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ABSTRACT

Arsenic (As) and fluoride (F^-) are known geogenic contaminants of groundwater and are reported to be hazardous for human health. The most widespread mode of poisoning by the two contaminants is through oral consumption of groundwater. Although a number of works have been completed in the field of As and F^- hydrogeochemistry, yet the study of co-contamination perspectives has remained a largely unexplored area. Arsenic and F^- have been detected in the groundwaters of many parts of the globe including India. Presence of As and F^- has also been reported from the state of Assam, India. However, proper study of their hydrogeochemistry and co-contamination behaviour is lacking. Therefore, this study was conducted to understand the co-contamination behaviour of As and F^- in the Brahmaputra flood plains (BFP) of Assam. The study investigates the extent and distribution of the two contaminants in the BFP, and further explores the factors influencing the possible pathways for co-contamination. For this purpose, in order to achieve proper results, comprehensive sampling was conducted for four years (2011-2014) in different seasons along the entire stretch of the BFP. In addition to this extensive study was carried out in the groundwater of the Jorhat district to understand and observe local trends which we could have missed in the larger BFP.

Natural weathering processes were found to have more control on the hydrogeochemistry of the region than anthropogenic activities. The water type in the BFP was found to be mainly of HCO_3^- type with mixed cations Na^+, K^+, Ca^{2+} and Mg^{2+}. The detection of different oxidation reduction potentials (ORPs) showed the presence of both oxidising and reducing aquifers, suggesting the presence of multiple aquifer systems in the BFP. Anthropogenic activities like groundwater abstraction seem to induce or create oxidising conditions in the aquifers; on the other hand reducing aquifers are likely to be influenced more by irrigation return flow and geogenic processes. Over all reducing conditions were found to be more prevalent, therefore reductive hydrolysis of Fe (hydr)oxides appeared to be the dominant process of As release in BFP. This finding was further supported by the strong correlation observed between As and Fe in the region. Depth seems to govern/influence As hydrogeochemistry but not F^- contamination as such.

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Principal components analysis (PCA) and hierarchical cluster analysis (HCA) reveal that Fe (hydr)oxides may be one of the sources of F^- and SO_4^{2-} as evident from the their formation close group alignments. This could be due to the fact that such oxides and hydroxides acts as adsorptive sites for anions like F^- and SO_4^{2-}. Presence of As bearing minerals like arsenopyrite (FeAsS) and walpurgite [$(BiO)_4UO_2(AsO_4)_2$-H_2O] in the soils and sediments indicated that the original source of As could be the above mentioned minerals as suggested by the mineralogical studies. The distribution of As and F^- suggested that occurrence of groundwater As was positively affected by river proximity (high As close to the river), while F^- distribution was negatively affected by proximity to the river. The extremely low values of F^- in the groundwater samples along the BFP suggested that the fluvial setting with high sedimentation and recharge rates is not suitable for F^- release, and F^- would be found rather at greater distance from the river. Arsenic occurrence was found to be discontinuous i.e. it occurred in patches or hotspots close to the river. Fluoride on the other hand seemed to occur in isolated localities with less recharge and more rock-water interaction. Alkalinity and pH were also found to affect mobilization of As and F^- throughout the year.

A detailed study of the Jorhat district with intensive groundwater sampling in the monsoon (June 2013, n = 26) and post-monsoon seasons (January 2014, n = 31) reveals that As mobilization is affected more by anthropogenic activities which is evident from the weak correlation of As and Fe and the high correlation of As and PO_4^{3-}. Further a high seasonal variation of As suggests that As mobilization in the Jorhat district depended to a great extent on groundwater recharge. Positive relation between As and SO_4^{2-} suggests the presence of sulphide oxidation in the Jorhat district. Lowering of water table in aquifers during the pre-monsoon season could lead to release of As from pyrite oxidation due to intrusion of oxygen into the aquifer system. This condition is opposite to the overall trend observed in the BFP i.e. release of As by reductive hydrolysis of Fe (hydr)oxides. Speciation studies by Visual MINTEQA2 v 3.1 suggests that the groundwater is under-saturated with mineral phases bearing As and F^-, therefore the level of As and F^- contamination is likely to increase in the future.

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As no good correlation was observed between As and F^- in the natural conditions, therefore an effort was made to understand the synergistic or the antagonistic dynamics of co-contamination at laboratory scale using sequential extraction procedure (SEP) and batched desorption experiment performed on soil/sediment. Arsenic fractionation was performed on 5 grab soil/sediment samples collected from the BFP to understand As phase distribution. Out of the 5 grab samples, 2 were river sediment samples while the rest were soil samples. The SEP selected for As fractionation extracted 5 “operationally defined” fractions of As. Fraction I and II are regarded as labile phases and are found to be removed or leached through anion exchange with sulphates and phosphates. Fraction III and IV are found to be associated amorphous and crystalline oxides and hydroxides of Fe respectively and together can be called the Fe (hydr)oxides associated As phase. The last or fraction V is regarded as the residual As and is found to be associated with sulphide phases like orpiment (As_2S_3). The total As extracted from the soil/sediment samples was found to show high positive correlation with the clay and organic matter content. Results of the SEP reveal that out of all the As fractions extracted, fraction II and the Fe (hydr)oxide associated fraction (III+IV) has the highest dependence on clay and organic matter content of the soil/sediments. This shows that breaking, modification and alteration of the functional groups of organic matter could facilitate the release of As from Fe (hydr)oxides. This process is likely to be a microbially mediated step which consumes O_2 leading to reducing conditions in the groundwater. The previous observations regarding the prevalence of reductive hydrolysis of Fe in the BFP along with the findings of the SEP were used to design the batch desorption experiment for studying the co-evolution of As and F^- from the soil/sediments.

Batch desorption experiment was designed to observe the leaching of As and F^- from the soil/sediment samples after spiking with a solution of known As and F^- concentration at acidic (pH 5) and alkaline conditions (pH 10). The experiment was conducted at two different conditions, one set of experiment was performed on raw soil/sediment samples, while the other set was conducted after removing the Fe (hydr)oxides from the soil and sediments. The Fe (hydr)oxide fraction was removed from the soil/sediment samples by using a CBD solution (Na-citrate + Na-bicarbonate + Na-dithionite). Leaching of As and F^- was observed in both sets of soil/sediment

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samples at acidic and alkaline conditions to observe the role of pH in the desorption mechanism. It was observed that raw soils desorbed much greater amounts of As and F^- than CBD treated soils. The possible reason could be the involvement of Fe (hydr)oxides. Iron (hydr)oxides coatings on soil and sediment particles are found to have a net positive charge, therefore this phase acts as a very good substrate for adsorption of F^- and As oxyanions. Removal of Fe (hydr)oxides effectively robs the CBD soil/sediment samples of their ability to complex and adsorb negatively charged species. Since the CBD soil/sediments adsorbed negligible amounts of As and F^- during the spiking process therefore the amount leached was also very minimal. Over all higher amounts of As and F^- were found to be released at alkaline conditions. Elevation in pH has been found to increase negative charge density on Fe (hydr)oxides surfaces ultimately leading to the achievement of the point of zero charge (PZC) when net surface charge becomes effectively zero. Under such conditions initially adsorbed negatively charged species are desorbed, since the PZC for Fe (hydr)oxides has been found to be between 8.5 and 9.3, therefore at pH 10 maximum desorption of As and F^- is observed.

The process of co-contamination can be further studied by the application of techniques like column leaching, multilayer sampling, isotope tracing and Fourier Transform Infrared (FTIR) spectroscopy. Surface water from the river Brahmaputra and it’s numerous tributaries could be harnessed as a source of drinking water after proper treatment to avoid the risks of As and F^- contamination.