Geochemical modeling and quality assessment of the surface waters from the Mouhoun River system, Burkina Faso: Implications of water–rock interactions and anthropogenic activities

Original Research Article

ABSTRACT

Major ion and heavy metal geochemistry was used to investigate the factors that control the Mouhoun River water quality in western Burkina Faso. Major cation concentrations was in the following decreasing order: $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$, reflecting silicate weathering. However, relatively high HCO_3^- and SO_4^{2-} concentrations could be related to dissolution of calcite and sulfide minerals, respectively. The average heavy metal concentrations in the riverine system were in the following order: $Fe_T > Ag > Mn > Zn > Pb > Cu > Ni > As_T > Cr > Hg > Co > Cd$ with Fe_T and Ag exceeding the World Health Organization permissible limits. Concentrations of all heavy metals, except Cr, were higher in the Mouhoun system compared to the average world river concentrations. Adsorption and speciation models showed that Zn, Ag, Cd, Co, Cr and Ni are likely to remain in their free ionic forms, and thus posing serious threats to aquatic life and human health. Ag-Hg-Ni-Cd association around Poura and Tenado on the principal component plot suggested that the widespread artisanal gold mining in these areas may have contributed to these metals' loading. In contrast, NH_4^+, Pb, Cu, Cr, As_T and Zn were clustered around a densely populated and industrialized Kou watershed, pointing to agricultural and industrial sources of these pollutants. Furthermore, the Kou River had the highest metal index followed by Tenado, Samendeni, Poura and Boromo. Hence, the chemistry of the Mouhoun River and its tributary appears to be mainly controlled by population density and various anthropogenic activities taking place in their drainage basins. The findings could provide avenues for sound and sustainable water resource management in a water scarce semi-arid environment.

Keywords: Surface water, Hydrogeochemistry, Major ions, Heavy metals, Geochemical modeling

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1. INTRODUCTION

The earlier agricultural system that allowed humanity to alter nature and mobilize necessary resources for cultural, scientific and technological progress, was practiced on the banks of the world's largest rivers such as the Huang, the He, the Indus, the Tigris, the Nile and the Euphrates [1,2]. In that sense, rivers are the most important inland water sources for domestic, agricultural and industrial supplies, and thereby play a central role in socio-economic development of many countries around the world. However, the quality of these finite resources, at any given point and time, can be under tremendous pressure from both natural and anthropogenic factors [3,4].. Natural factors such as droughts decrease river water availability and indirectly reduce its quality through competing demands, whereas the quality can be directly affected by flooding and sediment accumulation [5,6,7]. River water quality is also largely affected by the degree of water–rock interactions, soil erosion, dilution/evaporation effects and atmospheric deposition [8,9,10]. Because of their direct contact with various pollution sources and their relative short residence time, river waters are more exposed to point and non-point pollution sourcesthan groundwaters[11].

In order to protect river waters against pollution, the factors that control riverine pollutants' mobility and toxicity should be properly identified and assessed [12,13]. The hydrogeochemistry and water quality of world's large rivers are a function of several factors such as relief, tectonic and climate settings, underlying geology, soil types, riparian vegetation cover as well as pollution loads from various human activities [14,15]. In the rivers' long course through highly heterogeneous geological formations, these factors may vary considerably making the interpretation of the water quality difficult [16]. In contrast, smaller rivers, such as the Mouhoun River, flow through less diverse geology and climatic zones, and accordingly, the contribution of anthropogenic activities to pollutant loadings can be easily constrained through hydrogeochemical investigations[17]. For instance, quantification of river major ion compositions can reveal the relationships that may be exist between, chemical weathering and anthropogenic impacts and the river water quality [18,19,20].

Furthermore, heavy metals, with relatively high densities (≥ 5 g/cm^3), are among the pollutants that affect most river water quality, as they pose serious threats to human health and ecosystem functioning [21,22,23]. Although these metals can be released into the riverine system through chemical weathering of the underlying and pathway rocks, untreated or partially treated domestic and industrial wastewater and agricultural runoff, rich in heavy metals, are often discharged into urban and rural riverine systems [24,25,26].Once in the fluvial system, the heavy metals may be immobilized through precipitation or adsorption. The extent of these geochemical processes depends on pH, mineralogy, redox conditions and the availability of inorganic and organic ligands of the receiving environment [26]. Alternatively, the metals could be remained in their ionic forms, and end up in the groundwater system through infiltration [28,29]. Despite their low concentrations in the environment (0.01–100 µg/L), heavy metals distribution in natural waters is of great importance to hydrogeochemical and environmental investigations [30,31].Some heavy metals (e.g., Fe, Mn, Co, Ni, Cu and Zn) are micronutrients that play an important role in enzyme activities, and can be toxic to biota at high concentrations [32,33], whereas others such as such Cd, Pb, As and Hg are highly toxic even at low concentrations [34]. Heavy metals are non-biodegradable, and thus they are potentially toxic with serious ecological and human health ramifications [35]. Consequently, heavy metal environmental contamination is serious global concerns [36,37]. Not only these concerns urge environmental geochemists to thoroughly identify various sources of heavy metals in aquatic system, but also to gain better understanding of the factors that control their behavior and fate.

Several hydrogeochemical methods such as major ion ratios, scatter plots of ion concentrations and multivariate analyses have been traditionally used to study, characterize and evaluate river water quality [38,39,40]. Although these methods are effective in identifying geological controls on water composition and separating anomalous concentrations from natural background concentrations, they cannot adequately predict the behavior and fate of potentially toxic heavy metals in the aquatic systems [41,42,43]. As a result, a series of geochemical modeling such as saturation indices (SI), speciation and adsorption have been widely regarded as crucial for understanding and predicting heavy metal behavior in aquatic environments [44,45].

The Mouhoun River (former Black Volta River) is the largest permanent watercourse in Burkina Faso that flows around several towns including Bobo-Dioulasso, a major urban center and economic hub in the country. To the best of our knowledge, no studies have yet assessed hydrogeochemistry nor evaluated the factors that control the Mouhoun River water quality for human consumption. In order to reduce this gap of knowledge and provide policymakers with critical information on the river water quality, the main objectives of the present study were to use major ion ratios to highlight the influence of water–rock interaction on the Mouhoun River water, to determine the behavior and fate of selected heavy metals in the water column using R-mode factor analysis and geochemical modeling and to assess the suitability of river water for domestic consumption. Because of the relative short residence time of the flowing water, the extent of anthropogenic activities is likely to be the major factor controlling the Mouhoun River waters. We hypothesize that sampling sites that are located around larger human settlements will have the greatest pollution indices compared to those with smaller settlements.

2. Geographical and geological setting

The Mouhoun River basin, with a drainage area of 87,208 km^2 and total length of about 1,000 km, is part of the large international Volta River Basin [46]. This looped-shape river is fed by numerous springs in southwestern Burkina Faso. The basin is subdivided into three sub-basins namely Sourou (15225 km^2), Lower Mouhoun (54802 km^2) and Upper Mouhoun (20978 km^2) sub-basins. The storage capacity of the reservoirs in the Mouhoun River basin is about 438 million m^3 with an average annual filing rate of 65% [47].

The present study was undertaken in the Upper Mouhoun River at Samendeni and in its first major right-bank tributary (Kou River) in southwestern Burkina Faso and in the Lower Mouhoun River in midwestern and central plateau regions (Fig. 1). The Upper Mouhoun River is located in the southeastern edge of the Taoudeni sedimentary basin. This basin consists mainly of dolerites and fine pink and schistose sandstones. The river flows from southwest to northeast, and its basin belongs to Sudanian climatic zone with an average annual rainfall of 1143 mm [48]. Three sampling sites were also selected in the Lower Mouhoun River in Tenado (Midwest region) and Boromo and Poura in the central plateau region. These towns lie within a less wet Sudano-Sahelian climatic zone with an average annual rainfall of about 930 mm. The Lower Mouhoun River drains crystalline basement rocks of Precambrian age associated with the West Africa Craton and composed of a series of intermediate to basic volcanic rocks and some sandy conglomerates [49]. Two distinct types of savannahs are encountered in the study area namely woodland savannah and grassy savannah [50]. The Upper Mouhoun sub-basin is characterized by densely wooded savannah with tall to medium grasses, whereas grasslands interspersed with trees and shrub is found in the Lower Mouhoun sub-basin.

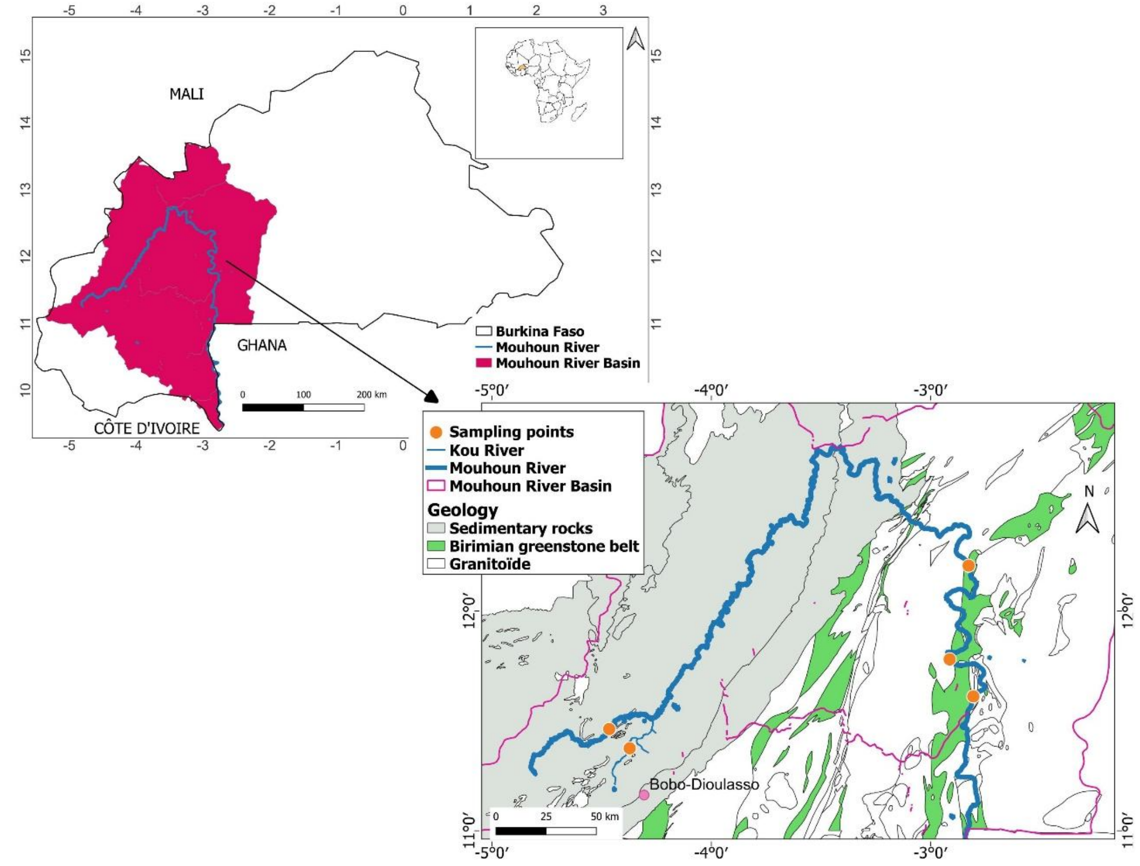


Fig. 1. Localization of the Mouhoun River basin and simplified map of the geology of southwestern Burkina Faso

3. Anthropogenic settings

In 2000, the Mouhoun River basin had about 4.5 million inhabitants, and the population is expected to reach 8 million in 2025. The Mouhoun River at Samendeni and the Kou River runs around Bobo-Dioulasso, a city of 904,920 inhabitants [51]. According to the last census in 2006, the populations were 48, 694 in Tenado, 14,885 in Boromo and 12,026 in Poura. The urbanization rate was 45,8 % in Samendeni and Kou, 16,4 % in Tenado, 9,6 % in Boromo and Poura in 2019. In addition to domestic water supply, the Mouhoun River water is used for washing, laundry, fishing, irrigation and small-scale hydropower generation. To meet urban population needs in vegetables and other agricultural products, many people are also involved in urban and peri-urban agriculture in the sampling towns, particularly in Bobo-Dioulasso. Thus, farming takes place in the riparian areas close to the waterbodies along with intensive application of agrochemicals. These activities are likely to be major sources of the river water pollution in the urban area, whereas cotton-growing, uncontrolled cattle grazing and lack of designated watering points for animals pose serious water pollution risks along the Mouhoun River banks in rural areas. Thus, the Mouhoun and Kou rivers are fed by agricultural runoff and domestic and industrial wastewaters of bordering cities and villages. Furthermore, the Mouhoun River basin is exposed to several artisanal gold mining sites, particularly around Tenado and Poura, which could be a major source of water pollution. Construction of dams (e.g., Samandeni and Lery dams) on the Mouhoun River could also cause accumulation of sediments and anthropogenic wastes in the waterbodies [52].

In Burkina Faso, where a lot of people lack access to clean drinking water and basic sanitation, several management strategies have been undertaken by the Mouhoun River Basin Authority through the Local Water Committees with the objective to reduce pollution loads and sediment transfer from riparian zones to the Mouhoun River system [48]. That is, a 100-m riparian buffer zone has been established around the Mouhoun River across the country. Thus, through a compensation scheme, farmers are encouraged to leave the 100-m zone. As a result, the Local Water Committees play a central role in reducing pollution loads through awareness campaigns about 100-m zone. Despite these efforts, population growth has resulted in larger abstraction of water to meet the increasing demand along with huge volumes of untreated or partially treated domestic and industrial effluents being discharged into the Mouhoun River [54].

4. Material and methods

4.1 Sampling and analysis

A suite of 15 surface water samples were collected at three points across the rivers' width in Kou, Samendeni, Tenado, Boromo and Poura using a 1000 mL clean glass immersion sampler during the late wet season 2022 (Fig. 2). These samples are representative of the Mouhoun River and its tributary, the Kou River. pH, electrical conductivity (EC) of the samples were measured *in-situ*, using a calibrated multi-parameter probe. The samples were filtered through 0.45 µm membrane filter and stored in clean unused polyethylene bottles. The filtered water samples were split into two portions. To avoid adsorption of cations onto the container, a portion of water samples was acidified with ultrapure nitric acid to a pH less than 2, and was subsequently used to determine major cation and heavy metal concentrations, whereas major anion concentrations were measured in non-acidified portion.

Back in the laboratory, major cations (i.e., Ca^{2+}, Mg^{2+}, Na^+ and K^+) plus total Fe (Fe_T) and Mn concentrations were determined by Flame Atomic Absorption Spectrophotometer (AAS), whereas those of major anions including Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-} and NH_4^+ were measured by UV-visible spectrometer. Bicarbonate concentrations were measured by titrating samples with 0.1 N HCl and methyl orange indicator. Total hardness (TH) of the samples was determined by EDTA titrimetric technique. A series of heavy metals including Ag, total As (As_T), Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn were analyzed on acidified samples by Inductively Coupled-Mass Spectrometer (ICP-MS). . Analytical grad standard stocks were used for the instrument calibrationThe detection limits of individual metals for AAS and ICP-MS were calculated using standard deviation of three runs of the blank samples. Concentrations of duplicate and external calibration data of multi-element standards were also used to determine analytical errors, and the results were within 10% error. Instrument calibration and sampling preparation were conducted using ultrapure analytical grad chemicals and Milli-Q water.

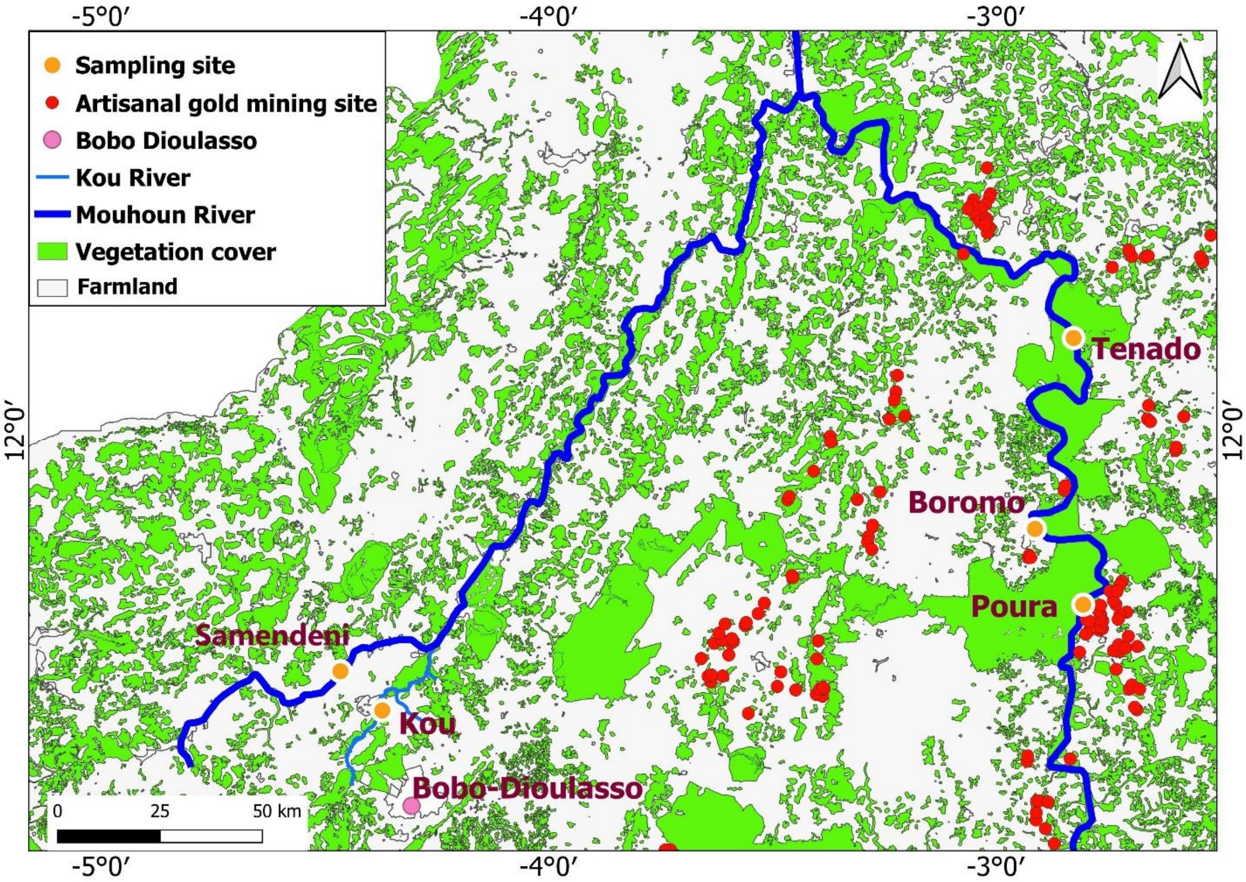


Fig. 2. Map showing the study area and major land use patterns within the Mouhoun River system in Burkina Faso

In this study, 26 variables were used for multivariate statistical analyses. Concentrations of some ions at certain sampling sites were censored (i.e., concentrations recorded as below the detection limit). Prior to multivariate statistical analyses, all variables (i.e., compositional data), except pH, EC and TH, were centered log-transformed (clr). Hence, one-way analysis of variance (ANOVA) was used to evaluate the differences in the mean of variables of the surface waters at significant values [55,56]. The degree of freedom (df), sum of square (SS) and mean square (MS) between the sampling sites and within sampling sites were determined. Also, F-value (i.e. MS between the clusters/MS within sampling sites) was calculated.

Additionally, R-mode factor analysis with principal component as extraction method was used to investigate the relationships between physico-chemical parameters of the water samples. To obtain stronger component or factor loadings, varimax rotation was applied. Variables loadings are correlation coefficients between the variable and the component. A loading close to ±1 indicates strong correlation between the variable and the component, whereas a loading close to 0 indicates weak correlation [57,58]. Variables with loadings greater than 0.75 are considered as strongly loaded on a component. In contrast, loadings of 0.4 and 0.5 to 0.75 correspond to weak and moderate loadings, respectively [59]. All statistical analyses were carried out using SPSS statistical software (ver. 23) and OriginPro2022.

4.2. Geochemical modeling

4.2.1. Saturation index

Saturation indices (SI) of a series of mineral phases were used to evaluate the degree of water–rock interactions. Through these indices, geochemical reactions that may control the river water chemistry are identified. These indices were calculated using Visual MINTEQ (Ver. 3.1), a chemical equilibrium code developed by [56], according to the following equation (Eq. 1):

$$SI = \log \frac{IAP}{KT} \quad (1)$$

Where IAP is the logarithm of ion activity product of the dissociated mineral and KT represents the equilibrium constant corrected to the mineral temperature. Visual MINTEQ was also used to calculate partial pressure of CO_2 (pCO_2), activity coefficients by the Davies equation and ionic strength (IS) of the water samples. Likewise, the dominant species of heavy metals were determined in the river water samples.

Average concentrations (mol/L) of hydrous ferric oxide ($Fe(OH)_3$ and individual heavy metals (i.e., Cd^{+2}, Cr^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2}) and ionic strength (IS in mol/L) were used in MINEQL+ a chemical equilibrium modeling system [59] to model the metal adsorption onto $Fe(OH)_3$ at different pH (4.5–8.5). Fitting of the data with Two-Layer model was described by [61]. Densities of strong (0.005 mol/mol Fe) and weak (0.2 mol/mol Fe) binding sites were used, whereas the specific surface area was assumed to be 600 m^2/g. The appropriate pH at which heavy metal species are likely to precipitate was also modeled using Hydra-Medusa equilibrium software [62].

4.2.2. Metal index calculation

The metal index (MI) is generally used to evaluate the overall surface and groundwater water quality for drinking and domestic purposes [62,63] and it is defined as (Eq. 2):

$$MI = \sum_{i=1}^{n} \frac{[M_i]}{(MAC)_i} \qquad (2)$$

Where [Mi] is the concentration of each metal and i is the sample, whereas MAC represents the maximum allowable concentration of the metals. Concentrations of 10 heavy metals including Ag, As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn were used in the present study to calculate MI. Based on the MI values, the following classes have been used to characterized surface water and groundwater quality [65,66] to very pure ($MI<0.3$), pure ($0.3<MI<1.0$), slightly affected ($1.0<MI<2.0$), moderately affected ($2.0<MI<4.0$), seriously affected ($4.0<MI<6.0$) and strongly affected ($MI>6.0$).

5. RESULTS AND DISCUSSION

5.1. Major ion characteristics

Physico-chemical parameters and major ion concentrations of the Mouhoun River system (main course and tributary) are presented in Table 1. Only pH, EC, TH and Na^+ varied significantly ($p < 0.05$) across the sampling sites (Table 2) with the following decreasing order: (Boromo>Tenado)Tenado>Boromo>Samendeni>Kou>Poura for pH and Poura>Tenado>Boromo>Kou>Samendeni for EC. Similarly, Poura and Tenado showed the highest TH concentrations followed by Boromo, Kou and Samendeni, whereas the highest Na^+ concentrations were found in Boromo and Poura. The relatively low pH, TH and Na^+ concentrations in the Upper Mouhoun River could be attributed to the lithological and vegetation cover differences[67]. The pH values were below the World Health Organization (WHO) recommended values for drinking water and ranged from 6.7 to 7.3 (6.9±0.2), indicating that the river waters were slightly acidic to circumneutral. Likewise, EC, which is an indicator of mineralization of natural waters, were low and varied across the sampling sites ($p = 0.00$) with an average value of 44±8 µS/cm. The low EC may be attributed to the high velocity of the surface water movement, short residence time and dilution effects during the wet season[68]. This, in turn, has led to lower dissolution, and thereby reducing solute concentrations [69].

With concentrations ranging from 44 to 78 mg/L (67±12 mg/L), HCO_3^- was the dominant major anion in the Mouhoun River system followed by SO_4^{2-} (8.48± 0. 49 mg/L), Cl^-, NO_3^-, PO_4^{3-} and NO_2^-. The predominance of HCO_3^- in the surface water samples could be related to the dissociation of calcite in the presence of CO_2[70,71]. Oxidation of organic matter could also contribute to the high HCO_3^- in surface waters [72]. Although all the major anions had concentrations largely below the WHO recommendation limits for drinking water, the low HCO_3^- (<100 mg/L) is an indicative of a poor water quality, which is only suitable for industrial activity [73]. In contrast, water with HCO_3^- concentrations comprised between 100 and 250 mg/L are considered having moderate quality and a concentration greater than 250 mg/L correspond to good water quality. Calcium and Na^+ are the most abundant cations, whereas Mg^{2+} had the lowest concentration. The pattern of major cation abundance based on their average concentrations is in following order: $Ca^{2+}>Na^+>K^+>Mg^{2+}$,with average concentrations of 8.82±4.3 mg/L, 8.17±7.31 mg/L, 4±0.4 mg/L and 1.2±1.6 mg/L, respectively. The dominance of Ca^{2+}, Na^+ and HCO_3^- in the waters can be explained by weathering of silicate minerals [74,75,76,77]. It can be noticed that average major ion concentrations of the Mouhoun River system are comparable to other world's rivers (Table 1; [78,79]). The low solute contents of the water are also reflected by low TH (30–70 mg $CaCO_3$/L with an average value of 55±11 mg $CaCO_3$/L). 9With TH less than 70 mg $CaCO_3$/L, the Mouhoun River system is considered as soft [80,81]. Hence, the cationic heavy metals such as Cd, Co, Cr, Cu and Pb are likely to be mobile in the water column.

Table 1. Summary Statistical of physico-chemical parameters and major ion concentrations in water samples from the Mouhoun River system (n = 15)

Parameter	Unit	Min	Max	Mean	SD	Median	World average[1]	WHO (2018)
pH		6.7	7.3	6.9	0.2	6.84	8	7.5-8.5
EC	µs/cm	28	51	44	8	49	–	300
TH	mg $CaCO_3$/L	30	70	55	11	54	–	300
HCO_3^-	mg/L	44	78	67	12	73	58	120
Cl^-	mg/L	<DL	2.6	1.2	0.9	1.7	7.8	250
NO_3^-	mg/L	0.1	0.51	0.33	0.11	0.3	1	10
NO_2^-	mg/L	0.03	0.05	0.04	0.01	0.04	–	–
PO_4^{3-}	mg/L	0.34	0.41	0.38	0.03	0.4	–	5
SO_4^{2-}	mg/L	7.6	9.53	8.48	0.49	8.52	11.2	250
Ca^{2+}	mg/L	8.82	23.65	16.41	4.29	16.83	15	75
Mg^{2+}	mg/L	1.2	6.6	3.3	1.6	3.39	4.1	50
Na^+	mg/L	8.17	36.94	17.18	7.31	18.8	6.3	200
K^+	mg/L	4	5.52	4.44	0.39	4.395	2.3	12
NH_4^+	mg/L	0.05	4.08	0.44	1.01	0.18	–	–

[1](Gaillardet et al., 1999; Meybeck, 2003)

Table 2. Analysis of variance of the hydrogeochemical parameters and centered log ratio-transformed (clr) major ion and heavy metal concentrationsof the surface waters from the Mouhoun River system.

Variable	SS	df	MS	F ratio	p level
pH	0.504	4	0.126	21.365	0.00
EC	984.74	4	246.185	688.951	0.00
TH	1102.4	4	275.6	5.679	0.01

clr.HCO_3-	0.22	4	0.055	1.582	0.25
clr.Cl^-	10.385	4	2.596	2.442	0.12
clr.NO_3^-	0.547	4	0.137	1.445	0.29
clr.NO_2^-	0.6	4	0.15	2.449	0.11
clr.PO_4^{3-}	0.317	4	0.079	1.544	0.26
clr.SO_4^{2-}	0.513	4	0.128	2.51	0.11
clr.Ca^{2+}	0.215	4	0.054	1.18	0.38
clr.Mg^{2+}	1.219	4	0.305	0.718	0.60
clr.Fe_T	1.838	4	0.46	8.722	0.00
clr.Mn	8.815	4	2.204	30.536	0.00
clr.Na^+	1.402	4	0.35	4.119	0.03
clr.K+	9.225	4	2.306	0.982	0.46
clr.NH_4^+	5.105	4	1.276	1.451	0.29
clr.Ag	13.491	4	3.373	1.259	0.35
clr.As_T	17.958	4	4.489	1.789	0.21
clr.Cd	4.801	4	1.2	0.603	0.67
clr.Co	5.689	4	1.422	2.125	0.15
clr.Cr	1.289	4	0.322	0.297	0.87
clr.Cu	9.703	4	2.426	2.268	0.13
clr.Hg	33.225	4	8.306	1.832	0.20
clr.Ni	147.362	4	36.841	1.877	0.19
clr.Pb	8.256	4	2.064	2.569	0.10
clr.Zn	13.697	4	3.424	8.411	0.00

SS = sum of square; df = degree of freedom; MS = mean square.

5.2.Geochemical processes controlling water chemistry

Interactions between surface water and host rocks is evaluated through several geochemical processes including water composition, chemical weathering, the extents of saturation of the aqueous solution with respect to various mineral phases, ion exchange, oxidation and reduction reactions and adsorption of metals onto secondary minerals [82]. These processes may increase or decrease major ion concentrations or enhance mobility and bioavailability of heavy metals in the aquatic systems [83,84].

In the presence study, the processes controlling the surface water chemistry was described by bivariate mixing plots of Ca^{2+}/Na^+ versus Na^+/Mg^{2+} and Ca^{2+}/ Na^+ versus HCO_3^-/Na^+ (Fig. 3a and 3b; [78]). According to the mixing plots, the Mouhoun River samples are clustered around the silicate end member, suggesting that silicate weathering is the dominant water–rock interaction that control the water chemistry. The influence of chemical weathering on the Mouhoun River water was further evaluated through a series of major ion scatter plots. If halite dissolution was the dominant process of Cl^- and Na^+ abundance in the river waters, the samples would plot along the 1:1 equiline (Fig. 3c). However, it could be noticed that half of the samples are plotted over and below 1:1, respectively. The excess of Na^+ over Cl^- suggesting other sources of Na^+ such as silicate weathering and ion exchange[85,86,87]. If weathering and dissolution of calcite, dolomite, anhydrite are dominating processes in the water system, the (Ca^{2+}+Mg^{2+}) versus (HCO_3^-+SO_4^{2-}) scatter plot will be close to the line 1:1 equiline (Fig. 3d). The silicate weathering can be indicated by the dominance of (HCO_3^-+SO_4^{2-}) over (Ca^{2+}+Mg^{2+}), whereas the dominance of (Ca^{2+}+Mg^{2+}) is indicative of reverse ion exchange [86]. In the present study, all samples, except those from Samendeni, showed a dominance of (HCO_3^-+SO_4^{2-}) over (Ca^{2+}+Mg^{2+}). This is a further indication that silicate weathering was the major lithogenic source of the dissolved ions in the Mouhoun River and its tributary. This was also corroborated by the Piper diagram (Fig. 4), which classified the Mouhoun River as Ca–HCO_3 dominant type, reflecting silicate weathering[88,89].

The saturation index (SI) is a factor that indicates mineral saturation due to water chemistry. If SI is greater than zero it indicates oversaturation of water by a given mineral, whereas values of less than zero suggests undersaturation of the mineral, if the mineral is available, will continue to dissolve until saturation. The SI values of carbonate and evaporate minerals for all samples in the Mouhoun River system were undersaturated, whereas those of Fe-oxyhydroxide minerals were oversaturated, indicating that the same geochemical processes are involved in the water chemistry across the sampling sites (Table 3). Ratios of Ca to Mg can be used to describe calcite and dolomite dissolution in water [90]. A Ca/Mg ratio greater than 1, suggests dissolution of calcite, whereas a value less or equal to 1 indicates dolomite dissolution. In the present study all samples had Ca/Mg> 1 (Fig. 3d), implying that in addition to silicate weathering, dissolution of calcite minerals contributes to the water chemistry.

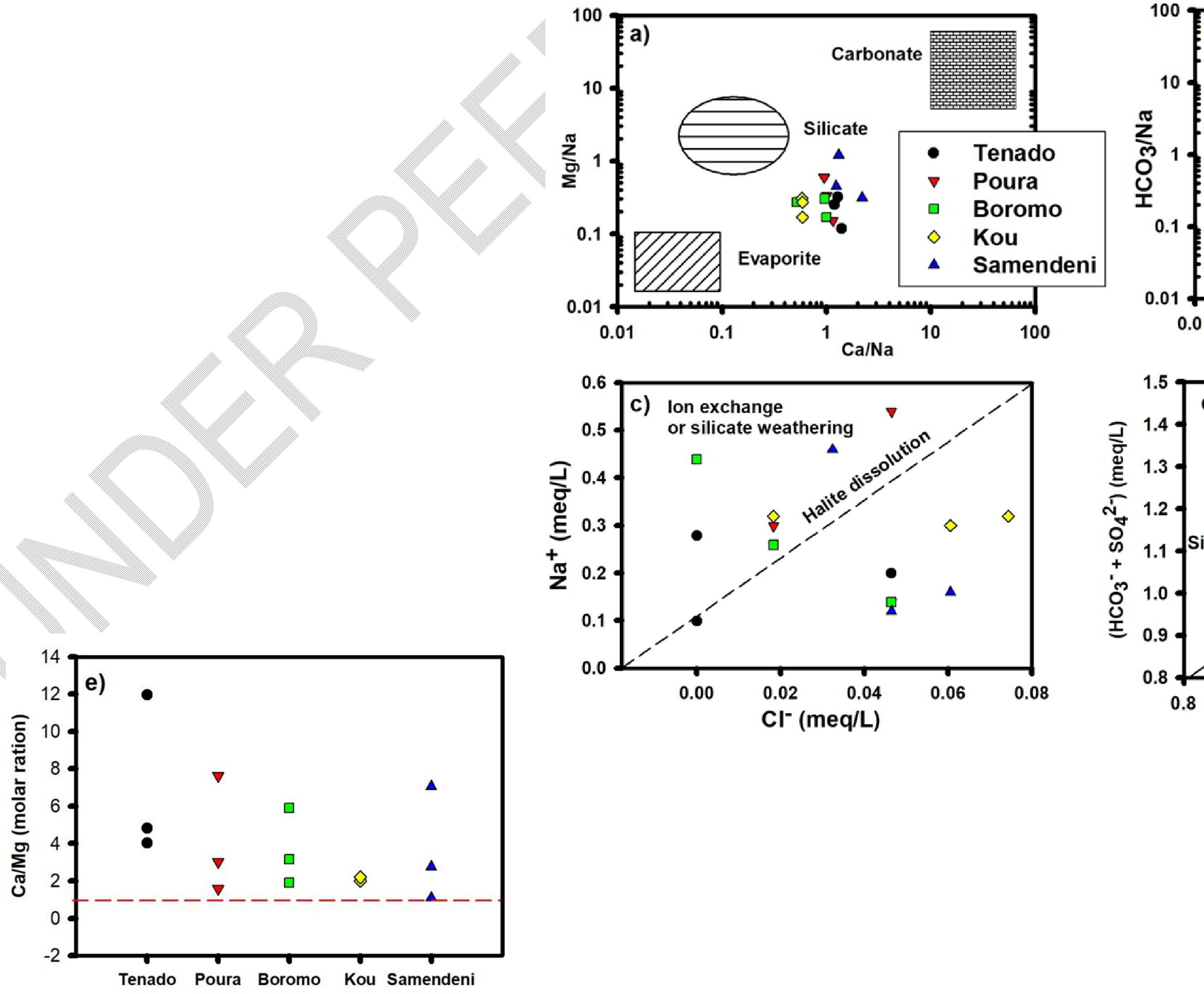


Fig. 3. a-b) Bivariate plots of Na+-normalized Ca^{2+} versus Mg^{2+} and Ca^{2+} versus HCO_3^- showing evaporitie, silicate and carbonate end-members. c-d) Relationships between major ion concentrations, highlighting the main geochemical processes controlling the Mouhoun River system chemistry. e) Scatter plot of molar ratios of Ca/Mg versus sampling sites. The samples with Ca/Mg ratios less than 1 indicate dolomite dissolution, whereas those with ratios greater than 1 correspond to calcite dissolution.

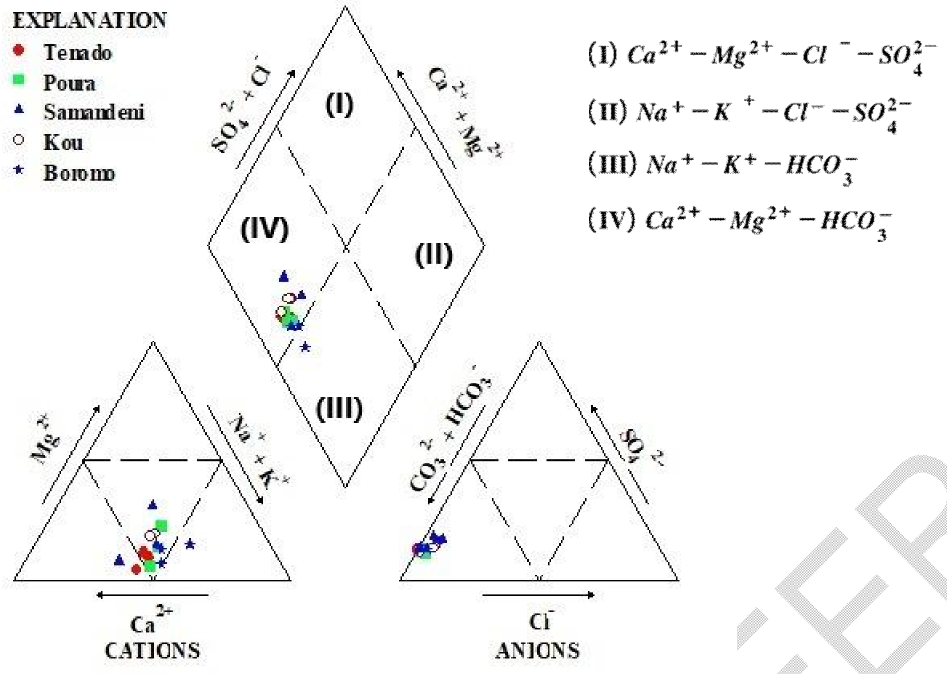


Fig. 4. Piper diagram [88] displaying the dominant water type of the Mouhoun River system

5.3. Distribution and geochemical modeling of river water

Only three variables (Fe_T, Mn and Zn) differed significantly among the sampling ($p<0.05$; Table 2). Two variables (Fe_T and Ag) had average concentrations above the WHO's permissible limits for drinking water (Table 4). The average concentrations of the heavy metals were lower than those measured in the mine-impacted Witwatersrand River [91], whereas the average concentrations of As_T, Cd, Cr, Cu, Ni, Pb and Zn were higher in the Rhine River compared to the Mouhoun River system [92]. Only the average concentrations of As_T and Cd in the Mississippi River were higher than those of the Mouhoun River basin system. However, the average concentrations of all metals, except Cr, were higher than the world average river concentrations[93]. The average concentrations of heavy metals in the Mouhoun River system followed the order of Fe_T>Ag>Mn>Zn>Pb>Cu>Ni>As_T>Cr>Hg>Co>Cd. The relative high concentrations of Fe_T, Mn and Hg in the Mouhoun River system with respect to the world rivers, can be attributed the local geology, pedogenic processes and widespread use of Hg in artisanal gold mining in the areas.

Table 3. Saturation indices of mineral phases, ionic strength (IS) and partial pressure (pCO_2) of surface water samples from the River system

Site	Sample	IS (M)	pCO_2 (atm)	Calcite	Aragonite	Dolomite	Anhydrite	Gypsum	Halite	Cupric Ferrite	Goethite	Ferrihydrite	Hematite
Tenado	T1	0.0024	0.0074	-1.2	-1.4	-3.0	-3.3	-3.0	-3.0	**16.0**	**7.2**	**4.5**	**16.7**
	T2	0.0025	0.0054	-1.0	-1.1	-2.9	-1.1		-10.2	**13.4**	**6.8**	**4.1**	**15.9**
	T3	0.0027	0.0064	-1.1	-1.2	-2.6	-3.2	-2.9	-10.2	**15.8**	**7.2**	**4.5**	**16.9**
Poura	P1	0.0025	0.0161	-1.6	-1.7	-3.5	-3.3	-3.0	-9.4	**14.1**	**6.9**	**4.2**	**16.3**
	P2	0.0027	0.0134	-1.5	-1.6	-3.0	-3.3	-3.0	-9.0	**14.1**	**7.0**	**4.3**	**16.4**
	P3	0.0025	0.0167	-1.5	-1.7	-3.8	-3.2	-2.9	-9.0	**14.4**	**6.9**	**4.2**	**16.2**
Samendeni	S1	0.0018	0.0072	-1.6	-1.7	-3.9	-3.3	-3.0	-9.3	**13.2**	**6.9**	**4.2**	**16.2**
	S2	0.0018	0.0057	-1.8	-1.9	-3.4	-3.5	-3.2	-9.5	**13.5**	**7.0**	**4.3**	**16.4**
	S3	0.0014	0.0097	-2.1	-2.2	-4.5	-3.6	-3.3	-9.3	**14.0**	**6.7**	**4.0**	**15.8**
Kou	K1	0.0020	0.0113	-1.6	-1.8	-3.4	-3.5	-3.2	-9.6	**15.1**	**7.3**	**4.6**	**17.0**
	K2	0.0020	0.0094	-1.6	-1.8	-3.5	-3.4	-3.2	-9.0	**14.7**	**7.3**	**4.6**	**17.0**
	K3	0.0020	0.0090	-1.6	-1.8	-3.4	-3.4	-3.2	-9.1	**15.0**	**7.3**	**4.6**	**17.1**
Boromo	B1	0.0022	0.0047	-1.1	-1.2	-2.8	-3.3	-3.0	-9.0	**15.4**	**7.4**	**4.7**	**17.2**
	B2	0.0023	0.0042	-1.0	-1.2	-2.4	-3.3	-3.1	-9.4	**15.9**	**7.4**	**4.7**	**17.1**
	B3	0.0030	0.0057	-1.2	-1.3	-2.5	-3.3	-3.0	-9.9	**15.7**	**7.3**	**4.6**	**17.0**

Table 4. Summary statistical of dissolved trace metal concentrations of the Mouhoun River system (n = 15) compared to other world large rivers as well as to word average river concentrations (μg/L)

Trace element	The Mouhoun River					World rivers					
	Min	Max	Mean	SD	Median	Mississippi[a]	Rhine[b]	Witwatersrand[c]	World average[d]	WHO (2018)	MAC[e] (2006)
Fe_T	400	1100	600	200	500	5	35	550000	66	300	300
Mn	24	235	89	75	57	10	5	200000	34	200	50
Ag	0.22	294.20	111.18	81.23	103.40	−	−	−	−	10	100.00
As_T	<DL	4.8	1.5	1.5	1.3	3	13	250	0.62	10	10
Cd	<DL	0.3	0.06	0.09	0	0.1	5.5	52	0.08	20	3
Co	0.1	1.0	0.4	0.3	0.3	−	−	−	0.15	2000	1000
Cr	0.2	4.7	1.2	1.3	0.7	0.5	33	4000	0.7	50	50
Cu	0.1	13.5	2.6	3.3	2	2	34	5400	1.5	10	1000
Hg	<DL	4	1.0	1.4	0.015	0.1	0.65	−	−	6	1
Ni	<DL	15.4	2.4	3.9	1.7	1.5	20	200000	0.8	10	20
Pb	0.8	22.8	8.3	6.5	7.3	0.2	27	6400	0.1	10	10
Zn	<DL	98.3	37.8	38.1	16.3	10	330	26000	0.6	50	5000

[a][94]; [b][95]; [c][92]; [d][93]; [e][96]

Several geochemical processes such as co-precipitation with metal-oxyhydroxides and adsorption onto the surface of river sediments are likely to control heavy metal distribution and bioavailability in the riverine system [97,98]. Once in the riverine system, behavior and fate of heavy metals will be a function of the environmental conditions such as pH, mineralogy of the drainage basin and oxidation potential [99,100]. Thus, heavy metals may remain in free ionic state in the water column, co-precipitate as secondary minerals or adsorbed onto the surface of the riverine sediments [101]. Speciation modeling showed that over 80% of Zn, Ag, Cd, Co, Cr and Ni remained in their free ionic forms within the river water pH range (Fig. 5a and 5b), more easily assimilated by living organisms [102,103]. Interestingly, the speciation modeling predicted that at pH values of 7.8 and 5.6, Cd^{2+} and Cu^{2+} will form labile $CdOH^+$ and $CuOH^+$, respectively (Fig. 7). Similarly, complexation of Co^{2+} and Ni^{2+} with OH to form labiles $CoOH^+$ and $NiOH^+$,will occur at pH 7, whereas formation of solid species of $Co(OH)_2$) and $Cd(OH)_2$) likely to occur for Co and Cd at pH 8.2 and Ni ($Ni(OH)_2$) for Ni at pH 9.8, suggesting that these metals are unlikely to be naturally removed from the water column. In general, cadmium (Cd(II)) precipitates around pH 8 in the form of hydroxides [104], which corresponds with our results. As a result, they pose serious threats to aquatic organisms and human health. Although about 90% of Zn was in the free ionic state (Zn^{2+}), zinc adsorption onto Fe-oxyhydroxides occurs at pH 6.2, which is within the river water pH range (6.7–7.3). Formation of zinc solid ($Zn(OH)_2$) is likely occurred at pH 7.8 (Fig. 7).

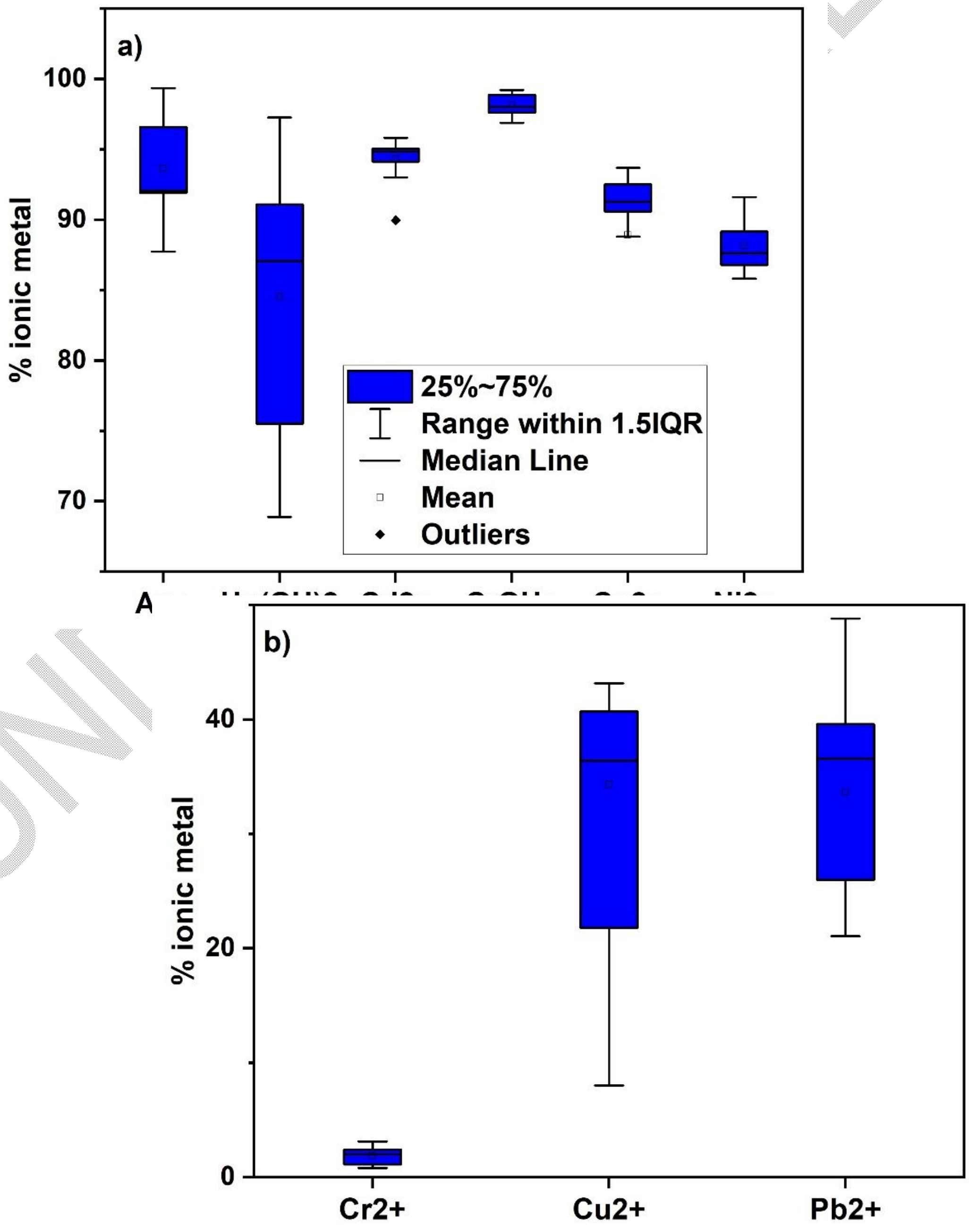


Fig. 5. Proportions of dissolved heavy metal distribution in the Mouhoun River system.

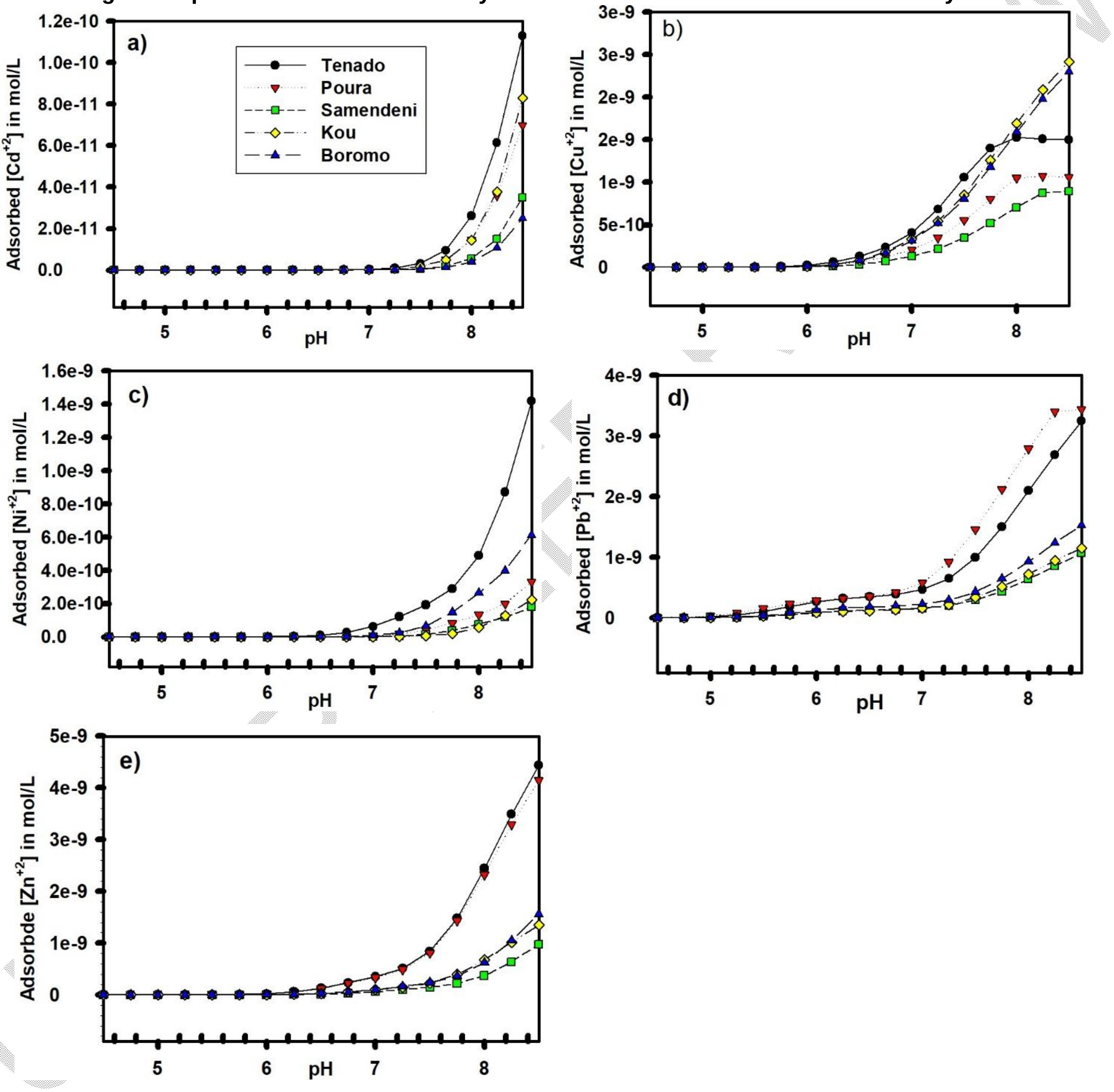
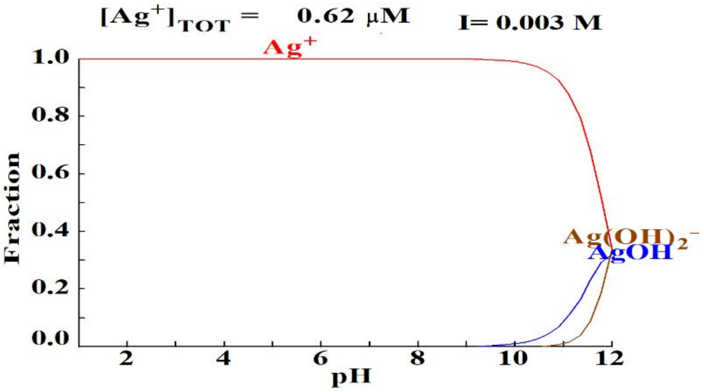
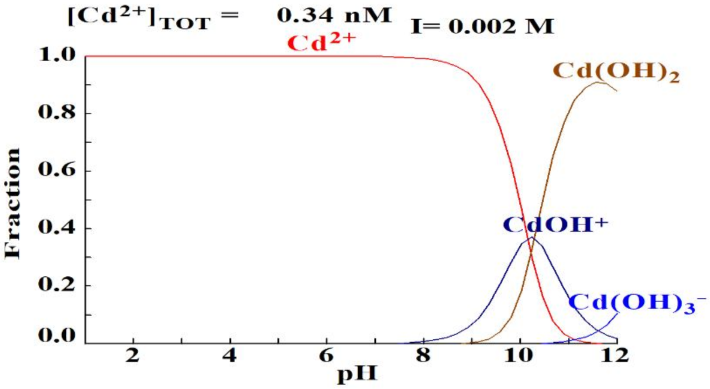


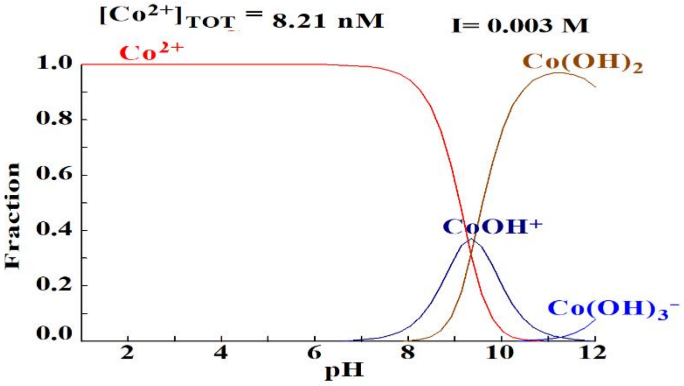
Fig.6. Expected average heavy metal concentrations adsorbed onto $Fe(OH)_3$ versus pH in water samples collected in different sites in the Mouhoun River basin.

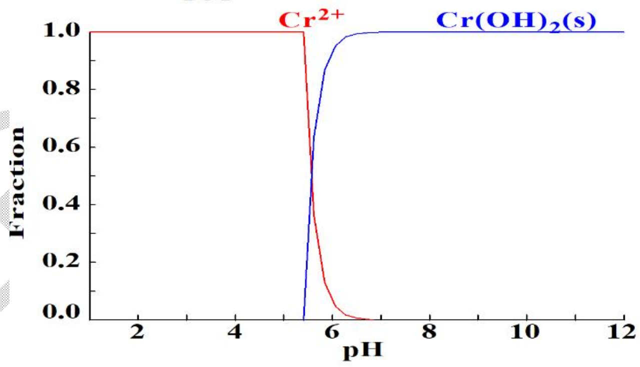
Behavior and fate of Cu and Pb in the riverine system were significantly different from other heavy metals. That is, only about 40% of these metals were in the form of Pb^{2+} and Cu^{2+} in the water column (Fig. 6b). Adsorption of Cu^{2+} and Pb^{2+} onto the Fe-oxyhydroxides started at pH 6.5 and 5.8, respectively. However, occurrence of solid forms of

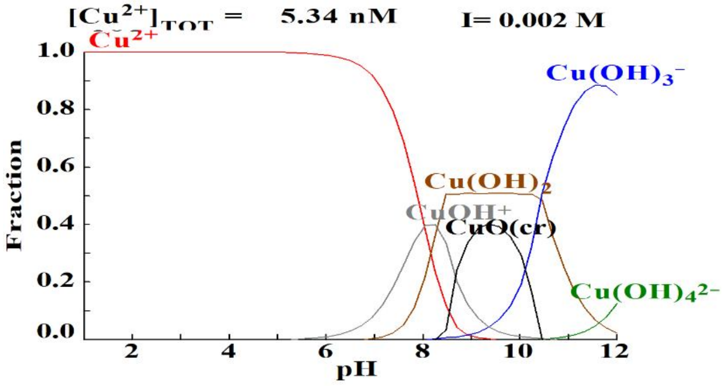
Cr(CrOH)$_2$), Cu (Cu(OH)$_2$), Hg (Hg(OH)$_2$) and Pb (PbOH)$_2$) is expected at pH 5.4, 7, 2.8 and 8.2, respectively. Adsorption and speciation modeling of heavy metal mobility in the river system was in the following decreasing order: $Ag^{+}>Cd^{2+}>Ni^{2+}>Co^{2+}>Zn^{2+}>Pb^{2+}>Cu^{2+}>Cr^{2+}>HgOH^{+}$. As a result, Ag and Cd may, not only pose serious threats to riparian population, but they may migrate into the groundwater system.

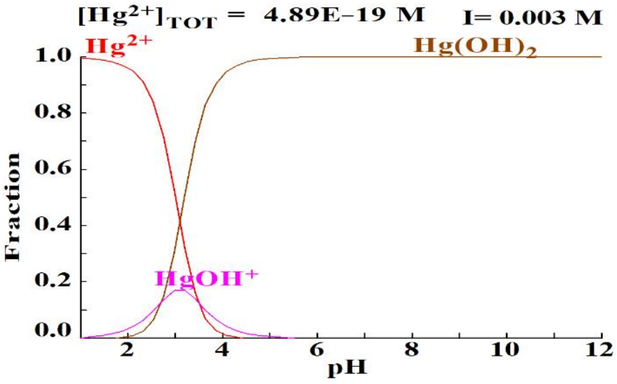












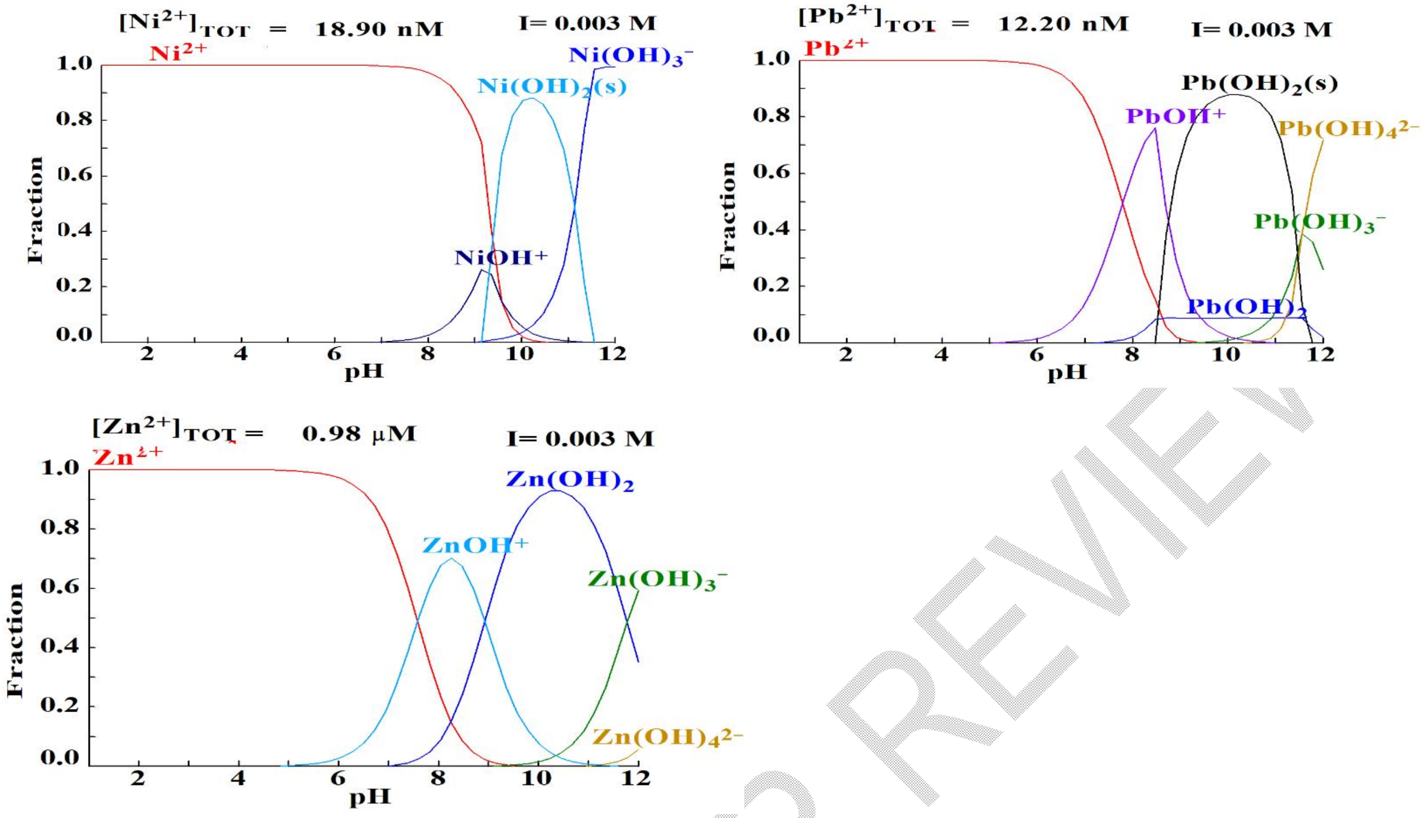


Fig. 7. Expected heavy metal species in the Mouhoun River water as a function of pH

5.4.Anthropogenic sources of heavy metals

To gain insight and understanding of the natural and anthropogenic processes that control distribution of major ions and heavy metals in the Mouhoun River system, R-mode factor was used. After varimax rotation [105], seven principal components (PCs) with eigenvalues greater than unity [106,107] and communalities of the variables close to 1 (Table 5). These components accounted for more than 80% of the total variance, which is reasonably good and can be relied upon to identify the potential sources of the hydrogeochemical parameters of the Mouhoun River system.

With 17% of the total of the variance, is the most important component among the seven components. Nitrite, PO_4^{3-} and SO_4^{2-} had strong positive loadings on PC1 and Mg^{2+} and HCO_3^- had moderate positive loadings on PC1. This component highlights the influence of sulfate of ammonia and phosphate-bearing fertilizers in the river drainage basin [104]. PC2 had high positive loading for NH_4^+ and strong negative loadings for K^+ and Ag. Furthermore, Na^+ and Cl^- had moderate positive and negative loadings on PC2, respectively. Such loadings on PC2 represent contribution of sewage or leakage of manure and fertilizers from agricultural activities under subsonic conditions to the riverine system [108]. PC3, which accounts 15.7% of the total variance, had high positive loadings for Fe_T, and Mn and moderate positive loading of Zn, Cd, and HCO_3^- representing effects of both water–rock interactions and urban solid wastes on the riverine chemistry. The inverse high loading of Pb on PC3 suggests that Pb was not derived from the same source as these heavy metals. Such a loading is usually ascribed to vehicular emissions and urban runoff around big agglomerations. With 11% of the total variance, PC4 was mainly dominated by NO_3^- and, to a lesser degree, EC, TH, Ca^{2+}, and HCO_3^-. Thus, PC4 could reflect atmospheric deposition and agricultural runoff. Indeed, the anthropogenic origin of NO_3^- would be much more related to agricultural fertilizers according to [109]. PC5 explained 9.3% of the total variance and had high positive loading for Cu and moderate loadings for Zn and Na^+. This component is likely to represent urban and domestic waste loadings into the river system. PC6 had high loading for Cr and a moderate loading for K^+, whereas Ni was negatively loaded, anthropogenic and natural sources of these elements (Fig. 8a). PC7 was characterized by high positive loadings for pH and Ca^{2+} and moderate loading for HCO_3^-, representing weathering of limestone and calcium carbonate bearing rocks and ion exchange processes [110] accompanied by an increase in pH. Further evidence to this end is provided by the high molar ratios of Ca/Mg of the samples. Mercury did not have loading on any principal component.

Table 5. R-mode varimax rotated factor analysis loadings (PC-PC7) of hydrogeochemical parameters of the Mouhoun River system

Variable	Component							
	PC1	PC2	PC3	PC4	PC5	PC6	PC7	Communalities
pH	0.03	0.24	-0.15	0.00	0.02	-0.06	**0.84**	0.789
EC	-0.64	0.38	-0.05	*0.45*	-0.13	0.24	0.27	0.895
TH	-0.41	0.41	-0.32	*0.51*	-0.49	-0.12	0.19	0.983
clr.HCO_3^-	0.46	0.36	*0.42*	0.37	-0.02	0.39	0.41	0.969
clr.Cl^-	0.28	-0.54	0.39	-0.10	0.21	0.03	-0.43	0.762
clr.NO_3^-	0.10	0.18	0.12	**0.85**	-0.22	0.08	0.15	0.854
clr.NO_2^-	**0.87**	0.17	0.05	-0.18	0.04	0.28	0.05	0.896
clr.PO_4^{3-}	**0.86**	0.00	0.24	0.15	0.01	0.27	0.20	0.935
clr.SO_4^{2-}	**0.87**	0.08	0.29	0.04	0.00	0.28	0.21	0.968
clr.Ca^{2+}	0.18	0.18	-0.06	0.42	-0.22	0.23	**0.70**	0.834
clr.Mg^{2+}	*0.67*	0.40	0.32	0.25	-0.16	-0.10	-0.27	0.871
clr.Fe_T	0.26	0.12	**0.90**	0.10	0.08	-0.09	-0.14	0.928
clr.Mn	0.24	-0.09	**0.88**	0.00	0.12	-0.06	-0.33	0.966
clr.Na^+	0.12	0.69	0.62	-0.42	0.45	0.17	0.09	0.940
clr.K^+	-0.09	**-0.94**	0.08	0.37	-0.09	0.42	0.39	0.975
clr.NH_4^+	0.20	**0.82**	0.09	-0.02	-0.04	-0.09	-0.12	0.922
clr.Ag	0.07	**-0.95**	0.09	-0.11	0.27	0.30	0.18	0.929
clr.As_T	0.05	0.14	-0.10	-0.10	-0.08	0.07	-0.07	0.939
clr.Cd	-0.04	-0.20	0.46	**-0.78**	-0.13	0.14	-0.02	0.884
clr.Co	0.12	0.14	0.01	0.12	**-0.81**	0.10	0.09	0.732
clr.Cr	-0.24	-0.10	-0.15	-0.17	-0.03	**0.88**	0.15	0.874
clr.Cu	-0.59	0.36	0.33	0.04	**0.72**	0.18	-0.12	0.741
clr.Hg	-0.28	-0.09	-0.12	0.01	0.28	0.27	0.13	0.656
clr.Ni	-0.20	0.30	-0.25	-0.19	-0.17	**-0.74**	0.15	0.785
clr.Pb	-0.03	0.15	**-0.76**	0.41	-0.13	-0.19	-0.08	0.923
clr.Zn	0.28	0.24	0.63	-0.14	0.62	0.10	0.23	0.888
% of Variance	17	16.9	15.7	11.0	9.3	9.0	8.9	
Cumulative %	17	34	50	61	70	79	88	

High loadings (≥0.75) are bold and moderate loadings (≥05≤0.75) are underlined.

The loading plot (Fig. 8) of three first PCs shows three grouping of the river hydrochemical parameters associated with the five sampling sites. That is, NO_3^-, PO_4^{3-}, Ca^{2+} and NO_2^-, representing agricultural runoff were clustered between Samendeni, Poura and Kou. Seven variables including Ag, Hg, K^+, Ni, Cl^-, TH and Cd were grounded around highly impacted artisanal gold mining areas of Poura and Tenado, whereas pH, Co, HCO_3^-, Na^+, Fe_T, EC and Mn, which are dominated by water–rock interactions were associated with Kou, and Boromo. Variables that directly related to organic matter decomposition (NH_4^+), vehicular emission (Pb) and industrial wastes (Cu, Cr, As_T and Zn) were clustered around Kou. The most affected site by anthropogenic activities was identified by using the metal index (MI). The MI values varied broadly from 4 to 15 with an average value of 7±16. Although the Mouhoun River water samples from Boromo had the lowest MI (4.8±1.1), these waters are considered as seriously affected. The highest MI (Fig. 8b) is measured in water samples from the Kou River (11.9±2) followed by Tenado (6.4±1), Samendeni (6.0±2) and Poura (5.7±07) from the Mouhoun River. It is noteworthy that the Kou River drains the surface runoff of Bobo-Dioulasso and its surroundings. The study clearly showed a positive correlation between the extents of urbanization and the quality of the surface water from the Mouhoun River system.

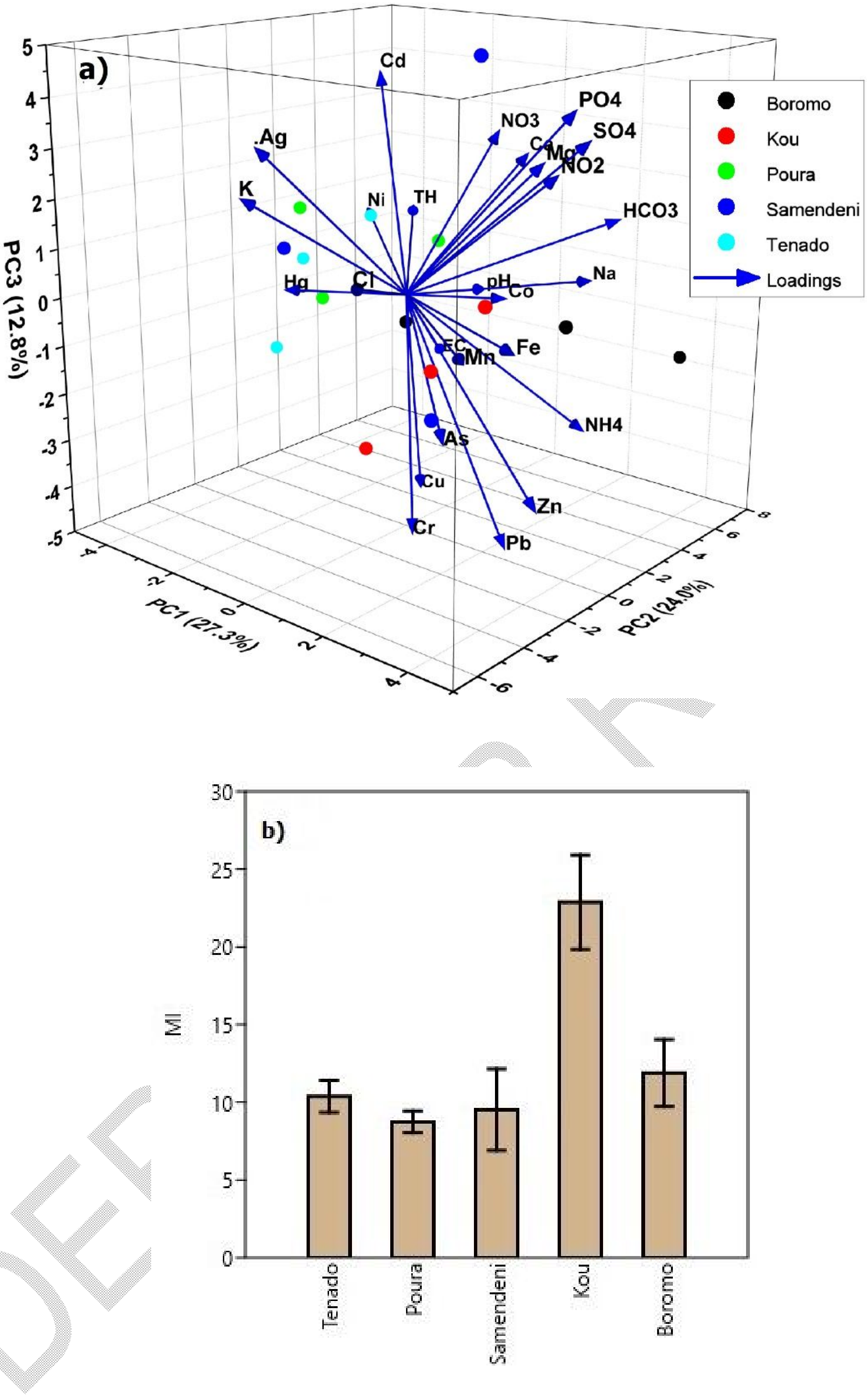


Fig.8. a) Biplot of two first dominant principal component loadings b) Heavy metal index distribution in different sites

6. CONCLUSION

The present study seeks to understand the factors that control the Mouhoun River water quality using a combination of statistical and geochemical modeling. The results of bivariate mixing plots, the major ion ratios and the Piper diagram successfully identified silicate weathering as the major lithogenic source of the dissolved ions in the Mouhoun River and its tributary (Kou River). However, anthropogenic activities such as industrial activities, farming, domestic effluents and artisanal gold mining appeared to enhance heavy metal loading the riverine system. With the highest urbanization level within its drainage basin, the Kou River, is, by far, the most affected by farming and industrial activities, whereas, areas with widespread artisanal gold mining such as Poura and Tenado, are more affected by Hg and Ag Water samples were oversaturated with respect Fe-oxyhydroxide minerals, suggesting that heavy metals may be co-precipitated with along with these minerals. However, adsorption and speciation modeling showed that all heavy metals, at various degree, are likely to remain in their ionic free species within the pH range of the riverine waters. Further studies including more samples and taking into account the effects of seasonal variations on the Mouhoun River water chemistry are highly recommended.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts

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COMPETING INTERESTS The authors declare no competing interests.

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