

Geochemical Characterization of Soil and Water From a Wastewater Treatment Plant in Gaza

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The aim of the study was to determine the interaction between the natural geochemistry and the anthropogenic effects through trace element profiles in one of the environmentally significant areas of the Gaza Strip. Five boreholes were dug in the area of the Gaza wastewater treatment plant. The geology, mineralogy, and geochemistry of the soil profiles were studied, and the geochemistry of wastewater, sludge, soil, and groundwater was identified by several analytical techniques. The study introduced the environmental baselines and the infrastructure needed for further research for the first time: the natural infiltration potential, the artificial recharge, and the agricultural activities of water and wastewater. The results of the geochemical investigations confirmed that the upper 40 cm of soil was found to be the affected zone by wastewater and sludge. Among 26 elements analyzed, only a few metals (As, Cd, Cr, Hg, Zn, and to a lesser extent Pb) showed relevance from the human health point of view. The metal accumulations in the soils were characterized by a large spatial variability, with some "hot spots" of Cu and Zn reaching topsoil concentrations of up to 240 and 2005 mg/kg, respectively. In spite of that, the results of the groundwater revealed that none of them was detected at concentrations that exceeded the WHO (World Health Organization) standards. Moreover, it was shown that both anthropogenic activities as well as seawater intrusion caused the high levels of nitrate and salinity.

Keywords Gaza, geochemistry, soil profile, wastewater treatment plant.

1. Introduction

Groundwater is the most precious natural resource in the Gaza Strip as it is the only source of water. The groundwater aquifer of Gaza is extremely susceptible to surface-derived contamination because of its largely unconfined nature and highly permeable sands and gravels. In the past decade, the aquifer has become the focus of experts and public concern. This concern has resulted from widespread salinity, nitrate and fluoride; from the detection of agricultural pesticides and fertilizers; and from increased pressures for urban development

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Address correspondence to B. H. Shomar, Institute of Environmental Geochemistry, University of Heidelberg, Im Neuenheimer Feld 236, 69120 Heidelberg, Germany. E-mail: bshomar@ugc. uni-heidelberg.de above the aquifer. As a first step to determine the reference levels of contaminants, it is necessary to know their contents in various environmental compartments. A few studies have been conducted in the area of wastewater and sludge but none in soil and groundwater. Studies of the interaction between environmental components of Gaza are completely lacking. Soils are one of the most precious natural resources of Gaza and they are prone to contamination from atmospheric and hydrological sources, but direct waste disposal causes a major impact on this limited natural resource, posing serious environmental concerns. Information on the soil macro- and micronutrient levels and trace elements could be of great interest for agricultural usage and artificial recharge of the groundwater aquifer (McBride *et al.*, 1997; Roemkens and Salomons, 1998; Wilcke *et al.*, 1998; Whittle *et al.*, 2002).

Metal mobility in soils depends on two main factors: (1) water transfer through the soil and (2) physicochemistry or biogeochemistry of the trace metals with the solid phase of the soil (sorption/desorption, precipitation/dissolution, complexation by the organic matter). Water transfer and chemical reactions depend on the chemical, mineralogical, and physical/hydrological properties of the different soil horizons (Cornu et al., 2001; Abrahams, 2002). As a matter of fact, pollution problems may arise if toxic metals are mobilized into the soil solution and are either taken up by plants or transported to the groundwater (Planquart et al., 1999). The concentrations of several potentially harmful contaminants, such as metals commonly found in sludges, limit their application on land. The high contents of Zn and Adsorbable Organic Halogen (AOX) in the sludges of Gaza are examples of such contaminants (Shomar et al., 2004a). By spreading sewage sludge on fields, the metal content of the soil drastically increases (Smith et al., 1996), inducing a potential risk of groundwater pollution, increased toxic metal mobility (e.g. organic complexing of the transition metals), plant toxicity, and metal contamination through the food chain (Mikac *et al.*, 1998; Cornu et al., 2001). Many investigations on the distribution of metals in relation to depth in the profiles of sludged soils have shown that, in the short term, relatively little downward movement of metals occurs below the depth of cultivation or of sludge application (Alloway and Jackson, 1991). Increases in metal concentrations below the depth of 30 cm did not appear to be significant compared to background values, suggesting that the movement of metals downward in the soil profile was minimal. However, several authors have reported a more pronounced movement of metals within the profiles of amended soils. Darwish and Ahmad (1997) have shown that sludge-borne Zn, Cu, Cd, and Pb moved down to a depth of 40 cm in soils referred to as saline, non-saline, sodic, and calcareous (except Zn in the calcareous soil). Although several trace metals have clearly migrated within the profiles, and therefore must have been in a soluble form at some time, their present concentrations in the leachates are very low. This indicates that after migration they have become fixed in more stable and insoluble forms (Planquart et al., 1999; Cornu et al., 2001; Hoffmann et al., 2002). The main goals of this study were: (1) to introduce all relevant information from the study area on hydrogeology, geochemistry, and geology; and (2) to study the geochemical characteristics of an on site column of wastewater, sludge, soil, and groundwater in the area of the Gaza central wastewater treatment plant.

2. Meteorology, Geology and Hydrology

There are two well-defined seasons: the wet season, starting in October and extending into April, and the dry season from May to September. The average daily mean temperature ranges from 25° C in summer to 13° C in winter, with the average daily maximum temperature ranging from 29° C to 17° C, and the minimum temperature ranging from 21° C to 9° C,

in the summer and winter, respectively. The daily relative humidity fluctuates from 65% in the daytime to 85% at night in the summer and between 60% and 80%, respectively, in the winter. The mean annual solar radiation is 2200 J/cm²/day (MEnA, 2000). There is a significant variation in the wind speed during the daytime, and the average maximum wind speed velocity is about 3.9 m/s. Moreover, storms have been observed in the winter with a maximum wind speed of about 18 m/s. Peak months of rainfall are December and January; the average annual rainfall is 335 mm/y (26 year average) (CAMP, 2000).

The coastal aquifer consists primarily of Pleistocene age Kurkar Group deposits, including calcareous and silty sandstones, silts, clays, unconsolidated sands, and conglomerates. Near the coast, coastal clays extend about 2–5 km inland, and divide the aquifer sequence into three or four sub-aquifers, depending upon the location. Towards the east, the clays pinch out and the aquifer is largely unconfined (PEPA, 1994). Within the Gaza Strip, the total thickness of the Kurkar Group is about 100 m at the shore in the south, and about 200 m near Gaza City. At the eastern Gaza border, the saturated thickness is about 60– 70 m in the north, and only a few meters in the south near Rafah. Local perched water conditions exist throughout the Gaza Strip due to the presence of shallow clays (MEnA, 2000).

From the results of pump tests carried out in the Gaza Strip, aquifer transmissivity values range between 700 and 5,000 square meters per day (m²/d). Corresponding values of hydraulic conductivity are mostly within a relatively narrow range, 20–80 meters per day (m/d). Most of the wells that have been tested are municipal wells screened across more than one subaquifer. Hence, little is known about any differences in hydraulic properties between these sub-aquifers. Specific yield values are estimated to be about 15–30% while specific storativity is about 10⁻⁴ from tests conducted in Gaza (CAMP, 2000).

Under natural conditions, groundwater flow in the Gaza Strip is towards the Mediterranean Sea, where fresh groundwater discharges into the sea. However, natural flow patterns have been significantly disturbed by pumping and artificial sources of recharge over the past 40 years. Within the Gaza Strip, large cones of depression have formed over large areas in the north and south. Water levels are presently below mean sea level in many places, inducing a hydraulic gradient from the Mediterranean Sea towards the major pumping centers and municipal supply wells (PEPA, 1994). Between 1970–1993, water levels dropped 1.6 m on average, mostly in the south. This is equivalent to 5 million cubic meters per year (Mm³/y) decline in overall aquifer storage on average, using a specific yield of 0.2 (CAMP, 2000).

It is estimated from available data that less than 10% of the Gaza's aquifer resource contains groundwater that meets the WHO drinking water standard for chloride (250 mg/l); primarily in the north and along the coastal sand dune areas of the Mawasi (southwest). The major documented water quality problems in the Gaza Strip are elevated salinity and nitrate concentrations in the aquifer. Depending on location, rates of salinization may be gradual or sudden. In Gaza City/Jabalia, chloride values are increasing at rates up to 10 mg/l per year in several wells. The lateral inflow of brackish water from Israel (chloride concentrations varying from 800 to 2000 mg/l) affects the water quality of a significant portion of the Gaza coastal aquifer, and is of a natural origin. Nitrate in 90% of the groundwater wells is more than 50 mg/l (CAMP, 2000).

Rates of aquifer replenishment are one of the most difficult parameters to derive. There is no simple method that can be applied to estimate recharge from rainfall in the Gaza Strip. This is primarily a function of the extreme climatological variability observed between rainfall stations and numerous influencing factors, such as soil types and irrigation practices. A pragmatic approach has been used for the Gaza regional model, which translates supporting information from other similar areas to the Gaza situation, and is guided by groundwater modeling (CAMP, 2000; MEnA, 2000).

3. Study Area, Materials and Methods

3.1 Location of the Study Area

The study area is the central wastewater treatment plant of the Gaza Strip, which lies to the southwest of Gaza City. The specific location within the plant is the drying lagoons, which are being used as filtration basins. Treated wastewater and produced sludge are disposed to open areas a few meters beside the plant itself. The plant is close to less urbanized and agricultural areas. Figure 1 shows the location of the Gaza Strip and a schematic illustration of the wastewater treatment plant as well as the five boreholes. The area has a long history of exposure to wastewater and sludge. Large areas have been used for the disposal of raw sewage effluents and untreated sludge from 1977 up to date. Due to the lack of functional and effective wastewater treatment plants associated with the absence of a wastewater



Figure 1. Location of the study area.

management system, the area of 50 ha was converted to a pure sewage disposal field and receives up to $10,000 \text{ m}^3/\text{day}$ of untreated or partially treated wastewater.

3.2 Sampling and Analysis

3.2.1 Sampling Considerations. As an independent project, 13 test borings were drilled at specified locations determined by an approved surveyor. The sampling locations were selected according to many justifications fitted to Gaza. The aquifer system, groundwater flow, available geological data, meteorological conditions, natural and anthropogenic factors, etc., are examples of these justifications. Because of the high cost of transportation and analysis, five test borings were chosen for this specific study to represent all locations (Figure 1). The five boreholes were selected to be: one borehole inside the existing treated wastewater pond, one borehole inside an old sludge drying pond, and three boreholes from the surrounding area. Each borehole is considered as a vertical study area starting from the surface, which is in some cases treated wastewater followed by sludge, then soil and finally groundwater. The ground surface at the site is covered with sand dunes of yellowish, fine sand.

3.2.2 Wastewater Samples. The sampling campaign was conducted in the period of 10 October-25 December 2002. The average depth of wastewater in the sampling site was 30 cm. A series of grab samples (8-10) were taken from two lagoons 1-2 days before the drilling process. The grab samples were combined in a container to form a composite sample. Finally, one liter of the mixture was taken in an acid-washed bottle and transferred to the laboratory, where it was filtered in an acid-washed filter holder and through 0.45 μ m pore size Sartorius membrane filters; the first few milliliters were used for rinsing, then discarded, and the filtrate was transferred to clean acid-washed polyethylene bottles and acidified by concentrated nitric acid (Ultrapur, Merck, v/v) to pH <2 and stored at 4°C until analyses by the inductive coupled plasma mass spectrometer (ICP/MS—Perkin Elmer-Sciex, Elan 6000) were performed. The other part of the wastewater was filtered with no additives and stored at 4°C for anion analyses by ion chromatography (IC DIONEX DX-120). Several parameters were measured during the fieldwork: temperature, electric conductivity, and pH; other parameters (Settleable solids SS, total suspended solids TSS, total dissolved solids TDS, chemical oxygen demand COD, and biochemical oxygen demand BOD₅) were measured a few hours later according to the American standard methods (APHA, 1995).

3.2.3 Sludge Samples. A continuous layer of sludge (15–25 cm depth) was found directly under the wastewater column of one site. The other four samples were collected from the neighboring sludge drying areas. Samples were collected in polyethylene containers. After collection, samples were freeze-dried to complete dryness; then they were ground and homogenized in an agate mortar and sieved through a mesh of 63-mm pore size. About 0.5 to 1.0 grams of the homogenized sample were dissolved in 10.5 ml concentrated hydrochloric acid (37%) and 3.5 ml concentrated nitric acid (65%) in 50 ml retorts. The samples were degassed (12 hours), then heated to 160°C for 3 h. After cooling to room temperature, the solutions were diluted with distilled water in 50 ml volumetric flasks and kept in 100 ml polyethylene bottles for analysis.

Elements were analyzed by different instruments; a flame atomic absorption (AAS vario 6—Analytik Jena) for determination of Ca, Cu, K, Li, Mg, and Na; an ICP/OES (VARIAN, VISTA-MPX) for determination of As, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sr, and Zn; and an energy-dispersive miniprobe multielement analyzer (EMMA-XRF) (Cheburkin and

Shotyk, 1996) for determination of Br, Rb, Se, Th, U, Y and Zr. Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of freezedried samples (50–100 mg) and Hg pre-concentration on a single gold trap by means of an AMA 254 solid phase Hg-Analyzer (LECO). Total carbon and sulfur were determined directly in dried samples by using a carbon-sulfur determinator (LECO CS-225); and finally, carbonates were measured directly by a carbonate bomb (Müller and Gastner, 1971). The total organic carbon (TOC) was calculated by the subtraction of inorganic carbon from total carbon. Adsorbable organic halogen (AOX) was determined by a Euroglas organic halogen analyzer from The Netherlands according to the DIN 38414 S18 Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung, Sludge and Sediment (Group S) Determination of AOX (DIN, 1989).

3.2.4 Soil Samples. Soil samples were obtained continuously from the five boreholes throughout the drilled depth. Three-inch-size split spoon sampling tubes (3" diameter $\times 24$ " long) were used to collect the samples. The samples were examined, described, and classified by geologists and geotechnical engineers. Natural beeswax was used to cap the ends of the sample tubes, as requested. The samples were properly labeled and placed in waterproof plastic bags before being placed in wooden boxes. Approximately 0.5 kg of soil was put in polyethylene cups and stored at 4°C during transport to laboratories where soil was dried in an oven at 50°C until constant weight. Then they were shipped to Germany in plastic sampling bags. The samples were sieved through a 20- μ m sieve and ground to a very fine powder by using a sand mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). Approximately 1-2 grams of the homogenized sample were dissolved with 10.5 ml of concentrated hydrochloric acid (37%) and 3.5 ml of concentrated nitric acid (65%) in 50 ml retorts. The digestion process of the soil samples was the same as the above-mentioned process for sludge samples. Al and Ba were analyzed by inductively coupled plasma optical emission spectroscopy (ICP/OES). AOX was analyzed by the same method as the sludge samples. In order to determine soil mineralogy, a semi-quantitative X-ray diffraction technique (XR Diffractometer, SIEMENS) (Moore and Reynolds, 1989) was used.

3.2.5 Groundwater Samples. Groundwater depth measurements were taken whenever groundwater was encountered in the boreholes, using a water-level indicator instrument. Groundwater samples were collected from the boreholes at the specified depths; they were sampled about one meter below the groundwater surface. Five groundwater samples were collected from the five boreholes. One-liter samples were collected and treated as the wastewater samples above. Several parameters were measured during the fieldwork: temperature, turbidity, electric conductivity, and pH. Elemental analysis was performed in the lab.

3.2.6 Quality Control. For quality control, analytical blanks and two standard reference materials with known concentrations of metals were prepared and analyzed using the same procedures and reagents. Precision for the results of soil and sludge samples was estimated using the reproducibility between the duplicates, and a coefficient of variation of less than 5% was found. The accuracy was evaluated using 20 aliquots of two river sediment standard reference materials—RS1 and RS3-Deutsche Industrie Norm (DIN, 1989, 1997). As an independent check of the trace element measurements of the soil and sludge, these were also measured in solid samples using the energy-dispersive miniprobe multielement analyzer (EMMA-XRF). A deviation of less than 5% from the certified values was found. The coefficient of variation for triplicates (2 samples and one standard) was less than 2% for all parameters. For the wastewater and groundwater analysis, standard reference materials 1643c

and 1643d were used for the determination of trace elements (National Institute of Standards and Technology, NIST, 1991, 1994) and SPS-WW2, wastewater level 2 (SPS, 2002).

4. Results

4.1 Wastewater

Table 1 shows the average values of parameters of the wastewater effluent. The general parameters indicate that the treatment plant was able to remove >92%, >88%, >60% of BOD₅, COD, and both total P and total N, respectively, under the existing treatment facilities. The table shows the metal content of the collected five composite wastewater samples, and these results agree with the findings of a three-year monitoring program conducted by Shomar *et al.* (2004a).

4.2 Sludge

In addition to the common metals analyzed in the sludge samples in many parts of the world, an additional eight elements were determined (Table 2). Seven of them had low

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Average	$SD(\sigma)$
7.7	0.3
26	1.7
0.1	0.03
1536	62
20	2.6
480	50
1.4	0.1
320	26
9	0.3
20	6.1
89	7.7
25	1.3
0.7	0.0
52	2.9
8	1.3
< 0.5	0.1
0.8	0.4
5	1.0
7	0.8
163	3.2
48	4.2
6	1.7
<2.5	0.2
42	12
	Average 7.7 26 0.1 1536 20 480 1.4 320 9 20 89 25 0.7 52 8 <0.5

Table 1Chemical characteristics of wastewater effluent (n = 3)

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Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
AOX (mg Cl/kg)	610 ± 68	600 ± 55	530 ± 62	510 ± 44	495 ± 52
As (ppm)	5.5 ± 0.8	2.1 ± 0.8	3.5 ± 0.7	5.4 ± 0.8	4.3 ± 0.6
Cr (ppm)	89 ± 6	68 ± 5	89 ± 7	111 ± 6	108 ± 11
C (%)	27 ± 0.7	19 ± 0.5	27 ± 0.8	26 ± 0.8	22 ± 1
Ca (%)	12.7 ± 0.3	9.0 ± 0.2	13.3 ± 1	10.5 ± 0.8	11.5 ± 0.4
Cd (ppm)	2.2 ± 0.8	1.5 ± 0.7	1.7 ± 0.3	2.0 ± 0.1	1.8 ± 0.3
Co (ppm)	3.3 ± 0.3	3.6 ± 0.2	0.9 ± 0.1	2.5 ± 0.2	2.4 ± 0.2
Cr (ppm)	89 ± 7	68 ± 5	89 ± 6	111 ± 11	108 ± 8
Cu (ppm)	304 ± 11	220 ± 8	288 ± 13	286 ± 14	281 ± 12
Fe (%)	1.5 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.5 ± 0.2	1.3 ± 0.1
Hg (ppm)	3.5 ± 0.5	2.6 ± 0.5	4.5 ± 1	3.2 ± 0.6	2.8 ± 0.5
K (ppm)	1836 ± 36	1808 ± 42	1673 ± 40	1810 ± 37	1605 ± 38
Li (ppm)	3.0 ± 0.2	2.5 ± 0.2	2.6 ± 0.2	3.4 ± 0.3	3.2 ± 0.3
Mg (%)	1.1 ± 0.3	0.9 ± 0.2	1.0 ± 0.1	1.0 ± 0.1	0.9 ± 0.1
Mn (ppm)	227 ± 8	188 ± 5	270 ± 7	261 ± 8	273 ± 10
Na (ppm)	9894 ± 26	10312 ± 42	7720 ± 35	3191 ± 22	4359 ± 25
Ni (ppm)	28 ± 5	21 ± 4	24 ± 5	26 ± 6	25 ± 5
Pb (ppm)	154 ± 5	111 ± 6	140 ± 11	156 ± 9	136 ± 8
Rb (ppm)	10.6 ± 0.7	11.5 ± 1	9.0 ± 0.5	9.9 ± 0.8	8.2 ± 1
S (%)	3.0 ± 0.3	2.1 ± 0.4	2.8 ± 0.2	3.1 ± 0.3	2.1 ± 0.1
Se (ppm)	2.6 ± 0.2	2.6 ± 0.2	5.0 ± 0.4	3.2 ± 0.4	3.0 ± 0.5
Sr (ppm)	651 ± 7	540 ± 9	984 ± 15	643 ± 32	730 ± 62
Th (ppm)	3.1 ± 0.2	0.0 ± 0	2.0 ± 0.2	2.4 ± 0.1	0.0 ± 0
U (ppm)	8.8 ± 0.6	5.7 ± 0.5	10.7 ± 1	10.5 ± 2	8.5 ± 0.4
Y (ppm)	7.1 ± 0.4	8.3 ± 0.5	5.8 ± 0.2	6.9 ± 0.3	8.1 ± 0.4
Zn (ppm)	2443 ± 46	1820 ± 66	2230 ± 84	2527 ± 72	2385 ± 78
Zr (ppm)	185 ± 5	164 ± 11	96 ± 9	103 ± 7	98 ± 11

Table 2Average chemical composition of five sludge samples (Average \pm SD σ , n = 3)

concentrations and only strontium (Sr) showed considerable amounts in the tested samples. Zinc in the sludge of Gaza (>2100 mg/kg) exceeds that of all standards of developed and industrialized countries for land application. As a very general parameter, the average AOX in the tested samples reached the mean value of 550 mg Cl/kg.

4.3 Soil

Due to the large set data obtained from the analysis of 160 soil samples, each having 26 parameters, this section will cover mostly the fifth soil profile, which represents the five profiles. The upper 40–50 cm represents a mixture of sludge and fine sand and its color starts from dark black in the surface layer up to very light dark downward. A well-distinguished soil appears from 20 cm depth and more.

The four examples of X-ray diffractograms (Figure 2) show that the soil mineralogy is mainly composed, in order of abundance, of quartz, calcite, kaolinite, and some feldspars. The soil texture, including the major components of each layer, is shown in Figure 3.





B. H. Shomar et al.



Figure 3. General geological features of the fifth soil borehole.

The soil-wastewater/sludge interaction and the trend of major parameters could be found in two profiles (1 and 2). The first is under the treated wastewater lagoon (Table 3) and the second is under the sludge, old drying area (Table 4). Selected depths of soil profile and their metal contents are shown in Table 5 and Figure 4.

The organic content of the soil decreased with depth from 26% organic carbon by weight in the surface sludge to less than 0.05% of 55 m depth, while the AOX in general is very low in the deep layers (less than 5 mg Cl/kg). The soil at the study plot was neutral to basic (pH 7.2–8 in 0.4–60 m), while the upper 40 cm of the sludge-covered soil was acidic (pH 4.8) due to high inputs of nitrate and sulfate loads from wastewater and sludge, which increase the acidity through the intensive mineralization and nitrification processes.

	Geoche	emical charact	eristics of slu	ıdge covered	l soil profile	e under wast	tewater lagoo	on (Average	\pm SD σ , n :	= 3)	
Parameter	$0 \mathrm{cm}$	5 cm	10 cm	15 cm	20 cm	25 cm	30 cm	35 cm	40 cm	45 cm	$50 \mathrm{cm}$
Org. C (%)	26 ± 4	26 ± 3	24 ± 3	22 ± 3	21 ± 3	20 ± 2	2 ± 1	2 ± 1	1 ± 0.3	1 ± 0.2	0.4 ± 0.1
Ca (%)	13 ± 2	10 ± 4	10 ± 3	13 ± 4	13 ± 4	10 ± 2	12 ± 2	1 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.4 ± 0.1
Cu (mg/kg)	237 ± 78	237 ± 68	157 ± 47	120 ± 40	77 ± 34	45 ± 10	18 ± 3	13 ± 3	5 ± 0.4	1 ± 0.4	2 ± 0.3
Fe (%)	1.3 ± 0.2	1.6 ± 0.3	1.8 ± 0.5	0.4 ± 0.1	0.2 ± 0.1	0.4 ± 0.2	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	0.2 ± 0.1	0.2 ± 0.1
Ni (mg/kg)	41 ± 7	38 ± 9	34 ± 8	13 ± 2	11 ± 1	6 ± 1	3 ± 0.5	2 ± 0.3	2 ± 0.1	2 ± 0.1	2 ± 0.2
Pb (mg/kg)	114 ± 38	76 ± 14	58 ± 11	33 ± 6	8 ± 1	3 ± 1	2 ± 0.4	1 ± 0.2	0.6 ± 0.1	0.1 ± 0	0.5 ± 0.1
Zn (mg/kg)	2197 ± 242	1276 ± 229	999 ± 114	217 ± 28	11 ± 1	8 ± 1	7 ± 0.8	4 ± 0.5	3 ± 0.7	5 ± 0.4	5 ± 0.6

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	Geochei	mical characte	ristics of sludg	ge covered so	oil profile u	nder sludge	drying area	(Average ±	: SD σ, n =	= 3)	
Parameter	0 cm	5 cm	10 cm	15 cm	20 cm	25 cm	30 cm	35 cm	40 cm	45 cm	50 cm
Org. C (%)	26 ± 4	25 ± 6	21 ± 4	20 ± 6	20 ± 4	19 ± 6	2 ± 0.5	2 ± 0.2	1 ± 0.1	1 ± 0.1	0.5 ± 0.2
Ca (%)	12 ± 3	13 ± 4	10 ± 2	14 ± 5	12 ± 3	3 ± 1	2 ± 0.4	0.6 ± 0.1	0.7 ± 0.2	0.5 ± 0.1	0.8 ± 0.1
Cu (mg/kg)	240 ± 66	210 ± 62	180 ± 51	132 ± 42	95 ± 33	52 ± 11	20 ± 4	17 ± 4	6 ± 0.7	2 ± 0.2	1 ± 0.1
Fe (%)	1.7 ± 1	1.5 ± 0.2	1.7 ± 0.1	0.5 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
Ni (mg/kg)	42 ± 8	39 ± 7	28 ± 8	14 ± 2	10 ± 2	6 ± 1	3 ± 0.2	2 ± 0.4	2 ± 0.2	3 ± 0.3	3 ± 0.7
Pb (mg/kg)	115 ± 24	82 ± 16	60 ± 14	27 ± 9	11 ± 2	3 ± 1	2 ± 0.1	1 ± 0.1	1 ± 0.1	0.2 ± 0.1	0.3 ± 0.1
Zn (mg/kg)	2005 ± 255	1700 ± 357	1102 ± 138	350 ± 89	42 ± 7	22 ± 5	9 ± 0.5	5 ± 0.6	3 ± 0.5	3 ± 0.3	3 ± 0.4

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	Table 5	
Chemical composition of soil	for selected depths of th	he fifth profile (Average \pm SD σ ,

				n = 3)			
Element	UC*	LC**	0.6 m	7.5 m	24.5 m	35 m	55 m
Al (%)	7.74	8.21	0.3 ± 0.1	1.7 ± 0.2	1.0 ± 0.1	0.7 ± 0.1	0.1 ± 0.1
As (mg/kg)	2	1.3	2.8 ± 0.2	2.1 ± 0.3	0.8 ± 0.1	3.6 ± 0.2	4.7 ± 0.4
Ba (mg/kg)	668	568	32 ± 4	79 ± 16	67 ± 11	66 ± 12	12 ± 2
Br (mg/kg)	1.6	0.28	0.0 ± 0	4.3 ± 0.8	1.4 ± 0.1	1.2 ± 0.3	1.0 ± 0.1
C (%)	0.32	0.06	0.9 ± 0.2	2.4 ± 0.4	0.8 ± 0.1	1.6 ± 0.2	1.3 ± 0.1
Ca (%)	2.95	4.86	3.2 ± 0.4	7.4 ± 1	2.2 ± 0.2	4.6 ± 0.8	4.2 ± 0.7
Cd (mg/kg)	0.102	0.101	0.06 ± 0	0.07 ± 0	0.04 ± 0	0.08 ± 0	0.1 ± 0
Co (mg/kg)	11.6	38	2.7 ± 1	9.8 ± 2	6.9 ± 2	4.3 ± 0.4	1.3 ± 0.1
Cr (mg/kg)	35	228	8 ± 1	34 ± 7	11 ± 3	12 ± 3	4 ± 1
Cu (mg/kg)	14.3	37.4	2.5 ± 0.6	26.1 ± 7	8.5 ± 3	3.6 ± 1	4.6 ± 2
Fe (%)	3.1	5.7	0.4 ± 0.1	1.7 ± 0.2	0.8 ± 0.2	0.7 ± 0.1	0.3 ± 0.1
Hg (μ g/kg	56	21	2.0 ± 0.4	2.0 ± 0.2	2.0 ± 0.2	2.0 ± 0.1	1.0 ± 0.1
K (%)	2.86	1.31	0.07 ± 0	0.17 ± 0.1	0.14 ± 0	0.07 ± 0	0.02 ± 0
Li (mg/kg)	22	13	1 ± 0.2	4.8 ± 1	3.9 ± 0.3	2.1 ± 0.2	0.5 ± 0.1
Mg (%)	1.35	3.15	0.1 ± 0.1	0.6 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.1 ± 0
Mn (mg/kg)	527	929	94 ± 11	251 ± 34	219 ± 80	148 ± 47	64 ± 14
Na (%)	2.57	2.12	0.12 ± 0	0.05 ± 0	0.05 ± 0	0.04 ± 0	0.03 ± 0
Ni (mg/kg)	18.6	99	6 ± 0.2	17 ± 4	13 ± 2	7 ± 1	2 ± 1
Pb (mg/kg)	17	12.5	0.8 ± 0.1	2.8 ± 0.3	1.7 ± 0.4	1.1 ± 0.4	0.6 ± 0.2
Rb (mg/kg)	110	41	10 ± 2	20 ± 4	20 ± 5	17 ± 4	7 ± 2
S (%)	0.95	0.41	0.01 ± 0				
Sr (mg/kg)	316	352	95 ± 12	133 ± 41	95 ± 24	63 ± 13	77 ± 9
Th (mg/kg)	10.3	6.6	0.0 ± 0	2.5 ± 0.8	0.0 ± 0	2.7 ± 0.7	0.0 ± 0
Y (mg/kg)	20.7	27.2	9 ± 2	21 ± 6	32 ± 8	14 ± 3	8 ± 1
Zn (mg/kg)	52	79	8 ± 2	26 ± 8	26 ± 7	14 ± 4	13 ± 4
Zr (mg/kg)	237	165	342 ± 44	254 ± 51	354 ± 58	188 ± 46	107 ± 28

(*) Upper Crust, and (**) Lower Crust: Turekian and Wedepohl, 1961.

4.4 Groundwater

Table 6 shows the concentration of the major anions and cations in the five groundwater samples. The average total dissolved solids (TDS) of groundwater is 1800 mg/l; and major ions of Cl, F, NO₃, SO₄, CO₃, PO₄, Na, Ca, Mg, and K are high. Tested groundwater of the area showed sulfate averages of 190 mg/l (Shomar et al., 2004a). Although it is assumed that fluoride is a natural constitutional of the groundwater of the Gaza Strip (Shomar et al., 2004b), F averages of the tested wells are 1.8 mg/l. The results of the fluoride contents by using IC are consistent with the results of the ISE. Phosphates were below the detection limit of the vanadate molybdate spectrophotometric method. Groundwater is oxygenated and Fe and Mn are in the oxidized soluble forms. The average dissolved oxygen (DO) was $6.7 \text{ mgO}_2/l$. Previous studies of the groundwater quality in the surrounding area revealed that many parameters (EC, TDS, Cl, NO₃, SO₄, F, Ca, Mg, and Na) are affected by seasonal variation; they are 30-60% higher in the summer (Shomar et al., 2004b).

The results for the metals indicate that all of them are within the WHO drinking water standards. Arsenic and iron for borehole number 2 are high; As is the same as the tentative



Figure 4. Examples of element profiles for borehole 5.

new WHO standard (10 μ g/l), while Fe is 1855 μ g/l, which is about 6 times higher than the WHO standard (300 μ g/l).

5. Discussion

The wastewater treatment plant was able to remove >92%, >88%, >60% of BOD₅, COD, and both total P and total N, respectively. This indicates that the majority of the metals have

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Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	WHO^*	LD^{**} ($\mu g/l$)
Temp. (°C)	22 ± 0.5	22 ± 0.6	23 ± 0.4	24 ± 0.7	21 ± 0.4		
Hd	6.7 ± 0.2	6.8 ± 0.3	7.1 ± 0.2	6.9 ± 0.2	6.7 ± 0.2	6.5-8.5	
$DO mgO_2/l$	6.4 ± 0.2	6.3 ± 0.2	6.9 ± 0.2	6.7 ± 0.3	7.1 ± 0.4		
EC mS/cm	2.65 ± 0.1	2.59 ± 0.2	2.6 ± 0.1	2.61 ± 0.2	2.65 ± 0.2		
Cl (mg/l)	560 ± 32	590 ± 35	505 ± 28	602 ± 34	595 ± 33	250	
NO ₃ (mg/l)	77 ± 7	85 ± 11	76 ± 9	89 ± 14	64 ± 7	50	
SO4 (mg/l)	135 ± 14	140 ± 17	160 ± 16	110 ± 9	123 ± 11	250	
F (mg/l)	1.7 ± 0.1	1.8 ± 0.2	1.7 ± 0.1	2.0 ± 0.1	1.9 ± 0.2	1.5	
PO4 (mg/l)	$<1\pm0.0$	$<1 \pm 0.1$	$<1 \pm 0.1$	$<1\pm0$	$<1 \pm 0.1$		
Na (mg/l)	320 ± 22	201 ± 24	370 ± 29	198 ± 18	231 ± 27	200	
Mg (mg/l)	90 ± 14	87 ± 9	110 ± 7	106 ± 10	119 ± 10		
Ca (mg/l)	128 ± 19	140 ± 20	133 ± 22	122 ± 19	143 ± 23		
Ag $(\mu g/l)$	$<0.5\pm0.1$	$<0.5\pm0.1$	$<0.5\pm0$	$<0.5\pm0.1$	$<0.5\pm0$		0.5
Al $(\mu g/l)$	28 ± 4	34 ± 7	27 ± 6	$<25 \pm 4$	29 ± 7	200	25
As $(\mu g/l)$	5 ± 1	10 ± 1	9 ± 2	7 ± 1	7 ± 2	10	2.5
Cd (µg/l)	0.7 ± 0.1	$<0.5 \pm 0$	$< 0.5 \pm 0.1$	$<0.5\pm0$	$<0.5\pm0$	ю	0.5
Co (μg/l)	$<0.3\pm0$	$<0.3\pm0$	$< 0.3 \pm 0.1$	$<0.3 \pm 0.1$	$< 0.3 \pm 0$		0.3
$Cr(\mu g/l)$	11 ± 2	29 ± 3	45 ± 3	23 ± 2	30 ± 3	50	2.5
Cu (μg/l)	$<1 \pm 0.1$	9 ± 1	3 ± 0.5	4 ± 0.2	2 ± 0.1	2000	1
Fe (μ g/l)	26 ± 4	1855 ± 245	28 ± 4	16 ± 2	26 ± 3	300	
$Mn (\mu g/l)$	$<1 \pm 0.1$	15 ± 3	$<1 \pm 0.1$	$<1\pm0$	$<1 \pm 0.1$	500	1
Ni (µg/l)	3 ± 0.2	6 ± 0.2	4 ± 0.1	3 ± 0.4	2 ± 0.2	20	0.5
Pb (μ g/l)	$<2.5\pm0.2$	2.6 ± 0.2	$<2.5 \pm 0.3$	$<2.5 \pm 0.3$	$<2.5\pm0.5$	10	2.5
Zn (μ g/l)	$< 10 \pm 2$	12 ± 2	$< 10 \pm 1$	12 ± 2	23 ± 3	3000	10
*WHO: Worl **LD: Limit o	d Health Organizat of Detection by the	tion Guidelines. ICP/MS in $(\mu g/l)$.					

Table 6Groundwater quality of five boreholes (Average \pm SD σ , n = 3)

323

been transferred from the wastewater to the sewage sludge where Zn, Pb, Cu, and Cr in the sludge were 2100, 125, 240, and 75 mg/kg, respectively. The new results agree with the findings of Shomar *et al.* (2004a); however, 20% may be lost in the treated effluent, depending on the solubility, and this may be as high as 40–60% for the most soluble metal, Ni (Scancar *et al.*, 2000). The average of Zn removal in the treatment process was 55%; this ratio finds its way to the sludge and this may explain the high contents of Zn in the sludge (>2100 mg/kg).

The most affected zone by wastewater and sludge is the upper 40-50 cm of the soil profile and the metal content decreased with depth. Element mobility sequence was $Ni > Ca > Cu \gg Fe$, where the concentrations in the upper 5 cm were 40 mg/kg, 10%, 240 mg/kg, and 1.5% and in the lower 40 cm were 2, 0.5, 5, and 0.3, respectively. This result agrees with that of Legret (1993) and Cornu (2001). Nickel is the most soluble metal in sludge, and thus the most mobile (Henry and Harrison, 1992). The general trend of the total Ni concentrations in each soil profile was a slight increase with depth. The distribution of Ni in a soil profile is related to the clay fractions; the higher the clay content, the greater the accumulation of Ni. The percent clay in the soil profiles increased due to the clay lenses in the 6.3 and 9.3 m depth, as did the total Ni concentrations. This could be supported by the explanation of the EPA (1995) that stated that Ni tends to accumulate in arid and semiarid soils as well. The sludge-covered soils were exposed to rainfall over the course of the study, which may have resulted in the leaching of Ni to the lower depths. It has been shown that soils with higher pHs have higher potentials for fixing Ni in less soluble forms than in soils with lower pHs (Abdel-Sabour, 1991). A mean comparison of total trace element concentrations in the upper 40 cm depth indicated that the uncovered soil had significantly lower Cu and Ni concentrations than the sludge-covered soils. In addition, the comparison of means from each soil profile indicated that there were no significant differences among the mean of most tested elements.

In soil, Ca is the most mobile, while Fe is the least mobile element (Sparks, 2002). The pH of the upper 40 cm for the sludge-covered soils increased slightly with depth. The results of the upper 40 cm of the soil profile were anticipated as the sludges that covered the soil surface contained low concentrations of the tested elements. The trend showed a definite increase in Cu within the upper 40 cm of all sludge-covered soils. This could be explained by the fact that the organic compounds of the sludge increased the solubility of Cu (Kabata-Pendias and Pendias, 1992). Total soil Cu concentrations were somewhat variable in the individual profiles.

The solubility, mobility and concentration of Pb and Zn are controlled by several mechanisms like organic matter, pH and soil structure (Sims and Patrick, 1978; Pepper *et al.*, 1983; Milner and Barker, 1989). The total Pb concentrations of the soil were basically uniform throughout the soil profiles. The heavy precipitation, in combination with the acidic environment of the upper sludge layer of pH 4.8 and the high contents of organic matter (26%), enhances the solubility and leaching processes of Pb from sludge. Pb concentration is high in the upper layers and decreases with depth. Even though the pH of the sandy layers was high, the concentrations of Pb and Zn were low due to the lack of organic matter and the effect of the downward water flow. Pb reached its minimum concentration (2.7 mg/kg) in the sandy soil at a depth of 40 cm. The leached Pb accumulated in the deep layers of clay at a depth of 5.5 and 25 m, where its concentrations are 4.2 and 3.6 mg/kg, respectively. The Pb profile in soil is similar to the Fe profile as well as to the organic matter profile. In comparison with Zn, organic matter is relatively more important in adsorbing Pb, but clay minerals are relatively more important in adsorbing Zn. Zn showed similar trend as Pb.

It was found that the soil metal content was affected by soil structure. Clay layers showed higher contents of major elements than soil layers. In clay layers Cd, Cr, Fe, Mn, Ni, Pb, and Zn were 0.1 mg/kg, 23 mg/kg, 6%, 930 mg/kg, 100 mg/kg, 13 mg/kg, and 80 mg/kg, respectively, while they were 0.04, 10, 0.7, 70, 8, 1, and 13, respectively, in other soil structures. Generally speaking, a trend of increase of most elements was observed from fine sand, sandstone, loose sandstone, sand clay, and clay. This conclusion agrees with the findings of several studies (Premovic *et al.*, 2001; Navas and Machin, 2002; Pearson *et al.*, 2002; USGS, 2004). Except for the upper half-meter of the soil profile, which is directly affected by sludge, the lateral distribution of elements was dependent on the physicochemical characteristics of the soil and not on depth.

The total contents of studied elements indicate that the concentrations of Zn, Mn, Cu, Fe, and partly As and Pb correlate with the clay content in the individual soil profile. The total content of Mn, Fe, Zn, and Cu in the individual soil horizons is proportional to their clay content (Martinek *et al.*, 1999). The trend showed that the layer of 6.3–9.3 m deep had high contents of Al, Ca, Cr, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, Y, Zn, and Zr, and to a lesser extent of Cd, Co, and Hg. Also, the soil samples of 35–55 m depth showed an increase in the contents of most elements. The Al figure shows the same trend of Ba, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Sr, Th, Y, and Zn. The figure of Cd shows the same trend of Rb and the Pb figure shows the same trend of S and Zr.

There is no significant difference between the mineralogy of the different depths of the fifth profile. Although the five boreholes were dug in around a 1 km^2 area, the layers were not continuous and this could be explained by the irregular deposition, sedimentation, and weathering rates. The stability rate under weathering conditions in the study area is gravel > sand > clay, where the clay layer is impermeable.

However, the results of groundwater revealed that it is highly polluted and all major parameters exceed regional and international standards; it was hard to judge that the major source of pollution is the leaching of these pollutants from the upper surface to the aquifer.

It is believed that the high concentrations of nitrate (>75 mg/l) in the area are caused by leaching of nitrate from wastewater to the aquifer (CAMP, 2000; Shomar *et al.*, 2004a). The results for the metals indicate that all of them are within the WHO drinking water standards (1998). Arsenic and iron for borehole number 2 are high; As is the same as the tentative new WHO standard (10 μ g/l), while Fe is 1855 μ g/l, which is about 6 times higher than the WHO standard (300 μ g/l).

6. Conclusions

A very good agreement was observed between soil physical characteristics and the vertical distribution of metals. The trend of most elements was: clay > sandclay > loose sandstone > sandstone > fine sand. The trend showed that the clay layer of 6–9 m depth had high contents of Al, Ca, Cr, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, Y, Zn, and Zr, and to a lesser extent of Cd, Co, and Hg.

Except for the upper half-meter of the soil profile, which is directly affected by water and sludge, the lateral distribution of elements was dependent on the physical characteristics of the soil and not on the depth.

The treated wastewater is a promising water resource for agriculture, and regular monitoring systems on soil, crops and groundwater should be adopted. Sludges, on the other hand, have high Zn (>2000 mg/kg) and AOX (>500 mg Cl/kg) concentrations, which exceed the standards of all industrialized countries for land application. Although the groundwater samples were collected from the aquifer below the wastewater treatment plant, no anomalous concentrations were found with respect to metals. However, several studies showed that elevated salinity, nitrate, chloride, and sulfate are believed to be a result of both anthropogenic and natural sources.

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