hydrology MDPI

Development of a hydrogeological conceptual model for shallow aquifers in the data scarce Upper Blue Nile Basin

Supplementary material

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Hydrochemistry field investigations

Sampling methodology

Sampling was conducted in accordance with accepted international standards and guidelines. A polypropylene syringe was rinsed several times in sample water prior to filling for sample collection. Sample water was collected directly from the hand pump or rope-and-washer pump outlet, from a collection bucket on a rope (typically a doctored 10-litre HDPE jerry can) or the point of emergence of a spring. New nalgene bottles were used for sampling, which were brought from the UK. Major ion samples were filtered through 0.2 μm Supor® Membrane into 125 ml bottles. Two 125 ml samples were collected and filtered at each sampling location, one for cation analysis and one for anions; the sample for cation analysis having the addition of three to four drops of nitric acid preservative. Stable isotope samples were collected in 60 ml bottles with no filtration or preservative. Care was taken to keep the bottles clean and avoid contamination during sampling. In addition to tightly capping, samples had their caps sealed further with electrical insulation tape to restrict the possibility of evaporation from the bottles.

Major ion hydrochemistry

Major ion analysis took place at ADSWE (Amhara Design & Supervision Works Enterprise) Laboratory in Bahir Dar, Ethiopia. Anion analysis was undertaken by a Palintest 2700 photometer utilising Dionex ion chromatography, with the exception of bicarbonate and carbonate that was analysed by titration. A Nova 300 Series utilising atomic absorption spectroscopy undertook cation analysis. Analysis equipment was calibrated in accordance with manufacturer's instructions.

Major ion analysis consisted of testing for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-} and NO_3^{-}. In addition, some samples were analysed for CO_3^{2-}, F^{-} and Fe^{2+}. Analysis for Fe^{2+} was deemed pertinent due to common red staining of filters during sampling. Samples were analysed for F^{-} because Ethiopia is known for having problems with fluorosis caused by groundwater, though excess F^{-} in groundwater is generally restricted to the Rift Valley.

A sample was collected in triplicate with one sample submitted blind to the laboratory and the third brought to the UK for analysis at Newcastle University. The average difference between measured concentrations of the samples tested by ADSWE was 16.6% and the average difference between measured concentrations of ADSWE vs Newcastle University tested samples was also high. The cause of the discrepancies was investigated and several possibilities can be ruled out:

- Contact with the laboratories indicated that all equipment had been recently calibrated.
- A review of manufacturers' datasheets and discussion with equipment operators revealed that the discrepancies are in excess of the tolerance of the analysis equipment.
- Following discussion with operators of such equipment at Newcastle University, the natural variations in hydrochemistry within a sample could not account for such discrepancies.
- The sample that appeared to contain excessive cations was retested at Newcastle University to determine if an erroneous result had been obtained. Almost identical concentrations were measured.

It is therefore suggested that individual samples with excessive cations had become contaminated. It is worth noting that, given the very low concentrations of all major ions, reduction of just 5 mg/l of calcium, magnesium and potassium would bring the ionic balance error within ±5%. A sample collected in duplicate during the second field visit and analysed at ADSWE and at Newcastle University showed an average difference between measured concentrations of just 1.3% further suggesting that the triplicate sample from the first visit had become contaminated.

Regarding the first field visit, ionic balance calculations in 82% of samples were within ±10% (the acceptable range for waters with low concentrations of ions) with an average ionic balance error of 6.6%. From the second field visit, 43.8% of samples were within ±10% and the average ionic balance error is 12.9%. Three possibilities are identified which could (singularly or together) be causing the high ionic balance errors:

Major ion concentrations within the groundwater samples are low, often at trace level. Therefore, trace elements, which are usually unimportant in calculating electroneutrality, are having an impact. For the first field visit, 73% of the ionic balance errors greater than ±5% are in the negative suggesting there are unanalysed cations affecting the ionic balance. To substantiate this claim, it was intended that subsequent testing regimes would include trace metal analysis such as aluminium and silica (considering the mineralogy of the shallow aquifer). Unfortunately, when the samples from the second visit were delivered to the ADSWE laboratory they informed us that such analysis could not be undertaken at that time due to a shortage of necessary equipment consumables. However, samples from the second visit in all but one case show high positive ionic imbalances and therefore an excess of cations perhaps indicating the presence of unanalysed anions. This suggestion of unanalysed ions influencing electroneutrality is supported by the higher EC of samples with greatest ionic balance error though analysed concentrations are not significantly different.

Because the major ion concentrations are low, small errors in concentration measurement (due to the equipment, the operator, or minor contamination) would be amplified when calculating percentage errors.

There is of course the third possibility that the major ion analysis is unreliable and significant conclusions should not be drawn from the groundwater chemistry analysis. As stated in the manuscript, the absolute concentrations are not presented with high confidence though the differences in water types are sufficiently evident that such possible inaccuracies in precision do not invalidate the usefulness of the data.

The results of the major ion analysis are presented in Tables S-1 and S-2. Considering the first field visit, there was not great variation among the shallow groundwater analyses. Considering the second field visit, there is not great variation among and between the shallow groundwater and surface water analyses though the deep groundwater has a different signature. The deep groundwater has low calcium and high sodium suggesting ion exchange. pH is high at 8.8 (possibly due to release of CO_2 from the water). The groundwater is likely to be old – as would be expected from boreholes >100 m deep – as it has high EC (>300 μS/cm), high bicarbonate and has taken time for Ca-Na exchange. Nitrate and sulphate are both low due to little human input and reducing waters. It may have been expected to see bicarbonate to sulphate exchange and this may have occurred followed by sulphate reduction, though there is no evidence of sulphide (not analysed but no smell). However, sulphide could have precipitated out as FeS_2, which is why iron concentration is lower than may be expected in a (suspected) low to zero dissolved oxygen water, though this sulphate reduction would have reduced the pH. Generally, the EC and ionic concentrations are lower than the first field visit, which indicates that at the end of the wet season the analysed groundwater had been recently recharged. However, repeat tests show very similar chemistries suggesting a longer (months rather than days/weeks) residence time. Surface water samples show similar chemistries to shallow groundwater samples though with EC at the lower end (around 100 μS/cm) and pH at the upper end (around pH 6.5).

Table S-1. Results of in-situ testing and laboratory analysis from first field visit in March/April 2015. All the samples are shallow groundwater.

Sample number	Location ID	In-situ field measurement			Calculated from EC	Laboratory analysis (mg/l)											Ionic balance error	Laboratory analysis (‰ VSMOW)	
		Temp. (°C)	pH*	EC (μS)	TDS (mg/l)	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}	CO_3^{2-}		$\delta^{18}O$	$\delta^{2}H$
SI/A/C 1	DW43	20.9	5.19	50.62	25	8.83	1.07	0.08	2.65	0.1	1.5	0.31	2.8	2.7	25.8	0	1.70%	-2.14	-0.17
SI/A/C 2	dw4	20.8	5.84	99.7	50	10.8	1.44	2.4	7.5	2.93	3.2	0.5	8.2	1.54	35.4	0	8.52%	-1.81	0.23
SI/A/C 3	CS42	22.1	5.31	48.67	24	14.1	2.42	0.08	5.13	0.01	0.8	0.8	2.4	2.34	50.2	0	3.11%	-1.56	-0.58
SI/A/C 4	DW56	22.9	5.53	171.9	87	12.5	2.28	0.08	0.15	0.01	2.6	0.21	1.5	4.85	48.8	0	-9.63%	-1.24	3.64
SI/A/C 5	DW73	20.3	5.83	130.7	66	14.6	2.37	1.73	0.42	0.2	0.5	0.22	1.1	4.37	52.0	0	2.26%	-1.55	1.98
SI/A/C 6	dw6	22.3	5.57	144.2	73	15.5	2.23	0.08	0.83	0.03	4.9	0.3	1.2	1.98	40.2	0	6.10%	-2.54	-3.58
SI/A/C 7	DW79	25.2	6.88	334.9	172	19.4	3.4	0.08	1.74	0.01	3.7	0.31	1.1	2.9	85.2	0	-10.08%	-1.91	no result
SI/A/C 8	DW79	25.2	6.88	334.9	172	17.5	3.07	0.08	3.43	0.01	4.1	0.41	2.3	3.05	80.3	0	-12.03%	-1.36	1.67
SI/A/C 9	DW79	25.2	6.88	334.9	172	41.9	16.7	9.0	0.99	0.002	5.597	0.116	1.167	2.822			15.89%	no sample	
SI/A/C 10	CS12	22	5.98	217.6	111	21.7	4.24	5.03	0.04	0.01	1.2	0.35	1.5	4.95	95.1	0	-2.08%	-1.48	0.27
SI/A/C 11	DW18	25.9	6.66	481.9	249	19.8	3.61	17.55	3.21	0.01	2.1	0.43	2.1	1.99	152.2	0	-10.90%	no result	0.59
SI/A/C 12	DW2	21.9	5.76	200.4	102	18.4	3.44	0.08	2.13	0.01	1.3	0.32	0.84	3.2	90.4	0	-12.03%	-1.83	-2.12
SI/A/C 13	dw10	22.1	5.69	44.29	22	10.1	1.78	2.87	1.03	0.01	1.4	0.33	0.92	2.65	38.5	0	3.37%	-1.95	-2.74
SI/A/C 14	DW21	24.7	6.17	174.0	88	17.4	2.81	4.6	1.54	0.01	1.3	0.4	6.2	1.48	60.2	0	5.60%	-1.85	0.76
SI/A/C 15	DW22	24	6.31	264.4	135	18.8	2.94	2.54	2.29	1.65	0.7	0.56	1.6	1.22	97.3	0	-9.30%	-2.86	-5.04
SI/A/C 16	dw15	23.4	5.69	196.8	100	18.7	3.12	0.1	1.14	4.3	1.7	0.28	1.4	2.37	86.1	0	-5.63%	no result	no result
SI/A/C 17	cs6	22.2	6.09	189.6	97	23.3	3.87	0.8	1.24	0.01	1.2	0.37	1.1	2.5	91.2	0	-2.00%	-1.97	-1.45
SI/A/C 18	dw30	21.9	5.99	309.4	159	27.1	3.18	0.19	9.06	0.7	2.7	0.25	1.2	4.12	125.4	0	-8.67%	-2.16	-0.02

Triplicate samples highlighted grey (SI/A/C7, 8 and 9) with the sample tested at Newcastle University highlighted darkest.

Table S-2. Results of in-situ testing and laboratory analysis from second field visit in October/November 2015.

Sample number	Location ID	Sample type	In-situ field measurement			Calculated from EC	Laboratory analysis (mg/l)										Ionic balance error	Laboratory analysis (‰ VSMOW)	
			Temp. (°C)	pH*	EC (µS)	TDS (mg/l)	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}		$\delta^{18}O$	$\delta^{2}H$
2SI/A/C1	DW56	Groundwater	22.9	5.61	167.7	107	15.88	6.5	8.65	1.91		2.70		1.10	10.50	51.85	22.09%	5.74	-0.47
2SI/A/C2	dw21	Groundwater	30.9	6.71	403.5	258	45.67	5.5	16.21	4.71		2.60		3.20	0.96	140.30	18.34%	-0.45	-0.41
2SI/A/C3	cs6	Groundwater	22.9	6	188.70	121	19.85	5.5	13.1	0.85		2.70		5.20	3.76	54.90	27.99%	3.46	-0.01
2SI/A/C4	DTW3	Deep Groundwater	22.9	8.77	315	202	2.55	4.05	34.1	1.84	0.01	0.90	0.47	1.10	0.98	97.60	8.23%	-3.98	-1.63
2SI/A/C5	dw31	Groundwater	21.8	5.55	136.4	87	14.73	5.01	10.4	1.24		2.20		8.10	3.70	51.85	17.72%	10.59	0.41
2SI/A/C6	D3	Deep Groundwater	21.8	8.81	335	214	0.97	4.51	34.5	1.86	0.01	2.50	0.64	0.50	1.44	97.60	6.23%	-1.02	-1.61
2SI/A/C7	RFL39	Rain										0.380		1.912	0.799			16.96	1.58
2SI/A/C8	DW43	Groundwater	20.5	4.77	46.26	27	4.89	6.02	5.33	1.34		1.20		8.30	4.20	24.40	19.71%	9.57	0.21
2SI/A/C9	CS42	Groundwater	22.2	4.77	58.44	37	6.25	4.03	3.01	1.08		1.20		7.20	4.50	27.45	6.35%	1.46	-0.29
2SI/A/C10	DW22	Groundwater	21.7	5.46	133.3	85	18.07	7.03	5.51	2.25		1.60		2.01	6.20	24.85	49.89%	11.39	0.72
2SI/A/C11	DW21	Groundwater	22.1	5.19	167.1	107	18.55	5.02	5.37	1.05		11.5		7.04	1.16	46.15	12.41%	8.79	0.59
2SI/A/C12	DW73	Groundwater	20.9	5.3	110.9	71	8.87	7.01	1.97	1.68		0.3		8.12	10.5	42.6	4.70%	4.19	0.33
2SI/A/C13	dw6	Groundwater	22.2	5.41	133.8	86	12.48	5.02	1.73	0.57		4.8		7.05	4.2	24.85	19.57%	4.81	0.30
2SI/A/C14	dw18	Groundwater																1.75	-0.04
2SI/A/C15	DW77	Groundwater	22.3	5.24	146.6	94												4.23	0.31
2SI/A/C16	dw2	Groundwater	22.5	6.43	289	185												6.37	0.11
2SI/A/C17	RFL46	Wetland stream	21.8	6.83	99.35	64												10.98	1.59
2SI/A/C18	CS12	Groundwater	22.8	5.98	217.6	139	17.56	5.05	6.27	2.01		1.2		6.1	11.5	60.35	9.50%	6.99	1.03
2SI/A/C19	CS12	Groundwater	22.8	5.98	217.6	139	15.85	6.71	3.92	3.86		2.67		8.22	9.41	60.26	7.55%	6.37	0.96
2SI/A/C20	RFL48	River	23.1	6.39	106.6	68												13.49	0.92
2SI/A/C21	RFL49	Wetland	30.9	6.71	256.1	164												16.42	1.85
2SI/A/C22	RFL50	Rain										0.541		1.225	0.935			51.30	5.90
2SI/A/C23	RFL39	Rain										1.122		1.063	1.102				
2SI/A/C24	RFL51	Wetland stream	20.3	6.84	83.26	53												23.14	0.35
2SI/A/C25	RFL52	Wetland stream	26.6	6.04	70.28	45	9.41	7.08	2.64	4.33		1.3		14	2.06	53.25	1.73%	23.44	0.92
2SI/A/C26	RFL53	River	23.1	6.18	91.1	58												21.97	0.64
2SI/A/C27	RFL55	River	22.3	6.27	93.45	60												23.13	1.29
2SI/A/C28	DW79	Groundwater	24.7	6.59	231.3	148	33.0	8.72	4.5	<1	0.001	2.119		1.146	6.485		86.43%	3.31	0.91
2SI/A/C29	cs9	Groundwater	23.2	5.75	124.8	79.8												2.65	0.50
2SI/A/C30	cs10	Groundwater	23.5	6.11	171.7	110												5.39	0.34
2SI/A/C31	RFL61	River	22.9	6.29	104.8	67	9.66	6.12	1.34	1.83		2.8		25.1	2.1	74.55	-26.00%	8.29	1.16

Duplicate samples highlighted grey (2SI/A/C18 and 19) with the samples tested at Newcastle University highlighted darkest.

Stable isotope

Analysis was undertaken by a LGR DLT-100 utilising laser spectroscopy at the School of Earth Science, Addis Ababa University, Ethiopia.

A sample was collected in duplicate with one sample submitted blind to the laboratory. A result was not obtained for δ²H for one of the samples whereas for δ¹⁸O the results differed by 28.8%. This percentage difference seems high though it is a percentage of a low result, which actually equates to only 0.55‰ VSMOW. Both results would plot in a very similar position on Figure 6 of the manuscript. The blind submitted during the second field visit varies by 8.9% (δ¹⁸O) and 6.8% (δ²H) with small absolute differences.

Unfortunately, analysis could not be completed on all of the samples. "No Result" on Table S-1, according to the laboratory, "means we haven't gotten good results for those analysis and we have discarded them". Each sample is analysed a number of times due to the sensitivity of the equipment and if the standard deviation of the results is above a certain threshold the result is rejected.

In-situ testing

A handheld Myron L Company Ultrameter II was used for in-situ water testing, calibrated immediately prior to the field visits. Testing was conducted in accordance with accepted international standards and guidelines. The sensor was thoroughly rinsed with sample water and the reading allowed to stabilise prior to a measurement being recorded.

The results of in-situ testing from the locations where samples were collected are presented with the laboratory results in Tables S-1 and S-2. Results from locations that had been tested a year previously during fieldwork by the Geological Survey of Ethiopia (GSE) are presented in Table S-3; there are eleven locations where testing was repeated. A total of 28 locations were subjected to testing in March/April 2015 following the 198 in February/March 2014 and a further 40 in October/November 2015.

Table S-3. Comparison of in-situ testing results from February/March 2014, March/April 2015 and October/November 2015.

Location code	Sample number	Oct/Nov 2015 pH *	Mar/Apr 2015 pH *	Feb/Mar 2014 pH	Oct/Nov 2015 EC (µS)	Mar/Apr 2015 EC (µS)	Feb/Mar 2014 EC (µS)	Oct/Nov2015 Temp. (^{o}C)	Mar/Apr 2015 Temp. (oC)	Feb/Mar 2014 Temp. (^{o}C)
DW73	SI/A/C 5 & 2SI/A/C 12	5.3	5.83	6.22	110.9	130.7	132.6	20.9	20.3	21.5
DW77	2SI 15	5.24	5.28	6.04	146.6	90.74	104	22.3	22.2	26.4
DW43	SI/A/C 1 & 2SI/A/C 8	4.77	5.19	5.82	46.26	50.62	56.8	20.9	20.9	18.9
DW56	SI/A/C 4 & 2SI/A/C 1	5.61	5.53	6.04	167.7	171.9	182.2	22.9	22.9	25.4
DW61			5.95	6.33		216.6	217		22.1	22.5
DW79	SI/A/C 7 8 9 & 2SI/A/C 28	6.59	6.88	7.35	231.3	334.9	320	24.7	25.2	26.7
DW18	SI/A/C 11		6.66	7.2		481.9	502		25.9	24.2
DW2	SI/A/C 12		5.76	6.32		200.4	203		21.9	23.3
DW21	SI/A/C 14 & 2SI/A/C 11	5.19	6.17	6.54	167.1	174	142	22.1	24.7	21.7
DW22	SI/A/C 15 & 2SI/A/C 10	5.46	6.31	6.69	264.4	264.4	200	24	24	26.4
dw6	2SI/A/C 13	5.41	5.57		133.8	144.2		22.2	22.3	
CS42	SI/A/C 3 & 2SI/A/C 9	4.77	5.31	6	58.44	48.67	49.7	22.2	22.1	23.5
cs6	2SI/A/C 3	6	6.09		188.7	189.6		22.9	22.2	
CS12	2SI/A/C 18 19	5.98	5.98		225.3	217.6	220	22.8	22.0	22.9
cs1		5.36	5.22		66.35	61.93		20.3	22.8	

The field tests gave remarkably similar EC measurements on both field visits, and to the previous period of testing 12-13 months earlier. The consistency of results indicates that the groundwater has consistent properties and, therefore, the laboratory samples are representative of shallow groundwater from this location.

In-situ radon-222 testing

A DURRIDGE RAD7 with the "Big Bottle System" was used for in-situ measurement of radon-222 concentration in water. Radon-222 testing was conducted in accordance with the Durridge Company Inc. manuals, comprising:

1. Equipment set up.
2. Purging of the equipment for at least 10 minutes and until a maximum internal relative humidity of 10% was achieved.
3. Careful sampling of water directly into the "big bottle" avoiding turbulent flow and degassing.
4. Running the test for at least 45 minutes with monitoring of radon-222 concentration, internal relative humidity and water temperature.
5. Removal of sample and minimum of 8-minute post-test purge before equipment disassembly.

The initial test was unsuccessful; purging took several hours to reduce the relative humidity to the correct level and following over an hour of testing the radon-222 concentrations were approaching zero. Considering the sample came from one of Dangila town's deep supply boreholes a concentration of several thousand Bq/m^3 would be expected. Later investigation revealed that a one-way valve, in place to prevent water from entering the RAD7 instrument, had been installed the wrong way round. Once the valve had been reinstalled correctly, the equipment operated satisfactorily.

Photographs of equipment set up and testing are shown in Figure S-1.

Figure S-1. Photographs showing radon-222 testing. The in-situ EC, pH, and temperature meter is also visible.