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SUMMARY AND CONCLUSION

Geochemical Investigation of Soil and Water on Polluted Areas in Mid-Nile Delta for Environmental Assessment

Contamination of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment. The objective of the present study is to obtain a clear idea about the effect of human activity (agricultural, urban and industrial) on the irrigation waters (drains and canal), bottom sediments, soils and plants as one of chain of environmental pollutions in the Mid-Nile Delta region.

The study was mainly concerned with the chemical partitioning of the heavy metals; Mn, Zn, Cu, Ni, Cd and Pb in the bottom sediments and soil samples irrigated by polluted waters from drains and to evaluate the effect of total metal concentrations on metal partitioning into different fractions. Emphasis on discharge of wastes of industries and municipal sewage of cities to irrigation water was considedred. It was stressed that knowledge of the total content of metals in soils and sediments provides only limited information about their chemical behaviour. In accordance, sequential extraction procedures have been used to fractionate heavy metals in polluted soils and bottom sediments.

The mobility and bioavailability of heavy metals in soils provide us with information to which extent these metals move and absorbed. Heavy metals are present in soil in different forms with varying degrees of mobility and availability. Levels of various forms and the rate with which the less mobile forms are transformed to the more mobile ones emphasized the environmental effect. Therefore metals in water soluble and exchangeable fractions would be readily bioavailable to the environment and metals in residual fraction are tightly bound and would not be expected to released under natural conditions.

In addition, chemical analysis of surface, squeezed and groundwaters was carried out and interpreted. Textural composition of soils and bottom sediments, carbonate content and organic matter were studied too.

The area of study occupied the Mid Nile Delta region and covers a total of 3794 km^2 and extends from Kafr El-Zaiyat and El-Mehalla El-Kobra in the south to the Mediterranean sea or Burullus Lagoon in the north. The main pollution sources in this area include agricultural (fertilizer and pesticides), urban (municipal dumps and septic tanks) and industrial activities. There are many industries such as fertilizers (Talkha and Kafr El-Zaiyat), oil & soap (Tanta & Kafr El-Zaiyat and El-Mehalla El-Kobra), sugar beet (Belkas & El-Hamoul), refining petroleum & oil and flax, Pepsi at Tanta and Soda & Salt, Pesticides & Chemicals, Financier & Industrial Egypt at Kafr El-Zaiyat occupying the study area. All these factories discharge their waste effluents to the canals and drains that are running from south to north discharging in lagoon Burullus or the Mediterranean sea.

A total of forty four water samples were collected mainly from drains. Only two samples represent the canal water and used as reference. In addition to these water samples, fourteen bottom sediment samples were collected from the polluted drains directly before the pump station. Above all, squeezed water was extracted from the bottom sediment samples just after collection of the samples for chemical analysis. Finally, fifty one samples were collected from seventeen soil profiles adjacent to the studied polluted drains and canals.

The studied bottom sediments from drains and canals are generally characterized by the following:

- They are composed mainly of silty clay texture.
- The clay content in the bottom sediments is generally higher than in the canal sediments.
- The carbonate content and the organic matter are usually high in some locations such as No. 3 and No. 4 due to the contribution of waste effluent from El-Nasr Fertilizer Factory and due to other human activities.

On the other hand, the studied soil samples have textural composition varied from clay, silty clay, sandy silty clay to sand. The clay content increases towards the Burullus lagoon and Mediterranean sea, accompanied by decrease of sand content. Carbonates and organic matter contents are generally high in the surface layers of the studied soil profiles and tend to decrease with depth. It was also found that organic matter is relatively high in soil profile No. 3 which is irrigated with municipal water, highly polluted by human activities.

Chemistry of the major elements Na^{+}, K^{+}, Ca^{++} and Mg^{++}; in the surface drainage water depends on the nature of pollution sources (agricultural, industrial and/or municipal), the distance from the source and the nearness to the sea or Burullus lagoon. Industries like; sugar, textile, Pepsi, industrial city of Dumyat El-Gedida, El-Nasr fertilizer are generally the main contributor of Na^{+}, K^{+}, Ca^{++} and Mg^{++} in their waste effluents. Sodium is the dominant cation followed by either calcium in the less saline water or magnesium in the saline ones; potassium has the lowest contents.

Chemistry of the anions confirmed that chloride is the dominant anions followed by sulphate in the saline water or carbonate and bicarbonate in sites greatly affected by waste effluent. The behaviour of chlorine is similar to sodium in the studied surface water of Mid Nile Delta and is always affected by the same factors controlling sodium distribution. Industries of sugar, fertilizers, textile and oil & soap are the main contributors of sulphate concentration in the drainage water of the Mid Nile Delta region. While, Pepsi, textile, fertilizer and oil & soap industries are the main contributors of CO^{--}_3. Mixed drainage water of agricultural, industrial and municipal affects also control the distribution of CO^{--}_3. The distribution of HCO^-_3 depend on the distance from source of pollution and the type of industries which are, arranged as: fertilizer > sugar > textile > chemicals & pesticides > petroleum refining > oil & soap > soda > salt > financier company > phosphate fertilizer.

On the other hand, the chemical characteristics of the major elements in the squeezed water of the bottom sediments revealed that all cations and anions except SO^{--}_4 are enriched in the squeezed water compared to the surface one according to the nature of pollution. Another, abrupt increase of the concentration of cations and anions in the squeezed water taken just after El-Nasr fertilizer factory and pump station No. 11 and El-Zeiny reflecting the effect of the wastewater of this factory and the lagoon water intrusion in the sediments of the surrounding area.

The chemical composition of the soil paste extract indicates that cations distribution in the different studied soil profiles are arranged in the order $Na^+ > Mg^{++} > Ca^{++} > K^+$ while the anions distribution is in the order $Cl^- > SO^{--}_4 > HCO^-_3 > CO^{--}_3$. The textural composition of the soil profiles plays an important role in the distribution of the soluble salts in the different layers. The increasing of sand content in the surface layer raise the rate of evaporation of the rising capillary water and hence increase the salt content in the surface layer. The chemical composition of the groundwaters and their depth as well as the nearness to the sea or Burullus lagoon play an important role in the distribution of the soluble salt in the subsurface layers too. However, the soils irrigated by canal water contain less soluble salts than those irrigated by wastewaters (mixed of agricultural, municipal and industrial drainage water) of pump station near to the sea or Burullus lagoon.

The chemical composition of the groundwater generally proved the dominance of chloride, bicarbonate and sulphate anions in the order $Cl^- > HCO^-_3 > SO^{--}_4$. The detected cations are Na^+, Mg^{++} in the saline water and Ca^{++} in the less saline water while potassium exhibits lower values.

Dealing with heavy metals contaminations in the surface drain water, significant special concentrations were recorded at locations close to El-Nasr fertilizer company and the laboratory of petroleum refining. Effect of discharge of such industrial effluents on the chemical composition of the surface water increased heavy metal concentrations. Furthermore, considerable concentration before and after pump stations in the Mid Nile Delta region was recorded and indicating the influence of mixing and type of drainage water. The behaviour and distribution of the studied Mn, Cu, Zn, Ni, Cd and Pb in the surface and squeezed waters reveal the following:

- Mn is enriched after some industries such as oil and flax (due to use manganese naphthens in the manufacturing of boiling flax oil), sugar beet, phosphate fertilizer, oil & soap, pesticides and chemicals.
- Cu showed a considerable concentration after manufacturing pesticides, chemicals and sugar (due to using of $CaCO_3$ as a raw material).
- Zn increased before and after pump stations due to use of pesticide as Radomil and Mancozeb for wheat, horsebean, maize and Zineb, zinc sulphate in rice planting.
- Ni reflected high concentrations after Kafr El-Zaiyat factories and companies. It have also considerable concentration after oil and soap factories of Tanta, El-Mehalla El-Kobra and Kafr El-Zaiyat due to the discharge of waste effluents of these factories which were being enriched with Ni as one of the manufacturing raw material. Ni metal was used as a catalyst agent.
- Cd exhibited a considerable concentrations in agricultural drainage water due to using phosphate fertilizer in planting processes. In addition to this, the effect of some industries of phosphate fertilizer, sugar beet, oil and soap, soda and salt and pesticides & chemicals which increase Cd in the irrigation water too.
- Pb increased after laboratory of petroleum refining, fertilizer company and oil & flax industry (due to use lead naphthene in the manufacturing of boiling flax oil).

The heavy metal contents determined in the squeezed water of the bottom sediments are significantly higher than that of the corresponding waters of canals and drains. This is attributed to the adsorption effect of the fine constituents of the bottom sediments (clay particles). So, variation in heavy metal contents of the squeezed water is generally related to the textural composition of the sediments. It was documented that Mn, Cu, Ni and Cd contents in the surface and squeezed waters are higher than the maximum permissible limits given by FAO, 1985, whereas Zn and Pb contents, on the other hand are lower than the permissible limits of FAO.

Study of chemical partitioning of heavy metals in the bottom sediments of the drains evaluates the effect of metal concentration on metal partitioning into different fractions, hence mobility and bioavailability can be deduced through metal movement in relation to metal fractions after determination of levels of the various fractions of each metal expressed in ppm and as percentage of total. It is concluded that:

- EXCH-fraction (exchangeable fraction) of Mn, Cu, Zn, Ni, Cd and Pb constitute a small portion of the total. Among the metal, Pb EXCH fraction represents a high portion of the total in the polluted and non polluted sediments. The abundance of metal ions in the EXCH fraction in the polluted sediments followed the sequence: Pb > Cu > Cd > Mn > Ni > Zn. It seems therefore, that bioavailability of Pb, Cu and Cd are more dominant in the EXCH fraction.
- The CARB-fraction (carbonate fraction) of Cd, Cu, Zn and Pb constitutes the high portions of the total among metals and are concentrated in the polluted sediments than in the canal sediments. The occurrence of CARB-metal fraction in the polluted sediments

varied markedly among metals and followed the order: Cd > Cu > Pb > Zn > Ni > Mn. The formation of insoluble $CdCO_3$ and $ZnCO_3$ in the aquatic environment has been significantly recognized. Cu present either with the organic or with sulphide components in the sediments and could possibly be mobilized from this phase by decomposition of the organic matter and the elevated carbon levels. Pb present mainly in the carbonate and Fe/Mn oxide phase becoming more important with depth. It was concluded that the bioavailability of Pb and Cd in CARB-fraction is highly pronounced.

- The sequence of metals associated with hydrous oxide of Mn EASR (easly reducible fraction) in the polluted sediments was: Pb > Mn > Zn > Cd > Cu > Ni while in the non-polluted canal sediments was: Pb >> Cd > Cu > Zn > Ni > Mn. The bioavailability of Pb and Mn are more dominant in the EASR-fraction.
- The portion of Metals occluded in the MODR-fraction (moderately reducible fraction) in the polluted sediments followed the sequence: Cu > Zn > Mn > Pb > Ni > Cd while in the non-polluted canal sediments was Zn > Cu > Cd > Mn > Ni > Pb. Thus the bioavailability of Cu and Zn is more common in the MODR-fraction.
- Metal complexation with the ORGS-fraction (sulphide and organic fractions) in the polluted bottom sediments followed the order: Mn > Pb > Ni > Cu > Cd > Zn, while in the canal sediments was: Zn > Ni > Mn > Cu > Cd > Pb.
- The RESD-fraction (residual fraction) of all metals constitutes the highest portion of the total content in the polluted bottom sediment and follow the order Ni > Zn > Mn > Cd > Cu > Pb.

- The distribution of heavy metals in the drain bottom sediments indicates that El-Nasr fertilizer company and industries & companies of Kafr El-Zaiyat city are considered to be the most contributors of heavy metal fractions.
- Concentrations of heavy metals in the bottom sediments of each location appear variable with regard to intensity of pollution.
- The distribution of heavy metals could be arranged according to relative abundance in the order: bottom sediments > squeezed water > surface water. Thus, the drain bottom sediments play a significant role in fixation of the delivered metals by the polluting sources.

Dealing with the heavy metals in various chemical fractions in the contaminated soils it is concluded that:

- Among the studied soils, profiles No. 3 and No. 17 represent the highest contamination with Mn, Cu, Zn, Ni and Pb. They contain a considerable high amounts in the nonresidual fractions.
- Excluding the residual fraction as the main container of all heavy metals, the bioavailability of heavy metals in the studied soils using sequential extraction follows that readily specifically sorbed > organically bounded > hydrous oxide bounded for Mn, Cu, Ni and Pb. So metals in these fractions would readily bioavailable to the studied soils, whereas the metals in the residual fraction are tightly bound and would not be expected to be released under natural conditions.
- A significant amount of total metals for Cu and Zn was associated with the nonresidual fractions, so they are the most bioavailable metals in the studied soils.
- The presence of Mn content in soils irrigated with sewage effluent is always follows residual > organically bounded > specifically

sorbed > hydroxides fractions. While those irrigated with industrial effluent, the trend was residual > specifically sorbed > organically bounded > hydrous oxides fractions.

- The behaviour of Cu in all studied soils is in the forms, residual > specific sorbed > organically bounded > hydrous oxides except profiles No. 2, No. 10, No. 11 and No. 12, the trend varies as residual > organically bounded > hydrous oxides > specific sorbed fractions.
- Fractionation of Zn content in all studied soils was residual > specific sorbed > hydrous oxides > organically bounded.
- Ni concentrations in soils depend largely on the nature of the parent material and is concentrated mainly in the residual fraction.
- The Cd content of various chemical fractions is affected by the type and nature of pollutants occurring in the irrigation water used and followed the order residual > specifically sorbed > organically bounded > exchangeable.
- Most of Pb amount is associated with the residual > hydrous oxides > specifically sorbed > organic fractions.
- It was found that the total content of Cd, Pb, Cu and Ni was higher than the average levels given by **Kabata-Pendias and Pendias (1992)**.

- The sources of heavy metals pollution include:
    - Talkha electrical Station wastewater and the municipal wastewater at Talkha are one of the main source of Mn, Zn, Cu, Ni and Pb to the adjacent studied area.
    - Air pollution is the main source of Pb, Zn, Ni, Mn, Cu and small amount of Cd at Tanta environ.
    - Ganag drain after Kafr El Zaiyat factories and companies is the main source of Cd, Pb, Cu, Zn, Ni and small amount of Mn.

- Fertilizer company at Talkha leads to higher accumulation of Mn, Cu and to moderate amount of Zn, Ni, Cd and Pb in the adjacent soils.
- El-Zeet drain after textile El Mehalla El-Kobra causes accumulation of Ni and Pb.
- El Tawella drain at El Rowdah village polluted the adjacent soils with Cd, Cu and Zn.

It is concluded that accumulation of heavy metals (Mn, Cu, Zn, Ni, Cd & Pb) in the surface layers of the studied soils was always higher than that in the subsurface ones. It is suggested that cycling through vegetation, atmosphere, heavy application of fertilization and adsorption or complexes by the soil organic matter are the main causes of heavy metals accumulation.

The application study carried out an accumulation of such heavy metals in some collected plants growing in the soils irrigated with drainage water proved that the concentration of Zn and Mn was within the normal range while that of Ni, Cu, Cd and Pb were higher than the normal range. Leafy vegetables have higher heavy metal contents than the other vegetables grown the same soil profiles. It was found also that heavy metal contents in roots and shoots were higher than in fruits and grains of the same plants such as wheat of profile 6, profile 7 and profile 17, which reflect different mobility of these metals within the plant and increase their concentrations in roots. Higher accumulation of Mn and Pb, moderate amount of Cu and Zn and lower concentration of Ni and Cd were recorded in clover plant of profile 8 (irrigated with El-Zeet drain after textile factory of El-Mehalla El-Kobra), profile 9 (irrigated with

Ganag drain after Kafr El-Zaiyat wastewater), profile 10 (irrigated with upper drain No. 8) and profile 17 (irrigated with canal water but located adjacent to the combustion of Tanta and high way between Tanta and El-Mehalla El-Kobra cities). As a matter of fact, the higher accumulation of the studied heavy metals could be due to the heavy application of different manure, sludge and commercial fertilizers. Polluted waters from different sources added also the high accumulation of these heavy metals.

It is clearly evidenced that the danger of output wastes by such factories containing high concentration of heavy metals affects the survival in the suffering area. Therefore, it is important to issue laws and show limitation for these factories to prevent polluting for the agricultural soils by wastes. **Abou El-Naga *et al.* (1999) and Zein *et al.* (2002b)** recommended that attention must be earnestly given to protection of the environment and commitment to the latest law issued 1994 in Egypt must be obligately taken for these factories. A part from the roles played by pollution control and soil chemistry, plant breading can make a vital contribution through the selection and utilization of crop genotypes which accumulate the last heavy metals.