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A novel high-frequency groundwater quality monitoring system

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Abstract High-frequency, long-term monitoring of water quality has revolutionized the study of surface waters in recent years. However, application of these techniques to groundwater has been limited by the ability to remotely pump and analyze groundwater. This paper describes a novel autonomous groundwater quality monitoring system which samples multiple wells to evaluate temporal changes and identify trends in groundwater chemistry. The system, deployed near Fresno, California, USA, collects and transmits high-frequency data, including water temperature, specific conductance, pH, dissolved oxygen, and nitrate, from supply and monitoring wells, in real-time. The system consists of a water quality sonde and optical nitrate sensor, manifold, submersible three-phase pump, variable frequency drive, data collection platform, solar panels, and rechargeable battery bank. The manifold directs water from three wells to a single set of sensors, thereby reducing setup and operation costs associated with multi-sensor networks. Sampling multiple wells at high frequency for several years provided a means of monitoring the vertical distribution and transport of solutes in the aquifer. Initial results show short period variability of nitrate, specific conductivity, and dissolved oxygen in the shallow aquifer, while the deeper portion of the aquifer remains unchanged—observations that may be missed with traditional discrete sampling approaches. In this aquifer system, nitrate and specific conductance are increasing in the shallow aquifer, while invariant changes in deep groundwater chemistry likely reflect relatively slow groundwater flow. In contrast, systems with high groundwater velocity, such as karst aquifers, have been shown to exhibit higher-frequency groundwater chemistry changes. The stability of the deeper aquifer over the monitoring period was leveraged to develop estimates of measurement system uncertainty, which were typically lower than the manufacturer's stated specifications, enabling the identification of subtle variability in water chemistry that may have otherwise been missed.

Keywords Water quality · Sonde · High frequency · Nitrate · Specific conductance, groundwater

Introduction

Groundwater is an essential source of drinking water in many parts of the world, and monitoring groundwater quality is important for resource protection, and may

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provide an early warning for water degradation. Groundwater quality monitoring has typically relied upon the collection of discrete samples analyzed to evaluate water quality and temporal variability (e.g., Chomycia et al. 2008; Koterba et al. 1995; Lindsey and Rupert 2012; Rupert 2008). However, data collection and analyses are labor intensive and expensive, often limiting the temporal resolution for groundwater assessments. Improvements in instrumentation and data transmission have led to the development of water quality monitoring instruments that analyze water chemistry (e.g., temperature, dissolved oxygen, specific conductance, pH, and nitrate) and transmit the data in real-time (Blaen et al. 2016; Pellerin et al. 2012), creating the opportunity for both high-frequency and long-term water quality monitoring networks (e.g., Meinson et al. 2016).

Autonomous water quality instrumentation was originally developed for oceanographic applications (e.g., Johnson et al. 2007). As the utility of such instrumentation was demonstrated, sensors have since become commonplace in surface water quality monitoring (e.g., Halliday et al. 2015). Real-time water quality data provides important information for managing and protecting the quality of water supplies (Carpenter et al. 2013), aquatic habitats (Downing et al. 2016), documenting ecosystem services (Kraus et al. 2017), and function (Snyder and Bowden 2014). Real-time water quality data is also useful to recreational users by providing information related to the presence and occurrence of harmful algal blooms (e.g., Boyer et al. 2007) and river conditions for swimming and fishing. The ability to sample frequently and over long periods has enabled routine investigation into solute transport and biogeochemical processes at rates commensurate with external forcing (Blaen et al. 2016; Kunz et al. 2017; Rode et al. 2016). Birgand et al. (2016) recently demonstrated the utility of high-frequency water quality sensors coupled to a manifold system in evaluating chemical variability at 12 different locations in a lake. While the use of high-frequency sensors in surface water studies has provided novel insights into biogeochemical processes (e.g., Etheridge et al. 2014; Lucas and Kudela 2015; Pellerin et al. 2012; Rode et al. 2016), few studies have focused on documenting high-frequency trends in groundwater quality.

Pumping groundwater for water quality sampling in aquifers with low groundwater velocities is essential to obtain representative samples for high-frequency monitoring. Time-series measurements from sensors installed inside monitoring wells suggest that in areas with low groundwater velocities, casing water, even at the screens, becomes stagnant and may not be representative of conditions in the surrounding aquifer. In addition, in situ instrumentation in supply wells is not feasible given the depth and presence of turbine impellers. While large water purveyors may have dedicated water quality monitors (e.g., SCADA (Supervisory Control and Data Acquisition)) on supply wells, these systems are purpose built for compliance of specific constituents and are therefore focused in areas with water contamination, rather than being applied to broader hydrologic studies. Previous studies have assessed groundwater quality with autonomous sampling systems. Granato and Smith (1999) developed and deployed the *Robowell*, an autonomous groundwater quality sampling system, for reactive-well monitoring in Massachusetts. In contrast to the study presented here, they limited the deployment to sub-annual time periods (weeks to months) and shallow depth (< 8 m). Opsahl et al. (2017) deployed a nitrate sensor down well in a karst groundwater system and observed rapid interactions with surface water hydrology. MacDonald et al. (2017) deployed a nitrate sensor down-well in both shallow overburden and fractured bedrock aquifers, identifying strong responses in nitrate concentration following recharge events, and resolving distinct zones of elevated nitrate by vertical profiling. Together, these studies further demonstrate the usefulness of high-frequency nitrate measurements for documenting surface water-groundwater interaction. While these efforts have successfully documented temporal changes in a single well using autonomous sensors, the approach outlined in this document enables long-term, unattended high-frequency sampling of multiple, co-located supply wells and a deep (> 30 m) monitoring well with a single set of water quality sensors to document the vertical distribution of water chemistry in the aquifers. Many monitoring wells are situated in remote locations, with no access commercial line power which has made sampling wells for continuous water quality challenging. The autonomous groundwater quality monitoring system described here can be deployed at most locations because it is based on a portable power source (solar panels and batteries). This system was developed as part of the U.S. Geological Survey National Water Quality Program trends work (https://water.usgs.gov/nawqa/studies/gwtrends/), with the aim to evaluate over what time scales groundwater quality is changing, identify drivers of those changes, and assess how this information may be better used to interpret decadal scale groundwater sampling data.

Materials and methods

Study area

The three wells instrumented for this study are located southeast of the city of Fresno, California, in the San Joaquin Valley (Fig. 1). The site is situated on the Kings River alluvial fan, a topographically low gradient area just west of the Sierra Nevada foothills. The climate in the southeastern San Joaquin Valley is Mediterranean and is characterized by hot, dry summers and cool, moist winters, with an average annual rainfall in Fresno of ~28 cm (Western Regional Climate Center 2015). Historically, land use was predominantly agricultural, but over the last 30 years has become increasingly urban, and housing developments have surrounded the wells sampled for this study.

The regional aquifer in the study area consists of three interconnected, unconfined alluvial layers: fluvial deposits of the Modesto and Riverbank Formations, coarse alluvium of the Turlock Lake Formation and North Merced Gravel, and finer grained continental sediments of the Laguna Formation (Marchand and Allwardt 1981). The alluvial fan sediments consist primarily of deposits which were derived from source materials in the Sierra Nevada during glacial episodes (Burow et al. 2007). Historic groundwater flow was from recharge along the mountain front in the east, west towards the valley axis. The city of Fresno, with

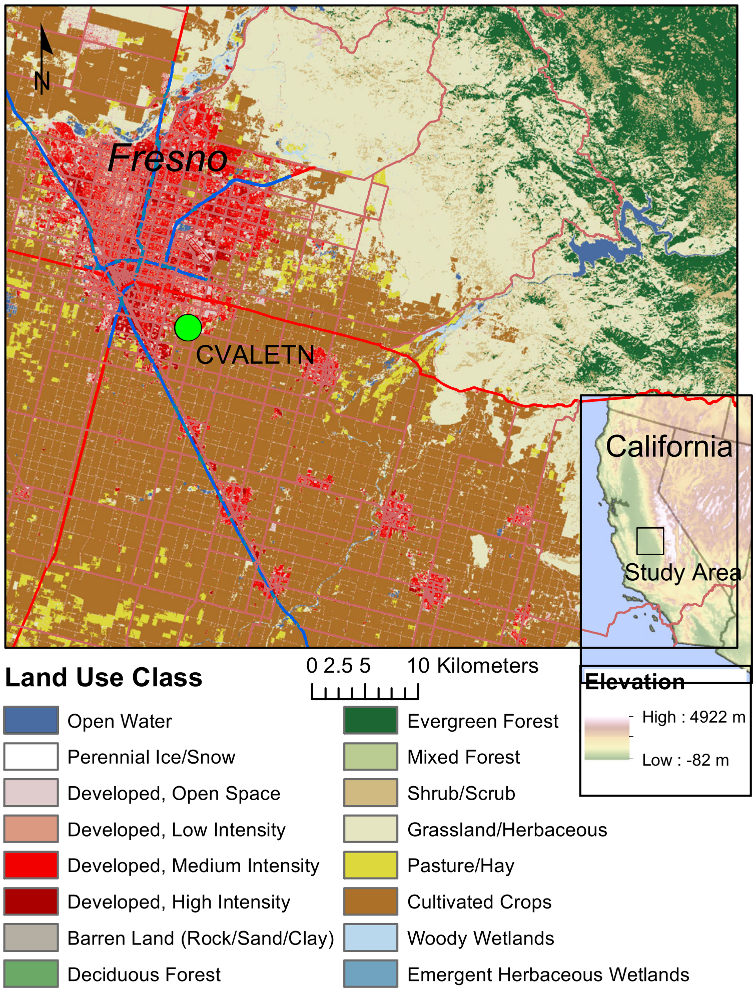

Fig. 1 Map of the southern San Joaquin Valley, California, showing the location of the Central Valley Enhanced Trends Network (cvaletn) wells, land use classes, and ground elevations

population of more than 500,000 (2013), relies almost exclusively on groundwater from this regional aquifer for its water supply (City of Fresno 2015). Groundwater flow and quality in the regional aquifer are affected by extensive agricultural and supply pumping and other land use activities. Nitrate exceeds the US Environmental Protection Agency Maximum Contaminant Levels (MCLs) in some groundwater in the area (Burow et al. 1998a; Irving and Kenneth 1987; Schmidt 1972; Wright et al. 2004) and exhibits temporal trends in concentration (Burow et al. 2007; Burow et al. 1998b; Schmidt 1972). The rates of transport of contaminants, particularly the vertical velocity, make this an ideal site to monitor the temporal variability of these compounds in the shallow and deep portions of the aquifer.

Well cluster

The three instrumented wells: one monitoring well and two supply wells represent different depths in the regional aquifer and are located within ~ 50 m laterally of one another. Two wells (CVALETN1–03 and CVALETN1–02, well depth 71 and 98 m below land surface (mbls), respectively) are screened in the Turlock Lake Formation and the North Merced Gravel (hereinafter referred to as ETN-03 and ETN-02). ETN-03, a shallow monitoring well, has a perforation interval from 65 to 68 mbls, and ETN-02, a supply well, has a perforation interval from 49 to 95 mbls and had a typical discharge rate of 1000 L per min (L/min) from September 2013 until 3 June 2014 and 1650 L/min after 1 September 2015. Historically, these wells both produce water with concentrations of nitrate > 10 mg/L (as N) (Arnold et al. 2016, 2017). The third well (supply well CVALETN1–01, hereinafter referred to as ETN-01; 189 mbls) is screened in the underlying Laguna Formation, has a perforation interval from 125 to 186 mbls, and had typical discharge rate of 1360 L/min from September 2013 until 20 April June 2015. The discharge rate was increased to 2650 L/min on 29 August 2015 and increased again to 3800 L/min on 13 January 2017. ETN-01 has concentrations of nitrate < 3 mg/L (Arnold et al. 2016, 2017).

Description of the sampling system

The autonomous groundwater quality monitoring system was designed to periodically sample the water quality of groundwater from several depths in an aquifer. The adaptable configuration lends itself to sample various combinations of well types including supply, domestic, and monitoring wells or piezometers. In the application presented here, two supply wells and one monitoring well were sampled regularly for water chemistry data using a water quality sonde and a nitrate sensor. The discharges from the supply wells were subsampled at the well head, while the monitoring well was sampled with a submersible pump. The sampling system consists of a solar panel array and charge controller, battery bank, high voltage direct current (DC) to alternating current (AC) inverter, submersible three-phase AC induction centrifugal pump, and variable frequency drive, as well as a data collection platform (DCP) that controlled system operation and transmitted water quality data to NWISWeb (Fig. S-1).

The monitoring well (ETN-03) was sampled using a Grundfos (Bjerringbro, Denmark) Redi-flo2 (RF2) submersible sampling pump coupled to a variable frequency drive (VFD). The RF2 was selected for its robust stainless steel construction, adjustable flow rate, and small (4.6 cm) outer diameter. These characteristics make the RF2 ideal for operation in 5 cm (2 in) inner diameter monitoring wells. Because the RF2's accompanying VFD was not designed for unattended monitoring, a custom system to power and operate the pump was developed. The power for the system was supplied by a 24VDC 200 Amp-Hour (Ahr) battery bank, 350 W 24 V solar panel array, a Morningstar Corporation SunSaver (Newtown, PA, USA) MPPT charge controller, and an AIMS Power (Reno, CA, USA) Global LF Series Pure Sine Wave PICOGLF20W24V230V model 24VDC to 240VAC split phase 6 kW pure sine inverter, which provided 240VAC split-phase power to the VFD (Fig. 2). An industrial VFD was selected based on the following criteria: (1) it can be started and stopped remotely, (2) it provides three-phase 220 V output with a power rating of at least 2 kW, and (3) the speed is adjustable from 0 to 400 Hz. Based on these requirements, the TECO Westinghouse (Round Rock, TX, USA) model A510 Heavy Duty AC Drive was selected.

The Campbell Scientific (Logan, UT, USA) CR1000 datalogger was selected as the DCP due to the high availability of peripheral control and sensing components, simple two-way telemetry setup, and advanced CrBasic scripting language. The DCP was programmed to control power distribution to sensors, solenoid valves, relays, high voltage, and high current contactors and to collect and store water quality data. Remote access was

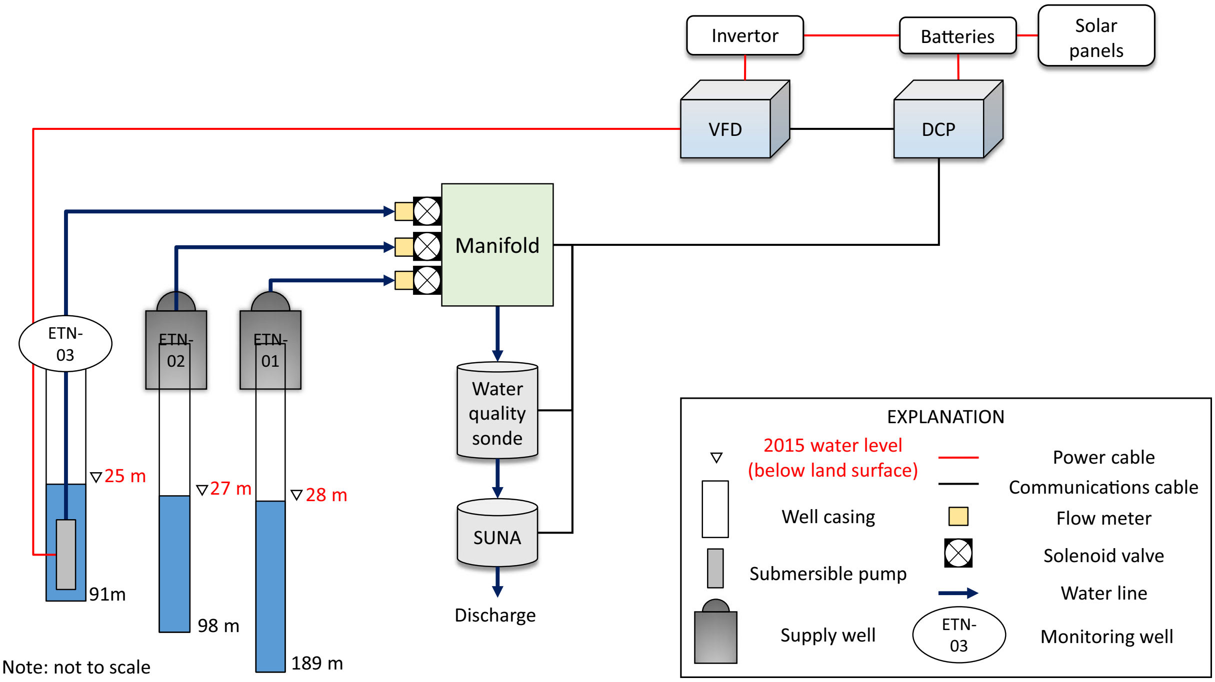

Fig. 2 Schematic of the autonomous groundwater monitoring system showing its major components including monitoring well pump configuration, variable frequency drive, sampling manifold, water quality sonde, optical nitrate sensor (SUNA), data collection platform (DCP), and power supply components

provided by a Raven XTV 3G cellular modem. The modem's power was cycled daily at midnight to prevent the occurrence of modem lockups, which can occur when the cellular signal quality (fidelity and strength) is diminished.

Power to the inverter was enabled using an in-line, 24 V, 200 A contactor (Fig. 2, Fig. S-1). Once the inverter was powered, the VFD was enabled by switching on a two-pole, 250 V, 30 A contactor. The pump was started by closing the VFD's run switch. The VFD was programmed with the RF2 pump specifications taken from the motor nameplate and operated in V/F mode. The variable frequency drive was adjusted to 330 Hz in order to calibrate the flow from the pump to an optimal 3.5 L/min of outflow to the system at 30 m of head. At this flow rate, the system consumed approximately 1300 W of electrical power at approximately 70% efficiency.

The supply wells typically operate 24 h per day, 7 days per week, and are sampled bi-hourly, with ETN-01 sampled on the even hours and ETN-02 sampled on the odd hours with the high-frequency sensors. Due to power constraints, the monitoring well (ETN-03) sampling interval ranged from daily to semiweekly depending on prevailing solar conditions. In the summer months, when solar input was high, the monitoring well was sampled on a daily interval. In the winter when weather conditions were cloudy or foggy, the sampling interval was reduced to semiweekly.

Discrete water quality samples were collected on a bimonthly basis to check and calibrate the high-frequency data and to provide analyses of additional isotopic and chemical constituents (Arnold et al. 2016, 2017). Discrete sample data for temperature, SC, DO, and pH were measured with a calibrated reference sonde (Xylem YSI EXO1). Nitrate plus nitrite (hereafter referred to as nitrate) samples were collected and analyzed at the USGS National Water Quality Lab using method 3156 colorimetry, DA, enzyme reduction-diazotization, which has a reporting limit of 0.04 mg/L (as mg/L-N) (Arnold et al. 2016, 2017). Discrete nitrate data, with associated uncertainties, are included on high-frequency plots for comparison.

High-frequency water quality monitoring protocols

Water temperature, specific conductance (SC) (electrical conductivity referenced at a temperature of 25 C), pH, and dissolved oxygen (DO) were measured at high frequency with a Xylem YSI EXO1 water quality sonde. Water temperature was measured to compensate SC, DO, and pH data for temperature dependence; however, it was not included in our analysis as it was not representative of aquifer conditions due to ambient temperature effects during water transit from the pump and well head to the sensors. Nitrate also was measured at high frequency with a Satlantic (Halifax, Nova Scotia, Canada) ultra-violet nitrate analyzer (SUNA) version two. The SUNA has a path length of 10 mm and was operated with a manufacturer provided flow cell. The SUNA was deployed in a water bath with constant circulation to minimize bias due to temperature oscillations (Pellerin et al. 2012) and to prevent SUNA overheating. Operation and maintenance of the SUNA were performed according to Pellerin et al. (2013). The SUNA exhibits a non-linear underestimate of nitrate concentration when nitrate is present > 5 mg/L (Fig. SI-3). Given the high concentration (> 10 mg/L) of nitrate in wells ETN-02 and ETN-03, it was necessary to correct for this bias. Following this correction, the sensor output was consistently ~ 1 mg/L above the laboratory measurements. Positive bias could be due to the presence of compounds that absorb in the UV spectrum. However, typical substances that absorb in the region where nitrate is detected (217–240 nm), such as sediments and DOC and salts, are present at relatively low levels in groundwater. To correct for the systematic bias, we adjusted sensor nitrate data to neighboring discrete laboratory values.

High-frequency water quality data from ETN-01 (available at: https://waterdata.usgs.gov/nwis/uv?site_no=364200119420001) was collected from 23 September 2013 until 31 December 2017. ETN-01 was inactive for two extended periods, 15 April 2015–1 October 2015 and 10 June 2016–11 October 2016. High-frequency water quality data from ETN-02 (available at: https://waterdata.usgs.gov/nwis/uv?site_no=364200119420002) was collected from 19 November 2013 until 27 September 2017. ETN-02 was not active from 2 June 2014 to 28 September 2015 and from 18 May 2016 to 27 March 2017 due to pump failure and its subsequent replacement. High-frequency data from ETN-03 (available at: https://waterdata.usgs.gov/nwis/uv?site_no=364200119420003) was collected beginning 22 April 2015 until 31 December 2017; however, tubing from the monitoring well pump to the instrumentation was disrupted and resulted in a gap in water quality data from 26 August 2016 until 9 December 2016. As part of a 10-year study, the instrumentation will be deployed from September 2013 to September 2022.

The four-way manifold is configured with three input lines and one output line and was mounted vertically on the wall to minimize the formation of bubbles (Fig. 2). The three input lines vary in distance from 9 to 30 m in length from the well head to the manifold. The input lines for the two supply wells are 0.95 cm (3/8 in) inner diameter, 1.27 cm (½ in) outer diameter, black-walled, Tygon® (Saint-Gobain Corporation, Courbevoie, France) R-3603 tubing, with foam insulation to reduce temperature effects and algal growth. The monitoring well input tubing is 0.95 cm inner diameter, Teflon-lined polyethylene, which is buried 40 cm below land surface, or encased in a 12-cm PVC conduit. All interconnections between equipment were made using 0.64 cm (1/4 in.) LinkTech Quick Couplings, Inc. (Ventura, CA, USA) 40PP Series polypropylene fittings. Starting Jan 2017, the tubing from the well head to the manifold for ETN-02 was changed to white 5/16″ PEX tubing contained in a 2 ½″ PVC conduit.

The three input lines connect to the supply wells ETN-01, ETN-02, and the monitoring well ETN-03, respectively. At each manifold port, the input line consisted of an SMC Corporation (Duluth, GA, USA) VX212DAB, 24 V normally closed solenoid valve, a GEMS (Plainville, CT, USA) FS-380P Series Flow Switch flow sensor, and a Zurn–Wilkins (Rexnord, WI, USA) brass pressure regulator (Fig. 2). The pressure regulator maintains a constant 25 psi to the flow system, just below the recommended maximum pressure for the sonde flow cell, despite fluctuations in pressure from the supply wells which may vary. Hose bibs were coupled to the outlet of the pressure regulators to adjust a constant flow rate of approximately 1.5 L/min to the instrumentation. The solenoid valves were powered and controlled programmatically by the DCP using a Campbell Scientific SDM-CD16AC relay module (Fig. S-1). The solenoid valves were operated in a mutually exclusive arrangement so that if flow is detected, one solenoid is always open at any given time to permit continuous flushing of the system instrumentation and tubing to prevent stagnation.

Water flow through the manifold was monitored to permit water quality measurements only when flow rates exceeded 1 L/min. As an additional control against sampling stagnant or city water back-flow, a magnetic air-flow deflectometer (Orion Fans AFM-01NO, Knight

Electronics, Inc., Dallas, TX, USA) was installed on each supply well and wired in series with the flow sensor switches to trigger data collection only when pumps were operating and providing water to the measurement system. The sample lines were flushed for 1 h prior to the 20-min measurement period, before switching to the next water source. A flush period of 1 h was determined to be adequate based on the stability (< 1% variance) in specific conductance readings collected at 1 hertz (Fig. S-2). Analyzed water was discharged to the sewer system as waste.

Water quality sensors were operated and maintained following Wagner et al. (2006). Water quality sensors were cleaned and calibrated every 6–8 weeks. Water quality was measured before and after sensors were cleaned to account for fouling drift. Following sensor cleaning, sensors were placed in calibration standards that bracketed the water quality conditions of the three wells to document sensor drift in between calibration visits. If the sum of the fouling and calibration drift errors was greater than the calibration criteria in Table 10 in *Wagner* et al. (2006), the record was corrected for drift using a linear correction (Wagner et al. 2006).

The data correction criteria presented in Wagner et al. (2006) are the minimum recommended uncertainties for high-frequency water quality data that is collected using approved USGS techniques. These uncertainties are, however, substantially larger than the sensor manufacturers' stated accuracies, which could be considered the minimum uncertainty as they are often determined in a controlled laboratory setting. The total measurement uncertainty for a given water quality parameter is likely a combination inherent sensor uncertainty as stated by the manufacturer plus the uncertainty associated with deployment, operation, and maintenance techniques. Because sensors are typically deployed in sites with natural variability, it is often very difficult to quantify a measurement systems total uncertainty. Given the high stability of the water chemsitry of ETN-01, as indicated by the lack of deviation of discrete grab samples from the median value, sensor performance at this site was used to estimate the high-frequency measurement system's operational uncertainty for measuring SC, DO, and pH and nitrate.

The water quality monitoring system's operational measurement uncertainty for each parameter was calculated as two times the median absolute deviation (MAD) over the entire monitoring period (Possolo 2015). Given the large difference in SC between wells (~ 300%), the uncertainty of SC is given as a percentage by normalizing the MAD by the median value and multiplying by 100. The operational measurement uncertainty for each parameter is listed in Table 2.

We operated and maintained the SUNA v2 optical nitrate sensor following Pellerin et al. (2013), though sensor drift was negligible over the study period. The nitrate sensor malfunctioned due to water ingress into the spectrometer and was therefore substituted with a SUNA v1 from 12 May 2016 to 23 August 2016 while the SUNA v2 was repaired and upgraded to a titanium body following a manufacturer recall.

High-frequency water quality data collection was halted when the flow rate fell below 1 L/min, or when battery voltage was below 9 V DC, during periods of low solar radiation. These conditions affected less than 1% of the data. Using pumping records from the City, data was excluded from the record if it was collected on days when the supply well pump was shut down for any part of the data and for any reason. Data spikes were removed from the record throughout. A data spike was identified as a spike and removed from the record if it exceeded the data–correction criteria presented in Table 10 in Wagner et al. (2006) relative to neighboring data points. For example, if the dissolved oxygen exceeded 0.3 mg/L relative to a neighboring value, it was removed from the record. For all parameters, the despiking process resulted in the elimination of less than 5% of the data points.

For the supply wells (ETN-01 and ETN-02), the EXO1 sonde measured DO, pH, and SC following the 1-h purge period. The daily median value is presented at midnight, and typically included 6–12 groups of samples collected throughout the day. For the monitoring well (ETN-03), the water quality sonde was sampled every minute for 30 min following a 70-min period of purging water from the well; the volume of water withdrawn (i.e., purge volume) typically represented three casing volumes. For SC, pH, and DO measured in ETN-03, the daily median value was the median of 30, 1-min burst data collected in the morning, typically 0910 to 0940 PST. For both the monitoring and supply wells, burst data for the nitrate monitor was only collected for 30 s (20–30 samples) at the end of the well sampling period due to limitations of sensor lamp overheating. For the monitoring well, ETN-03, the median of the 30-s burst was the basis for the daily median values because the well was sampled at most once per day.

The gray shading around the measured values (Figs. 3, 4, and 5) for SC, pH, and DO reflect the uncertainties listed in Table 10 from Wagner et al. (2006), which are set at 3%, 0.2, and 0.3 mg/L, respectively. The discrete samples were collected with the same model of water quality sonde as the sensor data; hence, the uncertainties for SC, pH, and DO (red bars Figs. 3, 4, and 5) also reflect the values from Table 10 (Wagner et al. 2006). For optical nitrate (Fig. 6), the manufacturer's stated uncertainty (gray shading) is ± 10% (Pellerin et al. 2013). The discrete sample nitrate uncertainty (red bars) is 3% (Arnold et al. 2016, 2017).

Results and discussion

Time series plots of the water quality parameters at each well were generated to evaluate the temporal variability in groundwater quality (Figs. 3, 4, 5, and 6). These plots include the uncertainties discussed in the preceding section; the gray bands are manufacturer's stated uncertainties and the green bands are the operational measurement uncertainties determined in this study using the stable water chemistry of ETN-01. Upon inspection, the uncertainty bands of the SC, pH, DO, and nitrate high-frequency data and the discrete data overlap, showing, in most cases, good agreement; confirming the accuracy of the high-frequency data from the autonomous instrumentation.

The median of the high-frequency and discrete data for each parameter were calculated for each well (Table 1) and plotted as solid lines: red for the discrete sample median and black for the high-frequency data median (Figs. 3, 4, 5, and 6). The high-frequency data and discrete data were then compared to these median value lines. When the associated error bars of the high-frequency and discrete parameter values overlap the median value lines, no temporal variability or trend is discernable. However, when either data set diverge from the median lines, this indicates a change in water quality and may represent short period variability or longer temporal deviations from steady-state conditions.

Specific conductance, pH, and dissolved oxygen variability

The water quality of the deep well, ETN-01, exhibited the least amount of variability of the three wells

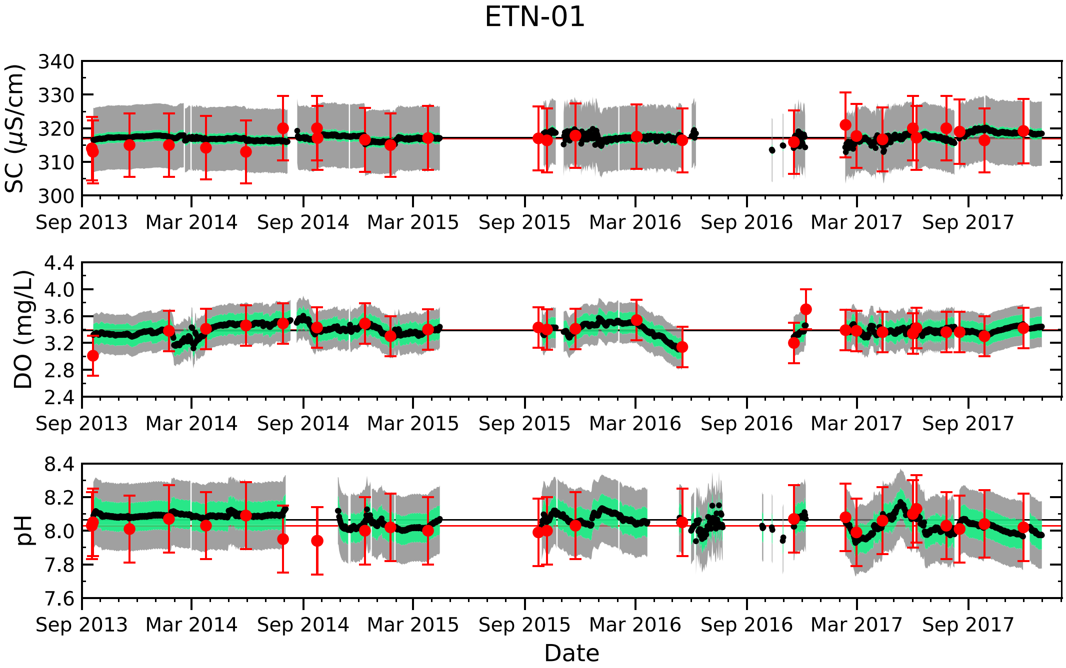

Fig. 3 High-frequency daily median (black dots) and discrete (red dots) water quality time series from the deep production well ETN-01. Gray and green bands surrounding the high-frequency data indicate manufacturer's stated and operational measurement uncertainty, respectively, as defined in the text. The red bars adjoining the discrete data indicate laboratory measurement uncertainty. Horizontal black and red lines indicate the median value for the period for the high-frequency and discrete data, respectively. No trends were identified by high-frequency or discrete measurements at this site

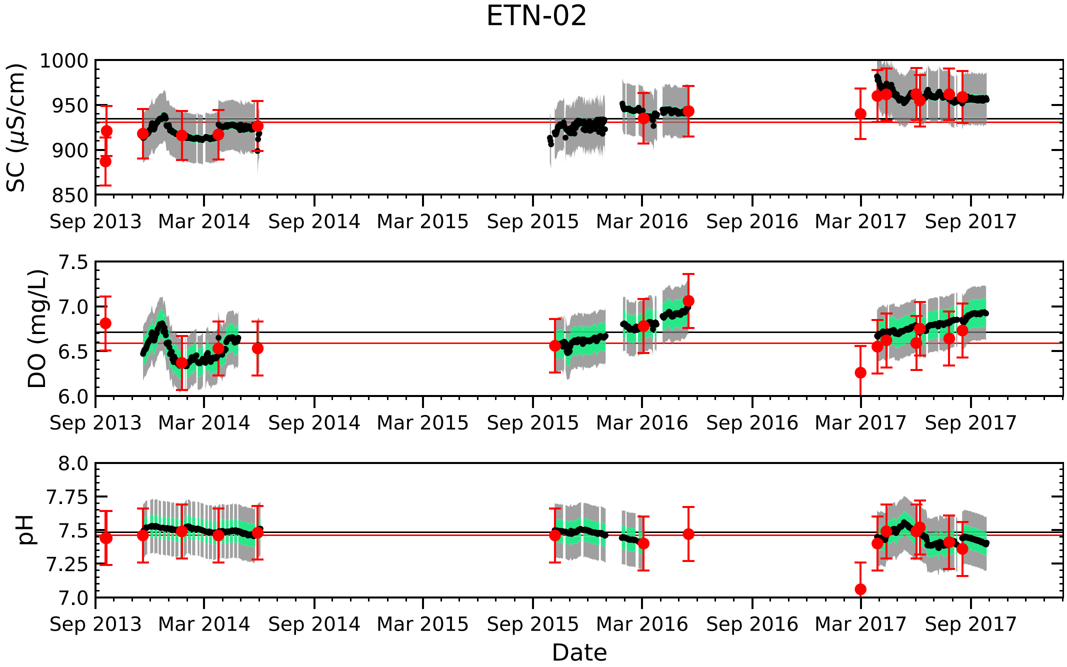

Fig. 4 High-frequency daily median (black dots) and discrete (red dots) water quality time series from the shallower production well ETN-02. Gray and green bands surrounding the high-frequency data and red bars adjoining the discrete data are ± error bars as defined in the text. Horizontal black and red lines indicate the median value for the period for the high-frequency and discrete data, respectively

monitored in this study. SC, DO, and pH did not deviate much from the median lines indicating the lack of short-period variability or trends (Fig. 3) during the study period. SC remained invariant over the

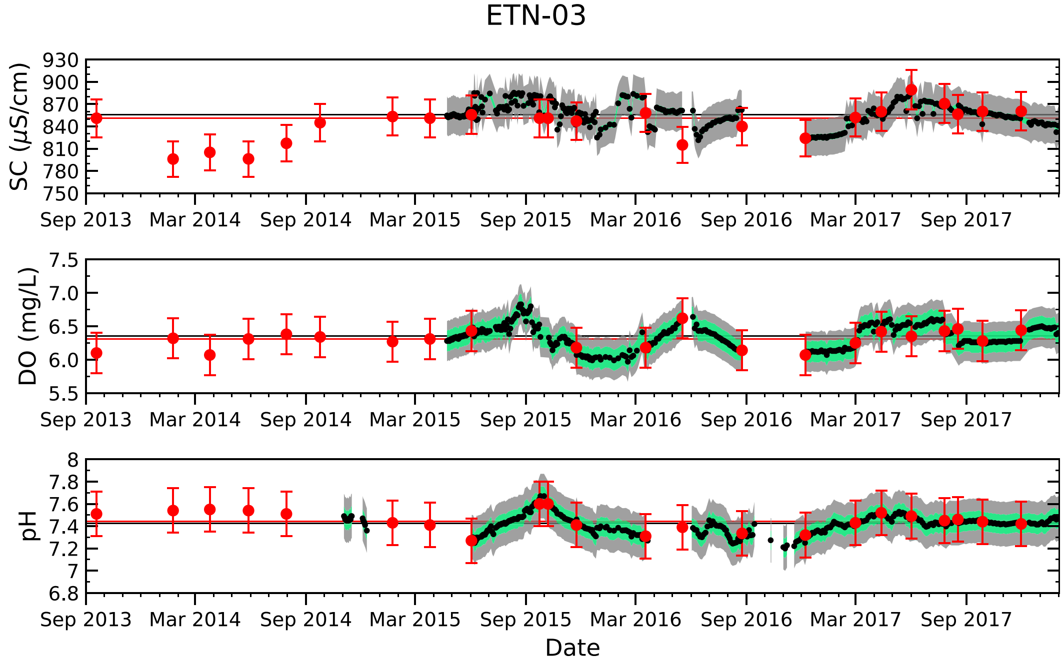

Fig. 5 High-frequency daily median (black dots) and discrete (red dots) water quality time series from the shallow monitoring well ETN-03. Gray and green bands surrounding the high-frequency data and red bars adjoining the discrete data are ± error bars as defined in the text. Horizontal black and red lines indicate the median value for the period for the high-frequency and discrete data, respectively

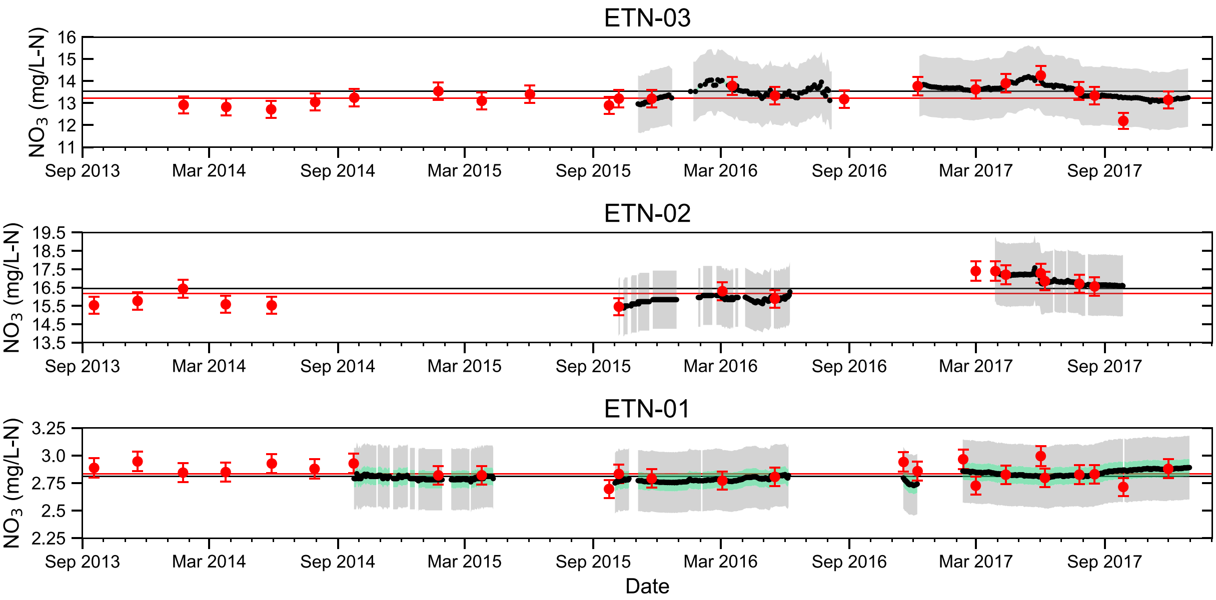

Fig. 6 High-frequency daily median (black dots) and discrete (red dots) nitrate concentration for the three wells ETN-01, ETN-02, and ETN-03. Gray bands adjoining the high-frequency data indicate ± 10% while the green bands indicate 0.09 mg/L, as determined in this study. Red bars above and below the discrete data indicate ± 3%

4-year record, near 317 µS/cm, as did the DO and pH at 3.4 mg/L and 8.1, respectively (Table 1). From the high-frequency data, it is possible to observe that no short period variability occurs in this record, something that could not be confirmed with discrete sampling, and groundwater quality in the deep production well was nearly constant over the 4-year record. This observation is perhaps not surprising given the depth of the well screen and aquifer lithology and is likely a result of long groundwater residence times. We used the natural stability in well ENT-01 to estimate our operational measurement uncertainty and found it to be equal to, or smaller than the manufacturer's stated uncertainty (Table 2).

At well ETN-02, SC and DO exhibited short period variability and trended higher over the period of record. The high-frequency and discrete data did not diverge from their respective median lines if the manufacturer stated uncertainties (gray bands in Fig. 4) are adopted; however, variability was identified when the operational measurement uncertainty (green bands Fig. 4) was applied. At ETN-02, SC increased from 899 µS/cm in 2013 to 982 µS /cm in 2017, with the maximum in April 2017. DO showed more variability than SC between 2013 and 2017, with a minimum in January 2014, and a maximum in May 2016, increasing from 6.3 to 7.0 mg/L. The pH was relatively invariable from 2013 to 2016 with a median value of 7.5 (Table 1). The first sampling event in 2017, after a long period during which the pump was replaced, had values of SC, DO, and pH which were lower than the median values of both the discrete and high-frequency

Table 1 Median water quality data for high-frequency sensor and discrete samples

Well name	Measurement type	SC (µS/cm)	pH	DO (mg/L)	Nitrate (mg/L-N)
ETN-01	Discrete	317	8.03	3.4	2.83
	High frequency	317	8.07	3.4	2.81
ETN-02	Discrete	940	7.46	6.6	16.40
	High frequency	935	7.48	6.7	16.18
ETN-03	Discrete	851	7.46	6.3	13.20
	High frequency	857	7.41	6.3	13.50

Table 2 Water quality measurement system operational uncertainty determined from median daily value water quality data collected at ETN-01 for the entire period of record

Water quality parameter	Operational measurement uncertainty = (2 * median absolute deviations)	Number of daily median values	Units
Specific conductance	0.51	1104	%
Dissolved oxygen	0.16	1103	mg/L
pH	0.01	1040	
Nitrate	0.09	758	mg/L

data, and probably do not represent aquifer conditions. Variability in the shallower well ETN-02 may be driven by trends in precipitation or pumping and the communication of the younger, shallower groundwater with the land surface.

Water quality in the monitoring well ETN-03 exhibited short period variability, likely seasonal in nature (Fig. 5). SC measured at high frequency varied from ~ 821 to ~ 885 μS/cm and has maxima in August 2015, February 2016, and May 2017, and minima in December 2015, June 2016, and December 2017. The higher frequency variability of water quality in this well was not apparent in discrete sample record. The DO also exhibited short period variability, with maxima in August of 2015, June 2016, and July 2017, and minimum in January and February of 2016 and 2017. The DO seasonal signal would have been missed if not for the continuous, high-frequency record. At ETN-03, pH has maximum in October 2015, July 2016, and May 2017. ETN-03 water chemistry did not exhibit any apparent trends, but did exhibit short period variability that was not identified in the discrete data, demonstrating the utility of autonomous instrumentation in documenting short-term variability in groundwater quality. Assessing trends in water-quality data exhibiting seasonal variability requires applying seasonal Kendall statistics and will be the subject of future data analyses.

Nitrate variability

Nitrate concentrations range from 2.73 mg/L in the well with the deepest perforations (ETN-01; 125 mbls) to 17.58 mg/L in the well with the shallowest perforations (ETN-02; 49 mbls); high nitrate concentrations likely result from historical and current agricultural land use surrounding the study site (Fig. 1). High-frequency nitrate data for all three wells overlap with the median lines when the manufacturer's stated uncertainty (± 10%) is adopted, resulting in no discernable variability or trends in the data (Fig. 6). However, if the operation uncertainty bands (green bands in Fig. 6) are adopted, then short-term variability and longer-term trends become apparent in the shallow wells. Nitrate values (discrete and high-frequency) in the deep well (ETN-01) do not deviate from the median lines, and thus do not exhibit trends or short-term variability. The nitrate data (discrete and high frequency) vary from 15.39 to 17.58 mg/L in well ETN-02 and from 12.93 to 14.20 mg/L in well ETN-03, suggesting that there is a trend of increasing nitrate concentrations and that the manufacturer's uncertainty for the high-frequency data may be overestimated. Rather, if the operational measurement uncertainty of ± 0.09 mg/L (nitrate) is adopted, then short period variability, as well as longer-term trends in high-frequency nitrate data, become apparent.

Nitrate is highest in ETN-02 which has the shallowest perforations (49 to 95 mbls) and overlaps the perforation interval of ETN-03 (65 to 68 mbls). One explanation for the vertical distribution of nitrate is that ETN-02 may draw in young, shallower groundwater that is high in nitrate, while ETN-03 has a deeper, shorter perforation interval, and samples older, deeper, lower-nitrate groundwater. This explanation is also supported by the SC and DO data discussed previously; ETN-02 has higher SC and DO values than ETN-03, which could be explained by its sampling shallower, higher SC, and nitrate groundwater that has more recently been at the land surface and subjected to agricultural land-use practices (Fig. 1).

High-frequency data provide greater resolution of temporal fluctuations in water chemistry, which helps to identify the drivers for groundwater chemistry change and help confirm longer-term trends. Preliminary analysis identified trends such as the increase in DO and SC in well ETN-02, which may be explained by the downward movement of water more recently exposed at the surface and rich in DO and higher in nitrate and SC. ETN-03, which is perforated deeper than ETN-02, but over a shorter interval, has lower SC and nitrate and exhibits sensitivity to short period variability in water chemistry. ETN-01, the deep supply well with a long perforation interval, had low concentrations of nitrate, SC, and DO, and high pH suggesting that it is isolated from short period changes in water chemistry and exhibited no trends in water quality.

While short period changes are mostly apparent in the shallow well ETN-03, high-frequency data from other hydrogeologic settings, particularly karst aquifers, may respond to precipitation events on the order of hours to days (Opsahl et al. 2017), and such changes in groundwater chemistry may only be captured by autonomous water quality sampling instrumentation. Moreover, comparisons of high-frequency time-series analyses between different hydrogeologic settings will provide insights on which settings are most appropriate for high-frequency measurements. Despite the similarity of water quality behavior captured by continuous and discrete sampling during the period and setting reported in this paper, over time and with development, the autonomous system may be more cost-effective than discrete sampling in some situations as well as providing data on episodic events that are not captured by scheduled discrete sampling events.

Conclusions and recommendations

An autonomous groundwater quality monitoring system was developed to sample three wells near Fresno, California, to evaluate temporal changes and identify trends in groundwater chemistry. The system collected and telemetered high-frequency data for over 4 years, including temperature, specific conductance, pH, dissolved oxygen, and nitrate, from supply and monitoring wells, in real-time. The system consists of a water quality sonde and optical nitrate sensor, multiway manifold, submersible pump and variable frequency drive, data collection platform, solar panels, and rechargeable battery bank.

High-frequency data provided greater temporal resolution of fluctuations in water chemistry than discrete field samples. The vertical distribution and transport of solutes in the aquifer were identified by patterns in the short period variability and longer-term trends of solutes in the aquifer. Nitrate, specific conductivity, and dissolved oxygen exhibited short period variability in the shallow aquifer, while the deeper portion of the aquifer remained unchanged. The difference in variability between the three wells likely reflects different connectivity with the surface, which is strongly influenced by the hydrogeologic setting. In shallow systems, fractured bedrock, or karst systems, where groundwater velocities are greater, high-frequency monitoring may identify variability missed by discrete sampling programs. Results from the groundwater monitoring also indicate that the shallow aquifer had higher nitrate, SC, and DO than the deeper aquifer, which could be explained by the more recent communication of shallow water to the land surface and exposure to agricultural land-use activities. In addition, nitrate concentrations in the shallow aquifers sampled by wells ETN-02 and ETN-03 are increasing, while the deep aquifer remains constant at low levels.

This study found that using one set of instrumentation reduces the cost of maintaining a water quality monitoring system in several ways. First, there is an immediate savings in up-front capital costs. Second, there is ongoing savings in the operation and maintenance of fewer sensors. There is a trade-off, however, if a sensor malfunctions, then data is interrupted at all stations that rely upon it. This problem also applies if there is sensor drift; it would likely affect all stations similarly. In addition, the water chemistry among wells may vary markedly, and a sensor must be calibrated and stable over a large dynamic range. Sensor specifications and calibration protocols should be carefully scrutinized prior to using a single sensor to sample many wells that differ greatly in the concentration and range of solutes. This difficulty is likely overcome by comparison to measurements collected on frequent discrete samples. Further, cycling between multiple water sources with a single set of instrumentation requires equilibration time prior to sampling, which necessarily impacts the minimum sampling rate. In this study, the equilibration time mandated that we sample the production wells at a bihourly rate. However, the equilibration time is expected to vary according to contrasts in water chemistry between sampling locations.

As this project continues, analysis of the high-frequency data in comparison with pumping rates, water levels, and other well operational variables may provide additional insight about how changes in hydrologic conditions affect short-term variability in water chemistry. Although the autonomous water quality system routinely collected high-frequency data over the course of several years, several challenges were encountered including sensor reliability, pump failure, and monitoring pump power supply requirements. The system was specified to sample the monitoring well daily. However, given lower than expected power system efficiency, it was only possible to sample the monitoring well two to three times a week depending on solar conditions. This was especially true during the winter months when cloud cover and fog were frequent. Based on our actual system efficiency, we recommend a solar system of 1200 to 1500 W in order to sample the monitoring well every day despite solar conditions.

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