Another Geological Disaster besides Earthquakes in Nepal: The Challenge of Eliminating Arsenic from Contaminated Groundwater in the Lowlands of the Country

Barbara Mueller

ABSTRACT

The lowlands of Nepal are severely affected by the arsenic (As) crisis causing serious health issues to the inhabitants using As contaminated groundwater as drinking water. The problem in Nepal has been more or less disregarded – whereas in other countries (e.g., Bangladesh) the problem had been recognized much earlier. There is clear evidence that the As concentration in groundwater is hardly dependent of climatic seasons whereas the concentration of Fe in groundwater is widely variable in pre- and post-monsoon. A substantial portion of this element is retained by clay minerals. During pre-monsoon clayey sediments are chemically weathered losing Na and K thus remaining relatively enriched in immobile compound like Fe and Al but as long as reduced conditions persist, As remains mobile. This article includes a brief overview on the overall situation concerning the issue of arsenic in groundwater as well as a discussion of the weak correlation or decoupling of aqueous As and Fe in the groundwater and the original reservoir of arsenic being incorporated in clay minerals and mitigation options. The study also sheds light on some socio-economic impacts of such changes on the livelihood of marginal communities residing downstream the affected areas.

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Keywords: Arsenic, Iron, Groundwater, Health Hazards

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1Bamugeobiochem, Horbenstrasse 4, 8356 Ettenhausen, Switzerland. Email: barbara.mueller@erdw.ethz.ch
1. Introduction

The disastrous earthquake dated 25th of April 2015 almost completely overlapped another human tragedy in the lowlands of Nepal: groundwater used as drinking or irrigation water severely contaminated with the extremely toxic chemical element arsenic (As). The naturally derived arsenic can reach limits that are perilous to human health if geological and geochemical conditions favor its release. The World Health Organization (WHO, 2001) has imposed a drinking water guideline with a value of 10 μg/L for arsenic. If this value is exceeded, health issues are likely to arise. Excess uptake of arsenic causes a range of detrimental health effects like characteristic skin lesions including pigmentation changes, mainly on the upper chest, arms and legs, and keratoses of the palms of the hands and soles of the feet and as the most severe effect, cancer (Smith et al., 2000; Shrestha et al., 2003; Maharjan et al., 2006; Adhikari & Ghimire, 2009; Pokhrel et. al., 2009; Yadav et al., 2011; Fillman et al., 2016). Dissanayake et al. (2010) have reported about a rate of 6.4% of arsenicosis for the population for 15 years and above, nearly the same rate as that found in Bangladesh. Further observations indicated that males had prevalence twice as high as females. According to a recent report by Nakamura (2016) based on surveys in the years 2012 and 2014 in the Nawalparasi district in the central Nepal, inhabitants hardly ever worry about the quality of the groundwater or do not understand the problems relating to high concentrations of arsenic. Although public campaigns on arsenic related hazards were organized, locals did not understand the advice given. The lack of medical facilities prevents the inhabitants of the Terai from clinical examinations, too. And lastly, most persons concerned do not show any interest for harvesting rainwater to be used as drinking water. The author of this article experienced this negligence during fieldwork in Nawalparasi district in October of 2015 and April of 2017. Moreover, the installed biosand filters are not handled or maintained correctly due to lack of proper and repeated instructions.

A geogenic source of Arsenic (As) is obvious and its elevated concentrations in natural groundwater is considered to be due to natural weathering of the Himalayan belt (Acharyya et al., 2000; Gurung et al., 2005; Guillot & Charlet, 2007; Guillot et al., 2015; Mueller, 2017). The sediments carried by the Ganga–Brahmaputra river system build up the Himalayan foreland basin and the Bengal fan – one of the largest modern fluvial deltas of the world (France-Lanord et al., 1993; Garzanti et al., 2004).

Arsenic is not found in high concentrations in the Earth’s continental crust - it is less abundant than several of the “rare-earth” elements. Beside its high content in the ubiquitous iron-sulphide pyrite, As is mainly concentrated in hydrous iron oxides and clay minerals. Arsenic can be easily dissolved from sediments into groundwater depending on pH, redox conditions, temperature, and solution composition. A limited type of source materials are now recognized as significant contributors to arsenic in water supplies: organic-rich or black shales, Holocene alluvial sediments with slow flushing rates, mineralized and mined areas (most often gold deposits), volcanogenic sources, and thermal springs. Natural arsenic in groundwater at concentrations above the drinking water guideline of 10 μg/L is not uncommon. Other specific geological settings can lead to be high arsenic concentrations: (i) closed basins in arid-to-semi-arid climates (especially in volcanogenic provinces) and (ii) strongly reducing aquifers, often composed of alluvial sediments but with low sulphate concentrations. Recent sediments in low-lying regions of low hydraulic gradient are characteristic of many arsenic-rich aquifers. Ordinary sediments containing 1 to 20 mg/kg (near crustal abundance) of arsenic can give rise to high dissolved arsenic (> 50 μg/L) if initiated by one or both of two possible “triggers” - an increase in pH above 8.5 or the onset of reductive iron dissolution. Other important factors promoting arsenic solubility are high
concentrations of phosphate, bicarbonate, silicate, and/or organic matter in the groundwater. These solutes can decrease or prevent the adsorption of arsenate and arsenite ions onto fine-grained clays and especially iron oxides. Arsenite tends to adsorb less strongly than arsenate often causing arsenite to be present at higher concentrations (Nordstrom, 2002; Smedley & Kinniburgh, 2002).

But the gravity of the arsenic contamination problem in the Bengal delta and Nepal was only recognized in 1998. The first report of arsenic contamination in groundwater above toxic levels in Nepal was made from the Terai Basin (Sharma, 1999). Twenty-four percent of samples analyzed (n = 18,635) from the Terai Basin exceeded the WHO limit of 10 μg/L (Shrestha & Shrestha, 2004). Since the first overall survey conducted by WHO (2001), only sporadic information on the situation has been published. Available documents later indicated that the region of As contamination extends even into the Terai region and that 24 districts in Nepal, including all 20 Terai districts and four hill districts, exhibiting arsenic contamination (Bhattacharya et al., 2003; Neku & Tandukar, 2003; Shrestha et al., 2003; FAO, 2004; Tandukar et al., 2005; Panthi et al., 2006; Maharjan et al., 2006; Pokhrel et al., 2009; Emerman et al., 2010; Thakur et al., 2011). Over 90% of the Terai population rely on groundwater from tube wells for drinking, household use, and irrigation (Guillot et al., 2015). The Terai itself is home to about 50% of the total Nepalese population; it contains over half of the total arable land although it constitutes less than 20% of Nepal’s surface.

In the following districts of the Terai the groundwater is most severely contaminated with arsenic: Nawalparasi, Bara, Parsa, Rautahat, Rupandehi, and Kapalivastu (Shrestha et al., 2014). Report prepared by Maharjan et al. (2005) indicated that 29% of more than 20,000 tube wells had arsenic concentrations exceeding the World Health Organization (WHO) guideline (10 μg/L), that the prevalence of arsenicosis varied between 1.3% and 5.1% [average of 2.6%; see Nepal Red Cross Society/Environment & Public Health Organization (NRCS–ENPHO), 2002; Yadav et. al., 2011] among four independent surveys, and that approximately 0.5 million people in Terai were at risk of consuming water with an arsenic concentration greater than 50 μg/L, the maximum permissible limit for Nepal (Shrestha et al., 2003). In a study by Dahal et al. (2008) the influence of arsenic-contaminated irrigation water on alkaline soils and arsenic uptake in agricultural plants at field level was monitored. The arsenic concentrations in irrigation water ranged from less than 0.005 mg/L to 1.014 mg/L and the arsenic concentrations in the soils fluctuated between 6.1 mg/kg to 16.7 mg/kg. The arsenic content in various parts of plants are found in the order of roots > shoots > leaves > edible parts.

All these reports led the decision makers of the government as well as non-governmental agencies involved in controlling water supply to initiate monitoring and mitigation measurements. As a consequence, in 2003 the National Arsenic Steering Committee (NASC) was constituted, involving major stakeholders from the drinking water and sanitation sector (Shrestha et al., 2003). The NASC worked in collaboration with the Environment Public Health Organization (ENPHO) to perform testing on 18,635 tube wells in 20 Terai districts, under a program called the “State of Arsenic in Nepal 2003”. All the data collected revealed that concentration of As varied both spatially and seasonally, suggesting the possibility of spatial variation due to conditions such as latitude, longitude and depth of the tube well. The temporal distribution of As showed seasonal dependence with lower concentration in winter and higher in summer (Yadav et al., 2012).

The objectives of this research is to evaluate the efficiency of the biosand filters, the modification of these filters as well as to understand the overall geological situation and its influence on future versions of these filters. The study also briefly sheds light on socio-
economic impact on everyday life of the people who are exposed to arsenic contaminated water.

The article is organized as follows: The following section discusses geological condition of Nepal’s Terai region. Section 3 provides an account of how arsenic is released to the groundwater in Terai region. Results are discussed in Section 4. Section 5 discusses socio-economic impact to the communities whereas Section 6 prescribes mitigation option of choice with alternative filters. Section 7 summarizes the study and prescribes policy actions.

2. Geological Situation of the Terai Region

Nepal is characterized by a diverse, rugged and undulating topography, geology and in general by a cold climate. The country is predominantly mountainous with flat low lands to the southern part having an approximately 6,000 rivers and rivulets. The topographic variations in Nepal are largely controlled by geology (BGS, 2001; Thakur et al., 2011). The geology of Nepal marks the transition where the Southern Gondwana land collided with the Northern Eurasian land lifting the sediments of the Tethys Sea to form the Himalayas. As a consequence, the southern and northern parts of Nepal differ widely in their geological formations and topography. The Archean crystalline formations deep beneath the Alluvium of the Terai as well as the marine sedimentary deposits forming the high Himalayas, and the Siwalik formation set up by the once east–west flowing rivers can be found within a very tight space (Yadav et al., 2015).

The outstanding mountain chain in the Himalayas including a central part, namely as the Nepal Himalaya, is formed by four major Himalayan tectonic units from north to south, respectively: (1) the Tethys Himalaya, delimited between the Indus-Suture Zone to the north and the South Tibetan Detachment System (STDS) to the south; (2) the Higher Himalayan Crystallines (HHC) confined between the Main Central Thrust (MCT) and the STDS; (3) the Lesser Himalaya (LH) divided into upper and lower Lesser Himalaya, is bordered between the MCT and the Main Boundary Thrust (MBT); and (4) the Siwaliks, delimited between the MBT and the Main Frontal Thrust (MFT) and the Quaternary foreland basin (Terai Plain). The mentioned units span a wide range of various rocks being metamorphic, sedimentary, and igneous in origin. This variety of rock types determine the differential erosion to account for some of the groundwater arsenic heterogeneity found in the foreland and delta (Gurung et al., 2005; Shah, 2008; van Geen et al., 2008; Guillot et al., 2015). The Terai Plain is an active foreland basin consisting of Quaternary sediments that include molasse units along with gravel, sand, silt, and clay. All major rivers of the Terai originate in the high Himalayas whereas minor rivers also emanate from the nearby Siwalik Hills. Fine sediments and organic material are deposited in inter-fan lowlands, in wetlands and swamps (Sharma, 1995). Major adsorption substrates and co-precipitation hosts for arsenic are prevailing throughout the finer-grained Siwalik facies, as iron mineralization, as sulphides, or as clays. In Nepal, the groundwater arsenic is of relatively local provenance, being derived directly from eroded Siwaliks (Stanger, 2005).

High monsoon precipitation (1,800-2,000 mm) and year-round snow-fed river systems recharge the Terai sediments, resulting in a high potential for groundwater resources. The aquifer system is highly sensitive to precipitation (Gurung et al., 2005).

The geology of the Terai region itself is on the whole comparable to the Bengal Delta Plain (BDP) and it is the continuation of Indo-Gangetic trough. The Terai Plain is covered by recent and older alluvium comprised in channel sand and gravel deposits and outwash deposits. The sediments were mainly deposited by braided rivers, which regularly changed their course. Consequently, clay, silt, sand, and gravel deposits of varying thicknesses occur
interlayered with each other. The Terai Plain has a multiple aquifer system (Yadav et al., 2011).

So far the most intensive studied Terai province or district of Nepal concerning local geology and arsenic contaminated groundwater is Nawalparasi. The lithology of the local sedimentary basin belongs to the Holocene alluvium that includes the present day alluvial deposits, channel sand and gravel deposits and outwash deposits (Yadav et al., 2014). The district has three distinct hydrogeological zones from north to south, respectively: (1) the Siwalik Hills, (2) the Bhabar recharge zone, and (3) the Terai Plain including unconsolidated Holocene floodplain sediments. The Narayani/Gandaki River (the major river) descends from the Higher Himalaya, flows along the eastern boundary of the Nawalparasi district and has made a major influence on the underlying unconsolidated Holocene fluvial deposits that includes the floodplain aquifer system. In the areas with fine-grained sediments, elevated concentrations of As are typically recorded (Brikowski et al., 2004, 2014; Diwakar et al., 2015). Guillot et al. (2015) describe in detail the lithology of sledge core samples from five drill holes showing various coarse (millimetric) to fine-grained (micrometric) sediments in the Narayani basin. Light-grey to dark grey sands; grey, greenish-grey to brown-grey and yellow–brown silts; and light-grey to black-grey, yellow–brown and black clay with occasional gravel layers could be distinguished. Macroscopic observations indicated that on average, the drilled sediments are composed of 33 % of silts; 30 % of grey to black clays, 27 % of brown clay, 9 % of fine-grained silt and sand and less than 1 % of calcrete. The detrital minerals in the silt fraction are dominated by quartz, biotite, muscovite, K-feldspar, calcite and dolomite as major phases and garnet, zircon, and monazite as heavy minerals. In the region of provenance of the Narayani basin, the Tethys Himalaya includes 10 km of various metasedimentary rocks (marbles, calc-schists, shales, quartzites) ranging from Cambrian to Jurassic as well as the Miocene Manaslu leucogranite emplaced within the Tethyan rocks of Nepal. The sediments evidently represent homogeneous mixtures of parent rocks of felsic origin.

3. Arsenic in Groundwater and Mechanisms of its Release to Groundwater in Terai

The worst affected districts by the arsenic crisis in Nepal include Nawalparasi (Western Region), Rautahat and Bara (Central Region) and Bardia (Midwestern Region). As already mentioned, in the Terai districts, elevated arsenic is found exclusively in the foreland basin, south of the Main Frontal Thrust (MFT), on the undisturbed floodplain. The aquifer itself is characterized by Ca-HCO₃ type water and is widely multi-contaminated, with the WHO guideline values exceeded for As, Mn and F in 80%, 70% and 40% of the cases, respectively. The middle portion of the floodplain is heavily contaminated with As, predominantly as As (III).

Knowledge of the provenance of the aquifer sediments is crucial for tracing the source of arsenic. As already pointed out there are two possible sources for the Terai sediments, the Siwalik hill and the higher Himalayas. Rare Earth Elements (REE) and other charged cation elements like Th, Sc, Hf, and Zr are highly immobile in most geological processes, and thus can be used for provenance studies. The observed enrichment of incompatible elements is highly indicative of a felsic source. Sediments hosting As-contaminated aquifers are most probably homogeneous mixtures of different types of rocks, with a felsic initial source. The As content of the groundwater within the Bengal delta is geologically controlled and those high concentrations of As are exclusively restricted to the Holocene sediments rich in organic matter. Average arsenic yield of the Terai sediments is within the range of common sediments (9 ppm). Abundances are greater in finer sediments such as black clay (maximum 31 ppm) than in coarser sediments (silt and fine sand, 3 ppm). These sediments represent
Homogeneous mixtures of a wide range of parent rocks of felsic composition. Significant As leaching rates indicate that the Terai sediments have high potential for arsenic release, depending on pH and redox conditions (Gurung et al., 2005).

In Nawalparasi district clays contain particularly high amounts of iron, in the range of 21.9–59.9 g/kg (2-6% in sediments). Together with the high levels of iron, high concentrations of aluminum were also extracted from the sediments (2.75-34.1 g/kg). Iron and aluminum in the sediments were positively correlated with arsenic, with correlation coefficients of 0.607 and 0.444, respectively. Arsenic is mainly retained in finer particles like clay minerals and it is also comprised in several other types of phases including ion exchange phases, carbonate and sulphide phases, ferric or manganese oxide and hydroxide phases, and organic soil matter phases also depending on pH and redox potential (Eh) (Nakano et al., 2014). Yadav et al. (2015) describe that As concentration varied from 0.22 to 0.64 ppm (mean 0.36 ppm) in sediment samples.

High As-containing aquifers also exhibit higher percentages of calcium, silica, aluminum, and iron. Arsenic occurs ordinarily in oxyanionic forms in aqueous environment. Available hydro-geochemical data for groundwater of the TAP (Terai Alluvial Plain) aquifers suggest a predominantly reducing environment, with high HCO$_3^-$, low SO$_4^{2-}$, and NO$_3^-$ concentrations. Elevated HCO$_3^-$ levels result primarily due to the oxidation of organic matter whereas low SO$_4^{2-}$ levels are the result of minor sulphate reduction (Bhattacharya et al., 2003). Yadav et al. (2012) found three types of tube wells that are used as a source of drinking water in the Terai region that all vary by depth. These three include shallow tube wells (STW) (less than 50 m deep), deep tube wells (DTW) (greater than 50 m deep), and dug wells (DW) (up to 20 m or more). A majority of them (98%) were STWs. Within the depths of DWs various As concentrations are found. The depth of deep tube wells ranged from 1 m to 183 m. Virtually, all (97%) of the tested tube wells that had As levels exceeding WHO guidelines, were of less than a depth of 20 m. At a depth of 21-50 m, 4.7% and 1.3 % of the water in tube wells had As concentrations that exceeded the 10 and 50 mg/L guideline levels, respectively. Similarly, at a depth greater than 50 m, tube wells exceeding the As concentration guideline values (10 and 50 mg/L) were significantly fewer in number. Most of the tested wells record a high arsenic concentration in March, and a low value in May and September. A general pattern of low arsenic - low piezometric level, high arsenic - high piezometric level can be observed (Shrestha et al., 2004).

Since the fundamental work by Nickson et al. (2000) several scientific articles about the specific situation and mechanisms of arsenic release to the groundwater in the Terai have been published. According to Nickson et al. (2000) the As in the groundwater derives from reductive dissolution of As-rich Fe oxyhydroxides that exist as a dispersed phase (e.g. as a coating) on sedimentary grains. The reduction is provoked by microbial degradation of sedimentary organic matter and the redox process that occurs after microbial oxidation of organic matter is triggered as soon as dissolved O$_2$ and NO$_3^-$ were consumed. Strong correlation between dissolved organic carbon (DOC) and As in groundwater suggests that the microbial degradation of organic matter in the sediment results in an overall reducing environment and facilitates the release of As in the groundwater (Halim et al., 2009). Aqueous arsenic is mostly retained by sorption onto Fe-, Mn-oxide or clay surfaces during high-redox, medium-pH conditions (i.e., about 5.5-6.5). This mechanism seems to be a widespread process. Consequently, desorptive release of arsenic occurs as groundwater becomes more reducing and alkaline (i.e., negative Eh and pH greater than 6.5), principally as the byproduct of bacterially-mediated FeOOH dissolution. Since the reducing agent is buried organic material and since the predominant adsorption substrate is goethite or its
analogues, with clay, high-iron and high-organic sedimentary environments are apparently premises for the modern release of arsenic (Stanger, 2005).

Arsenic (As, atomic number = 33) is a ubiquitous element, which ranks 20th in the earth’s crust. Arsenic exists in four oxidation states, +V (arsenate), +III (arsenite), 0 (arsenic), and −III (arsine). Its sensitivity to mobilization largely depends on the pH values notoriously found in groundwater (pH 6.5-8.5) under oxidizing and reducing conditions. The valency and species of inorganic arsenic are highly influenced by the redox conditions (Eh) and the pH of the groundwater. Arsenite, the reduced trivalent form [As (III)], is normally present in groundwater (assuming anaerobic conditions) while arsenate, the oxidized pentavalent form [As (V)], is present in surface water (assuming aerobic conditions). In general, inorganic arsenic species are more toxic than organic forms of arsenic for living organisms.

Bhattacharya et al. (2003) describe the groundwater in the Terai to be mostly of near-neutral to alkaline state within a pH range of 6.1-8.1. Redox potential (Eh) between -0.20 to -0.11 V suggest fairly reduced conditions in the aquifers. Low NO$_3^-$ coupled with elevated NH$_4^+$ concentrations in this groundwater seem to reflect the dissimilarity nitrate reduction in the aquifers. Moreover, redox levels (Eh less than -0.2 V) for sulphate reduction are sufficiently low, which facilitates the reduction of Fe$^{3+}$ and Mn$^{4+}$ in the aquifer sediments. The source of As in the subsurface environment is clearly geogenic, and in general mobilized through natural interaction of the aqueous phases with the aquifer sediments under anoxic conditions. The principally sub-oxic conditions, the dominance of As(III) and Fe$^{2+}$ species and the positive correlation between As and both NH$_3$ propose that oxidation of organic matter coupled with microbial mediated reductive processes are important for mobilizing As in the aquifers in the Terai (Diwakar et al., 2015). According to Brikowski et al. (2014), mitigation efforts concerning elevated arsenic in groundwater in Southeast Asia are hindered by persistent uncertainty about the proximal source of arsenic and mechanisms for its mobilization. Monsoon recharge refreshes the aquifers, temporarily minimizing arsenic concentrations. Post-monsoon, average groundwater compositions exhibit increasing trends in water–rock interaction (higher TDS, with cation exchange to form increasingly Na–HCO$_3^-$ waters), as well as in arsenic and iron concentrations. All the observations mentioned, strongly support a model of reductive mobilization of arsenic from adjacent clays into aquifers, influenced by repeated flushing during periods of appreciable rainfall. For a detailed review, see Mueller (2017).

4. Analysis of the System Fe-As-P in Groundwater of Nawalparasi District – Preliminary Results

4.1 Material and Methods

Co-workers from CAWST (Centre for Affordable Water Sanitation Technology) Calgary, Canada, in cooperation with ENPHO (Environment & Public Health Organization) Kathmandu, Nepal and Eawag (Swiss Federal Institute for Environmental Science and Technology), Dübendorf, Switzerland initiated sampling campaigns for groundwater in Nawalparasi in October 2015 and April 2017 due to the fact that recent surveys revealed that at least some of the installed iron-assisted bio-sand filters still had effluent arsenic concentrations exceeding the Nepal drinking water quality standard value (50 μg/l). The modified model of these filters now used in Nepal is known as Kanchan filter (Ngai et al., 2006; 2007). As stated by Singh et al. (2014) and CAWST, the Kanchan filters efficacy in field conditions operating for a long period has scarcely been observed. Therefore in October 2015 (post-monsoon) and April 2017 (pre-monsoon) field campaigns aiming to collect groundwater, intermediately filtered and effluent water, inspection of the filters at household levels and analysis of these samples for Fe, As and P were organized. 38 water samples from
identic filters in 2015 and 2017 were collected from hand pumps whereas the pumps were all run before sample collection to remove all standing water in the tube wells (Table 1). Households for sample collections were chosen according a register provided by ENPHO with filtered water exceeding the Nepal drinking water quality standard value (50 μg/L). Water samples were acidified with HNO₃ and sent to the laboratory in Switzerland for further examination.

Fe, As and P were determined by ICP-MS (Agilent Technology, 7500 Series, Agilent Technologies, Waldbronn, Germany) at Eawag, Dübendorf, Switzerland, after 1:20 dilution with 0.5 M HNO₃. Each measurement was conducted in triplicate. All ICP-MS determinations agreed to within 3–5% standard deviation (Wenk et al., 2014).

4.2 Results and Discussion

Other elements than Fe, As and P were determined but none of them were determined exhibiting concentrations above permissible limits. Fe and P are the fundamental elements concerning the As removal process in filters used in the Terai [so-called iron-assisted bio-sand filters based on zero-valent iron (ZVI)]. The removal efficiency of the filters over time correlates widely with the total iron in the groundwater as Fe forms adsorptive phases on the ZVI (Wenk et al., 2014). The main removal mechanism concerning As is due to spontaneous adsorption and co-precipitation of As with iron (II) and iron (III) oxides/hydroxides, formed in-situ during ZVI oxidation. Heterogeneous reactions at the oxidizing ZVI surface are complex and result in a variety of potential adsorption surfaces for As (III) and As (V) (Kanel et al., 2005). The average molar Fe/As ratio for the 36 samples listed in Table 1 adds up to 9.4 (post-monsoon) and 6 (pre-monsoon). Berg et al. (2008) report about an average molar Fe/As ratio between 60 and 68 in arsenic contaminated groundwater in the Hanoi area of Vietnam. The very low Fe/As ratio poses another serious issue regarding the performance of the filters. At this low Fe/As ratio other measures like enlargement of the iron surface or extension the contact time to increase the efficiency have to be considered. Phosphate interacts strongly with precipitating FeIII (hydr)oxides and competes with arsenic for sorption and incorporation, such that again additional iron is necessary to remove both arsenic and phosphate.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Number of samples</th>
<th>As (µg/l) 2015</th>
<th>Fe (mg/l) 2015</th>
<th>P (mg/l) 2015</th>
<th>As (µg/l) 2017</th>
<th>Fe (mg/l) 2017</th>
<th>P (mg/l) 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manari</td>
<td>12</td>
<td>331.3</td>
<td>2.1</td>
<td>0.14</td>
<td>281.9</td>
<td>1.05</td>
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<td>310.4</td>
<td>1.7</td>
<td>0.18</td>
<td>280.8</td>
<td>1.5</td>
<td>0.12</td>
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<tr>
<td>Ramgram</td>
<td>15</td>
<td>233.8</td>
<td>2.1</td>
<td>0.15</td>
<td>205.3</td>
<td>1.72</td>
<td>0.15</td>
</tr>
<tr>
<td>Sukauli</td>
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<td>1.18</td>
<td>0.08</td>
<td>260</td>
<td>1.0</td>
<td>0.08</td>
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<td>1.58</td>
<td>0.17</td>
<td>162</td>
<td>0.10</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*Note:* Samples collected in October 2015 (post-monsoon) and April 2017 (pre-monsoon). Standard deviation 3-5 % (Wenk et al., 2014)
Table 1 lists the average concentration of Fe, As and P classified into sampling localities in five communities in the district of Nawalparasi. Concentrations of Fe in pre-monsoon are distinctly lower than in post-monsoon season at all places. In Manari, Panchanagar, Ramgram and Tilakpur communities As concentrations are higher in post-monsoon; only in Sukauli community As exhibits a explicitly higher concentration in pre-monsoon. Results for Sukauli and Tilakpur communities are to be taken with caution as the number of samples is very limited. Figure 1 illustrates how the concentrations of Fe and As in raw water from tube wells differ between post-monsoon and pre-monsoon seasons. In only seven groundwater samples the concentration of As in post-monsoon is markedly higher than in pre-monsoon season. Evidently, the Fe content in groundwater extracted in pre-monsoon fluctuates is more prominent than As concentrations and Fe concentrations in post-monsoon season. Figure 2 shows the dependence of As concentrations from Fe concentrations from 38 groundwater samples analyzed. Although the correlation coefficients are weakly significant for both post- and pre-monsoon time, the dependence of As concentration from Fe is remarkably higher in post-monsoon season.

High monsoon precipitation (up to 2000 mm) and year-round snow-fed river systems recharge the Terai sediments and groundwater. The aquifer system remains highly sensitive to precipitation, especially the shallow aquifers. Most rainfall, however, is present as runoff and only 10% of the average rainfall of 1,600 mm infiltrates and recharges shallow aquifers at Nawalparasi (UNDP, 1989; Nakano et al., 2014). Recharge of the groundwater is caused by local infiltration of rainfall through permeable surfaces but the infiltration percentage may be low as there is also plenty of rejected rainwater in monsoon season due to oversaturation of the soil closely underlying the land surface (Yadav et al., 2014a). Most of the annual rainfall (around 75%) takes place during monsoon season from June to September, 20%
Figure 2: Concentration of As (µg/l) in dependence of Fe concentration (mg/l) from 38 raw water samples (Note: Correlation coefficients (r) are included in the diagrams. Even the linear relationships are not relevant for post-monsoon and pre-monsoon situations, r is eminently higher for post-monsoon time.)

during pre-monsoon season (March to May) and the remainder during the rest of the year (Dongol et al., 2005). There is a likely correlation between the late Quaternary climate conditions and the concentration of arsenic in the sediments (Guillot et al., 2015). Arsenic seems to be preferentially concentrated in sediments deposited during more arid periods. During humid periods the lower arsenic concentrations in sediments can be explained by the process of eluviations in sandy and silty sediments due to intensive summer monsoon rain. The results presented here do not apply a significant difference in arsenic concentration in the groundwater. In a few samples the arsenic concentration in post-monsoon is even higher than in pre-monsoon season. Shrestha et al. (2014) stated that 66.67 % of their samples taken showed a higher As concentration in pre-monsoon than in post-monsoon season. Yadav et al. (2014a) and Kurwadkar (2014) also report about higher concentrations of As in the groundwater of Nawalparasi district in pre-monsoon compared to monsoon season. Analysis from groundwater of the Kathmandu Valley suggests lower As concentrations in monsoon season than in pre-monsoon season (Japanese International Cooperation Agency/Environment and Public Health Organization (JICA/ENPHO), 2005). Yadav et al. (2014) described how As concentrations vary both spatially and seasonally, suggesting the possibility of spatial variation due to conditions such as latitude, longitude and depth of tube well. As most of the monsoon precipitation runs off, the shallow aquifers are not recharged to a major degree and reducing conditions can persist considering rapid sediment accumulation during monsoon season. Thus, groundwater contamination with As could be more prominent in post-monsoon season due to a only slight rise in water table and flooding (Pokhrel et al., 2009). The spatial and temporal variation of the As concentration in the groundwater certainly reflects the extremely heterogeneous sediments in the Terai region on a village-scale as well as the changes over time in redox conditions.

A striking feature shown in Figure 1 is the pronounced fluctuation of Fe concentrations in pre-monsoon time concerning all 38 groundwater samples collected. At a first glance this seems to be interpreted as variations in suspended loads of rivers feeding the alluvial plains between the different seasons and to variable degrees of water-sediment interaction. Arsenic is mainly incorporated in iron-hydroxides and oxides but a substantial portion of As is retained by clay minerals. According to Guillot et al. (2015) As concentrates in clayey sediments, associated with specific elements (Fe, Al, K and C). In arid periods (pre-
monsoon), when the rainfall is reduced, there is a minor terrigenous clastic input from the Higher Himalayan Crystallines and the black schists from the Lesser Himalaya but also from watershed soil erosion, which favored the development of swamp lands in the Ganga plain (Sharma et al., 2004). Such an environment can favor development of aquatic plants and bacteria, thus enhancing the strong weathering of initially suspended load particles (micas, clays), which are preferentially deposited in quiet hydraulic environments. Nevertheless, in this proximity clays are chemically weathered losing Na and K thus remaining relatively enriched in immobile compound like Fe and Al. As long as reduced conditions persists As remains relatively mobile. Most of the known wells record a high As concentration in March, and a low value in September (Shrestha et al., 2004). As already described in Figure 2, the correlation coefficients are weakly significant for both post- and pre-monsoon time, but the dependence of As concentration from Fe is remarkably higher in post-monsoon season. Fe concentrations in groundwater in post-monsoon are remarkably higher than in pre-monsoon season again reflecting higher weathering and dissolution rates in wet seasons as well as desorption and release of As from iron-hydroxides being rather formed in wet than in dry seasons. During post-monsoon average groundwater compositions exhibit increasing trends in water–rock interaction (higher TDS, with cation exchange to form increasingly Na–HCO$_3$ waters) as well as in arsenic and iron concentrations (Brikowski et al., 2014). Surficial sediments in the Terai exhibit extreme heterogeneity. Highly organic clays predominate in the shallow hydrologic system (the upper 50–100 m of surficial sediments contain greater than 70% clay), and aquifer hydraulic conductivities are two orders of magnitude lower than in the delta to the South. Low hydraulic conductivity of surficial fines limits infiltration, which likely enhances reducing conditions and mobilization of arsenic (Brikowski et al., 2014). Fine-grained minerals like clay are capable of adsorbing arsenic efficiently (Stanger, 2005; Chakraborty et al., 2007; Uddin, 2017) and can therefore also release a substantial amount of arsenic depending on local conditions. This weak correlation of aqueous As and Fe has also been observed by Dowling et al. (2002), van Geen et al. (2006), Diwakar et al. (2015) and may indicate decoupling between mobilization of As and Fe$^{2+}$. Decoupling between Fe$^{2+}$ and As may also result from sorption of Fe$^{2+}$ to other surfaces (i.e. clays) or precipitation of Fe(II) minerals, such as siderite. Groundwater in Nawalparasi is nearly saturated with respect to siderite in most samples collected for a study by Diwakar et al. (2015).

5. Health Problems and Socio-economic Impact to the Community

Any assessment of people at risk of arsenic poisoning is very difficult to conduct, particularly in areas where geochemical surveys are limited. Such assessment are broad and are based on four criteria: (1) prevalence of current recorded cases of arsenicosis, (2) likelihood of ingested concentrations exceeding 50 μg/L, (3) number of people living in exposed areas, and (4) likely ability of region to mitigate/mediate against contamination (Thakur et al., 2011). So far, in the following districts of the Terai, the groundwater is among the most severely contaminated with arsenic: Nawalparasi, Bara, Parsa, Rautahat, Rupandehi, and Kapalivastu districts (Shrestha et al., 2014). Although contamination of tube well water by arsenic in this area (Terai, Nepal) was first reported in 1999, till this day only sporadic information on the situation have been published. Amongst others, it was depicted that 29% of more than 20,000 tube wells had arsenic concentrations exceeding the World Health Organization (WHO) standard (10 μg/L), that the prevalence of arsenicosis varied between 1.3% and 5.1% among four independent surveys, and that approximately 0.5 million people in Terai were at risk of consuming water with an arsenic concentration greater than 50 μg/L. Reports included that the overall prevalence of arsenicosis among humans greater and equal to 15 years old was 6.9%, and that males had prevalence a twice as high as females
Arsenicosis usually develops after an exposure to arsenic over a prolonged period, generally 5 to 20 years. The first obvious signs of the disease are usually observed on the skin. The typical peculiarity of the changes include the appearance of small black or white marks (melanosis), then thickening of the skin on the palms and the feet (keratosis), followed by skin lesions and eventually skin cancer in a sequential development. Late phenomena like internal cancer take more than 10 years to develop. Patients are also complained of bronchitis, gastroenteritis and peripheral neuropathy. In advanced stages of arsenicosis, patients appear like leprosy patients due to the development of gangrenes over the entire body (Adhikari and Ghimire, 2009; Thakur et al., 2011). Early symptoms of arsenicosis (e.g., melanosis) seem to be reversible and can be stopped if exposure to arsenic is prevented.

New findings published by Fillman et al. (2016) show that As may have differing effects on human cell telomeres (a compound structure at the end of a chromosome) depending on the concentration: telomere length maintenance and increased telomerase expression at a lower concentration, versus shortening of telomeres, apoptosis, increased reactive oxygen species and decreased telomerase expression at a higher concentration. These mechanisms may be involved in the carcinogenic effects of arsenic and cadmium. Telomere attrition has been associated with a number of age-related diseases and health issues in adults, including inflammation, cardiovascular disease, type II diabetes, cancer, dementia, as well as psychosocial factors. This research project was conducted in the Terai of Nepal using salivary samples from the inhabitants.

The economy and the livelihoods of people living in the Terai are to a high degree dependent on the abstraction and consumption of groundwater as potable water. Factors such as economic status, literacy and profession are critical parameters of the vulnerability to arsenicosis. Various researches revealed that farmers, poor or illiterate persons are more prone to arsenic induced diseases. Patients of lower income groups were particularly more likely to face economic and social hardship. About half of the arsenicosis patients and particularly female patients faced difficulties receiving treatment (Thakur et al., 2011). Other factors that influence susceptibility to arsenicosis have been identified: nutritional status, addiction, dose response, different methylating capacity among individuals and population groups. The most severely affected area by the arsenic crisis is Ramgram municipality (Adhikari and Ghimire, 2009). In a study by Dahal et al. (2008) the influence of arsenic-contaminated irrigation water on alkaline soils and arsenic uptake in agricultural plants at field level was monitored. Moreover, groundwater in the Terai used for irrigation purposes of edible plants and vegetables like onion, cauliflower, rice, brinjal or potato was found to coerce uptake of arsenic by the mentioned plants. The continuous use of arsenic-contaminated water with an As concentration of more than 0.250 mg/L for irrigation on a longer period increases the risk of arsenic contamination in the food chain. Grimshaw (2016) explored a number of socio-economic factors which might influence the adoption of arsenic-eliminating devices. Willingness to pay was a key issue for many. There were others who believed that the government or NGOs should provide free water testing. Iron-assisted bio-sand filters (see section 6 below) were used by many but some households did not know how to repair them when broken. An acceptable price level has to be established for cooperation with business in Nepal and to promote use of arsenic-eliminating devices. This would help to establish local market conditions. But a key premise is simply that researchers, aid agencies, and government have to come forward to help community to spread the awareness among people about danger of arsenic toxicity, importance of analysis of arsenic in water, importance of arsenic safe water, and other social and socio-economic problems or they will not be able to combat the arsenic and similar contaminations (Chakraborty et al., 2013).
6. The Mitigation Option of Choice: Iron-assisted Bio-sand Filters

Initiated by a study of Sharma (1999), various organizations and agencies have conducted surveys on arsenic contamination of well water in Nepal. NRCS/ENPHO in 2003 have provided the following six types of mitigation options to the arsenicosis patients in all VDCs of Rautahat district: (i) two-Gagri (water vessel) filter, (ii) innovated dug well, (iii) arsenic iron removal plant (AIRP), (iv) tube wells from arsenic free aquifer, (v) modified bio-sand filter, and (vi) awareness program on nutrition. Later, Gagri filters and iron-assisted bio-sand filters (Kanchan filters) were usually applied to remove arsenic from well water in Nepal – these two filters were believed to be the best treatment option at household levels (Nakano et al., 2014; Yadav et al., 2011). To the best knowledge of the author solely Kanchan type filters are used in the district of Nawalparasi in 2017.

6.1 Kanchan filters

These days zero-valent iron (ZVI) media contained in iron-assisted bio-sand filters is preferably used to remove arsenic from water. The Kanchan filters are widely applied in the Terai. Under the applicable conditions to groundwater treatment, arsenate removal by zero-valent iron media involves surface complexation only and does not involve reduction to metallic arsenic. Therefore, removal of arsenic occurs through adsorption and co-precipitation during the formation of iron(III) hydroxides. The colloidal arsenic will be eliminated by a second filtration step using fine sand. These bio-sand filters in operation in Nepal as a point-of-use drinking water treatment option were originally designed by Dr. David Manz of the University of Calgary, Canada in the late 1990 with support of numerous organizations and individuals. The filters were modified to remove arsenic and tested in Nepal jointly by Massachusetts Institute of Technology (MIT) researchers; ENPHO, Nepal; Rural Water Supply and Sanitation Support Program (RWSSSP), Nepal; and CAWST, Canada, based on slow sand filtration and iron hydroxide adsorption principles (Thakur et al., 2011). Some prior field tests showed that this filter removes more than 95% arsenic on average and up to 99% in some cases (NRCS–ENPHO, 2003; Ngai & Walewijk, 2003). The filter also removes high levels of iron – up to 99%, with an average of 95%. Microbiological quality of this treated water is satisfactory (Shrestha et al., 2004). The award-winning household water filter known now as Kanchan Arsenic Filter (KAF) was constructed for simultaneous arsenic and pathogen removal. Indispensably, the KAF is constructed using locally available labor and materials and is optimized based on the local socio-economic conditions. The Kanchan Arsenic Filter combines the concept of a slow sand filter for intermittent use (i.e., a bio-sand filter base) with the innovation of a diffuser basin containing (rusty) iron nails for arsenic removal. On the whole the operation under the water quality conditions encountered in the Terai region of Nepal (total arsenic less than500 mg/L; phosphate less than 2 mg/L, pH less than 8) the iron nails may last up to 3 years before replacement is required (Ngai et al., 2006). In an evaluation study Ngai et al. (2007) report about a two-year technical and social evaluation of over 1000 KAFs deployed in rural villages of Nepal determined that the KAF typically removes 85–90% arsenic, 90–95% iron, 80–95% turbidity, and 85–99% total coliforms. They describe that 83% of the households continued to use the filter after 1 year, mainly motivated by the clean appearance, improved taste, and reduced odor of the filtered water, as compared to the original water source. Arsenic seems to be rapidly adsorbed onto the surface of the ferric hydroxide when arsenic-containing water is poured into the filter. Some arsenic-loaded iron colloids in the KAF are flushed on to the sand layer below, and are trapped in the top few centimeters of the fine sand due to straining. As ferric hydroxide particles exfoliate from the iron nails, new iron surfaces are created, providing additional arsenic adsorption capacity. Iron and arsenic do not migrate
through the sand media over time (Ngai et al., 2007). The filter container is either constructed out of concrete or plastic. The container itself is about 0.9 m tall 0.3 m in diameter (Figure 3). 5 to 6 kg of non-galvanized iron nails for arsenic removal is filled into the diffuser basin. Moreover, there is a standing water height of 5 cm above the sand layer. In addition, pathogens, iron and suspended material are removed from water through a combination of biological and physical processes: mechanical trapping, adsorption/attraction, predation, and natural death. Approximately 10–15 L/h of arsenic contaminated water can be treated by this filter. A filter is locally available at a cost of about 1,400 to 1,800 NRs (about US$20) per filter (Thakur et al., 2011). Figure 4 exhibits one of these operating filters in the district of Nawalparasi in October, 2015. Recent investigations indicate that the performance of these filters depends highly on the form of ZVI, filter design, water composition and operating conditions. Wenk et al. (2014) evaluated factors that influence the removal of arsenic and uranium with laboratory columns containing iron nails with six different synthetic groundwater at pH 7.0 and 8.4 over 30 days. Arsenic removal was 65–95% and strongly depended on the water composition during the first 10 days.

Arsenic removal at pH 7.0 was better than at pH 8.4 and high P combined with low Ca decreased As removal. After 10 days of operation, As removal decreased to 45–60% with all columns. The drop in performance over time is tentatively explained by decreasing release of iron to solution due to formation of layers of FeIII phases and calcite covering the iron surface. Mobile corrosion products contained ferrihydrite, Si-containing hydrous ferric oxides and amorphous Fe–Si–P phases. As a consequence, higher ZVI surface areas and longer contact times should lead to satisfactory As removal with Kanchan-type filters. Economical and auspicious methods are co-precipitation of As with naturally occurring or added FeII or FeIII, sorption or adsorption to inexpensive prefabricated sorbents or ion exchangers, or As removal with metallic iron. Phosphate is well known to interact strongly with precipitating FeIII (hydro)oxides and is an antagonist of As for sorption and incorporation, such that additional iron is essential to remove both arsenic and phosphate. Mainly, two arrangements could improve the performance of Kanchan filters are: (1) larger specific ZVI surface areas (e.g. by use of smaller nails) and (2) increased contact times by more controlled and restricted flow from the upper diffuser bucket. According to Singh et al. (2014) the Kanchan filters efficacy in field conditions operating for a long period has been scarcely observed. They confirm an efficiency of the Kanchan filters of only 54%, e.g. only 54% of the operating filters eliminated As to a safe level for human consumption in the in situ field conditions.

Ogata (2015) describes the deteriorating situation in Nawalparasi rigorously: 53.2% of KAF (Kanchan filters) and 96% of community-based safe water facilities were not effective. The coverage of safe water was reduced from 50.5% to 28.2% in Nawalparasi district, and 64.1% to 34.8% in all arsenic affected areas in Nepal, according the findings of this case study. Compared with other surveys the functionality of KAFs has deteriorated from 88.9% to 50%. The major reasons indicated not to use the KAFs anymore were: filter broken and filter leakage. Another major problem seems to be the deterioration of the filter material with time. The functionality of the filters decreased after a usage of more than two years. As a long term solutions Ogata (2015) suggests to extract groundwater from the deep aquifer after careful evaluation about the presence of an impermeable clay layer between the upper As contaminated and the deeper As free aquifer. Sealing of the borehole when drilling deep tube wells is crucial to avoid contamination of the deep aquifer by As. In a report, Nakamura (2016) states that the situation concerning the arsenic disaster in Nawalparasi as serious. Intake of As contaminated water extracted there is expected to increase the likelihood of developing various forms of cancer in 150-750 persons out of 100,000. In addition, the case study suggests using sand, aluminum powder or iron powder or a combination of these
measurements for eliminating As and to enhance the efficiency of the filtration process. Regular maintenance provided, Kanchan filters present a beneficial device to remove As from groundwater. Residents of the area have to be instructed carefully how to use and maintain the filters and have furthermore to be educated in basic knowledge of arsenic and related health issues as well as countermeasures.

Figure 3: Diagram of the Kanchan Arsenic Filter (KAF), showing the location and arrangement of its components (Source: Ngai et al., 2006)

Thakur et al. (2011) argued that an arsenic monitoring and mitigation program throughout the country could be effectively performed by an institution administratively and financially secured, with national and international collaborations. The arsenic groundwater monitoring program should be carried out at least twice in a year during pre-monsoon and post-monsoon period, since arsenic concentration in ground water varies seasonally. In addition, this institution should develop guidelines/regulations for installing new tube or dug wells. These guidelines should make mandatory tests prior to installing new tube wells, and also a tube well should not extract water from different aquifers, to avoid possible inter-
aquifer arsenic contamination, if possible. Provision of safe water options, periodic screening of water sources for arsenic, availability of trained doctors, regular availability of medicine, doorstep treatment, follow up on severe patients are the major recommendations.

7. Summary and Future Perspective

In addition to evaluate the factors that influence the removal of arsenic with laboratory columns containing iron nails and tests with modified KAFs explicitly amplifying research on the mechanism of dissolution of arsenic from sediments, mobility of arsenic in the groundwater, its chemical speciation, the influence of the geological environment, the origin of the geogenically derived arsenic as well as on the health impact on the concerned inhabitants of the Terai is highly required.

As already mentioned, the drop in performance over time by KAFs could tentatively be explained by the decreasing release of iron to solution due to the formation of layers of FeIII phases and calcite covering the iron surface. Higher ZVI surface areas and longer contact times should lead to more efficient As removal with Kanchan-type filters. As the Fe concentration in the groundwater of the Nepalese Terai is extremely low, the filters have to be modified accordingly, taking this low concentration of Fe into consideration. So far, this factor influencing the elimination of As considerably was never taken into account.

Residents of the concerned areas have to be instructed explicitly on the use and maintenance of the filters and have furthermore to be educated in basic knowledge of arsenic and related health issues as well as countermeasures.

References


