Water Quality Monitoring in the Pra Basin of Ghana

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Abstract

This study is a water quality monitoring of physicochemical and metals of potential toxicity in the Pra Basin of Ghana. Four samples were collected from each of the eight sampling sites from upstream to downstream of the basin. Six major physicochemical parameters namely pH, turbidity, nitrates, phosphate, Chemical Oxygen Demand, and Biological Oxygen Demand were monitored. Four metals of potential toxicity namely arsenic (As), lead (Pb), manganese (Mn), and iron (Fe) were also monitored. The measured pH, phosphate, and nitrates were all within the permissible level in all the sites studied. The turbidity, COD, and BOD were all above the permissible level in all the sites. Among the eight sites under study, only Barekese did not exceed the permissible level of the metals of potential toxicity. Arsenic concentration exceeded the permissible limit for all the sites except Barekese. All the sites recorded manganese concentration above the permissible level except Barekese and Brenase. Aside from Shamaa and Barekese, all the sites recorded lead concentrations above the permissible level. The *Igeo* in the study area is in the range of "uncontaminated" to "moderately" to "strongly" contaminated. Regarding manganese and arsenic enrichment, only Brenase was enriched with arsenic. Dunkwa, Akim, and Deboase were the only sites enriched with lead. The pollution load index indicates that none of the sites was polluted by any of the metals. Arsenic is the only metal that measured extreme contamination among the metals studied. The contamination factor of the metals is in the order arsenic > lead > manganese > iron. Dunkwa, Barekese, Adiembra, Deboase, and Shamaa all recorded low ecological risk for arsenic whereas Praso < Akim < Brenase in that order recorded moderate ecological risk for arsenic. Manganese and lead pose a low ecological risk in all the sites under study.

Subject Areas

Environmental Sciences

1. Introduction

Protecting water resources to ensure their sustainable use by future generations is a critical concern faced by developing countries. The early years of the industrial revolution in developed countries are no different from those of most developing countries presently. One is tempted to think that most developing countries are not taking advantage of the rich wealth of information available to avoid mistakes being repeated. During the revolution, little attention was paid to the environment and ecosystem sustainability, which is the case in most developing countries today. The situation in Ghana is a case in point. The release of elements of potential toxicity from legal and illegal mining sites and nutrients from agricultural fields is compounding the problem of pollution being caused by untreated wastewater from industries to water bodies. Unfortunately, regular monitoring of rivers in Ghana is not routine as it happens in other developed countries. The absence of routine monitoring has been compounded in Ghana by illegal mining, popularly known as "galamsey" ("gather them and sell") which has swallowed many other associated environmental problems due to the havoc it has caused to water bodies. Different ruling governments have tried many strategies to stop "galamsey" but yielded no fruitful results. The recent intervention has been operation vanguard which was introduced about six (6) years ago to stop illegal mining and introduce planting for food and jobs to take miners out of the mining sites. The present intervention was anticipated to reduce the problem emanating from "galamsey" to some extent and improve the quality of the water resources. As stated in my previous publications on integrated water resources management and water quality [1], observable features in the field seem to contradict what has been documented hence the need to constantly monitor the water resources and assess the ecological safety of the environment. This study is a follow-up on the 2016 monitoring that was done to assess the quality of the water resources after the first stage of implementation of integrated water resources management in the Pra Basin. The study showed a significant deterioration in the quality of the river after the first stage of implementation of integrated water resources management (IWRM). Interventions when introduced are meant for positive changes but sometimes the opposite is observed as was the case of that study. The new government's campaign promises to abolish galamsey and his subsequent introduction of "operation vanguard" to drive illegal miners out of their site have generated debates and doubts about its effectiveness and efficiency. Some section of the population believes that the intervention is impractical and targeted at the enemies of the government. These ideas have been rubbished by the state institutions responsible for regulating

mining in the country. One thing that remains undisputed is that there are no observable changes in the quality of the water esthetically. However, these observations are not enough, they must be scientifically proven, hence this monitoring. This study is extensive and covers the upstream through the midstream to the downstream and focused on both physicochemical parameters and some selected potentially toxic elements, unlike the previous study that considered only physicochemical parameters. In summary, in the present study, the physicochemical parameters will be assessed, and the levels and ecological toxicity of potentially toxic elements will be measured. Finally, some selected fishermen within the catchment of the river will be interviewed on the observed changes in fishing to augment the quantitative data gathered.

2. Study Area and Sampling

The study was carried out in the Pra basin with a population of 4.2 million and a growth rate of 2.2% per annum [2]. The basin cut across the Ashanti, Central, Eastern, and Western regions of Ghana with 43 administrative districts, municipal, and metropolitan assemblies. The climate is sub-equatorial wet and has two rainy seasons with May and July as the major rainy season and September-November as the minor season. The basin is located between Latitudes 50N and 70˚30'N, and Longitudes 20˚30'W, and 00˚30'W, in south-central Ghana. The basin is scattered with unregulated illegal mining sites, however, the eight sites which were considered for previous studies by Duncan *et al.*, [1] will be considered for this monitoring purpose. Sampling was done from the upstream to the downstream as displayed in Figure 1. The Pra River takes its source from the Kwahu plateau in the North and travels through 240 km to join the Gulf of Guinea in the town of Shama. A total of 40 water and soil samples each were collected from 8 sampling points, into laboratory-cleaned and rinsed 1.0 L polyethylene bottles and 0.1 L polyethylene containers respectively. Samples were collected from January to April 2022. Water samples were acidified with 0.24 M nitric acids (analytical grade) and kept in an ice chest (at 4˚C) and sent to the Water and Sanitation Laboratory at the University of Cape Coast for analysis. For the water samples, 50 mL of a well-mixed acid-preserved sample was transferred to a boiling tube and 5 ml HNO_3 was added. The mixture was heated at 130˚C in a graphite block digester till the volume was reduced to about 25 - 20 mL. The addition of nitric acid and heating was repeated until the solution became light-colored or clear. The solution was cooled and made to the desired volume using deionized water and filtering through Whatman no. 41 filter paper. Sediments were taken from Barekese where no illegal mining activities are identified as a control. In addition, laboratory blanks and duplicate samples were taken. The sediments were sampled from the riverbank using Ekman grab sampler into polyethylene bags. Sediment samples were transported to the laboratory and dried at room temperature for about seven to nine days. The dry sediment was crushed using a mortar and pestle to homogenize and sieved (0.2 mm)
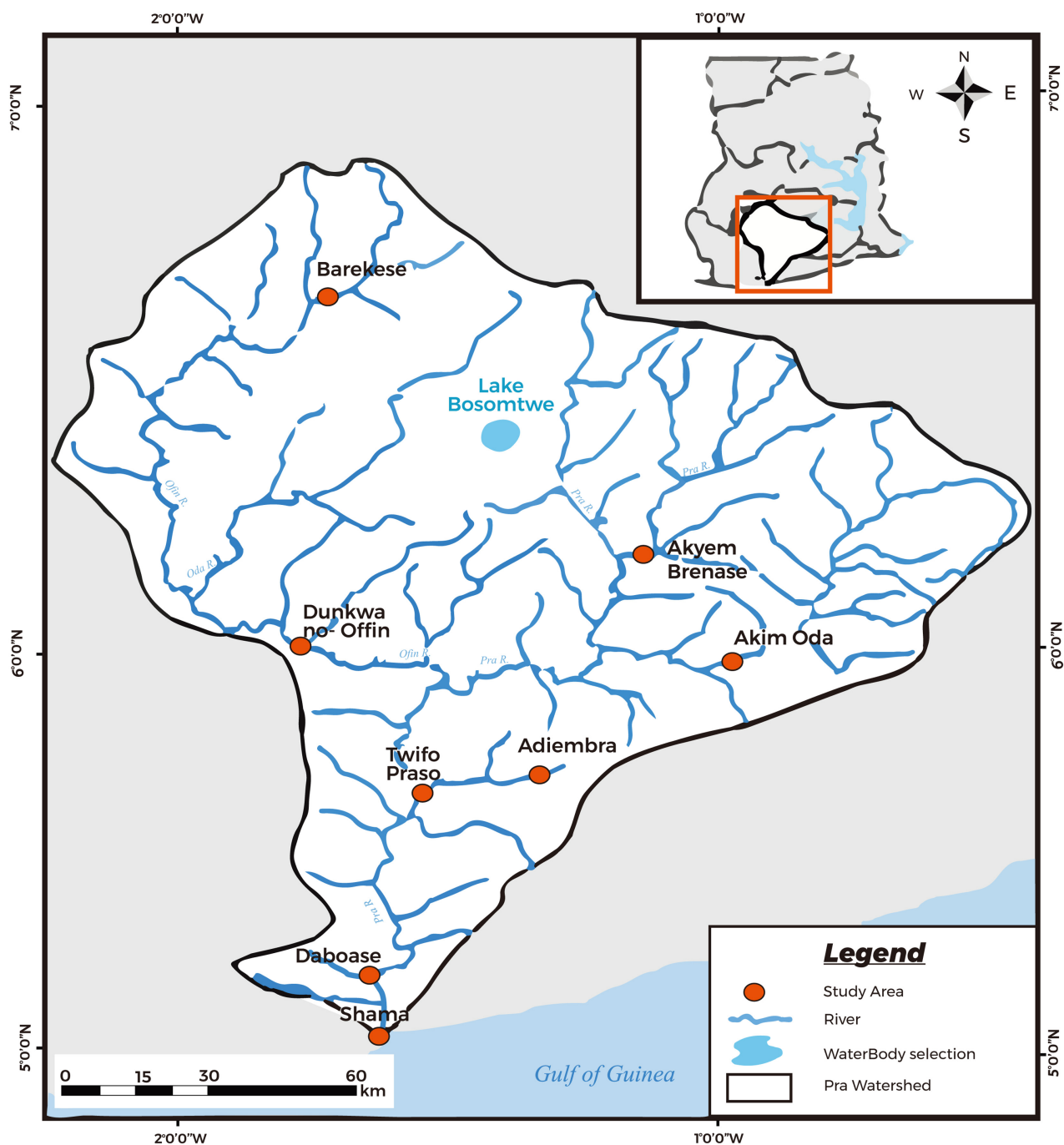
Figure 1. Sampling points in the Pra Basin.

to have dry fine samples. The sieved sediment was further ground with mortar and pestle until fine particles (<200 μm) were obtained [3]. About 2 g of the ground sediment was taken in a 100-mL beaker and 15 mL of concentrated HNO_3 was added. The content was heated at 130˚C for 5 hours until 2 - 3 mL remained in the beaker. The digested sediment was then passed through Whatman no. 41 filter paper and further washed with a 0.1 M HNO_3 solution and diluted to 100 mL volume [4]. US-EPA Method 3052 procedure for digestion was

followed [5]. The heavy metal determination was conducted using a dual atomizer and hydride generator atomic absorption spectrophotometer (model ASC-7000 No A309654, Shimadzu, Japan). All the samples were analyzed for arsenic (As), lead (Pb), manganese (Mn), and iron (Fe). The standard for AAS calibration was prepared by diluting standard (1000 ppm) supplied by MES Equipment Limited, Ghana. Matrix Spike recovery was in the range of 82% - 100%. The performance of the AAS was checked daily to ensure that the instrument is working according to the specifications. Concerning the interview, the focus was on any observed changes in fish harvest, species present, fish size, and what may account for the observed changes. All 8 fishermen were interviewed with one each from the eight sites. The questions were open-ended questions to allow the fishermen to express their views on the situation at stake. Questions such as 1) What changes have you observed in the fish harvest presently from the past? 2) What changes have you observed presently with the type of fish species in the river and their sizes from the past? 3) What will you associate any observed changes to?

3. Analytical Techniques and Accuracy Check

The heavy metal determination was conducted using a dual atomizer and hydride generator atomic absorption spectrophotometer (model ASC-7000 No A309654, Shimadzu, Japan). All the samples were analyzed for arsenic (As), lead (Pb), manganese (Mn), and iron (Fe). All reagents used were of the analytical grade from MES Equipment, Ghana. Ultrapure metal-free deionized water was used for all analyses. All glass and plastic wares were cleaned by soaking them in warm 5% (V/V) aqueous nitric acid for 6 hours and rinsed with ultrapure deionized water. The standard for ASS calibration was prepared by diluting standard (1000 ppm) supplied by MES Equipment Limited, Ghana. All measured results for soil samples were converted from milligrams per liter to milligrams per kilogram. Matrix Spike recovery was in the range of 85% - 100%. For ensuring that the quality of the research is maintained and produces reliable results, the performance of the AAS was checked daily to ensure that is working according to the specification. The indexes that would be employed in this study are briefly explained in the section that follows.

3.1. Assessment of Heavy Metal Pollution

The elements of potential toxicity in the water and soil will be interpreted using indexes such as the, geo-accumulation index, enrichment factor, pollution load index, contamination factor, and ecological risk assessment for soil samples.

3.2. Geo-Accumulation Index (*Igeo*)

In the year 1979, Muller [6] developed the geo-accumulation index to assess the level of elements of potential toxicity and metalloid elements in sediments by comparing the status of the current concentration with that of the pre-industrial

level [7]. The formula for its calculation is mathematically given as:

$$Igeo = \log 2 \left[\frac{[C_n]}{[1.5Bn]} \right] \tag{1}$$

where C_n is the concentration of metals in sediment (mg·kg^{-1}); Bn is a pre-industrial geochemical concentration or reference value of the heavy metal in a particular area; 1.5 is the background matrix correction factor due to lithogenic effects. In this study, iron (Fe) was used as the element of normalization for the reasons that follow: 1) its distribution in the natural environment is uniform and is the fourth major element in the earth's crust; 2) its geochemistry is alike to those many trace elements 3) commonly associated with fine solid surfaces [8]. The *Igeo* and its classification are presented in **Table 1**.

3.3. Enrichment Factor and Pollution Load Index

The enrichment factor is a very useful index for the assessment of the enrichment level of metals and metalloids in sediment. The factor was developed by Zoller [9] and is mathematically expressed as:

$$EF = \frac{A_i}{A_o} \Big/ \frac{B_i}{B_i} \tag{2}$$

$[A_i]$ and $[B_i]$ are the concentrations of elements A and B in mg/kg at sampling station i; $[A_o]$ and $[B_o]$ are the background concentrations of elements A and B mg/kg. Values estimated for EF from Equation (10) provide the pollution state of the sediment. Values of $0.5 \le EF \le 1.5$ are an indication that the metal concentration is a natural weathering process [10]. A value above 1.5 indicates the influence of anthropogenic activity [10] [11]. The five categories of contamination due to enrichment are shown in **Table 2**.

There is a strong relationship between the enrichment factor and the pollution load index (*PLI*). The pollution load index is defined as the nth root of the multiplication of the *EF* of metals involved and mathematically presented as:

$$PLI = \left(EF1 * EF2 * EF3 * EFn \right)^{1/n} \tag{3}$$

Table 1. *Igeo* classification.

Igeo value	Class	Designation of sediment quality
$Igeo \le 0$	0	Uncontaminated
$0 \le Igeo \le 1$	1	Uncontaminated to moderately contaminated
$1 \le Igeo \le 2$	2	Moderately contaminated
$2 \le Igeo \le 3$	3	Moderately to strongly contaminated
$3 \le Igeo \le 4$	4	Strongly contaminated
$4 \le Igeo \le 5$	5	Strongly to extremely contaminated
$Igeo > 6$	6	Extremely contaminated

Table 2. The degree of metal enrichment based on the enrichment factor (*EF*) classification.

EF	Degree of enrichment
<2	Depletion to mineral enrichment
$2 \leq EF < 5$	Moderate enrichment
$5 \leq EF < 20$	Significant enrichment
$20 \leq EF < 40$	Very high enrichment
$EF > 40$	Extremely high enrichment

A pollution index of 0 indicates excellence; 1 indicates baseline levels of the metals concerned, and values above 1 are indications of progressive deterioration [12]. The *PLI* shows the overall effect of all metals of the site under study [13].

3.4. Contamination Factor

The Contamination factor (C_f) is used to determine the contamination potential of elements of potential toxicity. The contamination factor evaluates individual metal contamination in soil with reference to background reference concentration values of the individual elements of potential toxicity. It is mathematically calculated as:

$$C_f = \frac{C_{\text{metal}}}{C_{\text{background}}} \tag{4}$$

C_{metal} represents the measured metal concentration in the soil sample, and $C_{\text{background}}$ is the background reference concentration values of the individual elements of potential toxicity. A study by Hakanson [14] classifies the C_f into seven categories as shown in Table 4.

3.5. The Ecological Risk Factor (E_r)

The ecological risk factor and its categorization are presented in Table 4. The ecological risk factor is used to assess the risk of soils based on their metal toxicity and environmental response factor. This risk assessment was first introduced by [14] and is calculated using the equation:

$$E_r = T_r \times C_f \tag{5}$$

T_r in the equation is the toxic response factor and C_f is the contamination factor. The toxic response factor of the metals that will be considered in this study is presented in Table 3 [14].

3.6. Potential Ecological Risk Index (*RI*)

The potential ecological risk index is used to assess the risk of soil to an environment with their description and categories presented in Table 4. It involves the comprehensive assessment of contaminated sites to establish their possible

Table 3. Toxic response factor of metals.

Metals	As	Mn	Pb
Toxic Response factor	10	1	5

Table 4. Ecological risk factor and potential ecological risk index.

Index	Category	Description	Reference
Contamination factor C_f	$C_f < 1$	Low contamination	[14] [16]
	$1 \leq C_f < 2$	Low to moderate contamination	
	$2 \leq C_f < 3$	Moderate contamination	
	$3 \leq C_f < 4$	Moderate to high contamination	
	$4 \leq C_f < 5$	High contamination	
	$5 \leq C_f < 6$	High to very high contamination	
	$C_f \geq 6$	Extreme contamination	
Ecological risk factor (E_r)	$E_r < 40$	Low risk	[17] [18]
	$40 \leq E_r < 80$	Moderate risk	
	$80 \leq E_r < 160$	Considerable risk	
	$160 \leq E_r < 320$	High risk	
	$E_r \geq 320$	Very high risk	
Potential Ecological Risk Index (RI)	$RI < 150$	Low risk	[19] [20]
	$150 \leq RI < 300$	Moderate risk	
	$300 \leq RI < 600$	Considerable risk	
	$RI \geq 600$	High risk	

ecological risk [15]. Based on Hakanson's study in 1980, the *RI* can be calculated using the equation:

$$RI = \sum E_r \tag{6}$$

4. Results and Discussion

The mean and standard deviations of the physicochemical parameters are presented in Table 5.

These parameters play a very important role in the survival of both micro and macro-organisms in an aquatic ecosystem. Any anthropogenic activities that have the potential to shift these parameters out of proportion in the environment have the potential to either destroy or cause organisms to migrate to a safe environment. Among the physicochemical parameters is the pH which is defined as the relative amount of free hydrogen and hydroxyl ions in a solution or water. The pH measures the acidity or basicity of a water body with a logarithmic

Table 5. Physicochemical parameters.

Par Site	pH	Turbidity NTU	TSS mg/L	Nitrates mg/L	NH$_3$-N mg/L	Phosphates mg/L	COD mg/L	(BOD) mg/L
Dunkwa	8.38 ± 0.07	28737.5 ± 81.84	2319.5 ± 75.74	3.54 ± 0.01	3.34 ± 0.19	1.51 ± 0.23	56.5 ± 8.96	27 ± 0.81
Praso	7.84 ± 0.37	536.75 ± 35.75	393 ± 5.47	1.64 ± 0.13	2.49 ± 0.39	1.26 ± 0.06	31.25 ± 2.22	18.13 ± 0.85
Akim	7.4 ± 0.08	767 ± 9.83	540.5 ± 34.1	2.68 ± 0.14	2.18 ± 0.04	1.02 ± 0.13	26.25 ± 1.71	12.5 ± 1.73
Barekese	8.9 ± 0.14	2.2 ± 0.18	2.45 ± 0.40	1.33 ± 0.20	0.25 ± 0.02	0.78 ± 0.12	28.25 ± 2.06	17.25 ± 0.95
Brenase	7.75 ± 0.52	661.25 ± 16.38	464.3 ± 14.80	2.17 ± 0.15	2.6 ± 0.40	1.31 ± 0.21	34.5 ± 1.29	22.25 ± 1.26
Adiembra	7.35 ± 0.05	636 ± 4.70	490.5 ± 39.0	3.62 ± 0.61	1.35 ± 0.89	0.40 ± 0.02	29.82 ± 5.99	13.12 ± 0.34
Deboase	7.36 ± 0.36	325.90 ± 9.2	249.5 ± 12.7	1.71 ± 0.04	1.16 ± 0.05	0.50 ± 0.07	39.75 ± 3.40	22.95 ± 2.10
Shama	8.17 ± 0.22	222.75 ± 13.76	213.5 ± 6.60	1.78 ± 0.16	1.44 ± 0.27	1.19 ± 0.16	38.25 ± 1	30 ± 4.08
WHO	6.5 - 8.5	0.5		50		5	25	50

Par = parameter; TSS = total suspended solids; NH$_3$-N = Ammonia nitrogen; COD = chemical oxygen demand; BOD = biological oxygen demand.

scale by using figures between 0 - 14 [21]. The closer the figure is to "0", the more acidic it is. For example, a stream or river with a pH of 3 is ten times more acidic than a river with a pH of 4. According to Taylor *et al.*, [22], a reduction in the pH in an aquatic environment has the potential to destroy the chemosensory ability of fish. This chemosensory ability when destroyed will affect the ability of the fish to locate its prey and survival in an ecosystem [23]. Even though there is no pH range that is said to be safe for fish, it is empirically known that the pH range of 5 - 9 is not directly lethal to fish [23]. The pH recorded in the study period was within the range safe for fish in the river (Table 5). The highest pH in the study area is below that of the previous studies [1]. The reduction in the pH in the basin is a good sign as a pH between 9 to 10 as recorded in the previous studies by Duncan *et al.*, [1] is lethal to fish survival [24].

Even though the present pH is within the range suitable for living organisms especially fishes to grow well, the situation on the field is totally different: the interview with the fishermen reveals that they continually experience low fish harvest and the disappearance of most fish species within the basin. This observation confirms that the quality of water cannot be determined by just one parameter. A parameter like total suspended solids (TSS) plays a very important role in the level of oxygen in the raw water and the survival of fishes that may not be able to dwell under anaerobic conditions. The diameter of suspended solids is usually less than 62 μm even though they usually travel as flocs in rivers and streams [25] [26]. The flocs have a high potential of influencing the water physically, chemically, and biologically [27]. A SS concentration of 8 mg·L^{-1} would reduce algae and macrophyte primary productivity by 3% - 13% whereas 500 mg·L^{-1} would cause severe abrasive damage to the leaves of aquatic moss [28] [29]. According to Francoeur and Biggs [30], suspended solids (SS) concentration of 0 - 6500 mg·L^{-1} would cause abrasive damage and reduced biomass of

periphyton. The measured SS ranged between 2.5 - 2319 mg·L^{-1}. The lowest concentration of SS is way below 8 mg·L^{-1}, and this is very much expected because that is the only sampling site that is not affected by anthropogenic activities such as illegal mining. Among the remaining seven sites, non-recorded concentrations below 200 mg·L^{-1}, According to [31] SS concentration of 200 mg·L^{-1} would cause a 50% reduction in the primary production of algae and macrophytes. This means that all six sites may potentially be experiencing this phenomenon resulting in the reduction in oxygen levels in the river and eventually affecting the survival of fish in such locations or environments. This could be one contributing factor to the disappearance of some fish species in the river that was revealed by fishermen during the interviews. The next quality parameter of interest is turbidity. Though turbidity and SS are related in some ways, there are also some differences. First, turbidity is a measure of only one of the many effects of SS and responds to factors aside from SS concentrations [27]. According to Bilottaa and Braziera [27], the particle size and shape of SS, the presence of phytoplankton, the presence of dissolved humic substances, and the presence of dissolved mineral substances have a great influence on the turbidity in water. Hence high turbidity does not imply high SS concentration. The measured turbidity is in a range of 2.5 - 28,737 mg·L^{-1}. Except for Berekese which recorded 2.5 mg·L^{-1}, all other sites recorded values at least 24 times the permissible value (Table 5). This is a concern that needs redress as many of the water treatment plants that finds themselves in the basin always suffer from the high cost of chemical application and clogging of pumps leading to the shutting down of water treatment plants and a resultant intermittent flow of water to consumers. Six months ago, the Sekyere Heman water treatment plant which is located downstream of the basin was shut down due to the above reasons. Nitrates are very essential plant nutrient however when present in high concentration causes water quality problems. According to the United States (US) EPA [32] nitrates when present in concentrations greater than required results in eutrophication with the consequential effect of high plant growth and changes in the type of plants and animals that leaves in such an environment. For infants, up to six months, ingestion of nitrate in concentrations above 45 mg·L^{-1} causes methemoglobinemia [33]. According to Camargo *et al*., [34], nitrate toxicity in animals increases with increasing nitrate and exposure time. A concentration of 10 mg NO$_3$-N/L during long-term exposure can adversely affect, at least, freshwater invertebrates, and amphibians [34]. However, for very sensitive freshwater species a maximum nitrate of 2 mg·L^{-1} is recommended. The nitrate concentration in the study area is below the WHO permissible limit of 50 mg·L^{-1} and below the level that can cause methemoglobinemia. The lowest nitrate concentration was recorded in the control site (Table 5). Phosphorus, though, is a very essential nutrient for plant growth and would cause explosive growth of plants and algae in surface water when present in excess [35]. Algae have a negative effect on fish in rivers and reservoirs because of their ability to deplete oxygen during respira-

tion and decomposition [36]. The depleted oxygen creates anoxic conditions, bad odor, and decoloration that not only make the water aesthetically unattractive but also cause the death of many sensitive aquatic organisms [13] [37]. The highest concentration of phosphate recorded (Table 5) is far below the permissible level of 5 as prescribed by WHO. The chemical oxygen demand (COD) is the amount of oxygen that must be consumed by reactions in a measured solution, or the amount of oxygen needed to oxidize the organic matter present in water. The COD indirectly measures the organic pollutants in a river, stream, or lake. The effect of illegal mining on COD cannot be underestimated. The COD of a river has serious implications on the fish population as overconsumption of oxygen in the river may result in anaerobic conditions that could force many fish species that cannot withstand such conditions to migrate or die. According to USEPA [38], COD less than 1 mg/L can be assumed to not be caused by anthropogenic sources and is expected to provide a suitable environment for ecosystem sustainability. For agriculture use, high COD interferes with the transfer of oxygen to the soil which may result in the death of rice plants in paddy [38]. None of the sampled sites recorded COD below 25 mg/L (Table 3). This is very worrying and may be attributed to the low and absence of certain fish species such as the carp within the study area. According to USEPA [38], for the oligotrophic and eutrophic lakes for oligosaprobic fish such as smelt, COD should be less than 3 mg/L and for the eutrophic lake where carp habitats, the COD should be less than 5 mg/L. Dunkwa town or site recorded the highest COD of 56.5 mg/L with Akim recording the least value of 26 mg/L. The values recorded are all very high and can attribute for the loss of most fish species and ecosystem sustenance. Biological oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a water body at a certain temperature over a specific period [39]. According to USEPA [40], a BOD of 1 mg/L is considered not to be caused by anthropogenic activities and can support the natural environment effectively. BOD of more than 3 mg/L is known to affect primary sedimentation and the process of filtration in conventional water treatment plants [40]. For environmental conservation, BOD should be less than 10 mg/L to prevent odor. BOD figures of more than 10 mg/L, are not suitable for water supply and fishery [40]. The measured BOD in the catchment ranges between 12 and 30 mg/L. The BOD in the catchment is therefore not suitable for water supply and fishery hence the frequent breakdown of water treatment plants and loss of certain fish species within the catchment. The measured BOD and COD are the main cause of the loss of certain fish species within the catchment. Regarding the interview, what came out so clearly with all the fishermen from the eight sites was that fish harvest in the river has gone down, whereas two out of the eight fishermen associate the problem with more people fishing from the same source of the river which in the past didn't experience that huge pressure of fishing, the remaining six associate the problem with unregulated illegal mining activities within the catchment. They

also said that there has been a disappearance of some fish species and a drastic reduction in the sizes of the fish they harvest presently as compared to the past. However, they could not give any explanation that could be linked to any scientific phenomenon accounting for the disappearing of fish species aside from the explanation two of the interviewee believe that "the gods may be angry with the way the rivers are being polluted".

4.1. Elements of Potential Toxicity

The studied elements of potential toxicity in the river are presented in Table 6. The element manganese was the only element in the water that was below the WHO standards in all the sites studied. The sites Dunkwa, Praso, Barekese, Shamaa, and Deboase all recorded arsenic values below the permissible limit. A study by Ahmed *et al.*, [41] reveals that nearly 100 million people globally drink water contaminated with arsenic. Arsenic is a highly toxic and carcinogenic metalloid that poses threats to many living organisms including humans [7]. The consumption of aquatic organisms such as fish contaminated by arsenic is the leading factor of arsenic toxicity. According to Shtangeeva [40], the total amount of arsenic produced globally through human activities is about 140,0000 tons per year which far outweighs that from volcanic activity (3000 tons per year) and other natural processes such as rocks and soil weathering (45,000 ton per year) put together. According to Hassan *et al.* [42], and Kapaj *et al.* [43], the ingestion of inorganic arsenic in humans has the potential to cause bladder and lung cancer. The sites Akim, Brenase, and Adiembra all recorded arsenic concentrations above the WHO threshold making the water not safe for any form of recreation such as swimming as observed in areas like Adiembra. The concentration of iron in water has been contented even though it has no serious health implications, it is an aesthetic contaminant. Thus, iron in its ferrous (soluble) form can be oxidized to ferric (insoluble) forming brown or reddish-brown color that stains clothes and could serve as a hiding place for pathogenic microbes. Iron is essential for good health as it helps in the transport of oxygen in the blood. Only two

Table 6. Elements of potential toxicity in water samples.

Sampling site	Arsenic (mg/L)	Iron (mg/L)	Manganese/(mg/L)	Lead (mg/L)
Dunkwa	0.004 ± 0.00	0.358 ± 0.04	0.031 ± 0.00	0.047 ± 0.02
Praso	0.003 ± 0.00	0.689 ± 0.07	0.101 ± 0.05	0.231 ± 0.01
Akim	0.026 ± 0.00	0.338 ± 0.01	0.049 ± 0.06	0.065 ± 0.02
Barekese	0.002 ± 0.00	0.141 ± 0.01	0.051 ± 0.01	0.033 ± 0.05
Brenase	0.044 ± 0.01	0.229 ± 0.08	0.086 ± 0.10	0.159 ± 0.08
Adiembra	0.015 ± 0.00	4.835 ± 0.50	0.032 ± 0.01	0.042 ± 0.04
Deboase	0.009 ± 0.00	0.553 ± 0.42	0.048 ± 0.02	0.072 ± 0.02
Shama	0.006 ± 0.00	0.398 ± 0.29	0.075 ± 0.01	0.179 ± 0.24
WHO	0.01	0.3	0.5	0.01

out of the studied sites recorded iron concentration below the permissible level. Iron concentrations as low as 0.3 mg/L will turn water into brownish red or brown. The remaining five sites all recorded iron in increasing order as Akim < Dunkwa < Shama < Deboase < Adiembra. This situation could contribute to the brownish color observed in almost all the rivers.

Human exposure to lead can damage the brain because it is a very powerful neurotoxin [44]. According to Mulvihill [44], lead is notoriously dangerous and has no safe level in the human body. According to America Centers for Disease Control and Prevention, fetuses, infants, and young children are at greater risk of lead poisoning than adults. In children, severe lead poisoning can result in irritability, weight loss, abdominal pain, fatigue, vomiting, lower IQ and hyperactivity, slowed growth, and seizures [44]. In adults lead poisoning causes high blood pressure, joint, and muscle pain, harm to reproductive health, and difficulty with memory. It must be stated here that even moderate to low-level exposure to lead can cause kidney impairment, anemia, hypertension, hearing loss, immune system dysfunction, and toxicity to the reproductive organs [45]. Though the Barekese sampling site does not experience any form of illegal mining, the concentration of lead in its water is about 3 times the permissible limit for drinking water. This is an indication that the soil in that area of the basin if not the entire basin may contain some substantial amount of lead soil from which any form of soil disturbance can introduce it into the water. The lead concentration in this study ranges from 0.231 - 0.033 mg/L. Praso recorded the lead concentration which is about 23 times the permissible level. This is very serious because the Pra River is the raw water source of the Daboase Water Treatment Plant, which does not have any dam or reservoir, and as a result, practices direct abstraction from the river. If conscious efforts are not put in place to treat the water to remove the lead during treatment, the treated water may likely contain lead thereby exposing consumers to long time lead exposure and the consequent danger of experiencing the threat listed above.

4.2. Elements of Potential Toxicity in Sediments

The mean and the standard deviation of the elements of potential toxicity concentrations for the sediments are presented in Table 7. Among all the elements of potential toxicity studied, only iron had concentrations below the WHO standard in all the sites (Table 7). The measured iron concentration though is below the WHO standard, it is the only metal with the highest concentration in all the sites indicating the dominance of the metal in Ghanaian soil. Iron according to WHO has no health implications in drinking water, however, it has much influence on the cost of treatment when it is in high concentration and must be oxidized from ferrous to ferric to precipitate out of water.

According to the Public Health Division of Delaware Health and Social Services (https://dhss.delaware.gov/dph/files/arsenicsoilfaq.pdf), arsenic when it is a few feet under the surface or deeper does not pose risk if the soil is not disturbed.

Table 7. The mean metal concentrations in sediments.

	Arsenic mg/kg	Iron mg/kg	Manganese mg/kg	Lead mg/kg
Dunkwa	25.67 ± 11.74	1716.33 ± 68.16	693.33 ± 126.19	99 ± 72.89
Praso	29.00 ± 7.65	2232.00 ± 685.36	822.00 ± 203.71	41.33 ± 10.89
Akim	29.33 ± 9.30	1545.33 ± 126.79	657..67 ± 68.42	66.67 ± 17.59
Barekese	5.00 ± 1.67	503.33 ± 163.03	442.00 ± 44.05	4.33 ± 1.28
Brenase	49.33 ± 8.91	2172.33 ± 944.24	422.00 ± 62.70	16.33 ± 2.52
Adiembra	26.67 ± 4.62	1555.67 ± 199.87	643.67 ± 47.50	50.33 ± 15.06
Deboase	9.67 ± 1.67	1473.00 ± 315.73	1573.00 ± 86.78	54.33 ± 22067
Shamaa	8.33 ± 2.28	11486.33 ± 0.20	1651.33 ± 109.07	4.67 ± 1.72
WHO	7	28,000	600	23

The measured concentration of arsenic is in the range of 5 to 49 mg·kg^{-1}. Only Barekese among the study sites recorded the lowest level of arsenic in sediments. The observed low concentration of the metal in Barekese is not strange as no observed human disturbance of the soil such as illegal mining occurs at that site. Brenase site recorded the highest arsenic concentration of seven times the permissible WHO value. The level of arsenic in all other sites except for Berekese is due to the disturbance of the soil through unregulated illegal mining activities. Shamaa site arsenic is very worrying because it serves as an estuary and as a result, attracts a lot of recreational activities exposing the users of such an environment to potential ingestion of the metalloid. Lead is a hazardous environmental contaminant due to its high ecotoxicity, detrimental medium, and its long-term effect on human health [46]. Lead is a soft, malleable, relatively inert metal that has been known and used by man since ancient times [39]. According to [39], lead abundance in the earth's crust is approximately 15 ppm; an equivalent of half an ounce of lead per ton of rock. Studies have shown that lead has the potential to restrict intelligence quotient (IQ) development and is a group 2A carcinogen by the international agency for Research on Cancer (IARC) [47] [48]. There are empirical pieces of evidence of lead pollution of soils and sediments that surround mining areas. A study of soil and sediments from mining areas around the Piedras Negras River by Mitchell *et al.*, [46] reveals mean lead concentrations of 434.7 and 2200.8 mg·kg^{-1} respectively. A study by Makombe & Gwisai in mine soils in Zimbabwe shows lead concentrations of 170.3 mg·kg^{-1} [49]. The toxic effect of lead on the nervous system is very alarming. The neurotoxicity of lead is alarming because a longitudinal study has shown that neurobehavioral effects, such as impaired academic performance and deficits in motor skills, have the potential to persist even after lead blood levels have returned to normal [50]. The lead concentration of the study area is in the range of 4 mg·kg^{-1} - 99 mg·kg^{-1} (Table 7). All the sites recorded concentrations above the permissible limit except Barekese and Shamaa. Barekese has not experienced any form of illegal mining activities as compared to the other sites hence the observed value.

Regarding the low value of lead in Shamaa, the reason could be the nature of the environment as there is always washing and mixing of the freshwater and seawater creating a unique soil environment. The nature of the soil at Shamaa is very sandy and loose and is likely to allow the washing of lead from the soil since there isn't so much organic matter to bind the inorganic lead hence it releases the metal to be washed away. Dunkwa which has experienced so much unregulated illegal mining activity recorded the highest lead concentration which is about four (4) times the permissible level in the soil. The level of lead in the sediment is associated with illegal mining because the areas under consideration are not urban to get exposed to many potential lead-polluting contributing sources such as lead base paints and the use of lead fuel.

The calculated *Igeo* of the metals is presented in Table 8. The measured *Igeo* in the study area is in the range of "uncontaminated" to "moderately to strongly contaminated". All the sites were uncontaminated with iron and manganese. Adiembra, Deboase, and Shamaa were all uncontaminated with arsenic. Dunkwa, Barekese, Praso, and Akim Oda in that order were all moderately contaminated with arsenic. The only site that was moderate to strongly contaminated with arsenic is Brenase. This means that half of the sites studied were moderately contaminated with arsenic and one out of eight sites was moderate to strongly contaminated. This is an indication that even though arsenic is naturally distributed in an average concentration of 1.5 - 5.5 $mg \cdot kg^{-1}$ [51], the measured concentrations in these sites far exceed the background concentration suggesting anthropogenic activities as the cause of the differences being observed. The activity of illegal mining in the areas of contamination is very much disturbing and this condition has been confirmed by other researchers as a contributing factor to arsenic contamination. According to Ali *et al.*, [4], gold mining is a primary source of arsenic contamination. The highest value of *Igeo* index was found in Brenase where unregulated illegal mining is all over. Concerning lead, only Dunkwa was moderately contaminated, the remaining seven sites were uncontaminated. The situation in Dunkwa concerning lead is expected as most of the

Table 8. Geoaccumulation index of the metals in sediments.

Sampling Site	Geoaccumulation index of metals in soil			
	Arsenic	Iron	Manganese	Lead
Dunkwa	1.290	−4.613	−0.376	1.521
Praso	1.466	−4.234	−0.131	0.261
Akim Oda	1.482	−1.443	−0.453	0.950
Barekese	1.345	−3.061	−1.026	−2.994
Brenase	2.232	−0.951	−1.093	−2.994
Adiembra	−1.070	−1.433	−0.484	0.545
Deboase	−0.119	−1.512	0.806	0.655
Shamaa	−0.334	−1.499	0.876	−2.885

rivers in the area have been diverted and the riverbed illegally mined for gold. Table 9 and Table 10 are the presentation of the enrichment and pollution load index of metals in the study area. Enrichment values less than or close to 1 are an indication that the primary source of the element of potential toxicity is natural. In that regard, all the sites except Brenase are not enriched with arsenic and manganese. The arsenic enrichment value of 1.59 measured for Brenase is coming from an anthropogenic source because all values greater than 1 indicate enrichment coming from an anthropogenic source [52] [53]. This means that Dunkwa, Akim, and Deboase lead enrichment is from anthropogenic sources (Table 9).

All other sites were not enriched with lead. The enrichment gives the effect of the individual metals at the sites however, the cumulative effect of the metals together can be determined using the pollution load index. The pollution load index (Table 10) indicates that none of the sites is being polluted by the cumulative effect of the metals. Though the metals are not polluting as shown in Table 10, however, most of these sites are being contaminated with these toxic metals (Table 11).

Table 9. Enrichment of sediment.

Heavy Metals	Dunkwa	Praso	Akim	Brenase	Barekese	Adiembra	Deboase	Shamaa
Arsenic	0.45	0.39	0.57	1.59	0.68	0.10	0.20	0.17
Manganese	0.24	0.22	0.26	0.53	0.12	0.25	0.64	0.67
Lead	1.73	0.56	1.29	0.26	0.06	0.97	1.11	0.09

Table 10. Pollution load index of metals at study sites.

PLI	Dunkwa	Praso	Akim	Brenase	Barekese	Adiembra	Deboase	Shamaa
	0.062729	0.015949	0.062768	0.072052	0.001583	0.007744	0.046544	0.003521

Table 11. Contamination factor of metals.

Sites	Contamination Factor			
	Arsenic	Iron	Manganese	Lead
Dunkwa	3.667	0.061	1.156	4.304
Praso	4.143	0.080	1.370	1.797
Akim	4.190	0.055	1.096	2.899
Barekese	0.714	0.018	0.737	0.188
Brenase	7.047	0.078	0.703	0.710
Adiembra	3.814	0.056	1.073	2.188
Deboase	1.381	0.053	2.622	2.362
Shamaa	1.190	0.410	2.752	0.203

Table 12. Ecological risk (*Er*) and potential ecological risk index (*RI*) of sediment.

Er	Dunkwa	Praso	Akim	Brenase	Barekese	Adiembra	Deboase	Shamaa
Arsenic	36.671	41.428	41.9	70.471	38.1	7.142	13.814	11.9
Manganese	1.155	1.37	1.096	0.703	0.737	1.072	2.621	2.752
Lead	21.521	8.984	14.493	3.55	0.941	10.941	11.810	1.015
RI	Dunkwa	Praso	Akim	Brenase	Barekese	Adiembra	Deboase	Shamaa
	59.347	51.782	57.489	74.727	39.778	19.155	28.245	15.702

The contamination factor of the metals is in the order arsenic > lead > manganese > iron. Arsenic is the only metal that recorded extreme contamination and this occurred in Branase where illegal mining is scattered everywhere without any regulation. The only site that recorded low contamination is Barekese which happens to be the control site. The remaining sites recorded arsenic contamination in the range of low to moderate contamination to high contamination. This is of concerned as part of these lands is still used by farmers for cassava and plantain farming. Lead recorded the high contamination at Dunkwa with Barekese recording the low contamination of lead. The order of lead contamination in the sites is Dunkwa > Akim > Deboase >Adiembra > Praso > Brenase > Shamaa > Barekese. Manganese contamination within the sites was in the range of moderate contamination to low contamination. The order of contamination in the sites is as follows Shamaa > Deboase >Dunkwa >Praso > Akim > Adiembra > Barekese > Brenase. Iron is the only metal that recorded low contamination at all the sites.

The grade ecological risk of a single metal (*Er*) and the potential ecological risk (*IR*) of the environment are presented in Table 12. The sites Dunkwa, Barekese, Adiembra, Deboase and Shamaa all recorded low ecological risk for the single metal arsenic. The remaining three sites recorded moderate ecological risk for arsenic in the order Praso < Akim < Brenase. The metals manganese and lead pose a low ecological risk to all the sites under study. The cumulative effect of all the metals at each study site and the potential ecological risk index of the metals at each study site are low (Table 4).

5. Conclusion

The study monitored the physicochemical parameters and metals and metalloids of potential toxicity in the Pra basin. In comparison to the previous study in the same locations within the basin, pH is found to have reduced and is now within the conducive range for fish survival. All the sites recorded phosphate and nitrate concentrations below the permissible limits. All the sites recorded BOD, COD, and turbidity above the permissible limits. Among the eight sites studied, only Barekese measured metals of potential toxicity within the permissible limit. The only metal of potential toxicity that didn't exceed the permissible limit in all the sites is iron. Arsenic concentration exceeded the permissible limit for all the

sites except Barekese. All the sites recorded manganese concentration above the permissible level except Barekese and Brenase. Aside from Shamaa and Barekese, all the sites recorded lead concentrations above the permissible level. The *Igeo* in the study area is in the range of "uncontaminated" to "moderately" to "strongly" contaminated. Regarding manganese and arsenic enrichment, only Brenase was enriched with arsenic. Dunkwa, Akim, and Deboase were the only sites enriched with lead. The pollution load index indicates that none of the sites was polluted by any of the metals. The only metal whose contamination factor is low in all the sites studied is iron. Arsenic is the only metal that measured extreme contamination among the metals studied. The contamination factor of the metals is in the order arsenic > lead > manganese > iron. Dunkwa, Barekese, Adiembra, Deboase, and Shamaa all recorded low ecological risk for arsenic whereas Praso < Akim < Brenase in that order recorded moderate ecological risk for arsenic. Manganese and lead pose low ecological risks in all the sites under study. It is recommended that constant monitoring of the basin be adhered to so that preventive measures that could help maintain the basin's ecosystem can be developed to safeguard the basin.

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Data Availability

The primary data used to support the findings of this study are available from the corresponding author upon request.

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Conflicts of Interest

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

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