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Evaluation of Some Trace Metals (Zn, Cd, Cu and Pb) in Sewage Sludge Samples Taken from Some Pumping Stations in Benghazi-Libya

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ABSTRACT

Due to the little data available on the levels of trace metals concentration in sewage sludge in and around Benghazi city, it was necessary to determine the current concentration, composition, distribution and sources of trace metals in the sludge of different wastewater treatment plants. Accordingly, raw sewage sludge samples collected from sixteen wastewater-pumping stations at Benghazi city have undergone evaluation of pH and some trace metals concentrations (mainly Zn, Cd, Cu and Pb) in dried sludge using atomic absorption spectrophotometry. Their monthly and spatial variations in sludge have been described.

Introduction:

Until the late 19th century, there have been much concern with the effective and safe disposal of the mankind liquid and solid wastes. The installation of sewerage systems for piping liquid wastes away from major population centers was the single greatest contributor to the dramatic reductions in infectious diseases which occurred during that time. The liquid wastes were usually discharged untreated to a river or the ocean but, with the increasing world population, improved sanitary systems and the adventure of more stringent standards on wastewater treatment, this option has become increasingly untenable [Raza, 2005; Świerk *et al*, 2007; Bigdeli *et al*, 2008; Olujimi *et al*, 2012; Yadav *et al*, 2013; Priestley, 1984; and Lim *et al*, 2006]. The processes applied to the treatment of sewage result in the separation of sewage into two streams, a clarified water containing 20-30 mg/l of suspended solids and a sludge stream of 1-3% solids dry weight, which contains 80-90% of nutrients and pollutants present in the raw sewage [Priestley, 1984]. The nature of the sewage sludge varies, depending on both the wastewater composition (mainly organic and inorganic materials, plant nutrients, trace elements, organic chemicals and some pathogens) and on the treatment processes used [Stehouwer, 1999]. Our current research deals with the evaluation of trace metals concentrations (mainly Zn, Cd, Cu and Pb) in dried sludge obtained from sewage sludge samples collected from pumping stations in and around Benghazi city, using atomic absorption spectrophotometry (AAS).

Benghazi city contains about 36 wastewater-pumping stations. Only sixteen pumping stations (Table 1) were chosen as sampling points for research. A monthly sample was collected from every station during the period of Jan.-Mar. (2006).

Table 1: Names, Locations, Numbers and Sizes of Chosen Pumping Stations as Sampling Points

Name of Pumping Station	Location	Station Number	Station Size
R, T, U	El-Sabri	1, 2, 3	small
V	Elthama	4	medium
GT_{13}	El-Masaken Turkya	5	small
GT_{11}	Aredzwawa	6	large
P	El-Fundik	7	medium
GT_7	El-Fundik	8	small
F	El-Salmani	9	medium
J	City center	10	medium
I	Bagdad station	11	medium
M	Eskabli	12	small
GT_3	Jamal Abdelnaser street	13	large
GT_1	El-keesh	14	large
GT_6	El-keesh	15	medium
Y	El-Qaria	16	medium

Experimental:

For determining the trace-metal concentrations, each dried sample was ground with glass pestle and mortar then passed through a 2mm mesh stainless steel sieve. The dried ground samples

were then stored in plastic bags into a refrigerator for analysis [Olsen, 1982]. The required temperature for trace-metal determination was 105 ^{0}C.

pH Measurements:

The pH for each sludge sample was measured using a pH meter, inserting the probe into the suspension of the sludge directly after sample collection [Gonzalez, 1995].

Digestion of Dried Sludge Material:

To a finely ground dried sludge (0.1 g) in a freshly cleaned Teflon bomb, 1 ml of aqua regia (HNO_3:HCl, 1:3 v/v) was added. The Teflon vessel was placed in a rack where hydrofluoric acid (1 ml) was carefully and slowly added. The bomb was tightly closed and placed on a hot-plate for 1 h then removed from the heat source and allowed to cool to room temperature. The contents of the bomb were transferred into a 25 ml volumetric flask by rinsing it several times with de-ionized water, adding the rinsing to the volumetric flask. The flask was shaken to complete the dissolution and the solution was made up to 25 ml with Milli-Q water. The solution was analyzed for trace metal by flame AAS.

Measurement of Trace Metal in the Digested Dried Sludge by Flame AAS [Bremner *et al*, 1982]:

The trace-metal determination was made by digestion with hydrofluoric and nitric acid mixture, where hydrofluoric acid and aqua regia are used to release the total metal content from dried sludge into solution in a sealed Teflon decomposition vessel referred to as a Teflon Bomb [U.S.EPA, 2001].
The metal standard solution was prepared for the calibration curve as follows:
An appropriate quantity of stock standard solution (1000 ppm) was diluted with Milli-Q water to the mark (50 ml) and shaken well. The calibration curve was determined according to the expected concentrations of the sample and linearity of the AAS response for the element considered. Standards for the calibration curve were prepared with at least three concentrations plus zero (the zero with no analyst).

Calculation:

$$\text{C } (\mu g/g) = \frac{(y - x)V.F}{wt}$$

C = Concentration of metal in the original sample (in µg/ g of dry weight).
y = Concentration of metal in sample solution (µg/ml).
V = Volume of dilution of digested solution (ml).
x = Mean concentration of metal in reagent blanks (ml).
wt = Dry weight of sample (g).
F = Dilution factor if needed (F =1, in the case of no further dilution than initial dilution during digestion procedure).

Results and Discussion

Spatial Variations in the Metal Concentrations of Sewage Sludge:

The area of study was divided into eight zones, each containing the neighboring pumping stations. The metal concentrations and pH ranges are all shown in Table 2.

Table 2: Regional Variation in pH and Metal Concentration at Different Zones of Benghazi City

Zone	Station	pH (range)	Zn (µg/g)	Cd (µg/g)	Cu (µg/g)	Pb (µg/g)
I	1,2,3,4	6.1-7.3	1374.3	9.1	143.66	143.66
II	5,6	6.3-7.3	2167.4	9.66	420.5	263.83
III	7,8	6.2-7.3	1239.8	8.08	464.42	223.17
IV	9	6.9-7.5	2181.3	9	145.5	295
V	10,11,12	6.0-7.9	1172.9	7.59	117.27	241.72
VI	13	6.7-7.1	1025	8.75	183.25	315
VII	14,15	6.9-7.1	1103.7	8	399.75	347.47
VIII	16	6.2-7.2	1950	5.75	170.37	255
Min		6.0	1025	5.75	117.27	223.17
Max		7.9	2181.3	9.66	464.42	422.5
Average		-----	1526.8	8.24	255.59	295.4
STD. Dev.		-----	489.8	1.21	145.33	65.44

The pH values range from acidic (6.00) to alkaline (7.97). Zones I, II, III and VIII had pH values ranging from acidic to neutral (6.1-7.2) whereas zones IV, VI and VII had almost neutral values ranging from 6.7 to 7.5. Zone V had wider pH range 6.0 to 7.9.

***Trace metals (Zn, Cu, Pb and Cd)**:*

Table 2 shows that, no differences in the contents of Cd were reported; its average concentration was 8.24±1.21 µg/g, whereas much more differences in the contents of Pb, Cu and Zn were obtained; their average concentration were 295.4±65.44, 255.59±145.33 and 1526.8±489.8 µg/g, respectively.

Many studies indicated that Lead, copper and cadmium might be found in significant concentrations in sewage sludge, whereas zinc typically presents the highest concentration [Marni *et al*, 2003].In our present work. Sewage sludges collected from different zones had lower content of Cd, but much higher content of Pb, Cu and Zn.

As shown in Fig.2, zone IV and II exhibited the highest levels of zinc (2181 and 2167µg/g, respectively), whereas the highest levels of cadmium were recorded in zone II (9.66 µg/g). Different levels of Cu were observed at all zones,

its highest levels were detected at zones III, II and VII (464, 420 and 399 µg/g, respectively), while its lowest content was detected at zone V (117 µg/g). Different values of Pb were also reported at all zones, the highest concentration of Pb was obtained at zone I (745 µg/g), while the lowest concentration was detected at zone V (241 µg/g).

Levels of metals detected at any zone are affected by the nature and activities in the surrounding area of each zone.

Unfortunately, it was difficult to identify exactly the nature of different zones at the study area, because most of them receive discharged wastewater not only from residential sources but also from health supplements, light industrial and commercial sources. Table 2 illustrates that zone V (city center) had the lowest contents of trace metals; zone V represents a residential area that contains commercial activities, whereas zone II (Elmasaken Turkya and Ared-Zwawa) exhibited the highest content of Zn, Cd and Cu, this area is famous with its high density of the workshops and light industrial activities, whereas zone I (Elsabri and Elthama) revealed the highest concentration of Pb, which may be related to the type of activities in the surrounding area.

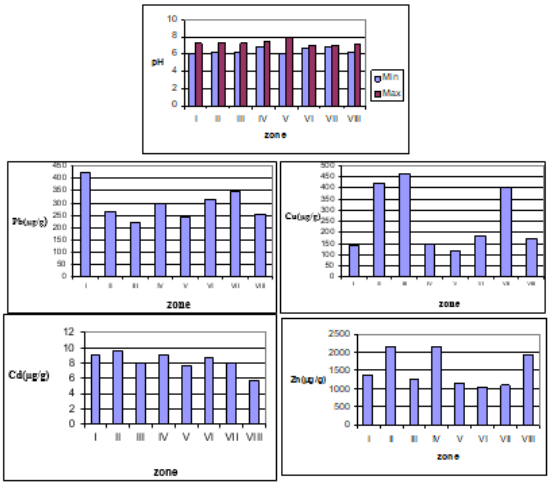

Fig. 1: Spatial Variations in the Metal Contents of Sludges Collected from Different Zones of Benghazi City.

In general, analysis of the sludge samples collected from the 16 wastewater-pumping stations revealed wide ranges in pH and wider ranges in the metal content: 6.06-7.97 for pH and 660-2359 for Zn, 5.62-11.50 for Cd, 112.58-698.16 for Cu and 162.16-745 for Pb (all in µg/g). The general trends for the metal content and the pH ranges of the sludge at the different wastewater pumping stations are shown in Fig. 2.

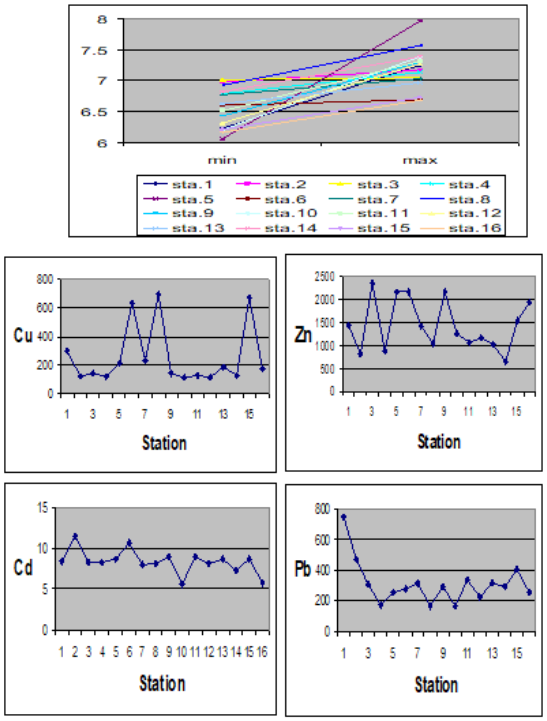

Fig. 2:General Trends for the pH ranges and the Metal Content (µg/g) at the Different Wastewater-pumping Stations.

Conclusions:

1. The wide ranges of sludge properties were mostly related to the variations in types of pumping stations, nature of surrounding area and illegal connections of sewage.
2. Sludges collected from each station had similar pH values and much more variations in their contents of each of Zn, Cu and Pb were obtained.
3. Considerably monthly variations were reported in the concentrations of trace metals (Zn, Cd, Cu and Pb), zinc was the most abundant metal followed by lead and copper, whereas cadmium was the lowest abundant.
4. the city center stations had almost the lowest contents of trace metal, stations of el-Masaken Turkya and Ared-Zwawa exhibited the highest content of Zn, Cd and Cu, whereas stations of Elsabri and Elthama exhibited the highest content of Pb.
5. Since sludges of the present study show an increase of their metal content in the order Zn > Pb > Cu > Cd, whereas sludges from literature show an increase in the order Zn > Cu > Pb > Cd, questions surrounding the high levels of Pb were raised.

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