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The Biogeochemical Differentiation and Movement of Arsenic within Groundwater Aquifers Amid Fluctuating Redox States

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Abstract

This widespread contamination of groundwater formation by natural sources of arsenic is an unprecedented environmental and public health crisis, especially in the deltaic and alluvial areas throughout the world. Geographical distribution and water solubility of arsenic is essentially controlled by the complex biogeochemical cycling of redox sensitive elements such as iron, manganese and sulfur under changing hydrodynamic conditions. This is a detailed study paper that methodologically reviews the processes that affect arsenic speciation and mobilization in different redox situations such as sub-daily variations associated with the tide, plus seasonal recharge of the groundwater and anthropogenic disturbance from agricultural activities. The traditional view is that the release of arsenic is due primarily to the reductive dissolution of the iron (oxyhydr) oxides, but from the current multi-scale evidence, there is strong evidence of an important geochemical separation of iron and arsenic. The separations of these due to the precipitation of secondary minerals like magnetite, green rust, and authigenic sulfides of different affinities to arsenite, (As (III)), and arsenate, (As (V)). In addition, this study examines kinetic constraints of arsenic oxidation by the biogenic manganese oxides (BMOs), their inhibitory effect in natural organic matter (NOM) and the evolution of integrated catalytic mechanisms such as bio-electro-Fenton processes. Inclusion of high-resolution spectroscopic data and use of reactive transport models like PHT3D and CD-MUSIC, has important implications regarding predictions and remediation in environments exposed to imminent hydro-climatic changes, as discussed in this article.

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1. Introduction:

Inorganic arsenic is one of the many hazardous metals (loids) that could increasingly threaten water safety globally. Geogenic arsenic is common in terrestrial ecosystems and the greatest concentration of occurrence is in the Holocene aquifers of the Ganges-Brahmaputra-Meghna (GBM) Delta, Holocene aquifers in the Hetao Basin, the Red River Delta, and in a few fractured volcanic systems that overlie fractures of sedimentary basins, such as in North-Central Mexico. Many individuals are exposed to levels of dissolved arsenic that always exceed the World Health Organization (WHO) interim guideline value of 10 micrograms per liter (µg/L).

The dynamics and diversification of arsenic in these aquifers are seldom stable. The process of transforming less mobile oxidized arsenic, as arsenate, As(V) - into more mobile and harmful reduced arsenic, as arsenite, As(III) - is in essence related to the redox potential (E_h) and pH of the local aquifer. In the past, literature revealed only one dominant model to explain the mobilization of this: mobilization via reductive dissolution of arsenic-containing iron (oxyhydr) oxides with the help of microorganisms. Thus, this model assumes that adding biodegradable organic material (a carbon source) to anoxic groundwater activates a heterotrophic microbial community that uses solid-phase ferric iron (Fe^{III}) as the final electron acceptor. This mineral structure is then broken down, putting the geochemically bound arsenic into the porewater.

However, the linear and uniformity of the reductive breakdown is increasingly challenged by field data that show strong geographical and temporal variability. Aquifers undergo continuous hydrodynamic disturbance leading to fluctuations in the redox conditions. Groundwater systems are continually and dynamically changing as a result of wave-induced circulation at the lake edge, sub-daily tidal pumping in estuaries by the coast, seasonal monsoonal recharge, and the regular flood and drying of rice paddy fields. Reaction zones that develop where oxygenated surface water meets anoxic ground water, promote the rapid, local mineral dissolution and re-precipitation cycles.

All these variable conditions contribute to complex biogeochemical processes, including the geochemical "decoupling" of iron and arsenic. Assuming reductive dissolution took place alone, concentrations of aqueous iron (Fe^{2+}) and arsenic would vary in a stoichiometric manner. In contrast, empirical observations indicate actively habitats that are strongly enriched in aqueous arsenic and strongly depleted of dissolved iron and vice versa. The intent of this article is to help clarify the specific processes that control the separation and mobility of as at different redox conditions. The use of predictive geochemical modeling to give insight to the complexities of as mobility, use of the scientific approach to study the kinetics of mineral alteration and the biological limits of sulfur and iron cycling is investigated.

2. Review of Literature: The conceptualisation of arsenic mobility has gone through a series of hydrogeochemical investigation. The first attempts were to explain the elevated arsenic contents by different natural processes, for example, by a degradation of carbonate minerals, changing the flushing rate of the aquifers, or by a flow of deep thermal waters, which, as a hypothesis, is named after the Pannonian Basin in Hungary. These processes occur in some geographical settings but the microbial reductive dissolution of (hydr) oxides has emerged as the most important process in deltaic ecosystems. In many instances there are specific bacterial communities that accelerate this dissolution process: e.g. Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans are known to be effective in iron phase modification under specific environmental conditions.

Despite this, a reduction solution model, the reductive dissolution model prevailed, although inconsistencies in later high-resolution field mapping were found. For example, solid phase analyses of sedimentary basins showed high concentrations of arsenic to often occur at the well depth where the reactive ferric (hydr)oxides, apparently, had been effectively eliminated, implying that there was additional trapping process. Because of this discovery, the hypostasis about biogeochemical decoupling originated. The focus of literature has been shifting towards the fate of

Fe^{2+} generated in reductive dissolution. There are unreacted precursor minerals, particularly ferrihydrite and lepidocrocite, which react with the increasing local aqueous Fe^{2+} concentrations to form mixed-valence secondary phases such as magnetite (Fe_3O_4), siderite ($FeCO_3$), and green rust. These secondary phases can also have selective adsorption behaviors and they often adsorb heavy metals and metalloids differently than their parent phases, thus changing their aqueous transport.

In addition to the study of iron, literature has developed to include regulatory roles of the cycle of sulfur and manganese. That anaerobically dominated communities can cause dissimilatory sulfate reduction, resulting in the production of hydrogen sulfide which should sequester metals as authigenic sulfides. However, studies indicate that this sequestration efficiency is dramatically affected by the arsenic specie before sequestration. By contrast, the biogenic manganese oxides (e.g. birnessite) have been exhaustively studied to see how fast they can oxidize As (III) to As (V). A key focus area in the study of this oxidation is the dynamics of the process, particularly regarding the possible surface passivation as a result of competing natural organic matter (NOM).

In the last years significant progress in the remediation technology has been reported, particularly related to the use of advanced oxidation processes (AOPs) in the groundwater system. The traditional Fenton reaction has been adapted and developed as bio-electro-Fenton systems in order to generate reactive oxygen species (ROS) in situ at neutral pH, to accelerate the oxidation of arsenite and hence link using the methodology of biogeochemistry in the environment to engineering in water purification.

3. Methods and Materials:

Institute-researchers combine high resolution solid-phase characterisation by microscopy, highly controlled biological microcosm incubations, and state-of-the-art reactive transport modelling to address the issues of arsenic differentiation and mobility in a comprehensive way. Combination of these strategies can provide a holistic picture of the transient physical and chemical processes of which they are a part.

3.1. Solid-Phase Spectroscopic Characterisation: In order to determine the exact coordination chemistry and oxidation state of arsenic in the host sediments, it would be required to use sophisticated spectroscopic methods. Micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy using synchrotron is extensively used for this purpose. Elemental maps and the ability to extract accurate sample spectra across the arsenic Kα edge of 11867 eV from -50 to +100\[span-40](start-span)[span-40](end-span) enables scientists to reliably measure the proportion of total arsenic attributable to individual solid-phase components of the sample (e.g., arsenate adsorption to ferrihydrite versus arsenite incorporation into minor iron sulfides). This is crucial in confirming elemental speciation and the original redox state of the sample for chemical extraction.

3.2. Microcosm and Kinetic Incubation Protocols: For the isolation of thermodynamic variables and rates of kinetic processes, advanced automated microcosm incubation procedures are followed. These systems allow precise execution of the variable redox cycles which resemble the oscillations of the oxidized ($E_h \geq +100$ mV) and reduced ($E_h \leq -100$ mV) processes occurring at coastal edges or at inundated paddy soils. Some bacterial species such as Desulfovibrio vulgaris (ATCC strain 7757) which tend to reduce sulfate instead of directly reducing iron and arsenic are added to synthetic groundwater buffered by carbonate. A series of these incubations include specific electron

donors (e.g., 10 mM lactate) and different sulfate concentrations (0.08 - 10 mM sulfate) to explore sulfidization of As (III/V)-bearing ferrihydrite. Theoretically "pure" experimental solid phases are often spiked with much higher levels of arsenic than are likely to be detected in natural samples, for example an arsenic level of 225 mg/kg or 9900 mg/kg on ferrihydrite.

For abiotic kinetic studies, the synthetic acid birnessite δ-MnO_2 is synthesized and it reacts with aqueous As (III) in predetermined buffering conditions. Empirical evidence indicates that the type of buffer used considerably influences the reaction rate as observed, for instance, in the Fe (II) - Fe(III) oxidation reaction where MES buffer (pH 6.75) and HEPES buffer (pH 7 and 7.25) gives a quite sluggish, non-first order reaction rate, while phosphate buffer gives true first order rate with a direct dependence on buffer concentration.

3.3. Reactive Tranceport and Surface Complexation Modeling: To develop models for prediction at aquifer scales from micro-scale measurements of kinetics, robust computational frameworks to enable modeling of Reactive Transport and Surface Complexation are required. The multidisciplinary transport simulator PHT3D, which successfully combines MODFLOW/MT3DMS and PHREEQC, is used to simulate groundwater arsenic distribution. One of the major goals of current modeling studies is to test how effective Surface Complexation Models (SCM) can be as opposed to simplified empirical distribution coefficients (K_d) for accurately capturing transient sorption phenomena in environments that change in redox status. Advanced supply chain management methodologies like the Charge Distribution MUltiSIte Complexation (CD-MUSIC) model are used to calculate standard-state intrinsic equilibrium constants of ion adsorption on specific crystalline surfaces of two mineral oxides, ferrihydrite and goethite, and thermodynamically take into account competitive complexation (e.g., arsenate and phosphate) in the system.

4. Discussion and Result:

4.1. Hydrodynamic Forcings and the Stratification of Redox Zones: The control on arsenic mobility in dynamic aquifers is primarily timers of hydro-biogeochemical interaction. Results have consistently shown that the sub-daily tidal flow produce strong physical pumping (increased transport of oxygen-rich surface waters into anoxic sediments) with frequency in the range of minutes or hours, but this high-frequency 'pumping' is often more than counterbalanced by larger tidal-scale seasonal changes.Observations show that remote boundary reactive aquifer purging is efficient when net groundwater outflow is significant, as in the rainy season when the groundwater recharge is high during the monsoon season. Consequently, there is a large reduction in concentration of dissolved as and Fe^{2+} in the vicinity of the channel. Such seasonal records of variation in both E_h and dissolved arsenic concentrations are significantly more pronounced than would be the variation due to tide alone. However, the spatial distribution of contamination risk is important: the bed sediments of paired channels can become saturated with arsenic and contain high concentrations of arsenic, primarily in its highly mobile form As(III) which can be suddenly mobilized following a physical disturbance or a resuspension event.

The future hydro-climatic changes (sea-level rise (SLR) and increased storm surge flooding) offer conflicting geochemical processes. Contrary logic on protection: laboratory inundation

experiments, simulating sea level rise, show that natural occurrence of high-sulphur concentration in marine waters provide effective protection as the reductive breakdown of ferric iron and arsenate is impeded in salt concentration of inundated sediment. The opposite situation is the freshwater inundation, where a strong reductive process after the low energy inundation resuspension event releases geochemically bound trace metals, and releases over 80% of the total bound as into the porewater by release.

4.2. Agricultural Interventions and Fluctuating Redox in Paddy Soils: The effects of the different redox states are more evident in agricultural contexts, such as in rice paddy fields, where purposeful and repeated soil inundation and de- watering take place. These hydrodynamic changes are purposefully induced, producing substantial fluctuations in E_h which results in rapid changes in as speciation and the direct threat to agricultural stability and human food supply system. Under baseline conditions of highly reduced environments ($E_h \leq +100$ mV), untreated natural soils exhibit considerable mobilisation of arsenic with concentrations in the pore water that range from 4.2 to 9.2 mg L^{-1}.

In response to this, often farming practices are aimed at improving soil vigor through organic soil amendments. The use of different amendments—lignocellulosic rice husk biochar (RH-BC), cow dung (CD) from birds and mixed biogas slurry (BGS)—produces distinct geochemical scenarios. The combination of raw organic carbon can stimulate the microbial reductive dissolution of iron oxides, however, under moderately reduced conditions ($E_h > +100$ mV) the resulting increase in pH from the degradation of the added organic solid can effectively be used to suppress the release of arsenic.

Dissolved arsenic (As) is decreased by a maximum of 3677% when CD is used. This immobilization is mostly due to the incorporation of carbon molecules and humic/fulvic acids that create very stable, macromolecular complexes with arsenic, making it immobile. Further, the Mn/Fe ratio of the extractable soil matrix is a critical thermodynamic stabilising component of soil's intrinsic chemical composition. The manganese oxides are more thermodynamically favorable terminal electron acceptors than the iron oxyhydroxides, which delays the onset of iron reduction. Microbial reduction of manganese results in greater pH in the pore water under inundation in soils rich with synthetic nanocrystalline manganese oxide (δ-MnO2). In environments where carbonate is abundant, this pH alteration works in tandem with microbial Fe- and S-reduction, catalyzing the widespread occurrence of siderite ($FeCO_3$) and mackinawite (FeS), and thereby decreasing the overall mobilization of As by up to 45% as compared to low-Mn soils.

4.3. Sulfur Cycling and Microbial Constraints

Dissimilatory sulfate reduction presents an alternative thermodynamic sink in environments where sulfate is abundant in the environment, such as salt water influenced aquifers or some sedimentary formations. Sulfate itself can be reduced by microorganisms, for example, Desulfovibrio vulgaris to give gaseous hydrogen sulfide which reacts quickly with available Fe^{2+} and primary iron oxides to give elemental sulfur and small amounts of iron sulfides like mackinawite (FeS).

By itself the efficacy of this route in sequestering arsenic is limited by the oxidation state of the metalloid. Incubation experiments have shown that sulfate reduction is not an effective means

of solubilizing or sequestering arsenic in environments that contain As (V), largely because the reduction of As (V) with biogenic sulfide is thought to be kinetrically impossible, and strongly recalcitrant. By contrast, incubations with sources of As (III) will retain the arsenic quickly, even if the retention is sometimes temporary, as As (III) co-precipitates directly into the authigenic sulfide phases. Thus, successful application of the arsenic mitigation method of sulfidization requires a microbial community that can reduce As (V) to As (III) as a first step and an anaerobic environment, and merely reduction via sulfate in anaerobic environment is not enough.

Conclusion: Arsenic concentrations in groundwater aquifers are geographically variable and sensitive to changes in groundwater composition (water solubility) and are controlled by complex biogeochemical processes which are especially sensitive to changing redox conditions in the groundwater. Presently available data shows that dynamic hydrologic processes, such as seasonal aquifer recharge, or deliberate flooding of agricultural fields, trigger rapid cycles of mineral transformation, at local scales, and largely independent from arsenic and the associated iron oxides. The differential sequestration of As (V) and As (III) causes the highly mobile and deadly arsenite plumes to persist in a dangerous manner as the initial ferrihydrite transforms to secondary mixed-valence minerals (e.g., magnetite and green rust).

Co-occurring geochemical cycles act as either accelerators and/or local obstacles. The natural deposition of sulfur is an effective sequestration method but it is totally prevented by the biological requirement for preceding $As (V)$ reduction. At the same time, the oxidative capability of biogenic manganese oxides constitutes a key natural factor for arsenic sequestration, but is very sensitive to passivation of the surface by natural organic matter and this can only be overcome by using highly selective ligands or by genetically engineered complex biologic oxidation methods (such as neutral pH bio-electro-Fenton or AsOB).The physical mechanisms operating at these boundaries of redox will inevitably become worse as hydro-climatic conditions change rapidly all over the world because of climate change and as seastands rise more frequently and monotonically in coastal areas, where, suddenly and without warning, rainfall patterns shift dramatically. The results gathered for this investigation suggest that more complex modeling than empirical solutions are necessary for present-day aquifer management, remedial engineering, and agricultural activity. There is a need for researchers and practitioners using models to forecast and mitigate the growing risk of environmental exposure to arsenic to use integrated kinetic-equilibrium reactive transport models (such as PHT3D and CD-MUSIC) that are able to accurately assess the various roles of the interface and include multicomponent surface complexation and non-linear biogeochemical decoupling.

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