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Distribution and mobility of geogenic molybdenum and arsenic in a limestone aquifer matrix

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ABSTRACT

To investigate the potential of Mo and As as possible geogenic contaminants, three sediment cores were examined to evaluate their mineralogical association, distribution and mobility. The cores were described and analyzed for total organic carbon (TOC), Ca, Mg, Si, Al, P, Sr, As, Mo, Fe, and S content. Except in the uppermost segment, limestone was the main lithology with the occasional presence of dolomite and clay. That change in lithology was also observed in the bulk chemical composition, where Ca, Mg and Sr concentrations increased with depth, while Si, Al and P concentrations decreased with depth. Minor minerals included pyrite (FeS_2), powellite ($CaMoO_4$) and ferrihydrite. The minimum, maximum, median and standard deviations for all analyzed elements, including As and Mo were comparable for all three cores. Molybdenum and As, however, varied significantly with depth and median As and Mo values were above their respective crustal averages of approximately 1.1 mg/kg and 1.5 mg/kg. The median values for As were 1.9 mg/kg in core DEP-1, 3.3 mg/kg in DEP-2 and 1 mg/kg in DEP-5. The median values for Mo were 2.3 mg/kg in core DEP-1, 2.5 mg/kg in DEP-2 and 2.5 mg/kg in DEP-5. Maximum concentrations for As were 101.9 mg/kg, 47.5 mg/kg and 56.2 mg/kg in cores DEP-1, DEP-2 and DEP-5, respectively. Maximum concentrations for Mo were 880 mg/kg, 123 mg/kg and 225 mg/kg in cores DEP-1, DEP-2 and DEP-5, respectively. Electron microprobe analyses of individual minerals revealed variable concentrations of As ranging from approximately 300 to 9000 mg/kg, in pyrite and up to 17,600 mg/kg in powellite ($CaMoO_4$). The Mo concentration in pyrite was consistently below the detection limit of approximately 100 mg/kg. In powellite the Mo concentration was up to 42 wt%.

A subset of 10 samples from different stratigraphic sections and with different As and Mo concentrations was further investigated to assess As and Mo mobility under changing physicochemical conditions. Leaching the aquifer matrix with a 1 M NaOAc solution at a pH of 8.1 removed more than 70% Mo in 8 of the 10 samples. The maximum value was 97%. In contrast to Mo, As was mobilized to a lesser degree. In 8 of the samples less than 30% were removed and the maximum was only 50%. Molybdenum, which seemed to be loosely bound to mineral and organic matter surfaces thus could easily be removed from the aquifer matrix, while As on the other hand should be much less mobile, because it occurred either tightly adsorbed by hydrous ferric oxide or as an impurity in pyrite. Thus, it is advisable to include Mo in the analytical program whenever elevated As concentrations are encountered in groundwater.

1. Introduction

Molybdenum (Mo) is considered an essential element, whose daily requirement for humans is approximately 0.3 mg (WHO, 2011), while at the same time high doses of Mo could be detrimental to human health. The recommendation by the World Health Organization (WHO) for drinking water is that Mo should not exceed 70 μg/L (WHO, 2011). Currently only anthropogenic Mo contamination seems to be of environmental interest and particularly in mining areas it is a well-known contaminant (Davies et al., 2005; Heijerick et al., 2012; Smedley et al., 2014; Zhai et al., 2013) where it is released during mining operations and due to weathering of mine tailings (Price et al., 1999). The deterioration of groundwater, however, is not exclusively due to the direct input of anthropogenic contaminants, such as the discharge of Pb due to battery recycling (e.g., Pichler, 2005). Another process leading to

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groundwater deterioration can be the mobilization of naturally occurring (geogenic) elements induced by anthropogenic perturbations of the physicochemical conditions in the aquifer (e.g., Amini et al., 2008; Ferguson and Gavis, 1972; Korte and Fernando, 1991; McNeill et al., 2002; Peters and Blum, 2003). This type of anthropogenic-induced contamination is a public health issue worldwide. In particular the ongoing catastrophic problems with arsenic (As) in Bangladesh and West Bengal are front-page stories in newspapers and scientific journals (e.g., Ahmed et al., 2006). There is the potential that geogenic Mo could be candidate for anthropogenic-induced widespread groundwater contamination as well. Marine sediments are known to accumulate Mo in organic matter (e.g., Tribovillard et al., 2004) and in pyrite (e.g., Helz et al., 2011, 1996). Since As is known to accumulate in the same two phases the physicochemical conditions that cause the release of As from the aquifer matrix should also release Mo.

Elevated arsenic (As) is a well-known problem in Floridan groundwater, whenever the physicochemical conditions in the aquifer are perturbed due to anthropogenic activities (Arthur et al., 2007; Jones and Pichler, 2007; Katz et al., 2009; Wallis et al., 2011). Thus As is routinely analyzed after completion of new wells, which led to the discovery of elevated As and Mo concentrations in groundwater in a rural area in central Florida (Pichler and Sültenfuß, 2010). There As concentrations of up to 350 μg/L and Mo concentrations of up to 5000 μg/L were measured. The value of 5000 μg/L is substantially above what could be considered “normal” for Mo concentrations in groundwater. Smedley et al. (2014) who studied Mo in Great Britain found a 10 to 90th percentile range of 0.08–2.44 μg/L with a median of 0.57 μg/L and a maximum observation of 230 μg/L in stream water samples (n = 11,600). In groundwater samples the 10 to 90th percentile ranged from 0.035 to 1.80 μg/L with a median of 0.20 μg/L and a maximum observation of 89 μg/L (n = 1735).

While some information about the occurrence and distribution of As in the Floridan aquifer matrix exists (e.g., Pichler et al., 2011), next to nothing is known about Mo. In this study, we present a first look at the distribution and mineralogical association of As together with Mo in a limestone aquifer of marine origin. To estimate As and Mo mobility, a modified extraction was carried out according to the procedure recommended by Pichler et al. (2001).

2. Study area

The study area is located in the municipality of Lithia southeast of Tampa Bay in the United Sates (Fig. 1). There, a multilayered aquifer system exists, which can be subdivided into three distinct hydrostratigraphic units, which are, from the top down: the Surficial Aquifer System (SAS), the Intermediate Aquifer System (IAS), and the Upper Floridan Aquifer System (UFA). Katz et al. (2007) provided detailed mineralogical and lithological descriptions of these units and their regional hydrogeology in central Florida, which were recently reviewed (Hughes et al., 2009). Relevant hydrogeological characteristics of these units are briefly summarized here.

The unconfined SAS consists of unconsolidated to poorly indurated clastic deposits with depths to the water table ranging from about 3 m to 15 m below land surface (Katz et al., 2009). The upper surface of the SAS is defined by the surface topography, which near the wells with high As concentrations is generally about 30 m above mean sea level (amsl) and ranges from about 65 m just to east of the high-As wells to near zero where it intersects Hillsborough Bay about 35 km to the west. Near the high-As concentration wells, the base of the SAS is 10 m amsl and dips to the west at a slope of approximately 0.001. The SAS generally is not used as a major source of water supply because of relatively low yields (less than 19 L/min), high Fe content, and the potential for contamination from the surface. Water table elevations in the SAS generally are above the potentiometric surface of the UFA, indicating downward groundwater flow through the IAS from the SAS to the UFA (Katz et al., 2009).

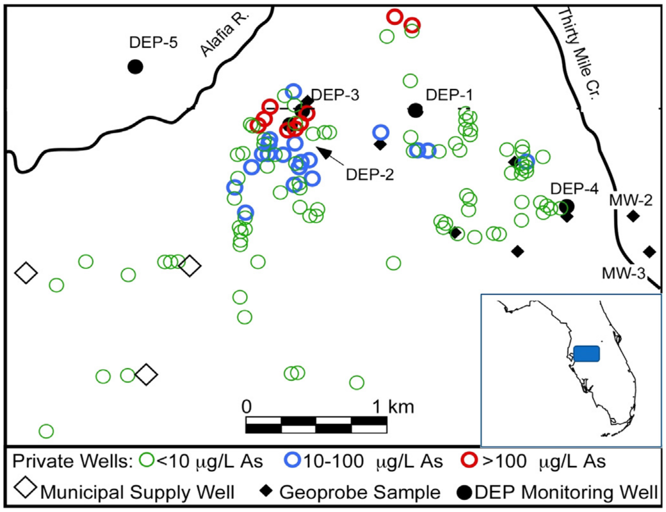

Fig. 1. Location of the study area showing domestic supply wells and their approximate As concentrations and the locations of the three cores, which were sampled for this study (DEP-1, DEP-2 and DEP-5).

The IAS consists of several water-bearing units separated by confining units, which are composed mainly of the siliciclastic Hawthorn Group with interlayered sequences of more and less permeable carbonates, sands and clays (Scott, 1988, 1990). The extent, thickness, and permeability of the IAS are variable, but generally control the downward leakage between the SAS and the UFA (Katz et al., 2009). Pyrite is found unevenly distributed throughout the Hawthorn Group and occurs mainly in its framboidal form (Lazareva and Pichler, 2007). Arsenic concentrations in the Hawthorn Group are generally less than 5 mg/kg, but can reach up to 69 mg/kg in samples with abundant pyrite (Lazareva and Pichler, 2007; Pichler et al., 2011). Near the highest As concentrations, the bottom of the IAS is about −30 m amsl and dips to the west at a slope of approximately 0.001.

The UFA is the major source of water supply within the study area and consists of permeable limestone and dolomite deposited in a shallow marine environment (Green et al., 1995; Miller, 1986). Carbonate deposition was interrupted at first periodically, and finally completely, with the influx of the siliciclastic sediments eroded from the Appalachian Mountains that form the IAS. Within the region of high As concentrations, the bottom of the UFA is about − 400 m amsl and dips to the west at a slope of approximately 0.001. Because of its high permeability, the Florida Geological Survey has been testing the UFA to serve as an underground reservoir for aquifer storage and recovery (ASR) systems. Detailed lithological, mineralogical, and geochemical studies of the two uppermost formations of the UFA, the Tampa Member and the Suwannee Limestone, showed that As is generally present in low concentrations (a few mg/kg), but is concentrated in minor minerals, such as pyrite, which may contain up to 11,200 mg/kg As (Lazareva and Pichler, 2007; Price and Pichler, 2006). The Tampa Member of the Arcadia Formation hydrostratigraphically belongs to the UFA, although it is the lowermost stratigraphic unit of the Hawthorn Group (Miller, 1986).