AGRICULTURAL LIVESTOCK:

ASSESSMENT OF COPPER EXPOSURE AND OF TOXICITY AND DEFICIENCY

FINAL REPORT FOR THE EUROPEAN COPPER INSTITUTE

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Table of Contents

List of Tables

List of Plates

List of Figures

1
INTRODUCTION

Copper and its compounds, together with other metals, are considered within the European Commission's Technical Guidance Document on Risk Assessment (TGD) as a class of chemicals of natural origin. Ambient concentrations of copper in the environment can thus be attributed to natural geochemical sources of the metal together with anthropogenic inputs that may have accumulated over time. Inputs of copper to the soil are to a degree countered by outputs which include uptake and removal in crops and pasture herbage and removal through erosion, leaching and downward migration. For example, it has been estimated that pasture herbage removes some 40-60 g Cu per hectare per year from the soil and that a similar amount is ingested by grazing cattle (both as herbage and soil). This is roughly compensated for by the return of copper to the soil in animal feces (MAFF, 1982).

The TGD is also concerned with bioaccumulation resulting from all exposure routes – air, water, soil and food and biomagnification – "accumulation and transfer of chemicals via the food chain, resulting in an increase of the internal concentration in organisms at higher levels in the trophic chain."

Secondary poisoning is concerned with "toxic effects in the higher members of the food chain which result from ingestion of organisms from lower trophic levels that contain accumulated substances." Agricultural livestock can be regarded in this category as their diets largely comprise pasture and forage plants and/or feedstuffs manufactured from crop plants. Because copper is an essential micronutrient for both plant and animal growth and health, this assessment must take into account issues concerned with deficiency as well as toxicity.

This review is restricted to agricultural livestock – cattle, sheep, pigs and poultry – that are primarily destined for human consumption and to the food chain transfer (soil to plant to plant-eating animal and soil to animal). It is based almost exclusively on cattle and sheep, as pigs and poultry are reared on formulated rations, which meet their dietary requirements, are usually raised under housed conditions, and may receive additions of copper compounds to promote growth. However, copper-rich excreta and slurry from pigs and poultry are sometimes intentionally applied or accidentally discharged onto pasture resulting in elevated copper exposure in grazing livestock.

The approach taken will be based on the concept that soil is an important source of copper to agricultural livestock (ruminants) via the food chain and that natural copper concentrations in soils vary widely in relation to the geochemical nature of the soil parent material. An assessment will be made of ranges in natural and ambient background concentrations of copper and of factors influencing the pathways soil-plant-animal and soil-animal (i.e., direct soil ingestion). Exposure will also be related to dietary feedstuffs, including hay and silage, growth promoters and mineral supplements. Information on copper levels in edible animal tissues will contribute towards human health risk assessment.

Critical values of copper in soil will be derived taking into account both natural and ambient background values for copper and will aim to provide a safe threshold for both toxicity and deficiency. It will be important to assess copper concentrations in soils related to the range of copper sufficiency in the diet within which neither deficiency nor toxicity may be expected in grazing ruminants.

2

THE SUPPLY OF COPPER

a) Grazing livestock – cattle and sheep

Copper in soils

Soil provides an important source of copper to plants and animals to meet their nutritional requirements. The total concentration of copper in soil tends to reflect that of the parent material, which may be the underlying rock, or material transported by wind, water or glacial activity. The variation in copper content of geological materials is shown in Table 1 taken from Landner *et al.* (2000) and shows a wide range of 4 to 200 mg/kg, with smaller concentrations in acid igneous rocks and sandstones and largest concentrations in basic igneous rocks and shales and clays.

Typical concentrations of copper found in agricultural soils have been reviewed by Landner *et al.* (2000). A general relationship is found between the total copper content of soil and the soil texture – the more sand sized particles, the lower the copper content (Table 2). For example, a study of copper concentration in soils developed from a sequence of sandstones in South Wales showed the total copper concentration in soil to reflect the coarseness of the sandstone formation, ranging from 13 mg/kg in coarser textured soils to 28 mg/kg in finer textured soils (Wood, 1975: Table 3). At the other extreme copper in soils developed from fine--grained marine black shales in England ranged up to 70 mg/kg (Leech, 1984), and chestnut soils weathered from basic rocks in the USSR ranged from 88-96 mg/kg (Aubert and Pinter, 1977). Landner *et al.* (2000) note data for total copper concentrations in soils from several countrywide surveys. Over 4000 unpolluted topsoil samples from Scotland showed a mean value of 18 mg/kg (Reaves and Berrow, 1984); 6000 topsoil samples from England and Wales had a median value of 18 mg/kg (McGrath and Loveland, 1992). 1,720 Swedish agricultural topsoil showed an arithmetic mean value of 14.6 mg/kg and a median of 11.1 mg/kg (Eriksson et al., 1997). in surface The average copper content of French soils has been reported as 20 mg/kg (Aubert and Pinter, 1977). Concentrations of copper soils of several other European countries have been listed by Kabata Pendias (2001) and show mean levels ranging between 13 and 24 mg/kg.

Angelone and Bini (1992) have reviewed data for trace element concentrations in soils of western Europe and record average (arithmetic mean) values for total Cu as - Austria 17 mg/kg; Belgium 17 mg/kg (range 8-30); Denmark 11.1 mg/kg (range 1.5-24); France 13 mg/kg (range 3-20); Germany 22 mg/kg (range 1-84); Italy 51 mg/kg (range 1-96); Netherlands 18.6 mg/kg (range 4-110); Norway 19 mg/kg (range 10-40); Portugal 13.2 mg/kg for soils on granite and 56.7 mg/kg for soils on schist; Spain 14 mg/kg (range 4-400, including some mined areas); Switzerland 15.6 mg/kg. A mean value of 1588 mg/kg for Greece is obviously influenced by soils contaminated by mining.

A recent analysis of the extensive data compiled from several sources for copper concentrations in European agricultural soils is summarized in Table 4, showing median and 90th percentile (PEC – predicted environmental concentrations) for seven countries; the overall median value is 14.7 mg Cu/kg DW and 90th percentile 30.7 mg Cu/kg DW (Heijerick and Van Sprang, 2003).

It has been noted by several authors that copper accumulates in top horizons of soil profiles, reflecting the bioaccumulation of the metal and recent additions from anthropogenic sources. However, this is not always the case as found in detailed studies of soil profiles in Devon and North Wales where soil forming (pedogenetic) processes have influenced the copper content of soil horizons, reflecting the influence of soil texture, organic matter content and drainage (Keeley, 1972). For example, the process of podzolization resulted in appreciably lower levels of copper in surface (0-40 cm – 6-16 mg/kg) horizons compared to deeper horizons (40-70 cm – 22-45 mg/kg. Strong evidence that copper is redistributed in the soil profile as an effect of podzolization, with removal from the A2 horizon and accumulation in the B horizon has also been cited in Scotland (Mitchell, 1964; 1971).

It must be stressed that depths of sampling and methods of analysis for "total" copper content of topsoils may well vary from one laboratory and country to another; thus the data reported in this section may not be strictly comparable.

Anthropogenic sources of copper in soils

It is not the aim of this section to detail the nature and distribution of anthropogenic copper inputs to agricultural land as this has been addressed elsewhere (see Kabata-Pendias and Pendias, 1992; Thornton, 1979; Baker and Senft, 1995; Landner *et al.,* 2000). It is sufficient to note that anthropogenic inputs of copper are widespread in Europe and may be described as historical, from past mining and smelting activities, recent and current. Point source emissions from mining, smelting and copper processing activities will have local inputs and may over time lead to marked accumulation of copper in surface soils. For example, copper was mined in southwest England from Roman to recent times and agricultural soils contain up to several hundred mg/kg Cu. Although this may be described as local contamination, the extensive nature of the mineral deposits and their intensive working, both mining and smelting, particularly in the 18th and 19th centuries, has given rise to copper contamination of soils of a regional nature (see Plate 1). The geochemical map for copper, taken from the *Wolfson Geochemical Atlas of England and Wales* (Webb *et al.*,1978), is based on the analysis of stream sediments and has been shown to delineate areas of elevated copper concentrations in soils (Abrahams and Thornton, 1994).

Diffuse emissions of copper into agricultural soils include the application of commercial fertilizers, particularly containing copper, the application of sewage sludge and pig slurry to land, the direct application of copper salts to soil or as liquid sprays to counteract copper deficiency in crops, and the use of copper-based fungicides and herbicides. Inputs of copper in sewage sludge to land have been extensively reviewed by Landner *et al.,* (2000). The EU Directive (86/278/EEC Directive) regulating the use of sewage sludge in agriculture stipulates the highest permitted loading rate of 12 kg copper/hectare per year. Many European countries have lower permissible rates, for example UK 7.5 kg/ha/yr and France 3 kg/ha/yr. Regulations in the above EEC Directive list limit values of copper in sludge for use in agriculture of 1000-1750 mg/kg DM, and for agricultural soils receiving sewage sludge of 50-140 mg/kg. However, this Directive is currently being revised and it is likely that limit values for copper in soil and sludge will be reduced.

The impact of sludge application on copper exposure in grazing livestock may vary from country to country depending on national policy. In Sweden sewage sludge may not be applied to pastures or arable land that will be used as pasture or if forage plants will be harvested within 10 months of application (Landner *et al.,* 2000).

Geochemical maps and atlases

Multi-purpose geochemical surveys based on the systematic sampling and analysis of rocks, soils, stream sediments and surface waters have now been carried out in 30 or more countries (Plant *et al.,* 1989). These provide spatial information on copper distribution in the surface environment. An example is shown in Plate 1 from the Wolfson *Geochemical Atlas of England and Wales* (Webb *et al.,* 1978), based on the analysis of c 50,000 stream sediment samples taken at an average density of 1 per 2.5 km^2. The lowest concentrations of copper in dark blue reflect areas underlain by sandstone and limestone formations in which copper deficiencies have been recognized in agricultural crops but where absolute/simple copper deficiency is rarely found in cattle and/or sheep. The areas shown in red in south west England have very high concentrations of copper, reflecting an area of copper-tin-arsenic mineralization that has been mined for several hundred years. *The Soil Geochemical Atlas of England and Wales* (McGrath and Loveland, 1992) also includes a map for copper, based on c 5,700 0-15 cm soil samples at a density of 1 per 25 km^2.

Equally important are geochemical maps showing the regional distribution of molybdenum, a metal occurring naturally in some rocks and soils at concentrations large enough to interact with copper in the grazing animal. As detailed in Section 3, molybdenum can induce copper deficiency in both cattle and sheep. The example of the molybdenum map from the *Wolfson Geochemical Atlas* is shown in Plate 2 and shows the considerable extent of high molybdenum areas, which are a potential hazard. It has been estimated that these areas may total as much as 0.81 M hectares. They are mostly underlain by marine black shales ranging in age from Cambrian to Recent. In several areas both clinical hypocuprosis and sub-clinical hypocupremia in cattle have been confirmed (Webb *et al*., 1968; Thomson *et al*., 1972).

More recently, consortia of European Geological Surveys have undertaken large sub-continental scale projects in geochemical mapping. The **NORDKALOTT** Project covered 200,000 km^2 in northern Finland, Norway and Sweden using a low sample density of 1 per 30 km^2 and a variety of different sampling materials (Bolviken *et al.*, 1986). The KOLA Project (1992 - 1998) covered 188,000 km^2 in northern Finland, Norway and Russia to map the environmental impact of Cu-Ni smelters (Reimann *et al.*, 1998). Samples of moss and three soil horizons were collected at a density of 1 per 300km^2. The area covered was then extended to 1,500,000 km^2 of Finland and north-west Russia at a density of 1 sample per 1,000 km^2 under the **BARENTS** Project (1999-2003). The **Baltic Soil Survey** (1996--2003) covered agricultural soils from 10 countries surrounding the Baltic Sea including Germany, Norway and Poland. Sampling was undertaken at a low density of 1 per 2,500 km^2 at depths of 0-25 cm and 50-75 cm from ploughed fields within an area of 1,800,000 km^2 (Reimann, *et al.*, 2000; 2003).

A new geochemical baseline, designed to establish the current levels of a range of natural elements, including copper, over Europe, due to the geology and to man-made influences, has recently been prepared by the **Forum of European Geochemical Surveys** (FOREGS, 1996). This is based on the systematic collection and analysis of a range of soil, sediment and water samples together. This survey covers an area of 4,250,000 km^2 at an average sample density of 1 per 5,000 km^2.

Forms of copper in soils and bioavailability

It is important to emphasize that copper is present in soils in many mineral and chemical forms which vary in their solubility and thus bioavailability. Only a small proportion of the total copper content of the soil may be available for uptake into plant roots.

Baker and Senft (1990) list six ‘pools’ of copper in soils classified according to their physical-chemical behavior.

These are:

Cu present as soluble ions and inorganic and organic compounds in soil solution

Exchangeable copper

Stable organic complexes in humus
Cu adsorbed by hydrous oxides of Fe and Mn
Cu adsorbed on the clay-humus colloidal complex
Crystal lattice-bound Cu in soil minerals

In relation to the exposure of cattle and sheep to copper in the soil, these forms must be viewed in terms of their potential uptake into pasture and forage species, i.e., bioavailability in the soil-plant system, and their bioaccessibility in the gastro-intestinal tract as a result of direct soil ingestion.

Laboratory-based methods to assess the bioavailability of copper have provided a focus for research since the 1960's. Copper availability to plants has been determined by a range of soil analytical tests, ranging from the use of single extractants such as EDTA, initially developed for the diagnosis of deficiencies in agricultural crops, to more complex, operationally defined sequential extraction procedures such as that developed by Tessier *et al.* (1979) and modified by Li *et al.* (1995), and the three-stage test developed by the European Union (Ure *et al.,* 1993). None of these tests provide an accurate assessment of copper uptake into plants from the wide range of soil types encountered – i.e., organic and inorganic, calcareous and non-calcareous, freely and poorly drained. An example is shown by soil testing over a wide range of UK grassland soils used for grazing, showing a strong significant relationship between EDTA-extractable Cu and total Cu (Figure 1). Both total and EDTA-extractable soil Cu showed a poor relationship with Cu in pasture herbage (UK Ministry of Agriculture, Fisheries and Food, unpublished data). Studies under UK farming conditions (Figure 6), supported by recent findings within a wide range of upland and moorland soil conditions in North Wales showing that water extractable soil copper did not correlate with soil pH but rather increasing with dissolved organic carbon, indicating organic complexation of free copper ions (Rieuwerts *et al*., 1999). However, no attempt was made to relate this finding to copper uptake by herbage.

Recent research into bioavailability has focused on soil solution chemistry and the concept of free ion activity (McLaughlin *et al.*, 2000). A further advance introduces a new concept of *effective concentration,* which includes both the soil solution concentration and the metal supplied to solution from the solid phase. This can be measured using the technique of *diffusion gradients in thin films* (DGT). Under experimental conditions, using 29 soils from different sources this measurement showed a linear relationship with plant content and is a promising quantitative measure of bioavailable copper in soils (Zhang *et al.*, 2001). However, until this new method is comprehensively tested under field conditions, it may be concluded that the best measure of copper availability to and uptake by plants remains that of determining the actual copper concentration in the plant tissue.

Chemical extraction procedures have also been used to determine metal availability from directly ingested soil and dust to farm livestock. The soil-animal pathway has been studied using

a) an *in vitro* Rusitec artificial rumen system to simulate extraction from dietary constituents and soils by cattle and sheep (McDonald and Suttle, 1983; Brebner, 1986). [This rumen simulation technique (Czerkawski and Breckenridge, 1977) aims to closely simulate rumen fermentation using artificial saliva.], and
b) *in vivo* studies on absorption and utilization of trace elements in livestock under experimental conditions, using well-established and reliable copper repletion techniques under experimental conditions in which the effects of soil and soil constituents including molybdenum, zinc and iron on copper absorption were determined using measurements of plasma-Cu, ceruloplasma-Cu, urine analysis and the analysis of rumen contents and rumen liquor collected by stomach tube.

Copper in pasture herbage and forage plants.

Although it is recognized that copper in the diet or pasture has little diagnostic value in ruminants unless other elements with which copper interacts are also determined (Underwood and Suttle, 1999), it is nonetheless useful to detail normal ranges over which (in the absence of copper antagonists) dietary sufficiency is to be expected, and those that might give rise to deficiency and toxicity.

Copper in forage and pasture depends on the availability of copper in the soil which is a function of Cu^{2+} activity in the soil solution at the root surface; uptake is a metabolically active process though much of the Cu^{2+} associated with plant roots may not be translocated into the shoot (Baker and Senft, 1995). The copper content of pasture is influenced by plant species, stage of growth, time of year and lime and fertilizer applications. Experimental applications of lime to an acid podzolic soil in Wales raised the soil pH from 4.7 to 6.0 but had little effect on the uptake of copper by either clover or the grass timothy (*Phleum pratense*), which averaged 2.5 and 2.0mg/kg DM respectively (Archer, 1971). This confirms the general recognition that legumes such as clover tend to take up larger amounts of copper than grasses (Baker and Senft, 1995). However, this is not always the case as shown in experimental work reported by Reith, (1975) in which clovers averaged 3.3 mg Cu/kg DM and ryegrass (*Lollium perenne*) averaged 4.8 mgCu/kg DM. Archer (1971) also cited work in Scotland showing that on soils of low copper status, the copper content of red clover fell below that of ryegrass, while on soils richer in copper, copper in red clover exceeded that in ryegrass (Mitchell *et al.*, 1956).

Reith (1975) reported that a doubling of yield of mixed pasture herbage resulting from the application of nitrogen fertilizer had no effect on the herbage copper content. On the other hand, application of $CuSO_4$ at a rate of 28.5 kg/ha in addition to nitrogen raised the copper content of clover from 3.0 to 10.1 mg/kg DM and ryegrass from 4.2 to 7.1 mg/kg DM.

Weed species in lowland pastures in northern England such as buttercup (16.6 mgCu/kg DM) and plantain (15.9 mgCu/kg DM) were richer in copper than associated grasses (4.2-8.2 mgCu/kg DM).

Kabata-Pendias (2001) has compiled data from several countries indicating that the copper content of plants growing in unpolluted soils rarely exceeds 20 mg/kg DM, with grasses averaging from 6-10mg/kg and clovers around 11 mg/kg DM. Species differences have been widely recorded with a general agreement that the normal range in plants is 5-20 mg/kg and that legumes tend to take up more than grasses (Burridge *et al.*, 1983; Baker and Senft, 1995). The copper content of common grasses has been shown to decrease with maturity more rapidly than that of red and white clover (Fleming, 1965). At a young stage of growth, cocksfoot (*Dactylis glomerata*) (12.9 mgCu/kg DM) contained more copper than red clover (10.8 mg/kg), but at maturity the red clover (8.4 mg/kg) contained more copper than the cocksfoot (4.0 mg/kg). Differences in the copper contents of inflorescence, leaf and stem between different species have also been noted (Fleming, 1963; Burridge *et al*., 1983). For example, Mitchell (1957) noted that the leaves of cocksfoot contained more copper than the stem and the inflorescence (5.9, 3.1 and 4.5mg/kg DM, respectively).

Studies on groups of sites at 15 locations in the UK have shown that the copper content of pasture herbage is fairly constant despite a wide range of total copper levels (3-70 mg/kg) in corresponding topsoils. Average copper contents in herbage ranged from 6-11 mg/kg DM, falling within the documented normal range for British pasture herbage of 2-15 mg/kg (ADAS, 1975). Seasonal differences were usually small and rarely exceeded 3mg/kg DM in herbage sampled in spring, summer and autumn (Leech and Thornton 1987). Further, no relationship was found between herbage copper levels and the total copper content of topsoils, in studies by Thomson (1971) and Leech (1984) (see Figures 2 and 3). However, further detailed studies into copper intake by sheep in 3 sheep rearing areas of England showed copper uptake by mixed pasture species to increase with increasing total soil copper content (Russell, 1987; see Figures 4a and 4b). For example, washed herbage on soils with 15 mgCu/kg DM contained 7.8-9.5 mgCu/kg DM rising to 12.5 mg/kg in herbage on soils with 35 mgCu/kg DM. This work was carried out on 23 farms covering a variety of soils. These were well-- drained brown earths and imperfectly drained brown earths with gleying of silty loam texture developed from Silurian and Carboniferous rocks in North Wales, pH 5.2-5.9 (mean 5.4); well-drained and imperfectly drained brown earths of silty loam texture developed from Silurian rocks and drift in the Lake District, pH 4.9-6.5 (mean 5.4); and well-drained and imperfectly drained calcareous and decalcified soils ranging in texture from sandy loam to silty clay developed on marine alluvian on Romney Marsh, pH 5.8-7.4 (mean 7.0). On land contaminated by historical copper mining in South West England, concentrations of copper in washed pasture herbage tended to increase with total soil copper content (Figure 5a) though relative accumulation (concentration of Cu in herbage/concentration of Cu in soil) decreased rapidly at higher soil concentrations, reflecting the homeostatic control of copper in the herbage tissues (Figure 5b: Abrahams and Thornton, 1994).

The variability in the copper content of the herbage at any one soil concentration (Figure 5a) can possibly be explained by differences in soil type, species composition of the sward, and the chemical and mineral nature of the soil contaminants, which in turn may influence bioavailability and uptake.

In the absence of copper antagonists, the UK Agricultural Research Council (1980) recommended dietary copper concentrations in excess of 10 mg/kg DM. This estimate is based on a factorial analysis of the need for copper to meet endogenous losses in feces and urine and the demands for growth, pregnancy and lactation (and wool production in sheep). Estimated requirements were 6.2-7.5 mgCu/kg diet for a pregnant ewe, up to 8.6 for a lactating ewe, 8-15 for a growing bullock and 8-14 for a lactating cow. Modern strains of pasture grasses and in particular Italian Ryegrass (*Lollium italicum*) usually contain less than this and indeed may fall below the critical level necessary to meet the dietary requirements of cattle and sheep. Further information on the growth and maintenance requirements for copper by ruminants resulted in Suttle (1983) estimating lower bovine requirements for copper than those estimated by ARC (1980); these ranged from 3-9mg/kg DM in the diet for sheep and 8-20 mg/kg DM for cattle. Further recommendations for copper requirements of sheep have been made by INRA (1989) of 7 mgCu/kg dietary DM for lambs and 10 mg/kg for lactating ewes. The recommendation for both growing cattle and dairy cows was 10mgCu/kg dietary DM (INRA, 1989; GfE, 2001).

Underwood and Suttle (1999) citing Minson (1990) note that “copper is unevenly distributed in temperate grasses, the leaves containing 35 percent higher concentrations than the stems; there is thus a tendency for values in the whole plant to decline during the grazing season.” They also note that forage copper is not influenced by soil pH.

In New Zealand, Cunningham (1950) reported the mean content of copper in “normal” pastures to be 11 mg/kg and found that ‘simple copper deficiency’, a disorder associated with low concentrations of copper in pasture, as opposed to a “complicated” or conditioned deficiency associated with pastures moderately low in copper and high in molybdenum, occurred in cattle and sheep maintained on pastures with a mean copper content of 3 mg/kg. Allcroft and Lewis (1957) noted that only rarely were pastures with mean copper values below 5 mg/kg found in Britain. Bennetts (1955) noted that in Western Australia stock remained healthy with pasture copper exceeding 6 mg/kg, signs of copper deficiency could be expected with values between 3 and 6 mg/kg and severe clinical manifestations of deficiency occurred with values below 3 mg/kg.

As noted earlier, excess dietary molybdenum will, in the presence of sulphur, induce copper deficiency in both cattle and sheep. Molybdenum-induced or ‘conditioned’ copper deficiency is widely recognized in the United Kingdom (Thornton, 1977). In New Zealand, 10 mg/kg Mo in the pasture dry matter has been found to cause copper deficiency if the copper content is ‘normal’, and 3-10 mg/kg is harmful if the copper intake is low (Cunningham, 1954). In England and Wales ‘conditioned’ copper deficiency is frequently associated with pasture molybdenum contents of 2-16 mg/kg; in Scotland 5-10 mg/kg has been reported as suspect (Mitchell, 1957); and in Ireland 5-25 mg/kg Mo (Walsh *et al*., 1952).

Experimental work with cattle has shown that with copper concentrations in the feed in the range of 3-10 mg/kg, and with concentrations of molybdenum of less than 2 mg/kg, animals do not respond to supplementary copper. If concentrations of molybdenum are in the range of 2-20 mg/kg and the copper concentrations are in the range of 5-20 mg/kg, copper supplementation results in weight gain (MAFF, 1982) – i.e., the animals have ‘conditioned’ copper deficiency. Copper:Molybdenum ratios in the diet have been used as a means of diagnosis, though Underwood and Suttle (1999) stress that they require flexible interpretation, with Cu:Mo ratios of <1 indicating a high risk of copper deficiency disorders and ratios of 1.0-3.0 indicating a marginal risk.

Excess intakes of other metallic cations can also induce copper deficiency in ruminants. Critical concentrations in pasture herbage that can cause copper deficiency have been recorded as Fe >350 mg/kg DM (Bremner *et al*., 1983); Zn >200 mg/kg DM (Agricultural Research Council, 1980) and Cd >3 mg/kg DM (Agricultural Research Council, 1980). Dietary Fe:Cu ratios of >100 may indicate a high risk of disorder and between 50-100 there is a marginal risk (Underwood and Suttle,1999).

Copper in other animal feed materials

Concentrations of copper in selected livestock feedstuffs established in several Members states are listed in Table 5 and mostly fall within the range of 2-20 mg/kg

DM. (cited in European Commission Opinion of the Scientific Committee for Animal Nutrition on the Use of Copper in Feeding Stuffs). A broader review worldwide (Table 6) provides general agreement with the EU data, though shows some higher copper contents in meals and cakes. A detailed listing for the US is shown in Table 7.

Soil Ingestion

The relative importance of ingested soil as a source of copper and other trace metals to grazing animals has been reviewed by Thornton (1983) and may be regarded as the soil-animal exposure pathway.

It has long been recognized that grazing animals involuntarily ingest soil along with grass. In Britain and New Zealand, cattle may ingest from 10 to over 100 g soil per kg herbage DM, and sheep, which graze closer to the ground, up to 300 g (Field and Purves, 1964; Healy, 1968, 1969, 1970; Thornton, 1974). The amount of soil ingested will depend on the type of pasture, management factors, soil type, season, and weather factors, such as rainfall intensity (Healy, 1969). Studies in Ireland showed that grazing sheep ingested up to 400 g soil per kg body weight over the period May to early September with ingestion rates related to rainfall and stocking rate. For a 60 kg animal, total soil ingested over a year was around 75 kg (McGrath, Poole, Fleming and Sinnot, 1982). Russell (1987) measured contamination of both herbage and feces by soil on 9 farms over an 18-month period showing the highest levels of contamination in winter months, when grass was in short supply. Soil ingestion by grazing sheep ranged up to 18% of dry matter intake (Figure 7).

Soil ingestion is thought to be an important pathway of metals into animals in areas where soils are contaminated with or contain naturally high concentrations of heavy metals. Studies in south-west and central England, in areas where past metalliferous mining and smelting have led to widespread soil contamination with one or more of the metals Cu, Pb, Zn, Cd and arsenic (As), have concluded that only a small proportion of these metals is taken up into the leafy material of pasture plants and that plant uptake is not the major pathway of these contaminants into grazing animals (Abrahams and Thornton, 1994).

In these studies, the rate of soil ingestion has been calculated using the titanium (Ti) content of feces as a stable marker, on the premise that Ti is present in relatively high concentration in soils (several thousand mg/kg and in very small amounts in herbage (usually less than 10 mg/kg DM). On soils heavily contaminated with copper in south west England, soil ingestion at rates ranging from 1.5 to 17.9% of dry matter intake gave rise to an estimated total intake of copper by cattle ranging from 113 to 396 mg Cu per day (Abrahams and Thornton, 1994; see Figure 8).

In addition, ingested soil may be an important source of nutrients to livestock, possibly providing beneficial quantities of Co, Cu, Se and Zn (Healy, McCabe and Wilson, 1970).

Collaborative studies between the Moredun Institute and Imperial College have shown under experimental conditions that when hypocupremic sheep are fed soil, at 100 g/kg DM, with a Cu-supplemented diet, the soil reduced the availability of dietary Cu by 50% (Suttle, Alloway and Thornton, 1975). This suggested that, either the soil was occluding Cu in the alimentary tract, or ingested soil was releasing a Cu antagonist.

Further experiments compared the effects of feeding hypocupraemic ewes three contrasting soil types,a "clay", a "chalk" and a "sand", using basal diets high or low in sulphur (S) (Suttle, Abrahams and Thornton, 1982). As the soils varied in their Fe content, an Fe treatment was included. On a Cu-repletion diet with high S, the two Fe-rich soils and FeSO4 reduced Cu absorption by c.50%, while the low Fe soil had no effect, suggesting that soil Fe might be the causal factor. However, with the low S diet, only Fe SO4 displayed an inhibiting effect on Cu absorption.

Repeated applications of sewage sludge to pasture over the period 1981 to 1994 (at an average annual application of 223 m^3 sludge per hectare) prior to grazing has resulted in increased uptake of copper into herbage. Untreated soils (2.5 cm) contained 38 mgCu/kg DW and sludged soils 83 and 120 mg/kg. In two experiments unwashed mixed pasture species ranged from 3.2-8.9 mg Cu/kg DM over the period May to November on untreated land and 5.1-17.9 mg Cu/kg DM where sludge had been applied (Wilkinson et al., 2001) Muscle tissue in grazing sheep, ranging from 3.6 to

4.8 mg Cu/kg DM did not show any increase in copper content on the treated land, though liver copper concentration increased from 63 to 197 mg Cu/kg DM in one experiment. This increase possibly reflected the application of sludge either through adhesion of sludge to the plant and/or ingestion of sludge-enriched soil. Copper--depleted sheep fed sludge-enriched topsoils (560-1700 mg Cu/kg DW) under experimental conditions showed significant increases in both blood and plasma copper content and in glutathione peroxidase activity, though the availability of the ingested copper was not considered to be high enough to cause toxicity and the majority of the copper was excreted in the feces (Suttle, Brebner and Hall, 1991).

Experimental application of Cu-rich pig slurry (429 mgCu/kg DM) applied at a rate of 15.6t DM/hectare to pasture increased the herbage copper content from 7.3 to a maximum of 10.2 mg Cu/kg DM (Suttle and Price, 1976). It should be noted that this still falls within the normal range of copper concentration in herbage dry matter. Experiments with Scottish blackface sheep in which copper absorption was measured as plasma content showed the proportion of the herbage copper available to the animal to be larger in the herbage treated with pig slurry than in the untreated herbage. The availability of copper in dried poultry waste was greater than in dry pigs slurry; the latter was similar to $CuSO_4$. Both dried pig slurry and dried poultry waste had a high proportion of EDTA-extractable Cu (78% and 64%, respectively), (Suttle and Price, 1976). The responses in plasma Cu showed similar availability from dried pig slurry (added to diet) as that of $CuSO_4$ (approximately 4%), indicating that slurry copper is partly bioavailable when ingested as a soil contaminant (Price and Suttle, 1975). However, once washed into the soil it causes little or no rise in herbage copper concentration and it may be concluded that the toxicity hazard associated with the recycling of Cu-rich pig slurries can be greatly reduced by suitable pasture management (Suttle and Price, 1976).

Nutritional requirements - Pigs

Nutritional anemia has been induced experimentally in baby pigs on a low copper diet. It has been estimated that a concentration of 4 mg Cu/kg DM in the diet is sufficient to meet the requirement of growing pigs up to 90 kg live weight (Agricultural Research Council, 1981). Copper requirements for pigs have also been reviewed by the European Commission Scientific Committee for Animal Nutrition (SCAN)(2003) and fall within the narrow range of 4-10 mgCu/kg dietary DM. AFRC (1990) recommend 4mg/kg for growing and adult boars; ARC (1981) 4 mg/kg for growing pigs up to 90 kg live weight; GfE (1987) 6 mg/kg for piglets, 4-5 mg/kg for growing pigs and 8-10 mg/kg for breeding sows and boars; INRA (1989a) 10 mg/kg for piglets, growing pigs and sows.

Growth promotion - Pigs

A recent review of the effect of copper fed at higher levels than those covering dietary requirements concluded that "up to 175 mg and further to 250 mg/kg feed, copper impacts on the growth and feed conversion of young pigs, from weaning to a body weight of approximately 25 kg (8-10 weeks of age). No significant effect is demonstrated in finishing pigs" (European Commission, 2003). However, it has been noted that copper supplementation of pig rations at 250 mg or even125 mg/kg Dm is not always a safe procedure and can result in copper toxicosis unless the diets contain sufficient iron and zinc (Underwood and Suttle, 1999; Suttle and Mills, 1966). A recommendation has been made that the period of authorization of feeding copper at a level of 175 mg/kg DM should be reduced to the first 10 weeks of the pigs life instead of the present period of four months of age (European Commission, 2003).

Nutritional requirements - Poultry

Underwood and Suttle (1999) state that definitive data on the copper requirements of chicks for growth or hens for egg production have not been reported. The National Research Council (1994) record copper requirements of 4, 2.5, and 8 mg/kg diet for growing chickens, laying hens and broilers, respectively. However, poultry rations invariably contain 8 mg Cu/kg DM or more and there are no reports of practical diets containing too little copper for poultry (Underwood and Suttle, 1999). SCAN (2003) have also covered copper requirements for poultry. The recommendation by GfE (1999) for growing chickens, laying hens and broilers is 7 mgCu/kg dietary DM. For turkeys these range from 6 mg/kg at 5-24 weeks and 15 mg/kg for poultry of 0-4 weeks.

Growth promotion - Poultry

Underwood and Suttle (1999) note "the effects of large copper supplements in poultry rations are highly variable, of doubtful economic significance and affected by the nature of the basal diet." They note that copper poisoning in poultry would not seem to occur until dietary concentrations reach 500 mg Cu/kg DM. Pesti and Bakalli (1996) report that copper between 125 and 250 mg/kg in the feedingstuff is effective in promoting growth of broiler chickens and can enhance the laying performance of hens and reduce levels of cholesterol in the egg.

3
COPPER ABSORPTION AND UPTAKE IN RUMINANTS

The rate of absorbability of dietary copper in ruminants is low and rarely exceeds 10%. It is greatly influenced by dietary molybdenum and copper and also by iron (Suttle, 1991). Citing several authors, Suttle introduces a review of copper interactions as follows: ”The interaction between copper, molybdenum and sulphur in ruminant nutrition is probably unique in its effects on health and production. No other interaction in ruminants is known to have the capacity to swing the nutritional status of its unsuspecting host from deficiency to toxicity while wholly natural foodstuffs are consumed. Sheep consuming a complete diet, low in sulphur and molybdenum and with a modest 12-20 mg/kg DM Cu can succumb to copper toxicity, while others grazing pasture of similar copper content but high in molybdenum and sulphur can give birth to lambs suffering from the copper deficiency disease swayback. Bovine copper deficiency is endemic in regions throughout the world, and a frequent feature is the presence of high molybdenum concentrations in pastures.”

The minimum requirement of absorbable copper has been estimated to be 2-5 mg/day for growing calves and heifers, while a milk-producing adult cow needs at least 5.5 mg Cu/day. Growing lambs require 0.2-0.5 mg of absorbable copper per day, while milk-producing ewes have a minimum requirement of 0.74 mg/day (Agricultural Research Council, 1980). Hartmans and Bosman (1970) note that the availability of copper increases as the herbage matures and that it is higher in hay than in fresh herbage stock. Experimental studies have confirmed that copper in hay and dried grass is more absorbable than that in fresh grass and silage (Suttle, 1980). Average absorbability of copper from hay was 7.3% compared with 4.9% from silage, 2.5% from herbage grazed in July and 1.4% from herbage grazed in September and October. It is suggested that the trend to conserve grass as silage rather than as hay may have contributed to a general decline in the copper status of ruminants in the UK.

The prediction of copper availability to ruminants from fresh grass may be carried out using an equation derived by Suttle (1983), based on copper repletion rates in hypocupremic sheep:

$$Acu = 5.72 - 1.297S - 2.785\log_e Mo + 0.227(Mo \times S)$$

Where Acu is the availability of dietary copper (%)

S is the sulphur concentration in g/kg DM

and Mo is the molybdenum concentration in mg/kg DM

This has only been tested for sulphur concentrations of <4,000 mg/kg and molybdenum concentrations of <6 mg/kg. Equations for the availability of dietary copper in silage and hay show less inhibitory effects of S and Mo (Underwood and Suttle, 1999).

The dietary requirements of ruminants with various levels of molybdenum and sulphur in the diet are shown in Table 8.

Leech and Thornton (1987) found that, under practical farming conditions in six regions of the UK where copper deficiency in cattle was recorded, this equation was frequently inappropriate as both herbage molybdenum and herbage sulphur levels exceeded these limits. Where the equation could be applied the Acu values ranged from 0.19 – 2.77% for pasture herbage harvested from May to September (i.e., the majority of the grazing season). This corresponded to estimated levels of available copper ranging from as little as 0.02 to 0.28 mg/kg DM, well below the minimum dietary requirements. In this study, which involved fifteen farms, three causal factors of copper deficiency were proposed on the basis of soil and herbage analysis:

1. absolute (simple) copper deficiency due to insufficient copper in the pasture to meet the dietary requirements of adult cattle (i.e.,‹ 6.2-7.5 mg/kg DM Cu proposed by Suttle,1983);

2. molybdenum-induced (conditioned) copper deficiency where herbage ranged from 2-9 mg Mo/kg DM and sulphur exceeded 1000 mg S/kg DM;

3. sulphur-induced copper deficiency in two industrialized areas where direct deposition of sulphur onto grassland could be anticipated.

The data in Table 9 illustrate the wide ranges in concentrations in both copper and molybdenum in soils and pasture herbage (sampled on 3 occasions) encountered on farms with bovine hypocupremia. The geometric mean values for copper and molybdenum in soils and herbage from 79 farms were 10 mg Cu/kg DM and 2.6 mg Mo/kg, respectively.

Further studies have shown that different equations for the prediction of copper availability are needed for various types of conserved pasture that differed by several orders of magnitude in copper availability at the same molybdenum and sulphur concentrations (Suttle, 1986). As noted earlier, the availability of copper from hay is greater than that of fresh grass and is usually higher from silage than from fresh grass, though this effect is lost as sulphur concentrations increase (Suttle, 2003).

As noted in Underwood and Suttle (1999), the ability of the feed to meet the copper requirements of ruminants or pose a risk of copper poisoning depends more on the absorbability (A_{cu}) than on the concentration of copper that it contains. A_{cu} varies widely in different foodstuffs as shown in table 11 (taken from Underwood and Suttle, 1999), showing that fresh grass is a poor source of copper, silage and hay are better sources, and *brassicas* and cereals are good sources. These values largely correspond with the statement that the rate of copper absorption from the diet in adult ruminants is <5% (ARC, 1980).

Underwood and Suttle (1999) note that ”Profound effects are predicted for both (molybdenum and sulphur) antagonists within commonly encountered ranges, the earliest, small rises in herbage molybdenum and sulphur having the largest inhibitory effects on Acu; it is arguable that a Cu x S interaction will rarely be fully independent of a molybdenum influence, though the work of Leech (1984) indicated that a sulphur-induced bovine hypocupremia could occur in areas with industrial sulphur pollution. The outcome of the antagonisms varies between forages, sulphur per se having an enhanced influence in silages and both antagonists having reduced influence in hays when compared with fresh grass.”

The low absorbability of copper from the diet may be attributable to digestive processes in the rumen with the production of reactive sulphide from sulphur in the diet, which interacts with copper released during rumen digestion to precipitate copper sulphide, which remains unabsorbed (Suttle, 1974; Bird, 1970). Copper released during post-rumen digestion may become bound to undigested dietary constituents. Suttle (1974b) notes that, as a result, the weaned lamb absorbs less than 10% of the dietary copper. In the presence of molybdenum and sulphur, thiomolybdates are formed which complex copper, reducing absorbability to as low as 1%. Thiomolybdates can also deplete body reserves of copper by interfering with the enterohepatic circulation of copper via biliary secretion (Suttle, 1991).

Underwood and Suttle (1999) tabulate the absorbability of copper (Acu %) in natural foodstuffs of low molybdenum content (<2mg/kg DM) to Scottish Blackface ewes ranging from 1.4-2.5% for grazed herbage, 4.9% for silage, 7.3% for hay, 6.7% for root brassicas, 12.8% for leafy brassicas and 9.1% for cereals. They also note that young milk-fed lambs can absorb 70-85% of the Cu ingested, while weaned lambs absorb less than 10%, as the process of absorption changes and the development of digestive processes in the rumen lead to the production of sulphide and much of the ingested copper may then be precipitated as copper sulphide which remains unabsorbed. As noted above, when the diet is enriched in molybdenum and sulfur, absorption of copper can be as little as 1%.

4
COPPER METABOLISM—TRANSPORT, STORAGE, AND EXCRETION

The subject of copper metabolism in both ruminants and non-ruminants has been covered by several authors, including Davis and Mertz (1987) and Underwood and Suttle (1999) and will not be detailed in this review. Points of particular significance are noted below.

Absorbed copper is transported in the blood to the liver where some is stored, some synthesized to ceruloplasmin and some subject to biliary secretion. Homeostatic control of copper supply is achieved mainly by storage in the liver and biliary secretion (Underwood and Suttle, 1999). This varies between species, with cattle storing less copper in the liver than sheep, and non-ruminants less than ruminants. Liver copper concentrations have been used as an indicator of the copper status of animals; they tend to indicate a deficiency when very low and toxicity when very high (Davis and Mertz, 1987). In newborn lambs liver copper values are lower than in adults and copper concentration continues to increase throughout life. In contrast, the liver copper concentrations of newborn calves are comparable to those found in adult cattle.

Urinary excretion of copper is usually small in all species and unaffected by copper intake, though Suttle (1987) has noted that urinary copper excretion may constitute 25% of the total copper loss in sheep and is higher in young than in old animals. A high proportion of ingested copper appears in the feces. Most of this is unabsorbed copper, but active excretion also occurs via the bowel (Davis and Mertz, 1987).

5
COPPER DISTRIBUTION IN ANIMAL TISSUES AND PRODUCTS

Davis and Mertz (1987) review numerous articles listing copper levels in animal tissues and note that in both cattle and sheep the largest proportion of body copper occurs in the liver as ruminants have a high capacity for hepatic storage. These authors note "Tissues containing relatively high concentrations of copper also include brain, heart and hair, intermediate concentrations – pancreas, skin, muscles, spleen and bone, and low concentrations – pituitary, thyroid, thymus, prostate, ovaries and testes. Liver, blood, spleen, lung, brain and bones are responsive to variations in dietary copper intake, whereas the muscle and heart are much less affected."

Underwood and Suttle (1999) also cover this subject and again note that "widely different copper concentrations are maintained in different organs, with heart and kidney being particularly enriched in sheep (3.1 and 3.6 mg Cu/kg fresh weight)" quoting Grace (1983). Grace also notes whole carcass copper concentrations (excluding liver) to be relatively low at 1.2 mg Cu/kg FW in sheep and 0.8 mg/kg FW in cattle. Chickens have higher carcass copper concentrations – 1.7 mg Cu/kg FW (Suttle, 1987a). The copper content of milk in Sweden has been recorded as 0. 13 mg Cu/kg FW (Sporndly, 1993), in dairy cows milk in the US as 0.15mg Cu/kg FW (and up to 0.2 mg/kg in animals on a high Cu diet) (National Research Council, 2001), and in the UK as 0.05 mg Cu/kg FW. Mean concentrations of copper in animal food products reported in the UK Total Diet Study are shown in Table 10.

A recent detailed review of copper levels in animal tissues has been produced by the European Commission Scientific Committee for Animal Nutrition on the use of copper in feedingstuffs (EC, 2003). The published data has focussed on results from experiments conduced with supplementary copper sulphate and also draw on some of the conclusions from Davis and Mertz (1987). They note "the distribution of total copper in the body varies with species, age and copper status of the animal. In general, levels in new-born animals are maintained throughout the suckling period, followed by a steady fall during growth to the time when adult values are recorded. The main target organ for copper is liver."

Cattle The copper retention in growing cattle is estimated at 0.5 to 1.2 mg Cu/kg body weight (ARC, 1980; CSIRO, 1990, Underwood and Suttle, 1999). Dietary supplementation enhances Cu retention in the liver and to a lesser extent in other edible tissues (Simpson et al., 1981). Muscle content remained independent from copper supply ranging from 3 to 4.2 mg/kg DM (approx. 0.75 to 1.05 mg/kg FW).

Sheep The concentration of copper in the liver of sheep is strongly correlated with copper intake (Dick, 1954) because of the high affinity of sheep liver to copper, which is greater than in other ruminant species, including goats (Zervas *et al.,* 1990). Copper in the sheep's muscle also increases with dietary Cu but to a lesser extent (i.e., dietary Cu at 7 mg/kg DM resulted in liver Cu of 300 mg/kg DM and muscle Cu of 5 mg/kg DM; Zervas *et al.,* 1990).

Pigs As a result of the practice of feeding copper to pigs as a growth promoter, numerous studies have measured copper storage in tissues. Liver copper storage does not increase up to 75 mg/kg total copper in the diet but increases markedly above 120 mg/kg feed, ranging up to nearly 600 mg/kg DM in the liver at a dietary Cu level of 250 mg/kg (Cromwell *et al.,* 1978). Copper content in muscle ranged from 2 to 5 mg/kg DM for diets ranging from 180 to 240 mg/kg Cu (Bradley *et al*., 1983). The authors of this review emphasized that piglets fed high levels of Cu at 240 to 283 mg/kg feed from weaning to 7 to 9 weeks of age store copper up to 505 to 537 mg/kg DM in the liver and up to 130 mg/kg DM in the kidney (Gipp *et al.,* 1973; Hedges and Kornegay, 1973; Shurson *et al.,* 1990).

SCAN (2003), citing a number of studies, noted that although there is no significant increase in copper storage in the liver up to 75 mg/kg of total copper in the diet, copper starts to increase dramatically when dietary copper exceeds 120 mg/kg in the feed, rising to nearly 600 mgCu/kg DM in the liver at a dietary intake of 270 mg/kg DM. However, when copper supplementation is withdrawn during an appropriate period prior to slaughter, copper levels in the liver fall markedly compared with those animals on unsupplemented diets. This is thought to be due to a progressive clearance of copper from the liver coupled with a dilution effect corresponding with an increase in size and weight of the liver.

Poultry Chickens have a high level of copper clearance (Beck, 1961; Aoyagi and Baker, 1993) and levels in liver (17-23 mg/kg DM) and kidney (16-24 mg/kg DM) are only marginally affected by dietary Cu supply. Copper levels in chicken muscle remain low (0.2 – 1.6 mg/kg) (Ledoux *et al*., 1991), and eggs (0.66 to 1.1 mg/kg DM) remain constant over a wide range of dietary Cu (Naber, 1979).

6
CLINICAL AND SUBCLINICAL COPPER DEFICIENCY AND MANIFESTATIONS

Clinical manifestations and pathological and metabolic responses to copper deficiency have been extensively reviewed and are usually associated with serum or plasma copper values of 3-4.5 µmol/l in both sheep and cattle, compared with a normal range of 9-15 µmol/l. Threshold levels of copper in the diet resulting in deficiencies are detailed in Section 3. Principal authors on these topics include Mills, 1983, 1987; Davis and Mertz, 1987; Suttle 1987; Underwood and Suttle, 1999. The main clinical consequences of copper deficiency are:

Anemia – arising as a result of severe, prolonged copper deficiency in most species. Copper is thought to be required for the maintenance of red blood cells. Blood copper values may fall as low as 1.5 – 3.0 µmol/l.

Bone Disorders – copper is essential for bone metabolism, though effects of deficiency vary between species. Osteoporosis and spontaneous bone fractures can occur in cattle and sheep.

Diarrhea (scouring) in cattle – this is most common in molybdenum-induced copper deficiency as in "teart scours" in UK and "peat scours" in New Zealand but can also occur in simple copper deficiency as in "scouring disease" in Holland.

Connective Tissue Defects - combination of bone and connective tissue defects can result in abnormal gait sometimes found in lambs on molybdenum-- rich pastures.

Neonatal Ataxia – a nervous disorder of lambs found in many parts of the world and caused by inhibition of myelin synthesis that in turn leads to degeneration of motor neurons in the brain and spinal cord and having a high mortality rate. Manifestation of the disease is uncoordinated hind leg movement. The disorder has local names including *swayback* in the UK and *lamkruis* in Holland. Lambs may either be affected at birth or several weeks later. It can be prevented by feeding supplementary copper to the ewe.

Depigmentation - this is one of the earliest signs of clinical copper deficiency in all species. Cattle show bleaching of brown hair or greying of black hair especially around the eyes. Black- wooled sheep are sometimes used as diagnostic markers.

Impaired Keratinization – changes in the growth and appearance of the hair and wool in cattle and sheep, with a thin wavy harsh coat common in cattle and a reduction in the quantity and quality of wool characterized by a loss of crimp in sheep.

Infertility – low fertility in cattle grazing copper deficient pastures has been found in several areas; this is associated with delayed or depressed estrus. Infertility has been experimentally produced in sheep associated in some cases with small dead fetuses.

Cardiovascular Disorders - "falling disease" occurring in cattle in Western Australia is due to cardiac lesions associated with copper deficiency which can result in sudden death due to acute heart failure usually after mild exercise or excitement. This disease of cattle has only rarely been reported elsewhere and has never been found in sheep grazing copper-deficient pastures.

Susceptibility to Infection - non-supplemented Scottish Blackface lambs kept under experimental conditions were four times more vulnerable to non-swayback mortality than Welsh Mountain lambs. Unsupplemented lambs showed significantly higher mortality than Cu-supplemented lambs providing clear evidence that decreased resistance to infection is a clinical consequence of Cu deficiency in sheep under field conditions (Woolliams *et al.,* 1986a).

Studies have shown that Welsh lambs irrespective of their dam's breed accumulated higher concentrations of copper in their liver than Blackface lambs, both on a low Cu diet (2.4 mg/kg DM) and a moderately high diet (8 mg/kg DM). The authors suggested the importance of the maternal breed in "determining the susceptibility both of the fetus and the young lamb to problems associated with Cu deficiency (Wiener *et al*., 1984a and b). Later experimental studies showed that unsupplemented Scottish Blackface lambs grazing improved hill pastures had lower concentrations of Cu in plasma and lower superoxide dismutase activity than Welsh mountain lambs, confirming that breed was an important determinant of copper deficiency (Woolliams *et al*., 1986b).

Growth retardation may result from copper deprivation in ruminants even in the absence of clinical manifestations. Under field conditions this is frequently associated with grazing pasture of low Cu:Mo ratio (<3.0 and often <1.0) (Underwood and Suttle, 1999). Copper supplementation of young cattle with low blood copper values (hypocupremia) was found to increase the live-weight gain from 10% to 70%, representing mean herd increases due to copper of 30 to 70 lbs per animal over a 6-- month grazing season (Thornton et al., 1972) on herbage pasture of normal copper content (7-14 mg/kg DM) and with elevated molybdenum content of 3-20 mg/kg DM. This provides a clear example of sub-clinical copper deficiency, which will respond to treatment.

It is likely that this sub-clinical deficiency will be widespread and largely unrecognised under practical farming conditions and may result in unrecognized economic losses within the European Union.

Copper deprivation does not cause problems in pigs or poultry fed natural feedstuffs (Underwood and Suttle, 1999).

7

CLINICAL AND SUBCLINICAL MANIFESTATIONS OF COPPER TOXICITY

Sheep are the most susceptible to copper toxicosis and are extremely intolerant of copper excess. The clinical features and biochemical and metabolic changes of copper toxicosis have been reviewed by Bremner (1998). In sheep, toxicosis develops as a two-stage process at intakes as low as 25 mg/kg (Bremner, 1979). In the first stage, copper accumulates in the liver sometimes up to 1000 mg/kg DM, with normal food intake and growth rate. The second phase then occurs suddenly, a hemolytic crisis with massive amounts of copper released from the liver into the bloodstream. This results in the rupture of red blood cells leading to severe anemia and jaundice, which is rapidly fatal. It is most commonly found in housed lambs, milk sheep and pedigree rams receiving large amounts of concentrates (Underwood and Suttle, 1999).

Chronic copper poisoning rarely occurs in grazing sheep under natural conditions except in susceptible breeds such as the North Ronaldsay and Texel. Genetic control of the sheep's copper status has been proposed as the causatory factor backed up with experimental studies. Indeed, it has been shown that there are large breed differences in the susceptibility to copper poisoning. Of common breeds crossed with Scottish Blackfaced females, liver copper storage (leading to toxicity) was greatest in Texel crosses followed by Suffolk crossed lambs, with East Friesland, Finnish Landrace and Scottish Blackface lower. Later trials with housed lambs showed consistently higher liver copper concentrations in Texel than in Suffolk lambs weaned onto a common complete diet containing 6.1mgCu/kg DM. Texel-cross lambs retain more than twice as much Cu in the liver than Blackface lambs (Woolliams *et al*., 1982). The genetic difference would seem to be due to the net retention of Cu from the diet rather than the partition of absorbed Cu (Wiener et al. 1978). In some breeds of sheep, in particular the Texel and Texel-cross, continued ingestion of copper at levels as low as 12 mg/kg DM can result in copper toxicosis (National Research Council, 1977; Woolliams *et al*., 1982). Underwood and Suttle (1999) cite Hartmans (1975) who notes that "complete sheep diets containing over 15 mg Cu/kg air-dried feed can cause copper poisoning." They stress that "it is difficult for feed compounders to keep values consistently below this limit, particularly when the feeds have been stored or processed in contact with copper-supplemented pig rations or when copper-rich constituents such as certain distillery by-products or palm-kernel cake are used." Underwood and Suttle (1999) note that "in parts of Australia and elsewhere, normal copper intakes together with very low levels of molybdenum (0.1 – 0.2 mg/kg DM) can cause copper poisoning." This has been found when sheep grazed on subterraneum clover, which may contain 10-15 mg Cu/kg DM but very little molybdenum. Davis and Mertz (1987) record that "sheep consuming excessive amounts of copper over a period of weeks to months with low molybdenum intake usually do not show toxic symptoms until the liver concentration of copper exceeds 150 µg/g wet weight. When this level of copper in the liver has been reached, the animal becomes listless, weak, tremulous, and anorexic. Hemoglobinemia, hemoglobinuria and icterus develop and mortality is often >75%." It is now considered that this 150 µg/g threshold is too low and that this is the level at which sub-clinical damage may occur. Clinical signs may develop over a wide range of liver copper concentrations of 250-1000 µg/g wet weight (Suttle, personal communication).

In the UK, during the period 1970-1990, the number of reported cases of copper poisoning in sheep rose to about 100 per year, due partly to the growing popularity of susceptible breeds, such as the Texel. Feeding trials on housed lambs showed twice copper accretion to be far greater in the Texel than in Charollais and Suffolk lambs and it was suggested that the continued hepatic Cu accretion in the Texel may reflect a breed-specific inability to cope with Cu overload (Suttle, Lewis and Small, 2002). These authors conclude that the current EC limit for copper in the diet of susceptible breeds of sheep of 17 mg Cu/kg DM is too high.

Indeed, feeding trials with cross-bred lambs under experimental conditions showed that the Texel cross (with Scottish Blackface ewes) responded to copper supplementation ($CuSO_4$ $5H_20$) giving 12 mg/kg Cu DM in the diet, with a liver copper level twice that of the Blackface lamb. Widespread anomalies in clinical biochemistry appear with a diet containing 20 mg Cu per kg DM and similar anomalies in some lambs with a diet of 12 mg Cu per kg DM emphasise the risk of

Cu toxicity in intensively fed lambs (Woolliams *et al.,* 1982). These results implied large breed differences in the susceptibility to copper poisoning, some breeds being at risk when given diets containing 12 mg Cu per kg DM for long periods. However, it is important to note that these feeding trials were based on diets supplemented with the salt $CuSO_4$, where the solubility and bioavailability would be considerably greater than that of copper in ingested pasture herbage and in accidentally ingested soil. These results must therefore be viewed with caution when attempting to set limits on copper in ovine diets.

It may be concluded that the increased use of more susceptible European breeds such as the Texel will increase the risk of copper toxicity in sheep (MacPherson et al., 1997; Woolliams *et al.,* 1982). Subclinical toxicity has been recorded in Suffolk and Texel-cross lambs fed diets containing 12 mg Cu/kg DM, a level often exceeded in commercial foodstuffs (Woolliams *et al*., 1982). North Ronaldsay sheep fed on a diet of terrestrial herbage were found to succumb to copper poisoning, despite a relatively high level of molybdenum in the diet (MacLachlan and Johnston, 1982). These animals are normally confined to a diet of seaweed with an average Cu content of 2.15 mg/kg DM and Mo content of 0.18 mg/kg DM; the experimental sheep were fed herbage and hay with an average Cu content of 2.15 mg/kg DM and Mo content of 1.46 mg/kg DM. Other sources of copper poisoning are: the use of copper sulphate in footbaths and spraying areas against snails which transmit fluke; copper-containing pesticides and fungicides in orchards where sheep graze; industrial copper waste in rivers and streams; slurry spreading from pig units (Kerr and McGavin, 1991); and poultry litter used as fertilizer or feed (Henderson, 1990). However, EEC legislation (Directive 86/278/EEC) imposes limit values for the addition of sewage sludge to soil of 12 kgCu/ha/y based on a 10-year average with a maximum soil concentration of 50-140 mgCu/kg DM. If these limit values were applied to animal manure, disposal of pig slurry and poultry litter onto agricultural land will not impose any adverse environmental effects (SCAN, 2003).

Cattle Chronic copper poisoning is less likely to occur in cattle than in sheep as they are able to excrete excess copper via the bile (Suttle, 1995). Some incidents of chronic copper poisoning have occurred as a result of pollution from base-metal mining activities in South Africa (Gunnow et al., 1991). Cases are not usually found under natural grazing conditions and there are no records of differences in susceptibility between breeds. There is however a recent report of chronic copper poisoning in grazing cattle in the UK (Livesey et al., 2002). Calves are susceptible to copper poisoning prior to weaning when fed copper-rich milk substitutes. Acute copper poisoning in cattle can result from excessive amounts by injection.

Pigs and Poultry Pigs and poultry appear to be comparatively tolerant of high dietary copper which is fed to both these species as a growth promoter in concentrations as high as 250 mg/kg. Diets containing 500mg/kg Cu will slow growth in the former and reduce egg production in the latter.

8

OCCURRENCE OF COPPER DEFICIENCY IN THE UK AND ELSEWHERE IN THE EU

Underwood (1966) noted “Copper deficiency occurs in grazing stock in many areas in every continent under a wide range of soil and climatic conditions.” Uncomplicated or simple copper deficiency in sheep and cattle is relatively uncommon and is associated with low levels of copper in soils and/or pasture herbage. This has been reported in New Zealand on pastures with a mean copper content of 3 mg/kg Cu DM, and sometimes as low as 2 in Australia and Florida. As noted in Section 2 of this report, pastures with less than 5 mg/kg DM are rarely found in Britain. Studies at Imperial College over a wide range of soil parent materials and taking into account seasonal differences in copper herbage content have only recorded a few instances of a pasture copper content of less than 5 mg/kg out of several hundred observations. It thus seems unlikely that simple copper deficiency is a problem in the UK. It is unlikely to be a problem elsewhere in the EU.

Underwood (1966) also notes “Conditioned copper deficiency occurs in sheep, cattle and goats over considerable areas in widely separated parts of the world.”

Swayback (enzootic ataxia) in sheep, a Cu-responsive disorder, is found under natural farming conditions and is thought to result from either dietary molybdenum or iron antagonism. Elevated molybdenum distribution in both soil and pasture is related to the presence of specific geological parent materials as shown in the geochemical map in Plate 2. In general, molybdenum in herbage increases with soil molybdenum content (see Figure 9) though it is influenced by soil pH, increasing over the range pH 4-8. Thus dietary Mo intake and its influence on Cu availability to the animal is related both to the presence of Mo in the soil and to soil pH.

Linked to the occurrence of swayback, accidental ingestion of soil, which may account for some 20 percent or more of the dry matter intake by sheep in winter months has been proposed under experimental conditions to significantly reduce the availability of copper to sheep and it has been shown that Fe released from ingested soil in the rumen may act as a copper antagonist.

The geographic distribution of farms on which swayback occurs in lambs in the UK and elsewhere in Europe has not as yet been mapped but its occurrence was thought to be widespread where precautionary supplementation with copper had not taken place. The increased occurrence of this disorder in certain years was associated with mild winters when soil ingestion was higher in the absence of snow cover. However, recent statistics from the Veterinary Laboratories Agency have shown a steady decline in swayback incidence and the disease is now considered to be rare in the UK. This may reflect a waning antagonism from pasture sulphur as industrial emissions of sulphur have fallen (Suttle, 2002).

As indicated in earlier sections, copper deficiency in cattle, both clinical hypocuprosis and sub-clinical hypocupremia, is usually associated with elevated Mo in the diet resulting in a conditioned deficiency. The widespread distribution of cattle with low blood copper (hypocupremia) in England is clearly shown in Plate 3 in which over 1700 herds were found to be copper deficient over the period 1977 – 1980, many of which were located in areas with molybdeniferous soils (Leech *et al*., 1982), in turn found in areas underlain by marine black shales containing elevated levels of Mo shown in the geochemical map (Plate 3).

Characteristic clinical signs of Cu deficiency were thought to develop annually in about 0.9% of the UK cattle population (MAFF, 1982). If the above applied worldwide, Mills (1985) estimated that "the approximate magnitude of the problem could be that 11.3 x 106 clinically identifiable cases of severe Cu deficiency develop in cattle annually". Numbers affected in the EU are not known. However, the prevalence of both bovine and ovine hypocuprosis has fallen over the past 15 years in the UK, perhaps reflecting a decline in industrial emissions of sulphur, a recognized antagonist (Suttle, 2002).

The extent of suspect high molybdenum land in England and Wales alone is now thought to exceed 400,000 hectares. Similar marine black shales outcrop in many parts of the world and in several countries in Europe. The degree to which molybdenum in these rocks and their associated soils influences the copper status of grazing animals is as yet unknown and must surely be a high research priority for the future.

9

OCCURRENCES OF COPPER TOXICITY IN THE UK AND ELSEWHERE IN THE EU

As noted in Section 7, copper toxicity in sheep and cattle is relatively rare and is usually associated with housed animals on artificial diets or those exposed to industrial pollution. Some breeds of European sheep including the Texel and North Ronaldsay are particularly susceptible and may suffer from copper toxicosis under natural grazing conditions. As noted in Section 7, the growing popularity of susceptible sheep breeds such as the Texel in the UK resulted in the number of reported cases of copper poisoning rising to around 100 incidents per year by 1990. However, this is a very small number out of an estimated UK sheep population of 19 million. The numbers of incidents are thought to have declined in subsequent years (Suttle, personal communication), though the reason for this is not known.

The Texel sheep originates from the island of Texel, one of the north-western islands off Holland where it has been known since Roman times. About 1933 the Texel was introduced to France and has since become established particularly in the northern provinces. The first Texels were imported to the United Kingdom from Holland in the 1970's. This breed has primarily been developed for meat. It is hardy and exceptionally thrifty. The breed's harsh native environment has led to the development of a sheep that thrives on poor pastures and requires only modest amounts of feed in the run-up to lambing and whilst suckling. Texels are now well known in Europe and the continents of Africa and South America as a provider of high-quality carcass. It transfers these qualities to its progeny when crossed with other breeds. By 1986 Texel-sired lambs accounted for 18% of all lambs slaughtered in the UK. In 2002 it was estimated that this had increased to over 30% of all lambs slaughtered (www.texel.co.uk , 2003), or about 970,000 lambs. Today in the UK 2,200 Texel flock masters notify births of around 56,000 lambs per year with 25,900 females and 1,400 males going into full pedigree registration. If mortality rates due to copper poisoning continue to occur at around 100 per year in the UK and all of these are Texel or Texel-cross lambs, the mortality rate for this the most susceptible breed remains very low at c 0.01%.

The total Dutch sheep population is currently estimated at 1.9 million spread over some 25,000 farms. The Texel breed because of its outstanding lean meat quality has become increasingly popular among Dutch sheep farmers. The Texel ram is used for pure Texel breeding purposes and as a sire in the production of lambs for slaughter in various crossbreeding programs The Dutch flock currently consist of 70% purebred Texel and 25% crossbred.

It is also considered that Texel cross lambs will be more susceptible to copper toxicity than other crosses though they are not usually crossed with the other susceptible breeds, the Suffolk and the Charollais.

The North Ronaldsay breed is mainly restricted to the Orkney Islands off the coast of Scotland though some may also be found in rare breed collections elsewhere. On the island of North Ronaldsay, they are mostly confined to a diet of seaweed with a very low copper content (1-3 mg Cu/kg DM) and are susceptible to copper poisoning when given a diet of terrestrial herbage of normal copper content (MacLachan and Johnstone, 1982). The numbers of this breed are too small and its occurrence too restricted to warrant further comment.

While clinical copper toxicosis resulting in a hemolytic crisis and subsequent death may be expected in susceptible breeds and their crosses when liver copper concentrations reach 1000 mg/kg DM, there is now evidence that liver damage and poor pregnancy outcome can arise at liver copper concentrations as low as 500 mg/kg DM. This liver damage can be detected by blood tests which show higher than normal levels of plasma aspartate amino-transferase that reflect enzyme leakage from damaged liver cells (Woolliams et al., 1982; Suttle, 1995). This provides the first clear evidence of a sub-clinical copper toxicity and raises the question as to whether the current EC limit for Cu in ovine diets of 17 mg Cu per kg DM is too high (Suttle, personal communication). The extent of this sub-clinical copper toxicity is at present unknown.

Derivation of Critical values for Copper in Soils in relation to both Deficiency and Toxicity

a) **Copper Deficiency**

Assessment of the extent to which shortages of minerals, including copper, in the diet limit life for stock production under practical farming conditions is subject to 5 sources of uncertainty (Underwood and Suttle, 1999):

Uncertainty regarding the effective mineral supply, i.e., amounts ingested, absorbed and utilized.
Uncertainty regarding the minimal demands of the livestock species, given the universal ability to conserve losses and redistribute what is retained.
Uncertainty surrounding the abrupt changes which physiological and environmental factors can cause in demand.
Uncertainty regarding the rate-limiting metabolic pathway when supply fails to meet demand.
Uncertainty arising from the poor correlations between conventional clinical biochemistry criteria and the activity of the rate-limiting pathways.

As noted in Section 8, simple or uncomplicated copper deficiency in grazing sheep and cattle is uncommon and is not likely to be a problem in the UK or elsewhere in the EU. The few cases reported worldwide have been associated with herbage copper concentrations of 3 mg/kg DM or less in Australia, New Zealand and Florida. In the UK field studies reported in previous sections (Leech, 1987; Russell, 1987) (see Figures 3 and 4b), no herbage copper levels of 5 mg/kg or less were found.

Thus, although simple copper deficiency in cattle and sheep is unlikely to occur under grazing conditions, it is perhaps useful to estimate critical soil copper levels on the basis of the recommendation of 10 mg Cu/kg DM dietary requirement (ARC, 1980; INRA,1989; GfE, 2001) as reported in SCAN (2003) and the revised upper value estimated by Suttle of 7.5 mg Cu/kg DM (neither of these would seem to take into account the potential antagonistic effect of dietary molybdenum and sulphur). Using the regression line from Russell (1987) -$y = 0.2x + 6.2$ $R2 = 0.6$, where y = the concentration of Cu in unwashed pasture herbage (mgCu/kg DM) and x = the concentration of Cu in the soil (mgCu/kg DM) (see Figure 4b), these would represent total soil copper concentrations of 29 mg/kg and 9 mg/kg respectively. However, this is a weak, though significant, relationship and the lower value is derived by extrapolation outside the levels of soil and herbage copper tested. In the author's opinion, these values should be regarded as tentative and should be treated with caution.

Pasture herbage growing in soils with less copper could in theory give rise to deficiency in grazing ruminants. In the opinion of the authors the latter value of 9 mg/kg would seem to be more appropriate and it is recommended that, as a precautionary measure, a total soil copper concentration of 10 mg/kg should be considered a critical value. The majority of the British soils studies exceeded this value as illustrated by the data in Figure 10 (Brebner, 1987). However, because of the interactive effect of molybdenum and sulphur on copper availability in the diet and because there is often a poor relationship between soil and herbage copper levels, it is concluded that soil copper data alone must be of very limited value in predicting the likelihood of copper deficiency disorders in ruminants. It is proposed that the above critical value can only be regarded as a guideline and must be considered in relation to factors that may influence the bioavailability of copper in the diet including pasture Mo and S and amounts of soil ingested.

In parallel, it is perhaps useful to record that, in relation to plant growth, assessment of the risk of copper deficiency based on concentrations of total copper in the soil is of limited value, since availability for uptake is of major importance. Nonetheless a "critical" total soil copper concentration of 5 mg Cu/kg DM has been set in France and 10mg/kg for mineral soils and 30 mg/kg for organic soils in some other countries (Shorrocks and Alloway, 1985, cited in Landner and Linderstrom, 1999).

Conditioned copper deficiency in both sheep and cattle is common in the UK and is likely to be common elsewhere in Europe. This is usually associated with excess molybdenum in the diet at values ranging from 2 to 25 mg Mo/kg DM. The source of the molybdenum is mostly marine black shale underlying bedrock, though some occurrences are found in estuarine and coastal alluvium (Thornton, 1968). It is difficult to derive a critical level of molybdenum in soil at which a herbage concentration of 2 mg/kg DM is to be expected, as availability and uptake of soil molybdenum into the plant is markedly influenced by soil pH, which ranges widely in the UK soils studied (pH 3.9 to 8.1; Brebner, 1987). Under managed UK pasture conditions, the pH of grassland soil would normally range from 6.0 to 7.5 depending on the nature of the parent material and liming policy. Within this range, a soil molybdenum concentration of 4 mg/kg or more was found to support pasture of 3 to 7 mg Mo/kg DM. This is confirmed by the work of Leech (1987) (see Figure 9). Under more acid upland and moorland conditions, the uptake of Mo would be less. It may be concluded that, as a general rule, a total soil molybdenum content of 4 mg/kg could be regarded as a level at and above which copper deficiency is likely to be found in grazing cattle and sheep. A sufficient copper supply may be expected when the Cu:Mo ratio in the diet is greater than 3.0.

Marine black shales are also found in France, Germany, Austria, Italy, Spain, Switzerland, Norway and Turkey, though the areas of molybdenum-rich soils associated with these are not documented, nor are livestock-related problems.

It is also recognized that sulphur, zinc and cadmium can induce copper deficiency in ruminants, usually under conditions of industrial contamination. As herbage values are likely to reflect atmospheric deposition as well as uptake from the soil, it is not possible to establish critical levels of these elements in soils. The decline in atmospheric inputs of sulphur resulting from pollution control measures may possibly account for the decline in both bovine and ovine copper deficiency over the past 15 years (Suttle, 2002).

In winter months when the rate of soil ingestion by sheep can reach 20 percent of DM intake, iron in the ingested soil can also act as a copper antagonist. Critical levels of iron have not been calculated as factors controlling its forms and bioaccessibility is not yet known.

b) **Copper Toxicity**

Because sheep are more at risk from copper toxicity than cattle, the following section is focused specifically on sheep. The EC limit for copper in the ovine diets of 17mg/kg DM is rarely found in pasture herbage. Studies in the UK have shown a normal range of 6 to 14 mg Cu/kg DM in pasture herbage grazed by cattle and sheep (Thomson, 1971, Leech, 1987; Russell, 1987).

Copper toxicosis in Texel and Texel-cross sheep may occur at dietary copper levels as low as 12 mg/kg DM, though this relatively low value relates to housed lambs fed a pelleted diet with hay that had been supplemented with copper as copper sulphate, where the bioavailability of copper may have exceeded that in pasture herbage. 12 mgCu/kg DM may be regarded as the high end of the normal range of copper concentrations in pasture herbage.

Studies attempting to relate copper in herbage dry matter with soil copper have produced conflicting results, with some showing no significant relationship (Thomson, 1971; Leech, 1987) (see Figures 1 and 2) and others showing herbage copper to increase with soil content (Russell, 1987). If the equation derived from the last study is used for a basis of comparison, the EC limit value of 17 mgCu/kg DM would relate to a total soil copper value of 60 mg/kg (see Figure 4b), though this is based on an extrapolation beyond the range of soil and herbage Cu values recorded in this study. This is well in excess of the median value reported for agricultural soils covering a wide range of parent materials in the UK (Brebner, 1987; see Figure 10), and the median value of 18 mg Cu/kg determined for 5692 surface soils in the soil geochemical survey of England and Wales (McGrath and Loveland, 1991). This latter survey showed 5% of the soil sampled, representing areas totalling approximately 2120 km^2, to exceed 60 mg Cu/kg. This value is appreciably higher than the average 90^{th} percentile concentration for copper in European agricultural soils and indeed exceeds the highest 90^{th} percentile (PEC) value listed (see Table 3). On the other hand, susceptible breeds of sheep fed a diet with 12 mgCu/kg DM may be adversely affected if exposed for long. It would not be appropriate to relate this level to total soil copper content as this value was derived under experimental housed conditions where copper was supplemented in the diet as a copper salt and bio availability may well have exceeded that of copper in herbage.

It should be recorded that the limit value for copper in soils to which sewage sludge is to be applied has been set under the EU Directive (86/278 EEC Directive) as 50-140 mg Cu/kg DM, while a provisional lower limits of 40 mg/kg has been agreed in Sweden and 60mg/kg in Germany.

10

CONCLUSIONS

Due to the limited knowledge and complex nature of factors controlling both copper bioavailability in soils and plant uptake and the importance of other dietary constituents including molybdenum, sulphur and iron, on copper absorption and utilization by the animal, it is not possible to provide firm threshold values of total soil copper concentration for deficiency and excess in grazing ruminants. However, on the basis of the data and studies reviewed in the previous sections, a range of 10-60 mgCu/kg DM in the soil may usually be regarded as adequate and in the absence of elevated molybdenum and/or sulphur, could normally be expected to provide a sufficiency and not an excess of copper to grazing cattle and sheep.

The development of reliable tests for "plant available" soil copper will in due course provide firmer data on which to assess critical levels. However, dietary interactions between copper, molybdenum and sulphur will always have an overriding influence on copper absorptability by the ruminant.

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Table 1
Typical copper concentrations in selected rock types of the earths crust (mg/kg)
after Thornton (1995) and Garrett (1998)

Rock type	**Copper concentration**	
	Range	**Average**
Igneous rocks		
Mafic, intermediate (e.g., basalt)	30 – 160	90
Intermediate, felsic (e.g., granite)	4-30	15
Sedimentary rocks		
Black shale	20-200	70
Shale	18-120	50
Sandstone	<1-30	15
Limestone	<1-20	4

Table 2
Typical total copper concentrations (mg/kg DM) found in soils on various parent materials (classified mainly by texture but also by approximate FAO/UNESCO soil group)
After Thornton (1979)

Soil Type	Classification	Copper content mg/kg
Peats	Histosols	15 - 40
Sandy soils on drift	Arenosols,Podzols	2 – 10
Sandy soils on granite	Arenosols,Podzols	10
Silty caly loams on shales	Gleysols, Cambisols	10
Clay on clay rocks	Mainly	10 – 27
Loam on basalt rock	Cambisols and others	40 – 150
Humic loams on chalk	Rendzinas	7 – 28

Table 3
Average copper contents and textures of soils derived from individual beds of the Old Red Sandstone formation (Upper Devonian) in South Wales.
Taken from Wood (1975)

Soil	Course Sand	Fine Sand	Silt and Clay	(µg/g)
Raglan Marl	14	50	3	28
St. Maughans Group	13	60	27	21
Brownstone	66	14	20	18
Tintern Sandstones	51	25	24	13

Table 4
Overview of Cu-PEC values in agricultural soils for different European countries
(Taken from Heijerick and Van Sprang, 2003).

	Agricultural soils	
	50th percentile (median) mg Cu/kg DW	**90th percentile (ambient) mg Cu/kg DW**
BELGIUM – De Temmerman et al. (2003)	10.1 (8.9 – 11)	16.1 (12.2 – 19)
DENMARK – EC-data set (2000)	7.8	
THE NETHERLANDS – ICA-data set	13.5	34.2
FRANCE – INRA/ASPIPET data set	13.8 – 14.9	28.0 – 30.8
FRANCE – EC-data set (2000)	14.4	31.2
GERMANY – EC-data set (2000)	14.4	33.5
GERMANY – LABO-data set	13 (4 – 33)	21.8 (8 – 55.4)
ITALY – ANPA-data set	33.1	59.1
SWEDEN – Eriksson et al. (1997)	12.0 (8 – 29)	21.6 (14 – 41)
Average for Europe + range	**14.7 (7.8 – 33.1)**	**30.7 16.1 – 59.1**

Note: different extraction techniques have been used in different countries; thus the data may not be strictly comparable.

Table 5

Copper in some feed materials (mg/kg DM)

Feed materials	Copper content (Range)
Alfalfa hay	7.3
Barley	3.5-7
Grass hay	9.0
Linseed	12-16
Maize	1.9-3.3
Maize silage	7.6
Oats	2.8-5
Rye	4-6
Sorghum	2.7-10
Soybean whole	12-15
Straw barley	1.7-5
Straw wheat	7

INRA= Institute National de la Recherche Agronomique (France)

DLG= Deutsche Landwirtschafts-Gesellschaft (Germany)

ACV= Afnemers Controle op Veevoeder (The Netherlands)

ADAS= Agricultural and Advisory Service (UK)

NRC= National Research Council (USA)

Table 6

Concentration of copper in animal feedstuff
Adapted from Davis and Mertz (1987) Underwood and Suttle (1999) and Kabata-Pendias (2001) and references within

Feed	**Cu concentration mg/kg dry weight Range**	
	White Clover	12.7-18.4
	Soybean	8.0-11.5
	Maize	1.7-5.0
	Wheat	3.0-3.7
	Oat	7.2-11.0
	Wheat	6.3-13.9
	Oat	6.3-11.0
	Corn	3.3-22.3
	Grasses	1.1-21.0
	Ryegrass	5.6-15.0
	Clover	2.0-29.0
	Soybean	9.0-22.3
	Legumes and oil seed	15-35
	Palm kernal cake	25-40
	Meat and fish meal	5-15
	Liver meal	80-100
Protein supple-ments	Leguminous seeds and oilseed meals	15-30

Table 7
The copper composition of feedstuffs most commonly fed to dairy cows
(National Research Council, 2001)

Feedstuff		Cu concentration Mean mg/kg DM	N
Alfalfa	Meal	9	110
Barley	Grain	6	241
	Malt	9	31
	Silage	7	291
Beet, Sugar	Dried pulp	11	152
Corn	Grain (dry)	3	-
	Grain and Cob	3	54
	Silage 32-38% DM	6	192
Grass-cool season	Pasture	10	13
	Hay	9	1,321
	Silage	9	879
Legumes-forage	Pasture, intensively managed	10	20
	Hay	9	4,242
	Silage	10	2,729
Linseed	Meal	19	5
Molasses	Beet sugar	22	7
	Sugar cane	59	11
Oats	Grain	8	183
	Hay	8	403
	Silage	9	212
Sorghum (grain dry)		6	64
Soybean	Hulls	10	72
	Seeds	13	27
	Silage	14	9
Sunflower (meal)		32	12

Wheat	Bran	11	22
	Grain	5	56
	Hay	8	110
	Silage	7	322
	Straw	6	120

Table 8
Dietary copper requirements of ruminants with various levels of Mo and S in the diet
(Reference MAFF, 1982 & Leech, 1984)

	Total Cu requirement mg/kg dry weight			
	Low Mo Low S	High Mo Low S	Low Mo High S	High Mo High S
Beef Cattle	11	14	20	36
Dairy Cattle	9	12	17	30
Suckler Cows	7	10	14	25
Pregnant Ewes	8	10	14	26
Growing Lambs	5	7	10	18

Table 9
Concentration of copper and molybdenum in soil and plants in areas identified to have incidence of bovine hypocupremia (After Leech, 1984)

	N	Median	90^{th} percentile	Range
Cu in soil				
Brayford	14	22.5	32	3-32
Glastonbury	14	45	65	19-65
Stow-on-the-Wold	9	16	29	10-29
Atherstone	14	17.5	53	10-58
Onecote	15	28	66	16-69
Masham	12	12	20	7-23
All data	78	20	54	3-69
Mo in soil				
Brayford	14	1.2	1.8	0.9-8.7
Glastonbury	14	10.4	30.2	4.1-41.3
Stow-on-the-Wold	9	1.9	4.0	1.7-6.2
Atherstone	14	1.8	3.3	0.7-8.4
Onecote	14	5.6	12.2	0.7-17.6
Masham	12	1.6	1.8	0.8-2..4
All data	77	1.9	10.4	0.7-41.3
Cu in plants				
Brayford	14	10.6	12.7	6.6-13.7
Glastonbury	15	10.4	13.3	6.5-13.6
Stow-on-the-Wold	9	8.6	10.1	6.5-10.1
Atherstone	14	11.0	13.1	7.4-13.8
Onecote	15	10.8	13.3	7.8-13.5
Masham	12	9.6	10.9	6.7-11.1
All data	79	10.5	12.6	6.5-13.8
Mo in plants				
Brayford	14	1.3	2.0	1.1-2.4
Glastonbury	15	6.6	13.8	2.7-37.8
Stow-on-the-Wold	9	1.5	1.9	1.2-2.1
Atherstone	14	1.7	2.5	1.3-2.7
Onecote	15	4.6	5.6	2.3-9.5

Masham	12	1.9	2.7	1.3-3.8
All data	79	2.2	6.6	1.1-37.8

Table 10

The mean concentration of copper in food (mg/kg fresh weight)

(Food Standards Agency, 2003)

Food	Mean concentration mg/kg fresh weight
Meat Products	1.4
Offal	50
Carcass Meat	1.3
Eggs	0.62
Milk	0.05
Dairy Produce	0.48

Table 11

Estimates of the absorbability of copper (A_{Cu},%) in natural foodstuffs of low molybdenum content (<2mg kg^{-1}DM) to Scottish Blackface ewes.

(From Underwood and Suttle, 1999)

Feed	**A_{Cu} (mean ± SD)**	**Number of estimates**
Grazed herbage (July)	2.5 ± 1.09	7
Grazed herbage (Sept/Oct	1.4 ± 0.86	6
Silage	4.9 ± 3.2	7
Hay	7.3 ± 1.8	5
Root brassicas	6.7 ± 0.9	2
Cereals	9.1 ± 0.97	3
Leafy brassicas	12.8 ± 3.2	5

SD, standard deviation

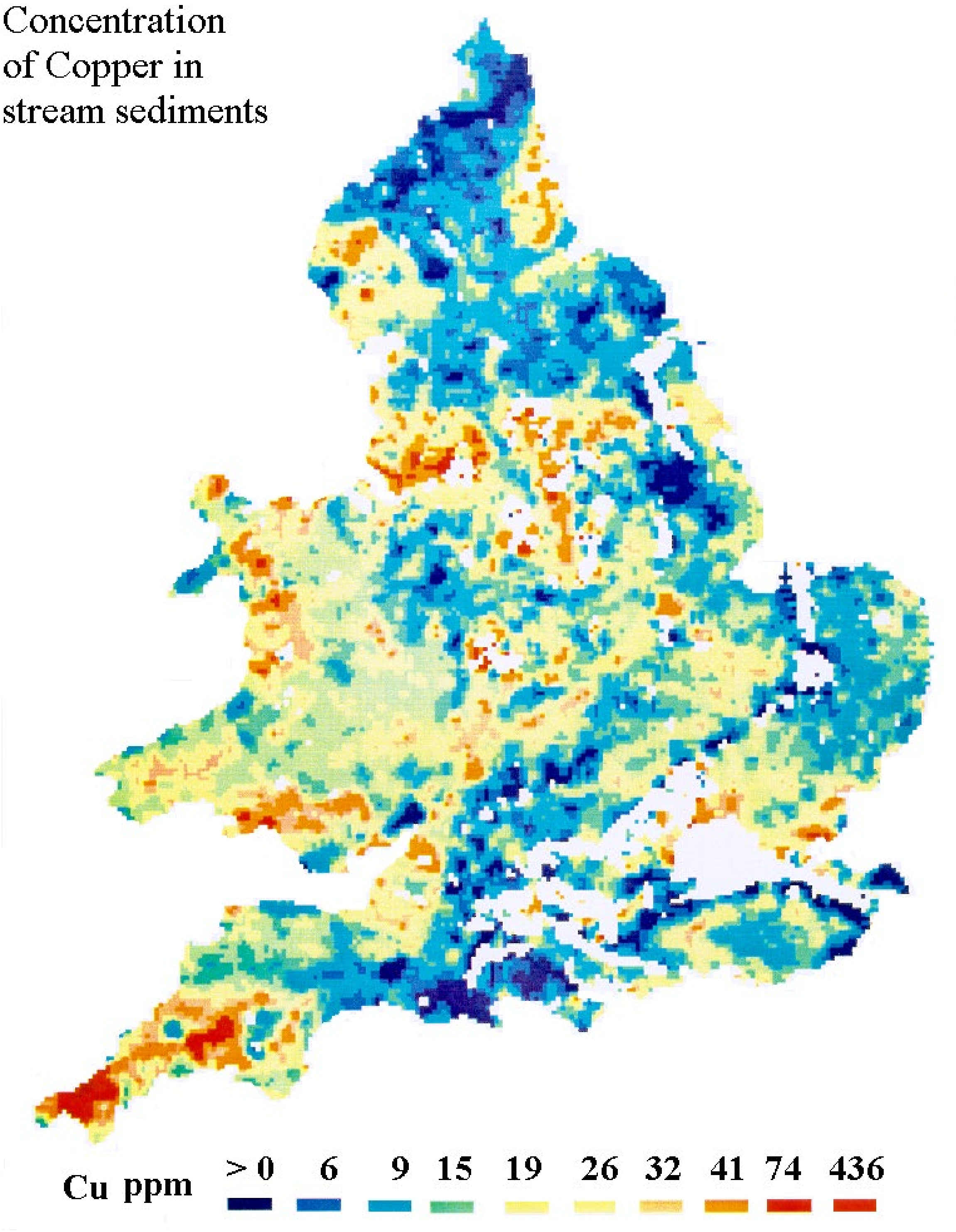


Plate 1
Distribution of copper in England and Wales
The *Wolfson Geochemical Atlas of England and Wales* (Webb *et al.*, 1978)

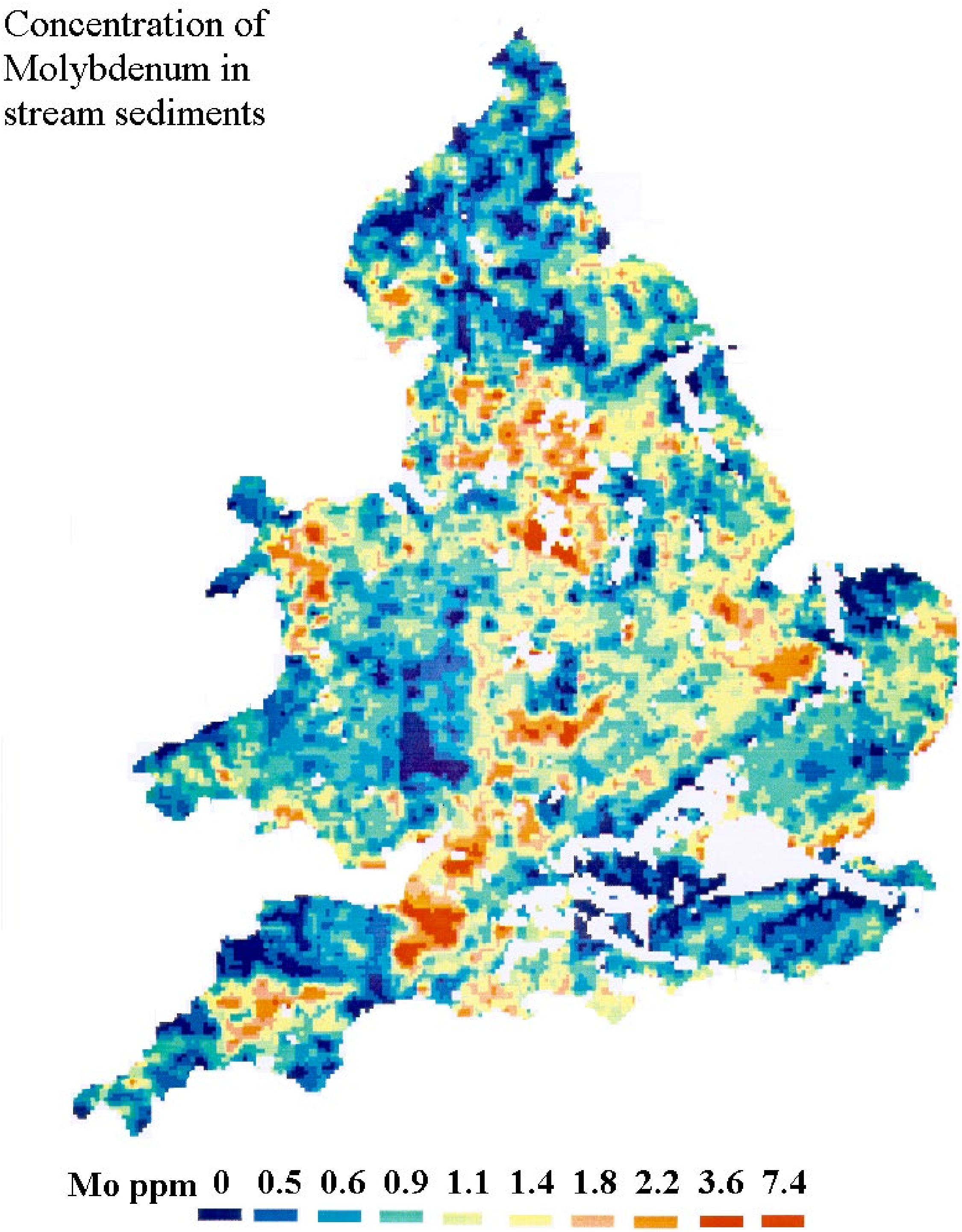


Plate 2
Distribution of molybdenum in England and Wales
The *Wolfson Geochemical Atlas of England and Wales* (Webb *et al.*, 1978)

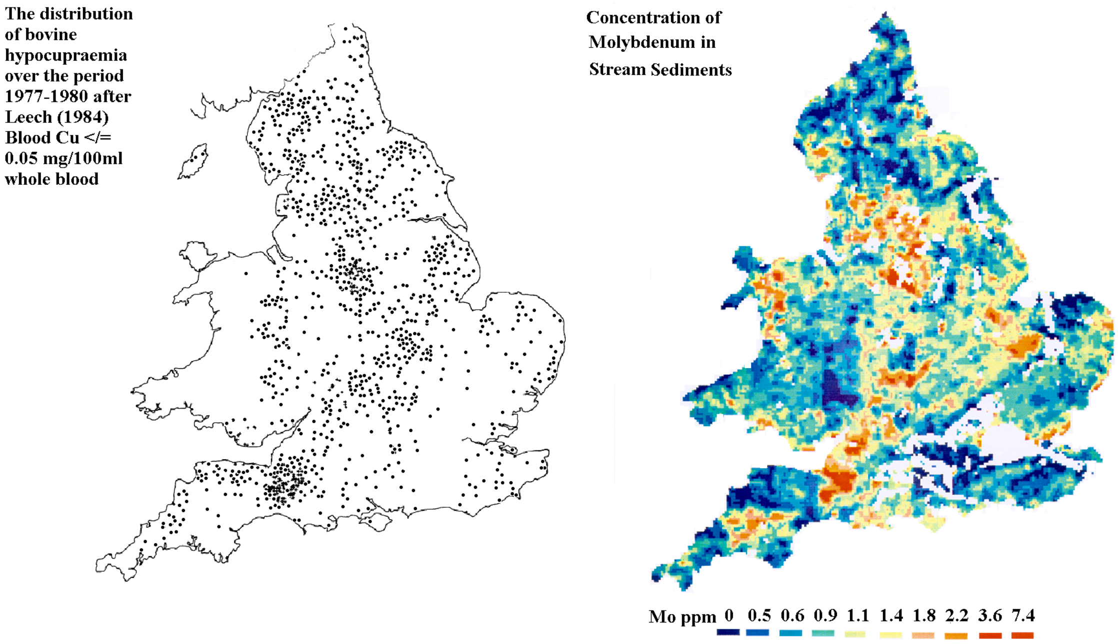


Plate 3
Spatial correlation between low blood copper levels in cattle herds and elevated molybdenum reported in stream sediments from the *Wolfson Geochemical Atlas*
(After Leech *et al.*, 1982, Leech, 1984 and Webb *et al.*, 1978)

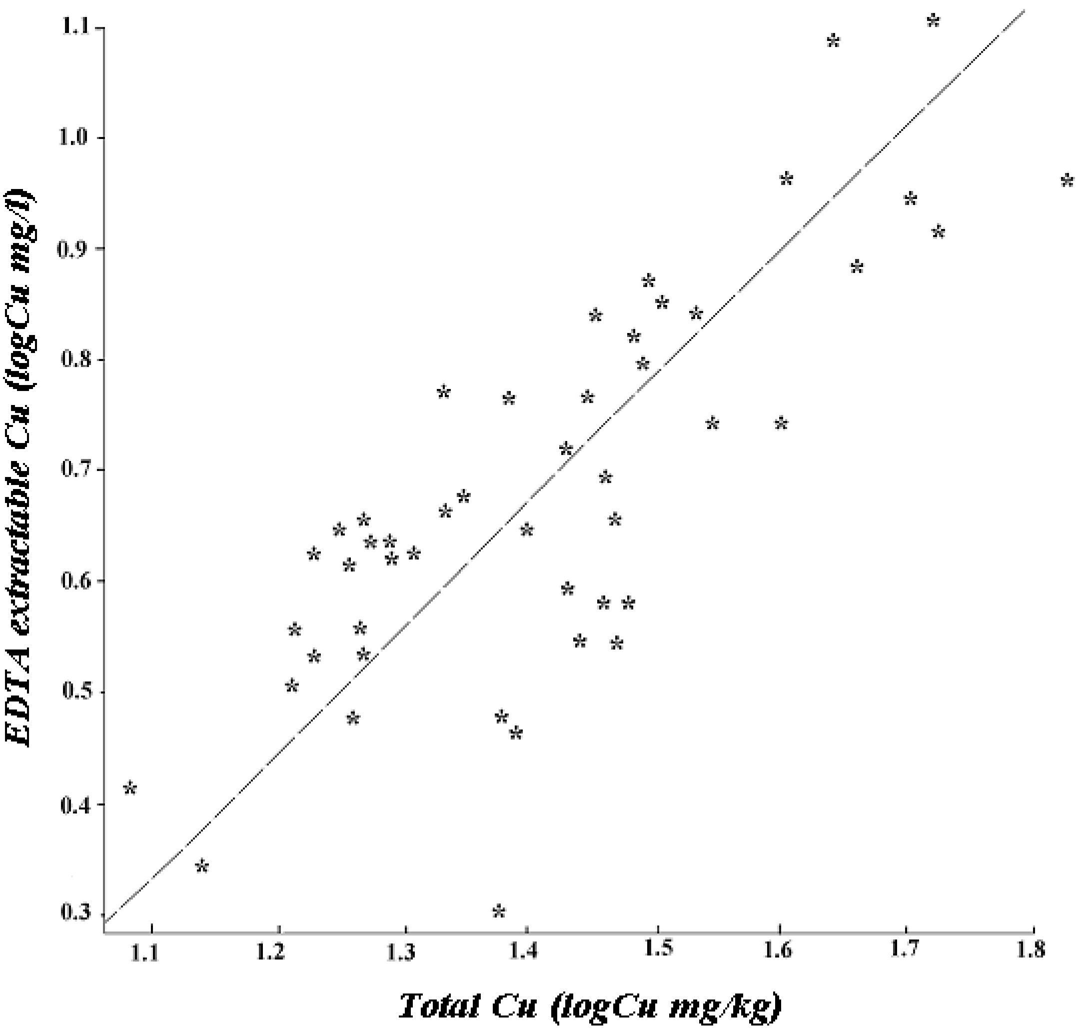


Figure 1
Relationship between total copper and available (EDTA extractable) copper in soil,
R = 0.806 (Unpublished data reproduced with permission of ADAS Consultancies Limited)

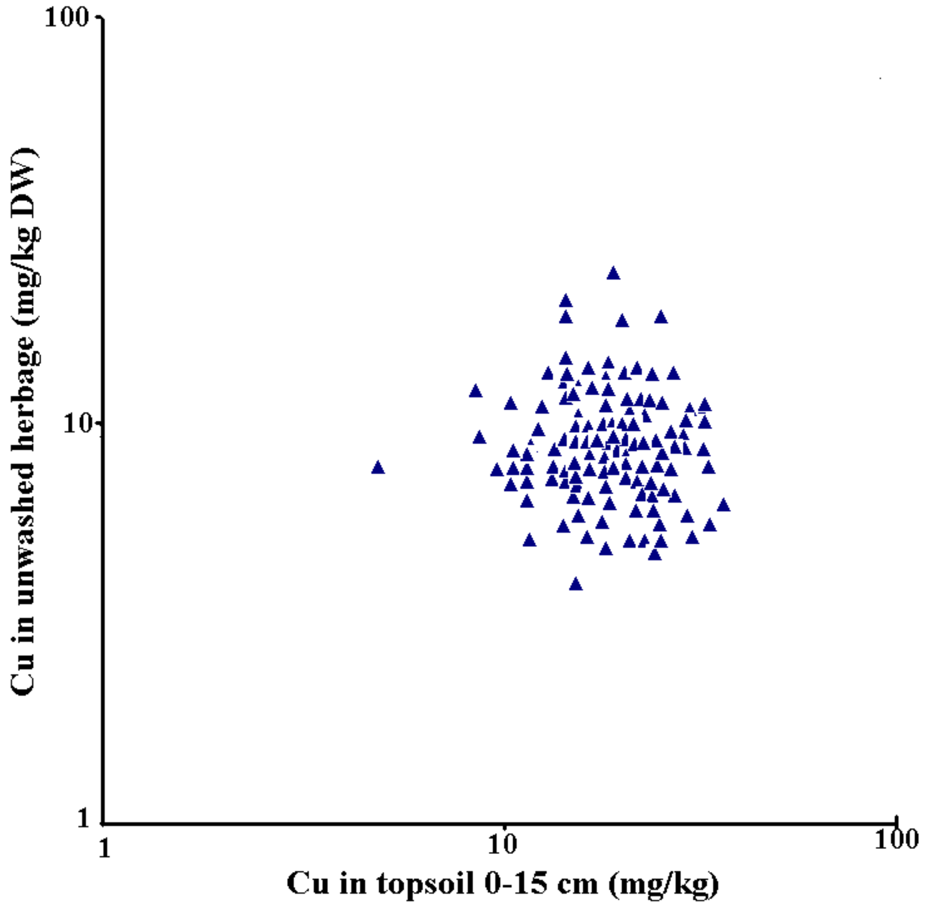


Figure 2
Relationship between copper in soil (0-15 cm) and copper in pasture herbage
(After Thomson, 1971)

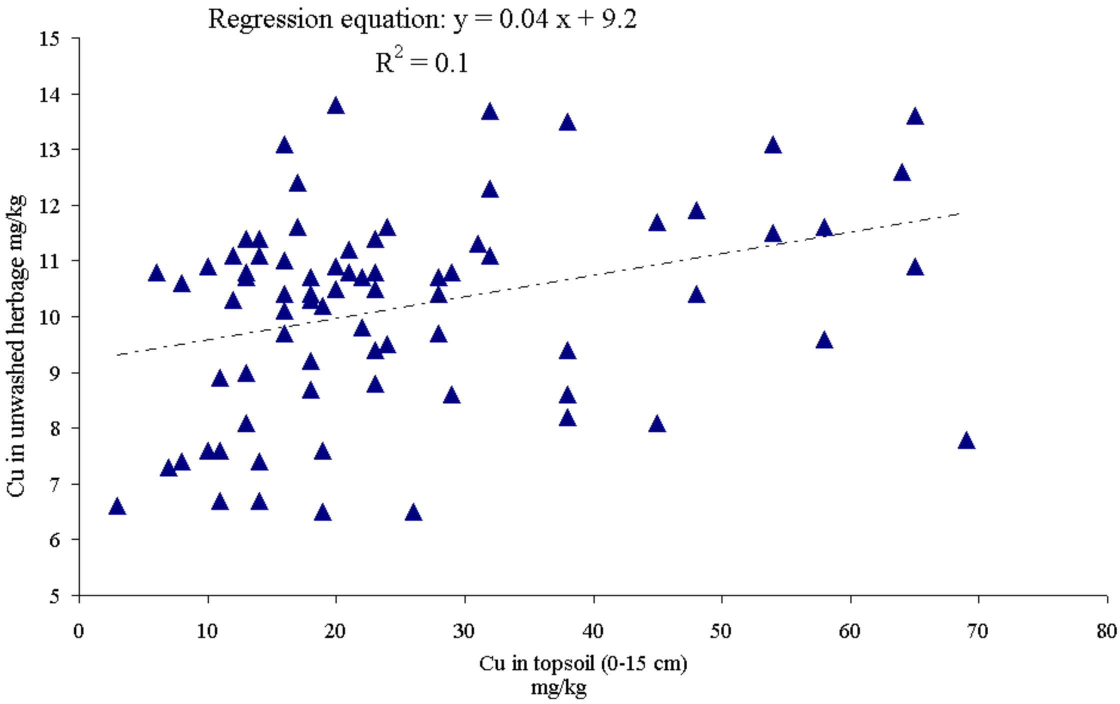


Figure 3

The relationship between the concentration of copper in soil and unwashed herbage from six study areas in England, concentration reported in µg/g dry matter (After Leech, 1987)

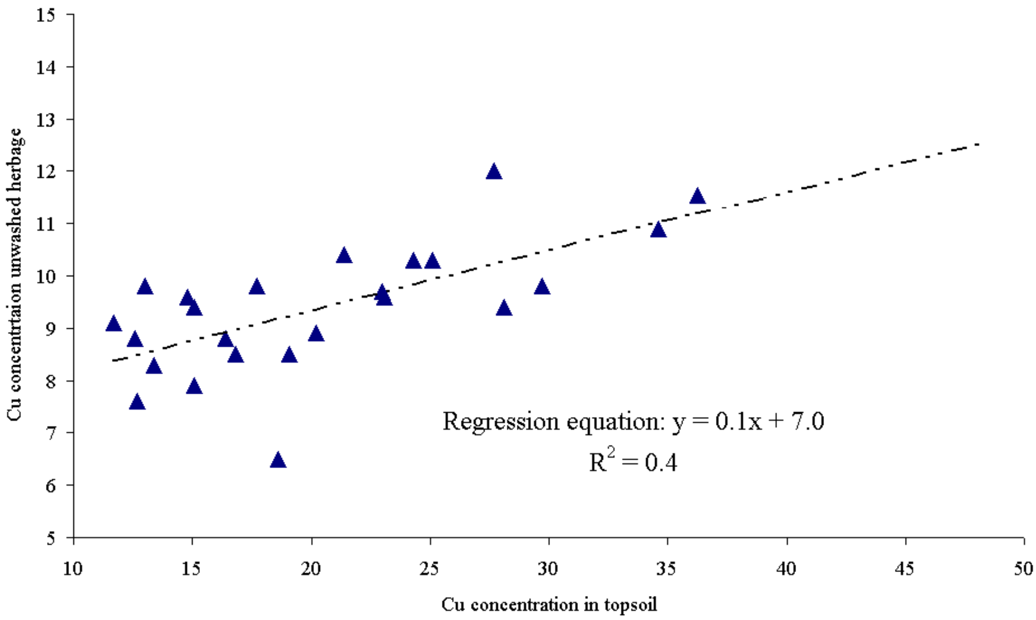


Figure 4a

Relationship between the concentration of copper in soil and washed herbage from three study areas in the UK, concentration reported in µg/g dry matter
(After Russell, 1987)

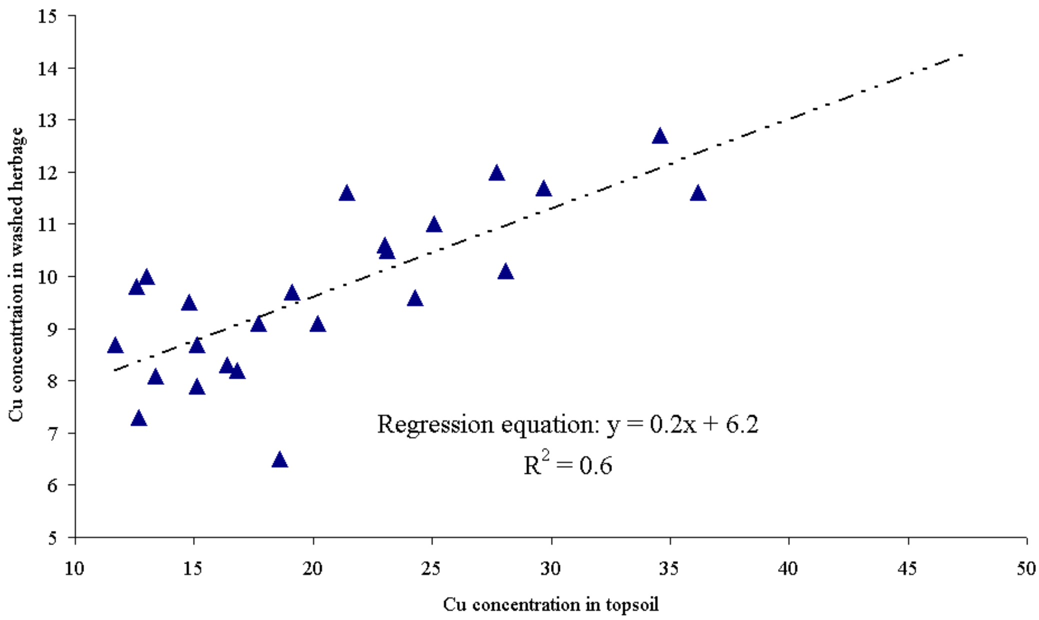


Figure 4b

Relationship between copper in soil and copper in unwashed herbage in three UK areas, concentration reported in µg/g dry matter
(After Russell, 1987)

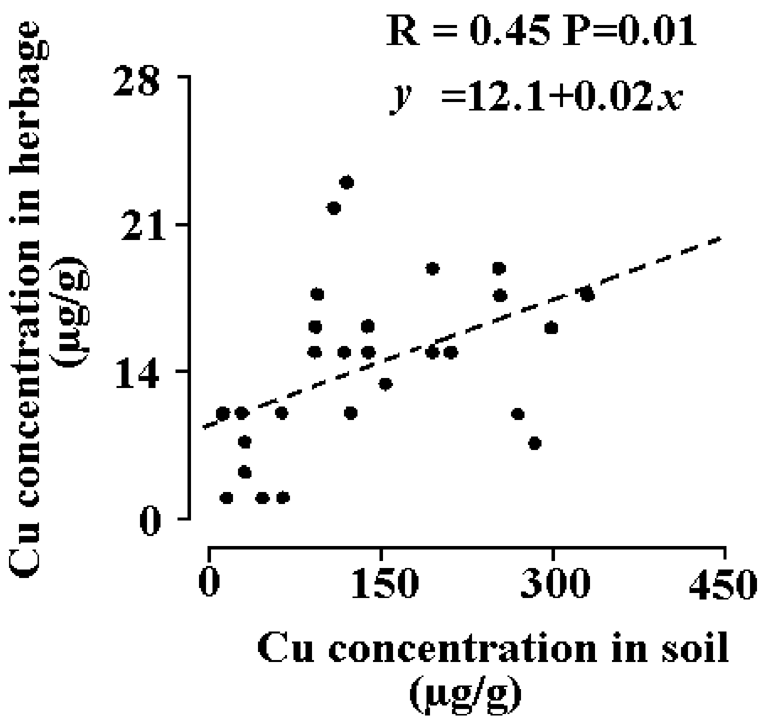


Figure 5a
Total concentration of copper in soils and pasture washed (April) in South West England (After Abrahams and Thornton, 1994)

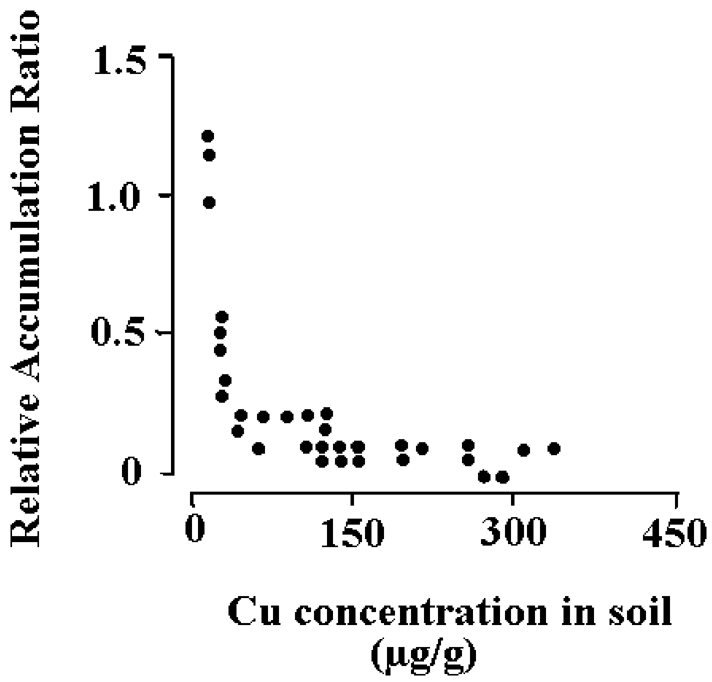


Figure 5b
Relative accumulation of copper in pasture herbage in South West England
(After Abrahams and Thornton, 1994)

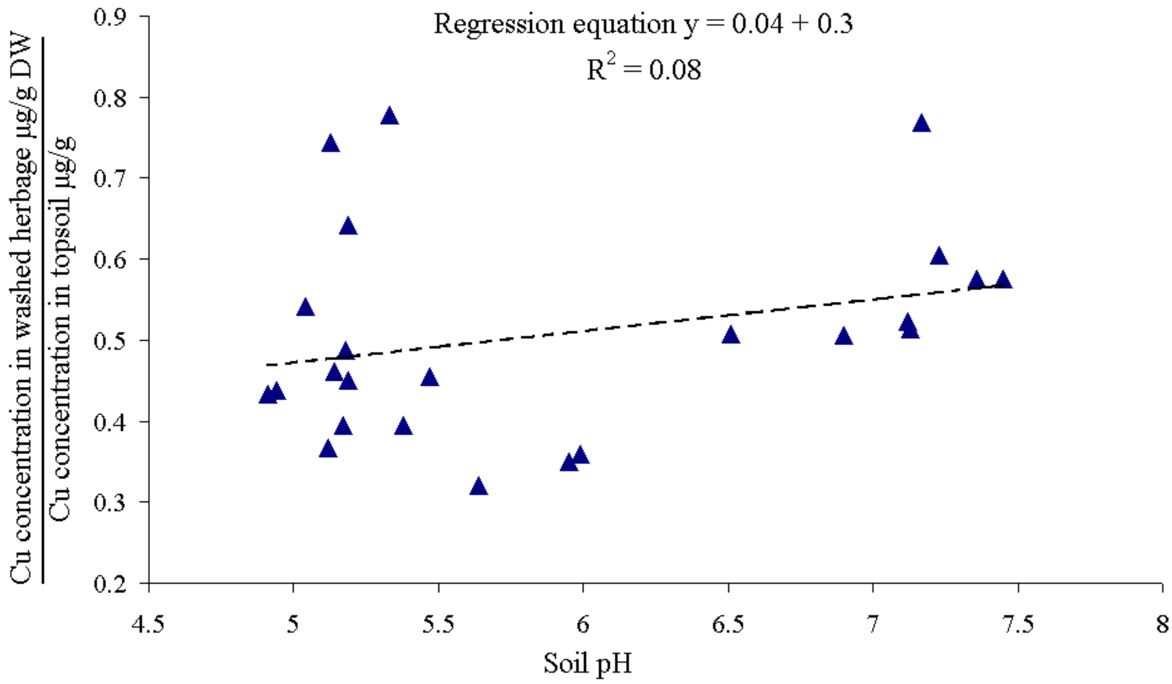


Figure 6

The bioavailability of copper in relationship to soil pH
(After Russell, 1987)

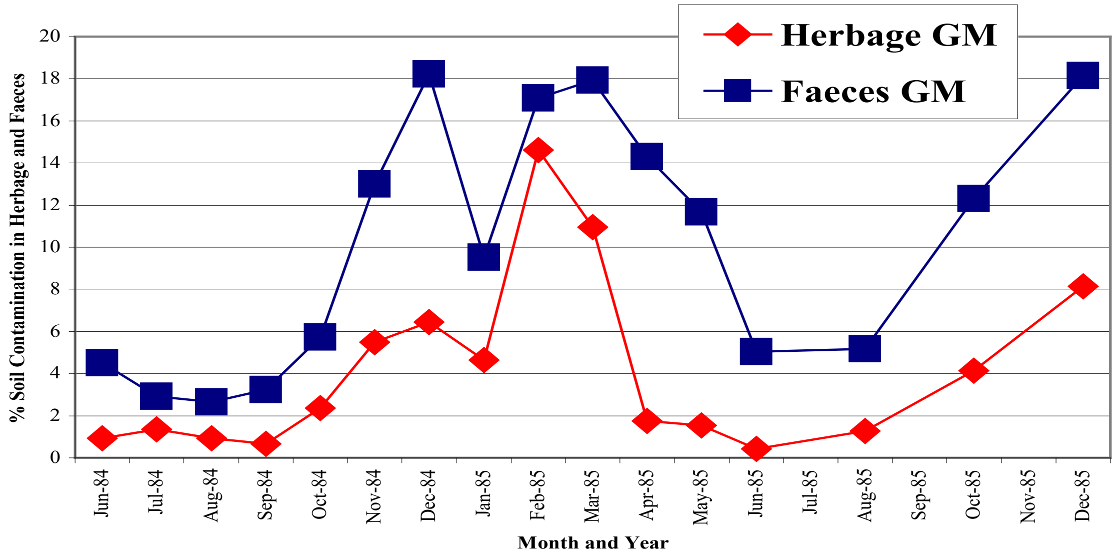


Figure 7

Seasonal variation of soil contamination in herbage and sheep faeces, geometric mean values from 9 farms sampled in The Lake District (After Russell, 1987)

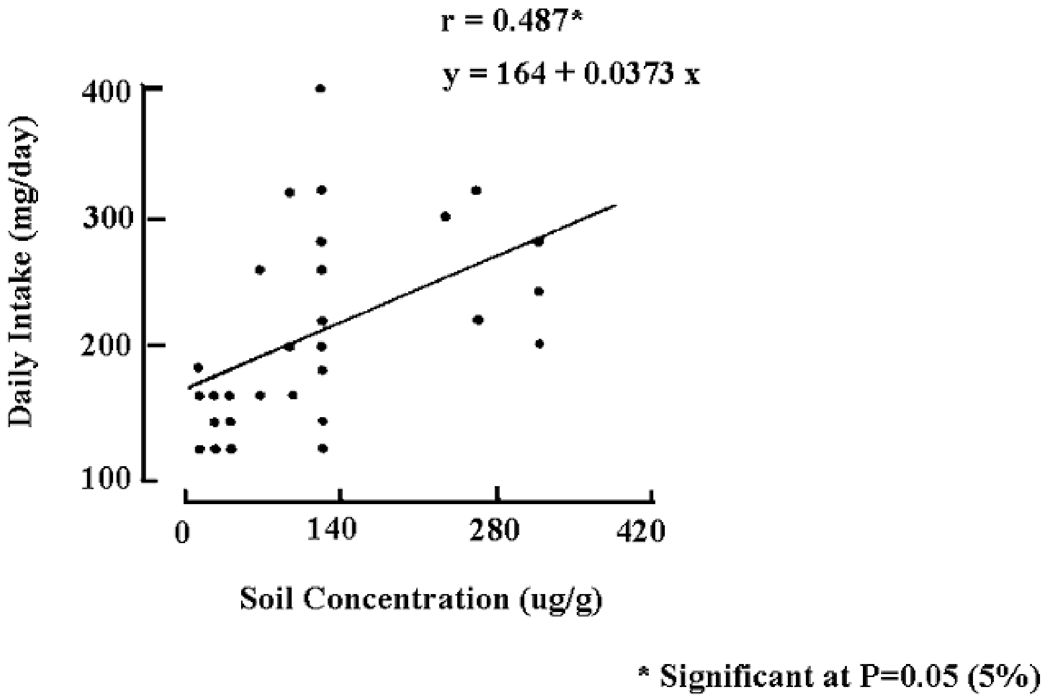


Figure 8
The calculated daily intake of copper by cattle at 12 study sites in South-West Britain
(Abrahams and Thornton, 1994)

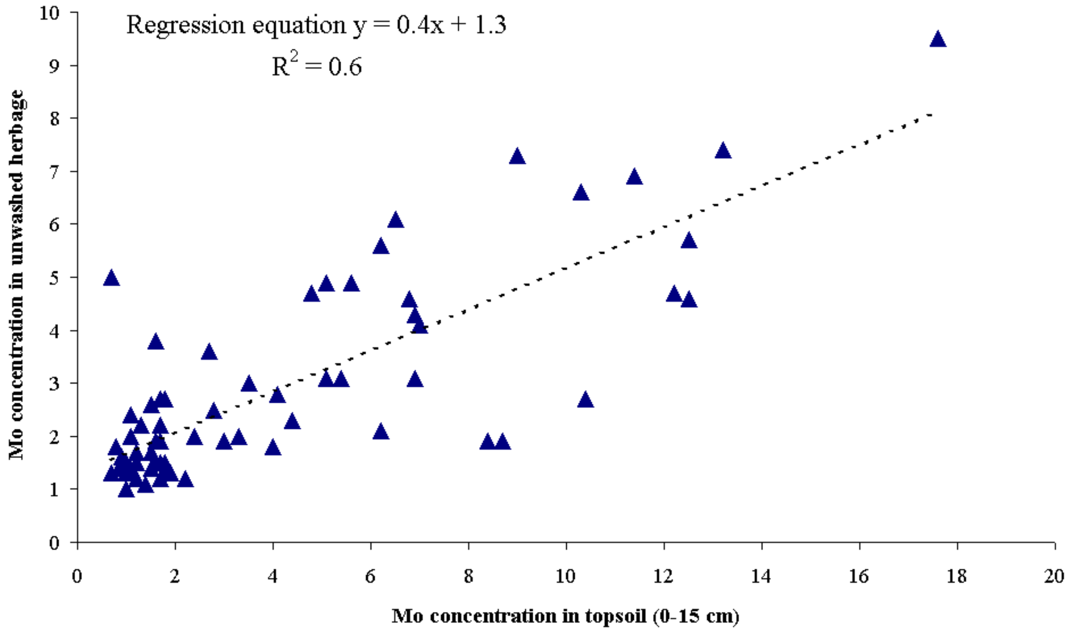
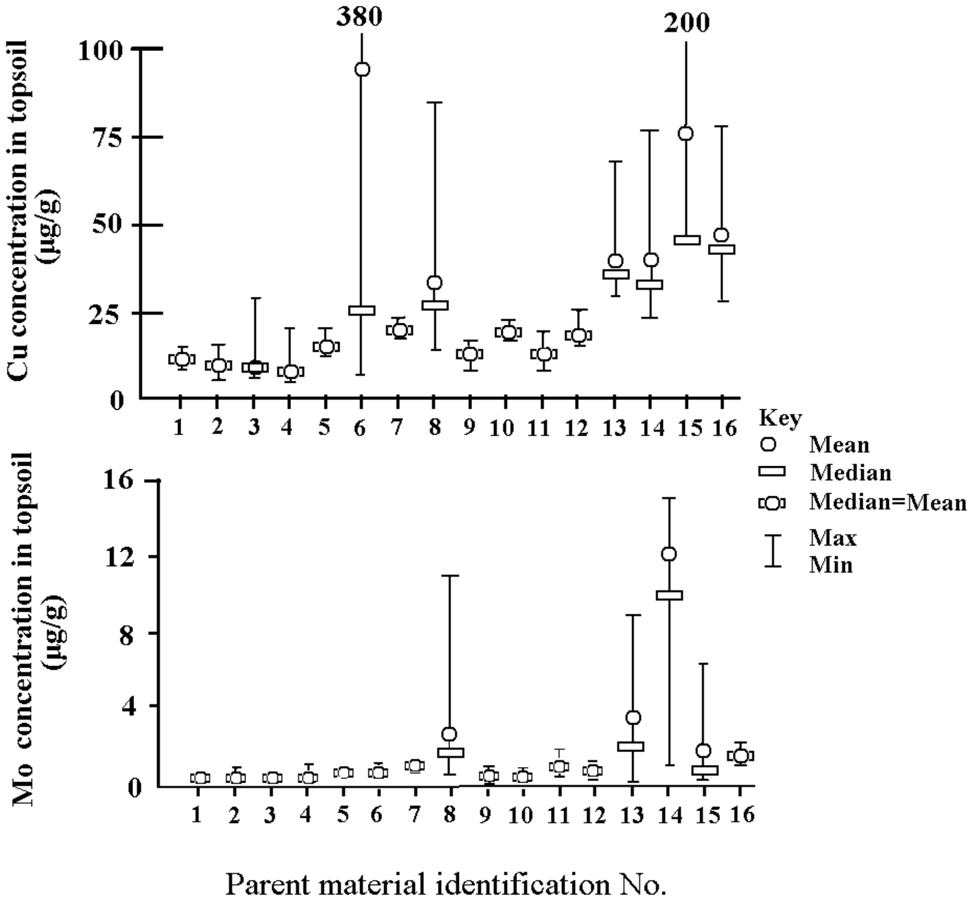


Figure 9

The relationship between the concentration of molybdenum in soil and unwashed herbage from 6 study areas in England, concentration reported in µg/g dry matter (After Leech, 1987)



Key to Parent Materials		
Identification No.	**N**	**Parent Material**
1	4	Chalk
2	8	Permo-Triassic New Red Sandstone
3	8	Devonian Old Red Sandstone
4	8	Lower Greensands
5	4	Upper Greensands
6	6	**Granite, with some mineralisation**
7	3	Carboniferous Milstone Grit
8	10	Carboniferous Limestone
9	11	Romney Marsh Alluvium
10	4	Oxford Clay
11	7	Silurian Shale: Moorland phase
12	6	Silurian Shale: Upland phase
13	9	Lower Lias Shale
14	4	Carboniferous Marine Black Shales
15	5	Devonian Shales, with some mineralisation
16	6	Carboniferous Culm Measures

Figure 10
The mean, median and range of copper and molybdenum in soils over a different parent materials in the UK (After Brebner, 1987)

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