

DATA QUALITY: DETECTION LIMITS ARE AN IMPORTANT DRIVER

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(with assists from Keith Chapman & Ron Morrow)
((and a late save by Spencer Bohaboy))



ENVIRONMENTAL SERVICES
CITY OF PORTLAND

working for clean rivers

conducted on the initial grab sample unless there is adequate volume of composite sample to conduct the analyses.

Test methods used must have quantitation limits less than or equal to those listed in the table below unless otherwise approved by the Department in writing. The permittee must ensure that all monitoring analysis reports contain both the quantitation limit and detection level as defined below:

Detection Level – the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Quantitation Limit – The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

For sample results below the detection level, the result shall be reported as "<DL" (e.g. <1.0). For sample results above the detection limit and below the quantitation limit, the results shall be reported as "eDL" (e.g. e1.0).

For metals, the minimum quantitation level (QL) shall be met for each metal as listed below using approved EPA methods. If there are no methods available to obtain the QL's listed below, the test method that provides the lowest QL shall be used. The method detection limit (MDL), the QL, and the test method used for each test shall be reported along with the results.

Parameter	QL (µg/L)
Arsenic	0.5
Cadmium	0.1
Chromium	0.4
Copper	10
Cyanide	5
Lead	5
Mercury	0.01
Nickel	10
Selenium	2
Silver	1
Zinc	5

This data will also be used to evaluate the reasonable potential to violate in-stream water quality standards. After evaluation of this data, the permit may be reopened to include permit limits resulting from the reasonable potential analysis.

- For influent and effluent cyanide samples, at least six (6) discrete grab samples shall be collected over the operating day. Each aliquot shall not be less than 100 mL and shall be collected and composited into a larger container which has been preserved with sodium hydroxide for cyanide samples to insure sample integrity.
- Composite samples of biosolids shall be collected from representative locations pursuant to Test Methods for Evaluating Solid Waste, Volume 2: Field Manual, Physical/Chemical Methods, November 1986, Third Edition, Chapter 9.

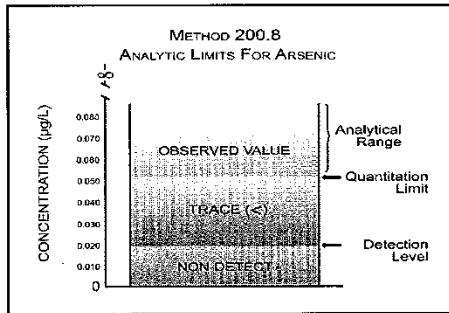
Inorganic pollutant monitoring must be conducted according to Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Second Edition (1982) with Updates I and II and Third Edition (1986) with Revision I.

DEFINITIONS REPEATED IN APPENDIX C:

analytic method as defined below⁶²:

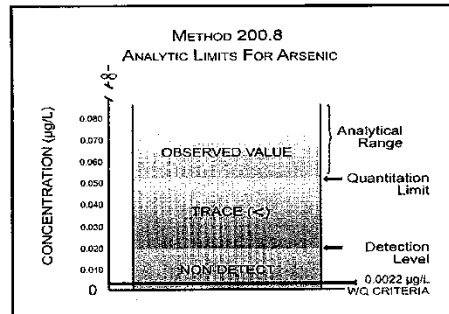
Detection Level⁶³: Same as the "Method Detection Limit" (MDL) derived using 40 CFR 136 Appendix B (40 CFR 136, Appendix B).

Quantitation Limit: Same as the Method Reporting Limit (MRL). It is the lowest level at which the entire analytic system must give a recognizable signal and acceptable calibration for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.



These are the definitions required by State and Federal regulation and are more practically described in the bullets and figure below.

- The QL is the lowest concentration at which a method can quantify a concentration of a pollutant in a sample.
- The DL is the lowest concentration at which a method can report (yes/no) a concentration of a pollutant in a sample, is greater than zero.
- For all analytic methods, the DL is always a lower concentration than QL.



Whenever possible, a permittee must use an analytic method with a QL that is lower than

⁶²There are a variety of analytic terms used that are roughly equivalent. For example:
Level of Detection = Detection Level = Method Detection Level (LOD = DL = MDL)
Level of Quantitation = Quantitation Limit = Method Reporting Limit (LOQ = QL = MRL)

⁶³ More plainly, the DL is the minimum concentration of a pollutant that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

THE RPA “DETECTION LEVEL” IS JUST THE OLD-FASHIONED MDL:

- Run ≥ 7 spiked reagent blanks ($n \geq 7$)
- Calculate the standard deviation (s)
- Look up the t-statistic for $n-1$ @ 0.99

$$DL = MDL = (t_{n-1, 1-\alpha = 0.99}) \bullet S_n$$

**IMPORTANT POINT:
THE DL (MDL) IS STATISTICALLY DERIVED**

PROBLEMS WITH THE MDL:

- RUN ON SPIKED BLANKS



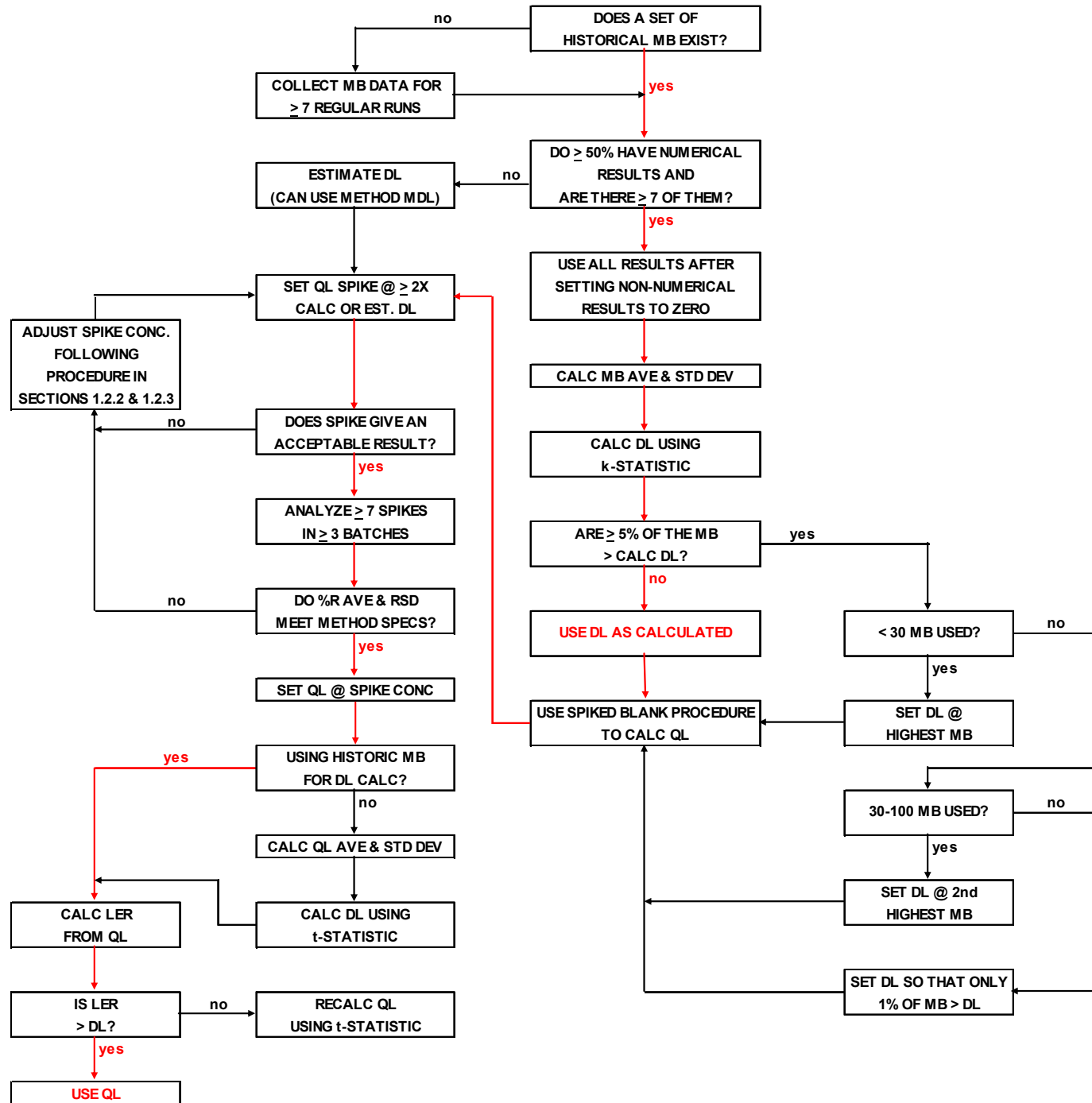
- RESULTS “ARTIFICIALLY” LOW



- NO RELATION TO REAL WORLD

WHY DIDN'T THE DEQ ALSO PICK A STATISTICAL METHOD FOR THE QL (MRL) ??

- THE PROPOSED METHODS ARE HORRENDOUSLY COMPLICATED.
- THERE'S NO AGREEMENT ON WHICH STATISTICAL METHOD IS BEST
- THE EPA OW DISAVOWED THE STATISTICAL METHOD PROPOSED BY ITS OWN WORKGROUP!



THE EPA OGWDW ATTEMPTED A PQL-LOQ RESCUE AND FAILED: THE INFAMOUS DISAPPEARING DOCUMENT:

The screenshot shows a web browser window displaying the EPA's website. The address bar shows the URL: <http://www.epa.gov/ogwdw000/standard/review/methods.html>. The page header includes the EPA logo and the text "U.S. ENVIRONMENTAL PROTECTION AGENCY". The main heading is "Ground Water & Drinking Water". Below this, there are navigation links: "Recent Additions", "Contact Us", and "Print Version". A search bar is also present. The breadcrumb trail reads: "EPA Home > Water > Ground Water & Drinking Water > Review of National Primary Drinking Water Regulations: Analytical Methods - Reassessment of Practical Quantitation Limits".

Review of National Primary Drinking Water Regulations: Analytical Methods - Reassessment of Practical Quantitation Limits

(This Issue Paper Is for Stakeholder Discussion and May Not Reflect Official EPA Policy)

BACKGROUND

The review of regulated contaminants will involve evaluating factors that contribute to the determination of a MCL. More specifically for analytical methods, the re-assessment will involve the re-evaluation of the Practical Quantitation Limits (PQLs) which were previously derived for some of the chemical contaminants at the time of promulgation of the NPDWRs. The purpose of this paper is to brief EPA stakeholders on the analytical methods-related issues for the 6-year review and the approaches EPA is considering for re-assessment of the PQL for these contaminants. With the help of stakeholder input, EPA will also consider developing a screening procedure to decide which PQL re-evaluation approach(es) will be most suitable for each regulated contaminant.

Analytical Methods Issues

The SDWA states that an MCL for a primary drinking water regulation must be set at a level at which "it is economically and technologically feasible to ascertain the level of such contaminant in water in public water systems..." [§1401(1)(C)(ii)], including quality control and test procedures to insure compliance [§1401(1)(D)]. According to section 1412 (b)(4)(B) of SDWA, EPA is to set the MCL as close to the MCLG as is feasible with the best available technologies. For the determination of some MCLs, the measurement capability may have been the limiting factor. This could be especially true for NPDWRs with MCLGs set at zero. Several NPDWRs having non-zero MCLGs may also have MCLs which were set due to the limits of the measurement capabilities.

Since the promulgation of pre-1996 SDWA contaminants, newer analytical methods for measuring SDWA contaminants have been approved. The approval of newer analytical techniques may have provided laboratories with the analytical capability to measure some contaminants at lower levels. The Agency would like to recommend to stakeholders that the chemical contaminants, whose MCLs were set due to the limits of the analytical capabilities, be selected as an initial group for PQL re-evaluation. Table 4 lists a few of the subject

The screenshot also shows a sidebar on the left with various navigation links such as "Drinking Water and Health Basics", "Frequently Asked Questions", "Local Drinking Water Information", "Drinking Water Standards", "List of Contaminants & MCLs", "Regulations & Guidance", "Public Drinking Water Systems", "Source Water Protection", "Underground Injection Control", "Data & Databases", "Drinking Water Academy", "Safe Drinking Water Act", and "National Drinking Water Advisory". The taskbar at the bottom shows several open applications including "Inbox - Microsoft Out...", "EPA Reassessment Of...", "Microsoft PowerPoint -...", and "EPA Ground Water ...". The system clock shows "11:04 AM".

THERE ARE EVEN DETECTION LIMIT CONSPIRACY THEORY SITES.....

The screenshot shows a Windows Internet Explorer browser window displaying the VanishingZero.org website. The browser's address bar shows the URL http://www.vanishingzero.org/vanishingzero/about_vz.html. The website's main header features the logo for "TOXILYTICAL RELATIVITY" and a navigation menu with items like "About VZ", "Categories", "About Vanishing Zero", "Recent Articles", and "Site Feeds".

About VZ
VanishingZero.org is a multidisciplinary project that seeks to foster the use of sound science in the determination of regulatory guidelines, public health policy, and consumer legislation. [Learn more about VZ.](#)

Categories
[Analytical Sciences](#)
[Economic Impact](#)
[Environmental Guidelines](#)
[General](#)
[Legal Implications](#)
[Media Responsibility](#)
[Medical Concerns and Public Health](#)
[Pharmaceutical Development](#)
[Political Accountability](#)

About Vanishing Zero
VanishingZero.org is a multidisciplinary project that seeks to foster the use of sound science in the determination of regulatory guidelines, public health policy, and consumer legislation. It is our hope that the interactive features incorporated into this web site will allow ongoing and constructive dialog toward these ends. Your support can make a difference in sound public policy, resource allocation, and job retention.

Why Vanishing Zero?
Technically, Vanishing Zero refers to the ability of analytical instrumentation to push the realm of the immeasurable down to unimaginably small levels. "Zero" keeps getting farther and farther away, both in distance and understanding. It is particularly manifested in the widening gap between instrument detection limits (sub-ppb) and toxicological regimens (ppm).

In the world of politics, regulation, and legislation, Vanishing Zero affords an excuse to advocate extreme measures to counter indeterminable or even negligible probability of risk. In other words, "If you can detect it to that limit, you should regulate it to that limit."

It's the 21st century's version of the Delaney Clause dilemma – dealing with a mindset that is inconsistent with the purpose and

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Site Feeds

The browser's taskbar at the bottom shows the Start button, several open applications including Microsoft Outlook, and the system tray displaying the time as 9:33 AM.

“WE BELIEVE DETECTION LIMITS SHOULD

GO AWAY!”*

David Coleman & Lynn Vanatta

Statistics In Analytical Chemistry

Part 26, Detection Limits

**LET'S WORK THROUGH THE RPA GUIDANCE AND
THEN SEE WHAT THE EPA HAS TO SAY ON ALL OF
THIS....**

Revised RPA IMD, Appendix C Quantitative Limits Tables
 Metals

EPA No.	Compound	Chemical Abstract Service Number (CAS)	Preferred Method	Freshwater Criteria		Saltwater Criteria		Human Health Consumption of		Drinking Water M.C.L.	Priority Pollutant	Quantitation Limit (ug/l)
				Acute (CMC) (ug/l)	Chronic (CCC) (ug/l)	Acute (CMC) (ug/l)	Chronic (CCC) (ug/l)	Water + Organism (ug/l)	Organism only (ug/l) except as noted			
2 H	Aluminum (pH 6.5-9.0)	7429905	200.8 / SM 3113									50
16	Antimony	7440360	200.8 / SM 3113					5.6	640		y	0.1
2	Arsenic	7440382	200.8 / SM 3113					0.022	0.0125	0.05mg	y	0.5
	Arsenic (II)		200.8 / SM 3113	360	190	69					y	50
	Arsenic (V)		200.8 / SM 3113								y	50
8 N	Barium	7440393	200.8 / SM 3113					1000		1.0mg		0.1
3	Beryllium	7440417	200.8 / SM 3113					0.0068	0.117		y	0.1
7 N	Boron	7440428	200.7									0.5
4	Cadmium	7440439	200.8 / SM 3113	3.9	1.1	43	9.3	10		0.010mg	y	0.1
	Chromium	7440473	200.8 / SM 3113								y	0.4
5a	Chromium (III)	16065831	200.7/200.8	1700	210	1100	50	170,000	3.433E6	0.05mg		10
5b	Chromium (VI)	18540299	218.6 / SM 3500	16	11	1100	50	50		0.05mg		10
6	Copper	7440508	200.8 / SM 3113	13	12	2.3	2.0	1300			y	10
20 H	Iron	7439896	200.8 / SM 3113		1,000			300				100
7		7439921	200.8 / SM 3113	32	3.2	140	5.8	50		0.05mg	y	5
22 H	Manganese	7439965	200.8 / SM 3113					50	100			2
8a	Mercury**	7439976	245.7 / 1631E / *	2.4	0.012	2.1	0.025	0.144	0.148	0.002mg	y	0.01
8b	Methylmercury **	22967926	1630						300 ug/kg	300 ug/kg L		0.00005
9	Nickel	7440202	200.8 / SM 3113	1400	160	75	8.3	134	100		y	10
10	Selenium	7782492	200.8 / SM 3113					10	4200	0.01mg	y	2
11		7440224	200.8 / SM 3113	4.5	0.12	2.7		50		0.05mg	y	1
12	Thallium	7440280	200.8					0.24	0.47		y	0.1
44 N	Tributyltin (TBT)	688733	GC/MS	0.46	0.063	0.37	0.01					Contact DEQ Lab
13	Zinc	7440666	200.8	120	110	95	85	7400	26000		y	5

All metals are in terms of "Total Recoverable"

Note: Human Health Criteria described in out of date and does not reflect current effective criteria.

Values shaded in blue are criteria based quantitation limits.

Values shaded in yellow are hardness dependant and not final criteria.

* For mercury, the City of Portland Environmental Lab is permitted to use method 200.8 as an approved alternative method for wastewater monitoring.

** For sources in the Willamette Basin, the permit writer should contact the TMDL basin coordinator to coordinate mercury monitoring efforts and ensure that adequate quantitation limits are met.

Note: Human Health Criteria listed here are incorrect. Please refer to most current guidance

**COPPER METHODS APPROVED AT 40 CFR 136
(DEQ RPA COPPER QL TARGET = 10 ug/L)**

ANALYTICAL TECHNIQUE	METHOD APPROVED				
	AT 40 CFR 136	OTHER	IDL	MDL=DL	MRL=QL
Flame AA	SM 3111	---	10	---	---
Graphite Furnace AA	SM 3113	1 ^a	---	---	---
Stabilized Temp. GFAA	EPA 200.9	---	---	0.7	---
Axial ICP	EPA 200.5	---	0.2	0.3	0.7
ICP	EPA 200.7	---	5.4	3	---
ICP/MS	EPA 200.8	---	0.03	0.5	---

^a Detection Level (= MDL???)

**ASSESSMENT OF THE 2005/2006 DEQ RPA
IMD: TABLE 8 PRACTICAL QUANTITATION
LEVELS**

by

**Chuck Lytle, City of Portland WPCL
February 26, 2007**

charles.lytle@portlandoregon.gov

“THERE’S NO WAY OUT OF HERE...”

2006-2007 ACWA/DEQ

AD HOC WORKGROUP ON DLs & QLs

- **Spencer Bohaboy, DEQ**
- **Brian Boling, DEQ**
- **Chris Redman, DEQ**
- **Keith Chapman, City of Salem**
- **Chuck Lytle, City of Portland**

FROM ASTM D 6512-00:

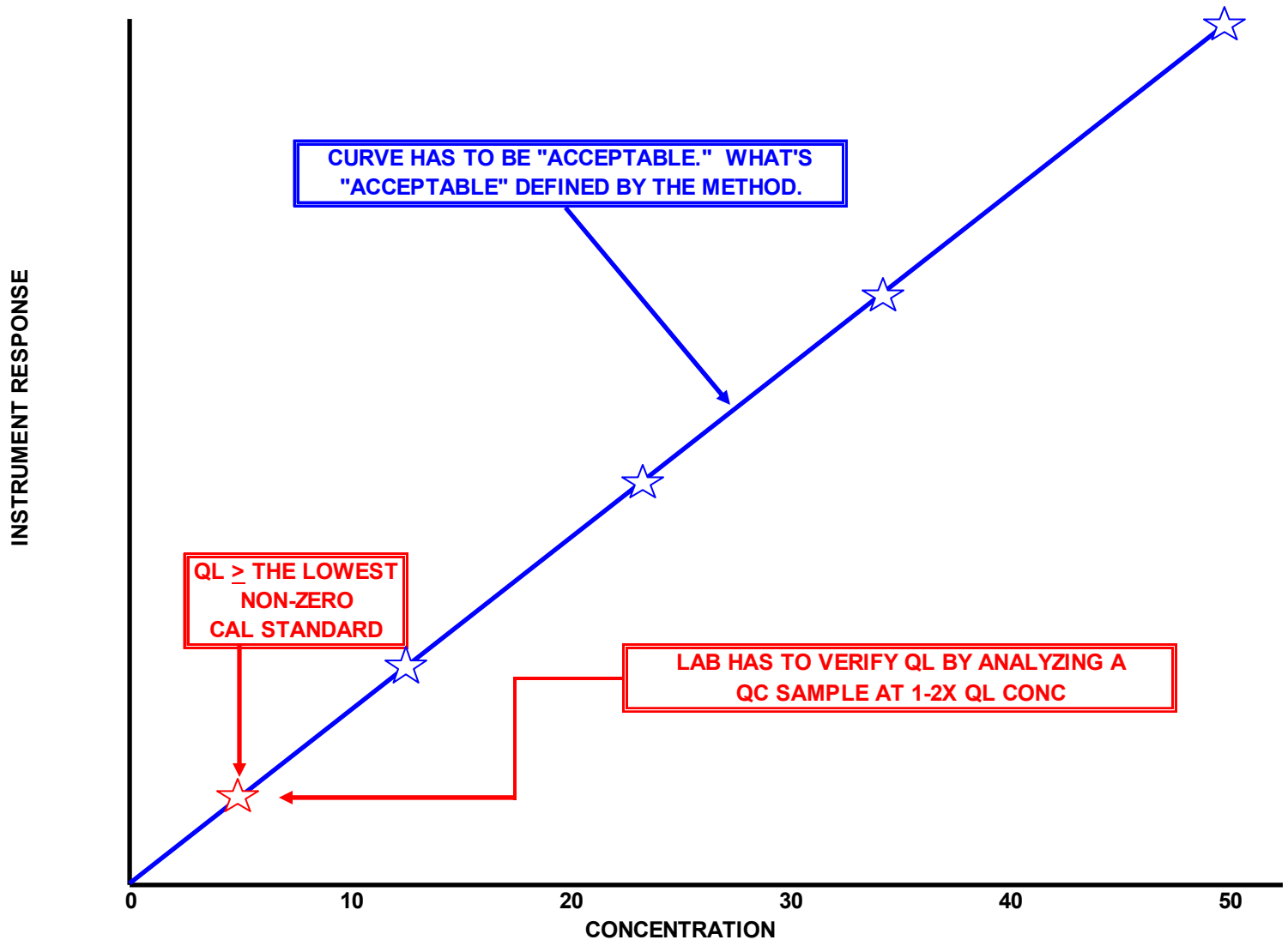
**STANDARD PRACTICE FOR INTER-LABORATORY
QUANTITATION ESTIMATE (IQE)**

“Routinely Achievable IQE – Most laboratories are able to attain the IQE detection performance in routine analyses, using a standard measurement system, at reasonable cost. The property is needed for a detection limit to be practically feasible. Representative laboratories must be included in the data to calculate the IQE.”

WORKGROUP OUTCOMES...

FOR **DLs**, USE THE TRADITIONAL METHOD AT 40 CFR 136.

FOR **QLs**, USE THE STANDARD METHODS (ALSO NELAC) PROTOCOL: MAKE IT \geq LOWEST CAL STD FROM AN ACCEPTABLE CAL CURVE. (IN THE PAST, THIS MEANT THE CURVE HAD TO HAVE A CORRELATION COEFFICIENT ≥ 0.995 .)



THUS...

THE DL (MDL) IS STATISTICALLY DERIVED

BUT

THE QL (MRL) IS OPERATIONALLY DEFINED.

THAT'S WHY YOU OFTEN SEE DLs LIKE THIS:

0.0237

AND QLs LIKE THIS:

4.00

Client: City of Portland
 Contact: Duane Linnertz

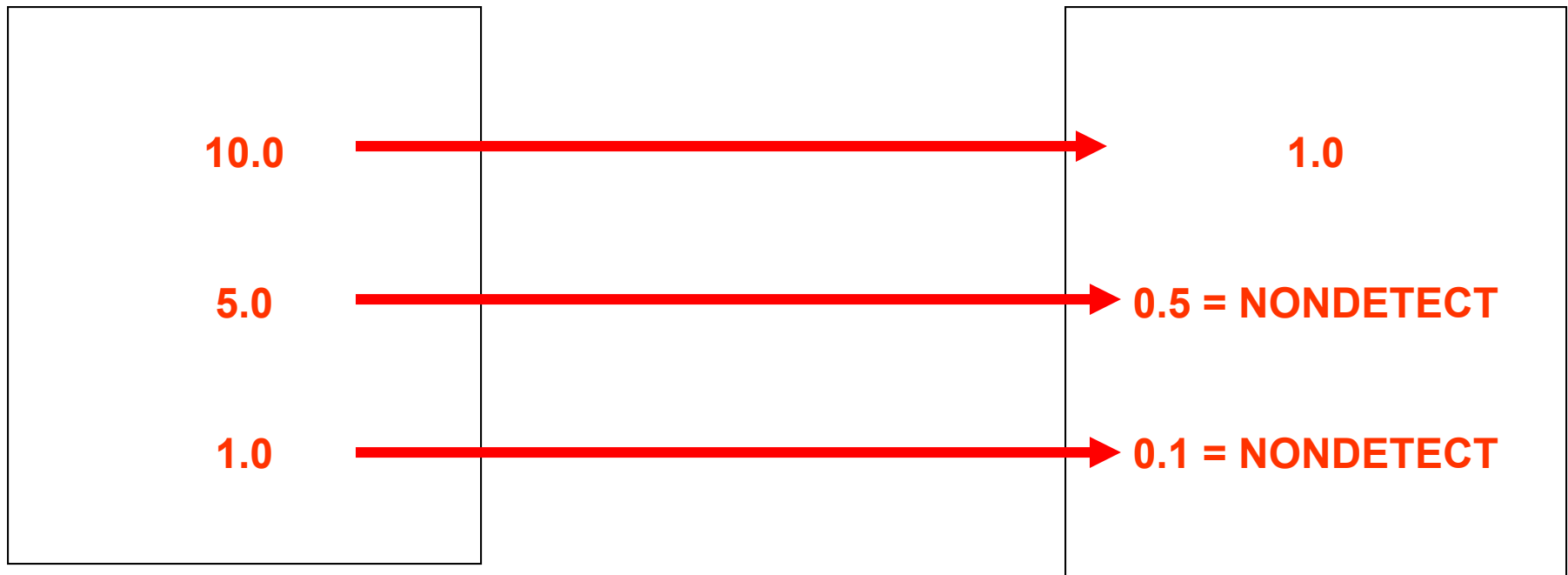
Bid Date: 02-November-2010
 Prices Expire: 30-June-2013

Method	Analyte	MDL	MRL	Units	Surr %Rec	Dup RPD	Matrix Spike Rec. RPD	Blank Spike Rec. RPD
EPA 8270m	Acenaphthene	0.0500	0.100 ug/l		-	35	26-135	35 26-135
EPA 8270m	Acenaphthylene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Anthracene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Benzo (a) anthracene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Benzo (a) pyrene	0.0500	0.100 ug/l		-	35	38-137	35 38-137
EPA 8270m	Benzo (b) fluoranthene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Benzo (ghi) perylene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Benzo (k) fluoranthene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Chrysene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Dibenzo (a,h) anthracene	0.100	0.200 ug/l		-	35	-	-
EPA 8270m	Fluoranthene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Fluorene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Indeno (1,2,3-cd) pyrene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Naphthalene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Phenanthrene	0.0500	0.100 ug/l		-	35	-	-
EPA 8270m	Pyrene	0.0500	0.100 ug/l		-	35	33-133	35 33-133
EPA 8270m	Fluorene-d10		Surrogate		25-125	-	-	-
EPA 8270m	Pyrene-d10		Surrogate		23-150	-	-	-
EPA 8270m	Benzo (a) pyrene-d12		Surrogate		10-125	-	-	-
RCRA-8 / ICP Metals								
in Soil								
EPA 6010B	Arsenic	0.429	5.00 mg/kg dry wt		-	40	75-125	40 80-120
EPA 6010B	Barium	0.163	2.00 mg/kg dry wt		-	40	75-125	40 80-120
EPA 6010B	Cadmium	0.0120	2.00 mg/kg dry wt		-	40	75-125	40 80-120
EPA 6010B	Chromium	0.135	2.00 mg/kg dry wt		-	40	75-125	40 80-120
EPA 6010B	Lead	0.268	5.00 mg/kg dry wt		-	40	75-125	40 80-120
EPA 6010B	Selenium	0.625	5.00 mg/kg dry wt		-	40	75-125	40 80-120
EPA 6010B	Silver	0.111	5.00 mg/kg dry wt		-	40	75-125	40 80-120
RCRA-8 / ICP Metals								
in Water								
EPA 6010B	Arsenic	0.00940	0.0500 mg/l		-	20	75-125	20 85-115
EPA 6010B	Barium	0.000200	0.0100 mg/l		-	20	75-125	20 85-115
EPA 6010B	Cadmium	0.000300	0.0100 mg/l		-	20	75-125	20 85-115
EPA 6010B	Chromium	0.00120	0.0100 mg/l		-	20	75-125	20 85-115
EPA 6010B	Lead	0.00370	0.0500 mg/l		-	20	75-125	20 85-115
EPA 6010B	Selenium	0.00900	0.0500 mg/l		-	20	75-125	20 85-115
EPA 6010B	Silver	0.00420	0.0200 mg/l		-	20	75-125	20 85-115

WHY DO THE MRLs (QLs) IN MY REPORT BOUNCE ALL OVER THE PLACE?

MRL (QL) = 1.0

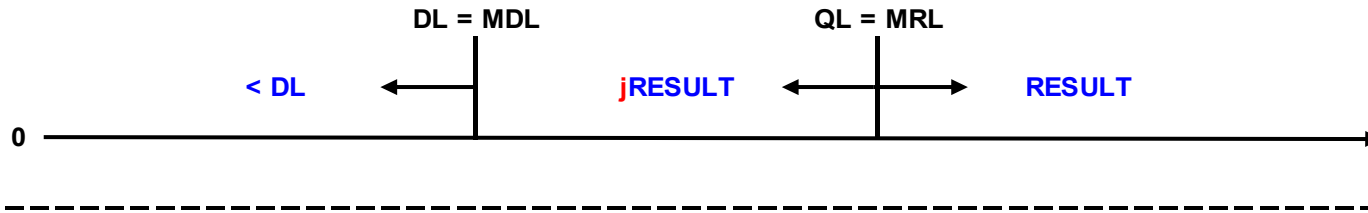
MRL (QL)
IS NOW 10.0



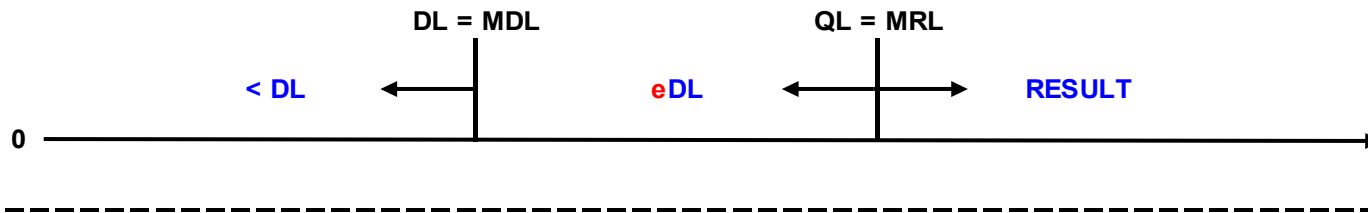
ORIGINAL SAMPLE
(CAN "SEE" ALL CONC.)

SAMPLE DILUTED 1:10
(CAN ONLY "SEE" 10.0)

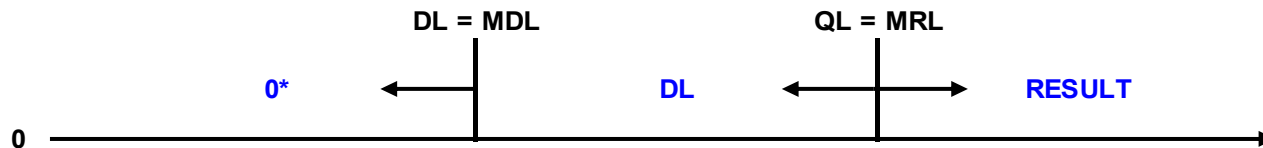
DATA REPORTING REQUIREMENTS FOR YOUR LAB



YOUR DMR/DMS DATA REPORTING REQUIREMENTS TO DEQ (P. 74)



NUMBERS DEQ WILL USE IN RPA CALCULATIONS (P. 75)



* 1/2 MDL used when calculating geometric mean: $(x_1 * x_2 * x_3 * \dots * x_n)^{1/n}$

DO NOT LET YOUR LAB USE THE TERM

“TRACE”

FOR ANY RESULT!!!

THIS TERM HAS NO MEANING!!!

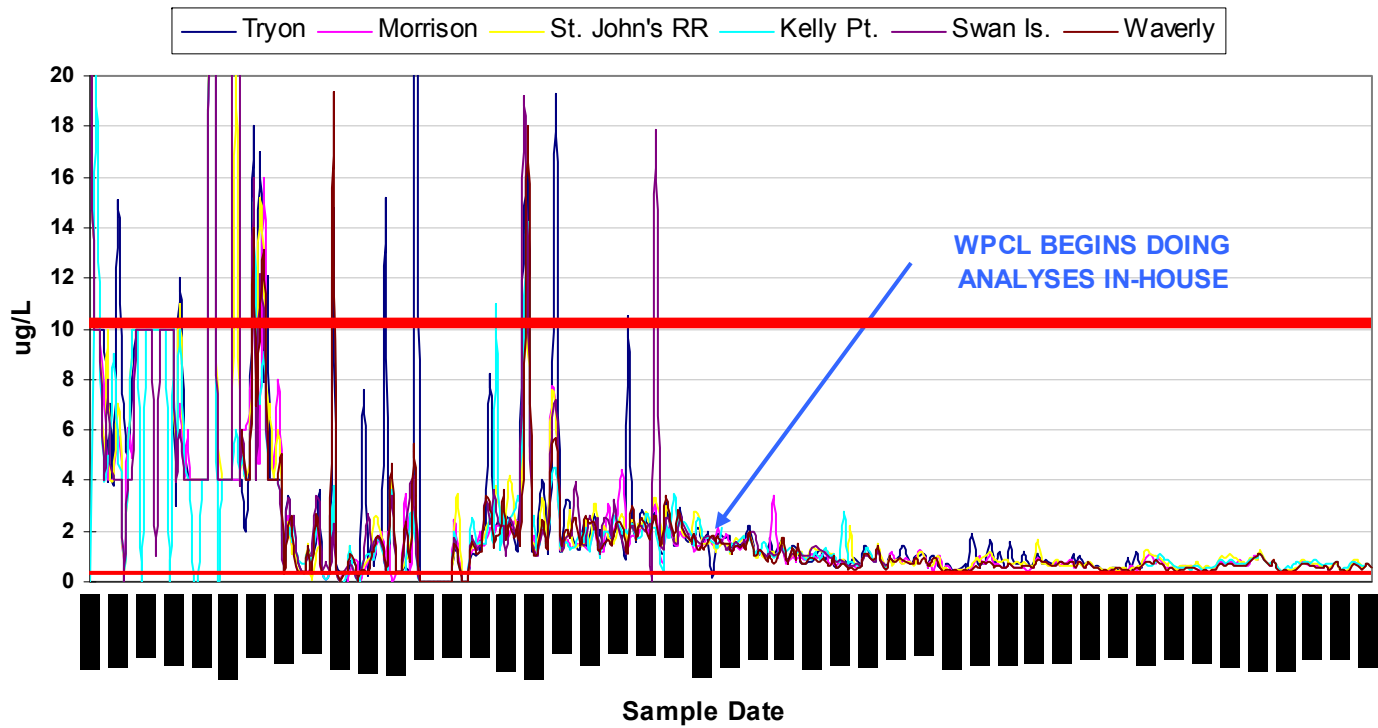
RESULTS BELOW THE DL SHOULD BE

REPORTED AS <DL....

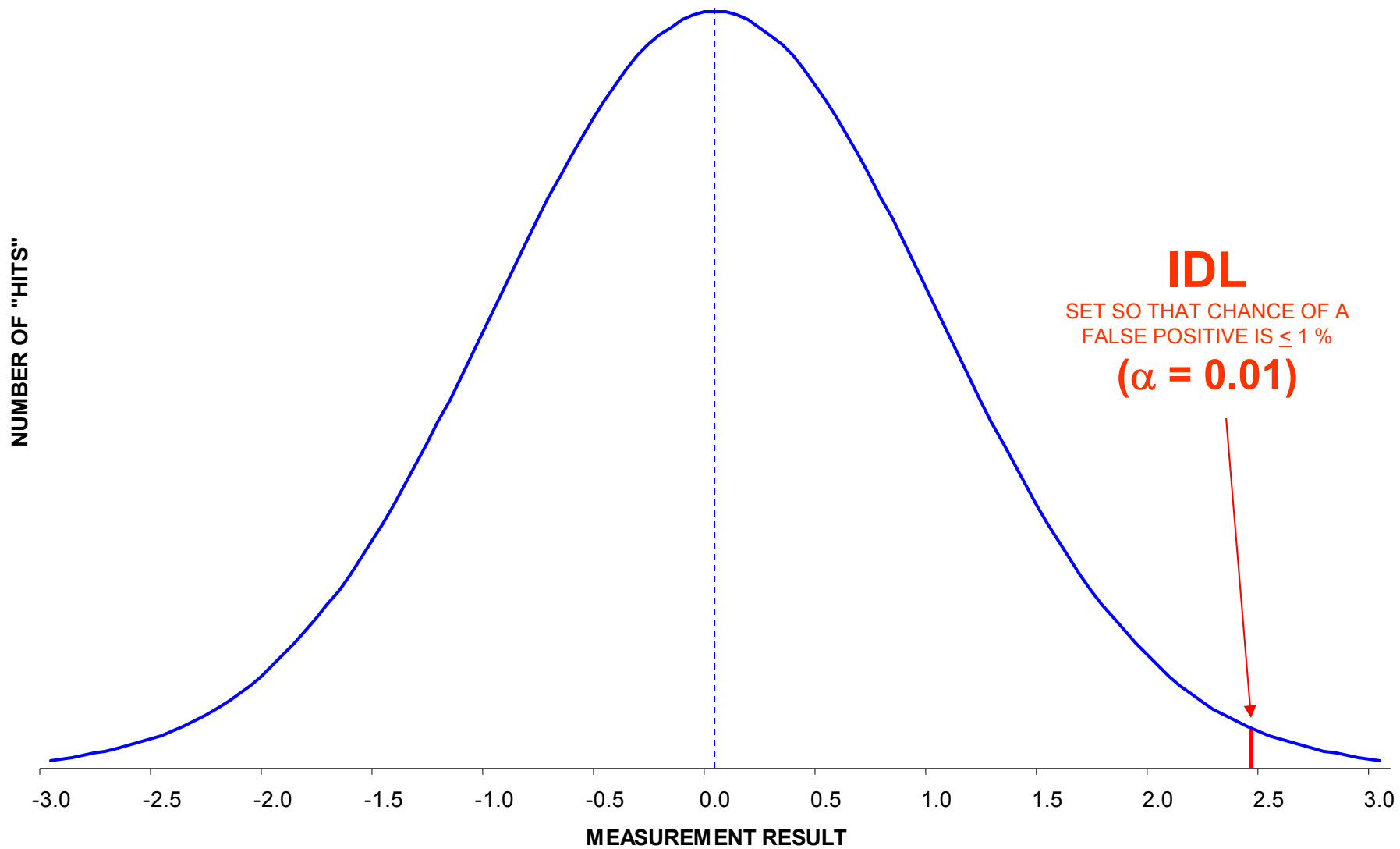
“nd” IS OKAY

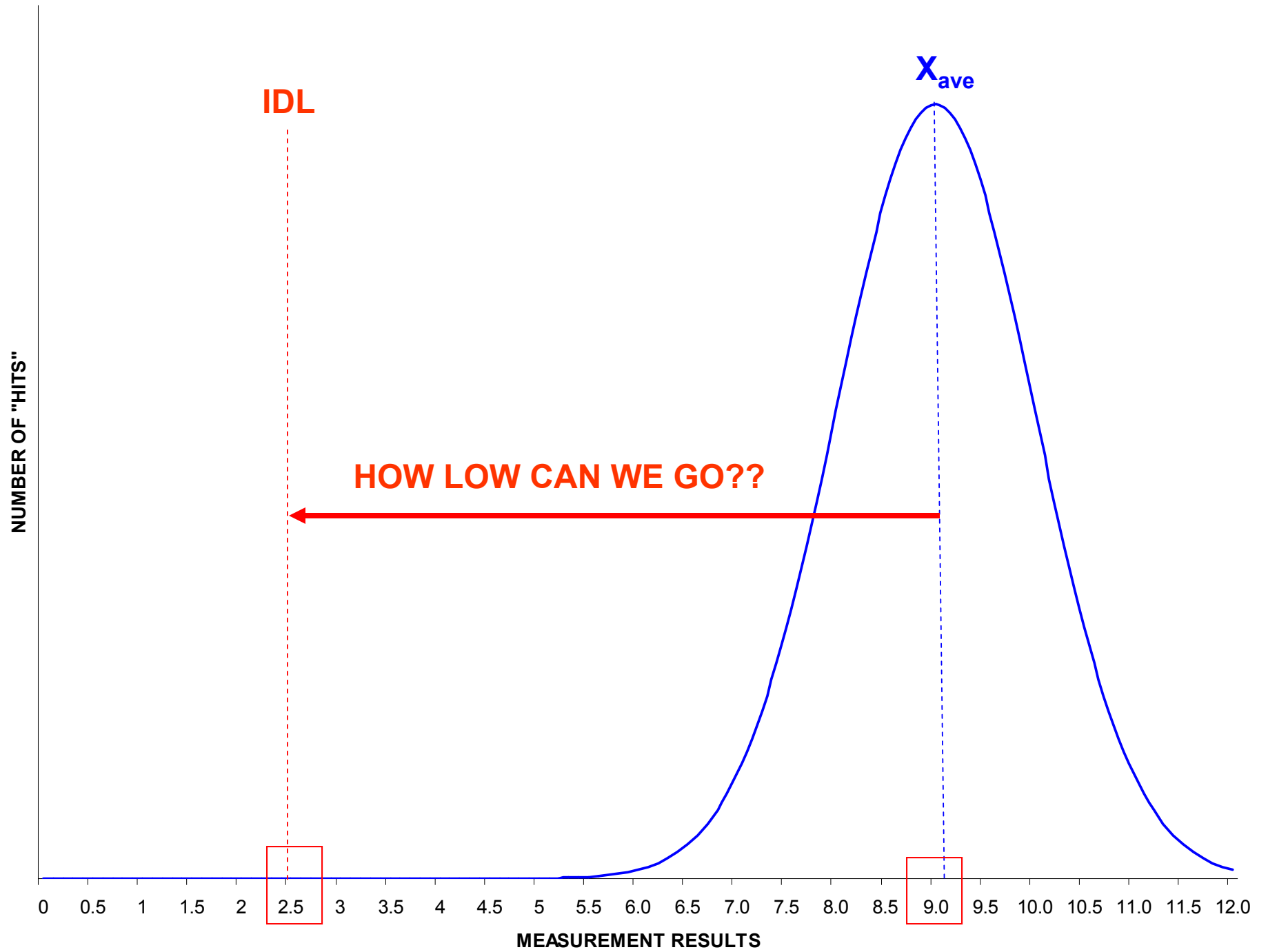
ONLY IF THE DL IS LISTED

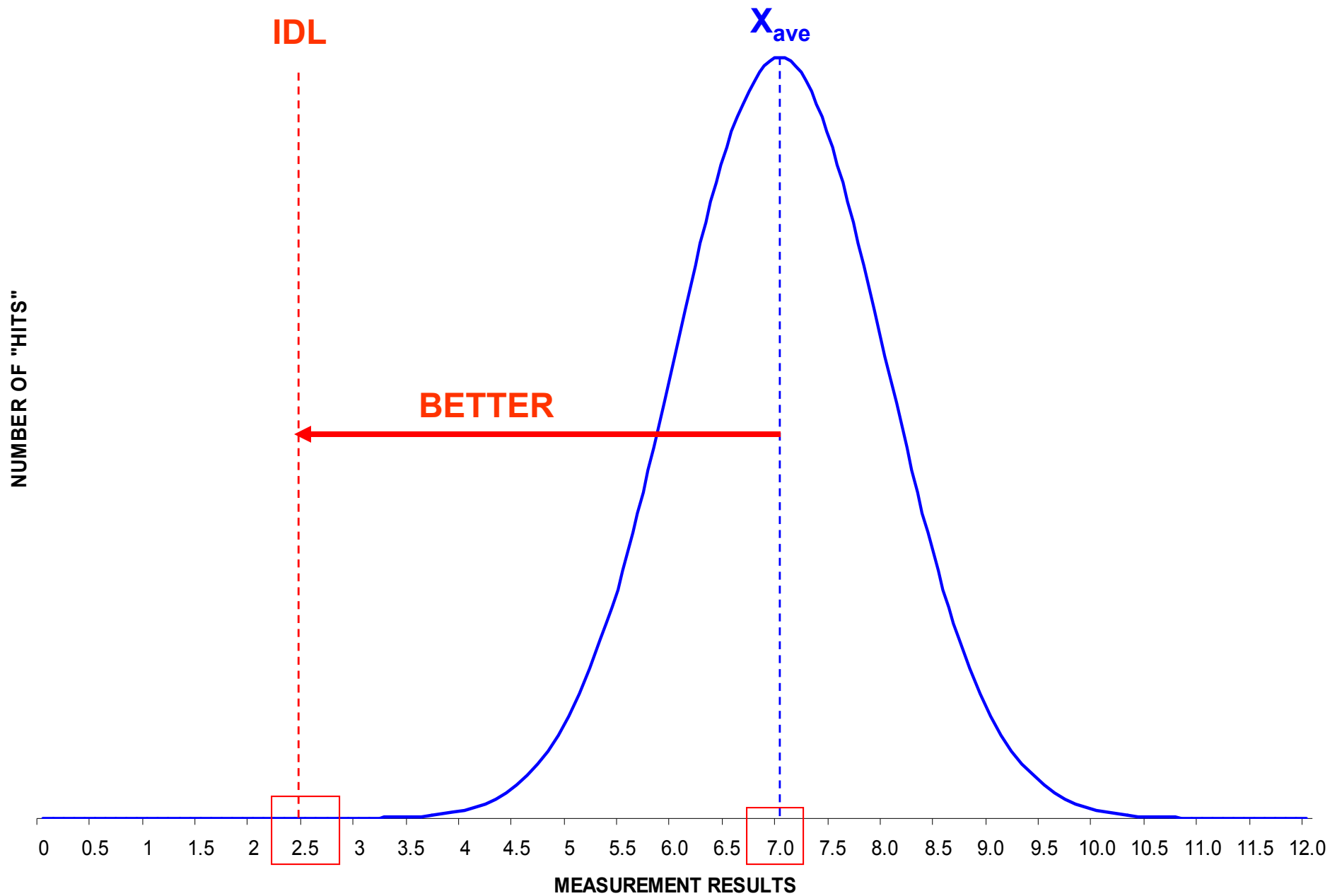
Willamette River Dissolved Copper Results 1993 - 2003

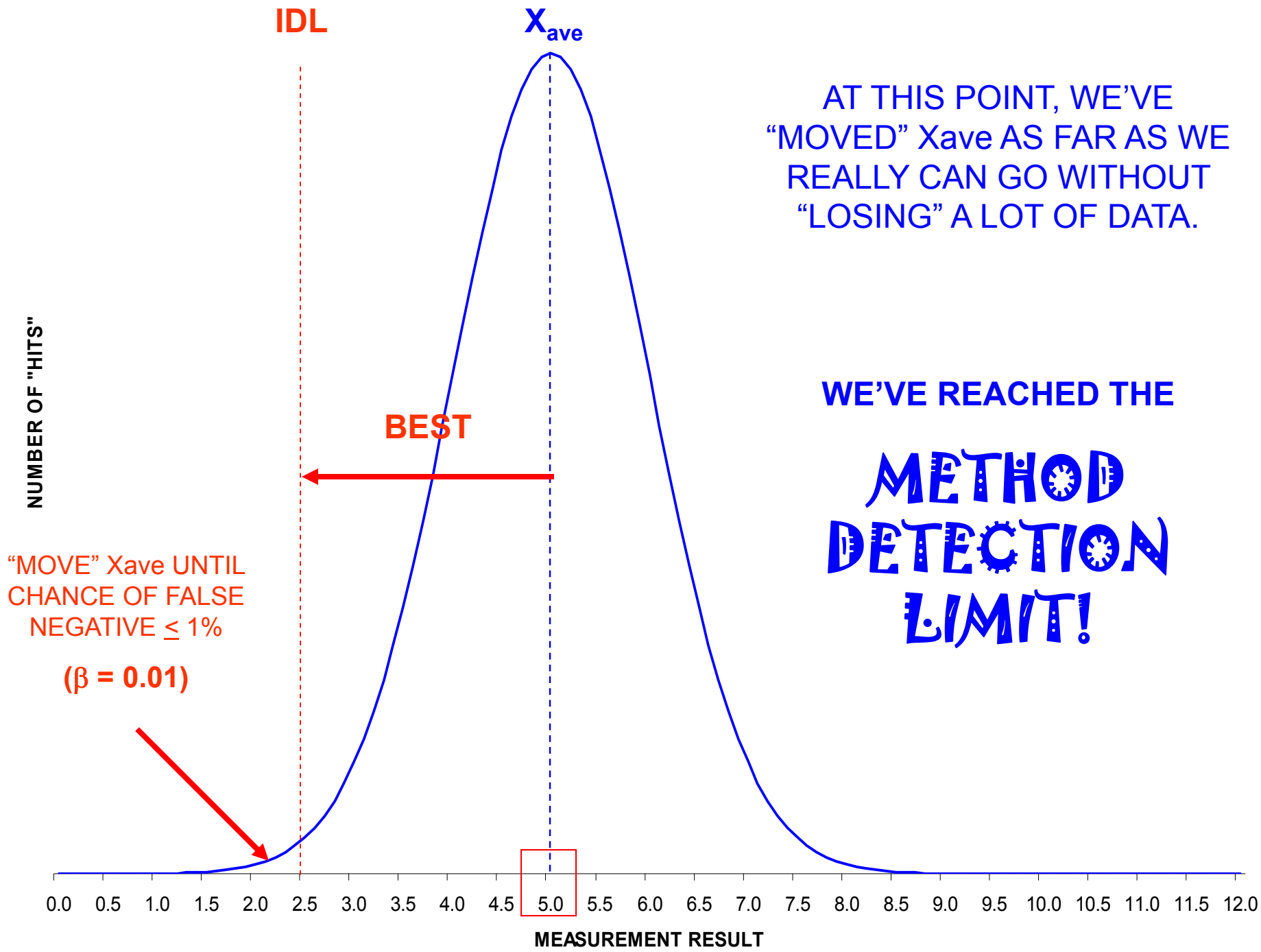


INTERMISSION









IDL

X_{ave}

AT THIS POINT, WE'VE
"MOVED" X_{ave} AS FAR AS WE
REALLY CAN GO WITHOUT
"LOSING" A LOT OF DATA.

NUMBER OF "HITS"

BEST

WE'VE REACHED THE

**METHOD
DETECTION
LIMIT!**

"MOVE" X_{ave} UNTIL
CHANCE OF FALSE
NEGATIVE $\leq 1\%$

$(\beta = 0.01)$

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5 10.0 10.5 11.0 11.5 12.0

MEASUREMENT RESULT

HOW DO YOU GO ABOUT SETTING
THE IDL SO THAT $\alpha = 0.01$ AND
THEN HOW DO YOU “MOVE” X_{ave}
SO THAT $\beta = 0.01$???

YOU ONLY HAVE SEVEN OR SO RESULTS.
WILL THIS GIVE A NICE, BELL-SHAPED CURVE?

ARE YOU SUPPOSED TO EYE-BALL WHERE THE 1% POINT IS?

(no)

YOU USE THE t -STATISTIC

WHAT IS THE t -STATISTIC?

(OTHER THAN BEING A JUST A BUNCH OF NUMBERS FOUND IN A TABLE AT THE
BACK OF SOME BOOK)

THE t -STATISTIC IS A FUDGE FACTOR!
IT COMPENSATES FOR THE FACT THAT YOU'LL

NEVER

HAVE ENOUGH RESULTS TO GIVE A “NICE” CURVE.

REMEMBER, WE ONLY USE 7 OR SO
RESULTS FOR CALCULATING A
DETECTION LIMIT.

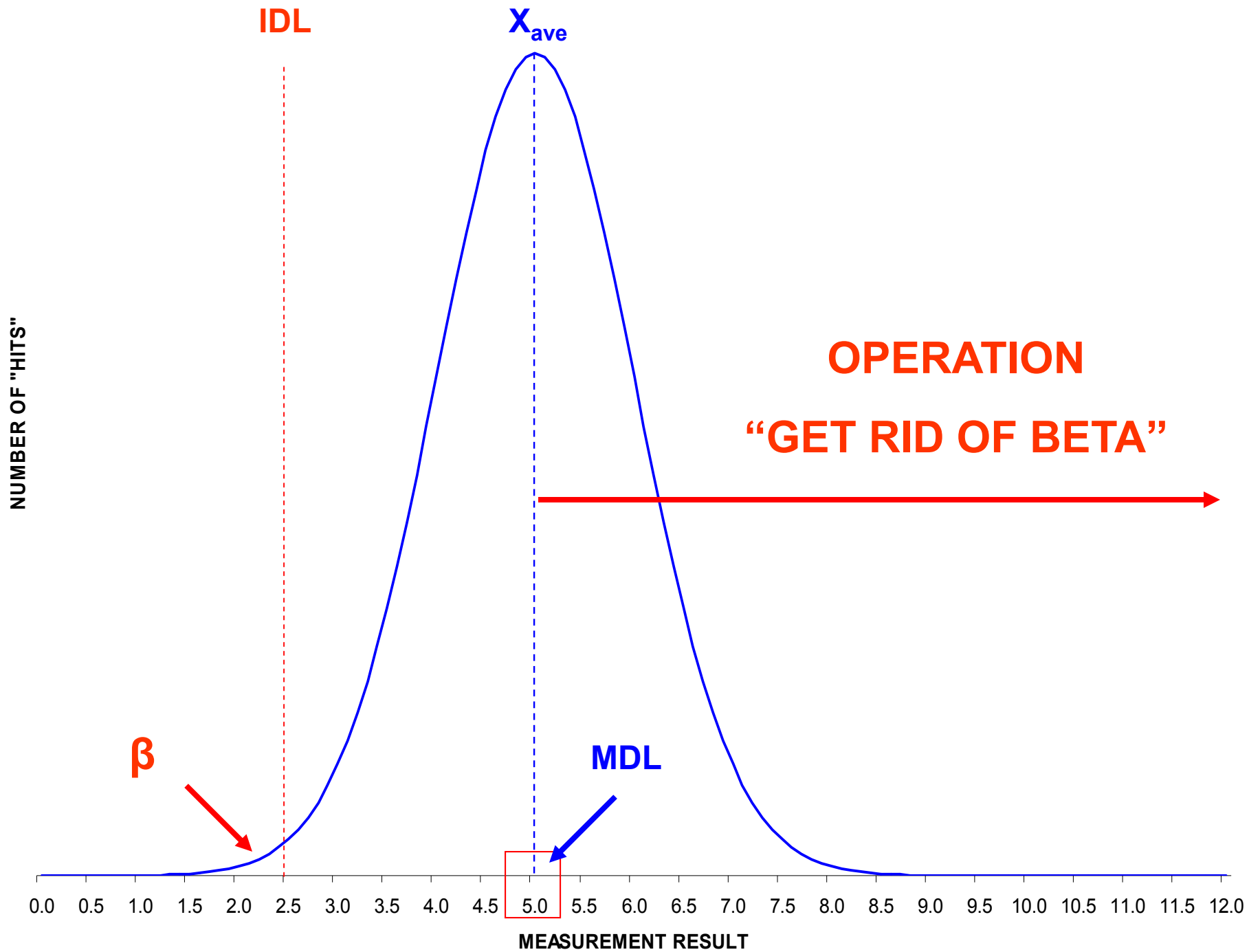
SO HOW “GOOD” IS OUR MDL?

(ANSWER: NOT VERY, WHICH IS WHY THE EPA WAS SUCCESSFULLY SUED OVER
THE USE OF THAT VERY EQUATION!)

IF THE MDL ISN'T SO HOT, HOW
ABOUT SETTING THE LIMIT HIGHER
SO WE CAN DO AWAY WITH ALL
THIS ALPHA-BETA NONSENSE?

AND THAT'S JUST WHAT THE EPA (AND LOTS OF OTHER PEOPLE) DECIDED TO
DO. AND THEY DECIDED TO CALL THIS A...

QUANTITATION LIMIT



**QUANTITATION LIMIT =
QL=PQL=LOQ=MRL= on and on**

