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Analysis of Organic Matter, Iron and Manganese in Soil of Arsenic Affected Singair Area, Bangladesh

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Abstract: This study evaluated the mutual relationship among arsenic, iron, manganese, total nitrogen and total organic carbon in the soil of arsenic affected area, Singair, Bangladesh and the results were compared with the other arsenic contaminated area in Bangladesh. The present investigation revealed that high concentration of iron (9138-22071 mg kg⁻¹) and manganese (22-80 mg kg⁻¹) were accompanied by the high concentration of arsenic (44-60 mg kg⁻¹) in arsenic polluted Singair area. In addition, the study showed that the soil of Singair (15-20 m) contained very high concentrations of total organic carbon ranged from 23100-42900 mg kg⁻¹ and the content of total nitrogen was also very significant in some soil samples, where the concentration of arsenic was high. Therefore, the research study can conclude that presence of total organic carbon, total nitrogen, iron and manganese has significant relationship with arsenic contamination in the soil of Bangladesh. However, the study found no significant relationship with arsenic and carbon nitrogen ratio in the soil of Singair.

Key words: Arsenic pollution, total organic materials, soil and sediment, groundwater

INTRODUCTION

The biogeochemical cycle of naturally-occurring arsenic in the terrestrial as well as aquatic environment has been extensively studied in recent years due to increased awareness of arsenic contamination and toxicity (Nickson *et al.*, 1998; Islam *et al.*, 2004). In Bengal Basin, some 25% of well that top ground waters from alluvial aquifers contain high (>0.005 mg L⁻¹) concentrations of arsenic, the consumption of which threatens the health of millions of people (Lubin *et al.*, 2007; Rahman *et al.*, 2005; Chakraborti *et al.*, 2002; Jain and Ali, 2000). It is now suspected that more than 100 million people worldwide ingest excessive amounts of arsenic through drinking water contaminated from natural geogenic sources (Lenny *et al.*, 2008).

Geochemical weathering of subsurface soil by natural process has caused an unacceptable level of dissolved arsenic in groundwater in many regions of the Indian subcontinent (Sudip *et al.*, 2008). Arsenic mobility and transport in the environment are strongly influenced by the association of arsenic with solid phases in soil and sediments (Keon *et al.*, 2001). Under aerobic conditions, arsenic occurs in soils in the form of arsenate (AsO₄⁻³), bound to clay minerals, Fe and Mn-(oxyhydr) oxides and to organic substances. Under natural conditions, the highest concentration of arsenic are found in groundwater as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favorable for arsenic mobilization and accumulation. Another study revealed that arsenic cycling in soil, sediment and natural water systems is driven by several possible microbial transformations, including both reduction and oxidation (Oremland and Stolz, 2003; Silver and Phung, 2005).

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The basic question of the origin of the organic matter that drives Bengal Basin aquifers toward reducing conditions conducive to arsenic mobilization remains unresolved (Van Green *et al.*, 2008). The relationships are not enough clear among arsenic and redox-active substances when environmental conditions are less oxidized and microorganisms participate in the oxidation and reduction of inorganic species such as arsenic, nitrogen, iron and manganese. For this reason, the knowledge of the sedimentary architecture and distribution of iron, manganese, arsenic and organic matter in Ganges alluvial sediments is necessary to develop a model to guide future aquifer development in a way that minimizes arsenic pollution.

The present research investigated the relationship of the total organic carbon, iron, manganese and total nitrogen with arsenic that allow arsenic to mobilize through soil, sediment and ground water.

MATERIALS AND METHODS

Sample Collection

The widespread arsenic occurrence in the active deltaic region of Bangladesh, Singair, sub-district area, which is located just east of the confluence of the Ganges-Brahmaputra River system, was chosen as the focus of study. The area of Singair, Manikgonj is about 209.6 km². The study area is densely populated and about 965 people live per square kilometer. The soil samples were collected through 15th to 18th January, 2004 from the depth of 15-20 m in the nine places of Singair sub-district, where, the groundwater is severely contaminated by arsenic. During sample collection, relevant biogeochemical histories of the samples were recorded.

Determination of Arsenic, Iron and Manganese

For arsenic detection, the silver diethyldithiocarbamate (SDDC) colorimetric method was employed (Greenberg *et al.*, 1998) that based on the evolution of arsine gas in which inorganic arsenic is reduced to arsine, AsH₃, by zinc in acid milieu, the arsine is bubbled through a solution of silver diethyldithiocarbamate, AgS.CS.N(C₂H₅)₂, in pyridine or chloroform; a red soluble complex is formed that can be measured photometrically at a specific wavelength of 535 nm.

Iron determination is carried out by hydroxylamine and with 1, 10 phenanthroline at pH 3.2 to 3.3. At the pH between 2.9 and 3.5, rapid color development was formed in the presence of an excess phenanthroline and the reddish-orange iron (II) complex absorbs at 515 nm (Greenberg *et al.*, 1998). Quantitative estimation of manganese in the digested samples was carried out using Ion Analyzer (C100 Series Multiparameter Bench Spectrophotometers) following permanganate oxidation method (Charlot, 1964). For each determination, same experiment was also done for standard solutions and blank tests were also done by using blank digest. With these values, each calibration curve was constructed against known concentrations. The concentrations of Fe and Mn were found from the graphs by putting the absorbance of these samples.

Determination of TOC and Total Nitrogen

The Walkley and Black (1934) method was used to determine the organic carbon content. In this procedure, organic carbon was determined using sulphuric acid and aqueous potassium dichromate (K₂Cr₂O₇) mixture. After complete oxidation from the heat of solution and external heating, the unused or residual K₂Cr₂O₇ (in oxidation) was titrated against ferrous ammonium sulphate. The used K₂Cr₂O₇, (the difference between added and residual K₂Cr₂O₇), gave a measure of organic carbon content of the soil. Determination of total Nitrogen (N₂) was performed by Kjeldahl's method.

RESULTS AND DISCUSSION

It is observed that the soil samples such as S-pond, S-3, S-4 and S-9 contained highest amount of arsenic, where, significant proportion of iron and manganese was also present (Table 1). In addition,

Table 1: Comparative amount of As, Fe, Mn, Total Organic Carbon and Total N in all soil samples

Sample ID	Total				Total organic carbon (%)	Total N (%)	C/N ratio
	As	Fe	Mn	C			
S-Pond	60	21180	75	42900	4.29	0.230	18.65
S-01	52	16877	48	28200	2.82	0.107	26.36
S-02	45	13320	35	26500	2.65	0.094	28.19
S-03	54.5	19422	61	23100	2.31	0.088	26.25
S-04	55	22071	70	27300	2.73	0.150	18.20
S-05	44	13731	45	24600	2.46	0.099	24.85
S-06	54	18510	56	29500	2.95	0.113	26.11
S-07	49	14514	50	30900	3.09	0.137	22.55
S-08	40	9138	22	23800	2.38	0.103	23.11
S-09	55	19437	80	33000	3.30	0.119	27.73

the most striking feature is that remarkable amount of arsenic was present where the concentration of total organic carbon (soil samples S-pond, 1, 4, 6 and 9) was high. Similarly, soil samples that contained low amount of arsenic, the content of total organic carbon was also low there.

The present finding also revealed that the average arsenic content in the investigated area was 50.85 mg kg^{-1} . Background levels of arsenic in soils can be 4 to 8 mg kg^{-1} in the areas irrigated with arsenic contaminated water and the soil level can reach up to 83 mg kg^{-1} (Chen *et al.*, 1995). Another study reported that the arsenic content in non-calcareous soils (AEZ 9) ranged from 4.85 to 12.20 mg kg^{-1} and that of non-calcareous soils (AEZ 11) ranged from 11.60 to 24.40 mg kg^{-1} (Jahiruddin *et al.*, 2000). Recently, the arsenic content of soil has found about 32 mg kg^{-1} from most highly affected area like Manikgonj district and Paba thana of Satkhira district.

So, it is the distribution of organic matter, particularly peat deposits, in the aquifer sediments that primarily control the arsenic pollution mechanism. Peat beds are common beneath the old Meghna Estuarine Floodplains and in Gopalganj-Khulna Peat Basins. Many wells in the area around Faridpur may be screened in waterlogged peat (Safiullah, 1998) and the aquifer in Laxmipur (stands on the confluence of Megna River) also contains peat (DPHE, 1999).

Arsenic in Bangladesh sediments will not be released from FeOOH unless organic matter is present to drive microbial reduction. The high amount of organic materials may drive microbial reduction. Bacteria microbes steal oxygen from the iron oxide coatings on the grains in order to process nutrients. This mechanism was proposed from a number of observations (Nickson *et al.*, 2000; Ravenscroft *et al.*, 2001). This reduction is driven by microbial metabolism of organic matter (Chapelle, 2000), especially by carbon. Another research by Bhattacharaya *et al.* (1997) has considered this mechanism to be more likely arsenic source than that of pyrite oxidation and the process has been documented to occur in groundwater. This action results in the release of iron and arsenic elements into the ground water.

In the present investigation, it is found that the concentration of arsenic correlates with the concentration of iron and manganese, which is similar to the results obtained in Faridpur (Safiullah, 1998). Generally, there is a good correlation observed between extractable iron, manganese and arsenic in soils around arsenic-enriched Singair areas which is also supported by the research on trace element and retention capacity of clays and metal oxides, particularly those of Fe, Al and Mn (Fox and Doner, 2002; Smedley and Kinniburgh, 2002). Overall, the conducting research study revealed that arsenic contamination in groundwater of Singair, Bangladesh has significant relationship with organic carbon, iron and manganese but there is no substantial correlation with carbon nitrogen ratio.

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