



Reply

Reply to a comment on “The distribution and mobility of geogenic molybdenum and arsenic in a limestone aquifer matrix”



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Hansard (2017) raised the issues that our statistical analysis did not justify the conclusions that (1) arsenic is of geogenic origin and that (2) pyrite is the primary source of As in the sedimentary sequence in Central Florida. We respond to those comments below.

Certainly, outliers can have a profound impact, and thus have to be treated with utmost care. Nevertheless, immediate dismissal of outliers purely based on a simple calculation of Cook's distance is not advisable in complex systems, such as the distribution of As in an aquifer matrix. There, an outlier can be indispensable to indicate a relationship in X–Y space, which is obscured for other samples due to analytical noise. Regardless, we did not rely on a statistical relationship between Fe, S and As to identify pyrite as the primary source of As, as stated by Hansard (2017). The use of linear regression analysis was more a thought experiment than a line of argumentation. The idea was to test if field observations and experimental/analytical data in such a complex system could be reproduced by a simple statistical method. Following that thought experiment, we provided a critical examination of the data set and its relationship to the linear regression analyses. We quote directly from Pichler and Mozaffari (2015): “Calculated and measured As are compared in

Fig. 9B. Many samples show good agreement between the measured and calculated As concentrations, i.e., they follow the dashed line in Fig. 9B. For those samples that lie significantly above the equal concentration line, calculated As concentrations were lower than those measured in the bulk sample. These results can be explained by the existence of other As sources such as, clays, organic material, hydrous ferrous oxides and powellite or an underestimation of the amount of pyrite. Samples that show a much higher calculated arsenic concentration compared to a measured result probably due to overestimation of pyrite abundance due to the presence of S from sources other than pyrite, e.g., gypsum or anhydrite.”

In his comment, Hansard (2017) noted that there was modest agreement between As, Fe and S, caused by an apparently well-known affinity between As and Fe. As a chalcophile element, As has a strong affinity for S and not Fe (Goldschmidt, 1937). A potential correlation between As and Fe is generally caused when As is adsorbed by Fe phases, such as ferrihydrite. However, this is not an affinity in a geochemical/mineralogical sense, because As is equally well adsorbed by clay minerals, as well as Al-, Mn- and other oxyhydroxides. In Central Florida ferrihydrite is only present in the matrix of the unconfined Surficial Aquifer System (SAS), because the Intermediate (IAS) and Upper Floridan Aquifer Systems (UFA) are suboxic (Sacks et al., 1995; Sacks and Tihansky, 1996). Of the three sediment cores studied by Pichler and Mozaffari (2015), core DEP-2 included data for the SAS and by separating SAS from IFA and UFA the relationship

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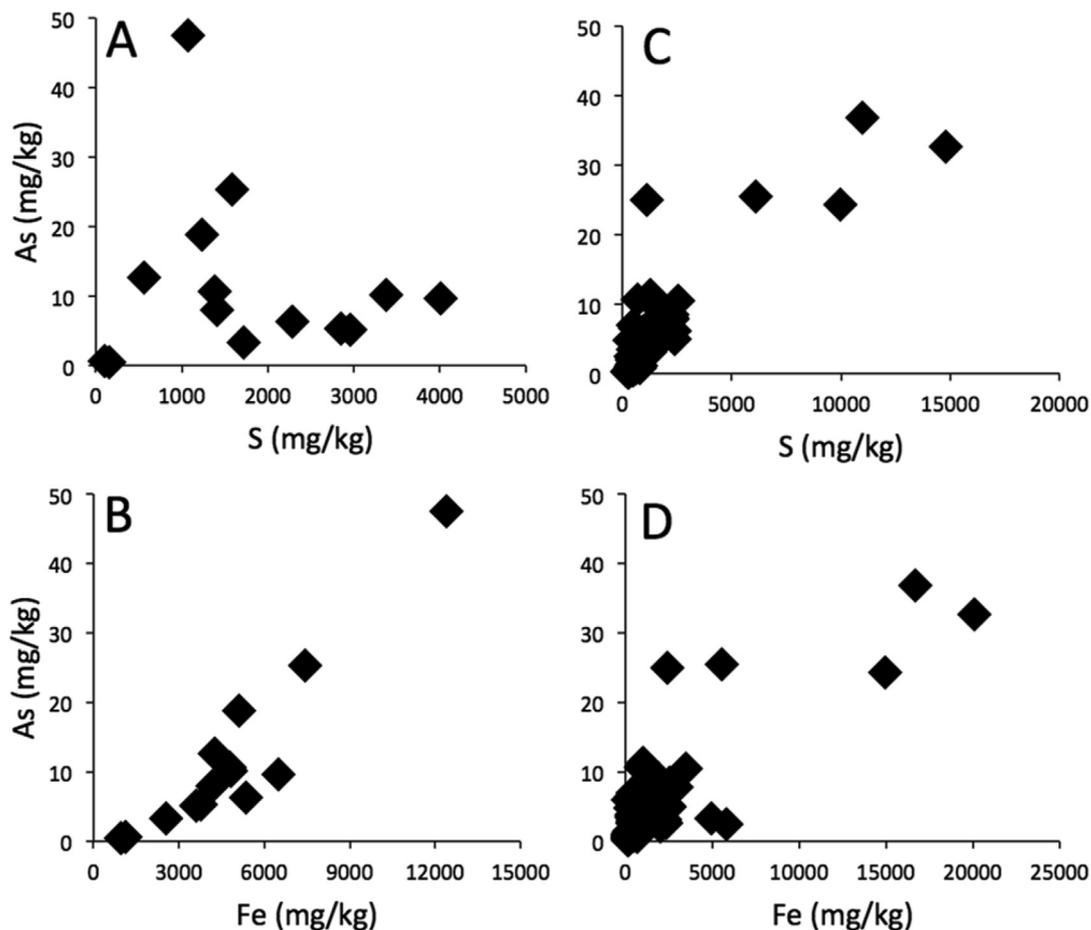


Fig. 1. X–Y diagrams for the concentrations of S vs. As and Fe vs. As in sediment samples from the Surficial Aquifer (A and B) and the Intermediate and Upper Floridan Aquifer (C and D) in the Lihtia area. Data is from Pichler and Mozaffari (2015).

between Fe, As and S can be further elucidated (Fig. 1). In the SAS there seems to be a correlation between Fe and As, but no correlation between S and Fe and As and S (Fig. 1A and B). This indicates that ferrihydrite is the likely source of As and that pyrite is not present. In the IAS and UFA on the other hand, there seems to be no correlation between S and As and Fe and As (Fig. 1C and D). However, the patterns for S and As and Fe and As are more or less identical indicating that Fe and S simultaneously affect the distribution of As in the IAS and UFA. This similarity can only be explained by the presence of a mineral phase, which contains all three elements, i.e., pyrite. It is noteworthy that groundwater in the SAS has no elevated As concentrations (Pichler et al., 2017), although the aquifer matrix contains equally high As concentrations as the IAS and UFA (Fig. 1). Further indicating that As bound to ferrihydrite is not a source of As in the Lithia area.

In closing Hansard (2017) stated that his statistical tests disagree with the observation that pyrite is the main primary source of As and that it remains unclear that As is of geogenic origin. He failed however to provide any other potential source and discarded multiple studies whose sole purpose was to determine the mineralogical association of As in the sedimentary sequence in Central Florida. More than 14 years of research into the source of As in the Floridan Aquifer in Central Florida did not identify any primary source of As other than pyrite (Arthur et al., 2002, 2007, 2005;

Jones, 2015; Jones and Pichler, 2007; Lazareva and Pichler, 2007; Pichler et al., 2011; Price and Pichler, 2002, 2006; Wallis et al., 2011). Extensive electron microprobe mapping demonstrated the close relationship between pyrite and As, because As was not analyzed in any other mineral phase (Fig. 2). Particularly compelling evidence was provided by Arthur et al. (2007) in the form of sequential extraction data (Fig. 3). They extracted the majority of As during the extraction step that targets sulfide minerals, such as pyrite.

The geogenic origin of elevated As in groundwater in the IFA and UFA is undoubtedly confirmed when considering the water management practice of aquifer storage and recovery (ASR) in Central Florida, where water is injected into a confined aquifer when it is plentiful and pumped from the aquifer when water is scarce. Those aquifers chosen for ASR are well removed from any potential source of agricultural or industrial contamination and are well protected from direct infiltration of surface water due to their confinement. Native (pre-injection) groundwater and recharge water generally have As concentrations below 2 µg/L, while concentrations in recovered water were as high as 130 µg/L. The cause of elevated As concentrations is the displacement of oxygen-free native groundwater with oxygenated surface water. As a result pyrite in the aquifer matrix is oxidized and dissolved causing the release of geogenic As (Arthur et al., 2005; Jones, 2015; Wallis et al., 2011).

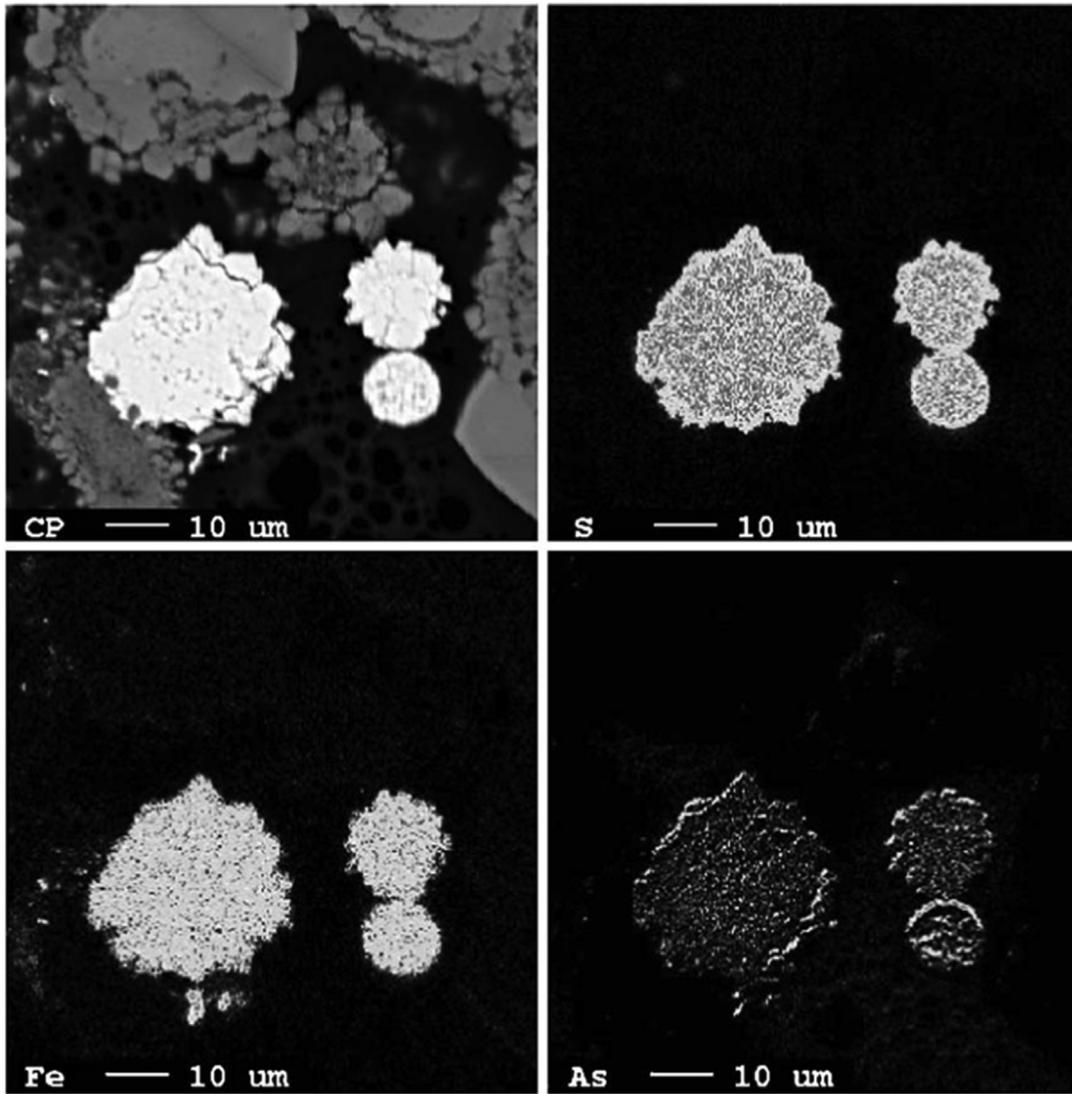


Fig. 2. Backscatter image (upper left) and S, Fe, and As element maps of framboidal pyrite and surrounding matrix in the Suwannee Limestone. The abundance of S, Fe, and As is shown in the upper right, lower left, and lower right, respectively (modified from Price and Pichler (2006)).

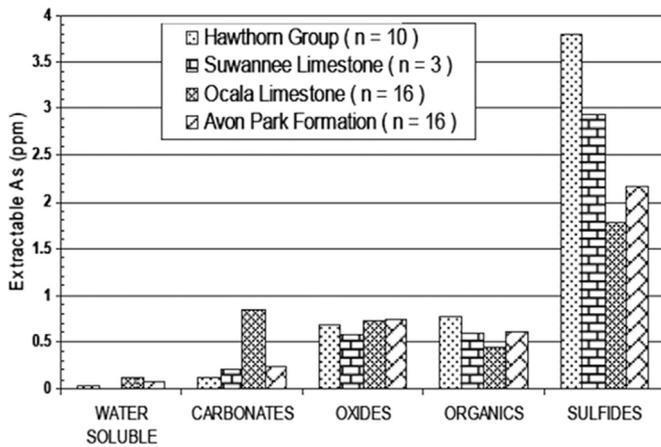


Fig. 3. Arsenic concentrations extracted during a five-step sequential extraction procedure for samples from Central Florida (including the Lithia area) (from Arthur et al., 2007).

References

- Arthur, J.D., Dabous, A.A., Cowart, J.B., 2002. Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. In: Aiken, G.R., Kuniansky, E.L. (Eds.), *U.S. Geological Survey Artificial Recharge Workshop Proceedings*. California, Sacramento, pp. 20–32.
- Arthur, J.D., Dabous, A.A., Cowart, J.B., 2005. *Water-rock Geochemical Considerations for Aquifer Storage and Recovery: Florida Case Studies*. Elsevier Ltd., Oxford.
- Arthur, J.D., Dabous, A.A., Fischler, C., 2007. Aquifer storage and recovery in Florida: geochemical assessment of potential storage zones. In: Fox, P. (Ed.), *Management of Aquifer Recharge for Sustainability, Proceedings of the International Symposium on Managed Aquifer Recharge*. Arizona, Scottsdale.
- Goldschmidt, V., 1937. The principles of distribution of chemical elements in minerals and rocks. *J. Chem. Soc.* 655–673.
- Hansard, P., 2017. A comment on “The distribution and mobility of geogenic molybdenum and arsenic in a limestone aquifer matrix”. *Appl. Geochem.* 77, 213–214.
- Jones, G.W., 2015. *Investigation of the Mechanisms for Mobilization of Arsenic in Two ASR Systems in Southwest Central Florida*. Geology. University of South Florida, Tampa, p. 80.
- Jones, G.W., Pichler, T., 2007. The relationship between pyrite stability and arsenic mobility during aquifer storage and recovery in southwest central Florida. *Environ. Sci. Technol.* 41, 723–730.
- Lazareva, O., Pichler, T., 2007. Naturally occurring arsenic in the Miocene Hawthorn Group, Southwestern Florida: implication for phosphate mining. *Appl. Geochem.* 22, 953–973.

- Pichler, T., Mozaffari, A., 2015. Occurrence, distribution and mobility of geogenic molybdenum and arsenic in a limestone aquifer matrix. *Appl. Geochem.* 63, 623–633.
- Pichler, T., Price, R.E., Lazareva, O., Dippold, A., 2011. Determination of arsenic concentration and distribution in the Floridan aquifer system. *J. Geochem. Explor.* 111, 84–96.
- Pichler, T., Renshaw, C.E., Sültenfuß, J., 2017. Geogenic As and Mo groundwater contamination caused by an abundance of domestic supply wells. *Appl. Geochem.* 77, 68–79.
- Price, R.E., Pichler, T., 2002. Naturally occurring arsenic in upper Floridan aquifer, southwest Florida: implications for aquifer storage and recovery. In: Kenny, J.F. (Ed.), *GroundWater/Surface Water Interactions*. American Water Resources Association, Middleburg, Virginia, pp. 387–392.
- Price, R.E., Pichler, T., 2006. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): implications for arsenic release during water–rock interaction. *Chem. Geol.* 228, 44–56.
- Sacks, L.A., Herman, J.S., Kauffman, S.J., 1995. Controls on high sulfate concentrations in the upper Floridan aquifer in southwest Florida. *Water Resour. Res.* 31, 2541–2551.
- Sacks, L.A., Tihansky, A.B., 1996. *Geochemical and Isotopic Composition of Ground Water with Emphasis on Sources of Sulfate in the Upper Floridan Aquifer and Intermediate Aquifer System in Southwest Florida*. U.S. Geological Survey, Tallahassee, p. 70.
- Wallis, I., Prommer, H., Pichler, T., Post, V., Norton, S.B., Annable, M.D., Simmons, C.T., 2011. Process-based reactive transport model to quantify arsenic mobility during aquifer storage and recovery of potable water. *Environ. Sci. Technol.* 45, 6924–6931.