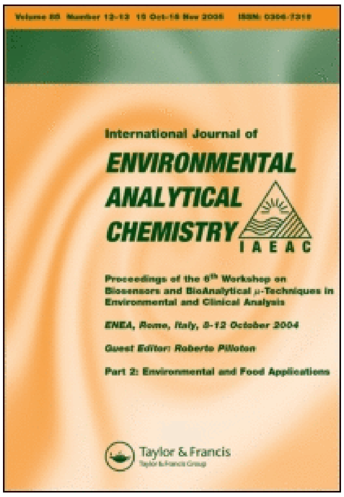

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ASSESSMENT OF TEMPORAL VARIABILITY TRENDS FOR INORGANIC PARAMETERS IN GROUND WATER

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The passage of environmental legislation in the United States has dramatically increased ground-water monitoring in the vicinity of point sources such as abandoned waste disposal sites, operational waste disposal sites, and municipal landfills. Even though these programs require sufficient sampling to define background conditions as part of the site characterization process, there is still a general absence of quantitative information on the magnitude and periodicity of temporal fluctuations for inorganic constituents in ground water. This paper presents an approach that has been used to develop an initial characterization of these temporal trends.

A search if on-going site investigation reports identified 18 facilities across the United States that had monthly monitoring data at a frequency of at least monthly for a period of one and a half years or longer (15 RCRA-C hazardous waste disposal facilities with monthly data for a period of 2–3 years, 2 research monitoring locations with biweekly monitoring data for a period of one and a half years, and a precious metal mining operation with daily monitoring data for a limited number of parameters for a period of one and a half years). The data from these site investigations were used to describe the temporal variability of several ground-water constituents including pH, specific conductance, sulfate, sodium, chloride, alkalinity, silica, iron, and manganese. An assessment of these data suggests that the magnitude of temporal ground-water fluctuations are on the order of 20 percent of the average concentration for chloride, 10 percent of the average concentration for sodium, manganese and specific conductance, 5 percent of the average concentration for alkalinity and pH, and essentially zero for silica. The apparent periodicities of these temporal fluctuations ranged from 40 weeks to approximately 2 years. The magnitude and periodicities in ground water are substantially smaller than those that have been reported and documented for the same constituents in surface waters. These differences are due to the fact that sunlight and wind, two energy factors that drive temporal cycles in surface water, do not exert a similar influence on the environmental chemistry of ground-water constituents.

KEY WORDS: Ground-water, inorganic parameters, monitoring, temporal trends.

INTRODUCTION

The passage of environmental legislation in the United States has increased the ground-water monitoring in the vicinity of point sources such as abandoned waste disposal sites, operational hazardous waste disposal sites, and municipal landfills. The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) supported site characterization programs at several thousand waste disposal facilities. These activities resulted in the prioritization of 1500 sites for inclusion on the National Priorities List and eventual remediation[1]. Subtitle C of the Resource Conservation and Recovery Act[2] requires regular ground-water monitoring at approximately 300 active hazardous waste disposal facilities that have received a permit to operate and an additional 1700 facilities that have filed for closure. The RCRA Subtitle D program[3], which was finalized in 1991, will require as many as 15,000 municipal landfills to conduct routine monitoring to detect and assess the impact of these facilities on local ground-water conditions. One factor that must be addressed in the sampling program at each of these facilities is the selection of a sampling frequency to characterize background temporal fluctuations. However, despite the magnitude of these combined monitoring efforts, there is still a general absence of information to define the magnitude and periodicity of temporal fluctuations for inorganic constituents in ground water.

Temporal fluctuations for several ground-water quality parameters have been reported and discussed in the technical literature. Seasonal fluctuations for calcium, magnesium, and bicarbonate have been reported for shallow ground water in Alberta with minimum concentrations occurring in the spring and maximum concentrations occurring in the summer[4]. Schmidt[5] has observed seasonal variation in nitrate concentrations due to agricultural activities at three locations in California. Temporal variation in nitrate and sulfate concentrations related to irrigation practices and water recharge have also been described by Spalding and Exner[6]. Montgomery *et al.*[7] have analyzed monitoring data from 11 disposal site/landfill facilities and have identified eight constituents (chloride, total dissolved solids, nitrate, sulfate, pH, iron, total kjeldahl nitrogen, and temperature) that displayed a tendency for seasonal behavior. However, the seasonal trends were only identified in 18 percent of the cases examined (individual parameters ranged from 6 percent of the cases to 50 percent of the cases). Furthermore, data for seven additional parameters (specific conductance, total organic carbon, ammonia, boron, fluoride, hardness, and sodium) did not display any seasonal tendency. The observed periodicities associated with the temporal cycles in ground-water data have ranged from minutes to decades[8].

Identified factors that can contribute to temporal variability in ground water include

(1) the timing and magnitude of recharge events (either natural or artificial)[5,7],
(2) changes in the composition of recharge water[5,7,9],
(3) localized pumping rates and patterns[5],
(4) changes in prevailing meteorological conditions[5],
(5) proximity to point and non-point sources of contamination[6,9], and
(6) aquifer stratigraphy[9].

A dominant characteristic of these factors is that their influence would be more pronounced in shallow aquifers. Since improperly functioning waste disposal sites and landfills would be expected to have their greatest initial impact on shallow aquifers, it is imperative that site monitoring programs are capable of distinguishing between changes due to temporal variability and those due to a site leakage event. A better understanding of temporal variability patterns can provide an improved technical basis for establishing effective sample collection frequencies in the ground-water monitoring programs at waste disposal sites and municipal landfills. The remainder of this paper shall present an assessment of temporal changes for inorganic parameters in ground water in the vicinity of waste disposal sites.

TEMPORAL MONITORING DATA

Data used in this report were obtained from three sources. One source was a database compiled as part of a project to characterize ground-water conditions near waste disposal facilities and to identify potentially useful monitoring parameters[10–13]. These data were a compilation of routine monitoring data from more than 500 RCRA and CERCLA site investigations across the country. A review of this project database identified 15 sites with multi-year records to define temporal fluctuations in ground-water quality. Each of these sites had 8 to 70 wells that were monitored approximately monthly for periods of two to three years.

The second source was a database compiled as part of an ongoing project to identify potential ground-water monitoring parameters for precious metal mining operations that utilize the heap leaching process. This data set consisted of routine monitoring data from 25 mining operations in Nevada. The data from one mine monitoring program was included in the temporal assessment study. The site monitoring program at this facility has produced daily observations for alkalinity, pH, and cyanide for a period of 18 months at three wells.

The third source of data was an EPA-funded research project to study temporal variability in ground water[8]. This study provided biweekly monitoring data from 12 wells at two sites in Illinois over a period of 78 weeks. A total of 24 parameters were monitored during this project.

The final data set used to assess temporal trends in ground water consisted of monitoring data from 16 waste disposal sites, one pristine site in Illinois, and one mining site in Nevada. Because these data were passively collected from diverse sources, the level of quality assurance/quality control varied with each subset of the data. The first subset (15 waste disposal sites) was produced by a single laboratory in accordance with quality assurance procedures established in the EPA Contract Laboratory Program. The third subset (2 Illinois sites) was generated in a research program in which the quality assurance samples (duplicates, matrix spikes, calibration standards, blanks, and external QC samples) represented 55 to 85 percent of the total number of samples analyzed. The ground-water data from the one mining facility is the only subset for which quality assurance procedures are not known.

DATA PRESENTATION PROCEDURE

A graphical, control-chart type procedure was used to summarize the monitoring data and assess temporal fluctuations. This approach simply consists of plotting the observed observation as a function of time. However, rather than plotting the actual concentration for each parameter, the data were normalized using the following multi-step procedure.

1. The data were tabulated by sampling location and date as shown in Table 1.
2. The data for a well were summed over the period of record and divided by the number of observations to produce a time-averaged concentration for that parameter at that well (Table 1).
3. The actual observations at a well were normalized to the calculated time-averaged concentration for that well (Table 2).
4. Steps 1 and 2 were repeated for each well in the ground-water monitoring network at the facility.
5. The normalized concentrations were then averaged across all wells to assess temporal trends that may be present at that facility.

The data normalization procedure described above was implemented for several reasons. First, there is no known or true value associated with environmental monitoring data

Table 1 Ground-water monitoring data for pH at R76, an active waste disposal site in Alabama.

Date	*Well A*	*Well B*	*Well C*	*Well D*	*Well E*
12/84	12.03	7.58	7.02	7.88	8.14
1/85	12.40	7.78	8.31	7.97	8.11
2/85	12.90	7.58	7.39	7.76	7.98
3/85	12.90	8.60	7.42	7.70	8.07
4/.85	12.20	7.49	6.86	7.58	8.40
5/85	12.40	7.60	9.54	7.53	7.98
Average	12.47	7.77	8.09	7.74	8.11

Table 2 Normalized ground-water monitoring data for pH at R76, an active waste disposal site in Alabama.

Date	*Well A*	*Well B*	*Well C*	*Well D*	*Well E*	*Average*	*Sigma*
12/84	0.96	0.98	0.87	1.02	1.00	0.97	0.05
1/85	0.99	1.00	1.03	1.03	1.00	1.01	0.02
2/85	1.03	0.98	0.91	1.00	0.98	0.98	0.04
3/85	1.03	1.11	0.92	0.99	0.99	1.01	0.06
4/85	0.98	0.96	0.85	0.98	1.04	0.96	0.06
5/85	0.99	0.98	1.18	0.97	0.98	1.02	0.08

(i.e., there is no baseline from which change or deviation can be measured). However, this approach creates an artificial known mean value over the period of record that can be used to visualize and quantify temporal fluctuations.

1. If there are no fluctuations in the data, the normalized concentration at each well for each sampling event will be 1.0 and the data will plot as a straight line with a slope of zero.

2. To the extent that systematic temporal variability is present in the data, the normalized data will deviate from the expected mean value of 1.0. The difference between the actual normalized concentration and the expected value of 1.0 provides an estimate of the magnitude of the temporal cycles while the number of consecutive observations above or below the expected value of 1.0 provides and estimate of the periodicity (frequency) of the temporal cycles.

A second reason for using this approach is tat it makes no a priori assumptions regarding the frequency of temporal cycles. Some of the conventional statistical procedures[14] require the user to assume a temporal cycle (i.e., annual) before the data are actually evaluated. If temporal cycles are present in the data, but at a frequency either shorter or longer than the assumed cycle, the data will be averaged across cycles and any temporal trend that may be present will be missed. A third reason for using this approach is that it minimizes the influence o spatial variability and extreme concentration values. a single high value can have a disproportionate effect on the mean of a set of data but this influence is limited by the normalization process. Also, dividing a set of values from one well by the average concentration for that well will not change the periodicity of any temporal fluctuations at that well. Finally, by using data from multiple wells, each well becomes an independent observation of the temporal cycles and a confidence interval can be calculated about the average normalized value for the aquifer being monitored.

RESULTS

The ground-water monitoring data were transformed using the method described in the previous section. The resultant temporal variability plots for each inorganic constituent are presented and discussed below.

pH

Site R-28 is a waste disposal site in the State of Illinois that monitors 28 wells on a monthly basis. The normalized pH data obtained from this monitoring program between January, 1984 and June, 1986 are summarized in Figure 1. At this facility, 94 percent of the individual normalized pH observations fall in the range of 0.95 to 1.05 and all of the monthly mean pH values, except those for December, 1985 and March, 1986, are within 5 percent of a value of 1.0. Also, except for the same two data points, the calculated 95 percent confidence intervals are on the order of plus or minus ten percent of the expected mean value of 1.0. Given that all of the calculated 95 percent confidence intervals, except for the two previously mentioned dates, overlap a value of 1.0, and the mean data plot as a straight line with a slope of zero, the plot of normalized pH as a function of time resembles that which would be expected if there was no temporal trend.

Normalized pH data from three additional site investigation programs are presented in Figure 2. Site R-77 is a waste disposal site in Texas with 30 monitoring wells. All of the mean normalized pH values for 9 quarterly surveys conducted between September, 1984 and September, 1986 fall within 1 percent of a value of 1.0 that would be expected if there was no temporal variability. Also, all of the calculated 95 percent confidence intervals are rather tight (plus or minus 0.05) and overlap a normalized mean value of 1.0. Site R-73 is a waste disposal site in Ohio that monitors 12 wells on a monthly basis. As with the previous examples, each normalized pH value falls within 3 percent of a value of 1.0 and the calculated 95 percent confidence intervals are generally less than 0.05. The third site in Figure 2 is a waste disposal site in California (R-87) that monitors 36 well on a monthly basis. Except for one value, the mean normalized pH is within 3 percent of a value of 1.0 and the calculated 95 percent confidence intervals are generally less than 0.05.

The data for a mining site in Nevada are presented in Figure 3. This site is of interest because the records provided (essentially) daily data for five wells for a period of one year. Ninety-three percent of the normalized pH values fall in the range of 0.95 to 1.05 which suggests that any long-term seasonal fluctuation is on the order of five percent or less.

In order to facilitate possible trend assessment of the pH data at the mining site, the data were plotted as a rolling average for periods of 30 days and 90 days (Figure 3). If this parameter displays temporal variability, the data should plot in a sinusoidal pattern that defines both the magnitude and periodicity of the fluctuation. An inspection of the data summaries indicates that the magnitude of the temporal fluctuations for pH are less than 2 percent of the mean value (7.65) at the site.

The results presented in Figures 1, 2, and 3 represent monitoring data for pH from 111 wells at 5 sites located in five different states. Two of the states are located in the west, two of the states are located in the temperate midwest, and one of the states is located in the south. Despite the geographical and hydrological differences that occur in these different regions of the country, each of the data summaries define an (approximate) linear plot with a slope of 0.0. The information in these Figures, which represents more

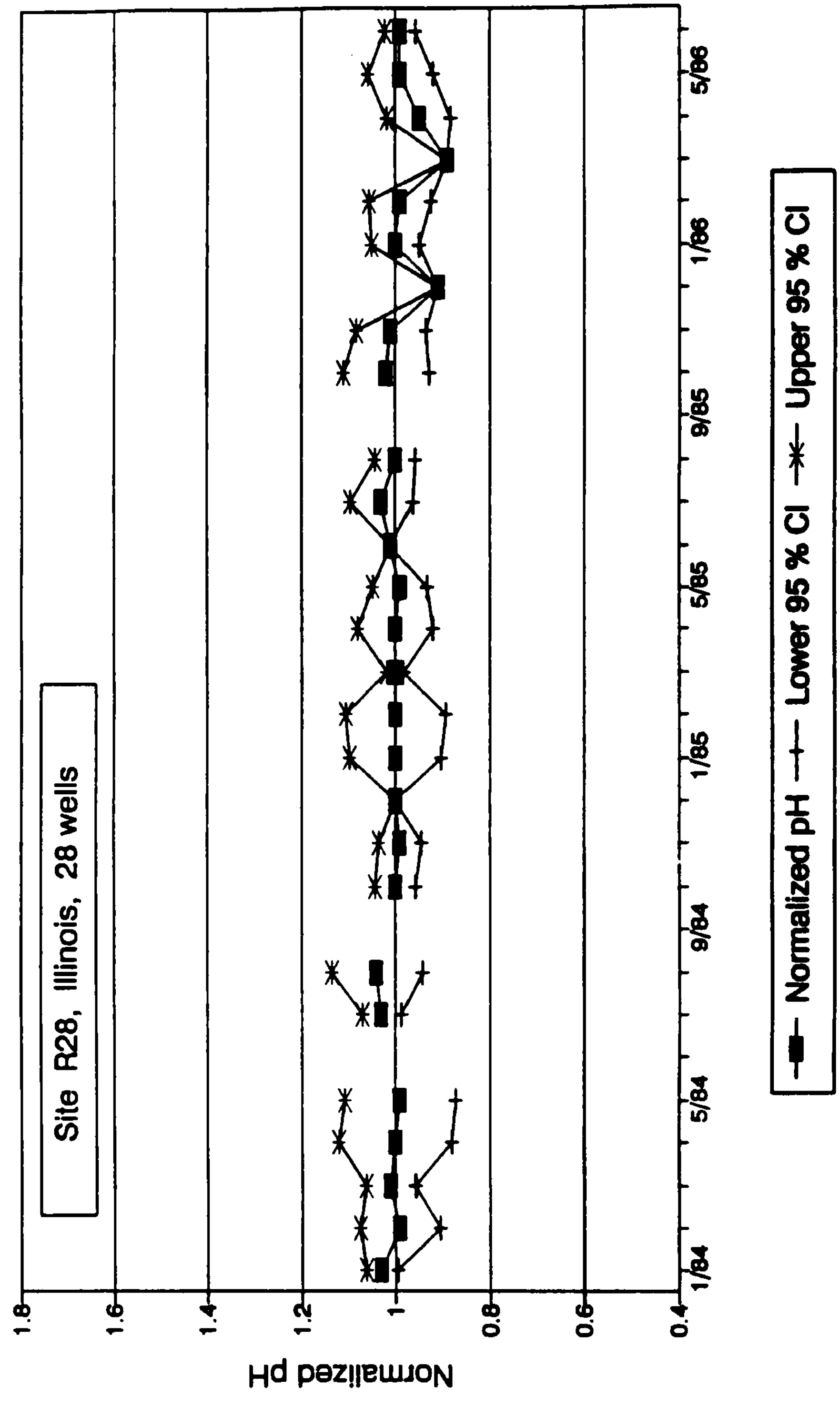


Figure 1 Normalized monitoring data for pH in ground water at site R 28 in Illinois.

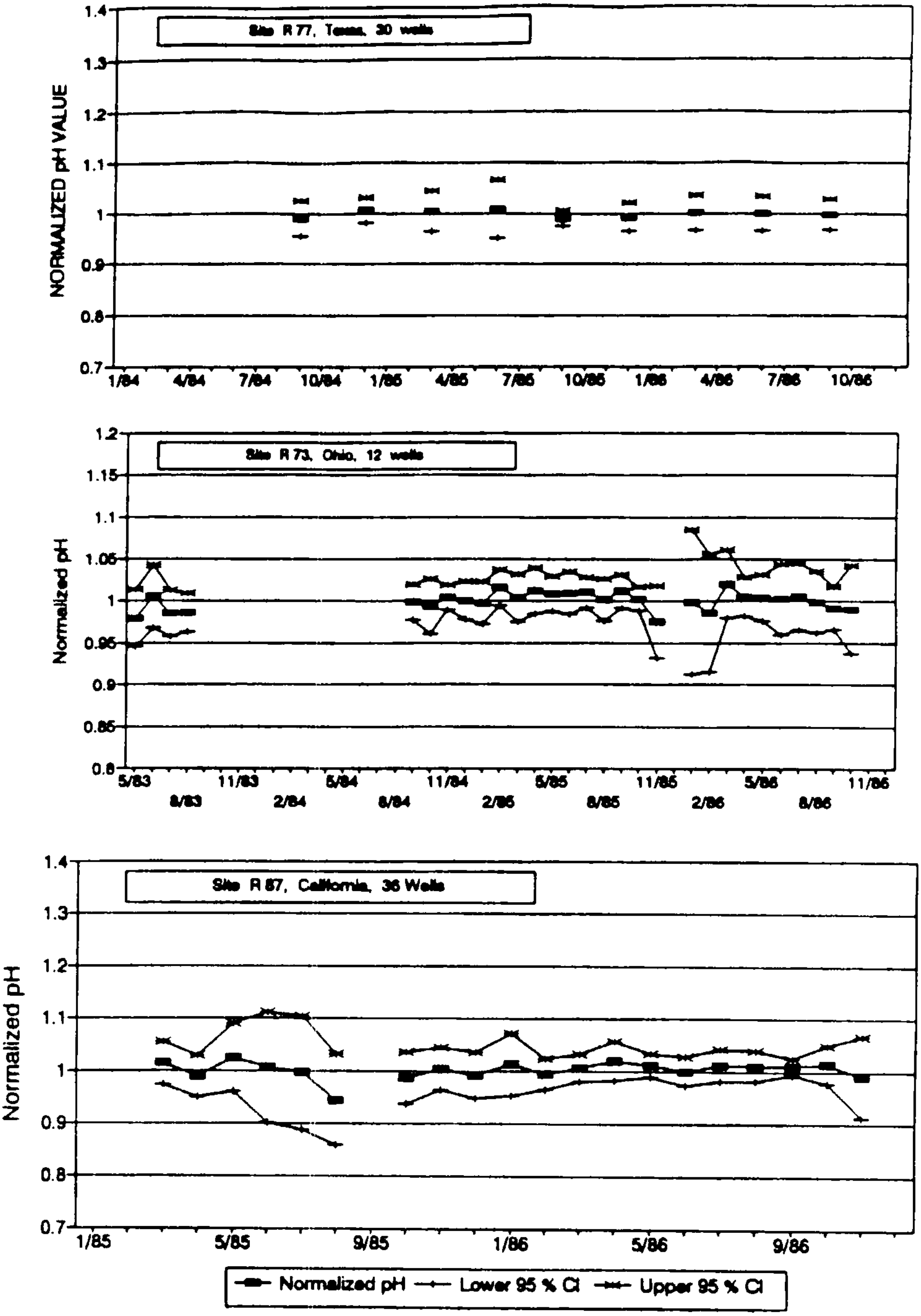


Figure 2 Normalized pH monitoring data from site investigations in Texas, Ohio, and California.

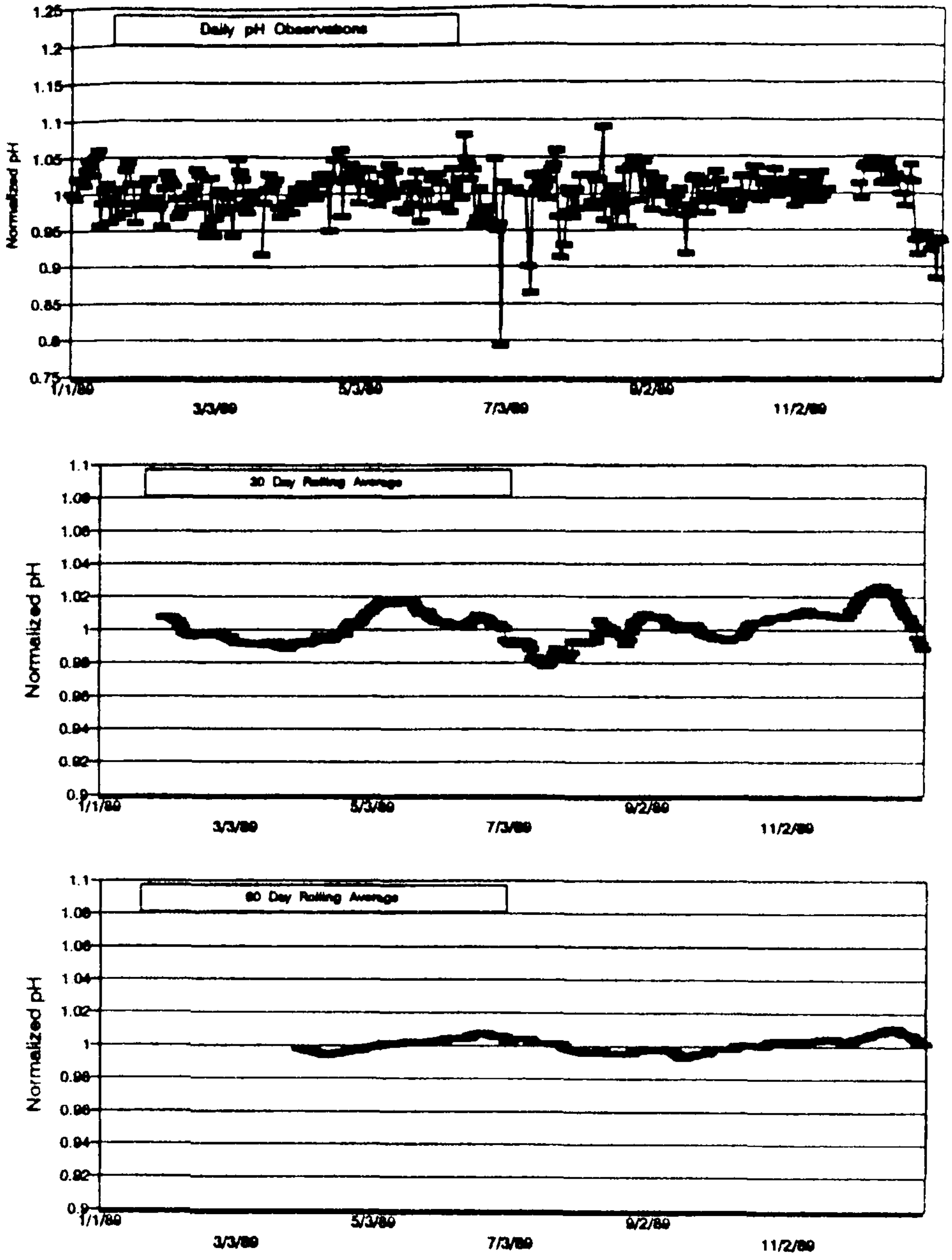


Figure 3 Daily monitoring results for pH from a mining site in Nevada.

than 230 well-years of monitoring data, indicates that ground-water pH does not display a pronounced tendency for seasonal fluctuation.

Alkalinity

Normalized alkalinity data for two small Illinois sites studied by Barcelona[8] are presented in Figure 4. These sites were monitored biweekly for a period of 78 weeks to establish a database for characterizing temporal variability patterns.

The mean value for each sampling period at the Beardstown site (E-1) is within 10 percent of a value of 1.0 that would be expected if there was no temporal fluctuation.

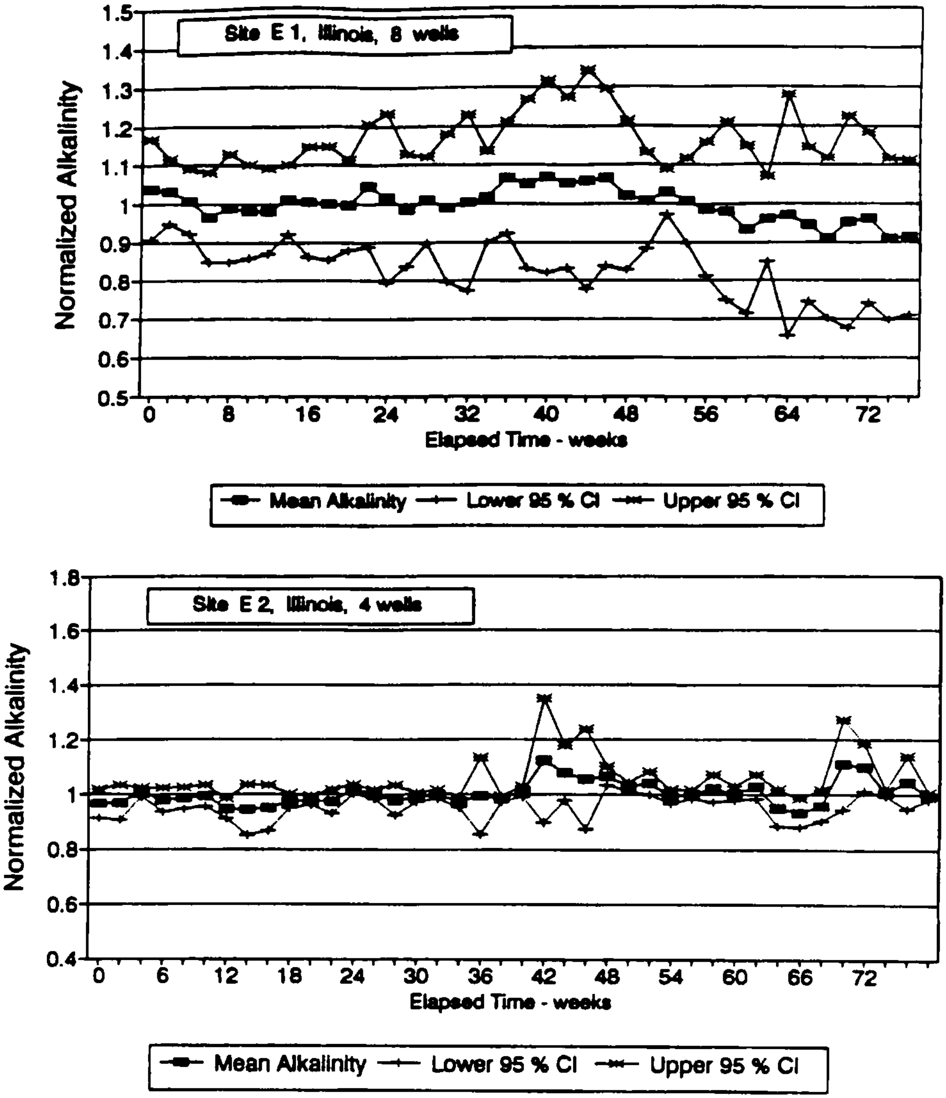


Figure 4 Biweekly ground-water monitoring results for alkalinity from two site investigations in Illinois.

Also, the 95 percent confidence interval for each sampling interval overlaps the expected mean value of 1.0. As a first approximation, these results would suggest that alkalinity does not display a pronounced tendency for temporal variability. However, a closer inspection of the alkalinity plot identifies a potential temporal trend. Specifically, beginning with the sixteenth sampling period, there are 12 consecutive values that fall above the mean expected value of 1.0 followed by at least 11 consecutive values that fall below the mean expected value of 1.0. The likelihood of 12 consecutive observations falling on the same side of the expected mean is 2^{12} or 0.024 percent. The likelihood of 11 consecutive observations falling on the same side of the mean is 2^{11} or 0.049 percent. Since control chart theory states that seven or more consecutive observations on the same side of the mean are an indication of a bias in the data, the trend in these data probably represent a real bias. In this case, the bias represents a temporal trend. The magnitude of this temporal trend is on the order of five to ten percent of the mean alkalinity concentration and the periodicity of the trend is at least 46 weeks ([11 sampling intervals + 12 sampling intervals]* 2 weeks per sampling interval).

The alkalinity results for the Sand Ridge site are also presented in Figure 4. These results are similar to the Beardstown results except the calculated 95 percent confidence intervals are smaller. Each of the mean concentrations, except for two values, are within ten percent of the expected mean value of 1.0 and each 95 percent confidence interval overlaps this value. Another similarity is the 13 consecutive observations above the expected mean value of 1.0 at the end of the monitoring program. Since the probability of this happening by accident is 0.01 percent $((1*100)/(2^{13}))$, this trend represents a temporal pattern for alkalinity. The magnitude of this pattern is approximately 10 percent of the mean alkalinity concentration and the periodicity is 13 sampling intervals * two weeks per sampling interval * 2 or 52 weeks.

Calcium

Normalized calcium data from the Sand Ridge site in Illinois[8] are presented in Figure 5. The data indicate very minor deviations from a mean value of 1.0 that would be expected if there were no systematic temporal fluctuation. Also, the calculated 95 percent confidence intervals are reasonably tight and are generally equivalent to only 10 percent of the expected mean value. These data suggest that calcium is not displaying a temporal trend at this pristine site located in a state forest.

Calcium data from a second industrial site in Illinois are also presented in Figure 5. Each of the calculated 95 percent confidence intervals for the 8 well monitoring network at this site overlap the expected mean value of 1.0 which would initially suggest that there is no temporal fluctuation over the period of record. However, as with the alkalinity data, there is a subtle indication of a temporal trend at the Beardstown site. Beginning with the second sampling period, there are twelve consecutive results below the expected mean value of 1.0. This event is immediately followed by 13–14 consecutive results above the expected mean value of 1.0. Since the probability of 12 consecutive points falling on the same side of a mean value is only $((1*100)/(2^{12}))$ or 0.02 percent while the probability of 14 consecutive points falling on the same side of a mean value is only $((1*100)/(2^{14}))$ or 0.006 percent, random chance is an unlikely explanation for the observed distribution. It is concluded that these data reflect a temporal trend with a magnitude equal to 10–20 percent of the mean calcium concentration at the site and a periodicity of approximately 52 weeks (26 sampling periods times 2 weeks per sample interval).

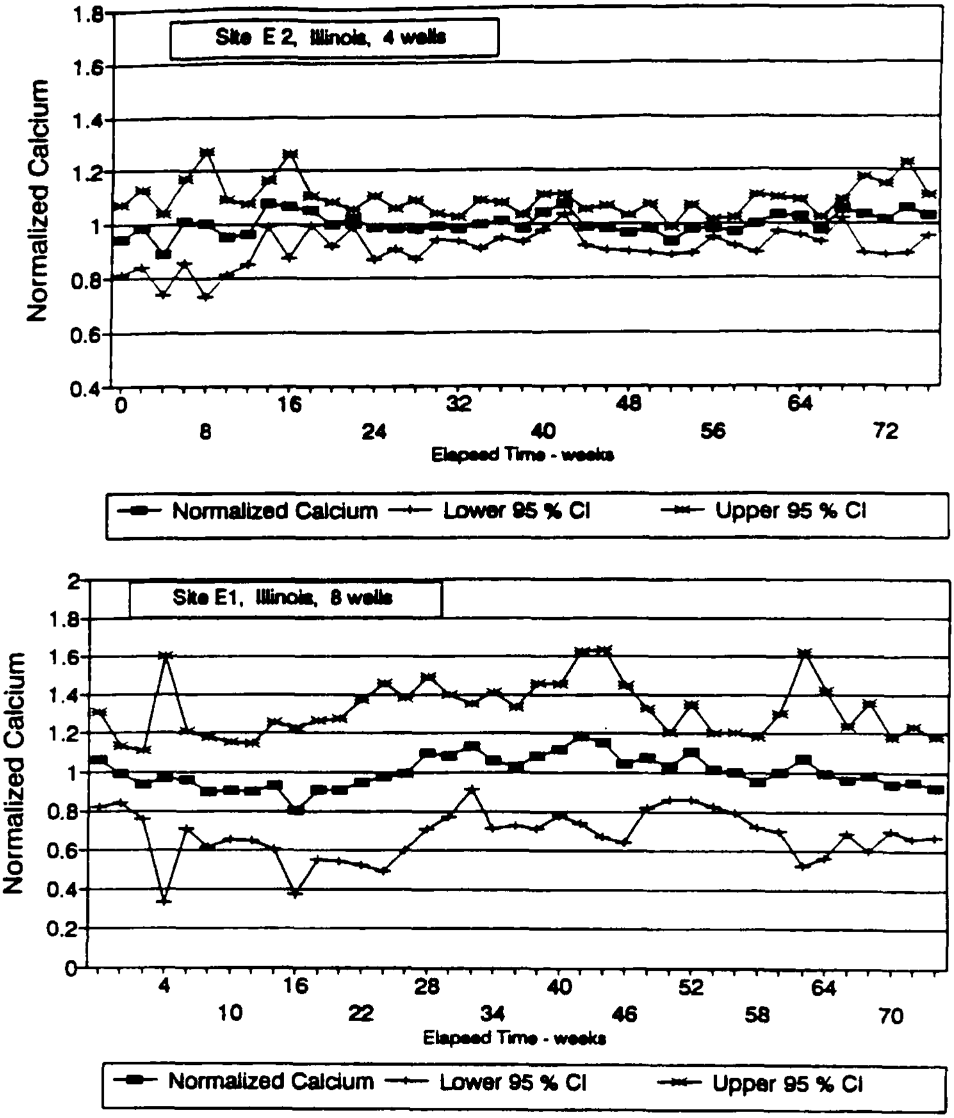


Figure 5 Biweekly ground-water monitoring results for calcium from two site investigations in Illinois.

Sulfate

Sulfate data from two site investigations are presented in Figure 6. The Sand Ridge site is an experimental site established by the Illinois Water Survey in the middle of a state forest[8]. Despite the rather large 95 percent confidence intervals associated with these data, there is a clear trend of increasing sulfate concentration with time. This trend has caused the sulfate concentration to increase from 80 percent of the mean concentration to 120 percent of them mean concentration in 78 weeks. Unfortunately, the sampling was not conducted long enough to determine whether this trend is part of a long-term temporal cycle or a long-term change in the system.

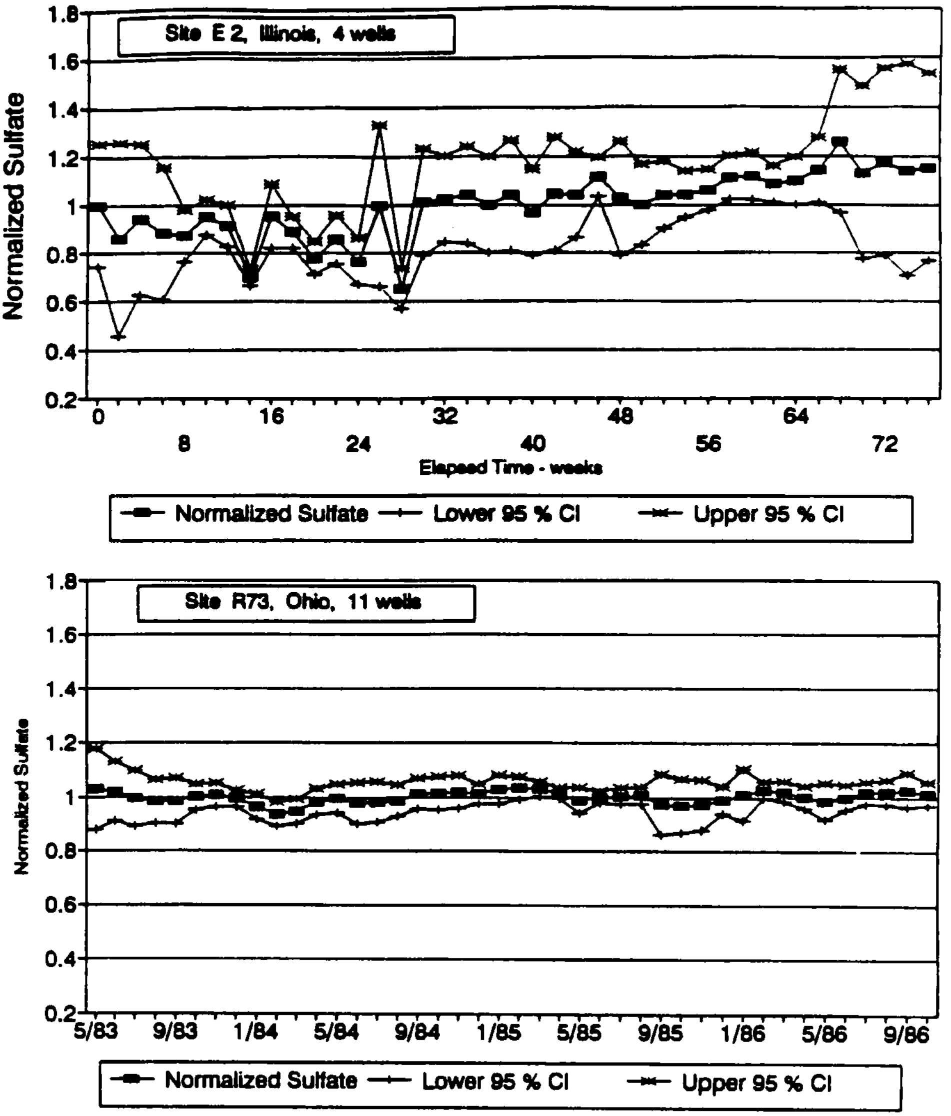


Figure 6 Temporal monitoring data for sulfate in ground water at sites in Illinois and Ohio.

The second site in Figure 6 for which sulfate data are presented is a waste disposal facility in Ohio. The majority of these monthly results (38 of 41 observations) are within five percent of the expected mean normalized concentration value. The 95 percent confidence intervals are generally less than ten percent of the normalized mean concentration and each overlaps the mean value. These results indicate that there is no strong tendency for a seasonal fluctuation of sulfate concentrations at this site.

Chloride

Chloride data[8] generated during monitoring of the Sand Ridge site in central Illinois are presented in Figure 7. This parameter obviously demonstrated temporal fluctuation at this site. The concentration fluctuated between 80 percent and 120 percent of the average site concentration for the first year and then doubled for a couple of months. Following the increase, the concentration leveled off in a level pattern with rather tight confidence limits. Despite the changes in chloride concentration over time, there is no indication of a seasonal or cyclic pattern in the data.

Chloride data[8] from a second site investigation in Illinois are presented in Figure 7. A

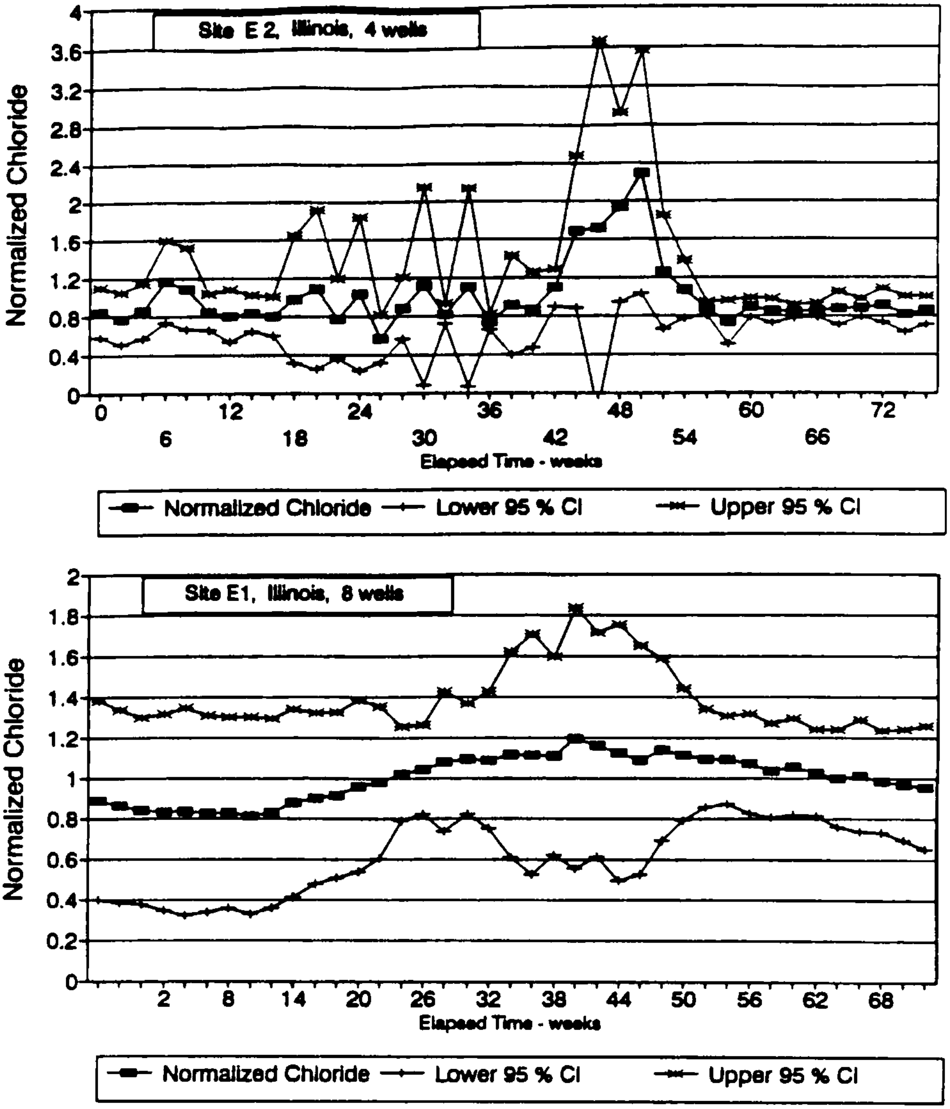


Figure 7 Biweekly ground-water monitoring data for chloride from two site investigations in Illinois.

sinusoidal pattern is clearly evident in the normalized data even though each of the 95 percent confidence intervals overlap the expected mean value of 1.0. However, the likelihood of 20 consecutive readings falling on the same side of the mean is extremely remote (2^{-20}). Therefore, these data suggest that chloride at this site has a temporal cycle with a magnitude of approximately 20 percent of the average concentration and a periodicity of approximately 80 weeks (20 observations per half cycle * two halves per cycle * two weeks per observation).

Sodium

Normalized monitoring data for sodium from two site investigations are presented in Figure 8. The first set of data is from the Sand Ridge site investigated by Barcelona, *et al.*[8]. These data would suggest that a slight sodium increase occurred over the one and one-half years that the site was monitored. The magnitude of this increase is approximately 10 to 20 percent of the mean sodium concentration. The sodium concentration increased from 90–95 percent of the average concentration at the beginning of the monitoring period to 105–110 percent at the end of the monitoring program. The period of record is not sufficient to distinguish between a long-term increase or a possible long-term temporal fluctuation.

Sodium data from a second site investigation are also presented in Figure 8. These data represent more than three years of monitoring data from four background wells at a waste disposal site in Ohio (R73). The results indicate a sodium increase of approximately 10 percent of the mean concentration from late 1983 to mid-1984.

However, since there is no corresponding temporal decrease, the increase probably represents either a spill or leakage event that was subsequently corrected or an analytical problem. Data for the two year period from 1984 through 1986 provide no indication of a seasonal cycle (the mean for each set of monthly monitoring data is within 5 percent of the expected mean concentration value and the 95 percent confidence intervals are rather tight and overlap the expected value of 1.0).

Silica and magnesium

Data for these two parameters from the Sand Ridge site in Illinois[8] are presented in Figure 9. Each of the biweekly sampling results for silica are within three percent of the expected mean concentration and the calculated 95 percent confidence intervals are generally less than 10 percent of the expected mean concentration. These data suggest that silica does not display a pattern of seasonal fluctuation. Ground-water data for magnesium at the same site are also presented in Figure 9. These results indicate that occasional short-term fluctuations on the order of two to six weeks have occurred for this parameter. However, there is no indication of any long-term, seasonal fluctuation for magnesium at this site.

Iron and manganese

Average normalized ground-water monitoring data for iron at a waste disposal site in Ohio are presented in Figure 10. These data indicate that iron has displayed a pattern of seasonal fluctuation at this site. The first of three apparent cycles occurs from June, 1983

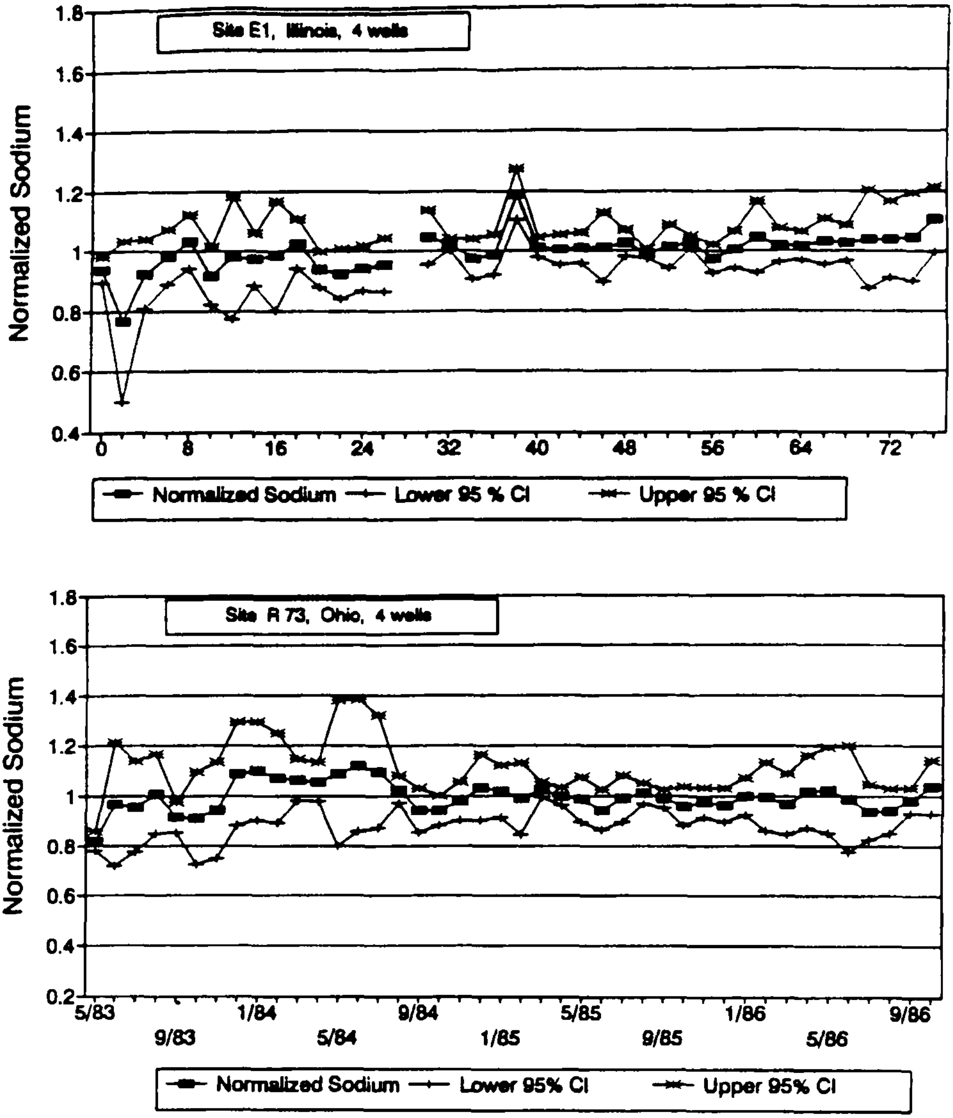


Figure 8 Temporal monitoring data for sodium in ground water at sites in Illinois and Texas.

until June, 1984. This cycle is followed by a shorter 9-month cycle (June, 1984 until March, 1985) and a third cycle of 11-months (March, 1995 until February, 1986). These results suggest that both the magnitude and the frequency of the temporal cycles are variable.

Manganese data from waste disposal site R 73 in Ohio are summarized in Figure 10. For this example, monthly data for a three and one-half year period have been presented using the same technique of data normalization. Except for occasional increases in the range of the 95 percent confidence interval about the mean (December, 1983; March, 1985; November, 1985; and April, 1986), the manganese data are clustered around the

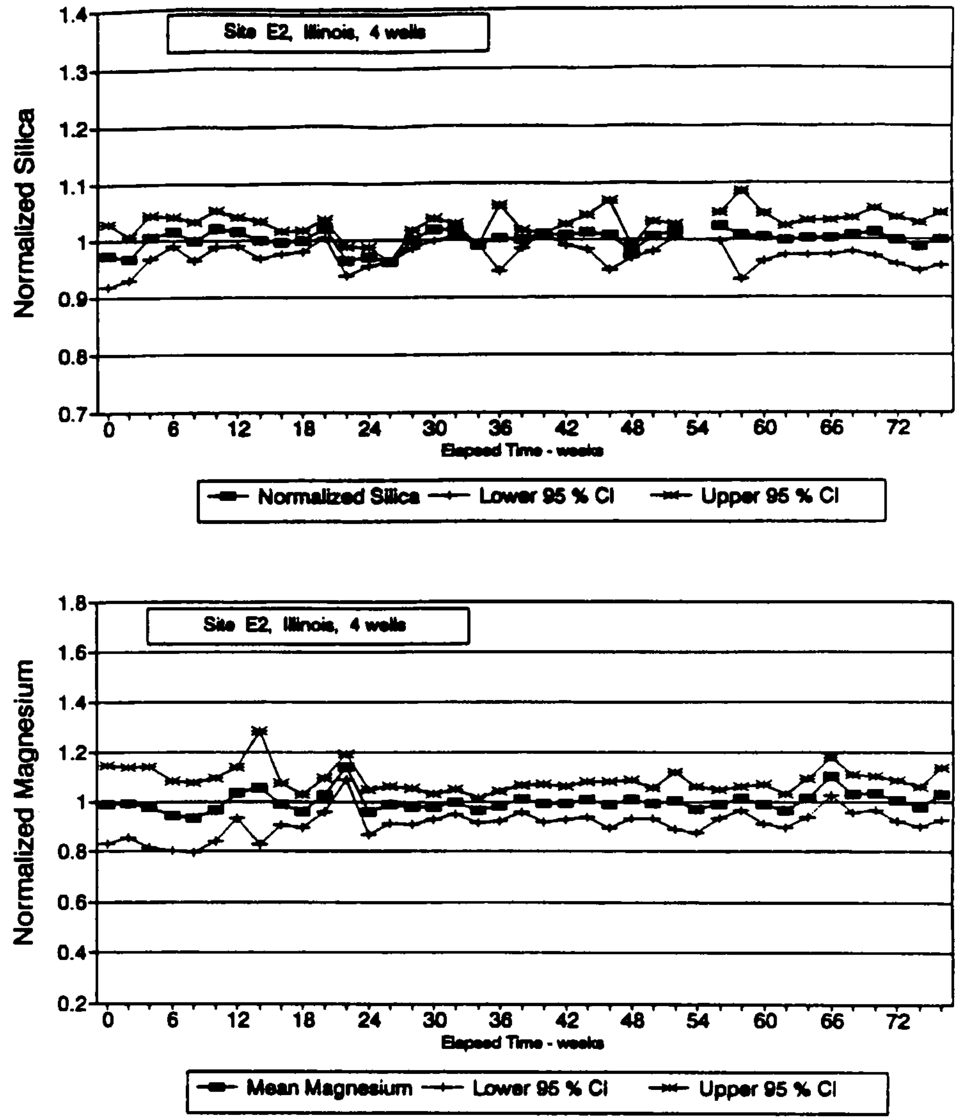


Figure 9 Temporal monitoring data for silica and magnesium in ground water from a site investigation in Illinois.

expected median value of 1.0. Beginning in Fall, 1983 and continuing until the summer of 1984, there is a series of consecutive observations below the expected mean value of the population. While the likelihood of such an event occurring by chance, there is no corresponding sequence of observation above the expected mean value of the population. Based on the monitoring data from this site, manganese does not display a pronounced seasonal fluctuation pattern.

Monitoring results for manganese at an industrial site in Illinois[8] are presented in Figure 10. The first 18 observations in this data set are below the mean concentration

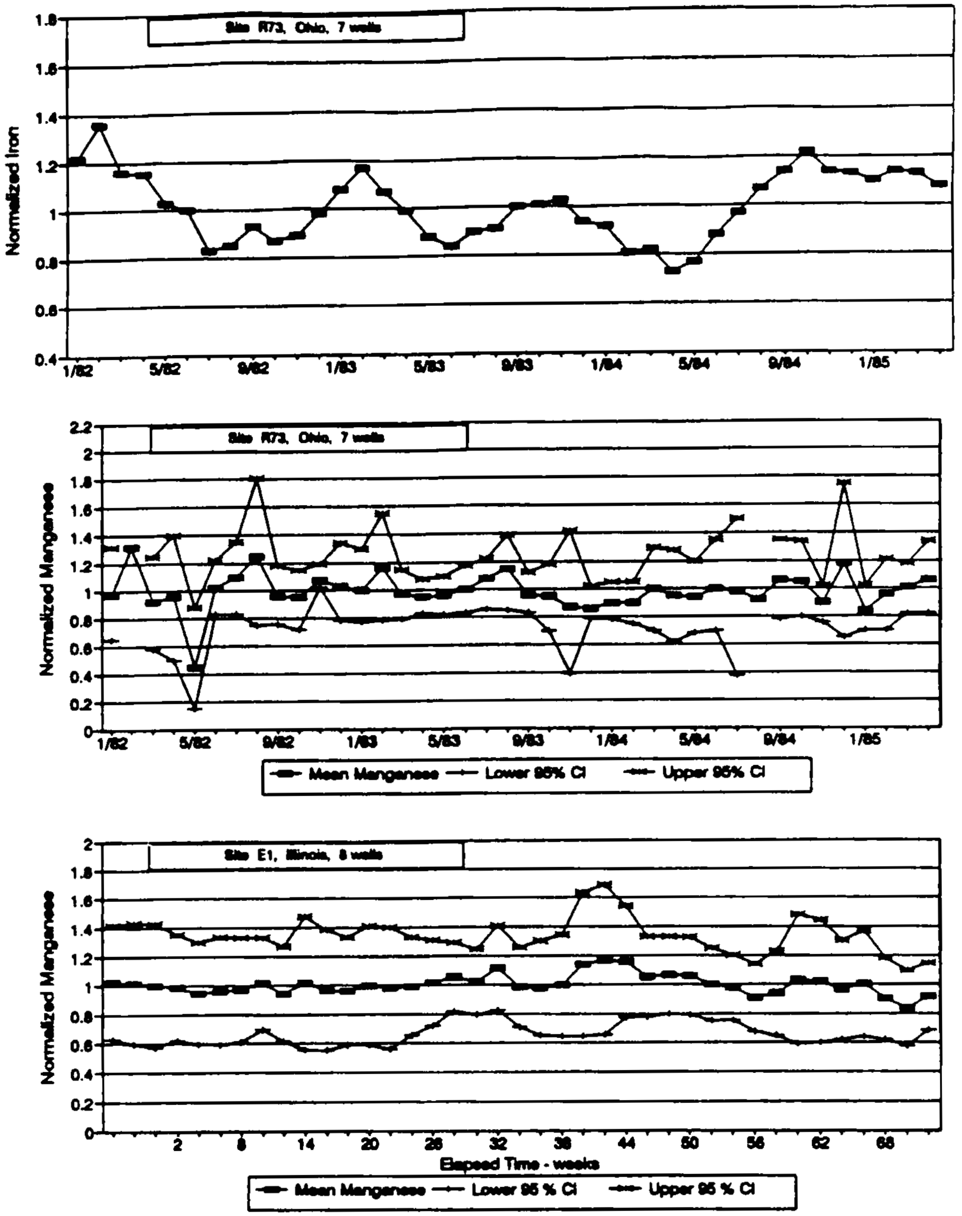
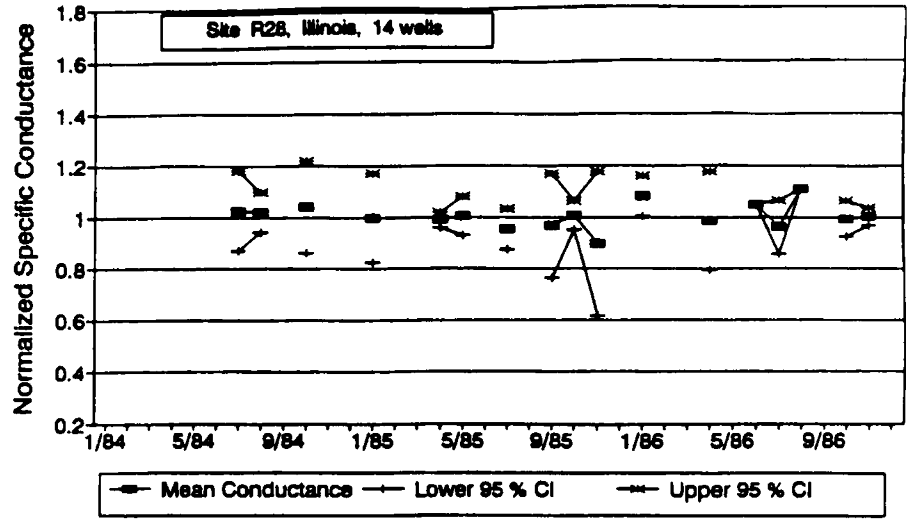


Figure 10 Temporal monitoring data for iron and manganese in ground water from site investigations in Ohio and Illinois.

value for the sample set. This is followed by a sequence in which 11 of 14 observations are above the mean concentration value for the sample set. If this pattern is due to temporal fluctuation, it would suggest a temporal cycle with a magnitude of approximately five to twenty percent of the mean concentration and a frequency of more than a year (16 observations per half cycle * two halves per cycle * 2 weeks per observation). A second point of note is that the 95 percent confidence intervals for manganese are larger than for the other parameters that have been summarized. This increased data variability complicates any attempt to identify temporal trends.

Specific conductance

Specific conductance monitoring data from two site investigations are presented in Figure 11. In the first example, a waste disposal site in Illinois (R 28), there is



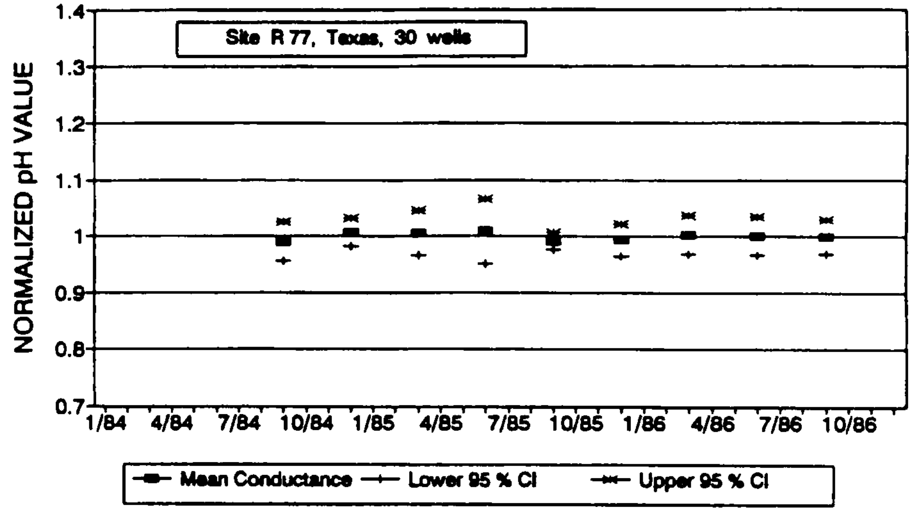


Figure 11 Temporal monitoring data for specific conductance in ground water from site investigations in Illinois and Texas.

considerable noise in the data as reflected by the magnitude and variability of the 95 percent confidence intervals. If there is a temporal pattern for this parameter at this site, the magnitude of this fluctuation is equal to less than 10 percent of the mean concentration.

The second example in Figure 11 is a waste disposal site in Texas (R 77). These data are from 30 wells that were monitored quarterly for a two-year period between September, 1984 and September, 1986.

As with each of the data sets previously discussed, each of the quarterly observations have a 95 percent confidence interval that overlaps the expected mean value for the population. This data set also has a subtle indication of a long-term temporal trend. Specifically, each of the quarterly mean values from September, 1984 until September, 1985 are below the expected mean value of the population while all of the results between October, 1985 and September, 1986, except for the July, 1986 results, are above the expected mean value of the population. This set of data suggests a temporal trend with a magnitude equal to 10 percent of the mean specific conductance and a periodicity of approximately two years.

A third set of temporal monitoring data for specific conductance is presented in Figure 12. These data are from 43 wells at a waste disposal site in Louisiana. These results are similar to those for the waste disposal site in Texas (Figure 11) in that the results for the first year are below the expected mean value for the population and the data for the second year are above the expected mean value for the population. This set of data suggests a possible temporal cycle with a magnitude equivalent to 10 percent of the mean concentration and a periodicity of approximately two years.

The final specific conductance example is from the Sand Ridge site in central Illinois[8]. Each of the biweekly observations are not different from the expected mean value for the population (Figure 12). However, there is a subtle indication of a long-term, low magnitude temporal cycle. Beginning with the thirteenth sampling interval, the normalized specific conductance is below the mean value of the population for 14 sampling periods or 28 weeks. This is followed by a period of at least 20 weeks during which the normalized conductance values are above the expected mean value. Since the probability of these events happening by chance is rather low (2^{-14} and 2^{-10}, respectively), the data from this site suggest a long-term specific conductance temporal cycle with a periodicity of more than 48 weeks. The concentration fluctuation during the temporal cycle is less than 10 percent of the mean specific conductance concentration at the site.

DISCUSSION

The need to address temporal variability of constituents in ground-water during a site monitoring program is well recognized. However, despite the importance of this factor in selecting adequate sampling frequencies, and the large number of site monitoring programs that have been conducted in the United States in the past 10 years, the present knowledge of temporal trends in ground water is not well developed. This situation is due, in part, to some estimates that extensive data sets for periods of 10 years[8] to 17 years[15] may be required to characterize these trends. Since resources are not generally available for studies of such duration, monitoring data from on-going site investigations were reviewed to obtain data sets that could be used for this purpose. As a result of this effort, data from several geographically diverse sites across the United States were compiled to describe long-term temporal trends for 11 inorganic parameters in ground water.

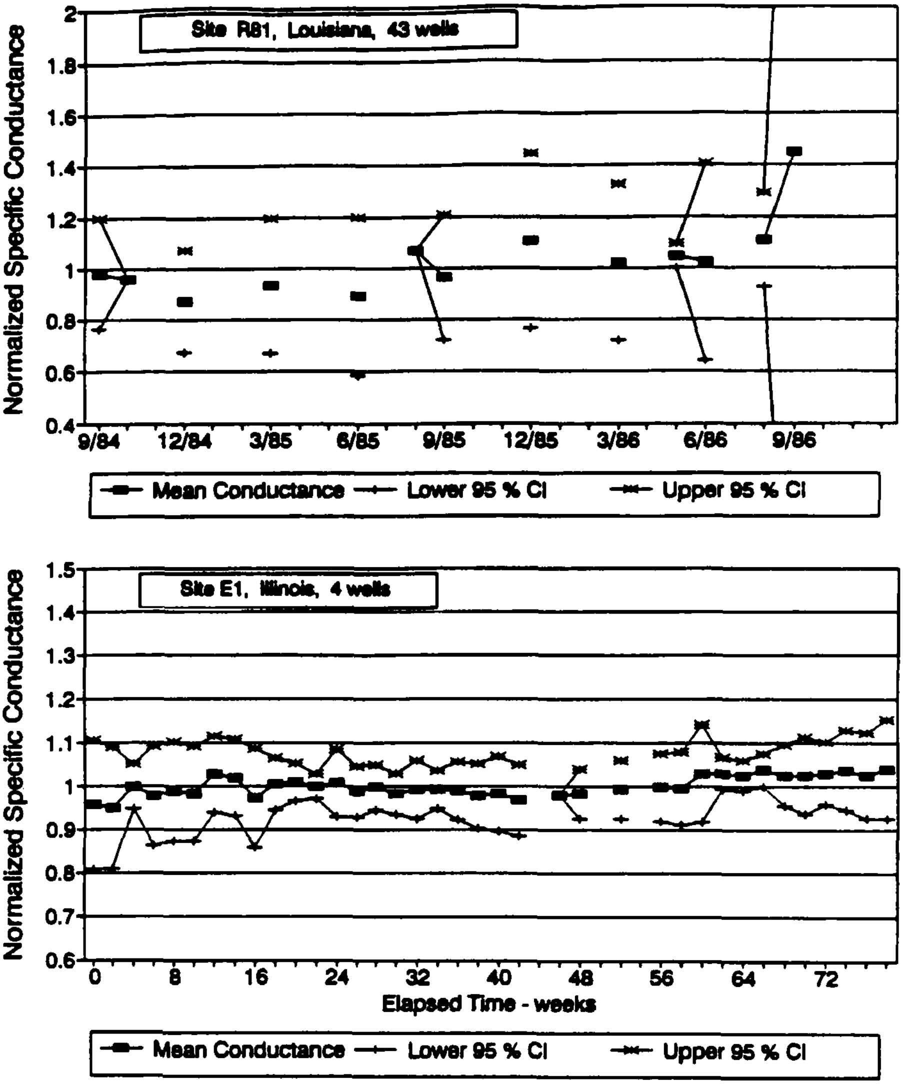


Figure 12 Temporal monitoring data for specific conductance in ground water from site investigations in Louisiana and Texas.

A graphical approach was used to summarize the data. However, rather than plotting actual concentrations as a function of time, a normalized concentration was used for this purpose. This technique was used for the following reasons:

1. The process minimizes the effects of spatial variability in the data. The pH data for the December, 1984 sampling event at a waste disposal site in Alabama (Table 1) ranges from 7.02 to 12.03 and the coefficient of variation for the raw data is 23.4 percent. After the pH readings are divided by the average pH at each monitoring location, the coefficient of variation for the normalized data drops to 6 percent.

2. The use of normalized data creates a relative baseline from which temporal fluctuations can be measured. As pointed out earlier, if there is no temporal variability in the data, each of the normalized data points will have a value of 1.0 and a plot of the data as a function of time will produce a straight line with a slope of zero. In effect, this approach provides a test of the null hypothesis that the ground-water constituents do not display any temporal variability. However, if there is a temporal pattern, the relative baseline provides a means to estimate the magnitude of the variability while the number of consecutive observations on either side of the baseline provides an estimate of the frequency of the temporal pattern.

3. One of the standard methods for deseasonalizing data[14] suggests that data from different cycles should be averaged. This was not done because the actual length of temporal cycles for ground-water constituents is not known. Instead, the individual observations were plotted over the entire period of record. As a result, several possible trends with a periodicity of more than a year were identified (chloride, specific conductance).

The temporal trends that were identified for each of the inorganic parameters were rather small. The magnitude of these fluctuations were less than 5 percent of the mean concentration for pH, silica, and magnesium; less than 10 percent of the mean concentration for alkalinity, sodium, and specific conductance; less than 20 percent of the mean concentration for calcium, sulfate, chloride, and manganese; and less than 40 percent of the mean concentration for iron. The assessment of low amplitude temporal fluctuations such as these are supported in three ways by the site monitoring data. First, the results from different site investigations converge on similar temporal estimates. For example, pH data from three different laboratories for five geographically diverse sites (California, Nevada, Texas, Illinois, and Ohio) indicate a temporal change of less than 3 percent of the mean pH at a site. Second, the use of normalized data provides a method to characterize temporal trends. If there is no temporal trend, the observations should randomly; distribute about the mean value. Although the possibility of a single observation falling on either side of a mean value is only 1/2, the possibility of n consecutive observations falling on the same side of the mean decreases to $1/2^{a}$. Since the likelihood of 10 or more observations occurring on the same side of the mean by chance is extremely remote ($< 1/2^{10}$ or < 0.00097), the fact that several inorganic parameters (i.e., alkalinity, calcium, chloride, and manganese) had ten or more consecutive measurements on the same side of the mean was considered a systematic bias that was interpreted as a temporal trend and estimated by the difference between the observation and the mean value. Third, the normalized data were used to calculate a rolling average or moving average concentration as a function of time. These plots should produce a maximum deviation from the mean when the number of observations being averaged is equal to half the temporal cycle. As illustrated with the daily pH data in Figure 3, rolling averages based on 5 days, 14 days, 30 days, 60 days, and 90 days did not produce a deviation of more than 2 percent.

The temporal change in concentration for inorganic parameters in ground water is much smaller than has been reported for the same parameters in surface water. For example, pH in ground water varied approximately 4 percent (2 percent/half cycle * 2) compared to 15–20 percent in the hypolimnion of surface waters; manganese in ground water varied by 20 percent (10 percent/half cycle * 2) compared to changes of 1000 percent or more in the hypolimnion of surface waters; and iron in ground water varied by 80 percent (40 percent/half cycle *2) compared to changes of 2000 percent or more in the hypolimnion of surface waters.

The reason for these differences between ground water and surface water is that temporal or seasonal variability is not a chemical property per se but, rather, it is a response to changes in equilibrium conditions. The following description of the phases in the thermal stratification of surface waters illustrates this point[16,17].

Phase I In the early spring, the conditions in a lake are vertically uniform. Because the water column is at the same temperature, water density is also constant and a gentle breeze is sufficient to mix and aerate the entire water column. Under these conditions, the concentration of water quality parameters are also vertically uniform.

Phase II As the summer season progresses, energy from the sun gradually warms the surface water of a lake. Since warmer water has a lower density, this water rises to the top and forms a less-dense surface layer. Eventually, the density difference between the warmer surface water and the cooler bottom water becomes sufficiently large that wind energy is no longer capable of mixing the entire water column. This condition restricts the transport of dissolved oxygen to the lower, hypolimnetic waters of a lake. When the dissolved oxygen is eventually depleted in this portion of the lake, the concentration of several water quality parameters change in response to the new equilibrium conditions (iron, manganese, and sulfide can increase by orders of magnitude; pH can decline by 1–2 pH units).

Phase III During the fall, the surface waters of the lake begin to cool. This reduces the density difference between the surface waters and the bottom waters until the wind can mix the entire water column. During the mixing process, the concentration changes that occurred in the hypolimnetic portion of the lake are reduced by mixing with the surface waters of the lake and dissolved oxygen is reintroduced to the entire water column. The new equilibrium conditions reverse the changes that occurred in Phase II and reestablish the conditions that were present in Phase I.

The seasonal variability that water quality parameters display in surface waters is a response to solar heating in the spring and summer, changes in water density with temperature, wind-driven mixing, and radiative cooling. Since the sun does not exert a direct influence on ground-water temperature, and wind energy is not effective at mixing ground water, the smaller temporal variability patterns observed for each inorganic parameter in ground water are consistent with smaller shifts in equilibrium conditions.

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