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J. Appl. Sci. Environ. Manage. Vol. 28 (4) 1281-1286 April 2024

Using Enrichment Factor Approach for Source Identification of Potentially Toxic Heavy Metals along Benin-Ore-Sagamu Expressway in Nigeria

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ABSTRACT: The variation in heavy metal concentration in different environment is dependent on the emission source. Source identification of heavy metal plays an important role in providing solution to its contamination in the atmosphere. Hence, the objective of this paper is to engage enrichment factor (EF) approach to evaluate the source identification of potentially toxic heavy metals along the Benin-Ore-Sagamu Expressway in Nigeria in four sampling locations (A, B, C and D) that are denoted with high traffic congestion. The source identification of Cu, Zn, Mn, Ni, Pd, Cd, Cr and Pb contamination in the study area were determined using appropriate standard methods. The EF values indicated for Cu ranged from (2.3-5.9), Zn (0.48-0.86), Mn (0.29-0.49), Ni (1.27-4.03), Pd (37012.18-59922.57), Cd (1909.11-2844.81), Cr (4.56-7.76) and Pb (0.77-4.64). The results suggest crustal source enrichment for Zn and Mn while Cu, Ni, Cr and Pb were enriched moderately. However, the EF values for Pd and Cd were found to be greater than 50, indicating extremely severe enrichment. The findings of this study provide evidence of anthropogenic impact on heavy metals pollution in the study area that is attributed to the intense vehicular traffic.

DOI: https://dx.doi.org/10.4314/jasem.v28i4.29

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Cite this Article as: RAJI, WA; JIMODA, LA; AJANI, AO; POPOOLA, AO (2024). Using Enrichment Factor Approach for Source Identification of Potentially Toxic Heavy Metals along Benin-Ore-Sagamu Expressway in Nigeria. *J. Appl. Sci. Environ. Manage.* 28 (4) 1281-1286

Dates: Received: 22 January 2024; Revised: 29 February 2024; Accepted: 23 March 2024 Published: 29 April 2024

Keywords: Pollution; Heavy metals; Source identification; Enrichment Factor; Crustal source; Anthropogenic.

Heavy metal concentrations in particulates vary for different environment as a result of contribution of different pollution sources. The two distinct sources contributing to heavy metals concentration in the environment are due to natural weathering of the rocks and minerals known as background or crustal level, and metals derived from human activities which is referred to as anthropogenic origin (Jadaa and Mohammed, 2023; Malik and Sandhu, 2023). These anthropogenic activities include biomass burning, mining and smelting of ore, effluents from industrial and domestic activities, and combustion of fossil fuel (Narjala, 2021). Combustion of fossil fuel has been reported as one of the major sources of some heavy metals (Tesleem and Akinade, 2023). However, asides the fuel combustion, non-exhaust of motor vehicles such as wear of tyre and brake linings, road abrasion, corrosion of batteries and galvanized parts such as tanks and radiator also contribute to heavy metals pollution (Singh and Devi, 2023; Rasheida, 2017). According to Denny *et al.* (2022), road dusts are potent media for transportation and distribution of heavy metals in urban environments, hence, people residing in communities that are 150-300 m away from roadside or highway are liable to potentially toxic heavy metals pollution (Gabe and Yonah, 2022). The

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heavy metals that are associated with transportation emissions include Copper (Cu), Iron (Fe), Zinc (Zn), Manganese (Mn), Nickel (Ni), Cobalt (Co), Palladium (Pd), Rhodium (Rh), Cadmium (Cd), Chromium (Cr) Titanium (Ti) and Lead (Pb) (Natasa *et al.*, 2023; Zhang *et al.*, 2021; Miroslaw *et al.*, 2020; Adamiec *et al.*, 2016; Ryszard, 2013). In order to assess and ascertain the main source contributing significantly to heavy metals pollution in the study area, an Enrichment Factor (EF) approach was adopted.

Enrichment factor is a widely used metric for determining how much the presence of an element in a sampling media has increased relative to average natural abundance due to human activities. EF can be calculated by normalizing metal concentrations to an element that varies minimally in concentration with respect to a sample reference metal which does not vary due to geogenic or anthropogenic processes (Ediagbonya, 2016). Generally, Iron (Fe), Aluminium (Al), Silicon (Si) and Titanium (Ti) are used as reference elements due to their abundance in the Earth's crust (Denny et al., 2022; Javid et al. 2021; Kadhum, 2020; Agnieszka, 2020; Mansour, 2016; Graciela et al. 2013). The Enrichment factor method has been employed as a tool for the assessment of heavy metals contamination in various environmental media by several researchers (Denny et al., 2022; Javid et al. 2021; Kantor et al., 2018; Kadhum, 2020; Agnieszka, 2020; Barbieri, 2016; Ediagbonya, 2016; Graciela et al. 2013). Hence, the objective of this paper is to engage enrichment factor approach to evaluate the source identification of potentially toxic heavy metals along the Benin-Ore-Sagamu Expressway in Nigeria.

MATERIALS AND METHODS

Four sampling locations (A, B, C and D) were selected for the sampling of heavy metals at Benin-Ore-Sagamu expressway during dry and wet season. These sampling locations are denoted with high traffic and a stop point for travellers. The sampled metals are metals associated with motor vehicles emissions which include, Copper (Cu), Zinc (Zn), Manganese (Mn), Nickel (Ni), Palladium (Pd), Cadmium (Cd), Chromium (Cr) Titanium (Ti) and Lead (Pb). The elemental concentrations of metals were obtained using Thermoscientific Nilton XL2 Energy Dispersive Xray Fluoresce (EDXRF). The quantitative measure of the extent of anthropogenic heavy metal pollution in the study area was determined using the EF method. This method requires elemental concentrations of metals in the sample and their concentrations in the Earth's crust with respect to the reference element. In this work, Titanium (Ti) was selected as the reference element because of its geochemical nature whose substantial amounts occur in the environment but has

no characteristic effects. The concentration of metals in the Earth's crust was obtained from the handbook published by William (2017). Equation 1 was used to obtain the EF of the metals.

$$EF_i = \left(\frac{C_i}{C_{ref}}\right)_s / \left(\frac{C_i}{C_{ref}}\right)_{bkg} \tag{1}$$

Where EF_i is enrichment factor for metal *i*, C_i and C_{ref} are concentrations ($\mu g/m^3$) of metal *i*, and reference element while subscripts *s* and *bkg* denote sampled and background metal level, respectively.

RESULT AND DISCUSSIONS

The Enrichment factor (EF) method was used to investigate the contribution of crustal and anthropogenic activities to heavy metal pollution in the study area because of its degree of perturbation that differentiates natural and anthropogenic sources. The pollution categories that are generally recognized for the identification of source of pollution include, EF \leq 1, no enrichment; $1 < EF \leq 3$, minor enrichment; $3 < EF \leq 5$, moderate enrichment; $5 < EF \leq 10$, moderately severe enrichment; $10 < EF \leq 25$, severe enrichment; $25 < EF \leq 50$, very severe enrichment; EF > 50, extremely severe enrichment (Zhang *et al.*, 2019; Walla and Anmar-Dharav, 2015). The Enrichment Factor (EF) of each metal is shown in Figure 1-8.

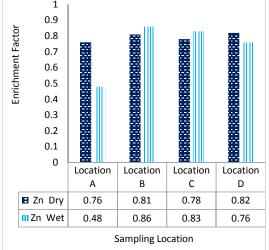


Fig 1: The EF of Zinc (Zn) across the Sampling Locations.

Figure 1 shows the Enrichment Factor (EF) of Zinc (Zn) across the sampling locations. The EF for Zn across the selected sampling locations were calculated for wet and dry seasons. The highest EF value (0.86) was recorded at location B while the lowest (0.48) was recorded at location A. All the values obtained were less than 1 in all the four locations. This is an indication that, Zn is attributed to crustal derived trace metal in the selected study area. This result outcome

is in accordance with the enrichment factor of Zinc reported by Ediagbonya (2016). However, the study carried out by Rajaram *et al.*, (2014) and Javid *et al.*, (2021) reported moderate and extremely severe enrichment of Zinc.

Figure 2 shows the Enrichment factor (EF) of Manganese (Mn) in the study area. The EF of Manganese (Mn) across location A, B, C, D in the dry and wet season were 0.36, 0.49, 0.38, 0.45 and 0.39, 0.29, 0.32, 0.5, respectively. It ranged between 0.29 - 0.5. The highest EF (0.5) was recorded at location D while the lowest EF (0.29) was recorded at location B in wet season. These values were found to be less than 1, indicating no enrichment of Mn in the study area. Acciai *et al.*, (2017) also reported no enrichment for Mn, this implies that Mn is a crustal derived metal.

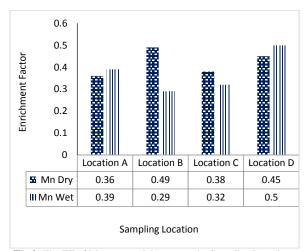


Fig 2: The EF of Manganese (Mn) across the Sampling Locations

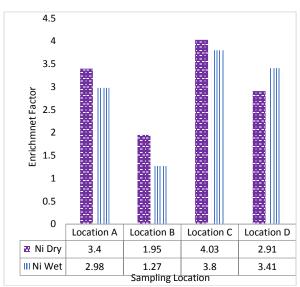


Fig 3: The EF of Nickel (Ni) across the Sampling Locations

Figure 3 shows the Enrichment factor (EF) of Nickel (Ni) in the study area. The EF of Nickel (Ni) across the sampling locations in the dry and wet season ranged from 4.03 - 2.91. The highest EF (4.03) was recorded at location C while the lowest EF (2.91) was at location D in the dry season. The EF values at location A in the dry season and location B (1.95, 1.27) showed a minor enrichment while others suggested moderate enrichment of Ni in the study area. This result outcome is similar to the EF value of Ni reported by Denny *et al.*, (2022) and Kui and Chang (2019).

Figure 4 shows the Enrichment Factor (EF) of Palladium (Pd) for wet and dry season across the sampling locations and their values were 42292.77, 52991.06, 45544.98, 59922.57 and 37012.18, 37234.49, 45274.77, 41587.07, respectively. The enrichment factor values for palladium were all found to be greater than 50, indicating extremely severe enrichment. Palladium is a well-recognized key tracer of non-exhaust brake wear, hence, it is suggested that Palladium pollution in this study is originated from vehicular emissions.

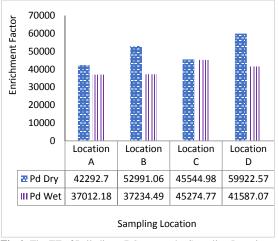


Fig 4: The EF of Palladium (Pd) across the Sampling Locations.

Figure 5 shows the Enrichment factor (EF) of Chromium (Cr) across the sampling locations. Chromium enrichment factor (EF) for wet and dry season across the sampling locations were 5.17, 5.63, 5.75, 5.65 and 5.88, 4.56, 5.06, 7.76 respectively. The EF values for Cr in all sampling locations were all greater than 5 except at location C (4.56), indicating moderately severe enrichment. Kui and Chang (2019) reported the contamination level of Chromium in the road dust to be a minor enrichment while, Abubakr *et al* (2018) reported Cr to be a crustal derived metal with no enrichment from anthropogenic activities.

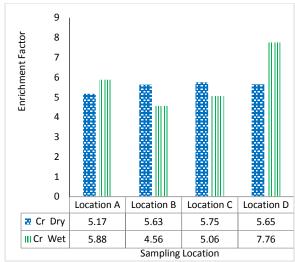


Fig 5: The EF of Chromium (Cr) across the Sampling Locations.

Figure 6 shows the enrichment factor (EF) of Cadmium (Cd) calculated across the selected sampling locations. The highest EF (2844.81) was recorded at location D while the lowest EF (1909.11) was recorded at location B in the dry season. In the wet season, the EF values at location A, B, C and D were 2301.95, 2023.23, 2268.45 and 1958.77, respectively. All EFs of Cd obtained were greater than 50, indicating extreme severe enrichment. This result is in agreement with the findings of Zhang *et al.*, (2020), who reported the contamination of Cd to be severely enriched. This implies that Cd, a highly poisonous metal is derived from anthropogenic source, specifically from the motor vehicles in this study.

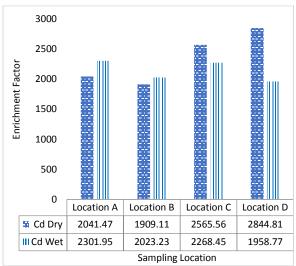


Fig 6: The EF of Cadmium (Cd) across the Sampling Locations.

Figure 7 shows the Enrichment factor (EF) of Copper (Cu) across the sampling locations. Copper EF for wet and dry season across the sampling locations were 2.54, 2.3, 2.51, 5.9 and 2.23, 2.37, 2.08, 2.97

respectively. The highest (5.9) enrichment factor was found at location D in the dry season. However, the EF values for Copper in all sampling locations were found to be lower than 3 except at location D (5.9), indicating minor enrichment to moderately severe enrichment. Agnieszka (2020) also reported the contamination level of copper in the road dust to be a minor enrichment. Copper is considered to be an anthropogenic derived metal which is obtained mainly from vehicle brake pads.

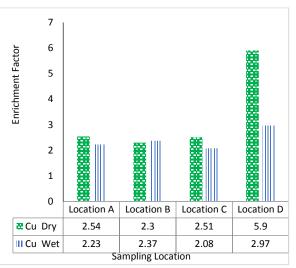


Fig 7: The EF of Copper (Cu) across the Sampling Locations.

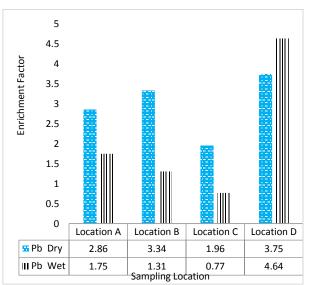


Fig 8: The EF of Lead (Pb) across the Sampling Locations.

The Enrichment Factor (EF) of Lead (Pb) in all selected sampling locations is shown in Figure 8. The EF of Lead (Pb) in the dry and wet season were 2.86, 3.34, 1.96, 3.75 and 1.75, 1.31, 0.77, 4.64 respectively. The highest (4.64) enrichment factor of Pb was recorded at location D and the lowest (0.77) recorded

was at location C in the wet season. These values suggested minor to moderate enrichment except at location C that indicated no enrichment of Lead (Pb) in the wet season. This result is consistent with the findings of Agnieszka (2020) who reported the contamination level of Lead (Pb) in the road dust to be a moderately enriched. This implies that Pb pollution is majorly from anthropogenic activities.

Conclusion: The source identification of potentially toxic metals such as Cu, Zn, Mn, Ni, Pd, Cd, Cr and Pb was determined using Enrichment Factor (EF) method. The EF of Zn and Mn in the study area indicates no enrichment which implies that they are derived from the Earth crust without the influence of vehicular emissions. While the EF of Cu, Ni, Cr and Pb were moderately enriched. However, the EF of Pd and Cd was found to be greater than 50, indicating extremely severe enrichment. The study shows that areas of heavy traffic or vehicular movements were indicative of the contribution of motor vehicles to the degradation of air quality as a result of air pollutants emission.

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