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Research article

GIS interpolation is key in assessing spatial and temporal bioremediation of groundwater arsenic contamination

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A R T I C L E I N F O

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A B S T R A C T

Arsenic (As) contamination in groundwater is a global crisis that is known to cause cancers of the skin, bladder, and lungs, among other health issues, and affects millions of people around the world. Due to the time and financial constraints associated with establishing in-depth monitoring programs, it is difficult to monitor and map arsenic concentrations over time and across large areas. The goal of this study was to determine the most accurate Geographic Information Systems (GIS) interpolation method for mapping the effects of bioremediation on groundwater arsenic sequestration across a local-scale study area in northwest Florida (~900 m^2) over the duration of a nine-month period (pre-injection, one-month post-injection, and nine-months post-injection). We used groundwater data collected from 2018 to 2019 to visualize arsenic contamination over time. Measured arsenic concentrations from 23 wells were grouped into three categories: (1) *decreasing*, (2) *fluctuating*, or (3) largely *unaffected* by the bioremediation procedure. The accuracy of three interpolation methods was also investigated: Inverse Distance Weighted (IDW), Ordinary Kriging (OK), and Empirical Bayesian Kriging (EBK). Statistical results using the leave-one-out cross validation (LOOCV) process showed that OK consistently provided the most accurate predictions of arsenic concentrations across space and time ([Root Mean Square Error (RMSE) = 0.265] and accurately predicted regulatory arsenic concentrations below 0.05 mg/L in nine of 11 wells, while IDW and EBK only accurately predicted four and five wells, respectively. While it was shown that OK tends to underpredict arsenic maxima, this did not affect the overall accuracy of the interpolation compared to results from EBK (RMSE = 0.297) and IDW (RMSE = 0.272). Overall, these interpolations aided in the interpretation of the extent of bioremediation, revealing the need for repeated injections to continuously remove arsenic from the groundwater. The study will provide guidance and evaluation methods for international and governmental organizations, industrial companies, and local communities on how to understand spatial and temporal distributions of arsenic contamination and inform bioremediation efforts at various scales in the future.

1. Introduction

Millions of people worldwide suffer from diseases caused by groundwater arsenic contamination (World Health Organization, 2019). Geogenic arsenic contamination is well known in regions like the Bengal Basin, yet anthropogenic sources of arsenic contamination, such as those produced at industrial and agricultural sites, can also be a threat to groundwater quality, especially in developed regions around the world (Woolson, 1983; Smedley and Kinniburgh, 2002). Most of these cases originate from the use of herbicides, pesticides, and other agricultural aids (Bencko and Foong, 2017; Lee et al., 2018). Arsenical herbicides are soluble in water, potentially leading to arsenic accumulation in underlying aquifers over time. Although arsenical herbicides and pesticides have been phased out beginning in the 1980s and barred from use by the U.S. Environmental Protection Agency (EPA) in 2009 (U.S. EPA, 2009), legacy contamination from industrial manufacturing sites and extensive field applications still pose a threat to groundwater quality today.

GIS has emerged as an effective tool for visualizing environmental contaminants. Often due to time and financial constraints, limited numbers of groundwater samples are collected in the field for chemical analysis, leading to sparse datasets that could diminish experimental results and conclusions (Liu et al., 2004). Interpolation of isolated well data can be used to predict values at unsampled locations using nearby measured values (Tobler, 1970) and fill in gaps in the conceptual site model. Three common interpolation methods for groundwater contamination mapping are Inverse Distance Weighting (IDW), Kriging,

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and Empirical Bayesian Kriging (EBK). IDW is a deterministic interpolation method which produces an estimated surface by considering the similarity between measured points and determining the optimum weight needed to control the influence of points at a certain distance (de Smith et al., 2020). IDW models adhere to Tobler's First Law (Tobler, 1970), in which measured values that are farther away from the point of estimation should be appropriately diminished or weighted based on this distance (de Smith et al., 2020). Kriging and EBK are both geostatistical interpolation methods, which differ from deterministic interpolation models in that they use the measured data points to describe a true population and then create an overarching model from this population to predict values at varying distances (de Smith et al., 2020). Kriging is a multistage process that uses a semivariogram to consider the distance and variation in the measured values to estimate unknown values (Paramasivam and Venkatramanan, 2019; de Smith et al., 2020). Kriging has a variety of mathematic models such as Simple Kriging, Universal Kriging, and Ordinary Kriging (OK). OK uses a location-dependent mean, and its semivariogram computes optimal weights (like IDW) and assigns weights to measured points to predict values at unsampled locations (Paramasivam and Venkatramanan, 2019; de Smith et al., 2020). EBK is a newly developed interpolation method that automates the intensive construction of a valid Kriging model through simulating the measured points (Magesh and Elango, 2019; ESRI, 2020b). Unlike Kriging, EBK utilizes multiple semivariograms and considers the uncertainty among them (ESRI, 2020b). Specifics regarding the mathematical basis of OK, EBK, and IDW interpolation are detailed in Xie et al. (2011), Krivorucko (2012a,b), Singh and Verma (2019), de Smith et al. (2020), and ESRI (2020b).

While interpolation is a common method used in GIS, disagreement still exists regarding the accuracy of interpolating contamination under different conditions for various pollutants. For example, Xie et al. (2011) investigated the performance of IDW and OK, along with Radial Basis Functions (RBF), across a 605 km^2 agricultural area in Beijing, China. They discovered that while OK was the most accurate in predicting soil heavy metal contamination, local maxima and minima were best preserved with IDW and RBF, as the maxima were underestimated with OK. Rabah et al. (2011) found that Kriging gave the most accurate interpolation results for groundwater chloride concentrations and water levels along the Gaza Strip (365 km^2). More recent studies like Mirzaei and Sakizadeh (2016) compared OK, EBK, and IDW in their ability to predict various groundwater quality parameters over 1100 km^2 in Khuzestan, Iran, through which they determined that EBK was the best method because it yielded the least error. However, they noticed that EBK and OK had strong smoothing effects in overestimating local minima, meaning that the interpolation overpredicted values around known low values and, thus, obscured the overall minima. Most recently, Singh and Verma (2019) investigated groundwater nitrate concentrations in Lucknow City, India (429.5 km^2) and found that Kriging, compared to IDW, was the most accurate method, while Magesh and Elango (2019) looked at groundwater fluoride concentrations in the Dindigul district, India (6267 km^2) and discovered that EBK, compared to IDW, had the least amount of error.

Interpolation methods have previously been used to understand the spatial distribution of groundwater arsenic. Shamsudduha (2008) examined different interpolation methods in their ability to predict arsenic concentrations in shallow aquifers across a very large study area in Bangladesh (144,000 km^2). The analysis found that OK was a better predictor of arsenic concentrations than IDW, but OK systematically underestimated arsenic maxima and had a strong smoothing effect at the regional scale. The study determined that the lack of sampling locations across a large study area with high spatial variability hindered the estimation of arsenic in shallow aquifers that were significantly influenced by biogeochemical processes. Although Gong et al. (2014) found that IDW, compared to several kriging models, performed best when accounting for well depth and elevation as covariates, they also noticed that the regional interpolation of arsenic across Texas (696,241 km^2) yielded a large degree of variation due to different aquifer and geologic properties. Overall, the selection of interpolation methods in groundwater studies proves to be site and scale specific.

Typically, groundwater arsenic remediation efforts involve ex-situ pump-and-treat methods; however, these treatments are expensive, take several months or years to reduce arsenic concentrations, and, most often, fail to remove enough arsenic to meet safe standards (Lee et al., 2000; Ford et al., 2007; Russo et al., 2010). An alternative technique proposed by Saunders et al. (1996) involves the in-situ bioremediation of arsenic by injecting a ferrous sulfate mixture with a source of organic carbon to stimulate indigenous sulfate-reducing bacteria (SRB) and biomineralize pyrite (Lee et al., 2018; Saunders et al., 2018; Fischer, 2020). Because arsenic has a high affinity for pyrite (Huerta-Diaz and Morse, 1992; Bostick and Fendorf, 2003; Lee et al., 2005), the working hypothesis is that dissolved arsenic can be sequestered via adsorption on the surface of iron sulfides (i.e., pyrite) or by co-precipitation under stimulated sulfate-reducing conditions. The technique has been shown to sequester groundwater arsenic through formation of biogenic pyrite in field-scale applications (Lee et al., 2018; Fischer 2020). However, the potential for both short-term (~one month) and long-term (~nine months) remediation using this technique is still unclear. Understanding both spatial and temporal patterns of the sequestration of arsenic is critical in evaluating the technique's remediation potential. Thus, the goal of this study is to determine the most accurate GIS interpolation method for mapping the effects of bioremediation on groundwater arsenic sequestration across a local-scale study area in northwest Florida (~900 m^2) over the duration of a nine-month period (pre-injection, one-month post-injection, and nine-months post-injection). We used groundwater data collected from 2018 to 2019 to conduct a high-resolution investigation into the visualization of arsenic contamination over time.

2. Materials and methods

2.1. Study site

The study by Fischer (2020) devised an in-situ arsenic bioremediation method to sequester arsenic for nine months at an arsenic contaminated industrial site in northwest Florida. The aquifer at the industrial site is part of the Surficial Aquifer System of Florida, mostly comprised of quartz-rich sand and sandy clay that extend to 6.0–7.6 m in depth (Lee et al., 2018). The aquifer has moderately oxidizing conditions and a shallow water table, measuring ~1.5 m in depth, with the general groundwater flow direction to the west and northwest at a rate of about 20 m/year (Fig. 1). The clean-up standard of this specific legacy site is 0.05 mg/L (Lee et al., 2018; Saunders et al., 2018). To reach this standard, an injectate consisting of 5 kg of ferrous sulfate, ~27 kg (60 lbs) of molasses, and ~1 kg (2 lbs) of fertilizer per 3785.4 L (1000 gallons) of water was used to stimulate bacterial sulfate reduction (Fischer, 2020). Twenty-three wells (11 injection wells and 12 monitoring wells) were installed across the ~900 m^2 site, with the injection wells placed hydrologically upgradient of the monitoring wells for the downgradient movement of the injectate to facilitate full-scale remediation (Fig. 1). The ferrous sulfate mixture was injected during the week of June 17, 2018. Groundwater samples were collected using a peristaltic pump prior to the injection as well as throughout the bioremediation process, until the end of the experiment during the week of March 17, 2019. Three time periods spanning the entire field experiment duration were chosen to determine the success of the bioremediation procedure using interpolation analyses: before the injection on May 15, 2018, one month after the injection on July 19, 2018, and nine months after the injection on March 18, 2019. Concentrations of arsenic in the water were measured by Agilent 7900 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) in the Department of Geosciences at Auburn University using EPA Method 6020 (U.S. EPA, 2014). Mineralogical and geochemical data of the precipitated biominerals formed from the

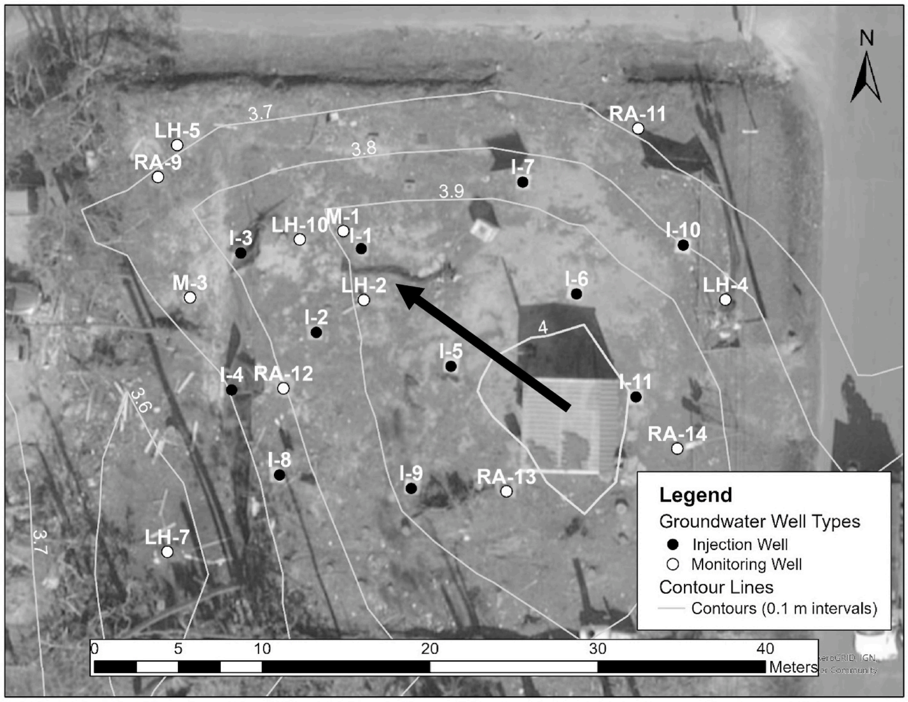

Fig. 1. Overview of study site in northwest Florida showing ground elevation (contours in meters), injection wells (in black), and monitoring wells (in white). The general direction of groundwater flow is toward northwest, as shown by the black arrow.

indigenous SRB to sequester arsenic can be found in Fischer (2020).

2.2. Interpolation and spatial analysis

IDW, OK, and EBK, interpolations were calculated and analyzed using ArcGIS Pro 2.4. The ArcGIS Pro Geostatistical Wizard was used to create interpolation maps for the three time periods spanning the bioremediation experiment. The Geostatistical Wizard allows one to manually create the best-fit model based on the statistical properties of the dataset. Additionally, the Geostatistical Wizard generates cross-validation and validation analyses of the interpolation surface such as leave-one-out cross-validation (LOOCV), which has been previously used as a cross-validation technique in environmental studies (Xie et al., 2011; Mirzaei and Sakizadeh, 2016). Through LOOCV, the program systematically removes each point in the interpolation, predicts its value by interpolating from the remaining points, and finally compares the predicted value to the measured value (Xie et al., 2011; Mirzaei and Sakizadeh, 2016). These validation outputs enable the user to determine which of the interpolation models is the most accurate representation for the dataset.

Arsenic concentrations were higher in the northwest region of the site and lower in the eastern and southern portions of the site. Arsenic showed a first order decrease in concentration across the study site over the three time periods. Consistent with best-practices (Lange and Krause, 2019), the first order trend was removed for each of the three interpolation methods to adhere to the assumption of Kriging that there should be no global trends in the dataset (Shamsudduha, 2008; Paramasivam and Venkatramanan, 2019). Additionally, arsenic concentrations were not normally distributed and were corrected using a log transformation in both the OK and EBK interpolation models (Gong et al., 2014; Singh and Verma, 2019), verified through the Geostatistical Wizard's Quantile-Quantile (QQ) Plots. For the OK interpolation, the kernel function was set to exponential and the function type to semivariogram, with the interpolation model optimized for goodness of fit and accuracy; all other variables were kept at their standard values. For the EBK interpolation, the transformation type was set to log empirical and the semivariogram model type was set to exponential; all other values were kept to their standards. The semivariogram power was kept at 100 simulations for improved operation, efficiency, and accuracy (Tomlinson, 2019). For the IDW interpolation, the weighting power was set to one, as this showed the lowest root mean square error (RMSE) compared to higher weighting powers. This implies that for the arsenic data, points farther away can still have a significant influence on the predictions (Xie et al., 2011).

The cross-validation indicators of RMSE and mean values as well as prediction and error plots were utilized to assess the validity and accuracy of the three interpolation methods throughout the bioremediation procedure. RMSE was used to directly assess the accuracy of the interpolation's predictions, as RMSE values closer to zero indicate that predicted values are numerically close to the measured values (Krause, 2019; Lange and Krause, 2019). The mean value denotes the average of the cross-validation (CV) errors and is important in determining any bias or smoothing effects in the interpolation model (Krause, 2019; Lange and Krause, 2019). Strong smoothing indicates that the interpolation either significantly overestimates local minima or underestimates local maxima, which inaccurately diminishes or obscures the contrast between the concentration changes across a site. Thus, if the mean is close to zero there is minimal bias; if the mean is above zero, the model systematically overestimates the actual values; while if the mean is below zero, the model consistently underestimates the values (Krause, 2019). Additionally, the measured arsenic concentrations were compared and plotted against the interpolation's predicted arsenic concentrations and the cross-validation errors. Final interpolation maps were created, and the interpolation surfaces were transformed from Geostatistical Analyst layers into rasters using the Geostatisical Analyst (GA) Layer to Raster tool.

3. Results

3.1. Measured arsenic concentrations

Spatial and temporal patterns were found among the results of bioremediation across the site. The 23 wells were grouped into three categories based on resultant arsenic concentrations over the course of the study: (1) *decreasing*, (2) *fluctuating*, or (3) largely *unaffected* (Fig. 2; Table S1 in Appendix A). Four wells showed continuously *decreasing* (1) arsenic concentrations throughout the nine months (LH-4, LH-10, M-1, and RA-9), three of which were located in the northwest portion of the site (LH-10, M-1, and RA-9) (Fig. 2a and b), in the downgradient direction of groundwater flow. The majority of wells (12/23) displayed large *fluctuations* (2) in arsenic concentrations over time (I-1, I-2, I-3, I-4, I-5, I-6, I-7, I-11, LH-2, LH-5, M-3, and RA-12). Several wells showed sharp decreases in arsenic concentration between the initial injection and one month reading, and then an increase in concentration between one and nine months (I-1, I-2, 1–3, 1–4, and I-11). Most wells with fluctuating arsenic concentrations were in the northwest portion of the site (I-1, I-2, I-3, I-4, LH-2, LH-5, M-3, and RA-12), with the remaining being injection wells located in the east (I-5, I-6, I-7, and I-11) (Fig. 2a). Finally, seven wells remained largely *unaffected* (3) by the injection, with arsenic concentrations showing no significant changes over time (I-8, I-9, I-10, LH-7, RA-11, RA-13, and RA-14) (Fig. 2b). These seven wells are found exclusively in the east and southwest sides of the site (Fig. 2a). The injection and monitoring wells in the east and southeast portions of the site maintained negligible concentrations of arsenic throughout the study (Fig. 2a). In contrast, wells in the northwest report the highest initial concentrations of arsenic, indicating a potential arsenic plume centered around injection well I-3 (Fig. 2a). Of the wells that reported arsenic concentrations above the site clean-up standard, two (LH-2 and M-1) decreased below 0.05 mg/L after nine months (Fig. 2b). Thus, the monitoring wells of LH-2 and M-1, with the potential addition of RA-9 and M-3, serve as best-case scenarios for demonstrating the success of the remediating mixture at the field site, with these wells depicting a significant reduction in arsenic to near or below the acceptable standard (Fig. 2b). Overall, arsenic concentrations were below the regulatory standard in 12 wells after one month and 11 wells after nine months.

3.2. Predicted arsenic concentrations with interpolation

The interpolation maps generated from the IDW, OK, and EBK methods show detailed differences in the overall accuracy of their predictions due to over- or underestimation (Fig. 3). All three methods predicted that the highest arsenic measurements were concentrated in the northwest, while lower concentrations (near or below 0.05 mg/L) were found primarily in the east and southeast of the study site.

Before the injection, EBK and IDW accurately predicted arsenic concentrations above 0.75 mg/L centered around well I-3, while OK underestimated this arsenic maximum (Fig. 3). Additionally, nine wells (I-8, I-9, I-10, LH-4, LH-7, LH-10, RA-11, RA-13, and RA-14) had measured concentrations below 0.05 mg/L (Fig. 2). The OK and EBK pre-injection interpolations successfully predicted arsenic concentrations in eight of these wells (missing LH-10), while IDW only accurately predicted four of the wells (missing I-8, I-9, LH-7, LH-10, and RA-13).

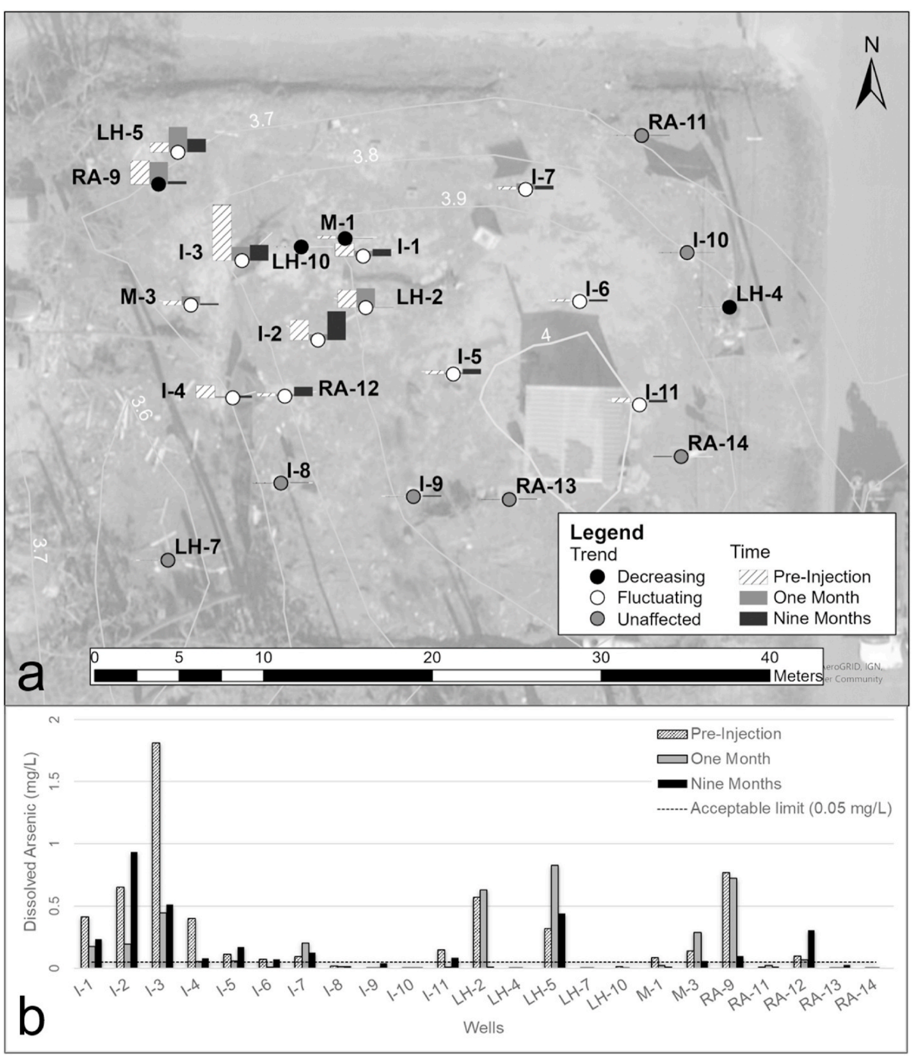

Fig. 2. Dissolved arsenic concentrations (mg/L) during the three sampling intervals at each injection and monitoring well shown in their respective locations and with ground elevation (contours in meters) (a) and on the bar chart (b) where the dashed line represents the site's acceptable arsenic limit of 0.05 mg/L.

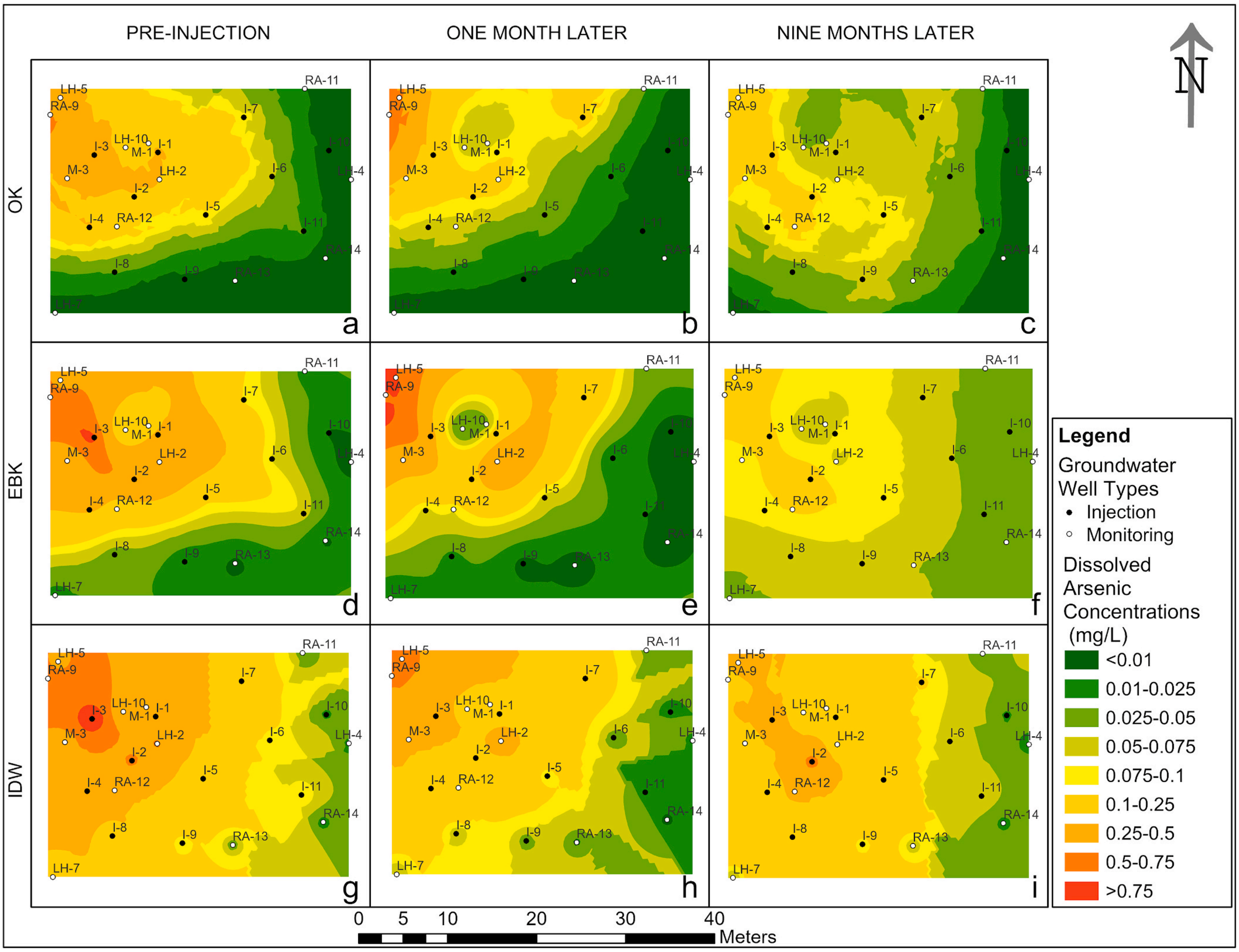

Fig. 3. Visualization of results of interpolation methods for different time periods: Ordinary Kriging (OK) for pre-injection (a), one month later (b), and nine months later (c); Empirical Bayesian Kriging (EBK) for pre-injection (d), one month later (e), and nine months later (f); and Inverse Distance Weighted (IDW) for pre-injection (g), one month later (h), and nine months later (i). Colors represent dissolved arsenic concentrations in milligrams per liter (mg/L) ranging from low (green) to high (red). Injection and monitoring groundwater wells, represented as groundwater sample locations, are depicted as black and white dots on the map, respectively. Groundwater flow moves in the northwest direction as shown by the black arrow in Fig. 1. (If viewing print version: for interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Moreover, IDW also over-predicted arsenic concentrations in these four wells, estimating values between 0.025 and 0.05 mg/L.

After one month of bioremediation, all interpolation methods predicted highest arsenic concentrations in the northwestern-most portion of the site, around wells LH-5 and RA-9 (Fig. 3b,e,h). However, only EBK predicted arsenic concentrations above 0.75 mg/L in these two wells, while OK and IDW predicted values of 0.5–0.75 mg/L. Yet, all three methods were inaccurate when compared to the measured values of 0.823 mg/L in LH-5 and 0.722 mg/L in RA-9. Both OK and EBK predicted low concentrations of arsenic around LH-10 and M-1 compared to the surrounding wells; however, EBK was more accurate in predicting concentrations below 0.05 mg/L at LH-10 and M-1 (Fig. 2). EBK correctly predicted all 12 wells with concentrations below the 0.05 mg/L standard (I-6, I-8, I-9, I-10, I-11, LH-4, LH-7, LH-10, M-1, RA-11, RA-13, and RA-14), OK accurately predicted 10 wells (missing LH-10 and M-1), and IDW accurately predicted eight wells (missing I-6, LH-7, LH-10, and M-1).

After nine months, the three methods indicated that the highest concentrations of arsenic existed in the northwestern portion of the site, extending from the northwest corner around LH-5 and RA-9 to slightly west of the center of the site at RA-12 (Fig. 3c,f,i). IDW predicted higher arsenic concentrations in this elevated area than both OK and EBK (0.5–0.75 to >0.75 mg/L compared to 0.25–0.5 mg/L). OK was the most accurate interpolation method in predicting regulatory arsenic concentrations, depicting nine of the measured 11 wells (I-8, I-10, LH-4, LH-7, LH-10, M-1, RA-11, RA-13, and RA-14) accurately below 0.05 mg/L (missing I-9 and LH-2), while IDW and EBK only accurately predicted four and five wells, respectively (IDW missed I-8, I-9, LH-2, LH-7, LH-10, M-1, and RA-13, and EBK missed I-8, I-9, LH-2, LH-10, M-1, and RA-13).

3.3. *Cross-validation analyses*

3.3.1. *Statistical results*

The RMSE and mean of the cross-validation values (mean CV) over the duration of the study from the IDW, OK, and EBK methods were used to assess the accuracy of each interpolation method in predicting arsenic concentrations across space and time. The RMSE values of the interpolations determined whether the predicted arsenic concentrations matched the measured concentrations, with values close to zero indicating a high prediction accuracy. Similarly, the mean CV values noted smoothing effects and bias in the interpolations, with values above zero indicating overestimation of arsenic concentrations and values below

Table 1
Statistical results of each interpolation method for each time period in the study. Interpolation methods used: Ordinary Kriging (OK), Empirical Bayesian Kriging (EBK) and Inverse Distance Weighted (IDW). Root Mean Square Errors (RMSE) and mean cross-validation values (Mean CV) are shown for each time-period. The global mean represents the averages of RMSE and Mean CV throughout the study.

	OK		EBK		IDW	
	RMSE	Mean CV	RMSE	Mean CV	RMSE	Mean CV
Pre-Injection	0.391	−0.034	0.49	0.113	0.399	0.046
One Month Later	0.163	−0.035	0.154	0.023	0.186	0.008
Nine Months Later	0.243	−0.023	0.225	0.046	0.233	0.026
Global Mean	0.266	−0.031	0.296	0.063	0.273	0.027

zero denoting underestimation of arsenic. Before the injection, OK had a RMSE of 0.391 and a mean CV value of −0.034 (Table 1). After one month, the RMSE decreased to 0.154, while the mean CV slightly decreased to −0.035. The RMSE for OK then increased to 0.243 and the mean CV increased to −0.023 after nine months. For the EBK interpolation, EBK reported a RMSE of 0.49 and a mean CV of 0.113 before the injection. Both the RMSE and mean CV then dropped to 0.154 and 0.023 after one month, respectively. After nine months, the RMSE and mean CV of the EBK interpolation both moderately increased to 0.225 and 0.046, respectively. The IDW interpolation had a RMSE of 0.399 and a mean CV of 0.046 before the injection, which both significantly decreased after one month to 0.186 and 0.008, respectively. Both the RMSE and mean CV increased to 0.233 and 0.026, respectively, after nine months (Table 1).

3.3.2. Prediction and error results

Besides the RMSE and mean CV values, prediction and error plots are automatically generated during the interpolation process. These plots were used to determine the accuracy of the three interpolation methods. Plots of the measured arsenic concentrations versus each interpolation's predicted arsenic concentrations as well as of the cross-validation errors versus the measured concentrations are shown in Fig. 4 (OK) and S1 in Appendix A (IDW and EBK). For the prediction plots, an accurate model would show a regression line that follows a slope of 1 indicating that the predicted concentrations align with the measured concentrations (Krause, 2019; Lange and Krause, 2019). Deviations from a slope of 1 indicate error in the model fit. OK showed a correlation slope of 0.419 for the predicted arsenic concentrations before the injection and a very strong correlation of 1.01 after one month (Fig. 4a). However, OK showed low correlation in its predicted concentrations after nine months, with a regression slope of 0.051. EBK had consistently weak correlation slopes for its pre-injection and nine-month predicted concentrations (0.226 and 0.237, respectively) but showed a strong correlation for its one-month concentrations (0.851) (Fig. 4b). IDW showed the weakest overall correlations of the three interpolation methods, with regression slopes of 0.409, 1.922, and 0.210 prior to the injection, one month after, and nine months after the injection, respectively (Fig. 4c). The average regression slope values for each of the interpolation methods throughout the bioremediation process were 0.489 for OK, 0.438 for EBK, and 0.209 for IDW. OK and EBK showed similar average error regression slopes of −0.708 and −0.706, respectively, while IDW showed the highest average error slope of −0.822 (Fig. S1).

4. Discussion

4.1. Arsenic concentrations across space and time

There were three trends in arsenic concentrations over the course of the nine-month bioremediation: (1) several wells (4/23) showed *decreasing* arsenic concentrations over time (LH-2, LH-10, M-1, and RA-9), (2) the majority of wells (12/23) displayed *fluctuating* patterns of arsenic concentrations, and (3) the seven remaining wells (I-8, I-9, I-10, LH-7, RA-11, RA-13, and RA-14) depicted *little to no change* in arsenic over time, remaining below the acceptable limit before and after the injection. Wells with a *decreasing* trend in arsenic were located in close proximity to injection wells and were first to exhibit reductions in arsenic (e.g., LH-10 and M-1), while those farther away (e.g., LH-2 and RA-9) depicted significant improvements in arsenic concentrations after nine months (Fig. 2). These findings can be explained by the slow velocity of groundwater at the site (20 m/y) and is representative of the amount of time it took the injectate to reach the wells located farther downgradient. In the 12 *fluctuating* wells, which displayed a striking contrast in arsenic concentrations, one of two scenarios likely occurred: (1) an influx of untreated groundwater increased arsenic over time or (2) the injectate did not reach its intended wells. The injection wells were predominantly located upgradient throughout the site (e.g. in the east or southwest), meaning that without repeated injections, they were susceptible to recontamination due to upgradient, untreated groundwater flowing into the site. This untreated groundwater was more oxidizing than the treated groundwater, potentially destabilizing the formed arsenian pyrite and releasing arsenic back into the groundwater. Thus, while the injectate effectively removed arsenic after one-month,

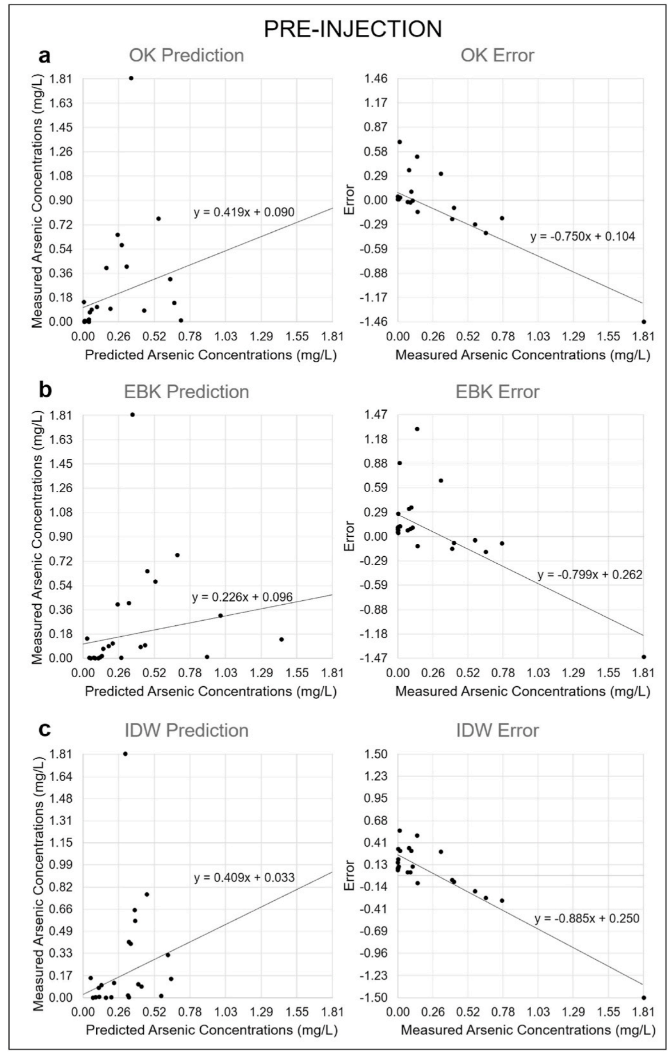

Fig. 4. The predicted arsenic concentrations and error values versus the measured arsenic concentrations before the injection from the OK, EBK, and IDW interpolation methods. Additional prediction and error plots for one- and nine-months post-injection can be found in Figure S1 in Appendix A.

untreated groundwater flowed into the site after nine months, which remobilized arsenic and induced a significant increase in arsenic in many of the injection wells located in the east and southwest (I-5, I-6, I-7, and I-11). In addition to the influx of untreated water, the injection and monitoring wells located around the arsenic plume in the northwest (I-1, I-2, I-3, I-4, LH-5, and RA-12) also showed increases in arsenic possibly due to a limited flow path of the injectate, and thus, the injectate did not effectively reach the intended wells. For instance, LH-5 was located far downgradient of surrounding injection wells (e.g., ~7.5 m downgradient of I-3 and ~12.5 m downgradient of I-1), and while a reduction in arsenic did occur after nine months, arsenic concentrations remained well above the standard. In contrast, the nearby monitoring well RA-9 showed a significant decrease in arsenic near the acceptable level, indicating that the injectate was preferentially flowing to RA-9 rather than to both wells equally. Thus, the increase in arsenic in many of the injection wells in the northwest could be explained by variations in the groundwater flow paths. In contrast to the *decreasing* and *increasing* arsenic trends, the trend of wells that appear largely *unaffected* by SRB bioremediation is due to the very low arsenic concentrations (5-10x less than 0.05 mg/L) reported in these wells. Due to these low concentrations, the wells exhibited only slight increases or decreases in arsenic throughout the nine months.

After examining and assessing the bioremediation trends in arsenic, this study definitively determined the importance of repeated injection treatments of contaminated groundwater. Repeated injections of the ferrous sulfate mixture would likely maintain reducing conditions and stabilize the arsenian pyrite for an extended period of time, even during the influx of untreated groundwater. Additionally, multiple injections may allow the variable groundwater flow to carry the injectate to the missed downgradient wells for full-scale remediation. New upgradient injection points near the missed wells may be needed if repeated injections still fail to reach these locations.

4.2. Accuracy of interpolation methods in determining arsenic concentrations

The high sampling resolution (23 wells) and a local-scale study area (~900 m^2) was key in demonstrating the accuracy of the interpolations and certainty in the overall findings of this study. Notably, the study's results differed from many previous environmental monitoring studies due to scale and sampling resolution, considering that most studies interpolated over very large areas (>100 km^2) with a lower sampling density. For instance, Mirzaei and Sakizadeh (2016) analyzed 65 wells over 1100 km^2, and Xie et al. (2011) analyzed 137 samples across an area half the size (605 km^2). Because Xie et al. (2011) had a much higher sampling resolution, this study aligned more closely to the results found by Xie et al. (2011) than Mirzaei and Sakizadeh (2016), in which OK showed consistent underprediction but overall accuracy in prediction. Studies that had a lower sampling resolution over a larger study area (e.g. Shamsudduha, 2008; Gong et al., 2014; Mirzaei and Sakizadeh, 2016) noted high uncertainty and discrepancies in their interpolations. Mirzaei and Sakizadeh (2016) found that although EBK yielded the least amount of error in their study, both EBK and OK showed strong smoothing effects and consistently overestimated local minima, which is problematic in regard to monitoring regulatory standards of groundwater contaminants. Similarly, Magesh and Elango (2019), who used 49 wells to interpolate fluoride over 429.5 km^2, reported high error in their ArcGIS Pro error plots and large RMSE values. Again, they saw a strong smoothing effect in both the EBK and IDW interpolations and a high error in their predictions at low concentrations. Both Shamsudduha's (2008) and Gong et al.'s (2014) interpolations of groundwater arsenic also highlighted how a low sample density yielded a lower prediction accuracy due to varying geology and biogeochemical processes over a large area. Considering these comparisons, our study benefited from a local-scale site (~900 m^2) with high-density data (23 wells) to increase the prediction accuracy, which allowed the study to effectively analyze and critique different interpolation methods.

The RMSE and mean CV values of the interpolations across space and time are reliable criteria to evaluate the accuracy of interpolation methods (e.g., Magesh and Elango, 2019; Singh and Verma, 2019). RMSE values close to zero indicate a high prediction accuracy, with the predicted (interpolated) arsenic concentrations closely aligning with the measured arsenic concentrations. By averaging the RMSE values of the three interpolation methods across the three sampling periods, OK showed the lowest global RMSE of 0.266, IDW had a RMSE of 0.273, and EBK depicted the highest global RMSE of 0.296 (Table 1). Because OK had the lowest overall RMSE and yielded consistently low RMSE values throughout the bioremediation process, OK had the highest accuracy in predicting arsenic concentrations over space and time. Accordingly, IDW and EBK had higher RMSE values, and, thus, a lower overall accuracy in predicting arsenic concentrations. The mean CV value is important for determining if a bias (underestimation or overestimation) exists in the interpolation model (Krause, 2019; Lange and Krause, 2019). Our results showed that OK had mean CV values below zero for each timepoint during the bioremediation process, with a global mean of −0.031 (Table 1). In contrast, EBK and IDW both systematically yielded mean CV values above zero, with global mean CV values of 0.063 and 0.027, respectively (Table 1). Thus, OK consistently underestimated arsenic concentrations, whereas EBK and IDW overestimated concentrations. The statistical results also indicate that OK is the most accurate of the three interpolation methods and that it tends to underpredict arsenic concentrations. Our results agree with the findings of Shamsudduha (2008), Xie et al. (2011), and Singh and Verma (2019), in which they reported OK as having the lowest RMSE and mean values.

In this study, OK was best overall in determining which wells had met regulatory arsenic concentrations (<0.05 mg/L) throughout the bioremediation process. This finding aligns with previous results by Xie et al. (2011), who concluded that OK had the "strongest ability" to accurately predict the overall trend in pollution across a site (Fig. 3a–c). However, OK consistently underestimated the local arsenic maxima that represented the arsenic plume on site. Yet, this trend of underestimation is also noted by Xie et al. (2011) and Mirzaei and Sakizadeh (2016). While this study confirms OK's trend in underestimation, there are no distinct instances of overprediction, perhaps due to the lack of a singular arsenic minima. Rather, there is a large area of low arsenic concentration (<0.05 mg/L), which OK accurately represented. Both EBK and IDW showed a tendency for overestimation, with EBK displaying a large smoothing effect on the data. EBK was less accurate overall compared to OK because it showed a consistent inclination for overestimation, especially in regard to wells around the local arsenic maxima of the plume, which aligns with findings from Mirzaei and Sakizadeh (2016) (Fig. 3e). The study also agrees with the large smoothing effect of EBK found by Magesh and Elango (2019) but provides a slight caveat, noting that the EBK method produces less systematic bias than IDW. In fact, the IDW method was the least accurate in predicting arsenic across the site, only accurately predicting concentrations <0.05 mg/L in a small fraction of the wells throughout the entire bioremediation process due to consistent overestimation, in contrast to Mirzaei and Sakizadeh's (2016) findings (Figs. 3g–i and 4c). Overall, OK was the most accurate interpolation method in predicting arsenic concentrations across space and time; EBK gave sufficient results but had a tendency for overestimation, and IDW showed the most inaccurate results and showed consistent problems with overestimation.

The RMSE and mean CV values represent the overall accuracy of the interpolation method, however, these measures may overshadow important nuances in predicting arsenic concentrations near the regulatory threshold, an important part of evaluating effective remediation. Plots of the CV errors versus the measured arsenic concentrations (Fig. 4) reveal the degree of smoothing in the model, depicting whether the errors are independent of the measured values. Moreover, the error plots can be used to carefully assess the error in the RMSE values and confirm the accuracy of these methods in predicting low concentrations.

If the error regression line is horizontal, then the model accurately predicts values across the entire range of the measured values. In this study, however, the regression line showed a negative slope, meaning the lowest values were underestimated while the highest values were overestimated (Krause, 2019). Considering this, OK and EBK showed moderate-to-high levels of systematic smoothing (bias) throughout the bioremediation process, reporting average error regression slopes of −0.708 and −0.706, respectively, while IDW depicted the highest systematic smoothing, with an average error slope of −0.822 (Fig. 4). Importantly, in the OK prediction plots, predicted arsenic at low concentrations closely aligns (near a 1:1 ratio) with the measured concentrations, but predicted concentrations deviate at high arsenic concentrations. Similarly, in the OK error plots, the error regression slopes intercept the y axis near zero, meaning that predicted arsenic concentrations at low concentrations (<0.05 mg/L) have a small amount of error (Fig. 4). Careful interpretation of the relative error across the wide range of arsenic concentrations reinforce the accuracy of OK for predicting arsenic concentrations near the regulatory threshold. For EBK and IDW, the predicted low concentrations show more distinct differences from the measured concentrations at low concentrations, evidenced by their error regression slopes have y intercepts significantly higher than zero throughout the experiment (Fig. 4b and c). All interpolation methods show that as arsenic concentrations increase, the amount of prediction error also increases, which explains the high degree of smoothing and potential bias seen at higher arsenic concentrations. OK was the most accurate of the three methods in its predictions overall and showed the least amount of error especially at concentrations near the regulatory threshold.

4.3. Methods and challenges of arsenic remediation

Several treatment methods have been developed to remediate water and groundwater arsenic contamination, with most facing efficacy or cost-related challenges. All methods would serve to benefit from interpolation and visualization of concentrations across space and time. Notable methods for arsenic remediation include co-precipitation with iron coagulants, filtration using ion exchange resins or membranes, adsorption by iron oxides, activated alumina, and ex-situ and in-situ bioremediation (c.f. Mondal et al., 2013). Yet, coagulation and filtration systems often become clogged, and adsorption filters using iron oxide or activated alumina create toxic sludge. These ion exchange, membrane, and adsorption filters also cannot effectively remove arsenite, the more toxic form of arsenic. Additionally, ex-situ remediation, or "pump and treat" techniques, involve pumping large quantities of groundwater for above-ground treatment, which is usually expensive (Pi et al., 2017). Considering these issues, in-situ bioremediation, as used in this study, appears as the most cost-efficient and effective method for groundwater arsenic removal. Low-cost remediating mixtures can be directly injected into the contaminated groundwater and stimulate bacteria to precipitate arsenic-sorbed biominerals, without producing any toxic by-products. Furthermore, iron (Fe), sulfate (SO_4), and hydrogen sulfide (H_2S) concentrations can be used to monitor the progress of in-situ arsenic bioremediation: initially, the injection would cause an increase in Fe, SO_4, and As (Fischer, 2020). Then subsequent concurrent decreases in Fe, SO_4, and As indicate the precipitation of As-sorbing pyrite, whereas H_2S, which is produced by sulfate reducing bacteria (SRB), reacts with Fe to produce pyrite for arsenic removal (Lee et al., 2018). No matter which method is used for arsenic bioremediation, there is a strong need for estimating concentrations in unmeasured areas. The results of this study indicate that interpolation is an effective way to aid in the interpretation and extent of bioremediation across space and time.

5. Conclusions

The spatial and temporal visualization of arsenic concentrations has been key to identifying the effectiveness of groundwater arsenic bioremediation. The results showed that 23 wells exhibited *decreasing*, *fluctuating*, or largely *unchanging* arsenic concentrations over the nine months of bioremediation. However, the wells with *fluctuating* arsenic concentrations saw increases in arsenic after one or nine months due to the influx of untreated groundwater over time and/or variations in the flow paths. Repeated injections would maintain reducing conditions throughout the site and, thus, prevent the untreated groundwater from destabilizing the arsenian pyrite.

Of the three examined interpolation methods, OK was the most accurate in predicting arsenic concentrations spatially and temporally throughout the bioremediation process. OK showed the lowest overall RMSE interpolation values and had mean CV values below zero throughout the bioremediation process. While these negative means indicated that OK underpredicted arsenic concentrations, the interpolation prediction and error analyses revealed that OK was the most accurate interpolation method, especially in determining the wells with low, regulatory arsenic concentrations of 0.05 mg/L. In contrast, EBK and IDW were consistently less accurate in predicting arsenic concentrations, both showing a tendency for overestimating and with IDW depicting larger prediction inaccuracies. These in-depth comparisons between OK, EBK, and IDW reveal the importance of using high-resolution sampling and a local-scale study area for accurate interpolations. In regard to mapping groundwater arsenic contamination specifically: when using OK as the interpolation method, researchers should be cognizant of the fact that actual lows and highs may be higher than predicted but overall accuracy across the site is reliable; whereas, with IDW and EBK, there will be significant instances of overestimation and a lower degree of accuracy overall. In conclusion, this study highlights the importance of high sampling resolution over a very small area, with both significantly increasing the accuracy of the interpolations and allowing the study to precisely analyze and compare the interpolations. Considering these important discoveries, this study can help inform governments, industry, and local communities of the best sampling and interpolation practices for effectively monitoring and mitigating arsenic contamination.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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