

Prepared in cooperation with the City of Independence, Missouri, Water Department

Concentration Comparison of Selected Constituents between Groundwater Samples Collected within the Missouri River Alluvial Aquifer using Purge and Pump and Grab-Sampling Methods, near the City of Independence, Missouri, 2013



Scientific Investigations Report 2015–5144

Cover. Background: Groundwater sampling well within the Independence well field, near Independence, Missouri, August 2013.
Upper right: Student technician observing water-quality properties at a groundwater sampling well within the Independence well field, near Independence, Missouri, August 2013.
Lower right: Groundwater sampling well at the City of Independence, Missouri, Water Department, near Independence, Missouri, August 2013.
Photographs by Shelley Niesen.

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By Heather M. Krempa

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Scientific Investigations Report 2015–5144

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior

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U.S. Geological Survey

Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2015

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Suggested citation:

Krempa, H.M., 2015, Concentration comparison of selected constituents between groundwater samples collected within the Missouri River alluvial aquifer using purge and pump and grab-sampling methods, near the City of Independence, Missouri, 2013: U.S. Geological Survey Scientific Investigations report 2015–5144, 19 p., <http://dx.doi.org/10.3133/sir20155144>.

ISSN 2328-0328 (online)

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Conversion Factors

[Inch/Pound to International System of Units]

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
inch (in.)	25,400	micrometer (μm)
foot (ft)	0.3048	meter (m)
Volume		
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
cubic inch (in ³)	0.01639	liter (L)
Mass		
microgram	35.27 x 10 ⁻⁸	ounce, avoirdupois (oz)
milligram	35.27 x 10 ⁻⁵	ounce, avoirdupois (oz)
gram	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	Pound, avoirdupois (lb)

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (μg/L).

Concentration Comparison of Selected Constituents between Groundwater Samples Collected within the Missouri River Alluvial Aquifer using Purge and Pump and Grab-Sampling Methods, near the City of Independence, Missouri, 2013

By Heather M. Krempa

Abstract

The U.S. Geological Survey, in cooperation with the City of Independence, Missouri, Water Department, has historically collected water-quality samples using the purge and pump method (hereafter referred to as pump method) to identify potential contamination in groundwater supply wells within the Independence well field. If grab sample results are comparable to the pump method, grab samplers may reduce time, labor, and overall cost. This study was designed to compare constituent concentrations between samples collected within the Independence well field using the pump method and the grab method.

Relative percent differences between environmental grab and duplicate grab samples were greater than 10 percent for 80 percent of the constituents. Duplicate grab samples were collected by tethering two grab samplers together, because the amount of water collected by each grab sampler is close to the amount necessary for analysis. The screened interval lengths of monitoring wells within the Independence well field is not conducive to collecting multiple grab samples by tethering samplers. The inability to collect required duplicate quality assurance samples may limit the use of grab samplers.

Concentrations between pump and grab samples were similar for analyzed nutrient species, the variability between methods was less than the variability between historical duplicate samples, and there were no significant differences determined. Major ion relative percent differences were less than 10 percent and root mean square error differences between methods and between historical duplicate samples were less than 1 milligram per liter with the exception of sulfate. Statistically significant differences were determined between pump and grab samples for sodium and fluoride. There is a strong association between major ion pump and grab samples based on bivariate plots and simple linear regressions. Variability between pump and grab samples of analyzed nutrients and

major ions may have minimal effect on the ability to monitor temporal changes and potential groundwater contamination threats.

Relative percent differences between methods were greater than 10 percent for most analyzed trace elements. Barium, cobalt, manganese, and boron had concentrations that were significantly different between sampling methods. Barium, molybdenum, boron, and uranium method concentrations indicate a close association between pump and grab samples based on bivariate plots and simple linear regressions. Grab sample concentrations were generally larger than pump concentrations for these elements and may be because of using a larger pore sized filter for grab samples. Analysis of zinc blank samples suggests zinc contamination in filtered grab samples. Variations of analyzed trace elements between pump and grab samples could reduce the ability to monitor temporal changes and potential groundwater contamination threats. The degree of precision necessary for monitoring potential groundwater threats and application objectives need to be considered when determining acceptable variation amounts.

Introduction

Protecting groundwater used for drinking water reduces public health risks and minimizes treatment costs (U.S. Environmental Protection Agency, 1987). Public water supply is a primary groundwater use in the United States, and 46 percent of the Nation's population uses groundwater for drinking water (U.S. Environmental Protection Agency, 2000). Amendments made in 1986 to the Safe Drinking Water Act established a nationwide program designed to protect groundwater used for public water supplies from a wide range of contaminants (U.S. Environmental Protection Agency, 1987). Contributing recharge areas and potential contaminants need to be identified to successfully protect these groundwater sources

(U.S. Environmental Protection Agency, 1987). Groundwater contaminants, such as arsenic, iron, and fluoride, can leach into groundwater from naturally occurring deposits. Anthropogenic contamination can result from many sources, including fuel storage, waste disposal, agricultural, and industrial practices. Long-term ambient water-quality monitoring programs that assess groundwater quality can potentially identify contamination threats before reaching supply wells.

The U.S. Geological Survey, in cooperation with the City of Independence, Missouri, Water Department (hereafter referred to as Independence), has historically collected water-quality samples using the purge and pump method (hereafter referred to as pump method) to identify potential contamination in groundwater supply wells within the Independence well field (Kelly, 2002a; Wilkison, 2011). Pump methods require purging the well before sampling by removing large volumes of water (generally at least three well casing volumes) until water-quality properties stabilize (see *Purge and Pump Sampling Methods*). Purging removes stagnant water and draws water into the well from the surrounding aquifer. The formation water that is drawn into the well is sampled.

No-purge grab sampling methods (hereafter referred to as grab method) collect water directly from a section of the well screen interval without well purging or the use of a pump (Parker and Clark, 2004; Savoie and LeBlanc, 2012). High hydraulic conductivity is necessary to maintain the same chemical and physical properties between the surrounding aquifer and the water at the sampled well section (Savoie and LeBlanc, 2012; U.S. Environmental Protection Agency, 2013).

If the necessary hydrogeologic conditions exist and grab sample results are comparable to the pump method, grab samplers may reduce time, labor, and overall cost. The pump method requires a pump, generator, and for the Independence well field, a spool of more than 100 feet of tubing, which can make sampling wells without vehicle access difficult. Grab sample equipment is lighter and more compact than pump equipment, allowing remote wells to be sampled more easily. Time required to deploy and collect grab samplers is minimal compared to the time necessary for pump method equipment setup and breakdown, purging, and equipment cleaning. This reduces the time required at each well, allowing more wells to be sampled within a given day, and reduces the total number of trips necessary to complete well sampling. Generators required to power pumps can introduce contamination from engine fumes and the large volumes of water removed during purging can result in pumping a well dry before samples are collected. Grab methods remove the risk of contamination from engine fumes because a generator is unnecessary and the potential for cross contamination is reduced because grab samplers are disposable.

Independence Well Field Background

Independence provides approximately 250,000 residents and surrounding communities with water from supply wells completed within the Missouri River alluvial aquifer (Missouri Department of Natural Resources, 2014; fig. 1). The U.S. Geological Survey (USGS), in cooperation with Independence, quantified groundwater travel times, contributing recharge areas, potential contamination areas, and designed a groundwater monitoring program for source water within the pumping and contributing recharge areas (Kelly, 2002a; Kelly, 2002b; Kelly, 2011). Several nonpoint and point contamination sources were identified within the contributing recharge area, including, but not limited to, landfill presence, sewage sludge application areas, commercial development, highway construction, a closed oil refinery, and agricultural activity (Kelly, 1996; Kelly, 2002a). These contamination threats increase the need to monitor the quality of groundwater supplied by Independence (Kelly, 1996; Kelly, 2002a; Kelly, 2011; Wilkison, 2011). During 1997 and 1998 a network of monitoring wells (see table 1 in Kelly, 2002a for detailed monitoring well information) was established within the area of supply wells (Independence well field, fig. 1) and groundwater sampling began. The current groundwater monitoring program was designed to assess water quality and monitor temporal changes in groundwater that has a simulated travel time of less than 10 years from monitoring well to supply well (10-year zone of contribution; Wilkison, 2011). Water-quality samples were collected from specific wells at various time intervals using the pump method with a portable submersible pump according to the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated) to target specific source areas, assess aquifer water quality, and identify potential contamination in sufficient time to take action before the contaminant reaches the supply well (Kelly, 2002a; Wilkison, 2011).

Sand and gravel deposits within the Missouri River alluvial aquifer have large hydraulic conductivities that allow for rapid groundwater flow through the aquifer, and groundwater levels within the aquifer respond rapidly to changes in river stage and pumping (Kelly, 2011). Grab samplers rely on high hydraulic conductivities and natural groundwater flow through the well screen to maintain an equilibrium between well water at the screened interval and the surrounding aquifer (Savoie and LeBlanc, 2012; U.S. Environmental Protection Agency, 2013). The rapid flow of groundwater within the Independence well field may create suitable conditions for the use of grab samplers, by maintaining a constant purged state, flushing wells with fresh alluvial groundwater rapidly after a disturbance or mixing (Kelly, 2002b; Kelly, 2011).

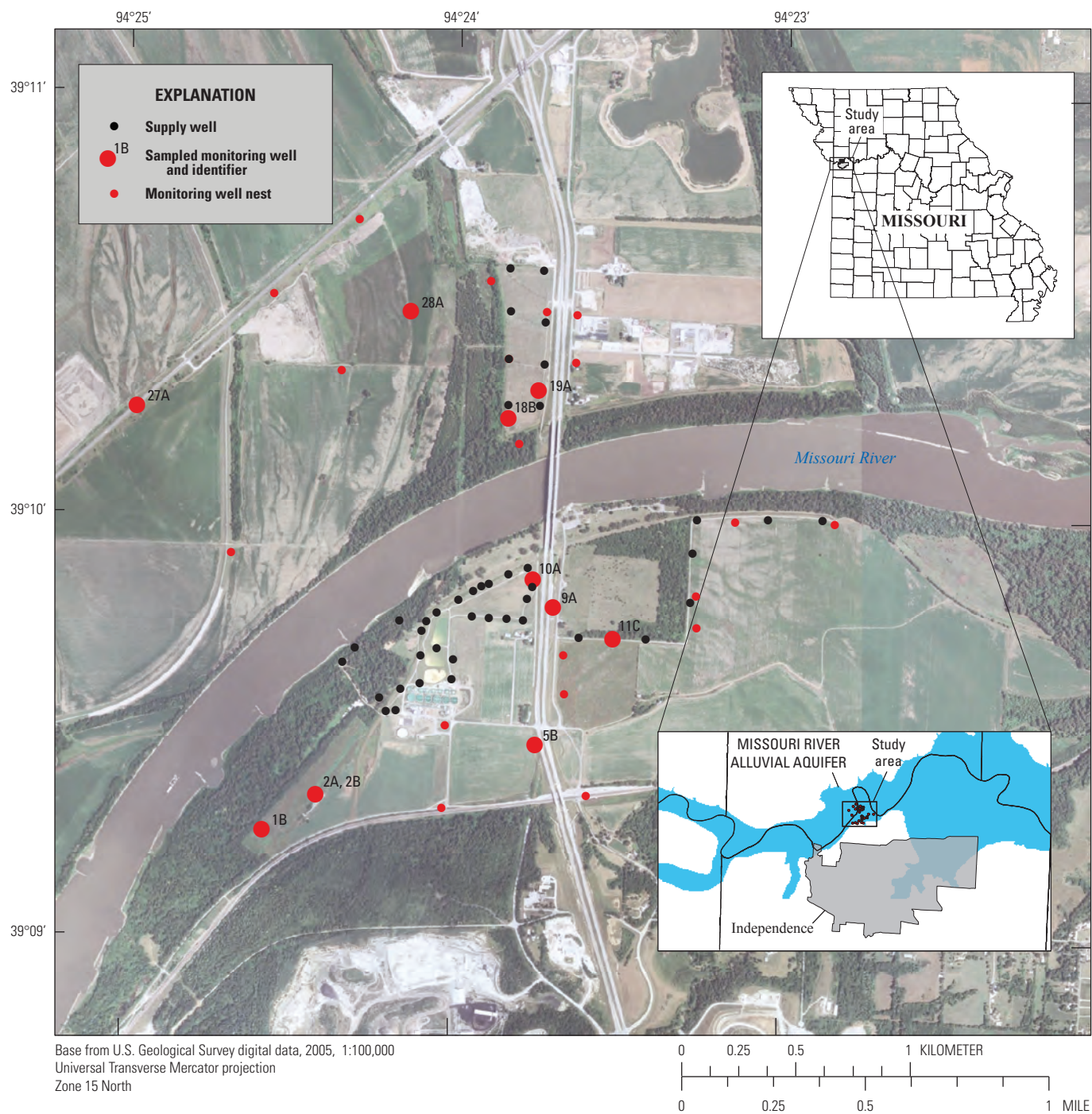


Figure 1. Study area and location of supply and monitoring wells within the Independence well field.

Purpose and Scope

The purpose of this report is to compare differences in analytical results between groundwater samples collected from monitoring wells within the Independence well field using two sampling methods, the conventional and previously-used pump method and the grab method. The U.S. Geological Survey, in cooperation with Independence collected samples during September and October 2013 from 11 selected monitoring wells within the Independence well field and concentrations of selected constituents, including nutrients, major ions, trace elements, and fuel compounds were compared.

Methods

This study was designed to compare constituent concentrations between samples collected within the Independence well field using the pump method and the grab method. Monitoring wells were sampled during 2013 and included those having groundwater travel times from monitoring well to supply well ranging from 0.5 years to 10 years (Kelly, 2011; Wilkison, 2011). Grab samples were collected by deploying HydraSleeve™ grab samplers in selected wells, allowing a calculated equilibrium period of 7 days, and retrieving samplers. Immediately following the collection of grab samples pump samples were collected. Because a 7-day equilibrium period was needed before the collection of grab samples, grab samples were collected before pump samples to reduce the duration between method sample collections. All sample bottles were rinsed and samples were preserved according to the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated) for both pump and grab samples. Samples were analyzed by the USGS National Water Quality Laboratory for nutrients according to methods described in Fishman (1993) and Patton and Kryskalla (2011), major ions according to Fishman (1989, 1993), trace elements according to Fishman (1989), Garbarino (1999), and Garbarino and others (2005), and fuel compounds according to Connor and others (1998).

Calculation of Equilibrium Period

Groundwater velocities determine the rate that fresh alluvial water will flush a monitoring well after a disturbance or mixing occurs. Deployment of grab samplers may cause a minimal amount of vertical mixing within the well. The duration required for well flushing after a disturbance was calculated using the lowest simulated groundwater velocities within the Independence well field (Kelly, 2011). The length of time required for groundwater to pass through the gravel pack and well casing of a monitoring well at the lowest simulated groundwater velocity (0.07 meters per day) within the 10-year contributing recharge area is 2.18 days. This is calculated using a 2-inch (0.0508-meter) diameter monitoring

well with a 2-inch thick gravel pack surrounding the well casing (0.1524 meters [which accounts for the well and the two sides of the gravel pack] divided by 0.07 meters per day equals 2.18 days). The greatest simulated duration for groundwater to pass through the gravel pack and well casing (2.18 days) was multiplied by three to account for differences in groundwater travel times outside of steady-state groundwater flow and grab samplers were left in each well at least 7 days before samples were collected.

Continuous Groundwater Quality

To identify water-quality property changes within a well before, during, and after pumping, dissolved oxygen (DO), pH, specific conductance (SC), and temperature were measured continuously (every 30 minutes) using the YSI 556 multiprobe system at the midpoints of the screened intervals in three selected wells (2B, 10A, and 28A; fig. 1; screened interval depths of 12.78 meters, 15.32 meters, and 27.43 meters, respectively). Water-quality probes were deployed before sampling and water-quality properties were recorded for approximately 2 weeks. Wells were then pumped with the water-quality probes in place. Probes were removed, inspected, and replaced after pumping. Recording continued for approximately another 2 weeks, after which probes were removed and data were reviewed.

Grab Sampler Methods

Grab samples were collected using the 1-liter HydraSleeve™ SuperSleeve 2-inch sampler (GeoInsight, 2010). The samplers were 91.4 centimeters long, consisted of a 4-mil-thick (0.004 inch) polyethylene collection chamber with a reed valve at the top that prevented filling before retrieval, was sealed at the bottom, and had an attached weight. An optional top weight was used to collapse the sampler, which allowed it to fill within a shorter water column height. Screened intervals of monitoring wells within the Independence well field were 1.5 meters long and were located at the bottom; therefore, a tether was used to lower and secure the empty sampler to rest just above the bottom of the well.

A small amount of vertical mixing of well water may occur during deployment; therefore, samplers were left in the well for at least 7 days to allow equilibrium and flushing of the well. After the equilibration period, each sampler was retrieved by quickly and smoothly pulling it through the water column by the tether. The reed valve opened as the sampler was drawn up, the collection chamber was filled, and the reed valve closed when the collection chamber was full to prevent water from other parts of the well from entering the sample. Water-quality samples were then collected from the collection chamber.

Samples included unfiltered samples (used to measure total concentrations) and filtered samples (used to measure dissolved concentrations). Filtered samples (nutrients, major ions,

and trace elements) were collected using a disposable syringe and were filtered using a fitted Whatman glass 0.70- μm -pore-size microfiber filter (hereafter referred to as 0.70- μm syringe filter). Filtered samples require the use of a 0.45- μm pore size capsule filter (see *Purge and Pump Sampling Methods*; U.S. Geological Survey, variously dated), which were not available for use with the disposable syringes. Use of 0.70- μm filters can introduce increased microbial activity and particle sizes into samples but this is expected to have had minimal impact on concentration results (Teresa L. Kirschling, National Water Quality Laboratory, written commun., 2014). Fuel samples were not filtered and were collected by inserting a discharge tube through the collection chamber wall to allow sample water to flow through the tube into the sample bottle.

Purge and Pump Sampling Methods

Pump samples were collected directly after grab sampling using standard pump sampling methods described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). Each well was pumped using a portable stainless steel pump with Teflon impeller. Field properties (DO, pH, SC, and temperature) were monitored using the YSI 556 handheld multiprobe system. Samples were collected after field property stabilization and included unfiltered samples (used to measure total concentrations) and filtered samples (used to measure dissolved concentrations). Filtered samples (nutrients, major ions, and trace elements) were filtered through a purged Pall GWV® high-capacity capsule filter with acrylic copolymer (Versapor®) filter membrane material with a 0.45-micrometer (μm) pore size (hereafter referred to as 0.45- μm capsule filter). Fuel samples were collected directly from the pump tubing and were not filtered. Before sampling the next well, equipment was cleaned according to procedures described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated).

Data Analysis

Constituent concentrations for pump and grab samples were compared using several diagnostic statistics. Some sample concentration variability is expected. As part of standard quality assurance procedures (U.S. Geological Survey, variously dated) duplicate pump samples were collected during historical (1998–2013) sampling of monitoring wells within the Independence well field. These duplicate pump samples (hereafter referred to as historical duplicate samples) were collected concurrently with environmental pump samples using standard pump methods (U.S. Geological Survey, variously dated) and were analyzed using the same methods. Historical duplicate pump samples include 23 nutrient samples during 1998 through 2013, 10 major ion and trace element samples during 2005 through 2013, and 6 fuel compound samples during 2009 through 2013. The difference between environmental

and historical duplicate samples represents the amount of variability between samples that can be expected under standard conditions from field and laboratory variability.

To quantify concentration differences between sample methods beyond what was expected, the variability between methods was compared to the variability between environmental and historical duplicate samples using root mean square error (hereafter referred to as RMSE) and relative percent difference (hereafter referred to as RPD). The RMSE measures the absolute (non-negative) value of the variation between environmental and historical duplicate sample concentrations (hereafter referred to as Historical Duplicate RMSE) and pump and grab sample concentrations (hereafter referred to as Method RMSE). The difference between the Method RMSE and the Historical Duplicate RMSE was calculated (hereafter referred to as RMSE Difference). A negative RMSE Difference is recorded when the Method RMSE is less than the Historical Duplicate RMSE and indicates less variation between methods than between environmental and duplicate samples. A positive RMSE Difference is recorded when the Method RMSE is greater than the Historical Duplicate RMSE and larger values indicate larger variation between methods compared to the variation between environmental and duplicate samples. A RMSE Difference that is close to zero indicates that the variance between methods is similar to the variance between environmental and duplicate samples.

The equation to calculate RMSE follows:

$$RMSE = \sqrt{\frac{e_1^2 + e_2^2 + e_3^2 + \dots + e_n^2}{n}} \quad (1)$$

where

- e is the difference between sample concentrations; and
- n is the total number of sample pairs.

The RPD measures the variation between sample concentrations as a percentage of the concentration pair's average value and the mean RPD is the average of all RPDs for a given constituent between environmental and historical duplicate sample concentrations (hereafter referred to as Historical Duplicate Mean RPD) and pump and grab sample concentrations (hereafter referred to as Method Mean RPD). A low Method Mean RPD indicates the differences between sample concentrations do not represent a large percentage of the mean concentrations. The differences between the Historical Duplicate Mean RPD and Method Mean RPD were calculated (hereafter referred to as RPD Difference). A negative RPD Difference is recorded when the Method Mean RPD is less than the Historical Duplicate Mean RPD and indicates less variation between methods than between environmental and duplicate samples. A positive RPD Difference is recorded when the Method Mean RPD is greater than the Historical Duplicate Mean RPD and larger values indicate larger variation between methods compared to the variation between environmental and duplicate samples. A RPD Difference that is close to zero indicates that

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the percent variance between methods is similar to the percent variance between environmental and historical duplicate samples.

The equation to calculate RPD follows:

$$RPD = \text{absolute value} \left(\frac{x_1 - x_2}{\left(\frac{x_1 + x_2}{2} \right)} \right) \times 100 \quad (2)$$

where

- x_1 is the pump or environmental sample concentration; and
- x_2 is the grab or historical duplicate sample concentration.

A Wilcoxon signed-rank test (hereafter referred to as Wilcoxon test; Wilcoxon, 1945) was used to determine if the median of the differences between the pump and grab samples was statistically different than zero. A significance level of 0.05 ($\sigma = 0.05$) was used; therefore, if the p -value is less than or equal to 0.05, the differences between sampling methods were significantly different.

Bivariate plots and simple linear regression techniques (Kenney and Keeping, 1962) were used for selected constituents to compare pump and grab sample concentrations. The equation for the linear line of best fit and coefficient of determination (R^2) were used to quantify the relation between sampling methods. A line of best fit slope value and a R^2 value that is close to 1.00 indicates a strong association between pump and grab sample concentrations. Concentrations of previously collected environmental and duplicate pump samples were included in plots to display the amount of expected variation and a line of equal concentration was included for reference.

To avoid false-positive quantification of a constituent, low concentrations were left-censored and reported as less than the method detection limit by the laboratory (Childress and others, 1999). Constituent concentrations were less than the method detection limit (left-censored) in several samples. There are many ways to handle censored data including estimating, substituting, or excluding. The small sample size of this study makes estimating censored values unreliable and substituting or eliminating censored data can skew results (Helsel, 2006). To avoid skewing differences between concentrations that were detected below and close to the detection limit, datasets that contained a large amount of left-censored data (greater than 10 percent was arbitrarily selected) were evaluated qualitatively and the RMSE, RPD, and Wilcoxon test p -value were not calculated. There were two concentration pairs that compared a censored value to an uncensored value in datasets that contained less than 10 percent censored data, including concentrations of orthophosphate with a left-censored environmental sample and an uncensored historical duplicate sample. Substituting the censored value with the detection limit (0.01; the largest potential value) or zero (the lowest potential value) resulted in no difference in the RMSE

and a 1.5 percent difference in the mean RPD. Substituting these censored values did not skew results excessively; therefore a value of one-half of the detection limit was used in place of these censored values. In comparisons where both values were left-censored a difference of zero was used.

Several datasets contained values that were below the laboratory reporting level and above the method detection limit. These values are flagged with an “E” (estimated) and the reported values were used in calculations. Values reported with the E qualifier are considered firm detections, although the precision of the value is frequently less than for values without this qualifier (Childress and others, 1999).

Quality Assurance

Quality assurance and quality control samples were collected during the current (2013) sampling period in accordance with standard quality assurance and quality control procedures (U.S. Geological Survey, variously dated). A blank sample was collected for fuel compounds and a duplicate sample was collected for both sampling methods. No fuel compounds exceeded the detection limit in the blank sample (table 1). There were three constituents (orthophosphate, chromium, and selenium) with RPDs between the current (2013) environmental pump and the current (2013) duplicate pump samples greater than 10 percent; however, absolute differences for these constituents were low (table 1).

RPDs between environmental grab and duplicate grab samples were greater than 10 percent for 80 percent of the constituents (table 1). Also, RPDs between environmental grab and duplicate grab samples (table 1) were greater than Method Mean RPDs between pump and grab samples (table 2) for 68 percent of the constituents that had calculated RPDs. This indicates that there was greater variability between environmental and duplicate grab samples (within method variability) than between the environmental pump and grab samples (between method variability) for most constituents.

Duplicate grab samples were collected by tethering two grab samplers together, because the amount of water collected by each grab sampler is close to the amount necessary for analysis. The grab samplers were left in the well for the calculated equilibrium period and, as the tether was pulled to retrieve the samplers, the duplicate sampler was lifted through the water column and filled directly after the environmental sampler was filled. The well screen length of monitoring wells within the Independence well field is 1.5 m, the sampler must be lifted 0.9 m to fill, and the top weight of the sampler is 0.3 m in length. Therefore, the environmental sampler was filled within approximately 1.2 m or 0.3 m below the top of the well screen. The water remaining within the screened interval is not sufficient to fill the duplicate sampler; therefore it was filled with water that remained from the screened interval, water that was drawn into the well while the first sampler was lifted, and water from above the screened interval. Because of this and the duplicate data results, the screened interval lengths

of monitoring wells within the Independence well field are not conducive to collecting multiple grab samples by tethering samplers. Quality assurance duplicate samples are included in the groundwater monitoring plan for the Independence well field (Wilkison, 2011). The inability to collect required quality assurance samples using two tethered grab samplers may limit the use of grab samplers. However, limiting the number of analyzed constituents per sample event or reducing the volume required for sample analyses by the laboratory such that sufficient volume for both an environmental and quality assurance sample can be obtained from one grab sample or two smaller samplers may allow grab sampler use. Further study may be necessary to determine if the collection of quality assurance duplicate samples by this method is appropriate.

Several zinc blank samples were collected during 2015 after the initial sample analysis because of large zinc concentration differences between pump and grab samples to determine if greater zinc concentrations in grab samples may have been caused by exposure to the grab sampler or from using a syringe and a 0.70- μm syringe filter instead of standard tubing and a 0.45- μm capsule filter. A grab sampler was soaked in deionized water in an enclosed Teflon container for 7 days (the duration of the calculated equilibrium period). An unfiltered sample, a sample filtered with standard tubing and a 0.45- μm capsule filter, and a sample filtered with a syringe and a 0.70- μm syringe filter were collected from the sampler as well as an unfiltered sample that was unexposed to the grab sampler; all samples were analyzed for zinc. The unexposed blank sample had a zinc concentration less than the detection limit (less than 2.0 $\mu\text{g/L}$, which was different than the 2013 detection limit presented in table 1). The unfiltered sample that was exposed to the sampler and the sample that was filtered with standard tubing and a 0.45- μm capsule filter had similar zinc concentrations below the laboratory reporting level and above the long-term method detection limit (2.16 $\mu\text{g/L}$ and 3.04 $\mu\text{g/L}$; Childress and others, 1999). The sample filtered with a syringe and a 0.70- μm syringe filter had the largest zinc concentration (13.15 μg). This suggests the syringe or filter may be a source of zinc contamination. Tracking temporal zinc changes within the Independence well field using zinc contaminated equipment could be problematic and further study may be necessary to remove the risk of zinc contamination.

Results of Concentration Comparison between Pump and Grab Samples

Continuous (every 30 minutes) groundwater quality was monitored before, during, and after pumping to determine the response of groundwater properties during pumping and the duration for properties to return to prepump values. Pump and grab sample nutrient, major ion, trace element, and fuel compound concentrations were compared using RMSE, RPD, and the Wilcoxon test. Constituents with greater than 10 percent censored data were compared qualitatively and the RMSE, RPD, and Wilcoxon test p -value were not calculated.

Continuous Groundwater Quality and Equilibrium Period

Water-quality properties remained fairly consistent during pumping in selected wells (Wells 2B, 10A, and 28A), with the exception of Well 2B specific conductance (SC; fig. 2), indicating water at the screened interval before pumping was likely similar to water drawn into the well from the aquifer during pumping. After the probes were removed and returned to the well, there were observed differences in dissolved oxygen (DO) in all wells, and in pH and SC in Well 2B. Values for DO returned to approximately prepurge values in less than one day. It took approximately 5 days for SC in Well 2B to return to values similar to those observed before pumping, and pH in Well 2B remained consistently smaller than prepurge values for 7 days before stabilizing at approximately prepurge values. Removing and returning the probe may have caused a disturbance affecting water quality similar to deploying a grab sampler; however, properties returned to prepurge, or approximately prepurge, and fairly consistent values within 7 days or fewer indicating the calculated 7-day period should be sufficient to attain the desired equilibrium conditions.

Comparison of Nutrient Concentrations between Pump and Grab Samples

Concentrations between pump and grab samples were similar for analyzed nutrient species (ammonia [as nitrogen, hereafter referred to as ammonia], nitrite plus nitrate [as nitrogen, hereafter referred to as nitrite plus nitrate], nitrite [as nitrogen, hereafter referred to as nitrite], and orthophosphate [as phosphate, hereafter referred to as orthophosphate]) and varied by less than 0.3 mg/L (table 3). Method Mean RPDs for ammonia and orthophosphate were greater than 10 percent (table 2); however the variability between methods was less than the variability between historical duplicate samples (RMSE Differences were negative), and there were no significant differences determined (p -values greater than 0.05; table 2).

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Table 1. Concentrations of quality assurance and environmental samples collected within the Independence well field during 2013 with absolute and relative percent differences near Independence, Missouri.

[RPD, relative percent difference; mg/L, milligram per liter; --, no data; <, less than and left-censored data; µg/L, microgram per liter]

Constituent (unit)	Well 1B; Station identification number 390920094243502	Well 10A; Station identification number 390951094234501				Well 20B; Station identification number 391023094235602			
	Blank	Environmental pump	Duplicate pump	Absolute difference	RPD	Environmental grab	Duplicate grab	Absolute difference	RPD
Nutrients									
Ammonia, as nitrogen (mg/L)	--	0.123	0.117	0.006	4.99	0.092	0.728	0.637	155
Nitrite plus Nitrate, as nitrogen (mg/L)	--	<0.04	<0.04	--	--	<0.04	<0.04	--	--
Nitrite, as nitrogen (mg/L)	--	<0.001	0.001	--	--	0.003	0.002	0.001	31.4
Orthophosphate, as phosphate (mg/L)	--	0.083	0.147	0.063	55.2	0.679	0.059	0.620	168
Major ions									
Calcium (mg/L)	--	81.9	83.6	1.70	2.06	165	176	10.7	6.29
Magnesium (mg/L)	--	22.9	22.7	0.180	0.79	26.0	34.7	8.71	28.7
Sodium (mg/L)	--	52.4	52.5	0.130	0.25	24.8	10.5	14.3	81.1
Silica (mg/L)	--	17.2	17.3	0.140	0.81	28.7	32.4	3.73	12.20
Chloride (mg/L)	--	23.2	22.6	0.615	2.68	9.32	6.83	2.49	30.9
Fluoride (mg/L)	--	0.402	0.402	0.000	0.00	0.170	0.165	0.005	2.99
Sulfate (mg/L)	--	172	167	4.98	2.94	43.9	52.4	8.51	17.7
Aluminum (µg/L)	--	<2.2	<2.2	--	--	4.29	2.73	1.56	44.4
Barium (µg/L)	--	329	328	0.900	0.274	328	518	190	44.8
Beryllium (µg/L)	--	<0.006	<0.006	--	--	0.027	<0.02	--	--
Cadmium (µg/L)	--	<0.016	<0.016	--	--	<0.03	<0.03	--	--
Chromium (µg/L)	--	0.594	0.439	0.156	30.1	0.311	<0.3	--	--
Cobalt (µg/L)	--	0.058	0.059	0.001	1.89	0.114	0.096	0.017	16.5
Copper (µg/L)	--	<0.8	<0.8	--	--	<0.8	<0.8	--	--
Iron (µg/L)	--	4,140	4,170	30.0	0.72	5,080	18,100	13,020	112
Lead (µg/L)	--	<0.025	<0.025	--	--	<0.04	<0.04	--	--
Lithium (µg/L)	--	27.0	28.3	1.23	4.45	28.3	34.6	6.39	20.3
Manganese (µg/L)	--	187	190	2.40	1.27	2,273	2,165	108	4.87
Molybdenum (µg/L)	--	2.901	2.967	0.066	2.25	<0.05	0.758	--	--
Nickel (µg/L)	--	0.782	0.808	0.026	3.32	1.10	0.899	0.205	20.5
Silver (µg/L)	--	<0.005	<0.005	--	--	<0.02	<0.02	--	--
Strontium (µg/L)	--	580	572	7.90	1.37	828	851	23.5	2.80
Thallium (µg/L)	--	<0.010	<0.010	--	--	<0.03	<0.03	--	--
Vanadium (µg/L)	--	<0.080	<0.08	--	--	0.235	0.086	0.149	92.6
Zinc (µg/L)	--	<1.4	<1.4	--	--	9.684	22.770	13.1	80.6
Antimony (µg/L)	--	<0.027	<0.027	--	--	0.229	0.055	0.174	122.40
Arsenic (µg/L)	--	0.721	0.742	0.021	2.84	4.07	6.52	2.45	46.4
Boron (µg/L)	--	65.6	69.0	3.39	5.04	105	112	6.70	6.17
Selenium (µg/L)	--	0.078	0.065	0.013	17.5	0.066	0.054	0.012	19.8
Uranium (µg/L)	--	0.159	0.158	0.001	0.820	0.049	0.136	0.087	94.17
Fuel compounds									
Benzene (µg/L)	<0.1	<0.1	<0.1	--	--	--	--	--	--
Ethylbenzene (µg/L)	<0.1	<0.1	<0.1	--	--	--	--	--	--
<i>tert</i> -Butyl methyl ether (µg/L)	<0.2	<0.2	<0.2	--	--	--	--	--	--
<i>m</i> - plus <i>p</i> -Xylene (µg/L)	<0.2	<0.2	<0.2	--	--	--	--	--	--
<i>o</i> -Xylene (µg/L)	<0.1	<0.1	<0.1	--	--	--	--	--	--
Toluene (µg/L)	<0.1	<0.1	<0.1	--	--	--	--	--	--
Xylene (µg/L)	<0.2	<0.2	<0.2	--	--	--	--	--	--

Table 2. Summary statistics for selected constituents comparing purge and pump samples with grab samples and environmental pump samples with historical duplicate pump samples from the Independence well field during 2013 and current (2015) drinking water standards near Independence, Missouri.

[RPD, relative percent difference; Method Mean RPD, mean relative percent difference between purge and pump and grab sample concentrations; Historical Duplicate Mean RPD, mean relative percent difference between historical duplicate samples and environmental pump samples; RMSE, root mean square error; Method RMSE, root mean square error between purge and pump and grab sample concentrations; Historical Duplicate RMSE, root mean square error between historical duplicate samples and environmental pump samples; Wilcoxon test, Wilcoxon signed-rank test; Wilcoxon *p*-value, Wilcoxon signed-rank test *p*-value; FMCL, federal maximum contaminant level; %, percent; mg/L, milligrams per liter; --, no data; µg/L, micrograms per liter]

Constituent	RPD			RMSE			Wilcoxon test	Drinking Water Standards ¹	
	Method Mean RPD	Historical Duplicate Mean RPD	RPD Difference	Method RMSE	Historical Duplicate RMSE	RMSE Difference	Wilcoxon <i>p</i> -value	FMCL	National secondary regulation
Nutrients	%			(mg/L)			--	(mg/L)	
Ammonia, as nitrogen	15.4	5.99	9.40	0.100	0.348	-0.248	0.10	--	--
Orthophosphate, as phosphate	47.7	51.9	-4.21	0.084	0.132	-0.048	0.97	--	--
Major ions	%			(mg/L)			--	(mg/L)	
Calcium	2.25	1.98	0.271	4.0	5.1	-1.1	0.83	--	--
Magnesium	1.88	1.19	0.692	0.889	0.751	0.138	0.70	--	--
Sodium	4.19	1.49	2.7	1.3	0.644	0.656	0.03	--	--
Silica	2.85	2.20	0.651	1.0	1.7	-0.7	0.83	--	--
Chloride	3.39	0.91	2.48	1.3	0.354	0.946	0.17	--	250
Fluoride	8.34	3.05	5.29	0.033	0.011	0.022	0.01	4	--
Sulfate	21.8	0.708	21.0	10.3	1.9	8.4	0.37	--	250
Trace elements	%			(µg/L)			--	(µg/L)	
Barium	32.3	4.92	27.4	158	38.4	120	0.00	2,000	--
Cobalt	19.6	7.33	12.3	2.0	0.1	1.9	0.02	--	--
Iron	26.4	2.21	24.2	2,910	322	2,590	0.08	--	300
Lithium	5.39	2.54	2.85	2.7	0.8	1.9	0.28	--	--
Manganese	19.3	1.02	18.3	404	17.0	387	0.00	--	50
Molybdenum	18.9	3.29	15.6	0.257	0.057	0.200	0.08	--	--
Nickel	8.40	5.51	2.89	1.5	0.3	1.2	0.58	--	--
Strontium	3.35	1.17	2.18	50.3	26.4	23.9	0.97	--	--
Arsenic	37.7	6.35	31.4	8.6	0.5	8.1	0.17	10	--
Boron	19.4	5.46	13.9	23.9	18.5	5.4	0.00	--	--
Uranium	18.9	1.50	17.4	0.060	0.009	0.051	1.00	0.03	--

¹U.S. Environmental Protection Agency (2009).

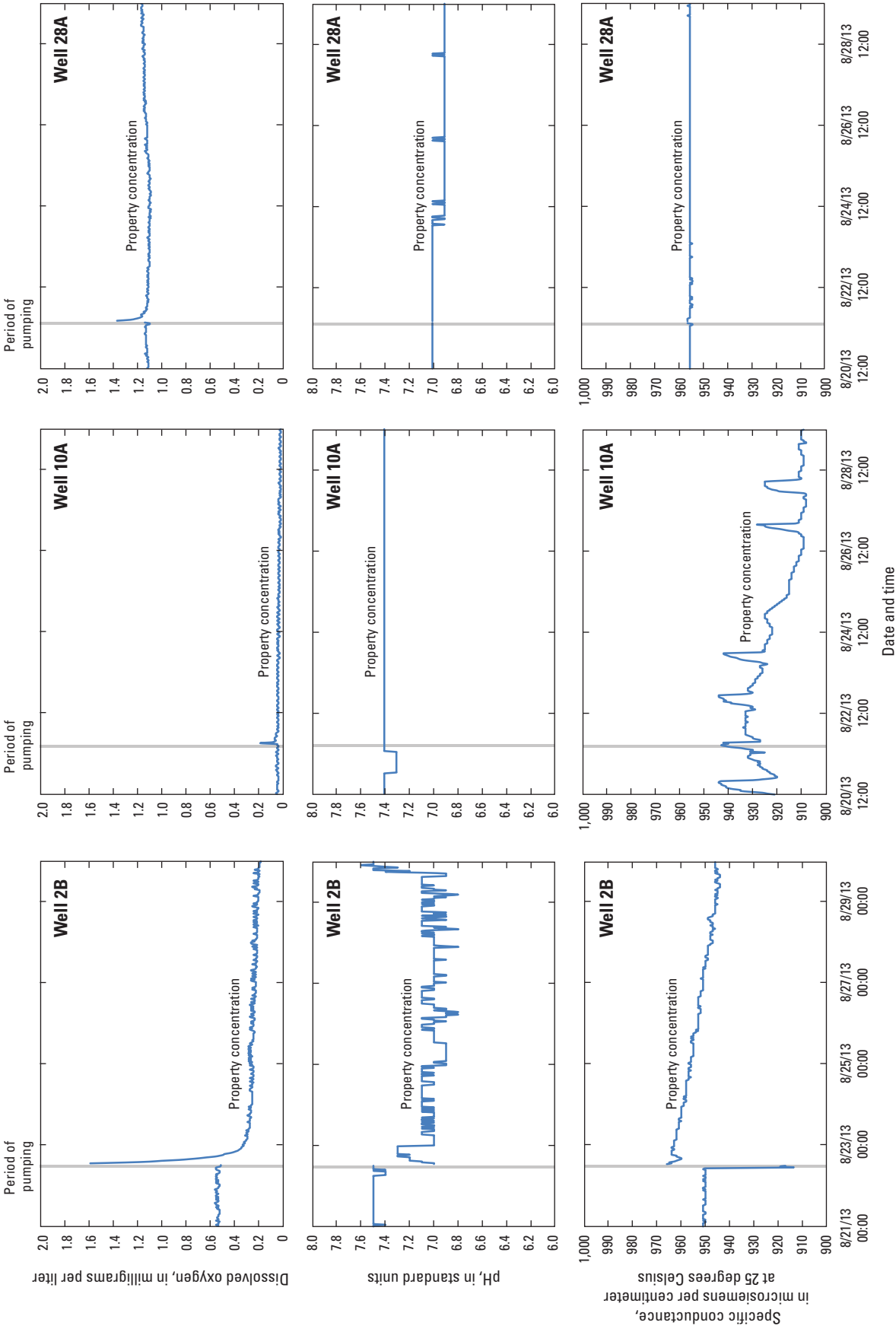


Figure 2. Concentrations of selected water-quality properties within three selected wells in the Independence well field before, during, and after pumping.

Table 3. Groundwater nutrient and major ion concentrations using pump and grab sampling method from the Independence well field and calculated absolute and relative percent differences near Independence, Missouri.

[mg/L, milligrams per liter; Grab, grab sampling method; <, less than and left-censored data; Pump, purge and pump sampling method; --, no data; RPD, relative percent difference; E, concentrations reported below the laboratory reporting level and above the long-term method detection limit]

Type of sample	Nutrients (mg/L)				Major ions (mg/L)						
	Ammonia, as nitrogen	Nitrite plus nitrate, as nitrogen	Nitrite, as nitrogen	Orthophosphate, as phosphate	Calcium	Magnesium	Sodium	Silica	Chloride	Fluoride	Sulfate
Well 1B, station identification number 390920094243502											
Grab	2.96	<0.04	0.003	0.09	187	45.4	20.5	36.6	11.8	0.13	59.3
Pump	3.21	<0.04	0.002	0.17	194	47.6	22.0	38.5	11.7	0.13	28.0
Absolute difference	0.254	--	0.001	0.079	6.50	2.20	1.49	1.90	0.03	0.00	31.30
RPD	8.23	--	37.80	59.25	3.41	4.74	7.03	5.06	0.22	0.00	71.67
Well 2A, station identification number 390923094242001											
Grab	2.15	<0.04	0.006	0.38	127	34.6	39.3	39.6	22.9	0.30	26.9
Pump	2.12	<0.04	0.006	0.52	122	33.0	38.6	38.5	25.0	0.29	36.4
Absolute difference	0.030	--	0.000	0.141	5.30	1.59	0.740	1.09	2.11	0.013	9.45
RPD	1.42	--	7.18	31.22	4.25	4.71	1.90	2.79	8.80	4.38	29.85
Well 2B; station identification number 390923094242002											
Grab	1.42	<0.04	0.003	0.60	113	27.3	53.4	34.1	28.9	0.33	74.6
Pump	1.55	<0.04	0.004	0.58	112	28.0	53.0	33.3	28.8	0.32	70.0
Absolute difference	0.132	--	0.001	0.022	1.80	0.650	0.41	0.860	0.065	0.011	4.58
RPD	8.88	--	19.56	3.68	1.60	2.35	0.77	2.55	0.23	3.41	6.34
Well 5B; station identification number 390924094234503											
Grab	0.34	<0.04	<0.001	0.03	184	31.0	63.2	25.8	104.5	0.19	149.7
Pump	0.32	<0.04	0.003	0.20	176	30.8	61.3	26.1	101.0	0.20	142.3
Absolute difference	0.020	--	--	0.169	7.80	0.184	1.93	0.260	3.49	0.007	7.36
RPD	6.18	--	--	148.07	4.33	0.60	3.10	1.00	3.40	3.58	5.04
Well 9A; station identification number 390948094234001											
Grab	0.15	<0.04	0.003	0.10	104	21.5	43.1	23.3	23.9	0.37	126.3
Pump	0.19	<0.04	<0.001	0.06	106	21.6	41.2	22.9	22.8	0.33	124.1
Absolute difference	0.036	--	--	0.044	1.40	0.180	1.93	0.390	1.11	0.046	2.28
RPD	20.94	--	--	54.31	1.33	0.84	4.58	1.69	4.74	13.22	1.82
Well 10A; station identification number 390951094234501											
Grab	0.076	<0.04	E0.002	0.168	79.26	23.1	52.8	17.1	24.0	0.409	175
Pump	0.123	<0.04	<0.001	0.083	81.87	22.9	52.4	17.2	23.2	0.402	172
Absolute difference	0.047	--	--	0.085	2.61	0.260	0.42	0.100	0.716	0.007	2.50
RPD	47.49	--	--	67.74	3.24	1.13	0.80	0.58	3.03	1.73	1.44
Well 11C; station identification number 390945094233003											
Grab	0.28	<0.04	<0.001	0.02	142	20.9	38.2	21.4	20.0	0.32	92.6
Pump	0.19	<0.04	<0.001	0.01	141	20.8	36.6	22.6	19.9	0.25	94.7
Absolute difference	0.092	--	--	0.006	0.800	0.170	1.61	1.21	0.051	0.067	2.09
RPD	39.16	--	--	38.12	0.57	0.82	4.30	5.49	0.26	23.63	2.23
Well 18B; station identification number 391014094235702											
Grab	0.49	<0.04	0.002	0.20	60	12.6	60.0	15.4	20.9	0.45	141.1
Pump	0.58	<0.04	<0.001	0.09	60	12.7	58.7	15.0	20.8	0.44	140.0
Absolute difference	0.084	--	--	0.111	0.060	0.160	1.27	0.380	0.017	0.013	1.15
RPD	15.78	--	--	78.31	0.10	1.26	2.14	2.50	0.08	2.92	0.82
Well 19A; station identification number 391018094234401											
Grab	0.26	<0.04	E0.001	0.17	65	16.5	55.8	17.1	19.4	0.44	149.2
Pump	0.27	E0.07	<0.001	0.14	66	16.7	54.6	16.2	20.0	0.41	149.9
Absolute difference	0.011	--	--	0.024	0.900	0.230	1.13	0.900	0.671	0.027	0.748
RPD	4.00	--	--	15.23	1.37	1.39	2.05	5.42	3.40	6.41	0.50
Well 27A; station identification number 391015094245802											
Grab	0.66	<0.04	0.003	0.19	145	36.9	12.2	34.3	8.3	0.22	0.2
Pump	0.71	<0.04	E0.002	0.17	147	36.6	11.0	34.4	7.9	0.21	0.7
Absolute difference	0.058	--	0.001	0.026	1.80	0.330	1.22	0.070	0.43	0.011	0.469
RPD	8.49	--	46.45	14.75	1.24	0.898	10.49	0.204	5.30	5.20	111.27
Well 28A; station identification number 391029094240202											
Grab	0.72	<0.04	0.003	0.16	160	38.3	15.9	32.9	8.8	0.26	19.7
Pump	0.79	<0.04	0.003	0.18	154	37.6	14.6	34.3	8.2	0.20	21.4
Absolute difference	0.066	--	0.000	0.024	5.20	0.730	1.37	1.38	0.670	0.063	1.71
RPD	8.78	--	1.68	14.19	3.31	1.92	8.99	4.10	7.87	27.21	8.32

RMSE differences and Method Mean RPDs were not calculated for nitrite plus nitrate or orthophosphate because these datasets were greater than 10 percent left-censored. All nitrite plus nitrate data were left-censored except one pump value which was below the laboratory reporting level and above the long-term method detection limit. Nitrite absolute differences did not exceed 0.002 mg/L (table 3). Variability between pump and grab samples of analyzed nutrients may have minimal effect on the ability to monitor temporal changes and potential groundwater contamination threats.

Comparison of Major Ion Concentrations between Pump and Grab Samples

Major ions (calcium, magnesium, sodium, silica, chloride, fluoride, and sulfate) had no censored data (table 3), their Method Mean RPDs were less than 10, and their RMSE Differences were negative or minimal (less than 1 mg/L) with the exception of sulfate (table 2). Although sulfate had a larger Method Mean RPD (21.8) and RMSE Difference (8.4) than other major ions, its concentrations between sampling methods were not significantly different (p -value = 0.37; table 2). Statistically significant differences were determined between pump and grab samples for sodium (p -value = 0.03) and fluoride (p -value = 0.01; table 2). Sodium, fluoride, and sulfate concentrations plot closely to their 1:1 line and their slopes and R^2 values are close to 1 (fig. 3), indicating a strong association between pump and grab samples based on bivariate plots and simple linear regressions. Grab sample concentrations were generally larger than pump concentrations and may be because of using a larger pore sized filter for grab samples. The Federal Maximum Contaminant Level (FMCL) for sulfate is 250 mg/L (U.S. Environmental Protection Agency, 2009), and the Method RMSE is 10.3 mg/L. The FMCL for fluoride is 4.0 mg/L (U.S. Environmental Protection Agency, 2009), and the Method RMSE was 0.033 mg/L. This indicates that the error between sulfate and fluoride pump and grab sample concentrations is substantially less than the level at which these ions need to be monitored. There is no FMCL for sodium (U.S. Environmental Protection Agency, 2009). If the Method RMSE is substantially less than the level at which the contaminant needs to be monitored (for example an established contaminant level) then the differences between sampling methods may not affect the ability to monitor for this constituent.

Method RMSEs, which indicate the amount of variation between pump and grab samples, is substantially less than the fluoride and sulfate FMCLs. Variability between pump and grab samples of analyzed major ions may have minimal effect on the ability to monitor temporal changes and potential groundwater contamination threats; however application objectives need to be considered in determining acceptable variation amounts.

Comparison of Trace Element Concentrations between Pump and Grab Samples

Differences in Method RMSE and Method Mean RPDs were calculated for 11 trace element constituents (out of 23 trace element constituents analyzed; table 2; table 4). Method Mean RPDs were greater than 10 percent for most analyzed trace elements (barium, cobalt, iron, manganese, molybdenum, arsenic, boron, and uranium). Lithium, nickel, and strontium had less than 10 percent Method Mean RPDs. Historical Duplicate Mean RPDs were less than 10 percent for analyzed trace elements (table 2). All analyzed trace element Method RMSEs were greater than Historical Duplicate RMSEs (table 2). Barium, cobalt, manganese, and boron had concentrations that were significantly different (Wilcoxon test p -value less than or equal to 0.05) between sampling methods (table 2).

Barium, molybdenum, boron, and uranium method concentrations plotted close to the 1:1 line on bivariate plots and had slopes and R^2 values that were close to 1.0, indicating a close association between pump and grab samples based on bivariate plots and simple linear regressions (fig. 3). Grab sample concentrations were generally larger than pump concentrations for these elements and may be because of using a larger pore sized filter for grab samples. Bivariate and simple linear regressions indicate cobalt, iron, manganese, and arsenic pump and grab sample relations were less direct, although cobalt and iron R^2 values were close to 1.0 (fig. 3). Manganese had a slope that was close to 1 (0.91), but had a low R^2 value of 0.57, likely due to two sampling method outliers (fig. 3). The cobalt method concentration relation was skewed by a single sample data pair—when this outlier is removed, the RMSE difference is negative (indicating smaller, more minimal differences between pump and grab samples than between environmental and duplicate samples) and the Method Mean RPD is less than 10 percent. However, this was the only data pair for cobalt having a concentration greater than 1 $\mu\text{g/L}$, which may indicate the relation between pump and grab sample concentrations is not strong at higher concentrations.

The Method RMSE is an indication of the mean difference between the pump and grab samples or the error between the two methods. If the Method RMSE is substantially less than the level at which the contaminant needs to be monitored (for example, an established contaminant level) then the differences between sampling methods may not affect the ability to monitor for this element. The FMCL for barium is 2,000 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 2009), and the Method RMSE concentrations was 158 $\mu\text{g/L}$ (table 2), suggesting the ability to detect and monitor for this element may not be affected by the use of grab samplers. Method RMSEs were greater than drinking water standards for iron, manganese, and uranium: the national secondary drinking water regulation for iron is 300 $\mu\text{g/L}$ and the iron Method RMSE

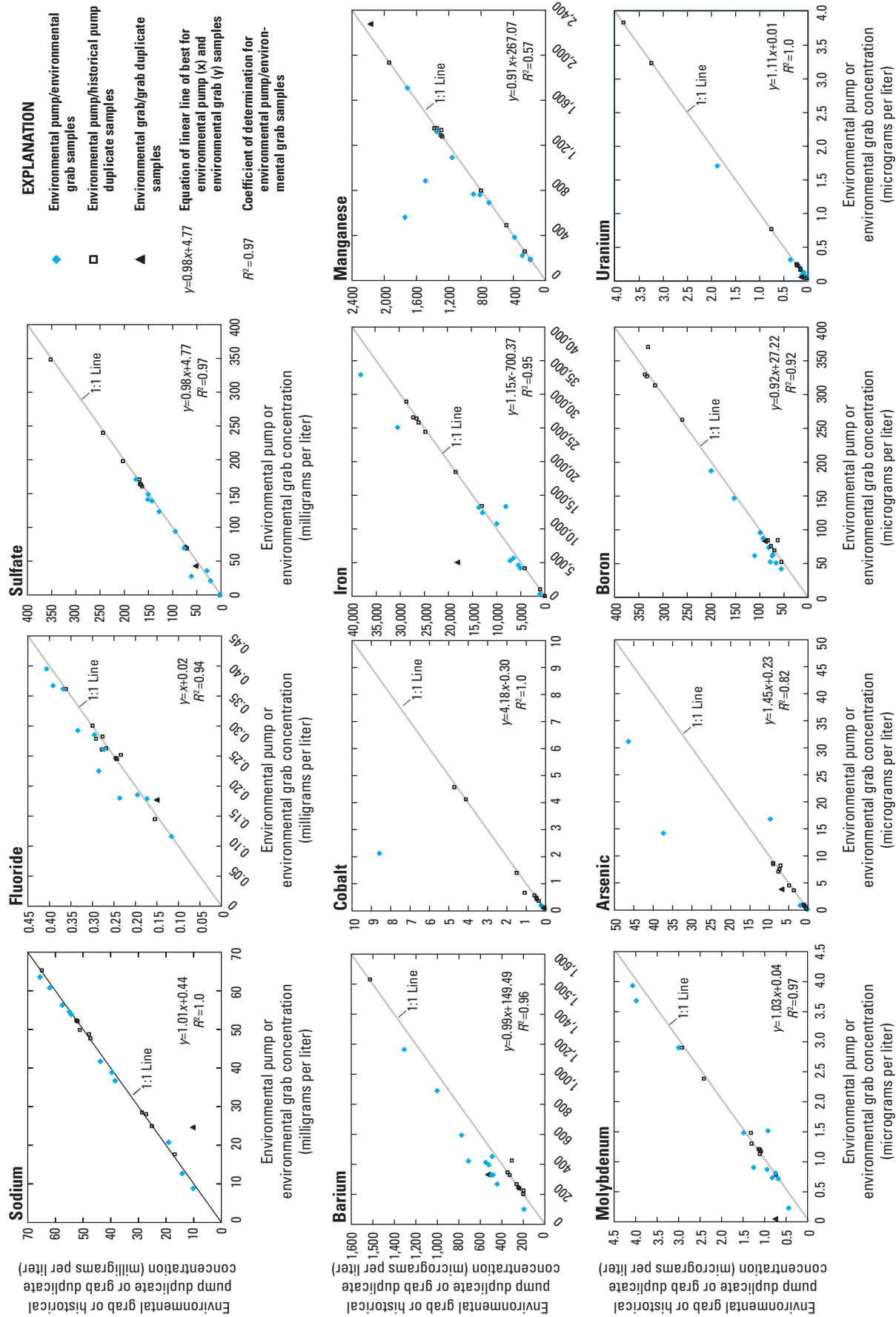


Figure 3. Comparison of concentrations of selected compounds between the purge and pump and samples collected using the grab-sampling method, with environmental and duplicate purge and pump samples.

was 2,910 µg/L; the national secondary drinking water regulation for manganese is 50 µg/L and the manganese Method RMSE was 404 µg/L; the FMCL for uranium is 0.03 µg/L and the uranium Method RMSE is 0.060 µg/L (table 2; U.S. Environmental Protection Agency, 2009). As such, the degree of error between pump and grab samples is greater than the level to which these elements have established guidelines. Iron and manganese concentrations, however, were determined above their national secondary drinking water regulations at all wells with both sampling methods. All instances where uranium concentrations were above its FMCL in pump samples the grab sample concentrations were also above its FMCL and vice versa except for samples collected in well 18B. Arsenic Method RMSE (8.6 µg/L; table 2) is close to its FMCL (10 µg/L; U.S. Environmental Protection Agency, 2009). Cobalt, lithium, molybdenum, nickel, strontium, and boron do not have FMCLs or national secondary drinking water regulations (U.S. Environmental Protection Agency, 2009).

Summary statistics were not calculated for 12 trace elements (aluminum, beryllium, cadmium, chromium, copper, lead, silver, thallium, vanadium, zinc, antimony, and selenium) that had datasets with greater than 10 percent left-censored data. These constituents had 106 data pairs with left-censored data and 84 percent of pairs were either both left-censored data or contained one left-censored value and one estimated (table 4). There were 26 data pairs without left-censored data, and RPDs between uncensored pump and uncensored grab sample concentrations ranged from 0 to 169 (table 4). Estimated concentrations are below the laboratory reporting level and above the long-term (typically 6-12 months) method detection limit (Childress, 1999) and were considered to be within a reasonable amount of difference from the left-censored data. Uncensored data paired with left-censored data were close to censoring levels (less than or equal to 0.01 µg/L) except for chromium and zinc. Chromium and zinc had larger differences between uncensored and left-censored data than other elements that contained left-censored data. There were six chromium data pairs containing one left-censored datum and in all pairs grab sample concentrations were less than the method detection limit and pump sample concentrations were above. It is not possible to determine if the higher concentrations of chromium in the pump samples were due to the introduction of chromium during pump procedures or from a reduced ability to detect chromium with the grab sample procedures and analyses. However, chromium pump concentrations paired with left-censored grab concentrations were small and, the greatest detected chromium concentration was 0.639 µg/L (table 4). The FMCL for chromium is 100 µg/L

(U.S. Environmental Protection Agency, 2009). Differences between pump and grab sample chromium concentrations were substantially smaller than established standards and these differences may not affect the ability to monitor chromium at levels close to the FMCL.

There were large differences in pump and grab sample zinc concentrations. Zinc concentrations in all pump samples were less than the method detection limit, except for one sample below the laboratory reporting level and above the long-term method detection limit. All grab sample zinc concentrations were greater than the method detection limit and the smallest concentration was 21.7 µg/L (table 4). Analysis of several zinc blank samples suggests the syringe or filter may be a source of zinc contamination. The zinc blank sample that was collected using deionized water exposed to the grab sampler and filtered with a syringe and a 0.70-µm syringe filter had a reported zinc concentration of 13.1 µg/L and was higher than the unfiltered blank sample and the blank sample filtered with standard tubing and a 0.45-µm capsule filter that were collected from the same water. Although, grab sample zinc concentrations were larger than pump sample concentrations the largest grab sample zinc concentration was 62.3 µg/L, which is substantially smaller than its FMCL of 5,000 µg/L (table 4; U.S. Environmental Protection Agency, 2009).

Variations of analyzed trace elements between pump and grab samples could reduce the ability to monitor temporal changes and potential groundwater contamination threats. It is unknown if concentration differences between the two sampling methods are due to the different sampling equipment, different sampling procedures, or from the use of different filters with different pore sizes. Tracking temporal zinc changes within the Independence well field with samples collected using zinc contaminated equipment could be problematic. The degree of precision necessary for monitoring potential groundwater threats and application objectives need to be considered when determining acceptable variation amounts.

Comparison of Fuel Compound Concentrations between Pump and Grab Samples

The concentrations of seven fuel compounds (benzene, ethylbenzene, *tert*-butyl methyl ether, *m*- plus *p*-xylene, *o*-xylene, toluene, and xylene) were analyzed, and there were no concentrations above the minimum detection limit (Childress, 1999) for either sampling method. It is not possible to determine if fuel compounds would be detected at similar concentrations.

Table 4. Groundwater trace element concentrations using purge and pump and grab sampling method from the Independence well field and calculated absolute and relative percent differences near Independence, Missouri.

[µg/L, micrograms per liter; Grab, grab sampling method; <, less than and left-censored data; Pump, purge and pump sampling method; --, no data; RPD, relative percent difference; E, concentrations reported below the laboratory reporting level and above the long-term method detection limit]

Type of sample	Trace elements (µg/L)											
	Aluminum	Barium	Beryllium	Cadmium	Chromium	Cobalt	Copper	Iron	Lead	Lithium	Manganese	Molybdenum
Well 1B, station identification number 390920094243502												
Grab	<6.6	490	<0.018	<0.048	<0.21	E0.110	<2.4	38,210	<0.075	21.1	1,713	0.484
Pump	<2.2	452	0.015	<0.016	<0.07	0.110	<0.8	32,920	<0.025	21.1	1,709	0.227
Absolute difference ¹	--	37.9	--	--	--	0.000	--	5,290	--	0.065	4.30	0.257
RPD ¹	--	8.05	--	--	--	0.000	--	14.9	--	0.308	0.251	72.2
Well 2A, station identification number 390923094242001												
Grab	<6.6	710	<0.06	<0.09	<0.9	E0.220	<2.4	30,560	<0.12	16.2	1,348	0.784
Pump	<6.6	422	<0.06	<0.09	<0.9	E0.190	<2.4	25,080	<0.12	16.4	1,321	0.809
Absolute difference ¹	--	289	--	--	--	0.030	--	5,480	--	0.168	27.3	0.026
RPD ¹	--	51.0	--	--	--	14.6	--	19.7	--	1.03	2.05	3.20
Well 2B; station identification number 390923094242002												
Grab	5.75	775	<0.02	<0.03	<0.3	0.138	<0.8	8,110	<0.04	26.0	701	0.964
Pump	E2.7	595	<0.02	<0.03	<0.3	0.124	<0.8	13,330	<0.04	25.6	692	1.514
Absolute difference ¹	3.05	180	--	--	--	0.014	--	5,220	--	0.420	8.90	0.550
RPD ¹	72.2	26.3	--	--	--	10.4	--	48.7	--	1.63	1.28	44.4
Well 5B; station identification number 390924094234503												
Grab	<2.2	550	0.012	E0.017	<0.07	0.12	<0.8	9,947	<0.025	28.9	1,489	0.867
Pump	<2.2	413	E0.011	<0.016	0.260	0.12	<0.8	10,770	<0.025	27.4	885	0.731
Absolute difference ¹	--	137	0.001	--	--	0.003	--	823	--	1.49	604	0.135
RPD ¹	--	28.4	12.0	--	--	2.70	--	7.95	--	5.29	50.9	16.9
Well 9A; station identification number 390948094234001												
Grab	<2.2	443	<0.006	<0.016	<0.07	0.08	<0.8	7,204	E0.025	27.8	385	1.530
Pump	<2.2	268	<0.006	<0.016	0.353	0.08	<0.8	5,256	<0.025	30.5	383	1.482
Absolute difference ¹	--	175	--	--	--	0.001	--	1,948	--	2.66	1.70	0.048
RPD ¹	--	49.1	--	--	--	0.637	--	31.3	--	9.13	0.443	3.19
Well 10A; station identification number 390951094234501												
Grab	E2.77	480	E0.012	E0.020	<0.07	0.070	<0.8	5,100	<0.025	31.2	189	3.04
Pump	<2.2	329	<0.006	<0.016	0.594	0.058	<0.8	4,140	<0.025	27.0	187	2.90
Absolute difference ¹	--	152	--	--	--	0.012	--	960	--	4.15	1.60	0.141
RPD ¹	--	37.5	--	--	--	18.7	--	20.8	--	14.3	0.851	4.75
Well 11C; station identification number 390945094233003												
Grab	<2.2	194	<0.006	0.121	<0.07	8.60	<0.8	1,019	<0.025	35.7	1,744	1.298
Pump	<2.2	100	<0.006	0.222	0.639	2.12	<0.8	310	<0.025	34.3	561	0.905
Absolute difference ¹	--	94.5	--	0.101	--	6.47	--	709	--	1.35	1180	0.393
RPD ¹	--	64.2	--	58.8	--	121	--	107	--	3.86	103	35.7
Well 18B; station identification number 391014094235702												
Grab	E3.0	497	<0.006	<0.016	<0.07	E0.04	<0.8	6,522	<0.025	26.1	894	4.025
Pump	<2.2	329	<0.006	<0.016	0.281	E0.04	<0.8	5,635	<0.025	26.7	766	3.683
Absolute difference ¹	--	168	--	--	--	0.000	--	887	--	0.610	128	0.342
RPD ¹	--	40.6	--	--	--	0.000	--	14.6	--	2.31	15.4	8.87
Well 19A; station identification number 391018094234401												
Grab	E2.7	520	<0.006	<0.016	<0.07	0.06	<0.8	5,493	<0.025	28.3	288	4.111
Pump	<2.2	397	<0.006	<0.016	0.253	E0.04	<0.8	4,615	<0.025	28.1	222	3.934
Absolute difference ¹	--	123	--	--	--	0.016	--	878	--	0.200	66.1	0.177
RPD ¹	--	26.9	--	--	--	33.2	--	17.4	--	0.709	25.9	4.40
Well 27A; station identification number 391015094245802												
Grab	E2.6	1,002	<0.006	<0.016	E0.08	0.09	<0.8	12,940	<0.025	35.1	1,158	0.728
Pump	<2.2	890	<0.006	<0.016	0.220	0.08	<0.8	12,390	<0.025	35.1	1,092	0.717
Absolute difference ¹	--	112	--	--	0.140	0.004	--	550	--	0.070	66.0	0.011
RPD ¹	--	11.8	--	--	93.3	4.61	--	4.34	--	0.20	5.87	1.47
Well 28A; station identification number 391029094240202												
Grab	6.5	1,308	0.019	E0.019	E0.1	0.12	<0.8	13,690	E0.035	37.6	813	0.985
Pump	74.3	1,165	E0.01	<0.016	0.166	0.13	<0.8	13,180	0.201	30.6	761	0.870
Absolute difference ¹	67.9	143	0.009	--	0.066	0.012	--	510	0.166	7.01	52.5	0.115
RPD ¹	168	11.6	60.1	--	49.7	9.84	--	3.80	141	20.6	6.67	12.3

16 Comparison of Constituents in the Missouri River using Two Sampling Methods, near Independence, Missouri, 2013

Table 4. Groundwater trace element concentrations using purge and pump and grab sampling method from the Independence well field and calculated absolute and relative percent differences near Independence, Missouri.—Continued

[µg/L, micrograms per liter; Grab, grab sampling method; <, less than and left-censored data; Pump, purge and pump sampling method; --, no data; RPD¹, relative percent difference; E, concentrations reported below the laboratory reporting level and above the long-term method detection limit]

Type of sample	Trace elements (µg/L)										
	Nickel	Silver	Strontium	Thallium	Vanadium	Zinc	Antimony	Arsenic	Boron	Selenium	Uranium
Well 1B, station identification number 390920094243502											
Grab	0.900	<0.015	1,077	<0.030	<0.240	25.4	<0.081	37.350	250.4	<0.09	0.124
Pump	0.796	<0.005	1,133	<0.010	<0.080	<1.4	<0.027	14.230	234.2	0.102	0.082
Absolute difference ¹	0.104	--	55.7	--	--	--	--	23.1	16.2	--	0.041
RPD ¹	12.3	--	5.04	--	--	--	--	89.6	6.69	--	40.1
Well 2A, station identification number 390923094242001											
Grab	E0.837	<0.06	989	<0.090	E0.298	24.6	<0.081	46.410	124.1	<0.15	<0.042
Pump	E0.834	<0.06	903	<0.090	E0.264	<6.0	<0.081	31.260	119.6	<0.15	<0.042
Absolute difference ¹	0.003	--	86.1	--	0.034	--	--	15.2	4.4	--	--
RPD ¹	0.359	--	9.10	--	12.1	--	--	39.0	3.64	--	--
Well 2B; station identification number 390923094242002											
Grab	0.863	<0.02	763	<0.030	<0.080	21.7	<0.027	9.621	116.4	E0.076	0.036
Pump	0.806	<0.02	774	<0.030	<0.080	<2.0	<0.027	16.850	108.9	E0.09	0.056
Absolute difference ¹	0.056	--	10.7	--	--	--	--	7.23	7.50	0.014	0.0
RPD ¹	6.76	--	1.39	--	--	--	--	54.6	6.66	16.9	44.3
Well 5B; station identification number 390924094234503											
Grab	1.302	<0.005	696	<0.010	E0.106	51.1	E0.032	0.130	191.3	0.061	0.364
Pump	1.394	<0.005	686	<0.010	E0.084	<1.4	E0.033	0.112	183.2	E0.046	0.306
Absolute difference ¹	0.092	--	10.4	--	0.022	--	0.001	0.019	8.10	0.015	0.059
RPD ¹	6.82	--	1.51	--	23.2	--	3.08	15.5	4.33	28.4	17.5
Well 9A; station identification number 390948094234001											
Grab	0.822	<0.005	626	<0.010	<0.080	62.3	<0.027	0.495	90.7	E0.051	0.175
Pump	0.914	<0.005	618	<0.010	<0.080	<1.4	<0.027	0.676	79.2	E0.058	0.202
Absolute difference ¹	0.091	--	7.80	--	--	--	--	0.182	11.5	0.007	0.027
RPD ¹	10.5	--	1.25	--	--	--	--	31.1	13.5	12.8	14.5
Well 10A; station identification number 390951094234501											
Grab	0.792	<0.005	559	<0.010	E0.087	39.1	<0.027	0.975	97.8	0.087	0.154
Pump	0.782	<0.005	580	<0.010	<0.08	<1.4	<0.027	0.721	65.6	0.078	0.159
Absolute difference ¹	0.010	--	21.2	--	--	--	--	0.254	32.2	0.009	0.005
RPD ¹	1.26	--	3.72	--	--	--	--	30.0	39.5	10.8	3.26
Well 11C; station identification number 390945094233003											
Grab	13.860	<0.005	710	0.051	0.582	33.1	0.131	1.859	92.7	0.166	1.873
Pump	8.875	<0.005	707	0.055	0.281	E2.8	0.105	0.829	76.9	0.610	1.695
Absolute difference ¹	4.99	--	2.80	0.003	0.301	30.3	0.026	1.03	15.8	0.445	0.178
RPD ¹	43.9	--	0.395	6.22	69.9	169	22.1	76.6	18.7	115	9.98
Well 18B; station identification number 391014094235702											
Grab	0.546	<0.005	427	<0.010	<0.080	54.4	<0.027	0.240	69.5	0.086	0.025
Pump	0.559	<0.005	424	<0.010	<0.080	<1.4	<0.027	0.257	52.7	0.068	0.032
Absolute difference ¹	0.013	--	2.30	--	--	--	--	0.017	16.8	0.018	0.007
RPD ¹	2.39	--	0.541	--	--	--	--	6.80	27.5	23.9	23.1
Well 19A; station identification number 391018094234401											
Grab	0.612	<0.005	470	<0.010	E0.093	44.5	<0.027	0.464	82.8	0.090	0.020
Pump	0.596	<0.005	461	<0.010	E0.086	<1.4	<0.027	0.355	63.9	0.087	0.024
Absolute difference ¹	0.015	--	8.40	--	0.007	--	--	0.109	18.9	0.003	0.004
RPD ¹	2.52	--	1.81	--	7.82	--	--	26.6	25.8	3.74	19.3
Well 27A; station identification number 391015094245802											
Grab	0.795	<0.005	1,114	<0.010	<0.080	24.0	<0.027	E0.048	101.9	E0.046	0.068
Pump	0.821	<0.005	1,103	<0.010	<0.080	<1.4	<0.027	E0.043	92.0	E0.051	0.067
Absolute difference ¹	0.026	--	11.0	--	--	--	--	0.005	9.89	0.005	0.001
RPD ¹	3.22	--	0.99	--	--	--	--	11.0	10.2	10.3	0.74
Well 28A; station identification number 391029094240202											
Grab	0.982	E0.006	1,084	E0.012	0.185	58.6	E0.028	0.255	138.1	0.071	0.083
Pump	0.958	<0.005	1,212	<0.010	0.244	<1.4	<0.027	0.180	77.1	E0.054	0.119
Absolute difference ¹	0.024	--	128	--	0.060	--	--	0.075	61.0	0.017	0.035
RPD ¹	2.48	--	11.1	--	27.8	--	--	34.4	56.7	27.8	34.9

¹ Calculated using raw values, which may result in greater accuracy than results calculated with presented values.

Summary and Conclusions

The U.S. Geological Survey, in cooperation with the City of Independence, Missouri, Water Department, has historically collected water-quality samples using the purge and pump method (hereafter referred to as pump method) to identify potential contamination in groundwater supply wells within the Independence well field. Pump methods require purging the well before sampling by removing large volumes of water. The formation water that is drawn into the well is sampled. No-purge grab sampling methods (hereafter referred to as grab method) collect water directly from a section of the well screen interval without well purging or the use of a pump. High hydraulic conductivity is necessary to maintain the same chemical and physical properties between the surrounding aquifer and the water at the sampled well section. If the necessary hydrogeologic conditions exist and grab sample results are comparable to the pump method, grab samplers may reduce time, labor, overall cost, and allow remote wells to be sampled more easily.

Independence provides approximately 250,000 residents and surrounding communities with water from supply wells completed within the Missouri River alluvial aquifer. Several nonpoint and point contamination sources for potential contamination were identified within the contributing recharge area. These contamination threats increase the need to monitor the quality of groundwater supplied by Independence.

This study was designed to compare constituent concentrations between samples collected within the Independence well field using the pump method and the grab method. To quantify concentration differences between sample methods beyond what was expected, the variability between methods was compared to the variability between environmental and historical duplicate samples using root mean square error (hereafter referred to as RMSE) and relative percent difference (hereafter referred to as RPD). The difference between pump and grab sample RMSE and environmental and historical RMSE was calculated (hereafter referred to as RMSE Difference). The mean RPD is the average of all RPDs for a given constituent between environmental and historical duplicate sample concentrations and pump and grab sample concentrations (hereafter referred to Method Mean RPD). A Wilcoxon signed-rank test was used to determine if the median of the differences between the pump and grab samples was statistically different than zero. A significance level of 0.05 ($\sigma = 0.05$) was used. Bivariate plots and simple linear regression techniques were used for selected constituents to compare pump and grab sample concentrations. Constituent concentrations were less than the method detection limit (left-censored) in several samples. Datasets that contained a large amount of left-censored data were evaluated qualitatively.

RPDs between environmental grab and duplicate grab samples were greater than 10 percent for 80 percent of the constituents. Duplicate grab samples were collected by tethering two grab samplers together, because the amount of water collected by each grab sampler is close to the amount

necessary for analysis. The screened interval lengths of monitoring wells within the Independence well field is not conducive to collecting multiple grab samples by tethering samplers. Quality assurance duplicate samples are included in the groundwater monitoring plan for the Independence well field. The inability to collect required duplicate quality assurance samples may limit the use of grab samplers. However, limiting the number of analyzed constituents per sample event or reducing the volume required for sample analyses by the laboratory such that sufficient volume for both an environmental and quality assurance sample can be obtained from one grab sample may allow grab sampler use.

Concentrations between pump and grab samples were similar for analyzed nutrient species (ammonia as nitrogen, nitrite plus nitrate as nitrogen, nitrite, and orthophosphate), the variability between methods was less than the variability between historical duplicate samples, and there were no significant differences determined. Variability between pump and grab samples of analyzed nutrients may have minimal effect on the ability to monitor temporal changes and potential groundwater contamination threats.

Major ion Method Mean RPDs were less than 10 percent and major ion RMSE Differences were negative or minimal (less than 1 milligram per liter [mg/L]) with the exception of sulfate. Statistically significant differences were determined between methods for sodium and fluoride. Sulfate, sodium, and fluoride concentrations plot closely to their 1:1 line and their slopes and coefficient of determination (R^2) values are close to 1, indicating a strong association between pump and grab samples based on bivariate plots and simple linear regressions. Variability between pump and grab samples of analyzed major ions may have minimal effect on the ability to monitor temporal changes and potential groundwater contamination threats.

Differences in Method RMSE and Method Mean RPDs were calculated for 11 trace element constituents (out of 23 trace element constituents analyzed). Method Mean RPDs were greater than 10 percent for most analyzed trace elements (barium, cobalt, iron, manganese, molybdenum, arsenic, boron, and uranium). Barium, cobalt, manganese, and boron had concentrations that were significantly different between sampling methods. Barium, molybdenum, boron, and uranium method concentrations plotted close to the 1:1 line and had slopes and R^2 values that were close to 1.0, indicating a close association between pump and grab samples based on bivariate plots and simple linear regressions. Grab sample concentrations were generally larger than pump concentrations for these elements and may be because of using a larger pore sized filter for grab samples. Bivariate and simple linear regressions indicate cobalt, iron, manganese, and arsenic pump and grab sample relations were less direct.

Summary statistics were not calculated for the 12 trace elements that had datasets with greater than 10 percent left-censored data. These constituents had 106 data pairs with left-censored data and 84 percent of pairs were either both left-censored or contained one left-censored value and one below

the laboratory reporting level and above the long-term method detection limit. There were 26 data pairs without left-censored data, and RPDs between uncensored pump and uncensored grab sample concentrations ranged from 0 to 169. Uncensored data paired with left-censored data for these 12 elements were close to censoring levels except for chromium and zinc. Analysis of several zinc blank samples suggests the syringe or filter may be a source of zinc contamination. Variations of analyzed trace elements between pump and grab samples could reduce the ability to monitor temporal changes and potential groundwater contamination threats. The degree of precision necessary for monitoring potential groundwater threats and application objectives need to be considered when determining acceptable variation amounts.

The concentrations of seven fuel compounds (benzene, ethylbenzene, *tert*-butyl methyl ether, *m*- plus *p*-xylene, *o*-xylene, toluene, and xylene) were analyzed, and there were no concentrations above the minimum detection limit for either sampling method. It is not possible to determine if fuel compounds would be detected at similar concentrations.

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