NITRATE POLLUTION IN GROUNDWATER OF SULAIMANIYAH CITY, KURDISTAN REGION, NE IRAQ

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ABSTRACT

This study deals with the nitrate pollution in groundwater of Sulaimaniyah city. Sixty eight water well samples and two water samples from "karez" were collected equally from the districts of the city. The samples collected from different aquifers (Quaternary sediments and Kometan and Tanjero formations) and from different depths. Majority of the water wells (63% of the groundwater in Sulaimaniyah city) is polluted with NO_3. The main source of this pollution by NO_3 in the groundwater comes from sewages. Waters of polluted wells are not suitable for drinking purposes.

تلوث المياه الجوفية بالنترات في مدينة السليمانية، إقليم كوردستان، شمال شرق العراق

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المستخلص

يتضمن هذا البحث دراسة تلوث المياه الجوفية في مدينة السليمانية بأيونات النترات. تم جمع 68 نموذج من مياه الآبار ونموذجين من مياه الكهاريز بشكل متساوي من أحياء المدينة. جمعت النماذج من المكامن المختلفة (مكمن ترسبات العصر الرباعي ومكمني تكويني كوميتان وتانجيرو) ومن أعماق مختلفة. إن غالبية مياه الآبار في منطقة الدراسة ملوثة بالنترات، ويأتي تلوث المياه الجوفية بالنترات في مدينة السليمانية من مياه الصرف الصحي ومياه هذه الآبار غير صالحة للشرب.

INTRODUCTION

Nitrate is the most highly oxidized form of nitrogen compounds, and is commonly present in surface and ground water, since it is the final product of the aerobic decomposition of organic nitrogenous matter (Bartram and Ballance, 1996). Nitrate pollution of the groundwater is a common occurrence in many parts of the world. Contamination of groundwater from point and non-point sources is one of the major pollution problems. Possible sources of nitrate pollution include domestic waste water, septic systems, manure applied to land, agricultural fertilizers, industrial effluent, human waste lagoons, animal feedlots, and native soil organic matter, as well as geologic sources (Helmut, 2000). Nitrate is very soluble in water and therefore, very mobile within soil solution. Nitrogen transformation in soils is also very complex and dynamic; has the potential to produce substantial N losses via leaching, ammonia volatilization, denitrification, and surface runoff (Cepuder and Shukla, 2002). The groundwater represents the major source of drinking water, in Sulaimaniyah city. In drinking water, if nitrate is in excess of 10 mg NO_3/ l, then may be toxic for infants and may be responsible for increasing in stomach cancer for others (Spalding and Exner, 1993). The primary health effect associated with human exposure to nitrate is methemoglobinemia, in which hemoglobin converts to methemoglobin. Low concentrations of methemoglobin (0.5 − 3%) occur in normal people, although concentrations up to 10% can occur without clinical signs.

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Concentrations above 10% can cause cyanosis, characterized by bluish skin and lips, and concentrations above 25% are associated with hypotension, rapid pulse and rapid breathing (NASS, 1995; Letterman, 1999 and Schmoll *et al*., 2006). Pacheco *et al.* (2001) have shown that boiling water, while it may kill bacteria, also concentrates the nitrate ions in solution. Since boiled water is used to prepare milk for infants, this practice is also worrisome, and thus, it should be discouraged (Pacheco *et al*., 2001).

Nitrate travels easily through the soil, carried by rain or irrigation water into groundwater supplies. Wells that tap groundwater may be affected. Shallow wells, wells in sandy soil or wells that are improperly constructed or maintained are more likely to have nitrate contamination. The maximum acceptable concentration (MAC) for nitrate in drinking water has been set at 50 ppm NO_3 (equivalent to 11.3 ppm NO_3–N) by the World Health Organization (WHO, 2006); in Iraqi Drinking Water Standards (IQS, 1996) is 40 ppm and in Canada (Canada, 2006) is 45 ppm NO_3 (~10 ppm NO_3–N). Nitrate concentrations in groundwater are typically less than 10 ppm, but can exceed that in areas of concentrated human sources (NASS, 1995). Much of the scientific literatures suggest that nitrate levels in groundwater have been generally increasing over time, unless there has been a change in local land use practices (Trojan *et al*., 2003). Areas influenced by substantial human activity had higher nitrate concentrations than pristine areas (Benson *et al*., 2007).

LOCATION

Sulaimaniyah city is located NE of Iraq, between latitude 35° 31' 26" – 35° 35' 37" N and longitude 45° 28' 48" and 45° 22' 10" E, covering an area of 90 Km^2 (Fig.1).

GEOLOGY OF THE AREA

The studied area is located in the Nubio-Arabian Platform of Phanerozoic tectonic unit of Middle East and belongs to the Unstable Shelf (Buday and Jassim, 1987). Geologic formations that crop out in the city, from the oldest to youngest are (Fig.2): Kometan Formation (Turonian) represented by white, light grey, thinly bedded limestone, locally silicified (Bellen *et al.*, 1959). Shiranish Formation is overlying Kometan Formation unconformably (Bellen *et al.*, 1959). The formation is exposed in NE, N and NW sides of the studied area, on the flanks of Goizha, Azmar and Piramagroon anticlines. Shiranish Formation (Late Campanian – Maastrichtian) is divided into two parts; the upper part (99 m) consists of blue marls, overlying the lower part (128 m), which consists of thinly bedded, marly limestone. The overlying formation is Tanjero with gradational contact (Bellen *et al.,* 1959 and Buday, 1980). Tanjero Formation (Late Campanian – Maastrichtian) with thickness of 1690 m consists of thinly bedded sandstone and marl, cross-bedded sandstone, rhythmic alternation of sandstone, marl and shale (Al-Rawi, 1981). Quaternary sediments are composed of alluvial sediments, which form fans along foothills of Goizha Mountain graded from gravels to sand and to clay particles.

HYDROGEOLOGY

Generally, all groundwater samples are collected from wells and "karez" that belong to three different aquifers, Kometan and Tanjero formations; and Quaternary sediments aquifers (Fig.3). Shallow Quaternary aquifer with (0 – 25) m depth represents a good and widespread aquifer in Sulaimaniyah city, which mostly includes alluvial fan sediments and in the southern part of the city floodplain sediments. The aquifer is composed of unconsolidated gravel, sand, silt and clay that yield a good quantity of water (Inter granular aquifer), but in some parts of the city the aquifer gives water only in wet seasons (Mustafa, 2006).

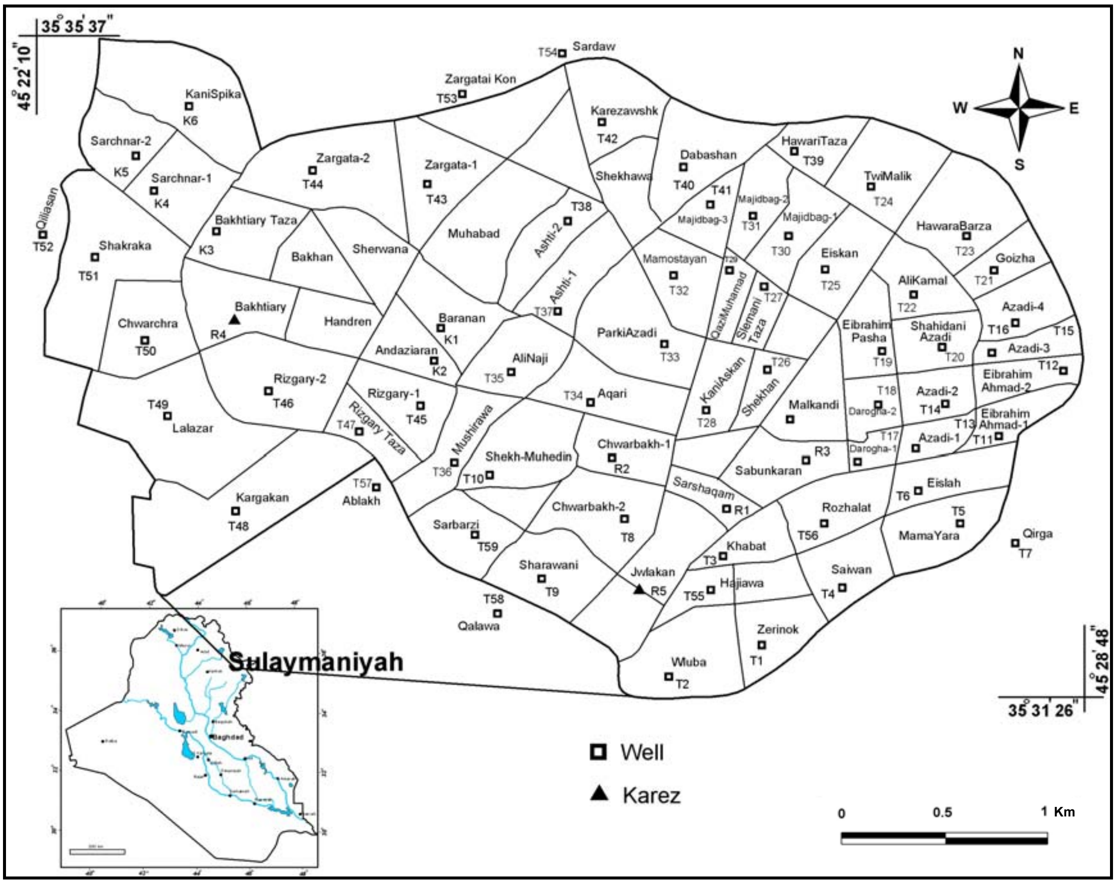

Fig.1: Location map of the studied area

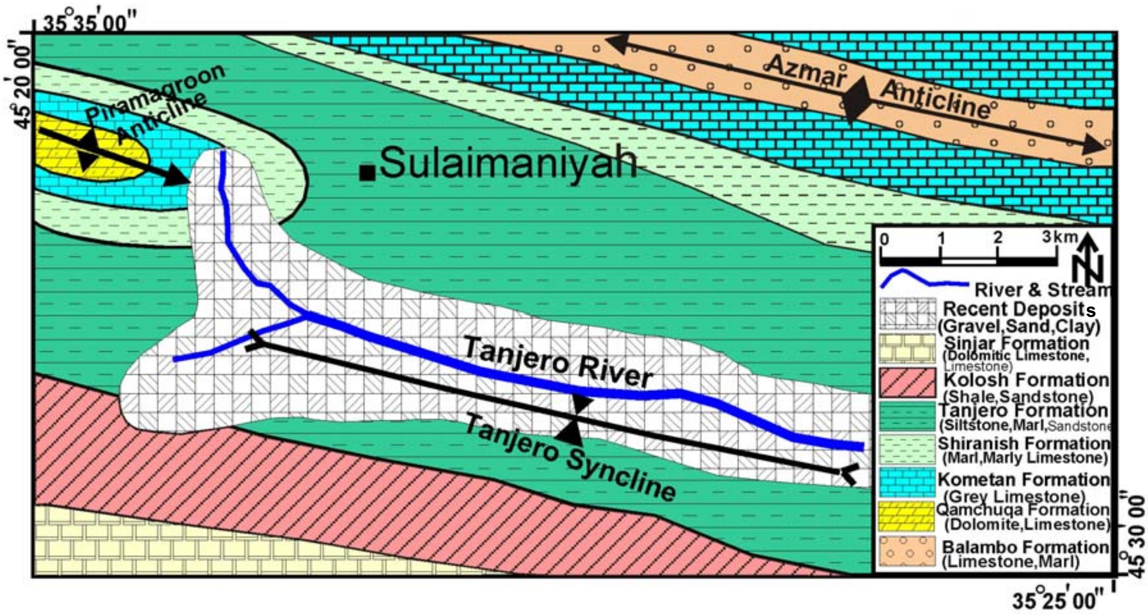

Fig.2: Geological map of the studied area (modified from Mustafa, 2006)

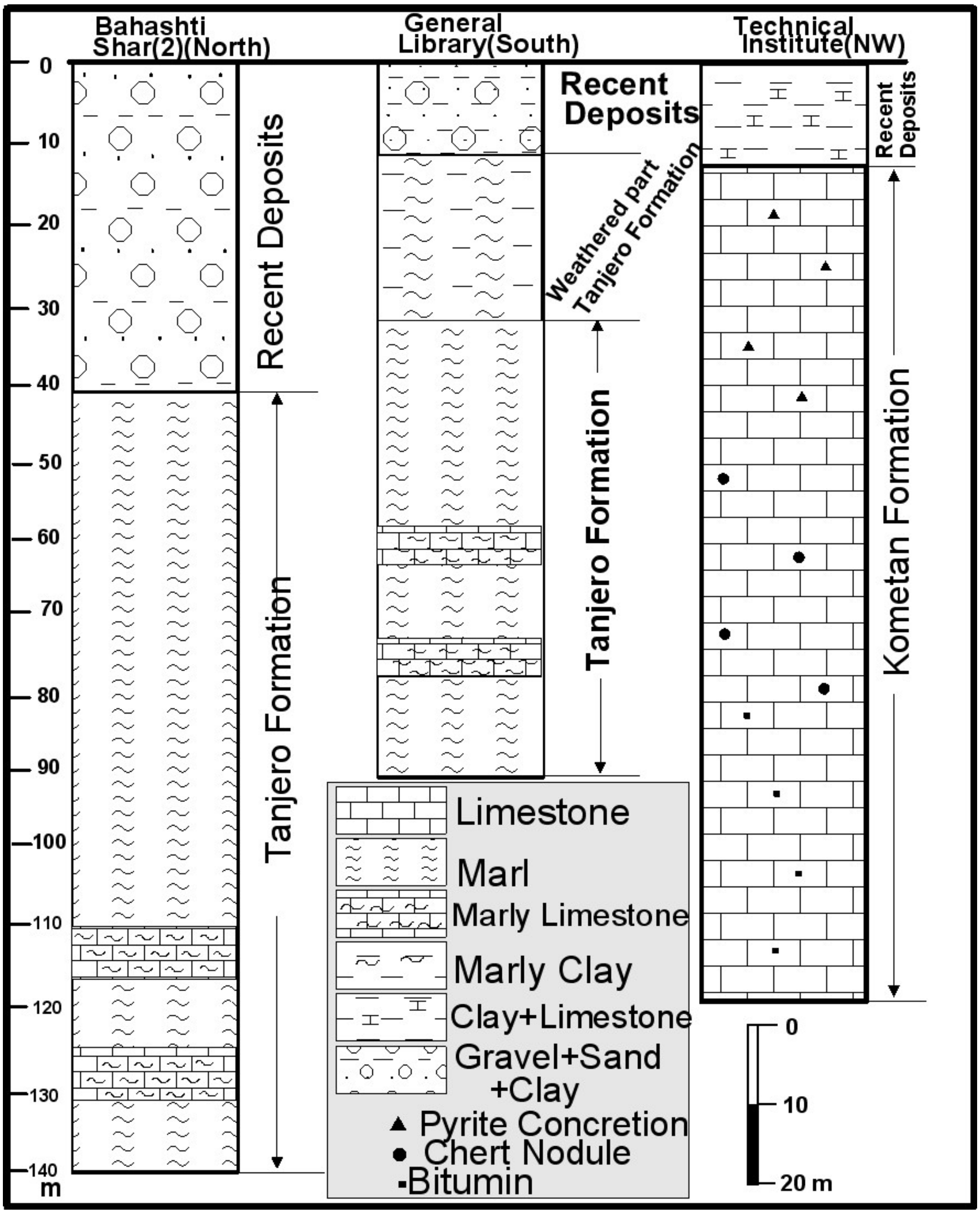

Fig.3: Stratigraphic succession of three wells in different parts of Sulaimaniyah city (Sulaimaniyah Groundwater Directorate)

Tanjero Formation aquifer represents medium to deep aquifer (25 – 120 m) composing of alternation of marly limestone, sandstone, marl and occasionally conglomerate beds. The aquifer is highly deformed and fractured that allow to form secondary porosity (Mustafa, 2006). Tanjero aquifer yields a good quantity of water (40 – 100) gal/ min in both dry and wet seasons and represents a semi-confined aquifer (Al-Manmi, 2002). Majority of the wells in the city are drilled within this aquifer. The general direction of the groundwater flow in Tanjero aquifer is from northeast to southwest (Fig.4) and this is related to the topography of the area.

Kometan aquifer represents a fractured, karstic aquifer in the area (Al-Rawi, 1990) situated in the northwest side of the city. The aquifer yields about (21 – 160) gal/min and represents a semi-confined aquifer (Al-Manmi, 2002).

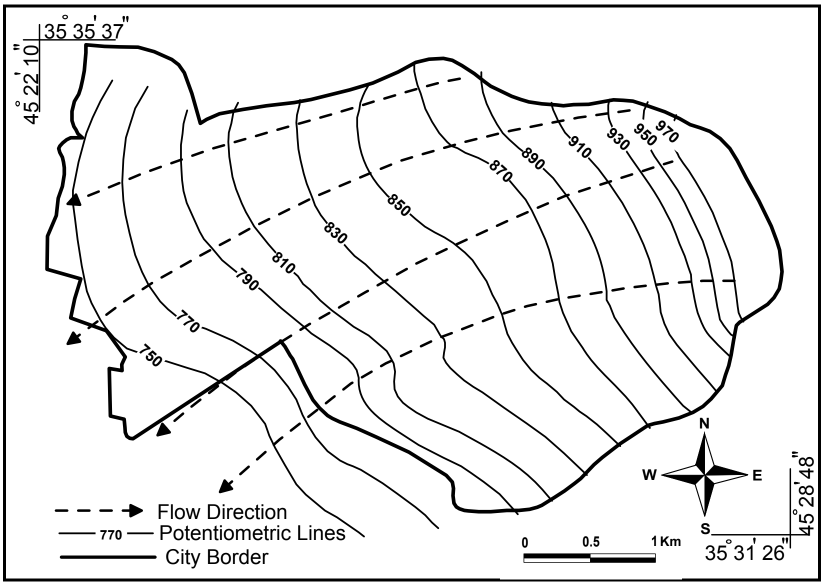

Fig.4: Direction of groundwater flow in Tanjero aquifer (Modified from Al-Manmi, 2002)

CLIMATE

The climate in the studied area is classified as moist type, showing seasonal variation between hot and dry in summer, and cold, rainy and relatively snowy in winter. Mean annual precipitation is 703.7 mm, mean annual air temperature is 19° C and mean annual evaporation is 2298.8 mm (Mustafa, 2006).

MATERIALS AND METHODS

Within Sulaimaniyah city, 68 wells (domestic and public) and 2 "Karez" (Bakhtiary and Jwlakan) were sampled between 24th January and 24th December 2006. Sampling sites were selected equally including most parts of Sulaimanyiah city (Fig.1). Samples were collected using pre-cleaned polyethylene bottles with capacity of 1.5 liter. Parameters like hydrogen ion concentration (pH), electrical conductivity (Ec), total dissolved solids (TDS), total hardness (TH), Alkalinity, chloride (Cl) and nitrate (NO_3) were analyzed (Table 1) for each sample in laboratory of Sulaimanyiah Environmental Protection Office using procedures of APHA (1998) (Table 2).

RESULTS

Concentration of NO_3, Cl, TDS, TH, alkalinity, pH and Ec are shown in Table (1). Hydrogen ion concentration ranges between 6.08 – 8.88 and majority of the samples are weak acidic, except sample T33 from Parki Azadi (central part of the city), which is strong acidic. Electrical conductivity ranges between (260 – 1921) µS/ cm with higher value in southeastern side of the city (Qirga district). Total dissolved salts showed wide variation (181 – 1229 ppm), displaying higher values in eastern, western and southern parts of the city, while northeastern and southwestern parts show lower values. Total hardness ranges between (15 – 620) ppm with maximum value in Qirga district and minimum value in Sardaw district. Maximum chloride concentrations in the collected samples is 518 ppm from Qirga well and minimum concentration appear in Hawara Barza well (23 ppm). Alkalinity varied from minimum value (16.3 ppm) in sample T46 to maximum 296 ppm in Lalazar district (sample T49), south of the city. Nitrate concentration in the analyzed samples shows wide range, varies from 0 ppm, in Shakraka well (sample T51) to maximum (60 ppm) in Qirga well. Generally, higher NO_3 values appear in the northeast, south to southwest districts of the city.

Table 1: Analyzed parameters of water samples

Sample No.	District	Depth (m)	pH	Ec	TDS	TH	Alkal.	Cl	NO_3
T1	Zerinok	60	6.94	537	N/A	380	169	128	56
T2	Wluba	42	7.01	550	N/A	220	205	107	51.6
T3	Khabat	150	7.98	1155	N/A	20	211	290	53
T4	Saiwan	25	7.1	670	428.8	300	180	77	57
T5	MamaYara	100	7.3	497	N/A	160	125	78	57.8
T6	Eislah	70	7.06	566	362.2	350	153	58	53.6
T7	Qirga	68	7.19	1921	1229	620	171	518	60
T8	Chwarbakh2	60	7	765	489.6	340	165	64	59
T9	Sharawani	55	6.42	573	N/A	460	263	121	57
T10	ShekhMuhedin	66	7.2	575	N/A	280	205	106	50
T11	E.Ahmad-1	55	6.67	848	542.7	185	175	78	57
T12	E.Ahmad-2	85	7.31	260	N/A	80	154	68	6.8
T13	Azadi-1	58	7.2	450	N/A	340	154	62	54.5
T14	Azadi-2	78	7.1	511	327	120	156	35	51.1
T15	Azadi-3	48	7.29	406	260	290	145	43	43.5
T16	Azadi-4	72	7.14	560	358	310	126	60	55.4
T17	Darogha-1	54	6.97	416	N/A	180	173	68	55
T18	Darogha-2	64	7.22	548	350.7	320	129	64	57
T19	E.Pasha	55	7.4	430	N/A	290	135	56	57.5
T20	Sh.Azadi	38	7	455	N/A	300	137	81	56
T21	Goizha	48	6.82	538	344	100	N/A	57	5.9
T22	Alikamal	49.5	7.02	454	291	250	147	29	40.8
T23	Ha.Barza	53	7.43	351	224.6	150	131	23	32.5
T24	Twimalik	67	7.16	379	242	150	143	30	18.2
T25	Eiskan	65	7.13	890	569.6	210	126	69	53.8
T26	Shekhan	63	7.34	327	209	200	200	40	41.7
T27	SlemaniTaza	45	7.3	614	392.9	195	166	50	50.6
T28	KaniAskan	50	6.6	890	N/A	350	368	120	44.6
T29	QaziMuhamad	50	7.08	50	420	340	187	68	47.1
T30	MajidBag1	60	7.29	488	312	160	125	71	55
T31	MajidBag2	54	6.08	507	325	230	138	36	52.6
T32	Mamostayan	48	7.37	543	347.5	200	153	46	55.2
T33	ParkiAzadi	/	8.88	365	N/A	104	150	43	28
T34	Aaqari	39	6.92	510	N/A	330	199	73	46.2
T35	Ali-Naji	37	7.38	315	201.6	340	274	141	50.4
T36	Mushirawa	63	7.28	283	181	214	220	36	0.7
T37	Ashti-1	54	7.02	586	375	210	170	50	52.2
T38	Ashti-2	50	7.18	530	339.2	130	148	28	52
T39	HawariTaza	36	7.12	561	359	200	147	18	54.2
T40	Dabashan	54	7.41	370	N/A	160	179	76	47.3
T41	MajidBag3	58	6.36	513	N/A	290	147	82	55
T42	Karezawshk	60	7.41	469	300	150	135	36	32.3
T43	Zargata-1	65	6.89	624	399	210	191	55	10
T44	Zargata-2	110	7.02	418	267.5	132	179	30	35.8
T45	Rizgary-1	42	6.83	802	513	390	284	43	0.85
T46	Rizgary-2	40	7.34	657	420		16.3	44	51.6
T47	RizgaryTaza	59	7.14	658	N/A	278	304	85	55
T48	Kargakan	100	7.2	504	N/A	300	216	42	30.35
T49	Lalazar	40	6.96	729	466.5	410	296	59	17.28
T50	Chwarchra	48	6.72	725	464	300	225	62	54
T51	Shakraka	58	7.5	450	N/A	90	171	44	0
T52	Qiliasan	100	6.71	1426	912.6	340	253	774	35.6
T53	Zarga.Kon	36	6.47	733	469	204	174	70	57
T54	Sardaw	50	7.06	535	N/A	15	216	60	11.9
T55	HajiAwa	50	7.07	754	482.5	360	167	88	58.8
T56	Rozhhalat	120	6.7	511	N/A	220	225	156	57
T57	Ablakh	51	7.24	886	567	270	132	220	54
T58	Qalawa	55	6.95	759	N/A	420	193	81	50

… continue Table (1)

Sample No.	Districts	Depth (m)	pH	Ec	TDS	TH	Alkal.	Cl	NO_3
T59	Sarbarzi	50	7.15	512	N/A	450	232	104	57
K1	Baranan	100	6.26	312	N/A	286	243	57	44
K2	Andaziaran	45	7.04	512	N/A	220	240	71	33.1
K3	Bakhtia.Taza	58	7.36	523	334.7	230	214	41	2
K4	Sarchnar1	60	6.85	710	454	280	189	51	54
K5	Sarchnar2	50	7.32	532	340	300	170	57	54.6
K6	KaniSpika	60	6.96	866	554.2	380	194	139	58
R1	Sarshaqam	14	6.97	790	505	360	241	67	53.5
R2	Chwarbakh1	17	6.78	1365	874	510	250	256	57
R3	Sabunkaran	20	6.65	850	544		251	63	54.6
R4	Bakhtiary	Karez	7.27	671	429.4	310	196	41	44.8
R5	Jwlakan	Karez	6.96	690	N/A	290	268	N/A	38
Ec in µS/ cm; TDS, TH, Alkalinity, Cl and NO_3 in ppm; N/ A= not analyzed; Depth in m									

Table 2: Procedures, techniques and methods used in sample analysis (APHA, 1998)

Test	Method	Instrument
NO_3	Ultraviolet screening	Spectrophotometer 220nm/ CECIL/ 2021
pH	Probe method	Portable multipara-meter/ Field Lab Analyzer
Ec	Probe method	Portable multipara-meter/ Field Lab Analyzer
TDS	Drying	Beaker, filter paper, oven
TH	EDTA titrimetric	Erlenmeyer flask, burette
Alkalinity	Titration	Radiometer Copenhagen
Cl	Argentometric method	Erlenmeyer flask, burette

DISCUSSION

Essentially, NO_3 values in the collected samples from the studied area are high. Evaluation and assessment of nitrate pollution is displayed as every aquifer alone as follow:

─ Quaternary Aquifer

Three wells (R1, R2 and R3) and two "karez" (R4 and R5) represent Quaternary aquifer (Table 1). Water of the mentioned wells is polluted with NO_3, which exceeds the maximum contamination level (MCL) (50 ppm) recommended by WHO (2006) and IQS (1996), while in the "karez" water (R4 and R5) the NO_3 concentration is high, which exceeds normal value in unpolluted groundwater (< 10 ppm) (Hamil and Bill, 1986 and NASS, 1995).

─ Tanjero Aquifer

From fifty eight studied wells, located in Tanjero aquifer (Table 1), thirty seven samples are polluted with NO_3 and exceed MCL. Twelve wells are highly contaminated, five samples are moderately contaminated and five samples show normal NO_3 concentrations (Table 1).

─ Kometan Aquifer

From six samples collected from wells in Kometan aquifer (Table 1), three of them (K4, K5 and K6) are polluted by NO_3, two of them (K1 and K2) show high concentrations and one sample (K3) is within normal NO_3 concentration (Table 1).

Generally, forty four wells show pollution with NO_3, which represent 63% of the groundwater in Sulaimaniyah city. The main source of NO_3 in the groundwater of

Sulaimaniyah city is from sewages, it is also confirmed by Al-Manmi (2002) in some wells of the city and by Mustafa (2006) in southern part of the city. It is also proved world wide in urbanized areas (Rao *et al*., 1996; Kacaroglu and Gunay, 1997; Cronin *et al*., 2003; Gulbahar and Elhatip, 2005; Gallardo *et al.*, 2005; Yuce *et al.*, 2006; Rao, 2006 and Benson *et al.*, 2007). An indication for the pollution of the groundwater by NO_3 from sewages is that the aquifers which are contaminated by sewages have a concentration of chloride higher than the water from the potable portion of the aquifer (Pacheco *et al*., 2001).

The Pollution of NO_3 is distributed in the whole Sulaimaniyah city along different aquifers (Quaternary, Tanjero and Kometan aquifers) and in different depths (Table 1) but the most infected areas extend from east to south, to the southwest (Fig.5). The contaminant (NO_3) from sewages may be transported within intergranular Quaternary aquifer, and at depth along vertical and horizontal fissures (Kometan aquifer) and micro fractures (Tanjero aquifer).

Poorly constructed wells may also account for the vertical transport (Cronin *et al*., 2003) and leaky wells can rapidly transmit contaminants from the sewage through low permeability strata into otherwise uncontaminated aquifers (Lacombe *et al*., 1995).

To release the NO_3 pollution problem in groundwater of Sulaimaniyah city it is recommended to use methanol as a reducing agent. Methanol should be pumped into the aquifer to reduce the nitrate (pentavalent nitrogen) to zero gas nitrogen, and the latter can be degassed leading to a decrease of nitrate concentrations in the aquifer (Merkel and Planer – Friedrich, 2005).

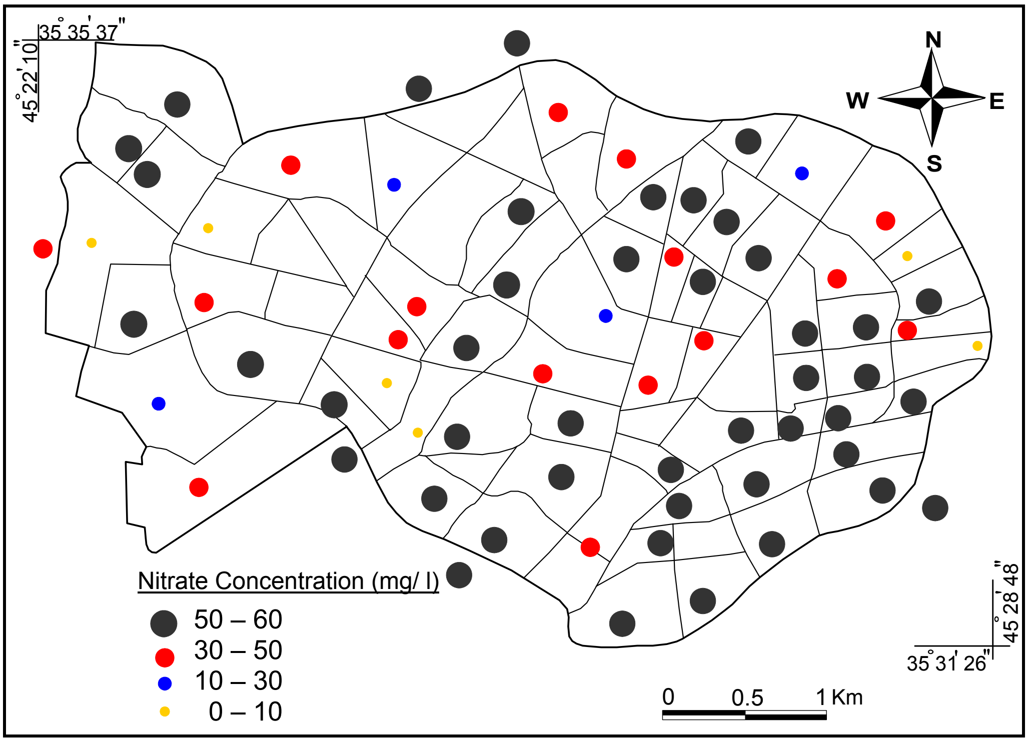

Fig.5: Distribution of nitrate in the groundwater of Sulaimaniyah city

CONCLUSIONS

- Concentrations of nitrate in groundwater of Sulaimaniyah city are high.
- NO_3 values in majority of the wells exceed the MCL.
- Water wells drilled in Quaternary sediments are polluted with NO_3.
- Majority of wells (37 wells) drilled in Tanjero Formation are polluted with NO_3.
- Half of water samples from Kometan Formation aquifer are polluted with NO_3, others show high concentration.
- About 63% of the groundwater in Sulaimaniyah city shows pollution with NO_3.
- The main source of groundwater pollution by NO_3 is sewages.
- The trend line of nitrate pollution in groundwater extends from east to south then to southwest of the city.
- The contaminant NO_3 transports to depth vertically and/ or horizontally within intergranular, fissured and fractured aquifers of Quaternary sediments; Kometan and Tanjero formations, respectively.
- Water of polluted and highly contaminated wells is not suitable for drinking purpose.

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