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Natural arsenic contamination of Holocene alluvial aquifers by linked tectonic, weathering, and microbial processes

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[1] Linked tectonic, geochemical, and biologic processes lead to natural arsenic contamination of groundwater in Holocene alluvial aquifers, which are the main threat to human health around the world. These groundwaters are commonly found a long distance from their ultimate source of arsenic, where chemical weathering of As-bearing minerals occurs. We propose a “GBH-As” model that ties together all of the important tectonic, biologic, and hydrologic processes that cause natural As release in groundwater in Holocene terrestrial deposits. Processes highlighted by the “GBH-As” model can explain the movement of arsenic from lithosphere to hydrosphere. However, we propose a factor that has increased dissolved As concentrations in Holocene aquifers to levels where human health is threatened: mechanical weathering associated with Pleistocene glaciation. Our model invokes erosion of mountain belts aided by glaciers, transport of arsenic by surface waters, adsorption of As by stream sediments, and deposition of stream sediments and organic matter in alluvial deposits. Subsequently, Fe(III)-reducing bacteria present in alluvial aquifers cause the release of sorbed As to groundwater under moderately reducing conditions.

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1. Introduction

[2] Arsenic is a common contaminant found in soils and groundwaters from both natural and anthropogenic sources. Natural geologic "non-point" sources of arsenic appear to be a greater threat to water quality worldwide. For example, arsenic is a common constituent in a variety of metallic sulfide ores [*Welch et al.*, 2000] and in coal deposits and associated host rocks [*Goldhaber et al.*, 2003]. Although the aforementioned As sources lead to contamination of groundwater at the scale of small regions, it is the Holocene alluvial aquifer setting that is currently exposing tens of millions people to high levels of arsenic in groundwater. This paper presents an overview of the tectonic, hydrogeology, geochemistry, and geomicrobiology of arsenic in the alluvial aquifers. Moreover, the widespread As contamination of groundwater in glacial tills worldwide indicates that arsenic mobilization could be enhanced by glacial erosion. Previous workers [*Acharyya et al.*, 2000; *McArthur et al.*, 2001] have proposed a connection between the retreat of continental glaciers at the end of the Pleistocene, which led to rise of sea and river base levels, and deposition of the Holocene alluvium which later hosts As-contaminated groundwater. Here, we document a number of settings around the world where mountain belts and/or glacial deposits appear to be the primary source of As, and propose that As released from these deposits ultimately can end up in alluvial aquifers by a complex series of events we call the Geo-Bio-Hydro arsenic (GBH-As) model.

[3] Although recent studies have linked the natural biogeochemical cycles of Fe and As to the widespread As contamination of shallow groundwater [*Korte*, 1991; *Welch and Lico*, 1998], the biogeochemical processes control As reactivity and mobilization as well as its sources and sinks remain poorly understood. The primary source of As is believed to be the weathering of As-rich minerals in the basin headwaters. Under aerobic conditions Fe(III) and Mn(IV) oxides remove As from surface water, but subsequent development of anaerobic conditions can reverse this process, leading to high levels of As in groundwater. Under progressively more reducing conditions, sulfate reducing bacteria (SRB) can also remove As by sequestering it in Fe-sulfides [*Huerta-Diaz and Morse*, 1992; *Saunders et al.*, 1997]. Thus bacterially mediated redox reactions involving organic carbon, Fe, Mn, and S may lead to cycling of As between solid minerals and groundwater. Our model stems from field data collected from our two research sites in the USA where biogeochemical and hydrogeologic conditions are similar to the worst As-contaminated areas in southern Asia. One of our sites where dissolved As levels are elevated is adjacent to Pleistocene glacial deposits in the midcontinent. The other site is not directly related to glacial deposits but contains higher levels of As in bio-epigenetic pyrite precipitated from groundwater. We also review recent literature that shows high As levels in glacial tills and associated groundwaters. Combining literature review and our own research, we propose that As cycling is generally controlled by weathering, adsorption, and bacterially mediated biogeochemical reactions, but glacial erosion may enhance As release to the point that threatens human health in the Holocene alluvial setting. Field data and geochemical models of arsenic reactivity and mobilization are presented in the auxiliary material[1].

2. Natural Arsenic Contamination of Holocene Alluvial Aquifers

[4] Arsenic occurs in elevated levels (>10 μg/L) in a variety of alluvial aquifers in countries such as USA, Hungary, China, Taiwan, Vietnam, Indian subcontinent, etc. [*Nickson et al.*, 2000; *Nordstrom*, 2002; *Dowling et al.*, 2002; *van Geen et al.*, 2003]. Unfortunately, the local population in a number of developing nations such as Bangladesh and India has turned to moderately shallow "tube-wells" in alluvial aquifers for water supplies because surface water resources have been polluted with human and animal feces.

[5] Bangladesh and West Bengal of India together form a large delta-dominated basin that comprises the proximal, eastern portion of the immense foredeep of the Himalayas. Formed by crustal loading during the Himalayan collision, this basin is over 20 km deep and is filled by synorogenic Cenozoic sequences derived from the eastern Himalayas [*Uddin and Lundberg*, 1998]. Two major Himalayan river systems, the Ganges and the Brahmaputra, dominate this dense fluvial network. The present-day Ganges-Brahmaputra delta may have started developing between 11,000 and 7,000 years ago during a glacial-interglacial transition, storing most of the sediments in the river floodplains [*Goodbred and Kuehl*, 2000]. The shallow groundwater aquifers in the Pleistocene

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[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gc/2004GC000803.

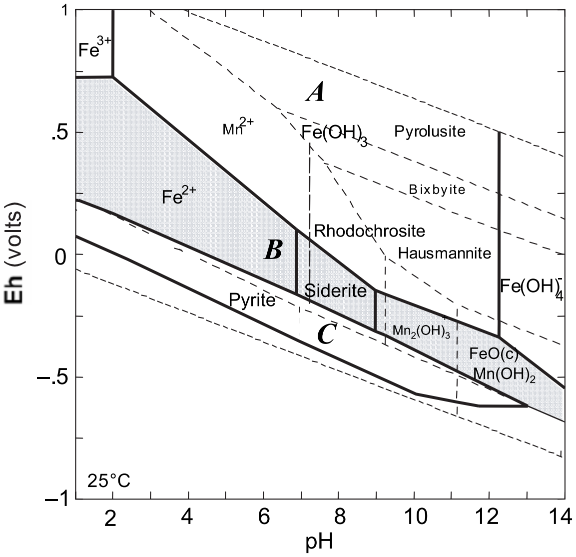

Figure 1. Eh-pH diagram calculated for average geochemical conditions in Fe-Mn-S-HCO_3-H_2O system. Activity of species: $Fe^{2+} = 10^{-4.5}$, $Mn^{2+} = 10^{-4.1}$, $SO_4^{2-} = 10^{-3.4}$, and $HCO_3^{-} = 10^{-2.6}$. Labels A, B, and C represent oxidizing, moderately reducing, and highly reducing groundwaters. This activity diagram was generated by the Geochemist's Workbench [*Bethke*, 1996].

and Holocene clastics range in depth from around 50 to 100 meters in most parts of Bangladesh [*Ahmed et al.*, 2004].

[6] Groundwater found in Holocene and Pleistocene alluvial aquifers occurs in three principal geochemical types (Figure 1). Groundwaters occurring near the water table in Holocene aquifers, or in the deeper oxidized Pleistocene units, have high Eh values, low dissolved As and Fe, and plot near field "A" in Figure 1. Pleistocene deposits are generally devoid of organic matter and oxidized with orange color of Fe- and Mn-oxyhydroxide minerals that strongly adsorb arsenic. Moderately reducing groundwaters plotting near field "B" of Figure 1 can have highly elevated As levels, and often elevated dissolved Fe(II) and Mn(II). These groundwaters usually occur in Holocene deposits containing abundant organic matter such as peat [*McArthur et al.*, 2001]. The redox condition of these waters is likely controlled by the metabolism of anaerobic Fe- and Mn-reducing bacteria [*Islam et al.*, 2004]. We have recently identified strains belonging to the genus *Geobacter* at the Kansas City Plant (KCP) site where reductive dissolution of Fe-oxyhydroxides released sorbed As [*Saunders et al.*, 2005]. As-rich groundwaters with similar geochemistry could precipitate authigenic siderite ($FeCO_3$) and/or rhodochrosite ($MnCO_3$) [*Saunders and Swann*, 1992; *Pal et al.*, 2002] as well (e.g., Figure 1). Very reducing groundwaters plot near field "C" in Figure 1 may or may not have any appreciable dissolved As. If biogenic sulfate reduction is limited by a minor amount of dissolved sulfate, then virtually all of the sulfate and only some of the As will be removed by As-bearing Fe-S solid phases [*Akai et al.*, 2004; *Kirk et al.*, 2004; *Zheng et al.*, 2004].

[7] *Korte* [1991] and *Saunders et al.* [1997] proposed that As is concentrated by its adsorption on Fe(Mn)-oxyhydroxides in the active stream sediments. Co-deposition of stream sediments with organic detritus in alluvial settings lead to the development of reducing conditions ("Type B" groundwaters in Figure 1) where As is released. Unfortunately in India and Bangladesh, hand-installed "tube-wells" are commonly installed at depths (~50–150 m) that tap these "Type B" groundwaters. Deeper and more expensive drill holes would be required to reach the "Type A" groundwaters in the underlying Pleistocene formations or perhaps some suitable "Type C" waters found under local biogenic sulfate reduction not limited by initial low sulfate concentrations.

[8] Although there is a growing consensus that reductive dissolution of Fe(Mn)-oxyhdydroxides is the most important As-release process in Holocene alluvial aquifers, the ultimate source of arsenic is not well understood. Recent research indicates that bedrock geology plays an important role [*Grosz et al.*, 2004]. The crustal abundance of As is about 2 mg/kg, and a variety of minerals contain minor amounts of As [*Welch et al. 2000*]. Thus weathering of a variety of rock types can lead to As-release to the hydrosphere. Rapid erosion associated with active tectonics (e.g., Himalayas) or glaciation expedited Holocene weathering of As-bearing minerals, leading to this recent "slug" of arsenic coursing through the hydrologic cycle.

3. Tectonic-Glacier Connection to Arsenic Enrichments

[9] There seems to be geographic correlation between countries where As-contaminated groundwaters in Holocene deposits and the presence of rapid tectonic uplift and extensive continental or alpine glaciers in the Pleistocene, particularly in southern Asia (Figure 2). This is an association in space and time (e.g., correlating to Holocene global warming and the retreat of glaciers) that led to our

Figure 2. Principal areas (yellow) covered by Pleistocene glacial ice in south Asia. Major occurrences of arsenic (red squares) in Bangladesh, Western Bengal (India), Pakistan, Vietnam, Thailand, and southern China are associated large alluvial or floodplain formed from glacial spillways. Arsenic contamination also occurs along the northern glacial outflow areas (not shown), including Inner Mongolia, Xinjiang, and Shanxi [*Nordstrom*, 2002].

hypothesis about the connection between tectonic uplift, glaciers, and natural As-contamination of groundwaters. The basic tenet of the hypothesis is that *enhanced* mechanical weathering of rocks by Pleistocene mountain-building or glaciation led to chemical weathering of the reactive, high-surface area glacial deposits upon Holocene warming. This renewed chemical weathering released As to the hydrosphere, and a series of linked biogeochemical processes have lead to As enrichment in Holocene alluvial aquifers.

[10] Recent research results in Europe and North America have shown a close connection between elevated As in groundwater and glacial deposits. For example, large parts of Hungary, centered between the Alps and Carpathians filled with thick alluvial and glacial sediments, contain As contaminated groundwaters in Holocene deposits [*Varsanyi et al.*, 1991; *Hungarian Geological Survey*, 1996]. The Cook Inlet basin of Alaska where more than half of the state's population reside in, shows this relationship quite clearly [*U.S. Geological Survey*, 2001] as wells tapping groundwater in tills commonly contain elevated As (Figure 3). In Saskatchewan, *Yan et al.* [2000] found many groundwaters in glacial tills had >100 μg/L As. Similarly, the areas with the most As-contaminated groundwaters in Washington State are in the Island County, where groundwaters occur in glacial till aquifers (Washington Department of Health, 2004; see http://www.doh.wa.gov/ehp/dw). Also, arsenic seems to be most elevated in glacial till aquifers in Minnesota [*Minnesota Pollution Control Agency*, 1998], Michigan [*Kolker et al.*, 2003], and Illinois [*Warner*, 2001].

[11] The essence of the GBH-As model is that it involves a chain of events including the weathering of As-bearing minerals (sulfides and silicates) in the headwaters, release of As to surface waters, sorption of As in surface waters by stream sediments containing reactive Fe-Mn-oxyhydroxides, deposition of those sediments in floodplains with organic matter, and bacterial reductive dissolution of Fe-Mn-oxyhydroxides. We suspect that "normal" weathering of average continental crust and movement of As through our hypothesized processes will not necessarily lead to groundwater with elevated As in river floodplains. The As flux in this situation is controlled by climate and weathering rates. The mechanical weathering related to active tectonic uplift and associated glacier erosion can provide a ready source of high-surface-area material, perhaps locally enriched in As. The retreat

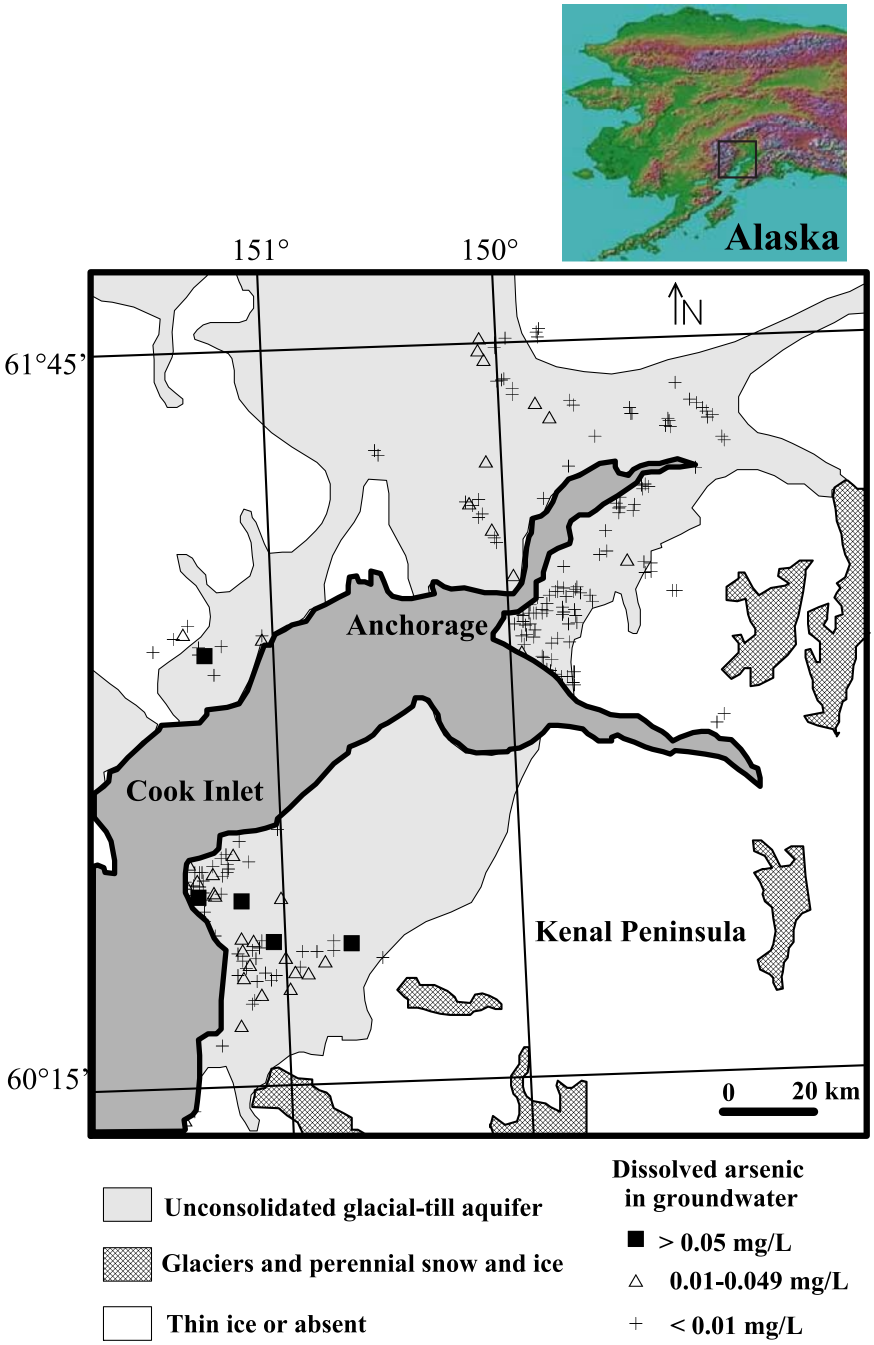

Figure 3. Geographic distribution of glacial tills and As-rich groundwater in Cook Inlet basin, Alaska [after *U.S. Geological Survey*, 2001].

of both continental and alpine glaciers provides a ready source of sediments, and the associated rise in ocean and base levels leads to extensive Holocene floodplain deposits. We propose that chemical weathering of those same materials set in process the chain of events leading to As contamination of groundwaters in Holocene alluvial and glacial deposits. Further, it is the low hydraulic gradients in these low-relief deposits that keep the As from being "flushed out" because of the slow groundwater movement.

4. Conclusions

[12] Although water-rock-bacteria interactions can explain a number of proximal examples of natural arsenic contamination of groundwaters, we pro-

pose a mechanism (the GBH-As model) and geochemical models to explain how arsenic can naturally contaminate groundwaters far from the ultimate As source. The model invokes geologic time and well documented geochemical and geomicrobiologic processes working in concert to cause long-distance of As transport. Active tectonic uplift and glaciation during Pleistocene enhanced mechanical weathering of bedrock with variable As content, setting the stage for Holocene chemical weathering which released As to surface waters. Sorption of As by Fe-oxyhydroxides in the slow-moving bed load of streams and rivers concentrated arsenic in these bottom sediments. Flooding or changes in river channels led to the deposition of these stream sediments along with transported organic matter. Subsequently, anaerobic conditions developed in groundwater hosted by these deposits and iron-reducing bacteria caused the reductive dissolution of As-bearing Fe(Mn)-oxyhyroxides, causing As release to these waters. This model can be used to predict other localities where As might naturally contaminate groundwaters.

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