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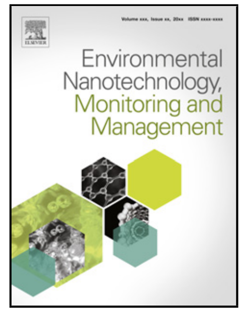

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Assessment of heavy metal pollution in the main Pra River and its tributaries in the Pra Basin of Ghana

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ABSTRACT

The Pra Basin is one of the Basins in Ghana with a high level of illegal mining activities. Heavy metal pollution in water bodies is common in areas where illegal mining is practiced. This study focused on the assessment of heavy metal pollution in the Pra Basin. The study was based on 216 water samples collected from 27 sampling points from the Pra River and two of its tributaries during the dry and wet seasons in 2017. Nine heavy metals namely arsenic (As), chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn), and iron (Fe) were assessed in this study. The metal concentrations (mgL^{-1}) in the water were as follows: Fe > Pb > Ni > Cu > Cr > Cd > Zn > Mn > As and in the dry season as Fe > Zn> Cu > Cr> Pb > Mn >Ni > Cd >As. Five metals exceed the safe drinking water guidelines making the water generally not safe for domestic activities like drinking and cooking. According to the Nemerow's Pollution Index (NPI) results, six metals namely Pb, Cd, Cr, Ni, Fe, Zn were the principal metal pollutants in both the dry and wet seasons whereas Mn, As, and Cu, were found not to contribute to the pollution effect. The water quality index confirms that the water quality is marginal to fair in the dry season and poor for 26 out of the 27 sites in the wet season. Generally the studied rivers (Pra, Offin and Oda) are polluted which is a serious threat to the health of inhabitants in villages which still use the water for cooking activities. The study recommends continuous monitoring of the polluting metals and the assessment of the river sediments to inform effective remediation measures.

Keywords: Heavy metals; River; Pollution; illegal mining; Pra Basin; Ghana

1 Introduction

The suitability of water for any purpose defines its quality. Globally, the quality of water is under serious threat due to anthropogenic activities such as urbanization, industrialization and unregulated mining (Jung, 2001; Sekabira, 2010). The threat could either affect the water physically, biologically or chemically (G. M. Carr & Neary, 2008). The United States Environmental Protection Agency (2000) defined heavy metals as metals with a specific gravity of 5 or greater or metallic element with high atomic weight which have the potential to damage living things at low concentrations. Heavy metal contamination of rivers, mostly from unregulated mining, is now a major concern in most developing countries such as India, Peru, Ghana etc. (Ali, 2016).

They are of great concern because of their public health consequences and their stress on ecology (Montuelle & Graillot, 2017). Exposure to heavy metals over a long period can cause memory impairment and damage to the nervous system (Rajendran, 2003). High accumulation of the metals can cause irreversible brain damage (Afrasiab, 2014). They are a threat to the environment because they are indestructible and can enter the food chain (Ololade, 2008). They can also affect invertebrates and fishes in the aquatic environment (Yi, 2011).

The alarming rate at which rivers in Ghana are getting polluted with heavy metals from untreated industrial waste is still a pending problem that has not been solved. The heavy metal pollution from industry has been compounded by that of unregulated/illegal mining. The Pra Basin has been experiencing unregulated mining in and around most of its major rivers for more than 30 years (WRC., 2012). The expansion of the illegal mining happened so fast that almost all the rivers in the basin which in the past 35 to 50 years were very useful to the riparian communities have become esthetically unattractive (Attuaquayefio & Folib, 2005). The unattractive nature notwithstanding, some riparian communities when faced with water supply crises depend on the rivers for domestic activities such as cooking and washing. In recent years major steps have been taken to improve water management in the Pra Basin (Pra Basin, 2012). Incorporated in the new management set-up is a river monitoring and evaluation unit with a task to conduct regular assessment of the rivers to see if there is any improvement or deterioration. Monitoring stations have been established along the Basin River since 2011. However, monitoring is not functioning effectively((WRC), 2011). Illegal mining is prevalence in the basin but heavy metal concentration is not used in classifying water quality. There has not been any scientific study of the heavy metal which pollutes the main Pra River from the upstream to the downstream of the basin. Therefore the objective of the study is to identify the heavy metals with a pollution threat and the extent of their threat using Nemerow's Water Pollution Index (NPI). We also assess the overall water quality with reference to the metals under study by employing the Canadian Council of Ministers of the Environment (CCME) Water Quality Index (WQI). The study will contribute in developing the right strategies and remediation measures in solving the threat posed by these metals in the basin and other comparable areas.

2 Materials and Methods

2.1 Study area and sampling

Ghana is drained by three main river systems; the Volta Basin system, South-Western Basin system, and the Coastal Basin system. The Pra Basin which is the study area forms part of the South-Western Basin which comprises of the Pra, Bia, Ankobra, and Tano rivers. A total of 17 artificial reservoirs are constructed nation-wide along the three main river systems for hydropower generation, irrigation, and water supply (Pra Basin, 2012). Nine (9) out of the 17 reservoirs are located in the study area which is why the quality of the water in the area is very important. Illegal mining sites are scattered all over the Pra Basin. All sampling sites were either within or around the illegal mining sites. Site 'LAK' was a control site located in the northern part of all the sites with no form of mining going on in the area. Kriging was used to develop a heat map for the polluting metals in all sampling sites. In this method, the field data was loaded in arcmap and the comma separated values (csv) file format converted into points. The Inverse distance weighted (IWD) interpolation tool was then used to run the interpolation for each element and displayed in figure 2. The study area is the largest among the three South-Western River Systems and occupies an area of 23000km^2 which is about 9.64% of the area of Ghana (Pra Basin, 2012). Studies conducted in the basin by the water resources commission of Ghana and that by Duncan (2016) reveals similar illegal mining activities in the entire basin. Due to the similar characteristics pertaining in the basin and accessibility difficulties, the main Pra River, and two of its tributaries (Offin and Oda) was considered for this study. The main Pra River takes it source from the Kwahu plateau from the eastern part of Ghana and flows through a distance of about 240km before joining the Gulf of Guinea. There are 43 administrative districts with about 42% of the households not having access to potable water i.e. tap water or approved wells (Pra Basin, 2012). Figure 1 presents the study area map. From a total of 27 sampling points, 216 water samples were collected in laboratory cleaned and rinsed 1.5-litre polyethylene bottles. Water samples were collected from January to April 2017 for the dry season and May to August 2017 for the wet season. Samples were acidified with 0.24M nitric acid (analytical grade) and kept at 4^{0}C in the dark before analysis.
FIGURE 1

2.2 Water quality parameter

Physico-chemical parameters such as pH, electrical conductivity, turbidity, and temperature were measured on the field. Temperature and pH were measured using a pH meter (model No. PHSB-320, BOQU instruments China). Conductivity was determined with the pen-type conductivity meter (model No. LH- P1318). Turbidity was measured by the portable 2100Q turbidity meter of the HACH United States of America.

2.3 Chemical and sample digestion

Deionized water supplied by University of Cape Coast Technology village was used in all the analysis. All standard solutions used were of the highest purity supplied by MES Equipment

Limited Ghana. The nitric and hydrochloric acids used for the digestion were all analytical grades and supplied by MES equipment. Water samples were filtered using a 0.45μm cellulose membrane filter and acidified to pH < 2 using analytical grade nitric acid. 50ml of a well-mixed acid preserved sample was transferred to a boiling tube and 5ml HNO_3 added. The mixture was heated at 130^{o}C in a graphite block digester till the volume reduced to about 25-20ml. 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.

2.4 Analytical technique and accuracy check

Nine (9) heavy metals namely arsenic (As), total chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn), and iron (Fe) were measured using dual atomizer and hydride generator atomic absorption spectrophotometer (model ASC-7000 No A309654, Shimadzu, Japan). All reagents used were of the analytical grade from MES Equipment Ghana. Ultrapure metal free deionized water was used for all analysis. All glassware and plastic were cleaned by soaking them in warm 5% (V/V) aqueous nitric acid for 6-7 hours and rinsed with ultrapure deionized water. The standard for the ASS calibration was prepared by diluting standard (1000 ppm) supplied by MES Equipment Ghana. All the results were expressed in mg/L. Matrix Spike recovery was in the range of 85% - 100%.

2.5 Assessment of heavy metals in water

In assessing the water quality in terms of the heavy metal load, two indices, the Canadian Council of Ministers of the Environment (CCME) Water Quality Index (WQI) and Nemerow's Pollution Index (NPI) were applied. These indices use the permissible levels of the parameters concerned as a reference point for assessment.

2.5.1 Canadian Council of Ministers of the Environment (WQI)

This index summarizes the overall quality of water by considering the number of variables not meeting the water quality objectives (scope); the number of times these objectives are not met (frequency) and the amount by which the objectives are not met (amplitude). The scope, frequency, and the amplitude together can provide a single value (0 -100) that describes the quality of the water. Once the CCME WQI value has been determined, the water quality can be classified as Excellent (95-100), good (80-94), fair (65-79), marginal (45-64) and poor (0-44). The CCME WQI provides a mathematical framework for assessing ambient water quality conditions relative to water quality objectives. In the mathematical framework, there should be at least a minimum of four sampling times with at least four variables; however, there is no limitation to the maximum numbers in the areas specified.

F_1 (Scope) represents the percentage of variables that do not meet their objectives at least once during the time period under consideration ("failed variables"), relative to the total number of variables measured. F_1 is mathematically expressed as:

$$F1 = \frac{Number\ of\ failed\ variable}{Total\ number\ of\ variables}\ x\ 100 \quad (1)$$

F_2 (Frequency) represents the percentage of individual tests that do not meet objectives ("failed tests"). It is mathematically expressed as:

$$F2 = \frac{Number\ of\ failed\ tests}{Total\ number\ of\ tests}\ x\ 100 \quad (2)$$

F_3 (Amplitude) represents the difference in amount between the failed test values and their objectives. The F_3 calculation involves three steps. The first step is to estimate the number of times the individual concentrations are greater than (or less than, when the objective is a minimum) the objectives (excursion). This is mathematically expressed as:

$$excursion = \frac{Failed\ test\ value}{Objective} - 1 \quad (3)$$

For the cases in which the test value must not fall below the objectives, the excursion is calculated as:

$$excursion = \frac{Objective}{Failed\ test\ value} - 1 \quad (4)$$

The ratio of the sum of excursions to the total test is referred to as the normalized test of excursion or nse.

$$nse = \frac{\sum_{i=1}^{n} excursion}{number\ of\ tests} \quad (5)$$

F_3 is then calculated by an asymptotic function that scales the normalized summed of the excursions from the objectives (nse) to yield a range between 0 and 100.

$$F3 = \frac{nse}{0.01nse + 0.01} \quad (6)$$

After calculating for the three F's, CCME WQI can be calculated as:

$$CCME\ WQI = 100 - \frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \quad (7)$$

2.5.2 Nemerows Pollution Index (NPI)

Nemerow's pollution index provides information on the extent of pollution of individual pollutants in a sampled area with reference to its standard value (Rathod, 2011). Whereas the WQI provides the general quality of the water, Nemerow's index identifies and establishes the extent of pollution of individual parameters at each sampling site. It is mathematically expressed as:

$$NPI = {}^{Ci}/_{Li} \quad (1)$$

Where C_i is the observed concentration of i^{th} parameter; L_i is the permissible limit of i^{th} parameter. Each value of the calculated NPI represents the relative pollution contribution by a single parameter. The calculated NPI when is less than or equal to 1 indicates the absence of pollution and any value above 1 indicate pollution.

2.5.3 Statistical analysis

Microsoft Excel 2010 was used to calculate the mean and standard deviations of the heavy metal concentration in the water samples. An independent t-test was used to assess the significance of the seasonal contribution to the variations in metal concentration and physicochemical parameters.

3 Results and Discussion

3.1 Water quality parameters

The mean values of the physico-chemical parameters are presented in table 1. The physical and chemical components of water are very important because they influence the stability of the water ecosystem as well as the chemical reactions which takes place in the water (Deborah, 1996). The pH of water is very important because it has a strong influence on the biological productivity (G. M. Carr, Neary, J. P., 2008) as well as the solubility of heavy metals in the water. The dry season pH (M = 7.22, SE = 0.08) was significantly different from that of the wet season (M = 6.85, SE = 0.01). The mean pH range of 5.08 to 8.94 and 5.5 to 9.67 recorded for both dry and wet seasons were all outside the WHO permissible limits (Table 1). The recorded pH ranges are not favorable for aquatic life (G. M. Carr, Neary, J. P., 2008). However, the mean pH of 6.86 and 7.22 was within the WHO permissible limits. Aquatic organisms have very narrow temperature tolerance; as a result, small changes in temperature can affect species such as algae, invertebrates, fishes etc. (G. M. Carr, Neary, J. P., 2008; Yi, 2011).The temperatures measured ranged from 27^0C to 32^0C and 27^0C to 30^0C for the dry and wet seasons respectively. The mean temperatures of the two seasons though were within the WHO standards were significantly different (table 1&5).The dry season showed a higher temperature (M = 29.10, SE = 0.24) than the wet season (M = 27.97, SE = 0.12). The significant temperature difference can have serious influences on aquatic species as well as some form of chemical reactions in the basin (Haiyan L., 2013). The mineral content of water which is usually made of the total dissolved solids is an important feature in the quality of the water (Deborah, 1996). Electrical conductivity is a measure of the dissolved salts and inorganic materials like sulfides and carbonates. Most water bodies have fairly constant conductivity; as a result, a sharp change in conductivity could be an indication of a possible pollution. The values of conductivity ranged from 97.2 to 948μs/cm and 1.05 to 609μs/cm for dry and wet seasons respectively. The mean conductivities of the two seasons were all within the WHO guideline value of 1000μscm^{-1}. Turbidity is a measure of the number of suspended solids in the water. It is very important because biodegradable suspended organic materials deplete available dissolved oxygen in water creating anaerobic conditions. The measured turbidity was ranged from 1.05 to 609NTU and 2.14 to 910NTU for the dry and wet seasons. There is a significant difference in the dry season turbidity (M = 285.33, SE = 29.7) and wet season turbidity (M = 535.01, SE =39.02). The higher turbidity value recorded for the wet season could be attributed to the high runoffs from the excavated fields and scouring of rivers during heavy downpours(G. M. Carr, Neary, J. P., 2008). High turbidity means more chemical usage for drinking water treatment plants in the basin.

TABLE 1

3.2 Metal concentration in water

The result of the heavy metal concentration in the water is shown in table 2. The concentration of the metals varied between the two seasons (figure 2). The metal concentrations (mgL^{-1}) in the water were as follows: Fe > Pb > Ni > Cu > Cr > Cd > Zn > Mn > As and in the dry season as Fe > Zn> Cu > Cr> Pb > Mn >Ni > Cd >As. The concentration of the metals Mn, As, and Cu was below the WHO permissible levels during the dry and wet season. An independent t-test was used to test the level of seasonal influence on the measured Pb concentration, $t(52) = -12.21$, $p = 0.00$, with the wet season showing higher Pb concentrations than the dry season (wet season M = 1.03; dry season M = 0.18). The mean concentration of Pb was 0.175 and 1.03mg/L for dry and wet season respectively. The values are far above the WHO permissible levels for drinking water. There was a significant seasonal variation in the Ni concentration. The wet season showed a higher Ni concentration (M = 0.33, SE= 0.08) than the dry season (M = 0.08, SE = 0.00). However, the observed mean concentrations of Ni for the dry and wet season were higher than the WHO guideline for drinking water (table 2&3). The higher levels of Pb and Ni in the wet season could be due to high turbidity and low pH (Table 1). Turbid water which contains suspended solids from a mining environment mostly carries heavy metals which dissolve under low pH. The concentrations of Pb and Ni (Table 3) in the wet season can also be attributed to the washing of the excavated sediments by runoff and scouring of river sediments during heavy rainfall into the river (G. M. Carr, Neary, J. P., 2008). The metals Cr, Fe, Cd, and Zn all recorded higher values in the dry season and vice versa (Figure 2). All the four metals had concentrations above the WHO guideline for drinking water. However, unlike Fe and Zn, there was no significant difference in the seasonal concentrations for the metals Cr and Cd (Table 4). Two reasons could account for the different concentrations in the two seasons. First, in the dry season, there was an increase in illegal mining hours and coverage due to the government order to stop all illegal mining by the end of March 2017. This catalyzed a lot of the miners to spend long periods working at the site to make enough money before the deadline. Second, dilution of rivers (G. M. Carr, Neary, J. P., 2008) during the wet season could account for the low concentration observed in Cr, Fe, Cd, and Zn. Reduction in the illegal mining in most part of the basin after March 2017 could also account for the low concentrations in the four metals during the wet season.

TABLE 2

TABLE 3

TABLE 4

3.3 Assessment of metal pollution

The summary of the Numerow's pollution index (NPI) and Canadian council of ministers of the environment water quality Index (CCMEWQI) is presented in table 5. The NPI values ranged from 0 to 99.6 and 0 to 257 during the dry and the wet seasons respectively, confirming that some of the metals did not contribute to the overall pollution effect in the study area ($0 \leq NPI > 1$). Even though Cd did not pollute all the sites in both dry and wet season, it was the metal with the highest pollution index at site ANK and ANY during the dry and wet season respectively (table 5). However, Pb polluted every site in both seasons indicating the persistence of the metal in the mining environment. On the general polluting effects of the basin by the metals, NPI results indicate that 11 of the sites were polluted by six metals whereas 12 sites were polluted by five metals, 3 sites were polluted by four metals and only 1 site was polluted by two metals during the dry season (Fig. 2). In the wet season, two sites were polluted with 5 metals, five sites polluted with four metals, sixteen sites polluted with 3 metals, three sites polluted with 2 metals and one site polluted with 1 metal (Fig. 2). The observed NPI values will serve as a guide in the choice of remediation measure to adopt at each study site. There wasn't much difference in the dry and wet season water quality index. The observed water quality index showed poor water quality for all the sites during the dry season except sites DDO and LAK which showed marginal (45-64) and fair (65-79) water quality respectively. Apart from site LAK which showed good (80-94) water quality in the wet season, all other sites observed poor (0-44) water quality. The observed water quality index for the study sites confirms the polluting effects of the study metals.

TABLE 5

FIGURE 2

4 Conclusions

The results identified Pb> Cd> Cr> Ni> Fe> Zn as the mean polluting order of the individual metals in the study sites for the dry and wet season (Fig. 2). The concentrations of the polluting metals were higher in the wet season than the dry season. The concentrations of the polluting metals were far higher than the permissible limit which is an indication that the Pra Basin is polluted by the studied metals. Among the six polluting metals, Cd showed the highest pollution index at site ANK and ANY during the dry and wet season. Metal pollution at the sites for the dry and wet season does not follow any pattern. Pb is the only metal among the six polluting metals identified to have polluted all the 27 sites during the dry and wet season. The water quality index confirms that the water quality is marginal to fair in the dry season and poor for the 26 out of the 27 sites in the wet season. Even though the contribution of unplanned urbanization and industrialization to heavy metal pollution of rivers in developing countries is a known phenomenon (Ali, 2016), the main cause of heavy metal pollution in the Pra Basin stems from the unregulated illegal mining activities. The pollution is a public health concern for the communities which still depend on these rivers for domestic activities such as cooking during water crises and those who feed on fishes from these rivers. The study results lead us to propose intensification of the monitoring in the basin to sustain the fear of arrest which has kept most of the illegal miners out of their sites. It further suggests the study of the levels of these metals in the river sediments to help in the choice of a holistic remediation process.

Conflict of interest

Conflict of interest

We declare as authors of this study that there is no conflict of interest. The study focused mainly on the content of heavy metals in the rivers of the Pra Basin of Ghana and its possible impact on public health and the environment. The work did not receive any financial support from any external organization

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Reference

(WRC), W. R. C. (2011). *Annual Report of the Water Resources Commission* Accra.

Afrasiab, K. T., Imrana, N. S., Pramuk, P., Mohammad, S., Ashraf, K., Mohammad W. K. and Sadat H. . (2014). Detection of heavy metals (Pb, Sb, Al, As) through atomic absorption spectroscopy from drinking water of District Pishin, Balochistan, Pakistan *International journal of Current Microbiology and Applied Science, 3*(1), 299-308.

Ali, M. M., Ali, M. L., Islam, Md. S., I., Rahman, Md Z. (2016). Priliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. *Environmetal Nanotechnology, Monitoring and Management, 5*, 27-35.

Attuaquayefio, D., & Folib, J. (2005). An overview of biodiversity conservation in Ghana: challenges and prospects. *West African Journal of Applied Ecology, 7*(1).

Carr, G. M., Neary, J. P. (2008). *Water quality for ecosystem and human health*: UNEP/Earthprint.

Deborah, C. (1996). Water quality assessments-A guide to use of biota, sediments and water in Environmental Monitoring. *UNESCO/WHO/UNEP*.

Haiyan L., A., S., Mingyi, L., Xiaoran, Z. (2013). Effect of pH, temperature, dissolved oxygen, and flow rate on overlaying water on heavy metals release from the storm sewer sediments. *Journal of Chemistry*, 11.

Jung, M. C. (2001). Heavy metal contaminiation of soils and waters in and around the Imcheon Au-Ag mine, Korea. *Appl. Geochem., 16*, 1369-1375.

Montuelle, B., & Graillot, D. (2017). Fate and effect of pollutants in rivers: from analysis to modeling: Springer.

Ololade, I. A., Lajide, L., Amoo, I. A (2008). Seasonal metal distribution in Ondo Coastal Sediment, Nigeria. *J. Appl. Sci. Environ. Mgmt., 12*(4), 11-18.

Pra Basin. (2012). *Pra Basin IWRM Plan*

Rajendran, P., Muthukrishnan J., and Gunasekaran P. (2003). Microbes in heavy metal remediation. . *Indian J. Exp. Biol., 41*(9), 935-944.

Rathod, S. D., Mohsin, M., Farooqui, M. (2011). Water Quality Index In & Around Waluj–Shendra Industrial Area Aurangabad.(MS). *Asian J. Biochem. Pharmaceut. Res, 1*(2).

Sekabira, K., Origa, H. O., Basamba, TA., Mutumba, G., Kakudidi, E. (2010). Assessment of heavy metal pollution in the urban stream sediments and its tributaries. *International Journal of Environmental Science & Technology, 7*(3), 435-446.

WRC. (2012). *National Integrated Water Resources Management Plan*

Yi, Y., Yang, Z., Zhang, S. (2011). Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze river *Environ. Pollut., 169*, 2575-2585.

Figures

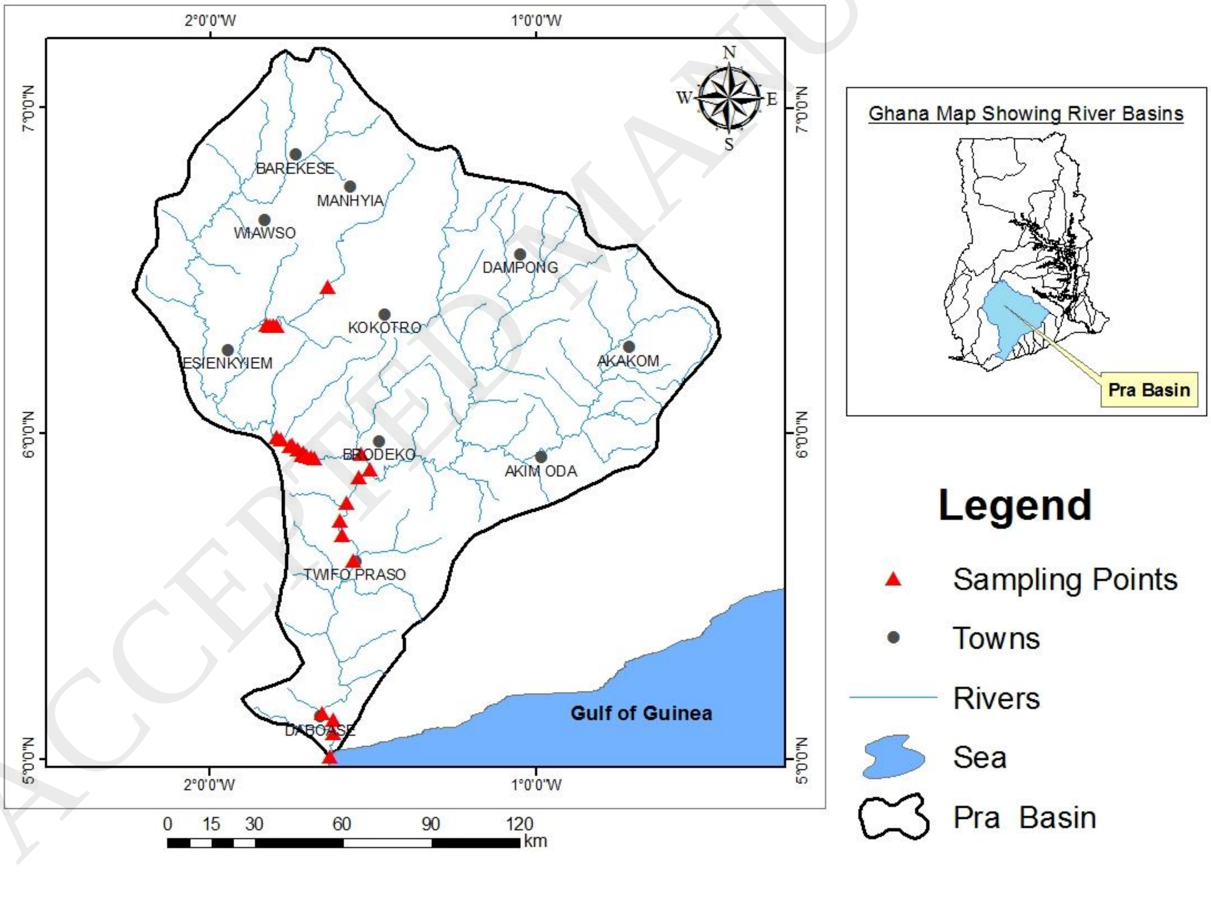
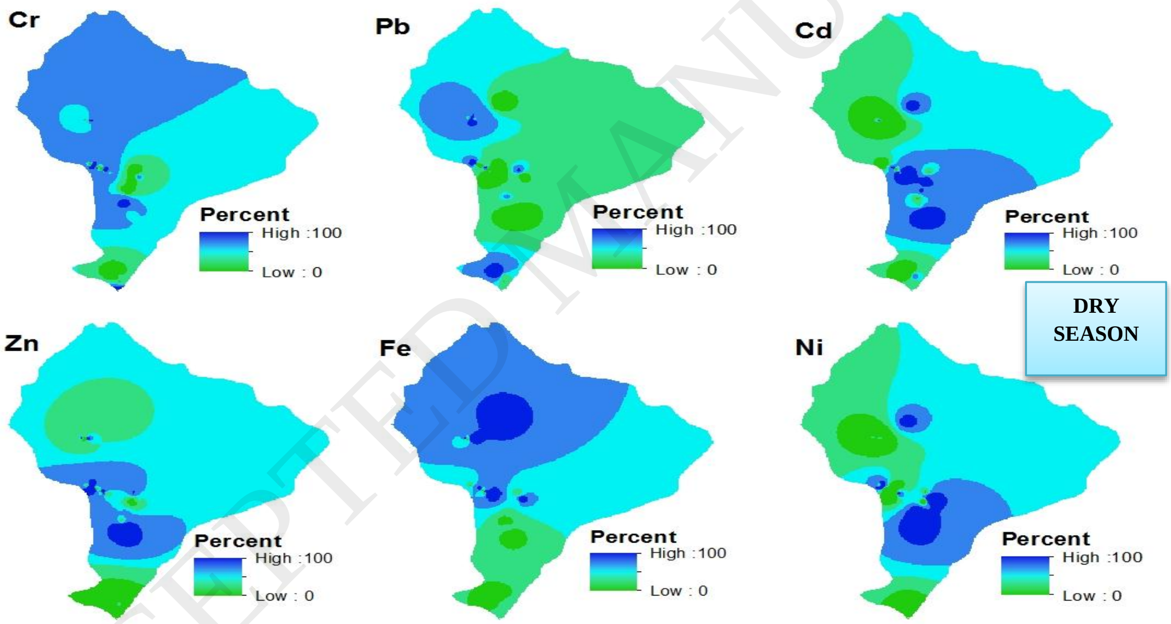


Fig.1. Map of the study area of the Pra River Basin, Ghana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Pb
Cd
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Fe
Ni
Percent
High :100
Low : 0
DRY SEASON

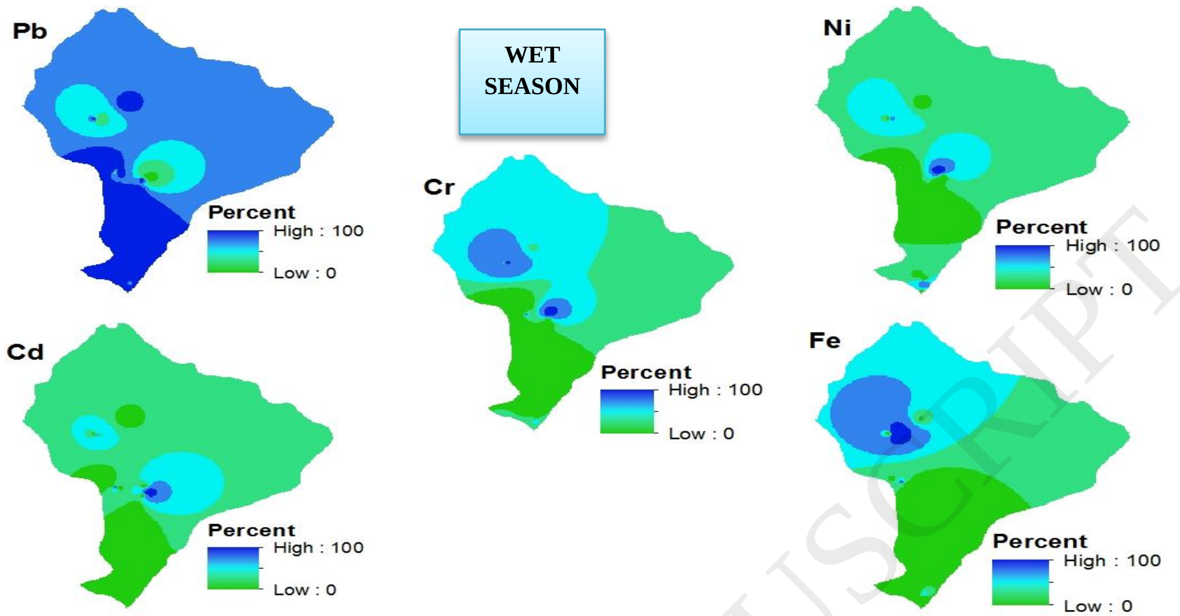

Fig. 2. Percentage distribution of polluting metals in the Pra Basin Rivers

Table 1
Water quality parameters of the Pra River and its tributaries in the Pra Basin of Ghana

Sites	Temperature ºC		pH		Electrical Conductivity(μs cm^{-1})		Turbidity (NTU)	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Lake(LAK)	29.58	27.85	**8.82**	8.96	9.38	131.28	**1.42**	**171.87**
Oda (OD1)	28.00	27.00	7.39	7.20	252.00	178.15	**74.95**	**303.75**
Oda (OD2)	28.20	28.08	7.76	7.30	255.75	187.30	**80.93**	**346.75**
Oda (OD3)	28.13	27.63	7.37	7.52	282.00	168.40	**93.15**	**358.50**
Oda (OD4)	27.75	27.45	7.24	7.36	261.25	168.15	**73.48**	**132.75**
Praso Town (PT)	27.75	27.13	7.06	**6.36**	165.08	123.83	**347**	**788**
Praso Subinso (PS)	27.63	27.63	7.20	**6.41**	174.35	124.15	**358.75**	**639.75**
Twifo Agona (TAG)	**30.70**	28.33	7.16	**6.41**	180.30	128.38	**278.50**	**740.50**
Twifo Kotokyire (TK)	**31.20**	28.68	7.05	6.54	210.20	106.75	**339.25**	**623.50**
Assin Awisam (TAW)	**31.13**	28.13	6.93	**6.46**	226.00	111.58	**407.25**	**666.50**
Assin asaman (AAS)	**31.10**	28.88	7.06	**6.44**	281.75	229.50	**376.25**	**603.00**
Assin Nyardom (ANY)	29.93	28.43	7.09	6.80	252.75	144.78	**364.50**	**622.75**
Dunkwa Town (DT)	28.13	27.48	6.92	6.73	248.50	138.70	**297.75**	**693.25**
Dunkwa Upstream (DU)	28.20	27.48	7.24	6.73	169.50	149.46	**490**	**704.00**
Dunkwa Breman (DBR)	27.63	27.25	7.38	6.62	293.50	142.58	**509.5**	**584.25**
Dunkwa Downstream(DDO)	29.30	28.55	7.39	6.89	274.75	133.98	**401.75**	**490.75**
Dunkwa Ankaase (DAN)	29.13	28.20	7.08	6.49	313.00	135.88	**231.25**	**407.25**
Dunkwa Kojokrom (DKO)	**30.53**	29.25	7.10	6.88	278.75	137.05	**498.5**	**803**
Appiah Nkwanta (ANK)	**30.48**	28.50	7.40	7.13	252.00	127.93	**366.8**	**657.75**
Dunkwa Edwuma (DED)	29.68	28.50	7.34	**6.47**	241.25	115.48	**342**	**779.25**
Dunkwa Akropong (DAK)	29.85	28.48	**6.10**	6.78	223.65	124.93	**473**	**631.00**
Dunkwa Kyekyere (DKY)	**30.63**	28.63	7.01	6.54	224.75	134.10	**366.75**	**692.75**
Anhwia Nkwanta (AAN)	28.75	27.68	7.27	7.19	344.75	245.50	**50.53**	**71.83**
Beposo (BEP)	28.10	27.55	6.68	6.88	162.10	150.50	**325.50**	**589**
Daboase (DAB)	28.13	27.60	7.48	6.68	154.50	157.25	**304.50**	**544**
Atwereboanda (ATW)	28.75	27.90	7.21	6.61	917.50	531.50	**213.75**	**373.25**
Shama (SHA)	27.50	27.05	7.30	6.79	361.25	363.50	**36.78**	**426.25**
Average± SD	29.10±0.20	27.97±0.27	7.22± 0.19	6.86±0.22	259.65±13. 96	170.02±81. 23	285.33±40. 79	535.01± 78.00
Average Max	32	30	8.94	9.67	950	948	609	910
Average Min	27	27	5.08	5.5	3.7	97.2	1.05	2.14
WHO (2011)	25-30		6.5-8.5		1000		5	

Bolded figures are above WHO standards.

Table 2
Mean metal concentration (mg/L) in water sample in the Pra Basin and maximum permitted concentration in water (mg/L) during dry season

Sites	Dry Season								
	As exp -3	Zn	Pb	Cu	Cd	Fe	Mn	Cr	Ni
LAK	0.745	1.141	**0.016**	0.031	**0.004**	1.916	0.051	0.045	0.014
OD1	1.746	**4.430**	**0.489**	0.340	**0.016**	**5.660**	0.163	**0.146**	0.068
OD2	1.734	**4.097**	**0.050**	0.368	**0.047**	**5.718**	0.173	**0.149**	**0.073**
OD3	0.674	**3.246**	**0.467**	0.333	**0.028**	**5.045**	0.168	**0.243**	**0.073**
OD4	0.994	1.263	**0.245**	0.367	**0.047**	**5.518**	0.267	**0.212**	**0.090**
PT	2.164	**6.215**	**0.057**	0.595	**0.084**	**3.446**	0.095	**0.199**	**0.131**
PS	1.603	**6.545**	**0.099**	0.213	**0.036**	**3.928**	0.028	**0.244**	**0.119**
TAG	3.736	**3.647**	**0.164**	0.295	**0.035**	**2.998**	0.033	**0.217**	**0.114**
TK	1.168	**4.065**	**0.114**	0.188	**0.049**	**4.118**	0.021	0.039	**0.136**
TAW	1.861	1.811	**0.108**	0.257	**0.056**	**5.219**	0.101	**0.071**	0.057
AAS	2.750	2.745	**0.058**	0.091	**0.035**	**5.254**	0.062	**0.137**	**0.119**
ANY	1.094	**4.963**	**0.190**	0.229	**0.035**	**4.131**	0.124	**0.290**	**0.074**
DT	1.023	**4.324**	**0.502**	0.079	BDL	**6.226**	0.115	**0.127**	**0.131**
DU	3.197	**5.487**	**0.021**	0.071	**0.028**	**4.007**	0.007	**0.269**	**0.142**
DBR	2.246	**7.435**	**0.086**	0.657	**0.036**	**4.563**	0.197	**0.204**	0.000
DDO	2.762	0.234	**0.048**	0.054	**0.042**	**5.012**	0.157	0.019	0.063
DAN	2.235	**6.081**	**0.579**	0.183	**0.028**	**5.825**	0.094	**0.126**	**0.091**
DKO	0.603	**5.199**	**0.026**	0.230	**0.017**	**5.458**	0.041	**0.326**	0.015
ANK	1.939	**4.573**	**0.077**	1.676	**0.027**	**3.716**	0.061	**0.076**	0.052
DED	1.612	**3.842**	**0.106**	0.317	**0.029**	**4.951**	0.057	**0.151**	0.009
DAK	2.254	1.890	**0.013**	1.636	**0.040**	**4.569**	0.018	**0.102**	**0.083**
DKY	2.118	1.994	**0.018**	0.340	**0.043**	**5.361**	0.047	**0.100**	0.069
AAN	1.883	2.272	**0.047**	0.292	**0.041**	**6.037**	0.297	**0.154**	**0.086**
BEP	1.849	**3.188**	**0.105**	0.474	**0.048**	**4.835**	0.306	**0.169**	0.068
DAB	2.314	2.907	**0.697**	0.422	**0.046**	**4.431**	0.177	**0.285**	**0.198**
ATW	1.108	2.155	**0.122**	0.428	**0.045**	**5.467**	0.327	**0.475**	**0.083**
SHA	1.647	1.623	**0.162**	0.218	**0.048**	**5.768**	0.295	**0.468**	**0.083**
Average ±SD	1.893 ±0.756	3.703±1.771	0.175±0.192	0.394±0.392	0.037±0.017	4.784±0.897	0.129±0.099	0.187±0.115	0.08 ±0.048
Max	7.930	9.252	0.894	3.824	0.161	7.768	0.520	0.820	0.541
Min	0.051	0.000	0.000	0.000	0	1.124	0.000	0	0

WHO(2011)	0.01	3	0.01	2	0.003	2	0.4	0.05	0.07

Bolded figures are above WHO standards; BDL = below detection limit

Table 3

Mean metal concentration (mg/L) in water sample in the Pra Basin and maximum permitted concentration in water (mg/L) during wet season

Sites	Wet Season								
	As exp -3	Zn	Pb	Cu	Cd	Fe	Mn	Cr	Ni
LAK	0.076	BDL	**0.032**	0.037	BDL	1.725	BDL	0.020	0.025
OD1	1.431	BDL	**1.492**	0.118	**0.007**	**6.905**	BDL	**0.164**	**1.514**
OD2	1.407	BDL	**1.200**	0.458	BDL	1.197	0.166	**0.275**	**0.176**
OD3	0.798	BDL	**1.170**	0.222	BDL	1.601	BDL	**0.252**	**0.201**
OD4	2.438	BDL	**1.135**	0.178	**0.499**	1.729	0.021	**0.110**	**0.246**
PT	1.414	BDL	**1.098**	0.334	BDL	**2.265**	BDL	**0.072**	**0.128**
PS	0.997	BDL	**1.189**	0.346	BDL	1.634	BDL	0.040	**0.133**
TAG	1.585	BDL	**1.454**	0.310	BDL	1.883	BDL	**0.094**	**0.120**
TK	0.663	BDL	**0.770**	0.201	BDL	1.841	BDL	**0.070**	**0.106**
TAW	0.595	BDL	**0.870**	0.326	BDL	**2.086**	BDL	0.016	**0.146**
AAS	0.948	BDL	**0.568**	0.155	**0.771**	**2.197**	BDL	**0.493**	**0.221**
ANY	1.620	BDL	**0.677**	0.341	BDL	1.426	BDL	**0.460**	**1.935**
DT	1.025	BDL	**0.810**	0.305	BDL	1.132	BDL	0.019	**0.128**
DU	1.065	BDL	**0.926**	0.151	BDL	**3.984**	BDL	0.039	**0.118**
DBR	0.803	BDL	**0.994**	0.487	BDL	**2.339**	BDL	0.018	**0.335**
DDO	1.591	BDL	**0.900**	0.019	BDL	**9.847**	BDL	0.033	**0.166**
DAN	2.171	BDL	**1.139**	0.306	BDL	**2.826**	BDL	0.030	**0.268**
DKO	1.351	0.722	**0.830**	0.196	BDL	**2.283**	BDL	0.043	**0.198**
ANK	1.484	BDL	**1.123**	1.385	BDL	0.792	BDL	0.029	**0.232**
DED	1.205	BDL	**1.223**	0.152	**0.370**	1.505	BDL	0.048	**0.158**
DAK	1.438	BDL	**1.335**	0.751	BDL	0.443	BDL	**0.126**	**0.243**
DKY	1.321	BDL	**1.186**	0.132	BDL	**2.338**	BDL	**0.260**	**0.200**
AAN	0.969	BDL	**1.215**	0.383	BDL	**3.257**	BDL	**0.150**	**0.257**
BEP	1.494	BDL	**0.993**	0.382	BDL	**5.150**	BDL	**0.077**	**0.191**
DAB	0.856	BDL	**1.470**	0.195	BDL	1.690	BDL	**0.134**	**0.316**
ATW	0.817	BDL	**0.916**	0.370	BDL	0.762	BDL	**0.146**	**0.902**

SHA	0.878	BDL	**0.971**	0.179	BDL	1.735	BDL	**0.113**	**0.206**
Average ± SD	1.201±0.483	0.027±0.139	1.025±0.307	0.312±0.263	0.061±0.184	2.493±1.998	0.007±0.032	0.123±0.126	0.329 ±0.434
Max	5.435	1.166	3.752	1.978	0.148	4.019	0.5846	1.473	0.537
Min	0.00	0.000	0.000	0.008	0	1.341	0	0	0
WHO(2011)	0.01	3	0.01	2	0.003	2		0.05	0.07

Bolded figures are above WHO standards; BDL = below detection limit

Table 4

Independence t-test for heavy metals and physicochemical parameters

Parameter	Season	mean	SD	SE	MD	DF	Sig (2-tailed)	t
Temperature	1	29.10	1.25	0.24	1.13	52	0.00	4.24
	2	27.97	0.60	0.12				
pH	1	7.22	0.44	0.08	0.37	52	0.01	2.76
	2	6.85	0.53	0.01				
EC	1	259.65	148.91	28.66	89.62	52	0.01	2.68
	2	170.02	89.34	17.19				
Turbidity	1	285.32	154.41	29.7	-249.68	52	0.00	-5.07
	2	535.01	203.70	39.02				
Zinc	1	3.61	1.84	0.35	3.58	52	0.00	10.09
	2	0.03	0.14	0.03				
Lead	1	0.17	0.19	0.04	-0.85	52	0.00	-12.21
	2	1.03	0.31	0.06				
Cadmium	1	0.04	0.02	0.00	-0.02	52	**0.50**	- 0.68
	2	0.06	0.18	0.04				
Iron	1	4.78	1.01	0.19	2.32	52	0.00	5.37
	2	2.47	2.00	0.39				
Chromium	1	0.19	0.11	0.02	0.06	52	**0.06**	1.92
	2	0.12	0.13	0.02				
Nickel	1	0.08	0.04	0.00	-0.24	26.22	0.01	-2.92
	2	0.33	0.43	0.08				

SD= standard deviation; SE= standard error; MD = mean difference; DF= degree of freedom; SED = standard error difference; EC = Electrical Conductivity; Season 1 = dry season; Season 2 = wet season; $P < 0.05$

Table 5

Pollution index and water quality index for dry and wet seasons

Sites	NPI dry season						WQI	NPL wet season					WQI
	Zn	Pb	Cd	Fe	Cr	Ni		Pb	Cd	Fe	Cr	Ni	
LAK	0.38	**1.6**	**1.33**	0.95	0.9	0.2	68	**3.2**	0	0.88	0.4	**0.36**	85
OD1	**1.48**	**48.9**	**5.33**	2.83	**2.92**	0.97	31	**149**	**2.33**	**3.48**	**3.28**	**21.6**	31
OD2	**1.37**	**5.0**	**15.7**	2.86	**2.98**	**1.04**	35	**120**	0	0.59	**5.5**	**2.51**	37
OD3	**1.08**	**46.7**	**9.33**	2.52	**4.86**	**1.04**	30	**117**	0	0.80	**5.04**	**2.87**	38
OD4	0.42	**24.5**	**15.6**	2.76	**4.24**	**1.3**	31	**113**	**166**	0.86	**2.2**	**3.51**	31
PT	**2.07**	**5.7**	**28**	1.72	**3.98**	**1.87**	42	**109**	0	**1.13**	**1.44**	**1.83**	37
PS	**2.18**	**9.9**	**12**	1.96	**4.88**	**1.7**	32	**118**	0	0.82	0.8	**1.90**	38
TAG	**1.22**	**16.4**	**11.667**	1.49	**4.34**	**1.63**	35	**145**	0	0.94	**1.88**	**1.71**	37
TK	**1.36**	**11.4**	**16.3**	2.06	0.78	**1.94**	36	**77**	0	0.92	**1.4**	**1.51**	40
TAW	0.60	**10.8**	**18.6**	2.61	**1.42**	0.81	37	**87**	0	**1.04**	0.32	**2.09**	40
AAS	0.92	**5.8**	**11.7**	2.63	**2.74**	**1.7**	38	**56.8**	**257**	**1.10**	**9.86**	**3.16**	32
ANY	**1.65**	**19**	**11.7**	2.06	0.73	**1.05**	34	**67.7**	0	0.71	**9.2**	**27.6**	39
DT	**1.44**	**50.2**	0.00	3.11	**2.54**	**1.87**	37	**81**	0	0.57	0.38	**1.83**	40
DU	**1.83**	**2.1**	**9.33**	2.00	**5.38**	**2.02**	39	**92.6**	0	**1.99**	0.78	**1.69**	38
DBR	**2.48**	**8.6**	**12**	2.28	**4.08**	0	36	**99.4**	0	**1.17**	0.36	**4.79**	37
DDO	0.08	**4.8**	**14**	2.51	0.38	0.9	55	**90**	0	**4.92**	0.66	**2.37**	38
DAN	**2.03**	**57.9**	**9.33**	2.91	**2.52**	**1.3**	29	**113**	0	**1.43**	0.6	**3.83**	37
DKO	**1.73**	**2.6**	**5.66**	2.73	**6.52**	0.21	41	**83**	0	**1.14**	0.86	**2.83**	39
ANK	**1.52**	**7.7**	**99.6**	1.86	**1.52**	0.74	45	**112**	0	0.40	0.58	**3.31**	41
DED	**1.28**	**10.6**	**9.66**	2.48	**3.02**	0.13	36	**122**	**123**	0.75	0.96	**2.26**	33
DAK	0.63	**1.3**	**13.3**	2.28	**2.04**	**1.19**	44	**133**	0	0.22	**2.52**	**3.47**	44
DKY	0.67	**1.8**	**14.3**	2.68	**2**	0.98	42	**118**	0	**1.17**	**5.2**	**2.86**	36
AAN	0.76	**4.7**	**13.6**	3.02	**3.08**	**1.23**	41	**121**	0	**1.63**	**3**	**3.67**	36
BEP	**1.06**	**10.5**	**16**	2.41	**3.38**	0.97	33	**99.3**	0	**2.58**	**1.54**	**2.73**	37
DAB	0.97	**69.7**	**15.3**	2.22	**5.7**	**2.83**	28	**147**	0	0.85	**2.68**	**4.51**	37
ATW	0.72	**12.2**	**15**	2.73	**9.5**	**1.19**	32	**91.6**	0	0.38	**2.92**	**12.8**	41

SHA	0.54	**16.2**	**16**	2.88	**9.36**	**1.17**	28	**97.1**	0	0.87	**2.26**	**2.94**	39.
Mean	1.203	17.281	15.568	2.391	3.548	1.184	37.593	102.322	20.309	1.235	2.467	4.687	39.185
Standard	1 ≤						100	1 ≤					100