

# The Effect of Kawergosk Oil Refinery Wastewater on Surrounding Water Resources

Shuokr Qarani Aziz

Department of Civil Engineering, College of Engineering,  
Salahaddin University–Erbil, Iraq; Corresponding author,  
shuokr.aziz@su.edu.krd, shoker71@yahoo.com, H/P: 00964  
750 462 5426

Enas Sa'ad Fakhrey<sup>2</sup>

Department of Dams and Water Resources Engineering,  
College of Engineering, Salahaddin University–Erbil, Iraq

**Abstract-** Kawergosk oil refinery is one of the biggest refineries in Kurdistan Region-Iraq. The refinery lies on Khabat District and the produced wastewater disposed to Greater-Zab River (GZR). The effect of Kawergosk refinery wastewater (KRWW) on the surrounded water sources was studied by examining the characteristics of KRWW, GZR and the groundwater. The impact of the KRWW on the surface and groundwater sources were examined via measuring parameters of pH, oxidation-reduction potential (ORP), phenol, oil and grease, fluoride, salinity, dissolved oxygen (DO), five day biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), BOD<sub>5</sub>/COD, color, ammonia-nitrogen (NH<sub>3</sub>-N), nitrite, nitrate, zinc, potassium, turbidity, chloride, electrical conductivity (EC), total dissolved salts (TD Salts)... etc. To assess effect of KRWW on GZR, two locations of GZR were selected one of them was at the disposing point (i.e. mixing point between the GZR and KRWW) and the other was before disposal of KRWW to the river. The results of pH, ORP, oil and grease, TDS, Salinity, NH<sub>3</sub>-N, EC, nitrite, nitrate, SS, turbidity, chloride, total acidity, total alkalinity, and total hardness showed that the GZR was polluted at the mixing point. For evaluating the effect of KRWW on the groundwater, two groundwater sites were chosen, one of them close to the refinery near Small Agulan village, and the second one was far from the refinery near Al-Jadida village. Results illustrated that commonly KRWW had not effect on the groundwater.

**Keywords:** oil refinery, wastewater, Greater-Zab River, groundwater, pollution, Erbil

## I. INTRODUCTION

Erbil wastewater composes of domestic sewage, industrial wastewater and storm water [1]. Petroleum refinery effluents (PRE) are wastes originating from industries primarily engaged in refining crude oil and manufacturing fuels, lubricants and petrochemical intermediates [2]. These effluents are a major source of aquatic environmental pollution. Petroleum refinery wastewater (PRWW) comprises different amounts of hazardous pollutants [2–4]. However, the concentration and type of pollutant present in the water totally depends on the type of oil and the refinement process [5]. Although concerted efforts have been made to replace fossil fuels, crude oil remains an important raw material. The need to satisfy the ever-increasing global energy demand, which is expected to soar by 44% over the next two decades, makes the processing of crude oil and the generation of PRE globally important issues [2]. The process of refining crude oil consumes large amounts of water. Consequently, significant volumes of wastewater are generated. In literature, the volume of PRE generated during processing is 0.4–1.6 times the amount of the crude oil processed. Large volumes of water are used during the refining process in oil refineries which subsequently generates huge quantity of wastewater. The refinery wastewater mostly contains high levels of pollutants which are similar to those identified in crude oils [2-5].

If produced wastewater from oil refiners disposed to the natural environment, it causes problems to the water sources. In Erbil City, surface runoff from both sides of Greater-Zab River (GZR) mixes with the river water. Produced wastewater from Kowergosk oil refinery (KOR) may mix with surface runoff and later enter to the river, or may it mixes directly with water sources. On the other hand and due to absence of lining of conveying channels, the formed wastewater may percolate to groundwater and contaminate the groundwater source. As a result, wastewater from KOR may affect surface water (GZR) and groundwater (wells water) sources. The goals of the present work were: 1) to study the characterization of Karergosk oil refinery wastewater, GZR and groundwater close to Kawergosk Refinery area, and 2) to show the effect of PRWW at Kowergosk area on the surrounded water sources (i.e. GZR water and ground water). Thus far, this kind of the study has not been conducted yet.

## II. MATERIALS AND METHODS

### A. Description of the Sites

Erbil province is the capital of Iraqi Kurdistan with about two million populations and situated in the northeast of Iraq. Its

boundaries extended from longitude 43° 15' E to 45° 14' E and from latitude 35° 27' N to 37° 24' N. Erbil city is currently served by two types of water resources.

KOR locates on 36.3179° Latitude and 43.7573° Longitude. Fig. 1 shows the location of the Refinery. KOR is about 30 km far from Erbil City. The Kourkosk Refinery, the fourth largest in Iraq and the largest private sector one, is a private, local investment in Kurdistan.

The GZR is the largest Tigris tributary in terms of water yield. Its headwaters originate in the Ararat Mountains in Turkey. The headwater topography is characterized by steep slopes, with several tributaries and wadis (Khazir, Rubar-i-Shin, Rukuchuk and Rubat Mawaran Rivers) flowing into the Greater Zab. This perennial stream has a total length of 462 km and flows mainly in Iraq before discharging into the Tigris River 49 km south of Mosul.

Well water samples from Small Agulan and Jadida Villages were collected. Small Agulan village located on 36.327° latitude and 43.736° longitude. Jadida village is located on 36.257° latitude, 43.783° longitude and an altitude of 377.074 m.



Figure1. Satellite image for the study area

## B. Sampling Process and Analysis

The samples were collected over three seasons to cover wet, hot and normal weather days. In January, March, and May of 2015 the samples were collected in plastic containers of 2L working volume and transported to the laboratory immediately. The samples were stored in the refrigerator at 4° C prior to experimental use to avoid any biological activities and changes in samples' characteristics [6].

First of all, numerous tests have been conducted each time to evaluate the characteristics of each of (KRWW, groundwater, and surface water).

The following parameters were tested: pH, oxidation-reduction potential (ORP) (mV), total dissolved salts (TD Salts) (mg/L), Salinity (PSU), temperature (°C), atm. press. (mmHG), total solids (TS) (mg/L), total suspended solids (TSS) (mg/L), total dissolved solids (TDS) (mg/L), total volatile solids (TVS) (mg/L), total non-volatile solids (TnVS) (mg/L), total acidity (mg/L), total alkalinity (mg/L), total hardness (mg/L), five-day biochemical demand (BOD<sub>5</sub>) (mg/L), BOD<sub>5</sub>/COD, turbidity (FTU), chloride (mg/L), chemical oxygen demand (COD) (mg/L), color (Pt.co), ammonia –nitrogen (NH<sub>3</sub>-N) (mg/L), dissolved oxygen (DO) (mg/L), electrical conductivity (EC) ms/cm, nitrite (mg/L), nitrate (mg/L), zinc (mg/L), potassium (mg/L), phenol (mg/L), and oil and grease (mg/L) for each of the first six samples.

The experiments were conducted in the Sanitary and Environmental Laboratory, Civil Engineering Department, College of Engineering, Salahaddin-University, Erbil.

### 1. Kawergosk Refinery Wastewater

For the whole study period, the treated and untreated wastewater samples from KOR were collected as shown in Figs. 2 and 3.



Figure 2. The untreated wastewater



Figure3. The treated wastewater

### 2. Greater-Zab River Water

To examine the changes that the KRWW may cause to the GZR, samples before and after mixing PRWW with GRZ were collected. Fig. 4 shows the KRWW channel that disposes to the GZR.



Figure 4. The mixing point between the GZR and the disposed wastewater

### 3. Groundwater

To show the impact of PRWW from KOR on the groundwater, two samples from Small Agulan Jadida Villages were tested (Figs. 5 and 6).

#### C. Analytical Methods

All the tests were performed in accordance to the standards methods of the APHA [6]. The method used to each parameter is explained in Table I.

Tests like TS, TSS, TDS, TVS, and Tn-VS confirmed using filter paper (thickness=0.33 mm, weight=55 gm/m<sup>2</sup>) and electrical oven (matest-(40-220) °C and Lenton-model EF-11/8B, made in England, max. temp.=1100 °C).



Figure5. Small Agulan's village location according to the refinery



Figure 6. Jadida's village location according to the refinery

### III. Result and discussions

The results for the aforementioned tests and methods are illustrated below for each of the KRWW, GZR and the ground water.

#### A. Kawergosk Refinery Wastewater

##### 1. Characteristics of KORWW

The conducted tests on the collected samples of the KRWW during the three months are listed in Table II.

It can be noticed from the obtained data that higher values of ORP, TD Salts, TS, TSS, TDS, T. hardness, chloride, and EC were noticed for the treated wastewater than the raw wastewater. This is due to adding chemicals to the raw wastewater for the treatment process in the refinery. The temperature of the processed wastewater was noticed to be less than the temperature of the raw wastewater because of that the wastewater treatment process includes aeration and exposure to the atmosphere which will lead to cool down the influent wastewater, further information are given in Process description.

By comparing the results that gained in Table II with the Iraqi Environmental Standards [8]; pH, temperature, zinc, and NO<sub>3</sub> were found to be within the limit, while TSS, BOD<sub>5</sub>, COD, and phenol found to exceed the allowable limits.

For the Environment Protection Regulations [9], TSS, NH<sub>3</sub>-N, NO<sub>2</sub> and NO<sub>3</sub> were not more than the limit of the standard, only chloride and oil and grease were more than the allowable limit for the mentioned standard.

TABLE I ILLUSTRATION OF ANALYTICAL METHODS

No.	Parameter	Details of method
1	pH	HANNA Multiparameter Meter (HI9829-00202)-
2	ORP	HANNA Multiparameter Meter (HI9829-00202)-
3	DO	HANNA Multiparameter Meter (HI9829-00202)-
4	TD Salts	HANNA Multiparameter Meter (HI9829-00202)-
5	Salinity	HANNA Multiparameter Meter (HI9829-00202)-
6	Temperature	HANNA Multiparameter Meter (HI9829-00202)-
7	Atm. Press.	HANNA Multiparameter Meter (HI9829-00202)-
8	TS	Method 2540B [6]
9	TSS & MLSS	Method 2540D [6]
10	TDS	Method 2540B [6]
11	TVS	Method 2540E [6]
12	TnVS	Method 2540B [6]
13	Acidity	Method 2310 [6]
14	Alkalinity	Method 2320 [6]
15	Hardness	Method 2340 [6]
16	BOD <sub>5</sub>	Method 5210B [6]
17	Oil & grease	Method 2530 [6]
18	Turbidity	HANNA Turbidity meter-LP 200
19	Chloride	Titration Method [7]
20	COD	Method 10067, Manganese III reactor digestion method, HACH DR/3600 spectrophotometer
21	Color	Method 8025, Platinum-Cobalt Standard method <sup>1,2,3</sup> , HACH DR/3600 spectrophotometer
22	NH <sub>3</sub> -N	Method 8038, Nessler method <sup>2</sup> , HACH DR/3600 spectrophotometer
23	EC	Wissenschaftlich-Technische Werkstätten-LF-42
24	Nitrite	Method 10019, Diazotization method, HACH DR/3600 spectrophotometer
25	Nitrate	Method 10020, Chromotropic acid method, HACH DR/3600 spectrophotometer
26	Zinc	Method 8009, Zincon method <sup>2</sup> , HACH DR/3600 spectrophotometer

27	Potassium	Method 8049, Tetraphenylborate method, HACH DR/3600 spectrophotometer
28	Phenol	Method 8047, aminoantipyrine method <sup>2</sup> , HACH DR/3600 spectrophotometer

TABLE II CHARACTERISTICS OF KAWERGOSK REFINERY WASTEWATER (KRWW)

No.	Parameter	Units	January/2015		March/2015		May/2015		Disposing Standards
			UnWW	TWW	UnWW	TWW	UnWW	TWW	
1	pH	-	9.15	8.01	7.5	6.43	6.57	5.91	6-9.5[8]
2	ORP	mV	4.1	150.3	-428.8	-93.3	-381.2	60	
3	TD Salts	mg/L	1738	2261	1294	1424	778	1784	
4	Salinity	PSU	1.84	2.42	1.26	1.46	0.73	1.85	
5	Temp.	°C	11.98	7.71	57.8	29.71	65	32.89	<35[8]
6	Atm. Press.	mmHG	719.1	719.1	736.8	737.6	731.8	731.1	
7	TS	mg/L	1700	1600	1400	1800	1100	2700	
8	TSS	mg/L	800	600	600	400	400	1600	60[8], 35 [9]
9	TDS	mg/L	900	1000	800	1400	700	1100	
10	TVS	mg/L	600	500	200	200	200	400	
11	TnVS	mg/L	1100	1100	1200	1600	900	2300	
12	T. Acidity	mg/L	20	8	64	10	56	12	
13	T. Alkalinity	mg/L	140	84	188	64	120	16	
14	Hardness	mg/L	156	268	160	192	120	480	
15	BOD <sub>5</sub>	mg/L	-	-	-	-	155	75	<40[8]
16	BOD/COD	-	-	-	-	-	0.32	0.26	
17	Turbidity	FTU	201.3	73.4	354.0	33.4	221.0	53.0	
18	Chloride	mg/L	333.3	453.3	327.8	478	334	634	750 [9]
19	COD	mg/L	-	-	-	-	485	298	<100[8]
20	Color	Pt.Co	157	124	1032	119	2180	1187	Nil [8]
21	NH <sub>3</sub> -N	mg/L	12.5	2.9	14.3	2.33	14.3	3.25	Nil [8], 1 [9]
22	EC	µs/cm	1692	2268	3628	2850	3626	1494	
23	Nitrite	mg/L	-	-	-	-	95	15	1 [9]
24	NO <sub>3</sub>	mg/L	-	-	-	-	100	19.75	50[8], 10[9]
25	Zinc	mg/L	-	-	-	-	0.51	0.01	0.2[8]
26	Potassium	mg/L	-	-	-	-	1.4	0.7	
27	Phenol	mg/L	-	-	-	-	3.5	0.39	0.01-0.05[8]
28	Oil & grease	mg/L	-	-	-	-	17.36	1.53	None permitted [8], 10 [9]

UnWW: The untreated wastewater

TWW: The treated wastewater.

Other investigators tested the general characteristics of Erbil's city wastewater (Table III). By comparing the results of the current study with the results by these investigators, it can be noticed that turbidity, EC, TDS, Cl, alkalinity, pH, and BOD were less than the results of the current study [11-15]. Also, the alkalinity of the current study was less than the lower recorded alkalinity by the investigators.

Regarding treatment processes, biological treatment processes are inefficient because the BOD/COD<sub>5</sub> value was less than 0.5. In literature, researchers applied physical-chemical processes added to biological techniques for treatment of low biodegradability ratio such landfill leachates [4, 16-19]. Finally, the obtained characteristics commonly agree with the published works [2-5, 20-21].

From Table II, sometimes the values of measured TWW were higher than UnWW; this phenomenon returns to the treatment processes for produced raw wastewater from KOR. The descriptions of the treatment processes are given in Section 2.

## 2. Process Description

The oily wastewater enters in the plant, by means of pumping, in the mechanical stage, consisting of a Corrugated Plates Interceptor (CPI). At the inlet of the CPI exists also a bypass connection to the sewer channel. In this stage a gravity separation of suspended particles, oil and water, process based on density differences, happens. Sand and sludge, with a higher density than the water, fall to the bottom, while the oil, with a lower density than the water, remains at the top.

After the first treatment in the CPI, the wastewater overflows to the mixing tank where happens in the chemical addition. Cationic polyelectrolyte is used for supporting the coagulation and flocculation processes. Caustic soda is used for pH regulation.

Downstream the mixing tank, the wastewater reaches the Dissolved Air Flotation (DAF) unit. Its purpose is to collect the sludge flocs formed in the mixing tank. To improve the separation efficiency, a part of the waste water at the outlet of the DAF is recirculated and enriched with compressed air which enhances the flotation of the particles with lower density than the water. The flocculating agents used in this stage change the size of flocs and their sedimentation speed, as a consequence of the electro-mechanical agglomeration of the particles. Flocculating agents are organic polyelectrolytes.

Fine hydrocarbon particles can be eliminated only by air flotation. This method is based on the principle of accelerated emersion of fine particles. Fine air bubbles carry dispersed matter from the bottom to the top of the waste water product particles attach themselves to the air bubbles and float to the surface with increased speed.

After passing the DAF unit, the oily wastewater, with low concentration of oil and suspended solids, is collected in a pit. The pit is divided in two zones: hot water zone and cooled water zone. From the "hot water zone", the wastewater is lifted to a cooling tower where its temperature is decreased. The discharge of the cooling tower is done in the other zone of the pit "cooled water zone". From here, two submersible pumps lift the pre-treated wastewater to the biological tanks. In the biological tanks, is fed also the non-oily wastewater stream, without any pre-treatment.

Another unit for the treatment is absorption, absorption of organic dissolved substances, as a slow method. Absorption occurs either through a surface effect or with the help of the complex action of enzymes, as the organic substance is deposited on the surface or inside the cells. The reactions happen as soon as sludge and water come into contact. Suspensions and colloidal substances must be divided into smaller particles before such absorption. Dissolved organic substances initially adhere to the surface or are collected inside the biomass cells.

The separation between the biomass and treated water takes place in a lamella clarifier downstream the biological treatment. The treated water separated of the biomass overflows to the treated water channel, while the settled sludge is recirculated back in the biological tank. Because of biomass growth, excess biological sludge has to be taken out of the system based on specific calculations and measurements [22].

## B. Characteristics of GZR Water

The mentioned 28 tests were conducted on both of the collected samples from the GZR. The obtained results with comparison with the standards are shown below in Table IV.

According to the mentioned standards in Table V [23], GZR was severely polluted in May (i.e. DO=0.14 mg/L), but it was moderately polluted in the other months (January and March); this may returns to rainfall and melting of snow





TABLE IV CHARACTERISTICS OF GREATER-ZAB RIVER WATER SAMPLES

NO.	Parameter	Units	January/2015		March/2015		May/2015		WHO standards [10]
			Normal river	Mixed river	Normal river	Mixed river	Normal river	Mixed river	
1	pH	-	8.32	8.36	7.84	8.21	7.56	8.07	6.5-9.6
2	ORP	mV	134.4	136.7	193	204.55	28.01	47.6	
3	DO	mg/L	9.11	9.04	5.95	3.86	0.17	0.14	
4	TD Salts	mg/L	414	711	213	401	210	353	
5	Salinity	PSU	0.41	0.72	0.21	0.4	0.2	0.35	
6	Temperature	°C	6.3	5.77	13.37	17.34	17.11	20	30
7	Atm. Press.	mmHG	719.6	719.5	738.5	732.3	732.9	732.2	
8	TS	mg/L	900	1100	500	700	800	1100	
9	TSS	mg/L	500	600	200	300	600	700	30
10	TDS	mg/L	400	500	300	400	200	400	500
11	TVS	mg/L	200	300	200	300	400	500	
12	TnVS	mg/L	700	800	300	400	400	600	
13	T. Acidity	mg/L	12	28	8	12	8	16	
14	T. Alkalinity	mg/L	178.8	244	160	262	140	224	
15	T. Hardness	mg/L	170	280	196	296	156	268	
16	BOD <sub>5</sub>	mg/L	0.2	0.6	0.2	1.8	4.2	10.4	10
17	BOD/COD	-	-	-	-	-	0.85	0.73	
18	Turbidity	FTU	10.6	16.29	19.8	24.36	149	172.4	5.82
19	Chloride	mg/L	2.4	13.4	6	18	4	14	
20	Color	Pt.Co	49	57	26	42	27	784	
21	NH <sub>3</sub> -N	mg/L	0	0.3	0	0.1	0	0.9	
22	EC	ms/cm	388	664	358	805	338	776	500
23	Nitrite	mg/L	-	-	-	-	3	4	
24	Zinc	mg/L	-	-	-	-	0	0.01	
25	NO <sub>3</sub>	mg/L	-	-	-	-	8.25	31.5	
26	Phenol	mg/L	-	-	-	-	0.17	0.18	0.2
27	Oil and Grease	mg/L	-	-	-	-	0	0.08	

TABLE V WATER QUALITY STANDARD FOR RIVERS [23]

No.	Water Quality/Item	Non (Slightly) polluted	Lightly-polluted	Moderately-polluted	Severely-polluted
1	Dissolved Oxygen mg/L	DO $\geq$ 6.5	6.5>DO $\geq$ 4.6	4.5 $\geq$ DO $\geq$ 2.0	DO<2.0
2	BOD <sub>5</sub> mg/L	BOD <sub>5</sub> $\leq$ 3.0	3.0<BOD <sub>5</sub> $\leq$ 4.9	5.0 $\leq$ BOD <sub>5</sub> $\leq$ 15	BOD <sub>5</sub> >15.0
3	TSS mg/L	TSS $\leq$ 20.0	20.0<TSS $\leq$ 49.9	50 $\leq$ TSS $\leq$ 100	TSS>100
4	NH <sub>3</sub> -N mg/L	NH <sub>3</sub> -N $\leq$ 0.5	0.5< NH <sub>3</sub> -N $\leq$ 0.99	1 $\leq$ NH <sub>3</sub> -N $\leq$ 3	NH <sub>3</sub> -N>3
5	Point sources	1	3	6	10
6	Pollution Index Integral Value	S $\leq$ 2	2<S $\leq$ 3	3.1 $\leq$ S $\leq$ 6	S>6

It is clear from Table IV that the disposed wastewater from the KOR changed most of the GZR characteristics. ORP, TD Salts, salinity, temperature, TS, TSS, TDS, TnVS, acidity, total alkalinity, total hardness, chloride, COD, NH<sub>3</sub>-N, EC, zinc, phenol, nitrate, nitrite, and oil and grease values were increased at the mixing point of the river with the wastewater.

### C. Characteristics of Groundwater

Table VI shows the characteristics of two wells taken from the aforementioned locations.

TABLE VI CHARACTERISTICS OF WELL SAMPLES

NO.	Parameter	Units	January	March		May		Well and GW standard
			Agulan Well	Jadida Well	Agulan Well	Jadida Well	Agulan Well	
1	pH	-	8.43	7.21	7.52	7.46	7.49	Nil [8], 6.5-8.5 [21]
2	ORP	mV	124.4	629.8	253.05	20.9	93.4	
3	TD Salts	mg/L	549	330	285	280	276	
4	Salinity	PSU	0.55	0.32	0.275	0.27	0.27	
5	Temperature	°C	19.62	21.8	19.66	24.7	22.61	Nil [8]
6	Atm. Press.	mmHG	719.4	731.5	734.5	722.9	728.8	
7	TS	mg/L	700	400	400	900	700	
8	TSS	mg/L	200	300	200	0	200	Nil [8]
9	TDS	mg/L	500	100	200	900	500	1000 [25]
10	TVS	mg/L	100	300	300	400	300	
11	TnVS	mg/L	600	100	100	500	400	
12	T. Acidity	mg/L	20	8	8	20	12	
13	T. Alkalinity	mg/L	186	232	210	136	148	
14	T. Hardness	mg/L	180	246	260	160	204	500 as CaCO <sub>3</sub> [25]
15	Turbidity	FTU	0.5	0.38	0	1.58	0.24	< 5 [25]
16	Chloride	mg/L	9.4	21	10	12	10	Nil [8]
17	COD	mg/L	-	-	-	9	13	Nil [8]
18	Color	Pt.Co	23	17	18	13	14	No discoloration [8], 10 [25]
19	NH <sub>3</sub> -N	mg/L	0	0	0	0.3	0	0.005
20	EC	ms/cm	511	542	551	554	553	
21	Nitrite	mg/L	-	-	-	1	2	3 [11]
22	Zinc	mg/L	-	-	-	0	0.01	0.1[8], 3 [11]
23	NO <sub>3</sub>	mg/L	-	-	-	20	30	50 [8]
24	Phenol	mg/L	-	-	-	0.18	0.17	
25	Oil and Grease	mg/L	-	-	-	0	0	Nil [8]

According to [10], both wells were within the mentioned ranges, zinc was less than 0.1 mg/L and nitrate was less than 50 mg/L. The obtained results were compared with the WHO drinking water standard [10, 26] as well. The achieved results of pH (6.5-8.5), TDS (<1000), total hardness (<500), zinc (<3), turbidity (<5), and nitrite (<3) were remained within the range. According to [8], turbidity (<10 NTU) and chloride

(<200 mg/L) were remained within the range. In January and March, color and T. alkalinity values were exceeded the limits. Aziz [27] examined ground water quality in Iskan Quarter in Erbil City during Aug 2001 to July 2002, he concluded that sample collection of groundwater one or times per year is enough. Furthermore, the author stated that temperature of ground water remain around 22°C [27]. On the

other hand, Daham et al. [28] studied evaluation of ground water in Erbil City for drinking and domestic purposes. Practically, the ground water in Erbil City used as source for water supply (beside of water treatment plants on the GZR) in the City. Commonly, the obtained results in the present work agree with published data.

#### IV. CONCLUSIONS

Based on the obtained results, and comparing with the standards the following conclusions were outlined:

- a. The wastewater that resulted from the KOR contained high levels of pollutants.
- b. The GZR quality at mixing point with the treated KRWW was affected and polluted.
- c. The surrounded ground water sources were slightly polluted and not totally affected by the KRWW.

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