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## EFFECTS OF CESSPOOL SYSTEMS ON GROUNDWATER QUALITY OF SHALLOW BEDROCK AQUIFERS IN THE RECHARGE AREA OF WADI FATIMAH, WESTERN ARABIAN SHIELD, SAUDI ARABIA

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An investigation of the potential contamination of groundwater from on-site domestic wastewater systems blasted in weathered and fractured bedrock in the upper reaches of Wadi Fatimah basin, western Saudi Arabia, was conducted during April, 2005. Impacts of on-site systems on the shallow aquifer are shown by the elevated concentrations of nitrate and chloride. The chemical analyses results of the groundwater samples, collected from private domestic wells in a residential site, show that the nitrate concentration in groundwater exceeded the maximum contaminant level of 45 mg/l. It ranges from 151 to 556 mg/l with an average of about 236 mg/l which is greater than the average background (16.3 mg/l) of the nitrate concentration in the undeveloped region within the wadi basin. The high nitrate content is a widespread pollutant that is a serious threat to public health. Nitrate contamination is generally observed in close proximity to potential point waste sources. The dominant groundwater movement in the area is the major factor contributing to the groundwater deterioration by nitrate that has leached from on-site wastewater disposal systems. The chloride-nitrate relationship has been used to differentiate the potential sources of chloride. No faecal coliforms were detected in the groundwater samples, even in samples with the highest nitrate concentrations, suggesting that residence time in fractured and weathered bed rocks was sufficient for bacterial die-off.

## **INTRODUCTION**

The shallow aquifer in the Wadi Fatimah basin in the western Arabian Shield is considered the principal source of water supplies to the towns and villages. During the past two decades a rapid growth of population and development in these areas has led to concern about potential water quality impacts, due to the absence of municipal sewer services. Disposal of sewage in the residential areas have been accomplished almost exclusively through the use of conventional on-site sewage systems. A traditional on-site sewage system consists of a cesspool and a subsurface absorption system (Figure 1). The cesspool is a shallow pit with different lengths and widths, and average depth of about 2 meters. It is poorly designed and often built by bricks. Under ideal conditions, the effluent is assimilated and treated within the top soil as well as the weathered and fractured column immediately below and adjacent to the cesspool. No regulations are implemented for setback distance and lot sizes requirements and its design and/or installation, to ensure that the vertical separation between the bottom of the cesspool and the water table is large enough so that unsaturated conditions will be maintained even during wet seasons.

Several investigations in the literature discussed the fate and movement of chemical constituents of septic/cesspool effluent into shallow groundwater (e.g. Duda and Cromartie, 1982; Yates, 1985; Scandura and Sobsey 1997; Amade, 1999; Rose et al., 1999; Whitehead and Geary. 2000). Generally, most concern appears to be related to  $NO_3^-$  and bacterial contamination of aquifers because of possible health problems from  $NO_3^-$ . Recently, investigations carried out in the Wadi Fatimah by Sharaf et al., (2004) and the Saudi Geological Survey (2004) have shown that many of the domestic water supply wells, particularly in the upper reaches of the wadi, extract waters with high  $NO_3^-$  concentration (120 mg/l) which is greater than the acceptable maximum contamination level (MCL) of 45 mg/l (10 mg/l of nitrate-nitrogen) by the World Health Organization (1998, 2000). The high  $NO_3^-$  contents of the groundwater are commonly linked to nitrogen-based fertilizers, with no particular attention given to the possible groundwater pollution by on-site sewage disposal systems used in these regions.



Figure 1. Traditional cesspool system used within the wadi basins. (not to scale).

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In this study, the upstream part of the Wadi Fatimah basin, where Alsail Alkabir town lies on a shallow aquifer, was selected to identify any adverse groundwater quality impacts arising from onsite wastewater disposal systems.

## **DESCRIPTION OF THE STUDY AREA**

During the last 15 years, Alsail Alkabir town has grown rapidly; more than 2000 residents are living within the town. This town is located at the recharge area of the Wadi Fatimah drainage at an altitude of about 1200 meters above sea level (Figure 2).

The rock types of the study area consist mainly of a batholith of pink granite, surrounded by intrusive rocks mainly of dioritic and granodioritic composition. The batholith has a roughly circular outline about 7 km in diameter, and the contact of the pluton with its country rocks is sharp. The area has a gentle slope towards the west (Moore and Al-Rehaili, 1989). Quaternary deposits are found along the Wadi Harad that trend in a south to northeast direction (Figure 3). These deposits range in size from course sand to pebbles and gravel, and they serve as a permeable conduit for the percolation of surface water into the aquifers. In several places, the surface of the batholith is completely weathered down to about a depth of 0.5 m.

Over the study area, the rainfall is irregular and has a torrential nature. The annual average rainfall is about 180 mm. The rainfall season is from December to May. December and January receive nearly 70% of the annual rainfall. During the rest of the year, rainfall is limited to isolated events. The general recharge source of the aquifer has been commonly attributed to infrequent runoff events, which infiltrate to the water table promptly through the zone of aeration. During the



Figure 2. Location map of the study area.



Figure 3. Well location map.

recharge processes, the thin alluvial deposits overlying the bedrock become partly saturated. For a short period of time after rainfall, the water level declines considerably owing to the combined effects of evaporation and subsurface infiltration. The water table is shallow and varies between 3.4 to 6.4 m below the wadi floor. The wadi channel is topographically lower than the surrounding areas by nearly 1.5 m. Most of the existing wells in this area have been dug into the bedrock and almost entirely penetrate the weathered and fractured zones. The major groundwater pumping is from these zones, whereas supplies from the surficial deposits overlying the bedrock are commonly temporary and may be completely depleted during the dry period (Alyamani and Hussein, 1995). Most of the drilled wells are placed along the main course of Wadi Harad. The most common type of well construction is the large diameter well, with an average diameter of 3 meters. The thickness of the fractured and weathered zones of about 13 m.

The groundwater is under unconfined conditions and the groundwater flow is from southeast to northwest (Figure 3). Due to the presence of a fault-filling dike on the northern side, which acts as water barrier, the groundwater flow has been modified towards the west throughout Wadi Alyamaniyyah (Alyamani and Bokhari, 2003).

## **METHODOLOGY AND SAMPLING COLLECTION**

During April 2005, a total of 23 groundwater samples were collected from private domestic water supply wells of the Wadi Harad (Figure 3). For comparison purposes, the background of groundwater chemistry was determined in nine samples (Table 1) that were collected from wells in Wadi Alaf, which least likely to be impacted by human activity. Groundwater temperature and

Variable	Average	backgrou	<sup>†</sup> Rain water		
	groundw	ater chem	chemistry		
	Wadi Ala	af (sample	s=9)	(samples=5)	
	Max	Min	Average	Average	
Na <sup>+</sup>	74.3	45.0	62.6	2.8	
Ca <sup>2+</sup>	168.0	77.4	108.5	3.5	
$Mg^{2+}$	29.7	13.1	21.2	1.2	
HCO <sub>3</sub> -	190.6	139.4	167.6	14.0	
$SO_4^{2-}$	73.6	56.4	66.8	4.1	
Cl-	89.4	56.9	71.2	5.9	
NO <sub>3</sub> -	28.7	2.04	16.3	-	
$\mathrm{NH_4}^+$	0.017	0.010	0.0122	-	
$PO_{4}^{3-}$	0.10	0.046	0.063	-	
Fe	0.13	0.005	0.0485	-	
Mn	0.008	0.004	0.0064	-	
Zn	0.079	0.008	0.0293	-	
Pb	0.0049	0.0015	0.0037	-	
В	1.26	0.37	0.653	-	
TDS	572.1	433.4	515.4	-	
DO	1.51	1.04	0.32	-	
BOD (5-day)	-	-	-	-	
Water temp. (°C)	30.4	33.9	30.6	-	
pН	7.44	7.56	7.11	7.3	

Table 1. Background concentrations (mg/l) of groundwater and rain water.

† After Alyamani and Hussein (1995).

pH were measured in situ. All the groundwater samples were analyzed for major ions including calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sodium (Na<sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and chloride (Cl<sup>-</sup>). Inorganic nutrients included (nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ammonia (NH<sub>4</sub><sup>+</sup>) as nitrogen and phosphorus (PO<sub>4</sub><sup>3-</sup>), and trace elements including lead (Pb), boron (B), manganese (Mn), zinc (Zn), and iron (Fe). Each well was pumped for at least 5 minutes prior to sampling. These analyses were carried out in the Faculty of Earth Sciences Laboratories, King Abdulaziz University. These elements were analyzed using the standard methods (APH/AWWA/WPCF, 1989) and an ICP-Optical Emission Spectrometer, Optima 2000 DV. In the laboratory, the groundwater samples were biologically analyzed for total coliform, fecal coliform and fecal streptococci, dissolved oxygen (DO) and biological oxygen demand (BOD). The results of these chemical analyses are given in Table 2.

### **RESULTS AND DISCUSSION**

A comparison of the values in Table 2 with background concentrations in Table 1 indicates that the total dissolved solids (TDS) are generally elevated by an order of magnitude above the average background concentrations, with nitrate and chloride concentrations being significantly elevated (Table 2). The Cl concentrations range from 103 to 289 mg/l, with an average of about 161.9 mg/l which is higher than the average reference of undeveloped area by an order of magnitude (71 mg/l). The NO<sub>3</sub><sup>-</sup> concentrations increased from 151 to 556 mg/l with an average of about 235.9 mg/l, which is 15 times higher than the average background concentrations (16.3 mg/l). The concentration of SO<sub>4</sub><sup>2-</sup> in water varies from 77.9 to 185 mg/l with an average of about 133.5 mg/l. The high concentrations of SO<sub>4</sub><sup>2-</sup> are probably due to the oxidation of pyrite (FeS<sub>2</sub>), which is a very common accessory mineral in the country rocks (Moore and Al-Rehili, 1989). The other major constituents such as Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> are slightly above the background

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Sample No.	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	Cŀ	$NO_3^-$	NO <sub>2</sub>	$NH_4^+$	PO <sub>4</sub> <sup>3-</sup>
1	67	185.2	45.8	197.7	104	161	151	0.054	0.013	0.896
2	46	165.5	44.6	132.2	156	109	244	0.072	0.021	0.945
3	109	198.3	46.2	200.1	139	197	274	0.058	0.005	0.792
4	48	144.2	32.9	187.0	87	133	294	0.064	0.029	0.859
5	66	185.2	50.6	188.2	97	199	153	0.005	0.014	0.654
6	33	165.4	39.9	187.0	107	163	271	0.085	0.013	0 965
7	82	195.4	45.9	234.7	77.9	157	232	0.049	0.005	0.802
8	45	193.6	52.0	226.3	143	144	197	0.005	0.004	0.843
9	55	177.2	41.3	194.2	119	121	177	0.003	0.001	4 16
10	30	178.8	55.1	172.7	161	103	397	0.071	0.023	1.10
10	39	1/0.0	54.9	1/2./	101	103	162	0.033	0.022	1.30
11	49	406.5	34.8	262.1	102	136	201	0.003	0.004	0.820
12	00	1/3.1	40.4	202.1	102	1/4	561	0.030	0.010	0.829
13	82	113.4	59.8	207.3	108	289	556	0.092	0.403	0.95
14	66	187.2	35.6	115.5	185	151	188	0.045	0.005	0.078
15	78	191.1	37.0	128.6	112	175	167	0.003	0.061	0.087
16	67	191.1	36.7	123.9	133	133	201	0.006	0.038	0.093
17	71	177.5	38.8	139.2	173	143	156	0.07	0.074	0.090
18	84	175.2	35.7	186.4	156	154	188	0.042	0.013	0.082
19	97	210.9	37.1	132.2	106	168	218	0.063	0.053	0.067
20	77	175.1	35.3	168.1	177	163	191	0.022	0.001	0.84
21	86	175.5	35.1	154.8	174.5	187	186	0.046	0.001	0.065
22	81	128.4	38.5	190.6	117	198	266	0.043	0.001	0.065
23	67	164.3	36.5	220.7	183	145	184	0.005	0.023	0.097
Max	109	408.5	59.8	262.1	185	289	556	0.092	0.403	4.16
Min	33	113	32.9	115.5	77.9	103	151	0.003	0.001	0.065
Average	67.9	185.2	42.5	178.2	133.5	161.9	235.9	0.0443	0.0367	0.721
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Sample No.	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> -	SO4 <sup>2-</sup>	Cl	NO <sub>3</sub> -	NO <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>
Sample No.	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> -	<b>SO</b> <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> -	NO <sub>2</sub>	$NH_4^+$	PO <sub>4</sub> <sup>3-</sup>
Sample No.	Na <sup>+</sup> 67	Ca <sup>2+</sup> 185.2	Mg <sup>2+</sup> 45.8	HCO <sub>3</sub> - 197.7	$SO_4^{2-}$ 104	Cl- 161	<b>NO</b> <sub>3</sub> <sup>-</sup> 151 244	NO <sub>2</sub> 0.054	NH <sub>4</sub> <sup>+</sup> 0.013	<b>PO<sub>4</sub><sup>3-</sup></b> 0.896
Sample No. 1 2 3	Na <sup>+</sup> 67           46           100	Ca <sup>2+</sup> 185.2 165.5	Mg <sup>2+</sup> 45.8 44.6	HCO <sub>3</sub> <sup>-</sup> 197.7 132.2 200.1	$SO_4^{2-}$ 104 156 120	Cl <sup>-</sup> 161 109	<b>NO</b> <sub>3</sub> <sup>-</sup> 151 244 274	<b>NO</b> <sub>2</sub> 0.054 0.072	NH <sub>4</sub> <sup>+</sup> 0.013 0.021	<b>PO<sub>4</sub><sup>3-</sup></b> 0.896 0.945
Sample No. 1 2 3 4	Na <sup>+</sup> 67           46           109           48	Ca <sup>2+</sup> 185.2 165.5 198.3	Mg <sup>2+</sup> 45.8 44.6 46.2	HCO <sub>3</sub> - 197.7 132.2 200.1	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139	CI <sup>+</sup> 161 109 197	NO <sub>3</sub> - 151 244 274	NO <sub>2</sub> 0.054 0.072 0.058	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005	<b>PO<sub>4</sub><sup>3-</sup></b> 0.896 0.945 0.792
Sample No. 1 2 3 4 5	Na <sup>+</sup> 67           46           109           48	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87	Cl <sup>-</sup> 161 109 197 133	NO <sub>3</sub> - 151 244 274 294 152	<b>NO<sub>2</sub></b> 0.054 0.072 0.058 0.064	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005 0.029	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859
Sample No. 1 2 3 4 5 (	Na <sup>+</sup> 67           46           109           48           66           22	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97	Cl <sup>-</sup> 161 109 197 133 199	<b>NO</b> <sub>3</sub> <sup>-</sup> 151 244 274 294 153	NO <sub>2</sub> 0.054 0.072 0.058 0.064 0.005	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005 0.029 0.014	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654
Sample No. 1 2 3 4 5 6 7	Na <sup>+</sup> 67           46           109           48           66           33	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107	Cl <sup>-</sup> 161 109 197 133 199 163	<b>NO<sub>3</sub></b> - 151 244 274 294 153 271	NO <sub>2</sub> 0.054 0.072 0.058 0.064 0.005 0.085	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005 0.029 0.014 0.013	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965
Sample No. 1 2 3 4 5 6 7 7	Na <sup>+</sup> 67           46           109           48           66           33           82	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9	Cl <sup>-</sup> 161 109 197 133 199 163 157	<b>NO<sub>3</sub></b> - 151 244 274 294 153 271 232	NO <sub>2</sub> 0.054 0.072 0.058 0.064 0.005 0.085 0.049	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005 0.029 0.014 0.013 0.005	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802
Sample No.           1           2           3           4           5           6           7           8	Na <sup>+</sup> 67           46           109           48           66           33           82           45	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143	Cl <sup>-</sup> 161 109 197 133 199 163 157 144	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 477	NO <sub>2</sub> 0.054 0.072 0.058 0.064 0.005 0.085 0.049 0.005	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005 0.029 0.014 0.013 0.005 0.004	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843
Sample No.           1           2           3           4           5           6           7           8           9	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121	NO <sub>3</sub> -           151           244           274           294           153           271           232           197           177	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.005	NH <sub>4</sub> <sup>+</sup> 0.013 0.021 0.005 0.029 0.014 0.013 0.005 0.004 0.025	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16
Sample No.           1           2           3           4           5           6           7           8           9           10	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121 103	NO <sub>3</sub> -           151           244           274           294           153           271           232           197           177           387	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.005           0.005           0.005           0.004           0.025           0.022	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30
Sample No.           1           2           3           4           5           6           7           8           9           10           11	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8 408.5	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121 103 158	NO <sub>3</sub> -           151           244           274           294           153           271           232           197           177           387           163	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.005           0.005           0.005           0.005           0.004           0.025           0.022           0.004	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8 408.5 175.1	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121 103 158 174	NO <sub>3</sub> -           151           244           274           294           153           271           232           197           177           387           163           381	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.004           0.025           0.022           0.004           0.016	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8 408.5 175.1 113.4	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289	NO <sub>3</sub> -           151           244           274           294           153           271           232           197           177           387           163           381           556	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.004           0.025           0.022           0.004           0.016           0.403	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8 408.5 175.1 113.4 187.2	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.004           0.022           0.004           0.016           0.403	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8 408.5 175.1 113.4 187.2 191.1	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045	NH4+           0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.004           0.025           0.022           0.004           0.016           0.403           0.005	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 193.6 177.2 178.8 408.5 175.1 113.4 187.2 191.1 191.1	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133	Cl <sup>-</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.056           0.092           0.045	NH4+           0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.004           0.025           0.022           0.004           0.016           0.403           0.005	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 195.5 177.2 178.8 408.5 175.1 113.4 187.2 191.1 191.1 177.5	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201 156	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.056           0.092           0.045           0.003           0.0045	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.004           0.025           0.004           0.016           0.403           0.005           0.005	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 177.2 178.8 408.5 175.1 113.4 187.2 191.1 191.1 177.5 175.2	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201 156 188	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.0045           0.0045           0.0045           0.003           0.0045           0.003           0.0045	NH4+           0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 177.2 178.8 408.5 175.1 113.4 187.2 191.1 191.1 177.5 175.2 210.9	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201 156 188 218	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.0045           0.0045           0.0045           0.0045           0.0045           0.0045           0.0045           0.0045           0.0045           0.0045           0.0042	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.004           0.025           0.004           0.016           0.403           0.005           0.005           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77	$\begin{array}{c} \mathbf{Ca^{2+}} \\ 185.2 \\ 165.5 \\ 198.3 \\ 144.2 \\ 185.2 \\ 165.4 \\ 195.4 \\ 195.4 \\ 195.4 \\ 195.4 \\ 195.4 \\ 195.4 \\ 177.2 \\ 178.8 \\ 408.5 \\ 175.1 \\ 113.4 \\ 187.2 \\ 191.1 \\ 177.5 \\ 175.2 \\ 210.9 \\ 175.1 \\ \end{array}$	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201 156 188 218 218 191	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.0045           0.0045           0.0045           0.0045           0.0045           0.0045           0.006           0.07           0.042           0.063	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.005           0.004           0.025           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.84
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77           86	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.5 175.1 113.4 187.2 191.1 191.1 177.5 175.2 210.9 175.1 175.5	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3 35.1	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1 154.8	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177 174 5	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163 187	NO3 <sup>-</sup> 151           244           274           294           153           271           232           197           177           387           163           381           556           188           167           201           156           188           218           191           186	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.0045           0.003           0.0045           0.003           0.0045           0.0045           0.0045           0.0045           0.0042           0.063           0.022           0.046	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.004           0.025           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.84 0.065
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21           22	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77           86           81	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.5 175.1 113.4 187.2 191.1 177.5 175.2 210.9 175.1 175.5 128.4	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3 35.1 38.5	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1 154.8 190.6	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177 174.5 117	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163 187 198	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201 156 188 218 191 186 266	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.0045           0.003           0.0045           0.003           0.0045           0.0045           0.0045           0.0045           0.0042           0.063           0.022           0.046           0.043	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.005           0.005           0.005           0.005           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.84 0.065 0.065
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21           22           23	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77           86           81           67	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.5 175.1 113.4 187.2 191.1 191.1 177.5 175.2 210.9 175.1 175.5 128.4 164.3	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3 35.1 38.5 36.5	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1 154.8 190.6 220.7	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177 174.5 117 183	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163 187 198 145	NO <sub>3</sub> -           151           244           274           294           153           271           232           197           177           387           163           381           556           188           167           201           156           188           218           191           186           266           184	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.006           0.071           0.045           0.003           0.0045           0.003           0.0045           0.0045           0.0042           0.063           0.022           0.046           0.043           0.005	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.004           0.025           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001           0.001	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.84 0.065 0.065 0.097
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21           22           23           Max	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77           86           81           67           109	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.5 175.1 113.4 187.2 191.1 191.1 177.5 175.2 210.9 175.1 175.5 128.4 164.3 408.5 128.4 164.3 164.3 165.5 128.4 165.5 128.4 165.5 128.4 165.5 165.5 175.5 1	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3 35.1 38.5 36.5 59.8	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1 154.8 190.6 220.7 262.1	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177 174.5 117 183 185	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163 187 198 145 289	NO3 <sup>-</sup> 151           244           274           294           153           271           232           197           177           387           163           381           556           188           167           201           156           188           191           186           266           184           556	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.055           0.005           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.006           0.07           0.045           0.003           0.006           0.07           0.042           0.063           0.022           0.046           0.043           0.005	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.029           0.014           0.013           0.005           0.005           0.005           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001           0.001           0.023	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.84 0.065 0.065 0.097 4.16
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21           22           23           Max	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77           86           81           67           109           33	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.5 177.2 178.8 408.5 175.1 113.4 191.1 177.5 175.2 210.9 175.1 175.5 128.4 164.3 408.5 113.4	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3 35.1 38.5 36.5 59.8 32.9	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1 154.8 190.6 220.7 262.1 115.5	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177 174.5 117 183 185 77.9	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163 187 198 145 289 103	NO3 <sup>-</sup> 151           244           274           294           153           271           232           197           177           387           163           381           556           188           167           201           156           188           191           186           266           184           556           151	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.055           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.006           0.07           0.045           0.003           0.0045           0.0045           0.0045           0.0045           0.0045           0.0042           0.043           0.005           0.005           0.005           0.005	NH <sub>4</sub> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.029           0.014           0.013           0.005           0.005           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001           0.001           0.0023           0.403	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.84 0.065 0.065 0.097 4.16 0.065
Sample No.           1           2           3           4           5           6           7           8           9           10           11           12           13           14           15           16           17           18           19           20           21           22           23           Max           Min	Na <sup>+</sup> 67           46           109           48           66           33           82           45           55           39           49           68           82           66           78           67           71           84           97           77           86           81           67           109           33	Ca <sup>2+</sup> 185.2 165.5 198.3 144.2 185.2 165.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 195.4 177.2 178.8 408.5 175.1 113.4 187.2 191.1 177.5 175.2 210.9 175.1 175.5 128.4 164.3 408.5 113 185.2	Mg <sup>2+</sup> 45.8 44.6 46.2 32.9 50.6 39.9 45.9 52.0 41.3 55.1 54.8 40.4 59.8 35.6 37.0 36.7 38.8 35.7 37.1 35.3 35.1 38.5 36.5 59.8 32.9 42.5	HCO <sub>3</sub> - 197.7 132.2 200.1 187.0 188.2 187.0 234.7 226.3 194.2 172.7 148.7 262.1 207.3 115.5 128.6 123.9 139.2 186.4 132.2 168.1 154.8 190.6 220.7 262.1 115.5 128.2	<b>SO</b> <sub>4</sub> <sup>2-</sup> 104 156 139 87 97 107 77.9 143 119 161 152 102 108 185 112 133 173 156 106 177 174.5 117 183 185 77.9 122 5	Cl <sup>+</sup> 161 109 197 133 199 163 157 144 121 103 158 174 289 151 175 133 143 154 168 163 187 198 145 289 103 161 0	NO <sub>3</sub> - 151 244 274 294 153 271 232 197 177 387 163 381 556 188 167 201 156 188 218 191 186 266 184 556 151 235 0	NO2           0.054           0.072           0.058           0.064           0.005           0.085           0.049           0.055           0.071           0.055           0.003           0.056           0.092           0.045           0.003           0.006           0.07           0.045           0.003           0.0045           0.003           0.0045           0.0045           0.0045           0.0042           0.045           0.0042           0.046           0.043           0.005           0.0022           0.046           0.092           0.003	NH <sub>4</sub> <sup>+</sup> 0.013           0.021           0.005           0.029           0.014           0.013           0.005           0.029           0.014           0.013           0.005           0.004           0.025           0.004           0.025           0.004           0.016           0.403           0.005           0.061           0.038           0.074           0.013           0.053           0.001           0.0023           0.403           0.403           0.023	PO <sub>4</sub> <sup>3-</sup> 0.896 0.945 0.792 0.859 0.654 0.965 0.802 0.843 4.16 1.30 1.02 0.829 0.95 0.078 0.087 0.093 0.090 0.082 0.067 0.093 0.090 0.082 0.065 0.097 4.16 0.065 0.097

Table 2. Chemical analyses results of the groundwater in the study area (mg/l).

concentrations. Concentrations of  $NH_4$  are rather low and varied from 0.001 to 0.403 mg/l, whereas the  $NO_2$  concentrations ranged between 0.003 to 0.092 mg/l with an average of 0.044 mg/l. On the other hand, there were significant differences in the concentrations of  $PO_4^+$  and B

where both elements are higher than the average background. The average concentration of  $PO_4^+$  is 0.721, while it ranges between 0.065 and 4.16 mg/l, and only 14 of 23 samples exceeded 0.70 mg/l.

Boron concentrations varied from 0.8 to 8.54 mg/l and the average reaches 2.29 mg/l. The Pb concentrations range between 0.0022 and 0.039 mg/l, with an average of 0.0152 mg/l. From the 23 samples, only 7 samples are greater than the drinking water standard (0.01 mg/l). The groundwater was oxygenated where the dissolved oxygen (DO) ranged between 0.8 and 2.45 mg/l, with an average of about 1.50 mg/l. Oxygen enters groundwater through recharge of oxygen-enriched water that percolates down through the aerated zone. The biological oxygen demands (BOD) varies from zero to 1.22 mg/l and average of about 0.451 mg/l

The study area represents the recharge zone of the Wadi Fatimah basin. It receives a yearly recharge rate greater than 180 mm/yr. One would expect that the prevalent chemical composition of the groundwater would be relatively close to that observed either in rain water or at least to that in the undeveloped area (Table 1). Instead concentrations are much higher than those in the background chemistries of both rain water and groundwater in the undeveloped area, particularly of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>. It has also been observed that the NO<sub>3</sub><sup>-</sup> concentrations are randomly distributed. The variations in NO<sub>3</sub><sup>-</sup> contents and the other constituents along the main course of Wadi Harad might be attributed to the changes of local flow in fractured media or might have been affected the enrichment of NO3<sup>-</sup> from off-site sources. However, the variability may also indicate that the groundwater has been affected by on-site sewage disposal systems in the study area. In unsewered residential areas and shallow groundwater, both NO<sub>3</sub><sup>-</sup> and Cl are the most significant contaminants associated with domestic wastewater (EPA, 2004). Chloride (Cl<sup>-</sup>) is a good indicator parameter of sewage impacts because it is not subject to adsorption, ion exchange, or oxidation-reduction reactions. To differentiate the potential sources of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in the groundwater of the study area; the plots of  $NO_3^-$  vs Cl<sup>-</sup>, Na<sup>+</sup> vs Cl<sup>-</sup>, Cl<sup>-</sup> vs  $NO_3^-$  + Na<sup>+</sup> and  $NO_3^-$  vs dissolved oxygen (DO) are shown in Figures 4 and 5. The relationship between NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> in an area of known cesspool system contamination is shown in Figure 4a. It appears that Cl almost increases linearly with increasing  $NO_3^-$  with a correlation coefficient (r<sup>2</sup>) of about 0.61. The relationship between Na and Cl ions shown in Figure 4b might be practically utilized to identify the concentration due to evaporation processes (Eugster and Jones, 1979). However, Figure 4b shows a weak correlation with  $r^2 = 0.30$ . The data also indicate that the points are randomly distributed and lie far from the halite dissolution line (1:1), indicating that halite salt resulting from the evaporation processes is not the potential source for Cl<sup>-</sup> ion. The observed deviation of the data points from the dissolution line might be the result of an excess of Cl<sup>-</sup> ions. It is more likely that the Cl ions entered the groundwater by wastewater discharged from on-site systems. Figure 5a shows that neither Na<sup>+</sup> nor NO<sub>3</sub><sup>-</sup> are by themselves sufficient to account for the Cl<sup>-</sup> in the groundwater. But together these two elements do balance to some extent ( $r^2 = 0.71$ ) the concentration trend of Cl<sup>-</sup>. The contribution of  $NH_4^+$  to the overall nitrate concentrations in the groundwater can be depicted from the positive relationship between  $NO_3^-$  and dissolved oxygen (DO) (Figure 5b). It demonstrates that the  $NH_4^+$ concentrations in the groundwater may be lost due to microbial conversion to nitrate by the nitrification process. However, in oxic conditions, the ammonia in sewage can be oxidized to nitrate that normally occurs in the unsaturated zone before effluent percolates to groundwater.

Coliform bacteria were not detected, even in samples with the highest  $NO_3^-$  concentrations, suggesting that substantial residence time of these waters in fractured and weathered rocks was sufficient for bacterial die-off (Geary and Whitehead, 2001).



Figure 4. Correlation diagrams showing the relationship between (a) NO<sub>3</sub> vs Cl; and(b) Na vs Cl.



Figure 5. Correlation diagrams showing the relationship between (a)  $Na+NO_3 vs Cl$ ; and (b)  $NO_3 vs$  dissolved oxygen (DO).

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Two significant factors may account for the movement of contaminants from on-site wastewater systems to the groundwater. Firstly, in the local groundwater flow system (Figure 3) the domestic wells are surrounded by areas where cesspools are present. The general flow direction of the groundwater, which is from southeast to northwest direction, seems to be passing through areas with cesspools before it arrives at the domestic wells. Figure 6 represents a conceptual pollutant transport model in fractured media from the cesspool areas to the groundwater storage in the study area (not scale). Effects of groundwater flow on the groundwater contamination can be traced from the maximum values of  $NO_3^-$  (556 mg/l) and Cl<sup>-</sup> (289 mg/l) that were found in well no. 13. This well is located in the vicinity of the "Almegat Mosque", which is close to the wadi course. Almegat Mosque is a holy place visited annually by several thousands of pilgrims before starting the pilgrimage to Makkah, the holy city. It is expected that a large amount of sewage water seeps through the weathered and fractured zones to the wadi. The volume of wastewater that is derived from the mosque is unknown, but it seems to be quite large as evidenced by the high concentrations of  $NO_3^-$  and Cl. Also, when a number of homes are built in close proximity to their cesspool leaching field, they may together exceed the rock and sediment's absorption capacities.

On the other hand, under the prevailing groundwater flow and  $NO_3^-$  pollution of the recharge zone, the  $NO_3^-$  can easily move further down and follow the groundwater flow direction in this area. Therefore great concern should be paid to contaminant flow to other surrounding areas particularly the Wadi Alyamaniyyah sub-basin downgradient, where the groundwater flowpath has been modified toward the wadi sub-basin (Figure 3). It may necessary to assess the groundwater quality and to identify any impacts arising from on-site wastewater disposal systems being utilized in this area.

Questions must be posed as to the adequacy under the new U.S. EPA regulations of the minimum thicknesses requirement (between 0.9-1.2m) of soil to prevent bacteria and viruses from entering groundwater (EPA, 2000). It must be kept in mind that the EPA manual requires 1.2 m of unsaturated subsoil beneath the invert of the percolation trench. In many parts of the area studied, the water table is within 2.0 to 3.0 m of the surface particularly in wet weather, where the thickness of unsaturated zone decreases. This figure therefore must be taken into consideration with many other factors mentioned above and not used on its own.



Figure 6. Conceptual model of contaminant flow from the cesspool to the groundwater body in the study area (not to scale).

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It is beyond the objective of this paper to present a comprehensive assessment of cumulative and comparative risk for the study area. The average concentration of  $NO_3^-$  is about 235.9 mg/l. This is 5 times above the risk value of the drinking water level (45 mg/l; with 10 mg/l of nitratenitrogen). Increasing  $NO_3^-$  concentrations will continue as long as on-site systems contribute significantly to the risk value. Therefore, to deal with potentially degrading water quality from cesspool wastewater systems, as well as to decrease exposure risk, regulations for cesspool systems in this area should be implemented.

### CONCLUSIONS

In the study area nitrate represents the chemical of greatest concern in the groundwater under unsewered developments. The nitrate concentration in the groundwater ranges between 151 and 556, mg/l with an average of about 235.9 mg/l. This value exceeds the drinking water standard. Impacts from on-site cesspool systems on the shallow aquifer are obvious as evidenced by the elevated concentrations of  $NO_3^-$  and Cl. Nitrate contamination is generally observed in close proximity to potential point waste sources. Coliform bacteria have not been detected in the groundwater samples, which may be because the residence time of these waters in fractured and weathered rocks was sufficient for bacterial die-off. Lot-size and setback distances of the cesspool are critical factors in determining the amount of natural attenuation that occurs between the location where cesspool effluents enter the aquifer, and the nearest downgradient point of groundwater withdrawal. Recommendations are provided for better source water protection.

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#### **REFERENCES**

- Alyamani, M.S., and A Y. Bokhari. 2003. Salinity problems of groundwater in parts of Wadis Fatimah and Usfan basins in western province of Saudi Arabia. Final Report. Project No. 201/424, Jeddah, Saudi Arabia, 102p. (in Arabic)
- Alyamani, M.S., and M.T. Hussein. 1995. Hydrochemical study of groundwater in recharge area, Wade Fatimah basin, Saudi Arabia. Geo Journal, Vol. 37.1, 81-89.
- Amade, L.J. 1999. Seasonal correlation of well contamination and septic tank distance. Groundwater, Vol. 37, No. 6, 920-923.
- APH/AWWA/WPCF. 1989. Standard methods for the Examination of Waste Wastewater. Washington, DC, American Public Health Association.
- Duda A.M., and K.D. Cromartie. 1982. Costal pollution from septic tank drainfields. Journal of Env. Eng. Div. Am.Soc. Civ. Eng., Vol. 108, 1265-1279.
- Eugster, H.P., and B.F. Jones. 1979. Behavior of major solutes during closed basin brine evolution. Am Journal of Sci., Vol. 279, 609-631.
- Environmental Protection Agency (EPA). 2000. Wastewater Treatment Manual: Treatment Systems for Single Houses.
- Environmental Protection Agency (EPA). 2004. Edition of Drinking Water Standards and Health Advisories EPA 822-R-04-005.
- Geary, P.M., and J.H. Whitehead. 2001. Groundwater Contamination from On-site Domestic Wastewater Management Systems in a Coastal Catchment, 9<sup>th</sup> National Symposium on Individual and Small Community

Sewage Systems Proceeding, American Society of Agricultural Engineers, St. Joseph, Michigan, 479-487.

- Moore, T.A., and M.H. Al-Rehaili. 1989. Geologic map of the Makkah quadrangle, Sheet21D, Kingdom of Saudi Arabia: Saudi Arabian Directorate General of Mineral Resources. Geoscience map GM-107C, 1:250,000 scale.
- Rose, J.B., D.W. Griffin, and L.W. Nicosia. 1999. Virus Transport from septic tanks to Coastal Waters. In: 10<sup>th</sup> Northwest On-site Wastewater Treatment Conference Proceedings, University of Washington, Seattle, WA, 71-80.
- Saudi Geological Survey. 2004. Strategic groundwater storage in Wadi Fatimah, Makkah region, Saudi Arabia. Technical report, SGS –TR- 2003-2.
- Scandura, J.E., and M.D. Sobsey. 1997. Viral and Bacterial Contamination of Groundwater from On-site Sewage Treatment Systems. Journal of Water Sciences and Techno., 11-12: 141-146.
- Sharaf, M.A., M.S. Alyamani, and A.M. Alsubani. 2004. Regional study of rare and trace elements in the groundwater of major wadi basins (An Numan, Usfan, and Fatimah) in western Saudi Arabia and their suitability for various purposes. Final report, Project No. (204/423), Jeddah, Saudi Arabia, 214p.
- World Health Organization (WHO). 1998. Guidelines for drinking water-water quality, 2<sup>nd</sup> ed. Addendum to volume 1, Recommendations, Geneva.
- World Health Organization (WHO). 2000. Report of Drinking Water Quality Committee Meeting, Berlin.
- Whitehead, J.H., and P.M. Geary. 2000. Geotechnical Aspects of Domestic On-site Effluent Management Systems. Australian Jour. of Earth Sci., Vol. 47, 75-82.
- Yates, M.V. 1985. Cesspool density and groundwater contamination. Groundwater, Vol. 23, 586-591.

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