

Ecological Health Risk Evaluation of Potentially Toxic Metals in Saline Soils Used for Table Salt Production in Awe Salt Mining Community of Nasarawa State

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Abstract

The assessment of potentially toxic metals (PTMs) in saline soils used for table salt production is critically important because salinity can enhance the solubility and transport of metals in soils. This study assessed the concentrations, contamination and ecological risks of selected PTMs in saline soils used for table salt production in Awe Salt Mining Community, Nasarawa State, Nigeria. Soil samples were collected and analyzed for metal (Al, As, Cr, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) concentration using Genius-IF energy dispersive X-ray fluorescence (EDXRF) spectrometer. Enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), degree of contamination (C_d), pollution load index (PLI) and ecological risk assessment (ERA) were evaluated using the measured concentrations of the PTMs. Result showed that Fe (37112.29±377.59–117044.29±993.20) was the most abundant metal. Elevated levels of Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn in the investigated saline soils exceeding their respective average shale reference levels were observed. EF values indicated that the investigated saline soils have very high enrichment of Co, Cr, Cu, Hg, Mn, Pb and Zn. CF values showed that Co, Cr, Cu, Hg, and Mn are probably responsible for the high contamination. C_d and PLI revealed high degree of contamination for all investigated saline soils. The presence Co, Cu and Hg may probably be the key controlling factor causing the potential ecological risk. These findings have provided valuable information for effective environmental management strategies and policy to alleviate the influence of PTMs generated from table salt mining environment.

Keywords: Saline soil, table salt mining, heavy metal, ecological risk, soil contamination

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Introduction

Saline soils are characterized by elevated concentrations of soluble salts. They are widespread in arid and semi-arid regions, and their physical and chemical properties significantly influence soil quality and ecosystem function [1]. High salinity does not only affect the soil structure and fertility but also enhances the mobility of various trace elements, including potentially toxic metals (PTMs), thereby increasing environmental and ecological risks [2, 3]. Saline conditions can alter the speciation, solubility, and transport of metals such as arsenic (As), cadmium (Cd), lead (Pb), copper (Cu), chromium (Cr) and zinc (Zn), potentially facilitating their movement into biotic and abiotic components of the ecosystem [4, 5].

Soils are a rich ecosystem, consisting of both living and non-living matter with varying levels of interaction between them. It is also a critical component due to its ability to accumulate pollutants produced by natural and anthropogenic activities such as from agriculture, industry, mining and vehicular movement. Different processes interact together to aid the movements of heavy metals in soil, and this includes processes of biological, chemical, and physical nature [6]. The ecological risk posed by PTMs in soils is a global concern because these elements are persistent, non-degradable, and can bioaccumulate in the food web, affecting soil organisms, plants, and humans [5]. Ecological risk assessment (ERA) provides a systematic framework to quantify the likelihood that environmental contamination may lead to adverse



ecological effects, typically by comparing measured concentrations of contaminants against established benchmarks and indices such as the contamination factor (CF), enrichment factor (EF), and ecological risk index (RI) [7]. Although ERAs have been extensively applied to agricultural and rehabilitated soils to understand the distribution and risks associated with PTMs (e.g., Poland, Saudi Arabia), similar assessments are limited for saline soils associated with artisanal and industrial salt production, particularly in West Africa [7, 8].

The assessment of potentially toxic metals (PTMs) in saline soils used for table salt production in the Awe Salt Mining Community of Nasarawa State is critically important due to the multi-faceted environmental and public health implications associated with heavy metal contamination in mining and saline environments. Mining and associated processing activities have been widely recognized as significant sources of heavy metal pollution, frequently leading to elevated concentrations of metals such as lead (Pb), cadmium (Cd), chromium (Cr), and others in soil, water, and biota, with resultant ecological and health risks [9–11].

Saline soils present unique challenges for metal mobility and bioavailability; high salinity can increase the solubility and transport of heavy metals, thereby enhancing their environmental risk relative to non-saline soils [7, 12]. This phenomenon underscores the need to investigate PTM behaviour specifically in salt-affected soils where traditional assumptions of metal retention and distribution may not apply. Despite this known susceptibility, there is a paucity of region-specific data on PTM concentrations and ecological risks within saline soils used for salt production, particularly in West African contexts such as Nigeria. Existing ecological risk studies in Nigeria have largely focused on non-saline soil systems affected by industrial, agricultural, or artisanal mining activities [9, 11, 13–16], but information on saline soil systems exploited for commercial salt production is limited or absent. Furthermore, PTMs are persistent, non-biodegradable, and capable of bioaccumulation in soil organisms and higher trophic levels, potentially entering food chains and threatening ecosystem services and human wellbeing [17].

The Awe Salt Mining Community in Nasarawa State, Nigeria, is involved in the extraction and production of table salt from saline soils which is a process that may influence soil salinity levels and the dynamics of PTMs in surface and subsurface environments. Nasarawa State has been identified as a region with active mining activities for various minerals, raising concerns about anthropogenic impacts on soil quality and associated ecological risks [11, 18]. Despite this, there is a paucity of studies investigating toxic metal distribution and the ecological risk linked to the use of saline soils for salt production in Nigeria. Addressing this gap is critical for

sustainable management of soil resources, human health protection, and environmental conservation within mining communities.

This study therefore aims to evaluate the concentrations of selected PTMs in saline soils used for table salt production in the Awe Salt Mining Community and to assess the associated ecological risk, thereby providing baseline data for future policy development and environmental management strategies.

Materials and Methods

Description of study area

Awe is a semi-urban community known for the occurrence of brine which is mined for salt production. It is located in southern Nasarawa State, North-Central Nigeria, at approximately latitude 8°05'N and longitude 9°15'E. The area lies within the Middle Benue Trough, a geologically important region known for mineralization and brine-bearing formations [19]. The terrain is gently undulating, with elevations ranging from 120 to 160 m above sea level. Awe experiences a tropical climate with distinct wet and dry seasons, and an average annual rainfall of about 1100–1500 mm.

Geologically, the Awe Formation is underlain by sedimentary rocks of Albian to Turonian age and is mainly composed of shales, sandstones, and siltstones. It is exposed around Old Awe Town due to erosion by River Baki Abu, contains shallow brine-saturated layers occurring at depths of about 4–38 m. These brine deposits support natural salt springs and make the area suitable for artisanal table salt production [20].

Sample collection and preparation

A total of fifty-five soil samples were collected from the 11 investigated sites using soil auger. Five composite soil samples were collected and analyzed from each of the investigated site. The investigated sites include 10 salt mining sites in Old Awe community and a control which is an arable farm located about 2 km away from Old Awe community. The investigated salt mining sites are not less than 120 m apart from each other. At each location of each investigated site, six quadrants were marked and, in each quadrant, four core soil samples were collected randomly at depth of 0–30 cm and mixed together to give a composite sample and five composite soil samples were collected at different locations for each investigated site. Foreign materials such as waste polythene and plastics, plant debris, pebbles etc. were removed from the soil samples. The soil samples were air-dried for 8 days, pulverized, sieved to less than 2 mm and then, stored in dried plastic containers for analysis. The coordinates of the sample locations were marked with a handheld global positioning system (GPS) and are shown in Fig. 1.

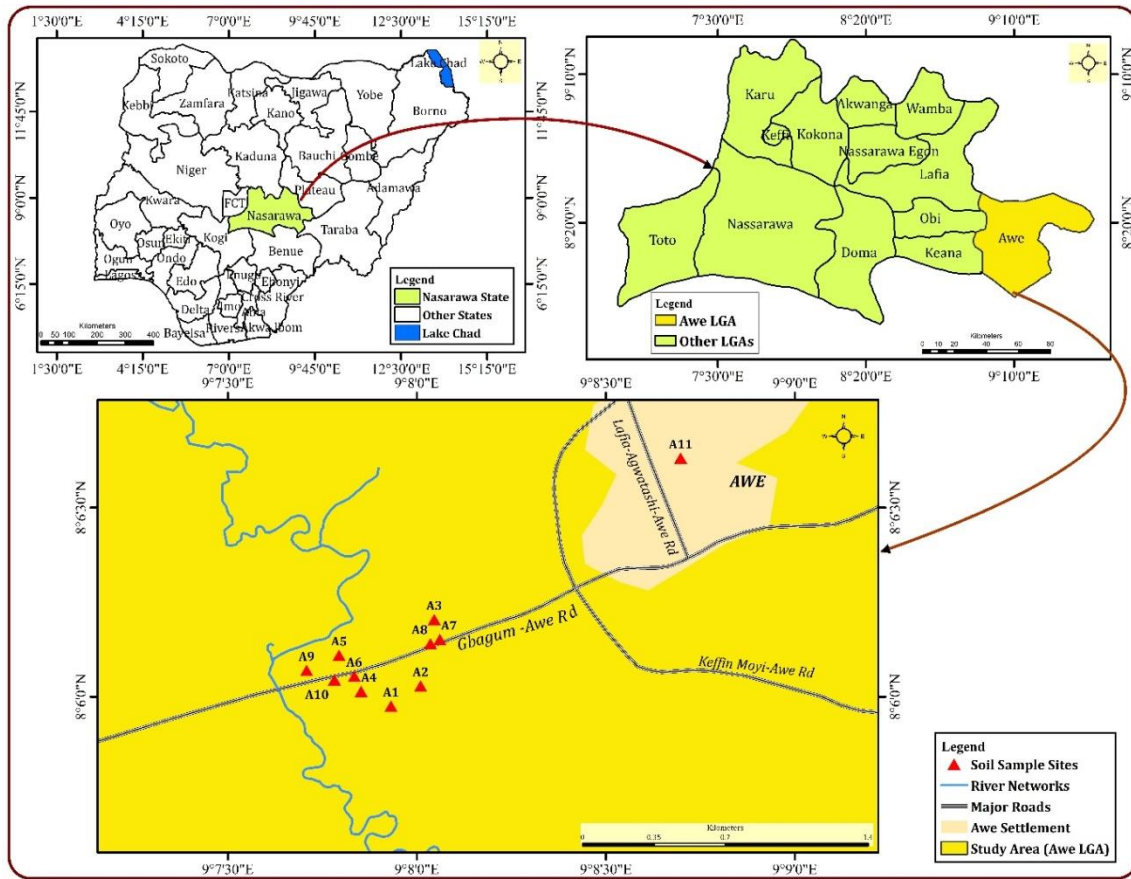


Figure 1: Map of the study area

Analysis of metals

About 25 g of the pulverized sample was placed in a prolene thin film covered sample cup. The lid of the sample cup was tightened shut to engage interlocks so as to avoid leakages or loose particles on the thin film layer. The sample cup was loaded/inserted in the sample turret of Genius-IF energy dispersive X-ray fluorescence (EDXRF) spectrometer. The EDXRF spectrometer was switched on and the X-ray lamp allowed to warm or stabilize for 30 min. It was set at the default mode to analyze the compositions of the soil samples to obtain a spectrum. The spectrum analysis was conducted on an XRS-FP Software

Quality assurance

Quality assurance and quality control were carried out using standard reference materials (SRMs), analyzing spiked samples and repetitive analysis. The percentage recoveries after spike analysis were within the range of 96.7–98.2%, thus indicating good accuracy and precision.

Estimation of contamination level

The extent of soils contamination by the analyzed metals was assessed using the following indices; the enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), and the ecological risk (RI); with principle based on the comparison of estimated values against reference values.

Enrichment factor (EF)

EF is commonly used to assess the contribution of anthropogenic and natural sources of metals in the investigated soils by normalizing the metal concentration in the sample with respect to a reference metal [21]. When EF is close to 1, it indicates a natural source while $EF > 1$ suggests an anthropogenic source. Enrichment factor (EF) can be estimated using Equation 1 [22]:

$$EF = \frac{(C_n/Fe)_{sample}}{(C_n/Fe)_{Background}} \quad (1)$$

Where $(C_n/Fe)_{sample}$ and $(C_n/Fe)_{Background}$ are ratios of metal and reference element (Fe) concentrations in the sample and background concentrations of the metal and reference element (Fe) respectively. The average shale value (ASV) described by Turekian and Wedepohl [23] is usually adopted as the background concentrations (for the metal and reference element). Five (5) contamination categories recognized on the basis of enrichment factor are; $EF < 2$, deficiency to minimal 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 [24].

Geo-accumulation index (I_{geo})

Muller [25] proposed I_{geo} as a single factor contamination index for qualitative assessment of metal pollution in soils. The geo-accumulation index (I_{geo}) was calculated on the basis of Umeh *et al.* [26]:



$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \quad (2)$$

Where C_n is the metal concentration in the examined sample; B_n is the geochemical background while the factor 1.5 is introduced to minimize the effect of possible variations in the background or control values which may be attributed to lithological variations [27]. Seven pollution levels were used to define the intensity of pollution based on the increasing value of geo-accumulation index as follows: $I_{geo} \leq 0$ unpolluted; $0 \leq I_{geo} < 1$ unpolluted to moderately polluted; $1 \leq I_{geo} < 2$ moderately polluted; $2 \leq I_{geo} < 3$ moderately to strongly polluted; $3 \leq I_{geo} < 4$ strongly polluted; $4 \leq I_{geo} < 5$ strongly to extremely polluted; $I_{geo} > 5$ extremely polluted [28].

Contamination factor (CF), degree of contamination (C_d) & pollution load index (PLI)

The contamination factor (CF) is a major tool for identifying the pollution and the contamination level in the samples. The level of contamination of the investigated soil samples by analyzed metals was expressed in terms of contamination factor (CF) and evaluated by employing the Equation 3 [29]:

$$CF = \frac{\text{Concentration of Metals in Soil}}{\text{Target (Background) Values}} \quad (3)$$

Nigerian Directorate of Petroleum Resources [30] target values for metals in soils (Table 1) were adopted as the target (background) values. The following contamination classes were adopted in explaining the contamination factor; $CF < 1$, low contamination; $1 \leq CF < 3$, moderate contamination; $3 \leq CF < 6$, high contamination and $CF > 6$, very high contamination.

Degree of contamination (C_d) is the sum of all contamination factors of the various metals [31]. Generalized model of Hakanson [32] equation for computing C_d was used in this study.

$$C_d = \sum_{i=1}^n (CF_i) \quad (4)$$

Where n is the number of metals studied and CF_i is the contamination factor for metal "i" in the sample. Four degree of contamination categories were used in the interpretation of degree of contamination values; $C_d < 8$, low degree of contamination; $8 \leq C_d < 16$, moderate degree of contamination; $16 \leq C_d < 32$, considerable degree of contamination; $C_d \geq 32$, very high degree of contamination.

Pollution Load Index (PLI) was used to estimate the magnitude of contamination by the simultaneous presence of analyzed metals in a sampling site [33]. PLI was calculated using Equation 5 as described by Onwuka et al. [14].

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \dots \times CF_n)^{1/n} \quad (5)$$

Where, n is the number of metals and CF is the contamination factor of each metal.

Ecological risk assessment

Potential hazard(s) from soil metal contamination was quantified using ecological risk (Er) factor and ecological risk index (RI).

Er is a single index quantitative expression of potential ecological risk of a given contaminant (metal) [32]. It was calculated using Equation 6;

$$Er = Tr \times CF \quad (6)$$

Tr is the toxic response factor presented in Table 1 while CF is the contamination factor of the metal. Five (5) risk levels employed in explaining the potential ecological risk posed by the presence of individual metal in the soil, are as follows: $Er < 40$, low potential ecological risk; $40 \leq Er < 80$, moderate potential ecological risk; $80 \leq Er < 160$, significant potential ecological risk; $160 \leq Er < 320$, high potential ecological risk; $Er \geq 320$, very high potential ecological risk.

Potential ecological risk index (RI) index evaluates the general pollution caused by the simultaneous presence of the 12 analyzed metals. It was calculated using the expression in Equation 7

$$RI = \sum_{i=1}^n Er \quad [7]$$

n is the number of the heavy metal considered; Er and RI are potential ecological risk factor of individual and multiple metals respectively. Four risk levels were used to explain the ecological risk posed sites by the presence of analyzed metals in the investigated site based on the value of ecological risk index: $RI \leq 150$ low ecological risk; $150 \leq RI < 300$ moderate ecological risk; $300 \leq RI < 600$ significant ecological risk; $RI > 600$ high ecological risk.

Results and Discussion

Heavy metal concentration

Table 1 presents the concentrations of 12 metals (Al, As, Cr, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) in the investigated saline soil samples obtained from 10 different locations/sites within the Awe salt mining community. The concentrations were compared to the average shale [23] and Department of Petroleum Resources [30] reference values. Heavy metal contamination in soil poses a significant ecological threat to the environment and to public health [34, 35], particularly because of their toxic nature and potential to bioaccumulate.

Cadmium (Cd), a known carcinogen, was found to be below instrumentation limit of detection in all the investigated soils, indicating the absence of any immediate threat of Cd contamination to the environment. Though this absence is favourable, it remains necessary to continuously monitor Cd levels in the study area because of its high mobility in saline soils [36]. Arsenic (As) and nickel (Ni) were the least occurring metals, appearing only in some of the investigated saline soils and below instrumentation detection limit in the control soil (A11). As was found in only sites A1 (8.52 ± 2.17 mg/kg), A4 (4.14 ± 0.63 mg/kg), A7 (2.95 ± 0.36 mg/kg), and A10 (6.63 ± 1.07 mg/kg), all of which had concentrations above the DPR [30] acceptable limit (1 mg/kg) for arable soil but below the average shale [23] value of 13 mg/kg. This suggests probable enhancement from both localized and natural geogenic activities [37]. Obiora et al. [38] reported similar range (6.9 – 7.7 mg/kg) of As level in

stream sediments around the Pb – Zn mining vicinity of Enyigba, southeastern Nigeria. Ni, on the other hand, was found in only samples A4 and A6. These isolated occurrences could be indicative of anthropogenic activities or site-specific geochemical inputs [39]. The concentrations of essential metals such as Fe, Mn, and Cu were elevated in the majority of the investigated saline soils, exceeding both the DPR [30] threshold (except Zn) and their levels in the control soil. Mn and Cu concentrations were above both their average shale

[23] reference values and DPR [30] acceptable limits. Fe concentrations in the investigated saline soils ranged from 38,644.06±384.69 to 117,044.29±993.20 mg/kg, which was much higher than the DPR [30] threshold of 38,000 mg/kg as well as Fe concentration in the control soil (37,112.29±377.59 mg/kg). These high Fe concentrations found are not unusual, as Fe deposits characterize the Awe locality [40, 11].

Table 1: Concentrations (mg/kg) of analyzed metals in the investigated saline soils

Sample	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
A1	16782.36 ±283.82	8.52 ±2.17	BDL	220.26 ±11.76	561.04 ±79.96	766.92 ±87.88	56255.95 ±573.54	50.94 ±8.72	2052.43 ±154.89	BDL	102.11 ±9.76	353.50 ±36.16
A2	952.94 ±99.16	BDL	BDL	198.24 ±8.08	431.05 ±94.16	1565.79 ±143.77	117044.29 ±993.20	175.94 ±24.10	4151.32 ±247.84	BDL	92.84 ±4.69	393.67 ±56.24
A3	18010.59 ±201.97	BDL	BDL	41.63 ±4.46	526.83 ±78.92	343.51 ±55.91	38644.06 ±384.69	BDL	1092.05 ±92.94	BDL	44.18 ±3.87	104.44 ±20.09
A4	8094.70 ±211.71	4.14 ±0.63	BDL	506.60 ±21.69	882.62 ±119.69	1334.11 ±95.84	50730.38 ±531.57	BDL	2377.72 ±153.88	330.03 ±84.29	119.23 ±6.07	200.85 ±32.14
A5	26470.59 ±217.64	BDL	BDL	168.87 ±10.98	622.62 ±92.60	726.97 ±79.87	88367.25 ±650.30	5.84 ±0.62	3748.58 ±170.39	BDL	120.68 ±11.58	297.26 ±22.84
A6	16528.24 ±251.62	BDL	BDL	682.82 ±20.06	759.46 ±86.82	1421.99 ±103.84	82408.02 ±657.29	19.38 ±3.72	3206.43 ±162.65	432.18 ±97.67	59.76 ±8.10	249.05 ±26.33
A7	10609.41 ±217.16	2.95 ±0.36	BDL	7.34 ±0.63	821.04 ±133.64	918.70 ±95.85	71510.75 ±692.23	92.60 ±4.76	2571.34 ±178.14	BDL	67.02 ±6.53	112.48 ±11.82
A8	28530.00 ±208.06	BDL	BDL	161.53 ±9.76	554.20 ±99.44	822.84 ±79.87	62963.59 ±537.39	148.16 ±10.85	2950.86 ±159.54	BDL	25.10 ±1.77	176.75 ±25.86
A9	32834.12 ±183.07	BDL	BDL	73.42 ±9.10	273.68 ±58.40	287.59 ±39.94	45218.80 ±370.60	BDL	1525.77 ±92.88	BDL	125.32 ±14.83	273.16 ±19.90
A10	22960.59 ±256.76	6.63 ±1.07	BDL	154.18 ±16.41	506.31 ±96.28	678.04 ±71.89	50163.84 ±510.45	BDL	1827.82 ±139.32	BDL	167.09 ±15.48	305.29 ±43.84
Mean	18,177.35 ±213.10	2.22 ±0.42	BDL	221.49 ±11.29	593.89 ±93.99	886.65 ±85.45	66330.69 ±593.73	49.29 ±5.28	2550.43 ±155.28	76.22 ±18.20	92.33 ±8.27	246.65 ±29.52
A11 (Control)	11244.71 ±225.90	BDL	BDL	14.69 ±1.17	800.51 ±95.76	423.40 ±55.91	37112.29 ±377.59	18.52 ±1.64	1649.69 ±108.42	BDL	31.39 ±2.11	103.74 ±39.90
ASV	80000.00	13.00	0.30	19.00	90.00	45.00	47200.00	0.40	850.00	68.00	20.00	96.00
DPR Target Values		1.00	0.80	20.00	100.00	36.00	38000.00	4.00	850.00	35.00	85.00	140.00
Tr		10.00	30.00	5.00	2.00	5.00	NA	40.00	1.00	5.00	5.00	1.00

Key: BDL = Below Detectable Limit; ASV = average shale value; DPR = Department of Petroleum Resources; Tr = Toxic Response Factor

Fe is essential for plant growth and chlorophyll synthesis, but when in excess could lead to cell death, reduced nutrient availability, and stunted growth in plants [41, 42]. Manganese (Mn), which when in excess, leads to phytotoxicity [43, 44], was also found to significantly surpassed both the average shale [23] reference values and DPR [30] tolerable limits. All copper (Cu) levels were higher in the investigated saline soils (287.59±39.94 – 1565.79±143.77) (except samples A3 and A9) than in the control soil sample (A11; 423.40±55.91), which is significantly above both the average shale [23] reference value and DPR [30] limits of 45 and 36 mg/kg, respectively. Zn level in all the investigated saline soils was above that of the control soil, average shale [23] reference value and DPR [30] acceptable limit (except sites A3 and A7) for arable soils. The high concentrations of Cu, Mn and Zn observed in the investigated saline soils could be attributed to anthropogenic contributions (likely stemming from table salt mining and processing activities, indiscriminate dumping of wastes, application of fertilizers, pesticides and herbicides etc.) to the saline nature (geogenic origin) of the soils which increases the geological concentrations of the

metals in the soil through diffuse pollution, wet and dry deposition of metals, erosion and downward leaching effects of metal. Salinity enhances the solubility, mobility and transport of metals in soil [45]. Cobalt (Co) levels were lowest in A7 (7.34±0.63 mg/kg), with A7 being much lower than the control, A11(14.69±1.17 mg/kg). Co levels in the investigated saline soils (except A7) were significantly higher compared to the control soil, average shale [23] value and DPR [30] limits of 14.69±1.17, 19 and 20 mg/kg, respectively. Aluminum (Al) levels in all the samples ranged from 952.94±99.16 mg/kg (A2) to 32834.12±183.07 mg/kg (A9), including the control. All soil samples were below the average shale value of 80,000 mg/kg [23], indicating their presence was mainly due to lithogenic sources. More toxic elements like mercury (Hg), lead (Pb), and chromium (Cr) had their mean concentrations exceeding their respective average shale values. Cr concentration in all the investigated soils (control soil inclusive) higher than the average shale [23] reference and DPR [30] acceptable limit values of 90 mg/kg and 100 mg/kg, respectively. Cr concentrations in the investigated saline soils ranges from 273.68±58.40 to



882.62±119.69 mg/kg with mean concentration of 593.89 mg/kg. Cr(VI), a known carcinogen, is very mobile in acidic soils [46]. Hg concentrations in the investigated saline soils varied between being non-detectable and 175.94 mg/kg, with mean value exceeding its level in the control soil as well as the average shale [23] reference value (0.40 mg/kg) and DPR [30] permissible limit (4 mg/kg). Serious contamination was indicated in samples A2 and A8 with extremely high levels of Hg. These high levels could be a result of enrichment from human activities from table salt mining and processing in the study area [47]. Pb levels ranged from 25.10±1.77 mg/kg to 167.09±15.48 mg/kg, indicating serious contamination. Samples A9 and A10 had dangerously high levels, which could be linked to anthropogenic activities of Pb – Zn mining in Adudu which is close to the study area, as well as contributions from the use or disposal of Pb-based products within the study area. Similar correlations have been made in urban studies where Pb accumulation was attributed residual pollution from Pb-containing paints and batteries [48, 49]. These elevated concentrations of Cr, Pb, and Hg in these saline soils raise significant health and safety concerns as they tend to pose long-term risks to consumers of salts produced from the investigated saline soils, if not properly refined or remediated [46, 47]. These metals exceeding average shale levels and DPR target limits may either coprecipitate or become entrapped in crystallized salt during evaporation [50]. These could pose a problem if the salt is not adequately purified during refining, thus leading to chronic exposure in populations that rely on locally processed salts with inadequate purification [51]. With these results indicating that certain metals such as Cr, Hg, Pb, Fe, Zn and Mn exceed critical thresholds, there is a need for regular testing to minimize the long-term ecological and health impacts of these metals.

Estimation of contamination level

Enrichment factor (EF)

The extent of enrichment of the analyzed metals in the investigated soils was explored using enrichment factor (EF) of the individual metals as shown in Table 2. EF is used to differentiate the contributions of natural origins

from anthropogenic sources of the metals [52]. The mean EF of metals in the investigated saline soils is as follows: Hg > Cu > Co > Cr > Pb > Mn > Zn > Ni > Al > As. The results showed that the investigated soils (including the control) are deficient to minimally enrich with aluminum (Al), arsenic (As) and cadmium (Cd). Iron (Fe) was used as reference element in this study. The investigated saline soils showed deficient to very high, moderate to significant and significant to very high levels of Co, Cr and Cu enrichment respectively. Hg enrichment of most of the investigated saline (A1, A2, A6, A7, A8) and control (A11) soils is at very high to extremely high level. Mn and Zn are enriched at deficient to moderate level in the investigated soils. Table 2 showed moderate enrichment of Ni in only two (A4 and A6) of the investigated saline soils while Ni is at deficient level in the other investigated soils. The investigated soils showed deficient to significant enrichment levels of Pb. Consequently, high EF value (EF>1) shows that the presence of Co, Cr, Cu, Hg, Mn, Pb and Zn in most of the investigated saline soils could be traced majorly to the salinity of the study area (underlying geogenic processes) being influenced by anthropogenic contributions from table salt mining processes as well as the mining of Pb – Zn, barite, gypsum and limestone [53] around the study area. Waris *et al.* [5] and Acosta *et al.* [4] reported that saline conditions can alter the solubility, and transport of metals such as copper (Cu), cadmium (Cd), chromium (Cr), manganese (Mn), iron (Fe), lead (Pb), and zinc (Zn), thus, potentially facilitating their movement into biotic and abiotic components of the ecosystem. The control soil showed deficient to minimal enrichment of Al, As, Cd, Co, Ni, Pb and Zn; moderately enrichment of Mn; significant enrichment of Cr and Cu, and extremely high enrichment of Hg. This shows that anthropogenic sources of these metals (Cr, Cu, Hg and Mn) in the investigated control soil, is a consequence of the geological nature and mineralization of the study area. The EF values signify anthropogenic sources (EF >1) for Cr, Cu, Hg, Mn, Pb and Zn as well as lithogenic or geogenic sources (EF <1) for Al, As, Cd, Co and Ni presence in the control soils.

Table 2: Enrichment factor (EF) of the analysed metals in the investigated soils

Sample ID	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
A1	0.18	0.55	0.00	9.72	5.23	14.31	Used as Reference Element	106.91	2.03	0.00	4.92	3.09
A2	0.01	0.00	0.00	4.20	1.93	14.04		177.47	1.97	0.00	1.88	1.65
A3	0.28	0.00	0.00	2.67	7.15	9.33		0.00	1.57	0.00	2.70	1.33
A4	0.09	0.29	0.00	24.78	9.13	27.59		0.00	2.60	4.52	5.56	1.95
A5	0.18	0.00	0.00	4.74	3.69	8.63		0.78	2.36	0.00	3.23	1.65
A6	0.12	0.00	0.00	20.56	4.84	18.11		27.77	2.16	3.64	1.71	1.49
A7	0.09	0.15	0.00	0.25	6.02	13.48		152.88	1.99	0.00	2.22	0.77
A8	0.27	0.00	0.00	6.37	4.62	13.71		277.82	2.60	0.00	0.94	1.38
A9	0.43	0.00	0.00	4.03	3.18	6.67		0.00	1.87	0.00	6.55	2.97
A10	0.27	0.48	0.00	7.63	5.29	14.18		0.00	2.02	0.00	7.87	2.99
Mean	0.19	0.14	0.00	8.49	5.11	14.01		74.29	2.12	0.82	3.76	1.93
A11 (Control)	0.18	0.00	0.00	0.98	11.32	11.97	58.92	2.47	0.00	1.99	1.37	

Table 3: Geo-accumulation index (I_{geo}) of the analysed metals

Sample ID	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
A1	-2.84	-1.19	0.00	2.95	2.06	3.51	-0.33	6.41	0.69	0.00	1.77	1.29
A2	-6.98	0.00	0.00	2.79	1.68	4.54	0.73	8.19	1.70	0.00	1.63	1.45
A3	-2.74	0.00	0.00	0.55	1.96	2.35	-0.87	0.00	-0.22	0.00	0.56	-0.46
A4	-3.89	-2.24	0.00	4.15	2.71	4.31	-0.48	0.00	0.89	1.69	1.99	0.48
A5	-2.18	0.00	0.00	2.57	2.21	3.43	0.32	3.28	1.56	0.00	2.01	1.05
A6	-2.86	0.00	0.00	4.58	2.49	4.39	0.22	5.01	1.33	2.08	0.99	0.79
A7	-3.49	-2.72	0.00	-1.96	2.60	3.77	0.01	7.27	1.01	0.00	1.16	-0.36
A8	-2.07	0.00	0.00	2.50	2.04	3.61	-0.17	7.95	1.21	0.00	-0.26	0.29
A9	-1.87	0.00	0.00	1.37	1.02	2.09	-0.65	0.00	0.26	0.00	2.06	0.92
A10	-2.39	-1.56	0.00	2.44	1.91	3.33	-0.49	0.00	0.52	0.00	2.47	1.08
Mean	-3.16	1.03	0.00	1.99	1.93	3.45	-0.24	6.15	0.84	1.88	1.13	0.55
A11 (Control)	-3.42	0.00	0.00	2.96	2.57	2.65	-0.93	4.95	0.37	0.00	0.07	-0.47

Geo-accumulation index (I_{geo})

I_{geo} was evaluated so as to determine the level of contamination of the investigated sites by individual analyzed metal [54, 55] and the evaluated I_{geo} values are given in Table 3. According to Muller (1969) classifications described by Onwuka *et al.* [11], I_{geo} values showed that the investigated saline sites are unpolluted by Al and As ($I_{geo} < 0$) but are polluted by Hg at strong to extreme level ($I_{geo} > 3$). All investigated saline soils are unpolluted to moderately polluted by Fe, Mn, Ni, Pb and Zn. However, they are polluted by Cu at moderate to extreme level ($I_{geo} > 2$) and are also moderately to strongly polluted by Cr. The level of Co pollution in the investigated saline soils ranges from unpolluted to extremely polluted. However, the control site is unpolluted by Al and Fe but moderately polluted by As, Co, Cr, Ni and Pb, unpolluted to moderately polluted by Mn and Zn, strongly polluted by Cu and extremely polluted by Hg. The concentration of Cd at the control site is below 1 mg/kg suggesting that the site could also be unpolluted by Cd in addition to the site being unpolluted by Al and Fe which was ascertained by the result. These observations show that the salinity of the investigated saline soils, human activities from table salt mining and processing as well as agricultural practices, increases the geological concentrations of these metals in the investigated saline soils (via diffuse pollution, wet and dry deposition of metals, erosion and leaching of mine wastes etc.) within the study area which leads to the increase in geo – accumulation of the analyzed metals over time [55].

Contamination factor (CF), degree of contamination (C_d) and pollution load index (PLI)

Table 4 presents the CF of the analyzed metals, C_d and PLI of the investigated soils. The results were interpreted using levels and classes proposed by Hakanson [32]. Results showed that the investigated saline soils are moderately ($EF = 1 - 3$) and highly ($EF > 6$) contaminated by Fe and Cu respectively. Some of the investigated saline soils are highly contaminated with As (A1, A10), Hg (A1, A2, A7 and A8) and Ni (A4 and A6). However, all the investigated soils (saline and control) are assumed to be lowly contaminated ($EF < 1$) by Cd since their Cd level is below 1 mg/kg. All investigated saline soils showed low to moderate contamination by Pb and Zn. The investigated saline

soils showed considerable to high level of Cr contamination as well as moderate to considerable level of Mn contamination. Cr contaminates the saline soils at moderate to high level. Therefore, the contamination of the investigated saline soils is dominated by Cu, Cr, Co, Fe, Mn, Hg, As, Mn and Ni. However, the control soil sample showed low contamination by As, Cd, Co, Fe, Ni, Pb, and Zn; moderate contamination by Mn, considerable contamination by Hg and high contamination by Cr and Cu. The high CF value (> 1) for Cu, Cr, Co, Fe, Mn, Hg, As, Mn and Ni in various investigated saline soils could be attributed to anthropogenic activities around the saline soils as well as activities associated with salt mining and processing which increase the geologic concentration of the analyzed metals in the investigated saline soils.

C_d is the summation of contamination factor (CF) for all contaminants (analyzed metals) in a given investigated soil sample [31]. The contamination degree of most (80 %) of the investigated saline soils (A1, A2, A4, A5, A6, A7, A8 and A10) are very high ($C_d > 32$). Their contamination is mainly due to the presence of Cu, Cr, Co, Fe, Mn, Hg (A1, A2, A5, A6, A7, and A8), As (A1, A4, A7, and A10), Mn and Ni (A4 and A6). The control sample showed considerable degree of contamination dominated by Cu and Cr. The various investigated saline soils are contaminated in the following decreasing order; A2 > A6 > A4 > A8 > A1 > A7 > A5 > A10 > A11 (Control) > A9 > A3. This indicates that the investigated saline soils are the most contaminated.

PLI value of zero, under zero, unity and above unity indicates perfection, unpolluted soil, presence of only pollutants baseline levels and progressive deterioration of soil quality respectively [56, 57]. Table 4 showed that the PLI values obtained in this study for all investigated soil samples (saline soils and control) are above unity. However, the control sample has the least PLI value when compared to the investigated saline soils (except A3). This is an indication of anthropogenic contribution to the geological presence of the metal pollutants in the investigated saline soils. PLI values (Table 4) show that pollution of the investigated soils follows a descending order: A6 > A2 > A4 > A1 > A8 > A10 > A5 > A7 > A9 > A11 (control) > A3. Thus, the saline soils are mostly polluted due to the exploration of common salt.

**Table 4: Contamination factor (CF), degree of contamination (C_d) and pollution load index (PLI) of the investigated soils**

Sample ID	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	C _d	PLI
A1	8.52	0.00	11.03	5.61	21.30	1.48	12.74	2.41	0.00	1.20	2.53	66.82	3.66
A2	0.00	0.00	9.91	4.31	43.49	3.08	43.49	4.88	0.00	1.09	2.81	113.56	3.97
A3	0.00	0.00	2.08	5.26	9.54	1.02	0.00	1.28	0.00	0.52	0.75	20.45	1.44
A4	4.14	0.00	25.33	8.83	37.06	1.34	0.00	2.79	9.43	1.40	1.43	91.75	3.81
A5	0.00	0.00	8.44	6.23	20.19	2.33	1.46	4.41	0.00	1.42	2.12	46.60	2.67
A6	0.00	0.00	34.14	7.59	39.49	2.17	4.85	3.77	12.35	0.70	1.78	106.84	4.15
A7	2.95	0.00	0.37	8.21	25.52	1.88	23.15	3.03	0.00	0.79	0.80	66.70	2.45
A8	0.00	0.00	8.08	5.54	22.86	1.71	37.04	3.47	0.00	0.29	1.26	80.25	2.80
A9	0.00	0.00	3.67	2.74	7.99	1.19	0.00	1.79	0.00	1.47	1.95	20.80	1.76
A10	6.63	0.00	7.71	5.06	18.83	1.32	0.00	2.15	0.00	1.97	2.18	45.85	2.72
A11 (Control)	0.00	0.00	0.73	8.01	11.76	0.98	4.63	1.94	0.00	0.37	0.74	29.16	1.59

Table 5: Ecological risk (Er) and potential ecological risk index (RI) of the analysed metals and investigated soils

Sample ID	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	RI
A1	85.20	0.00	55.15	11.22	106.50	0.00	509.60	2.41	0.00	6.00	2.53	778.61
A2	0.00	0.00	49.55	8.62	217.45	0.00	1739.60	4.88	0.00	5.45	2.81	2048.36
A3	0.00	0.00	10.40	10.52	47.70	0.00	0.00	1.28	0.00	2.60	0.75	73.25
A4	41.4	0.00	126.65	17.66	185.30	0.00	0.00	2.79	47.15	7.00	1.43	429.38
A5	0.00	0.00	42.20	12.46	100.95	0.00	58.40	4.41	0.00	7.10	2.12	227.64
A6	0.00	0.00	170.70	15.18	197.45	0.00	194.00	3.77	61.75	3.50	1.70	652.13
A7	29.50	0.00	1.85	16.42	127.60	0.00	926.00	3.03	0.00	3.95	0.80	1109.15
A8	0.00	0.00	40.40	11.08	114.30	0.00	1481.60	3.47	0.00	1.45	1.26	1653.56
A9	0.00	0.00	18.35	5.48	39.95	0.00	0.00	1.79	0.00	7.35	1.95	74.87
A10	66.30	0.00	38.55	10.12	94.15	0.00	0.00	2.15	0.00	9.85	2.18	223.30
A11 (Control)	0.00	0.00	3.65	16.02	58.80	0.00	185.20	1.94	0.00	1.85	0.74	268.20

Ecological risk assessment

Soils contaminated by toxic heavy metals can enter the human body via various exposure routes (such as oral ingestion, inhalation and dermal contact) and cause serious ecological and human health risks [58]. Saline soils from the study area (Awe) are commonly used for table salt production and agricultural activities which is usually consumed by man and animal. Thus, contaminated saline soils could pose serious risk to the environment considering its importance. Therefore, it is necessary to evaluate the ecological risk factor (Er) of the individual analyzed metals and ecological risk index (RI) of the investigated sites.

The toxicity of the analyzed metals in the investigated soils was estimated through the evaluation Er and RI. Er and RI classifications by Hakanson [32], was employed in the interpretation of Er and RI values of the analyzed metals as shown in Table 5. The Er of was not evaluated because Fe has no certified toxic response factor (Tr). The levels of Cd in the investigated soils were below instrumentation limit of detection. Thus, contamination risk from Cd at all the investigated sites could be assumed to be low due to low level of Cd in these investigated sites (< 1 mg/kg). The result shows that the potential ecological risk factors of Cr, Mn, Pb and Zn in all the investigate soils are low (Er < 40). Thus, Cr, Mn, Pb and Zndo not pose any ecological risk to the environment. However, Cu pose moderate to high ecological risk at most of the investigated sites for saline soils. There is low to high and low to moderate

potential ecological risks of Co and As contaminations respectively at the investigated saline soils. Hg and Ni have respectively very high (Er > 320) and moderate ((Er = 40 – 80) levels of potential ecological risks in most of the investigated saline soils where their levels were within instrumentation detectable limit. These implies that food crops, animals and old Awe community dwellers are exposed to high risk of Hg, Cu and Co poisoning at the investigated saline sites [59]. However, low risk of contamination from As, Co, Cr, Mn, Ni, Pb and Zn; moderate contamination risk from Cu, and high Hg contamination risk were observed at the control site.

The RI values of the analyzed metals showed that 60 % (A1, A2, A4, A6, A7 and A8) of the investigated saline soils are at risk of contamination with significant to high ecological risk index (RI > 600). Low to moderate risk of contamination was observed at the other investigated saline sites (A3, A5, A9 and A10) due to their ecological risk index (RI < 300). This implies that table salt miners, old Awe community dwellers, and arable farms in the community are exposed to toxic levels of Hg, Cu and Co through inhalation and dermal contact with the saline soils from the sites. Also, food crops grown on these sites are at high risk of being contaminated by Hg, Cu and Co which will be inimical to human health when consumed [59]. The high risk of contamination observed in most of the investigated saline soils could be attributed to saline nature (geologic origin) of the study area which aid the

mobility and transport of the PTMs during geochemical and anthropogenic processes. The decreasing sequence of potential ecological risk index (RI) of the investigated sites from the analysed metals is as follows: A2> A8>A7>A1>A6>A4>A11>A5>A10>A9 >A3.

Conclusion

The study successfully assessed the levels of PTMs and evaluated the associated contamination and ecological hazards indices in the investigated soils in the Awe salt mining community. The result showed elevated levels of Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn above the control (except Cr) and average shale reference values. Contamination assessment showed that investigated saline soils are deficient of Al, As and Cd. However, their EF values revealed that most are significantly enriched with Co, Cr, Cu, Mn, Pb and Zn. Geo-accumulation index (Igeo) showed that most of the investigated saline soils are moderately to extremely polluted by Co, Cr, Cu and Hg but are contaminated by Co, Cr, Cu, Fe, Hg, Mn and Zn. The degree of contamination (C_d) and pollution load index (PLI), revealed high degree of contamination for all investigated saline soils. However, ecological risk (Er) assessment showed that only the presence of Co, Cu and Hg pose high ecological risk (significant potential negative implications to human and animal health) in the investigated saline sites. The potential ecological risk index (RI) revealed that the presence of the analyzed PTMs can have serious adverse effect on plants, animal and human on the investigated saline sites. However, the control sites had low ecological risk index. Thus, this study confirms that salinity is the controlling factor influencing concentrations and environmental risks of analyzed metals in the investigated saline soils.

Conflict of interest: The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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