Original Paper



Groundwater Sampling: Flow-Through Bailer Passive Method Versus Conventional Purge Method

M. Gomo,^{1,2} D. Vermeulen,¹ and P. Lourens¹

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A study was conducted to assess the performance of the flow-through bailer groundwater sampling method against the conventional purge method based on the analysis of inorganic chemistry and total coliform parameters. Sampling was performed at three sites for a total of 43 monitoring wells. Samples were first collected by a bailer from inferred groundwater flow zones followed by the purging method. Analysis of variance of inorganic chemistry parameters measured in the bailered and purged groundwater samples was conducted at 99% confidence interval. Across the three sites, there was no statistically significant difference between all inorganic chemistry parameters measured in the bailered and purged samples. Further analysis was conducted to assess the probability (p) to which the observed difference among groups is attributable to the influence of random factors or the sampling methods (test factor). The probability that the observed differences between the tested groups is rather due to random chance and not to the influence of sampling methods. There are wells that show high influence of the sampling methods on the results and others showing minimum influence. The results suggest that well specific hydrogeology has an influence on the comparison of the sampling methods. Recommendations are therefore made for well specific evaluations prior to the adoption of the bailer passive sampling method. The total coliform counts in the bailered samples are much more elevated than in purged samples, which suggest that, for total coliforms and possibly other microbial analytes, purging is necessary.

KEY WORDS: Aquifer, Bailer, Groundwater sampling, Hydrogeochemistry, Purge and total coliforms.

INTRODUCTION

Groundwater sampling methods and techniques have continued to evolve over many decades. However, the question of whether to purge or not before collection of groundwater samples has remained under debate. While the purging methods have been in use for a very long time (USGS 1980; Barcelona et al. 1984, 1985; Barcelona and Helfrich 1986; Puls and Barcelona 1996), over the recent years, the field of groundwater sampling has seen the rise of passive (non-purge) sampling methods as a low-cost alternative to purging (Vroblesky and Hyde 1997; ITRC 2008; USEPA 2010; Savoie and LeBlanc 2012).

Unlike purging, passive methods collect groundwater from specific depths without active pumping of the water. Under natural conditions, groundwater from the adjacent aquifer formation continuously flows across the well through the screened casing (Robin and Gilham 1987), which presents an opportunity to collect representative

¹Institute for Groundwater Studies, Faculty of Natural and Agricultural Sciences, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa.

²To whom correspondence should be addressed; e-mail: GomoM@ufs.ac.za

groundwater samples without purging. A passive sampler can therefore be used to collect representative groundwater from a discrete position (flow zone) in a well that is naturally replenished without actively inducing stress into the aquifer media by pumping or other purge techniques. To facilitate continuous replenishment of water in the flow zone interval, the monitoring well has to be open or screened along groundwater flow zones.

Passive samplers such as flow-through stainless steel bailers (which have open/close valves at the top and bottom) have become increasingly popular particularly in the developing countries mainly because they can be manufactured locally, easy to use but also reusable. Although the purchase cost could be high, their long-term running and maintenance costs are relatively low in comparison with purging. Despite the wide and rapid adoption of these bailers as a passive method, their performances against the conventional purge method for inorganic chemistry and total coliform have not yet been scientifically assessed. For other determinants such as volatile organics (VOCs), there are a number of studies that have been conducted to compare the performance of other passive methods against the active purging method (Byrnes et al. 1996, Lundegard et al. 1997, Springer 1998). This study therefore presents an opportunity to assess the performance of flowthrough bailers against the conventional purging sampling method for the analysis of inorganic chemistry and total coliform determinants in order to improve the understanding of their applications.

The study utilizes three sites in South Africa representing different hydrogeology characteristics. Site 1 at Krugersdrift is an alluvial aquifer with pristine hydrogeochemical characteristics (Gomo et al. 2013). Site 2, the campus test site at the University of Free State is a bedding plane fractured-rock aquifer with fairly pristine hydrogeochemical characteristics. Site 2 is, however, used for research and study purposes, thus both the hydrogeology and hydrogeochemical characteristics might have been significantly altered over the years. Site 3 is in a mining area where monitoring wells were installed to monitor potential release and transportation of pollutants associated with mining activities.

METHODS AND MATERIALS

The study sites are located in South Africa. Sites 1 and 2 are located in the Free State Province

while site 3 is located Northern Cape Province (Fig. 1). In total, 43 wells were sampled in the following order: 12 at site 1; nine at site 2; and 22 at site 3. Each well is 150 mm in diameter. Additional information about the wells is given in the following sections.

Site 1: Krugersdrift Dam Site

The site consists of 15 wells. The wells have been drilled during a Water Research Commission (WRC) funded K5/2054 surface water/groundwater hydrology project. Twelve wells were successfully sampled by that project using a reusable stainless steel bailer flow-through and purging methods. The site consists of a shallow alluvial aquifer of less than 10 m thickness. With the exception of well BH1, all the other wells are drilled and screened into this alluvial aquifer. Well BH1 is screened in the deep low permeable un-weathered shale aquitard and is therefore isolated from the shallow (<20 meters below ground level) main alluvial aquifer. For this study, groundwater samples were successfully obtained from 12 of the 15 wells.

Geology

The study site is situated within the Karoo Basin, where Quaternary deposits are a major feature along rivers. The geology of the site mainly consists of calcrete, clay, silt and gravel-sand deposits that overlie low impermeable shale bedrock. Calcrete deposits at the site occur as outcrops and at shallow depth. The occurrence of calcrete in different forms and positions in the sediments possibly resembles different ages and/or stages of remobilization (McQueen 2006). The gravel-sand facies at the site are characterized by various textural and structural properties that have an influence on the groundwater flow properties due to their high hydraulic conductivity (Gomo 2011). The shale sedimentary deposits which sequentially consist of soft-weathered and fresh-hard sediments regionally represent the bedrock over which deposition and river flow occurred.

Hydrogeology

The study site consists of a shallow alluvial channel aquifer that is typical of the Quaternary

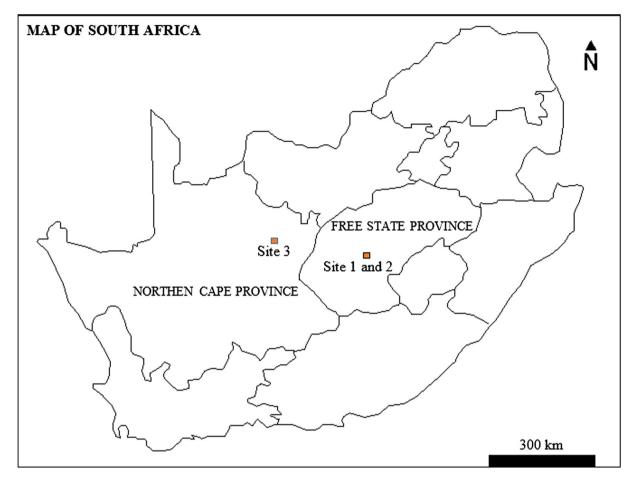


Figure 1. Map of South Africa showing the location of study sites in Northern Cape and Free State Provinces.

deposits of the Karoo Basin. Alluvial channel aquifers are generally hosted in laterally discontinuous layers of sand, silt and clay sediments deposited by a river in the channel, on the bank or flood plain (Barker and Molle 2004). Patches of calcrete outcrops are visible at the site.

The gravel–sand deposits represent the higher hydraulically conductive unit of the aquifer. In general, gravel–sand hydro-facies are typically characterized by high hydraulic conductivity due to their large grain size (Gomo 2011). Clay and silt sediments have high groundwater storage potential owing to their conceptually large porosity as influenced by small grain size. Due to its high hydraulic conductivity, the gravel–sand formation constitutes the main hydraulic groundwater flow zone of the alluvial aquifer where electrical conductivity (EC) anomalies are expected. As an example, Figure 2 shows the EC profile in one of the wells with an anomaly associated with the gravel–sand main

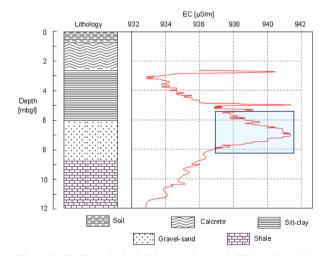


Figure 2. Well geological lithology log and EC profile with depth (mbgl—meters below ground level) at Krugersdrift site. The marked section of the profile shows the EC anomaly indicative of the groundwater flow zone from which samples were collected.

groundwater zone being visible at about 5 meters below ground level (mbgl). It should therefore be possible to identify the main groundwater flow zones in a typical alluvial aquifer from which samples can be collected using a bailer. The wells are screened along the gravel–sand main groundwater flow zone. The length of the screens varies from one well to the other depending on the flow zone thickness as influenced by subsurface heterogeneities.

Site 2: Institute of Groundwater Studies (IGS) Campus Test Site

The campus test site was established in 1990 at the University of the Free State in Bloemfontein, South Africa. The site covers an area extent of approximately 180×192 m², and consists of 35 percussion and nine core wells. For this study, groundwater samples were successfully obtained from less than 30 m deep at the nine wells. Site 2 is used for research and study purposes, and thus both the hydrogeology and hydrogeochemical characteristics might have been significantly altered over the years. Several tracer injection tests with table salt (sodium chloride) have been conducted at this site. It can therefore be expected that the concentration of these two constituents could be elevated in some of the wells and could provide a good opportunity to also compare the two sampling methods in a contaminated aquifer scenario.

Geology and Geohydrology

The campus test site is underlain by a series of mudstones and sandstones from the Adelaide Subgroup of the Beaufort Group of formations in the Karoo Sequence. Previous studies (Botha et al. 1998) indicate that the campus test site is composed of three aquifer systems. Aquifers 1 and 3 occur in the relatively low permeable but high storage mudstone and carbonaceous shale, respectively. Aquifer 2 consists of a horizontal fracture zone, which according to Botha et al. (1998), developed as a consequence of the weathering of the rock between two bedding planes. With the surrounding shale and mudstone formations being of low permeability but high storage, this fractured zone is the main hydraulically conductive zone. Monitoring wells are therefore screened along the bedding plane fracture main flow zone, while the length of the screens

varies from one well to the other depending on the flow zone thickness.

In these aquifers, fractures typically form preferential flow paths for groundwater and in some cases the contaminants. Since flow is mainly confined to fractures and not the entire thickness of the formation, identification of flow zones using EC profiling should be possible in most of the instances. This is mainly because EC anomalies would distinctively occur along these fractures, which are targeted for bailer sampling. The purging pump intake was placed within the flow zone.

Site 3: Mining Area

Site 3 is a mining area with monitoring wells being installed to monitor potential release and transport of pollutants associated with mining activities. Information on the site geology and hydrogeology is limited due to restricted access related to confidentiality of information. Regionally, the geology mainly consists of banded iron formations. Although site information is limited, for the sake of comparing between bailer and purge methods, the site can still yield very useful information. Many sites exist that do not have information on geology, well construction and other key hydrogeological features, yet sampling still has to be done. This is very common in developing countries, where borehole data bases are still very much being developed. This site can therefore be a good example of such sites with limited data and information available prior to sampling. At this site, groundwater samples were successfully obtained from 22 wells. The wells are generally screened along the fractures, but background information about the wells is limited. The screened fractures were targeted for bailer sampling after their location from EC profiles. Samples were first obtained using a bailer and thereafter purging of three well volumes.

Sample Collection

Wells were profiled with an EC probe to locate groundwater flow zones, from which samples were collected using a flow-through metal stainless steel bailer into prepared sample containers. A flowthrough bailer minimizes disturbances and mixing of the groundwater. The bailer was lowered slowly at the rate of about 2 cm/s to the intended zone. Dur-

ing lowering, the top and bottom valves of the bailer were open to enable the bailer to pass through the water with minimum displacement to reduce the disturbances. Once the intended horizon is reached, the top and bottom valves are instantaneously closed and the bailer is retrieved to the surface. The containers were rinsed three times with the sampled water prior to collection of the sample. The bailer was also rinsed with deionized water before sampling from the next well. Samples collected from the groundwater flow zones are regarded to be representative of aquifer hydrogeochemical conditions as the water is continuously replenished by natural flows. With the aid of well geology logs, EC anomalies were inferred to represent groundwater flow zones within the wells. For illustration purposes, see the EC profile for one of the wells at site 1 that is presented in Figure 2. It must be highlighted that identification of the groundwater flow zones where natural replenishment occurs in wells, from which samples can be collected, is very important prior to sampling. While EC profiles and well logs can provide insights into the location of potential flow zones, this process remains highly subjective as it is also influenced by site-specific conditions and therefore is a potential source of random error contributing to sampling variability. It is possible that thermal convection associated with season turnover could affect the results if sampling is done in a winter season (Vroblesky et al. 2007). However, for the purpose of comparing the two sampling methods, the influence of random errors during sampling was assumed to be evenly distributed across sampling wells and the sampling method (test factor) was considered as the main source of variability between concentrations of the constituents measured in bailered and purged samples.

After collection of samples with the bailer method, samples were then collected using a purging pump at discharge rates of between 0.02 and 0.06 l/s (for sites 1 and 2). Samples were only collected after the stabilization of total dissolved solids (TDS) and EC. At site 3, wells were purged by pumping (discharge rates of 0.1–0.3 l/s) three well volumes (traditional approach) of the stagnant water in the well column before samples were collected.

The groundwater samples were collected in summer, which is typical of hot and wet weather in Southern Africa. It is possible that thermal convection associated with season turnover could affect the results if sampling is done in a winter season. In regions where thermal convection associated with season turnover is known or expected to occur, well specific comparisons should be conducted for winter and summer for comparative purposes. In South Africa, air temperatures do not significantly change seasonally, so it is likely that seasonally induced inwell convection does not impact the results of the present study.

Laboratory Analysis

Bailered and purged groundwater samples from the three sites were analyzed for the dissolved constituents of major ions and trace elements. The analysis was conducted by the Institute of Groundwater Studies (IGS) laboratory of the University of Free State in South Africa. All the analyses were conducted based on the guidelines provided in the Standard Methods for the Examination of Water and Wastewater (APHA 2005). The ion balance error (IBE) for the analysis was between -6 and +8. Samples from sites 1 and 2 were also analyzed for total coliforms as general determinant of microbial quality. The coefficient of variation of the laboratory analysis was calculated for metals $(\pm 6.5\%)$, major ions ($\pm 2.4\%$) and total coliforms ($\pm 8\%$) for this particular study.

Data Analysis and Interpretation

Purging is generally regarded as an established sampling method (USGS 1980; Barcelona et al. 1984, 1985; Barcelona and Helfrich 1986; Puls and Barcelona 1996) and is thus used as a control method for comparative reference of the bailer.

Analysis of Variance

One-way analysis of variance (ANOVA) tests were conducted to determine if there is any statistically significant difference between inorganic chemistry parameters measured in the bailered and purged groundwater samples. The ANOVA between the two sampling methods was conducted for each well and not across the wells. This is because hydrogeology characteristics across different wells might vary as influenced by heterogeneity and that could be another source of variation besides the sampling methods themselves. In a single well, the only source of variation between the two sets of parameters is assumed to be the methods of sample collection, which is what the study seeks to investigate. The Microsoft excel 2010 program was used to perform one-way ANOVA. Analysis of variance at 99% confidence interval ($\alpha = 0.01$) was used to test the following hypothesis:

- The null hypothesis is that the means of all inorganic chemistry parameters measured in the samples collected using the bailer and purge methods in each specific well are equal; and
- The alternative hypothesis is that the mean of all inorganic chemistry parameters measured in the samples collected using the bailer and purge methods from each specific well are not equal.

The test wells are primarily sampling aerobic groundwater; however, localized anaerobic conditions due to pollution or other reducing factors cannot be ruled out. In wells sampling anaerobic groundwater, there is a potential that water within the well casing may contain lower concentrations of redox sensitive metals than aquifer water because of oxidation effects related to diffusion of oxygen at the water surface or to mixing effects due to convection, vertical advection, or other in-well disturbances (Vroblesky et al. 2007). In order to evaluate the potential influence of the redox sensitive conditions of the aquifers, ANOVA was also conducted for data sets without redox sensitive parameters. Redox sensitive parameters that were considered are pH, sulfate, bicarbonate, nitrate, iron and manganese.

Coefficient of Variation Analysis

In order to assess the variation between the total coliforms microbial parameter measured in purged and bailered groundwater samples, the coefficient of variation (CV) was used. The CV was used because, between the two groups, there is only one microbial parameter measured, which is not sufficient to perform ANOVA. The CV (Eq. 2) is a measure of spread that describes the amount of variability relative to the mean. It is calculated by multiplying relative standard deviation (RSD) (Eq. 2) by 100.

$$RSD = \frac{s}{\bar{x}}$$

where *s* is standard deviation and \bar{x} is the mean.

$$CV(\%) = 100RSD \tag{2}$$

By hypothesizing that the bailer and purge methods can both collect equally representative groundwater samples, the CV can be used as a measure of the precision/repeatability between the two methods. In a similar study, Rong (1998) also used CV to analyze parameters measured in purged and non-purged groundwater samples data. Smaller CV indicates higher precision between the two methods, which implies closeness in the results. Larger CV indicates low precision between the two methods, which implies lack of agreement of the results. A CV of zero shows that the methods perfectly replicate each other in collecting representative samples. It is rather difficult to say what CV range is acceptable, but for the purpose of this study $\pm 5\%$ is regarded as an acceptable measure of repeatability.

While the CV parameter itself is always a positive parameter, for the purpose of this study, negative values were also used in order to show which sample has higher counts of total coliforms between the two methods of collection. The following convention was therefore adopted: CV > 0 indicates total counts in purged sample > bailered; CV < 0indicates total counts in purged sample < bailered; and CV = 0 indicates no variation.

RESULTS AND DISCUSSION

The results constitute of two components, AN-OVA of inorganic chemistry parameters (site 1, 2 and 3) and analysis of CV of the total coliform microbial parameter (sites 1 and 2).

Site 1: Krugersdrift Alluvial Channel Aquifer

ANOVA of Inorganic Chemistry Parameters

Laboratory results of the inorganic chemistry parameters measured in the groundwater samples collected using the bailer and purge methods, respectively, are presented in Table 1. Table 2 shows results of one-way ANOVA of inorganic chemistry parameters analyzed between bailered

Table 1. Inorganic chemistry parameters measured in groundwater samples collected from the Krugersdrift alluvial aquifer using the bailer
and purge methods

Well no. ^a	pН	EC	Ca	Mg	Na	Κ	HCO ₃	F	Cl	Br	NO ₃ (N)	SO_4	Ba	Fe	Ni	Si	Sr	V	Zn
BH1B	7.62	87.1	39.94	29.89	129.08	5.87	412	0.68	57.5	0.41	0.475	25.9	0.159	0.047	0.021	22.62	0.911	0.051	0.025
BH1P	7.70	87.7	36.81	41.12	116.89	7.06	410	0.57	63.52	0.42	0.214	30.0	0.103	0.024	0.020	21.76	0.685	0.048	0.021
BH3B	7.69	94.8	28.96	40.70	154.82	7.47	453	0.80	65.79	0.42	0.071	30.7	0.094	0.043	0.021	25.96	0.6	0.059	0.035
BH3P	7.68	94.8	27.51	38.61	144.26	7.06	452	0.83	65.06	0.51	0.084	30.0	0.091	0.022	0.021	24.71	0.566	0.056	0.018
BH4B	7.66	80.1	39.33	42.78	102.51	7.23	383	0.53	56.96	0.37	0.170	22.6	0.105	0.019	0.021	24.46	0.717	0.047	0.025
BH4P	7.77	80.1	36.25	39.66	95.68	6.93	382	0.51	57.17	0.40	0.173	22.9	0.094	0.022	0.028	23.02	0.648	0.040	0.025
BH5B	7.74	90.1	32.24	50.20	102.73	7.11	443	0.67	60.51	0.39	< 0.05	25.0	0.088	0.018	0.025	27.46	0.673	0.040	0.024
BH5P	7.67	88.7	35.69	54.24	113.78	7.72	435	0.68	60.77	0.57	< 0.05	24.7	0.103	0.017	0.027	29.44	0.741	0.041	0.022
BH6B	7.70	87.2	35.85	45.70	105.63	7.30	418	0.62	57.55	0.37	0.094	25.3	0.099	0.017	0.022	24.97	0.671	0.054	0.022
BH6P	7.75	87.8	35.23	45.52	106.60	7.33	420	0.66	57.91	0.36	0.092	25.5	0.098	0.017	0.023	26.14	0.668	0.053	0.025
BH7B	7.76	88.7	35.24	47.70	109.62	7.55	428	0.62	59.45	0.41	< 0.05	25.7	0.106	0.018	0.025	26.8	0.681	0.053	0.020
BH7P	7.81	88.8	32.50	45.88	104.24	7.25	427	0.66	59.01	0.48	0.086	25.8	0.101	0.041	0.022	25.71	0.634	0.050	0.019
BH8B	7.83	92.9	31.04	40.96	126.91	7.26	443	0.71	65.55	0.52	0.103	29.8	0.082	0.024	0.021	24.81	0.6	0.053	0.031
BH8P	7.82	94.6	31.05	42.93	129.96	7.22	453	0.70	65.39	0.46	0.102	30.3	0.086	0.019	0.019				
BH9B	7.78	93.6	32.96	46.35	135.30	7.18	448	0.70	64.55	0.70	< 0.05	31.5	0.094	0.02	0.023	23.85	0.662	0.064	0.019
BH9P	7.81	87.7	33.66	41.91	123.30	7.18	413	0.61	60.99	0.37	0.140	27.7	0.089	0.019	0.023	24.56	0.629	0.057	0.017
BH11B	7.84	86.0	36.01	40.89	105.35	7.29	400	0.55	62.03	0.50	0.101	29.0	0.089	0.017	0.017	20.95	0.66	0.044	0.021
BH11P	7.83	83.6	33.00	39.80	100.56	7.03	400	0.53	59.32	0.37	0.085	25.5	0.095	0.017	0.020	22.13	0.623	0.049	0.019
BH12B	7.84	83.6	35.78	39.34	99.53	7.01	408	0.54	58.51	0.33	< 0.05	24.8	0.086	0.021	0.017	21.02	0.624	0.041	0.023
BH12P	7.88	83.1	37.34	43.91	106.80	7.50	399	0.56	57.06	0.36	0.052	24.4	0.099	0.018	0.021	24.18	0.688	0.050	0.025
BH13B	7.75	87.1	38.48	42.02	108.66	7.56	418	0.55	60.75	0.67	< 0.05	20.9	0.09	0.046	0.018	21.66	0.676	0.019	0.022
BH13P	7.92	83.1	35.85	42.79	104.08	7.31	395	0.59	57.14	0.35	0.067	22.6	0.103	0.021	0.023	23.65	0.674	0.050	0.015
BH15B	7.83	81.9	40.54	40.40	82.71	6.52	398	0.40	54.64	0.24	< 0.05	20.1	0.109	0.022	0.020	21.46	0.605	0.026	0.024
BH15P	7.96	78.9	40.26	41.38	86.11	6.61	380	0.44	55.3	0.32	0.226	21.2	0.109	0.017	0.021	22.74	0.6	0.043	0.021

Ion concentrations are measured in mg/l and EC in mS/m ^aSuffix B = bailered sample; suffix P = purged sample

Sumx D = banered sample, sumx r = purged sample

 Table 2. Results of one-way ANOVA of inorganic chemistry parameters analyzed between bailered and purged groundwater samples from each well at Krugersdrift alluvial aquifer

Well no.	MS	F	p Value	F _{crit}
BH1	0.502895	5.52E-05	0.99	7.395597
BH3	8.620935	0.00077	0.98	7.395597
BH4	6.064889	0.000782	0.98	7.395597
BH5	3.95884	0.000372	0.98	7.444136
BH6	0.562692	6.06E - 05	0.99	7.395597
BH7	4.298504	0.000425	0.98	7.444136
BH8	7.28797	0.000677	0.98	7.395597
BH9	112.7508	0.010774	0.92	7.444136
BH11	7.390366	0.00087	0.98	7.395597
BH12	0.951763	0.000105	0.99	7.444136
BH13	31.62656	0.00344	0.95	7.444136
BH15	5.072255	0.000611	0.98	7.444136

MS—Mean squares, F—test statistic, p value—is the probability of calculating a given test statistic assuming that the means of your groups are identical and F_{crit} critical statistic

and purged groundwater samples per well at Krugersdrift alluvial aquifer.

For all the 12 wells, the *p* values are greater than 0.01 (significance level) and test statistic (*F*) is less than the critical value (F_{crit}) ($F < F_{crit}$). The null hypothesis of equal inorganic chemistry parameters means for the two data sets is therefore accepted.

This implies that with 99% confidence level it can be concluded that there are no statistically significant differences between all inorganic chemistry parameters measured in bailered and purged groundwater samples per well.

However, the absence of significant differences does not imply that the two methods give the same

results. Further analysis of the p value was used to indicate the probability to which the observed difference (even if not significant) among groups is attributable to influence of random factors or the sampling methods (test factor). The smaller the pvalue, the more likely that the observed difference is due is to the influence of the sampling method. There is at least 92% probability that the observed difference (even if not significant) between the tested two groups in all the 12 of the wells is rather due to random chance and not to the influence of sampling methods (tested factor). In three of the 12 wells, the probability that the differences observed between the tested two groups is rather due to random chance and not to the influence of the sampling methods is at least 99%. This probability is indicated by the *p* values in Table 2. There is therefore only 1% probability that the observed variance could be due to the influence of the sampling methods. The three wells therefore show minimum influence of the sampling methods on the results.

CV Analysis for Total Coliforms

Figure 3 shows the CV between total coliforms analyzed in purged and bailered groundwater samples collected from the alluvial aquifer. Also shown in Figure 3 is the + or -8% CV for the laboratory analysis. Only one well, BH12, has a CV within $\pm 8\%$ of the laboratory analysis. This implies that for the 10 samples whose CV is above $\pm 8\%$ of the laboratory analysis, there are other factors con-

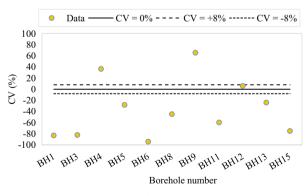


Figure 3. Coefficients of variations between total coliforms analyzed in purged and bailered groundwater samples from the Krugersdrift alluvial aquifer. CV > 0 indicates ion concentrations in purged sample > bailered. CV < 0 indicates ion concentrations in purged sample < bailered. CV = 0 indicates no variation.

tributing to the variation between the concentration of the purged and bailered samples. Assuming the influence of other factors to be evenly distributed across the wells, the sampling method becomes the main source of variation.

The results show a consistent trend between the CV of total coliforms analyzed in purged and bailered samples. Only three samples have a CV>0(total coliforms in purged sample > bailered) while for the majority of the samples (8) the CV < 0 (total coliforms in purged sample < bailered). In eight of the 12 samples, the bailered samples had higher total coliform counts as compared to the purged ones. This could be attributed to chemical and physical changes that might occur in the stagnant water inside the well column. While at a flow zone the groundwater is not necessarily stagnant, the water in the well column can still interact with the atmosphere and could influence the microbial activities. Examples of such influences include temperature changes and degassing. With long residence times in the well column, water temperatures rise and bacterial levels increase (LeChevallier 2003). Roudnew et al. (2014) reported significantly greater virus-like particles (particles/ml) in unpurged groundwater water as compared to the purged, which point toward a similar trend to results of this study. The findings of this study suggest that for microbial analysis, purging is vital in order to obtain samples representative of conditions from the aquifer that are less affected by these external factors in comparison with the bailered samples.

Site 2: Campus Test Site at University of the Free State

ANOVA of Inorganic Chemistry Parameters

Laboratory results of the inorganic chemistry parameters measured in the groundwater samples collected using the bailer and purge methods, respectively, are presented in Table 3. Table 4 shows results of one-way ANOVA for inorganic chemistry parameters analyzed between bailered and purged groundwater samples per well at Krugersdrift alluvial aquifer.

For all nine wells, the *p* values are greater than 0.01 (significance level) and the test statistic (*F*) is less than the critical value (F_{crit}) ($F < F_{crit}$). The null hypothesis of equal inorganic chemistry parameters mean for the two data sets is therefore accepted.

Table 3. Inorganic chemistry parameters measured in groundwater samples collected from the campus test site using the bailer and purge
methods

Well no. ^a	pН	EC	Ca	Mg	Na	Κ	HCO ₃	F	Cl	Br	NO ₃ (N)	SO4	Al	В	Ba	Fe	Ni	Se	Si	Sr	V	Zn
5B	6.81	90.1	88.0	39.7	61.4	5.65	335	0.37	89	0.83	3.82	98.5	0.040	0.114	0.07	0.03	0.022	0.02	19.14	0.784	0.01	0.05
5P	6.93	111	94.4	42.2	92.1	6.68	330	0.56	121	0.89	4.37	141.8	0.054	0.152	0.08	0.03	0.027	0.03	16.41	0.947	< 0.01	0.05
U07B	6.83	87.2	83.2	34.7	66.0	5.00	329	0.31	97	0.64	2.35	72.2	0.078	0.107	0.07	0.03	0.022	0.02	18.50	0.850	0.01	0.06
U07P	6.95	84.9	80.7	35.6	55.4	5.18	332	0.34	67	0.67	3.09	72.6	0.068	0.104	0.06	0.040	0.024	0.02	19.34	0.688	0.011	0.04
13B	6.89	69.1	91.8	37.2	60.9	5.20	349	0.28	77	0.62	3.24	87.2	0.042	0.135	0.09	0.07	0.023	0.03	18.87	1.030	0.011	0.04
13B	6.81	87.8	88.6	37.4	58.6	5.25	347	0.39	77	0.65	3.32	86.9	0.070	0.124	0.09	0.05	0.027	0.02	18.95	0.901	0.011	0.05
U014B	6.92	86.5	83.6	37.3	59.7	5.61	357	0.37	70	0.55	3.58	74.2	0.034	0.130	0.06	0.03	0.022	0.02	20.35	0.705	0.015	0.06
U014P	6.85	83.6	86.3	38.0	59.7	5.56	356	0.37	71	0.59	3.55	76.1	0.028	0.128	0.07	0.03	0.025	0.02	20.25	0.731	0.015	0.03
15B	6.91	80.6	92.9	26.6	79.5	3.31	332	0.42	79	0.78	3.10	96.7	0.027	0.160	0.09	0.03	0.020	0.03	17.12	1.976	< 0.01	0.04
15P	6.91	73.7	72.7	32.6	48.8	4.74	329	0.41	47	0.30	2.55	54.2	0.034	0.096	0.05	0.08	0.022	0.02	18.34	0.653	< 0.01	0.03
U020B	6.91	89	91.3	35.0	62.1	4.69	324	0.30	86	0.80	3.00	95.5	0.044	0.112	0.06	0.03	0.020	0.02	18.55	1.073	< 0.01	0.05
U020P	6.87	84.9	83.1	36.5	53.8	5.29	339	0.31	69	0.64	3.25	73.5	0.099	0.106	0.06	0.04	0.024	0.02	19.91	0.694	0.012	0.05
U023B	6.94	76.1	80.4	32.4	45.1	4.14	344	0.39	44	0.32	2.49	58.8	0.198	0.092	0.07	0.09	0.021	0.02	20.20	0.914	0.012	0.05
U023P	6.97	74.9	79.6	32.7	45.5	4.19	340	0.34	43	0.32	2.26	56.6	0.057	0.102	0.07	0.07	0.022	0.03	19.51	0.829	0.012	0.04
26B	6.95	106	97.6	38.0	75.2	4.77	322	0.28	149	0.46	2.66	78.2	0.075	0.107	0.07	0.03	0.020	0.02	18.37	1.226	< 0.01	0.05
26P	6.96	83.7	79.7	35.4	53.2	5.03	336	0.40	67	0.56	3.30	64.7	0.048	0.109	0.05	0.03	0.022	0.03	19.81	0.686	0.011	0.04
UN-P	7.11	172	140.1	39.4	171.3	4.82	324	0.29	418	0.51	1.71	56.2	0.091	0.104	0.16	0.06	0.020	0.02	17.11	2.913	$<\!\!0.01$	0.04
UN-B	7.09	76	76.5	32.4	42.5	3.84	323	0.37	50	0.29	2.79	56.3	0.051	0.072	0.06	0.05	0.027	0.02	19.60	0.728	< 0.01	0.03

Ion concentrations are measured in mg/l and EC in mS/m $\,$

^aSuffix B = bailered sample, suffix P = purged sample

 Table 4. Results of one-way ANOVA of inorganic chemistry parameters analyzed between bailered and purged groundwater samples from each well at the campus test site

Well no.	MS	F	p Value	F _{crit}
U05	426.5951	0.066215	0.80	7.35
U07	36.83835	0.006601	0.94	7.31
U013	3.053544	0.000497	0.98	7.31
U014	0.040685	6.43E-06	1.00	7.31
U015	397.805	0.071882	0.79	7.31
U020	40.57844	0.007166	0.93	7.31
U023	2.509353	0.000441	0.98	7.31
U026	492.5821	0.084293	0.77	7.31
UN	10,520.03	1.112309	0.30	7.31

MS—Mean squares, F—test statistic, p value—is the probability of calculating a given test statistic assuming that the means of your groups are identical and F_{crir} —critical statistic

This implies that with a 99% confidence level it can be concluded that there is statistically no significant difference between all inorganic chemistry parameters measured in bailered and purged groundwater samples per well.

However, there is no consistency on the percentage probability which gives a measure of the differences attributable to the tested factor (sampling methods). For the campus test site aquifer, this probability varies from 30 to 100%. In only one of the nine wells, the probability that the observed differences between the tested two groups is rather due to random chance and not to the influence of sampling methods is at least 99% (Table 4). In the remaining eight wells, there is therefore at least 1% probability that the observed variance is due to the influence of the sampling methods. There is therefore a higher chance that the sampling methods will not agree in these eight wells.

In order to illustrate the difference between the wells that shows a higher probability of the influence of sampling methods to those ones with lowest the probability, data from wells (U014, p = 100%) and (UN, p = 30%) are further analyzed. Figure 4 shows a scatter diagram presenting the concentration of parameters measured in bailered groundwater samples plotted against purged samples for wells; UN (a) and U014 (b). Line 1:1 shows the line through

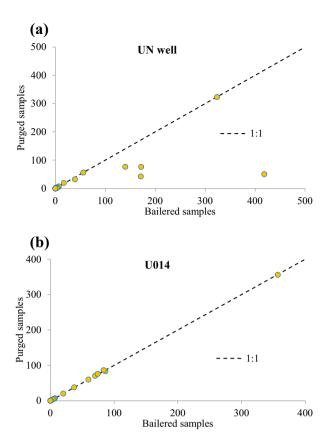


Figure 4. Scatter diagram showing the concentration of all inorganic chemistry parameters measured in bailered samples plotted against purged groundwater samples from wells UN (a) and U014 (b) at the campus test site.

which all samples must plot if the concentrations in the bailered and purged samples are equal. Unlike for U014 well, UN has four samples that plot far away from the 1:1 line. This strongly indicates a poor agreement between the methods even though there is statistically no significant difference between two groups means (Table 4). There is therefore clear evidence on the influence of sampling methods on the measured concentration in the UN well as reflected by the low probability value.

Potential Influence of Sodium-Chloride Salt Tracer

It has been highlighted that site 2 is used for research and study purposes and that sodium–chloride has been injected numerous times during tracer tests. In order to evaluate the potential influence of sodium–chloride on the results of the study, further comparison was conducted for the sodium and

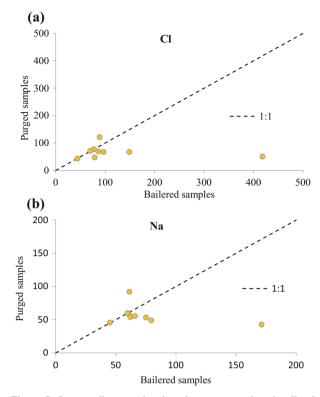


Figure 5. Scatter diagram showing the concentration (mg/l) of chloride (**a**) and sodium (**b**) measured in bailered samples plotted against purged groundwater samples from the at the campus test site.

chloride constituents between bailered and purged samples with the help of scatter plots. Scatter diagram showing the concentration of chloride (a) and sodium (b) measured in bailered samples plotted against purged groundwater samples is presented in Figure 5.

From Figure 5, it is clear that the concentration of chloride and sodium measured in bailered samples are generally elevated in comparison with the purged ones. It is possible that during purging the pump may have diluted the plume associated with sodium-chloride tracers by mixing it with "uncontaminated" water from the surroundings of the aquifer resulting in lower concentrations in the purged samples. In contaminated or anaerobic aquifers, bailer sampling and purging will most likely result in significantly different concentrations in comparison with a fresh aerobic aquifer. Purging would give more of a weighted average of concentrations due to pumping from the surroundings of the aquifer, but mixing and dilution are also possible.

Furthermore, in this fractured-rock aquifer system, it is also possible that one or more flow paths may intersect the screened or open interval of the well, thereby increasing the potential for mixing and dilution of the purged sample (McCarthy and Shevenell 1998). In a typical Karoo single-plane fractured-rock aquifer, any form of pumping (including purging) will initially draw water from the fractures during linear flow and later from the matrix as bilinear flow and later radial (van Tonder et al. 2002), which can also lead to the mixing of groundwater prior to sample collection (Gomo and Vermeulen 2015). Well specific evaluations for both sampling methods would therefore improve the understanding of contaminants distribution and spread.

CV Analysis for Total Coliforms

Figure 6 shows the CV between total coliforms measured in purged and bailered groundwater samples collected from the bedding plane fractured-rock aquifer. Only one well (U013) has a CV within the laboratory analysis CV of $\pm 8\%$ while the rest of the wells have values of over 20%. The results do not show a consistent trend between the CV of total coliforms analyzed in purged and bailered samples. Four of the samples have a CV > 0 (total coliforms in purged sample > bailered) while the other five samples have a CV < 0 (total coliforms in purged sample < bailered). Given that the sampled wells at this site are drilled into a highly hydraulically connected bedding plane fracture, this trend might have been caused by the interference and mixing effect during

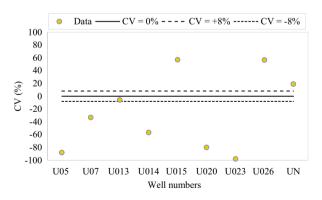


Figure 6. Coefficients of variation between total coliforms analyzed in purged and bailered groundwater samples collected from the campus test site. CV > 0 indicates ion concentration in purged sample > bailered. CV < 0 indicates ion concentration in purged sample < bailered. CV = 0 indicates no variation.

purging. It is, however, clear that the total coliform counts measured in the bailered samples are much more elevated (Table 5) as compared to the purged ones. This is attributed to chemical and physical changes that might occur in the well column which creates conducive conditions to promote growth for microbes.

Site 3: Mining Area

ANOVA of Inorganic Chemistry Parameters

Laboratory results of the inorganic chemistry parameters measured in the groundwater samples collected using the bailer and purge methods are presented in Table 6. Table 7 shows results of oneway ANOVA of inorganic chemistry parameters analyzed between bailered and purged groundwater samples per well at the mining site.

For all the 22 wells, the *p* values are greater than 0.05 (significance level) and test statistic (*F*) is less than the critical value (F_{crit}) ($F < F_{crit}$). The null hypothesis of equal inorganic chemistry parameters means for the two data sets is therefore accepted. This implies that with a 99% confidence level it can be concluded that there is no statistically significant difference between all inorganic chemistry parameters measured in bailered and purged groundwater samples per well.

There is, however, no consistency on the calculated percentage probability (Table 7) that gives a measure of variance attributable to the tested factor (sampling methods). For this site, the probability varies from 26 to 100%. In only nine of the 22 wells, the probability that the observed difference between the bailered and purged samples is rather due to random chance and not to the influence of sampling

 Table 5. Total coliform counts measured in bailered and purged samples

Well no.	Bailered	Purged
U05	4110	260
U07	3870	1940
U013	4880	5480
U014	19,860	5480
U015	308	1120
U020	14,140	1570
U023	1610	17
U026	430	1553
UN	820	1203

 Table 6. Inorganic chemistry parameters measured in groundwater samples collected from the mining site using the bailer and purge methods

Well no. ^a	pН	EC	Ca	Mg	Na	Κ	HCO ₃	Cl	SO_4	$NO_{3}(N)$	Al	Fe	Mn	F	Ba	Zn
E2 B	7.20	62.10	81.24	36.28	14.84	3.09	248.00	40.72	73.50	0.28	0.01	0.02	< 0.01	0.97	0.02	< 0.01
E2 P	7.19	63.20	80.55	36.06	14.37	3.16	246.00	40.05	73.70	0.22	$<\!\!0.01$	0.01	$<\!0.01$	0.93	0.01	$<\!\!0.01$
E3 B	7.21	62.00	83.62	32.75	13.90	2.74	245.00	32.64	72.20	0.30	$<\!\!0.01$	0.01	$<\!0.01$	1.15	$<\!\!0.01$	$<\!\!0.01$
E3 P	7.22	63.20	85.03	33.09	13.84	2.67	248.00	32.99	71.10	0.28	$<\!\!0.01$	0.01	$<\!0.01$	1.21	$<\!\!0.01$	$<\!\!0.01$
E4 B	7.17	89.00	104.53	56.91	23.44	3.95	340.00	55.90	112.80	1.16	$<\!\!0.01$	0.01	$<\!0.01$	0.69	$<\!\!0.01$	$<\!\!0.01$
E4 P	7.13	90.10	102.74	55.54	23.31	3.81	343.00	56.10	113.80	1.17	$<\!\!0.01$	0.01	$<\!0.01$	0.65	$<\!\!0.01$	$<\!\!0.01$
E15 B	6.19	11.80	9.32	4.83	8.65	0.84	23.60	10.36	12.15	3.43	0.08	0.08	0.01	0.03	0.01	$<\!\!0.01$
E15 P	6.15	14.90	11.62	6.01	7.07	0.59	17.30	17.47	11.91	3.22	0.16	0.15	0.01	0.08	0.02	0.01
E17 B	7.28	56.10	59.68	35.69	9.72	2.47	207.00	49.68	35.52	0.47	$<\!\!0.01$	0.02	0.02	0.30	0.04	$<\!\!0.01$
E17 P	7.50	55.00	59.73	35.38	8.83	2.24	201.00	51.05	34.55	< 0.05	$<\!\!0.01$	0.02	0.06	0.26	0.03	0.01
E24 B	7.38	255.00	222.35	159.12	187.54	3.54	259.00	202.27	1135.00	2.90	$<\!\!0.01$	0.02	0.01	0.01	0.01	$<\!\!0.01$
E24 P	7.40	256.00	221.02	157.39	187.31	3.62	261.00	206.05	1164.00	3.63	$<\!\!0.01$	0.05	0.01	0.19	0.01	0.01
E25 B	7.24	219.00	293.36	70.98	186.75	8.01	225.00	167.12	933.00	11.76	$<\!\!0.01$	0.07	0.05	$<\!0.10$	0.04	0.01
E25 P	7.38	216.00	298.24	72.61	180.77	7.74	233.00	165.49	953.00	11.13	$<\!\!0.01$	0.13	0.04	0.20	0.04	0.01
E27 B	7.39	122.00	122.40	69.86	56.30	4.64	303.00	85.30	311.88	0.99	$<\!\!0.01$	0.04	0.09	0.90	0.03	0.01
E27 P	7.30	123.00	124.97	70.85	57.58	4.69	303.00	88.74	314.99	0.83	$<\!\!0.01$	0.04	0.04	1.49	0.03	0.01
E28 B	7.15	141.00	177.87	51.00	83.01	7.56	243.00	180.49	376.81	6.43	0.01	0.05	0.02	< 0.10	0.02	0.01
E28 P	6.88	135.00	181.30	49.25	84.00	6.65	255.00	172.24	367.26	5.90	$<\!\!0.01$	0.01	$<\!0.01$	0.21	0.01	0.01
E29 B	7.49	49.00	23.59	26.46	40.62	4.13	143.00	82.30	85	< 0.05	$<\!\!0.01$	0.04	0.07	$<\!\!0.01$	0.03	0.01
E29 P	7.32	70.30	75.63	30.09	40.51	3.07	148.00	94.30	106.90	8.77	0.01	0.06	0.20	0.01	0.01	$<\!\!0.01$
E30 B	7.65	90.80	101.33	34.19	40.32	3.67	182.00	137.90	111.40	5.64	$<\!\!0.01$	0.05	0.01	0.02	0.01	0.01
E30 P	7.40	86.10	103.77	33.90	40.12	2.97	185.00	135.60	110.30	5.78	$<\!\!0.01$	0.04	0.01	0.04	0.01	$<\!\!0.01$
G2 B	6.71	18.90	17.75	9.90	7.79	1.92	63.60	15.40	9.23	1.44	0.01	0.10	0.02	0.06	0.01	0.01
G2 P	6.39	16.00	15.11	8.10	5.11	1.48	51.00	17.43	7.36	1.13	$<\!\!0.01$	0.03	0.06	0.07	0.01	$<\!\!0.01$
G3 B	6.82	24.90	17.96	11.59	12.41	2.22	41.30	33.01	39.29	0.10	$<\!\!0.01$	0.05	1.35	$<\!\!0.01$	0.04	0.01
G3 P	7.42	46.10	35.69	25.35	19.85	3.81	101.00	50.87	55.80	6.29	$<\!\!0.01$	0.08	0.01	0.11	0.02	0.01
G8 B	7.95	55.00	27.09	52.30	15.73	5.55	259.00	24.58	12.47	0.56	0.01	0.04	0.01	0.05	0.03	$<\!\!0.01$
G8 P	7.96	55.00	33.05	51.61	15.61	5.41	264.00	25.23	12.72	0.54	0.01	0.04	0.01	0.04	0.03	0.01
G9 B	7.60	11.90	8.15	6.42	8.01	1.79	35.70	21.76	0.64	< 0.05	0.01	0.03	0.01	0.02	0.01	$<\!\!0.01$
G9 P	7.28	27.90	26.15	18.10	8.27	2.00	112.00	20.39	5.99	0.61	$<\!\!0.01$	0.05	0.07	0.07	0.01	0.01
G10 B	6.65	14.40	13.30	5.66	6.31	0.76	14.70	42.28	0.77	< 0.05	0.01	0.04	0.01	0.07	0.01	$<\!\!0.01$
G10 P	7.34	27.20	26.97	13.71	11.02	1.81	90.40	22.57	12.76	2.27	$<\!\!0.01$	0.13	0.03	0.07	0.01	0.01
GA01a B	7.75	87.30	91.37	55.44	24.24	3.09	305.00	76.70	86.50	1.40	$<\!\!0.01$	0.05	0.01	0.03	0.01	0.01
GA01a P	7.79	87.90	92.20	55.91	24.15	3.05	308.00	76.50	86.60	1.38	$<\!\!0.01$	0.03	0.01	0.07	0.01	0.01
GA02a B	7.74	86.20	85.09	51.56	24.98	3.29	237.00	96.80	68.80	12.63	$<\!\!0.01$	0.03	0.01	0.07	0.03	0.01
GA02a P	7.82	86.10	84.08	51.27	25.12	2.90	241.00	94.90	68.50	12.58	$<\!\!0.01$	0.03	0.01	0.09	0.01	0.01
GA03 B	7.73	114.00	114.78	70.59	34.89	3.90	342.00	151.32	117.25	0.63	$<\!\!0.01$	0.03	0.01	1.00	0.03	0.01
GA03 P	7.62	115.00	114.44	70.62	34.65	3.97	344.00	149.65	116.63	< 0.05	$<\!\!0.01$	0.03	0.01	$<\!0.10$	0.03	0.01
GA04a B	8.02	100.00	53.30	57.40	77.59	2.25	112.00	121.51	292.99	0.57	$<\!\!0.01$	0.03	0.01	$<\!\!0.10$	0.03	$<\!\!0.01$
GA04a P	7.80	102.00	89.64	51.48	58.67	2.65	157.00	116.06	267.82	< 0.05	$<\!\!0.01$	0.03	0.26	$<\!0.10$	0.04	0.01
GA04b B	7.90	100.00	46.46	47.69	95.78	1.29	133.00	126.42	253.38	< 0.05	$<\!\!0.01$	0.04	0.07	< 0.10	0.02	$<\!\!0.01$
GA04b P	8.03	120.00	88.79	60.15	108.63	1.57	164.00	134.93	353.83	0.95	$<\!\!0.01$	0.07	0.35	< 0.10	0.02	0.01
KLM4 B	7.88	59.10	66.28	35.38	13.39	1.93	214.00	45.33	53.09	2.57	$<\!\!0.01$	0.03	0.01	0.20	0.02	0.01
KLM4 P	7.81	59.00	66.75	34.85	12.64	1.86	214.00	45.04	50.13	2.61	< 0.01	0.03	0.01	0.26	0.02	0.02

Ion concentrations are measured in mg/l and EC in mS/m

^aSuffix B = bailered sample; suffix P = purged sample

methods is at least 99% (Table 7). Measured concentrations in these wells are less likely to be affected by the type of sampling method used. In the remaining 13 wells, there is therefore more than 1% probability that the observed variance is due to the influence of the sampling methods. There is a higher chance that the tested sampling methods will not agree in these wells.

Potential Influence of Inorganic Chemistry Redox Sensitive Parameters

Line graphs showing calculated p values from ANOVA of all parameters and those without redox sensitive parameters in each well at sites 1, 2 and 3 are presented in Figure 7. The results generally show lower p values for ANOVA conducted with-

	fr	om each well at the mining site		
Well name	MS	F	p Value	F _{crit}
E2	0.247582	6.19E-05	0.99	7.56
E3	0.818161	0.000204	0.99	7.56
E4	0.096716	1.31E - 05	1.00	7.50
E15	0.844239	0.019164	0.89	7.56
E17	2.203071	0.000821	0.98	7.56
E24	35.13319	0.000428	0.98	7.56
E25	17.2759	0.000302	0.99	7.56
E27	5.0705	0.00047	0.98	7.56
E28	3.956607	0.000299	0.99	7.64
E29	1317.581	0.653611	0.63	7.64
E30	0.488154	0.000135	0.99	7.56
G2	17.35543	0.082334	0.78	7.56
G3	813.7197	1.523182	0.23	7.56
G8	3.709573	0.000889	0.98	7.56
G9	503.224	1.151589	0.29	7.56
G10	387.8046	1.214841	0.28	7.56
GA01a	0.692708	0.000112	0.99	7.56
GA02a	0.000966	2.39E-07	1.00	7.56
GA03a	0.030756	3.57E-06	1.00	7.56
GA04a	23.23418	0.003835	0.95	7.56
GA04b	1861.598	0.235884	0.63	7.72
KLM4	0.547299	0.000185	0.99	7.56

 Table 7. Results of one-way ANOVA for inorganic chemistry parameters analyzed between bailered and purged groundwater samples from each well at the mining site

MS—Mean squares, F—test statistic, p value—is the probability of calculating a given test statistic assuming that the means of your groups are identical and F_{crir} —critical statistic

out redox sensitive parameters, which is in contrast to expectations that these parameters would be more affected by the sampling methods resulting in higher p values being calculated. If the redox sensitive parameters were affected by the sampling methods, it would be expected that the ANOVA conducted without these parameters will yield larger p values indicating less influence of the sampling methods. The influence of the redox sensitive parameters can therefore be regarded as minimum on the study.

Results also show very small differences (<6%) between p values for the ANOVA conductivity with all parameters and those conducted without redox sensitive parameters at site 1. With the exception of only four wells (E15, E29, G3 and G10), the results from site 3 show nearly equal (<5% difference) p values for ANOVA conducted without redox sensitive parameters, which are in contrast to expectations that these parameters would be more affected by the sampling methods, resulting in higher p values being calculated. There is therefore no evidence to suggest that the redox aquifer conditions could have influenced the results of this comparative study.

CONCLUSIONS AND RECOMMENDATIONS

Analysis of variance of inorganic chemistry parameters measured in bailered and purged groundwater samples was conducted in each well. Results at all three sites show that with 99% confidence level there was statistically no significant differences between all inorganic chemistry parameters measured in bailered and purged groundwater samples from each well. However, the absence of significant differences does not imply that the two methods give the same results. Further analysis of the p values was used to indicate the probability to which the observed difference (even if not significant) among groups is attributable to influence of random factors or the sampling methods (test factor). The smaller the p value, the more likely that the observed difference is due to the influence of the sampling method. In 13 of the 43 wells, the probability that the observed difference between the bailered and purged samples is rather due to random chance and not to the influence of sampling methods is at least 99%. Depending on well specific conditions, it should be possible to obtain results of the bailer method that are very similar to those of the purging method.

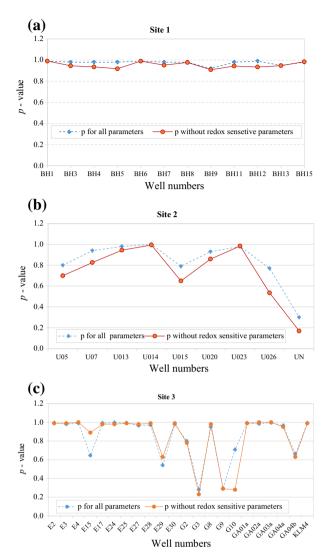


Figure 7. Line graphs showing calculated p values from the ANOVA of all parameters and those without redox sensitive parameters in each well at sites 1 (a), 2 (b) and 3 (c).

The results of this study suggest that that in some cases bailers can obtain samples that are statistically comparable to purged samples. However, as discussed, the success of bailers to collect samples representative of aquifer water would depend on site-specific factors such as hydrogeology, hydrogeochemistry, depth of sample collection, well development and construction among others. The adoption of the bailer sampling method, like many other passive approaches, cannot therefore be recommended without some considerations. As a general guide it is recommended that:

- Site-specific evaluations are done per well before bailers can be adopted;
- Such evaluations can be based on the analysis of variance between all-important inorganic chemistry determinants (according to monitoring program and project goals) measured in bailered and purged samples at 99% confidence level. At this confidence level, adoption of bailers can be scientifically justified if:
 - There is no significant difference between the two groups; and
 - There is at least 99% probability that the observed statistical difference (even when not significant—indicated by the *p* value) is attributable to random chance and not to the influence of sampling methods (tested factor).
- When passive sampling has been adopted for long-term monitoring, comparison must be made to the conventional purging method. The interval for comparison would probably vary due to factors such as site conditions, monitoring frequency among others. Comparisons at the start, middle and end of the monitoring program would help to assess the performance of passive methods against purging methods; and
- For one-off sampling exercises, purging is recommended.

The total coliform counts measured in the bailered samples, as an indication of the microbial quality, are much more elevated as compared to the purged samples. Unpurged samples are prone to chemical and physical changes that might occur in the well column. The findings suggest that for microbial analysis, purging is necessary to collect water from the aquifer that is less affected by changes that might occur within the well column.

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REFERENCES

- APHA. (2005). Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association (APHA). 20001-3710.
- Barcelona, M. J., Gibb, J. P., Helfrich, J. A., & Garske, E. E. (1985). Practical guide for groundwater sampling. ISWS Contract Report 374. Champaign, Illinois: Illinois State Water Survey. https://www.orau.org/PTP/PTP%20Library/li brary/EPA/samplings/pracgw.pdf. Accessed July 5, 2016.
- Barcelona, M. J., & Helfrich, J. A. (1986). Well construction and purging effects on ground-water samples. *Environmental Science and Technology*, 20(11), 1179–1184.
- Barcelona, M. J., Helfrich, J. A., Garske, E. E., & Gibb, J. P. (1984). A laboratory evaluation of groundwater sampling mechanisms. *Groundwater Monitoring and Remediation*, 4(2), 31–41.
- Barker, R., & Molle, F. (2004). Evolution of irrigation in south and Southeast Asia: comprehensive assessment research report 4. Colombo: International Water Management Institute (IWMI). http://www.iwmi.cgiar.org/assessment/files/pdf/pub lications/ResearchReports/CARR5.pdf. Accessed July 12, 2016.
- Botha, J. F., Verwey, J. P., Van der Voort, I., Vivier, J. J. P., Buys, J., Colliston, W. P., & Loock, J. C. (1998). Karoo aquifers: Their geology, geometry and physical properties. Report to Water Resources Commission. WRC Report No: 487/1/98. Bloemfontein, South Africa: Institute for Groundwater Studies.
- Byrnes, J. P., Jeffrey E. B., & Bealer L. J. (1996). Evaluation of well purging in ground-water sampling for BTEX and MTBE. In Proceedings of the 1996 Petroleum Hydrocarbon Organic Chemicals in Ground Water Conference, Houston, Texas, National (Vol. 221). Dublin, Ohio: Ground Water Association. http://info.ngwa.org/gwol/pdf/960162465.PDF. Accessed August 3, 2016.
- Gomo, M. (2011). A groundwater-surface water interaction study of an alluvial channel aquifer. Ph.D. thesis. Bloemfontein: University of the Free State. http://scholar.ufs.ac.za:8080/ xmlui/bitstream/handle/11660/1882/GomoM(1).pdf?sequence= 1&isAllowed=y. Accessed March 30, 2016.
- Gomo, M., van Tonder, G. J., & Steyl, G. (2013). Investigation of the hydrogeochemical processes in an alluvial channel aquifer located in a typical Karoo Basin of Southern Africa. *Environmental Earth Science*, 70, 227–238.
- Gomo, M., & Vermeulen, D. (2015). An investigative comparison of purging and non-purging groundwater sampling methods in Karoo aquifer monitoring wells. *Journal of African Earth Sciences*, 103, 81–88.
- ITRC. (2008). Diffusion/passive samplers. Washington, DC: Interstate Technology & Regulatory Council (ITRC). http:// www.itrcweb.org/teampublic_DPS.asp. Accessed September 16, 2008.

- LeChevallier, M. W. (2003) Conditions favouring coliform and HPC bacterial growth in drinking water and on water contact surfaces. In 2003 World Health Organization (WHO). Heterotrophic Plate Counts and Drinking-water Safety. London: Published by IWA Publishing. ISBN: 1 84339 025 6.
- Lundegard, P. D., Williams, K., Martinez, A., & Daugherty, S. (1997). Net benefit of well purging reevaluated. *Environ*mental Geosciences, 4(3), 111–118.
- McCarthy, J., & Shevenell, L. (1998). Obtaining representative groundwater samples in a fractured and Karstic formation. *Groundwater*, 38(2), 251–260.
- McQueen, K. G. (2006). Calcrete geochemistry in the cobar-girilambone region, New South Wales. New South Wales: Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME). http://www.crcleme. org.au/Pubs/OPEN%20FILE%20REPORTS/OFR%20200/ OFR%20200%20Regional%20Calcrete%20Geochemistry5. pdf. Accessed August 15, 2016.
- Puls, R. W., & Barcelona, M. J. (1996). Low flow (minimal drawdown) ground-water sampling procedures. U.S. Environment Protection Agency, EPA/540/S-95/504. https://www. epa.gov/sites/production/files/2015-06/documents/lwflw2a.pdf. Accessed July 17, 2016.
- Robin, M. J. L., & Gilham, R. W. (1987). Field evaluation of well purging procedures. Groundwater Monitoring and Remediation, 7(4), 85–93.
- Rong, Y. (1998). Groundwater sampling: To purge or not to purge. *Environmental Geosciences*, 5(2), 57–60.
- Roudnew, B., Lavery, T. J., Seymour, J. R., Jeffries, T. C., & Mitchell, J. G. (2014). Variability in bacteria and virus-like particle abundances during purging of unconfined aquifers. *Groundwater*, 52(1), 118–124.
- Savoie, J. G., & LeBlanc, D. R. (2012). Comparison of no-purge and pumped sampling methods for monitoring concentrations of ordnance-related compounds in groundwater, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, 2009–2010: U.S. Geological Survey Scientific Investigations Report 2012–5084. http://pubs.usgs.gov/sir/ 2012/5084. Accessed June 24, 2016.
- Springer, K. (1998). No Purging ground-water sampling proposal for gasoline compounds in New Jersey unconfined aquifers. In Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference: November 11–13, 1998, Houston, Texas (p 474). Ground Water Association.
- USEPA. (2010). Low stress (low flow) purging and sampling procedure for the collection of groundwater samples from monitoring wells: Chelmsford, Mass., U.S. Environmental Protection Agency (USEPA), Region 1, EPASOP–GW 001, revised Accessed January 19, 2010.
- USGS. (1980). National handbook of recommended methods for water data acquisition. Reston, VA: US Geological Survey (USGS).
- van Tonder G. J., Bardenhagen I., Riemann, K., van Bosch, J., Dzanga, P., Xu, Y. (2002). Manual on pumping test analysis in fractured-rock aquifers. Water Research Commission (WRC) of South Africa, Report number 1116/1/02, ISBN No 1 86845 861 X. Pretoria.
- Vroblesky, D. A., Casey, C. C., & Lowery, M. A. (2007). Influence of dissolved oxygen convection on well sampling. *Ground Water Monitoring and Remediation*, 27(3), 49–58.
- Vroblesky, D. A., & Hyde, W. T. (1997). Diffusion samplers as an inexpensive approach to monitoring VOCs in ground water. *Ground Water Monitoring and Remediation*, 17, 177–184.