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Viewpoint

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Should Monitoring of Molybdenum (Mo) in Groundwater, Drinking Water and Well Permitting Made Mandatory?

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Molybdenum (Mo) is considered an essential element, whose daily requirement for humans is up to 300 μg, although high doses are considered detrimental to human health.[1] The tolerable upper intake level by the Food and Nutrition Board (FNB) of the U.S was set to 2000 μg per day. With regard to drinking water, the United States Environmental Protection Agency determined that the "Lifetime Advisory Level" for Mo is 40 μg/L, and the World Health Organization published a recommendation that Mo should not exceed 70 μg/L. Molybdenum intake from drinking water should be of no concern considering that its concentration in natural water is generally 1 to 2 μg/L.[2] Anthropogenic activities, however, can have a detrimental effect on ground and surface water Mo concentrations. Particularly in mining areas and near coal ash landfills, Mo is a well-known contaminant of environmental concern.[1] Another process detrimental to groundwater quality is the mobilization of naturally occurring (geogenic) toxic elements from the aquifer matrix due to anthropogenic perturbations. In particular, the ongoing catastrophic problems with arsenic (As) in Bangladesh and West Bengal are front-page stories in newspapers and scientific journals. Thus, geogenic contamination is critical to water quality and particularly in poor urban and rural settings, the risk of geogenic contamination can be high. Drinking water is often not supplied centrally and rarely tested, if at all. Recent observations point to Mo as another potential candidate for anthropogenic-induced geogenic contamination. During the random survey of a newly installed irrigation well in rural central Florida, more than 300 μg/L Mo were measured by the Florida Department of Environmental Protection (FDEP). Following this discovery, 93 nearby domestic supply wells (DSW) were sampled and analyzed. Of those, 34 wells had Mo concentrations above 40 μg/L with a maximum value of 4740 μg/L.[3] Such concentrations correspond to a Mo intake greater than the tolerable upper intake level set by the FNB.

The mean concentration of Mo in the Earth's crust is between 1 mg/kg and 2 mg/kg,[2] although concentrations can be significantly higher in marine sediments deposited under oxygen-depleted conditions, where Mo is trapped in organic matter and pyrite. Among many other recent reports, Pichler and Mozaffari[4] for example, reported up to 880 mg/kg for the aquifer matrix in central Florida, which is a marine limestone of Eocene to Miocene age. However, the Mo concentration in the aquifer matrix is not necessarily the controlling factor for elevated Mo in the corresponding groundwater. As seen in the studies by Pichler and Mozaffari[4] and Pichler, Renshaw and Sültenfuß[3] Mo concentration in the aquifer matrix and in groundwater were not related. In their study three monitoring wells (DEP-1, DEP-2, and DEP-3) were chosen for the analysis of aquifer matrix and groundwater. Well DEP-1 had 880 mg/kg Mo in the aquifer matrix and 700 μg/L in groundwater, well DEP-2 had 123 mg/kg and 5050 μg/L and the control site DEP-5 had 225 mg/kg and 1 μg/L, which suggests anthropogenic disturbance as the controlling factor and not its natural abundance in the aquifer matrix. The release of Mo was ascribed to the rapid introduction of oxygen into the aquifer, followed by Mo release due to the oxidation of pyrite and organic matter. The abundance of DSW effectively increased the local scale permeability of the aquifer, causing the mixing of oxygen-rich surface and deeper anoxic groundwater across a confining unit.

The rapid introduction of oxygenated water into a reducing aquifer also occurs during aquifer storage and recovery (ASR) operations. The basic principle of ASR is to inject treated excess water into an aquifer to be recovered during times of increased demand. One well-studied example is from Florida, where 55 ASR facilities are currently in operation or have permission for construction, which cyclically inject oxygenated water into the anoxic upper Floridan Aquifer System, whose aquifer matrix is a marine limestone of Eocene to Miocene age. In Orange County the FDEP took 307 water samples from the injection and several monitoring wells during several ASR cycles (Figure 1). Of those, 113 had As concentrations above the U.S. Environmental Protection Agency (EPA) drinking water standard and 199 Mo concentrations above the U.S. EPA

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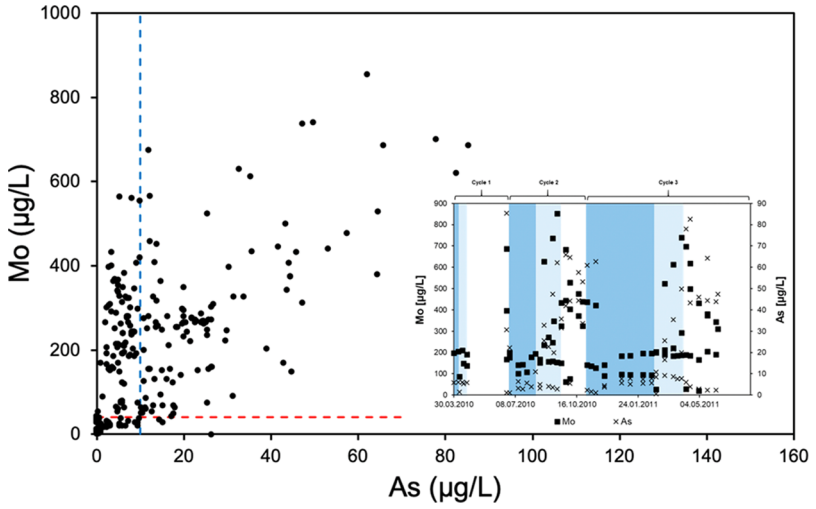

Figure 1. As and Mo concentrations in 307 water samples collected during three ASR cycles.[5] The dashed lines indicate 10 μg/L and 40 μg/L for As and Mo, respectively. The inset shows concentrations of Mo and As during periods of injection (dark blue), storage (light blue) and recovery (white).

recommended maximum of 40 μg/L. In total 202 samples had either too much As or Mo (Figure 1). Observations of elevated Mo as a result of ASR operation, however, were not limited to the Orange County facility. For example, the maximum Mo concentrations measured at the Peace River and Punta Gorda ASR facilities were 289 μg/L and 675 μg/L, respectively.[5] Thus, it becomes clear that besides the well-known issues of As release, the release of Mo from the aquifer matrix also had a negative impact on groundwater quality during ASR operation, with concentrations in excess of health-based threshold values by more than 10 times as observed at ASR sites in Florida.[5] Yet, despite those observations, Mo is not a standardized parameter in monitoring programs during ASR.

In summary, it seems that in marine sediments deposited under reducing conditions, including limestone, the release of Mo is catalyzed by a change from reducing to oxidizing. This phenomenon was documented for groundwater in the Floridan Aquifer System, whose aquifer matrix consists mainly of limestone of Eocene to Miocene age that was deposited under reducing conditions. Hence, it is conceivable that elsewhere groundwater extracted from aquifers of marine origin could have equally high Mo concentrations, if the physicochemical equilibrium between aquifer matrix and groundwater would be perturbed. This type of geogenic contamination can occur on such small scales that it remains unnoticed in regional or national groundwater monitoring networks, as seen in the study by Pichler, Renshaw, and Sültenfuß.[3] We would therefore recommend:

(1) more routine measurements of Mo in groundwater on a reconnaissance scale,

(2) mandatory testing of groundwater from aquifers suspected to contain elevated Mo concentrations, such as those described above,

(3) that during water rights licensing for ASR as part of a drinking water supply, Mo should be part of the risk study to evaluate its potential mobilization.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Chappell, W. R.; Meglen, R. R.; Moure-Eraso, R.; Solomons, C. C.; Tsongas, T. A.; Walravens, P. A.; Winston, P. W. *Human Health Effects of Molybdenum in Drinking Water*; U.S. Environmental Protection Agency: Cincinnati, OH, 1979.

(2) Smedley, P. L.; Kinniburgh, D. G. Molybdenum in natural waters: A review of occurence, distributions and controls. *Appl. Geochem.* **2017**, *84*, 387−432.

(3) Pichler, T.; Renshaw, C. E.; Sültenfuß, J. Geogenic As and Mo groundwater contamination caused by an abundance of domestic supply wells. *Appl. Geochem.* **2017**, *77*, 68−79.

(4) Pichler, T.; Mozaffari, A. Occurrence, distribution and mobility of geogenic molybdenum and arsenic in a limestone aquifer matrix. *Appl. Geochem.* **2015**, *63*, 623−633.

(5) Fischler, C.; Hansard, P.; Ladle, M.; Burdette, C. *A Review of Selected Florida Aquifer Storage and Recovery (ASR) Sites and Their Geochemical Characteristics*; Florida Geological Survey Report of Investigation, Tallahassee, 2015; p 216.

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