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Invited Review

Molybdenum in natural waters: A review of occurrence, distributions and controls

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ABSTRACT

Molybdenum is an essential trace element for human, animal and plant health and has played an important part in the evolution of life on earth. Nonetheless, exposure to the element can be harmful and although the evidence for symptoms in humans is sparse, it has been linked with a number of health conditions in animal models. Molybdenum is present in trace quantities (1–10 mg/kg) in most rocks and soils and at concentrations less than, and often orders of magnitude less than, 10 μg/L in most freshwaters. It is the most abundant transition metal in open seawater (10 μg Mo/L) owing to the dominance, and low chemical reactivity, of the molybdate ion (MoO_4^{2-}).

The 2011 WHO Guidelines for Drinking-Water Quality (fourth edition) advised a health-based value of 70 μg/L for Mo but this is no longer promulgated as a formal guideline value as WHO consider such concentrations to be rarely found in drinking water. This is indeed usually the case, but there are instances where currently-used drinking waters do exceed 70 μg Mo/L. We therefore recommend more routine measurement of Mo in water, at least on a reconnaissance scale, in order to improve knowledge on occurrence in water used for potable supply. Where multi-element analytical procedures are already used (e.g. ICP-MS), the marginal cost of adding Mo to the list of elements to be analysed should not be great.

We have reviewed nine areas in the world where high concentrations of Mo in freshwater, and in some cases drinking water, have been found: Argentina, Jordan, Qatar, Ethiopia, UK, USA (three) and Chile. These represent a range of geochemical environments. A common theme of the high-Mo occurrences is (i) oxic, alkaline conditions where, as for seawater, the Mo occurs as the stable molybdate ion; groundwater in oxic, alkaline conditions within volcanogenic sediments can have exceptionally high Mo concentrations (up to hundreds of μg/L) where felsic volcanic ash is present; (ii) anoxic, non-sulphidic waters where Mo can be released to solution by reductive dissolution of Mn and Fe oxides or by release from degradation of organic matter, notably within high-Mo organic-rich muds, black shales or oil shales; or (iii) surface waters or groundwater impacted by metal sulphide mining and/or mineralisation, in particular occurrences of porphyry deposits. Under such conditions, Mo concentrations can reach several tens to several hundreds of μg/L and while not all are otherwise suitable for drinking water, some are.

Much of the basic geochemistry of Mo in oxic natural environments is now quite well understood. Critically, its behaviour is redox-sensitive like its near neighbours in the Periodic Table, W and V. At the near-neutral pH values characteristic of most natural waters, Mo is rather weakly sorbed and formation of Mo minerals is either not indicated or is extremely slow. Molybdenum becomes less mobile when converted to thiomolybdates under the strongly reducing conditions found in some present-day ocean basins (e.g. the Black Sea), fjords, stratified lakes and confined aquifers. This leads to concentrations of around 100 mg Mo/kg or more in black shales and other organic-rich mudstones. However, despite the many studies of these water bodies and the importance of Mo as a palaeoredox indicator, the mechanism of the highly-efficient and diagnostic scavenging of Mo in euxinic (H_2S-rich) waters remains uncertain. Possibilities include the formation of an as yet unidentified Mo-Fe-S mineral or solid solution, or the scavenging by some pre-existing solid such as a sulphide or oxide mineral, or organic matter. The possible role of dispersed and reduced natural organic matter has become more prominent in recent

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years but this has proven difficult to quantify and the mechanism of binding is poorly understood. Molybdenum isotope studies now play an important role in constraining reaction pathways.

At a more fundamental level, there is a lack of up-to-date thermodynamic and kinetic data for many of the reactions of importance for Mo in the natural environment and this limits the ability of current geochemical models to predict its fate and transport. This is particularly true for the strongly reducing conditions where Mo partitions to the solid phase, leading to the formation of the Mo-rich shales. Even the existence of reduced aqueous Mo species (e.g. in the Mo(V) and Mo(III) oxidation states) in natural waters is uncertain. These uncertainties will only be resolved with focused laboratory experiments using the benefits of modern instrumentation, combined where necessary with supporting molecular dynamics calculations.

The mobility of Mo in aqueous systems has to date received far more attention in the marine than the freshwater setting. The value of Mo speciation as an indicator of redox conditions and of stable-isotopic variations as a tracer, can have more value in the arena of environment and health, and studies of the element's mobility in aqueous systems can be useful for themes varying from radioactive waste disposal, sustainability of unconventional hydrocarbon exploitation and wider surficial pollution.

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