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Geochemical Baseline and Contamination Level Assessment of Antimony (Sb) in Sediment around Agbaou Gold Mine, Côte d'Ivoire

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Agbaou is one of the most recent gold mine exploitation sites in Côte d'Ivoire. Little studies are discussed on the geochemical baseline concentration of trace metals in the wetland sediments around Agbaou gold mine. The main objectives of this study were to establish geochemical baseline values and to assess the pollution status of antimony (Sb). The geochemical baseline concentration of Sb (GBC_{Sb}) was estimated using linear regression method. In this study, total Sb concentration was analysed in sediment (10 sediment samples) collected around Agbaou gold mine site. The average Sb concentration was 5.63 ± 2.50 µg.g^{-1} ranging from 2.50 to 11.3 µg.g^{-1}. The spatial distribution of Sb showed a tendency to accumulate near gold mine site. Moreover, the

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GBC_{Sb} (5.72 µg.g^{-1}) was slightly higher than the average concentration found in sediments. GBC of Sb was used to calculate the anthropogenic contribution rate (R) which exhibited a positive value (R > 0) for all samples, indicating that the sediments were influenced by gold mining activities. Due to lack of local baseline value in the study area, the GBC_{Sb} obtained could be used as reference value for Sb contamination level assessment in the sediments.

Keywords: Antimony; geochemical baseline; gold mine; sediment; anthropogenic contribution.

1. INTRODUCTION

Gold mining activities are classified among the main sources of heavy metals in environment [1]. Through processing, milling and disposal tailings a considerable number of gases, aerosols and particulate matter containing metals that can be fixed by sediments [2]. Sediments polluted by heavy metals can pose direct harm to benthonic organisms, plants and human health. Heavy metals in sediments can be released into overlying water by reactivation and then affect the health of aquatic ecosystem and humans which are at the top of food chain [3]. Among trace metals, antimony (Sb) and its compounds are matter of concern since trace metals exposure can result in acute toxicity effects on the skin, eyes, lungs, intestines, stomach, liver, kidney, and heart [4]. Identified as a toxic pollutant, U.S. Environmental Agency (USEPA) [5] and European Union (EU) [6] Sb induced priority interest in many countries. Antimony contamination levels in soil/sediment is mainly assessed using index evaluation methods [7,8]. Whereas, these contamination levels result vary considerably with background concentration. Furthermore, the conventional background (e.g., metal concentrations in the crust, preindustrial concentrations) does not consider the natural variation of metals across regions [9,10]. In fact, a geochemical baseline levels have been used as reference values in assessments of the degree of pollution based on sediments [11]. Linear regression with inert elements (Mn, Fe, or Al) that are not influenced by anthropogenic activities can be used to define geochemical threshold.

In Côte d'Ivoire, several widespread studies are focused on sediments and biota contamination by trace metals. Overall, these studies indicated that sediment collected in urban area [12] in gold mining area [13] and in agricultural areas (Ouattara et al., 2019) were obviously contaminated by arsenic, cadmium and mercury. The upper continental crust (UCC) concentration established by Wedepohl [14] which reflect the average content of the element in Earth's crust, used as background values in these studies, does not account for the significant anthropogenic influence on the geochemical processes occurring in the specific studied areas. Despite, several studies conducted in different regions of the country to estimate contamination levels, no study has yet discussed the geochemical baseline concentration in sediment impacted by gold mining exploration. The main objective of this study was to estimate Sb contamination level in sediment and geochemical baseline value using statistical methods.

2. MATERIALS AND METHODS

2.1 Study Area

Agbaou village (06 08 °N, 05 11°W) is located in central southern of Côte d'Ivoire is a sub-Saharan nation in southern West Africa. The study area was carried out in wetlands around the Agbaou gold mine, which the exploitation permit covers an area of 334 km^2. The geology dominated by the Archean-Proterozoic man Shield, which forms the southern half of the larger West African Craton, which makes it a mining area. Gold occurs in mesothermal auriferous sulfide (pyrite + pyrrhotite) assemblage associated with quartz veins (Technical report, 2012). Started in the third quarter of 2013, the operations consist mainly to open pit mining and gravity/CIL facilities, with an average gold mined grade estimated of 1.97 g/t Au. The climate is equatorial, with average annual temperature range between 21 and 33°C and the precipitation reaching up to 1900 mm. The study area is drained by Bandama River.

2.2 Sampling and Chemical Analysis

A total of 10 top 0 – 5 cm sediment samples were collected during summer and winter periods from February to December in 2015 (Fig.1). In order to take the local variability into account, each sample (300 g) was made of five sub-samples collected using a Van Veen stainless steel grab (with an area of 0.02 m^2). Samples were then put into ice bags and transported to the laboratory, stored in a deep-freeze unit before the drying procedure. Sediment samples were air-dried at room temperature, ground with an agate mortar to pass through a 63 µm sieve and stored in polyethylene zip-type bags for further analysis. All sampling devices were cleaned by rinsing with pure water and kept in 0.1 M HNO_3 (68%, Fischer Scientific) for several days before sampling.

Sediment samples (0.5 g) were digested in triplicate with aqua regia (HNO_3: HCl; 3:9; v/v) in a microwave system (Milestone Ethos 1 microwave, Shelton, US) following Method 3051 A [15,5]. The Sb, Al and Fe concentrations in the digested sediment samples were analyzed using inductively coupled plasma-optical emission spectrometer (ICP OES Icap 6200, Termo Fisher, Cambridge, UK). Accuracy and precision of the analytical procedures were evaluated through the analysis of the certified reference material CRM CNS 301-04-050 (Sigma-Aldrich; Missouri, U.S.A) for freshwater sediment. The measured concentrations fell within the range of certified values, and the recoveries varied between 95% and 110%. Arcgis 10.2.1 software as used for Sb

2.3 Geochemical Baseline Concentration (GBC) of Sb in Sediments

GBC concentration has been widely applied to differentiate between anthropogenic and natural source concentrations of trace metals in sediments or soils [16,8,17]. The GBC calculation requires a normalization method base on linear regression equation obtained from the correlation of concentration between the element in question (in this case, Sb), and a conservative reference element [18]. This study used inert elements (Al and Fe) reference. The geochemical baseline model was defined by the following equation:

$$C_{Sb} = a \times C_{inert} + b \qquad \text{(Eq.1)}$$

Where C_{Sb} and C_{inert} are the concentrations of Sb and of the inert element (Al and Fe), respectively, while a and b are the regression constants.

In the scatterplot described by Eq. (1), data within the 95% confidence limit were characterized as naturally sourced. Data outside the 95% confidence limit were characterized as having anthropogenic sources [16]. Data from the anthropogenic sources were removed, and a linear regression was fitted to the remaining data from natural sources with new regression constants (c and d). We subsequently arrived at the following equation:

$$C_{Sb} = c \times \bar{C}_{inert} + b \qquad \text{(Eq. 2)}$$

Where C_{Sb} is the GBC_{Sb} (µg/g) and $\bar{C}_{inert}$ is the average concentration of the inert element sample inside the 95% confidence limit (µg/g) and c and d are the new regression constants. Using the average concentration of remaining data for inert element, the naturally sourced Sb concentration was obtained. This value was defined as the GBC value of Sb.

2.4 Anthropogenic Contribution of Sb Calculated by GBC

According to previous study, the geochemical baseline can also be used to calculate the influence of anthropogenic activities in the various sampling using the GBC method [17,18]. Therefore, the contribution rate (R) of anthropogenic input on the Sb source in the sediment from Agbaou gold mine, was calculated as follows (Eq.3)

$$\mathrm{R}\,(\%) = \frac{C_{metal} - C_{baseline}}{C_{baseline}} \times 100 \qquad \text{(Eq.3)}$$

Where C_{metal} and $C_{baseline}$ are the concentrations (in $\mu g.g^{-1}$) of Sb at each sampling point, and GBC concentration ($\mu g.g^{-1}$) at each sampling site, respectively. If R > 0, it indicates anthropogenic input; R ≤ 0, it indicates natural source.

2.5 Statistical Analysis

Statistical analysis was performed using STATISTICA (ver. 7.0) packages significant Pearson's (r) correlation coefficients were determined and mean metal concentration was compared using one-way analysis of variance, ANOVA, at 5% significance level, after testing for normality of the data.

3. RESULTS

3.1 Concentration Level of Antimony in Sediment

The concentrations of Sb in sediments were presented in Table 1. Sb concentrations varied from 2.5 $\mu g.g^{-1}$ to 11.3 $\mu g.g^{-1}$. The average concentration of Sb in sediment was 5.63 ± 2.50 $\mu g.g^{-1}$. The highest concentration was found at A4 sampling sediment point, which was enclosed to the gold mine site. Whereas, the lowest concentration of Sb was recorded at A7 sampling point.

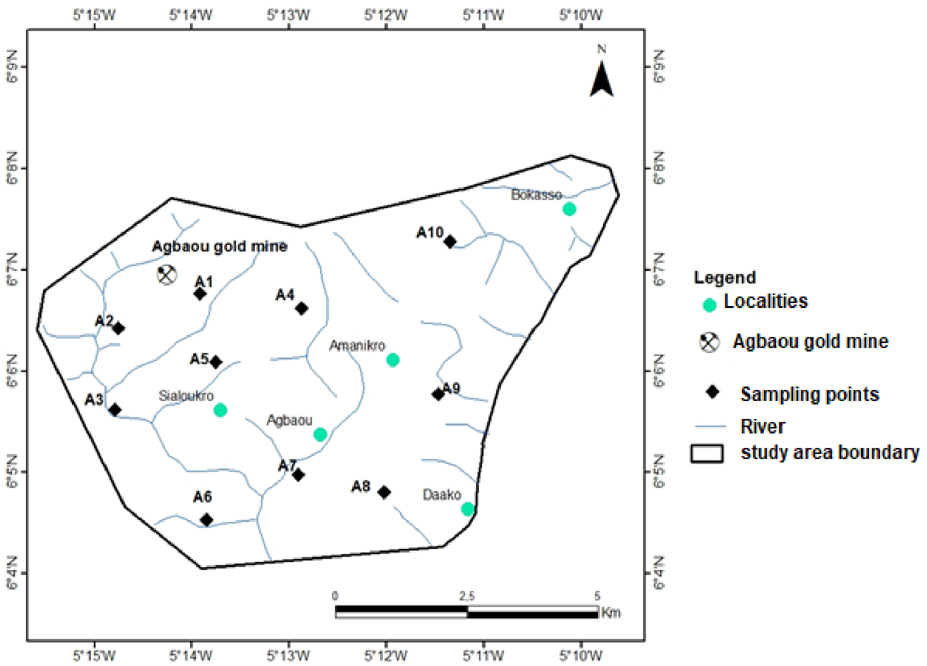

Fig. 1. Study and sampling points location

Table 1. Sb concentrations in sediment collected around Agbaou gold mine

Sampling points	Sb concentrations (µg.g)$^{-1}$
A1	6.02
A2	7.10
A3	8.00
A4	11.3
A5	4.90
A6	4.77
A7	2.50
A8	5.10
A9	3.70
A10	2.90
Mean	**5.63**
SD	**2.50**

SD : the standard deviation

3.2 Spatial Distribution of Antimony

Antimony spatial distribution map was outlined in Fig.2. It appears clearly that the higher content of Sb was found at sampling points near of the gold mine. Whereas, beyond gold mine equipment, Sb concentrations in sediment decrease significantly.

3.3 Anthropogenic Contribution of Sb Calculated by GBC

The GBC of Sb (GBC_{Sb}) and its anthropogenic distribution were then calculated. The principle selection of the inert elements was as follows : (1) the inert element was significantly correlated to the naturally occurring concentrations of the elements of interest ; (2) the reference element was not added or only added in the natural quantity by anthropogenic sources ; (3) the reference element was stable and not subject to environmental influences such as reduction/oxidation, adsorption/desorption, and other diagenetic processes ; and (4) the concentration of the reference element could be accurately determined quantitatively [19]. In this study, the relationship among the two inert elements (Al and Fe) and Sb concentrations in the sediments are presented in Fig. 3.

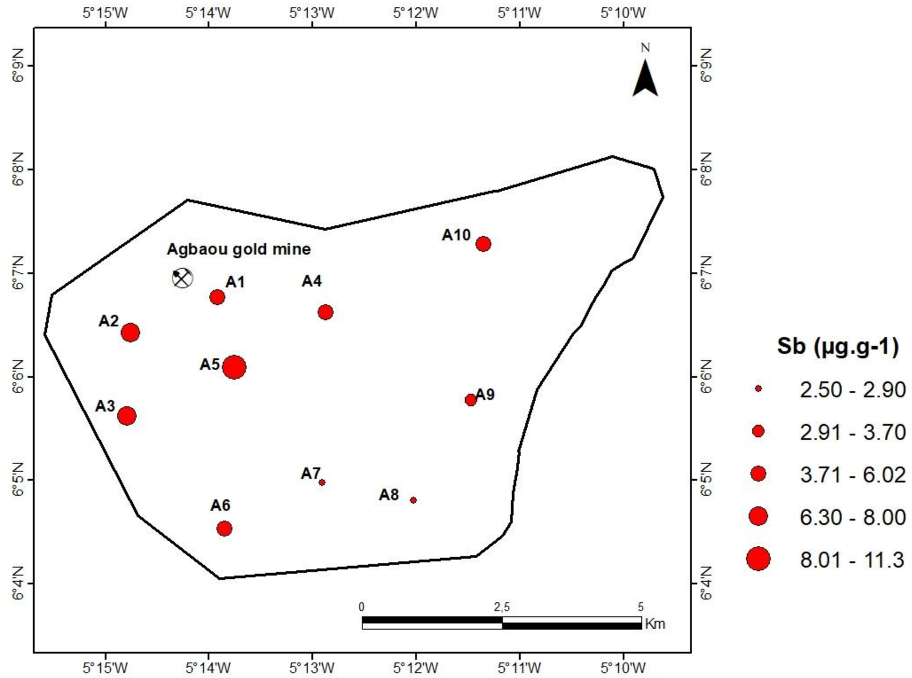

Fig. 2. Spatial distribution of Sb concentration in sediment

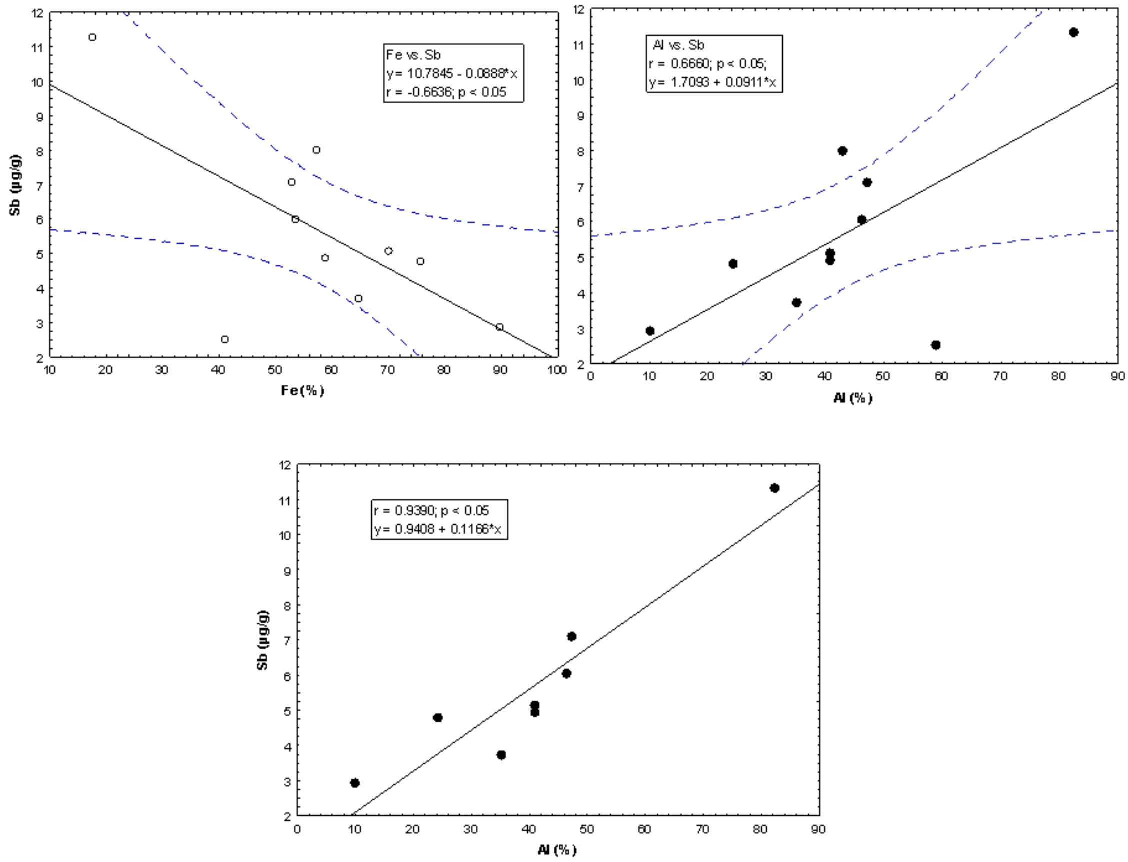

Fig. 3. Inert elements screening and establishment of geochemical baseline concentration of Sb in sediment

The r value of Al (r = 0.6660) obtained was higher than the one of Fe element (r = -0.6636). According to principle of selection above, Al was chosen as the inert (reference element) to evaluate the GBC_{Sb} values in sediments. Based on the method presented previously, the sampling points outside the 95% confidence limit were characterized as anthropogenic sources and were removed and the remaining data were used to determine the GBC_{Sb}. In terms of above Equation (2), a value obtained for GBC_{Sb} was 5.72 µg. g^{-1} which was approximate to the average of Sb concentration in sediment (5.63 ± 2.50 µg. g^{-1}). This suggested a slight influence of anthropogenic sources on the Sb content in sediments.

According to Equation (3), the average contribution of Sb was (252%), which suggested that the Sb in sediment was mainly originated from anthropogenic source. Highest anthropogenic contribution values (400%), was exhibited in sediment from samples A4, indicating that anthropogenic input was present in this sample.

3.4 Statistical Analysis

The Pearson correlation coefficients for Sb concentration and previously physicochemical parameters (total organic carbon (TOC) content, clay+ silt and pH) in sediments from Agbaou gold mine are presented in Pearson matrixes below (Table 2).

Pearson statistical analysis indicated negative relationship between Sb concentration and TOC and Clay + silt ($p < 0.05$), whereas Sb concentration showed weak but positive correlation with pH_{H2O}. This probably indicates that Sb distribution in sediment was not determined by TOC and fine grain size.

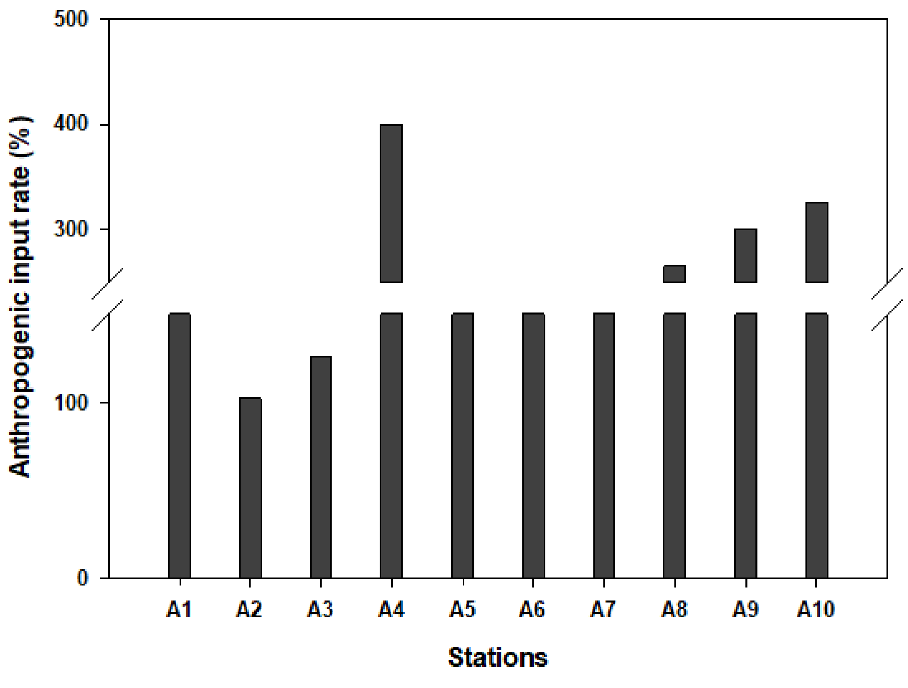

Fig. 4. Anthropogenic contribution of Sb in sediment collected around Agbaou gold mine

Table 2. Correlation matrix for Sb concentrations, TOC and Clay+silt

	Sb	**Clay + silt**	**pH_{H2O}**	**TOC**
Sb	1			
Clay + silt	-0.06	1		
pH_{H2O}	0.39	-0.76	1	
TOC	-0.39	-0.40	0.40	1

4. DISCUSSION

In current study, Sb baseline concentration was determined with geochemical baseline concentration in sediment collected around Agbaou gold mine. Agbaou gold mine exploration and commercial exploitation were started in 2012 and remain active. Unfortunately, the lack of "natural background" that strictly refers to the pristine geochemical composition does not exist, and forced researchers to use upper continental crust (UCC) concentration determined by Wedepohl [14] as natural background concentration value for trace metals. The Sb concentrations were less than the ones recorded in sub-regions. Indeed; Sb concentrations reported in Ghana (6.88 ± 0.38 µg/g); Nigeria (20.2 µg/g) and, South Africa (11±6 – 24±7 µg/g) [20-22]. gold mining areas. The low levels of antimony might be that tailings rain-washed into the water bodies have low levels or no antimony. The mining activities may probably release extremely low levels of antimony into the environment, and that the sediment are unaffected by the mining activities with regards to antimony release. Secondly, the relatively low level of antimony is probably since anthropogenic antimony inputs are either very low or non-existent. Nevertheless, the spatial distribution showed that the hot spots of Sb concentration were observed around the gold site, where it could have been transferred to the river by water erosion process. Similarly, Sb pattern distribution was observed near mining areas in Iran [23], Bolivian [24] and Macedonia [25].

The regression analysis is often used to construct geochemical baseline, for it can the influence of anthropogenic and reveal the geochemical natural background concentrations of elements [26-28]. In this study, the geochemical baseline concentration of Sb was 5.72 µg. g^{-1}, and positive anthropogenic contribution (R > 0) was found. These suggested that Sb in sediment from Agbaou gold mine demonstrate high anthropogenic influence. Whereas, the slight anthropogenic influence was observed somewhere. In overall, due to the lack of antimony geochemical baseline value for the study area, our result (GBC_{Sb} = 5.72 µg. g^{-1}) could be used as comparative reference to explore the environmental quality or evaluate the disturbance (natural or anthropogenic) degree in the future.

Although geochemical baseline study was approved method, our study present certain limitations. The sample size was very small and a statistically appropriate number of sediment samples from impacted and control sites should be included. On the other hand, certain limitations such as diversity in the sampling media and information on the concentration levels of organic compounds should be consider in further research.

5. CONCLUSION

This study aimed to identify the possible pollution source of antimony in the sediment collected near Agbaou gold mine site based on the metal geochemical baseline calculated by statistical methods. The average concentration of Sb was 5.63 ± 2.50 µg. g^{-1}, which was less than the ones reported in sub-regions. The spatial distribution of Sb in sediment confirmed that Sb concentration decreased as one further away from the gold mine. However, Pearson's correlation between Sb contents and physico-chemical parameters (TOC, clay+silt, and pH) revealed that Sb distribution in sediment was not affected by fine grain size particles and the organic carbon contents. The geochemical baseline concentration (GBC) of Sb in surface sediment was 5.72 µg.g^{-1}. The anthropogenic contribution rate reaches up to 400 %, indicating high anthropogenic originate inputs.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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