Groundwater contamination by salinity, microoorganisms and nitrogen compounds in Zahedan city, southeastern Iran

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Research Article

Keywords: Wastewater discharge well, Groundwater exploration, Nitrate, Water treatment plants, Urban groundwater, Waste disposal

Posted Date: December 1st, 2021

DOI: https://doi.org/10.21203/rs.3.rs-920120/v1

Abstract

Generally, the quality and availability of groundwater resources can be affected by urbanization. In this research, various impacts of urbanization on the height of the water table and quality of groundwater in an urban aquifer has been investigated for Zahedan city, Iran. The investigations indicated that the widespread use of wastewater discharge wells in the city area had increased the elevation of the water table by 2 to 6 meters and had reduced the salinity of shallow groundwater. The effluent in the city's sewage channel with high EC had no effect on the groundwater quality in the city due to the fact that the channel was cement-lined within the city area. Microbial surveys showed that elevated total coliforms were present in groundwater throughout the city area while fecal coliforms were only present at a limited number of sampling sites. In the central areas of the city, where the groundwater abstraction takes place at high rates from deep wells, the pollution was less. The wastewaters had high level of total coliform and fecal coliform contamination due to the discharge of domestic wastewater through wells and the dumping of solids wastes. The urban water supply network and water treatment plants samples were free of any microbial contamination. Finally, nitrate concentrations in the groundwater were high (27-392 mg/L) and in the wastewater were much higher (up to 600 mg/L).

1. Introduction

Groundwater is important for water supply in most of the urban centers in Iran. In fact, for food production and drinking water supply, groundwater is largely used in the world and has greatly contributed to development of cities (Drangert and Cronin 2004; Minnig et al. 2018; Moeck et al. 2017; Morris et al. 2007; Howard 2002). Due to a rapidly increasing global population and the demand for fresh water, the importance of groundwater resources has also greatly increased. However, the fairly easy access to these water resources in many urban areas has also caused significant environmental impacts due to changes in the water balance caused by the process of urbanization (Kalhor and Emaminejad 2019; Sheng et al. 2020; Bai et al. 2017).

Both the quality and availability of groundwater resources can be affected by increasing urbanization. This is because of the growth in the population density of the urban area and the increased demand for water, and the greater levels of waste production (Khazaei et al. 2004). The increase of roads and building density in urban areas extends the impermeable area and can change the natural drainage system at a local or regional scale. The increased coverage of impermeable surfaces in urban areas increases the proportion of rainfall that becomes runoff (Oka 1993; Hall 1984; Khazaei et al. 2004). If this runoff is routed to unlined sewerage systems or ponded increased groundwater recharge may take place (Rushton et al. 1988; Khazaei et al. 2004). Additionally, another source of groundwater recharge can be leakage from the water supply network system in an urban area (Lerner 2002).

The process of urbanization can also cause changes in quality of groundwater beneath urban areas. These changes include increasing concentrations of nitrogen compounds due to poor solid waste and wastewater management practices, increased groundwater salinity, groundwater contamination by petroleum compounds, and as well as microbiological contamination (Ibe and Njemanze 1999). Therefore, urbanization may affect the water table, the flow direction, and the water quality of aquifer. The outcome of these effects may result in critical environmental problems. In such conditions, to address these problems and to prevent further degradation, it needs to effective management of the groundwater. However, efficient management is only possible when the various impacts of urbanization on quantity and quality of groundwater are known (Khazaei et al. 2004).

To assess of impacts of urbanization on groundwater, researchers have used remote sensing techniques and geographical information systems (Al-Bakri and Al-Jahmany 2013; Chaudhary et al. 1996; Lalbiakmawia 2015; Mukherjee 2008; Solomon and Quiel 2006; Kalhor and Emaminejad 2019), hydrogeochemical investigations (Khazaei et al. 2004; Sheng et al. 2020; Minnig et al. 2018; Zhang et al. 2020; Li et al. 2009; Keraita et al. 2003), modeling (Khazaei et al. 2004; Zhang et al. 2019; Lamichhane and Shakya 2020; Lamichhane and Shakya 2020; Palanca-Tan R 2017) and microbiological approaches (Khazaei et al. 2004; Hynds et al. 2012; Michalopoulos et al. 2016; Vasudevan et al. 2020; Nowicki et al. 2019).

In the Zahedan city, the rapid growth of urbanization and lack of use of wastewater collection and treatment systems, as well as lack of urban development planning can cause groundwater pollution, and spatial and temporal changes in the elevation of the water table. The city's sewage disposal system is carried out without urban planning and wastewater systems installed by individuals are commonly unregulated. Wastewater in the area is commonly discharged through hand-dug wastewater discharge wells which can cause groundwater contamination by sewage. In addition to causing groundwater contamination, the widespread use of wastewater discharge wells can increase the elevation of the water table.

In the northern and northeastern parts of the city, the water table is close to the ground surface and in this part of the city, due to the inefficiency of the water supply network, the domestic water supply for some residents is supplied through hand-dug wells (Fig. 1a). Therefore, due to the close proximity water supply wells to the wastewater discharge wells, there is a high risk of local water supplies being contaminated with microorganisms and chemical compounds derived from sewage. In addition, there is a flow of domestic sewage into the streets of city, which mainly flows to the channels of sewer in the city and has increased the potential for the transport of pollution to the groundwater and the spread of the disease (Fig. 1b and c). In the city, 14 water treatment plants exist that treat water supplied from the Zahedan aquifer. In addition, part of the water supply of the city is provided from a freshwater source that transfers water from the Chah-Nimeh reservoir about 250 Km north of Zahedan city. Hence, the objective of this study is to assess various impacts of urbanization on the elevation of the water table and on groundwater quality. This study has evaluated characteristics of groundwater contamination beneath Zahedan city through the evaluation of: (i) the temporal and spatial variation of the water table elevation and of groundwater EC; (ii) the assessment of changes in the chemical composition of groundwater beneath the urban area (iii), the assessment of the effects of a saline water channel in the city (iv); the use of a water mixing model; and (v) the assessment of the extent and severity of groundwater contamination by nitrate, nitrite, and microorganisms.

2. Materials And Methods

2.1. Site description

The Zahedan city overlies the Zahedan aquifer within the Zahedan catchment which covers an area of about 146 km^2 in the Sistan and Baluchestan provinces in Iran. The average annual precipitation in the area from 2003 to 2017 was 72.46 mm. Numerous basement rock units outcrop as isolated hills within the plain. These rock units are comprised of igneous rocks and old (upper Cretaceous and Palaeocene) and young (middle Tertiary) flysch materials which are exposed in surrounding mountains and individual hills (Fig. 2). The old flysch is composed of alternating layers of sandstones, shales, mudstones, siltstones, and thin layers of limestone. The young flysch is observed in the southern and western parts of the catchment as hills and in the eastern and northern parts as mountains, and consists of conglomerates, sandstones, thin layers of marl, shales, mudstones, and siltstones along with evaporite beds containing halite and gypsum. These evaporites in the young flysch can cause the degradation of groundwater quality in the study area. The mountains with a northwest-southeast trend in the areas to the south, west, and northwest, are formed from granite rock of Eocene - Oligocene age.

The Zahedan plain has gradually filled with material that was derived from the erosion of the surrounding mountains. In part the plain, the alluvial material has formed an unconfined aquifer known as the Zahedan aquifer that which has a saturated thickness that ranges from 20 - 40 m. In the study area, the rivers are ephemeral and their flow direction is generally towards the northeast. According to Khazaei et al. (2004), the water table in Zahedan city has been a general decline since 1977 due to over-abstraction. In some places, the extent of this decline has reached about 20 m.

2. 2. Sampling And Analysis

In total, 191 water samples were collected for this study from groundwater, sewage, the water supply network, and from water treatment plants (Fig. 3). The collected samples were chemically analysed for the major ions, nitrate and nitrite, and also for the assessment of microbial contamination in 2017 and 2018. To remove suspended particles, water samples were filtered in situ using a 0.45 µm syringe filter and then moved to clean polyethylene bottles (Fig. 1d). Samples that were collected for the analysis of major cations were treated with HNO_3 (the purity of 65%) to ensure that ions stayed in solution and did not adsorb onto sample container walls. Then the samples were sent to relevant laboratories for chemical analysis. Values of temperature, electrical conductivity (EC), and the pH of water samples were measured at the sampling site. The major cations (Ca, Mg, Na and K), the anion HCO_3, and other anions (SO_4, Cl, nitrate and nitrite) were analyzed using an ICP-MS device, titration, and ion chromatography (ICP) device respectively (Fig. 1e). To evaluate the uncertainty of the measurements, the ion balance equation was used and the ionic balance error for each water sample was calculated to be less than 5%. The physicochemical characteristics of various water samples in the study area are shown in Table 1.

In order to undertake microbial analysis and for the preparation of special media for bacterial culture, the water samples were transferred to the laboratory for the investigation of the total coliforms and fecal coliforms, and the number of heterotrophic microorganisms. Hence, three methods of multi-tube fermentation, presence-absence, and purplate were used according to standard methods for water and wastewater testing (Roodgar et al. 2017).

Table 1

The physicochemical characteristics of various water samples in the study area (EC in µS/cm and ions in mg/L)

Sample	Name	pH	EC	Ca	Na	Mg	K	Cl	SO_4	HCO_3	NO_3	NO_2	NH_3	Error
Well sampling points	Q	7	7550	240	1575	214	50	1280	2036	750.54	296.9	<0.1	1.99	2.1
	A_1	6.78	15280	308	3082	422	100	3910	3020	988.93	46.4	<0.1	0.00	-0.8
	A_2	7.69	4750	160	910	54.4	13	887	1283	164.21	29.3	<0.1	0.14	-2.3
	A_3	6.79	9340	330	1660	288	42	1850	2063	741.03	391.8	<0.1	3.69	0.1
	A_4	7.51	11220	462	2260	317	37	2450	2740	725.9	213.6	<0.1	2.67	2.5
	A_5	7.02	10460	408	1840	407	44	2185	2760	634.64	312.2	<0.1	3.68	0.4
	A_6	7.27	9010	214	1870	148	48	1880	1757	758.11	47.6	36.6	1.05	1.3
	A_7	6.89	6150	238	1157	119.4	29	1164	1177	963.56	81.7	<0.1	1.76	-1
	A_8	7.75	8930	132.26	1316	327.56	33.6	1600	1831.4	709.06	141.4	<0.1	-	-2.7
	A_9	7.3	4530	152.3	626	129.76	12.6	717	890.2	653.92	38.9	13.1	-	-4.3
	A_{10}	7.29	12770	349.5	2100	375.68	39.9	2743.2	2595	712.97	117	10.6	-	-1.3
	A_{11}	7.49	9630	589.18	1316	178.36	33.6	1564.8	2624	468.48	166	<0.1	-	-3.2
	A_{12}	7.9	9560	238.88	1470	298.89	36	1605.6	2017	619.76	287	<0.1	-	-0.2
	S_1	7.25	5070	255	848	104	24	703	1560	412.36	150.2	<0.1	0.15	-2.1
	S_2	7.19	4710	183	820	84.7	22	760	1278	397.48	153.5	<0.1	0.21	-4.2
	S_3	7.44	3190	124	570	39.5	14	412	967	336.72	34.85	<0.1	0.17	-4.4
	S_4	7.79	4570	100.5	930	47.6	22	602	1100	544.12	354.2	<0.1	0.25	-4.3
	S_5	7.16	12710	452	2300	309	39	2995	3000	401.14	221.5	<0.1	1.74	-2.5
	S_6	7.4	6830	168	1250	171.6	50	1107	1626	622.2	377.3	<0.1	0.24	-1.9
	S_7	7.31	8040	507	1270	244	34	1588	1948	541.68	157.4	<0.1	2.65	2.5
	S_8	7.05	6720	209	1248	132	32	1156	1467	662.95	152.9	<0.1	0.65	0
	S_9	6.46	6010	173	1200	111	30	1157	1000	1071.16	55.2	19.2	0.14	-0.7

Table 1
(continued)

Sample	Name	pH	EC	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3	NO_2	NH_3	Error
Well sampling points	F_1	6.75	8410	406.81	225.5	1210	36	1825	1388.3	620.74	47.9	<0.1	-	0.8
	F_2	7.45	6970	312.8	136.32	1126	24	1367	1477	206.79	226	<0.1	-	0.2
	F_3	7	5708	314.63	124.42	742	16	739.8	1235.6	513.62	177.2	<0.1	-	0.8
	F_4	6.98	5440	302.6	144.1	707	16.5	781.85	1396	242.78	123.15	<0.1	-	1.1
	F_5	7.15	6330	424.85	91.61	879	13.5	714	1816.1	336.23	205	<0.1	-	0.5
	F_6	7.34	5480	301.99	125.37	755	16.4	707.8	1350.4	380.39	229.6	<0.1	-	0.7
	F_7	6.87	5852	272.94	104.73	858	18.5	982.6	1023.5	434	111.7	<0.1	-	1.9
	F_8	7.03	4930	174.75	147.99	725	20.5	785.6	974.3	485.07	127.8	<0.1	-	0.6
	F_9	7.17	6240	216.43	120.29	891	20	1057.5	1065.6	389.42	71.2	<0.1	-	0.5
	F_{10}	6.97	5960	324.25	138.51	803	18	707.6	1685.6	260.84	183.8	<0.1	-	0.7
	F_{11}	7.15	6060	305.81	121.74	896	21	744.4	1719.6	273.52	184.8	<0.1	-	0.5
	F_{12}	6.83	5480	256.51	158.19	767	19.5	704.25	1513.85	239.12	255.3	<0.1	-	0.4
	F_{13}	7.18	4510	121.08	105.63	762	22	721.8	917.2	447.74	33.2	<0.1	-	1.3
	F_{14}	7.16	3530	73.93	73.89	567	20	451.5	613.2	533.14	27.1	<0.1	-	0.5
	F_{15}	7.26	6310	314.63	128.3	975	19	1050.6	1166.2	653.19	240.25	<0.1	-	0.6
	F_{16}	7.58	6001	335.26	88.19	863	24	592.8	1670.6	429.44	191.8	<0.1	-	0.5
	F_{17}	7.26	8290	327.85	204.12	1315	14.5	1709.1	1512.2	603.9	48.2	<0.1	-	0.3

Table 1 (continued)

Sample	Name	pH	EC	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3	NO2	NH_3	Error
Well sampling points	F_{18}	7.21	5380	214.58	114.59	759	22	606.4	1100	649.04	176	<0.1	-	0.3
	F_{19}	6.84	6410	210.42	137.54	1092	24.5	1349.35	716.7	849.12	161.95	<0.1	-	0.4
	F_{20}	7.18	6580	302.1	163.78	950	24.8	1114.8	1008.8	872.3	189.6	<0.1	-	0.7
	F_{21}	7.21	7790	300.6	186.87	1245	24.5	1355.7	1516.5	713.94	203.45	<0.1	-	0.3
	F_{22}	7.28	5340	251.3	68.28	801	16.8	635.6	1088.2	567.06	197	<0.1	-	0.4
	F_{23}	7.12	3630	97.6	103.2	595	24	539.64	752	507.52	34.96	<0.1	-	0.3
	F_{24}	7.06	5660	143.89	99.39	947	32.2	587.6	1163.4	605.12	393.4	<0.1	-	0.4
	F_{25}	6.84	4880	150.3	129.52	739	22.5	765	918.1	558.76	28.5	<0.1	-	0.7
	F_{26}	6.99	11770	456.91	364.5	1744	22.5	2104.6	2750.8	561.44	154.2	<0.1	-	0.5
	F_{27}	6.99	7680	377.95	169.37	1170	21	1489.7	1428.6	519.96	183.75	<0.1	-	0.7
	F_{28}	7.11	6610	204.41	160.38	1115	25.8	904.1	1440.4	793.49	213.8	<0.1	-	0.5
	F_{29}	7.34	5870	108.22	75.33	1162	19	630.9	1456.6	606.34	231.5	<0.1	-	0.7
	F_{30}	7.09	7250	199.6	141.18	1330	28	1271.4	1353.5	670.51	179.8	<0.1	-	1.5
	F_{31}	7.11	5400	220.44	103.28	780	27	607.15	1215.5	541.68	132.55	<0.1	-	0.7
	F_{32}	7.03	7460	268.54	130.01	1303	26.4	1105.6	1454.2	711.5	372.7	<0.1	-	-5
	F_{33}	6.89	5800	276.92	75.09	972	19.5	998.5	913.6	692.72	181.8	<0.1	-	1.1
	F_{34}	7.17	6140	184.37	153.82	1030	22.8	1217	869	901.09	142	<0.1	-	-1.5

Table 1 (continued)

Sample	Name	pH	EC	Ca	Na	Mg	K	Cl	SO_4	HCO_3	NO_3	NO_2	NH_3	Error
water treatment plants	Fw_1	6.08	360	0.72	66	1.99	1.8	61.62	7.85	44.16	53.36	<0.1	0.05	-5
	Fw_2	6.42	239	3.85	42	2.58	0.9	32.86	13.36	43.19	14.31	<0.1	0.00	2.6
	Fw_3	6.47	287	4.01	57	3.06	0.9	32.05	12.48	97.36	15.34	<0.1	0.09	-0.8
	Fw_4	6.26	505	3.53	97	3.69	4.8	107.88	20.08	39.04	40.99	<0.1	0.02	0.6
	Fw_5	6.59	161.8	1.68	31	2.87	1.9	23.9	14.26	17.81	21.92	<0.1	0.05	3.1
Urban network of water supply	Uz_1	6.89	9080	319.04	1453	223.56	25	1941.8	1469	756.64	66.4	<0.1	0.01	-0.2
	Uz_2	7.26	1800	69.1	162	36.74	6.2	238.82	363.92	281.58	48.94	<0.1	1.78	-5
	Uz_3	7.99	1246	20.84	127	20.22	5.6	132.46	240.62	285.48	4.68	<0.1	0.09	-5
	Uz_4	6.68	8120	254.91	1372	203.63	43.2	1872.2	1412	875.96	44	<0.1	0.06	-3.6
	Uz_5	7.7	1240	43.77	114	48.5	5.8	155.98	285.2	253.76	6.66	<0.1	1.19	-5
	Uz_6	7.73	1237	43.29	114	44.23	5.8	137.54	251.38	247.66	6.16	<0.1	0.13	5
	Uz_7	7.83	1234	43.29	122	49.09	5.8	154.92	283.34	248.88	7.2	<0.1	0.12	5
	Uz_8	6.63	6300	310.62	891	141.67	21.5	1313.1	1362	656.36	210.2	<0.1	0.04	5
	Uz_9	6.98	1796	69.9	240	37.62	5.6	244	378.2	197.88	55.28	<0.1	2.88	-4.7
	Uz_{10}	8.24	1252	42.24	138	47.97	5.4	138.7	261.22	225.94	7.36	<0.1	< 0.01	-3.7
	Uz_{11}	8.1	1242	56.43	140	34.31	5.8	148.86	276.38	228.63	6.92	<0.1	0.01	5

Table 1 (continued)

Sample	Name	pH	EC	Ca	Na	Mg	K	Cl	SO_4	HCO_3	NO_3	NO_2	NH_3	Error
Sewage sampling points	Sw_1	7.41	2340	75.03	190	73.09	27	314.96	338.12	16.62	0	6.8	16.40	5
	Sw_2	7.57	6500	196.39	760	181.52	30.8	1305.5	1565.8	14.96	0	8.6	0.37	-5
	Sw_3	7.07	2890	90.18	415	47.39	25	492.15	384.45	12.76	0	<0.1	0.16	-1.1
	Sw_4	7.78	18600	614.83	2866	437.89	69.6	3026.5	4754.5	46.14	628	<0.1	-	-0.2
	Sw_5	7.84	18110	621.24	2798	438.86	66.7	3029	4711.5	47.33	573.5	<0.1	-	-0.6
	Sw_6	7.65	19000	921.84	2772	521.48	76.8	3262.8	4616.4	37.11	468.4	94.8	6.01	5
	Sw_7	7.9	17820	799.2	3000	445.66	69	3357.5	4872	64.15	594	<0.1	-	-0.1
	Sw_8	8.05	17900	698.19	2900	443.23	69.6	3188.5	4649	56.18	520	<0.1	-	0.1
	Sw_9	7.71	18400	708.61	2900	452.95	69.6	2861	3799.5	86.87	427	<0.1	-	0.1
	Sw_{10}	7.69	18360	695.79	2965	444.2	69	3423.5	4677.5	52.37	494	<0.1	-	0.1
	Sw_{13}	7.92	12440	510.62	1779	298.4	44.1	2147.5	2893	42.32	337.5	<0.1	-	-0.4
	Sw_{14}	8.07	12420	515.43	1803	346.03	44.1	1913.5	2523.5	64.59	231.5	<0.1	-	-0.6
	Sw_{15}	7.54	9980	367.13	2000	300.35	52.8	2675.2	3467	14.32	168.4	<0.1	2.81	-1.7
	Sw_{16}	7.72	10460	331.06	2176	214.33	52.8	2832.4	3766.8	11.34	143	<0.1	2.65	-5

2.3. Modeling and statistical methods

Statistical analysis

Pearson's correlation coefficients for depth, discharge (Q), nitrate concentration, and percentage of microbial contamination were calculated according to normalized data.

Mixing calculations

In this research, the mixing ratio of water samples was estimated on the local scale. According to Scheiber et al. (2018) to define the composition of end-members and their percentage in each water sample, the procedure was included:

i. Classifying various water sources as end-members.
ii. Determining the hydro-chemical properties of end-members and mixed water samples.
iii. Choosing hydro-chemical species to be applied in the assessment.
iv. Determining the standard deviation of each species in end-members and water samples as uncertainty.
v. Import the data to the MIX code.
vi. Estimating the mixing ratios in each water sample.

The MIX code is constructed on the method of maximum likelihood for obtaining the mixing ratios (Scheiber et al. 2018). The MIX PROGRAM v1.0 (Carrera et al. 2004) was used to evaluate mixing ratios in case of uncertain endmembers. The methodology of this approach was that in conservative species coming from a definite number of endmembers, which were mixed in a definite number of samples with various ratios (Scheiber et al. 2018) with the minimum error value. For every species, it is essential to consider a standard deviation to describe the reliability of results and measurements (Scheiber et al. 2018). Therefore, errors of analytical and sampling should be considered.

3. Results And Dissection

3.1. Flow direction

Maps of iso-potential and groundwater flow direction in Zahedan city for 2003 and 2018 (Fig. 4a) showed that groundwater flow tends to the center and east of the study area. The difference in groundwater table height between 2002 and 2018 in the study area (Fig. 4b) indicated that the height of the water table in the outside of the city is decreasing but is increasing within the city area. Therefore, the time series elevations of the water table for two observation wells outside the urban area (P4 and P5) and two observation wells within the city area (P25 and P27) were considered (Fig. 5a and b). It can be natural for such a phenomenon to occur in cities without a sewage collection system, such as Zahedan. However, due to an existing large number of exploitation wells in the city (155 wells) and low rainfall (average annual rainfall, 72.46 mm), large rises in the height of the water table would not be expected to take place. Therefore, other factors must have contributed to the observed rise in the the elevation of the water table. The most probable factor could be the effect of the freshwater transfer scheme from Zabol to Zahedan city, which commenced in 2003 and has continued to the present. After the initiation of this project, the amount of groundwater abstraction in the city area has decreased by 500 L/s from the aquifer in the city of Zahedan. Since 2011, almost no groundwater has been discharged by the water and wastewater company in the city, and that volume has been provided by the transferred freshwater from Zabol. Additionally, the transfer of water to Zahedan city has accelerated urban development in the city area. Therefore, with the increase of water consumption and the infiltration of domestic wastewater into groundwater through wastewater discharge wells, the water table has risen at a higher rate than would have otherwise been expected.

Therefore, in addition to the effect of transferred water on the quantity of groundwater in the study area, it is expected to affect the quality of groundwater too. Hence, the time series of EC in groundwater of some exploitation wells for outside (Fig. 5c) and inside the city (Fig. 5d) as well as in precipitation, have been considered from 2004 to 2017. These diagrams showed that the EC of groundwater has had a decreasing within the city area and an increasing trend outside of the city. Since the temporal variation of precipitation does not have a specific trend, the effect of precipitation on EC can be negligible. Therefore, due to groundwater abstraction and reduction of the height of the water table in the aquifer and extraction of groundwater with a higher salinity from the depths of the aquifer, a decrease in the quality of the pumped groundwater is occurring over time in the study area. This condition is observed for wells outside of the city. However, due to the transferring of Zabol's water and its consumption in the city and its infiltration through wastewater discharge wells, there has been an increase in groundwater quality (i.e., a reduction in salinity) within the city area. Also, urban floodwater and sewage are discharged outside of the city (northeast) through the sewage channels (Fig. 1b). The floor and walls of these channels in the inner parts of the city are covered with cement while for the outskirts of the city there is no cement cover. Therefore, the probability of penetration of floodwater and sewage into the ground is low in urbanised areas. As a result, it can be said that they had no effect on the aquifer while there is a possibility of sewage and urban flood penetration into the ground.

3.2. Water type

The chemical composition of the analysed water samples was determined using a Piper trilinear diagram. This assessment indicated that the chemical composition of groundwater was of $NaSO_4$ and NaCl types. The spatial distribution of water type for groundwater showed that the $NaSO_4$ type of composition occurred in the aquifer in the western and southern parts of the study area (Fig. 6a).

Water samples from the water supply network, like groundwater, had $NaSO_4$ and NaCl composition types. Water samples from the supply network near the northeastern outskirts of the city had a NaCl composition type (samples Up1, Up4, and Up8: see Fig. 6b) while for other parts of the city water, the reticulated water supply had a $NaSO_4$ composition type.

The chemical composition of water from the city's water treatment plants was of $NaHCO_3$ and NaCl composition types. These water treatment plants are located mainly in the central and northeastern parts of the city. Among these stations, the stations located in the central part of the city area have a $NaHCO_3$ water composition type, while the stations located in the surrounding area have a NaCl water composition type (Fig. 6c).

3.3. Salinity

The electrical conductivity of groundwater was found to vary between 3190 to 15280 µS/cm in the study area. The lowest EC was found in well S3 in the west and the highest electrical conductivity in well A1 in the southeastern part of the study area. However, in the study area, wells have various depth and in the saturated part of the aquifer, the entire length of the walls of the wells equipped with screens. Therefore, these differences of the EC can be resulted due to vertical salinity gradient in the aquifer. In general, if well A1 is ignored, the EC of groundwater has increased from the west to the northeastern parts of the study area (Fig. 7). This distribution is consistent with the groundwater flow direction in the study area (Fig. 4a).

Water with a low EC (about 1200 µS/cm) is distributed from the water supply system in the western and southern parts of Zahedan city. The infiltration of this domestic water through wastewater discharge wells into groundwater is one of the reasons for lower groundwater electrical conductivity in this part of the city. By contrast, in the eastern and northeastern parts of the city, water with high EC (about 7000 µS/cm) is distributed in the water supply network, and the infiltration of this water through wastewater discharge wells affected the quality of groundwater in these areas. Another possible source of increased EC in the groundwater is the presence of wastewater from the municipal water and wastewater treatment plant in the Zahedan city. This wastewater is saline and has an electrical conductivity of about 20,000 µS/cm. This water is transported through a cemented channel from the city center in a northeasterly direction, and then enters a natural waterway on the outskirts of the city and leaves the city limits (Fig. 7b and 1b).

In order to identify the effect of this saline water on the quality of groundwater resources, the relationship between the electrical conductivity of pumped wells to the distance from in the cemented cemented and unlined parts of the saline water discharge channel for each well was determined (Fig. 7c). The results indicated that in areas where saline wastewater is flowing in unlined parts of the channel and in a natural waterway, with a moderate correlation coefficient ($r = -0.5$), the electrical conductivity increases with proximity of wells to the channel. However, for the lined sections of the channel, there was no significant relationship between the distance with electrical conductivity ($r = -0.15$). Hence, saline wastewater has no role in decreasing groundwater quality in the city, but does influence groundwater quality outside of the city.

Except in special cases, the EC in groundwater usually increases with increasing the well's depth while the relationship of electrical conductivity with the depth of the well has a partly negative trend in the groundwater of the study area (Fig. 8). As mentioned that time variation of EC and water table in the groundwater outside the city (urbanization) have an increasing and decreasing trend respectively. This indicates the salinity of groundwater increases with depth in the aquifer outside of the city area. However, this is not the case inside of the city area as indicated by the negative relationship between EC and well depth. To examine this issue, a few points should be considered. The saline sewage channel inside the city has a cemented cover and prevents the effects of this source of saline water on the groundwater of wells with deeper depths in the center of the city. By contrast, the infiltration of saline sewage on the outskirts of the city has affected the quality of groundwater that is pumped from shallow exploitation wells. In addition, the presence of Zabol's water in the water supply network with low electrical conductivity and infiltration through wastewater discharge wells into groundwater has reduced electrical conductivity inside the city. Also, in shallow wells on the outskirts of the city, evaporation can increase the TDS in groundwater. Finally, these shallow wells are located mainly in the northern part of Zahedan, at the end of the groundwater flow path in the study area, where water travels a longer distance and contains a higher TDS content. Therefore, according to the above, it can be stated that inside the city, like outside the city, in the direction of depth, there is an increase in the salinity of the groundwater. Since the shallow wells are located in parts with high salinity, a false negative relationship between well depth and salinity is created.

3.4. Water mixing model

According to physicochemical characteristics and groundwater flow direction, on a local scale, a water mixing model with the three end-members was considered. The end-members were included groundwater in the western (W.G), southern (S.G), and northwestern (NW.G) parts of the city, and Zabol's water (Z.W). Initially, all physicochemical characteristics of groundwater samples were selected for quantifying the mixing ratios of end-members in the different water samples. According to the principal component analysis (PCA), in this first analysis, a total of the variance of 74% was gained with six major factors or five eigenvectors. The first principal component explains 32% of the variance and most of the components (factors) contribute positively with the exception of EC, SO_4, Cl, Na, Ca, K and Mg. The second, third and fourth principal component explains 11%, 9%, 8%, 7% and 6% of the variance respectively. Omitting the physicochemical characteristics was used step by step in the PCA analysis to achieve the most variance. Finally, EC, Ca, Mg, Na, Cl and SO_4 were considered, and the third eigenvector explains 89% of the total variance. As mentioned by MIX PROGRAM software (Vazquez-Suñe and Carrera 2004) with respect to the minimum error value, the percentages of the end-members in each groundwater resources were calculated. In this research errors of analytical and sampling were considered for minimum error value (standard deviation values ranged from 5–10%). However, after calibration, the mixing ratios in each groundwater sample were obtained. The results showed that the Z.W and NW.G have the highest fraction of mixing in the groundwater resources of the study area. The NW.G is detected with the most percentage in the northern parts of the city and its impact decreases to the south of the city (Fig. 9a). Moreover, in that part of the city where the Z.W has the most recharge to the water supply network, the Z.W has the most mixing with groundwater resources (Fig. 9b).

3.5. Nitrogen compounds

Nitrate concentration varied from 27 to 392 mg/L (as N) in the groundwater of the study area. Since the WHO (2017) considers 50 mg/L (as N) as the maximum concentration of nitrate in international standards for drinking water, about 82% of the water samples were higher than that. Therefore, it indicated that groundwater was unhealthy for humans in the urban area of Zahedan. The high level of nitrate in groundwater is most likely due to the infiltration of wastewater through wastewater discharge wells, which is one of the main sources of the groundwater recharge in the study area. As there is no agriculture and large industry in the city of Zahedan, and the most probable source of nitrate is likely to be the infiltration of domestic and hospital wastewater through wastewater discharge wells in the study area. The distribution map of nitrate ion showed that nitrate had an increasing trend to the north of the region (Fig. 10a). The minimum and maximum contents of nitrate were located in well F14 and A3 in the southwestern and northern parts of the study area respectively. In the northern areas of Zahedan city, where nitrate had a higher concentration, the water table was very close to the ground surface (water table depth was less than one meter). In this part of the region, due to the inefficiency of the drinking water piping network (because of low water pressure or blocked water meter), some house wells have been dug for domestic water supply (Fig. 1a). These wells are mainly located near the wastewater discharge wells and therefore have the potential to affect the health of residents who use their own wells for domestic water use. Additionally, the elevated concentrations of nitrate in groundwater in the northern part of the city may be due to seepage from the sewage system, as the floor and walls of the main sewage channel in this area are unlined.

According to the results of groundwater analysis in the study area, nitrite ion was detected in only five samples that related to wells F20, A10, A9, A6 and S9 (Fig. 10b). Nitrite concentrations varied between <0.1 and 37 mg/L with the highest concentrations being observed in well A6 in the eastern part of the study area. Since nitrite is the intermediate compound between ammonia and nitrate, its stability in water is low and it is rapidly converted to ammonia or nitrate. Therefore, it generally has a low concentration in water samples. However, the presence of this ion in the water samples can be confirmed the contamination of groundwater with sewage. Although high nitrite concentrations may be associated with other sources of contamination.

The minimum and maximum concentrations of ammonia ions in groundwater sources were < 0.01 and 3.69 mg/L, respectively. The highest concentration of this ion was in well A3 in the northern part of the study area and the lowest concentration was measured is in well A1 in the southeastern part of the study area. The distribution map of ammonia ion showed that this ion had an increasing trend to the north of the region (Fig. 10c).

3.6. Microbial contamination

The results of the microbial analysis of groundwater showed that in the first stage (possible stage) from 43 samples only 4 samples (including S3, F4, F8 and F19) were free of contamination that were mostly located in the central part of the study area while other water samples showed contamination at this stage.

Samples with positive and negative signs of contamination from the previous stage moved to the confirmation stage. In this stage, it was found that 6 samples (including S3, F4, F8, F15, F16 and F19) were free of contamination and the other samples showed negative signs of contamination. At this stage, the positive contamination indicated the presence of coliforms in the groundwater of the study area. In this stage, like the possible stage, in the central part of the study area, the amount of contamination was low (Fig. 11a). Considering that the number of exploitation wells was higher in this part area, it can be concluded that increasing the amount of groundwater abstraction was one of the factors that had reduced pollution; Because with the increase of discharge, the drawdown cone also increased and the volume of groundwater abstraction from deeper depths increased and the percentage of groundwater participation that affected by wastewater discharge wells and sewage, decreased. The bacteria that were detected include Escherichia coli, Enterobacter, Klebsiella and Citrobacter. However, it cannot be said for sure that groundwater has fecal contamination. This is because coliforms do not necessarily have a fecal origin, and the presence of contamination must be confirmed in the complementary stage to ensure the presence of fecal coliforms. The samples analyzed in the possible stage transferred to the complementary stage too. The results of the analysis showed that at this stage seven samples were contaminated and the other samples were not. Contamination of the samples at this stage confirmed the presence of fecal coliforms in the groundwater. Wells contaminated with fecal coliforms include S2, A3, A9, S10, F10, F18, and F38 (Fig. 11b).

Due to the fact that with increasing fecal contamination, the amount of nitrate is expected to increase, the correlation of these two parameters was considered for the sampling sites (Fig. 11c) and this Figure confirmed that. The fecal contamination did not have any trend in the groundwater of the study area and the polluted groundwater had an irregular point distribution. Therefore, sources of the microbial contamination were from discrete points in the study area rather from diffuse pollution. A field survey of contaminated sites showed that well A3 was drilled near a wastewater discharge well and sewer channel that was unlined, as it did not have a cement lined floor and walls. Well A9 is located near a livestock yard in the west of Zahedan city and so animal wastes are likely to be the source of microbial contaminated at this sampling site. The well S2 is located in a garden and the presence of animal manure as a fertiliser may be the cause of contamination of the well. On the ground surface, no evidence of microbial contamination sources had been observed for other wells. Hence, it was possible that the effluent from wastewater discharge wells had somehow spread to the groundwater of the pumping wells.

Microbiological analysis of the water samples related to the sewage channel indicated that all the samples were contaminated in all three stages. As a result, it can be said that sewage channels in all areas were contaminated with coliforms and feces. Domestic wastewater and wastewater from the municipal water and wastewater treatment plant were discharged into these channels. Moreover, sometimes the remains of animal carcasses and their excrement and garbage are dumped into channels by butchers (Fig. 1c).

Samples from the water treatment plants and municipal water supply network were analyzed using the presence-absence method, because of the low probability of contamination for these samples. The results showed that all samples were free of microbial contamination.

The results of testing for heterotrophic microorganisms indicated that that, like the multi-tube fermentation method, the number of heterotrophic microorganisms in the central part of the study area was lower than the other parts of the area (Fig. 12a). Samples from wells S1, S2, A6, A7, F11 and F13 had the highest amount of heterotrophic microorganisms. Moreover, the amount of these microorganisms inside the water treatment plants was low and in the range of 25-5 Cfu/mL (Fig. 12b). Also, the number of microorganisms in the sewer was very high, and more than 5700 Cfu/mL.

The correlation coefficient between the variables of discharge and depth of exploitation wells, nitrate and the most probable number of coliform in three stages in samples with coliform contamination (Table 2) showed that there was a positive correlation between the first, second and third stages. Also, the positive correlation between nitrate and the third stage of fecal contamination indicated that they can have the same source. The stages of determining microbial contamination showed a negative correlation with the depth and discharge of wells. As seen before in the central part of the city, where the water exploitation rate was high, the contamination was also lower than in other areas. On the other hand, due to the fact that wastewater discharge wells have less depth than exploitation wells, with increasing the depth of exploitation wells, most of the groundwater abstraction takes place at a much greater depth than discharges from the wastewater discharge wells. This enables sufficient groundwater travel time for microorganisms to dies off and to be filtered by the aquifer sediments.

Table 2

Correlation between well's depth, discharge (Q), nitrate concentration and percentage of microbial contamination (three stages of 1, 2 and 3) related to groundwater resources in the Zahedan city

	Q	**Depth**	**NO_3**	**Stage 1th**	**Stage 2th**	**Stage 3th**
Q	1					
Depth	0.539	1				
NO_3	-0.089	-0.136	1			
Stage 1th	**-0.860**	**-0.718**	0.076	1		
Stage 2th	**-0.868**	**-0.727**	0.061	**0.996**	1	
Stage 3th	-0.453	**-0.850**	**0.584**	**0.509**	**0.504**	1

4. Conclusions

In this study, various impacts of urbanization on the elevation of the water table and water quality in an urban aquifer had been investigated for Zahedan city, Iran. The assessment of the groundwater hydrochemistry indicated that the groundwater had a $NaSO_4$ composition type in the western part of the city and a NaCl composition on the eastern side of the city. The highest concentration of nitrate measured in groundwater within the city area is currently 392 mg/L, compared to a maximum level of 295 mg/L that was measured 16 years ago. The transfer of water from Zabol (the Chah-Nimeh reservoir) to Zahedan city has improved the salinity of Zahedan aquifer and also has increased the height of the water table in the city. At the time of Khazaei et al.'s (2004) research, the groundwater table had dropped by 5 to 15 meters while after 16 years this study showed that the height of the water table has increased by about 2 to 6 meters within the city area, while outside the city water table elevation has decreased by about 2 to 8 meters. Saline effluent with an electrical conductivity of about 20,000 µS/cm from a wastewater treatment plant in the city is discharged to a cement lined channel. Consequently, there is negligible seepage from the channel and no groundwater impacts from this effluent within the city area, whereas groundwater quality has been degraded in the northern outskirts of the city where the discharge channel is unlined.

This study showed that fecal contaminants in groundwater in the Zahedan city were from point sources due to the proximity of groundwater sampling sites to wastewater discharge wells, sewers and to the use of manures for the fertilizing of green spaces. Also groundwater in the northern and outskirts of the city were generally free from the effects of fecal contamination. However, groundwater in this part of the city had elevated total coliform levels and the highest nitrate concentrations measured in groundwater.

An investigation of the relationship between depth and pumping rate of groundwater with the amount of microbial contamination showed deep wells with a high pumping rate had less microbial contamination and nitrate than in shallow wells. Therefore, in order to prevent the spread of pollution in the city of Zahedan, it is recommended that shallow wells with low pumping rates are not used for drinking water supply. However, increasing the depth of water supply wells would also increase the salinity of pumped groundwater.

The use of wastewater discharge wells has improved the salinity and the availability of groundwater in the aquifer under the city and can even be said to be it is one of the main sources of aquifer recharge. However, elevated total-coliform levels in the aquifer and high concentrations of nitrate and ammonium in groundwater in this area indicate the effect of wastewater discharge wells on groundwater quality. Samples from water treatment plants did not show microbial contamination but showed elevated concentrations of nitrate. The urban water supply network had a favorable situation both in terms of the absence of microbial contamination and in terms of nitrate, and this showed the high efficiency of the water supply distribution network of Zahedan city. Sewage in the city of Zahedan had a very high microbial and chemical pollution. The total coliform and fecal microbiological tests of all samples were positive. Nitrate in wastewater was also very high (up to 600 mg/L). Therefore, sewage can be considered one of the main sources of groundwater pollution in the city and it is important that measures should be taken to prevent the release of sewage into groundwater.

Declarations

Funding Information and Conflicts of Interest

This research was partially supported by Iran National Science Foundation (INSF) under founding No: 99027840. There are no conflicts to declare.

Acknowledgements

The authors would like to thank the Research Council of University of Sistan and Baluchestan, and Sistan and Baluchestan water & wastewater Co. for their support.

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Figures

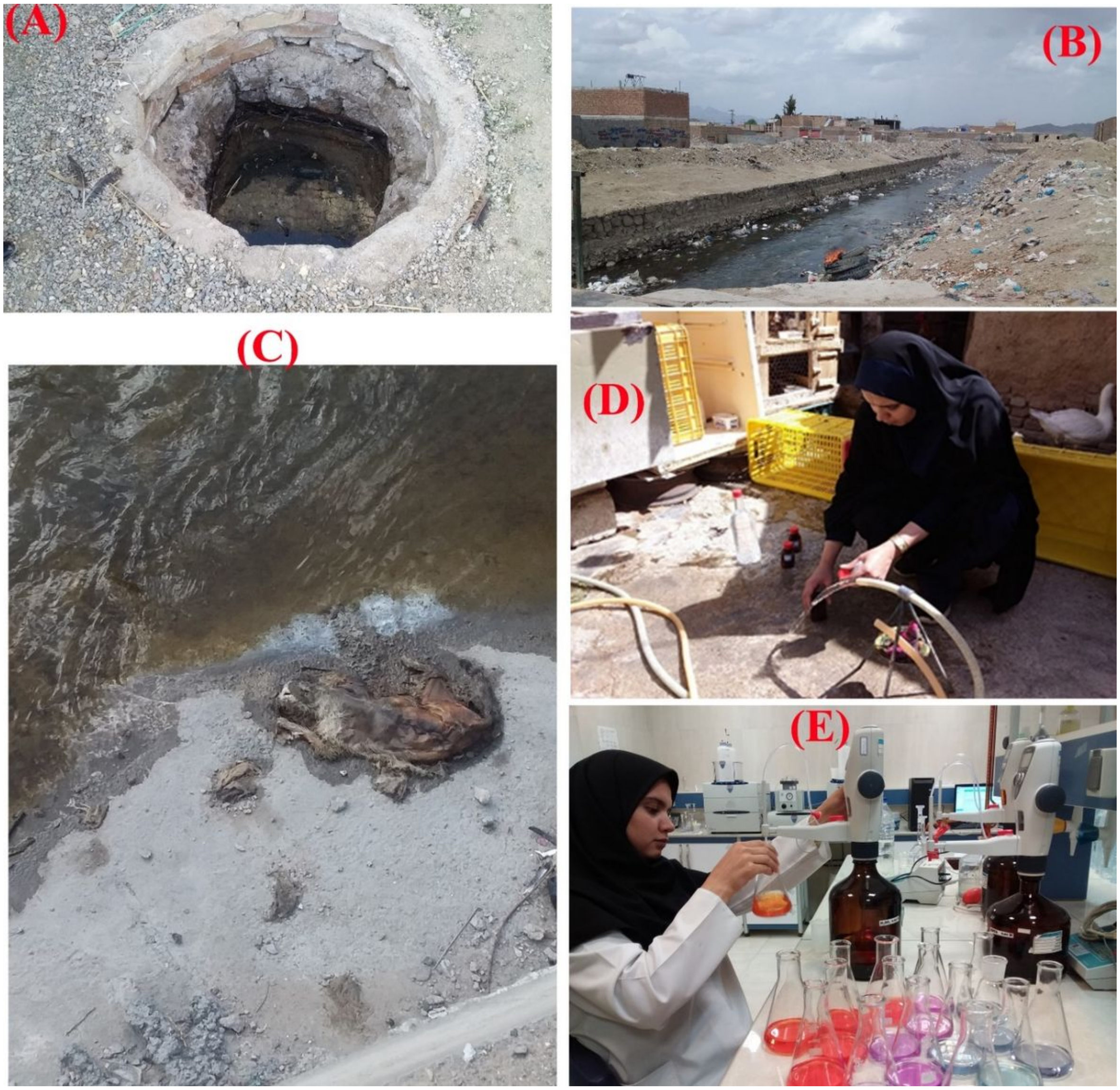

Figure 1

A shallow hand-dug well in downstream of the city (a), sewage channel, garbage and the remains of animal carcasses and their excrement in channels (b and c), water sampling in situ (d) and water analysis in laboratory (e)

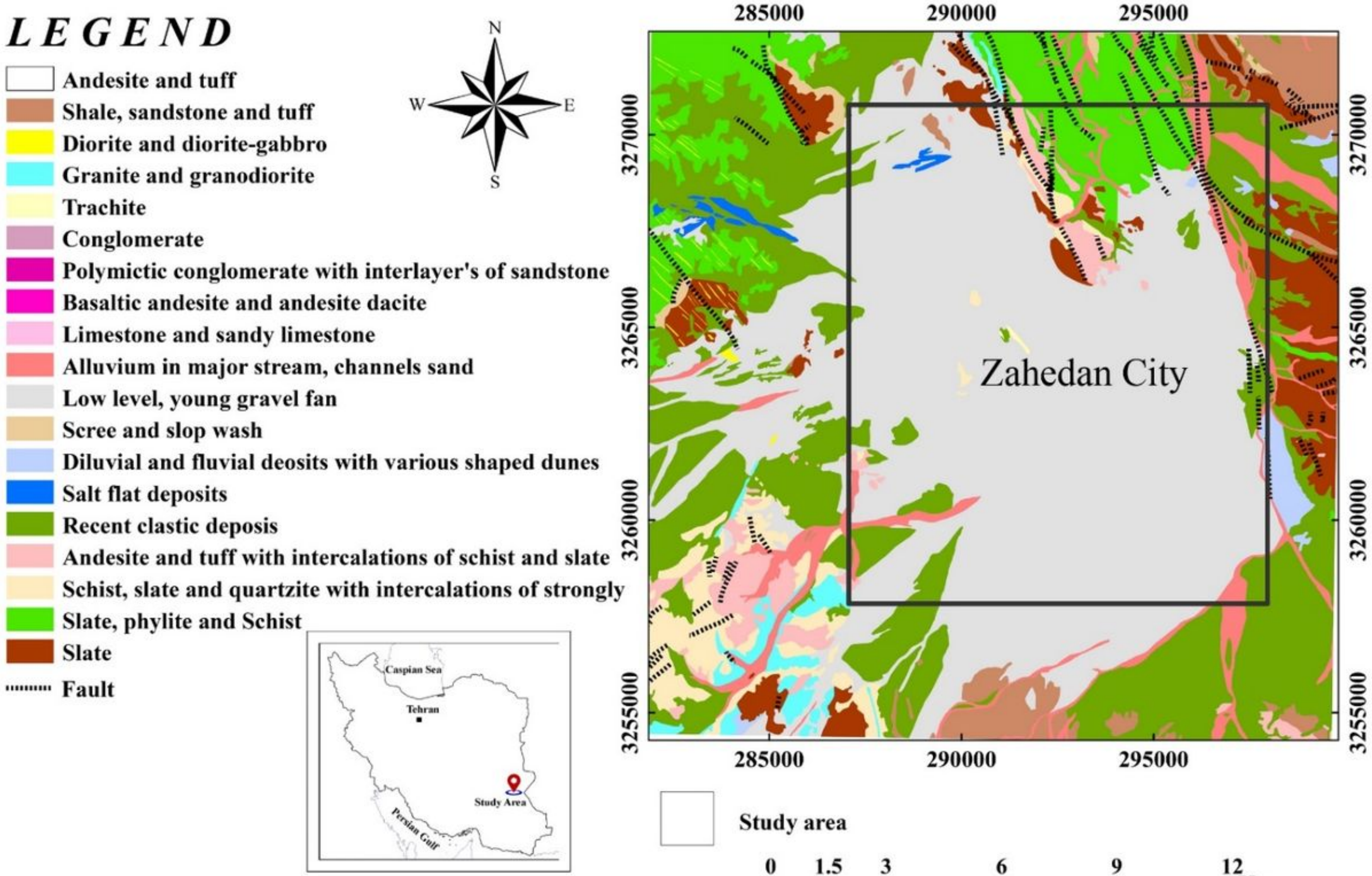

Figure 2

Geology map and location of the study area

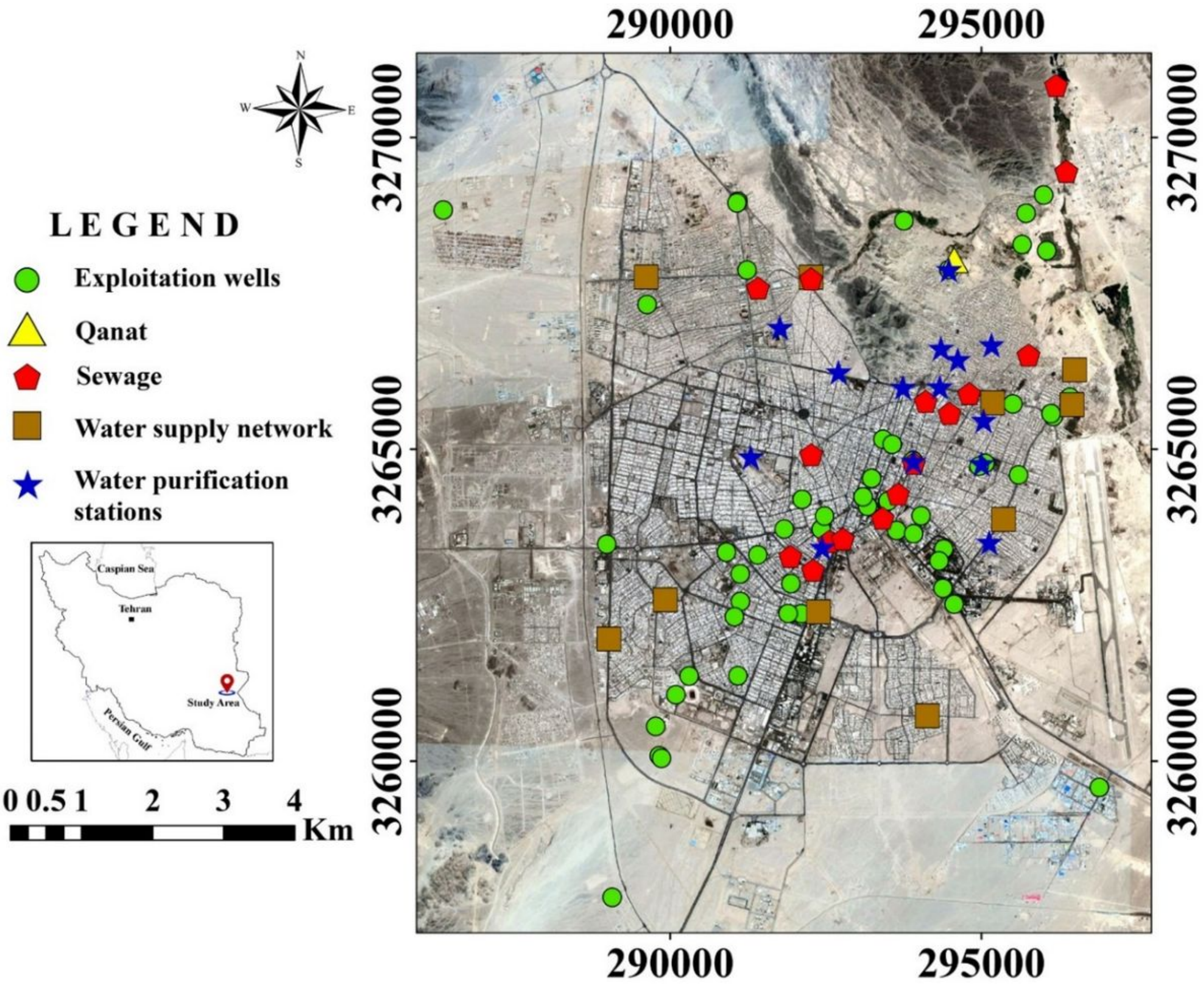

Figure 3

Spatial distribution map of the water samples from groundwater, sewage, water supply network and water treatment plants (or water purification stations) in the study area

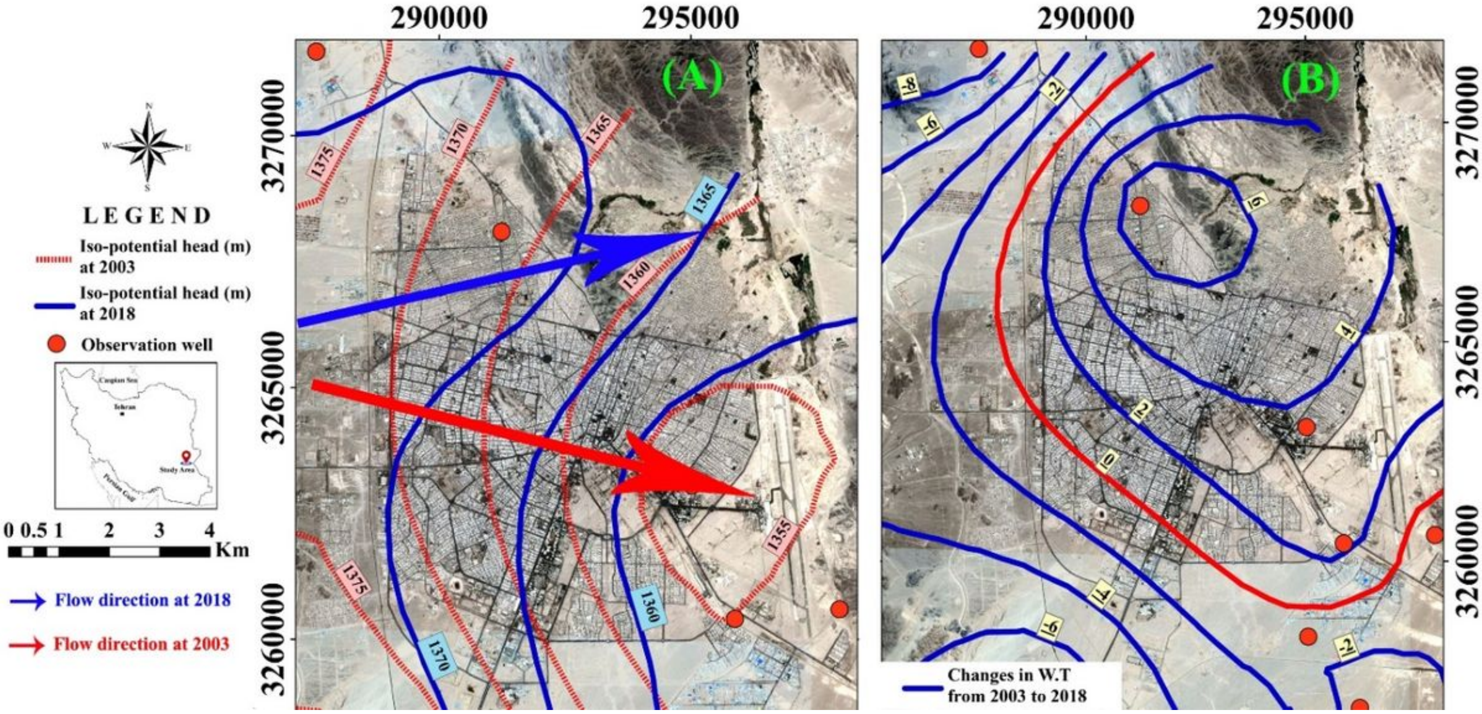

Figure 4

Groundwater flow direction in 2003 and 2018 (a) and spatial changes in water table from 2003 to 2018 (b)

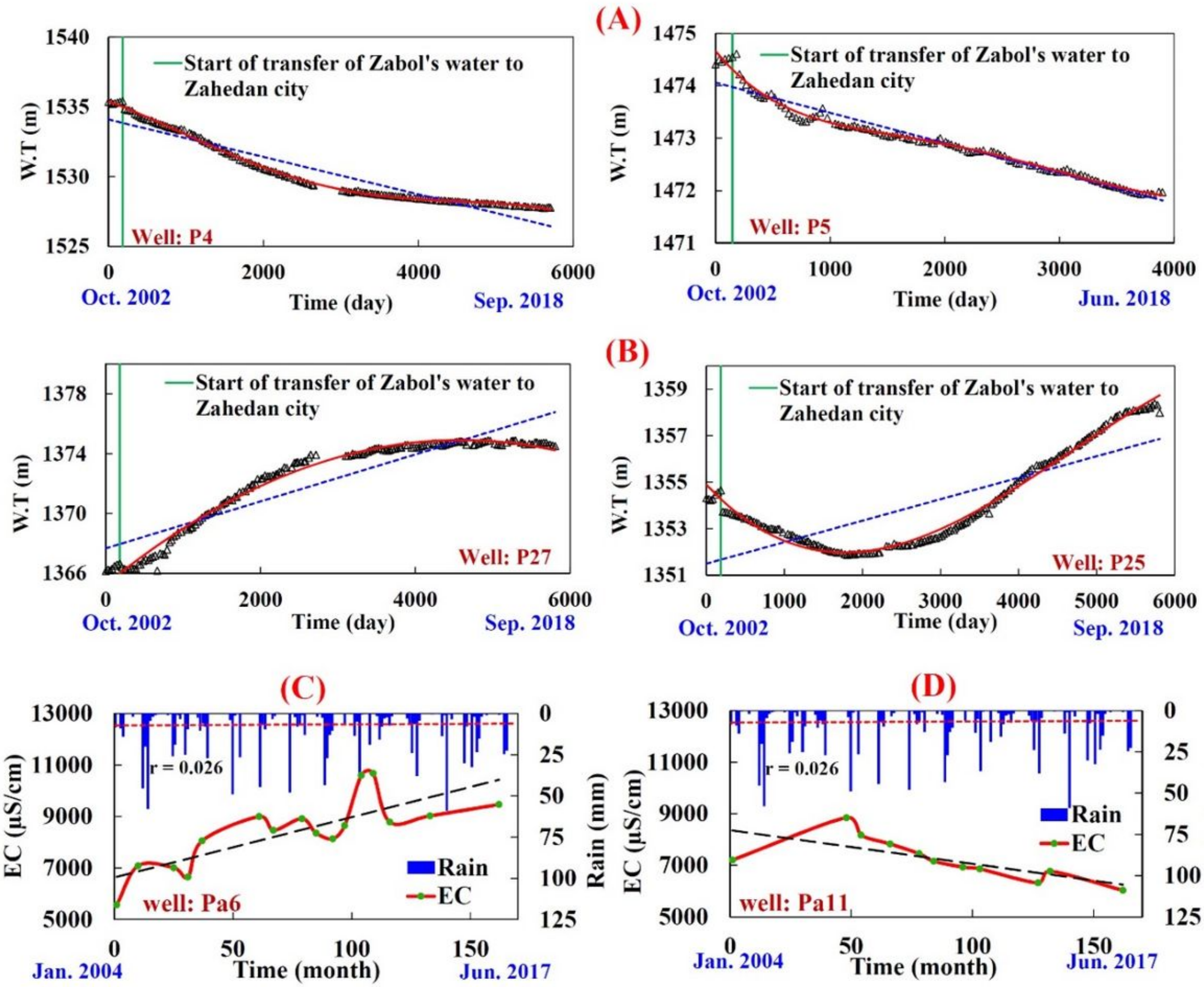

Figure 5

Time variation in water table in some of observation wells from 2003 to 2018 for outside the city (a) and inside the city (b) and time variation in rainfall and EC of groundwater for outside the city (c) and inside the city (d) after transfer of Zabol’s water to Zahedan city

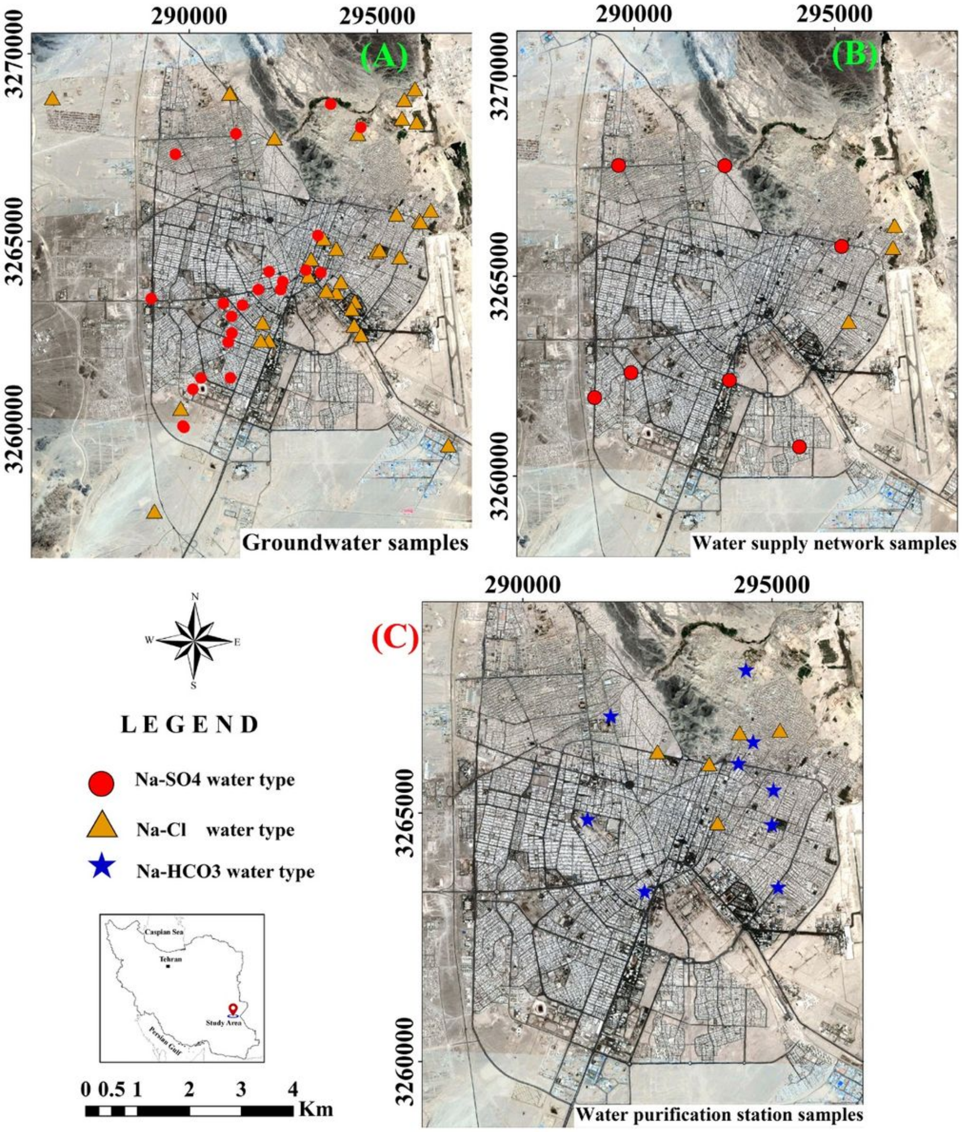

Figure 6

Spatial distribution map of the water type for groundwater (a), water supply network (b) and water treatment plants (c) in the study area

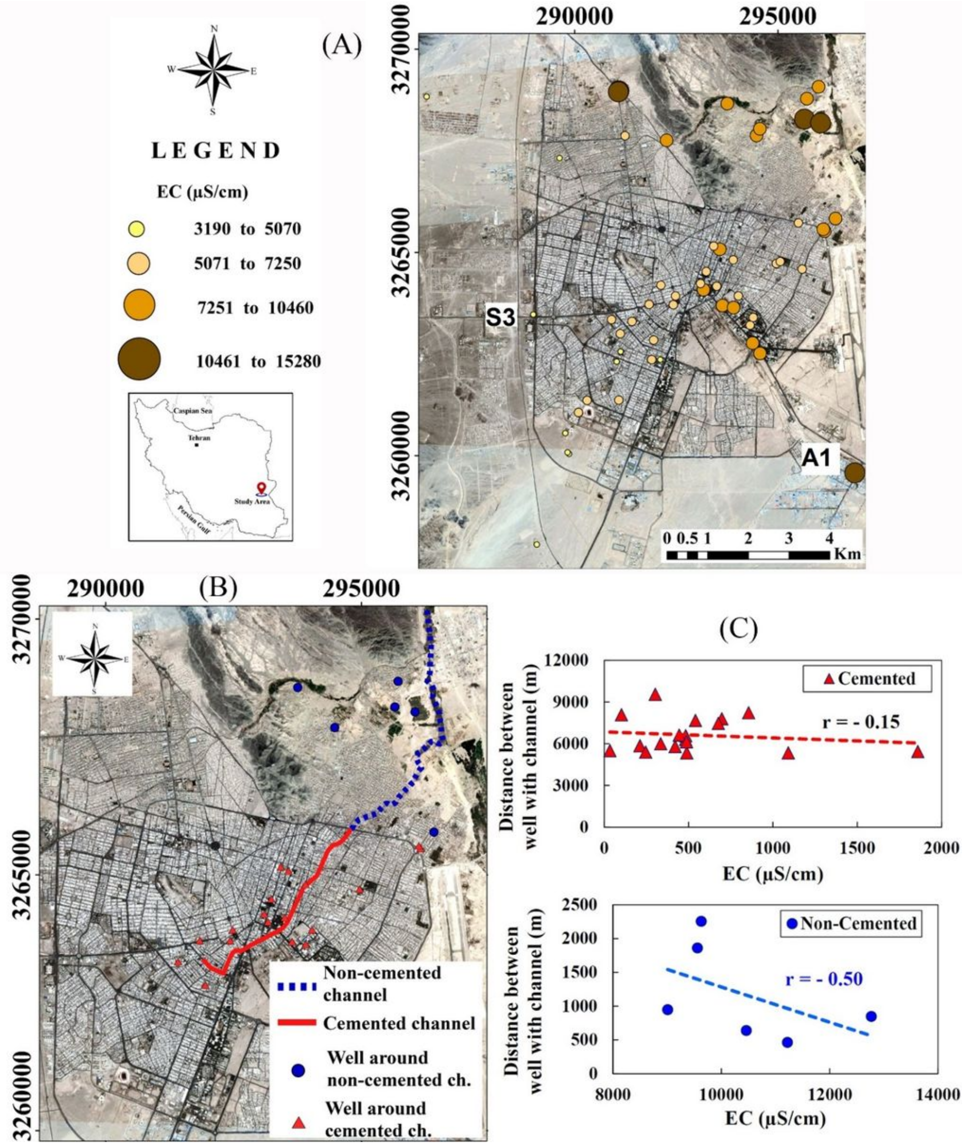

Figure 7

The spatial distribution map of EC in groundwater in the study area (a), the position of sewage channel (b) and the relationship of the distance between pumping wells to saline water channel with EC for areas of the non-cement channel (c) and the cemented channel (d)

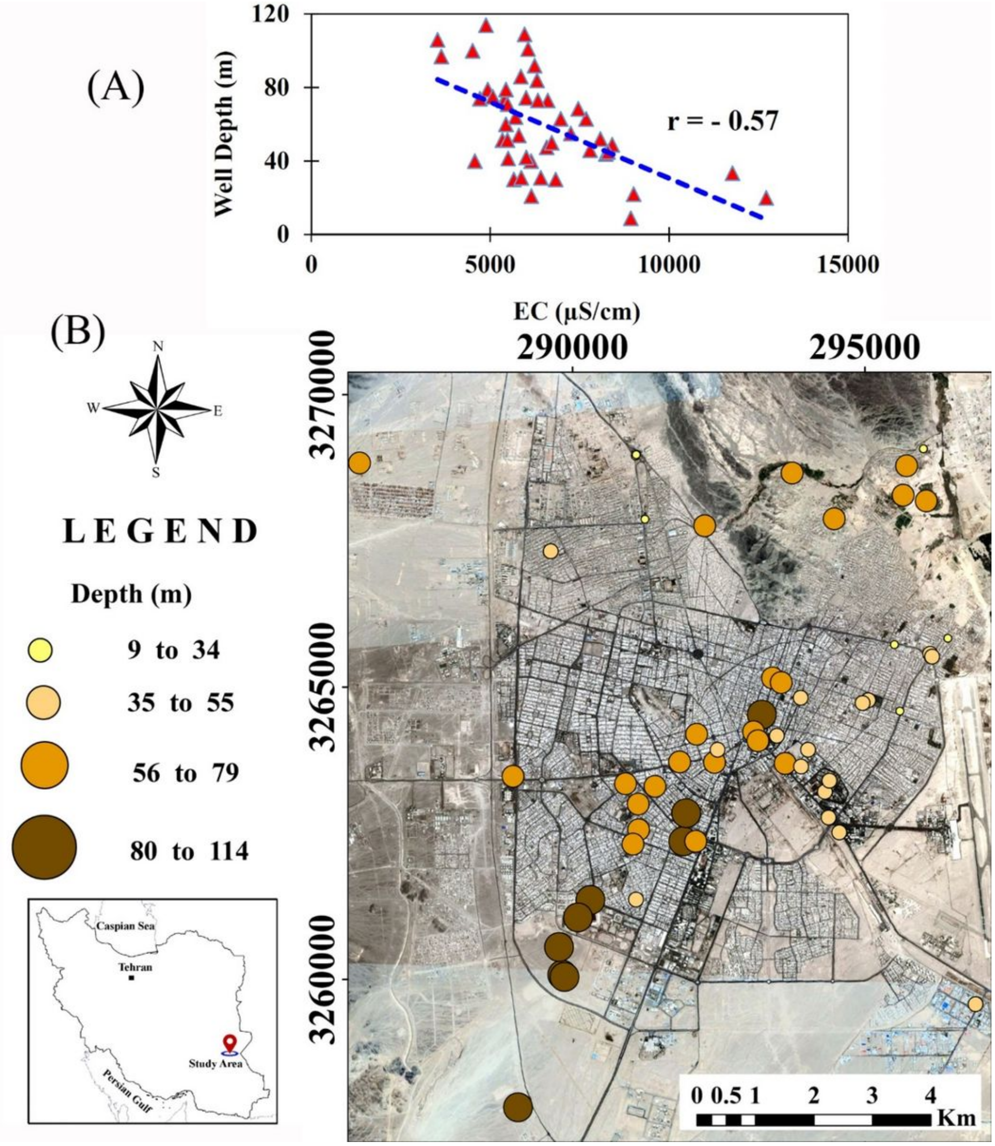

Figure 8

Relationship of EC with well's depth (a) and the spatial distribution map of exploitation well depth in the study area (b)

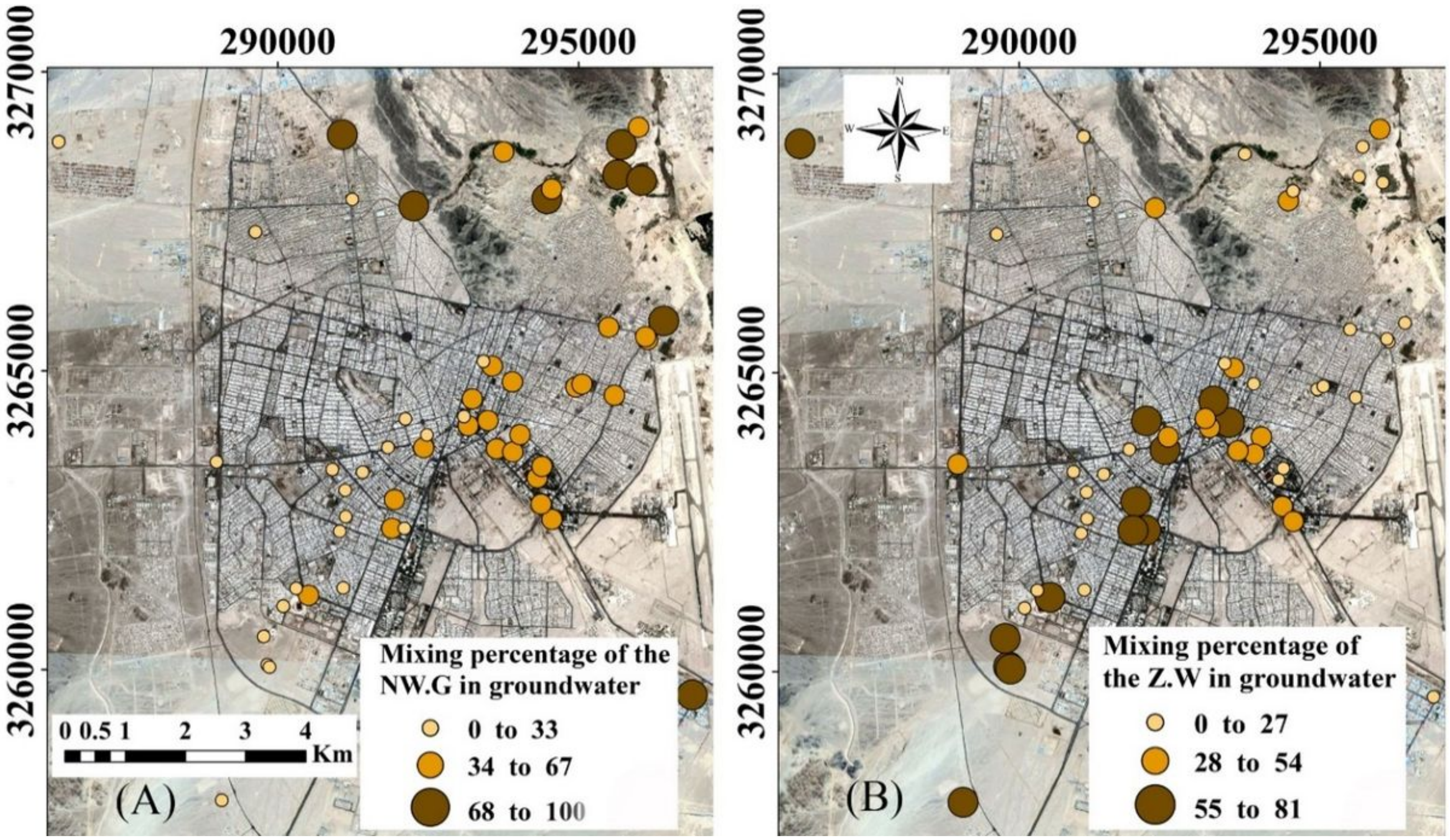

Figure 9

Mixing percentage of NW. G (a) and Zabol's water (Z.W) (b) in the groundwater of the study area.

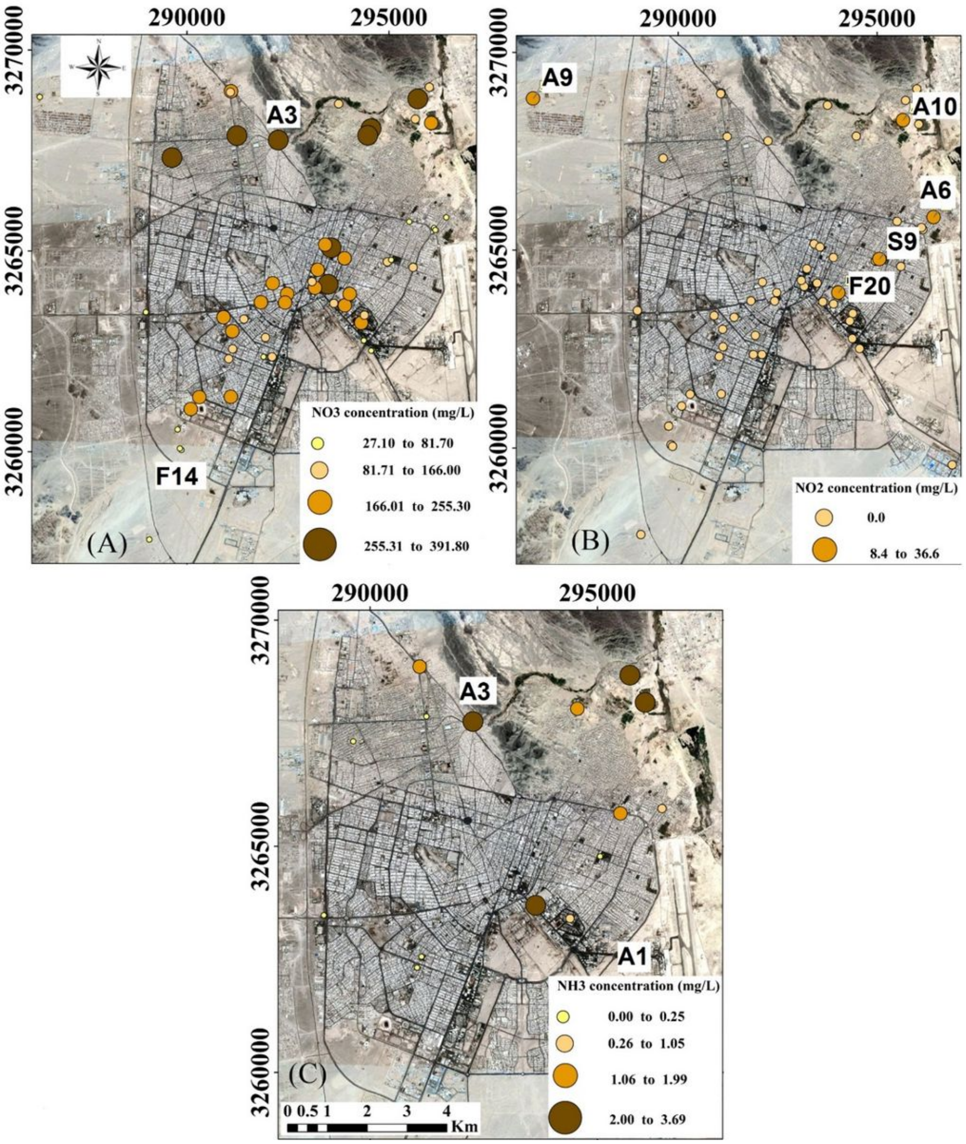

Figure 10

The distribution map of nitrate (a), nitrite (b) and ammonia (c) in the groundwater of the study area

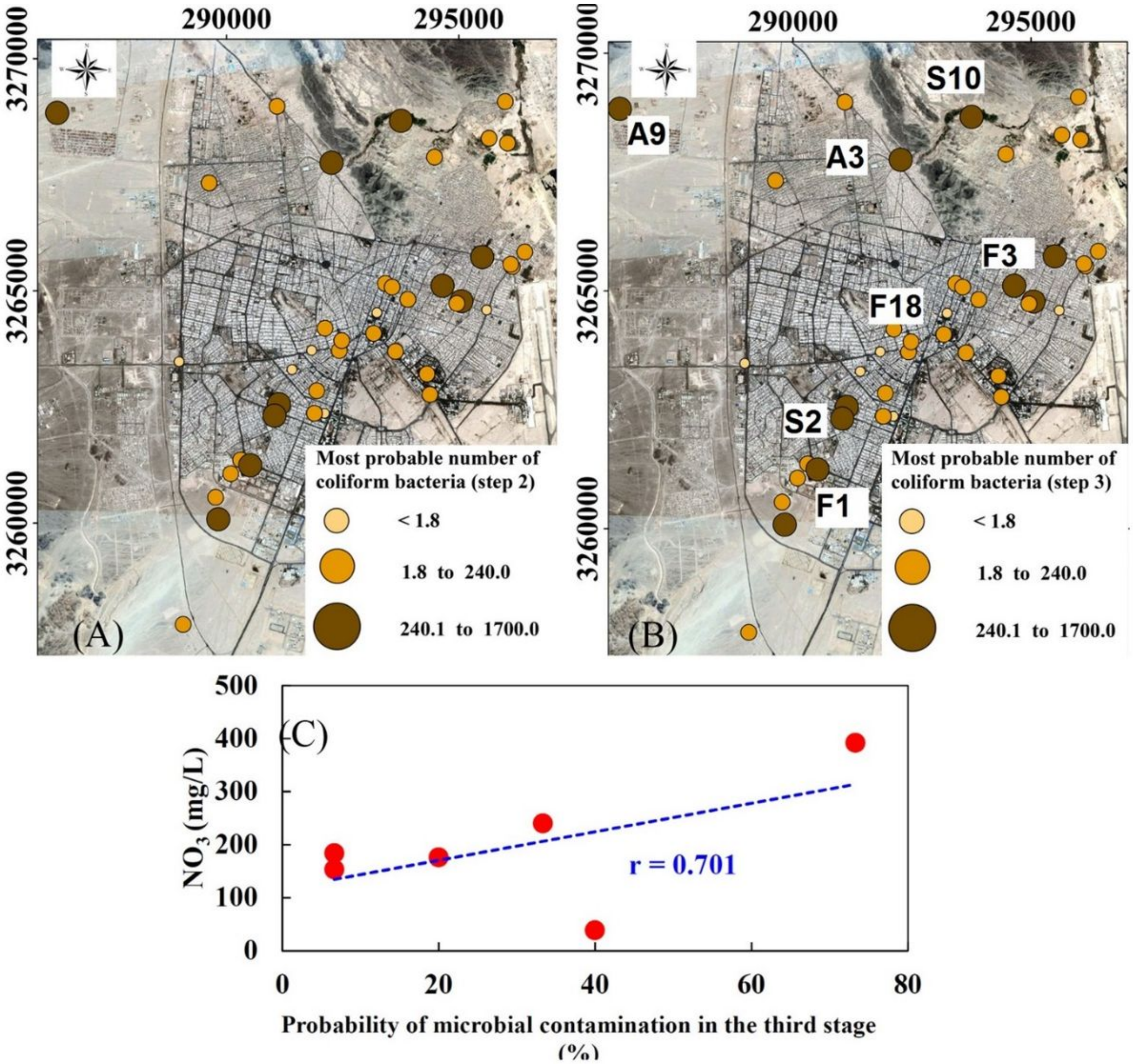

Figure 11

Distribution map for a most probable number of coliform in the second phase (confirmation) (a) and in the third phase (supplementary) (b) related to groundwater resources in the study area, and the relationship between nitrate content and the probability of contamination in the third stage for contaminated groundwater samples (c)

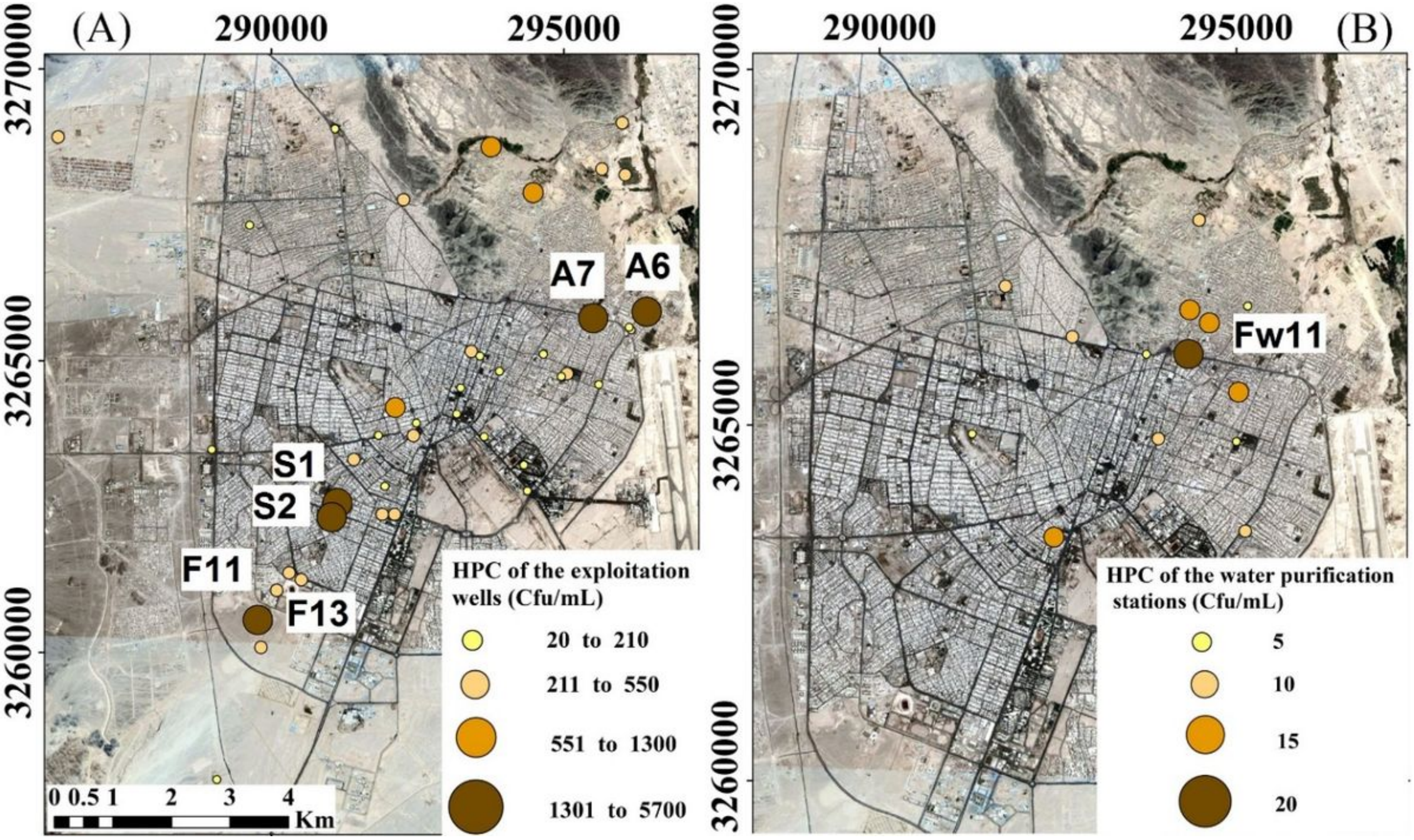

Figure 12

Distribution map of distribution of heterotrophic microorganisms related to groundwater resources (a) and related to water treatment plants (b) in the Zahedan city