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Arsenic in groundwater and redox conditions in the Bengal delta – possible in situ remediation

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Abstract

Widespread arsenic contamination in groundwater in the Bengal Delta seems to be largely natural depending on reducing conditions in the aquifers. Reduction of ferric hydroxides with adsorbed arsenic species occurs at intermediate depth. In situ remediation might be achieved by artificial recharge stabilising the ferric hydroxides. It might however be problematic to keep the aquifer oxic. Sulphate levels are generally low and sulphur deficiency for crops common. The low sulphate levels favour methane fermentation over sulphate reduction. Application of gypsum to the surface soils might favour immobilisation of the arsenic in the form of sulphides.

INTRODUCTION

Widespread arsenic contamination of the groundwater in the Bengal delta has been detected threatening about 100 M people. Around 30 % of a large number of wells have been found to have arsenic contents in excess of the Indian and Bangladeshi health limit of 50 mg/L (DPHE/BGS, 2000; Salamatullah, 2000). The mobilisation of arsenic in the groundwater in the Bengal delta has been explained by two hypotheses, the oxidation of arsenopyrite on one hand (Das et al., 1994) and the reduction of ferric hydroxides serving adsorbants for anionic arsenic species (Bhattacharya et al., 1997; Nickson et al., 2000). These two hypothesis infer very different conditions in the soil zone. Thus it is warranted to look at the redox conditions in the soil zone.

During the recent decades the groundwater extraction increased manifold due to intensified cultivation, mostly of paddy rice. The draught of groundwater has generally not resulted in declining groundwater levels (Chadha and Sinha Ray, 1999) but might have increased the oscillation of the groundwater level. This in turn has been considered to cause a pumping of oxygen into the subsoil (Das et al., 1994).

SOIL REDOX CONDITIONS

The cultivation of wetland rice implies a cover of standing water on the fields during most of the growth period. If two crops per year are taken, water will be standing on the fields for about 200-300 days depending on the cultivar used (Tran Kim Tinh, 2000). As diffusion of gas, including oxygen, is very slow in water this implies a lid on the terrain what concerns the possibility for oxygen to enter into the subsoil. This is also manifested in the physiology of rice plants which are supplied with aerenchyma which allows the plant to make the immediate surrounding of the root oxic. However, the oxic zone, Radial Oxygen Loss zone (ROL), extends just to a maximum of a couple of centimetres from the root tips and becomes vary thin along a mature root (Armstrong, 1979; Colmer et al, 1998) (Fig. 1). In the Bengal delta the ferric/ferrous redox-couple is the one which is active in the ROL zone while profiles in rice fields show gley phenomena along the root channels.

The oxic zone causes problems in acid sulphate soils in that pyrite oxidises (van Breemen and Pons, 1978). In the inner part of the Mekong delta pyrite occurs up into the top soil (Tran Kim Tinh, 2000). This is due to frequent flooding because of tides entering up the Mekong river delta. The outer portion of the Mekong delta is slightly higher elevated due to increased erosion and sediment transport during the last 3-4000 years when the catchment of the river has become inhabited and subject to slash and burn cultivation. The Bengal delta has, except for the coastal portion, low sulphate concentrations and hence little sulphide formation. The sulphate content in a set of groundwater samples from Nadia district in West Bengal (von Brömssen, 1999; Hermansson, 1999) is depicted in Fig. 2.

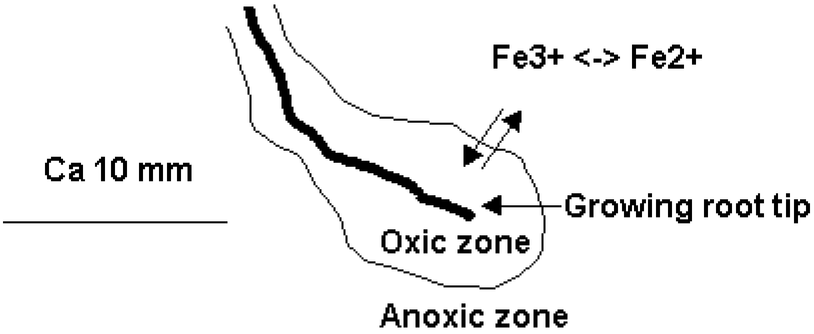

Figure 1. Radial oxygen loss around a growing root tip of rice. Modified after Tran Kim Tinh (2000).

Considerable amounts of nitrogen is applied in agriculture in West Bengal, in the order of 60 kg/ha/crop. In addition there is a substantial nitrogen fixation by blue green algae in rice fields, of almost the same order (Khan et al, 1994). While similar nitrogen inputs in well drained soils in semi-arid regions results in a noticeable leaching of nitrate very little nitrate has been detected in soil water and groundwater in the Bengal delta. A maximum of a couple of mg/L has been observed (von Brömssen, 1999; Hermansson, 1999). With a recharge rate of about 1000 mm/year this means a leaching of about 5 kg/ha/year. With a yield of about 2000 kg/ha the nitrogen removal by the rice crop is about 25 kg N/ha/crop. Thus there must be sizeable of at least more than 50 kg/ha/crop in losses by some other pathway which most likely is through denitrification. This is verified by Abao et al. (1996) who has found that the fallow season is characterised by denitrification manifested as nitrous oxide emission. The growth season in paddy rice is characterised by methane emission (Singh et al, 1998). Methane emission is recorded in several instances in connection with well-drilling in the Bengal delta (Ahmed et al. 1998). Rice cultivation produces 3-4000 kg/of straw per crop and in addition to that around 1000 kg/ha of root bio-mass or 400 kg/ha C (Diaz et al, 1994). Especially the root bio-mass is a very good substrate for methane fermentation (Yoshiba et al, 1996). The production of methane may as much as 45 g/m^2 per crop (Yagi, 1997). The latter figure is equivalent to about 300 kg/ha C. Thus a large fraction of the root bio-mass seems to be converted to methane.

While ferric reduction is observed in the soil zone it obviously becomes more abundant towards depth as is reflected by increasing concentrations of ferrous iron in groundwater at intermediate depths down to 50-60 m in the observations from Nadia (Fig. 2).

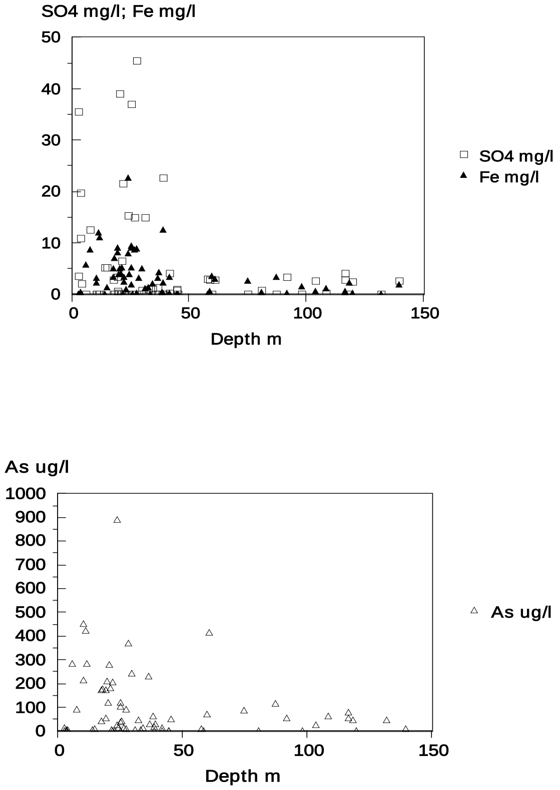

Figure 2. Depth-wise distribution of sulphate, iron and total arsenic in groundwater in Nadia district in West Bengal, India.

As mentioned above, the sulphate levels are low in the Bengal delta. This has manifested itself as sulphur deficiency in crops (Bhuiyan and Islam, 1986; Haque, 1994). Sulphate isotope ratios in the order of + 7-8 $^{o}/oo$ show an enrichment compared to surface water.

This could reflect discrimination by sulphate reduction. However, there seems still to be a shortage of sulphate as electron acceptor. Sulphate reduction and methane emission occurs at much the same redox level and as CO_2 is abundant methane fermentation may be advantaged. Smell of hydrogen sulphide is seldom observed.

In addition to rice fields there are of course other environments like better drained portions where habitations are placed. Even here there is a heavy load of organic matter from human activities but certainly more oxidising conditions. Such areas in general occupy a minor fraction of the landscape. Another possible pathway for oxygen into the aquifers could be through wells. However, most wells are lined tubewells giving little chance for the gas diffusion into the groundwater zone. Wherever they are screened they provide a water-flow into to wells. Summarising it seems unlikely that any oxygen should be able to diffuse into the subsoil. Thus as is found by several researchers the ferric reduction hypothesis seems to be the likely one.

The depthwise distribution of species shown in Fig. 2 have been recorded elsewhere e. g. by Nickson et al, (1998) and by Chadha and Sinha Roy (1999). The diagram infers a redox sequence as the one shown in Fig. 3. Naturally there are considerable spatial variations even in a small scale which is shown by the scatter of the points especially at depth between 10-60 m depth**.**

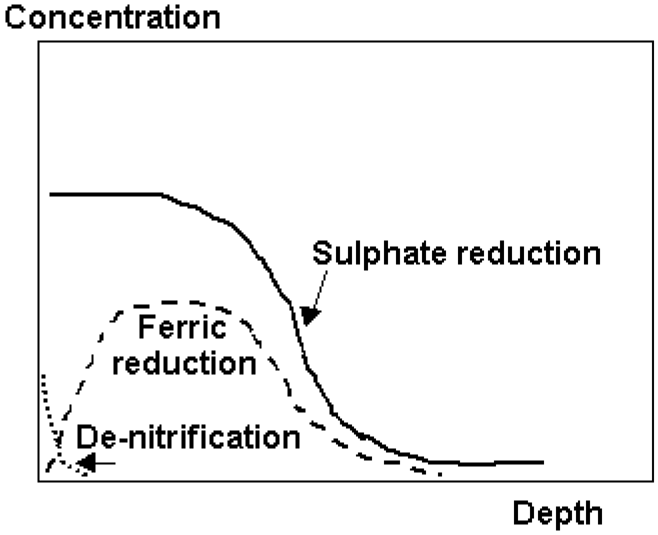

Figure 3. Redox sequence in the Bengal Delta aquifers inferred from data in Fig. 2.

POSSIBLE IN SITU REMEDIATIONS

Redox conditions vary largely in space and time. However based on the above discussion a simplified scheme may be implied (Fig. 2). As arsenic follows iron there seems to be essentially two alternatives in immobilising the arsenic in situ. Either pushing down the redox cline between oxic and anoxic conditions or lifting up the strongly reducing conditions at depth. The former may be achieved by artificial infiltration or reinfiltration by aerated groundwater. The latter process is often used in the Nordic countries to remove iron (Frycklund and Jacks, 1997). This can be fairly easily done into open aquifers by recharge ponds. One problem encountered is that oxygen solubility is fairly small at the high ambient temperature, around 6 mg/L only. This may consumed if some organic matter from algal growth on the pond accumulates at the bottom of the pond. Some other oxidant could be added e. g. nitrate. Nitrate can act as a electron acceptor inhibiting the redox to drop to the ferric/ferrous stage.

If the aquifer is more or less confined recharge wells has to be used. This requires usually very a very good water quality. However, an indigenous Indian design used for recharge of flood water in Kacchh in Gujarat seems to sustain even muddy water (Raju and Ferruokhi, 1996). It has by now functioned for 8 years placed in dams in nallahs (seasonal rivers). In this case the risk for depletion of oxygen may be minimised by using small dams around the recharge well. More elaborate recharge arrangements are available like VYREDOX (Seppanen, 1992). This implies much higher investments.

The other option, lifting the strongly reduced zone, may be achieved by addition of gypsum to the soil. In addition to that it hopefully should immobilise the arsenic in sulphides it will alleviate the sulphur deficiency in rice (Bhuiyan and Islam, 1986) and it will decrease methane emission. The sulphate reduction and methane fermentation occurs at much the same redox level and the addition of sulphate will enable the sulphate reducers to compete more successfully for the organic substrate with the methane fermenting bacteria (Andales et al, 1993).

This short review of redox conditions of the rice field environment does not give support to the possibility of oxygen entry into the subsoil. All evidence indicate that the oxygen is consumed in the very soil zone and that anoxic conditions prevail already in the root zone.

CONCLUSIONS

A literature review and field observations of the soil zone of redox indicators such as gley phenomena and soil water chemistry supports the reduction hypothesis what concerns the arsenic mobilisation. There seems to be little likelihood that oxygen can pass down to the groundwater zone causing pyrite oxidation.

In situ remediation might be achieved by artificial infiltration, lifting the redox level above the presently dominating the ferric/ferrous or by lifting the strongly reduced redox conditions at depth by promoting sulphate reduction.

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