Mapping and screening risk assessment of heavy metals concentrations in soils of the Bahr El-Baker Region, Egypt

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Mapping the spatial distribution of soil pollutants is essential for delineating contaminated areas of Bahr El-Baker Soils, Egypt. Geostatistical interpolation and kriging was used to estimate pollutant levels in soils. The X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) analyses results showed similarity of the studied soils in the most of chemical and mineralogical (dominant montmorillonite) properties; thus revealing to these exposed soils the same geological and pedological conditions. These soils exhibited that they possess both permanent and variable surface charges due to smectite minerals, amorphous iron oxides, and organic matter which ensures high metal sorption capacity thus, increasing the cation-exchange capacity (CEC) values. The spatial patterns showed the homogeneity in Cd, Pb, Cr, and Ni contents. In contrast, Cu and Zn contents, since their data distributions were characterized by great variation and high skewness (1.27 and 1.22 respectively). The best fit model for Cd and Pb were Circular and Exponential model with Mean Standardized (MS) values for them -0.0255 and 0.0600, respectively which is closest to zero. Root Mean Square Standardized (RMSS) values for Cd and Pb were 1.096 and 0.9789 respectively which are closest to 1. The best fit model for Zn was Pentaspherical model (MS = 0.0002) and Rational Quadratic model for Ni and Cr with -0.0029 and -0.0046 MS, respectively which is closest to zero. The data showed that the concentrations of heavy metals Zn, Cr, Ni, and Pb measured in these soils are still under the threshold values. However, the concentrations of Cd and Cu in some soils exceeded the threshold values for non-polluted soils. Since the whole study area (17818.93 ha) became contaminated by Cd, and 6370.23 ha only became contaminated by Cu. Although, this study is a screening presentation which helps to identify the important areas to sample in the future, the results indicate that these soils are still able to load with over concentrations of these metals and retained them, since they do not reach their saturation capacities except for Cu and Cd in some areas. But under bad management with continuous accumulation of these toxic metals in the environment, region will be exposed to real disaster. Geostatistics provides effective methods to quantify the contaminated soil which support decision-making about redevelopment scenarios or remediation techniques.

Key words: Heavy metals, geostatistics, risk assessment, Egypt.

INTRODUCTION

The world has changed and the priorities have been shifted from agricultural production towards environmental issues. Sustainable use of soil resources in a broad global perspective will be an important challenge for future soil science (Omran, 2008). The overexploitation for example, of resources in agriculture has led to environmental degradation: soil erosion, the greenhouse effect, and heavy metals pollution. Environmental limitations of the resource must be determined and...
considered in order to develop a sustainable reuse and agricultural strategy. Due to rapid increase in population, Egypt is expanding its agricultural land require reuse of agricultural drainage water for irrigation. About 12 billion m³ (BCM) of water are drained yearly, and only about 4.2 BCM are currently being reused. Approximately, one million acre in the Nile delta depends on drainage water for irrigation (Abu, 2011). Reusing this drainage water without suitable treatment may cause adverse effects on soil, crop, animal, and human health. One of the most polluted drains in Egypt is Bahr El-Baqar drain (Abdel-Shafy and Aly, 2002).

Bahr El-Baqar drain receives untreated waste water starting from east of Cairo, at the discharge point of El-Gebel El-Astaf and then joined by the Belbeis drain, down to the confluence with the Qalubiya drain. The length of the main drain is 170 km discharges in El-Manzala Lake and has two main branches, Qalubiya drain and the Bhables drain (Taha et al., 2004). It receives and carries the greatest part of wastewater (about 3 BCM/year) into Lake Manzala through a very densely populated area of the Eastern Delta passing through Qalubia, Sharkia, Ismailia and Port Said Governorates. Four main sources of pollutants which cause deterioration in Bahr El-Baqar region are: The industrial activities in Shoubra El-Khema including metal production, food processing, detergents and soaps manufacturing, textile finishing and paper production, industrial activities in Zagazig area; Wastewater discharged from Belbeis drain to Bahr El-Baqar, and domestic discharge received from rural areas around Bahr El-Baqar drain. Saad (1997) concluded that 58% of the total drainage water of Bahr El-Baqar drain comes from agricultural drainage, 2% from industrial drainage and 40% from domestic and commercial drainage.

Bahr El-Baqar drain has received considerable concern by many researchers since it is a polluted drain flowing into Lake Manzala. Ali et al. (1993) studied the effect of prolonged use of drain water for irrigation on the total heavy metals content of southern Port-Said soils. Water quality, chemical composition, and hazardous effects on Lake Manzala water and living organisms caused by Bahr El-Baqar drain water has also been investigated (Rashed and Holmes, 1984; Khalil, 1985; Ezzat, 1989). The discharge of industrial, agricultural and municipal wastewaters in Bahr El-Baqar drain led to contamination of the soil which are dependent on this drain in their irrigation (Bahr El-Baqar). These soils receive many kinds of pollutants especially, heavy metals such as lead, cadmium, nickel, and mercury which are considered the most hazardous (Park and Shin, 2006).

Cd and Pb are considered as the most important environmental pollutants which are quite toxic even at low concentration in agricultural soils because of the potential harmful effects (Onweremadu and Duruigbo, 2007; Yobouet et al., 2010). Lead is now considered a major environmental health hazard in both developed and developing countries. Lead is an important metal from the viewpoint of environmental toxicology (ATSDR, 1999). Lead measured exhibit the importance of the anthropogenic sources and particularly, the influence of global atmospheric inputs from leaded gasoline compared to regional and local industrial emissions. Its sources include lead smelter, battery manufacturer, paper and pulp industry, pipes, paints, solders, glass, pottery glazes, rubber, plastics, insecticides, boat and ship fuel and ammunition industry etc. Most lead processing industries are established in or around Bahr El-Baqar region and Gasoline used in gas stations also contained tetraethyl lead as an anti-knock additive which contributes to soil contamination. The results of IMM (2003) emphasized the influence of leaded gasoline as a source of lead contamination in soil in areas of high vehicle traffic.

The toxic effects of cadmium have received as much attention as those of lead. Its sources in the environment are metal plating, cadmium- nickel battery manufacture, phosphate fertilizers, paints and pigments manufacture, and alloy industries (Kadirvelu and Namasivayam, 2003). It can be found in reservoirs and soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Cigarettes also contain cadmium. Cadmium is a by-product of the mining and smelting of lead and zinc metallic nickel is produced from sulfide and silicate-oxide ores. Nickel is included in various metal alloys, stainless steels, and electroplating. Zinc fertilizers, sewage sludges and atmospheric dust of industrial origin are the principal sources of Zn accumulation in soils. Thus, these heavy metals were selected to represent as indicator on the pollution degree in this region.

Spatial distribution of some important heavy metals is essential to assess their effects on soil and to delineate contamination. Heavy metals are detrimental to the environment because of their non-biodegradable and persistent nature. Soils are an important sink for these metals due to their high metal retention capacities. The assessment and mapping of the soil heavy metals can contribute to sustainable use of soil resources aimed at mitigating soil degradation and increasing crop production. Remediation of soil contaminated by heavy metals is a serious environmental and technological issue worldwide. Geostatistical interpolation, or kriging, is being used to estimate the spatial distribution of pollutants in soil (Baraba et al., 2001; Van Meervenne and Goovaerts, 2001; Kumar et al., 2007; He and Jia, 2004; Woo et al., 2009). Ordinary Kriging (OK), disjunctive kriging, and lognormal kriging were used to produce the spatial patterns of heavy metals and to quantify the probability of heavy metal concentrations higher than their guide values (Liu et al., 2005).

So, the question still not answered yet is “What is the risk assessment of soil heavy metals for sustainable soil
resources in Bahr El-Baqar region? To the best of our knowledge, no reports were available on the Lead and Cadmium spatial distribution which indicate the pollution degree in this region. Consequently, the objective of this study is to evaluate and map the spatial distribution of heavy metals from contaminated soils in Bahr El-Baker region. In order to achieve the main objective, three specific objectives are identified. First, is to identify the components of these soils and the types of clay minerals associated with them. Second, is to map the spatial distribution of heavy metals and thirdly, to identify and map the potential hazards and screening risk associated with heavy metals contamination in these soils. Screening risk assessment provides risk maps and priority based on risk sources.

MATERIALS AND METHODS

Study area and methodology

The study area is located in northern Egypt, Bahr El-Baqar region, between 32° 05’ to 32° 16’ Longitude and 30° 56’ to 31° 07’ Latitude (Figure 1). The choice of the Bahr El-Baqar region implies that the local specific land-cover/land-use and environmental problems are represented. The area is an arid region that is experiencing significant land use change due to an extensive irrigation system that is converting semi-natural areas into arable land. Environmental protection in Bahr El-Baqar region is faced with critical problems due to the increasing population, demolishing natural resources, environmental pollution, land-use planning as well as others. The study area covers an area of 17818.93 ha. Soils which are adjacent to El Manzala Lake are described by UNDP (1979) as saline alkali low-lying clay which is lacustrine deposits. The land surface is flat, gently sloping towards the north and ranges in elevation from below sea level to 4 m. a. s. I in the highest point (Fathi et al., 1971). A reconnaissance visit was performed for the study area to get acquainted with different landscape features, land-use and land-cover patterns. The extensive field surveys were guided with a Global Positioning System (GPS) receiver. Nine soil samples were collected from Bahr El-Baqar region. The samples were air-dried and crushed with a wooden pestle and mortar to pass through a 0.5 mm mesh-screen. The electrical conductivity (EC) of soils was determined using 1:2 soil to solution (H2O) ratio. Particle size distribution was determined by the pipette method (Gee and Bauder, 1986). Soils were also characterized for their carbonate content (Allison and Moodie, 1965). Soil pH was measured in deionized water (pHw) and in 0.01 M CaCl2 (pH CaCl2) (in 1: 2.5 suspensions). Organic carbon (OC) was determined by wet digestion (Walkley and Black, 1934). Cation-exchange capacity (CEC) was determined for the soils samples by Na-method (Chapman, 1965). Figure 2 shows the overall methodology used in this study.

Mineralogical analysis

The mineral composition of soils samples were identified by X- Ray Diffraction (XRD) technique using a Philips X-ray diffractometer with cobalt target (λ= 1.791 Å) and a nickel filter at 40 KV and 20
mA. The selected scanning speed was 1°/min. The aluminum mould of the diffractometer was filled with an average sample thickness of 1.0 mm. The phases were identified by correlation with the corresponding standard X-RAY CARDS (ASTM) (Whittig and Allardice, 1986). The chemical composition of the studied soils was determined by X-Ray Fluorescence (XRF) (Philips, PW2400).

Geostatistical approach

Out of different Kriging techniques, the ordinary Kriging (OK) method was used in the present study because of its simplicity and prediction accuracy in comparison to other Kriging methods (Isaaks and Srivastava, 1989). OK is one of the most basic kriging methods (Meuland and Van Meirvenne, 2003). OK assumes the model: \( Z(s) = \mu + \epsilon(s) \). Where \( Z(s) \) is the main variable of interest, and \( \epsilon(s) \) are random errors. OK assumes stationarity of the mean and considers \( \mu \) to be a constant, but an unknown, value. Non-stationary conditions were taken into account by restricting the domain of stationarity to a local neighbourhood and moving it across the study area. After normalization of data for interpolation of heavy metals, kriging methods were used for predicting spatial distribution of some soil heavy metals characteristics such as: Pb and Cd. Variogram was drawn for selecting suitable model for fitness on experimental variogram and less Mean Standardized (MS) value was used. With the use of cross-validation and Root Mean Square Standardized (RMSS), the best method of interpolation was selected. More detailed explanations of the Geostatistical method.
are given by Isaaks and Srivastava, (1989); Stein, (1999); Yamamoto, (2000); Gringarten and Deutsch, (2001) and Omran (2011). We proceeded to prepare the map of heavy metals based on this interpolation and the help of Geographical Information System (GIS). Geostatistical analyses were performed using the Geostatistical analyst extension available in ESRI ArcMap v 10 (ESRI, 2011).

Heavy metals hazard mapping

Soil quality standards for heavy metals are often based on the total soil heavy metal concentration. For agriculture, one of the key aspects is safe food production and the degree to which heavy metals are affected on the plants or soil organisms, or leach to the groundwater largely depends on a combination of the soil properties and the source of the metals in the soil. In a national survey of the quality of crops, Wiersma et al. (1986) found that for wheat, the maximum acceptable concentration of Cd (0.15 mg kg\(^{-1}\) fresh weight) was exceeded in 6% of the samples; for barley, this was 24%, and for oats 10%. For Pb (maximum acceptable concentration: 0.5 mg kg\(^{-1}\) fresh weight) Considering the thresholds concentration used in this study as Cd =3, Pb= 300, Cu= 140, Zn= 300, Ni= 75, Cr= 150 according to European Union Standards (EU, 2002).

RESULTS AND DISCUSSION

Characterization of the soils samples

Table 1 shows the Physico-chemical properties of the soils. The concentration of each heavy metal was always controlled by different parameters (soil pH, iron and aluminum oxide content, clay content, organic matter and cation exchange capacity), which are heavy metal specific. The soils were similar in their texture with clay content from 46.1 to 80%. These soils which are adjacent to El Manzala Lake are described by UNDP (1979) as heavy saline alkali low-lying clay which is lacustrine deposits. However, the current EC values ranged between 1.2 and 2.92 dSm\(^{-1}\) which are not considered saline. These results indicate that these soils have continuous leaching as it was used as aquaculture which is not used in that region in the past. This is the reason why it was classified previously as a saline soil. The organic matter varied from 1.57 to 3.55 g kg\(^{-1}\). These soils are used as fishponds and have some residual of organic feeding on surface soil which is the reason why the OM content is high. Soil organic matter plays an important role not only in iron oxidation and reduction but also forms complexes with any soluble iron that is released. The organic matter extract, doubtless, chelates with iron and holds it for a time in a soluble condition and can be transported within the plant tissues (Allison, 1973). The CEC values ranged from 64.3 to 97.75 cmol\(_e\) kg\(^{-1}\). Most of the soils have neutral reaction (7.30 to 7.85) with differences between pH\(_w\) and pH\(_{CaCl_2}\) close to or greater than the unit. This difference refers to the soils that have positive charges on their surfaces which have amorphous iron oxides and organic matter. The %CaCO\(_3\) ranged from 5.2 to 29.2%, and the highest values is related to their content of CaO and Loss on ignition (LOI) % as appeared in XRD, XRF analyses and noticed from shells in the field.

<table>
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<tr>
<th>Sample no.</th>
<th>pH(_w)</th>
<th>pH(_{CaCl_2})</th>
<th>EC (dSm(^{-1}))</th>
<th>CEC (Cmol(_e) Kg(^{-1}))</th>
<th>CaCO(_3)%</th>
<th>OM (%)</th>
<th>Mechanical composition (%)</th>
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</tr>
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<td>8.29</td>
<td>2.92</td>
<td>78.49</td>
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Mineralogical studies

Figure 3 and Table 2 illustrate the XRD patterns and XRF analysis for the mineralogical composition and chemical analysis respectively, of the soils collected from Bahr El-Baker region. Montmorillonite was the main mineral composition of clay fraction for all soils. Except for the soil No 9, illite was associated with montmorillonite minerals. The iron oxides minerals were not detected by XRD in all soils in spite of the fact that XRF showed the presence of iron close to 15%. These results indicated that the iron oxides are presented as amorphous form in these soils. The crystalline form of iron oxides was detected in three soils (soil No 2, 6 as a magnetite form and soil No 4 as a pyrite form). Pyrite form of iron oxide indicated that this area is under redox situation. Fe-rich (hydroxyl) sulfates represent the main oxidation products of pyrite. These soils exhibited that they possess both surface permanent and variable charges due to smectite.

Table 1. Physico-chemical characteristics of studied soils from Bahr El-Baker region.
minerals, amorphous iron oxides, and organic matter. Since phyllosilicates are together with Fe oxides, the two major constituents of the great majority of soils, and that of the organic fraction is generally lower than a few percentage; these minerals have a negative (phylllosilicates) or positive (layer double hydroxides) permanent charge (that is, pH-independent) arising from isomorphic lattice substitutions. That result is the reason
for increasing the values of CEC for the most soils under the study. The montmorillonite mineral as the dominant clay mineral ensures high metal sorption capacity (Veeresh et al., 2003) which provides the soil with high cation exchange capacity. CEC regulating the sorption of heavy metals by soils (Kuo and Baker, 1980; Hooda and Alloway, 1998; Appel and Ma, 2002). These minerals consist of the so-called primary minerals, either inherited from the parent material (quartz, titanium oxides and feldspar etc) or introduced to the environment by industrial activities (for example, zinc and nickel oxide and willemite released by smelters), and secondary minerals such as phyllosilicates, oxides of Fe, Al and Mn, and sometimes carbonates, which may also have a lithogenic origin. While the coarse soil fraction may be more important from the standpoint of soil physics and to trace the origin of the pollution, the fine materials are the most reactive soil separation from a chemical point of view, and hence, the most important in order to assess the impact of metal contaminants to ecosystems. The mineral colloidal fraction consists predominantly of phyllosilicates and variable amounts of Fe and Mn oxides, while the organic colloidal fraction is represented by humic substances. These

<table>
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<th>SiO2</th>
<th>Al2O3</th>
<th>P2O5</th>
<th>K2O</th>
<th>CaO</th>
<th>MgO</th>
<th>*SO3</th>
<th>Na2O</th>
<th>Fe2O3</th>
<th>MnO</th>
<th>Cu</th>
<th>Zn</th>
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<td>0.73</td>
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<td>14.29</td>
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<td>280.30</td>
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<td>201.18</td>
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<td>75.85</td>
<td>93.41</td>
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* = not free, LOI= Loss on ignition.

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<th>Threshold concentration *EUS</th>
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</table>

Adopted from Baize, 1997; * EUS= European Union Standards (EU 2002).
nanoparticles have a large surface area, and are characterized by a surface charge which attracts labile ions (Manseau et al., 2002). Table 3 shows that the maximum Cd, Cu, and Zn contents in the soils were equal to 17.37, 280.30, and 215.58 mg kg\(^{-1}\) respectively. The total extracted fractions comprises of both the residual and the non-residual portion of that fraction bound to silica. These levels were far above the average concentrations in the earth's crust (Baize, 1997; Hasan, 2007; Yobouet et al., 2010) and the threshold concentration of European Union Standards (EU). Table 3 indicates these soils were heavily polluted with Cd and Cu metals that are part of the most dangerous industrial and municipal waste (Hasan, 2007).

Cadmium is a by-product of the mining and smelting of lead and zinc. It can be found in reservoirs and soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Lead is accumulated in the surface soil horizon because of its low mobility and strong association to soil constituents as organic matter, minerals of the clay fraction, and oxides of iron and manganese (Pendias and Pendias, 2001). The net effect on Pb adsorption is controlled by the relative binding strengths between the soil surface sites and the metal and the complex reactions between the organic acid and the metal (Wu et al., 2003).

### Table 4. Correlation coefficient (R\(^2\)) relationships between trace and major elements and the physico-chemical soil parameters.

| Parameters | pHw | OM | CaCO\(_3\) | CEC | clay | SiO\(_2\) | Al\(_2\)O\(_3\) | P\(_2\)O\(_5\) | K\(_2\)O | CaO | MgO | Fe\(_2\)O\(_3\) | MnO | Cu | Zn | Ni | Pb | Cd | Co | Cr |
|------------|-----|----|-----------|-----|------|---------|-------------|-------------|--------|------|-----|-----------|-----|----|----|----|----|----|----|
| pHw        | 1   |    |           |     |      |         |             |             |        |      |    |           |     |    |    |    |    |    |    |
| OM         | -0.658 | 1  |           |     |      |         |             |             |        |      |    |           |     |    |    |    |    |    |    |
| CaCO\(_3\) | 0.025 | 0.616 | 1         |     |      |         |             |             |        |      |    |           |     |    |    |    |    |    |    |
| CEC        | -0.777* | 0.538 | 0.124 | 1   |      |         |             |             |        |      |    |           |     |    |    |    |    |    |    |
| clay       | -0.679* | 0.408 | 0.153 | 0.917** | 1   |         |             |             |        |      |    |           |     |    |    |    |    |    |    |
| SiO\(_2\)  | 0.362 | -0.819** | -0.862** | -0.293 | -0.346 | 1         |             |             |        |      |    |           |     |    |    |    |    |    |    |
| Al\(_2\)O\(_3\) | 0.354 | -0.784* | -0.803** | -0.226 | -0.291 | 0.988** | 1         |             |        |      |    |           |     |    |    |    |    |    |    |
| P\(_2\)O\(_5\) | -0.693* | 0.545 | 0.080 | 0.352 | 0.261 | -0.482 | -0.560 | 1        |        |      |    |           |     |    |    |    |    |    |    |
| K\(_2\)O    | 0.433 | -0.847** | -0.650 | -0.151 | -0.072 | 0.805** | 0.786* | -0.453 | 1    |      |    |           |     |    |    |    |    |    |    |
| CaO        | -0.189 | 0.674* | 0.878** | 0.063 | 0.145 | -0.944** | -0.933** | 0.336 | -0.816** | 1 |      |    |           |     |    |    |    |    |    |    |
| MgO        | 0.798** | -0.726* | -0.113 | -0.811** | -0.688* | 0.411 | 0.389 | -0.598 | 0.417 | -0.133 | 1 |      |    |           |     |    |    |    |    |    |    |
| Fe\(_2\)O\(_3\) | 0.097 | -0.332 | -0.483 | 0.015 | -0.060 | 0.394 | 0.311 | 0.123 | 0.523 | -0.468 | 0.045 | 1 |      |    |           |     |    |    |    |    |    |    |
| MnO        | 0.858** | -0.617 | -0.016 | -0.901** | -0.788* | 0.256 | 0.202 | -0.417 | 0.203 | 0.000 | 0.847** | 0.106 | 1 |      |    |           |     |    |    |    |    |    |    |
| Cu         | -0.523 | 0.244 | -0.152 | 0.819** | 0.755* | 0.029 | 0.069 | 0.143 | 0.286 | -0.299 | -0.614 | 0.318 | -0.820** | 1 |      |    |           |     |    |    |    |    |    |    |
| Zn         | -0.825** | 0.669* | 0.039 | 0.570 | 0.416 | -0.432 | -0.471 | 0.927** | -0.487 | 0.219 | -0.835** | 0.053 | -0.654 | 0.339 | 1 |      |    |           |     |    |    |    |    |    |    |
| Ni         | 0.085 | -0.336 | -0.461 | -0.326 | -0.414 | 0.574 | 0.612 | -0.366 | 0.112 | -0.427 | 0.320 | -0.417 | 0.122 | -0.336 | -0.278 | 1 |      |    |           |     |    |    |    |    |    |    |
| Pb         | 0.126 | -0.356 | -0.620 | 0.035 | -0.070 | 0.572 | 0.516 | -0.083 | 0.609 | -0.687* | -0.027 | 0.915** | -0.003 | 0.433 | -0.032 | -0.213 | 1 |      |    |           |     |    |    |    |    |    |    |
| Cd         | -0.231 | 0.423 | 0.551 | 0.660 | 0.663 | -0.405 | -0.285 | -0.248 | -0.226 | 0.350 | -0.316 | -0.207 | -0.432 | 0.450 | -0.076 | -0.328 | -0.193 | 1 |      |    |           |     |    |    |    |    |    |    |
| Co         | 0.263 | -0.383 | -0.325 | -0.482 | -0.521 | 0.503 | 0.541 | -0.443 | 0.084 | -0.319 | 0.451 | -0.516 | 0.296 | -0.503 | -0.400 | 0.969** | -0.335 | -0.352 | 1 |      |    |           |     |    |    |    |    |    |    |
| Cr         | -0.243 | 0.195 | -0.223 | -0.148 | -0.266 | 0.077 | 0.068 | 0.264 | -0.363 | -0.105 | -0.289 | -0.479 | -0.128 | -0.302 | 0.390 | 0.606 | -0.305 | -0.491 | 0.589 | 1 |      |    |           |     |    |    |    |    |    |    |

*Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level.

References:

The range between the minimum and 4 mg kg\(^{-1}\) the clay proportion. However, Cu, and Zn. Zn and Fe in the soils, the CEC, there is a positive correlation with clay, Cd, Cu, Zn, and OM; however, it has a negative correlation with Mg and Mn. A significant relationship is found between Cd, Cu content and clay content. Considering all soil samples, Pb, Ni and Cr content is not significantly related to clay content. Surprisingly, there is no significant relationship between organic matter content and heavy metal concentration, except for Zn. Also, there is no significant relationship between P\(_2\)O\(_5\) content and heavy metal concentration, except for Zn. Cd presents a positive relationship with CaCO\(_3\). CaCO\(_3\) has a positive correlation with Cd and Ca; however, it has a negative correlation with Cu and Pb, Si, and Al.

### Spatial distribution of soil heavy metals

The summary statistics results which are shown in Table 5 indicated that the mean value of soil Pb, Cu, and Zn concentrations were 43.096, 122.96, 133.25 mg kg\(^{-1}\) respectively, and the range between the minimum and maximum values were 21, 218.53, 116.4 mg kg\(^{-1}\) respectively, which was large. The mean value of soil Cd, Cu, and Ni concentrations is 17.37, 280.30, 79.86 mg kg\(^{-1}\), respectively which is much higher than the EUS threshold levels (3, 140 and 75 mg kg\(^{-1}\), respectively) presented in Table 3. There are great variations and high skewness for Cu and Zn (1.27 and 1.22). The spatial patterns of Cu and Zn concentrations revealed that the spatial distribution is not homogeneous. The histogram results which are summarized in Table 5 also indicate that the data distribution has great variation and is right tailing which need transformation. Table 6 and Figure 4

### Table 5. Summary statistics of soil heavy metals concentrations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean</th>
<th>Min.</th>
<th>Med.</th>
<th>Max.</th>
<th>SD</th>
<th>Skewness</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>12.702</td>
<td>10.27</td>
<td>12.45</td>
<td>17.37</td>
<td>2.2108</td>
<td>0.984</td>
<td>3.276</td>
</tr>
<tr>
<td>Pb</td>
<td>43.096</td>
<td>31.75</td>
<td>44.23</td>
<td>52.40</td>
<td>6.2916</td>
<td>-0.219</td>
<td>2.510</td>
</tr>
<tr>
<td>Cu</td>
<td>122.96</td>
<td>61.77</td>
<td>97.53</td>
<td>280.30</td>
<td>73.35</td>
<td>1.267</td>
<td>3.318</td>
</tr>
<tr>
<td>Zn</td>
<td>133.25</td>
<td>99.18</td>
<td>120.37</td>
<td>215.58</td>
<td>37.03</td>
<td>1.221</td>
<td>3.688</td>
</tr>
<tr>
<td>Ni</td>
<td>67.83</td>
<td>61.32</td>
<td>64.42</td>
<td>79.86</td>
<td>6.914</td>
<td>0.913</td>
<td>2.245</td>
</tr>
<tr>
<td>Cr</td>
<td>111.57</td>
<td>93.41</td>
<td>116.06</td>
<td>134.06</td>
<td>13.48</td>
<td>0.064</td>
<td>1.977</td>
</tr>
</tbody>
</table>

SD= Standard deviation.

### Table 6. Fitted parameters of the variogram models for heavy metals parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Models</th>
<th>Prediction errors</th>
<th>Mean</th>
<th>RMS</th>
<th>ASE</th>
<th>MS</th>
<th>RMSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Circular</td>
<td></td>
<td>-0.090</td>
<td>2.410</td>
<td>2.219</td>
<td>-0.0255</td>
<td>1.096</td>
</tr>
<tr>
<td>Pb</td>
<td>Exponential</td>
<td></td>
<td>0.799</td>
<td>6.566</td>
<td>6.593</td>
<td>0.0600</td>
<td>0.979</td>
</tr>
<tr>
<td>Cu</td>
<td>K-Bessel</td>
<td></td>
<td>-0.878</td>
<td>43.965</td>
<td>56.604</td>
<td>-0.0037</td>
<td>0.717</td>
</tr>
<tr>
<td>Zn</td>
<td>Pentaspherical</td>
<td></td>
<td>0.161</td>
<td>33.565</td>
<td>34.817</td>
<td>0.0002</td>
<td>0.985</td>
</tr>
<tr>
<td>Ni</td>
<td>Rational Quadratic</td>
<td></td>
<td>-0.056</td>
<td>7.197</td>
<td>7.334</td>
<td>-0.0029</td>
<td>0.975</td>
</tr>
<tr>
<td>Cr</td>
<td>Rational Quadratic</td>
<td></td>
<td>-0.061</td>
<td>9.769</td>
<td>11.504</td>
<td>-0.0046</td>
<td>0.803</td>
</tr>
</tbody>
</table>

RMS= Root Mean Square, ASE= Average Standard Error, MS= Mean Standardized, RMSS= Root Mean Square Standardized.
Figure 4. Cross validation and semivariograms model for some heavy metals parameters.
list the cross validation results to examine the validity of
the fitting models and parameters of semivariograms (for
example, Cd and Pb). The best fit model for Cd and Pb
were Circular and Exponential model with MS values for
them -0.0255 and 0.0600 respectively, which is closest to
zero. RMSS values for Cd and Pb were 1.096 and 0.9789
respectively which are closest to 1. The best fit model for
Zn was Pentaspherical model (MS = 0.0002) and
Rational Quadratic model for Ni and Cr with -0.0029 and
-0.0046 MS respectively, which is closest to zero. The
RMSS value for Zn, Ni and Cr are 0.985, 0.975 and 0.803
respectively which is closest to 1. When the average
estimated prediction standard errors are close to the root-
mean-square prediction errors from cross-validation, you
can be confident that the prediction standard errors are
appropriate (Johnston et al., 2001). Figure 5 shows the
distribution maps of heavy metals based on this
interpolation.

Vulnerability mapping of heavy metals for
agricultural purposes

Soil resources degradation is an issue of significant
societal and environmental concern in Bahr El-Baker
region. Soil represents a major sink for heavy metals,
which can then enter the food chain via plants or leaching
into ground water. In order to prevent soil pollution before
it occurs and avoid the future need for costly remediation
efforts, GIS can be used to assess the soil pollution
potential. The Geostatistical Analyst can be used to map
the probability that any heavy metals values exceed the
threshold. The heavy metals vulnerability maps for
agricultural purposes are shown in Figure 6. The whole
area is divided into two classes on the basis of hazard,
low and high. Most of the soil samples fall in the low
hazard classes. Pb, Cr, Ni and Zn metals concentrations
are under the threshold value in soils which falls in the
low hazard category. However, only Cd falls in the high
hazard category. The whole study area (17813.93 ha)
was contaminated with Cd. Part of Cu metal falls under
the threshold (6370.23 ha) and the other area falls above
the threshold as shown in Figure 6.

Conclusion

The obtained results of this study can be concluded
based on the three specific objectives which are identified
in the introduction. First, is to identify the components of
these soils and the types of clay minerals associated with
them. X- Ray Fluorescence and X- Ray Diffraction
analyses were used to identify the components of these
soils. The similarity of these soils in most of physico-
chemical and mineralogical (dominant montmorillonite)
properties revealed that these soils are exposed to the
same geological and pedological conditions. These soils
exhibited that they possess both permanent and variable
surface charges due to smectite minerals, amorphous
iron oxides, and organic matter which ensures high metal
sorption capacity and increasing the CEC values.
Second, is to map the spatial distribution of the some
heavy metals. Geostatistical analyses were used to map
the spatial distribution of some heavy metals. The spatial
patterns and the histogram results of Cu and Zn
concentrations revealed that the spatial distribution was
not homogeneous and the data distribution has great variation and high skewness. The best fit model for Cd and Pb were Circular and Exponential model with MS values for them -0.0255 and 0.0600, respectively which is closest to zero. RMSS values for Cd and Pb were 1.096 and 0.9789 respectively which are closest to 1. The best fit model for Zn was Pentaspherical model (MS = 0.0002) and Rational Quadratic model for Ni and Cr with -0.0029 and -0.0046 MS, respectively which is closest to zero.

The best fit model for Zn is Pentaspherical model (Mean Standardized = 0.0002) and Rational Quadratic model for Ni and Cr with a -0.0029 and -0.0046 Mean Standardized respectively which is closest to zero. The RMSS values for Zn, Ni and Cr are 0.985, 0.975 and 0.803 respectively which is closest to 1. When the average estimated prediction standard errors are close to the root-mean-square prediction errors from cross-validation, then you can be confident that the prediction standard errors are appropriate.

Third, is to identify and map the potential hazards associated with heavy metals contamination in these soils. The abundance of heavy metals measured in these soils decreases as follows: Cd > Cu > Zn > Cr > Ni > Pb. Total concentrations of Cd and Cu in some soils exceed the thresholds values for non-polluted soils. The most important heavy metals with regards to potential hazards in studied soils are Cu and Cd. The total study area (17818.93 ha) is contaminated with Cd, however, part of the area (6370.23 ha) is contaminated with Cu metal.

Finally, this study is only a screening application that will help in identifying the most important areas to sample in the future with much greater detail. Consequently, the resulting spatial distribution maps will continue to change. However, these soils by their properties are still able to load with over concentrations of these metals and retained them since they do not reach their saturation capacities except for Cu and Cd in some areas. However, under bad management and aquacultural activity (the continuous redox conditions) with continuous accumulation of these toxic metals in the environment, this region will be exposed to a real disaster. These results are essential for understanding the heavy metals

Figure 6. Heavy metals vulnerability maps of the studied soils in Bahr El-Baker region.
process which serves as a basis for quantitative considerations. Protection against the threat is critical for sustainable land management. Precise measures and efficient methods for soil and water quality must be created. So, in order to prevent soil and water pollution before it occurs and avoid the future need for costly remediation efforts, further research will be to answer the question "Is the concept of soil and water quality for sustainable land management fake or genuine?"

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UNDP Staff (1979). Suez Canal Region integrated Agricultural Development Study. EGY 176/001-6, Report No. 3.


