

Original Research Article

Pollution Assessment of Heavy Metals As, Cu, Pb and Zn in the Sirba Greenstone Belt Soils (Liptako, Niger)

ABSTRACT

The Sirba greenstone belt was Niger's main gold province. Soil geochemical data from the Sirba gold prospecting campaign carried out from 1989 to 1994 by the Japanese International Cooperation, prior to the advent of gold mining in the region were used in this work. The aim of this work was to establish geochemical background and to assess soil pollution for As, Cu, Pb and Zn. Geochemical data from 16,696 soil samples (analyzed by AAS) had been used to define geochemical background. The median method to calculate the threshold value on log-transformed data was used. Geochemical background data were used to assess the pollution of each element using the Contamination Factor, and multi-element pollution using the Pollution Load Index. The geochemical background values obtained were: As (27 mg/Kg), Cu (151.99 mg/Kg), Pb (12.50 mg/Kg) and Zn (145 mg/Kg). Soil Contamination Factor values for As (Min = 0.02, Mean = 0.99, Max = 442.07), Cu (Min = 0, Mean = 0.31, Max = 8.95), Pb (Min = 0.04, Mean = 0.29, Max = 43.12) and Zn (Min = 0, Mean = 0.39, Max = 8.58), and Pollution Load Index values (Min = 0.01, Mean = 0.28, Max = 3.86) show higher arsenic contamination and some samples with high global pollution (PLI > 1). The pollution and gold mining areas were mainly developed in the soils with high arsenic Contamination Factor values. The arsenic in the soils of the Sirba was therefore thought to have originated from gold mineralization.

Keywords: Sirba, Geochemical Background, Soils, Gold mining, Contamination Factor, Pollution Load Index

1. INTRODUCTION

Toxic elements such as As, Cd, Cu, Hg, Pb, Zn, etc. had given rise to major environmental concerns due to their toxicity, their non-biodegradable nature, their persistence, which means they have a strong tendency to accumulate in the food chain (Bing et al., 2016; Olivero-Verbel et al., 2015; Salam et al., 2016; Tyopine et al., 2018; Zhong et al., 2014). This accumulation posed a serious threat to living organisms, including humans (Radziemska and Fronczyk, 2015; Song et al., 2015; Vaverková and Adamcová, 2014). Accumulation of metals in soils beyond their natural cycle and control led to soil pollution (Tyopine et al., 2018). Pollution was the set of processes that cause toxicity and present a risk to human health (Thornton, 1995). Soil pollution had become a major environmental concern worldwide (Alshahri and El-Taher, 2018; Gupta et al., 2014; Liu et al., 2006). Soil was one of the main ecosystems on which human beings depended for their survival and development (Wang et al., 2019). Soils were an important reservoir for metals in terrestrial ecosystems (Gulan et al., 2017; Hamedan et al., 2016; Li et al., 2013; Santos-Francés et al., 2017; Tyopine et al., 2018). Food security remains an important aspect of human life, and the vital role of soil in agricultural and food production was evident in the fact that the quality of agricultural products consumed by people throughout the food chain depended on the condition of the soil (Okerefor et al., 2019).

Toxic metals in the natural environment existed as trace elements in the crust (Facchinelli et al., 2001; Gope et al., 2018). They were introduced into the environment through anthropogenic or natural processes (Barik et al., 2018; de-Lima et al., 2020; Ghrefat et al., 2021; Tyopine et al., 2018; Wang et al., 2019). The natural origin of heavy metals was linked to soil parent materials (Rodríguez Martín et al., 2013; Santos-Francés et al., 2017; Wang et al., 2019). Anthropogenic origin was due to industrial activities, urban planning, etc. (de-Lima et al., 2020; Sarkar et al., 2017; Wang et al., 2019).

Determining the level of pollution was the key to solving the problem of soil pollution (Jiang et al., 2020; Yuan et al., 2014). A soil quality assessment required knowledge of the background values of metals in soils (Baize and Sterckeman, 2001; Konstantinova et al., 2021). Establishing geochemical reference concentrations of metals in soil enabled precise pollution assessment and provided a basis for pollution control (Jiang et al., 2020). Reference geochemical concentrations referred to natural levels of metals in soil that were not influenced by anthropogenic activities (Jiang et al., 2020; Sierra et al., 2007). In many regions, reference geochemical data were not available, so it was necessary to establish local geochemical background or baselines (Li et al., 2015; Tian et al., 2017). Geochemical background had been defined as “the normal abundance of an element in a geological body whose equilibrium had not been disturbed by the presence of a mineral deposit” (Khan et al., 2021; Licht, 2020; Wei et al., 2021). The geochemical threshold corresponded to the upper limit of normal background fluctuation, i.e. the boundary between the geochemical background and the geochemical anomaly (Franklin et al., 1991; Konstantinova et al., 2021). It was used to identify areas where element concentrations were abnormally high (Reimann et al., 2018). It could also be used to assess soil contamination and pollution (Baize and Sterckeman, 2001). Several approaches had been used to determine the geochemical threshold value (Konstantinova et al., 2021; Reimann et al., 2005). For geochemical data with asymmetric distribution (Gonçalves et al., 2022; Suresh et al., 2012), Reimann *et al.*, 2005 had suggested calculating the threshold from the median (Gonçalves et al., 2022; Konstantinova et al., 2021; Santos-Francés et al., 2017; Suresh et al., 2012).

Assessing the degree of pollution through the content of chemical elements in the soil could be done by calculating pollution indices (Santos-Francés et al., 2017). Geochemical indices, such as Contamination Factor (CF) and Pollution Load Index (PLI), could be used to assess metal pollution in soil (Chon et al., 1998; Tomlinson et al., 1980). The Contamination Factor (CF) was used to express the level of contamination for each metal in the soil (Barik et al., 2018). The Pollution Load Index (PLI) as introduced by Tomlinson et al. (1980), assessed the extent of multi-element pollution (Barik et al., 2018; Gope et al., 2018; Hamedan et al., 2016; Hossain et al., 2022). Several authors had used the Contamination Factor (CF) and the Pollution Load Index (PLI) to assess soil pollution (Akay and Özyaytekin, 2022; Baah et al., 2023; Fagbenro et al., 2021; Fodoué et al., 2022; González-Valoys et al., 2021; Luo et al., 2020; Quiroz et al., 2022; Raji et al., 2023; Sawadogo et al., 2023; Sutkowska et al., 2023; Wiafe et al., 2022).

The aim of this work is to determine geochemical background values of As, Cu, Pb and Zn for soils and to assess soil pollution in the Sirba greenstone belt.

2. MATERIAL AND METHODS

2.1. Study area

The Sirba greenstone belt belongs administratively to the Tillabéri region in the south-western part of the Republic of Niger. The Tillabéri region was divided into three climatic zones: the Sahelo-Saharan zone in the north (150 and 300 mm/year), the Sahelian zone in the center (300 and 600 mm/year) and the Sahelo-Sudanian zone in the south (600 to 700 mm/year) (Abass-Saley, 2024). Temperatures range from 17°C in December to 45°C in May (Seyni et al., 2014). The relief comprised several geomorphological complexes: granitic domes, lateritic hills, quartz vein buttes and dune belts. Fig. 1c of the elevation map highlighted the geomorphic complexes. Three types of soil were associated with these geomorphological complexes: sandy soils made up of coarse sands forming more or less mobile dunes in places; sandy-clay soils in valley bottoms, depressions and ponds, characterized by dense vegetation; and highly eroded lateritic soils, located on plateaus and occupied by sparse vegetation. The study area's hydrographic network was made up of Niger and Sirba rivers.

Geologically, the Sirba greenstone belt is located in the Niger's Liptako. The latter corresponded to the NE end of the Léo-Man's ridge (Fig. 1a) on the West African craton (Machens, 1973). The Liptako geological formations (Fig. 1b) were Lower Proterozoic in age (Bessoles, 1977). They were formed by alternating greenstone belts, granitoids, Neoproterozoic and Mio-Pliocene sediments (Dupuis et al., 1991; Machens, 1973; Pons et al., 1995). The greenstone belts consist of metabasalt, meta-sediments, meta-volcano-sediments, meta-volcano-plutonites, tuffs and rhyolitic breccias (Ama Salah et al., 1996; Soumaila et al., 2004). The granitoids consist of granites, tonalite, trondhjemite and granodiorite intersected by sills and basic dykes (Dupuis et al., 1991; Pons et al., 1995).

Gold mineralization in the Liptako is closely linked to major regional faults and to the nature of the metamorphism affected rocks (Klockner, 1995). Two types of gold mineralization had been identified in Liptako (Jica, 1995; Saint-Martin, 1999): syn-sedimentary exhalative gold mineralization associated with graphitic clays (Jica, 1995; Saint-Martin, 1999) and quartz vein gold mineralization controlled by fractures and regional faults (Jica, 1995; Klockner, 1995; Saint-Martin, 1999; St-Julien, 1992). Gold mineralization was also related to gabbro, quartz diorite and rhyolite dyke (Saint-Martin, 1999). Gold mineralization in the Sirba greenstone belt occurred mostly in quartz veins in association with sulfides (Saint-Martin,

1999). In this region, the gold mining was the main source of non-agriculture income. Traces of gold panning had existed since the advent of the 1984 drought in Niger (Amadou, 2002; Hilson et al., 2019; Pétot, 1995; Yonlihinza, 2011). Gold panning really took off in the region with the mining boom of the 2000s. Industrial gold mining began in the Sirba in 2007.

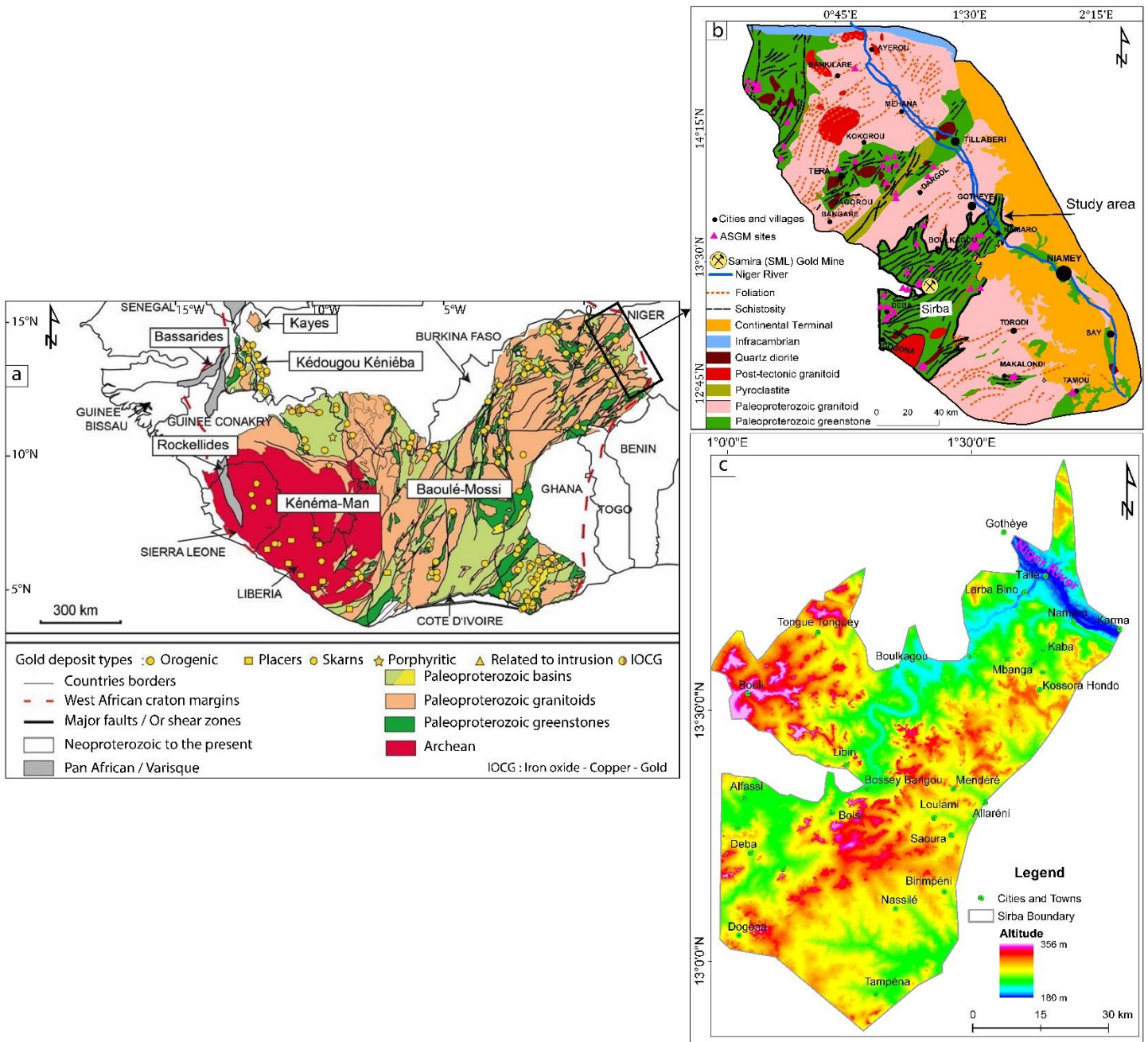


Fig. 1. Geological map of the Léo-Man Ridge (a) (Milési et al., 2004) and location of gold deposits (Markwitz et al., 2016), geological map of the Liptako area (b) (Machens, 1967) and the Sirba area elevation map (c).

2.2. Geochemical Data

The geochemical data of the study come from the 1989-1994 geochemical prospecting campaign carried out by the International Cooperation of the Japanese Metals Mining Agency under the Jica project, at a time when gold mining was almost non-existent in the region. As, Cu, Pb and Zn analytical results from 16,696 Sirba soil samples were used. Fig. 2a shows the map of the sample collection points. The analysis was performed by Chemex Labs Ltd. North Vancouver, B.C, in Canada. As, Cu, Pb and Zn content of the soil samples were determined in ppm (1 ppm = 1 mg/Kg) by Atomic Absorption Spectrometry (AAS) after HNO₃-aqua regia digest of soil samples. Fig. 2b shows the situation in 2024 of the Sirba greenstone belt with the development of gold mining.

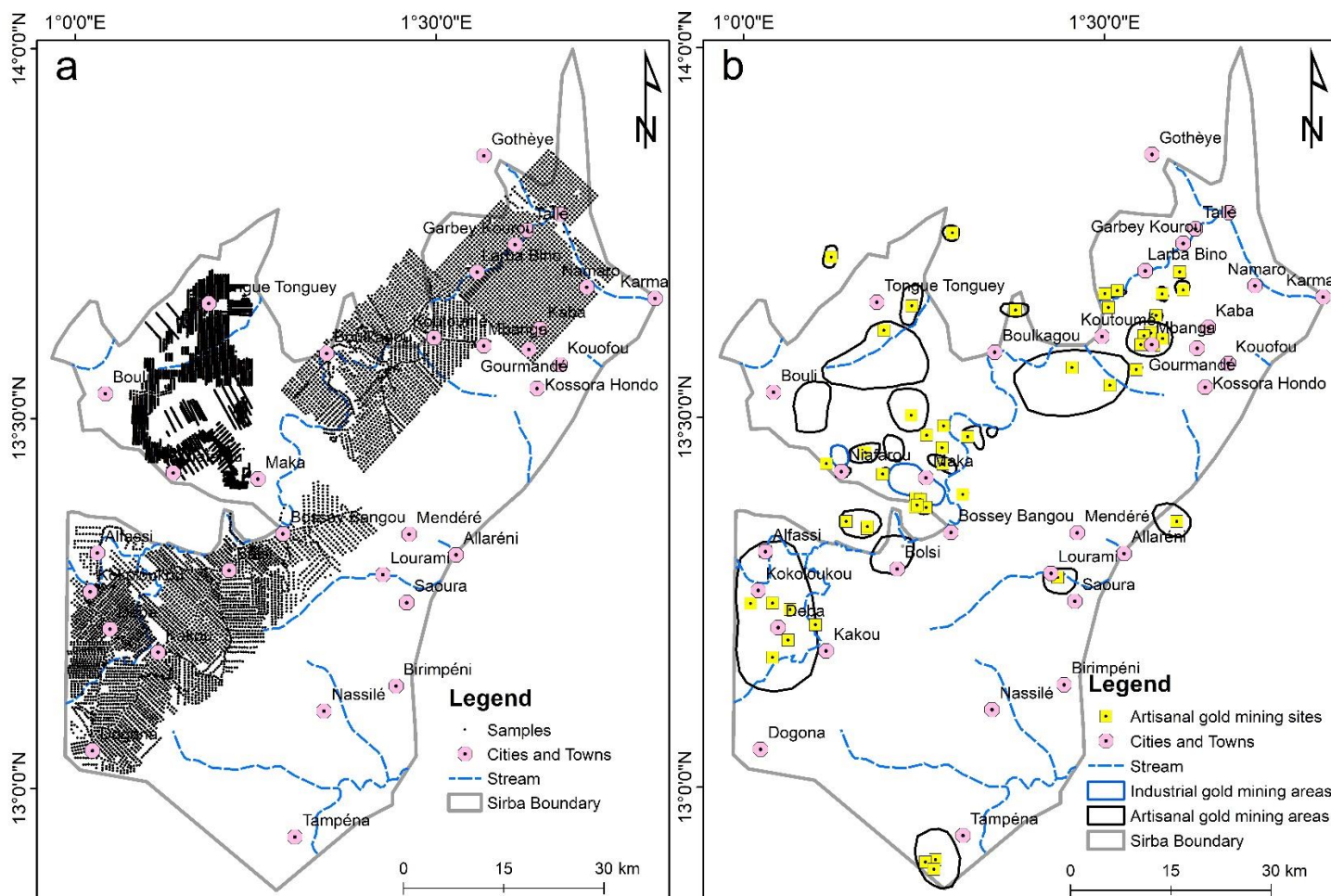


Fig. 2. Map of the sample collection points (a) and the Sirba greenstone belt situation in 2024 (b).

2.3. Geochemical Threshold Calculation

The distribution of geochemical data is generally asymmetrical and strongly skewed to the right (Gonçalves et al., 2022; Reimann et al., 2018). The Kolmogorov-Smirnov normality test (Mishra et al., 2019) was applied to the data to check their distribution. This test is applied if the number of samples is greater than fifty (Normadiah and Yap, 2011). The correct approach for determining the geochemical threshold would therefore be to calculate it on log-transformed data (base 10), then retransform the result and use these values as the threshold according to formula 1 (Gonçalves et al., 2022; Konstantinova et al., 2021; Reimann et al., 2018).

$$\text{Th res hold} = \text{Median} + 2 * \text{MAD} \quad (1)$$

where MAD is the Median Absolute Deviation.

2.4. Pollution Assessment Indexes

Two indices were used to assess the level of contamination of each element and the level of multi-element pollution of the soil: the Contamination Factor and the Pollution Load Index.

The Contamination Factor (CF) was used to assess the level of contamination for each metal in a soil sample (Alshahri and El-Taher, 2018; Barik et al., 2018; Ferati et al., 2015). It was the ratio of the concentration of each element in the soil sample (C_m) to the value of the geochemical background of the same element (GB) (Formula 2) (Gope et al., 2018; Haris et al., 2017; Hossain et al., 2022).

$$CF = \frac{C_m}{GB} \quad (2)$$

CF values have been classified into four groups to reflect the soil contamination levels: Low contamination ($CF < 1$); Moderate contamination ($1 < CF \leq 3$); Considerable contamination ($3 < CF \leq 6$); Very high contamination ($CF > 6$) (Barik et al., 2018; Gope et al., 2018; Tashakor et al., 2018).

The Pollution Load Index (PLI) as suggested by Tomlinson et al. (1980) (Formula 3), was the root n of the n number of Contamination Factor (CF) values multiplied together (Bassey et al., 2015; Bhuiyan et al., 2015; Ferati et al., 2015; Gope et al., 2018; Hossain et al., 2022; Tian et al., 2017; Zhao et al., 2014).

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \cdots \times CF_n)} \quad (3)$$

where n is the number of studied metals and CF is the Contamination Factor.

There is no pollution if $PLI < 1$. Soil is polluted by several metals if its $PLI > 1$ (Hossain et al., 2022).

To better represent the spatial distribution of Contamination Factor (CF) and Pollution Load Index (PLI) values for Sirba soil samples, a GIS-based mapping approach was used to represent the different CF and PLI classes according to the coordinates of the sampling points.

3. RESULTS AND DISCUSSION

3.1. Geochemical Threshold

Table 1 shows the descriptive statistics and p-value of the Kolmogorov-Smirnow normality test (decision 5%). The data do not follow a normal distribution (p-value = 0). They were skewed to the right (Skewness > 0). Table 2 shows the statistics of the transformed data. Table 3 shows the threshold values and the determined values for the geochemical background (in mg/Kg) for As, Cu, Pb and Zn, elements in the Sirba soils. The obtained geochemical background values for Sirba soils are: As (27 mg/Kg), Cu (151.99 mg/Kg), Pb (12.50 mg/Kg) and Zn (145 mg/Kg).

Table 1. Descriptive statistics and p-value of the normality test

Element	NT	Mean	SD	Skewness	Min	Max	p-value
As (mg/Kg)	16696	26.73	135.69	44.78	0.5	11936	0
Cu (mg/Kg)	16696	46.97	47.57	3.36	0.5	1360	0
Pb (mg/Kg)	16696	3.67	6.04	47.43	0.5	539	0
Zn (mg/Kg)	16696	56.83	67.61	3.57	0.5	1250	0

NT: Total number; SD: Standard deviation; Min: Minimum; Max: Maximum

Table 2. Log transform data statistical values

Element	NT	Mean	SD	Min	Median	Max	MAD
Log10_As	16696	0.63	0.73	-0.30	0.48	4.08	0.48
Log10_Cu	16696	1.46	0.47	-0.30	1.49	3.13	0.35
Log10_Pb	16696	0.35	0.45	-0.30	0.30	2.73	0.40
Log10_Zn	16696	1.53	0.44	-0.30	1.51	3.10	0.33

Table 3. Threshold and geochemical background values

Element	NT	TH	GB (mg/Kg)
As	16696	1.43	27.00
Cu	16696	2.18	151.99
Pb	16696	1.10	12.50
Zn	16696	2.16	145.64

TH: Threshold; GB: Geochemical Background

3.2. Pollution Assessment

Table 4 shows the descriptive statistics for the Contamination Factor (CF) and Pollution Load Index (PLI) values for As, Cu, P and Zn elements in the Sirba soils. Fig. 3 shows the spatial distribution of As (Fig. 3a), Cu (Fig. 3b), Pb (Fig. 3c)

and Zn (Fig. 3d) Contamination Factor (CF) assessment classes for the Sirba soils in 1994, at a time when gold mining did not exist in the region. Fig. 4 shows the spatial distribution of As (Fig. 4a), Cu (Fig. 4b), Pb (Fig. 4c) and Zn (Fig. 4d) Contamination Factor assessment classes of the Sirba soils in 1994, with the spatial distribution of the gold mining areas and sites in 2024, thirty years after sampling.

Table 4. Descriptive statistics for CF and PLI values for As, Cu, P and Zn in Sirba soils.

Index	NT	Mean	SD	Min	Maximum
CF As	16696	0.99	5.03	0.02	442.07
CF Cu	16696	0.31	0.31	0	8.95
CF Pb	16696	0.29	0.48	0.04	43.12
CF Zn	16696	0.39	0.46	0	8.58
PLI	16696	0.28	0.27	0.01	3.86

Fig. 5a shows the spatial distribution of As, Cu, Pb and Zn PLI assessment classes for Sirba soils in 1994, at a time when gold mining did not exist in the region. Fig. 5b shows the spatial distribution of As, Cu, Pb and Zn PLI assessment classes of Sirba soils in 1994, with the spatial distribution of gold mining areas and sites in 2024.

3.3. Discussion

As, Cu, Pb and Zn elements show an asymmetrical distribution in the Sirba greenstone belt soils. As (Min = 0.5 mg/Kg, Max = 11936 mg/Kg, Skewness = 44.78) and Pb (Min = 0.5 mg/Kg, Max = 539 mg/Kg, Skewness = 47.43) were more asymmetric than Cu (Min = 0.5 mg/Kg, Max = 1360 mg/Kg, Skewness = 3.36) and Zn (Min = 0.5 mg/Kg, Max = 1250 mg/Kg, Skewness = 3.57).

The geochemical background values for the Sirba soils (1994 pre-industrial period) obtained from the geochemical threshold values were: GB As = 27 mg/Kg, GB Cu = 151.99 mg/Kg, GB Pb = 12.50 mg/Kg and GB Zn = 145 mg/Kg. The GB As (27 mg/Kg), GB Cu (151.99 mg/Kg) and GB Zn (145 mg/Kg) values for the Sirba soils were higher than the values for the average concentration of these elements in the upper continental crust, as given by Hans-Wedepohl (1995): As (2 mg/Kg), Cu (14.3 mg/Kg) and Zn (52 mg/Kg). This difference could be explained by the fact that the geochemical threshold was always higher than the natural geochemical background, as well explained by ADEME (2018). Only the GB Pb value (12.50 mg/Kg) of the Sirba soils was slightly lower than the average lead concentration in the upper continental crust (Pb = 17 mg/Kg) as given by Hans-Wedepohl (1995).

Geochemical background values for Sirba soils were used to calculate pollution assessment indices (Contamination Factor and Pollution Load Index) for As, Cu, Pb and Zn. The arsenic Contamination Factor (CF As) gives higher values (Min = 0.02, Mean = 0.99, Max = 442.07) than copper (CF Cu) (Min = 0, Mean = 0.31, Max = 8.95), lead (CF Pb) (Min = 0.04, Mean = 0.29, Max = 43.12) and zinc (CF Zn) (Min = 0, Mean = 0.39, Max = 8.58). Only the mean value of the arsenic Contamination Factor is very close to 1 (CF As \approx 1). This shows that Sirba soils have overall moderate arsenic contamination. The overall average Cu, Pb and Zn contamination of the Sirba soils was very low. The pollution Load Index values (Min = 0.01, Mean = 0.28, Max = 3.86) show that multi-element pollution was low (Mean PLI = 0.28), even though some samples have PLI > 1 (Max PLI = 3.86), thus presenting high global pollution. The multi-element (As, Cu, Pb, Zn) pollution was mainly concentrated in the soils of the NE part of the Sirba greenstone belt.

Overlaying the gold mining areas on the CF and PLI classification shows that areas presenting high multi-element pollution and high levels of As, Cu, Pb and Zn Contamination Factor were areas that had subsequently been subjected to gold mining. High arsenic concentrations in gold mining areas may be associated with gold mineralization. In fact, gold mineralization at Sirba and Liptako was associated with sulfides rich in As and other metals (Cd, Cu, Pb, Zn, Hg, etc.) such as pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, etc., as shown by Abass-Saley (2024), Jica (1995) and Saint-Martin (1999). The weathering of sulfide-rich rocks (pyrite, arsenopyrite, etc.) could mobilize their metals and metalloids, which end up in soils. The release of metals and metalloids into soils from the weathering of sulfide-rich rocks was observed by Weightman (2020). This could explain the presence of As, and Cu, Hg, Pb, Zn in the soils of the Sirba greenstone belt which is the Niger's largest gold province. Arsenic in the soils of the Sirba greenstone belt therefore came from the gold mineralization.

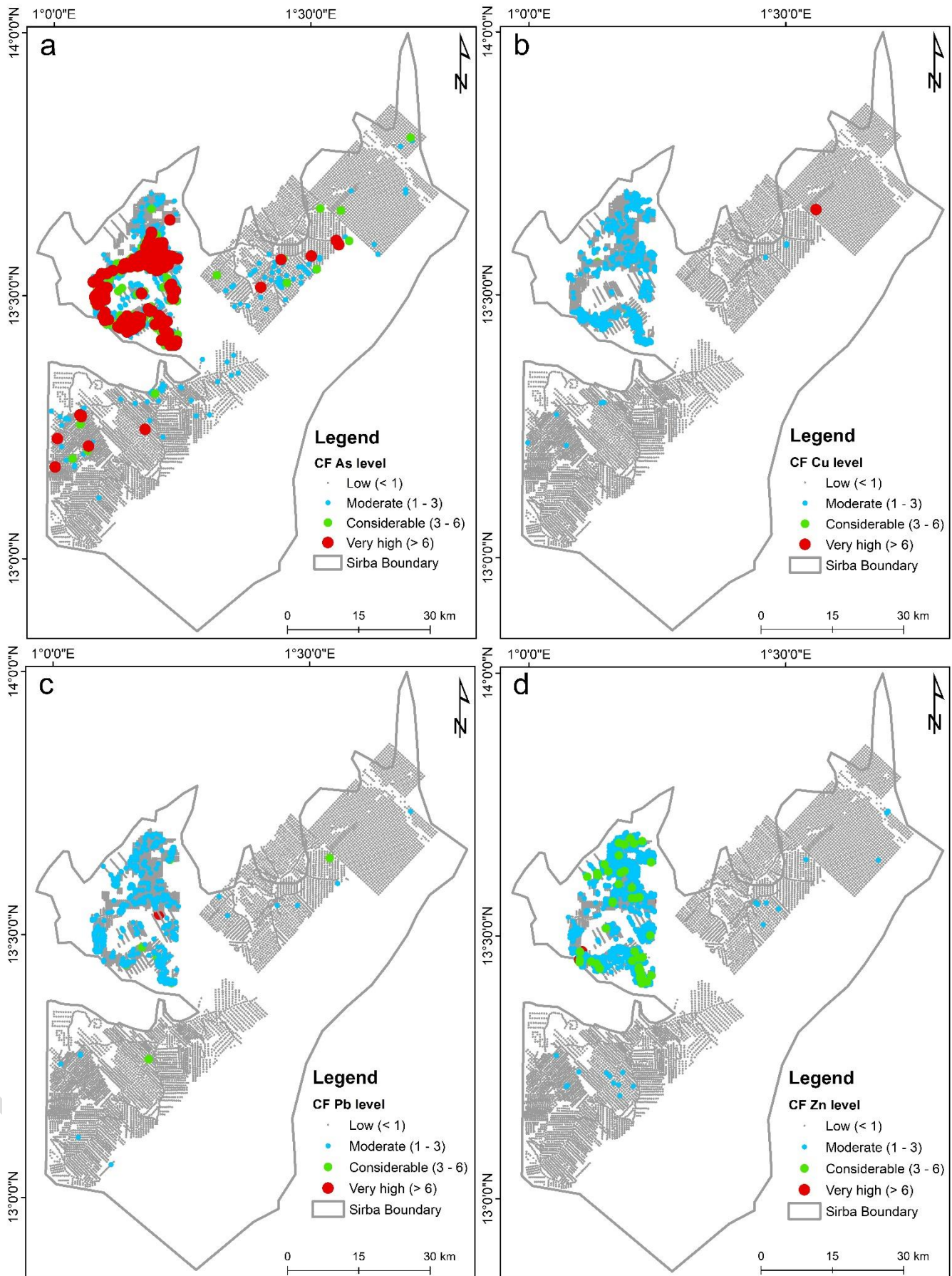


Fig. 3. Spatial distribution of As, Cu, Pb and Zn CF assessment classes for Sirba soils in 1994.

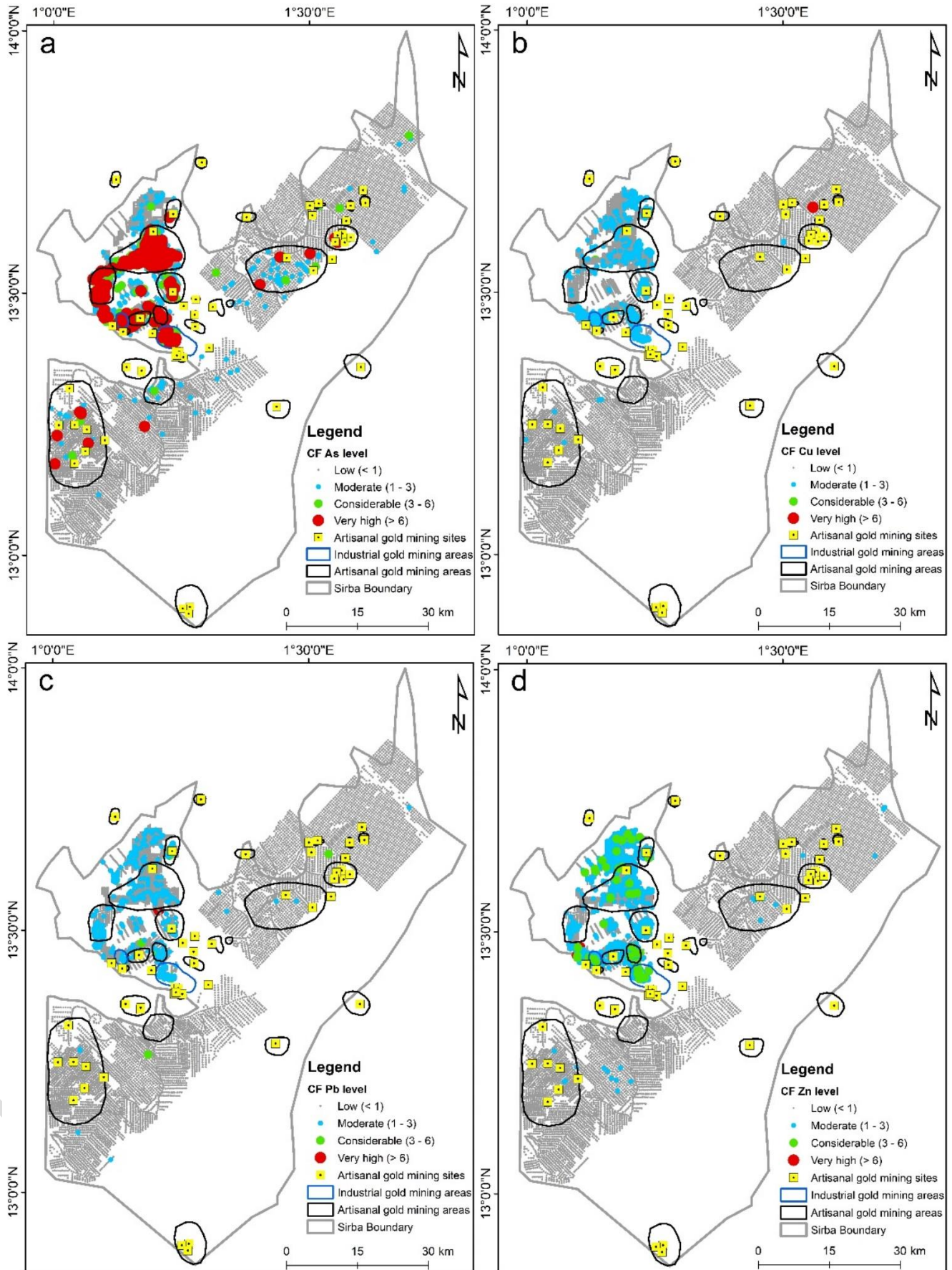


Fig. 4. Spatial distribution of Sirba soils CF classes in 1994 and gold mining areas and sites in 2024.

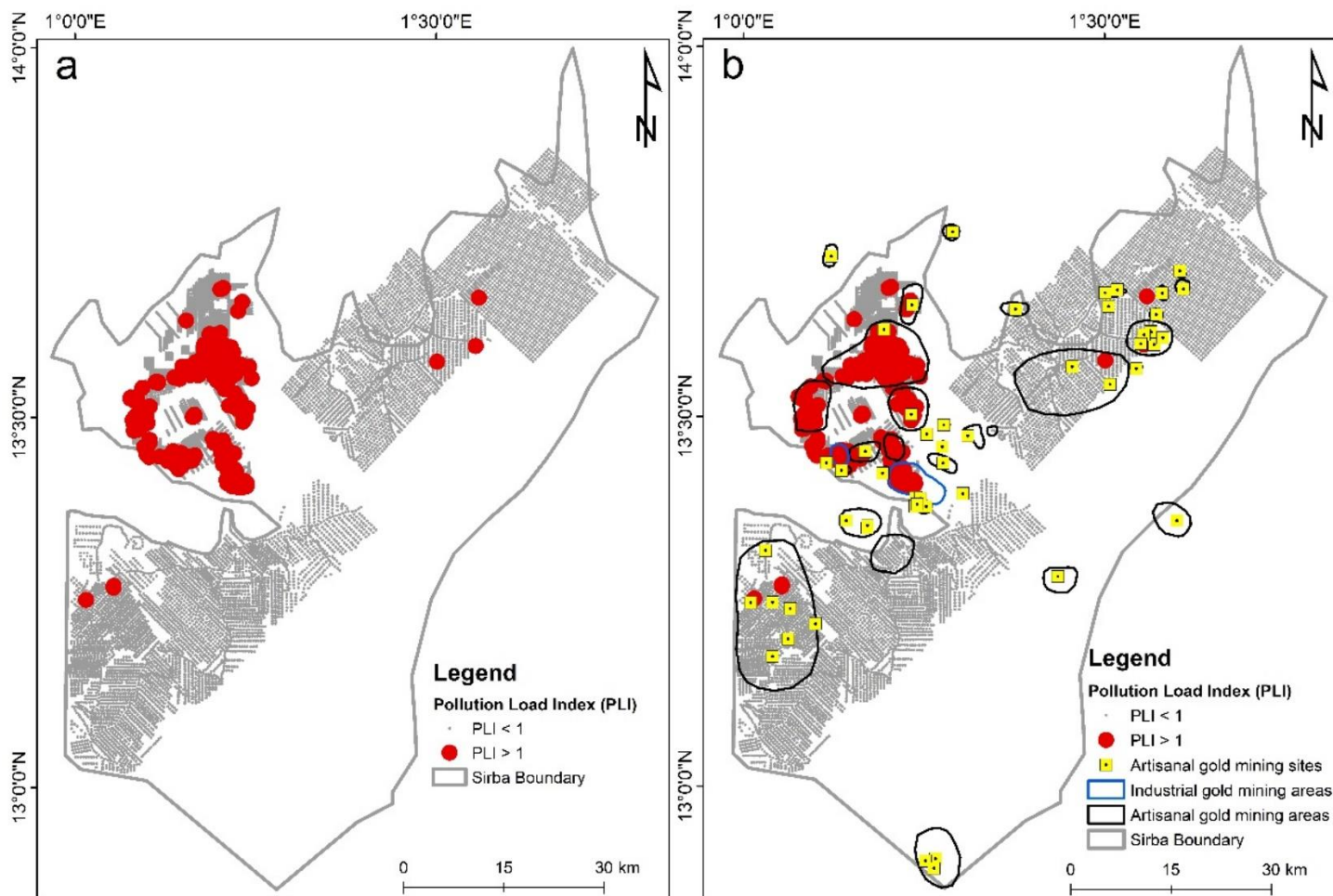


Fig. 5. Spatial distribution of Sirba soils PLI classes in 1994 (a) gold mining areas and sites in 2024 (b)

4. CONCLUSION

Soil geochemical data from the Sirba greenstone belt had made it possible to define As, Cu, Pb and Zn geochemical background values for the Sirba region. The geochemical background values were used to calculate pollution assessment indices (Contamination Factor, Pollution Load Index) for As, Cu, Pb and Zn elements. The Contamination Factor values showed that arsenic contamination was highest in soils, while copper, lead and zinc contamination was low in Sirba soils. The average of Sirba soils multi-element (As, Cu, Pb and Zn) pollution (PLI) was low. There was, however, some heavily polluted areas. This multi-element pollution developed mainly in the soils of the NE part of the Sirba belt, which had high arsenic Contamination Factor values. The Sirba gold mining areas had developed on zones with high pollution indices, particularly arsenic. The arsenic in the soils of the Sirba greenstone belt was therefore thought to have originated from gold mineralization.

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 this manuscript.

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