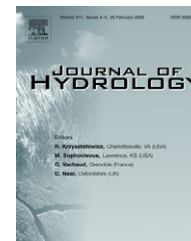


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# Observations on elemental concentrations of groundwater in central Benin

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Regional  
characterization

**Summary** Groundwater samples were collected at over 100 locations in Benin, West Africa, for the purpose of characterizing region-wide spatial variation in groundwater quality as indicated by concentrations of a number of elements measured within the samples. Analytic techniques ranged from field measures of conductivity and pH, to characterization of major and trace element concentrations using ICP-MS and ICP-OES. Five methods of data analysis were applied to the resulting data set: indicator variables, parameter plots, cluster analysis, variogram analysis, and principal component analysis (PCA). A number of observations are developed from these analyses including regional trends in concentrations and variation of concentration of major and trace elements in specific geologic settings. Perhaps most significant is the identification of a region in the southern portion of the study area where the element chemistry shows high spatial variability. This region had not been identified in prior studies of the regional geochemistry. The mechanisms leading to this variability remain under study. The results presented provide significant insight into the regional variation in groundwater elemental chemistry for Benin. Further, they provide further illustration of the utility of applying multiple data analysis techniques to assessment of regional water quality data sets.

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## Introduction

Spatial variation in element concentration in groundwater is being characterized for central Benin, West Africa. The

goals of this characterization include provision of a baseline from which to perform region-specific characterization and delineation of significant natural variations in water quality that may impact human health or utility of the water for domestic or agricultural use. The work discussed herein is motivated by the need to develop fundamental understanding in an effort to provide a foundation for management of relatively scarce groundwater resources.

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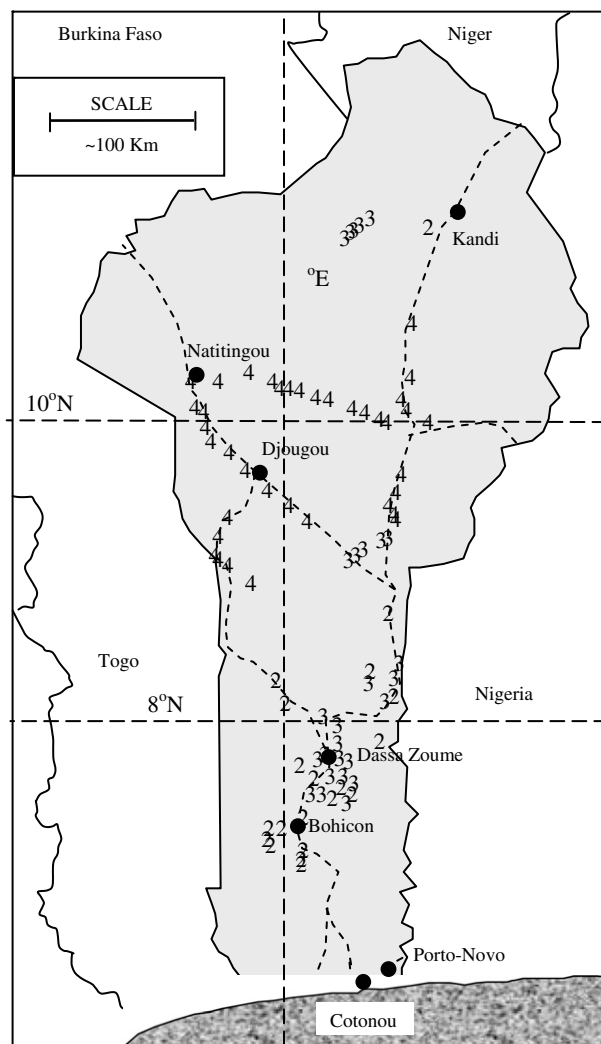
The study reported below follows on the example of a number of other authors who have used statistical methods, in combination with data sets on elemental concentrations in water, to differentiate structure and sources represented in groundwater systems. A number of authors have, for example, reported on the analysis of the chemistry of precipitation (e.g., Berg et al., 1994; Reimann et al., 1997; Freyrier et al., 1998; Goni et al., 2001), and groundwater (e.g., Farnham et al., 2000; Kraemer et al., 1996). Goni et al. (2001), Freyrier et al. (1998) and others, for example, have used spatial patterns of groundwater chemistry to link groundwater quality to precipitation, with emphasis on the impact of sea spray, natural dry fallout and anthropogenic effects. Similarly, Kraemer et al. (1996) used ICP-MS and Ion Chromatography to characterize trace elements to relate groundwater chemistry to flow pathways in Death Valley, California. Farnham et al. (2003, 2000) have discussed the use of a number of statistical methods for the interpretation of groundwater element data. Hence, as suggested in the literature, element analysis utilizing ICP-MS (inductively coupled plasma-mass spectrometry), ICP-OES (inductively coupled plasma-optical emissions spectrometry) and related instrumentation provides a powerful tool, when combined with data analysis techniques, for characterizing spatial patterns in groundwater chemistry.

The present manuscript details the spatial description, at the regional scale, of groundwater elemental concentrations in central Benin. Samples were collected over three field seasons and assessed using several data analysis methods. The present study provides initial indication of regional trends in elemental concentrations, the degree of spatial variability in elemental composition, and regions of interest from the standpoint of unusual element concentrations and/or potential impact on human health.

## The study area

The study area, central Benin, West Africa, is bounded by latitude  $\sim 7^{\circ}$  N through  $\sim 11^{\circ}30'$  N and longitude  $\sim 1^{\circ}20'$  E through  $\sim 3^{\circ}$  E (an area of approximate dimension 500 km by 180 km; see Fig. 1). Based on the work of Lelong (1963) and Azonsi and Adjomayi (2005), it is known that Benin is an intertropical savanna with between 900 and 1500 mm of annual precipitation. The climate progresses from sub-equatorial in the south (with two rainy seasons: April through July and September through November) to tropical in the north (with one rainy season: May through September). Annual potential evapotranspiration is estimated to vary spatially from a mean value of 1350 mm in the south to 1700 mm in the north. Rainfall exceeds evapotranspiration for approximately 6 months out of the year in the south and 3 months out of the year in the north, thus providing the opportunity for recharge of the groundwater. Although a significant hydrologic monitoring network is available, the details of the hydrologic cycle, particularly in the study area, remain poorly defined.

The geology of Benin is largely composed of igneous and metamorphic Precambrian rocks (approximately 80% of the country including the entire study area) (Boukari, 1980, 1982, 1989). Sedimentary sequences (approximately 20% of the country) can be found in the coastal basin in southern Benin (Mesozoic and Cenozoic), the Paleozoic basin of Kandi



**Figure 1** Simplified map of Benin, West Africa, with select cities, major roads and approximate sample locations shown (exact latitude and longitude of samples available electronically from the primary author). The numbers represent approximate location of wells sampled with the number representing the year of sampling (2, 3, and 4 representing, respectively, 2002, 2003, and 2004).

in northeastern Benin, and the Cambrian basin of Pendjari in northwestern Benin (Pouget, 1955; Affaton, 1975; Istituto Ricerche Breda, 1982).

Within the study area, the metamorphic formations consist primarily of complex, undifferentiated migmatites but also include granulitic complexes and diverse gneisses, with less abundant amphibolites, mica schists, pyroxenites, serpentinites, quartzites and marbles (Affaton, 1975; BRGM, 1978; Istituto Ricerche Breda, 1982, 1987). The igneous formations are primarily composed of complexes of syn-tectonic to post-tectonic intrusions (granite with a medium to fine grain, granodiorite, monzodiorite, diorites, gabbros, diabase, and basalt) but also include some volcanic rocks (basalt and rhyolite). Volcanic sequences are also present and consist of felsic to intermediate rocks (Boussari, 1975) with veins of quartz, pegmatite, and diabase in various combinations.

The hydrogeology within the study region is based on fractured rock formations with minimal matrix porosity such that groundwater is derived primarily from regions of alteration or fractures. Alteration is most common in the upper 10–20 m of the subsurface and is associated either with shallow fracture networks or zones of disaggregation leading to formation of sand lenses and/or saprolites. Fractures are present beneath the zone of weathering, with fractures and joints forming potential groundwater flow routes. The fractures are generally sub-vertical, but variable in orientation.

Based on this geology, water supplies within the crystalline rocks of Benin are commonly developed from three ranges of depth that are differentiated by available porosity:

- Superficial aquifers in the shallow, altered rock. These aquifers exhibit an interstitial porosity and are commonly exploited as water supplies based on large-diameter, hand-dug wells.
- Deep fractured rock, with groundwater flow reliant solely on the porosity of the fractures. Development is pursued through drilling, typically with air hammers, to median depths of 60 m (Guiraud, 1975; Engalenc, 1978). These wells are commonly equipped either with submersible pumps (where electricity is available and demand is sufficient to warrant construction of a centralized supply) or with manual pumps (hand or foot pumps).
- Fracture zones at the transition between the superficial aquifers and the deep aquifers. While these depths may exhibit behavior associated with both fracture flow and interstitial porosity, their behavior tends towards that of fractured media. These zones have been exploited both through construction of hand-dug wells and through drilling.

Land use in the region includes small acreage agriculture, rural residential, small urban, and undeveloped. Faced with the scarcity and poor quality of surface water, much of the population originally invested in large-diameter, hand-dug wells that penetrated only into the upper, weathered zones. Difficulties with these wells were observed both in terms of maintaining water quality and in terms of declining water levels between rainy seasons and during droughts. In the 1980s, programs were initiated to alleviate the water problems via installation of small-diameter, drilled wells penetrating into the deep fractured zones. As these wells penetrated to the deep fractures, it was anticipated that there would be the additional benefit of lower risk of direct anthropogenic contamination. Those drilled wells with a relatively small capacity (0.7–5 m<sup>3</sup>/h) were equipped with manual (hand or foot) pumps, whereas select deep wells were equipped with submersible pumps in order to provide water supply for towns and villages with higher population density.

The wells sampled in this study are all in the deep aquifer and are equipped with manual pumps. Each was drilled by air hammer (with rotary drilling occasionally employed to penetrate altered rock near the surface) and was screened at the depth of the most productive fracture zone. Casing with grout was used to seal the well above the screen. Depths range from ~50 m in the southern por-

tion of the study area to ~70 m in the northern portion of the region. By focusing solely on wells drilled by air hammer, screened at the zone of production, and equipped with manual pumps, the variation in well chemistry related to variable methods of drilling, completion, or sampling (e.g., possible variation from high-capacity pumps found in the larger cities to buckets used in large-diameter wells throughout the country) is substantially reduced, thus reducing one important variable in the analysis of the resulting data.

## Field sampling campaigns

A preliminary field sampling campaign was conducted in the year 2000 and included sampling of 20 wells. Although the resulting data base was considered unreliable due to difficulties in sampling and analysis protocols, this initial sampling effort aided significantly in guiding the design of the long-term sampling strategy (e.g., Galbis-Reig, 2001). Based on results derived from this initial effort, three field campaigns (2002–2004) were pursued and have provided data for this study. With sampling locations as shown in Fig. 1, these three field campaigns resulted in collecting samples from 37, 28, and 43 groundwater wells, respectively. Field methods are discussed in the following section.

Based on these field campaigns, samples were returned to the University of Notre Dame for analysis via a number of analytical devices including ICP-MS (inductively coupled plasma-mass spectrometry), ICP-OES (inductively coupled plasma-optical emission spectrometry) and specific ion electrodes.

The distribution of sampling points in Benin has involved a compromise between sampling for specific purposes (e.g., analysis of elevated concentration of nitrate and uranium in the southern portion of the study site) and sampling for the purpose of developing estimates of spatial structure (e.g., estimation of the variogram). While sampling to characterize specific contamination scenarios leads to a desire to concentrate sampling in specific regions, optimizing the estimate of the variogram leads to a desire to distribute sampling throughout the region of study (e.g., Journel and Huijbregts, 1978; Conwell et al., 1997, others). With respect to Benin, assessment of the distribution of data following the 2003 sampling campaign demonstrated that the data were heavily clustered in the south-central region. In order to provide a distribution of samples more consistent with estimation of spatial statistics, the samples collected in the summer of 2004 were located based on a sampling design dedicated to increasing the utility of the data set for spatial statistical analysis. The result of this sample distribution is discussed below.

## Field methods used

As a result of the fact that the wells sampled within this study were actively in use by local populations, it was difficult to follow standard sampling procedure (purging multiple well bore volumes prior to collecting a sample). However, substantial effort was made to sample in a manner that would produce reliable data. The following summarizes the field methods employed:

- 1 As noted above, only drilled wells equipped with manual (hand or foot) pumps were included in this analysis. Thus data from hand-dug wells and/or wells equipped with submersible pumps were not included in the data analysis discussed below.
- 2 All wells sampled had been in active production by the local population within the previous 24 h. Further, the majority of wells were in active production when approached for sampling. Hence, concern regarding clearing of multiple well volumes prior to sampling was considered minimal as the water within the wells is refreshed (by pumping) on a nearly continuous basis. Despite this, our field procedure required, for any well not actively being pumped when we arrived for sampling, pumping a minimum of 100 cycles prior to collecting the sample. This level of cycling produces an estimated 100 l of water, thus it is recognized that it does not ensure complete flushing of the wellbore volume (with an estimated volume between 200 and 800 l). However, this cycling did ensure flushing of the pump cylinder and drop pipe (the pipe leading from the pump cylinder to the surface), which has a total estimated volume of approximately 15 l. Hence, it was assumed that the regular use of these wells combined with the 100 cycles pre-sampling was an adequate compromise between following standard development procedures and managing time spent at each sampling location (as well as concern by the local population regarding our monopolizing their pump).
- 3 Immediately after sample collection, 60 ml of water was filtered through a 0.45  $\mu\text{m}$  filter and acidified with 1.5 ml of concentrated nitric acid. A second 60 ml sample was collected without filtration or acidification. These samples were returned to the University of Notre Dame for elemental analyses. Due to the remote field conditions, these samples could not be refrigerated prior to return to the United States with lag periods as long as  $\sim 14$  days.
- 4 An additional container of approximately 3 l of well water was collected to be tested at the site for temperature, pH, conductivity, and turbidity. As our equipment has improved over the 3 years of sampling, dissolved oxygen and salinity were added to the parameters sampled in the field, as was nitrate during the 2003 campaign. For consistency, only pH and conductivity are assessed from these parameters in the spatial analysis discussed below.

Beyond the scope of this paper, select samples were also collected for analysis of oxygen and nitrogen isotopes (Crane, 2005).

### Analytical methods used

The non-acidified/unfiltered samples were analyzed in the Notre Dame laboratory for chloride and fluoride using specific ion electrodes which were calibrated against standards ranging from 1.7 mg/l to 500 mg/l for chloride and 0.85 mg/l to 49.5 mg/l for fluoride. Samples which were acidified and filtered were analyzed for both major and minor elements. Major elements were determined using ICP-OES. Minor and trace elements were determined using ICP-MS. In addition to well samples, samples of the nitric acid (diluted into distilled water) were analyzed.

Although samples from 2002 and 2003 were originally analyzed in the fall of those years (Roope, 2003), respectively, using a Fisons quadrupole PQII STE ICP-MS, a new Thermofinnegan Element 2 high resolution magnetic sector ICP-MS was brought on-line in the fall of 2004. This unit has allowed greater precision in the measurement of trace elements. Hence, all samples were reanalyzed on this new unit and it is the results of analysis from this newer unit that are discussed below. Samples from 2002 and 2003 were kept refrigerated and acidified prior to analysis using the Element 2. The resulting list of parameters used in our analysis is provided in Table 1. As discussed in the following paragraphs, additional elements were analyzed, but were eliminated from further analysis due to excessive numbers of non-detects (e.g., Al, Cs, Re, Sb, Bi, Th) or mass interference without an alternative isotope for analysis on the ICP-MS (e.g., Sc, As, Se, following on the work of Stetzenbach et al., 1994).

Internal standards (Be, Ge, Y, In, Tb, and Tl) were used in the ICP-MS analyses of the water samples to correct for machine drift. Based on these estimates of drift on the internal standards, measured intensities for all samples were corrected for drift, background (blank) intensity, and then assessed against calibration curves based on the standards prepared from stock solutions of known concentration. All dilutions were conducted gravimetrically for greater accuracy. Finally, where possible, multiple isotopes were run for the same element in an effort to identify and avoid mass interferences on the ICP-MS. For Cr, Ti and Ni, two isotopes were analyzed for each element. In each case, the abundances measured for the two isotopes were different, with the isotope anticipated to be impacted by interference [e.g.,  $^{47}\text{Ti}$  with Si ( $^{28}\text{Si}^{18}\text{OH}$  and  $^{30}\text{Si}^{16}\text{OH}$ );  $^{53}\text{Cr}$  with  $\text{Cl}^-$  ( $^{35}\text{Cl}^{18}\text{O}$  and  $^{37}\text{Cl}^{16}\text{O}$ );  $^{60}\text{Ni}$  with Mg and  $\text{Cl}^-$  ( $^{25}\text{Mg}^{35}\text{Cl}$ )] giving the higher abundance and showing positive correlation with an interfering element (e.g., Cl or Si). The isotopes exhibiting the lower abundances show no such correlations – these data are used in our analyses.

While all samples were analyzed for  $^{45}\text{Sc}$ ,  $^{75}\text{As}$  and  $^{77}\text{Se}$ , these data are not reported for the following reasons. For  $^{45}\text{Sc}$ , a broad positive correlation was observed with Si (interference of  $^{28}\text{Si}^{16}\text{OH}$ ;  $^{29}\text{Si}^{16}\text{O}$ ); for  $^{75}\text{As}$ , a broad positive correlation was observed with Cl (interference of  $^{40}\text{Ar}^{35}\text{Cl}$ ); for  $^{77}\text{Se}$  broad positive correlations were observed with Ca and Cl, indicating abundances are enhanced by the  $^{40}\text{Ca}^{37}\text{Cl}$  (as well as the  $^{42}\text{Ca}^{35}\text{Cl}$ ) polyatomic interference. While the samples were re-run at medium and high resolution to try and resolve the element signal from that of the interference, the element signals were below detection at these higher resolutions.

Calibration standards and reference materials SLRS-3 (Riverine Water, NRC Canada; McLaren, 1994) and NIST 1643d (Trace Metals in Water) were included at several points in each analytical run on the ICP-MS in order to determine precision and accuracy of the results (Table 2a). Examination of results for the reference materials indicates that ICP-MS results for  $\text{Mg}^{25}$  were not reliable. As Mg was also analyzed using the ICP-OES, the ICP-MS results were not utilized in the statistical analysis. With respect to  $\text{Fe}^{57}$ , it was observed that the reference values for the low resolution on the ICP-MS were quite poor. Hence, Fe was rerun at medium resolution with substantially better results. However, Fe



**Table 1** Elements for which analytical results were used in the statistical analyses

Element or parameter	Mean/standard deviation/estimated detection limits of results with units indicated	Comments
	<i>Parameters included in final analysis</i>	<i>Analysis method</i>
Ti <sup>49</sup>	1.7/2.9/0.7 ppb	ICP-MS
V <sup>51</sup>	11.8/11.5/0.2 ppb	ICP-MS
Cr <sup>52</sup>	3.3/7.8/0.7 ppb	ICP-MS
Co <sup>59</sup>	0.52/0.62/0.02 ppb	ICP-MS
Ni <sup>62</sup>	9.4/56/1.0 ppb	ICP-MS
Cu <sup>63</sup>	3.1/4.5/0.2 ppb	ICP-MS
Mo <sup>95</sup>	2.7/3.9/0.03 ppb	ICP-MS
Sn <sup>118</sup>	0.06/0.13/0.04 ppb	ICP-MS
Pb <sup>206</sup>	0.38/0.39/0.02 ppb	ICP-MS
U <sup>238</sup>	12.8/59/0.003 ppb	ICP-MS
Mn <sup>55</sup>	106/165/0.03 ppb	ICP-MS
Zn <sup>64</sup>	75.7/158/0.4 ppb	ICP-MS
Sr <sup>88</sup>	0.39/1.01/0.06 ppm	ICP-MS and ICP-OES
Ba <sup>137</sup>	0.15/0.15/0.04 ppm	ICP-MS
Fl	0.54/0.72/~0.1 ppm	Specific ion electrode
Cl	24.5/44.4/~1.0 ppm	Specific ion electrode
Na <sup>330.237</sup>	24.9/20.9/2.4 ppm	ICP-OES
Mg <sup>285.213</sup>	21.2/17.1 /0.40 ppm	ICP-OES
Al <sup>308.215</sup>	0.04/0.06/0.12 ppm	ICP-OES
Si <sup>251.611</sup>	37.6/14.4/0.62 ppm	ICP-OES
P <sup>213.617</sup>	0.06/0.09/0.02 ppm	ICP-OES
S <sup>181.975</sup>	4.5/11.4/0.07 ppm	ICP-OES
K <sup>776.490</sup>	9.6/12.6/0.26 ppm	ICP-OES
Ca <sup>317.933</sup>	48.3/44.2/1.41 ppm	ICP-OES
Fe <sup>238.204</sup>	0.39/1.00/0.01 ppm	ICP-OES*
pH	6.25/0.54	Field probe
Conductivity	434/364 $\mu$ S/cm	Field probe
Latitude	N/A	N/A
Longitude	N/A	N/A

Elements analyzed by ICP-MS include the mass analyzed whereas those analyzed by ICP-OES include the wavelength used in the laboratory analysis.

\* Fe was run on both the ICP-MS and the ICP-OES. As Fe concentrations were more consistent with the reference concentrations used with the ICP-OES, only these results are reported here.

was also run on the ICP-OES with a range of result concentrations more consistent with the concentrations in the reference solution used with the OES. Hence, a choice was made to use only the ICP-OES data for Fe in the statistical analysis below.

All samples were also analyzed on a Perkin Elmer 3300 XL ICP-OES for major ions. Following a similar method to that detailed above for the ICP-MS, internal standards (Y and In) were used to correct for machine drift. Final measured counts were corrected for drift, background (blank) intensity, and then assessed against calibration curves based on the standards prepared from stock solutions of known concentration. All dilutions were conducted gravimetrically for greater accuracy. Multiple wavelengths were run for each element to allow comparison of calibration curves and consistency with reported values for the reference solutions. The wavelengths used in the statistical analysis below were selected based on their providing better calibration curves for the range of sample concentrations and greater reproducibility of standards and reference materials than the alternate wavelength.

As with the ICP-MS, calibration standards and reference materials SLRS-3 and NIST 1643d were included at select points in each analytical run in order to determine precision and accuracy of the results (Table 2b). It was observed in completing this comparison with reference solutions that none of the wavelengths for the ICP-OES provided reasonable results for Ba. As Ba<sup>137</sup> data from the ICP-MS were considered reliable, only these values are used in the statistical analysis.

### Data analysis methods used

As discussed by previous authors, use of multiple data analysis techniques can provide substantial insight into the information contained in a data base of water quality data (e.g., Farnham et al., 2000 and others). In the present study, analysis of the final element concentrations (as well as the field values for conductivity, pH, latitude, longitude and select concentration ratios) was performed in multiple stages including exploratory data analysis, indicator vari-

**Table 2** Results for the ICP-MS analysis of standard reference materials NIST 1643d (trace elements in water) and the National Research Council of Canada SLRS-3 (Riverine Water) (Panel a)<sup>a</sup> and results for the ICP-OES analysis of standard reference materials NIST 1643d and the NRCC SLRS-3 (Panel b)<sup>b</sup>

	NIST 1643d				CRC SLRS-3			
	Average (N = 8)	Standard deviation	Certified value	95% Confidence (± value)	Average (N = 5)	Standard deviation	Certified value	95% Confidence (± value)
<i>Panel a</i>								
V <sup>51</sup>	34.42	0.97	35.1	1.4	0.55	0.10	0.3	0.02
Cr <sup>52</sup>	17.67	0.72	18.5	0.2	0.34	0.05	0.3	0.04
Cr <sup>53</sup>	17.92	1.02	18.5	0.2	1.13	0.31	0.3	0.04
Fe <sup>57</sup> (low range)	222.49	63.15	91.2	3.9	108.0	10.1	100	2
Co <sup>59</sup>	24.70	0.55	25	0.59	0.041	0.005	0.027	0.003
Ni <sup>60</sup>	58.69	1.10	58.1	2.7	1.02	0.03	0.83	0.08
Ni <sup>62</sup>	56.28	1.55	58.1	2.7	0.92	0.12	0.83	0.08
Cu <sup>63</sup>	20.37	0.91	20.5	3.8	1.38	0.09	1.35	0.07
Cu <sup>65</sup>	20.70	1.20	20.5	3.8	1.38	0.11	1.35	0.07
As <sup>75</sup>	55.94	1.20	56.02	0.73	0.83	0.03	0.72	0.05
Se <sup>77</sup>	11.58	1.54	11.43	0.17				
Mo <sup>95</sup>	116.5	3.86	112.9	1.7	0.21	0.038	0.19	0.01
Cd <sup>111</sup>	7.37	0.81	6.47	0.37	0.018	0.002	0.013	0.002
Sb <sup>121</sup>	55.47	2.22	54.1	1.1	0.16	0.006	0.12	0.009
Pb <sup>206</sup>	18.15	0.88	18.15	0.64	0.071	0.009	0.068	0.007
Pb <sup>207</sup>	19.01	1.00	18.15	0.64	0.072	0.009	0.068	0.007
Pb <sup>208</sup>	19.27	1.09	18.15	0.64	0.073	0.009	0.068	0.007
U <sup>238</sup>					0.044	0.003	<b>0.045</b>	<b>0.005</b>
Mg <sup>25</sup>	6044	1719	7989	35				
Mn <sup>55</sup>	35.28	2.90	37.66	0.83	3.19	0.27	3.9	0.3
Fe <sup>57</sup> (medium range)	93.62	8.22	91.2	3.9	89.0	4.97	100	2
Zn <sup>64</sup>	75.14	5.09	72.48	0.65	1.75	0.35	1.04	0.09
Zn <sup>66</sup>	72.48	3.74	72.48	0.65	1.69	0.33	1.04	0.09
Sr <sup>88</sup>	302.43	5.78	294.8	3.4	31.23	4.74	<b>28.1</b>	
Ba <sup>137</sup>	517.71	18.86	506.5	8.9	14.37	0.96	13.4	
<i>Panel b</i>								
	NIST 1643d			CRC SLRS-3				
	Average (N = 2)	Certified value	95% Confidence (± value)	Average (N = 4)	Standard deviation	Certified value	95% Confidence (± value)	
Na 330.237	15.12	22.07	0.64	1.96	0.48	2.3	0.2	
Mg 285.213	8.60	7.989	0.0035	1.72	0.01	1.6	0.2	
Al 308.215	0.19	0.1276	0.0035	0.11	0.00	0.031	0.003	
Si 251.611	3.08	2.7		1.93				
K 766.490	2.53	2.356	0.0035	0.62	0.03	0.7	0.1	
Ca 317.933	31.64	31.04	0.50	6.05	0.04	6.0	0.4	
Fe 238.204	0.07	0.0912	0.0039	0.08	0.00	0.1	0.002	

<sup>a</sup> Only those elements reported for the reference material are tabulated. Numbers in bold are not certified values. Data are reported in ppb.

<sup>b</sup> Only those elements used in the analysis and reported in the reference materials are tabulated. Numbers in bold are not certified values. Data are reported in ppm.

able analysis, variogram analysis, cluster analysis and principal component analysis. These five levels of analysis allowed delineation of: (i) spatial patterns in single parameters, (ii) relationships among pairs of parameters (or parameter ratios), (iii) statistical (spatial) structure in single parameters (or parameter ratios), (iv) clusters of samples of similar chemical composition, and (v) groupings of parameters which describe the overall variability ob-

served in the data. The combination provided a multifaceted analysis strategy.

Spatial patterns in single parameters were investigated through use of indicator variables determined for multiple target levels for each of the measured parameters. Specifically, for each target level, each sample was assigned either as 0 (sample value below the target level for the parameter of interest) or as 1 (sample value greater than or equal to

the target level for the parameter of interest). Spatial plots were then generated contrasting the locations at which the indicator variable was equal to one versus equal to zero (for a particular parameter and a particular target level), thus providing the ability to highlight spatial patterns for each of the parameters.

Relationships among pairs of parameters were studied visually via plotting each parameter against every other parameter via linear, semi logarithmic, and log–log plots (following on the exploratory data analysis techniques of Tukey, 1977). Further, ratios anticipated to provide insight into relationships in groundwater quality were also assessed (these included Na/Cl, Si/Cl, Si/Ca, Si/Sr, and Si/U). Visual analysis (versus calculation of correlations) allowed identification of interactions between pairs of parameters regardless of whether the interactions were characterized as linear trends or more complex patterns.

Variogram analysis provided a measure of the spatial statistical structure in individual parameters, assessed over the sample locations. Although the details of generating variograms are beyond the scope of the present manuscript (see Journel and Huijbregts, 1978 and others for details), the variogram (classically called the semivariogram) is here estimated as one-half the sum of the squared differences in parameter values for a series of distance classes ( $h_j < |h| \leq h_k$ ), where  $|h|$  is the magnitude of separation distance between two sample locations (without consideration of the angle of separation). Estimated drift (spatial variation in the mean parameter value) was removed from each parameter prior to estimation of the variogram.

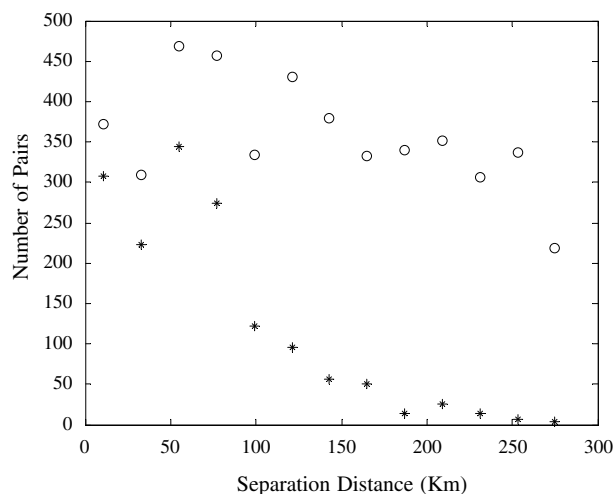
Variogram analysis requires careful design of the spatial distribution of data points so as to obtain adequate numbers of data pairs in each distance class of interest. As indicated above, the 2004 sampling campaign was designed to provide appropriate spatial distribution of data points. The difference in distribution of data pairs before and after the 2004 sampling campaign is shown in Fig. 2 for a lag-distance class of approximately 20 km. It is concluded, based on this distribution of sample pairs, that the overall distribution of sampling locations, while somewhat over-weighting the southern portion of the study area, is sufficient for assessing spatial statistical structure within the data.

In order to investigate clustering among the samples and patterns among the parameters (excluding latitude and longitude), cluster analysis and principal component analysis were applied to the data (e.g., Salman and Ruka'h, 1999). Cluster analysis (Kaufman, 1990; Aldenderfer and Blashfield, 1984) was applied to the original data without correction for spatial drift. Within our work, cluster analysis involved estimation of the Euclidian distance,  $D_{m,n}$ , between two sample points,  $x_m$  and  $x_n$ , defined as the square root of the sum of the square differences of each of the  $M$  parameter (concentration) values,  $P_{\gamma}$ , for those samples:

$$D_{m,n} = \left\{ \sum [P_{\gamma}(x_m) - P_{\gamma}(x_n)]^2 \right\}^{0.5}$$

Cluster analysis allowed identification of groups of sample points that have similar chemical compositions based on this Euclidian distance.

Principal component analysis allowed identification of structure or groupings among the parameters (e.g., Jolliffe, 2002; Farnham et al., 2003). Although various approaches



**Figure 2** Change in number of pairs by distance class through addition of the 2004 data (stars are pre-2004 whereas circles are post 2004). The goal was to maintain approximately uniform numbers of data pairs through a separation distance of approximately 300 km (approximately 1/2 the maximum separation distance in the study area).

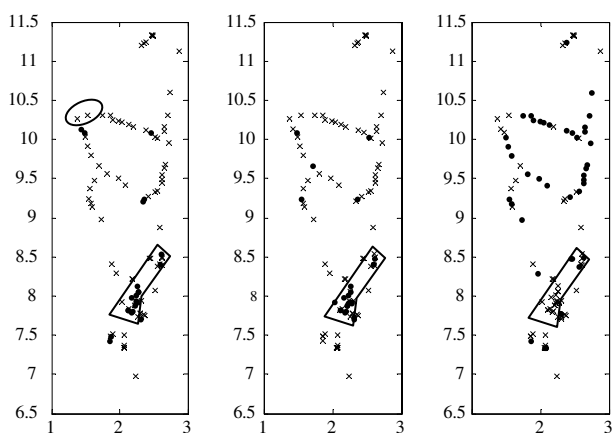
are available for principal component analysis, the choice was made for the present analysis to transform each parameter to a standardized normal distribution. The analysis was then applied to these transformed data. The results provide indications of groups of parameters that explain variability within the transformed data set.

## Results

Summary statistics are provided in Table 1 as are estimates of detection limits for each parameter. In the following paragraphs, the general results for each analysis technique are presented. These results are then integrated in the analysis section of this manuscript.

### Indicator variable analysis

Indicator variable analysis was utilized to explore the data for spatial structure within individual variables. This analysis led to a number of observations that were consistent across multiple elements. Fig. 3, for example, shows all sample locations with the locations of high values for pH (left), conductivity (center), and P (right), where high values are plotted with dots and low values are plotted as 'x's. It is noted that there is close spatial correspondence in southern Benin of sample locations with high values of conductivity and high values of pH (as indicated by the samples enclosed by the box). This region also corresponds to sample locations showing low concentrations of P (as indicated by the lack of circles in this region). Elevated values in this region were observed for a number of parameters, including: conductivity, pH, Fe, Ca, S, Mg, Na, Cl, Fl, Zn, Mn, and Mo. Parameters showing relatively low concentrations in this region include: P, Sn and, to a lesser degree, Si. In addition, a number of parameter ratios showed decreased magnitude in this region: examples include Si/Cl,



**Figure 3** Indicator variable analysis illustrating consistent clustering of high pH (left), high conductivity (middle), and low phosphorus (right) in south-central portion of study area (indicated in figure). High values are indicated by dots whereas low values are plotted with 'x's. The threshold value for pH was 6.7, conductivity was 0.55 mS/cm, and phosphorus was 0.05 mg/l. The oval in the upper left portion of the left figure indicates two wells which are also identified by a number of the data analysis techniques.

Si/Conductivity and P/U. As discussed below, this region is identified by a number of the analysis techniques as being a region with an elemental composition substantially different than that observed for the majority of the study region.

A second observation identified using indicator variables was the difference in chemical composition of two wells in the northwest portion of the country. These two wells are shown by the oval in the left image of Fig. 3. Although not obvious from these plots, these two points had extremely low values for conductivity and pH as well as very low concentrations for a number of major and minor elements (including Si and P in addition to Ca, Na, etc.). Examination of the geology indicates that these two wells are drilled into a substantially different lithology than the other wells sampled in this study (the region is dominated by quartzite). Hence, water from these wells exhibits a substantially different element composition.

### Plotting of parameter pairs

Exploratory analysis using parameter plots provided a number of insights into the data. A summary of the relationships discussed below are contained in Table 3.

First, as might be anticipated from geochemical arguments, there were a number of positive relationships identified (increase in one parameter accompanied by an increase in the second parameter: the relationship may be linear or non-linear). Such relationships were observed, for example, among Na, Cl, K, Ca, Mg, and conductivity. There were also a number of positive relationships between major elements (as well as conductivity and pH) and trace elements. Examples include positive relationships between Ca (as well as a number of other major elements) and the trace elements U and V. A select number of inverse relationships (increase in one parameter accompanied by a de-

crease in the second parameter) were also identified. The predominant elements involved in inverse relationships were Si and P, each against a number of the major and trace elements. Finally, drift in parameter values was identified through plotting individual parameter values against latitude and longitude.

Parameter plots also allowed identification of outliers and local deviation in regional trends. For example, the two points in northwestern Benin identified in Fig. 3 appeared as outliers in several of the parameter plots in the form of concentrations significantly below those of other wells in the region. In addition, locally increased concentrations in a number of major and trace elements were observed at a select number of locations at the lower latitudes (e.g., between latitudes 7.5° N and 8° N). This local increase in concentration is apparent for example in the variation of Na with latitude as shown in Fig. 4. Finally, for several parameters, the wells north of 11° N latitude show increased mean concentration as compared to the mean concentrations observed south of 11° N (again, the variation of Na with latitude shown in Fig. 4 provides an example of this type of deviation).

### Variogram analysis

Variogram analysis (using both variogram clouds and variograms averaged over distance classes) was applied to each of the elements following transformation into log space and then removing linear drift in the log-data (with the exception of pH for which no logarithm was taken). The variograms discussed were omni-directional such that no dependence on orientation of the data pairs is considered in this analysis. Outliers were identified and removed through an iterative process based on analysis of the variogram cloud (plot of squared difference versus separation distance for each data pair, prior to averaging over distance classes – see Journel and Huijbregts, 1978; for further discussion of the variogram and variogram clouds).

As noted above, the spatial sampling pattern was designed so as to allow estimation of the variogram over maximum distances of approximately 1/2 the largest dimension of our study area with approximately equal number of pairs of data in each distance class. Sufficient data points are available to provide reasonable numbers of data pairs (e.g., greater than 40) for distance classes as small as 5.0 km. At distances classes of approximately 20 km, the number of data pairs in each class is approximately 300.

Fig. 5a illustrates the variogram for pH for two different distance classes (5.0 and 20 km, respectively). The similarity in the underlying variogram structure for these two lag distances indicates that the refinement of distance class is likely sufficient for interpretation of the spatial behavior of pH for lag distances greater than approximately 5–10 km. Similar to several of the variograms calculated from the project data, the variogram for pH shows an initial nugget effect and relatively smooth rise to a sill, with a structure similar to an exponential model (e.g., Journel and Huijbregts, 1978).

Fig. 5b shows a second common pattern observed. Shown for sodium and a distance class of 20 km, the variogram shows a relatively constant value at short lags followed by a rise at large lag distances. This structure is relatively con-

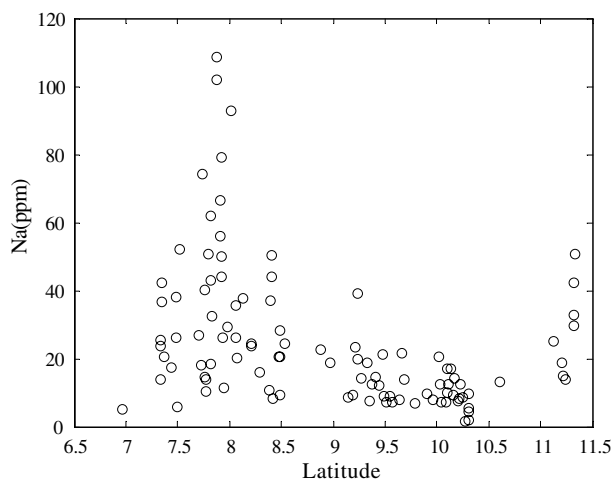


**Table 3** Relationships among parameters recorded during process of plotting each pair of parameters

Parameter	Positive relationship <sup>a</sup>	Negative relationship <sup>a</sup>	Possible outliers
Cond.	pH, Ca, Cl, Fl, Cr, K, Mg, Na, Ba, Sr, U, Ti	P, Lat, Si	2 below 0.04
pH	Cond, Ca, Sr	P, Cu	3 below 5.0
Cl	Cond, Ca, K, S, Mg, Na, Fl, Sr, Mo, Ba, Sr, U, Mn, V	Lat, P	0
Fl	Cond, Cl, S, Na, Mo	Lat, P	2 above 5 ppm
Ca <sup>313</sup>	Cond, pH, K, Mg, Na, Cl, Fl, Sr, Mn, U, Mo, S, V	Lat, P	0
K <sup>776</sup>	Long, Cond, pH, Ca, S, Mg, Na, Cl, Fl, Ba, Sr, U, Mo, V	Lat	2 above 40 ppm
S <sup>181</sup>	Cond, Ca, K, Mg, Na, Cl, Fl, Sr, Ti, U	Si	0
p <sup>213</sup>		Cond, pH, Mg, Na, Mn, Mo	2 below 0.03
Si <sup>251</sup>	P	Cond, pH, Cl, S, Mo	1 above 100, 4 below 10
Mg <sup>285</sup>	Cond, pH, Ca, K, Na, Cl, Ba, Sr, V	Lat, P	2 below 10.
Na <sup>330</sup>	Long, Cond, pH, Ca, K, S, Mg, Cl, Fl, Ba, Sr, U, Mo	Lat, P, Si	2 below 3 ppm
Ba <sup>137</sup>	Cond, Mg, Sr, V	Lat	3 below 10 ppb
Sr <sup>88</sup>	Cond, pH, Ca, K, S, Mg, Na, Cl, Ba, U, V, Ti	Lat, P	1 above 3000 ppb, 2 below 10 ppb
Zn <sup>64</sup>	Ni		0
Mn <sup>55</sup>	Na, Fl, Co, Ti	Lat, P	0
U <sup>238</sup>	Long, Cond, Ca, K, S, Na, Cl, Fl, Sr, Mo	Si	0
Pb <sup>206</sup>	Cu, Ni, Cr		0
Sn <sup>118</sup>	Complex relationship with several parameters		0
Mo <sup>95</sup>	Cond, pH, Ca, K, Mg, Na, Fl, Mn, U	P, Si	0
Cu <sup>63</sup>	Pb, Ni	pH	0
Ni <sup>62</sup>	Si, Zn, Pb, Cu, Co, Cr, Ti	Lat	2 above 100 ppb
Co <sup>59</sup>	Mn		0
Cr <sup>52</sup>	Pb		0
V <sup>51</sup>	Si, Mg, Ba		4 below 0.6 ppb
Ti <sup>49</sup>	Long, Cond, S, Mg, Na, Cl, V	Lat, P	1 above 10 ppb

A reported positive or negative relationship should not be interpreted, here, as an indication of the value of the correlation coefficient as not all relationships were linear and several that were identified were relatively weak relationships. Long = longitude, Lat = latitude, Cond = conductivity.

<sup>a</sup> Positive relation = increase in one parameter generally corresponds to increase in other parameter; negative relation = increase in one parameter generally corresponds to decrease in other parameter; number obvious outliers = number of points identified as possible outliers based solely on parameter plots.



**Figure 4** Variation in concentration of Na versus latitude (degrees north latitude) illustrating select location with high Na concentrations between 7.5° N and 8° N and increasing mean concentrations north of 11° N.

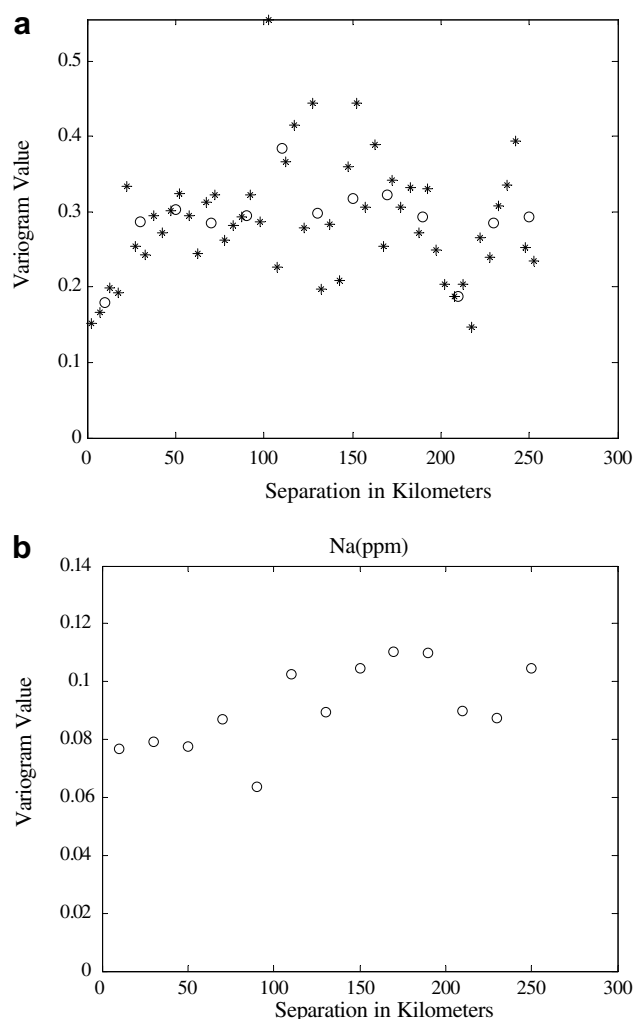
sistent with a Gaussian-variogram model and was observed for many of the major elements.

Table 4 provides a summary of which parameters provided variograms with identifiable structure and, where appropriate, the estimated nugget, range and sill of the variogram.

### Cluster analysis

Cluster analysis was performed on standardized parameter values (value minus the mean and divided by the standard deviation) excluding latitude and longitude and using Euclidian distance as the measure of difference between sample locations. No corrections were made for drift, nor were the variables transformed into log space.

Results were assessed using the resulting dendrogram and plots of the spatial distribution of groups. An example of a graph of spatial groups is shown in Fig. 6. Specifically, Fig. 6 provides a spatial map of the location of the 70 sample locations that have the most similar parameter values (smallest separation distances on the dendrogram) shown by the 'x' symbol versus the remaining sample locations



**Figure 5** (a) Variogram for pH using distance classes of 5.0 km (stars) and 20 km (circles) illustrating a possible nugget of approximately 0.15, a range of approximately 50–100 km, and a sill of approximately 0.3. (b) Variogram of Na for 20 km distance classes illustrating the Gaussian-type behavior of many of the major and trace elements.

that demonstrate larger variation in parameter values (larger separation distances) as represented by the dots on the figure. The largest cluster outside of the main cluster of 70 sample locations involves only 3 wells, hence all points outside the large cluster have relatively distinct chemistries.

Two primary observations are made with respect to these results. First, there is a cluster of wells in south-central Benin (see Fig. 6) where the chemistry is highly variable as indicated by the number of points in this region which are not in the large cluster. This region coincides with the region of elevated concentration of several elements identified through the parameter plots and as identified with the indicator variable analysis (compare with Fig. 3) and is discussed further below. Second, two wells in the north-western portion of the sampling region form a separate cluster (identified by the oval in Fig. 6), consistent with the results obtained through the exploratory data analysis and indicator variable analysis indicating that these two wells

have element chemistries substantially different than the majority of other wells (compare with Fig. 3).

### Principal component analysis (PCA)

For PCA, all parameters with the exception of pH were first transformed into log space and then standardized (through subtraction of the transformed mean and division by the transformed standard deviation). Those parameters judged to have excessive values below detection limit were removed from the analysis. Latitude and longitude were not included in the analysis. The resulting data set included 23 parameters.

The results of the PCA, provided in Table 5 for the first three components, show that the first three components explained 35%, 13%, and 10% of the total variance, respectively. Hence, approximately 60% of the variability in the transformed data set is explained by the first three components.

Looking at the weights within the individual components, it is observed that the first component is dominated by positive loadings with approximately uniform weights ( $\sim 10\text{--}11\%$  each) from Na, Mg, Ca, and Conductivity. A second group of elements each contributes weights of  $\sim 6\text{--}8\%$  (Cl, Fl, Sr, and K). Hence, the first component reflects, to a large degree, major elements within the groundwater system.

The second component is dominated by several trace metals (Cu, Pb, Ni, Zn, Co, Cr), thus implying that the variation in groundwater chemistry is described, independent of the major elements, by variation in the dissolved trace metals. The third component is dominated by Si, Sn, Cr, and V.

These results imply nearly complete separation of large loadings on the parameters in the first three components (e.g., Cr is the only parameter that has high loading in more than one component) with no significant negative loadings of the major contributors. One interpretation of this result, consistent with the results from the other analysis techniques and classical interpretation of principal components in mixed systems, is that these three components represent different, but not competing, sets of processes or mechanisms that have impacted the groundwater chemistry (i.e., there is no indication of mixing).

### Analysis

The data presented herein, along with the combination of analysis methods, lead to several observations regarding groundwater characteristics in the study area. Many of these observations are further supported by comparison of the sample locations with their hydrogeologic setting as derived from examination of a hydrogeologic map available for this region (Carte Géohydraulique, 1985). Among the observations are:

### Regional geologic control

The results confirm that major changes in geology can result in identifiable changes in elemental composition. While this observation was expected, it provides confidence in the methodology, particularly in terms of the statistical meth-

**Table 4** Results of variogram analysis for the logarithm of the data

Parameter	Drift correction	Structure	Nugget	Range (km)	Sill
Cond (mS/cm)	Y	Y	0.07	120	0.10
pH <sup>a</sup>	N	Y	0.17	100	0.31
Cl (ppm)	Y	Y	0.18	110	0.28
Fl (ppm)	Y	N	0.08	N/A	N/A
Va (ppb)	N	Y	0.21	>300	>0.30
Cr (ppb)	Y	Y	0.16	280	0.22
Co (ppb)	Y	Y	0.16	90	0.28
Ni (ppb)	Y	N	0.07	N/A	N/A
Cu (ppb)	N	Y	0.17	150	0.28
Mo (ppb)	Y	Y	0.2	200	0.34
Sn (ppb)			Excessive non-detects		
Pb (ppb)	N	N	0.065	N/A	N/A
U (ppb)	Y	N	0.68	N/A	N/A
Mn (ppb)	N	Y	0.35	220	0.85
Zn (ppb)	Y	N	0.30	N/A	N/A
Sr (ppb)	Y	Y	0.08	150	0.11
Ba (ppb)	Y	N	0.17	N/A	N/A
Na (ppm)	Y	Y	0.075	250	0.125
Mg (ppm)	Y	Y	0.08	150	0.14
Al (ppm)			Excessive non-detects		
Si (ppm)	Y	N	0.035	N/A	N/A
P (ppm)			Excessive non-detects		
S (ppm)			Excessive non-detects		
K (ppm)	Y	Y	0.02	250	0.07
Ca (ppm)	Y	Y	0.10	200	0.16

Drift correction indicates whether or not a correction was necessary for observed drift in the data. Structure refers to: (Y) = the presence of a consistent increase in the value of the variogram with separation distance, (N) = a pure nugget effect. Range and sills are estimated where possible within the variability of the data based either on exponential or Gaussian variogram models. Results presented here are for a lag distance of approximately 28 km, with use a lag distance of ~5 km to clarify behavior at small separation distances.

<sup>a</sup> pH variogram based on pH, not log(pH), values.

odology used to identify spatial changes in groundwater chemistry. This observation is supported by the identification of two wells in northwestern Benin (in the region of Natintinguou, and as identified in Figs. 3 and 6) and a group of wells in northern Benin (west of Kandi), which demonstrate differences in elemental composition as compared to the regional analysis, while maintaining similar elemental compositions within each group. These differences were identified through the parameter plots, indicator variables, and cluster analysis. They were further supported through examination of the reported geology at the location of the wells. The two wells near Natintinguou, for example, are in a quartzite, which contrasts with the gneiss present at the vast majority of the other well sites.

### Spatial trends

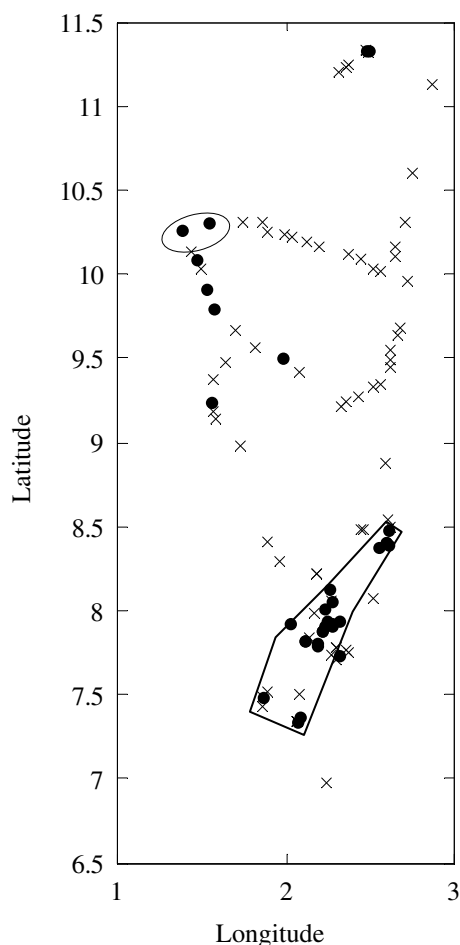
Spatial trends in the elemental composition were identified. These include decline in mean concentration with latitude for major elements such as Cl, Na, Mg, and K, as well as for trace elements such as Ba and Ni. Subtle increases in mean concentration with latitude were also observed for select trace elements such as P. Select trace elements also showed a tendency towards increasing concentration with

longitude, including U, Mo, and Ni. It is anticipated that these large-scale trends result from regional variation in mineralogy, as well as variation in precipitation patterns.

The variograms indicate that variation in the drift-corrected element concentrations may show correlation, for select elements, over significant distances (e.g., 100–200 km). This is consistent with the observation that large regions of the study region are of a relatively consistent geology. It is noted further, for those variograms showing structure, that the nugget effect is often a significant percentage of the sill (e.g., 50% or greater – see Table 4), implying that variability at the local scale (in addition to analytical error) is a significant part of the overall variability in observed concentrations. Additional studies at much shorter lag distances would likely help to separate the impact of analytical error from local variability. Unfortunately, such studies are not possible at the present time in this region of Benin.

### South-central Benin

The most significant unanticipated result of the statistical analyses was the identification of the region in south-central Benin (identified by the indicator variable and cluster anal-



**Figure 6** Results from cluster analysis showing locations of the 70 wells with the smallest separation distances (x) versus those wells that fell outside of this group (the dots). It is noted that a cluster of wells exists in south-central Benin (enclosed region on the plot) for which each well has an elemental composition that is quite different from all other wells (including other wells in this cluster). The region is similar to the region identified using indicator variable analysis. The two wells in the northwestern portion of the study area identified by the previous methods are also identified by cluster analysis (the two points in the oval).

yses as outlined in Figs. 3 and 6) for which the groundwater exhibits an element composition that is both substantially different than the average composition observed in the remainder of the study region and variable (spatially) from well to well within this region. This region had not been previously identified through hydraulic or chemical methodologies as being unique or exceptional.

Two analysis methods were used to further explore the data from this region. Both methods involved separating the total data set into two subsets based on cluster analysis as shown in Figs. 6. Of the 34 samples excluded from the primary cluster, 25 were located within the region of interest. While these 25 samples could have been assessed separately based solely on geographic proximity, a decision was made to base separation of the data on a consistent measure, in this case the cluster analysis, rather than an arbitrary choice based solely on geographic location.

These two data sets were then assessed via exploratory data analysis. The results of this analysis demonstrated two primary features. First, the points included in the smaller data set, particularly those identified to be from the region of interest, were significantly over-represented in the higher concentrations of the major elements. Second, the data in the smaller data set demonstrated a higher variation than the data in the larger group of samples. Both of these observations indicate that the water in this region is significantly different, in terms of concentrations, than the water in the larger region of Benin. However, the analysis also indicated that the data in both groups tended to follow very similar trends between parameters.

The second assessment of these data was performed using principal component analysis as applied to the same two subsets of the entire data set. Component weights were compared for: (i) the entire data set, (ii) the larger data subset (those points within the large cluster), and (iii) the smaller data subset (those points excluded from the large cluster). Consistent with the discussion provided above for the entire data set, the first component was reflective of the major elements for all three data sets. Further, consistent across the three data sets, the first significant appearance of Si was in the third component.

Review of the parameter weights in the first component show that all three data sets have significant weights on conductivity, Ca, Na, Mg and Cl; i.e., several of the major elements. Significant differences occur, however, for select elements, including Fl, Sr, Ti, and K. Generally, the larger subset shows more consistency with the entire data set than does the smaller subset. Hence, there is consistency among the entire data set and two subsets as expressed in the major elements. However, the two subsets show significant difference in terms of the contribution of the secondary elements.

This difference among the three data sets is further highlighted in the third component (the first component with significant contribution from Si for each of the data sets). Although all three show significant weight on Si, there are substantial differences in the remaining parameter weights. As compared to the weights for the full data set, for example, the smaller subset shows significantly increased weights on Fl, Cu, K and pH with reduced weights on V and Cr (as well as a lower weight on Si). The larger subset shows greater weight on Ti and lower weight on Si (as compared to the full data set). Although not based in geochemical analysis, these results imply that there is a significant difference between the two subsets of the data regarding the interplay among the parameter groupings.

In attempting to identify unique controls on elemental composition consistent with the original assessment of the complete data set and the analysis of the data subsets, patterns in geology, land-use, and precipitation were considered. Following on Tardy (1969), it is anticipated that each of these may impact groundwater chemistry and variability in this chemistry.

Reviewing the hydrogeology of Benin (Carte Hydrogéologique, 1985) and associated discussion in Boukari (1982), it is observed that the south-central region of the study area that was identified via data analysis (Figs. 3 and 6), more so than other regions within the study area, is characterized by relatively rapid changes in rock type, with variation among



**Table 5** Results of the principal component analysis – first three components

Parameter	Principal component 1		Principal component 2		Principal component 3	
	Loading	Weight	Loading	Weight	Loading	Weight
% Variance explained:	34.9		12.7		9.6	
Cl	0.25	<b>0.06</b>	0.08	0.01	-0.14	0.02
Fl	0.26	<b>0.07</b>	-0.02	0.00	0.05	0.00
Ti	0.19	0.03	0.13	0.02	0.23	0.05
V	0.17	0.03	0.01	0.00	0.39	<b>0.15</b>
Cr	-0.02	0.00	0.29	<b>0.09</b>	0.30	<b>0.09</b>
Co	0.10	0.01	0.31	<b>0.10</b>	-0.20	0.04
Ni	0.04	0.00	0.38	<b>0.15</b>	-0.21	0.05
Cu	-0.03	0.00	0.45	<b>0.20</b>	0.08	0.01
Mo	0.22	0.05	0.09	0.01	-0.12	0.01
Sn	-0.04	0.00	-0.07	0.00	0.39	<b>0.15</b>
Pb	0.02	0.00	0.44	<b>0.20</b>	0.10	0.01
U	0.22	0.05	-0.02	0.00	-0.17	0.03
Mn	0.17	0.03	0.08	0.01	-0.216	0.05
Zn	0.04	0.00	0.34	<b>0.12</b>	-0.15	0.02
Sr	0.29	<b>0.08</b>	-0.14	0.02	0.00	0.00
Ba	0.19	0.03	0.08	0.01	0.15	0.01
Na	0.32	<b>0.10</b>	0.05	0.00	-0.11	0.01
Mg	0.32	<b>0.10</b>	-0.06	0.00	0.12	0.01
Si	0.02	0.00	0.06	0.00	0.48	<b>0.23</b>
K	0.28	<b>0.08</b>	0.07	0.00	0.17	0.03
Ca	0.33	<b>0.11</b>	-0.10	0.01	0.04	0.00
pH	0.22	0.05	-0.22	0.05	-0.11	0.01
Cond	0.33	<b>0.11</b>	-0.09	0.01	-0.02	0.00

The score is the value associated with the individual parameter for the given component and represents the directional cosine of rotation in parameter space. The weight is the square of the score and represents the percent contribution of the parameter value to the resulting component.

gabbros, gneisses, and granites and associated significant variations in mineralogy. While this variability may not provide an immediate explanation for the elevated concentrations of major elements in this region, it does provide potential insight into increased variability of both the major and trace elements.

Previous assessments (e.g., Carte Hydrogeologique, 1985) also indicate that the reliability of water supply is substantially lower in the south-central region than it is elsewhere in the study area. Reliability, in this environment, is closely related to water storage capacity of the fractured rock and the overlying depth of weathered rock. Lower reliability, as measured by critical drop in water level during droughts, is an indication that there is minimal storage within this particular region, suggesting a thin weathered zone and minimal storage within the fractures (Boukari, 1982). This environment results in greater sensitivity and response to water quality variations of recharge waters. Further, in this setting, opportunity for dissolution of major and trace elements may vary spatially due both to variation in residence time in the weathered zone and fractured zones (resulting from spatial variation in depth of weathering) as well as minimal mixing and more rapid response to local variation in quality of recharge waters. As such, impact of application of agricultural chemicals such as lime and fertilizers (as well as sensitiv-

ity to other anthropogenic contaminants) may be more significant in this region than in regions where a deeper weathered zone would tend both to minimize the impact of these chemicals and smooth the spatial/temporal variation in recharge chemistry related to application of these chemicals.

Finally, review of precipitation patterns in Benin illustrates that this region represents a region of transition from the southern sub-equatorial to the northern tropical climates. Hence, the variability in timing and, more importantly, chemical composition of precipitation may be greater in this region than in regions further to the south or further to the north.

This discussion of the relatively unique element chemistry in the identified region of south-central Benin indicates that this region is more complex than the remainder of the study area in terms of groundwater quality. The importance of this complexity is highlighted by the observations both that all of the wells for which elevated uranium concentrations have been observed (with a maximum observed concentration of 491 ppb) are located within this region and that the government agency in Benin responsible for water quality issues (Direction de l'Hydraulique) has reported that the highest incidence of nitrate contamination is reported in this general region of Benin. Hence, the results from this data analysis effort

highlight the need for further study of the source waters and mechanisms impacting groundwater quality in this region of Benin.

## Conclusions

This study has provided baseline elemental chemistry data for description of groundwater quality in central Benin, West Africa. Results from this study have included identification of dependence of element concentrations in groundwater on geology, spatial trends in these concentrations, regions of deviation from these trends, and dominant features of the elemental composition. In addition, this work has provided a baseline for continuing studies of spatial and temporal variations in groundwater quality due to natural and anthropogenic processes. Consistent with the work of other authors (Farnham et al., 2003, 2000), it is noted that the combination of the five analysis techniques (exploratory analysis, indicator variables, cluster analysis, variogram analysis, and PCA) allowed identification of trends in the element concentrations, confirmation of those trends, and examination of groupings of data across both physical space (e.g., latitude and longitude) and parameter space (e.g., the groups of parameters identified by PCA).

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