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NATTS TAD Revision 3

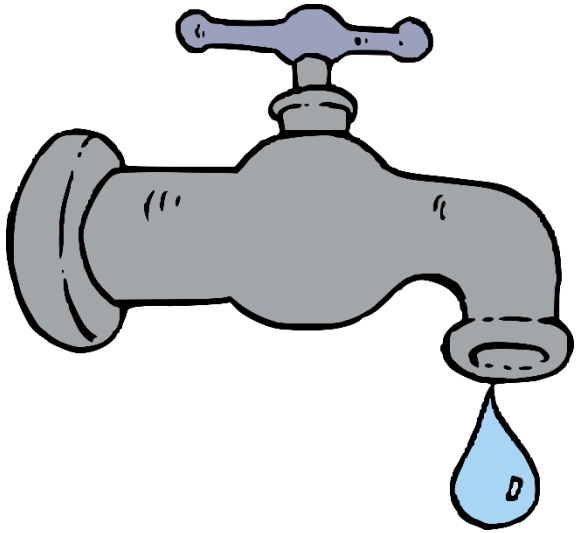
Method Detection Limits

Method Update Rule vs 40 CFR Part 136

Method Detection Limits

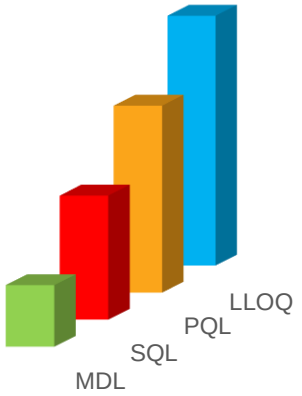
- Agenda:
  - Background of detection limits
  - MDLs as they relate to the NATTS network
  - MDL Method Update Rule
  - Determining MDLs via Method Update Rule
  - Analysis of reported AQS data to examine impact of MUR
  - Example scenario

- The *method detection limit* (MDL) is defined as 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.
- Initially designated for water analyses, but adapted for many other matrices.



Detection Threshold Terms

- Common terms related to the detection threshold
  - Method Detection Limit (MDL) – defined by 40 CFR Part 136 App B
  - Limit of Detection (LOD) – TNI term for detection, not quantitation
  - Sample Quantitation Limit (SQL) – typically ~3x the MDL
  - Practical Quantitation Limit (PQL) – typically 5x the MDL
  - Lower Limit of Quantitation (LLOQ) – typically the lowest calibration standard level
  - Method Reporting Limit (MRL) – lowest quantifiable concentration, often set at the LLOQ



Method Detection Limits

- MDLs are controversial
- You may have heard (or said yourself):
  - "MDLs are flawed because they are a theoretical value."
  - "MDLs don't reflect real-world conditions."
  - "MDLs don't take into account the sample media background."
  - "We don't trust values around the MDL."

NATTS Network MDLs

- MDLs are necessary to properly assess risks, particularly at the ambient concentrations measured by the NATTS network
- Concentration data must be qualified according to relationship with MDL and SQL so data users can assign proper confidence
- Consistent determination of analyte MDLs ***across all NATTS laboratories*** ensures results are comparable
- MDLs aren't going away anytime soon

Method Detection Limits

- 40 CFR Part 136 App B prescribes preparation and analysis of a minimum of 7 spikes in matrix. The MDL is calculated by multiplying the standard deviation of the measured concentrations by the appropriate student's T.

$$MDL = s \cdot T$$

- Compare the determined MDL to the nominal spiked value.

$$MDL < spike\ value < 10x\ MDL$$

NATTS MDLs – TSAs

- TSAs of NATTS network laboratories found that very few laboratories determined MDLs correctly per 40 CFR Part 136 Appendix B or were not determining them annually.
  - Analyzed a standard directly without matrix 7 times
  - Analyzed one or two samples annually to “verify” the MDL
  - Prepared one spiked sample and analyzed this sample 7 times
  - Prepared 7 spiked samples not including all portions of the matrix
  - Did not ensure that the nominal spiked value was 1- to 10-fold the determined MDL

MDLs – Method Update Rule

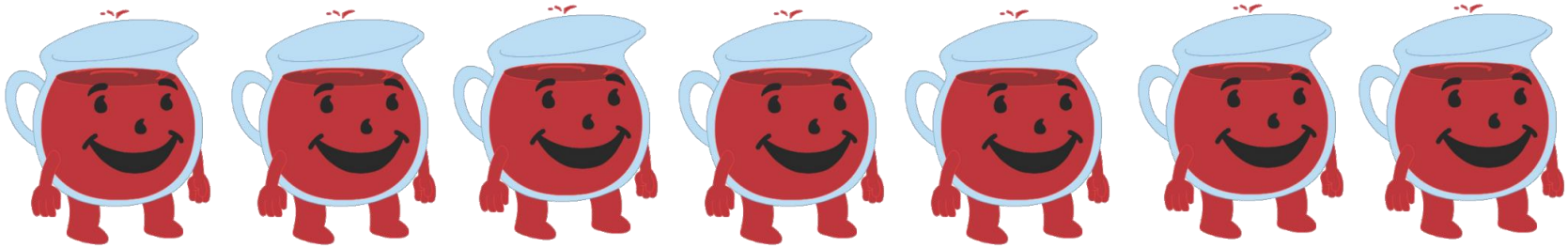
- Draft Revision 3 of the NATTS TAD adopts the Method Update Rule
- Why adopt the Method Update Rule…?
  - MDLs determined by 40 CFR Part 136 Appendix B do not take into account the sample collection media.
  - TO-11A permits up to 0.150 µg/cartridge, or 0.104 µg/m^3 assuming 1.44 m^3 collected volume. This exceeds the MDL MQO of 0.08 µg/m^3.
  - An analysis of AQS data and laboratory reported MDL data indicate that little to no additional data would be qualified as < MDL following adoption of the MUR.

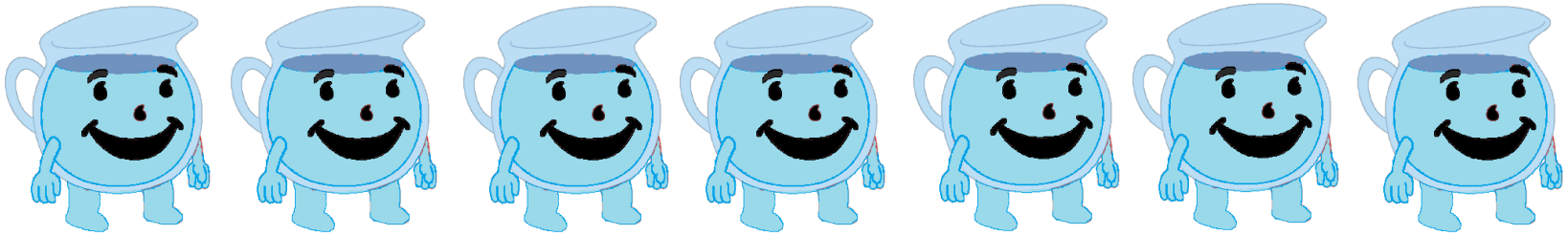
MDLs – Method Update Rule

- Improvements to 40 CFR Part 136 Appendix B:
  - Incorporates the background attributable to the sample collection media
  - More closely approximates real-world conditions
    - Incorporates temporal variability – requires minimally three separate batches for sample preparation and analysis over minimally three separate dates
- Still requires sample preparation in a laboratory in a clean matrix
- Does not address that the determined MDL is theoretical

MDL – Method Update Rule

- Prepare a minimum of 7 spikes and 7 blanks over the course of three or more different preparation batches





MDL – Method Update Rule

- Determine the MDL as per 40 CFR Part 136 Appendix B

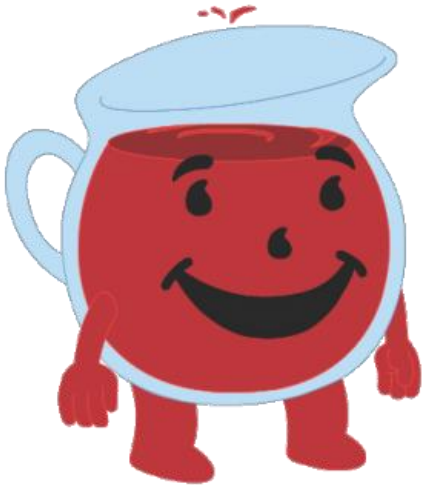
$$MDL_{sp} = s_{sp} \cdot T$$

- Determine an additional MDL based on the analysis of the blanks
  - Calculate the average ($\bar{x}_b$) and standard deviation (s_b) of the blanks.
  - Multiply the blank standard deviation (s_b) by the appropriate student's T value and add this to the average blank value ($\bar{x}_b$).

$$MDL_b = (s_b \cdot T) + \bar{x}_b$$

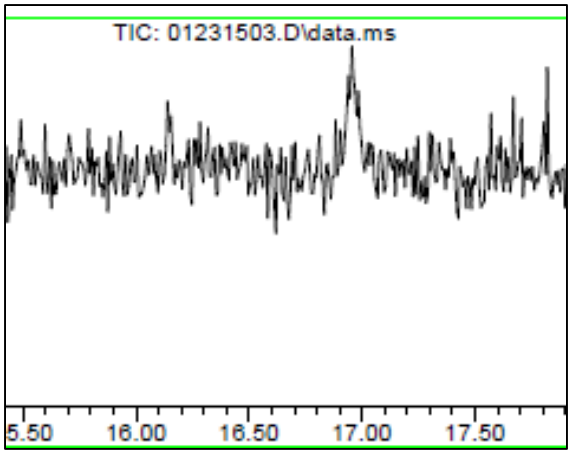
MDL- Method Update Rule

- Compare MDL_{sp} and MDL_b
- **<u>Whichever is higher</u>** is reported as the laboratory MDL



MDLs – Determining Spike Levels

- Choose a spiking level by considering:
  - Previously acceptable MDL studies and related experience
  - Concentration where qualitative identification criteria are lost
  - Concentration at which the signal to noise ratio is ~3 to 5-fold
  - Analysis of a suite of blank samples – calculate the standard deviation and multiply by 3



Method Update Rule - NATTS

- MDLs (mean or median) were polled from laboratories participating in the NATTS PT for metals, VOCs, PAHs, and carbonyls.
- These “typical” laboratory MDLs were all below the NATTS MDL MQO or 10^{-6} cancer risk except acrolein (3 ppt) and 1,1,2,2-tetrachloroethane (~10-fold).
- This indicates laboratories are sufficiently sensitive to meet NATTS MDL MQOs or cancer risk metrics.

VOCs (ppbv)		
	typical MDL	MDL MQO or 10^{-6} cancer risk
Acrolein	0.042	0.039
Benzene	0.024	0.041
1,3-Butadiene	0.024	0.050
Carbon tetrachloride	0.020	0.027
Chloroform	0.020	0.100
1,2-Dibromoethane	0.025	NA
1,2-Dichloroethane	0.026	NA
Dichloromethane	0.027	0.600
1,2-Dichloropropane	0.026	NA
cis- 1,3-Dichloropropene	0.020	0.066
trans-1,3-Dichloropropene	0.021	0.066
1,1,2,2-Tetrachloroethane	0.027	0.0025
Tetrachloroethylene	0.020	0.025
Trichloroethylene	0.020	0.037
Vinyl chloride	0.028	0.043

Method Update Rule - NATTS

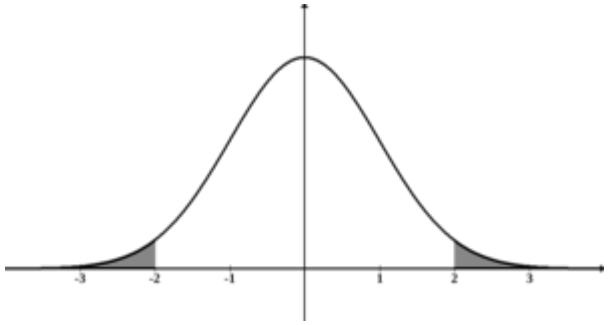
Metals (ng/m^3)			
	Typical MDL		
	High Volume Metals	Low Volume Metals	MDL MQO or cancer risk 10^{-6}
Antimony	0.0094	0.028	20
Arsenic	0.0231	0.106	0.23
Beryllium	0.0014	0.034	0.42
Cadmium	0.0020	0.014	0.56
Cobalt	0.0048	0.013	10
Lead	0.0069	0.067	15
Manganese	0.0051	0.166	5
Nickel	0.0051	0.293	2.1
Selenium	0.0123	0.182	2000

Carbonyls (ppbv)		
	typical MDL	MDL MQO or cancer risk 10^{-6}
Acetaldehyde	0.0254	0.250
Benzaldehyde	0.0253	NA
Formaldehyde	0.0265	0.064
Propionaldehyde	0.0163	NA

PAHs (ng/m^3)		
	typical MDL	MDL MQO or cancer risk 10^{-6}
Acenaphthene	0.222	300
Anthracene	0.219	300
Benzo(a)pyrene	0.347	0.91
Fluoranthene	0.257	300
Fluorene	0.237	300
Naphthalene	0.473	29
Phenanthrene	0.249	300
Pyrene	0.228	300

Method Update Rule - NATTS

- NATTS data were pulled from AQS covering 2003-2010 and binned according to percentiles:
  - 5, 10, 25, 50, 75, 90, & 95%
- These binned data were compared to the typical MDLs to determine whether the specific percentile was above or below the typical MDL.



Method Update Rule - NATTS

VOCs (ppbv)								
analyte	typical MDL	reported data (percentile)						
		5	10	25	50	75	90	95
Acrolein	0.042		no data in table					
Benzene	0.024	0.15	0.26	0.41	0.64	1.00	1.59	2.09
1,3-Butadiene	0.024	0.00	0.00	0.00	0.04	0.09	0.18	0.27
Carbon tetrachloride	0.020	0.00	0.25	0.48	0.57	0.65	0.75	0.82
Chloroform	0.020	0.00	0.00	0.00	0.10	0.18	0.34	0.59
Tetrachloroethylene	0.020	0.00	0.00	0.00	0.09	0.20	0.40	0.61
Trichloroethylene	0.020	0.00	0.00	0.00	0.00	0.04	0.08	0.11
Vinyl chloride	0.028	0.00	0.00	0.00	0.00	0.00	0.02	0.03

Green cells indicate concentrations less than the typical MDL.

Method Update Rule - NATTS

carbonyls (ppbv)								
analyte	typical MDL	reported data (percentile)						
		5	10	25	50	75	90	95
Acetaldehyde	0.03	0.44	0.57	0.85	1.30	2.00	2.99	3.77
Formaldehyde	0.03	0.61	0.86	1.41	2.22	3.50	5.08	6.50

PAHs (ng/m^3)								
analyte	typical MDL	reported data (percentile)						
		5	10	25	50	75	90	95
Benzo(a)pyrene	0.347	0.000	0.000	0.000	0.031	0.100	0.244	0.404
Naphthalene	0.473	7.806	12.498	27.385	55.675	100.622	164.229	213.253

Green cells indicate concentrations less than the comparison MDL.

Method Update Rule - NATTS

metals - high volume (ng/m³)								
analyte	typical MDL	reported data (percentile)						
		5	10	25	50	75	90	95
Arsenic	0.023	0.080	0.160	0.310	0.550	0.920	1.600	2.210
Beryllium	0.001	0.000	0.000	0.000	0.000	0.010	0.080	0.100
Cadmium	0.002	0.000	0.000	0.050	0.090	0.170	0.340	0.600
Lead	0.007	0.650	0.900	1.400	2.410	4.020	7.220	10.000
Manganese	0.005	0.920	1.240	2.020	3.640	7.900	18.400	28.390
Nickel	0.005	0.050	0.210	0.610	1.000	1.900	3.360	5.050

metals - low volume (ng/m³)								
analyte	typical MDL	reported data (percentile)						
		5	10	25	50	75	90	95
Arsenic	0.106	0.000	0.060	0.240	0.450	0.770	1.160	1.480
Beryllium	0.034	0.000	0.000	0.000	0.000	0.010	0.030	0.040
Cadmium	0.014	0.000	0.000	0.040	0.070	0.120	0.220	0.340
Lead	0.067	0.520	0.800	1.370	2.330	4.130	6.950	9.420
Manganese	0.166	0.600	1.030	2.390	5.210	9.610	15.410	20.270
Nickel	0.293	0.000	0.000	0.340	0.860	1.740	5.200	10.300

Green cells indicate concentrations less than the comparison MDL.

Method Update Rule - NATTS

- Blank data (lot blanks, field blanks, trip blanks, and lab blanks) were polled from AQS from 2003-2010 to determine a mean or median blank value for each analyte.
- To approximate the MDL_b for each analyte in a worst case scenario, the typical MDL in the previous step was added to the mean or median blank value.
- $MDL_b \geq$ typical MDL in all cases.

Method Update Rule - NATTS

- In the following slides:
  - Green = less than the typical MDL and MDL_b
  - Red = less than the MDL_b
  - Orange = MDL_b > MDL MQO

Method Update Rule - NATTS

VOCs (ppbv)										
analyte	typical MDL	blank value	MDL_b	reported data (percentile)						
				5	10	25	50	75	90	95
Acrolein	0.042	not in AQS	0.042	no data in table						
Benzene	0.024	0.050	0.074	0.15	0.26	0.41	0.64	1.00	1.59	2.09
1,3-Butadiene	0.024	0.000	0.024	0.00	0.00	0.00	0.04	0.09	0.18	0.27
Carbon tetrachloride	0.020	0.003	0.023	0.00	0.25	0.48	0.57	0.65	0.75	0.82
Chloroform	0.020	0.002	0.022	0.00	0.00	0.00	0.10	0.18	0.34	0.59
Tetrachloroethylene	0.020	0.000	0.020	0.00	0.00	0.00	0.09	0.20	0.40	0.61
Trichloroethylene	0.020	0.000	0.020	0.00	0.00	0.00	0.00	0.04	0.08	0.11
Vinyl chloride	0.028	0.000	0.028	0.00	0.00	0.00	0.00	0.00	0.02	0.03

Green cells indicate concentrations less than the comparison MDL.

Method Update Rule - NATTS

carbonyls (ppbv)										
analyte	typical MDL	blank value	MDL_b	reported data (percentile)						
				5	10	25	50	75	90	95
Acetaldehyde	0.025	0.038	0.063	0.44	0.57	0.85	1.30	2.00	2.99	3.77
Formaldehyde	0.026	0.052	0.079	0.61	0.86	1.41	2.22	3.50	5.08	6.50

PAHs (ng/m^3)										
analyte	typical MDL	blank value	MDL_b	reported data (percentile)						
				5	10	25	50	75	90	95
Benzo(a)pyrene	0.347	0.008	0.355	0.000	0.000	0.000	0.031	0.100	0.244	0.404
Naphthalene	0.473	1.229	1.703	7.806	12.498	27.385	55.675	100.622	164.229	213.253

Orange cells indicate MDLs which exceed the NATTS MDL MQO.
Green cells indicate concentrations less than the comparison MDL.

Method Update Rule - NATTS

metals - high volume (ng/m³)

analyte	typical MDL	blank value	MDL_b	reported data (percentile)						
				5	10	25	50	75	90	95
Arsenic	0.023	0.036	0.059	0.080	0.160	0.310	0.550	0.920	1.600	2.210
Beryllium	0.001	0.003	0.004	0.000	0.000	0.000	0.000	0.010	0.080	0.100
Cadmium	0.002	0.053	0.055	0.000	0.000	0.050	0.090	0.170	0.340	0.600
Lead	0.007	0.302	0.309	0.650	0.900	1.400	2.410	4.020	7.220	10.000
Manganese	0.005	0.757	0.763	0.920	1.240	2.020	3.640	7.900	18.400	28.390
Nickel	0.005	0.446	0.451	0.050	0.210	0.610	1.000	1.900	3.360	5.050

metals - low volume (ng/m³)

analyte	typical MDL	blank value	MDL_b	reported data (percentile)						
				5	10	25	50	75	90	95
Arsenic	0.106	0.090	0.196	0.000	0.060	0.240	0.450	0.770	1.160	1.480
Beryllium	0.034	0.004	0.037	0.000	0.000	0.000	0.000	0.010	0.030	0.040
Cadmium	0.014	0.035	0.048	0.000	0.000	0.040	0.070	0.120	0.220	0.340
Lead	0.067	0.046	0.113	0.520	0.800	1.370	2.330	4.130	6.950	9.420
Manganese	0.166	0.146	0.312	0.600	1.030	2.390	5.210	9.610	15.410	20.270
Nickel	0.293	0.259	0.552	0.000	0.000	0.340	0.860	1.740	5.200	10.300

Green cells indicate values less than the typical MDL and MDL_b.
Red cells indicate values less than the MDL_b.

Example MDL Scenario

Lab Q determined their formaldehyde MDL by preparing and analyzing 8 spiked cartridges (spiked at 0.030 µg/cartridge) and 8 blanks.

aliquot	measured concentration (µg/cartridge)	
	Spikes	Blanks
1	0.1685	0.1412
2	0.1651	0.1399
3	0.1701	0.1402
4	0.1673	0.1405
5	0.1692	0.1408
6	0.1686	0.1403
7	0.1705	0.1402
8	0.1696	0.141
average	0.1686	0.1405
stdev	0.0017	0.0004
student's T	2.998	2.998
calculated MDL	0.0052	0.0013
calculated MDL + blank average	NA	0.1419
spike value/calculated MDL	5.8	NA

The MDL_b of 0.1419 is higher than the MDL_{sp} of 0.0052 µg/cartridge and is reported as the laboratory MDL (0.0985 µg/m^3).

Summary

- With rare exception existing MDLs meet MDL MQOs.
- Draft NATTS TAD Revision 3 adopts the MUR.
- The MUR includes temporal variability and matrix background in the MDL determination.
- Under a worst case scenario, MDLs by the proposed MUR meet the MDL MQOs with the exception of formaldehyde, and with the exception of cadmium and nickel, no additional data would be flagged as < MDL for these methods.

Thank you

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