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Arsenic and other trace elements in groundwaters and surface waters in the gold mining region of the Nigerien Liptako (Southwestern Niger)

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Abstract

The Nigerien Liptako in southwest Niger has gold mineralisations in Birimian formations (Paleoproterozoic) that have been mined for several decades. The objective of this study was to document the concentrations of arsenic and other toxic trace elements in groundwaters, river waters, suspended particulate matter and sediments and discuss the potential influence of artisanal gold mining on arsenic and trace elements enrichment. For this, forty-three groundwater samples (boreholes and wells) were analysed in mined and unmined areas. Surface waters, suspended particulate matters and sediments were sampled in three rivers at stations upstream and downstream from mining sites. Rock samples extracted from mine galleries were collected for mineralogical and geochemical characterization. In groundwater, arsenic concentrations ranged from 0.018 to 202 µg/L, exceeding drinking water guidelines (10 µg/L) in three artisanal gold mining areas. Manganese exhibited concen-trations exceeding the potability limit in 23% of the samples, mainly in the Continental Terminal aquifer. In rivers, arsenic was the element most enriched in suspended particulate matter and sediments, but its concentration in water did not exceed 3 µg/L. Mineralogical analysis of rocks showed traces of arsenic in association with iron oxides, suggesting a release of arse-nic in groundwater by desorption. The consumption of these waters rich in arsenic or manganese presents serious risks for health. These data represent the first large-scale investigation of arsenic and trace elements concentrations in groundwaters and surface waters in the Nigerien Liptako, where no or very scarce water quality measurements have been published yet.

Keywords Nigerien Liptako · Arsenic · Artisanal gold mining · Trace elements · Environment health

Introduction

Gold mining is a potential source of high groundwater As concentration (Smedley and Kinniburgh 2002). The local disruption of chemical equilibrium in aquifer material generated by mine workings can lead to displacement of elements naturally present in the rocks, such as arsenic and trace metals. These elements are mobilized towards the water where they can reach concentrations harmful to the health of consumers. In West Africa, gold mining has undergone significant development since the 1980s, with an acceleration in the last five years. The Liptako–Gourma (L.G.) region in West Africa straddles the borders shared by three countries, Niger, Mali and Burkina Faso. The area is rich in industrial and artisanal gold mines. Few studies investigated As concentration values in groundwater and surface water in gold mining areas from LG. In northern Burkina Faso, the presence of arsenic levels up to 1630 µg/L was shown in wells and boreholes in the Birimian rock aquifers in the locality of Ouahigouya. About 560,000 people are potentially exposed to groundwater arsenic contamination in this area (Smedley et al. 2007; Bretzler et al. 2017). In Mali, groundwater arsenic concentrations ranged from 0.8 to 132 µg/L in the village of Sanso, next to the Au Sanso mine, and it was accompanied by manganese at concentrations of 2.52 to 5200 µg/L (Bokar et al. 2020). These data suggest that As and trace

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elements enrichment in groundwaters in gold mining areas in the Liptako–Gourma region is of concern.

In the Nigerien Liptako, there has been no large-scale investigation to document arsenic and trace elements concentrations in water resources. Tankari et al. (2014) revealed the existence of significant water contamination by arsenic and trace elements in the vicinity of the Komabangou artisanal gold mining zone (Tillabéri, Niger). Wastewater from cyanide treatment exhibited extremely high concentrations of As, Cu, Mn, Ni, Pb and Zn (Tankari et al. 2014, 2019). In groundwater, average concentration values were 19 µg/L for As and 98 µg/L for Mn (Tankari et al. 2014). Apart from the Komabangou artisanal gold mining site, no survey of arsenic and other trace elements in the water resource has been carried out. The objective of the present study was to make a preliminary diagnosis of the levels of arsenic and trace metals in groundwaters, surface waters, river sediments and suspended particulate matter in gold mining areas in the Nigerien Liptako and to identify the source of these elements in water and the mobilization processes. For this, two sampling surveys were carried out in 2019 and arsenic and trace elements were analysed in water and solid samples. The two redox species of arsenic were also determined for a better insight into As mobilization processes. The source rocks were analysed by Scanning Electron Microscopy coupled to Energy Dispersive Spectroscopy (SEM–EDS) to find out the main mineral phases bearing arsenic and trace elements.

Materials and methods

Study area

General description

The study area is located in the southwestern part of Niger, next to the border with Burkina Faso and Mali, and lies between longitudes 0°30′ W and 3°48′ E, and latitudes 12°12′ S and 15° N. It occupies the eastern part of the Nigerien Liptako and the western edge of the Iullemenden basin and covers the Nigerien part of the Niger River watershed with its tributaries on the right bank (Dargol, Sirba and Goroubi) and on the left bank (Kori of Ouallam, Dallol Bosso and Dallol Maouri) (Fig. 1a, b, c). The Liptako-Gourma (L.G.) zone covers an area of 370,000 km^2. The Nigerien Liptako corresponds to the NE portion of the Man Dorsal (West African Craton). It mainly consists of the Birimian (Paleoproterozoic) formations. Gold has been mined at an artisanal level for decades in the area and there are currently over 100 artisanal gold mines in operation employing approximately 500,000 gold miners. Artisanal gold mining began in 1983, after a terrible drought and has increased in recent years with the arrival of refugees due to insecurity in the Sahel. The extraction of gold in this area is considered to be a source of major environmental and health impacts (Barro-Traoré et al 2008; Ochieng et al. 2010, Adama et al. 2012; Ouédraogo and Amyot 2013; Adama et al. 2017; Bretzler et al. 2017; Tankari 2014, 2019; Ibrahim et al. 2019, Bintou et al. 2020, Bokar et al. 2020), but its production contributes to the increase of the gross domestic product (GDP) and employment for many West African countries.

In the study area, the problem of water resource depletion has been increasing in recent years in relation with irregular rainfall, recurrent droughts in the Sahel, combined with an increasing demand for water, in relation with the rapid growth of the population (Ousmane et al. 2006). Degradation of water quality due to gold mining would further increase pressure on water resources.

Geology

The geology of the study area consists of the Precambrian basement of the Liptako-Gourma to the west and the Iullemenden sedimentary basin to the east. The Nigerien Liptako consists of alternating greenstone belts and granitoid plutons oriented in a general NE–SW direction (Fig. 2a, NNW–SSE geological section of the study area (A–B)). The belt formations consist of metasediments, metavolcanosedimentary and metavolcanoplutonic formations (Machens 1973; Pouclet et al 1990; Ama Salah 1996; Abdou et al 1998; Soumaila 2000; Soumaila et al 2004) which are composed of sandstone rocks (graywackes), mica-schists, shales, quartz-schists, rhyolitic tuffs and breccias and green rocks (pyroxenites, amphibolites, epidotites, chlorite-schists, metabasalts, metagabbros). A variety of granitoid rocks including diorite, granodiorite and granites were intruded the greenstone belts, following the main structural trends (Dupuis et al. 1991; Cheilletz et al. 1994; Pons et al. 1995; Soumaïla et al. 2005). The cover formations are formed of 5 to 50 m thick alterite, alluvium and colluvium.

The Continental terminal consists of the "Ader Doutchi siderolithic series" (Ct^1), the "lignite clay-sand series" (Ct^2) and the "Middle Niger claystone series" (Ct^3) (Greigert 1966). A geological section from Favreau (2000) is available in Fig. S1.

Hydrogeology

The study area is characterized by discontinuous aquifers of the Liptako-Gourma basement (Fig. 2b, NNW–SSE hydrogeological section of the study area (C–D)), generalized aquifers of the Continental terminal formations (Fig. S1) and alluvial aquifers. The discontinuous aquifers are those of the alterites, the volcano-sedimentary series and the granite-gneiss formations (Ousmane 1988). The thickness

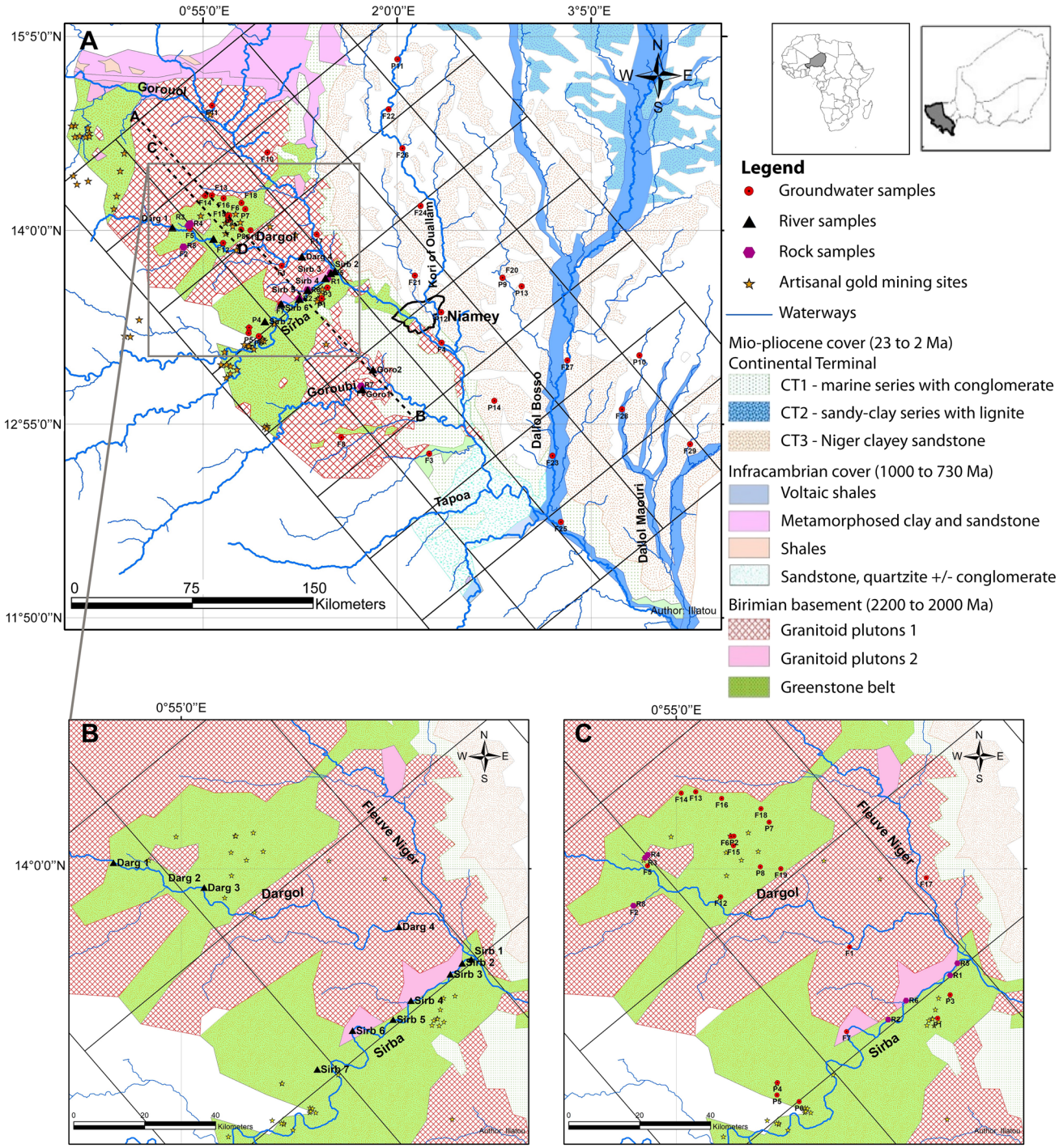

Fig. 1 Location of sampling sites, artisanal gold mining sites, sampling grid, geology of the area and geological and hydrogeological cross sections (**a**) and zoom on the Dargol and Sirba watersheds showing river sampling sites (**b**) or rock and groundwater sampling sites (**c**)

of alteration varies from 10 to 20 m in the granite-gneissic domain (Guiraud and Travi 1990), and from 15 to 40 m in the shale and greenstone domain with a predominance of clay (Kamagaté et al. 2007). The recharge mechanism and groundwater origin of the fissured and fractured Liptako basement aquifers have been described through piezometric methods and hydrogeochemistry (Babaye et al. 2018). The Continental terminal aquifers (Fig. S1) form three horizons recognized from bottom to top as Ct^1, Ct^2, and Ct^3 (Leduc and Karbo 1996). It is characterized by a weakness of the reserves in contact with the base and thickening of the aquifer series from the border of the Nigerien Liptako

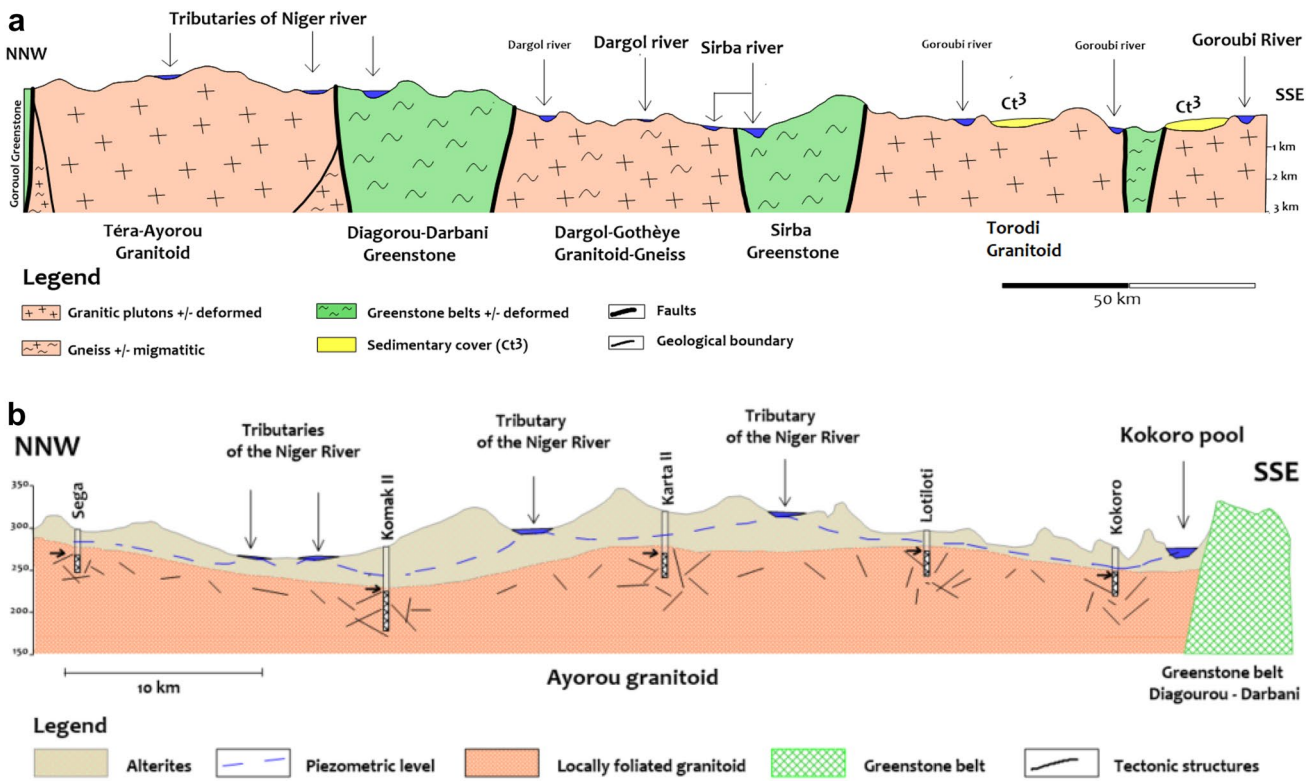

Fig. 2 NNW–SSE geological section of the Nigerien Liptako showing the succession of granitoid plutons and greenstone belts (**a**) and NNW–SSE hydrogeological section showing the alteration aquifer in the Ayorou pluton (**b**)

basement to the east of the study area. Isotopic analysis of the Ct aquifers has confirmed their current renewal (Leduc and Taupin 1997; Le Gal La Salle et al. 2001; Favreau et al. 2009). Their recharge is ensured by the direct infiltration of rainwater in the permeable outcrop areas and especially the emptying of water bodies (ponds) in the low-lying areas of the valleys, particularly in the Dallol Bosso and Kori of Ouallam sectors (Favreau 2000; Guéro 2003). Their annual recharge estimated through geochemical, hydrogeophysical and hydrodynamic approaches is 25 mm/year over the decades 1990–2000 (Favreau et al. 2009). The alluvial aquifers are contained in formations resulting from alluvial deposits of the Niger River or from tributary valleys.

Sampling

Sampling strategy

The sampling area covers the hydrographic basin of the Niger River in the Nigerien part, distributed on both sides of the two banks constituting the Niger River and its tributaries over an approximate area of 400 km × 200 km (80,000 km^2). A preliminary study of the area according to its size, the types of anthropic activities that may release metallic pollutants into the environment, as well as the heterogeneity of the geological formations oriented perpendicular to the direction of the Niger River was carried out. This study allowed the placement of a systematic sampling grid of 50 km × 50 km, superimposing the direction of the Niger River and perpendicular to the Sirba River in the N45 direction (Fig. 1). The aquifers involved are the discontinuous Liptako-Gourma basement aquifer (fractured or weathered) and alluvial aquifers on the right bank, and the Continental terminal (CT) aquifer on the left bank. On the right bank, the groundwater sampling points were chosen on the basis of the spatial distribution of artisanal gold mining sites, according to their proximity to the tributaries of the Niger River and considering their accessibility. On the left bank, proximity to the tributaries of the Niger River, notably the Kori of Ouallam and the Dalol Bosso, was mainly taken into consideration, as well as the size of the surrounding population.

The selection of surface water sampling points was guided by the morphology of the watershed and the spatial distribution of the gold-panning sites relative to the rivers. These rivers are the Dargol, the Sirba and the Goroubi. The northernmost Goroual River, which has been affected by intense gold-panning activities in the past, could not be sampled during the study period because of insecurity problems. The Dargol River lies south of a former large gold-panning site in Niger (Komabagou) and receives water from

surrounding sites. On the river Sirba, several placer gold mining sites have been identified. The Goroubi River is not directly involved in the artisanal exploitation of gold but is located downstream several former gold-panning sites such as Tangounga, on the border between Burkina and Niger. Four stations were selected on the Dargol river (Darg 1 to Darg 4), seven stations on the Sirba river (Sirb 1 to Sirb 7), and two stations on the Goroubi river (Goro 1 and Goro 2).

Rock sampling

Samples of Nigerien Liptako rocks (basalt, granite, diorite, schist, quartz vein, quartzite and gneiss) were collected near major artisanal gold mining sites and at mineralized areas to examine the relationship between their mineralogical composition and trace metal concentrations in water (R1 to R8, Fig. 1).

Water sampling

Groundwater Forty-three (43) water points were sampled for groundwater. Thirty samples were collected during the high-water periods between June and August 2019, and thirteen during the low water period in April and May in 2019. Depth of boreholes and wells ranged from 30 to 98 m on the right bank and down to 150 m on the left bank. The sampling was carried out on wells and boreholes regularly used for drinking water by the population. The water was collected in 1-L polyethylene bottles. The main physico-chemical parameters (pH, conductivity) were measured in situ using a calibrated multiparameter HACH®. Water was filtrated through 0.22 µm cellulose acetate disposable filter with a syringe, and distributed into polyethylene bottles for the determination of trace element (60 ml), major anions and cations (10 ml) and arsenic speciation (10 ml). The vials for trace element analysis and arsenic speciation were previously cleaned with 10% nitric acid (v:v) for 48 h and then rinsed three times with ultrapure water (Milli-Q®) in a clean room at the HydroSciences Montpellier laboratory. For alkalinity, vials (50 ml) were filled with unfiltered water to prevent air entry. The samples for trace element analysis were acidified with 60 µl of nitric acid (15 M HNO_3, Suprapur, Merck). Samples for arsenic speciation were preserved with 100 µL of 8.7 M acetic acid solution and 100 µL of 50 g/L EDTA solution (Samanta and Clifford 2005). All water samples were kept at 4 °C during transport (cool box) and storage until analysis.

River water At each station on the rivers Sirba, Dargol and Goroubi, the main physico-chemical parameters (pH, conductivity) were measured and both water and surface sediments were sampled. Water (1 l) was collected in a polyethylene bottle and filtrated (250 ml to 500 ml) using a 500 ml Nalgene filtration unit and manual vacuum pump on PVDF 0.22 µm filters. The filters were previously cleaned in 1% nitric acid, rinsed with ultrapure water, dried, weighed and preserved in a filter-box until use. Once filtrated, water was distributed into vials for trace elements, major anions and cations, arsenic speciation as described for groundwaters. For alkalinity, vials were filled with unfiltered water. The filter with suspended particulate matter (SPM) was recovered and stored in the filter-box, then air-dried in a desiccator and weighed before acid digestion.

Sediment sampling

Fine surface sediments were collected after the rainy season (July 2019), while the waters begin to recede. They were sampled at each station in the river bed, under water in the main stream, using a spatula and stored in polypropylene vials, then frozen and freeze-dried before further processing.

Sample processing and analysis

Digestion procedure

Rocks and sediments were crushed in an agate mortar before acid digestion.

Samples were processed in a clean room class 10,000 at the HydroSciences laboratory. All consumable (vials, pipette tips…) was acid-cleaned before use and reagents were of Suprapur quality (Merck). Filter with SPM, sediments (50 mg) and rocks (50 mg) were digested in PTFE vials using a microwave oven (Ultrawave, Milestone) and a mixture of 15 M HNO_3 (3 ml), 9.5 M HCl (1 ml) and 22.6 M HF (1 ml). The temperature program was as follows: 5 min at 100 °C, then 5 min at 150 °C, and finally 10 min at 200 °C. The solution was evaporated to dryness at 70–80 °C. The residue was redissolved in 3 ml of 15 M HNO_3, ultrasonicated for 20 min and heated at 100 °C on a hot plate during 10 min. After cooling, the solution was transferred in a 30 ml vial and completed with 27 mL of ultrapure water. This solution was diluted ten times with ultrapure water for ICP-MS analysis. To control the quality of analytical results, a certified reference material (NIST 2711a) and a blank of procedure were processed as for samples.

Chemical and mineralogical analyses

Trace element concentrations in water, SPM, sediment and rock samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on the AETE-ISO platform of OSU OREME (University of Montpellier) using routine procedures. Depending on the conductivity values, the water samples were diluted one, two or three times prior to analysis. A certified reference water

(SLRS-6) was analysed to check the quality of the analysis. Measured concentrations were within the uncertainty of the certified values for all studied elements (Al, As, B, Ba, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Zn) and the analytical error (relative standard deviation) was better than 5%, except for Cd (8%). In addition, accuracy was within 10% of the certified values for the reference material NIST 2711a for all elements (except 19% for B) and blank contribution was negligible (< 1% for all elements, except for Ba, Cr, Pb < 5%) confirming that no contamination occurred during the digestion procedure.

Redox arsenic species were analysed by anion-exchange chromatography (25 cm, 4.1 mm inner diameter Hamilton PRP-X100 column) using a Spectra Device SCM1000 solvent delivery pumps coupled to ICP-MS (Héry et al. 2014). Major anions and cations in water samples were analysed by DIONEX ICS-1000 ion chromatography at HydroSciences Montpellier laboratory. Alkalinity was determined by acid titration. The analysed compounds are HCO_3^-, F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-} for the anions and Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+ for the cations. The reliability of the results of the major element analyses was validated after the calculation of the ionic balance values ($-7 < BA < +7$). The calculated values are considered acceptable (< 10%). The software used for the data analysis (Piper diagram), is DIAGRAMME from the University of Avignon.

Mineralogical analyses were performed by scanning electron microscopy coupled with Energy Dispersive Spectroscopy (SEM–EDS) at the C2MA laboratory of IMT Mines Alès, after the preparation of polished thin slides.

Enrichment factors

Trace element enrichment factors (EF) in suspended particulate matter and sediments were calculated according to the following equation:

$$F = \frac{\left(\frac{[M]}{[Al]}\right)_{sample}}{\left(\frac{[M]}{[Al]}\right)_{av.crust}},$$

where $([M]/[Al])_{sample}$ represents the ratio between element concentration and aluminium concentration in the sample and $([M]/[Al])_{av.crust}$ represents the ratio between average element concentration and aluminium concentration in the earth surface continental crust (average Upper Continental Crust, Taylor and McLennan 1995). Due to the lack of published data for the geochemical composition of sediments in the study region, the upper continental crust value is used as reference in the calculation of the enrichment factor even though it may not reflect the regional background values.

Statistical treatment

The statistical analyses were performed with the R free software. Groundwater trace elements concentrations data were analysed by non-parametric test Mann–Whitney; the p values were obtained at the level of $p < 0.05$.

Results

Rocks

Table 1 shows the concentrations of arsenic and other trace elements in the different types of rocks collected in the gold exploitation zones and the main mineralogy inferred from SEM–EDS analysis (Fig. S2). The selected rocks are associated with gold mineralisations and hence represent the material extracted and processed on gold-panning sites that represents a potential source of geogenic metallic contaminants for the surrounding hydrosystems.

The As content of the rocks ranged between 0.4 and 8.3 µg/g (Table 1). These concentrations were in the same order of magnitude than the average values for basalt (2.3 µg/g), granite (1.3 µg/g), diorite (1 µg/g), schist (1.1 µg/g), quartzite (5.5 µg/g) and gneiss (1.1 µg/g) reported by Smedley and Kinniburgh (2002). Arsenopyrite (FeAsS) was not detected by SEM in the rock samples of the studied area. Arsenic was present as traces (~ 0.8%) in Fe/Mn oxides in the schist sample from Doumba (Fig. S2).

The most remarkable result was the high Mn (85 mg/g) and Ba (27 mg/g) contents in the sample of the quartz vein (quartz diorite) from the Torodi pluton (Goroubi watershed) (Table 1). This was consistent with the detection of Mn oxide and Ba carbonate by SEM (Fig. S2). Barium was also detected as barite ($BaSO_4$) in the basalt sample from Sirba A (village of Talé), despite the low Ba content (84 µg/g) in this rock (Table 3). The concentrations of Co, Mn, Ni, and Cr were enriched relatively to the average composition of the upper continental crust for most types of rocks from the studied area while Ba, Cd, Cu concentrations exceeded average values in some samples. There was no Co, Ni, or Cr minerals detected by SEM. These elements were detected as traces (~ 2% Co; ~ 3% Ni, ~ 0,4% Cr) in association with Fe/Mn oxides in the schist sample from Doumba (Fig. S2). Several metal sulphides were detected by SEM in the magmatic rock samples of the study area: pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and other sulphide minerals consisting of pyrrhotite ($Fe_{1-x}S$), chalcocite (Cu_2S) and pentlandite ((Fe, Ni)S) were detected in the basalt sample (Fig. S2).

Table 1 Concentration (in % or µg/g) of major and trace elements and mineral phases in selected rock samples

Sample name	Watershed	Type of rock	Al (%)	Ca (%)	Fe (%)	K (%)	Na (%)	Mg (%)	As (µg/g)	B (µg/g)	Ba (µg/g)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)	Mn (µg/g)
R1	Sirba	Basalt	8.35	9.05	6.87	0.123	2.03	4.82	0.368	8.66	82.6	0.034	67.5	209	3.27	833
R2	Sirba	Granite	12.4	5.79	5.34	3.12	5.63	1.71	1.08	4.64	1232	0.066	121	61.3	12.1	928
R3	Dargol	Schist	4.72	0.050	7.26	0.008	0.006	11.5	8.28	1.01	15.2	0.014	120	3425	20.7	758
R4	Dargol	Quartzite	0.055	0.034	0.071	0.007	0.008	0.114	0.423	2.36	3.32	0.012	195	26.2	1.32	11.6
R5	Sirba	Basalt	7.47	8.70	7.47	0.058	1.16	4.34	1.02	5.36	83.7	0.098	85.5	187	86.1	1449
R6	Sirba	Diorite	9.24	6.85	6.49	1.14	1.92	4.40	2.56	11.2	441	0.125	70.8	313	64.5	1145
R7	Goroubi	Quartz diorite (quartz vein)	0.647	0.099	0.447	0.043	0.027	0.024	2.24	1.09	26,898	0.664	740	22.6	143	84,768
R8	Dargol	Gneiss	1.66	10.0	3.72	0.128	0.250	5.41	1.49	1.74	75.0	0.591	72.4	1297	1.6	1268
Average composition of the upper continental crust**			8.04	3.00	3.50	2.80	2.89	1.33	1.5	15	550	0.098	10	35	25	600

Sample name	Watershed	Type of rock	Ni (µg/g)	Pb (µg/g)	Zn (µg/g)	Published As concentrations*	Sulphides	Mineralogy oxides	Other
R1	Sirba	Basalt	100	0.512	29.4	2.3	Not analysed		
R2	Sirba	Granite	37.7	9.39	81.9	1.3	Not analysed		
R3	Dargol	Schist	1523	0.648	65.4	1.1		Co-, Ti-, Fe-, Mn-oxides	Quartz
R4	Dargol	Quartzite	12.5	0.220	2.36	5.5	Not analysed		
R5	Sirba	Basalt	113	0.631	67.6	2.3	Cu-, Ni-, Fe- sulphide		Quartz, Ba sulphate, Ti-Aluminosilicate
R6	Sirba	Diorite	80.9	5.27	71.9	1	Not analysed		
R7	Goroubi	Quartz diorite (quartz vein)	99.6	5.25	78.7	5.5/1		Ce-, Mn- oxide	Ba carbonate
R8	Dargol	Gneiss	613	3.34	81.3	1	Not analysed		
Average composition of the upper continental crust**			20	20	71				

*Smedley et al. 2002

**Taylor and McLennan (1995)

Groundwater

The main physico-chemical parameters and concentrations of major and trace elements in groundwater are presented in Table 2.

Most groundwater samples showed calcic and magnesian bicarbonate facies, for the two geological environments (Nigerien Liptako and CT^3) (Table 2, Fig. S3). A few samples in the CT^3 geologic environment exhibited a sodium potassium chloride or a calcium magnesium chloride and sulphate composition type (Table 2). Ten samples had nitrate concentration above drinking water guidelines (Nigerien standard: 45 mg/L), eight in LG geological environment, two in CT geological environment. The origin of nitrate was attributed in the study area to the use of fertilizers and manure for agriculture and to human settlements (Salihou-Djari et al. 2018).

Trace element concentrations in groundwaters were highly variable within each geological environment (Fig. 3). Arsenic concentrations exceeded drinking water guidelines (10 µg/L) in four samples, all in LG geological environment (Fig. 4, Table 2). The two samples with the highest As concentrations corresponded to wells in Nbanga (203 µg/L) and Boulounjounga (190 µg/L) on the Sirba watershed. Both were located in a gold mining area and have been dug decades ago for gold extraction; the water recovered from these wells during dewatering is used for drinking water purpose by the surrounding population. Comparatively, the well in Sefa Moussa exploited since 2017 for gold extraction exhibited lower As concentration (2.5 µg/L). The two samples with 16 µg/L of As corresponded to boreholes close (< 1 km) to the old (> 40 years) Komabangou mining site; they have been drilled specifically for drinking water supply. In CT, only one sample exceeded 1 µg/L (borehole from Sona, 2.1 µg/L of As). Considering all data, arsenic concentrations were significantly higher ($p < 0.05$) in LG geological environment than in CT geological environment. The oxidized arsenate species predominated in all groundwater samples analysed, except in the well from Sefa Moussa, where the reduced species arsenite (As(III)) predominated at low concentration (2.5 µg/L).

Manganese concentrations exceeded guidelines in ten samples, both in LG and CT geological environments (Fig. 5, Table 2). However, considering all data, Mn concentrations were higher ($p < 0.05$) in CT geological environment than in LG geological environment (Fig. 3). Barium concentrations exceeded Nigerien drinking water guidelines (100 µg/L) in nineteen samples, both in LG and CT geological environments (Table 2); however, only one sample exceeded WHO guidelines (1300 µg/L). Two samples exceeded boron drinking water guidelines and one sample exceeded nickel guidelines, all in CT geological environment (Table 2). Other trace elements Al, Fe, Co, Cu, Zn, Cd and Pb did not exceed drinking water guidelines (Table 2). No strong correlation was found, neither between trace element concentrations and hydrochemical parameters, nor among trace elements.

Rivers

Water

Surface water of the Rivers Sirba, Dargol and Goroubi exhibited calcic and magnesian bicarbonate hydrochemical facies (Fig. S3). One sample on the river Sirba (village Larba) contained more chloride and sulphate (Table 2).

The concentrations of arsenic and other trace elements in the dissolved phase were compared with published values for the Niger River and to world rivers averages (Table 2). Arsenic concentrations were at maximum five times higher than world rivers average (no data available for the river Niger); they were higher in the River Sirba ($[As]_{average} = 1.5 \pm 0.9$ µg/L, $n = 7$) than in the Rivers Dargol ($[As]_{average} = 0.3 \pm 0.2$ µg/L, $n = 4$) and Goroubi ([As] = 0.13–0.19 µg/L, $n = 2$). In the river Sirba, arsenic concentration increased between stations Sirb6 and Sirb3, located upstream and downstream from a gold-panning area. Arsenite (As(III)) represented more than 70% of total As concentration in the river Sirba. In the River Dargol, arsenate predominated at low concentration (0.58 µg/L at station Darg 1).

Manganese, Co, Zn and Ba were the elements most enriched in the dissolved phase compared to the River Niger or to world river averages, up to a factor 323 for Mn, 50 for Co, 26 for Zn and 29 for Ba.

Suspended particulate matter and sediments

Concentrations of arsenic and other trace elements in suspended particulate matter and sediments are presented in Table 3, together with enrichment factors relatively to upper continental crust. Concentrations in SPM were generally similar or lower than world river averages, except Cd at the most downstream station (Sirb 1) in the river Sirba (Table 3). They were highly correlated ($r^2 > 0.7$) to the content of Al (for Co, Cr, Cu, Fe, Ni, Pb, Zn) and Fe (for B, Ba, Co, Cr, Cu, Ni, Pb, Zn). The correlation ($r^2 > 0.7$) was also found in sediments between some of the trace elements and Al (for Ni, Pb, Zn) or Fe (for As, Co, Cr, Cu).

Arsenic exhibited the highest enrichment factors in both SPM and sediments, with maximum values in the river Sirba (EF = 6 to 14 in SPM and EF = 10 to 59 in sediments). The highest EF (EF = 59) was reached for sediments at station Sirb3, located downstream from a gold-panning area. For other trace elements, enrichment factors were generally lower than 4, except locally for Cd (Sirb 1) and Mn (Sirb 2)

Table 2 Main physico-chemical parameters and concentrations of major and trace elements in goundwater (wells and boreholes) and surface water. For arsenic, percentage of arsenite and arsenate are mentioned, when available

	Sample name	Latitude	Longitude	Sampling date (wet (W)/dry (D) period)	Watershed	Geological environment	Structure	Water use	Aquifer type	Geological formation	Depth (m)
Groundwater	P1	13.61857	1.57649	17/04/2019, D	Sirba	LG	Well	Gold extraction	Alterites	Green rocks	34
	P2	14.08278	1.06320	13/06/2019, D	Dargol	LG	Well	Drinking water	Alterites	Altered schists	60
	P3	13.67982	1.61183	13/06/2019, D	Sirba	LG	Well	Gold extraction	Alterites	Green rocks	40
	P4	13.45657	1.17384	17/07/2019, W	Sirba	LG	Well	Gold extraction	Alterites	Green rocks	50
	P5	13.42506	1.17241	17/07/2019, W	Sirba	LG	Well	Drinking water	Alterites	Green rocks	10
	P6	13.40817	1.22886	17/07/2019, W	Sirba	LG	Well	Drinking water	Alterites	Green rocks	20
	P7	14.11846	1.15282	22/09/2019, W	Dargol	LG	Borehole	Drinking water	Alterites	Green rocks	67
	P8	14.00492	1.13031	22/09/2019, W	Dargol	LG	Borehole	Drinking water	Fractures	Fractured granite	67
	P9	13.73522	2.59041	09/05/2019, D	Dallol Bosso	CT	Well	Drinking water	CT3	CT	28
	P10	13.30080	3.35514	09/05/2019, D	Dallol Maouri	CT	Borehole	Drinking water	CT3	CT	35
	P11	14.95680	2.00260	23/08/2019, W	Kori of Ouallam	CT	Well	Drinking water	CT3	CT	60
	P12	13.54170	2.24770	08/09/2019, W	Kori of Ouallam	CT	Well	Drinking water	CT3	CT	39
	P13	13.68700	2.69720	08/09/2019, W	Dallol Bosso	CT	Well	Drinking water	CT3	CT	40
	P14	13.04690	2.54340	04/09/2019, W	Niger river	CT	Borehole	Drinking water	CT3	CT	50
	F1	13.80142	1.35662	07/05/2019, D	Dargol	LG	Borehole	Drinking water	Alterites	Fractured granite	48
	F2	13.90552	0.80816	24/04/2019, D	Dargol	LG	Borehole	Drinking water	Alterites	Fractured granite	72
	F3	12.75132	2.17564	08/05/2019, D	Tapoa river	LG	Borehole	Drinking water	Alterites	Fractured granite	46
	F4	13.37128	2.25026	09/05/2019, D	Niger river	LG	Borehole	Drinking water	Alterites	Fractured granite	88
	F5	14.00770	0.84406	25/04/2019, D	Dargol	LG	Borehole	Drinking water	Alterites	Green rocks	60
	F6	14.08214	1.05564	13/06/2019, D	Dargol	LG	Borehole	Drinking water	Alterites	Altered schists	70
	F7	13.58624	1.34927	17/07/2019, W	Sirba	LG	Borehole	Drinking water	Alterites/Fractures	Fractured granite	64
	F8	12.84236	1.68933	17/07/2019, W	Goroubi	LG	Borehole	Drinking water	Fractures	Fractured granite	38
	F9	13.12687	1.79868	17/07/2019, W	Goroubi	LG	Borehole	Drinking water	Fractures	Basement	59
	F10	14.43487	1.27655	07/08/2019, W	Niger river	LG	Borehole	Drinking water	Fractures	Fractured gneiss	57
	F11	14.69694	0.96663	07/08/2019, W	Niger river	LG	Borehole	Drinking water	Fractures	Fractured amphibolite	50
	F12	13.92861	1.02971	25/08/2019, W	Dargol	LG	Borehole	Drinking water	Alterites	Green rocks	90
	F13	14.19542	0.96625	25/08/2019, W	Dargol	LG	Borehole	Drinking water	Fractures	Fractured granite	55
	F14	14.19206	0.92973	25/08/2019, W	Dargol	LG	Borehole	Drinking water	Fractures	Fractured granite	57
	F15	14.05856	1.06229	16/07/2019, W	Dargol	LG	Borehole	Drinking water	Alterites	Green rocks	40
	F16	14.17848	1.03224	25/08/2019, W	Dargol	LG	Borehole	Drinking water	Alterites	Basement/Green rocks limit	52
	F17	13.97690	1.55150	10/09/2019, W	Niger river	CT	Borehole	Drinking water	CT3	CT	75
	F18	14.15232	1.13172	22/09/2019, W	Dargol	LG	Borehole	Drinking water	Alterites	Green rocks	65
	F19	14.00009	1.18231	22/09/2019, W	Dargol	LG	Borehole	Drinking water	Fractures	Fractured granite	48

Table 2 (continued)

	Sample name	Latitude	Longitude	Sampling date (wet (W)/dry (D) period)	Watershed	Geological environment	Structure	Water use	Aquifer type	Geological formation	Depth (m)
	F20	13.73399	2.58975	09/05/2019, D	Dallol Bosso	CT	Borehole	Drinking water	CT2	CT	154
	F21	13.74667	2.10003	29/08/2019, W	Kori of Ouallam	CT	Borehole	Drinking water	CT3	CT	90
	F22	14.67630	1.95355	23/08/2019, W	Kori of Ouallam	CT	Borehole	Drinking water	CT3	CT	60
	F23	12.73883	2.86820	22/09/2019, W	Dallol Bosso	CT	Borehole	Drinking water	CT3	CT	30
	F24	14.13664	2.13246	29/08/2019, W	Kori of Ouallam	CT	Borehole	Drinking water	CT3	CT	64
	F25	12.36859	2.91603	30/08/2019, W	Niger river	CT	Borehole	Drinking water	CT3	CT	54
	F26	14.45816	2.03066	23/08/2019, W	Kori of Ouallam	CT	Borehole	Drinking water	CT3	CT	49
	F27	13.27214	2.95275	19/08/2019, W	Dallol Bosso	CT	Borehole	Drinking water	CT3	CT	30
	F28	12.99932	3.25716	19/08/2019, W	Dallol Maouri	CT	Borehole	Drinking water	CT3	CT	98
	F29	12.80400	3.63700	28/12/2019, D	Dallol Maouri	CT	Borehole	Drinking water	CT3	CT	57

	Sample name	Conductivity (µS/cm)	T°C	pH	Ca^{2+} (mg/L)	Cl^- (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Br^- (mg/L)	F^- (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	SO_4^{2-} (mg/L)
Groundwater	P1	783	32	7.54	43.8	7.01	1.24	43.7	58.5	< 0.02	0.28	497	13.5	< 0.08	53.8
	P2	473	32	6.80	53.2	6.76	3.07	20.8	15.0	< 0.02	0.37	213	29.4	n.d	7.51
	P3	828	24	7.10	104	7.91	0.88	29.3	36.7	< 0.02	0.21	460	88.1	n.d	40.6
	P4	1003	32	7.54	12.5	17.3	5.75	18.9	54.4	< 0.02	< 0.08	n.d	1.11	< 0.08	19.2
	P5	86	30	5.81	1.74	0.75	0.26	0.68	0.38	< 0.02	< 0.08	29.2	0.84	< 0.08	0.47
	P6	69	34	5.92	6.50	6.12	8.31	1.85	2.40	< 0.02	0.14	28.4	8.62	< 0.08	2.46
	P7	117	20	5.81	11.6	3.20	3.33	3.50	3.19	< 0.02	< 0.08	31.7	11.5	< 0.08	14.2
	P8	597	19	6.47	60.3	3.65	1.00	42.0	24.4	< 0.02	< 0.08	291	39.8	< 0.08	71.2
	P9	196	32	5.99	21.2	4.76	1.58	14.0	1.78	< 0.02	0.05	62.4	43.2	0.21	1.70
	P10	211	33	6.19	5.25	3.46	7.38	29.1	5.89	< 0.02	0.24	110	< 0.04	< 0.08	16.6
	P11	405	31	5.42	30.9	7.86	3.13	21.6	11.7	0.06	0.16	12.1	136	0.26	11.9
	P12	292	31	6.27	36.0	12.8	3.78	10.6	6.34	< 0.02	0.38	177	0.20	< 0.08	0.82
	P13	198	31	5.96	14.2	7.01	6.22	18.6	4.00	< 0.02	< 0.08	63.6	41.9	< 0.08	3.49
	P14	58	31	5.60	3.20	1.17	0.55	8.84	0.50	< 0.02	< 0.08	12.4	22.2	< 0.08	0.58
	F1	576	32	6.51	49.2	18.8	0.80	69.8	8.71	0.15	0.43	321	25.9	0.31	12.6
	F2	638	34	6.65	45.0	9.29	3.43	82.3	15.9	0.17	0.65	393	13.8	0.18	17.0
	F3	522	33	6.89	47.7	3.00	2.69	32.2	25.6	< 0.02	0.15	337	0.08	< 0.08	26.8
	F4	604	36	6.50	43.1	23.9	4.82	45.6	29.5	< 0.02	0.29	317	0.12	< 0.08	46.7
	F5	935	34	6.46	92.0	16.5	4.39	65.7	34.1	0.29	0.19	289	77.5	< 0.08	195
	F6	742	36	7.43	67.6	10.6	1.37	69.6	23.3	< 0.02	0.31	460	42.3	n.d	33.8

Table 2 (continued)

	Sample name	Conductivity (µS/cm)	T°C	pH	Ca^{2+} (mg/L)	Cl^- (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Br^- (mg/L)	F^- (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	SO_4^{2-} (mg/L)
	F7	469	30	6.5	n.d	44.0	4.93	27.3	15.1	n.d	n.d	82.3	93.0	n.d	4.22
	F8	487	28	6.59	53.0	2.52	3.21	21.6	19.4	< 0.02	< 0.08	322	4.92	< 0.08	4.80
	F9	344	28	8.68	25.0	7.86	6.64	15.6	16.6	< 0.02	0.49	95.0	31.0	< 0.08	2.73
	F10	329	31	6.19	36.1	6.03	2.37	20.2	9.15	< 0.02	0.15	194	17.3	< 0.08	5.40
	F11	1095	34	6.56	98.9	35.7	1.92	94.1	35.1	< 0.02	< 0.08	268	321	< 0.08	21.4
	F12	498	28	6.89	46.9	2.62	3.86	37.8	20.7	< 0.02	0.54	350	11.1	< 0.08	4.53
	F13	847	28	7.38	73.8	18.7	8.83	24.2	54.1	< 0.02	< 0.08	419	111	< 0.08	23.0
	F14	672	28	6.96	45.4	6.30	6.16	76.1	15.3	< 0.02	< 0.08	465	1.00	< 0.08	11.5
	F15	448	28	6.96	44.3	6.13	3.40	25.3	16.1	< 0.02	0.48	150	30.6	< 0.08	9.64
	F16	470	28	6.96	55.9	5.61	4.47	14.4	23.2	< 0.02	< 0.08	333	6.89	< 0.08	6.14
	F17	963	33	6.96	41.7	25.2	1.55	178	15.9	< 0.02	1.49	524	47.4	< 0.08	43.5
	F18	926	21	6.59	102	26.6	3.41	69.5	28.8	< 0.02	< 0.08	404	159	< 0.08	20.7
	F19	648	20	6.32	65.5	16.2	2.04	28.2	27.4	< 0.02	< 0.08	187	144	< 0.08	26.3
	F20	1337	33	7.11	54.3	121	10.3	209	25.5	0.62	1.77	339	0.54	< 0.08	254
	F21	64	31	5.35	4.79	2.86	4.26	2.48	1.37	< 0.02	< 0.08	4.64	14.1	< 0.08	8.76
	F22	524	29	6.24	50.3	5.87	3.71	13.9	13.7	< 0.02	0.29	202	0.68	< 0.08	82.5
	F23	1142	31	5.24	15.3	9.88	1.03	12.9	4.49	< 0.02	< 0.08	8.42	24.4	< 0.08	4.76
	F24	1275	31	6.96	55.8	121	9.53	199	26.4	< 0.02	1.01	181	2.35	< 0.08	242
	F25	70	31	5.79	3.42	0.86	1.61	1.08	0.61	< 0.02	< 0.08	22.3	3.55	< 0.08	0.71
	F26	817	28	6.42	80.5	53.3	7.56	65.6	24.7	0.36	0.41	263	0.44	< 0.08	164
	F27	1605	31	5.96	62.3	252	71.2	183	19.3	< 0.02	< 0.08	93.4	162	< 0.08	141
	F28	72	31	5.57	3.10	0.97	0.54	1.71	0.78	< 0.02	< 0.08	12.9	3.34	< 0.08	0.95
	F29	417	25	7.60	7.80	23.9	5.10	79.6	5.00	0.17	1.61	223	< 0.04	< 0.08	< 0.50

	Sample name	Al (µg/L)	As (µg/L)	As(III)/As_{tot} (%)	As(V)/As_{tot} (%)	B (µg/L)	Ba (µg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Cr (µg/L)	Fe (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
Groundwater	P1	2.96	203	0	100	24.3	29.7	0.005	0.384	8.08	0.103	0.860	1.56	3.56	0.037	12.7
	P2	7.74	0.714	0	100	30.0	37.0	0.004	0.188	1.72	1.16	5.26	0.314	0.125	0.034	3.61
	P3	3.96	2.54	100	0	17.7	2.98	0.013	0.179	1.13	0.041	4.09	2.36	0.131	0.013	0.675
	P4	4.53	190	n.d	n.d	14.1	86.6	0.004	9.79	1.97	0.037	5.60	956	6.15	0.021	2.41
	P5	86.1	0.130	n.d	n.d	11.0	33.2	0.002	0.048	0.326	0.332	40.9	2.26	0.783	0.023	2.19
	P6	74.2	0.086	n.d	n.d	11.4	32.6	0.001	0.070	1.23	0.182	40.6	0.546	0.655	0.041	9.85
	P7	34.6	0.253	n.d	n.d	13.7	50.0	0.004	0.111	0.763	0.125	17.3	16.7	0.766	0.042	1.41
	P8	2.61	15.8	n.d	n.d	20.3	5.39	0.007	0.041	0.298	0.174	0.547	0.152	0.361	0.027	0.624

Table 2 (continued)

Sample name	Al (µg/L)	As (µg/L)	As(III)/As_{tot} (%)	As(V)/As_{tot} (%)	B (µg/L)	Ba (µg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Cr (µg/L)	Fe (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
P9	0.262	0.005	n.d	n.d	1.98	3.16	0.011	0.053	3.66	0.008	0.751	3.14	0.180	0.912	7.95
P10	11.2	0.078	n.d	n.d	118	72.9	0.016	6.79	4.17	0.258	6.56	121	11.2	0.071	34.7
P11	67.7	0.038	n.d	n.d	15.6	131	0.141	5.59	0.410	0.137	6.05	657	24.2	0.015	39.0
P12	13.9	0.360	n.d	n.d	11.8	158	0.005	5.46	0.188	0.069	62.6	581	6.57	0.035	1.61
P13	4.59	0.048	n.d	n.d	4.70	94.5	0.050	0.227	1.51	0.055	1.82	17.7	1.87	0.030	10.9
P14	10.9	0.028	n.d	n.d	6.71	14.7	0.014	0.285	0.500	0.063	19.5	24.0	0.481	0.369	8.82
F1	7.91	0.183	0	100	14.0	458	0.007	0.048	1.17	0.035	3.16	1.87	0.218	0.045	3.12
F2	3.33	0.149	0	100	8.04	275	0.007	0.058	0.756	0.145	0.648	1.20	0.280	0.014	1.48
F3	5.97	0.298	0	100	4.57	201	0.008	0.027	1.76	0.082	2.48	0.354	0.312	0.037	2.24
F4	2.03	0.365	n.d	n.d	27.7	54.8	0.008	0.197	8.62	0.113	1.23	73.6	2.36	0.020	5.86
F5	43.5	0.681	n.d	n.d	45.5	443	0.049	0.240	3.29	0.970	23.5	4.52	4.38	0.484	37.5
F6	1.44	2.03	0	100	7.28	3.35	0.003	0.035	0.143	0.026	1.40	0.273	0.067	0.020	34.9
F7	11.8	0.116	n.d	n.d	14.8	146	0.006	0.050	0.431	0.169	11.7	0.899	0.677	0.038	6.13
F8	19.1	0.177	n.d	n.d	5.81	284	0.017	0.011	0.680	0.295	2.55	0.639	0.418	0.121	57.0
F9	22.5	0.043	n.d	n.d	3.69	109	0.005	0.030	0.417	6.02	0.432	1.90	0.659	0.012	6.62
F10	0.593	0.049	n.d	n.d	13.0	178	0.004	0.006	1.13	0.021	0.331	0.240	0.552	0.031	1.17
F11	1.48	0.061	n.d	n.d	24.5	244	0.004	0.498	0.680	0.159	0.530	0.122	0.165	0.030	4.49
F12	6.98	15.5	n.d	n.d	14.1	191	0.005	0.024	0.345	0.220	2.06	0.138	0.081	0.006	1.27
F13	5.30	0.371	n.d	n.d	72.9	347	0.023	0.420	10.8	8.82	1.22	0.386	0.218	0.687	14.4
F14	0.638	0.079	n.d	n.d	50.9	1344	0.003	0.016	0.231	0.035	0.583	0.558	0.066	0.061	2.32
F15	3.94	5.07	n.d	n.d	16.5	45.3	0.002	0.087	0.235	0.903	1.45	0.089	0.379	0.034	0.564
F16	2.23	0.209	n.d	n.d	21.6	296	0.006	0.018	0.343	0.189	0.395	0.998	0.349	0.032	6.38
F17	1.82	2.12	n.d	n.d	11.8	135	0.009	0.087	2.79	0.034	0.846	24.5	0.141	0.052	6.54
F18	2.23	0.293	n.d	n.d	7.84	60.0	0.007	0.295	1.30	0.187	0.294	0.227	0.133	0.032	2.02
F19	1.85	0.067	n.d	n.d	7.65	10.7	0.003	0.029	0.276	0.058	0.363	0.517	0.156	0.056	13.8
F20	2.59	0.071	n.d	n.d	1 377	30.6	0.003	0.016	0.119	0.008	7.28	70.1	0.045	0.006	0.866
F21	20.9	0.018	n.d	n.d	5.35	29.1	0.069	2.08	3.70	0.038	15.1	42.4	4.54	0.155	9.68
F22	1.20	1.10	n.d	n.d	93.8	43.8	0.001	3.48	0.228	0.013	12.1	758	4.78	0.005	39.6
F23	4.48	0.063	n.d	n.d	2.10	1.69	< 0.001	18.0	0.157	0.027	103	420	9.13	0.020	12.8
F24	3.30	0.130	n.d	n.d	1 092	27.7	0.003	0.016	0.196	0.009	2.96	49.0	0.357	0.029	94.7
F25	2.55	0.054	n.d	n.d	12.6	108	0.004	0.008	8.90	0.015	1.57	0.872	0.264	0.991	14.5
F26	2.44	0.091	n.d	n.d	191	34.9	0.000	0.059	0.104	0.016	0.947	116	0.196	0.009	1.65
F27	1.73	0.153	n.d	n.d	41.3	227	0.053	3.45	2.36	0.063	27.2	611	2.81	0.389	21.5
F28	4.03	0.042	n.d	n.d	5.14	31.5	0.017	0.193	150	0.677	0.819	3.70	1.14	3.16	71.7
F29	3.50	0.028	n.d	n.d	446	128	0.001	0.057	0.532	0.015	101	17.8	0.095	0.068	6.84

Table 2 (continued)

	Sample name	Latitude	Longitude	Sampling date (wet (W)/dry (D) period)	Watershed	Geological environment	Structure	Water use	Aquifer type	Geological formation	Depth (m)
Surface water	Sirb 1	13.76947	1.65249	18/04/2019, D	Sirba	ES	River		Sirba	LG	0
	Sirb 2	13.75928	1.62998	16/05/2019, D	Sirba	ES	River		Sirba	LG	0
	Sirb 3	13.73168	1.59957	16/05/2019, D	Sirba	ES	River		Sirba	LG	0
	Sirb 4	13.66488	1.49981	16/05/2019, D	Sirba	ES	River		Sirba	LG	0
	Sirb 5	13.61660	1.45443	16/05/2019, D	Sirba	ES	River		Sirba	LG	0
	Sirb 6	13.49008	1.26186	17/07/2019, W	Sirba	ES	River		Sirba	LG	0
	Sirb 7	13.58827	1.35160	17/07/2019, W	Sirba	ES	River		Sirba	LG	0
	Darg 1	14.01499	0.74457	18/04/2019, D	Dargol	ES	River		Dargol	LG	0
	Darg 2	13.95177	0.97476	25/04/2019, D	Dargol	ES	River		Dargol	LG	0
	Darg 3	13.85238	1.46900	07/05/2019, D	Dargol	ES	River		Dargol	LG	0
	Darg 4	13.95177	0.97476	07/05/2019, D	Dargol	ES	River		Dargol	LG	0
	Goro 1	13.11141	1.80470	07/05/2019, D	Goroubi	ES	River		Goroubi	LG	0
	Goro 2	13.22084	1.86547	07/05/2019, D	Goroubi	ES	River		Goroubi	LG	0
Reference values	CMA NN										
	WHO guidelines										
	CMA NF										
	CMA NC										
	Niger river*										
	World river average*										

	Sample name	Conductivity (µS/cm)	T°C	pH	Ca^{2+} (mg/L)	Cl^- (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Br^- (mg/L)	F^- (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	SO_4^{2-} (mg/L)
Surface water	Sirb 1	107	32	6.28	5.57	1.43	3.47	5.88	2.69	< 0.02	0.17	55.5	< 0.04	< 0.08	0.39
	Sirb 2	145	31	6.20	12.0	4.05	5.40	9.53	4.75	< 0.02	0.21	93.5	0.05	< 0.08	1.05
	Sirb 3	488	31	6.74	21.0	74.0	15.4	83.6	11.2	0.45	0.58	99.6	6.67	< 0.08	29.2
	Sirb 4	389	30	7.24	27.1	11.7	25.0	18.7	16.6	0.15	0.52	266	0.07	< 0.08	1.34
	Sirb 5	284	33	6.43	25.5	8.09	10.8	13.7	11.0	< 0.02	0.36	192	< 0.04	< 0.08	2.02
	Sirb 6	41	25	5.80	3.02	1.42	3.82	1.92	1.03	< 0.02	< 0.08	18.2	2.59	< 0.08	1.12
	Sirb 7	104	25	n.d	2.26	1.14	0.60	1.33	0.50	< 0.02	< 0.08	n.d	0.08	< 0.08	0.78
	Darg 1	163	25	6.27	15.0	3.24	7.66	7.14	5.77	< 0.02	0.60	104	< 0.04	< 0.08	3.59
	Darg 2	179	25	6.21	10.5	10.8	12.3	13.0	3.90	0.07	0.34	n.d	4.68	< 0.08	8.35
	Darg 3	308	33	7.24	30.6	6.80	7.42	22.9	6.14	< 0.02	0.51	88.4	1.93	< 0.08	3.95
	Darg 4	159	36	6.16	11.1	3.96	8.96	12.6	3.72	< 0.02	0.26	89.4	4.70	0.12	3.15
	Goro 1	45	25	5.86	3.66	1.20	5.22	1.43	1.26	< 0.02	< 0.08	23.0	1.98	< 0.08	1.10
	Goro 2	30	25	5.74	2.72	0.96	2.95	1.00	0.92	< 0.02	< 0.08	13.9	3.06	0.13	0.88

Table 2 (continued)

	Sample name	Conductivity (µS/cm)	T°C	pH	Ca^{2+} (mg/L)	Cl^- (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Br^- (mg/L)	F^- (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	SO_4^{2-} (mg/L)
Reference values	CMA NN														
	WHO guidelines														
	CMA NF														
	CMA NC														
	Niger river*														
	World river average*														

	Sample name	Al (µg/L)	As (µg/L)	As(III)/As_{tot} (%)	As(V)/As_{tot} (%)	B (µg/L)	Ba (µg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Cr (µg/L)	Fe (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
Surface water	Sirb 1	7.52	0.738	100	0	7.71	50.8	0.210	0.081	1.72	0.104	9.02	2.30	0.786	0.096	4.30
	Sirb 2	20.2	1.72	100	0	11.3	109	0.013	0.135	1.35	0.082	21.3	9.88	0.902	0.034	4.97
	Sirb 3	28.0	2.91	70	30	38.9	280	0.041	0.865	5.67	0.300	21.3	4.36	3.77	0.060	8.80
	Sirb 4	17.9	2.25	100	0	32.1	660	0.035	0.455	2.20	0.108	13.4	37.1	1.96	0.037	11.0
	Sirb 5	15.6	1.65	100	0	22.8	256	0.461	0.441	2.37	0.098	5.84	68.9	1.32	0.046	12.0
	Sirb 6	821	0.614	n.d	n.d	12.7	62.7	0.052	0.437	3.45	1.08	590	21.7	1.56	0.521	15.7
	Sirb 7	133	0.531	n.d	n.d	11.9	55.7	0.033	1.99	1.06	0.196	82.5	66.7	1.11	0.112	10.2
	Darg 1	563	0.576	0	100	26.0	141	0.115	0.372	3.00	0.965	431	12.7	1.49	0.520	3.25
	Darg 2	550	0.306	n.d	n.d	74.4	296	0.003	0.190	3.29	1.00	234	1.01	1.39	0.146	3.07
	Darg 3	11.2	0.339	n.d	n.d	18.3	272	0.052	0.133	1.29	0.133	15.2	1.39	0.741	0.042	4.99
	Darg 4	356	0.153	n.d	n.d	15.9	179	0.026	0.404	1.91	0.306	181	161	0.694	0.363	3.64
	Goro 1	135	0.186	n.d	n.d	13.8	39.8	0.028	0.271	2.16	0.298	86.8	8.69	1.16	0.070	6.77
	Goro 2	19.9	0.130	n.d	n.d	7.37	27.2	0.020	0.140	1.13	0.164	15.4	3.37	0.715	0.037	5.46
Reference values	CMA NN		10				100	5		1000	50		100		50	5000
	WHO guidelines	200	10			2400	1300	3		2000	50		400	70	10	3000
	CMA NF	200	10			1000	700	5		2000	50		50	20	10	
	CMA NC		10			5000	2000	7		2000	50		120		5	
	Niger river*	76				3.2	30		0.040	0.63	0.45	105	0.50	0.29	0.039	0.89
	World river average*	32	0.62			10.2	23	0.08	0.148	1.48	0.7	66	34	0.801	0.079	0.60

*From Gaillardet et al., 2003

n.d. not determined

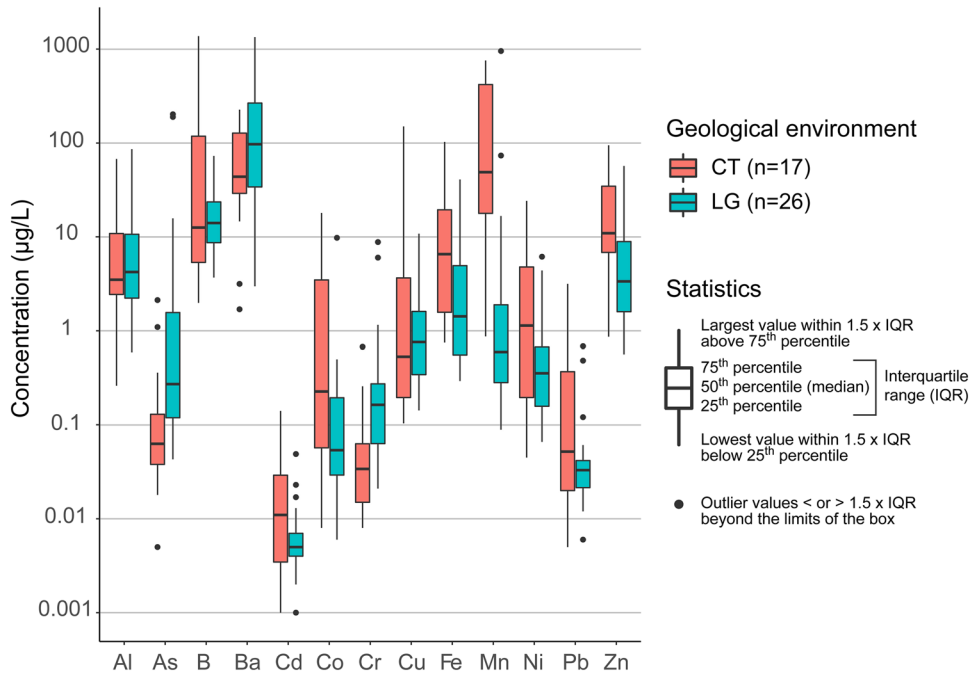

Fig. 3 Comparison of dissolved concentration (µg/L) of trace elements in the two contrasted geological environments CT (in red) and LG (in blue)

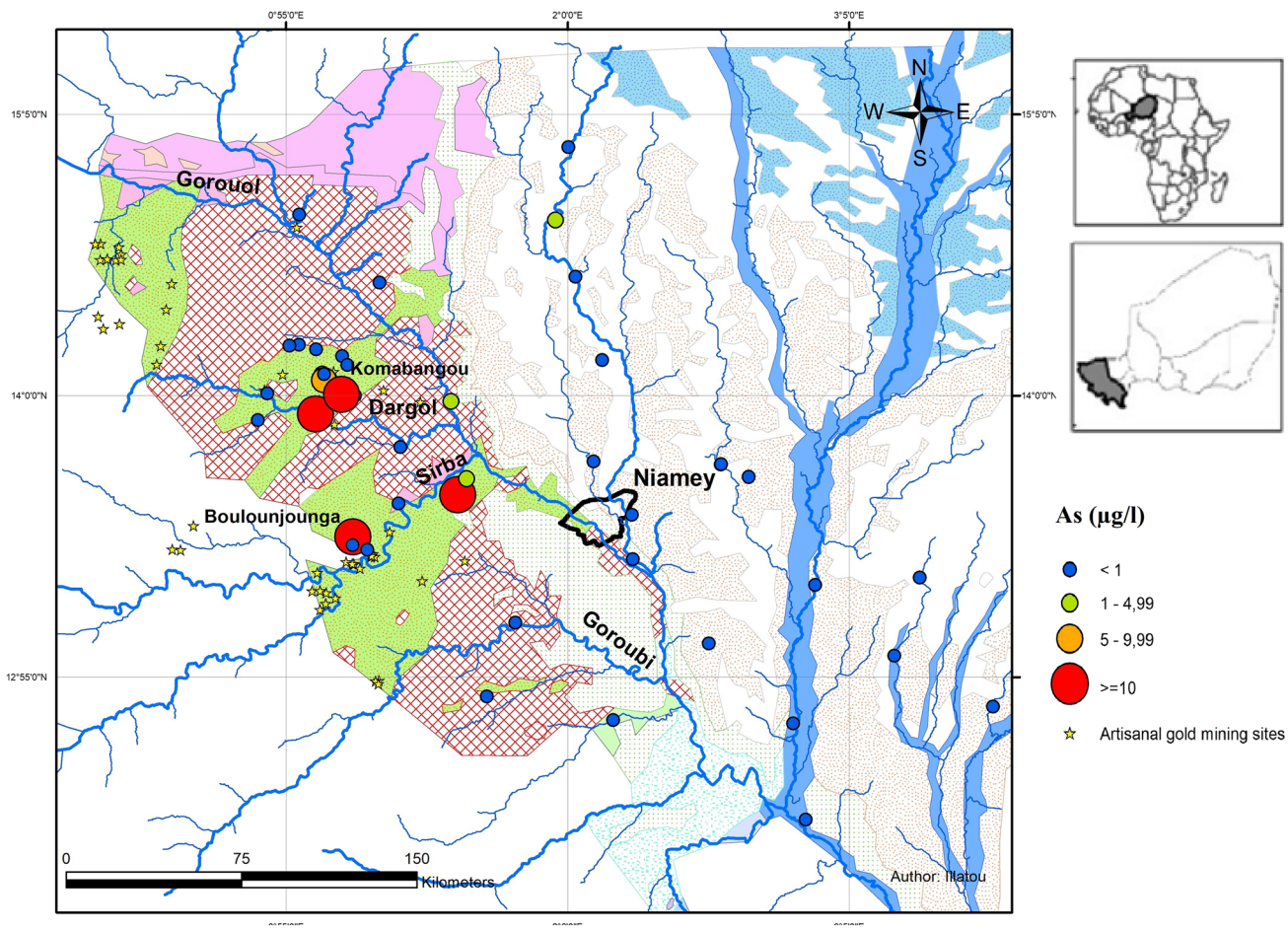

Fig. 4 Distribution of As concentrations in the studied area

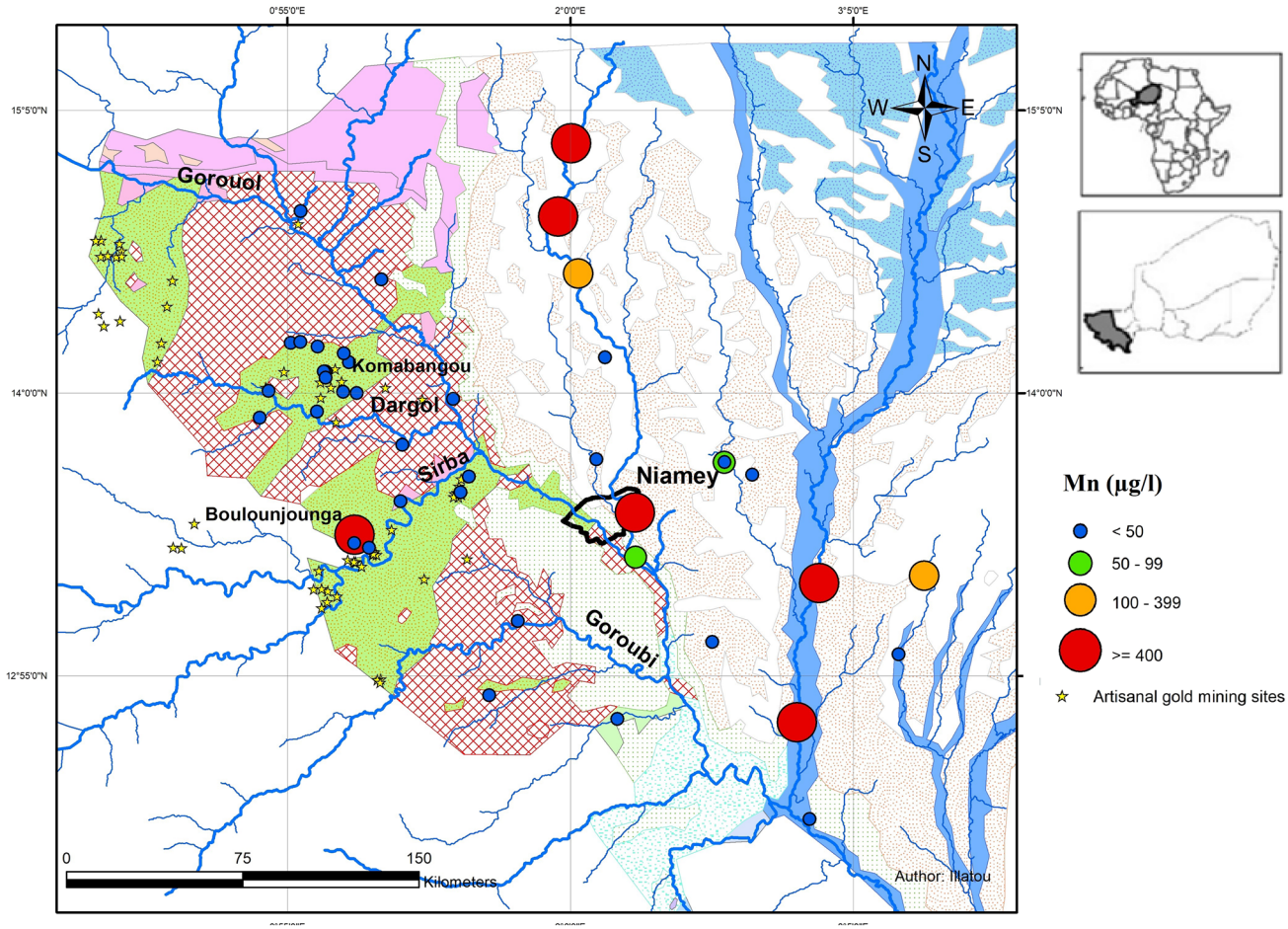

Fig. 5 Distribution of Mn concentrations in the studied area

in SPM and more extensively for B ($EF_{average} = 6 \pm 4$) and Cr ($EF_{average} = 8 \pm 5$) in sediments.

Discussion

Arsenic in groundwaters and rivers

Our study evidenced 23% of groundwater samples that exceeded drinking water guidelines for As or Mn. For As, exceedances of guidelines were exclusively encountered in the LG geologic formation, in alterite greenstone aquifers of the Birimian formations. There was no boreholes or wells with high As concentrations in the alluvial aquifers of the Continental Terminal. The four groundwater samples with the highest arsenic concentrations have been taken from wells or boreholes located in or near the gold artisanal mining sites of Mbanga ([As] = 203 µg/L), Boulounjounga ([As] = 190 µg/L) and Komabangou ([As] = 15.8 µg/L and 15.5 µg/L). The wells from Mbanga and Boulounjounga have been dug to exploit vein gold deposits, and reached the water table, thus providing a water resource to the surrounding population. At Komabangou, the two boreholes exceeding 15 µg/L have been drilled for drinking water supply. Previous data from Tankari et al. (2014, 2019) showed similar values in groundwater at Komabangou (As = 19 µg/L, Tankari et al. 2014; As = 3 µg/L, Tankari et al. 2019) and in water from the gravimetric gold extraction process (As = 20 µg/L) while the As concentration was hundred times higher (As = 2429 µg/L) in the water from the cyanidation gold extraction process. In soils, average As concentrations were two orders of magnitude higher in the gold exploitation zone than outside this zone (Tankari et al. 2019). Thus, Au mineralisation was a source of high-As groundwater at Komabangou. Our study revealed that, besides Komabangou, two other artisanal gold mining sites (Mbanga and Bouloundjounga) in the Nigerien Liptako exhibited even higher groundwater As concentrations. The reason for such elevated As concentrations in wells P1 (203 µg/L) and P4 (190 µg/L) may be related to their original purpose (gold extraction rather than drinking water supply) and age (they have been exploited since the 1980's). It

Table 3 Concentrations and enrichment factors in SPM and sediments from the rivers Sirba, Dargol and Goroubi. Al and Fe concentrations in %, other trace element concentrations in µg/g. World river averages are given for SPM when available (Viers et al. 2009)

River	Sample name	Al		As				B				Ba				Cd				Co				Cr			
		SPM	Sediment	SPM		Sediment		SPM		Sediment		SPM		Sediment		SPM		Sediment		SPM		Sediment		SPM		Sediment	
		%	%	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF
Sirba	Sirb 1	11.2	1.9	12.8	6.1	4.2	11.9	32.1	1.5	15.7	4.5	499	0.7	144.5	1.1	21.0	153.4	0.03	1.4	24.9	1.8	5.6	2.4	123	2.5	42.1	5.1
	Sirb 2	0.95	0.8	1.80	10.1	3.7	26.4	2.12	1.2	17.6	12.5	126	1.9	71.9	1.4	0.035	3.0	0.03	3.2	3.27	2.8	3.8	4.0	11.9	2.9	49.8	15.2
	Sirb 3	4.65	2.1	5.19	6.0	22.5	58.7	5.94	0.7	22.5	5.9	124	0.4	188.2	1.3	0.027	0.5	0.05	1.8	9.60	1.7	17.1	6.7	65.9	3.3	188.5	21.1
	Sirb 4	2.41	1.6	2.95	6.5	5.0	17.2	4.27	1.0	18.6	6.4	140	0.8	437.8	4.1	0.020	0.7	0.03	1.5	5.34	1.8	6.5	3.4	32.3	3.1	42.5	6.2
	Sirb 5	1.28	0.9	1.73	7.3	1.8	10.1	4.58	1.9	7.9	4.6	69.9	0.8	157.5	2.5	0.027	1.7	0.02	1.8	2.85	1.8	2.5	2.2	15.1	2.7	28.9	7.1
	Sirb 6	1.38	0.4	2.10	8.2	1.8	25.2	1.86	0.7	9.1	12.4	31.6	0.3	27.4	1.0	0.020	1.2	0.01	1.5	1.92	1.1	1.6	3.3	13.7	2.3	15.4	9.1
	Sirb 7	6.52	2.7	17.0	14.0	6.2	12.1	30.3	2.5	28.0	5.5	412	0.9	272.3	1.5	0.067	0.8	0.04	1.3	20.8	2.6	12.2	3.6	118	4.1	68.3	5.7
Dargol	Darg 1	11.3	5.6	5.63	2.7	5.2	4.9	14.7	0.7	13.3	1.3	237	0.3	253.4	0.7	0.268	2.0	0.06	0.9	11.9	0.8	14.1	2.0	104	2.1	103.3	4.2
	Darg 2	10.7	2.1	5.28	2.6	1.7	4.3	11.4	0.6	10.3	2.6	401	0.5	165.9	1.1	0.057	0.4	0.02	0.7	18.3	1.4	5.8	2.2	138	3.0	40.6	4.4
Goroubi	Goro 1	5.22	1.7	1.95	2.0	1.4	4.4	4.77	0.5	9.6	3.0	125	0.4	144.6	1.2	0.018	0.3	0.02	0.8	6.52	1.0	5.7	2.7	53.6	2.4	37.4	5.0
	Goro 2	11.6	3.4	6.20	2.9	7.1	11.1	13.4	0.6	15.8	2.5	288	0.4	163.3	0.7	0.044	0.3	0.06	1.4	19.7	1.4	11.4	2.7	159	3.1	84.2	5.6
World River av		**8.72**		**36.3**				No data				**522**				**1.55**				**22.5**				**130**			

River	Sample name	Cu				Fe				Mn				Ni				Pb				Zn			
		SPM		Sediment		SPM		Sediment		SPM		Sediment		SPM		Sediment		SPM		Sediment		SPM		Sediment	
		µg/g	EF	µg/g	EF	%	EF	%	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF	µg/g	EF
Sirba	Sirb 1	52.6	1.5	11.0	1.9	5.26	1.1	1.4	1.7	2832	3.4	214.6	1.5	71.5	2.6	13.3	2.8	22.8	0.8	6.7	1.4	137	1.4	18.9	1.1
	Sirb 2	5.03	1.7	5.8	2.5	0.49	1.2	1.0	3.0	816	11.5	285.8	5.1	6.38	2.7	6.2	3.3	2.80	1.2	8.5	4.6	12.1	1.4	12.4	1.9
	Sirb 3	21.5	1.5	37.1	5.8	2.11	1.0	8.2	9.2	242	0.7	407.1	2.7	29.2	2.5	32.8	6.4	5.82	0.5	8.5	1.7	29.8	0.7	35.6	2.0
	Sirb 4	12.0	1.6	12.8	2.6	1.21	1.2	1.5	2.1	468	2.6	1292.4	11.1	15.4	2.6	12.2	3.1	3.36	0.6	5.7	1.5	18.4	0.9	16.5	1.2
	Sirb 5	5.77	1.5	5.4	1.9	0.61	1.1	0.7	1.8	373	3.9	146.1	2.1	8.12	2.6	4.7	2.0	2.08	0.7	4.3	1.8	11.1	1.0	8.9	1.1
	Sirb 6	5.12	1.2	3.6	2.9	0.69	1.2	0.5	3.2	36.5	0.4	58.4	2.0	7.05	2.1	3.5	3.6	1.85	0.5	2.2	2.2	11.2	0.9	6.0	1.7
	Sirb 7	40.6	2.0	18.9	2.2	4.64	1.6	2.7	2.2	622	1.3	399.0	2.0	55.7	3.4	23.9	3.5	14.5	0.9	9.7	1.4	65.2	1.1	30.1	1.2
Dargol	Darg 1	30.2	0.9	33.9	1.9	3.93	0.8	3.7	1.5	220	0.3	795.0	1.9	55.0	2.0	48.1	3.5	12.4	0.4	15.2	1.1	73.1	0.7	66.7	1.4
	Darg 2	40.5	1.2	11.8	1.8	5.16	1.1	1.3	1.4	494	0.6	210.4	1.3	68.1	2.6	16.6	3.1	17.4	0.7	6.5	1.2	74.2	0.8	23.1	1.2
Goroubi	Goro 1	15.9	1.0	8.1	1.5	1.87	0.8	1.0	1.4	117	0.3	144.3	1.1	29.6	2.3	13.5	3.2	6.35	0.5	5.8	1.4	36.0	0.8	19.0	1.3
	Goro 2	39.5	1.1	16.6	1.6	5.31	1.0	5.5	3.7	268	0.3	261.4	1.0	78.2	2.7	25.3	3.0	21.9	0.8	15.6	1.8	101	1.0	56.7	1.9
World River av		**75.9**				**5.81**				**1679**				**74.5**				**61.1**				**208.0**			

n.d. not determined

can be hypothesized that digging for decades toward deeper and deeper horizons in the mineralized zone favoured water/rock interaction and subsequent As mobilization. The process could take a certain amount of time; the contamination could not be effective until months or years after the beginning of pumping (Bonnemaison 2005). In this respect, well P3, located in Sefa Moussa, a few kilometres from well P1, had lower As concentration (As = 2,5 µg/L). Gold extraction began in 2017 at this site. Similarly, well P5, located a few kilometres from well P4, had lower As concentrations (As = 0.13 µg/L). This well was dug especially for drinking water supply; thus, groundwater at this site was not readily to interact directly with gold mineralization.

The detection of high-As groundwater at several sites in the study area demonstrates that the problem could be widely distributed in the gold extraction zones in Nigerien Liptako. These results agree with those of Smedley (1996) and Smedley et al. (2007) who reported groundwater As concentrations up to 141 µg/L in similar Birimian lithology in northern Ghana and up to 1630 µg/L in the region of Ouahigouya in Burkina Faso. In all these regions, a high spatial variability in groundwater As concentrations was evidenced at a local scale, which makes a prediction of groundwater As concentrations difficult. Regarding the primary arsenic source, arsenic-rich pyrite and arsenopyrite have been associated to gold mineralisation in the Birimian greenstone belt (e.g. Milési et al. 1989, 1992; Bourges et al. 1998; Smedley et al. 2007; Béziat et al. 2008; Sangaré et al. 2014). The oxidation of sulphide minerals is an important As mobilization mechanism (Smedley et al. 2002). Here, bulk analysis of the rocks collected in the vicinity of the artisanal mining sites showed As concentrations slightly higher than common values in shale and diorite. SEM–EDS analyses showed the presence of sulphide minerals, but no detectable levels of As in these sulphides. The only As source identified by SEM was related to Fe-oxides. Sample of schist showed Fe-oxides with 0.8 wt.% As. Secondary Fe-oxides have been suggested as a possible primary source of arsenic in groundwater in zones of mineralised Birimian volcano-sedimentary rocks in Burkina Faso (Smedley et al. 2007). Sulphate released during the initial oxidation of sulphides may have been flushed from the aquifer some time ago. Arsenic may be released from Fe-oxides by desorption. This process is favoured at high pH due to the anionic character of arsenate that competes for sorption sites with bicarbonate at the surface of Fe-oxides (Smedley and Kinniburgh 2002). Results of arsenic speciation in the present study showed that arsenate predominated in the well from Mbanga where the highest As concentration (203 µg/L) has been measured. However, no correlations were evidenced in the present study between pH or bicarbonate concentrations and arsenic concentrations, probably because of the few high As concentration data available.

The Boulonjounga and Mbanga artisanal gold mining sites where the two highest groundwater As concentrations have been evidenced are both located near the Sirba River. In this river, gold miners extract gold by panning. Our analysis showed that dissolved As concentrations in the river Sirba were higher than in the rivers Dargol and Goroubi and also higher than the world river average. SPM and sediments of the Sirba river were the most enriched with As. Moreover, station Sirb3, located downstream a gold-panning area exhibited higher dissolved As concentration than station Sirb6, located upstream. This suggests that artisanal gold extraction in the river Sirba had an impact on arsenic mobilization to surface water, although the resulting As enrichment was relatively low. The predominance of arsenite upon arsenate suggests that As(V), which is the thermodynamically stable species in the oxidizing conditions of the Sirba river remains immobilized on SPM and sediments. At stations along the river Dargol, draining the Komabangou gold extraction area, where groundwater As concentrations around 16 µg/l have been measured, no As enrichment was evidenced in surface water. The strong correlation ($r^2 = 0.83$) between As and Fe in sediments from the three rivers suggests that Fe-oxides control As mobility in surface waters in the study area, as generally observed (Smedley and Kinniburgh 2002).

Other trace elements in groundwaters and rivers

Nine groundwater samples, corresponding to 21% of the samples, had Mn concentrations exceeding the French drinking water guidelines (50 µg/L), seven exceeded the Nigerien drinking water guideline (100 µg/L) and five exceeded the WHO guideline (400 µg/L). Several studies have shown that Mn could have neurodevelopmental effects in children exposed to concentrations higher than 50 µg/L (WHO Guideline 2017). The risk of neurotoxic effects on children starts to increase when the concentration in drinking water exceeds 100 µg/L (Bouchard et al. 2011). The highest concentration of Mn (956 µg/L) was found together with arsenic (190 µg/L) in the well of the artisanal gold mining site of Boulounjounga. At this site, the well was close to a manganese deposit highlighted in the Niger Mineral Plan (Franconi et al. 1984). Several manganese deposits have been identified in the West African craton including in Mali, Burkina Faso, Ghana and Côte d'Ivoire with occurrences in the volcano-sedimentary belts (Hein and Tshibubudze 2016). At Komabangou, Tankari et al. (2014, 2019) found Mn concentrations of 98 µg/L and 36 µg/L in groundwater while in gravimetric gold processing waters and cyanidation gold processing waters, Mn concentrations reached 1.60 mg/L and 108.43 mg/L, respectively, suggesting a link between Mn and gold mineralisation. Our analysis of rocks clearly showed the presence of manganese oxides in diorite sample

from the quartz vein and in the shale sample. These Mn oxides explain the high Mn concentrations in the groundwater sample from Boulounjounga. However, as with As, the high-Mn groundwaters were very locally distributed in the right bank area. Mn enrichment in surface water from the rivers Sirba, Dargol and Goroubi, compared to the Niger River, and local Mn enrichment in SPM and sediments compared to UCC confirm the influence of Mn deposits on water geochemistry in the right bank tributaries.

The other groundwater samples with high Mn concentrations were located in the Ct^3 aquifer, mainly along the left bank tributaries of the Niger River. High manganese concentrations had previously been highlighted in this area; at Tillakaina village, in the Tillabery region, Salihou-Djari et al. (2018) found Mn concentration of 140 µg/L in the Ct^3 aquifer waters. The processes at work for Mn mobilization in this area deserve further research.

Among the other trace elements, Ba, B and Ni showed a few localized groundwater enrichments. The origin of Ba in the LG geological environment was clearly related to the gold mineralisation according to the high content (85 mg/g) in the sample of diorite from the quartz vein, while the origin of Ba, B and Ni enrichments in groundwater in the CT geological environment will deserve further research.

Conclusion

Arsenic and manganese are contaminants of concern in groundwaters of the Nigerien Liptako. Arsenic concentrations exceeding drinking water guidelines (> 10 µg/L) were associated to alterite aquifer of the Birimian greenstone belt. The highest As contents were evidenced in old wells mined for gold extraction since the 1980s and used for drinking water purpose, suggesting a relationship between the elevated arsenic concentrations found in groundwater and gold mining. The origin of As in the water of the alterite aquifer is probably related to desorption from iron/manganese oxides. Wells and boreholes with high As concentrations were highly dispersed throughout the Nigerien Liptako and it is therefore difficult to predict the As concentration at the regional scale and at the scale of a mining site as well. In the rivers, As enrichment was evidenced in SPM and sediments draining artisanal gold mining sites but dissolved As did not exceed ~ 1 µg/L. Manganese is another trace element of concern in groundwaters of the studied area. Concentrations exceeding WHO drinking water guidelines (400 µg/L) were recorded in aquifers of the Continental Terminal geological environment.

This study showed that it is essential to carry out an inventory of the concentrations of arsenic and other trace elements in the boreholes and wells of all the former artisanal gold mining sites in Nigerien Liptako, to characterize the polluted areas and to find alternative water supply for the population living in the vicinity of these sites. Further investigations would be necessary to assess the level of As and Mn exposure of the populations living in these areas. Because of the development of artisanal gold mining in the region and the pressure on water resource availability, the establishment of long-term monitoring programs for arsenic and trace metal levels in boreholes used as water supplies by the population in gold-rich zones is absolutely required. Furthermore, non-geologic pollutants such as mercury and cyanides, used in gold extraction, should be investigated in the water resources in the area.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

Declarations

Conflict of interest The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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