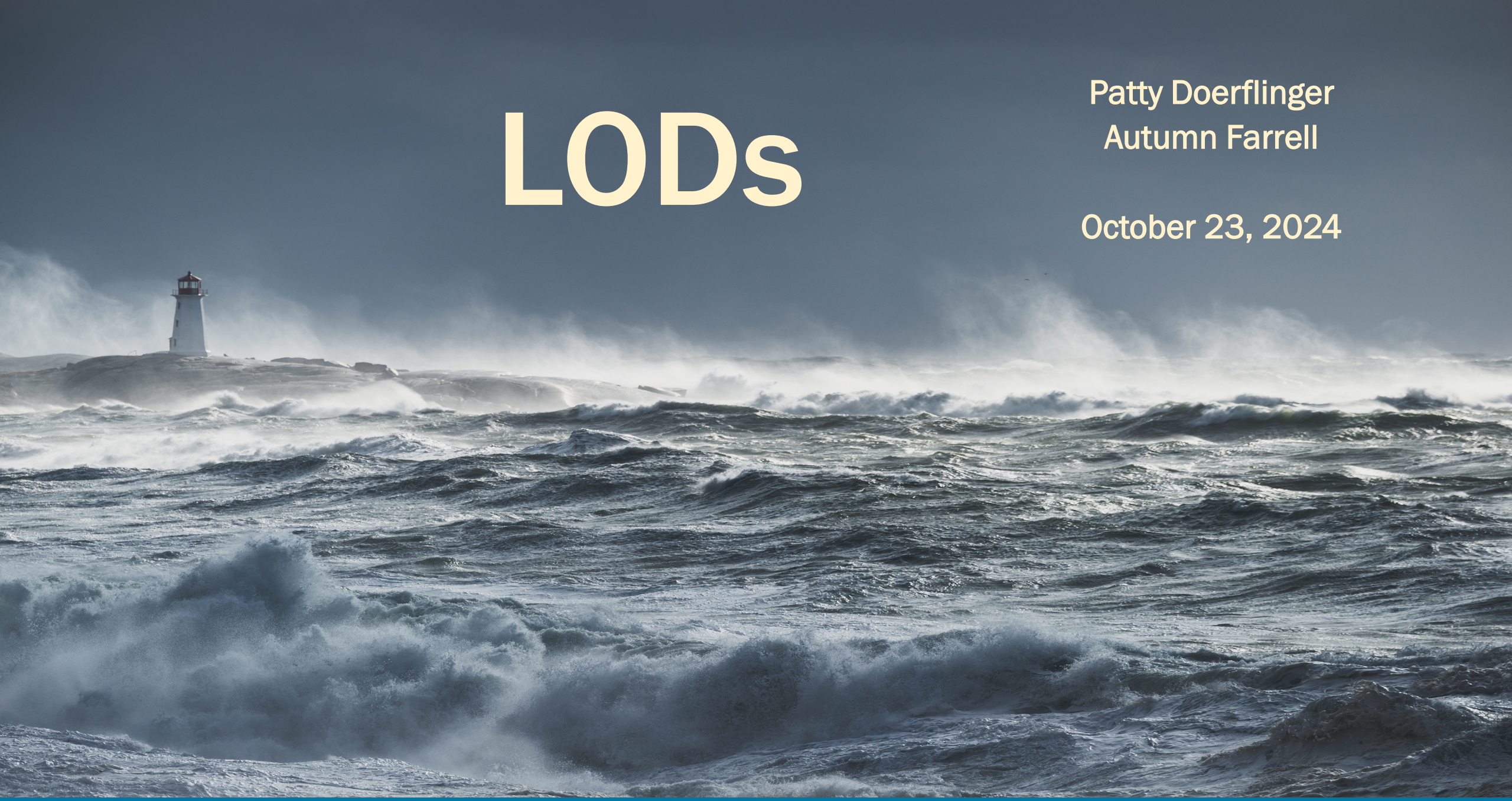
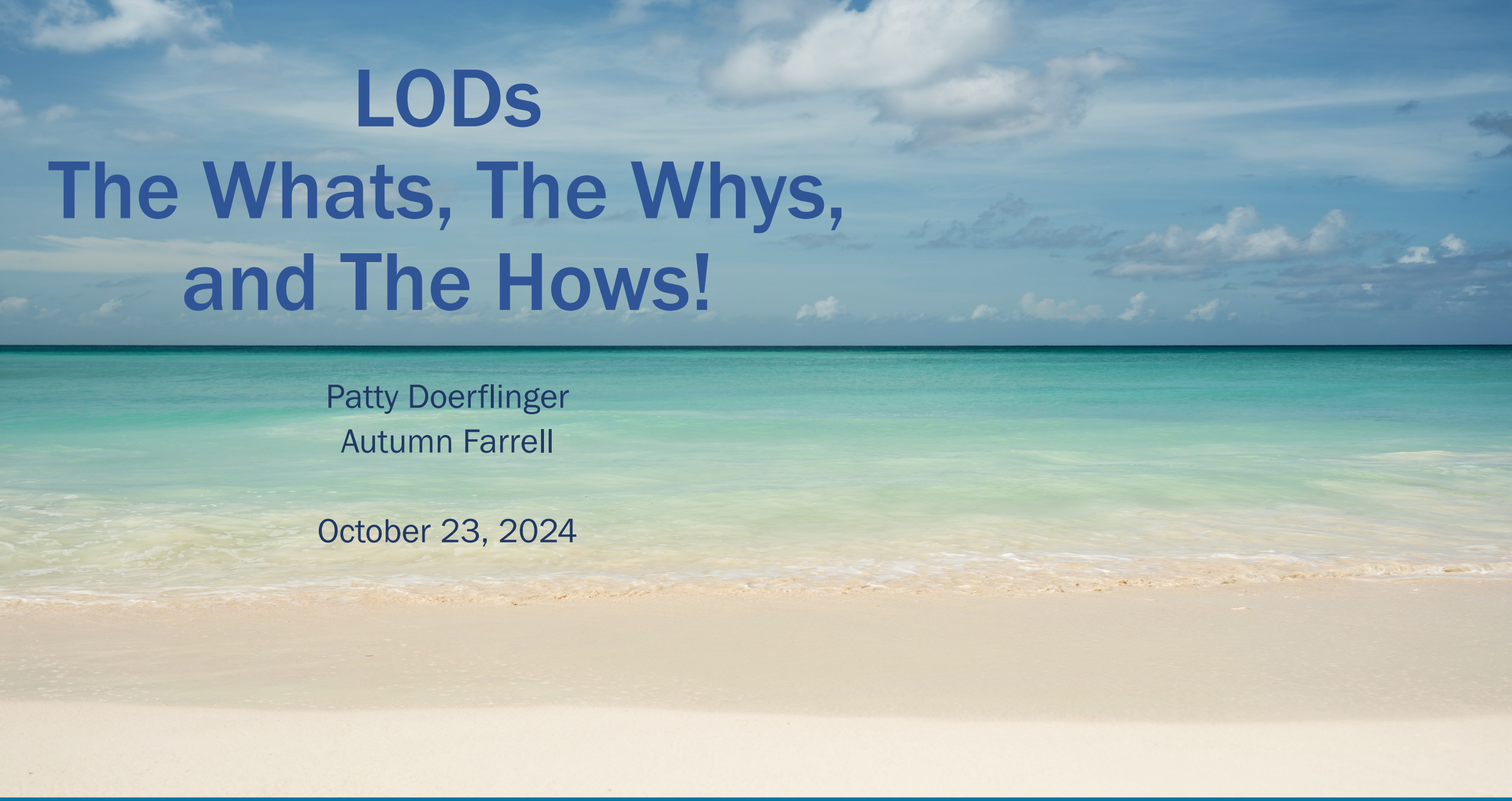
LODs

Patty Doerflinger
Autumn Farrell

October 23, 2024





LODs
The Whats, The Whys, and The Hows!

Patty Doerflinger
Autumn Farrell

October 23, 2024

Disclaimer

This presentation is to try to help you understand LODs.

Exact definitions and technical jargon have been avoided.

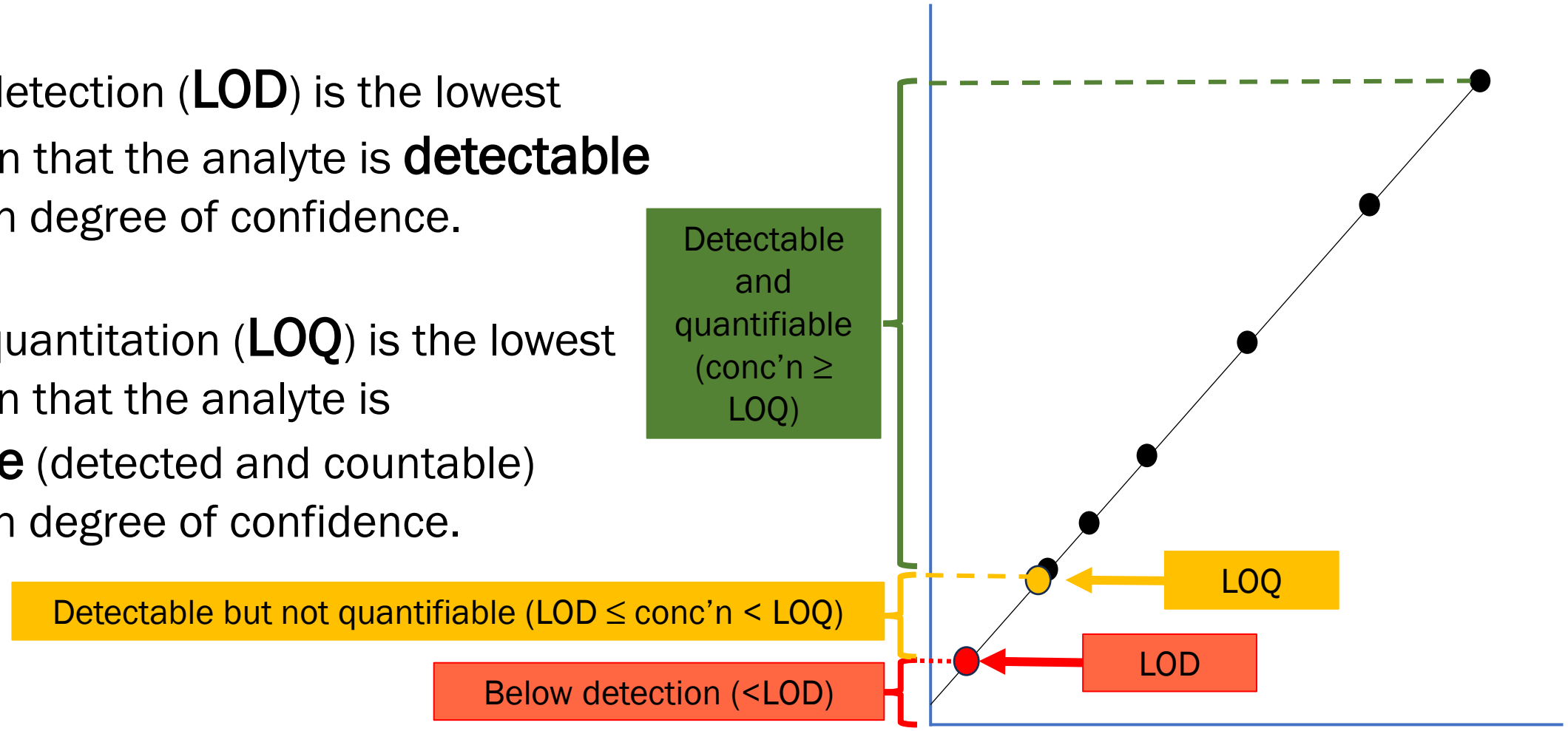
There is a lot more to the LOD determination that likely does not apply to this audience's testing, so it will not be covered here.

What is an LOD?

The department considers the LOD to be equivalent to the method detection limit (MDL).

The limit of detection (**LOD**) is the lowest concentration that the analyte is **detectable** with a certain degree of confidence.

The limit of quantitation (**LOQ**) is the lowest concentration that the analyte is **quantifiable** (detected and countable) with a certain degree of confidence.



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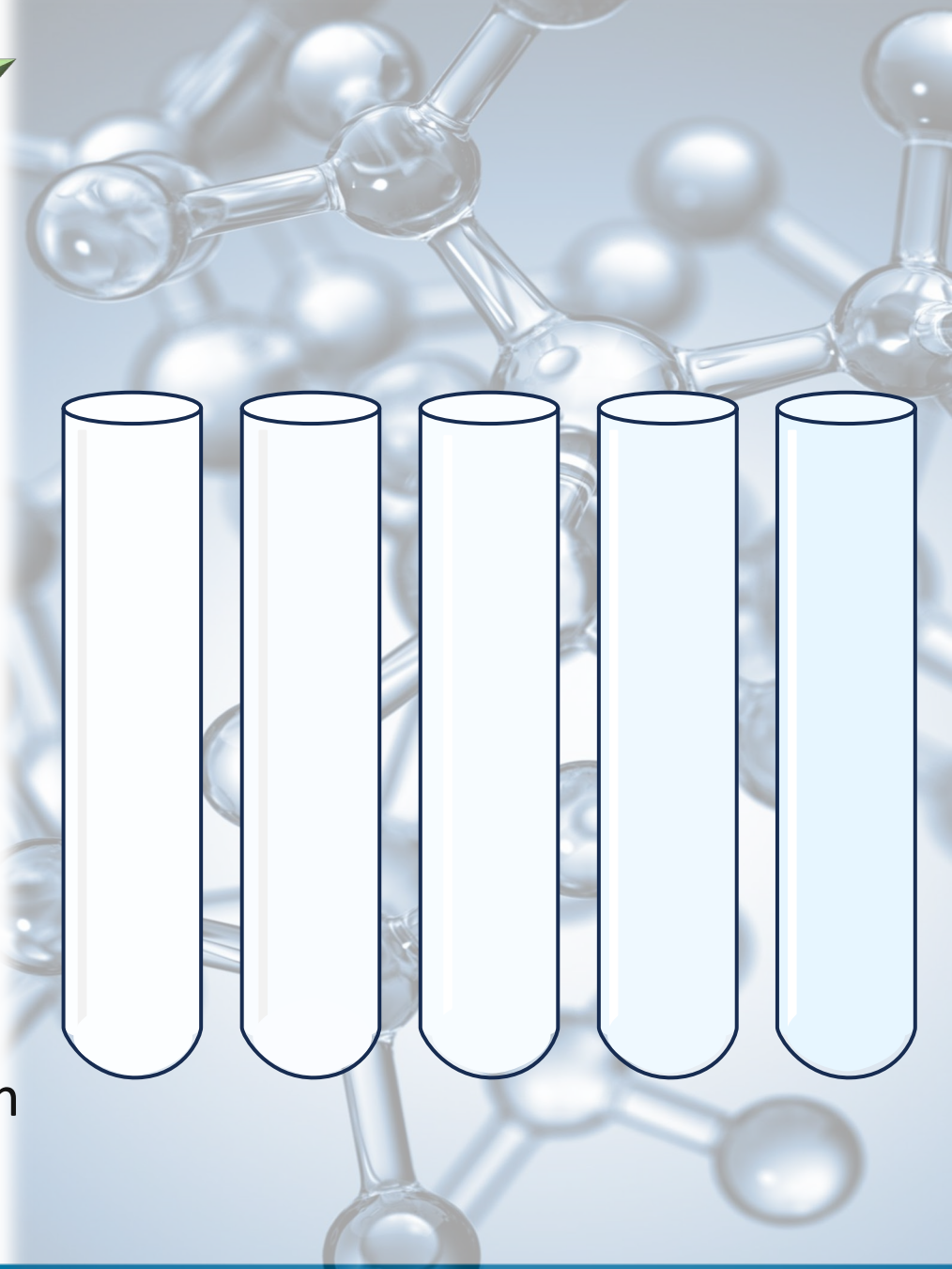
Why do we need an LOD?

- It is always possible that the analyte is present in the sample at a concentration below your LOD, so it's important that your LOD is low enough for the intended use of the data.
  - For example, if your permit limit is 0.075 mg/L for phosphorus, and your LOD for is 0.1 mg/L, then you know that your analysis is inadequate. You could have a “<LOD" result and the sample result would still not meet permit limits.
  - If your LOD is 0.05 mg/L, then a “<LOD" result indicates that the sample result is in compliance with your permit.



How do we determine the LOD?

"Initial" LOD

Do NOT redo the initial LOD unless needed. Only do the initial LOD when:

- you change methods.
  - For example: the lab changed from ammonia by ISE to Hach Test N Tube.
- a significant change has occurred that could affect sensitivity.
  - For example: the lamp was replaced in the spectrophotometer which may cause a significant change in sensitivity.
- the spiked blank concentration is changed.
  - For example: the lab changed the quarterly spiked blanks from 0.5 mg/L to 0.1 mg/L

How do we determine the LOD?

"Initial" LOD

Collect the Data

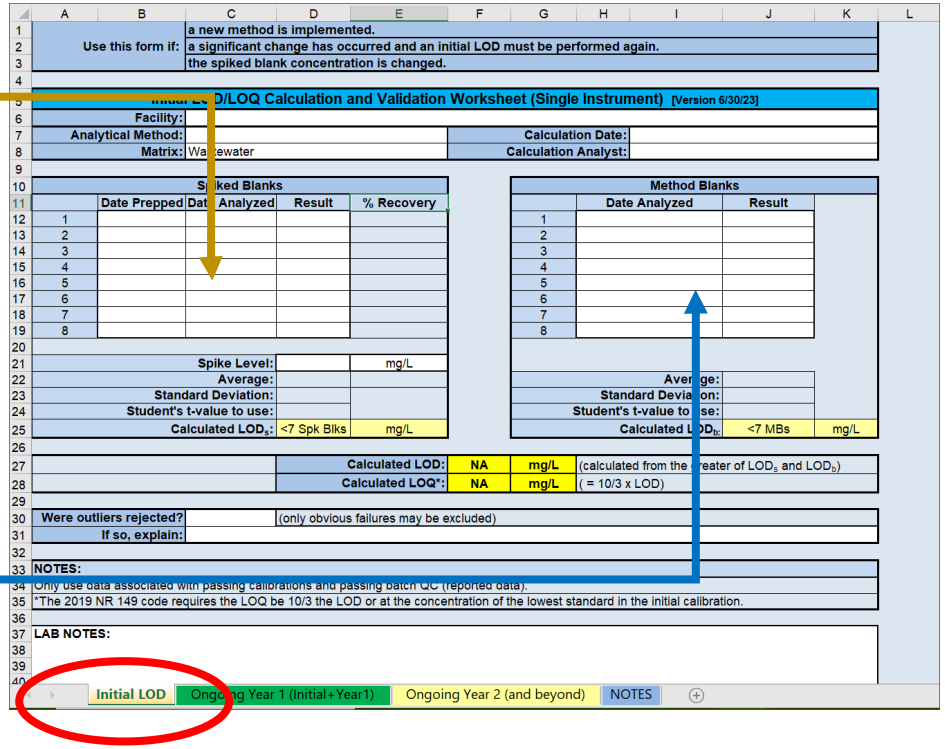
Prepare and analyze <u>at least</u>:

7 spiked blanks on at least **3 different days**

and

7 method blanks on at least **3 different days**

Enter the Data



Use this form if: a new method is implemented. a significant change has occurred and an initial LOD must be performed again. the spiked blank concentration is changed.

D/LOQ Calculation and Validation Worksheet (Single Instrument) [Version 6/30/23]

Facility:

Analytical Method: Calculation Date:

Matrix: Wastewater Calculation Analyst:

Spiked Blanks				
	Date Prepped	Date Analyzed	Result	% Recovery
1				
2				
3				
4				
5				
6				
7				
8				
Spike Level:				mg/L
Average:				
Standard Deviation:				
Student's t-value to use:				
Calculated LOD_s:			<7 Spk Blks	mg/L

Method Blanks		
	Date Analyzed	Result
1		
2		
3		
4		
5		
6		
7		
8		
Average:		
Standard Deviation:		
Student's t-value to use:		
Calculated LOD_b:		<7 MBs mg/L

Calculated LOD: NA mg/L (calculated from the greater of LOD_s and LOD_b)

Calculated LOQ*: NA mg/L (= 10/3 x LOD)

Were outliers rejected? (only obvious failures may be excluded)

If so, explain:

NOTES:

Only use data associated with passing calibrations and passing batch QC (reported data).

*The 2019 NR 149 code requires the LOQ be 10/3 the LOD or at the concentration of the lowest standard in the initial calibration.

LAB NOTES:

Initial LOD | Ongoing Year 1 (Initial+Year1) | Ongoing Year 2 (and beyond) | NOTES

"Ongoing" LOD

How do we determine the LOD?

Collect the Data

Prepare and analyze at least:

2 spiked blanks every quarter in separate batches

Have some system to remind yourself to do these each quarter.

Be sure the spiked blanks are in separate batches or different days each quarter.

and

Usual method blanks

You don't need to do any special LOD method blanks.

"Ongoing" LOD

How do we determine the LOD?

Every year, calculate and assess the LOD.

Collect the Data

- 2 spiked blanks every quarter in separate batches

and

- Usual method blanks

Enter the Data

Which data?

Always use the last 24 months of spiked blanks.

ONLY include the initial LOD data if it is was done within the last 24 months.

Ideally, use all method blank (MB) data from last 24 months.

If you have a LOT of MB data, you also have the option to use whichever of these that provides more data: at least the last 6 months of MBs or at least the 50 most recent MBs.

"Ongoing" LOD

Year 1 (Initial+Year1)

How do we determine the LOD?

Collect the Data

2 spiked blanks every quarter in separate batches

Usual method blanks

Enter the Data

	Spiked Blanks (include all LOD data generated within the last 2 years)				
7		Date Prepped	Date Analyzed	Result	% Recovery
8	Initial LOD 1	12/1/23	12/1/23	0.09200	92%
9	Initial LOD 2	12/1/23	12/1/23	0.08700	87%
10	Initial LOD 3	12		0.10100	101%
11	Initial LOD 4	12		0.09400	94%
12	Initial LOD 5	12/4/23	12/4/23	0.10200	102%
13	Initial LOD 6	12/5/23	12/5/23	0.09900	99%
14	Initial LOD 7	12/5/23	12/5/23	0.08900	89%
15	Initial LOD 8				
16	Q1 A	1/13/24	1/13/24	0.10200	102%
17	Q1 B	1/20/24	1/20/24	0.09000	90%
18	Q2 A	4/1/24	4/1/24	0.08100	81%
19	Q2 B	4/		0.09100	91%
20	Q3 A	7/		0.10400	104%
21	Q3 B	7/15/24	7/15/24	0.11000	110%
22	Q4 A	10/10/24	10/10/24	0.09600	96%
23	Q4 B	10/17/24	10/17/24	0.09600	96%
24					
25			Spike Level (same as initial):	0.10000	mg/L
26			Average:	0.09560	96%
27			Standard Deviation:	0.00756	
28			Student's t-value to use:	2.624	
29			Calculated LOD_s:	0.0198	mg/L
30					

Initial Data

Year 1 Data

Initial LOD | Ongoing Year 1 (Initial+Year1) | Ongoing Ye

ONLY include the initial LOD data if it is was done within the last 24 months.

Always use the last 24 months of spiked blanks.

"Ongoing" LOD

Year 1 (Initial+Year1)

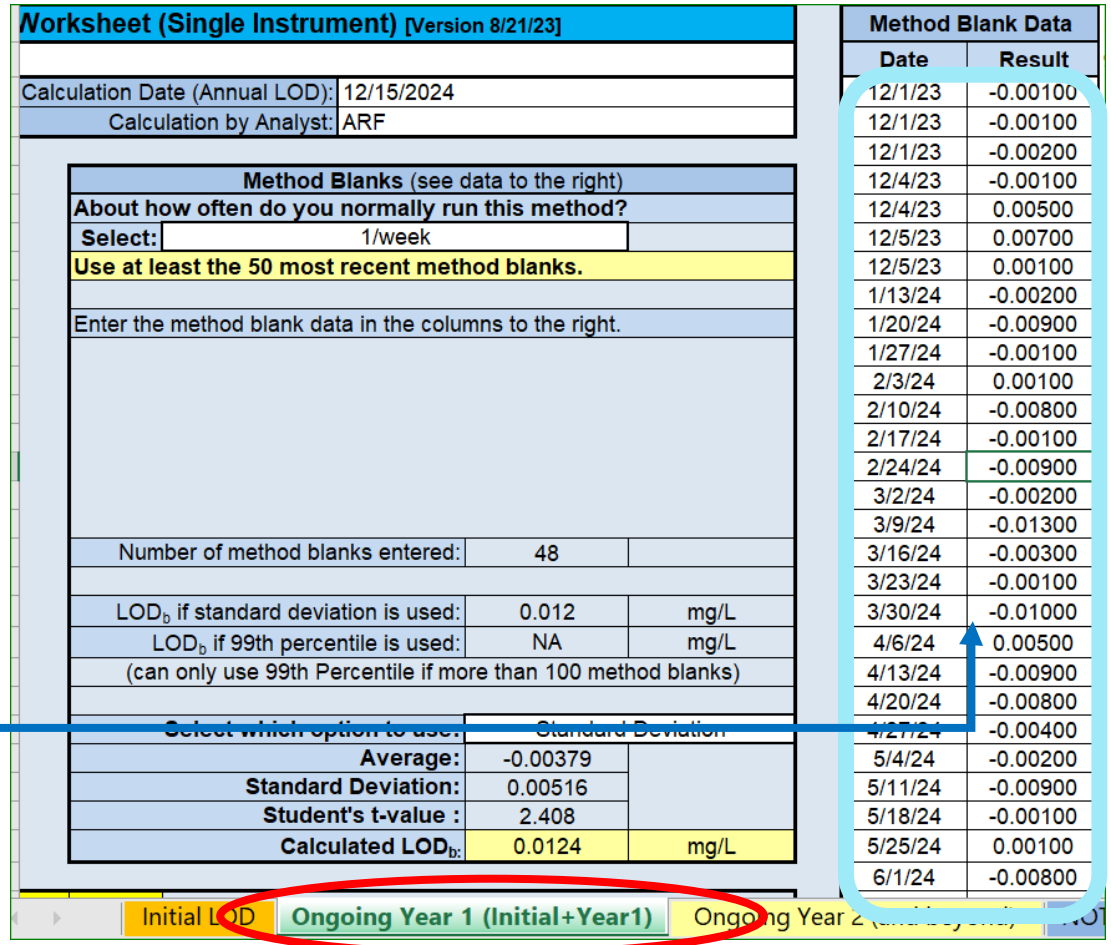
How do we determine the LOD?

Collect the Data

2 spiked blanks every quarter in separate batches

Usual method blanks

Enter the Data



Worksheet (Single Instrument) [Version 8/21/23]

Calculation Date (Annual LOD):	12/15/2024
Calculation by Analyst:	ARF

Method Blanks (see data to the right)

About how often do you normally run this method?

Select: 1/week

Use at least the 50 most recent method blanks.

Enter the method blank data in the columns to the right.

Number of method blanks entered:	48	
LOD_b if standard deviation is used:	0.012	mg/L
LOD_b if 99th percentile is used:	NA	mg/L

(can only use 99th Percentile if more than 100 method blanks)

Select which option to use:	Standard Deviation	
Average:	-0.00379	
Standard Deviation:	0.00516	
Student's t-value :	2.408	
Calculated LOD_b:	0.0124	mg/L

Initial LOD | Ongoing Year 1 (Initial+Year1) | Ongoing Year 2 (and beyond) | NOT

Method Blank Data

Date	Result
12/1/23	-0.00100
12/1/23	-0.00100
12/1/23	-0.00200
12/4/23	-0.00100
12/4/23	0.00500
12/5/23	0.00700
12/5/23	0.00100
1/13/24	-0.00200
1/20/24	-0.00900
1/27/24	-0.00100
2/3/24	0.00100
2/10/24	-0.00800
2/17/24	-0.00100
2/24/24	-0.00900
3/2/24	-0.00200
3/9/24	-0.01300
3/16/24	-0.00300
3/23/24	-0.00100
3/30/24	-0.01000
4/6/24	0.00500
4/13/24	-0.00900
4/20/24	-0.00800
4/27/24	-0.00400
5/4/24	-0.00200
5/11/24	-0.00900
5/18/24	-0.00100
5/25/24	0.00100
6/1/24	-0.00800

Ideally, use all MB data from last 24 months.

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"Ongoing" LOD

Year 2 (and beyond)

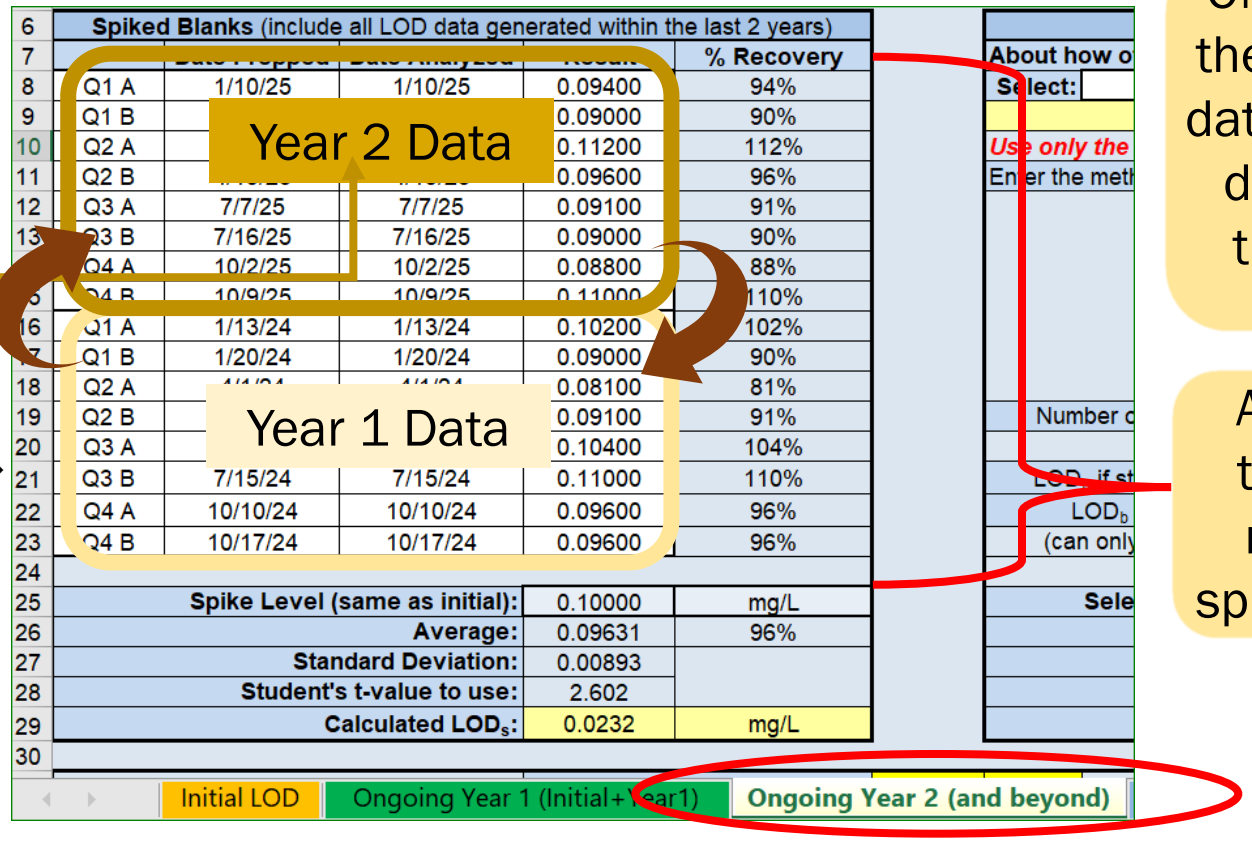
How do we determine the LOD?

Collect the Data

2 spiked blanks every quarter in separate batches

Usual method blanks

Enter the Data



ONLY include the initial LOD data if it is was done within the last 24 months.

Always use the last 24 months of spiked blanks.

"Ongoing" LOD

Year 2 (and beyond)

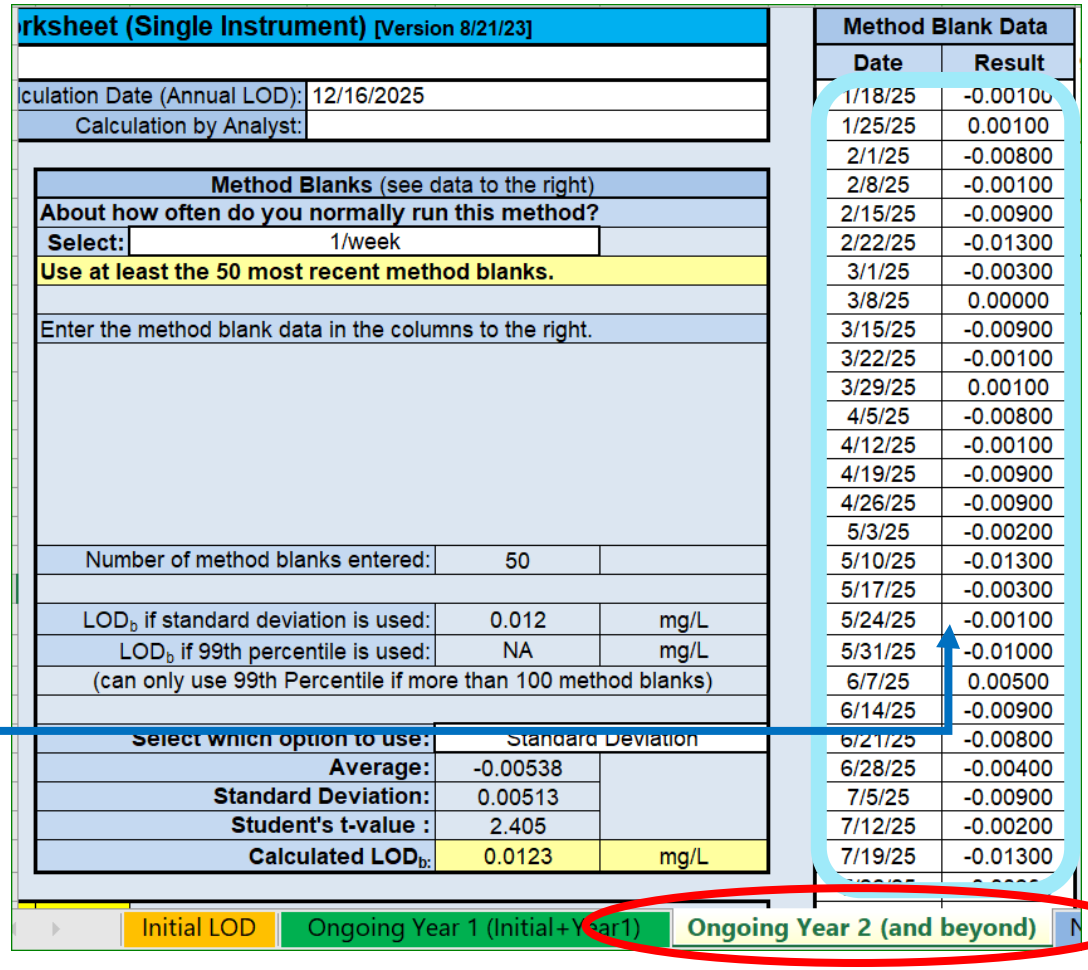
How do we determine the LOD?

Collect the Data

2 spiked blanks every quarter in separate batches

Usual method blanks

Enter the Data



rksheet (Single Instrument) [Version 8/21/23]

culation Date (Annual LOD):	12/16/2025
Calculation by Analyst:	

Method Blanks (see data to the right)

About how often do you normally run this method?

Select: 1/week

Use at least the 50 most recent method blanks.

Enter the method blank data in the columns to the right.

Number of method blanks entered:	50	
LOD_b if standard deviation is used:	0.012	mg/L
LOD_b if 99th percentile is used:	NA	mg/L

(can only use 99th Percentile if more than 100 method blanks)

Select which option to use:	Standard Deviation	
Average:	-0.00538	
Standard Deviation:	0.00513	
Student's t-value :	2.405	
Calculated LOD_b:	0.0123	mg/L

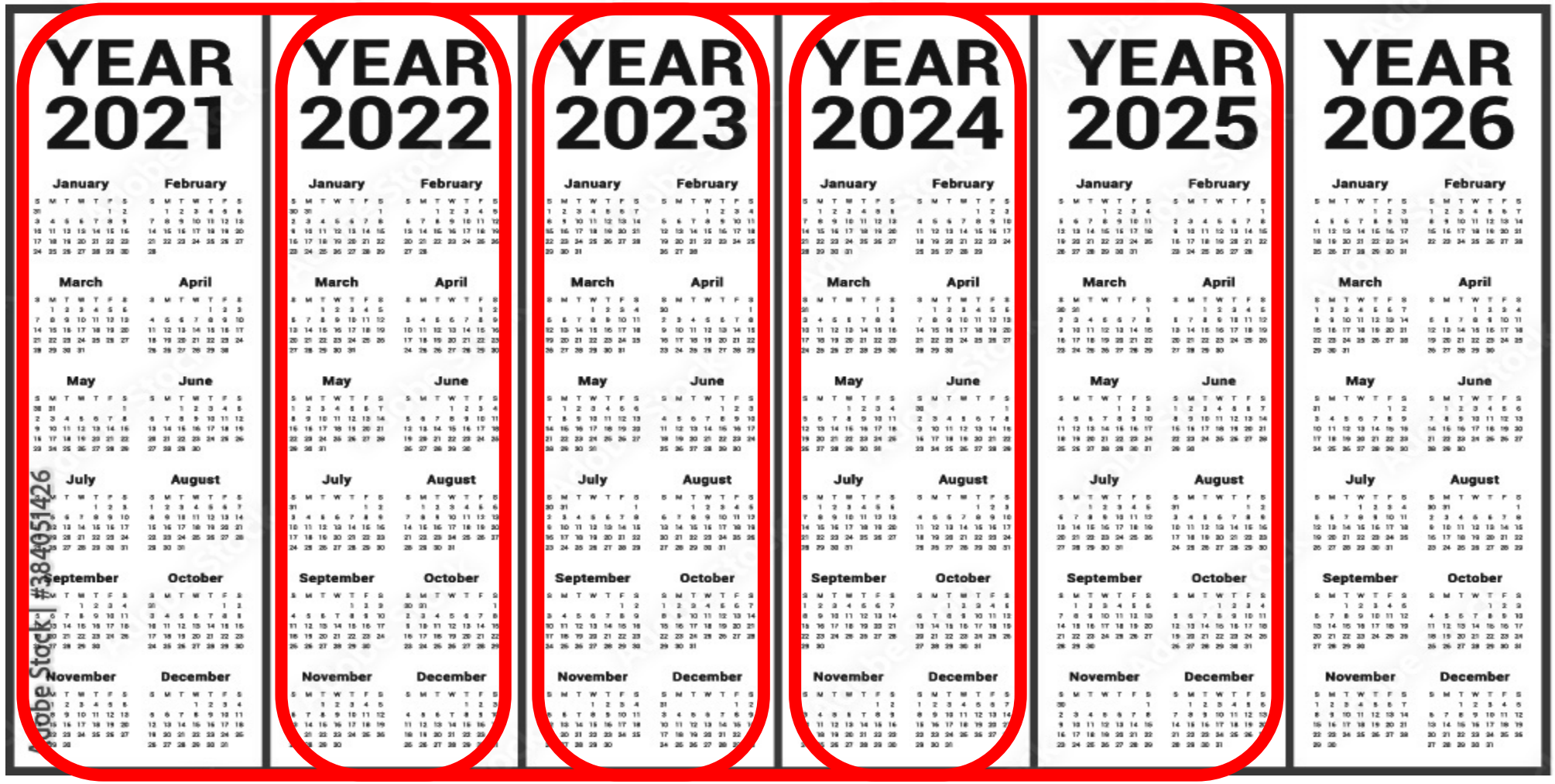
Initial LOD | Ongoing Year 1 (Initial+Year1) | Ongoing Year 2 (and beyond)

Method Blank Data	
Date	Result
1/18/25	-0.00100
1/25/25	0.00100
2/1/25	-0.00800
2/8/25	-0.00100
2/15/25	-0.00900
2/22/25	-0.01300
3/1/25	-0.00300
3/8/25	0.00000
3/15/25	-0.00900
3/22/25	-0.00100
3/29/25	0.00100
4/5/25	-0.00800
4/12/25	-0.00100
4/19/25	-0.00900
4/26/25	-0.00900
5/3/25	-0.00200
5/10/25	-0.01300
5/17/25	-0.00300
5/24/25	-0.00100
5/31/25	-0.01000
6/7/25	0.00500
6/14/25	-0.00900
6/21/25	-0.00800
6/28/25	-0.00400
7/5/25	-0.00900
7/12/25	-0.00200
7/19/25	-0.01300

Ideally, use all MB data from last 24 months.

“Ongoing” LOD

How do we determine the LOD?



"Ongoing" LOD

Assessment

How do we determine the LOD?

Every year, calculate and assess the LOD.

Collect the Data → Enter the Data → Assess the Data

Calculated LOD:	**0.023**	**mg/L**	(calculated from the greater of L
Calculated LOQ*:	**0.077**	**mg/L**	(= 10/3 x LOD)
Existing LOD:	0.019	mg/L	
Can the existing LOD be left unchanged?	YES		
Is spike level okay (<5% spiked blanks <0)?	YES		

If the new LOD is close enough to the existing LOD (and most method blanks are <LOD), you can continue to use the existing LOD.

If the new LOD is not close enough to the existing LOD (or too many method blanks are >LOD), you MUST use the new LOD.

Calculated LOD:	**0.043**	**mg/L**	(calculated from the greater of L
Calculated LOQ*:	**0.142**	**mg/L**	(= 10/3 x LOD)
Existing LOD:	0.019	mg/L	
Can the existing LOD be left unchanged?	**NO**		**Use the new calculated LOD.**
Is spike level okay (<5% spiked blanks <0)?	YES		

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"Ongoing" LOD

Tips

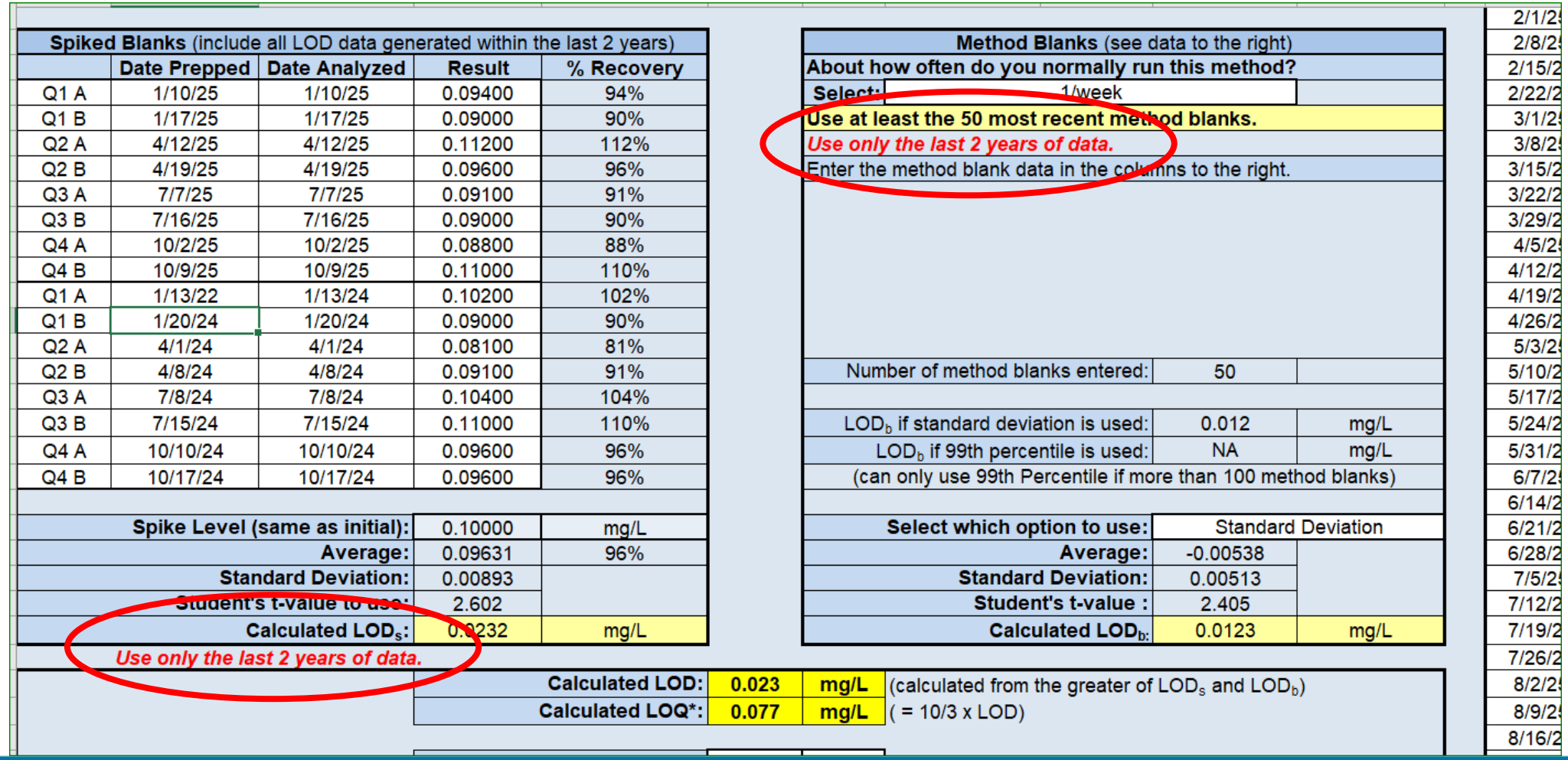
How do we determine the LOD?

- Every analysis:
  - Report results to LOD
- Every quarter:
  - Run 2 spiked blanks
- Every year:
  - Calculate LOD and update if needed
    - 2 years of spiked blanks
    - 2 years of method blanks

"Ongoing" LOD

Tips

How do we determine the LOD?



Spiked Blanks (include all LOD data generated within the last 2 years)

	Date Prepped	Date Analyzed	Result	% Recovery
Q1 A	1/10/25	1/10/25	0.09400	94%
Q1 B	1/17/25	1/17/25	0.09000	90%
Q2 A	4/12/25	4/12/25	0.11200	112%
Q2 B	4/19/25	4/19/25	0.09600	96%
Q3 A	7/7/25	7/7/25	0.09100	91%
Q3 B	7/16/25	7/16/25	0.09000	90%
Q4 A	10/2/25	10/2/25	0.08800	88%
Q4 B	10/9/25	10/9/25	0.11000	110%
Q1 A	1/13/22	1/13/24	0.10200	102%
Q1 B	1/20/24	1/20/24	0.09000	90%
Q2 A	4/1/24	4/1/24	0.08100	81%
Q2 B	4/8/24	4/8/24	0.09100	91%
Q3 A	7/8/24	7/8/24	0.10400	104%
Q3 B	7/15/24	7/15/24	0.11000	110%
Q4 A	10/10/24	10/10/24	0.09600	96%
Q4 B	10/17/24	10/17/24	0.09600	96%

Spike Level (same as initial):	0.10000	mg/L
Average:	0.09631	96%
Standard Deviation:	0.00893	
Student's t-value to use:	2.602	
Calculated LOD_s:	0.0232	mg/L

Use only the last 2 years of data.

Method Blanks (see data to the right)

About how often do you normally run this method?

Select: 1/week

Use at least the 50 most recent method blanks.

Use only the last 2 years of data.

Enter the method blank data in the columns to the right.

Number of method blanks entered:	50	
LOD_b if standard deviation is used:	0.012	mg/L
LOD_b if 99th percentile is used:	NA	mg/L

(can only use 99th Percentile if more than 100 method blanks)

Select which option to use:	Standard Deviation	
Average:	-0.00538	
Standard Deviation:	0.00513	
Student's t-value :	2.405	
Calculated LOD_b:	0.0123	mg/L

Calculated LOD:	0.023	mg/L	(calculated from the greater of LOD_s and LOD_b)
Calculated LOQ*:	0.077	mg/L	(= 10/3 x LOD)

2/1/25
2/8/25
2/15/2
2/22/2
3/1/25
3/8/25
3/15/2
3/22/2
3/29/2
4/5/25
4/12/2
4/19/2
4/26/2
5/3/25
5/10/2
5/17/2
5/24/2
5/31/2
6/7/25
6/14/2
6/21/2
6/28/2
7/5/25
7/12/2
7/19/2
7/26/2
8/2/25
8/9/25
8/16/2

Watch for red alerts.

If you're sure you are just using the last 2 years of data, check for typos.

"Ongoing" LOD

Tips

How do we determine the LOD?

When you do the annual LOD calculation, fill in that date:

Ongoing LOD/LOQ Calculation and Verification Worksheet (Single Instrument) [Version 8/21/23]			
Facility:	**Acme Labs**		
Analytical Method:	SM 4500-P E	Calculation Date (Annual LOD):	12/15/2024
Matrix:	Wastewater	Calculation by Analyst:	ARF

Even though you do parts of the LOD determination each quarter, you only need to do the calculation and verification once per year. That is an important date to record.

"Ongoing" LOD

Tips

How do we determine the LOD?

If you set up a spreadsheet for the next year, you may put a reminder here:

Ongoing LOD/LOQ Calculation and Verification Worksheet (Single Instrument) [Version 8/21/23]			
Facility:	Acme Labs		
Analytical Method:	SM 4500-P E	Calculation Date (Annual LOD):	(DUE Dec 2025)
Matrix:	Wastewater	Calculation by Analyst:	

If you set up a spreadsheet for the next year, also be sure to update (if needed) or enter the existing LOD:

Calculated LOD:	0.023	mg/L	(calculated from the greater of LOD_s and LOD_b)
Calculated LOQ*:	0.077	mg/L	(= 10/3 x LOD)
Existing LOD:		mg/L	
Can the existing LOD be left unchanged?	NO		Use the new calculated LOD.
Is spike level okay (<5% spiked blanks <0)?	YES		

How do we determine the LOD?

When getting ready to enter data for the next year…

Before you delete any data, be sure to save a copy. You need to keep the data used to calculate the annual LOD.

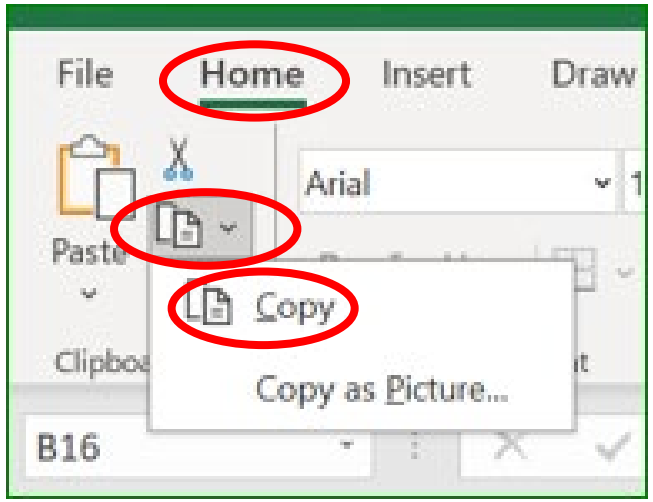
- When you're done doing the annual calculation, enter the date on the spreadsheet.
- File, "Save" the current LOD spreadsheet (e.g., "Phos 2024").
- File, "Save As…" and rename the LOD spreadsheet for the next year (e.g., "Phos 2025").
- In the new spreadsheet (e.g., "Phos 2025,") delete the data that will be more than 2 years old (e.g., from 2023). Delete all spiked blanks and method blanks that will be more than 2 years old.

"Ongoing" LOD

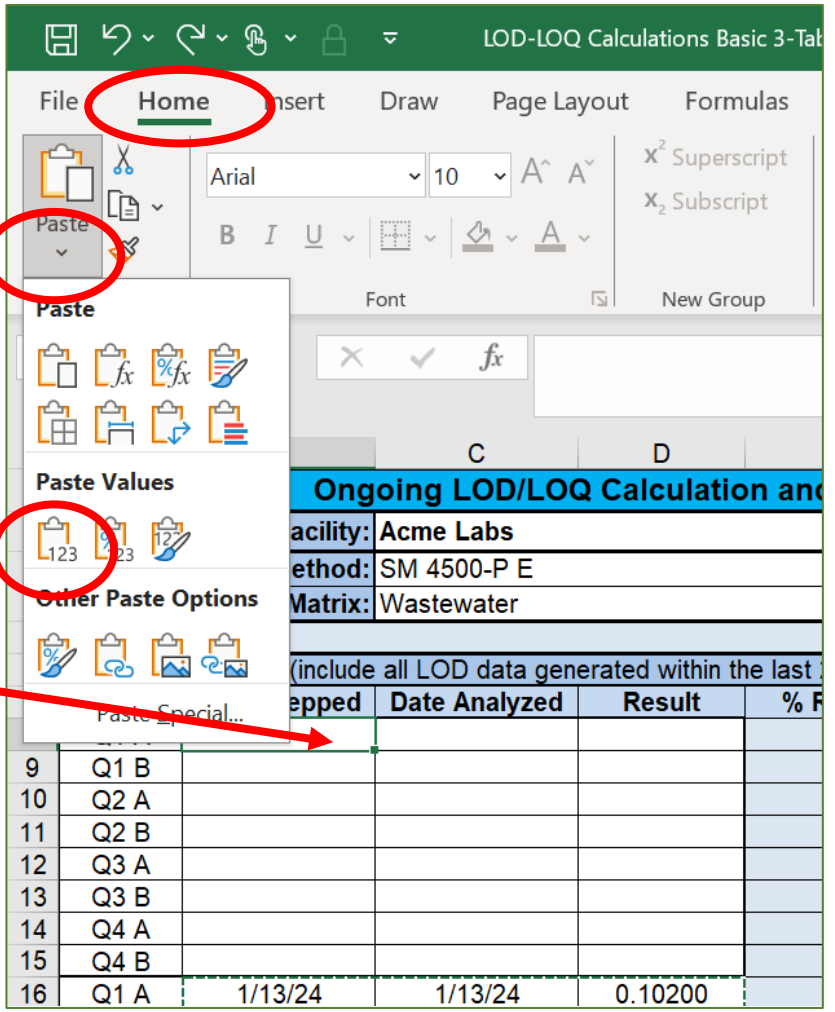
Tips

How do we determine the LOD?

1. To copy cells and move them in Excel, select the cells you want to move (click and drag), select **Home** > **Copy** (or Ctrl + C).



2. Then select the upper left cell where you want to paste the date.
3. Then, **Home** > **Paste** > drop down arrow, and > Values (V).
4. Delete the duplicate data.



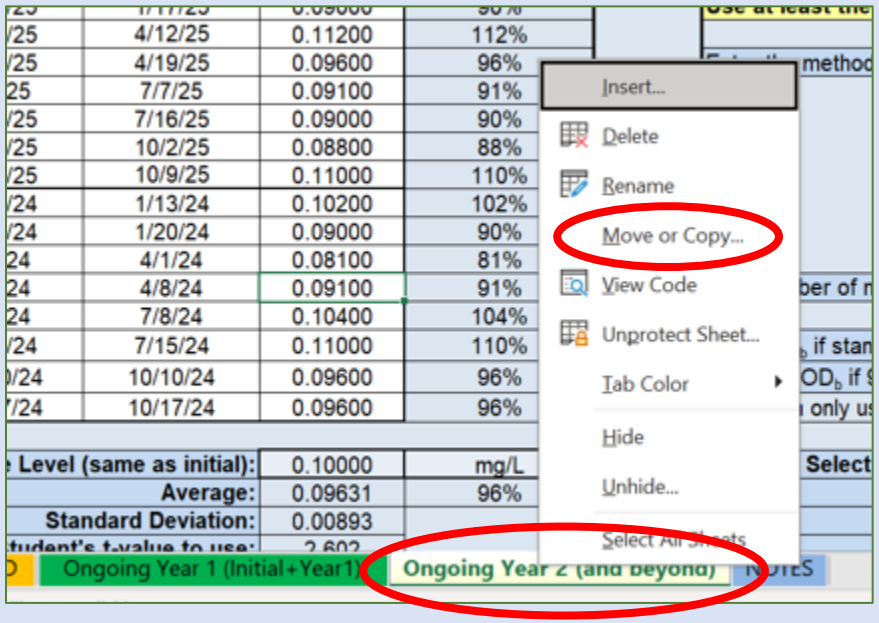
This method will keep the formatting the same. There are other ways of doing the same thing.

"Ongoing" LOD

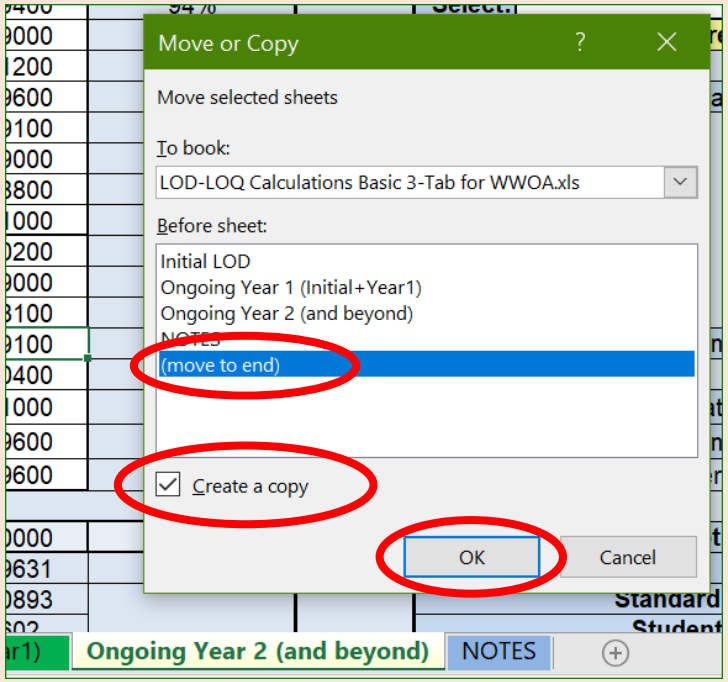
Tips

How do we determine the LOD?

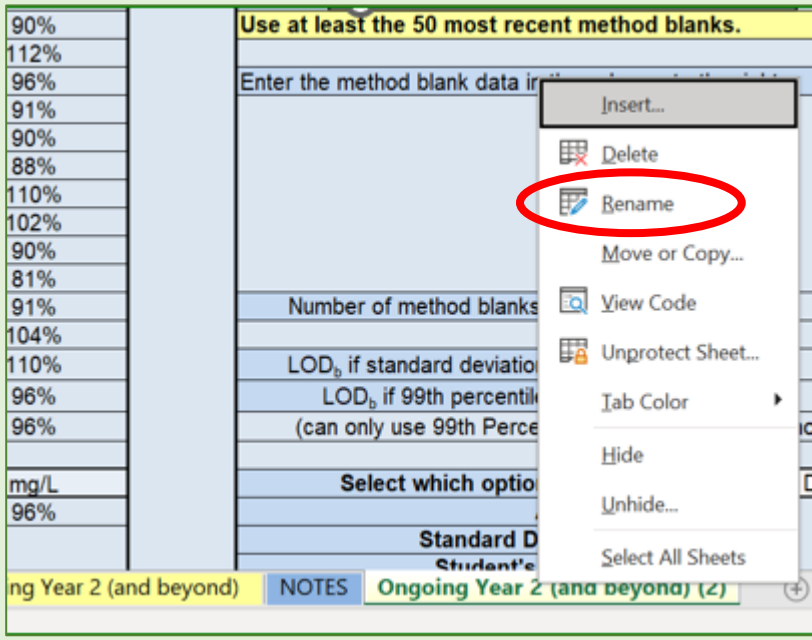
1. To copy a tab in Excel, right-click on the "Ongoing Year 2 (and beyond)" tab. Select "Move or Copy…"



2. Then select "(move to end)," check the box to "Create a copy," then "OK."



3. Then, right-click on the "Ongoing Year 2 (and beyond) (2) tab, and rename. Type a name, and press "enter."



Questions

CONNECT WITH US

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"WILD WISCONSIN:
OFF THE RECORD"