

An Approach for Evaluating the Progress of Natural Attenuation in Groundwater

**GROUNDWATER RESOURCES ASSOCIATION
of California**

GRACast Web Conference

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U.S. EPA/ORD/NRMRL

RESEARCH AND DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Statistics is not a substitute for common sense.

Furthermore, statistics is not a substitute for good site characterization and hydrogeology.

Concentrations in a well can attenuate simply because the plume moved away from the well.

Pay particular concern to your monitoring well network.



Performance Monitoring of MNA Remedies for VOCs in Ground Water. 2004. Pope, D., S. Acree, H. Levine, S. Mangion, J. van Ee, K. Hurt and B. Wilson. EPA/600/R-04/027.

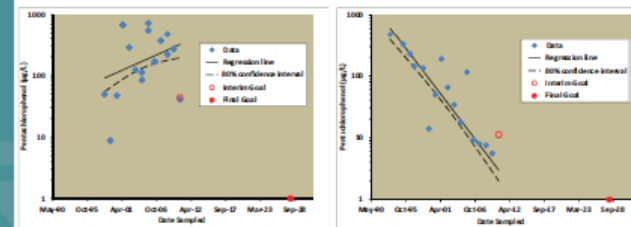
Available

<http://www.epa.gov/ada/gw/mna.html>



[http://www.epa.gov/nrmrl/
gwerd/publications.html](http://www.epa.gov/nrmrl/gwerd/publications.html)

An Approach for Evaluating the Progress of Natural Attenuation in Groundwater



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Publications

General Information	Topics	Type	Year
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Year

- | | | |
|------------------------|------------------------|------------------------|
| • 2011 | • 2003 | • 1996 |
| • 2010 | • 2002 | • 1995 |
| • 2009 | • 2001 | • 1994 |
| • 2008 | • 2000 | • 1993 |
| • 2007 | • 1999 | • 1992 |
| • 2006 | • 1998 | • 1991 |
| • 2005 | • 1997 | • 1990 |
| • 2004 | | • 1989 |

2011

[An Approach for Evaluating the Progress of Natural Attenuation in Groundwater \(PDF\)](#) (84 pp, 956 KB) (EPA/600/R-11/204) December 2011 | [Comparison of Initial Year of Review Cycle to Final Year of Review Cycle \(.xls\)](#) (2 pp, 60 KB) | [Regression MNA \(.xls\)](#) (3 pp, 56 KB)

An Approach for Evaluating the Progress of Natural Attenuation in Groundwater (pdf)

Comparison of Initial Year of Review Cycle to Final Year of Review Cycle (.xls)

Regression MNA (.xls)


RESEARCH & DEVELOPMENT
Building a scientific foundation for sound environmental decisions

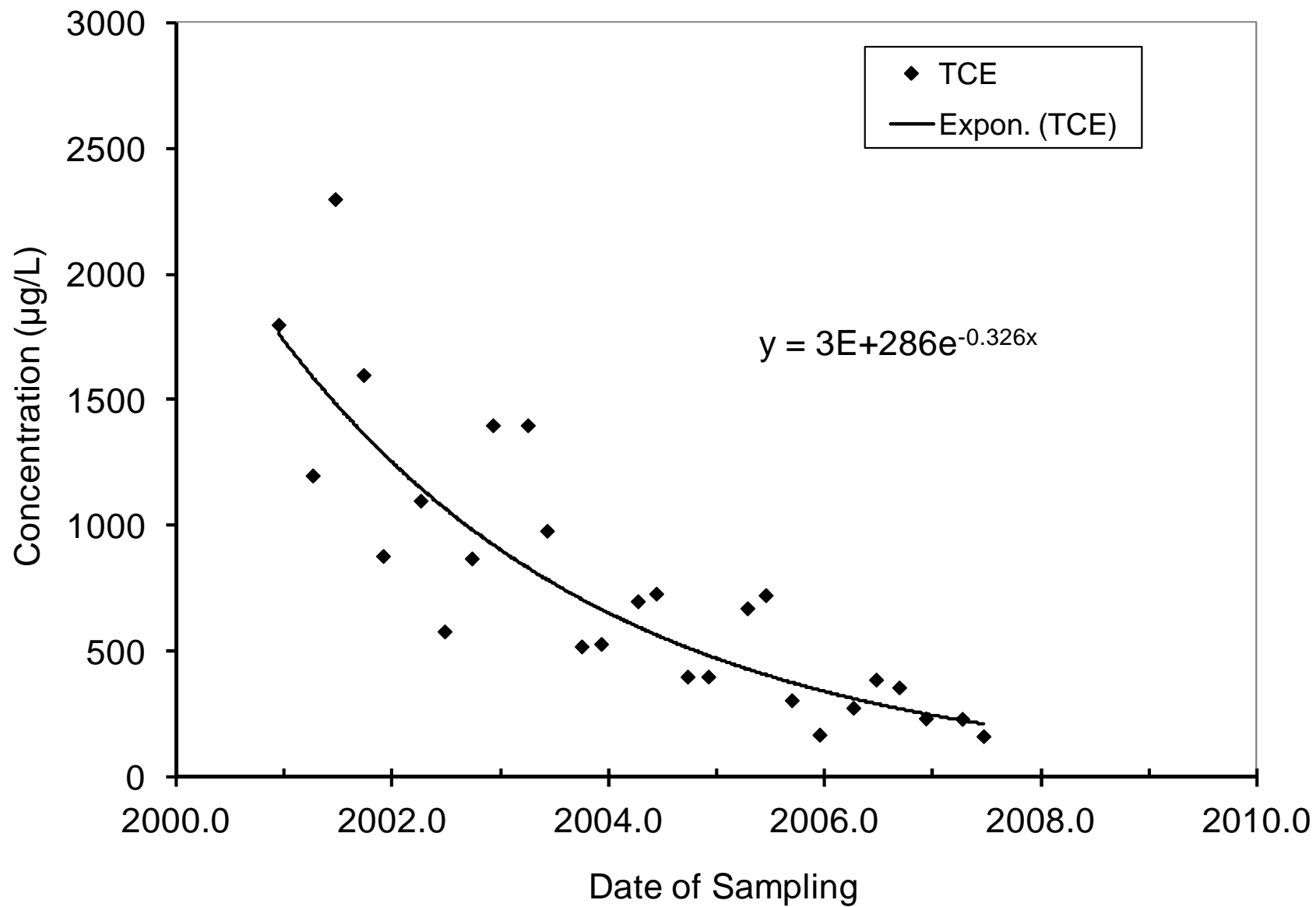
We have good statistical methods to:

- (1) determine whether concentrations of a contaminant are attenuating over time,
- (2) determine the rate of attenuation and confidence interval on the rate,
- (3) determine whether concentrations have met a particular clean up goal.



We have not applied statistical methods to determine whether the extent of attenuation seen in a five year review is adequate to meet the ultimate cleanup goal in a predetermined time frame.





For the purposes of illustration, assume the ROD specified that the site would reach the clean up goals (the MCLs) by 2018.

Will attenuation of TCE meet the goals?



$$C/C_o = e^{-kt}$$

C/C_o = concentration reduction

k = first order rate constant for
attenuation

t = time elapsed



$$t = - \ln(C/C_o) / k$$

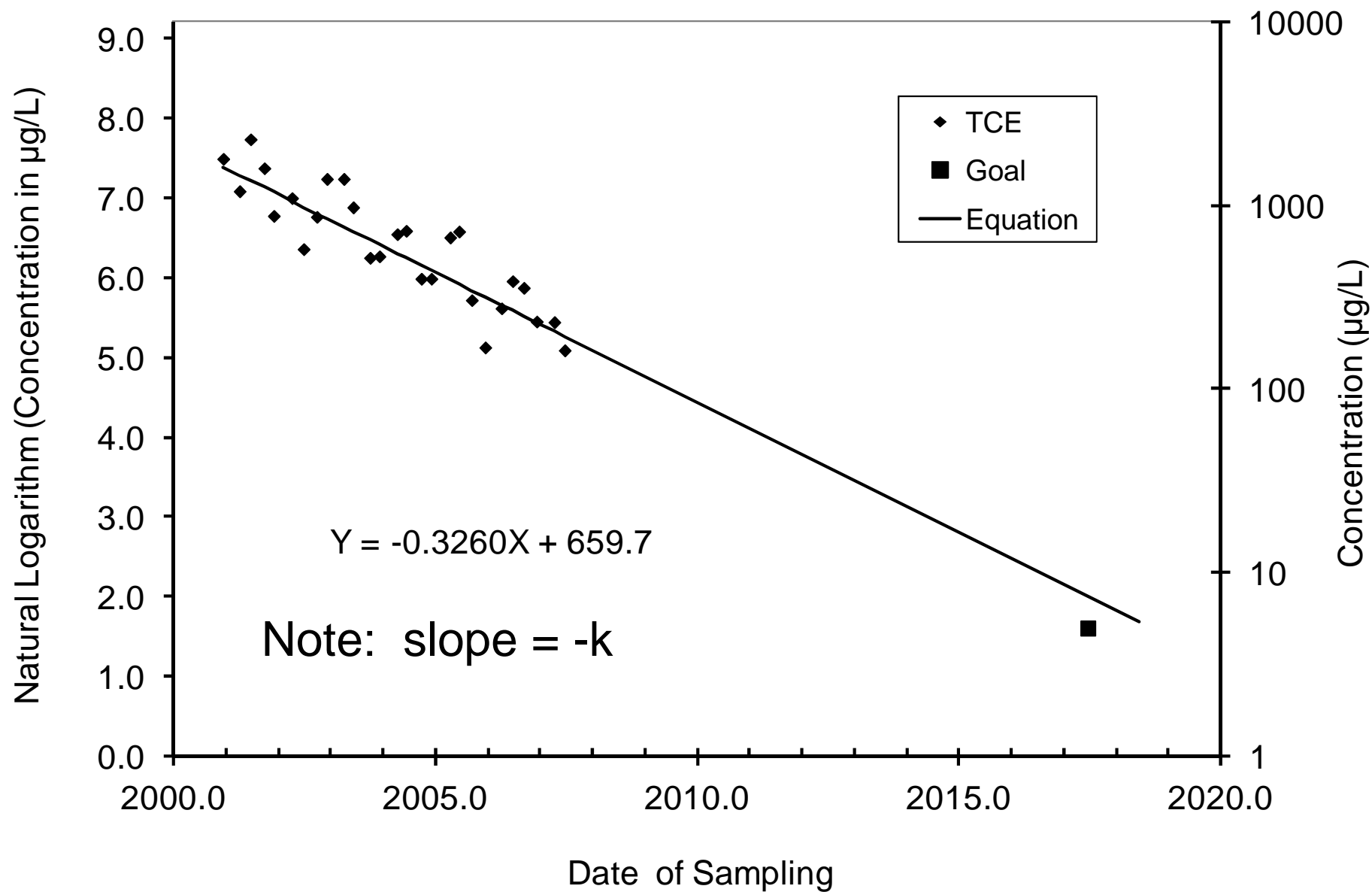
C = cleanup goal = 5 µg/L

C_o = max of 2300 µg/L in 2001

k = 0.321 per year

t = 19 years or 2020





How can we tell from the monitoring data when the rate of attenuation is adequate to attain the goal?

Compare the monitoring data to a interim goal that would be adequate to attain the long the long term goal.



$$C_{ig} = C_o \left(\frac{C_g}{C_o} \right)^{1/n}$$

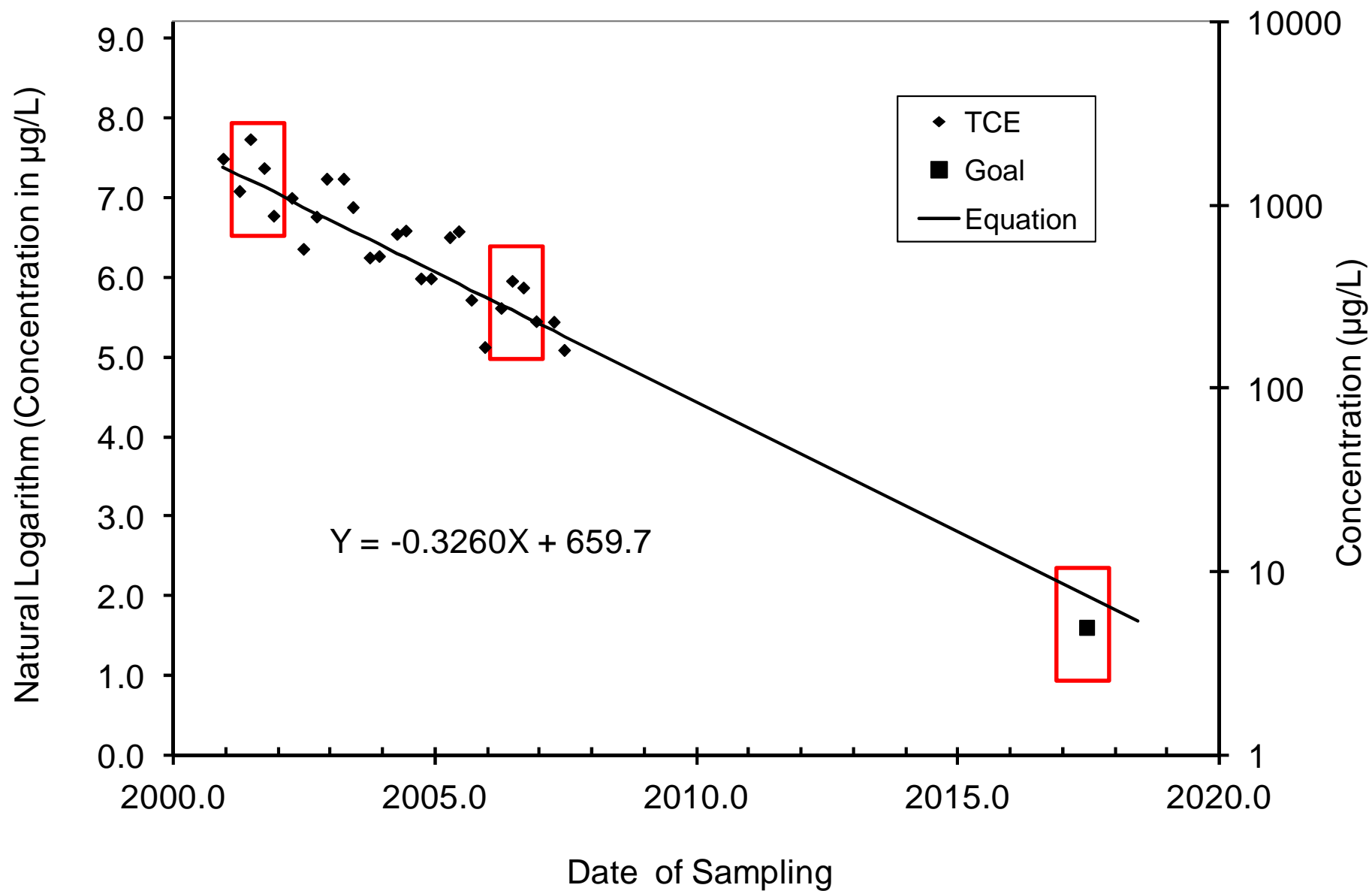
C_{ig} is the interim goal at the end of the first review cycle. This is the maximum concentration that must be attained if the rate of attenuation is adequate to meet the final clean up goal.

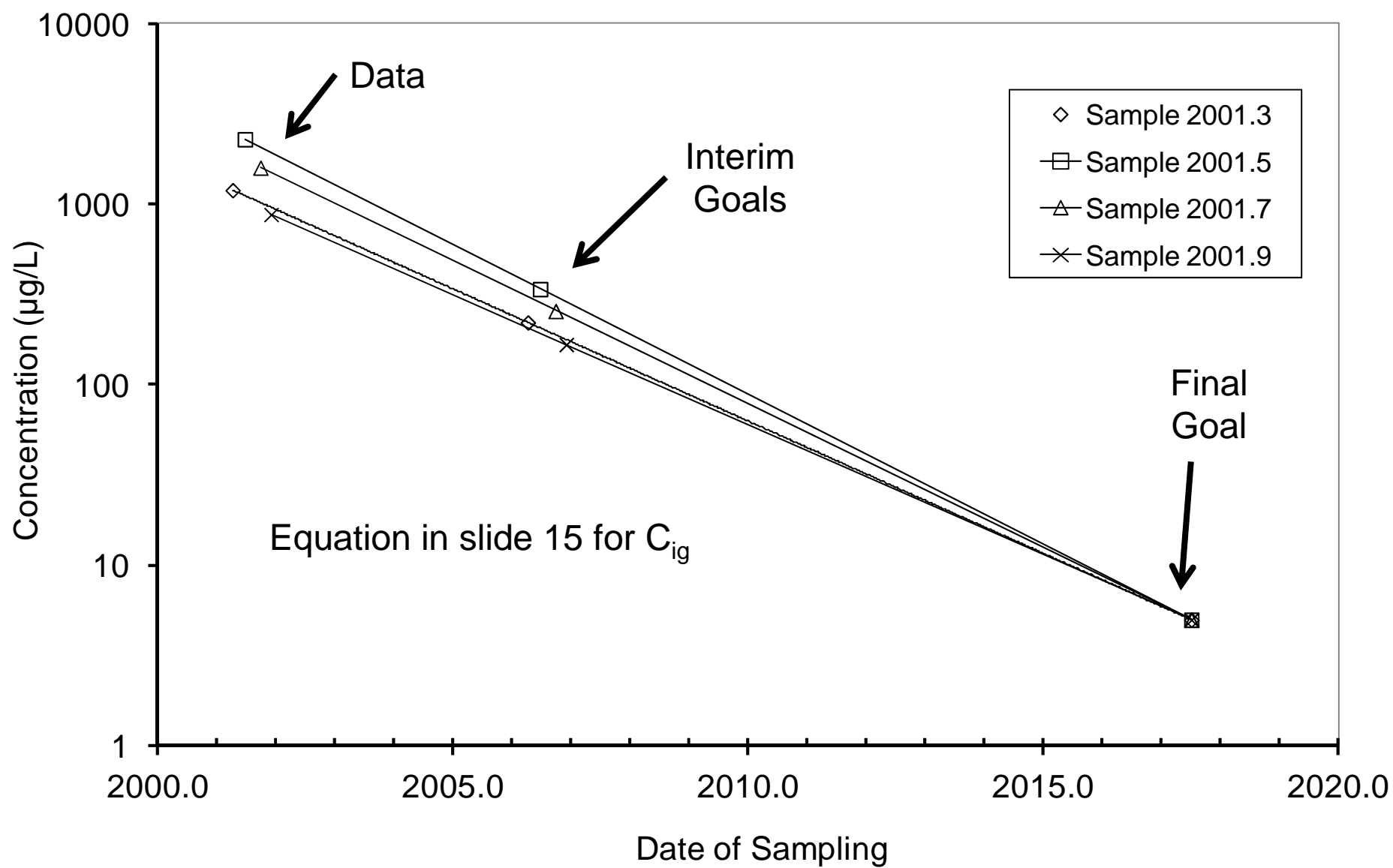
C_o is the concentration at the start of the first review cycle.

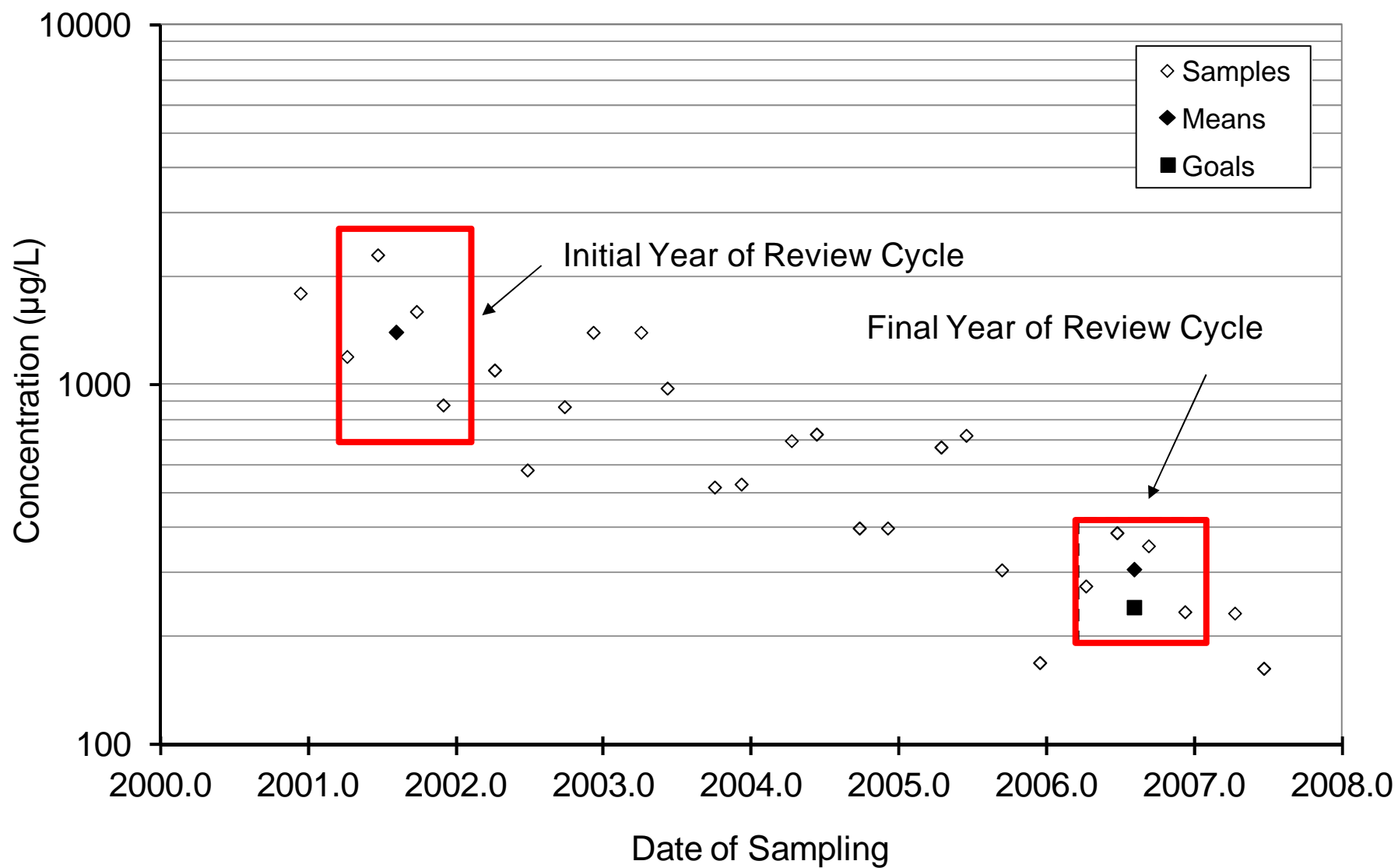
C_g is the final clean up goal.

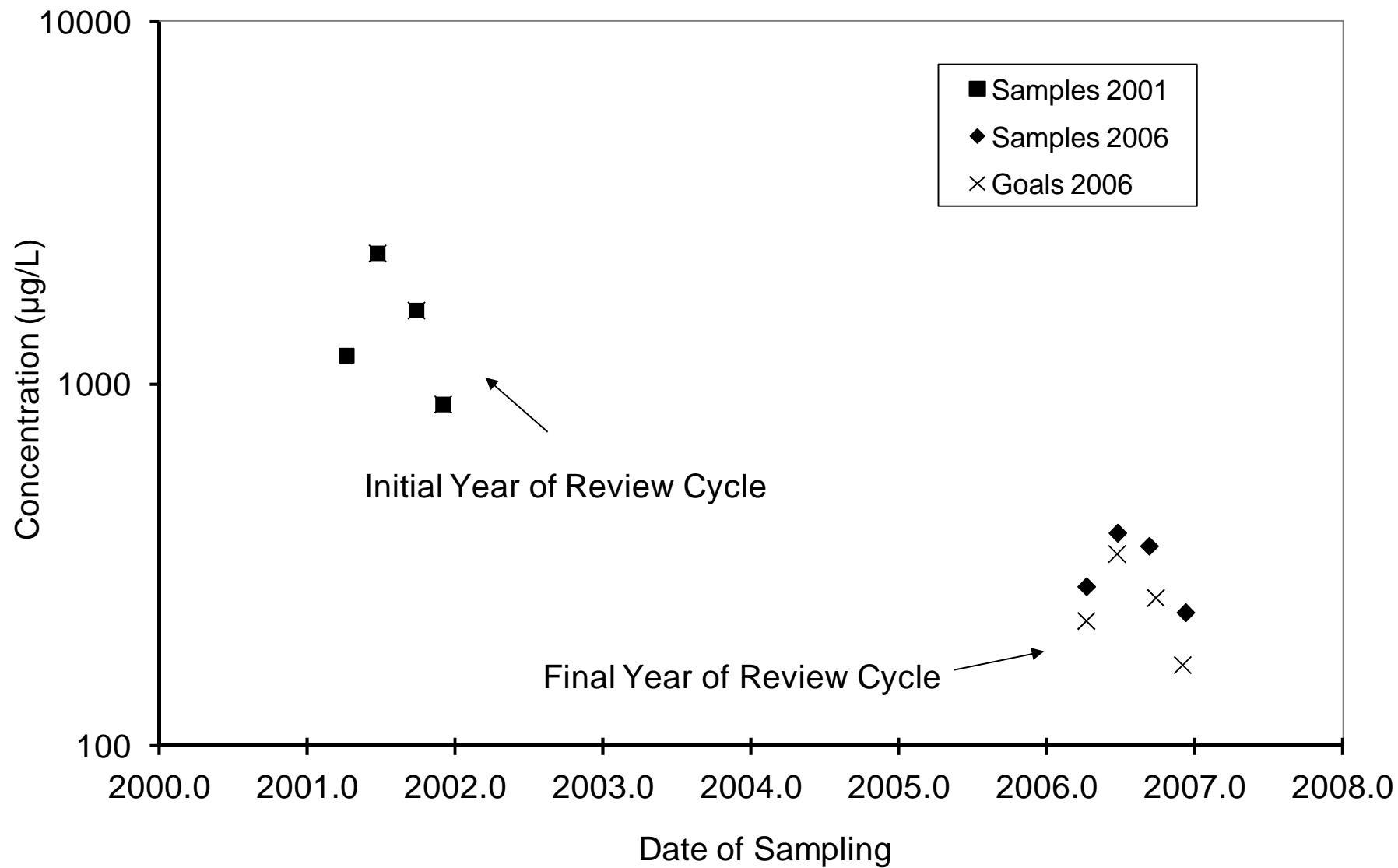
n is the number of review cycles that can be completed from the time of the start of the first review cycle to the time when the goal is to be obtained.



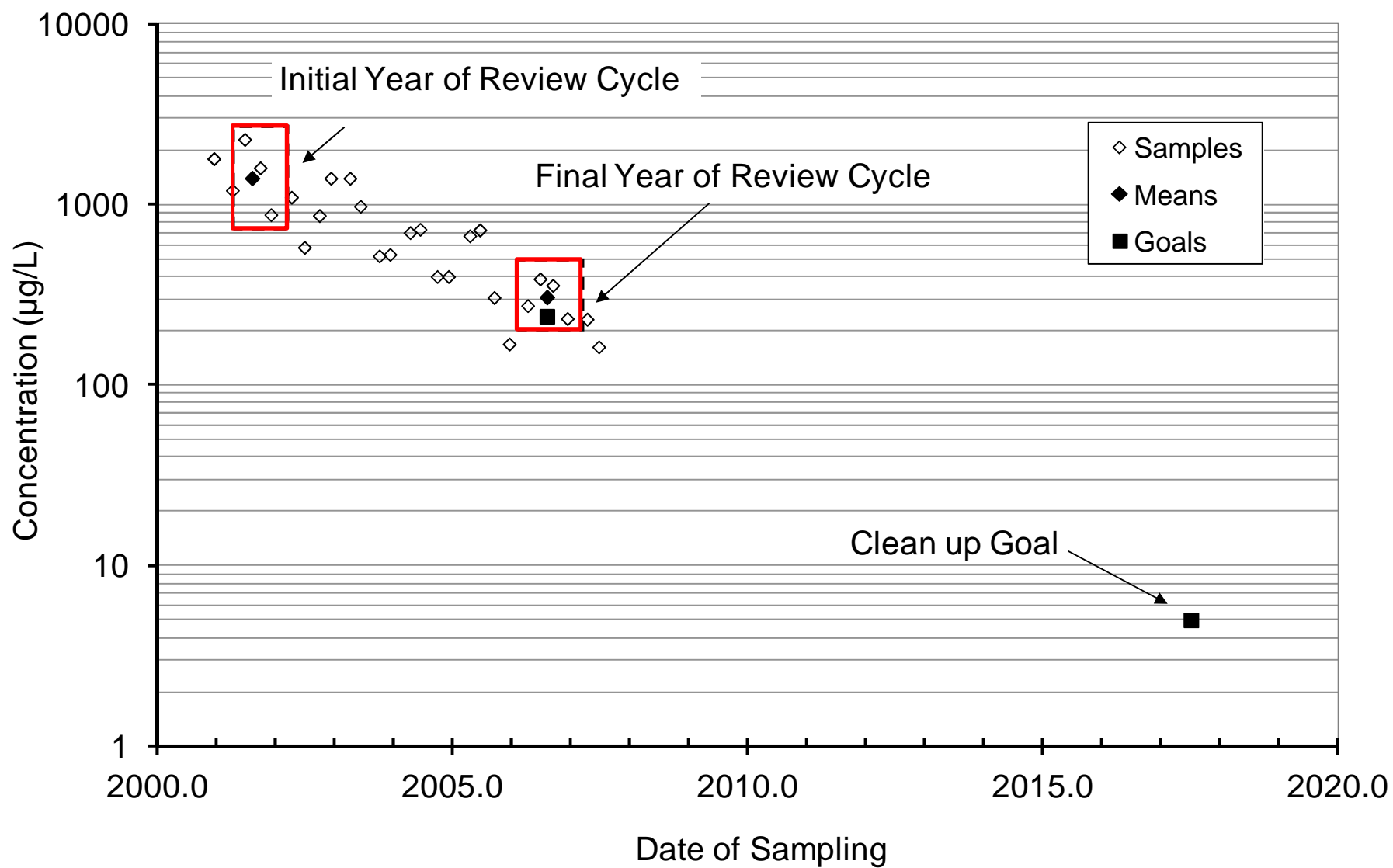








Notice that the concentrations required to be adequate are less than the actual concentrations.



You can't use statistics to prove that something is the same. We can't prove that attenuation is adequate to meet the goal.

You can use statistics to prove that something is different with a predetermined possibility of error.

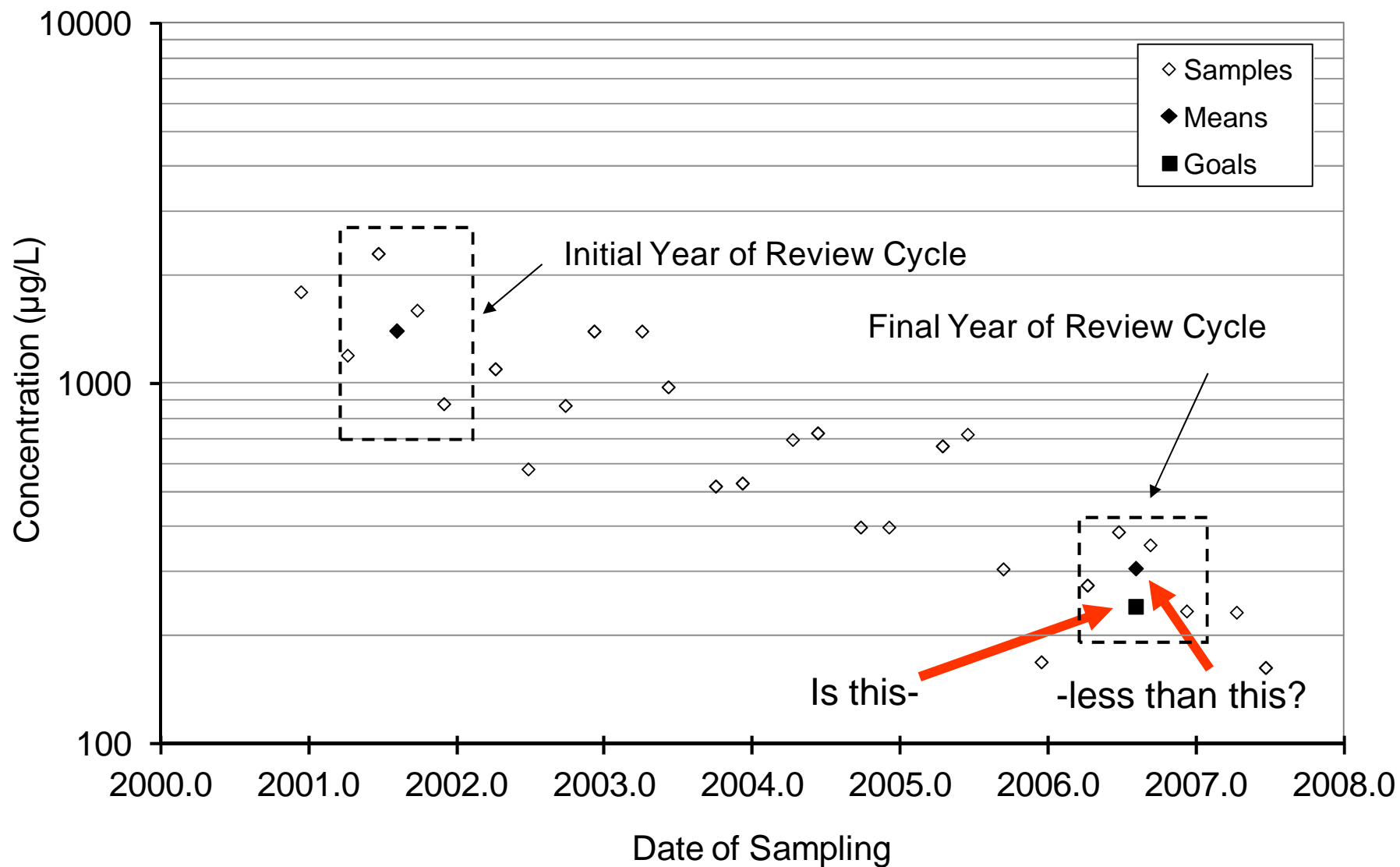
We can test if attenuation is not adequate to meet the goal at some level of confidence.



The following decision criterion will be used to determine if attenuation is adequate to meet the long term goal.

If the mean of the interim goals in the final year of the review cycle is less than the mean of the samples in the final year at some predetermined level of confidence, then attenuation will not be adequate to attain the goal.





We will use a t -test for the difference of means to compare the mean of the samples in the final year to the mean of interim goals.

To satisfy an important condition required to apply a t -test, we will conduct the calculations on the natural logarithm of the concentrations.



Data entry for
EvalMNA.xls

Data to be
entered are
formatted in red.

Copy new data
over the
example data.

	A	B	C	D	E	F
1						
2		Comparison of Initial Year of Review Cycle t				
3						
4		Date	Concentration	LN Conc.	Mean	Geometric
5			µg/L		LN Conc.	Mean of
6						Conc. (µg/L)
7						
8						
9						
10		Initial Year	Initial Year	Initial Year	Initial Year	Initial Year
11		n ₁ =?				
12		4				
13		4/4/2001	1200	7.090		= Co
14		6/19/2001	2300	7.741		
15		9/23/2001	1600	7.378	7.247	1404
16		11/28/2001	880	6.780		
17						
18						
19						
20		Final Year	Final Year	Final Year	Final Year	Final Year
21		n ₂ =?				
22		4				
23		4/5/2006	276	5.620		= Ci
24		6/21/2006	388	5.961		
25		9/7/2006	357	5.878	5.729	308
26		12/6/2006	234	5.455		
27						
28						
29						
30						

Enter α , the Acceptable Probability of Error

	J	K	L	M	N	O
1						
2						
3	Attenuation	Probability	Degrees	Critical Value	Difference	Attenuation
4	Factor	of Error	Freedom	Student's	of Means	Factor (Ci/Co)
5	<i>Ci/Co</i>	α one-tailed	in	<i>t</i>	required to be	required to be
6			Student's	(2 α , d.f.)	significant at	significant at
7			<i>t</i>		various levels	various levels
8					of α one-tailed	of α one-tailed
9						
10			4.755			
11						
12		0.4		0.271	-0.064	0.938
13		0.3		0.569	-0.134	0.875
14		0.2		0.941	-0.222	0.801
15		0.15		1.190	-0.280	0.756
16	0.219	0.1		1.533	-0.361	0.697
17		0.05		2.132	-0.502	0.605
18		0.025		2.776	-0.654	0.520
19		0.010		3.747	-0.883	0.414
20		0.005		4.604	-1.085	0.338
21		0.0025		5.598	-1.319	0.267
22						
23						

	P	Q	R	S	T
1					
2	Setting Interim Goals (C_{ig}) for Final Year of Review Cycle				
3					
4	Final Goal	Time Interval*	Time Interval	Interim	LN <i>Cig</i> required
5	or MCI	between years	from initial	Goal (<i>Cig</i>)	to be adequate
6	($\mu\text{g/L}$)	in review cycle	year to goal	required	to meet goal
7		(years)	(years)	to be on track	
8				to meet	
9				Final Goal	
10				($\mu\text{g/L}$)	
11					
12					
13	5	5	16	216	5.377
14				339	5.825
15		* length of review cycle		264	5.575
16				175	5.164
17					
18					
19					

	Z	AA	AB	AC	AD
1					
2					
3					
4	Probability	Degrees	Critical Value	Difference	
5	of Error	Freedom	Student's	of Means	
6	α one-tailed	in	t	required for	
7		Student's	(2α , d.f.)	C_i to be	Attenuation
8		t		statistically	Adequate
9				different	to Attain Goal?
10				from C_{ig}	
11		5.795			
12					
13	0.4		0.267	-0.049	No
14	0.3		0.559	-0.102	No
15	0.2		0.920	-0.168	No
16	0.15		1.288	-0.235	No
17	0.1		1.476	-0.270	No evidence not adequate
18	0.05		2.015	-0.368	No evidence not adequate
19	0.025		2.571	-0.470	No evidence not adequate
20	0.01		3.365	-0.615	No evidence not adequate
21	0.005		4.032	-0.737	No evidence not adequate
22	0.0025		4.773	-0.872	No evidence not adequate
23					
24					



If the mean of the interim goals in the final year of the review cycle is less than the mean of the samples in the final year at some predetermined level of confidence, then attenuation will not be on track to attain the goal.

These data indicate that natural attenuation over the review cycle is not adequate to meet the goal.

There is a 15% chance of error in that finding. An error in this case would mean that MNA truly is on track.



Most of the time in statistics, you use the statistical test to protect yourself from accepting something in the data that you want to accept, when that something in the data is really not true.

A higher level of confidence, or lower probability of error, is good. You reduce the chance of making a mistake.



Statisticians recognize two types of error in drawing an inference from a data set.

Type I error draws an inference from the data set when the inference is not true.

Type II error fails to draw an inference from the data set even though the inference is true



Type I error sees something that is really not there.

Type II error fails to see something that really is there.



Prior to selection of MNA as a remedy, the default presumption is that the rate of attenuation **is not** adequate to attain the cleanup goal by the specified time



If the null hypothesis (the expected behavior) is that the rate of attenuation **is not** adequate to attain the cleanup goal by the specified time (H_0)

and-

the rate of attenuation **is truly not** adequate to attain the cleanup goal by the specified time (H_0 is true)-

but we reject H_0 anyway and say the rate **is** adequate,

that is a Type I error.



The probability of Type I error is described by α .

To protect from Type I error we want α to be as small as possible.

The confidence in a test is $1-\alpha$.

If α were 0.05, the confidence would be 0.95 or 95%



After selection of MNA as a remedy, the default presumption is that the rate of attenuation **is** adequate to attain the cleanup goal by the specified time.

It says so in the ROD.



If the null hypothesis (H_0 , the expected behavior) is that the rate of attenuation **is** adequate to attain the cleanup goal by the specified time

and-

the rate of attenuation **is truly not** adequate to attain the cleanup goal by the specified time (H_0 is false)-

but we fail to reject H_0 anyway, and say the rate **is** adequate,

that is a Type II error.



The probability of Type II error is described by β .

To protect from Type II error we want β to be as small as possible.

The values of β and α are inversely related.

The power of a test is $1-\beta$.



Evaluation of MNA prior to a ROD

The null hypothesis (H_0) is-

The rate of attenuation **is not** adequate to attain the cleanup goal by the time specified.

	H_0 is true	H_0 is false
Fail to Reject H_0	Correct Decision	Type II error (probability β)
Reject H_0	Type I error (probability α)	Correct Decision



Five year review after a ROD is signed

The null hypothesis (H_0) is-

The rate of attenuation **is** adequate to attain the cleanup goal by the time specified.

	H_0 is true	H_0 is false
Fail to Reject H_0	Correct Decision	Type II error (probability β)
Reject H_0	Type I error (probability α)	Correct Decision



Both types of error are important to an evaluation of natural attenuation after MNA is selected for a site.

Someone who is trying to support the use of MNA might want to determine that MNA is adequate to attain the goal.

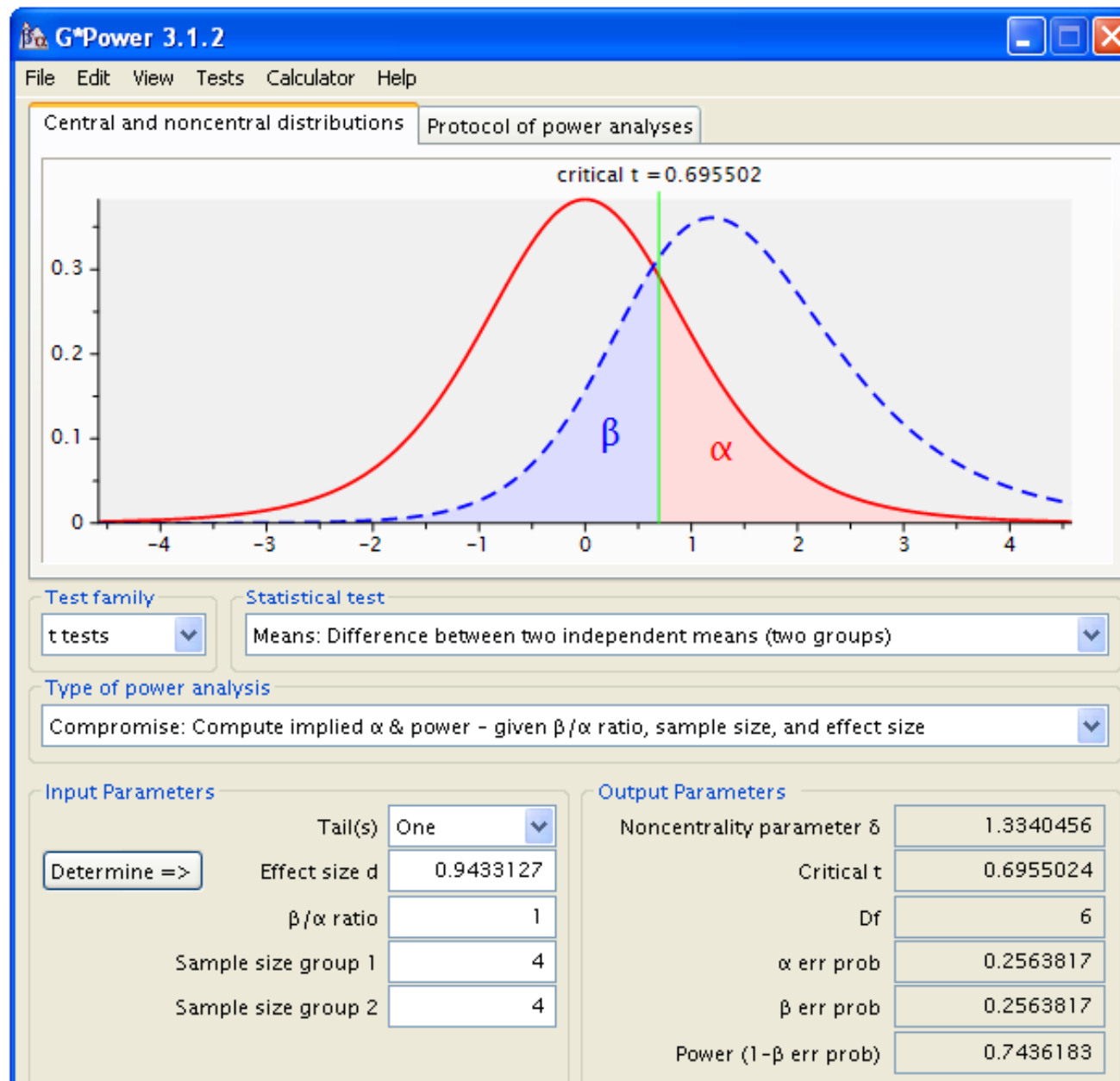
This person would want to minimize Type I error, and would select small values of α and corresponding large values of β .



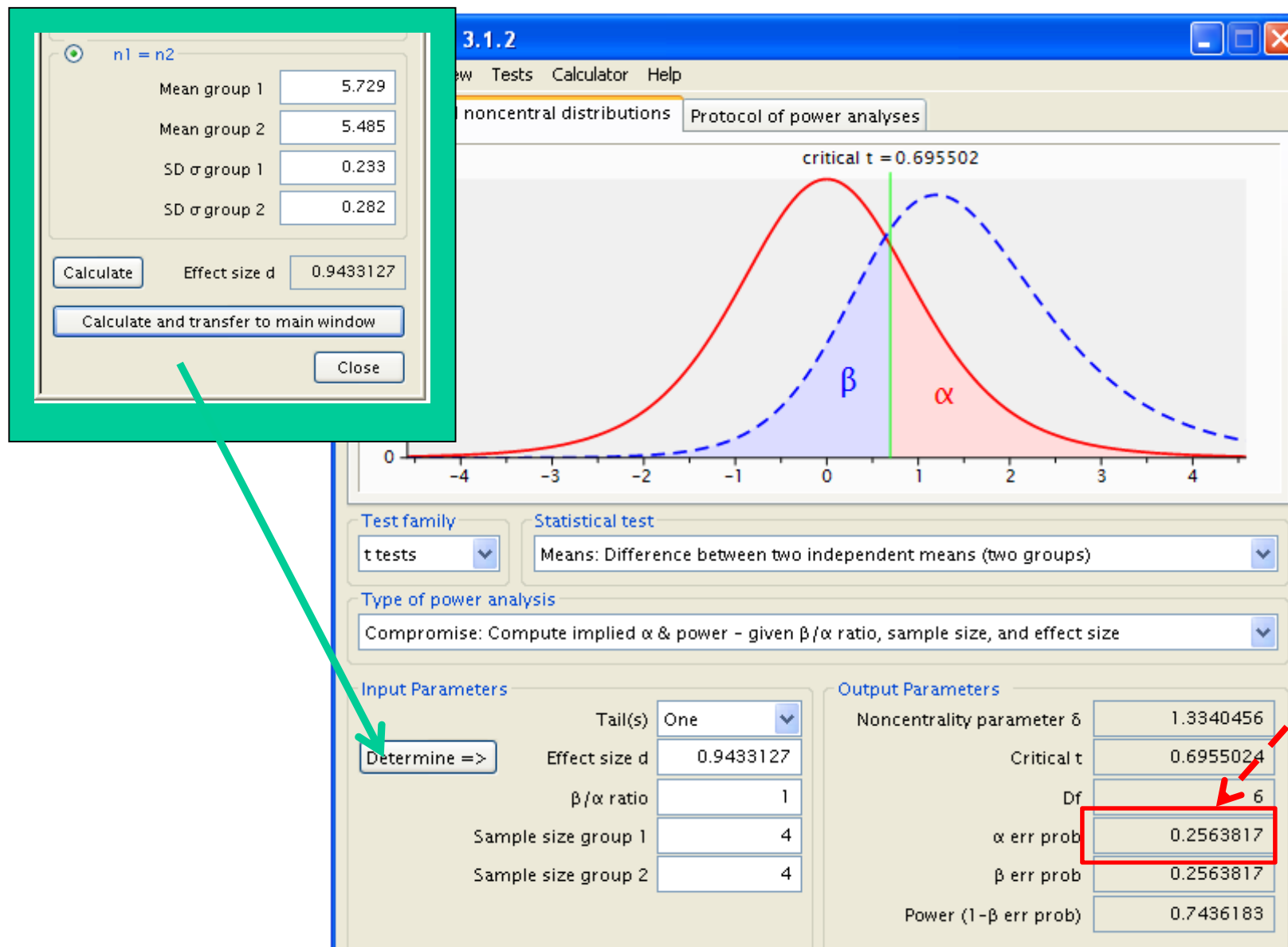
Alternatively, someone who is concerned that attenuation is not adequate to meet the long term goal would want to be sure that the statistical test warns that attenuation is not adequate, when in fact, attenuation is not adequate.

This person would want to minimize Type II error, and would select large values of α and corresponding small values of β .





<http://www.psych.uni-duesseldorf.de/abteilungen/aap/gpower3/download-and-register>



1	Z	AA	AB	AC	AD
2					
3					
4	Probability	Degrees	Critical Value	Difference	
5	of Error	Freedom	Student's	of Means	
6	α one-tailed	in	t	required for	
7		Student's	(2α , d.f.)	C_i to be	Attenuation
8				statistically	Adequate
9				different	to Attain Goal?
10				from C_{ig}	
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21	0.005		4.032	-0.737	No evidence not adequate
22	0.0025		4.773	-0.872	No evidence not adequate
23					



The values of α and β depend on n .

As n increases, the values of α and β decrease.

If α and β are not adequate to support site specific needs for decision making, increase the number of samples.

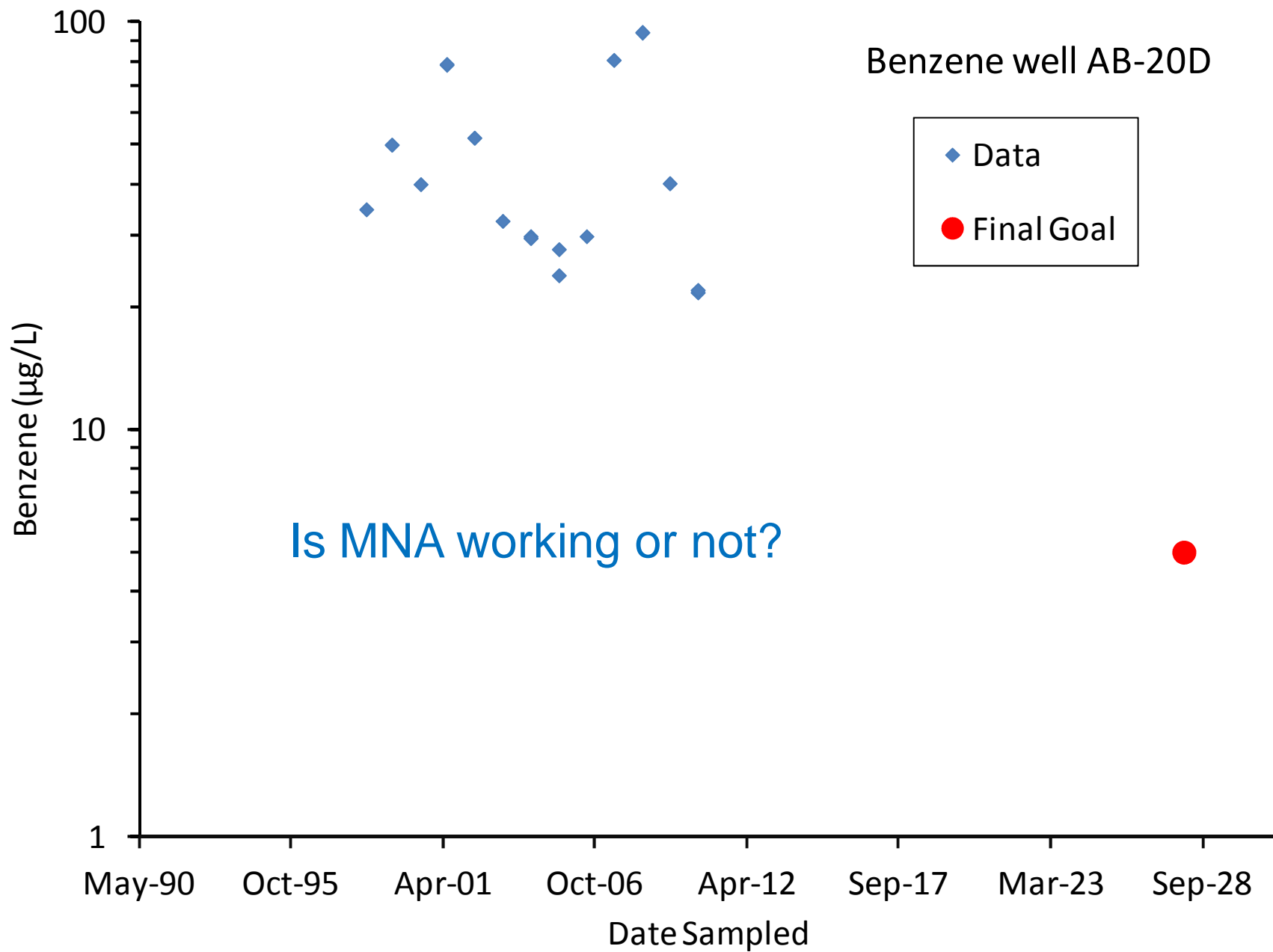


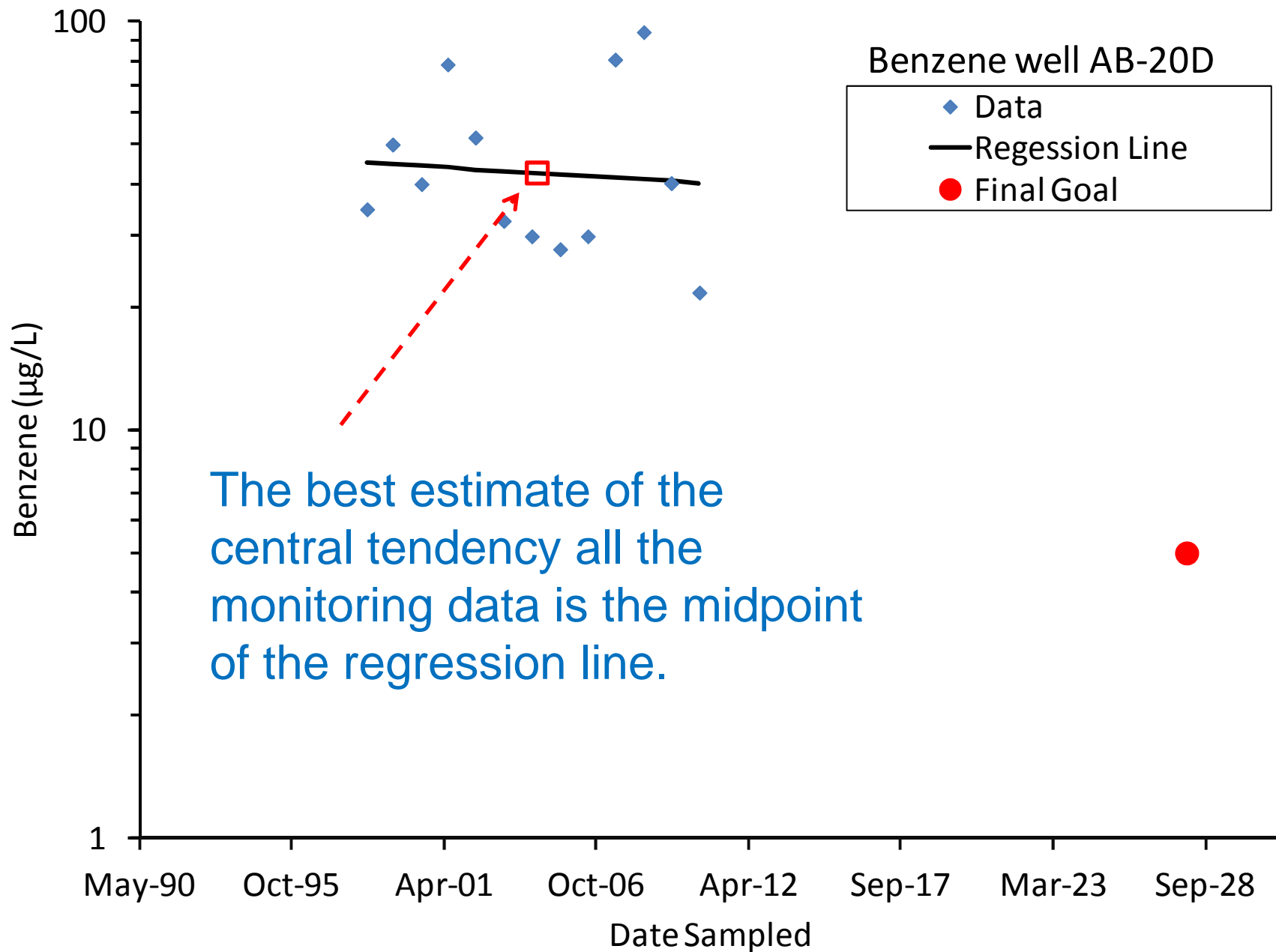
What if you want to analyze all the data, not just the first and final year?

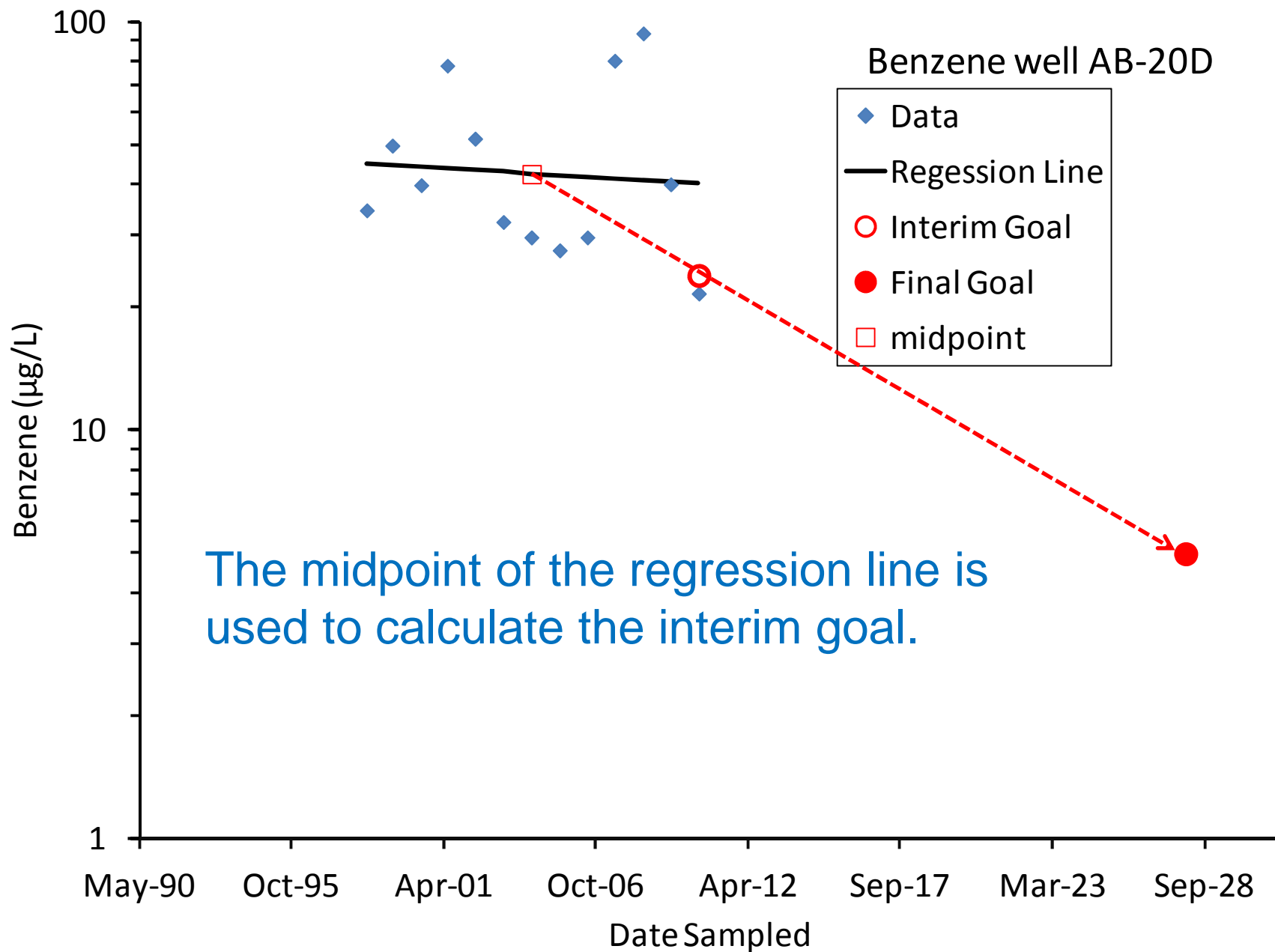
What if there is something “atypical” about the first or final year of data?

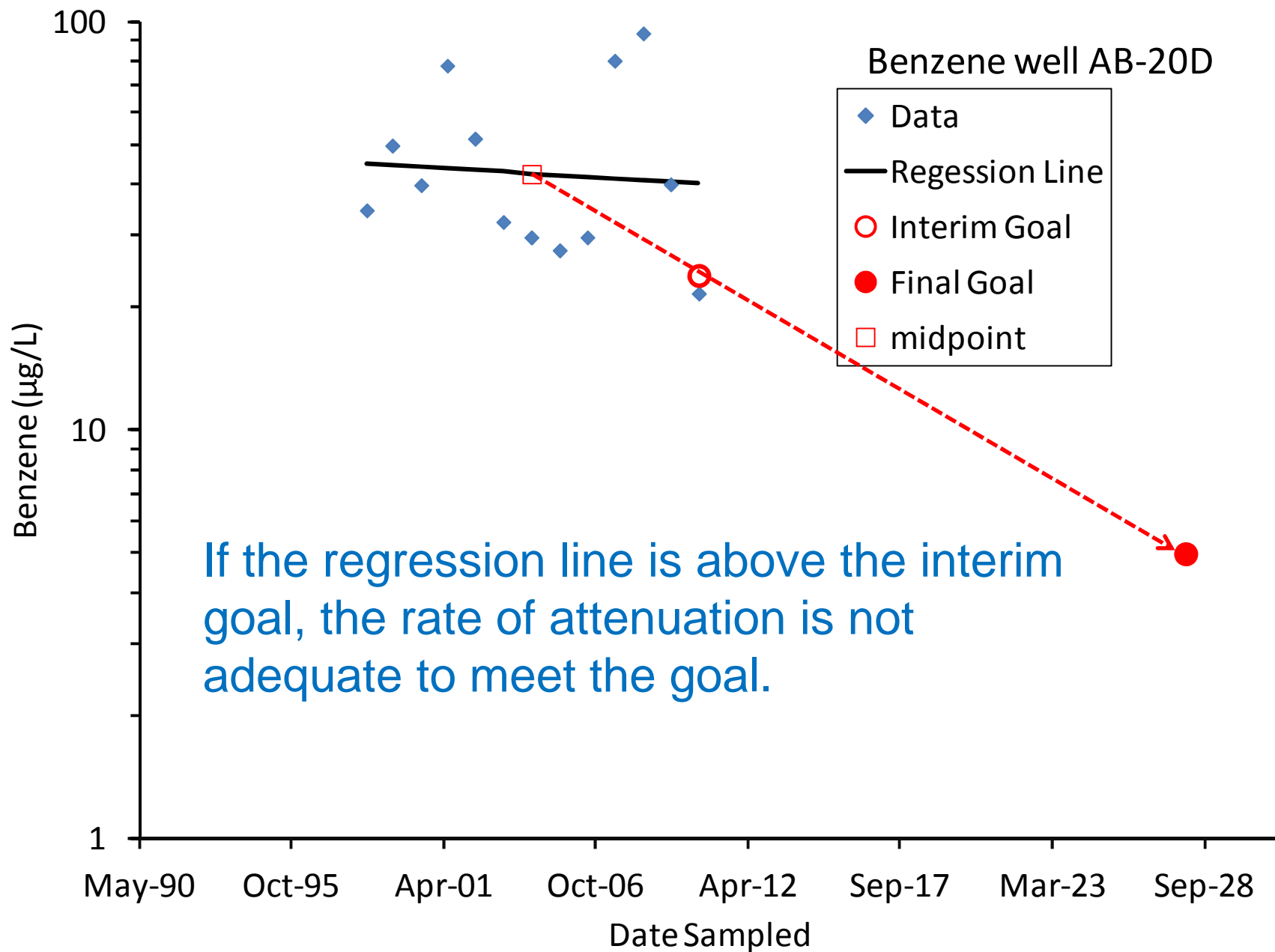
What if you only have one sample in each year?











But what about the uncertainty in the data?

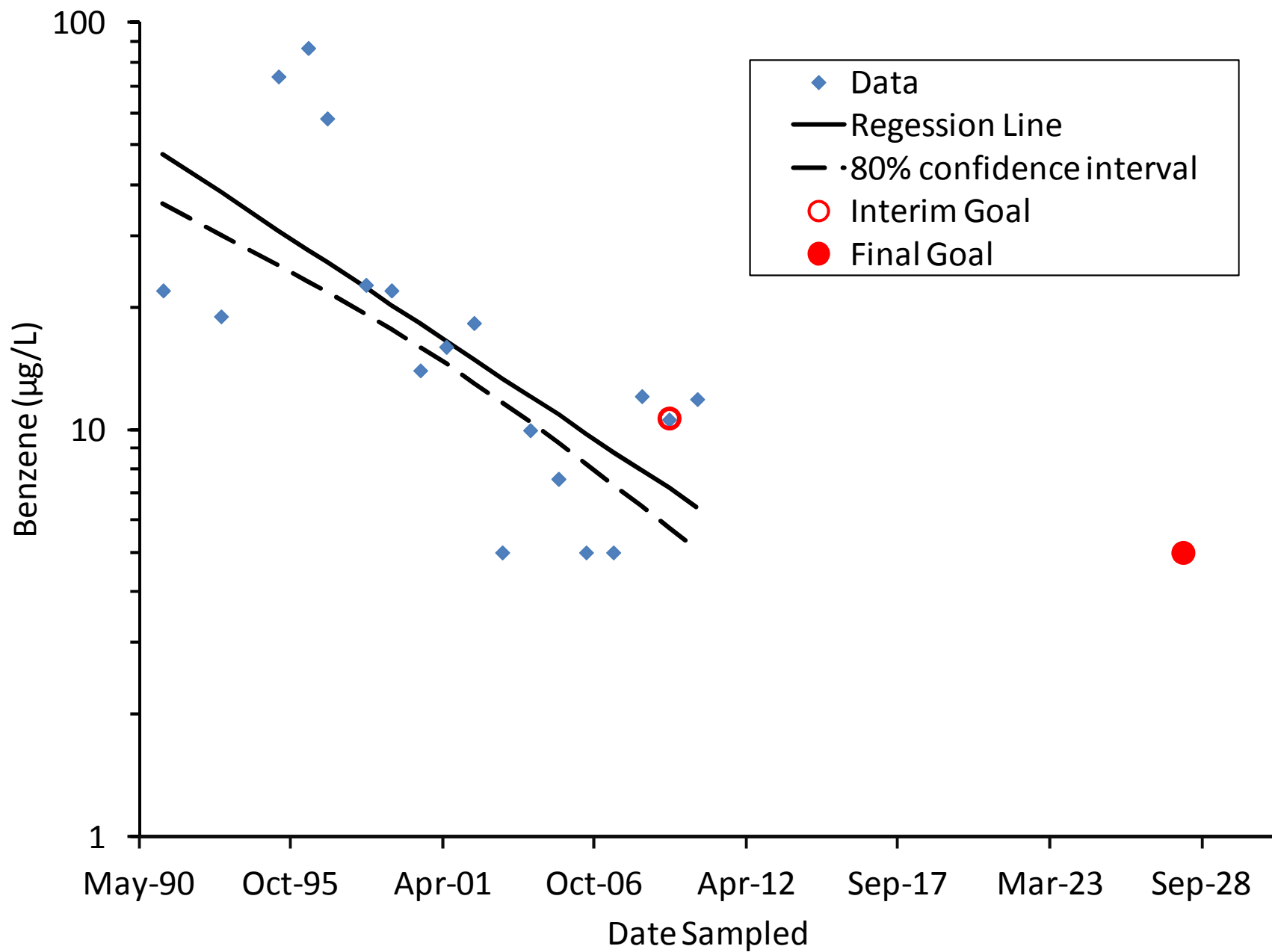


You can compare the statistical confidence bands on the regression line.

Put all the possibility of error on values less than the line.

Calculate a one-tailed confidence band, and compare the confidence band to the interim goal.





Regression MNA (.xls)



	Date	Y Value	Number of	Ln Y	Date or X	X ²	Σ X
	Julian	µg/L	Samples		Decimal Years		
							48098
Interm goal→	12/6/2006	219.7			2006.9		
Final goal→	1/1/2017	5			2017.0		
Data →	4/4/2001	1200	1	7.090	2001.3	4005039.23	
	6/19/2001	2300	2	7.741	2001.5	4005872.11	
	9/23/2001	1600	3	7.378	2001.7	4006924.28	
	11/28/2001	880	4	6.780	2001.9	4007647.73	
	4/4/2002	1100	5	7.003	2002.3	4009040.01	
	6/24/2002	580	6	6.363	2002.5	4009928.12	
	9/24/2002	870	7	6.768	2002.7	4010936.97	
	12/4/2002	1400	8	7.244	2002.9	4011715.62	
	4/1/2003	1400	9	7.244	2003.2	4013009.88	
	6/5/2003	980	10	6.888	2003.4	4013722.91	
	9/30/2003	520	11	6.254	2003.7	4015006.52	
	12/5/2003	530	12	6.273	2003.9	4015730.70	
	4/7/2004	700	13	6.551	2004.3	4017091.46	
	6/8/2004	730	14	6.593	2004.4	4017771.92	
	9/22/2004	400	15	5.991	2004.7	4018935.43	
	12/1/2004	400	16	5.991	2004.9	4019703.88	
	4/12/2005	672	17	6.510	2005.3	4021153.15	
	6/13/2005	724	18	6.585	2005.5	4021833.96	
	9/9/2005	306	19	5.724	2005.7	4022800.37	
	12/12/2005	169	20	5.130	2005.9	4023832.79	
	4/5/2006	276	21	5.620	2006.3	4025085.06	
	6/21/2006	388	22	5.961	2006.5	4025931.01	
	9/7/2006	357	23	5.878	2006.7	4026788.03	
	12/6/2006	234	24	5.455	2006.9	4027777.01	

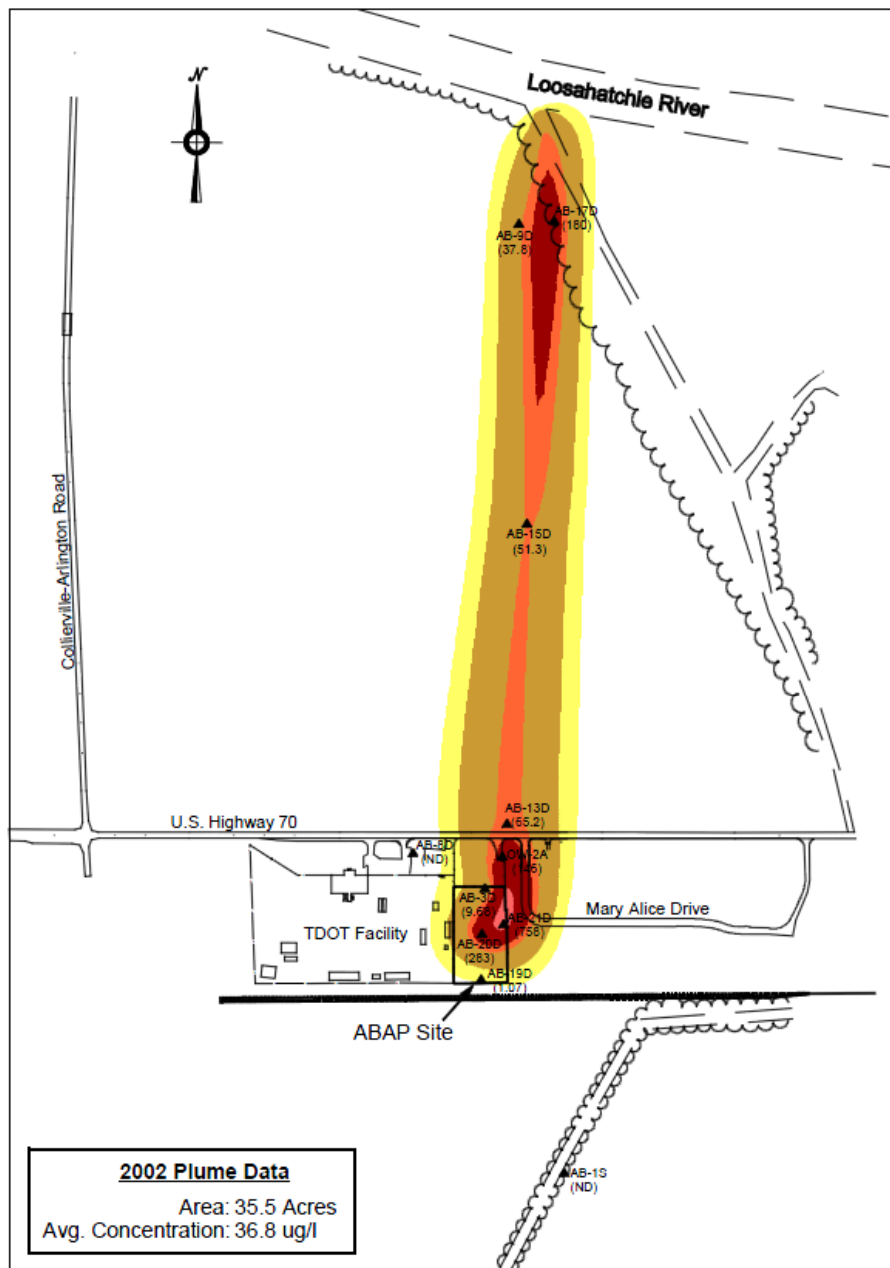


	AE	AF	AG	AH	AI	AJ
13		First Confidence Interval				
14		α	critical value	Length	Value	
15			t	Natural Logarithm	Confidence Interval	
16				Confidence Interval		
17						
18		0.2	0.858266052			
19						
20						
21						
22				0.122566043	1375.9	
23				0.116066186	1297.2	
24				0.108079572	1203.9	
25				0.102761589	1143.5	
26				0.093023586	1035.1	
27				0.087234873	971.0	
28				0.081164881	902.5	
29				0.076924563	852.6	
30				0.070934232	774.9	
31				0.068305015	734.7	
32				0.064997457	666.5	
33				0.064028396	630.3	
34				0.064077957	566.5	
35				0.065017305	536.5	
36				0.067948022	488.3	
37				0.070713736	458.5	
38				0.077438028	406.5	
39				0.081164881	383.9	
40				0.086959046	353.9	
41				0.093688968	324.2	
42				0.102444409	291.3	
43				0.108652414	270.9	
44				0.115137577	251.7	
45				0.122825439	231.2	
46						



	AJ	AK	AL	AM	AN	AO
13		Second Confidence Interval				
14		α	critical value	Length	Value	
15			t	Natural Logarithm	Confidence Interval	
16				Confidence Interval		
17						
18		0.05	1.717144335			
19						
20						
21						
22				0.245219516	1217.1	
23				0.232215165	1155.0	
24				0.216236241	1080.5	
25				0.205596482	1031.7	
26				0.186113529	943.1	
27				0.174531974	889.8	
28				0.16238766	832.1	
29				0.153903999	789.5	
30				0.141919064	721.8	
31				0.136658755	686.1	
32				0.130041279	624.5	
33				0.128102466	591.2	
34				0.128201622	531.3	
35				0.130080989	502.7	
36				0.135944514	456.2	
37				0.141477914	427.1	
38				0.154931296	376.2	
39				0.16238766	354.0	
40				0.173980123	324.4	
41				0.187444768	295.2	
42				0.204961895	262.9	
43				0.217382334	243.0	
44				0.230357286	224.3	
45				0.245738494	204.4	
46						

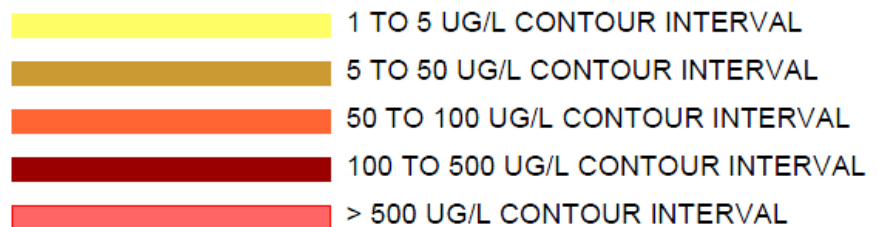


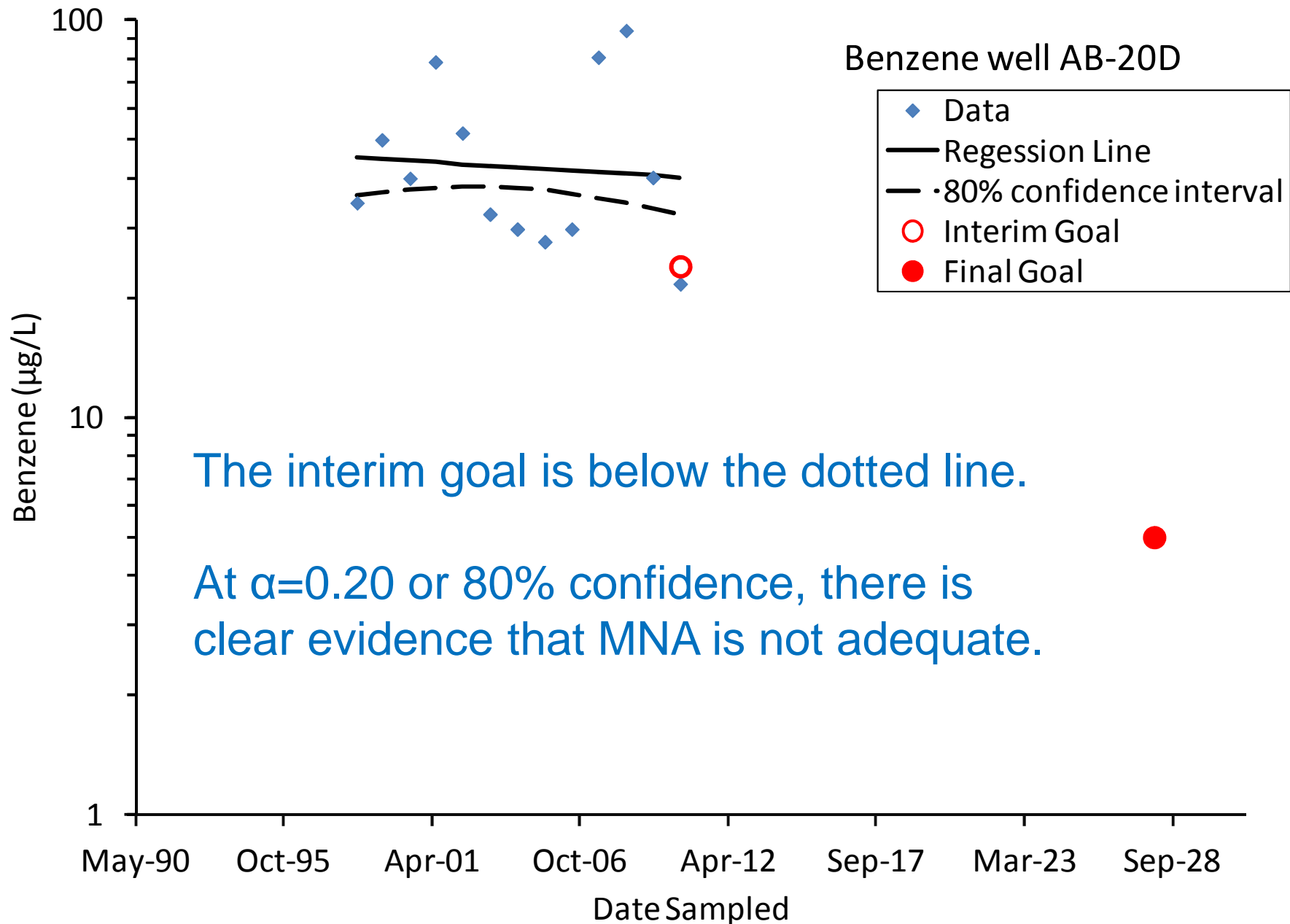


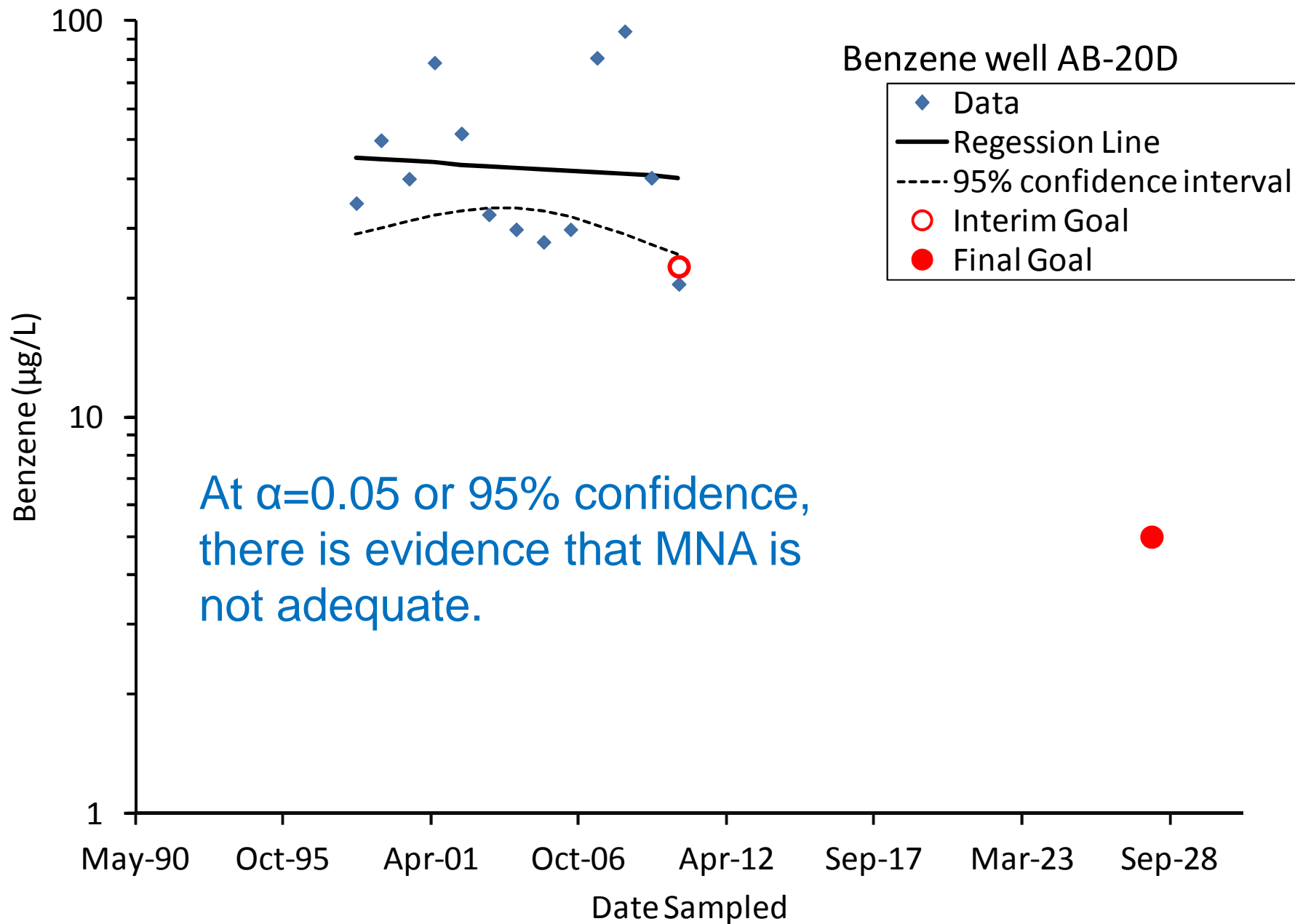
Pentachlorophenol (PCP)

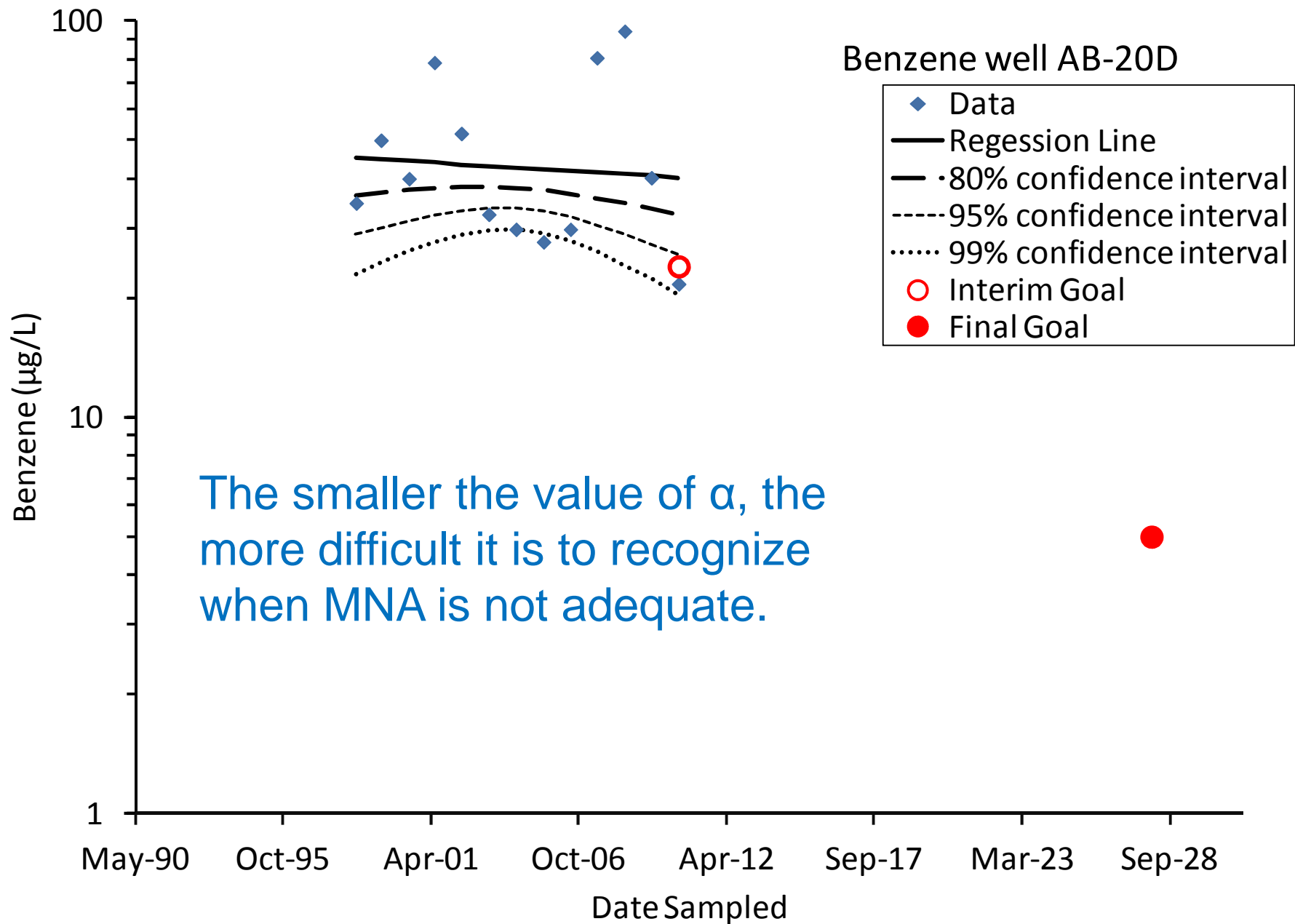
Ground Water flow

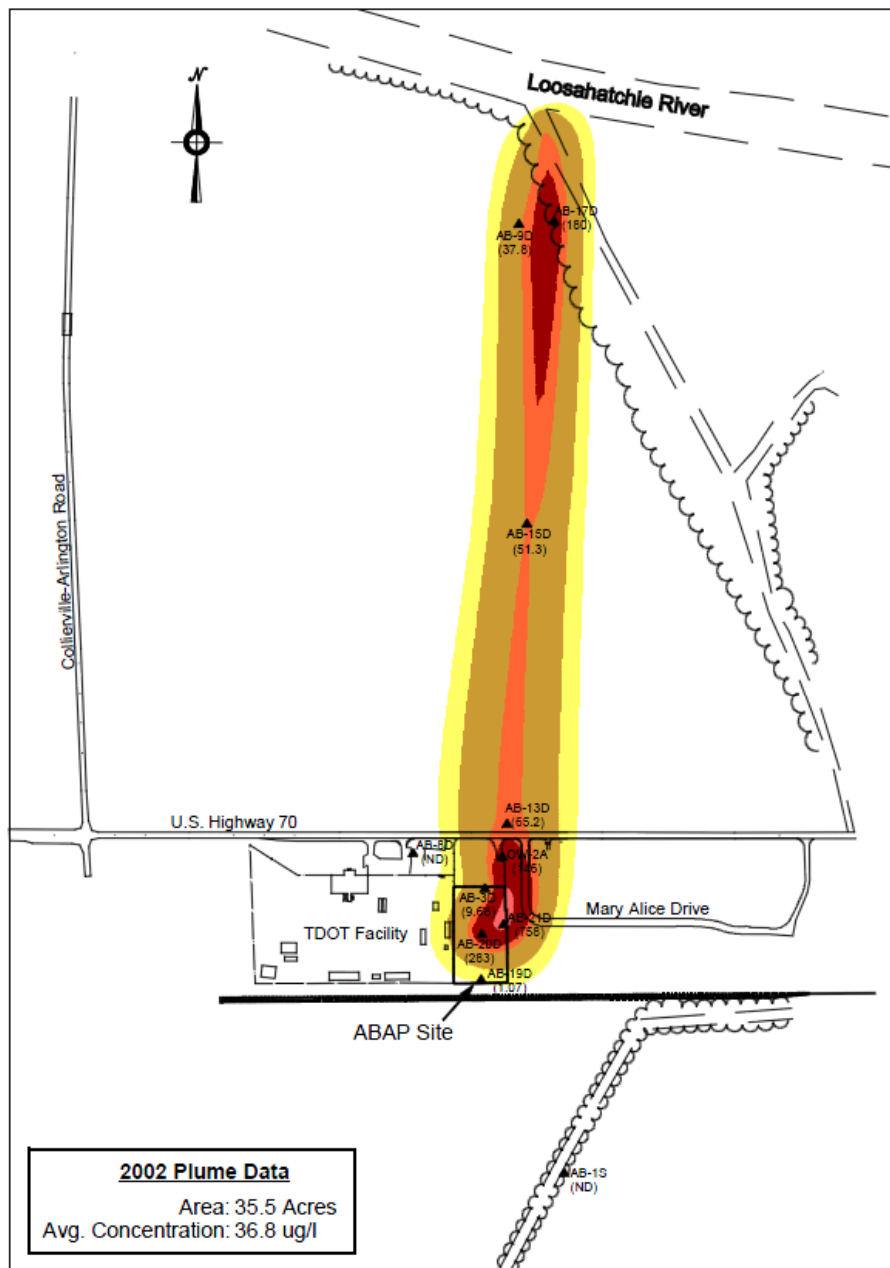
LEGEND











Pentachlorophenol (PCP)

Ground Water flow

LEGEND

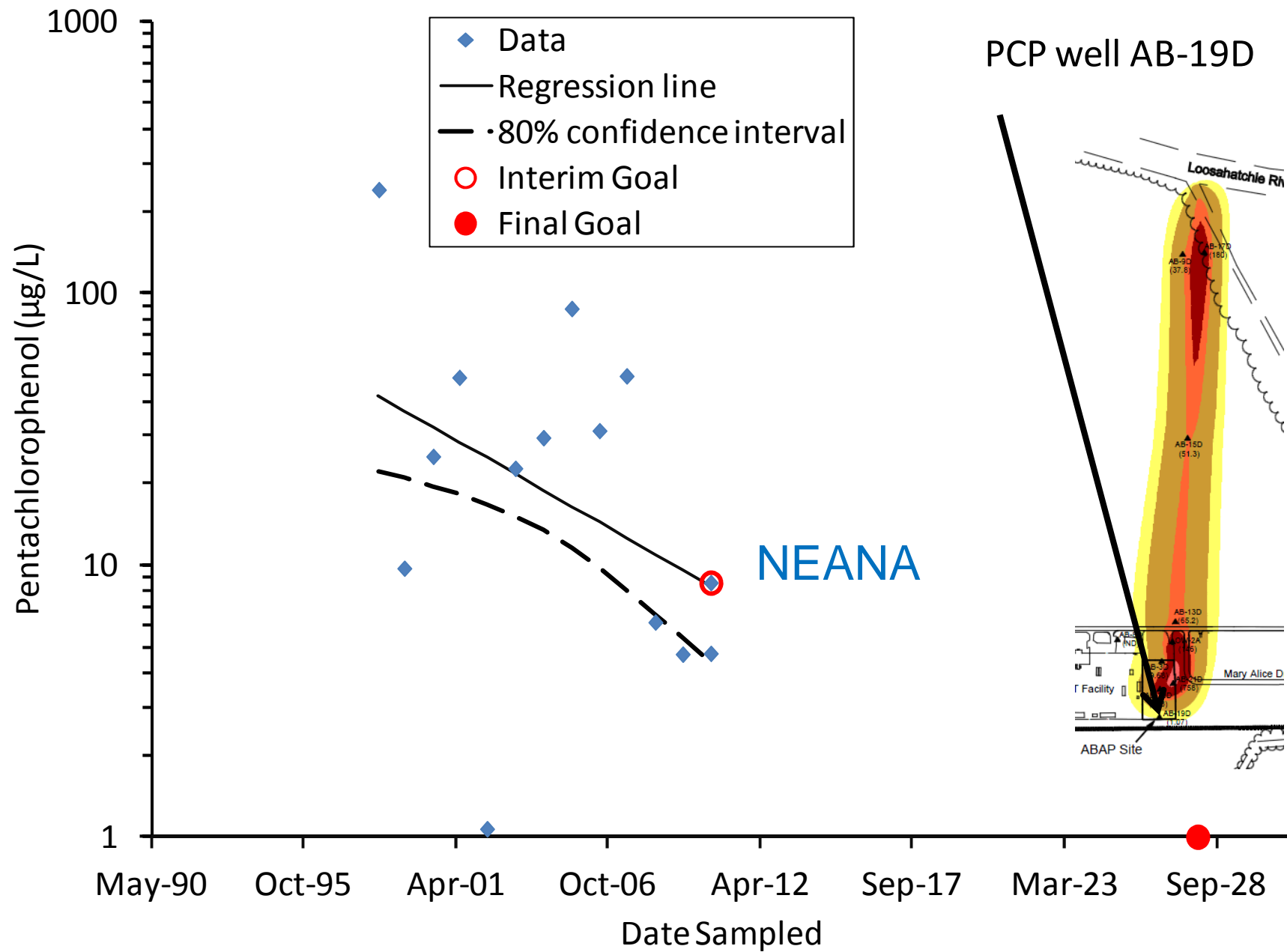


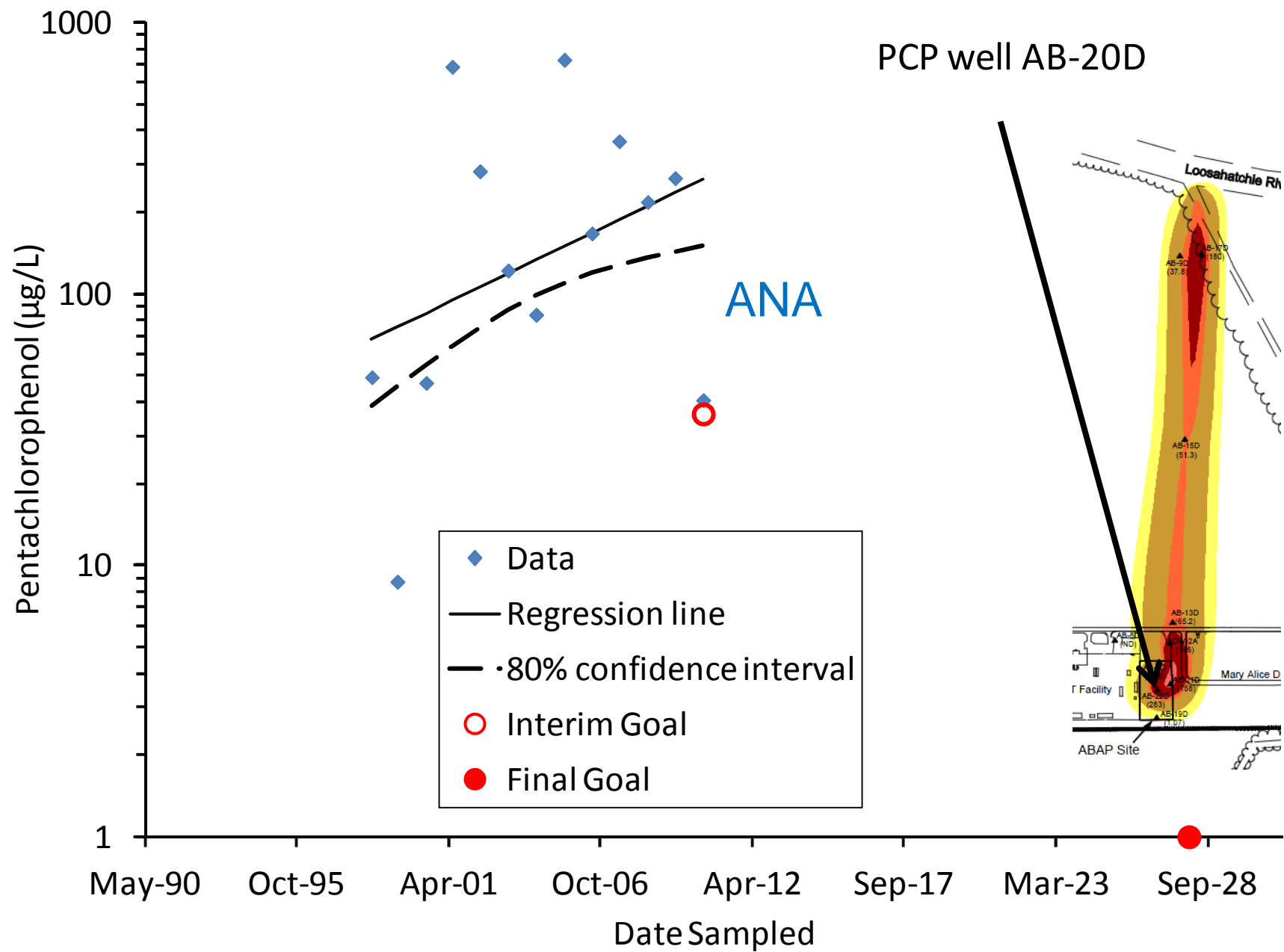
For purposes of this presentation:

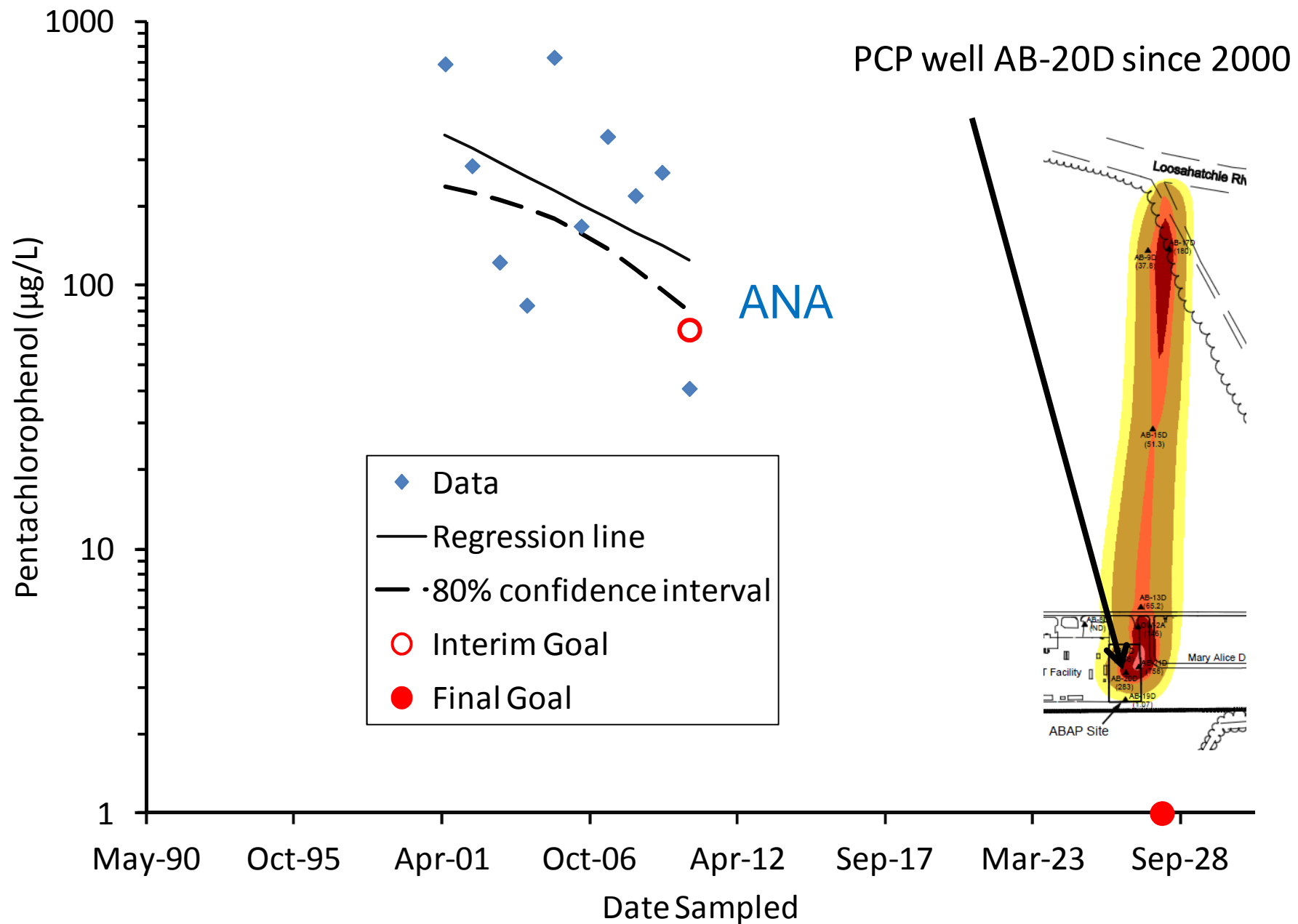
ANA means the rate of attenuation is not adequate at the selected level of confidence. There might be a problem here.

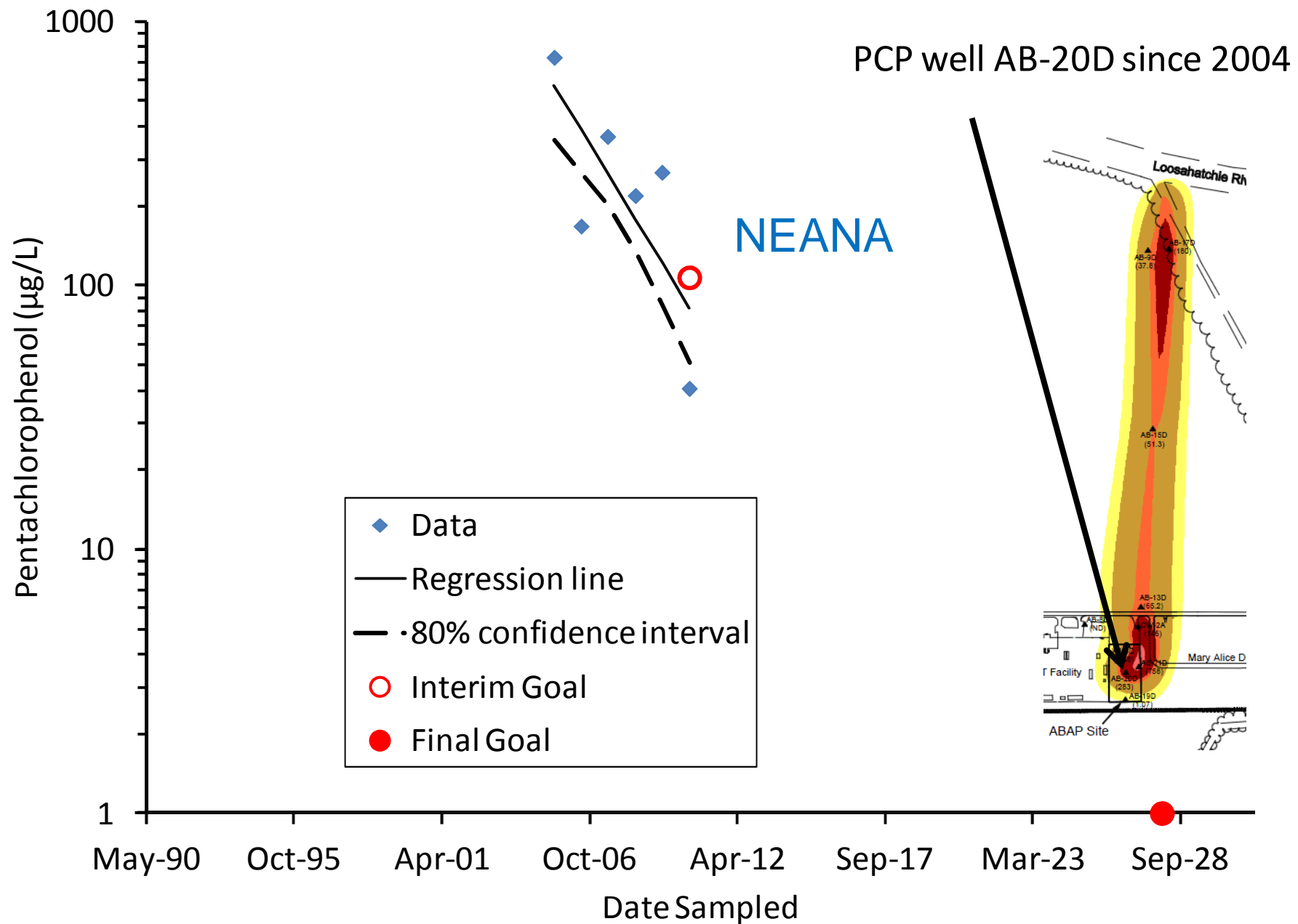
NEANA means no evidence at the selected level of confidence that the rate of attenuation is not adequate to attain the concentration based goal by the time specified. This is good, move on.

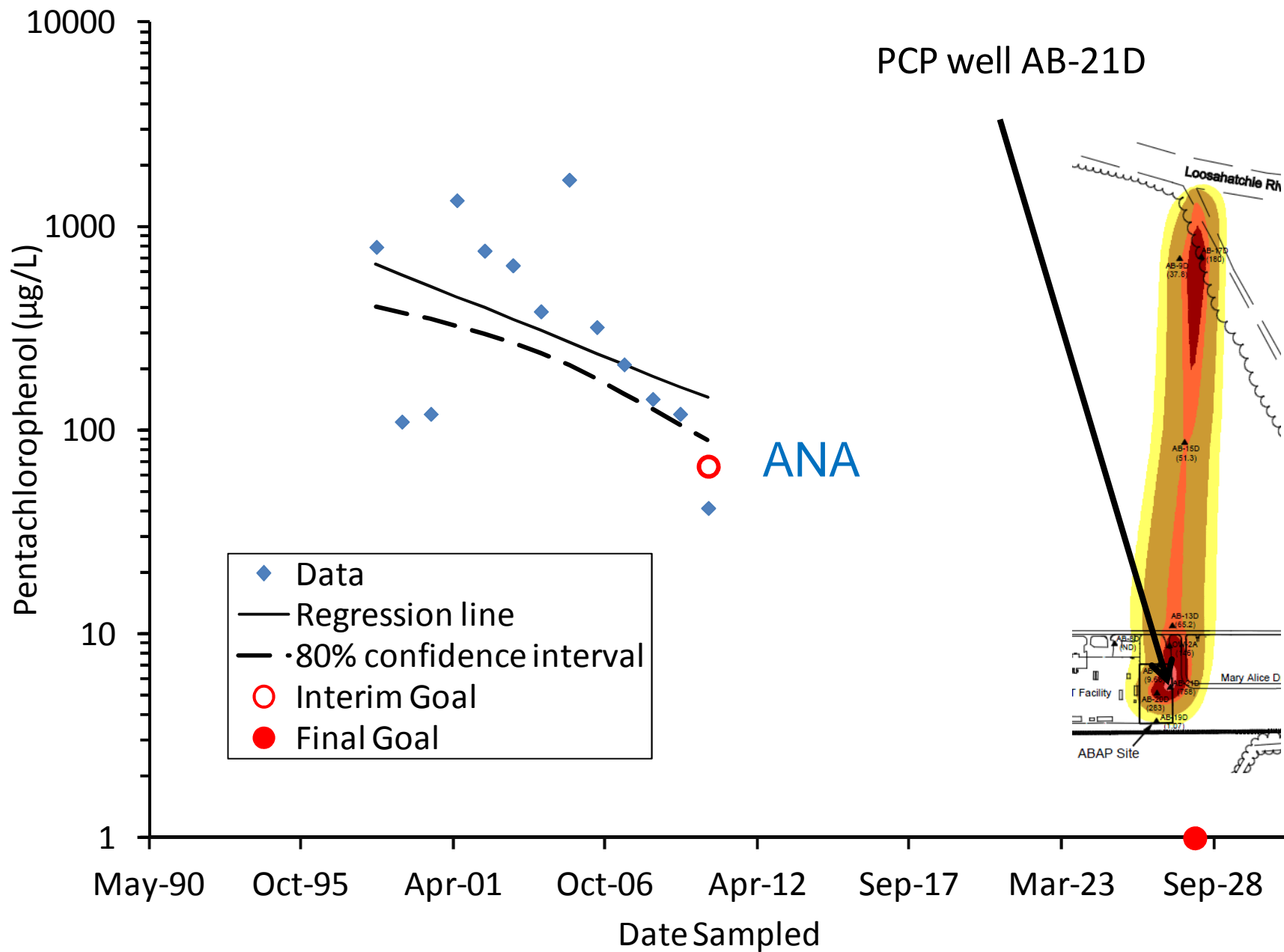


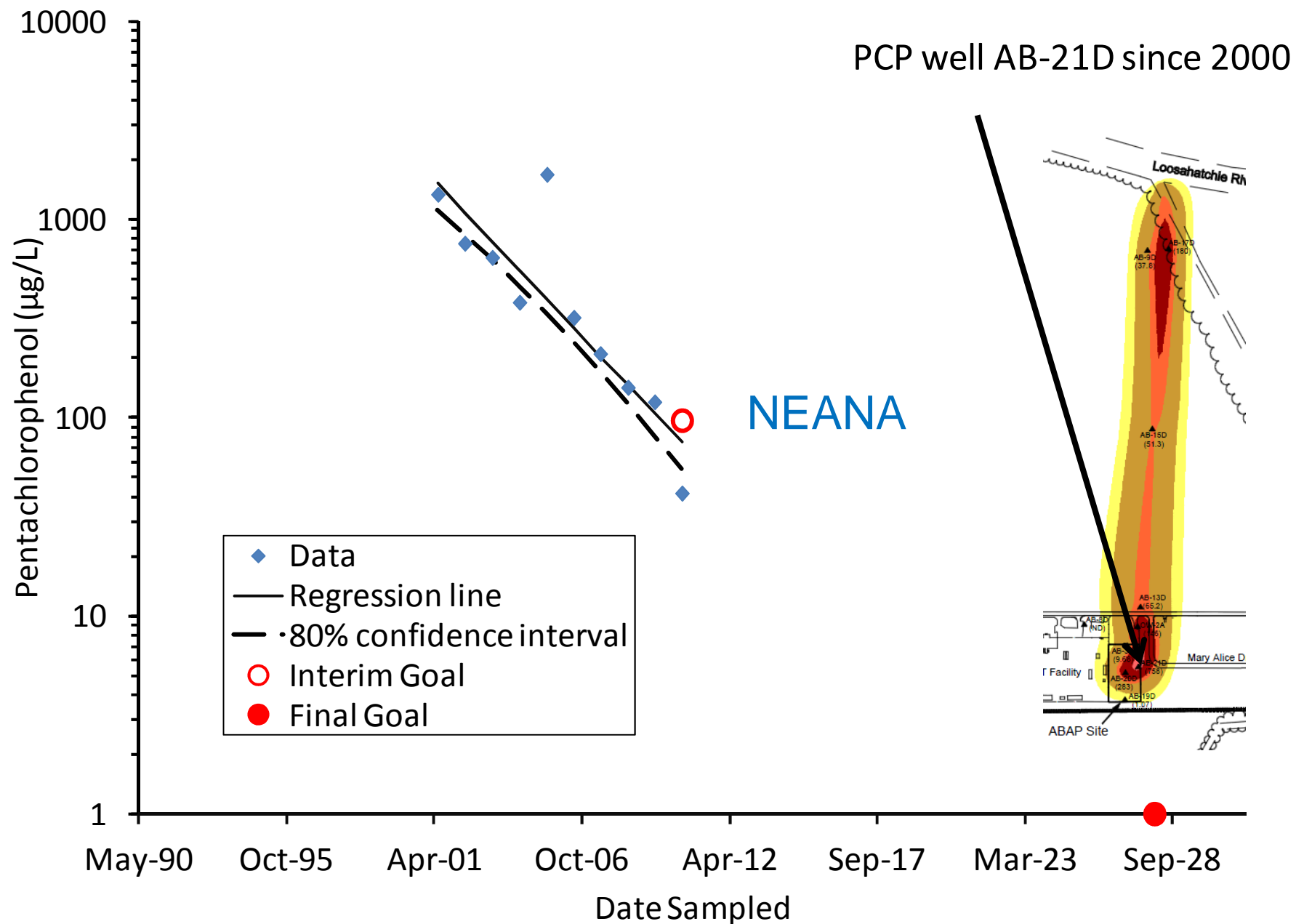


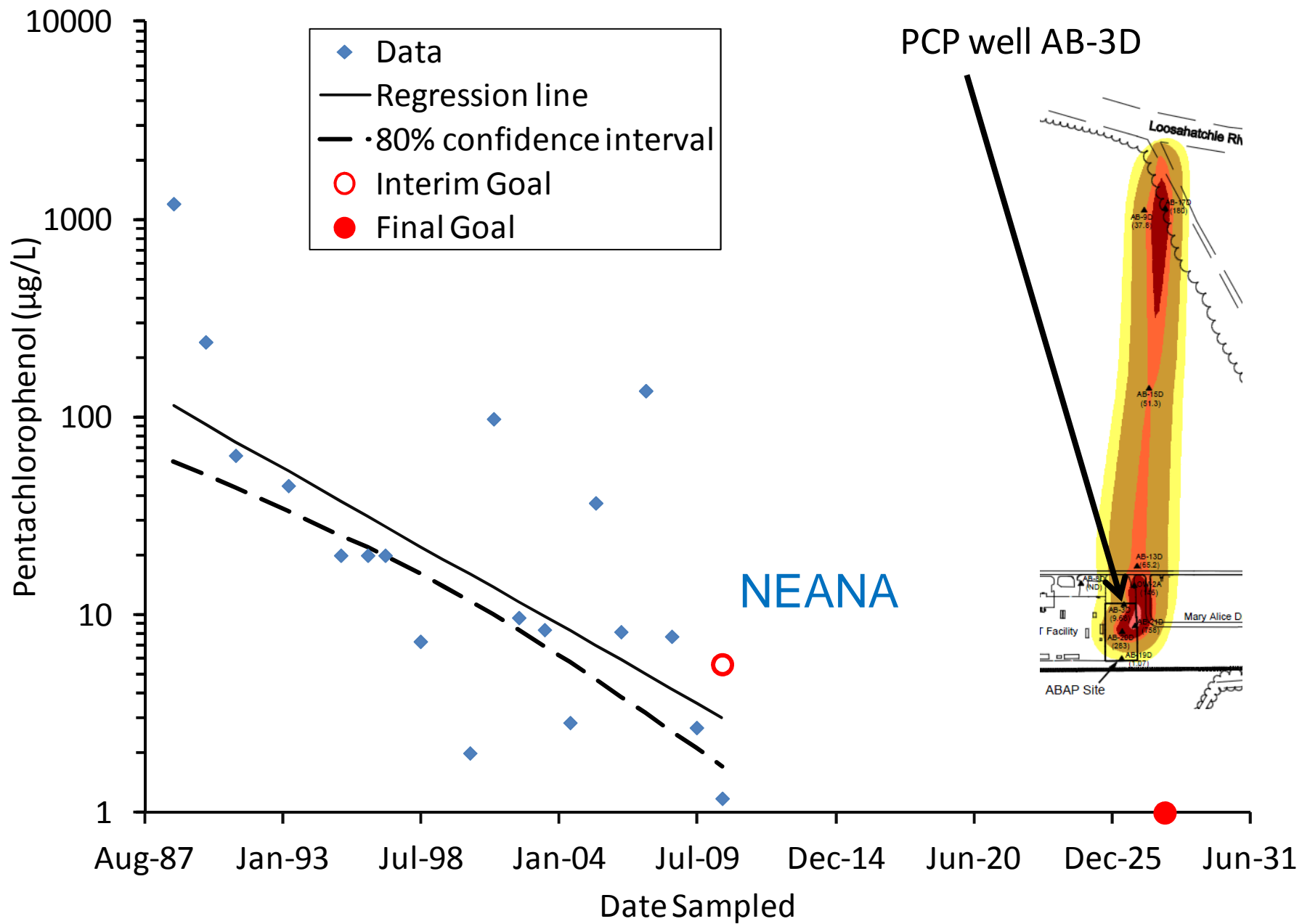


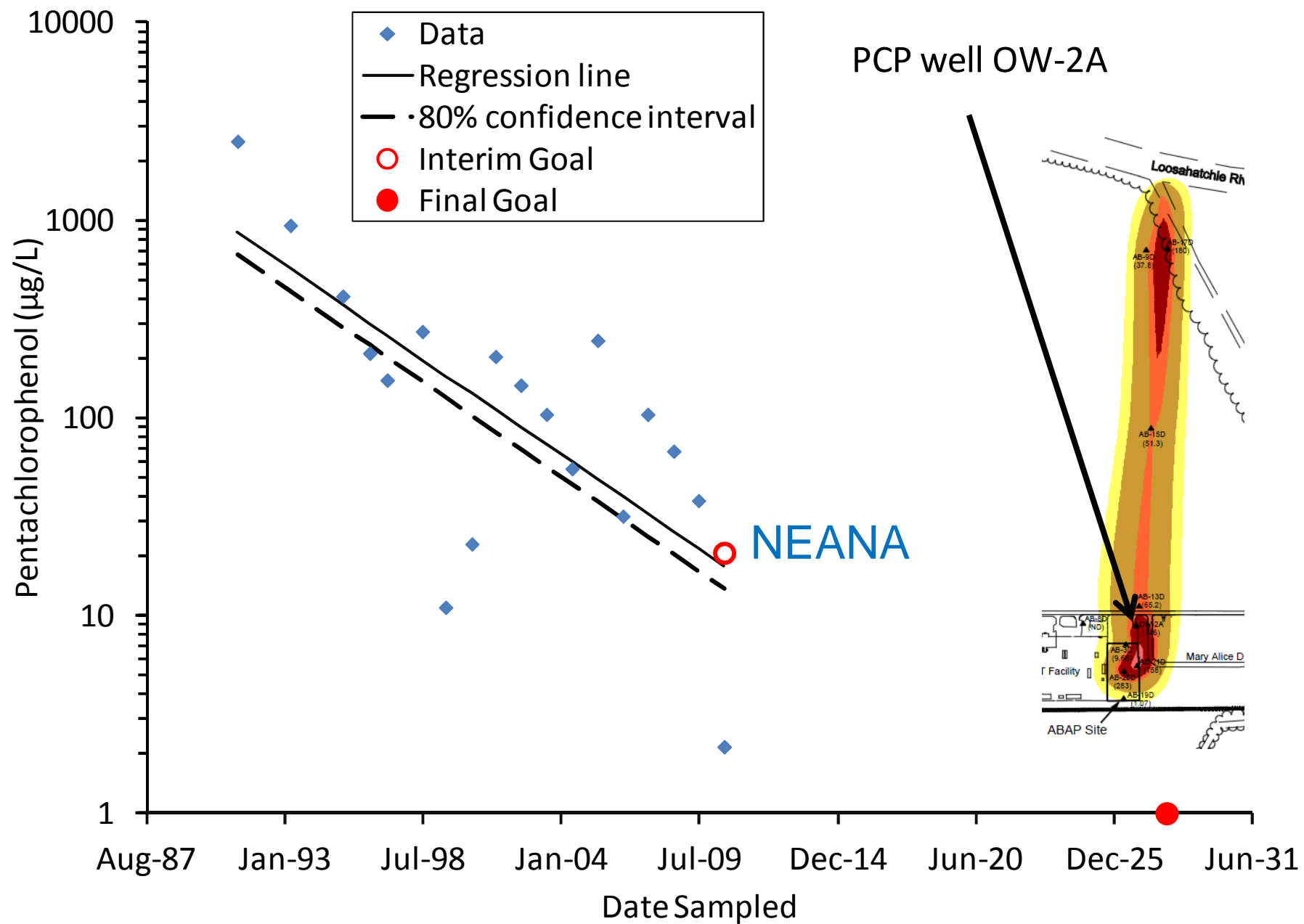


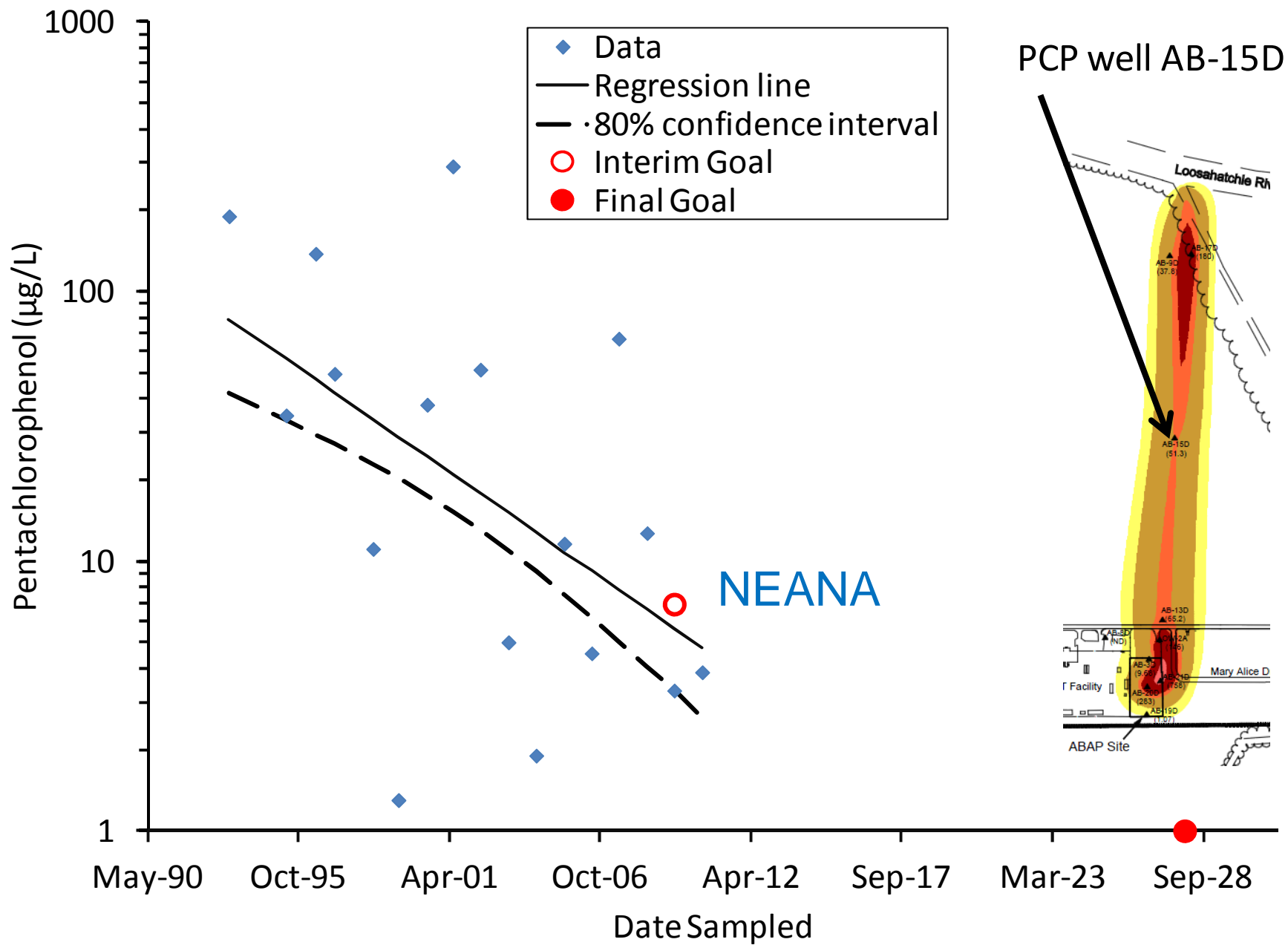


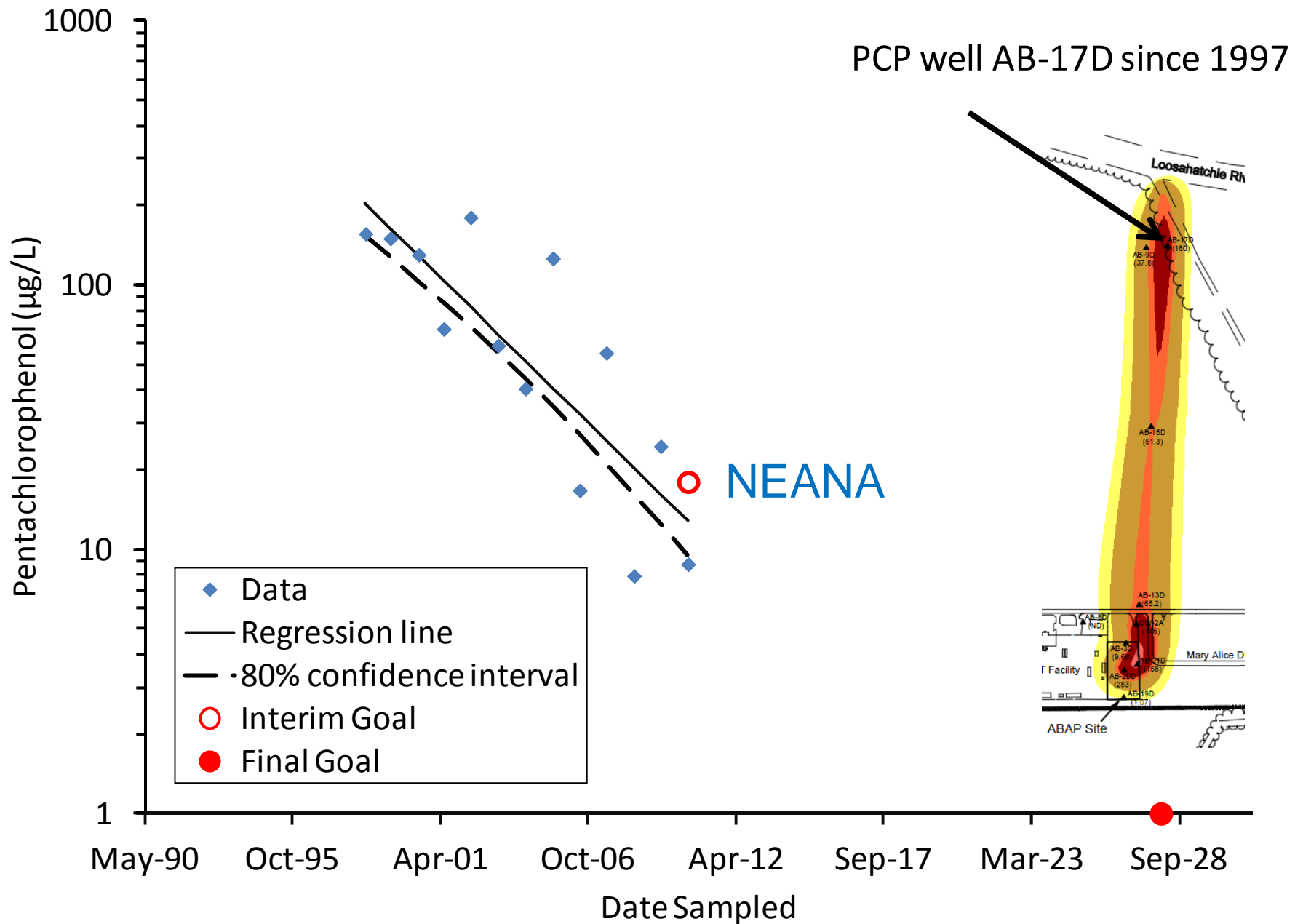


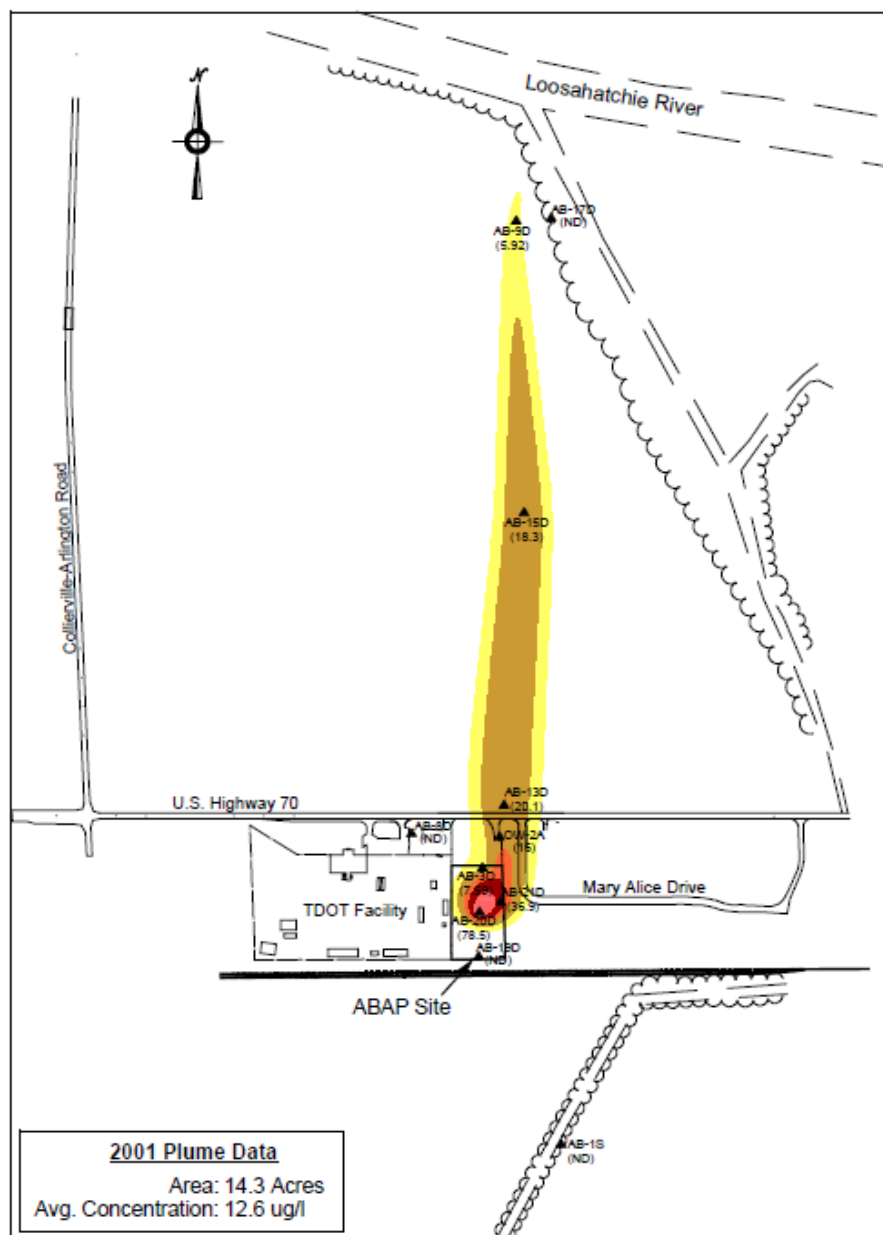












Benzene

Ground Water flow

LEGEND



