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Molybdenum in British drinking water: a review of sources and occurrence and a reconnaissance survey of concentrations

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BRITISH GEOLOGICAL SURVEY
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Molybdenum in British drinking water: a review of sources and occurrence and a reconnaissance survey of concentrations

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Front cover

Agden Reservoir, south Yorkshire (a source of drinking water for Sheffield)

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Foreword

This report presents the findings from a Defra-funded project, managed by the Drinking Water Inspectorate (DWI), entitled “A review of data on molybdenum in drinking water and a survey of molybdenum and other trace elements in drinking water” (Defra project WT02062, DWI file reference DWI 70/2/211). The project was a collaboration between the British Geological Survey (BGS) and the Centre for Ecology & Hydrology (CEH) and was carried out during the period December 2006 to June 2008.

Acknowledgements

Staff of BGS Keyworth, notably Chris Johnson, are thanked for access to data for and background information on molybdenum concentrations in stream sediments, soils and streamwaters from the G-BASE database for Great Britain. Thanks are also due to staff of the Geological Survey of Northern Ireland (GSNI), notably William Smyth, Mark Patton and Dee Flight for equivalent G-BASE data for Northern Ireland. Data for lakewaters from Esthwaite Water and Lake Windermere were kindly supplied by Philip Rowland of CEH Lancaster. Groundwater molybdenum data were collated from the BGS Wallingford groundwater database by Chris Milne. River-water data from the LOIS data set were kindly provided by Colin Neal (CEH Wallingford).

We are grateful to Alan Lawlor and Philip Rowland of the CEH Lancaster laboratory for carrying out the ICP-MS analysis of water samples from the drinking-water surveys.

Contents

FIGURES

TABLES

Summary

Although there is no statutory limit for molybdenum in UK or European drinking water, the WHO since 1993 have recommended a health-based guideline value for molybdenum in drinking water of 70 µg L^{-1}. This report provides an assessment of the occurrence and distribution of molybdenum in UK surface waters, groundwaters and drinking waters in order to assess the implication for the UK water industry should legislation to limit the concentrations of molybdenum in drinking water, commensurate with the WHO guideline value, be introduced in the coming years.

A survey has been carried out of molybdenum (Mo) concentrations in drinking water from twelve public-supply sources distributed across England & Wales, monitored up to four times over an 18-month period, together with domestic taps from three of their supply areas. As the scale of the survey was limited, a formal probability-based survey design was not possible. Instead a purposive sampling approach was adopted, focusing on those regions where the risk of exceedence of the WHO guideline value, based on available surface-water and groundwater data, was believed to be greatest. The design adopted was therefore non-probabilistic and not able to provide statistical estimates of probabilities of exceedence. However, it was considered appropriate for reducing uncertainty over sources of greatest risk. Public-supply sources included five groundwater sources (one a mine sough), four river sources and three upland reservoir sources.

For three of the public-supply sources investigated, molybdenum concentrations for all samples were below the detection limit of 0.03 µg L^{-1}. For the remaining nine sources, analysis of variance confirmed that significant differences existed in molybdenum concentration between sites but not within sites at different sampling times. Although concentrations in surface waters were generally more variable than in groundwaters, the results did not show evidence of a notable seasonal effect. All analysed concentrations were more than an order of magnitude lower than the WHO guideline value for Mo of 70 µg L^{-1}.

Tapwater samples were analysed from eight households in each of three areas: Bangor (Gwynedd), Mickleover (Derbyshire) and Haverhill (Suffolk). Sampling at each tap involved collection of a morning first-draw (pre-flush) sample and a post-flush sample. Analysis showed a remarkable uniformity in molybdenum concentrations at each location, the variability being very small between houses (old and new), between pre- and post-flush samples, and between the tapwater and respective source-water samples. The results suggest that water distribution pipework has a negligible effect on supplied tapwater molybdenum concentrations. All tapwater samples from Bangor had molybdenum concentrations below detection limit, consistent with those in the public-supply source water. Tapwaters from Haverhill were not significantly different from their source waters ($p > 0.05$). Mickleover tapwaters had lower Mo concentrations than source waters. The differences were statistically significant ($p < 0.001$), although their absolute magnitude was small. There was a possible tendency ($p=0.04$) for post-flush samples at Mickleover to have slightly higher molybdenum concentrations than pre-flush samples. Such a difference may be due to adsorption of molybdenum onto surfaces (pipes, encrusted minerals) during overnight standing of water in the pipes. Again, the magnitude of the differences was small. Analysis of other trace elements by the ICP-MS technique used, revealed significant differences in concentrations of copper (Cu), zinc (Zn), nickel (Ni) and lead (Pb) between pre-flush and post-flush water samples. In two pre-flush samples, concentrations of Ni or Pb were above drinking-water limits, although in all cases, post-flush waters were compliant. These high concentrations most likely derive from metal pipework in the domestic distribution system during overnight standstill. Pre-flush Pb concentrations were generally higher in water from older properties.

A compilation has also been made of available data for molybdenum in streams, rivers, lakes and groundwaters, together with stream sediments, soils and rocks in the UK. The data derive from a combination of the BGS and GSNI 'G-BASE' databases (geochemical baseline data for streamwater, stream sediment and soil), the BGS groundwater database, CEH data from the Land-Ocean Interaction Study (LOIS) project which characterised quality of river waters in eastern England, and CEH data from the Environmental Change Network (ECN) for lakewater quality in Cumbria. Data have also been collated from the open literature.

The results indicate that concentrations of molybdenum in rocks, sediments and soils in the UK are typically less than 10 mg kg^{-1}. Higher concentrations (>20 mg kg^{-1}) can be found in some argillaceous deposits, especially black shales and other sulphide-rich deposits. Relatively high molybdenum concentrations are also found in some ironstones and granites. Concentrations of molybdenum in 65,447 stream sediments from England & Wales (G-BASE data) range up to 309 mg kg^{-1} but with a 90th percentile value of just 2.9 mg kg^{-1}. Analysis of 5874 stream-sediment samples from Northern Ireland showed concentrations ranging up to 86 mg kg^{-1} but with a 90th percentile of 6.7 mg kg^{-1}.

Concentrations of molybdenum in surface waters and groundwaters in Britain are usually very low. Analyses of 96 lakewater samples monitored in 2004 from Lake Windermere and Esthwaite Water in Cumbria have concentrations of 0.1 µg L^{-1} or less. Analyses of 11,562 streamwater samples from the G-BASE dataset have a range of <0.05–230 µg L^{-1} although the 10–90th percentile range is much narrower, 0.08–2.45 µg L^{-1}, with a median value of just 0.57 µg L^{-1}. Analyses of water samples from the LOIS rivers also typically have median concentrations <1 µg L^{-1}, although sites on the Rivers Calder, Don, Trent, Great Ouse and Thames have higher median values, in the range 3–10 µg L^{-1}. The highest observed streamwater concentrations in both the G-BASE and LOIS datasets appear to be from the River Aire and its tributaries in south Yorkshire. In the River Aire, concentrations had a notable correlation with river flow, being highest under low-flow conditions. Concentrations in several low-flow samples were close to the WHO guideline value (tens of µg L^{-1}) though rarely exceeded it. The high values in this area are interpreted as the result of contamination by coal-mine drainage and possibly other industrial contaminants. The River Aire in its industrial reaches is not used as a source of public drinking-water supply because of its recognised polluted condition.

Molybdenum data for 1398 groundwater samples from the BGS groundwater database have a range of <0.1–120 µg L^{-1} but with a 10–90th percentile range of 0.1–1.5 µg L^{-1} and a median of 0.12 µg L^{-1}. Only three samples (0.21%) have concentrations in excess of the current WHO guideline value. Median concentrations distinguished by source type (springs, boreholes, wells, mine drainage) are all close to or less than 1 µg L^{-1}, although relatively high concentrations characterise mine-drainage waters (0.60–6.0 µg L^{-1}, median 1.4 µg L^{-1}). These are likely derived by the release of molybdenum following oxidation of sulphide minerals. Relatively high molybdenum concentrations appear to be a particular feature of reducing (anaerobic) groundwaters and groundwaters with prolonged residence times in host aquifers. The highest observed concentrations are found in reducing groundwaters from greensand aquifers (Lower Greensand, Carstone, Spilsby Sandstone).

The ranges observed in both groundwaters and surface waters indicate that molybdenum concentrations in Britain rarely occur in excess of or approaching the WHO guideline value for molybdenum in drinking water. In the event that a new drinking-water limit at a comparable concentration (70 µg L^{-1}) is introduced for molybdenum in national or European legislation in the coming years, our results suggest that molybdenum should not pose a significant problem for the UK water-supply industry.

1 Introduction

1.1 BACKGROUND

Molybdenum is an essential trace element for human health. WHO estimates that adults have a daily requirement for molybdenum of 100–300 µg. Nonetheless, high doses can be detrimental and in 1993, WHO introduced a health-based guideline value for molybdenum in drinking water of 70 µg L^{-1}. There are currently no EC or national limits for molybdenum in drinking water, although it is possible that future amendments to the EC Drinking Water Directive will incorporate a new limit for the element at a concentration comparable to the WHO guideline value. National regulation would follow from such a Directive amendment.

Since water companies, the Environment Agency and local authorities currently have no statutory obligation to test for molybdenum in water supplies, there appear to be few if any data available for molybdenum in public and private drinking-water sources. More data are available from a number of organisations on concentrations in natural (untreated) groundwaters and surface waters. Drinking water in England & Wales is provided from a combination of these water sources, and so such databases provide potentially important information for assessing the likely concentrations of molybdenum in drinking water. However, these data have not previously been collated or evaluated on a national scale.

1.2 PROJECT OBJECTIVES

The objectives of this project, as specified in the Defra terms of reference, were to:

1) identify all relevant studies, in the published and grey literature, that establish concentrations of molybdenum in drinking water and relevant source waters in England & Wales;

2) assess broadly the quality of the studies identified, in terms of the scope of the study and the performance of the analytical methods used;

3) summarise the findings of the studies and identify any catchment/aquifer characteristics that may be associated with high molybdenum concentrations;

4) devise a survey of drinking water from up to 12 sources for England & Wales to assess the ranges[1] of observed concentrations (the survey to cover all major types of source and taking account of possible seasonal variations in concentration and any possible effects of plumbing metals through the use of first-draw samples from random daytime visits and fully flushed samples);

5) conduct the survey in accordance with best practice in terms of sampling and analysis, including appropriate analytical quality control (analysis to include total metals, not just soluble metals);

6) in addition to molybdenum, analyse for and report other trace elements that can be determined using the same analytical technique;

7) report the findings of the survey, identifying possible implications for waters supplies should a standard be set at 70 µg L^{-1}.

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[1] The terms of reference required the estimation of maximum, mean and minimum molybdenum concentration in drinking water

This report presents a collation of available data on the concentrations and distributions of molybdenum in surface waters, groundwaters, and drinking waters, as well as rocks, stream sediments and soils in the UK. The data have been compiled from various databases held by BGS and CEH as well as information provided in the open and grey literature. The available data have been used to design a sampling survey of drinking water from 12 public-supply sources in England & Wales, and water from 24 domestic taps taken from three towns/suburbs supplied by these sources. A statistical evaluation of these data has been carried out to characterise the spatial distributions and temporal variations of molybdenum. The results presented in this report should provide the UK water industry with a better understanding of the occurrence of molybdenum in drinking water and its implications for drinking-water monitoring and supply.

2 Molybdenum occurrence and distribution

2.1 PHYSICAL AND CHEMICAL PROPERTIES

Molybdenum is a transition metal that occurs in a range of oxidation states, from -II to VI, though in nature the predominant states are Mo(IV) and Mo(VI). Its occurrence in variable oxidation states means that molybdenum participates in a number of redox reactions.

Molybdenum has a number of naturally-occurring isotopes: ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo and ^{100}Mo. The most abundant of these is ^{98}Mo (24%). Molybdenum is strongly chalcophile and its behaviour is closely linked to that of sulphur. It also has properties similar to tungsten and vanadium.

2.2 MOLYBDENUM IN PLANT AND ANIMAL HEALTH

Molybdenum is an important nutrient for a range of biological functions in animals, plants and microorganisms. It is an essential constituent of enzymes that catalyse redox reactions (Stiefel, 1996). Molybdenum interacts with copper and sulphate in organisms and the complex interactions between these compounds can lead to problems in biological systems which relate to both molybdenum deficiency and excess.

Molybdenum is important in plant growth and is added to some fertilisers in trace amounts to enhance crop production. It also has a role in nitrogen fixation (Bostick et al., 2003). However, excessive molybdenum concentrations have been linked to abnormal plant growth (Das et al., 2007). Molybdenum availability to plants from soils is known to be pH-dependent, being greatest in alkaline soils (National Research Council, 1980).

Molybdenum has a particularly large health impact on ruminant animals. In goats, Mo deficiency has been linked to reduced fertility and increased mortality (Expert Group on Vitamins and Minerals, 2003). High dietary molybdenum intakes inhibit the uptake of copper and lead to copper-deficiency disorders (Suttle, 1991; Shen et al., 2006). Symptoms of molybdenum toxicity are similar to those for copper deficiency which include anaemia, anorexia, diarrhoea, joint abnormalities, osteoporosis and hair discoloration. In sheep, copper deficiency leads to the neurological condition, swayback. This has long been recognised in the UK, particularly in parts of Somerset and Derbyshire (Thornton and Webb, 1979).

Shen et al. (2006) described symptoms of a similar condition known as 'shakeback' disease in yaks from the Qing Hai-Tibetan Plateau. Symptoms included emaciation, unsteadiness, shivering backs and reduced appetite (though not hair discoloration). Many of the symptoms were consistent with molybdenum-induced copper deficiency. Although the mean molybdenum concentration in the soils of the affected area was only 4.85 ± 0.21 mg kg^{-1} (dry weight), the mean Cu/Mo ratio in forage was 1.34 ± 0.36 compared to 8.12 ± 1.31 in control areas. A critical minimum Cu/Mo ratio in ruminants has been taken at around 2:1 (Suttle, 1991).

Animal studies using rabbits and mice have also linked high intakes of dietary Mo with weight loss, anorexia, premature deaths and reduced fertility (Expert Group on Vitamins and Minerals, 2003). The toxic effects were seen with administration of Mo(VI) but not Mo(III) (as molybdenite).

In humans, molybdenum has an important function in the activity of xantine oxidase, sulphite oxidase and aldehyde oxidase (Momcilovic, 1999; Expert Group on Vitamins and Minerals, 2003). Molybdenum is said to have beneficial effects for patients with sulphite sensitivity and asthmatics. It has also been claimed to reduce the incidence of dental caries.

Data documenting molybdenum toxicity in humans are limited. Water-soluble molybdenum compounds are taken up readily through the lungs and digestive tract. The physical and chemical state of molybdenum, the route of exposure, and factors such as dietary copper and sulphur concentrations all likely affect toxicity. Effects of acute molybdenum toxicity in humans include diarrhoea, anaemia and gout. Chronic occupational exposure has been linked to weakness, fatigue, lack of appetite, anorexia, joint pain and tremor. Cases of pneumoconiosis have also been reported (Expert Group on Vitamins and Minerals, 2003). No data are currently available on molybdenum carcinogenicity. Despite the above observations, recognised cases of molybdenum toxicity in humans are rare.

WHO first promulgated a guideline value for molybdenum in drinking water in 1993 (WHO, 1993). The value introduced was 70 $\mu g\ L^{-1}$ on the basis of limited toxicological studies on Mo in drinking water in humans. This value has been upheld in the WHO (2004) guidelines.

2.3 MOLYBDENUM IN MINERALS, ROCKS AND SOILS

2.3.1 Molybdenum in minerals and rocks

Molybdenum occurs as a major constituent in the sulphide minerals molybdenite (MoS_2) and the oxides wulfenite ($PbMoO_4$) and powellite ($Ca(Mo,W)O_4$). Being chalcophile, it also occurs at variable concentrations in other sulphide minerals including pyrite (FeS_2), galena (PbS) and sphalerite (ZnS). Molybdenum is therefore often concentrated in sulphide-rich ore zones, and commonly associated with high concentrations of uranium, antimony, arsenic, vanadium, barium, copper, lead and zinc (BGS, 2007).

In igneous and metamorphic rocks, average concentrations are around 1–2 mg kg^{-1} (Table **2.1**). Concentrations in sedimentary rocks depend largely on the concentrations of organic sulphur and carbon present and as a result, tend to be higher in shales and muds than in sandstones and carbonates. Das et al. (2007) suggested that Mo concentrations in shales were around 30 mg kg^{-1}. Black shales can have particularly high Mo concentrations, being found in association with organic sulphur compounds, again often in combination with U and V. BGS

Table 2.1 Typical concentrations of molybdenum in the crust, as well as rocks, sediments and soils from Britain and elsewhere.

Rock type	Average (range) mg kg^{-1}	Number analyses	Reference
Upper crust	1.5		BGS (2007)
Basalt	1.0		BGS (2007)
Granite	2.0		BGS (2007)
Shale	33 (32–34)		Das et al. (2007)
Black shale, Cariaco Trench	50–200		Lyons et al. (2003)
Antarctic marine sediment	0.79 (0.41–1.3)	21	Waheed et al. (2001)
Limestone	0.4		BGS (2007)
Sewage-sludge amended soil	8.3		Bettinelli et al. (2000)
Stream sediments, England & Wales	<0.5–3.6*		Imperial College (1978)
Stream sediments, England & Wales	$0.40^{\#}$ (<0.1–309)	65,447	BGS unpublished data
Average soil	(1–2)		Jarrell et al. (1980)
Soil	(0.03–43)		Das et al. (2007)
Topsoil, Humber-Trent, England	2.2 (0.4–43)	6559	BGS (2007)
Soil, Northern Ireland	<0.1–7.6	6937	Smyth (2007)
Soil, Spain	0.80 (0.32–1.2)	5	Campillo et al. (2002)

*10–90th percentiles; #median value

(1999) reported concentrations of molybdenum up to 70 mg kg^{-1} in black shale deposits in Britain. Lyons et al. (2003) found concentrations of 50–200 mg kg^{-1} in laminated marine sulphidic shales from the Cariaco Trench off Venezuela. As a result of this association, Mo has been used as an indicator of sulphidic, anoxic environments in the sedimentary record (Bostick et al., 2003; Tribovillard et al., 2004). Molybdenum has also been suggested as a useful proxy for original organic matter content in sediments (Wilde et al., 2004). Relatively high Mo concentrations are also found in ironstones. By contrast, concentrations in limestone are typically <1 mg kg^{-1} (Table 2.1).

2.3.2 Molybdenum in stream sediments

Stream sediments can have very variable molybdenum concentrations although concentrations are usually less than around 10 mg kg^{-1}. The distribution of molybdenum (and other trace elements) in stream sediments from England & Wales was described in the Wolfson Geochemical Atlas (Imperial College, 1978). In this study, molybdenum was analysed by fusion of samples with $KHSO_4$, formation of the toluene dithiol complex and

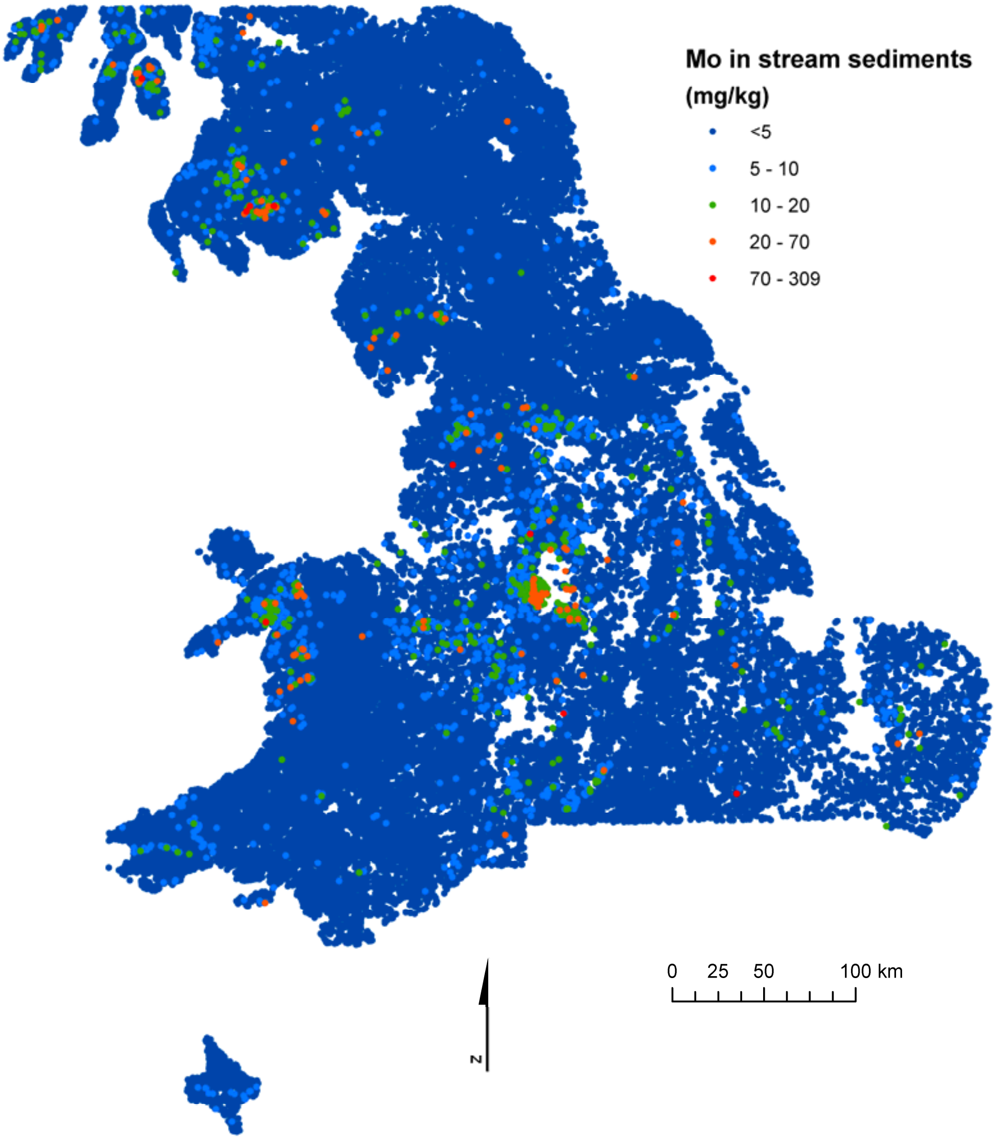

Figure 2.1 Variation in molybdenum concentration in stream sediments in parts of England, Wales and Scotland (G-BASE data, BGS).

extraction into toluene, followed by spectrophotometric analysis. The method had a detection limit of 0.5 mg kg^{-1}. Samples fell in the range <0.5–3.6 mg kg^{-1} (10–90th percentiles). Mapping of the results showed that concentrations were relatively high in stream sediments derived from argillaceous deposits of the Millstone Grit Group (Carboniferous) in Derbyshire. These contain a relative abundance of black shale deposits. High concentrations were also a feature of sediments derived from the Palaeozoic deposits of north Wales and Lias and Rhaetic deposits (dominantly shales) from south-west and central England.

From the BGS G-BASE dataset of stream sediment samples, 65,447 molybdenum analyses from England & Wales (downloaded December 2006) had an observed range of <0.1–309 mg kg^{-1} with a median of 0.4 mg kg^{-1}. The 10th to 90th percentile range was <0.1–2.9 µg L^{-1}. The samples were analysed either by digestion followed by ICP-OES or by x-ray fluorescence spectroscopy. Of the analysed samples, 99% had molybdenum concentrations <10 mg kg^{-1}. The spatial distribution of Mo in the stream sediments is shown in Figure 2.1. As with the Wolfson data, relatively high concentrations are seen in sediments from the Leek-Buxton area which are derived from Namurian black shales on the margins of the Derbyshire Dome. High concentrations (>20 mg kg^{-1}) are also found in sediments derived from the Cairnsmore of Fleet Granite in south-west Scotland and the Arran Granite in the Firth of Clyde, as well as sediments derived from shales and volcanic tuffs of Cambro-Ordovician age in north Wales (Figure 2.1).

Recent BGS G-BASE data collected for 5874 samples of stream sediments in Northern Ireland gave a range of 0.1–86 mg kg^{-1} with a mean of 1.2 mg kg^{-1}. The 10th–90th percentile range was 0.3–6.7 mg kg^{-1} (Lister et al., 2007).

2.3.3 Molybdenum in soils

Regional variations in concentrations of Mo in top soils from Great Britain, analysed as part of the BGS G-BASE survey are shown in Figure 2.2. The largest contiguous dataset is from the Humber-Trent area from which molybdenum concentrations are in the range 0.4–43 mg kg^{-1} (6559 samples) with a median of 2.2 mg kg^{-1} (BGS, 2007). Median values in these samples distinguished by parent rock type are typically in the range 1–3 mg kg^{-1}. BGS (2007) noted that relatively high median values were found for soils derived from the Carboniferous Limestone, Coal Measures and Cretaceous ironstones and clays and lowest median values for soils on the Triassic Sherwood Sandstone, Mercia Mudstone, Chalk and blown sands. Relatively high Mo concentrations were also found in top soils around the urban centres of Sheffield, Leeds and Bradford. Figure 2.2 shows that relatively high concentrations are seen on soils developed on the argillaceous deposits of the Millstone Grit Group to the west of the Derbyshire Dome, in correspondence with high molybdenum concentrations seen in the stream sediments from this area (Figure 2.1). Locally high Mo concentrations are also seen in some soils developed on argillaceous rocks of the Coal Measures Group in the West Midlands. However, in most analysed samples of top soil, concentrations are <6 mg kg^{-1}.

G-BASE soil datasets also include data for deep soils. Of 25,673 deep-soil analyses, the observed range in molybdenum concentrations was <0.6–885 mg kg^{-1} with a median of 1.4 mg kg^{-1}. Molybdenum concentrations are to some extent elevated in the deep soils of the Millstone Grit of Derbyshire, as for top soils. However, concentrations in the deep soils appear overall to be slightly lower than the equivalent top-soil concentrations at given locations. BGS (2007) suggested that anomalously high molybdenum concentrations observed in some of the top soils are linked at least in part with atmospheric pollution (deposition of molybdenum-rich aerosols derived from coal combustion) (BGS, 2007). A soil sample from the Humber-Trent area with an anomalously high molybdenum concentration of 885 mg kg^{-1}

had correspondingly high concentrations of chromium, nickel, copper and tin and was considered to have been contaminated with industrial waste (BGS, 2007).

From G-BASE data for soils in Northern Ireland, Mo concentrations in 6937 samples had a range of <0.1–7.6 mg kg^{-1} with a mean of 0.97 mg kg^{-1} and a 10th to 90th percentile range of 0.29–1.6 mg kg^{-1} (Smyth, 2007).

2.3.4 Anthropogenic sources

Molybdenum can be distributed in the environment as a result of industrial or agricultural contamination. Molybdenum is a component of steel alloys and welding rods and is used as an additive in lubricants, as a corrosion inhibitor and in the manufacture of tungsten, pigments and ceramics. It is added to cast iron for hardness control at concentrations of 250–450 mg kg^{-1} (Morrison et al., 2006). It is also a component of stainless steel.

Molybdenum can be distributed in the environment as a result of fossil-fuel combustion, leaching from fly ash and mobilisation from mine wastes (Morrison and Spangler, 1992; Zhang and Reardon, 2003). It is also used in agriculture to counteract molybdenum deficiency in crops (WHO, 2004).

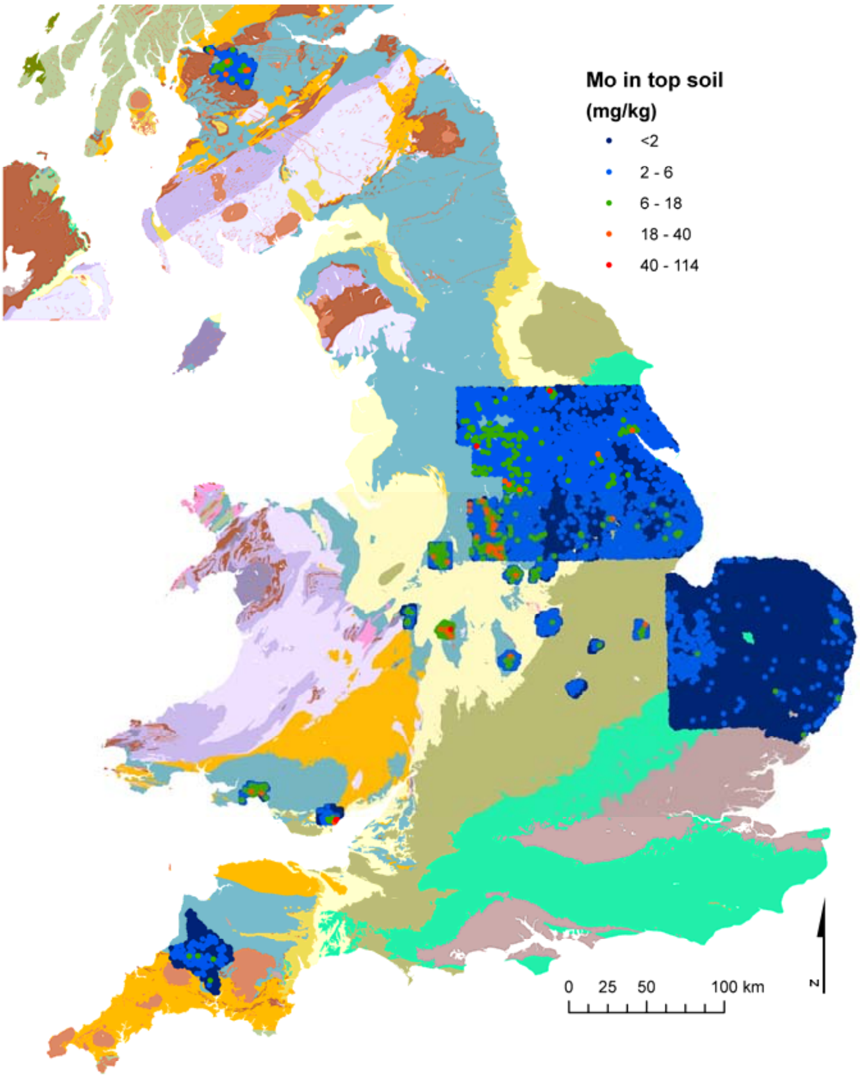

Figure 2.2 Variation in molybdenum concentration in top soils in parts of England, Wales and Scotland (G-BASE data, BGS).

2.4 MOLYBDENUM IN WATER

2.4.1 Molybdenum in stream and river waters

Reimann and de Caritat (1998) quoted a median Mo concentration in streamwaters worldwide of 0.5 µg L^{-1} (Table 2.2). Observed median concentrations in British streams and rivers are usually comparable with this value but concentrations are variable. Neal and Robson (2000) summarised the data for samples of river water collected as part of the Land-Ocean Interaction Study (LOIS). These analyses were carried out by ICP-MS at the CEH-BGS Wallingford laboratory. Neal and Robson (2000) found that median concentrations in rivers from 18 sites in eastern England were mostly <1 µg L^{-1}, but with medians of 3–10 µg L^{-1} in the Rivers Calder, Don, Trent, Great Ouse and Thames. The highest median (20.7 µg L^{-1}) was obtained for samples from the River Aire (maximum observed concentration 70.3 µg L^{-1}; Table 2.2; Figure 2.3). This river flows through an urban and industrial catchment and water at the sampling point, downstream of Leeds, was taken by Neal and Robson (2000) and Neal and Davies (2003) to be strongly impacted by industrial contamination. The river is well known to be one of the most polluted in Britain and it is not used for public supply in its industrial reaches. Only one sample from the LOIS sample set had a molybdenum concentration in excess of the WHO guideline value for drinking water of 70 µg L^{-1}. The river water samples showed evidence of strong seasonal variability, with highest

Table 2.2 Concentrations of molybdenum in rainwater, surface waters and groundwaters.

Water type	Average (range) µg L^{-1}	Number	Reference
Rainwater	0.2		Neal et al. (1994)
Streamwater			
World median streams	0.5		Reimann and de Caritat (1998)
Streams, Wales	<9 (<9–200)	13,337	BGS (1999)
Streams, Humber-Trent	0.68 (0.06–2.7*)		BGS (2007)
River Tweed (Teviot)	0.39 (0–4.2)	119	Neal and Robson (2000)
River Wear	1.46 (0.20–10.3)	55	Neal and Robson (2000)
River Swale (Catterick)	0.61 (0–5.00)	172	Neal and Robson (2000)
River Nidd	0.78 (0–4.32)	184	Neal and Robson (2000)
River Ure	0.51 (0–3.0)	180	Neal and Robson (2000)
River Ouse (Acaster)	0.95 (0–4.47)	144	Neal and Robson (2000)
River Derwent	0.90 (0–26)	173	Neal and Robson (2000)
River Wharfe	0.72 (0–4.92)	192	Neal and Robson (2000)
River Aire	23.5 (0.32–70.3)	196	Neal and Robson (2000)
River Calder	4.70 (0.57–19.7)	176	Neal and Robson (2000)
River Don	8.88 (0.70–20.1)	180	Neal and Robson (2000)
River Trent	5.05 (1.75–9.80)	153	Neal and Robson (2000)
River Great Ouse	3.34 (1.1–40.2)	58	Neal and Robson (2000)
River Thames (Day's Lock)	2.85 (0.5–10.0)	108	Neal and Robson (2000)
River Thames (Howbery Park)	2.80 (0.91–9.60)		Neal et al. (2000a)
Upland streams (baseflow), Wales	0.20^{m} (0–14.7)	67	Neal et al. (1998)
Upland stream (stormflow), Wales	0.36^{m} (0–11.2)	67	Neal et al. (1998)

^{m}: median. BGS (1999) data are analysed by ICP-OES; all others determined by ICP-MS
*: 10th, 90th percentile values

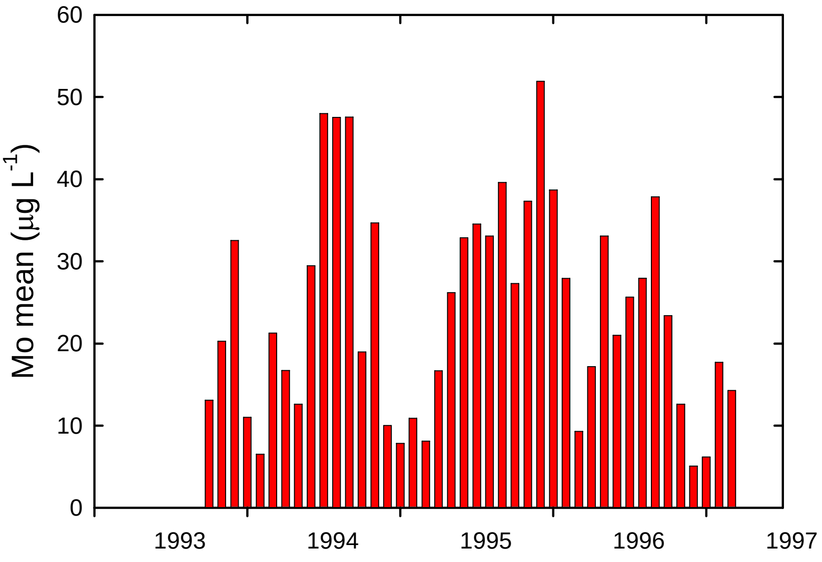

Figure 2.3 Monthly mean molybdenum concentrations in water from the River Aire (data from Neal and Robson, 2000).

concentrations occurring during summer months (Figure 2.3) when river flow is lowest and least diluted by storm water (Figure 2.4).

Neal et al. (2000a) also reported molybdenum data for the River Thames (Howbery Park, Oxfordshire) between the years 1997–1999. The highest reported maximum value for the site was 1588 µg L^{-1} but this was highly unusual and the next highest observed concentration was 9.6 µg L^{-1}. These data were also determined by ICP-MS. The range quoted in Table 2.2 is believed to be representative for the site as it compares closely with concentrations obtained from nearby Day's Lock. The River Thames is used for public supply in some places and there is a risk that this may be a source of relatively high Mo concentrations. Nonetheless, the observed concentrations are usually still an order of magnitude less than 70 µg L^{-1}.

Neal et al. (2000b) suggested that Mo in the River Great Ouse in Bedfordshire may be derived from contamination from the car components industry at Bedford. They also found

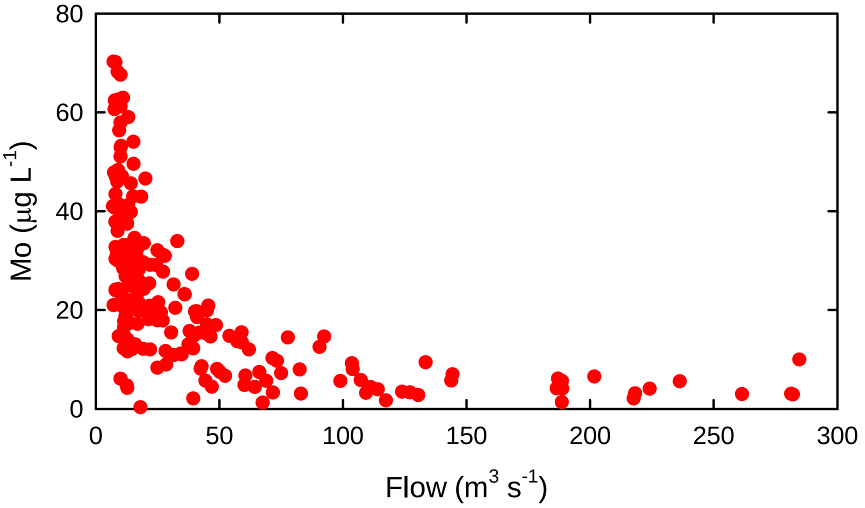

Figure 2.4 Molybdenum concentrations versus river flow in the River Aire (data from Neal and Robson, 2000).

occasionally high molybdenum concentrations in the particulate fraction of river-water samples from this area.

Data for streamwaters collected during stream-sediment sampling for the BGS G-BASE project are shown for selected areas in England & Wales in Figure 2.5. Water sampling is a relatively recent addition to the G-BASE sampling campaign and so areal coverage of water samples is more limited than that for stream sediments. Data are focussed on regional blocks, with sampling only within blocks. The samples therefore do not represent a complete British population of possible sites according to a formal survey design, although within blocks there is a gridded design. The G-BASE streamwater data are predominantly from small streams of a size that would not be used for significant public water supply. They were generally collected at low flow, with the intention of reflecting groundwater (or at least subsurface water) concentrations.

From 10,822 analysed streamwater samples in the G-BASE dataset, the observed Mo range was <0.05–230 µg L^{-1} with a median of 0.57 µg L^{-1} and mean of 1.33 µg L^{-1} (Table 2.3). 12 samples (0.1%) had molybdenum concentrations greater than 70 µg L^{-1}. Most analysed samples derive from the Humber-Trent area. Here, molybdenum concentrations were largely in the range 0.06–2.7 µg L^{-1} (10–90th percentile range) (BGS, 2007). Relatively high concentrations (up to 11 µg L^{-1}) were found in streams on the Triassic Sherwood Sandstone that have received a component of coal-mine drainage.

Figure 2.5 also shows that relatively high concentrations are clustered around tributaries of

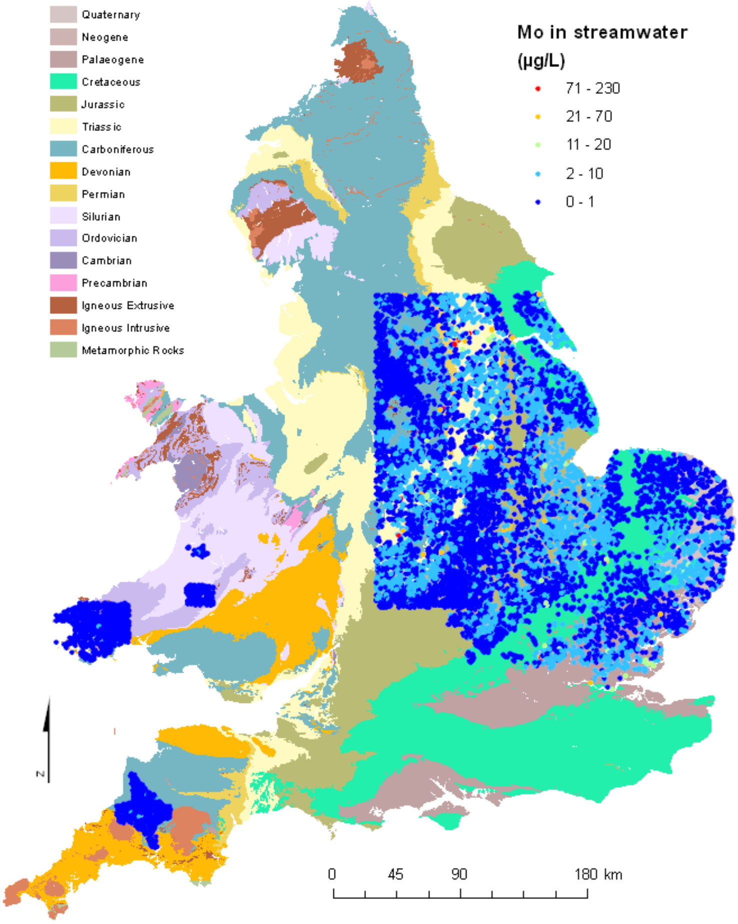

Figure 2.5 Variation in concentrations of molybdenum in streamwater from parts of England & Wales (data from the BGS G-BASE database; 11,562 samples).

Table 2.3 Summary statistics for molybdenum concentrations in streamwater, from the BGS G-BASE database.

Parameter	Value (µg L^{-1})
Minimum	<0.05
10th percentile	0.08
Median	0.57
Mean	1.33
90th percentile	2.45
Maximum	230
Number of samples	11,562

the River Aire in South Yorkshire. This supports the observed high concentrations in samples from the River Aire itself noted by Neal and Robson (2000). In this area, inputs to the drainage network from coal-mine drainage are considered the most likely cause of the elevated molybdenum concentrations. High concentrations were also found in streams close to Drax and Eggborough power stations (230 µg L^{-1} and 152 µg L^{-1} respectively). Potential sources in these include contamination from coal and fly ash. High Mo concentrations are also found in streams around Corby, Northamptonshire and some former collieries.

The G-BASE dataset revealed variable concentrations of molybdenum in streams draining Quaternary deposits, reflecting their variable mineralogy and provenance. Streams draining alluvium in the Trent Valley commonly had concentrations in the range 10–20 µg L^{-1} (BGS, 2007). By contrast, generally low concentrations were found in streams draining the Lincolnshire Limestone and Chalk (median 0.2 µg L^{-1}) (BGS, 2007). This is in accord with low molybdenum concentrations observed in limestones themselves (Table 2.1). Concentrations of molybdenum in G-BASE streamwater samples from Wales and south-west England are universally low, all being ≤10 µg L^{-1} and most <1 µg L^{-1} (Figure 2.5).

Additional G-BASE molybdenum data for streamwaters in Wales are available from 13,337 filtered, acidified water samples which were analysed for a range of trace elements using ICP-OES (BGS, 1999). The detection limit for molybdenum by this method was 9 µg L^{-1}. Only 210 samples exceeded this value; the median was <9 µg L^{-1} and the highest concentration was 200 µg L^{-1} (Table 2.2). Most of the detectable concentrations were from north-west Wales and from streams draining Mercia Mudstone (Triassic) and Lias (Jurassic) deposits in south-east Wales. The highest concentrations often correlated with relatively high concentrations of dissolved copper, zinc and lead as well as high sediment molybdenum concentrations. A large number of these were associated with sulphide mineralisation. For example, high molybdenum concentrations were found in water from the Parys Mountain mineral mine on Anglesey, a well-documented area of sulphide mineralisation and trace-metal mobilisation. Some high molybdenum occurrences were linked with high concentrations of dissolved phosphorus and are believed to be due to contamination with sewage effluent (BGS, 1999).

Neal et al. (1998) summarised the data for samples of river water collected under stormflow and baseflow conditions from 67 upland catchments across Wales. Many of the streams in the survey drain acidic catchments with land-use largely consisting of coniferous forest. Analyses were determined by ICP-MS. Results revealed low molybdenum concentrations under both baseflow and stormflow conditions, with median values being 0.20 µg L^{-1} and 0.36 µg L^{-1} respectively. The highest observed concentration in the study was 14.7 µg L^{-1} (Table 2.2). The observation of generally low concentrations supports the observations from the BGS G-BASE dataset for Wales.

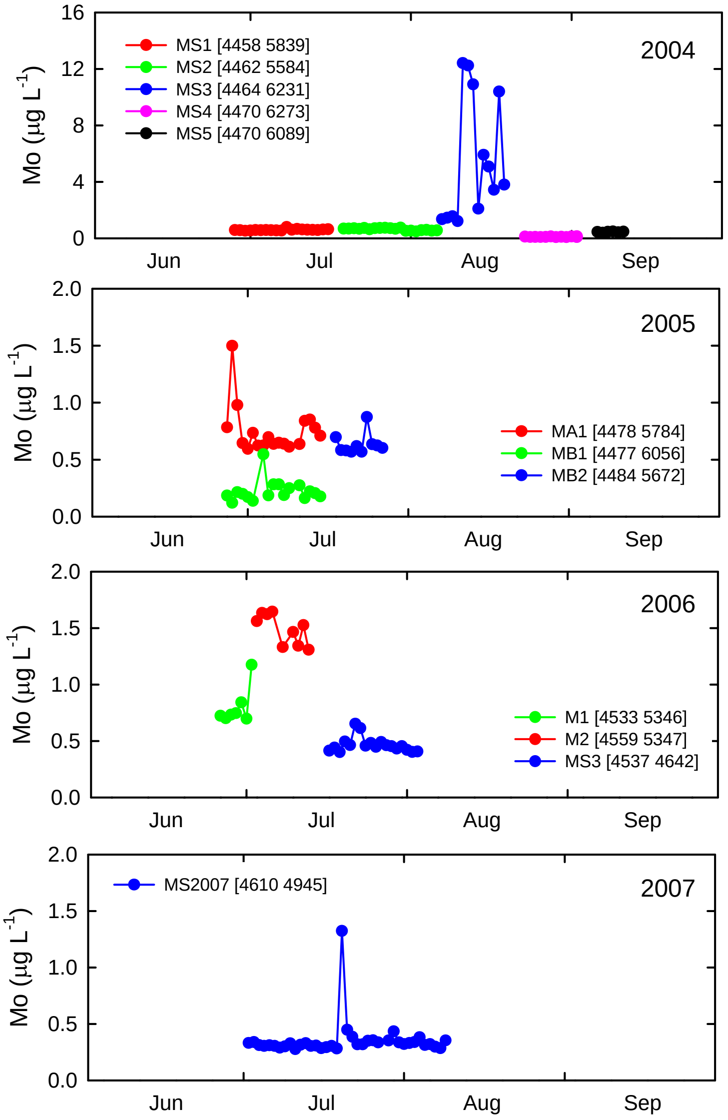

Figure 2.6 Molybdenum concentrations in streamwaters from monitoring sites in East Anglia, collected over the period 2004–2007 (BGS G-BASE data).

During the course of G-BASE streamwater sampling, additional samples for chemical analysis have been collected from defined monitoring sites typical of those being sampled in the study area (i.e. first-order streams). Molybdenum data for streamwater monitoring sites in East Anglia, the most recent area investigated, are given for the years 2004–2007 in Figure **2.7**. Results show that concentrations are often variable both within and between sites. Between-site variations probably relate mainly to variations in local geology and soil compositions, and temporal variability to varying flow rates. For example, the notable spike in molybdenum concentration at site MS2007 in July 2007 correlates with a major rainfall event on 20th July. Increased turbidity was noted to accompany the increased stream flow rates and may be responsible for the increased concentrations. One of the sites (MS3, 2004) had much higher concentrations than the other sites (1.2–12 µg L^{-1}) for reasons which are unclear. Nonetheless, the concentrations of all samples were significantly less than 70 µg L^{-1}. Most sites had concentrations some two orders of magnitude less.

Table 2.4 Summary statistics for Mo in monitored water samples in lake water from Esthwaite Water and Lake Windermere (North Bank and South Bank), sampled during 2004 (data from CEH Lancaster, provided by P. Rowland, 2007).

	Esthwaite Water	Windermere (north bank)	Windermere (south bank)
Min	0.069	0.048	0.050
Max	0.162	0.150	0.157
Median	0.099	0.086	0.094
Mean	0.100	0.090	0.096
Std dev	0.021	0.021	0.022
Number	32	32	32

Recent BGS G-BASE data for streamwaters from Northern Ireland (5899 samples) gave a range of <0.02–28 mg kg^{-1} with a mean of 0.35 mg kg^{-1} and a 10th to 90th percentile range of 0.03–0.82 mg kg^{-1} (Ander et al., 2007).

2.4.2 Molybdenum in lake water

Few data could be found for Mo concentrations in lake waters. However, regular monitoring of water in Lake Windermere and Esthwaite Water is carried out using ICP-MS by CEH Lancaster. Summary statistics for monitoring data for the period April to November 2004 taken from two sites at Windermere and one site at Esthwaite Water are shown in Table 2.4. Concentrations are in all cases low and within a narrow range, with median values at the three sites being <0.1 µg L^{-1} and maxima of just over 0.1 µg L^{-1}.

2.4.3 Molybdenum in groundwater

Data for molybdenum in British groundwater have been collated from the BGS groundwater database. The available groundwater data have a relatively wide spatial coverage, but sampling has been sporadic and to some extent opportunistic. The BGS groundwater samples were collected at sites not necessarily used for public water supply. They therefore comprise a different population from water-supply abstraction boreholes, although the extent of the population chemical differences (within the same aquifer or aquifer section) may be minor. These groundwater sample data may therefore be taken as a first approximation to concentrations in water from public-water-supply boreholes.

The database contains Mo data for samples analysed by two different methods: ICP-MS and ICP-OES. Typical laboratory detection limits given for these two methods respectively are 0.1 µg L^{-1} and 20 µg L^{-1}. Only the ICP-MS data have been evaluated here as the majority of samples have concentrations of less than 20 µg L^{-1}. The ICP-MS data date from 1992 to 2006 and have been analysed in BGS laboratories in Wallingford or Keyworth or by a commercial laboratory in Canada.

A statistical summary of the groundwater data from Great Britain is shown in Table 2.5. The observed range is <0.1–120 µg L^{-1}. The highest observed concentrations are from borehole waters, although only three samples (0.21%) have concentrations in excess of the WHO guideline value of 70 µg L^{-1}. Median concentrations in samples from springs, boreholes, wells and mine drainage are all around 1 µg L^{-1} or less. Samples of mine drainage have the highest median value and all samples in this category have concentrations above detection limits. This is consistent with mine waters being impacted by oxidation of molybdenum-bearing sulphide minerals.

Table 2.5 Summary statistics for molybdenum in groundwaters from Britain (BGS unpublished data). All concentrations are in µg L^{-1}.

	Springs	Boreholes	Shallow wells	Mine drainage	Other	Total
Min	<0.1	<0.1	<0.1	0.60	0.1	<0.1
10th percentile	0.10	0.10	0.10	0.80	0.19	0.10
Median	0.10	0.20	0.46	1.40	0.55	0.12
Max	5.00	120	9.64	6.00	14	120
90th percentile	0.40	1.50	4.30	3.91	1.19	1.50
Number	183	1176	21	14	4	1398

The regional distribution of groundwater molybdenum concentrations is shown in Figure 2.7. In general, where high molybdenum concentrations have been measured, these are at single locations, with nearby samples showing much lower concentrations. However, there are a few locations where several boreholes in the same vicinity have elevated concentrations. The most notable example is in Lincolnshire. Here, relatively high groundwater molybdenum concentrations are largely associated with the greensand aquifers (Lower Greensand, Carstone, Spilsby Sandstone). The source of the molybdenum in these groundwaters is uncertain but may be associated with iron oxides which are relatively abundant in these aquifers. Highest Mo concentrations in groundwaters from the greensand aquifers tend to occur under reducing conditions. This is consistent with molybdenum mobilisation resulting from iron-oxide reduction.

2.4.4 Molybdenum in drinking water

At the timing of writing, no data could be found for molybdenum concentrations in British public drinking-water supplies. Recent unpublished BGS data for 55 samples of British bottled mineral waters (natural mineral waters and spring waters, taken from a wide variety of aquifer lithologies) had a range in Mo concentrations of <0.009–2.62 µg L^{-1} and a median of 0.077 µg L^{-1}. Results were for unfiltered water samples, analysed by ICP-MS.

Likewise, limited information is available for drinking-water samples from other parts of the world. From an investigation of US public drinking-water supplies carried out in 1962, Durfor and Becker (1964) reported median molybdenum concentrations in the range 1–4 µg L^{-1} with a maximum observed value of 68 µg L^{-1}. In another study of US tapwaters, Greathouse and Craun (1979) detected molybdenum in 30% of 3676 analysed samples and found a range of <1–53 µg L^{-1}.

Yao and Byrne (1999) described the analysis of chromium and molybdenum in natural waters using long-pathlength absorbance spectroscopy. As part of the verification of the method, they analysed Mo(VI) in five bottled mineral waters (each analysed in duplicate). These were from unspecified sources, but were probably bottled in the USA. The average concentrations of Mo(VI) were 0.56, 0.58, 3.8, 4.1 and 26 µg L^{-1}. Molybdenum(VI) is likely to be the dominant form and therefore these concentrations should be representative of the total concentrations present in the water.

In addition, Escudero et al. (2008) found concentrations of Mo(VI) in drinking-water samples from their laboratory in Sun Luis, Argentina of 1.23 ± 0.08 µg L^{-1}. Again, this is probably representative of the total molybdenum in the water samples.

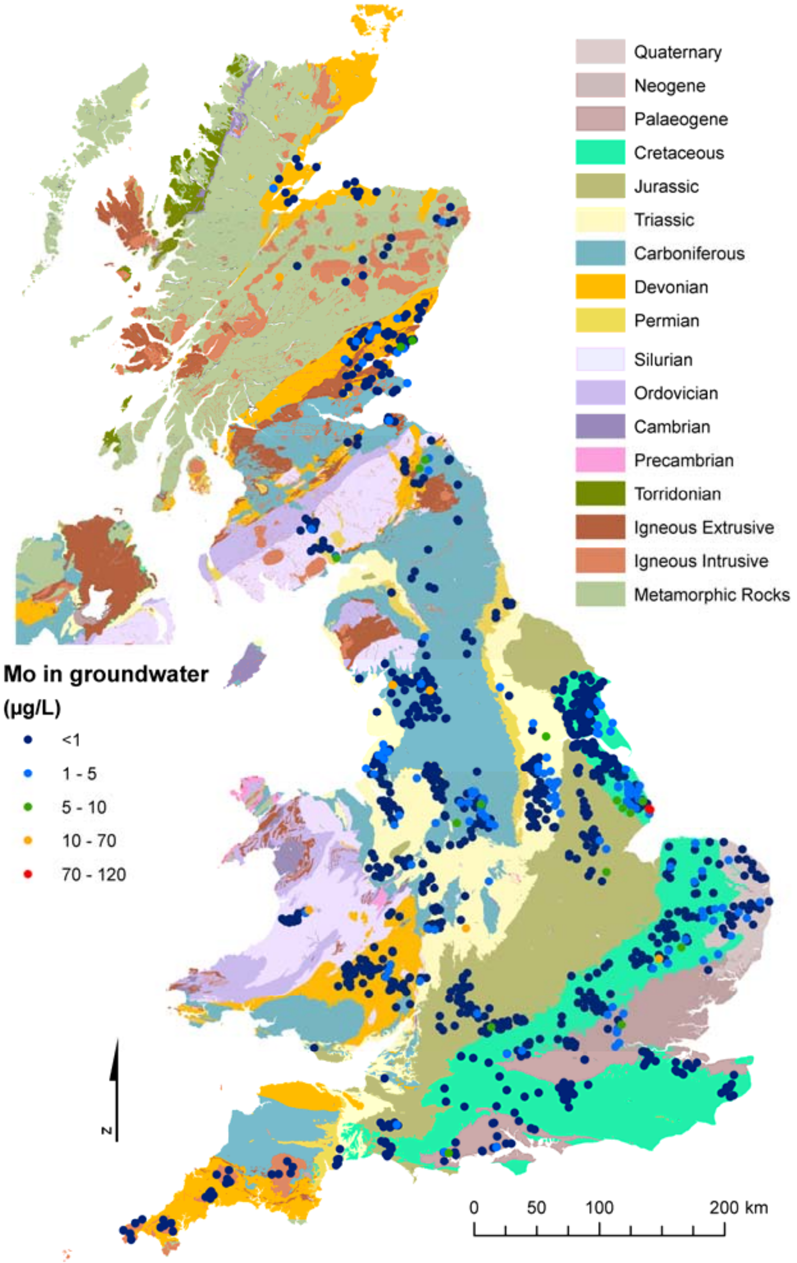

Figure 2.7 Variation in concentrations of molybdenum in groundwater from England & Wales (data from the BGS groundwater database; 1398 samples).

3 Molybdenum mobility in the environment

Molybdenum concentrations in water are controlled to a significant extent by redox conditions and pH. In oxic waters at pH>5, molybdenum occurs principally as the molybdate oxyanion (MoO_4^{2-}). This means that molybdenum can be present as a stable soluble species under the conditions of many natural waters.

Sorption reactions also have a strong control on molybdenum mobility. The molybdate ion adsorbs readily to iron oxides (e.g. hydrous ferric oxide) at low to neutral pH (Kaback and Runnells, 1980; Dzombak and Morel, 1990; Morrison and Spangler, 1992) as well as to aluminium oxides (Goldberg et al., 1996). It also adsorbs strongly to manganese oxides and some clays under acidic conditions. Sorption to carbonate minerals is insignificant (Goldberg et al., 1996).

Under reducing conditions, molybdenum immobilisation has been attributed to the reduction of molybdate (Mo(VI)) to Mo(IV) and precipitation as MoS_2 (e.g. Amrhein et al., 1993). This can be described by the half-reaction:

$$MoO_4^{2-} + 2e^- + 2HS^- + 6H^+ \rightarrow MoS_2 + 4H_2O.$$

However, the kinetics of MoS_2 precipitation are slow and the mineral is rarely seen in natural systems (Erickson and Helz, 2000; Bostick et al., 2003). Molybdenum more likely co-precipitates with FeS or FeS_2 under such reducing sulphidic environments (Helz et al., 2004). This gives rise to the often high concentrations of Mo found in sulphide minerals. Helz et al. (1996) suggested that HS^- ions present under S-reducing conditions could transform conservative dissolved molybdate to reactive thiomolybdate species which are more susceptible to scavenging by Fe-rich particles and S-rich organic matter (Vorlicek et al., 2004). In sulphidic solutions, molybdate can undergo sulphidation in a series of steps, leading through monothio-, dithio- and trithio- to tetrathiomolybdate. Though thermodynamically unstable, these intermediate (Mo(VI)) thiomolybdates could become dominant in sulphide-rich environments (Erickson and Helz, 2000). Lyons et al. (2003) suggested that organic matter could have an important role to play in thiomolybdate formation.

Under reducing conditions, molybdate (MoO_4^{2-}) and tetrathiomolybdate (MoS_4^{2-}) have also been observed to adsorb onto synthetic pyrite (Bostick et al., 2003). Adsorption of the MoO_4^{2-} ion to pyrite was noted to be greatest at low to neutral pH, although MoS_4^{2-} sorption remained strong even at high pH. Bostick et al. (2003) suggested that molybdate sorption to pyrite was reversible while the sorption of tetrathiomolybdate likely forms strong inner-sphere complexes and is therefore less mobile. They also concluded that thiomolybdate species could be important controls on the concentrations of molybdenum in reduced sulphidic sediments. Vorlicek et al. (2004) concluded that Mo-Fe-S cuboidal structures on pyrite, observed by x-ray spectroscopy, must involve reduction of Mo(VI) in order for them to be stabilised. They suggested that zero-valent sulphur was an important factor in reducing the Mo.

Experimental column studies have shown that molybdenum can be mobilised from aquifer sediments under reducing conditions in response to reductive dissolution of iron and manganese oxides (Schlieker et al., 2001). Concentrations of molybdenum in a sand column with acetate as a reducing agent increased modestly to $1.8\ \mu g\ L^{-1}$ as a result of reduction of iron-manganese oxides, but decreased further along the column as a result of sulphate reduction and the co-precipitation of molybdenum with FeS (Schlieker et al., 2001).

This spatial variation in dissolved Mo concentrations has also been observed in aquifers. Smedley and Edmunds (2002) investigated molybdenum in groundwaters from the East Midlands Triassic Sandstone aquifer. The aquifer outcrops in central Nottinghamshire but is confined in east Nottinghamshire and Lincolnshire by poorly-permeable marls and mudstones of the Mercia Mudstone Group. Smedley and Edmunds (2002) found that molybdenum concentrations were low in oxic, unconfined groundwaters in Nottinghamshire (Figure 3.1) but increased progressively downgradient (up to 3.5 µg L^{-1}) in the confined, reducing part of the aquifer further eastwards. This they concluded was probably a result of reductive dissolution of iron oxides; manganese oxides were observed to be of low abundance in the aquifer. Concentrations of molybdenum in old, deep, saline groundwaters further down the groundwater flow gradient in Lincolnshire were lower (<2 µg L^{-1}) as a result of incorporation into precipitating sulphide (FeS).

Dalai et al. (2005) reported concentrations of molybdenum up to 0.5 µg L^{-1} in fresh river waters of the Chao Phraya estuary, Thailand. Estuarine waters (salinity up to 25 ‰) had molybdenum concentrations up to 11 µg L^{-1}. The molybdenum concentration of seawater is taken to be around 10 ±1 µg L^{-1} but Dalai et al. (2005) concluded that the molybdenum concentrations of the most saline estuarine waters studied were higher than could be achieved by simple mixing of freshwater and seawater. The authors concluded that the excess dissolved molybdenum observed was derived by reductive mobilisation, principally of manganese oxides, from Gulf of Thailand bottom sediments.

Morrison et al. (2006) reported high concentrations of molybdenum and uranium mobilised by oxidation reactions at a uranium tailings site in Colorado, USA. They observed the

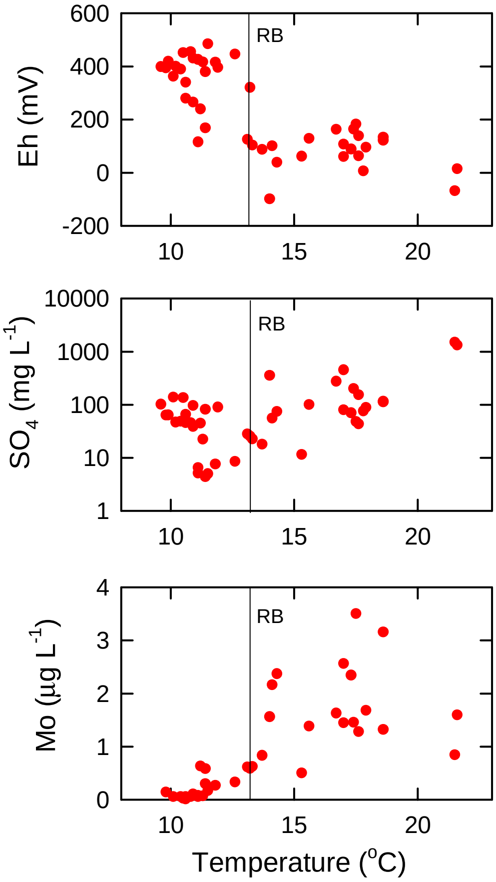

Figure 3.1 Variation in redox potential (Eh), SO_4 and Mo in groundwater from the East Midlands Triassic Sandstone aquifer (after Smedley and Edmunds, 2002). Groundwater temperature increases eastwards in response to increasing borehole depth and groundwater residence time and is here used as an indicator of the position of groundwater samples along the flow line. A redox boundary (RB) is observed close to the confined/unconfined interface.

unexpectedly early breakthrough of molybdenum from a permeable reactive barrier composed of zerovalent iron (ZVI) installed to treat the uranium-molybdenum-rich waters. Influent molybdenum concentrations were around 4.8 mg L^{-1}. The ZVI in the barrier was observed initially to reduce dissolved molybdenum concentrations in the effluent to around 0.1 mg L^{-1}, although after 250 days, concentrations increased to as much as four times the influent concentration because of desorption of molybdenum. Investigation of the ZVI barrier revealed that the breakthrough related to the precipitation of calcite, Fe oxide and S minerals in pore spaces which reduced the permeability of the permeable reactive barrier and led progressively to flow via preferential flowpaths and ultimately to complete bypass of the ZVI horizon.

Significant factors that appear to give rise to increased molybdenum concentrations in groundwaters therefore appear to include the generation of reducing conditions, relative abundance and instability of molybdenum-rich minerals (e.g. iron oxides, sulphide minerals) in the aquifer, and groundwater residence time.

4 Reconnaissance survey of molybdenum in drinking water in England & Wales

4.1 SAMPLING SURVEY DESIGN

4.1.1 Treated public-supply survey

The main purpose of a survey of public-water-supply sources is to identify the extent of risk of exceedence of the WHO guideline value of 70 µg L^{-1} Mo. This purpose is not the same as the common objective of a survey, which is to estimate a population mean of some variable of interest. The difference in purpose has a strong influence on the choice of survey design. Ultimately it would be desirable for every public-water-supply source to conform to the WHO guideline value (or EC drinking-water limit). A non-exhaustive survey can never guarantee this. Where there are limited resources, it is instead necessary to focus sampling attention on those sources where the risk is considered *a priori* to be higher, on the basis of an examination of existing data.

The terms of reference were to sample up to 12 sources from England & Wales, covering all major types of water source: groundwater, rivers and upland reservoirs. Evidence from available data suggests that, at a national scale, the probability of exceedence in water from any source is very small. Estimation of this proportion on a national scale, using simple random sampling, and scoring each site according to pass or fail, would require a much larger sample to determine this small proportion with reasonable accuracy. If say four groundwater samples, collected by simple random sample, showed no exceedences, then a Bayesian statistical analysis based on a binomial distribution and using standard assumptions, would give a 95% confidence interval of (.0001,0.44) for the true probability. This is not very informative, but compliance in all four samples is much the most likely outcome of simple random sampling if the true probability is very small (<0.01). This (binomial) approach takes no account of the continuous nature of the molybdenum concentration, but the extreme skewness of the values means that distributional assumptions needed for other techniques are questionable, particularly for spatially correlated data. There are also insufficient data to attempt formal stratification, although this might be a good option with a larger sample.

In view of the inadequacy of data acquirable under the terms of reference for a formal probability-based survey design, a purposive sampling approach was adopted, focusing on those regions where the risk of exceedence is believed to be highest. Such a scheme may be interpreted within the terminology of the Water Framework Directive (WFD) as “operational monitoring”, designed to “establish the status of those bodies identified as being at risk of failing to meet their environmental objectives”. Operational monitoring generally follows an impact assessment or surveillance monitoring identifying water bodies at risk. This approach involves selection of monitoring points within the water bodies at risk that are representative of the relative risks. While the present sampling scheme does not fall within the remit of the WFD, the investigation is similar in kind and there is good reason to conform to WFD recommendations in monitoring.

The most prominent groundwater source at risk on the basis of examination of data that existed prior to the study was the Spilsby Sandstone in the vicinity of Skegness. Elsewhere there are clusters of elevated Mo concentrations in parts of Cambridgeshire and Derbyshire and south-west of Birmingham. Groundwater sources in these areas were therefore targeted for monitoring.

It was considered highly unlikely that upland reservoirs have Mo concentrations above the WHO guideline value. However, apart from parts of Cumbria, upland areas have not been investigated previously. G-BASE data suggest that relatively high concentrations exist in sediment in streams draining parts of North Wales and the Peak District. Public-supply sources from these areas were therefore also selected as reservoir monitoring sites.

River sources flowing through industrial areas, particularly former mining areas, were also targeted for monitoring. For rivers, it was considered important that sampling included low- as well as high-flow samples, since there is clear evidence that for many rivers, concentrations are higher under low-flow conditions (albeit water abstracted at low flow from rivers and stored in reservoirs may have undergone some dilution through mixing of waters of varying residence times).

4.1.2 Domestic tapwater survey

The purpose of sampling tap water in this study was to determine whether there is any effect of pipework on Mo concentrations in drinking water. This is most easily achieved by measuring the difference in concentrations between water leaving a treatment works and water delivered to household taps. Molybdenum might either be lost or gained in the system and this might depend on both the nature of the pipework and the chemical composition of the source water. It may also depend on the residence time of water in the pipework.

In the absence of any knowledge of possible changes in the supply line, it was considered sensible to investigate a limited number of areas with known supply sources, with several taps in each area. For this reason, sampling design incorporated taps supplied from three of the surveyed supply areas, one from each of the main water source types (groundwater, river, upland reservoir water). This would be most likely to encompass samples with variable

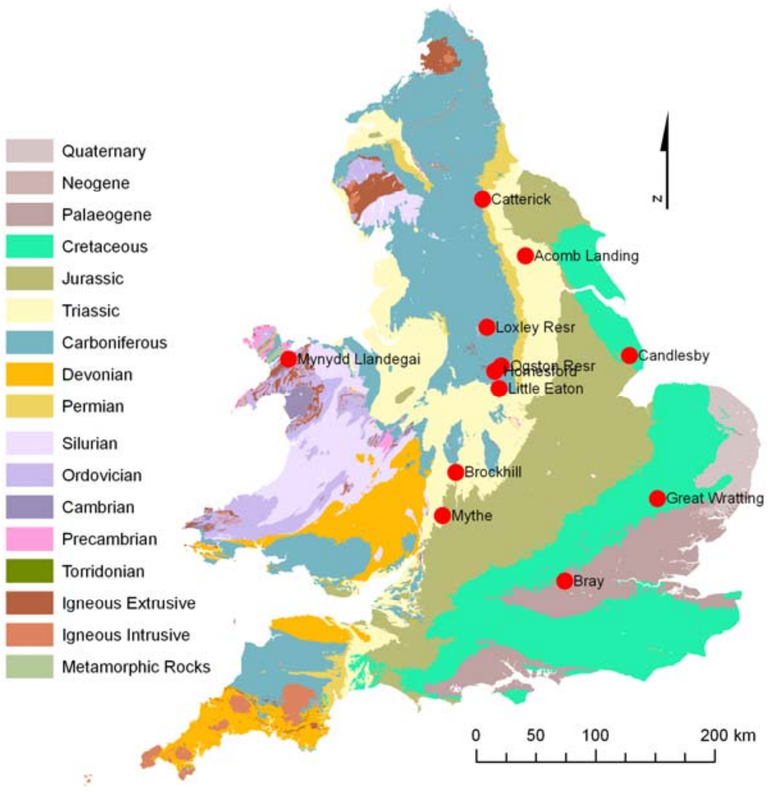

Figure 4.1 Sampling locations of the public-supply sources.

Table 4.1 Public-supply sources and supply areas.

Site	Production	Source	Supply area
Groundwater sources			
Brockhill	100 L/s	Brockhill bhs	Reddich
Candlesby	70 L/s	Candlesby bhs and Welton bhs, (Skarsby Res).	Burgh-Le-Marsh, Skegness, Welton-Le-Marsh and other local supplies
Catterick	197 L/s	Catterick bhs and Morris Grange Res.	Scotch Corner, Dolton supply system
Great Wratting	155 L/s	Gt Wratting bhs and Wixon bhs	Haverhill, Boyton Res, Hundon Res, Little Thurlow booster
Homesford	580 L/s	Sough (including old lead mines)	Alfreton and Ripley
River sources			
Acomb Landing	312 L/s	River Ouse	West York
Bray	232 L/s	River Thames	Camberley, Fleet, Surrey Hill Res. and Frith Hill Res.
Little Eaton	1620	River Derwent	Derwent Valley Aqueduct, Derby, Littleover and Mickleover
Mythe	N/A	River Severn	Cheltenham, Dursley and Gloucester
Reservoir sources			
Loxley	N/A	Strines Res., Dale Dyke, Agden Res.	Sheffield and some local farms
Mynydd Llandegai	70 L/s	Llugwy Res. (45–60 L/s) and Marchlyn Res. (10–20 L/s)	Bangor (50 L/s), Bethesda
Ogston	695 L/s	Ogston Res.	Whiteborough Res., Higham Res. – Chesterfield, parts of Sheffield, north Notts, north Derbys

Abbreviations: bh: borehole, Res.: reservoir; N/A: not available

major-ion chemistry (e.g. soft vs. hard water). It was also desirable to select supply sources with variable Mo concentrations. This approach required delay in surveying of tapwater until the results of the earliest public-supply-source surveys were available. Taps were selected from a mixture of buildings with old and new plumbing, and sampling included first morning draw from the mains and after flushing to clear pipework within the building. Some near-replication was attempted by sampling within the same street (assuming the same mains source and similar plumbing). Actual site selection depended heavily on obtaining permission and access to sample from householders.

4.2 SAMPLING AND ANALYTICAL METHODOLOGY

4.2.1 Public-supply survey

A map of sample locations is given in Figure 4.1. Details of the selected public-supply sites and their corresponding supply areas are given in Table 4.1 and details of water treatment at each site are given in Table 4.2. Twelve sites in total were visited, of which eleven were sampled four times. Sampling dates were March–May 2007, July 2007, November–December

Table 4.2 Water-treatment details for the survey sites.

Site	Treatment
Groundwater sources	
Brockhill	Cl_2 – F dosing
Candlesby	Rapid sand filter – sodium hypochlorite – SO_2 – H_3PO_4 dosing
Catterick	Cl_2 – H_3PO_4 dosing
Great Wratting	Aeration – GAC – Cl_2 – SO_2 – PO_4 dosing
Homesford	GAC – Cl_2 – H_3PO_4 – SO_2
River sources	
Acomb Landing	$Al_2(SO_4)_3$ – rapid sand filters – slow sand filters – GAC – Cl_2 – SO_2 – MSP (added to reduce Pb content)
Bray	Pre-ozone – Cl_2 – PAC 18% coagulation – sand filters – H_{2SO4} (summer algae only) – inter-ozone – GAC – Cl_2 – SO_2
Little Eaton	$Fe_2(SO_4)_3$ coagulation – sand filter/anthracite filter – GAC – Cl_2 – SO_2 – H_3PO_4
Mythe	Settling tanks – $Al_2(SO_4)_3$ / $Fe_2(SO_4)_3$ – sand filters – ozone – sodium hypochlorite – SO_2 – lime – GAC
Reservoir sources	
Loxley	$Fe_2(SO_4)_3$ – lime – dissolved air filtration (DAF) – filters – hypochlorite –lime – MSP
Mynydd Llandegai	Lime – sand filters – Cl_2 – lime – H_3PO_4 dosing
Ogston	$Fe_2(SO_4)_3$ coagulation – sand filter/anthracite filter – GAC – Cl_2 – SO_2 – H_3PO_4

Abbreviations: GAC= Granular activated carbon, MSP=monosodium phosphate

2007 and March 2008. Water from one site (Homesford) could only be sampled twice during the study because of long-term engineering works at the site. Of the twelve sites, five were from groundwater sources (four boreholes, one mine sough), four from river sources and three were from upland reservoirs. Duplicate samples were taken at three of the sites during the surveys.

Sampling and sample preservation were carried out following DWI recommended procedures (DWI, unpublished). Water samples were taken from the 'final' supply tap at the treatment works after the tap had been allowed to run for the specified flush time (labelled on the tap, usually between five and ten minutes). Samples were collected in factory-new 125 mL Nalgene™ HDPE bottles pre-washed in 10% Aristar™ nitric acid, rinsed with ultrapure water (ASTM type I reagent grade water, including a UV cracker) and dried. Each bottle was prior dosed with 1.25 mL Aristar™ nitric acid (equivalent to1% v/v, pH<2, following best practice documented in ISO 5667 Part 3:2003). Bottles were then sealed in a self-seal bag ready for use in the field. After filling, sample bottles were returned to the self-seal bag and stored in a cool box for transportation to the laboratory. Samples were sent to the analytical laboratory within two weeks of batch collection and were stored in a refrigerator (<5ºC) prior to analysis.

During the sampling, on-site measurements were also made of electrical conductivity, alkalinity (as HCO_3, by titration with H_2SO_4) and pH of flushed water.

Collected water samples were pretreated by heating overnight at 80ºC in the BGS Wallingford laboratory in order to dissolve any particulate matter and trace elements adsorbed to bottle walls (DWI, unpublished). Bottles were allowed to cool and aliquots were then decanted into pre-washed (10% HNO_3) and rinsed 30 mL Nalgene™ LDPE bottles ready for analysis.

Sampling included the preparation of two field blanks (separate sampling rounds) which were taken through the same procedure as the samples. In addition, a 10 µg L^{-1} standard solution (10,000 mg L^{-1} stock solution, traceable to NIST) was also prepared with each sample batch and analysed along with the batches. Heated (80ºC) and unheated aliquots of this solution were analysed for comparison.

4.2.2 Domestic tapwater survey

Three towns/suburbs were selected for the tapwater survey. These were Bangor (Gwynedd), supplied by Mynydd Llandegai treatment works, Mickleover (Derbyshire), supplied by Little Eaton treatment works, and Haverhill (Suffolk), supplied by Great Wratting treatment works. The selection was made on the basis that supply areas were clearly identifiable and encompassed sources from upland reservoir, river water and groundwater.

Samples were taken from eight domestic properties in each of the three areas (i.e. 24 domestic taps). Sampling was carried out over the period 28th November to 4th December 2007, coincident with the third monitoring round of the public-supply sources. In each source area, four taps were from relatively modern houses (post-1990) and four from older houses (pre-1960s).

Both pre- and post-flush samples were taken from each tap. The pre-flush sample was collected first thing in the morning in order to assess the chemical composition of water that had been in the pipes overnight. The post-flush sample was taken after the tap had been allowed to run to waste for 2–3 minutes. In each case, samples were from the normal source of drinking water in the household (usually the kitchen tap). Sampling packs and detailed instructions were given to residents to carry out the sampling themselves the following morning in order to ensure that first-draw samples could be taken.

Samples were collected in Nalgene™ bottles precleaned with acid and rinsed with deionised water. These were not pre-dosed with acid. Following standard procedures (DWI, unpublished), a 1L sample of pre-flush water was collected (HDPE Nalgene™ bottles). Post-flush samples were collected in 125 mL HDPE bottles. Bottles were collected from the household the same day and transported in a cool box. Samples were acidified (1% v/v Aristar HNO_3) in the BGS Wallingford laboratory as soon as possible after collection (within a few hours). The subsequent protocol was identical to that for the public-supply samples. Laboratory blanks and standards were also collected and processed along with the tapwater samples.

In most cases the responses from residents were very positive and it was possible to obtain four samples from the same street, or within very close proximity. Several participants were interested in the results of the survey and have been sent copies of the analysis by letter.

4.2.3 Chemical analysis

All samples were analysed for Mo and other trace elements at the CEH Environmental Analysis Laboratory in Lancaster using a Perkin Elmer DRCII ICP-MS instrument. The laboratory procedure is UKAS-accredited (SOP 3504; testing laboratory 2506). Standard reference material validation data for Mo from the laboratory are given in Table 4.3. The quoted detection limit for Mo from validation tests is 0.03 µg L^{-1}.

Determinands analysed at the same time as Mo were Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, Ti, U, V, W and Zn. The detection limit for Mo in all sample batches was 0.03 µg L^{-1} (4σ on the blank) except for samples S07-00782–S07-00793 (sampling round 2) which were 0.06 µg L^{-1} due to sample dilution. During the course of the

Table 4.3 Laboratory validation and QC monitoring data for molybdenum.

Reference material	Certified/nominal concentration ($\mu g\ L^{-1}$)	No. replicates	Mean	sd	% recovery
Method validation					
SLRS-4	0.21	12	0.19	0.01	92
1643e	121	12	119	11.2	98
TMRain-95	0.17	12	0.16	0.02	97
ICPMS-QC	5	12	5.12	0.21	102
ICPMS-QC (low)	0.5	12	0.54	0.01	107
Routine QC monitoring data					
TMRain-95	0.17	37	0.16	0.02	95
ICPMS-QC	5	55	4.97	0.14	99

ICPMS-QC: certified standard from an external supplier

analysis, eight measurements of CRM SLRS-4 were also made. These gave a mean value of 0.19 $\mu g\ L^{-1}$ with a standard deviation of 0.01 $\mu g\ L^{-1}$ (certified value 0.21 ±0.02 (2σ) $\mu g\ L^{-1}$).

Four analyses of a BGS Wallingford laboratory blank gave values of <0.06 $\mu g\ L^{-1}$ (three being <0.03 $\mu g\ L^{-1}$). Out of eight CEH laboratory blanks, seven had Mo concentrations <0.03 $\mu g\ L^{-1}$; the eighth being 0.034 $\mu g\ L^{-1}$. The two field blanks each had Mo concentrations <0.03 $\mu g\ L^{-1}$. No blank correction was applied to the Mo data.

Prepared 10 $\mu g\ L^{-1}$ standard solutions (unheated) gave a mean value of 9.44 $\mu g\ L^{-1}$ (standard deviation 0.24 $\mu g\ L^{-1}$); four pretreated standard solutions (heated at 80ºC) gave a mean value of 9.53 $\mu g\ L^{-1}$ (standard deviation 0.13 $\mu g\ L^{-1}$).

Results for three duplicate samples (Acomb Landing round 4; Brockhill round 2; Candlesby round 2) showed variations of <5% between analysed Mo concentrations.

4.3 RESULTS

4.3.1 Treated public-supply sources

Chemical analysis results from the four public-supply sampling rounds are given in Appendix 1A and 1B. Waters from the survey sites have mostly near-neutral pH values (most acidic Brockhill, pH range 6.5–6.7; most alkaline Little Eaton, pH 7.0–8.3). Electrical conductivity measurements show that the least mineralised waters are from Mynydd Llandegai (71–97 $\mu S\ cm^{-1}$) while the most mineralised are from Great Wratting (929–1120 $\mu S\ cm^{-1}$). Waters from Mynydd Llandegai also had the lowest alkalinity values (≤18 $mg\ L^{-1}$ as HCO_3), consistent with them being soft water. These results are in line with variations expected between surface waters and groundwaters. Considerable variability in trace-element concentrations between sites is also observed (Appendix 1). Temporal variability is apparent for a number of trace elements, especially in the river-water samples. However, no clear temporal trends are apparent from the limited available data.

Variations in Mo concentrations between sampling rounds at each of the sites are shown as boxplots in Figure 4.2. For Brockhill (groundwater), Loxley (reservoir) and Mynydd Llandegai (reservoir), all measured concentrations were below the detection limit of 0.03 $\mu g\ L^{-1}$. Of the sources with detectable Mo, there appears to be more seasonal variability in concentrations in surface-water sources than in groundwaters. Figure 4.2 also suggests that differences exist in overall mean concentrations, although all sources have concentrations well below the WHO guideline value for Mo of 70 µg L^{-1}.

Analysis of variance has been applied separately to groundwater and surface water sources, restricted to sites with detectable Mo concentrations. The analysis confirms significant differences between sources ($p < 0.05$), but no significant consistent difference between batches within sites. There is therefore no evidence of a consistent seasonal effect.

4.3.2 Domestic tapwater survey

MOLYBDENUM

Chemical data from the tapwater survey are given in Appendix 2A and 2B. The relationship between public-supply source and tapwater Mo concentrations for the three surveyed areas is shown in Figure 4.3. The uniformity in Mo concentrations in each source area is striking, in comparison with concentration differences between sources. Only relatively small variability exists between houses (old and new), between pre- and post-flush samples, and between the tapwater and source-water samples. This suggests that tapwater concentrations for these samples are largely unaffected by processes occurring within the water distribution pipework.

Of the areas surveyed, the greatest variation in Mo concentrations between houses occurs at Haverhill. However, analysis of variance (on the basis of AIC minimisation) detects no significant difference in concentrations between houses or between tapwater and source water ($p > 0.05$).

Data for Mo in tapwaters from Mickleover show that concentrations do not differ significantly between houses, although tapwater concentrations are lower than source concentration. While this difference is statistically significant ($p < 0.001$), the magnitude of the difference is very small in relation to the concentrations measured. At Mickleover, source water and tapwater were sampled on 27 and 28 November 2008 respectively, rather than on the same day. Since the Mickleover source is the River Derwent at Little Eaton, which has

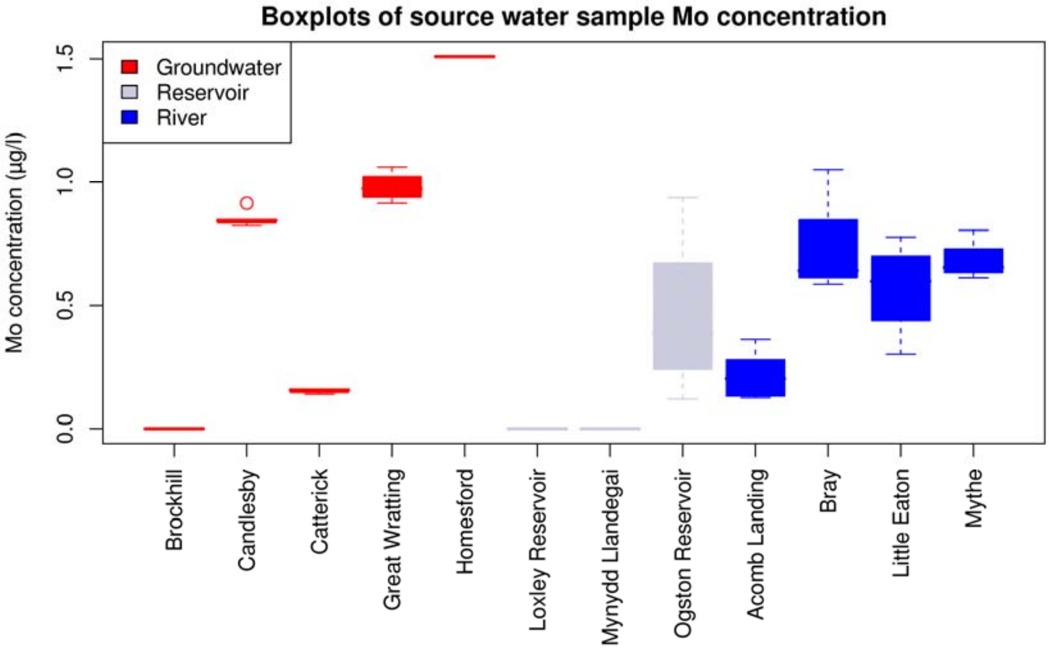

Figure 4.2 Boxplots of public-supply source molybdenum concentrations from the four sampling rounds (outliers are shown as circles).

comparatively variable Mo concentration (Figure 4.2), the difference in timing of sampling may be the cause of the difference in source and tapwater concentrations. There is an indication that post-flush concentrations are significantly higher than pre-flush for this source (p=0.04), though the absolute concentrations and differences are very small.

At Bangor, all analysed Mo concentrations in the tapwater samples were below the detection limit of 0.03 µg L^{-1} and corresponded with the concentrations determined at the supply source.

OTHER TRACE ELEMENTS

A detailed statistical analysis of the data for other analysed trace elements in the tapwater samples is beyond the scope of this report. However, the data (Appendix 2) show some notable differences in chemistry between areas, consistent with chemical compositions of the respective source waters.

One striking observation in the dataset is the significant differences in concentration of some trace elements between pre- and post-flush samples. Pre-flush samples commonly contain much higher concentrations of Ni, Cu, Zn, Pb and to some extent Cd than post-flush samples. These elements most likely derive from the metal pipework in the distribution system and are therefore most concentrated in the water that has been stored in the pipes overnight. One sample had a concentration of Ni in excess of the drinking-water limit for Ni of 20 µg L^{-1} (26 µg L^{-1}) and one had a concentration of Pb in excess of the current drinking-water limit of 25 µg L^{-1} (199 µg L^{-1}), though the excesses were not in the same sample. A further sample had a lead concentration just in excess of the 2013 drinking-water limit of 10 µg L^{-1} (11.2 µg L^{-1}). In each case, the post-flush samples had concentrations well below the respective limits (Appendix 2). For Pb, the concentrations in samples from old houses (pre-1960s) were significantly higher than for new (post-1990) houses, likely due to the presence

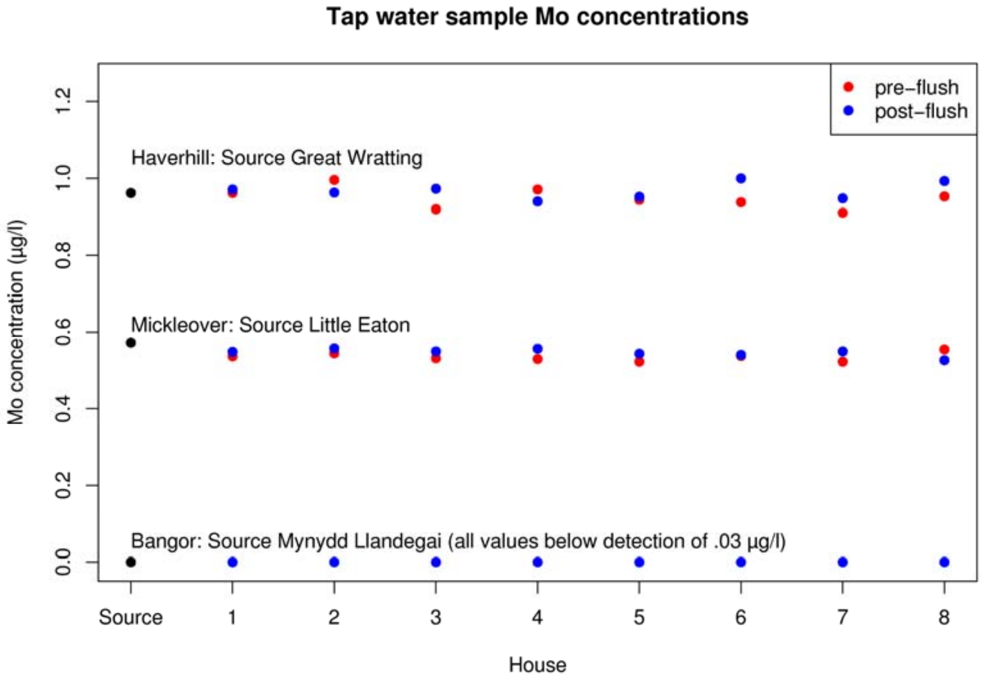

Figure 4.3 Molybdenum concentrations in tapwater samples from three surveyed locations compared to their respective public-supply sources (households 1–4 are 'new' properties; 5–8 are 'old' properties; see Appendix 2).

of lead pipes (and/or solder) in the plumbing systems.

There is a tendency for post-flush samples to have slightly higher concentrations of Cr than pre-flush samples, though as with Mo, the magnitude of the increases is small. All samples had concentrations at least two orders of magnitude less than the drinking-water limit for Cr of 50 $\mu g\ L^{-1}$.

The reason for the slightly higher concentrations of both molybdenum and chromium in post-flush samples compared to pre-flush samples is unclear. It is possible that adsorption of molybdenum and chromium (both of which form oxyanions in oxic neutral-pH waters) onto pipework, solder or any encrusted minerals in the plumbing system could have occurred. If such a process has occurred, it might be expected to affect overnight standing water to a greater extent than flowing water. While the observation is interesting, this conclusion remains speculative without further information.

5 Conclusions and implications

Collated data for molybdenum in geological materials and waters suggest that concentrations are usually low. Rocks, sediments and soils usually have concentrations <10 mg kg^{-1} with higher concentrations possible in clay deposits, particularly black shales. Relatively high concentrations are also possible in ironstones and some granites. Concentrations observed in sediments from Britain are up to 309 mg kg^{-1}, although this is atypical.

Molybdenum concentrations in waters are usually <1 µg L^{-1} and often <0.1 µg L^{-1}. Analyses of more than 11,000 streamwater samples in England & Wales from the BGS G-BASE dataset had a 10–90th percentile range of 0.08–2.45 µg L^{-1} and a median of 0.57 µg L^{-1}. Analyses of river waters under the LOIS project also revealed median concentrations typically <1 µg L^{-1} at monitored sites although higher concentrations were found at sites on the Rivers Calder, Don, Trent, Great Ouse and Thames. The highest observed concentrations in both the LOIS and G-BASE datasets were from the River Aire and its tributaries in south Yorkshire. These were highest when water flows were low and in the River Aire, some low-flow concentrations approached the WHO guideline value (although only one sample exceeded it). The anomalously high concentrations are most likely caused by contamination with coal-mine drainage, although other industrial pollutants could also be responsible.

Concentrations of molybdenum in lake waters from Cumbria appear to have universally low concentrations, around 0.1 µg L^{-1} or less. Groundwater concentrations are more variable, ranging between <0.1–120 µg L^{-1}. Nonetheless, the vast majority of samples in the BGS groundwater dataset have concentrations well below the WHO guideline value for molybdenum in drinking water of 70 µg L^{-1}. Only three samples (0.21%) had concentrations >70 µg L^{-1}.

Data for molybdenum from a survey of 12 public-supply sources distributed across England & Wales and for tapwater surveys from three of these supply areas indicated a clear variability in concentrations between sources. However, results from sampling sources up to four times (March–May 2007, July 2007, November–December 2007 and March 2008) revealed no discernible seasonal trends. In addition, little change in molybdenum concentrations was observed between source water and tapwater, suggesting that inputs of molybdenum to the drinking water from the pipe distribution system were negligible. In some cases, post-flush samples had slightly higher Mo concentrations than pre-flush samples but the increases compared to morning first-draw samples were of small magnitude and not of practical significance.

Notable differences were found between pre-flush and post-flush samples in concentrations of the trace metals Pb, Ni, Cu and Zn. Highest concentrations were present in pre-flush waters, and for Pb, higher concentrations were in pre-flush waters from older properties. The drinking-water limits for Pb (currently 25 µg L^{-1}) or Ni (20 µg L^{-1}) were exceeded in two pre-flush samples, although all post-flush samples had concentrations below the respective limits.

If the molybdenum data collected in the surveys are representative of UK source waters and tapwaters, then concentrations of molybdenum are at least an order of magnitude below the drinking-water threshold of 70 µg L^{-1}. The probability of any UK source concentrations occurring above this threshold cannot be computed from the data collected. Such an event would be so far from the measured values as to be outside the range of meaningful extrapolation.

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Appendix 1 Chemical data for water samples from the public-supply survey

APPENDIX 1A DATA FOR SELECTED TRACE ELEMENTS

ID number	Locality	Source type	Sample date	pH	EC (µS cm^{-1})	HCO$_3$ (mg L^{-1})	Round	Li (µg L^{-1})	Be (µg L^{-1})	Al (µg L^{-1})	Sc (µg L^{-1})	Ti (µg L^{-1})	V (µg L^{-1})	Cr (µg L^{-1})	Mn (µg L^{-1})	Co (µg L^{-1})	Ni (µg L^{-1})	Cu (µg L^{-1})	Zn (µg L^{-1})
S07-00434	Acomb Landing	River	01-May-07	7.08	446	117	1	4.65	<0.003	11.4	0.247	4.90	0.446	0.469	0.276	0.123	0.612	0.619	3.99
S07-00786	Acomb Landing	River	18-Jul-07	7.09	484	89.0	2	5.75	<0.006	5.88	0.741	4.16	0.551	0.405	2.46	0.037	1.23	0.717	4.85
S07-01157	Acomb Landing	River	27-Nov-07	6.87	498	101	3	4.27	0.006	<0.6	0.401	3.42	0.365	0.392	0.194	0.035	0.512	0.558	4.35
S08-00565	Acomb Landing	River	12-Mar-08	7.10	330	61.6	4	2.42	0.01	3.07	0.284	3.24	0.264	0.312	0.089	0.017	0.196	0.524	3.06
S08-00566	Acomb Landing	River	12-Mar-08				4	2.47	0.01	2.98	0.298	3.29	0.27	0.318	0.09	0.015	0.205	0.705	5.1
S07-00427	Bray	River	03-Apr-07	7.38	747	154	1	5.58	<0.003	44.1	0.967	1.10	0.757	0.573	0.063	0.232	1.21	2.99	4.57
S07-00787	Bray	River	19-Jul-07	7.80	625	241	2	5.97	<0.006	73.8	1.30	1.31	1.12	0.376	0.036	0.081	0.971	1.03	<2.00
S07-01161	Bray	River	29-Nov-07	7.34	699	223	3	7.75	<0.003	17.8	1.04	1.19	0.829	0.412	0.2	0.102	1.37	102	5.71
S08-00569	Bray	River	14-Mar-08	7.31	690	219	4	5.35	0.021	22.8	0.809	1.17	0.64	0.44	0.145	0.069	0.747	34.8	8.63
S07-00431	Brockhill	Groundwater	04-Apr-07	6.51	474	80.5	1	9.45	0.13	2.82	1.76	2.17	2.13	0.656	0.357	0.085	2.28	2.06	3.38
S07-00777	Brockhill	Groundwater	16-Jul-07	6.60	460	84.1	2	10.1	0.155	3.24	1.67	2.00	2.43	0.749	0.377	<0.006	4.53	2.86	6.43
S07-00778	Brockhill	Groundwater	16-Jul-07	6.60	460	84.1	2	9.24	0.14	3.39	1.64	2.00	2.37	0.701	0.36	<0.006	2.93	2.72	4.94
S07-01154	Brockhill	Groundwater	26-Nov-07	6.71	453	135	3	11.9	0.149	<0.6	1.27	1.51	2.07	0.713	0.295	<0.006	3.83	2.56	8.29
S08-00560	Brockhill	Groundwater	10-Mar-08	6.52	435	118	4	9.83	0.123	2.0	1.39	1.83	1.53	0.587	0.342	<0.006	4.40	2.93	13.9
S07-00423	Candlesby	Groundwater	26-Mar-07	7.46	708	215	1	17.5	<0.003	<0.6	1.77	5.80	0.159	0.219	0.31	0.029	0.022	1.66	1.2
S07-00788	Candlesby	Groundwater	20-Jul-07	7.84	682	321	2	18.2	<0.006	<1.20	1.43	4.84	0.251	0.32	0.331	<0.012	<0.020	1.49	<2.00
S07-00789	Candlesby	Groundwater	20-Jul-07	7.84	682	321	2	18.7	<0.006	<1.20	1.46	5.07	0.261	0.316	0.191	<0.012	<0.020	0.999	<2.00
S07-01162	Candlesby	Groundwater	03-Dec-07	7.69	772	340	3	16.0	0.012	<0.6	0.927	2.59	0.301	0.458	1.76	<0.006	1.89	19	35.5
S08-00568	Candlesby	Groundwater	13-Mar-08	7.42	767	317	4	11.6	0.023	<0.6	1.08	3.88	0.223	0.413	0.196	<0.006	<0.010	0.831	<1.00
S07-00433	Catterick	Groundwater	01-May-07	7.43	647	260	1	20.9	<0.003	<0.6	1.03	4.81	0.249	0.451	0.135	0.106	0.083	5.59	5.84
S07-00785	Catterick	Groundwater	18-Jul-07	7.69	526	187	2	19.2	<0.006	<1.2	0.979	4.20	0.275	0.345	0.025	<0.012	<0.020	2.95	2.82
S07-01159	Catterick	Groundwater	28-Nov-07	7.40	670	268	3	19.1	0.003	<0.6	0.675	3.04	0.342	0.483	0.234	<0.006	<0.010	8.08	15.6
S08-00564	Catterick	Groundwater	12-Mar-08	7.28	645	249	4	15.7	0.013	<0.6	0.663	3.40	0.171	0.466	0.114	<0.006	2.91	12.8	8.08
S07-00425	Great Wratting	Groundwater	30-Mar-07	7.28	1080	223	1	22.3	<0.003	1.08	3.09	5.08	0.429	0.405	0.375	0.715	4.62	3.9	6.27
S07-00790	Great Wratting	Groundwater	20-Jul-07	7.62	929	354	2	24.2	<0.006	<1.20	2.88	5.16	0.447	0.306	0.336	0.438	3.88	2.33	5.66
S07-01163	Great Wratting	Groundwater	04-Dec-07	7.44	1120	364	3	20.9	0.004	<0.6	1.92	3.46	0.474	0.379	0.36	0.48	5.48	5.38	12.1
S08-00570	Great Wratting	Groundwater	17-Mar-08	7.24	1110	352	4	18.7	0.009	0.879	2.15	4.42	0.437	0.454	1.38	0.537	3.07	3.23	5.58
S07-00428	Homesford	Sough	04-Apr-07	7.21	621	162	1	4.88	<0.003	0.879	0.901	5.97	0.264	0.58	0.253	0.132	2.68	1.37	389
S07-00783	Homesford	Sough	17-Jul-07	7.40	583	189	2	4.96	<0.006	<1.2	0.844	4.62	0.251	0.512	0.273	<0.012	2.24	1.16	375
S07-00429	Little Eaton	River	04-Apr-07	8.24	651	123	1	6.4	<0.003	2.58	0.774	5.32	0.225	0.613	0.185	0.188	2.24	0.57	22.3
S07-00781	Little Eaton	River	17-Jul-07	7.00	233	47.5	2	1.7	0.01	41.2	0.685	5.55	0.222	0.576	1.85	0.04	0.857	0.484	71
S07-01156	Little Eaton	River	27-Nov-07	7.60	629	155	3	5.75	<0.003	<0.6	0.53	3.36	0.318	0.454	0.907	0.078	2.21	0.485	23.2
S08-00563	Little Eaton	River	11-Mar-08	8.29	629	169	4	5.35	0.003	1.18	0.508	5.63	0.198	0.346	0.222	0.033	2.14	0.384	21.5

ID number	Locality	Source type	Sample date	pH	EC (µS cm^{-1})	HCO_3 (mg L^{-1})	Round	Li (µg L^{-1})	Be (µg L^{-1})	Al (µg L^{-1})	Sc (µg L^{-1})	Ti (µg L^{-1})	V (µg L^{-1})	Cr (µg L^{-1})	Mn (µg L^{-1})	Co (µg L^{-1})	Ni (µg L^{-1})	Cu (µg L^{-1})	Zn (µg L^{-1})
S07-00435	Loxley Reservoir	Reservoir	01-May-07	7.70	216	6.8	1	1.92	<0.003	8.17	0.801	4.81	0.196	0.295	0.576	0.034	0.733	1.49	4.98
S07-00784	Loxley Reservoir	Reservoir	18-Jul-07	7.77	194	9.39	2	1.77	<0.006	12.4	0.774	4.52	0.197	0.322	1.06	0.022	0.670	0.476	7.81
S07-01158	Loxley Reservoir	Reservoir	28-Nov-07	7.59	201	119	3	1.97	0.017	1.01	0.52	3.23	0.221	0.262	4.98	0.047	0.793	2.05	6
S08-00567	Loxley Reservoir	Reservoir	12-Mar-08	7.75	197	116	4	1.9	<0.003	14.1	0.603	4.43	0.163	0.174	5.23	0.069	1.05	2.3	7.87
S07-00426	Mynydd Llandegai	Reservoir	02-Apr-07	8.03	71.0	18.0	1	0.29	<0.003	38.3	0.208	2.66	0.215	0.444	1.99	0.022	0.92	3.44	5.22
S07-00779	Mynydd Llandegai	Reservoir	16-Jul-07	7.37	97.0	14.5	2	0.201	0.01	53	0.125	1.36	0.221	0.522	1.95	0.01	0.553	2.35	6.94
S07-01160	Mynydd Llandegai	Reservoir	29-Nov-07	7.80	97.2		3	0.285	0.027	43.1	0.053	2.58	0.339	0.582	2.84	0.014	0.645	2.6	3.7
S08-00561	Mynydd Llandegai	Reservoir	10-Mar-08	7.16	81.2		4	0.284	0.009	41.9	0.131	1.95	0.225	0.324	2.12	<0.006	0.353	1.79	3.87
S07-00432	Mythe	River	04-Apr-07	7.60	721	109	1	7.49	<0.003	14.5	0.664	4.36	0.894	0.503	0.044	0.172	0.998	1.02	3.38
S07-00776	Mythe	River	16-Jul-07	7.15	506	85.3	2	3.84	0.004	10.7	0.877	5.41	0.547	0.557	0.077	0.046	0.84	0.965	2.53
S07-01153	Mythe	River	26-Nov-07	7.24	628	106	3	7.71	<0.003	1.23	0.653	3.19	0.711	0.43	0.058	0.07	0.881	1.91	3.38
S08-00559	Mythe	River	10-Mar-08	7.22	582	124	4	4.52	0.01	6.5	0.602	3.52	0.565	0.397	1.42	0.04	0.445	0.708	2.53
S07-00430	Ogston Reservoir	Reservoir	04-Apr-07	7.56	446	59.7	1	2.95	<0.003	0.614	0.558	4.94	0.236	0.448	0.394	0.105	1.71	0.922	5.33
S07-00782	Ogston Reservoir	Reservoir	17-Jul-07	7.76	370	61.6	2	3.01	<0.006	<1.2	0.462	4.46	0.274	0.381	4.27	0.058	1.51	0.896	5.24
S07-01155	Ogston Reservoir	Reservoir	27-Nov-07	7.66	481	109	3	3.82	0.017	<0.6	0.24	3.09	0.361	0.269	1.07	0.068	2.07	1.14	2.17
S08-00562	Ogston Reservoir	Reservoir	11-Mar-08	7.26	440	104	4	2.94	0.004	0.935	0.308	3.68	0.156	0.321	21	0.1	1.41	1.57	11

EC: electrical conductivity (25ºC)

APPENDIX 1B DATA FOR SELECTED TRACE ELEMENTS (CONT'D)

ID number	**Locality**	**Source type**	**Sample date**	**Round**	**As (µg L^{-1})**	**Se (µg L^{-1})**	**Rb (µg L^{-1})**	**Sr (µg L^{-1})**	**Mo (µg L^{-1})**	**Cd (µg L^{-1})**	**Sn (µg L^{-1})**	**Sb (µg L^{-1})**	**Cs (µg L^{-1})**	**Ba (µg L^{-1})**	**W (µg L^{-1})**	**Pb (µg L^{-1})**	**U (µg L^{-1})**
S07-00434	Acomb Landing	River	01-May-07	1	0.312	0.349	1.53	303	0.281	0.036	0.041	0.303	0.007	94.9	<0.01	0.35	0.358
S07-00786	Acomb Landing	River	18-Jul-07	2	0.379	0.347	2.14	277	0.364	0.014	0.085	0.251	<0.004	98.5	<0.02	0.406	0.139
S07-01157	Acomb Landing	River	27-Nov-07	3	0.27	0.201	1.49	303	0.203	0.032	0.058	0.189	<0.002	76.8	<0.01	0.33	0.079
S08-00565	Acomb Landing	River	12-Mar-08	4	0.207	0.218	0.813	145	0.126	0.017	<0.006	0.133	<0.002	47.7	<0.01	0.114	0.06
S08-00566	Acomb Landing	River	12-Mar-08	4	0.203	0.181	0.831	148	0.132	0.017	<0.006	0.134	0.002	48.8	<0.01	0.13	0.062
S07-00427	Bray	River	03-Apr-07	1	0.477	1.01	2.03	334	0.587	0.006	0.087	0.14	0.002	12.8	0.089	0.135	0.389
S07-00787	Bray	River	19-Jul-07	2	0.672	0.933	2.71	316	1.05	<0.004	0.107	0.171	<0.004	15.5	0.096	<0.120	0.368
S07-01161	Bray	River	29-Nov-07	3	0.533	0.498	2.31	366	0.639	0.011	5.74	0.281	<0.004	13.4	0.06	3.41	0.346
S08-00569	Bray	River	14-Mar-08	4	0.469	0.628	2.03	269	0.644	0.012	1.5	0.265	0.003	10.8	0.064	1.25	0.338
S07-00431	Brockhill	Groundwater	04-Apr-07	1	1.32	0.944	0.124	70.5	<0.03	0.042	0.054	<0.01	<0.002	129	0.011	0.124	0.059
S07-00777	Brockhill	Groundwater	16-Jul-07	2	1.33	0.946	0.126	67.3	<0.03	0.043	0.107	<0.01	<0.002	131	<0.01	0.115	0.065
S07-00778	Brockhill	Groundwater	16-Jul-07	2	1.29	0.817	0.121	64.5	<0.03	0.041	0.321	<0.01	<0.002	127	<0.01	0.085	0.065
S07-01154	Brockhill	Groundwater	26-Nov-07	3	1.24	0.434	0.095	66.7	<0.03	0.035	0.092	<0.01	<0.002	115	<0.01	0.08	0.055
S08-00560	Brockhill	Groundwater	10-Mar-08	4	1.16	0.489	0.10	55.5	<0.03	0.036	<0.006	<0.01	<0.002	93.1	<0.01	0.107	0.041
S07-00423	Candlesby	Groundwater	26-Mar-07	1	0.349	0.366	2.53	583	0.849	<0.002	0.042	0.05	0.013	24.1	0.014	<0.060	0.015
S07-00788	Candlesby	Groundwater	20-Jul-07	2	0.205	0.566	2.73	710	0.823	<0.004	0.076	<0.02	<0.004	25.6	<0.02	<0.120	0.004
S07-00789	Candlesby	Groundwater	20-Jul-07	2	0.218	0.389	2.73	709	0.844	<0.004	0.08	<0.02	<0.004	25.3	<0.02	<0.120	<0.004
S07-01162	Candlesby	Groundwater	03-Dec-07	3	0.365	0.131	2.4	598	0.834	0.003	0.752	<0.01	0.013	24.8	<0.01	4.81	0.012
S08-00568	Candlesby	Groundwater	13-Mar-08	4	0.339	0.162	2.35	573	0.914	<0.002	<0.006	<0.01	0.011	28.6	<0.01	<0.060	0.019
S07-00433	Catterick	Groundwater	01-May-07	1	0.19	1.21	3.0	444	0.154	0.017	0.151	<0.01	0.046	151	<0.01	0.077	0.651
S07-00785	Catterick	Groundwater	18-Jul-07	2	0.227	0.807	3.17	403	0.14	<0.004	0.123	<0.02	0.029	150	<0.02	<0.120	0.68
S07-01159	Catterick	Groundwater	28-Nov-07	3	0.162	0.404	2.89	424	0.159	0.016	0.077	0.028	0.046	150	<0.01	0.313	0.751
S08-00564	Catterick	Groundwater	12-Mar-08	4	0.166	0.526	2.83	347	0.161	0.016	<0.006	<0.01	0.041	126	<0.01	0.269	0.704
S07-00425	Great Wratting	Groundwater	30-Mar-07	1	3.37	2.17	2.33	3320	1.06	0.004	0.069	0.098	0.028	51.5	<0.01	0.102	0.66
S07-00790	Great Wratting	Groundwater	20-Jul-07	2	3.31	1.16	2.36	2990	0.984	<0.004	0.072	0.056	0.012	48.5	<0.02	<0.120	0.563
S07-01163	Great Wratting	Groundwater	04-Dec-07	3	3.07	0.982	2.13	3060	0.962	<0.002	0.081	0.080	0.029	48	<0.01	0.211	0.609
S08-00570	Great Wratting	Groundwater	17-Mar-08	4	3.43	1.16	2.07	2480	0.915	0.002	0.01	0.130	0.024	46.7	<0.01	<0.060	0.644
S07-00428	Homesford	Sough	04-Apr-07	1	0.509	3.0	0.998	461	1.51	2.17	0.041	0.084	0.06	66.2	<0.01	14.8	1.81
S07-00783	Homesford	Sough	17-Jul-07	2	0.491	2.62	1.02	446	1.51	2.04	0.083	0.058	0.046	64.4	<0.02	15.9	1.8
S07-00429	Little Eaton	River	04-Apr-07	1	0.214	1.49	2.22	258	0.778	0.079	0.064	0.46	0.014	126	0.018	0.098	0.682
S07-00781	Little Eaton	River	17-Jul-07	2	0.24	0.64	0.844	100	0.303	0.342	0.124	0.066	0.014	25.3	<0.01	2.75	0.358
S07-01156	Little Eaton	River	27-Nov-07	3	0.265	0.679	2.24	210	0.572	0.052	0.06	0.588	0.017	101	<0.01	0.095	0.559
S08-00563	Little Eaton	River	11-Mar-08	4	0.232	0.848	2.16	175	0.624	0.045	0.057	0.408	0.042	92.5	0.021	0.061	0.381
S07-00435	Loxley Reservoir	Reservoir	01-May-07	1	0.194	0.321	1.45	32.9	<0.03	0.011	0.047	0.033	0.008	28.7	<0.01	<0.060	<0.002
S07-00784	Loxley Reservoir	Reservoir	18-Jul-07	2	0.224	0.366	1.49	38.2	<0.06	<0.004	0.075	<0.02	<0.004	25.9	<0.02	0.132	<0.004
S07-01158	Loxley Reservoir	Reservoir	28-Nov-07	3	0.266	0.214	1.31	33.7	<0.03	0.009	0.057	0.032	0.003	22.5	<0.01	0.407	<0.002

ID number	Locality	Source type	Sample date	Round	As (µg L^{-1})	Se (µg L^{-1})	Rb (µg L^{-1})	Sr (µg L^{-1})	Mo (µg L^{-1})	Cd (µg L^{-1})	Sn (µg L^{-1})	Sb (µg L^{-1})	Cs (µg L^{-1})	Ba (µg L^{-1})	W (µg L^{-1})	Pb (µg L^{-1})	U (µg L^{-1})
S08-00567	Loxley Reservoir	Reservoir	12-Mar-08	4	0.189	0.177	1.21	32.1	<0.03	0.026	<0.006	0.04	0.005	22.7	<0.01	0.123	<0.002
S07-00426	Mynydd Llandegai	Reservoir	02-Apr-07	1	0.167	0.101	0.249	9.83	<0.03	0.007	0.039	<0.01	0.004	1.29	<0.01	0.119	0.015
S07-00779	Mynydd Llandegai	Reservoir	16-Jul-07	2	0.191	0.23	0.195	8.25	<0.03	0.01	0.093	0.021	0.003	1.39	<0.01	0.091	0.016
S07-01160	Mynydd Llandegai	Reservoir	29-Nov-07	3	0.219	0.114	0.186	8.86	<0.03	0.007	0.055	<0.01	0.004	1.06	<0.01	0.146	0.016
S08-00561	Mynydd Llandegai	Reservoir	10-Mar-08	4	0.168	0.157	0.25	9.36	<0.03	0.009	0.029	0.013	0.003	1.32	0.014	0.076	0.028
S07-00432	Mythe	River	04-Apr-07	1	0.532	0.884	1.8	273	0.805	0.017	0.037	0.16	0.007	90.4	0.016	<0.060	1.94
S07-00776	Mythe	River	16-Jul-07	2	0.454	0.595	1.97	163	0.655	0.011	0.095	0.312	0.006	61.7	<0.01	<0.060	0.153
S07-01153	Mythe	River	26-Nov-07	3	0.471	0.454	1.89	223	0.655	0.01	0.051	0.178	0.013	64.9	<0.01	0.18	0.105
S08-00559	Mythe	River	10-Mar-08	4	0.408	0.516	1.49	1700	0.613	0.013	0.007	0.163	0.02	63.5	0.016	<0.060	0.282
S07-00430	Ogston Reservoir	Reservoir	04-Apr-07	1	0.312	0.727	1.82	101	0.410	0.016	0.04	0.228	0.003	82.7	<0.01	<0.060	0.273
S07-00782	Ogston Reservoir	Reservoir	17-Jul-07	2	0.362	0.788	2.32	107	0.362	0.005	0.091	0.239	<0.004	83.6	<0.02	<0.120	0.107
S07-01155	Ogston Reservoir	Reservoir	27-Nov-07	3	0.367	0.509	2.26	113	0.937	0.007	0.069	0.275	<0.002	53.6	<0.01	<0.060	0.776
S08-00562	Ogston Reservoir	Reservoir	11-Mar-08	4	0.232	0.533	1.58	85	0.120	0.019	0.052	0.175	0.003	72.6	<0.01	0.235	0.039

Appendix 2 Chemical data for tapwater samples

APPENDIX 2A DATA FOR SELECTED TRACE ELEMENTS

ID number	Locality	Li (µg L^{-1})	Be (µg L^{-1})	Al (µg L^{-1})	Sc (µg L^{-1})	Ti (µg L^{-1})	V (µg L^{-1})	Cr (µg L^{-1})	Mn (µg L^{-1})	Co (µg L^{-1})	Ni (µg L^{-1})	Cu (µg L^{-1})	Zn (µg L^{-1})	As (µg L^{-1})	Se (µg L^{-1})	Rb (µg L^{-1})	Sr (µg L^{-1})
S07-01166	Mickleover 1A-N	4.29	<0.003	2.5	0.508	3.13	0.226	0.082	1.00	0.082	5.83	7.48	164	0.266	0.692	2.02	204
S07-01167	Mickleover 1B-N	4.21	<0.003	16.5	0.497	3.38	0.263	0.126	1.75	0.093	2.31	1.04	60.2	0.291	0.748	2.12	209
S07-01168	Mickleover 2A-N	3.99	0.007	3.14	0.504	3.19	0.247	0.070	1.02	0.079	2.78	48.1	193	0.282	0.651	2.09	210
S07-01169	Mickleover 2B-N	4.94	<0.003	1.77	0.606	3.29	0.174	0.197	0.815	0.076	2.26	3.91	64.3	0.257	0.637	2.13	209
S07-01170	Mickleover 3A-N	5.15	<0.003	4.76	0.583	3.12	0.197	0.140	1.88	0.096	4.09	13.1	180	0.297	0.715	2.10	211
S07-01171	Mickleover 3B-N	5.39	<0.003	6.31	0.601	3.41	0.214	0.168	1.40	0.086	2.38	1.38	62.6	0.30	0.771	2.16	213
S07-01172	Mickleover 4A-N	4.99	<0.003	3.75	0.558	3.15	0.204	0.115	0.871	0.074	2.29	19.1	170	0.285	0.668	1.98	203
S07-01173	Mickleover 4B-N	5.24	<0.003	2.13	0.597	3.21	0.214	0.126	0.809	0.076	2.18	1.70	67.4	0.278	0.685	2.13	211
S07-01174	Mickleover 5A-O	4.39	<0.003	4.51	0.545	3.25	0.229	0.136	0.813	0.060	2.19	18.5	82.6	0.289	0.731	1.95	212
S07-01175	Mickleover 5B-O	5.02	<0.003	2.91	0.563	3.19	0.229	0.164	0.726	0.067	1.88	1.62	67.8	0.292	0.725	2.08	220
S07-01176	Mickleover 6A-O	4.89	<0.003	2.64	0.547	3.18	0.231	0.153	0.675	0.067	1.85	3.56	68.3	0.283	0.718	2.05	219
S07-01177	Mickleover 6B-O	4.88	<0.003	2.17	0.537	3.18	0.221	0.119	0.676	0.066	1.83	4.93	65.4	0.295	0.568	2.03	217
S07-01178	Mickleover 7A-O	4.95	<0.003	1.78	0.55	3.04	0.237	0.101	1.08	0.069	2.23	24.6	85.9	0.317	0.721	2.08	212
S07-01179	Mickleover 7B-O	4.85	0.013	0.962	0.615	3.11	0.219	0.165	1.08	0.075	2.20	2.20	63.8	0.285	0.632	2.12	214
S07-01180	Mickleover 8A-O	5.19	<0.003	24.8	0.597	3.52	0.253	0.160	2.28	0.101	2.32	6.49	73.7	0.313	0.78	2.20	217
S07-01181	Mickleover 8B-O	4.79	<0.003	23.2	0.561	3.45	0.234	0.156	2.09	0.095	2.19	1.34	59.1	0.313	0.725	2.02	201
S07-01182	Bangor 1A-N	0.488	<0.003	14.8	0.10	1.95	0.211	0.191	3.01	0.017	0.499	106	7.52	0.259	0.139	0.318	9.77
S07-01183	Bangor 1B-N	0.439	0.009	14.0	0.111	1.92	0.181	0.235	2.75	0.015	0.262	7.14	1.78	0.242	0.138	0.326	9.31
S07-01184	Bangor 2A-N	0.448	0.015	13.6	0.112	2.00	0.181	0.197	3.14	0.023	6.66	58.0	17.6	0.285	0.113	0.332	9.74
S07-01185	Bangor 2B-N	0.449	<0.003	14.8	0.106	1.92	0.175	0.238	2.88	0.016	0.501	3.13	2.31	0.247	0.097	0.323	9.40
S07-01186	Bangor 3A-N	0.431	0.016	12.5	0.103	1.92	0.180	0.167	2.23	0.015	0.697	33.4	5.67	0.253	0.069	0.328	9.32
S07-01187	Bangor 3B-N	0.433	0.003	15.0	0.102	1.96	0.164	0.233	2.74	0.015	0.355	3.75	2.59	0.248	<0.030	0.328	9.27
S07-01188	Bangor 4A-N	0.450	0.009	14.8	0.116	2.09	0.174	0.214	2.76	0.018	0.610	87.9	9.92	0.267	0.103	0.333	9.43
S07-01189	Bangor 4B-N	0.486	0.015	15.4	0.147	2.02	0.147	0.204	3.88	0.020	0.627	54.4	18.9	0.239	0.079	0.339	9.82
S07-01190	Bangor 5A-O	0.429	0.018	13.6	0.117	2.07	0.161	0.176	3.05	0.020	0.916	87.4	20.4	0.236	0.164	0.312	9.22
S07-01191	Bangor 5B-O	0.462	0.024	20.2	0.132	2.11	0.183	0.275	2.63	0.016	0.241	9.42	1.70	0.254	0.097	0.341	9.35
S07-01192	Bangor 6A-O	0.423	0.011	15.2	0.099	2.05	0.158	0.167	2.18	0.014	0.511	36.9	13.3	0.238	0.106	0.318	8.76
S07-01193	Bangor 6B-O	0.444	0.009	22.9	0.123	2.18	0.194	0.237	2.48	0.015	0.264	13.6	4.18	0.255	0.131	0.342	9.76
S07-01194	Bangor 7A-O	0.438	0.021	20.6	0.11	2.03	0.164	0.169	2.46	0.018	1.53	94.9	3.28	0.235	0.136	0.34	9.54
S07-01195	Bangor 7B-O	0.452	<0.003	20.3	0.119	2.13	0.171	0.225	2.55	0.015	0.414	5.09	1.65	0.260	0.074	0.344	9.45
S07-01196	Bangor 8A-O	0.414	0.018	19.3	0.097	2.12	0.168	0.156	3.07	0.017	0.970	11.3	4.85	0.242	<0.030	0.326	9.02
S07-01197	Bangor 8B-O	0.445	<0.003	19.5	0.098	2.15	0.163	0.201	2.65	0.015	0.482	3.72	2.67	0.24	0.138	0.335	9.18

ID number	**Locality**	**Li (μg L^{-1})**	**Be (μg L^{-1})**	**Al (μg L^{-1})**	**Sc (μg L^{-1})**	**Ti (μg L^{-1})**	**V (μg L^{-1})**	**Cr (μg L^{-1})**	**Mn (μg L^{-1})**	**Co (μg L^{-1})**	**Ni (μg L^{-1})**	**Cu (μg L^{-1})**	**Zn (μg L^{-1})**	**As (μg L^{-1})**	**Se (μg L^{-1})**	**Rb (μg L^{-1})**	**Sr (μg L^{-1})**
S07-01198	Haverhill 1A-N	23.1	<0.003	<0.6	1.98	3.37	0.326	<0.040	0.25	0.422	15.85	76.3	99.9	3.29	0.952	2.12	3070
S07-01199	Haverhill 1B-N	22.3	0.005	<0.6	2.03	3.37	0.303	0.067	0.241	0.410	3.96	6.46	10.8	3.26	0.982	2.14	3080
S07-01200	Haverhill 2A-N	23.1	0.007	<0.6	2.15	3.53	0.350	0.049	0.456	0.441	5.05	86.4	76.6	3.45	1.11	2.24	3200
S07-01201	Haverhill 2B-N	21.6	<0.003	<0.6	2.05	3.45	0.343	0.110	0.221	0.414	4.15	9.90	11.8	3.33	0.999	2.17	3120
S07-01202	Haverhill 3A-N	20.6	0.011	<0.6	1.96	3.29	0.382	<0.040	0.253	0.404	4.21	79.9	32.3	3.20	0.933	2.07	2980
S07-01203	Haverhill 3B-N	20.4	0.018	<0.6	1.98	3.31	0.376	0.102	0.199	0.41	3.91	8.40	14.6	3.33	1.05	2.16	3110
S07-01204	Haverhill 4A-N	21.4	<0.003	<0.6	2.13	3.46	0.384	<0.040	0.263	0.431	4.32	34.7	38.7	3.40	0.996	2.18	3090
S07-01205	Haverhill 4B-N	21.6	<0.003	<0.6	2.29	3.73	0.386	0.079	0.415	0.462	4.30	7.38	14.1	3.42	1.17	2.14	3100
S07-01206	Haverhill 5A-O	20.1	0.006	<0.6	2.14	3.31	0.390	<0.040	0.367	0.405	26.2	295	93.3	3.03	0.941	2.11	3050
S07-01207	Haverhill 5B-O	20.5	<0.003	<0.6	2.22	3.59	0.420	0.142	0.165	0.391	5.19	21.4	9.51	3.36	1.11	2.15	3070
S07-01208	Haverhill 6A-O	19.9	<0.003	<0.6	2.16	3.45	0.422	0.042	0.172	0.393	4.55	41.3	123	3.35	0.899	2.13	3080
S07-01209	Haverhill 6B-O	20.9	<0.003	<0.6	2.50	4.00	0.261	0.042	0.16	0.404	4.22	4.07	8.65	3.30	0.865	2.21	3190
S07-01210	Haverhill 7A-O	21.8	<0.003	<0.6	2.27	3.60	0.260	0.075	0.131	0.368	5.05	141	44.7	3.19	0.823	2.48	2990
S07-01211	Haverhill 7B-O	22.0	<0.003	<0.6	2.50	4.01	0.277	<0.040	0.139	0.401	4.39	4.64	5.56	3.22	1.09	2.44	2970
S07-01212	Haverhill 8A-O	21.9	<0.003	<0.6	2.58	4.09	0.310	<0.040	0.148	0.412	6.64	48.5	147	3.32	1.07	2.13	3080
S07-01213	Haverhill 8B-O	22.0	<0.003	<0.6	2.51	3.92	0.324	<0.040	0.167	0.411	4.41	3.36	9.60	3.38	1.08	2.18	3130

A: Pre-flush sample (first-morning draw); B: post-flush sample, same tap
N: New house (post 1990); O: old house (pre-1960s)

APPENDIX 2B DATA FOR SELECTED TRACE ELEMENTS (CONT'D)

ID number	Locality	Mo (µg L^{-1})	Cd (µg L^{-1})	Sn (µg L^{-1})	Sb (µg L^{-1})	Cs (µg L^{-1})	Ba (µg L^{-1})	W (µg L^{-1})	Pb (µg L^{-1})	U (µg L^{-1})
S07-01166	Mickleover 1A-N	0.536	0.316	0.042	0.479	0.022	76.9	<0.01	0.672	0.498
S07-01167	Mickleover 1B-N	0.548	0.281	0.047	0.525	0.023	81	<0.01	1.86	0.504
S07-01168	Mickleover 2A-N	0.544	0.371	0.114	0.512	0.022	74.8	<0.01	0.725	0.615
S07-01169	Mickleover 2B-N	0.557	0.310	0.06	0.495	0.026	77.1	<0.01	0.645	0.597
S07-01170	Mickleover 3A-N	0.531	0.339	0.056	0.492	0.023	76.5	<0.01	0.919	0.567
S07-01171	Mickleover 3B-N	0.549	0.290	0.054	0.510	0.022	81.2	<0.01	1.00	0.515
S07-01172	Mickleover 4A-N	0.529	0.363	0.144	0.463	0.021	72.2	<0.01	0.769	0.584
S07-01173	Mickleover 4B-N	0.556	0.332	0.053	0.491	0.022	78.7	<0.01	0.674	0.580
S07-01174	Mickleover 5A-O	0.522	0.353	0.048	0.421	0.030	53.4	<0.01	3.06	0.800
S07-01175	Mickleover 5B-O	0.543	0.352	0.054	0.460	0.031	65.0	<0.01	2.67	0.757
S07-01176	Mickleover 6A-O	0.537	0.337	0.042	0.463	0.031	63.2	<0.01	1.80	0.771
S07-01177	Mickleover 6B-O	0.540	0.330	0.047	0.448	0.032	63.9	<0.01	1.67	0.751
S07-01178	Mickleover 7A-O	0.522	0.356	0.036	0.472	0.025	69.0	<0.01	1.90	0.734
S07-01179	Mickleover 7B-O	0.549	0.312	0.060	0.530	0.022	76.9	<0.01	1.20	0.543
S07-01180	Mickleover 8A-O	0.554	0.345	0.053	0.549	0.023	75.6	<0.01	4.86	0.620
S07-01181	Mickleover 8B-O	0.526	0.279	0.043	0.480	0.022	74.6	<0.01	3.06	0.518
S07-01182	Bangor 1A-N	<0.03	0.004	0.051	<0.01	0.007	1.49	<0.01	1.56	0.006
S07-01183	Bangor 1B-N	<0.03	0.003	0.040	<0.01	0.007	1.57	<0.01	0.061	0.009
S07-01184	Bangor 2A-N	<0.03	0.007	0.027	<0.01	0.006	1.58	<0.01	0.175	0.008
S07-01185	Bangor 2B-N	<0.03	0.004	0.043	<0.01	0.006	1.64	<0.01	<0.060	0.011
S07-01186	Bangor 3A-N	<0.03	0.004	0.029	<0.01	0.007	1.53	<0.01	0.512	0.007
S07-01187	Bangor 3B-N	<0.03	0.004	0.043	<0.01	0.007	1.60	<0.01	<0.060	0.009
S07-01188	Bangor 4A-N	<0.03	0.006	0.063	<0.01	0.011	1.42	<0.01	0.464	0.009
S07-01189	Bangor 4B-N	<0.03	0.007	0.436	<0.01	0.007	1.55	<0.01	0.364	0.008
S07-01190	Bangor 5A-O	<0.03	0.005	0.037	<0.01	0.006	1.78	<0.01	0.633	0.008
S07-01191	Bangor 5B-O	<0.03	<0.002	0.054	<0.01	0.007	1.79	<0.01	0.438	0.011
S07-01192	Bangor 6A-O	<0.03	0.003	0.042	0.012	0.007	1.56	<0.01	3.29	0.009
S07-01193	Bangor 6B-O	<0.03	0.003	0.054	<0.01	0.007	2.17	<0.01	1.83	0.011
S07-01194	Bangor 7A-O	<0.03	0.006	0.782	<0.01	0.007	1.99	<0.01	199	0.010
S07-01195	Bangor 7B-O	<0.03	0.004	0.147	<0.01	0.007	1.84	<0.01	4.47	0.011
S07-01196	Bangor 8A-O	<0.03	0.005	0.047	<0.01	0.006	1.80	<0.01	0.113	0.011
S07-01197	Bangor 8B-O	<0.03	0.003	0.055	<0.01	0.007	1.80	<0.01	<0.060	0.011
S07-01198	Haverhill 1A-N	0.962	0.020	0.071	0.078	0.023	46.3	<0.01	0.364	0.656
S07-01199	Haverhill 1B-N	0.971	0.003	0.052	0.112	0.022	46.2	<0.01	<0.060	0.659
S07-01200	Haverhill 2A-N	0.996	0.010	0.059	0.106	0.022	48.5	<0.01	0.179	0.691
S07-01201	Haverhill 2B-N	0.963	<0.002	0.038	0.077	0.020	47.1	<0.01	<0.060	0.674

ID number	Locality	Mo (μg L^{-1})	Cd (μg L^{-1})	Sn (μg L^{-1})	Sb (μg L^{-1})	Cs (μg L^{-1})	Ba (μg L^{-1})	W (μg L^{-1})	Pb (μg L^{-1})	U (μg L^{-1})
S07-01202	Haverhill 3A-N	0.920	0.004	0.039	0.141	0.021	45.4	<0.01	0.218	0.660
S07-01203	Haverhill 3B-N	0.973	0.003	0.035	0.076	0.021	46.9	<0.01	<0.060	0.679
S07-01204	Haverhill 4A-N	0.971	0.008	0.106	0.073	0.023	47.4	<0.01	0.255	0.691
S07-01205	Haverhill 4B-N	0.940	0.004	0.039	0.077	0.020	46.4	<0.01	0.113	0.678
S07-01206	Haverhill 5A-O	0.944	0.041	0.742	0.117	0.022	46.7	<0.01	8.96	0.676
S07-01207	Haverhill 5B-O	0.952	0.003	0.057	0.079	0.021	46.5	<0.01	3.63	0.699
S07-01208	Haverhill 6A-O	0.938	0.014	0.048	0.071	0.024	46.8	<0.01	5.10	0.693
S07-01209	Haverhill 6B-O	1.00	<0.002	0.040	0.086	0.023	47.4	<0.01	1.44	0.669
S07-01210	Haverhill 7A-O	0.911	0.010	0.049	0.082	0.026	32.8	<0.01	1.90	0.651
S07-01211	Haverhill 7B-O	0.948	0.002	0.038	0.073	0.026	31.5	<0.01	1.55	0.639
S07-01212	Haverhill 8A-O	0.953	0.029	0.054	0.079	0.021	46.4	<0.01	11.2	0.633
S07-01213	Haverhill 8B-O	0.993	0.005	0.046	0.077	0.021	47.1	<0.01	2.29	0.648

A: Pre-flush sample (first-morning draw); B: post-flush sample, same tap
N: New house (post 1990); O: old house (pre-1960s)

Appendix 3 Detection limits for analysed trace elements

Element	Detection limit (µg L^{-1})	Element	Detection limit (µg L^{-1})	Element	Detection limit (µg L^{-1})
Li	0.003	Co	0.006	Cd	0.002
Be	0.003	Cu	0.02	Sn	0.006
Al	0.6	Zn	1	Sb	0.01
Sc	0.05	As	0.008	Cs	0.002
Ti	0.04	Se	0.03	Ba	0.06
V	0.02	Rb	0.002	W	0.01
Cr	0.04	Sr	0.03	Pb	0.06
Mn	0.006	Mo	0.03	U	0.002
Ni	0.01				

Detection limits for samples S07-00782 to S07-00793 inclusive (sampling round 2) have detection limits double those listed above due to dilution during analysis