

Trace metals in cocoa soils exposed to illegal gold panning in central west Côte d'Ivoire.

Abstract

Côte d'Ivoire, the world's leading cocoa producer, is facing the challenge of illegal gold washing, which is likely to jeopardise its goal of a sustainable cocoa farming system. This is due to the degradation of soil resources through trace metal contamination (TM). The aim of this study is to determine the levels of copper (Cu), cadmium (Cd), lead (Pb) and arsenic (As) contamination in cocoa growing soils in Bonikro. 70 soil samples were collected using the toposequential method, processed and sent to the laboratory for analysis. The results show that TM levels vary significantly depending on the topographical position and depth of the soil. However, these levels are below tolerable **limits**. There are significant correlations between pH and TM, which vary with depth and topographic position. A strong positive correlation was observed at depth between pH and Pb ($r = 0.82$) and Cd ($r = 0.71$), whereas at the surface the correlations were negative for the same elements. This indicates that pH plays a crucial role in the evolution of TM concentrations. In conclusion, this study highlights the fact that cocoa-growing soils have TM levels below tolerable thresholds, but with significant variation as a function of depth and topographic position. Soil pH appears to be a determining factor in the mobility of TMs, which has important implications for the sustainable management of soils and the environment. Further research is needed to refine these observations and improve natural resource management.

Comment [DS1]: Mention tolerable limits ?

Keywords: Gold panning, trace metal, cocoa, soil management, **environment**.

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1. Introduction

Cocoa in Côte d'Ivoire generates more than 30% of export earnings and contributes more than 15% of gross domestic product (GDP) [1][2]. However, recent studies show a decline in the yields of cocoa plantations, partly due to the ageing of the plantations. This ageing of orchards, combined with climate change, is making certain regions increasingly marginal for cocoa production [3]. This is compounded by the state of soil fertility and soil acidification [4]. Soil acidification leads to the solubilisation of metals such as aluminium (Al), iron (Fe) and manganese (Mn), which then bind nutrients, particularly phosphorus (P) in tropical soils. In addition to these difficulties, for more than fifteen years cocoa farming has been facing a new challenge linked to the development of the mining sector.

Mining is known to be an activity that can lead to the degradation of soil resources through their contamination with trace metal (TM) such as lead (Pb), cadmium (Cd), arsenic (As) and copper (Cu) [5]. However, studies on the soil contamination levels of artisanal miners, who are generally illiterate farmers engaged in illegal and clandestine gold panning, remain patchy, and the case of the Bonikro mining area in west-central Côte d'Ivoire is illustrative. The remaining cocoa plantations are under attack from illegal gold panners, with the result that waste is dumped at various sites, which may contain chemical elements that accumulate

in the soil [6]. This situation could therefore jeopardise Côte d'Ivoire's goal of a sustainable cocoa farming system [7]. The aim of this study is to determine the level of TM contamination (Pb, Cd, As and Cu) in cocoa growing soils in Bonikro. In the current context, the aim is to assess the level of contamination of agricultural soils in this region, which is currently dominated by illegal gold panning, in order to identify the factors contributing to this contamination. The results will then be used to make recommendations for the sustainable management of agro-systems in mining areas and for environmental protection.

2. Material and Methods

2.1. the study site

The study was carried out in Bonikro, located in central west Côte d'Ivoire, in the Divo department. The department covers an area of approximately 3,577 km² and lies between latitudes 05°40' and 06°10' North and longitudes 05°30' and 04°40' West (Figure 1). The climate is transitional equatorial, with two rainy seasons and two dry seasons. The average annual rainfall is 1,400 mm and the average annual temperature is 25.3°C. The soils are predominantly ferralitic, highly desaturated and divided into three groups: plinthosols, ferralsols and gleysols. All these soils are the result of long and intense weathering, with a clay fraction composed mainly of kaolinite [8].

2.2. Soil sample collection and processing

Soil samples were collected from several cocoa plots in Bonikro using the toposequence method. A 30°N toposequence was opened and soil samples were drilled from 0-20 cm and 20-40 cm from the topographic positions to the shallows, with a rate of 10 samples per topographic level. The choice of sampling point per topographic position was based on the ability to report metal contamination of the soil. A total of 70 soil samples were collected from the study area. These samples were transported to the laboratory, crumbled by hand and then approximately 500 g of soil was dried in a room at room temperature according to ISO standard 11464:2006. After drying, each sample was sieved through a square mesh sieve ($\emptyset = 2$ mm) to collect the fine soil for laboratory analysis.

Comment [DS3]: Date of sample collection.

2.3. Chemical analysis of soils

Determination of soil pH

The fine soil obtained from each sample was divided into two parts. The first part was used to determine soil pH according to the method recommended in ISO 10390:2021. Specifically, 10 g of fine soil from each sample was placed in a 100 ml plastic beaker with 50 ml of distilled water. The mixture was stirred for 1 hour and then the pH was measured using a glass electrode in a dilute soil suspension. The reading was taken when the digital display of the pH meter had stabilised.

Determination of soil TM content

The TM content of the samples was determined by inductively coupled plasma atomic emission spectrometry (ICPAES) after mineralisation by hot acid etching of the samples with aqua regia (1/3 HNO₃ and 2/3 HCl).

2.4. Statistical analysis

All analyses were performed using R software. After checking for homogeneity and normality within groups, a one-way ANOVA followed by a Student-Newman-Keuls (SNK) test comparison was used to identify significant differences between the means of ETM content by topographic level at the 5% p threshold.

3. Results

3.1. Spatial distribution of trace metals (TM)

Analysis of the vertical variation of TM content and pH shows that depth has a significant effect on the content of Pb, Cd, As and pH in the soil. Cd (0.003 mgkg⁻¹), As (6.21 mgkg⁻¹) and pH (6.46) in the soil are significantly lower at depth (20-40 cm) than at the surface (0-20 cm), while Pb (0.16 mgkg⁻¹) is significantly higher at depth (20-40 cm). The Cu content shows no significant difference whatever the depth (Table 1).

Comment [DS4]: Level of significance.

Table 1. Average TM and pH levels as a function of depth and topographic position

Depth	TM (mgkg ⁻¹)				Acidity
	Pb	Cd	As	Cu	pH
Vertical variation					
0-20 cm	0,07b	0,04a	9,36a	6,65a	7,2a
20-40 cm	0,16a	0,003b	6,21b	6,46b	6,7b
Lateral variation					
Topographic position	Pb	Cd	As	Cu	pH
Lowland (BF)	0,13ab	0,03b	7,71b	7,84b	6,9b
Low lying area (BV)	0,16a	0,05a	7,03b	7,05b	7,9a
Top of slope (HV)	0,05c	0,02b	14,11a	9,39a	6,5c
Mid-slope (MV)	0,10b	0,003c	4,61c	3,54d	7,2b
Summit (S)	0,12ab	0,015bc	5,46c	4,95c	6,5c
Tolerable limit values(mgkg ⁻¹)	50	1,5	20	140	6,5-7,5

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The letters assigned to the averages (a, ab, b and c) represent the statistical differences between the average levels, where the values sharing the same letter are not statistically different from one another.

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3.2. TM distribution along the toposequence

Figures 1 to 5 illustrate the distribution of ETM values and soil pH along the toposequence around the gold mine. Analysis of the trends reveals a number of significant observations.

The elements As, Cd, Cu, Pb and pH show significant variations in content between positions BF, BV, HV, MV, S and depths 0-20 cm and 20-40 cm:

- The mean pH value (Fig.1) varies between positions BF, BV, HV, MV and S at depth 0-20 cm with a mean of about 6.70 ± 0.326 . At a depth of 20-40 cm, the average pH shows more pronounced variations, with an average of around 6.34 ± 0.58 at MV and 6.33 ± 0.578 at BF.

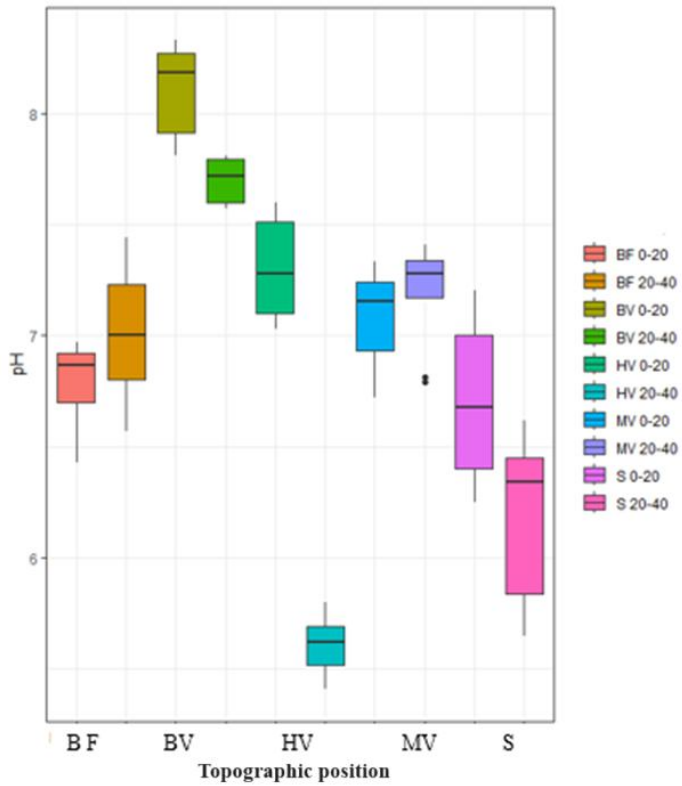


Figure 1 : Distribution of pH values according to topographic position

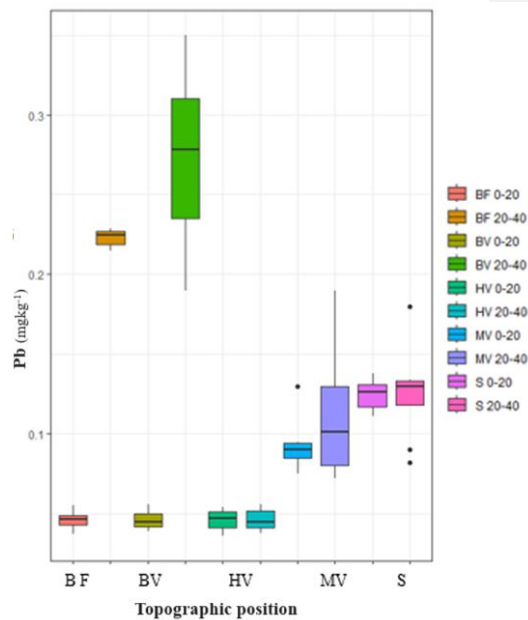
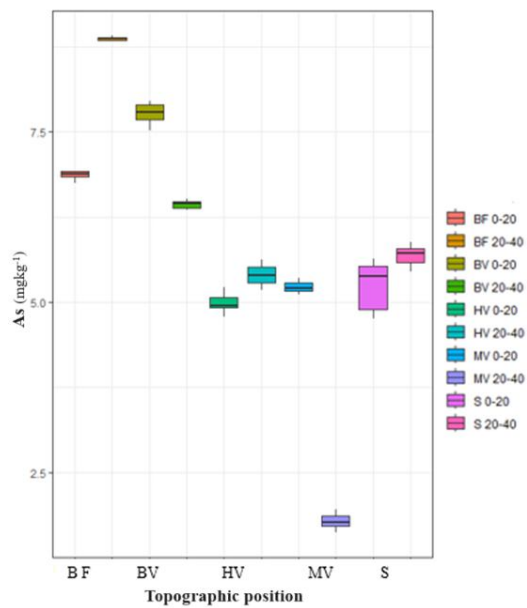


Figure 2 : Distribution of As content according to topographic position

Figure 3 : Distribution of Pb content according to topographic position

- The mean As contents (Fig. 2) are relatively similar between the BF, BV, HV, MV and S positions at 0-20 cm depth, with a mean of about $5.25 \text{ mgkg}^{-1} \pm 0.32$. However, at 20-40 cm depth, the mean As content decreases significantly to about $0.03 \text{ mgkg}^{-1} \pm 0.004$, indicating a different distribution in the deeper soil horizons. However, at depths of 20-40 cm, the mean As content decreases significantly to around $0.03 \text{ mgkg}^{-1} \pm 0.004$, indicating a different distribution in the deeper soil horizons.

- The average Pb content (Fig. 3) is very low at depths of 0-20 cm, with an average of about $0.002 \text{ mgkg}^{-1} \pm 0.0004$ at MV. At depths of 20-40 cm the average Pb content increases significantly to around $4.80 \text{ mgkg}^{-1} \pm 0.19$ at MV.

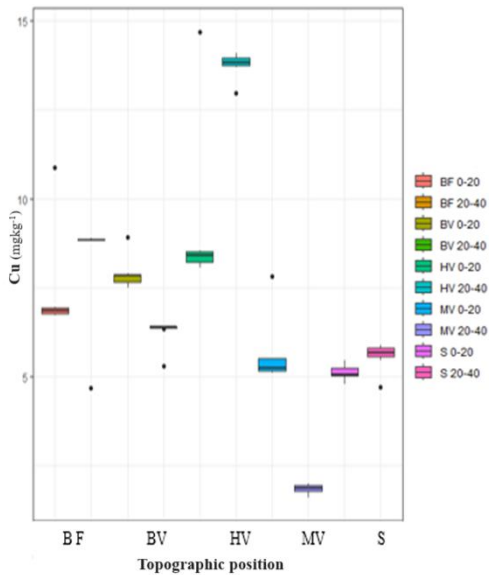


Figure 4: Distribution of Cd content according to topographic position

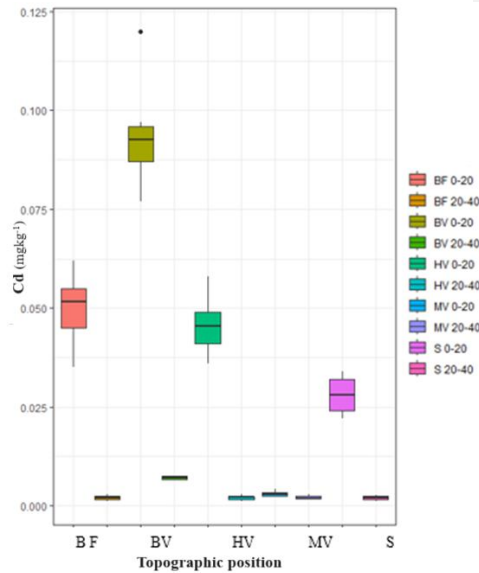


Figure 5: Distribution of Cu content according to topographic position

- Mean Cd contents (Fig. 4) varied between the BV and HV positions at depths of 0-20 cm, with a mean of approximately $5.10 \text{ mgkg}^{-1} \pm 0.18$ at BV and $6.70 \text{ mgkg}^{-1} \pm 0.33$ at HV. At depths of 20-40 cm, the mean Cd content decreased significantly at BV (approximately $0.12 \text{ mgkg}^{-1} \pm 0.009$) while remaining relatively stable at HV.

- The mean Cu content (Fig. 5) shows a significant difference between BF and MV positions at depths of 0-20 cm, with a mean of $6.70 \text{ mgkg}^{-1} \pm 0.33$ at BF and $5.68 \text{ mgkg}^{-1} \pm 0.13$ at MV. At depths of 20-40 cm, mean Cu concentrations show similar variations for all positions, with a mean of around $4.80 \text{ mgkg}^{-1} \pm 0.19$.

The trend analysis shows that the concentration of lead (Pb) in the soil varies significantly with depth. The coefficients for the different depths indicate that the Pb concentration tends to decrease with increasing depth. This trend is particularly pronounced for the HV position where the Pb concentration decreases significantly ($p < 0.001$). This suggests that lead levels in soil are higher at the surface (shallower) and decrease with depth.

As for cadmium (Cd), the trend analysis shows that the concentration of this metal also varies with depth. The depth BV coefficient indicates an increase in Cd concentration with depth, although this trend is not statistically significant. However, the MV depth shows a significant decrease in Cd concentration ($p = 0.00454$). This suggests that cadmium may accumulate more at the soil surface, while its concentration decreases with depth.

For arsenic (As), the results of the trend analysis show significant variations in concentration as a function of depth. The positive coefficient for the HV depth indicates a significant increase in arsenic concentration with depth ($p < 0.001$). In contrast, depths MV and S show opposite trends with significant negative coefficients. This suggests that arsenic may be more abundant at depth and less abundant at the soil surface.

For copper (Cu), the trend analysis shows significant variations in concentration as a function of depth. Depth BV shows a significant negative relationship with Cu, indicating that Cu concentration decreases with depth ($p = 0.0234$). Depth HV shows the opposite trend with a significant increase in copper concentration ($p < 0.001$). Similarly, depths MV and S show significant negative coefficients, also suggesting a decrease in copper concentration with depth.

For soil pH, the results of the trend analysis indicate significant variations with depth. Depth BV showed a significant positive relationship with pH, indicating that soil pH tends to increase with depth ($p < 0.001$). In contrast, depth HV showed a significant negative relationship with pH ($p = 0.00353$). Depths MV and S also show coefficients suggesting variations in pH with depth, although the trends are not as pronounced.

Table 2. Correlation between different variables as a function of depth

	0 – 20 cm					20 – 40 cm				
	Pb	Cd	As	Cu	pH	Pb	Cd	As	Cu	pH
Pb	1					1				
Cd	-0,641	1				0,715	1			
As	-0,812	0,241	1			-0,501	-0,117	1		
Cu	-0,893	0,692	0,851	1		-0,258	0,127	0,96	1	
pH	-0,546	0,728	0,218	0,612	1	0,821	0,642	-0,778	-0,597	1

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Overall, there were average to strong positive correlations between Cd, Cu, As and pH at all depths, and average to strong negative correlations between Pb, As and Cu at all depths (Table 2). However, there were differences between surface (0-20 cm) and depth (20-40 cm) correlations. There was a strong positive correlation at depth between pH and Pb ($r = 0.82$) and Cd and Pb (0.71), whereas at the surface the correlation was negative ($r = -0.54$) and ($r = -0.64$). The same observation is made for As ($r = -0.77$) and Cu ($r = -0.59$) with pH, which show negative correlations at depth, while at the surface there are positive correlations.

4. DISCUSSION

4.1. Mobility of TM in soil

The results of the spatial distribution of the concentrations of trace metals (As, Cd, Cu, Pb) and soil pH show that the concentrations vary significantly with topographic position and depth. The Cu content showed a slight variation with depth. This variation could be attributed to Cu migration and redistribution processes in the soil profile. In fact, [9] observed a gradual decrease in Cu content as a function of depth along a forest toposequence.

For cadmium, the results show that the content of this metal decreases with increasing depth. This is because cadmium tends to bind to soil particles, especially clay and humus. According to the work of [10], the content of organic matter in the soil could influence the retention of cadmium. This could explain the observed variation in cadmium levels with depth, as different depths could have different organic matter contents. Pb is a metallic element that is not very mobile in soil. Its high affinity with organic matter explains its high concentration in surface horizons [11]. In our case, the high concentration of Pb in the 20-40 cm horizon can probably be explained by the cultivation work in the cocoa plots.

The work of [12] showed a decrease in arsenic levels with increasing soil depth along a toposequence. According to this work, this trend could be attributed to vertical migration of arsenic from deeper geochemical sources. [13] showed that arsenic concentrations were higher in middle and upper slope areas. This distribution could be attributed to erosion and runoff processes of arsenic-rich particles from higher to lower areas of the toposequence.

4.2. Relationship between TM and pH

It is also important to note that soil pH can influence TME availability and mobility [14][15]. Our results show a strong relationship between pH and TMs. There is a strong positive correlation at depth between pH and Pb ($r = 0.82$) and Cd and Pb (0.71), whereas at the surface the correlation is negative ($r = -0.54$) and ($r = -0.64$). The same observation is made for As ($r = -0.77$) and Cu ($r = -0.59$) with pH, which show negative correlations at depth, while at the surface there are positive correlations. These results are in line with those of [16] and [17], who found either a decrease or an increase in the uptake of TM with pH, depending on the soil type. According to [18], metal concentrations are higher at $pH < 6$. This explains the low levels found in this study.

The correlations between the metals themselves give us information about the complex interactions that exist between the different MTEs in the soil. Among the MTs, we observe a relatively strong positive correlation ($r = 0.73$) between As and Cu, suggesting a certain consistency in their concentrations at different depths and positions. We also observed a very strong negative correlation ($r = 0.64$) between Pb and As, indicating that higher concentrations of one are associated with lower concentrations of the other.

5. Conclusion

The aim of this study was to determine the level of contamination of cocoa growing soils by illegal gold washing. The various results show that the levels of TM (Pb, Cd, Cu and As) in the soil are below tolerable thresholds. However, the levels vary according to the different topographic segments and the depth of the horizons. The pH could play an important role in

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the evolution of the TM levels, as it is strongly correlated with them. These results may have important implications for the sustainable management of soils and the environment. They also provide important insights into the distribution and interactions of metals in soils, which may have important implications for ecosystem health and soil quality. Further studies with larger samples could help to refine these relationships and provide more detailed information for effective management of natural resources.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Or authors name separated by & Snoeck, D., Koko, L., Joffre, J., Bastide, P., & Jagoret, P. (2016)

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Use of et al. After first author name

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