Retooling To Calculate Initial and Annual MDLs Following Revision 2 of 40CFR136 Appendix B

August 8, 2024

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Today's Topics

- MDL Calculating/Evaluation – as it was
- MDL Calculating/Evaluation – as it is
- The Gaps to Resolve
- Evolution and Validation
- Resources

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MDLs - Past

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MDLs - then

- 7 (or more) replicates
- MDL = $t_{(n-1,1-\alpha=0.99)} \times S$
- Easily presented in a table:

Date Analyzed:	1/1/2023				**Instrument**		test instrument					Matrix:	
Method ID/Description	TestMethod			ug/L	**Analyst:**		TestMe					Aqueous:	x
					Notes:		TestBatch123					Solid:	
Prep Method / Date	Test Prep				**Quality Assurance**			TestQA				Other:	
	Spike	MDL #1	MDL #2	MDL #3	MDL #4	MDL #5	MDL #6	MDL #7	**AVE.**		**SD**	**MDL**	**RL**
Analyte	**ug/L**	**ug/L**	**ug/L**	**ug/L**	**ug/L**	**ug/L**	**ug/L**	**ug/L**	**ug/L**	**%R**	**ug/L**	**ug/L**	**ug/L**
Demo Analyte	5.000	4.100	4.250	4.400	4.300	4.900	4.300	4.800	4.436	89%	0.30	0.94	10

Evolution

- Integrated into LIMS
- Specialized Query
- Flexibility
  - Time Periods
  - Multiple Instruments or by Instrument

Evolution

Method 8290 Detection Limit Study

Type: 40 CFR 136 App B MDL

Laboratory Eurofins Sacramento

Preparation Method: 8290_P_Sox

Limit Group HR - 8290 - 8290A - Solid - RL_MDL_LOD

Analysis Dates: 12/1/2021 to 3/1/2022

Analyte	Spike Amount	Replicate Measurements 1	2	3	4	5	6	7	8	AVG pg/g	% Rec Mean	Std Dev	Calc MDL	Current MDL	RL
1,2,3,4,6,7,8-HpCDD	5.0	5.6683210	5.171299	5.285586	5.253890	5.524724	5.444683	5.362383		5.387270	107.74	0.171547	0.539174	0.853	5
1,2,3,4,6,7,8-HpCDF	5.0	6.3202906	5.226993	5.275540	5.209861	5.360481	5.141398	5.345311		5.411411	108.22	0.408049	1.282498	1.15	5
1,2,3,4,7,8,9-HpCDF	5.0	5.6596148	5.115876	5.297064	5.236044	5.302183	5.282266	5.258664		5.307387	106.14	0.167813	0.527439	0.955	5
1,2,3,4,7,8-HxCDD	5.0	5.4027800	5.308719	5.467327	5.426619	5.366428	5.149821	5.298854		5.345792	106.91	0.105640	0.332027	1.04	5
1,2,3,4,7,8-HxCDF	5.0	5.8971344	5.201839	5.324915	5.348007	5.338160	5.305214	5.242753		5.379717	107.59	0.234309	0.736435	1.58	5
1,2,3,6,7,8-HxCDD	5.0	5.2994397	5.117214	5.204235	5.436150	5.637551	5.541081	5.444980		5.382950	107.65	0.185307	0.582422	0.768	5
1,2,3,6,7,8-HxCDF	5.0	5.9252004	5.235611	5.406759	5.416472	5.466521	5.342789	5.256349		5.435671	108.71	0.231877	0.728790	1.38	5
1,2,3,7,8,9-HxCDD	5.0	5.4649298	5.363958	5.277760	5.441585	5.423400	5.497040	5.398189		5.409552	108.19	0.072474	0.227788	1.05	5
1,2,3,7,8,9-HxCDF	5.0	5.4871231	5.306548	5.353197	5.551487	5.526214	5.442765	5.440670		5.444001	108.88	0.088809	0.279128	1.32	5
1,2,3,7,8-PeCDD	5.0	5.4972735	5.343922	5.255803	5.430625	5.380665	5.509540	5.419648		5.405354	108.10	0.088407	0.277865	0.628	5
1,2,3,7,8-PeCDF	5.0	5.7436764	5.324232	5.432748	5.348209	5.376609	5.243918	5.415676		5.412153	108.24	0.159022	0.499808	1.39	5
2,3,4,6,7,8-HxCDF	5.0	5.5519711	5.381468	5.317165	5.409006	5.396260	5.406492	5.430587		5.413278	108.26	0.070874	0.222757	1.29	5
2,3,4,7,8-PeCDF	5.0	5.3068721	5.157431	5.222504	5.201204	5.298636	5.228634	5.158049		5.224761	104.49	0.060219	0.189270	1.11	5
2,3,7,8-TCDD	1.0	1.2996374	1.310418	1.199494	1.317239	1.258757	1.241981	1.265161		1.270384	127.03	0.042127	0.132407	0.161	1
2,3,7,8-TCDF	1.0	1.4617963	1.110271	1.119649	1.130540	1.161829	1.137936	1.170978		1.184714	118.47	0.124086	0.390004	0.368	1
OCDD	10.0	14.335107	11.27160	11.10512	10.60379	11.31134	11.17743	10.77609		11.51150	115.11	1.272259	3.998710	3.61	10
OCDF	10.0	13.063083	10.85891	10.83468	10.61439	11.23661	10.58280	11.05841		11.17841	111.78	0.862444	2.710663	2.47	10

Batch-Sample List: 559045-8 559045-9 559045-10 559086-27 559086-28 559200-7 559200-8

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MDLs - Now

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MDLs - Now

- Calculate spikes and blanks
- Many replicates
- Extended time period
- Options for blank calculation
- On-going comparison

Gaps

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New Considerations

- Quarterly checks
- Multiple spike concentrations
- MDL_b ??
- MDL_b vs MDL_s
- $MDL_{Current}$ vs MDL_{Calc}
- Clean Presentation
- Data in LIMS?

Output Appearance?

Analyte

1,2,3,4,6,7,8-HpCDD

Current MDL	Current RL
0.853	5

Calculations Avg pg/g	Spike amount	% Rec Mean	Std Dev	Reps	Stud T	Calc MDL
0.9727835	0.75	129.70	0.076593	8	2.998	0.229627

Evaluation 2 MDL < RL	RL / MDL	Mean / MDL	MDL>10% Spike Amnt	Recovery 50-150%
Pass	21.8	4.2	Pass	Pass

Lab ID	Anal Date	Batch	Samp	Analyst	Method	Prep Method	Equipment	Result	Units	Exclude
320-103472-A-27-BN	09/17/2023	706684	9	Stephens, Kyle	8290	8290_P_Sox	DFS 1	1.065839164	pg/g	
320-103472-A-17-BN	09/20/2023	707706	11	Bennett, David	8290	8290_P_Sox	12D5	1.039606756	pg/g	
320-103474-A-15-AN	09/22/2023	708232	4	Cox, Joshua B	8290	8290_P_Sox	DFS 1	0.963412515	pg/g	
320-103474-A-8-AMI	09/24/2023	708405	18	Bennett, David	8290	8290_P_Sox	12D5	0.845889882	pg/g	
320-105651-A-27-AN	10/22/2023	714904	4	Bojorquez, Courtney	8290	8290_P_Sox	DFS 1	0.920744187	pg/g	
320-105651-A-17-AN	10/29/2023	716614	4	Bennett, David	8290	8290_P_Sox	12D5	0.924850848	pg/g	
320-105652-A-8-AMI	11/02/2023	717478	4	Bennett, David	8290	8290_P_Sox	12D5	1.054726783	pg/g	
320-105652-A-15-AN	11/04/2023	718185	4	Stephens, Kyle	8290	8290_P_Sox	DFS 1	0.967198038	pg/g	

1,2,3,4,6,7,8-HpCDF

Current MDL	Current RL
1.15	5

Calculations Avg pg/g	Spike amount	% Rec Mean	Std Dev	Reps	Stud T	Calc MDL
0.9079681	0.75	121.06	0.101041	8	2.998	0.302922

Evaluation 2 MDL < RL	RL / MDL	Mean / MDL	MDL>10% Spike Amnt	Recovery 50-150%
Pass	16.5	3	Pass	Pass

Lab ID	Anal Date	Batch	Samp	Analyst	Method	Prep Method	Equipment	Result	Units	Exclude

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Better?

Overall Summary

Method	EPA 314.0/NA													Reviewer	SN3k		
Matrix	Aqueous													Review Date	06/09/2023		
Analyte	Spike Conc	Unit	RL	MDL	Calc MDL	MDLb Option	MDLs	MDLb (99th)	MDLb (t-stat)	MDLb (Max)	CalcMDL/MDL	RL/CalcMDL	Spike/MDL	Blank Hits > MDL (%)	Comment		
Perchlorate	0.499	ug/L	1.000	0.110	0.192930	MDLb (Max)	0.192930		0.000000	0.000000	1.75	5.18	4.53	0.0	Acceptable, no change needed.		

Blank Evaluation

Analyte	Unit	RL	MDL	Mean Result	Std Dev	N (Total)	N (Actual)	Stud T	Min Val	Max Val	Blank Hits > MDL (%)	Zeros (%)	MB Censored	MDLb (99th)	MDLb (t-stat)	MDLb (Max)
Perchlorate	ug/L	1.000	0.110	0.000000	0.000000	53	53	2.400	0.000	0.000	0.0	100.0	No	NC	0.000000	0.000000

Spike Evaluation

Analyte	Spike Cor	Unit	RL	MDL	Calc MDL	RL/CalcMDL	Mean/CalcMDL	CalcMDL/MDL	Mean Result	Mean/Spike (%)	Std Dev	N	Min Val	Max Val	Stud T	Spike > CalcMDL	Spike < RL
Perchlorate	0.4985	ug/L	1.000	0.110	0.192930	5.18	2.58	1.75	0.497441	99.8	0.070980	12	0.402	0.620	2.718	Yes	Yes
Perchlorate	0.4990	ug/L	1.000	0.110	NC	NC	NC	NC	NC	NC	NC	2	0.518	0.534	NC	N/A	N/A

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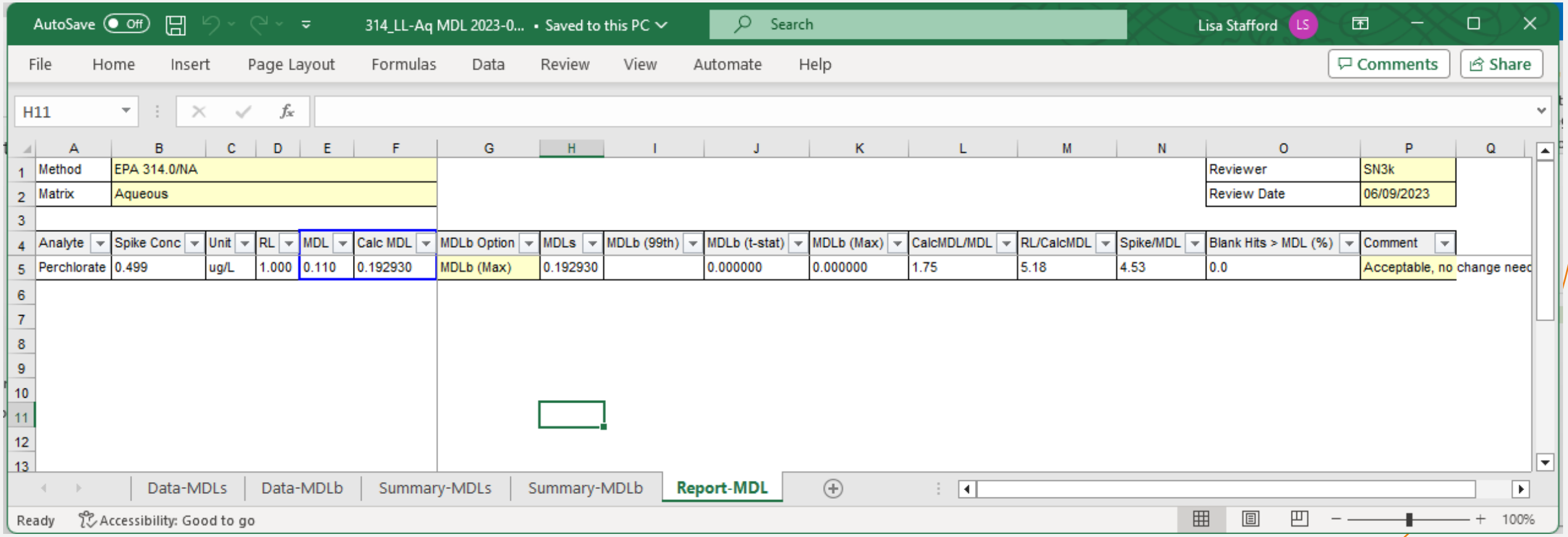
Single File!



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	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	Method	EPA 314.0/NA													Reviewer	SN3k	
2	Matrix	Aqueous													Review Date	06/09/2023	
3																	
4	Analyte	Spike Conc	Unit	RL	MDL	Calc MDL	MDLb Option	MDLs	MDLb (99th)	MDLb (t-stat)	MDLb (Max)	CalcMDL/MDL	RL/CalcMDL	Spike/MDL	Blank Hits > MDL (%)	Comment	
5	Perchlorate	0.499	ug/L	1.000	0.110	0.192930	MDLb (Max)	0.192930		0.000000	0.000000	1.75	5.18	4.53	0.0	Acceptable, no change neec	
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11																	
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Data-MDLs | Data-MDLb | Summary-MDLs | Summary-MDLb | Report-MDL

Ready | Accessibility: Good to go | 100%

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Evolution & Validation

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Brainstorming

Existing Data Queries (“Control Chart”)

Exportable

Excel Read-able

Logical Process, therefore programmable

Evolution?

- Specifications
  - Import
  - Calculate
  - Compare/Evaluate
- Formatting
  - Retain imported data
  - Summarize Separately
  - Evaluation/Comparison
- User Interface

Iterations

- 4 versions over 6 months before initial release
  - Bug testing
  - Logic errors corrected.
- Fully reprogrammed version 2 years later
  - Added checks
  - Calculations refined
  - Improved Functionality
  - Code Efficiency
  - Use of inherent Excel functions

Resources

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Expenditure

- Initial: 120 person-days for the first four versions
- Revamp (version 5):
  - 120 person-hours to program
  - 40 person-hours to test and validate.

Gains

- Time
  - Simple MDLs: 30 min/MDL
  - Complex MDLs: 4-6 hours/MDL
- Presentable Summary
- Traceable Data

How to do this at home…

Spike Data:

- Concentration of each analyte
- Measured value for each analyte (preferably before rounding)
- Traceability Info (trace to prep and analysis)/sample ID
- Make sure all concentrations/measured values are in the same units (may need to massage data after export?)
- Helpful to have RL and MDL in export, can be added to summaries manually later.
- Format as table: Analyte Name, sample ID, Concentration, Measured, units

How to do this at home…

Blank Data:

- Result for each analyte (even if ND),
  - to < MDL,
  - before rounding
  - Same units as spike
- Traceability Info (trace to prep and analysis)/sample ID
- Helpful to have RL and MDL in export, can be added to summaries manually later.
- Format as table: Analyte Name, sample ID, concentration, units.

Crunching the data…

- Pivot tables can summarize blanks and spikes
  - Calculate Mean/SD & count number of values (n).
  - Insert summarized data into the summary table
- Useful functions for calculations and collating data:
  - vlookup
  - t.inv(0.99, n-1)
  - percentile.inc(data range, 0.99)
  - If() (blanks>MDL%, etc)

Acknowledgements

The following individuals were instrumental in bringing the “Cruncher” to life:

Brayden Dutrow

Kathryn Chang

Pamela Schemmer