Sources identification and contamination assessment of heavy metals in soil of Middle Nile Delta, Egypt

Atef M. Abu Khatita \(^a\)^, Roman Koch \(^c\) and Abdullah O. Bamousa \(^a\)

\(^a\)Geology Department, Faculty of Science, Taibah University, Al Madinah, Saudi Arabia; \(^b\)Geology Department, Al Azhar University, Cairo, Egypt; \(^c\)GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Erlangen, Germany

ABSTRACT
Sedimentological and geochemical studies are integrated to determine the potential of heavy metals in the Middle Nile Delta soil. Four sources of trace elements were identified; a geogenic source includes Fe, Co, Cr, Ni and V, along with Ca that partly enhanced by anthropogenic input, and three dissimilar anthropogenic sources grouped the elements as follow; As, Pb, Zn Cu, Ba and P which derived mainly from industrial activities; Ba, Pb, Zn and Cu group is likely dispersed by traffic emissions, and P, As and Cu elements group which influenced by agrochemical application and drain water irrigation. The concentrations of studied elements increasing with decreasing the particle size. Moreover, two groups of mineral assemblages of soil are recognized; the first group deposited with one particle fraction and inherited from parent materials. The second one includes non-silicate minerals clasts, deposited with more than one fraction and most likely of anthropogenic source.

1. Introduction
Trace elements occur naturally in the soil with specific concentration depending essentially on the parent materials and pedogenic processes but their concentration can significantly enhance by the different human activities. These concentrations may cause direct and indirect adverse effects for fauna, flora and human health. Along with other anthropogenic activities such as urbanization, off-road driving, overgrazing, salinization, oil contamination, industrial activities and quarrying, heavy metals contamination results in faster land degradation on regional scale [1]. Moreover, heavy metals contamination can also impact the groundwater by soil–water interaction throughout the water cycle. From an environmental point of view, drought is an important factor of hydrological cycle process and soil–water interaction. The long periods of droughts, scarcity of water and the huge variation in precipitation records are recorded in the regional scale in Kuwait [2–5], Iraq [6] and Iran [7]. Many attempts tried to evaluate and distinguish between the elements that of natural or geogenic origin than those of man-made or anthropogenic ones. These attempts demonstrate that the most important factors that dispersing the concentration of trace elements in the soils are; agrochemical practices of the cultivated soils [8,9], industrial and mining activities [10,11] and urbanization such as waste disposal, urban effluent, traffic and vehicle exhausts [12–15].

Recently, the application of enrichment factor [16–19] and statistical techniques e.g. cluster analysis [20–22] are using as an effective tool to distinguishes between the geogenic and/or anthropogenic input of trace elements within the soil. In general, elemental distribution in soils is controlled by the parent materials, soil textures, climate, while its partitioning in a soil depends on pH, Eh, clay minerals, CEC, organic matter, Fe–Mn oxides, microbial activities, soil–water contents, the concentration of element itself and others [23–25].

Nile Delta region represents an essential agricultural and economic sector for Egypt where it contains the most fertile soil, commercial districts along with huge fertilizer and chemical factories. Unfortunately, all these activities are interlocked under the absence of environmental awareness. Assessment of the soil contamination in the Nile Delta is quite rare so far [8,26]. The aim of the present investigation is to delineate the relative degree of contamination of the different land use soil in the study area to identify the potential sources of trace element contaminations. The study started with the petrographical description of the surface soil samples of the middle Nile Delta area, its texture and mineralogical composition. The concentration and enrichment factor of selected elements in the soil of different land uses (urban, industrial and cultivated) are assessed and discussed, where the local natural unpolluted Nile sediment was used as a background [27]. Moreover, distributions of the elements within the different particle
sizes were presented. The study presents a database in order to recover the soil functions and reducing the environmental degradation in the Nile Delta region.

2. Materials and methods

2.1. Study area and soil sampling

Nile Delta is the green area that begins from Cairo at the south where the river Nile splits into two Damietta and Rosetta branches to the Mediterranean coast of Egypt. The climate in the Nile Delta is recognized by scarce rainfall with an annual average rainfall of about 37 mm, which usually occurs from October to March. The study area (between 30° 42’ to 30° 55’ N and 30° 42’ to 31° 06’ E) covers the middle sector of the Nile delta which seriously suffer from more than one sources of pollution. Agricultural activities consume a whopping amount of fertilizers, pesticides and insecticides, particularly after the construction (by 1964) of Aswan High Dam. Moreover, it has an important transportation hub with one of the densest highway networks and contains the most important industrial and eldest commercial cities in Egypt; Kafr El Zyat and Tanta cities. Cotton ginning and oil and soap are the major industries in Tanta while Kafr El Zyat contains the greatest fertilizers, pesticides and insecticides factories in Egypt.

Twenty-six soil samples (Figure 1) were collected from different characteristic soil types (7 agricultural, 10 urban and 9 industrial soil samples) of the middle sector of Nile Delta. The samples (0.50–1.00 kg) were collected by using a plastic shovel to avoid the iron contamination and stored in plastic bags.

2.2. Analytical techniques

The petrography of the different soil types was investigated under the polarizing microscope based on 12 prepared thin sections of different soil types (4 cultivated, 4 urban and 4 industrial soil types). Sieving analysis was carried out to investigate the potential impact of soil particle size (> 200 μm, 125–200, 63 μm–125 μm, 36–63 μm and < 36 μm) on the heavy metals content. X-ray diffractometry was applied on 26 soil samples to determine the mineral assemblage. Moreover, the previously separated particle size fractions were subjected to XRD analyses to study the effect of particle size on the composition of different mineral phases. The bulk powdered samples were investigated as random powder mounts with a Siemens D5000 X-ray diffractometer equipped with a secondary monochromator. For all investigations, the angular range was from 2 to 65° 2θ with a step size of 0.020° 2θ and a measuring time of 2s/step. A copper tube was used with 40 kV and 30 mA. The determination of the phases was made using EVA (version is 14.0) software (Bruker AXS, Coventry, UK) and quantitative analysis was performed by Rietveld refinement. For optimum results, the X-ray diffraction (XRD) patterns were fitted using TOPAS (version is 4.2) software from Bruker AXS. All studied elements were analysed by X-ray fluorescence technique. All analytical techniques used in this study have been carried out at the Geozentrum Nordbayern (GZN), Erlangen, Germany.

2.3. Enrichment factor

Enrichment factor calculation is expressed according to Zoller et al. [28] as the following:

$$EF_x = \frac{X/E_{ref}}{(X/E_{ref}) \text{ background}}$$

where X is the concentration of interest element, $E_{ref}$ is the reference element for normalization. The Nile sediments are used as a natural (local) background [27] and Al is used as a reference element to minimize particle size effects [17, 29].

3. Results and discussion

3.1. Soil texture

The grain size analysis indicates that, all soil categories (except for one industrial soil sample) are classified as silty clay soil based on Shepard [30] and clayey soil according to USDA [31] (Figure 2). This result may reflect different land use types where cultivated soils display homogenous particle size that reflects the original sediment (Nile flooding sediment) underwent only very few changes. On the other hand, urban and industrial soils are severing from admixtures of various allochthonous particles and particles deriving from different human activities. Fertilizer particles are easily dissolved in cultivated soil to supply their ions to the pore water and finally to the roots system of the plants. So admixed particles may have been just dissolvable fertilizers, which therefore will have may not have had a long effect on a change of the original sediment to coarse particle sizes. By contrast, urban and industrial soils hold accumulated insoluble particles of anthropogenic origin [32].

3.2. Mineralogical composition

X-ray diffractometry revealed that the studied soil samples are consisting predominantly of clay minerals (59.5 wt.%), quartz (21.6%), Plagioclase (5.5 wt.%), amphiboles (2.4 wt.%) along with magnetic minerals (2.4 wt.% of magnetite and titanomagnetite), pyroxene (1.5 wt.%), K-feldspars (1.3%), biotite (0.6 wt.%) with a small amount (1%) of garnet, epidote. These minerals have a primary sedimentary source and indicate metamorphic and basic or intermediary affinity of the parent material. Calcite (2.1 wt.%), gypsum (0.8 wt.%), apatite (0.3 wt.%) and halite (0.2 wt.%) are also identified which most probably have different sources. These minerals
may be present as relics of fertilizer particulates dispersed on the surface soil surface and redistributed by wind. In this circumstance, the minerals assemblage distribution throughout the soil sizes fractions can be used to indicate their sources.

The average mineralogical contents in various particle sizes of the different soil types are listed in Table 1. Commonly the amounts of quartz and clay minerals exhibit opposite trends in regard to the particle size fractions. The finer the particle size is, the more clay mineral occurs and vice versa for quartz. Quartz content increases from the finer to the coarser fraction (9.3–15.5 wt.% respectively) in the cultivated soil is likewise for the industrial soil type. The reverse trend of the urban soil sample might indicate that large admixed of clay fragments in the soil. where clay contents increase from finer to coarser fractions (from 66.9 wt.% to 73.7 wt.%) and vice versa for quartz which decreases from 13.1 to 10.4 wt.%. Feldspars did not display a special trend.

Neither heavy minerals nor magnetic minerals display a clear trend to a specific fraction. The lowest amounts (1.3–2.8 wt.%) of calcite occur in urban soil sample while the highest amount (5.9–9.9%) presents in an industrial soil sample (8S). The other industrial soil sample (14S) and a cultivated one contain average amounts of calcite (2.4–3.2 wt.%). A relatively high calcite amount (4.8%) in cultivated soil most probably due to fertilizer deposited on the surface soil.

Gypsum and halite are registered in an industrial soil sample (14S), whereas these mineral phases are missed in the other surface soil types. Both phases can originate in-situ due to sea water evaporation but can also be transported by wind and deposited from any other place.

In respect to the average amounts of the mineral phases that recognized in different particle size fractions, the distribution of the mineral assemblages is more obvious.
Table 1. Mineral phases (in %) in various grain size fractions in different types of surface soil.

| Sample                  | Fraction (μm) | Quar. ( %) | Plag. ( %) | K-fld. ( %) | Mg. ( %) | Calc. ( %) | Amph. ( %) | Pyro. ( %) | Gran. ( %) | Bit. ( %) | Ep. ( %) | Ap. ( %) | Hal. ( %) | Gyp. ( %) | Sum  |
|-------------------------|---------------|------------|------------|-------------|----------|------------|------------|-----------|------------|----------|---------|---------|----------|---------|-------|-------|
| US cultivated soil      | > 200         | 67.7       | 15.5       | 4.7         | 1.2      | 3.1        | 4.8        | 1.7       | 0.8        | 1.4      | 0.1     | -       | -        | -       | 100   |
|                         | 125- 200      | 74.7       | 11.2       | 5.0         | 0.9      | 2.0        | 2.4        | 2.2       | 0.6        | 0.4      | 0.5     | -       | -        | -       | 100   |
|                         | 63- 125       | 72.7       | 13.5       | 4.7         | 0.9      | 1.0        | 2.4        | 2.5       | 1.0        | 0.9      | 0.3     | 0.1     | -        | -       | 100   |
|                         | 36- 63        | 71.3       | 12.6       | 5.6         | 1.0      | 1.8        | 2.3        | 2.7       | 1.0        | 0.9      | 0.6     | 0.1     | -        | -       | 100   |
|                         | <36           | 73.4       | 9.3        | 5.8         | 1.5      | 2.5        | 2.7        | 2.3       | 1.0        | 0.9      | 0.4     | 0.1     | -        | -       | 100   |
| IS cultivated soil      | > 200         | 38.0       | 46.7       | 3.1         | 1.1      | 0.6        | 5.9        | 1.3       | 1.7        | 1.1      | 0.5     | -       | -        | -       | 100   |
|                         | 125- 200      | 35.5       | 51.2       | 3.9         | 1.1      | 1.3        | 6.4        | 2.0       | 0.5        | -        | -       | 0.2     | -        | -       | 100   |
|                         | 63- 125       | 42.6       | 36.3       | 6.0         | 1.3      | 1.2        | 7.3        | 2.7       | 1.1        | -        | 1.0     | 0.4     | -        | -       | 100   |
|                         | 36- 63        | 56.0       | 18.5       | 5.9         | 1.2      | 1.0        | 9.9        | 2.8       | 1.7        | 0.3      | 1.0     | 1.4     | 0.2     | -      | 100   |
|                         | <36           | 62.6       | 12.7       | 5.8         | 1.6      | 1.9        | 9.6        | 2.9       | 2.2        | 0.3      | 0.4     | 0.3     | 0.1     | -      | 100   |
| US industrial soil      | > 200         | 59.5       | 17.7       | 5.4         | 0.8      | 1.6        | 3.2        | 3.5       | 1.5        | 0.8      | 0.9     | 0.1     | -        | 2.4     | 2.7   |
|                         | 125- 200      | 56.7       | 16.2       | 6.0         | 1.5      | 1.4        | 2.4        | 2.3       | 2.7        | 2.0      | 1.2     | -       | 0.1      | 2.5     | 4.9   |
|                         | 63- 125       | 58.1       | 19.6       | 4.9         | 1.2      | 1.4        | 2.7        | 2.5       | 1.4        | 0.7      | 0.4     | -       | 0.1      | 2.9     | 4.0   |
|                         | 36- 63        | 59.8       | 11.3       | 5.9         | 1.1      | 2.1        | 2.6        | 3.1       | 1.9        | 1.2      | 0.5     | 0.3     | 0.2      | 2.2     | 7.8   |
|                         | <36           | 63.0       | 9.2        | 5.4         | 0.8      | 2.2        | 3.0        | 3.5       | 1.5        | 0.9      | 0.6     | -       | 0.1      | 1.1     | 8.7   |
| 25S urban soil          | > 200         | 73.7       | 10.1       | 5.2         | 1.3      | 2.4        | 2.1        | 2.1       | 1.3        | 0.6      | 0.7     | 0.1     | -        | -       | 100   |
|                         | 125- 200      | 74.1       | 10.6       | 5.2         | 1.0      | 2.9        | 1.3        | 2.0       | 1.2        | 0.3      | 0.7     | 0.2     | 0.2      | -       | 100   |
|                         | 63- 125       | 71.6       | 14.0       | 5.0         | 1.1      | 1.9        | 1.6        | 2.4       | 1.2        | 0.4      | 0.6     | 0.2     | 0.1      | -       | 100   |
|                         | 36- 63        | 65.6       | 16.4       | 6.0         | 1.2      | 1.9        | 2.6        | 2.3       | 1.9        | 0.2      | 0.9     | 0.8     | 0.2      | -       | 100   |
|                         | <36           | 66.9       | 13.4       | 6.8         | 1.2      | 2.8        | 2.8        | 1.6       | 2.7        | 0.2      | 1.0     | 0.8     | 0.2      | -       | 100   |

Amph. = amphiboles, Ap. = apatite, Bt. = biotite, Calc. = calcite, Ep. = epidote, Gar. = Garnet, Gyp. = gypsum, Hal. = halite, K-fld. = K- feldspars, Mag. = magnetite+ hematite+ titanomagnetite minerals, Plag. = plagioclase, Pyro. = pyroxene and Qz.= quartz.

Two groups of mineral assemblages are recognized and distributed through different soil particle size (Figure 3). The first group comprises mineral that gathered in one particle size fraction and my inherited from parent materials from which the Nile soil was originated (Ethiopian highlands and Lake plateau of Africa with contributions of Pan-African complex that exposed in the Egyptian Eastern Desert). Along with clay and quartz, clay in finer and quartz in coarser fractions, this group comprises plagioclase, feldspars, garnet and mafic minerals (biotite, pyroxene and amphiboles). The second group includes mineral clasts, assembled in more than one fraction such as apatite and calcite and are most likely of the anthropogenic source due to the grinding raw material of phosphate in the fertilizer factory of Kafr El Zayat in the industrial zone.

4. Petrography

The examined soil samples exhibit porphyroelastic fabric where flakes of biotite and plagioclase are embedded in a fine-grained ground mass (Figure 4(A)). In the most cultivated soil samples, quartz is dominant with rounded to sub-rounded medium-sized grains, (Figure 4(B)) which most probably relics of primary eolian sediments. In opposite, angular and subangular quartz grains are prevalent in both industrial and urban soil samples. This probably indicates that, the cultivated soils are consisting predominantly of original flooding sediments from the Nile, while industrial and urban soils are mixtures of Nile sediments with allochthonous materials and anthropogenic sand grains, etc.

Black rounded to sub-rounded particles are very common in industrial soil samples than the others (Figure 4(C)). They indicate extensive mixing of soil with other particles transported and deposited via industrial dust [32]. Scanning electron microscope combined with EDX revealed that these black particles are spherules in shape and composed mainly of Fe oxides with inclusions of P and Ca which indicates the industrial origin due to the grinding processes of raw phosphatic materials (e.g. apatite, Ca₅[PO₄]₃(F,Cl,OH)) fertilizer plants (Figure 4(D)). In addition, Ca my enhanced due to the deposition of carbonate particles (e.g. limestone) of geogenic dust since Egypt and its surrounding countries of arid climate are impacting by the considerable amount of carbonates particles caused from deposited dust aerosols during humid conditions and other weather conditions [33] as listed in Table 2.

4.1. Geochemistry

Since the soil of the study area was originated from the same sources under the same circumstances, it is supposed to be very similar in composition, but the anthropogenic inputs can differ the concentration of some trace elements there based on the land use management. The statistical parameters of studied trace elements in the Middle Nile Delta soils of different land uses are listed in Table 3. As, Pb, Cu, Zn Ce, Sr, Ba.
Figure 3. Distributions of identified minerals in various grain size fractions of surface soil and sediment samples.

Along with Ca and P, are revealing high concentration in the industrial soil than the others. While the other studied elements (e.g., Fe, Mn, Ni, Co, Cr and V) do not exhibit significant variation in concentration among different types, cultivated soils display a relatively high content of these elements than the others.

In cultivated soil samples, the mean concentration of P, Zn, Mn, Fe, Ni and Cu that are essential nutrients for plant are, 1258, 105.3, 1197, 70,619, 80.6 and 61.3 ppm, respectively. It is observed that the sample (105) that collected close to industrial zone reveals the highest value of As (9 ppm) and Zn (111 ppm), while the soil (sample 21C) that irrigated by waste drain water reveals the highest content of Ce, Cu and Pb and organic carbon (95, 90, 29 ppm and 3.57%, respectively) relative to the other soils, which are irrigating by Nile fresh water.

The calculated enrichment factors (as listed in Figure 5) ordered the elements in the following order: Cu (3.1) > As (2.2) > P (1.9) > Mn (1.7) > Zn (1.5) > Ca (1.4) > Pb (0.7) ≈ Ce (0.7). Even cultivated soil that irrigated by wastewater displays relatively high Pb content, these soil types still unenriched in Pb. This result
Figure 4. Internal structures and particles of soil samples; (A) plagioclase (Pl), biotite (Bt) flakes and other particles (pyrite, black) are embedded in a fine-grained ground mass. + Nic; (B) rounded to sub-rounded quartz grains, // Nic.; (C) black spherules of industrial source in clayey sediment, // Nic.; (D) SEM photomicrographs with a corresponding EDX of separated magnetic spherules with martasitic pattern surface structure.

Table 2. Average particle size and mineralogical percentages of deposited dust in Egypt and the Middle East compared to global dust samples [33].

| Sector          | Size particles% | Minerals% |
|-----------------|-----------------|-----------|
|                 | Sand | Mud | Quartz | Carbonates | Feldspars | Clay | Others |
| Kuwait [34]     | 37   | 63  | 38     | 45         | 10        | 2    | 5 |
| Ahwar-Iraq [4]  | 3    | 97  | 13     | 80         | 8         | 0    | 0 |
| Manamah-Bahrain [5] | 12 | 87  | 32     | 41         | 10        | 3    | 15 |
| Walameen-KSA [35] | 40 | 61  | 62     | 13         | 24        | 1    | 0 |
| Ain-Emirates [36] | 97 | 4   | 26     | 52         | 20        | 1    | 0 |
| Dubai-Emirates [37] | 17 | 82  | 21     | 45         | 6         | 0    | 27 |
| Amman-Jordan [32] | 30 | 70  | 21     | 68         | 4         | 7    | 0 |
| Tripoli-Libya [38] | 20 | 81  | 64     | 27         | 5         | 4    | 0 |
| Biougra-Morocco [32] | 12 | 88  | 46     | 46         | 8         | 1    | 0 |
| Cartagena-Colombia [39] | 10 | 90  | 66     | 0          | 33        | 0    | 1 |
| Cairo-Egypt [33] | 10  | 90  | 51     | 34         | 15        | 0    | 0 |
| Bald Hill-Australia [40] | 9  | 90  | 57     | 0          | 21        | 14   | 7 |
| Average         | 25   | 75  | 41     | 38         | 14        | 2    | 5 |

may document that, the cultivated soil is affected predominantly by agrochemical inputs and atmospheric deposition. Beside to its industrial origin, the applications of Cu-containing liquid fungicides, dead and decayed macroalgae (CuSO4-bearing) from Nile irrigation water [41]. As and Zn are most probably enhanced due to atmospheric deposition or fertilizer applications along with the occurrence of Ca and P. Abu Khatita [27] stated that, Ca-rich and P-bearing calcareous particles of high Ca and P contents are commonly observed in cultivated soils.

Urban soil reveals the lowest concentration of Ba (369 ppm), Cu (50.3 ppm), Ni (66 ppm), V(187 ppm) and P (1183 ppm) compared to the other land uses while the Zn (123 ppm) and Pb (25.3 ppm) contents are higher than that of cultivated soils. The two highest contents of Pb and Zn (56–49 ppm and 173–198 ppm of samples 19S and 27S, respectively) were recorded in samples that collected from the commercial zone of Tanta city where the traffic is very busy. Automobile exhausts and ultrafine particles that are braded from tyres and breaks, losses of lubricants and corrosion are the main sources of enriched the urban soil in Zn and Pb [42]. Moreover, the highest content of As was observed in samples collected from the windblown of industrial zone.

The calculated enrichment factor revealed that the urban soils are enriched in Cu, As, Zn, Ca, Pb, Mn and Ce by EF = 3.1, 2.5, 2.4, 2.3, 2.0, 1.7,1,4,1.2, respectively. Enrichment of both P and Ca most probably from deposition industrial dust of fertilizer plants in the surrounding industrial zone. Numerous Ca-bearing minerals and P-bearing calcareous particles
Table 3. Concentration of selected chemical elements (ppm) in Nile delta soils ($n = \text{number}$) and descriptive statistical data (range, mean, standard deviation and variation coefficient) for element concentrations in all soil categories (cultivated, urban and industrial).

|     | All soil categories $n = 26$ | Cultivated soil $n = 7$ | Urban soil $n = 10$ | Industrial soil $n = 9$ |
|-----|------------------------------|--------------------------|---------------------|-------------------------|
|     | range | mean | SD. | VC. | Range | mean | SD. | VC. | range | mean | SD. | VC. | range | mean | SD. | VC. | range | mean | SD. | VC. |
| As  | 1–14  | 5.9  | 2.5 | 43  | 3–9   | 5.9  | 2.2 | 37  | 1–7   | 5.0  | 1.7 | 34  | 4–14  | 6.9  | 3.3 | 48  |
| Ba  | 299–1103 | 429  | 146 | 34  | 383–479 | 430  | 29  | 7   | 305–451 | 396  | 50  | 13  | 299–1103 | 466  | 245 | 53  |
| Ce  | 50–118 | 80   | 16.5| 21  | 59–95  | 73   | 12.6| 17  | 50–118 | 80.2 | 18.0| 22  | 61–115 | 84.4 | 17.4| 21  |
| Co  | 10–40 | 31   | 6.3 | 21  | 32–40  | 34.7 | 2.6 | 7   | 10–38  | 29.4 | 8.0 | 27  | 19–35  | 29.2 | 5.5 | 19  |
| Cr  | 84–186 | 128  | 22.4| 18  | 114–148 | 133  | 12.4| 9   | 84–186 | 127.3| 29.1| 23  | 86–158 | 124.6| 21.5| 17  |
| Cu  | 24–139 | 61.8 | 29.1| 47  | 52–90  | 61.3 | 13.8| 22  | 24–98  | 50.3 | 22  | 45  | 25–139 | 75   | 40  | 53  |
| Ni  | 36–94 | 70.6 | 15.3| 22  | 72–94  | 80.6 | 7.8 | 10  | 36–94  | 66   | 18.9| 29  | 47–88  | 68.0 | 12.8| 19  |
| Cr  | 84–186 | 128  | 22.4| 18  | 114–148 | 133  | 12.4| 9   | 84–186 | 127.3| 29.1| 23  | 86–158 | 124.6| 21.5| 17  |
| Cu  | 24–139 | 61.8 | 29.1| 47  | 52–90  | 61.3 | 13.8| 22  | 24–98  | 50.3 | 22  | 45  | 25–139 | 75   | 40  | 53  |
| Ni  | 36–94 | 70.6 | 15.3| 22  | 72–94  | 80.6 | 7.8 | 10  | 36–94  | 66   | 18.9| 29  | 47–88  | 68.0 | 12.8| 19  |
| Pb  | 12–182 | 30.7 | 33  | 107 | 15–29  | 19   | 5.5 | 28.8 | 12–56  | 25.3 | 14.8| 59  | 16–182 | 45.6 | 52.2| 115 |
| Sr  | 235–492 | 308  | 54  | 18  | 254–303 | 283  | 16.3| 6   | 235–409 | 294  | 48.6| 17  | 275–492 | 342.4| 65.4| 19  |
| V   | 96–240 | 192  | 36  | 19  | 201–240 | 215  | 12.7| 6   | 96–231 | 187  | 41.7| 22  | 123–229 | 179  | 35  | 20  |
| Zn  | 88–689 | 143  | 115 | 81  | 103–111 | 105  | 2.8 | 3   | 98–198 | 123  | 34.0| 28  | 88–689 | 193.0| 189.1| 98  |
| Ca  | 25372–64109 | 38569 | 9513 | 25  | 29589–37665 | 34020 | 2658 | 8   | 25372–63465 | 37050 | 10400 | 28  | 28874–64109 | 43795 | 10204 | 23  |
| Fe  | 16786–76724 | 62583 | 12730 | 20  | 76165–68401 | 70619 | 2697 | 4   | 16786–76724 | 59344 | 17315 | 29  | 44832–72108 | 59931 | 9280  | 15  |
| Mn  | 434–1549 | 1099 | 224 | 20  | 1046–1293 | 1179 | 100 | 8   | 434–1549 | 1080 | 325 | 30  | 813–1293 | 1059 | 154  | 14  |
| P   | 1021–6721 | 1816 | 1548 | 85  | 1060–1475 | 1282 | 131 | 10  | 1021–1362 | 1183 | 103 | 9   | 1318–6721 | 2936 | 2303 | 78  |
| O.C.| 0.34–3.9 | 1.3  | 0.9 | 73  | 1.53–3.57 | 2.3  | 0.7 | 32  | 0.34–3.91 | 1.1  | 1.0 | 96  | 0.72–2.34 | 1.3  | 0.6  | 43  |
were recorded in the surface horizon of the urban area [32].

Compared to the other types, the industrial soil exhibit the highest content of As, Ba, Ce, Cu, Pb, Sr, Zn, P and Ca with an average concentration of 6.9, 466, 84.4, 75.0, 45.6, 342, 193 ppm, 3,936 ppm and 43,795 ppm.

The highest concentrations of P, Sr and Ca were observed in the industrial zone samples. On the other hand, the sample collected from south Tanta city, close to the rubber factory, presents the highest content of Ba (1103 ppm), Zn (689 ppm), Pb (182 ppm), Ce (115 ppm), Cu (139 ppm) and As (14.0 ppm).

Based on the enrichment factor, P is the highest enriched element (6.0) followed by Cu (4.7), Zn (3.8), As (3.4), Pb (2.2), Ca (2.1), Mn and Ni (1.9). Abu Khatita et al. [32] demonstrate that, anthropogenic particles gathered from the industrial area proved the occurrence Ba, Cu, Zn and derived from chemicals, pesticides, insecticides and fertilizer plants. On the other hand, increasing the concentration of As, Ba, Ce, Cu, Pb and Zn in in Tanta city mainly due to rubber battery cases, and moulded products factory. Rubber industry represents the industrial source of Ba [43].

Figure 6 illustrates the comparison between the concentration of studied elemental to average soil values (AS) worldwide of Bowen [44] and to average upper continental crust values (CC) after Wedepohl [45]. Except Ba Sr and Cr, the average concentrations of studied elements, particularly P which increases up to 3.7, are higher in the Middle Nile Delta area.

Cluster analysis is achieved to recognize the factor(s) that affect the distributions and elemental concentration through the studied soil types. Two main categories of variables can be identified (Figure 7). First category comprises As, Cu, Pb, Ce, P, (O.C.), Zn, Ca, Sr and Ba. On the other hand, the second category consists of Al, Fe, Mn, Mg, Ni, Co, Cr and Ti. Al and Ti are generally considered as a reference element and hardly affected by anthropogenic influences [46–48].

Therefore, the cluster analysis may indicate that proves that he elements that clustered in the second category reflects the lithological source materials and reflects Fe-rich clay and the mafic affinity of parent materials of the studied soil that characterized by considerable concentrations of, Fe, Mn, Mg, Ni, Co, Cr [27,44,49]. In opposite, the other studied elements that of the first category are mainly of anthropogenic origin.

4.2. Effect the particles sizes on elemental concentration

Particle size considered an important factor controlling sediment capacity for concentrating and retaining trace elements [50]. Due to their large specific surface
Figure 7. Dendrogram of elements analysed in all soil types according to multivariate cluster analysis using Ward’s method (WARD 1963) based on 19 variables in 26 soil samples.

area, fine particles represent the main site for the accumulation of trace elements than the coarse particles [51]. Figure 8 shows the concentration of studied trace elements through different particle size fractions. It is observed that, the concentration of all elements in the different soils increase when particle size decreasing. While As, Ba, Ce, Co, Ni, Pb, V and Zn are accumulated in the < 36 μm fraction, Cr and Sr and have the highest concentration in the 63–36 μm particles. In opposite, Cu is distributed in another pattern. Firstly, its concentration decreases with decreasing particle size and then increases once again in the finest fraction. This pattern most probably indicates that Cu has more than one source of contamination.

5. Conclusion

Based on the sedimentological and geochemical investigation, contamination of soil in the Middle Nile Delta has been evaluated. The study demonstrates the following conclusions:

- Two assemblages of mineralogical contents of the soil were identified; the first assemblage comprises clay minerals, quartz, K-feldspars, plagioclase, amphiboles, pyroxene, biotite and garnet which reflect the parent materials from which the soil was formed. Other minerals assemblage includes calcite, apatite and gypsum and supposed to be derived from allochthonous particles and admixed with soil.
- Common black rounded particles that distinguished petrographically indicate the complete mixing of urban and industrial soils with anthropogenic particles that transported there by wind from industrial sources. SEM-EDX examination reveals that, these particles are spherules in shape and composed mainly of iron oxide bearing-Ca, P.
- Enrichment factor and cluster analysis classified the studied elements into two groups; the first group represents Fe, Co, Cr, Ni, Mn and V, which are mainly of geogenic origin and reflects Fe-rich clay and the mafic affinity of parent materials of the studied soil, while the second group comprises As, Cu, Zn, Pb, Ce and P, Ca along with Sr and Ba which are predominantly affected by the anthropogenic sources rather than the geogenic ones.
- Cultivated soils display the minimum concentration of heavy metals the enrichment of P, Ca, As and Cu in this type of soil most probably due to the application of superphosphate fertilizer insecticides and fungicides. The soil irrigated by waste drain water is characterized by relatively high concentrations of Cu and Pb.
- The urban areas generally characterized by the high concentration of Pb, Ce, Cu, Zn, in high traffic area and As, P and Ca at the areas that located in the wind blow direction of the industrial zone.
- The industrial soils display the highest contents of P, Ca, As and Zn which are originated mainly from fertilzer plants and chemical, pesticide factory. While the extremely high concentrations of As, Ba, Ce, Cu, Pb and Zn found in soil that close to rubber and battery cases and the moulded products factories.
It has been documented that, the concentration of heavy metals in soil increasing with decreasing the particle size fraction.

These findings indicated that more attention should be paid to; grinding processes of the raw phosphatic materials in fertilizer plants, which lead to the dispersion of this raw material everywhere; extensive efforts and planning must be carried out in urban and industrial areas to reduce the number of vehicles in order to mitigate the amount of emissions. In addition, preventing irrigation with inadequately treated wastewater.

Figure 8. Average concentrations and distributions of selected trace elements in various grain size fractions of soil samples.

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No potential conflict of interest was reported by the author(s).

ORCID
Atif M. Abu Khatita http://orcid.org/0000-0003-4206-0178
Abdullah O. Bamousa http://orcid.org/0000-0001-6107-4503

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