Environmental Consequences of Soil Heavy Metal Contamination in Gharyan Regions, Libya: A Comprehensive Study

Raja allafi
Department of Chemistry/ Gharyan's Faculty of Science/ Gharyan University/ Gharyan/ Libya

Rabia A. Anwesre

Ali M. Al-Saleh
School of Chemical Engineering University Technology Mara/ Shah Alam/ Selengor/ Malaysia
Northern technical University Iraq

Nuha Khalaefa
Department of Chemistry/ Gharyan's Faculty of Science/ Gharyan University/ Gharyan/ Libya

Hadi H. Mahid
School of Chemical Engineering University Technology Mara/ Shah Alam/ Selengor/ Malaysia

ABSTRACT

The proximity of military encampments and barracks to groundwater reservoirs and agricultural regions in Gharyan has raised environmental and health apprehensions among local inhabitants. Given the potential hazards, an analytical study was initiated to gauge the extent of soil contamination in areas influenced by military activities. This research aimed to determine the concentrations of select heavy metals (zinc, copper, lead, and cadmium) in soil samples sourced from specific sites associated with military engagements. Additionally, the study evaluated the soil's pH levels. Soil specimens were amassed from three primary locations: the former Sahban camp, the Abu Ghaylan zone, and an area affiliated with the Eighth Battalion. A fourth specimen, taken from a non-affected region, was a control. Sampling was conducted at three depth intervals: 0-20 cm, 20-40 cm, and 40-60 cm. The quantification of heavy metals was accomplished using atomic absorption spectroscopy (220GQER006). When juxtaposed with the control specimen and standards set by the World Health Organization, samples from the military-influenced sites exhibited elevated concentrations of lead, copper, and cadmium. Distinctly, the Eighth Battalion-associated site (sample 3) demonstrated the highest lead content at 2093 mg/Kg. Meanwhile, the Sahban campsite (sample 1) recorded a peak copper concentration of 460 mg/Kg, and cadmium was most pronounced in sample 3 at 45.8 mg/kg. In contrast, zinc concentrations were found to be within permissible thresholds. The pH analysis showed the soil to be mildly alkaline, with values ranging from 6.9 to 8.77.

Keywords: Heavy metals - chemical pollution - soil pH - military activity - atomic absorption, and Libya.
INTRODUCTION

Environmental pollution is increasingly recognized as a paramount global concern, especially when juxtaposed with other urgent issues. The rising focus on environmental pollution can be ascribed mainly to its profound effects on human health (Dubey et al., 2014a). The evolution of human society, marked by burgeoning urban industrial hubs and technological progression, has transitioned human structures from rudimentary to intricate systems. Heavy metal contamination is a severe environmental problem due to its persistence in the environment and nonbiodegradable nature, leading to its accumulation up to toxic levels (An et al., 2004). However, the term “heavy metals” refers to any relatively dense and high atomic weight metals and are also known for their potential toxicity in environmental contexts (S. Mishra et al., 2006). The term heavy metal is applied to cadmium, mercury, lead, and arsenic, and all of which appear in the World Health Organization’s list of 10 chemicals of primary public concern (Sevinç-Özakar et al., 2022). Heavy metals (HMs) found in a particular mining site depend on the type of ores discovered; however, South Africa is well known to be resourced in these minerals for industrialization improvement (Nour and El-Sorogy, 2017; Ghani et al., 2022a). Furthermore, the presence of HMs in the environment might be due to the industrial effluent that flows directly into the water system or through the contaminated soil percolates, which changes the concentration of the underground water systems (Liu et al., 2010). However, it has ushered in adverse environmental ramifications, leading to environmental degradation impacting both living beings and the broader ecosystem (Kciuk et al., 2023). Technological and scientific advancements have introduced an array of environmental contaminants alien to the natural environment (Ghani et al., 2022b). This influx can be primarily associated with the onset of new industrial chemicals, which were erstwhile unidentified (Dubey et al., 2014b). Soil is particularly vulnerable to pollutants, acting as a primary receptacle and filter, amassing various contaminants (Nour and El-Sorogy, 2017; Ghani et al., 2022a).

Soil contamination by noxious chemicals has surfaced as a pressing environmental issue, posing threats to public health and resulting in economic repercussions, underscored by its profound implications for human welfare and economic ramifications (Liu et al., 2010).

The primary culprits of soil pollution encompass the use of pesticides and chemical fertilizers in agriculture, industrial waste discharge, emissions from the oil sector, and repercussions of military activities (Dubey et al., 2014b).

This trend correlates with expanding diverse industries, resulting in an amplified usage of chemicals across sectors like medicine, agriculture, construction, and manufacturing (Muhammad et al., 2022). As a result, global incidences of such pollution have surged. A notable body of research detailing the bioaccumulation of chemical pollutants in organisms reaching levels that pose significant threats Click or tap here to enter text. Prolonged contact with these substances can potentially instigate grave health concerns, including cancer and congenital anomalies, given their rising occurrence rates (Saeeda and Futuristic, 2018; Shao et al., 2020). Heavy metal contamination is a severe environmental problem due to its persistence in the environment and nonbiodegradable nature, leading to their accumulation up to toxic levels (Sevinç-Özakar et al., 2022).

However, the term “heavy metals” refers to any relatively dense and high atomic weight metals, also known for their potential toxicity in environmental contexts (Alloway, 2012; Dubey et al., 2014b). Heavy metals are applied to cadmium, mercury, lead, and arsenic, all appearing on the World Health Organization’s list of 10 chemicals of primary public concern (Okbah et al., 2018).

Elevated exposure to pollutants, like unintentional chemical spills, yields observable health outcomes, potentially culminating in premature deaths or escalated incidences of grave illnesses (Ouali et al., 2018a; Allaq et al., 2021; Allaq et al., 2023). Particularly in developing countries, there is an uptick in such diseases stemming from weak regulatory measures and a pervasive lack of public awareness (Allaq et al., 2023). The extraction and utilization of raw terrestrial resources,
combined with agricultural, chemical, and military waste disposal, have significantly increased. Such activities amplify the risks of environmental degradation, especially soil pollution (Paunov et al., 2018).

Military Activities and Soil Contamination: Impacts and Regulations

Prolonged military engagements in mineral-rich terrains can result in lingering chemical residues in soils. The stability of these pollutants is predominantly dictated by factors such as soil oxidation, pH, humidity, and other inherent soil characteristics. As time progresses, there's an augmented accumulation of heavy metals and metals stemming from oxides in the soil. Consequently, global conflict zones become major reservoirs for heavy metal contaminants, impacting terrestrial and aquatic ecosystems (Liu et al., 2010). A notable example is lead, which can be introduced into the soil through complex mineralogical and chemical transformations (Dubey et al., 2014a; Liu et al., 2010).

To address the ramifications of military-induced pollution, regulatory frameworks analogous to those governing industrial pollution have been instituted (Mayouf, 2012). These frameworks aim to remediate and preserve the ecological integrity of sites compromised by military actions, recognizing the acute threats they pose to human well-being and the environment. The prevalence of heavy metal residues in areas influenced by military undertakings can introduce toxins into both land and water ecosystems, jeopardizing diverse life forms (Elbagermi et al., 2012). Areas under military usage or impacted by warfare can negatively influence the livelihoods of nearby communities, including sectors like agriculture, livestock farming, and hunting (Abd-Alsalam et al., 2022). The ensuing accumulation of toxins in the soil poses dire threats to crop yield, food quality, and the broader environmental wellness (Nour, 2019).

While measures to conserve and rehabilitate industrial zones are in place across nations, their specifics can vary due to differing foundational goals for ecological protection and remediation. In contrast, soil contamination in military and conflict zones is often evaluated against specialized criteria, such as military-specific soil concentration standards or agricultural-based benchmarks (Nour and El-Sorogy, 2017; Okbah et al., 2018).

Heavy Metal Concentrations in Soil: Environmental Implications and Regulatory Frameworks

The Environmental Protection Agency exclusively delineates protocols concerning the presence of explosive compounds in soils (ELhariri et al., 2020). These protocols establish permissible chemical concentrations in environmental matrices. However, these guidelines are primarily accessible to a limited group of countries (Elosta and Abulkreeb, 2022).

Notably, while heavy metals are indigenous components of the Earth's crust, their escalated concentrations in soils are becoming increasingly alarming(Ahmed et al., 2017). This concern stems from potential repercussions on food safety and potential contamination of groundwater and surface water (Elbagermi et al., 2013). Some of these metals, despite being detrimental in high concentrations, are vital in trace amounts for human well-being. However, an excessive accumulation can imperil human health by contaminating water bodies, affecting the quality of both surface and groundwater (Elbagermi et al., 2020).

Such metals can be introduced to the environment both from the natural geological composition of the Earth and anthropogenic activities, including industrial emissions, urban waste disposal, and certain agricultural practices. From a scientific perspective, chemists and environmentalists identify heavy metals based on their density (Metwally and Fouad, 2008).

In the natural environment, heavy metals, beneficial in trace amounts for plant physiology, include zinc (Zn), iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu) (Metwally and Fouad, 2008; Abd-Alsalam et al., 2022). The concentration of such metals in the soil largely depends on the composition of the parent rock (Nour, 2019). Notably, basic igneous rocks have a higher
concentration of certain metals like chromium and manganese, in contrast to sedimentary rocks, which tend to be lower in metals like cadmium and mercury (Garbowski et al., 2023).

Moreover, heavy metals' affinity towards soil particles facilitates their interaction with various soil compounds, undergoing oxidation, reduction, and precipitation reactions (Nour and El-Sorogy, 2017). Such interactions determine the mobility of these metals within the soil matrix. The potential risks arising from this mobility encompass the uptake of these metals by plants and possible contamination of groundwater (Banana et al., 2016). It is paramount to realize that mobility is determined not just by the metal type but also by the soil's physicochemical properties (Nour and El-Sorogy, 2017).

Contemporary research has indicated a shift in climatic patterns, with global temperatures rising between 0.6 to 0.9°C over the past century (Okbah et al., 2018). This spike in temperatures over recent decades has outpaced naturally occurring climatic variations. Such climatic alterations have consequences on soil dynamics (ELhariri et al., 2020). Specifically, temperature and soil moisture levels regulate contaminants' behaviour in the soil. Soil moisture, acting as a solvent, can facilitate the transport of heavy metals deeper into the ground, jeopardizing groundwater quality and aiding in plant uptake of these metals (Saleh and Farouk, 2017; Elosta and Abulkrereb, 2022).

Temperature-Driven Translocation of Heavy Metals in Soil and its Implications in Military Zones

The influence of soil and atmospheric temperatures on the transportation of heavy metals is significantly modulated through transpiration (Yahya et al., 2020; Saleh et al., 2022). Fluctuations in temperature directly impact the rate of evaporation, particularly transpiration. As this rate increases, plants' water absorption accelerates, enhancing the uptake of heavy metals (Hamid et al., 2022). Concurrently, with rising temperatures, certain chemical reactions within the soil facilitate the release of heavy metals from their complexes. This results in their integration into the soil solution, potentially leading to soil leaching into groundwater or plant uptake, introducing heavy metals into various living organisms (Saleh et al., 2022).

Research from different countries has shown increased heavy metal concentrations in areas associated with military activities and conflicts (ELhariri et al., 2020; Yahya et al., 2021). This conclusion is drawn from soil samples, both surface and from varied depths. Detailed soil analyses from military training regions in Canada, Korea, the US, and former conflict zones in Spain indicate pronounced levels of lead and ammonium, with noticeable increases in copper and cadmium concentrations. A separate study analysing samples from eight US locations reported elevated concentrations of copper and lead (Ahmed et al., 2017; Saeeda and Futuristic, 2018). However, nickel, antimony, and zinc were found in lower quantities than expected. The pH of these samples varied significantly, from highly acidic at 4.4 to moderately alkaline at 8.2. In a similar study from Australia's military training areas, the pH ranged from a very acidic 5.3 to an alkaline 9.2. Heavy metal analysis of these samples showed high levels of lead and antimony, whereas copper and zinc concentrations were relatively low (Saleh and Farouk, 2017).

In a specific case study from Gharyan, impacted by military operations during the Libyan War from 2010 to 2019, four distinct soil samples were evaluated. Using atomic absorption spectroscopy, the concentrations of lead, cadmium, zinc, and copper were identified and subsequently compared against the World Health Organisation's (WHO) recommended (Elbagermi et al., 2013; Mlitan et al., 2013; Amin et al., 2020)

Diverse Soil Characteristics in Varied Topographies: Opportunities and Challenges in Libyan Agriculture

The soils in this region have formed across a wide range of topographical settings, with elevations ranging from 400 to 880 m above sea level (Amin et al., 2020). There exist numerous
variations of these soils, each manifesting unique attributes based on the specific factors influencing their formation. Generally, these soils are recognized for their advantageous properties, making them suitable for cultivating various agricultural products, given the availability of sufficient water resources (Elmanafi and Elqutaan, 2019). However, challenges arise due to certain intrinsic features, such as the prevalent presence of cinnamon mountainous soil. This particular soil type is noted for its light texture and delicate structure, leading to its reduced water retention capacity, which in turn contributes to the region's arid conditions. The soil's shallow depth, high salt concentration, and limited nutrient content make it prone to wind erosion (Saeeda and Futuristic, 2018). Moreover, the salinity present in specific areas intensifies its vulnerability. The limited application of the soil is notably affected by its location in regions where groundwater transit occurs (Ahmed et al., 2017).

This situation suggests potential avenues for optimizing its use. Predominantly, the cultivation in these areas comprises rain-fed crops like wheat, barley, olives, almonds, figs, and pomegranates, highly dependent on the volume of rainfall received (Supervision et al., 2022). Previous literature predominantly centered around investigating pollutants stemming from industrial establishments and civilian actions. Remarkably, there appears to be a void in academic contributions from Libya specifically addressing the military's impact, with no analogous studies identified (Saeeda and Futuristic, 2018; Elmanafi and Elqutaan, 2019).

Heavy Metals in Agriculture: Impacts on Plant Metabolism and Health

Human-driven activities, including industrialization and agriculture, contribute to the escalating heavy metal content in soils (Yahya et al., 2020). Consequently, toxic metals accumulate extensively in agricultural zones (Elmanafi and Elqutaan, 2019). Certain trace elements benefit plants, but many, like lead, cadmium, and copper, can harm plant growth and metabolism (Garbowski et al., 2023). Elevated concentrations of these metals can inhibit plant growth and pose potential threats to health as they accumulate in plants, animals, and eventually humans (Amin et al., 2020). The concentration of metals in plants is influenced by plant species and the prevailing environmental pollution (Ara et al., 2018).

Lead, historically present due to its unique physical and chemical properties, is a predominant environmental toxin. It accumulates because of its resistance to biodegradation, thus posing mounting environmental risks. Lead alters various plant enzymes, most notably affecting the Chloramphenicol acetyltransferase (CAT) enzyme responsible for detoxifying peroxides. Interestingly, while low lead concentrations boost CAT activity, higher concentrations lead to enzyme inactivation, primarily due to ROS. Lead's interference extends to chlorophyll synthesis, ATP synthesis, and oxidative phosphorylation (An et al., 2004). Its profound impact on respiratory functions in plants is evident, with observations like reduced respiration in corn root tips post-high lead exposure (Zamani et al., 2013). Notably, lead's impact on chloroplast ATP synthesis disrupts membrane stability (An et al., 2004).

Cadmium, pervasive in products like batteries and chipsets, poses environmental threats (An et al., 2004). Plants readily absorb it, which, upon entering the food chain, may affect animals and humans. Cadmium impedes metalloproteins and metalloenzymes by binding to them, causing functional disruptions (Mishra et al., 2006). Although essential to plants in trace amounts, its excess can be detrimental, showing symptoms such as reduced photosynthesis (Liu et al., 2010).

Similarly, copper, a vital micronutrient, becomes problematic in higher concentrations (Mayouf, 2012). Originating from industrial wastes, agricultural activities, and pesticides, excessive copper affects cellular functions, notably impairing membrane transport systems (An et al., 2004; Hassan and Elssaidi, n.d.; Mayouf, 2012). As plants confront heavy metal stress, there is an upsurge of reactive oxygen species (ROS), which can harm plant molecules. In defence, plants induce specific metabolic shifts, such as synthesizing secondary metabolites like antioxidant enzymes and phenolic compounds (Nour and El-Sorogy, 2017; Elosta and Abulkreb, 2022). These compounds, besides providing protection, possess potential pharmacological benefits. Nevertheless, there is a
research gap on how these soil contaminants impact the physiological responses of medicinal plants and their therapeutic potential (Ara et al., 2018; Hassan and Elssaidi, n.d.).

MATERIALS AND METHODS

Atomic absorption spectroscopy variant 220 GQER006, BOECO vibrating device, BOECO pH mete device, Sensitive balance, and heater. Nitric acid (HNO₃), and Hydrogen peroxide, (H₂O₂) (Hassan and Elssaidi, n.d.; Metwally and Fouad, 2008).

Sampling Area:

In Gharyan, four distinct samples were collected from zones that had witnessed military activities. These zones are uniquely distinguished by the presence of cinnamon silicate soil. This particular soil composition is predominantly observed in the north-western terrains, especially within the mountainous landscapes of Gharyan. Fig. (1) provides a comprehensive illustration of this soil's extensive distribution throughout the specified area (Supervision et al., 2022).

Soil samples were collected from three sites known for military operations. These sites include the former Sahban camp (designated as sample 1), the Bu Ghilan site (designated as sample 2), and the former 8th Battalion (designated as sample 3). Additionally, a control sample was taken from a location significantly distant from military activity. Multiple samples were retrieved on three separate occasions from each site. The samples were categorized by depth: the first layer ranged from 0-20 cm, the second from 20-40 cm, and the third from 40-60 cm across all specified locations.

Sample soil preparation and analysis:

pH analysis:

In the experimental procedure, the sample mass was precisely determined to be 25 grams, utilizing a high-precision analytical balance. The measured sample was then transferred into a plastic centrifuge tube. Following this, an equivalent mass of 25 grams of distilled water was introduced into the system. The sample and solvent were combined thoroughly by subjecting the tube to a 30-minute agitation in a mechanical shaker. Upon completion of the shaking period, the resultant mixture was subjected to quantitative analysis using the appropriate spectroscopic equipment.

Measuring soil pH:

Each soil sample was accurately weighed to two grams using a precision analytical balance. The samples were then placed into sterile containers and mixed with 10 ml of nitric acid in a 1:1 volume ratio. This mixture was subsequently heated to 95 degrees Celsius to facilitate the complete evaporation of the liquid component. After cooling, 2 ml of distilled water and 3 ml of 30%
hydrogen peroxide were added to the residue. The mixture was heated once more and allowed to cool, followed by filtration. The filtrate was then transferred into a 100 ml volumetric flask, ensuring thorough rinsing of the original container with distilled water to carry over any remaining traces of the sample. The volume in the volumetric flask was then brought up to the mark with additional distilled water. Post-digestion, the prepared samples were ready for quantitative analysis with the appropriate instrumentation.

Statistics Results:
The statistical analysis utilized the SAS software package (version 9.1). The means derived from three replicates of all physicochemical and biological parameters were assessed using one-way ANOVA. To discern significant differences between the means, Turkey's Honestly Significant Difference (HSD) test, a studentized range test, was employed.

RESULTS AND DISCUSSION

pH analysis
The results shown in the urban soil of the study area were listed in (Table 1). The pH levels of all soil samples were within the range of slightly alkaline to moderately alkaline (6.9 - 8.77). Samples 1 and 3 were deemed to possess a neutral quality, but sample 2 was characterized as essential.

Table 1: The results of cluster analysis of basic directions of research.

<table>
<thead>
<tr>
<th>Name of Sample</th>
<th>Deep</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sahban camp</td>
<td>0-25</td>
<td>7.25</td>
</tr>
<tr>
<td></td>
<td>25-50</td>
<td>7.27</td>
</tr>
<tr>
<td>Boghilan site</td>
<td>0-25</td>
<td>8.13</td>
</tr>
<tr>
<td></td>
<td>25-50</td>
<td>8.13</td>
</tr>
<tr>
<td>8th Battalion</td>
<td>0-25</td>
<td>6.90</td>
</tr>
<tr>
<td></td>
<td>25-50</td>
<td>6.94</td>
</tr>
<tr>
<td>Control of Sample</td>
<td>0-25</td>
<td>8.77</td>
</tr>
<tr>
<td></td>
<td>25-50</td>
<td>8.77</td>
</tr>
</tbody>
</table>

Concentration of heavy metals in the soil
Table (2) shows the concentrations of every compound within samples, including the study geographical area, arising from three locations, as previously mentioned.

Table 2: The concentrations of every compound within samples

<table>
<thead>
<tr>
<th>Name of Sample</th>
<th>Deep</th>
<th>Lead (Pb)</th>
<th>Copper (Cu)</th>
<th>Zinc (Zn)</th>
<th>Cadmium (Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sahban camp</td>
<td>0-20</td>
<td>1855.10</td>
<td>451.24</td>
<td>24.10</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>1880.60</td>
<td>460.0</td>
<td>24.7</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>1890.66</td>
<td>460.38</td>
<td>25.33</td>
<td>23.4</td>
</tr>
<tr>
<td>Boghilan site</td>
<td>0-20</td>
<td>1610.3</td>
<td>340.50</td>
<td>24.04</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>1614.1</td>
<td>361.3</td>
<td>24.2</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>1615.7</td>
<td>363.01</td>
<td>24.40</td>
<td>30</td>
</tr>
<tr>
<td>8th Battalion</td>
<td>0-20</td>
<td>2035</td>
<td>341.7</td>
<td>25.21</td>
<td>44.1</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>2883</td>
<td>344.0</td>
<td>26.1</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>2093</td>
<td>349.1</td>
<td>26.5</td>
<td>45.8</td>
</tr>
<tr>
<td>Control of Sample</td>
<td>0-20</td>
<td>0</td>
<td>33.2</td>
<td>15.11</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Lead (Pb)
Table (3) summarizes the concentrations of the assessed components in four soil samples, as discussed in the section 'Concentration of Heavy Metals in Soil.' Additionally, Fig. (2) provides a comparative evaluation of lead concentrations within these samples. The lead concentration in Sample 1 is estimated to be approximately -1890.661855 mg/kg. In contrast, Sample 2 displays a
lead concentration of around -1615.716103 mg/kg. Furthermore, Sample 3 reveals a lead concentration of 3 mg/kg, with a reported analytical value of 2093.12035 mg/kg (Jung and Thornton, 1996). Sample 4, classified as uncontaminated ('clean'), recorded lead values ranging from 0 mg/kg to 1 mg/kg (Hachani et al., 2020). Notably, the concentrations in all three contaminated samples exceed the established safe limit of 50-300 mg/kg. Sample 3, in particular, manifested the highest attention among the samples. The augmented levels are ascribed to pollution, historical weapon use, and a substantial clay percentage in the soil's initial composition. Lead is categorized as an element with low mobility in soils. Literature suggests that the mean lead concentration in non-contaminated soil is about 17 mg/kg, with surface soil lead levels typically fluctuating between 10 and 76 mg/kg (Ouali et al., 2018a). Lead interaction in soil is predominantly affected by organic matter and clay content (Ouali et al., 2018b). There is a propensity for lead to adhere strongly to organic substances, especially at pH levels exceeding 4, and to the surfaces of clay particles in soils with high clay content (Hachani et al., 2020). The solubility of this element in alkaline soils is increased due to its ability to form complexes with particular organic molecules, promoting a phase change from a solid to a more bioavailable liquid form (Alloway, 2012; Chen, 2000).

**Fig. 2:** compares the lead amounts observed in the materials under analysis

**Copper (Cu)**

In the analysis depicted in Fig. (4), the copper concentration in Sample 1 was found to be -460.38451.24 units, which seems to be an erroneous recording. Sample 2, however, displayed a copper concentration ranging from 363.0 to 340.51 mg/kg. Sample 3 had a concentration of 349.1 units, whereas Sample 4a recorded values not exceeding 33.7 mg/kg. Excluding the sample classified as 'clean,' all measured concentrations surpassed the permissible range of 50 to 140 mg/kg. The observed variation among the samples may be attributed to differences in soil pH, contaminant levels, and the extent of exposure each military region experienced (Xu et al., 2006). Copper, naturally occurring in the earth's crust, varies in concentration from 2 to 50 mg/kg depending on the composition of the parent rock. As an essential micronutrient for plant life, copper's bioavailability in the soil is modulated by factors such as pH levels and organic matter content (Poggere et al., 2023). It tends to be more soluble under conditions of low pH and low organic content, leading to higher concentrations of copper complexes (Zamulina et al., 2022). Studies have indicated that up to 90% of copper in soil solutions can form complexes with organic matter, accumulating primarily in the topsoil in association with organic layers. Soil contamination
Environmental Consequences of Soil...........

with copper arises from various sources, with agricultural chemicals, especially insecticides, being a significant contributor. Furthermore, industrial activities like mining and power generation contribute to elevated levels of copper in the soil, resulting in potentially harmful accumulations that can adversely affect plant health and biodiversity, as cited in references (Andráš et al., 2021; Poggere et al., 2023).

Fig. 3: Comparison of copper concentrations in the study samples

Zinc (Zn)

Fig. (3) delineates the variation in zinc concentrations found within the surveyed sites. Analysis revealed that Sample 1's zinc concentration fluctuated between 24.10 and 24.7 mg/kg, Sample 2's concentration varied from 25.33 to 24.4 mg/kg, while Sample 3's levels were within 26.5 to 25.33 mg/kg. In stark contrast, Sample 4 presented a concentration range of 14.6 to 14.0 mg/kg. Notably, each of these measurements is below the threshold established by the World Health Organization, which stipulates a normative range of 150 to 300 mg/kg for zinc in soil. The soil's inherent characteristics heavily influence zinc accumulation in the soil (Moffett et al., 2003). The origin of the soil plays a pivotal role; zinc is typically found in greater quantities in soils originating from basaltic and granitic formations (H. Liu et al., 2005). Conversely, soils stemming from sedimentary and sandy origins are often characterized by lower zinc concentrations, suggesting a potential deficiency of this element (Stephan et al., 2008). Zinc mobility within the soil matrix highly depends on several soil parameters, with soil pH particularly influential (Rutkowska et al., 2015). Acidic conditions promote zinc dissolution, whereas neutral pH conditions result in moderate mobility of zinc. Alkaline conditions, however, lead to increased adsorption of zinc onto the silicate clay minerals and oxides present in the soil, consequently diminishing its solubility and mobility. These findings underscore the complexity of zinc dynamics in soil environments (Dumoulin et al., 2017).
Fig. 4: Comparison of Zinc concentrations in the study samples

**Cadmium (Cd)**

Fig. (5) presents the cadmium concentrations measured in four distinct samples. Sample 1 revealed cadmium levels between 22.4 and 23.4 mg/kg. In comparison, Sample 2 showed levels ranging from 29 to 30 mg/kg. Sample 3's concentrations were between 44.1 and 45 mg/kg, while Sample 4's levels were below 3.6 mg/kg. Except for Sample 4, the concentrations in all samples exceeded the safety limits set by the World Health Organization, which are between 1 and 3 mg/kg. Cadmium is recognized as a toxic element to all life forms, even at low levels (K. Liu et al., 2015). Studies have shown that cadmium can adversely affect various enzymes within the human body when consumed, posing significant health risks (Dumoulin et al., 2017). Cadmium contamination in soils is on the rise, largely attributable to emissions from industrial processes, such as the manufacturing of cadmium-containing products like paints and batteries. The release of cadmium is particularly associated with the combustion of fuels in industrial operations and its use in certain pesticides and agricultural fertilizers, especially those that are phosphate-based (De Oliveira et al., 2016). Cadmium is highly mobile in soil environments and is soluble, leading to substantial plant absorption (Marković et al., 2019). These characteristics make cadmium a particularly dangerous element as it can leach into groundwater and ascend through the food chain via plant uptake, affecting various trophic levels (Wu et al., 2021). Its high solubility and bioavailability to plants underscore its potential to contaminate the food supply. It also highlights the necessity for stringent monitoring and regulation to mitigate its environmental and health impacts (Marković et al., 2019; Wang et al., 2019; Wu et al., 2021).
CONCLUSION

The study's results reveal significant elevations in lead, copper, and cadmium levels in samples 1, 2, and 3, highlighting the critical issue of heavy metal pollution. In stark contrast, the zinc content at the four analyzed locations did not exceed established safety benchmarks. Moreover, the moisture content of all samples remained below 0.58%, with pH values demonstrating consistent neutrality to slight alkalinity, ranging from 6.9 to 8.77. Pertinently, these findings contribute to the ongoing discourse on Heavy Metals in Agriculture: Impacts on Plant Metabolism and Health, revealing potential disturbances to plant biological functions and the ensuing health risks for humans. The interaction of heavy metal accumulation with the sustainability of agricultural practices poses considerable threats, pointing to an imperative demand for extensive research. Such research should investigate the influence of these metals on plant metabolism and their subsequent entry into the human diet. Therefore, a comprehensive investigative strategy is necessary, incorporating diverse analytical techniques and innovative methods to dissect further the intricate relationships between heavy metals and organic molecules in agricultural settings. This research should also examine residual heavy metals from past military operations, notably ordnance, and explosives, due to their significant environmental contamination potential. In light of the negative effects of heavy metals on plant vitality and human health, it is advisable to prohibit agricultural use of these contaminated areas. The risk of heavy metals entering the food chain via bioaccumulation calls for immediate intervention to remediate affected sites, particularly in vulnerable regions like Camp Eighth, near groundwater resources. Prompt and effective remediation is paramount to protect groundwater integrity and prevent further ecological and public health issues.

REFERENCES


