DISTRIBUTION ET SOURCES DES ELEMENTS TRACES (Article 2)

Seasonal variations in processes driving manganese and iron concentrations above drinking water guidelines in the unregulated shallow aquifer of Cotonou (Southern Benin)

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Abstract

Urbanization combined with the production of domestic and industrial waste in expanding West African cities are a significant contributor of elevated level of metallic trace elements of groundwater, which are a greatest risk to human health. The Fe and Mn concentrations in the unregulated shallow aquifer of Cotonou (Benin) intermittently exceed concentrations of Beninese drinking water guidelines (100 µg/L and 300 µg/L for Mn and Fe respectively). The processes controlling the elevated Fe and Mn concentrations (up to 999 and 643 µg/L) were analysed in three urban neighborhoods of Cotonou with distinct hydrogeological contexts: Ladji is seasonally inundated by water from the Lake Nokoué, Agla is subject to inundations and is located in a swampy low-lying area, and St Jean is located at higher elevations where there is no inundation or ponds. The concentrations of trace elements and Rare Earth Elements (REE) in groundwater, surface-water and soil were determined from a total of 142 samples acquired between June 2017 to June 2018 by Spectrometry (Q-ICP MS). Results of this study highlight that infiltration of waters from shallow ponds are a key element in driving elevated Mn and Fe concentrations and their role is multi-faceted. Firstly, the ponds transmit high loads of dissolved inorganic carbon (DOC) to the aquifer that is used in the reductive dissolution of the Mn-bearing minerals (Mn (IV) (oxyhydr)oxides). In-aquifer Fe-mineral dissolution is unlikely due to the super-saturation of common Fe-oxyhydroxide minerals for these groundwaters. Relatively low Ce/Ce* anomalies at Agla (1.06) compared with Ladji (1.08) may indicate higher organic matter transfers to the groundwater from the ponds in Agla, compared with the ponds in Ladji. Secondly, the ponds are a significant source of both Fe and Mn, with concentrations up to 1742 and 561 in Agla, and 1232 and 235 in Ladji. The lake (with Mn concentrations up to 970) is also likely to contribute to high concentrations of Mn in groundwater at Ladji. The analysis of sediments at each site also highlighted the accumulation of Fe in the unsaturated zone where the sediments are clay-rich.

The increases in Mn and Fe concentrations in the shallow aquifer predominantly occurs during the dry season; when this unregulated water resource is most solicited by local residents living in underprivileged areas.

Key words: Surface water and groundwater, reductive condition, organic matter, iron and manganese concentrations, human health risks

1. Introduction

In 2014, according to statistical data, 1.8 billion people are using water sources of dubious quality; and in 2030, the global demand for water resources is expected to increase by 50 per cent (UNDP 2018). In Africa, World Bank predictions in 2005 show that 75 to 250 million people will have difficulty reaching their water needs in 2020 (WWAP 2017). Urbanization in many expanding West African cities, combined with the significant production of domestic and industrial waste, incineration waste, the use of fertilizers and agrochemicals contribute to the contamination of urban soils and water resources by metallic trace elements (Weissmannová and Pavlovský 2017). The high contamination of groundwater and surface water by metallic trace elements represents the greatest health risk to human health (Ritter et al. 2002; Merkel, and Offiong 2003; Ogunlaja et al. 2019). In addition, due to their non-biodegradable nature and persistence in the environment, trace elements can accumulate in the soil and/or pass through the unsaturated zone, which may increase the potential risk to groundwater and to the immediate population (Ogunlaja et al. 2019). The trace elements can be found in groundwater either during water-rock interactions or from different sources of anthropogenic activities (Schneider 2016). The determination of trace elements in the soil solution makes it possible to quantify the contents of dissolved trace elements that can be directly transferred between soil compartments to shallow groundwater. The mobility of trace element such as As, Fe and Mn is highly dependent upon the concentration of dissolved organic carbon (DOC) due to its ability to change the redox conditions and microbial abundances. DOC concentrations in groundwater are higher in urban areas compared to natural or agricultural areas (McDonough et al. 2020).

The processes of precipitation, mineral dissolution, adsorption/desorption, complexation/dissociation and oxidation/reduction control the mobility and availability of trace elements in the soil and groundwater (Leung and Jiao 2006; Sun et al. 2010 ; Ye et al. 2019). Many studies have focused on the presence and monitoring of trace elements in groundwater and drinking water. For example, in South West Palestine (Malassa et al. 2013) have shown that groundwater is contaminated with trace elements such as Pb, Al, Cr, Co, Ni, Cu, Zn, Tl, Bi, Mn, Ag, Cd and Mo. It is clear that studies on the presence and determination of these elements in groundwater, surface water and soil are an important issue for human health and the environment.

The study area is located in Cotonou (south of Benin) and is the most urbanization city of the country with intense human activities that produce a huge amount of solids wastes and sewages (Yadouléton 2015). Groundwater is becoming increasingly vulnerable to contamination from sewage, septic tanks and seawater, such as Nokoué Lake (Houéménou et al. 2019). Unmonitored and untreated shallow groundwater is used by populations through large diameter wells for domestic uses. Cotonou groundwater in the Quaternary aquifer is not recommended to be used for drinking water because of its vulnerability to contaminants (Boukari et al. 1996). Economic reasons and proximity to groundwater lead the underserved populations to use this resource for washing only, but it commonly ends up for drinking, dish washing, shower and cooking water supplies (Houéménou et al. 2019). The underprivileged areas of the city are subject to greater groundwater quality issues, and this also corresponds to the parts of the city where the residents are more dependent on the groundwater as a domestic water resource. There is very limited data on the water quality notably on trace elements in groundwater and ponds in Cotonou. On the rare studies conducted on trace elements in shallow groundwater (Maliki 1993; Boukari 1998; Yehouenou Azehoun Pazou et al. 2009), none has examined their spatial and temporal concentration variations in different hydrogeological environments. In addition, no studies have been able to implement the vertical distribution of soluble trace elements in the unsaturated area in Cotonou. This study on trace elements contamination is mainly carried out on groundwater, ponds and Lake Nokoué in three neighborhoods with different hydrogeological contexts. The first (Ladji) which overflows towards the small wet season is bordering Lake Nokoué, the second (Agla) is subject to inundation during both the small and large wet seasons is located in a swamp low land and the third (St Jean), where there is no long-term surface inundation. We analyse the spatio-temporal distribution and concentration of trace elements in shallow groundwater and surface water at each site. The results in this study highlight that manganese (Mn) and iron (Fe) concentrations are the only trace elements to reach concentrations above guidelines proposed for drinking water. Thus, we analyse the processes, and temporal variations of these, resulting in the elevated Mn and Fe concentrations in the shallow groundwater of Cotonou. This study aims to assess the vulnerability of the Cotonou coastal aquifer to trace element pollutants, the influence of different inundation and hydrogeological processes (including the role of inundation and recharge by the Lake Nokoué) and the risks to human health.

2. Study area

2.1 Description and soil types in study area

The city of Cotonou is bordered by the Lake Nokoué in the North, and the Atlantic Ocean to the South (Fig. 1). Cotonou is located in the hot and humid sub-equatorial climate zone, characterized by two annual rainy seasons (March to July and September to October) and two dry seasons (November to March and August). As shown in Figure 1A, the different types of soil in Cotonou are: i) tropical ferruginous soils leached without concretions on Quaternary sand (orange color), ii) hydromorphic soils leached on Quaternary sand (blue color), iii) hydromorphic soils with little humus on clay alluvial material (green color) and iv) soils with little hydromorphic development on coastal marine sands.

The hydromorphic soils common in the coastal areas of southern Benin are characterized by a long-term oxygen deficit that promotes redox processes. These soils are classified as highly to moderately acidic pH soils (Azontonde 1991; Igue et al. 2013)

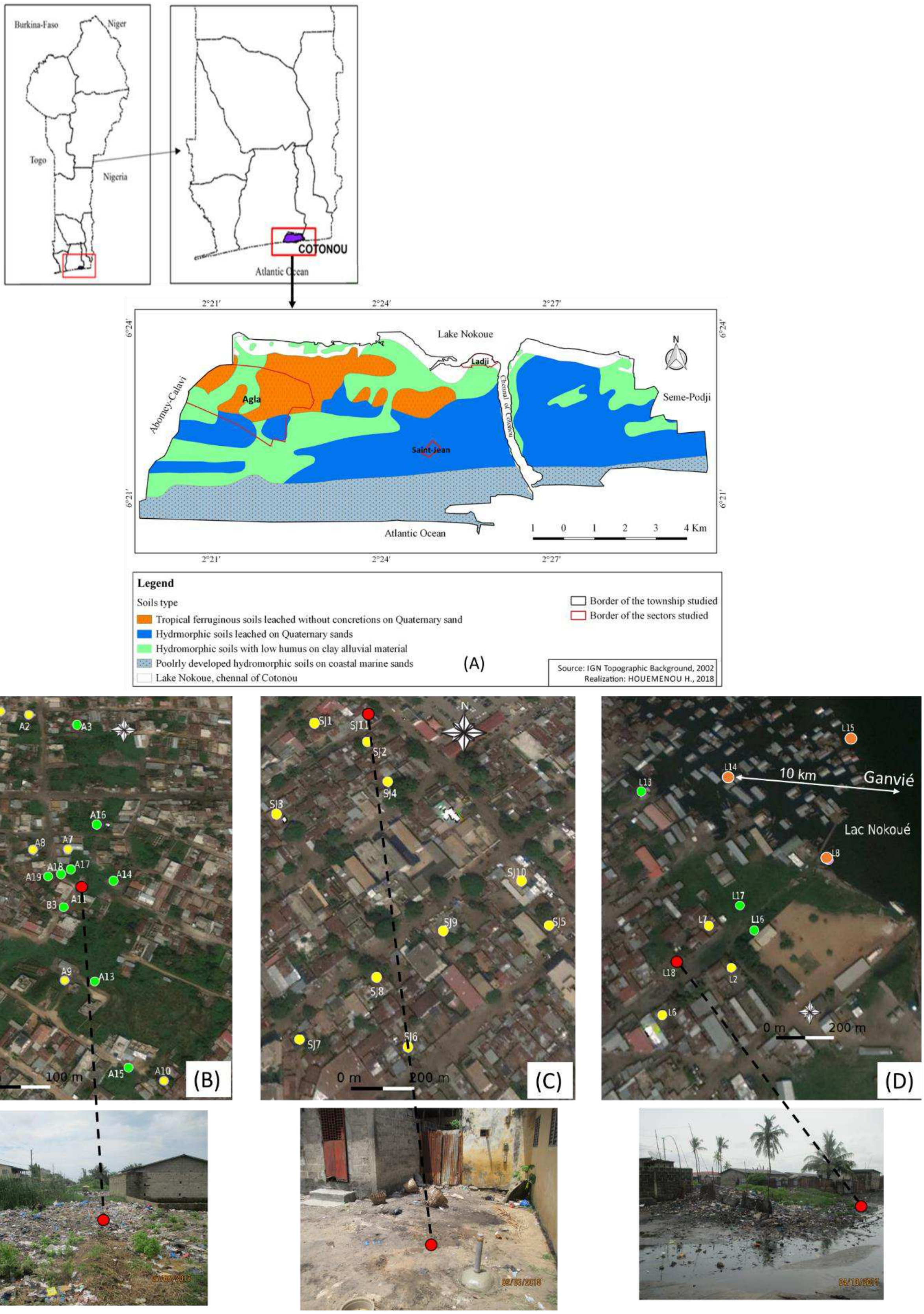


Figure 1. (A) Soil types in Cotonou; (B)Location of sampling sites at Agla; (C)Location of sampling sites at St Jean, (D)Location of sampling sites at Ladji.

(Groundwater sample for Yellow color; Pondwater sample for green color, Lake samples for orange color and Soils samples for red color. G4, G5, G6 and G7 are located in the Ganvié lacustrine village at 10 km from sampling point L14.

2.2 Geology and granulometry

Cotonou is located in the coastal sedimentary basin comprised of Quaternary (Holocene) sediments, which include facies of the littoral plain (sands) and alluvial deposits, underlain by sediments from the Mio-Pliocene (Continental Terminal), Paleocene and Upper Cretaceous (Maliki 1993). The Cotonou aquifer is based on the Quaternary aquifer identified at the level of the coastal sedimentary basin.

The particle size fractions found in "Holocene sediments" are composed of fine to medium sand (85%), silt (5.5%) and clay (9%). The content of fine particles (silts + clays) is less than 17% and those of sands can reach 95% (Oyédé 1991). They are therefore homogeneous sediments with a low clay content. Most of the silicates present in the barrier beaches are, in addition to silica itself, clays. These are kaolinite and smectites (including montmorillonite) for yellow sands and smectites only for white and brown sands. Traces of limestone from recent marine or coastal (lagoon) deposits frequently strewn with shell debris are also present (Boukari 1998). The granulometric analysis carried out by Oyédé (1991) and Maliki (1993) on the PU2 piezometer (not far from the beach and about 200 m from the Atlantic Ocean) made it possible to obtain the lithological section shown in the Figure 2.

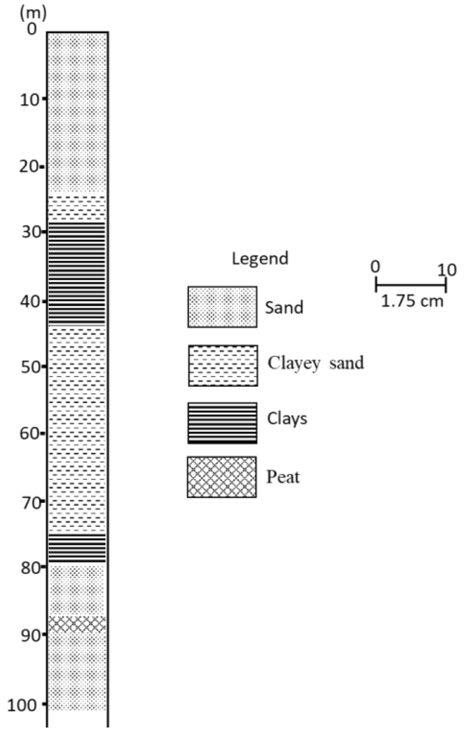


Figure 2. Lithological section of the PU2 piezometer ((Maliki (1993) modified))

2.3 Groundwater contamination by iron and manganese

The iron may have an oxidation state of +2 or +3. The stability of the ions Fe^{2+}, Fe^{3+}, $Fe(OH)^{2+}$, and $Fe(OH)^{+}$ with respect to $Fe(OH)^{3}$ and $Fe(OH)^{2}$ precipitate or colloidal depends on pH, Eh, and the composition of the solution. Manganese presents three possible oxidation states in such environments rather than two (+2, +3, and +4) and can form a wide variety of mixed-valence oxides (Hem 1985). The chemistry of manganese is somewhat like that of iron. In general, manganese occurs as Mn^{2+}, which easily oxidizes to MnO_2 and may form stable organic complexes, as iron does. The main sources of Fe^{2+} include the dissolution of iron (II) bearing minerals and the reduction of iron oxyhydroxides (Fe-OOH) present in the sediments and clay minerals such as smectites (Appelo et al. 1994).

Very few studies have actually focused on metallic trace elements in groundwater and surface water. This is due to the absence or the limited data base on water resources in the coastal zone of southern Benin compared to other African countries. Moussa Boukari (1998) had shown that total iron contents are generally between 0.1 and 0.2 mg/L, which is below the WHO (World Health Organization) guideline of 0.3 mg/L. As far as zinc is concerned, the levels are between 0.5 and 1 mg/L and are also not harmful to water quality. Nevertheless, sectors with high zinc contents (2 to 3.5 mg/L) corresponding to the Central Cotonou area were obtained during the same period. The study carried out on well and borehole water used at the Houéyiho market garden site in Cotonou showed that these irrigation waters are contaminated with cadmium, lead and manganese; metallic trace elements produced from household waste used for fertilization (Yehouenou Azehoun Pazou et al. 2009). Low quality physico-chemical water can effectively promote the contamination of vegetable cultures and compromise human health.

In the shallow aquifer of the Godomey wellfield in southern Benin, high contents of total iron (0.5 mg/L in the Togba wells) and lead (0.18 mg/L in a well in Hèvié) were recorded. These values are above the Beninese standard of 0.3 and 0.05 mg/L respectively (Dovonou et al. 2015).These values are similar to those of (Azokpota 2005) who found iron and lead contents of 0.8 mg/L and 0.16 mg/L respectively in the waters of wells in the Cotonou districts where dyeing activities are carried out.

Inadequate wastewater management contributes to groundwater contamination by metallic trace elements in urban areas; and the consumption of wastewater poses risks of poisoning to human health (Roufai 2012). The toxicity of trace elements such as lead to human health can affect brain and nervous system development and increase the risk of high blood pressure and kidney damage (WHO 2018).

3. Material and methods

3.1 Water sampling

In the three neighborhoods in Cotonou, thirty-eight (35) sampling sites were selected as representative groundwater, ponds and Lake of the study area (Fig. 1A). In each neighborhood, groundwater wells were selected for sampling and, where/when possible, surface water samples (permanent and temporary pools, as well as Lake Nokoué) were also included. Groundwater was sampled from the Quaternary aquifer via the large-diameter wells. The wells are separated by an average distance of ~200 m within the same neighborhood.

The trace elements and major ions of waters were analyzed 6 times between November 2016 to June 2018 in February (main dry season), June (main wet season) and October (small wet season), resulting in a total of 77 groundwater and 50 surface water samples. Other samples were collected in the centre of the Lake (G1, G2, G3) and near the Ganvié lacustrine village (G4, G5, G6 and G7) during dry season.

3.2 Soil sampling

In February 2018 (dry season), three soil profiles were carried out in Ladji, Agla and St Jean sites at L18, A11 and J11 respectively. Sites A11 and L18 are old garbage landfills (respectively, from 5 to 10 years), while J11 is a soil without landfills (Fig. 1). The samples were taken with a 5*20 cm auger. Soil samples were collected from the soil surface (horizon above the natural terrain) and every 20 cm depth of the unsaturated zone. The depth of investigation, which corresponds to the thickness of the unsaturated zone, is 40 cm for A11, 80 cm for L18 and 120 cm for J11. A total of fifteen (15) soil samples were collected and stored in polyethylene bags before being transported to the laboratory.

3.3 Water extraction method

For the analysis of metallic trace elements and major ions in soils, 200 g of soil is leached in 200 mL of milliQ water. The leachate is obtained after mixing by a stirrer for 1 hour and centrifugation for 10 minutes at 4000 laps per minutes. This extraction method used by (Blondel 2008) and (Cras 2005), promotes the leaching of elements weakly bound to the solid fraction of the soil and makes it possible to determine the distribution of the total content of trace elements and ions..

Water samplings from extraction, from groundwater and surface water were filtered in situ with disposable PP syringe and Durapore membrane (0.22 µm) and stored in acid washed HDPE bottles. Aliquots for cations and trace elements were acidified with ultrapure HNO_3 (1‰ v/v) to pH 2.

3.4 Analytical methods

Groundwater and surface water temperature (T°C), pH, redox potential (Eh), Electrical conductivity (EC), and dissolved oxygen (DO) were measured *in situ* using a WTW 3430i portable digital multiparameter.

Major ions are analyzed using the DIONEX model ICS-1100 ion chromatograph at the Hydrogeology Laboratory of the University of Avignon. The quality of the chemical analysis is verified by the calculation of ionic balances and validated if the value obtained is less than or equal to 5%.

Trace elements (Li, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ba, Pb, and U) and the Rare Earths Elements (REE) were analyzed with Q-ICP MS (iCAP Q, Thermo Scientific® equipped with an Argon Gas Dilution in-line system) at 1% v/v HNO3- at the AETE-ISO (Analyse des Elements en Trace dans l'Environnement et Isotopes) technical platform of the OSU OREME, University of Montpellier. The Argon Gas Dilution in-line system allows us to introduce the highly mineralized samples without previous dilution. Precision error was typically < 5%. SLRS-6, fresh water reference material, and CASS-6 and NASS-6 seawater reference materials for trace metals (National Research Council, Canada) were analyzed every 20 samples to check the analysis accuracy. Mean results are within the range of certified uncertainties. Precision error was typically < ± 5%. The results are presented in Tables 2, 3 and 4. The Ce/Ce* ratios were calculated using formula $Ce/Ce^{*}= Ce_{NASC}/(La_{NASC} * Pr_{NASC})^{0.5}$.

3.5 Granulometric method

The granulometric analysis was performed on the fifteen (15) soil samples collected. After removing the fraction less than 0.063 mm, each soil sample was subjected to a dry granulometric analysis on a sieve column (AFNOR series, Association Française de Normalisation). The sieves are shaken using mechanical systems such as Ro-TAP. The grains are classified according to their diameter and the fractions retained on the successive sieves (2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, 0.063 mm) are weighed. The classification adopted for the nature of sediments is that defined by Blott and Pye (2001). The particle size composition is expressed as a percentage (%) of the total sample weight.

3.6 Statistical analysis

The distribution of trace elements in water was done using descriptive analysis based on arithmetic average, minimum, maximum and standard deviation. The chemical analysis data were processed by PCA and AC using XLSTAT (Microsoft Excel add on). The PCA was used to classify sample locations on an observation chart, the trace elements and ions concentrations were analyzed to generate a correlation circle and associated Pearson's correlation matrix (significance level of 5%). The main objective of Cluster Analysis (CA) is to reveal an underlying relationships that is presumed to exist within a set of PCA observations. The degree of correlation between traces elements is represented by the distance between the clusters. Minerals that influence the solubility of the elements were identified by calculating the saturation index using PHREECQ 3.5.0 with wateq4f.

3.7 Geochemical modelling

The potential for dissolution and precipitation of the Mn- and Fe-bearing minerals was investigated with PHREEQC geochemical model (Parkhurst and Appelo, 1999). The results for the calculated saturation indices (SIs) for the common manganese oxide such as minerals Manganite (MnOOH), Bixbyite (Mn_2O_3), Pyrolusite (MnO_2), Hausmannite (Mn_3O_4) and iron oxide minerals such as Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Geothite (FeOOH), freshly precipitated hydrous ferric oxide or ferrihydrite ($5Fe_2O_3$. $9H_2O$) are presented in the results.

4. Results

4.1 Trace element and rare earth element concentrations in surface waters and groundwater

The spatial distribution of trace elements such as Li, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ba, Pb, and U in groundwater and surface water (ponds and Lake Nokoué) is different at each site as shown in the Figure 3.

In Ladji, the means concentrations are in decreasing order Mn>B>Fe>Ba>Li>Al>Zn>V>U>Mo>As >Ni>Cr>Cu>Co>Pb. The most abundant elements are Mn, B, Fe, Ba, Li, Al, Zn, V, U and Mo with means values of 192.8±185.8, 165.07±4, 129.8±261.6, 105.6±110.3, 22.9±30.4, 17.1±18.2, 17.1±18.2, 6.4±7.6, 5.1±8.5 and 3.4±3.4 respectively (Table 1). The most abundant elements are B, Mn, Ba, Li, Fe, Al, Mo, Zn, V in Lake (saline water). Fe, V, Zn and Al are higher in groundwater and ponds compared to Lake Nokoué. On the other hand, Li, Ba, B and Mn are high in groundwater and Lake Nokoué compared to ponds. Mo and U are high only in groundwater (Fig. 3). Thus, the high values observed in groundwater could be due to influence of Lake water infiltration, anthropogenic contamination or mineral dissolution reactions.

In Agla, the means concentrations (µg/L) of trace elements in groundwater samples are in decreasing order Ba>Mn>Fe>B>Al>Zn>V>Mo>U>Cu>As>Ni>Cr>Li>Co>Pb. The most abundant elements are Ba, Mn, Fe, B, Al, Zn, V and Mo with means values of 126.6±109.3, 114.1±139.5, 39.5±24.5, 26.9±22.2, 16.1±12.7, 2.6±3.2 and 2.6±2.7, respectively (Table 1). Like in groundwater, Agla ponds have high concentrations for the same trace elements (Fe, Mn, Ba, B, Al, Zn, Mo and V) but in a different order. The decreasing order in pond is Fe>Mn>B>Al>Ba>Zn>V>Mo>Ni>Cu>Cr>Li>As>Co>U>Pb. Fe, Mn, B, Al, Mo and V have higher concentrations in ponds compared to groundwater (Fig. 3). This trend highlights the influence of ponds on groundwater in discharge areas due to surface water infiltrations.

In St Jean, the means concentrations were found to be in the decreasing order of B>Zn>Al>Mn>Fe >Ba>V>Mo>As>Cu>Ni>Cr>U>Li>Co>Pb. The most abundant elements are B, Zn, Al, Mn, Fe, Ba, V and Mo. The average values are of (µg/L) 54.6±21.1 for B, 24.8±21.9 for Zn, 23.5±16.0 for Al, 20.8±16. for Mn, 18.8±32.9 for Fe, 13.2±5.5 for Ba, 11.2±4.8 for V and 6.0±4.4 for Mo (Table 1). The anthropogenic contamination from leaching and mineral dissolution reactions was also evident. The concentration of Zn, V and Mo are high in St Jean groundwater compared with Ladji and Agla.

The large standard deviation values observed for Mn, B, Fe, Ba, Li, Al, Zn, V and Mo may indicate variability among the sampling sites. An example (Fig. 3), the high values obtained in Agla for Ba during the dry season at A4 (208 µg/L), A5 (260 µg/L) and A11 (414 µg/L), for Mn during the wet season at A2 (454 µg/L) and A9 (248 µg/L). In Ladji, L18 (472 µg/L) for Ba, L18 (999 µg/L) for Fe, L2 (341 µg/L), L7 (439 µg/L), L18 (643 µg/L) for Mn during the dry season. In St Jean, J5 (165 µg/L) for Fe, J5 (21µg/L) for Mo and J6 (90 µg/L) for Zn during wet season.

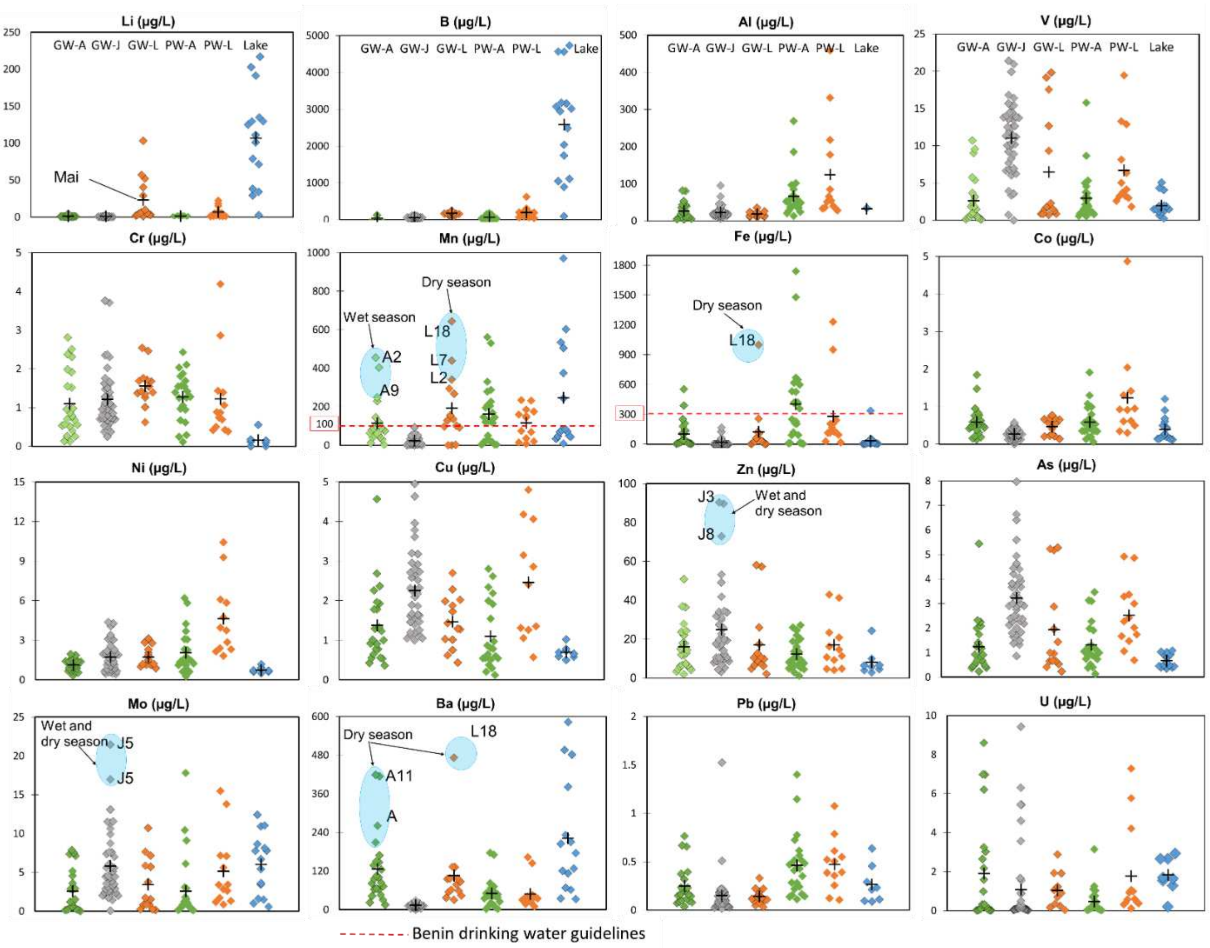


Figure 3. Concentration of trace elements in groundwater and surface waters for Agla, Ladji and Saint Jean sites. GW-L: Groundwater sampled in Ladji, GW-J: Groundwater sampled in St Jean, GW-A : Groundwater sampled in Agla, PW-L : Pond water sampled in Ladji, PW-A : Pond water sampled in Agla, Lake : Nokoué Lake

The REE concentrations of groundwater samples (Annex 10 and 11) are listed and the North American Shale Composite (NASC) normalized REE patterns are presented in Fig. 4. The total REE concentrations (∑REE) ranged from 0.3 to 5.7 µg/L in St Jean, from 0.6 to 6.3 µg/L in Ladji and from 1.4 to 23.2 µg/L in

Agla. The total REE concentrations in groundwater samples from St Jean and Ladji are lower than those from Agla. Despite the similarity between the signatures of the REEs in groundwater (Fig. 4), small negative anomaly is observed in groundwater samples, when normalized by NASC. The Ce/Ce* ratios in groundwater varied from 0.41 to 1.11, from 0.67 to 1.08 and from 0.69 to 1.06 respectively in St Jean, Ladji and Agla. The lower Ce/Ce* anomalies are more pronounced during the small wet season (October) compared to the dry season (February).

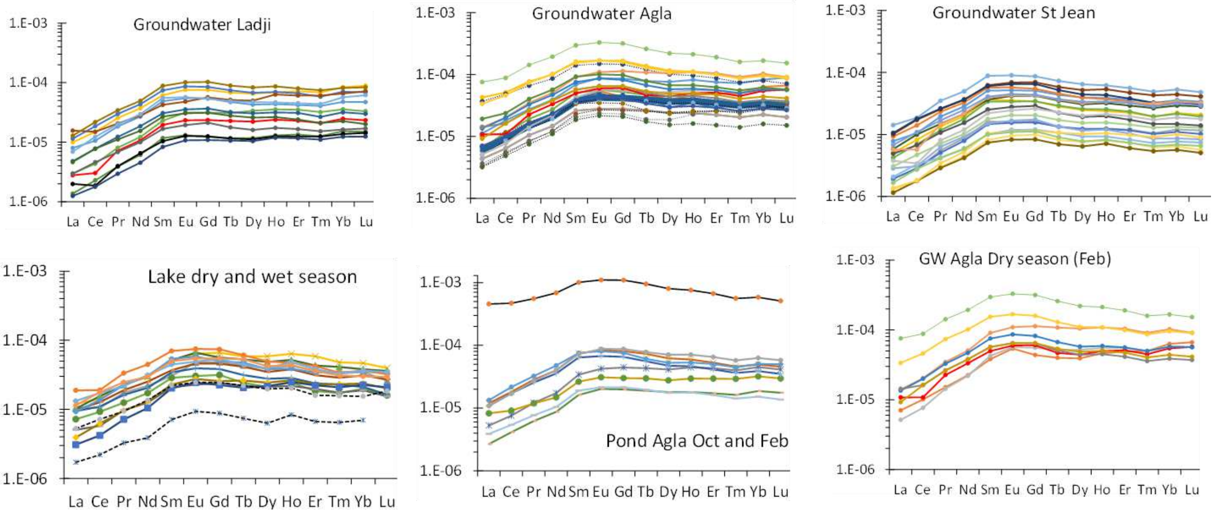


Figure 4. Shale-normalized REE patterns for groundwater and surface water

From all of the trace elements analyzed in groundwater from Agla, St Jean and Ladji, Fe and Mn are the only elements to reach concentrations above drinking water guidelines (Fig. 3; Annex 10 and 11). The Beninese quality standard for drinking water for Mn is 100 µg/L (which varies a lot from the WHO guideline) and for Fe it is 300 µg/L. Mn and Fe are above these concentrations in groundwater, pond water and lake water at Agla and Ladji, but not at groundwater from Saint Jean. At Agla, 33.3 and 8.7 % of groundwater samples, 68.2 and 50.0 % for pond water are above the Benin guideline for Mn and Fe respectively in drinking water. At Ladji, 64.3 and 7.1 % of groundwater samples, 53.8 and 15.4 % for pond water are above the Benin guideline for Mn and Fe respectively. Lake water is only above the Benin guideline for Mn, and includes 40.0 % of the samples.

Table 1: Concentration of metallic trace elements (µg/L) in groundwater and surface water of Agla, Ladji and St Jean sites

	Li	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ba	Pb	U
GW-L	1.16-103.16	94.61-244.22	9.83-35.57	0.71-19.84	0.62-2.54	0.42-643.74	1.29-999.19	0.14-0.77	0.89-3.13	0.43-2.69	2.09-58.22	0.23-5.28	0.15-10.74	29.97-472.32	0.03-0.33	0.04-2.88
n=14	22.89±30.35	165.07±39.00	18.44±7.01	6.44±7.60	1.58±0.50	192.89±185.86	121.89±261.64	0.46±0.22	1.73±0.75	1.46±0.66	17.10±18.19	1.93±1.91	3.38±3.44	105.66±110.30	0.14±0.07	1.04±0.89
GW-J	0.03-2.12	25.42-115.57	6.823-94.94	0.72-21.41	0.24-3.76	0.36-64.09	1.01-165.54	0.06-0.57	0.44-4.37	1.00-6.18	3.14-90.40	0.85-6.64	1.45-21.44	3.76-28.03	0.02-1.53	0.03-5.43
n=40	0.65±0.52	54.62±21.12	23.54±16.01	11.23±4.80	1.22±0.79	20.77±16.86	18.85±32.98	0.27±0.12	1.74±1.08	2.44±1.24	24.88±21.95	3.10±1.35	6.01±4.41	13.21±5.49	0.15±0.24	0.48±1.06
GW-A	0.11-4.39	12.92-125.94	3.85-81.95	0.11-10.70	0.13-2.81	3.69-454.55	3.44-554.74	0.12-1.85	0.32-1.94	0.36-4.57	1.96-50.87	0.24-5.44	0.03-7.87	15.07-418.51	0.04-0.76	0.02-8.60
n=23	1.02±0.88	39.46±24.51	26.92±22.21	2.64±3.24	1.10±0.84	114.11±115.75	101.97±139.48	0.59±0.40	1.13±0.43	1.37±0.97	16.04±12.69	1.24±1.12	2.56±2.74	126.67±109.34	0.25±0.20	1.91±2.71
PW-L	1.03-22.06	41.61-619.44	28.34-458.90	1.82-19.47	0.38-4.19	7.32-235.38	17.85-1232.31	0.30-6.71	1.81-10.42	0.57-4.80	4.08-42.93	0.69-4.92	0.85-15.49	9.50-163.11	0.11-1.08	0.11-7.27
n=13	6.56±7.21	187.70±149.69	124.25±136.02	6.68±5.35	1.220±1.113	115.62±82.41	277.70±371.23	1.65±1.93	4.63±0.84	2.45±1.45	17.02±13.20	2.52±1.32	5.12±4.73	48.91±47.61	0.43±0.27	1.77±2.37
PW-A	0.23-4.15	8.51-174.03	13.29-268.87	0.56-15.78	0.11-2.48	3.03-561.08	4.05-1741.78	0.13-1.91	0.25-6.19	0.12-8.85	1.17-27.15	0.37-3.46	0.13-17.81	2.36-176.13	0.11-1.40	0.02-3.14
n=22	1.67±1.01	67.83±47.44	66.97±58.06	3.14±3.45	1.27±0.62	168.52±156.01	420.03±447.96	0.62±0.42	2.04±1.57	1.91±2.37	12.24±7.70	1.37±0.89	2.77±4.41	51.53±44.16	0.46±0.32	0.50±0.68
Lake	2.67-216.72	92.67-4729.87	29.72-34.89	0.23-5.06	0.0-0.55	8.38-970.45	2.34-336.02	0.12-1.20	0.49-1.40	0.49-1.02	2.23-24.39	0.34-1.08	0.59-12.43	32.50-583.11	0.07-0.64	0.21-2.93
n=15	106.47±65.19	2575.46±1421.21	32.31±0.97	1.96±1.39	0.11±0.14	247.68±287.38	35.98±84.25	0.39±0.33	0.84±0.27	0.71±0.16	6.02±5.54	0.68±0.27	6.04±3.93	221.49±179.79	0.19±0.16	1.27±0.92
WHO 2018			200			400	300		70	2000	5000	10	70	700	10	30
BENIN*		5000			50	100	300		20		3000	50		1000	50	30

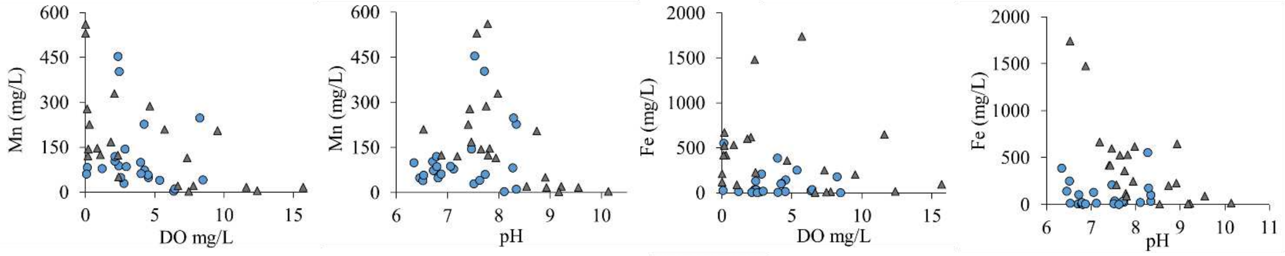
Concentration are in µg/L, range (Minimum–Maximum) and Average±SD). GW-L: Groundwater sampled in Ladji, GW-J: Groundwater sampled in St Jean, GW-A : Groundwater sampled in Agla, PW-L : Pond water sampled in Ladji, PW-A : Pond water sampled in Agla, Lake : Nokoué Lake, n= number of samples, *Guidelines for drinking water quality in Benin.

4.2 Spatial variations of Mn and Fe concentrations and associated variations in groundwater chemistry

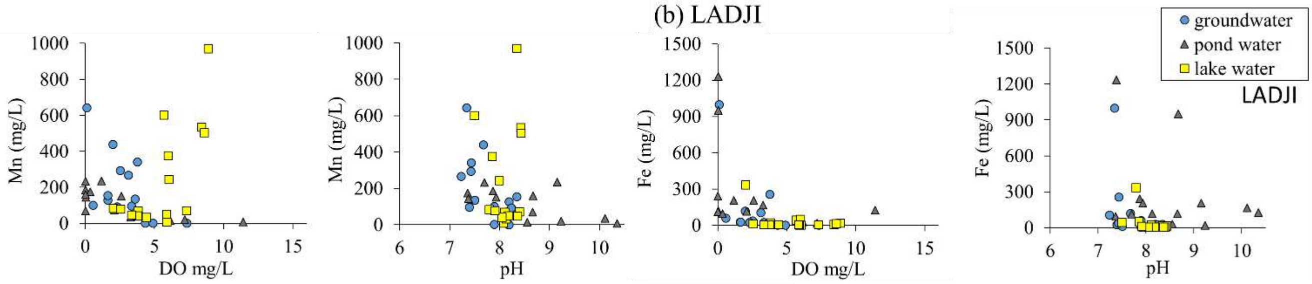
4.2.1 Changes in groundwater Mn and Fe concentrations with DO and pH

The pH values are relatively similar for groundwater from Ladji (6.7-7.8) and St Jean (6.7-8.1), and from the lake (6.9-7.9). In comparison, Agla has some sites where groundwater is lower, with pH values ranging between 5.8-7.8. In addition, the ranges of dissolved oxygen (DO) at Agla also show lower minimum values (0.0 - 8.5 mg/L) compared with Ladji (0.1 – 7.3 mg/L) and at St Jean (0.7 - 7.8 mg/L). The Figure 5 illustrates that the high Mn concentrations at Ladji and Agla (up to 643 and 454 µg/L respectively) are associated with DO values < 5 mg/L and circumneutral pH. The highest Fe concentrations at Agla and Ladji (555 and 999 µg/L respectively) are associated with very low DO concentrations (<1 mg/L). Other sites with relatively high Fe concentrations (ie. 100-400 µg/L) there is no correlation with either DO or pH.

(a) AGLA



(b) LADJI



(c) St JEAN

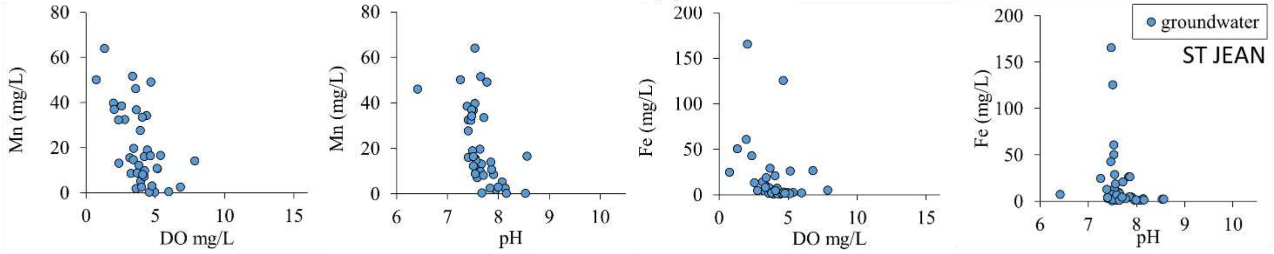


Figure 5. DO and pH with Mn and Fe concentrations in groundwater, pond water and lake water for all sites.

4.2.2 Mn and Fe mineral saturation indices

The calculated values of the saturation indices (SIs) show a difference between common Fe and Mn minerals (Fig. 6). The groundwater samples in Ladji, Agla and St Jean are undersaturated or near saturation ($SI \leq 0$) with Mn-bearing minerals such as manganite (MnOOH), bixbyite (Mn_2O_3), pyrolusite (MnO_2) hausmannite (Mn_3O_4) and ferrihydrite $Fe(OH)_3$. This suggests that the dissolution of these minerals could contribute to the increase of Mn and Fe concentrations in groundwater. In contrast in Ladji and Agla, some samples at St Jean showed $SI>0$ indicating that the precipitation process of Mn-bearing minerals may promote to the low Mn concentrations in groundwater at St Jean. In comparison, the supersaturation ($SI > 0$) with Fe minerals such as hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite (FeOOH) and also ferrihydrite suggest that there is little potential for the dissolution of Fe-bearing minerals to contribute to the high Fe concentrations in groundwater

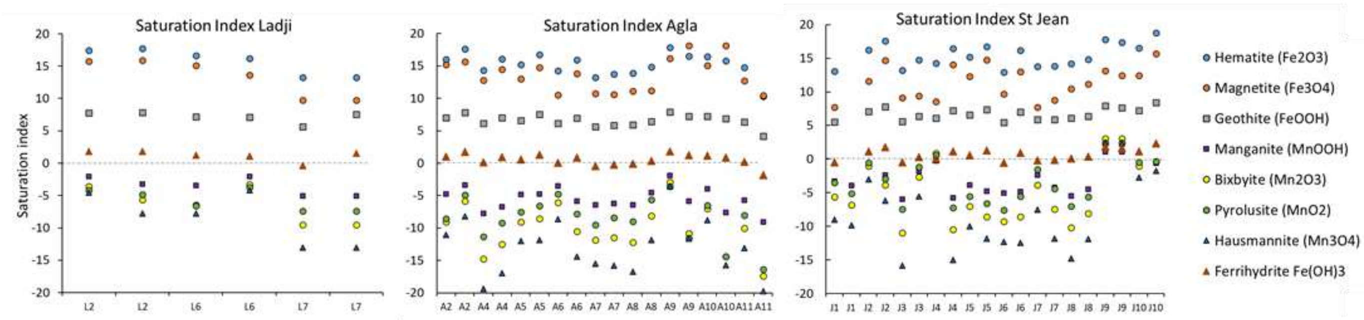


Figure 6. Saturation indices of Mn- and Fe- bearing minerals for groundwater sampled at Agla, Ladji and St Jean.

4.2.3 Principal Component Analysis for Mn and Fe

The variations of Fe and Mn with key chemical parameters (DO, pH, DOC, NH_4) in the shallow groundwater of the Cotonou coastal aquifer as well as major ions (data from Houéménou et al. 2019) and other trace elements (Li, B, Al, V, Zn, Mo and Ba) in Nokoué Lake are analysed using a PCA (Principal Component Analysis). Table 2 and Figure 7 summarize the PCA results in groundwater and Lake, respectively.

In Ladji, F1 and F2 axis explain 73.9% of the total variance (Table 3). The main F1 axis (46.3% of the variance) is shows that Mn and Fe are positively correlated with DOC and NH_4. These two elements (Fe and Mn) are negatively correlated with pH and DO. This indicates that the increase in Mn and Fe concentrations in groundwater may be due to an increase in DOC and NH_4. The PCA analysis on Lake Nokoué samples (Fig. 7.) shows that Ba, Fe, Zn, Mn and V sites have a different origin than Cl, Na, Ca, SO_4, Li and B. The high concentrations of Fe and Mn in Lake Nokoué (e.g. sites G5, G6 and G7) are not due to contact with the Atlantic Ocean, unlike the ions Cl, Na, Ca, SO_4, Li and B.

In Agla, three axis are extracted, together explaining 86.7 % of the total variance. F1 axis (42.7 % of the variance) shows a strong positive correlation between Mn with NH_4, DOC and pH and weakly correlated with DO. Fe shows a positive but weak correlation with NH_4, DOC, pH and DO. On the F2 axis, NH4 is negatively correlated to DO. Fe is correlated with F3 axis.

In St Jean, the three axis F1, F2 and F3 are considered, describe 72.1 % of the total variance. On F1 axis, Mn and to a lesser extent Fe are negatively correlated with pH and DO. F2 axis is positively correlated with NH_4, COD and negatively correlated with DO, Fe and Mn. On F3 axis, Fe and COD are moderately correlated.

The anaerobic decomposition of organic material which contribute an increase of NH_4 concentrations could play significant role in the increase of Fe and Mn concentrations in Agla and Ladji compared in St Jean. The input of high DOC concentrations in groundwater in Agla and Ladji via ponds can promote the reductive dissolution of iron and manganese oxide minerals.

Table 2: Matrix of principal components

	Ladji			Agla			St Jean		
Parameters	Component			Component			Component		
	F1	F2	F3	F1	F2	F3	F1	F2	F3
pH	-0.44	**0.79**	0.14	**0.82**	0.38	-0.29	**0.75**	0.11	0.12
DOC	**0.75**	0.46	0.00	**0.92**	0.02	-0.25	-0.14	**0.71**	**0.54**
NH4	**0.54**	**0.68**	0.38	**0.59**	**-0.71**	-0.18	-0.24	**0.68**	-0.47
Mn	**0.89**	-0.30	0.02	**0.67**	-0.40	0.38	**-0.77**	-0.32	-0.25
Fe	**0.75**	-0.41	0.33	0.30	0.07	**0.90**	-0.46	-0.28	**0.61**
DO	**-0.60**	-0.34	**0.68**	0.40	**0.83**	0.09	**0.83**	-0.23	-0.05
% total variance	46.31	27.63	12.24	42.75	25.02	18.95	35.60	20.23	16.23
Cumulative %	46.31	73.94	86.18	42.75	67.78	86.73	35.60	55.83	72.06

Bold Figures indicating values ≥ 0.5, show a high correlation

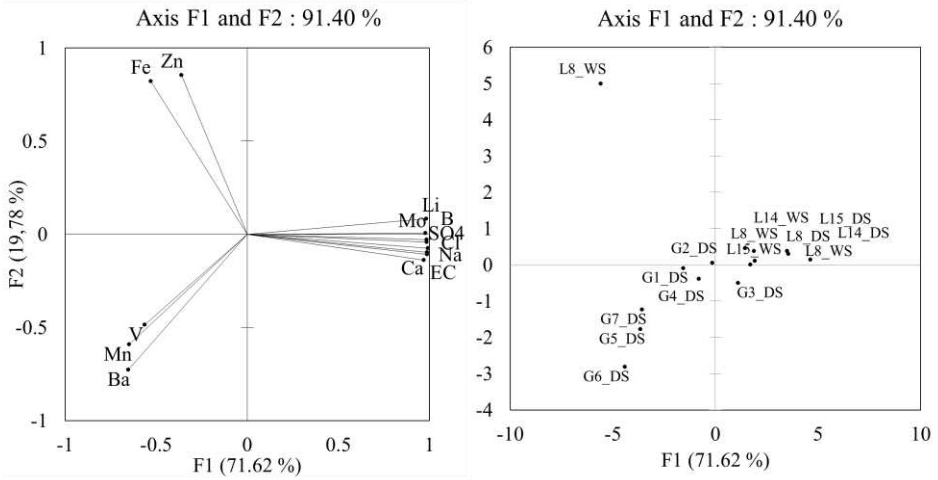


Figure 7. Principal Component Analysis in Lake samples. WS (Wet Season), DS (Dry season).

4.3 Seasonal changes in groundwater Mn and Fe concentrations and associated changes in groundwater chemistry

For the 23 groundwater sampling sites, there are time series for seasonal Mn and Fe concentration data between 2017 and 2018 (Fig. 8). Greatest seasonal changes in Mn and Fe concentrations were observed between October (small wet season) and February (dry season). For groundwater sampled at L2 and L7 in Ladji, dry season conditions results in increases in Mn (by 341-439 µg/L) and Fe (by 119-256 µg/L) compared to small wet season. The Mn concentrations at site L11 and L6 sites do not follow the same evolution as Fe during the dry season. Mn increases (up to 155 µg/L for L6 and 135 µg/L for L11) while Fe remains relatively low (12 and 27 µg/L for L11 and L6, respectively).

In Agla, groundwater at six of the eight wells sampled (A4, A5, A6, A8 and A10) show an increase in Mn (by 61-101 µg/L) and Fe (by 23-555 µg/L) during dry season. The small wet season shows an increase in Mn concentrations at A2 (up to 455 µg/L), A7 (up to 120 µg/L) and A11 (up to 79 µg/L) associated with a decrease in Fe (up to 39 µg/L for A2, 7 µg/L for A7 and 61 µg/L for A11).

In St Jean, seven of the ten groundwater wells (J1, J2, J4, J6, J7, J8 and J9) show an increase in Mn (by 13-93 µg/L) associated with a decrease in Fe (by 1- 4 µg/L) during the dry season. The same trend is observed during the wet season at J5 where the Mn increased from 39 to 64 µg/L while Fe decreased from 61 to 50 µg/L. Some sites such as A9 and L2 have relatively high Mn and Fe concentrations during the small wet season (October) and the dry season (February).

From these sites with time series data, the dry season result in Mn concentrations above the drinking water guidelines for 44.4 % of the sites at Agla, and for all of the sites at Ladji. The dry season also results in 22.2 % of the sites at Agla with Fe concentrations that are above the drinking water guideline.

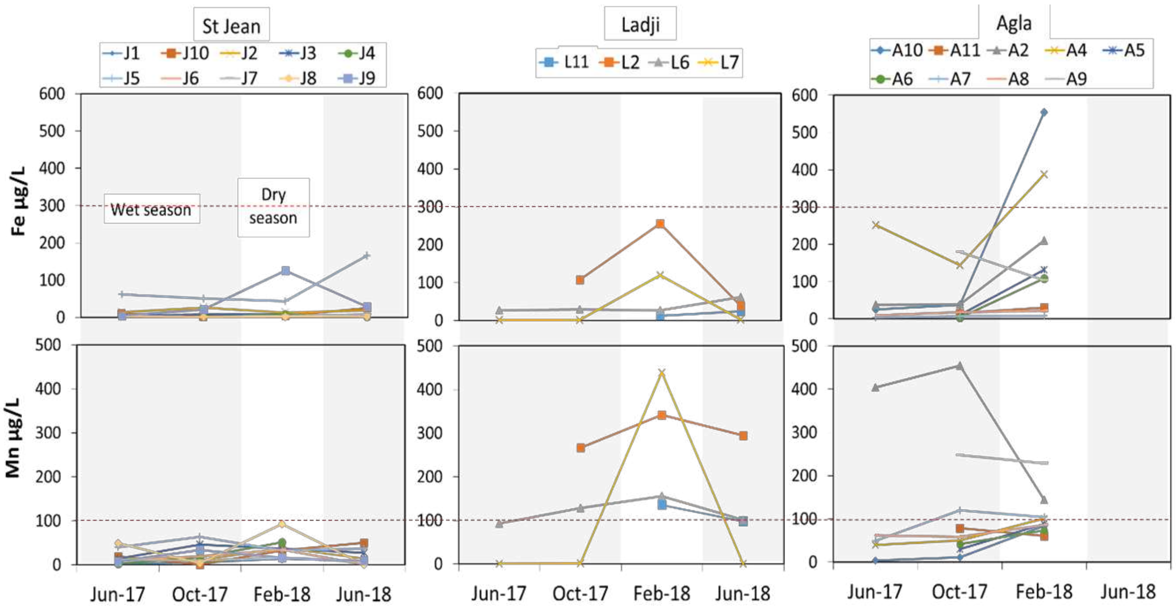


Figure 8. Temporal variation between Mn and Fe at each site with time series data at St Jean, Ladji and Agla compared with the Benin drinking water guideline (red dotted line).

The percentage changes between the months of February (dry season) and October (small wet season) are showed in Figure 9. These graphs highlight the increases in both Mn and Fe (Fig. 9a) during the dry season (February) compared with the small wet season (October) for most of the samples. However, there are a few outlying samples at St Jean and Agla that show dry season decreases in both Mn and Fe concentrations.

For Mn concentrations the changes between the wet and dry seasons are negatively correlated with dissolved oxygen (DO), with a greater correlation observed at St Jean (R^2 = - 0.8) compared with Agla (R^2 = - 0.1) (calculations of Ladji correlations were not possible due to small sample size; Fig. 9b). The low correlation at Agla is due to 2 samples that have small Mn increases (8-23%) in the wet season associated with a wet season increase in DO. Mn concentration changes are also negativewith pH, with a greater correlation observed at St Jean (R^2 = -0.4) compared with Agla (R^2 = -0.8) (Fig. 9c). In comparison, seasonal changes in the Fe concentrations are not correlated with DO concentrations, with an R^2 of -0.04 at Agla, and -0.06 at St Jean (Fig. 8e) and neither not with pH (R^2 of -0.06 and -0.01 at Agla and St Jean respectively; Fig. 9f).

The seasonal changes in Fe and Mn concentrations are weakly positive with the Ce/Ce* anomaly at St Jean ($R^2 = 0.2$ for Mn and 0.04 for Fe) where dry season increases are associated with Ce/Ce* increases (Figs. 8d and g). In contrast, at Agla the Ce/Ce* anomaly mostly decreases with increases in Mn and Fe. This could indicate the effects of high organic matter on Ce/Ce* anomalies at Agla, since this area has many low elevation areas that are frequently inundated, and is discussed further below.

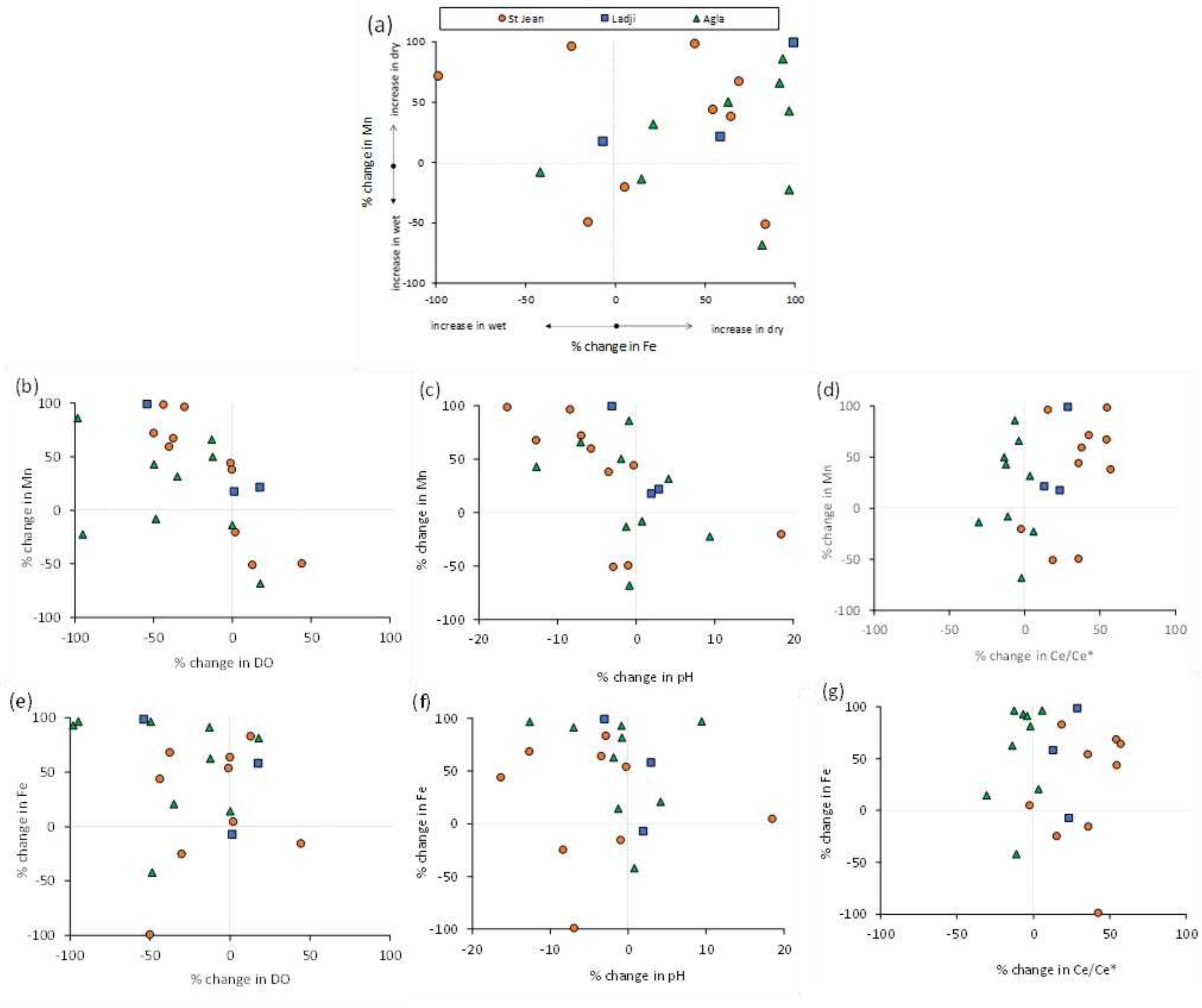


Figure 9. Percentage change in both dry and wet seasons at each site with time series data at St Jean, Agla and Ladji.

4.4 Soil profiles and trace elements

The soils studied in L18 (Ladji), A11 (Agla) and J11 (St Jean) sites show textural variability between sites (Fig. 10). Overall, the unsaturated zone of the coastal aquifer in Cotonou is of sandy and silt-clayey-sandy type except in certain areas where there is a low gravel content. During soil analysis, the depth of the unsaturated zone ranged from 40 cm at Agla, 80 cm at Ladji and 120 cm at St Jean. In Ladji, the soil sampling site (L18) is characterized by a silt-clay-sand texture with an average of 52.8% silts and clay, 45.7% sand and 1.4% gravel (Fig. 10o). The surface horizons (0-20 cm) and at depths closer to the saturated zone (60-80 cm) contain sediments composed respectively of fine to medium low clay sand and clayey sands compared to the intermediary horizon (20-60 cm) where clay and silt have accumulated. In Agla, the sampling soil site (A11) is dominated by a sandy-clayey texture with an average of 76% sand, 19.8% clay and 4.1% gravel (Fig. 10n). There is a horizon consisting of medium to coarse clayey fine sands (0-20cm) and an accumulation horizon of very little clayey medium fine sand (20-40cm). In St Jean, J11 site is characterized by a sandy texture with an average of 98.3% sand, 1.6% clay and silt, and 0.1% gravel (Fig. 10m). The soil site at St Jean shows a homogeneous profile of medium sand along the unsaturated zone (0-120 cm).

The vertical evolution of the electrical conductivity (EC), major ions (NO_3, Ca, Cl, Na, HCO_3) and trace elements (Fe, Mn, Zn, Al, B, V, Ba, Mo) in the soil leaching are presented in Figure 9. Water from soil leaching in Agla and Ladji was extracted from sediments collected from garbage landfills compared to St Jean that was collected from soil without a landfill. The EC is higher in Agla and Ladji (landfill sites) compared to St Jean (no landfill). The EC at the surface horizon (0-20 cm) ranges from low values at St Jean (92-156 µS/cm), medium values at Ladji (448-796 µS/cm), and higher values at Agla (1525-1617 µS/cm). At greater depths (>20 cm), values decrease at St Jean (35-67 µS/cm) and Agla (up to 288 µS/cm), whereas at Ladji the EC values increase (1080-1217 µS/cm)

In Ladji (Fig. 10i), the increase in EC is greater between 40-60 cm and is accompanied by an increase in major ions including Na (167.9-212.7 mg/L) and Cl (58.9-77.9 mg/L) compared to Ca and HCO_3 which remain relatively stable throughout the profile. NO_3 only accumulates on the soil surface, indicating the contribution of relatively recent contamination due to human activities (Zhou, Peng, and Pan 2004; Bouih et al. 2005; Kadjangaba et al. 2018). The figures 10i, j and k show that most trace elements (with the exception of B and Mo) accumulate in the surface horizon (at 20 cm depth) and gradually decrease in concentrations with depth (up to 60 cm). The silty-clayey texture present on the horizon at 20-60 cm probably facilitated the retention of these trace elements during surface water leaching (landfill waste water, ponds and lake water). The concentration of Fe (up to 9632.2 µg/L) in this clay-rich zone is particularly elevated compared with other trace elements, including Al (5704.2 µg/L), V (17.9 µg/L), Mn (138.7 µg/L), Zn (632.4 µg/L) and Ba (62.4 µg/L).

In Agla (Fig. 10h), the increase in EC in the sallow zone (0-20 cm depth) is associated with an accumulation of HCO_3 (382-500 mg/L), Cl (73.3 to 100.6 mg/L), Na (56.4 to 81.0 mg/L), Ca (104.3 to 112 mg/L) and trace elements such as Fe (665.1 to 1192.9 µg/L), Zn (8.9 to 15.5 µg/L) and Ba (18.5 to 25.9 µg/L). Mo (from 29.5 to 8.3 µg/L), Mn (from 69.5 to 3.7 µg/L), B (from 217.6 to 28.8 µg/L) decrease with depth compared to NO_3 (from 0 to 14.7 mg/L), V (from 9.3 to 51.4 µg/L) and Al (from 72.5 to 309.7 µg/L) that increase with depth. Thus, high concentrations of HCO_3, Cl, Na, Ca, Fe, Zn and Ba in horizons close to the soil surface may be due to enrichment from the surface water or related to the evaporation effect (Houéménou et al. 2019). In ponds, the concentrations of Fe and Ba are high, up to 1741.7 µg/L and 176.1 µg/L, respectively.

In St Jean (Fig. 10d), the high EC observed in the surface horizon (0-20 cm) is accompanied by an relatively high concentrations of Cl (20.5 mg/L), Mn (139.5 µg/L), Zn (487.1 µg/L) compared to HCO_3, Na, Ca and Mo which remains relatively stable throughout the profile. NO_3, Ba, B, V, Al and Fe are accumulated both in the soil surface and in the deep horizon. The quasi-sandy texture of the sediments (Fig. 10m) seems to promote the transfer of pollutants from the unsaturated zone to accumulate in groundwater. The respective concentrations in the surface horizon and in the deep horizon for each element are 2.3 and 3.7 mg/L for NO_3, 23.1 and 7.4 µg/L for Ba, 7.8 and 5.8 µg/L for V, 9.5 and 13.7 µg/L for B, 4255.1 and 4569.3 µg/L for Al, 2267.4 and 1132.5 µg/L for Fe respectively.

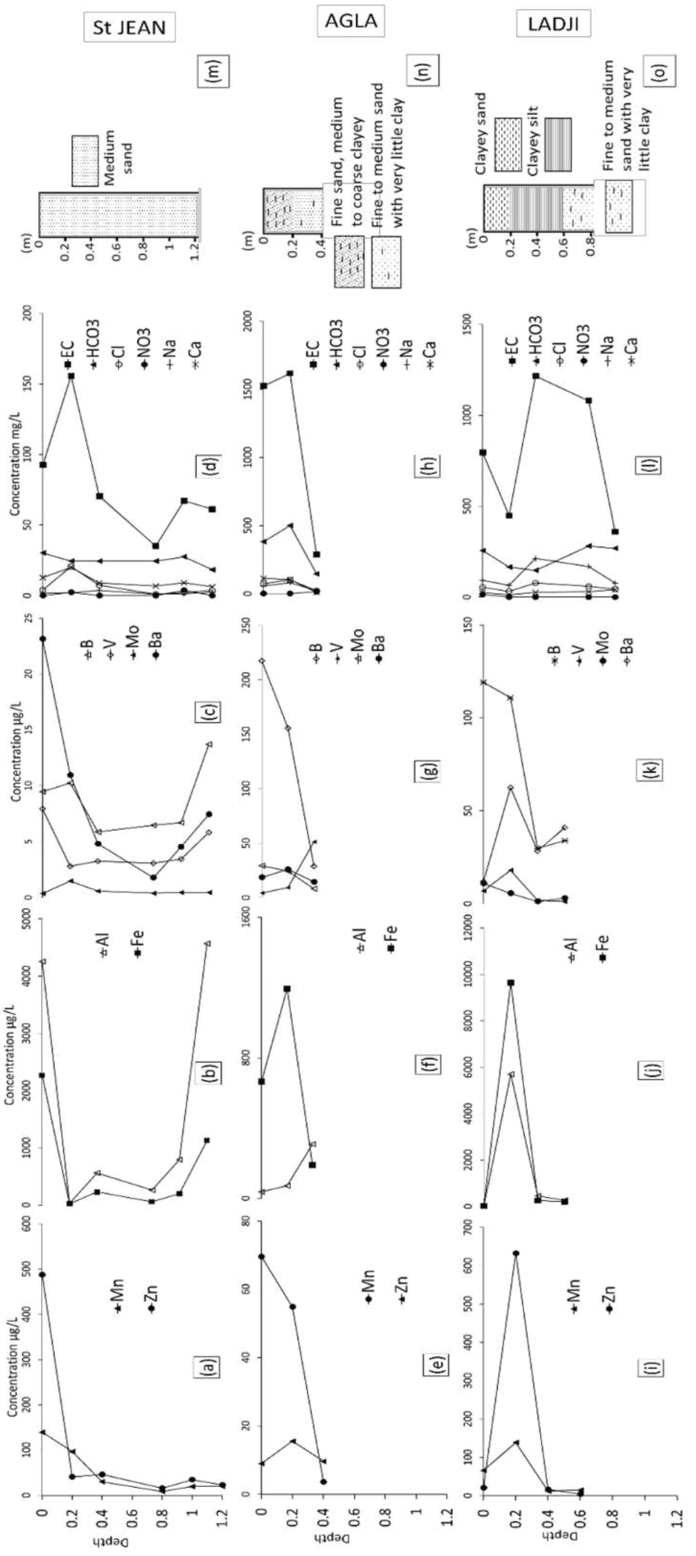


Figure 10. Vertical evolution of EC (µS/cm), major ions (mg/L) and trace element (µg/L) contents. Profile J11 (a, b, c and d); Profile A11 (e, f, g and h); Profile L18 (i, j, k and l)

5. Discussion

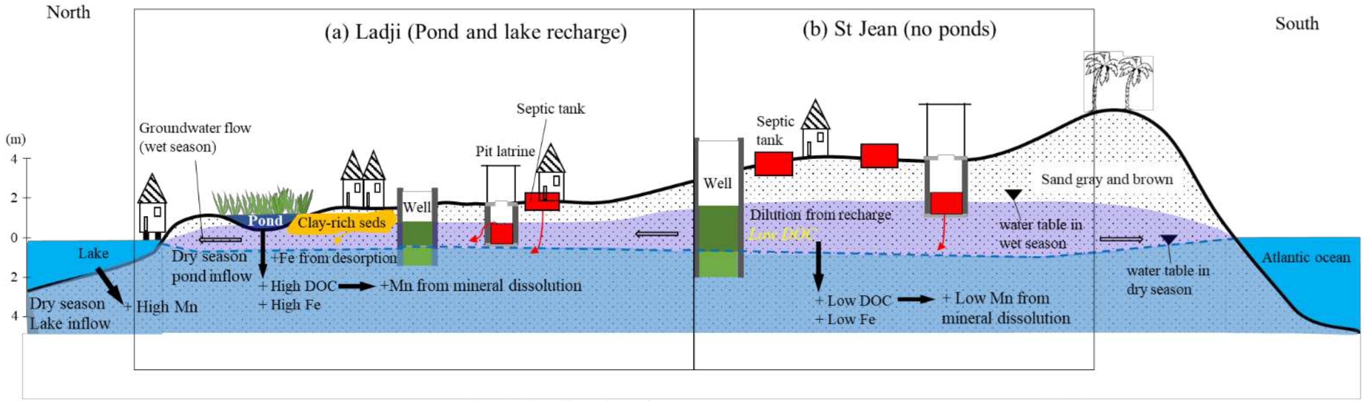
5.1 Processes controlling Fe and Mn concentrations

A schematic of the main processes controlling Fe and Mn concentrations at each site are presented in Figure 11. The dissolution of Fe/Mn oxide-hydroxide minerals in reduced aquifers is a common source of Fe and Mn in groundwater (Hem 1972; Thomas et al. 1994). The oxides of Fe (III) and Mn (IV) previously formed under oxidizing conditions are reduced to Fe (II) and Mn (II) which are readily mobilized in the aquifer (Gounot 1994; Borch et al. 2010). According to Thomas et al. (1994), the reductive dissolution of manganese oxides occurs for the Eh values ranging from 100 to 600 mV where the pH ranges from 5-8 (pH values observed in this study range from 5.8 to 8.1). In comparison, the microbial decomposition of organic matter and the reductive dissolution of Fe(III) oxyhydroxides occurs under more anaerobic conditions; within the Eh range from 0 to -500 mV. Eh values of groundwater from this study ranges from 42 – 598 mV. This suggests that redox-controlled mineral dissolution reactions at all sites are likely a main factor controlling the high concentrations of Mn in solution but not Fe. In addition, in Agla, the increases in Mn concentrations in the dry season are weakly correlated with decreases in groundwater DO concentrations (Fig. 9b), whereas the increases in dry season Fe concentrations are not correlated with changes in DO concentrations (Fig. 9e). The results of the geochemical modelling also confirm that groundwater has the potential to dissolve several common Mn-bearing minerals (Fig. 6). On the contrary, groundwater samples were super-saturated with respect to common Fe oxide-hydroxide minerals, thus indicating that mineral dissolution was not a major driver of high Fe concentrations in groundwater at all sites sampled in this study.

The reductive dissolution of the Mn-bearing minerals (Mn (IV) (oxyhydr)oxides) that mobilises Mn in groundwater may be driven by the transfer of young organic matter from pond waters into the aquifers. Dissolved organic carbon (DOC) concentrations in groundwater are elevated at Agla and Ladji (average DOC = 13.8 and 13.9 mg/L respectively) compared with St Jean (average DOC = 7.1 mg/L), which is likely due to recharging waters from ponds (DOC data from Houéménou et al., 2019). The ponds at both Agla and Ladji have high DOC concentrations (average DOC = 24.3 and 27.83 mg/L respectively) compared with the lake water (average DOC = 3.1 mg/L). From the PCA, increases in Mn are correlated with increases in DOC at Ladji and Agla. McDonough et al. (2020) showed that reduced dissolved species of Fe(II) and Mn(II) are positively correlated with DOC concentrations in groundwater. Thus, the redox conditions favoring the increase in Fe and Mn are largely controlled by the increase in COD. Mn-oxides and Fe-oxides are used as alternative electron acceptors to DO in the presence of DOC under anoxic conditions by bacteria (Appelo et al. 2005). Organics matter can stabilize Fe and Mn in waters by forming organic complexes with them, leading to elevated Fe and Mn concentrations in groundwater (Weng et al. 2007; McDonough et al. 2020).Where there are high organic matter compositions in reducing groundwater conditions this can result in a decrease in the Ce/Ce* anomalies (Davranche et al., 2015). The effects of increased mixing with organic matter on the Ce/Ce* anomalies are predominantly observed at Agla, where the change in Ce/Ce* anomaly during the dry season is low compared with Ladji and St Jean (Fig. 9.d). This may indicate higher organic matter transfers to the groundwater from the ponds in Agla, compared with the ponds in Ladji. The anaerobic decomposition of organic material can also result in elevated concentrations of NH_4 and decreases in NO_3 in reducing waters (Lovley 1991; Ferro 2003). According to the PCA, Mn are well correlated with NH_4 at Ladji and Agla relating its release to organic matter decomposition and the source of Mn appears to be the Mn-oxides being reduced.

The infiltration of Mn and Fe from surface waters into the aquifer during the dry season may also contribute to increases in groundwater Mn and Fe concentrations at Ladji and Agla. Surface waters include the infiltration of pond water or lake water into the aquifers. From a previous study in Ladji (Houéménou et al. 2019), the ^{18}O and ^{2}H data indicate that there is dry season mixing between the lake and groundwater, and there are evaporation processes that effect groundwater major ion chemistry. Therefore, these processes also potentially control trace element concentrations. According to the PCA analysis, the high concentrations of Fe and Mn in Lake Nokoué are not due to contact with the Atlantic Ocean. In addition, the reference values certified by the National Research Council Canada (Canada 2016), Fe and Mn (μg/L) have low levels in seawater (CASS-6: 2.22 ± 0.12 for Mn, 1.56 ± 0.12 for Fe). Instead, the high Fe and Mn concentrations in the lake water may be due to desorption mechanisms from sediments (Russak, Sivan, and Yechieli 2016). At Ladji, where there is both infiltration from lake and pond water, it is the recharge from pond water that potentially contributes to the high Fe concentrations because lake water Fe concentrations are below maximum groundwater values (Fig. 5b). In contrast, it is the recharge from lake water that potentially contributes to the elevated concentrations of Mn in groundwater (Fig. 5b). According to Weng et al. (2007) and Pezzetta et al (2011), the release of iron and manganese in groundwater can be enhanced by contact with a saline solution. In Agla, in many areas the decrease in rainfall between the small wet to the dry season results in a change from (sub)artesian groundwater to hydraulic heads that are below the ground surface. Therefore, the numerous ephemeral ponds at Agla in the small wet season have the potential to recharge the aquifer during the dry season and stable isotope values have confirmed this pond water recharge (Houemenou et al., 2019). Ponds analysed in this study have both Fe and Mn concentrations higher than groundwater (Fig. 5a). Therefore, direct infiltration from pond waters at Agla has the potential to result in both the high Fe and Mn concentrations in groundwater. In West Bengal and Bangladesh, the studies showed that the addition supply of organic matter caused by infiltration from surface water may promote a release of supplemental amounts of Fe and Mn into groundwater (Neidhardt et al. 2013; Farooq et al. 2010; Sutton et al. 2009)

Desorption and sorption processes of Fe and Mn, in either the unsaturated or saturated zone may also contribute to changing Fe and Mn concentrations. The soil samples highlight that Fe concentrations are relatively high in the unsaturated zone in areas where the sediments are rich in clay, such as at Ladji (Fe up to 9632.19 μg/L) compared with the relatively clay-poor soil profiles of St Jean (Fe up to 2267.4 μg/L) and Agla (Fe up to 1192.9 μg/L). In comparison, Mn concentrations between soil profiles are less variable, with concentrations up to 138.6, 139.5 and 69.5 μg/L at Ladji, St Jean and Agla. Therefore, spatial variations in the infiltration of Fe in water from the land's surface (pond water or rainfall runoff) to the water table is likely to be heavily influenced by the location of clay-rich sediments in the unsaturated zone. In addition, the transfer of trace elements from the soil can depend on other factors, including soil water chemistry (e.g. pH) and organic matter composition (e.g. Tahervand and Jalali, 2016). Since the contamination of groundwater from septic and sewerage systems in the three regions is common (Houéménou et al. 2019), the evolution of trace element concentrations from the unsaturated to the saturated zone is also likely to be influenced by inputs from waste water during leaching (Leung and Jiao 2006). According to Toribio and Romanyà (2006) and Kania et al. (2019), the high organic matter (e.g. sewage and septic tank) content of sediments can influence the mobility of trace elements, either they are retained in the sediments by the organic matter bound to the particles (e.g. Mn and Zn) or promote their leaching by the mobility of the organic matter.



(c) Agla (Pond recharge)

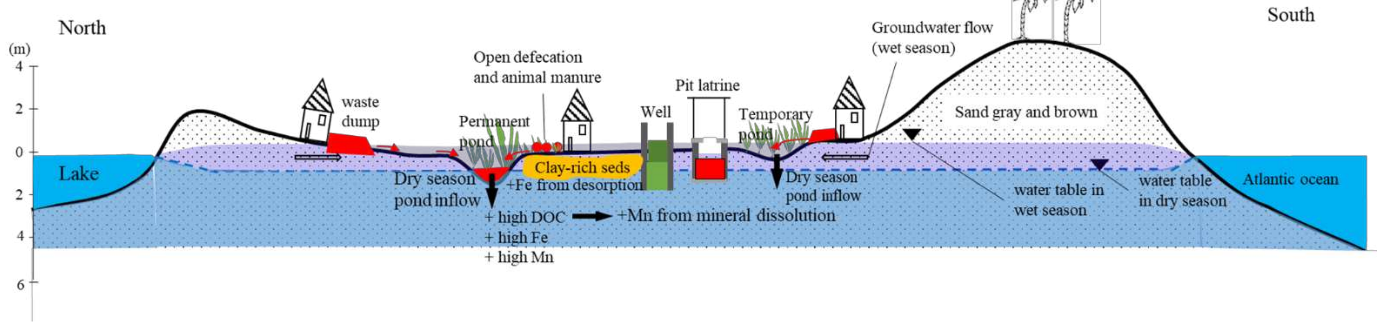


Figure 11. Schematic of conceptual model for Mn and Fe contamination sources at (a) Ladji, (b), St Jean and (c) Agla.

5. 2 Human health risks

Diseases related to trace element contamination of drinking water are major risks to human health. The concentrations of trace elements analysed in shallow groundwater at each of the three sites (Ladji, Agla and St Jean) in Cotonou were compared to WHO (2018) and national guidelines for drinking water quality, Decret N⁰ 2001-094 (Table 1). The results show that the concentrations of the trace elements in groundwater of studied area (with the exception of Mn and Fe) are below the guidelines drinking water quality in the Republic of Benin and those established by the World Health Organization (WHO 2018). Mn concentrations are above Benin drinking water guidelines (300 µg/L) at L2, L7, L6, L18 sites in Ladji and at A4, A2, A7 and A9 sites in Agla. Fe concentrations are above Benin drinking water guidelines (100 µg/L) at A4 and A10 in Agla and at L18 sites in Ladji (Fig. 3). In Brong-Ahafo, Ashanti and Western regions (Ghana), drinking water in Ghana produced from groundwater is contaminated by iron and manganese with concentrations above respectively 300 µg/L and 400 µg/L, the drinking-water guideline value commonly accepted for Fe and Mn (Buamah et al. 2008). Drinking water contaminated with manganese can pose a significant risk to human health. The United States Environmental Protection Agency report (USEPA 2004) mentioned that the health effects included lethargy, increased muscle tonus, tremor and mental disturbances. In both Bangladesh and the United States, children who consumed well water with an average Mn concentration of 793 µg/L, were exposed at the risk for Mn-induced neurotoxicity (Wasserman et al. 2006).

6. Conclusion

This study developed a quality dataset on trace element concentrations in Cotonou groundwater, which can serve as a resource for future research on the geochemistry of Mn and Fe in particular. Geochemical data showed that groundwater is contaminated by Fe and Mn, the only trace elements with concentrations are below the Beninese health guideline (100 µg/L and 300 µg/L for Mn and Fe respectively). Mn concentrations are above Benin drinking water guidelines (300 µg/L) at L2, L7, L6, L18 sites in Ladji and at A4, A2, A7 and A9 sites in Agla. Fe concentrations are above Benin drinking water guidelines (100 µg/L) at A4 and A10 in Agla and at L18 sites in Ladji. The high Mn concentration is explained by dissolution process from water-rock interaction. Also, given the increase of DOC and redox condition (low Eh), the high Mn and Fe in groundwater is controlled by denitrification process in reduced environments and by Fe-reducing microorganism decomposition. Drinking water contaminated with manganese can pose a significant risk to human health. The main factors controlling Mn and Fe concentrations in groundwater are redox conditions which are explained by increase of Fe and Mn in dry season when Eh values are ranged from 42 to 500 mV. In reduced environments (low Eh), denitrification process is followed by the reductive dissolution of Mn oxides. The presence of organic matter and microbial activities contribute to the increase in the Fe concentration in groundwater. The scale of the problem of increase Mn and Fe concentrations in the analyzed groundwater highlights the need for wider sampling in the coastal aquifer in southern Benin.

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