California's Surface Water Ambient Monitoring Program

Quantitation and Reporting Limits 101

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Moss Landing Marine Laboratories

California Water Boards

SWAMP Surface Water Ambient Monitoring Program

Quantitation and Reporting Limits 101

- Definitions of Quantitation Limits
- Surface Water Ambient Monitoring Program Reporting Limits Requirements
- Determining Program/Project Reporting Limits
- Working with a Laboratory and Reporting Limits
- Documents for Communication of Reporting Limits
- Comments on Reporting in the Context of Reporting Limits
- New Developments – Stay Tuned to EPA
- Conclusion
- Reporting Limits 102

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Outcome

- A general understanding of common quantitation limit terms
- An understanding of the differences between quantitation limits
- The SWAMP requirements for reporting limits and SWAMP resources
- A brief introduction to determining reporting limits
- Tips for ensuring labs can hit reporting limits

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Text and References

- There are several slides with a significant amount of text and definitions.
- There are also several slides that show tools and list web site addresses, phone numbers, and email addresses.
- We will not be going over these verbatim; they are included so that you may use the slides later as a reference.

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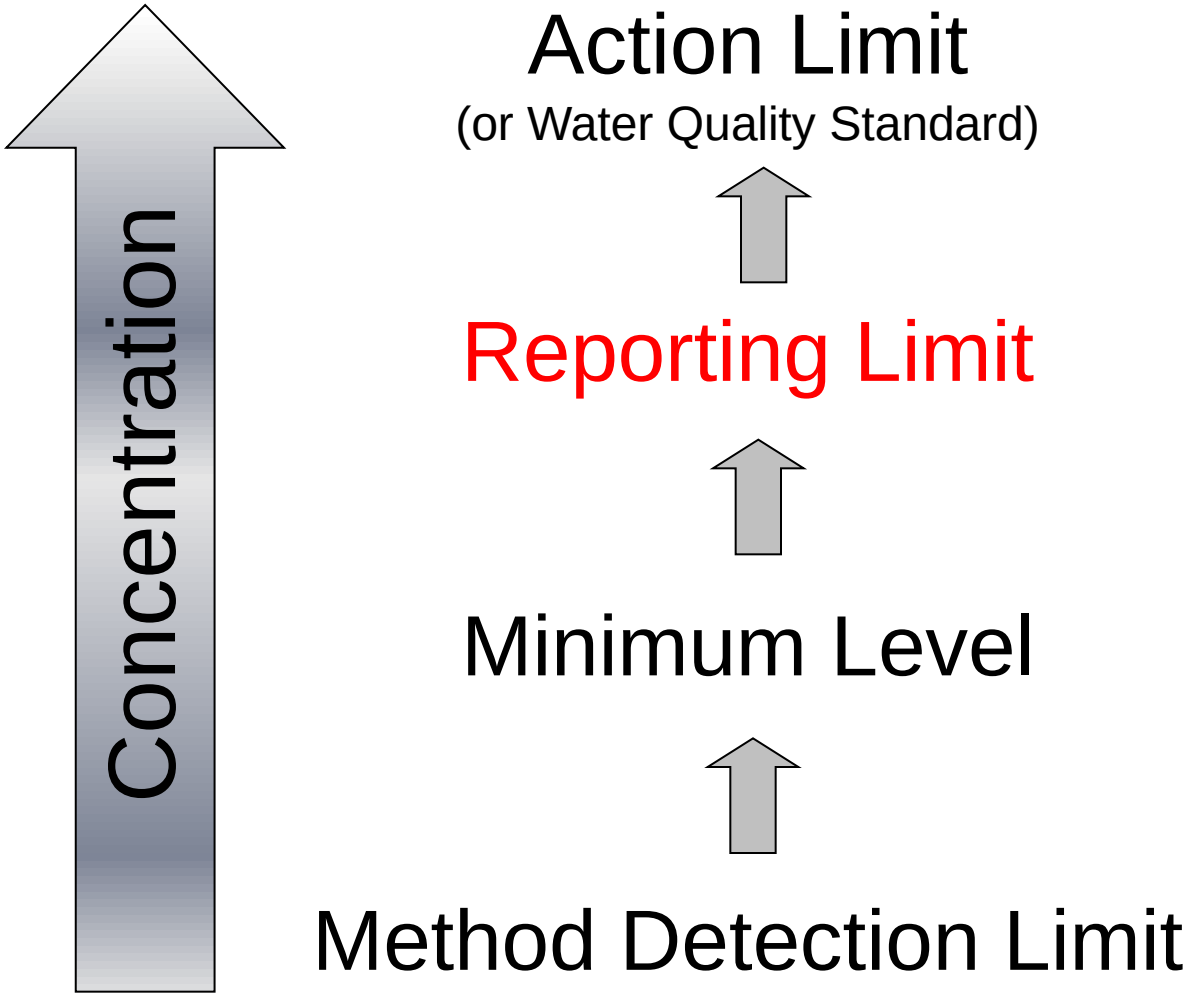

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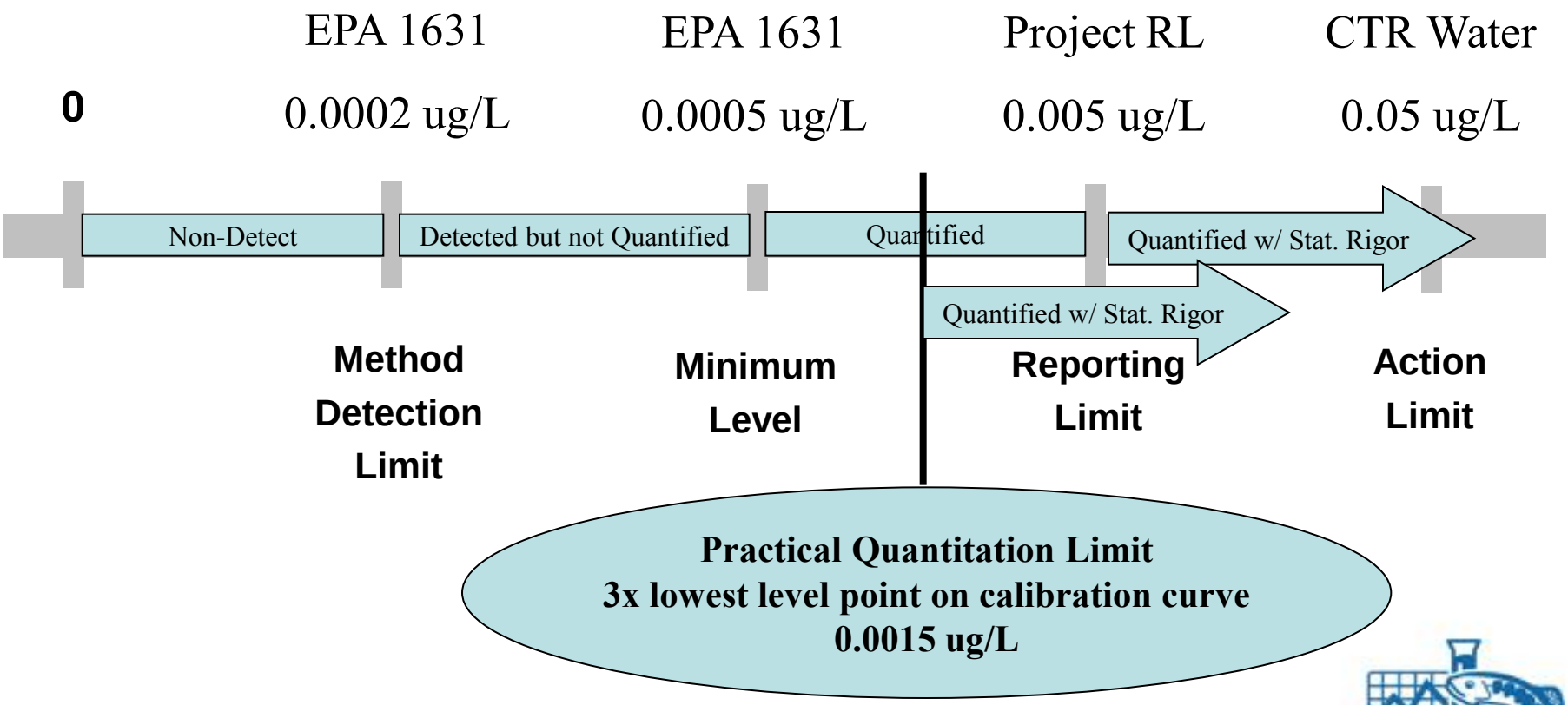

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Definitions of Quantitation Limits

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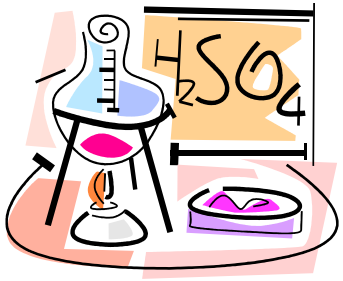
Method Detection Limit



Sample Prep + Analyses + Lab = MDL

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Method Detection Limit

- 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11
  - Google: e-CFR title 40 part 136, go to App. B
- Definition: The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. (40 CFR Section136 Appendix B)
- The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

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Method Detection Limit

- A laboratory determines its MDLs by analyzing a minimum of seven replicates.
- MDL replicate percent recovery acceptance criterion is defined by the range of the percent mean recovery ± 2 times the percent relative standard deviation (%RSD) found for the seven replicates. If any of the seven replicates fails this acceptance criterion, then the analyst discards all results and performs another set of seven replicates.
- The spiking concentrations used to determine an MDL are between 1 and 10 times the calculated MDL.
- This should be determined annually, or at least verified annually.

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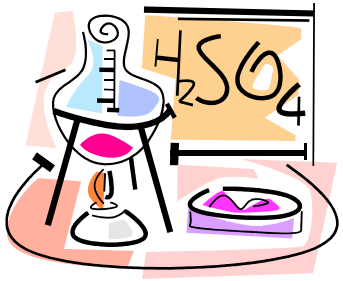
Method Detection Limit



Sample Prep + Analyses + Lab = MDL

7 spike replicates

MDL = lowest level signal is produced

A signal is <u>detected</u>

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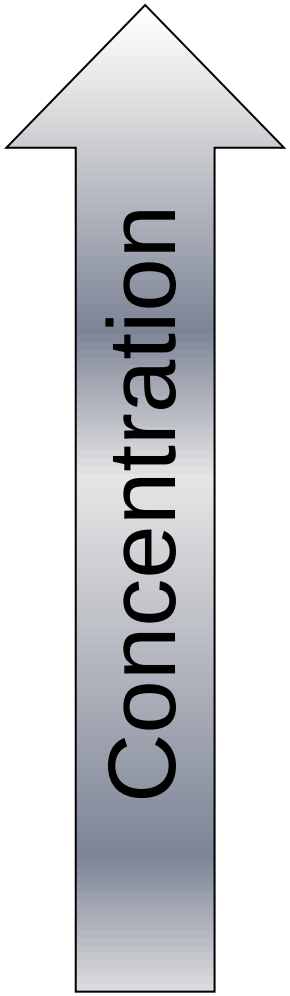

Method Detection Limit

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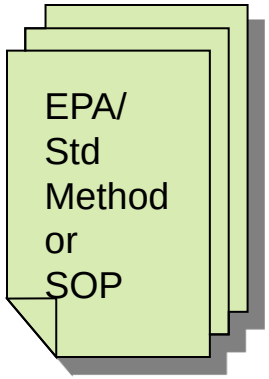
Minimum Level



MDL X (3.18)

Method + MDL + Factor = ML

ML = lowest point on calibration curve

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Minimum Level

- US EPA definition.
- The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point 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.
- The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10n, where n is an integer. (EPA definition)
- Minimum levels are used in some EPA methods.

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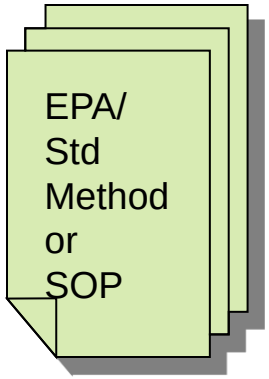
Minimum Level



MDL X (3.18)

Method + MDL + Factor = ML

ML = lowest point on calibration curve

A signal is <u>quantified</u>

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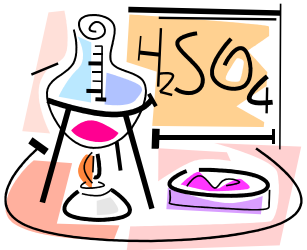
Method Detection Limit



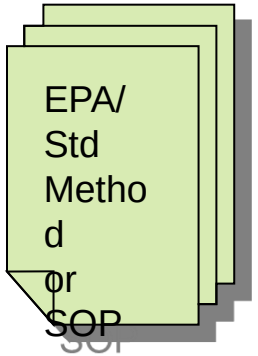
Sample Prep + Analyses + Lab = MDL

7 spike replicates

MDL = lowest level signal is produced

A signal is <u>detected</u>

Minimum Level



MDL X (3.18)

Method + MDL + Factor = ML

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A signal is <u>quantified</u>

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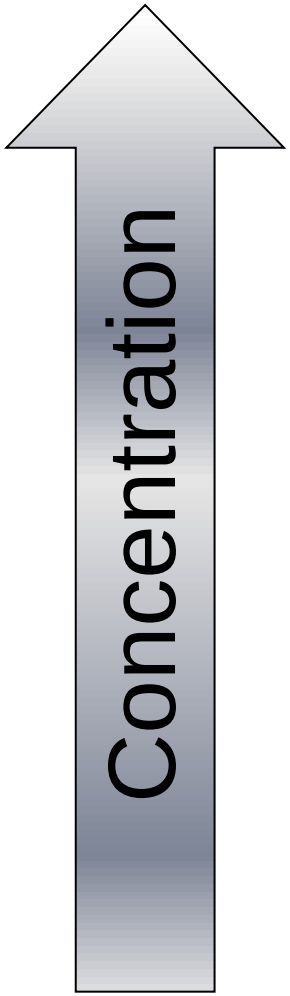

Minimum Level

Method Detection Limit

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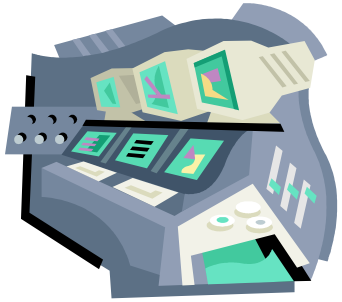
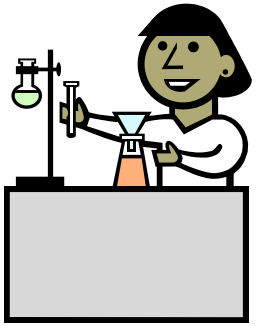
Practical Quantitation Limit





X (2-10)

Instrument + Analyst + Factor = PQL

***** or *****

PQL = 3x lowest point on calibration curve

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Practical Quantitation Limit

- Several different definitions.
- A quantity set at two to ten times above the method detection limit (MDL). By raising the MDL by a factor of two to ten, serving as a “safety factor,” commercial laboratories hope to quantify the environmental sample concentrations with a degree of certainty.
- The degree of the factor (2-10) is decided by the analytical laboratory depending upon the skill and experience of the analyst, the quality of the instrument, and the nature of the sample objectives.

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Practical Quantitation Limit

- The lowest level that can be reliably achieved during routine laboratory operating conditions. The PQL is approximately two to five times the calculated MDL. (Vermont Department of Environmental Conservation)

- The lowest concentration where the 95% confidence interval is within 20% of the true concentration of the sample. The percent uncertainty at the 95% confidence level shall not exceed 20% of the results for concentrations greater than the PQL. (United States Department of Energy)

- 3x the lowest point on the calibration curve (common practice with commercial labs)

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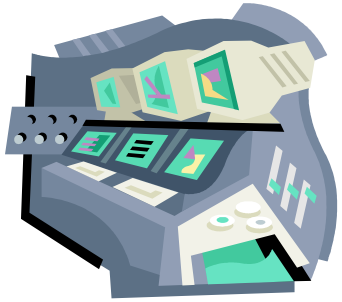
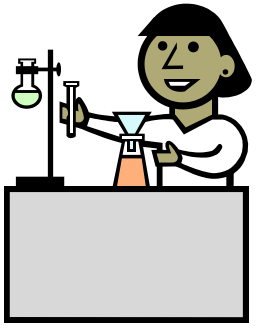
Practical Quantitation Limit





X (2-10)

Instrument + Analyst + Factor = PQL

A signal is quantified

***** or *****

PQL = 3x lowest point on calibration curve

A signal is quantified *with* statistical rigor

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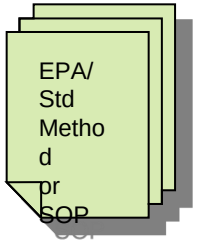
Sample Prep + Analyses + Lab = MDL

7 spike replicates

MDL = lowest level signal is produced

A signal is detected

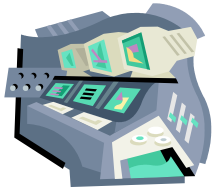


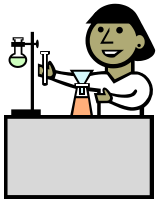
MDL X (3.18)

Method + MDL + Factor = ML

ML = lowest point on calibration curve

A signal is quantified





X (2-10)

Instrument + Analyst + Factor = PQL

A signal is quantified

***** or *****

PQL = 3x lowest point in calibration curve

A signal is quantified *with* statistical rigor

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- MDL = Method Detection Limit

  Detected

- ML = Minimum Level

  Quantified

- PQL = Practical Quantitation Limit

  Quantified

  If 3x the lowest point on calibration curve

  Quantified *with* Statistical Rigor

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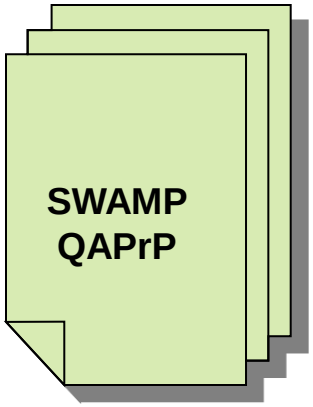
Reporting Limit



Program + Data Use = RL

(Action Limit)

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Reporting Limit

- Several different definitions.
- An instrument-dependent quantity based on the lowest point on the calibration curve. (Massachusetts Department of Environmental Protection)
- A limit imposed upon the reporting laboratory. The RL is usually demanded by the client or regulatory guidelines, and is basically associated with method detection limits (MDLs) or practical quantitation limits (PQLs). (California Regional Water Quality Control Board – Los Angeles Region)
- The RL should have statistical rigor in order to be used in reporting

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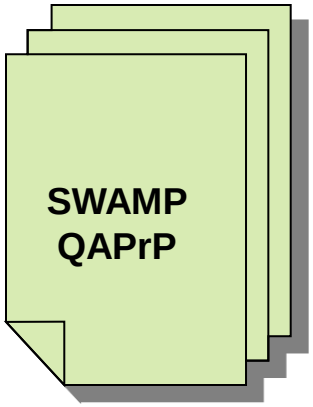
Reporting Limit



Program + Data Use = RL

(Action Limit)

A signal is <u>quantified</u> *with* <u>statistical rigor</u>

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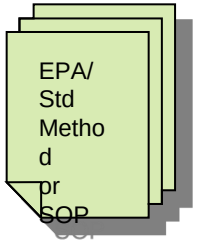
Sample Prep + Analyses + Lab = **MDL**

7 spike replicates

MDL = lowest level signal is produced

A signal is detected

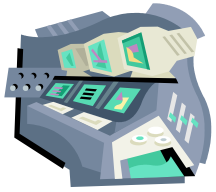


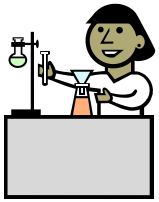
MDL X (3.18)

Method + MDL + Factor = **ML**

ML = lowest point on calibration curve

A signal is quantified





X (2-10)

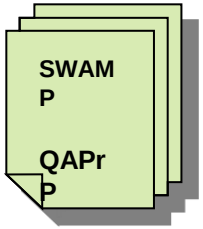
Instrument + Analyst + Factor = **PQL**

A signal is quantified

*** or ***

PQL = 3x lowest point in calibration curve

A signal is quantified *with* statistical rigor



Program + Data Use = **RL**

(Action Limit)

A signal is quantified *with* statistical rigor

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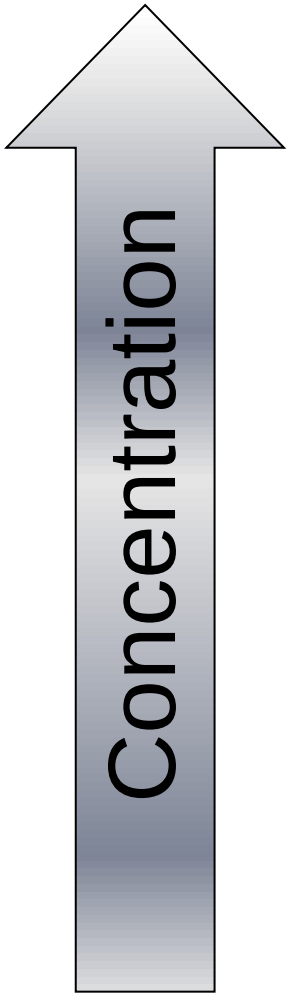

Reporting Limit

Minimum Level

Method Detection Limit

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- MDL = Method Detection Limit
  Detected

- ML = Minimum Level
  Quantified

- PQL = Practical Quantitation Limit
  Quantified

  If 3x the lowest point on calibration curve
  Quantified *with* Statistical Rigor

- RL = Reporting Limit
  Action Limit
  Quantified *with* Statistical Rigor

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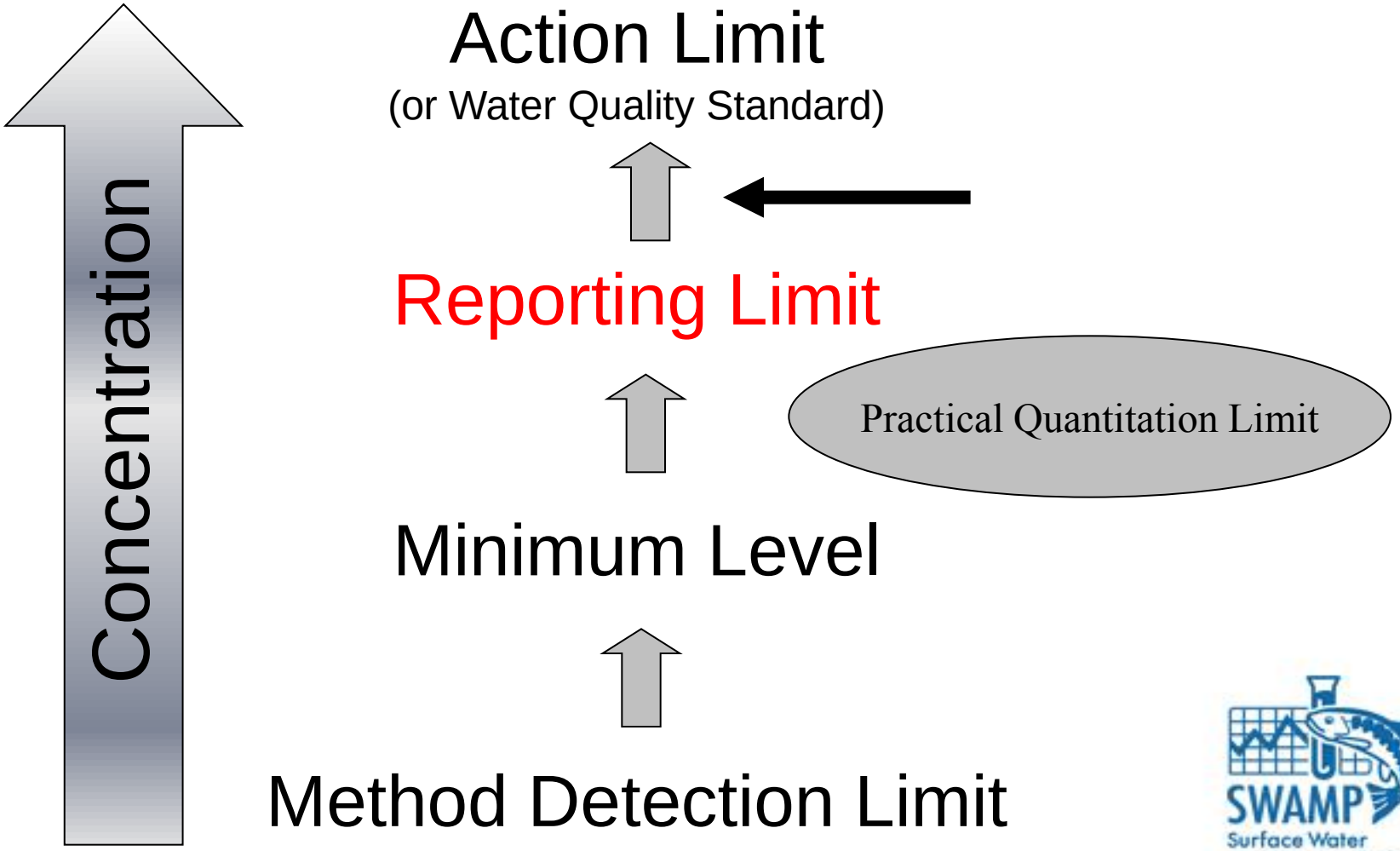

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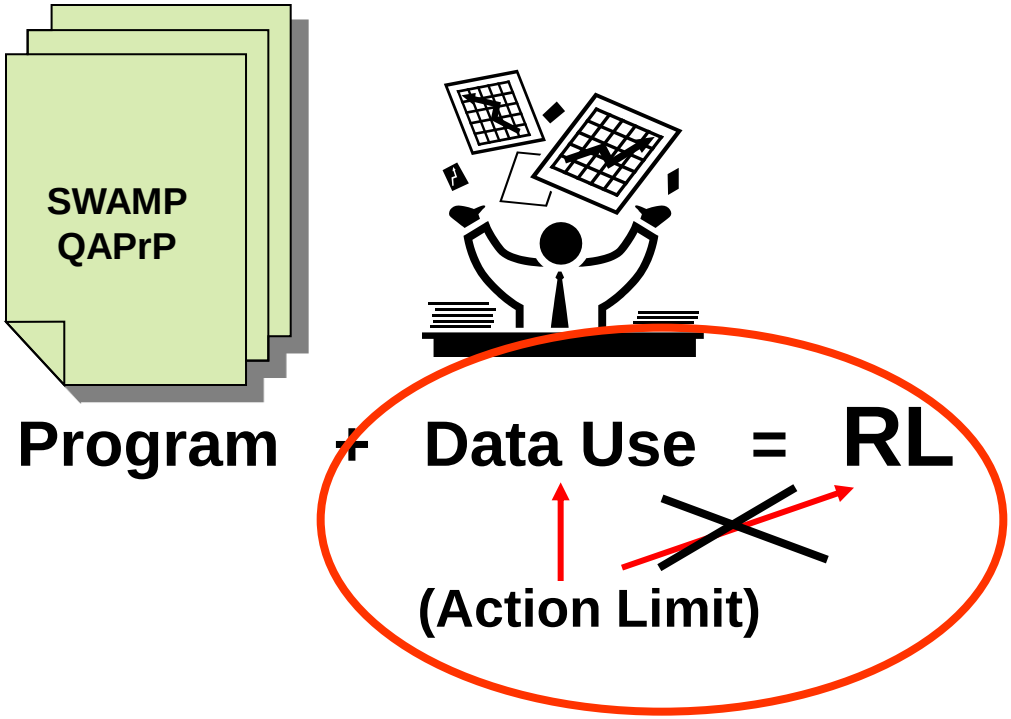
Reporting Limit



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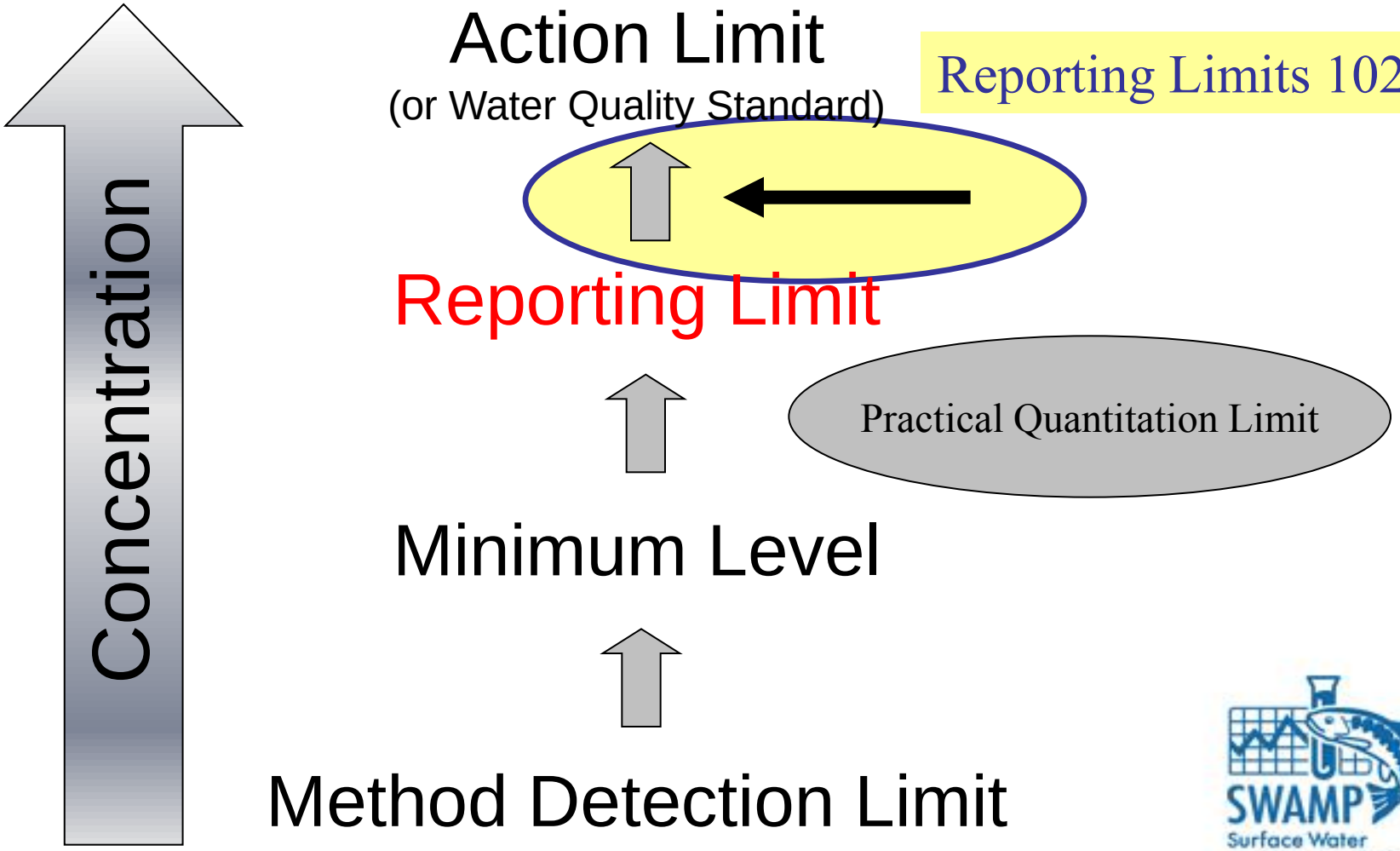

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Method Detection Limit

Minimum Level

Reporting Limit

Action Limit

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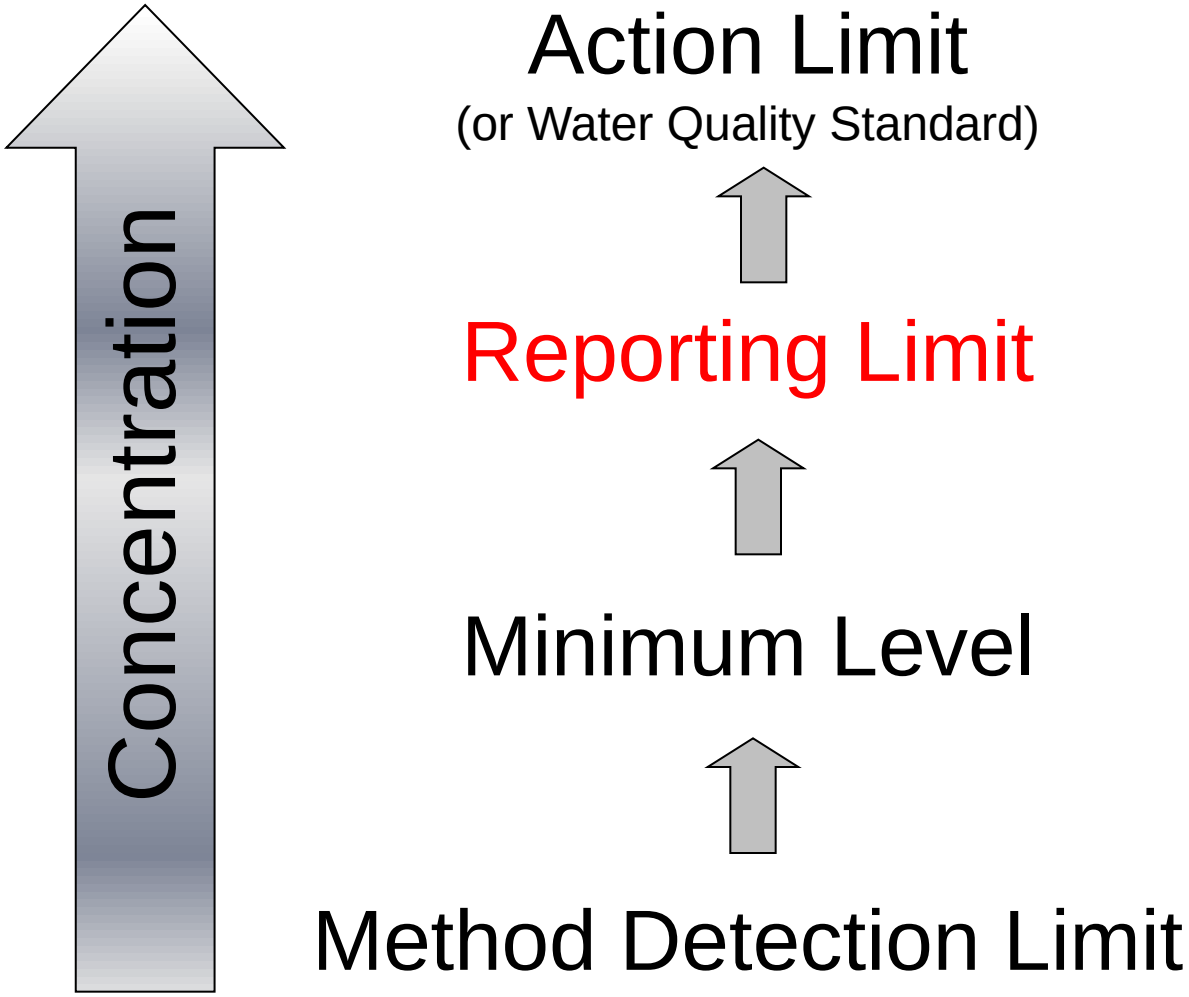
Definitions of Quantitation Limits



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Surface Water Ambient Monitoring Program Reporting Limit Requirements

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SWAMP Reporting Limits

- Target, not required
- Appendix C 2008 SWAMP QA Program Plan
- Currently under revision with a draft of new tables anticipated late 2012

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Where Do I Find the SWAMP Requirements?

- SWAMP 2008 QA Program Plan
  - http://www.waterboards.ca.gov/water_issues/programs/swamp/tools.shtml#qa
  - Google search: SWAMP QAPrP
  - Appendix C: Reporting Limits
- Bioassessment, algae, P-Hab
  - http://swamp.mpsl.mlml.calstate.edu/resources-and-downloads/standard-operating-procedures
  - Google search: SWAMP Bioassessment SOP
- Call/email the SWAMP QA Help Desk
  - 206-525-0491
  - swampqa@mlml.calstate.edu
- Read the SWAMP-Comparability FAQ
  - http://swamp.mpsl.mlml.calstate.edu/faqs

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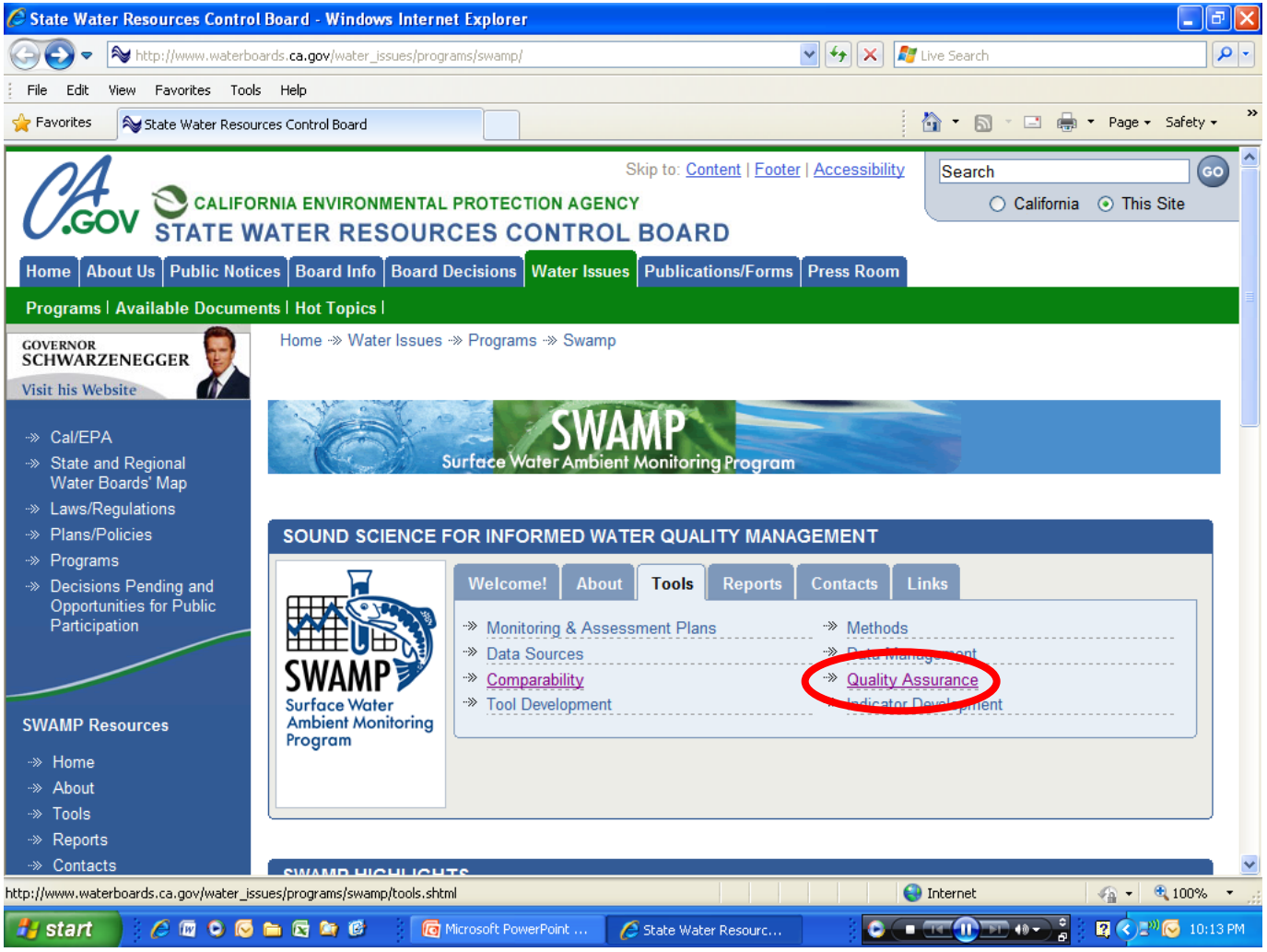
State Board SWAMP Website



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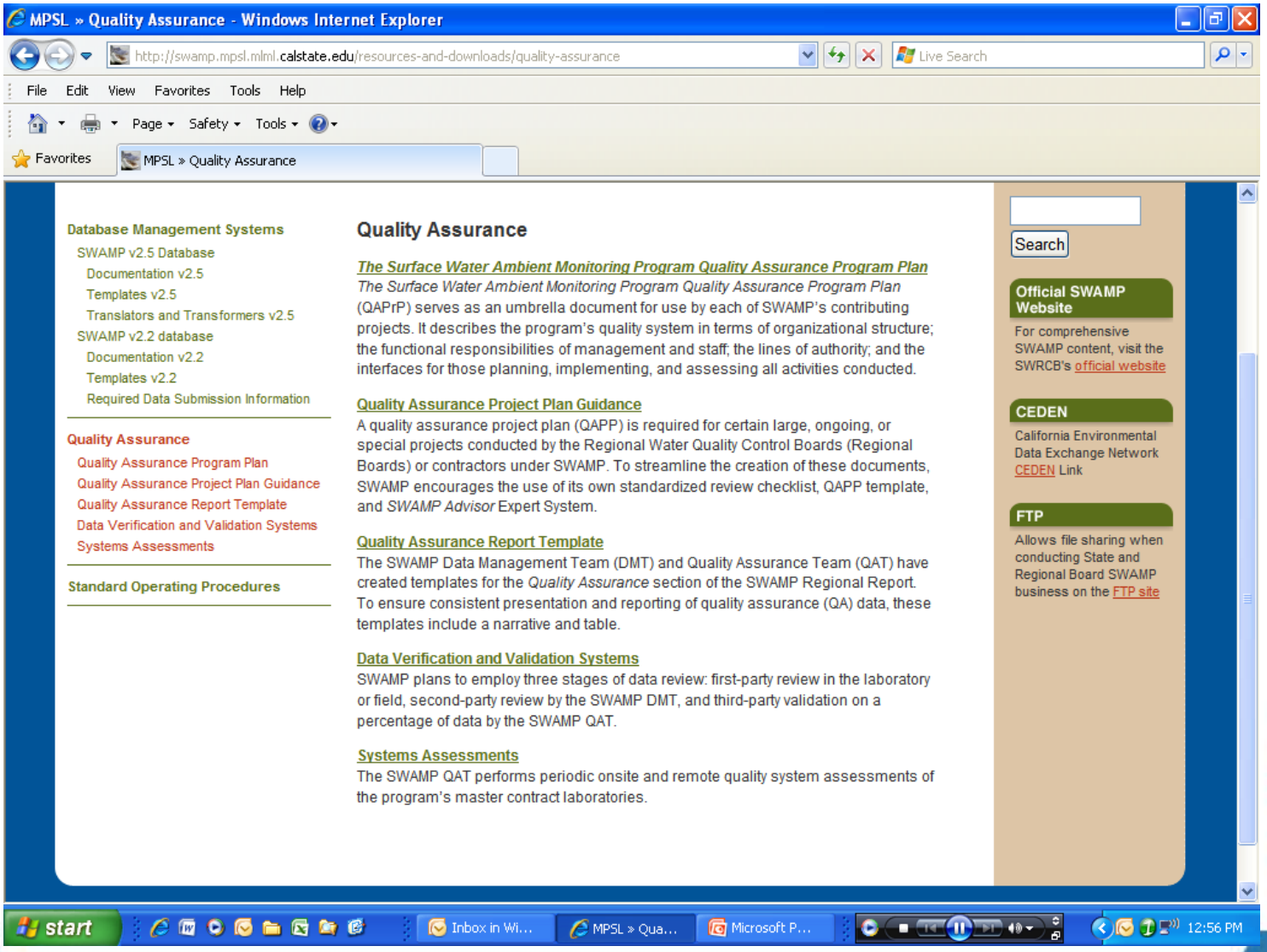
SWAMP Website Hosted by MLML



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Determining Program/Project Reporting Limits

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How do I determine program/project RLs?

- Program/project reporting limits should be based on the use of the data.
  - This may include, but is not limited to, water quality standards, assessment thresholds, TMDLs, regulatory contexts, and use of results with other testing (such as toxicity testing).
- You can find additional information to help determine RLs by looking in the SWAMP QAPrP, the project QAPPs, basin plans, the CTR, and in the analytical methods.
- It is important to understand that you cannot set reporting limits below the lowest level of state-of-the-art analytical capabilities.
- Consider cost/benefit
  - Lower RL may mean less resources for field samples
  - Ensure RL is based on data use

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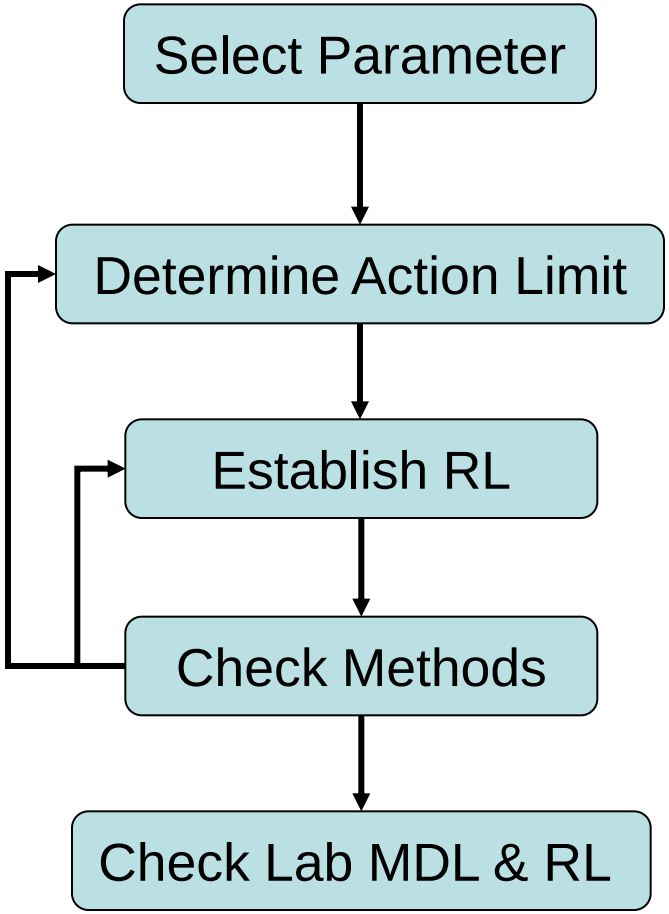

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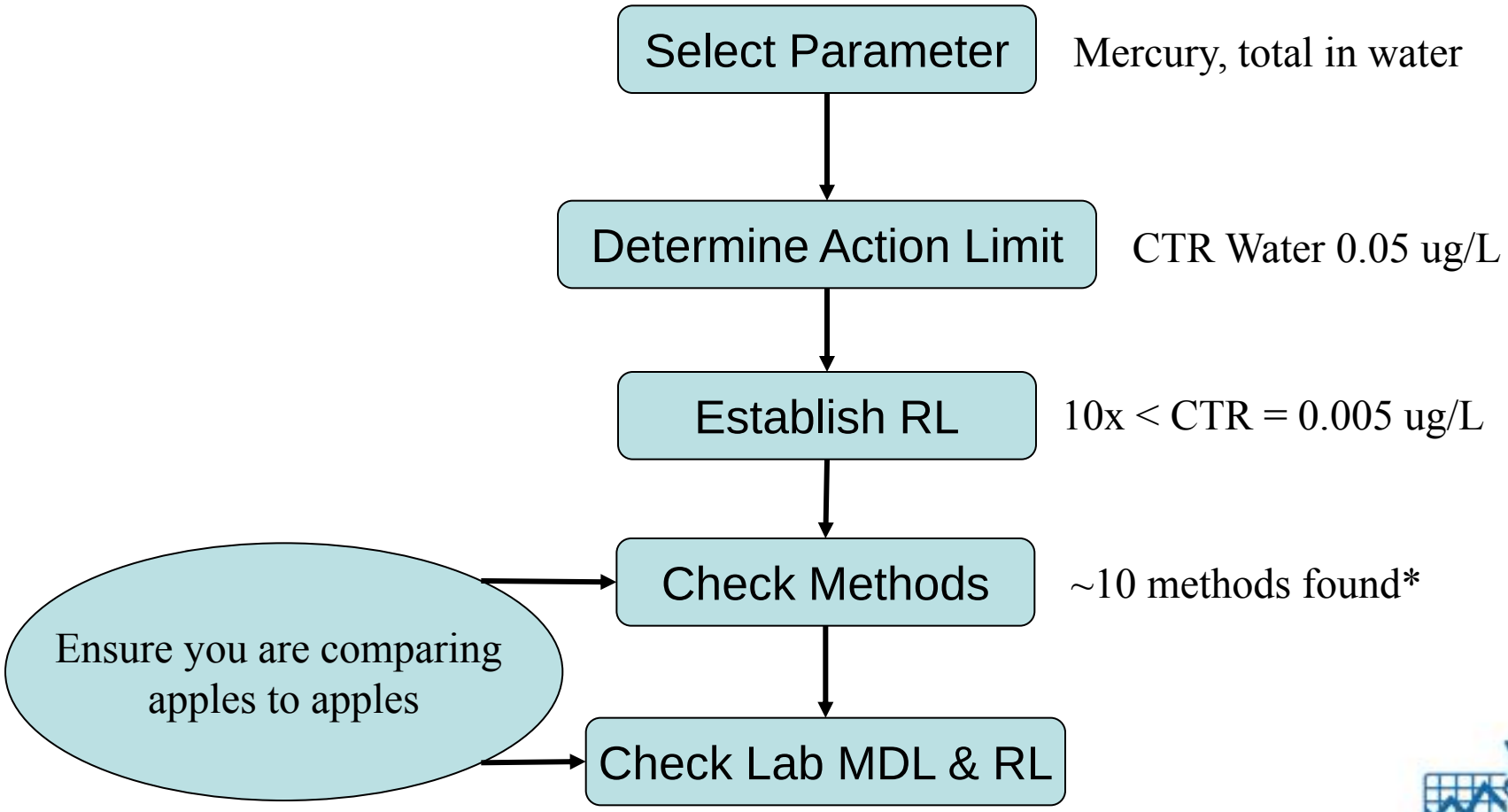

* Use NEMI to find methods: www.nemi.gov

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Method Search

Method #	Source	Detection Level	Detection Type
200.8	EPA	0.2 ug/L	MDL
200.7	EPA	7 ug/L	MDL
245.1	EPA	0.2 ug/L	RNGE
I-1462	USGS	0.5 ug/L	RNGE
I-7462	USGS	0.5 ug/L	RL
D6502	ASTM	1 ug/L	ML
1631	EPA	0.0002 ug/L	MDL
245.7	EPA	0.0018 ug/L	MDL

RL = 0.005 ug/L

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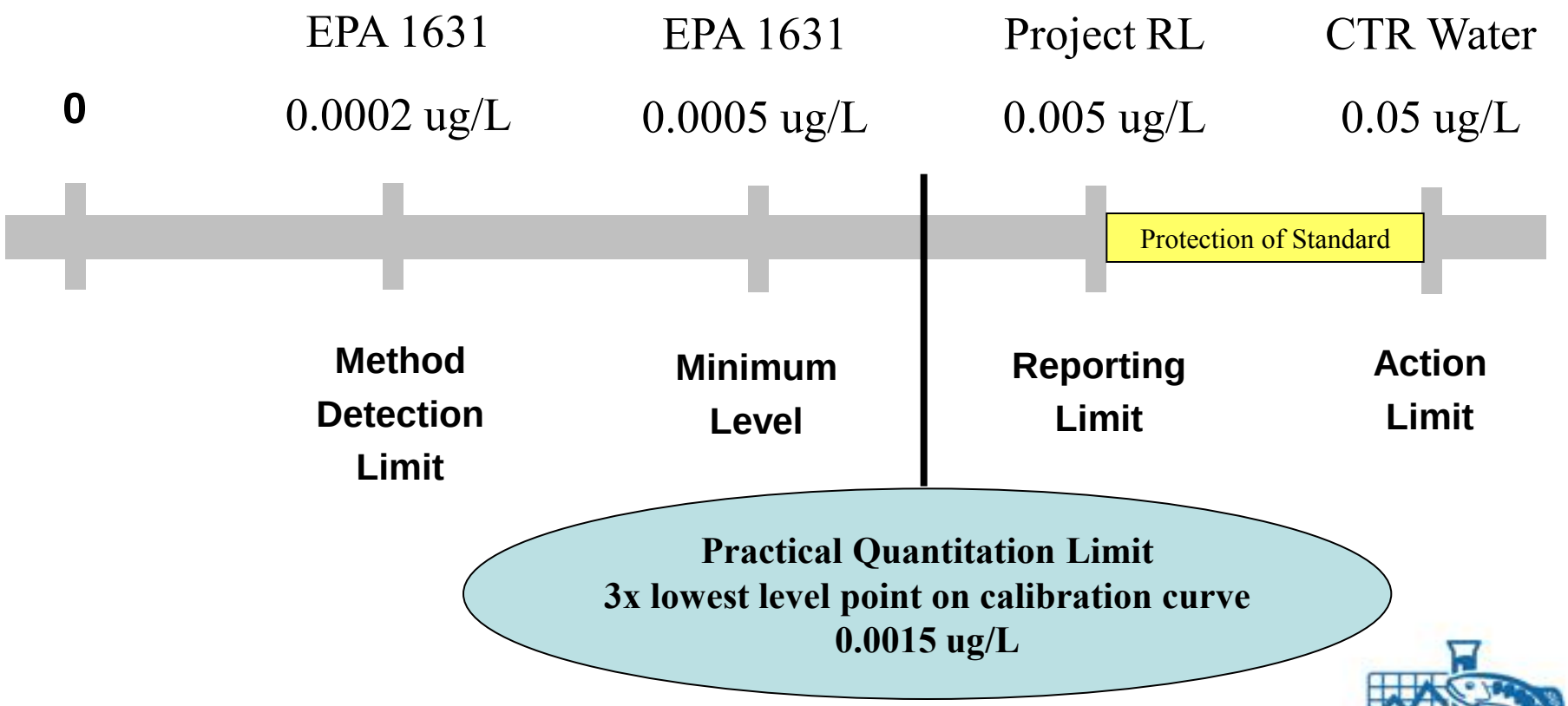

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Working with a Laboratory and Reporting Limits

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Laboratory Reporting Limits

- Generally, a laboratory will establish its reporting limits based on the lowest point in the calibration curve or as 3x the lowest point in the calibration curve. Another method is to set the RLs at 2-5 times the MDL.

- It is easy for a laboratory to misrepresent these terms, so when selecting a lab for your project, be sure to gather the appropriate information.

- Ask to see how MDLs, PQLs, RLs are determined. If the lab can not supply that information quickly, this is a red flag.

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Selecting a Laboratory

Program/project should:

- Supply parameter list to lab
  - List of analyte/matrix combinations to lab along with RL requirements

Lab should:

- Provide list of RLs and MDLs, including methods or SOPs and any modifications (in writing)
- Define how the RLs are determined (are they PQLs, MLs, etc.)
- Identify if they will comply with all the program/project or QC requirements
- Have a designated QA Officer

Both should:

- Include reporting limits as part of the written contract

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Documents for Communication of Reporting Limits

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How should RL requirements be communicated?

Reporting limits should be communicated:

- In legal documents such as permits and contracts;
- During project planning and coordination meetings;
- Within a QA Program or Project Plan; and
- During the laboratory selection process.

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Permits and Contracts

- Specifying RL requirements directly into legal documents such as permits and contracts
  - Improves communication between data producer and data users
  - Prompts all parties/organizations to clarify important project details

- Suggestions for Legal Documents
  - MQOs (i.e., QC samples types, quantities, and limits)
  - Holding Times
  - Methods
  - Reporting Limits (and MDLs)
  - Reporting Formats & Timelines
  - Subcontracting work

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Comments on Reporting in the Context of Quantitation Limits

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Reporting

When reporting data, other terms worth understanding include:

- **Not Detected (ND)**: Sample result is less than MDL; Analyte being tested cannot be detected by the equipment or method.

- **Detected Not Quantifiable (DNQ)**: Sample result is between the MDL and the ML. These results may be reported as the measured value (not negative) with a flag that is carried all the way through data storage, handling, and reporting.

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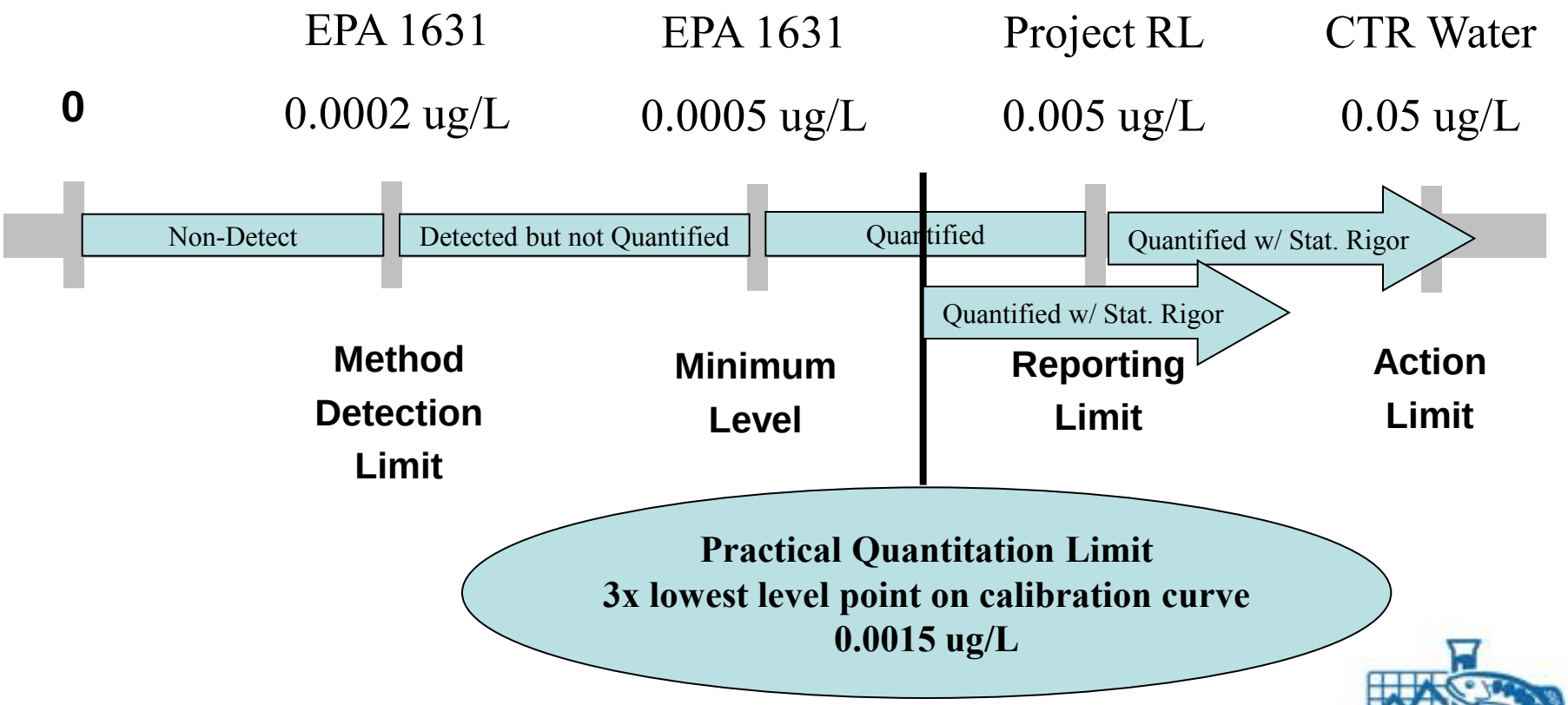

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New Developments – Stay Tuned to EPA

- US EPA Report December 2011
- A Laboratory Study of Procedures Evaluated by the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs
- http://water.epa.gov/scitech/methods/cwa/det/upload/fac_report_2009.pdf
- Study found that the procedures for determining method detection/quantitation are flawed.
- “none of the procedures tested consistently generated accurate estimates of the lowest concentration” page 88
- Note that the study itself lacked in statistical power and real-world applicability in terms of # of labs and methods

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Conclusion

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Outcome

- A general understanding of common quantitation limit terms
- An understanding of the differences between quantitation limits
- The SWAMP requirements for reporting limits and SWAMP resources
- A brief introduction to determining reporting limits
- Tips for ensuring labs can hit reporting limits

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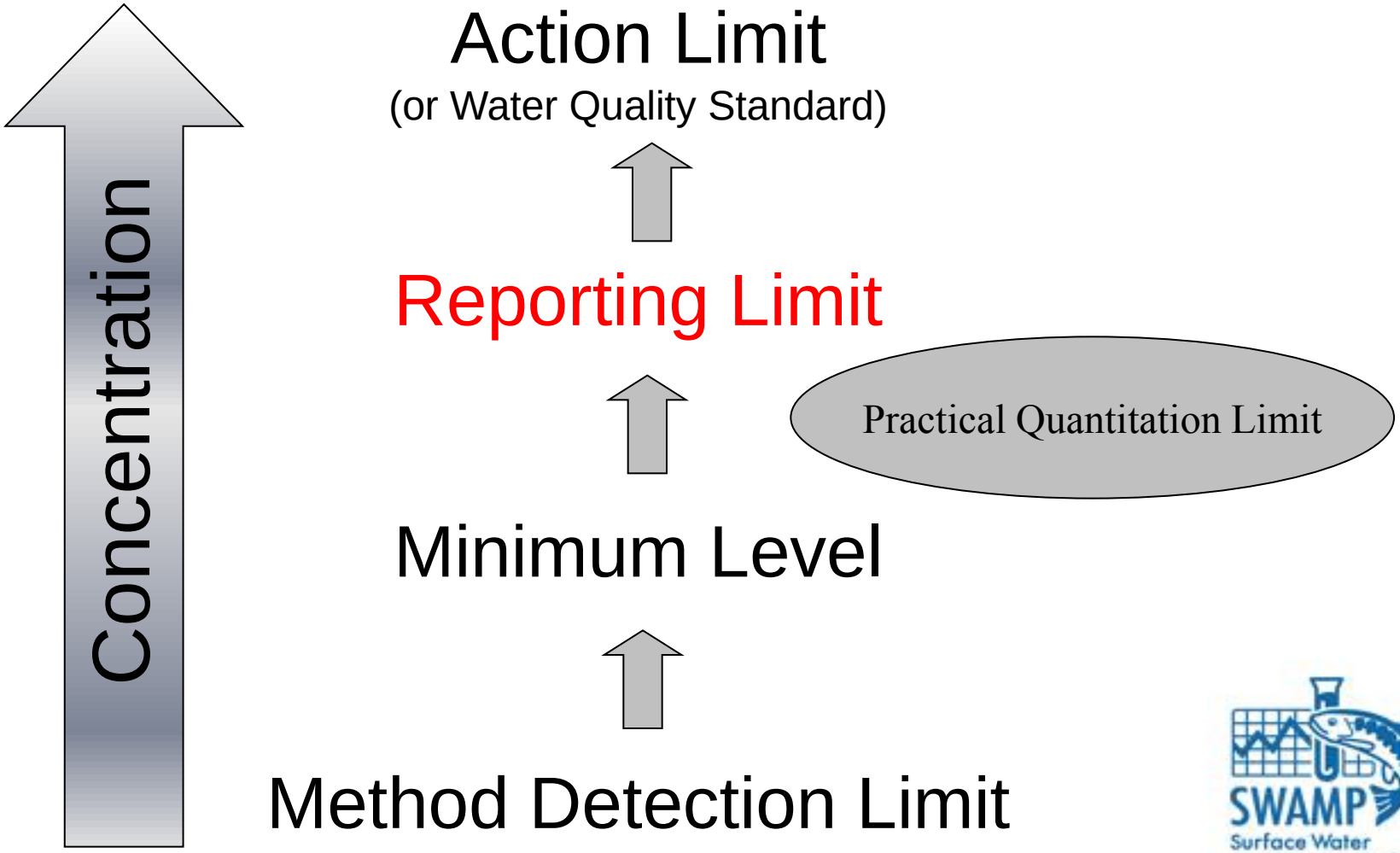

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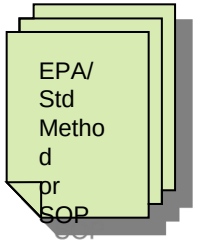
Sample Prep + Analyses + Lab = MDL

7 spike replicates

MDL = lowest level signal is produced

A signal is detected

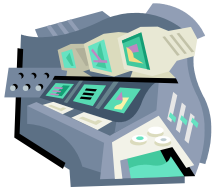


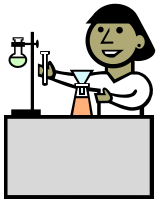
MDL X (3.18)

Method + MDL + Factor = ML

ML = lowest point on calibration curve

A signal is quantified





X (2-10)

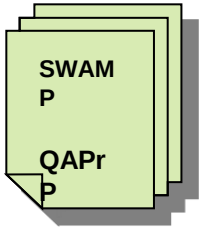
Instrument + Analyst + Factor = PQL

A signal is quantified

***** or *****

PQL = 3x lowest point in calibration curve

A signal is quantified *with* statistical rigor



Program + Data Use = RL

(Action Limit)

A signal is quantified *with* statistical rigor

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0

Method Detection Limit

Minimum Level

Reporting Limit

Action Limit

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Reporting Limits 102

- Examples of setting reporting limits for different Water Board uses
- Can the action limit (e.g., assessment threshold/water quality standard) and RL be the same?
- Can standards be below method capabilities?
- How to set reporting limits when chemistry results are tied to other data, such as toxicity testing
- Benefits to statistical rigor using an RL of 3x the lowest point on calibration curve
- How to work with results that are between the MDL and RL – results that are detected but not quantified
- I need lower RLs and MDLs – what can I do?

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Where do I get help?

SWAMP QA Help Desk
(206) 525-0491
swampQA@mlml.calstate.edu

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The QA Research Group at Moss Landing Marine Laboratories

Specializing in the Quality Assurance associated with all areas of environmental science such as in-stream flow, bioassessment, P-Hab, chemistry (including ultra-trace and speciation), toxicity testing, statistical analysis, field measurements, and database structures. If you would like to contract with the QA Research Group, please contact Beverly H. van Buuren.

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Moss Landing Marine Laboratories

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SWAMP QA Program Resources

- SWAMP 2008 QA Program Plan
  - http://www.waterboards.ca.gov/water_issues/programs/swamp/tools.shtml#qa
- SWAMP QA Help Desk
  - 206-525-0491
  - swampqa@mlml.calstate.edu
- SWAMP Advisor (QAPP-creation software)
  - http://swamp.waterboards.ca.gov/swamp/qapp_advisor/
- SWAMP Web Site (Google search: SWAMP QA Help)
  - http://swamp.mpsl.mlml.calstate.edu/
  - http://www.swrcb.ca.gov/water_issues/programs/swamp/tools.shtml

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