Factors affecting temporal variability of arsenic in groundwater used for drinking water supply in the United States

Joseph D. Ayotte [a,*], Marcel Belaval [b], Scott A. Olson [a], Karen R. Burow [c], Sarah M. Flanagan [a], Stephen R. Hinkle [d], Bruce D. Lindsey [e]

[a] U.S. Geological Survey, 331 Commerce Way, Pembroke, NH 03275, USA
[b] U.S. Environmental Protection Agency, Boston, MA, USA
[c] U.S. Geological Survey, Sacramento, CA, USA
[d] U.S. Geological Survey, Portland, OR, USA
[e] U.S. Geological Survey, New Cumberland, PA, USA

HIGHLIGHTS

- Arsenic concentrations mostly vary by small amounts but in many wells vary substantially.
- Variability due to sampling and analysis is controlled by careful use of replicate sample data.
- Concentrations in public supply wells vary more than in private domestic wells.
- The overall variability appears related to seasons of the year, implying potential process controls.
- The most variable concentrations relate to variation in geochemical conditions.

ARTICLE INFO

ABSTRACT

The occurrence of arsenic in groundwater is a recognized environmental hazard with worldwide importance and much effort has been focused on surveying and predicting where arsenic occurs. Temporal variability is one aspect of this environmental hazard that has until recently received less attention than other aspects. For this study, we analyzed 1245 wells with two samples per well. We suggest that temporal variability, often reported as affecting very few wells, is perhaps a larger issue than it appears and has been masked by datasets with large numbers of non-detect data. Although there was only a slight difference in arsenic concentration variability among samples from public and private wells ($p = 0.0452$), the range of variability was larger for public than for private wells. Further, we relate the variability we see to geochemical factors—primarily variability in redox—but also variability in pH and major-ion chemistry. We also show that in New England there is a weak but statistically significant indication that seasonality may have an effect on concentrations, whereby concentrations in the first two quarters of the year (January–June) are significantly lower than in the second two quarters (July–December) ($p < 0.0001$). In the Central Valley of California, though not statistically significant ($p = 0.4169$), arsenic concentration is lower in the first quarter of the year but increases in subsequent quarters. In both regions, these changes appear to follow groundwater levels. It is possible that this difference in arsenic concentrations is related to groundwater level changes, pumping stresses, evapotranspiration effects, or perhaps mixing of more oxidizing, lower pH recharge water in wetter months. Focusing on the understanding the geochemical conditions in aquifers where arsenic concentrations are concerns and causes of geochemical changes in the groundwater environment may lead to a better understanding of where and by how much arsenic will vary over time.

Published by Elsevier B.V.

1. Introduction

The problem of the occurrence of arsenic in groundwater has gained worldwide attention, and studies in high-exposure regions of the world have established its human carcinogenicity (Smedley and Kinniburgh, 2002). Additional health effects have been increasingly linked with arsenic exposure, including associations with diabetes, heart disease, and H1N1 viral susceptibility (Kozul et al., 2009). One aspect of the arsenic environmental hazard problem that has not been well characterized is the degree to which temporal variability occurs in well water. Temporal variability of concentrations of arsenic in drinking water is a potential

concern for human-health studies in which long-term exposure is often based on one arsenic measurement to represent 20 or more years of use of drinking water from wells (Karagas et al., 1998; Nuckols et al., 2011). Temporal variability may also pose challenges for water treatment practices where municipalities or private well owners seek to reduce arsenic concentrations. Although studies have reported the presence or absence of temporal variability of arsenic in public or private groundwater supplies, emphasis to date has been on documentation of the presence or absence of variability, and these studies often lack conclusive evidence of trends or controls on variability (Ayotte et al., 2003; Belitz et al., 2003; Burgess et al., 2007; Cheng et al., 2005; Erickson and Barnes, 2005; Focazio et al., 2000; Hinkle and Polette, 1999; Karagas et al., 2001; Meliker et al., 2007; Nadakavukaren et al., 1984; Ravenscroft et al., 2006; Seiler, 2004; Sengupta et al., 2006; Sorg et al., 2014; Steinmaus et al., 2005; Thundiyil et al., 2007). Most studies reveal that, for water from the vast majority of wells, arsenic concentration is not particularly variable; however, some reveal significant fluctuations over time. Often, the ability to explain variation is limited due to small numbers of samples exhibiting significant variability. Furthermore, although some studies suggest that a number of wells show variability that is significant, it is unclear what factors or mechanisms are associated or controlling.

In the United States, governmental agencies recommend testing private water supplies for various contaminants on a periodic basis (usually 1–3 years) to determine whether concentrations are changing (U.S. Environmental Protection Agency, 2010). This recommendation is intended to be protective of public health and the 1–3 year frequency is assumed adequate to detect any changes in concentrations before exposure risks become elevated; however, the extent to which these recommendations are successful is unclear. Public water supplies in the United States are subject to the protections of the Safe Drinking Water Act, which requires periodic testing of water for arsenic, the frequency of which is predetermined but can be reduced when arsenic concentrations are substantially lower than the maximum contaminant level (MCL) of 10 μg/L (U.S. Environmental Protection Agency, 2001). The lack of more detailed information on temporal variability may reflect the prevailing focus on occurrence and distribution of arsenic in groundwater used for drinking water (particularly private domestic supplies) and on the perception that variability over time is generally low.

Variation in concentrations of arsenic in groundwater may arise in response to natural or anthropogenic factors. Natural variation in arsenic concentrations might be expected to occur in response to climatic and seasonal changes such as wet and dry periods (Berg et al., 2001; Cheng et al., 2005; Nadakavukaren et al., 1984), however, these factors have rarely been directly linked to variation in arsenic concentrations (Thundiyil et al., 2007). Studies that have identified seasonal signals in arsenic concentrations frequently have been unable to identify whether correlations between arsenic variability and seasonal effects reflect advection of seasonal fluxes of recharge through aquifers (seemingly at odds with the fact that dispersion tends to smooth out such fluxes in many groundwater systems) or seasonally varying pumping stresses on aquifers. Anthropogenic factors that may affect arsenic variability may be more complex and include land development, addition of solutes to the groundwater system (Harte et al., 2012), or human-induced flow-system changes, including well development, groundwater pumping, or aquifer storage and recovery (Ayotte et al., 2011; Focazio et al., 2000; Gotkowitz et al., 2004; Katz et al., 2009; Price and Pichler, 2006; Schreiber et al., 2003). It is also unclear whether natural processes can cause significant or widespread changes in arsenic concentration in groundwater over periods of weeks to years. Indeed in many studies of temporal variability of arsenic, identification of systematic variability has been elusive (Focazio et al., 2000; Hinkle and Polette, 1999; Mackenzie et al., 2000; Sorg et al., 2014). The objectives of this study are (1) to characterize the amount of temporal variability of arsenic in groundwater using existing data from wells used for drinking water, collected at various time scales, and (2) for wells that vary significantly, to examine factors that may relate to the cause of variability such that potential controlling processes can be identified.

2. Data and methods

2.1. Well selection

This study evaluates five independent datasets of arsenic concentrations in well water used for drinking-water supply, mostly from New England but also from California and other parts of the United States. The datasets are from (1) U.S. Geological Survey (USGS) National Water-Quality Assessment Program (NAWQA) private domestic and public wells across the United States, (2) private domestic wells in the Lamprey River basin in southeastern New Hampshire, (3) public wells in New England, (4) private domestic wells near the Mottolo Superfund site in southeastern New Hampshire, and (5) private domestic wells in southeastern New Hampshire (Fig. 1; Table 1). The datasets were chosen because of interest in arsenic variability in New England and elsewhere as well as based on the quality of data. The nationwide data from NAWQA were included because they add national context and were of high quality, meaning that the data were well suited for comparison of concentrations within a well.

In all, data were compiled from 1245 public and private drinking water wells with temporal data (Supplemental information). The data cover spatial scales ranging from regional to local and temporal scales of sample collection ranging from less than one year to more than a decade. Most wells had only two samples, although a small percentage had additional samples; as such, only two-sample comparisons were made for this study. Some data were for filtered samples, but most samples were not filtered, owing to the fact that they were drinking water wells; only filtered-to-filtered or unfiltered-to-unfiltered sample comparisons were made.

All analyses had a laboratory reporting level less than or equal to 1 μg/L and a common reporting level was used on a per sample pair basis. Where concentrations were reported as less than 1 μg/L, a value of 1 μg/L was assumed to be the actual value; this had the conservative effect of rendering many of the comparisons within wells to be within noise limits associated with random sampling and analysis error. Samples were collected according to protocols associated with each study, but typically water was collected from just ahead of the pressure tank (in domestic well settings) or from the designated sampling spigot (public wells) into acid-rinsed polyethylene bottles and preserved with nitric acid to a pH of less than 2. The NAWQA samples were analyzed according to various methods, using inductively coupled plasma (ICP) atomic-emission spectrometry, ICP mass spectrometry, graphite-furnace atomic absorption (AA) spectrometry, and hydride generation AA (Faires, 1993; Fishman and Friedman, 1989; Garbarino, 1999; Ivahnenko et al., 2001). All other samples were analyzed using U.S. Environmental Protection Agency (EPA) method 200.8 (U.S. Environmental Protection Agency, 1994). The individual datasets used in this study are described in more detail below.

For the USGS NAWQA dataset, two samples each were collected from 312 public and private wells in major aquifers across the United States about 10 years apart from 1993 to 2010 (Fig. 1). Samples were collected through a 0.45 μm filter according to the same protocols and analyzed at the USGS National Water-Quality Laboratory (Koterba et al., 1995; Lapham et al., 1995).

For the Lamprey River basin dataset, two samples each were collected from 148 domestic wells in bedrock across the basin (about 475 km^2) from June to September 2004 and May to June 2005. The unfiltered water samples from drinking-water taps were analyzed at the New Hampshire Department of Environmental Services (NHDES) Laboratory, at an EPA contract laboratory, and the EPA National Air and Radiation Environmental Laboratory.

For the New England public wells dataset, 2 to 29 measurements per well were obtained for 607 public wells in bedrock from 1995 to 2008.

Locations of wells used in this study

A

MAXIMUM ARSENIC CONCENTRATION, ug/L

National Water Quality Assessment Program Domestic and Public-Supply Wells

○ < 1.0

● 1 to 10

● > 10

☐ Conterminous United States

B

MAXIMUM ARSENIC CONCENTRATION, ug/L

○ < 1.0

● 1 to 10

● > 10

Data source

Private Domestic Wells

☐ Lamprey River Basin

◊ Mottolo Superfund

△ Southeast New Hampshire

Public-Supply Wells

○ New England Public-Supply Wells

☐ New England, United States

New Hampshire

Maine

Vermont

Lamprey River Basin

Mottolo Superfund

Massachusetts
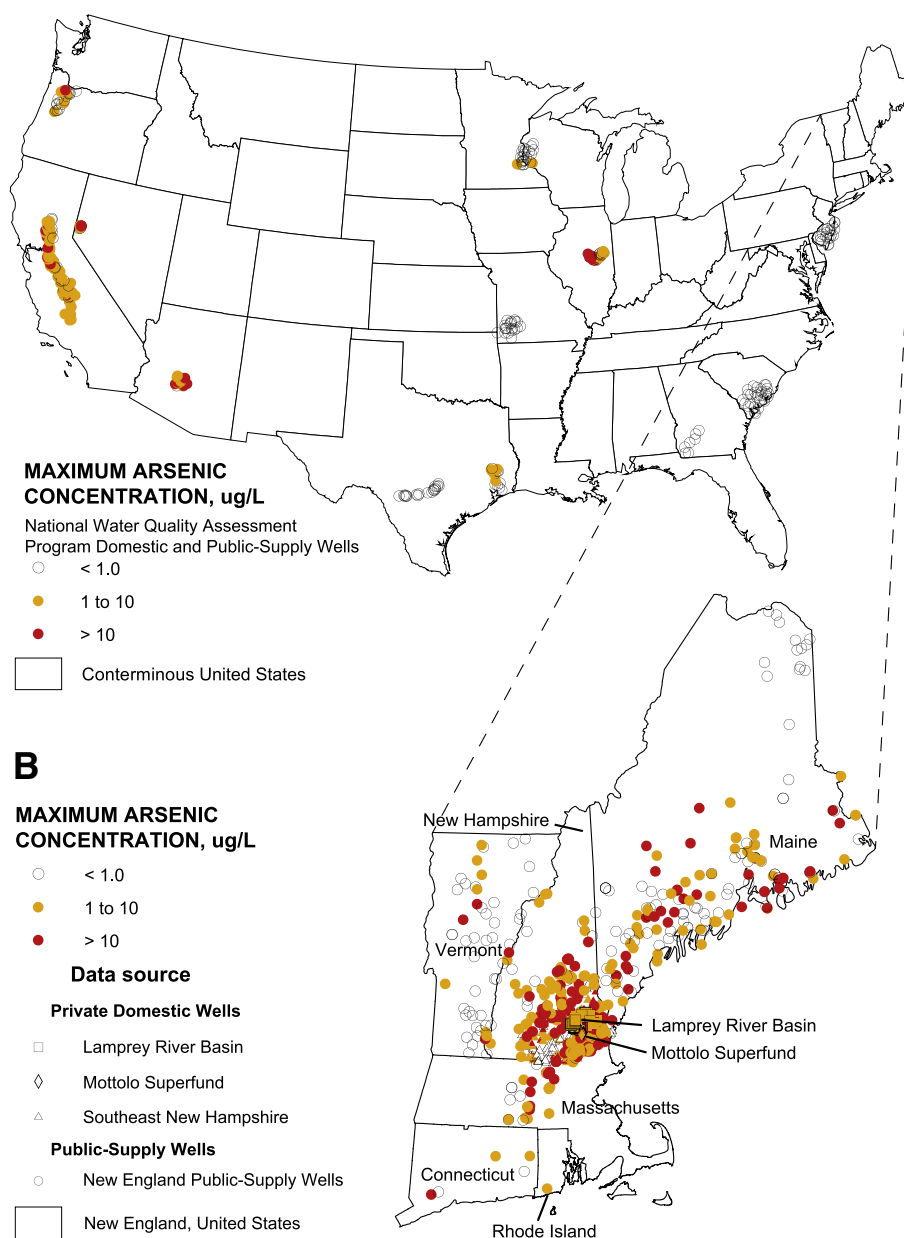
Connecticut

Rhode Island

Fig. 1. Locations of wells and maximum concentrations of arsenic for wells with temporal arsenic data in A, the United States and B, New England. Wells are colored by concentration range and symbols (in B) denote data source.

For wells with three or more measurements, the two most recent were used. The average time between measurements was 2 years to comply with monitoring frequency requirements for inorganic contaminants specified by regulations under the authority of the Safe Drinking Water Act (40 CFR §141.23).

For the private wells dataset near the Mottolo Superfund site, two (and occasionally 3) unfiltered samples were obtained from 35 private wells in bedrock from June 2009 to June 2010 and were analyzed at the NHDES Laboratory. Some wells are affected by anthropogenic contamination from former disposal of organic and nitrogen waste (New Hampshire Department of Environmental Services, 2010).

For the southeastern New Hampshire dataset, two unfiltered samples were collected from 143 domestic wells in bedrock in 2002 and 2012. Samples were collected by homeowners according to detailed

instructions provided with sample bottles. The USEPA region 1 Laboratory analyzed the samples.

2.2. Development of variables

Variables were developed for the analysis of potential factors that affect temporal variability of arsenic in water from wells. In particular, variables that are surrogates for changes in redox processes, such as changes in iron, manganese, and dissolved oxygen, were used to relate redox changes to changes in concentrations of arsenic. Well water pH also was used. For some wells, changes in concentrations of major ions were used to indicate changes in groundwater chemistry. Because most of the data on arsenic were originally collected for other purposes and were compiled retrospectively for this study, they do not generally

Table 1
Summary of differences in arsenic concentrations based on two samples per well.
[LRB, Lamprey River Basin; MOT, Mottolo Superfund Site; PSW, New England public-supply wells; NAWQA, National Water Quality Assessment Program; SNH, Southern New Hampshire].

Data source	Range of years for samples	Percent of wells with arsenic ≥ 1 in both samples	Number of wells	Arsenic difference, in micrograms per liter												
				Mean	Minimum	Percentile										Maximum
						1st	5th	10th	25th	50th	75th	90th	95th	99th		
Private domestic wells																
LRB	2003–2005	54.7	148	0.5	−5	−5	−1	0	0	0	0	2	3	5		37
MOT	2009–2010	88.6	35	25	−57	−57	−42	−11	−2.4	−0.4	0	8	23	1000		1000
NAWQA	1993–2008	45.2	290	−0.1	−11	−8	−2	−1	0	0	0	1	1.5	6		15
SNH	2003–2013	58.7	143	−0.1	−16	−7.9	−5.1	−3.5	−0.31	0	0.43	1.3	3.1	17		30
Public-supply wells																
NAWQA	1994–2007	68.2	22	3.0	−5	−5	−5	−4	−2	0	0	0	1	90		90
PSW	1995–2008	60.6	607	8.5	−73	−22	−9	−4	−1	0	0	2	4	46		3000
All data	1993–2013	57.0	1245	4.9	−73	−16	−6	−2.6	0	0	0	1	3	29		3000

contain consistent types of information across datasets. For example, the Lamprey River basin dataset contains data on pH, dissolved oxygen, and specific conductance along with concentrations of arsenic, whereas the datasets of the public well generally contain only data on iron and manganese.

In New England, the estimation of water-level conditions under which a sample was collected was based solely on the date of sample collection, as it pertains to typical groundwater levels. For this classification, samples were divided into quarters of the year based on the sample date. In general, the third and fourth quarters of the year have the greatest depths to groundwater, and the first and second quarters have shallower depths to groundwater. In this way, the hydrologic condition was inferred based on typical hydrographs of monthly groundwater levels. For most of the wells that were sampled as part of the NAWQA program, water level data were available, and these data were used directly. One hypothesis is that variability in arsenic concentrations may be related to variability in groundwater levels, which may in turn be indicative of time-varying proportions of contributions of water from different parts of the aquifer to wells. Water levels tend to be shallowest in the winter and spring months and deepest in the summer and fall months, and arsenic concentrations, if collected during each of these time periods at the same well can be compared.

2.3. Statistical analyses

Datasets generally had two samples per well except for a small number of public wells in New England and wells at the Mottolo Superfund site, both of which had three or more samples; in those cases, the last two samples were used in the evaluation. Differences in the samples (sample 2 minus sample 1) were compared by various groupings using graphical and group-comparison methods, such as the Mann–Whitney two-group test and the Kruskal–Wallis multiple group test (Helsel, 2005; Helsel and Hirsch, 1992). Pairwise comparisons were

used to evaluate overall changes in paired sample data using the Wilcoxon–Pratt test, which considers change in the entire data distribution in determining trend and provided a means for comparing datasets (Hothorn et al., 2008; Lindsey and Rupert, 2012; Pratt, 1959; Rupert, 2008). These tests indicate possible upward or downward patterns based on the median difference between paired samples. Contingency table tests and the associated chi-square statistic were used to determine whether increases or decreases in redox or other geochemical indicators lead to increases or decreases in arsenic concentrations (Helsel and Hirsch, 1992). Derivative metrics such as the pooled mean relative standard deviation between replicate pairs also were used in the analysis in order to determine confidence intervals for each sample (Apodaca et al., 2006).

2.4. Quality control

Replicate samples represent samples collected sequentially at a well and analyzed to determine the amount of variability in a measured arsenic concentration that is attributable to sample collection and laboratory analytical error. Analyses of the variability in arsenic concentrations was done with and without samples with overlapping confidence intervals, as indicated, in order to show how the relations that were identified are affected by inclusion or exclusion of those samples. Replicate variability can be characterized by the relative standard deviation (RSD) of the two samples (Apodaca et al., 2006). Mean RSD values (by dataset) ranged from 1.8% to 8.3% of the measured values (Table 2).

From the pooled mean RSD of replicate well pairs for each dataset, an upper and lower confidence interval can be computed and applied to the environmental samples. Where confidence intervals from environmental sample pairs overlap, it is not possible to say with certainty that the difference in arsenic concentrations between those sample pairs is due to environmental variability or sample collection, handling, and analysis.

Samples from the NAWQA, Lamprey River basin, Mottolo Superfund, and southeastern New Hampshire arsenic studies have associated

Table 2
Variability of replicate data by source of data.
[NAWQA, USGS National Water-Quality Assessment Program; MOT, Mottolo Superfund Site, New Hampshire; LRB, Lamprey River Basin, New Hampshire; SNH, Southeast New Hampshire.]

Water-supply well data source	Consistent detections	Mean concentration of replicate sets			Mean standard deviation (µg/L)	Mean relative standard deviation (percent)
		Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)		
NAWQA	25	1	4.3	89	0.2	4.6
MOT	5	3.5	15	53	0.3	1.8
LRB[a]	6	1.9	13	24	0.8	8.3
SNH[b]	11	1.9	12	37	0.31	3.1

[a] Replicates analyzed at different laboratory.
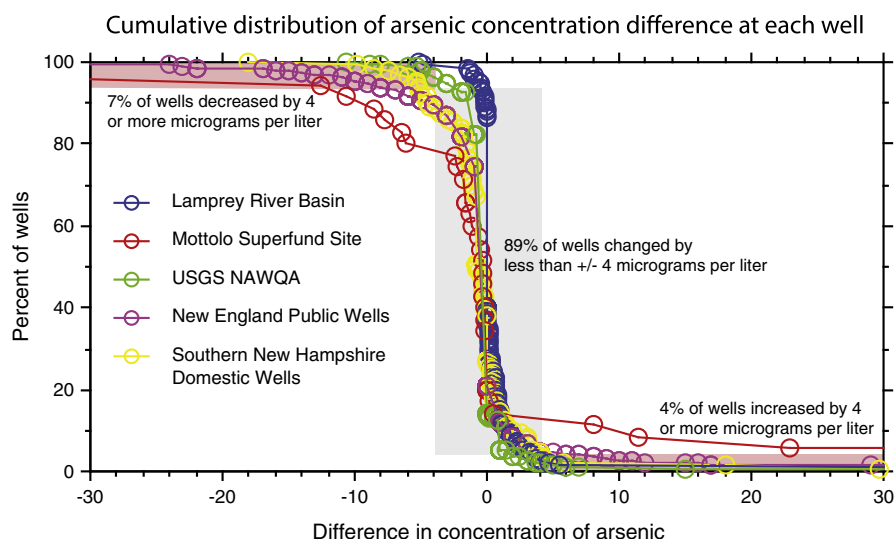[b] Replicates only on second sample.

Fig. 2. Difference in concentration of arsenic between samples for wells used in this study (difference equals sample 2 minus sample 1). Most wells (middle 89%) had concentrations that varied by less than 4 µg/L. However, 11% of wells (7% decreased and 4% increased) had arsenic concentrations that varied by 4 to ≥30 µg/L.

replicate samples. There were no replicate data available for the public wells in New England, so the highest value of 8.3% from Table 2 was applied to the data from those wells to compute confidence intervals.

Quality control (QC) data for the NAWQA samples included replicate samples from 50 wells across the United States and, excluding those that had nondetect values, had a mean RSD of 4.6% (n = 25), with only two sites showing values that differed by more than 50%. These replicate data, which are a subset of data collected by NAWQA, were less variable than the arsenic replicates in the complete set (RSD = 7.6%; n = 202) (Apodaca et al., 2006). The five Mottolo Superfund site replicates collected during sampling were analyzed by the same laboratory and had a mean RSD of 1.8% (Table 2). The southeastern New Hampshire arsenic study replicates were collected for the second sampling period only (10 years after the initial sample collection) and had a mean RSD of 3.1% (n = 11) (Table 2).

The Lamprey River basin replicates are not true replicate samples because the environmental samples were analyzed by one laboratory and subsequently a second laboratory analyzed the same bottles. Two standard reference samples also sent to the second laboratory revealed a 1.2 µg/L bias so all QC data were adjusted by this factor. These data, excluding the censored values, had a mean RSD of 8.3% (Table 2).

3. Results

Temporal variability of arsenic concentrations within each well (from two samples per well, collected over time frames of days to decades) was generally small[1] in water samples from 89% of all private and public drinking-water wells used in this study. This variability appears to support the conclusion that changes in concentrations over time are not a widespread phenomenon. However, it is important to keep in mind that about 43% of wells used in this study had concentrations reported as <1 µg/L in both samples; this means that the percentage of wells with high variability in concentration of arsenic will always appear to be low. What is not clear from these numbers, but is important for the fraction of wells with measurable concentrations (>1 µg/L), is that a large percentage (>43%) of wells with measureable arsenic have significant arsenic variability, underscoring the objectives of this study.

Increases or decreases in concentrations of arsenic >±4 µg/L, however, were observed for about 11% of all wells used in this study

[1] For this paper, small was considered to be ≤±4 µg/L, although other thresholds could have been used.

(133 of 1245 wells) and increased to 19% of wells when considering only those sites that had measurable concentrations of arsenic (133 of 710), indicating that variability is indeed a concern for water supply wells (Fig. 2; Table 1).

3.1. General variability

Variability in overall concentrations of arsenic, for all wells, was evaluated statistically by evaluating whether the concentration of arsenic in sample 2 was greater than or less than the concentration in sample 1 (termed arsenic difference, Table 3), while accounting for those samples that indicate no change. Some datasets showed an increase in the concentration of arsenic between the two samples, whereas others showed a decrease. Tests for changes by source of data indicate that there were overall increases in two datasets and decreases in three (Table 3). The private well samples for the Lamprey River basin and southeastern New Hampshire studies had overall increases in concentrations of arsenic but only the concentration increase in the well samples in the Lamprey River basin study was statistically significant. The public wells in New England had an overall decrease in concentrations of arsenic, as did the wells in the Mottolo Superfund and NAWQA datasets.

The NAWQA dataset was further divided into wells in the lower Illinois River basin and the Central Valley of California because these two subsets represent concentrations of arsenic that are affected by distinctly different geochemical processes that will be described later in this article. In the lower Illinois River basin, processes associated with reductive dissolution of iron oxyhydroxides and reductive desorption from oxyhydroxides are likely controls on arsenic variability (Thomas, 2007). In the Central Valley of California, arsenic variability may be affected by increasing residence time of the groundwater (Anning et al., 2012) as well as the introduction of oxidizing recharge water (through irrigation) with high concentrations of dissolved solids (Jurgens et al., 2009).

Arsenic variability was greater for public than for private wells. Although individual datasets are described in Table 1, the concentrations from all public wells (excluding those with overlapping confidence intervals) are more variable than those from private domestic wells (Fig. 3A). It is important to note, however, that most wells used in this part of the analysis are located in New England. Twenty-two of the 629 public wells are in Texas, Nevada, Illinois, or South Carolina. The interquartile range for the public wells (n = 161) is 8 µg/L compared with 2.9 µg/L for the private domestic wells (n = 183). The coefficient

of variation for samples at each well also was significantly greater for the public wells tested than for the private wells (Fig. 3B).

For community and noncommunity public wells in New England, arsenic concentrations were similarly variable. Community wells serve the largest populations (such as municipalities and housing developments) and generally have higher pumping rates than noncommunity wells (which serve motels, restaurants, and schools, for example). The interquartile ranges of differences in concentrations of arsenic for community and noncommunity wells, excluding samples with overlapping confidence intervals, were 8.5 μg/L and 8 μg/L, respectively (Fig. 4A). The coefficient of variation for samples at each well was not statistically different for community and noncommunity wells (Fig. 3B). The effect of elapsed time between samples from the data used in this study appears unrelated to changes in concentrations of arsenic over time—that is, the amount of time elapsed between samples was not related to the concentration of arsenic in samples—and therefore no further discussion is included on elapsed time between samples.

3.2. Inferred geochemical factors related to arsenic variability

Commonly measured constituent data or water properties were used to indicate the geochemical (redox, pH, major ions) status of the groundwater. Surrogate information has been used effectively for relating to single measurements of constituents such as arsenic (Ayotte et al., 2011; Harte et al., 2012; McMahon and Chapelle, 2008; Thomas, 2007); however, when there is variation in a surrogate constituent, analysis is lacking on how arsenic concentrations vary.

In this study, examination of the change in a constituent in or property of water was done by individual dataset rather than combined because not all datasets had paired measurements of the same constituents nor did all data within datasets have measurements of these constituents or properties (Table 4). For example, concentrations of dissolved iron or manganese were available for each of the two arsenic samples per well for some datasets, whereas others had information on dissolved oxygen or pH or oxidation–reduction potential. Further, using pooled relative standard deviation data from multiple replicate pairs per dataset (Table 2), upper and lower 95th-percentile confidence intervals were computed for each measurement, and data with overlapping confidence intervals were alternately included and excluded from the analyses as indicated in Table 4 and as described below.

3.2.1. Lamprey River basin private wells

Measurements of dissolved oxygen taken at the time of sample collection indicate that increases in concentrations of arsenic correspond to decreases in dissolved oxygen concentrations (Table 4). More than 80% of wells where the dissolved oxygen decreased also showed increases in arsenic (regardless of whether or not samples with overlapping confidence intervals were excluded). Conversely, 80 to 86% of samples from wells where dissolved oxygen increased had arsenic decreases (Table 4). The differences in dissolved oxygen among samples from the same well range from − 7.6 to 1.6 mg/L, which are relatively large, indicating that the water pumped from these wells may reflect temporally variable groundwater fluxes possibly caused by temporally variable pumping stresses.

3.2.2. Private wells near the Mottolo Superfund Site

Inferred redox status based on measurements of redox indicators (such as dissolved oxygen, iron, and oxidation–reduction potential) taken at the time of sample collection indicate that high concentrations of arsenic corresponded to a reducing conditions (Harte et al., 2012). Taking this finding further and analyzing paired temporal samples from private wells adjacent to the Mottolo Superfund site, concentrations of arsenic generally decreased when the concentrations of iron at a well decreased (Table 4). Although it is unclear what controlled changes in redox conditions and arsenic concentrations over time, time-varying fluxes of anoxic groundwater resulting from the

degradation of organic compounds at the Mottolo Superfund site and moving toward the private wells could explain these patterns. In this way, temporal variability in arsenic concentrations may be attributable to localized anthropogenic contamination that has largely been remediated. In these wells, the resulting changes in redox state unexpectedly resulted in changes in arsenic concentrations. Such patterns are not unexpected at small spatial scales, but these types of waste-related temporal patterns are unlikely to operate at the large spatial scales and may not be applicable to general resource investigations.

3.2.3. New England public wells

Measurements of arsenic and manganese in samples from public wells in New England indicate that changes in manganese concentrations correspond to changes in concentrations of arsenic (Table 4). About 60% of wells showed a decrease in concentrations of arsenic when there was an associated decrease in the concentration of manganese; similarly, about 60% of wells showed increases in concentrations of arsenic when concentrations of manganese increased. The strength of these relations improves when wells with overlapping 95% confidence intervals are excluded—71% of wells showed a decrease in concentrations of arsenic when concentrations of manganese decreased, and 62% of wells showed an increase in concentrations of arsenic when concentrations of manganese increased. Similar to other datasets in this study, this correlation suggests that change in concentrations of arsenic is associated with changes in redox status of the water being pumped. For these data, the cause of changing chemistry (both manganese and arsenic) is not known. However, the associations in the trends between manganese and arsenic likely would relate to similar processes, such as flow system perturbations.

3.2.4. Lower Illinois River basin private wells

Samples from private wells in the glacial aquifer in the Lower Illinois River basin, though few in number, indicate that changes in iron were related to changes in arsenic (Table 4). Nearly all samples showed an arsenic increase when iron increased; the opposite also was true. The significance of this result is questionable because of the small number of wells (Table 4). Nevertheless, this result provides additional evidence that changes in redox conditions often are associated with changes in concentrations of arsenic in water from wells.

3.2.5. Central Valley private wells

Changes in concentration of arsenic from private well samples in the unconsolidated sand and gravel aquifer in the Central Valley of California, unlike most of the other wells analyzed, did not appear to respond to changes in redox but rather were related to changes in some major ions, such as calcium, magnesium, and sulfate (Table 4). There were no significant changes in the concentration of arsenic related to changes in the concentrations of dissolved oxygen, manganese, or iron. However, the effect of decreases in the concentrations of calcium, magnesium, and sulfate resulted in modest increases in the percentage of wells (55% to 60%) with increases in concentrations of arsenic (Table 4); however, increases in the concentrations of these major ions were associated with significant percentages (70% to 80%) of wells decreasing in concentrations of arsenic. This result is consistent with recent studies that have described increases in the concentrations of calcium, sulfate, and bicarbonate in groundwater that were related to increased irrigation and the addition of gypsum as a soil amendment, resulting in mobilization of uranium (Jurgens et al., 2009). In this study, increases in these major ions are associated with decreased concentrations of arsenic, which may be an indication of increasing proportions of young recharge water, which is diluting groundwater that contains arsenic, or geochemically limiting the mobility of arsenic. Increases in concentrations of sulfate, however, may be indicative of increasingly oxidizing conditions, which would cause decreases in concentrations of arsenic such as those indicated in Table 4.

Table 3

Trends in concentrations of arsenic based on two samples per well.

[LRB, Lamprey River Basin; MOT, Mottolo Superfund Site; PSW, New England public-supply wells; SNH, Southern New Hampshire; NAWQA, National Water Quality Assessment Program; LIRB, Lower Illinois River Basin; CV, Central Valley of California; p-values bolded were significant at alpha = 0.05.]

Water-supply well data source	Supply type	Number of wells	Average time between samples (years)	Change in concentration of arsenic, in percent			Overall change	Wilcoxon-signed rank p-value
				Increase	Decrease	No change		
LRB	Private	148	0.81	**20.3**	15.2	64.6	Increase	**0.0063**
PSW	Public	607	2.5	19.6	**25.4**	55.0	Decrease	**0.0159**
SNH	Private	143	10	**36.4**	31.5	32.2	Increase	0.8281
MOT	Private	35	0.34	16.2	**70.3**	13.5	Decrease	**0.0174**
NAWQA All	Mixed[a]	183	9.4	7.1	11.7	81.2	Decrease	0.0866
NAWQA LIRB	Private[b]	25	11	44.0	20.0	36.0	Increase	0.1244
NAWQA CV	Private	104	8.4	20.2	**32.7**	47.2	Decrease	**0.0248**

[a] Mixed public and private; does not include LIRB and Central Valley NAWQA wells.

[b] One was a public supply.

3.3. Seasonal effects on arsenic variability

The seasonal effect on concentrations of arsenic traditionally has been difficult to characterize, but one method is to consider whether concentrations measured at different times of the year, as a group, are different from each other. Comparing these results to typical hydrographs of water levels for groundwater wells indicate possible reasons for variability.

For all New England wells in the study, samples were categorized by identifying the quarter of the year in which the sample was taken and comparing the distributions of concentrations among quarters. Overall, concentrations of arsenic were lowest in the first quarter (January through March) and were highest in the fourth quarter (October through December) (Fig. 5A). At the same time, groundwater levels were generally deeper in the third and fourth quarters than in the first and second quarters (Fig. 5B). The fact that higher arsenic concentrations occur when groundwater levels are deepest suggests that arsenic concentrations in well water may be controlled, in part, by the proportions of the youngest, less geochemically evolved groundwater components to the oldest, more geochemically evolved groundwater components; the proportions of groundwater ages in turn may be affected by pumping, which can mix dissimilar groundwater, or other aquifer stresses, such as high or low groundwater conditions.

Similarly, in the Central Valley of California, samples collected in periods with deeper water levels had a slight though apparent increase in concentrations of arsenic, (Fig. 6A, B). This is most apparent for quarters 1 and 2, where an increase in depth to water corresponded to a noticeable increase in arsenic concentrations. Water levels remained moderately deep in quarters 3 and 4, which corresponded to relatively high 75th percentile (and above) concentrations of arsenic. Although these relations are weak, the general pattern may be suggestive of a water-level effect.

4. Discussion

The concentrations of arsenic in most wells analyzed for this study varied over time by small amounts (less than ± 4 μg/L); however, some varied by much larger amounts. This finding is common for
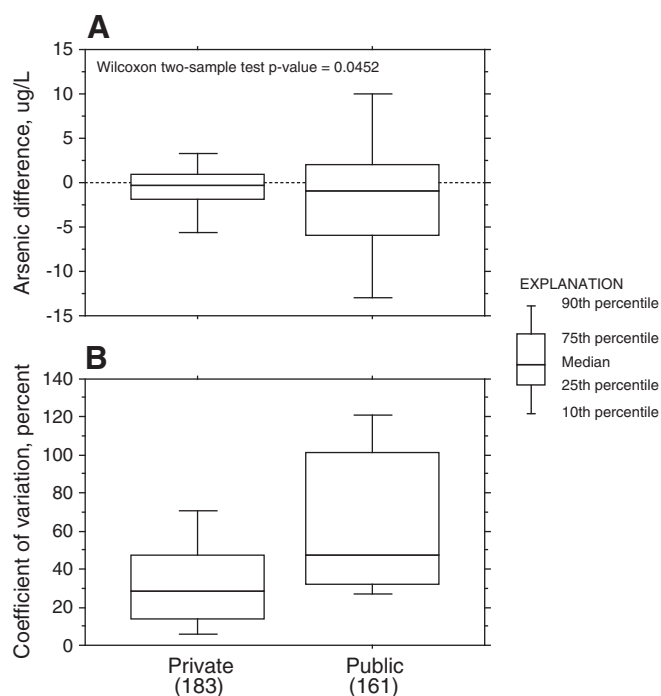

Fig. 3. (A) Box plot of the difference in concentration of arsenic between samples (sample 2 minus sample 1) in each well for private and public wells. (B) Box plot of the coefficient of variation between sample 1 and sample 2, for private and public wells. The number in parentheses is the number of wells sampled.
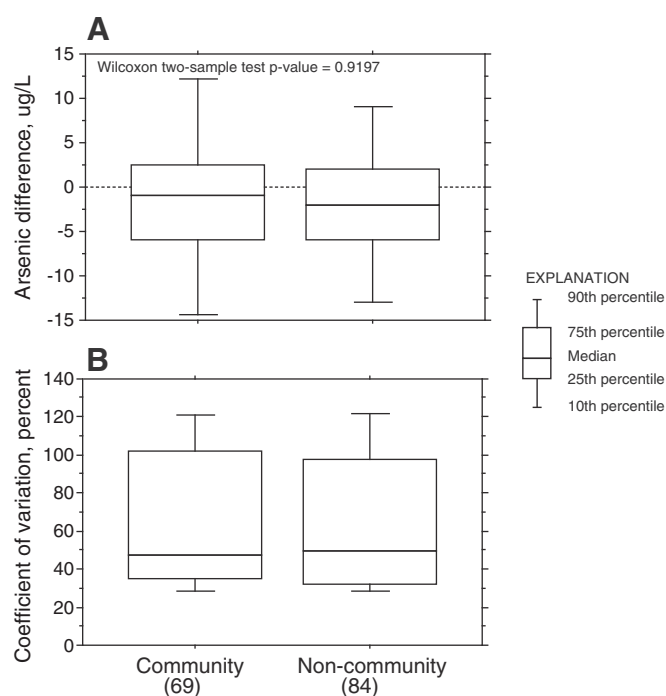
Fig. 4. (A) Box plot of the difference in concentration of arsenic between samples (sample 2 minus sample 1) in each well for public wells, by well type. (B) Box plot of the coefficient of variation between sample 1 and sample 2, by well type. The number in parentheses is the number of wells sampled.

Table 4

Effect of changes in surrogate variables for geochemical conditions on temporal variability of arsenic in groundwater.

[As, arsenic; LRB, Lamprey River Basin; PSW, New England public-supply wells; MOT Mottolo Superfund Site; NAWQA, National Water Quality Assessment Program; LIRB, Lower Illinois River Basin; CV, Central Valley of California; NVBR, Nevada Basin and Range; percentages and p-values bolded were significant at alpha = 0.05, for samples without overlapping confidence intervals.]

Water-supply well data source	Supply type	Number of wells	Includes arsenic differences with overlapping 95% confidence intervals	Percentage of wells with increase or decrease in arsenic by potential controlling factor				Chi-square p-value
PSW	Public	–	–	Mn decreased		Mn increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		62	Y	60.0	40.0	40.6	59.4	0.1273
		38	N	**70.6**	**29.4**	**38.1**	**61.9**	**0.0461**
LRB	Private	–	–	Dissolved oxygen decreased		Dissolved oxygen increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		42	Y	**17.1**	**82.9**	**85.7**	**14.3**	**0.0002**
		20	N	**20.0**	**80.0**	**80.0**	**20.0**	**0.0149**
MOT	Private	–	–	Fe decreased		Fe increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		27	Y	**94.1**	**5.9**	**50.0**	**50.0**	**0.0078**[b]
		23	N	**93.3**	**6.7**	**37.5**	**62.5**	**0.0037**[b]
NAWQA LIRB	Private[a]	–	–	Fe decreased		Fe increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		16	Y	60.0	40.0	18.2	81.8	0.0944[b]
		5	N	**100**	**0.0**	**0.0**	**100**	**0.0253**[b]
NAWQA CV	Private	–	–	Sulfate decreased		Sulfate increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		54	Y	45.0	55.0	70.6	29.4	0.0625
		38	N	**44.4**	**55.6**	**80.0**	**20.0**	**0.0233**
NAWQA CV	Private	–	–	Ca decreased		Ca increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		55	Y	**42.1**	**57.9**	**72.2**	**27.8**	**0.0288**
		38	N	**42.9**	**57.1**	**75.0**	**25.0**	**0.0475**
NAWQA CV	Private	–	–	Ca and Mg decreased		Ca and Mg increased		–
		–	–	As decreased	As increased	As decreased	As increased	–
		51	Y	**40.0**	**60.0**	**72.2**	**27.8**	**0.0301**
		36	N	**41.7**	**58.3**	**75.0**	**25.0**	**0.0497**

[a] One well is a public well.

[b] More than 75% of the cells have expected counts less than 5; chi-square may not be a valid test.

studies of temporal variability in the United States and, in many cases, internationally, which has generally led to the conclusion that arsenic is not particularly variable in natural groundwater. Although this is a reasonable conclusion in general, it also has been an impediment to understanding what processes affect temporal variability, particularly for wells that have large differences in concentrations of arsenic over time. In this study, changes in iron, manganese, and dissolved oxygen, that are related to time-varying redox conditions in well water, were found to relate to variability in concentrations of arsenic. Other geochemical factors such as changes in pH and some major ions, such as calcium, magnesium, and sulfate also were related to arsenic variability.

The fact that arsenic concentrations in private wells were least variable and in public wells were most variable suggests that aspects of well operation such as high or variable pumping rates or seasonality of pumping affect variability (Fig. 2; Table 1). Private wells from this study that are not affected by systematic contamination (NAWQA, Lamprey River basin, and southeastern New Hampshire wells) had the least amount of variability (Fig. 2). However, private wells that were affected by redox changes caused by a nearby waste site (Mottolo Superfund wells) had greater variability than all other wells used in this study. The private wells near the Mottolo Superfund site are recently known to be affected by changed redox conditions (more reducing) associated with former volatile organic compound contamination at the waste site (Harte et al., 2012; Hoffman, 2010). The data led to the conclusion that the effects of the now mostly removed contaminants (organic solvent) caused redox changes in groundwater that were much more far reaching than expected, affecting concentrations of arsenic in the adjacent, down gradient, local groundwater.

Changes in surrogate variables for indicating reducing redox conditions in water samples, such as decreased dissolved oxygen and oxidation–reduction potential and increased iron and manganese, along with other geochemical changes, such as increased pH, were related to increases in arsenic; this relation was particularly observable in samples from the Northeastern United States. Increases in some major ions, such as calcium and sulfate, in the Central Valley were related to decreases in concentrations of arsenic (a signature that may be indicative of well-documented gypsum dissolution associated with irrigated agriculture) (Jurgens et al., 2009; Schoups et al., 2005). It also is possible that high proportions of less chemically evolved, more oxidizing recharge water with high concentrations of calcium and sulfate could be inhibiting arsenic mobility or may simply be diluting the water that contains high concentrations of arsenic. Although the reasons for this relation is unclear, the relation suggests that focusing on the causes of the geochemical changes as indicated by surrogate variables may help resolve the reasons for observed changes in concentrations of arsenic over time.

Seasonal variability was observable within the data from New England (Fig. 5A, B) and in the Central Valley (Fig. 6A, B). One hypothesis is that low groundwater levels may indicate less dilution with oxidizing, lower-pH water (such as from recharge or irrigation water), resulting in increases in dissolved arsenic. Also, geochemical conditions that inhibit arsenic mobility, such as slightly acidic pH or oxidizing conditions would be greater during periods of increasing groundwater levels (greater recharge) than during periods of decreasing groundwater levels (periods of recession). Although these data were not originally collected to determine such relations, that it was observable suggests that these processes could be affecting changes in concentrations of arsenic.

The extent to which changes in arsenic concentrations in wells occur in areas not covered by data used for this study or on the individual well scale is unclear but is of concern because it appears that either changes in redox or other geochemical conditions affect arsenic concentrations over time or systematic changes are affecting arsenic as well as other solute concentrations.
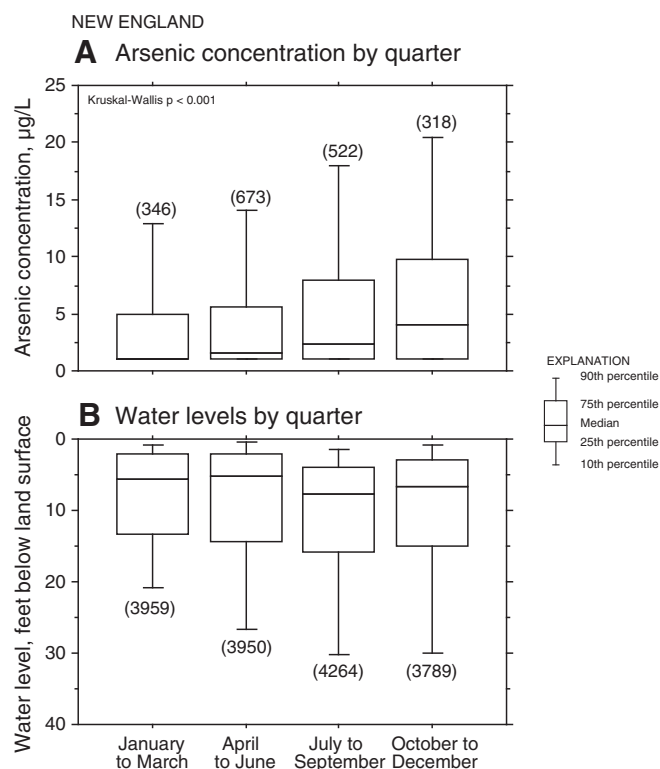
NEW ENGLAND

Fig. 5. A, Box plot of arsenic concentrations from all wells in New England (from this study; includes two samples per well) and B, box plot of water levels by quarter for wells in New Hampshire (from the National Water Information System, since 1990). The number in parentheses is the number of samples.
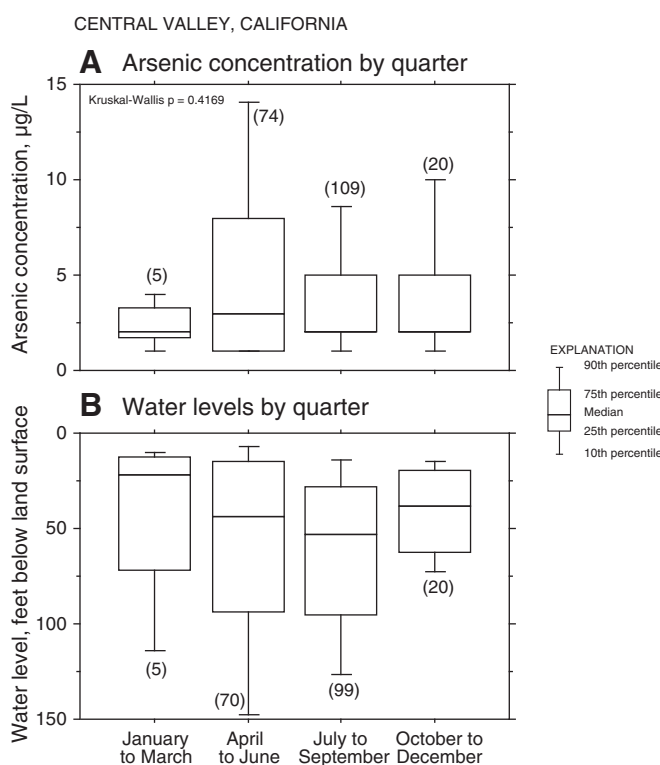
CENTRAL VALLEY, CALIFORNIA

Fig. 6. A, Box plot of arsenic concentrations from wells in the Central Valley (from this study; includes two samples per well) and B, box plot of water levels by quarter for the same wells in the Central Valley of California. The number in parentheses is the number of samples.

4.1. Implications for public and private well use

An important concern is the magnitude of arsenic variability in public and private wells. For example, concerns about variability in public wells may relate more to treatment efficacy or costs, whereas the concerns for private wells also may include whether the presence of the contaminant is known and whether it is being treated.

Although evident from the datasets that are described in Table 1, the concentrations of contaminants from all public wells (excluding those with overlapping confidence intervals) are more variable than those from private wells (Fig. 3). In many ways, this is a positive finding because the private wells, with assumed lower variability are generally not regulated and therefore are less often tested than public wells. For public wells with high-variability, higher than normal frequency monitoring is often required.

For private wells, less variability might appear to imply that infrequent monitoring could be considered sufficient; however, it is clear from the examples herein that local changes in geochemical conditions can cause large temporal changes and that those changes may not be obvious to the typical well owner unless routine testing is conducted.

From analyses of the data used in this study we can deduce that variability in concentrations of arsenic occurs and is, in part, systematic in that it can be related to variations in indicator variables that act as surrogates for geochemical processes. Applying this deduction in the larger context of worldwide arsenic contamination areas can help to predict where variability may be most problematic. Identification of processes that can potentially affect concentrations of arsenic could allow for management of groundwater resources to minimize exposure to arsenic. For example, consideration of groundwater flow paths and zones of contribution to public wells could be evaluated not just in terms of potential for contaminants to reach the supply well but also in terms of whether geochemical changes caused by contaminants might extend beyond the reach of the contaminants themselves and affect changes in concentrations of arsenic over time. Evaluation of geochemical variation, whether as changes in redox or changes in solute loads in an area over multiple time scales, may lead to more informed decisions about management of existing water-supply wells and where new supply wells can be best sited.

Consideration of the potential for variability in concentrations of arsenic or other contaminants could and perhaps needs to be part of the evaluation of sources of groundwater supplies, whether from different aquifers in the same area or from different parts of the same aquifer. In this way, groundwater and aquifer geochemistry that may be more or less favorable for time-varying mobilization of geologically sourced contaminants can be adequately evaluated. More complete evaluation of mobilization mechanisms that include a temporal component can lead to more informed decision making ability.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.02.057.

References

Anning DW, Paul AP, McKinney TS, Huntington JM, Bexfield LM, Thiros SA. Predicted nitrate and arsenic concentrations in basin-fill aquifers of the southwestern United States. U.S. Geological Survey; 2012. p. 78.

Apodaca LE, Mueller DK, Koterba MT. Review of trace element blank and replicate data collected in ground and surface water for the National Water-Quality Assessment Program, 1991–2002. Reston, VA: U.S. Geological Survey; 2006.

Ayotte JD, Montgomery DL, Flanagan SM, Robinson KW. Arsenic in groundwater in eastern New England: occurrence, controls, and human health implications. Environ. Sci. Technol. 2003;37(10):2075–83.

Ayotte JD, Szabo Z, Focazio MJ, Eberts SM. Effects of human-induced alteration of ground-water flow on concentrations of naturally-occurring trace elements at water-supply wells. Appl Geochem 2011;26(5):747–62.

Belitz K, Dubrovsky NM, Burow K, Jurgens B, Johnson T. Framework for a ground-water quality monitoring and assessment program for California. Sacramento: U.S. Geological Survey; 2003. p. 78.

Berg M, Tran HC, Nguyen TC, Pham HV, Schertenleib R, Giger W. Arsenic contamination of ground water and drinking water in Vietnam: a human health threat. Environ. Sci. Technol. 2001;35(13):2621–6.

Burgess W, Ahmed KM, Carruthers A, Cheetham H, Cobbing J, Cuthbert M, et al. Trends in arsenic concentration at tubewells in Bangladesh: conceptual models, numerical models, and monitoring proxies. In: Bhattacharya P, Mukherjee A, Zevenhoven R, Bundschuh J, Loeppert H, editors. Trace metals and other contaminants in the environment. Elsevier; 2007. p. 63–83.

Cheng Z, van Geen A, Seddique AA, Ahmed KM. Limited temporal variability of arsenic concentrations in 20 wells monitored for 3 years in Araihazar, Bangladesh. Environ. Sci. Technol. 2005;39(13):4759–66. http://dx.doi.org/10.1021/es048065f.

Erickson ML, Barnes RJ. Well characteristics influencing arsenic concentrations in ground water. Water Res 2005;39:4029–39.

Faires LM. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of metals in water by inductively coupled plasma-mass spectrometry. Denver, CO: U.S. Geological Survey; 1993. p. 28.

Fishman MJ, Friedman LC. Methods for determination of inorganic and organic constitu-ents in water and fluvial sediments. Reston, VA: U.S. Geological Survey; 1989. p. 545.

Focazio MJ, Welch AH, Watkins SA, Helsel DR, Horn MA. A retrospective analysis on the occurrence of arsenic in ground-water resources of the United States and limitations in drinking-water-supply characterizations. U.S. Geological Survey; 2000. p. 21.

Garbarino JR. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium using inductively coupled plasma-mass spectrometry. Reston, VA: U.S. Geological Survey; 1999. p. 31.

Gotkowitz MB, Schreiber ME, Simo JA. Effects of water use on arsenic release to well water in a confined aquifer. Ground Water 2004;42(4):568–75.

Harte PT, Ayotte JD, Hoffman A, Révész K, Belaval M, Lamb S, et al. Heterogeneous redox conditions, arsenic mobility, and groundwater flow in a fractured-rock aquifer near a waste repository site in New Hampshire USA. Hydrogeol J 2012;1–13. http://dx.doi.org/10.1007/s10040-012-0844-4.

Helsel DR. Nondetects and data analysis: statistics for censored environmental data. 1st ed. New York: John Wiley & Sons, Inc.; 2005.

Helsel DR, Hirsch RM. Statistical methods in water resources. New York: Elsevier Science Company, Inc.; 1992.

Hinkle SR, Polette DJ. Arsenic in ground water of the Willamette basin. U.S. Geological Survey; 1999. p. 29.

Hoffman A. Mottolo Superfund Site Summary. Retrieved March 25, 2011, 2011, from. http://des.nh.gov/organization/divisions/waste/hwrb/fss/superfund/summaries/mottolo.htm, 2010.

Hothorn T, Hornik K, van de Wiel MA, Zeileis A. Implementing a class of permutation tests: the coin package. J Stat Softw 2008;28:1–23.

Ivahnenko T, Szabo Z, Gibs J. Changes in sample collection and analytical techniques and effects on retrospective comparability of low-level concentrations of trace elements in ground water. Water Res 2001;35(15):3611–24.

Jurgens BC, Fram MS, Belitz K, Burow KR, Landon MK. Effects of groundwater develop-ment on uranium: Central Valley, California, USA. Ground Water 2009;49:913–28.

Karagas MR, Tosteson TD, Blum J, Morris JS, Baron JA, Klaue B. Design of an epidemiologic study of drinking water arsenic exposure and skin and bladder cancer risk in a U.S. population. Environ Health Perspect 1998;106(Suppl. 4):1047–50.

Karagas MR, Le CX, Morris S, Blum J, Lu X, Spate V, et al. Markers of low-level arsenic exposure for evaluating human cancer risks in a U.S. population. Int J Occup Environ Health 2001;14(2):171–5.

Katz BG, McBride WS, Hunt AG, Crandall CA, Metz PA, Eberts SM, et al. Vulnerability of a public supply well in a karstic aquifer to contamination. Ground Water 2009;47(3):438–52.

Koterba MT, Wilde FD, Lapham WW. Ground-water data-collection protocols and proce-dures for the National Water-Quality Assessment program—collection and documen-tation of water-quality samples and related data. U.S. Geological Survey; 1995. p. 113.

Kozul CD, Ely KH, Enelow RI, Hamilton JW. Low-dose arsenic compromises the immune response to influenza A infection in vivo. Environ Health Perspect 2009;117(9):1441–7. http://dx.doi.org/10.1289/ehp.0900911.

Lapham WW, Wilde FD, Koterba MT. Ground-water data-collection protocols and proce-dures for the National Water-Quality Assessment Program—selection, installation, and documentation of wells, and collection of related data. U.S. Geological Survey; 1995. p. 69.

Lindsey BD, Rupert MG. Methods for evaluating temporal groundwater quality data and results of decadal-scale changes in chloride, dissolved solids, and nitrate concentra-tions in groundwater in the United States, 1988–2010. U.S. Geological Survey; 2012. p. 46.

Mackenzie A, Audette R, Chen W, Schopflocher D. Arsenic in ground water from domestic wells in three areas of northern Alberta. Edmonton: Alberta Health and Wellness; 2000. p. 40.

McMahon PB, Chapelle FH. Redox processes and water quality of selected principal aquifer systems. Ground Water 2008;46(2):259–71.

Meliker JR, Wahl RL, Cameron LL, Nriagu JO. Arsenic in drinking water and cerebrovascular disease, diabetes mellitus, and kidney disease in Michigan: a standardized mortality ratio analysis. Environ Heal 2007;6(1):4.

Nadakavukaren JJ, Ingermann RL, Jeddeloh G, Falkowski SJ. Seasonal variation of arsenic concentration in well water in Lane County, Oregon. Bull Environ Contam Toxicol 1984;33(1):264–9.

New Hampshire Department of Environmental Services. Mottolo Superfund Site. Re-trieved August 10, 2010, 2010, from http://des.nh.gov/organization/divisions/waste/hwrb/fss/superfund/summaries/mottolo.htm, 2010.

Nuckols JR, Beane Freeman LE, Lubin JH, Airola MS, Baris D, Ayotte JD, et al. Estimating water supply arsenic levels in the New England bladder cancer study. Environ Health Perspect 2011;119(9):1279–85. http://dx.doi.org/10.1289/ehp.1002345.

Pratt JW. Remarks on zeros and ties in the Wilcoxon signed rank procedures. Am Stat Assoc J 1959;54(287):655–67.

Price RE, Pichler T. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): implications for arsenic release during water-rock interaction. Chem Geol 2006;228:44–56. [(1-3 spec. iss.)].

Ravenscroft P, Howarth RJ, McArthur JM. Comment on "Limited temporal variability of arsenic concentrations in 20 wells monitored for 3 years in Araihazar, Bangladesh". Environ. Sci. Technol. 2006;40(5):1716–7. http://dx.doi.org/10.1021/es058017a.

Rupert MG. Decadal-scale changes of nitrate in groundwater of the United States, 1988–2004. J Environ Qual 2008;37(5_Suppl):S240–8. http://dx.doi.org/10.2134/jeq2007.0055.

Schoups G, Hopmans JW, Young CA, Vrugt JA, Wallender WW, Tanji KK, et al. Sustainabil-ity of irrigated agriculture in the San Joaquin Valley, California. Proc Natl Acad Sci U S A 2005;102(43):15352–6. http://dx.doi.org/10.1073/pnas.0507723102.

Schreiber ME, Gotkowitz MB, Simo JA, Freiberg PG. Mechanisms of arsenic release to ground water from naturally occurring sources, Eastern Wisconsin. In: Welch AH, Stollenwerk KG, editors. Arsenic in groundwater: geochemistry and occurrence. Boston: Kluwer; 2003. p. 259–94.

Seiler RL. Temporal changes in water quality at a childhood leukemia cluster. Ground Water 2004;42(3):446–55.

Sengupta MK, Mukherjee A, Ahamed S, Hossain MA, Das B, Nayak B, et al. Comment on "Limited temporal variability of arsenic concentrations in 20 wells monitored for 3 years in Araihazar, Bangladesh". Environ. Sci. Technol. 2006;40(5):1714–5. http://dx.doi.org/10.1021/es051492o.

Smedley PL, Kinniburgh DG. A review of the source, behaviour, and distribution of arsenic in natural waters. Appl Geochem 2002;17:517–68.

Sorg TJ, Chen AS, Wang L. Arsenic species in drinking water wells in the USA with high arsenic concentrations. Water Res 2014;48:156–69. http://dx.doi.org/10.1016/j.watres.2013.09.016.

Steinmaus CM, Yuan Y, Smith AH. The temporal stability of arsenic concentrations in well water in western Nevada. Environ Res 2005;99(2):164–8. http://dx.doi.org/10.1016/j.envres.2004.10.003.

Thomas MA. The association of arsenic with redox conditions, depth, and groundwater age in the Glacial Aquifer System of the Northern United States (pp. 26). Reston: U.S. Geological Survey; 2007.

Thundiyil JG, Yuan Y, Smith AH, Steinmaus C. Seasonal variation of arsenic concentration in wells in Nevada. Environ Res 2007;104(3):367–73.

U.S. Environmental Protection Agency. Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry, Revision 5.4, methods for the determination of metals in environmental samples, Supplement I; 1994 [Washington, D.C.].

U.S. Environmental Protection Agency. National primary drinking water regulations; arse-nic and clarifications to compliance and new source contaminants monitoring. Feder-al Register: United States Government. Retrieved from http://www.epa.gov/fedrgstr/EPA-WATER/2001/January/Day-22/w1668.htm, 2001.

U.S. Environmental Protection Agency. Private drinking water wells: what you can do. Re-trieved Aug 10, 2010, from http://www.epa.gov/privatewells/whatyoucando.html, 2010.