Geogenic arsenic in groundwater of Burkina Faso

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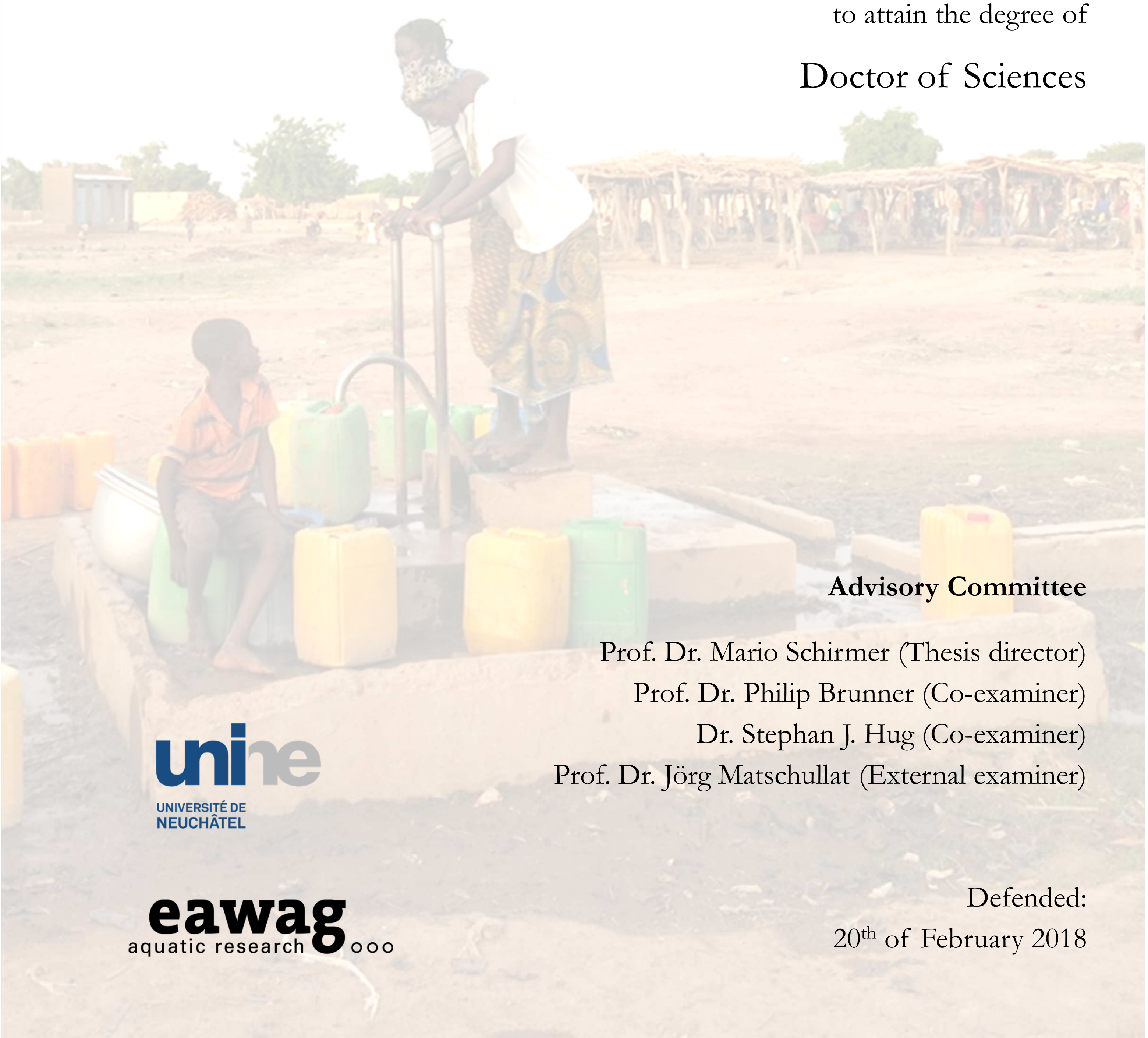

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In memory of

Annette Johnson

1958 – 2015

With gratitude and appreciation

Summary

In the semi-arid West African Sahel belt, rural populations often rely on groundwater from fractured aquifer systems for their drinking water needs. Recent evidence has shown that some tube wells in northern Burkina Faso are affected by arsenic (As) concentrations above the World Health Organisation's (WHO) 10 μg/L guideline value. Arsenic is hypothesised to stem from geogenic (naturally occurring) sources, specifically sulphide minerals occurring in ore zones. Arsenic is a potent carcinogen and long-term exposure even to low concentrations can lead to greatly increased risks of developing cancers of the internal organs (lung, bladder, kidney), as well as a range of other serious adverse health effects.

Compared to the widely reported and intensely studied cases of geogenic As in Asia and Latin America, Burkina Faso and the greater West African region are noticeably data-scarce. However, before risks to human health can be assessed and mitigation measures initiated on a large scale, a comprehensive assessment of the origins, dynamics and magnitude of groundwater As contamination is necessary. This dissertation aims to contribute to these issues by investigating i) which regions in Burkina Faso are most at risk of As-contaminated groundwater, ii) whether temporal aspects such as groundwater residence time and seasonality influence As concentrations and iii) the suitability of low-cost, low-tech zero-valent iron-based technologies for As removal.

A comprehensive dataset encompassing both new and existing measurements of tube well As concentrations from different regions of Burkina Faso (n = 1498) revealed that 15% were above 10 μg/L. By using these measurements for calibration, as well as data extracted from readily available geological and mineral deposit maps as independent predictor variables, As prediction models were computed using multivariate logistic regression. The best predictors for high As were schists and volcanic rocks belonging to the Birimian formation, which has undergone considerable mineralisation resulting in high-class metal ore deposits. Combining the resulting hazard maps with population density data led to the estimation that ~560,000 people in Burkina Faso, roughly 3% of the population, are potentially exposed to As > 10 μg/L in their drinking water.

The high spatial variability in tube well As concentrations observed in the above-mentioned dataset highlighted the need for a more detailed investigation regarding As sources and release mechanisms, as well as the influence of the hydrological system on As concentrations. Hydrochemical and multi-tracer (noble gases, ^{3}H, ^{2}H, ^{18}O) sampling was performed in a small study area (~80 km^{2}) in South-Western Burkina Faso. This first dataset of dissolved noble gases in West African fractured crystalline bedrock aquifers gave the unexpected insight that groundwater bodies with residence times > 10^{3} a can already be found at depths less than <50 m, as suggested by $^{3}He/^{4}He$ ratios of ~10^{-8}. This finding questions the sustainability of future increasing groundwater extraction in light of a rapidly growing population. Elevated As concentrations > 10 μg/L, found in oxic groundwater of circum-neutral pH, were not correlated to any other analysed parameter, nor related to groundwater residence times. This corroborates the hypothesis that the proximity to sulphide minerals ($Fe(As,S)_2$, FeAsS) in mineralised zones is likely the principal factor influencing As concentrations in groundwater.

Nevertheless, the exact mechanisms controlling excess aqueous As concentrations under these pH/Eh conditions remain elusive and require further investigation.

Where switching to an uncontaminated water source is not feasible, water treatment to remove As is necessary. Sand filters with small iron nails as a Fe-oxide source for As sorption and co-precipitation were tested in remote rural households in northern Burkina Faso with groundwater As concentrations of 400 – 1350 µg/L. Laboratory column experiments revealed that entrapped air in the nail layer can severely lower As removal efficiency due to decreased water/nail contact time and preferential flow paths. Modification of the field filters to avoid these issues and ensure constant nail saturation resulted in As removal efficiencies of 75 – 90 %, but effluent As still remained mostly > 50 µg/L, therefore not adhering to drinking water guidelines. These filters may be suitable to remove As when input concentrations are lower (10 – 100 µg/L), or as an emergency measure to lower total As exposure. A household filter containing granular ferric hydroxide (GEH®) consistently removed As to below 10 µg/L. Such commercial adsorbents however are expensive and not locally available, leading to challenges of affordability and long-term financial sustainability in these low-income settings.

This dissertation has exposed the widespread occurrence of geogenic As in groundwater of Burkina Faso and advanced understanding of As-affected fractured aquifer systems. These results are relevant to the greater West African region, where similar geological and hydrogeological conditions occur. A first estimation of more than half a million people exposed to As > 10 µg/L in Burkina Faso alone should spur the initiation of further scientific research, as well as mitigation activities involving stakeholders from the health, water supply and rural development sectors. Considering the social and economic burden induced by As-related mortality, reducing As exposure is an investment in future generation's health and productivity.

Résumé

Dans les régions sahéliennes semi-arides d'Afrique de l'Ouest, l'eau souterraine des aquifères fracturés permet de satisfaire les besoins en eau potable des populations rurales. Au nord du Burkina Faso, des études récentes ont montré que l'eau de certains forages contient de l'arsenic (As) à des concentrations supérieures à la norme de 10 μg/L définie par l'Organisation Mondiale de la Santé (OMS) et également adoptée par le Burkina Faso. Cet arsenic serait d'origine géogénique (c'est-à-dire naturelle) et trouverait en particulier sa source dans des sulfures présents dans les gisements de minerais. L'arsenic a un fort potentiel cancérigène: une exposition à long-terme, même à de faibles concentrations, augmente le risque de cancers des organes internes (poumons, vessie, reins), ainsi que d'autres effets néfastes pour la santé.

Au Burkina Faso et plus généralement en Afrique de l'Ouest, les données sur la présence d'arsenic géogénique sont extrêmement rares, contrairement à d'autres régions telles que l'Asie ou l'Amérique du Sud, où de nombreuses études ont été effectuées sur ce sujet. Cependant, avant d'évaluer les risques pour la santé humaine et de développer des solutions à grande échelle, il est nécessaire de déterminer les sources, la dynamique et l'ampleur de la contamination des eaux souterraines à l'arsenic. Cette thèse a pour but de répondre à ces questions en étudiant: 1. quelles sont les régions du Burkina Faso où le risque de contamination des eaux souterraines à l'arsenic est élevé; 2. comment la concentration en arsenic est influencée par des paramètres temporels tels que le temps de résidence des eaux souterraines et la saisonnalité; 3. la faisabilité des technologies de traitement basées sur l'élimination de l'arsenic par oxydation du fer à valence zéro, simples et peu coûteuses.

Une base de données compilant 1'498 mesures d'échantillons d'eau, anciennes et nouvelles, provenant de forages de diverses régions du Burkina Faso montre que dans 15% des forages, la concentration en arsenic est supérieure à 10 μg/L. Ces données ont été utilisées comme points de calibration, et les cartes géologiques et minières existantes comme variables indépendantes d'une régression logistique multivariée. Cette modélisation a permis la création de cartes de prédiction de la présence d'arsenic dans les eaux souterraines. Les meilleurs prédicteurs d'une haute concentration d'arsenic dans l'eau souterraine sont les schistes et les roches volcaniques de la formation birimienne, qui ont subi une minéralisation importante, se développant ainsi en gisements de minerais de haute qualité. Les cartes de risques ainsi obtenues, couplées aux données sur la densité de population, nous permettent d'estimer qu'environ 560'000 personnes au Burkina Faso (soit 3% de la population) sont exposées au risque de consommer de l'eau pouvant contenir une concentration d'arsenic supérieure à 10 μg/L.

Les mesures réalisées ont montré une grande variabilité spatiale de la concentration en arsenic dans les eaux de forages. C'est la raison pour laquelle des recherches supplémentaires concernant les origines, les mécanismes de libération de l'arsenic et l'influence des systèmes hydrologiques ont été nécessaires. Une campagne d'échantillonnage hydrochimique et de traçage avec des gaz nobles (^{3}H, ^{2}H, ^{18}O) a été réalisée dans une zone d'étude (~80 km^{2}) au sud-ouest du pays. Ce tout premier jeu de données de gaz nobles dissous dans les aquifères en

milieu fracturé dans le socle cristallin de l'Afrique occidentale a permis de montrer qu'à des profondeurs inférieures à 50 m, il existe des eaux souterraines ayant un temps de résidence supérieur à 1000 ans, correspondant à des rapports isotopiques d'hélium ($^3He/^4He$) d'environ 10^{-8}. Cette découverte inattendue met en question la durabilité des ressources en eau souterraine dans un contexte d'augmentation rapide de la population. Les concentrations élevées en arsenic (> 10 µg/L) détectées dans les eaux souterraines où des conditions oxiques et de pH neutre prédominent ne sont liées à aucun autre paramètre hydrochimique mesuré ni au temps de résidence. Cela renforce l'hypothèse que la proximité de sulfures ($Fe(As,S)_2$, FeAsS) dans les zones minéralisées est probablement le principal facteur influençant les concentrations en arsenic dans les eaux souterraines. Cependant, les mécanismes exacts engendrant la concentration excessive aqueuse d'arsenic sous ces conditions de E-pH ne sont pas encore bien connus et demandent davantage de recherche.

Lorsqu'il est impossible de s'approvisionner à une source d'eau non contaminée à l'arsenic, le traitement de l'eau est nécessaire. Un essai pilote sur le terrain avec des filtres à sables contenant des clous en fer comme source d'oxyde de fer pour l'adsorption et la co-précipitation de l'arsenic a été mené dans une zone rurale au nord du Burkina Faso où les concentrations en arsenic dans l'eau souterraine oscillaient entre 400 et 1350 µg/L. Parallèlement, des essais en colonnes au laboratoire ont révélé que l'air piégé dans la couche de clous peut drastiquement réduire le rendement d'élimination de l'arsenic dans les filtres, à cause de la diminution du temps de contact entre l'eau et les clous et des écoulements préférentiels. Grâce à une modification des filtres sur le terrain, une saturation en eau de la zone des clous a pu être obtenue et les rendements d'élimination de l'arsenic ont ainsi atteint 75 à 90%. Cependant, dans la majorité des cas, l'eau traitée gardait une concentration en arsenic supérieure à 50 µg/L, ce qui n'est pas conforme aux normes de potabilité de l'eau. Ces filtres peuvent donc s'avérer efficaces pour traiter l'arsenic lorsque les concentrations en entrée sont relativement basses (10 – 100 µg/L). Ils pourraient également être employés comme une solution d'urgence pour diminuer l'exposition totale à l'arsenic. Le remplacement des clous en fer par de l'hydroxyde ferrique granulaire (GEH) a permis d'obtenir une concentration en arsenic dans l'eau traitée systématiquement inférieure à 10 µg/L. La construction d'un filtre avec ce type de média adsorbant industriel est néanmoins limitée par son coût élevé et son manque de disponibilité sur le marché local, menaçant ainsi la durabilité et de viabilité financière à long terme de cette solution dans les pays à bas revenus.

La présente thèse a visé à caractériser la présence géogénique de l'arsenic dans les eaux souterraines du Burkina Faso et à mieux comprendre le fonctionnement des aquifères fracturés soumis à cette contamination. Les résultats obtenus sont utiles pour d'autres régions d'Afrique occidentale ayant des conditions géologiques et hydrogéologiques similaires à celles du Burkina Faso. Un demi-million de personnes sont à risque de consommer de l'eau contaminée à l'arsenic à une concentration supérieure à 10 µg/L : cette première estimation devrait inciter le lancement de nouveaux travaux de recherches scientifiques mais également encourager les acteurs de la santé, de l'approvisionnement en eau potable et du développement rural à s'impliquer pour la mise en œuvre de solutions de traitement. Vu les conséquences sociales et économiques liées à l'empoisonnement chronique par l'arsenic, réduire l'exposition à ce poison représente un investissement important dans la santé et la productivité des générations futures.

Keywords

Groundwater, drinking water quality, arsenic, hydrochemistry, geogenic contamination, sulphide minerals, hazard maps, statistical modelling, logistic regression, health threat, fractured aquifers, noble gases, isotope tracers, residence time, adsorption, filtration, water treatment, zero-valent iron, semi-arid, Burkina Faso, West Africa

Mots clés

Eau souterraine, qualité de l'eau potable, arsenic, hydrochimie, contamination géogénique, sulfures, cartes de risque, modélisation statistique, régression logistique, risque sanitaire, aquifères fracturés, gaz nobles, traceurs isotopiques, temps de résidence, adsorption, filtration, traitement de l'eau, fer zéro, semi-aride, Burkina Faso, Afrique de l'Ouest

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1 Introduction

1.1 Context

In September 2015, the UN General Assembly adopted the Sustainable Development Agenda 2030, which includes the Sustainable Development Goal (SDG) 6, committing Member States to "Ensure availability and sustainable management of water and sanitation for all" by 2030 (United Nations, 2017a). For the first time, safe drinking water quality (with respect to pathogens AND chemical water quality) was included in this framework, presenting a global framework for the provision of drinking water that is also free of contaminants such as arsenic (As). The African population is growing rapidly, particularly in countries of the Sahel, whose current population is projected to more than double within the next 30 years (United Nations, 2017b). This will ultimately lead to the increased exploitation of water resources in this semi-arid region, particularly groundwater. In order to minimise overexploitation or the extraction of water with inadequate quality, a sound scientific knowledge base of local and regional hydrological processes is mandatory to aid decision-making. In particular, the capacity of local scientists and research and higher education institutions needs to be strengthened. This thesis was part of a larger research effort attempting to contribute to this complex issue through scientific collaborations between the *Institut International de l'Ingénierie de l'Eau et de l'Environnement (2iE)* in Ouagadougou, Burkina Faso and several Swiss research institutions (*EPFL, HEIG-VD* and *Eawag*). With funding from the Swiss Agency for Development and Cooperation (SDC), the "*Programme 3E" (Eau, Énergie, Environnement)* dealt with questions of sustainable energy production, the spread of water-borne disease and, relevant to this dissertation, the occurrence and mitigation of As-contaminated groundwater in Burkina Faso.

1.2 Arsenic as a naturally occurring groundwater contaminant

Groundwater containing As above permissible levels is a world-wide occurrence and many millions of people rely on such water for their daily drinking water needs, with potentially serious and chronic consequences on their health. Even though high groundwater As concentrations can also be a result of anthropogenic activities such as mining or industrial activities, these tend to be more localised, whereas the large-scale groundwater contamination affecting whole geographic regions is generally a result of naturally occurring (geogenic) processes. Arsenic is present in commonly occurring minerals of the Earth's crust (see e.g. Matschullat (2000) and Smedley and Kinniburgh (2002)). However, it is not simply the content of As in an aquifer mineral that governs As concentrations in natural waters, but rather ambient environmental conditions such as the pH and redox potential of groundwater that control As speciation, solubility and sorption. Three main As mobilisation mechanisms occurring in natural groundwater systems have been identified (Ravenscroft et al., 2009):

1) Reductive dissolution: in strongly reducing environments, often generated by the microbial reduction of organic matter, Fe(III)-hydroxides with adsorbed As are reduced and dissolve, releasing As(III) to solution

2) Alkaline desorption: at pH-values > 8, As(V) bound to metal oxides is desorbed

3) Sulphide oxidation: when exposed to oxygen, sulphide minerals such as $Fe(S,As)_2$ or FeAsS are oxidised and can release As to solution

Geothermal sources can also result in significant As concentrations in groundwater, but are generally more localised. Arsenic mobilised via reductive dissolution is dominantly responsible for the widespread and widely documented cases of geogenic As contamination of groundwater in the young alluvial floodplain aquifers of South and South-East Asia, with 45 million people estimated to be exposed to As-contaminated water (> 10 μg/L) in Bangladesh alone (Flanagan et al., 2012). Examples of alkaline desorption dominated systems are the Chaco-Pampean plains of Argentina and the Lagunera region of northern Mexico (Smedley & Kinniburgh, 2002). Aquifers where As results from sulphide oxidation are of special relevance to this dissertation and will be discussed in more detail in the following section.

1.3 Groundwater arsenic in mineralised zones

Sulphide minerals, especially arsenian ("As-rich") pyrite ($Fe(S,As)_2$) and arsenopyrite (FeAsS), can be important sources of As to groundwater. Sulphide minerals are present in mineralised zones worldwide, and are especially common in hydrothermal vein- or disseminated-style deposits, where they can occur in mineral assemblages with quartz and precious metals such as Ag or Au (Evans, 2014). The oxidation of arsenopyrite when in contact with oxygen-containing groundwater may be described by the following reaction:

$$FeAsS + \frac{7}{2}\,O_2 + 4H_2O \rightarrow Fe(OH)_3 + H_3AsO_4 + SO_4^{2-} + 2H^+$$

In an open system, the reaction will continue until the reaction products, Fe(III)-(hydr)oxides, coat the sulphide surfaces and prevent further sulphide oxidation (Smedley, 1996). In such oxidising conditions, As occurs as As(V) and has a high affinity to sorb to the produced Fe(III)-(hyrd)oxides (Dixit & Hering, 2003). In a closed system, such as a deep aquifer, sulphide oxidation may continue until all oxygen is consumed, resulting in reducing conditions in the aquifer and dissolved Fe(II) and As(III) species. The speciation and solubility of As released from sulphide oxidation is subsequently closely linked to Eh and pH conditions in the aquifer, which can vary greatly from region to region, depending on local geology, geochemical evolution of groundwater and flow patterns. It is therefore impossible to propose a generic, globally applicable conceptual model for groundwater As occurrences in sulphide oxidation-dominated areas. This is exemplified by numerous studies investigating As in the fractured bedrock aquifers of the north-eastern USA and eastern Canada (e.g. Ayotte et al. (2003); Bondu et al. (2017); Lipfert et al. (2006); Ryan et al. (2013); Yang et al. (2015)), who all agree on sulphide minerals as the As source, but have proposed differing scenarios to explain the elevated As concentrations in relation to the groundwater pH, Eh and As speciation measured in boreholes in their respective study areas.

1.4 Human health impacts of arsenic exposure

Arsenic is a non-essential element for humans and highly carcinogenic. Even low concentrations, for example in the µg/L-range as occur in natural waters, can lead to adverse health effects after prolonged exposure.

Few easily identifiable symptoms of arsenicosis exist. The only frequently occurring visible clinical manifestations are skin lesions, which can arise within months or after years of exposure (Naujokas et al., 2013). Hyperpigmentation (melanosis) often occurs on the trunk of the body, whereas keratosis predominantly affects the palms and soles (Sengupta et al., 2008). Links have been established between As exposure and a wide range of other medical conditions, including chronic pulmonary diseases, anaemia, hypertension and peripheral vascular disease (Guha Mazumder, 2008; Naujokas et al., 2013; Sengupta et al., 2008; Smith et al., 2005). In addition, As exposure can lead to an increased mortality from acute myocardial infarction (heart attacks) and has been made responsible for a range of negative health impacts on children, including impaired cognitive development, increased infant mortality and reduced birth weight (Smith & Steinmaus, 2009).

The most severe health concern however is the increased risk of developing cancers of the skin or internal organs, especially the bladder, kidney and lung (Smith et al., 1992). Cancer rates continue to increase even decades after As exposure has stopped, showing a distinct latency pattern (Steinmaus et al., 2013; Yuan et al., 2010). Recent findings have shown that *in utero* or early childhood As exposure is sufficient to generate increased cancer mortality in later adult life (Smith et al., 2012; Steinmaus et al., 2014).

Large-scale epidemiological studies in Bangladesh have demonstrated a clear dose-response relationship between As exposure via drinking water and all-cause mortality (Argos 2010, Sohel 2009). The exposure group drinking water between 10-50 µg/L were slightly more likely to die from chronic disease than the control group, with mortality rising considerably at exposure concentrations > 150 µg/L. Flanagan et al. (2012) estimated that up to 1 in 18 deaths in Bangladesh are arsenic-related, leading to a huge social and economic burden in lost life years and productivity. The provision of clean drinking water to populations exposed to As concentrations, especially > 150 µg/L, therefore needs to be a priority.

1.5 Mitigation strategies for arsenic-affected areas

Arsenic mitigation can present a considerable challenge in low-income, rural settings due to a combined effect of limited financial ability, lack of infrastructure, a weak enabling environment and low awareness levels among the population (Johnson et al., 2014). Water treatment often first comes to mind when considering As mitigation, but exploiting an alternative, As-free water source may be simpler and less cost-intensive. Well-switching was preferred by the population over technological solutions such as water treatment filters in As-affected regions of Bangladesh (Ahmed et al., 2006; Inauen et al., 2013). Complementing these investigations, Johnston et al. (2010) came to the conclusion that As treatment filters on household or community levels were too pricey for the poor and too complicated to maintain. Nevertheless, in certain settings or as an interim measure, As removal may certainly be appropriate and unavoidable. Arsenic treatment plants on municipal scales, employing coagulation-filtration techniques, adsorption on filter beds or reverse osmosis, can successfully provide treated water for thousands of consumers, as examples from Europe, North and South America and Asia have shown (Hering et al., 2017). Numerous techniques that are suitable for small, decentralised community systems or on household scales have been developed and tested in the last decades (see Amrose et al. (2015); Deschamps and Matschullat (2011); Eawag (2015); Malik et al. (2009); Mohan and Pittman (2007) for comprehensive reviews). No single technique is suited to all conditions though, with a number of site-specific considerations having to be taken into account: groundwater chemistry, consumer preferences and habits, availability of raw materials, ease of handling and maintenance (Hug et al., 2008; Osterwalder et al., 2014). A technology that is successful in densely populated, humid Bangladesh with groundwater from shallow, young sedimentary aquifers, may not be so in remote villages of the semi-arid Sahel, supplied with water from fractured crystalline bedrock aquifers.

1.6 Study site

Burkina Faso is a land-locked country in the West African Sahel belt and shares borders with Mali, Niger, Benin, Togo, Ghana and Ivory Coast (Fig. 1.1). The climate is hot and semi-arid, with rainfall restricted to a monsoon season in June – September. A rough NE-SW rainfall gradient exists, with average total annual precipitation of ~450 mm in the far north-east to ~1100 in the south-west (Source: Direction de la Météorologie du Burkina). Three quarters of the land surface of Burkina Faso belongs to the Volta watershed and is drained by the Mouhoun (Black Volta), Nakambé (White Volta) and Nazinon (Red Volta). The original savannah and steppe vegetation has largely been decimated by livestock grazing, agriculture and firewood collection (Stéphenne & Lambin, 2001). 70% of Burkina Faso's population of 19 million (United Nations, 2017b) still live in rural areas and chiefly rely on rain-fed subsistence agriculture of millet, sorghum, maize, cotton, beans and peanuts. In the last decades, numerous small dams have been constructed to catch surface runoff during the monsoon. Along their shores, more irrigation-intensive crops such as rice, fruits and market garden vegetables are cultivated.

Fig. 1.1 Geographical location of Burkina Faso

The geology of Burkina Faso is dominated by Paleoproterozoic crystalline basement rocks belonging to the West African craton and covering roughly three quarters of the country. Volcanic and meta-sedimentary rocks of the Birimian Formation (2240 – 2170 Ma) were intruded by massive granitic batholiths during the Eburnean orogeny (2210 – 1800 Ma) (Castaing et al., 2003a). The Birimian formation has undergone considerable mineralisation, leading to the formation of mineral deposits, particularly gold (Au) in hydrothermal quartz-sulphide veins or disseminated in the host rock.

1.6.1 Hydrogeology

Millions of years of intense in-situ bedrock weathering have formed a dense fissure and fracture network that now constitutes the aquifers of the region (Lachassagne et al., 2011;

Soro et al., 2017). Shallow groundwater (down to ~20 m below ground level) can be found in the highly weathered, clayey saprolite, but is vulnerable to drops in water level during the long dry season and to anthropogenic pollution from human settlements and agricultural activities (Huneau et al., 2011; Nikiema et al., 2010). The deeper, fractured bedrock aquifer represents a more secure groundwater resource. In general, groundwater levels are lower in the arid north of the country (~25-35 m b.g.l.) as opposed to the more humid south (~5 – 15 m b.g.l.) (Filippi et al., 1990). Estimations of annual groundwater recharge are scarce for Burkina Faso. Filippi et al. (1990) made recharge estimations using water balance-based hydrological models for nine sites throughout the country, estimating 47 mm/a for the most arid site (annual rainfall ~500 mm) and 260 mm/a for the most humid site (~1100 mm annual rainfall), but the authors also argue that these values may be overestimated. Apambire et al. (1997) and Dapaah-Siakwan and Agyekum (2008) cite sources that propose annual recharge between 2.5 – 4 % of annual precipitation, which seems more reasonable and also corresponds to figures given by Martin and Van De Giesen (2005). Little is known about the exact recharge mechanisms. Stable isotope investigations (^{2}H, ^{18}O) show that water generally does not undergo significant evaporation (e.g. due to prolonged surface exposure) before recharge, and that the strong rain events at the height of the rainy season contribute most significantly to groundwater recharge (Huneau et al., 2011; Jasechko & Taylor, 2015). The fractured aquifers respond very differently to precipitation due to highly heterogeneous physical aquifer properties, with delays of between one to four months seen until groundwater levels react to the monsoon (Compaore et al., 1997; Filippi et al., 1990; Tirogo et al., 2016).

1.6.2 Rural drinking water supply

Due to a lack of perennial surface water resources, rural drinking water production relies heavily on groundwater from these aquifers. Tube wells with depths between 30 – 90 m and equipped with hand pumps tap groundwater from fractured bedrock (Courtois et al., 2010), while dug wells with depths < 25 m reach shallower aquifers in the weathered saprolite (Fig. 1.2). The yields of these wells are not very high, typically between 1 – 5 m^{3}/h (Courtois et al., 2010).

Groundwater quality has, until recently, not been thoroughly investigated in Burkina Faso. Only in 2004 did a study in the northern province of Yatenga reveal that numerous tube wells were affected by As concentrations above the WHO guideline value of 10 μg/L, with maximum measured concentrations of up to 1630 μg/L (COWI, 2004; Smedley et al., 2007).

Fig. 1.2 Examples of hand pump types commonly installed in tube wells in Burkina Faso. The picture on the left shows an "India" hand pump, on the right a "Volanta" hand pump.

A high prevalence of skin lesions was also observed in villagers drinking water from high-As sources (Barro-Traoré et al., 2008; Somé et al., 2012). Smedley et al. (2007) attributed the elevated As to stem from sulphide minerals in auriferous zones, as occur in the Birimian volcano-sedimentary rocks. Generally good water quality with respect to drinking water standards (except NO_3^-) was found in shallow dug wells by Nikiema et al. (2010) and (2013). Overall, many open questions still exist concerning the origin and dynamics of As concentrations in aquifers of Burkina Faso.

1.7 Objectives

This dissertation attempts to advance scientific understanding on the overarching topic of arsenic-affected groundwater in Burkina Faso on multiple spatial and temporal scales and using a diverse set of methods. The following broad research questions were addressed:

1) What is the magnitude of geogenic As contamination in Burkina Faso, which regions are especially at risk and how many people are potentially affected?

2) Do temporal aspects such as groundwater residence time and seasonal fluctuations have an influence on the occurrence, distribution and concentrations of As in fractured crystalline bedrock aquifers?

3) Which low-cost, low-tech technologies are suitable for As drinking water treatment in Burkina Faso? Can zero-valent iron-based household filters effectively remove As below 10 μg/L?

These objectives are addressed in three separate studies that compose the main research chapters of this thesis and are herewith briefly outlined:

Groundwater arsenic contamination in Burkina Faso, West Africa: Predicting and verifying regions at risk (Chapter 2):

In many countries, field testing of groundwater As concentrations lags behind due to a lack of resources such as funding, equipment and know-how. Hazard prediction maps identifying regions which are most at risk and should be prioritised in drinking water surveys can be useful tools for authorities and scientists alike (e.g. Ayotte et al. (2006); Rodríguez-Lado et al. (2013); Winkel et al. (2008)). Multivariate logistic regression was used to find the statistically most significant predictors for groundwater As from a range of independent geological and mineralogical variables. The model was calibrated and validated with As measurements from various regions in Burkina Faso. By combining population density data with the resulting hazard maps, estimations of the number of people potentially exposed to As-contaminated groundwater in Burkina Faso could be made.

Hydrogeochemical and multi-tracer investigations of arsenic-affected aquifers in semi-arid West Africa (Chapter 3):

Apart from the hypothesis that As stems from sulphide minerals in auriferous zones (Sako et al., 2016; Smedley et al., 2007), little is known about the processes governing As occurrence in the West African fractured bedrock aquifers. Especially the influence of groundwater residence time and seasonal monsoon precipitation on As concentrations has not been investigated. In order to capture small-scale variability, field measurements and sampling was carried out in a small study area (~80 km^2) in south-western Burkina Faso. In addition to major ions, trace elements and stable isotopes (^{18}O, ^{2}H), dissolved noble gases were sampled for the first time in these shallow to moderately deep fractured aquifers. ^{3}He/^{4}He ratios gave new insights on groundwater residence time, leading to an improved conceptual model of groundwater As occurrence.

Arsenic removal with zero-valent iron filters in Burkina Faso – field and laboratory insights (Chapter 4)

Arsenic mitigation activities are still largely unexplored in Burkina Faso, but increasing interest from authorities, NGOs and donors has shown the necessity of viable solutions. Currently, tube wells identified as contaminated are closed by the authorities, often without replacement.

Building up on the efficient As removal of the Fe(0)-based SONO household filter in Bangladesh (Hussam & Munir, 2007; Neumann et al., 2013), it was hypothesised that similar systems can be effective in Burkina Faso, considering that groundwater contains As(V) and has an optimal pH-range (6.5 – 7.5) for As adsorption to Fe(0). A key to the success of the SONO filter is its composite iron matrix, composed of fine iron shavings. A similar material, free from oily residues, could not be located in Burkina Faso. Pilot filters were therefore constructed with small, locally available iron nails as an Fe-oxide source and tested for nine months in households with highly contaminated tube wells (~400 - ~1300 μg As/L). In parallel, a laboratory study with filter columns enabled testing different filter set-ups and finding the optimal conditions for As removal with respect to flow rate, contact time and pH.

Despite their distinct topics and stand-alone character, the chapters are nevertheless connected and build up on each other. The broad, country-scale assessment presented in Chapter 2 gives a first overview of the magnitude of As contamination and serves as a foundation for the two follow-on studies. The large spatial heterogeneity in As occurrences warranted a more detailed, catchment-scale approach (Chapter 3) allowing an evaluation of dynamic processes not covered by the static, low-resolution geological data of Chapter 2. Finally, the third study addresses As mitigation on the scale of single households and tube wells and with a temporal resolution of days, detail that is necessary to capture fluctuations in a filter’s performance.

The principal findings of this thesis and their relevance are discussed in Chapter 5, including suggestions for future fields of research.

2 Groundwater arsenic contamination in Burkina Faso, West Africa: Predicting and verifying regions at risk

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Abstract

Arsenic contamination in groundwater from crystalline basement rocks in West Africa has only been documented in isolated areas and presents a serious health threat in a region already facing multiple challenges related to water quality and scarcity. We present a comprehensive dataset of As concentrations from drinking water wells in rural Burkina Faso (n=1498), of which 14.6% are above 10 μg/L. Included in this dataset are 269 new samples from regions where no published water quality data existed. We used multivariate logistic regression with As measurements as calibration data and maps of geology and mineral deposits as independent predictor variables to create As prediction models at concentration thresholds of 5, 10 and 50 μg/L. These hazard maps delineate areas vulnerable to groundwater As contamination in Burkina Faso. Bedrock composed of schists and volcanic rocks of the Birimian formation, potentially harbouring As-containing sulphide minerals, has the highest probability of yielding groundwater As concentrations >10 μg/L. Combined with population density estimates, the As prediction models indicate that ~560,000 people are potentially exposed to As-contaminated groundwater in Burkina Faso. The same As-bearing geological formations that are positive predictors for elevated As concentrations in Burkina Faso also exist in neighbouring countries such as Mali, Ghana and Ivory Coast. This study's results are thus of transboundary relevance and can act as a trigger for targeted water quality surveys and mitigation efforts.

2.1 Introduction

Despite the increased construction and development of centralised water distribution systems and piped water supplies in sub-Saharan Africa during the last decades, small-scale groundwater abstraction via hand-dug wells or village hand pumps is often the sole source of drinking water for rural populations (MacDonald et al., 2009; Martin & Van De Giesen, 2005). Especially in the arid and semi-arid regions of the Sahel belt, where surface water resources can dry out completely in the long dry season, rural areas rely on groundwater for their drinking water supply (Edmunds, 2008). In general, groundwater is regarded as having good drinking water quality and to be predominantly free of pathogens, but chemical constituents may present a hazard that is often discovered late or not at all due to insufficient testing and surveying of water quality (MacDonald & Calow, 2009; UNICEF, 2008).

This is the case for As, which can occur naturally in groundwater in concentrations that can lead to serious and chronic health effects after prolonged consumption (Naujokas et al., 2013). As exposure has not only been linked to the development of a variety of cancers, but also to developmental, neurological, respiratory and cardiovascular effects (Argos et al., 2010; Naujokas et al., 2013; Yuan et al., 2010; Yuan et al., 2007). The World Health Organisation (WHO) has imposed a drinking water guideline concentration for As of 10 µg/L, which has also been adopted by Burkina Faso (MAHRH/MS, 2005; WHO, 2011). Large-scale geogenic contamination of groundwater with As in South and Southeast Asia (e.g. Bangladesh, India, Cambodia, Vietnam) has received a lot of attention in the last two decades (e.g. Bhattacharya et al. (1997); Flanagan et al. (2012); Smith et al. (2000), Berg et al. (2007)). The phenomenon is still relatively unknown and little studied in West Africa though (Ahoulé et al., 2015), where fractured aquifers composed of weathered crystalline bedrock predominate. This is a totally different system to the young sedimentary aquifers of As-affected regions in Asia, where As is released by reductive dissolution (Ahmed et al., 2004). Studies in Ghana and Burkina Faso have shown that the oxidation of As-containing sulphide minerals found in rocks of the Birimian formation is the primary process responsible for high As levels found in some groundwater (Asante et al., 2007; Barro-Traoré et al., 2008; Buamah et al., 2008; Sako et al., 2016; Smedley, 1996; Smedley et al., 2007; Somé et al., 2012). However, an understanding of the extent of the problem and a detailed investigation of the sources and geological conditions leading to As contamination is currently lacking.

Since testing wells for As contamination is expensive and time consuming, maps identifying areas that are especially vulnerable to this kind of pollution are largely missing. However, they would be a useful tool for decision makers by helping to focus efforts where they are most needed. Such groundwater vulnerability assessment and mapping is a growing field, with more and more studies focussing on finding methods to assess the vulnerability of aquifers to contaminants such as nitrate or pesticides (Nolan & Hitt, 2006; Nolan et al., 2002; Ouedraogo et al., 2016; Sorichetta et al., 2013).

Specifically concerning As, statistical modelling to predict the spatial occurrence of As and highlight areas where safe drinking water predominates has been performed successfully at different scales, from global to regional, and in a range of different geological terrains (Ahn & Cho, 2013; Amini et al., 2008; Ayotte et al., 2016; Ayotte et al., 2006; Dummer et al., 2015; Rodríguez-Lado et al., 2013; Shamsudduha et al., 2015; Winkel et al., 2008; Winkel et al., 2011; Yang et al., 2012). Fundamental to the development of such models is knowledge of the geochemical processes leading to the occurrence of high As in groundwater, as well as finding the predictor variables (proxies) to explain these. Since geogenic As is by definition of geological origin, such proxies are usually geological variables, but various environmental parameters, such as temperature or precipitation, that influence geochemical processes in groundwater may also be relevant (Amini et al., 2008).

The concentration of As in groundwater is not only related to the abundance of As found in minerals in the aquifer matrix, it is also a function of solubility, which is governed predominantly by pH and redox conditions (Dixit & Hering, 2003; Hug & Leupin, 2003). In China, for example, Rodríguez-Lado et al. (2013) found elevated groundwater As concentrations in sedimentary basins and river valleys to be strongly associated with Holocene sediments, soil salinity, fine subsoil texture and an elevated Topographic Wetness Index, which functioned as proxies for chemically reducing environments with high As solubility. In the case of As release due to sulphide mineral oxidation in crystalline basement rocks, different proxies must be taken into account, as has been shown by Ayotte et al. (2006), Yang et al. (2012), Ahn and Cho (2013) and Dummer et al. (2015) who modelled a positive correlation between As occurrence and certain mineral-bearing geological formations.

The goal of this study is to investigate the distribution and magnitude of geogenic groundwater As concentrations in Burkina Faso in order to better identify affected areas and populations. We carried out a country-wide As survey and created As prediction models based on three different concentration thresholds (5, 10 and 50 μg/L) taking into account the geochemical processes and conditions responsible for elevated As in groundwater in West Africa. The models were calibrated using a spatially limited As measurement dataset and then validated with measurements from other regions in Burkina Faso to ensure country-wide validity. As is often the case in developing countries, datasets of physical parameters such as geology, hydrogeology, mineral resources and climate were not available to the same extent or resolution as in industrialised nations. For this study, only surface parameters were available. The depth of individual boreholes and lithological logs were not available. Therefore, another goal of this study was to investigate whether a reliable hazard model for As can be produced in light of data scarcity. Due to the large number of countries in the West African region and the difficulty in collecting the necessary data for each individual country, we chose a single "model" country for which to create As prediction models. Burkina Faso was selected because some existing studies already show elevated groundwater As but are limited in their spatial extent (Barro-Traoré et al., 2008; COWI, 2004; Nzihou et al., 2013; Ouédraogo & Amyot, 2013; Sako et al., 2016; Smedley et al., 2007; Somé et al., 2012). The same geological formations that harbour As-containing sulphide minerals in Burkina Faso are also found in neighbouring countries such as Mali, Niger, Ivory Coast, Ghana and Benin (Schlüter, 2008). Therefore, this study is relevant to the greater West African region and should spur increased discussion and mitigation efforts concerning As contamination and its health effects.

2.2 Hydrological and geological setting and its relevance to elevated As concentrations

Burkina Faso has a hot and dry semi-arid climate, with rainfall restricted to one rainy season per year from June to September. Rainfall is higher in the south-west than in the more arid north and east. Groundwater recharge occurs during the rainy season with smaller total amounts in the north than in the south-west, but can be spatially highly heterogeneous (Filippi et al., 1990; Martin & Van De Giesen, 2005). Geomorphologically, Burkina Faso is relatively flat, with most of the country lying between 250 and 400 m a.s.l. (Fig. 2.1). 65% of the land area of Burkina Faso is covered by the Volta basin and is drained by the Mouhoun, Nazinon and Nakambé rivers (Black, Red and White Volta) (Martin & Van De Giesen, 2005).

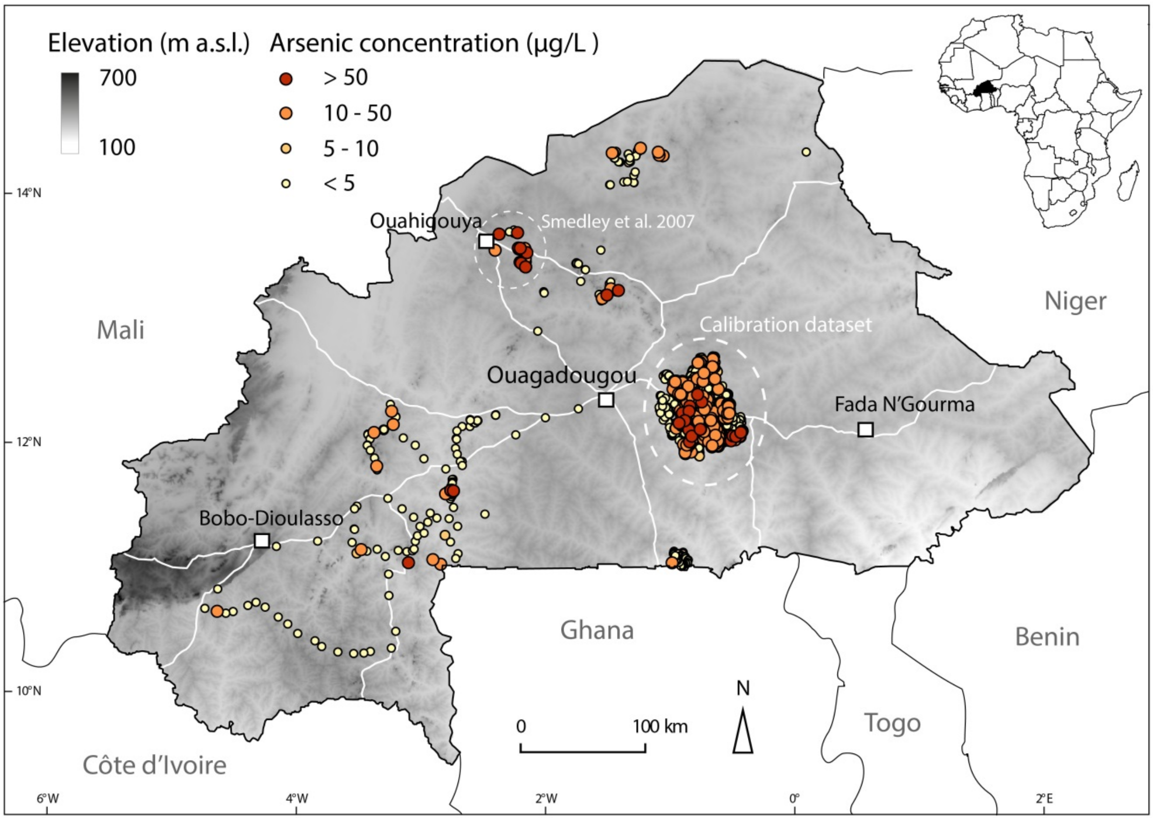

Fig. 2.1 Overview of the study area, giving the location of groundwater As measurements used in this study (n=1498). The calibration dataset from the Province of Ganzourgou (source: Unicef/BUMIGEB) is represented by the large cluster of points east of Ouagadougou (n=1184). The remaining points comprise the validation dataset (n=314), which includes data from Smedley et al. (2007) (n=45) and the new measurements presented in this study (n=269).

Between the in-tact crystalline bedrock at depth and the ground surface, a typical tropical hard-rock weathering profile exists and controls the local hydrogeological properties, explained in more detail in Courtois et al. (2010) and Nikiema et al. (2013). The top few metres of the ground surface are usually composed of a laterite crust, underlain by a few tens of metres of weathered clayey saprolite, which represents the upper part of the aquifer. This then merges into the so-called fissured layer (densely fissured and fractured weathered bedrock), which can extend to a depth of 80-100 metres below ground level and acts as the main aquifer for groundwater storage (Courtois et al., 2010). In rural areas, boreholes for drinking water abstraction with hand pumps are drilled into the fissured layer and have depths ranging from 35-90 metres. Hand-dug wells tapping shallower aquifers in the weathered saprolite layer may also be used for drinking water purposes.

A large part of Burkina Faso is covered by Paleoproterozoic crystalline basement rocks. These comprise belts of (meta-)volcanic, metasedimentary and plutonic rocks of the Birimian Formation, as well as large intrusive bodies of Eburnean granitoids (granite, tonalite, granodiorite) (Fig. 2.2). The Birimian volcano-sedimentary belts (also known as Birimian greenstone belts) were formed as part of an island-arc system between 2240 and 2170 Ma. They are composed of varied volcanic and plutonic rocks, including basalt, andesite, rhyolite and gabbro, that occur next to schists, quartzite and chert (Castaing et al., 2003a). The Birimian formation has undergone considerable mineralisation that was synchronous with regional metamorphism and deformation. This led to the formation of high-grade ore deposits, primarily gold and to a lesser extent other metallic ores. Gold deposits principally occur within or adjacent to quartz veins that formed later than the host rock (Béziat et al., 2008). Native gold can occur directly within deformed quartz veins, or as gold particles disseminated in the alteration halos of unfolded quartz veins. Both mineralisation types are directly associated with the occurrence of sulphide minerals such as pyrite (FeS_2) and arsenopyrite (FeAsS) (Béziat et al., 2008; Bourges et al., 1998; Castaing et al., 2003a). Pyrite can incorporate minor and trace elements into its mineral structure and As concentrations in pyrite can occur up to 10 wt% (Abraitis et al., 2004). The oxidation of such sulphide minerals when in contact with oxygen-containing groundwater and subsequent release of As to solution can lead to considerably elevated groundwater As concentrations (Verplanck et al., 2008; Walker et al., 2006; Yang et al., 2015). In general, depending on the redox conditions in the subsurface, As should stay in solution in its reduced form As(III) if reducing conditions are prevalent, but should be tightly adsorbed to iron hydroxides if conditions are oxidising (Dixit & Hering, 2003). Nevertheless, Smedley et al. (2007) measured clearly elevated As concentrations in oxidising groundwater in Burkina Faso and hypothesised that these high concentrations occur in the direct vicinity of mineralised zones where the As loading in groundwater can be very high locally.

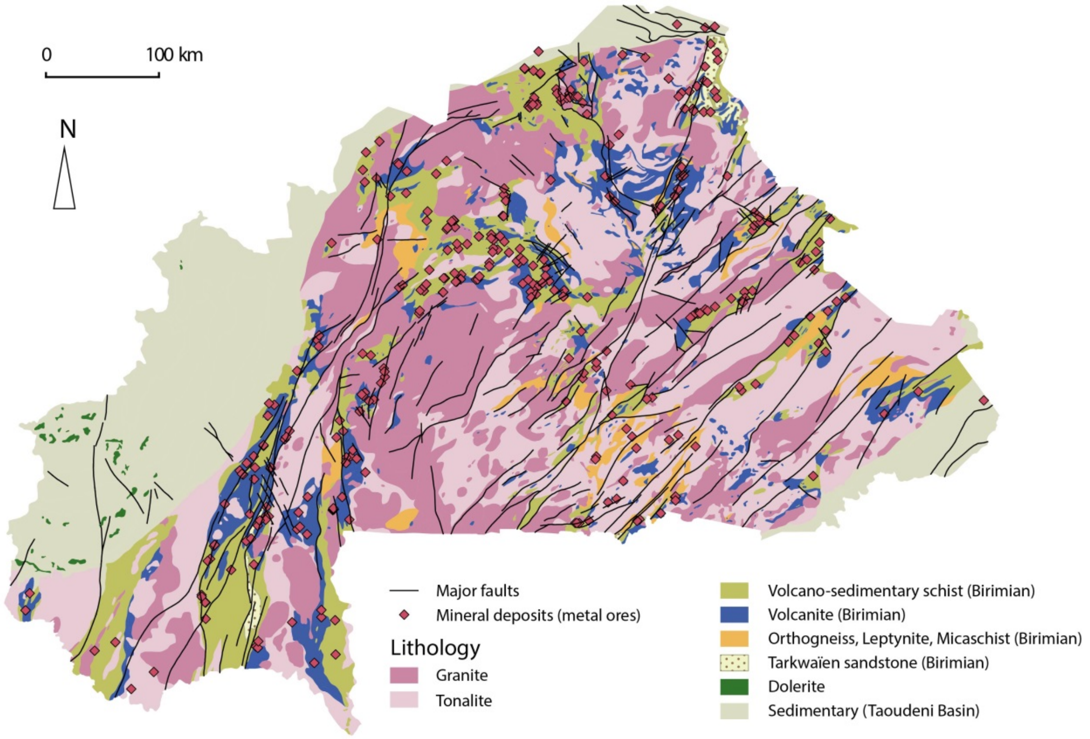

Fig. 2.2 Simplified geological map of Burkina Faso, showing the main rock types, major faults and the location of mineral deposits (metal ores). Modified from Castaing et al. (2003b)

2.3 Methods

2.3.1 Data collection and processing

2.3.1.1 Arsenic concentration measurements

A dataset (n=1498) of georeferenced groundwater As concentration measurements from boreholes in rural areas was used in this study to calibrate and validate the As prediction model (Fig. 2.1). The dataset includes both new and existing data (Table 2.1). Included in the 1498 measurements are 269 new groundwater samples taken specifically for this study from 2014 to 2016 in different regions of Burkina Faso (Table 2.1, Fig. 2.1). Samples originate from village boreholes equipped with hand pumps (types India, Volanta or Vergnet). We followed standard sampling and laboratory analysis procedures as described in similar studies (Berg et al., 2008; Buschmann et al., 2007). On-site parameters (temperature, pH, electrical conductivity, O_2 concentration and redox potential) were measured in a flow-through cell connected to the pump spout. Water sampling was performed after on-site parameters had stabilised, generally after 5-10 minutes. All sampled boreholes are pumped nearly continuously during the day by local residents for drinking water production, hence water was never stagnant in the pipes during sampling. Samples for major cations and minor and trace element analysis (including As) were collected in acid-washed polypropylene bottles, filtered through 0.45 μm filters and acidified with concentrated HNO_3 suprapure to a pH < 2. An unfiltered, non-acidified aliquot was collected for analysis of anions, DOC and TIC. Samples were stored below 4°C whenever possible. Analysis was performed in the laboratories of Eawag, Switzerland, using ICP-MS (Agilent 7500 cx) for cations and trace elements, ion chromatography for anions (ICS-2001 Dionex) and a carbon analyser (TOC Shimadzu) for TIC and DOC.

Table 2.1 Arsenic concentration measurements (n=1498) used for model calibration and validation

	Province	**No. of samples**	**% > 10 μg/L As**	**Source**
Calibration data	Ganzourgou	1184	15.5 %	Unicef/BUMIGEB
Validation data	Yatenga	45	42 % *	Smedley et al., 2007
	Nahouri	52	2 %	This study
	Soum	38	13 %	This study
	Balé	31	16 %	This study
	Various (South-West)	101	9 %	This study
	Bam	22	14 %	This study
	Boulkiemdé	15	0 %	This study
	Various	10	20%	This study

* Non-random sampling specifically targeting As-affected boreholes

Also included in the total dataset of 1498 samples are 1184 As measurements obtained through a study commissioned by Unicef Burkina Faso and carried out by the "Bureau des Mines et de la Géologie du Burkina" (BUMIGEB) in 2010 to measure As concentrations in drinking water boreholes in the province of Ganzourgou, 50 km east of Ouagadougou (Table 2.1). Samples were measured in the laboratories of BUMIGEB using Atomic Absorption Spectroscopy (AAS). Depths of individual boreholes are not known, however a separate database of 434 boreholes from the province of Ganzourgou contains depths ranging from 35 to 90 metres, with a mean of 51 metres. In addition to the Ganzourgou data, 45 As measurements from the Ouahigouya region (Yatenga province) in northern Burkina Faso were provided by Smedley et al. (2007).

2.3.1.2 Model variables

Independent predictor variables

Georeferenced map data with a country-wide coverage were considered as predictor variables for the As prediction model. As groundwater As in Burkina Faso is thought to originate from sulphide minerals in mineralised zones, focus was set on assembling predictor variables that could indicate such mineralisation, such as lithological variables and distances to mineral deposits, faults and granitic intrusions (Table 2.2). The Geological and Mineral Deposit Map of Burkina Faso at a scale of 1:1,000,000 (Castaing et al., 2003b) was used to extract major lithologies, faults and the location of mineral deposits of metal ores (e.g. gold, zinc, chromium, manganese) (Fig. 2.2). In addition to the location of mineralised zones, groundwater flow and residence time may also play a role in As concentrations. Due to the heterogeneity of fractured bedrock aquifers, mapping such parameters on a regional or country-wide scale is problematic (Dewandel et al., 2012). As possible proxies for hydrological processes related to groundwater flow and residence time we chose the “drainage direction” and “flow accumulation” datasets of the Hydrosheds database (Lehner et al., 2008). These data are derived from the digital elevation model (DEM) of the Shuttle Radar Topography Mission (SRTM).

The predictor data layers were converted to raster format (if originally in vector format such as polygon, line or point) with a resolution of 30 arc seconds (1 km on the equator) using standard tools available in the open source QGIS and GRASS software packages (GRASS Development Team, 2015; QGIS Development Team, 2015). The distances to faults, mineral deposits, and granitic rocks were calculated within a buffer zone of a maximum of 10 km away from the feature.

Table 2.2 Predictor variables used in the As prediction model

Predictor variables	Type	Format	Source
Volcano-sedimentary schist (Birimian)	Categorical	Polygon	BUMIGEB/BRGM (Castaing et al., 2003b)
Volcanite: basalt, andesite, rhyolite (Birimian)	Categorical	Polygon	
Orthogneiss (Birimian)	Categorical	Polygon	
Granite	Categorical	Polygon	
Tonalite	Categorical	Polygon	
Distance to faults	Continuous	Raster	
Distance to mineral deposits (metal ores)	Continuous	Raster	
Distance to granitoid rocks	Continuous	Raster	
Drainage direction	Continuous (30 arc seconds)	Raster	HydroSHEDS/WWF (Lehner et al., 2008)
Flow accumulation	Continuous (30 arc seconds)	Raster	

Dependent variable (Arsenic concentration measurements)

In order to be compatible with the predictor variables, the calibration dataset of As concentration measurements was converted from point to raster format and concentrations aggregated to one value per 1 km^2 pixel by using the maximum As concentration if more than one measurement fell into the pixel. We chose the more conservative maximum value instead of averaging concentrations in order to ensure that high-As boreholes remain in our analyses and are not "diluted" by surrounding low concentrations. As such, the original calibration dataset of 1184 individual As measurements was reduced to 877 measurements, with 39% above 5 µg/L, 19% above 10 µg/L and 2% above 50 µg/L. The aggregated concentration values were binary-coded according to the chosen threshold (above threshold = 1, below threshold = 0) and used as the dependent variable in the logistic regression model. We chose the threshold values of 5, 10 and 50 µg/L to represent the full concentration range of the dataset. Furthermore, 10 µg/L is the WHO and national drinking water guideline value and therefore of greatest relevance for drinking water. Discussions also exist in Burkina Faso of raising the guideline value to 50 µg/L, a value that is used in some other As-affected countries, such as Bangladesh. The calibration dataset from Ganzourgou Province has a limited spatial extent (4000 km^2) but very dense borehole coverage within this area. All predictor variables are present in this zone and any potential spatial bias is therefore limited. On the other hand, the validation dataset (composed of the 269 new samples described in this study, plus 45 samples from Smedley at al. (2007)), is spatially well distributed and includes locations from the north, south and west of Burkina Faso (Fig. 2.1).

2.3.2 Geospatial hazard modelling

Logistic regression was used to model the probability of As occurring over three concentration threshold values. This method is extensively used in a variety of fields to determine the relationship between a binary dependent outcome variable and a number of independent predictor variables (Hosmer et al., 2013). Specifically, logistic regression models the log(odds), which is defined as the probability P that an event occurs relative to the probability that it fails to occur *(1 – P)*, (e.g. As being above/below the threshold concentration), as the linear combination of a set of independent predictor variables $x_1 \ldots x_k$ with model coefficients $\beta_1 \ldots \beta_k$ (Hosmer et al., 2013):

$$\log(odds) = \log\left(\frac{P}{1-P}\right) = \beta_0 + \beta_1 x_1 + \ldots + \beta_k x_k$$

Removing the logarithm then gives the probability:

$$P = \frac{e^{(\beta_0 + \beta_1 x_1 + \ldots + \beta_k x_k)}}{1 + e^{(\beta_0 + \beta_1 x_1 + \ldots + \beta_k x_k)}}$$

The exponential of the model coefficients exp(β) being greater than 1 indicates an increasing effect of the predictor variable on the dependent variable, while a value less than 1 denotes a decreasing effect.

Logistic regression modelling was carried out within the R statistical environment (R Core Team, 2015). We have followed similar procedures as described in detail in Rodríguez-Lado et al. (2013). Univariate logistic regressions for the three chosen thresholds of 5, 10 and 50 μg/L were performed separately on each predictor variable using the whole calibration dataset as the dependant variable. The drainage direction and flow accumulation datasets were discarded from further analyses as they did not prove to be significant predictors for elevated As at the

95%-confidence level in the univariate models (p-values > 0.05) (Table 2.3). The orthogneiss, tonalite and "distance to faults" predictors were also not significant (Table 2.3), but were nevertheless kept for further analyses. Orthogneiss belongs to the partly mineralised Birimian formation and could potentially be linked to As contamination, tonalite is a widespread rock type in Burkina Faso with a large spatial coverage (Fig. 2.2) and fault zones as areas of increased fracturing and/or deformation are also hypothesised to be potential proxies for mineralised zones.

Table 2.3 Results of univariate logistic regression models for three concentration thresholds. Significant values at the 95%-confidence level ($p < 0.05$) are highlighted in bold font

Predictor variables	**p-values**		
	5 µg/L	**10 µg/L**	**50 µg/L**
Volcano-sedimentary schist (Birimian)	**<0.001**	**<0.001**	**<0.001**
Volcanite: basalt, andesite, rhyolite (Birimian)	**0.01**	**<0.001**	0.99
Orthogneiss (Birimian)	0.22	0.15	0.99
Granite	**0.002**	**<0.001**	**0.01**
Tonalite	0.40	0.06	0.44
Distance to faults	0.67	0.42	0.19
Distance to mineral deposits (metal ores)	**<0.001**	0.87	**0.02**
Distance to granitoid rocks	**<0.001**	**<0.001**	**<0.001**
Drainage direction	0.14	0.63	0.31
Flow accumulation	0.59	0.81	0.93

The remaining eight predictor variables were used for multivariate logistic regression. Instead of single-algorithm models, which are vulnerable to the number and location of the calibration data, we chose to create an ensemble model from numerous base models (ensemble members) for more robust results (Rodríguez-Lado et al., 2013). The calibration dataset was randomly split into training (75%) and testing (25%) portions for multivariate logistic regression with stepwise selection (both directions), whereby predictor variables are automatically retained or removed according to the Akaike Information Criterion (AIC) (Akaike, 1974). This procedure was repeated 100 times, creating 100 models each calculated with a different subset of training data. These models were then used to calculate probabilities for the testing data subsets, whereby the Hosmer-Lemeshow goodness-of-fit test at the 95%-confidence level was applied to assess the accuracy of the model, i.e. whether the model is consistent with the testing data that were not used to calibrate it (Hosmer et al., 2013). Models with a significant Hosmer-Lemeshow test ($p < 0.05$) indicate that there is no relationship between predicted and observed data. Models with a high p-values ($p > 0.05$) in this test were therefore retained. Of the remaining ensemble members, a weighted mean of the model coefficients ($\beta_{1\ldots k}$) was calculated to generate a final ensemble model for each of the three threshold concentrations. Weighting was applied according to the frequency that a predictor variable was retained by stepwise selection in the ensemble members. In this way, predictor variables that occurred frequently in many ensemble members received a higher weighting and greater relative importance in the final ensemble model than variables that were retained in relatively few ensemble members. Variables that were present in less than 5 out of a maximum of 100 ensemble members were not considered for the final model. See Fig. 2.3 for a summary of the above-mentioned procedure. A Receiver Operating Characteristics (ROC) curve was computed on the final ensemble model using the whole calibration dataset to assess how well the model discriminates between low and high risk observations (Fawcett, 2006). For this, the rate of true positives (sensitivity) was plotted against the rate of true negatives (specificity) and the area under the curve (AUC) computed. An AUC value of 0.5 denotes a model that is no better than a random model, and a value of 1 would be a perfect prediction.

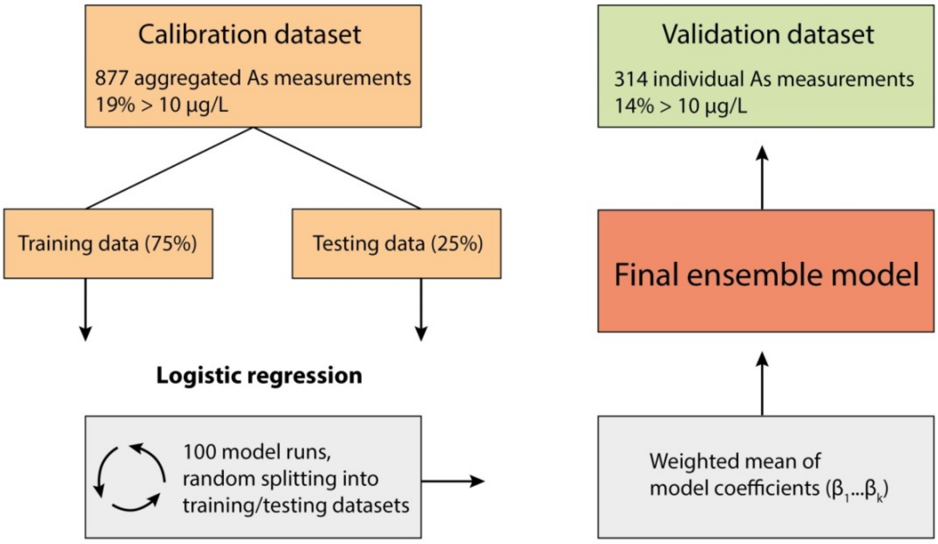

Fig. 2.3 Overview of the logistic regression modelling procedure

2.3.3 Hazard map generation

The final model coefficients were used to generate hazard maps showing the modelled probability of groundwater As concentrations exceeding the threshold concentrations of 5, 10 and 50 µg/L. The cut-off value to distinguish between low- and high-risk areas was chosen where the sensitivity and specificity of the model were equal (Rodríguez-Lado et al., 2013; Winkel et al., 2008). To calculate how many people are potentially affected by elevated As in their drinking water, we combined the hazard map with population density estimates obtained from the Center for International Earth Science Information Network - CIESIN - Columbia University (2016).

2.4 Results and Discussion

2.4.1 Arsenic concentration data

The full chemical analysis performed on the 269 new groundwater samples presented in this study will only be discussed briefly here to give a broad overview of water chemistry. Results are summarised in Table 2.4 and show that groundwater is generally near-neutral in pH, contains dissolved oxygen and is largely of good chemical quality for drinking. Arsenic is by far the contaminant of greatest concern, with 9.6% of samples above the WHO and national guideline value of 10 µg/L. Arsenic speciation measurements were carried out on few samples (n=31) from the province of Balé, about 180 km south-west of Ouagadougou and show that As is predominantly present as As(V), confirming the findings of Smedley et al. (2007). No other trace elements show significantly high concentrations and dissolved iron concentrations are typically very low. Nitrate concentrations are high in some boreholes, with 5.6% of samples above the WHO guideline value of 50 mg/L (Table 4). Drinking water boreholes are generally located in the immediate vicinity of human dwellings and are also used for watering livestock, therefore human and animal waste is a likely source of nitrate to groundwater (Huneau et al., 2011; Nikiema et al., 2010). Geogenic fluoride contamination is restricted to the southern province of Nahouri close to the village of Tiébélé, where the fluoride concentrations of only a few samples were slightly above the WHO guideline value of 1.5 mg/L (Table 2.4). This region is directly adjacent to Bongo district of northern Ghana, where geogenic fluoride contamination originating from alkaline granitic rocks has been extensively documented (Alfredo et al., 2014; Apambire et al., 1997; Salifu et al., 2012).

Table 2.4 Summary results of field and laboratory analyses performed on new groundwater samples

Parameter	Unit	Minimum	Maximum	Mean	Median	St.Dev	n	WHO guideline	% > guideline
pH	-	4.85	8.18	6.75	6.86	0.45	221	-	-
EC	µS/cm	26.0	2311	369	339	219	220	-	-
O_2	mg/L	0.40	6.26	2.22	2.01	1.13	134	-	-
Temp.	°C	26.7	33.0	30.9	31.0	0.98	221	-	-
Eh	mV	69	305	250	281	64	21	-	-
DOC	mg/L	0.25	3.1	0.42	0.25	0.48	269	-	-
TIC	mgC/L	1.5	112	42	39	22	269	-	-
HCO_3	mg/L	7.5	560	212	197	110	269	-	-
F	mg/L	< 0.1	2.55	0.28	0.19	0.36	269	1.5	2.6
Cl	mg/L	< 0.1	129	4.11	1.23	10.8	269	-	-
Br	mg/L	< 0.1	0.63	0.07	0.05	0.06	269	-	-
NO_3	mg/L	< 0.1	1060	17.8	4.6	69.7	269	50	5.6
SO_4	mg/L	< 0.1	1250	9.90	0.83	80.9	244	-	-
PO_4	mg/L	< 0.1	14.8	0.18	0.05	0.99	244	-	-
Li	µg/L	< 0.1	94.2	15.9	11.9	15.0	269	-	-
B	µg/L	< 5	332	13.0	5.6	31.5	269	2400	-
Na	mg/L	0.7	172	21.6	18.2	16.4	269	-	-
Mg	mg/L	0.2	110	14.9	13	11.8	269	-	-
Al	µg/L	< 0.1	1952	13.1	1.5	119	269	900 (HB)	0.3
Si	mg/L	5.2	53.3	26.7	25.5	10.4	269	-	-
K	mg/L	0.16	45.0	2.41	1.51	3.75	269	-	-
Ca	mg/L	0.6	318	30.8	27.3	30.2	269	-	-
V	µg/L	< 0.02	67.5	9.63	6.78	10.6	269	-	-
Cr	µg/L	< 0.02	13.6	0.54	0.15	1.25	269	50	0
Mn	µg/L	< 0.02	1101	26.8	4.77	83.9	269	400 (HB)	-
Fe	µg/L	< 0.3	6043	155	7.35	548	269	-	-
Co	µg/L	< 0.02	4.71	0.19	0.04	0.50	269	-	-
Ni	µg/L	< 0.02	9.51	0.74	0.38	0.99	269	70	0
Cu	µg/L	< 0.1	31.7	1.77	0.66	3.37	269	2000	0
Zn	µg/L	< 0.1	3187	62.0	7.85	247	269	-	-
As	µg/L	< 0.02	421	7.56	0.4	38.8	269	10	9.6
Se	µg/L	< 0.02	4.32	0.32	0.09	0.64	269	40	0
Sr	µg/L	8	3048	259	182	312	269	-	-
Mo	µg/L	< 0.02	144	3.53	0.86	14.3	269	70 (HB)	1.1
Cd	µg/L	< 0.01	3.94	0.04	0.005	0.25	269	3	0.3
Sb	µg/L	< 0.01	16.7	0.20	0.05	1.02	269	20	0
Ba	µg/L	< 0.1	539	53.6	15.3	81.4	269	700	0
La	µg/L	< 0.01	0.59	0.04	0.01	0.08	269	-	-
Ce	µg/L	< 0.01	1.06	0.06	0.014	0.15	269	-	-
W	µg/L	< 0.02	9.97	0.31	0.075	0.84	269	-	-
Tl	µg/L	< 0.02	0.37	0.02	0.01	0.03	269	-	-
Pb	µg/L	< 0.02	8.28	0.25	0.06	0.72	269	10	0
Th	µg/L	< 0.01	< 0.01	< 0.01	< 0.01	0.00	269	-	-
U	µg/L	< 0.02	8.96	0.21	0.01	0.90	269	30	0

HB: health-based value, no formal guideline value established

The complete As concentration dataset of 1498 measurements demonstrates that elevated levels of As in groundwater are found in numerous provinces (Fig. 2.1, Table 2.1) and are not restricted to northern Burkina Faso where most previous studies were carried out (Barro-Traoré et al., 2008; Smedley et al., 2007; Somé et al., 2012). Of all 1498 collected measurements, 14.6 % contained As concentrations above the national and WHO guideline value of 10 μg/L and 2.3% above 50 μg/L. 84% of elevated As concentrations (those above 10 μg/L) fall into the range of 10 – 50 μg/L, and very high concentrations (above 50 μg/L), which are especially relevant to people's health, are much less frequent.

2.4.2 Arsenic and lithology

The percentage of samples above the given As thresholds according to the host rock type is presented in Fig. 2.4. Although As concentrations above 5 μg/L are found in all rock types with only a slight preference for Birimian lithologies, those above 10 and 50 μg/L are increasingly more likely to be only found in volcano-sedimentary schists and volcanic rocks (basalt, andesite, rhyolite) of the Birimian formation and are much less common in groundwater from granitic rocks (granite, tonalite, granodiorite). This supports findings from previous studies (e.g. Smedley et al. (2007)) that As is linked to the occurrence of sulphide minerals in volcano-sedimentary rocks of the Birimian formation. Geogenic As in groundwater is much less common in granitic areas, which have not undergone widespread alteration or hydrothermalisation processes leading to the formation of mineral deposits.

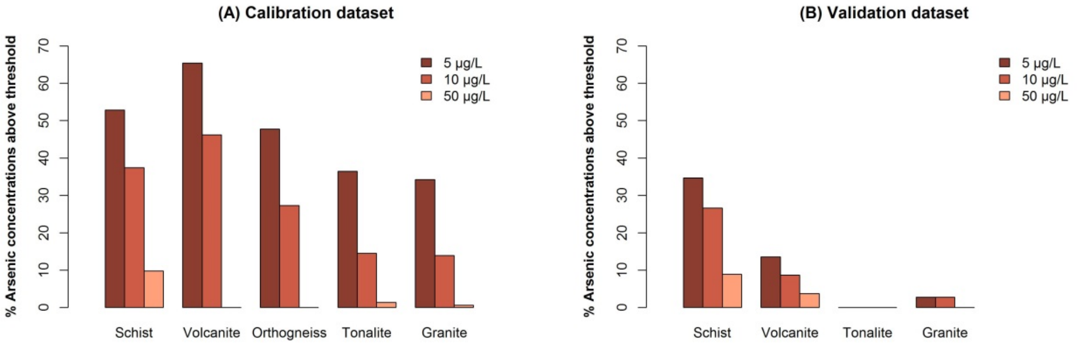

Fig. 2.4 Bar graphs showing the distribution of As concentrations above the chosen threshold value in relation to the lithology of the aquifer. A) displays the calibration dataset (aggregated to one As value per 1 km² pixel as was used for modelling, n=877), B) the validation dataset (n=314). The rock type "Orthogneiss" does not occur in areas where water was sampled for the validation dataset and is therefore not represented on the graph on the right.

Arsenopyrite and pyrite occurrence in the Birimian greenstone belts has been documented in numerous studies, e.g. Milési et al. (1992), Béziat et al. (2008). Unfortunately, data on As concentrations in pyrite minerals in Burkina Faso were not available. A database of geochemical analyses of 482 rock samples taken throughout Burkina Faso in both granitic and volcanic/metamorphic terranes (Castaing et al., 2003a) showed few samples (n=27) that had As concentrations greater than the upper crustal abundance of 5.7 mg/kg given in Hu and Gao (2008). All of these high-As samples were located within the Birimian greenstone belts and were volcanic, meta-volcanic or meta-sedimentary rocks, with the highest As concentration of 55 mg/kg being measured in a meta-basalt sample. Arsenic in groundwater can be assumed to originate from sulphide minerals in such rocks, however identifying the sources of high concentrations in specific boreholes would require very local, in-depth geochemical studies with rock samples ideally being taken during borehole drilling.

Groundwater As concentrations are subject to a great degree of spatial variability, with As-affected wells often in direct proximity to "safe" wells. This effect is observed in nearly all As-affected areas worldwide, regardless of the geological setting and As mobilisation mechanism and indicates that As concentration in groundwater is influenced by very local, small-scale conditions (Fendorf et al., 2010; Van Geen et al., 2003). In Burkina Faso, the occurrence of potentially As-containing sulphide minerals (e.g. pyrite, arsenopyrite) is linked to gold-bearing quartz veins that are heterogeneously distributed within the volcano-sedimentary schists and volcanic rocks of the Birimian belts. The occurrence of sulphide minerals can therefore vary over a scale of meters, depending on the size of mineralised veins. Smedley et al. (2007) hypothesised that As(V) may reach high dissolved concentrations in direct proximity to these mineralised zones, where it may be in equilibrium with secondary Fe-oxides having high sorbed As(V) loads. In addition, groundwater may flow in fractures that are totally isolated from each other. It is plausible that anoxic/suboxic zones may develop in such fractures, locally favouring the desorption of As(III) bound to Fe-oxides as has been suggested by Yang et al. (2015). Whether a borehole intercepts a groundwater flow path very close to a mineralised zone is likely the main factor affecting whether or not elevated As is present in the well.

2.4.3 Predicting arsenic-affected areas

Logistic regression was performed on the calibration dataset for the three chosen thresholds using eight explanatory variables as predictors for elevated groundwater As occurrence. For all three thresholds, only some of the lithological variables were significantly related to the presence of elevated As as shown by the mean model coefficients (Table 2.5), whereas the distance variables (faults, mineral deposits, granitic intrusions) did not have a significant influence on the final ensemble model. Volcano-sedimentary schists of the Birimian formation increase the odds of wells having elevated As for all three thresholds. Birimian volcanites (basalt, andesite, rhyolite) and Birimian orthogneiss are also positive indicators for As being above 5 and 10 μg/L. The higher the As concentration, the fewer variables were significant in the model, with volcano-sedimentary schist being the dominant variable, causing a 4–fold and 17-fold increase in the odds of As being above 10 μg/L respectively 50 μg/L (Table 2.5). The probability maps in Fig. 2.5 highlight areas that are vulnerable to elevated groundwater As, showing probabilities of As exceeding the specified threshold values.

Table 2.5 Weight-averaged coefficients (β), standard deviation and frequency per 100 model runs of predictor variables that were retained in the final ensemble models. The averaged p-value of the Hosmer-Lemeshow (HL) goodness-of-fit test for the significant ensemble members is given in the last column (p-values ≤ 0.05 were discarded).

Predictor variables	**Coefficient β**	**Exp(β)**	**St. dev.**	**Freq. in analyses**	**p-value HL test**
	5 μg/L threshold				
Volcano-sedimentary schist (Birimian)	0.7	2.01	0.12	89	0.87
Volcanite (Birimian)	1.19	3.29	0.24	90	
Orthogneiss (Birimian)	0.33	1.39	0.35	46	
Distance to granitic intrusions	0.04	1.03	0.76	6	
	10 μg/L threshold				
Volcano-sedimentary schist (Birimian)	1.3	3.67	0.11	98	0.91
Volcanite (Birimian)	1.68	5.37	0.26	98	
Orthogneiss (Birimian)	0.74	2.1	0.2	83	
	50 μg/L threshold				
Volcano-sedimentary schist (Birimian)	2.82	16.77	0.54	27	0.93
Tonalite, granodiorite	0.48	1.61	1.37	8	

The highest probabilities (0.7) are calculated for the threshold of 5 μg/L, meaning that there is a 70% chance of finding As concentrations above 5 μg/L in a well in this region. The low AUC value (0.57, Fig. 2.6) denotes rather poor discriminating power of the model. This is not surprising for this low threshold and reflects the nature of the calibration data: water with As greater than 5 μg/L is well-represented in all rock types used as predictor variables, with only a slight preference for lithologies of the Birimian formation (Fig. 2.4). The lack of a clear, distinguishing predictor variable means that the specificity and sensitivity of the model are low, as high As values are frequently classified into low-risk areas and vice-versa. The AUC for the 10 μg/L model of 0.63 is also not very high. This also indicates that high As values are often found outside the regions classified as "high risk", reflecting the heterogeneity of the calibration dataset and the inability to find a clear predictor for high As. Even though As concentrations >10 μg/L are mainly found in volcanites and volcano-sedimentary schist, some occurrences are also found in granitic rocks (granite and tonalite) (Fig. 2.4), which were not determined to be significant predictors. These As measurements therefore plot as high values in low-risk areas, which reduces the model's specificity. The best AUC is calculated for the threshold of 50 μg/L, where volcano-sedimentary schists are the clearest predictor of high As concentrations and the few high values are correctly classified.

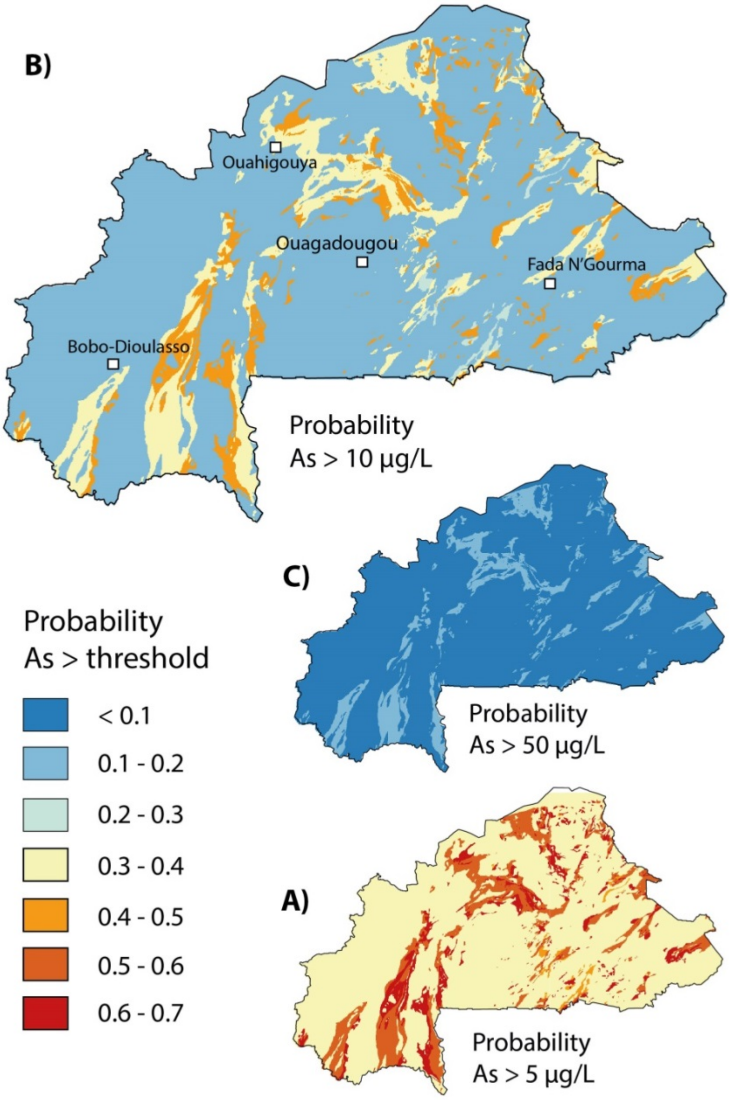

Fig. 2.5 Modelled probability of groundwater As concentrations exceeding the threshold values of A) 5 µg/L, B) 10 µg/L and C) 50 µg/L

Even though mineral deposits are hypothesized to be excellent proxies for mineralised zones, they were not a significant predictor for As in the logistic regression model. This is not surprising when we consider that mineralised zones exist where mineral exploration may not have taken place yet or that are too limited in extent to be economical for mineral extraction. Nevertheless, such areas are still potential As sources and may yield elevated groundwater As concentrations even though they are not documented in the mineral deposits dataset. Most of the high-As samples in the calibration dataset are from areas more than 10 km from documented mineral deposits. We therefore see the incompleteness of the mineral deposit dataset we used as the reason for its poor performance in predicting As-affected areas, and not the unsuitability of mineralised zones as As-predictors as such.

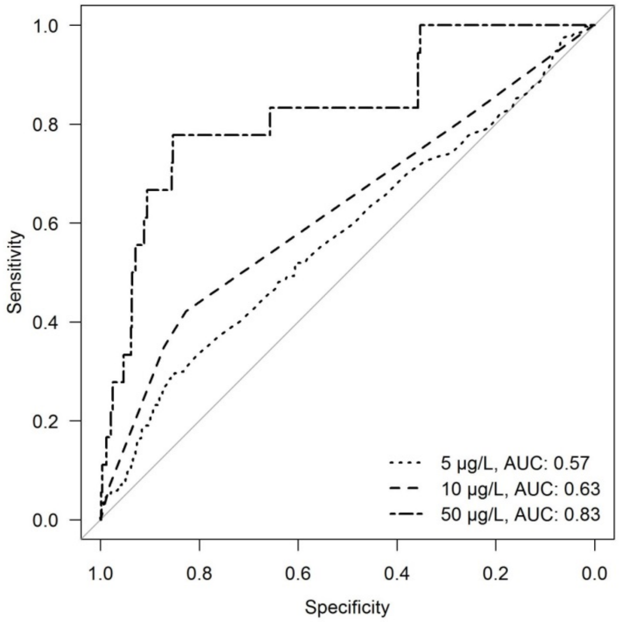

Fig. 2.6 Receiver operating characteristics (ROC) curves for the calculated logistic regression models using three different thresholds. The area under the curve (AUC) is displayed in the legend.

2.4.4 Model validation

The validation dataset, composed of 314 independent groundwater As measurements was used to verify the validity of the prediction model in other regions of Burkina Faso outside of the geographical distribution of the calibration dataset. The validation data are located in the north, south and west of the country (Fig. 2.1) with 14% of concentrations above 10 µg/L. The 10 µg/L probability map was first classified into "high risk" and "low risk" zones by taking 0.2 as the probability cut-off value. The validation data were then plotted on this map and the rate of correct classification calculated (Fig. 2.7). Results presented in Table 2.6 show that 91% of high As values (> 10 µg/L) were correctly classified into high-risk areas (sensitivity, true positives), with only 9% plotting in low-risk regions (false negatives). For the low As concentrations, 39% of these were correctly classified into low-risk areas (specificity, true negatives), with the remaining 61% in high risk areas (false positives). The high rate of false positives again reflects the nature of the As concentration database, with only few high-

As wells being scattered among a majority of As-safe wells. From a drinking water quality perspective, the high rate of false positives is less worrying, as finding good water quality in a high-risk area is a positive outcome. Much more important is the good performance of the model in predicting high-risk areas, with very few high-As values plotting in low-risk areas.

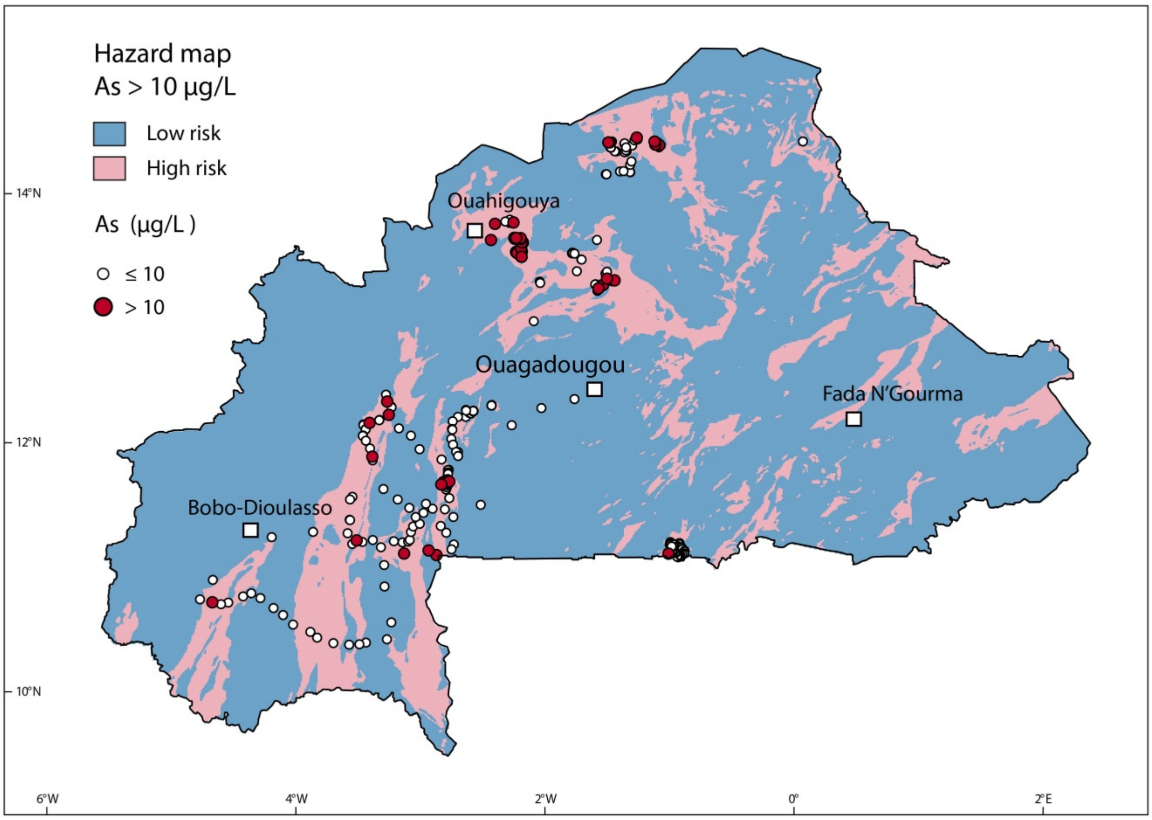

Fig. 2.7 Arsenic hazard map divided into "high" and "low" risk zones according to the probability cut-off of 0.2 of the 10 µg/L prediction model, overlain by the validation dataset of As measurements (n=314).

Even though the presented hazard maps highlight areas at greater risk of As contamination, they cannot accurately predict high As concentrations of individual boreholes, since the spatial resolution of predictor variables is much coarser than the small-scale variability that can occur between boreholes. Such data cannot represent the extremely localised processes leading to highly varying As concentrations in wells situated within hundreds of metres of each other. Ideally, to more accurately predict As occurrence in Burkina Faso, one would need highly detailed maps of gold and/or sulphide mineral deposits (showing individual mineral veins) on a country-wide scale, as well as borehole logs showing the lithological structure and location of water-bearing fractures at depth.

Table 2.6 Model validation results

Validation dataset, n=314	No. of samples	Predicted > 10 µg/L (high risk)	Predicted ≤ 10 µg/L (low risk)
Observed > 10 µg/L (high As)	44	40 (91% true positives)	4 (9% false negatives)
Observed ≤ 10 µg/L (low As)	269	165 (61% false positives)	104 (39% true negatives)

2.4.5 Population at risk

Using large-scale and readily available geological data and a detailed dataset of As measurements, we have produced a statistically sound hazard map predicting areas that are more likely to contain high concentrations of geogenic groundwater As in Burkina Faso. By combining predicted high-risk areas (> 20% chance of finding high As concentrations) with population density, the total population at risk of drinking water elevated in As (> 10 µg/L) were estimated (Fig. 2.8). Burkina Faso sustains a largely rural population, with only 30% living in urban areas (UNICEF and World Health Organization, 2015). Altogether, about 4 million people, which is roughly one-fifth of the total population of 17.3 million, live in designated high-risk areas. Of these, 2.8 million are estimated to be rural inhabitants. Considering the calculated statistical probability that about 1 in 5 boreholes in these high-risk regions are contaminated with As, about 560,000 people in rural areas are potentially exposed to contaminated groundwater. Since groundwater is the main source of drinking water in rural areas and As treatment techniques are as yet very rarely implemented, we consider this figure to be a valid estimate. This is a daunting number for one of the poorest and least-developed countries that is already facing numerous issues concerning water and sanitation (UNDP, 2015; UNICEF and World Health Organization, 2015). Even though large-scale targeted medical studies have not been undertaken to the authors' knowledge, As-related health issues can be expected to be widespread and result in a considerable burden of disease and reduced productivity and life expectancy in the Burkinabè population. In addition, socio-economic, demographic and political conditions will contribute considerably to a population's total vulnerability to As exposure (Singh & Vedwan, 2015).

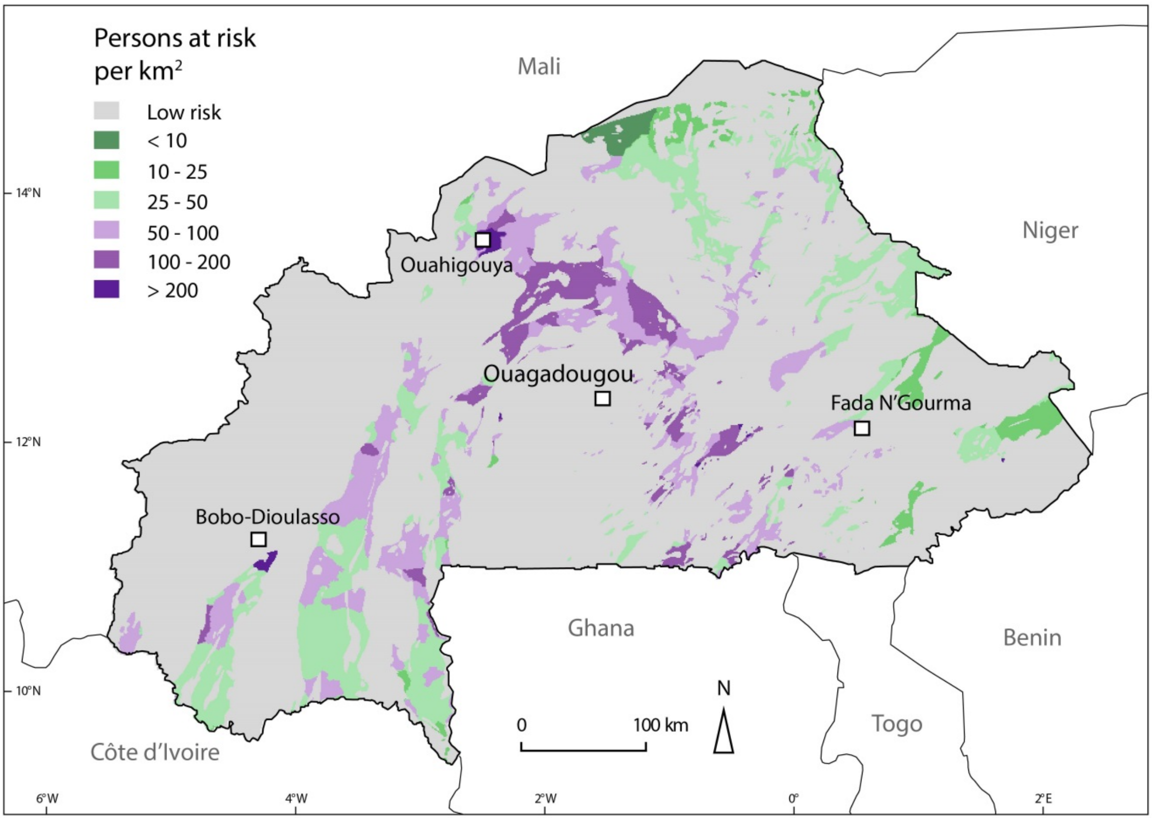

Fig. 2.8 Estimated number of persons at risk of being exposed to groundwater As concentrations >10 µg/L per km² in Burkina Faso. Population density data from the Center for International Earth Science Information Network - CIESIN - Columbia University (2016)

2.4.6 Relevance for arsenic mitigation in Burkina Faso and the greater West African region

The presented As hazard maps are aimed as a tool for water resource authorities to conduct drinking water surveys in areas where they are most needed. The testing of each drinking water well in high-risk regions is still necessary, as relatively few high-As wells are generally distributed among many low-As wells. The current practice is to close As-affected wells with a chain or to dismantle them to prevent water abstraction by the population. Often a replacement well is not drilled in the vicinity, leading to water shortages and greatly increased walking distances and hardship for women and children in charge of water collection. Closing a well without replacement only makes sense if an alternative, As-free well is nearby, which may certainly be the case since several drinking water boreholes are often installed in a village.

Well-switching has proved to be a popular mitigation option in As-affected regions in Bangladesh and is preferred over technological solutions such as water treatment filters (Ahmed et al., 2006; Inauen et al., 2013). Only where alternative, As-safe wells are too far away does on-site As treatment or the drilling of a new well make sense. Some success and encouraging results have already been seen in Burkina Faso with the installation of community-scale As treatment filters by 2iE-Fondation based on commercially available iron-hydroxide filter materials, though this is not yet widespread (Ouedraogo, 2016). The installation of a filter needs careful operation and maintenance, trained local staff, frequent water quality monitoring, replacement of filter material when saturated, and, above all, the necessary funding for sustainable, long-term operation. These can be daunting tasks for remote rural communities and need to be addressed before any upscaling of filter techniques is possible. Therefore, switching to alternative, As-free wells, where possible, is definitely the preferred mitigation option in Burkina Faso at the moment.

The As hazard model generated may also be relevant in Burkina Faso's neighbouring countries, as the volcanites and volcano-sedimentary schists of the Birimian formation, which proved to be the most reliable predictor for high As, also cover large areas of Ghana, the Ivory Coast, Mali, Niger and Benin. A transboundary hazard map for the whole West African region, calibrated and validated with local data would be a first step in creating awareness of geogenic As contamination on a more regional scale and initiating necessary mitigation in affected areas.

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3 Hydrogeochemical and multi-tracer investigations of arsenic-affected aquifers in semi-arid West Africa

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Abstract

The semi-arid Sahel regions of West Africa rely heavily on groundwater from shallow to moderately deep (< 100 m b.g.l.) crystalline bedrock aquifers for drinking water production. Groundwater quality may be affected by high geogenic arsenic (As) concentrations (> 10 µg/L) stemming from the oxidation of sulphide minerals (pyrite, arsenopyrite) in mineralised zones. These aquifers are still little investigated, especially concerning groundwater residence times and the influence of the annual monsoon season on groundwater chemistry. To gain insights on the temporal aspects of As contamination, we have used isotope tracers (noble gases, ^{3}H, stable water isotopes (^{2}H, ^{18}O)) and performed hydrochemical analyses on groundwater abstracted from tube wells and dug wells in a small study area in south-western Burkina Faso. Results revealed a great variability in groundwater properties (e.g. redox conditions, As concentrations, water level, residence time) over spatial scales of only a few hundred metres, characteristic of the highly heterogeneous fractured underground. Elevated As levels are found in oxic groundwater of circumneutral pH and show little relation with any of the measured parameters. Arsenic concentrations are relatively stable over the course of the year, with little effect seen by the monsoon. Groundwater residence time does not seem to have an influence on As concentrations, as elevated As can be found both in groundwater with short (< 50 a) and long (> 10^{3} a) residence times as indicated by ^{3}He/^{4}He ratios spanning

three orders of magnitude. These results support the hypothesis that the proximity to mineralised zones is the most crucial factor controlling As concentrations in the observed redox/pH conditions. The existence of very old water portions with residence times > 10^3 years already at depths of < 50 m b.g.l. is a new finding for the shallow fractured bedrock aquifers of Burkina Faso, suggesting that overexploitation of these relatively low-yielding aquifers may be an issue in the future.

3.1 Introduction

Shallow to moderately deep (< 100 m b.g.l.) groundwater from fractured, crystalline bedrock aquifers constitutes the most important drinking water resource in rural and peri-urban areas of many sub-Saharan countries (MacDonald et al., 2012; MacDonald & Calow, 2009), for example in Burkina Faso, West Africa (Barbier et al., 2006). However, in this region, groundwater quality can be affected by high levels of geogenic arsenic (As), released through the oxidation of sulphide minerals occurring in the volcano-sedimentary schists and volcanic rocks of the Birimian formation (Ahoulé et al., 2015). Such As contamination has been shown to contaminate groundwater throughout Burkina Faso (Barro-Traoré et al., 2008; Bretzler et al., 2017; Sako et al., 2016; Smedley et al., 2007; Somé et al., 2012) and neighbouring Ghana (Asante et al., 2007; Buamah et al., 2008; Smedley, 1996). An estimated 560,000 people are potentially exposed to elevated As concentrations via their drinking water in Burkina Faso alone (Bretzler et al., 2017). The serious and chronic health effects of prolonged exposure to As-contaminated water include the development of a variety of cancers as well as developmental, neurological and cardiovascular diseases (Argos et al., 2010; Naujokas et al., 2013).

In comparison to the well-known cases of large-scale groundwater As contamination in South and South-East Asia which have been extensively addressed, geogenic As in the fractured crystalline bedrock aquifers of West Africa is less thoroughly investigated (Ahoulé et al., 2015; Nikiema et al., 2013). To the best of our knowledge, no work has yet looked into the influence of the annual monsoon on As concentrations, nor has the residence time of As contaminated groundwater in this region been investigated. Tracers such as noble gases, stable water isotopes (^2H, ^{18}O) and tritium (^3H) have shed light on groundwater mobility and flow paths of high-As waters in South-East Asia (Klump et al., 2006; McArthur et al., 2010). Isotope tracers as tools for determining groundwater origin and residence times have rarely been employed in the West African Sahel. The few existing studies have mostly focussed on aquifers of the large sedimentary basins, for example the Chad basin (Chad, Nigeria), the Iullemeden basin (Niger) and the Taoudeni basin (western Burkina Faso, Mali) (Beyerle et al., 2003; Huneau et al., 2011; Maduabuchi et al., 2006; Rueedi et al., 2005a; Rueedi et al., 2005b). Age-dating of deep groundwater (> 100 m b.g.l.) of these sedimentary formations using ^{14}C and noble gases revealed residence times of several thousands to tens of thousands of years, with recharge having occurred during wetter and cooler climatic periods in the Sahel. On the other hand, the shallow aquifers (both sedimentary formations and weathered crystalline bedrock) used extensively for drinking water production in West Africa are thought to contain mostly modern groundwater with residence times of less than 65 years (Lapworth et al., 2013) with some authors estimating that groundwater abstraction can be developed substantially without over-exploitation (MacDonald et al., 2012; Martin & Van De Giesen, 2005). The application of tracers also capable of identifying old water components (e.g. ^{4}He) in the shallow crystalline bedrock aquifers has yet to be carried out.

Considering large population growth (Gerland et al., 2014) and planned intensification of irrigated agriculture in sub-Saharan Africa (MacDonald et al., 2012), groundwater use will increase in the future and both water quality assessments and the sustainability of increased exploitation are vital information for decision makers. Regarding these challenges and to gain insights on the temporal aspects of As groundwater contamination, we used tracers (noble gases, ^{3}H, ^{2}H, ^{18}O) and performed hydrochemical analyses and seasonal sampling on a shallow to moderately deep groundwater system affected by geogenic As contamination. Recently, a broad, nationwide groundwater quality survey revealed the widespread occurrence of As-affected aquifers in Burkina Faso (Bretzler et al., 2017). Following up on these findings, the present study focuses on small-scale heterogeneities in these aquifers, investigated in a small study area (~80 km^{2}). The properties of fractured rock aquifers are generally difficult to predict and in Burkina Faso, detailed, site-specific information on geological and hydrogeological conditions at depth, as well as borehole characteristics are usually not available. The chosen approach can give indications on groundwater residence times and environmental conditions at the time of recharge and may also aid in understanding the occurrence, distribution and geochemistry of As-affected groundwater.

3.2 Study Area

The study site of Poura is located about 250 km south-west of Burkina Faso's capital city Ouagadougou and is typical of the relatively flat, highly weathered Central Plateau of Burkina Faso (Fig. 3.1). The studied area covers about 80 km^2 and terrain elevations range from 330 m a.s.l. in the slightly hilly east to 230 m next to the Mouhoun river in the west. The administrative community of Poura has about 10,000 inhabitants and comprises the main town of Poura Mine, as well as several nearby villages (Poura Village, Kankele, Darsalam, Toécin, Basnéeré, Mouhoun 3, Bologo) (Fig. 3.1). Poura lies within the Sahelian-Soudanian climate zone, experiencing dry conditions for most of the year, with a distinct wet season from June to September. For the years 2003-2015, the mean annual precipitation in the town of Boromo (25 km north-west of Poura) was 930 mm, mean annual potential evapotranspiration 1800 mm and the mean annual minimum/maximum temperatures 22.3 °C and 35.5 °C (Source: Direction de la Météorologie du Burkina). Poura was the location of Burkina Faso's first state owned gold mine, in operation from 1961 to 1966 and from 1984 to 1996. Currently, informal artisanal goldmining is widespread at several locations within the study area.

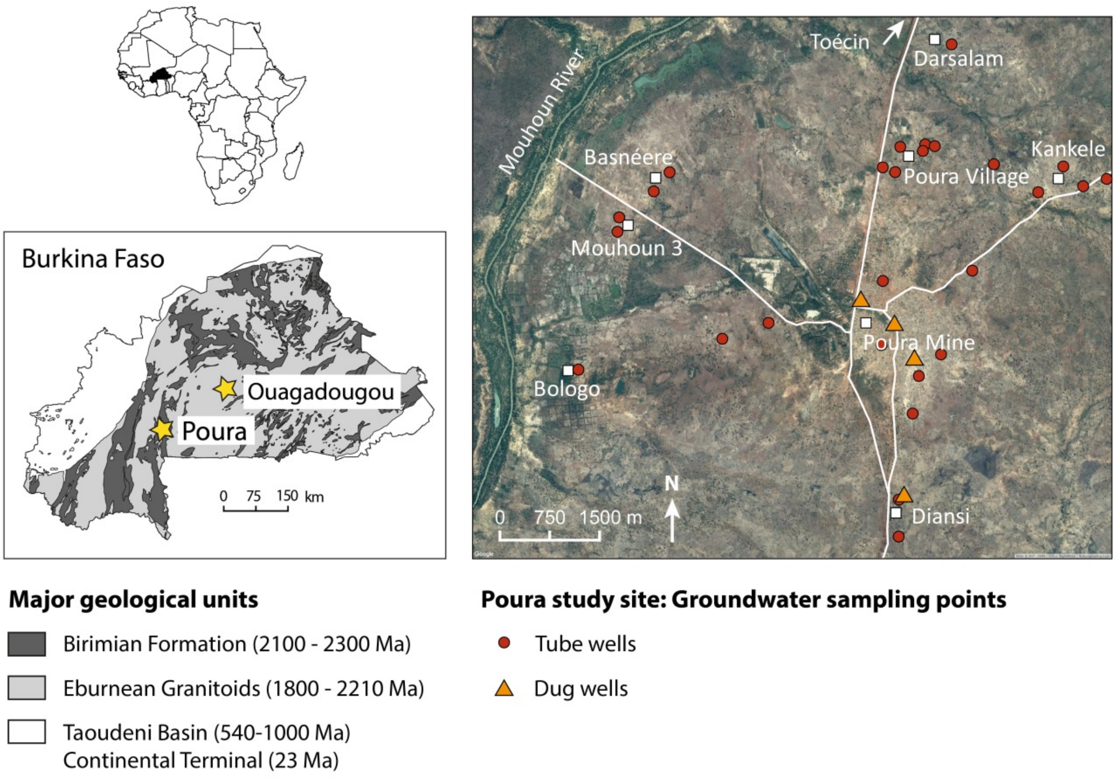

Fig. 3.1 Location of the study area and groundwater sampling points

3.2.1 Geology

Apart from sedimentary rocks belonging to the Taoudeni Basin and the Continental Terminal formation, the geology of Burkina Faso is dominated by crystalline bedrock of varying lithologies formed during the Paleoproterozoic era (2300 – 1600 Ma) (Fig. 3.1). Large granitic bodies (granite, granodiorite, tonalite) of the Eburnean orogeny occur next to belts of meta-sedimentary and (meta)-volcanic rocks that cross the country from SW-NE and belong to the Birimian formation (Castaing et al., 2003b) (Fig. 3.1). The study site of Poura is located on one such Birimian belt (the Boromo greenstone belt) in a shear zone dominated by N-S trending structures. Poura is underlain by series of intermediate to basic volcanic rocks (andesite, andesitic tuff, rhyolite) and some sandy conglomerates belonging to the Tarkwaïen group that act as host rocks for mesothermal gold-quartz vein deposits (see detailed geological map in section 3.4.1) (Kote et al., 2003; Milési et al., 1992). Occurring with these quartz veins are sulphide minerals, predominantly pyrite (FeS_2) and arsenopyrite (FeAsS). In addition to these quartz vein-associated gold deposits, disseminated-style deposits occur within a few kilometres of Poura Mine at the gold mining districts of Larafella and Loraboué, where gold and sulphide minerals occur disseminated within the host rock (Bamba et al., 2002; Béziat et al., 2008).

3.2.2 Hydrogeology

The fractured rock aquifers of Burkina Faso (and large parts of West Africa) are a result of intense alteration weathering processes leading to a characteristic weathering profile. Numerous studies in the last 20 years have shown that weathering processes, rather than tectonics, are primarily responsible for the creation of the dense fissure and fracture network that forms these aquifers (Courtois et al., 2010; Koita et al., 2013; Lachassagne et al., 2011; Soro et al., 2017). A typical weathering profile is made up of, from top to bottom, i) a few metres of ferricrete/laterite or iron/bauxite crust, ii) several tens of metres of clayey saprolite resulting from prolonged, in-situ decomposition of the parent rock through weathering iii) several tens of metres of densely fissured parent rock and iv) the fresh, unfractured bedrock. The saprolite layer can in itself be divided into a so-called alloterite sub-unit consisting mostly of clays, lying above a less weathered isalterite sub-unit (lower clay content, parent rock structure preserved). The thicknesses of the individual layers can vary greatly according to lithology and ancient or current topography and erosion processes (Bamba, 1996; Koita et al., 2013).

The saprolite layer has increased groundwater storage (Campaore 1997), whereas the fissured/fractured bedrock is seen to have a more conductive function due to its increased secondary permeability. From the few available lithologs and literature sources available for Poura and its vicinity (e.g. Bamba (1996)), it could be deduced that saprolite and fissured layer thicknesses vary greatly within this small area, with average thicknesses of 27 m and 33 m respectively (Stolze, 2015).

Groundwater in the study area is exploited for domestic purposes via tube wells equipped with hand pumps. Shallow dug wells (5-25 m deep) usually tap groundwater from the saprolite layer and are vulnerable to seasonal water level changes and surface pollution. Tube wells with depths between 36 - 90 m (mean depth 61 m, n = 20) are often drilled all the way to the fresh bedrock. This is a typical tube well depth distribution in Burkina Faso, as seen in a study of by Courtois et al. (2010) who investigated the properties of nearly 15,000 tube wells. Borehole screens are placed within the fissured layer, often in multiple layers (up to three screened sections per borehole) corresponding to fissures with high hydraulic conductivity (Stolze, 2015). Tube well yields vary, with maximum yields of ~8 m^3/h. Generally, very little technical information about tube wells in this area could be sourced, with inaccuracy and inconsistencies certainly posing a problem in the few available borehole logs. An evaluation of static water level data measured in different field campaigns combined with a numerical groundwater flow model has shown the relative groundwater flow direction to be from NE-SW towards the Mouhoun river (Stolze, 2015).

3.3 Methods

3.3.1 Hydrochemistry and stable isotopes (^2H, ^{18}O)

Within the study area, we located and sampled all existing community tube wells (equipped with hand pumps of the types India, Volanta or Vergnet, n = 29) and a selection of dug wells (n = 4). We followed standard sampling and laboratory analysis procedures as described in similar studies (Berg et al., 2008; Buschmann et al., 2007). On-site parameters (temperature, pH, electrical conductivity, O_2 concentration and redox potential) were measured in a flow-through cell connected to the hand pump spout. Water sampling was performed after on-site parameters had stabilised, generally after less than 10 minutes. All sampled tube wells are pumped nearly continuously during the day by local residents for drinking water, hence water was never stagnant in the pipes before sampling. Samples for major cations and trace element analysis (including As) were collected in acid-washed polypropylene bottles, filtered through 0.45 μm filters and acidified with concentrated HNO_3 suprapure to a $pH < 2$. An unfiltered, non-acidified aliquot was collected for the analysis of anions, dissolved organic carbon (DOC), total inorganic carbon (TIC) and stable isotopes of water (^2H, ^{18}O). For As speciation, filtered samples were passed through an alumosilicate cartridge which retains As(V) (Meng & Wang, 1998) and then acidified. Samples were stored below 4°C whenever possible. Analysis was performed in the laboratories of Eawag, Switzerland, using ICP-MS (Agilent 7500 cx) for cations and trace elements, ion chromatography for anions (ICS-2001 Dionex) and a carbon analyser (TOC Shimadzu) for TIC and DOC. Stable isotope (^2H and ^{18}O) analysis was performed using cavity ring-down laser spectroscopy (Picarro L1 102-I). After the initial sampling campaigns in February and April 2015, a selection of tube wells (n=19) and dug wells (n=3) were re-sampled in the months during and after the rainy season (August 2015 – February 2016) to investigate seasonal changes in hydrochemistry. Gaps in the dataset result from malfunctioning hand pumps or prolonged inaccessibility to the study site due to surface flooding during the rainy season. Seasonal changes in static water levels were only measured at dug wells and tube wells equipped with "India" type hand pumps which allowed easy access to the water table with a dipper. Hand pumps of the type "Volanta" and "Vergnet" have to be dismantled and pump and tubing removed from the borehole before a dipper can be lowered.

3.3.2 Noble gases and tritium

The noble gases He, Ne, Ar, Kr and Xe and the radioactive hydrogen isotope ^3H (tritium), act as tracers for environmental processes (Aeschbach-Hertig et al., 1999; Aeschbach-Hertig & Solomon, 2013; Beyerle et al., 1999). Their concentrations and isotope ratios in groundwater can give indications of groundwater dynamics, residence times and mixing ratios (Kipfer et al., 2002). Atmospheric noble gases dissolve in groundwater during recharge. The dissolution of entrapped air bubbles below the groundwater table may lead to a supersaturation of atmospheric noble gases with respect to equilibrium concentrations (excess air) (Aeschbach-Hertig & Solomon, 2013; Kipfer et al., 2002). Helium in groundwater can stem from several different reservoirs which have distinct $^3He/^4He$ isotope ratios. Atmospheric He ($^3He/^4He = 1.384 * 10^{-6}$ (Clarke et al., 1976)) dissolves in groundwater during recharge, while radiogenic He (He_{rad}) is a daughter product of the U-Th decay series and is constantly emanated from minerals in the Earth's crust. Radiogenic He may result from different sources: 1) produced in-situ in the aquifer (Andrews, 1985), 2) as external input from the Earth's crust ("crustal flux") (Torgersen & Clarke, 1985) and 3) as stored ^{4}He released from very old crustal rocks through weathering (Heaton, 1984) or diffusion (Solomon et al., 1996). Radiogenic He accumulates in groundwater, has a typical ^{3}He/^{4}He signature of 10^{-9} to 10^{-7} (Tolstikhin, 1984) and can be used to date groundwater with residence times > $10^{2\text{-}3}$ years (Kipfer et al., 2002). Helium can also be emitted directly from the Earth's mantle in Rift zones or other volcanically and tectonically active regions and has He isotope ratios of around 10^{-5} (Mamyrin & Tolstikhin, 1984). Tritiogenic ^{3}He (^{3}He$_{tri}$) is produced as a direct product of the radioactive decay of tritium (^{3}H, half-life 12.3 a), a process that can be used to date groundwater with short residence times (< 50 a) (Kipfer et al., 2002).

As noble gases are also present in the atmosphere, it is vital to avoid any air contact while sampling groundwater for noble gas analysis in order to avoid contamination. At the selected tube wells (n = 12), the hand pump and connected pipes had to be dismantled and removed from the borehole to allow for the insertion of a small submersible pump (type Comet-Combi) connected to a 12V battery. The pump was typically installed 5-6 m below the water table at depths between 12-25 m b.g.l.. Groundwater was pumped until on-site parameters (temperature, pH, EC, O_2, Eh) were stable and then filled into gas-tight copper tubes and tightly clamped (Beyerle et al., 2000). The analysis of noble gas concentrations (He, Ne, Ar, Kr, Xe), isotope ratios (^{3}He/^{4}He, ^{20}Ne/^{22}Ne, ^{36}Ar/^{40}Ar) and ^{3}H was performed at the Noble Gas Laboratory of ETH Zurich by noble gas mass spectroscopy (Beyerle et al., 2000).

3.4 Results and Discussion

3.4.1 Hydrochemistry

The sampled groundwater has varying hydrochemical signatures despite the close spatial proximity of the samples, with closest distances between tube wells being ~200 m. A summary of all measured parameters is displayed in Table 3.1. Tube well water has circumneutral pH (6.3 -7.2), whereas dug wells generally show more acidic values (pH 5-6). Electrical conductivities range from 195 – 624 µS/cm for tube wells, with only two dug wells having much lower mineralisation. Dissolved oxygen is generally present in a range of 0.1 - 2 mg/L for tube well water (few exceptions with higher values) and groundwater can be classified as oxic (Eh 380-500 mV). Three tube wells, on the other hand, have mildly reducing values of 270-290 mV and dissolved O_2 of 0.8 – 1 mg/L.

Table 3.1 Summary of measured chemical parameters for tube wells and dug wells

		Tube wells				**Dug wells**			
	Unit	**Min**	**Max**	**Median**	**n**	**Min**	**Max**	**Media**	**n**
Depth	m (b.g.l.)	36	89	57	20	6.7	13	7.4	4
pH	-	6.25	7.21	6.93	29	4.97	7.28	5.52	4
EC	µS/cm	195	624	399	29	52	485	217	4
O_2	mg/L	0.13	6.30	1.02	29	0.8	3.93	3.86	4
Temp	°C	30.3	32.9	31.3	29	29.4	30.9	30.4	4
Eh	mV	271	502	425	24	458	508	484	4
DOC	mg/L	< 0.5	2.80	1.20	29	0.6	3.1	2.05	4
TIC	mgC/L	30	88	54	29	1.9	65.8	12.6	4
HCO_3	mg/L	150	439	271	29	9	329	63	4
F	mg/L	< 0.1	0.25	0.09	29	< 0.1	0.17	< 0.1	4
Cl	mg/L	< 0.1	8.97	0.59	29	1.74	41.0	3.52	4
Br	mg/L	< 0.1	0.05	0.05	29	< 0.1	< 0.1	< 0.1	4
NO_3	mg/L	< 0.1	33.1	3.66	29	0.87	51.4	17.5	4
SO_4	mg/L	< 0.1	11.1	0.99	29	0.26	4.59	2.10	4
PO_4	mg/L	< 0.1	0.15	0.05	29	< 0.1	0.40	< 0.1	4
Li	µg/L	1.9	44.9	9.3	29	0.6	7.6	1.94	4
B	µg/L	< 5	34.8	14.1	29	< 5	22.1	< 5	4
Na	mg/L	4.2	68.6	19.6	29	3.4	35.9	14.4	4
Mg	mg/L	9.8	41.5	19.9	29	1.55	19.4	4.45	4
Al	µg/L	0.8	16.3	4.3	29	12.3	221	41.6	4
Si	mg/L	7.6	28.3	19.7	29	6.67	28.1	7.15	4
K	mg/L	0.16	0.80	0.31	29	0.81	4.63	1.18	4
Ca	mg/L	15.4	56.8	35.6	29	2.4	40.6	8.4	4
V	µg/L	0.09	33.8	3.97	29	0.25	6.19	0.56	4
Cr	µg/L	< 0.02	1.19	0.06	29	0.05	1.09	0.32	4
Mn	µg/L	0.09	147	3.18	29	13.6	46.5	20.0	4
Fe	µg/L	< 0.3	2953	12.4	29	4.9	86.7	48.9	4
Co	µg/L	< 0.02	1.32	0.03	29	0.18	2.71	2.23	4
Ni	µg/L	< 0.02	1.98	0.19	29	1.14	3.53	3.05	4
Cu	µg/L	< 0.1	3.25	0.40	29	0.5	2.8	1.33	4
Zn	µg/L	1.0	741	5.4	29	3.1	20.3	10.1	4
As	µg/L	< 0.02	333	2.83	29	< 0.02	6.53	0.28	4
A(V)	%	94	100	99	18	60	89	75	4
Se	µg/L	< 0.02	0.99	0.13	29	< 0.02	0.08	0.045	4
Sr	µg/L	55	313	144	29	17	172	58	4
Mo	µg/L	< 0.02	5.96	0.80	29	0.18	0.67	0.21	4
Cd	µg/L	< 0.01	0.75	0.01	29	< 0.01	0.02	< 0.01	4
Sn	µg/L	< 0.02	0.39	0.34	29	< 0.02	0.38	0.36	4
Sb	µg/L	< 0.02	0.94	0.09	29	0.11	0.16	0.12	4
Ba	µg/L	< 0.1	265	0.70	29	8.6	147	28.2	4
La	µg/L	< 0.01	0.05	0.01	29	< 0.02	0.56	0.22	4
Ce	µg/L	< 0.01	0.076	0.01	29	0.02	0.64	0.32	4
W	µg/L	< 0.02	3.76	< 0.02	29	< 0.02	0.44	< 0.02	4
Tl	µg/L	< 0.02	<	< 0.02	29	< 0.02	0.14	< 0.02	4
Pb	µg/L	< 0.02	0.21	0.04	29	< 0.02	0.24	0.16	4
U	µg/L	< 0.02	0.06	< 0.02	29	< 0.02	<	< 0.02	4
$\delta^{18}O$	‰(VSMOW)	-5.56	-3.52	-4.37	17	-4.46	-3.95	-4.3	4
$\delta^{2}H$	‰ (VSMOW)	-36.2	-19.1	-26.0	17	-27.1	-23.9	-25.9	4

Arsenic concentrations above the WHO guideline value of 10 μg/L were found in five tube wells, the highest concentration being 333 μg/L (Fig. 3.2). The pH values of these high-As samples belong to the higher values measured (> 7.0), with dissolved O_2 concentrations < 1 mg/L (one exception) (Fig. 3.2). No linear relationship between the depth of tube wells and As concentrations was seen. Similarly, no clear trends between As and any other measured parameter could be observed. The positive correlations between As and W and Mo concentrations observed in waters from auriferous zones in northern Burkina Faso by Smedley et al. (2007) cannot be seen in Poura (Fig. 3.3), which may be due to regional differences in mineralisation and mineral assemblages. An exception is antimony (Sb), where the highest concentrations were measured in the samples having elevated As (Fig. 3.3). Nevertheless, the measured Sb concentrations are still relatively low (< 1 μg/L). Relationships between dissolved Sb and As in groundwater (though with much higher Sb concentrations) have been described by Verplanck et al. (2008) and attributed to the co-occurrence of stibnite (Sb_2S_3) with arsenopyrite and pyrite in auriferous zones. Antimony ores are found in Burkina Faso (Kote et al., 2003), though are not specifically described in the area of Poura. Antimony is probably a minor constituent of the mineralised zones in Poura and released together with As during sulphide mineral oxidation, though the aqueous geochemical behaviour of Sb is essentially different to that of As (Mitsunobu et al., 2006).

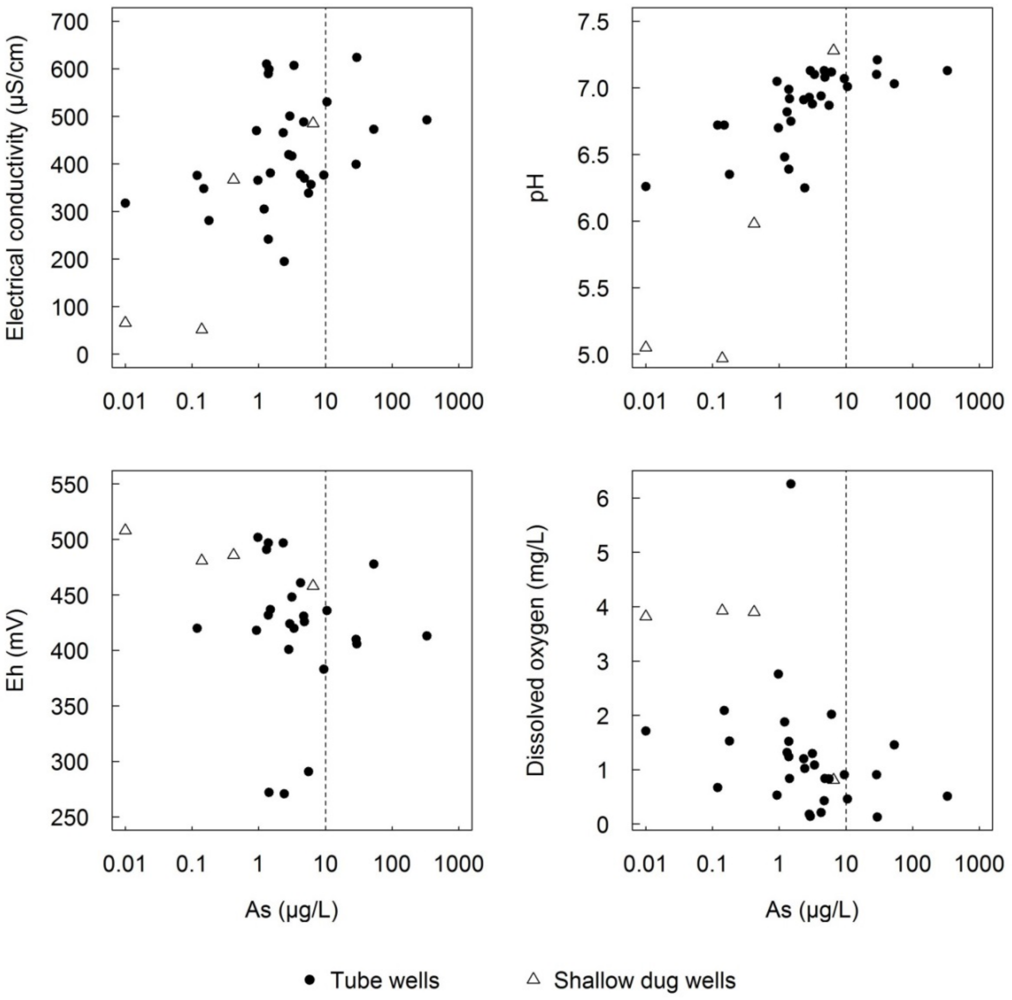

Fig. 3.2 Scatter plots of groundwater As concentrations versus pH, Eh, O_2 and electrical conductivity. Note the log scale on the x-axes. The dashed line represents the WHO drinking water guideline value for As of 10 µg/L (WHO, 2011).

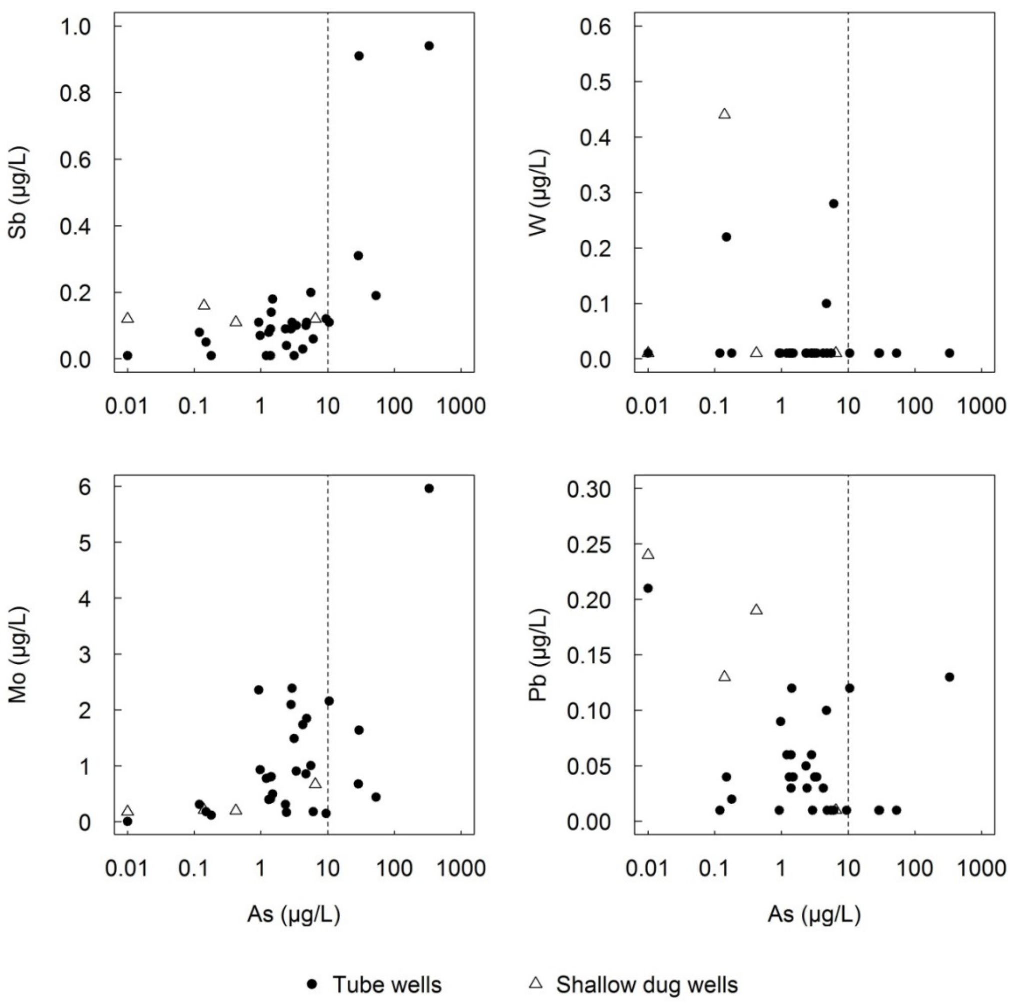

Fig. 3.3 Groundwater As concentrations plotted against trace metals commonly found in auriferous zones (Sb, Mo, W, Pb). The dashed line indicates the WHO drinking water guideline value for As of 10 µg/L.

Due to the oxic nature of the groundwater, As is predominantly found as As(V) (Table 3.1). In this state, and at circumneutral pH, dissolved As chemistry is strongly controlled by sorption to Fe(III) hydroxides (Dixit & Hering, 2003). Dissolved Fe concentrations are generally also very low, with only three tube wells with mildly reducing signature having significant Fe concentrations (Fig. 3.4). These wells do not show elevated As though, indicating that reductive dissolution of As from Fe hydroxides is most likely not the source mechanism of high groundwater As. Even though the analysis of filtered and unfiltered samples revealed that some particulate Fe occurs (generally lower dissolved Fe concentrations in filtered than in unfiltered samples), As does not seem to be bound to these iron hydroxide solids, as filtered and unfiltered As concentrations are nearly identical (Fig. 3.5).

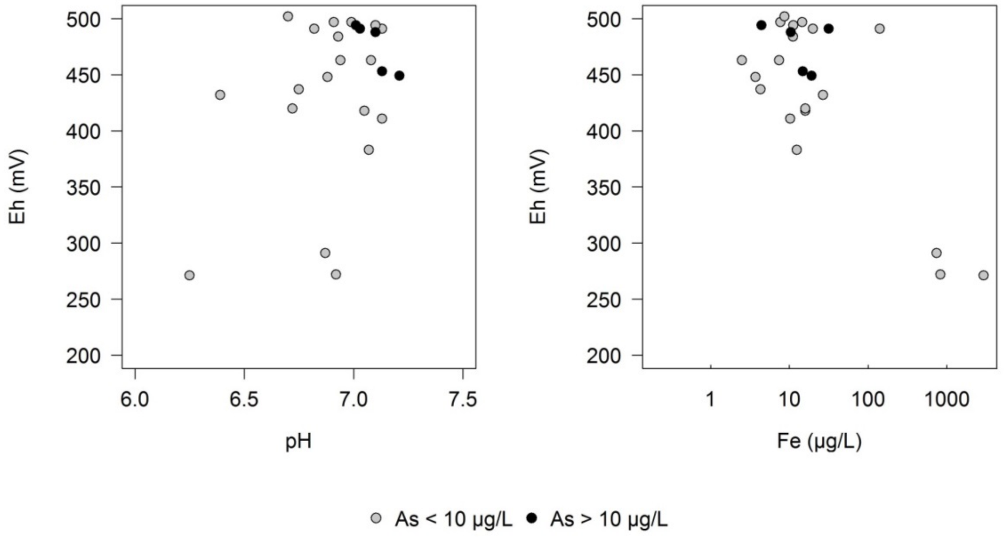

Fig. 3.4 Redox potential of tube well water plotted against pH and dissolved Fe concentrations

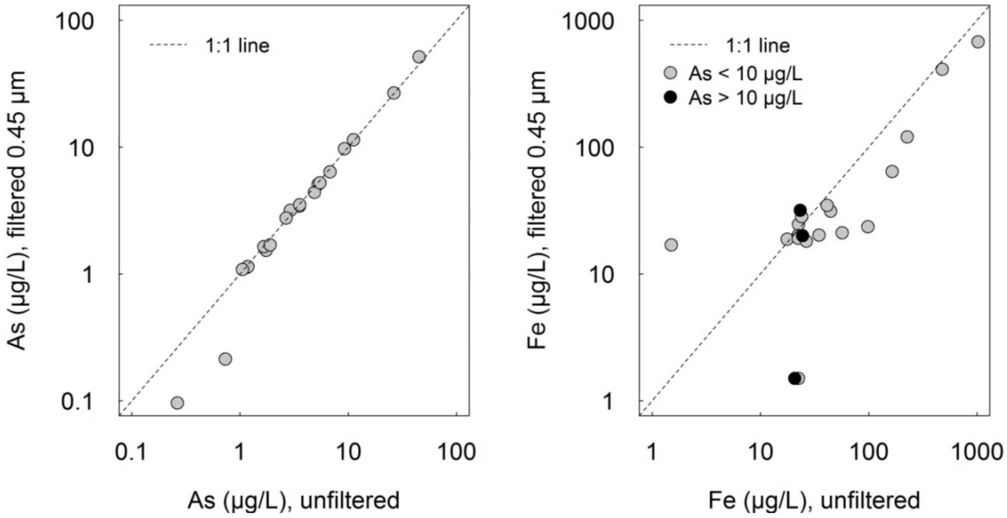

Fig. 3.5 Arsenic and iron concentrations in filtered and unfiltered samples

The spatial variability of As concentrations is high and does not show any clear pattern. Highly contaminated wells (e.g. PO-1, 333 µg/L) can be found within a few hundred metres of uncontaminated wells (e.g. PO-2, 2.4 µg/L) (Fig. 3.6). This also reflects the very heterogeneous distribution of mineralised areas, which in Poura occur as gold and sulphides (mainly pyrite and arsenopyrite) associated to quartz veins. Such quartz veins may have widths of only a few metres to tens of metres and extend from a few hundred metres to several kilometres, with the surrounding metamorphic/volcanic host rock being comparatively sulphide-free (Béziat et al., 2008). As already postulated by Smedley et al. (2007), the direct proximity to mineralised zones (quartz veins with associated sulphides) must play a major role in influencing groundwater As concentrations. The high dissolved As concentrations can only be explained by a very high As release in the direct vicinity of sulphide mineral occurrences, as with increasing distance from the As source, dissolved As(V) should rapidly adsorb to Fe(III) hydroxides in the oxic, circumneutral pH conditions. This can also partly explain the large variability in As concentrations over short distances.

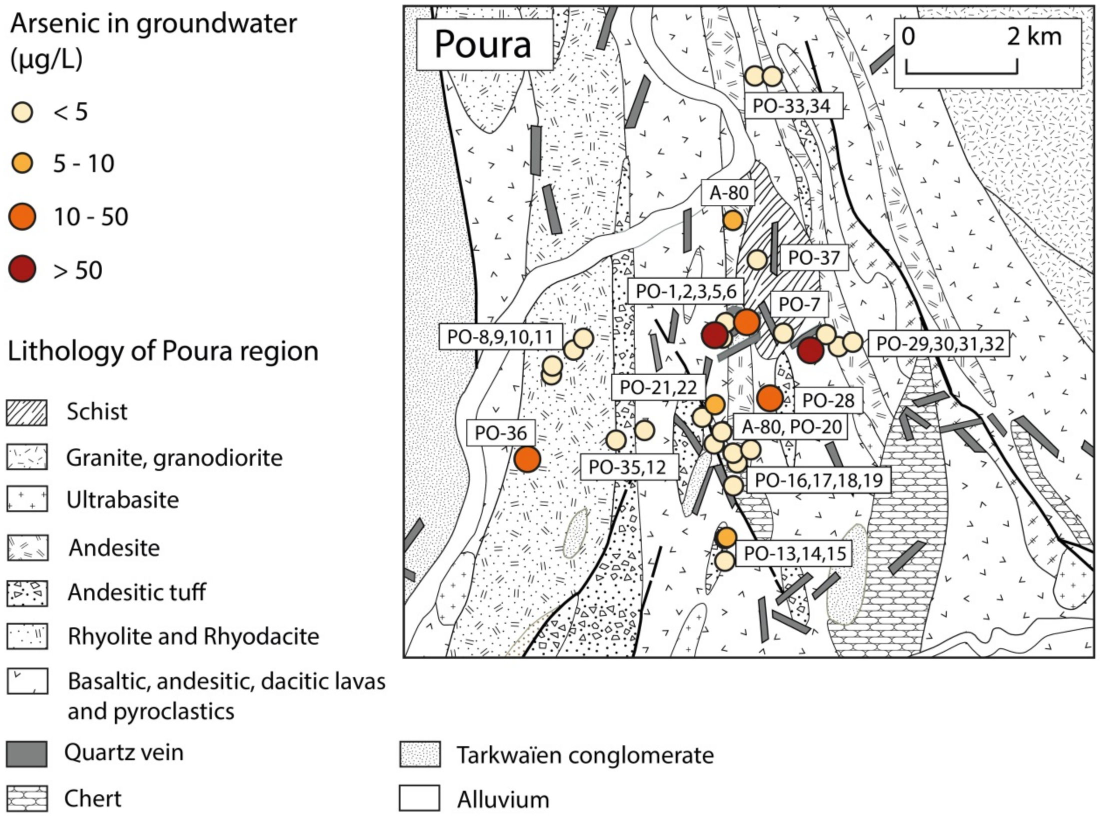

Fig. 3.6 Map showing the variability in groundwater As concentrations, as well as the geological characteristics of the study area. Geological map source: Ouedraogo et al. (2003)

The hydrochemical signatures of dug wells can also be very variable, reflecting the different layers of the aquifer, their geochemistry and state of weathering. The three shallowest dug wells (PO-18, PO-20 and PO-22, depths 6-7 m) source their groundwater from the upper saprolite layer, that is highly weathered. The water has very little geochemical evolution (low pH, low electrical conductivity, low concentrations of major elements, low As), is probably recently recharged and can be clearly distinguished from the tube well groundwater. By contrast, the deeper dug well (PO-14, 13 m) has a pH and element concentrations that are similar to those of groundwater tapped by tube wells (e.g. Fig. 3.2, Fig. 3.3), as well as an elevated As concentration of 6.5 µg/L (rising to 12 µg/L during the rainy season, see section 4.4, Fig. 3.12). Clearly this well reaches geochemically more evolved groundwater from the lower saprolite. The geochemical signature of the laterite/ferricrete and saprolite layers can vary significantly at different sites, according to the chemistry of the bedrock but also due to the geomorphological evolution of the weathering profile (Bamba, 1996; Bamba et al., 2002). In addition to in-situ weathering of the parent rock, material eroded from hillslopes may be incorporated into the weathering profile, changing the geochemical signature of some layers. Bamba et al. (2002) found well-conserved sulphide minerals and still elevated As content in some ferricrete and saprolite (upper 12 m) in the vicinity of Poura, whereas other nearby profiles were depleted in most major and trace elements, and dominated by residual Fe and Al hydroxides. From the limited data available in this study and especially without analysing the geochemical composition of the aquifer material at the site of the sampled dug wells, it is not possible to draw conclusions on the main process governing the chemistry of dug well water. We hypothesise that the geochemistry of the aquifer material plays a greater role than the (generally short) groundwater residence time, with elevated groundwater As concentrations occurring if sulphide minerals are still present in the saprolite. Where intense weathering has caused the dissolution of the sulphides and Fe and Al hydroxides predominate, the shallow, slightly acidic groundwater has very low mineralisation and As chemistry (if present) should be controlled by sorption to the abundant ferric material.

From a drinking water perspective, As is the only parameter of major health concern in the investigated groundwater samples. Elevated nitrate (NO_3^-) concentrations affect some dug wells and shallow tube wells, but only surpass the WHO drinking water guideline value of 50 mg/L (WHO, 2011) in the case of one dug well (Fig. 3.7). The five shallowest tube wells (< 50 m) all have NO_3^- concentrations between 15 and 35 mg/L, whereas concentrations in tube wells > 45 m in depth stay below 5 mg/L (one exception). The sources of NO_3^- are most likely of anthropogenic origin, supported by the very low background concentrations in the deeper wells and a positive correlation between NO_3^- and Cl^- concentrations (Fig. 3.7). Wells are usually constructed in the direct vicinity of human settlements without protection zones, and human and animal waste are most likely a direct source of NO_3^- to groundwater. Fertiliser application in the dominating subsistence agriculture is another possible NO_3^- source.

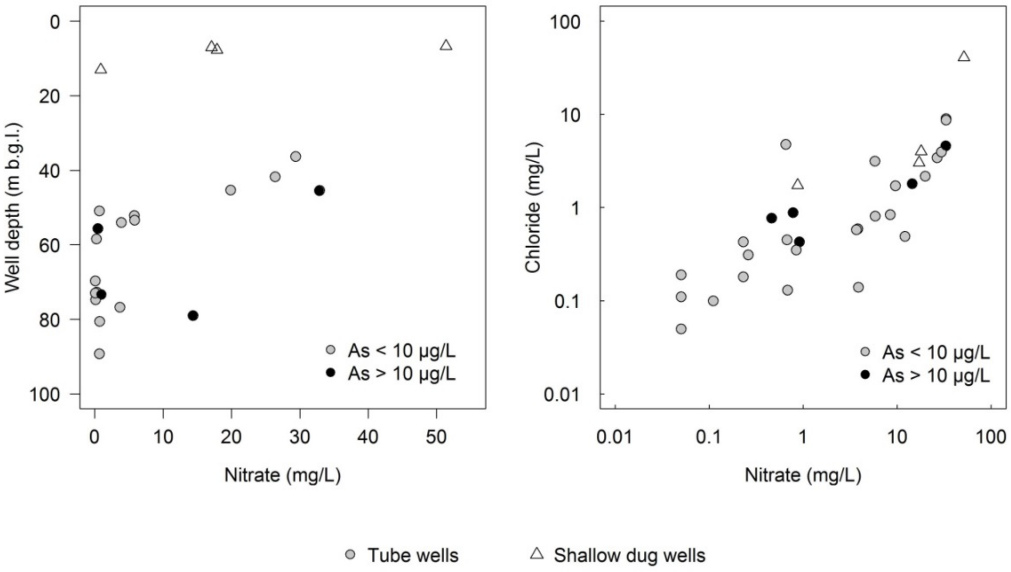

Fig. 3.7 Groundwater nitrate (NO_3^-) concentrations plotted versus well depth and chloride (Cl^-) concentrations

3.4.2 Stable isotopes (^2H, ^{18}O)

The stable water isotopes ^2H and ^{18}O are tracers for physical processes that water molecules may be subjected to in the hydrological cycle, such as evaporation, condensation, thawing and freezing. Stable isotope ratios in rainfall vary significantly globally, with these variations attributed to a number of usually temperature-related effects leading to isotope fractionation in large air masses ("continental effect", "latitude effect" and "altitude effect") (Rozanski et al., 1993). The isotope composition of tropical rainfall, however, is less dependent on temperature, but rather related to the amount of rainfall ("amount effect") (Dansgaard, 1964; Rozanski et al., 1993).

Time series of stable isotope measurements of rainfall are very scarce in the Sahel region of West Africa, with only two stations of the Global Network of Isotopes in Precipitation (GNIP), Bamako (Mali) and Niamey (Niger) having data spanning more than 10 years. Together with much shorter data series from the stations of Bobo-Dioulasso, Barogo, Houndé and Nasso in Burkina Faso, we determined the Local Meteoric Water Line (LMWL) for the study region (Fig. 3.8). The isotope ratios of precipitation have a very large range from

-10 to 5 ‰ ($\delta^{18}O$) and -60 to 30 ‰ (δ^2H). A clear "amount effect" can be observed for the collected precipitation values (Fig. 3.9). Sporadic rain events at the beginning and end of the dry season (May, June, September, October) are characterised by enriched isotopic ratios, whereas the heavy and frequent rainfalls of July and August generally have more depleted values.

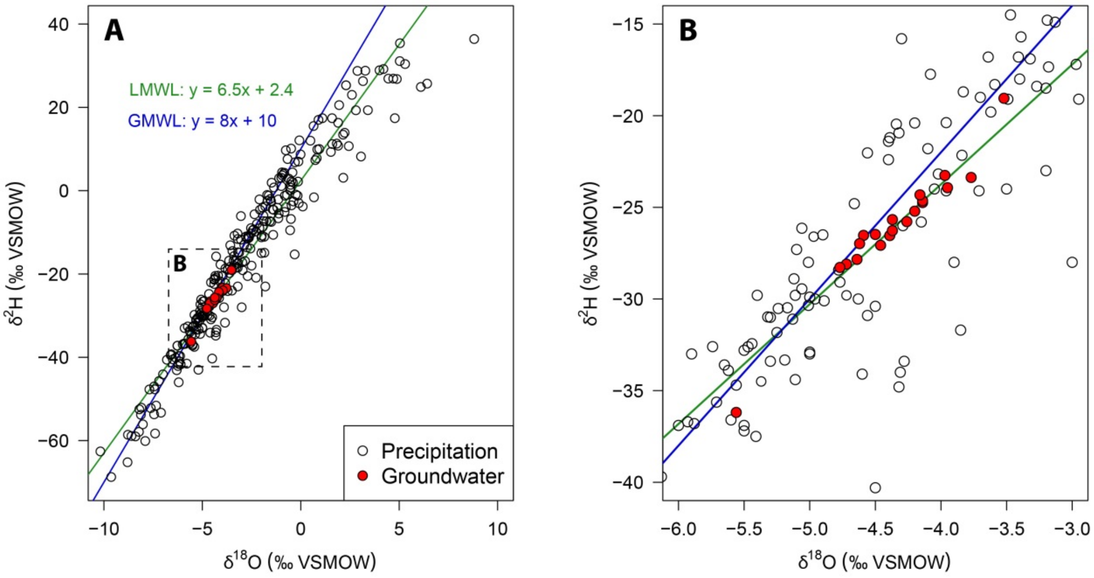

Fig. 3.8 Stable water isotopes of the sampled groundwaters in Poura and of precipitation from the following GNIP stations: Burkina Faso: Bobo-Dioulasso (2010-2015), Houndé (2004-2005), Nasso (2004-2005), Barogo (1988-1989), Mali: Bamako (1962-1979, 1991-1998), Niger: Niamey (1992-1999, 2009-2015). LMWL: Local Meteoric Water Line, GMWL: Global Meteoric Water Line. Precipitation data source: Global Network of Isotopes in Precipitation (GNIP), IAEA/WMO

The groundwater samples from the Poura study site plot in the more depleted precipitation spectrum (Fig. 3.8), indicating that strong rain events during already humid conditions at the height of the rainy season most likely lead to groundwater recharge. This supports similar findings of authors investigating groundwater recharge mechanisms in tropical African aquifers (Jasechko & Taylor, 2015; Taylor et al., 2013). In addition, the groundwater samples all plot on or near to the LMWL (Fig. 8), indicating that the water was not subjected to evaporation during groundwater recharge. This confirms observations made by other authors in the West African Sahel (Beyerle et al., 2003; Compaore et al., 1997; Huneau et al., 2011;

Lapworth et al., 2013; Lutz et al., 2011) and supports the earlier conclusion that the Cl^- vs. NO_3^- relationship is probably pollution- rather than evaporation-influenced.

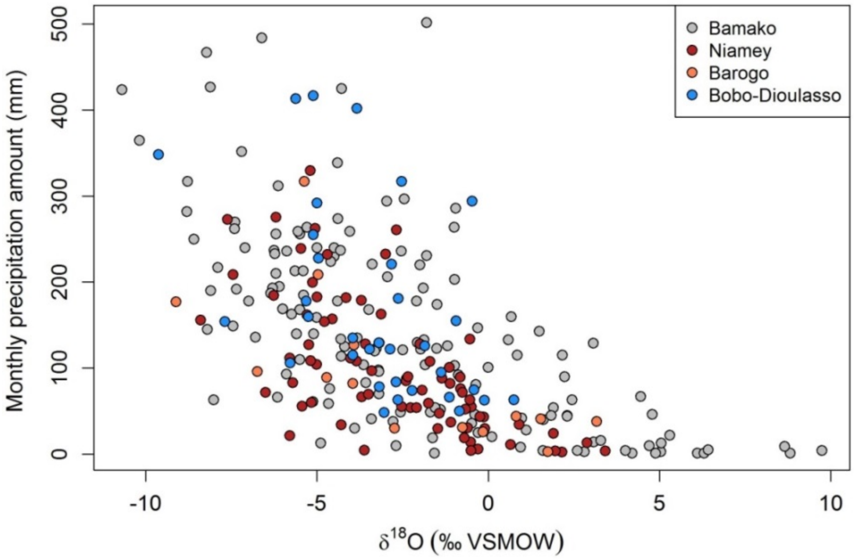

Fig. 3.9 Monthly precipitation amounts from the GNIP stations Bamako (1962-1979, 1991-1998), Niamey (1992-1999, 2009-2014), Barogo (1988-1989) and Bobo-Dioulasso (2010-2015) plotted against the mean monthly stable oxygen isotope ratio, illustrating a clear "amount effect" in isotope fractionation.

3.4.3 Noble gases and tritium

Of the twelve noble gas samples obtained from tube wells during field work in February 2016, ten delivered reliable results. Two samples were apparently air-contaminated. The results reveal a very large range in He concentrations and $^3He/^4He$ ratios varying over three orders of magnitude, whereas the concentrations and isotope ratios of the atmospheric noble gases (Ne, Ar, Kr, Xe) are relatively similar for all samples (Table 3.2). For this reason, the focus of this section will lie on the presentation and discussion of the He results.

Table 3.2 Results of noble gas analysis. Measurement errors are typically between 1 – 2% for total gas concentrations, about 0.1% for Ne and Ar isotope ratios and between 1% - 3% for He isotope ratios. (n.d.: not determined, STP: standard temperature and pressure, TU: tritium units)

Well ID	**Well Depth**	**^3H**	**He**	**Ne**	**Ar**	**Kr**	**Xe**	**$^3He/^4He$**	**$^{20}Ne/^{22}Ne$**	**$^{40}Ar/^{36}Ar$**
	m (b.g.l.)	TU	[10^{-8}] cc STP/g	[10^{-7}] cc STP/g	[10^{-4}] cc STP/g	[10^{-8}] cc STP/g	[10^{-9}] cc STP/g	[10^{-6}]		
PO-1	74	0.82 ± 0.07	6.50	2.54	3.18	6.24	7.75	1.61	0.1031	293.6
PO-37	45	n.d.	8.42	2.87	3.33	6.35	7.72	1.33	0.1031	292.6
PO-28	n.d.	n.d.	169	2.70	2.74	4.95	5.62	0.0796	0.1027	292.2
PO-30	46	1.81 ± 0.04	7.80	2.54	3.09	6.07	7.45	1.21	0.1029	293.7
PO-36	56	< 0.5	205	2.37	3.11	6.23	7.58	0.0667	0.1030	293.6
PO-7	51	< 0.5	283	2.83	3.46	6.88	8.32	0.0558	0.1031	294.3
PO-2	n.d.	1.53 ± 0.08	7.88	3.05	3.61	6.91	8.39	1.47	0.1033	293.6
PO-31	77	n.d.	37.1	12.3	8.78	13.6	14.1	1.25	0.1029	294.0
PO-17	73	< 0.5	11.1	2.62	3.29	6.52	8.10	0.864	0.1030	294.5
PO-10	81	n.d.	46.5	4.40	4.32	7.98	9.46	0.358	0.1030	293.4

By plotting the $^3He/^4He$ ratio against the Ne/He ratio, potential noble gas end members can be identified (Fig. 3.10). The ten groundwater samples are spread on a nearly ideal two-component mixing line between He from atmospheric sources with high $^3He/^4He$ ratios and radiogenic He ($^4He_{rad}$) characterised by very low $^3He/^4He$ ratios. The five samples close to the atmospheric He end member (PO-1,2,30,31,37) are shifted slightly to higher $^3He/^4He$ values than apparent from the mixing line (Fig. 3.10). This shift is likely induced by tritiogenic ^3He ($^3He_{tri}$) production from the decay of tritium (^3H). Measureable ^3H, though in low concentrations (0.8 – 1.5 TU), was determined in three of these samples (Table 3.2). They most likely contain at least some water that was recharged after the 1950s. In all other samples, ^3H was below detection (indicating pre-bomb recharge) or could not be determined due to high residual He concentrations in the samples after noble gas extraction. Such high residual gas concentrations usually occur when total He concentrations in the samples are high due to a dominance of radiogenic He, pointing to groundwater with long residence times and probably no or very little bomb-emitted ^3H. One sample, PO-31, has clearly higher concentrations of the atmospheric noble gases (Ne, Ar, Kr and Xe) than all other samples (Table 3.2), which may be interpreted as the influence of excess air. This tube well has by far the largest water table fluctuation over the wet season of all monitored tube wells (n = 8) with a rise of at least 12 m, responding rapidly to the first rains (see section 3.4.4). Such a rapid water table rise can lead to the entrapment and partial dissolution of air bubbles from the unsaturated zone, resulting in the supersaturation of dissolved gases in groundwater (excess air) compared to atmospheric equilibrium (Heaton & Vogel, 1981).

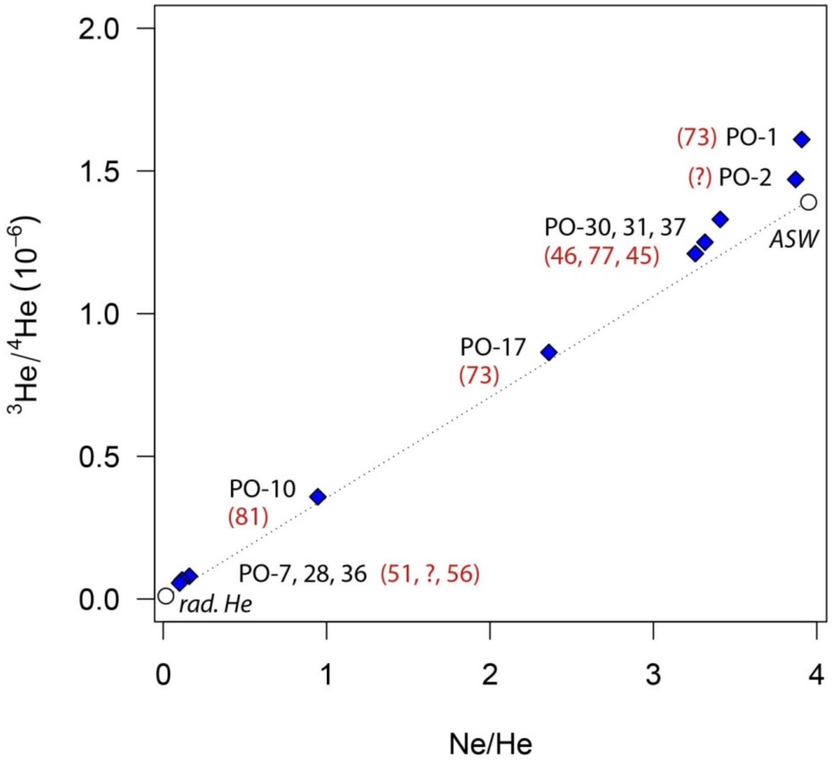

Fig. 3.10 Helium isotope ratio and Ne to He ratio of the sampled groundwater. The dotted line represents the mixing line between the atmospheric (air-saturated water, ASW) and radiogenic He end members. Samples are labelled with the well ID (in black), the corresponding depth of each well (in metres b.g.l.) is given in brackets with red font.

Three samples (PO-7, 28 and 36) stand out with very low $^3He/^4He$ ratios (Table 3.2, Fig. 3.10). Such dominance of ^4He concentrations over ^3He can only be explained by radiogenic ^4He accumulation from U/Th decay. The influence of mantle-derived He can be ruled out, as its very high $^3He/^4He$ ratios of 10^{-5} (Mamyrin & Tolstikhin, 1984) are not observed in our samples, nor would mantle He be expected considering the geological conditions of the study area. If $^4He_{rad}$ stems exclusively from in-situ, constant-rate production in the aquifer, the sampled groundwater must have been in contact with the minerals emanating ^4He for very long timescales (> 10^3 years) in order to accumulate such high ^4He concentrations. By using the average U and Th concentrations of rock samples (andesite, dacite) in the study area (U:

0.4 ppm, Th: 1.1 ppm, database appendix to Ouedraogo et al. (2003)), we calculated a ^{4}He production rate of 8 * 10^{-14} cm^3STP/g_{rock}/a as demonstrated in e.g. Craig and Lupton (1976); Torgersen and Clarke (1985). By assuming a rock density of 2.5 g/cm^3 and porosities ranging from 0.5 % to 5 % for an andesitic rock, we could further estimate groundwater age ranges of about 70 – 700 ka for sample PO-7, 40 – 400 ka (PO-28) and 50 - 500 ka (PO-36). These numbers are very rough indications only and may be overestimated if the other mentioned He sources (e.g. crustal flux or stored He, see section 3.3.2) also contribute to the total He concentrations. Local connections and discontinuities may exist to very deep fracture zones (as described, for example, in Courtois et al. (2010)), that may act as conduits to He-rich fluids rising from deeper crustal layers. The Paleoproterozoic rocks with ages above 2 Ga that form the aquifers may have also accumulated a large ^{4}He pool (by U/Th decay) since their formation, some of which may be released over mineral surfaces during subsurface weathering. As explained in Section 3.2.2, the studied aquifers and their fracture porosity represent a deep weathering profile formed over many millions of years. Other studies have found though, that the He release due to weathering is insignificantly small compared to the in-situ production and crustal flux (Heaton, 1984; Torgersen & Clarke, 1985). Overall, we lack detailed information to accurately quantify the $^4He_{rad}$ accumulation and therefore cannot calculate a quantitative groundwater residence time. However, it can be assumed with some certainty that the samples with high ^{4}He concentrations contain portions of groundwater that had long residence times in the order of thousands of years and were cut off from the modern water cycle.

The tube wells with very low ^{3}He/^{4}He ratios do not follow a spatial trend in the study area and are found in close proximity to wells with a more modern signature. All sampled tube wells are similar in depth. In general, the most likely scenario to explain the high variations in ^{4}He concentrations is that some water-carrying fractures, even at depths of less than 50 m b.g.l. remain isolated from modern recharge and can carry very old, slow-moving groundwater. Groundwater exploited via the tube wells often represents a mixture of groundwater from different fissured zones (tube wells may be screened in two or three distinct sections (Stolze, 2015)), which is also visible in the atmospheric to radiogenic He mixing ratio presented in Fig. 3.10. The wells PO-10 and PO-17 most likely represent mixtures of groundwater with short and long residence times, while the fractions of modern water increase in samples plotting towards the atmospheric-influenced He endmember. “Old” water dominates where samples plot towards the radiogenic He endmember.

It could be expected that groundwaters with residence times > 10^3 years can also be distinguished from waters with much younger components by their hydrochemical and isotopic profiles. This is only the case to a certain extent. When comparing $^3He/^4He$ with $\delta^{18}O$ values, the "old" groundwaters have more depleted $\delta^{18}O$ values, though the differences to modern-influenced groundwater are only slight (Fig. 3.11). If groundwater had been recharged during a different, cooler climatic regime than at present, one would expect clearly more depleted $\delta^{18}O$ values than found in groundwater recharged by modern precipitation (e.g. Beyerle et al. (2003)). The Sahel has certainly experienced periods of much cooler climate, though these have also alternated with climatic regimes similar to the present (Beyerle et al., 2003; Edmunds, 2009; Lézine & Casanova, 1989). Groundwater with residence times > 10^3 years therefore does not necessarily have to display very different $\delta^{18}O$ and δ^2H values to that fed by modern recharge. Supporting this statement, some groundwater samples with ^{14}C-ages > 5 ka dated by Huneau et al. (2011) in sedimentary formations of south-west Burkina Faso and Mali using ^{14}C exhibited similar $\delta^{18}O$ values as modern groundwater. Similarly, no large differences were seen in $\delta^{18}O$ values of groundwaters in Mali and Senegal with ages ranging from modern to late Pleistocene (Edmunds, 2009). The sampled groundwaters in Poura most probably represent mixtures of old and some modern water, meaning that a more depleted $\delta^{18}O$ signature from a cooler climatic regime may be "diluted" by modern water portions with more enriched $\delta^{18}O$ values. No clear relationship can be observed between the degree of groundwater mineralisation as an indicator of prolonged water-rock interaction (given here as electrical conductivity (EC)) and groundwater residence time, though the three samples with low $^3He/^4He$ ratios have some of the highest EC values of all sampled tube wells (Fig. 3.11). Only strontium (Sr) shows some positive relationship with the $^3He/^4He$ ratios (Fig. 3.11), the old waters having higher Sr concentrations than water with modern influence. This is indicative of more mature groundwater with longer water-rock interaction.

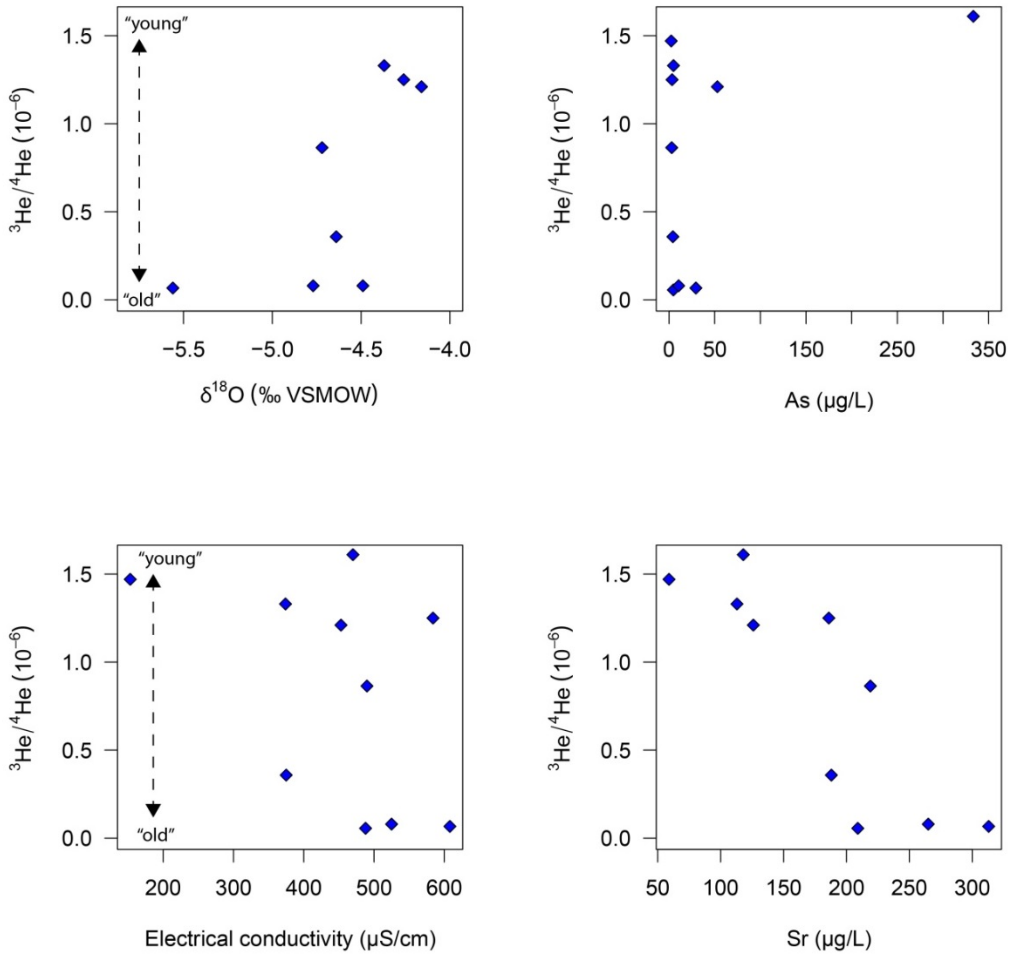

Fig. 3.11 Helium isotope ratios (^{3}He/^{4}He) as an indicator of groundwater residence time plotted against other measured hydrochemical and isotopic parameters. The terms "young" and "old" refer to groundwater with short or long residence times as inferred from noble gas data.

Arsenic-affected tube wells capture groundwater with ^{3}He/^{4}He ratios spanning three orders of magnitude (Fig. 3.11). Elevated As concentrations are therefore found both in "old" groundwater, as indicated by very low ^{3}He/^{4}He ratios (tube well PO-28, PO-36) as well as in tritium-containing, "modern" water (e.g. tube well PO-1, PO-30). Prolonged water-rock interaction, taking place over thousands of years in waters with long residence times, therefore does not seem to be a key factor in promoting elevated As concentrations. These results, in combination with hydrochemical data described in section 3.4.1, further support the hypothesis of previous studies (e.g. Smedley et al. (2007)) that attribute elevated As concentrations (as As(V) in predominantly oxic waters) to result from sulphide mineral oxidation in auriferous zones. The proximity to such zones is most likely the main factor promoting the development of high As concentrations.

3.4.4 Seasonal changes

Very few data exist on the influence of the annual monsoon on groundwater hydrochemistry in the West African crystalline bedrock aquifers. Specifically, temporal changes in As concentrations have not been investigated yet. Seasonal monitoring of groundwater levels revealed that tube wells in the study area respond differently to the monsoon. Gaps in the dataset do not allow a detailed interpretation, but general trends are visible. The water levels of some tube wells (e.g. PO-31) peak towards the end of the monsoon (October), whereas others only reach their highest level in December (PO-7), half a year after the onset of the rainy season (Fig. 3.12). The very late water level peak for the two tube wells abstracting water with long residence times (PO-7 and PO-28) is another indicator that these wells tap water from fractures that are at least partially isolated from modern, infiltrating water.

Results from hydrochemical sampling reveal that As levels in the study area do not vary greatly over the year (Fig. 3.12). A slight dip in concentrations can be observed in most wells during August-October, corresponding to the highest groundwater levels. Thus, there seems to be a slight dilution effect as uncontaminated water reaches the aquifer after the onset of the rains. As water levels recede again, concentrations stabilise. The only clear rise in As concentrations can be observed for the dug well PO-14, though this does not correspond to a rise in water level, which comes later (Fig. 3.12). Near-surface aquifers tapped by dug wells can be more vulnerable to fluctuations in water level, pH and redox conditions, possibly also affecting the mobility of trace elements.

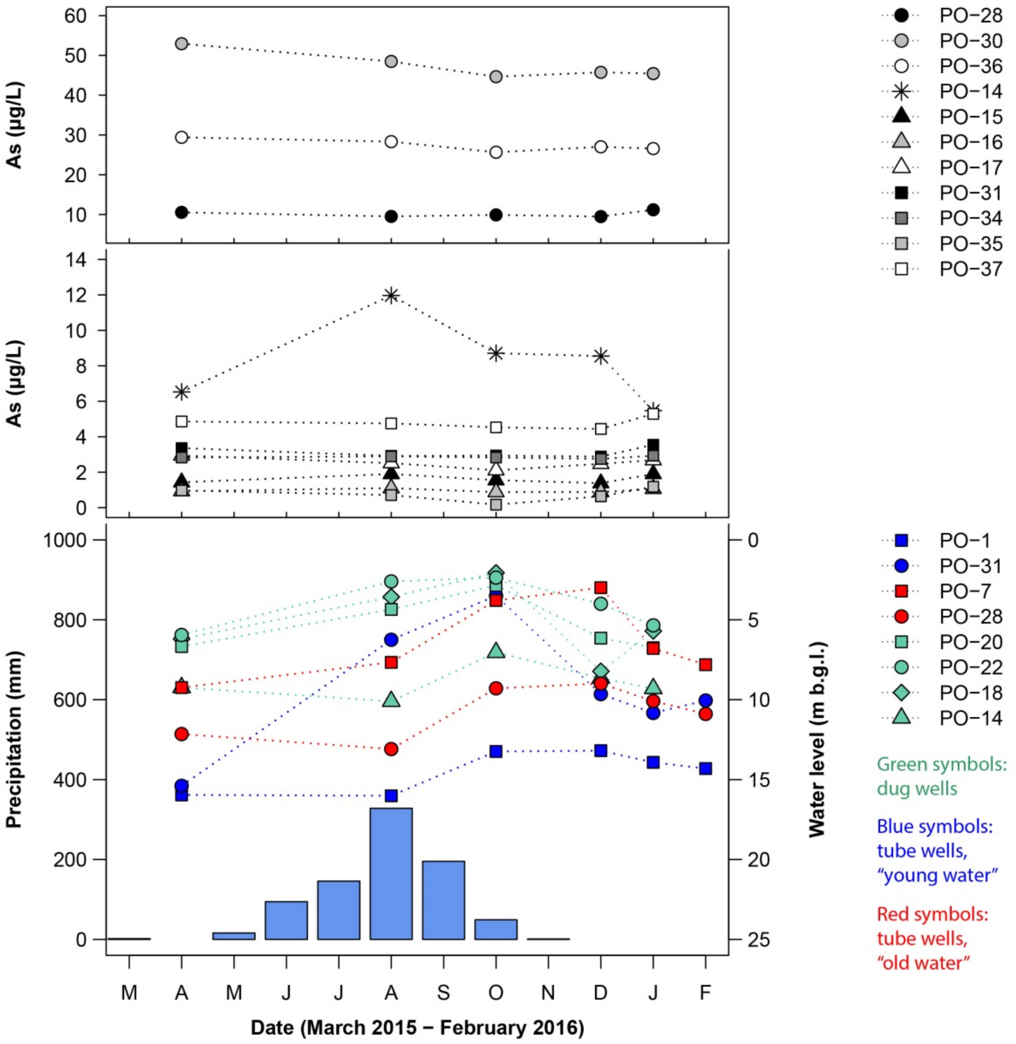

Fig. 3.12 Top graphs: Groundwater As concentrations measured in irregular intervals over the course of one year, from March 2015 to February 2016. Bottom graph: Static water level changes in a selection of tube wells and dug wells. The terms "young" and "old" water refer to groundwater with short or long residence times as inferred from noble gas data. The lowest water levels would be expected at the beginning of the rainy season, which cannot be seen in this data set as no samples exist from this period. The legend refers to the individual well IDs. Precipitation data is for the town of Boromo, about 25 km from Poura (Source: Direction Générale de la Météorologie du Burkina)

3.5 Summary and Conclusions

This study aimed to investigate As-affected aquifers in fractured crystalline bedrock in West Africa by employing hydrochemical analyses in combination with isotope tracers. Results showed that a high variability in chemical and physical groundwater properties exist, influenced both by the geochemistry of the host rock (e.g. mineralised zones) but also by the highly heterogeneous fissured and fractured underground. Groundwater with varying elemental chemistry, redox conditions and residence times can co-occur over spatial scales of only a few hundred metres (Fig. 3.13). The application of noble gas tracers yielded new insights into the groundwater residence time distribution of these aquifers. In addition to modern, recently recharged groundwater with residence times of < 50 years, we could show the existence of very old water portions with residence times > 10^3 years already at depths of < 50 m below ground level, representing non-renewable groundwater resources. This is valuable information, as previous studies generally attributed shallow groundwater in West Africa to dominantly have residence times between 30-60 years (Lapworth et al., 2013). We hypothesise that some water-bearing fractures remain disconnected from modern recharge and carry old, very slow-moving water. Discontinuities to the fresh, unweathered bedrock may also enable fluids from deeper layers to rise up (Fig. 3.13).

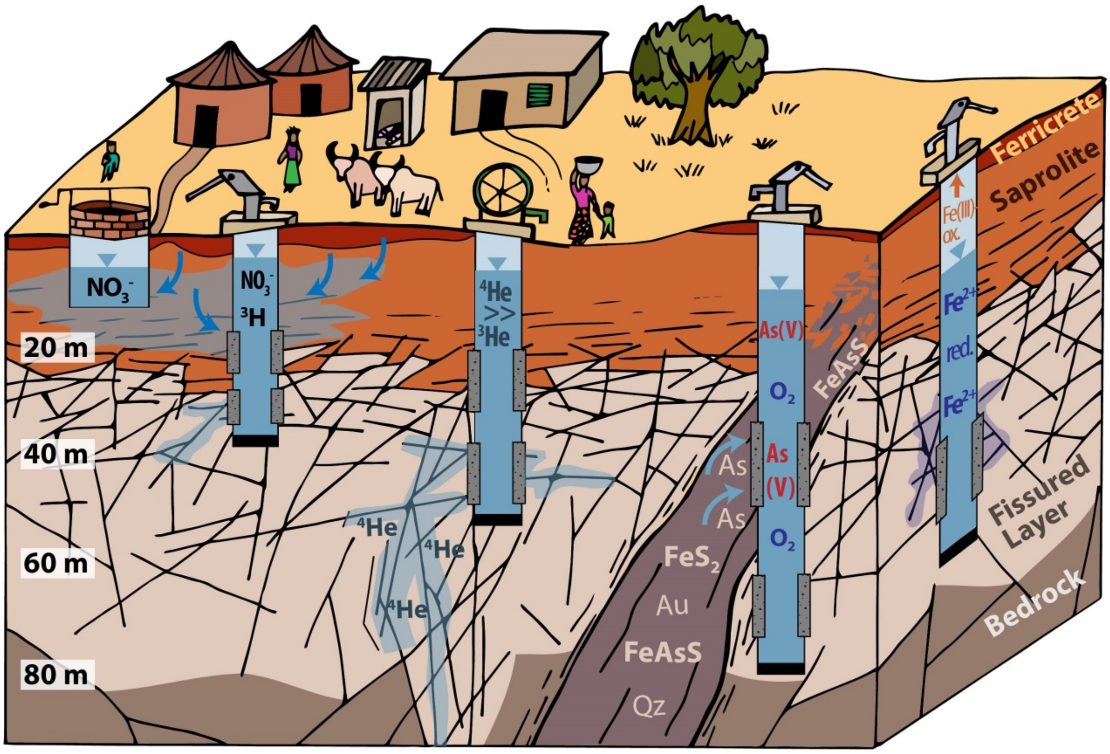

Fig. 3.13 Overview diagram illustrating the highly variable physical and chemical groundwater properties observed in the study area. From left to right: i) Groundwater in dug wells and shallow tube wells dominated by modern recharge and at times affected by pollution from settlements, livestock or agriculture. ii) Tube wells tapping groundwater with long residence times (> 10^3 years, high ^4He concentrations) from fractures isolated from the modern water cycle, possibly with connections to deeper crustal zones. iii) Geogenic As contamination in wells directly dissecting mineralised zones, where As is released from sulphide minerals (FeAsS, FeS_2) by oxidation and found in oxic groundwater as dissolved As(V). iv) Locally mildly reducing conditions (Eh < 300 mV) leading to high dissolved Fe concentrations. The diagram is not drawn to scale.

Elevated As concentrations (> 10 µg/L) were found in oxic tube well groundwater with both short (< 50 years) and long (> 10^3 years) residence times and at different depths. The deepest of the four sampled dug wells also had a slightly elevated As concentration. Arsenic concentrations therefore do not seem to be influenced by groundwater residence time and increased water-rock interaction. In the absence of any clear correlations of As with other hydrochemical or isotopic parameters, we hypothesise that, in the observed oxidising conditions and at circum-neutral pH, solely the direct proximity to sulphidic mineralisations associated with quartz veins is relevant for generating the observed high As concentrations via sulphide oxidation. The annual monsoon season and associated changes in groundwater levels seem to have little effect on As concentrations in tube wells, with only a very slight dilution effect observed in some wells. For drinking water provision, As remains of great concern. Affected wells are impossible to identify via factors such as well depth, redox potential, oxygen concentration or other hydrochemical parameters, therefore water analysis with advanced analytical techniques is always necessary. The alternative abstraction of groundwater via shallow dug wells cannot be recommended, as these may also contain As and are more vulnerable to nitrate and microbiological contamination. Large-scale groundwater quality surveys targeting As should be a focus for national authorities, especially in the Birimian mineralised zones where As-affected groundwater is more likely to occur than in the large granitic terrains (Bretzler et al., 2017).

Extensive groundwater exploitation for irrigation and industrial purposes is still relatively rare in Burkina Faso. With a rapidly rising population and increasing industrial and agricultural development, groundwater use will certainly increase in the future (Barbier et al., 2006). Considerable capacity for groundwater storage exists in the aquifers of the Sahel and seasonal monsoonal rainfall is clearly responsible for widespread modern groundwater recharge (Lapworth et al., 2013; Leduc et al., 1997; MacDonald et al., 2012; Martin & Van De Giesen, 2005). The relatively low-yielding crystalline bedrock aquifers have previously been estimated as being resilient to increasing extraction rates and climate change (MacDonald et al., 2012; Martin & Van De Giesen, 2005). Nevertheless, in light of the results of this study and the fact that groundwater residence times are still very little investigated in these systems, this statement may be too general. Aquifers yielding water with residence times > 10^3 years may certainly be vulnerable to unsustainable exploitation. Without the application of age-dating tracers such as noble gases, ^{3}H and ^{14}C, these waters are very difficult to identify, as their chemical signatures can be similar to those of water containing higher fractions of modern recharge. The relatively small noble gas dataset of this preliminary study limits the depth of interpretation that is possible. Nevertheless, the results show that more in-depth studies involving age-dating tracers in the fractured bedrock aquifers of semi-arid West Africa are necessary to gain a more complete picture of groundwater residence times.

Acknowledgements

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4 Arsenic removal with zero-valent iron filters in Burkina Faso – field and laboratory insights

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Manuscript in preparation

Abstract

Groundwater contaminated with geogenic arsenic (As) is a widespread occurrence in Burkina Faso and frequently used as drinking water despite adverse health effects. Where switching to an alternative, uncontaminated source is not feasible, As removal is the only option to supply water adhering to guideline values. To make As removal as affordable as possible, this study focussed on testing low-cost, low-tech filter systems based on zero-valent iron (Fe(0)), specifically SONO filters, which have shown success in As-affected regions of Bangladesh but have not at all been explored in West Africa. Due to a lack of suitable, clean scrap iron filings, the active Fe(0) bed was constructed using small-sized iron nails. Three nail-based filters were tested for nine months in remote rural households in northern Burkina Faso with tube well As concentrations of 400 – 1350 μg/L and daily filtered volumes of 40 – 60 L. A fourth filter containing granular ferric hydroxide (GEH®) acted as a reference for comparing the efficiency of the nails with an established, industrially-produced adsorbent. In parallel, laboratory filter columns using nails were run for five months to find the set-up for optimal As removal, with special attention given to the influence of input pH, flow rate and water/nail contact time. The field nail filters displayed lower than expected As removal efficiency (65 - 86%) in the first six months of operation. The column experiments revealed that trapped air in the nail layer greatly lowers As removal due to decreased water/nail contact time. Measures taken to avoid entrapment of air and increase contact time (raising the outlet to keep the water level permanently above the nail layer) only lead to a partial improvement in the field filters, with effluent concentrations still > 50 μg/L. Similar structural modifications were very successful

in the columns, where As removal efficiency was consistently above 95% and effluent concentrations frequently < 10 μg/L. The tested nail-based systems therefore have potential, but the efficiency needs to be urgently increased for field applications with high As input concentrations. Finding scrap iron shavings with a high specific surface area should be a priority. The GEH filter removed As to < 10 μg/L consistently, but represents a high-cost material that is not affordable for rural communities in Burkina Faso in the long term.

4.1 Introduction

Groundwater contaminated with geogenic Arsenic (As) is widely used as drinking water in West African countries. In Burkina Faso, 560,000 people in rural communities are estimated to rely on water from contaminated tube wells (Bretzler et al., 2017). Well-switching to uncontaminated sources has proven to be an effective As mitigation measure in other countries, e.g. Bangladesh (Inauen et al., 2013). However, due to the different climatic and geological conditions in Burkina Faso (semi-arid climate, lower water tables, fractured crystalline bedrock aquifers) and resulting elevated cost of drilling, villages may only be supplied by few community tube wells equipped with hand pumps. As a result, switching to uncontaminated wells is not always feasible. Therefore, water treatment removing As may be necessary to supply drinking water adhering to the WHO (and Burkinabè national) guideline value of 10 μg/L.

Considerable research has been undertaken in the last decades in finding effective As removal technologies for low- and middle-income regions, spurred by the “As crises” in Asia and Latin America (Bundschuh et al., 2010; Litter et al., 2012; Mohan & Pittman, 2007). Due to the affinity of As to bind to Fe-oxides, Fe-based materials have been amongst the most successful and widespread solutions. Industrial adsorption media, such as granular ferric hydroxide (GEH®) or Bayoxide®, can be very effective in removing As due to their high specific surface areas, but the comparatively high cost of the material often makes it unaffordable for low-income rural communities. On the other hand, technologies based on low-cost and generally available metallic Fe (zero-valent iron, Fe(0)) such as scrap iron or iron nails have been shown to be promising and partly successful in low-income settings at both the household and community level (Chaudhari et al., 2014; Chiew et al., 2009; Neumann et al., 2013; Ngai et al., 2007; Smith et al., 2017). The corrosion of Fe(0) leads to the formation of dissolved Fe(II) and various mixed Fe(II)/Fe(III) and Fe(III) phases that act as sorbents for both As(III) and As(V) (Leupin & Hug, 2005). The design and efficiency of the different systems can vary considerably. Kanchan filters use iron nails as an Fe oxide source, but some studies have shown that the contact time between nails and water is too short, limiting As removal efficiency (Chiew et al., 2009; Singh et al., 2014; Smith et al., 2017). The community-scale system developed by the Indian Institute of Technology Bombay (IITB) utilises a similar concept as Kanchan filters, but is more effective as water/nail contact time is increased (Chaudhari et al., 2014). Also NIS ("nails-in-sand") filters developed in China have attempted to increase water/nail contact time and yielded promising results (Smith et al., 2017). SONO filters, developed in Bangladesh, utilise fine scrap iron shavings (composite iron matrix, CIM) instead of nails and have a higher specific surface area and therefore corrosion rates (Hussam & Munir, 2007). A sand filter after the Fe layer removes residual Fe from the water.

Arsenic removal is dependent on various factors and no technology performs consistently well for all water types. The presence of high P concentrations competing with As for adsorption sites can considerably reduce As uptake, as can Si (Leupin & Hug, 2005; Leupin et al., 2005; Roberts et al., 2004; Sun et al., 2006; Tyrovola et al., 2006; Wenk et al., 2014). Arsenate (As(V)) sorbs preferentially over arsenite (As(III)) to Fe-oxides in the prevailing pH conditions of natural waters (Dixit & Hering, 2003), and groundwater containing mainly As(III) may have to undergo pre-oxidation before the main As removal step. Technologies therefore have to be chosen and/or adapted to suit local groundwater composition, pH and redox state (Hug et al., 2008).

To our knowledge, no studies have been undertaken to investigate suitable low-cost, low-tech Fe-based As removal options adapted to conditions in West Africa, and specifically in Burkina Faso. Considering the already described technologies using Fe(0), the aim of this study was not to develop a new removal system, but rather to benefit from the state of the art and adapt and test existing technologies. In contrary to the often reducing groundwater systems in lowland Asia dominated by As(III), geogenic As in Burkina Faso stems from the oxidation of sulphide minerals (e.g. arsenian pyrite, arsenopyrite) in mineralised zones and occurs as As(V) under oxic conditions (Bretzler et al., 2017; Smedley et al., 2007). Together with low P concentrations (< 0.05 mg/L) and circum-neutral pH, conditions are relatively favorable for As(V) adsorption onto iron oxide phases. Dissolved Fe concentrations, on the other hand, are generally very low (< 100 μg/L) and not sufficient for As removal without additional Fe-sources (Berg et al., 2006). Considering that Burkina Faso is one of the poorest countries in the world, filters should be constructed exclusively from low-cost, locally available materials and be reliable and robust in operation. We chose the SONO technology as the basis for filter materials and designs in Burkina Faso, as SONO filters are well studied, need very little maintenance and can be operated for years without exchanging the Fe matrix (Hussam & Munir, 2007; Neumann et al., 2013).

The challenge for reproducing SONO filters outside of Bangladesh is finding the right Fe(0) material to replicate the Composite Iron Matrix (CIM), the active filter bed where As is adsorbed. CIM is a layer of loose, pre-corroded iron filings and turnings that are produced free of lubricant and oils. For this study, it was not possible to find similar suitable iron filings, at least not in a quantity necessary for multiple filters, especially considering a possible later scale-up if pilot tests should prove successful. The least costly form of clean iron with a reasonably high specific surface were small iron nails. Filters with iron nails are used in Nepal and Cambodia (Kanchan filters), but this filter design often results in insufficient contact times with the iron nails exposed to air between filtrations (Chiew et al., 2009). This leads to different corrosion reactions and products than in SONO filters, where the iron matrix is embedded between two sand layers and remains anoxic between filtrations (Neumann et al., 2013; Wenk et al., 2014). The purpose of this study was to test filters that use the same design as SONO filters, but with locally available iron nails instead of the finer iron turnings and filings, and to determine the filter performance under different operating conditions. As a reference, we also conducted field tests at the same location with filters of the same design, but with granular ferric hydroxide (GEH®) as the active layer.

In parallel to field testing of filters, laboratory experiments with different filter column designs were carried out to find the set-up with optimal As removal. In addition, the still open question of the influence of flow rate and water/nail contact time on As removal could be addressed in detail in the laboratory. The field filters and laboratory columns were monitored over nine months and five months, respectively, to evaluate filter performance, Fe(0) corrosion and As removal efficiency over longer time scales.

4.2 Materials and Methods

4.2.1 Field experiment

The field experiment took place in the village of Souriyala in northern Burkina Faso (Province de Bam). The village was already a focus site of the partner NGO "Le soleil dans la main" and villagers were familiar with previous NGO activity and interventions. Two tube wells with highly elevated As concentrations (~ 450 and ~ 1000 µg/L) had previously been identified.

4.2.1.1 Filter construction and set-up

Altogether four household As removal filters were constructed, three using iron nails as an Fe-oxide source and one using Granular Ferric Hydroxide (GEH®) as an As adsorbent (Fig. 4.1, Table 4.1). GEH is a granular medium (grain sizes 0.2 – 2 mm) with an iron content of 610 g/kg and a specific surface area of 300 m^2/g (GEH Wasserchemie, 2013). The GEH filter was constructed to compare the As removal efficiency of the nail-based filters with an established and well-studied sorbent. In the nail filters, two different nail sizes were used, 20 mm x 1 mm (Filter F-1 and F-2) and 12 mm x 1 mm (Filter F-4). The filters were built following the basic design of the SONO filter by Hussam and Munir (2007), with some adaptions, mainly the replacement of scrap iron shavings by iron nails. In addition, gravel was placed at the bottom of the bucket around the tap entrance instead of brick chips, and the charcoal layer was omitted. The sand layers were composed of fine quartz sand with grain sizes of 0.4-0.8 mm. The nails (8 kg per filter) underwent some pre-treatment for cleaning and to start the corrosion processes (several 12-24h cycles of soaking in water or vinegar, followed by drying), as described in Hussam and Munir (2007) and Smith et al. (2017) for the iron filings used in SONO filters. The sand, nail and gravel layers in the filter were separated by a double layer of fine plastic (polyethylene) mosquito netting. The bottom bucket only contained gravel and sand to remove any Fe particles and dissolved Fe(II) leaving the upper bucket (Fig. 4.1). In order to reduce the flow velocity and increase water/nail contact times in filters F-1, F-2 and F-4, the taps of the top bucket were fixed into position using tape so that water left the bucket at about 8 – 12 L/h. The tap of the GEH filter was left unchanged, with flow rates being > 20 L/h.

Due to an unsatisfactory As removal efficiency after six months of filter operation (see Results, section 4.3.1) and following new insights attained during the laboratory experiments, the nail-based filters were structurally modified in October 2017. The outlet tube of the first bucket was raised to ensure that the water level stayed above the nail layer, which consequently remained permanently saturated. The top fine sand layer was replaced by gravel (mixed grain sizes of 2 – 20 mm) to enable any trapped air in the nail layer to escape more easily (Fig. 4.1).

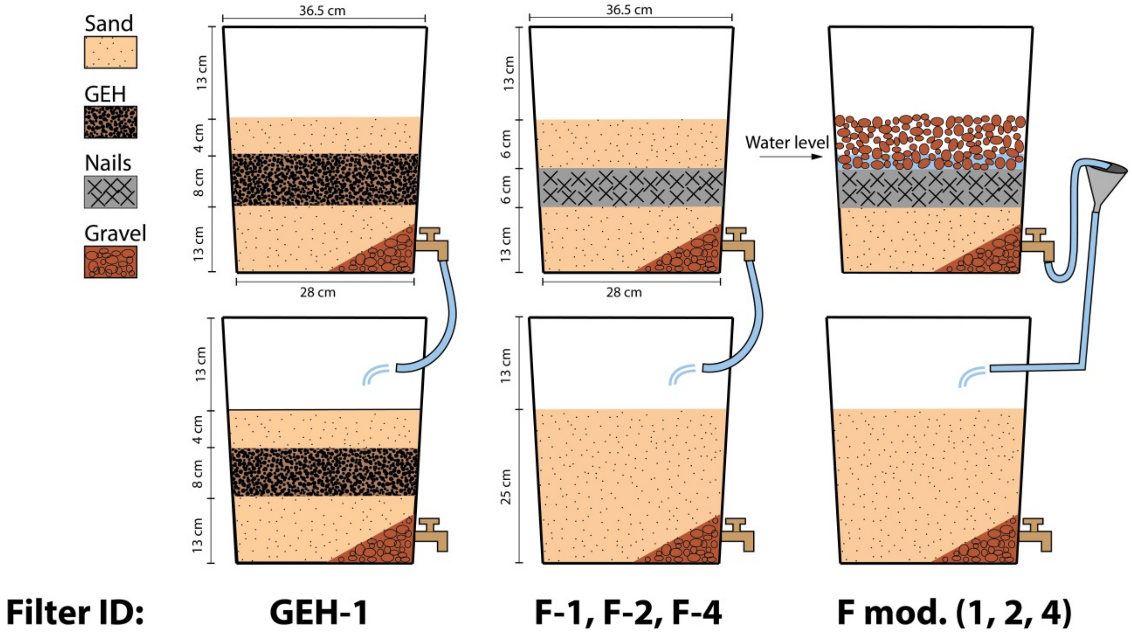

Fig. 4.1 Overview of the different filter designs installed in the field experiment. The three filters containing nails (F-1, F-2, F-4) were all modified to the setup on the far right (F mod.) in October 2017 as a result of insights attained during the laboratory experiments. The GEH filter remained unchanged.

4.2.1.2 Filter implementation and operation

Initial meetings with village elders and decision makers were held in February 2017 to present the project and discuss filter implementation. The filters were installed in the village of Souriyala Hollé in households recommended by village heads as being reliable and willing to participate. Villagers were instructed to filter three 20 L jerrycans of groundwater per day (morning, midday and evening). Considering the very hot climate and large families (the total fertility rate is 5.4 live births per woman (United Nations, 2017b)), 60 L is a realistic daily need in drinking and cooking water of a rural family. During the rainy season (July-September), only two jerrycans were filtered daily (40 L), as villagers often spent the whole day on the fields tending their crops. Sampling of input water and filtered water was initially performed weekly in the first two months after filter installation, then twice-monthly by an employee of the NGO. Due to accessibility problems to the village during the rainy season, sampling was more sporadic from August to October. Samples were collected unfiltered in 5 mL pre-acidified vials (HNO_3 suprapure) and shipped to Eawag, Switzerland for analysis using ICP-MS (Agilent 7500cx). In addition, filtered samples (0.2 µm) were taken on a monthly basis and As speciation investigated using silicate filter cartridges that retain As(V) (Meng & Wang, 1998).

Table 4.1 Main characteristics of the four test filters installed in the village of Souriyala, Province de Bam, Burkina Faso

Filter ID	As input conc. (µg/L)	Iron source	Flow rate
F-1	600-1350	8 kg nails (20 mm x 1 mm)	8 – 12 L/h
F-2	400-600	8 kg nails (20 mm x 1 mm)	8 – 12 L/h
F-4	400-600	8 kg nails (12 mm x 1 mm)	8 – 12 L/h
GEH-1	600-1350	14 kg GEH	> 20 L/h

4.2.2 Laboratory experiments

Column experiments were started in July 2017 in the laboratories of Eawag, Switzerland, four months after the launching of the field experiment in Burkina Faso. The aim of the laboratory experiment was to construct and compare different filter designs and operations that would also be viable in a field setting in order to find the best set-up for optimum As removal efficiency. In particular, the influence of the nail/water contact time was investigated by varying the flow velocity. Furthermore, the influence of variations in the pH and As speciation (As(III) and As(V)) of the influent water were investigated. An additional important factor that was found with the laboratory columns was accumulation of air in the iron layer, which seriously lowered As-removal when it occurred. Different measures to remove trapped air and to avoid its formation were explored.

4.2.2.1 Filter column construction

Initially, three different filter column variations were tested in duplicate (L-1A/L-1B, L-2A/L-2B, L-3A/L-3B), with L-2A/L-2B being identical in their set-up to filters F-1, F-2 and F-4 tested in Burkina Faso (Fig. 4.2, Table 4.2). Cylindrical acrylic glass columns with a total length of 300 mm and an inner diameter of 32 mm were used. The vertical dimensions of the nail and upper sand layer were kept the same as for the field columns (60 mm), while the bottom sand layer was reduced. Sand and nail layers were separated by a fine polyester cloth.

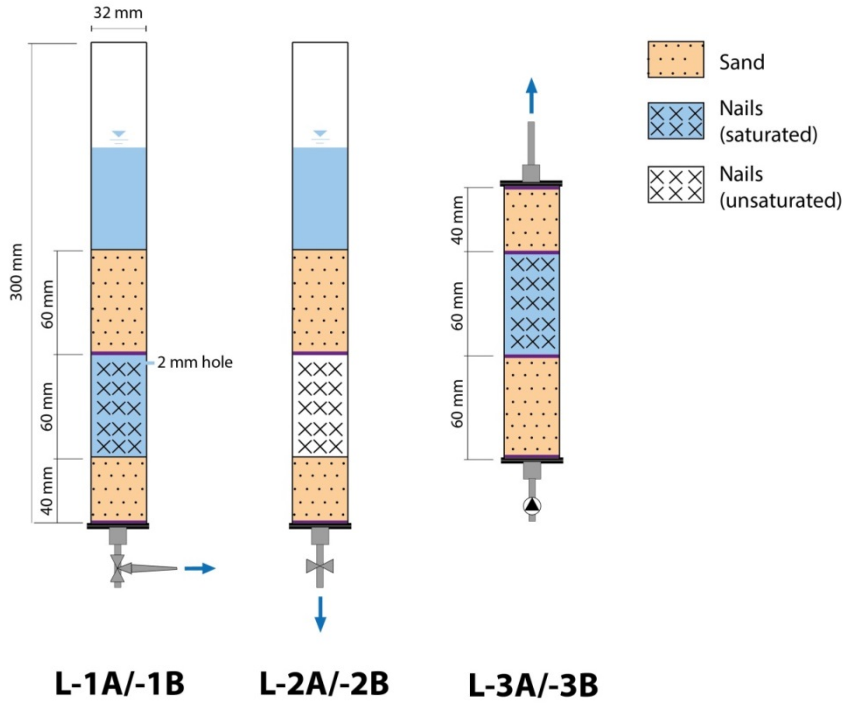

Fig. 4.2 Diagram showing the set-up of the three different filter columns initially constructed in July 2017. Columns L-2A and L-2B represent the same set-up as filters F-1, F-2 and F-4 installed in Burkina Faso. Columns L-1A and L-1B were operated with a constantly water-saturated nail layer, as were the up-flow columns L-3A and L-3B.

Table 4.2 Characteristics of filter columns constructed for the laboratory experiment

Column ID	Operation period	Nail size (mm)	Direction of flow	Specific characteristics
L-1A / L-1B	Jul-Dec 2017	12 x 1.0	Downflow, gravity driven	Water-saturated nail layer
L-2A / L-2B	Jul-Aug 2017	12 x 1.0	Downflow, gravity driven	Same design as field filters F-1, F-2 and F-4. Temporarily unsaturated nail layer (low outlet)
L-3A / L-3B	Jul-Aug 2017	12 x 1.0	Upflow, peristaltic pump	Closed filter column, no headspace, constantly saturated filter bed
L-4	Sept-Dec 2017	23 x 1.5	Downflow, gravity driven	Constantly water-saturated nail layer (raised outlet)
L-5	Sept-Dec 2017	23 x 1.5	Downflow, gravity driven	Constantly water-saturated nail layer (raised outlet). Top sand layer replaced by gravel. Same design as modified field filters (F_{mod}. 1, 2, 4)

4.2.2.2 Influent water composition and flow rate

Natural groundwater was used as influent water for the columns, with some adjustments to the water composition to mimic groundwater chemistry in Burkina Faso. Freshly pumped groundwater from a groundwater well on the Eawag campus (Switzerland) was diluted 1:1 with deionised water to halve the concentrations of all constituents. The Si concentration was raised to 10-15 mg/L by adding $Na_2SiO_3*9H_2O$, the pH adjusted to 7.0 ± 0.5 with CO_2 and As(V) spiked to attain the desired As concentration (500 μg/L or 1000 μg/L). A comparison of the water composition of the two tube wells in Burkina Faso with the Swiss groundwater adjusted in the laboratory is presented in Table 4.3.

Table 4.3 Chemical composition of influent groundwater in Burkina Faso and adjusted groundwater used for the laboratory column experiments

Location		**Souriyala Hollé (BF) old well**	**Souriyala Hollé (BF) new well**	**Eawag (CH) groundwater**	**Eawag adjusted groundwater, inflow for columns**
Filter IDs		**F-2, F-4**	**F-1, GEH-1**		**All columns**
pH		7.02	6.38	8.27	6.5 – 7.5
EC	μS/cm	666	352	674	365
DO	mg/L	1.31	2.65		
Temp	°C	31.3	30.6		
Redox	mV	361	398		
DOC	mg C/L	1.2	1	1.3	0.8
Alkalinity	mmol/L	7.7	4	5.8	3.1
Cl	mg/L	2.2	0.7	48.3	24.6
NO_3-N	mg NO_3-N/L	<0.25	<0.25	2.7	1.3
SO_4	mg/L	12.6	5.9	29	14
Na	mg/L	41	14	31	18
Mg	mg/L	39	30	16	8.0
Ca	mg/L	61	20	103	51
K	mg/L	1.5	0.8	4.6	2.7
P	mg/L	< 0.01	< 0.01	< 0.01	< 0.01
Si	mg/L	20.3	7.8	4.5	10 - 15
Fe	μg/L	60	68	< 10	< 10
As	μg/L	419	1000	< 0.1	500 - 1000

An influent water volume of 113 mL (correspondingly downscaled from the 20 L applied in the field per filtration) was pumped into the columns three times daily. All columns were operated in gravity driven down-flow mode (to reflect conditions in the field filters) except L-3A and L-3B, which were operated in reversed up-flow to maintain a constantly saturated nail layer. The approximate flow rate of 10 L/h used in the field was downscaled to an ideal rate of 1.77 mL/min for the columns (Table 4.4). This flow rate could only be constantly maintained for columns L-3A and L-3B (up-flow controlled by a peristaltic pump), whereas the gravity-filtered columns experienced variations in flow rate during each filtration due to the changes in water level and hydrostatic pressure. This effect cannot be avoided and also occurs in the field filters. The flow rate could be regulated using a tap at the outflow of the columns. The columns were filmed with a time lapse camera (30 second resolution), the video recordings giving the duration of each filtration cycle per column. Together with the volume of the collected water, an average flow rate could be calculated for each filtration.

In columns L-1A and L-1B a small hole (ø 2 mm) was drilled at the top of the nail layer. The hole was opened when needed, allowing trapped air in the nail layer to escape and closed once the water level reached the top of this layer. By changing the size and geometry of the column outlet (see Fig. 4.2), the hydraulic resistance was increased, impeding water to freely drain out of the nail layer during each filtration cycle and resulting in constant nail saturation (Fig. 4.2). Measures to avoid and to remove trapped air were not taken for columns L-2A and L-2B, where water drained out of the nail layer after each filtration and the trapped gas phase could not escape due to the small pore space of the moist sand above. The nail layer in columns L-2A and L-2B subsequently remained constantly unsaturated and water flowed over the nails in preferential flow paths during each filtration.

Table 4.4 Comparison of dimensions, iron surface area and flow conditions of all studied filters and columns. The last column of the table displays values of a column experiment using the Composite Iron Matrix of SONO filters for comparison (data from Wenk et al. (2014))

		Field filters			**Laboratory nail columns**		**SONO columns**
		F-1, F-2	**F-4**	**GEH-1**	**L-1A/ L-1B, L-2A/ L-2B, L-3A/ L-3B**	**L-4, L-5**	
Fe filter bed diameter	mm	310		310	32		32
Fe bed length	mm	60		200	60		90
Fe bed volume	cm^3	4529		15095	48.3		72.3
Mass of Fe	g	8000		14000	100		160
Bulk density	g/L	1766		927	2070		2210
Particle size	mm	20 x 1	12 x 1	-	12 x 1	23 x 1.5	2 x 1 x 0.2
Specific surface area	m^2/g	0.000521	0.000529	300	0.000529	0.00035	0.00165
Water volume per filtration	mL	20000		20000	113		100
Time for filtration	min	120		30	64		60
Flow rate	mL/min	166		667	1.77		1.67
Velocity in empty column	mm/s	0.037		0.147	0.037		2.07
Empty bed contact time (EBCT)	s	1630		1359	1630		2605
Contact time with Fe	s	1265		1359	1201		1874
Fe contact time x surface	$s * m^2/L$	1500	1525	378000000	1789	1182	9514

4.2.2.3 Column adjustments

The laboratory columns L-1A, L-1B, L-2A, L-2B, L-3A and L-3B were operated for six weeks in July/August 2017. At the end of this period, columns L-2A and L-2B were de-installed, as results had shown that trapped air accumulated in the nail layers resulted in insufficient As removal. The up-flow columns L-3A and L-3B were also discontinued, as they yielded similar results as the down-flow columns L-1A and L-1B, which better represent the conditions in the gravity driven filter in the field. Instead, two additional columns were constructed (column L-4 and L-5), where the nail layer was constantly kept saturated by raising the outlet to 1-5 mm above the upper limit of the nail layer. (Fig. 4.3, Table 4.2). In column L-5, the top sand layer was additionally replaced by gravel, to enable any trapped air to move into the large pore spaces provided by the gravel. Columns L-4 and L-5 also received 113 mL of influent water (~1000 µg/L) three times daily.

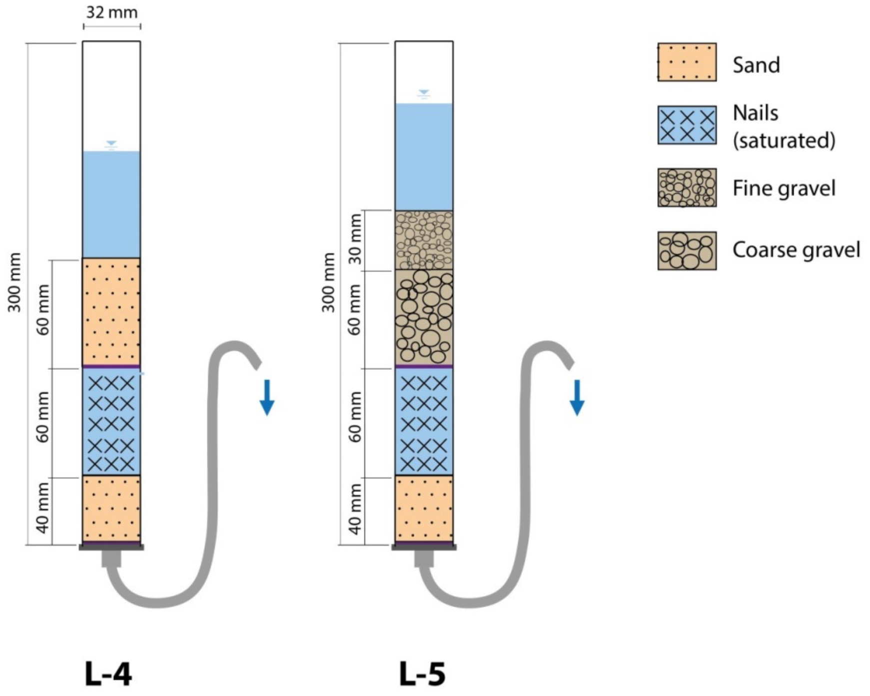

Fig. 4.3 Schematic representation of columns L-4 and L-5, that were constructed after the decommissioning of columns L-2A/L-2B and L-3A/L-3B in September 2017. The raised outflow ensures that the water level always remains above the nail layer.

4.2.2.4 Aqueous sampling and analysis

In the first two weeks after installation, effluent water was sampled after each filtration (three times daily). This was then reduced to daily sampling (mixed samples of three filtrations) and later three times a week (mixed samples of seven filtrations). When inflow pH was low (< 7) and the column effluent contained visible Fe solids, filtered samples (0.2 µm) were additionally taken. Every time new influent groundwater was mixed, a sample was taken for analysis. The pH and dissolved O_2 values of the influent water were measured three times per week. All water samples (influent and effluent) were acidified with HNO_3 suprapure and analysed for total concentrations of As, Ca, Mg, K, P, Si, Mn and Fe using ICP-MS (Agilent 7500cx).

4.2.2.5 Solid sampling and analysis

The solid phases that developed on the surface of the nails were investigated using X-ray diffraction (XRD). Some nails and water of column L-3A were removed from the column under exclusion of air and shaken overnight to dislodge the coating of the nails. The slurry with suspended solids was removed from the nails and then centrifuged. The concentrated black residue was spread on a silicon wafer, dried under an N_2 atmosphere and analysed with X-ray diffraction (Panalytical Expert[3] Powder with Co source) twice for 60 minutes. Between the two measurements, the sample was exposed to air.

4.3 Results

4.3.1 Field experiment

The filters F-1, F-2, F-4 and GEH-1 had been monitored over a period of nine months at the time of writing (Fig. 4.4). Filter F-1 and GEH-1 received water from the same tube well, with very high inflow As concentrations fluctuating between ~500 and ~1350 µg/L. Filters F-2 and F-4 were operated with water from the slightly less contaminated well (~350 - ~600 µg/L). The lowest inflow groundwater As concentrations were observed during the months of the rainy season (Jul – Oct) (Fig. 4.4).

The capacity of the nail-based filters to remove As varied considerably over the 9 month monitoring period (Fig. 4.4). From March to September, filter F-1 showed an average As removal efficiency of 65%, F-2 77% and filter F-4, which contained the smaller sized nails, 86%. None of these filters removed As consistently to less than 50 µg/L, with filter F-4 overall showing the most promising results. Only the GEH-based filter (GEH-1) always yielded effluent As concentrations of < 10 µg/L and an As removal efficiency of 99%.

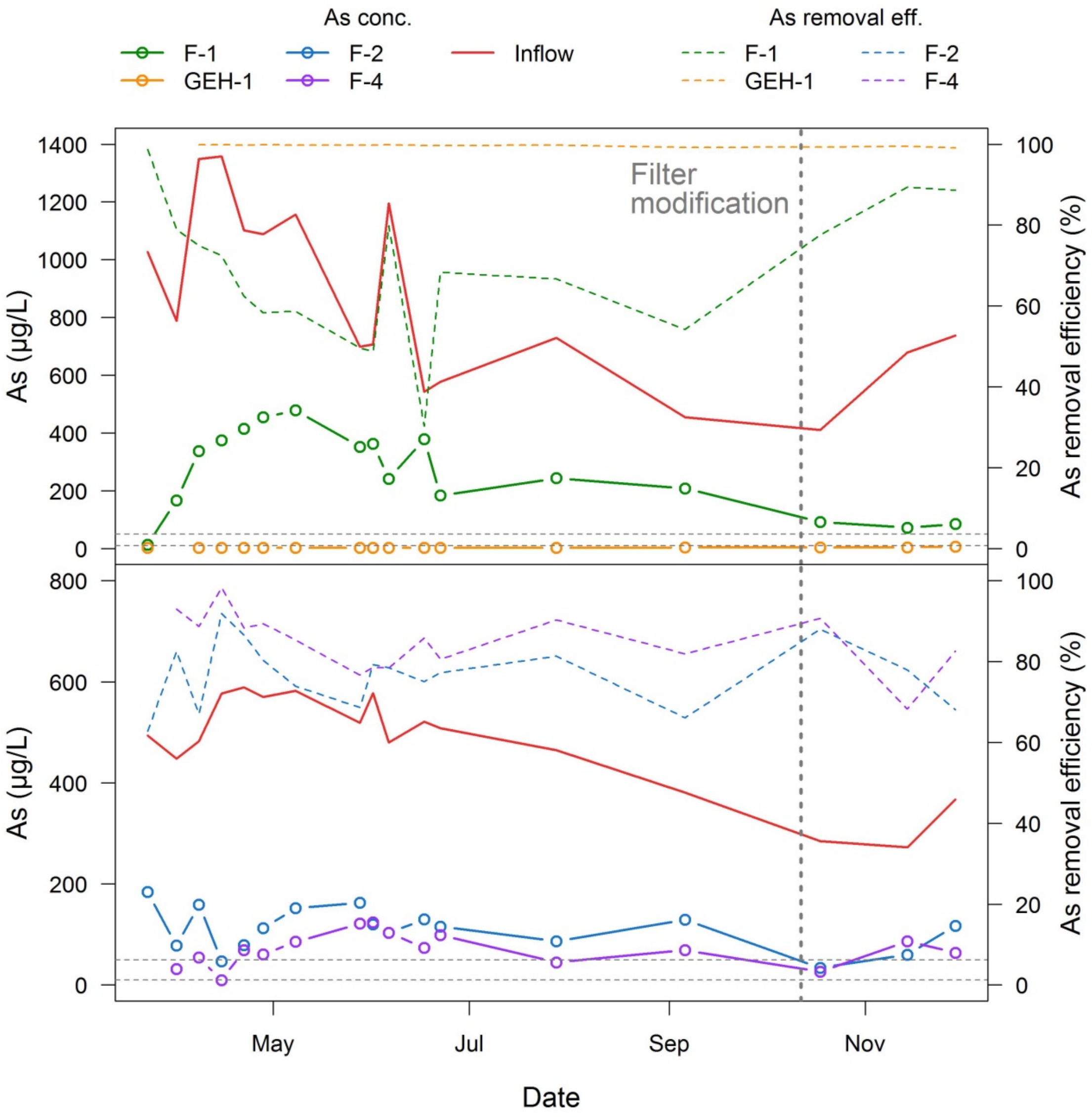

Fig. 4.4 Diagram showing the performance of the four filters installed in the village of Souriyala. The top diagram depicts the inflow and outflow As concentrations and As removal efficiency (second y-axis, dashed lines) of filter F-1 (nail-based) and GEH-1, the bottom diagram for the two nail-based filters F-2 and F-4. The horizontal dashed grey lines indicate the 10 µg/L and 50 µg/L values. The vertical dashed line marks the date of the filter modification.

After the structural modification of the nail-based filters in October 2017 (see Fig. 4.1 for details of the set-up), the mean As removal efficiency of filter F-1 improved markedly to 85%, though the outflow As concentrations were still slightly above 50 µg/L due to the very high As inflow (Fig. 4.4). An even clearer improvement was achieved in Filters F-2 and F-4 in the week after the modification, with As concentrations in filtered water dropping to below 50 µg/L and removal efficiency rising to 90%. Unfortunately, both filter's performance then worsened again, with effluent concentrations of 60 – 100 μg/L. A possible reason could be insufficient control of flow conditions and the positions of the outlets by the users, leading to fast flow or a drop in water level. In general, filter F-4 performed consistently better than F-2 over the whole operation period, most likely due to the smaller nail size used in F-4 and correspondingly higher specific surface area and Fe-oxide production.

The Fe concentrations in the filtered water of F-1, F-2 and F-4 were always below 150 μg/L, showing that the sand filter in the bottom bucket is sufficient to remove the Fe-oxides and remaining Fe(II) in the water after passing the nail layer.

4.3.2 Laboratory experiments

4.3.2.1 Arsenic removal

The performance of all columns over the total operation period of five months is illustrated in Fig. 4.5. The filter columns L-1A/L-1B, L-2A/L-2B and L-3A/L-3B were continuously run for six weeks (Jul-Aug) with three filtration cycles daily. Arsenic concentrations in the outflow of columns L-1A/L-1B and L-3A/L-3B (with a constantly saturated nail layer) always remained below 25 μg/L, and below 10 μg/L in 82% (L-1A/L-1B) and 70% (L-3A/L-3B) of samples. The mean As removal efficiency for columns L-1A/L-1B and L-3A/L-3B was 98.5% during this period. Columns L-2A/L-2B, having the same set-up as the filters in the field initially had, performed less well. Arsenic concentrations in these columns were always above 10 μg/L and frequently above 100 μg/L, with mean As removal efficiencies of 80% (L-2A) and 90% (L-2B). In contrast to columns L-1A/L-1B and L-3A/L-3B, a gas phase developed in the nail layer of columns L-2A and L-2B. The moist sand layer above the nails prevented this gas phase from escaping. Water therefore trickled quickly over the nail layer in preferential flow paths during each new filtration cycle, resulting in a very short nail/water contact time. The better performance of column L-2B in comparison to L-2A (Fig. 4.6, top graph) can be attributed to a 1.5 cm thick water-saturated layer which developed at the bottom of the nail layer of L-2B after three weeks of operation.

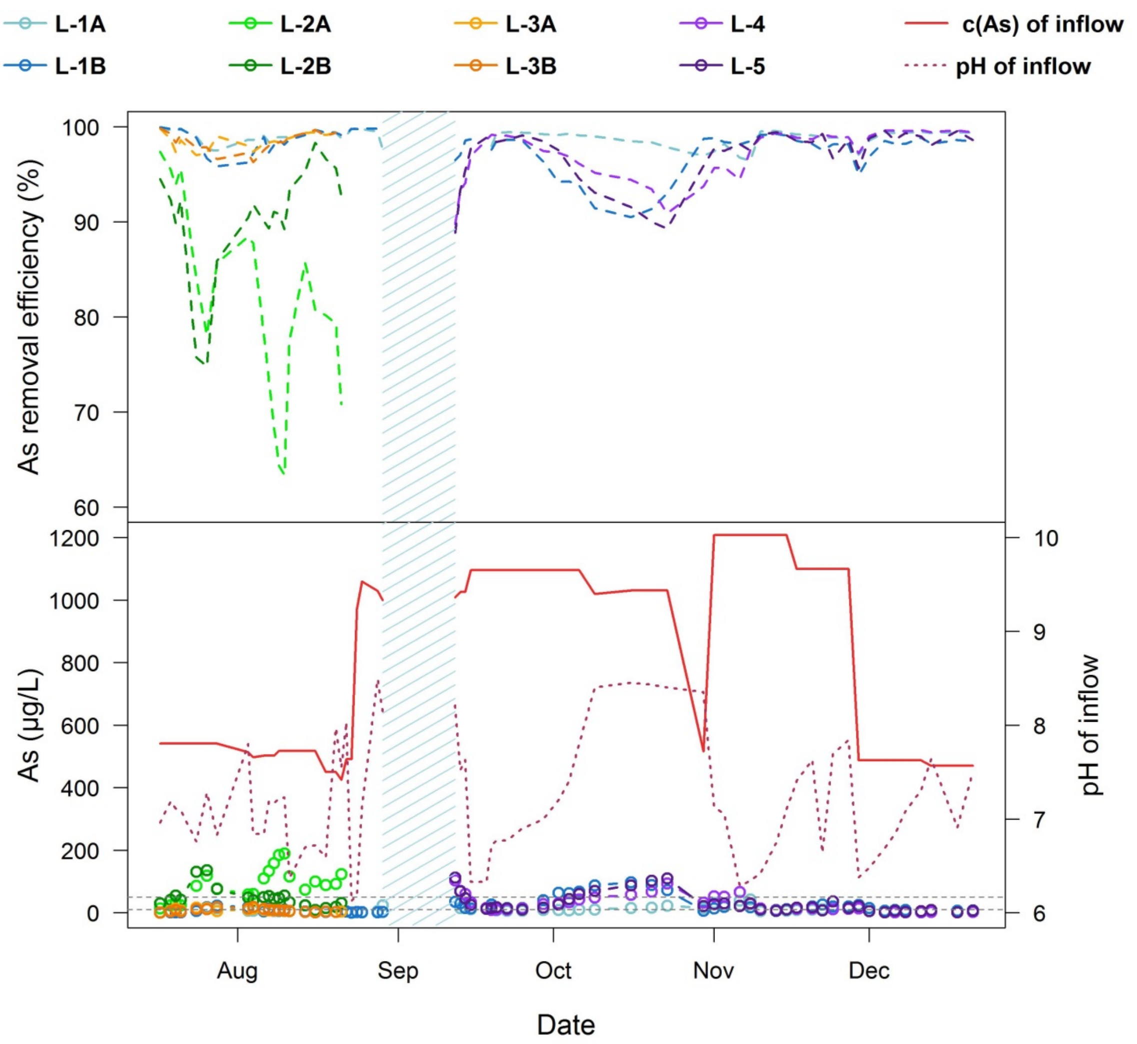

Fig. 4.5 Arsenic removal efficiency (top diagram) and influent/effluent As concentrations (bottom diagram) of the column experiments conducted from July to December 2017. The shaded area represents a pause in column operation of roughly two weeks. Columns L-2A/L-2B and L-3A/L-3B were dismantled after six weeks of operation (end of August) and the new columns L-4 and L-5 started in mid-September. The dashed grey horizontal lines indicate the 10 µg/L and 50 µg/L values.

Columns L-1A/L-1B were kept operational after the deactivation of columns L-2A/L-2B and L-3A/L-3B and showed continuously good As removal, with the exception of a period of three weeks in October when the input pH was very high at 8.5 (Fig. 4.5). The new columns constructed in September (L-4 and L-5), with a raised outflow to keep the nail layer saturated, also displayed very good As removal, despite the larger nails used in these columns (Fig. 4.5). With the exception of the high-pH period and the first days after column construction when the nails were not yet sufficiently corroded, As concentrations in columns L-4 and L-5 remained below 50 μg/L in 95% and below 10 μg/L in 36% of samples. The mean As removal efficiency for both columns was 97%.

4.3.2.2 Fe and Ca concentrations

The pH-value of the influent water was observed to be highly influential on the Fe corrosion rate, Fe(II) production and the rate of Fe(II) oxidation (Fig. 4.6, Fig. 4.7). At an influent pH < ~ 6.5, Fe concentrations in the column effluent rose markedly due to the increased H^+ availability for corrosion and the decreased oxidation rate for Fe(II). The collected effluent water was clearly orange-coloured from Fe(III) precipitates formed after the water left the column. A comparison between As concentrations of filtered and unfiltered samples during this period show that As leaving the columns sorbs to these Fe(III)-oxides, with aqueous As concentrations generally being lower in filtered than unfiltered samples (Fig. 4.8). In contrast, virtually no Fe was present in the effluents during a period of very high pH-values (> 8.0) in October, with effluent Fe concentrations below 0.02 mg/L in all columns. This also had a clear effect on As removal, with outflow As concentrations rising due to a lack of freshly produced Fe(III)-oxides for co-precipitation (Fig. 4.7). Apparently there was also a reduced rate of Fe(0) corrosion and production of fresh Fe(II,III)-oxides in the nail layer of the columns at high pH. In general, the Fe(II) production rate at pH 6.5 - 7.5 seems to be sufficient for an effective As removal. Effluent Ca concentrations show a similar pattern as Fe (Fig. 4.7) and rose above influent levels during the low-pH phases, possibly due to the dissolution of $CaCO_3$ that accumulated on the nail surfaces when the pH was > 7.5 (Wenk et al., 2014).

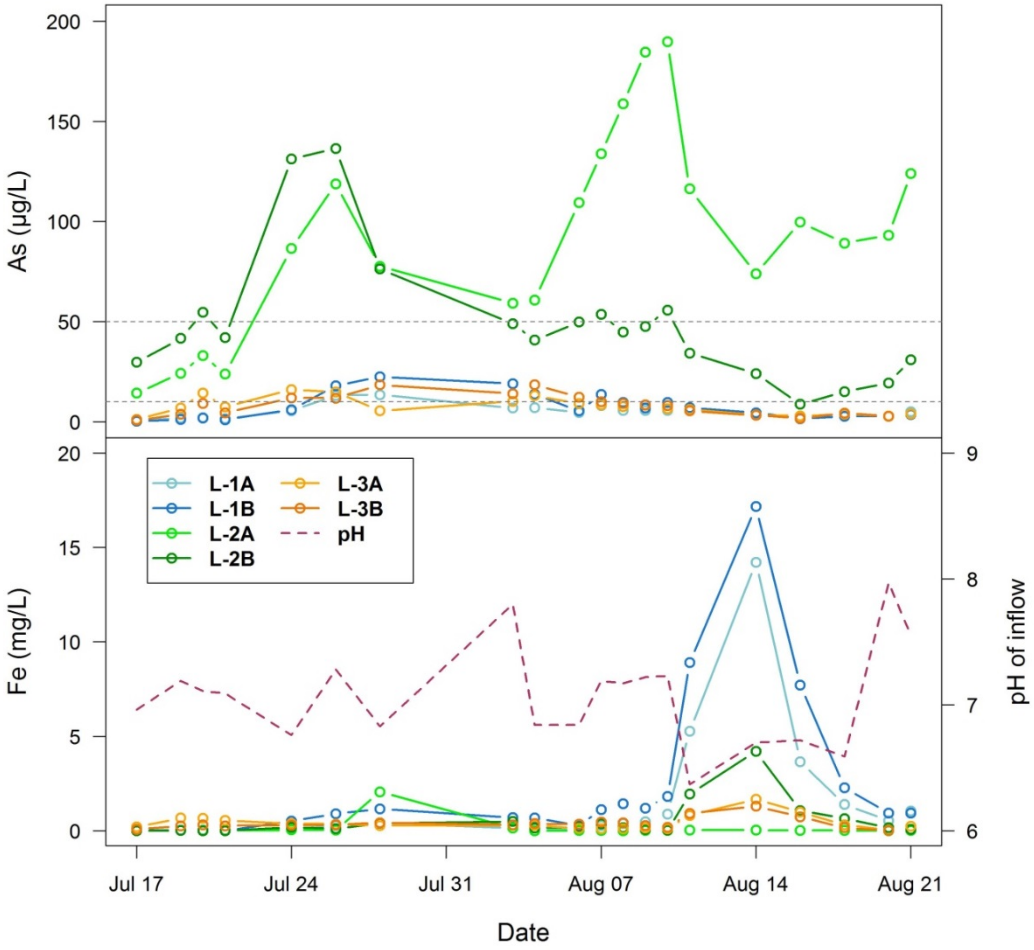

Fig. 4.6 Arsenic and Fe concentrations in columns 1, 2 and 3. The inflow As concentration is between 450 and 500 µg/L (Fig. 4.5). The dashed grey horizontal lines indicate the 10 µg/L and 50 µg/L values.

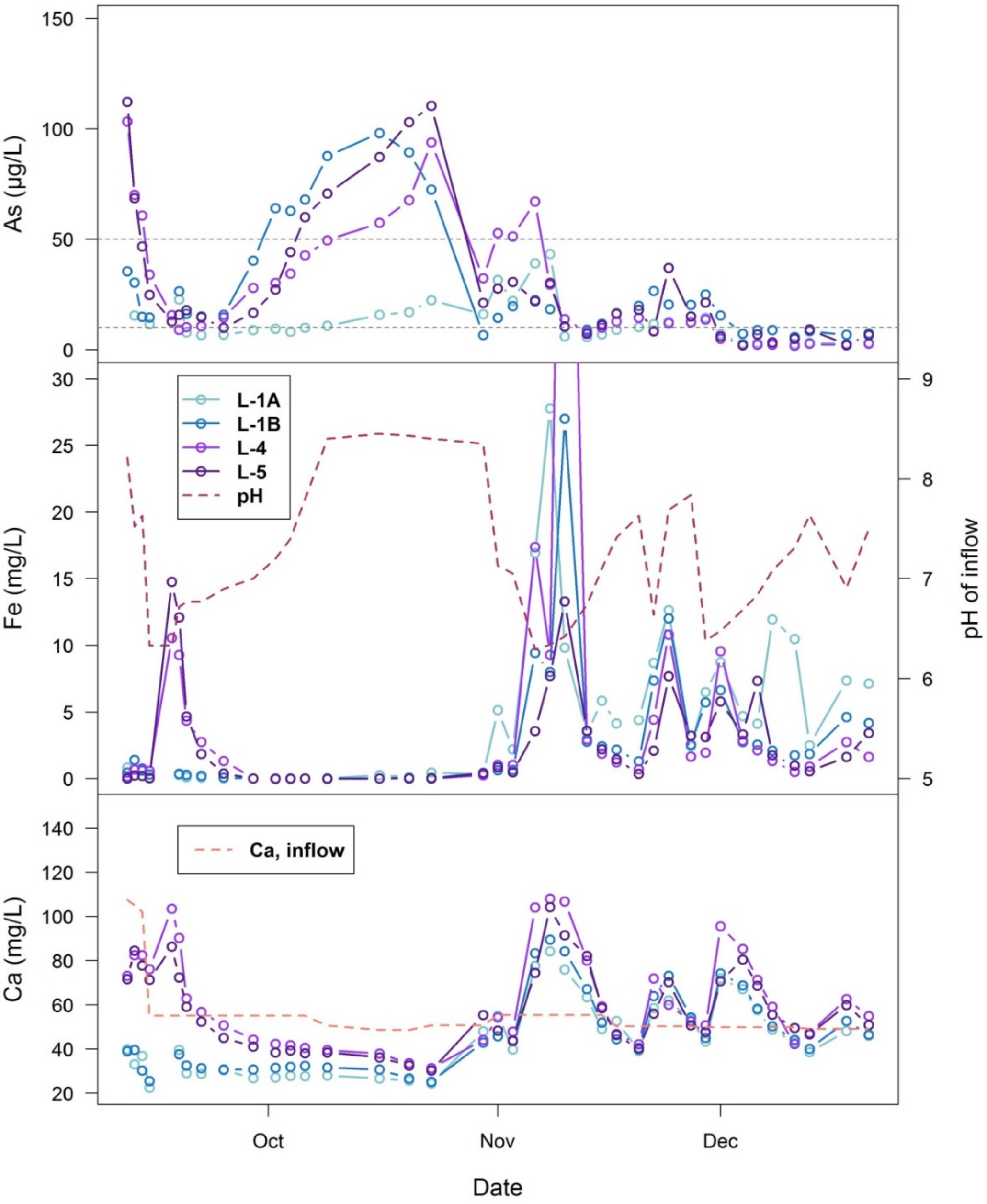

Fig. 4.7 Arsenic, Fe and Ca concentrations in columns L-1A/L-1B, L-4 and L-5. The inflow As concentration is between 450 and 1200 µg/L (see Fig. 4.5). The dashed grey horizontal lines indicate the 10 µg/L and 50 µg/L values. Arsenic concentrations from mid-November onward are those measured in filtered samples (0.2 µm).

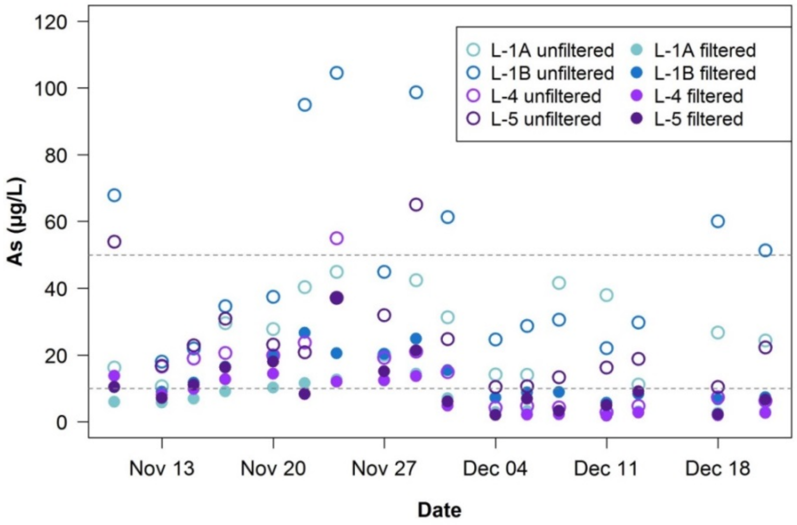

Fig. 4.8 Arsenic concentrations in unfiltered and filtered (0.2 µm) samples of columns L-1A/L-1B, L-4 and L-5. The dashed grey horizontal lines indicate the 10 µg/L and 50 µg/L values.

4.3.2.3 Influence of flow rate on arsenic removal

The rate at which the inflow water flowed through the filter bed was expected to have an influence on the effectiveness of As removal, with higher flow rates leading to decreased As removal. The results presented in Fig. 4.9 indicate that this is not the case. The As concentration curves of columns L-1A/L-1B and L-3A/L-3B follow a similar pattern, while the flow rates of L-3A/L-3B are kept constant by the peristaltic pump and those of L-1A/L-1B fluctuate (Fig. 4.9). The rise in As concentrations after July 24th, affecting both column types, therefore does not seem to be caused by the peak in flow rate of L-1A/L-1B, but must have a different reason. Similarly, As removal for columns L-1A/L-1B, L-4 and L-5 follows similar patterns, while the flow rates of L-4 and L-5 are at times ten times greater than those of L-1A/L-1B (Fig. 4.9).

4.3.2.4 Arsenic removal with As(III) inflow

In order to test the As removal efficiency of the columns when As occurs in its reduced form, As(III), columns L-1A/L-1B were run with As(III) in the inflow water (instead of As(V)) for a period of two weeks. Arsenic concentrations in the outflow water did not change significantly after the switch to As(III), staying mostly below 10 µg/L (Fig. 4.10). This suggests that As(III) is sufficiently oxidised to As(V) in the columns, as As(V) is the better sorbent to Fe-oxides.

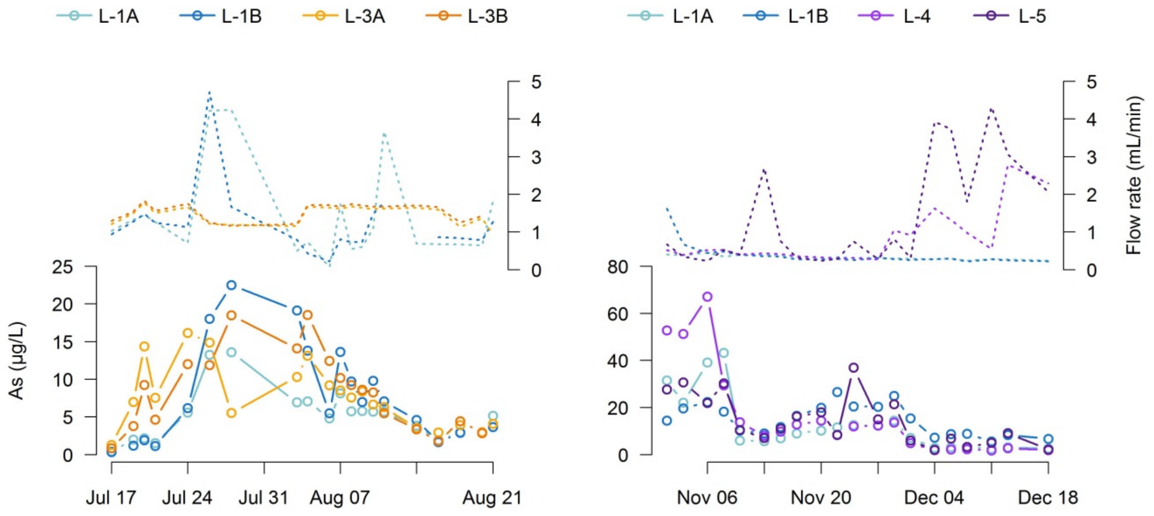

Fig. 4.9 Diagrams showing a comparison of effluent As concentrations (bottom graphs) with flow rate (top graphs) of columns L-1A/L-1B, L-3A/L-3B and L-4 and L-5.

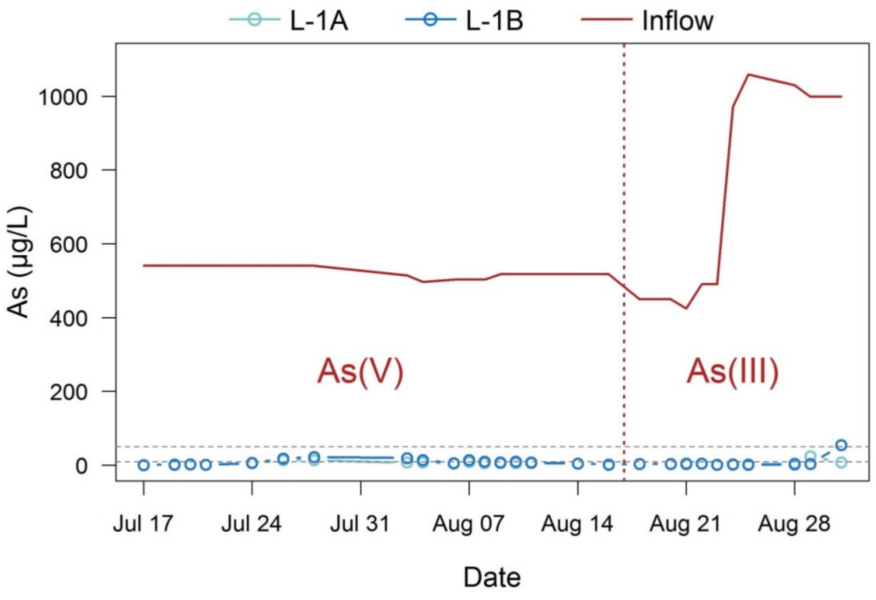

Fig. 4.10 Comparison of effluent As concentrations of columns L-1A/L-1B when inflow As speciation changes. The dashed grey horizontal lines indicate the 10 µg/L and 50 µg/L values.

4.3.2.5 X-ray diffraction (XRD) of nail surfaces

The most dominant phase identified in the X-ray diffractogram was magnetite (Fig. 4.11). The other detected Fe-phase was carbonate green rust. After the sample had been exposed to air, the peak intensity of the unstable green rust had clearly decreased due to oxidation, while all other identified phases remained stable. The presence of calcium carbonate and quartz was also indicated in the diffractogram, the latter possibly resulting from contamination by the sand used in the columns.

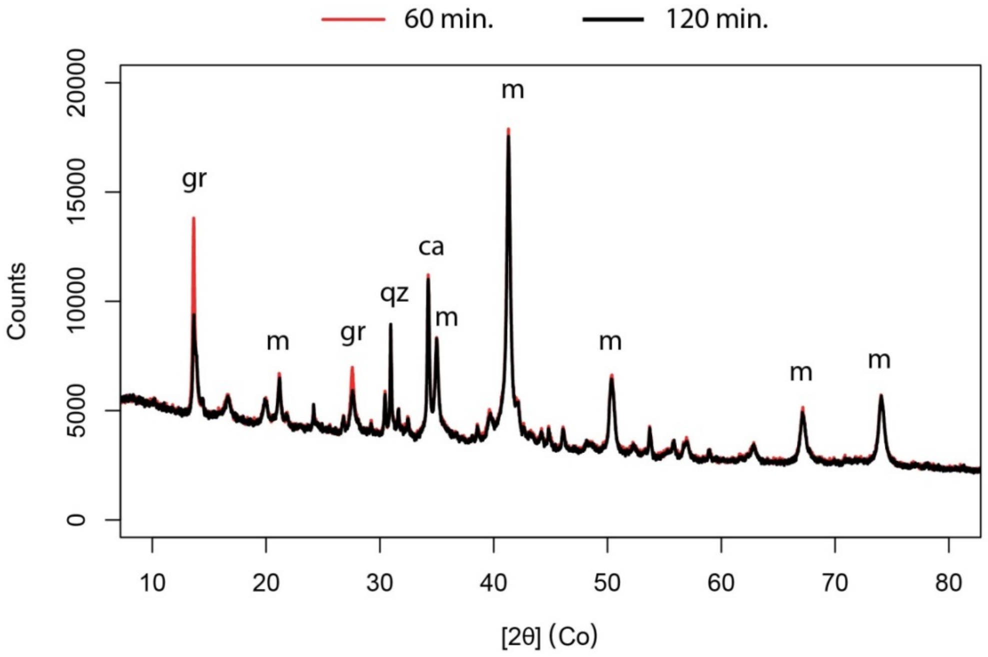

Fig. 4.11 X-ray diffractogram of the powdered surface layer formed on the nails of column L-3A. The lower-case letters in the spectrum identify the following solid phases: m: magnetite (Fe_3O_4), gr: carbonate green rust ($Fe_3(CO_3)(OH)$), ca: calcium carbonate ($CaCO_3$), qz: quartz (SiO_2)

4.4 Discussion

The oxidation of Fe(0) to Fe(II) and Fe(III) in oxygen-containing water is the main chemical reaction occurring in the nail layer of the columns and filters and can be summarised in the following equations:

$$2Fe(0) + O_2 + 4H^+ \rightarrow 2Fe(II) + 2H_2O \qquad 1)$$

$$2Fe(II) + 0.5O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+ \qquad 2)$$

$Fe(OH)_3$ in equation 2 represents Fe(III)(oxy)(hydr)oxide phases such as FeOOH, ferrihydrite or poorly crystalline Fe phases (Neumann et al., 2013; Senn et al., 2015). If As is present in solution, it can sorb to and co-precipitate with the Fe phases formed during Fe corrosion:

$$As(V) + xFe(III) + yFe(II) \rightarrow As(V)\ containing\ Fe(II, III)\ phases \qquad 3)$$

As(V) generally sorbs better to Fe-phases than As(III), but even if As occurs as As(III) in water, the formation of reactive intermediates (H_2O_2, Fe(II, III, IV)) during the oxidation of Fe(0) and Fe(II) by O_2 can lead to the oxidation of As(III) to As(V) (Katsoyiannis et al., 2008). This explains the still good As removal observed in the filter columns when they were operated with As(III) instead of As(V) (Fig. 4.10). With increasing filter/column age, the generally amorphous Fe(II, III)-phases can undergo structural transformation to more crystalline and stable compounds such as magnetite (Fe_3O_4) (Neumann et al., 2013). Magnetite was observed on the six week old surface of the nails (XRD data, Fig. 4.11). Magnetite formation is thought to have a positive effect on filter performance as it is less voluminous than the red amorphous Fe-oxides, preventing filter clogging (Neumann et al., 2013). In addition, As is tightly bound in its crystal lattice and should not be remobilised from the nails when the filter is not needed any more, making filter disposal unhazardous (Hussam & Munir, 2007; Neumann et al., 2013).

One of the main problems limiting As removal efficiency that was identified during the laboratory study was the presence of trapped air in the nail layer (columns L-2A/L-2B) and subsequent Fe/water contact times of only a few seconds, leading to decreased Fe(II) and Fe(III) production. This phenomenon most probably also occurred in the filters in the field during the first six months of operation, explaining their less-than-expected As removal and leading to a change in filter design. The presence of air in the filters had not been expected, as SONO filters (similarly constructed), are not reported to experience this problem. Most likely, the higher surface area of SONO's Composite Iron Matrix (CIM) (Table 4.4), smaller pore size and higher capillary forces in comparison to the nails retains water in the CIM instead of letting it freely drain out. Raising the water level permanently above the nail layer (columns L-4 and L-5) increased nail/water contact time and greatly improved As removal in the laboratory columns. The only partial success seen in the modified field filters at the time of writing is difficult to explain. It is possible that the raised outflow tube of filters F-2 and F-4 was pushed too far down into the recipient funnel by household users, lowering the water level again below the nail layer.

In the laboratory, As removal was still effective even when flow rates greatly exceeded 1.77 mL/min (equivalent to 10 L/h in the field). Because of the large volume of standing water in the columns with saturated nail layers, a considerable percentage of the water drained during each new filtration cycle is standing water from the previous filtration, that has actually been in contact with Fe-oxides in the column for hours (depending on the frequency of filtration). These pauses between filtration cycles provide time for Fe(0) oxidation, solid phase formation and As incorporation. The flow rate that the column or filter is operated at, is therefore not necessarily an indicator of the real contact time between water and Fe-phases, provided that pauses of several hours between filtration cycles are respected to increase contact time. This also reflects the real situation in households in Burkina Faso, where water is filtered 2-3 times daily.

Besides contact time, other important factors influencing As removal in the conducted experiments were the pH of the inflow water and the specific surface area of the nails. At pH > 8, corrosion is slow and Fe(II) is very short-lived (few minutes to seconds (Millero et al., 1987), oxidising and precipitating quickly as Fe(III)(oxy)(hydr)oxides on surfaces. Arsenic in the water then has less contact to the Fe(0) surface, where Fe(II) and Fe(III) are formed and As is removed via co-precipitation with Fe(III) (Katsoyiannis et al., 2008; Wenk et al., 2014). This is illustrated in the clear drop in As removal efficiency when inflow water had a pH of ~8.5.

The specific surface area of a filter material is an important parameter as it determines the number of adsorption sites and the accessibility of the contaminant to the adsorbent (Crittenden et al., 2012). In the case of the nails, the higher the specific surface area, the higher Fe corrosion and the more Fe(II) and Fe(III) is produced for As sorption. In a direct comparison, filter F-4 generally outperformed F-2, the former using smaller nails with a slightly higher specific surface area (Table 4.4). The very effective As removal of the GEH filter in comparison to the nail filters is not surprising, considering that the specific surface area of GEH is six orders of magnitude larger than that of the nails (Table 4.4). In addition, GEH is composed of stable, oxidised Fe(III)-phases and does not need to undergo the oxidation steps of Fe(0).

Even though As removal efficiency was high in the modified filters F-1, F-2 and F-4 (75-90%), they did not remove As to levels below 50 µg/L. This is certainly connected to the very high As concentrations (up to 1350 µg/L) of the two tube wells and the large volumes of water filtered per day (40 – 60 L), conditions that are at the extreme end for nail-based filters. Other studies employing nail-based filters mostly worked with input concentrations < 400 µg/L (Chaudhari et al., 2014; Chiew et al., 2009; Ngai et al., 2007; Singh et al., 2014; Smith et al., 2017). Filters F-1, F-2 and F-4 (mod.) have similarities to the Chinese NIS ("nails-in-sand") filter developed and tested by Smith et al. (2017). NIS filters are constructed using fewer nails (5 kg) but larger volumes of sand and were shown to remove As to less than 50 µg/L for six months, but the As inflow concentrations were lower (150 – 300 µg/L) and less water was filtered per day (~20 L), limiting comparability with the filters in Burkina Faso.

4.5 Significance and Implications

To our knowledge, zero-valent iron-based household filters were field-tested for the first time in As-affected areas of West Africa. Despite the widespread occurrence of As-contaminated wells in this region (Ahoulé et al., 2015; Bretzler et al., 2017), As mitigation activities are still almost non-existent compared to Asian or South-American countries. In Burkina Faso, tube wells identified as As-affected are usually closed by the authorities without replacement. Due to the extreme poverty and very low purchasing power of rural communities in Burkina Faso, utilising a low-cost, low-tech As removal method exclusively sourced from locally available materials was a priority of this study. Nails were chosen as an Fe-source as they are cheap, widely available and do not need elaborate cleaning, but have the considerable drawback of a low specific surface area compared to the Fe shavings/turnings used in SONO filters. Finding large quantities of suitable scrap metal shavings for a SONO-type composite iron matrix proved challenging in Burkina Faso. Countless small street-side workshops fabricating steel into furniture, doors or window frames exist, but cutting and sawing is often not mechanised and iron scraps that result have highly heterogeneous sizes and fall onto the unpaved ground, where they mix with other detritus and dust. Larger workshops and enterprises cutting with rotary blades produce greater amounts of scrap Fe shavings, but these are usually contaminated with machinery oils used to grease the blades, rendering them useless for drinking water treatment. For the moment, small-sized nails are therefore the simplest and cleanest source of Fe(0) for As removal.

The tested filters did not undergo any maintenance during the trial period of nine months, nor did users report any clogging. The combined effect of low specific surface area of the filter material, very high As input concentrations (450 – 1300 µg/L) and high filtered volumes (40 – 60 L/d) resulted in effluent As concentrations staying above 50 µg/L. Nevertheless, As-concentrations were reduced by an average of ~ 70% for influent concentrations of 400-1300 µg/L and by an average of ~ 80% for influent concentrations of 300-600 µg/L. In the absence of other sources for drinking water and more efficient filters, the tested filters can be an emergency measure to reduce the exposure to As, but their efficiency needs to be improved urgently. The laboratory column experiments show that the limit of 10 µg/L can be reached with controlled operating conditions.

Nevertheless, consistent effluent concentrations below 10 µg/L are unlikely under field conditions with high input As concentrations, but the filters might be suitable for less contaminated wells where As is between 10 – 100 µg/L. Further field trials would be needed to confirm this hypothesis. 80 – 90% of As-affected tube wells in Burkina Faso have concentrations between 10 and 100 µg/L (Bretzler et al., 2017). The need for As-removal technologies in this concentration range is therefore large, especially considering that there is growing evidence of arsenic’s low-dose health effects (Schmidt, 2014). Nevertheless, the high-As tube wells (concentrations > 100 µg/L) remain of largest health concern for the population, with the cancer risk rising greatly at these exposure levels (Argos et al., 2010; Sohel et al., 2009). GEH proved to be an effective adsorbent for treating such water to levels < 10 µg/L, but affordability becomes an issue, especially considering that the filter material needs to be replaced once its As uptake capacity is exhausted. 1 kg of small iron nails costs roughly 2 euros at a hardware store in Ouagadougou, with prices expected to be lower for bulk quantities. 1 kg of GEH, on the other hand, amounts to 5-8 Euros, excluding considerable costs for shipping and import. Even using low-cost filter materials such as nails, sand and gravel, As removal may still be unaffordable to rural communities in Burkina Faso and other means of financing or subsidies may be necessary to provide clean water. Arsenic treatment solutions such as the presented nail-based filters can provide opportunities for local entrepreneurs or social businesses, but first, their efficiency needs to be improved. A focus should lie on finding or producing suitable scrap iron filings and turnings with a high specific surface area to use in a SONO-style composite iron matrix.

Acknowledgements

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5 Conclusions and Perspectives

This dissertation provides novel insights into the occurrence, distribution and dynamics of geogenic arsenic contamination in groundwater of Burkina Faso. The interdisciplinary approach touched on numerous fields of environmental science, ranging from statistical modelling and GIS applications via hydrochemistry and isotope hydrology to the engineering of water treatment systems. This broad scope allowed an interpretation of the subject from a variety of angles and on multiple scales, not only investigating natural processes, but also offering solutions to ultimately improve human health. In the following sections, the main findings of this work will be discussed and future fields of research proposed.

5.1 Arsenic hazard prediction modelling

The ability to predict areas where aquifers are especially at risk of geogenic As contamination is a powerful tool for water resources management. In Chapter 2 of this thesis, it was demonstrated that certain geological formations and rock types, extracted from low resolution geological maps, have a higher probability of yielding arsenic-containing groundwater above the chosen threshold values than others. Specifically, basalt, andesite and schists of the Birimian formation were positive predictors for elevated groundwater As. The resulting hazard maps feature "high-risk" regions where the statistical probability of drawing As-contaminated groundwater lies above 20% (for concentrations > 10 μg/L). This may seem like a low value, but actually reflects the large spatial heterogeneity of the dependent variable (arsenic concentrations in tube wells), where one As-affected well may be located within hundreds of meters of a "safe" well. The spatial resolution of the independent predictor variables is too low to explain this high variability, hence the statistical model returns low probabilities. Despite being ineffective at predicting As on the scale of individual wells, the maps nevertheless highlight areas where water testing for As contamination should be prioritised. The combination with population density figures led to the estimation that ~560,000 people in Burkina Faso, roughly 3% of the population, are exposed to drinking water with As > 10 μg/L. The Birimian formation with its hydrothermal alteration zones and extensive gold mining is found in other West African countries (Ghana, Ivory Coast, Niger, Mali and Guinea), with some groundwater As occurrences already confirmed, especially in Ghana (e.g. Asante et al. (2007); Buamah et al. (2008); Smedley (1996)). Widening the focus of the As prediction model from Burkina Faso to the whole region would be an obvious next step, involving the collection of groundwater quality measurements and the harmonisation of geological and mineral deposit data from individual countries.

Using predictor variables that more accurately delineates sulphide-bearing mineralised zones would be of high relevance for producing more accurate models predicting As groundwater occurrences in West Africa. An aspect that was not explored in this work, but harbours great potential is the interpretation of satellite-derived remote sensing data. Such techniques are widely used for mineral exploration purposes, both by identifying faults and fracture zones that localise ore deposits and by recognising hydrothermally altered rocks and minerals by their spectral characteristics (Sabins, 1999). Secondary Fe minerals such as goethite and jarosite, formed as weathering products of pyrite can be identified on the Earth's surface by processing multispectral ASTER (*Advanced Spaceborne Thermal Emission and Reflection Radiometer*) images (Gabr et al., 2010). For good image classification, field campaigns for ground truthing purposes are generally additionally necessary. The high resolution given by ASTER (30 x 30 m) provides considerable potential for the use in As prediction maps, as it matches the highly resolved dependent variable (arsenic concentrations in individual tube wells). Geophysical mapping such as airborne electromagnetic surveying (AEM) is also applied for identifying mineralised zones, and can measure changes in conductance, caused for example by the presence of ore zones, up to a depth of several hundred metres (Palacky, 1993). Data resolution varies depending on the system used and the flight paths, and data processing can be complex (Brodie & Sambridge, 2006). In addition, AEM data is seldom available on a country-wide coverage and may also be expensive to acquire.

Additional flexibility is given by the choice of the statistical model. The present work was restricted to logistic regression, which has been demonstrated to be robust and suitable for modelling groundwater contaminants (e.g. Amini et al. (2010); Nolan et al. (2002); Podgorski et al. (2017); Rodríguez-Lado et al. (2013); Winkel et al. (2008)). However, machine-learning modelling approaches, with the ability to learn complex patterns in data, have lately been successfully applied for predictive contaminant modelling (Jones et al., 2017; Nolan et al., 2015) and may outperform logistic regression (Ayotte et al., 2016). Nevertheless, from the experiences gained in this dissertation, the quality and accuracy of the final prediction model will be more influenced by the quality of the input data than by the statistical modelling approach applied.

5.2 Arsenic dynamics and relation to groundwater residence times

West Africa is a data-scarce region concerning even the most basic hydrogeological data such as static groundwater levels. Yet not only the geochemical trigger (e.g. sulphide oxidation), but also the hydrological regime controls As occurrences, and knowledge of basic flow patterns, residence times and seasonal water table fluctuations is a prerequisite for understanding As dynamics (Smedley & Kinniburgh, 2002). The high resolution sampling campaign in Poura, described in Chapter 3, captured the spatially heterogeneous distribution of hydrochemical parameters and yielded novel insights into groundwater residence times of these shallow to moderately deep fractured bedrock aquifers. The application of noble gas tracers revealed that some tube wells extract groundwater with very low $^{3}He/^{4}He$ ratios and ages > 10^3 a. The hypothesis that As would be predominantly found in geochemically evolved waters with long residence times, where prolonged water rock interaction, silicate weathering and oxygen consumption might lead to favourable conditions for As mobilisation could not be confirmed. Arsenic was both found in wells where residence times are > 10^3 a and those dominated by modern recharge with residence times < 50 a. Groundwater with As(V) > 10 µg/L had a pH of 7.0 – 7.2 and Eh of 400 – 470 mV, therefore neither alkaline desorption of As from Fe-(hydr)oxides, nor their reductive dissolution is a likely scenario. In addition, As was not bound to colloidal or particulate Fe. We therefore hypothesise that high As concentrations only occur in direct proximity to the sulphide mineral source. Here, As loadings would be very high and not all released As sorbed on Fe(III)-(hydr)oxides precipitating on mineral surfaces after pyrite oxidation. A further influence on soluble As concentrations may be the release of already sorbed As due to the aging and increasing polymerisation and crystallisation of Fe(III)-(hydr)oxides, leading to a reduction in their sorption capacity (Senn et al., 2018).

Fractured aquifers present a very complex flow environment and groundwater abstracted from tube wells probably represents a mixture of water from different fracture zones with potentially varying hydrochemical signatures and residence times (Bondu et al., 2017). Tube wells in Burkina Faso may be screened in several sections, corresponding to fractures with high hydraulic conductivities. To gain insights on the origin of As-containing water portions, future fieldwork should concentrate on isolating different parts of the borehole using inflatable packers and selectively pumping only from certain fracture zones (Yang et al., 2015). A borehole camera could be used to locate the position of screens, as borehole documentation is frequently lacking or inaccurate. Further potential would lie in solid sampling and geochemical analysis of aquifer material to prove the hypothesis that sulphide minerals are As sources. Drilling and extracting cores next to an As-affected well to identify mineral assemblages and their As content would finally shed light on this issue.

Hydrogeological field work in rural West Africa is often restrained by hand pumps preventing access to the boreholes. Dissolved gases, for example, cannot be sampled from the well spout as oxygen from the air would contaminate the sample. It was demonstrated in this thesis that it is possible to remove the hand pump and tubing in order to have access to the borehole with a portable pump, though this should always be undertaken by a mechanic knowledgeable in dismantling these types of hand pumps. The dataset of dissolved noble gases resulting from this field campaign is unique for shallow to moderately deep (< 100 m) crystalline bedrock aquifers in West Africa and should initiate follow-on studies in other regions to confirm the measured low ^{3}He/^{4}He ratios. Noble gas analysis is time consuming and costly, therefore the utilisation of recently developed portable gas mass spectrometers allowing on-site measurements should also be considered (Brennwald et al., 2016).

As presented in Chapter 3, the influence of monsoon precipitation (June - September) on tube well As concentrations in Poura was marginal, with only a slight dilution effect seen in some samples. However, the two tube wells regularly sampled over nine months for the filter study in northern Burkina Faso, Province de Bam (Chapter 4) displayed As concentrations that nearly halved during August to October. A third As-affected tube well had stable concentrations (data not shown). These variations again demonstrate the very heterogeneous nature and varying hydrological response of the studied fractured aquifers and highlight the need to further investigate seasonal effects.

5.3 Arsenic mitigation options

Field- and laboratory-scale experiments with zero-valent iron-based filters highlighted the complexity of As removal in low-income settings. Despite removing between 75 – 90% of As, the guideline value of 10 μg/L was not reached with the nail-based filters due to a combination of factors such as low specific surface area of the used iron nails and very high As input concentrations (400 – 1350 μg/L). Future research should concentrate on finding a suitably fine scrap iron material in Burkina Faso to experiment with SONO-style filters. In addition, Fe(0)-based community systems treating water directly at the source (tube well) need more consideration (Chaudhari et al., 2014), as it is easier to control operating conditions than in households. The trade-off between cost and efficiency of a system remains the major challenge. Granular ferric hydroxide (GEH®) is certainly an effective and suitable material for As removal in Burkina Faso, but comes at considerable cost, needs replacement when saturated and is not locally available. Arsenic removal systems in developing countries are frequently installed with donor money, but are usually not financially sustainable in the long term (Johnston et al., 2010). It is becoming increasingly clear that entrepreneurship and business model innovation are options that need to be explored to make water services in developing countries more financially sustainable and also affordable to the lowest income levels (Gebauer & Saul, 2014).

The existence of high As in groundwater of northern Burkina Faso has been known for over a decade (COWI, 2004; Smedley et al., 2007), yet national authorities and administration are still at an early stage in dealing with this issue. This dissertation has demonstrated that As occurs throughout Burkina Faso and is a health threat to potentially over half a million inhabitants that needs to be urgently addressed. Arsenic mitigation is complex and requires a holistic approach (Johnston et al., 2014). From experiences gained not only during this dissertation, but also from previous projects (Bretzler & Johnson, 2015) and literature sources, the following section offers recommendations on how to approach As mitigation, aimed at decision makers in Burkina Faso. The list is not exhaustive and some of the proposed aspects may already be at varying stages of being addressed, but all are highly relevant if As mitigation is to succeed.

5.4 Recommendations

Identification of As-related health symptoms

The education and training of rural doctors and health care workers on identifying arsenicosis and linking certain symptoms (e.g. skin lesions) with possible drinking water As exposure needs to be implemented. An early diagnosis of As-related health effects can help pinpoint villages or regions where wells should be tested and is a first step to initiate mitigation measures.

Arsenic testing of tube wells

Water quality testing of tube wells located in "high-risk" regions designated by the As hazard map needs to be prioritised. Every tube well should be tested due to the high spatial variability in concentrations. For drinking water exposure assessment, water should be sampled unfiltered (but acidified for sample stabilisation), as As may be adsorbed to particulate Fe(III)-phases in the water, which will be removed by filtration. This phenomenon was not observed in Burkina Faso in this study, with filtered and unfiltered As concentrations generally being very similar (Chapter 3), but does occur in other regions (e.g. Yang et al. (2015)), hence unfiltered sampling is preferred. To the author's knowledge, large drinking water surveys have been carried out in the last years, mandated by government and international agencies, but results need to be transparent and accessible to researchers, consultants and NGOs working in the water sector.

Strengthen decentralised laboratory capacity

The As-testing capacity of laboratories outside of Ouagadougou needs to be built up and/or strengthened. Priority should be in regional centres on or close to the Birimian greenstone belts, for example Ouahigouya, Kongoussi, Djibo, Dori, Fada n'Gourma, Bobo-Dioulasso, Gaoua and Boromo. Field test kits, though not always 100% reliable (George et al., 2012), can identify As in the relevant concentration ranges for human health exposure and allow a rapid screening (van Geen et al., 2014). Promising methods utilising the processing of mobile phone photos for more precise colorimetric measurement of As are in development, e.g. *Akvo.org* and Haque et al. (2018).

Prioritise high exposure groups

Arsenic mitigation for the population drinking water with As > 150 µg/L is the most urgent from a public health point of view and needs to be prioritised (Argos et al., 2010; Sohel et al., 2009). The rural population in Burkina Faso generally only has access to the most basic health care services and cancer treatment is not possible. The resulting cancer deaths will result in a considerable social burden of lost life years and economic burden in lost productivity in the coming decades (Flanagan et al., 2012; Sauerborn et al., 1995). Investments in As-avoidance schemes (e.g. drilling of replacement wells) or As removal technologies, though involving substantial sums, are small in relation to the economic losses that will incur if As exposure continues unabated. Due to the latency period of up to 40 years of As-related cancers, the effects of As mitigation measures taken now will only be felt in several decades (Steinmaus et al., 2013).

Epidemiological research

Identifying As-affected tube wells needs to be accompanied by large-scale epidemiological studies involving the exposed population, as have been carried out in Bangladesh (Argos et al., 2010; Sohel et al., 2009). They are the only means to quantify and prove the effect of As exposure on human health in Burkina Faso and subsequently justify As mitigation. Such studies require a large effort and investment from the state of Burkina Faso, but probably also from international donors. Partnerships with international research teams already having experience in similar studies on As-related topics would be highly beneficial. Not to be underestimated is the language barrier, as knowledge of English is limited in Burkina Faso even in a university context. Most As-related studies have been carried out in English- or Spanish-speaking environments, and very few in francophone countries.

Data and knowledge exchange

The exchange of data and information on As-related activities between institutions and authorities in the involved sectors, namely health, geology/mineral resources, rural development and drinking water supply needs to be facilitated. This involves stakeholders from government bodies, international donors, NGOs, research facilities and consulting offices. Such an initiative is very challenging, but even regular national and international conferences held in Burkina Faso exclusively on the topic of As in groundwater, where stakeholders from all sectors are represented, can be a start (Johnson et al., 2014). With increasingly improved and widespread internet availability, online data platforms for data exchange and visualisation offer new possibilities that should be explored and further developed.

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