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GEOCHEMICAL STUDIES OF ARSENIC AND SOME HEAVY METALS IN SOUTH-EAST ENGLAND

by

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B.Sc (Hons) London

A Thesis Submitted in Part Fulfilment for the
degree of
Doctor of Philosophy in Environmental Physical Science
in the
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Darwin College January, 1983

To my Parents and Andrew

"To doubt everything or to believe everything are two equally convenient solutions; both dispense with the necessity of reflection"

H. Poincaré

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ABSTRACT

The soils of the Weald of South-East England are derived from a complex variety of sedimentary materials, which exhibit strong geochemical variation. This thesis describes detailed research into the biogeochemistry of Arsenic and other heavy metals of the Weald.

A short review and introduction to the geology and soil types of the area is presented. The importance of As and human health is emphasised.

Soil samples were taken along eight transects at various points across the geological boundaries and two other specific Wealden areas. The "total" concentration of As, Cu, Zn, Mn, and Fe; DTPA - extractable Cu, Mn, Zn and Fe; Bray P-1 extractable As; LOI (%) and pH were all determined using the fine earth fraction.

To perform analysis for As a sensitive method of detection in the range 0-1.0 μg/g by hydride generation coupled to atomic absorption spectrophotometry was developed and refined. The majority of the Wealden soils have As contents typical of the published data for these soil types. Romney Marsh soils exhibited the highest levels of ($\overline{x}$=15 μg/g). An examination of stream sediments indicated that localized pollution had occurred. This anomaly is rationalised in terms of drainage and soil chemistry. A strong correlation was found for Fe-As ($p<0.001$).

Trials performed with various plant types in As-spiked soils show a relationship between soil concentration and plant uptake. Yield decreases and plant uptake vary with soil type and crop. The effects were found to be most marked in a calcareous soil with low phosphate content.

Extractions indicated Bray P-1 to be useful in determining plant availability.

Abundance levels for Cu, Mn, Zn and Fe are presented. Argillaceous deposits usually contain greater concentrations than arenaceous. A strong positive correlation was found between Zn and Cu ($p<0.001$) for all soils.

The DTPA extractions are discussed with regard to soil parent material. Generally increased levels of total elements imply increases in available concentrations.

A statistical analysis of the results is reported.

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CHAPTER ONE

INTRODUCTORY STATEMENTS

Currently there is much interest in the geochemistry of heavy metals and their influence on human health. Attention has concentrated on the potentially toxic elements lead, mercury and cadmium. Relatively little public attention has been focused on the problems of arsenic in the environment, although it is widely recognized as a toxin.

Most research in this country so far has been concerned with the geochemical distribution of arsenic in the south-west (Peterson *et al.*, 1979). In contrast this thesis concentrates on the abundance of arsenic in the soils and plants of south-east England. One of the main bases for this investigation is the pioneering work of Webb *et al.* (1978) at Imperial College, which may be regarded as a template for more definative studies.

In this introductory chapter the techniques of Geochemical Reconnaissance are outlined, and a comprehensive review of environmental problems connected with the geochemistry of As is presented. It concludes with an outline of the objectives of each chapter.

1.1 Geochemical Reconnaissance Techniques

The requirement for systematic data on trace element levels over the United Kingdom has been partly satisfied by geochemical reconnaissance surveys based on stream sediment sampling conducted by the Applied Geochemical Research Group (AGRG) of Imperial College.

In 1969 over a period of ten weeks, nearly 50,000 samples of active stream sediment were taken from tributary drainage over the 165,760 km^2 of England and Wales, at an average density of 1 per 2.5 km^2. Samples were taken 20 m from tributary-road intersections wherever the upstream catchment area did not exceed 25 km^2. Urban and obviously contaminated areas were avoided, and sampling was restricted over ground underlain by calcareous rocks, where there is little surface drainage.

The <200 μm fraction (oven-dried at c.80 °C) was analysed by direct reading spectrography for Al , Ba , Ca , Co , Cr , Cu , Fe , Ga , K , Li , Mn , Ni , Pb , Sc , Sn , Sr and V . Cd and Zn were analysed by absorption spectrometry, and As and Mo by colorimetry.

The data were computer mapped using a special moving average smoothing technique to reduce sampling and analytical variability. These maps have since been published as the Wolfson Geochemical Atlas (Webb *et al.*, 1978).

It is based on the assumption that each sediment sample is a composite of the erosion products of rock, overburden and soil upstream from the sampling point, and hence reflects the mean concentration of elements in the catchment area (Hawkes and Webb, 1962).

The Atlas has three main functions:

a) area selection for mineral exploration

b) delineating areas of trace element disorders in crops and livestock

c) environmental studies including land-use and public health, for example water and food quality, and medical geography.

The geochemical maps were found to reflect closely changes in bedrock composition revealing areas of low Co, Cu, Mn and Zn, and high As, Cd, Cu, Zn, Ni, Cr and Mo (Thornton and Plant, 1980).

The optimum range of trace elements in soils is often narrow and both deficiencies and excesses can give rise to serious agricultural problems such as crop failure or livestock death. However, subclinical effects can be more insidious as in many cases they remain undetected, and these marginal areas may be of considerable economic importance. For example, the only observable effects of moderate Cu deficiency in cereals in East Anglia was a slight reduction in the filling of grain on previously normal and otherwise healthy plants (Pizer, *et al.*, 1966). Therefore, there was a need for geochemical maps to focus attention on suspect areas.

The possible relationship between trace element distribution and human disease is still a controversial subject, and causal relationships are limited. Variations in the prevalence of dental caries have been related to the distribution of Pb (Anderson and Davies, 1980), and iodine distribution with endemic goitre. Another aim of the Atlas is to assist in the selection of sampling locations for epidemiological studies.

Care must be taken in the interpretation of geochemical mapping. In many cases it is capable of indicating changes in bedrock and soil which would not be apparent from geological maps. However, many factors affect the solubility and availability of trace elements, some of which are discussed by Plant and Moore (1979). For example, natural enrichment can occur in moorland areas where Mn and Fe are mobilised in low Eh/pH conditions and leached into surface waters where they re-precipitate into the stream sediments.

In the introduction to the Atlas Webb *et al.* stressed that regional geochemical maps only highlight areas of interest which need to be investigated by more detailed surveys. The basin-structure of the Weald exhibited strongly ovoid patterns for Al , Ba , As , Co , Cu , Ga , Fe and Mn accompanied by moderate patterns for Ni , K , V and Zn . A "high" As anomaly was revealed on the Romney Marsh. While some of these may be enhanced by secondary environmental factors, others may well be related to the geochemistry of the various sediments.

1.2 Arsenic in the Human Environment

This section contains a review of the environmental problems associated with As and draws on modern scientific literature from a wide variety of fields.

1.2.1 Natural Sources

Arsenic usually exists in nature in sulphide ores, arsenopyrite being the most common arsenic-bearing mineral. Arsenic trioxide is obtained principally as a by-product in the smelting of Cu , Pb or Au ores mainly in Canada, Australia and Brazil. The largest known deposit occurs at Boliden in Sweden where the sulphide ore contains 10% arsenic which is disposed of by sinking in concrete containers in deep water (Kipling, 1977). In Britain, arsenopyrite occurs in close proximity to the Cu and Sn-bearing minerals in the south-west, and was regarded as an impurity until the latter part of the 19th Century (Thomas, 1980).

When these ores are smelted, the volatilised oxides are trapped by electrostatic precipitators, and arsenic trioxide is refined from this. Most commercially available arsenic compounds are produced from As_2O_3 .

1.2.2 Uses

Many of the major uses for arsenic compounds are listed in Table 1.1.

Historically, arsenic has been known for its medicinal and toxic properties. However, with the advent of the industrial revolution in the 19th Century, exposure to arsenic became more widespread among the populace. Arsenical pigments were one of the main sources. These included all types of paper wrappings, toys, fabrics, paints, soaps and sweets. Other workers were exposed in the manufacture of sheep dip and other pesticides and a variety of chemicals (Schroeder and Balassa, 1966).

Agriculture has been one of the main commercial outlets for arsenical compounds. "Paris Green" was first used as an insecticide in France at the beginning of the 19th Century, but was replaced by lead and calcium arsenate because of their reduced toxicity (Kipling, 1977). Since then $PbHAsO_4$ has been widely used as an insecticide in vineyards and apple orchards worldwide (Elfving, *et al.*, 1978; Aten, *et al.*, 1980).

Sodium arsenite is another multipurpose arsenical compound which is used for weed control, sheep dip and is a potato vine defoliant. In Britain it is the only arsenical on the list of Approved Products for Farmers and Growers, and is recommended for the control of winter moths (apples and pears), pear slug sawfly (cherries), and earthworms and leatherjackets (turf).

Arsenicals are used in the poultry industry to control coccidiosis and as a growth promotant (Isaac, *et al.*, 1978). Derivatives of phenylarsonic acid are employed as a growth stimulant in pigs.

In agriculture inorganic compounds have largely been replaced by organic arsenicals, carbamates and organic phosphates, with a corresponding reduction of arsenic reaching the soil (Walsh, *et al.*, 1977).

In medicine arsenicals have long been used as stimulants and tonics. From the 19th Century onwards, an inorganic arsenic

Table 1.1

Arsenic Compounds Used in Industry, Agriculture and Medicine (Kipling, 1977)

Arsenic Compound	Formula	Common Name	Uses
Arsenic	As		Alloying Additive Electronic devices Veterinary Medicines
Arsenic pentoxide	As_2O_5	Arsenic Oxide Boliden salts	Chemical intermediate Defoliant Wood preservative
Arsenic trioxide	As_2O_3	Arsenic Arsenolite White arsenic Arsenious oxide	Insecticides and fungicides Glass Chemicals Anti-fouling paints Taxidermy Timber preservation
Arsenic trichloride	$AsCl_3$	Butter of arsenic	Pharmaceuticals
Arsine	AsH_3		Stabilizing selenium In transistors
Calcium arsenate	$Ca_3(AsO_4)_2$		Insecticide, herbicide
Copper arsenite	$CuHAsO_3$	Scheele's green	Larvicide
Copper aceto-arsenite	$3CuOAs_2O_3Cu(OOCCh_3)$	Paris Green Emerald Green	
Orpiment	As_2S_3		Depilatory- fireworks - pigment
Potassium arsenate	KH_2AsO_4	Macquer's salt	Preservation of hides Textile printing Fly papers
Potassium arsenite	$KH(AsO_2)_2$	Fowler's solution	Medicine

Table 1.1 (Cont'd.)

Arsenic Compound	Formula	Common Name	Uses
Realgar	As_2S_2		Pigment; Depilatory
Lead arsenate	$PbHAsO_4$		Pesticide; growth regulator
Sodium arsenate	Na_2HAsO_4 Na_3AsO_4	Wolman salts	Wood preservative Calico printing Insecticide; Weed killer
Sodium arsenite	$NaAsO_2$		Herbicides; Pesticides Corrosive inhibitor Fluorescent lamps
Magnesium arsenate	$Mg_3(AsO_4)_2$	Atoxyl	Tyrpanicide
Sodium arsanilate	$NaH_2C_6H_4AsO(OH)(ONa)$		Pharmaceutical manufacture

compound known as Fowler's solution (potassium arsenite) containing 7.6 g/ℓ As has been used for the treatment of leukemia, psoriasis, chronic bronchial asthma, and as a tonic (Martindale, 1977). The daily dosage could often be up to 30 mg As . This and other common medicinal preparations which contain arsenic, including Donovan's solution (arsenic and mercuric iodides) and asiatic pills (arsenic trioxide and black pepper) are now rarely prescribed.

Prior to the introduction of antibiotics, organic arsenic compounds were used for the treatment of syphilis and trepanematosis. Some are still used as antiparasitic drugs.

1.2.3 Arsenic Pollution

Considering the widespread use of arsenic in the past, there must inevitably be unwanted additions to the biosphere resulting in elevated levels in soils, sediments, waters, plants and animals. The relationships between these can be seen in Figure 1.1:

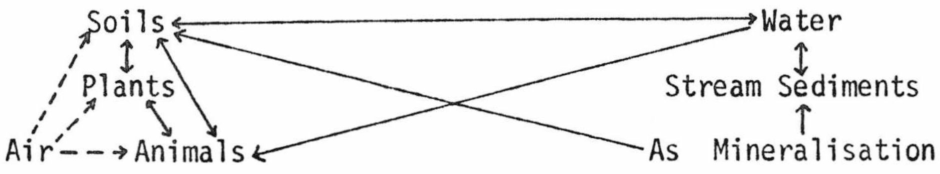


Figure 1.1 Possible movement of arsenic in the environment

The most important source of As pollution is undoubtedly emissions from smelters and their distribution through the atmosphere. Although most modern smelters have electrostatic precipitators, smelting has in the past been a major contribution to the environment. There are many examples of this in the literature including Crecelius *et al.* (1974); Amasa (1975); Låg (1978); Adamson (1980) and Mudroch and Copobianco (1980). This form of enhancement is worldwide. Mine spoil also enhances As in the local environment. Benson *et al.* (1981) reported soil levels of c.20,000 μg/g As developed on old minespoil in south-west England. Here As tolerant flora can, in some cases, accumulate As up to 1% of their dry weight.

Secondary lead smelters have also been reported to release As (Temple, *et al.*, 1977). Small amounts of As are alloyed with Pb in the production of battery plates and this could be of importance at Sheerness in Kent, where whole cars are smelted.

Arsenic is present to some degree in most coal in Britain and some is emitted when the coal is burnt. Hence elevated levels might be expected near coal-fired power stations. The residue, fly ash, is used to neutralise tips and wasteland and can produce elevated levels of As in soils and crops (Gutenmann, *et al.*, 1979).

The second most important source of As enhancement is from agricultural practices. As already outlined in 1.2.2, arsenical compounds were widely employed for many problems. Ultimately they find their way into the soil and drainage systems, and possibly animals. Elfving *et al.* (1979) reported an accumulation of As in small mammals living on an old orchard site sprayed with $PbHAsO_4$. Unintentional enrichment can occur through inorganic fertilizer applications which Senesi *et al.* (1979) feel could be significant. Certainly poultry and swine manure can contain high levels through the use of arsenic compounds as growth stimulants.

The weathering of natural mineralized areas can mobilise As into the drainage system and hence the soils and sediments of the surrounding environment. Soils have been examined around the Dartmoor granite As anomaly. Those within the metamorphic aureole contained more As (up to 250 µg/g) and Cu than soils developed from unmetamorphosed Devonian, Carboniferous and Permian rocks to the north (Aguilar-Ravello, 1974; Colbourn, *et al.*, 1975). The enhanced levels in the metamorphosed shales and granites are thought to be the result of hydrothermal activity at the time of the granitic intrusion. These soils however, contain far less As than the contaminated sites in the Tamar area. Thoresby and Thornton (1979) reported a maximum of 1200 µg/g As in pasture soils associated with exploited mineralised areas.

Klumpp and Peterson (1979) found that the Carnon River which drains an area with a long history of mining activity, contained 1.8-42.1 µg/ℓ As decreasing towards the Carrick Roads estuary. Macrophytes were found to be important accumulators of As with mean levels of up to 100 µg/g As (dry weight) but biomagnification did not occur up the food chain.

From this section it can be seen that as a result of natural mineralisation and human activities As has been redistributed and could pose a serious pollution problem.

1.2.4 Arsenic and Human Health

Since As is present in air, food and water in varying concentrations, it is continually absorbed by the mouth, lungs and possibly skin. However, it has not been shown to be an essential constituent of the human body.

Arsenic is toxic to most higher plants, to all animals having central nervous systems, and to certain lower organisms. As III is much more toxic than As V. Stored As is widely distributed in man in the liver, kidney, spleen, skin, bone, abdominal viscera, and especially in low-level metabolic tissues such as hair and nails.

Acute As poisoning in humans can result upon ingestion of 20 mg of As , but long-term arsenosis may remain undetected for years. The toxic effects of As are generally:

1. Systematic vascular poisoning, a paralytic action on smooth and cardiac muscle leading to haemorrhage;
2. Mitotic poisoning, blockage of chromosomal mitotic metaphase during cellular division;
3. Protoplasmic poisoning, a combination with certain enzymic sulphydryl groups which causes inhibition of various oxidative systems requisite in tissue respiration (Luh, *et al.*, 1973).

Industry has not been a major cause of As poisoning in Britain, except in the manufacture of pesticides and pigments. Exposure to sodium arsenate in sheep dip factories has caused ill-health and death. The agricultural use of As in Europe is a well-described hazard. Vineyard workers especially developed signs of As-poisoning, including melanosis of the body, particularly over the back, chest and abdomen. In the Rhine and Moselle districts of Germany, arsenical insecticides have been banned since 1942 (Kipling, 1977).

Prolonged therapeutic administration of arsenic compounds, particularly Fowler's solution can result in dermal lesions and liver disease (Fowler, *et al.*, 1979).

High concentrations of As in water supplies has been a further cause for concern. Tseng *et al.* (1968), published a report on an area on the south-west coast of Taiwan where artesian well water with a concentration of 0.01-1.82 mg/ℓ As used over a period of c.45 years caused 20% of the population to suffer from Blackfoot disease (a peripheral vascular disorder resulting in gangrene of the extremities). Similar outbreaks have occurred in Cordoba, Argentina (Astolfi, *et al.*, 1981). The WHO (1970) maximum level of As in piped supplies of drinking water is 0.05 mg/ℓ .

With the exception of some kinds of fish, crustaceans and seaweed, most foods contain low levels of As . Thoresby and Thornton (1979) demonstrated that little soil As passed into the shoots of normal pasture plants or into the edible parts of barley, strawberries and lettuce. In non-accumulator plants phytotoxicity occurs before dangerous levels are reached. Surface contamination with pesticides can increase the concentrations of As in plants (Gur *et al.*, 1979), but again to only a small degree in the edible parts.

Terrestrial organisms seldom contain more than 1 μg/g (dry mass) As whereas the corresponding value for marine organisms can be more than 100 μg/g (Lunde, 1977).

The safe level of As in food will depend on its form and bioavailability, the concentration of other elements present which may affect absorption and retention, and the proportion of the entire diet. There is insufficient information to produce an absolute limit, but WHO (1973) recommends that the maximum acceptable load of As be tentatively placed at 0.05 mg per kg body weight per day.

Involuntary inhalation and ingestion of As in particulate form can occur. Smelting of metals, burning of coal, and use of arsenical pesticides are major sources of airborne As . Bowen (1979) reported 0.6 ngAs/m^3 air at S.T.P. at Shetland (uncontaminated) and a range of 1.5-53 ng/m^3 over Europe as a whole. Arsenic acid is used to desiccate 2-3 million acres of cotton annually in the USA. Miller *et al.* (1980) measured an average As content of 7.8 μg/m^3 in the breathing zone of ground rig applicators. The current US standard is 10 μg/m^3 . The highest exposure in insecticide manufacturing and distribution is usually in the mixing, screening, drying, bagging and drum-filling operations.

Regardless of the mode of introduction, As is rapidly excreted from the human body, mainly through the urine, but to some extent in the faeces (Buchet, *et al.*, 1980).

Arsenic has been suspected as a possible carcinogen since 1820, when Paris reported a cancerous disease of the scrotum amongst Cu smelter workers in Cornwall. Later an association between Fowler's solution and skin cancer was postulated by Hutchinson (1887). However, despite many attempts it has not been possible to show conclusively any carcinogenic effect of As in experimental animals (Hernberg, 1977).

The first epidemiologic report of a connection between occupational As exposure and cancer was published by Hill and Faning (1948). They reported an excess of cancer (29.3% observed as opposed to 12.9% expected) of the skin and lungs among workers manufacturing sodium arsenite sheep-dip. Since then many other studies have been published. Pinto and Bennett (1963) found 41.9% deaths of lung cancer occurred amongst Cu smelter workers exposed to As compounds compared to 23.7% expected. Other reports include Lee and Fraumeni, 1969; Pinto, *et al.*, 1977; Axelson, *et al.*, 1978.

The reported latency period for As-induced cancer seems to be long. Lee and Fraumeni (1969) reported average latent periods of 34, 39 and 41 years respectively for heavy, medium and light exposure categories.

High levels of As in drinking water have been reported as the causal agent for excess skin cancer (Tseng, *et al.*, 1966;

Tseng, 1977). Clough (1980) suggested that the high rate of melanoma found in the SW hospital region might be related to high levels of As in the region.

There is a vast amount of literature on this subject, but four good reviews are Hernberg (1977); Fowler, *et al.* (1979); Axelson (1980) and Pershagen (1981).

1.3 Objectives of this Thesis

In order to produce an objective assessment of As and other heavy metals in south-east England, and their importance to agriculture and human health this thesis will concentrate on the following topics:

1. The geological and pedological characteristics of the study area (Chapter 2);
2. The use of a rapid and precise technique for the measurement of As at low levels in a variety of environmental samples (Chapter 3);
3. The occurrence and controls of As in the soils of the Weald (Chapter 4);
4. The uptake and distribution of As in wheat, radishes and beans (Chapter 5);
5. The abundance of Cu , Zn , Mn , and Fe in Wealden soils;
6. The 'available' concentration of Cu , Zn , Mn , Fe and As in soils in the south-east.

CHAPTER TWO

THE GEOLOGY AND SOILS OF THE WEALD

2.1 Location

The area commonly called the Weald is the dominant landscape feature of south-east England (Figure 2.1). It lies within the counties of Kent, Sussex, South Surrey and West Hampshire, and is naturally delineated by the North Downs (from Farnham to Folkestone), the South Downs (from Petersfield to Beachy Head), and the Butser Hills.

Figure 2.1 Sketch map to show the location of the Weald

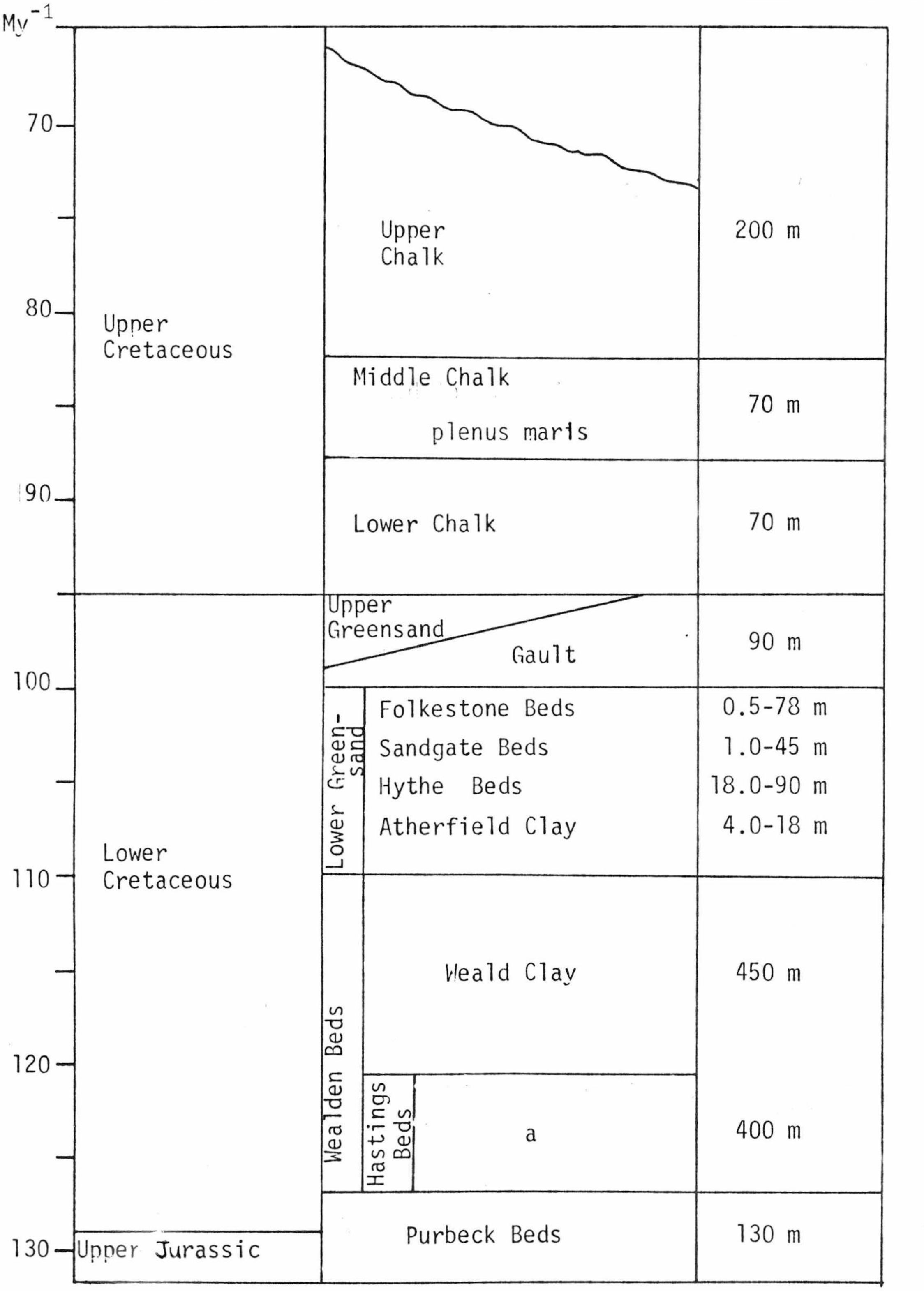
Geologically, the Weald continues across the straits of Dover in the Bas Boulonnais of north-east France, where a semi-circle of chalk hills form the eastern counterpart of the Butser Hills.

2.2 Geology

2.2.1 Stratigraphy

The oldest rocks exposed are of Upper Jurassic age, and older formations are only known in boreholes (Gallois, 1965; Rawson, *et al.*, 1978). The stratigraphical range of surface outcrops in the Weald is dominated by the Cretaceous period. Table 2.1 gives a summary of the formations, including local names. These are mapped in Figure 2.2. All the rocks are of sedimentary origin, laid down under various depositional conditions.

There is a long history of stratigraphical research in the Weald commencing with the studies of Topley (1875), and a concise review has recently been published by Gibbons (1981). Since the details of formation are well-documented, only the most salient points will be given here. The object is to describe the lithology of the parent material (including drift), of the soils of the region. Other major reviews used in this text are: Gallois (1965); Smart, *et al.* (1966); Green and Fordham (1973); Rawson *et al.* (1978) and Fordham and Green (1980).



Period	Formation			Maximum Thickness
Upper Cretaceous	Upper Chalk			200 m
	Middle Chalk plenus marls			70 m
	Lower Chalk			70 m
Lower Cretaceous	Upper Greensand Gault			90 m
	Lower Green-sand		Folkestone Beds	0.5-78 m
			Sandgate Beds	1.0-45 m
			Hythe Beds	18.0-90 m
			Atherfield Clay	4.0-18 m
	Wealden Beds		Weald Clay	450 m
		Hastings Beds	a	400 m
Upper Jurassic	Purbeck Beds			130 m

a. Upper Tunbridge Wells Sand
Grinstead Clay
Lower Tunbridge Wells Sand
Wadhurst Clay
Ashdown Beds

Table 2.1 A Stratigraphic Record of Mesozoic Rocks Exposed in the Weald

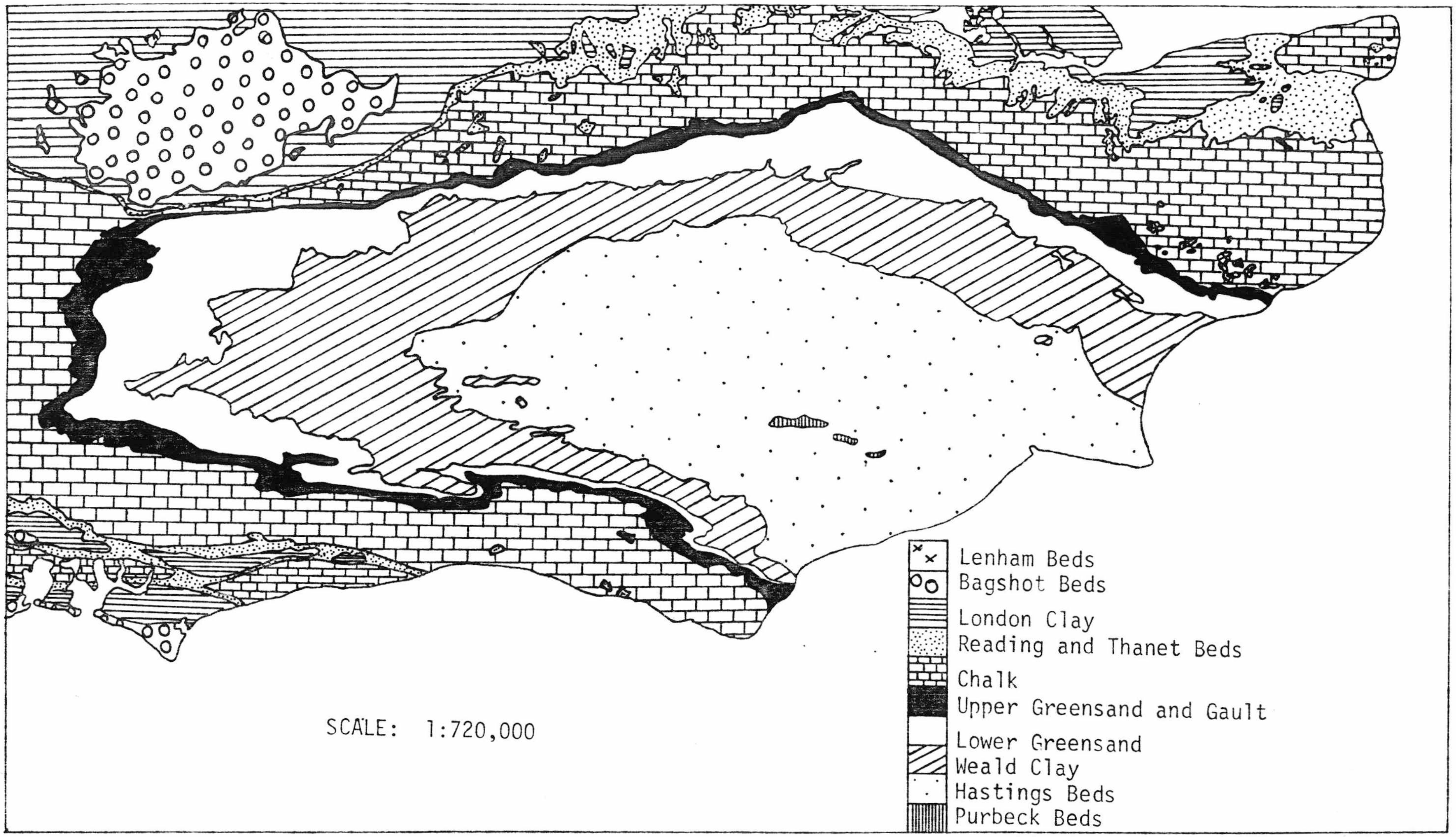


Figure 2.2 Geological Map of the Wealden Area, S.E. England

(Blyth, F.G.H. and M.H. de Freitas. 1976. A Geology for Engineers. Edward Arnold, London.)

2.2.2 Details of Formation

2.2.2.1 Purbeck Beds (Upper Jurassic)

These beds are the oldest exposed rocks in the Weald Economically valuable gypsum and anhydrite deposits occur at the base, and indicate initial semi-arid conditions. The higher Purbeck Beds consist of soft dark shales containing thin beds of hard, pale limestones and yellow-brown sandstones. These formed in waters of variable salinity through cycles of shallow water, tidal flats, and non-deposition (West, 1975). They represent part of a major regression at the end of Upper Jurassic sedimentation.

2.2.2.2 Wealden Beds

The Wealden Beds are divided into the Hastings Beds and Weald Clay (Table 2.1) and vary considerably in facies and thickness, reflecting an unstable sedimentary environment.

The oldest Wealden Beds, the *Hastings Beds* can be subdivided into the Ashdown Beds, Wadhurst Clay, Grinstead Clay and Tunbridge Wells Sand, the nomenclature of which is discussed by Bristow and Bazley (1972). They are an alternating group of sandy and more argillaceous units which thicken to 400 m towards the centre of the Weald.

The Purbeck Beds are succeeded conformably by the *Ashdown Beds* which consist of fine-grained siltstones and sandstones with subordinate beds of shale and mudstone. Over much of the formation the sandstones are massive and quartzose, often forming a conspicious landmark, such as the cliffs at Fairlight. The outcrop is not continuous.

The *Wadhurst Clay* marine transgression is marked by the top Ashdown Pebble Bed. This formation is made up of soft, dark-grey shales and pale-grey mudstones with thin bands of siltstone, shelly limestone and clay ironstone. The Tilgate Stone (a calcareous sandstone about 1 m thick) occurs at several horizons, and was quarried for building and roadstone, particularly in the Hastings area. The most persistent ironstone occurs as nodules and tubular masses near the base of the formation, and was the basis of the Wealden Iron industry in Kent and east Sussex. The outcrop is much faulted and does not occur over a large area due to outliers of the overlying Tunbridge Wells Sand, and to erosion through the soft shales to the underlying Ashdown Sand. The beds thicken westwards to a maximum of 70 m .

The *Tunbridge Wells Sand* is divided into upper and lower parts separated by the Grinstead Clay in the western Weald. It is not possible to make this subdivision in the east, where the outcrop is faulted. The Lower Tunbridge Wells Sand comprises interbedded silts and sandstones overlain by a massive sandrock known as Ardingly Stone. This formation varies from 20-50 m .

Grinstead Clay is similar in lithology to Wadhurst Clay, and consists of shales and mudstones with thin beds of silt, clay ironstone, and limestone. The outcrop is very broken and is a maximum of 23 m thick.

The Upper Tunbridge Wells Sand is dominated by siltstones and thin sandstones, with reddish mottled ("catsbrains") clays. The horizons are indistinct and the lithologies impersistent. This formation is rarely exposed and grades into the overlying Weald Clay.

The *Weald Clay* comprises grey shales and mudstones with subordinate bands of thin sandstones, siltstones and shelly limestones, with conspicuous bands of red clay. These lithofacies are arranged in cyclic sequences, units varying from 1-100 m (Allen, 1975).

Topley (1875) believed that a sequence of seven sandstones and limestones could be recognised in the Weald Clay and this has been confirmed. The most important sandstone is known as Horsham Stone which is up to 10 m thick. The main limestone formation is a maximum of 0.3 m thick and is known locally as Bethersden "marble".

The Weald Clay covers an extensive area surrounding the Hastings Beds, and is thickest in the Western Weald, where it may attain 450 m (Thurrell, *et al.*, 1968). It is most sandy in the west, and clays become more frequent towards London. Marine influences are least in the eastern end of the basin (Allen, 1975). Small inliers occur in the Lower Greensand near Guildford, Dorking and Maidstone.

The origin of the Wealden Beds has been studied by Allen for many years. They were initially thought to be deltaic in origin (Allen, 1959), but are now believed to represent sedimentation in a fault-bounded basin, where a variable salinity mudplain was periodically transformed into braided sandbars by powerful overloaded streams (Allen, 1975; 1981).

2.2.2.3 Lower Greensand

The divisions of the Lower Greensand are given in Table 2.1. It has been described in detail by Casey (1961a) and Middlemiss (1975). Towards the end of Weald Clay deposition the conditions of sedimentation became more saline as the sea transgressed into the area between the London platform and Brittany. The Lower Greensand was laid down in a variety of shallow-water environments.

The *Atherfield Clay* lies unconformably on the Wealden Beds (Holmes, 1959) indicating some erosion before deposition. This clay is composed of clay ironstone and impersistent beds of fine-grained sandstone in the lower part of the formation. It reaches a maximum of about 20 m in the north-west Weald and thins eastwards to less than 0.6 m . Exposures are rare due to landslips along the Hythe Beds escarpment.

The upper beds of the Atherfield Clay are sandy and grade into the *Hythe Beds*. This formation indicates a rejuvenation of the London platform source area because of the relative abundance of phosphate pebbles, probably from the erosion of Jurassic rocks (Middlemiss, 1975). The lithology of the Hythe Beds varies considerably. They consist of alternate layers of hard sandy limestones ("rag") and glauconitic calcareous sandstone ("hassock").in Kent and east Sussex. The beds become more arenaceous westwards where they are composed of grey/green sandstones with subordinate lenticular bands of chert. The beds thicken westwards where they attain a maximum of 90 m .

A period of tectonic movement followed the deposition of the Hythe Beds and resulted in the erosion of the Lower Cretaceous sediments north of Guildford. The lower divisions of the Sandgate Beds, the Bargate Beds, was built up in the western Weald and comprises a pebbly calcareous sandstone. This is overlain by ferruginous clayey sands and silts known as the Puttenham Beds which mark the re-advance of Lower Greensand sedimentation.

The *Sandgate Beds* are more variable than any of the other Lower Greensand formations. In Kent they consist of green-grey sandstones and grey glauconitic mudstones with a basal phosphatic nodule bed resting disconformably on the Hythe Beds. Westwards they pass into more varied facies. Important seams of Fullers Earth occur locally. The Sandgate Beds reach a maximum of about 45 m in the south-west Weald and thin rapidly eastwards into glauconitic silts approximately 10 m thick at Eastbourne.

The *Folkestone Beds* are mainly poorly consolidated quartzose sands containing pebble and clay seams, with veins and "doggers" of hard ferruginous sandstone ("carstone"). The sands are generally yellow-brown due to limonite staining, but "silversands" do occur. From the coast the beds thicken inland into false-bedded sands reaching a maximum of about 80 m . Over much of the formation the top of the Folkestone Beds is marked by a series of glauconitic sands and clays containg phosphatic nodule beds. However, near Midhurst the junction is marked by a thin ferruginous pebble bed.

In Sussex the Lower Greensand formation thins south-eastwards and the beds lose their individuality until at Eastbourne the whole series is represented by thin glauconitic loams withphosphatic nodules beneath the Gault.

2.2.2.4 Gault Clay and Upper Greensand

The Gault and Upper Greensand have been described in detail by Owen (1975). The initial deposition of these rocks was marked by a marine transgression. The Gault and Upper Greensand are part of the same sequence, the former composed of argillaceous material and the latter arenaceous.

The *Gault* can be subdivided into upper and lower divisions and is a fossiliferous blue-grey soft mudstone. The Upper Gault is calcareous. Phosphatic nodule beds occur at the junction between the divisions and at contact with the Folkestone Beds. The thickness of the formation varies considerably, but it generally increases westwards to a maximum of 90 m .

The Upper Gault thins westwards into its lateral equivalent of *Upper Greensand* (Figure 2.2), in which three broad rock types occur. Poorly consolidated siltstones which form a junction with the Gault are overlain by a series of sandstones known as "Malmstone". The top of the Upper Greensand usually consists of clayey, glauconitic sandstones. From a maximum of 60 m , it thins eastwards.

2.2.2.5 Chalk

A detailed description of the petrology of the chalk has been published by Hancock (1975).

Slow subsidence that began during Lower Gault deposition culminated in the production of a large marine basin which affected much of central and western Europe. The chalk accumulated in this basin as a calcareous ooze. During this period there was little land available for erosion due to high eustatic sea levels, and a probably arid climate, therefore little land derived material is present in the chalk.

Chalk is a soft, white friable limestone consisting of >95% $CaCo_3$. Most of the fine material is calcite secreted by planktonic marine organisms known as coccoliths (Black, 1953). Mixed with this are smaller quantities of coarser calcareous fragments from other plankton and bivalves. Although initially the chalk appears to be uniform, a variety of distinct lithologies are present which are thought to represent changes in sea depth which Hancock (1975) believed usually ranged from 100-600 m . Three main subdivisions are recognised (Table 2.1).

The *Lower Chalk* is the least pure formation, containing up to 50% non-calcareous material in the lowest beds. The basal bed is a sandy glauconitic marl of 3 m thick and usually contains iron and phosphatic modules. Above this lies interbedded grey marl and limestone, which increases in the proportion of limestone up the sequence to grey massively bedded chalk. The Plenus Marls dominate the top of the formation.

Melbourne Rock is the lowest bed of the *Middle Chalk* and comprises a hard nodular yellow-grey limestone. This is succeeded by massively bedded white chalk with seams of thin grey marl in the upper part. Flints and beds of nodular chalk occur in the top 10 cm .

The *Upper Chalk* is the thickest and purest (97-99% $CaCO_3$) of the three formations. The lower beds are characterised by many thin bands of hard nodular chalk, but most of the Upper Chalk consists of soft, white chalk with flints.

Chalk deposition terminated with the uplift of the Wealden sediments at the commencement of the Tertiary era, and erosion of the Cretaceous sediments began. The sea in the early part of the Tertiary alternately advanced and retreated on this new land, depositing marine or estuarine sands and clays to the north and south of the Weald. Tertiary Beds are only found today lying upon the Chalk to the north (London Basin) and south-west (Hampshire Basin) of the Weald. The overall tendency towards uplift culminated with earth movements contemporaneous with those which built the Alps. The whole area was raised above sea level and folded roughly east to west. This dome was slowly eroded centrally down to the Weald Clay and underlying Hastings Beds. Slight tilting occurred in the late Tertiary causing the sea to encroach on the lowland and producing a second Wealden Shelf, buried by marine sands which remain only as remnants. Later the land was lifted relative to sea level and further erosion took place, producing a landscape very similar to that of today.

The Tertiary sediments are not important in this study and are only mentioned for completeness. Further details can be found in Smart, *et al.* (1966).

2.2.3 Drift Formations

Accumulations of clay, loam, sand, gravel and calcareous material overlying solid rock are collectively known as "Drift". Much of Drift deposits overlying Cretaceous rocks in the Weald formed during the cold climate of the Quartenary glaciation. In the early Pleistocene the climate lapsed into glacial conditions, which at their culmination covered the whole of Britain north of the Thames. Three main glaciations are recognised alternating with the warm interglacial periods, determiningmost of the major features of the present landscape.

Under these conditions the subsoil remains permanently frozen while the topsoil seasonally thaws causing the land to heave and disintegrate. An incomplete tundra vegetation probably existed. The summer meltwater streams, unable to penetrate the subsoil, carved deep valleys above the permafrost, carrying masses of material downslope to be deposited as fans in valleys and at the base of scarps. This material is collectively termed "Head" and the process of movement solifluction. In interglacial periods the deposits were redistributed by streams and rivers.

The main Drift deposits are listed in Table 2.2, and are described overleaf.

2.2.3.1 Plateau Dift and Clay-with-Flints

Nearly all the deposits on or fringingthe Downland plateau can be conveniently grouped into this category (Loveday, 1962).

Clay-with-flints is a dark-brown/red unbedded clay containing flints and some manganiferous patches. The base rests irregularly on the Chalk and locally occupies solution

Table 2.2

Drift Deposits

(Fordham and Green, 1980)

Age	Climate	Deposit	Conditions of Formation
Holocene (Recent)	Temperate	Sand, shingle Alluvium, peat	Sea level fluctuations and development of marshlands
Pleistocene	Periglacial and warm interglacial	River gravels Undifferentiated head Coombe deposits Dry valley deposits Brickearth Angular Chert Drift Plateau Dift and Clay-with-flints	Staged uplift; valleys, escarpments and plaints of present landscape formed by sub-aerial erosion. Assorted drift from solid rocks and loess is partly reworked, contributing to younger drift

pockets and pipes. It is believed that Clay-with-flints is the result of chalk solution and eroded Tertiary strata mixed by cryoturbation (Catt and Hodgeson, 1976).

Plateau Drift is a heterogeneous deposit ranging from clayey to sandy material. It is usually a reddish flinty clay which is often mottled, with locally sandy pockets indicating varied sources. Flinty, loamy or silty layers are common over the clay. The sandy and loamy dift varies widely and consists of red/yellow clay loam to sand containing hard ironstone and occasional flints and is usually mapped as Sand in clay-with-flints.

Plateau Dift and clay-with-flints once formed a virtually continuous sheet across the Downs, but the outcrop is now much dissected by dry valleys.

2.2.3.2 Angular Chert Drift

This consists of angular chert in a sand/clay matrix resting on the higher Lower Greensand ridge. It reflects the lithology of the underlying Greensand and probably developed in a similar way to Plateau Drift, mainly from disrupted Hythe and Sandgate Beds.

2.2.3.3 Brickearth

This is a general term to describe silty deposits of varying age, mainly late or post-glacial. These loams are red/

brown to buff in colour and are unbedded apart from rare flint layers. Normally they are sandy but every gradation exists from sand to a heavy clay loam. Some deposits are calcareous and $CaCO_3$ can be found as "race" nodules suggesting leaching from above and redeposition.

Brickearth has formed from a variety of processes, including the deposition of wind-blown dust on land and in water, and the periglacial erosion of local bedrock.

2.2.3.4 Coombe and Dry Valley Deposits

These deposits are the best example of Drift produced by Pleistocene solifluction.

Coombe deposits are unbedded accumulations of broken chalk and flint fragements in a pale chalky silt matrix. They are characteristically found at the base of coombes dissecting the chalk escarpment, but are also present wherever the slopes have been steep enough for downhill movement, and in some cases spread out over the Upper Greensand and Gault outcrops.

Dry valley deposits are heterogeneous, with Coombe deposits usually buried by Drift which Smart *et al.* (1966) regarded as old alluvium formed when the water table was higher than at present. Since then some infilling, probably by hillwash, has occurred.

2.2.3.5 Undifferentiated Head

Deposits which are mapped as Head vary in age, thickness and lithology. On the chalk the Head consists of flinty clay loams and is mostly derived from the clay-with-flints. Head >1 m thick can be found over the Gault Clay and is composed of brown/blue flinty clayloams. Thick Head on the Lower Greensand is classed as Angular Chert Drift. Deposits are rarely found on the Wealden Beds.

2.2.3.6 River Gravels

These were laid down during the development of the present drainage system and occur either on valley slopes above the water course, or capping nearly flat hilltops and benches. The main component is usually flint mixed with siltstones and ironstones from the Wealden, and Cherts from the Lower Greensand formations.

2.2.3.7 Alluvium and Peat

Peat is locally extensive and occurs in the alluvial tracts of some streams and at springs which are common at the junction between the Folkestone and Sandgate Beds. It is also an important part of the deposits which form the Romney Marsh.

Alluvium has accumulated upon the floodplains of most of the larger rivers in the Weald, and consists of muds, silts and fine sands. The largest areas of alluvium have collected in the coastal regions of Pevensey Levels and Romney Marsh. These flatsare made up of a composite alluvium composed of both river and marine deposits of differing ages. As the Romney Marsh is an important region in this study, the development of this landform will be described in greater detail.

The Romney Marsh

The main review relevant to this section is that of Green (1968).

The Romney Marsh is a general name used to describe several marshes, the two largest being the Romney Marsh proper and Walland Marsh. The Romney Marsh occupies the northern part and is separated from the Walland Marsh by the Rhee Wall. Its landward boundary is the Royal Military Canal (Figure 2.3).

The Marsh deposits (10-35 m) lie on Hastings Beds and Weald Clay in which rivers excavated a broad valley during the Pleistocene when sea level was much lower. Marine sediments and upland materials from Wealden rocks, principally Hastings Beds and Weald Clay, drained by the River Rother have gradually accumulated during several fluctuations in sea level in the old Romney Bay in the lee of off-shore spits and beaches formed by the sea (Lewis, 1932). Most sediments include some calcareous material in the form of finely comminuted sea shells.

About 1000 BC there was a period of low sea level and a luxuriant forest vegetation developed. Later when the sea

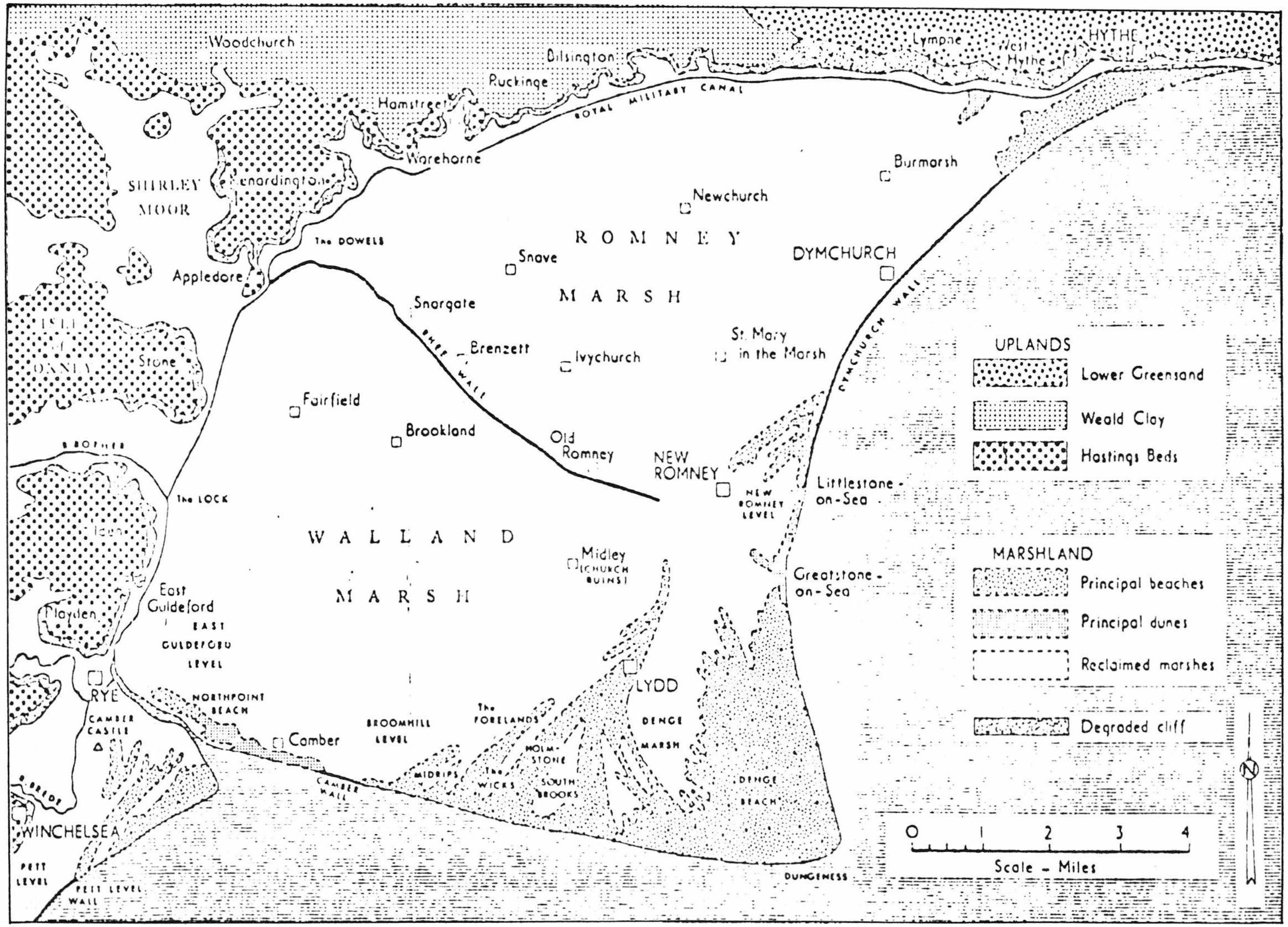


Figure 2.3 Romney Marsh and Adjacent Lands
(Green,1968.)

level rose these were buried as peat deposits. Subsequent deposition of sediments was very complex as changes in sea level have continued to present times. Sand banks and single spits were formed and then later removed; river courses were changed by tides and currents, and lagoons and tidal flats silted up to develop as salt marshes; long-established land was flooded, partly eroded and then recovered with fresh sediments.

The sediments which comprise the Romney Marsh can be seen in cross-section in Figure 2.4. The top few metres include all texture grades from sandy to clay, as well as peat and shingle. The shingle is largely composed of flint pebbles (98%) derived from Sussex Chalk which have accumulated and been reworked in Romney Bay over a long period. Dungeness Point is the largest shingle structure in Britain. With time the peat has been changed by erosion and compaction beneath mineral deposits; differential shrinkage through drying and partly wastage by oxidation. It is now a maximum of 2 m thick and is important as a soil parent material where it is within 0.105 m of the surface. (See Figure 2.4 overleaf.)

Post-peat deposits are commonly >2 m thick. Deposition occurred over 2,000 years with the formation of sedimentary patterns of contrasting age and complexity in different parts of the Marsh. Younger marshland with thicker post-peat alluvium forming a high land is calcareous throughout, whereas the adjacent land is mostly non-calcareous at the surface, and in some parts contains no detectable native lime due to pedological decalcification. The Marsh can therefore

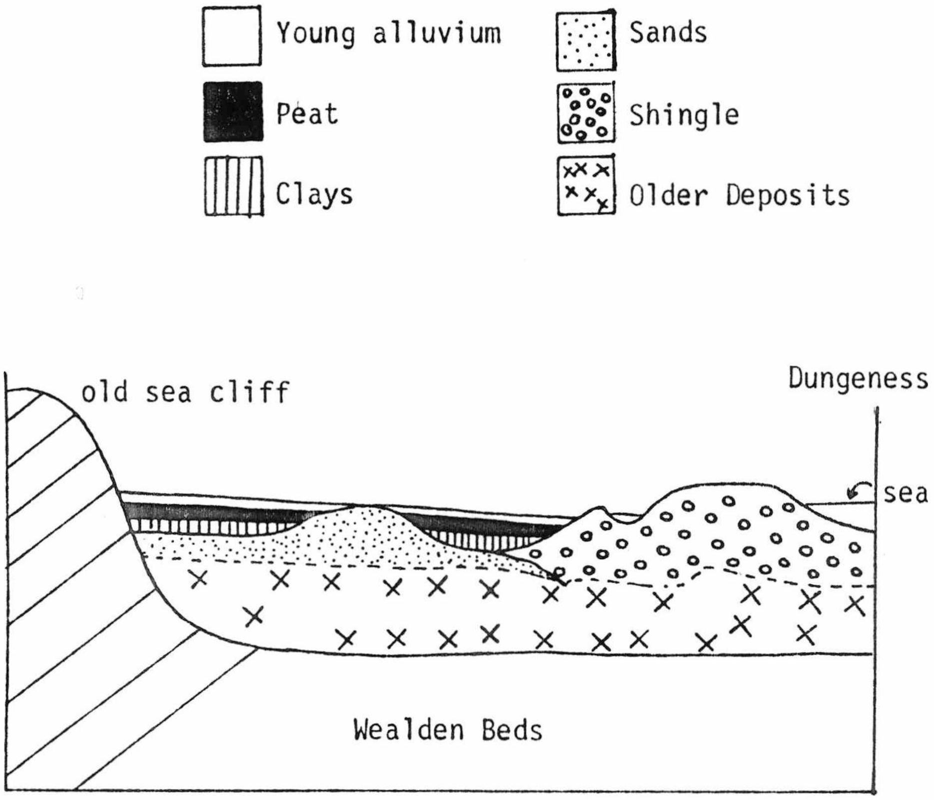


Figure 2.4 Sketch Cross-Section of the Romney Marsh

be divided into decalcified (old and calcareous (new) Marshland (see Figure 2.5 overleaf.)

Romney Marsh now comprises a series of enclosures, the youngest having been completed less than 100 years ago.

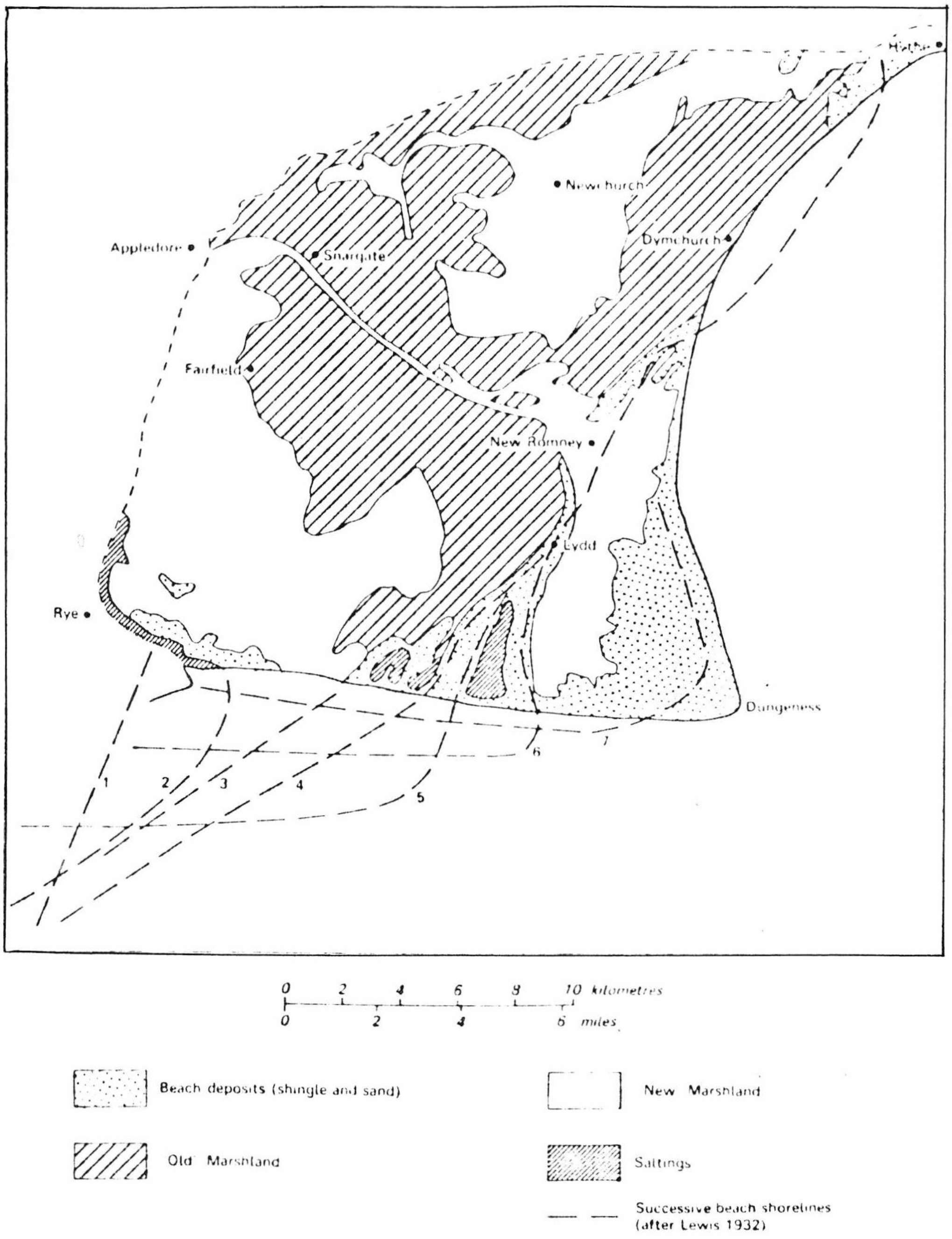


Figure 2.5 Location of Decalcified (Old) and Calcareous (New) Marshland (Fordham and Green, 1980.)

2.2.4 Structure

The Wealden uplift is a large shallow dome, with the main fold axis running aproximately east-west. Regional dips away from this are only one or two degrees, but in numerous subsidiary folds steeper dips are present.

The Hastings Beds contain long fault belts between which there are large areas of lightly folded rocks, but the surrounding Weald Clay is relatively undisturbed as the stresses were absorbed by bedding plane slip. The Lower Greensand and chalk were folded with minimal fracturing, with the intervening Gault Clay behaving similarly to the Weald Clay.

A generalised section of the Weald can be seen in Figure 2.6.

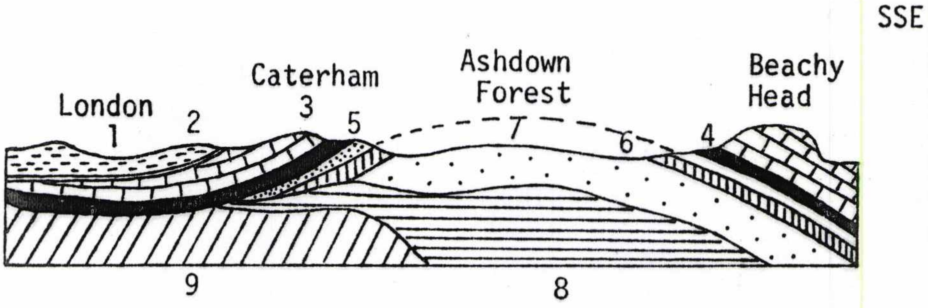


Figure 2.6 X-Section of Weald

1. London Clay
2. Woolwich and Reading Beds and Thanet Sands
3. Chalk
4. Gault Clay and Upper Greensand
5. Lower Greensand
6. Weald Clay
7. Hastings Sands
8. Jurassic
9. Palaeozoic

2.3 The Soils of the Weald

The main review used in this section is that of McRae and Burnham (1975).

Soils can be classified according to the horizons present and other properties, for example particle size and drainage. The determination of soil horizons is described by Hodgeson (1978). The dominant soil series found in the Weald are mapped in Figure 2.7, and the divisions are further detailed in Table 2.3. (See overleaf.)

2.3.1 Dominant Soils of the Weald

2.3.1.1 Rendzinas

Rendzinas are thin (<35 cm) calcareous soils which occur only on the steep upper and middle slopes of the escarpment of the Downs. They are typically black or brown in colour and are high in silt, probably due to loessial contamination. The original woodland has given way to a closely grazed sward.

2.3.1.2 Brown Calcareous Earths

Rendzinas pass into brown calcareous soils on late Pleistocene solifluction deposits or recent hillwash along the footslope of much of the North and South Downs. Often this chalk Head covers the surface outcrop of the Lower Chalk

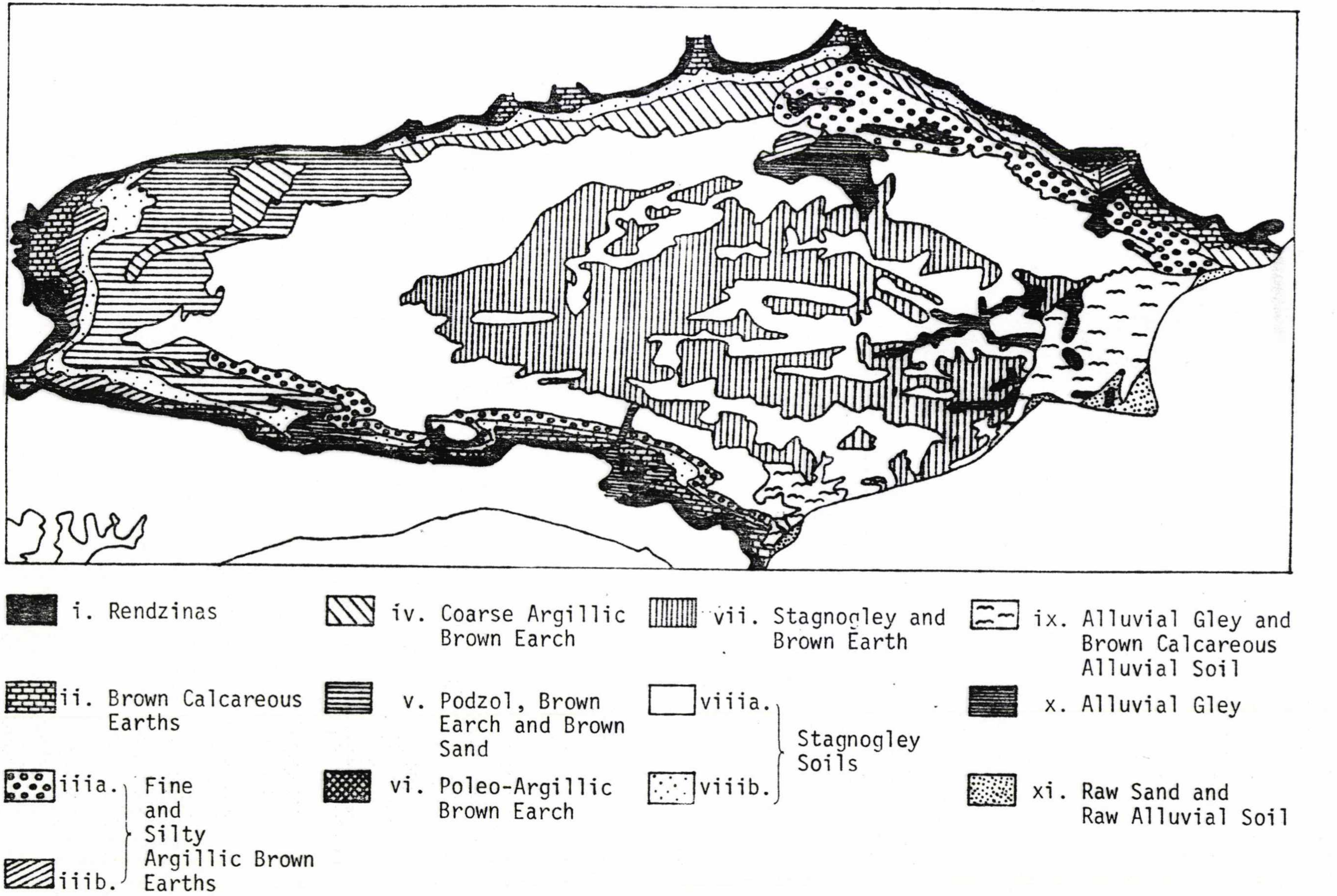


Figure 2.7 The Dominant Soil Series in the Weald Scale: 1:720,000

(McRae and Burnham,1975.)

Table 2.3

The Main Wealden Soil Groups

Soil Association	Dominant Soil Group	Texture	Parent Material
i	Rendzina	Silty, calcareous	Chalk and and very chalky drift
ii	Brown, calcareous earth	Silty, calcareous	Drift
iiia	Argillic brown earth	Fine loamy silty	Lower Greensand with or without superficial drift
iiib	Argillic brown earth	Fine loamy silty	Brickearth, Upper Greensand
iv	Argillic brown earth	Coase loamy and loamy	Cherty Hythe Beds and Head or Drift over Folkestone Beds
v	Podzol Brown earth and Brown Sand	Sandy	Folkestone Beds Sandgate Beds Hythe Beds
vi	Paleo-argillic brown earth	Loamy over clayey	Angular Chert Drift
vii	Stagnogley and brown earth	Loamy or silty	Hastings Beds or derived Drift
viiia	Stagnogley soil	Clayey Silty or sandy Silty or loamy over clay	Wealden Clays Siltstone and Sandstone Bands Drift over Wealden Clays

Table 2.3 (Cont'd.)

Soil Association	Dominant Soil Group	Texture	Parent Material
viiib	Stagnogley	Clayey Loamy or silty over clay	Gault Clay Drift over Gault Clay
ix	Alluvial gley and brown calcareous alluvial soil	Loamy or clayey	Marine alluvium
x	Alluvial gley	Clayey, loamy or silty	River or Marine alluvium
xi	Raw sand and raw alluvial soil	Sandy and fragmental	Dunes and beaches

and Gault Clay. These soils are pale brown and less calcareous than the rendzinas due to a higher silt content. They are variable in depth but of great agricultural value as they are well-drained and fertile. Lime induced deficiencies of Fe and Mn can occur.

2.3.1.3.1 Fine Loamy and Silty Argillic Brown Earths

Brown earths cover the largest area in lowland England. Fine loamy and silty argillic brown earths developed mainly on drift over or derived from the Lower Greensand. The majority of these soils occur on the Hythe Beds (rag and hassock) in Mid- and East-Kent, and along the outcrop of the Lower Greensand in Sussex. This is some of the best land in the Weald and the soils are usually deep, permeable, friable and retain enough winter rain to sustain crops through all but very severe droughts. Around Maidstone much of the land supports fruit growing (the mid-Kent fruit belt), and elsewhere high yielding vegetable and arable crops are grown.

2.3.1.3.2 Fine Loamy and Silty Argillic Brown Earths

The soils found in this group are developed on brickearth around Wye and on the Upper Greensand in the western Weald. The brickearth soil is dark brown with a silt loam topsoil overlying a paler horizon from which clay has been illuviated into a reddish silty clay loam horizon. These soils are fertile and easy to till and support a wide variety of crops.

However care has to be taken to avoid structural damage through plough pans.
The dominant soil on the Upper Greensand contains much silt and fine sand. These soils are renowned for their high fertility.

2.3.1.4 Coarse Loamy and Loamy Argillic Brown Earths

These have formed on the Lower Greensand, mainly from the Folkestone Beds, Bargate Beds and parts of the Hythe Beds. Their composition is determined not only by the lithology of the underlying rock, but also by the presence of the superficial drift. This variability yields land of mixed quality. The poorest soils are left as heathland and are very acid. The deeper soils are easily worked, but are liable to drought due to their sandy nature.

2.3.1.5 Podzols, Sandy Brown Earths and Brown Sands

These occur in the western Weald supporting woodland, heaths and poor agricultural land on the Lower Greensand. These soils have formed mainly on the steep slopes of the Hythe Beds where podzols, and coarse sandy acid brown earths can be found. The overlying Sandgate Beds and Folkestone Beds are similar but with a less rugged topography. To summarise, these soils are infertile, acidic, coarse textured and therefore drought stricken in summer. Without liming and fertilization, crops fail.

2.3.1.6 Paleo-Argillic Brown Earths

Paleo-argillic brown earths have developed on the clay-with-flints and Plateau Drift of the Wealden downland. Clay has been illuviated from the upper horizons to form a clayey subsoil, probably when the climate was warmer than at present.

Similar soils are found on the Angular Chert Drift on the higher part of the Hythe Beds around Maidstone. Gleying can sometimes occur as the parent material in a reddish stony clay.

Most of these soils support woodland or rough grazing.

2.3.1.7 Stagnogley Soils and Brown Earths

The Hastings Beds sandstone varies from hard sandstone and siltstone to fine sands and silts, and occasional drift. Many of the soils have a compact subsoil which causes the development of springs and seepage lines.

Stagnogely soils are the most common and are characterised by mottles produced by reduction and mobilization of Fe and Mn in water and reoxidation during summer. Loamy to fine sandy soils occur where drainage is better, and silty or loamy drift forming brown earth is common on footslopes. Podzols can also be found in woodland on the Ashdown Beds.

These soils are typically acid, infertile and poorly drained, and much of the land is under woodland or pasture.

2.3.1.8.1 Stagnogley Soils

This is the most extensive soil association in the Weald and contains soils developed on the Hastings Clays and the Weald Clay. Surface water-logging occurs in the winter when precipitation cannot percolate through the fine subsoil, but the soil becomes extremely hard when dried out in summer. Sandstone, siltstone and limestone bands can be found in the Weald Clay which gives rise to lighter textured soils.

Land of this classification is mainly used for pasture or cereal growing, dominantly wheat which prefers heavy ground.

2.3.1.8.2 Stagnogely Soils

This association coincides with the Gault Clay Vale. These soils are similar to the Weald Clays, but also contain some heavy calcareous soils. Unlike Wealden Clays, Gault Clay is montmorillonitic and thus cracks widely in summer with a prismatic structure. These soils may be very acid.

The calcareous Upper Gault and derived Head tend to be better drained, but again develop the structure described above.

Composite soils can occur where drift is present. The Gault Clay soils are more versatile than the Wealden Clays and can grow a variety of crops.

2.3.1.9 Alluvial Gley Soils and Brown Calcareous Alluvial Soils

These soils are mainly found on the Romney Marsh which has been mapped in detail by Green (1968). The principal soil differences in the Marsh deposits are determined partly by the variability of sediments and geomorphology, which respectively govern soil texture and drainage, and partly by time. There is a wide variation in age; the Old Marshland (Figure 2.5) was settled before the 9th Century and therefore pedological processes have proceeded further. These include incorporation of organic matter, decalcification and leaching of soluble salts, and development of structure. The soil parent materials can be seen in Figure 2.8.

Former creeks in the Old Marshland are marked by ridges of about 1.5 m which developed as a result of differential shrinkage under the adjacent sediments which are thin or absent under the creek. They are capped by decalcified and moderately well-drained brown alluvial soils. The land between the creeks or "pools" is occupied by poorly-drained alluvial gley soils, usually of a clay texture which have been decalcified to a depth of 40-60 cm and which usually overlie peat at a depth of 1-2 m . These clayey soils are more extensive in the north-east of Romney Marsh.

Former creeks in the New Marshland are now lowlying swampy areas bounded by loamy levee type ridges with better drained brown calcareous alluvial soils. These grade into clayey deposits approximately 1 m lower with alluvial gley soils which can be calcareous at the surface. These dominate in the north-east of the Marsh, but in the east there is a greater proportion of loamy brown calcareous soils. The

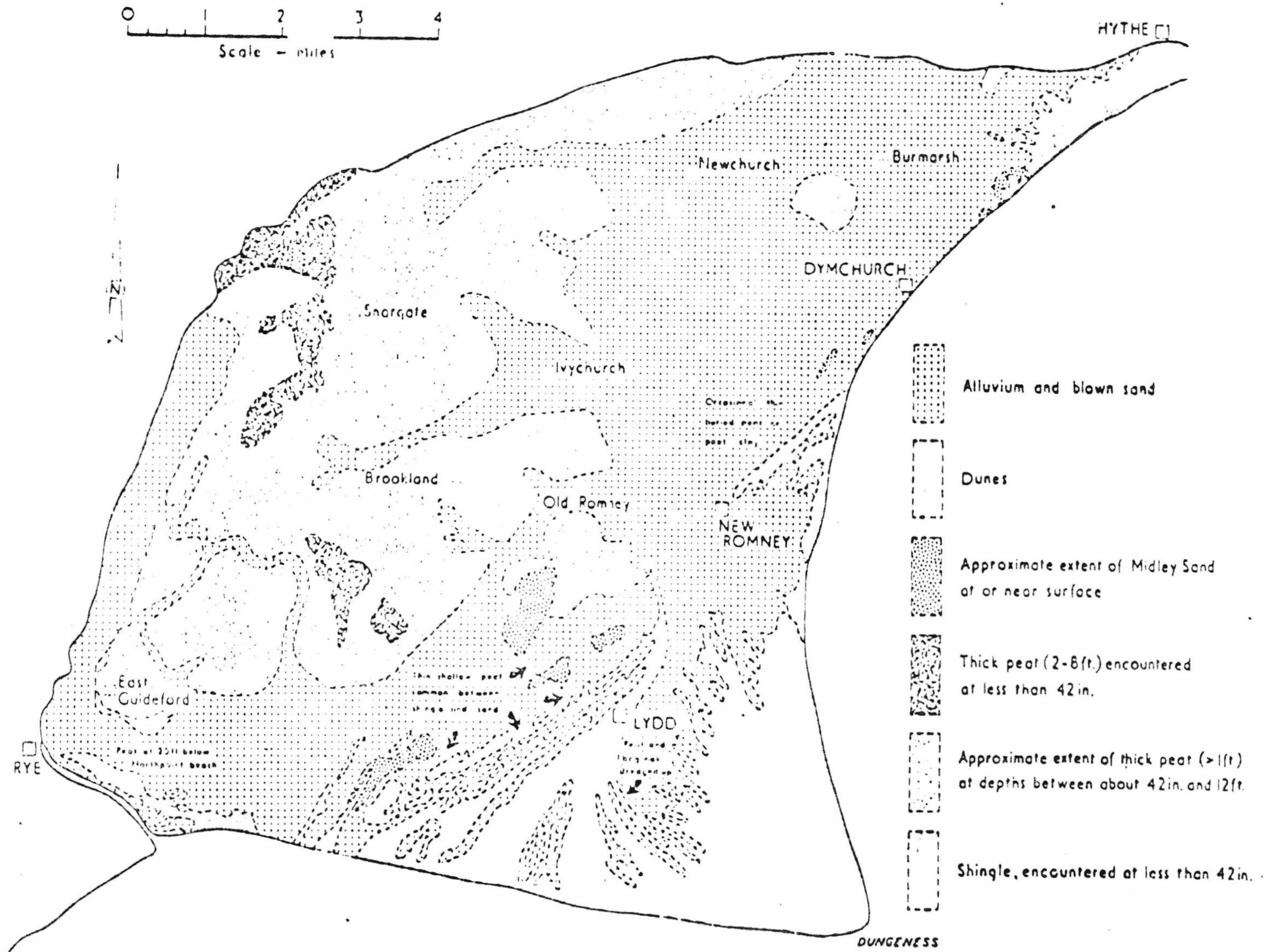


Figure 2.8 Romney Marsh Soil Parent Materials
(Green, 1968.)

soil series of the Romney Marsh can be seen in Table 2.4 overleaf.

Agriculturally, the Romney Marsh is very rich and with improved drainage much pasture has gone over to arable crops, including potatoes, peas, oilseed rape, strawberries, and cereals. Soil structure problems can occur in wet seasons but the main limiting factor is exposure.

2.3.1.10 Alluvial Gley Soils

Non-calcareous clayey alluvial gley soils can be found on the flood plains of the major water courses in the Weald. These soils are limited in use due to their heavy and wet natures.

Near Tunbridge and Ashford the alluvium passes into silty argillic gleys which can be drained and utilized for a variety of crops.

2.3.1.11 Raw Sands and Alluvial Soils

Raw soils are undeveloped immature deposits found on coastal sand and shingle. For example, the Dungeness shingle ridges have ungleyed raw alluvial soils.

Table 2.4

Drainage and Texture of the Soils of the Romney Marsh

(Green, 1968)

Drainage	Subsurface Texture	DOMINANT TEXTURE OF B HORIZON (30-75 cm)					
		COARSE		MEDIUM		FINE	
		Stony	Loamy Sand or Sand	Loam or Sandy Loam	Clay Loam	Clay Loam Over Silty Clay	Silty Clay or Clay
Well-Drained	Similar to B	Beach Bank[1]	Lydd[2] Midley[2]				
Imperfectly Drained	Similar to B		Greatstone[3]				
Imperfectly or Moderately Well-Drained	Similar or Finer Texture Below 75cm			Snargate[2]	Finn[2]	Brenzett[2] Walland[3]	Dymchurch[2] Newchurch[3]
	Loam to Sand Below 75cm to at least 105cm			Romney[3]	Agney[3]	Ivychurch[2] Guildford[3]	
Poorly or Very Poorly Drained	Thick Peat Occurs Between 60-105cm					Dowels[2] Fairfield[3]	
	Thich Peat Occurs Less Than 60cm						Appledore[2]

1. Beach Bank soils are locally calcareous
2. Decalcified soils
3. Calcareous Soils

2.4 Conclusions and Summary

1. The Weald of south-east England is extremely diverse geologically and pedologically.

2. Sediments range from the highly calcareous chalk to siliceous sands, clays and gypsum deposits. Grain size is also variable. Drift is extensive.

3. In general, the soils reflect the variety of underlying parent material, though Romney Marsh is an exception. Agriculture is diverse and generally prosperous.

CHAPTER THREE

SAMPLING AND ANALYTICAL TECHNIQUES

Introduction

This chapter presents a comprehensive account of the analytical techniques employed in this research with particular emphasis on the detection of arsenic, including a review of possible methods.

The main requirement of the research was an efficient, precise and sensitive technique for arsenic determination in a variety of environmental matrices. This was achieved by modifying recent developments in the field of hydride generation as a general method for Atomic Absorption analysis.

3.1 Sampling

3.1.1 Soil Sampling

The Wealden study area was sampled along eight transects at various points across the geological boundaries and more intensely locally in two sub-areas; one on the Romney Marsh and the second near Hythe. Approximately one sample was taken per square kilometre in these areas (Figure 3.1). Each sample was taken at least 100 m from major roads, and anomalous headland was avoided. Drainage vegetation and topographical features, as well as soil characteristics, were noted at each site.

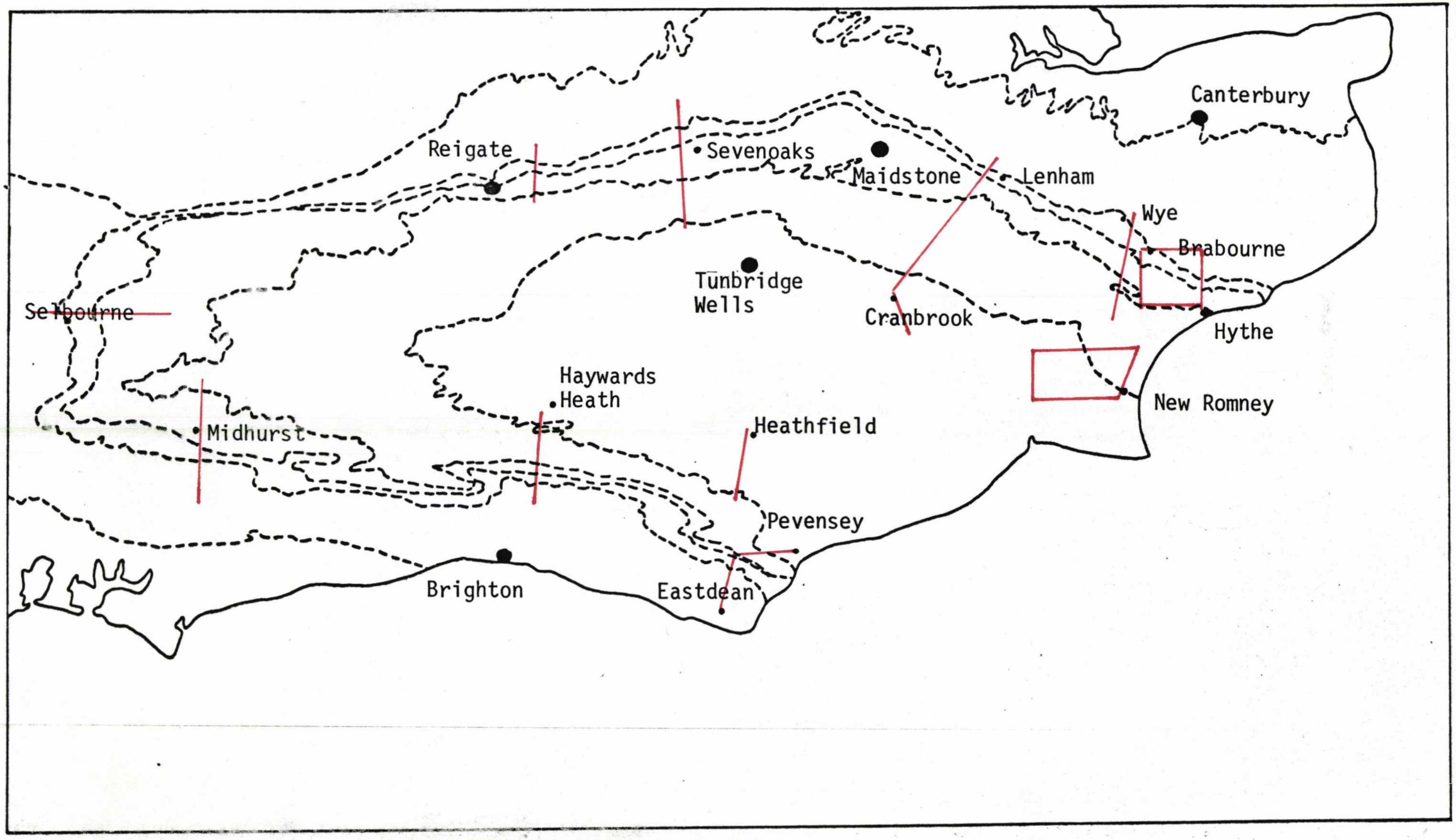


Figure 3.1 Location Map to Show the Soil Sampling Sites

Composite samples were made up of nine subsamples, taken to a depth of 25 cm in a W transverse using a steel screw auger. This is the approximate depth of the mixed plough layer and was constant for all sample points. The collected soil was placed in clean, labelled plastic bags to avoid contamination.

Several other sites were sampled to compare with the Wealden soils. These were taken from the Devonian Greenstones, Cambourne, Cornwall, on the Marlstone Rockbed near Melton Mowbray, Leicestershire, and from the Devonian Wealden counterpart in the Bas Boulonnais, France. Full details of all sample sites, including grid references are recorded in Appendix 1 .

3.1.2 Stream Sediment Sampling

Stream sediment samples were taken on the Romney Marsh only. These were collected using a single core auger pushed into a constant depth. For analysis purposes, these were then treated as soil samples.

Grid references are given in Appendix 1 .

3.2 Sample Preparation

3.2.1 Soils and Sediments

The samples were air-dried in the laboratory, and crushed and homogenised in a ceramic mortar and pestle to pass a 2 mm (10 mesh) plastic sieve. Care was taken not to crush gravel and stones. The resultant <2 mm fine earth fraction was stored in screw-capped bottles to await analysis.

3.2.2 Plant Material

Details of cultivation are given in Chapter 5.

To obtain precise results, freshly harvested plant material was quickly and thoroughly washed with distilled water to remove any surface deposits, and immediately dried in a forced-air oven at 65°C for 24 hours, since decay begins soon after sampling (Lockman, 1980). Samples were then ground and homogenised in a Wiley Mill with stainless steel blades and stored in sealed containers until analaysed.

3.3 Analytical Techniques

3.3.1 Arsenic Analysis

3.3.1.1 Historical Review of Arsenic Determination

Several recent reviews have been published on this subject, the major ones used here are: Luh, *et al.* (1973); Talmi, *et al.* (1975); Peterson, *et al.* (1978); Robbins and Caruso (1979) and Brooks *et al.*(1981).

Early analytical methods for arsenic determination such as Reinsh's method, Marsh's test, and Gutzeits test were qualitative rather than quantitative in nature, and results from these should therefore be treated with caution.

Several spectrophotometric methods can be used for quantitative analysis. The two most widely employed are silver-diethyldithiocarbamate (Ag-DDC) and ammonium molybdate. Both are usually carried out in conjunction with an arsine generation method. Arsine is passed through a 5% solution in pyridine and the intensity of the red colour is measured at 533 nm. Beer's Law is obeyed over the range 0-20 μg As/ml, the detection limit being <0.1 μg/ml (American Public Health Association, 1971). The molybdenum blue procedure is often considered more suitable because of its reliability and general freedom from interferences (Small and McCants, 1961). Arsine is generated by the reaction of H_2SO_4/HCl with mossy zinc and bubbled into a solution containing ammonium molybdate hydrazine sulphate, where the subsequent reaction forms a molybdenum heteropolyblue arsenic complex. Absorption is measured at 840 nm and is linear up to 2 μg/ml As.

Neutron activation analysis has been widely used for the determination of As in biological and environmental samples. The element is monoisotopic in nature (^{75}As) and is converted to ^{76}As by irradiation. The time required for this can range from a few minutes to several hours depending on the As content. The resultant γ-rays from ^{76}As are measured. Elevated levels of ^{24}Na, ^{42}K, and ^{58}Cl can interfere and various methods have been devised to overcome this problem. Detection limits are dependent on matrix composition, but Peterson *et al.* (1978) have reported a limit of 4 ng for orchard leaves. High equipment and operating costs are associated with this method.

Polarography can be utilised for As analysis by D.C. and square wave polarography, anodic stripping from a Pt electrode, and by differential pulse polarography. The latter seems to be one of the most sensitive electrometric methods available. Buldini *et al.* (1980) quantified As(111). As(V) and organic arsenic by a difference method with a detection limit of 1 μg/ℓ in water.

Arsenic has also been determined by coulometry. Woolson *et al.* (1971) compared this with the molybdenum blue method and found no apparent difference in accuracy, although coulometry was more precise.

Routine measurements can be made by X-ray fluorescence providing that the concentration is ≥10 μg/g . Preconcentration is necessary for lower levels. These techniques include evaporation, precipitation, ion-exchange and solvent extraction. For example, Carvalho and Hercules (1978) adsorbed arsine onto filter paper impregnated with mercury (11) chloride solution to give a detection limit of 3 ng , but the method is slow. Equipment costs are high and experienced technicians are required.

Atomic fluorescence spectrometry has also been used in conjunction with hydride generation techniques and a detection limit for arsenic of 5 ng has been reported by Nakahara *et al.* (1979).

Normal D.C. arc excitation flame emission spectrometry has a detection limit of 10 µg/g due to inadequate excitation energies. This can be improved by use of a matrix buffer and by co-precipitation with iron (111) hydroxide. However, plasma discharge sources are much more efficient and levels as low as 0.1 µg/ml in aqueous samples (Kirkbright *et al.*, 1973) and 0.001 µg in generated arsine samples (Lichte and Skogerboe, 1972) can be detected.

However, the most widely applicable instrumental technique for quantifying As is atomic absorption spectrometry (AAS). Conventional AAS does not provide the required sensitivity, mainly because the optimal analytical absorption line of 193.7 nm is in the ultraviolet range of the spectrum, where a 60% background absorption is encountered. The detection limit here is approximately 2 µg/ml with a similar sensitivty (Thompson and Reynolds, 1978). The introduction of the argon/hydrogen flame (Kahn and Schallis, 1968) reduced background absorption to 15% but the cool flame increased chemical interferences. To reduce these Holak (1969) generated arsine by a zinc/HCl reaction and finally passed it into an argon/hydrogen flame:

$$Zn + 2HCl \rightarrow ZnCl_2 + 2H \xrightarrow{As^{3+}} AsH_3 + H$$

Many papers have since been published based on this reaction.

The production of arsine is slow, particularly as As(V) must be first reduced to As(III). Absorbance peaks were broad so reservoirs were introduced to store the arsine and release it as a whole to give a sharper more reproducible peak (Fernandez and Manning, 1971).

A second, more effective method used to generate hydrides is the acid/sodium borohydride reaction:

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H^+$$

$$\xrightarrow{As^{3+}} \quad AsH_3 + H_{2(excess)}$$

Since its introduction by Braman *et al.* (1972) $NaBH_4$ has virtually replaced the metal/acid reaction. Although tablets of $NaBH_4$ have been used, solutions are now generally employed, and this has encouraged the development of mechanised procedures (Pierce, *et al.*, 1976; Vijan, *et al.*, 1976; Agemian and Cheam, 1978; Agemian and Bedek, 1980; Agemian and Thompson, 1980; and Arbab-Zavar and Howard, 1980). $NaBH_4$ generated hydrides have been treated in many of the ways used with the acid/zinc reaction. In the majority of modern hydride techniques, arsine is passed directly into a heated quartz cell (c. 1000°C), which acts as the atom reservoir. Heating can be electrical (Thompson and Thoresby, 1977; Wauchope, 1976), or by mounting the cell above the air-acetylene flame (Thompson and Thomerson, 1974; Evans, *et al.*, 1979). Detection limits are typically 1 ng/ml .

The $NaBH_4$ reaction is rapid and prereductants are not needed for mixtures of As(III) and As(V) below pH 1 where instrument response is related to concentration (Arbab-Zavar and Howard 1980). However, if organic arsenic species are not decomposed to inorganic forms, an under estimation of "total" arsenic can result due to comparison with inorganic standards (Hinners, 1980). Large excesses of elements capable of forming hydrides in the presence of the element of interest can interfere. This can be overcome by the addition of ethylenediamine-tetraacetic acid (EDTA) before reduction (Howard and Arbab-Zavar, 1981).

Electrothermal methods using a graphite furnace have been developed, but interferences are more common. The introduction of electrodeless discharge lamps has greatly improved the sensitivity and precision of analyses.

Other methods of analysis include ion-exchange (Tam, *et al.*, 1978), paper electrophoresis (Reay and Asher, 1977), paper chromatography (Miketukova, 1968), and gas chromatography (Andreae, 1977).

The detection limits of methods commonly used for arsenic analysis are summarised in Table 3.1 overleaf.

3.3.1.2 The Determination of Arsenic in this Research

Introduction

Experience with the molybdenum-blue colourimetric method showed that it was slow and tended to suffer from poor precision.

Table 3.1

Methods Commonly Used for Arsenic Analysis

Technique	Reported Detection Limit
Colourimetric:	
Ag-DDC	0.1 μg/ml[1]
Molybdenum Blue	
Neutron Activation	0.004 μg/g[2]
Polarography	0.001 μg/ml[3]
X-ray Fluorescence:	10.0μg/g
Preconcentration	0.003 μg/g[4]
Atomic Fluorescence Spectrometry	0.005 μg/ml[5]
Atomic Emission Spectrometry:	
D.C. arc	10.0 μg/g[6]
D.C. plasma (aqueous)	0.1 μg/ml[7]
(hydride)	0.001 μg[8]
Atomic Absorption Spectrometry	
Atom Reservoir: air-acetylene	2.0 μg/ml[9]
argon-hydrogen	0.1 μg/ml[6]
quartz tube	0.001 μg/ml[10]
graphite furnace	0.001 μg/ml[6]

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1. American Public Health Association (1971)
2. Peterson *et al.*(1978)
3. Buldini *et al.*(1980)
4. Carvalho and Hercules (1978)
5. Nakahara *et al.* (1979)
6. Brooks *et al.* (1981)
7. Kirkbright *et al.* (1973)
8. Lichte and Skogerboc (1972)
9. Thompson and Reynolds (1978)
10. Thompson and Thoresby (1977)

The determination of arsenic by $NaBH_4$ hydride generation coupled to atomic absorption spectrophotometry with thermal atomisation reviewed previously was employed in this investigation. The method used in this study modifies and incorporates details from a variety of literature reports.

Experimental

Reagents and Glassware

All chemicals used were of analytical grade unless otherwise stated; solutions were prepared with double distilled deionised water. Glassware was soaked in "pyroneg" and thoroughly rinsed with distilled water before use. Stock solutions of 1000 μg/ml arsenic were prepared from arsenic trioxide (AsIII) and sodium arsenate (AsV). Solutions of lower concentration were prepared from these. Laboratory reagent grade $NaBH_4$ was made up fresh each time as a stabilised 2% solution in 1N sodium hydroxide. A certified reference material, antimony-arsenic ore CD-1 was taken up into solution by treatment with $HF/HClO_4$ and used as a known standard of 0.066 μg/ml As.

Apparatus

The apparatus is shown schematically in Figure 3.2. The custom-made hydride generator cell was constructed from a Quickfit B19 socket fitted with two-side arms and a trap at the base for the removal of waste. A Dreschel head admitted the nitrogen carrier-gas into the generator cell. The side-arm near the base of the cell was angled and sealed

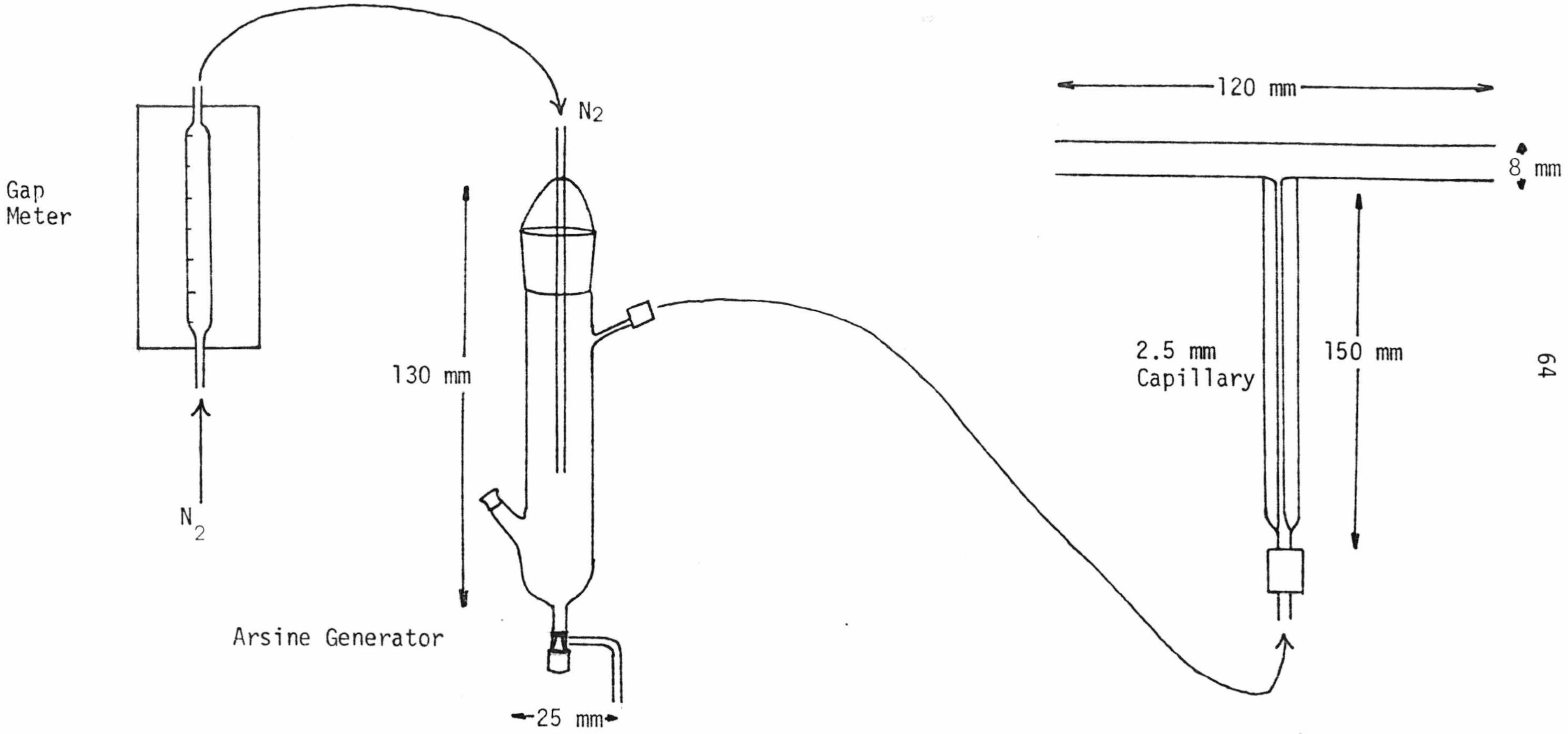


Figure 3.2 Schematic Diagram of the Hydride Generation Apparatus

with a subaseal No.13 for the injection by Eppendorf pipette of sample and $NaBH_4$. The narrow side-arm near the top of the cell made a gas-tight seal via a swagelock with a short length of polypropylene tubing which carried the hydrides to the quartz furnace cell.

The quartz tube atomiser (12 cm × 8 mm i.d.) was mounted 1 cm above the burner head of a Pye Unicam SP90 Atomic Absorption Spectrophotometer, and was heated with an air-acetylene flame. It was important to align the tube to obtain the maximum signal possible.

The carrier gas flow was monitored by a gas meter calibrated to give a steady nitrogen flame of $2.5\ cm^3/s$ (150 ml/min.).

The absorption signal was recorded by a Servoscribe chart recorder, set at 1 cm per min. The following spectrophotometer conditions were maintained throughout: wavelength, 193.7 nm; lamp current, 10 mA; low gain 9; slit width, 1 mm.

Sample Digestion

Several acid mixtures have been used to extract arsenic from sediments, soils and plant material. Gorusch (1959) showed that a HNO_3-$HClO_4$ mixture is an efficient means of recovering As without losses. However, Kang and Valentine (1977) showed that the order of decreasing acid interference was $HNO_3 > H_2SO_4 > HClO_4$. The action of HNO_3 in digests was investigated in greater detail by Brown *et al.* (1981) who showed that NO_3^- and HNO_3 are not serious inhibitors of

AsH_3 evolution but reduced nitrogen oxides (NO_2^-, etc) produced in sample digestion were. Heating HNO_3 digests will remove reduced forms of nitric acid.

As previously mentioned organoarsenic compounds must be destroyed to yield a true "total" As value. A $HNO_3/HClO_4$ acid mixture is sufficiently oxidising to break down these compounds (Agemian and Thompson, 1980).

Aluminium hot-blocks have been used for the digestion of soils and vegetation (Vijan, 1976). The use of long test tubes in the block produces a refluxing action during digestion, and coupled with the ease of temperature control makes it a very efficient and reproducible sample processing technique. A large number of samples can be digested simultaneously.

Hot-Block Construction

The dimensions of the hot-block can be seen in Figure 3.3 overleaf.

Borosilicate glass test tubes (150 × 16 mm) were used in the block to digest the samples. The block was placed on a Gallenkamp con-tem-plate hotplate, and the temperature was monitored by a thermometer suspended in glycerol in one of the tubes.

Digestion Procedure

0.100 g of prepared sample (soil, sediment or vegetation) was weighed into a test tube. To this was added 3 ml of a

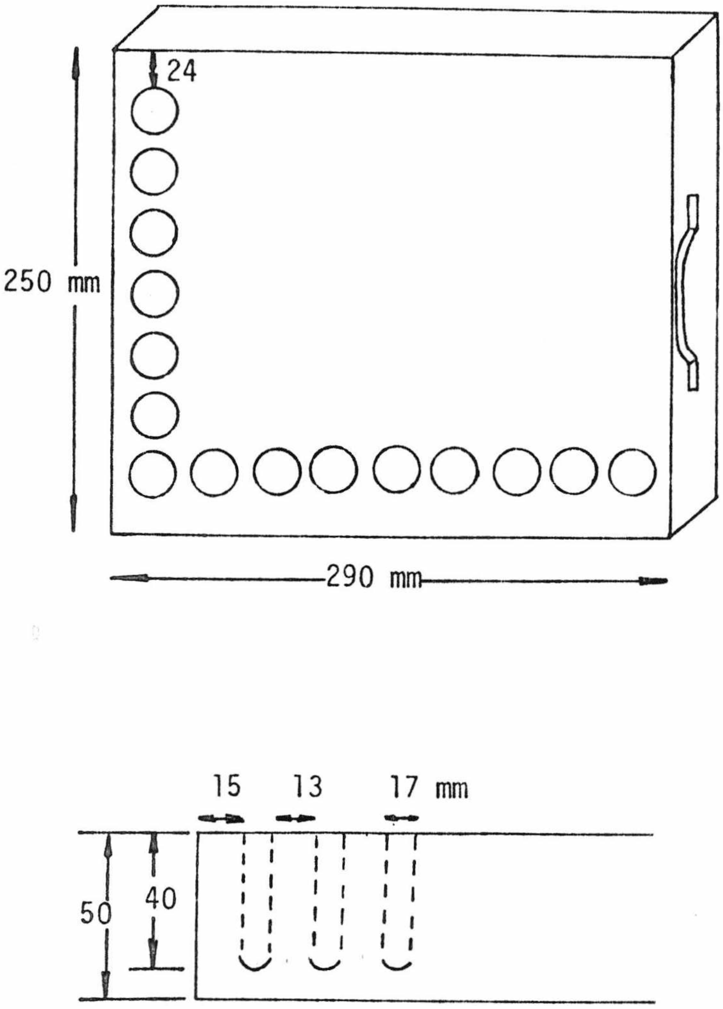


Figure 3.3 Details of Hot-Block Dimensions

4:1 mixture of $HNO_3/HClO_4$ (70%) acids. The tubes were placed in the aluminium block in a fume cupboard for one hour at room temperature. Sixty tubes plus a reagent blank could be processed simultaneously. After that time period anti-bumping granules were added to the tubes and the block gradually heated up to 200 °C . This temperature was maintained for at least three hours until a clear solution of low volume was obtained containing a white siliceous residue. The samples were then allowed to cool to room temperature, and the residue was leached and made up to volume with 1.5 N HCl to give an arsenic concentration not greater than 0.1 μg/ml .

When vegetation containing low concentrations of As was digested, the procedure was multiplied up and carried out in conical flasks with refluxing bubbles (see Section 3.2.1). This however was less efficient than the hot-block and therefore took longer to complete.

Hydride Generation

The optimum conditions required for arsenic determination by hydride generation have been investigated in some detail by Arbab-Zavar and Howard (1980). The cell dimensions, carrier gas flow-rate, $NaBH_4$ concentration and sample acid concentration are inter-related and determine the rate of hydride generation and therefore the shape of the absorption signal. By experimentation the optimum conditions for this apparatus were found to be: N_2 flow rate 150 ml/min.; 1 ml of 2% $NaBH_4$ in 1N NaOH reacting with 1 ml of sample in 1.5 N HCl . Under these conditions As(III) and As(V) were detected with equal sensitivity.

Arsenic Determination Procedure

The AAS was switched on and the quartz tube heated in the normal air-acetylene flame for ten mins. to warm up and stabilise. Meanwhile the N_2 flow was adjusted to the correct rate. 1 ml of standard was introduced through the injection port followed by 1 ml of $NaBH_4$ injected directly into the standard. The absorption response was immediate. When the signal had returned to the base line, the waste was removed via the tap on the generator cell, and after allowing a few seconds for the ingressed air to be swept from the system, the procedure was repeated until a uniform response was obtained.

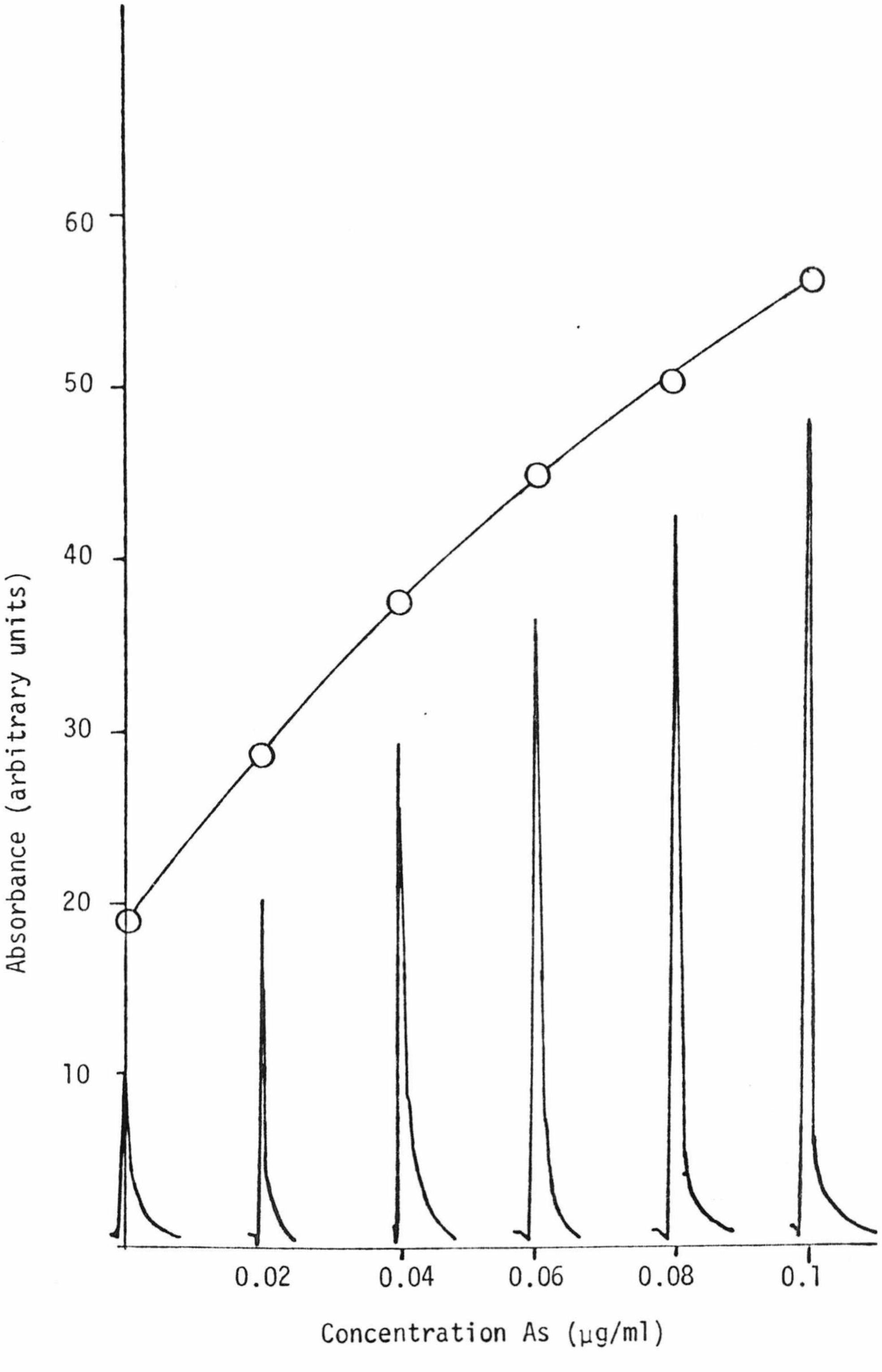
Calibration was carried out before and after each batch of samples and all readings were duplicated. The standard reference material CD-1 was also included in each batch. The absorption signals were measured as peak heights and the readings for a particular sample averaged and a blank correction made. Figure 3.4 shows typical calibration traces and the resulting graph. The response was found to be linear over the range 0-0.1 μg/ml As.

Discussion of Method

Initially the $NaBH_4$ solution was injected above the sample/standard, but this was found to give a broad variable peak due to uneven mixing. By afixing a 50 mm (11/10) needle onto the pipette tip and injecting directly into the acidified solution a sharp reproducible peak response was obtained. It was found to be important to adopt a consistent technique for injection, as slow or interrupted use produced poorly defined peaks.

After the quartz tube had been conditioned for use, it had

Figure 3.4 An Example of a Typical Arsenic Calibration Graph



a limited life expectancy of about 400 injections. This was due to the gradual build-up of sulphates, especially sodium sulphate, on the wall of the tube which eventually cracked as a result of differential cooling when the flame was extinguished. The coating must become bonded in the glass matrix because soaking in HF failed to remove any appreciable amount of it. Howard and Arbab-Zavar (1981) passed the hydride gas flow through the lead acetate scrubber to remove hydrogen sulphide and through a sodium hydroxide drying trap. It was found by the author that the inclusion of these interrupted the gas flow and gave less reproducible results. The NaOH pellets tended to fuse in the trap after only about twenty injections and becameinefficient and therefore it was decided to adopt the simple system described and replace the quartz tube as necessary.

A background value was found through the inclusion of blanks. The As here was thought to originate from the $NaBH_4$ and this agrees with the findings of other workers (Thompson and Thomerson, 1974).

No interferences were detected in standard solutions of As(V) containing 1.0 μg/ml Cu and Zn , 10.0 μg/ml Mn and 50.0 μg/ml Fe. These levels were greater than those normally found in soil digests where the dilution factor was frequently greater than 100.

Large dilutions could be a possible source of error and care was taken to minimise this possibility.

The sample digestion was found to be sufficiently oxidising to break down organic arsenic compounds since a sharp peak response was obtained (organic arsenic compounds have a boiling point of +55° C compared to +2° C for inorganic arsenic (V) and therefore if any were present double or broad peaks would have been obtained).

A major advantage of this method is the speed of analysis. It was found that one injection could be made per minute.

3.3.1.3 Extraction of "Available" Arsenic

Available As was extracted by shaking 2 g of the fine earth fraction with 20 ml of Bray-Pl solution (0.025 N HCl - 0.03 N NH_4F) for 5 mins and centrifuging (Bray, 1948; Aggett and Aspell, 1980). The supernatant was dried in an oven overnight and the residue digested and analysed as described in 3.3.1.2.

3.3.2 Analysis of Copper, Iron, Manganese, and Zinc by Atomic Absorption Spectrophotometry

Introduction

One of the main advantages of analysis by atomic absorption is the lack of spectral interferences enabling sample dissolution to be confined to dissolution of the sample, or simple extraction of the elements of interest. Therefore handling errors are minimised and analyses can be performed rapidly and reproducibly.

Since the basic principles of AAS are well-known they will not be described here. Further details can be found in Thompson and Reynolds (1978).

3.3.2.1 "Total" Metal Digestion Procedure

2.000 g of the fine earth fraction (< 2 mm) was weighed into 100 ml conical flasks. To this was added 20 ml conc. HNO_3 A.R. and the flasks were loosely stoppered with a glass condensing bubble. The samples were refluxed for 3-4 days until no further nitrogen dioxide was evolved and the soil was a light grey colour indicating that all the organic matter was decomposed. They were then evaporated to dryness. 5 ml of 6N HNO_3 was added to the residue and after approximately one hour this was filtered, washing the siliceous residue thoroughly and made up to 25 ml with deionised water, thus giving an approximate final concentration of 1N HNO_3 which is suitable for atomic absorption.

NOTE: This does not release metals trapped in the crystal lattice.

3.3.2.2 Extraction of Available Mn, Cu, Zn and Fe

An extracting solution of 0.005 M diethylenetriamine-pentaacetic acid (DTPA), 0.01 M calcium chloride ($CaCl_2$) and 0.1 M triethanolamine (TEA) buffered at pH 7.3 was prepared. 20 ml of the DTPA extractant was shaken with 10 g of soil (< 2 mm) at 25°C for 2 hours. The slurry was filtered and analysed by AAS.

Since Fe and Mn deficiencies are most prevalent on calcareous soils, the extractant was designed to avoid excessive dissolution of $CaCO_3$ and release occluded micronutrients which are normally unavailable. This was achieved by buffering TEA at pH 7.3 and including soluble Ca^{2+}. At pH 7.3 $CaCO_3$ dissolves only slightly and reaches equilibrium at a CO_2 partial pressure of approximately ten times the atmosphere (Lindsay and Norvell, 1978).

3.3.2.3 Determination of Cu, Fe, Mn, and Zn

The validity of each determination was checked by the inclusion of "blank" controls and replicates of samples. All equipment was cleaned before use with "decon" (a chelating agent) to reduce external contamination. Samples were analysed as quickly as possible to reduce metal adsorption onto the surface of the storage container.

Measurements were made using a Pye-Unicam SP 90 under the following operating conditions. (See Table 3.2 overleaf.)

Calibration solutions were made up using the appropriate extractant from the sample processing.

3.3.3 Other Analytical Techniques

3.3.3.1 pH

The pH of each soil was determined by shaking a mixture of 1:2.5 w/v of soil and deionised water for ten minutes and then introducing a pH probe into the slurry (combined

Table 3.2

Atomic Absorption Operating Conditions for Cu , Fe , Mn and Zn

Element	Wavelength (nm)	Maximum Lamp Current (mA)	Optimum Level µg/ml	Sensitivity µg/ml	Interferences
Cu	324.8	5	0.5-10	0.1	None
Fe	372.0	15	20.0-200	2.0	None
Fe	248.3	15	0.2-20	0.1	*
Mn	279.5	12	2.0-20	0.1	None
Zn	213.9	10	0.1-4	0.025	None

* Ionisation occurs at low levels

glass electrode and calomel half cells). The stable recording was measured by a Radiometer Copenhagen PHM 62 standard pH meter which had previously been calibrated with buffers of pH 4,7 and 9 . This equipment is accurate to ±0.01 pH units. (Avery and Bascombe, 1974.)

3.3.3.2 Calcium Carbonate Content

The method used was that described by Bascombe (1961). The apparatus can be seen in Figure 3.5.

Procedure

The dye and the acid were saturated with CO_2 by decomposing about 1 g $CaCO_3$ with acid in flask F and leaving for half an hour with taps A and B closed. After saturation the flask was replaced by a 250 ml conical containing a weighed representative subsample of air-dry soil (< 2 mm). Suitable weights for a 0-100 ml graduated manometer are:

20 g	for soils containing	<5% $CaCO_3$
10 g		<10%
5 g		10-20%
0.5 g		>30%

See Figure 3.5 overleaf.)

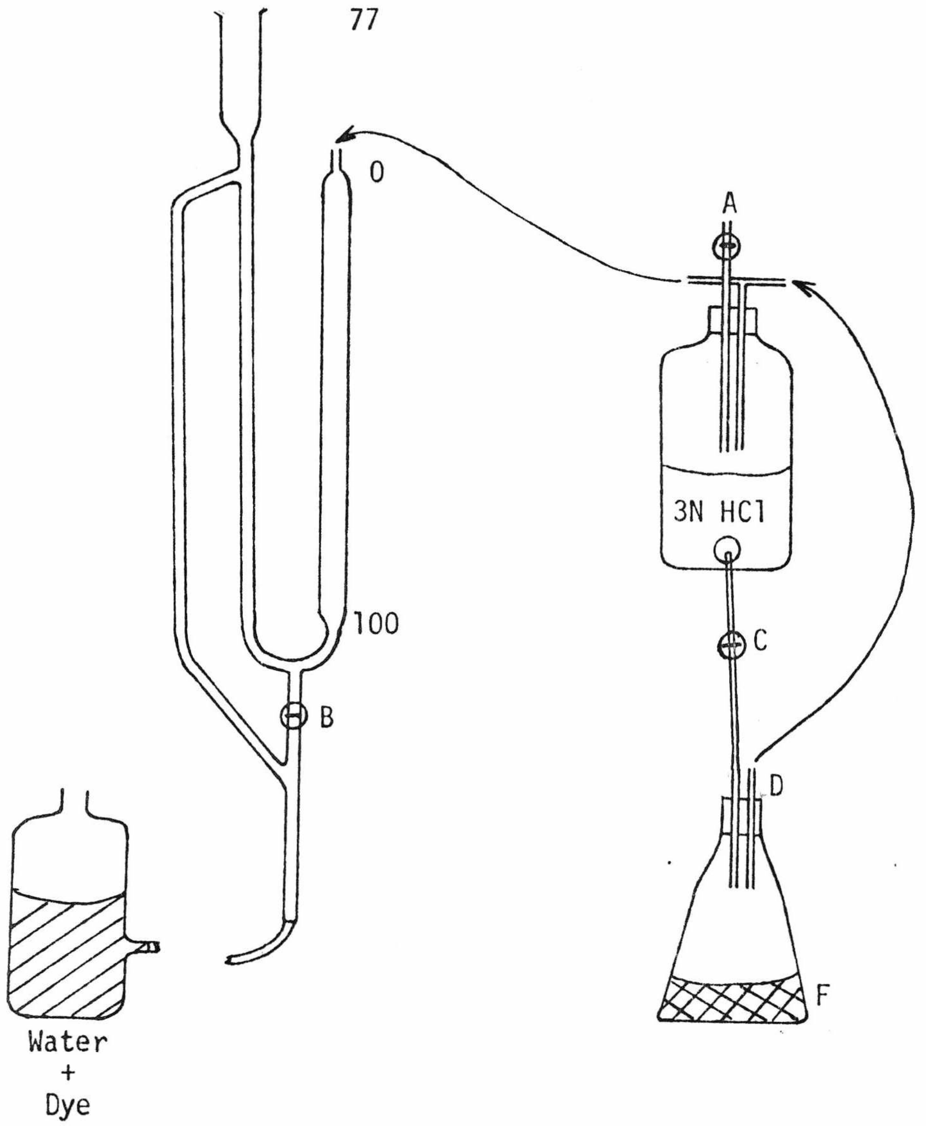


Figure 3.5 The Calcimeter used in this Study

Tap A was opened and a moist bung (D) was inserted into F. The reservoir was filled until the liquid was above the 0 ml graduation, and was then lowered to this mark by using tap B. Tap A was then closed and the acid inlet C opened until the sample became fluid. The efficiency of the apparatus was increased by agitating the sample with a magnetic stirrer. Further acid was added until all reaction ceased and a constant equal level was shown on the manometer. The volume of CO_2 evolved was measured and the air temperature and barometric pressure noted. The recovery was checked by decomposing 0.5 g $CaCO_3$.

The result is expressed as $CaCO_3$ equivalent as there may be some $MgCO_3$ in the samples.

$$\% \ CaCO_3 = \frac{\text{vol. } CO_2 \text{ (ml)}}{\text{mass sample (g)}} \times \frac{\text{barometric pressure (mm Hg)}}{\text{temperature } {}^0C + 273} \times K$$

where

$$K = \frac{273 \times 100}{760 \times 224} = 0.1604$$

3.3.3.3 Loss on Ignition (LOI%)

The organic matter content was determined using the method outlined by Avery and Bascombe (1974). Approximately 5 g of soil was placed in weighed cruicibles and put in an oven overnight at 105°C to remove hygroscopic water. These were then placed in a desiccator and weighed when cool. Following this they were heated in a muffle furnace at 850°C for a minimum of 30 mins (longer is needed for calcareous soils). When they had cooled sufficiently to be handled with tongs they were then replaced in the desiccator to prevent the re-entry of water and then finally weighed when cold. Re-ignition to constant mass was used to check completion.

$$\text{LOI\%} = \frac{\text{mass oven dry soil (g) - mass ignited soil (g)}}{\text{mass oven dry soil (g)}} \times 100$$

and for calcareous soils:

$$\text{Corrected LOI\%} = \text{LOI\%} - 0.44 \times CaCO_3 \ \%$$

3.3.3.4 Particle Size Analysis

The procedure followed was the Pipette Method of Smith and Atkinson (1975).

10 g of the fine earth fraction (< 2 mm) was weighed into a tall 600 ml beaker. 50 ml of H_2O_2 (30 vol) was added and the mixture left to stand for one hour when a further 50 ml was added and warmed gently until the reaction subsided indicating all the orgnaic matter was decomposed. The mixture was boiled for a few minutes, allowed to cool, and diluted to about 200 ml with distilled water. Carbonate was removed by the addition of 25 ml of 2N HCl to the suspension, which was allowed to stand for one hour with frequent stirring. The solution was tested with litmus paper to make sure that it was acid. The soil solution was then filtered through a Buchner funnel (Whatman No.50), and washed with water to remove the acid. The soil was dried as much as possible and transferred to the beaker where 200 ml of distilled water was added.

To disperse the soil particles so they are non-aggregated in suspension, all the clay particles were saturated with sodium ions. This was achieved by adding 2 ml of 2N NaOH and stirring for 15 mins. The suspension was then transferred to a one litre measuring cylinder and made up to the mark with distilled water. The settling velocities of particles through 10 cm of water have been calculated and their settling times are given in Table 3.3. To determine the proportion of silt and clay present the temperature of the liquid was taken and the settling time before sampling at 10 cm determined.

Table 3.3

Settling Times of Fine Sand and Silt Through 10 cm of Water

(Smith and Atkinson, 1975)

Temperature °C	Fine Sand		Silt	
16	5 min	19 sec	8 hr	51 mins
17	5	10	8	37
18	5	3	8	24
19	4	55	8	12
20	4	48	8	0
21	4	41	7	48
22	4	34	7	37
23	4	28	7	26
24	4	22	7	16

The cylinder was stoppered and shaken for one minute to re-suspend all the sediment. It was placed on a bench and a 20 ml pipette inserted 30 sec. before the designated sampling time. The pipette was held exactly 10 cm above the surface of the sample by a piece of card. The extracted 20 ml aliquot was ejected into a previously oven-dried and weighed evaporating basin and was evaporated at 105°C, cooled in a desiccator and reweighed.

$$\text{Silt + clay in sample} = \text{weight of aliquot} \times \frac{1000}{20}\ \text{g}$$

The cylinder was reshaken and allowed to stand for eight hours in a position of uniform temperature. The sampling was repeated and the weight of clay in the sample calculated as above.

The sand content of the sample was determined by decanting the supernatant liquid and washing the sediment into a tall 600 ml beaker. A mark was made 10 cm from the base and the beaker filled to this mark with distilled water. The sediment was stirred and allowed to stand for the appropriate time for the sand to settle out (Table 3.3) and the supernatant liquid discarded. This process was repeated until the liquid was clear at the correct time. The sand was dried and weighed as before.

3.3.3.5 Adsorption Characteristics of Soils

The adsorption capacity of soils was estimated using the method of Hiltbold *et al.* (1974).

Duplicate 5 g soil samples were equilibrated with 5 ml of an aqueous 50 μg/ml As(V) solution. The suspension was shaken overnight on a horizontal reciprocating shaker and then centrifuged. The concentration of arsenic in the supernatant liquid was determined as in Section 3.3.1.2.

Equilibrium distribution coefficients (K_d) were calculated using:

$$K_d = \frac{C_0 - C}{C} \quad (V/W)$$

where C_0 is the initial As concentration; C is the As concentration in the supernatant liquid; V is the volume of solution used, and W is the weight of soil taken.

3.4 Estimation of Analytical Precision

Introduction

Commonly within-batch precision is estimated by repeatedly analysing one or more samples and calculating the standard deviation. There are however, drawbacks associated with this method:

i. the sample taken for repeat analysis may not represent the series as a whole because chemical composition of the matrix varies

ii. extra preparation is required to maintain homogeneity over long periods

iii. precision estimates are likely to be unrealistically low if the samples are analysed consecutively and are known to the analyst

iv. large numbers of recordings have to be made to obtain a realistic standard error, and this reduced analytical efficiency

v. the variation of standard deviation with concentration is not determined.

The methods described by Thompson and Howarth (1976) remove or reduce the above drawbacks. They are based on the duplicate analysis of all, or a random selection of the samples. To obtain an accurate estimation of precision, each duplicate must be treated as a separate sample and analysed in random order. All duplicated analyses can be found in Appendix 2.

Each soil sample was replicated for the determination of As , and the precision was calculated as follows. (Based on Thompson and Howarth, 1976).

i. From the duplicate analyses the means of the pairs and the corresponding difference between them are calculated i.e. (x+y)/2 and (x-y).

ii. The duplicates were arranged in increasing order of concentration means.

iii. The mean concentration and the median difference for successive groups of 9 in the list, ignoring any remainder less than nine were obtained.

iv. The linear regression of the medians on the means was calculated:

Mean Concentration of Duplicates	Median Difference Between Duplicates
3.1	0.2
4.7	0.4
5.4	0.3
5.9	0.5
6.2	0.4
6.6	0.4

Mean Concentration of Duplicates	Median Difference Between Duplicates
7.0	0.5
7.6	0.5
8.0	0.5
8.3	0.6
9.0	0.5
9.9	0.4
11.0	0.9
11.9	1.0
13.4	1.0
14.8	0.7
16.2	0.4
16.9	1.1
17.9	0.6
22.0	0.8
208	4.9

Precision (p_c) here is specified as the coefficient at concentration C

$$p_c = \frac{\sigma_0}{c} + k$$

where

σ_0 is the standard deviation at zero concentration (i.e. the intercept)

k is the slope of the linear regression

From this the variation of precision with concentration for As was found to be:

$[As]_{\mu g/g}$	P_c
5	9.4%
10	5.8%
15	4.6%
20	4.0%

v. the detection limit (c_d) was calculated from

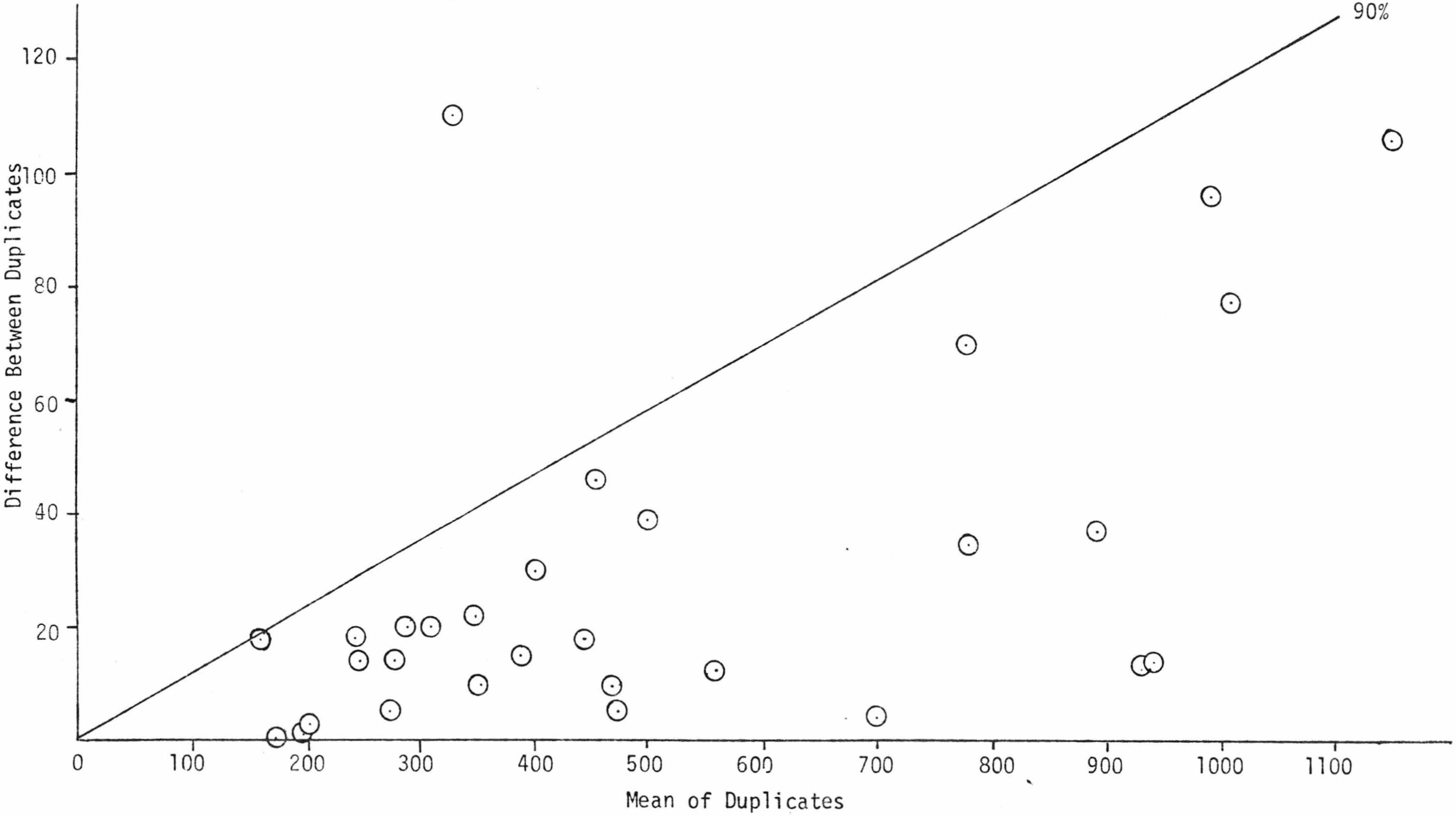
$$c_d = \frac{\sigma_0}{1-k}$$

and was found to be 0.37 μg/g As .

A comparatively small number of replicates were processed for the other elements analysed in this study. Thompson and Howarth (1976) state that for a specified relationship between standard deviation and concentration, it is possible to predict the frequency distribution of absolute differences at any given concentration, assuming that the Gaussian curve is followed. Observation of the actual distribution of a small number of experimentally determined values makes it possible to determine whether the experimental precision exceeds the specification. Assuming a 10% precision the 90th percentile was calculated via the method of Thompson and Howarth (1976) for each set of replicates.

Each set of replicates was found to obey the 10% precision specification. An example is shown for "total" Mn in Figure 3.6. The point above the line is thus quite obviously a wild result, since the rest of the set obeys the specification.

Figure 3.6 Plot to Show the Reproducibility of Manganese Determinations



CHAPTER FOUR

ARSENIC IN WEALDEN SOILS

4.1 Occurrence and Geochemistry of Arsenic in Rocks and Soils

4.1.1 Arsenic Distribution

Arsenic,a metalloid, is ubiquitous in nature occuring in most rocks and soils in detectable concentrations. It is regarded as a chalcophile element and is concentrated in mineral deposits. The principal arsenic minerals include:

realgar	As_4S_4
orpiment	As_2S_3
cobaltite	CoAsS
niccolite	NiAs
arsenopyrite	FeAsS

Arsenopyrite is the most common arsenic mineral and is frequently associated with ores of Sn , W , Ag and Cu . Arsenic is also found in minor quantities in most of the common sulphides and secondary oxidation products, particularly sulphates.

Table 4.1

The Mean Distribution of As in Rocks (μg/g) (Bowen, 1979; Rose *et al.* 1979)

Average Crystal Abundance	Igneous Rocks	Shales	Sedimentary Rocks Sandstones	Carbonates
2	1.5	13	1	1

There is very little variation in the arsenic content of igneous rocks (Boyle and Jonasson, 1973) and from Table 4.1 it can be seen that amongst sedimentary rock types, As is concentrated in the finer-grained deposits. Sulphide ores, sedimentary iron and manganese ores, and rock phosphates may contain as much as 2,000 μg/g As (Table 4.2)

Table 4.2

Typical Ranges and Levels of As in Various Deposits (μg/g) (Krauskopf, 1955; Bowen, 1979)

Lignite	Phosphorites	Sediments	
		Iron-Oxide	Manganese-Oxide
1-55	30	10-700	70

In general, soils tend to reflect the chemical composition of their parent materials. Table 4.3 is a compilation of recently documented reports which illustrates the natural range of abundance levels for As in soil types.

Table 4.3

Arsenic Concentrations in Uncontaminated Soils

Mean Soil As (μg/g)	Range	Country	Reference
6.0			1
	5-15	Sweden	2
	0.1-30		3
7.2	0.1-55	Worldwide	4
	8-13	China	5
	<5-100	Britain	6
	0.2-40	U.S.A.	7
11.4	0.12-22	Italy	8

1. Bowen (1979)
2. Lindau (1977)
3. Aten *et al.* (1980)
4. Boyle and Jonasson (1973)
5. Group on Natural Background Values of Soils (1980)
6. Thornton and Webb (1980)
7. Walsh *et al.*(1977)
8. Polemio *et al.* (1980)

From this it can be seen that the ranges are fairly similar worldwide. The higher value shown for Britain is as a result of natural mineralisation in the south-west.

4.1.2 Arsenic Soil Chemistry

Walsh and Keeney (1975) have published a good review on the behaviour of inorganic arsenicals in soils.

Arsenic is a member of Group V in the Periodic Table and is believed to be very similar to phosphorous in behaviour. It is, however, more mobile than P and can undergo valence state changes under the range of redox conditions likely to be found in soils (Bohn, 1976). Under reducing conditions elemental As and arsine ($AsIII^-$) are the stable forms. Arsenate (AsV^+) is thought to be the stable form in aerated soils with arsenite ($AsIII^+$) present in mildly reducing conditions.

All these valence states can form C-As compounds and are readily interconverted by microbial activity (Wood, 1974). Thus arsenite added to a well-drained aerated soil with significant biological activity is oxidised rapidly to arsenate as demonstrated by Porter and Peterson (1977), who showed AsIII mine spoil to be now mainly AsV. Conversely, arsenate in reducing conditions can be converted through arsenite to dimethylarsinic acid. Atkins and Lewis (1976) found that gaseous arsenic evolution was a function of organic matter and moisture content. The greatest loss occurred from reducing soils with a high organic matter content. Davies (1980) envisaged the reactions of arsenic to be those shown in Figure 4.1.

The concentration of soluble As in soils is a function of the adsorption capacity of the soil. Among the cations that react with

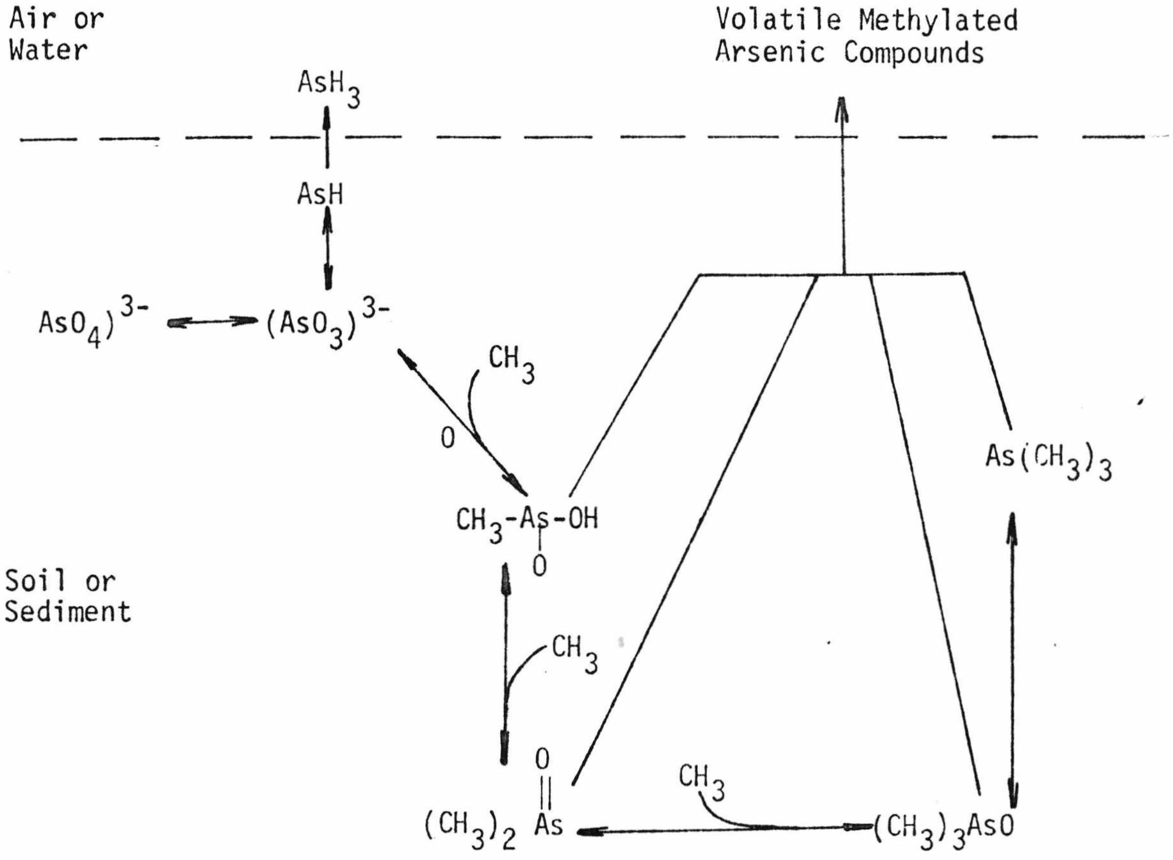


Figure 4.1 Biogeochemical Reactions of Arsenic

As are Fe , Al , Ca and Mg . The main constituents which control arsenic solubility appear to be iron and aluminium compounds. Woolson *et al.* (1971), Jacobs, *et al.* (1970) and Livesay and Huang (1981) found that As adsorption was linearly related to oxalate extractable Fe and Al is soils (mainly Fe and Al hydroxides). Many hydrous oxides generate a significant number of positive charges as the pH falls. For example, goethite (α-FeOOH) is positively charged below pH 8-8.5 and gibbsite (γ-$Al(OH)_3$) below pH 9, and anions would be electrostatically attracted to these species.

Clay minerals also seem to be important in arsenic retention in soils. Johnson and Hiltbold (1969) found that 90% of As was associated with the clay fraction in an organoarsenic treated soil. Thus arsenic would be expected to be more mobile in a sandy soil than a fine-texture clay soil. This also provides an obvious explanation for the high As abundances found in shales relative to sandstones (Table 4.1). This relative immobility has been noted by various workers, for example Aten *et al.*(1980), and Peterson (1979) reported that arsenic-rich acid sites which had remained undisturbed for 70 years showed only limited movement down the soil profile.

Extractable As decreases with time from As-treated soils (Jacobs, *et al.*,1970; Woolson, *et al.*, 1973) which demonstrates the importance of adsorption mechanisms. This is further supported by the fact that phosphate anions appear to be preferentially adsorbed compared to arsenate (Woolson *et al.*,1973) and the high proportion of arsenate removed by neutral salts (Jacobs *et al.*,1970).

Thus arsenate in soils is mainly retained through sorption processes (Walsh *et al.*,1977).

4.1.3 Arsenic Distribution in South-East England as Shown by the Wolfson Geochemical Atlas

Published data on arsenic in south-east England are limited to geochemical reconnaissance surveys based on stream sediment sampling presented in the Wolfson Geochemical Atlas of England and Wales

(Webb *et al.*, 1978) described in Chapter One.

Figure 4.2 is a compilation of the stream sediment data for As, based on the Wolfson Atlas. The summary in Table 4.4 gives a general indication of relative abundances which might be expected if the soil chemistry reflects the parent material.

The highest concentration of As in south-east England is found on the Romney Marsh. Examples of the values found by the Applied Geochemistry Research Group were kindly communicated by Dr. I. Thornton of Imperial College. The full data supplied are included in Appendix 3. From these the mean value in Romney Marsh stream sediments was 38.5 µg/g ; the median was 29 µg/g , and the range of values was from 14-136 µg/g . These values are obviously greater than the other sediments introducing the possibility

Table 4.4

Approximate Arsenic Concentrations in Stream Sediments from the Wolfson Geochemical Atals (Webb *et al.*, 1978)

Bedrock	Mean As (µg/g)
Romney Marsh Alluvium	15 - ≥ 30
Chalk	0 - ≥ 7
Gault Clay	0 - ≥ 7
Upper Greensand	
Lower Greensand	0 - ≥ 7
Weald Clay	7 - ≥ 15
Hastings Beds	0 - ≥ 7

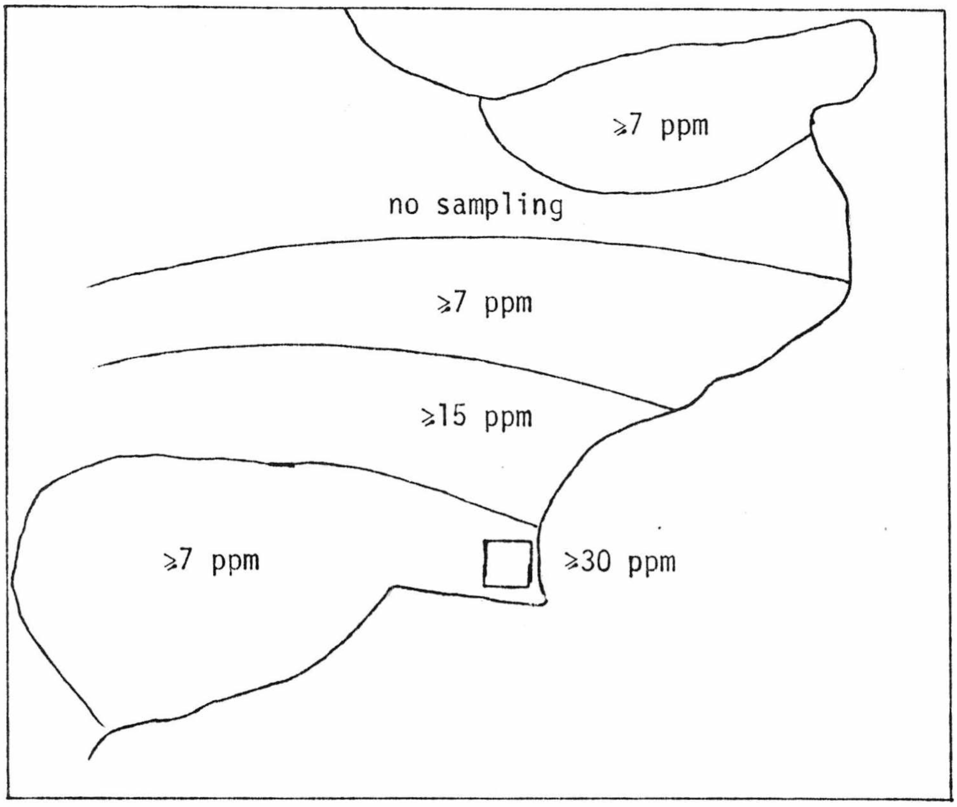


Figure 4.2 Diagrammatic Geochemical Map of Arsenic in Stream Sediments in South-East England, Adapted from the Wolfson Geochemical Atlas (Webb, *et al.*, 1978)

of pollution enhancing the levels on the Romney Marsh.

The following sections of this chapter document As data for the individual soils of the Weald, with particular reference to Romney Marsh. A point of especial interest was to investigate whether the apparently raised level of As in stream sediments is also found in the soils.

4.2 Results

(All analytical data are included in Appendix 4.)

4.2.1 The Distribution of Arsenic in Wealden Soils

The abundance of arsenic in Wealden soils is summarised in Table 4.5. The ranges are within those published (Table 4.3), but the mean concentrations of As in Romney Marsh soils and stream sediments, and Weald Clay soils are rather high. However, they agree with the expected values derived from the Geochemical Atlas (Table 4.4).

From Table 4.5 it can be seen that the Romney Marsh, Chalk and Weald Clay samples have an approximately normal distribution. The Gault Clay/Upper Greensand distribution is slightly skewed, and the Lower Greensand and Hastings Beds are more markedly skewed. The Gault Clay/Upper Greensand distribution may be explained by the fact that they are two separate populations. The Upper Greensand has a significantly lower As concentration than Gault Clay ($p < 0.01$). This explanation cannot be applied to the Lower Greensand where there is no difference between the As concentrations found in the Folkestone, Sandgate and Hythe Beds. The skew here is a result of five high

Table 4.5

The Abundance of Arsenic in Wealden Soils and Stream Sediments

Parent Material	n	$\overline{x}$	σ_D	Range	Median
Romney Marsh Alluvium	48	15.0	3.0	8.1-20.8	15.0
Drift Deposits	19	9.3	5.0	3.6-24.9	8.2
Chalk	23	6.4	2.5	2.4-13.7	6.3
Gault Clay/ Upper Greensand	22	7.1	2.3	2.6-12.1	6.6
Lower Greensand	35	9.6	6.4	1.7-27.5	7.7
Weald Clay	12	11.9	5.0	3.3-18.5	11.1
Hastings Beds	16	9.1	4.0	4.2-17.9	7.9
All Soils	175	10.4	5.2	1.7-27.5	8.8
Stream Sediments	8	25.8	25.5	5.2-76.5	13.9

values. The Hastings Beds can be subdivided into the Tunbridge Wells sand, Wadhurst Clay and Ashdown Beds. The coarser Tunbridge Wells Sand and Ashdown Beds are significantly lower than the fine textured Wadhurst Clay at $p < 0.001$ and $p < 0.01$ respectively, producing a skewed distribution. The Drift Deposits are also skewed, but there is such a large sample variation in this group that this might be expected.

The difference between the mean values obtained has been tested in a t-matrix (Table 4.6). The soils developed on the Romney Marsh are higher than those on the Weald Clay at $p < 0.01$ and all other Wealden soils at $p < 0.001$. Although the Romney Marsh is known to be partly derived from the Weald Clay and Hastings Beds, obviously there is a distinct difference between them. This can be seen more clearly in the frequency histogram Figure 4.3, which is distinctly bimodal. However, if the values for the Wadhurst Clay are compared with Romney Marsh the difference is not significant. Similarly, if the Weald Clay samples, excluding two sandy soils (1M, 2M) are compared with Romney Marsh soils there is no significant difference at $p=0.05$ level. Therefore, it seems debatable as to whether the Romney Marsh soils are enhanced.

The change in As concentration with parent material can be seen in the cross-sections Figure 4.4 (i-ix). From these it may be noted that generally argillaceous sediments contain a higher arsenic content than arenaceous sediments (Table 4.1). The relative abundance in these depoits may be summarised as:

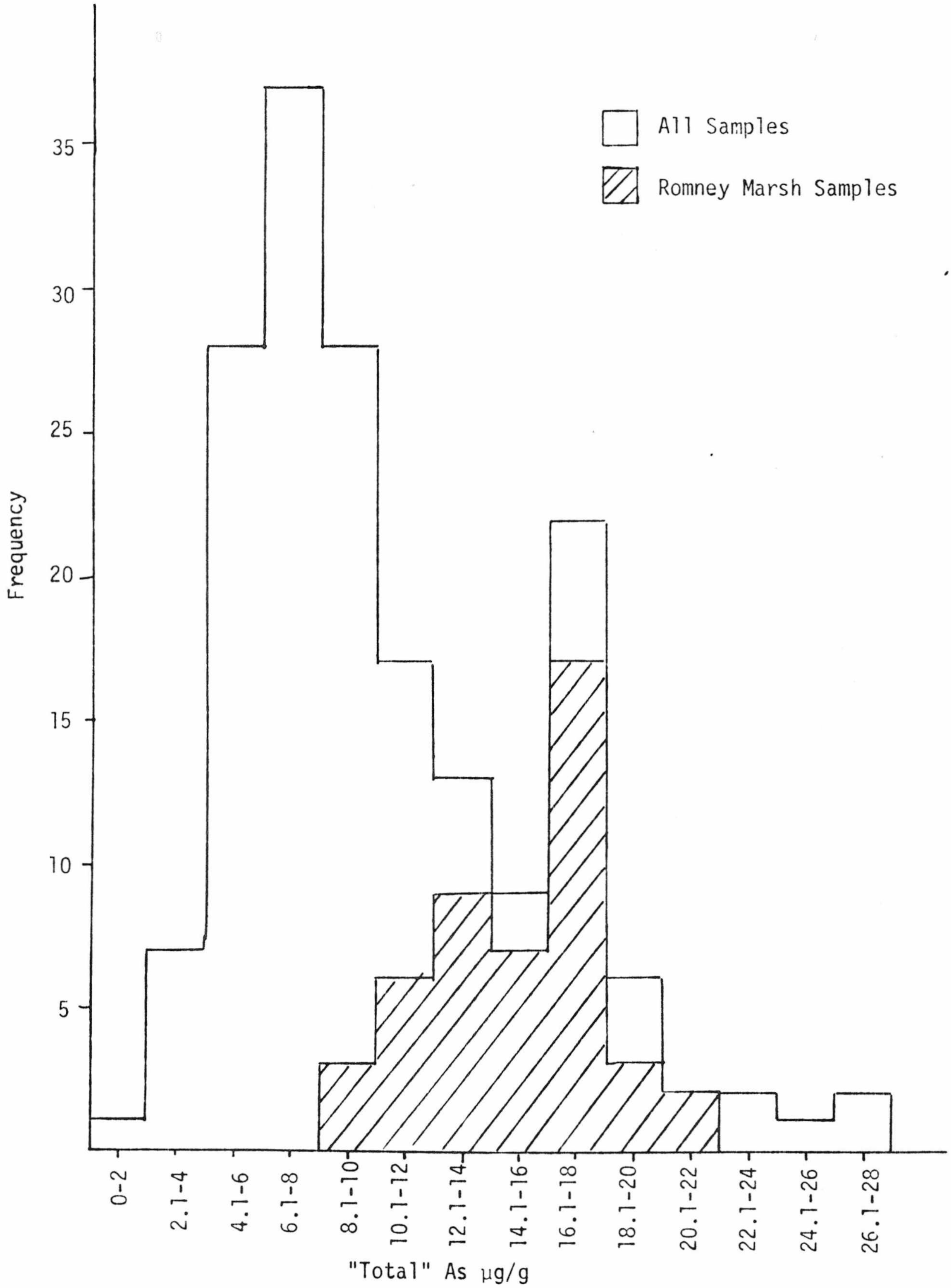
Table 4.6

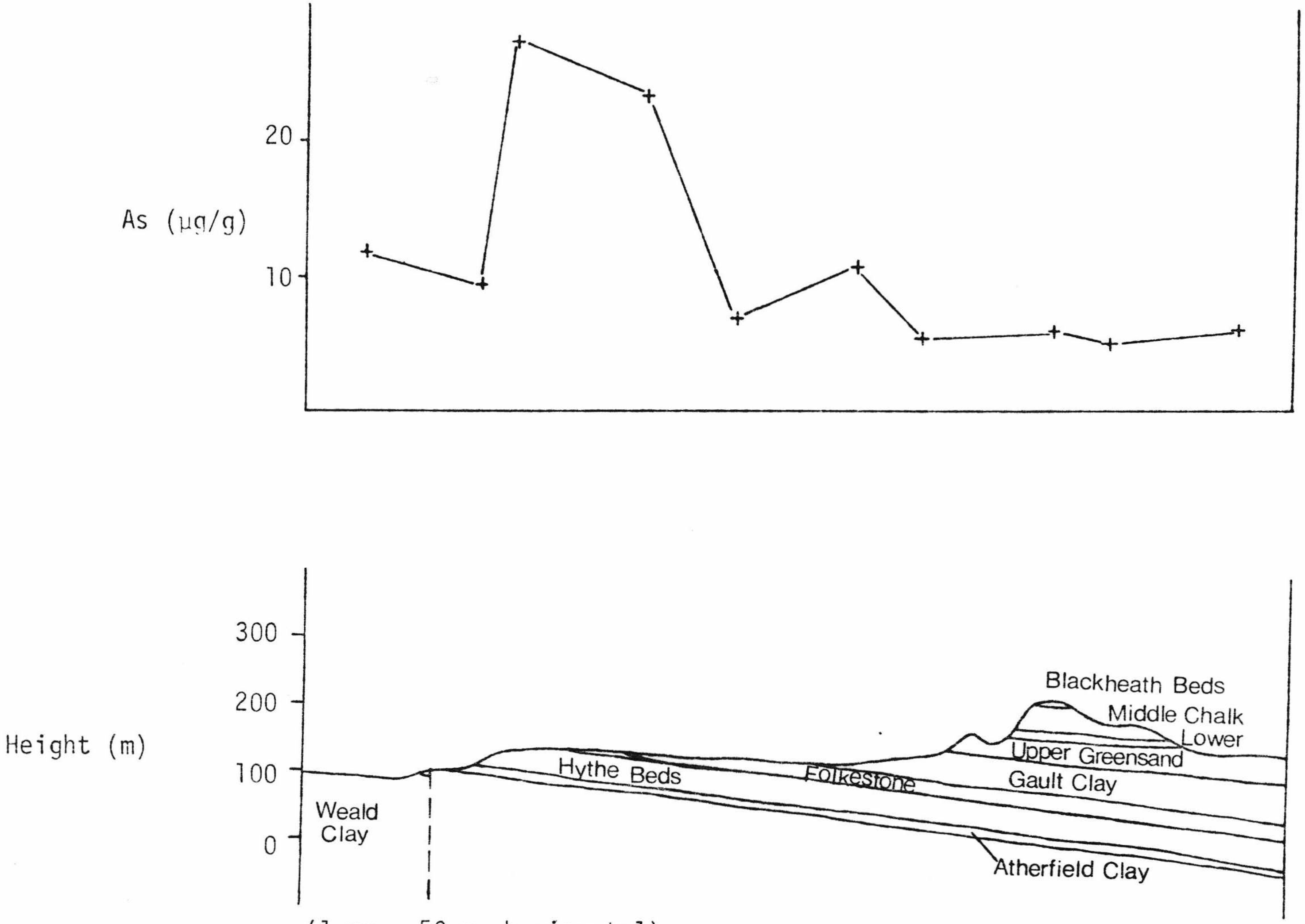
t-Matrix of "Total" As in Wealden Soils

	Romney Marsh	Drift	Chalk	Gault and Upper Greensand	Lower Greensand	Weald Clay	Hastings Beds
Romney Marsh		6.079^4	13.237^4	11.957^4	5.288^4	2.953^3	6.719^4
Drift			2.496^2	3.390^3	0.178	1.413	0.130
Chalk				1.011	2.308^1	4.450^4	2.667^2
Gault and Upper Greensand					1.766	3.820^4	1.642
Lower Greensand						1.134	0.289
Weald Clay							1.642
Hastings Beds							

1. $p < 0.05$ 2. $p < 0.02$ 3. $p < 0.01$ 4. $p < 0.001$

Figure 4.3 Frequency Distribution of "Total" Arsenic in Wealden Soils





(1 mm = 50 m horizontal)

Figure 4.4i Cross-Section of Bletchingly Transect (1-10R) Showing Arsenic Concentration at the Various Locations

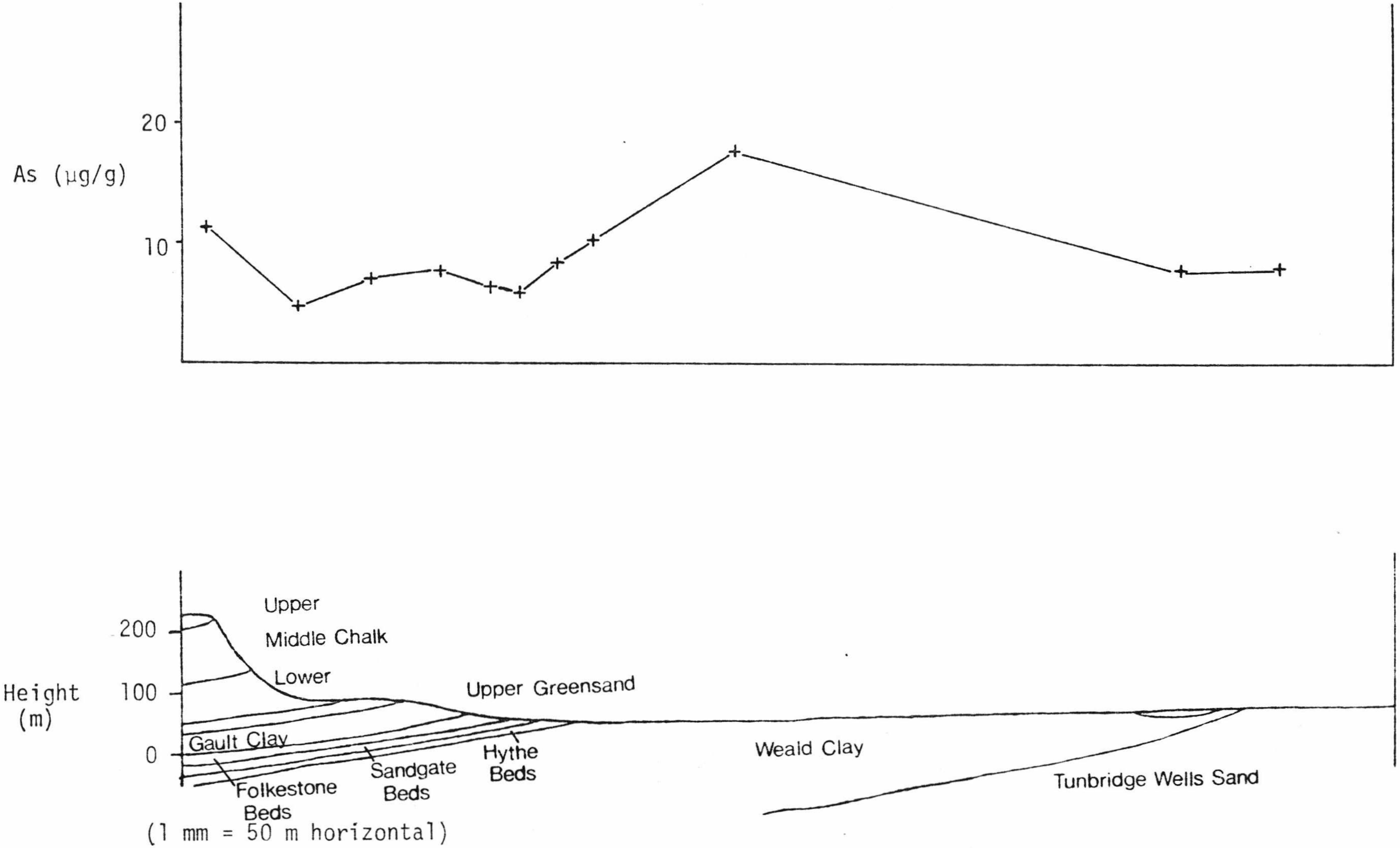
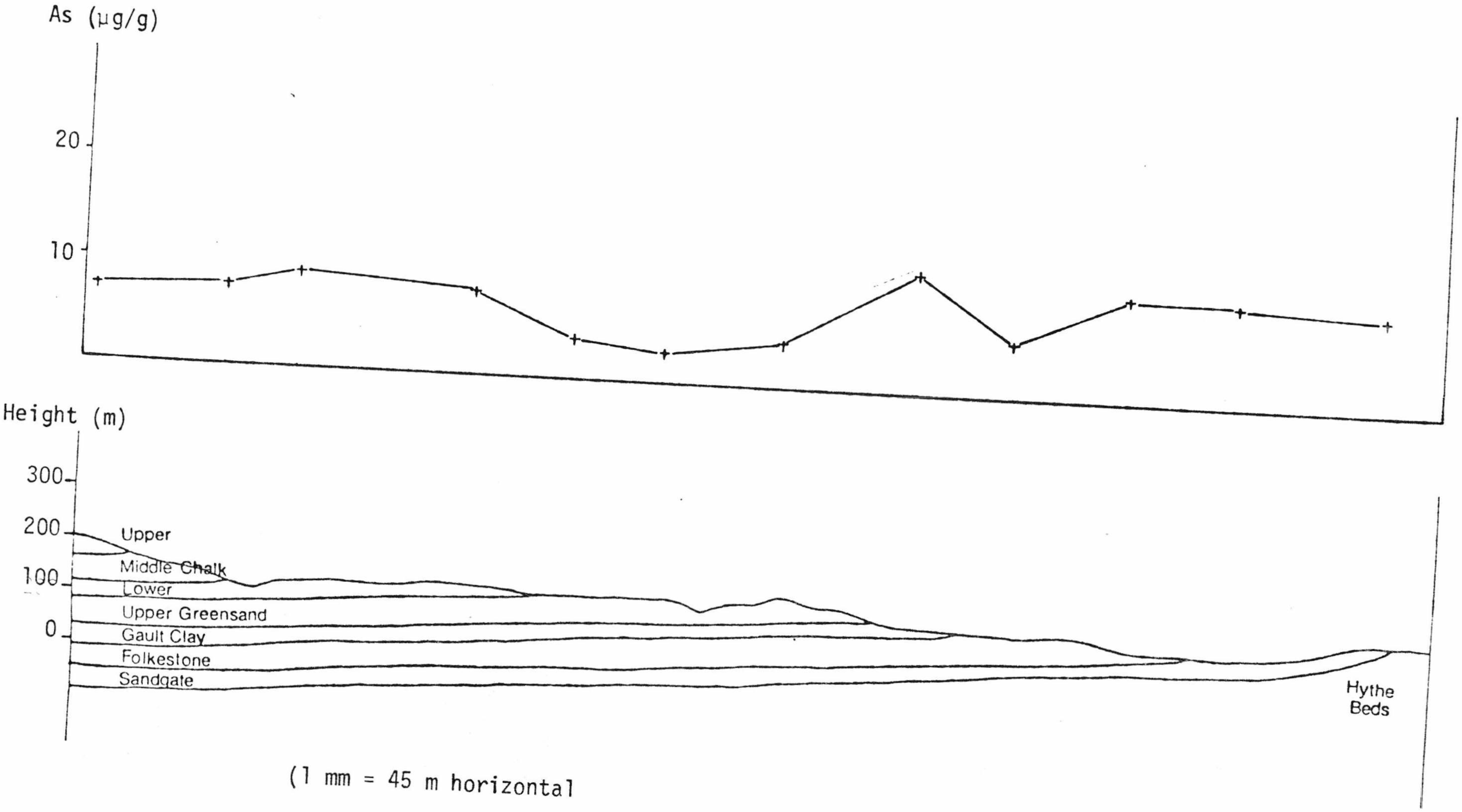


Figure 4.4ii Cross-Section of Ditchling Transect (1-11BD) Showing Arsenic Concentration at the Various Locations



(1 mm = 45 m horizontal

Figure 4.4(iii) Cross-section of SelbourneTransect (1-12L) Showing Arsenic Concentration at the Various Locations

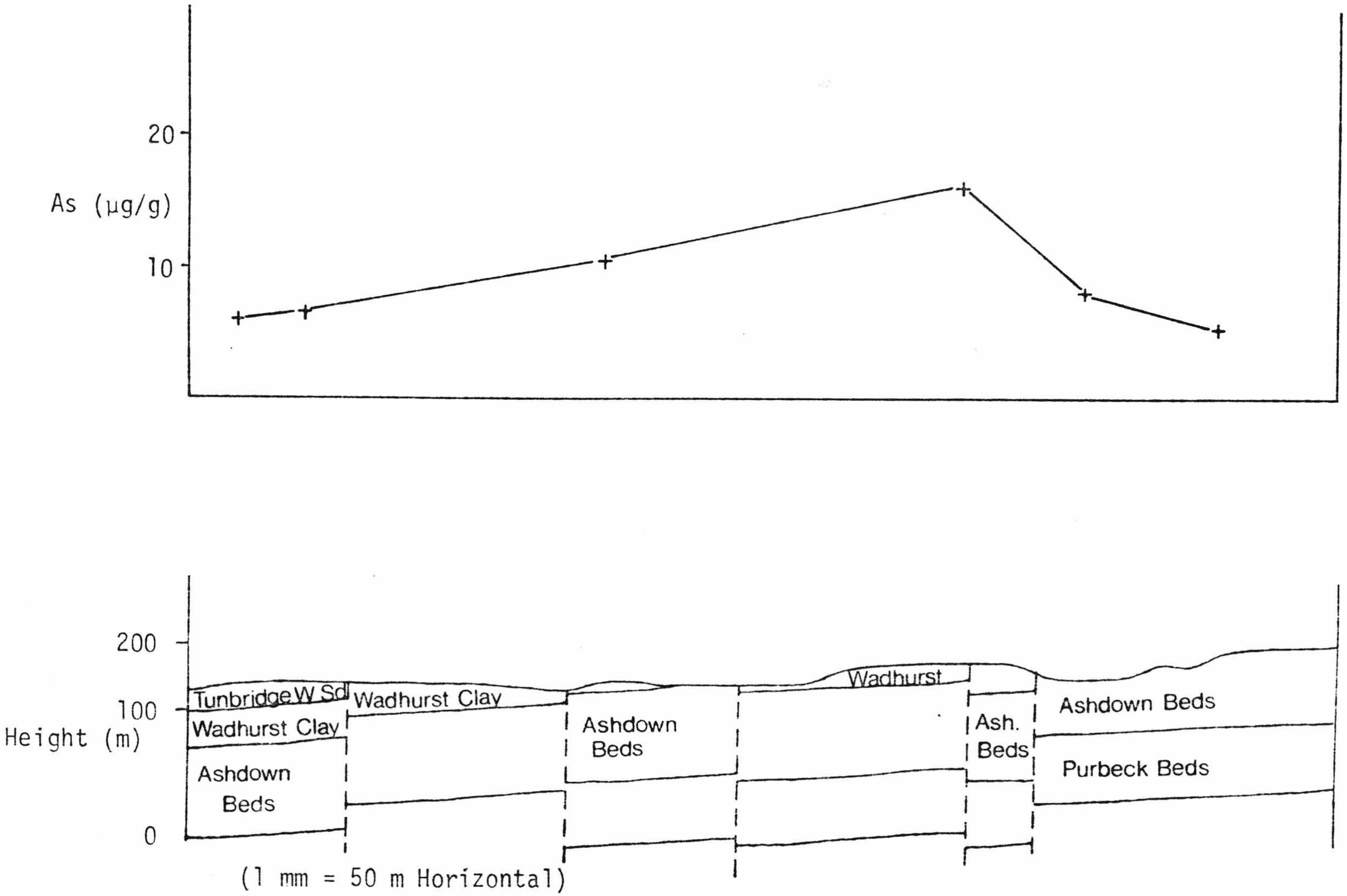
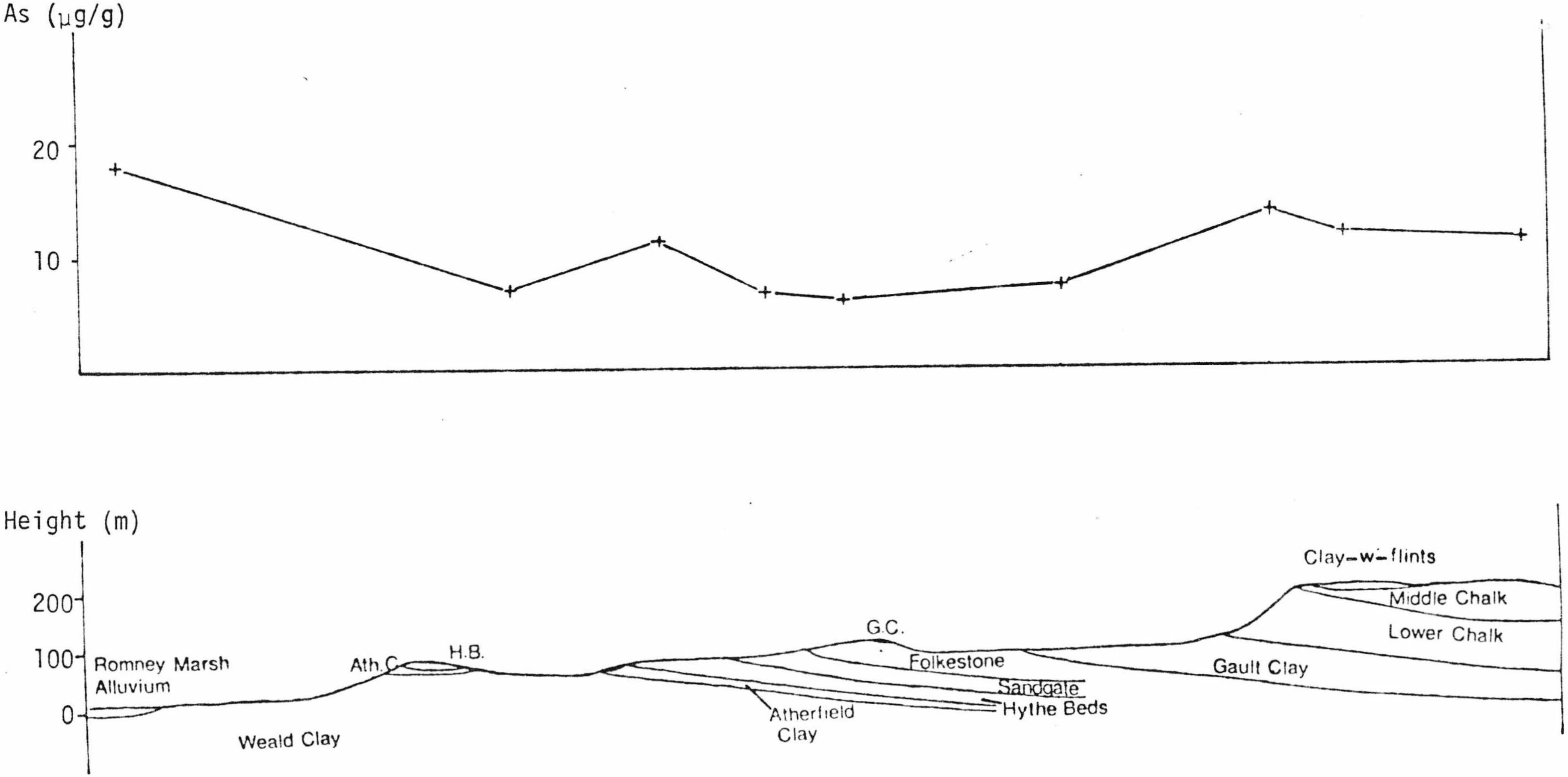


Figure 4iv Cross-Section of Heathfield Transect (7-12P) Showign Arsenic Concentration at the Various Locations



(1 mm = 45 m horizontal)

Figure 4.4(v) Cross-section of Hastingleight Transect (1-9K) Showing Arsenic Concentration at the Various Locations

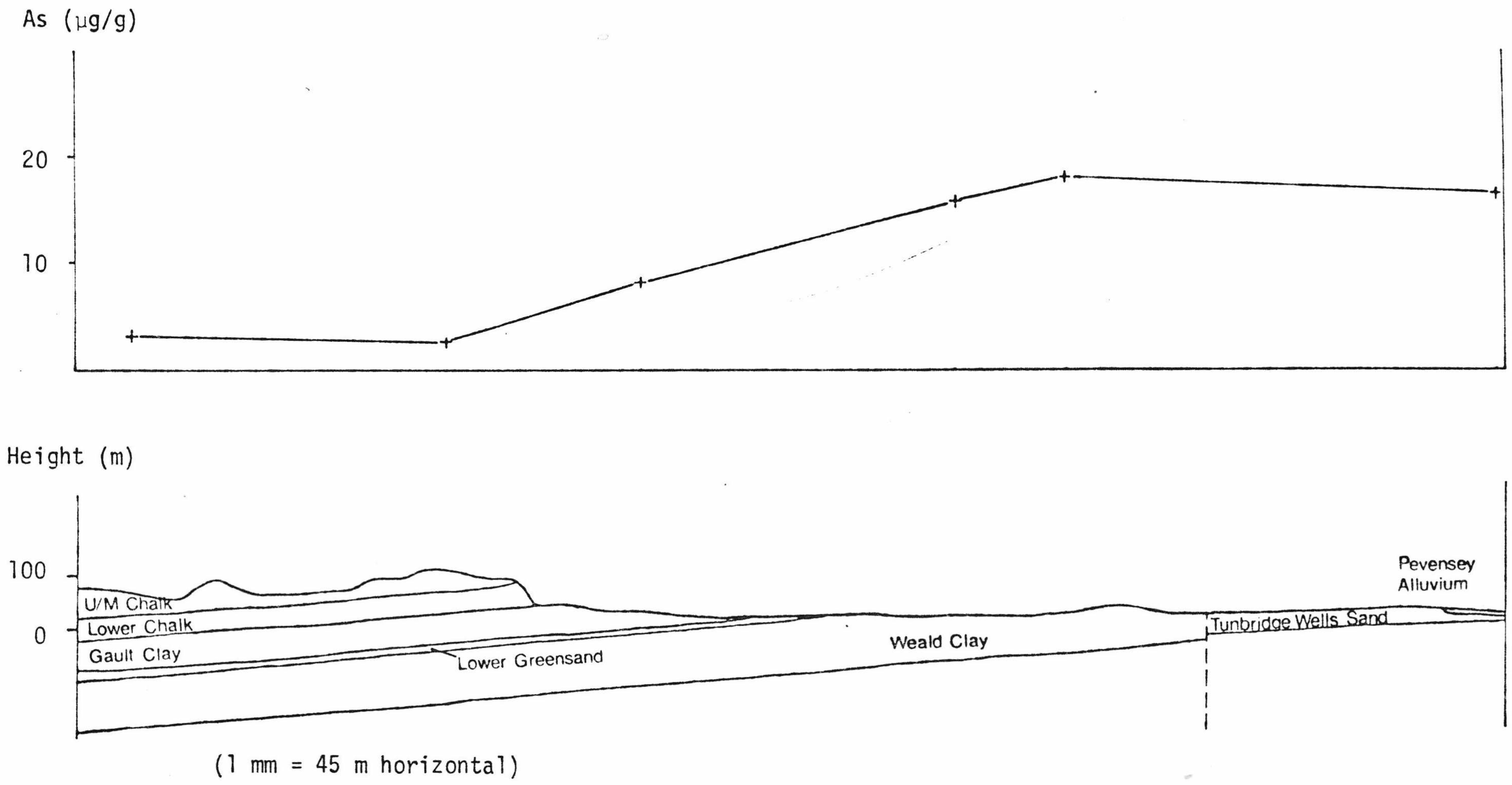


Figure 4.4(vi) Cross-Section of Pevensey Transect (1-6P) Showing Arsenic Concentration at the Various Locations

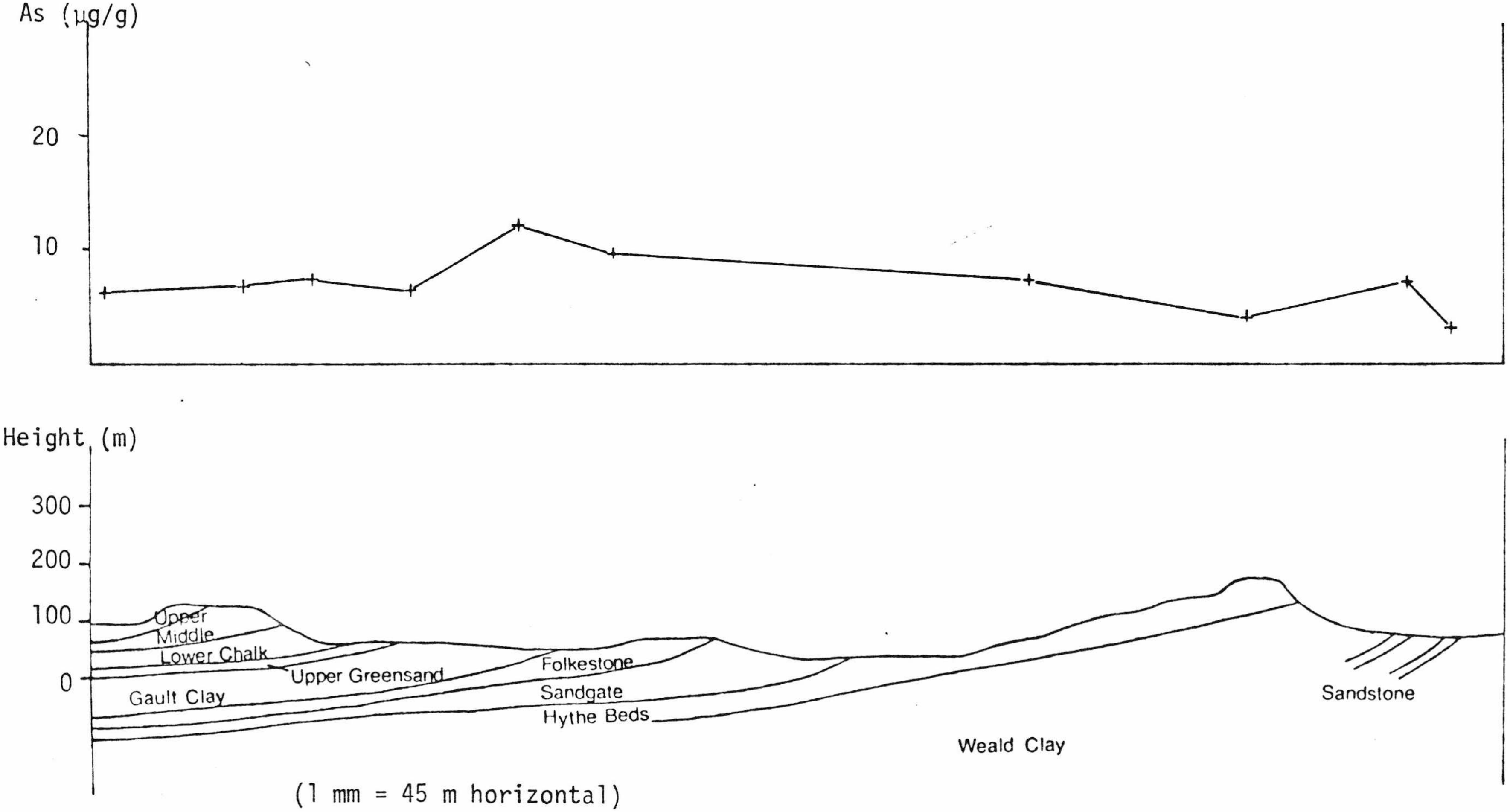


Figure 4.4(vii) Cross-section of Midhurst Transect (1-10M) Showing Arsenic Concentration at the Various Locations

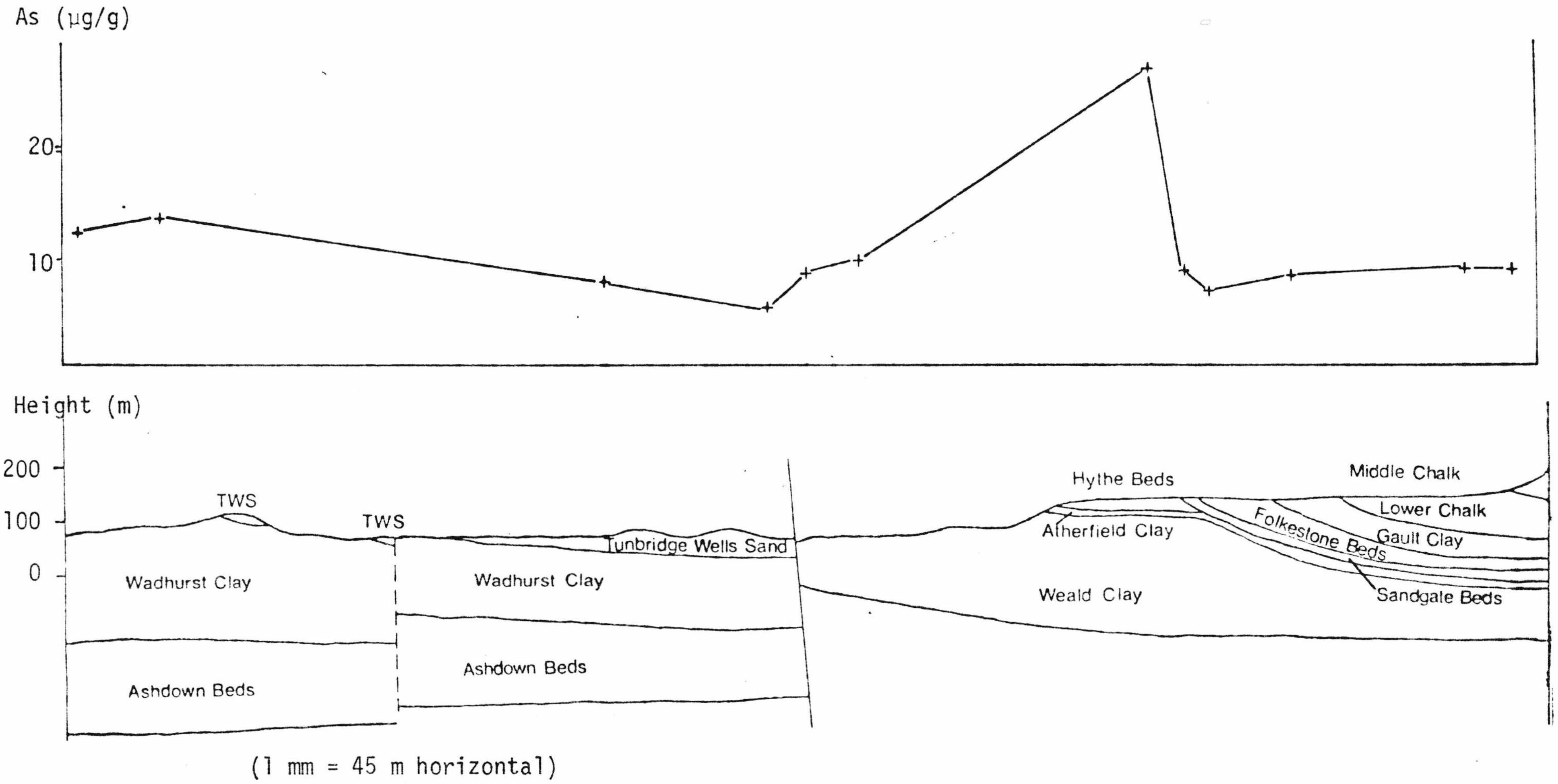
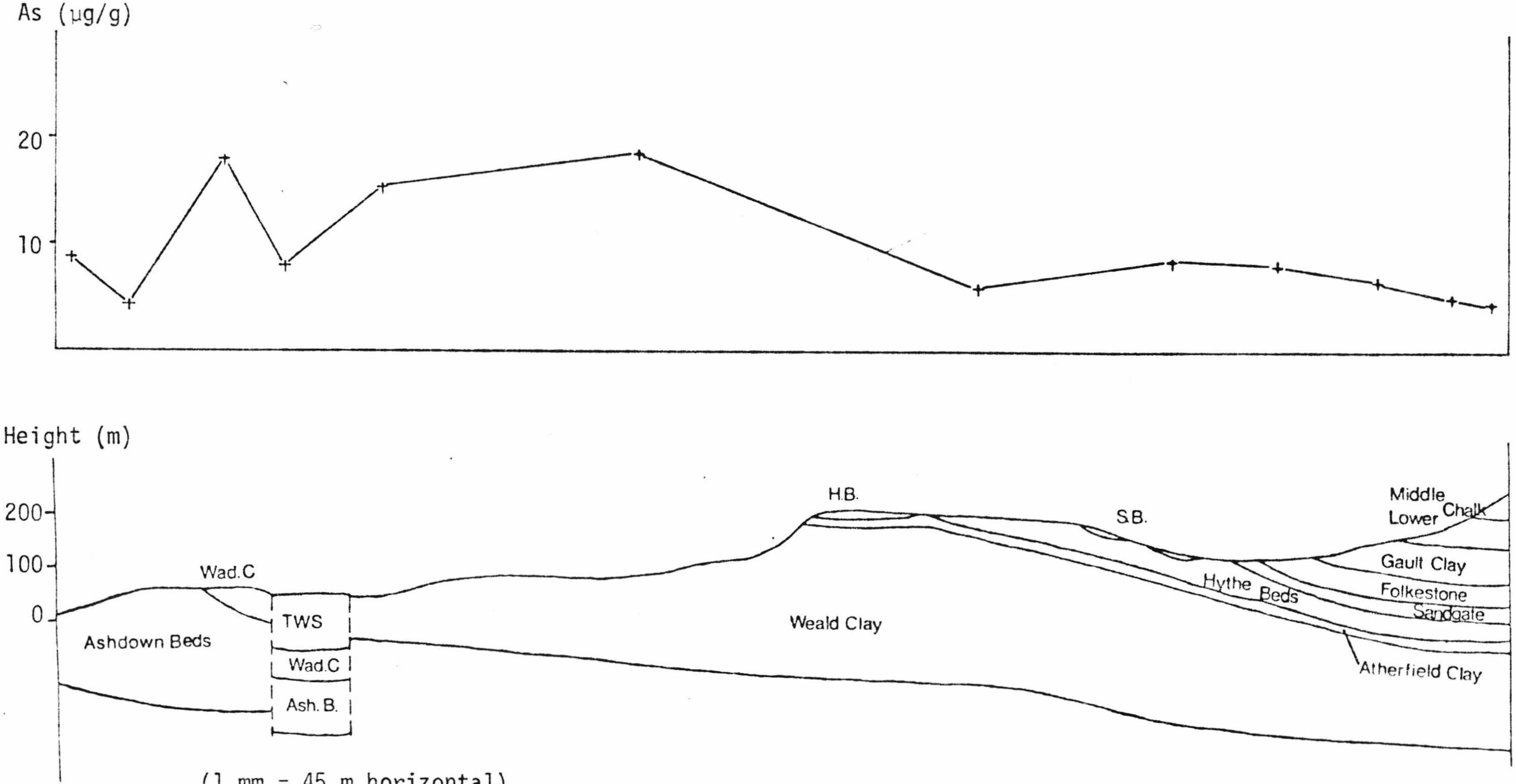


Figure 4.4(viii) Cross-Section of Lenham Transect (1-12D) Showing Arsenic Concentration at the Various Locations



(1 mm = 45 m horizontal)

Figure 4.4(ix) Cross-Section of Brasted Transect (1-12BP) Showing Arsenic Concentration at the Various Locations

Romney Marsh = Wadhurst Clay > Weald Clay > Lower Greensand
> Gault Clay > Tunbridge Wells Sand = Ashdown Beds
= Chalk > Weald Clay Sandstone > Upper Greensand

It is also interesting to note that sample 1P on the Pevensey Levels contains 16.4 μg/g As since McRae and Burnham (1975) stated that from a limited reconnaissance it appears that this marsh is a similar landform to the Romney Marsh.

From the cross-section Figure 4.4 it can be seen that in most cases:

Upper Chalk < Middle Chalk < Lower Chalk
[As] →

This is to be expected as the Lower Chalk is the most impure and contains phosphatic and iron nodules which from Table 4.2 are known to contain higher concentrations of As . Similarly, the Wadhurst Clay would be expected to contain a high As concentration as its locally abundant clay ironstone was the basis for the Wealden Iron Industry (Chapter Two).

A value of 6.7 μg/g As was determined for a soil from the Devonian Wealden counterpart in the Bas Boulonnais indicating that similar As levels may be found in France.

4.2.2 Controls on Arsenic Abundances - Inter-Element Relationships

4.2.2.1 Fe-As

"Total" Fe and As are positively correlated in all the Wealden soil types. Values for r are given in Table 4.7. Significant correlations are found in all groups. When all the data are plotted on a scatter diagram (Figure 4.5), there

Table 4.7

Correlation Coefficients for "Total" Fe-As According to Soil Parent Material

Parent Material	Correlation Coefficient (r) for Fe-As
Romney Marsh Alluvium	0.699^2
Chalk	0.665^2
Gault/Upper Greensand	0.390^1
Lower Greensand	0.694^2
Weald Clay	0.889^2
Hastings Beds	0.814^2
All Soils	0.436^2

1. $p < 0.1$, > 0.05 2. $p < 0.001$

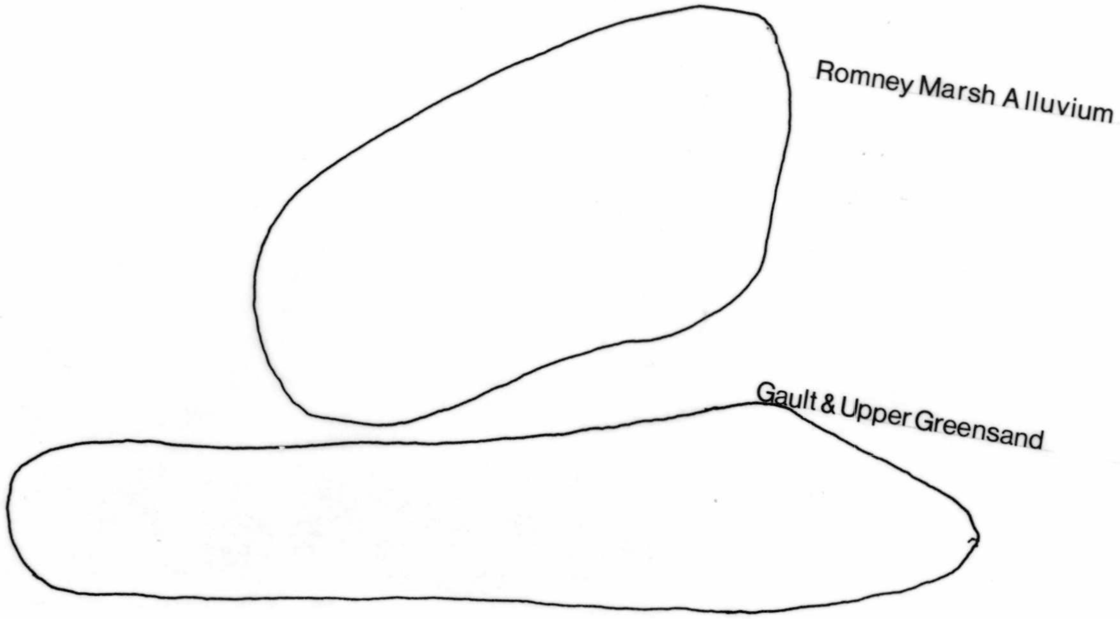
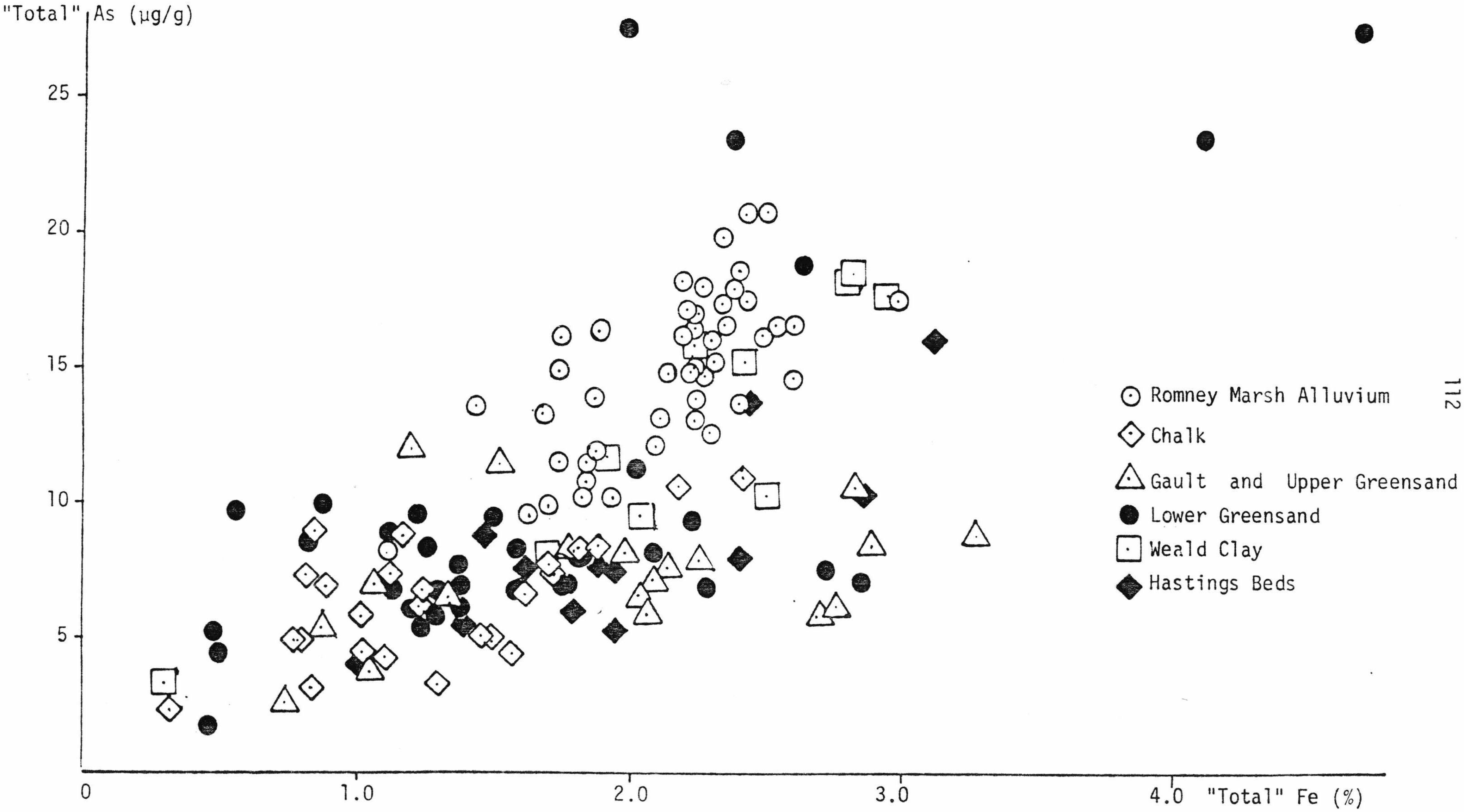

Romney Marsh Alluvium
Gault & Upper Greensand

Figure 4.5 Graph of Arsenic Against Iron in Wealden Soils



appears to be at least two distinct fields of variation as shown by the transparent overlay. Separations like these are a result of differences in slope. To investigate this a reduced major axis method (RMA) was employed (Miller and Kahn, 1962), which is described in Appendix 5. The RMA regression data are listed in Table 4.8. To compare the slopesof two separate reduced major axes the z statistic is determined. The derived z values in Table 4.9 shows that the Fe-As slope for soils on the Romney Marsh is significantly different from the Chalk and Gault/Upper Greensand. The slope of the latter is also significantly different from all the parent materials except for Chalk ($p < 0.05$). The calculated regression lines (slope of RMA) are illustrated in Figure 4.6, clearly showing that Gault/Upper Greensand are different from the other soil parent materials.

4.2.2.2 As-Mn

The correlation between "total" As-Mn is only significant for four of the soil parent materials (Table 4.10).

Again it is possible to discern fields of variation which are graphed in Figure 4.7, and outlined in the overlay. The Chalk and the Rommney Marsh alluvium samples separate from the rest due to their high and low manganese concentrations respectively.

Possible mechanisms for this relationship will be further discussed later.

Table 4.8

Reduced Major Axis Regression Data for Fe:As

Soil Parent Material	K slope	r	n	S_k STD Error of K
Romney Marsh Alluvium (RM)	8.57	0.699	48	0.88
Chalk (Ch)	5.10	0.665	23	0.79
Gault Clay and Upper Greensand (GC)	3.03	0.390	22	0.59
Lower Greensand (LG)	6.88	0.694	35	0.84
Weald Clay (WC)	6.10	0.889	12	0.81
Hastings Beds (HB)	6.90	0.814	16	1.00

Table 4.9

Z Statistics Matrix for Fe:As (See Appendix 5)

	RM	Ch	GC	LG	WC	HB
RM		2.93[2]	5.23[3]	1.39	2.06[1]	1.25
Ch			2.10[1]	1.54	0.88	1.41
GC				3.75[3]	3.07[2]	3.33[2]
LG					0.67	0.01
WC						0.62
HB						

[1] $p < 0.05$ [2] $p < 0.01$ [3] $p < 0.001$

RM = Romney Marsh Alluvium

Ch = Chalk

GC = Gault Clay and Upper Greensand

LG = Lower Greensand

WC = Weald Clay

HB = Hastings Beds

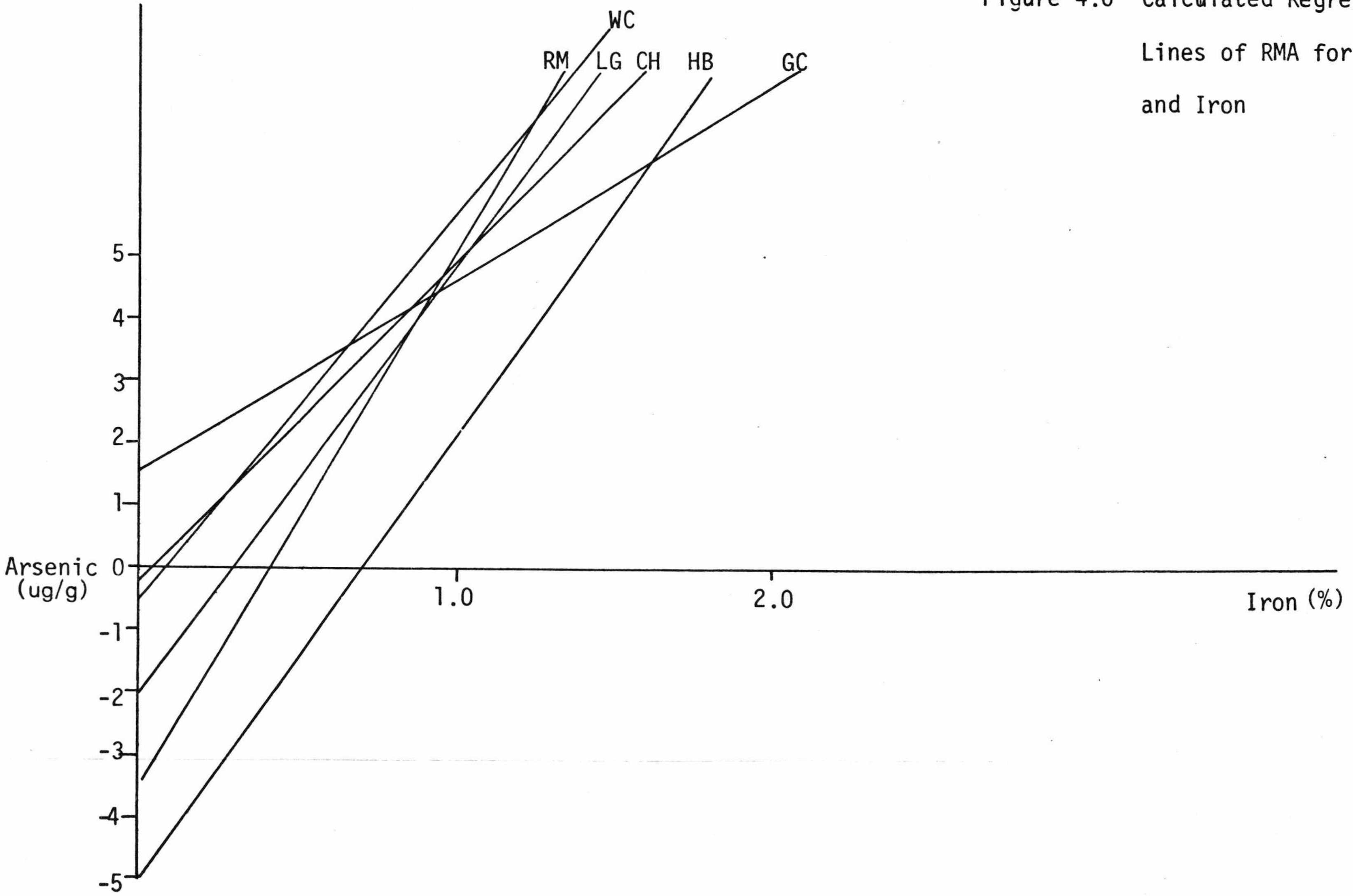


Figure 4.6 Calculated Regressions Lines of RMA for Arsenic and Iron

Table 4.10

Correlation Coefficients for "Total" As-Mn for Varying Soil Parent Materials

Parent Material	Correlation Coefficient (r) for As-Mn
Romney Marsh Alluvium	0.274[1]
Chalk	0.544[3]
Lower Greensand	0.310[1]
Weald Clay	0.767[2]

1. $p < 0.1, > 0.05$ 2. $p < 0.01, > 0.001$ 3. $p < 0.001$

4.2.2.3 As-Zn

A weak relationship was also observed between "total" As:Zn . Again this was only statistically significant in the soil parent materials listed in Table 4.11. When the data are plotted (Figure 4.8) it can be seen that the Romney Marsh samples again partially separate from the remainder.

4.2.3 Arsenic in Romney Marsh Stream Sediments

As only eight samples were taken, the complete results are given in Table 4.12. It is immediately apparent that there is a wide range in As concentration in the sediments suggesting a variable nature of enhancement. These results are very similar to those communicated by Thornton, although a less extreme range is

Figure 4.7 Graph of Arsenic Against Manganese in Wealden Soils

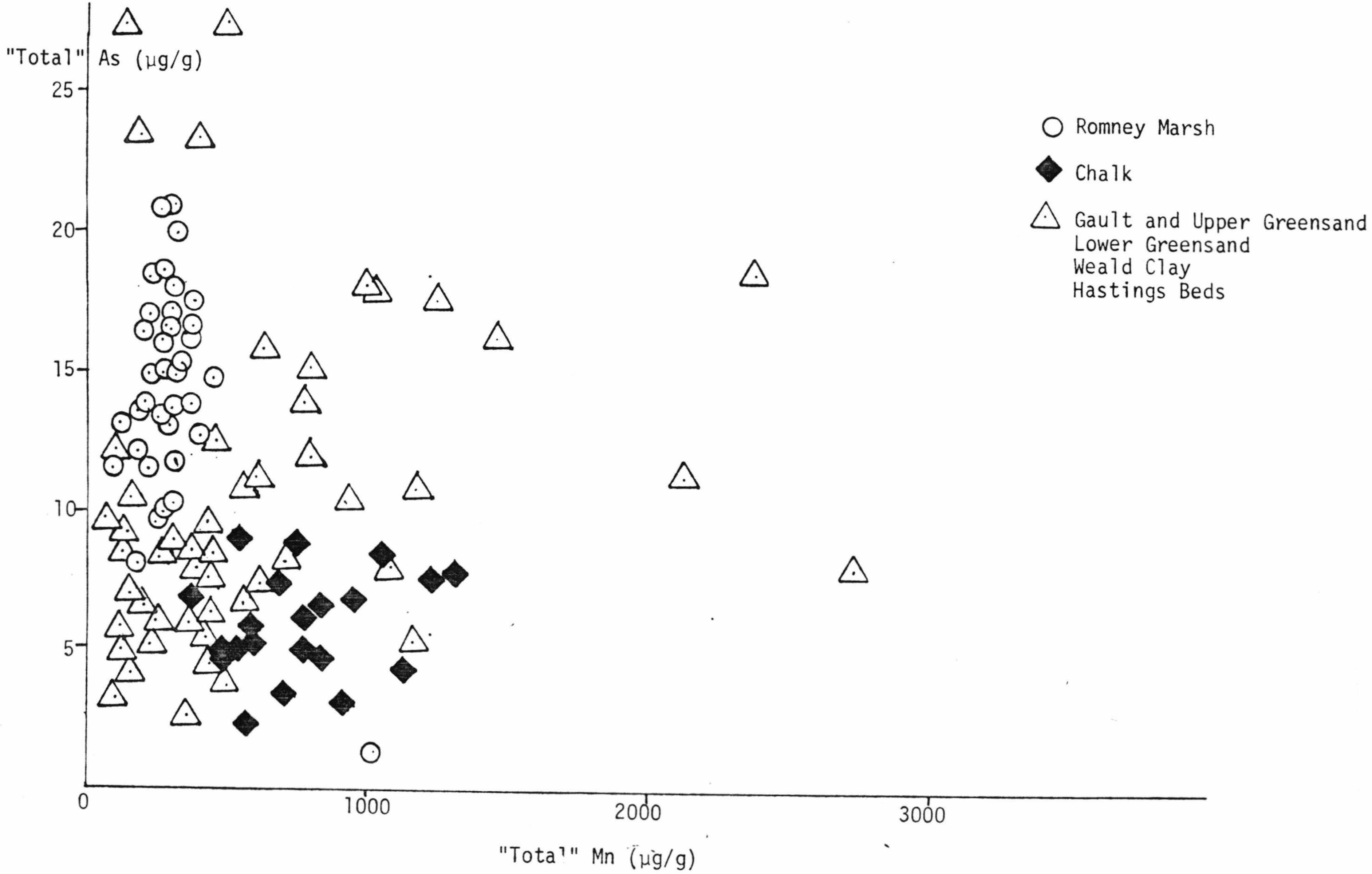


Table 4.11

Correlation Coefficient Values for "Total" As-Zn for Several Soil Parent Materials

Parent Material	Correlation Coefficient (r) for As:Zn
Romney Marsh Alluvium	0.513^4
Chalk	0.352^1
Weald Clay	0.601^3
Hastings Beds	0.731^2

1. $p < 0.1$, 2. $p < 0.05$, 3. $p \leq 0.01$,
4. $p < 0.001$

apparent. From Table 4.5 it can be seen that the distribution is markedly skewed, and when As in Romney marsh soils and stream sediments are plotted as a cumulative frequency graph (Figure 4.9) there is a distinct break in slope at ≥20 μg/g As which suggests that pollution has occurred above that level (cf. Davies, 1980). Also there is no correlation between "total" Fe-As in the sediments which may again suggest an extraneous As source although it is difficult to be categorical with so few samples.

The mean As level in stream sediments is high (25.8 μg/g As), but the mean values for other elements in these sediments are normal (the abundance levels for Cu , Zn , Mn and Fe are discussed in Chapter 6), therefore there is only a clear enhancement in arsenic in stream sediments.

Figure 4.8 Graph of Arsenic Against Zinc in Wealden Soils

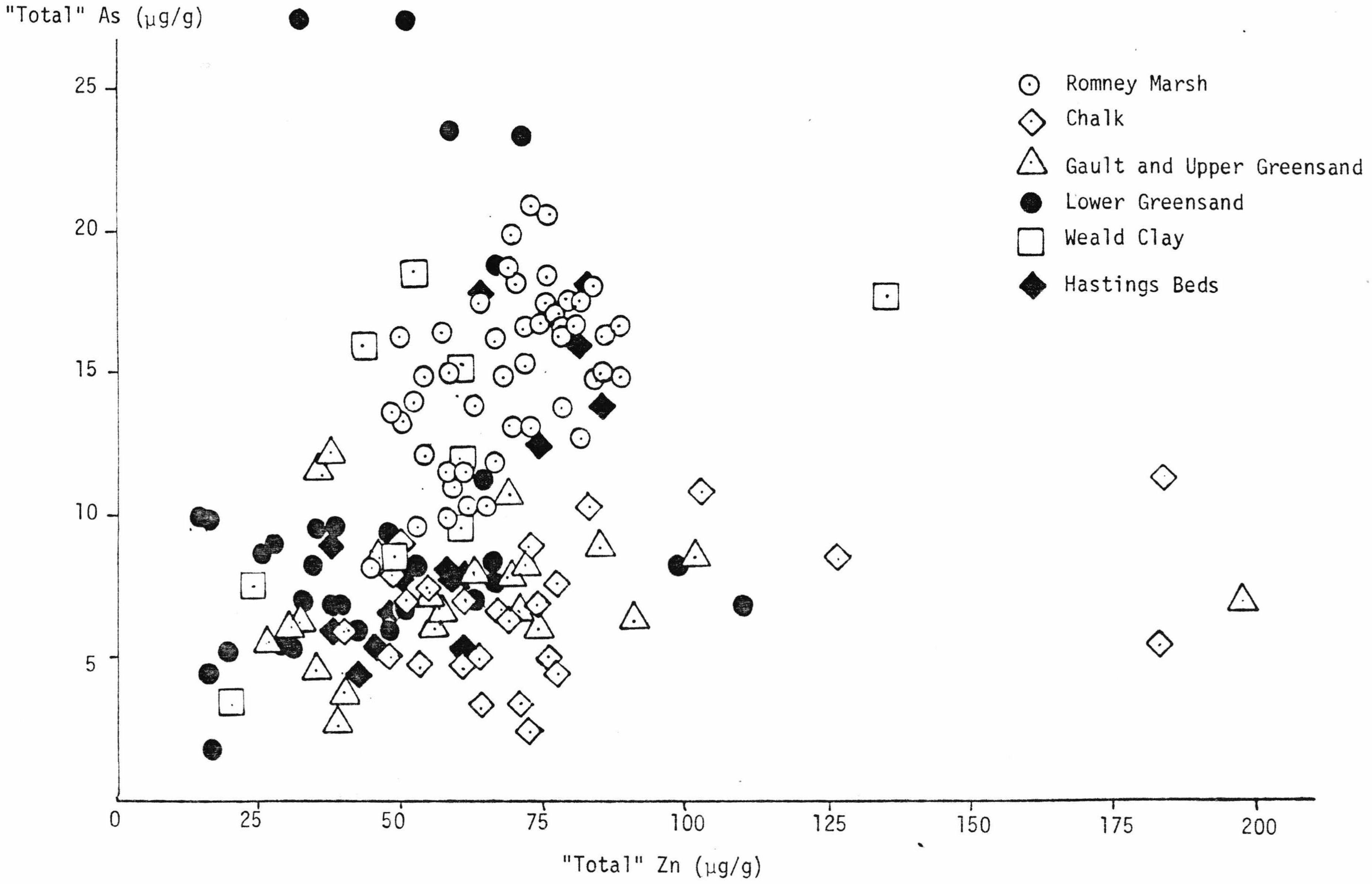


Figure 4.9 Cumulative Frequency Plot of Arsenic in Romney Marsh Soils and Stream Sediments

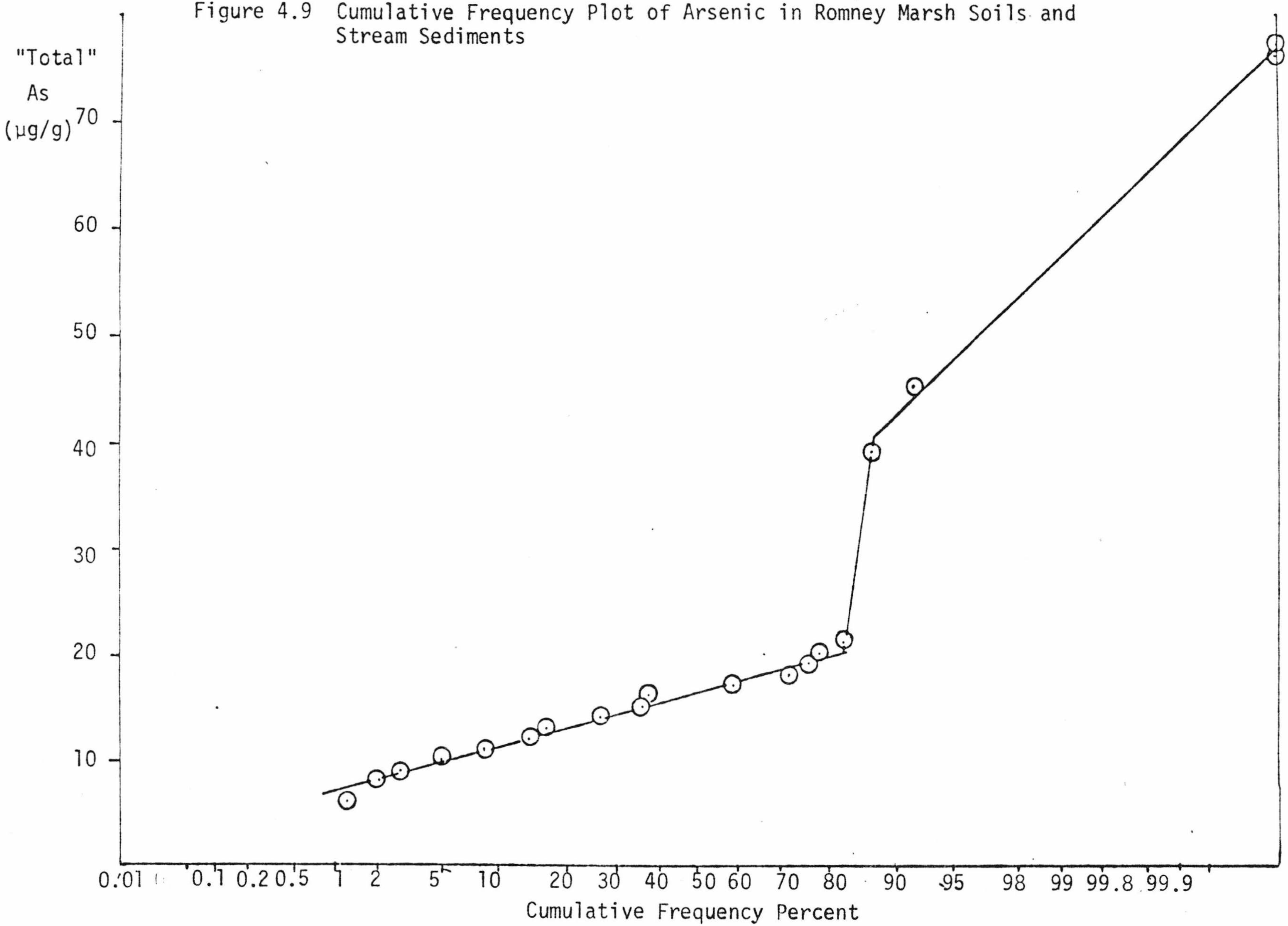


Table 4.12

Abundance of As , Cu , Mn , Zn and Fe in Romney Marsh Stream Sediments

Sediment No.	As	Cu	μg/g Mn	Zn	Fe%
7SS	5.9	5.6	156.0	44.0	1.66
41SS	16.2	7.8	223.0	54.0	2.68
47SS	11.6	9.1	97.0	58.5	2.25
44SS	38.9	2.5	78.4	22.2	2.01
5SS	5.2	3.1	91.7	31.6	1.08
42SS	7.4	2.5	73.0	29.9	1.35
39SS	44.8	15.6	180.0	72.2	1.26
6SS	76.5	9.5	61.0	60.2	2.73

4.3 Discussion

It is unlikely that any significant pollution has increased the As content of Romney Marsh soils because of the normal distribution exhibited in Figure 4.3 and the narrow standard deviation in Table 4.5. Also, all Romney Marsh soil samples lie below the break in slopeof the cumulative frequency histogram Figure 4.9. This is further supported by the similarity between the concentration found in the Wadhurst Clay, Weald Clay proper and the Romney Marsh.

The Lower Greensand group contains five high values. On reflection, this does not seem unreasonable if the Fe values are also high, as these sediments contain ferruginous sands and phosphatic nodules locally

(Chapter Two) and from Table 4.7 it is apparent that Fe is strongly associated with As in soils. However, two of the samples 3R and 4R do not contain a correspondingly high value of Fe . These soils lie within the soil group (iv) (Chapter Two), coarse loamy and loamy argillic-brown earths which tend to be very sandy and in places very acid. However, the two soils in question are pH 6.3 and pH 7.2 respectively and contain an adequate supply of Cu , Zn , Mn and Fe and may therefore have been utilised for fruit growing. Their high As levels could possibly be a result of lead arsenate sprays.

The good correlation between Fe:As is expected from previous observations by other workers (for example, Section 1.2), and can be explained partly by our knowledge of adsorption processes in soils. The surface charge of oxides, hydroxides, organic materials and other colloids with constant surface potential results from ionisation of surface atoms, or from chemical adsorption of dissolved ions onto the surface. The surface of a stable oxide, for example Fe_2O_3 , contains ions which are not completely co-ordinated into that lattice and thus give rise to electric charges at specific locations. These surfaces are regarded as being always hydroxylated in an aqueous environment. Therefore, depending on the pH the reverse reaction of dissociation of water from the surface can occur giving rise to a negative or positive surface site:

$$MOH^0 \rightleftharpoons MO^- + H^+_{(aq)} \quad (1)$$

$$MOH^0 \rightleftharpoons M^+ + OH^-_{(aq)} \quad (2)$$

(This simplified system is explained in more detail in Mott, 1970)

For Fe-oxides at approximately pH 6.5-8.5 the surface is uncharged which is termed the zero point of charge (zpc) Figure 4.10, so that natural Fe-oxides are usually positively charged (Parks and de Bruy-, 1962). Therefore, as As exists in an aqueous environment as $HAsO_4^{2-}$, $H_2AsO_4^-$ and H_3AsO_3 (Ferguson and Gavis, 1972) adsorption of the arsenic anion by the positively charged Fe-oxides would be expected to take place.

The relationship of Mn:As is not so obvious, as the OH on the

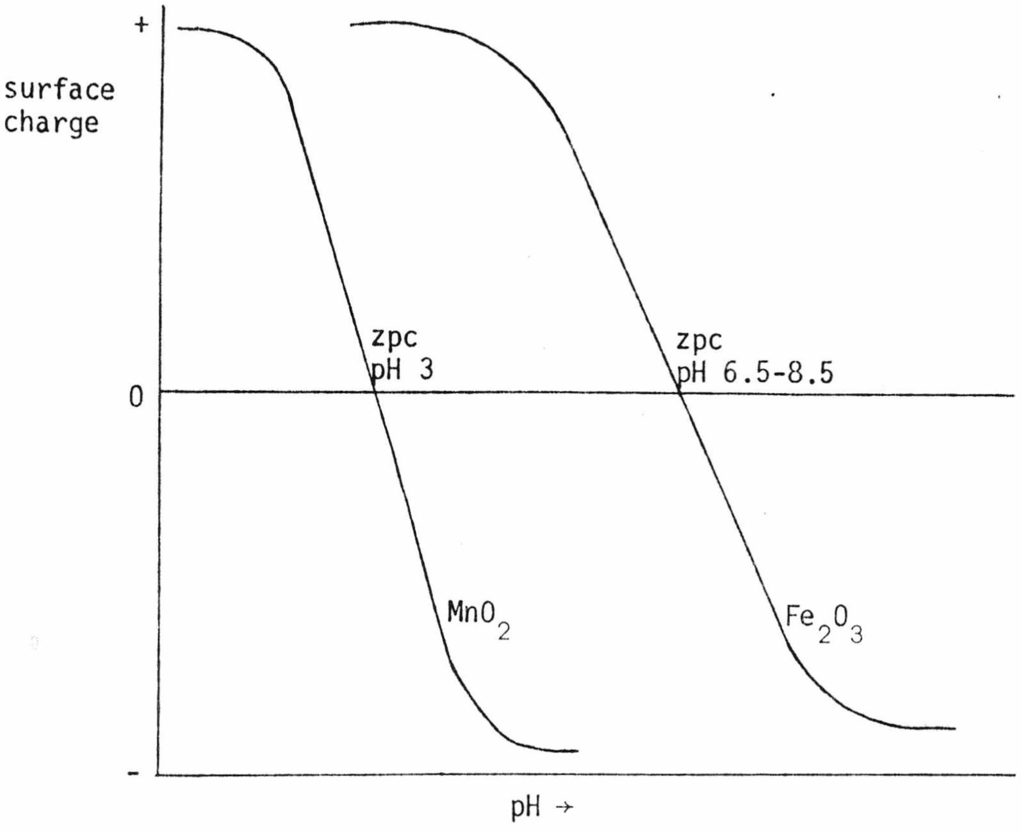


Figure 4.10 Diagram of Surface Charge on Mn- and Fe-oxides as a Function of pH (Rose *et al.*, 1979)

surface to a Mn-hydroxide tends to dissociate in a manner analogous to other weak acids and equation 1 applies. The extent of dissociation depends on pH , and the surface of most colloidal Mn-oxides and hydroxides has a strong negative charge. The zpc is approximately pH 3 (Figure 4.10). Under very acid conditions excess of H^+ is adsorbed to the surface and it has a positive charge, however this pH is not reached in the soils studied. As will be seen later in Chapter 4, there is a relationship between Fe and Mn because the chemistry of Mn resembles Fe very closely (Krauskopf, 1967), and therefore there appears to be an Mn-As relationship because of the strong Fe-As correlation. This would be expected from Table 4.2, which shows the levels of As expected in Mn-oxides.

The Zn:As correlation, although weak, could be important in the mobility of As . Zinc minerals weather to Zn^{2+} is solution in neutral/ acid conditions. Unlike Cu^{2+} , the simple ion remains dominant up to about pH 9 , and occurs in soil solution or adosrbed on clays, oxides and organic matter, with a small amount retained in clay mineral lattices. Compounds of Zn with the common anions of surface solutions are soluble in neutral and acid solutions, and therefore move readily in most natural waters (Mortveld *et al.*, 1972).

The large range of As in the Romney Marsh stream sediments indicates pollution. In the past soluble arsenical compounds were widely used for the control of external parasites on sheep and residual solution dumped at the treatment site. This has been commmunicated to the author by local shepherds. This couldbe the main source of As enhancement. Hounslow (1980) postulated a model for the leaching of As from landfills, but this could be adapted for the Romney Marsh system

(Figure 4.11). Zone A is oxygenated containing insoluble Fe^{3+} and adsorbed and soluble arsenate. Zone B is anaerobic and mildly reducing and is typical of shallow ground water. Soluble ferrous iron moves readily in this environment as does soluble arsenite. In strongly reducing zone C insoluble iron sulphide and co-precipitated arsenic sulphides are present.

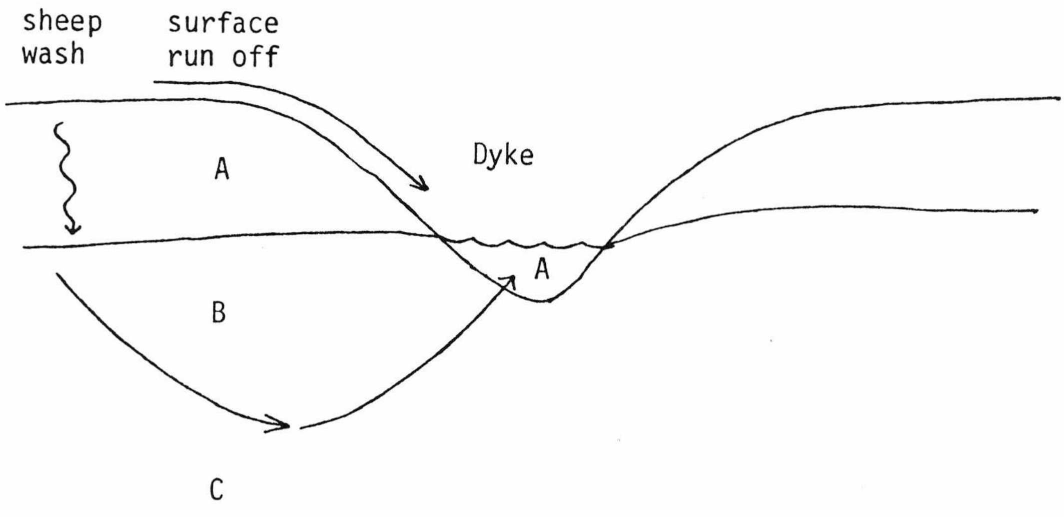


Figure 4.11 Diagrammatic Section of Romney Marsh Showing Three Generalised Aqueous Environments

Unusually high metal values in stream sediments have been noted where Mn- and Fe-oxides mobilised by reducing ground waters (zone B) have been precipitated in the stream. This process is common in glaciated areas and other regions of poor drainage, moderate to high rainfall and a cool climate. The Romney Marsh has considerable drainage problems because most parts are periodically below sea level. The fields are mostly bounded by water courses which discharge at low tide into the sea. In the summer the sluices are shut to prevent the land from drying out. Therefore, at low Eh/pH conditions in Zone B , maintained by the Marsh's unique drainage system, Fe^{2+} is mobilised with arsenite. which at a precipitation barrier such as the dyke zone A will precipitate out as Fe^{3+} , and As is strongly scavenged from solution in Fe-rich environments, either by formation of Fe-compounds or by adsorption on Fe-oxides and will be preferentially retained in Fe-rich soils. Horsnail *et al.* (1969) reported an enrichment factor of 5 for As in sediments in Wales affected by Fe- , Mn-oxide precipitation. Clement and Faust (1981) found that the releaseof As from contaminated sediments was highly dependant on the reduction of Fe^{3+} to Fe^{2+} . This explanation is further supported by the presence of reddish/brown ferric hydroxide precipitates commonly found in Romney Marsh dykes.

Another possible source of As is as an impurity in H_2SO_4 used to desiccate potato vines prior to harvesting (Chapter One). Potatoes are extensively cultivated on the Marsh and H_2SO_4 is a widespread treatment.

As Romney Marsh soils have not been shown to be polluted, the author would suggest the major route of contamination to be via surface runoff from arsenical sheep dips, especially as these are always situated next to the dykes.

4.4 Conclusions

1. The majority of Wealden soils are unpolluted and agree with other published soil data and the Wolfson Geochemical Atlas.

2. The soils can be listed according to As concentration:

Romney Marsh = Wadhurst Clay > Weald Clay > Lower Greensand,
> Gault Clay > Tunbridge Wells = Ashdown Beds
= Chalk > Weald Clay Sandstone > Upper Greensand

Generally argillaceous deposits contain more As than arenaceous deposits.

3. There is a strong Fe-As correlation, and weak Mn-As and Zn-As relationships.

4. Romney Marsh soils have been shown to contain similar As concentrations to the Weald Clay and Hastings Beds from whence they are derived.

5. High As values may be expected in ferruginous deposits such as the Wadhurst Clay and Lower Greensand.

6. Localised pollution may be found on loamy Lower Greensand soils which may have been utilised for fruit production and subjected to arsenical sprays.

7. Localised pollution has occurred in Romney Marsh stream sediments, probably as a result of the dumping of arsenical sheepdip solutions and possibly as a contaminant in H_2SO_4 potato vine spray.

CHAPTER FIVE

ARSENIC IN PLANTS

5.1 Introduction

The availability of arsenic to plants is governed by the total concentration in the soil and by the form in which it occurs. Usually a high concentration in the soil is only reflected to a small degree in plants (Thornton, 1980). Either the element is in a form unavailable for plant uptake, or the regulatory processes within the plant itself limit uptake.

There is a considerable variation in the sensitivity of plants to high levels of soil arsenic, for example potatoes are highly tolerant compared to legumes (Jacobs *et al.*, 1970).

Bioaccumulation would be hazardous to animals and humans, but fortunately recent studies have shown that the edible parts of plants seldom accumulate dangerous levels of As (Thoresby and Thornton, 1979). There is also usually a difference in the distribution of As amongst the various plant parts. Various studies of arsenic in vegetation have found substantially lower concentrations in the edible parts (Elfving *et al.*, 1978; Aten *et al.*, 1980).

Plant growth stimulation has been observed at low levels of arsenic additions to soils, although As is not considered as an essential element for plant growth. The reason for this is not apparent, but

Jacobs *et al.*,(1970) postulate that this may be due to the displacement of phosphate by arsenate with a resulting increase in phosphate availability, or the stimulation may be similar to that obtained by other pesticides (for example 2,4-D). Crop yield usually decreases with high arsenic concentrations.

No satisfactory treatment has beenfound to overcome soil arsenic toxicity. Application of iron salts has been suggested to remove it from the soil solution, but the amount needed is uneconomic. Alternatively deep ploughing to expose the arsenate to more sites for fixation is thought to be one of the most economic methods (Benson, 1953). Phosphate has been found to be a strong inhibitor of arsenate uptake by plant roots in solution culture systems (Asher and Reay, 1979), however attempts to reduce arsenic toxicity in soil-grown plants have produced divergent results. For example, Woolson *et al.*,(1973) found that with one soil arsenic toxicity decreased with phosphate addition, but with another soil toxicity increased with phosphate addition. Clearly the same arsenic level may be phytotoxic at one soil fertility level, but not at another.

One objective of this research was to estimate the adsorption capacity of three soils of varying physical and chemical properties:

i) a Brown Earth on the Hythe Beds OS 189 10903575 (LG)

ii) a Non-calcarcous surface water gley on Gault Clay
OS189 14603795 (GC)

iii) a Brown Calcareous soil on the Lower Chalk OS189 14503930 (CH)

Another objective was to establish the phytotoxic response and plant uptake of arsenate by three crops:

i) *Phaseolus vulgaris* var. Canadian Wonder, an example of a legume (bean)

ii) *Raphaneous sativus*, var. Scarlet Globe, an example of a root crop (Radish)

iii) *Triticum aestivum* var. Mardler, an example of a cereal crop (wheat).

5.2 Experimental Detail

5.2.1 Pot Experiments with Treated Soils

The soils were collected from the three sites listed above, to a depth no greater than the plough layer (ca. 25 cm). The soils were spread out to dry, and broken up by hand in the laboratory. They were further reduced to a particle size of < 5 mm and thoroughly mixed to homogenise each soil type. A final weight of 36 kg per soil was required, for three replicates of each treatment for the three crops.

Sufficient $Na_2HAsO_4.7H_2O$ was weighed and mixed thoroughly with 0.5 kg of soil to give the desired final concentration of 0,10,50 and 100 µg/g As in 9 kg . Care was taken to ensure that the spiked 0.5 kg soil was thoroughly mixed with the rest. 1.0 kg of treated soil was weighed into each 130 mm pot, watered and left fallow to equilibrate for one month before planting. All pots were placed on saucers to prevent the loss of As by leaching and after planting were watered from the bottom.

The beans were planted on 12th May 1981 at a rate of two per pot; the wheat was planted on 13th May 1981 at ten seeds per pot, and the radish seeds at five per pot on 16th May 1981. Initially, the pots were placed in a "polytunnel" until germination when they were moved into the open to grow normally. The pots were arranged randomly. Watering was carried out as necessary. One fertiliser application was given in the form of "phostrogen" at the recommended level (NPK 10-10-27; Mg 1.3% , Fe 0.4% , Mn 200 mg/kg).

Unfortunately, the wheat plants had to be sacrificed after one month due to a very bad infestation of septoria (a mildew). However, the beans and radishes were grown to maturity and were washed, dried and analysed as described in Chapter Three. Analysis of the three soils was also performed according to previously described procedures.

5.2.2 Pot Experiments with Untreated Soils

A second group of pots were set up to investigate the uptake of arsenic by wheat on arsenic-rich soils from

i) Cambourne, Cornwall an area in which Cu-Sn-As mineralisation was extensively worked in the 18th and 19th centuries;

ii) an area near Melton Mowbray, where the iron-rich marlstone rockbed is naturally high in arsenic;

iii) Romney Marsh stream sediment samples,

and

iv) high arsenic soils from the Lower Greensand.

Grid references are given in Appendix 1.

The wheat variety Mardler was grown at a rate of ten seeds per pot in the laboratory for a month before the crop was harvested. Soil and plant analyses were performed as described in Chapter Three.

5.3 Results

5.3.1 Treated Soil Pot Experiments

The chemical properties of the three soils used are given in Table 5.1 and the physical properties in Table 5.2 enabling them to be classified according to the particle size classes (Figure 5.1) of England and Wales (Hodgson, 1978).

Table 5.1

The Chemical Properties of the Soils Cultivated

Soil	pH	"Total" µg/g As	 Cu	 Mn	 Zn	 Fe%
Lower Chalk	8.15	3.4	11.3	697	71.4	1.31
Gault Clay	7.26	8.8	12.2	353	85.2	3.3
Lower Greensand	6.96	7.0	11.8	387	62.4	2.86

Table 5.2

Particle Size Anlaysis of the Soils Cultivated

Particle Size (%)	Lower Chalk	Gault Clay	Lower Greensand
Sand	27.4	18.4	53.4
Silt	16.5	20.0	19.5
Clay	14.0	47.0	20.5
LOI%	5.43	9.75	4.02
$CaCO_3$	36.3	1.65	0.92

From Table 5.2 it can be seen that the Gault Clay would be expected to have the greatest adsorption capacity due to its high clay and silt content. Using the method outlined in Chapter Three the adsorption capacities of these soils were found to be:

Gault Clay	$3.02\ K_d$
Lower Chalk	$1.32\ K_d$
Lower Greensand	

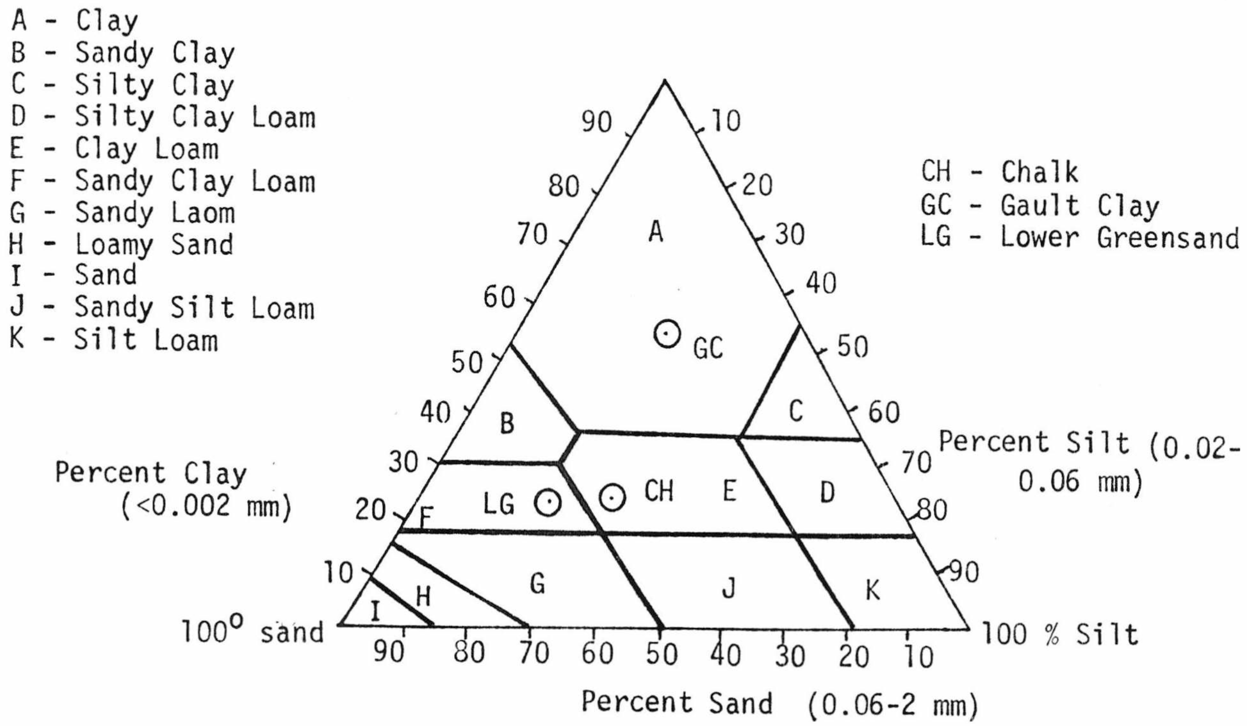


Figure 5.1 Particle Size Classification on the Three Cultivated Soils

The Gault Clay adsorption capacity is more than twice the other two soils, and the importance of this will be discussed later.

The growth of radishes in the As-treated soils is given in Table 5.3. The data are expressed on a yield dry weight basis and as a percentage relative to the background growth. The latter is plotted in Figure 5.2. For all soils the yield was increased at the 10 μg/g As treatment as has been observed by other workers (see Introduction). Thereafter, yield decreases with increasing As concentration, although the reduction is non-linear. There is a distinct difference in growth between the soil types and the plant part. The radish foliage on the Lower Chalk exhibits the lowest yield reduction, which is surprising when the radish bulb is considered. These show only 17.6% growth compared to the background plants. On the whole yield reduction is greatest in the bulb. Generally radish growth on these soils is in the order:

Gault Clay > Lower Greensand > Lower Chalk

The amount of arsenic needed to reduce growth by 50% (GR_{50}) (Woolson, 1973) can be calculated from Figure 5.2 and was found to be 43 μg/g and 40 μg/g As for radish bulbs on the Lower Greensand and Lower Chalk respectively. The decrease in yield in radish bulbs is initially rapid between 10-50 μg/g As added, but flattens out between 50-100 μg/g As .

The yield data for the beans and wheat are given in Table 5.4. The percentage yield relative to the background growth are plotted

Table 5.3

Radish Growth Response to Sodium Arsenate Treatments on Three Soils

(Weight/Plant Dry Mass (g))

Soil	μg/g As	Foliage	% of control	Bulb	% of control
Lower Chalk	0	0.114	100.0	0.017	100.0
	10	0.124	108.8	0.019	111.8
	50	0.117	102.6	0.007	41.2
	100	0.096	84.2	0.003	17.6
Gault Clay	0	0.199	100.0	0.028	100.0
	10	0.204	102.5	0.037	132.3
	50	0.195	98.0	0.026	92.9
	100	0.167	83.9	0.025	89.3
Lower Greensand	0	0.155	100.0	0.020	100.0
	10	0.183	118.1	0.025	125.0
	50	0.091	58.7	0.009	45.0
	100	0.066	42.6	0.007	35.0

in Figures 5.3 and 5.4. The wheat exhibits an increase in growth at the 10 μg/g As applied level whereas the beans do not. Again yield reduction is lowest on the Gault Clay for both crops. The beans show a much greater sensivity to applied As than the wheat, which does not fall below 50% yield on any of the soils. The GR_{50} can be calculated for the beans, giving values of 24 μg/g As applied for lower Greensand and 52 μg/g As for the Lower Chalk. For both crops yield decreases with increasing As concentration and is non-linear.

The levels of arsenic in the plant material are presented in

Figure 5.2 Graph of Yield Against Added Arsenic for Radishes

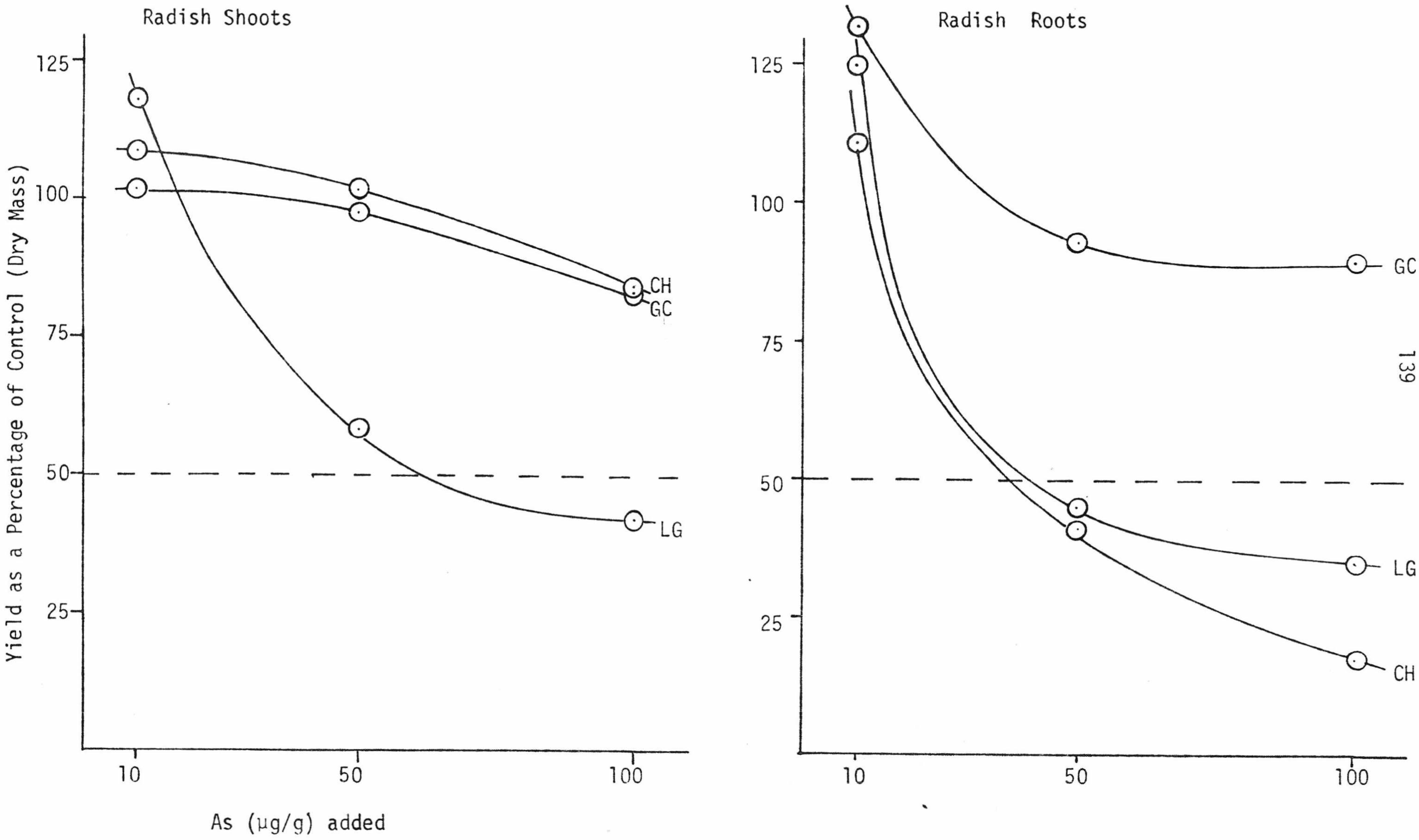


Table 5.4

Plant Growth Response to Sodium Arsenate Treatments (Weight/Plant Dry Mass (g))

Soil	μg/g As	Beans (Aerial Parts)	% of Control	Immature Wheat	% of Control
Lower Chalk	0	0.789	100.0	0.070	100.0
	10	0.719	91.1	0.081	115.7
	50	0.409	51.8	0.050	71.4
	100	0.18	22.8	0.042	60.0
Gault Clay	0	1.141	100.0	0.133	100.0
	10	1.04	91.1	0.140	123.9
	50	0.95	83.3	0.09	79.6
	100	0.833	73.0	0.077	68.1
Lower Greensand	0	1.172	100.0	0.069	100.0
	10	0.832	71.0	0.079	114.5
	50	0.368	31.4	0.049	71.0
	100	0.325	27.7	0.04	57.9

Figure 5.3 Graph of Wheat Yield Against Added Arsenic

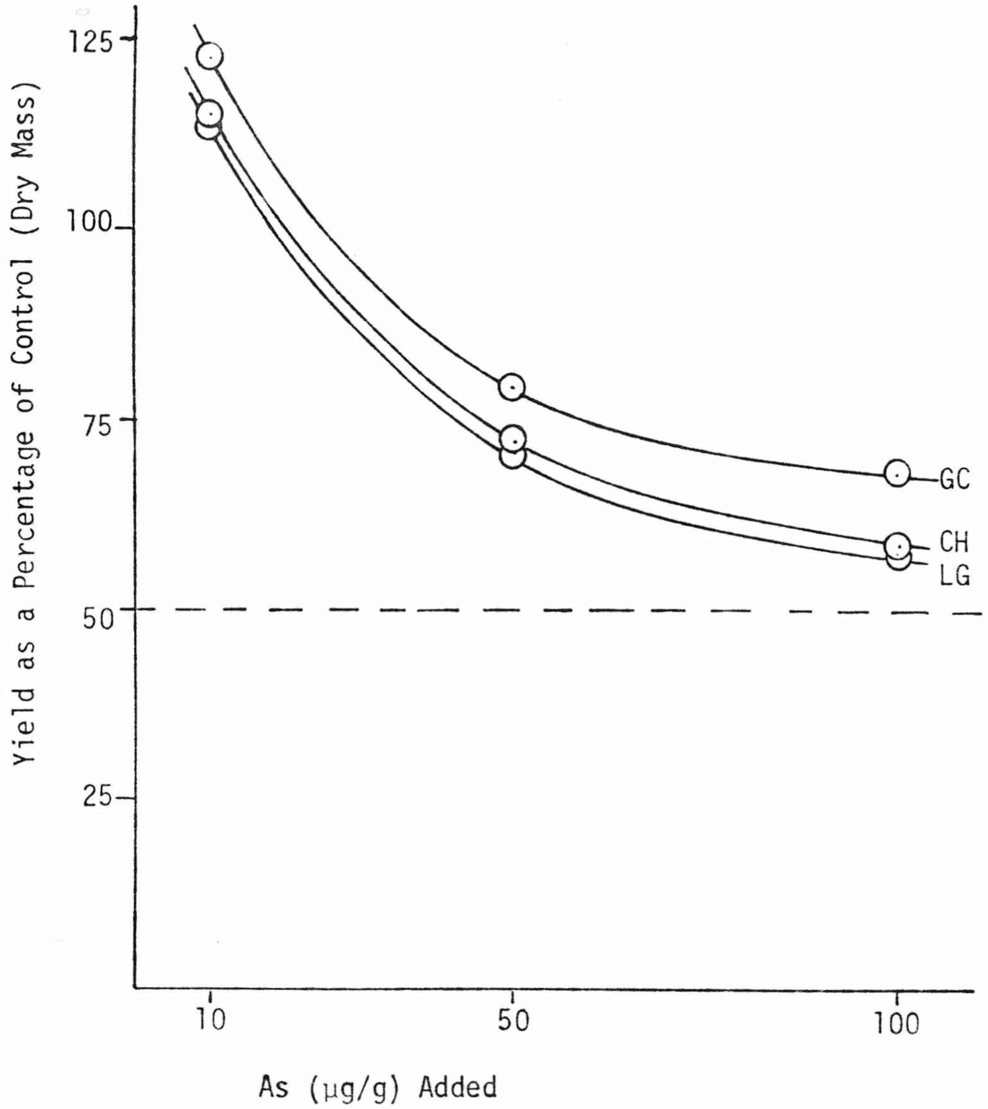


Figure 5.4 Graph of Bean Yield (Aerial Parts) Against Added Arsenic

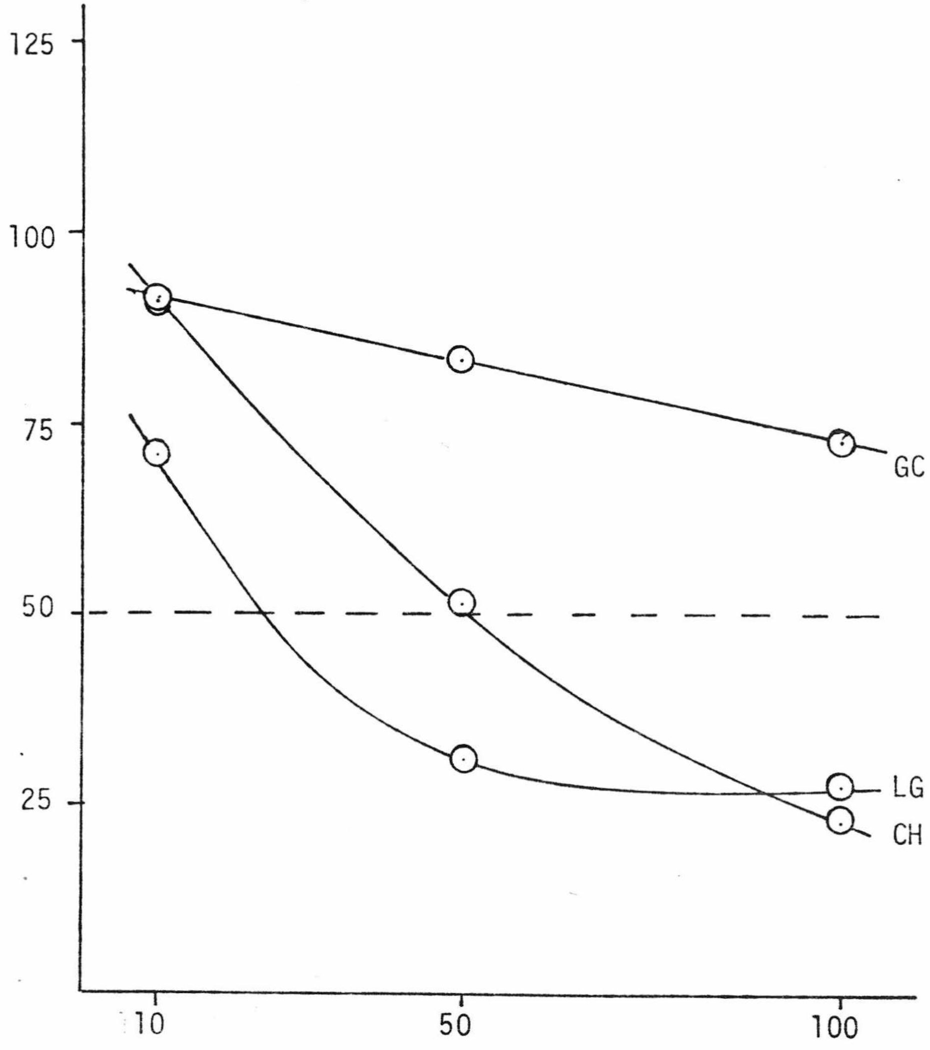


Table 5.5. Clearly the plant concentration increases with increasing soil arsenic. Correlations were made between plant As and soil As-treatment. The resulting correlation coefficients are given in Table 5.6 and are highly significant. These were used to determine the amount of As present in radish bulbs and the aerial part of beans at the GR_{50} level (Table 5.7). Comparatively little As is taken up into the bean pods and at the highest level of As on the Lower Chalk no pods were produced at all, suggesting that phytotoxicity occurs before high levels are accumulated. (See Table 5.4-7)

One might expect root crops to contain high levels of arsenic when grown in treated soil and this appears to be the case as the highest concentrations are found in the radish bulbs and bean roots. However, Walsh *et al.*(1977) believe that most of the As is confined to the epidermis, probably due to minute quantities adhering to the surface.

The concentrations of As found in the various plant parts have been plotted for the 10 and 100 μg/g As-treatments on each soil type in Figures 5.5-7. From these it can be seen that the plant parts can be generally classified:

plant roots > vegetative tissue > reproductive tissue

← As uptake

Arsenic residues are considerably lower in plants grown on the Gault Clay at the 100 g/g As treatment than on either of the other two

Table 5.5

Arsenic Concentration on (µg/g Dry Mass) in Plant Material Grown on Three Arsenic Amended Soils

Soil Developed On:	Gault Clay				Lower Greensand				Lower Chalk			
Plant Material / As µg/g added	0	10	50	100	0	10	50	100	0	10	50	100
Wheat (immature)	0.24	1.67	6.25	9.9	0.57	3.24	11.8	21.6	0.36	5.56	11.7	21.5
Radish Foliage	0.24	1.50	6.16	7.47	0.21	2.89	23.8	43.7	0.3	5.13	18.7	29.2
Radish Bulbs	0.33	0.85	4.8	8.77	0.58	1.88	52.7	117	0.51	3.10	87.0	255
Bean Stems	0.19	0.85	2.19	3.42	0.12	1.38	4.62	4.75	0.10	1.72	8.23	41.6
Bean Leaves	0.22	2.12	4.03	4.43	0.54	1.97	7.73	14.0	0.45	4.59	13.9	26.0
Bean Roots	0.41	2.45	6.62	11.9	0.68	2.9	8.96	17.2	0.33	2.97	38.0	126
Bean Pods	0.03	0.24	1.14	1.14	0.05	0.30	1.16	1.78	0.06	0.32	1.13	non prod.

Table 5.6

Correlation Coefficients of Plant Arsenic with Soil As-Treatment

Soil Plant Material	Lower Chalk	Gault Clay	Lower Greensand
Wheat	0.989	0.992	0.999
Radish Foliage	0.990	0.950	0.998
Radish Bulbs	0.986	0.998	0.996
Bean Stems	0.951	0.990	0.897
Bean Leaves	0.998	0.885	0.999
Bean Roots	0.979	0.997	0.999
Bean Pods	0.999 (excl. 100 μg/g)	0.886	0.989

$r = 0.878 \quad p < 0.05$

$r = 0.934 \quad p < 0.02$

$r = 0.959 \quad p < 0.01$

$r = 0.991 \quad p < 0.001$

Table 5.7

Concentration of As (µg/g) in Beans and Radish Bulbs at the GR_{50} Level

As (µg/g) at GR_{50} (dry Mass)	Lower Greensand	Lower Chalk
Bean: Leaves	3.90	14.2
Stems	1.98	17.8
Pods	0.55	1.18
Radish Bulbs	46.6	86.4

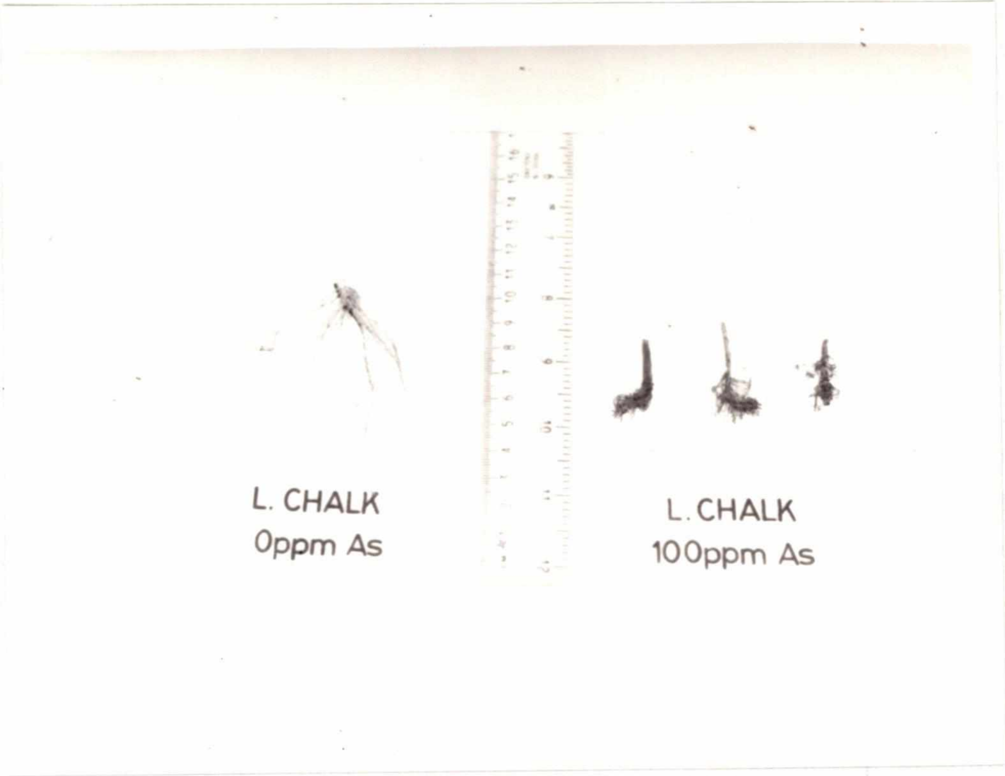
Photograph 1: Bean Plants Grown on the Lower Chalk

Photograph 2: Radish Plants Grown on the Lower Chalk

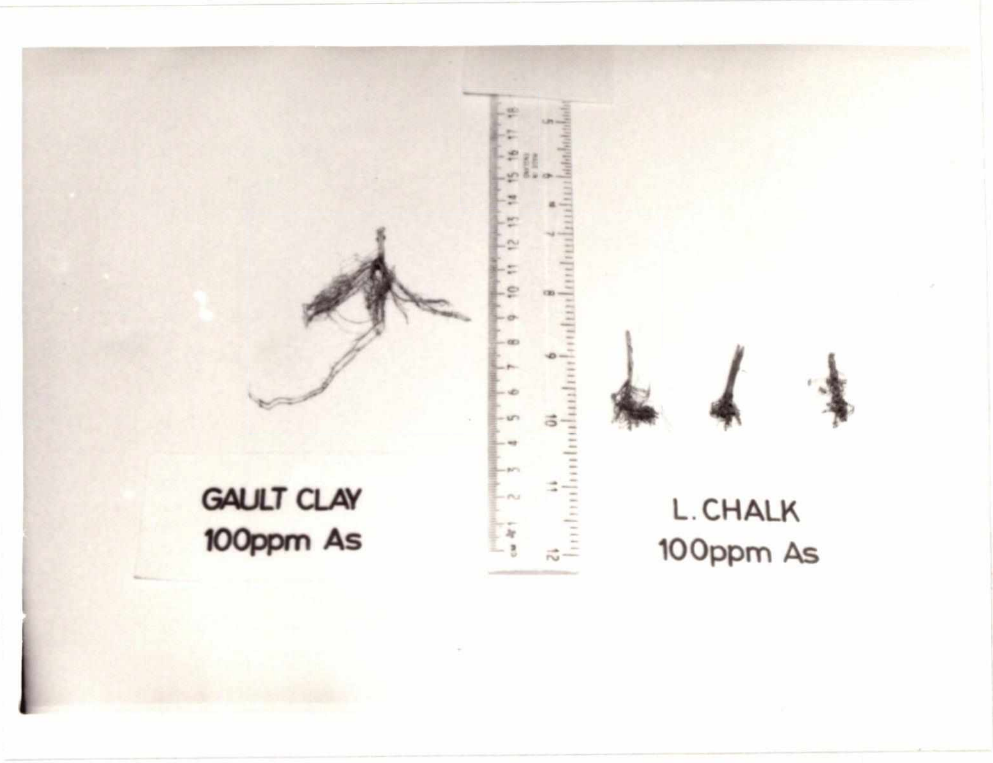
Photograph 3: Bean Plants Grown on the Gault Clay

Photograph 4: Radish Plants Grown on the Gault Clay

Photograph 5: Bean Plants Grown on the Lower Greensand



Photograph 6: Roots of Bean Plants Grown on the Lower Chalk.



Photograph 7: Comparison of Bean Roots Grown on the Gault Clay and Lower Chalk

Figure 5.5 Variations in Arsenic Content at Specific Doping Levels on the Lower Chalk

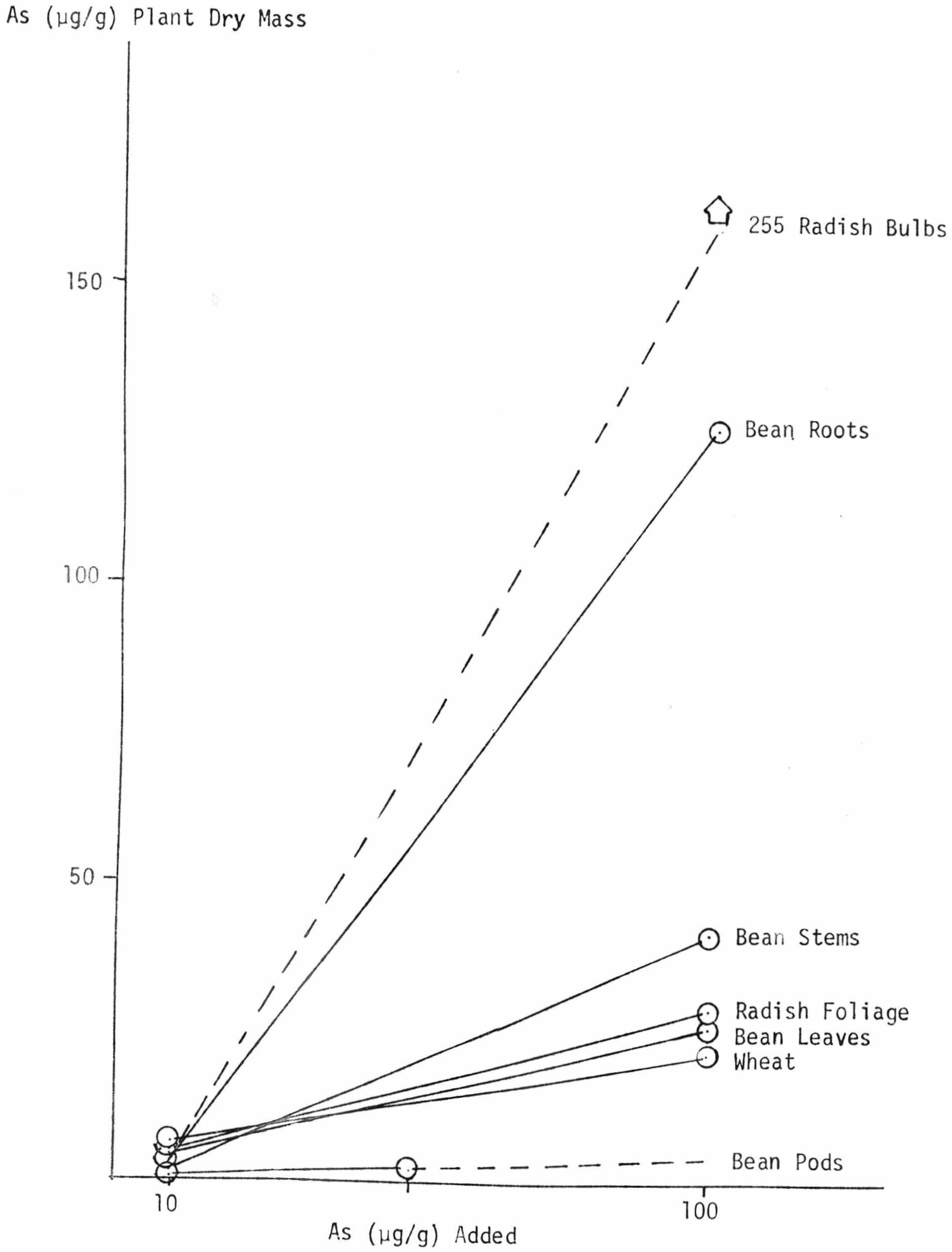


Figure 5.6 Variations in Arsenic Content at Specific Doping Levels on Gault Clay

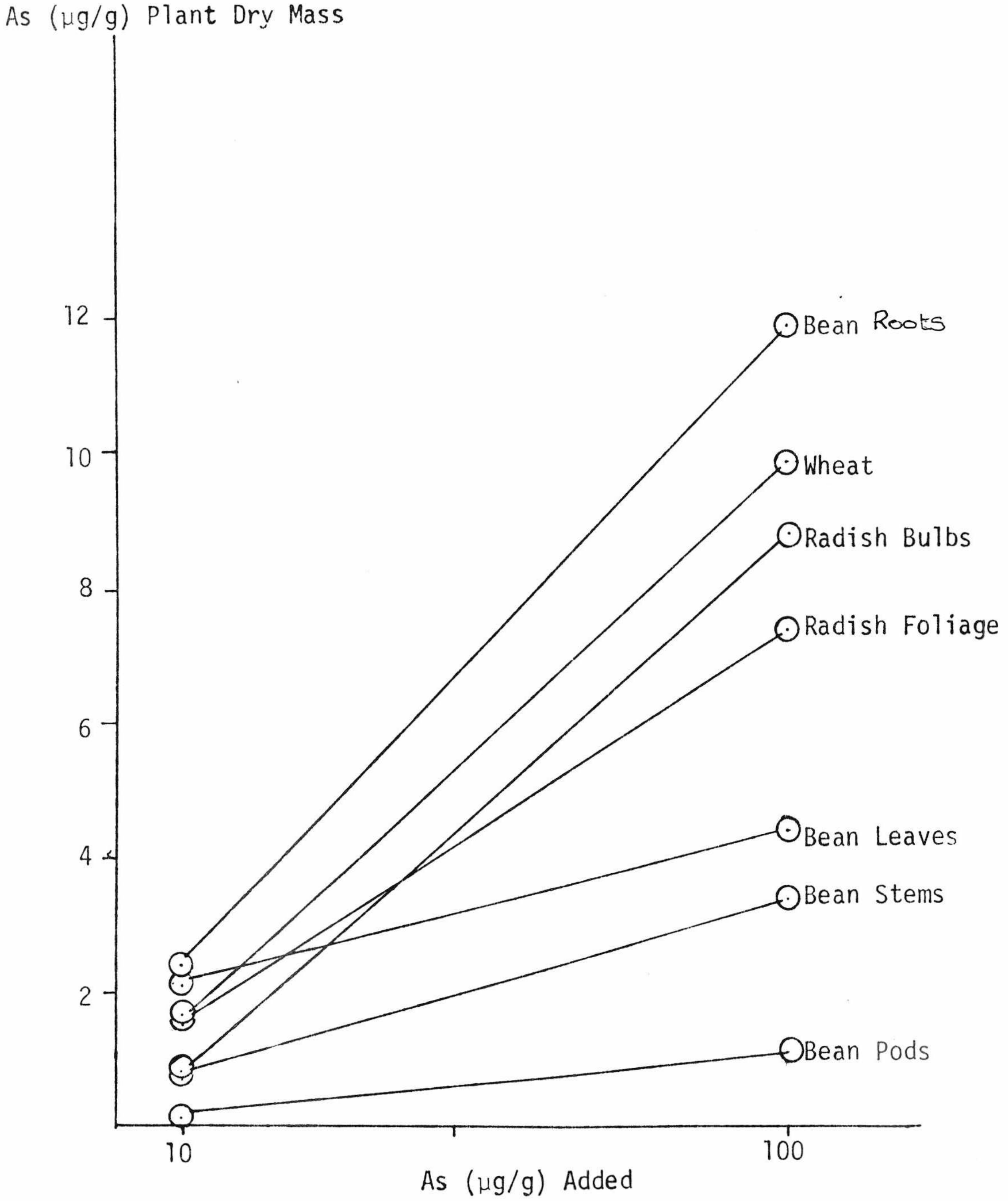
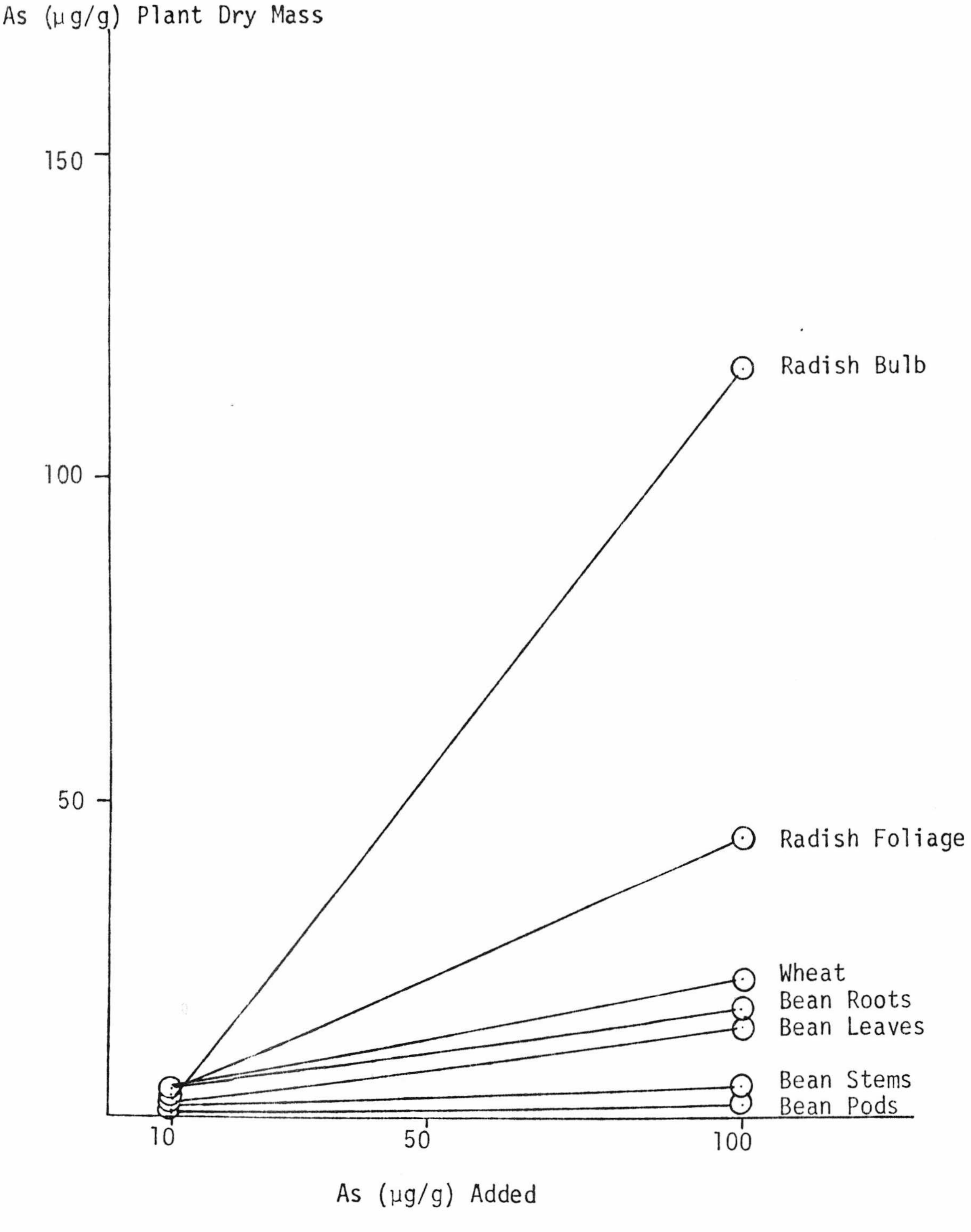


Figure 5.7 Variations in Arsenic Content at Specific Doping Levels on the Lower Greensand



soils. In fact the radish bulbs on the Lower Greensand and Chalk would seem to be actively taking up As , as the residue levels are greater than the applied concentration. Arsenic uptake is greatest in the radishes followed by the wheat and least in the beans (excluding the roots). This is similar to the yield reductions, and the crop sensitivity could be said to be in the order:

Beans > Radishes > Wheat

On the whole, the plants seem to be most severely affected on the calcareous soil, as generally the yield reductions and plant residue levels are the highest. This was visually apparent throughout the experiment. An obvious gradation from 0-100 μg/g As-applied could be seen in plant height and health. Those at the highest As-level had small and often mishapen leaves. Photographs 1 and 2 show the difference between growth at the 0 and 100 μg/g As level for beans and radishes. In comparison there is no detectable difference between the sample plants grown on the Gault Clay (Photographs 3 and 4). Similar stunting to the Chalk was found in plants grown on the treated Lower Greensand soil (Photograph 5), but only after harvest at the end of the experiment was yield reduction and As-uptake found to be less severe than the chalk. On harvesting the beans a brown rot was found to have developed in the roots of plants grown on the Chalk at the highest As-application (Photograph 6 and 7). They were extremely stunted and few root nodules could be found when compared to similar plants grown in Lower Chalk control pots and Gault Clay 100 μg/g As-treatment. The above ground symptoms were similar to those caused by drought and have been observed by other workers (Thomas, 1980).

5.3.2 Untreated Soil Pot Experiments

The physical and chemical properties of the soils used in this section are presented in Table 5.8, along with the amount of As determined in wheat grown on these soils.

The Cambourne soils contain elevated levels of all the elements studied, presumably as a result of past mining activities. The high As concentration in the Marlstone Rockbed is probably associated with the high Fe-content. The Romney Marsh stream sediment samples and the Lower Greensand soils have been discussed in the previous chapter.

The graph of wheat As against "total" soil As is presented in Figure 5.8. The plant As increases with soil As . However, one sample (44SS) contains a high level of As considering its total soil content. The element here must be in a form more available for plant uptake and therefore total soil arsenic should not be relied upon to predict plant levels. Surprisingly small amounts were taken up by the plants compared with the large concentrations in the soil. Even at 1000 μg/g soil As the wheat contained less than 6 μg/g As (dry mass).

5.4 Discussion

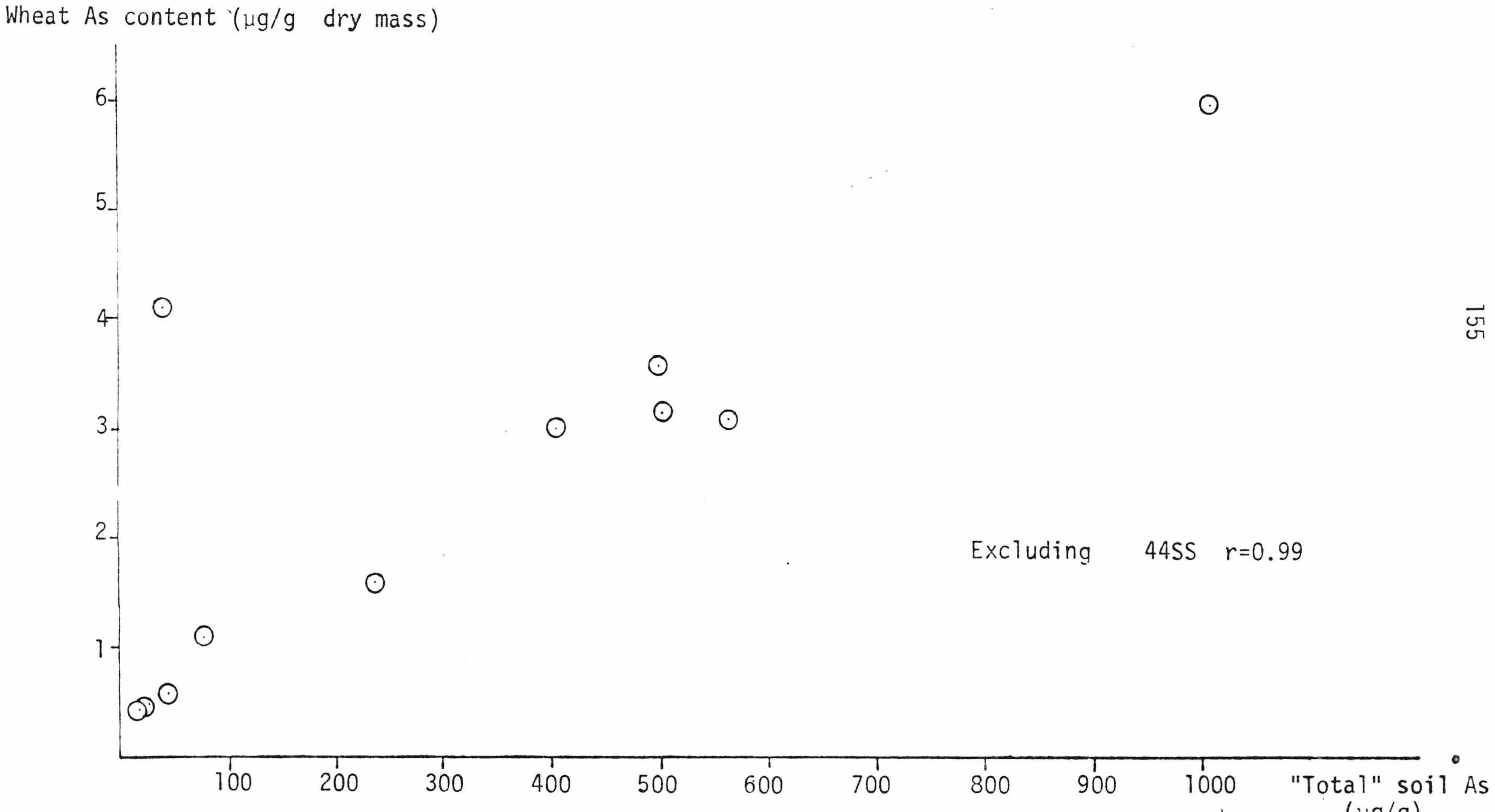
"Total" soil arsenic showed a good correlation with plant arsenic residue concentrations. However, considerably more As was taken up by soils on the 100 μg/g As-treated soil then on the 1000 μg/g As Cambourne sample, suggesting that other factors have to be taken into account.

Table 5.8

Physical and Chemical Properties of Untreated Pot Experiment Soils

Location	Soil No.	"Total" (µg/g)							Wheat As (µg/g)
		As	Cu	Mn	Zn	Fe%	LOI%	pH	
Cambourne Devonian Greenstones	C1	404	432	728	363	2.77	14.0	6.31	3.02
	C2	500	265	1067	481	4.07	7.14	6.75	3.58
	C3	501	326	1533	378	5.13	9.31	6.55	3.32
	C4	1009	640	992	886	4.65	12.8	6.17	5.94
	C5	236	200	1785	430	4.16	11.8	7.57	1.71
Melton	1BY	43.1	11.8	368	54.5	3.24	8.78	7.47	0.52
Mourbray	2BY	56.5	29.8	1225	258	24.0	13.7	6.87	3.20
Romney Marsh Alluvium	44SS	38.9	2.5	78.4	22.2	2.01	1.68	8.12	4.25
	6SS	76.5	9.5	61.0	60.2	2.73	6.01	7.97	1.19
Lower Greensand	4R	23.3	16.1	391	71.6	2.41	4.29	7.20	0.46
	6D	27.5	6.8	493	50.7	4.72	5.00	7.27	0.48

Figure 5.8 Graph of Wheat Arsenic Content Against Soil Arsenic



Some soils have a greater adsorption capacity than others as shown in Chapter Four. In these experiments the Gault Clay removed more than twice the amount of As from solution than the Lower Greensand and Chalk soils, presumably because of its higher clay and iron content (Tables 5.1-2). This resulted in a much lower yield reduction and plant tissue As content for all three crops than the other soils. However, having shown that the Chalk and Lower Greensand soils have a similar adsorption capacity, it was surprising to find that plants grown on the Chalk were more damaged and had higher As levels. Benson (1976) has also noted that added As is more toxic to flora on calcareous soils. To understand this more fully phosphates in calcareous soils must be examined. A detailed account may be found in Greenland and Hayes (1981).

Phosphates are strongly and specifically adsorbed in soils. They are poorly desorbable from hydrous oxides by concentration reductions, but are effected by pH changes. However, their behaviour is complicated by calcium carbonate onto which phosphates are preferentially sorbed.

The $CaCO_3$ crystal and structure are well understood, the usual form in soil being calcite. This has a rhombohedral crystal face with alternate Ca^{2+} and CO_3^{2-} ions on the surface. $CaCO_3$ usually has an associated diffuse layer as it is partially soluble. Either Ca^{2+} or CO_3^{2-} ions may leave the surface plane which results in a net charge of opposite sign which tends to retain the "escaping" ions in a diffuse layer. Thus other anions could be incorporated. Also the solvated surface may adsorb potential determining ions such as H^+ or OH^- and so acquire charge.

The predominant form of phosphate ions in solution in calcareous soils ($pH > 7.5$) are HPO_4^{2-} and $H_2PO_4^-$. Those which are specifically adsorbed on $CaCO_3$ surfaces must initially form ($CaHPO_4$) complexes or be adsorbed by displacement of CO_3^{2-} ions by HPO_4^{2-}. With increasing equilibrium of phosphate ions, multilayer formations are gradually built up as precursors for the formation of dicalcium phosphate crystallites which in alkaline soil change to the most basic calcium phosphate.

The adsorption mechanisms are not as well defined on $CaCO_3$ surfaces as on oxides and more work is required. However, it is not surprising that the concentration of available P in soils is determined by the form of calcium phosphate.

This affinity of $CaCO_3$ for phosphates becomes more important when it is realised that the Lower Chalk soil used in this experiment had a phosphate concentration of 14 µg/g as opposed to the recommended level of 40 µg/g required for optimum plant growth. The amount available for plant uptake was therefore very low.

Both phosphate and arsenate are absorbed by identical carrier mechanisms in most cells, and plants have difficulty in discriminating between them. Thus it is important that arsenic detoxification be rapid and continuous so that plants may survive in low phosphate soils. Benson *et al.* (1981) have linked their work on As metabolism in marine algae with that in higher plants.

Under high phosphate conditions, marine algae have been shown to absorb arsenate much as those under phosphate stress. Arsenite is produced by reduction of arsenate and is tightly bound by sulphydryl proteins and is insoluble in non-reactive solvent systems. This suggests that As pollution of high phosphate waters or soils could be damaging to algae and plants as it would ultimately saturate the sulphydryl groups of essential enzymes and inhibit photosynthesis or other metabolic processes.

Under arsenate stress very little As remains bound to proteins. The arsenite or arsenate is rapidly converted through a sequence of soluble intermediates to non-toxic products. The hazard of As accumulation may be ameliorated by excretion mechanisms, by removal by bacterial activities, andby storage of As in non-toxic neutral unreactive forms.

Most terrestrial plants, especially those in phosphate deficient soils are associated with mycorrhiza. These fungi exchange phosphate collected from the soil for plant glucose or sucrose. In low P soils mycorrhiza may be reducing and methylating arsenate to produce trimethylarsine. Plant roots possess ample reserves of phosphoenolpyruvate for reaction with trimethylarsine to produce trimethylarsonium lactate. The toxicity of this has not been established, but by analogy with closely related structures it should be non-toxic.

Therefore, considering the low availability of phosphate in calcareous soils, and the inability of plants to differentiate between arsenate and phosphate, it is to be expected that high levels of arsenic would be found in the crops grown on the Lower Chalk.

The forms of As in the soil and the mechanisms of translocation in the plant are not understood. From the results section it can be seen that in the bean plants generally the As tissue concentrations are:

roots > leaves > stems > pods

Porter andPeterson (1975) noted an increase in As concentration in leaves with age and suggested that this was possibly a detoxification process. The plant reduces its As content through the senescence and loss of old leaves.

The As content of edible plant tissue is naturally of importance to human helath, but the levels found in the bean pods in this experiment do not pose a hazard. Unfortunately, the wheat could not be grown to maturity. However, Thoresby and Thornton (1979) found in a study of the Tamar area that although the As concentration of barley grain increased with soil As, it did not exceed 0.4 μg/g As (dry mass) even when the soil contained >300 μg/g As. Therefore, it is unlikely that cereals would take up large amounts of As. In contrast, the radish results cause concern. Woolson (1973) published a value of 76.0 μg/g As (dry mass) in radish bulbs which is approximately 8 μg/g As on a fresh weight basis and exceeds the U.S. Public Health tolerance limit of 2.6 μg/g As (Walsh *et al.*, 1977). The GR_{50} for radish bulbs grown on the Lower Greensand and Chalk soils at the 100 μg/g As level were 46.6 and 86.4 μg/g As respectively (Table 5.7), and would also be above this tolerance level. However, a 50% cropping failure is economically unacceptable and high As levels are unlikely to be found in saleable root crops.

At present in the United Kingdom there is not sufficient information on sources of foodstuffs and dietry habits to make valid safety recommendations. These would depend on the form, bioavailability and proportion in the overall diet of arsenic in foodstuffs. In this investigation root crops may pose a hazard either by minute quantities adhering to the tuber or by direct plant uptake.

5.5 Conclusions

1. Adsorption capacities for the three experimental soils are in the order:

   Gault Clay > Lower Greensand = Lower Chalk

2. Yield decreases with increasing As concentration are essentially non-linear for all crops cultivated on each soil type in this investigation.

3. For all crops the yield reductions vary with the soil type:

   Gault Clay > Lower Greensand > Lower Chalk

   ← Yield

4. Wheat and radishes showed a yield increase at the 10 μg/g applied As level, whereas the beans did not.

5. Crop yield reductions were in the order:

   Beans > Radishes > Wheat

6. Good correlations were found between "total" soil As and plant As concentration in all pot experiments.

7. Crop As uptake varied with the soil type:

Lower Chalk > Lower Greensand > Gault Clay

[As] →

8. Plant variety As uptake was in the order:

Radishes > Wheat > Beans

9. Plant tissue can generally be classified as:

Roots > Vegetative Tissue > Reproductive Tissue

← [As]

10. High arsenic residues in Gault Clay are unlikely to be available for plant uptake due to the high adsorbances capacity of the soil. However, high concentrations may be found in root crops grown on arsenic-rich Lower Greensand and Chalk soils, especially if the soils are low in phosphate.

11. Phytotoxicity is likely to occur before harmful levels are taken up into bean pods.

CHAPTER SIX

THE "TOTAL" CONCENTRATION OF COPPER, ZINC, AND IRON IN WEALDEN SOILS

6.1 Introduction

Heavy metals are present in all uncontaminated soils as a result of weathering from their parent materials. In Britain this is bedrock or overburden transported by wind, water or glaciation. The influence of parent material may be modified by pedogenetic processes leading to mobilisation and redistribution within the soil profile and between soil types.

The natural range in rocks and soils is very wide as can be seen in Table 6.1. Sandstones and acid igneous rocks usually contain smaller amounts than fine-grained sediments and basic igneous rocks.

In agricultural soils the concentration of one or more of these elements may be increased in several ways:

i) Pesticide

Approximately 10% of the chemicals approved for use as insecticides and fungicides in the UK are based on compounds which contain Cu , Hg , Mn , Pb or Zn and are applied to a wide variety of crops (MAFF, 1978).

Table 6.1

Approximate Values of Cu , Zn , Mn and Fe (μg/g) Found in Rocks and Soils

(after Krauskopf, 1967; Bowen, 1966, 1979)

Element	Igneous		Sedimentary			Soils	
	Granite	Basalt	Limestone	Shale	Sandstone	Typical	Range
Cu	13	90	4	45	1-10	20	2-100
Fe	27,000	56,000	17,000	48,000	29,000	38,000	7,000-550,000
Mn	400	1,500	1,100	850	10-100	850	100-4,000
Zn	52	100	20	95	16	50	10-300

ii) Fertilisers

Some soils are deficient in heavy metals which are essential for plant growth and may be supplied either as a foliar spray or as soil additions. In the U.K. Cu and Mn deficiencies are the most important. This will be discussed further in Chapter Seven.

iii) Aerial Emissions

Most fossil fuels contain some heavy metals and industrial processes involving metal smelting and/or refining often result in large aerial inputs to soils and plants. For example, Little and Martin (1972) found high concentrations of Cd , Pb and Zn in soils adjacent to the Avonmouth, smelter, Bristol.

iv) Sewage Sludges

The practice of adding sewage sludge to agricultural land is well established. It is a useful means of disposal as well as a cheap source of N and P , and may improve the physical structure of the soil. The heavy metal content depends on the source of the sludge, but they may well accumulate in soils especially when sludges from industrial areas are applied. Typical concentrations can be found in Table 6.2.

v) Animal Slurries

The value of a supplement of $CuSO_4$ in pig fattening diets to give improved food conversion ratios is now well-recognised

(Unwin, 1977). Levels of up to 250 μg/g $CuSO_4$ have been

Table 6.2

Concentrations of Heavy Metals (μg/g dry mass) in 42 Sewage Sludges From England and Wales

(Berrow and Webber, 1972)

Metal	Median	Range
Cd	-	<60-1,500
Co	12	2-260
Cr	250	40-8,800
Cu	800	200-8,000
Fe	21,000	6,000-62,000
Mn	400	150-2,500
Mo	5	2-30
Ni	80	20-5,300
Pb	700	120-3,000
Sn	120	40-700
Zn	3,000	700-49,000

added with increased levels of Zn and Fe (Kornegay *et al.*, (1976). 80-95% of the dietary Cu and similar amounts of Zn and Fe are excreted in the manure, nearly all of which is spread on agricultural land. This has given rise to concern about applying these potentially toxic metals to the soil.

Cu, Zn Mn and Fe are essential to both plant and animal life (Thornton and Webb, 1980), but there is little published information on the background concentrations to be found in south-east England, apart from the Wolfson Geochemical Atlas (Chapter One). The abundance levels found in stream sediments are given in Table 6.3. The aim of this section is to establish the range and distribution of Cu , Zn Mn and Fe in Wealden soils. (See Table 6.3 overleaf.)

6.2 Results

All data are given in Appendix 4.

6.2.1 "Total Results

The summarised "total" Cu results are presented in Table 6.4 and generally fall within the soil ranges in Table 6.1. The Romney Marsh, Chalk, Lower Greensand and Weald Clay all have approximately normal distributions. However, the Romney Marsh and Hastings Beds have low ranges and standard deviations compared with the others. The Drift Deposits have a skewed distribution, probably as a result of their heterogeneity. This factor may also promote skewness in the Gault/Upper Greensand and Hastings Beds samples. The lowest

Table 6.3

Ranges of Cu , Mn , Zn (μg/g) and Fe (%) Published for Stream Sediments in the Wolfson Geochemical Atlas

Parent Material	Cu	Fe	Mn	Zn
Chalk	0-≥30	0-≥3	250-≥1000	0-≥100
Upper Greensand/ Gault	0-≥30	1-≥3	125-≥1000	0-≥100
Lower Greensand	0-≥7	1-≥4	0-≥500	0-≥50
Weald Clay	7-≥30	2-≥5	500-≥2000	50-≥100
Hastings Beds	0-≥15	1-≥4	0-≥1000	0-≥100

concentrations of Cu are to be found in the Lower Greensand soils, but to determine whether there is any real difference between the soil parent materials a t-matrix was constructed and can be found in Appendix 4.

From this it can be seen that the Lower Greensand contains significantly less Cu than the others, and the Romney Marsh less than the Weald Clay and Hastings Beds.

Overall the distribution of Cu in soils in the south-east is normal as shown by Figure 6.1.

The "total" zinc results are summarised in Table 6.5. All deposits show a normal distribution apart from the Drift Deposits and Chalk samples. The Romney Marsh, Lower Greensand and Hastings

Table 6.4

Summarised "Total" Copper ($\mu g/g$) Results for Wealden Soils and Stream Sediments

Parent Material	n	$\overline{x}$	σ_D	Range	Median
Romney Marsh	48	11.6	2.3	6.4-15.9	11.3
Drift Deposits	19	13.3	7.4	6.5-37.1	11.4
Chalk	23	12.7	4.7	6.9-29.2	12.3
Gault Clay/ Upper Greensand	22	12.8	6.2	6.6-31.4	11.9
Lower Greensand	35	9.3	4.5	2.1-22.1	9.0
Weald Clay	12	15.9	6.9	5.5-29.9	15.6
Hastings Beds	16	12.9	3.6	8.7-18.6	12.0
All Soils	175	12.0	5.03	2.1-37.1	11.4
Stream Sediments	8	7.0	4.5	2.5-15.6	6.7

Beds show the least deviation and therefore have the smallest ranges. Again the Lower Greensand have the lowest values, but to separate the others a t-matrix was drawn (Appendix 4). This confirms that the Lower Greensand is significantly lower in Zn than all the other samples, and also reveals that the Chalk deposits are significantly higher than the Romney Marsh and Hastings Beds. The Romney Marsh

Figure 6.1 Frequency Distribution of "Total" Copper in Wealden Soils

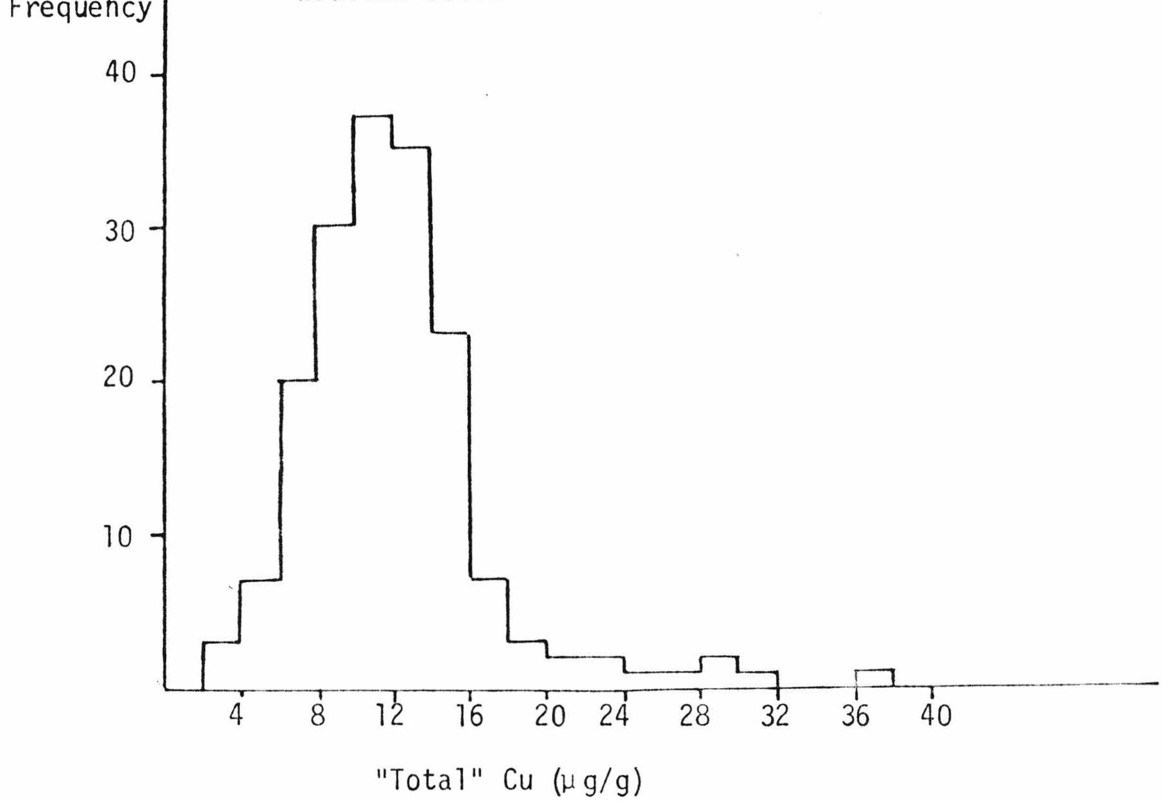
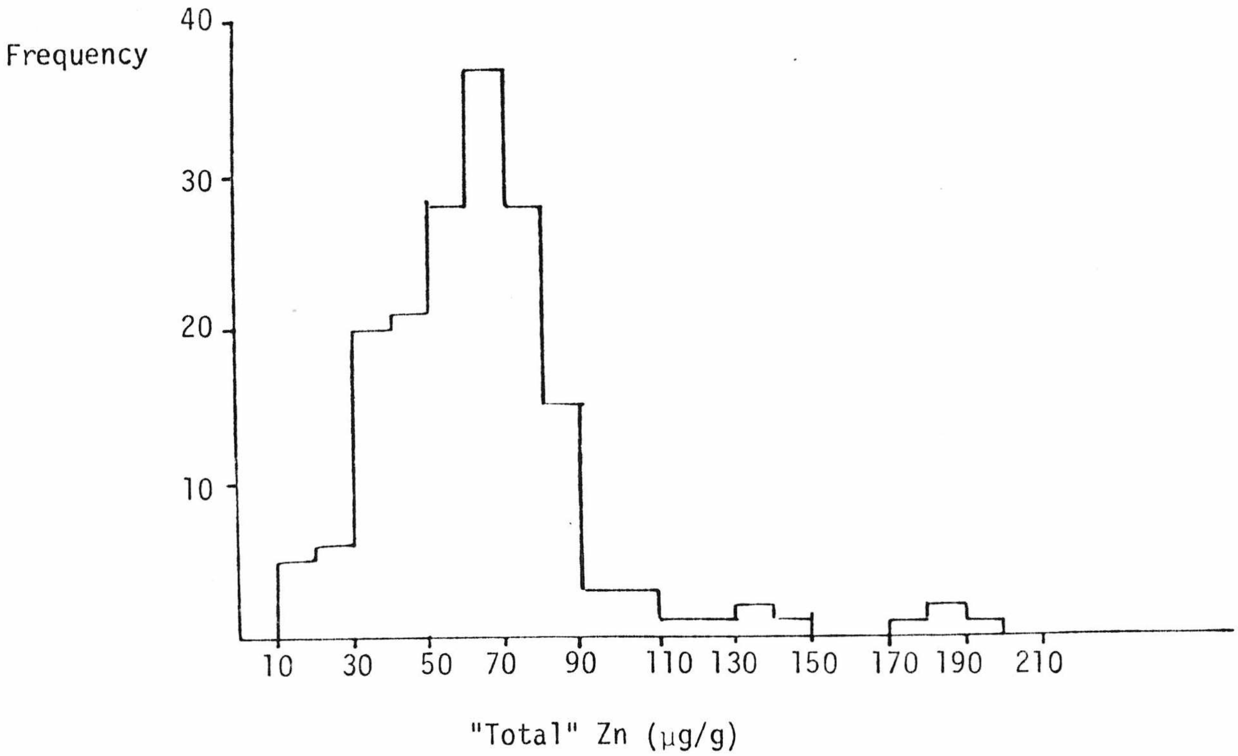


Figure 6.2 Frequency Distribution of "Total" Zinc in Wealden Soils



soils are also higher than the Hastings Beds.

The frequency distribution (Figure 6.2) for all the soils is normal.

The summarised Mn results are found in Table 6.6. Only the Romney Marsh and the Gault/Upper Greensand populations show approximately normal distributions. This is reflected in the "All Soils" frequency graph (Figure 6.3) which is skewed. All the soil parent materials have large ranges.

The "total" Mn t-matrix (Appendix 4) demonstrates that the Romney Marsh is lower than all the other soils except for the Lower Greensand. The Drift Deposit samples are higher than the Lower Greensand. The Chalk soils contain a greater concentration of Mn than the Drift Deposits, Gault/Upper Greensand and the Lower Greensand. The Gault Clay/Upper Greensand samples are lower than the Weald Clay and Hastings Beds.

From Table 6.1 the abundance of Mn would be expected to be in the order carbonates>shales>sandstones. Mn is most abundant in limestone because of its easy oxidation to Mn^{2+}, and the similarity in solubility between $MnCO_3$ and $CaCO_3$ (Krauskopf, 1972). The Romney Marsh values are low when it is considered that this landform is derived from the Weald Clay and Hastings Beds.

The "total" iron results are summarised in Table 6.7. All The soil parent materials have approximately normal distributions which is again emphasised by the "All Soils" populations. (Figure 6.4). The Lower Greensand soils have the greatest range which is to be expected because of iron-bearing sands mentioned in Chapter Two.

From the t-matrix in the Appendix 4 , it can be seen that the Chalk samples are significantly lower than all the other soil parent

Table 6.5

The Abundance of "Total" Zinc ($\mu g/g$) in Wealden Soils and Stream Sediments

Parent Material	n	$\overline{x}$	$\overline{\sigma}_D$	Range	Median
Romney Marsh	48	69	11.7	44.8-88.6	70.1
Drift Deposits	19	75.8	40.4	36.5-175	63.2
Chalk	23	78.5	37.8	40-184	69.7
Gault Clay/ Upper Greensand	22	63.1	36.7	26.6-198	56.4
Lower Greensand	35	45.6	22.1	14.7-110	40.7
Weald Clay	12	60.0	30.5	20.3-135	56.5
Hastings Beds	16	57.9	14.1	37.6-84.8	57.6
All Soils	175	63.9	29.1	14.7-183	61.2
Stream Sediments	8	46.6	17.5	22.2-72.2	49.0

materials as would be expected from Table 6.1. Also the Romney Marsh are higher than the Drift Deposits, Gault/Upper Greensand and Lower Greensand formations.

The ovoid patterns of the stream sediment data presented in the Wolfson Geochemical Atlas (Webb *et al.*, 1978) are confirmed by the soil chemistry when Table 6.3 is compared with Tables 6.4-7.

Table 6.6

The Abundance of "Total" Manganese (µg/g) in Wealden Soils and Stream Sediments

Parent Material	n	$\overline{x}$	$\overline{\sigma_D}$	Range	Median
Romney Marsh	48	256	75.6	70.4-430	262
Drift Deposits	19	492	363	125-1307	335
Chalk	23	835	381	355-2123	763
Gault Clay/ Upper Greensand	22	362	147	101-710	378
Lower Greensand	35	265	200	17-938	190
Weald Clay	12	718	626	78.7-2368	617
Hastings Beds	16	792	626	315-2729	461
All Soils	175	454	395	17-2729	348
Stream Sediments	8	120	58.9	61-223	94.3

Figure 6.3 Frequency Distribution of "Total" Manganese in Wealden Soils

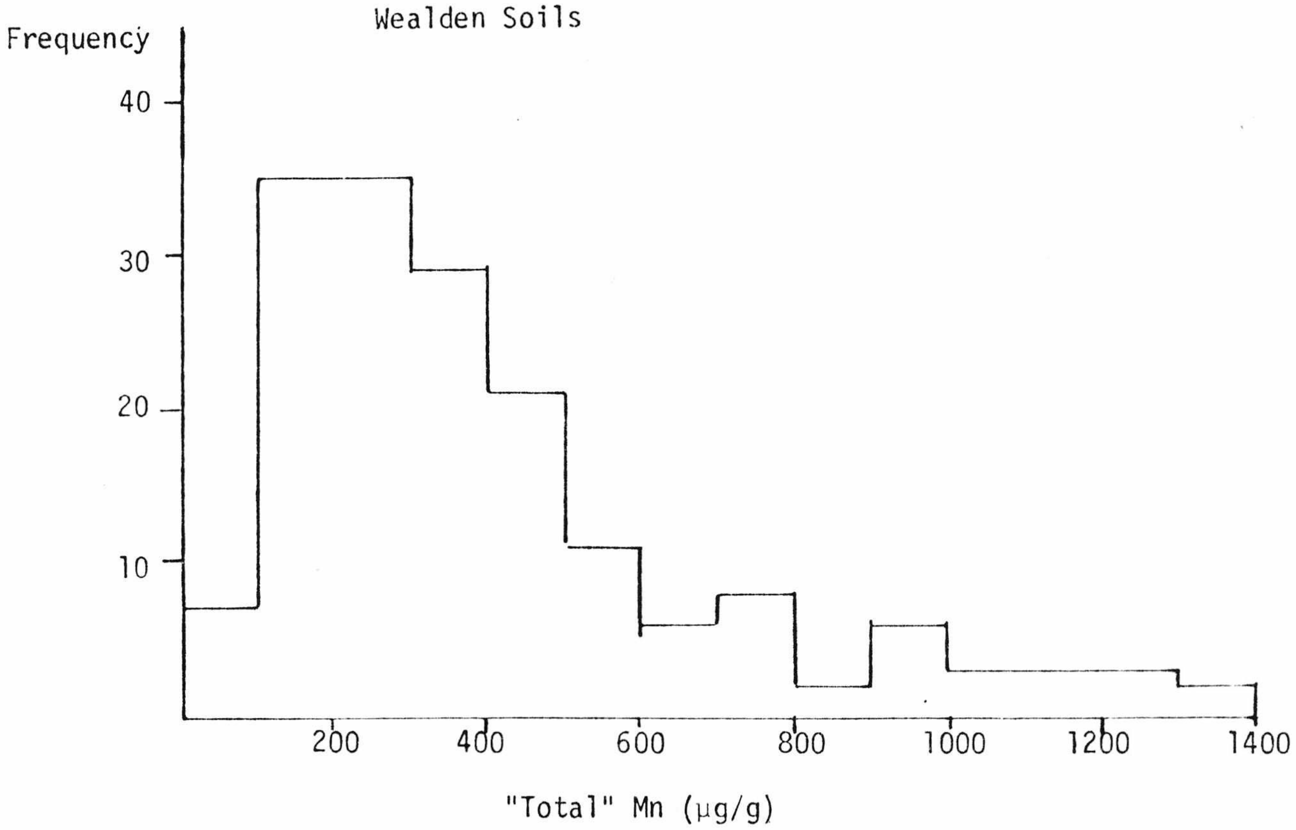


Figure 6.4 Frequency Distribution of "Total" Iron in Wealden Soils

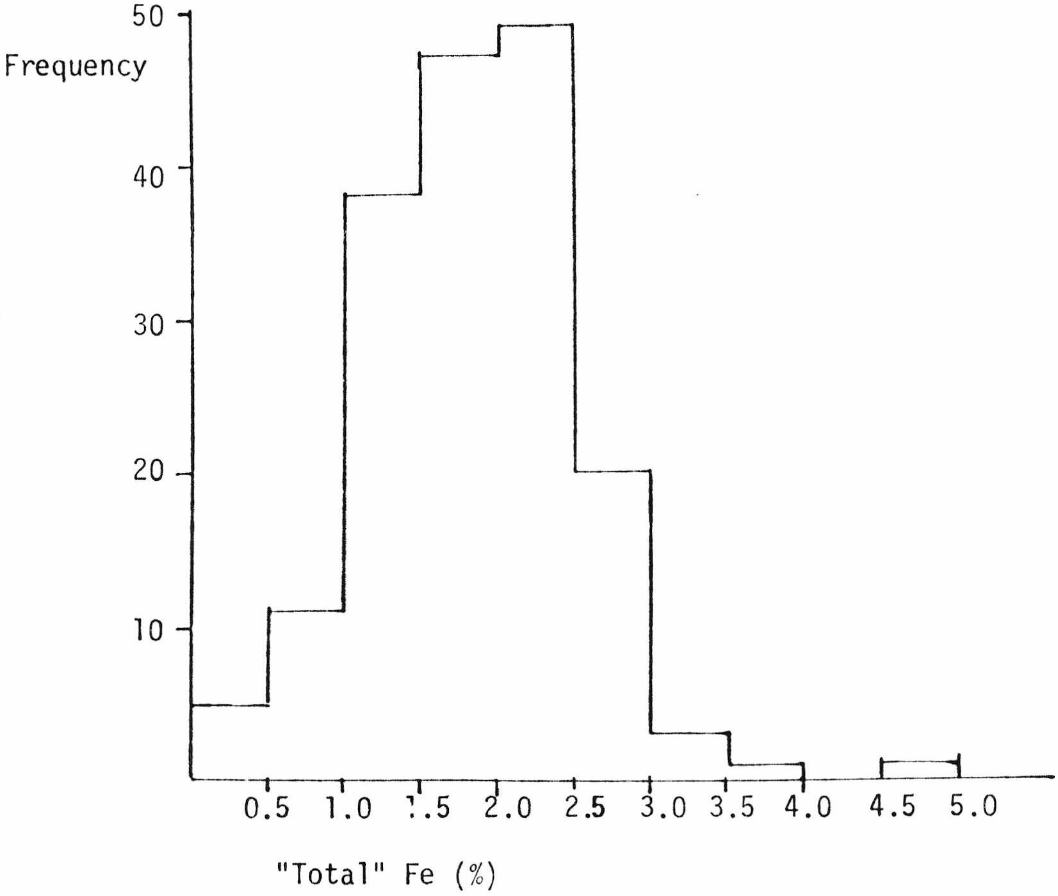


Table 6.7

The Abundance of "Total" Iron (%) in Wealden Soils and Stream Sediments

Parent Material	n	$\overline{x}$	$\overline{\sigma}_D$	Range	Median
Romney Marsh Alluvium	48	2.16	0.35	1.12-3.01	2.25
Drift Deposits	19	1.82	0.49	1.26-2.89	1.70
Chalk	23	1.30	0.49	0.32-2.43	1.24
Gault Clay/ Upper Greensand	22	1.83	0.76	0.75-3.30	1.91
Lower Greensand	35	1.70	0.93	0.46-4.72	1.48
Weald Clay	12	2.03	0.82	0.30-2.97	2.15
Hastings Beds	16	2.04	0.58	1.04-3.14	1.92
All Soils	175	1.86	0.69	0.30-4.72	1.85
Stream Sediments	8	1.88	0.64	1.08-2.73	1.84

6.2.2 Inter-Element Associations

Correlation coefficients were calculated for each combination of element pairs (Table 6.8) and the following observations can be made.

6.2.2.1 Zn:Cu Ratios

From Table 6.8 it can be seen that Zn and Cu are very strongly positively correlated. The Zn-Cu antagonism is

Table 6.8

Correlation Coefficients for Pairs of the Elements Studied

Parent Material	Correlation Coefficient (r) for: Zn:Cu	Cu:Mn	Cu:Fe	Mn:Zn	Mn:Fe	Zn:Fe
Romney Marsh Alluvium	0.738[3]	0.632[3]	0.638[3]	0.572[3]	0.611[3]	0.785[3]
Drift Deposits	0.920[3]	0.514[1]	0.084	0.721[3]	0.053	0.111
Chalk	0.705[3]	0.210	0.527[2]	0.532[2]	0.735[3]	0.591[2]
Upper Greensand/Gault Clay	0.905[3]	0.071	0.313	0.153	0.131	0.305
Lower Greensand	0.740[3]	0.399[1]	0.238	0.325	0.441[2]	0.416[1]
Weald Clay	0.821[3]	0.114	0.610[1]	0.281	0.585	0.744[2]
Hastings Beds	0.952[3]	0.340	0.630[2]	0.430	0.388[1]	0.670[2]
All Soils	0.602[3]	0.105	0.095	0.137	0.026	0.109

1. $p > 0.05$ 2. $p > 0.01$ 3. $p > 0.001$

well-documented. Brar and Sekhon (1976) found that Cu competitively inhibited Zn absorption by wheat seedlings. Hawf and Schmid (1967) reported similar findings. Chaudry *et al.* (1973) found that Cu applications had no effect on Zn uptake by rice plants, but applications of Zn depressed Cu uptake. This antagonism is also important in animal nutrition. Zn deficiency is still of pressing importance to pork producers employing high supplemental levels of $CuSO_4$ as a growth stimulant. Symptoms include a dry, cracked condition of the skin known as parakeratosis (Allaway, 1975) which is linked with cell division.

When "total" Cu is plotted again Zn (Figure 6.5) a reasonably tight scatter is obtained. However, if an RMA is calculated (Appendix 5), the Chalk samples are found to give a significantly different slope from the other soil parent materials, except the Gault Clay/Upper Greensand. From the transects (Figure 6.6i-iii), it can be seen that the Zn concentration is higher in the Chalk relative to Cu. This phenomenon may be partially explained by the fact that Zn^{2+} is strongly adsorbed on magnesian carbonates because it is spatially matched with Mg^{2+} ions in the $MgCO_3$ crystal surface lattice (Greenland and Hayes, 1981).

Zn/Cu ratios are of some interest in studies which have attempted to relate trace element inbalances with human diseases. For example, cancer of the stomach in parts of North Wales has been correlated with the Zn/Cu ratio in garden soils (Stocks and Davies, 1964), although this theory

Figure 6.5 Scatter Plot of Cu Against Zn for all Soils

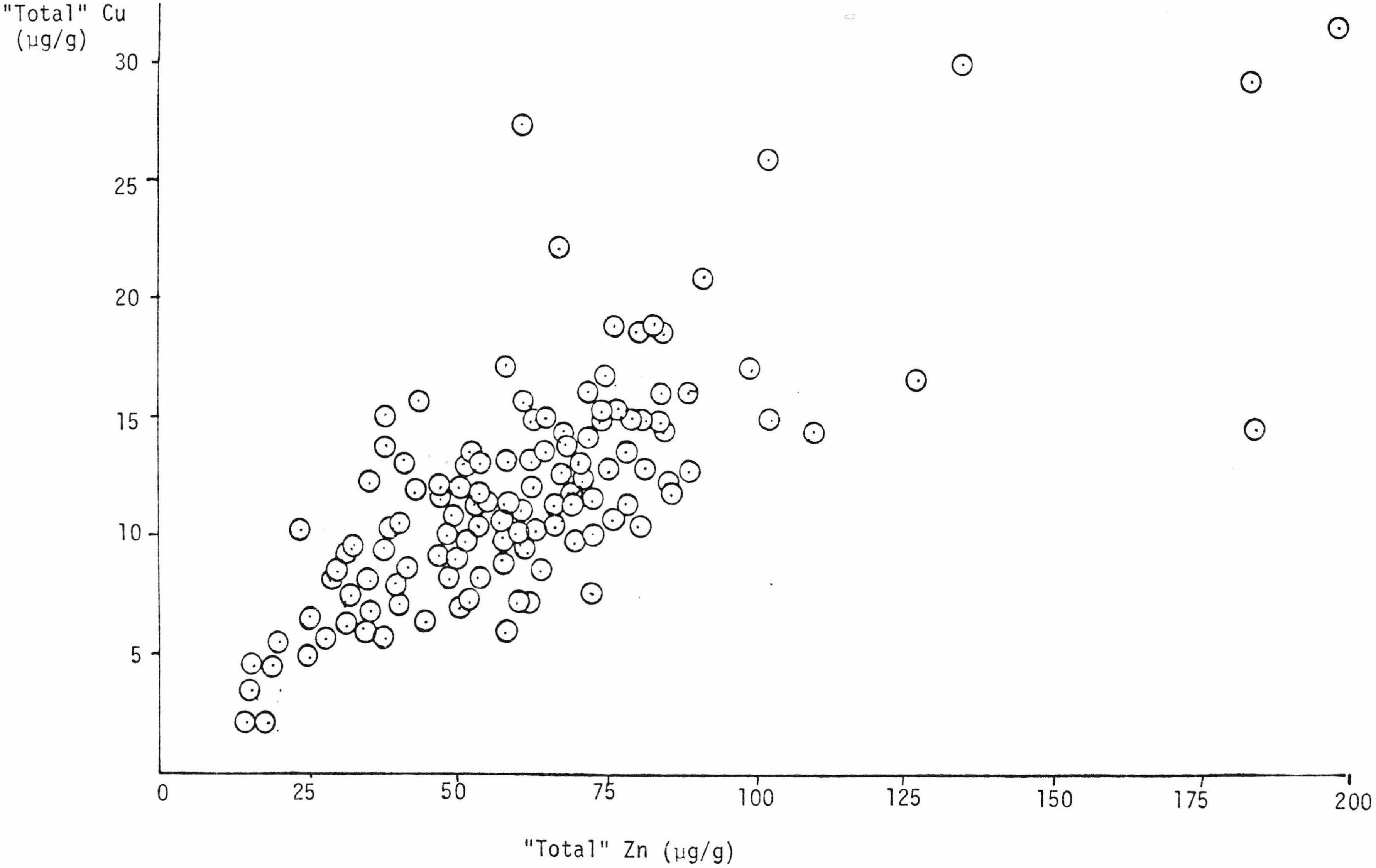


Figure 6.6(i) Cross-Section of Pevensey Transect (1-6P) Showing the Relationship Between Copper and Zinc

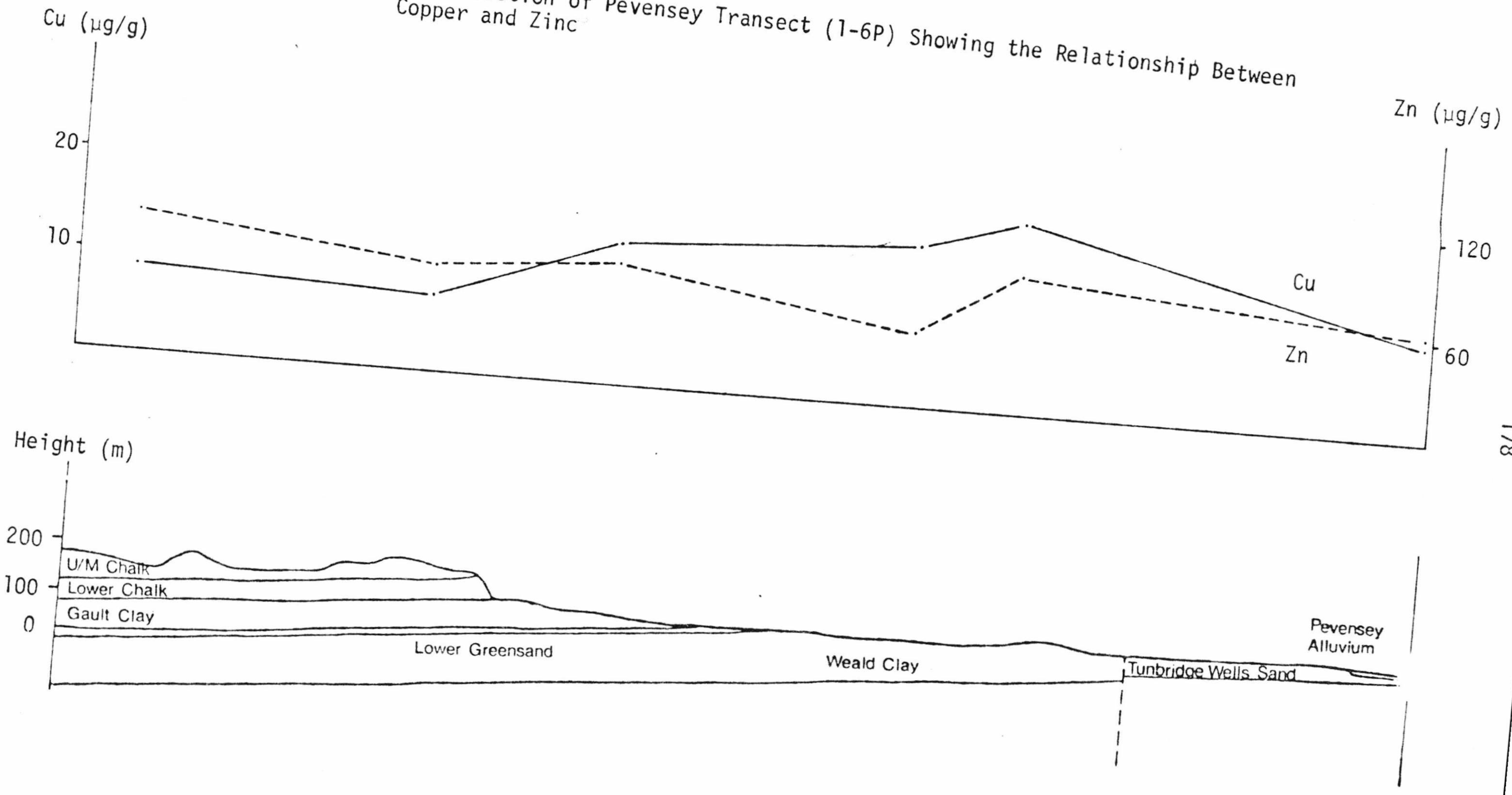


Figure 6.6(ii) Cross-Section of Hastingleigh Transect (1-9K) Showing the Relationships Between Copper and Zinc

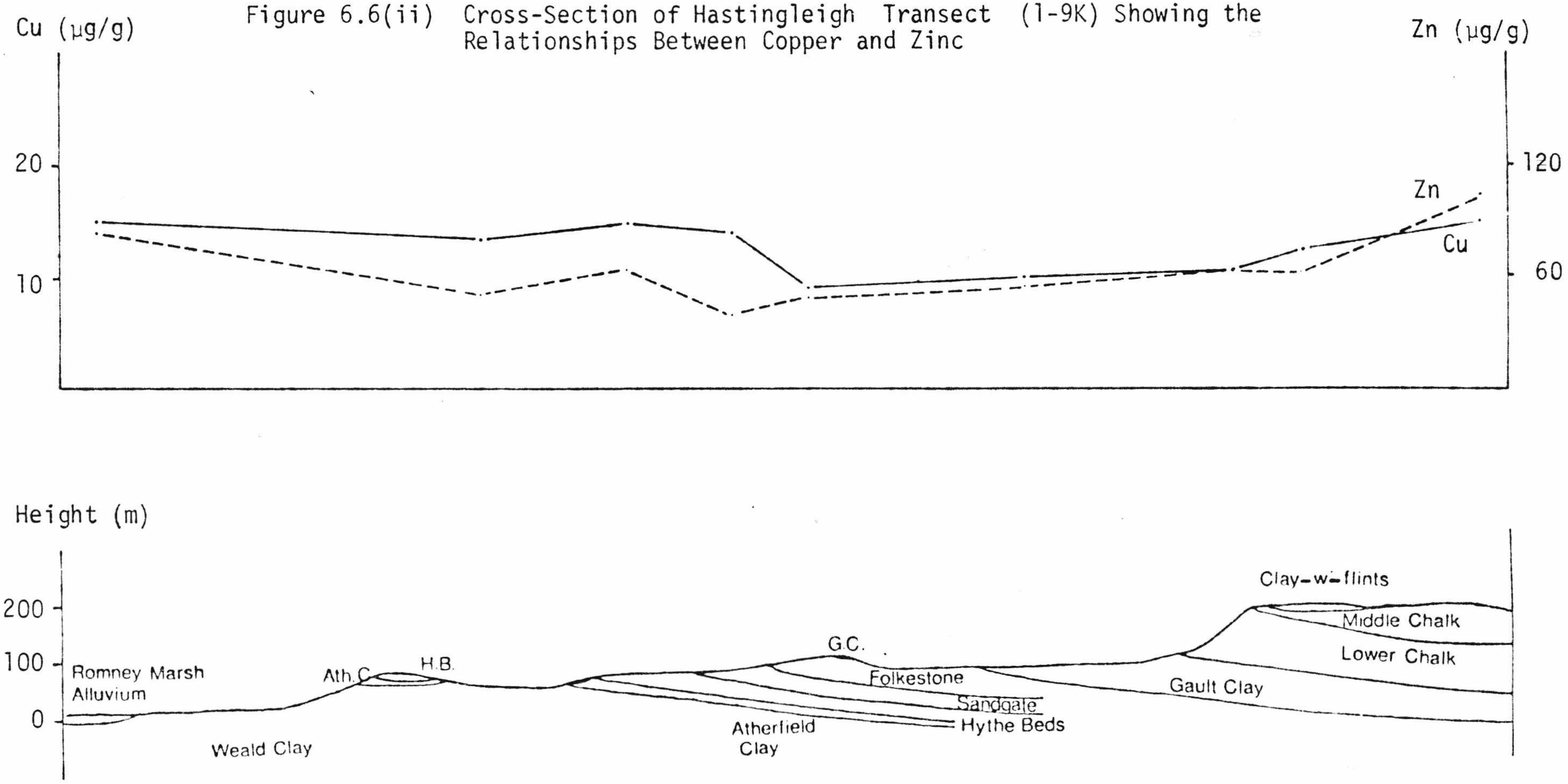
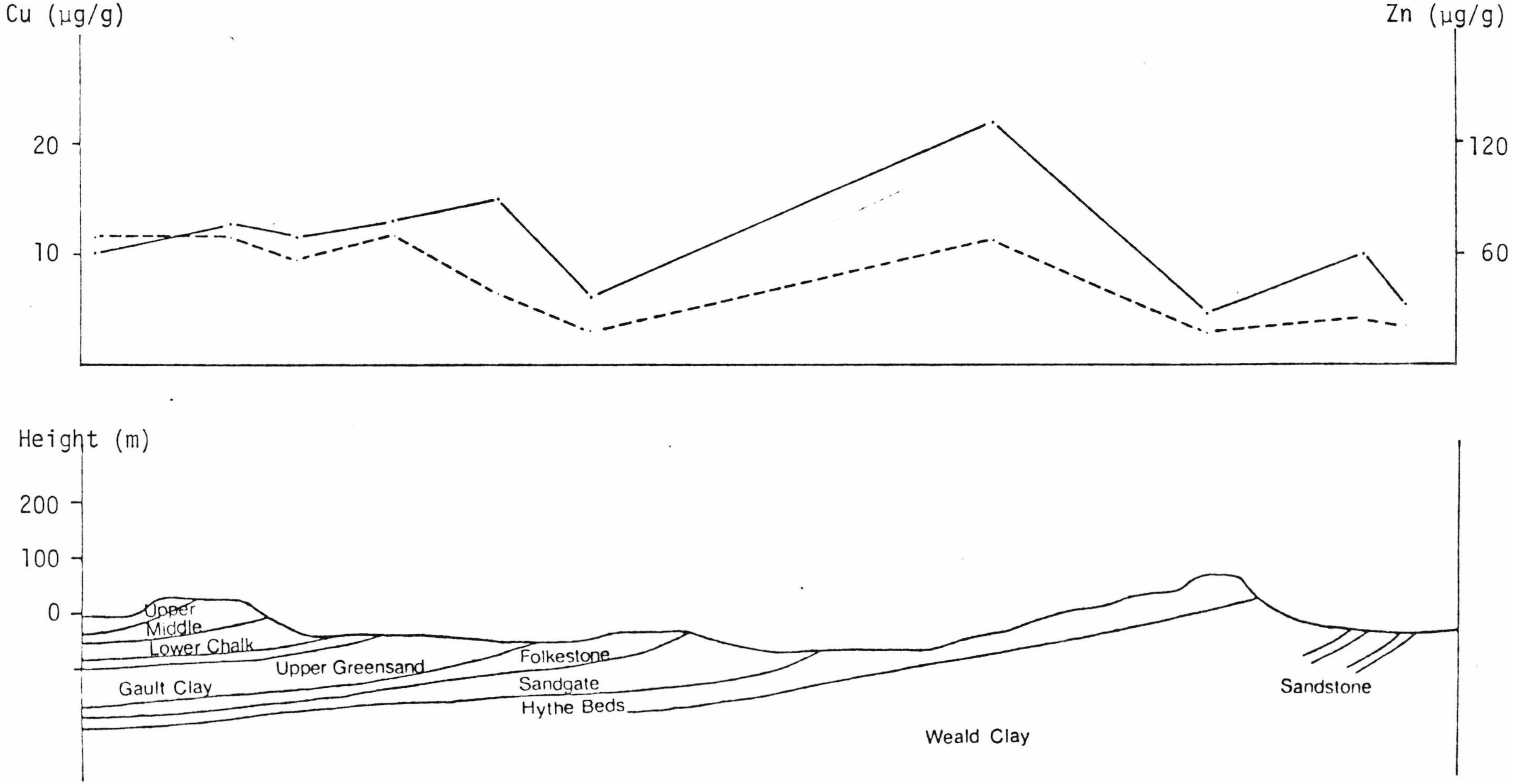


Figure 6.6(iii) Cross-Section of Midhurst Transect (1-10 M) Showing the Relationship Between Copper and Zinc



has not been substantiated by further work. However, recent studies of stomach cancer in south-east England (Clough, 1982) suggest that those areas which draw their water supplies from the Chalk aquifer have a high incidence of stomach cancer than those which draw water from the Lower Greensand (for example, Ashford, Cranbrook, Tenterden). The nitrate levels in these waters have been investigated in this context, but Zn/Cu ratios should perhaps also be considered.

6.2.2.2 Other Ratios

Fe and Mn oxides may hold significant proportions of some heavy metal ions in soils. There is evidence from electron microprobe analysis of surface soils that Cu and Zn are concentrated in, and distributed equally between, the Mn and Fe oxides (Norrish, 1975). Therefore, it would not be unexpected to find correlations between these elements.

From Table 6.8 it is apparent that there is no significant overall relationship for any pair. Cu/Fe , Mn/Fe and Zn/Fe show the most consistent relationships overall the soil parent materials. Of the individual soil groups, the Romney Marsh has strong correlations for all the element pairs, and the Chalk for most pairs. The Romney Marsh landform contains a very uniform group of soil types. However, homogeneity *per se* does not denote a direct association, but it may influence the factors which would otherwise cause statistical scatter. Groups of wider provenance, for example, the Lower Greensand, may lose significance due to their heterogeneous nature.

6.3 Conclusions

1. The abundance levels for "total" Zn , Cu , Fe and Mn in soils in south-east England are typical of values for soils as documented in recent scientific literature.

2. Soils derived from the Lower Greensand consistently have lower abundance levels than the other parent materials. This almost certainly reflects their arenaceous character.

3. The Romney Marsh soils have a low absolute level of Mn .

4. As might be expected from abundance levels in limestones, the Chalk soils have the highest concentrations of Mn , and the lowest Fe levels.

5. The Lower Greensand soils show a wide range for Fe due to the occurrence of iron-bearing sands.

6. The ovoid element distribution patterns of the Wolfson Geochemical Atals (Webb *et al.*, 1978) are traceable to the soil parent material.

7. Zn and Cu are very strongly positively correlated ($p<0.001$) for all the soils.

8. The Chalk Zn/Cu ratio is significantly different from the other soil parent materials, except the Gault Clay/Upper Greensand.

9. The Romney Marsh gave good correlations for all the element pairs ($p<0.001$).

CHAPTER SEVEN

"AVAILABLE" COPPER, ZINC, MANGANESE, IRON AND ARSENIC IN WEALDEN SOILS

7.1 Introduction

The optimum range of elements in soils is narrow and both deficiencies and excesses can produce problems such as crop failure and death of livestock. Subclinical effects such as lowering of crop yields and loss in animal production are often unrecognised and these losses may be of considerable economic significance.

As farming practices intensify and greater demands are made on the land possibly depleting elemental reserves, previously marginal situations may become a problem.

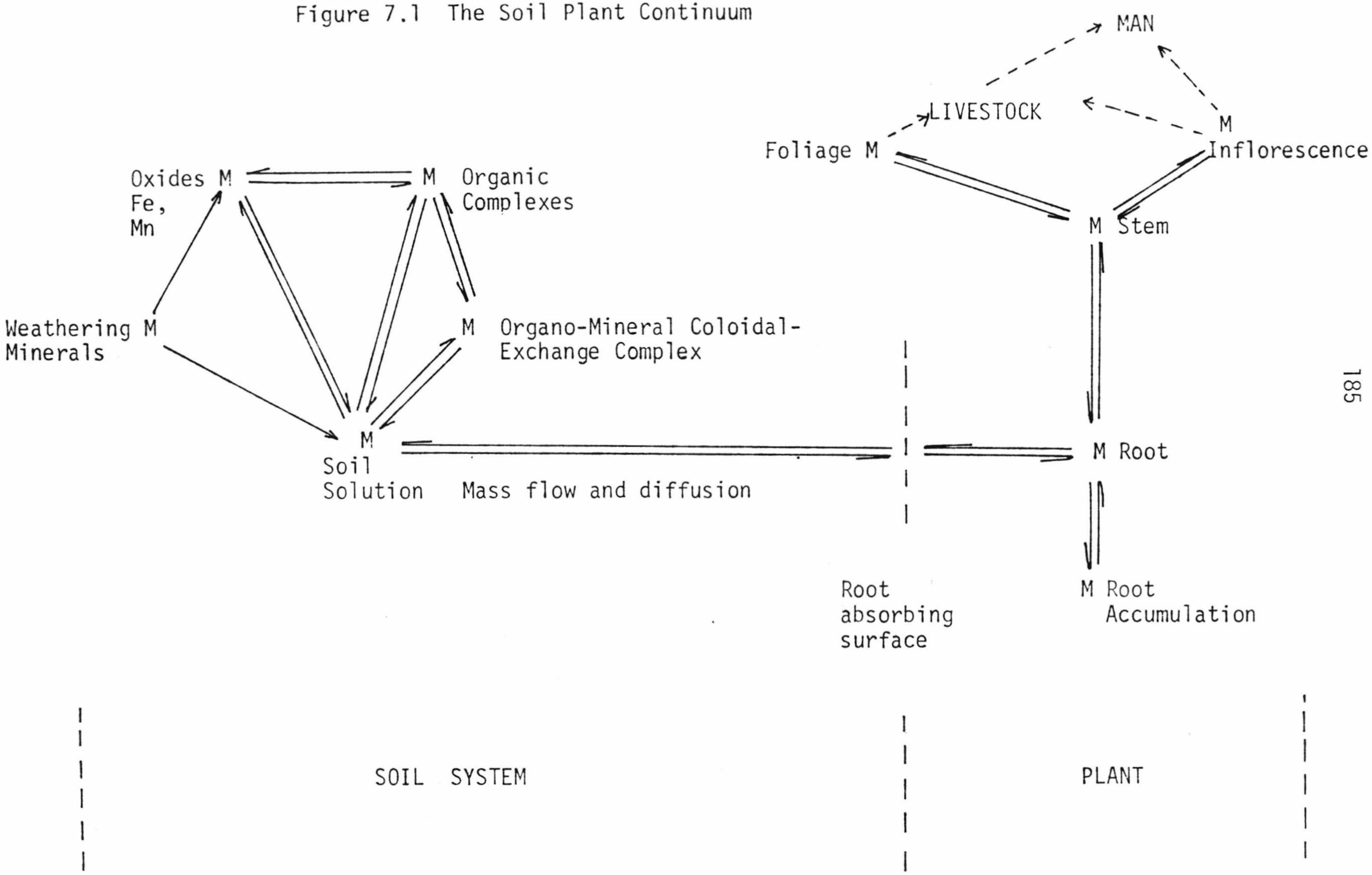
7.1.1 Physico-Chemical Properties of Soils

The total trace element content of soils is largely determined by the parent material and the effects of climate, relief, time and living organisms acting upon these (Jenne, 1968). The distribution of metals within the soil, and the interaction of these with plants, and animals is represented by Figure 7.1.

The major labile pools of trace elements in soils are:

1. Soil solution (metals as ions, and soluble complexes)
2. Organo-mineral cation exchange complex (minerals adsorbed)

Figure 7.1 The Soil Plant Continuum



3. Hydrous oxides of Fe , Mn , Al (metals sorbed)
4. Organic complexes (metals complexed: large molecules insoluble; small soluble)
5. Minerals (metals within the crystals - released during chemical weathering).

The nature of the element and the relative proportions of the phases present will determine distribution. The availability of metals to plants and animals depends on their predominant form in the soil. Extraction techniques are used to estimate the supply of a particular element to growing crops.

7.1.1.1 Inorganic Phase Equilibria

Soils comprise a dynamic system in which numerous chemical reactions are occurring simultaneously. The environment is constantly changing due to fluctuating temperatures, respiring microorganisms, changing O_2 and CO_2 levels, alternating moisture levels and other important factors. Inorganic solid compounds such as crystalline minerals, and amorphous Fe and Mn oxides establish solubility levels for these metals by releasing free ions if the solution level drops below its equilibrium level, or conversely by precipitation if the solution level exceeds the equilibrium level. Thus, solid phases participate in the dynamic equilibria involving soil solution, soil exchange complex, adsorption surfaces, uptake and release of nutrients by microorganisms and removal of elements by plants (Mortveld *et al.*, 1972).

7.1.1.2 Sorption on Hydrous Oxides

The production and stability of hydrous oxides is dependent on Eh/pH conditions, and the activities of micro-organisms. Sorption of metals is controlled principally by pH, the concentration of metal ions, and of alternative complexing agents in solution. Clay minerals are frequently coated with oxides.

7.1.1.3 Ion Exchange Capacities

This property is due almost entirely to the clay and silt fractions, organic matter, and hydrous oxide content of a soil. Clay minerals and organic molecules bind together to form a colloidal organo-mineral complex of net negative charge. This charge is a result of isomorphous substitution in the clay lattice, from the ionisation of hydroxyl groups in silica tetrahedra, from unsatisfied OH^- and O^{2-} groups at the crystal edge and from carboxylic and phenolic groups on humic substances. Cations may be adsorbed in several forms such as Cu^{2+}, $ZnOH^+$ (Greenland and Hayes, 1981). The ions are held by Coulombic and Van der Waals forces and are surrounded by water molecules in a double diffuse layer near the colloid surface.

The behaviour of H^+ is an anomaly as although monovalent, it behaves as a polyvalent ion. In acid conditions many H^+ ions counteract the net negative charge, so that many heavy metals are in solution and hence available to plants due to the H^+ dominated cation exchange complex. This may, in very acid conditions, lead to toxic conditions. The pH can be increased by liming, but carried too far over-liming can lead to lime-induced deficiencies as metals become unavailable in free solution.

7.1.1.4 Organic Complexes

The ability of soil organic matter to form stable combinations with metal ions is well established. Some of the metals occurring naturally in soil, or introduced in fertilizers are held as insoluble complexes and are thus unavailable to plants. On the other hand, many metals that would ordinarily convert to insoluble precipitates at the high pH values found in productive agricultural land are maintained in solution through chelation (Mortveld *et al.*, 1972).

7.1.2 The Distribution of Cu, Zn, Mn and Fe in Soils

Copper exists in soils as Cu^{2+} and $CuOH^{+}$ adsorbed on other minerals, organic matter, and Fe and Mn oxides; and as ions in solution. While the solution remains oxidising and slightly acidic Cu^{2+} may remain in solution. When the pH becomes higher than about 6.5 the complex $CuOH^{+}$ becomes dominant and at >pH 7.0 any one of several precipitates may appear (Mitchell, 1964; Mortveld *et al.*, 1972).

Weathering of silicates or carbonates containing manganese where oxygen is limited gives Mn^{2+} in solution. A large part of this (84-99%) may be sorbed in complexes. Under oxidising conditions a large number of adsorbed higher oxides may form for example, MnO_2, with only a small proportion of manganese existing in clays. Compounds of Mn^{2+} are at least slightly soluble at pH 7.0 or higher. Bacteria are thought to be important in oxidation/reduction reactions (Mortveld, *et al.*, 1972; Krauskopf, 1972). The role of micro-organisms is related to the essentiality of Mn in the oxidation of organic matter (Cotter and Mishra, 1968).

Zinc minerals weather to Zn^{2+} in solution in neutral/acid conditions. Zinc occurs in soil solution or adsorbed on clays, oxides, and organic matter. Most Zn on average is present as Al- and Fe-oxides bound and in residual forms (Iyengar *et al.*, 1981).

The distribution of Fe in soils is affected by soil formation processes pH , redoxstatus, and chelation are of most important in Fe soil chemistry. Fe^{3+} , $FeOH^{2+}$ and $Fe(OH)_2^{+}$ will predominate in acid conditions and $Fe(OH)_3$, $Fe(OH)_4^{-}$ in alkaline. Microorganisms may affect transformations of Fe in several ways (Alexander, 1977). At normal pH values (>6.0) chemical oxidation of Fe^{2+} becomes the dominant process. Some bacteria and fungi are active in decomposing organic matter which has been binding Fe , thus allowing it to precipitate as the hydroxide.

Little is known of the distribution of As in soils, but many workers have correlated extractable As with plant uptake (Jackson and Levin, 1979). Extractants used include Bray P-1 , 0.5N $NaHCO_3$, and 0.05N HCl + 0.025N H_2SO_4 (Walsh, *et al.*, 1977).

7.2 Results

All results are recorded in Appendix 4.

7.2.1 DTPA Extractions for Cu , Zn , Mn , Fe

Lindsay and Norvell (1978) tentatively proposed critical deficiency levels for the four elements shown in Table 7.1.

7.2.1.1 Copper

A summary of the DTPA extractions from the various soil parent materials can be found in Table 7.2. The lowest values are from the Lower Greensand soils as might be expected from the "total" results in the previous chapter. (See Table 7.2.) Only two of these soils are close to the 0.2 μg/g critical level and several contain <1.0 μg/g extractable Cu . None of the other soil types appear to be deficient.

Table 7.1

Threshold Deficiency Levels for DTPA Extractions

Element	Critical Level (μg/g)
Cu	0.2
Zn	0.8
Mn	1.0
Fe	4.5

Caldwell (1971,1976) listed areas of Cu deficiency which in South-East England include shallow organic chalk loams

Table 7.2

Summarised Values of DTPA Extractions from Wealden Soils (µg/g Cu)

	n	$\overline{x}$	$\overline{0}_D$	Range	Median
Romney Marsh Alluvium	36	1.8	0.6	1.08-3.52	1.68
Drift Deposits	19	2.32	1.66	1.06-41.8	1.78
Chalk	20	1.98	1.12	1.06-6.04	1.72
Gault/Upper Greensand	19	2.32	1.18	1.24-5.5	2.10
Lower Greensand	31	1.68	1.08	0.16-4.62	1.50
Weald Clay	10	3.46	2.28	0.64-8.82	3.30
Hastings Beds	8	2.40	1.02	0.72-4.00	2.46

(rendzinas), and loamy sands derived from the Lower Greensand.

Copper deficiencies in various crops produce abnormal colouring and development, lowered quality in fruit and grain, and lowered grain yields. Martens (1976) found tentative levels for Cu of

Deficient <2.4 (µg/g) in whole wheat plants
Intermediate 2.4-3.0 20 cm high
Adequate >3.0

Sheep are particularly prone to "swayback", a disease where the myelin sheath of the central nervous system is not laid down during the gestation period. This is associated with hypocupraemia probably due to dietry Cu deficiency and excess Mo.

7.2.1.2 Zinc

Zinc deficiency is unrecognised in British field crops (Thornton and Webb, 1980) although marginal deficiencies are possible. This is confirmed by the summary Table 7.3, where it can be seen that the levels are for the most part more than adequate. It is interesting to note that although the Lower Greensand contained the lowest "total" values, the extractable concentration is high. Compounds of Zn are soluble in neutral and acid solutions and is therefore known as one of the most mobile of the heavy metals (Mortveld *et al.*, 1972). (See Table 7.3)

7.2.1.3 Manganese

Overall none of the soils appear to be deficient from the results presented in Table 7.4. Archer (1976) listed the soils most susceptible to Mn deficiency in the south-east as the Gault Clay, Romney Marsh Alluvium and River Alluvium. The Romney Marsh has low "total" Mn as noted in Chapter Six and is mainly alkaline. Deficiences are most commonly found on peats, mineral soils with high organic matter content and where the pH is >6.0 (Batey, 1971). Surprisingly all the alkaline soils examined here appear to have an adequate amount of available Mn . (See Table 7.4)

7.2.1.4 Iron

The proposed critical level for Fe deficiency is 4.5 μg/g

Table 7.3

Summarised Values of DTPA Extractions From Wealden Soils (μg/g Zn)

	n	$\overline{x}$	σ_D	Range	Median
Romney Marsh Alluvium	36	2.97	1.30	0.97-7.92	2.80
Drift Deposits	19	6.22	9.56	0.86-41.7	3.17
Chalk	20	5.66	2.66	2.06-11.3	5.56
Gault/Upper Greensand	19	3.56	1.72	1.34-7.36	3.34
Lower Greensand	31	5.20	7.20	1.00-40.6	3.36
Weald Clay	10	2.24	0.76	0.92-3.16	2.22
Hastings Beds	8	2.20	1.17	1.04-4.20	1.62

Table 7.4

Summarised Values of DTPA Extractions from Wealden Soils (μg/g Mn)

	n	$\overline{x}$	σ_D	Range	Median
Romney Marsh Alluvium	36	13.4	7.80	4.38-22.0	11.7
Drift Deposits	19	31.5	25.7	6.06-117	22.7
Chalk	20	29.3	32.2	13.1-159	19.0
Gault/Upper Greensand	19	16.3	15.9	4.8-75.6	13.4
Lower Greensand	31	15.3	11.5	3.12-50.0	11.8
Weald Clay	10	30.2	22.0	16.3-69.6	21.5
Hastings Beds	8	25.8	14.6	13.4-58.4	20.3

and from Table 7.5 it can be seen that the lowest levels are found in soils developed on the Gault Clay and Chalk, although they contain sufficient concentrations. Fe behaves similarly to Mn and decreases in availability with increasing pH.

Table 7.5

Summarised Values of DTPA Extractions from Wealden Soils (μg/g Fe)

	n	$\bar{x}$	σ_D	Range	Median
Romney Marsh Alluvium	36	125	84.6	42.7-361	94.8
Drift Deposits	19	142	77.4	38.9-306	143
Chalk	20	47.8	25.7	21.0-112	39.2
Gault/Upper Greensand	19	142	67.8	18.2-283	137
Lower Greensand	31	178	127	44.0-664	152
Weald Clay	10	137	69.6	36.1-208	124
Hastings Beds	8	155	79.8	36.0-265	161

7.2.2 Sample Correlations

The strongest correlations were found between "total" and available Cu which are listed in Table 7.6 and plotted in Figure 7.2. This relationship was also observed by Alloway and Davies (1971). The correlation between "total" and available was found to be much weaker for Zn and Mn .

Table 7.6

Correlations of Total:Available Metal

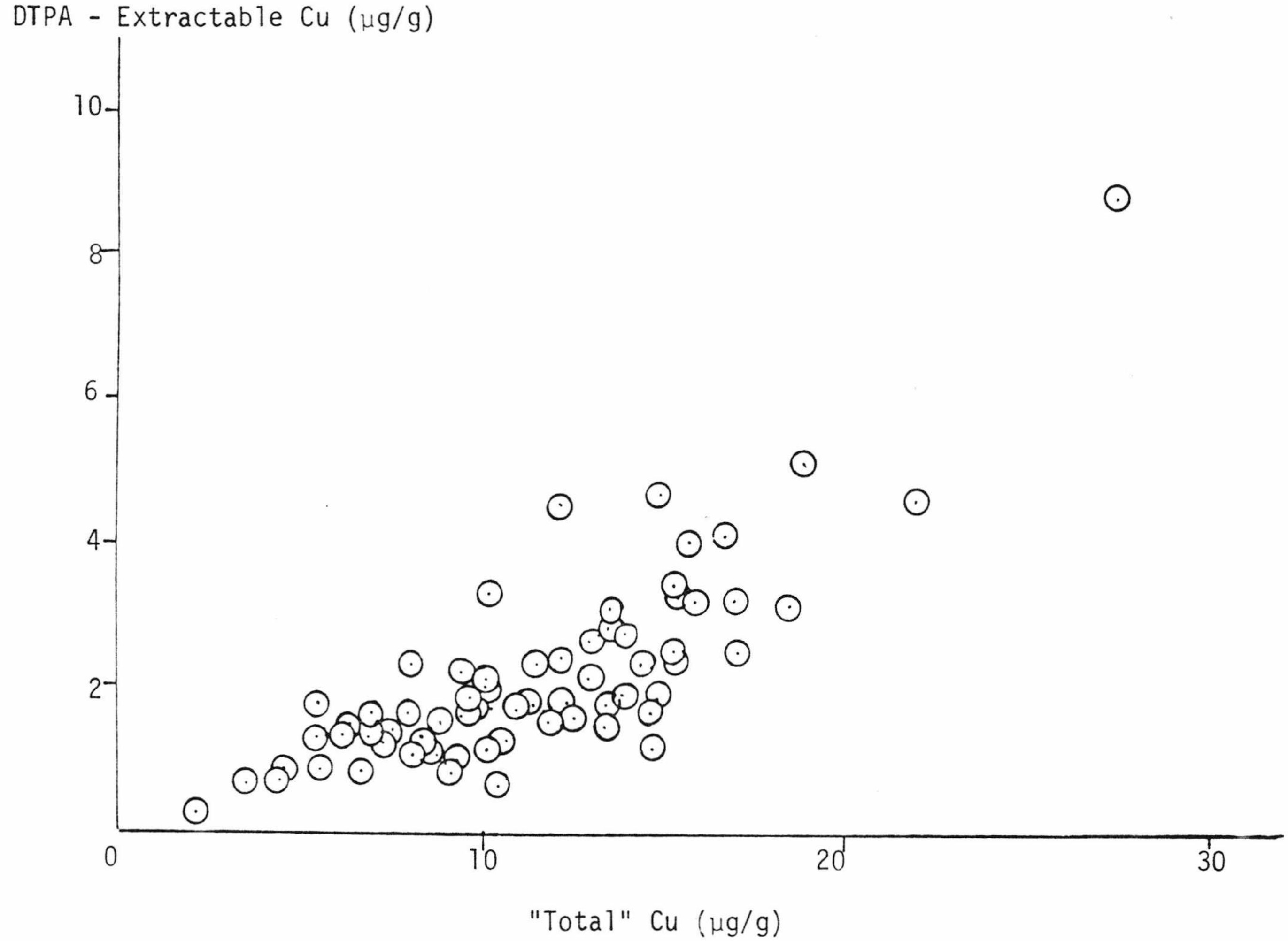
Soil Parent Material	Coefficient of Correlation (r) Cu	 Zn	 Mn
Romney Marsh Alluvium	0.802^3	0.265	0.152
Drift Deposits	0.940^3	0.807^3	0.329
Chalk	0.843^3	0.744^3	0.335
Gault/Upper Greensand	0.841^3	0.056	0.094
Lower Greensand	0.848^3	0.610^3	0.699^3
Weald Clay	0.904^3	0.555^1	0.732^2
Hastings Beds	0.827^3	0.178	0.652^1

1. $p<0.1$, 2. $p<0.01$, 3. $p<0.001$

Cu is believed to be strongly complexed by soil organic matter (Baker, 1974) and Hodgson *et al.* (1966) reported that 98% of the Cu in soil solution was in an organic complexed form. However, only two correlations were found between DTPA extractable Cu and LOI% (Hastings Beds $r=0.753$, Weald Clay $r=0.585$).

Misra and Mishra (1969) found that organic matter was closely associated with the retention of Mn in an exchangeable form. The destruction of organic matter or its addition decreased or increased the exchangeable form of Mn respectively. Again only two correlations

Figure 7.2 Graph of "Available" Against "Total" Copper



could be found in this investigation (Hastings Beds r=0.632 , Chalk r=0.867).

Manganese deficiencies are most often observed on poorly-drained high pH soils containing high organic matter (Cooke, 1961). This relationship between available Mn and pH again was not reflected very clearly in the results (Table 7.7), although stronger correlations were found for pH:DTPA extractable Fe.

Table 7.7

Correlations of DTPA-Mn and Fe With pH

Soil Parent Material	Coefficients of Correlation (r) for pH:DTPA-Mn	pH:DTPA-Fe
Romney Marsh Alluvium	-0.265	-0.849[3]
Drift Deposits	-0.594[1]	-0.860[3]
Chalk	-0.361	-0.466
Gault/Upper Greensand	-0.759[3]	-0.777[3]
Lower Greensand	+0.101	-0.803[3]
Weald Clay	-0.527	-0.336
Hastings Beds	-0.508	-0.934[3]

1. $p<0.05$ 3. $p<0.001$

7.2.3 Bray P-1 Extractable Arsenic

These results are given in Table 7.8. The high As soils (especially C1-5) have relatively low extractable values, for example C4 has a total concentration of 1009 μg/g As but only 3.59 μg/g is Bray P-1 extractable. This was previously discussed in Chapter Five.

Available As correlates well with total soil As ($r=0.637$, $p<0.001$) illustrated in Figure 7.3, and with total plant concentration from the pot experiments in Chapter Five ($r=0.742$, $p<0.01$) plotted in Figure 7.4. Thus Bray P-1 would appear to be a good extractant for the determination of available As, in agreement with Benson (1976).

7.3 Conclusions

1. Copper deficiencies are likely to occur in soils developed on the Lower Greensand.

2. Zinc levels appear to be adequate on all soil parent materials found in the Weald.

3. No Mn deficiencies were found in this study despite the fact that Mn is known to be less available in alkaline soils.

4. Iron values are again adequate but would be expected to be low on Chalk and Gault Clay soils.

Table 7.8

Values for Extractable Arsenic

Soil	Bray P-1 Extractable As (μg/g)
LG	1.48
1BY	0.95
2BY	1.58
41SS	0.75
39SS	2.81
3BD	1.91
6D	1.06
C2	3.75
C1	3.87
7LB	2.32
C3	2.83
11BP	1.92
GC	2.21
12D	1.58
CH	0.60
C5	1.08
6SS	1.12
1P	2.00
4R	1.22
12P	2.40
1	1.97
C4	3.59
44SS	1.79
3B	2.09

Figure 7.3 Bray P-1 Extractable Arsenic Against "Total" Soil Arsenic

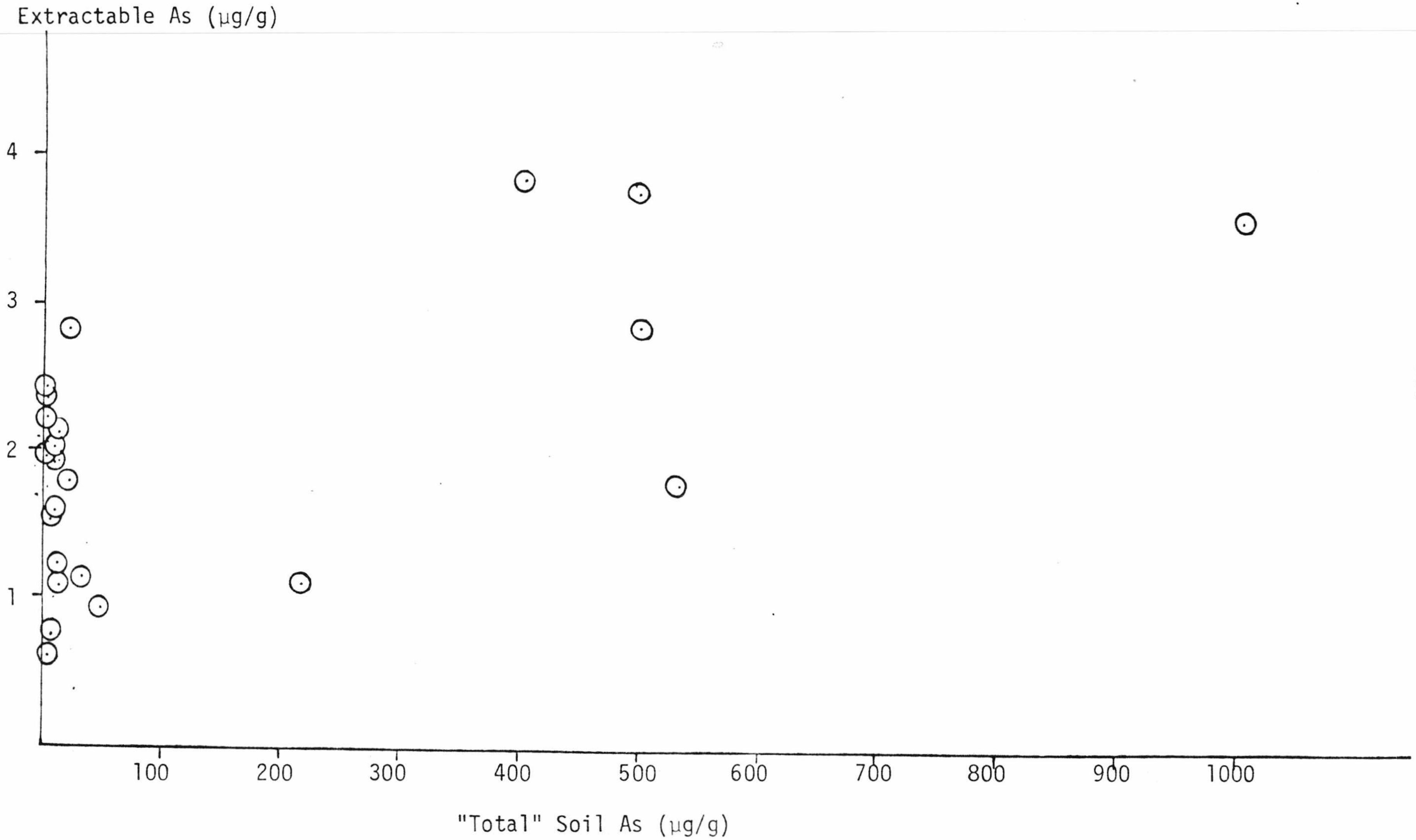
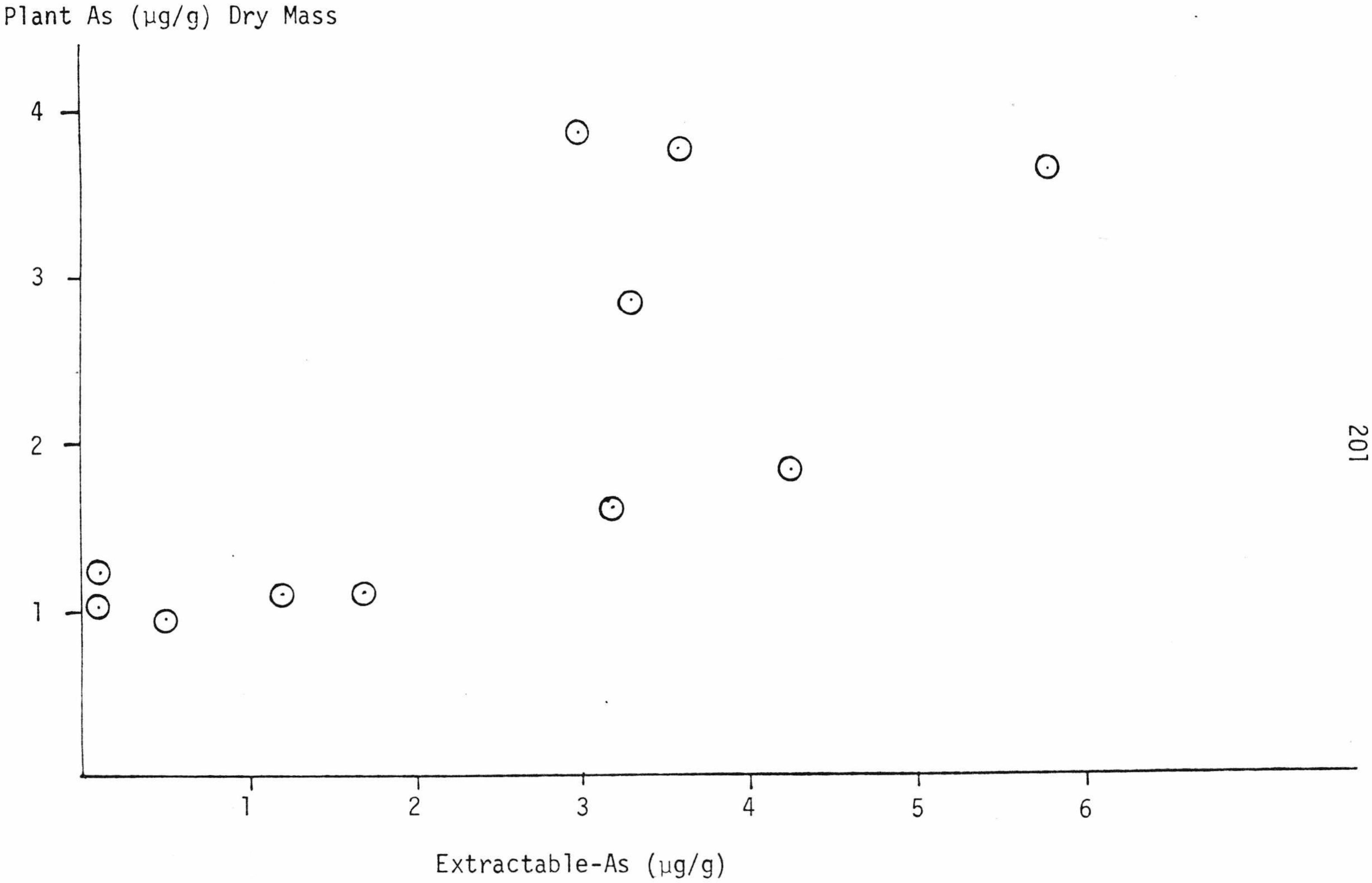


Figure 7.4 Plant Arsenic Content Against Bray P-1 Extractable Arsenic



5. Strong correlations were found between "total" and DTPA-extractable-Cu , and weaker relationships between "total" and available Zn and Mn . Generally increased levels of total elements imply increases in available concentrations (except for Fe).

6. An increase in pH is associated with a decrease in the availability of Fe.

7. Bray P-1 would seem to be a good extractant for the determination of plant available arsenic.

CHAPTER 8

CONCLUDING REMARKS

This thesis has demonstrated that As may be determined with accuracy, precision and sensitivity using $NaBH_4$ hydride generation coupled to AAS with thermal atomisation. The efficiency of the process depends on the operating conditions. The optimum conditions are described in Chapter 3. As (III) and As (V) were detected with equal sensitivity precluding the need for pre-reductants.

It was found to be important to inject the $Na BH_4$ directly into the acidified sample to obtain a sharp reproducible peak response. The quartz tube had to be conditioned for use and had a limited life expectancy due to the build-up of sulphates. No interferences were experienced.

The use of an aluminium hot-block for the digestion of soils, sediments and vegetation was found to be an efficient and reproducible sample processing technique. A 4:1 mixture of HNO_3 - $HClO_4$ was a suitable combination for the extraction of As, destroying organoarsenic compounds.

An estimation of the analytical precision of As with concentration was made based on the duplicate analysis of all the samples. This varied from 9.4% at the 5ug/g level to 4.0% at 20 ug As/g. The detection limit was 0.37 ugAs/g.

The abundance of As in Wealden soils was found to be within published ranges. Although the Romney Marsh soils and stream sediments, and Weald Clay soils are rather high they agree with expected values as suggested by the Wolfson Geochemical Altas (Webb et al, 1979).

In general, the argillaceous sediments of the Weald contain more As than the arenaceous sediments, as might be anticipated from trace element studies of sediments.

When the difference between the mean values obtained was tested the Romney Marsh was found to contain more As than all other soils except for the Wadhurst Clay and Weald Clay.

High values may be expected locally on the Lower Greensand and Wadhurst Clay where ferruginous deposits and phosphatic nodules are present.

"Total" Fe and As are strongly positively correlated in all the Wealden soil types, which can be explained by adsorption processes. Fe-oxides are usually positively charged in soils and thus adsorption onto these by arsenic anions would be expected to take place.

The range of As concentrations found in Romney Marsh stream sediments indicates that localised pollution has occurred. Historically, residual solutions of arsenical compounds used as sheep dips were dumped at the treatment site, which from OS maps can be seen to be adjacent to dykes. Fe-oxides may be mobilised by reducing ground waters and precipitated out into dykes where oxygenating conditions prevail. As is strongly scavenged from solution in Fe-rich environments and would be concentrated in sediments.

From the pot experiments (Chapter 5) the adsorption capacity of a Gault Clay soil was found to be more than twice that of a Lower Greensand and Lower Chalk soil, and hence yield decreases and crop uptake of As was least on the Gault soil.

Wheat and radishes showed yield increases at the 10ug/g applied As level which may be a result of phosphate displacement by arsenate.

Correlations between plant As content and soil As treatment were found to be highly significant.

The bean plants were most severely affected by As additions, especially on the Lower Chalk where no pods were produced, suggesting that phytotoxicity occurs before high levels are accumulated.

Plant tissues contain different amounts of As and can be generally classified as:-

Roots > Vegetative Tissue > Reproductive Tissue

←←←←←←←←As

Therefore higher concentrations may be expected in root crops.

On the whole crop As content was greatest on the calcareous soil, probably due to the limited available amount of phosphate. Plants have difficulty in differentiating between phosphate and arsenate (Benson et at, 1981).

From the untreated soil pot experiments plant As also increased with soil concentration, but only small amounts were taken up.

The basin structure of the Weald exhibited strongly ovoid patterns for Cu, Fe, Mn and Zn traceable to the soil parent material (Chapter 6).

Soils derived from the Lower Greensand reflect their arenaceous character with generally low abundance levels, although as has already been mentioned, they may be high in Fe due to iron-bearing sands.

The Romney Marsh soils are consistently low in Mn giving rise to a local deficiency known as 'Marsh spot'.

Zn and Cu are very strongly positively correlated ($p<0.001$) for all the soil types. Zn was found to be high in the chalk soil samples relative to Cu. The chalk soils also have the highest concentrations of Mn.

The DTPA extractions revealed that Cu deficiencies are likely to occur in soils developed on the Lower Greensand. Deficiencies might also be expected on the chalk soils. Surprisingly, however, they appear to contain adequate supplies, both from the "total" determinations and from the extractions.

Zinc deficiencies have been unrecognised in British field crops in the past and none are recognised here.

Although Mn and Fe deficiencies are known to occur on alkaline soils, none were revealed. However, an increase in pH was found to correlate with a decrease in the availability of Fe.

Generally increased levels of total elements are reflected by increases in available concentrations (except Fe).

Bray P - 1 may be a useful extractant in determining the availability of As.

This thesis has described several aspects of the geochemical dispersion of Arsenic in the soils and stream sediments of South-East England. The pot experiments add to our knowledge of the bioavailability of the element.

There was insufficient time to investigate further problems concerned with As in the environment. Amongst suggestions for further research are the following:-

1. The geochemical studies of As in the Weald may be extended into the French counterpart, where older Wealden rocks are exposed which are only known from bore holes in South-East England.
2. The movement of Fe and As in the Marsh system may be investigated further by measuring the redox potentials of soil and sediments down the profile near sheep washes.
3. The analysis method for As may be further refined to allow the separation and determination of As species within the soils and sediments.
4. The aerial emissions from the smelter at Sheerness, Kent could be monitored where As and Pb may be released from melted battery plates (see Page 10), thus enhancing levels locally. This may be of importance when considered in conjunction with aspects of human health.

APPENDIX 1

SAMPLE SITES FOR SOILS AND SEDIMENTS

Hythe Sector OS189

No.	Grid Reference	Soil Parent Material
1	103416	Head
2	116412	Lower Chalk
3	111404	Gault Clay
4	108403	Gault Clay
5	112398	Folkestone Beds
6	108397	Alluvium
7	103387	Head Brickearth
8	116385	Folkestone Beds
9	125388	Folkestone Beds
10	124394	Head
11	123406	Head
12	145392	Combe Drift
13	146384	Gault Clay
14	147379	Gault Clay
15	148358	Hythe Beds
16	147362	Sandgate Beds
17	122358	Head Brickearth
18	113352	Hythe Beds
19	107355	Hythe Beds
20	108366	Hythe Beds
21	103373	Hythe Beds
22	125377	Head Brickearth
23	124364	Head Brickearth
24	133396	Lower Chalk
25	114378	Head Brickearth

Hythe Sector OS189 (Cont'd.)

No.	Grid Reference	Soil Parent Material
26	132388	Gault Clay
27	135404	Sand in Clay-with-Flints
28	124414	Lower Chalk
29	143408	Lower Chalk
30	147413	Lower Chalk
31	137418	Clay-with-Flints
32	134369	Folkestone Beds
33	136357	Sandgate Beds
34	134377	Head
1W	076453	Middle Chalk
2W	077456	Clay-with-flints

Romney Marsh Sector OS189

No.	Grid Reference	Soil Parent Material
1B	049296	Alluvium:Clay
2B	045305	Alluvium:Clay
3B	054303	Alluvium:Clay
4B	056294	Alluvium:Clay
5B	057282	Alluvium:Clay
6B	057275	Alluvium:Clay
7B	067274	Alluvium:Sand
8B	034307	Alluvium:Clay
9B	065296	Alluvium:Clay
10B	064304	Alluvium:Clay
11B	083294	Alluvium:Clay
12B	074274	Alluvium:Clay
13B	067286	Alluvium:Sand
14B	076295	Alluvium:Clay
15B	084287	Alluvium:Clay
16B	074266	Alluvium:Clay
17B	065264	Alluvium:Sand
18B	029303	Alluvium:Clay
19B	032292	Alluvium:Clay

Romney Marsh Sector OS189 (Cont'd.)

No.	Grid Reference	Soil Parent Material
20B	028291	Alluvium:Clay
21B	023283	Alluvium:Sand
22B	027274	Alluvium:Clay
23B	023264	Alluvium:Clay
24B	038265	Alluvium:Sand
25B	034272	Alluvium:Clay
26B	037287	Alluvium:Clay
27B	046265	Alluvium:Sand
28B	053269	Alluvium:Clay
29B	043282	Alluvium:Clay
30B	049277	Alluvium:Clay
31B	073305	Alluvium:Clay
32B	087302	Alluvium:Clay
33B	072282	Alluvium:Clay
34B	081277	Alluvium:Clay
35B	082265	Alluvium:Sand
36B	978313	Peat
37B	974297	Alluvium:Sand
38B	963289	Alluvium:Sand
39B	962297	Peat
40B	961292	Alluvium:Sand
41B	008285	Alluvium:Clay
42B	013283	Alluvium:Clay
43B	042260	Alluvium:Clay
44B	051246	Alluvium:Sand
45B	064279	Alluvium:Clay
46B	047327	Alluvium:Clay
47B	043328	Alluvium:Clay

N.B. All the soil series on the Romney Marsh are represented in this group of samples

Bas Boulonnais Sample (Northern France)

Taken from the Devonian at La Parisienne Quarry near Ferques.

Pevensey-Polegate-Eastdean Transect OS199

No.	Grid Reference	Soil Parent Material
1P	652049	Alluvium
2P	613044	Weald Clay
3P	603048	Weald Clay
4P	575039	Gault Clay
5P	566022	Upper/Middle Chalk
6P	555995	Upper/Middle Chalk

Bletchingly Transect OS187

No.	Grid Reference	Soil Parent Material
1R	326489	Weald Clay
2R	327498	Hythe Beds
3R	326503	Hythe Beds
4R	328512	Folkestone Beds
5R	332518	Folkestone Beds
6R	325524	Gault Clay
7R	325528	Gault Clay
8R	325538	Blackheath Beds
9R	321537	Middle Chalk
10R	312536	Upper Greensand

Four Marks-Selbourne Transect OS186

No.	Grid Reference	Soil Parent Material
1L	689346	Upper Chalk
2L	702349	Middle Chalk
3L	709351	Clay-with-Flints
4L	725347	Lower Chalk
5L	735348	Upper Greensand

Four Marks-Selbourne Transect OS186 (Cont'd.)

No.	Grid Reference	Soil Parent Material
6L	742343	Upper Greensand
7L	753339	Upper Greensand
$7L_B$	753337	Upper Greensand
8L	765343	Gault Clay
9L	774341	Folkestone Beds
10L	801339	Folkestone Beds
11L	810343	Sandgate Beds
12L	822352	Bargate Beds

Fernhurst-Midhurst Transect OS197

No.	Grid Reference	Soil Parent Material
1M	894269	Weald Clay:Sandstone
2M	895265	Weald Clay:Sandstone
3M	895253	Hythe Beds
4M	890234	Hythe Beds
5M	886197	Folkestone Beds
6M	881190	Gault Clay
7M	879181	Gault Clay
8M	876172	Lower Chalk
9M	876167	Middle Chalk
10M	885154	Upper Chalk

Lenham-Benenden Transect OS188,189

No.	Grid Reference	Soil Parent Material
1D	899530	Middle Chalk
2D	901525	Lower Chalk
3D	891514	Gault Clay
4D	884510	Folkestone Beds
5D	881509	Sandgate Beds
6D	879505	Hythe Beds

Lenham-Beneden Transect OS188,189 (Cont'd.)

No.	Grid Reference	Soil Parent Material
7D	867481	Weald Clay
8D	866477	Weald Clay
9D	798388	Tunbridge Wells Sand
10D	797373	Tunbridge Wells Sand
11D	804329	Wadhurst Clay
12D	805324	Wadhurst Clay

Brasted-Chiddingstone-Penhurst Transect OS188

No.	Grid Reference	Soil Parent Material
1BP	465571	Middle Chalk
2BP	468569	Lower Chalk
3BP	472563	Gault Clay
4BP	474554	Folkestone Beds
5BP	481548	Sandgate Beds
6BP	482529	Hythe Beds
7BP	487497	Weald Clay
8BP	488472	Weald Clay
9BP	498453	Tunbridge Wells Sand
10BP	504439	Wadhurst Clay
11BP	513439	Ashdown Beds
12BP	519439	Ashdown Beds

Heathfield-Hellingly Transect OS199

No.	Grid Reference	Soil Parent Material
7P	597199	Ashdown Beds
8P	599189	Ashdown Beds
9P	596180	Wadhurst Clay
10P	598154	Wadhurst Clay

Heathfield-Hellingly Transect (Cont'd.)

No.	Grid Reference	Soil Parent Material
11P	597131	Tunbridge Wells Sand
12P	592128	Tunbridge Wells Sand

Hastingleigh-Bilsington Transect OS189

No.	Grid Reference	Soil Parent Material
1K	057342	Alluvium
2K	065376	Weald Clay
3K	066389	Hythe Beds
4K	072397	Sandgate Beds
5K	077402	Folkestone Beds
6K	081421	Gault Clay
7K	089438	Clay-with-Flints
8K	089444	Clay-with-Flints
9K	077454	Middle Chalk

Brighton-Ditchling Transect OS198

No.	Grid Reference	Soil Parent Material
1BD	340215	Tunbridge Wells Sand
2BD	341207	Tunbridge Wells Sand
3BD	341160	Weald Clay
4BD	339158	Weald Clay
5BD	337155	Hythe Beds
6BD	336153	Sandgate Beds
7BD	338152	Folkestone Beds
8BD	337147	Gault Clay

Brighton-Ditchling Transect OS198 (Cont'd.)

No.	Grid Reference	Soil Parent Material
9BD	339142	Upper Greensand
10BD	336136	Lower Chalk
11BD	333129	Upper Chalk

Banbury Samples OS129

No.	Grid Reference	Soil Parent Material
1BY	694232	London Clay
2BY	707236	Marlstone Rockbed

Cambourne Samples

No.	Grid Reference	Soil Parent Material
C1	629391	Devonian Greenstones
C2	609388	Devonian Greenstones
C3	615380	Devonian Greenstones
C4	599376	Devonian Greenstones
C5	580366	Devonian Greenstones

Romney Marsh Stream Sediments OS189

No.	Grid Reference	Soil Parent Material
6SS	063278	Clay Alluvium
39SS	962297	Peat
44SS	051246	Sandy ALluvium
7SS	047327	Clay Alluvium
5SS	070266	Sandy Alluvium
47SS	053328	Clay Alluvium
42SS	013283	Sandy Alluvium
41SS	008285	Sandy Alluvium

APPENDIX 2

PRECISION REPLICATES

Arsenic in Soils Within Batch Precision

Mean of Duplicates ($\overline{x}$)	Difference Between Duplicates (x_1-x_2)	Mean of Duplicates ($\overline{x}$)	Difference Between Duplicates (x_1-x_2)
1.7	0.1	5.4	0.6
2.4	0.8	5.5	0.3
2.6	0.1	5.8	0.1
3.2	0.2	5.8	0.5
3.3	1.9	5.9	0.2
3.4	0.2	5.9	0.1
3.6	0.4	5.9	0.4
3.7	0.2	5.9	0.5
4.2	1.2	5.9	0.6
4.3	0.3	5.9	0.6
4.4	0.1	5.9	0.8
4.4	0.8	6.0	0.2
4.6	0.0	6.0	0.4
4.6	0.4	6.0	0.7
5.0	0.5	6.2	0.1
5.0	0.8	6.2	0.1
5.0	1.0	6.2	0.6
5.1	0.2	6.3	0.4
5.2	0.2	6.3	0.5
5.2	0.3	6.3	1.2
5.3	0.2	6.4	0.4
5.3	0.4	6.4	0.6
5.3	0.5	6.5	0.6
5.4	0.1	6.6	1.9

Arsenic in Soils within Batch Precision (Cont'd.)

Mean of Duplicates ($\bar{x}$)	Difference Between Duplicates (x_1-x_2)	Mean of Duplicates ($\bar{x}$)	Difference Between Duplicates (x_1-x_2)
6.7	0.1	8.1	0.3
6.7	0.1	8.1	0.7
6.7	0.3	8.2	0.0
6.7	0.4	8.2	0.5
67.	0.8	8.2	0.5
6.8	0.2	8.2	0.5
6.8	0.6	8.2	0.6
6.9	0.0	8.2	0.8
6.9	0.0	8.3	0.4
7.0	0.1	8.3	0.7
7.0	0.4	8.5	0.2
7.0	0.7	8.5	1.0
7.0	0.5	8.5	1.4
7.1	1.5	8.6	0.3
7.2	0.8	8.8	0.2
7.4	0.3	8.8	0.6
7.5	0.2	8.9	0.0
7.5	0.5	8.9	0.8
7.5	1.2	9.0	0.4
7.6	0.1	9.1	0.5
7.6	0.5	9.3	0.5
7.7	0.1	9.4	1.0
7.7	0.6	9.5	0.4
7.7	1.8	9.5	0.1
7.9	0.1	9.6	1.3
7.9	0.6	9.7	1.4
7.9	0.6	9.9	0.6
7.9	0.6	9.9	0.3
8.0	0.0	10.2	1.5

Arsenic in Soils within Batch Precision (Cont'd.)

Mean of Duplicates ($\bar{x}$)	Difference Between Duplicates (x_1-x_2)
10.3	0.0
10.3	0.4
10.4	1.0
10.6	1.0
10.8	0.3
10.8	0.8
11.2	0.5
11.2	1.0
11.2	2.2
11.5	0.5
11.5	0.9
11.5	1.0
11.5	1.1
11.6	0.7
11.8	0.1
11.8	1.9
11.9	1.7
12.1	0.9
12.1	1.2
12.5	1.0
12.6	1.3
13.1	1.0
13.1	1.0
13.3	0.7
13.6	0.3
13.7	0.7
13.7	1.0
13.8	0.7
13.8	1.2
13.9	1.2
14.7	0.2
14.8	0.0
14.8	0.7
14.9	0.5
14.9	0.6
15.0	1.3
15.2	0.9
15.2	0.7
15.9	0.3
16.1	0.3
16.1	0.3
16.2	0.4
16.2	1.8
16.2	0.6
16.2	1.5
16.4	2.0
16.4	0.4
16.5	2.3
16.6	0.7
16.6	0.7
16.6	0.8
16 6	2.8
17.0	1.1
17.2	3.0
17.4	1.1
17.4	1.8
17.5	1.0
17.5	0.6
17.6	0.7
17.9	0.2

Arsenic in Soils within Batch Precision (Cont'd.)

Mean of Duplicates ($\overline{x}$)	Difference Between Duplicates ($x_1 - x_2$)	Mean of Duplicates ($\overline{x}$)	Difference Between Duplicates ($x_1 - x_2$)
18.0	0.4	27.5	2.0
18.0	0.8	38.9	0.30.3
18.1	0.6	43.0	4.94.9
18.3	2.1	44.8	0.30.3
18.5	0.4	76.5	13.13.0
18.6	0.8	236	44.0
18.6	2.2	404	64.0
19.8	0.5	500	49.0
20.7	3.6	501	2.0
20.8	0.6	566	13.0
23.3	0.7	1005	313
23.5	0.1		
24.9	3.1		
27.4	1.3		

Plant As Precision

Sample 1	Sample 2	Mean of Duplicates	Difference Between Duplicates
1.65	1.69	1.67	0.002
5.93	6.57	6.25	0.64
10.3	9.57	9.90	0.73
0.23	0.25	0.24	0.002
1.48	1.52	1.50	0.004
5.87	6.46	6.16	0.59
7.76	7.18	7.47	0.58
0.86	0.84	0.85	0.002
5.23	4.36	4.80	0.87
8.74	8.80	8.77	0.06
0.83	0.87	0.85	0.004
3.48	3.37	3.42	0.11
4.27	4.59	4.43	0.32
0.36	0.46	0.41	0.10
2.15	2.75	2.45	0.60
12.4	11.4	11.9	1.0
0.25	0.24	0.25	0.001
1.09	1.16	1.13	0.007
0.60	0.55	0.57	0.005
24.0	19.3	21.6	4.7
1.23	1.53	1.38	0.3

"Total" Cu (μg/g) Within Batch Precision

Soil	Cu_1	Cu_2	Mean	Difference
17	7.4	8.0	7.7	0.6
7B	12.9	12.7	12.8	0.2
8	2.3	1.8	2.1	0.5
15	5.9	6.0	5.9	0.1
24	10.3	10.9	10.6	0.6
25	7.5	6.2	6.8	1.3
30	15.2	15.3	15.2	0.1
3B	10.5	10.9	10.7	0.4
16	7.5	8.3	7.9	0.8
34	7.5	7.2	7.4	0.3
26	12.4	12.0	12.2	0.4
19	14.0	13.8	13.9	0.2
31	9.3	8.8	9.1	0.5
20	13.4	12.8	13.1	0.6
2	14.8	15.3	15.0	0.5
2B	10.0	10.4	10.2	0.4
13	19.9	22.0	20.9	2.1
12	21.9	21.0	21.4	0.9
4B	11.6	12.0	11.8	0.4
2W	17.1	16.3	16.7	0.8
25B	12.5	13.1	12.8	0.6
20B	12.6	13.2	12.9	0.6
1W	16.9	16.1	16.5	0.8
35B	9.6	10.8	10.2	1.2
10M	10.4	9.8	10.1	0.6
LP	17.0	17.2	17.1	0.2
12D	17.4	16.0	16.7	1.4
7P	8.5	10.8	9.6	2.3
GC	11.5	12.9	12.2	1.4
Ch	11.0	11.5	11.3	0.5
LG	11.5	12.0	11.8	0.5
2BD	12.0	11.6	11.8	0.4
9P	18.4	18.9	18.6	0.5

"Total" Zn (μg/g) Within Batch Precision

Soil	Zn_1	Zn_2	Mean	Difference
30	72.6	74.7	73.6	2.10
19	65.0	70.0	67.5	5.00
7B	85.2	92.0	88.6	6.8
3B	73.8	78.4	76.1	4.6
26	62.6	63.1	62.8	0.5
15	57.4	60.5	59.0	3.10
34	39.5	41.6	40.6	2.10
17	42.6	50.3	46.5	7.7
8	16.8	16.9	16.9	0.1
16	37.1	42.0	39.6	4.9
25	38.3	34.7	36.5	3.6
24	39.2	40.7	40.0	1.5
2	59.0	62.6	60.8	3.6
20	50.7	52.4	51.6	1.7
31	40.4	52.2	46.3	11.8
13	87.0	95.0	91.0	8.0
20B	75.7	80.7	78.2	5.0
2W	97.0	99.0	98.0	2.0
2B	61.5	64.5	63.0	3.0
25B	73.2	82.8	78.0	9.6
4B	82.4	89.0	85.7	6.6
1W	131	124	128	7.0
35B	55.9	63.3	59.6	7.4
LP	98.7	101	99.9	2.3
10M	68.1	71.3	69.7	3.2
12D	75.3	74.3	74.8	1.00
9D	46.1	48.2	47.2	2.1

"Total" Zn (μg/g) Within Batch Precision (Cont'd.)

Soil	Zn_1	Zn_2	Mean	Difference
GC	89.1	81.2	85.2	7.9
CH	60.5	64.4	62.5	3.9
LG	72.2	70.6	71.4	1.6
2BD	52.6	54.9	53.8	2.3
7P	57.6	63.5	60.6	5.9
9P	80.0	80.4	80.2	0.4

"Total" Mn (μg/g) Within Batch Precision

Soil	Mn_1	Mn_2	Mean	Difference
7B	236	254	245	18.0
15	177	177	177	0.0
19	945	931	938	14.0
17	279	272	276	5.0
30	936	923	930	13.0
3B	240	254	247	14.0
2	471	476	474	5.0
31	463	473	468	10.0
20	550	563	557	13.0
4B	281	301	291	20.0
35B	148	166	157	18.0
12	796	761	779	35.0
25B	275	289	282	14.0
2B	362	340	351	22.0
13	432	478	455	46.0

"Total" Mn (μg/g) Within Batch Precision (Cont'd.)

Soil	Mn_1	Mn_2	Mean	Difference
20B	305	325	315	20.0
2W	434	452	443	18.0
C2	977	1055	1016	78.0
C3	1583	1528	1556	55.0
C4	944	1044	992	96.0
LP	869	906	888	37.0
10M	777	770	774	7.0
12D	519	480	500	39.0
1P	323	334	329	11.0
4M	197	198	198	1.0
6BP	207	210	209	3.0
GC	358	348	353	10.0
CH	394	379	387	15.0
LG	699	695	697	4.0
2BD	412	382	397	30.0
7P	1202	1096	1149	106.0
9P	1519	1377	1448	142.0

"Total" Fe (%) Within Batch Precision

Soil	Fe_1	Fe_2	Mean	Difference
3B	2.35	2.53	2.44	0.18
17	1.78	1.96	1.87	0.18
30	1.19	1.31	1.25	0.12
19	2.73	2.56	2.65	0.17
20	2.34	2.24	2.29	0.10
31	2.08	1.92	2.00	0.16
2	1.72	1.43	1.58	0.29
4B	2.48	2.64	2.56	0.16
12	1.41	1.49	1.45	0.08
2B	2.15	2.35	2.25	0.20
13	2.72	2.84	2.78	0.12
20B	2.34	2.38	2.36	0.04
2W	3.00	2.71	2.86	0.29
25B	2.31	2.51	2.41	0.20
C1	3.75	3.61	3.68	0.14
C2	4.48	4.59	4.54	0.11
C3	6.74	6.55	6.65	0.19
LP	2.89	2.91	2.90	0.02
10M	1.38	1.20	1.24	0.08
12D	2.17	2.08	2.13	0.09
GC	3.33	3.28	3.31	0.05
CH	2.87	2.86	2.87	0.01
LG	1.31	1.31	1.31	0.0
2BD	1.59	1.65	1.62	0.06
7P	1.99	1.99	1.95	0.08
9P	3.24	3.24	3.14	0.20

APPENDIX 3

ARSENIC IN ROMNEY MARSH STREAM SEDIMENTS DETERMINED BY THE APPLIED GEOCHEMISTRY RESEARCH GROUP, IMPERIAL COLLEGE

(Thornton, 1979)

Grid Reference (OS189)	[As]µg/g in Romney Marsh Stream Sediment
061304	39
079262	27
069259	27
067275	56
067283	44
054295	14
053272	22
042266	136
049304	18
040304	27
036257	29
037287	52
031281	46
028287	29
036304	21
034308	50
018284	39
023276	41
024269	14

APPENDIX 4

"TOTAL" CONCENTRATION OF As, Cu, Mn, Zn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE ROMNEY MARSH

Soil No.	µg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
1B	16.1	11.2	251	66.6	2.31	7.81	8.73
2B	13.8	10.2	351	63.0	2.25	7.74	4.55
3B	20.7	10.7	247	76.1	2.44	7.31	8.19
4B	16.2	11.8	291	85.7	256	7.60	6.35
5B	14.7	14.4	430	84.5	262	7.94	6.91
6B	16.2	11.3	336	78.0	2.20	7.62	6.06
7B	14.8	12.8	245	88.6	2.15	6.70	7.28
8B	15.2	12.7	312	72.1	2.32	5.80	8.69
9B	16.6	10.3	262	80.7	2.36	7.31	10.7
10B	17.5	12.8	217	81.6	2.45	7.41	9.39
11B	13.1	10.1	97.5	73.1	2.12	6.54	12.5
12B	17.4	11.2	201	60.4	2.44	7.23	6.01
13B	16.6	12.5	353	74.6	2.55	8.04	5.09
14B	11.5	9.2	70.4	61.7	1.75	5.92	7.50
15B	18.0	12.3	179	70.7	2.28	7.51	4.68
16B	18.6	13.8	262	69.1	2.41	6.97	4.61
17B	13.3	7.10	235	50.5	1.69	7.97	3.29
18B	19.8	9.8	309	69.6	2.36	8.00	6.06
19B	12.6	14.8	381	81.6	2.30	6.36	7.39
20B	16.6	12.9	315	78.2	2.36	7.77	5.83

"TOTAL" CONCENTRATION OF As , Cu , Mn , Zn AND Fe; pH AND LOI% IN SOILS DEVLOPED ON THE ROMNEY MARSH (Cont'd.)

Soil No.		µg/g			Fe%	pH	LOI%
	As	Cu	Mn	Zn			
21B	11.9	12.8	282	66.5	1.89	7.85	7.69
22B	14.9	15.9	301	84.9	2.23	6.73	10.2
23B	14.8	12.7	290	68.2	2.27	7.87	4.37
24B	13.9	7.2	184	52.5	1.88	5.75	9.84
25B	13.7	12.8	282	78.0	2.41	7.38	7.94
26B	16.6	15.9	346	88.4	2.62	7.82	7.04
27B	9.9	9.9	245	58.2	1.71	7.22	7.50
28B	17.4	12.6	388	75.4	2.35	7.79	6.65
29B	16.5	11.3	281	71.4	2.25	7.59	8.46
30B	20.8	11.1	295	73.0	2.52	7.75	4.45
31B	13.1	11.3	270	69.1	2.25	7.98	7.55
32B	17.2	13.6	282	79.3	2.22	7.49	5.19
33B	17.0	13.6	203	77.7	2.26	5.25	6.30
34B	18.3	10.2	199	75.6	2.20	6.59	8.44
35B	10.8	10.2	157	59.6	1.85	8.05	2.50
36B	10.2	13.1	293	62.1	1.95	5.39	9.37
37B	10.3	15.0	285	65.0	1.84	7.93	9.02
38B	8.1	6.4	162	44.8	1.12	8.18	5.00
39B	17.5	15.3	359	79.2	3.01	8.07	9.32
40B	9.5	11.3	220	52.7	1.64	8.20	6.29
41B	12.1	8.1	160	54.3	2.10	7.99	6.99
42B	13.6	9.2	157	48.4	1.45	7.77	3.76
43B	14.9	8.3	198	54.1	1.75	8.33	5.05
44B	16.2	8.9	176	49.8	1.76	7.61	4.77
45B	15.0	13.2	248	58.4	2.24	7.43	8.74
46B	11.5	10.0	194	58.2	1.85	6.24	8.63
47B	16.4	9.0	179	57.5	1.90	6.08	7.80
1K	18.0	14.8	286	83.9	2.39	7.29	7.51

"TOTAL" CONCENTRATION OF As , Cu , Mn , Zn AND Fe ; pH AND LOI% IN SOILS DEVELOPED ON DRIFT DEPOSITS

Soil No.	µg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
1P	16.4	9.6	328	63.2	2.20	6.47	11.68
7K	13.7	10.3	561	63.2	1.33	5.53	9.33
8K	11.5	12.6	550	60.5	1.61	5.91	7.51
3L	9.1	15.6	965	78.7	1.73	5.53	6.73
17	8.2	7.7	225	47.0	1.87	6.84	7.52
7	6.3	8.1	215	43.0	1.48	5.95	6.98
22	6.0	13.9	282	68.0	1.76	6.49	4.65
23	6.2	11.4	158	53.0	1.60	7.77	4.36
25	7.5	6.8	243	36.5	1.63	7.42	3.54
1	6.4	37.1	672	175.0	1.54	7.21	10.2
10	11.8	13.4	207	78.0	2.89	7.33	7.97
11	8.2	21.8	1307	146.0	2.50	7.39	11.0
34	5.5	7.4	125	40.5	1.26	5.74	5.84
31	8.2	9.1	468	46.0	2.00	7.08	3.59
2W	11.2	16.7	443	98.0	2.89	4.92	9.09
27	24.9	6.5	197	48.0	1.81	4.89	7.19
12	3.6	22.4	778	135.0	1.45	7.78	5.47
6	5.9	9.6	335	41.0	1.81	6.64	4.59
8R	5.8	13.0	1290	120.0	1.22	7.33	8.70

"TOTAL" CONCENTRATION OF As , Cu , Mn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE CHALK

Soil No.	µg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
5P	2.4	7.61	560	73.2	0.32	8.01	8.23
6P	3.2	8.4	904	64.6	0.84	8.02	7.84
9R	5.0	8.3	539	48.6	0.79	8.00	7.66
1L	7.0	6.9	355	61.6	0.90	7.29	7.36
2L	7.6	15.4	1215	77.7	1.73	7.94	7.02
4L	7.9	10.9	1304	49.0	1.71	7.69	6.43
8M	7.5	11.6	666	55.0	1.14	7.85	7.89
9M	6.7	12.3	826	68.0	1.63	8.12	5.65
10M	6.3	10.1	770	69.7	1.24	7.70	9.72
1D	8.9	11.4	740	72.4	1.18	7.89	6.84
2D	9.0	9.8	531	51.2	0.85	7.85	7.34
1BP	4.4	13.5	1119	77.7	1.12	8.13	6.62
2BP	5.0	8.7	474	63.9	0.78	8.21	3.82
9K	10.8	14.8	1164	103.0	2.19	7.24	19.5
1W	8.5	16.5	1044	127.0	1.89	7.60	22.6
29	5.3	29.2	603	183.0	1.47	7.75	9.30
24	5.9	10.6	585	40.0	1.03	8.25	4.17
28	6.9	17.8	763	76.0	1.51	7.78	6.66
30	4.6	15.2	930	74.0	1.25	7.85	7.20
2	4.6	15.0	473	61.0	1.58	7.85	6.71
10D	11.2	13.0	814	53.5	1.03	8.27	4.66
11BD	3.4	14.6	2123	184.0	2.43	7.36	17.8
CH		11.3	697	71.4	1.31	8.15	5.43

"TOTAL" CONCENTRATION OF As , Cu , Mn , Zn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE GAULT CLAY AND UPPER GREENSAND

Soil No.	µg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
4P	8.2	14.0	710	72.1	2.00	7.72	7.23
6R	10.6	13.3	546	69.7	2.85	7.66	8.73
7R	5.4	6.6	424	26.6	0.89	7.96	5.38
8L	11.5	6.8	125	36.4	1.54	6.57	9.24
6M	12.1	15.0	101	37.8	1.21	6.31	9.31
7M	6.5	13.0	177	70.6	1.35	7.61	8.56
3D	8.3	12.0	249	47.1	1.82	6.86	11.1
3BP	6.6	10.6	554	56.8	2.05	8.05	6.52
6K	7.2	10.1	416	54.9	2.10	6.41	11.3
4	5.9	9.7	373	56.0	2.08	6.32	11.4
14	8.5	25.8	384	102.0	2.93	6.86	11.8
26	7.9	12.2	194	63.0	2.27	7.80	9.58
3	5.9	14.8	244	74.0	2.71	7.00	8.16
13	6.2	20.9	455	91.0	2.78	6.89	11.5
8BD	7.7	11.7	390	68.9	2.15	7.93	8.94
gC	8.8	12.2	353	85.2	3.3	7.86	9.75
10R	6.0	7.0	354	30.8	1.21	7.96	3.98
5L	3.7	8.1	495	40.0	1.06	6.46	5.73
6L	2.6	10.3	348	38.9	0.75	7.30	7.09
7L	4.4	8.1	427	35.3	1.13	6.48	6.95
7LB	6.2	7.4	262	32.3	1.01	5.23	8.96
9BD	7.0	31.4	382	198.0	1.08	7.89	9.00

"TOTAL" CONCENTRATION OF As , Cu , Mn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE LOWER GREENSAND

Soil No.	μg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
5K	5.9	9.2	105	48.1	1.25	6.48	3.83
4BP	8.2	17.0	152	99.0	1.26	5.40	6.67
4D	6.8	14.5	178	110.0	1.39	7.01	4.93
5M	9.7	3.6	75.1	16.8	0.56	5.57	3.66
9L	5.1	4.6	109	18.8	0.48	6.47	3.79
10L	9.9	2.1	47.2	14.7	0.89	4.95	4.87
4R	23.3	16.1	391	71.6	2.41	7.20	4.29
5R	6.7	6.2	426	31.9	1.13	6.80	3.36
5	5.2	7.1	207	31.0	1.25	6.57	4.42
32	5.3	8.2	106	29.0	1.48	6.47	7.85
8	1.7	2.1	17	17.0	0.46	3.50	7.07
9	6.9	9.0	141	33.0	1.77	6.98	5.28
7BD	6.3	7.2	156	60.1	1.35	7.58	3.27
4K	6.7	13.9	186	38.0	1.28	5.78	6.30
5BP	8.2	6.1	409	35.2	1.59	6.04	3.47
5D	8.6	4.7	118	25.6	0.82	4.62	5.68
11L	9.5	5.6	48.1	38.3	1.23	5.47	6.67
16	6.7	7.9	127	39.5	1.59	6.76	4.90
33	9.3	10.0	280	48.0	2.24	6.79	8.29
6BD	5.9	7.1	193	40.7	1.76	5.87	6.15
12L	8.9	5.6	373	28.1	1.11	6.93	3.54
3K	11.2	14.8	600	64.2	2.04	7.79	3.86
6BP	5.8	13.2	208	41.3	1.30	7.35	5.67
6D	27.5	6.8	493	50.7	4.72	7.27	5.00
3M	4.3	4.5	140	15.9	0.49	6.80	2.74
4M	7.7	22.1	203	66.9	1.38	5.73	4.96

"TOTAL" CONCENTRATION OF As , Cu , Mn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE LOWER GREENSAND (Cont'd.)

Soil No.	µg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
2R	9.4	12.2	416	35.5	1.50	5.53	5.45
3R	27.4	9.4	129	32.6	2.01	6.30	4.36
15	23.5	5.9	177	59.0	4.14	6.65	9.22
18	8.1	10.4	525	53.0	2.10	6.32	5.70
19	18.6	13.9	938	67.5	2.65	7.79	5.01
20	6.8	13.1	556	51.0	2.29	5.89	5.66
21	7.5	10.4	483	54.0	2.74	7.14	4.11
5BD	8.3	10.3	190	66.2	1.83	7.41	8.68
LG	7.0	11.8	387	62.4	2.86	6.96	4.02

"TOTAL" CONCENTRATION OF As , Cu , Mn , Zn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE WEALD CLAY

Soil No.	As	Cu	µg/g Mn	Zn	Fe%	pH	LOI%
2P	18.1	18.9	983	82.7	2.83	6.14	7.90
3P	15.9	15.7	619	43.4	2.25	6.73	8.60
1R	11.8	15.4	786	60.5	1.91	7.67	5.56
1M	3.3	5.5	78.7	20.3	0.30	6.51	3.97
2M	7.4	10.2	612	24.2	0.82	6.38	4.22
7D	9.6	27.3	418	61.2	2.05	6.08	9.21
8D	8.5	11.9	437	43.7	1.82	7.79	4.99
7BP	18.5	10.3	2368	52.5	2.84	4.12	6.44
8BP	15.2	15.7	785	61.2	2.44	6.12	8.44
2K	7.0	13.4	141	51.4	1.60	5.65	8.56
3BD	17.6	29.9	1231	135	2.97	7.09	11.0
4BD	10.3	16.0	157	83.5	2.52	5.83	13.0

"TOTAL" CONCENTRATION OF As , Cu , Zn AND Fe; pH AND LOI% IN SOILS DEVELOPED ON THE HASTINGS BEDS

Soil No.			µg/g		Fe%	pH	LOI%
	As	Cu	Mn	Zn			
9BP	7.9	12.1	372	50.1	1.86	4.83	7.54
9D	5.4	9.2	428	47.1	1.40	7.49	4.53
10D	7.7	17.1	471	57.7	1.73	7.27	4.21
1BD	7.9	14.8	2729	61.8	1.88	7.36	5.96
2BD	7.6	11.8	397	53.8	1.62	6.62	5.38
11P	6.4	11.5	420	47.6	1.96	6.70	4.27
12P	6.0	9.5	332	38.4	1.80	7.48	4.52
10BP	17.9	13.5	1011	64.1	2.90	5.20	9.33
12D	12.5	16.7	450	74.2	2.12	4.97	13.4
11D	13.8	18.3	758	84.8	2.44	7.42	5.27
9P	16.1	18.6	1448	80.2	3.14	6.39	7.89
10P	10.4	14.3	925	68.3	2.86	8.38	6.09
11BP	4.2	8.7	393	42.3	1.04	6.30	5.39
12BP	8.8	9.6	315	37.6	1.48	4.73	5.18
7P	5.3	9.6	1149	60.6	1.95	6.68	4.86
8P	8.0	11.4	1069	57.5	2.41	6.22	4.37

"TOTAL" CONCENTRATION OF As , Cu , Mn , Zn AND Fe; pH AND LOI% IN STREAM SEDIMENTS ON THE ROMNEY MARSH

Sediment No.	µg/g				Fe%	pH	LOI%
	As	Cu	Mn	Zn			
7SS	5.9	5.6	156	44.0	1.66	8.10	2.97
41SS	16.2	7.8	223	54.0	2.68	8.40	2.58
47SS	11.6	9.1	97	58.5	2.25	7.67	6.46
44SS	38.9	2.5	78.4	22.2	2.01	8.12	1.68
5SS	5.2	3.1	91.7	31.6	1.08	7.62	2.20
42SS	7.4	2.5	73	29.9	1.35	7.58	1.08
39SS	44.8	15.6	180	72.2	1.26	6.33	78.8
6SS	76.5	9.5	61	60.2	2.73	7.97	6.01

DTPA - EXTRACTABLE Cu , Zn , Mn AND Fe (μg/g) FROM ROMNEY MARSH SOILS

Soil Number	Cu	Zn	Mn	Fe
1B	1.58	5.54	11.5	127.0
2B	1.08	0.98	8.54	47.6
3B	1.62	3.51	10.7	60.2
4B	1.49	1.86	8.23	76.9
5B	1.89	2.21	9.51	59.0
6B	1.60	2.64	13.2	63.1
7B	1.70	7.92	9.47	126.0
8B	2.20	2.58	10.1	256.0
9B	1.68	3.75	10.4	84.0
10B	2.04	3.21	12.9	93.0
11B	1.71	3.71	5.28	222.0
12B	1.77	1.33	18.1	133.0
13B	1.55	2.06	15.2	100.0
14B	1.55	3.90	4.67	326.0
15B	1.58	2.12	24.6	191.0
16B	2.23	1.61	14.7	162.0
17B	0.70	1.33	8.60	52.6
18B	1.24	2.27	14.5	95.8
19B	3.52	3.98	48.0	323.0
20B	1.90	2.46	16.1	80.3
21B	2.57	4.51	11.2	78.1
22B	2.65	3.90	13.7	163.0
23B	1.68	2.09	14.9	63.8
24B	1.26	3.25	22.0	231.0
25B	2.01	3.30	24.2	47.9
26B	3.41	3.26	13.3	66.8
27B	1.10	4.13	6.00	159.0

DTPA - EXTRACTABLE Cu , Zn , Mn , AND Fe (μg/g) FROM ROMNEY MARSH SOILS

Cont'd)

Soil Number	Cu	Zn	Mn	Fe
28B	2.04	2.68	14.3	93.0
29B	1.39	2.87	8.27	61.8
30B	1.22	1.55	7.11	69.1
31B	1.59	2.12	9.88	59.3
32B	2.54	3.49	15.5	93.7
33B	2.55	3.35	21.5	361
34B	1.49	2.72	11.7	144
35B	1.09	2.91	4.36	42.7
1K	1.80	2.28	11.6	111

DRIFT DEPOSITS DTPA RESULTS (μg/g)

Soil Number	Cu	Zn	Mn	Fe
1P	1.80	2.84	13.3	219.0
7K	1.08	3.36	45.2	143.0
8K	1.59	2.05	48.7	159.0
3L	2.41	6.14	66.5	222.0
17	1.71	3.18	18.6	206.0
7	1.63	4.07	22.7	174.0
22	2.00	2.66	15.4	151.0

DRIFT DEPOSITS DTPA RESULTS (μg/g) (Cont'd.)

Soil Number	Cu	Zn	Mn	Fe
23	2.29	2.09	8.28	53.1
25	1.20	1.02	13.1	49.3
1	7.69	41.8	22.4	80.5
10	1.42	1.60	17.7	112.0
11	5.11	11.0	40.2	101.0
34	1.06	1.02	6.07	205.0
31	1.17	0.86	22.1	39.0
2W	1.78	4.25	117.0	256.0
27	1.26	3.27	38.2	306.0
12	4.29	7.51	23.0	63.3
6	2.00	1.64	27.4	110.0
8R	2.58	17.8	33.1	62.8

CHALK DTPA EXTRACTIONS (μg/g)

Soil Number	Cu	Zn	Mn	Fe
5P	1.39	5.20	22.6	55.6
6P	1.30	6.74	35.5	25.8
9R	1.09	5.05	16.7	21.0
1L	1.33	7.96	18.8	110.0
2L	2.48	5.30	18.4	69.7
4L	1.61	2.17	13.7	33.6

CHALK DTPA EXTRACTIONS ($\mu g/g$) (Cont'd.)

Soil Number	Cu	Zn	Mn	Fe
8M	2.32	6.15	16.1	63.1
9M	1.74	2.71	24.1	40.6
10M	2.00	7.78	32.8	112.0
1D	1.71	3.72	14.4	21.2
2D	1.65	3.10	15.7	31.0
1BP	1.77	5.89	19.1	29.5
2BP	1.08	2.40	14.1	31.5
9K	1.08	7.55	57.4	37.9
1W	1.06	11.3	159.0	47.7
29	6.04	11.2	23.1	44.0
24	1.72	2.06	17.4	33.8
28	2.78	5.86	24.1	58.1
30	3.12	5.12	29.4	32.3
2	2.24	5.80	13.1	57.8

GAULT CLAY/UPPER GREENSAND DTPA EXTRACTIONS (μg/g)

Soil Number	Cu	Zn	Mn	Fe
4P	2.71	2.07	8.10	70.9
6R	2.72	2.52	6.42	80.0
7R	1.36	3.66	9.30	75.5
8L	1.31	3.34	8.19	234
6M	4.82	4.60	13.4	283
7M	2.11	5.35	7.17	117
3D	2.23	3.87	12.1	192
3BP	1.30	1.34	6.06	66.5
6K	1.80	2.82	18.7	172
4	1.60	2.86	19.8	216
14	5.50	5.86	13.7	125
26	2.48	1.48	9.78	94.2
3	1.60	1.44	15.2	152
13	3.58	4.38	18.7	197
10R	1.62	1.84	5.00	18.2
5L	2.30	6.00	34.0	181
6L	2.13	7.36	14.8	101
7L	1.62	2.64	14.7	137
7LB	1.25	4.30	75.6	175

LOWER GREENSAND DTPA EXTRACTIONS (μg/g)

Soil No.	Cu	Zn	Mn	Fe
5K	0.98	7.22	5.65	105
4BP	3.28	40.60	5.98	279
4D	2.29	12.80	3.85	108
5M	0.64	2.70	11.10	166
9L	0.85	4.18	9.78	153
10L	0.25	5.06	4.55	292
4R	3.20	5.16	7.46	87.2
5R	1.32	2.00	24.6	89.9
5	1.42	3.48	13.0	98.4
32	0.98	1.58	5.52	251
8	0.16	2.60	3.12	664
9	1.70	1.00	6.90	242
4K	1.80	1.86	13.5	159
5BP	1.58	2.18	24.0	112
5D	0.83	2.56	19.4	341
11L	1.34	10.80	12.1	410
16	1.20	1.32	4.86	111
33	1.88	3.68	17.9	176
12L	0.79	2.90	13.4	62.6
3K	1.79	1.85	11.7	44.0
6BP	1.51	3.73	8.49	88.8
6D	0.91	1.58	23.7	75.2
3M	0.71	3.06	6.71	108
4M	4.63	11.7	18.2	131
2R	4.49	3.37	28.7	208
3R	2.24	1.66	6.26	157
15	0.88	4.56	11.0	293
18	1.98	6.08	50.0	145
19	2.36	3.44	29.9	49.3
20	2.16	2.48	40.0	152
21	2.12	3.88	32.1	173

WEALD CLAY DTPA EXTRACTIONS (μg/g)

Soil No.	Cu	Zn	Mn	Fe
2P	5.10	2.52	33.1	141
3P	3.97	2.09	22.5	106
1R	3.41	2.71	20.5	71.0
1M	1.83	2.98	12.1	205
2M	3.33	1.88	68.8	96.9
7D	8.82	3.01	20.5	176
8D	1.47	1.41	16.3	36.1
7BP	0.64	0.93	69.4	82.5
8BP	3.27	3.17	31.0	209
2K	2.83	1.68	7.57	248

HASTINGS BEDS DTPA EXTRACTIONS (μg/g)

Soil No.	Cu	Zn	Mn	Fe
9BP	2.46	4.21	24.7	265
9D	0.73	1.26	18.7	36.0
10D	2.48	1.05	16.8	66.5
10BP	3.09	2.93	58.4	192
12D	4.01	3.56	34.5	214
11D	3.09	1.50	13.5	122
11BP	1.58	1.42	22.0	129
12BP	1.86	1.75	17.8	219

T-MATRIX OF "TOTAL" Cu IN WEALDEN SOILS

	RM	DD	Ch	UG/G	LG	WC	HB
RM	X	1.439	1.327	1.181	3.009^3	3.620^4	1.717^1
DD		X	0.320	0.236	2.469^1	0.978	0.200
Ch			X	0.061	2.755^3	1.623	0.146
UG/G				X	2.459^1	1.339	0.058
LG					X	3.771^4	2.827^3
WC						X	1.514
HB							X

1. $p < 0.1$ 2. $p < 0.02$ 3. $p < 0.01$ 4. $p < 0.001$

T-MATRIX OF "TOTAL" Zn IN WEALDEN SOILS

	RM	DD	Ch	UG/G	LG	WC	HB
RM	X	1.068	1.597	1.014	6.245^3	1.644	3.113^2
DD		X	0.223	1.054	3.564^3	1.159	1.683
Ch			X	1.385	4.184^3	1.461	2.072^1
UG/G				X	2.252^1	0.249	0.537
LG					X	1.764^1	2.041^1
WC						X	0.244
HB							X

1. $p < 0.1$ 2. $p < 0.01$ 3. $p < 0.001$

T-MATRIX OF "TOTAL" Fe IN WEALDEN SOILS

	RM	DD	Ch	UG/G	LG	WC	HB
RM	X	3.204^2	8.506^3	2.512^1	3.145^2	0.851	1.001
DD		X	3.417^2	0.049	0.523	0.898	1.217
Ch			X	2.796^2	1.892^1	3.310^2	4.294^3
UG/G				X	0.550	0.716	0.927
LG					X	1.091	1.343
WC						X	0.038
HB							X

1. $p < 0.1$ 2. $p < 0.01$ 3. $p < 0.001$

T-MATRIX OF "TOTAL" Mn IN WEALDEN SOILS

	RM	DD	Ch	UG/G	LG	WC	HB
RM	X	4.321^3	10.18^3	-1.792^1	0.035	3.995^3	5.898^3
DD		X	2.965^2	1.542	2.977^2	1.277	1.769
Ch			X	5.440^3	7.447^3	0.689	0.267
UG/G				X	1.966^1	2.570^1	3.121^2
LG					X	3.812^2	4.547^3
WC						X	0.310
HB							X

1. $p < 0.1$ 2. $p < 0.01$ 3. $p < 0.001$

KEY:

RM - Romney Marsh Alluvium

DD - Drift Deposits

Ch - Chalk

UG/G - Upper Greensand/Gault

LG - Lower Greensand

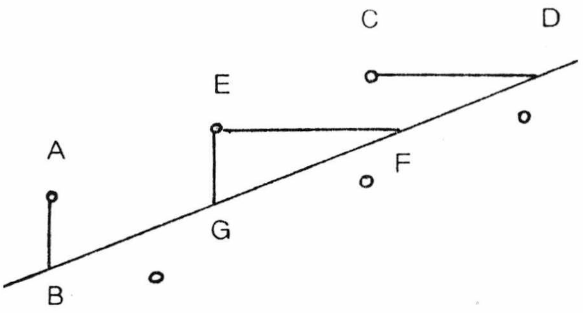
WC - Weald Clay

HB - Hastings Beds

APPENDIX 5

THE REDUCED MAJOR AXIS CORRELATION (R.M.A.) (Miller and Kahn, 1962)

The reduced major axis correlation is used when there is no clear justification to choose either of the dimensions as the independent variable. Thus a RMA minimises the sum of the areas of triangles EFG rather than the sum of the squares of the deviations measured as AB or CD



For a RMA in the form of a straight line $y=b+kx$ where

the slope $K = \frac{Sy}{Sx}$ (S = the standard deviation)

the standard error of the slope

$$S_K = \frac{S_y}{S_x}\sqrt{\frac{1-r^2}{n}}$$ (n = the sample size
r = the correlation coefficient)

The intercept $b=\bar{y}-\bar{x}K$

To compare the slopes of two separate reduced major axes the z statistic is determined.

$$z = \frac{K_1 - K_2}{\sqrt{S_{K_1}^2 + S_{K_2}^2}}$$

z is the referred to in the t-tables which gives the areas of the normal curve for n-2 degrees of freedom.

RMA FOR "TOTAL" Cu:Zn

	K	r	n	S_K
RM	5.09	0.738	48	0.50
DD	5.46	0.920	19	0.49
Ch	8.04	0.705	23	1.19
GC/UG	5.92	0.905	22	0.54
LG	4.91	0.740	35	0.56
WC	4.42	0.821	12	0.73
HB	3.92	0.952	16	0.30

z-STATISTIC MATRIX FOR "TOTAL" Cu:Zn IN WEALDEN SOILS

	RM	DD	Ch	UG/G	LG	WC	HB
RM	X	0.372	2.269^1	0.814	0.175	0.604	1.308
DD		X	1.990	0.453	0.537	0.942	0.651
Ch			X	1.612	2.366^1	2.612^2	3.375^3
UG/G				X	0.963	1.331	2.182^1
LG					X	0.431	1.067
WC						X	0.493
HB							X

1. $p < 0.05$ 2. $p < 0.02$ 3. $p < 0.01$

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