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Cattan, R.

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An investigation of the risks for human health from bio-available and bio-accessible arsenic in the Tamar catchment using human hair bio-markers and geochemical data

Richard Cattan

Project Advisor: Charlotte Braungardt, School of Geography, Earth & Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, PL4 8AA

Abstract

Geologic mineralisation and anthropogenic exploitation in the Tamar catchment of south-west England have resulted in an environment enriched with arsenic, a recognised carcinogen and systemic toxicant that can target many organs in the human body. This study examined geochemical data from the catchment and found particularly high arsenic contamination around the historic mining districts of Callington and Gunnislake, where maximum concentrations of 39 µg L^{-1} in stream waters, 11000 mg kg^{-1} in stream sediments, and 15000 mg kg^{-1} in topsoils were found in certain areas.

Hair samples from 91 catchment residents were analysed using inductively-coupled plasma mass spectrometry. The arsenic levels found in their hair ranged from 4.87 to 1150 µg kg^{-1}, with a geometric mean of 43.1 µg kg^{-1} and 95% confidence interval of 33.7 to 55.2 µg kg^{-1}. Most samples (59.3%) were within the typical range found in hair from people unexposed to arsenic, but three samples exceeded the expected value of 1000 µg kg^{-1} of arsenic in hair based on accepted dietary intake. Statistical tests indicated the main influences on arsenic bio-availability were living within 5 km of an arsenic-contaminated area, or growing and/ or consuming locally-grown food. The hair arsenic concentrations were significantly correlated with copper, phosphorus and zirconium in topsoils, and pH and conductivity in stream waters. A multiple regression equation was derived to relate bio-availability with bio-accessibility and indicate parts of the catchment where humans may have high arsenic levels in their hair, highlighting the arsenic bio-availability risks of areas in the south of the catchment.

This study contributes to the limited available data on human bio-markers of arsenic exposure in the catchment. The incorporation of geochemical and bio-marker data in a combined bio-accessible and bio-available multiple regression model offers a robust alternative for human health risk assessment, and the fitted model could guide land use planning and remediation of areas at risk from arsenic-related health problems. It could also be used with epidemiological studies of disease incidence in the catchment.

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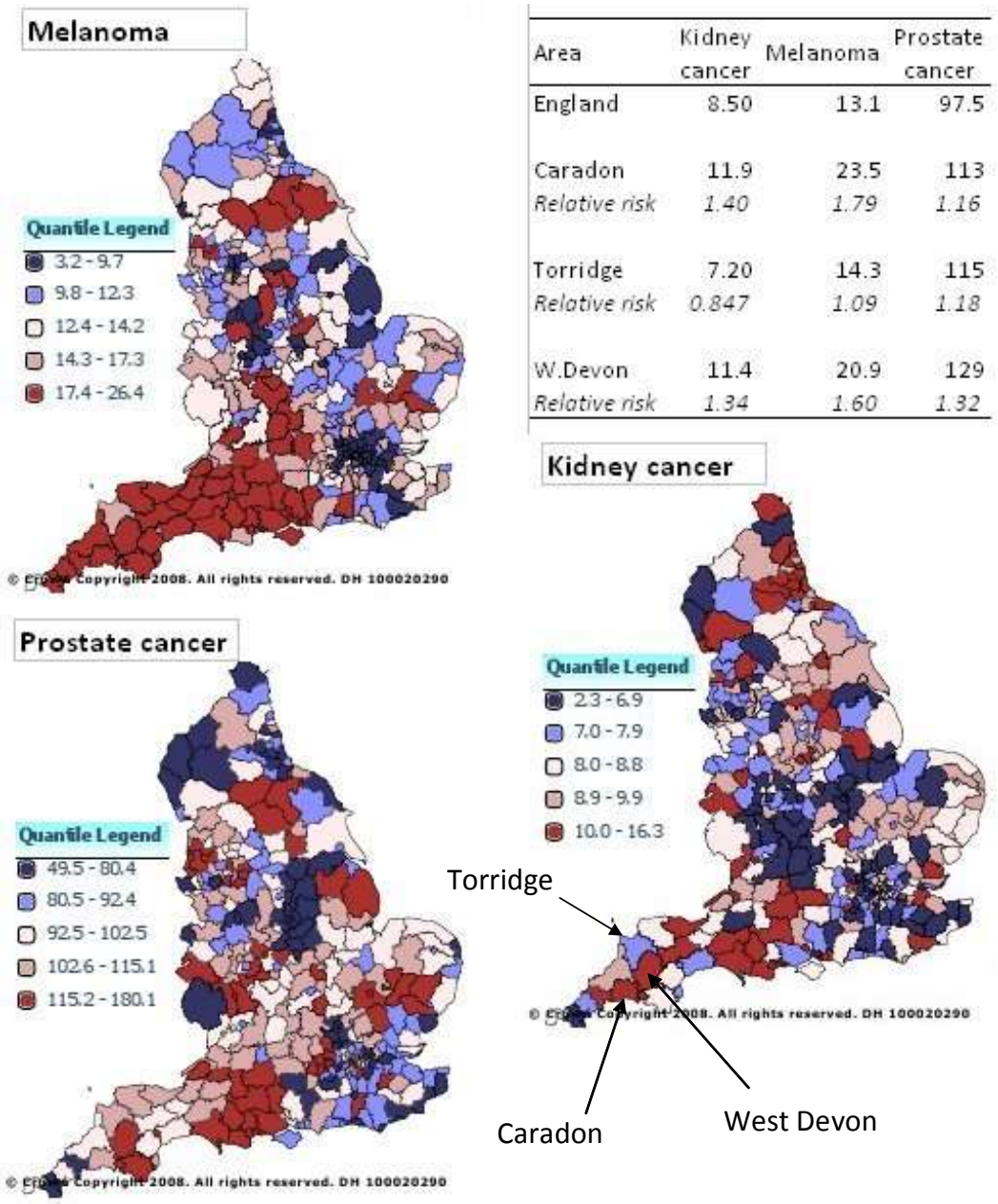
1. Introduction

Arsenic (As) is a steel grey, brittle, crystalline metalloid, the 20th most abundant element in the Earth's crust and naturally present in small amounts in rock, soil, dust, water, air and biological tissues (Bhattacharya *et al* 2007). It has been used as a medicine and as a poison since the time of the Ancient Greeks, and was one of the main causes of fatal poisoning in early 19th century England. On the other hand, Dr. Fowler's solution containing 1% potassium arsenite ($KAsO_2$) was first proposed as a medicine in 1786 and was still available in the United States until the 1950's (Hindmarsh & McCurdy, 1986). As is an inexpensive by-product of the smelting of many metals such as copper (Cu) and iron (Fe), and today it is mostly used in agriculture for pest control, wood preservatives and veterinary medicines. It is also used in the semi-conductor industry and for treating tropical diseases such as African sleeping sickness and amoebic dysentery (Tchounwou *et al*, 2004).

As is a mutagen, teratogen and the only human carcinogen with adequate evidence of risk from both inhalation and ingestion (Bhattacharya *et al* 2007). It can target the skin and the respiratory, cardiovascular, gastrointestinal, renal and nervous systems. The skin is the major organ of As accumulation and the kidneys are the major route of As excretion (Morton & Dunnette, 1994). Epidemiological studies in Bangladesh, South America and Taiwan have shown significant increases in the risk of skin, liver and bladder cancer associated with high As contamination of drinking water (Tchounwou *et al*, 2004). Guideline values for As in drinking water have recently been lowered from 50 µg L^{-1} to 10 µg L^{-1} in the United States and Canada because adverse health effects were found with lower concentrations than previously thought (Kapaj *et al*, 2006; Health Canada, 2006).

The south-west region of England suffers high metal and metalloid contamination due to the historical exploitation of geological mineralisation in the area (Thornton & Farago, 1997). As enrichment in the Tamar catchment is well-documented; several studies have reported elevated levels in environmental media and human bio-markers compared to other areas of England (Colbourn *et al* 1975; Farago *et al*, 1997; Kavanagh *et al*, 1998; Peach & Lane, 1998; Farago & Kavanagh, 1999; Rawlins *et al*, 2003; Rieuwerts *et al*, 2006; Button *et al*, 2009). Contamination is particularly evident around the historic mining districts of Callington and Gunnislake, where the processing of As was anecdotally associated with skin disorders and skin cancers (Hamilton, 2000). Today, the Caradon, Torridge and West Devon districts have relatively high incidence of kidney cancer, melanoma and prostrate cancer (Figure 1), but it has proved difficult to link As exposure with morbidity or mortality in the region. High cancer incidence in the Tamar valley was reported in 1868, 1936 and 1962 but the exact causes could not be identified, and a more recent study of a possible link between As and bladder cancer incidence in south-west England found no evidence for an ecological association (Farago *et al*, 1997).



Area	Kidney cancer	Melanoma	Prostate cancer
England	8.50	13.1	97.5
Caradon	11.9	23.5	113
Relative risk	*1.40*	*1.79*	*1.16*
Torridge	7.20	14.3	115
Relative risk	*0.847*	*1.09*	*1.18*
W.Devon	11.4	20.9	129
Relative risk	*1.34*	*1.60*	*1.32*

Figure 1: Melanoma, prostate cancer and kidney cancer incidence for all persons in England averaged over the calendar years 2003 to 2005 (Cancer e-Atlas, © Crown Copyright, available online at www.ncin.org.uk/index_files/eatlas.htm, accessed 17 March 2010). The relative risks for Caradon, Torridge and West Devon districts are proportional to incidence in England.

Understanding exposure is important for managing human health risks: exposure includes the presence, abundance and mobility of an element in the environment (its bio-accessibility), and its ability to access target organisms and cause toxicity (its bio-availability). This study integrates chemistry, statistics and geographical information systems to combine bio-available risks represented by bio-marker data and bio-accessible risks represented by significantly correlated geochemical data. One advantage of this combination is that it does not rely on the analysis of a single element to assess its own health risks, but incorporates a number of environmental factors which may have more influence on bio-accessibility and therefore bio-availability. A further

advantage is the use of established laboratory and statistical techniques in the method of investigation.

The primary objective of this study is to add to the limited body of research on human bio-markers in the Tamar catchment. The secondary objective is to conduct a holistic examination of the bio-accessible and bio-available factors of As exposure in the Tamar catchment. The final objective is to propose a model for a human health risk assessment which could inform the management and possible remediation of areas at risk, and provide insight for epidemiological studies of clinical disease in the catchment.

The bio-geochemistry, exposure pathways and toxicology of As are reviewed in the next section to characterise the risks to humans living in the catchment. The physical and socio-economic features of the Tamar catchment and previous studies of As are described in Section 3 to establish the nature and scale of the As hazard in the region. The methods of investigation are described in Section 4 and the results are discussed in Section 5. The findings are presented in Section 6 along with improvements which may be made for future research.

2. Arsenic in the environment

2.1. Sources of arsenic

As is widely distributed in nature: concentrations in the Earth's crust range from 0.5 to 2.5 mg kg^{-1} and over 200 As-containing minerals have been identified (Kabata-Pendias & Mukherjee, 2007). Of these, 60% are arsenates, 20% are sulphides and sulphosalts, while the remaining 20% are arsenides, arsenites, oxides, silicates and elemental As. The ability of As to bind with sulphur (S) ligands means it tends to be found with sulphide-bearing minerals such as arsenopyrite (FeAsS), the most common As-containing mineral (Elmsley, 2001). This mineral is typically found in sedimentary formations rich in organic matter such as shales and peat deposits. As is also often found in galena (PbS) and chalcopyrite ($CuFeS_2$). The As content of minerals ranges from 0.02 to 0.5% but can be up to 5% in pyrite minerals (Thornton & Farago, 1997).

As concentrations in igneous and sedimentary rocks are commonly around 2 mg kg^{-1}. Most rocks contain from 0.5 to 2.5 mg kg^{-1} but finer-grained argillaceous sediments can have 10 to 15 mg kg^{-1} (Table 1) (Alloway, 1995).

Table 1: Common As concentrations in major rock types (mg kg^{-1}, adapted from Kabata-Pendias, 2001 and Kabata-Pendias & Mukherjee, 2007).

Magmatic rocks	Ultramafic rocks	Dunites, peridotites, pyrozenites	0.5 – 1.0
	Mafic rocks	Basalts, gabbro	0.5 – 2.5
	Intermediate rocks	Diorites, syenites	1.0 – 2.5
	Acid rocks	Granites, gneisses	1.0 – 2.5
	Acid rocks (volcanic)	Rhyolites, trachytes, dacites	1.5 – 2.5
Sedimentary rocks	Argillaceous sediments		5 – 13
	Shales		5 – 13
	Sandstones		0.5 – 1.2
	Limestones, dolomites		1.0 – 2.4

Soils contain more As than rocks and have normal concentrations ranging from 1 to 40 mg kg^{-1}, but most are in the lower half of this range (Table 2). The main sources of As in soils are parent material from the underlying bedrock, or material transported by wind and water. Lowest As levels are found in sandy soils and those derived from granites, while higher amounts are usually found in alluvial soils and soils rich in organic matter. Elevated soil As generally occurs in mineralised areas, for example soils close to sulphide ore deposits may contain up to 8000 mg kg^{-1} (Thornton & Farago, 1997). Acid sulphate soils can also accumulate a high proportion of native As due to the presence of pyrite.

Table 2: Typical As content of surface soils in different countries (mg kg^{-1}, dry weight, Kabata-Pendias, 2001).

Soil type	Country	Range	Mean
Podzols and sandy soils	Canada	1.1 – 28.9	5.8
	Japan	1.2 – 6.8	4.0
	Korea	2.4 – 6.8	4.6
	UK	5.1 – 6.8	
	US	<0.1 – 30	5.1
Loamy and clay soils	Canada	1.3 – 16.7	4.8
	Thailand	7.2 – 18.4	12.8
	US	1.7 – 27	7.7
Fluvisols	UK	20 – 30	25
Soils on mafic rocks	UK	5.0 – 8.2	
Forest soils	Norway	0.6 – 5.0	2.2
	US	<0.1 – 93	7
Various soils	Bulgaria	2 – 10.4	5.6
	Canada	<1 – 30	5.8
	Italy	4 – 197	41
	Japan	0.4 – 70	11
	Norway	0.7 – 8.8	2.5
	UK	4 – 95	16.3
	US	<1 – 93	7

The world's rivers contain average As levels of 0.11 to 0.94 µg L^{-1} but in areas of sulphide mineralisation this can range from 100 to 5000 µg L^{-1} (Alloway, 1995). The seas and oceans contain 1.2 to 3.7 µg L^{-1} with the majority sorbed to suspended particulate matter (SPM) (Kabata-Pendias & Mukherjee, 2007). As is emitted naturally to the atmosphere by sea-salt aerosols, soil-derived dusts, forest fires and volcanic eruptions, which can compose 20 to 40% of all natural As emissions. As concentrations in air have been recorded from 2 to 53 ng m^3 in urban regions but only 0.007 ng m^3 at the South Pole.

Anthropogenic activities have a major influence on the distribution of As in the environment. The major As minerals have been mined in their own right in the past, but are currently recovered from sludge and flue dust during the smelting of Cu, zinc (Zn), lead (Pb), gold (Au) and silver (Ag) ores. In 2000 global production was estimated as 27.9 kt yr^{-1} (Kabata-Pendias & Mukherjee, 2007). Agriculture has used As for over 100 years: until the 1970s around 80% of As production was used in pesticide manufacture, although this has now declined to around 50% due to its toxicity (Alloway, 1995). However, agriculture's reliance on As has not declined: organic arsenicals composed 90% of pesticide production in 2000, and small quantities are still legitimately used as

animal feed additives to promote growth in chickens, turkeys and pigs (Elmsley, 2001). Industrial applications include copper-chromium-arsenate for glass and wood preservatives, gallium arsenide in semiconductors, and arsine gas in the microchip industry (*ibid.*). EU industrial emissions to the atmosphere were estimated to be 177 t yr^{-1} in 2000, mostly from coal combustion (Kabata-Pendias & Mukherjee, 2007). Mining and industrial activities can disperse As widely and play a significant role in the contamination of soils, water and air (Bhattacharya *et al* 2007), and globally there are many terrestrial hotspots of elevated As due to geochemical enrichment or mining and processing.

2.2. Speciation and mobility

As forms covalent compounds or occurs as an anionic species. Pentavalent arsenate (As^V, H_2AsO_4), is stable under oxidising conditions, but trivalent arsenite (As^{III}, H_2AsO_3) is predominant under reducing conditions (Figure 2) (Centeno *et al*, 2007). Inorganic As compounds can be methylated by micro-organisms to produce methylarsonic acid (MMA, $CH_3AsO(OH)_2$), dimethylarsinic acid (DMA, $(CH_3)_2AsO(OH)$) and trimethylarsine oxide (TMAO, $(CH_3)_3AsO$) under aerobic conditions, and volatile and easily oxidised methylarsines under anaerobic conditions (Thornton & Farago, 1997).

As often forms more volatile and soluble phases than its associated major elements Fe and S, and is therefore more widely dispersed. There are significant atmospheric fluxes, an estimated 7% of which is vapour and the remainder particulate (Alloway, 1995). Roasting of As ores and burning of As-rich coal releases arsenic trioxide (As_2O_3), which may react with air and be deposited onto soils (Thornton & Farago, 1997). The residence time for As in the atmosphere is estimated to be 9 days as methylated forms are rapidly oxidised to inorganic forms that adsorb to dust particles, settle out or are washed from the atmosphere by rain (Hindmarsh & McCurdy, 1986).

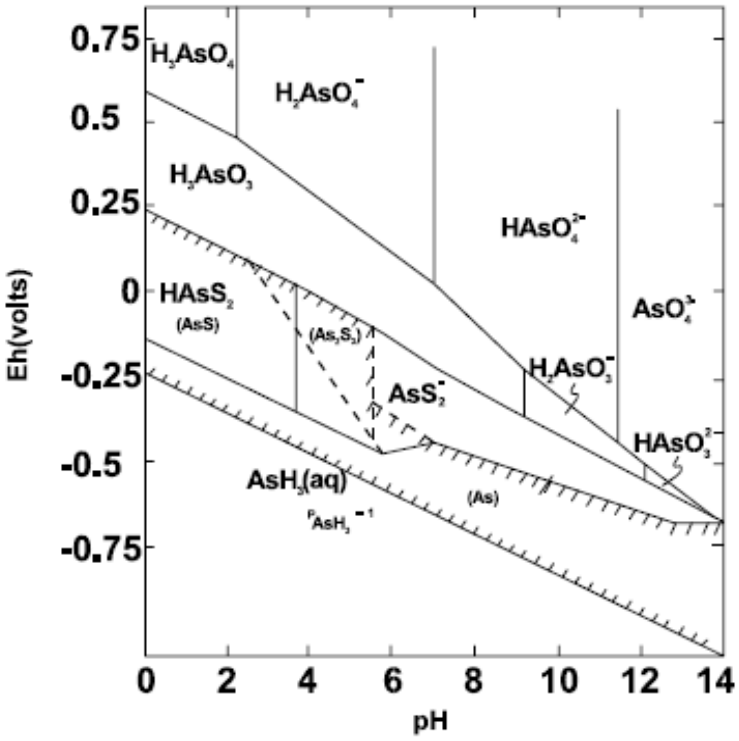


Figure 2: Eh-pH diagram for As at 25 °C and 1 atmosphere (WHO, 2001). Solid species are shown in brackets in the cross-hatched area.

Arsenic sulphides oxidise easily with weathering, yielding As minerals and compounds that are readily soluble in freshwaters such as arsenous acid (H_3AsO_3) and arsenic acid (H_3AsO_4). However, migration is limited by strong adsorption with clays, hydroxides and organic matter (Kabata-Pendias, 2001). As^V and As^{III} form insoluble salts with cations (usually Fe) and generally remain in suspension until settled out into sediments. As in groundwater is often reduced to As^{III} because of the higher pH and lower Eh conditions. Less co-precipitation with cations occurs in these environments and As is likely to remain in solution. Complex organic As compounds are found in the marine environment, but only a very minor fraction of total As remains in solution in seawater and most is adsorbed to SPM (Thornton & Farago, 1997).

As reactions in soil depend on the presence of clay minerals, Fe and/ or aluminium (Al) oxides, and organic matter, which all influence sorption, solubility and oxidation rate. As typically forms insoluble complexes with Fe and clay particles and normally has a long residence time of 9400 years in soil (Hindmarsh & McCurdy, 1986). As^V is readily fixed by soil components: arsenates of Fe and Al dominate in acid soils (Thornton & Farago, 1997), and are less soluble than calcium arsenate ($Ca_3(AsO_4)_2$), the main chemical form in calcareous soils. As^{III} is most soluble at ambient pH but relatively immobile at elevated pH, where As^V is less strongly adsorbed to the soil (Alvarez-Benedi *et al*, 2005). As is more mobile in sandy or low-clay soils especially at higher pH.

As is a constituent of many terrestrial plants but concentrations are seldom in excess of 1 mg kg^{-1} and are generally well below that found in the soil (Bhattacharya *et al* 2007). Lower levels are found in plants grown on clays and silts but plant bio-availability of As can be five times greater in sandy soils (Alloway, 1995). Little is known about the biochemical role of As in plants but it is taken up passively with water-flow, trans-located throughout the plant and accumulated in the roots and old leaves (Kabata-Pendias, 2001). The effect of As on crop quality and yield is a major worldwide concern, particularly for paddy rice because the submerged soil creates reducing conditions where As^{III} can depress rice growth (Yan-Chu, 1994).

Elevated As levels are found in valueless ore material discarded by mining activities. The exposed wastes and finely-ground mining spoils are highly vulnerable to wind erosion, and have high water erosion risks due to low pH, low water retention capacity, and low cation exchange capacity (Meza-Figueroa *et al*, 2009). The degree of stabilisation of the spoil also affects wind dispersal and drainage pathways. Poorly stabilised spoil can be intensely eroded: heavy rainfall events will erode spoil contents downstream, leaving the remaining tailings dry and susceptible to wind erosion; surrounding areas can be subjected to airborne metal-laden particles which can be inhaled.

2.3. Human exposure pathways

The direct ingestion of As in water, crops and soils are the most influential pathways for human As exposure. Humans can be exposed by dermal absorbance, particularly by As_2O_3 which is more lipid-soluble than As^V, but the absorption rate may be insufficient to cause clinical problems (Hindmarsh & McCurdy, 1986). As may also be inhaled which is particularly relevant for occupational exposure, for example workers in a smelting operation, but most inhaled As is not absorbed directly from the respiratory tract and instead is regurgitated and subsequently ingested (Al Rmalli *et al*, 2005).

Food is a major source of As exposure: it may be cooked using contaminated water; As

can accumulate in crops; meat and poultry products may contain As legitimately used as a growth stimulant; or animals may have accumulated As from contaminated fodder. Fish and crustaceans are known to contain high As levels but usually as non-toxic arsenobetaine (AsB, $(CH_3)_3As^+CH_2COO^-$) (Khan *et al*, 2009). Seafood has highest As concentrations of the food groups while meats and cereals contain more As than vegetables, fruit and dairy products (WHO, 2001). The UK Government's Total Diet Study (Table 3) estimated the average UK diet includes a daily As intake of 65 µg day^{-1} for the general population and 17 µg day^{-1} for vegetarians (Al Rmalli *et al*, 2005).

Table 3: Total As concentrations in samples from various food groups in the 1999 Total Diet Study (FSA, 2004), ranked by the maximum value found in each range.

Food group	Range of total As concentration (µg kg^{-1})
Fish	1106 – 8423
Poultry	<2.1 – 169
Miscellaneous cereals	3.2 – 26
Potatoes	<1.4 – 18
Nuts	<4.3 - 11
Meat products	<2.1 – 8.2
Eggs	<1.4 – 7.6
Bread	<2.1 – 7.5
Other vegetables	2.7 – 7.4
Green vegetables	<0.5 – 6.3
Fresh fruit	<0.9 – 5.5
Dairy produce	<2.1 – 3.4
Milk	<0.5 – 0.7

The incidental ingestion of soil results from hand-to-mouth activities and from soil particles attached to food. It is the main source of non-dietary exposure to As, particularly in contaminated areas, and children are especially at risk because they exhibit more hand-to-mouth behaviours than adults (Basta *et al*, 2002). As in soils is 50% less bio-available than soluble As in water, which is considered to be 100% bio-available.

As in drinking water is one of the most significant environmental causes of cancer, and the groundwater of several countries is greater than the World Health Organisation (WHO) drinking water guideline of 10 µg L^{-1} (Kapaj *et al*, 2006). The prevalence of waterborne diseases in developing countries such as India, Bangladesh and Thailand meant many surface water sources of drinking water were replaced by tube-wells to extract groundwater. These programmes often inadvertently caused serious health problems from the use of As-contaminated groundwater (Bhattacharya *et al* 2007).

Recent research concerns the transfer of As from groundwater to soil to crops which is a particular problem where contaminated groundwater is intensively used for irrigation (Khan *et al*, 2009). In Bangladesh it is estimated that around 100 t of As is contained in waters used for irrigation during the dry season each year. The bio-accessible As in these waters may leach to surface or ground waters or accumulate in soils and/ or crops. In China it is reported that rice yields reduce by 10% in soils with As concentrations of 25 mg kg^{-1} (Bhattacharya *et al* 2007).

2.4. Arsenic toxicology

Total As in the human body averages around 7 mg, varying between 0.5 and 15 mg, and the regular intake may be as low as 10 µg day^{-1} (Elmsley, 2001). A unique metabolic role for As in humans has not been found (Hindmarsh & McCurdy, 1986), but ingested soluble forms of As are absorbed from the gastro-intestinal tract and mainly transported to the organs by the blood. It is metabolised in the liver by a two-step process where reduction transforms inorganic As from As^{V} to As^{III}, which is then transformed into MMA and DMA by oxidative methylation (Basta *et al*, 2002). The biological half-life of inorganic As is about 10 hours and around 60 to 75% of ingested inorganic As is excreted by the kidney within 48 hours: 60 to 80% as DMA; 10 to 20% as MMA; and 10 to 20% as inorganic As (Yanez *et al*, 2005). Organic As compounds such as AsB are efficiently absorbed and rapidly excreted, but inorganic species tend to accumulate over longer periods in bone, skin, nails and hair (Bhattacharya *et al* 2007). Inorganic As can constitute around 85% of total As in keratinous tissue and trivalent species are generally better absorbed by hair than pentavalent species (Raab & Feldmann, 2005).

Small doses of As stimulate the production of haemoglobin and influence the metabolism of the arginine amino acid, Zn and manganese (Mn). The drug Trisenox contains As_2O_3 and is used for treating promyelocytic leukaemia by stimulating the production of normal red blood cells which have become crowded out by cancerous white blood cells (Elmsley, 2001). However, As is a systemic toxicant and recognised carcinogen of the skin and lungs that affects many other organ systems, such as the gastrointestinal, cardiovascular and renal systems (Centeno *et al*, 2007). Evidence suggests methylation activates As as both a toxin and a carcinogen (Button *et al*, 2009), and its toxicity varies with its metabolites: As^{III} is most toxic, followed by As^{V}, MMA, DMA, AsB, and arsenocholine (AsC, $(CH_3)_3As^{+}CH_2CH_2OH$) (Al Rmalli *et al*, 2005). The most common mode of toxicity is the inactivation of an enzyme system by binding with various biological ligands and blocking their action. Other mechanisms include chromosomal abnormalities and oxidative stress. The severity of exposure relates to its source, its chemical form, and the dose and duration of exposure (Kapaj *et al*, 2006).

Acute As poisoning can induce vomiting, colic, diarrhoea and dehydration. Large doses can cause coma, likely heart failure and death within 48 hours: doses in excess of 100 mg are generally considered to be lethal (Elmsley, 2001). Major poisonings have accidentally occurred in modern times; 130 Japanese infants died after consuming dried milk contaminated with As in 1955, and more than 400 Japanese people were poisoned by soy sauce contaminated with inorganic As in 1956 (Hamilton, 2000).

Prolonged As exposure can cause chronic dermatitis which can eventually lead to skin cancer, and As_2O_3 fumes have been linked with lung cancer. The prolonged ingestion of geogenic As from contaminated drinking water can lead to chronic health disorders: in the Bengal Basin around 70 million people were exposed to chronic As poisoning over

many years (Centeno *et al*, 2007). Widespread arsenicosis led to instances of disfiguration, keratosis (leprosy-like skin lesions) and cancerous growths. Prolonged accumulation of As in the skin, hair and nails can lead to hyperpigmentation (flushed appearance, freckles), keratosis, and increased risks of skin, internal organ and lung cancers (Kapaj *et al*, 2006).

As intoxication risks increase as a function of exposure and duration, and a risk threshold can be assumed if inorganic As only reaches target organs when an individual's methylation capacity is saturated. However, only limited data support this assumption, and a risk threshold cannot be assumed if some inorganic As always reaches target organs regardless of methylation capacity (Tchounwou *et al*, 2004). Sub-clinical effects have proven difficult to link with As exposure, and the deterministic or stochastic nature of the dose-response relationship requires further clarification at present.

2.5. Measuring human exposure

Concentrations in human hair are widely accepted as a measure of toxic element exposure and hair is well suited to assess chronic As exposure (Sanz *et al*, 2007). It is a biological polymer and over 80% of its dry weight is made up of keratins, which are proteins containing a high percentage of S-containing amino acids. As has an affinity for sulfhydryl groups and the human metabolic pathway for As includes accumulation in S-rich hair and nails. The hair matrix is isolated from other metabolic processes once formed and concentrations measured in hair can reflect the mean level of As in the human body over two to five months (Gault *et al*, 2008). Furthermore, metal concentrations found in hair samples can be up to ten times higher than in blood or urine (Sanz *et al*, 2007), which are more useful for assessing acute exposure.

Hair As levels in Novia Scotia, Canada have been reported as less than 1000 µg kg^{-1}: in contrast, people in West Bengal exposed to contaminated drinking water have been reported with hair As ranging from 3000 to 10000 µg kg^{-1} (Le, 2002). People with no known excess exposure generally have hair As concentrations ranging from 20 to 200 µg kg^{-1}. Following several studies, the WHO considers 1000 µg kg^{-1} to be the expected value based on accepted dietary levels (Hindmarsh, 2002), while the Canadian government considers 5000 µg kg^{-1} of hair As to be evidence of significant ingestion (Peach & Lane, 1998).

Hair has a rigid and robust structure that is fairly resistant to degradation and is easy to collect, transport and store. A key challenge in measuring contaminant levels in hair is to remove external (exogenous) contamination of the sample, which is typically done with a pre-washing procedure. Common detection limits for As are in the range 0.4 to 0.5 µg L^{-1} under inductively-coupled plasma mass spectrometry (ICP-MS) (Morton *et al*, 2002). The ICP-MS technique broadly involves the ionisation of a sample and discrimination of the ionic mass of the analyte of interest (Jarvis *et al*, 1992). A concentric glass nebuliser aspirates the liquid sample with high temperature argon (Ar) to form an aerosol of droplets (Figure 3). Smaller droplets pass through a glass spray chamber and are mixed with more heated Ar gas to form an Ar plasma flame. The hot plasma atomises then ionises the sample, which is passed through a pumped vacuum system to remove the ions. The mass spectrometer separates ions according to their mass-to-charge ratio using a quadrupole mass filter (a four metal rod array aligned in a parallel diamond pattern). A particular combination of DC and AC electrical potential is applied to the array so only an ion with a specific mass-to-charge ratio is allowed to pass through to

an electron multiplier detector. These ions hit the surface of the detector and emit secondary electrons which are attracted to the positively-charged end of the detector where further electrons are emitted on collision. A cascade effect is created and the number of electrons is counted. The number of ions hitting the detector is proportional to the number of electrons and analyte concentrations can be derived using calibration standards.

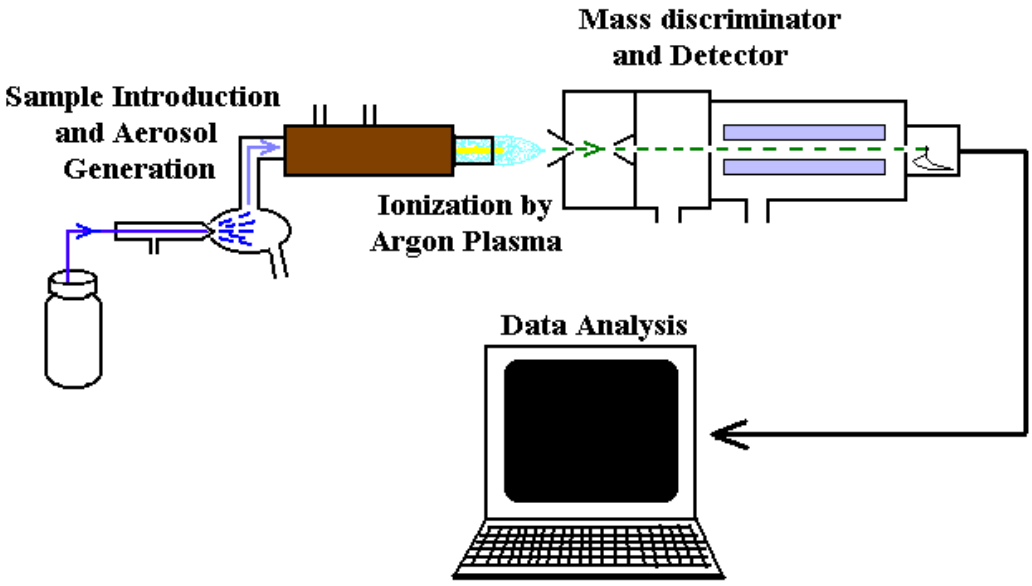


Figure 3: Schematic of the ICP-MS technique (Worley & Kvech, no date).

Polyatomic interferences can occur in mass spectrometry where ions such as Ar and chlorine (Cl) come together and form the same mass as the analyte of interest (Tanner *et al*, 2002). Physical interferences can also arise from differences in viscosity between liquid samples and calibration standards, and can affect the efficiency of nebulisation and transport to plasma (Jarvis *et al*, 1992).

3. The Tamar catchment

3.1. Physical characteristics

The River Tamar rises 6 km from the Atlantic Ocean at Bude in the north of the region, flowing south for nearly 80 kilometres to the English Channel and setting the boundary between the counties of Devon and Cornwall in the south-west of England. The river is classed as 'fairly responsive' with base flow index of 0.47 at the tidal limit at Gunnislake, and a mean annual flow of 30 $m^3 s^{-1}$ with occasional instantaneous flows greater than 100 $m^3 s^{-1}$ (Mighanetara *et al*, 2009). The freshwater Tamar catchment covers 920 km^2 and has maximum altitude of 586 m. Dartmoor in the east reaches over 500 m and Bodmin Moor in the west reaches over 300 m. Northern parts are elevated to around 200 m and the southern reaches of the catchment have elevation of less than 200 m. Average rainfall between 1961 and 1990 was 1216 mm yr^{-1} (Rawlins *et al*, 2003).

The bedrock geology is mostly Carboniferous sandstones and argillaceous sedimentary rocks in the northern area, the granite outcrops of Dartmoor and Bodmin Moor to the east and west respectively, and mostly fine-grained sedimentary rocks and chert to the south (Figure 4). The middle and upper catchment areas have a succession of folded sandstones and shales, with the proportion of sandstones falling against the shales from the middle to the lower areas (Langston *et al*, 2003). The underlying rocks have low permeability and porosity which limits groundwater flow and storage (Mighanetara *et al*, 2009). Granitic intrusions around 270 million years ago formed metamorphic aureoles around the granite bosses of Bodmin Moor and Dartmoor, and geological mineralisation, most common in the southern part of the catchment, resulted in high As enrichment compared to other areas of England (Webb, 1978).

Typical brown earth soils dominate the catchment and are prone to slight seasonal waterlogging. The soil types include 78% slightly acid to acid loamy soils, 9% slightly acid to acid loamy and clayey soils, and a further 9% blanket bog peat and very acid upland soils (Cranfield University, 2004). The soils overlying the Bude Formation in the north are more clayey than those of the south, which contain a fine silty fraction. Acidic podzols lie over the granite outcrops of Dartmoor and Bodmin Moor (Rawlins *et al*, 2003).

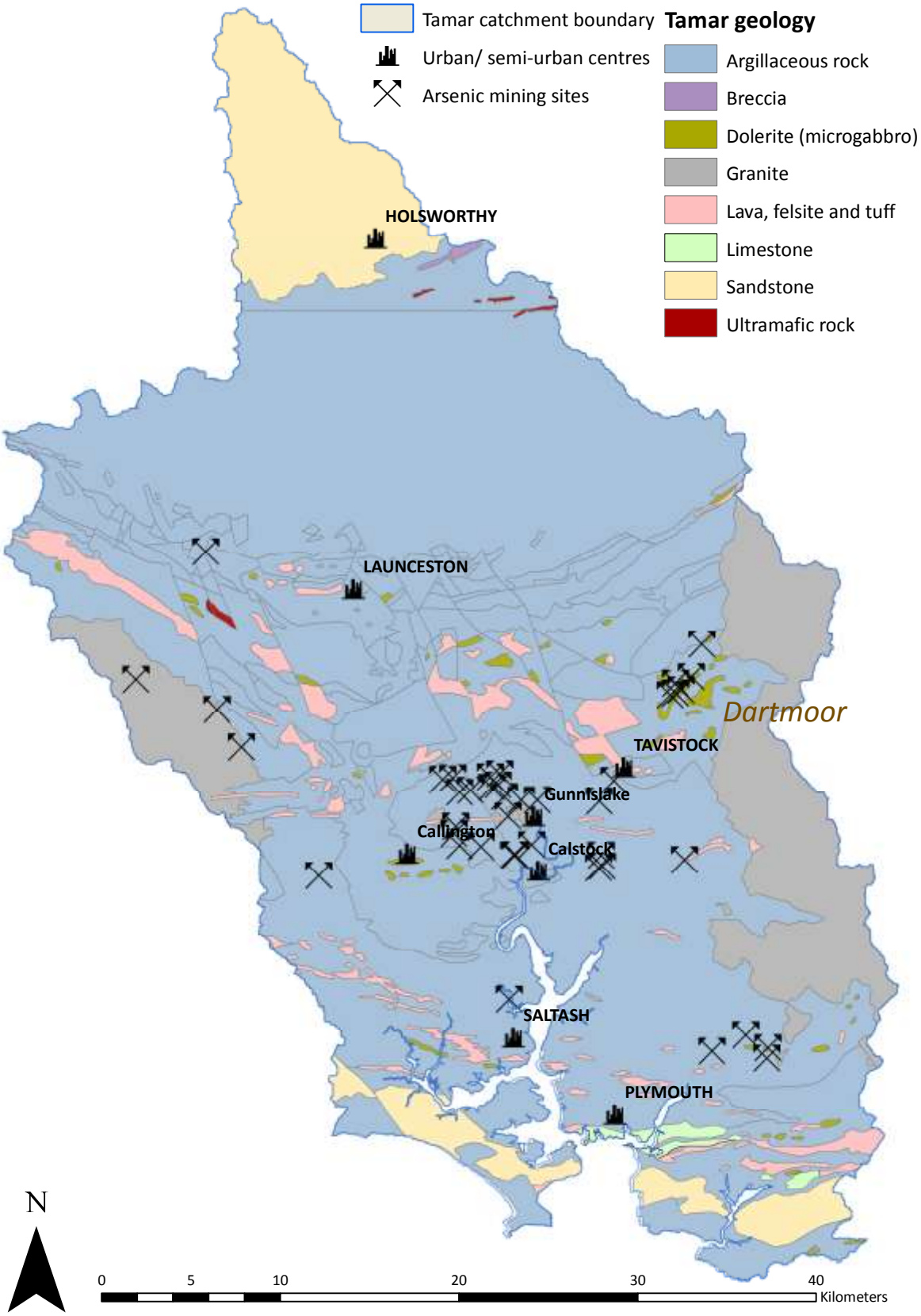


Figure 4: Bedrock geology and former As mining sites in the Tamar catchment. Geology data and the urban/ semi-urban centres were supplied by British Geological Survey/ EDINA (© Crown Copyright). Mining data was provided by the Environment Agency.

3.2. Land use and population

Land use in the Tamar catchment is predominately agricultural: 56% is grassland (78% of which is improved grassland); 21% is arable land; 12% is woodland; and 7% urban, suburban or rural-developed areas (CEH, 2002). Pasture and deciduous forest is evenly distributed throughout and arable land is most common in the north and west (Figure 5). The human population of the catchment is just over 374000 with 240000 (64%) resident in the City of Plymouth (ONS, 2001). Elsewhere the population is concentrated around urban or semi-urban centres where some areas have developed around farming communities and old mining villages (Figure 6).

3.3. Legacy of mining activities

Mining for metalliferous deposits of tin (Sn), Cu, Pb, Ag, Fe, As, Zn, tungsten (W) and Mn has been a feature of the catchment since the middle of the 18th century. The most important mineral resources were found in an 18 km x 6 km belt running east to west from the edge of the Dartmoor granite (Langston *et al*, 2003), and the principle economic minerals were FeAsS, $CuFeS_2$ and PbS. Sulphide ores were more prominent than Sn around Gunnislake and the Tamar Valley where 60% of the historic mine workings are located (Rawlins *et al*, 2003). FeAsS was considered a waste material at first but was mined from 1870: at the peak of mining activity during the mid to late 19th century most of the world's Cu and As supply came from the Gunnislake and Calstock mining district (Langston *et al*, 2003). As was commonly mined around Gunnislake but it was not produced further north.

The last mines closed around 1950 (Rawlins *et al*, 2003) but the influence of mining on the environment continues to this day. The catchment has been physically modified by the development of drainage adits to take mine water directly to the river, and large heaps of mine spoil, remains of engine houses and smelters are abundant around the old mining sites. Extremely high As concentrations are found in surface soils on or around spoil heaps, for instance up to 52000 mg kg^{-1} in the Devon Great Consols (DGC) mining area of the Tavistock district, and around 700 km^2 of land is affected when deposition from smelting processes is included (Farago *et al*, 1997). Significantly, most metals were transported to Wales as concentrated ores for smelting, but As was calcined in the Tamar Valley, where disused calciners around the old mining sites have been found to be highly contaminated with As compounds (Mighanetara *et al*, 2009). Large areas of land are un-vegetated due to high phyto-toxicity and poor nutrient availability, and there are significant risks of wind erosion and inhalation or ingestion of particulates.

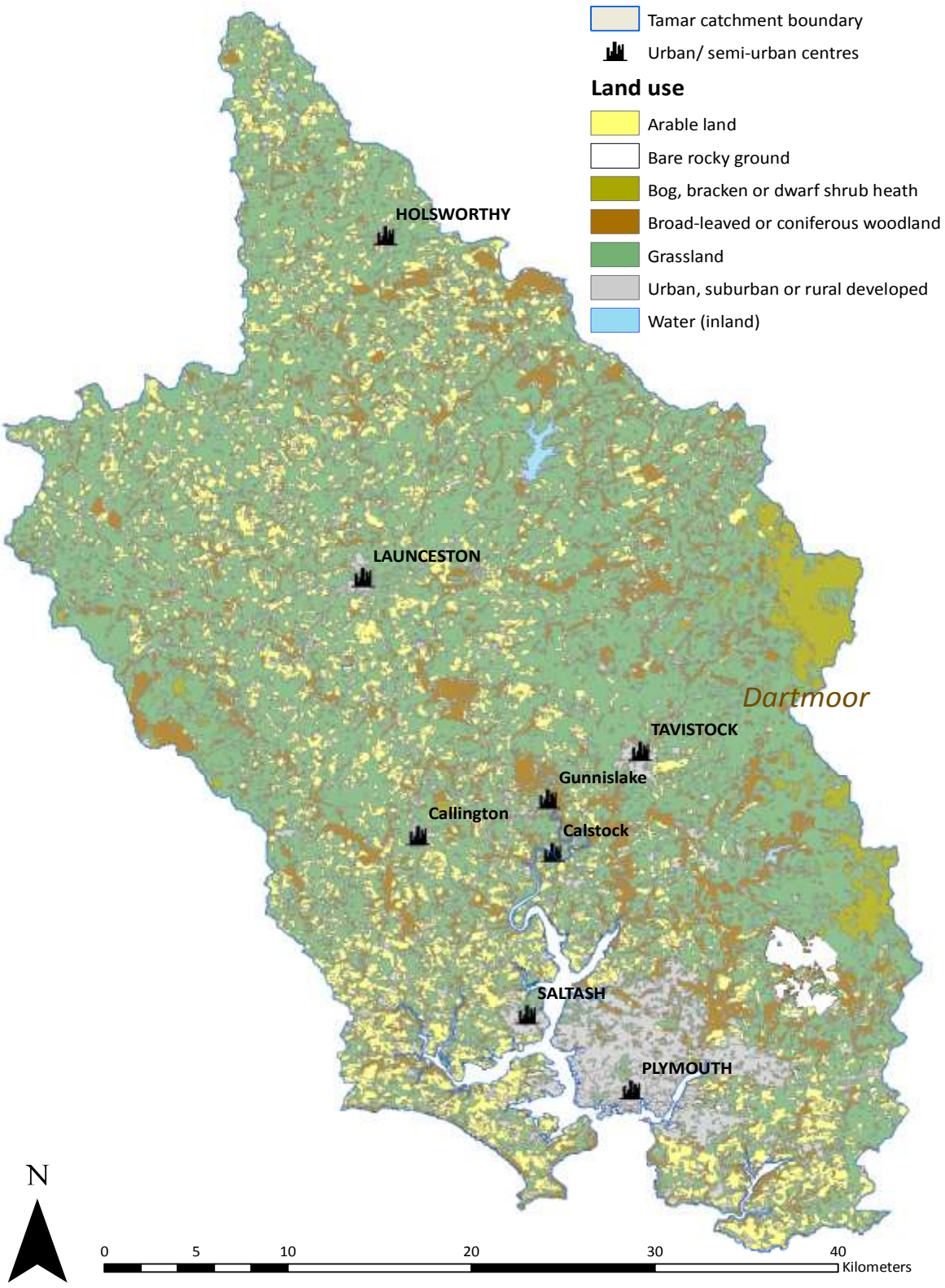


Figure 5: Land use categories in the Tamar catchment (CEH, 2002). Urban/ semi-urban centres were courtesy of EDINA (© Crown Copyright).

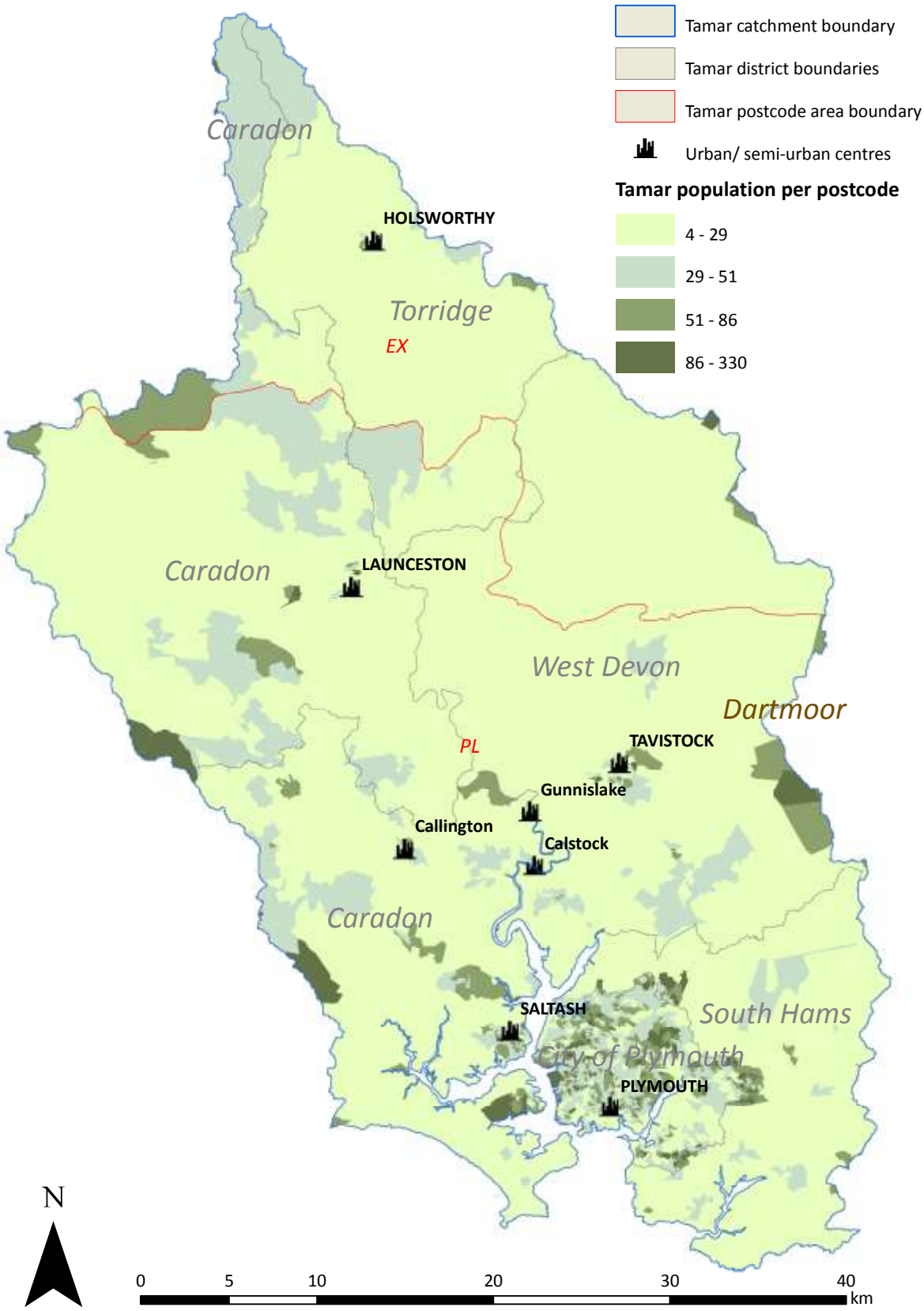


Figure 6: Resident population in the Tamar catchment by census output area averaged over postcode. Population, postcode and district boundaries are © Crown Copyright (source: National Statistics / Ordnance Survey). The locations of urban/ semi-urban centres were supplied by EDINA (© Crown Copyright).

3.4. Arsenic in the Tamar environment

In 2002 the BGS surveyed approximately 73% of the catchment for the G-BASE project. Elevated total As concentrations were reported in stream waters, stream sediments and topsoils around historic mining sites in the south and west of the catchment: the maximum value for each type of sample were found within two to three km of Callington and Gunnislake (

Table 4) (Rawlins *et al*, 2003). All zones except the southern zone have median As stream water concentrations in the typical range (Section 2.1), but the WHO drinking water guideline of 10 µg L^{-1} was exceeded by 1% of stream water samples (Figure 7). Nearly all (98%) sediment samples exceeded the Canadian interim freshwater sediment quality guideline with 54% of samples breaching the probable effect level (Figure 8) (CCME, 2002). Note these guidelines are for the protection of aquatic life rather than human exposure; there are no equivalent guidelines for the UK or Europe. The lowest soil As levels were found overlying the Bude and Crackington formations in the north, but median levels in the southern zone are higher than typically found (Section 2.1) and overall 35% of topsoil samples exceeded the Soil Guideline Value for residential use of 32 mg kg^{-1} (Figure 9) (EA, 2009). As concentrations were strongly correlated with Cu levels in all three sample media, implicating mining activities as the source of enrichment.

Table 4: Summary of G-BASE results for As in the Tamar catchment (Rawlins *et al*, 2003). Water samples were taken from 1st and 2nd order streams and topsoil samples were taken from a depth of 0 to 15 cm. Samples are evenly divided into survey zones according to their latitudinal map coordinates.

		Survey zones:			
Sample media	Statistic	All	North	Centre	South
Stream sediments (mg kg^{-1})	*n*	488	164	161	163
	Median	19.15	12.9	17.1	48.5
	Inter-quartile range	13.0 - 44.7	9.45 – 15.9	13.3 – 38.4	27.3 – 97.7
	Range	4.40 – 11000	4.40 – 27.7	7.20 – 550	9.9 – 11000
Stream waters (µg L^{-1})	*n*	488	164	161	163
	Median	0.70	0.60	0.60	1.10
	Inter-quartile range	0.50 – 1.10	0.40 – 0.70	0.50 – 0.90	0.70 – 2.60
	Range	0.20 – 33.8	0.20 – 5.70	0.20 – 8.50	0.20 – 33.8
Topsoil (mg kg^{-1})	*n*	468	158	155	155
	Median	22.3	16.4	23.1	46.8
	Inter-quartile range	16.5 – 42.0	13.9 – 19.9	17.5 – 35.9	32.3 – 82.8
	Range	6.80 – 15000	7.20 – 41.4	6.80 – 276	13.8 – 15000

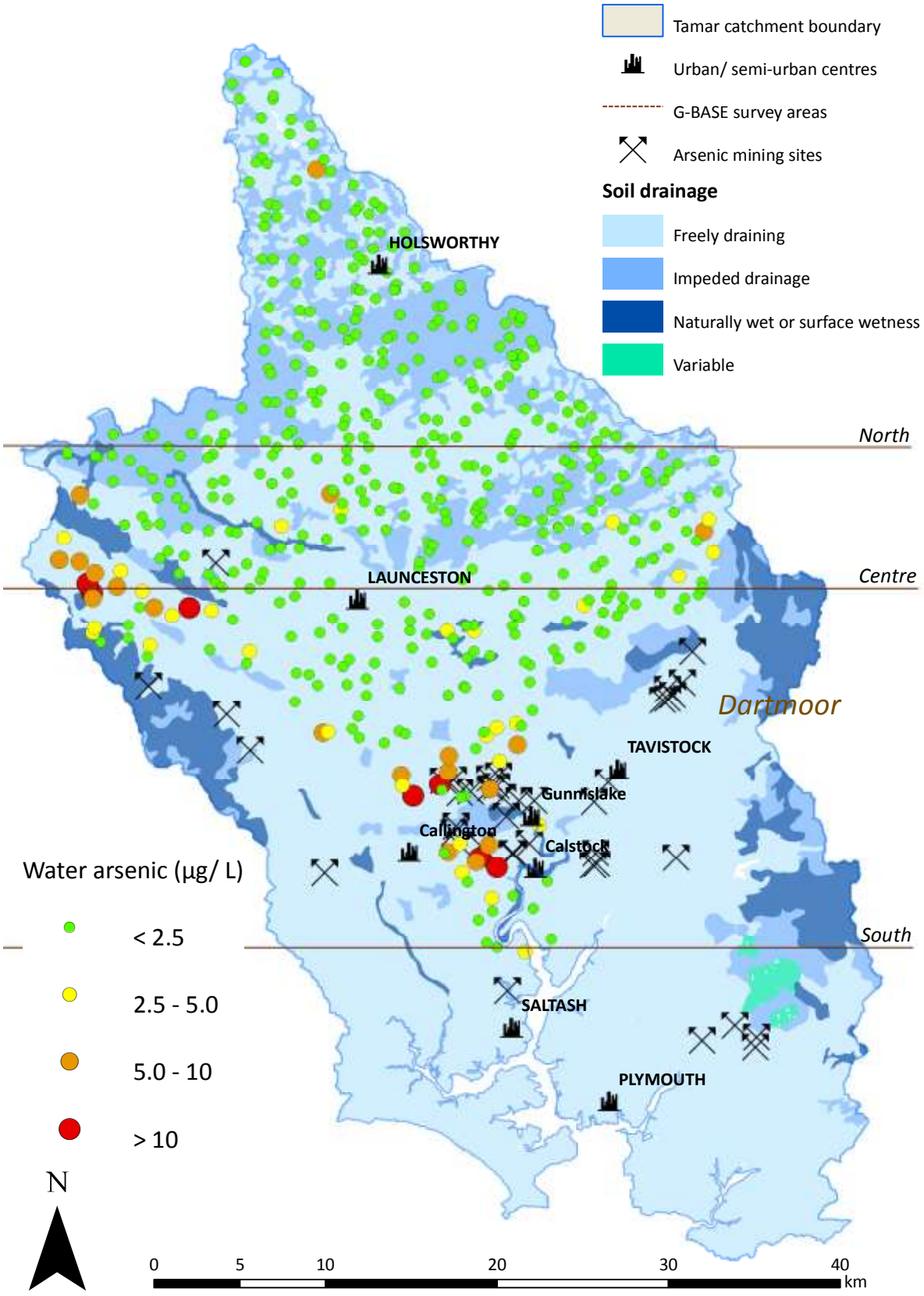


Figure 7: G-BASE As concentrations in stream waters and soil drainage types of the catchment (Rawlins *et al*, 2003; Cranfield University, 2004). Red symbols indicate levels higher than the 10 µg L^{-1} drinking water guideline (WHO, 2001). The locations of urban/ semi-urban centres were supplied by EDINA (© Crown Copyright), and mining data was provided by the Environment Agency.

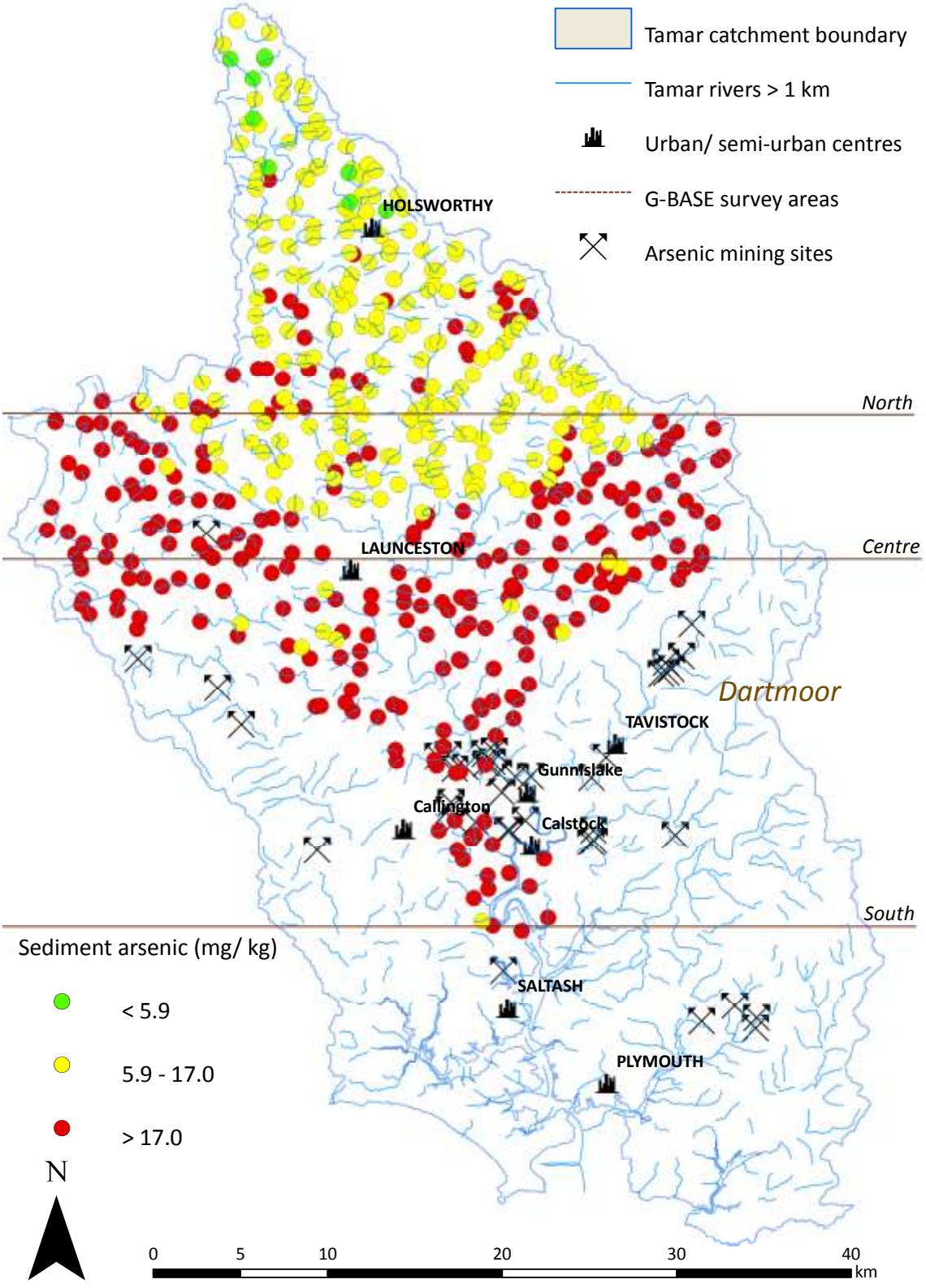


Figure 8: G-BASE As concentrations in stream sediments of the catchment (Rawlins *et al*, 2003). Red indicates levels higher than Canadian interim freshwater sediment quality guideline; yellow indicates levels higher than the probable effect level (CCME, 2002). The locations of urban/ semi-urban centres were supplied by EDINA (© Crown Copyright), and mining data was provided by the Environment Agency.

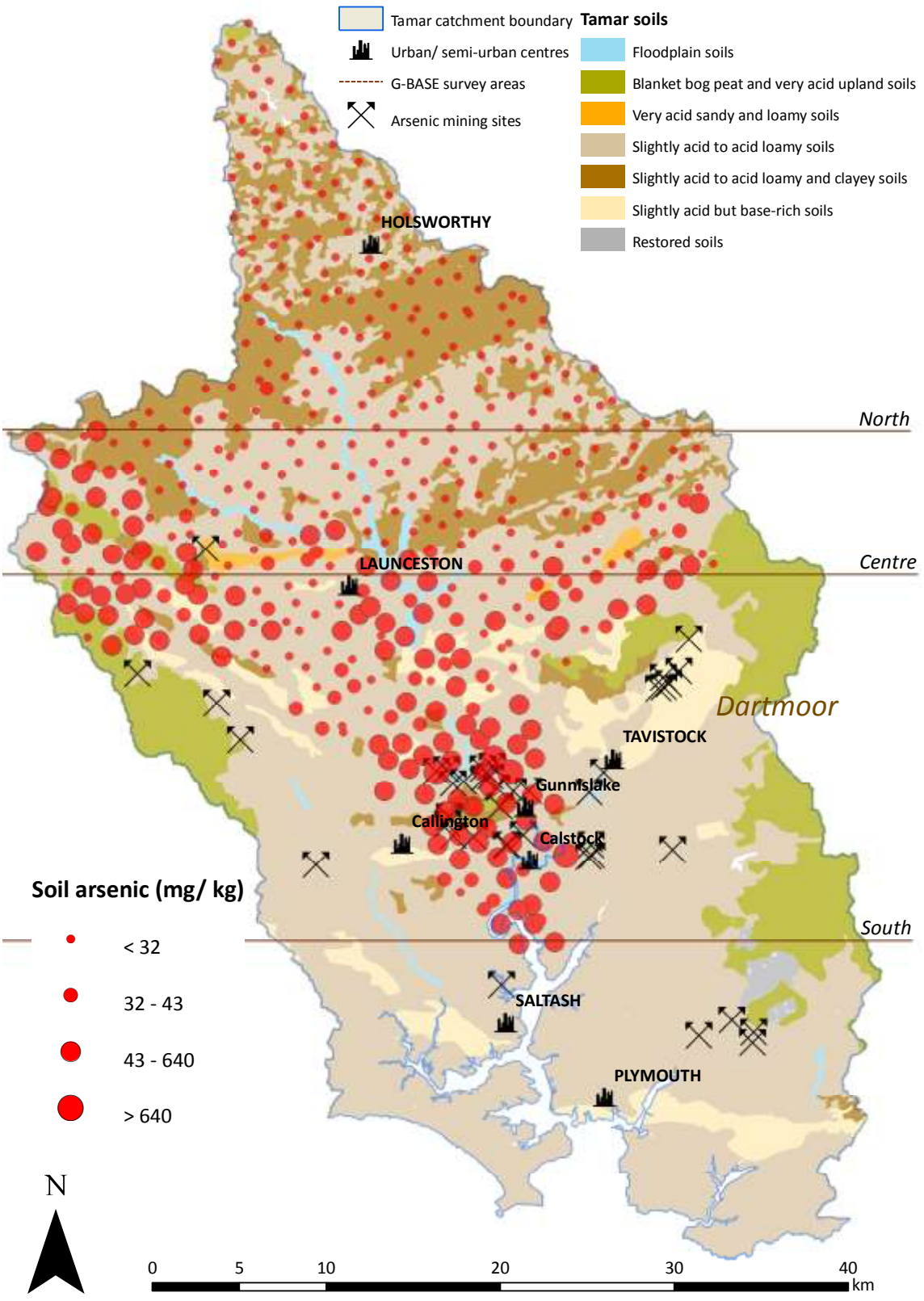


Figure 9: G-BASE As concentrations in surface soils and soil types of the catchment (Rawlins *et al*, 2003; Cranfield University, 2004). As levels are classified according to Soil Guideline Values: 32 mg kg^{-1} for residential use, 43 mg kg^{-1} for allotments, and 640 mg kg^{-1} for commercial use (EA, 2009). Restored soils are mostly from quarry and opencast spoil. The locations of urban/ semi-urban centres were supplied by EDINA (© Crown Copyright), and mining data was provided by the Environment Agency.

The G-BASE results for As in topsoils of the central and southern zones are higher than the range of 0.5 to 143 mg kg^{-1} found in UK rural soils, and all zones are higher than the range of 1.75 to 32 mg kg^{-1} found in UK urban soils (EA, 2009). Another BGS study analysed environmental samples from DGC and found As concentrations in the mine soils ranging from 249 to 68924 mg kg^{-1}, with a median value of 2105 mg kg^{-1} (Klinck *et al*, 2005). X-ray absorption near edge structure (XANES) analysis indicated that As^{V} was the dominant species in the mine wastes. Natural run-off from calciner ash piles contained 6577 µg L^{-1} of total As, and As^{III} was the main species found in surface waters and tailings water leachates. The authors concluded there was a toxic risk associated with the mine soils.

A more recent study focused on 25 drainage adits and streams in the Gunnislake and Calstock mining area, and found As concentrations of 1.3 to 560 µg L^{-1} in the dissolved phase and 1.0 to 1600 µg L^{-1} in the particulate phase (Mighanetara *et al*, 2009). Eight adits and 10 streams exceeded the WHO drinking water guideline, and 12 water courses breached the EC Dangerous Substances Directive (76/464/EEC) List II Water Quality Standard for As of 50 µg L^{-1}. The total As flux from the surveyed water courses was estimated as 1400 kg yr^{-1}; split 50% between dissolved and particulate phases. The authors noted high erosion risks from mine waste deposits located on or near the banks of the Tamar and tributaries: sediment taken from one stream running through a mine waste pile contained up to 186000 mg kg^{-1} As.

As exposure in the home environment of the south-west region has been explored in several studies. In Gunnislake and the DGC area As concentrations ranged from 24 to 3740 mg kg^{-1} in household dusts, and from 120 to 52600 mg kg^{-1} in garden soils (Farago & Kavanagh, 1999; Rieuwerts *et al*, 2006). Mean concentrations in the study areas were significantly higher than mean levels for the control areas used in each study. The more recent study found no relationship between levels of As in house dust and garden soils, but noted that 45% of study participants visited local mining sites at least once per week on average (Rieuwerts *et al*, 2006). The direct ingestion of As-contaminated soil and dust is suggested to be the most likely exposure pathway for humans in the Tamar catchment due to the regulation of contaminants in food and public water supplies. The maximum As concentration in water from the consumer's tap was 1.15 µg L^{-1} in 2008 (DWI, 2009). The exception to this may be where home-grown food and/ or private water supplies are consumed. There are no published studies of As in foodstuffs grown within the Tamar catchment, but there are an estimated 20000 to 30000 private boreholes in the catchment, including within old mining areas, which receive limited or no water treatment. Many of these private water sources are unregistered, but three wells tested by Carrick District Council contained As concentrations of 11, 60 and 80 µg L^{-1} (Farago *et al*, 1997).

Human biomarkers of As exposure in the Tamar catchment have been the subject of only a few studies. Urine samples from 24 residents of the Gunnislake and DGC area were analysed using high performance liquid chromatography coupled with ICP-MS (HPLC-ICP-MS) (Kavanagh *et al*, 1998). This study found that total As concentrations were significantly higher than those of the control group. Furthermore, inorganic As was detected in 88% of the study group's samples but was below the limit of detection in the control group's samples. Questionnaires completed by all study participants revealed no significant difference in diet between the two groups. The authors concluded that the Gunnislake and DGC area residents were chronically exposed to inorganic As from ingestion of soils and dusts.

Another biomarker study used particle-induced X-ray emission (PIXE) to analyse hair collected from 36 Cornish residents of Callington, Camborne, Gunnislake and Redruth (Peach & Lane, 1998). Hair As concentrations ranged from 1690 to 3330 µg kg^{-1} at the 95% confidence interval with an arithmetic mean value of 2510 µg kg^{-1}. 91% of the residents had hair As levels greater than 1000 µg kg^{-1}, the expected amount established by the WHO, and 21% had hair As concentrations greater than 5000 µg kg^{-1}. The results were found to be significantly higher than those for the control group in this study, which featured residents of Oxfordshire and Wiltshire.

In 2009 a pilot study used ICP-MS to analyse toenail samples provided by eight Devon residents who lived near an old As mine (Button *et al*, 2009). Total As concentrations ranged from 858 to 25981 µg kg^{-1} and were significantly elevated compared to the control group, which consisted of nine Nottinghamshire residents. The sample wash solutions were also analysed to determine exogenous As contamination as an indicator of environmental As levels. Higher concentrations were found in the exposed group compared to the control group, suggesting significantly higher levels of environmental As in Devon.

4. Methodology

4.1. Sample collection

Ethical approval for this study was granted by the Ethics Committee of the Faculty of Science and Technology at the University of Plymouth. Hairdressing businesses in Callington, Gunnislake, Holsworthy and Launceston permitted human hair samples to be collected on their premises. Customers of each business who consented to their hair being used in the study completed a brief questionnaire to record physical factors, such as their age, and lifestyle factors, such as whether they grew and/ or consumed locally-grown food. Participants' identities remain anonymous and their samples and questionnaires have been removed from this study at their request.

All hair samples examined for this study were taken from participants by staff members of each hairdressing business. Hair was cut or shaved directly from a random location on the head and immediately placed in a small polyethylene bag which was tied and labelled with an identifying code linked to each participant's questionnaire and consent form. All samples were returned to the laboratory later the same day and stored out of direct sunlight in a cardboard box.

4.2. Sample preparation and analysis

All laboratory equipment was soaked in 10% v/v hydrochloric acid (HCl) for at least 24 hours and rinsed in Milli-Q de-ionised water (MQ) before use; all reagents used in the study were of analytical grade.

Each hair sample was washed prior to digestion following a protocol established by the International Atomic Energy Agency (IAEA), who use human hair to monitor global trends of element levels in the environment (IAEA, 1976). Samples were removed from their polyethylene bags and placed in plastic centrifuge tubes. Samples were completely covered with acetone ($(CH_3)_2CO$, Fisher Scientific, Loughborough, UK), securely capped and shaken on a mechanical platform shaker (Stuart SSL1 Lab-Scale Orbital Shaker, Keison Products of Chelmsford, UK) for 10 minutes at 200 rpm. The acetone was drained off and the samples were covered by MQ before further shaking for 10 minutes. The MQ was drained off and the same acetone-MQ process repeated twice more before a final acetone step. The tube caps were loosened and samples were left to dry in an oven (BS Size Two, Weiss-Gallenkamp of Loughborough, UK) for approximately two hours at 60°C.

PTFE microwave digestion vessels were used to digest each sample. Each vessel was cleaned before use by adding 3 ml of 70% concentrated nitric acid (HNO_3, Fisher Scientific, Loughborough, UK), heating for two minutes at 50% power in a microwave (650 W power rating, model R2V16, Sharp Electronics (UK) Limited, Uxbridge, UK), rinsing with MQ and drying with tissue paper. Approximately 250 mg of each sample (or all available material when the sample amount was lower) was placed in a digestion vessel using plastic tweezers. 4 ml HNO_3 and 1 ml of 30% hydrogen peroxide (H_2O_2, Fisher Scientific, Loughborough, UK) was added and each vessel loosely capped. Samples were left overnight in a ducted fume cupboard to allow easily oxidised materials to be destroyed at low temperature. The vessels were then securely sealed and the samples heated in the microwave at 50% power for two minutes. The liquid digests were then filtered into glass volumetric flasks and diluted with MQ.

Ten samples were selected for replicate analyses to assess the precision of laboratory procedures used in the study. A human hair certified reference material (CRM) (NIES CRM No. 13, National Institute for Environmental Studies (NIES), Japan) was also prepared to assess the accuracy of procedures; the dry powder CRM was not washed before analysis. A blank sample and four external calibration standards in the range 2 to 100 µg L^{-1} were prepared using MQ and 1000 mg L^{-1} As solution (SpectrosoL 14250, Merck Pty. Limited, Feltham, UK). Total As concentrations in all samples and standards were analysed by ICP-MS using an X Series 2 (Table 5) (Thermo Elemental, Winsford, UK).

Table 5: ICP-MS operational settings for the analysis of total As in hair samples.

Power (kW)	1.40
Coolant (L Ar min^{-1})	13.0
Auxiliary (L Ar min^{-1})	0.70
Nebuliser (L Ar min^{-1}))	0.86
Nebuliser type	Concentric glass
Spray chamber type	Glass with impact bead
Dwell time (m s^{-1})	40.0

A collision cell was deployed before the quadrupole mass filter with 7% hydrogen in helium mixture bled into the cell at 4 ml min^{-1} to fragment any polyatomic interference. To avoid physical interferences calibration standards were matrix-matched with an independently prepared 100 µg L^{-1} As solution, and an internal standard spike of 1% v/v indium was added to all standards and samples.

4.3. Statistical and spatial analyses

Sample results were collated and summarised using Microsoft Excel XP 2002 (Microsoft Corporation). Hair As data was log-transformed to fit a normal distribution where at least 68% of the samples lay within one standard deviation of the mean, and 100% of the samples lay within three standard deviations.

Log-transformed data was categorised by physical and lifestyle factors according to participant questionnaire responses and statistically tested for significant differences using Statgraphics Plus version 5.1 (Statistical Graphics Corporation). Dixon's *Q*-test was used to identify potential outliers in the data. Parametric tests were used where the variances of sample subsets were not different: *t*-statistics were calculated to compare two unmatched subsets and one-way ANOVA *F*-statistics to compare more than two unmatched subsets. Non-parametric tests were used where the variances of the sample subsets were different: Mann-Whitney (Wilcoxon) *W* statistics to compare two unmatched sample subsets, and Kruskal-Wallis *H* statistics to compare more than two unmatched subsets. The test prefix (with confidence limit subscripted), calculated statistic and associated probability (*P*) are shown in brackets in the text to indicate which test has been used.

Spatial analysis of the sample results was conducted using ArcMap version 9.3.1 (ESRI Inc.). Postcode data from participant questionnaires was used to create mapped polygons of hair As levels, which were spatially joined to G-BASE survey point data contained in each postcode. Pearson's product moment correlations (R) and Spearman's rank order correlations (R_S) between hair As measurements and G-BASE data were calculated using SigmaPlot for Windows version 11 (Systat software Inc.). Significantly related hair As values and G-BASE data were used to derive a multiple regression equation using the least squares method in Statgraphics. Hair As values were estimated for the G-BASE survey area by fitting the model to G-BASE data and interpolating the results using the inverse distance weighting function in ArcMap (cell size of 250 m and a fixed distance of 1500 m).

5. Results and discussion

5.1. Accuracy and precision

Thirty-six replicate measurements had relative standard deviations (RSD) ranging from 15 to 145% (Figure 10), indicating reasonable precision of the method. A mean total As concentration of 74.7 µg kg^{-1} was measured in the human hair CRM with an upper 95% confidence limit of 88.1 µg kg^{-1}. This is significantly below ($t_{0.05}$ = 5.99, P = 0.009) the quoted reference value for As of 100 µg kg^{-1} dry weight (NIES, 1996), and implies an extraction efficiency of 74.7%.

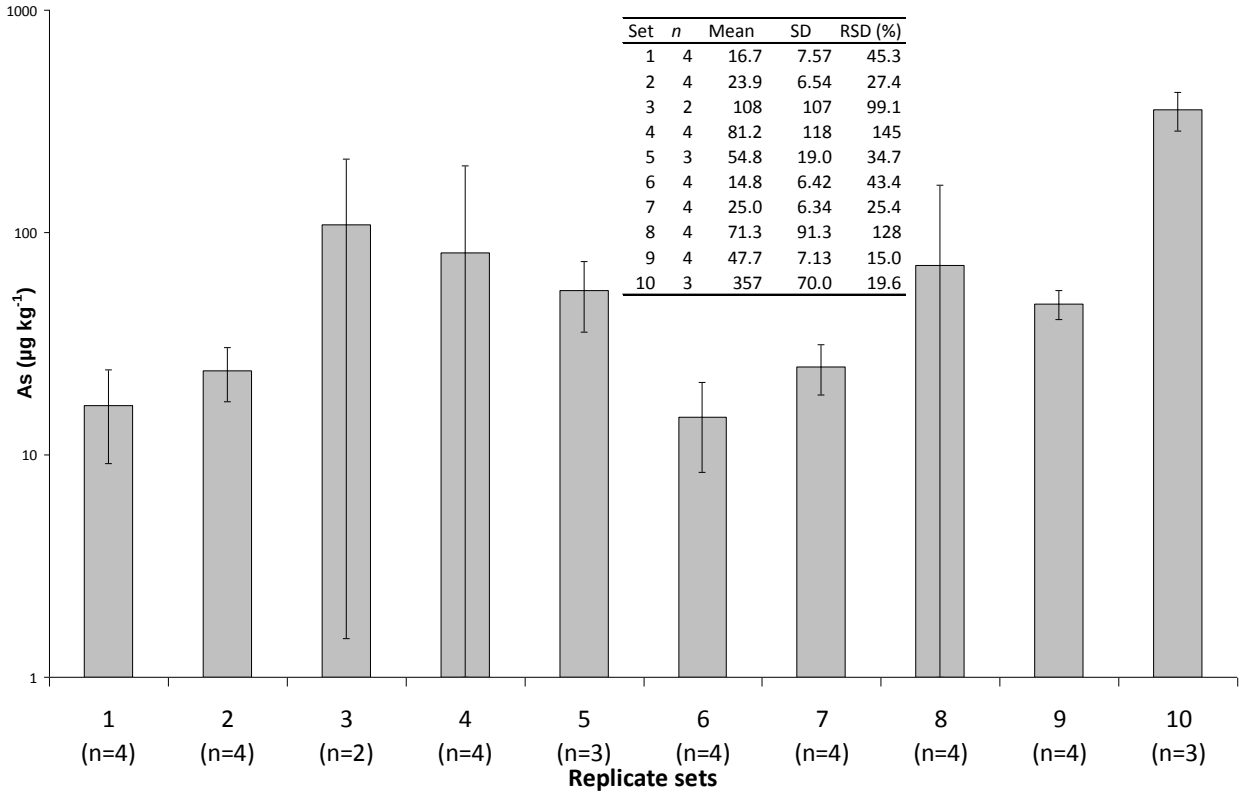


Figure 10: Assessment of laboratory precision showing mean replicate measurements on a logarithmic scale; error bars represent the standard deviation.

As levels in hairs from the head of one individual can vary greatly (Hindmarsh, 2000), but exogenous contamination is one of the most important sources of error when collecting samples. It is recommended that hair samples be cut directly at the skin in the occipital region at the back of the head (Müller & Eckard, 1997), but in this study no attempt was made to control where hair was taken from participants' heads. Error may also have been introduced while transferring hair samples between vessels in the laboratory. Moisture retention in the hair matrix after washing and oven-drying was another problem observed in the laboratory: this could influence the weight of measured samples and affect the calculation of As content. Hair samples could not be weighed before washing because small amounts of sample were sometimes lost during the draining of wash liquids. The discrimination of exogenous As from As metabolised and secreted in hair (endogenous As) has been the subject of several studies. The washing procedure could be a confounding factor if both exogenous and endogenous As are

removed from the sample. It has been claimed the IAEA protocol does not remove endogenous As (Yanez *et al*, 2005), but other studies suggest there is no accepted washing procedure that can distinguish between endogenous and exogenous As (Morton *et al*, 2002).

5.2. Arsenic levels in catchment residents

Hair samples were collected from 96 individuals at five hairdressing businesses in Callington, Gunnislake, Holsworthy and Launceston. None of the participants asked for their hair sample to be removed from the study. The limit of detection (LOD) for the method was 0.023 µg L^{-1}, representing the noise from three standard deviations of the mean blank signal. The average weight of hair sample used in the laboratory was 217 mg, ranging from 3.00 to 273 mg.

Five samples from Gunnislake were below LOD and are excluded from the results. The As concentrations of the remaining 91 hair samples ranged from 4.87 to 1150 µg kg^{-1} with a positively-skewed distribution of results (Table 6). Three samples exceeded 1000 µg kg^{-1} which is the expected value based on accepted dietary levels (WHO, 2001). These samples were not determined to be outlying values ($Q_{0.05}$ = 0.007, P < 0.350), but excluding these three samples the next highest hair As value was 380.1 µg kg^{-1}.

Table 6: Summary statistics of hair As concentrations for all samples and by sources of samples.

Statistic	All samples	Callington	Gunnislake	Holsworthy	Launceston
n	91	27	12	24	28
Geometric mean (µg kg^{-1})	43.1	88.7	43.4	29.2	30.0
95% confidence interval (µg kg^{-1})	33.7 – 55.2	53.3 – 148	17.7 – 106.3	21.3 – 40.0	21.8 – 41.2
Range (µg kg^{-1})	4.87 - 1150	11.7 - 1130	4.87 – 1150	7.49 – 244	6.23 - 291

The hair As levels were significantly lower than previously found in the region (Section 3.4), but those results may not be comparable because substantially different techniques were employed. For instance, samples were washed once in hexane and rinsed in distilled water, then pressed into pellets using a steel die and heated hydraulic press. A PIXE technique was used where 13 of 36 samples (36%) were below LOD whereas only five of 96 samples (5%) were below LOD using extraction and determination by ICP-MS. The earlier study collected samples from Callington, Gunnislake, Cambourne and Redruth but made no distinction between sources of samples in the results. The latter two areas are outside the Tamar catchment and cannot be considered in this study.

Compared to typical hair As concentrations (Section 2.5), 59.3% of the samples were within the normal unexposed range, 27.5% were below and 13.2% were above. The

range of As levels in hair samples from participants in Holsworthy and Launceston in this study is very similar to a study of unexposed urban residents of Umeå and Luleå in north-east Sweden. The participants in this research (n = 114) had no known occupational exposure and their hair As levels ranged from 34 to 319 µg kg^{-1} (Rodushkin & Axelsson, 2000). If the three samples exceeding 1000 µg kg^{-1} are excluded, the Swedish study is also very similar to those samples from Callington and Gunnislake.

5.3. Physical and lifestyle influences

There were no significant differences in the concentrations of As in hair samples collected in this study based on gender ($t_{0.05}$ = 1.30, P = 0.199) or age groups ($F_{0.05}$ = 0.870, P = 0.423) (Table 7). Participants' ages were categorised according to how active they might be in the outdoors, and therefore more exposed to environmental As. Two of the samples exceeding 1000 µg kg^{-1} were from males, one aged 19 to 38 and the other aged 59 to 88, and the third sample was from a female who was also in the age group 59 to 88. It is difficult to relate levels of As in hair to more general factors such as age and gender because a large number of other factors can contribute to exposure (Khan *et al*, 2009). Peach & Lane (1998) reported no significant differences between the genders in hair As concentrations, and also found the male exposed population had significantly higher levels than the control group, but the female exposed population did not. Archer *et al* (2005) found higher hair As levels in individuals aged over 30, but this trend was only confirmed in urine data for males but not females.

Table 7: Hair As levels grouped by physical factors; residence refers to the number of years the participant has lived at their current postcode.

Physical factors	Category	*n*	Geometric mean (µg kg^{-1})	95% confidence interval (µg kg^{-1})	Range (µg kg^{-1})
Gender	Female	34	34.9	23.3 – 52.4	4.87 – 1150
	Male	57	48.9	35.9 – 66.7	7.49 – 1130
Age group [1]	19 to 38	34	46.7	32.2 – 67.6	7.49 – 1101
	39 to 58	31	34.5	23.6 – 50.3	6.23 – 380.1
	59 to 88	25	51.5	28.8 – 92.1	4.87 – 1150
Residence (years)	≤ 5	21	57.1	30.1 – 108	6.23 – 1150
	6 to 15	33	40.9	26.6 – 63.0	4.87 – 1130
	> 15	36	38.7	28.3 – 52.8	8.61 – 380.1

The participants' number of years of residence was categorised as short term (less than or equal to five years), medium term (6 to 15 years) or long term (more than 15 years). As levels did not vary significantly between different categories of residence ($F_{0.05}$ =

[1] One male participant in Callington provided a hair sample but did not complete a questionnaire therefore the total sample size is 90 for all factor categories except gender and source of sample.

0.740, $P = 0.480$). Two of the samples exceeding 1000 µg kg^{-1} were from short term residents who had lived in their area for five years, while the other had been living in their area for six years. Peach & Lane (1998) obtained hair samples from long-term residents in their earlier study but gave no information about number of years of residence or how this influenced their results.

The use of private water supplies instead of regulated public supplies caused no significant difference in As concentrations in participants' hair ($t_{0.05} = 0.448$, $P = 0.655$) (Table 8). Many studies of As exposure focus on drinking water as the primary driver for risk, especially as dissolved As species have high bio-availability (Khan *et al*, 2009). It is surprising that no significant difference was found for this factor considering the geological profile of the catchment and the private wells tested by Carrick District Council (Section 3.4). Although the number of these participants is low ($n = 8$) this does represent 9% of all participants. Furthermore all three samples that exceeded 1000 µg kg^{-1} were taken from participants who received their water from regulated supplies. There is very limited data available on private water supplies in the region so it cannot be assumed to be a source of high As exposure. Indeed, individuals using their own water supplies may be more aware of possible risks and take necessary precautions.

Table 8: Hair As levels grouped by lifestyle factors: the factor 'Local food' refers to whether the participant grew or consumed locally-grown food; the category 'Mains' indicates the participant received South West Water regulated water supplies.

Lifestyle factors	Category	*n*	Geometric mean (µg kg^{-1})	95% confidence interval (µg kg^{-1})	Range (µg kg^{-1})
Water supplies	Mains	82	44.0	33.8 – 57.3	4.87 – 1150
	Private	8	36.0	16.3 – 79.3	11.5 – 225
Local food	No	58	37.6	27.1 – 52.0	4.87 – 1150
	Yes	32	55.7	38.5 – 80.7	11.5 – 1130
Time spent outdoors (days per month) [1]	≤ 3	23	54.6	29.0 – 103	8.61 – 1150
	4 to 7	26	32.8	20.2 – 53.2	4.87 – 380.1
	8 to 27	21	43.4	31.2 – 60.4	7.49 – 333
	30	19	49.7	30.2 – 81.5	13.6 - 369
Smoker	No	70	43.6	33.0 – 57.8	4.87 – 1150
	Yes	20	41.8	23.9 – 72.9	7.49 – 1101
Hair dyed	No	66	50.2	37.3 – 67.6	7.49 – 1150
	Yes	24	28.6	18.7 – 43.9	4.87 – 244

Time spent outdoors was categorised as rarely (three days or less each month), occasionally (four to seven days), frequently (eight to 27 days), and every day (30

[1] The total sample size is 89 for this factor because one person did not answer this question.

days). There were no significant differences between categories of time spent outdoors ($H_{0.05}$ = 3.35, P = 0.341), whether they smoked cigarettes or tobacco ($t_{0.05}$ = 0.141, P = 0.888), or whether they dyed their hair ($t_{0.05}$ = 1.98, P = 0.051). Smoking cigarettes is a potential confounding factor due to As added to commercial cigarettes, but Rodushkin & Axelsson (2000) also report no significant difference in hair As between those who smoked and those who didn't. Of the three samples that exceeded 1000 µg kg^{-1} one participant smoked cigarettes or tobacco while none of these participants dyed their hair or spent any time in the outdoors.

Participants who grew or consumed locally-grown food were found to have significantly higher As levels than those who didn't ($W_{0.05}$ = 1179, P = 0.035) (Figure 11) although only one of the samples exceeding 1000 µg kg^{-1} was from a participant who used local food. However, participants using local food and private water supplies had more than three times the hair As level than those using private water supplies but not local food, and medium to long term residents who were using local food had hair As concentrations around twice as much as medium to long term residents who weren't using local food. Despite these findings, no significant interactions between participants' use of local food and any other factor were found (Table 9). This is unexpected; growing food locally would involve more time spent outdoors and therefore regular exposure to environmental As. Participants' responses may have an element of bias because of the aspirational value of growing or consuming locally-grown food in English society. Additionally the two-way ANOVA for local food and time spent outdoors had low statistical power of 0.159, suggesting sample sizes in each category were not representative.

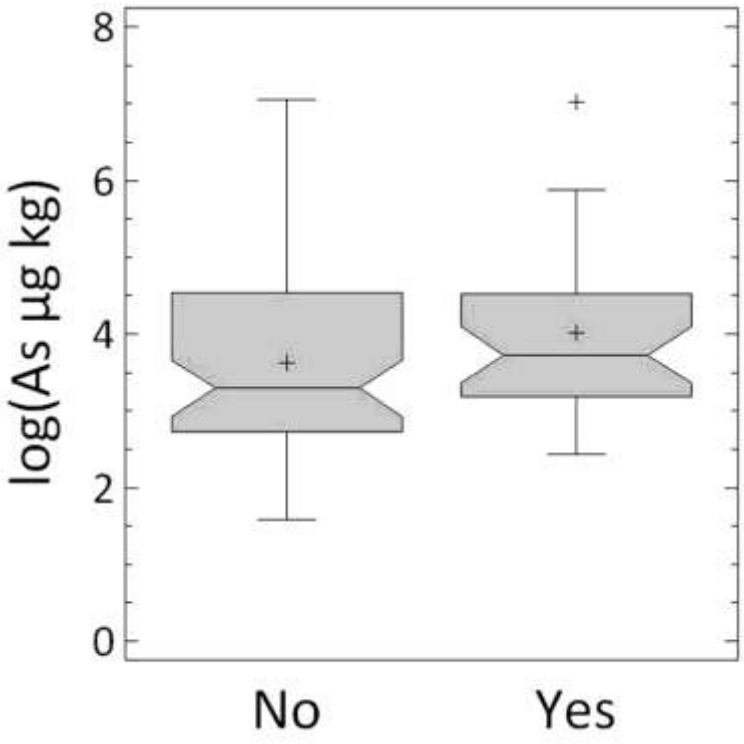


Figure 11: Box and whisker plot of hair As levels and use of local food. 'No' and 'yes' refers to whether participants grew or consumed locally-grown food.

Significant correlations between As concentrations in hair and dietary intake have been observed in previous studies (Al Rmalli *et al*, 2005; Khan *et al*, 2009). Dietary intake of As is generally related to the geographic source of the food and the level of As enrichment found there, and it is estimated that people living in As-contaminated areas ingest 30 times more As from food than people living in non-contaminated areas(Khan *et al*, 2009). In addition, As bio-accessibility is generally higher in soils contaminated by anthropogenic activities than in soils enriched geogenically (Smith *et al*, 2009).

Table 9: Hair As levels for the 'Local food' category grouped by physical and lifestyle factors. The two-way ANOVA *F* statistic and probability is shown in brackets for each factor.

Physical or lifestyle factors	Category	*n*		Geometric mean (µg kg^{-1})		Range (µg kg^{-1})	
		Local food = 'Yes'	Local food = 'No'	Local food = 'Yes'	Local food = 'No'	Local food = 'Yes'	Local food = 'No'
Gender	Female	13	21	37.4	33.5	11.5 – 150.2	4.87 – 1150
($F_{0.05}$ = 0.831, *P* = 0.364)	Male	19	37	73.2	40.1	16.9 – 1130	7.49 – 1101
Age group	19 to 38	10	24	47.7	46.3	21.1 – 295	7.49 – 1101
($F_{0.05}$ = 0.402, *P* =	39 to 58	8	23	49.5	30.4	11.5 – 223	6.22 – 380.1
0.670)	59 to 88	14	11	66.7	37.0	16.9 – 1130	4.87 – 1150
Residence (years)	≤ 5	5	16	70.3	53.5	26.8 – 295	6.23 – 1150
($F_{0.05}$ = 1.475, *P* =	6 to 15	11	22	82.3	28.8	11.5 – 1130	4.87 – 296
0.235)	> 15	5	20	70.3	37.8	26.8 – 295	8.61 – 380.1
Water supplies	Mains	27	55	55.6	39.2	16.7 – 1130	4.87 – 1150
($F_{0.05}$ = 0.858, *P* = 0.357)	Private	5	3	56.5	16.9	11.5 – 357	15.3 – 19.7
Time spent outdoors	≤ 3	5	18	54.3	54.7	11.5 – 1130	8.61 – 1150
(days per month)	4 to 7	4	22	100.3	26.8	23.4 – 223	4.87 – 380.1
($F_{0.05}$ = 1.574, *P* =	8 to 27	11	10	64.7	28.1	20.8 – 333	7.49 – 71.4
0.202)	30	11	8	43.8	59.0	16.9 – 357	13.6 - 369
Smoker	No	27	43	57.3	36.8	11.5 – 1130	4.87 – 1150
($F_{0.05}$ = 0.133, *P* = 0.716)	Yes	5	15	48.1	39.8	20.9 – 98.6	7.49 – 1101
Hair dyed	No	25	41	63.7	43.4	16.9 – 1130	7.49 – 1150
($F_{0.05}$ = 0.034, *P* = 0.854)	Yes	7	17	34.6	26.5	11.5 – 129	4.87 – 244

5.4. Spatial distribution

The spatial distribution is represented by hair As values aggregated to participants' postcodes (Figure 12). Higher levels are apparent in the southern zone of the G-BASE survey area, and the overall distribution pattern is similar to the G-BASE survey results, particularly those for As in topsoils (Figure 13). However there were no significant differences in hair As concentrations between G-BASE survey zones ($H_{0.05}$ = 3.14, P = 0.208). The participants lived in 70 different postcodes and 13 different postcode districts (the first three or four characters of a postcode) within the catchment. There were no significant differences in participants' mean hair As concentrations between postcode districts ($H_{0.05}$ = 17.4, P = 0.134), although 90% of samples were concentrated in just five postcode districts and the remaining districts did not have representative samples. There was also no significant difference in hair As levels between the 'EX' postcode area (n = 27) and the 'PL' postcode area (n = 63) ($W_{0.05}$ = 1044, P = 0.893).

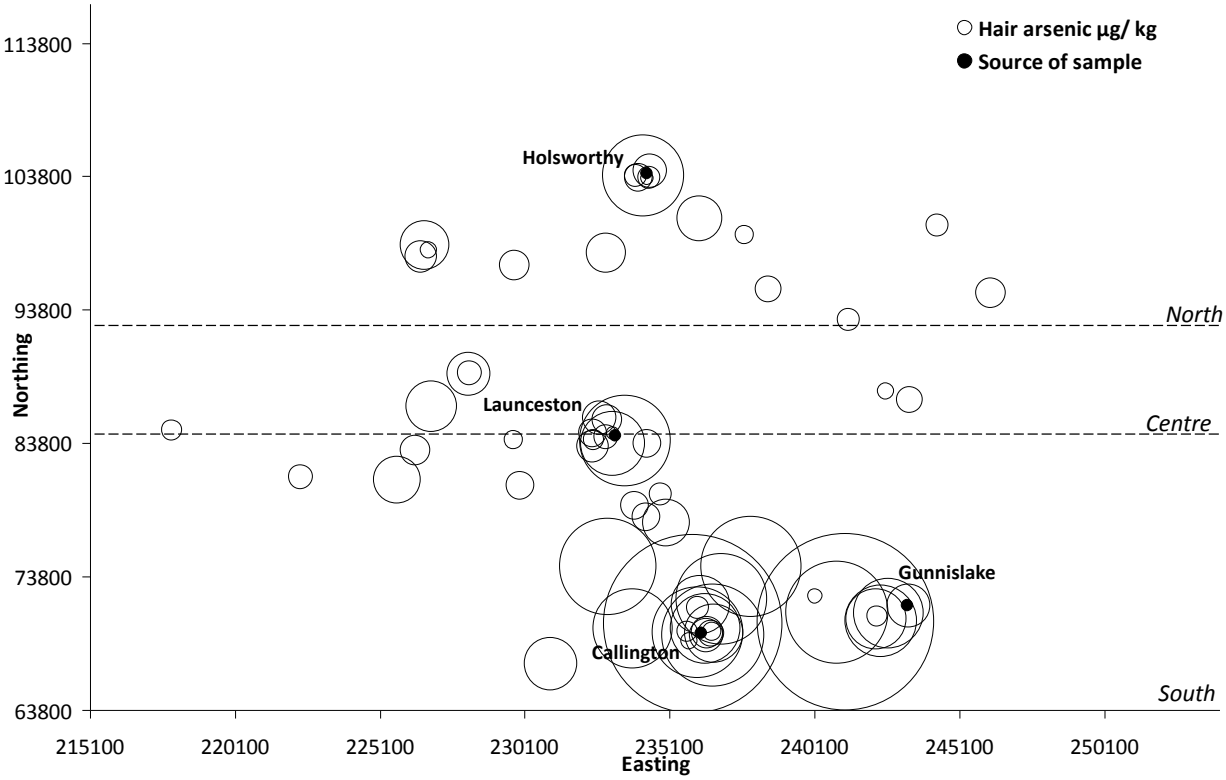


Figure 12: Spatial representation of total As concentrations in hair samples. The size of each transparent circle represents the mean hair As value in each postcode; the black dots show the sources of hair samples. The northing and easting scales cover the same area as the G-BASE survey of the catchment. G-BASE survey zones are shown as dashed lines; these represent the zones described previously in Table 4

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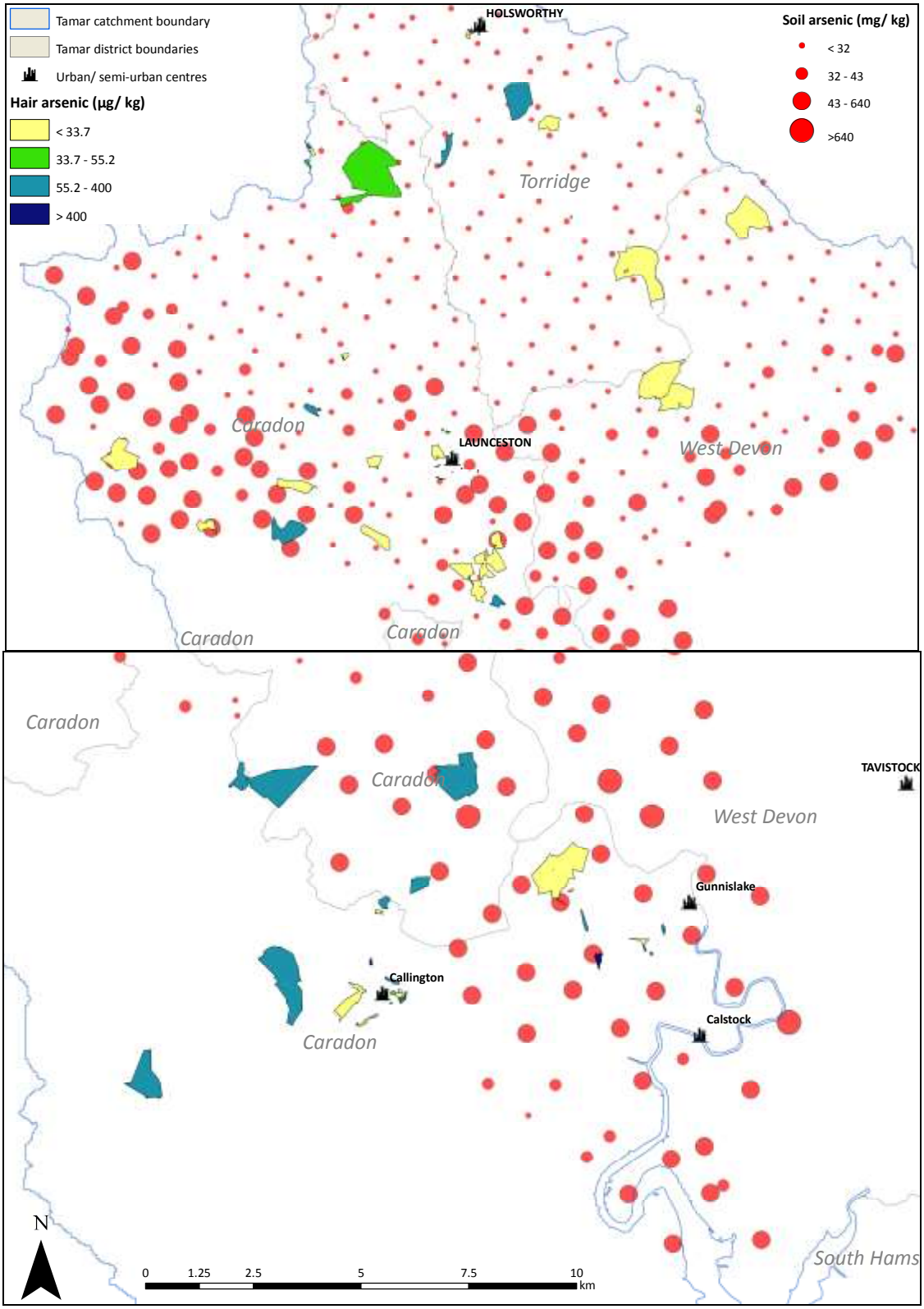

Figure 13: Hair As levels aggregated to participants' postcodes categorised as below, within, and above 95% confidence limits (Table 6), and G-BASE results for soil As (Rawlins *et al*, 2003). The top section shows the area around Holsworthy and Launceston, the bottom section the area around Callington and Gunnislake. District boundaries are © Crown Copyright (source: Ordnance Survey), and the locations of urban/ semi-urban centres were courtesy of EDINA (© Crown Copyright).

The source of samples was used as a proxy indicator for spatial distribution of hair As levels because 61% of participants lived within 5 km of each hairdressing business. Callington participants had significantly higher As concentrations than Holsworthy and Launceston participants ($H_{0.05}$ = 11.3, P = 0.010) (Figure 14). Hair As in samples from Gunnislake participants were not significantly different to those from any other location ($H_{0.05}$ = 0.215, P = 0.898). Two of the samples that exceeded 1000 mg kg^{-1} were from participants in Callington while the other was from a participant in Gunnislake.

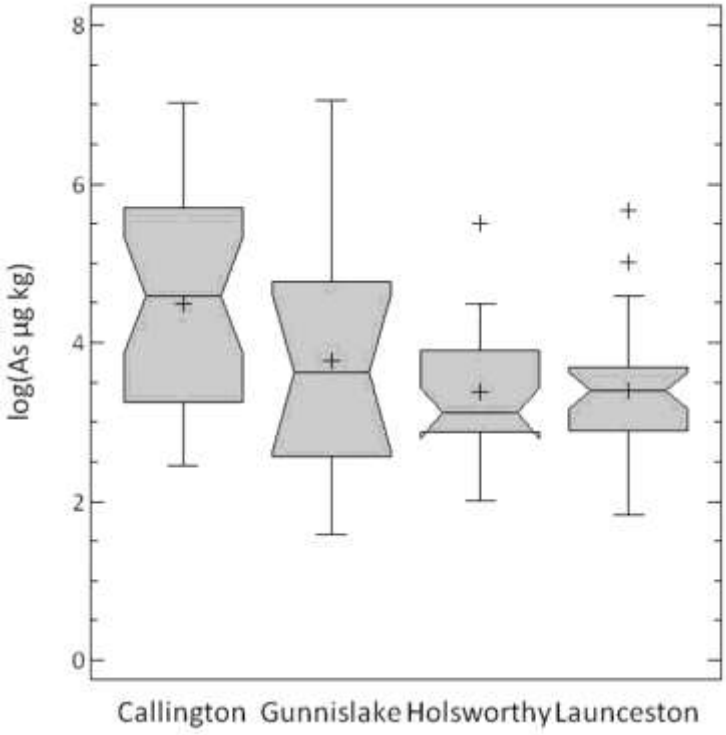

Figure 14: Box and whisker plot of hair As levels and the sources of hair samples.

No significant interactions between the sources of samples and any other factor were identified. However, Callington and Gunnislake participants using local food had twice the hair As levels than those who weren't: this is consistent with the findings above (Figure 11) and other studies (Khan *et al*, 2009). Callington and Gunnislake hair samples from short term residents had higher As concentrations than medium or long term residents, and the oldest group of Callington participants had nearly twice the level of hair As than the youngest group. The former is unexpected because longer residence in a contaminated area would suggest higher exposure to environmental As. The latter seems more consistent because older participants may have been resident for longer, and may have accumulated more As over time. These findings were not confirmed in Holsworthy or Launceston however, and the difficulty may be caused by the large number of factors that contribute to As exposure and uptake. For instance, human nutrition can be an important factor: studies in Bangladesh estimated 69% of arsenicosis patients were malnourished, i.e. where their body mass index was less than 20 kg $m^{2\ -1}$, and found higher susceptibility to arsenicosis in people with poor nutritional status (Khan *et al*, 2009). It has also been shown that high carbohydrate, high protein or high fat diets can increase the effects of As toxicity.

5.5. Bio-available and bio-accessible arsenic

Hair As concentrations aggregated to postcodes were spatially matched to 28 different G-BASE samples of stream sediments, stream waters and topsoils. A multi-element correlation found four elements were significantly correlated at the 99% confidence level (two inversely and two positively correlated), and a further six elements were significantly correlated at the 95% confidence level (Table 10). The pH and conductivity (Eh) of stream waters were also significantly correlated at the 95% confidence level. A one-to-one relationship was found between hair As levels and soil pH and Eh, but these are excluded because only two measurements were spatially matched in each case.

Table 10: Spearman's rank correlations between hair As and G-BASE data ordered by strength of relationship (R_s). Probabilities shown in bold indicate significant relationships at the 99% confidence level.

Sample media	G-BASE analyte	*n*	Correlation with mean hair As (R_s)	Probability (*P*)
Topsoils	P	13	-0.759	**0.00181**
Topsoils	Zr	13	0.717	**0.00528**
Stream waters	Li	15	0.715	**0.00235**
Topsoils	Cu	13	-0.681	**0.00948**
Topsoils	Rb	13	-0.678	0.0103
Stream sediments	Bi	15	-0.629	0.0116
Topsoils	Bi	13	-0.622	0.0222
Stream waters	U	15	0.605	0.0166
Stream waters	pH	15	0.565	0.0275
Topsoils	Ga	13	-0.551	0.049
Stream sediments	Ba	15	0.549	0.0325
Stream waters	Eh	15	0.538	0.0367

Hair As levels were most strongly correlated with soil As (R_s = -0.391, *P* = 0.179) of the three different G-BASE sample media while As in stream waters had no linear relationship (R_s = 0.041, *P* = 0.873). This could suggest soil is the main As exposure pathway for humans, but there were no significant correlations between As in G-BASE sample media and hair As levels. It is widely accepted that the use of total element concentrations overestimates risks of contaminant exposure (Smith *et al*, 2009), but in addition elemental concentrations simply indicate partitioning in particular environmental media. It is environmental conditions and geochemical associations that influence a substance's mobility between partitions and therefore bio-accessibility and bio-availability. As itself could be relatively stable in an environmental partition and therefore have less influence on bio-accessibility than the presence or mobility of other elements or different levels of acidity.

A significant relationship (Figure 15) was found between log-transformed data for hair As concentrations and five independent variables from the G-BASE dataset: Cu,

phosphorus (P) and zirconium (Zr) in topsoils; and pH and Eh in stream waters ($F_{0.10}$ = 89.95, P = 0.079). The fitted model provided a good description of the available data (R^2 = 99.8%, mean absolute error = 0.015, Durbin-Watson statistic = 2.92), the standardised residuals of the model were not correlated with any independent variable, and there was good linearity in the residuals for each component.

Log (Hair As) = 10.2889 + (0.193964 * (log (soil P)) + (3.50989 * (log (soil Zr)) + (0.809624 * (log (soil Cu)) – (17.9355 * (log (water pH)) + (1.3589 * (log (water Eh))

Figure 15: Multiple regression equation for hair As (response variable) and five independent (predictor) variables

Cu is closely associated with As: the ratio of median soil As to median soil Cu was 0.748 across the G-BASE survey area, ranging from 0.780 in the central zone to 1.03 in the southern zone (
Table 4 and

Table 11), and they had a significantly strong linear relationship (R = 0.941, P < 0.001). Areas in the south and west of the survey area had five to 10 times more As in the topsoils than Cu (Figure 16), which could be due to Cu ore extraction and subsequent As enrichment around the old mining areas. The negative correlation between soil Cu and hair As suggests decreasing amounts of Cu release As, which becomes more bio-accessible and hence bio-available. Minerals such as $CuFeS_2$ may be weathered to release H_3AsO_3 or H_3AsO_4, and soil Cu had a significantly non-linear but weak relationship with As in stream waters (R = 0.159, P < 0.001).

Table 11: Summary G-BASE results for Cu, P and Zr in topsoils of the Tamar catchment (Rawlins *et al*, 2003). Samples are evenly divided into survey zones according to their latitudinal map coordinates.

G-BASE analyte	Statistic	Survey zones: All	North	Centre	South
Soil Cu (mg kg^{-1})	*n*	468	158	155	155
	Median	29.8	19.4	29.6	45.5
	Inter-quartile range	19.6 – 42.7	14.9 – 25.6	22.2 – 37.7	35.2 – 64.8
	Range	2.40 – 2660	5.10 – 41.6	3.30 – 298	2.40 – 2660
Soil P (mg kg^{-1})	*n*	467	157	155	155
	Median	20.5	16.5	22.0	23.0
	Inter-quartile range	13. 5 – 32.0	11.1 – 26.7	13.9 – 30.8	15.4 – 42.4
	Range	0.10 – 238	2.90 – 92.3	0.10 – 85.6	4.50 – 238
Soil Zr (mg kg^{-1})	*n*	468	158	155	155
	Median	230.1	250.2	228	212
	Inter-quartile range	202 – 260.2	225 – 286	207 – 260.3	188 – 238
	Range	129 – 575	129 – 372	129 – 575	132 – 355

As and P share similar ionic radii and consequently have similar behaviours: both commonly form oxy-anions in the +5 oxidation state, but phosphate (PO_4^{3-}) is stable over a much wider range of redox potential and pH than As^V (Alvarez-Benedi *et al*, 2005). Soil PO_4^{3-} had a significantly slight linear correlation with As in stream waters ($R = 0.270$, $P < 0.001$) but no significant relationship with soil As, suggesting that PO_4^{3-} mobilises As by competing for adsorption sites. However, the fitted model only includes available P, which had a significantly slight linear relationship with soil As ($R = 0.285$, $P < 0.001$) and As in stream waters ($R = 0.214$, $P < 0.001$). Its negative relationship with hair As suggests that as P is taken up in soils and becomes less available, As becomes more bio-accessible and hence bio-available. The ratio of soil As to soil P is 1.09 across the G-BASE survey area, ranging from 0.994 in the northern zone and 2.04 in the southern zone. There is one area near Launceston and several areas near Callington and Gunnislake where there is 100 times more As in the topsoils than P (Figure 17). As^V shares similar exchange dynamics with PO_4^{3-} and may be taken up by plants as a PO_4^{3-} analogue in these areas (Mkandawire & Dudel, 2005), and the excess soil As may be more mobile between partitions because P is more stable.

Zr is closely associated with silica and has an affinity for sandy soils (Rawlins *et al*, 2003), where As does not accumulate and can be much more mobile, especially at higher pH. Zr soil content is highest in the northern zone of the G-BASE survey area, which could indicate a higher sandy fraction than topsoils in the central and southern zones. Soil Zr's positive relationship with hair As suggests the increased mobility leads to increased bio-availability, but Tamar catchment soils are predominately loamy (Section 3.1 and Figure 9) and therefore have higher potential for As accumulation.

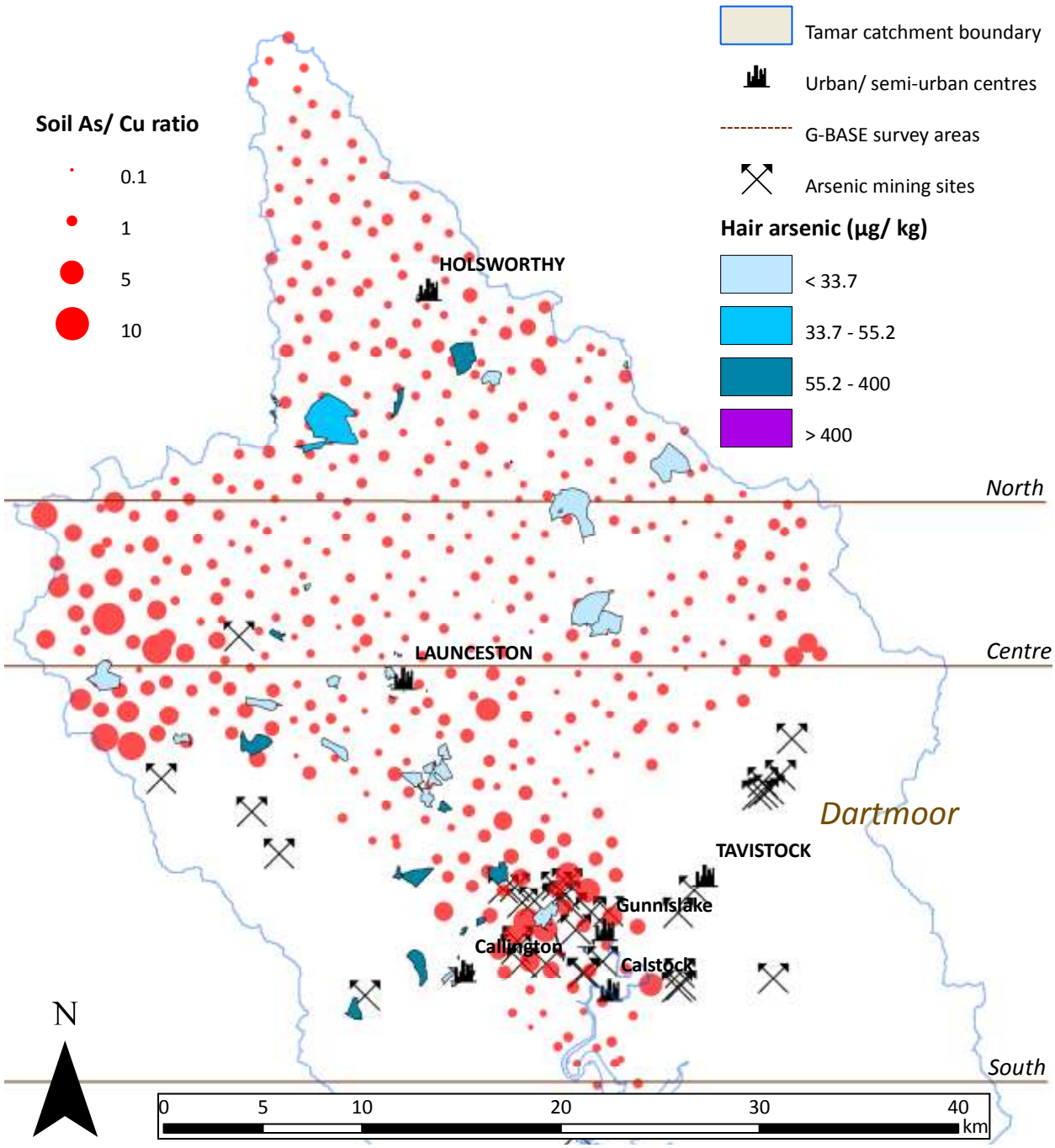

Figure 16: Ratios between soil As and soil Cu in the G-BASE survey area (Rawlins *et al*, 2003), and hair As concentrations aggregated to participants' postcodes. The locations of urban/ semi-urban centres were supplied by EDINA (© Crown Copyright) and mining data was provided by the Environment Agency.

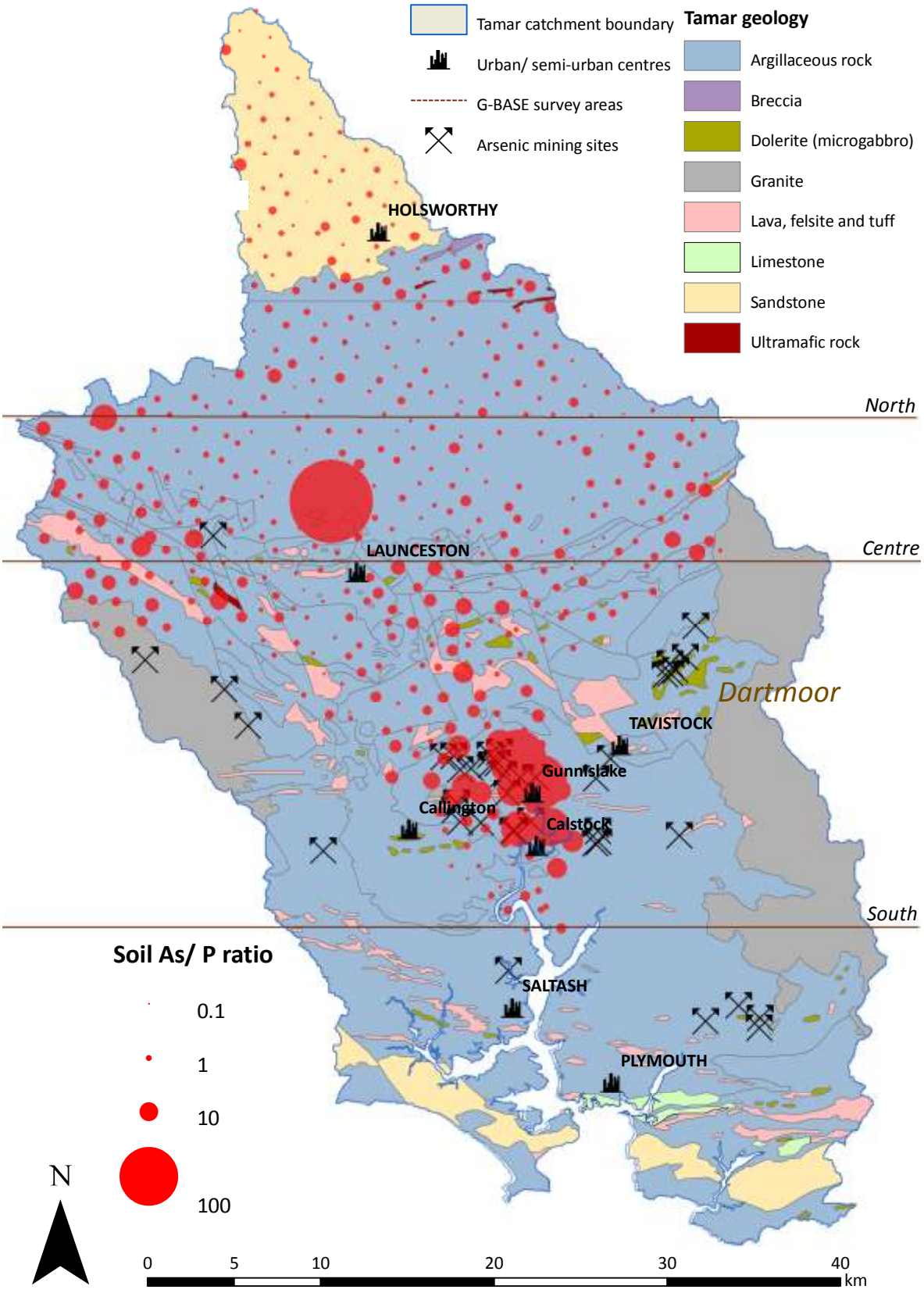

Figure 17: Ratios of soil As and soil P in the G-BASE survey area (Rawlins *et al*, 2003). Geology data and the urban/ semi-urban centres were supplied by British Geological Survey/ EDINA (© Crown Copyright). Mining data was provided by the Environment Agency.

Eh and pH are less strongly related to hair As than the other independent variables but are known controlling factors of As mobility (Section 2.2). Both are positively related with hair As suggesting bio-availability is higher at elevated pH. Soil As is more mobile at higher pH although this tends to be in the form of As^{V} rather than As^{III}, which is relatively immobile at high pH (Alloway, 1995). This could mean As^{V} is the more relevant bio-available species, which is consistent with the soil types found in the Tamar catchment (Sections 2.2 and 3.1)

Fitting the model to the G-BASE dataset for the catchment indicates the areas where residents may have the highest hair As levels surround the historic mining districts in the south of the G-BASE survey area (Figure 18). This is consistent with the bio-available concentrations of As found in hair samples in this study, and the environmental As concentrations shown in the G-BASE survey results (Table 4). The model is also consistent with the BGS risk assessment of As in the catchment's topsoil (Rawlins *et al*, 2003). This used physiologically-based extraction tests on soil samples to estimate As bio-accessibility as 20% of total As concentrations, and also found the highest risk in the south of the G-BASE survey area.

A limitation of the multiple regression model is the inherent inter-relationships between the independent variables. In addition many other factors apart from those included in the model influence As morbidity and mortality. Both bio-availability and bio-accessibility vary with speciation, for example soluble As salts can have 100% bio-availability while inorganic As in mine tailings can have less than 10% (Khan *et al*, 2009). The exposure pathway may have an effect, for instance the bio-accessible fraction of a contaminant may vary with different soil particle sizes; one study shows increasing As bio-accessibility with decreasing particle size (Smith *et al*, 2009). Bio-availability can be determined by the target organism and its individual attributes (host factors) of age, gender, size and weight, nutritional status, genetics and behaviours (Khan *et al*, 2009). Human metabolism is also important and is influenced by many factors such as cations in the diet and variable absorption capability among individuals.

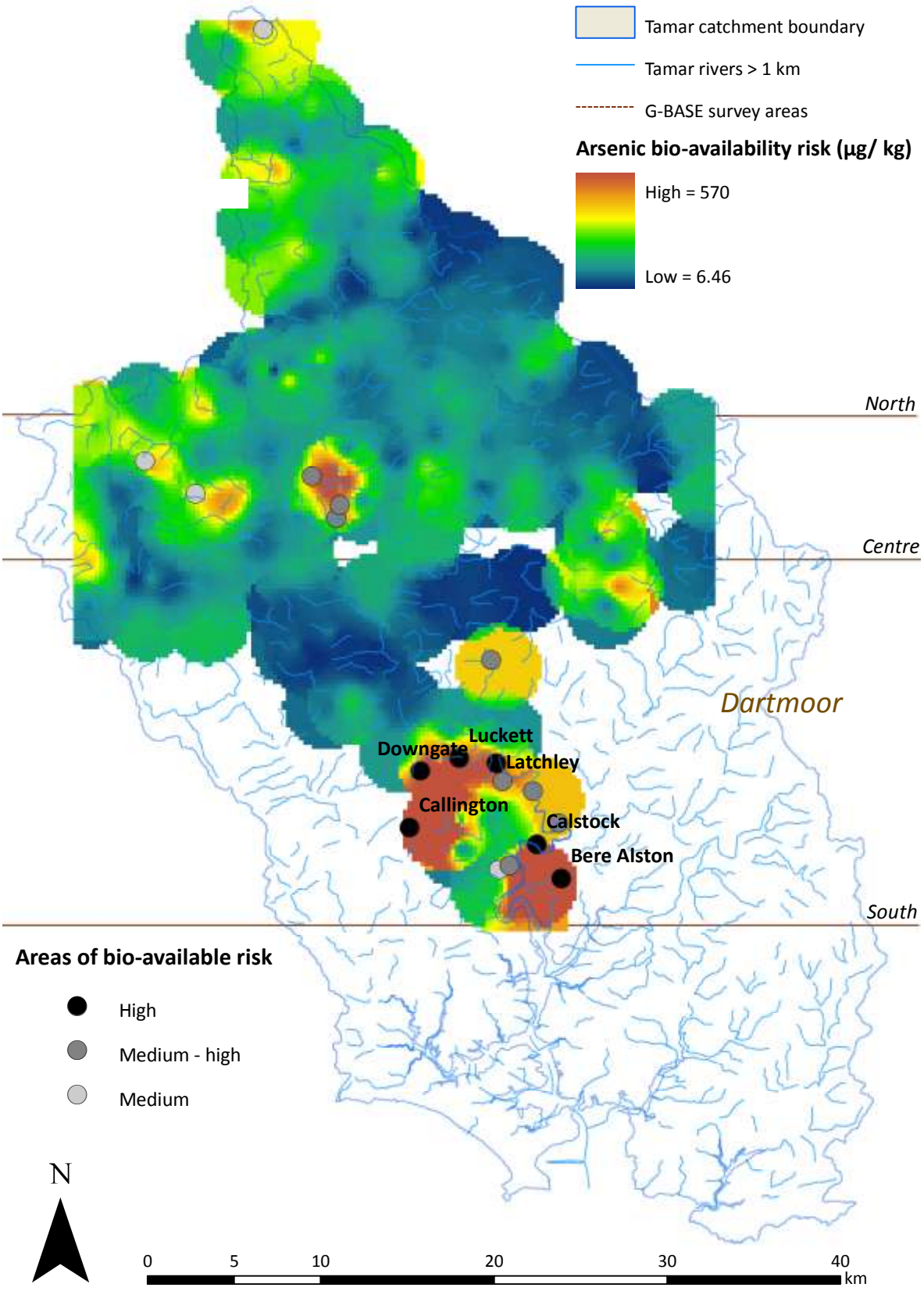

Figure 18: Spatial representation of As bio-availability risk for the Tamar catchment. The model is derived from concentrations of P, Cu and Zr in topsoils, and the pH and Eh of stream waters. Areas which have high risks are named on the map.

6. Conclusions

The majority of participants in this study had hair As levels in the typical unexposed range, which remains true after accounting for the implied extraction efficiency of the method (Sections 5.1 and 5.2). However, there are three examples of high As bio-availability that are more consistent with previous human bio-marker studies in the catchment (Section 3.4). These high levels could signal an excess accumulation of trivalent inorganic As in some catchment residents that may affect their health, and it may not be accurate to assume a threshold for As intoxication (Section 2.4). In this context even the low concentrations of As in hair from Holsworthy and Launceston participants may not be acceptable as 'background' levels of As exposure. An additional concern is the significant risks for children who tend to have higher As exposure as they generally spend more time in the outdoors, play on the ground and engage in more frequent hand-to-mouth behaviours than adults.

The primary drivers for As exposure in the Tamar catchment are whether an individual lives within 5 km of an As-contaminated area or whether they grow and/ or consume locally-grown food, although these two factors were unrelated in this study (Section 5.3). Influential physical and lifestyle factors for As exposure were difficult to identify because of the large number of different factors that affect the bio-availability of As for an individual. The small sample sizes in some categories of physical or lifestyle factor meant some statistical tests had low power. The questionnaire design could also have been more precise, for example the questionnaire did not differentiate between growing and eating locally-grown food, which may involve more or less time outdoors, or ask for the frequency of this habit.

The multiple regression equation relates As bio-availability and bio-accessibility under environmental conditions in a holistic manner: the independent variables influence the presence of As (Cu and Zr) and its mobility between partitions (P, Eh and pH) (Section 5.5). Elevated As in environmental media (Section 3.4) and high As bio-availability represented by hair As concentrations (Section 5.4) coincide around the historic mining districts of Callington and Gunnislake in the south of the catchment. The fitted model provides a good match with risk assessments completed using other methods, and offers a robust alternative based on established geochemical knowledge.

The model presented in this study pinpoints the significant role of P in the bio-availability of As. This highlights a separate issue concerning the agricultural use of P fertilisers, which is particularly relevant for the Tamar catchment because its land use is dominated by agriculture (Section 3.2). The widespread use of these fertilisers increases their leaching potential and presents a threat to water quality and the eutrophication of surface waters. An additional consequence could be the exacerbation of As bio-accessibility and hence the increased bio-availability of As for humans.

The sample methodology used in this study could be improved in a number of ways. The potential for exogenous contamination of samples could be reduced by rinsing hands and equipment before taking hair from skin at the occipital region of the head (Section 5.1). Several samples from each individual could be aggregated to overcome the inherent variability in the sample matrix. The number of different vessels used to collect and prepare samples in the laboratory could be reduced to remove handling difficulties. Wash liquids or spiked and un-spiked control samples could be analysed to determine the extraction efficiency and a correction factor for the results. Hair samples

could also be freeze-dried after washing to remove all moisture before weighing.

A more formal arrangement could be adopted for collecting hair samples from volunteers to enable the necessary improvements in the sample methodology. The volunteers could also provide more detailed information on physical and lifestyle factors affecting individual exposure to As. A detailed survey could collect data about their occupation, medical history, and their dietary intake of As, particularly from home-grown or allotment-produced foods. It could also collect data on the volunteers' nutritional status, which may be significant for As bio-availability.

A major limitation of this study is the lack of data on As speciation in the G-BASE survey samples and human hair samples. As toxicity varies with speciation (Section 2.4) which varies with environmental conditions and geochemical associations (Section 2.2); therefore speciation data is essential for a more accurate health risk assessment. HPLC-ICP-MS or direct speciation methods such as XANES can determine As speciation in human hair but research is required in this area to differentiate variability due to the methylation of inorganic As in the human body or from external accumulation such as washing hair in As-contaminated water.

A future investigation should include more users of private water supplies: although this factor did not significantly affect hair As levels in this study, without geochemical data on the As status of these water sources it cannot be discounted as a potentially significant exposure pathway for some residents of the catchment. Children must also be included because they may have the highest risks of As bio-availability. A more general aim should be to increase the number and geographic distribution of hair samples to improve the database of human bio-marker information for the catchment, and to provide greater confidence in the statistical analyses. A project could be conducted over a landscape-level scale or on a smaller scale such as the Callington and Gunnislake area. The multiple regression model used in this study is easily scalable and could incorporate more independent variables if necessary. The addition of a more extensive dataset could allow the bio-availability model to be used as a guide for land use planning and remediation efforts where necessary. It could also be used in conjunction with epidemiological studies to explore possible links between environmental As and incidences of clinical disease in the catchment.

In addition there must also be a review of dose-response studies for As as it is further characterised by toxicological research; this may influence the current acceptable level of As that is expected in human hair. Where practicable P should be included in a proposed bio-marker and geochemical sampling strategy to confirm the significant relationship between environmental P and bio-available As. Temporal studies could obtain information on annual farm nutrient budgets to determine whether bio-available As varies over time with agricultural applications of P.

In light of the high bio-available As values found in catchment residents in this study, and the uncertainty surrounding the As dose-response relationship, there is an urgent need to increase the database of human bio-marker research in the catchment and to conduct As speciation studies to provide a better understanding of the human health risks from As in the Tamar catchment.

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