



August 21, 2009

Submitted Electronically to : miller.scott@epa.gov

Mr. Scott Miller
Remedial Project Manager
Superfund Remedial and Technical Services Branch
U.S. Environmental Protection Agency, Region 4
Atlanta Federal Center
61 Forsyth Street
Atlanta, Georgia 30303-8960

**Subject: Evaluation of Monitored Natural Attenuation in Groundwater
Agrico Site, Pensacola, Florida
EPA ID: FLD 98022 1857**

Dear Mr. Miller:

In accordance with the U.S. Environmental Protection Agency's (EPA) request to perform a quantifiable evaluation of the effectiveness of the Monitored Natural Attenuation (MNA) remedy for the Agrico site, Pensacola, Florida, URS Corporation (URS) on behalf of ConocoPhillips, Inc., merger successor to Conoco, Inc. and Williams representing Agrico Chemical Company is submitting this Report for the Agrico site in Pensacola, Florida. This report "*Evaluation of Monitored Natural Attenuation in Groundwater*" was prepared by William A. Huber, Ph.D., Quantitative Decisions (Rosemont, Pennsylvania) and presents the results of the MNA evaluation for the site.

This report was prepared using the guidance provided by EPA as part of the request to complete this evaluation. Additionally, Dr. Huber has presented recommendations for data analysis using different statistical procedures than indicated in the supplied EPA documents for some of the calculations. All methods used in this report conform to EPA objectives and the EPA conceptual model of attenuation.

Should you have any questions or require additional information regarding this report, please contact Ms. Terry D. Vandell (ConocoPhillips) at (580) 767-6561 or Mr. Phil Roberts (Williams) at (918) 573-0757.

Sincerely,

Jeffrey R. Wagner, P.G., V.P.
Principal Hydrogeologist

JRW:lc

cc: Walsta Jean-Baptiste – FDEP, Hazardous Waste Cleanup Section, Tallahassee (1 copy + 1 CD)
Mike Kennedy – FDEP, Northwest District, Pensacola (1 copy + 1 CD)
Phil Roberts– Williams (1 copy + 1 CD)
Terry Vandell-Bell – ConocoPhillips (1 copy + 1 CD)

R E P O R T

EVALUATION OF MONITORED
NATURAL ATTENUATION IN
GROUNDWATER
AGRICO SITE
PENSACOLA, FLORIDA
EPA ID: FLD 980221857

Prepared by
William A. Huber, Ph.D.
Quantitative Decisions
Rosemont, Pennsylvania

Prepared for
ConocoPhillips, Inc.
Ponca City, Oklahoma

and

Williams, Inc. on behalf of
Agrico Chemical Company
Tulsa, Oklahoma

August 21, 2009



URS Corporation
1625 Summit Lake Drive
Suite 200
Tallahassee, Florida 32317
Tel: 850.574.3197
12805561.00000

Evaluation of Monitored Natural Attenuation in Groundwater

Agrico Site, Pensacola, Florida

August 19, 2009

EXECUTIVE SUMMARY	1
Is attenuation working?	1
How long will it take?	1
What changes can reasonably be anticipated?	1
What are the uncertainties?	1
Recommendations	2
INTRODUCTION	3
Purposes of this report	3
History and setting	3
Sources	4
Monitoring	5
Objectives	5
Management	5
BACKGROUND	6
Groundwater conditions	6
Configuration and flow	6
Quality	6
Theories of constituent fate and transport	7
The remedy	10
Remedial objectives	10
The groundwater monitoring program	11
EPA guidance on assessing MNA	12
Objectives of this evaluation	13
METHODS	14
The statistical model of attenuation and its assumptions	14
Consequences of advection and dispersion	14
Nature of the variability	17
Statistical procedures	17
Evaluating the data	17
<i>Outlying, atypical, and non-representative data</i>	<i>18</i>
Estimating point attenuation rates and their confidence limits	19
<i>The statistical model</i>	<i>19</i>
<i>Estimating the parameters</i>	<i>20</i>
<i>Computing confidence intervals</i>	<i>21</i>
<i>Interpreting the results</i>	<i>22</i>
Estimating cleanup times and their confidence limits	23
<i>Estimating the time when cleanup is achieved</i>	<i>23</i>
<i>Confidence limits for the cleanup time: an incorrect method</i>	<i>24</i>
<i>Computing confidence limits for the cleanup time</i>	<i>25</i>
<i>Interpreting the results</i>	<i>28</i>
Setting periodic review targets to assess whether attenuation is on track to meet the goals	28
<i>Analysis of the t-test</i>	<i>29</i>

<i>A better procedure</i>	30
<i>Interpretation</i>	31
Other analytes	33
RESULTS	34
Overview and summary of the fluoride data	34
Upgradient of the source area	34
Source area (Surficial Zone)	34
Central portion of the plume (“elevated” concentration area)	35
Fringes of the plume	36
Background	36
Statistical results	37
Point attenuation rates	37
Cleanup dates	39
Proposed review targets	39
Other analytes	40
Overview	40
Chloride	41
Nitrate	41
Combined Radium	42
Sulfate	43
Arsenic and Lead	43
CONCLUSIONS	44
REFERENCES	45
TABLES	48
Table I Monitoring Well Function	48
Remarks	48
Table II Reproduction of Table I-3 in [Wilson <i>et al.</i> 2005]	50
Remarks	50
Table III Unused Fluoride Data	51
Remarks	51
Table IV Dates of Apparent Peak Fluoride Concentrations	52
Remarks	52
Table V Estimated Fluoride Attenuation Rate and Prediction Limit Calculations	53
Remarks	53
Table VI Estimated Radium Attenuation Rates and Prediction Limit Calculations	55
Remarks	55
Table VII Summary of Remaining Radium Histories	56
Remarks	56
FIGURES	57
Figure 1 Well Locations, Groundwater Elevations, and Flow Directions	57
Main producing (deep) zone, November 2008	57
Surficial Zone, November 2008	57
Figure 2 Time <i>versus</i> Concentration Plots for One-Dimensional Advection and Dispersion	58

Figure 3 Inverse Regression and Fiducial Confidence Limits	59
Figure 4 Fluoride Time Series	60
Explanations	60
Legend	60
Main Producing Zone	61
Surficial Zone	63
Figure 5 Apparent Date of Peak Fluoride Concentration <i>versus</i> Groundwater Elevation	65
Figure 6 Fluoride Attenuation in AC-35D (Near Bayou Texar)	66
Figure 7 Time Series of Additional Analytes	67
Chloride	67
<i>Main Producing Zone</i>	67
<i>Surficial Zone</i>	69
Nitrate	71
<i>Main Producing Zone</i>	71
<i>Surficial Zone</i>	73
Combined Radium Activities	75
<i>Main Producing Zone</i>	75
<i>Surficial Zone</i>	77
Sulfate	79
<i>Main Producing Zone</i>	79
<i>Surficial Zone</i>	81
Figure 8 Scatterplot Matrix by Well	83
Remarks	83
INDEX	84

Executive Summary

Is attenuation working?

Yes.

The data show that mechanisms for attenuation are in place throughout the area and the effects of the source remedy (implemented in 1997) are propagating downgradient (that is, easterly), as expected. Decreases in concentrations have now been observed in the most upgradient groundwater and are imminent in the furthest downgradient wells.

How long will it take?

Much of the groundwater will reach the target concentrations within two to three decades. Within the groundwater discharge zone next to Bayou Texar, the time to clean up could be longer. In that area, precise estimates of the cleanup date cannot be made at this time, but will become possible as monitoring continues.

What changes can reasonably be anticipated?

Point attenuation rates at most wells should continue to increase. This means the cleanup will likely proceed more quickly than currently estimated. Eventually, concentrations of all constituents of concern will be decreasing at all wells throughout the area. For a time the attenuation will mostly occur—and has occurred to varying degrees, depending on how quickly each constituent moves—in the upgradient areas (the western portion), but eventually the downgradient areas will catch up.

What are the uncertainties?

All predictions and estimates assume the groundwater conditions will continue to evolve in the future as they have done in the past.

Statistical uncertainty is low: data are consistent within each well and show relatively little random variability. This implies there is no need to increase the monitoring frequencies.

The groundwater moves through zones whose physical conditions vary: permeability changes, groundwater gradients change slightly, and thicknesses change. The chemical environment of the groundwater also varies, causing changes to occur in the rates at which constituents are transported. This variation modifies the expected relationships among spatially related wells and also shows up as random variability within the data for each well.

The hydrogeological conditions at the downgradient end of the site, near Bayou Texar, are more complex than a simple one- or two-dimensional conceptual model would suggest.

Also, the effects of the source remedy have not yet fully appeared there, making accurate predictions at these locations difficult at this time.

At present, nitrates are attenuating slowly due to the apparent retardation of their movement in groundwater. This is unlikely to delay cleanup because all nitrate concentrations are close to or below their target. It will take more monitoring data and more time to estimate a cleanup time with suitable precision.

Many factors control the attenuation of radium activity in a complex fashion. Radium should be considered a secondary indicator of progress, as it reflects improvements in overall chemical conditions in the groundwater, and is most useful for corroborating the results of the other constituents of concern.

Recommendations

(1) Continue the current monitoring program, with the following considerations:

- The current measurement frequencies, typically annual, are appropriate for the cleanup period (up to 70 years from 1997).
- There appears little need to measure arsenic or lead: these substances are rarely detected and, where they are, have decreased in concentration. (Occasional measurements of arsenic and lead might be warranted at wells immediately downgradient of any suspected residual source areas.)

(2) As additional data are obtained, periodically update the point attenuation rate estimates, because they are likely to increase (especially in the wells most downgradient).

(3) For data analysis, use the statistical procedures described herein:

- Ordinary Least Squares regression (of log concentrations versus time) to estimate point attenuation rates.
- Fiducial confidence intervals (based on inverse regression) for cleanup times.
- Prediction limits to assess progress from one review period to another.

Introduction

Quantitative Decisions was retained in March 2008 to “consider the use of the most appropriate analytical / statistical methods to evaluate” groundwater monitoring data, “including but not limited to the method[s] suggested by EPA.” Interest focuses on the “point decay rates” as defined in [Newell *et al.* 2002].

Purposes of this report

This report presents our evaluation of the data. It aims to:

- (1) Provide and justify a scientific and statistical framework for articulating and addressing the question of natural attenuation of fluoride (and other constituents) in the groundwater plume.
- (2) Use all relevant data to assess the point attenuation rates of constituents in the monitoring wells.
- (3) Measure uncertainty and evaluate its influence on estimates and decisions made with the monitoring data.
- (4) Propose criteria for assessing whether the attenuation remains on track to clean up the groundwater in the future.
- (5) Identify any additional data needs.

The following narrative begins with a brief overview of the scientific, regulatory, and management context in which the groundwater monitoring has been conducted. It then provides background information about groundwater conditions, the work that has been done to improve them, and relevant US EPA guidance. This is followed by a long section, necessarily technical in nature, describing and justifying the methods used. A narrative summary of the results follows, amplified and supported by the appended tables and statistical graphics. Our conclusions and recommendations complete the report.

History and setting

This brief section¹ is provided to make the report self-contained. It relies on recent annual reports ([URS 2008 and 2009]), to which the reader is referred for further details.

¹ Short summaries, like this one, accompany the report as a guide to the reader. They are set within a border for easy recognition.

Sources

The Agrico site itself (“Site”), at 118 East Fairfield Drive, Pensacola, FL, was the location of phosphate fertilizer and sulfuric acid manufacturing from 1891 until 1975. In 1987 a groundwater assessment by the Florida DEP concluded that Site-derived materials, primarily fluoride and sulfate, had entered the groundwater. There are seven constituents of concern. Five are water-soluble inorganic ions and two are heavy metals (arsenic and lead, which can occur in various chemical species with varying properties). Fluoride predominates: concentrations measured in some locations have been almost two orders of magnitude greater than the cleanup target of 4 mg/L.

All constituents except radium could originate in Site-derived materials. All of them also have potential non-Site sources. However, fluoride is a characteristic residue of the historical manufacturing processes.

The constituents are transported under the influence of groundwater that moves through a sand and gravel aquifer whose hydraulic head drops approximately 30 feet in approximately one mile between the Site and Bayou Texar. The groundwater ultimately discharges beneath the bayou.

By 1997, onsite constituent sources had been stabilized with cement, consolidated over dry sediments underlying the site, and covered with an impervious engineered cap. (We will refer to the previous locations of these constituents as the “former source area.”) A subsurface slurry wall further protects these materials from water that otherwise could exfiltrate from a nearby stormwater impoundment. These actions effectively removed the original source of the Site-derived constituents to the groundwater. As a result, groundwater quality began changing, first beneath the former source area, thereby detaching the constituent plumes from their sources. Over time, these changes will propagate downgradient.

As related in [URS 2009], the EPA and FDEP have identified additional sources of the same or similar groundwater constituents at nearby or hydraulically upgradient sites. These include

- “Site 348” (the “Kaiser Site”), with “a history of fertilizer” dating back at least to 1926, located 3000 feet south of the Agrico facility (shown on Figure 1). It appears to have introduced ammonia, chloride, radium, and nitrates into the groundwater upgradient of wells AC-6S and AC-6D.
- Non-point sources of nitrates “throughout the southern half of Escambia County.”

Such non-Site sources help explain various localized anomalies apparent in the data.

Monitoring

By 1998, the US EPA had selected and approved an operations and maintenance plan to carry out monitored natural attenuation (MNA) intended to clean the residual contaminants in the downgradient groundwater. Seven analytical parameters—arsenic, chloride, fluoride, lead, nitrates and nitrites (together²), radium-226 and radium-228 (as total activity), and sulfate—are monitored in 40 wells, most of which are sampled once each year. This monitoring network is designed and operated to track the downgradient passage, dispersal, and ultimate discharge into Bayou Texar of the now-detached plumes of constituents.

Objectives

“Initial modeling results” indicated that cleanup targets, of which the most stringent is 4 mg/L fluoride, are likely to be met in all wells by 2067.

Management

The US EPA has conducted five-year reviews in 2000 and 2005 and will conduct another in 2010. This next review is expected to inquire about the effectiveness of the remedy: is attenuation working? How long will it take? What are the uncertainties?

This report addresses these questions by analyzing all the available, relevant monitoring data. It relies on the narrative, data, and figures in the 2008 Annual Report [URS 2009], where further background information about the Site can be found.

² In 2006, nitrites were removed from the list of constituents of concern. Subsequent measurements were converted, by a URS calculation, into concentrations of nitrate only.

Background

Groundwater conditions

This is a brief summary of relevant information from the most recent annual report [URS 2009].

Configuration and flow

The groundwater moves through three hydrogeologic units: the “Surficial Zone,” a low-permeability zone, and the “Main Producing Zone”:

Surficial: Up to 100 feet thick, quartz sand to gravel with “highly discontinuous” thin beds of clay, silt, and limonite-cemented sandstone. Groundwater migrates downward into the main producing zone.

Low-permeability: Semi-confining, variable lithology, typically poorly sorted. 20 to 50 feet thick. “Low vertical permeability.”

Main Producing: Moderate- to well-sorted sand and gravel. Gradual changes occur in depth, grain size distribution, and sorting. 10% to 40% interbedded clays. About 100 feet thick. Discharges into the bayou.

Before the 1997 remedial action, groundwater passing through the former source area created a plume of dissolved constituents in the Surficial Zone. This plume progresses in a “limited” spatial fashion before entering the Main Producing Zone (“deep zone,” for brevity). Flow is easterly in the Main Producing Zone. Any vertical flow is controlled by “head variations between zones.” The vertical gradients of course are downward where the plume enters the Main Producing Zone. They then appear to be relatively small until the groundwater reaches Bayou Texar, where—in textbook fashion—the water flows upward to discharge into the bottom of the bayou. The flow overall is “primarily controlled” at the groundwater discharge boundary in the bayou. This analysis is supported by water district numerical models, 1993-97. Compare the two panels of Figure 1, which show contours of groundwater heads in the surficial and deep zones. 59 private irrigation wells have been identified in this area. Using water level monitoring data from 2003 through 2008, URS concludes the private wells do not “adversely affect” the direction of groundwater flow. There is a moratorium on new well construction in the area.

Variations in regional groundwater levels tend to “mimic” rainfall patterns. Cumulative precipitation decreased from 1997 to 2001, increased to 2005, and has been declining since.

Quality

Table 3 of [URS 2009], “Field Parameter Results,” documents groundwater that is moderately acidic (pH 3.88 to 6.53 in the Main Producing Zone, 4.14 to 6.51 in the Surface

Zone) and generally oxidizing (field measurements of oxidation-reduction potentials range from -290 to 370 mV but are typically 150 – 250 mV).

Dissolved oxygen (DO) ranges from less than 0.1 mg/L to over 8 mg/L. In the Main Producing Zone, wells in the plume tend to be oxygen depleted (about ½ mg/L or less). There are two exceptions: adjacent wells AC-28D and AC-9D2 exhibit moderate amounts of DO (1 to 3 mg/L). Wells AC-6D and NWD-4D, which are supposed to monitor the periphery (“fringe”) of the plume (see Table I), have essentially no DO. Fluoride has not been detected in either of these wells.

Specific conductance (SC), ranging from 66 to 1749 µs/cm, is a clear marker of plume wells (as one would expect for dissolved ionic species like fluoride, chloride, sulfates, and nitrates). Within the apparent Main Producing Zone plume, SC exceeds 300 µs/cm; at the other wells of this zone, SC is less than 200 µs/cm. The conductance in AC-6D is about twice that of its upgradient, sidegradient, and downgradient wells. (AC-6D appears to be influenced by another upgradient source.)

Theories of constituent fate and transport

The information about Site history, constituent sources, and groundwater conditions implies that most plume constituents typically originated within distinct source areas and moved by flowing with the groundwater (advection) and via dispersion. This section explains how the origin and transport of the combined radionuclides (radium) are substantially different.

All constituents of concern are ionic species characteristic of Site-derived materials. All of them also occur naturally to some degree in rocks and soils, dissolve in groundwater, and move with it. Chemical and physical interactions of these constituents with the porous medium (“matrix” or “substrate”) through which the groundwater moves slow them down to varying degrees and cause them to be spread out (“dispersion”). The speeds with which the constituents move relative to the groundwater flow speed are known as “retardation factors.” These can vary somewhat by location and over time. They are influenced by ambient geochemical conditions, especially the presence or absence of materials that compete with the constituents for the same chemical interactions. Thus, although the groundwater may flow from the source into the Bayou within a decade, most of its dissolved constituents will take a decade or more to make the same trip.

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. The next paragraphs explain what is happening.

“Combined radium” is the total measured activity of two isotopes, radium-226 (^{226}Ra) and radium-228 (^{228}Ra). Their half-lives are 1600 years and 5.8 years, respectively. They are present due to the natural occurrence of uranium-238 (^{238}U) and thorium-232 (^{232}Th) in minerals of the matrix. ^{238}U decays indirectly, via other uranium and thorium isotopes, to

^{226}Ra , and ^{232}Th decays directly to ^{228}Ra . Thorium is highly immobile in the groundwater [Porcelli & Swarzenski 2003]. Uranium can be mobile but its “sorption ... by soils is low at pH values less than 3, increases rapidly with increasing pH from 3 to 5, reaching a maximum in the pH range from 5 to 7 ...” [Vidal *et al.* 2009]. Radium itself tends to be relatively immobile. “The alkaline earth Ra, and to a greater extent the less soluble actinide Th, are readily removed from groundwater by water-rock interactions, and so are strongly depleted” [Porcelli & Swarzenski 2003].

Once the radium is in the groundwater, its mobility depends on many chemical factors, including the total amount of dissolved solids (especially nitrates as noted in [Szabo *et al.* 2005]); the amounts of similar ionic species like calcium, strontium, and barium; the pH; the cation exchange capacity; Redox conditions; iron content; organic matter; and amounts of anions like sulfates (which can cause the radium to (co-)precipitate out of solution). “Adsorption exerts a strong control on Ra in dilute groundwater. Adsorption constants are strongly dependent upon the type of substrate, solution composition (*e.g.*, Eh, pH, and other cations), and temperature” [Porcelli & Swarzenski 2003].

This tendency to adsorb onto the substrate greatly retards the movement of radium (and thorium). Therefore, the excess radium (compared to background concentrations) measured downgradient of the Site must have entered the groundwater from the aquifer substrate itself due to changes in the groundwater chemical conditions. These changes altered the chemical quasi-equilibrium between radium, uranium, and thorium in the groundwater, thereby increasing the radium concentrations in the groundwater. Because most of the excess radium activity is from ^{228}Ra , and this isotope is short lived³, it must result from decay of ^{232}Th in the nearby substrate: it cannot have come from any isotope of uranium, even indirectly.

These origins and mechanisms distinguish radium from the other constituents in important ways:

- The appearance of radium in the groundwater reflects the passage of a plume of altered groundwater conditions through the aquifer substrate, not the direct introduction of radium from the Site itself.
- Changes in groundwater radium activities over time only reflect changes in overall groundwater conditions.
- The movement and the concentrations of radium are likely to be reduced in the future as conditions in the plume return to background, especially as pH rises (becomes more neutral).
- ^{228}Ra decays relatively quickly into a stable element (lead), whereas the other constituents of concern undergo little or no intrinsic decay at all. (The amounts of

³ The half-life of 5.75 years for ^{228}Ra implies the majority of it observed in any groundwater sample was created from ^{232}Th within the last decade (and over 90% within the last two decades).

radium corresponding to the observed activities are so tiny that any lead eventually produced will be in quantities far too small to measure⁴.)

Consequently, the advection-dispersion theory of fate and transport used to justify the statistical calculations, as described later below, applies only indirectly to the combined radium activity. For wells where the combined radium data conform to the statistical assumptions, calculations can be carried out and will produce reasonable results. It is likely that future improvements in groundwater quality, as reflected in reduced concentrations of the other constituents, will also reduce the combined radium activity as a collateral effect.

Retardation factors of constituents, where available in the literature, are tabulated below. The comments implicitly acknowledge that the retardation factor is not a constant, intrinsic property of a substance; in particular, it can depend on the concentration of the substance itself (a “non-linear isotherm”) and on the ambient geochemical conditions. The table therefore reports the retardation factors for sites with conditions closest to this plume. Of course, where site-specific information is available, that is preferred. The ensuing data analysis shows that the mobile constituents in this plume are taking one to two decades to migrate from the source to the bayou, implying their retardation factors lie within the literature ranges.

⁴ Relating radium activity to its chemical concentration provides a useful perspective. One picoCurie (pCi) is defined to be an activity producing 2.22 decays per minute (dpm). The ²²⁸Ra half-life of 5.75 years, or 3.02E⁶ minutes, implies its decay rate per minute is $\ln(2)/3.02E^6 = 2.29E^{-7}$. One gram of ²²⁸Ra constitutes 2.665E²¹ atoms, thereby producing an activity of $2.665E^{21} \times 2.29E^{-7} / 2.22 = 2.73E^{14}$ pCi. Inversely, 1 pCi of activity reflects only $1/2.73E^{14} = 3.37E^{-15}$ gm of Ra.

The largest ²²⁸Ra activity recorded in November 2008 is 10.9 pCi/L [URS 2009 Table 8], equal to 4.00E⁻¹⁴ g/L = 0.00000004 parts per billion (ppb). This concentration is the aqueous portion of a system comprising adsorbed radium and radium in water: the total amount of radium equals the retardation factor (*R*) times the aqueous concentration. Since the value of *R* is uncertain, we carry out order-of-magnitude calculations from now on. Because the half-life of ²²⁸Ra is several years, and because each atom of ²²⁸Ra eventually produces one atom of lead of slightly lower mass, at equilibrium approximately $0.00000001 \times R$ ppb of lead will be created annually. Let us assume all the lead produced somehow remains adsorbed and that recent conditions continue into the indefinite future. To conservatively estimate total lead production, assume the radium retardation factor equals the upper limit of the literature values (around 1E⁴). Even so, several million years would be needed to produce one part per million, a barely detectable quantity.

Analyte	Retardation Factor	Comments	Reference
Fluoride	1.31 – 80	pH 3.9 – 4.1	Bégin <i>et al.</i> 2003
Nitrate	1.35 – 32	Slightly acidic soils at 20 mg/L nitrogen concentration	Mikołajków 2003
Radium	57 – 21,000	In sand (3 observations)	Quoted by Smith & Amonette 2006
Radium	100 – 10,000	Very rough approximation	Porcelli & Swarzenski 2003
Radium	4300 – 38,000	pH 4.3 to 5.2 in silty loam and sandy soils ⁵	USEPA 2004
Thorium	1000 – 1,000,000	Very rough approximation	Porcelli & Swarzenski 2003

The remedy

The remedy, monitored natural attenuation, is characterized by (but not limited to) numerical concentration targets and an associated monitoring program: how many wells are in each aquifer, purposes of monitoring, frequencies of monitoring, and analytical methods and detection limits.

Remedial objectives

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	Basis
Arsenic	0.05 mg/L	Former MCL
Chloride	250 mg/L	FL standard
Fluoride	4 mg/L	2 mg/L for potable supply
Lead	0.015 mg/L	
Nitrates ⁶	10 mg/L	
²²⁶ Ra + ²²⁸ Ra	5 pCi/L	MCL
Sulfate	250 mg/L	FL standard

These standards have not been exceeded by measurements of lead or arsenic in any sample since 1999, nor is there any evidence (in the form of increases over time in any well or high

⁵ “[For] site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential.” [USEPA 2004], emphasis in the original.

⁶ Represented in the database primarily by combined nitrite + nitrate concentrations (as N). Nitrite was “deleted from the site’s analyte list” in 2006 [URS 2009 p. 4-2].

variability) that they are likely ever to be exceeded. Of the remaining analytes, fluoride is likely to drive the remedy: its movement through aquifers is retarded [Bégin *et al.* 2003] and its concentrations are greater multiples of its cleanup target than are the concentrations of the other analytes.

The groundwater monitoring program

Forty wells are monitored. Fourteen are screened in the Surficial Zone and the remaining 26 are screened in the underlying Main Producing Zone.

The wells are situated by design in five kinds of “target zones,” as suggested in EPA guidance for MNA of inorganics [USEPA 2007]. These are the “original source area,” the zones “with highest contaminant concentrations,” “fringe portions within the plume,” “outside the plume,” and background areas—“areas representative of uncontaminated settings” [*ibid.* pp 20-21]. The role of each well is reflected in information about its location (especially with respect to groundwater flow paths) and observed concentrations as described in Table I. Figure 1 shows their locations.

Depending on their monitoring functions, wells have been sampled twice a year, once a year (“periodic” monitoring), or once in each five-year EPA review period. Fluoride and many (but not always all) of the other constituents of concern are measured in each sample. Water level measurements are made in each well at least once a year, regardless of sampling frequency.

Frequency	Zone	Wells	Function
Biannual (became annual in May 2008)	Surficial	AC-7SR, AC-33S, AC-34S	Source area monitoring.
Annual	Main Producing	AC-2D, AC-3D, AC-8D, AC-12D, AC-13D, AC-25D, AC-29D, AC-30D, AC-35D, NWD-4D	Primarily within the current or projected path of the plume.
	Surficial	AC-2S, AC-3S, ACB-31S, ACB-32S	Near the source area.
Quinquennial (every 5 years, approx.)	Both	23 remaining wells	“Fringe” wells and sentinels.

Samples are measured for the seven analytes having performance standards (*q.v.*) (plus some field parameters not evaluated here). The analytical methods and typical laboratory reporting limits achieved (for analytes that have been undetectable in at least one sample) are

Analyte	Target	EPA Method	Reporting Limit
Arsenic	0.05 mg/L	6010 B	0.01 mg/L
Chloride	250 mg/L	325.2	---
Fluoride	4 mg/L	340.2	0.2 mg/L
Lead	0.015 mg/L	6010 B	0.005 mg/L
Nitrates ⁷	10 mg/L	353.2	0.05 mg/L
²²⁶ Ra + ²²⁸ Ra	5 pCi/L	903.1, 904	---
Sulfate	250 mg/L	375.4	5 mg/L

In particular, [Keith 1996] documents that the fluoride analytical methods are precise (less than 4% relative error) and accurate (99% recoveries).

EPA guidance on assessing MNA

This overview describes the EPA conceptual model of attenuation, its implicit assumptions, and its objectives.

The most recent US EPA guidance document is [USEPA 2007]. Other relevant EPA documents include an OSWER directive [USEPA 1999], a monograph on calculating attenuation rates [Newell *et al.* 2002], another monograph on MNA of an organic compound (MTBE) [Wilson *et al.* 2005], and conference training presentations [Wilson 2008a and b]. These documents present and rely on a consistent conceptual model of attenuation, which we dub the “EPA conceptual model.”

In this conceptual model, the first line of evidence for MNA is “...historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points” [Wilson 2008a]. A “clear and meaningful trend” is characterized as a condition where the “first order rate constant for attenuation over time is greater than zero at some predetermined level of confidence” [*ibid.*]. Three aspects of this are notable:

- 1) Attenuation is assumed to be first order, at least approximately.
- 2) “Attenuation over time” appears to mean the “concentration *versus* time attenuation rate” or, equivalently, the “point attenuation rate” of [Newell *et al.* 2002]. Thus, the “first order” attenuation of item (1) implies that exponential decrease of concentrations should be observed in samples obtained at individual monitoring points. This assumption, in the alternative form of a postulated linear decrease of the log concentrations over time, underlies the statistical techniques described in [Wilson 2008a and b].

⁷ Represented in the database primarily by combined nitrite + nitrate concentrations. Nitrite was “deleted from the site’s analyte list” in 2006 [URS 2009 p. 4-2].

- 3) Logarithms of the measured concentrations will depart from this expected linear behavior in ways that should be considered random. Therefore, estimates and decisions based on the data will be uncertain. That uncertainty should be managed by statistical procedures conducted at an appropriate level of confidence.

The first and third of these might not apply in all situations. Therefore, in the “Methods” section below, we describe how to determine where and when these assumptions apply, how, where, and when they might be violated, and what the consequences of that are for evaluating MNA at the Site.

The EPA guidance does not specify how monitoring data should be selected and assessed for quality, nor does it address how to account for variability and uncertainty (except indirectly in the context of a groundwater model). We let scientific and statistical principles guide data selection, as discussed below in the section on statistical procedures.

In addition to “extract[ing] a first order rate constant and [a] confidence interval on the rate constant” [Wilson 2008a], the objectives stated in the EPA documents are summarized in [Wilson 2008b] as

- seeing whether the attenuation observed to date “is on track to meet the ultimate cleanup goal in a predetermined time frame,”
- to “set reasonable expectations for the extent of attenuation that should be attained” at a designated (intermediate) future time, and
- seeing whether “it is possible to evaluate natural attenuation” over a given (future) time interval.

In short, the EPA asks, what is a reasonable range in which the true attenuation lies, has cleanup proceeded quickly enough, how long will it take, and can the monitoring program deliver data useful for future reviews?

Objectives of this evaluation

To address the EPA concerns, this report identifies the monitoring data that conform to the EPA conceptual model, uses standard statistical methods to derive estimates of rate constants and cleanup times, provides confidence intervals for these estimates, and assesses the implications of the remaining data that do not conform to the conceptual model.

Methods

The statistical model of attenuation and its assumptions

This is a technical section whose purpose is to justify and document the statistical procedures used, especially those that improve on procedures appearing in some EPA documents. It adopts a conventional probability model for the random variability. As a reference for understanding the spatial and temporal patterns in the data, it relies on a one-dimensional advection-dispersion model of solute transport in groundwater, with appropriate modifications to understand the actual three-dimensional situation.

Consequences of advection and dispersion

Because we are prepared to treat some variability in the analytical data as random, for a conceptual model of constituent transport it suffices to consider average concentrations during sufficiently long times and over sufficiently large (macroscopic) portions of the media through which the groundwater travels. This allows characterizing the spatial distribution of the constituent as a definite “plume.” (Different constituents may form different plumes.) At any point the plume travels in the direction of, and proportional to the speed of, the groundwater itself, but will be retarded by interactions of the constituent with the geologic media through which it passes. In addition, and approximately independently of this motion, the plume spreads by means of hydrodynamic dispersion and molecular diffusion ([Bear & Verruijt 1987], Chapter 6). Again, actual variations from this approximation of *average* plume motion will be treated as random variations.

In regions sufficiently far from a source (“10s to 100s of meters,” [Anderson 1984]), the behavior of the plume can be learned from that of an idealized one-dimensional situation (as if the water were flowing in a relatively thin, uniform, homogeneous aquifer past a source of large lateral extent, so that lateral dispersion—up and down, left and right—can be ignored). The governing equation is the *advection-dispersion equation*

$$\left[D_t + uD_x - dD_x^2 - \lambda \right] f(x, t) = 0 \quad (1)$$

where $f(x, t)$ is the concentration, x is the signed distance from the source, t is time, D is the partial differentiation operator, u is the (retarded) flow speed of a solute (like fluoride) in the groundwater, d is a (longitudinal) dispersion coefficient, and λ is a decay rate (zero or positive) for any substance undergoing intrinsic first-order decay [Runkel 1996, NAS 2000]. (For constituents of concern unlikely to exhibit any such decay⁸, take $\lambda = 0$.) At

⁸ λ is retained in the advection-dispersion equation because processes such as conversion of fluoride to gaseous F_2 with losses to the atmosphere, or permanent binding to materials in the geologic matrix, could make λ nonzero. The rate for alpha decay of ^{226}Ra , at $\lambda = 0.000433$, is negligible. The rate for beta decay of ^{228}Ra of 0.12 is large. See [Argonne 2005].

time 0, introduce a fixed source of concentration C_0 at the location $x = 0$, then remove it at time t_0 . For times $t \geq t_0$ after the source is removed, the physically meaningful solution to (1) equals⁹

$$f(x, t) = C_0 [C(x, t) - C(x, t - t_0)] \quad (2)$$

where

$$\begin{aligned} C(x, t) &= c_\gamma(x, t) + c_{-\gamma}(x, t), \\ c_\gamma(x, t) &= \frac{e^{\rho(x)(1-\gamma)}}{2} \operatorname{erfc}\left(\frac{x - ut\gamma}{2\sqrt{dt}}\right), \\ \rho(x) &= \frac{ux}{2d}, \quad \gamma = \sqrt{1 - \frac{4d\lambda}{u^2}}, \text{ and} \end{aligned} \quad (3)$$

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-t^2} dt \text{ (the complementary error function).}$$

The time behavior is determined by the second factor of (3), the complementary error function. As is recommended in all the EPA references, it is best to study its logarithm. The log concentration is *not* linear in time, but eventually it is to an excellent approximation. This follows from the asymptotic relationship

$$\operatorname{erfc}(z) \sim \frac{e^{-z^2}}{z\sqrt{\pi}} \quad (4)$$

for large values of z . It implies that for sufficiently large t , $\ln f(x, t)$ is approximately linear with slope equal to $-\lambda - u^2/(4d)$. For a substance that is not intrinsically decaying, the decay rate λ is zero, implying the slope of $\ln f(x, t)$ eventually approximates $-u^2/(4d)$. This value depends only on the speed of the substance in the groundwater (u) and its dispersivity (d), which is primarily a property of the geologic medium. From this many useful insights follow:

⁹ Appendix II of [Newell *et al.* 2002] invokes the “Domenico solution” to a two-dimensional advection-dispersion equation. It is actually an approximation, not a true solution. Subsequent discussion in the literature found it often to be too inaccurate for modeling the effects of lateral dispersion (see [West *et al.* 2007] and [Guyonnet & Neville 2004]): it “typically underpredicts concentrations” and one “cannot ascertain the degree of underprediction without a comparative study...” [West *et al.*, *op. cit.*] Along the plume centerline (its “spine”), the Domenico solution is the same as the one-dimensional equation discussed here.

- (1) Because the aquifer is relatively homogeneous, d should be approximately constant. Therefore, attenuation rates are eventually proportional to the squares of the transport speeds, u^2 (which can depend on the constituent).
- (2) Therefore, within the upgradient and middle portion of the Main Producing Zone, where groundwater gradients are approximately the same, the eventual slope of $\ln f(x, t)$ will not vary from well to well: *all* the wells there should eventually exhibit similar attenuation rates.
- (3) At the wells furthest downgradient, where the groundwater discharges into Bayou Texar, the groundwater speeds may decrease. Evidence for this is provided in [URS 2009] Figure 4, a “Hydrogeological Conceptual” diagram of groundwater flow (in cross section). It depicts the groundwater discharging vertically beneath the Bayou. Vertical permeabilities of geological strata can be one to two orders of magnitude less than horizontal permeabilities, causing the rate of rise in groundwater elevation to be decreased proportionately. (Because the groundwater continues to move laterally as well, its speed is not reduced as much as that. For example, groundwater emerging at a 45 degree angle will still move at 70% or more of its original speed. (See [Bear & Verruijt 1987], Chapter 2.)
- (4) At any fixed location within the aquifer, the history of concentration over time will chronicle the effects of two competing terms in formula (2). The first one, $C(x, t)$, is the effect of the source migrating past. If the source is never removed, this term *always increases* but eventually levels off at a maximum concentration. The second one, $-C(x, t - t_0)$, is the effect of the source removal at time t_0 . It is the delayed reward for the source remedy that was completed in 1997. This term acts inversely to the first: after a lag of approximately time t_0 , it begins to reduce the concentration, slowly at first, but then at an accelerating rate. Eventually it dominates the first term: attenuation wins out. However, before this occurs, there must be a time during which the two terms—historical contamination and subsequent attenuation—are approximately equal. This is exhibited as a long, flat peak in the concentration *versus* time plot. The peaks at far downgradient wells are longer and flatter than the peaks for wells nearer the former source.
- (5) The time of the peak concentration at any point in the aquifer depends on how long it took the substance to reach it. Concentrations will peak first immediately near the source. At the furthest downgradient points, they will not peak until the source removal effect has propagated, moving at the speed of the substance itself.

Figure 2, showing theoretical plots of concentration *versus* time for various solutions to the one-dimensional advection-dispersion equation, illustrates most of these points.

Nature of the variability

The one-dimensional advection-dispersion model is an idealized reference for our analysis. The data will depart from its predictions in some ways that will appear (and be treated as) random, in other ways that will be revealed as systematic (and therefore should be identified and characterized), and in ways that may be a combination of the two.

Causes of non-systematic (random) variation include temporal variation in the system, such as precipitation and tides, microscopic variability in the geologic media, heterogeneity in the magnitude and spatial distribution of the source (before it was treated), and sampling, handling, and analytical variability. At any given well, these will be manifested as relatively small variations in concentration over time, both above and below its predicted trajectory.

Possible systematic departures from the reference include two dimensional and three dimensional effects, large-scale inhomogeneity in the geology, long-term climate change, and long-term land use change. For example, to the next order of approximation the fluoride plume is two-dimensional: it spreads laterally through the Main Producing Zone as it travels downgradient. This has predictable effects. For instance, wells near the fringes of the plume will be affected by dispersion from the higher-concentration areas of the plume. This will slightly delay the onset of peak concentrations in the fringes. Possible systematic changes in the future suggest, as always, caution in the use of long-term predictions, which always rely on assuming things will continue to evolve in the future as they have in the past.

Variation of a mixed nature may include substantial changes in groundwater elevation. Over a long term these can create systematic departures from the conceptual model; over the short term, they might appear to be random effects.

The statistical analysis, therefore, proceeds by first describing the general behavior of the data: how closely do the time series of concentrations at each well conform to scientific expectations? It then evaluates how the data depart from that general behavior, seeking to classify departures into systematic and (apparently) random differences. Any systematic differences call for explanation and perhaps further investigation. The random differences will be managed statistically, resulting in intervals (ranges) of estimates to reflect the consequent uncertainty.

Statistical procedures

Evaluating the data

Only data representing attenuating conditions are valid for calculating attenuation rates. This section provides a scientific and statistical basis for choosing which wells and data are suitable for evaluating MNA.

The advection-dispersion model applies only in the plume-related zones, roughly delineated by those wells with the highest fluoride concentrations and those on the “fringe.” The concentrations within or near the original source area may also exceed the cleanup target, but they might not decrease over time in the straightforward log-linear fashion suggested by this conceptual model. Concentrations beyond the plume will reflect ambient conditions (unrelated to the Site, but not necessarily pristine or in a steady state, either), which can fluctuate unpredictably over time. Therefore, the data evaluation depends on the role each well plays in the monitoring. In particular,

- Concentrations in plume wells will not start decreasing consistently until the peak of the plume passes. For these wells, we need to identify the date of peak concentration. Measurements at earlier dates are not relevant to estimating attenuation rates. In fact, even measurements around the peak are not useful, either (and can be misleading): some time has to elapse—more for the further downgradient wells—before asymptotic attenuation rates are approached.
- Concentrations measured before the source treatment was complete in spring 1997 are relevant only for background and outside-of-plume wells.
- Wells in the original source area are expected to encounter lower concentrations over time, but might not do so according to the predictions of the advection-dispersion model. In particular, concentrations in these wells could be especially subject to the “mixed” forms of variability (*q.v.*) arising from variations in groundwater elevation.

For estimating a point attenuation rate at a well, we first estimate when the plume peak passed by. Except where noted, this estimate coincides with the date the maximum observation occurred. To conservatively *underestimate* cleanup times and *overestimate* the magnitude of random variation, and because relatively few observations would otherwise be available at many wells, the maximum value and all subsequent measurements are used for the estimates. In all cases, data before the source cleanup date in 1997 are excluded.

Outlying, atypical, and non-representative data

Table III lists additional fluoride data excluded from the point attenuation rate analysis. It indicates the reasons used to exclude each value.

Experience tells us that the first samples obtained from a well often differ from all subsequent samples, likely due to the recent disturbance associated with well construction and development. These differences are usually manifest in most or all of the measurements made of those samples: thus, they simultaneously appear as outliers for many parameters. This is apparent in the data at wells AC-35D and AC-36D, where concentrations of most analytes in the initial samples (obtained in November 1999) are atypically low. Although both these wells are near Bayou Texar, they are far from each other and separated by other wells without such problematic results, ruling out any geographically localized phenomenon as a possible explanation.

An unusual pattern of relatively low concentrations appears in some wells for samples obtained in 1999 through 2001. This affects fluoride concentrations (among other analytes) in wells AC-3D, AC-12D, and AC-25D. Apart from the two or three samples taken during this period, all other results closely fit a solution of the advection-dispersion equations, formula (2). Including these anomalously low results would be statistically invalid because the resulting regression lines would not correctly describe the temporal pattern of the data, leading to misleading statistical estimates.

All radium measurements made in January 2004 are suspect [USACE 2005] and are likely biased high. They have been retained in the database and shown in the statistical graphics, but usually are not used in statistical calculations.

Estimating point attenuation rates and their confidence limits

This method of estimating point attenuation rates and confidence limits uses linear regression of log concentrations against time as described in EPA documents.

The statistical model

We have shown, following formula (4), that within wells affected only by the plume, eventually the log concentrations will decrease linearly over time. It is appropriate to use logarithms for statistical analysis, too, for otherwise the amount of the random variation will depend on the concentrations (a form of *heteroscedasticity*). For this reason alone the EPA references consistently recommend using a logarithmic transformation (*e.g.*, [Newell *et al.* 2002] Example 1, [Wilson 2008a] slides 31-35, and [Wilson 2008b] slides 42-45).

The data for any given well and constituent form a sequence of (time, concentration) pairs (X_i, Z_i) , $i = 1, 2, \dots, n$. The underlying linear relationship posited between time and log concentration is

$$Y_i = \ln(Z_i) = \beta_0 - \beta_1 X_i. \quad (5)$$

Two parameters appear in this formula: β_0 is the y-intercept and β_1 is the point attenuation rate. They are assumed to be constant properties of the well and constituent but are not directly observable. The task of statistical analysis is to estimate them from these data. However, formula (5) is incomplete: as we have noted, the data will exhibit random variations around the values predicted by the formula. Let the random variation for pair i be written ε_i , which may be positive or negative, so that

$$Y_i = \beta_0 - \beta_1 X_i + \varepsilon_i. \quad (6)$$

We will refer to the values $\beta_0 - \beta_1 X_i$ as the “true” (log) concentrations, bearing in mind that they cannot be observed directly. The actual observation at time X_i , expressed as a logarithm, differs from the true value at that time by ε_i , a random variation.

The implicit assumptions in the EPA documents are that

- (i) The statistical expectation of each ε_i is zero. This means there is no systematic bias to the variations.
- (ii) The sizes of the potential variations of each ε_i are the same. These are measured by their standard deviation, which we call σ . Its value is unknown but can be estimated from the data.
- (iii) The variations are statistically independent of each other. This will often be the case provided the monitoring frequency is sufficiently low: this gives any random fluctuation appearing at a well enough time to go away before the next sample is obtained.
- (iv) To compute confidence intervals, assume the variations are Normally distributed. This assumption need only hold approximately, but among its important implications are that outliers—the occasional large variations—should be considered surprises worth further analysis.

The conventional abbreviation for this set of assumptions is

$$\varepsilon_i \underset{iid}{\sim} N(0, \sigma^2) : \quad (7)$$

the variations are independently and identically distributed according to the Normal distribution of mean zero and variance σ^2 .

Estimating the parameters

Ordinary Least Squares is the method of choice to estimate the parameters β_0 , β_1 , and σ for the statistical model given by (6) and (7). (σ is a legitimate third parameter and is of more than statistical interest. Like β_0 and β_1 , it characterizes conditions at the well. Small values indicate concentrations in the well are decaying at a consistent rate. The value of σ is unlikely to be any smaller than sampling and analytical variability, though, which for a well-run field program is around 10%, equal to 0.10 on a logarithmic scale.) Formulae for the estimators appear in any book on regression or linear models; we have relied on [Draper & Smith 1981]. These formulas agree exactly with the results produced by Excel's "Regression" add-in used in [Wilson 2008a and b].

In the notation of [Draper & Smith 1981], b_0 estimates β_0 , b_1 estimates the rate constant β_1 , and s^2 estimates σ^2 . The formulas (after adjusting for the minus sign we have placed before β_1 in (6) to agree with the EPA convention of estimating a *decay* rate rather than a slope) are

$$\begin{aligned} b_1 &= -S_{XY} / S_{XX} \\ b_0 &= \bar{Y} + b_1 \bar{X} \\ s^2 &= (S_{YY} - b_1^2 S_{XX}) / (n - 2) \end{aligned} \quad (8)$$

where the following auxiliary statistics are computed¹⁰ from the data:

$$\begin{aligned} \bar{X} &= \sum_{i=1}^n X_i / n \\ \bar{Y} &= \sum_{i=1}^n Y_i / n \\ S_{XX} &= \sum_{i=1}^n (X_i - \bar{X})^2 \\ S_{XY} &= \sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y}) \\ S_{YY} &= \sum_{i=1}^n (Y_i - \bar{Y})^2. \end{aligned} \quad (9)$$

These are unique, well-defined estimates when at least three observations ($n \geq 3$) are made over at least two distinct times (S_{XX} is not zero). All three estimates in (8) are unbiased: their expectations equal the parameters they are intended to estimate.

The attenuation rates can be converted to half-lives via the formula

$$\text{half-life} = \text{Ln}(2) / \text{rate} \approx 0.693 / \text{rate}. \quad (10)$$

Computing confidence intervals

The formulae in (8) include an estimate, s^2 , of the common variance of the variations ε_i . From this flow all assessments of statistical uncertainty. Its square root, s , is directly proportional to the *standard error of the point attenuation rate*,

$$se(b_1) = s / \sqrt{S_{XX}}.$$

The standard error estimates how much b_1 is likely to differ from the true point attenuation rate β_1 .

Because lower attenuation rates imply longer times to clean up, *one-sided lower confidence limits* for β_1 are of interest. After specifying the amount of confidence desired (typically

¹⁰ These computations can be carried out in spreadsheets or calculators using functions for the average (arithmetic mean), and variance. For example, in Excel we can name the range of x-values “X”, the range of y-values (the log concentrations) “Y”, and the data count “N”. A simple set of formulas is $N = \text{COUNT}(X)$, $\bar{X} = \text{AVERAGE}(X)$, $\bar{Y} = \text{AVERAGE}(Y)$, $S_{XX} = N * \text{VARP}(X)$, $S_{YY} = N * \text{VARP}(Y)$, and $S_{XY} = \text{SUMPRODUCT}(X, Y) - N * \bar{X} * \bar{Y}$.

90% to 95% is used in all the EPA documents), compute the corresponding upper percentile¹¹ of the appropriate Student t distribution. The distribution to use has $n - 2$ degrees of freedom. Obtain a lower confidence limit for β_1 by subtracting this multiple of the standard error of b_1 from b_1 itself:

$$LCL(\beta_1) = b_1 - t(n - 2, \text{confidence}) * se(b_1). \quad (11)$$

Determining the critical value $t(n - 2, \text{confidence})$ is complicated by different conventions. With Excel, for example, this value is computed as $TINV(n - 2, 2 * \text{confidence})$: note the factor of two that is needed.

Interpreting the results

The estimate b_1 is the attenuation rate derived from the data. It is a rate of decrease in the natural logarithm of concentrations per unit time. When it is small in size (less than about 0.25), $100b_1$ can be interpreted accurately as *the percentage decrease in concentration per unit time*.

(To see this, write $Z(t)$ for the concentration at time t , $Z(t+1)$ for the concentration one unit of time later, and let $Y(t)$ and $Y(t+1)$ be their logarithms. Then b_1 estimates the change in logarithm $Y(t+1) - Y(t)$. The relative decrease in concentration per unit time is

$$\begin{aligned} \frac{Z(t+1) - Z(t)}{Z(t)} &= \frac{e^{Y(t+1)} - e^{Y(t)}}{e^{Y(t)}} = e^{Y(t+1) - Y(t)} - 1 \\ &= e^{b_1} - 1 = b_1 + \left(\frac{1}{2}b_1^2 + \dots + \frac{1}{k!}b_1^k + \dots \right) \approx b_1. \end{aligned}$$

The error in this Taylor Series approximation is close to $\frac{1}{2}b_1^2$ when b_1 is small, which is

$\frac{1}{2}b_1$ times as great as b_1 itself. Thus, the error made in interpreting $100b_1$ as a

percentage decrease per unit time is relatively small provided $\frac{1}{2}b_1$ is also small. This

analysis also shows that interpreting $100b_1$ as a percent decrease per unit time (conservatively) underestimates the attenuation, because the terms dropped from the Taylor Series are all positive.)

¹¹ By definition, the confidence equals the probability that a variable having the Student t distribution (with $n - 2$ degrees of freedom) is less than or equal to the percentile. In all cases, the percentile for a confidence of 50% is zero and percentiles for confidences greater than 50% are positive. Except for the smallest values of n , the percentiles for typical confidences in the range 80% to 95% will lie between 1.3 and 3. This information is useful for spot checks of spreadsheet calculations, especially when the desired confidence can be specified arbitrarily.

The lower confidence limit $LCL(\beta_1)$, as given by formulae (8) through (11), assesses uncertainty. Assuming the statistical model given in formulae (6) and (7) is correct, the LCL is a value likely to *underestimate* the true attenuation rate (β_1). Due to the random variations in the data, there is a small chance the LCL is greater than the true attenuation rate. This chance equals 100% minus the confidence: thus, it is 10% for 90% confidence and only 5% for 95% confidence.

Estimating cleanup times and their confidence limits

This uses the method of inverse regression [Draper & Smith 1981]. It comports with EPA objectives and the EPA conceptual model of attenuation but is a different method than indicated in EPA documents. (The method of those documents is ad hoc and has no name.)

Estimating the time when cleanup is achieved

We can use the estimated attenuation rate b_1 to assess when a target concentration will be reached: that is, when cleanup has succeeded. This is done by inverting equation (5) and solving for the cleanup date X upon replacing the parameters by their estimates (β_0 by b_0 and β_1 by b_1):

$$Y = \ln(\text{Target}) \simeq b_0 - b_1 X \text{ implies}$$

$$X \simeq \frac{b_0 - \ln(\text{Target})}{b_1}. \quad (12)$$

This method extrapolates the least squares regression line until it reaches the logarithm of the target concentration: see Figure 3 for an illustration.

Some of the EPA references estimate the cleanup time, but details are missing. We can deduce the methods from published examples. For instance, Table I-3 in [Newell *et al.* 2002] (reproduced below as Table II) estimates the time to reach a cleanup goal (“Target”) of 20. Let us call the first sample time X_1 and the most recent sample time X_n . In its leftmost columns Table I-3 displays the concentrations Z_1 (“first sample 1993”), Z_n (“last sample 2000”), and b_1 (“estimated rate ... required”). The next value, “estimated ... time required,” equals

$$\frac{Y_n - \ln(\text{Target})}{b_1} = \frac{\ln(Z_n) - \ln(\text{Target})}{b_1}. \quad (13)$$

Adding this duration to the last sample date X_n extrapolates to another estimated cleanup time:

$$X^* \simeq \frac{Y_n - \ln(\text{Target})}{b_1} + X_n. \quad (14)$$

For example, in the first line of the table (for well MW-5), $Z_n = 420$ (implying $Y_n = \ln(420) = 7.55$) and $b_1 = 0.188/\text{yr}$. Because $\ln(\text{Target}) = \ln(20) = 3.00$, we obtain

$$(Y_n - \ln(\text{Target})) / b_1 = (7.55 - 3.00) / (0.188/\text{yr}) = 16 \text{ years}$$

after X_n (the year 2000), as the table indicates. The estimated cleanup date therefore is sometime in 2016.

Formulae (12) and (14) usually give different answers. The former uses only the parameter estimates while the latter (the EPA estimate) also involves the most recent datum (X_n, Y_n). We can compare the two estimates by subtracting (12) from (14) and invoking the model equations (6):

$$X^* - X = \frac{(\beta_0 - b_0)}{b_1} + \left(1 - \frac{\beta_1}{b_1}\right) X_n + \frac{\varepsilon_n}{b_1}. \quad (15)$$

The difference is the sum of three terms: one is proportional to the difference between the true intercept β_0 and its estimate b_0 ; another is proportional to the most recent time X_n ; the third is proportional to the random error inherent in the most recent log concentration Y_n (and this error is magnified by dividing it by b_1). The first two terms will likely balance each other out and sum almost to zero, but the third term is problematic: although all three terms involve random values, when sufficient data are available the regression line (as determined by the estimates b_0 and b_1) tends to be less variable than ε_n because it is based on all data points. This unnecessarily introduces additional uncertainty into the estimated cleanup date. **Therefore, for this report, we have used the more reliable estimates based on (12).**

Confidence limits for the cleanup time: an incorrect method

Table I-3 of [Newell *et al.* 2002] also illustrates a method that purports to compute upper confidence limits on the times to clean up. This method replaces the estimated attenuation rate b_1 in formula (14) by its lower confidence limit. Thus, it extrapolates from the most recent value by means of a conservatively slow estimate of the attenuation rate. Although this intuitively makes sense, it will not achieve the intended level of confidence. To see why not, rewrite (14) in terms of the model (6), which for the most recent observation asserts $Y_n = \beta_0 - \beta_1 X_n + \varepsilon_n$:

$$\frac{Y_n - \ln(\text{Target})}{b_1} = \frac{[\beta_0 - \ln(\text{Target}) - \beta_1 X_n] + \varepsilon_n}{b_1}. \quad (16)$$

The first term in square brackets on the right hand side is not random: it is a combination of constants (although two of them, the betas, are unknown). The second term in the numerator, ε_n , has a Normal distribution with zero expectation (assumption (7)). This makes the entire numerator Normally distributed. The denominator, b_1 , has a Normal distribution with β_1 for its expectation (see [Draper & Smith 1981] for a demonstration) and is *correlated* with the numerator (because b_1 includes a nonzero multiple of ε_n).

The distribution of a ratio of correlated Normal variables has been characterized but is complicated: see [Cedilnik *et al.* 2004] for detailed formulas and a discussion. It is not a Normal distribution. Therefore, it is incorrect to use percentiles of Student t distributions to compute confidence limits, as in (11) (and implicitly in Table I-3). (It is nevertheless possible that in some cases these percentiles might still give good confidence limits, as we show below for a variant of this approach. The reason, though, is not that the procedure is theoretically good, but that it accidentally happens to approximate a good confidence limit procedure.)

A bigger flaw with this approach is that the standard deviation of the numerator in (16), σ , is relatively large. The standard error of the denominator, b_1 , will decrease as more data are collected, but by assumption σ remains constant. This builds an irreducible amount of uncertainty into the Newell *et al.* confidence limits. That is not how confidence limits should behave: they ought to converge to the quantity being estimated (the date cleanup is attained) as the amount of data increases. This flaw is identical to the error discussed after formula (15), which arises from basing the extrapolation on a single datum (the most recent). According to the model given by (6) and (7), the most recent datum is not any more reliable than any other datum and is less certain than averages of the data. It is true that the more recent data may be more “representative” of future results if one is concerned that the rate of attenuation may be changing over time. That, however, presupposes a different model for the concentrations: one that has not been explicitly specified and therefore cannot be evaluated statistically or scientifically. This point is taken up again and addressed with the prediction limit methods discussed below on page 30, “A better procedure.”

Computing confidence limits for the cleanup time

There is a relatively simple resolution of this problem: compute a “fiducial limit” based on “inverse regression” [Draper & Smith 1981]. The idea is to create confidence envelopes for the fitted line and then find the range of dates where these envelopes enclose the target concentration. This is a natural extension of the approach in [Newell *et al.* 2002], page 9, which “rearranges” the regression equation to express time in terms of concentration, exactly as we did in formula (12).

To begin, note that the intuitive approach can be improved by extrapolating from the *point of averages* instead of extrapolating from the most recent measurement (or from any particular measurement). This point has coordinates $(\bar{X}, \bar{Y})$, signifying an average (log) concentration $\bar{Y}$ attained at the average sampling date $\bar{X}$. The regression line (8)

necessarily passes through this point. Moreover, the abscissa $\bar{Y}$ is Normally distributed, uncorrelated with the estimated point decay rate b_1 , and has a standard error that decreases to zero as the amount of data increases. The time to clean up can be estimated by starting here and extrapolating, yielding an estimated cleanup date of

$$\hat{X}_0 = (\bar{Y} - Y_0) / b_1 + \bar{X} \quad (17)$$

(where, for brevity, $Y_0 = \text{Ln}(\text{Target})$).

The second step is to note that for any time X (past or future) we can compute an upper confidence limit for the fitted (log) concentration at X . The need for a confidence limit arises from uncertainty about both β_0 and β_1 : we are not exactly sure of the true intercept and true slope, so the true line really could lie within a range of possible lines. The fitted log concentration at X can be written

$$\hat{Y}(X) = \bar{Y} - b_1(X - \bar{X})$$

and the standard error of the fitted value equals

$$se(\hat{Y}(X)) = s \left(\frac{1}{n} + \frac{(X - \bar{X})^2}{S_{xx}} \right)^{1/2}.$$

The fitted value is Normally distributed, whence as before (in formula (11)) an upper confidence limit can be constructed the form

$$UCL(X) = \hat{Y}(X) + t(n-2, \text{confidence}) * se(\hat{Y}(X)).$$

As X varies, the UCL traces a hyperbolic arc lying above the fitted line: see Figure 3. To find the “upper fiducial limit,” or “inverse confidence limit for X given Y_0 ” ([Draper & Smith 1981] section 1.7), find the largest solution X of the equation

$$Y_0 = UCL(X), \quad (18)$$

if such a solution exists. This can be solved with the quadratic formula, giving¹²

$$UCL(X) = \bar{X} + \frac{D_0 + g \sqrt{D_0^2 + (1 - g^2) S_{xx} / n}}{1 - g^2}, \text{ where} \quad (19)$$

¹² This formula is equivalent to [Draper & Smith 1981] equation 1.7.6. We write g^2 here in place of the g in [Draper & Smith 1981]. Our version is a little easier to compute with a spreadsheet.

$$D_0 = (\bar{Y} - Y_0) / b_1 \text{ (estimated cleanup duration after } \bar{X} \text{),}$$

$$g^2 = \frac{t^2 s^2}{b_1^2 S_{xx}} \text{ (an auxiliary calculation), and}$$

$$t = t(n - 2, \text{confidence}) \text{ (a Student } t \text{ percentile).}$$

(A lower confidence limit on the cleanup time is obtained by using the negative square root $-g$ in (19).) A solution does not necessarily exist; it makes sense only when b_1 is positive (attenuation occurs) and $g^2 < 1$. The latter is equivalent to $LCL(b_1) > 0$; that is, an upper confidence limit for the cleanup time exists only when there is confidence that attenuation really is occurring. [Draper & Smith 1981] suggest that computing confidence limits on the cleanup time is “not of much practical value” unless $g^2 < 0.2$, although they do not provide any justification for such an omnibus statement.

When g^2 is relatively small, a good approximation is obtained by expanding (19) in a power series in its positive square root g and stopping after the linear term, yielding

$$UCL(X) \approx \bar{X} + D_0 + g\sqrt{D_0^2 + S_{xx}/n} + \dots \quad (20)$$

Note that g^2 is small when, relative to the estimated variance s^2 , the estimated attenuation rate b_1 is large, the variance of sample times S_{xx} is large, and t is small (that is, extremely high confidence is not required). In short, any combination of fast attenuation, long history of monitoring, large amounts of data, relatively small variation around a linear decay curve, and/or modest confidence needs will assure the approximation (20) is a good one. Also note that as the monitoring continues and data are collected over a longer period of time, $UCL(X)$ converges to $\bar{X} + D_0$, the estimated time to clean up, as one would expect of a genuine confidence limit.

When, in addition, there are large amounts of data (large n) or the estimated time to clean up is relatively far into the future ($D_0^2 \gg S_{xx}$), expression (20) is close to the time we would compute by starting at the point of averages and extrapolating forward with formula (17) using an upper confidence limit of the slope (formula (11)):

$$UCL(X) \approx \bar{X} + (\bar{Y} - Y_0) / (b_1 - t(n - 2, \text{confidence}) * se(b_1)) \quad (21)$$

This second, simpler, but approximate approach connects the fiducial limit (19) to a version of the intuitive (but flawed) approach suggested in [Newell *et al.* 2002]. The difference is that this one extrapolates from the point of averages, not from the most recent result. Simulations of a wide range of realistic cleanup situations indicate the approximate UCL of (21) varies between a few days and about 100 days earlier than the exact one of (19); the larger differences occur when cleanup will take a long time.

For this report, **we do all confidence limit calculations using the exact formula (19)**. As a check of the calculations, we have also computed the approximation (21), but do not

report its results. The approximate dates are typically within two months of the correct dates and none differ by more than five months.

Interpreting the results

Inverse regression uses the data to estimate the time X when the target (log) concentration Y will be achieved in the model (5). The *concentration observed* at time X is actually given by formula (6), which adds in the random variation. It is likely that additional monitoring beyond the true cleanup time will be needed, because (a) the estimated cleanup time will be (slightly) uncertain, (b) the observations occurring around that time could, by chance, remain above the cleanup target for a while, and (c) only monitoring can confirm the statistical assumption that future conditions are similar to past conditions. The situation in (b) is illustrated (with simulated data) in Figure 3, where cleanup occurs in early 2004 but the observed concentrations exceed the target until late 2009. Thus, although cleanup might in theory be attained by a certain date, it is likely additional monitoring will be needed past that date in order to confirm the cleanup target has actually been attained.

An upper confidence limit on the cleanup time is a statistical procedure that uses the data to overestimate the time needed. Because the data have a random component, the upper confidence limit itself is random. It is chosen to have a high probability—its confidence—of exceeding the time when cleanup really is attained. When a high level of confidence is specified, such as the 95% chosen here, decisions based on a correctly formulated confidence limit are unlikely to be in error through the action of chance differences between the observations and the true concentrations.

Setting periodic review targets to assess whether attenuation is on track to meet the goals

This uses the linear regression results to compute prediction limits. Again, it comports with the EPA objectives and conceptual model but is superior to the procedure suggested in some EPA documents (a t-test), which logically conflicts with the conceptual model.

Suppose we already have some monitoring data, that monitoring is planned to continue in the near future, and at the end of a specified review period all the data, new and old, will be re-evaluated to assess whether attenuation is progressing satisfactorily. Is the review period going to be sufficiently long to detect further attenuation or not? The US EPA document [Wilson 2008b] proposes to answer this question with a t-test. The examples there compare a sequence of four consecutive monitoring results to a sequence of four consecutive monitoring results obtained during a later period. This constitutes an eight-sample dataset $(X_{j1}, Y_{j1}), (X_{j2}, Y_{j2}), (X_{j3}, Y_{j3}), (X_{j4}, Y_{j4})$ selected from the monitoring history for the purpose of this comparison. The subscript $j = 1$ designates the early samples and $j = 2$ designates the later samples. Again the Y_i are the logarithms of the concentrations.

Analysis of the t-test

A merit of the approach in [Wilson 2008b] is that it reduces the uncertainty associated with one future sample by considering a sequence of four (or some other specified number) of future samples. Unfortunately, *the proposal to use a t-test for this comparison conflicts with the EPA's basic conceptual model*. The probability model for the t-test, to be compared to that of the original model in formulas (6) and (7), is

$$Y_{ji} = \mu_j + \varepsilon_{ji}, \quad \varepsilon_{ji} \underset{iid}{\sim} N(0, \sigma^2).$$

The parameter μ_1 is the mean concentration for the first set of samples, whose concentrations thereby are assumed to vary randomly but *not* to vary systematically over time. The parameter μ_2 is the mean concentration for the second set of samples, which again are assumed not to vary systematically over time. By using two parameters for these mean concentrations, this model accommodates the possibility that μ_1 and μ_2 might differ. This allows for change (that is, attenuation) to occur, but only in the time intervening between the two sets of samples, *not during the times when each set is collected*. When the duration of each set of samples is small compared to the intervening time, this might be a reasonable approximation. However, in the worked examples of [Wilson 2008b] this condition does not hold: each group of four samples is collected over a nine month period and only 24 months intervene between the average sample dates.

The amount of the error can be determined by comparison to the original model. By definition, the t-statistic is the ratio of a difference in average (log) concentrations to the standard error¹³ of that difference,

$$t = \frac{(\bar{Y}_1 - \bar{Y}_2) - (\mu_1 - \mu_2)}{se(\bar{Y}_1 - \bar{Y}_2)}, \text{ writing}$$

$$\bar{Y}_1 = \frac{1}{4} \sum_{i=1}^4 Y_{1i}, \quad \bar{Y}_2 = \frac{1}{4} \sum_{i=1}^4 Y_{2i}, \quad se(\bar{Y}_1) = \sqrt{\frac{1}{3 \cdot 4} \sum_{i=1}^4 (Y_{1i} - \bar{Y}_1)^2},$$

$$se(\bar{Y}_1 - \bar{Y}_2) = \sqrt{\frac{1}{3 \cdot 4} \sum_{i=1}^4 (Y_{2i} - \bar{Y}_2)^2}, \text{ and } se(\bar{Y}_1 - \bar{Y}_2) = \sqrt{se(\bar{Y}_1)^2 + se(\bar{Y}_2)^2}.$$

The t-statistic has a Student t distribution (with $4-1 + 4-1 = 6$ degrees of freedom) under the null hypothesis $\mu_1 = \mu_2$; this depends on the fact that the expected values of $se(\bar{Y}_1)^2$

¹³ This differs from the formula displayed on p. 63 of [Wilson 2008b], which incorrectly uses the standard deviation in the denominator. For groups of four samples, the standard deviation equals twice the standard error.

and $se(\bar{Y}_2)^2$ are both $\sigma^2 / 4$. The original model of attenuation, though, implies the expected value of $se(\bar{Y}_1)^2$ is actually

$$\mathbb{E}\left[se(\bar{Y}_1)^2\right] = \sigma^2 / 4 + \frac{\beta_1^2}{3 \cdot 4} \sum_{i=1}^4 (X_{ji} - \bar{X}_j)^2 \text{ with}$$

$$\bar{X}_j = \frac{1}{4} \sum_{i=1}^4 X_{ji}.$$

The additional term (following $\sigma^2 / 4$) is proportional to the square of the attenuation rate (β_1^2) and to the variance of the monitoring dates when the group of samples is obtained. It reflects the variation in the log concentrations we would expect to see during the monitoring period because attenuation is occurring. The t-test neglects this entirely, resulting in a larger denominator than is appropriate. Consequently, the size of the t statistic will be too small, *making it less sensitive to changes in concentration* than it is intended to be.

A better procedure

Let us review the situation. Given all the monitoring data collected to date, we can estimate the parameters of the original EPA model as given by the formulas in (8). Later, at the end of the review period, we will have collected additional monitoring data. The question to be asked then is *whether or not these additional data are consistent with the previous estimates*. If there is a lot of variability in the data relative to the true amount of attenuation (that is, if σ is large compared to $\beta_1 (\bar{X}_2 - \bar{X}_1)$), it will be difficult to

determine whether any change in the attenuation rate has occurred. Thus, we want to be able to test hypotheses concerning attenuation rates during the intervening time and we want to know whether these tests will have sufficient power to detect changes in rates that would be of interest or concern.

It is difficult to directly test a change in attenuation rate, because the resulting concentrations during the second monitoring period will depend on precisely when the rate changed between the two periods. This problem is avoided by predicting the second-period values based on the first-period rate estimates and then comparing the actual values observed during the second period to the predicted ones. This is called a *prediction interval* test.

Because more than one measurement is made during the future comparison period, there are many kinds of predictions that could be made: we might predict the largest value, the smallest, their average, or something else. In the spirit of the t-test suggestion of [Wilson 2008b], we propose predicting the *average* value during the second monitoring period. Usually only values obtained on a single future date are predicted, but it is straightforward

to extend the theory presented in [Draper & Smith 1981] section 1.4 to averages, as we will now describe.

As before, estimate b_0 , b_1 , and s from all the available monitoring data observed at times $X_1, X_2, \dots, X_n$, using all the notation and formulas of (8) and (9). With them we aim to predict the average of a future set of data planned for times $X_{n+1}, X_{n+2}, \dots, X_{n+k}$. (By the time the test is actually conducted, those future monitoring events will already have occurred, so there is no uncertainty about these future times.) Let

$$\bar{X}_0 = \frac{1}{k} \sum_{i=n+1}^{n+k} X_i$$

be the average future monitoring date. Then the predicted mean value at this average date equals

$$\hat{Y}_0 = b_0 - b_1 \bar{X}_0$$

and its *standard error of prediction* is

$$sep = s \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(\bar{X}_0 - \bar{X})^2}{S_{xx}}} . \quad (22)$$

The predicted value and the standard error of prediction depend on the future sampling dates. The further out they are in the future, the larger the standard error of prediction becomes. This captures the statistical hazards of extrapolation.

For a one-sided test, determine the value of t as before: it is the upper percentile of the Student t distribution, still with $n - 2$ degrees of freedom, corresponding to the percentage given by the desired significance level. The upper prediction limit is

$$upl = \hat{Y}_0 + t^* sep . \quad (23)$$

A lower one-sided prediction limit (for identifying significant *increases* in attenuation rate) is obtained by subtracting $t^* sep$ instead of adding it.

Exponentiating the prediction limits produces prediction limits for the *geometric mean* of the future results.

Interpretation

In conjunction with a planned monitoring schedule (consisting of one or more future times X_{n+1} through X_{n+k}) the calculations (22) and (23) provide a prediction limit for each well where conditions for attenuation have been established. Once those observations have been made, the prediction limits are recalculated if necessary to reflect the actual

monitoring. Then the average of the new log concentrations in each well is compared to its prediction limit.

The null hypothesis is that attenuation continues in the future at the same true rate (not the estimated rate) at which it occurred during the past. If the actual mean result

$$\bar{Y}_0 = \frac{1}{k} \sum_{i=n+1}^{n+k} Y_i$$

exceeds *upl*, this test rejects the null hypothesis. There are many possible explanations for a rejection: the attenuation rate may have changed (that is, β_1 is now different), there may have been a sudden overall change in concentration (that is, β_0 has changed), the variance of the errors has changed (that is, σ^2 has changed), some combinations of these changes may have happened, or even that the entire model is no longer appropriate. Thus, this test can be applied before the attenuation rate settles down near its asymptotic level: especially at wells where the plume has just passed, the two-sided test (comparison to both the upper and lower prediction limits) might detect accelerating attenuation.

We recommend conducting a two-sided test, because if the attenuation rate is changing, even if it is increasing, then older data should be dropped from the rate calculations. If the null hypothesis is rejected, then the time at which the attenuation rate changed needs to be estimated. This could have been any time during the period from X_1 through X_{n+k} . (Because its estimate can be informed by additional data, hydrogeological considerations, and so on, it is not possible to give a general-purpose procedure for doing this.) The attenuation rate can be re-estimated from the remaining data and prediction limits can be computed for the next review period, and so on until cleanup is complete.

Even when the null is not rejected, older data might need to be dropped for future analysis due to a slowly accelerating attenuation rate. This could be assessed formally with a test for a quadratic term in the regression [Draper & Smith 1981] or, more simply, by examining the residuals for serial correlation and conducting a runs test: the acceleration will be apparent as a sequence of positive residuals sandwiched between sequences of negative residuals.

This use of two-sided prediction limits can be viewed as a formal quality control scheme to detect when attenuation is deviating from expected tolerances. When it does, if an intervention is indicated it is taken, but in any case the dataset is updated with the new monitoring results, older data are removed from the calculations, and quality control is restarted. This point of view is discussed (and advocated) in EPA guidance documents for groundwater monitoring statistical procedures ([USEPA 1989] and [USEPA 1992]). However, that EPA guidance describes procedures only for situations where no attenuation is expected.

Other analytes

In principle, every analyte can be evaluated using the methods just described. However, the proportions of nondetects for arsenic and lead are so high that most numerical methods are inapplicable. For the same reason, they are also unnecessary: it is clear these need no cleanup.

With the introduction of additional analytical parameters, more statistical methods become possible. To limit the length and complexity of this report, we have resorted to just one: graphical display of scatterplots, broken down by well and groundwater zone. This display provides qualitative, visual assessment of correlations between the analytes. It would become cumbersome to quantify these correlations because a procedure is needed to deal with the nondetects (which can be plotted at arbitrary locations, such as the corresponding detection limit, but which do not have unique numerical values suitable for computing correlation coefficients). Moreover, even on log-log plots the scatterplots exhibit some curvature: that is, the relationships among the analytes are nonlinear.

Results

This section provides a narrative summary based on graphs—log concentration versus time—and tables of the results.

This narrative focuses on the fluoride data, because this constituent appears to be driving the cleanup and will determine when cleanup is complete. At the end of this section the remaining constituents of concern are reviewed.

Overview and summary of the fluoride data

Figure 4 plots all the log fluoride concentrations against time for each well. The following narrative summarizes the data by well function (as documented in Table I). It reaches two conclusions. First, the data at all wells outside the former source area are consistent with the expectations established by the advection-dispersion conceptual model. Second, a subset of wells can be identified in which the peak fluoride concentrations have passed and attenuation is occurring. These wells are candidates for further statistical analysis to estimate the attenuation rates and cleanup times. They are the ones listed in Table IV for which (a) the date of peak concentration has passed and (b) enough data—at least three observations—are available to perform a regression analysis.

The term “history” will refer to the time series of concentrations of a given analyte measured at a given well.

Upgradient of the source area

Concentrations in ACB-31S, ACB-32S, and PIP-D have never exceeded the reporting limit of 0.2 mg/L. This establishes the reporting limit as a reasonable reference concentration for identifying the plume.

Before the source removal was completed in 1997, concentrations in AC-2D were greater than the target of 4 mg/L but less than 6 mg/L. After the source removal, concentrations have been less than the target and decreasing slowly.

Source area (Surficial Zone)

This is monitored by wells AC-7SR, AC-33S, and AC-34S. They have been sampled twice yearly since 1997. The concentrations are attenuating but not at a uniform rate. Late in 2004, sudden changes occurred at all three wells, increasing the concentrations. This kind of variability can occur when the groundwater system is disturbed; for example, when rising groundwater levels cause local changes in flow directions or cause the groundwater to intercept residual source materials that had been dry. The most recent concentrations in all three wells are nevertheless below the target.

Central portion of the plume (“elevated” concentration area)

This is monitored by wells AC-2S, AC-3D, AC-9D, AC-12D, AC-13D, AC-24D, AC-25D, AC-28D, AC-29D, AC-30D, and AC-35D. After accounting for outlying data as previously described, all histories are consistent with the qualitative description of the one-dimensional advection-dispersion model. In this model, the salient properties of each well are the time when peak concentrations occur, how much the peak concentrations exceed the target, and the asymptotic post-peak attenuation rates. Because the latter two are addressed by the statistical analysis below, the focus here is on estimating and understanding the peak times.

Until a peak has definitely passed, it is usually not possible to tell exactly when it has occurred or will occur: the random variation in the data usually exceeds the slight curvature in the peak, especially for the broader peaks expected in the more downgradient wells, thereby obscuring the peak itself. Therefore only a semi-quantitative estimate of peak times is attempted here. Informing this estimate is the understanding that a peak does not necessarily coincide with the time of highest observed concentrations. There are two reasons for this. One is that time elapses between observations. A planned monitoring event is unlikely to coincide exactly with the peak time. The other is that the observations, because they include random error, differ slightly from the true concentrations. (This is the distinction between formula (5), the true concentration, and formula (6), the observation.) Therefore, for many wells only a reasonable range of possible peak times can be provided.

Table IV summarizes our assessment of apparent peak years in these wells, along with two additional wells (AC-2D and AC-22D) located at edges of the plume where a peak might be identified.

The advection-dispersion model suggests the peak time at a well will be approximately proportional to how long it takes fluoride to travel from the former source to the well. This is directly proportional to the time it takes groundwater to make the same trip. In a homogeneous aquifer with uniform groundwater gradient, that time is in turn proportional to the difference in groundwater elevations between source and well. This suggests that a scatterplot of apparent peak year against a typical groundwater elevation will be roughly linear, at least for wells along the center of the plume.

Away from the center, two additional things happen: groundwater must travel further and more slowly to reach a given elevation and lateral dispersion accounts for more of the fluoride transport. Dispersion effects become greater the further downgradient one goes, too. This implies that wells along the fringes will experience peak concentrations later than predicted by this linear relationship, the peak concentrations will be lesser, and the peaks will be flatter (in plots of concentration against time). The further along the fringe (that is, side-gradient), the later the peak should occur.

Figure 5 shows this scatterplot. With one exception, it conforms closely to the model's predictions. Wells AC-3D, AC-29D, AC-30D, and AC-35D delineate the center of the plume. They lie closely along a line that adds 0.4 years per foot of elevation decrease. The

peaks of the remaining wells are indeed delayed, causing their points on the plot to lie above this line. As expected, the amount of delay typically is greater for the wells farther out in the fringes of the plume. (If this pattern were perfect, then the peak in AC-13D likely has not yet occurred, but will occur around 2010.) The exception is AC-2S, which monitors the Surficial Zone immediately downgradient of the former source area. As such, it may share some of the non-random variability experienced by the other source area wells (as described in the preceding section), which could be obscuring the apparent peak time.

If the patterns suggested by the model and this scatterplot hold for the entire plume—and there is no evidence that they will not—then we may conclude that **peak concentrations have already occurred in most of the area occupied by the plume**, especially in the areas of highest concentration. Peak concentrations likely have not yet occurred in areas that are both far downgradient and along the plume fringes. Depending on the location, the peaks will occur sometime between now and 2017, approximately.

Fringes of the plume

These areas are represented by wells **AC-3S**, AC-26S, **NWD-2S**, **AC-5D**, AC-6D, AC-8D, AC-10D, AC-11D, AC-14D, AC-21D, **AC-22D**, **AC-23D**, AC-26D, **AC-36D**, and NWD-2D. Fluoride has been detected only in the six wells with bold names. It has exceeded the target of 4 mg/L only in NWD-2S. Its maximum concentration was 5.2 mg/L. The model and the data (although few in number) indicate the peak passed about a decade ago and attenuation is occurring. The two results obtained in 2004 and 2008 are less than the target.

The concentrations in AC-22D have increased from less than 1 mg/L to 3.1 mg/L in 2008. The peak probably has not yet passed through this well. When it does, it is possible the fluoride concentrations will then exceed the target of 4 mg/L. This would be consistent with the model, it would not indicate an unexpected development, and it is not in itself cause for taking any additional remedial action.

In the future, as the plume continues to disperse further, it is possible that fluoride will appear in low concentrations in more of the fringe wells.

Background

No fluoride has ever been detected in AC-5S, AC-24S, AC-27S, NWD-4S, AC-27D, or NWD-4D.

Well AC-6S is both the remaining background well and is downgradient of sources at Site 348 (the Kaiser Site, *q.v.*) Fluoride in its samples appears to have peaked at less than 1 mg/L sometime between 1997 and 2008. This well is slightly downgradient and primarily sidegradient of NWD-2S, a Surficial Zone fringe well (also downgradient of Site 348) in which fluoride has exceeded the target. At locations downgradient of NWD-2S, we expect to observe a delayed peak concentration, lower peak concentrations, and (initially) slower attenuation rates. The data at AC-6S, although few in number, confirm this expectation.

Together, the histories at NWD-2S and AC-6S indicate NWD-2S lies near a hypothetical line in the Surficial Zone where peak fluoride concentrations equal the cleanup target. Downgradient of that line (at locations to the southeast like AC-6S), peak concentrations in the Surficial Zone, whenever they occur or have occurred, will not exceed the target.

Statistical results

This section discusses and interprets the results collected in Table V. They are accompanied by assessments of uncertainty in the form of statistical intervals or limits.

Point attenuation rates

Table V calculates attenuation rates for five of the six wells identified in Table IV as candidates for statistical calculation: AC-2D, AC-2S, AC-3D, AC-29D, and AC-30D. (Well AC-35D will be discussed separately.)

Calculations are based on all the post-peak observations that can be identified. The numbers of post-peak observations in each well range from 7 through 11, which is adequate for this calculation due to the small estimated variability (s , which estimates the value of σ in formula (7)).

The maximum concentrations confirm these wells have exhibited among the highest fluoride concentrations in the monitoring program, making them appropriate for a conservative assessment of the duration of cleanup for the entire plume. The maximum concentration in AC-2D is low (below the cleanup target) because this well monitors a relatively upgradient portion of the Main Producing Zone. It is likely affected by dispersion of fluoride upgradient from points where the plume enters this zone from the Surficial Zone.

The estimated rates are given in changes of logarithm per year. Because they are small (less than 0.25), they can be interpreted as average percent change per year in the concentrations themselves. These rates vary with well location:

- At the upgradient well AC-2D, the rate is low (5.4% per year, 13 year half-life: see formula (10)). This is expected of any well affected primarily by dispersion, which includes many of the fringe wells, because concentrations will be low, the peak will be spread out for a long time, and attenuation rates, although positive, will not reach their asymptotic limits for very long times.
- Wells AC-2S, AC-3D, AC-29D, AC-30D, and AC-35D march down the apparent “spine” of the plume starting at the former source and progressing to the edge of Bayou Texar. The theoretical plots in Figure 2 illustrate the expected patterns: peaks will be sharper and occur earlier closer to the source and be flatter and occur later further from the source. Consequently, at any given time conditions in the upgradient wells will be closer to the asymptotic attenuation rates expected eventually to hold everywhere. A pattern of decreasing attenuation rates should be

observable in these wells, and it is, with one exception: with an estimated value of 35.7% per year (half-life 1.9 years), attenuation in AC-30D is much greater than it should be. The data suggest no explanation. However, this well lies within a local anomaly in the groundwater heads observed in 2007 [URS 2008]. Something unusual about groundwater conditions here may be causing this rapid decrease in fluoride concentrations. Extrapolating these data to a future cleanup date should be done with caution, if at all, until this situation is understood.

- Estimates of the size of random errors (s) vary from 8% to 21% (a relative range of $21:8 = 2.63$). These estimates incorporate some amount of random natural variability in the true concentrations, variability in sampling, handling, and analysis¹⁴, and may be further increased by departures from the perfect linear model posited by formula (6). These low values indicate such forms of variability are limited, enabling relatively narrow confidence intervals to be computed from relatively little data (7 to 11 points in these cases). Also, as a rule of thumb, estimated standard deviations that cover less than a 3:1 range are probably not statistically distinguishable, especially not when each one is estimated with only 5 to 9 degrees of freedom. This indicates there is no unusually large amount of variability at any of these wells.
- The 95% lower confidence limits on the attenuation rates are all positive, confirming that attenuation occurs throughout the spine of the plume.
- The best estimates of cleanup dates, which assume these attenuation rates were attained within the last five years (see the “Mean Date” line in the table) and will continue unchanged in the future, range from 1997 to 2041. (The date of 2010 for AC-30D is less reliable than the others due to doubts that the advection-dispersion model appropriately describes the rapid attenuation observed there.) All these dates are conservative in the sense that attenuation rates should increase in the future, especially in the more downgradient wells, which would cause the cleanup targets to be attained sooner than the estimates. Furthermore, by using as many post-peak observations as possible, some observations close to the peak—when attenuation rates were almost zero—have inevitably been included. This tends to lower the estimated rates.

Well AC-35D is the furthest downgradient along the spine of the plume, next to Bayou Texar. The long flat peak there has probably occurred, but this event was so recent that the attenuation rate is just beginning to accelerate. This pattern is consistent with the spatial trends in attenuation rates discussed in wells AC-2D, AC-2S, AC-3D, and AC-29D. The rate estimate based on all the non-outlying data is 3.3% per year, while the rate estimate based on the three most recent results is 14.4% per year (4.8 year half-life), more than four times greater. See Figure 6 for a plot of the data and the two regression lines. The former

¹⁴ Fluoride in water is measured by EPA method 340.2 [URS 2008]. The analytical variability of this method has been estimated in a laboratory study at 3% to 3.6% [Keith 1996].

estimate does not represent future attenuation, but the latter estimate, based on so few data, is uncertain. Due to this uncertainty, a 95% upper confidence limit for the cleanup date cannot be computed, because equation (18) has no solution. The cleanup date estimated from the last three observations is in 2032.

As additional data are collected from AC-35D in the future, more reliable estimates of ongoing attenuation rates and dates to attain cleanup will become possible.

Similar analyses of all these wells show that attenuation rates have been accelerating, as expected, and will continue accelerating in the future. Eventually, all wells should exhibit rates similar to those achieved at the most upgradient wells: such as 21.9%/year in AC-2S and 14.4%/year in AC-3D.

Cleanup dates

Table V provides one-sided upper and lower 95% confidence limits for the cleanup dates for wells where such limits can reasonably be computed. Upper limits conservatively (pessimistically) estimate the last dates at which we can reasonably expect the target concentrations to be attained, assuming attenuation rates remain the same in the future as they have been since the peak of the plume passed by. Lower limits optimistically estimate the first dates at which we can reasonably expect the target concentrations to be attained.

The upper limits for these wells (which track the spine of highest concentrations down the plume) range from 1998 through 2069 (one year through 72 years after the source remedy was completed in 1997). The lower limits range up to 2030. The length of this 39 year interval of uncertainty is due primarily to recent passage of the plume's peak concentrations past most of the wells. This limits the data available to represent the post-peak attenuation. The uncertainty will decrease, at first very quickly, as more monitoring data are obtained.

No confidence limits for the cleanup dates were computed for AC-35D because its value of g^2 , computed using either three or eight monitoring results, is too large for the limits to be useful: recall that [Draper & Smith 1981] suggest g^2 should be less than 0.20.

The furthest upper limit for cleanup, in 2069, is probably too conservative. It is estimated from data in well AC-29D. It is possible the attenuation rate in this well will increase from the current estimate of 6.4%/year, perhaps doubling or tripling to equal the rates observed further upgradient (as indicated by the advection-dispersion model). Such an increase would advance the time of cleanup several decades.

Proposed review targets

The wells in the spine of the plume are monitored annually. Using a sequence of four future results would cover a relatively long period and not be very timely: the average collection date of such a sequence would be 1.5 years before the most recent observation. To counter this effect, we have computed prediction limits instead for the average of the

last two observations made in the next five-year review period. These are planned for November 2012 and November 2013.

These assumptions are the basis of the prediction limit calculations in the last panel of Table V. As with the other statistical intervals, a confidence of 95% is used. Here are some examples to illustrate their interpretation. The upper prediction limit (UPL) of 3.5 mg/L in AC-30D indicates not only that this well will be cleaned by 2013, but also that cleanup is likely to be confirmed by the monitoring results in 2012 and 2013. The lower prediction limit (LPL) of 5.8 mg/L in AC-3D indicates it is likely more time will be needed after 2013 for concentrations to attenuate below 4 mg/L.

The prediction interval for AC-35D does not seem much of an improvement on the recent data, which at 120 and 150 mg/L suggest the UPL of 160 mg/L is an unlikely average value for the concentrations five years into the future. This is because the UPL is based on using the eight most recent values, most of which were obtained just as the peak of the plume appears to have been passing and little attenuation was yet occurring. As previously discussed, it is likely attenuation is accelerating. The planned comparison of the average of the 2012 and 2013 observations to the LPL will test this hypothesis.

Other analytes

This section briefly reviews the data for the other six constituents besides fluoride. Figure 7 displays time series of all data by analyte and well.

Overview

- Different constituents exhibit different behavior because they have different retardation factors, the former source was heterogeneous, and some may have other sources. Nevertheless, the pattern of a detached plume migrating downgradient holds for each analyte.
- The constituents fall into four groups according to the data and the behavior predicted by theory:
 - i. **Fluoride and chloride.** Fluoride is the principal indicator of the plume and drives the remedy. Chloride is highly correlated with it, chemically similar, and in much lower concentrations relative to the cleanup target. Therefore chloride will attenuate with the fluoride.
 - ii. **Nitrate and sulfate.** These appear to move more slowly than fluoride and chloride, so definite peak concentrations in all wells have not yet been observed. Nevertheless, (a) the advection-dispersion theory implies they will attenuate and their point attenuation rates will accelerate; and (b) their present concentrations are so low that cleanup targets have been attained at most wells. Therefore the success of MNA for nitrate and sulfate appears imminent, although it is not yet possible to estimate the cleanup dates.

- iii. Combined radium activities.* These serve as indicators of the overall plume and will decrease as the plume is cleaned up. The attenuation rates and cleanup times can be calculated for key wells in the plume: the results are consistent with those for fluoride and serve to corroborate them.
 - iv. Arsenic and lead.* These have attained their cleanup targets.
- Apart from the combined radium results, target concentrations of the other analytes were exceeded recently only in wells AC-12D, AC-13D, AC-25D, and AC-35D.
 - Attenuation rates and cleanup dates can be estimated for radium at 13 wells. Cleanup is estimated to occur by 2025 in these wells. The confidence in this date is good except at three wells whose results exhibit relatively high variability: AC-3D, AC-12D, and AC-30D.

Chloride

Chloride measurements exceed the target of 250 mg/L in the most recent (2008) data only in wells AC-25D and AC-35D.

Scatterplots of the fluoride and chloride data, broken down by well, shows these two analytes are strongly correlated except in AC-2S. Indeed, the chemical composition of samples from AC-2S differs markedly from that of all other wells: although fluoride in AC-2S has been high (due to its position immediately downgradient of the former source area), concentrations of chloride, sulfate, and radium have been relatively low and highly variable.

The strong correlation of chloride with fluoride is an expected consequence of the chemical similarity of these halogen anions. The chloride cleanup target is substantially greater than the fluoride target relative to typical concentrations. Therefore chloride targets will be reached before the fluoride targets are reached, making it unnecessary to perform separate statistical analyses of the chloride data.

Nitrate

Most measurements in the database are between 1 and 20 mg/L. In 2008, the target of 10 mg/L was exceeded only in wells AC-9D (13 mg/L), AC-12D (12 mg/L), AC-13D (13 mg/L), AC-35D (11 mg/L), and AC-6S (11 mg/L).

The post-1997 time series plots of nitrate suggest it is more retarded in the groundwater than fluoride. The greater retardation:

- Causes the peak concentrations to be reached at later times and
- Spreads the peaks over longer times.

As with fluoride, the most upgradient wells (AC-2D and AC-3D) were the first to exhibit a peak concentration. They show signs of gradual attenuation after peak concentrations were reached around 1997 – 2001 and 2001 – 2003, respectively. The wells further downgradient, such as AC-29D and AC-30D, may have exhibited peaks a little later, *circa* 2005. Those furthest downgradient, such as AC-35D and AC-36D, might have recently exhibited peaks, but the onset of significant attenuation still lies in the future.

The relatively low concentrations compensate for the slower changes: to attenuate the maximum recent concentration of 13 mg/L to 10 mg/L over the next 59 years requires an average decrease of less than 0.5% per year. Because the attenuation rates for fluoride are already an order of magnitude greater than this, and the advection-dispersion theory implies that eventually the attenuation rates for all constituents will accelerate and all eventually be equal (to $u^2/(4d)$ as discussed after equation (4)), we can expect nitrate eventually to attenuate below its cleanup target. It is not yet possible, however, to estimate the time to attain cleanup with adequate precision.

Combined Radium

The January 2004 results were deprecated in the 2005 five-year review [USACE 2005] but nevertheless remain in the database and are shown in the figures for completeness. The January 2004 data were removed before performing the statistical calculations. (Including the January 2004 data, which tended to be biased high, typically increases the estimated attenuation rates, because the high values recorded in 2004 exaggerate the apparent decrease in activity observed during the last five years.)

Thirteen of the wells exhibit sufficient amounts of data for estimates of attenuation to be carried out, including key wells in the “spine” of the plume. Table VI provides the results. The most recent measurements in eight of these wells exceed the cleanup target of 5 pCi/L. Estimated annual attenuation rates range from 3.1% to 25%. The estimated cleanup dates extend to 2025. There are not enough data yet to compute confidence limits for most of the cleanup dates.

Recall that radium is not an independent indicator of plume conditions: the combined activities reflect changes induced by gradual improvements in groundwater quality. The results for these 13 wells thereby serve to corroborate the estimates obtained for the other constituents. In particular, their attenuation rates are similar to the fluoride attenuation rates.

Table VII summarizes data for the rest of the wells (27 of them). Radium is sampled once every five years at most of them not because it needs to be monitored everywhere but only, it seems, to assure at least one measurement of every constituent of concern is obtained at each monitoring well during each five year interval. Because of this low sampling frequency, it is not possible to estimate attenuation rates or cleanup times with reasonable confidence, nor is this infrequent monitoring intended to support such an analysis. None of these 27 wells exhibits any substantial or sudden increase in combined radium activity. 20

of the 27 most recent results are less than the cleanup target. The largest result, 10.39 pCi/L, is approximately twice the target.

Sulfate

Sulfate measurements exceed the target of 250 mg/L in the most recent (2008) data only in wells AC-12D and AC-13D. Because there is no strong evidence yet that peak concentrations have been reached in these two wells, no estimates of attenuation rates or time to clean up can be derived using the methods of this report.

Arsenic and Lead

These analytes have rarely been detected. There is enough evidence to demonstrate that cleanup of both has been achieved.

Conclusions

This evaluation supports, strengthens, and refines the narrative description of groundwater conditions appearing in the 2008 Annual Report [URS 2009].

The statistical methods described here are appropriate, objective, and sound. For correct, accurate results, they should be used in place of statistical methods illustrated in the EPA guidance documents. Their chief limitation, which is shared by the methods they replace, is that they focus on the histories of monitoring at individual wells: they do not consider spatial relationships among the wells.

Fluoride results will determine cleanup progress. In the context of a conceptual model of groundwater flow and chemical fate and transport implicit in EPA documents, these data indicate that attenuation is working. Attenuation will eventually occur everywhere at the Site.

Where sufficient data are now available (which is primarily in wells closest to the former source area and downgradient of it), they indicate the cleanup target concentrations will be reached much earlier than the planned 70 year duration. Cleanup dates cannot yet be projected for the easternmost wells (those furthest downgradient or sidegradient).

Conditions immediately upgradient of Bayou Texar are likely to depart from the advection-dispersion model used here: the groundwater encounters different permeabilities as it begins to flow upwards and it might become more saline. This adds to the difficulty in estimating when cleanup will be attained at wells in these locations. Projections will become possible as monitoring progresses and the full effects of the source remedy reach those wells.

Although cleanup dates cannot yet be predicted for every well, this limitation is not due to lack of data. More frequent monitoring would not help identify when peak concentrations occur in wells: that depends on the progress of attenuation. The existing monitoring frequencies are effective for the objectives of the MNA program. As additional data are collected in the future, and the existence and extent of attenuation can be characterized with more precision, it may become advisable to reduce the monitoring frequencies at many wells.

References

- Argonne, 2005: *Natural Decay Series: Uranium, Radium, and Thorium*. Argonne National Laboratory, EVS, Human Health Fact Sheet August 2005. Available at <http://www.ead.anl.gov/pub/doc/natural-decay-series.pdf> . Accessed 5/12/2009.
- Anderson, M, 1984: Movement of Contaminants in Groundwater: Groundwater Transport—Advection and Dispersion. National Academy Press.
- Bear, J and A. Verruijt, 1987: *Modeling Groundwater Flow and Pollution*. D. Reidel , Dordrecht.
- Bégin, L, J Fortin, and J Caron, 2003: *Evaluation of the Fluoride Retardation Factor in Unsaturated and Undisturbed Soil Columns*. Soil Sci. Soc. Am. J. **67**:1635-1646. Available at <http://soil.scijournals.org/cgi/content/full/67/6/1635> . Accessed 5/7/2009.
- Cedilnik A, K Košmelj, and A Blejec, 2004: *The Distribution of the Ratio of Jointly Normal Variables*. Metodološki zvezki, Vol. 1, No. 1, 2004, 99-108. Available at <http://mrvar.fdv.uni-lj.si/pub/mz/mz1.1/cedilnik.pdf> . Accessed 4/13/2009.
- Draper, NR and H Smith, 1981: *Applied Regression Analysis*, Second Edition. John Wiley & Sons, New York.
- Guyonnet, D and C Neville, 2004: *Dimensionless Analysis of Two Analytical Solutions for 3-D Solute Transport in Groundwater*. J. Contaminant Hydrology **75** pp 141-153.
- Keith, LH, 1996: *Compilation of EPA's Sampling and Analysis Methods*. Second Edition, Revised. CRC Press.
- Mikołajków, J, 2003: Laboratory methods of estimating the retardation factor of migrating mineral nitrogen compounds in shallow groundwater. Geological Quarterly **47** no. 1 pp 91-96.
- National Academy of Sciences, 2000: *Natural Attenuation for Groundwater Remediation*. Washington, DC: National Academy Press.
- Newell CJ, HS Rifai, JT Wilson, JA Connor, JA Aziz, and MP Suarez, 2002: *Calculation and Use of First-Order Rate Constants for MNA Studies*. EPA/540/S-02/500 (Issue paper).
- Porcelli, D and PW Swarzenski, 2003: *The Behavior of U- and Th-series Nuclides in Groundwater*. Reviews in Mineralogy and Geochemistry **52** no. 1 pp 317-361.
- Runkel, RL, 1996: Solution to the Advection-Dispersion Equation: Continuous Load of Finite Duration. J. Env. Eng. **122** No. 9 pp 830-832.

Szabo, Z, VT DePaul, TF Kraemer, and B Parsa, 2005: Occurrence of Radium-224, Radium-226, and Radium-228 in Water of the Unconfined Kirkwood-Cohansey Aquifer System, Southern New Jersey. USGS Scientific Investigations Report 2004-5224, Reston, VA.

URS Corporation, 2008: *Draft 2007 Annual Report*. Agrico Site, Pensacola, Florida. Supplied as text of sections 1-10 together with Figures 4, 5, and 6.

URS Corporation, 2009: *2008 Annual Report*. Agrico Site, Pensacola, Florida, Operable Units One (OU-1) and Two (OU-2) (with all figures and tables). March 31, 2009.

USACE, 2005: Second Five-Year Review Report for Agrico Chemical Company, Operable Units 1 and 2, Pensacola, Escambia County, Florida. U.S. Army Corps of Engineers Mobile District, Alabama.

USEPA, 1989: Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities. Interim Final Guidance. Washington, DC (EPA/530-SW-89-026).

USEPA, 1992: Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities. Draft Addendum to Interim Final Guidance. Washington, DC (EPA/530-R-93-003).

USEPA, 1999: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17P, April 21, 1999.

USEPA, 2004: Understanding the Variation in Partition Coefficient, K_d , Values. Volume III: Review of Geochemistry and Available K_d Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium. Washington, DC (EPA 402-R-04-002C).

USEPA, 2007: *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water*. Volume 1, Technical Basis for Assessment. Washington, DC (EPA/600/R-07/139).

Vidal M, A Rigol. and CJ Gil-García, 2009: Soil-radionuclide interactions. In Quantification of radionuclide transfer in terrestrial and freshwater environments for radiological assessments (Draft). International Atomic Energy Agency. Available at <http://www-ns.iaea.org/downloads/rw/projects/emras/draft-final-reports/trs-364-wg-tecdoc.pdf#page=74> . Accessed 6/26/2009.

West, MR, BH Kueper, and MJ Unger, 2007: *On the Use and Error of Approximation in the Domenico (1987) Solution*. Ground Water **45** No. 2 pp 126-135.

Wilson, JT, 2008a: *Extracting Rate Constants for MNA from long-term monitoring data*. Presentation to the NARPM Annual Training Conference, Portland, Oregon, July 9, 2008.

Wilson, JT, 2008b: *An approach for Five Year Review to see if MNA on track for the clean up goal*. Presentation to the NARPM Annual Training Conference, Portland, Oregon, July 9, 2008.

Wilson, JT, PM Kaiser, and C Adair 2005: *Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites*. EPA/600/R-04/1790.

Tables

Table I Monitoring Well Function

Target zone	Concentration history	Wells (S=surface, D=deep)
Upgradient of the source area (but not necessarily background)	Various, depending on distance from the source, but typically near background (no detectable fluoride).	ACB-31S, ACB-32S; AC-2D⁽¹⁾ , PIP-D
Source area	Possibly high in the past (if in the source area), potentially highly variable ⁽²⁾ .	AC-7SR , AC-33S, AC-34S
Elevated concentrations (along flow paths emanating from the source zone)	After 1995-97, similar to predictions by the one-dimensional advection-dispersion model.	AC-2S⁽³⁾ ; AC-3D , AC-9D , AC-12D , AC-13D , AC-24D , AC-25D , AC-28D , AC-29D , AC-30D , AC-35D
Fringe portions of the plume (may be considered inside or outside the plume)	Concentrations usually less than the target (4 mg/L fluoride), potentially more variable than most, eventually decreasing over time as predicted by the one-dimensional advection-dispersion model.	AC-3S ⁽⁴⁾ , AC-26S, NWD-2S⁽⁵⁾ ; AC-5D, AC-6D, AC-8D, AC-10D, AC-11D, AC-14D, AC-21D, AC-22D, AC-23D, AC-26D, AC-36D, NWD-2D ⁽⁵⁾
Background areas	No detectable fluoride (unless affected by different known sources).	AC-5S, AC-6S ⁽⁵⁾ , AC-24S, AC-27S, NWD-4S; AC-27D, NWD-4D
Totals		14 shallow; 26 deep.

Remarks

The maximum fluoride concentration observed in **bold wells** exceeds the cleanup target of 4 mg/L.

(1) AC-2D appears downgradient on the map, but is actually upgradient when the 3D flow pattern is considered.

- (2) If concentrations are high, typically the peak concentration occurred shortly after the source cutoff (1995-1997). If concentrations are low, usually they are relatively variable.
- (3) AC-2S has a peak in 2002, not 1997. [URS 2009] notes it as an “elevated concentration area well.”
- (4) AC-3S is beyond (east) of the connection between the shallow and deep zones and therefore intercepts, at most, a downgradient fringe of the plume within the shallow zone that is not expected to move laterally.
- (5) Wells AC-6S, NWD-2S, and NWD-2D appear to lie hydraulically downgradient of Site 348: see Figure 1. Concerning these locations, [URS 2009] remarks that “effects by site 348 (Kaiser) [are] possible.” Fluoride concentrations less than 1 mg/L are detected in AC-6S.

Table II Reproduction of Table I-3 in [Wilson *et al.* 2005]

	Concentrations		Estimates		90% Confidence Limits		95% Confidence Limits	
	First result ⁽¹⁾ 1993	Last result ⁽²⁾ 2002	Rate ⁽³⁾ (/yr)	Time ^{(4), (5)} (yr)	Rate (/yr)	Time ⁽⁵⁾ (yr)	Rate (/yr)	Time ⁽⁵⁾ (yr)
MW-5	1900	420	0.188	16	0.127	24	0.109	28
MW-11	2200	146	0.453	4.4	0.365	5.4	0.337	5.9
MW-6	270	51.2	0.29	3.2	0.246	3.8	0.231	3.8

Remarks

- (1) Z_1 .
- (2) Z_n .
- (3) b_1 .
- (4) Agrees with formula (13).
- (5) Based on an incorrect method: see *Estimating cleanup times and their confidence limits*, p. 23.

Table III Unused Fluoride Data

Well	Comment	Date	Raw value
AC-3D	Outlier; suspect	11/1/99	14
	Outlier; suspect	11/1/00	18
	Outlier; suspect	11/1/01	13
AC-3S	Outlier	9/1/97	1.4
AC-5D	Outlier	9/1/97	3.6
	Pre-peak; outlier; suspect	11/1/99	0.52
	Pre-peak; outlier; suspect	11/1/01	1.7
AC-24D	Outlier; pre-peak?	9/1/97	8.5
AC-25D	Pre-peak; outlier; suspect	11/1/99	2.6
	Pre-peak; outlier; suspect	11/1/00	3.3
	Pre-peak; outlier; suspect	11/1/01	2.9
AC-30D	Pre-peak; outlier?	9/1/97	15
	Pre-peak; outlier?	11/1/99	18
	Pre-peak; outlier?	11/1/00	11
	Pre-peak; outlier?	11/1/01	11

Remarks

Only the month of each observation is available; these are rounded down to the first of the month in the database.

There is no evidence that the outliers are bad data. They could reflect temporary changes in groundwater conditions brought about, say, by local fluctuations in groundwater elevations.

Table IV Dates of Apparent Peak Fluoride Concentrations

Well	Apparent peak year	Range	Comments
AC-2S	2002	1998-2004	1999-2001 data may be unrepresentative
AC-3D	1997	1997-2003	1999-2001 data may be unrepresentative
AC-9D	----	by 2008	Sampling too infrequent to estimate a peak
AC-12D	2008	after 2007	
AC-13D	2008	after 2007	
AC-24D	2006+	after 2004	Sampling is infrequent
AC-25D	2008	after 2007	
AC-28D	2007+	after 2006	Sampling is infrequent
AC-29D	2000	1997-2000	
AC-30D	2002	before 2003	1999-2001 data may be unrepresentative
AC-35D	2005	before 2007	Peak is very flat; 1999 value is unrepresentative
AC-2D	1997	1997-2000	
AC-22D	2007+	after 2007	Sampling is infrequent

Remarks

As the ranges of estimates indicate, these estimates of peak years are rough. They are nevertheless consistent with each other and with the advection-dispersion model, as illustrated in the scatterplot of Figure 5.

Enough post-peak observations are available at wells shown in bold to attempt a statistical analysis of their attenuation rates.

Because wells with “infrequent” sampling are along the fringes of the plume, they do not require annual sampling. Although this staid pace delays the time when statistical analysis can be performed on the data, the concentrations in these wells are presently so low, and changing so slowly, that no such analysis is warranted.

Table V Estimated Fluoride Attenuation Rate and Prediction Limit Calculations

	AC-2D ⁽¹⁾	AC-2S	AC-3D	AC-29D	AC-30D	AC-35D ⁽²⁾
Count ⁽³⁾ (<i>n</i>)	10	8	7	11	7	3-8
Max. value ⁽⁴⁾ , mg/L	3.5	210	46	65	61	160-170
Recent ⁽⁴⁾ , mg/L	2.0	54	18	31	8.0	120
<i>b</i>₁ (rate), /year⁽⁵⁾	0.054	0.219	0.144	0.064	0.357	0.144-0.033
half-life, years	13	3.2	4.8	11	1.9	4.8-21
<i>b</i> ₀ (intercept), log	0.964	4.735	3.483	3.745	3.394	
<i>s</i>	8%	20%	12%	17%	21%	6%-8%
LCL(rate) ⁽⁶⁾ , /year	0.038	0.160	0.098	0.037	0.276	
UCL(rate) ⁽⁶⁾ , /year	0.070	0.279	0.191	0.092	0.439	
Cleanup year	1997	2020	2019	2041	2010	2032

Inverse Regression Calculations ⁽⁸⁾						
	AC-2D	AC-2S	AC-3D	AC-29D	AC-30D	AC-35D ⁽⁹⁾
Mean date ($\bar{X}$) ⁽¹⁰⁾	5/23/2004	5/24/2005	11/24/2005	10/14/2003	11/24/2005	
<i>D</i> ₀ , years	-7.330	14.757	13.533	37.807	4.596	
<i>t</i> (<i>n</i> -2, 95%) ⁽⁷⁾	1.860	1.943	2.015	1.833	2.015	
<i>g</i> ²	0.084	0.073	0.104	0.182	0.052	4.02/0.578
UCL(cleanup)⁽⁶⁾	1998	2025	2025	2069	2011	
LCL(cleanup)⁽⁶⁾	1993	2016	2016	2030	2009	

Prediction Limit Calculations (for the average of planned 2012 and 2013 results)						
	AC-2D	AC-2S	AC-3D	AC-29D	AC-30D	AC-35D ⁽¹¹⁾
$\hat{Y}_0$	0.505	2.872	2.259	3.199	0.357	4.774
<i>sep</i>	0.0959	0.289	0.198	0.192	0.348	0.123
<i>t</i> (<i>n</i> -2, 97.5%) ⁽¹²⁾	2.262	2.447	2.571	2.262	2.571	2.447
UPL (mg/L)	2.1	35.8	15.9	37.8	3.5	160
LPL (mg/L)	1.3	8.7	5.8	15.9	0.58	87.6

Remarks

- (1) Ordered from upgradient to downgradient. AC-2D is upgradient of the plume in the main producing zone. AC-2S is immediately downgradient of the source in the Surficial Zone. Groundwater subsequently flows into the main producing zone and passes through AC-3D, AC-29D, and AC-30D in that order.
- (2) A summary of two calculations is provided, based on the last three observations or all eight non-outlying observations. The latter clearly underestimate future attenuation rates, but the former do not provide enough certainty to compute a 95% upper confidence limit on the cleanup date.

- (3) Number of post-peak data used. All values were quantified (that is, not non-detects).
- (4) The maximum and most recent values are shown for reference; they are not part of the calculations.
- (5) Calculations were carried out in double-precision arithmetic (about 15 significant figures). Results are rounded for presentation.
- (6) Confidence limits are one-sided limits at 95% confidence. Equivalently, the interval from LCL(rate) to UCL(rate) is a symmetric 90% two-sided confidence interval for the attenuation rate and the interval from LCL(cleanup) to UCL(cleanup) is a symmetric 90% two-sided confidence interval for the date when the target concentration is reached.
- (7) 95% percentile of the Student t distribution with $n - 2$ degrees of freedom, rounded to three decimal places. (More decimal places were used in the calculations.)
- (8) See the formulas at (19).
- (9) Estimates are too uncertain to carry out inverse regression.
- (10) To keep the results unbiased, 15 days have been added to all sample dates to account for the method of recording dates as the first of their month.
- (11) Based on eight observations.
- (12) For a 95% two-sided test, the limits are computed using the 97.5 percentile of the Student t distribution.

Table VI Estimated Radium Attenuation Rates and Prediction Limit Calculations

Well	2008 Result (pCi/L) ⁽¹⁾	Attenuation rate (/year)	Estimated cleanup date	95% UCL	<i>s</i>	<i>n</i> ⁽²⁾	LPL ⁽³⁾	UPL ⁽³⁾
AC-2D	2.164	0.076	Done	Done	9%	8	1.1	1.9
AC-3D⁽⁵⁾	12.12	0.09	2017	---	26%	5	1.2	44.6
AC-8D	1.736	0.087	Done	Done	9%	9	1.0	1.6
AC-12D⁽⁴⁾	8.48	0.031	2025	---	6%	6	5.7	9.5
AC-13D⁽⁵⁾	7.27	0.077	2014	---	10%	5	2.8	11.0
AC-25D⁽⁵⁾	6.18	0.11	2010	---	15%	5	1.2	11.0
AC-29D⁽⁵⁾	12.34	0.14	2014	---	17%	5	1.9	20.1
AC-30D^{(4), (5)}	8.49	0.086	2015	2023	16%	8	3.5	9.8
AC-35D⁽⁵⁾	7.07	0.18	2010	---	25%	5	0.5	17.5
AC-36D ⁽⁵⁾	3.82	0.037	Done	Done	20%	8	1.4	5.3
NWD-4D	5.76	0.25	2008	---	24%	5	0.29	8.3
AC-2S	<0.044	0.39	Done	Done	109%	10	0.00	0.17
AC-3S ⁽⁵⁾	0.43	0.10	Done	Done	39%	9	0.12	1.03

Remarks

- (1) The cleanup target is 5 pCi/L (picoCuries per liter). Rows for wells whose 2008 results exceed this are shown in **bold**.
- (2) All data from 1/2004 have been excluded.
- (3) Two-sided 95% prediction limits. (Each limit, taken on its own, is a one-sided 97.5% limit.)
- (4) An unusually high value observed in January 2004 influences the statistics. Removing it would reduce the attenuation rate but also reduce *s* (the variability of the random component). As a result, the estimated cleanup date would move further into the future, but its upper confidence limit would move forward (to 2096 for AC-12D, 2023 for AC-30D).
- (5) g^2 exceeds 0.2, indicating the 95% UCL for the cleanup date may be unreliable.

Table VII Summary of Remaining Radium Histories

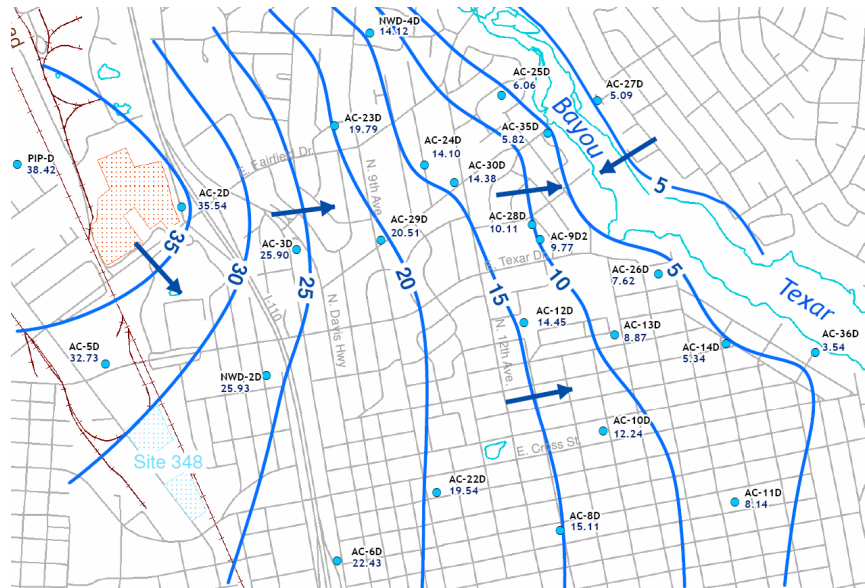
Well	2008 Result (pCi/L) ⁽¹⁾	Post- remediation results ⁽²⁾	Frequency ⁽³⁾	Comments
AC-5D	2.22	2	5 years	
AC-6D	7.24	3	1 year	
AC-9D	9.42	2	5 years	AC-9D2, AC-9D3, and AC-9D4
AC-10D	3.33	2	5 years	
AC-11D	2.76	2	5 years	
AC-14D	3.86	2	5 years	
AC-21D	4.11	2	5 years	
AC-22D	3.99	2	5 years	
AC-23D	6.47	2	5 years	
AC-24D	10.39	2	5 years	
AC-26D	<0.18	2	5 years	
AC-27D	3.55	2	5 years	
AC-28D	8.50	2	5 years	
NWD-2D	2.61	2	5 years	
PIP-D	3.73	4	1 year	Monitoring began 2005
AC-5S	1.71	2	5 years	
AC-6S	6.31	2	5 years	
AC-7SR	1.43	2	1 year	Monitoring began 2003
AC-24S	1.75	2	5 years	
AC-26S	2.04	2	5 years	
AC-27S	0.32	2	5 years	
ACB-31S	7.27	2	1 year	Monitoring began 2003
ACB-32S	1.20	2	1 year	Monitoring began 2003
AC-33S	2.59	2	1 year	Monitoring began 2003
AC-34S	2.20	2	1 year	Monitoring began 2003
NWD-2S	1.89	2	5 years	
NWD-4S	2.03	2	5 years	

Remarks

- (1) The target is 5 pCi/L. Results exceeding this are in **bold**.
- (2) “Post-remediation” includes the 1997 values, but (because of data quality problems discussed in the text) does not include the January 2004 values.
- (3) Some monitoring frequencies were changed from 5 years to 1 year in November 2007, as indicated. The quinquennial measurements were made in the nominal years 1997, 2003 (actually in January 2004) and 2008.

Figure 1 Well Locations¹⁵, Groundwater Elevations, and Flow Directions

This is Figure 6 in [URS 2009].



This is Figure 5 in [URS 2009].

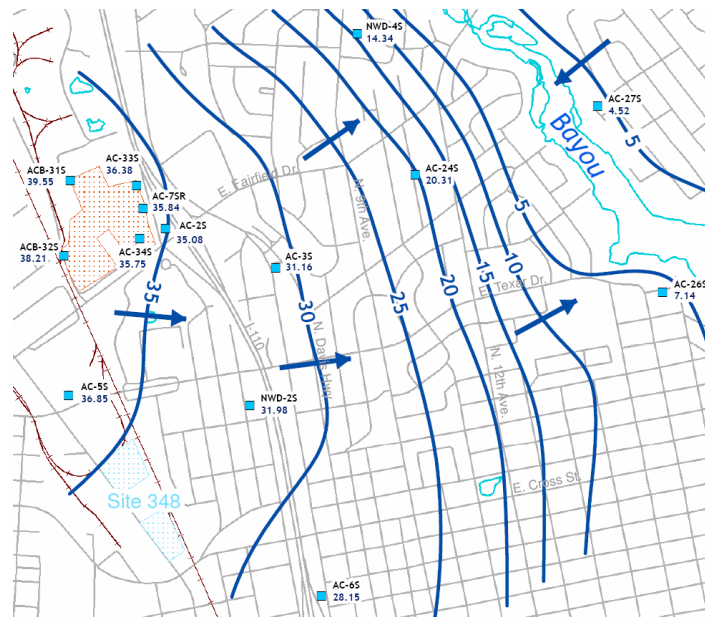
Monitoring well

Former source area

Groundwater flow direction

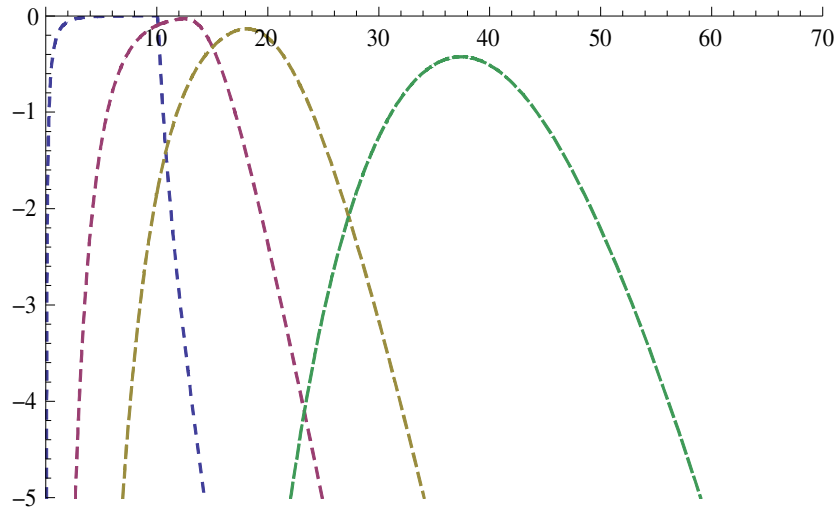
Groundwater elevation (feet NGVD)

Elevation contour (five foot interval)



¹⁵ AC-21D does not appear in these maps. Other maps in the annual reports place it halfway between AC-5D and NWD-2D.

Figure 2 Time versus Concentration Plots for One-Dimensional Advection and Dispersion



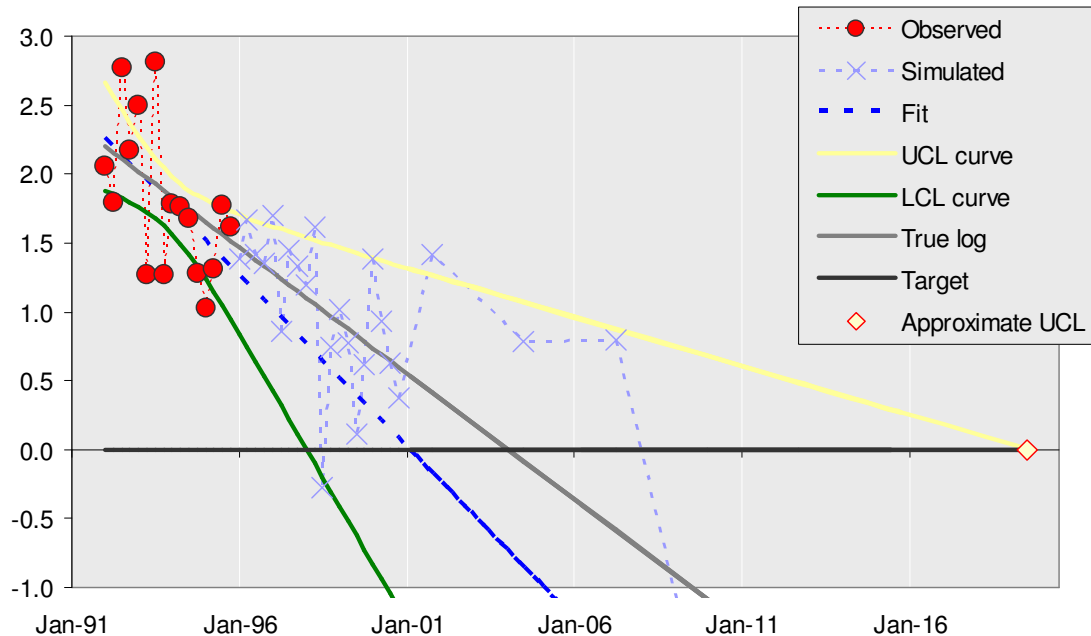
Horizontal coordinates are time in years (t) and vertical coordinates are logarithms of the decrease in concentration compared to the maximum (that is, $\text{Ln}(C/C_0)$). A logarithm of -5, for example, represents $e^{-5} = 0.7\%$ of the maximum concentration: over two orders of magnitude reduction.

The four solutions shown here are for wells 0.1, 1, 2, and 5 kilometers downgradient of a source that was removed after ten years ($t_0 = 10$). This hypothetical substance moves at 0.15 km/year with a dispersion coefficient $d = 10,000 \text{ m}^2/\text{year}$. These values do not necessarily reflect conditions at the Site: they were chosen only to afford an illustration that works on approximately the same time scale.

Eventually, at large times all four curves will closely approximate lines of a common slope of $-(150 \text{ m/year})^2 / (4 \times 10,000 \text{ m}^2/\text{year}) = -0.56/\text{yr}$. It is clear, though, that this slope is not approached until some years after the peak concentration occurs. For example, in the green (rightmost) plot for the well five kilometers downgradient, the log concentration decreases from -0.5 at 40 years to -2.0 at 50 years, an average of -0.15/yr. This is one-half the rate of decrease over the next decade (50 years to 60 years on the horizontal axis) and only about one-quarter the eventual rate of decrease.

Sources present longer than ten years produce similar solutions, but their peaks are flattened (stretched horizontally) for proportionally longer periods.

Figure 3 Inverse Regression and Fiducial Confidence Limits



The estimated cleanup date is the date where the fitted line crosses the line $Y = \ln(\text{Target}) = 0$; in this example, it occurs in January 2001.

The “UCL curve” is the locus of 95% upper confidence limits and the “LCL curve” is the locus of 95% lower confidence limits for the fitted line. All the confidence limits are based on 16 observations obtained quarterly from 1992 through 1995.

For reference, the true model (“true log”) is also shown: simulated future data will tend to follow the true model rather than the fitted line, especially further into the future. The approximate 95% UCL and the 95% upper confidence limit for the time to reach the cleanup target of 1 (logarithm is 0) almost coincide where the UCL curve intersects the horizontal target line, July-August 2019. In this example, the prediction was that cleanup would be complete around January 2001, considerably ahead of the upper confidence limit (due to the relatively large variation in the observations). In the simulated data, the target concentration was actually reached around January 2004 as shown by the “true log” line. The first observation of a concentration below the target occurred in July 1998 but the next observation below the target did not occur until December 2009, eleven years later—and almost six years after the target was actually reached. This delay was due in part to the expanded temporal spacing of the data after 2002.

Figure 4 Fluoride Time Series

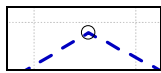
Explanations

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

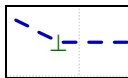
To enhance comparability, all plots show a common range of concentrations (on a logarithmic scale) and a common range of sample dates.

Data for wells AC-9D2, AC-9D3, and AC-9D4 have been combined into a single plot for monitoring point “AC-9D.”

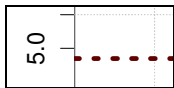
Legend



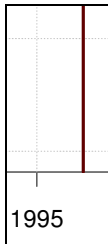
Quantified result



Nondetect (plotted at the reporting limit, always 0.2 mg/L)

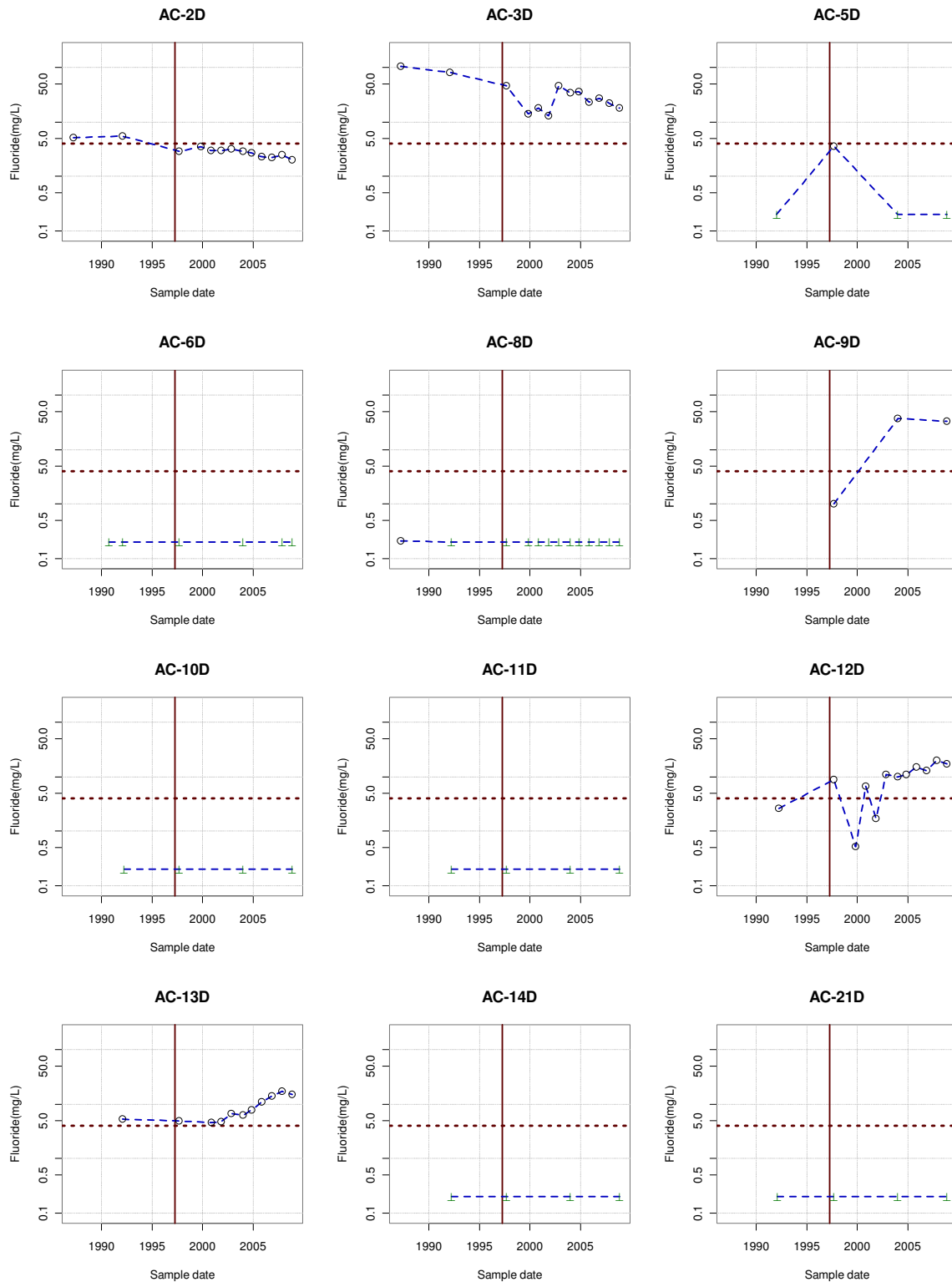


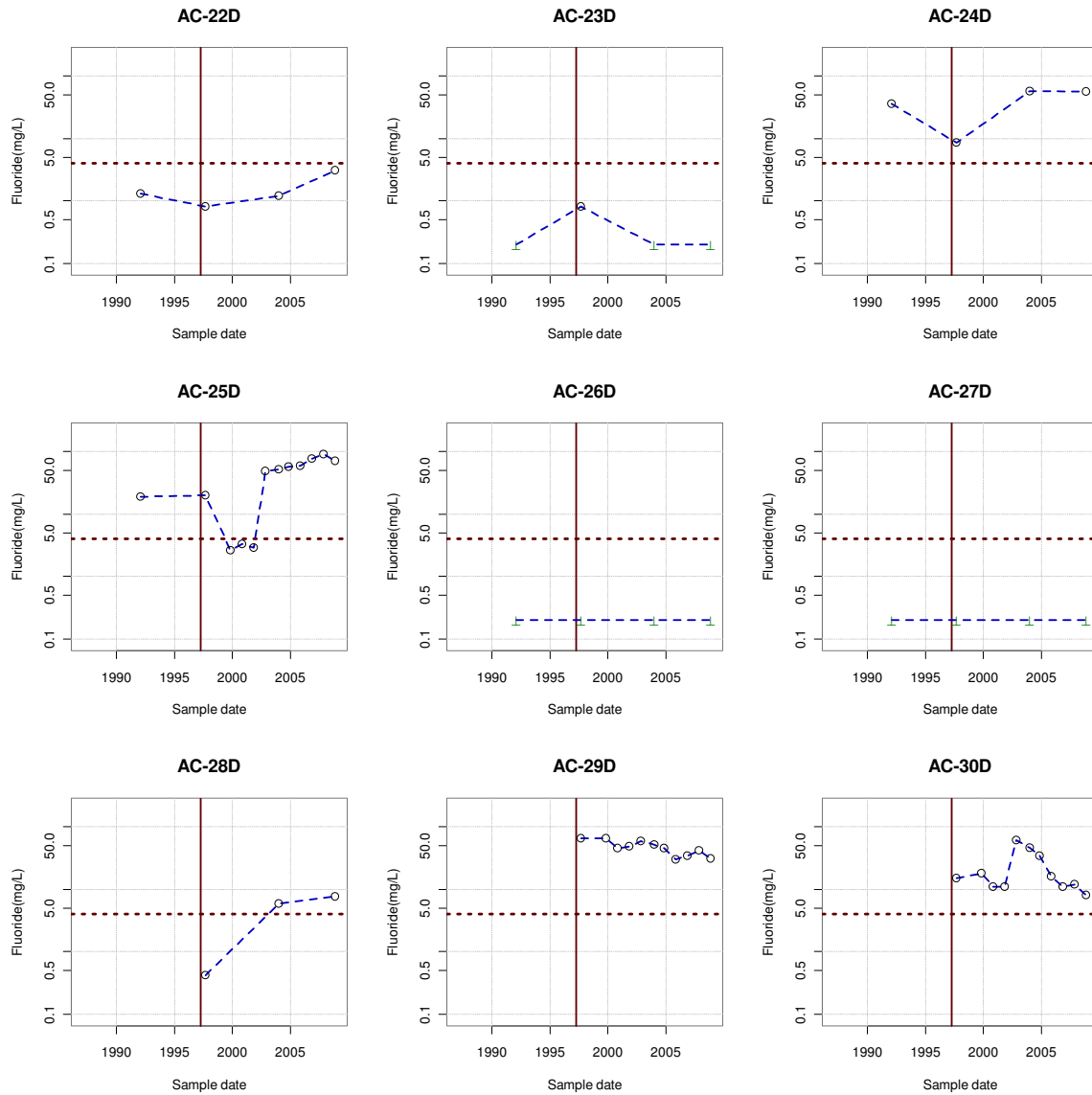
Target concentration (4.0 mg/L for Fluoride)

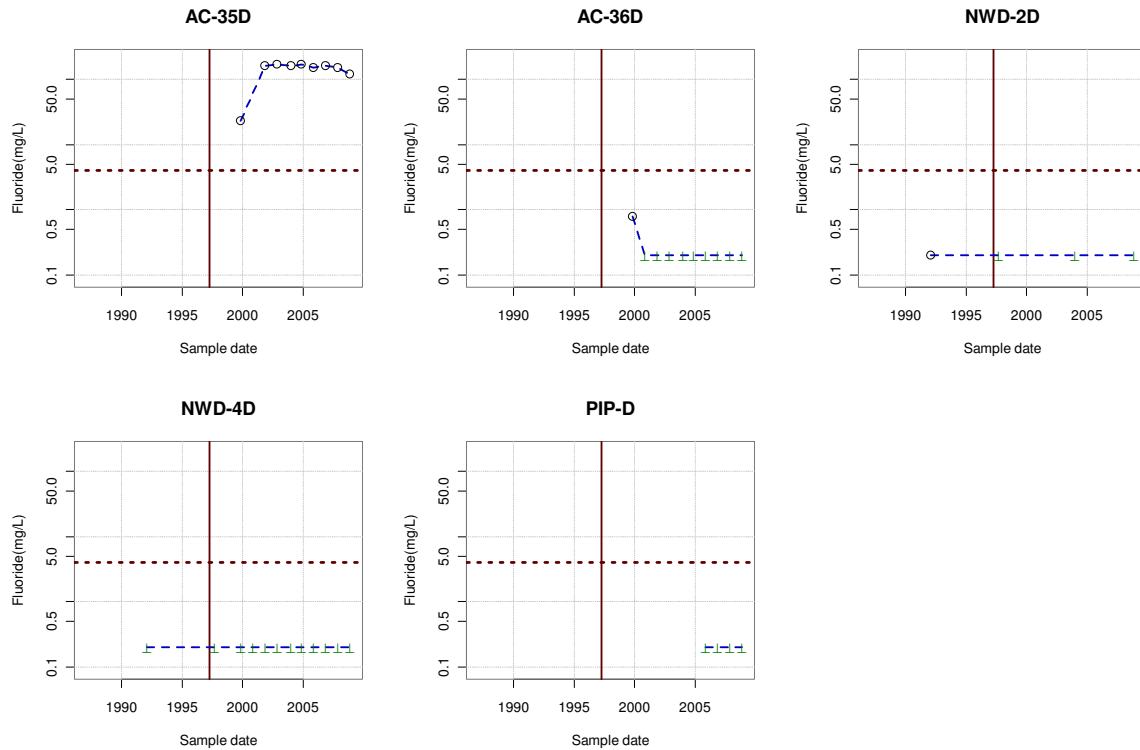


Date source remediation was completed (April 1997)

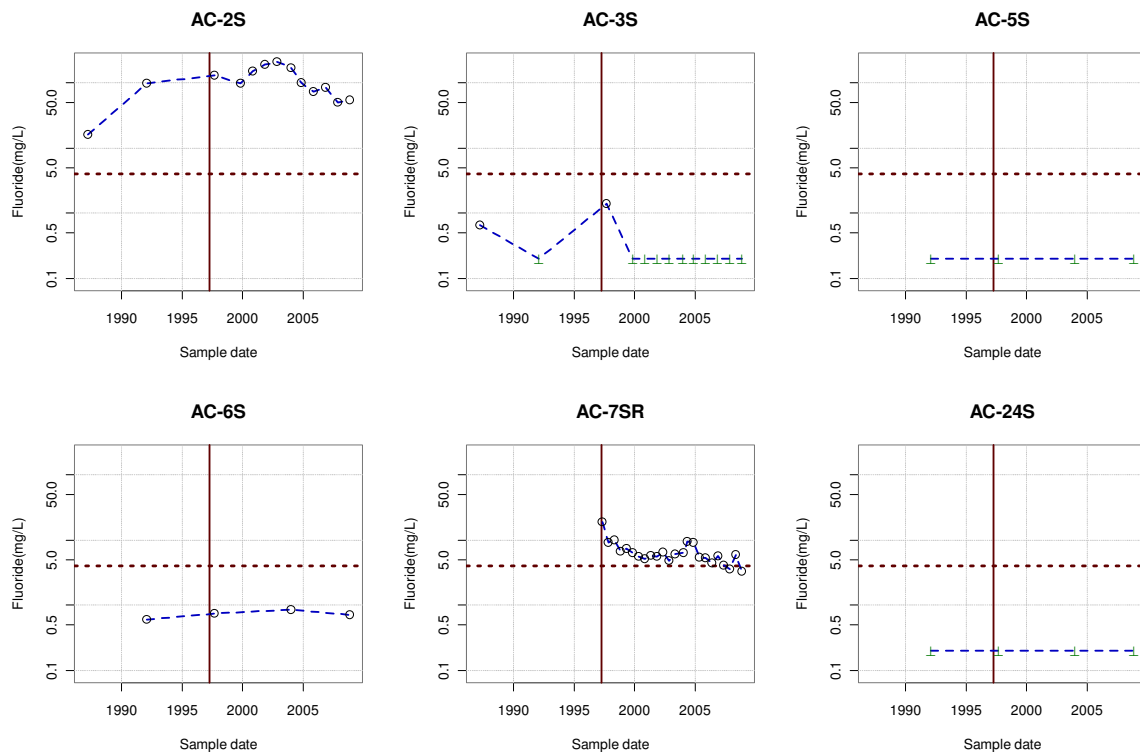
Main Producing Zone







Surficial Zone



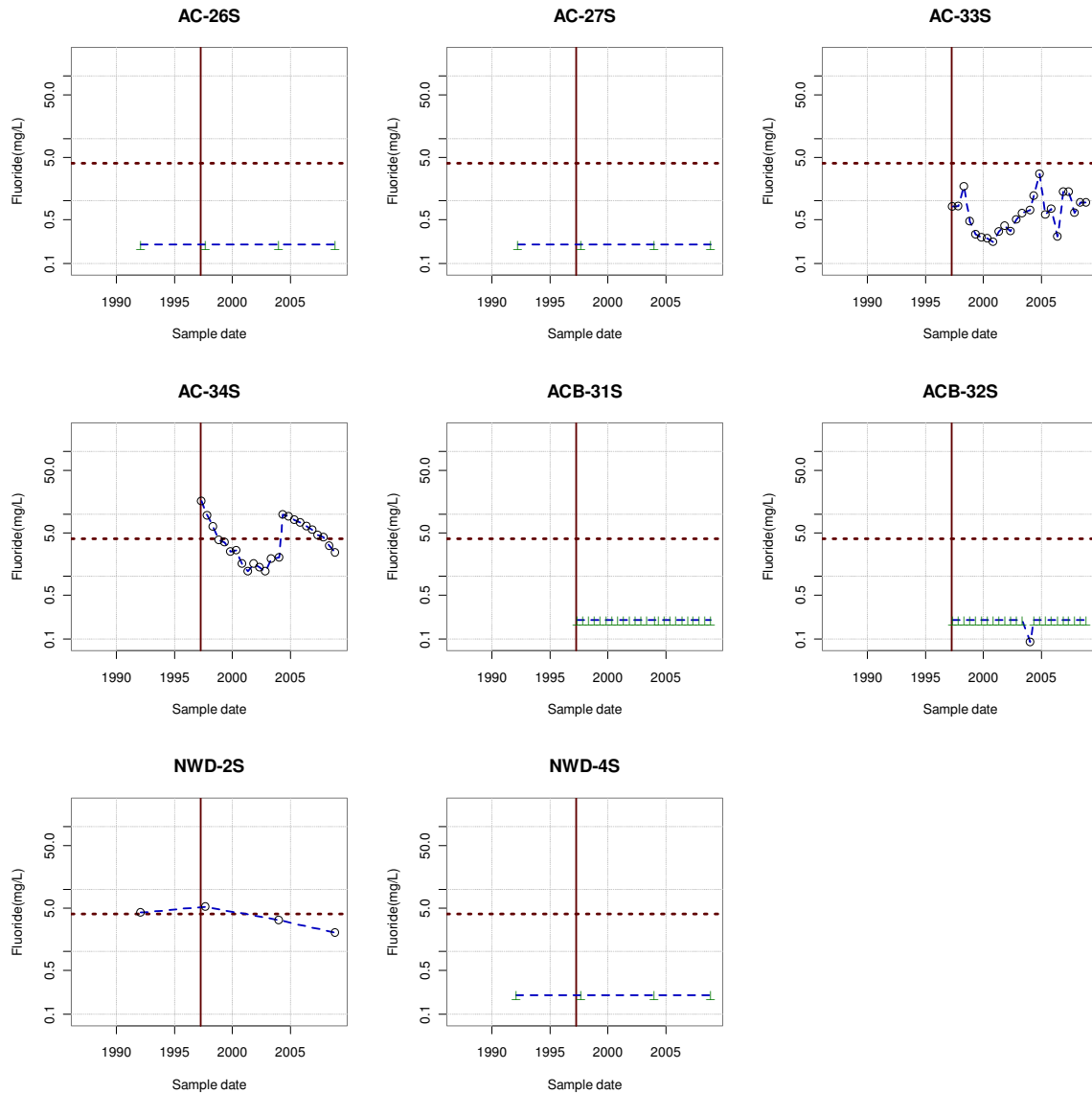


Figure 5 Apparent Date of Peak Fluoride Concentration *versus* Groundwater Elevation

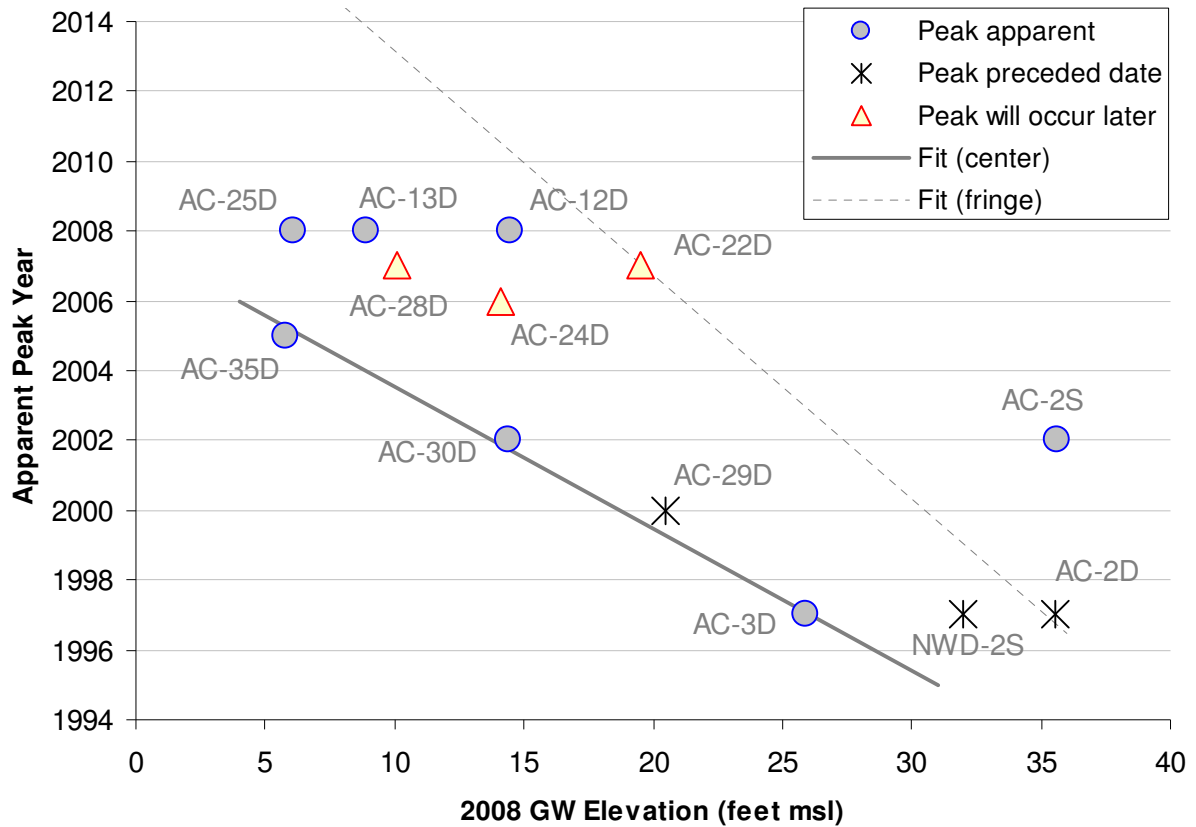
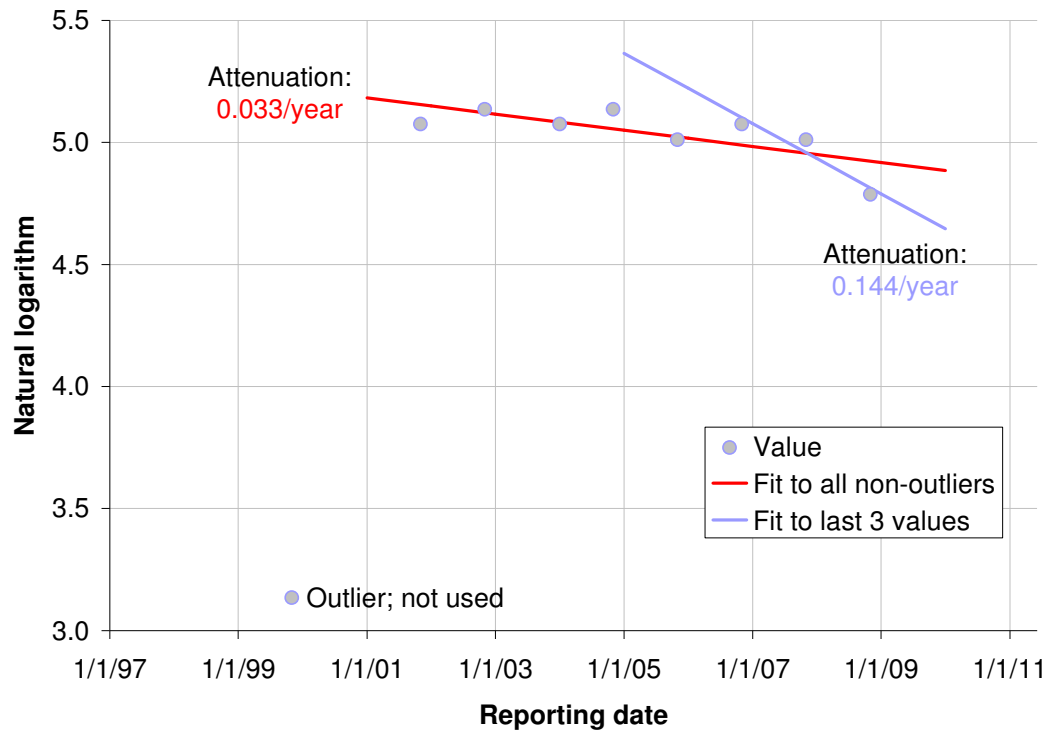


Figure 6 Fluoride Attenuation in AC-35D (Near Bayou Texar)

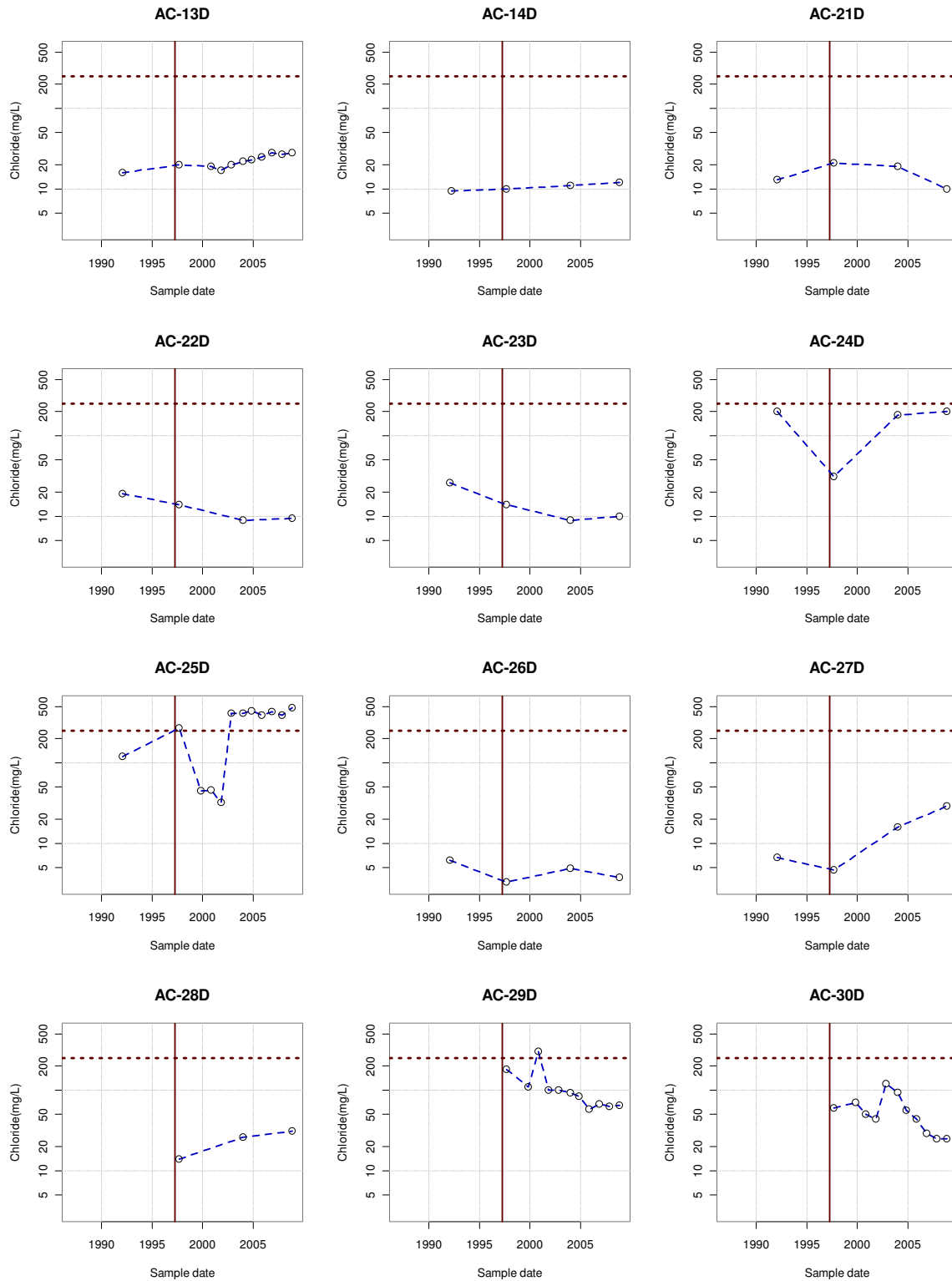


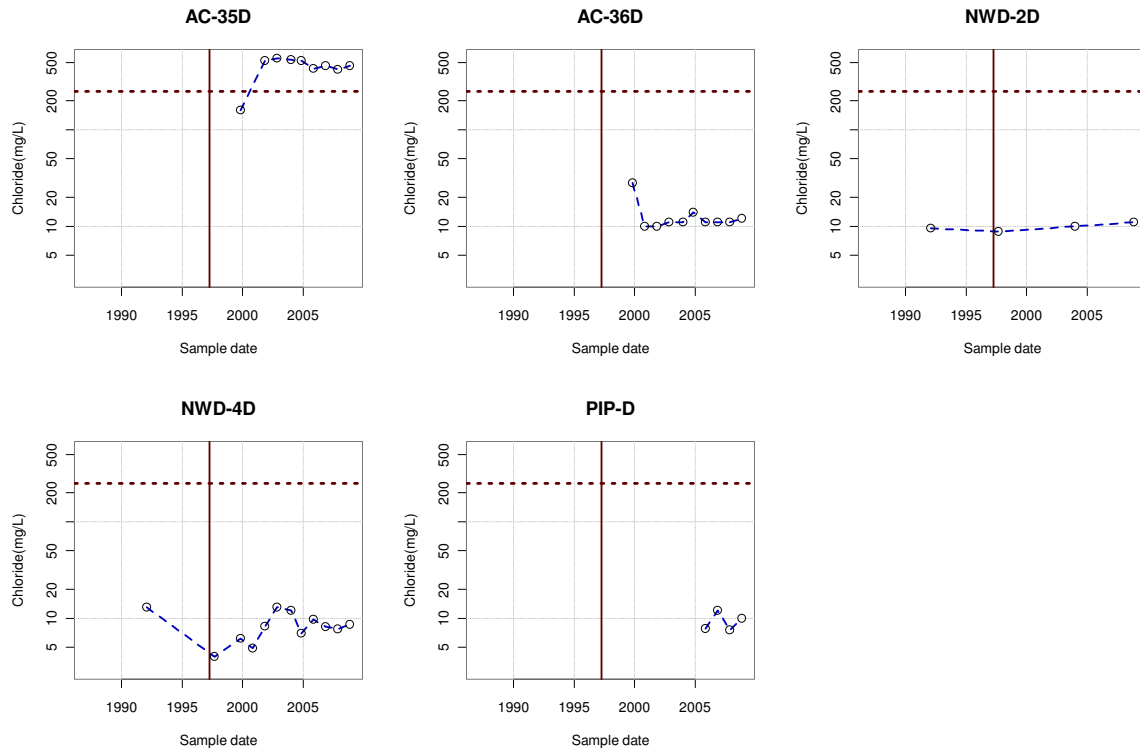
See Figure 4 for explanations and a legend. Only constituents that have not attained cleanup targets at all monitoring wells are shown: this excludes arsenic and lead.

The target is 250 mg/L.

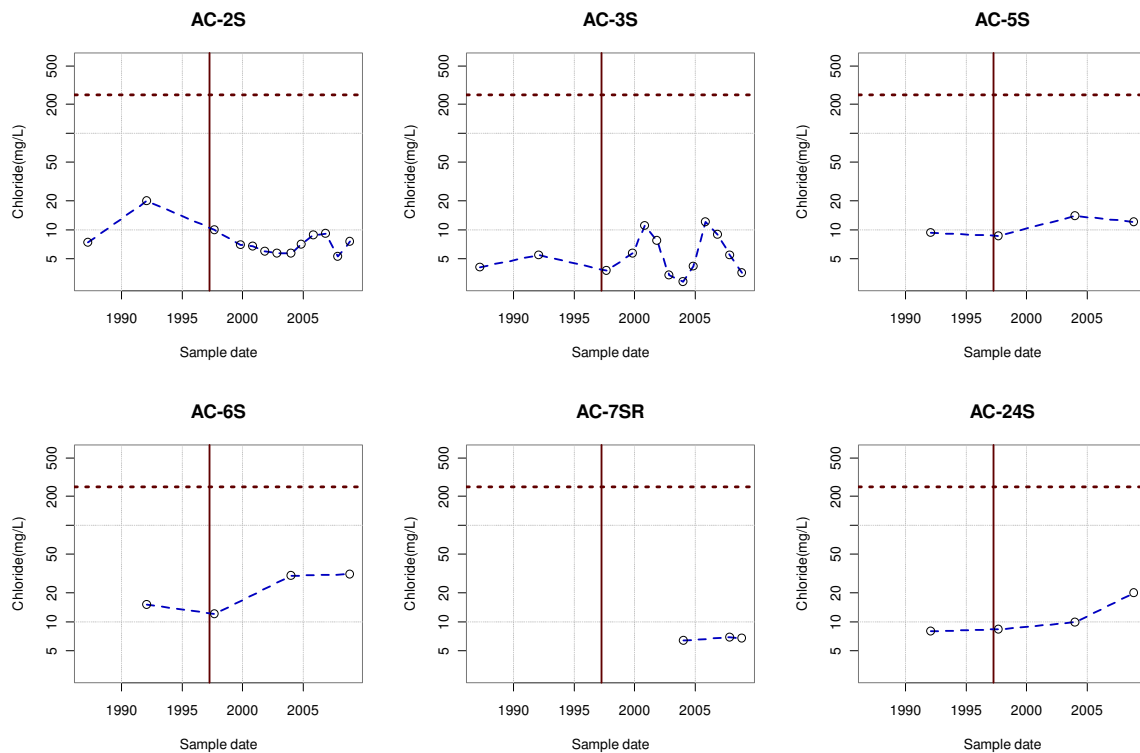
Figure 1 displays nine plots showing Chloride concentration (mg/L) versus Sample date for different AC types (AC-2D, AC-3D, AC-5D, AC-6D, AC-8D, AC-9D, AC-10D, AC-11D, AC-12D). The y-axis is logarithmic, ranging from 5 to 500 mg/L. The x-axis shows Sample date from 1990 to 2005. A vertical solid red line indicates the start of the test, and a horizontal dashed red line indicates the target chloride concentration (approximately 250 mg/L).

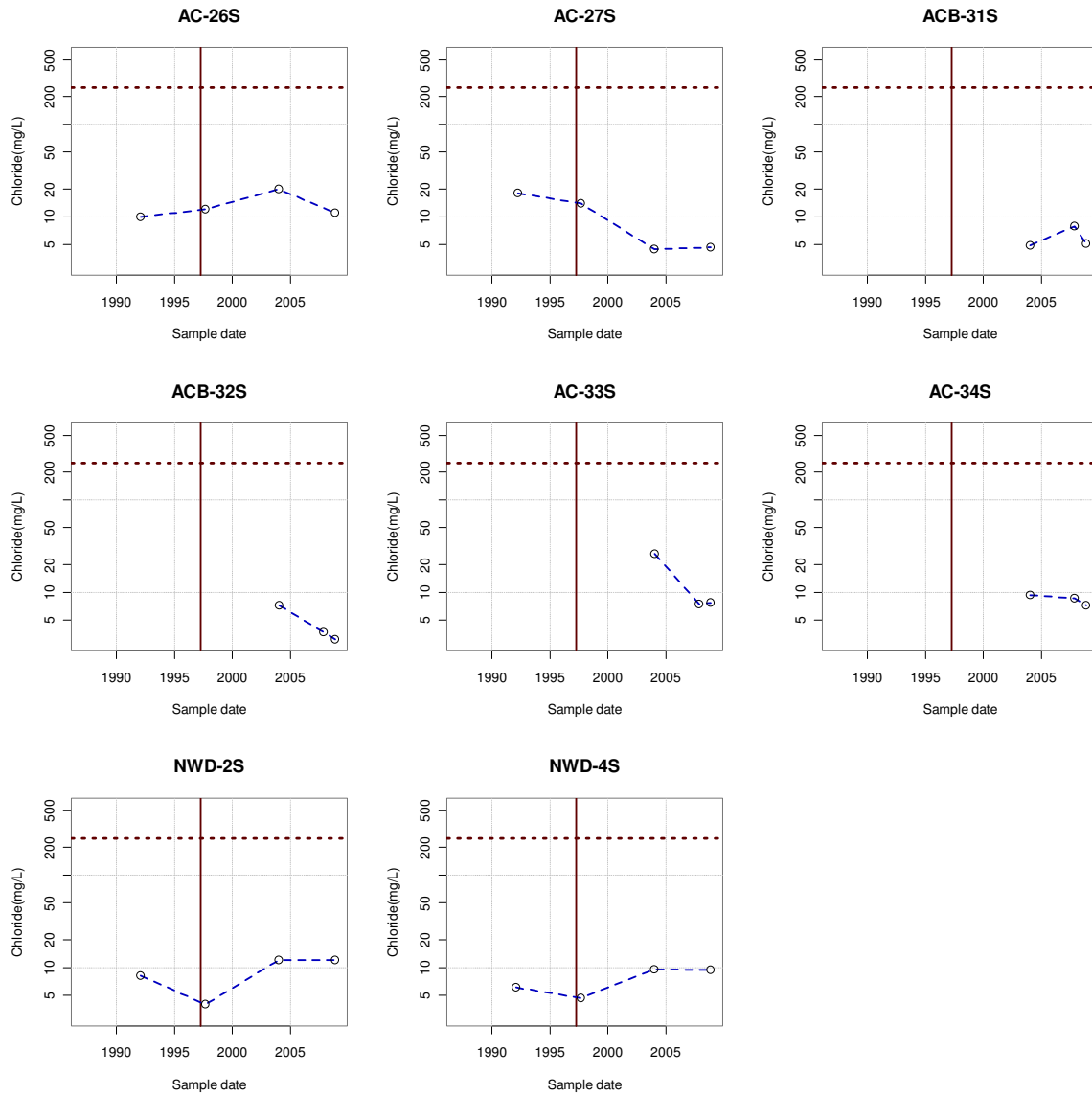
- AC-2D:** Chloride concentration starts around 15 mg/L, remains relatively stable until the test start, then decreases to approximately 10 mg/L by 2005.
- AC-3D:** Chloride concentration starts around 300 mg/L, decreases sharply after the test start to approximately 20 mg/L by 2005.
- AC-5D:** Chloride concentration starts around 15 mg/L, remains relatively stable until the test start, then decreases to approximately 10 mg/L by 2005.
- AC-6D:** Chloride concentration starts around 15 mg/L, decreases slightly after the test start to approximately 10 mg/L by 2005.
- AC-8D:** Chloride concentration starts around 15 mg/L, remains relatively stable until the test start, then increases to approximately 20 mg/L by 2005.
- AC-9D:** Chloride concentration starts around 5 mg/L, increases sharply after the test start to approximately 50 mg/L by 2005.
- AC-10D:** Chloride concentration starts around 10 mg/L, remains relatively stable until the test start, then increases to approximately 15 mg/L by 2005.
- AC-11D:** Chloride concentration starts around 10 mg/L, remains relatively stable until the test start, then increases to approximately 15 mg/L by 2005.
- AC-12D:** Chloride concentration starts around 10 mg/L, increases sharply after the test start to approximately 20 mg/L by 2005.





Surficial Zone

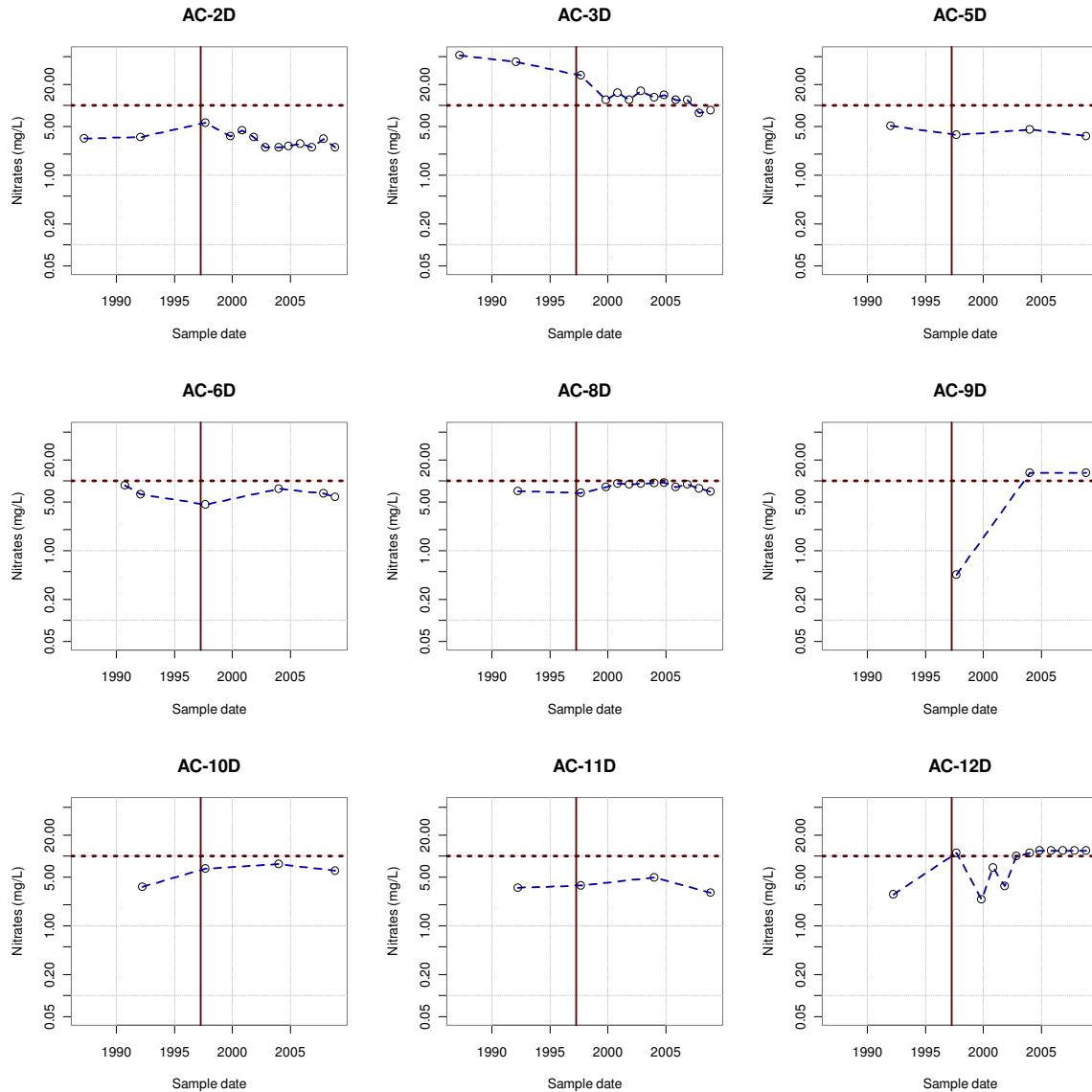


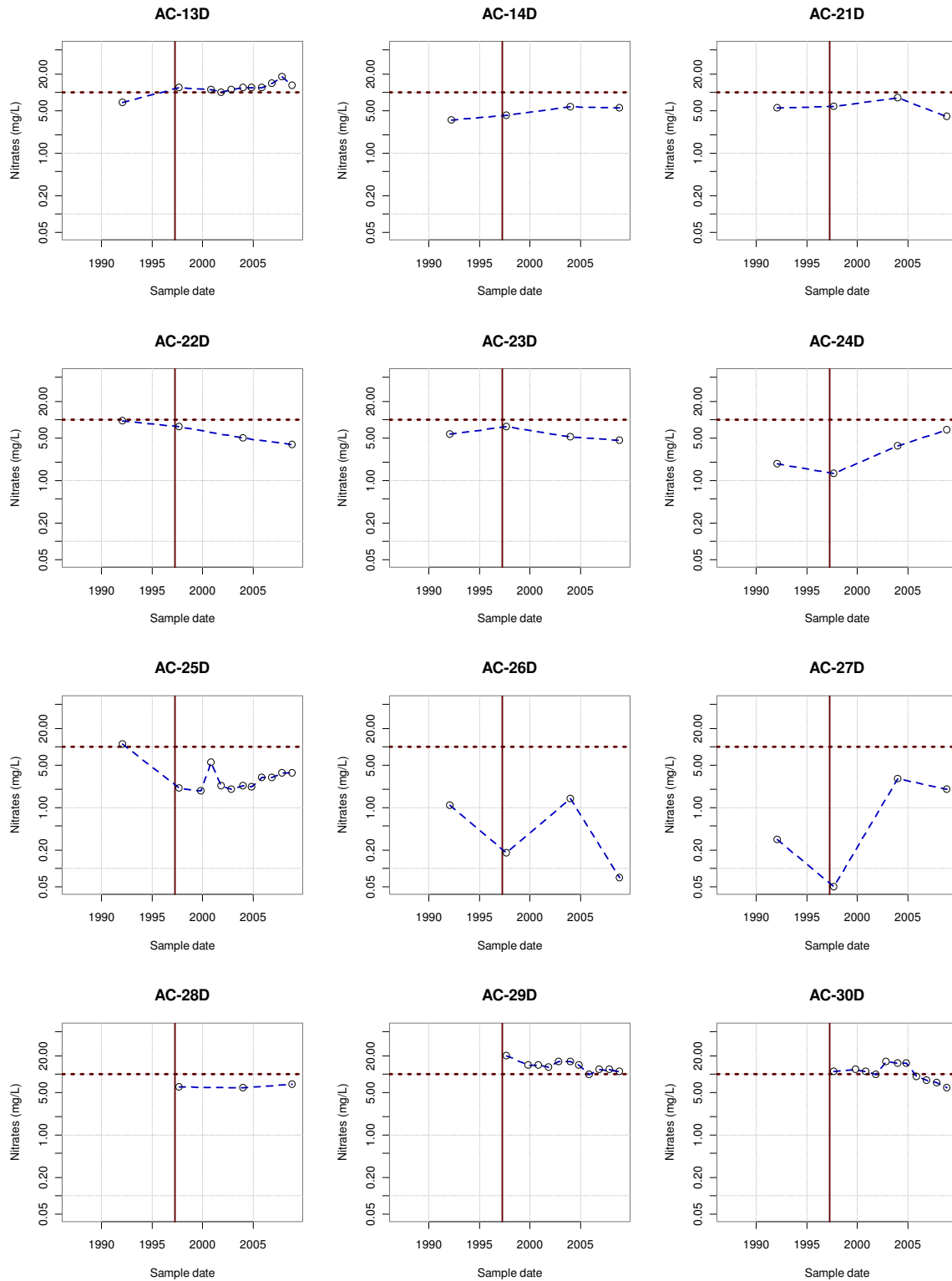


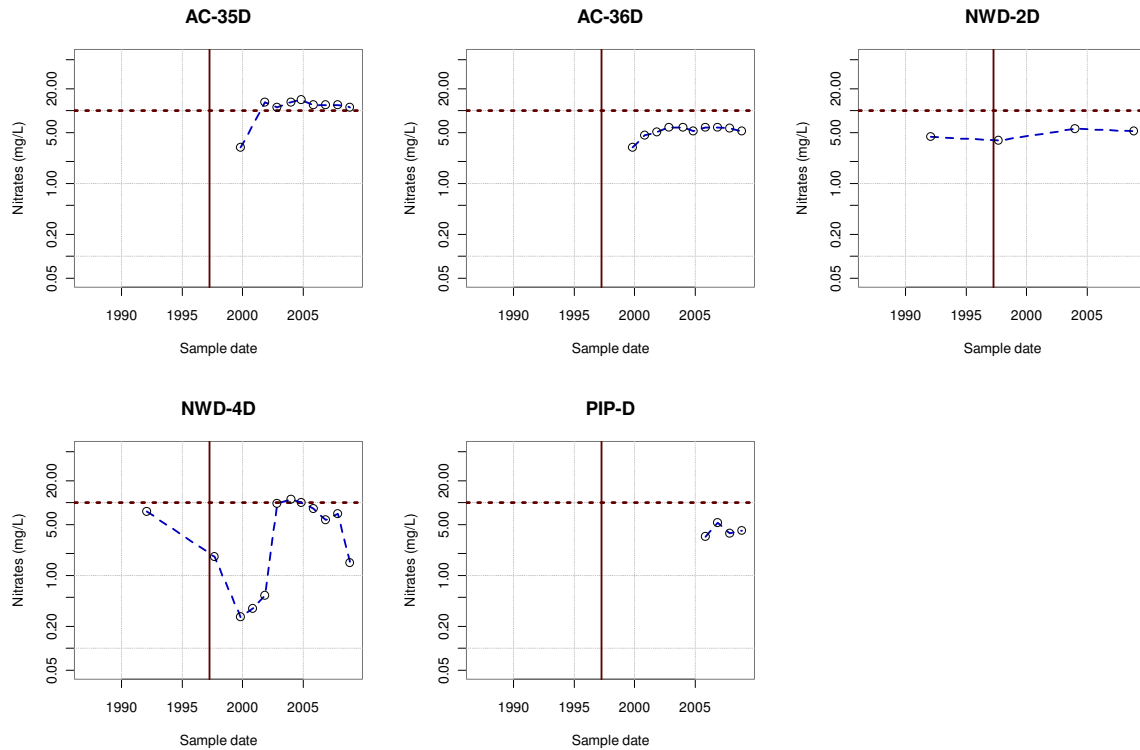
Nitrate

The target is 10 mg/L.

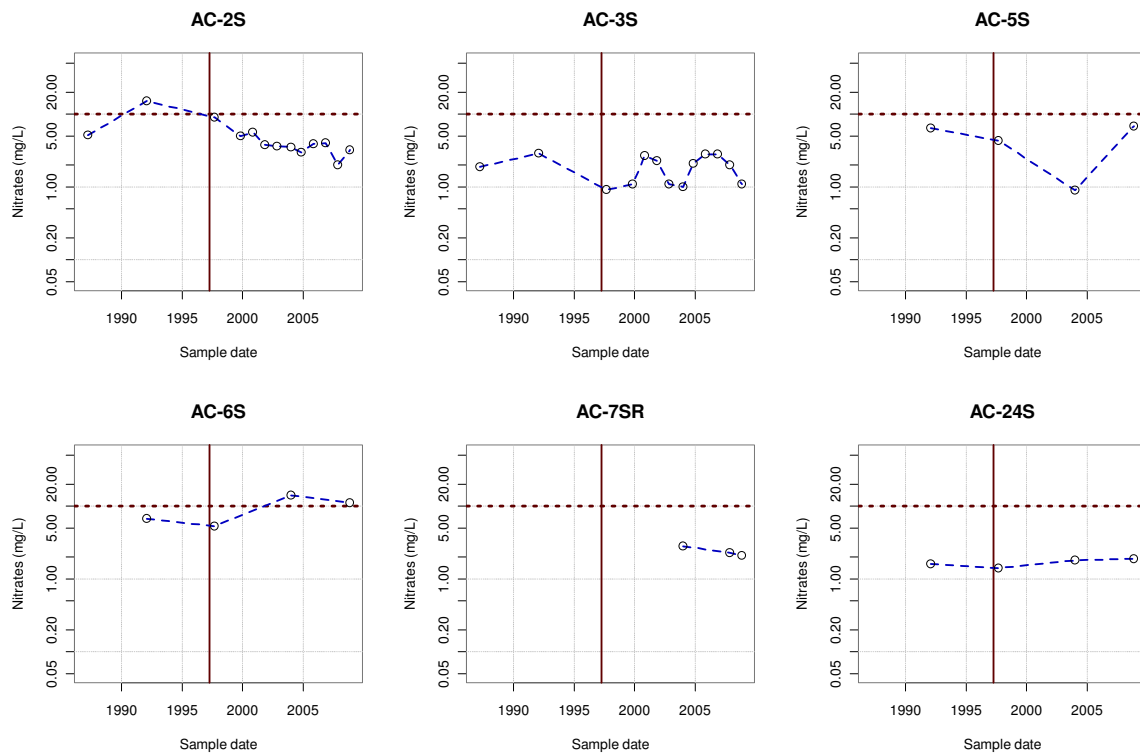
Main Producing Zone

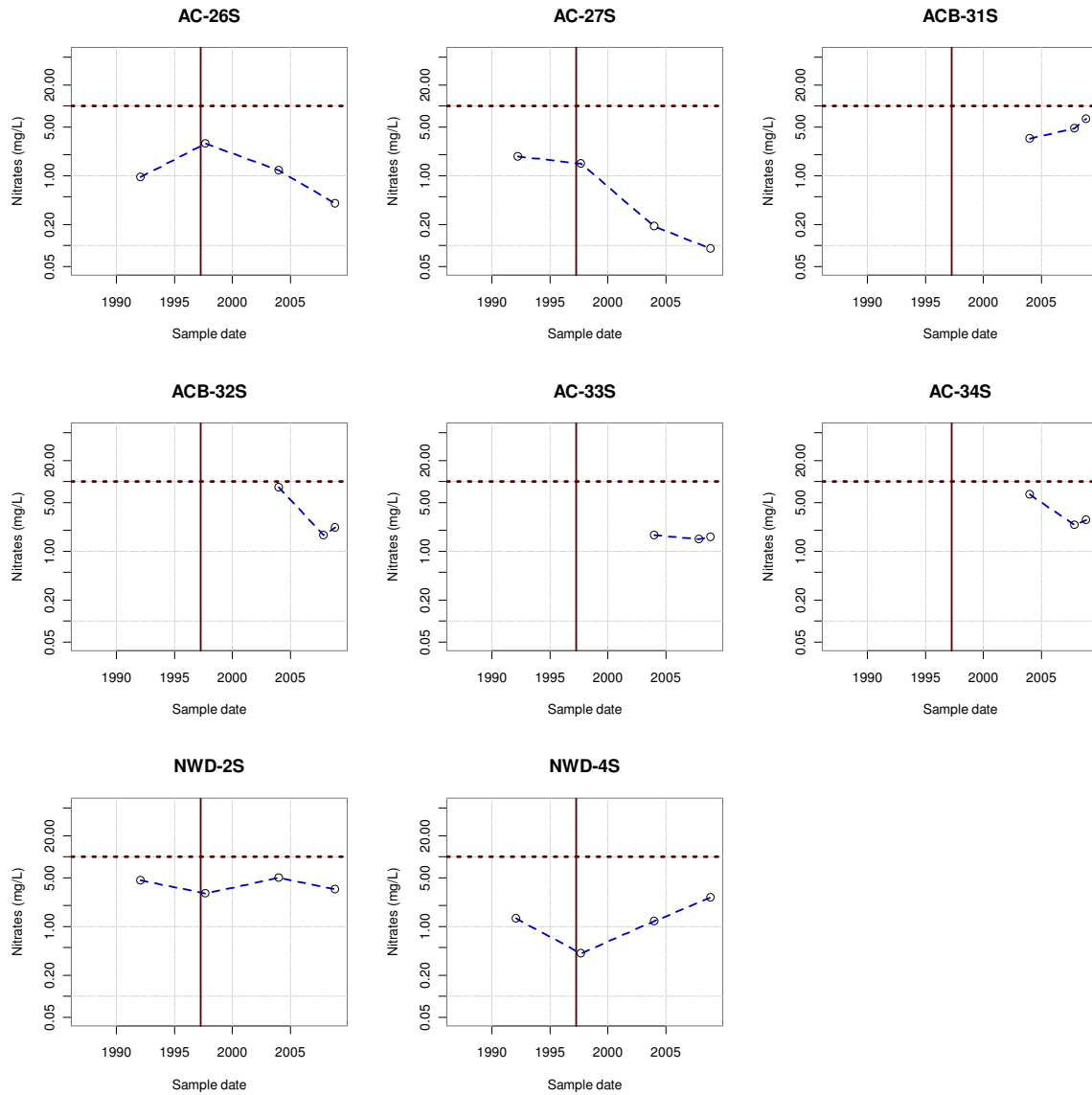






Surficial Zone

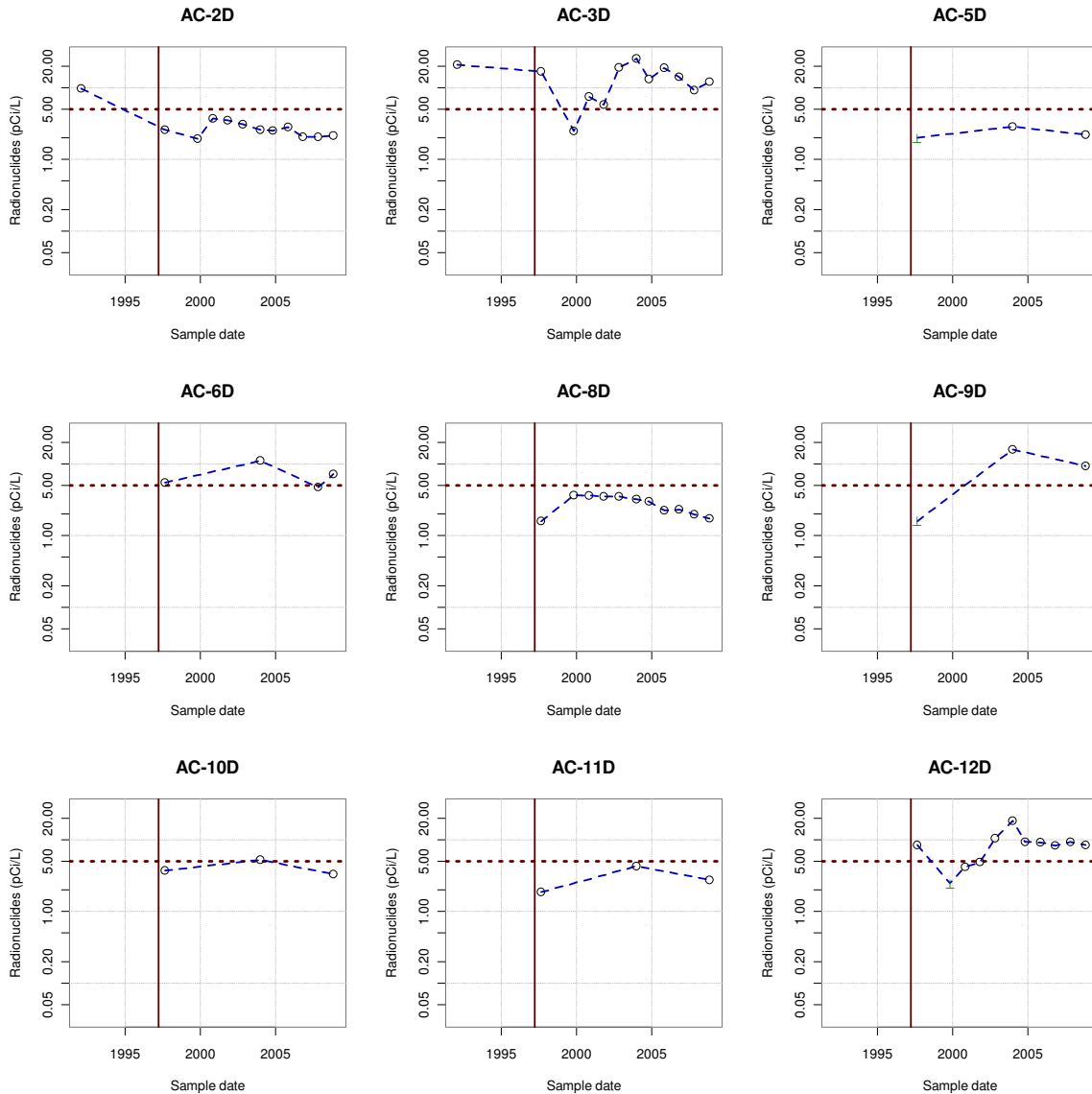


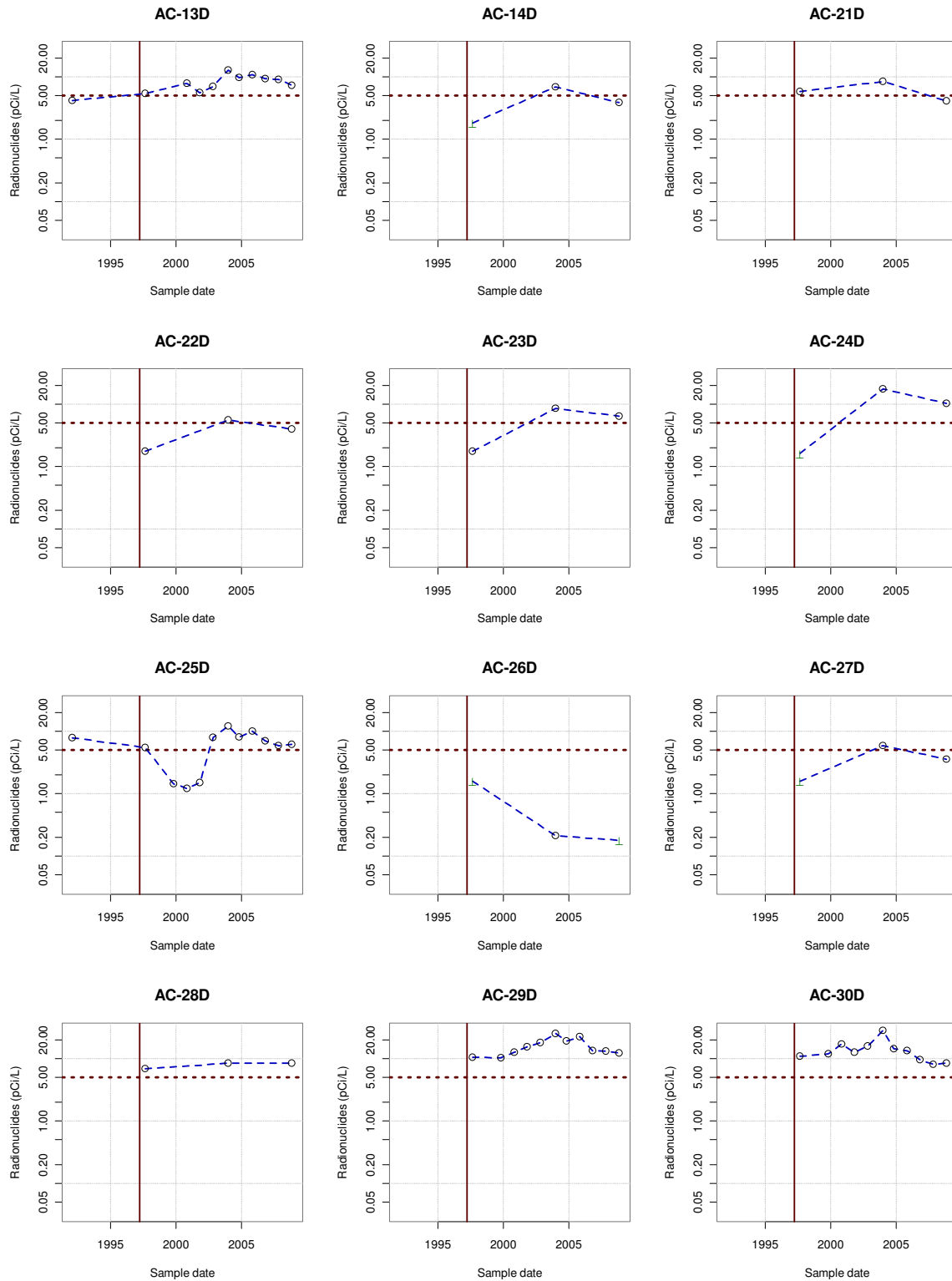


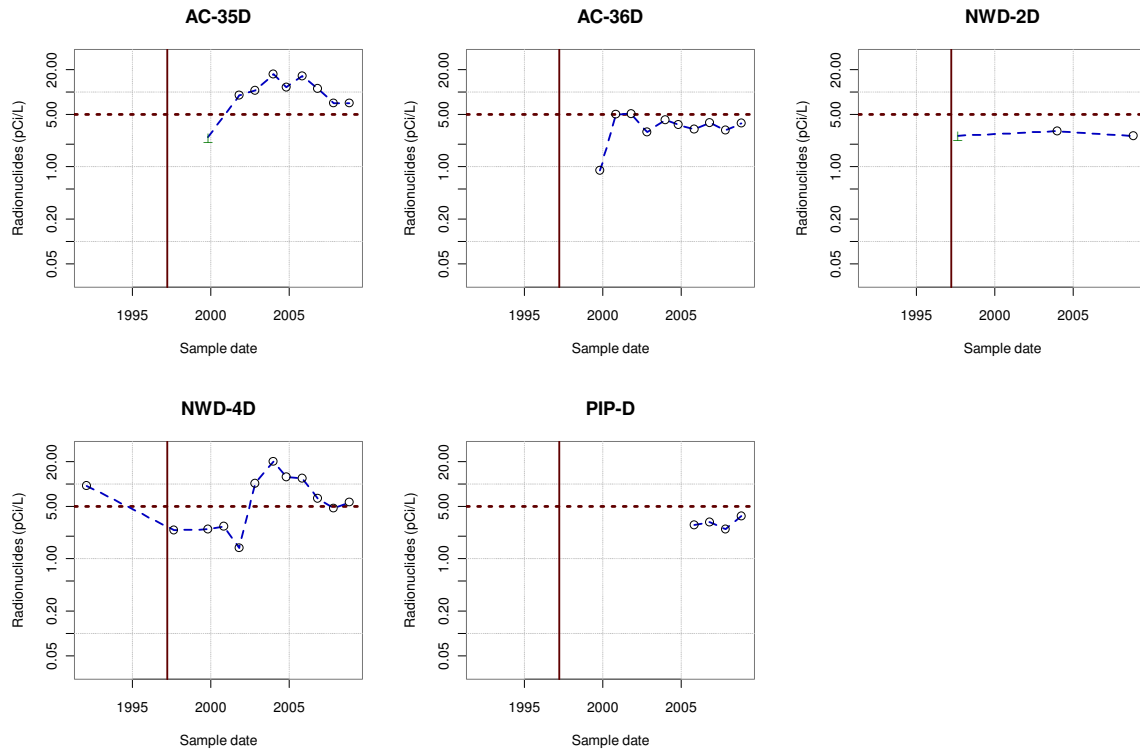
Combined Radium Activities

The target is 5 pCi/L.

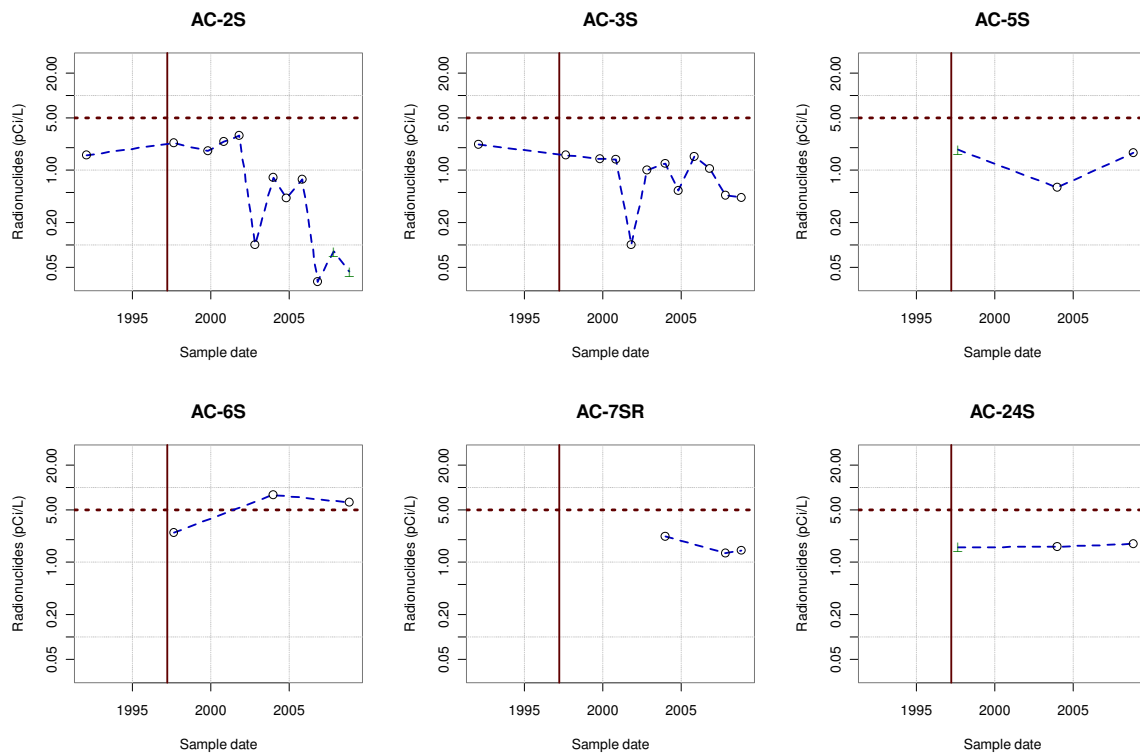
Main Producing Zone

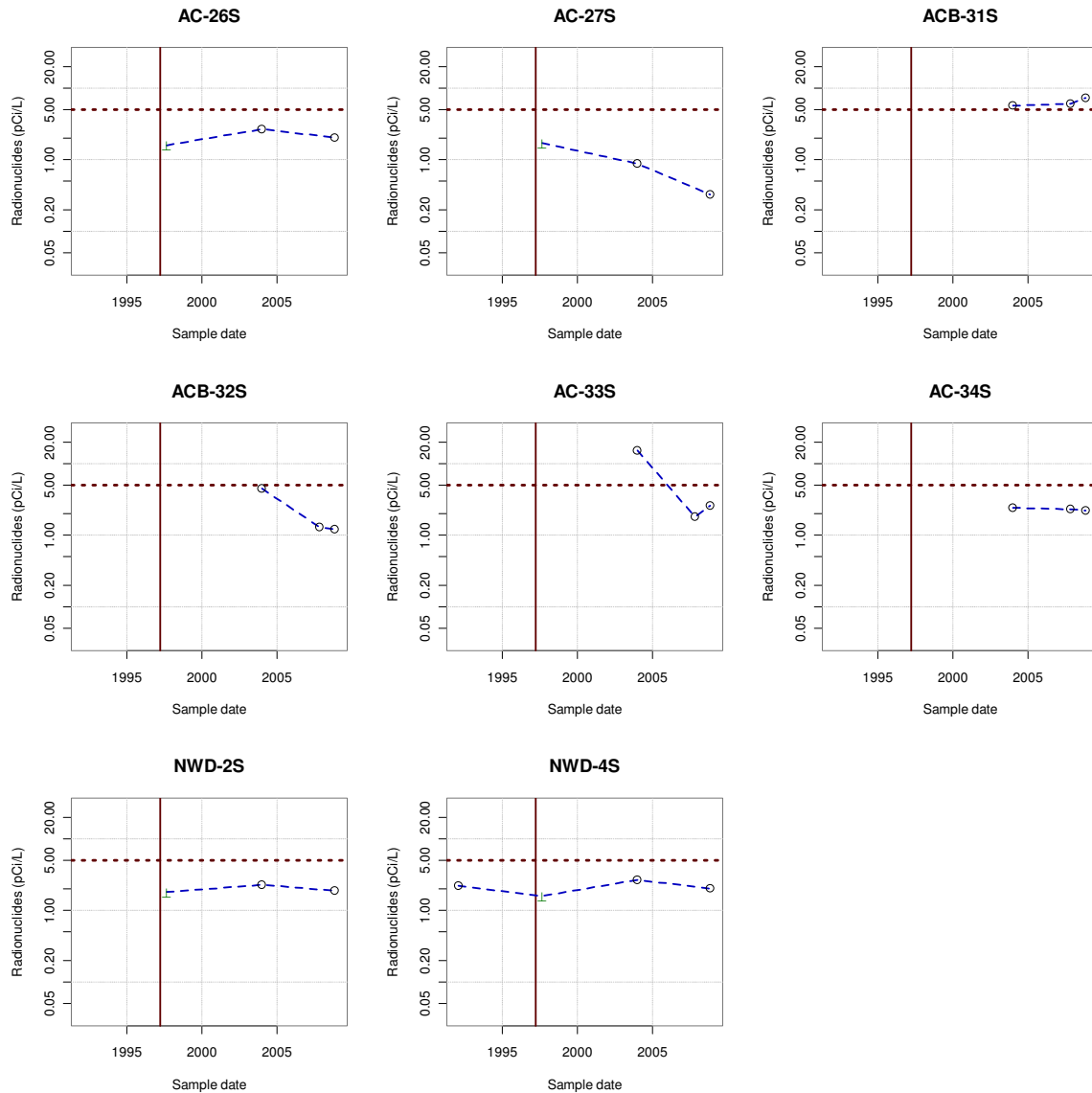






Surficial Zone

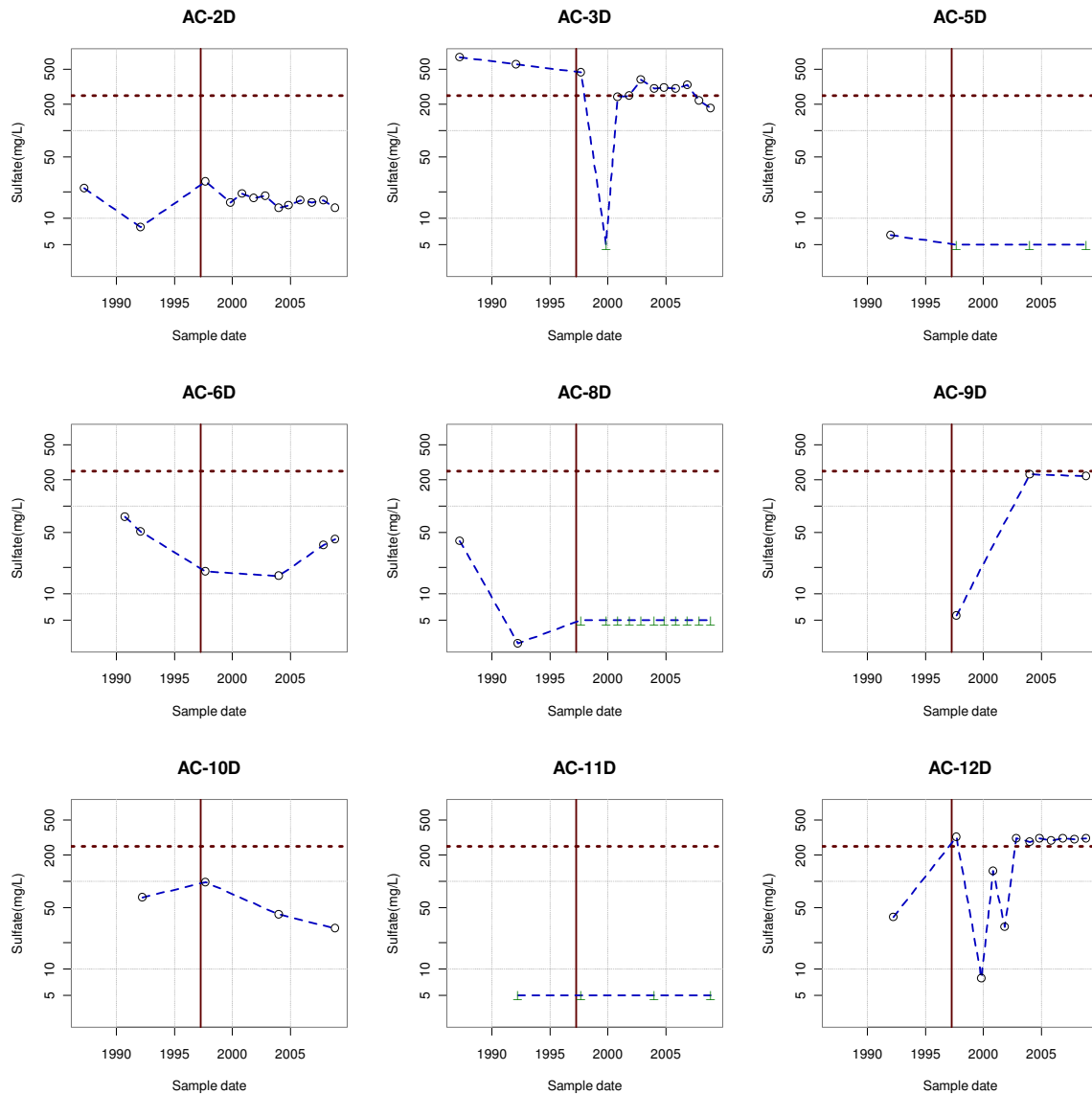


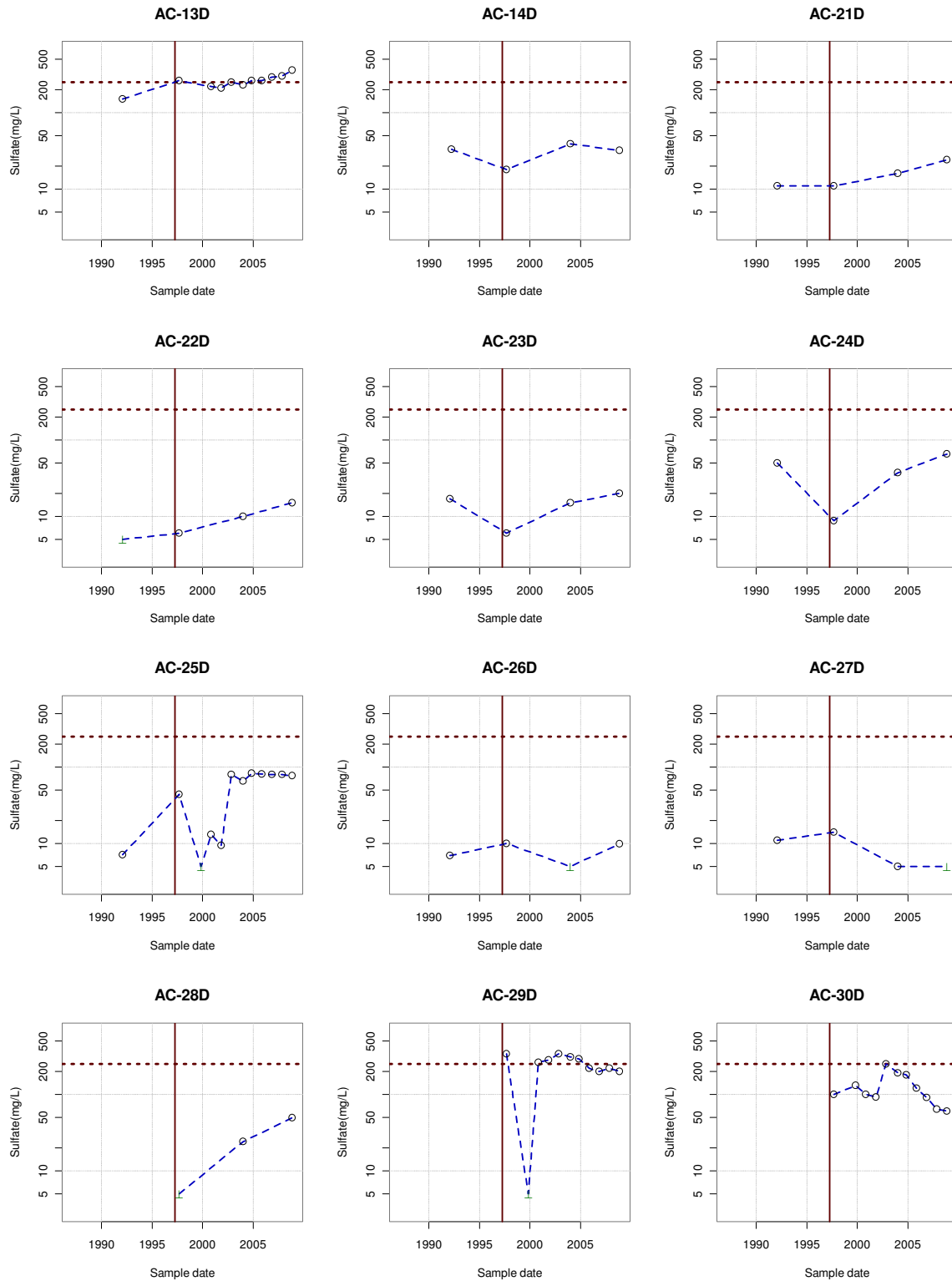


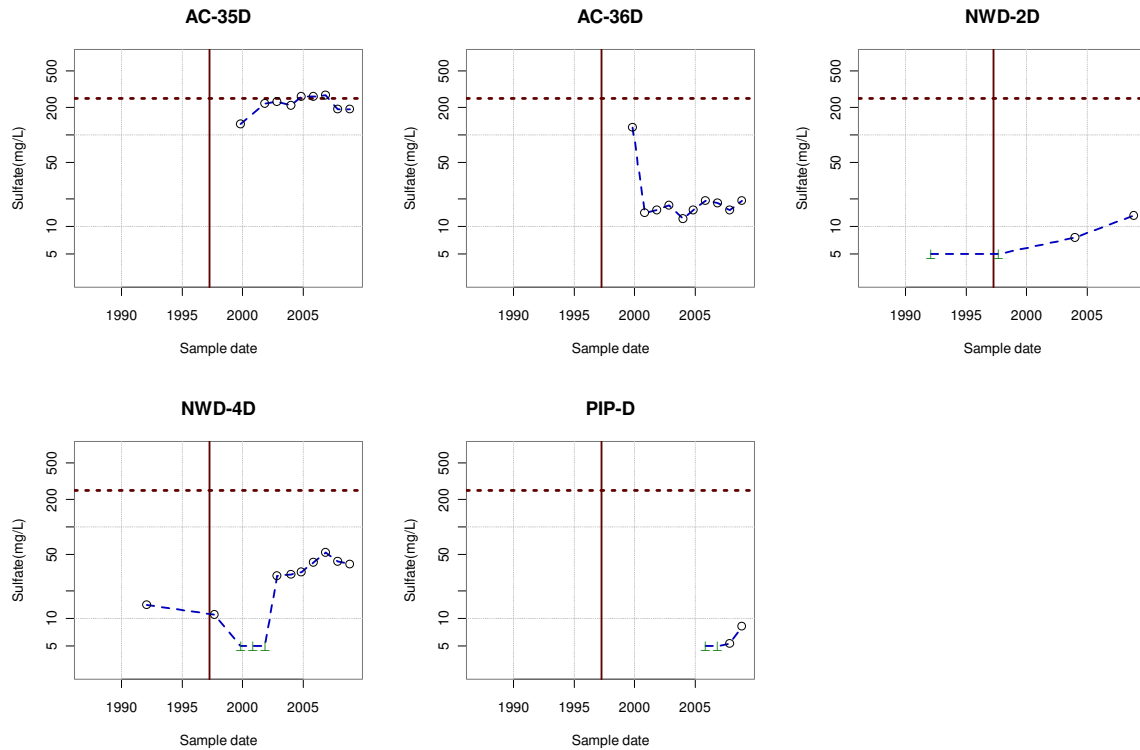
Sulfate

The target is 250 mg/L.

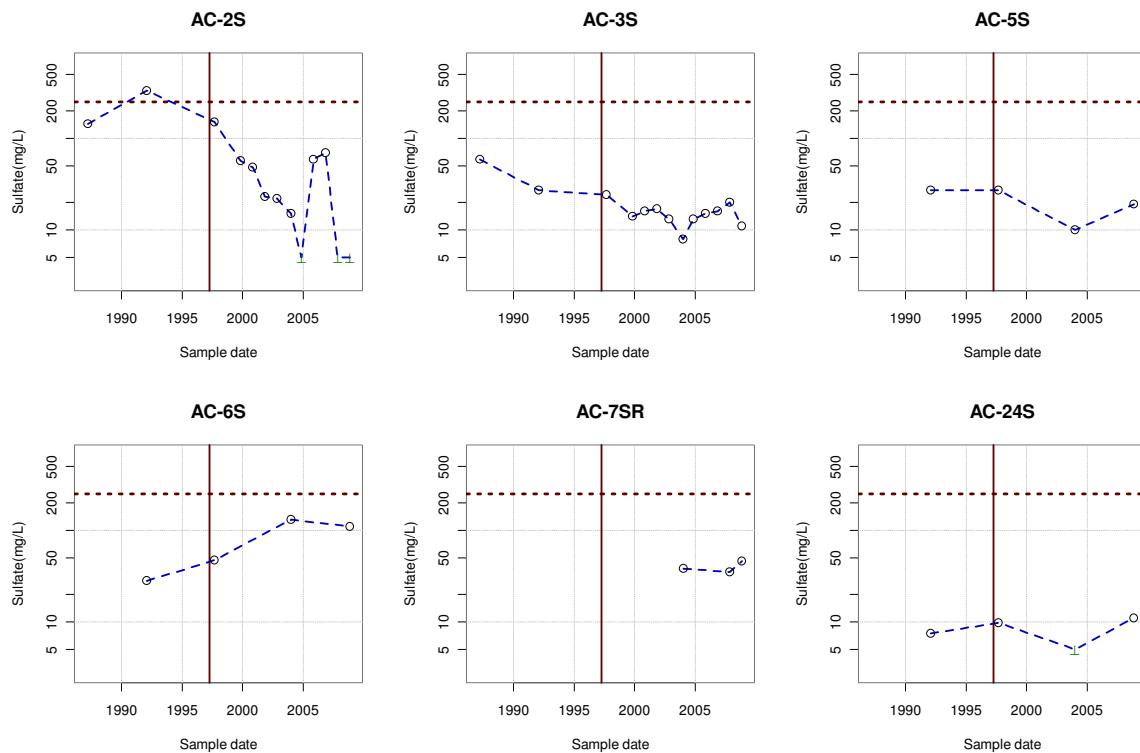
Main Producing Zone







Surficial Zone



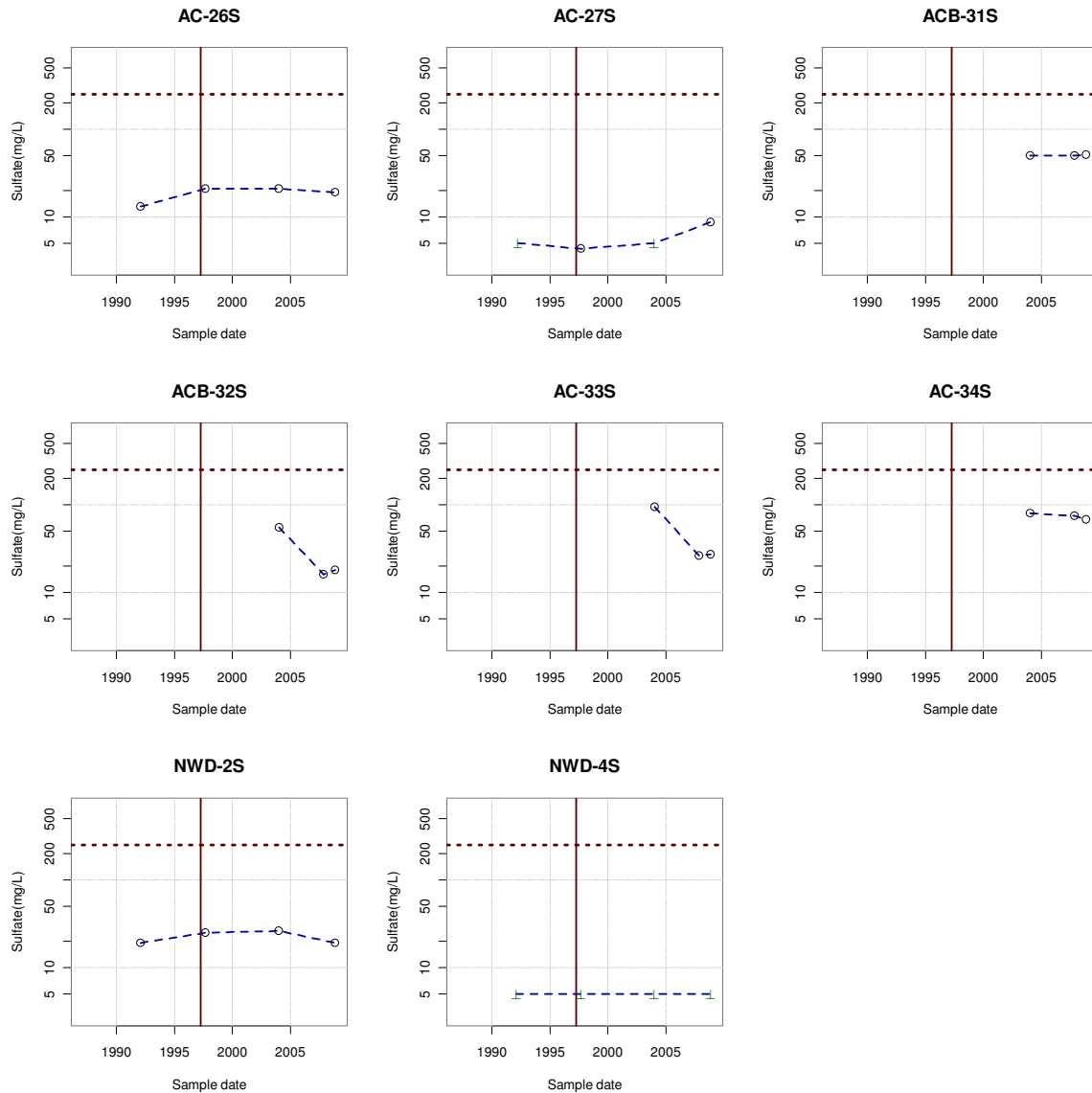
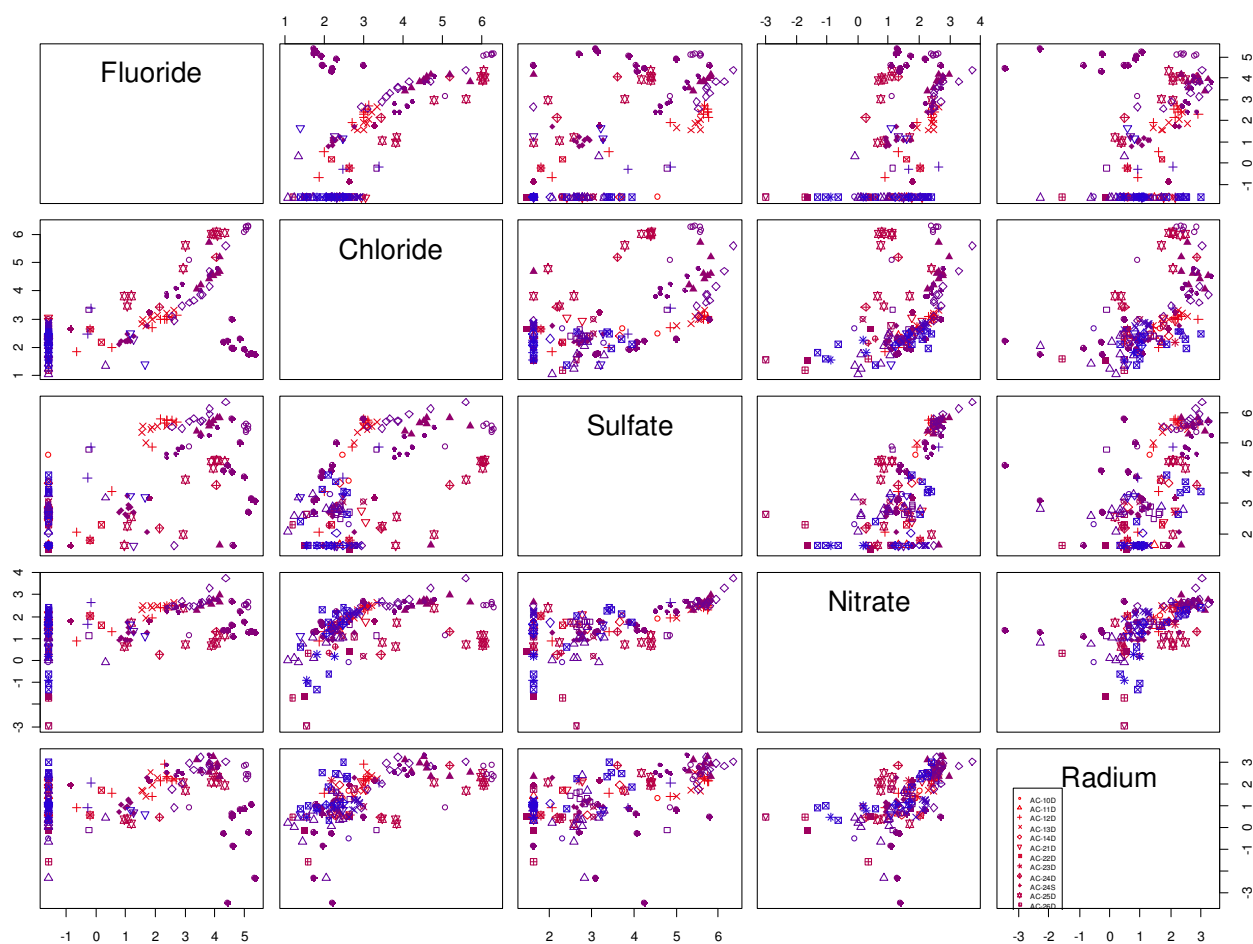


Figure 8 Scatterplot Matrix by Well



Remarks

- (1) Scales are natural logarithms. Original units are pCi/L for Radium and mg/L for all others.
- (2) “Radium” refers to the combined activity of radionuclides Ra^{226} and Ra^{228} .
- (3) “Nitrate” was combined nitrites and nitrates through 2006.
- (4) Nondetects are plotted at (the logarithms of) their reporting limits. Because reporting limits can vary, some quantified values may be less than many of the nondetects.
- (5) The combination of symbol shape and color identifies each well. (The software was unable to print a complete legend.)

Index

A

acceleration, 16, 32, 39, 40
acidic, 7, 10
ad hoc, 23
advection, 7, 9, 14, 15, 16, 17, 18, 19, 34, 35, 38, 39, 42, 44, 45, 48, 52, 58
Agrico site, i, 4, 5, 7, 8, 10, 13, 18, 36, 44, 46, 58
analyte, 10, 12, 33, 34, 40
approximation, 4, 10, 12, 14, 15, 16, 17, 20, 22, 25, 27, 29, 35, 36, 43, 46, 58, 59
aquifer, 4, 10, 14, 16, 35, 46
Arsenic, 2, 4, 5, 10, 12, 33, 43, 46, 67
assumption, 9, 12, 13, 14, 20, 25, 28, 40
asymptotic, 15, 18, 32, 35, 37
attenuation, i, 1, 2, 3, 5, 10, 12, 13, 14, 16, 17, 18, 19, 21, 22, 23, 24, 25, 27, 28, 29, 30, 31, 32, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 52, 53, 54, 55, 66
average, 12, 14, 20, 21, 25, 29, 30, 31, 32, 37, 38, 39, 40, 42, 51, 53, 58

B

background, 3, 5, 6, 8, 9, 11, 18, 36, 48
Bayou Texar, 1, 4, 5, 6, 7, 16, 18, 37, 38, 44, 66
bias, 19, 20, 42

C

certain, 25, 28, 53
Chloride, 4, 5, 7, 10, 12, 41, 67
cleanup, 1, 2, 3, 4, 5, 10, 11, 13, 18, 21, 23, 24, 25, 26, 27, 28, 32, 33, 34, 37, 38, 39, 40, 41, 42, 43, 44, 47, 48, 50, 51, 53, 54, 55, 59, 67
comparison, 28, 29, 30, 32, 40
conceptual model, 1, 12, 13, 14, 17, 18, 23, 28, 29, 34, 44
concern, 1, 2, 4, 5, 7, 9, 11, 14, 30, 34, 42
concerns, 13
conductance, 7
confidence, 2, 12, 13, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 38, 39, 40, 41, 42, 50, 53, 54, 55, 59
fiducial, 2, 25, 26, 27, 59
prediction, 2, 25, 28, 30, 31, 32, 39, 40, 53, 55, 59
conflict, 28, 29
conservative, 37, 38, 39
contamination, 5, 11, 12, 16, 45, 46
conventional, 14, 20
correlation, 25, 32, 33, 41
criterion, 3

D

data, 1, 2, 3, 4, 5, 6, 9, 10, 12, 13, 14, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 30, 31, 32, 34, 35, 36, 38, 39, 40, 41, 42, 43, 44, 46, 51, 52, 54, 55, 56, 59, 60
decay, 3, 8, 9, 14, 15, 16, 20, 26, 27, 45
degrees of freedom, 22, 29, 31, 38, 54
detection, 2, 7, 28, 30, 32, 36, 43, 48
dispersion, 7, 9, 14, 15, 16, 17, 18, 19, 34, 35, 37, 38, 39, 42, 44, 45, 48, 52, 58
distribution, 6, 14, 17, 20, 22, 25, 26, 29, 31, 45, 54
 Normal, 20, 25
 Student t distribution, 22, 25, 29, 31, 54
Draper & Smith, 20, 23, 25, 26, 27, 31, 32, 39, 45
duration, 23, 27, 29, 37, 44, 45

E

environment, 1
equation, 14, 15, 16, 23, 25, 26, 39, 42, 45
erfc, 15
estimate, 1, 2, 3, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 30, 31, 32, 34, 35, 37, 38, 39, 41, 42, 43, 44, 45, 50, 51, 52, 53, 54, 55, 59
Excel, 20, 21, 22
exfiltrate, 4
expectation, 20, 25, 36
extrapolate, 23, 24, 27
extrapolation, 25, 31

F

figure, 4, 5, 6, 11, 16, 23, 26, 28, 34, 35, 37, 38, 40, 42, 46, 52, 54, 57, 58, 59, 60, 65, 66, 67, 83
first-order, 14
fit, 19, 25, 26, 59
flaw, 25, 27
Fluoride, 3, 4, 5, 7, 10, 11, 12, 14, 17, 18, 19, 34, 35, 36, 37, 38, 40, 41, 42, 44, 45, 48, 49, 51, 52, 53, 60, 65, 66
formula, 16, 19, 21, 24, 25, 26, 27, 28, 29, 35, 37, 38, 50
frequency, 1, 2, 10, 11, 20, 42, 44, 56
fringe, 7, 11, 17, 18, 35, 36, 37, 48, 49, 52
future, 1, 3, 9, 13, 17, 25, 26, 27, 28, 29, 30, 31, 32, 36, 38, 39, 40, 42, 44, 53, 55, 59

G

gradient, 35
 downgradient, 1, 2, 4, 5, 7, 8, 16, 17, 18, 35, 36, 38, 40, 41, 42, 44, 48, 49, 53, 58
 sidegradient, 7, 36, 44
 upgradient, 1, 4, 7, 16, 34, 37, 39, 42, 44, 48, 53

groundwater, i, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14,
15, 16, 17, 18, 32, 33, 34, 35, 38, 41, 42, 44, 45, 46,
51, 53, 57, 60, 65
guidance, 3, 11, 12, 13, 32, 44, 46

H

half-life, 9, 21, 37, 38, 53
heteroscedasticity, 19
historical, 12, 16
history, 3, 4, 7, 16, 27, 28, 34, 48
homogeneous, 14, 16, 35
hyperbolic, 26
hypothesis, 29, 30, 32, 40

I

incorrect, 24, 25, 50
interpret, 22, 28, 31, 37, 40
intuitive, 25, 27
inverse, 2, 16, 23, 25, 26, 28, 53, 54, 59
ionize, 7, 8
irrigation, 6
isotherm, 9

J

justify, 3, 9, 14, 27

L

lateral, 14, 15, 35
Lead, 2, 4, 5, 9, 10, 12, 33, 43, 67
limit, 2, 10, 11, 12, 19, 21, 23, 24, 25, 26, 27, 28, 31, 32,
33, 34, 37, 38, 39, 40, 42, 50, 53, 54, 55, 59, 60, 83
linear, 9, 12, 13, 15, 18, 19, 20, 27, 28, 35, 38
local, 34, 38, 51
logarithm, 2, 12, 15, 18, 19, 20, 21, 22, 23, 24, 25, 26,
28, 29, 30, 32, 33, 34, 37, 53, 58, 59, 60
logarithms, 13, 19, 22, 28, 58, 83

M

macroscopic, 14
Main Producing Zone, 6, 7, 11, 16, 17, 37, 61, 67, 71,
75, 79
management, 3, 5, 47
microscopic, 17
MNA, 5, 10, 11, 12, 13, 17, 44, 45, 46, 47
monitored, i, 5, 10, 11, 34, 35, 39, 42, 46, 47

N

network, 5
Newell, 3, 12, 15, 19, 23, 24, 25, 27, 45
nitrates and nitrites, 2, 4, 5, 7, 8, 10, 12, 71, 83
null hypothesis, 29, 32

O

objectives, 5, 10, 12, 13, 23, 28, 44
one-sided, 21, 31, 39, 54, 55
Ordinary Least Squares, 2, 20
outlier, 18, 20, 35, 38, 51, 53
oxidation, 7

P

parameter, 5, 7, 11, 18, 19, 20, 21, 23, 24, 29, 30, 33
peak, 16, 17, 18, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43,
44, 49, 51, 52, 54, 58, 65
percentage, 22, 31
percentile, 22, 27, 31, 54
permeability, 1, 6, 16, 44
plume, 3, 6, 7, 8, 9, 10, 11, 14, 15, 17, 18, 19, 32, 34, 35,
36, 37, 38, 39, 40, 42, 48, 49, 52, 53
precipitation, 6, 17
prediction, 1, 2, 17, 18, 30, 35, 48
probability, 14, 22, 28, 29
propagate, 1, 4, 16

Q

quadratic, 26, 32
quality control, 32
quantify, 33, 54, 60, 83
quinquennial, 11

R

Radionuclides, 2, 4, 5, 7, 8, 9, 10, 19, 41, 42, 45, 46, 55,
56, 75, 83
random, 1, 13, 14, 17, 18, 19, 20, 23, 24, 25, 28, 35, 36,
38, 55
reasonable, 9, 13, 29, 34, 35, 42
recommend, 19, 32
reference, 3, 10, 14, 17, 34, 54, 59
regression, 2, 19, 20, 23, 24, 25, 28, 32, 34, 38, 45, 53,
54, 59
reject, 32
reliable, 24, 25, 38, 39
remediation, 1, 2, 5, 6, 10, 11, 16, 36, 39, 44, 45, 56, 60
residual, 2, 5, 32, 34
retardation, 2, 7, 9, 10, 40, 41, 45
review, 2, 5, 11, 28, 30, 32, 39, 40, 42, 46, 47
risk, 47

S

scatterplot, 33, 35, 36, 41, 52, 83
sensitive, 30
sentinel, 11
source, 1, 2, 4, 6, 7, 11, 14, 16, 17, 18, 34, 35, 36, 37, 39,
40, 41, 44, 48, 49, 53, 57, 58, 60
spatial, 6, 14, 17, 38, 44
spine, 15, 37, 38, 39, 42
standard, 10, 13, 20, 21, 22, 25, 26, 29, 31, 38

standard deviation, 20, 25, 29, 38
standard error, 21, 22, 25, 26, 29, 31
 sep, 31
stormwater, 4
Student t-test, 28, 29, 30
substrate, 7, 8
Sulfate, 4, 5, 10, 12, 41, 43, 79
Surficial Zone, 6, 11, 34, 36, 37, 53, 57, 63, 69, 73, 74,
 77, 81
systematic, 17, 20

T

table, 3, 7, 9, 11, 18, 23, 24, 25, 34, 35, 37, 38, 39, 40,
 42, 46, 48, 50, 51, 52, 53, 55, 56
target, 1, 2, 4, 10, 11, 12, 18, 23, 24, 25, 26, 28, 34, 35,
 36, 37, 39, 41, 42, 43, 44, 48, 54, 55, 56, 59, 60, 67,
 71, 75, 79
Taylor Series, 22
temporal, 14, 17, 19, 59
time series, 17, 34, 40, 41
trajectory, 17
transformation, 19
transport, 1, 4, 7, 9, 14, 16, 35, 44, 45
trend, 12

two-sided, 32, 54, 55

U

uncertainty, 1, 3, 13, 17, 21, 23, 24, 25, 26, 28, 29, 31,
 37, 39, 54
URS, 3, 4, 5, 6, 7, 10, 12, 16, 38, 44, 46, 49, 57
USEPA, 3, 4, 5, 10, 11, 12, 13, 14, 15, 19, 20, 22, 23, 24,
 28, 29, 30, 32, 38, 44, 45, 46, 47

V

variability, 1, 11, 13, 14, 17, 18, 20, 30, 34, 36, 37, 38,
 41, 55

W

Wilson, 12, 13, 19, 20, 28, 29, 30, 45, 46, 47, 50

Z

zone, 1, 6, 7, 11, 16, 17, 33, 34, 36, 37, 48, 49, 53, 57,
 60, 61, 63, 67, 69, 71, 73, 75, 77, 79, 81