Arsenic, manganese, and dissolved organic matter biogeochemistry in the Bengal Basin (India) and Southern Pampean plain (Argentina)

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SUMMARY: Arsenic (As) and manganese (Mn) biogeochemistry is intimately linked with dissolved organic matter (DOM) in subsurface aqueous environments. In this study, we explore the role of contrasting DOM quality on the distributions of Mn and As in groundwater. Tubewell and subsurface sediment samples were collected from Murshidabad, West Bengal (WB), India, as well as the Claromecó basin of Argentina. A parallel factor (PARAFAC) model is presented for WB samples that delineate key DOM components in sites characterized by high concentrations of both Mn and As (HMHA), and high Mn concentrations but low As (HMLA). An association between humic-like DOM and elevated As is clear, whereas Mn concentrations are high in the presence of both humic and protein-like DOM. In Claromecó basin groundwaters, an inverse relation between As and Mn is presented and future efforts are planned to incorporate the role of DOM.

1 INTRODUCTION

The arsenic (As) calamity in Southeast Asia has been a significant area of research for decades. More recently, concern over manganese (Mn) in drinking water has inspired work to assess the extent of Mn contamination and associated health impacts. Despite numerous reports of Mn inhibiting the intellectual development of children, increasing infant mortality rates, and causing Parkinson's like neurological disorders, the World Health Organization (WHO) revoked its Mn drinking water limit (0.4 mg L^{-1}) because naturally occurring levels were not of health concern (WHO, 2011). We argue that the data needs to be reassessed and the drinking water limit reconsidered.

Numerous papers have explored the relationship between Mn and As in groundwater. Early work demonstrated that Mn oxide reduction can stimulate dissolved As(III) oxidation and immobilization, and later experimentation by Ehlert *et al.* (2016) highlighted that greater Mn-oxide content in contaminated paddy soils lead to increased As retention. Field scale observations noting an inverse relation between dissolved Mn and As in groundwater have been attributed to this phenomenon, as well as variable redox potential (E_h). Yet, few studies to date have assessed the role of DOM in the coupled biogeochemical cycling of Mn and As (Vega *et al.*, 2017).

Dissolved organic matter plays a key role in metal(loid) geochemistry through electron shuttling catalyzing reduction pathways, complexation processes keeping solutes in solution, and labile organic carbon fueling heterotrophic microbial metabolisms. Recent advances in fluorescent and absorbance spectroscopic techniques have permitted qualitative analyses of DOM as it relates to As mobilization,

and fluorescence excitation emission matrices (EEMs) coupled with a PARAFAC model revealed associations between DOM and As, but did not include Mn (Kulkarni *et al.*, 2016). The purpose of this study was therefore to investigate the role of DOM in coupled Mn and As biogeochemical cycling by evaluating associations between these metal(loid)s in sites with statistically different DOM composition. This presentation emphasizes recently published work in Murshidabad, India, but also includes ongoing work in the Claromecó river basin of Argentina.

2 METHODS

2.1 Study area

Murshidabad, a district in West Bengal, India, is bisected by the north-south flowing River Bhagirathi. West of the river, aquifer sediments are reddish brown and are of Pleistocene age, whereas dark gray Holocene sediments dominate the east. Several studies have reported contrasting As concentrations in the Holocene (high As) and Pleistocene (low As) aquifers, and more recent work has revealed contrasting DOM quality in these distinct systems.

The Claromecó fluvial basin (CFB) is situated in the southern Chaco-pampean plain of Argentina. Late Pleistocene-Holocene aquifer sediments constitute the top of the sedimentary sequence covering the middle and lower basin, and are greenish-brown, mostly volcanoclastic and deposited by fluvio-eolian processes (Sosa *et al.*, 2017).

2.2 Sampling and analysis

In Murshidabad, 51 groundwater and 16 subsurface aquifer sediment samples were collected from two

sites located on the west side and four sites located on the east side of the river Bhagirathi. Water samples were analyzed for dissolved cations, anions, pH, alkalinity, E_h , DOC, and TDN; DOM was further characterized using EEMs followed by PARAFAC modeling. In the CFB, 29 well water samples were analyzed for dissolved cations, anions, pH, alkalinity, and E_h . Aqua regia digestions were performed on subsurface sediments in both regions to determine bulk concentrations of As, Fe, and Mn; XRF was also employed in the CFB.

3 RESULTS

3.1 Aquifer metal(loid) geochemistry

Within Murshidabad, the WHO limits for As ($10 \mu\text{g L}^{-1}$) and Mn (0.4 mg L^{-1}) were exceeded in 78% and 73% of the surveyed tubewells, respectively. Three sites were characterized by high concentrations of both As ($\sim 330 \mu\text{g L}^{-1}$) and Mn ($\sim 0.8 \text{ mg L}^{-1}$) ["HMHA"], while the remaining three sites had high Mn ($\sim 1 \text{ mg L}^{-1}$) but low As ($\sim 9 \mu\text{g L}^{-1}$) ["HMLA"]. HMLA sites had higher E_h but lower As and Fe concentrations, than HMHA sites. Arsenic concentrations exceeded the WHO limit in all CFB wells ($\sim 83 \mu\text{g L}^{-1}$), whereas Mn concentrations were consistently low ($\sim 0.003 \text{ mg L}^{-1}$). Bulk sediment concentrations for Fe, Mn, and As were statistically similar between HMHA and HMLA sites in Murshidabad, as well as both spatially and with depth in the CFB.

3.2 DOM-PARAFAC model

Four DOM components were determined by the PARAFAC model in Murshidabad: (C1) a terrestrial humic-like component; (C2) a humic-like component influenced by agriculture and wastewater; (C3) a protein-like component; and (C4) a microbial humic-like component (Fig. 1). Component 1 was significantly more abundant in HMHA sites, C3 and C4 were significantly more abundant in HMLA sites, and C2 was statistically similar between HMHA and HMLA sites.

4 CONCLUSIONS

The HMHA aquifers have reducing redox potentials that can mobilize Fe, Mn, and As, and the presence of humic-like DOM may be catalyzing these processes. Further, a greater proportion of wells in HMHA sites were saturated with respect to rhodochrosite relative to HMLA sites. This implies a net sink for Mn in HMHA sites, yet Mn concentrations were similar throughout all sites. It is postulated that rhodochrosite precipitation is inhibited by complexation mechanisms with humic-like DOM, keeping Mn in solution. In HMLA aquifers, Mn oxide reduction may be oxidizing As(III) and enhancing the potential re-adsorption of As(V) onto un-reduced or freshly precipitated Fe oxides. The fact that Mn concentrations are high in the presence of both humic-like and protein-like DOM suggests that

Figure 1. Excitation emission matrices (EEMs) for the four components of the DOM PARAFAC model and their relative distributions in high Mn, high As (HMHA) and high Mn, low As (HMLA) sites.

Mn mobilization may be independent of DOM quality. Future work necessitates experimental validation of the processes in Murshidabad and the application of fluorescence spectroscopic techniques in the CFB to understand the role of DOM quality in a high As, low Mn scenario.

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