

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 $70 \mu\text{g L}^{-1}$. 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 $0.03 \mu\text{g L}^{-1}$. 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 $70 \mu\text{g L}^{-1}$.

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 ($>20 \text{ mg kg}^{-1}$) 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 $0.1 \mu\text{g L}^{-1}$ or less. Analyses of 11,562 streamwater samples from the G-BASE dataset have a range of $<0.05\text{--}230 \mu\text{g L}^{-1}$ although the 10–90th percentile range is much narrower, $0.08\text{--}2.45 \mu\text{g L}^{-1}$, with a median value of just $0.57 \mu\text{g L}^{-1}$. Analyses of water samples from the LOIS rivers also typically have median concentrations $<1 \mu\text{g L}^{-1}$, although sites on the Rivers Calder, Don, Trent, Great Ouse and Thames have higher median values, in the range $3\text{--}10 \mu\text{g L}^{-1}$. 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 $\mu\text{g L}^{-1}$) 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 $<0.1\text{--}120 \mu\text{g L}^{-1}$ but with a 10–90th percentile range of $0.1\text{--}1.5 \mu\text{g L}^{-1}$ and a median of $0.12 \mu\text{g L}^{-1}$. 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 $1 \mu\text{g L}^{-1}$, although relatively high concentrations characterise mine-drainage waters ($0.60\text{--}6.0 \mu\text{g L}^{-1}$, median $1.4 \mu\text{g L}^{-1}$). 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 ($70 \mu\text{g L}^{-1}$) 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.