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# Evaluation of Monitored Natural Attenuation in Groundwater, Report #2

## Agrico Site, Pensacola, Florida

### October 23, 2013

## Introduction and Background

This report presents the second analysis of monitored natural attenuation (MNA) in groundwater monitoring data collected at the Agrico Site in Pensacola, Florida through 2012. It follows the methods and recommendations conveyed in the URS Corporation (URS) August 19, 2009 *Evaluation of Monitored Natural Attenuation In Groundwater, Agrico Site, Pensacola, Florida* prepared by Dr. William A. Huber as submitted to and accepted by USEPA Region IV and FDEP. This MNA evaluation also is supplementary and supports the regression analyses and concentration trend analysis presented in the URS 2012 Annual Report (March 29, 2013).

Because the 2009 MNA submittal provides all background information and descriptions of the procedures, the present report summarizes the 2009 results, proceeds to describe the new data, applies the procedures to the collective dataset, and interprets the results. It concludes with recommendations for future groundwater monitoring.

### *Background: the 2009 results*

The 2009 MNA Report recommendations and ensuing actions were:

(1) Continue the current monitoring program. The measurement frequencies at that time, typically annual, were found to be appropriate for the cleanup period (up to 70 years from 1997). Based on the 2009 evaluation, EPA on October 15, 2009 requested that the AC-9D2, AC-24D and AC-28D sampling frequency be changed from every 5 years to annual. The request was implemented beginning with the November 2009 sampling event.

(2) Discontinue monitoring arsenic and lead. This recommendation was implemented. For separate reasons, arsenic is still being monitored in groundwater from monitoring well AC-2S.

(3) Periodically apply the following formal analyses of the data:

a. Estimates of point attenuation rates (using Ordinary Least Squares regression of log concentrations against time), anticipating that over time they would eventually accelerate.

b. Estimates of cleanup times (based on inverse regression), anticipating that they would remain stable on average.

c. Calculation of upper prediction limits (UPLs) and lower prediction limits (LPLs) for future data in order to anticipate progress between review periods.

d. Comparison of the most recent data to the previous prediction limits to assess the most recent progress.

The recommended calculations have been performed where possible and are described below. (They are applicable only to parameters in wells that have exceeded their cleanup targets and have exhibited the peak concentrations expected from a groundwater plume migrating past the wells.)

The 2009 evaluation was based on limited data (often the minimum amount needed to perform the statistical procedures) and the results were accordingly uncertain. As time goes on and more data are collected, the results will become less variable and more reliable. Changes in projections (such as the confidence limits and prediction limits that are calculated) between 2009 and 2013 were to be expected and are noted herein. Future changes in projections will also naturally occur, but on the whole are expected to be smaller in magnitude than the changes documented here.

### *Performance standards*

Monitored natural attenuation is part of a coherent set of actions intended to limit and reduce the concentrations of Site-derived materials in the groundwater. The EPA has established "performance standards" for the area. These are concentrations to be achieved throughout the groundwater plume; that is, cleanup targets:

| **Analyte** | **Target** | **Natural Logarithm** | **Basis** |
|---|---|---|---|
| Chloride | 250 mg/L | 5.52 | Florida standard |
| Fluoride | 4 mg/L | 1.39 | 2 mg/L for potable supply |
| Nitrates[1] | 10 mg/L | 2.30 | |
| $^{226}Ra + ^{228}Ra$ | 5 pCi/L | 1.61 | MCL |
| Sulfate | 250 mg/L | 5.52 | Florida standard |

[1] Represented in the database primarily by combined nitrite + nitrate concentrations (as N). Nitrite was approved for deletion by EPA from the site's analyte list in 2006.

## The Data

Data were collected and recorded by URS and delivered in an Excel spreadsheet comprising the entire history of relevant monitoring data from October, 1990 through November, 2012 (consisting of 2,471 rows, one per observation). They represent monitoring results for seven parameters at 44 wells: chloride, fluoride, nitrate as N (“nitrate-n”), nitrates plus nitrites as N (“nitrate+nitrite, n”), radium-226, radium-228, and sulfate.

The information for each observation includes a numeric result (if detected) or a detection limit (if not detected) along with the usual identifying information: sample date, sample location name (consisting of a well name and the unit it monitors), and name of analytical parameter, along with additional information including three “qualifier” fields.

Results were flagged as “nondetects” whenever a detection limit was provided *and* at least one of the following occurred:

- the `DL_QUALIFIER` was “J”, “U”, or “<” *or*
- the `WC_QUALIFIER` was “U” or “<” *or*
- the `RESULT` value was nonzero but less than the detection limit (and the parameter was not a measurement of radiation activity) *or*
- the `RESULT` was zero.

Some records represent replicate measurements: that is, multiple results obtained for a parameter at a well on the same date. To avoid biasing the subsequent calculations, groups of replicate measurements were merged into a single value by taking the arithmetic average of the separate numeric values. Whether or not at least one of the replicates is a nondetect, or whether all the replicates are nondetect, was also recorded. The resulting database contains 2,457 separate observations.

### *Preprocessing for the formal statistical analyses*

Calculations were conducted separately for each analytical parameter, with the most attention paid to fluoride. The most stringent performance standard—that is, the one currently expected to take the longest time to reach—is that for fluoride (4 mg/L). This parameter therefore is of principal interest.

Because many of the earliest results had previously been noted as unusual and necessarily preceded the onset of natural attenuation, which only began in earnest by April 1997 when the source remedial activities were completed, all data before 1995 were eliminated.

Next, only wells having at least one value above the performance standard were retained for evaluation. For fluoride, these are wells AC-12D, AC-13D, AC-24D, AC-25D, AC-28D, AC-29D, AC-2S, AC-30D, AC-34S, AC-35D, AC-3D, AC-7SR, AC-9D2, and NWD-2S.

An initial graphical survey of the data indicated some outlying values, especially for fluoride during the 1990's and early 2000's. At this point these were manually flagged as outlying, which enabled the statistical procedures optionally to exclude them. Outliers *are* routinely shown in graphical displays in this report.

Because the amount of data available for the planned analyses is still relatively small, ranging from four to about two dozen observations per parameter per well, unusual or outlying values can have important effects on the results. To counter this, a *robust* version of ordinary least squares (OLS) fitting was used, implemented as "iteratively re-weighted least squares" (IWLS or IRLS). This method initially uses OLS, then examines the residuals and downweights those that are far from the fitted curve. Subsequent iterations use weighted least squares, with unit weights assigned to most points and weights smaller than 1 assigned to the downweighted points. After each iteration, points are re-weighted according to the amount by which they deviate from the fit. The procedure is continued until convergence. In effect, it fits all or most of the data without allowing large departures from the fit to affect it adversely. Calculations were performed using the \`rlm\` function in the \`MASS\` add-in to the \`R\` statistical computing platform, version 2.15.0 [Ripley *et al.* 2013].

In the 2009 MNA submittal, *ad hoc* methods were used to identify ranges of possible peak times at each well. In order to establish a more objective procedure, these peaks are now provisionally identified by regressing the log concentrations over time and including a quadratic term to allow for the "curvature" near the peak. This means that the temporal evolution of the non-outlying data $y_i$ = log(result) is approximated as

$$y_i = \beta_0 + \beta_1 t_i + \beta_2 t_i^2 + \varepsilon_i \qquad (1)$$

where $t_i$ denotes the date of observation (in years), $\beta_0$, $\beta_1$, and $\beta_2$ are constant coefficients, and $\varepsilon_i$ are independent random variables representing deviations between the observations (on the left hand side) and the values as computed on the right hand side. The date of any peak can be identified by estimating the coefficients as $b_0$, $b_1$, and $b_2$, respectively, and computing the value $t_{\text{peak}} = -b_1 / (2b_2)$ provided $b_2$ actually is negative (for otherwise this formula identifies an apparent "trough," or local minimum, of the concentration). (All these fits are presented graphically in Appendix 2.)

Only wells that have passed their apparent peaks (or had no peaks but have consistently exhibited declining concentrations over time) are candidates for further statistical analysis. In order to carry out that analysis, a sequence of at least three observations is needed. Because most sampling is annual, the estimated peak must therefore occur before the year 2013 – 3 = 2010. Once the peaks are found, subsequent analysis of natural attenuation is performed on all data occurring on or after the peak. (If no peak is found, all the data are used.) Thus the calculations reflect *average* attenuation during the period from the peak to the present. As discussed in the 2009 submittal, this method conservatively underestimates point attenuation rates and overestimates cleanup dates. It is expected that as data accumulate over time, a less conservative procedure can be adopted which more accurately reflects current attenuation rates rather than average rates. (Rates are, by definition, zero at any peak and accordingly make the average look smaller than current rates.)

Because data before (approximately) 2000 tend to have many outlying or unusual values, additional judgment was applied to limit the data used for some analyses, as noted in appropriate sections below. In all cases the most recent data were retained back to a well- and parameter-specific date, before which older data were not used.

To evaluate the combined radium results and to assess parameter correlations, it was necessary to match $^{226}Ra$ and $^{228}Ra$ data by time and location (to sum them) and to match all data, regardless of analyte, by time and location (to compare them). To facilitate this, all data were assigned to a "period" consisting of the calendar year in which the sample was taken. In case multiple results were available, they were averaged to represent the entire period. The average was flagged with indicators of whether any or all of its aliquots were considered nondetects. Data were then joined by well and period identifiers. The $Ra^{226}$ and $Ra^{228}$ results were summed into a combined radium value whenever both were available and otherwise the combined radium result was flagged as missing.

# Results

## *Fluoride*

### Peak detection

The candidate wells for natural attenuation analysis, and their estimated peak dates, are

| AC-7SR | NWD-2S | AC-2S | AC-3D | AC-29D | AC-24D | AC-30D | AC-34S | AC-35D |
|---|---|---|---|---|---|---|---|---|
| 1995.7 | NA | 1996.1 | 1979.9 | NA | 2009.6 | 2002.8 | NA | 2002.6 |

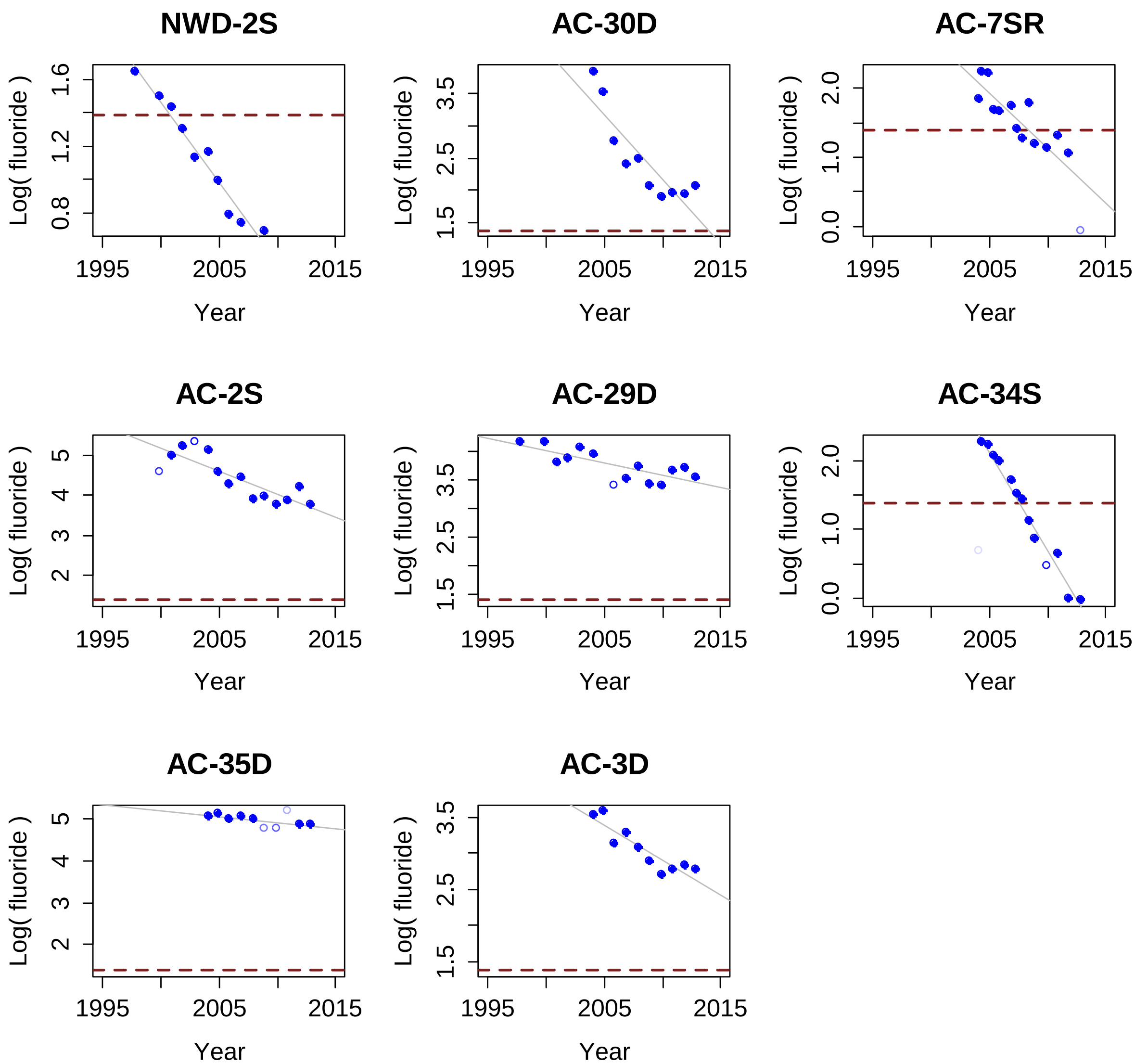
The "NA" results indicate no peak was found before 2010: further analysis will show whether concentrations in those wells should be considered increasing or decreasing. As in the 2009 submittal, the wells are ordered approximately from upgradient to downgradient, left to right.

Any peak estimated to have occurred on or before the beginning of data collection (1995) merely reflects the presence of a downwards trend without significant evidence of a preliminary peak. Wells located within or immediately downgradient of the source would exhibit such behavior. Possibly, natural variation in observations made in wells somewhat further from the source (a few hundred meters) could mask the peak and lead to such early estimates. In any event, it is evident that fluoride has been decreasing in AC-7SR, AC-2S, and AC-3D, where early peaks are estimated.

The recent peak estimate of 2009.6 for AC-24D indicates that observations just before and just afterwards—that is, the most recent ones—must have been relatively constant (which is the case). The estimate of this peak is influenced by an unusually low concentration observed in 1997. Due to the sparse monitoring (every five years until 2009 and annually since then), this estimate of the peak time may be unreliable and could change substantially when more data are collected.

### Line fitting

The (robust) OLS fits are shown as slanted gray lines in the following plots. The dots represent the data, with open dots showing data that were downweighted by the IWLS procedure (lighter open dots were downweighted more than the darker open dots: an example appears in the plot for AC-34S). For reference, thick dashed horizontal red lines are drawn at the performance standard of 4 mg/L. All plots show the natural logarithms of the fluoride results on the vertical axis. They share the same range of dates from 1995 to 2015, but allow the range on the vertical axis to vary so that the most detail can be seen. (The interval from 2012—the most recent year in the dataset—to 2015 is shown to facilitate visual extrapolation of the data into the near future.)



All data following a possible visually apparent peak at each well are included:

### Data selection

| Well | Starting date |
|---|---|
| AC-7SR | 2004 |
| AC-2S | 1999 |
| NWD-2S | 1995 |
| AC-3D | 2003 |
| AC-29D | 1995 |
| AC-30D | 2003 |
| AC-34S | 2004 |
| AC-35D | 2001 |

These eight wells show decreases over time and therefore remain viable candidates for the attenuation analysis. The relatively close scatter of the data around the lines in these plots indicates the fits are sufficiently good approximations to the data to be useful for further attenuation analysis.

### Point attenuation rates

| | N data | Half-life (yr) | Rate (/yr) | LCL (/yr) | UCL (/yr) | MSE % |
|---|---|---|---|---|---|---|
| AC-7SR | 24 | 8.89 | 0.078 | 0.055 | 0.101 | 23.0 |
| AC-2S | 14 | 6.08 | 0.114 | 0.069 | 0.159 | 36.3 |
| NWD-2S | 10 | 7.15 | 0.097 | 0.082 | 0.111 | 8.2 |
| AC-3D | 10 | 7.15 | 0.097 | 0.067 | 0.127 | 17.3 |
| AC-29D | 14 | 16.12 | 0.043 | 0.022 | 0.064 | 24.0 |
| AC-30D | 10 | 3.48 | 0.199 | 0.127 | 0.272 | 46.3 |
| AC-34S | 14 | 2.43 | 0.285 | 0.253 | 0.317 | 18.0 |
| AC-35D | 10 | 23.90 | 0.029 | 0.006 | 0.051 | 6.9 |

The amount of data available for each well ranges from 10 through 24 separate observations, adequate for characterization of the slopes and potentially for extrapolation into the future. The half-lives are typically short, with three-quarters of them between 2.4 and 8.9 years.

(Because judgment was used in determining which of the earliest data were likely not to represent subsequent attenuation, and thereby to exclude from the analysis, the sensitivity of the results presented in this and the following tables was assessed by computations using slightly different amounts of data at each well. Of course the estimates, the confidence limits, and the prediction limits do change slightly, but none of these changes appreciably affect any of the conclusions.)

The LCL (lower confidence limit) and UCL (upper confidence limit) are each one-sided 95% confidence limits for the rate. For example, the LCL for AC-29D of 0.022/yr is constructed to have a 95% chance of being *less* than the true average point attenuation rate during the period covered by these data (1997 through 2012, according to the plot). Because all LCLs are positive, these results indicate concentrations have been decreasing exponentially over time at all eight of these wells.

The MSE (mean squared error) measures the vertical scatter of the points around their fitted lines (on the logarithmic scale). Small values indicate a close match between the line and the data; larger values suggest some mismatches or larger variability. A value above 0.50 (50%) coupled with a low rate would make it difficult to extrapolate forward with adequate reliability. These MSE values are all small enough to support extrapolation. The relatively large MSE of 36% at AC-2S is due to a nonlinear sequence of values observed between 2000 and 2005. To improve the fit (and lower the MSE), one might view the outlying value in 1999 as being uncharacteristically low, in which case the estimated rate would be substantially higher; or one might view the outlying peak in 2002 as being uncharacteristically high, in which case the estimated rate would be slightly lower. Resolving the question of which of these older data, if either, is characteristic of the trend will need to await future data: as time progresses, older data will have progressively less bearing on the estimates.

The relatively large MSE of 46% at AC-30D is due to an apparent change in trend during the last three years. This causes the fitted line to be less steep than it was previously and increases the scatter of all the data around the line. The mean of the most recent two values exceeds the upper prediction limit computed in 2009 (see below), providing evidence of a recent decrease in the point attenuation rate at this well.

### Estimated cleanup dates

| | Cleanup year | LCL year | UCL year | 2009 estimate | LCL (2009) | UCL (2009 |
|---|---|---|---|---|---|---|
| AC-7SR | 2008.5 | 2007.8 | 2008.8 | NA | | |
| AC-2S | 2033.3 | 2029.5 | 2038.3 | 2020 | 2016 | 2025 |
| NWD-2S | 2000.8 | 2000.3 | 2001.3 | NA | | |
| AC-3D | 2025.7 | 2022.7 | 2030.2 | 2019 | 2016 | 2025 |
| AC-29D | 2060.8 | 2052.2 | 2073.1 | 2041 | 2030 | 2069 |
| AC-30D | 2014.0 | 2012.8 | 2015.8 | 2010 | 2009 | 2011 |
| AC-34S | 2007.6 | 2006.9 | 2007.5 | NA | | |
| AC-35D | 2133.9 | 2109.9 | 2173.7 | 2032 | NA | NA |

The estimated cleanup dates are obtained by extrapolating the fitted lines forward until they reach the performance standard. The LCL and UCL are "fiducial intervals" around those estimates, constructed *via* inverse regression as described in the 2009 submittal. They function similarly to the confidence limits for the rates: the LCL is constructed to have a 95% chance of being too early, while the UCL is constructed to have a 95% chance of being too late. For comparison, the 2009 estimate and its LCL and UCL are copied from Table V in the 2009 submittal: they were based on data available through 2008.

Because the UCLs for cleanup date at AC-7SR and NWD-2S are in the past, the data provide significant evidence that the performance standard has been met at these wells.

As noted in the introduction, data collected since 2009 are *expected* to change the estimated cleanup dates. It is of interest to evaluate whether those changes tend to stay within the confidence intervals. The preceding table lists five 2009 estimates. Confidence intervals could be established for four of them. In all cases, either the new estimate of the cleanup year is beyond the 2009 UCL or the 2009 estimated cleanup year is before the new LCL.

These apparent inconsistencies may be partially due to how data have been selected for analysis. There are three kinds of wells: those whose peaks came early and are now showing high attenuation rates; those whose peaks are uncertain because concentrations are not changing rapidly; and those that clearly have not yet experienced their peaks. The five wells with 2009 cleanup date estimates are all in the middle group, where uncertainty is greatest. The estimates and the confidence limits for these wells are sensitive to how data are selected for fitting and they will be highly uncertain in any case because the expected acceleration of attenuation rates has not yet set in.

### Retrospective prediction limits

To check that attenuation is proceeding as expected, current data are compared to prediction limits based on previous data. In the 2009 submittal, prediction limits were computed for the average (geometric mean) of planned 2012 and 2013 data. Because the 2013 data have not yet been collected, this comparison will be made by averaging the two most recent data—usually from 2011 and 2012—and comparing those to retrospectively computed prediction limits based only on the data that were available at the time of the 2009 submittal.

| | LPL (mg/L) | UPL (mg/L) | Geo mean (mg/L) | Value 1 | Value 2 | Date 1 | Date 2 |
|---|---|---|---|---|---|---|---|
| AC-7SR | 2.02 | 5.85 | **1.65** | 2.9 | 0.94 | 2011.9 | 2012.8 |
| AC-2S | 11.99 | 190.70 | 54.07 | 68.0 | 43.00 | 2011.9 | 2012.9 |
| NWD-2S | 1.71 | 2.40 | 2.05 | 2.1 | 2.00 | 2006.9 | 2008.9 |
| AC-3D | 7.81 | 31.10 | 16.49 | 17.0 | 16.00 | 2011.9 | 2012.9 |
| AC-29D | 15.47 | 43.24 | 37.88 | 41.0 | 35.00 | 2011.9 | 2012.9 |
| AC-30D | 1.04 | 4.21 | **7.48** | 7.0 | 8.00 | 2011.9 | 2012.9 |
| AC-34S | 0.75 | 1.38 | 0.98 | 1.0 | 0.97 | 2011.9 | 2012.9 |
| AC-35D | 83.52 | 157.72 | 130.00 | 130.0 | 130.00 | 2011.9 | 2012.9 |

These 2009 prediction limits (shown in the "LPL" and "UPL" columns) form an interval constructed to have a 95% chance of including the mean value (the "Geo mean" column). For six of the eight wells, the intervals indeed cover the prediction interval. In AC-7SR, the recent values have been lower than predicted, due primarily to the very low value of 0.94 mg/L observed in late 2012 (shown in the "Value 2" column, with its sample date in the "Date 2" column). In AC-30D, the recent values have been higher than predicted.

These results constitute significant evidence that recent concentrations in AC-7SR are lower than anticipated and recent concentrations in AC-30D are higher than anticipated.

### Prospective prediction limits

To set the stage for the next five-year review, provisional prediction limits have been calculated for the geometric mean of hypothetical data to be collected on or near the middle of 2017 and 2018.

| | LPL (mg/L) | UPL (mg/L) |
|---|---|---|
| AC-7SR | 0.39 | 2.0 |
| AC-2S | 9.72 | 53.7 |
| NWD-2S | 0.56 | 1.0 |
| AC-3D | 4.98 | 14.3 |
| AC-29D | 14.69 | 43.4 |
| AC-30D | 0.44 | 7.3 |
| AC-34S | 0.13 | 0.3 |
| AC-35D | 89.1 | 136 |

### Spatio-temporal considerations

The most distant estimated cleanup date is in 2134 for AC-35D (the one-sided 95% confidence limits are 2110 to 2174). This well is far downgradient of the site, located just west of the Bayou. In 2009 it was not possible to estimate a cleanup date for this well, because it had not yet exhibited signs of attenuation. As the 2009 submittal explained, attenuation at any location is expected to occur only when a plume—whose leading edge is becoming more spread out over time—finally passes that location. Before and during that period, concentrations of the primary constituents (fluoride and chloride) will appear to be randomly fluctuating around a stable (peak) level. Beginning a few years after the peak, depending on how variable the data are, attenuation will become noticeable in the time series plots but be impossible to estimate: this is where AC-35D was in 2009. (A comment in Table IV of the 2009 submittal noted "Peak is very flat.") As more time passes, the attenuation rate will first become estimable, yet be unrealistically low and uncertain. This seems to be where AC-35D is now. The attenuation rate will increase over time, but its estimates may vary erratically at first. Once a peak has been *definitively* identified and then approximately eight observations are available during the subsequent accelerating period, it will become possible to make a reliable estimate of the attenuation rate.

The salient consequences of this analysis are

1. Wells that presently exhibit low attenuation rates will (a) have wide confidence levels for time to cleanup and (b) may exhibit wide swings in the estimated time to cleanup until the plume definitively passes them by.

2. Predicted times to cleanup for the most-downgradient wells in the central portion of the plume, which includes AC-35D, AC-30D, AC-29D, AC-28D, and AC-24D, will be unrealistically long until the plume clearly passes those wells.

"Clearly passes" in the second point refers to that future time when accelerating and consistent attenuation are exhibited. At the time the peak is first (tentatively) identified at any well, its presence is highly uncertain. Even afterwards, changes in local groundwater velocities may cause deviations from the theoretical ideal of a single peak passing through each fixed monitoring point. Higher-concentration portions of the plume may spread laterally under the influence of varying flow directions and cause periods when attenuation is masked by the lateral movement of the plume.

## *Radium*

### Trends over time

The reader is referred to the August 19, 2009 MNA report, pages 7-13, for discussion of radium fate and transport. As stated, *"Radium, however, is so strongly retarded under any conditions that the elevated radium activities observed downgradient cannot reasonably be attributed to radium released near the Site."* In Table VI of the 2009 submittal, attenuation rates were estimated for 11 deep monitoring well locations and two shallow well locations. Most were based on five to eight observations. As a result of these relatively small amounts of data, prediction limits for the mean 2012/2013 combined radium values covered wide ranges, often spanning an order of magnitude or greater. Presently, four additional observations obtained in 2009 through 2012 are available.

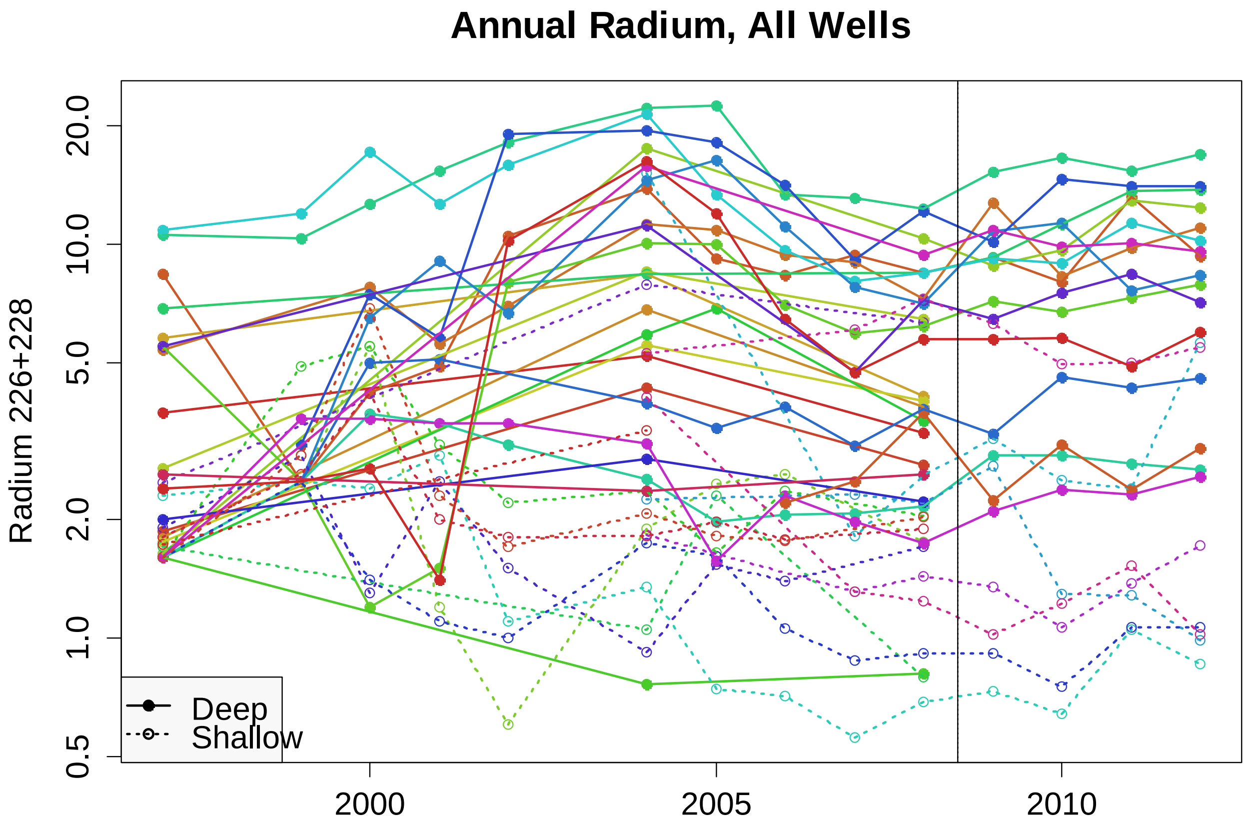
The analysis begins with an overview of the combined radium data, plotted as overlaid time series. The next figure uses a logarithmic axis (showing activity in pCi/L), differentiates wells by color, and uses different symbols to distinguish deep wells from surficial wells. General impressions afforded by this plot are

1. There has been less temporal variation during the last four years than previously.

2. The rate of attenuation that had been apparent in many wells during the 2004 – 2008 period has generally not continued.

3. Radium activity however, appears to be stable—neither significantly increasing nor decreasing—during the last four years.

4. Radium activity in deep wells (typically 2 to 15 pCi/L)—the ones monitoring the Main Producing Zone—tend to be higher than those in shallow wells (typically ½ to 5 pCi/L), which are the ones monitoring the Surficial Zone.




Apparent exceptions to the impression of recent stability occur in AC-34S, whose combined radium activities have decreased from 2.73 pCi/L in 2009 to 0.98 in 2012, and in AC-28D, whose activities have increased from 9.26 pCi to 13.78. To assess the significance of these changes, consider the 23 wells monitored for radium between 2009 and 2012. Consider any such group of 23 wells that *hypothetically* have stable activities over time but exhibit random variation around their long-term values. Among the 4! = 24 possible ways in which a sequence of four values can be ordered, there is exactly one way in which they start high and consistently decrease each time. With fluctuations occurring randomly around a stable level, all 24 ways are equally likely. Thus, 23/24—almost one—of these wells is *expected* to exhibit such a decreasing pattern (and, by the same reasoning, one well is expected to exhibit a consistently *increasing* pattern). The occurrence of one increasing sequence and one decreasing sequence out of 23 wells therefore is no surprise. Moreover, the amounts of change in these two monotonic sequences are typical of the amounts of change occurring in the other 21 wells. Therefore what has recently been observed in AC-34S and AC-28D is neither statistically significant nor of concern, but rather helps to reinforce the impression of overall stability in combined radium activities throughout the monitoring area.

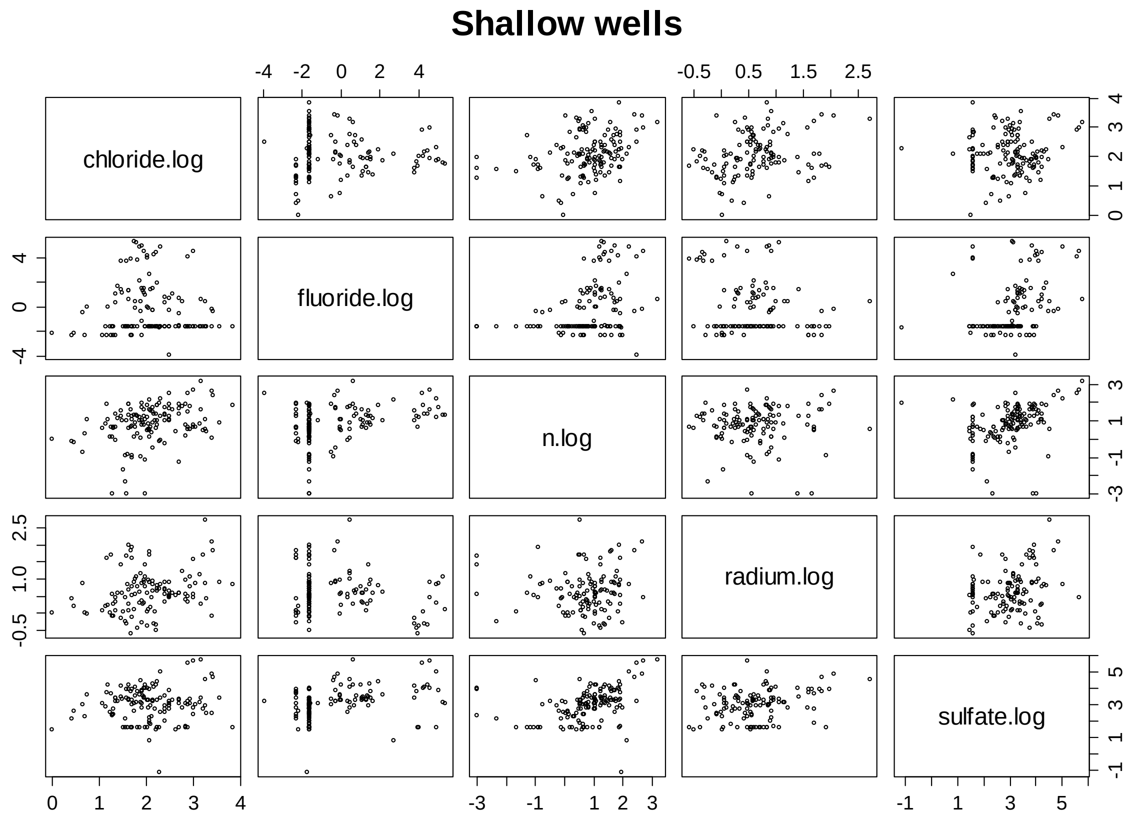
### Correlations with other parameters

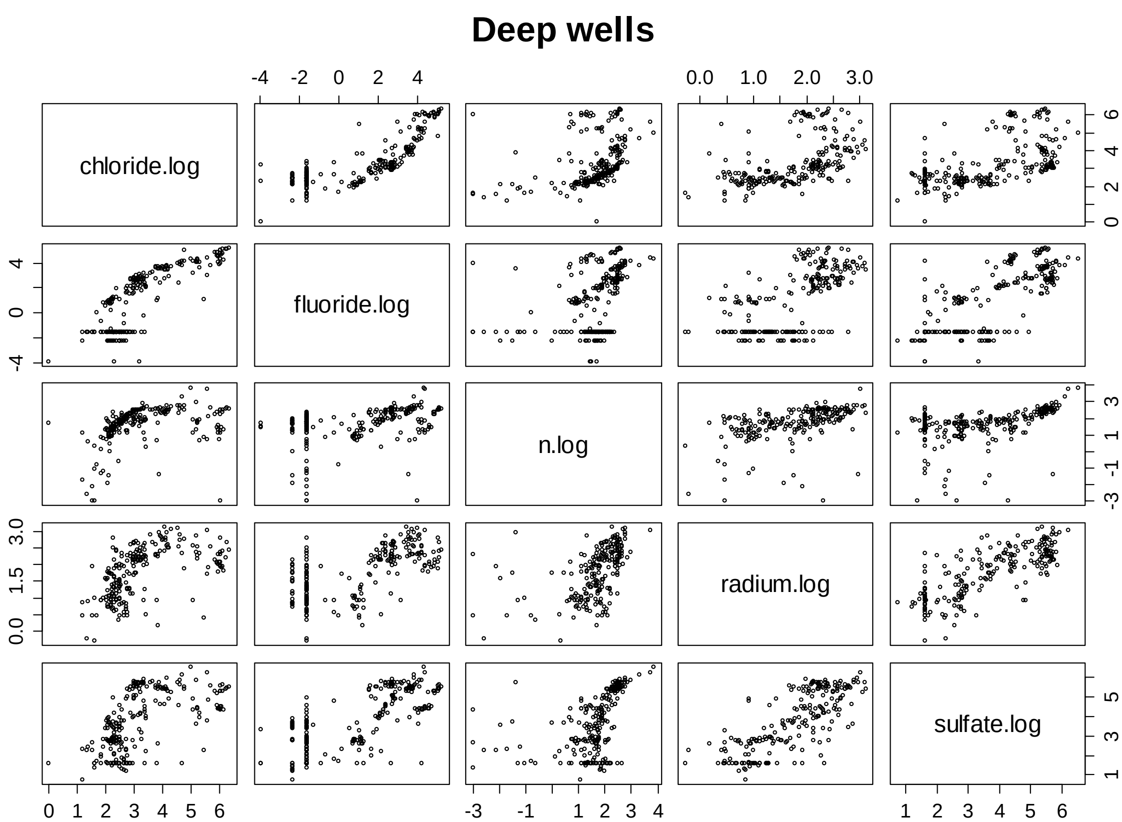
To what extent, then, should combined radium still be considered an "indicator of the overall plume"? This question can be addressed by exploring the relationships between the radium results and the rest of the monitoring parameters.

(Before proceeding, a technical issue has to be managed. From the original seven parameters, combined radium was created by summing two of them ($^{226}$Ra and $^{228}$Ra). Two others, Nitrate as N and Nitrate+nitrite as N, are almost equivalent and closely related to each other. To use them effectively, the values of the latter, in cases where they were missing, were imputed from values of the former by regressing their logarithms and using the resulting least-squares fit to provide estimates. The relationship is so close and accurate that this imputation likely introduces little error, while enabling fullest use of the nitrate-related data.)

After these preliminaries, four variables are left to study in connection with combined radium: chloride, fluoride, nitrates, and sulfate. For geochemical reasons (as discussed in the 2009 submittal) a positive correlation with sulfate is expected. If indeed radium is created in groundwater from the site-derived plume—either directly or indirectly—then positive correlations with fluoride and chloride should also be evident.

An informative way to assess such correlations is with a scatterplot matrix. This is an array of scatterplots, each comparing one variable to another. As usual, logarithmic scales will be used. Because of the distinct difference in typical radium concentrations observed in the deep and surficial wells (*q.v.*), separate scatterplot matrices for each hydrological unit were generated.


Shallow wells
chloride.log
fluoride.log
n.log
radium.log
sulfate.log


Deep wells
chloride.log
fluoride.log
n.log
radium.log
sulfate.log

Within the surficial (shallow) wells, the expected correlations are *not* found. The second column of scatterplots from the right displays the relevant information: each of these scatterplots displays combined radium activities on the horizontal axis and concentrations of the other parameters on the vertical axis. The most important of these compares fluoride to radium: here, the correlation is strongly *negative*. The largest fluoride concentrations are associated with the *smallest* radium activities, forming a separated "cloud" of a dozen points in the upper left of that scatterplot. Complementing this is a cloud of about a dozen points at the lower right, where radium has the highest activity and fluoride concentrations are low or not detected.

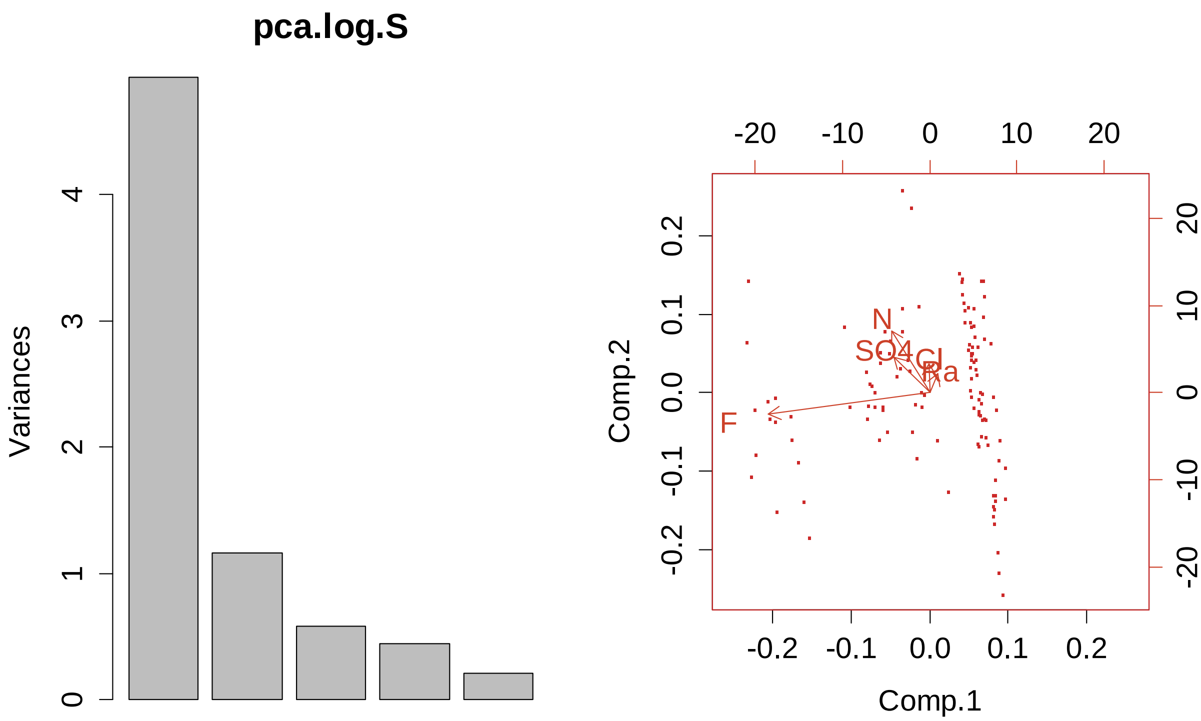
<u>The correlations between radium and the other parameters are weak to nonexistent in the shallow wells.</u> There is some hint of a weak positive association between radium and chloride.

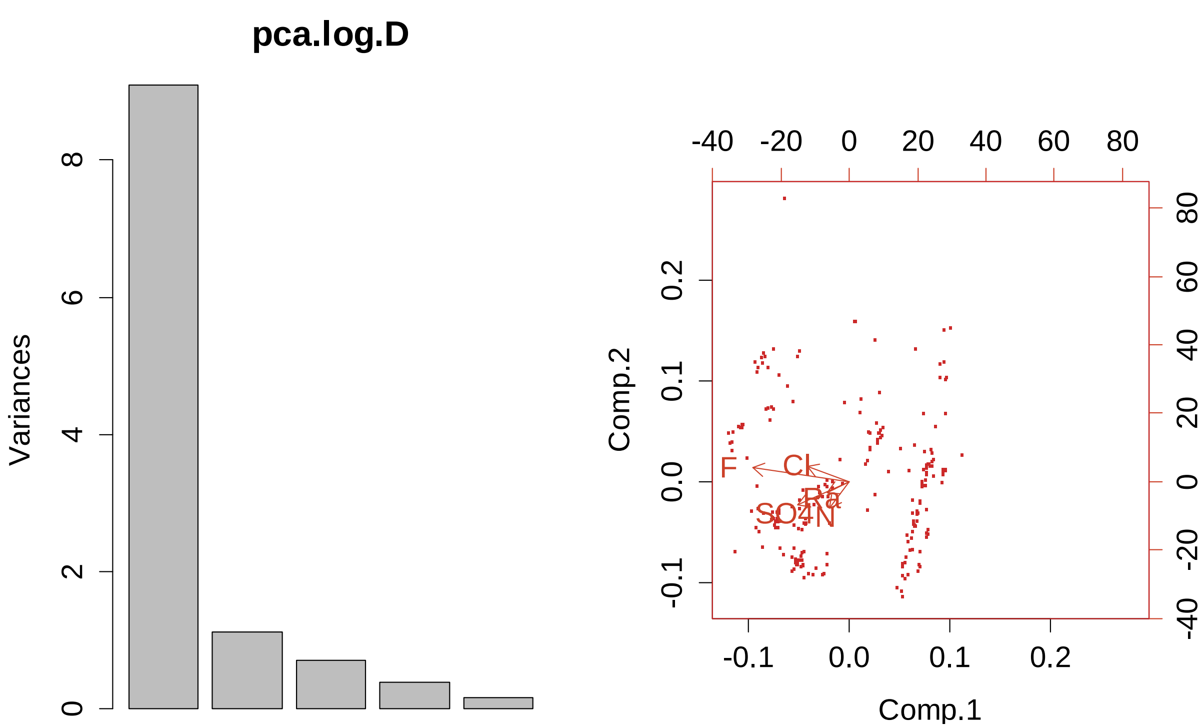
The scatterplot matrix for the deep wells, in contrast, exhibits the expected positive correlations between combined radium and the other parameters. For fluoride the correlation is partially hidden by the nondetects, but it is still clear and strong: the largest fluoride concentrations are consistently associated with the largest radium concentrations, as shown by the large cloud of points in the upper right corner of that scatterplot. The correlation of radium with sulfate suggested by chemical theory is apparent and strong. Its correlations with chloride and nitrate echo those with fluoride and sulfate, respectively, and may indeed be the indirect results of strong chloride-fluoride and nitrate-sulfate correlations.

A numerical way to study a set of mutual correlations among parameters is *Principal Components Analysis*, or PCA [Davis 1986]. This exploratory statistical method finds a relatively small set of linear combinations of the parameters that account for most of the variation in their values. It is a multivariate extension of the visualization carried out in a scatterplot: when we view a cloud of points and assess it for correlation, we are evaluating the degree to which it is long and thin and not just a diffuse circular blob. When it is long and thin, both variables tend to increase and decrease together (or they vary oppositely when the correlation is negative). The linear combination in PCA associated with the long direction of the cloud is the sum of the two variables. In the perpendicular (narrow) direction in the cloud, the associated linear combination is the difference of the variables (taken in either order). The linear combinations (or "principal components") computed in PCA have similar interpretations when more than two variables are involved.

Judgment is needed when performing PCA. Among the decisions made by the analyst are whether to use the original values or their logarithms and whether to analyze the correlations or the *covariances* of the variables. (The covariances can be thought of as correlations, weighted by the amount of variation of the variables.) For these data, the result of PCA does not materially change when these decisions are varied. The following summarizes the PCA based on logarithms (which is consistent with the use of logarithms throughout this analysis) and the use of covariance to measure the associations among the variables.

Because substantial differences in the covariances between the two hydrological units were exhibited in the scatterplot matrices, PCA was performed separately for each unit. The results of a PCA can be summarized with two plots: a “scree plot” showing the contribution of each principal component to the total variation and a “biplot” which graphically shows the contributions of each variable to the largest two principal components.



In both cases, the scree plots (at left) show the components are dominated by the first one, which is typical of groundwater plumes: the first component reflects the overall concentrations. The second components, albeit small, provide some power to indicate how the different parameters are interrelated. For the surficial wells, shown as "pca.log.S," the biplot (at the right) contains one small dot for each sample (representing the vector of chloride, fluoride, nitrate, radium, and sulfate values for that sample). The axes, labeled "Comp .1" and "Comp. 2," are the first two principal components. The vector of five (log) concentrations in each sample has been replaced by its pair of "loadings" on the principal components, effectively projecting the five dimensions of data into a two-dimensional plane. Because the first two principal components were used for the projection, as much of the variation in the data as possible is being shown. Because the remaining three principal components have small variances (as displayed in the scree plots), these two-dimensional approximations can be expected to represent the data accurately, justifying the following interpretation.

The dots in the biplots appear to stratify into three discrete levels according to the value of the first component: a near-vertical sequence of points ranging horizontally between 0.05 and 0.1, a more diffuse cloud between -0.1 and 0.0, and another vertical sequence near -0.2. These patterns echo—and effectively combine into one plot—the ten scatterplots shown in the scatterplot matrix for the shallow wells. In particular, the observations with high fluoride and low radium correspond to the third stratum in the biplot and the observations with fluoride nondetects correspond to the first stratum. Evidently, the stratification reflects different levels of fluoride. This is indicated by the vectors in the biplot: fluoride ("F") stands out by itself, pointing in a direction that separates the strata. Nitrates and sulfates ("N" and "SO4") form a cluster of two nearly similar vectors, pointing along the directions within the strata. This means that points of any given stratum in that biplot likely can be distinguished by either their nitrate or sulfate concentration, both of which are highly correlated within that stratum. Finally, the very small vectors for radium and chloride ("Ra" and "Cl") indicate that neither of these parameters plays a strong role in accounting for the variation in the data.

The same three strata show up in the deep wells. This time, though, all five parameters appear to contribute (to some small extent) to the stratification: their vectors in the biplot point in approximately the same direction that the fluoride vector points. This bears out the impression from the earlier scatterplot matrix that all five parameters are strongly mutually correlated.

## Conclusions

The recent stable trends in the combined radium activities indicate there is little or no point attenuation of radium throughout the plume within either of the hydrological units, but there are no significant increases. Any short-term trends that may be apparent in the data are not statistically significant: they are consistent with random variation around values that are stable over time. It is therefore not meaningful to estimate attenuation rates or "cleanup" times for radium.

There are clear differences in conditions between the hydrological units: radium activities tend to be greater in the deep wells and they are strongly correlated with the concentrations of all the other parameters. Within the surficial unit, the relatively low radium activities (many, but not all, of which are below the target of 5.0 pCi/L) and the lack of strong correlations (even those predicted on general chemical principles) suggest that the observed radium may be unrelated to any site-derived plume and perhaps reflects naturally occurring concentrations.

### *Monitoring Frequency*

The current monitoring frequency at many wells is once per year. Is this optimal? The answer to that question may vary from well to well according to its role in the monitoring system, the statistical characteristics expected of future observations, and the need and timeliness of any active response to possible changes in conditions.

- The characteristics of future observations *in wells where the peak of the plume has passed* will likely be similar to those in the past: they should exhibit the same amount of apparently random variation around a decreasing trend.
    - When that amount of random variation is relatively small, confidence in future projections can be high, suggesting less frequent monitoring is necessary.
    - Where temporal correlation among observations is high, future data can be predicted with greater confidence.
- Large or sudden changes in wells near the source or—at the other extreme—wells just upgradient of the receptor (the Bayou) might indicate a need for a relatively quick reaction, whereas such changes in wells in the middle of the plume would likely indicate no immediate need for action.
    - If, in any event, concentrations are substantially below their targets, then even large increases in them would be of less environmental concern.

If monitoring frequencies are decreased at wells where attenuation has appeared to begin, then over time less data will be available and consequently the confidence limits for the times to cleanup will be wider and prediction limits for future values will be higher. This will not be problematic at wells that have already met their cleanup targets or whose targets are not in the distant future: these wells are not driving the duration of the overall cleanup.

Nitrates present a problem: in many wells that otherwise exhibit low concentrations of fluoride, chloride, radium, and sulfate, nitrates may be more variable and sometimes exceed their target. Especially in the shallow zone monitoring points, this is consistent with a secondary surficial source of nitrates (such as past agricultural applications). Whether or not nitrates need annual monitoring, or monitoring that is as frequent as the other parameters, is beyond the scope of the present analysis to determine.

Applying these criteria systematically to the data identifies the following wells as the best candidates for a reduced monitoring frequency.

| Well | Characteristics |
|---|---|
| AC-3S | Upper to mid-plume; all parameters are below targets. |
| AC-5S | South of site and almost side-gradient; all parameters are below targets (but nitrates exhibit relatively high variability). |
| AC-7SR | At eastern boundary of site. Fluoride appears to be attenuating consistently and has fallen below its target. All other parameters are below their targets. |
| ACB-32S | At western (upgradient) boundary of site. All parameters are well below targets (many values are nondetects) and some, like sulfate, are attenuating rapidly. |
| AC-8D | Mid-plume, southern end. No evidence of fluoride. All other parameters are very stable. Nitrate appears to attenuate slowly, as if a separate nitrate-bearing plume had passed by (with a peak around 2003). |
| AC-36D | Near the Bayou, serving as a sentinel. No evidence of fluoride. All other parameters are very stable. Nitrate appears to attenuate slowly, as if a separate nitrate-bearing plume had passed by (with a peak around 2006). |
| PIP-D | Upgradient of the site. Low concentrations of all parameters. No evidence of fluoride. |

A reduction of frequency to once every two years appears justified in these wells from the data alone. A greater reduction might be suitable but would need additional justification based on the role of each well in the monitoring program and the confidence in the understanding of this plume, the forces affecting it, and the likelihood that conditions continue to change slowly.

## Summary and Recommendations

**Fluoride continues to determine the progress of natural attenuation at this site.** The statistical modeling and testing of the fluoride data has been carried out as described in the 2009 submittal, including:

- Principled selection of data for analysis:
    - Wells exhibiting concentration trends characteristic of attenuation were identified.
    - Outlying data were detected, evaluated, and appropriately downweighted in subsequent analyses.

- Least-squares fitting of log concentrations *versus* time, by well.
- Estimation of point attenuation rates and their corresponding half-lives, with confidence limits constructed for the rates to establish they are all significantly positive.
- Estimation of cleanup dates, with confidence limits constructed to assess the uncertainty in time to cleanup.
- Comparison of recent data to prediction limits based on older data, providing an assessment of progress toward cleanup at this intermediate stage.
- Construction of provisional prediction limits to project the ranges of concentrations likely to be observed in 2017-2018.

Some minor technical improvements have been implemented:

- A robust version of least-squares fitting helps to identify and downweight outlying data.
- Least-squares fitting with a quadratic term is useful for objective identification of likely dates of peak concentration.

**The least-squares fits provide good descriptions of the data.** The point attenuation rates continue to be sufficiently high in most wells to indicate cleanup targets will be attained before 2062. The projected ranges of cleanup dates remain approximately the same as before.

**Concentrations in well AC-30D are greater than projected from previous data**: they recently average 7.5 mg/L compared to a projection of 1.0 to 4.2 mg/L. Consequently, although cleanup at this well was expected by now, it has not yet occurred. Nevertheless, the point attenuation rate has been high at this well, averaging a decrease of 22% per year. Assuming that some rate of decrease—albeit perhaps not this great—continues in the future, then within five years the average observed values are projected to lie between 0.4 and 5.7 mg/L, below or near the performance standard. Because concentrations in this well are so close to the cleanup target, it is not determining the duration of the remedy.

**The projected cleanup dates in most wells (where concentrations have peaked) remain between the present and 2061.** Dates further into the future do appear among the estimates at wells where the peak of the plume has not yet been reliably identified. Those dates are unreliable, will likely decrease during future reviews, but are expected eventually to become reliable and consistent projected cleanup dates as at the other wells.

**Combined radium activities have stabilized** during the last four years of monitoring. Radium exhibits different characteristics in the two hydrogeological units. In the surficial unit, radium does not appear to be a reliable indicator of a site-derived plume. In the main producing zone, radium does appear associated with the other monitoring parameters, and therefore should exhibit the same trends over time as those other parameters.

### *Recommendations*

**Seven wells are good candidates for a reduced monitoring frequency**. These wells, and the reasons for the reduction, are listed under the heading "Monitoring Frequency" above. A reduction from annual to biennial (once every two years) monitoring is easily justifiable from the data; a greater reduction may be appropriate in the future, provided it is supported by additional lines of evidence.

Although the data indicate that some monitoring wells are candidates for a reduced monitoring frequency, the PRPs have chosen to maintain the frequencies specified by the existing monitoring plan. As more data become available in the future, the appropriateness of the monitoring frequencies should continue to be re-evaluated with reference to the role of each well in the program.

## References

Davis, John C. *Statistics and Data Analysis in Geology*. Second Edition, 1986. John Wiley & Sons, New York.

Ripley, Brian *et al*. *Support Functions and Datasets for Venables and Ripley's MASS*. April 3, 2013. Available at http://cran.r-project.org/web/packages/MASS/MASS.pdf.

URS Corporation, 2009. Evaluation of Monitored Natural Attenuation in Groundwater. Agrico Site. Pensacola, Florida. EPA ID: FLD980221857. Prepared by William A. Huber, Ph.D. (Quantitative Decisions). August 19, 2009.

# Appendix 1: Tables

## Table I Outlying Fluoride Data

The following records were explicitly flagged as outliers based on visual examination of the time-series graphics and preliminary statistical analyses.

| Date | Well | Mean result | Number of replicates | Any NDs? |
|---|---|---|---|---|
| 1999.882 | AC-3D | 14.00 | 1 | |
| 2000.889 | AC-3D | 18.00 | 1 | |
| 2001.869 | AC-3D | 13.00 | 1 | |
| 1990.748 | AC-12D | 24.00 | 1 | |
| 1990.748 | AC-13D | 8.60 | 1 | |
| 1992.089 | AC-13D | 5.30 | 1 | |
| 1997.738 | AC-13D | 4.90 | 1 | |
| 1992.133 | AC-24D | 36.00 | 1 | |
| 1993.784 | AC-28D | 3.10 | 1 | |
| 1997.738 | AC-28D | 0.42 | 1 | |
| 1997.352 | AC-34S | 16.00 | 1 | |
| 1997.858 | AC-34S | 9.50 | 1 | |
| 1998.337 | AC-34S | 6.30 | 1 | |
| 1998.893 | AC-34S | 3.80 | 1 | |
| 1999.876 | AC-34S | 2.50 | 1 | |
| 2000.372 | AC-34S | 2.60 | 1 | |
| 2000.870 | AC-34S | 1.60 | 1 | |
| 2001.352 | AC-34S | 1.20 | 2 | |
| 2002.882 | AC-34S | 1.20 | 1 | |
| 2003.345 | AC-34S | 1.90 | 1 | |
| 2004.035 | AC-34S | 2.00 | 1 | |
| 1999.882 | AC-35D | 23.00 | 1 | |
| 2002.885 | AC-35D | 0.08 | 1 | TRUE(1) |
| 1990.748 | NWD-2S | 0.78 | 1 | |

### Remarks

(1) The value listed was chosen uniformly and randomly between 1/100 and 1 times the detection limit.

Due to the use of a robust fitting method, some values listed as outliers in the 2009 submittal were not explicitly labeled as such for these analyses. The reason for labeling any values as outliers at all is that least-squares methods are most sensitive to values at the extreme ends of the date ranges: the oldest and the most recent. The most recent are probably more reliable and certainly more current, but the oldest no longer reflect current or even average conditions during the time period. Therefore, any data obtained near the beginning of the monitoring period which appear grossly inconsistent with the subsequent data were flagged as outliers.

## Appendix 2: Time-Series Plots

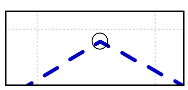
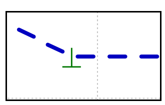
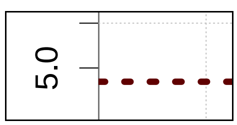
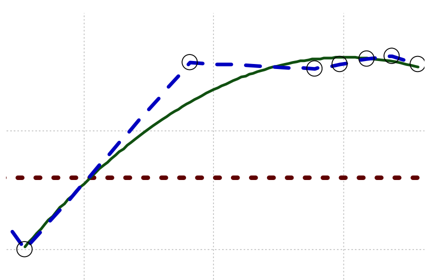
### Explanations

Plots are presented in alphabetical order of well name within each groundwater flow zone.

To enhance comparability, all plots show a common range of concentrations (on a logarithmic scale) and a common range of sample dates.

The superimposed curves display the *quadratic* fits used to identify possible peaks., both to serve as documentation of the peak identification procedure and to display a simple summary of temporal trends. The curves span all observations after the beginning of 1995. (Remediation was completed near this time, in April 1997, and most of the data were collected after this date.) **It is not valid to project these fits forward in time**; they are reliable primarily at the location of any peak, if it exists. They should be considered unreliable for small datasets, especially those of just three or four observations.

### Legend

| Symbol | Explanation |
|---|---|
|  | Quantified result |
|  | Nondetect (plotted at the reporting limit) |
|  | Target concentration (4.0 mg/L for Fluoride) |
|  | Fitted quadratic curve |