GROUNDWATER QUALITY IN THE VICINITY OF ABA-EKU DUMPSITE, IBADAN, SW NIGERIA: A DETAILED REPORT. *ONI, A. A.^{1, 2} and HASSAN, A.T.¹ http://dx.doi.org/10.4314/ejesm.v6i6.2

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Abstract

Groundwater contamination by landfill leachate is a recognized socio-economic and environmental problem in many countries. The Aba-Eku dumpsite was upgraded and the present study undertaken to characterize groundwater quality in the vicinity of the site to assess the effectiveness of the upgrades. Twenty three parameters were assessed in two groundwater wells (GW1 and GW2 located 600m from the site) over a twenty-month period using Inductively Coupled Plasma Spectroscopy and Ion Chromatography. Data were analyzed using t-test, ANOVA and correlation coefficients. Phosphates and nitrites were below detection limits. Suspended solids: [42.96±67.68 mg/l]; COD-[9.80±4.07mg/l]; and four metals [Pb: 0.047±0.029; Cu: 0.017±0.009; Ni: 0.012±0.011; Cr: 0.014±0.019 mg/l] were elevated in the up-gradient well GW1. However, only lead was significant (p<0.05). Fifteen parameters were elevated in GW2 down-gradient, of which nine including: pH: 8.15±0.11, dissolved solids: 241.39±62.89; magnesium: 28.25±17.52; chloride: 38.19±16.80; sulphate: 27.00±9.62 and cadmium: 0.070±0.045 mg/l were significant (p<0.05). Mean lead, GW1-0.047±0.029; GW2-0.015±0.018; cadmium GW1-0.028±0.047; GW2-0.070±0.045 and iron GW1-0.82±0.61; GW2-2.43±4.33 mg/l levels in both wells exceeded regulatory limits. Correlation results [GW1:TSS-COD;0.713;p<0.01; GW2:TSS-COD:0.262] indicated that the turbid nature of GW1 reflected in higher levels of TSS appeared to be composed of organics and may have contributed to lead mobilization in this well. Zinc mobilization in both wells was strongly pH dependent [GW1: pH-Zn: -0.491;p<0.01; GW2:pH-Zn: -0.682;p<0.05]. Seasonal variations were less distinct. However, increased leachate influx into GW2 resulted in significantly elevated wet season levels of pH, nitrates, sulphates, chloride and TDS. There is urgent need for remediation in view of the health implications of these pollutants.

Key words: Groundwater, Aba-Eku dumpsite, landfill leachate, Remediation.

INTRODUCTION

Sanitary landfills are expensive to construct and maintain. Hence, upgrading dumpsites to sanitary landfills in phases is advocated to provide a cost-effective means of groundwater protection (Allen, 2001; Diaz and Savage, 2002). Groundwater contamination by landfill leachate is a recognized socio-economic and environmental problem (Rapti-Caputo and Vaccaro, 2006). The release of leachate into the groundwater aquifer leads to the formation of a complex contaminant plume that fundamentally alters the chemical properties of the aquifer (Jorstad et al. 2004). Leachates may introduce pathogens and various contaminants into groundwater (Salman, 1999).

The Aba-Eku landfill site, located at km 13 along Akanran – Ijebu Igbo road in Ona-Ara

¹Department of Zoology, University of Ibadan, Nigeria ²Institute of Applied Ecology, Shenyang, China. *Corresponding Author: adeyoni2006@yahoo.co.uk Local Government Area, is a major repository of municipal solid wastes in Ibadan - Nigeria. It has been used as an open dump since 1994. Reports of the death of some domestic animals attributed to the impacts of the dumpsite necessitated the upgrading to landfill, possibly in phases. It was thus upgraded and commissioned in 1998. Evidence of upgrading is shown by a system of pipes (Aluko and Sridhar, 2005), located 250m down-gradient of the site, which drains the leachates into a central collecting pond. The pond appears to be a constructed wetland and is equipped with aquatic macrophytes (Ipomoea aquatica forsk and Lemna sp.) which have been demonstrated to have high leachate purification properties (Aluko and Sridhar, 2005).

Information obtained from the Waste Management Board indicates that a clay liner containment system was also installed (Shittu, 2000, Pers. Comm;). Poor funding may however have hampered upgrading efforts and presently, disposal does not follow standard landfilling practices. The site is located within 600m of Aba-Eku community. This makes investigation of its environmental impact imperative. Thus, it becomes necessary to carry out detailed characterization of groundwater in the vicinity of the site to assess the effectiveness of upgrades. Previous studies (Hassan and Oni, 2009) were carried out over a three month period, which is inadequate for proper characterization of the groundwater. In addition, fewer parameters were assessed. Thus, this study involves a detailed characterization of groundwater in the vicinity of Aba-Eku

dumpsite in order to provide more information on the effectiveness of the above containment measures aimed at ground and surface water protection.

Materials and Methods Study Area

The Aba-Eku landfill is located at Km 13, along Akanran– Ijebu-Igbo road in Ona-Ara Local Government Area of Oyo state (Figure 1). Two wells in Aba-Eku community were chosen as groundwater sampling points and designated GW 1 and GW 2 respectively. Both wells were at up- and down-gradient locations 600m from the dumpsite. Twenty three parameters were evaluated over a twenty month period using Inductively Coupled Plasma Spectroscopy and Ion Chromatography methods.



Figure 1 Map of Ona-Ara LGA (inset) showing the Aba-Eku Dumpsite and groundwater sampling points (GW 1 and GW 2)

Sampling, preservation and analytical methods for collected groundwater

Groundwater samples were obtained from GW 1 and GW 2 via a pulley system. Samples

were collected in pre-washed polyethylene bottles, and taken to the laboratory where they were stored at approximately 4°C until analysis. Analytical parameters were determined from January 2003-September 2004. The following parameters were determined in the groundwater as given below:

- ▶ pH [pH meter model PHS-3B];
- Total Dissolved Solids (TDS) and Electrical Conductivity (EC) [WTW conductivity meter LF 95 model].
- Total Suspended Solids (TSS); and Chemical Oxygen Demand (COD) [APHA, (1998)]

The metals and cations were preserved as follows: 100ml sample was acidified with 1ml concentrated nitric acid (HNO_3) for preservation prior to digestion and analysis. Parameters determined included: Cadmium, Chromium, Lead, Nickel, Copper, Zinc, Calcium, Magnesium, Potassium, Iron and Manganese. They were analysed after nitricperchloric acid digestion (APHA, 1998) using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Perkin Elmer Optima 3000 at the Institute of Applied Ecology, Shenyang, China.

The following anions and ammonium: NH_4^+ were determined using an Ion Chromatograph IC 1010 model (detection limit <0.005) at the Shenyang University, Shenyang China:-Sulphates, Chloride, Nitrates, Nitrites and Phosphates. Chemical Oxygen Demand (COD) was tested as an index of organics present. Data were analysed using Independent Samples T-Test, Analysis of Variance (ANOVA) and correlation coefficients.

Results and Discussion

Of the twenty-three parameters determined, two (phosphates, nitrites) were below detection limits. Lead, copper, nickel, chromium, TSS and COD were elevated in the up-gradient well GW 1. Of these, only lead was significant (p<0.05; Tables 1-5). Although turbidity was not determined, the higher amounts of suspended solids reflected in the turbid nature of the water in GW 1. Furthermore, COD and TSS in GW 1 correlated significantly and positively with each other (0.713; Table 6), implying that organics may contribute substantially to suspended solids in this well. Organics may form stable complexes with metals particularly lead, enhancing mobility, thus explaining the higher lead levels in GW 1 (Deiss et al., 2004; Pivato and Raga, 2006). Fifteen parameters were elevated in the well

GW 2 down-gradient of the dumpsite (Tables 2 and 4). While pH, TDS, electrical conductivity (EC), magnesium, potassium, chloride, nitrate, sulphate and cadmium were significantly higher in GW 2 (p<0.05; ANOVA), other parameters such as total solids, iron, manganese, zinc, calcium and ammonium were higher but not significant (p<0.05; ANOVA; Tables 2 and 4). Of the above parameters, mean values of lead, cadmium and iron exceeded one/both regulatory limits (WHO; FMEnv) in both wells, while nitrate exceeded regulatory limits occasionally in GW 2. Other parameters were within the limits (Tables 1-4).

Another important observation was that low mobility metals such as lead and copper [Mulligan *et al.* (2001); Deiss *et al.*, (2004)] were highest in the up-gradient well GW 1; while high mobility metals (cadmium, zinc) [Christensen *et al.* (1996); Kugler *et al.* (2002)] were highest down-gradient in GW 2. The degree of mobility of a metal in the environment is associated with risk assessment. The more mobile the metal is, the more risk associated with it (Mulligan *et al.*, 2001).

Metals are indestructible elements that can accumulate in biological tissues (Chofqi *et al.*, 2004). Lead is a serious cumulative body poison. Water, air and food are the entry routes into the body system. It can be toxic at very low concentrations (Rajaratnam *et al.*, 2002), and may cause mild to chronic effects such as anemia, headaches, fatigue, nephritis, scaring and shrinking of the kidney tissues. It may also damage the liver, brain, reproductive and central nervous systems and may also cause death (Ghaedi *et al.*, 2006).

Cadmium has also been reported to have neuro-toxic effects (Chofqi et al., 2004). Furthermore, it has higher potentials to bioconcentrate in living tissues, compared to lead and zinc (Hsu et al., 2006). Chronic health problems associated with cadmium toxicity include bone disease, lung edema, renal dysfunction, liver damage and anemia (Chaudri et al., 2001). Iron on the other hand, affects plumbing and appliances through scale formation or corrosion, and may also impart taste and odors to water. The moderately high concentrations of chloride, nitrates, sulphates, ammonia, iron and zinc in GW 2 proved to be tracers for groundwater contamination (Mor et

al., 2006) and suggests that the groundwater quality has been affected by leachate percolation. Marzougui and Mammou, (2006) also observed high concentrations of these contaminants in groundwater surrounding the Henchir El Yahoudia dump site, Tunisia. High nitrate levels may cause health problems in infants and animals (Wakida and Lerner, 2005). A number of significant correlations were obtained in the groundwater. In both wells, pH had a significant negative correlation with zinc, and also with nickel in GW 2. This implies that zinc mobility in the groundwater and to a lesser extent nickel, appears to be strongly pH dependent. In GW 1, total suspended solids and total solids also had a high significant correlation (0.984, p < 0.01); implying that the suspended solids are the major contributors to the total solids content of the well. Suspended solids also correlated well with COD (0.713, p<0.01), an association which has been explained earlier. COD also correlated fairly with total solids (0.636, p<0.01) - (Table 6).

In both wells, the exchangeable cations, calcium, magnesium and potassium correlated significantly with each other. Cadmium also correlated significantly (p <0.01) with these cations in GW 2. A similar correlation has been reported earlier in the soil (Oni, 2010), where cadmium correlated significantly and positively with these cations, as well as with the CEC of the soils. This may imply that cation exchange may also play an important role in the mobilization of this metal in the soils into the groundwater. Iron (Fe) and manganese (Mn) correlated significantly (p<0.01) in both wells (Tables 6-7). The correlations among the exchangeable cations; and between iron and manganese are possibly due to similarities in association, and the role of iron and manganese in redox reactions (Christensen et al., 2001). Other correlations in GW 2 include a number of metal-to-metal correlations: Zn correlated with Ni (0.698); Cr (0.689). In addition, Zn and Ni each correlated negatively with pH at -0.682 & -0.674, all at p<0.01 respectively (Table 7). The inter-correlations among the metals may be suggestive of similar geo-genic or anthropogenic origins.

pH, TDS, nitrates, sulphates and chloride were elevated in GW 2 down-gradient of the dumpsite, particularly in the wet season. The landfill environment is mainly alkaline and increased leachate influx during this period, may lead to increased wash-out into GW 2, raising the water pH. There may also be increased leaching out of soluble salts from the refuse, transporting them down-gradient into the groundwater. Increased levels of COD (p<0.05) and suspended solids and COD prevailed in GW 1 in the wet season, and may have also contributed to high lead levels in GW 1 due to the formation of soluble complexes with the organic matter as earlier explained. Other parameters showed no distinct patterns, but in general were elevated in dry or wet season in either well.

Conclusion

In general, most parameters were well controlled in the groundwater. However, two toxic metals lead, cadmium; as well as iron were major issues of concern, as they exceeded both local and international regulatory limits, thus highlighting the need for remedial measures to be put in place at the site.

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	Ca	Mg	K	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr
Jan. 03	16.03	2.94	2.17	0.52	0.028	0.035	0.408	0.085	0.031	0.015	0.012
Feb. 03	31.53	1.91	1.61	1.046	0.158	0.026	0.158	0.037	0.017	0.022	0.005
Mar 03	19.56	3.43	2.68	0.175	0.002	0.010	0.062	0.042	0.008	0.00	0.036
Apr. 03	17.03	2.91	2.52	0.819	0.025	0.030	0.156	0.08	0.035	0.022	0.011
May 03	6.39	2.40	2.05	1.182	0.048	0.011	0.104	0.062	0.017	0.009	0.005
Jun. 03	11.43	3.30	2.04	1.662	0.032	0.025	0.245	0.051	0.024	0.014	0.051
Jul. 03	6.75	3.00	1.81	0.408	0.008	0.012	0.064	0.038	0.011	0.003	0.003
Aug 03	5.16	3.59	1.73	0.656	0.010	0.009	0.115	0.042	0.017	0.044	0.052
Sep. 03	#	#	#	#	#	#	#	#	#	#	#
Oct. 03	10.16	5.23	1.90	0.498	0.004	0.009	0.22	0.012	0.008	0.012	0.052
Nov 03	50.16	6.71	3.40	1.079	0.044	0.017	0.212	0.024	0.021	0.002	0.038
Dec. 03	10.46	3.30	1.82	0.329	0.030	0.012	0.086	0.048	0.017	0.023	0.009
Jan. 04	12.19	4.11	1.40	0.398	0.012	0.003	0.038	0.028	0.02	0.006	0.00
Feb. 04	9.83	3.23	1.45	0.232	0.004	0.004	0.030	0.032	0.015	0.022	0.001
Mar.	11.03	4.39	2.31	1.389	0.118	0.018	0.110	0.043	0.022	0.008	0.001
Apr. 04	3.78	1.69	0.98	2.64	0.071	0.031	0.145	0.054	0.224	0.00	0.006
May 04	9.09	3.32	1.74	0.519	0.02	0.021	0.00	0.033	0.017	0.003	0.000
Jun. 04	9.24	2.82	2.10	1.461	0.025	0.021	0.00	0.018	0.018	0.007	0.000
Jul. 04	10.95	2.78	2.48	0.472	0.057	0.014	0.00	0.041	0.017	0.005	0.000
Aug. 04	13.34	3.02	2.16	0.29	0.018	0.018	0.00	0.028	0.011	0.00	0.000
Sep. 04	16.44	3.80	1.87	0.708	0.046	0.023	0.00	0.145	0.019	0.018	0.000
AV	14.03	3.39	2.01	0.82	0.04	0.02	0.11	0.05*	0.03	0.01	0.01
SD	10.46	1.12	0.52	0.61	0.04	0.01	0.11	0.03	0.05	0.01	0.02
WHO/FMEnv Lmi	ts 150	200	200	0.3/1.0	0.4	2.00	5.00	0.01/0.05;	0.003/0.01	0.07	0.05

Table 1 Cations and heavy metals in GW 1 over the study period

#: Not sampled; Data highlighted exceeded one/both regulatory limits on the stated dates. *Significant at p < 0.05

	Ca	Mg	K	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr
Jan. 03	WD	WD	WD	WD	WD	WD	WD	WD	WD	WD	WD
Feb. 03	9.89	7.15	4.33	0.00	0.000	0.004	0.029	0.00	0.019	0.012	0.000
Mar. 03	12.20	9.08	4.98	0.046	0.000	0.006	0.058	0.002	0.015	0.012	0.000
Apr. 03	7.62	8.98	3.14	0.313	0.002	0.010	0.076	0.020	0.016	0.009	0.005
May 03	17.99	49.35	19.32	0.665	0.038	0.000	0.170	0.052	0.125	0.005	0.028
Jun. 03	87.52	84.95	52.49	0.468	0.109	0.000	1.169	0.007	0.213	0.025	0.012
Jul. 03	27.46	32.91	32.45	0.432	0.025	0.002	0.161	0.000	0.079	0.005	0.000
Aug. 03	16.72	35.68	16.02	0.082	0.010	0.000	0.070	0.018	0.088	0.002	0.000
Sep. 03	#	#	#	#	#	#	#	#	#	#	#
Oct. 03	29.29	39.61	19.52	0.385	0.033	0.020	0.209	0.057	0.100	0.008	0.000
Nov. 03	20.56	24.31	8.73	0.451	0.043	0.017	0.514	0.041	0.065	0.030	0.000
Dec. 03	6.75	21.01	6.11	0.612	0.018	0.004	0.000	0.003	0.056	0.015	0.000
Jan. 04	9.44	30.38	7.86	7.925	0.196	0.035	0.000	0.023	0.073	0.000	0.000
Feb. 04	7.65	21.68	6.09	0.530	0.042	0.000	0.004	0.016	0.057	0.020	0.017
Mar. 04	47.79	36.70	12.27	16.87	0.487	0.035	2.480	0.034	0.095	0.033	0.042
Apr. 04	10.91	26.97	6.58	2.709	0.079	0.034	0.251	0.011	0.064	0.000	0.000
May 04	21.86	19.07	6.05	4.455	0.109	0.028	0.097	0.000	0.050	0.000	0.000
Jun. 04	14.46	17.63	7.27	0.095	0.020	0.000	0.013	0.000	0.042	0.006	0.002
Jul. 04	19.82	23.30	8.50	8.382	0.156	0.033	0.022	0.001	0.054	0.000	0.000
Aug. 04	23.36	27.83	11.04	0.392	0.002	0.000	0.288	0.000	0.070	0.007	0.026
Sep. 04	15.69	20.10	17.51	1.281	0.028	0.000	0.072	0.002	0.047	0.000	0.000
AV	21.42	28.25*	13.17*	2.43	0.07	0.01	0.299	0.02*	0.07*	0.01	0.007
SD	18.79	17.52	11.96	4.33	0.11	0.01	0.59	0.02	0.04	0.01	0.01
HO/FMEnv	150	200	200	0.3/1.0	0.4	2.00	5.00	0.01/0.05;	0.003/0.01;	0.07	0.05

Table 2 Cations and heavy metals in GW 2 over the study period

WD: Well Dry; #: Not sampled. Data highlighted exceeded one/both regulatory limits on the stated dates. *: Significant at p < 0.05.

	рН	TDS	TSS	TS	EC(µs/cm)	COD	Cl	N0 ₃	NH4 ⁺	S04 ²⁻	0.005< P04 ³⁻ /N0 ²⁻
Jan. 03	-	-	-	-	-	-	-	-	-	-	-
Feb. 03	7.74	97.20	40.28	137.48	194.40	5.29	3.108	0.915	0.280	1.688	N/D
Mar. 03	7.62	53.40	0.00	53.40	106.90	7.35	6.395	2.497	0.252	2.251	N/D
Apr. 03	-	-	-	-	-	-	-	-	-	-	-
May 03	7.60	77.90	146.96	224.86	155.70	15.28	6.091	3.127	0.127	3.271	N/D
Jun. 03	7.40	71.30	119.44	190.74	142.70	18.67	1.712	0.589	0.050	1.925	N/D
Jul. 03	7.62	58.90	0.00	58.90	117.90	12.43	1.558	4.050	0.069	1.969	N/D
Aug. 03	7.82	55.90	0.00	55.90	111.80	7.96	3.797	4.187	0.261	2.748	N/D
Sep. 03	#	#	#	#	#	#	#	#	#	#	#
Oct. 03	7.82	54.90	0.00	54.90	109.70	11.37	4.247	4.211	0.087	3.244	N/D
Nov. 03	-	-	-	-	-	-	-	-	-	-	-
Dec. 03	7.60	74.10	0.00	74.10	148.30	4.19	6.605	0.291	0.049	2.359	N/D
Jan. 04	7.51	90.70	0.00	90.70	181.20	5.82	4.488	2.885	0.084	2.213	N/D
Feb. 04	8.10	78.80	0.00	78.80	157.70	9.45	4.450	4.029	0.041	3.132	N/D
Mar. 04	7.93	91.30	24.47	115.77	182.95	6.92	7.383	2.282	0.059	4.077	N/D
Apr. 04	7.91	71.30	40.65	111.95	141.90	6.24	5.299	1.471	0.328	3.742	N/D
May 04	7.94	80.10	45.55	125.65	160.20	10.40	6.265	5.083	0.033	3.687	N/D
Jun. 04	7.89	95.60	246.03	341.63	191.10	16.63	8.070	2.161	0.097	5.708	N/D
Jul. 04	8.04	76.60	21.82	98.42	153.30	8.48	6.457	1.388	0.005	3.607	N/D
Aug. 04	8.02	94.30	43.04	137.34	188.60	9.68	7.514	0.595	0.087	3.563	N/D
Sep. 04	7.93	79.20	2.12	81.32	158.20	10.40	5.696	0.133	0.089	3.320	N/D
ĀV	7.79	76.56	42.96	119.52	153.09	9.80	5.24	2.35	0.118	3.088	ND
SD	0.20	14.47	67.68	74.57	28.96	4.07	1.92	1.58	0.098	0.997	ND
WHO/FMEnv		250						50/10	1.5	50	

Table 3 General parameters, anions and organic matter (COD) in GW 1 over the study period

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: Only cations and heavy metal results are presented for these months. ND: Below detection limit (0.005<); #: Not sampled.

	pН	TDS	TSS	TS	EC(µs/cm)	COD	Cl	N0 ₃	NH_4^+	S04 ²⁻	$P0_4^3/N0^2$
Jan. 03	WD	WD	WD	WD	WD	WD	WD	WD	WD	WD	WD
Feb -Apr. 03	-	-	-	-	-	-	-	-	-	-	-
May 03	8.31	235.00	23.89	258.89	469.00	7.56	35.48	9.594	0.349	26.776	N/D
Jun. 03	8.08	192.00	8.49	200.49	385.00	8.49	39.89	21.67	0.505	23.075	N/D
Jul. 03	8.16	331.00	14.34	345.34	660.00	10.16	68.98	38.00	0.459	43.295	N/D
Aug. 03	8.20	224.00	6.31	230.31	449.00	8.08	17.14	0.300	0.193	11.045	N/D
Sep. 03	#	#	#	#	#	#	#	#	#	#	#
Oct. 03	8.25	279.00	5.55	284.55	549.00	2.16	58.48	11.431	0.068	34.955	N/D
Nov. 03	7.98	123.90	30.80	154.70	247.90	9.53	14.00	0.008	0.188	11.347	N/D
Dec. 03	8.20	249.00	6.73	255.73	498.00	9.00	36.63	0.410	0.000	27.613	N/D
Jan. 04	8.04	194.00	29.34	223.34	388.00	8.93	26.39	0.364	0.216	21.237	N/D
Feb. 04	8.16	224.00	2.77	226.77	450.00	4.39	29.95	0.545	0.000	25.965	N/D
Mar. 04	7.90	205.00	-	205.00	410.00	13.58	21.69	0.282	0.731	20.424	N/D
Apr. 04	8.14	136.30	3.00	139.30	272.30	11.17	18.16	0.198	0.102	16.296	N/D
May 04	8.21	256.00	9.18	265.18	514.00	9.82	35.62	7.332	0.265	30.089	N/D
Jun. 04	8.10	278.00	8.47	286.47	555.00	7.93	47.49	6.060	0.000	32.679	N/D
Jul. 04	8.30	300.00	12.00	312.00	604.00	11.24	49.35	3.497	0.371	32.614	N/D
Aug. 04	8.13	288.00	4.96	292.96	576.00	7.48	48.65	9.598	0.159	31.521	N/D
Sep. 04	8.22	347.00	-	347.00	696.00	9.12	63.16	44.23	0.000	43.022	N/D
ĀV	8.15*	241.39*	11.85	248.29*	482.7*	8.67	38.19*	9.60*	0.225	26.997*	ND
SD	0.11	62.89	9.41	57.53	125.64	2.66	16.8	13.70	0.212	9.615	ND
WHO/FMEnv		250						50/10	1.5	50	

Table 4 General parameters, anions and organic matter (COD) in GW 2 over the study period

: Only cations and heavy metal results are presented for these months. WD: well dry; ND: Below detection limit (0.005<); #: Not sampled. Data highlighted exceeded one/both regulatory limits on the stated dates. *: Significantly different (p < 0.05).

Physico-chemical			GW 1				GW 2	
parameters (mg/l	Range (dry)	Range (wet)	Mean ± SD(D)	Mean ± SD(W)	Range (dry)	Range (wet)	Mean ± SD(D)	Mean ± SD(W)
except otherwise			(dry)	(wet)			(dry)	(wet)
PH (no unit)	7.51-8.10	7.40-8.04	$7.75 \pm 0.22a$	$7.82 \pm 0.20a$	7.90-8.20	8.08-8.31	$8.06 \pm 0.12b$	8.19 ± 0.08b
COD	4.19-9.45	6.24-18.67	$6.50 \pm 1.84a$	$11.59 \pm 3.85b$	4.39-13.58	2.16-11.24	$9.09 \pm 3.26a$	$8.47 \pm 2.49a$
TSS	0.00-40.28	0.00-246.03	$10.79 \pm 17.45a$	$60.51 \pm 78.85a$	2.77-30.80	3.00-23.89	$17.41 \pm 14.72a$	$9.62 \pm 6.03a$
TDS	74.10-91.30	54.90-95.60	83.73 ± 4.31a	74.18 ± 4.16a	123.9-249.0	136.3-347.0	199.18 ±21.0b	260.57 ±18.47c
EC (µs/cm)	148.3-182.9	109.7-191.1	$167.5 \pm 8.60a$	$148.3 \pm 8.3a$	247.9-498.0	272.3-696.0	$398.8 \pm 42.1b$	$520.8 \pm 36.9c$
Ca	9.83-50.16	3.78-17.03	$20.10 \pm 14.11a$	9.98 ± 4.18a	6.75-47.79	7.62-87.52	$16.33 \pm 14.61b$	$24.39 \pm 20.85b$
Mg	1.91-6.71	1.69-5.23	$3.75 \pm 1.41a$	$3.16 \pm 0.85a$	7.15-36.70	8.98-84.95	21.47 ± 10.63 b	$32.20 \pm 19.86b$
K	1.40-3.40	0.98-2.52	$2.11 \pm 0.69a$	$1.95 \pm 0.40a$	4.33-12.27	3.14-52.49	$7.20 \pm 2.71a$	16.66 ± 13.92b
Fe	0.18-1.39	0.29-2.64	$0.65 \pm 0.46a$	0.94 ± 0.69 ab	0.00-16.87	0.082-8.38	$3.78 \pm 6.43b$	1.64 ± 2.49 ab
Mn	0.002-0.158	0.004-0.071	$0.050 \pm 0.06a$	0.030 ± 0.021 a	0.000-0.487	0.002-0.156	$0.112 \pm 0.179a$	$0.051 \pm 0.050a$
Cu	0.003- 0.035	0.009-0.031	$0.016 \pm 0.011a$	$0.019 \pm 0.008a$	0.000 -0.035	0.000-0.034	$0.014 \pm 0.015a$	0.011 ± 0.014 a
Zn	0.030-0.408	0.000-0.245	$0.138 \pm 0.125a$	0.087 ± 0.091 a	0.000-2.48	0.013-1.169	$0.441 \pm 0.918a$	$0.217 \pm 0.313a$
Pb	0.024-0.085	0.012-0.145	$0.042 \pm 0.019a$	$0.050 \pm 0.035a$	0.000-0.041	0.000-0.051	0.017 ± 0.016b	0.014 ± 0.020 b
Cd	0.008-0.031	0.008-0.224	0.02 ± 0.007 ab	0.035 ± 0.06 ab	0.015-0.095	0.016-0.213	0.054 ± 0.03 bc	0.080 ± 0.051 c
Ni	0.000-0.023	0.000-0.044	$0.012 \pm 0.009a$	$0.011 \pm 0.012a$	0.000-0.023	0.000-0.035	$0.017 \pm 0.011a$	0.005 ± 0.007 a
Cr	0.000-0.038	0.000-0.052	$0.013 \pm 0.015a$	$0.015 \pm 0.022a$	0.000-0.042	0.000-0.028	$0.008 \pm 0.016a$	$0.006 \pm 0.010a$
Cl	3.11-7.38	1.56-8.07	$5.40 \pm 1.63a$	$5.16 \pm 2.14a$	14.00-36.63	17.14-68.98	$25.73 \pm 8.53b$	43.85 ± 16.77b
N0 ₃	0.291-4.029	0.133-5.083	$2.15 \pm 1.36a$	$2.45 \pm 1.75a$	0.008-0.545	0.198-44.23	$0.32 \pm 0.20b$	13.81 ± 14.80c
S0 ₄ ²⁻	1.688-4.077	1.925-5.708	$2.62 \pm 0.85a$	$3.34 \pm 1.01a$	11.35-27.61	11.05-43.30	$21.32 \pm 6.35b$	29.58 ± 9.95c
$\mathrm{NH_4}^+$	0.041-0.280	0.005-0.328	$0.103 \pm 0.10a$	$0.112 \pm 0.097a$	0.000-0.731	0.000-0.505	$0.227 \pm 0.299a$	$0.225 \pm 0.178a$

Table 5 Seasonal variation in the parameters in the groundwater wells

Table 6 Correlation coefficient matrix for GW 1

	Са	Mg	К	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr	COD	Cl	NO ₃	${\rm NH_4}^+$	SO ₄ ²⁻	EC	рН	TDS	TSS	TS
Са	1.000																				
Mg	0.514*	1.000																			
к	0.632**	0.540*	1.000																		
Fe	-0.049	-0.227	-0.185	1.000																	
Mn	0.301	-0.233	-0.049	0.484*	1.000																
Cu	0.164	-0.347	0.058	0.526*	0.408	1.000															
Zn	0.284	0.161	0.177	0.243	0.123	0.471*	1.000														
Pb	-0.039	-0.210	-0.026	0.064	0.106	0.463*	0.114	1.000													
Cd	-0.205	-0.365	-0.435	0.734**	0.222	0.441	0.151	0.120	1.000												
Ni	-0.109	-0.076	-0.223	-0.153	0.017	-0.053	0.187	0.252	-0.210	1.000											
Cr	0.197	0.469*	0.284	0.034	-0.282	-0.125	0.505*	-0.195	-0.111	0.296	1.000										
COD	-0.293	-0.002	0.249	0.231	-0.300	0.147	0.140	0.016	-0.212	-0.146	0.218	1.000									
Cl	-0.074	0.016	0.383	-0.027	0.039	0.045	-0.567*	0.007	0.005	-0.316	-0.430	-0.166	1.000								
NO₃	-0.411	0.303	-0.150	-0.270	-0.425	-0.516*	-0.038	-0.447	-0.170	0.048	0.171	0.111	-0.191	1.000							
$\mathbf{NH_4}^+$	0.234	-0.430	-0.300	0.403	0.297	0.293	0.326	0.045	0.532*	0.173	0.266	-0.335	-0.142	-0.061	1.000						
SO ₄ ²⁻	-0.385	-0.001	0.137	0.312	-0.009	0.224	-0.409	-0.077	0.176	-0.263	-0.340	0.262	0.728**	0.063	-0.183	1.000					
EC	0.338	-0.259	-0.086	0.176	0.518*	0.308	-0.353	-0.024	-0.056	-0.165	-0.696**	-0.056	0.404	-0.386	-0.206	0.354	1.000				
рН	-0.092	-0.043	-0.023	-0.057	0.103	0.123	-0.491*	0.011	0.133	-0.026	-0.392	-0.194	0.482	0.095	-0.103	0.632**	0.254	1.000			
TDS	0.337	-0.262	-0.091	0.180	0.518*	0.311	-0.352	-0.023	-0.050	-0.166	-0.697**	-0.057	0.404	-0.387	-0.202	0.355	1.000**	0.254	1.000		
TSS	-0.136	-0.357	0.163	0.504*	0.080	0.362	0.004	-0.132	0.020	-0.188	-0.100	0.713**	0.258	-0.124	-0.054	0.543*	0.392	-0.108	0.393	1.000	
TS	-0.058	-0.375	0.130	0.492*	0.173	0.389	-0.065	-0.124	0.008	-0.203	-0.226	0.636**	0.313	-0.188	-0.088	0.561*	0.550*	-0.048	0.551*	0.984**	1.000

** - p, 0.01; * - p, 0.05

	Са	Mg	к	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr	COD	Cl	NO₃ ⁻	NH4 ⁺	SO42-	EC	рН	TDS	TSS	TS
Са	1.000																				
Mg	0.840**	1.000																			
к	0.835**	0.875**	1.000																		
Fe	0.216	0.068	-0.131	1.000																	
Mn	0.406	0.254	0.044	0.963**	1.000																
Cu	-0.007	-0.077	-0.301	0.754**	0.671**	1.000															
Zn	0.694**	0.465*	0.334	0.662**	0.813**	0.298	1.000														
Pb	0.089	0.321	0.065	0.137	0.221	0.218	0.276	1.000													
Cd	0.837**	0.997**	0.860**	0.075	0.265	-0.076	0.480*	0.341	1.000												
Ni	0.476*	0.260	0.184	0.197	0.377	-0.062	0.698**	0.288	0.294	1.000											
Cr	0.367	0.354	0.138	0.449	0.545*	-0.020	0.689**	0.327	0.376	0.472*	1.000										
COD	0.130	-0.094	-0.076	0.622**	0.582*	0.448	0.453	-0.345	-0.106	0.087	0.129	1.000									
Cl	0.087	-0.014	0.353	-0.263	-0.319	-0.345	-0.274	-0.299	-0.042	-0.360	-0.179	-0.259	1.000								
NO₃ ⁻	0.269	0.192	0.598*	-0.285	-0.257	-0.426	-0.075	-0.277	0.163	-0.213	-0.149	-0.019	0.773**	1.000							
${\rm NH_4}^+$	0.668**	0.537*	0.470	0.624**	0.708**	0.307	0.746**	0.135	0.537*	0.369	0.520*	0.567*	-0.088	0.070	1.000						
SO 4 ²⁻	-0.044	-0.175	0.181	-0.154	-0.232	-0.271	-0.277	-0.343	-0.197	-0.379	-0.114	-0.185	0.960**	0.729**	-0.117	1.000					
EC	-0.121	-0.238	0.105	-0.132	-0.250	-0.361	-0.316	-0.401	-0.263	-0.466	-0.104	-0.160	0.887**	0.641**	-0.114	0.903**	1.000				
рН	-0.327	-0.087	-0.002	-0.443	-0.577*	-0.266	-0.682**	-0.086	-0.106	-0.674**	-0.324	-0.394	0.463	0.230	-0.355	0.454	0.537	1.000			
TDS	-0.120	-0.234	0.109	-0.137	-0.254	-0.361	-0.316	-0.388	-0.259	-0.465	-0.104	-0.172	0.893**	0.642**	-0.117	0.906**	1.000**	0.538*	1.000		
TSS	-0.080	0.045	-0.019	0.302	0.363	0.235	0.053	0.437	0.050	0.140	-0.034	0.262	-0.241	-0.033	0.335	-0.238	-0.316	-0.345	-0.316	1.000	
TS	-0.054	-0.162	0.087	0.059	-0.160	-0.240	-0.392	-0.262	-0.178	-0.404	0.077	-0.134	0.868**	0.517	0.193	0.876**	0.988**	0.520	0.988	-0.165	1.000

Table 7 Correlation coefficient matrix for GW 2

** - p, 0.01; * - p, 0.05