A CASE STUDY IN PRECISION (BASED ON THE 2010 NMP DATASET)

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BACKGROUND ON NMP

- National Monitoring Programs (NMP) annual report
- Includes data from NATTS, UATMP, and CSATAM program sites
- Includes data generated from EPA's contract laboratory

- http://www.epa.gov/ttn/amtic/uatm.html

METHODS UNDER THE NMP

- VOCs (TO-15)*
- Carbonyl Compounds (TO-11A) *
- PAHs (TO-13)*
- Metals (PM10*& TSP)
- Hexavalent Chromium (ASTM D7614-12)*
- SNMOC

* NATTS program Method

WHAT IS PRECISION?

- According to the NMP annual report, precision is *"the level of agreement realized between independent measurements performed according to identical protocols and procedures"*.
- *Method precision*, which includes both *sampling and analytical precision,* quantifies random errors associated with collecting ambient air samples and analyzing the samples in the laboratory.

METHOD PRECISION

- Method precision is evaluated by comparing concentrations measured as duplicate or collocated samples and calculating the corresponding Coefficient of Variation.
- EPA's NMP Method Quality Objective (MQOs) is 15 percent CV.
- Some analytical methods meet the MQO and others do not.

METHOD PRECISION FOR THE NMP

Exceedences of the MQO are largely driven by the following factors:

- The inclusion of measurements below the experimentally-determined method detection limits (MDLs);
- The substitution of 1/2 MDLs for non-detects;
- Concentration differences for very small concentrations can result in large CVs (i.e., the RPD between 0.001 ng/m^3 and 0.002 ng/m^3 is 100 percent).

A CASE STUDY IN PRECISION

- The purpose of this study is to see how precision results are affected if these factors are removed from the calculations and if the program MQO for precision is met.
- Using an iterative process, the CV was recalculated multiple times after adjusting the dataset to remove an additional aspect from the list above each time.
- Only data generated by the EPA contract laboratory is included in this analysis.

HOW IS METHOD PRECISION CALCULATED?

- The calculation for CV using two variables is:

$$CV = 100 * \sqrt{\frac{\sum_{i=1}^{n} \left[\frac{(p-r)}{0.5 * (p+r)}\right]^2}{2n}}$$

Where p = primary; r = duplicate or collocate;
and n is the # of pairs

ITERATIONS

- Include all pairs and sub in ½ MDL for non-detects (whats currently done in NMP report);
- Include all pairs and sub in 0s for non-detects;
- Require at least one of the two concentrations in a pair be greater than or equal to the MDL, with zeros subbed in for non-detects;
- Require both values to be numerical (excluded pairs with one non-detect);

ITERATIONS (CON'D)

- Require both concentrations to be greater than or equal to the MDL;
- Require both concentrations to be greater than or equal to the Sample Quantitation Limit (SQL);
- Require both concentrations to be greater than or equal to 5 times the MDL;
- Require both concentrations to be greater than or equal to the bottom of the calibration curve.

EXCEPTIONS

- Excludes results for acrolein for TO-15
- Excludes results for acetonitrile for TO-15
- Excludes results for Sum of Knowns, Sum of Unknowns, and TNMOC for SNMOC
- Excludes replicate analysis

CURRENT PROCEDURE (SUB IN ½ MDL FOR ND)

Method	Average CV (%)	Count of Pairs
Hexavalent Chromium	**33.01**	121
Metals Analysis	**23.54**	1538
SNMOC	**20.35**	1819
TO-11A	6.91	1212
TO-13	**20.35**	477
TO-15	**19.03**	3393

*Program MQO is 15%

*Bolded CV = exceeds DQO

ITERATION #1 (SUB IN 0 FOR ND)

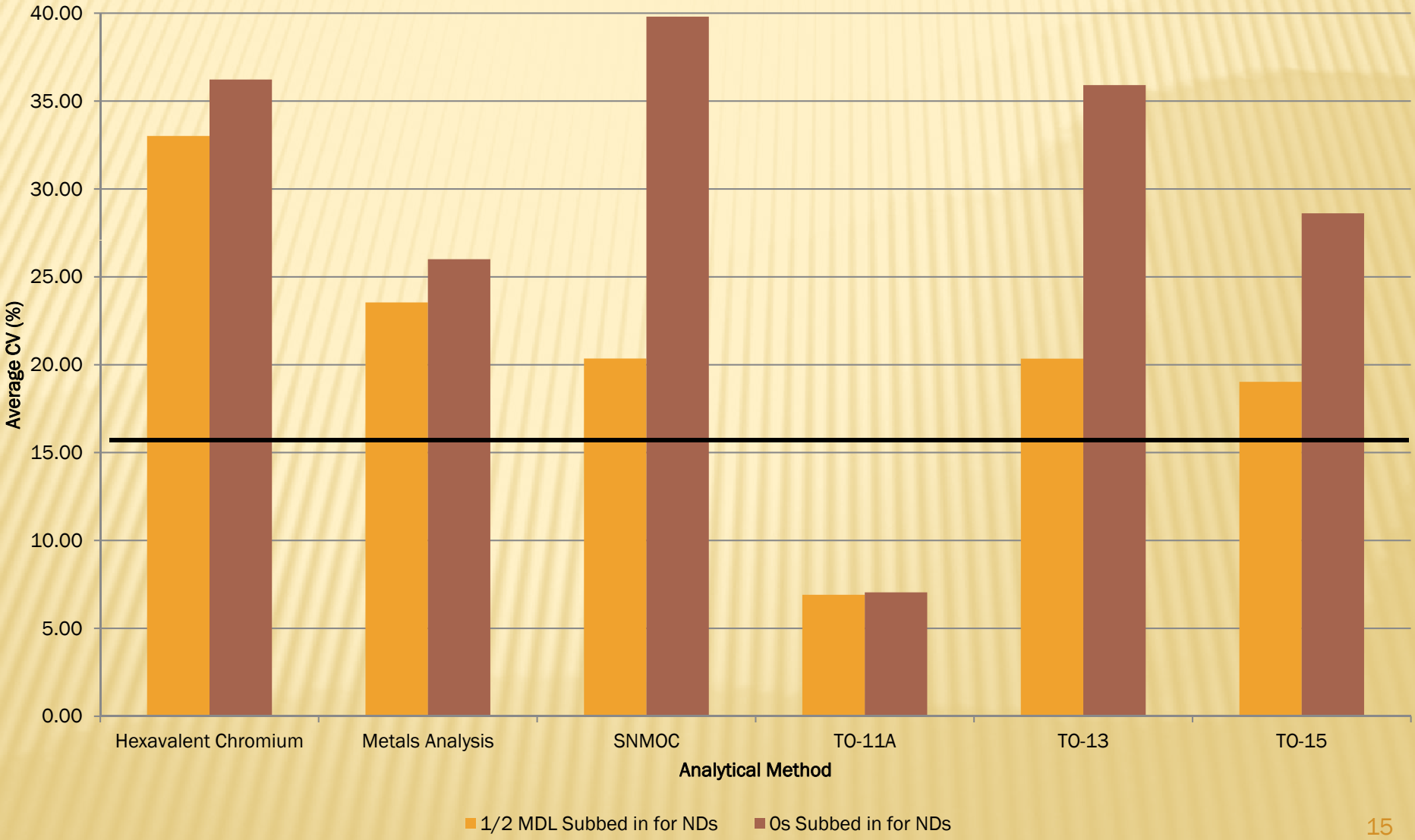
Method	Average CV (%)	Count of Pairs
Hexavalent Chromium	**36.23**	121
Metals Analysis	**26.00**	1538
SNMOC	**39.80**	1819
TO-11A	7.05	1212
TO-13	**35.91**	477
TO-15	**28.61**	3393

*Program MQO is 15%

COMPARISON

Method	½ MDL Sub	0 Sub
Hexavalent Chromium	**33.01**	**36.23**
Metals Analysis	**23.54**	**26.00**
SNMOC	**20.35**	**39.80**
TO-11A	6.91	7.05
TO-13	**20.35**	**35.91**
TO-15	**19.03**	**28.61**

COMPARISON


40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs

ITERATION #2 (1 > MDL & SUB IN 0 FOR ND)

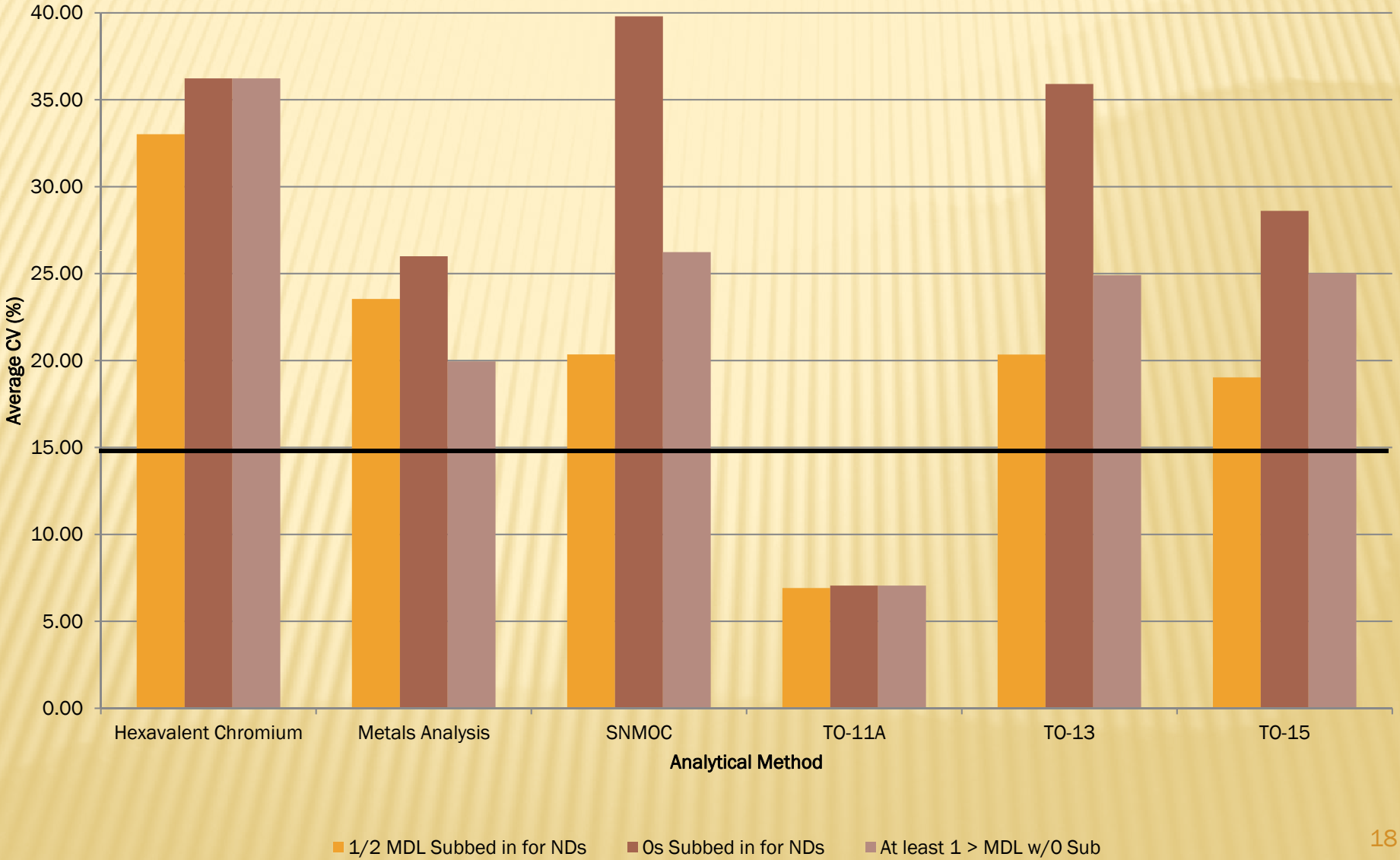
Method	Average CV (%)	Count of Pairs	
Hexavalent Chromium	**36.23**	121	121
Metals Analysis	**19.96**	1240	1538
SNMOC	**26.24**	1356	1819
TO-11A	7.05	1212	1212
TO-13	**24.90**	403	477
TO-15	**25.02**	3116	3393

*Program MQO is 15%

COMPARISON

Method	½ MDL Sub	0 Sub	1>MDL,0 Sub
Hex Chrome	**33.01**	**36.23**	**36.23**
Metals Analysis	**23.54**	**26.00**	**19.96**
SNMOC	**20.35**	**39.80**	**26.24**
TO-11A	6.91	7.05	7.05
TO-13	**20.35**	**35.91**	**24.90**
TO-15	**19.03**	**28.61**	**25.02**

COMPARISON


40.00
35.00
30.00
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20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs
At least 1 > MDL w/0 Sub

ITERATION #3 (EXCLUDES ANY PAIRS W/ ND)

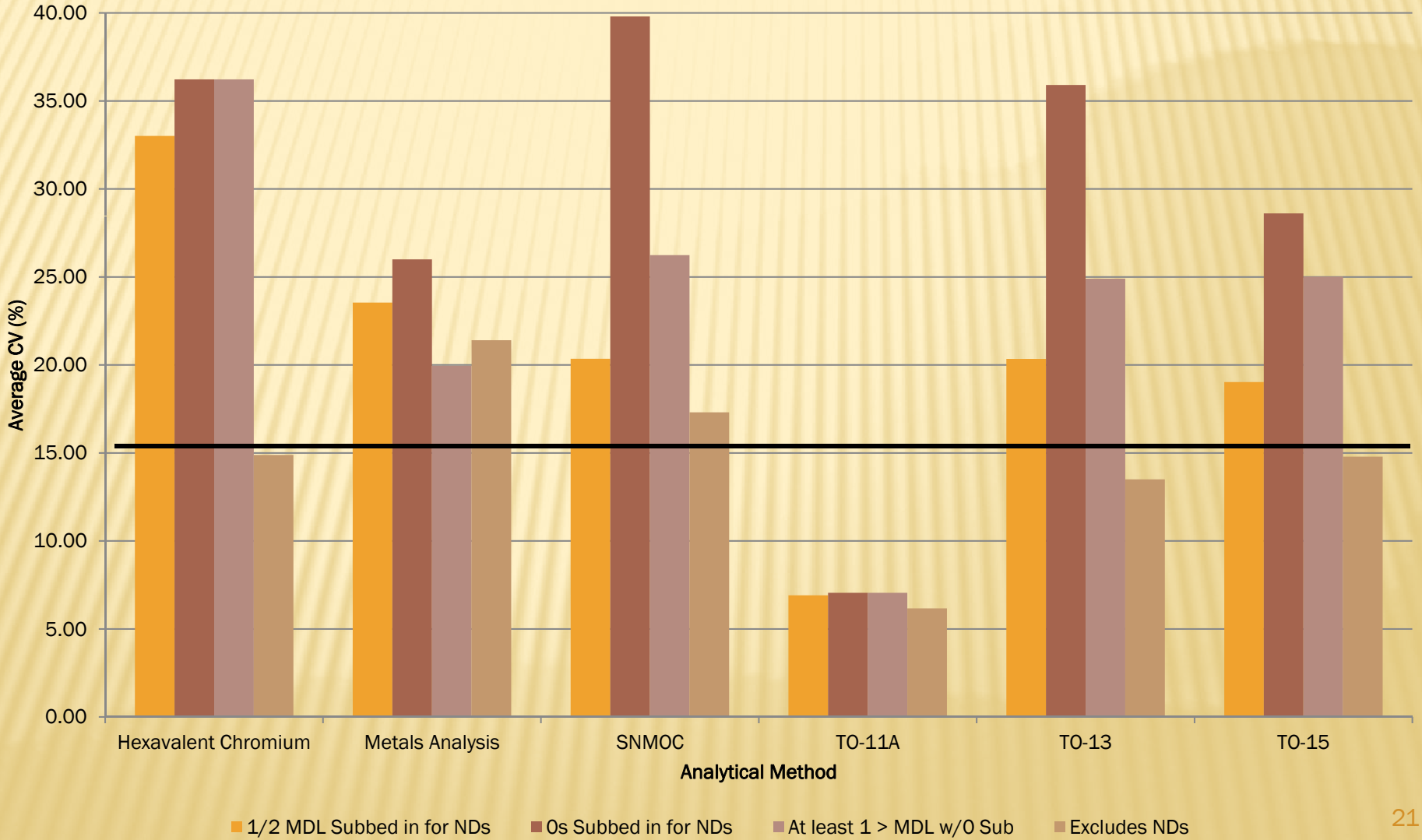
Method	Average CV (%)	Count of Pairs	
Hexavalent Chromium	14.89	112	121
Metals Analysis	**21.40**	1523	1240
SNMOC	**17.31**	1627	1356
TO-11A	6.17	1209	1212
TO-13	13.50	439	403
TO-15	14.79	3246	3116

*Program MQO is 15%

COMPARISON

Method	½ MDL Sub	0 Sub	1>MDL,0 Sub	Exclude NDs
Hex Chrome	**33.01**	**36.23**	**36.23**	14.89 ↓
Metals	**23.54**	**26.00**	**19.96**	**21.40** ↑
SNMOC	**20.35**	**39.80**	**26.24**	**17.31** ↓
TO-11A	6.91	7.05	7.05	6.17 ↓
TO-13	**20.35**	**35.91**	**24.90**	13.50 ↓
TO-15	**19.03**	**28.61**	**25.02**	14.79 ↓

COMPARISON


40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs
At least 1 > MDL w/0 Sub
Excludes NDs

ITERATION #4 (EXCLUDES <MDL)

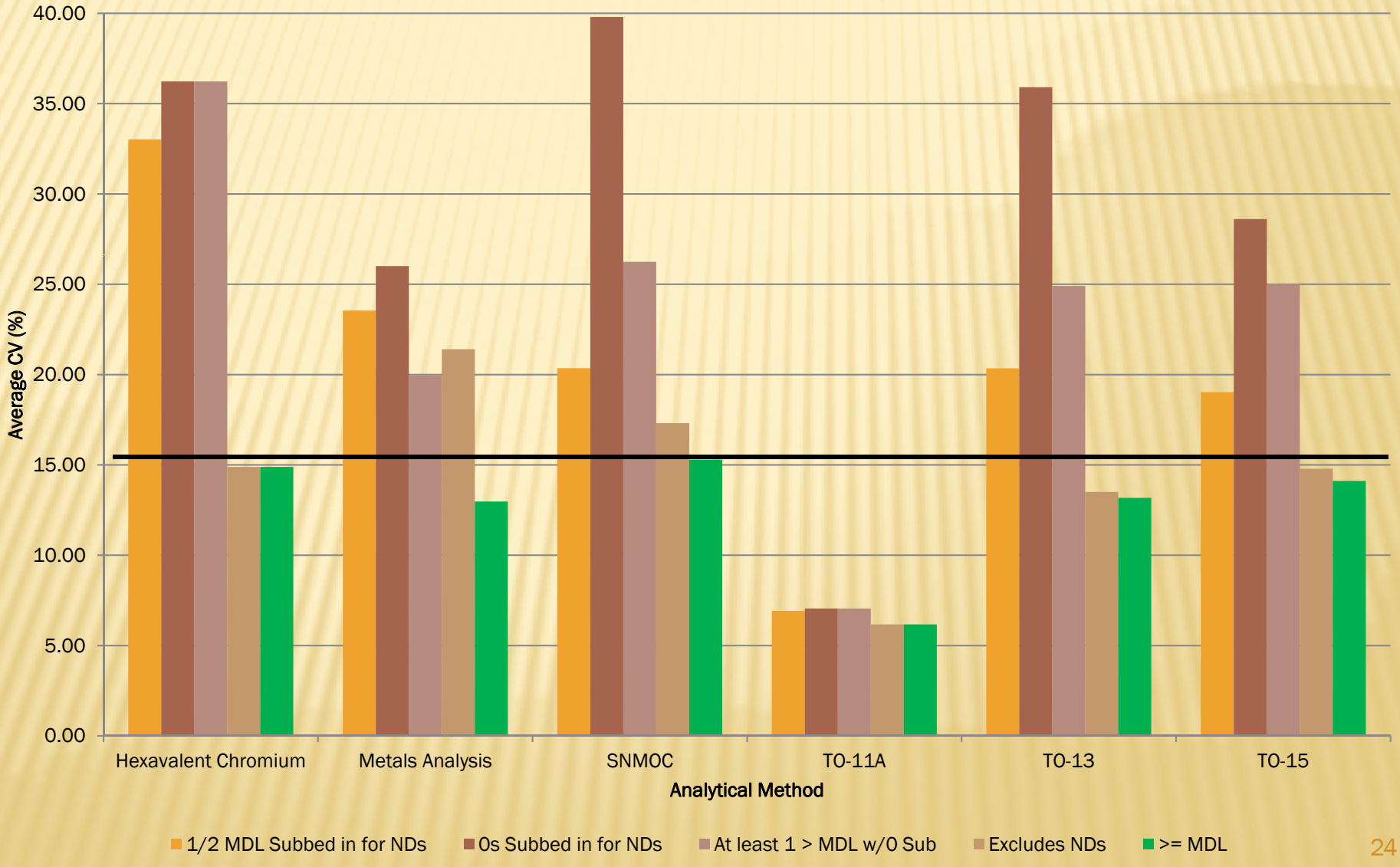
Method	Average CV (%)	Count of Pairs	
Hexavalent Chromium	14.89	112	112
Metals Analysis	12.97	1178	1523
SNMOC	**15.29**	1191	1627
TO-11A	6.17	1209	1209
TO-13	13.18	378	439
TO-15	14.11	2935	3246

*Program MQO is 15%

COMPARISON

Method	½ MDL	0 Sub	1>MDL, 0 Sub	Exclude NDs	>MDL
Cr6+	**33.01**	**36.23**	**36.23**	14.89	14.89
Metals	**23.54**	**26.00**	**19.96**	**21.40**	12.97
SNMOC	**20.35**	**39.80**	**26.24**	**17.31**	**15.29**
TO-11A	6.91	7.05	7.05	6.17	6.17
TO-13	**20.35**	**35.91**	**24.90**	13.50	13.18
TO-15	**19.03**	**28.61**	**25.02**	14.79	14.11

COMPARISON


40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs
At least 1 > MDL w/0 Sub
Excludes NDs
>= MDL

ITERATION #5 (EXCLUDES <SQL)

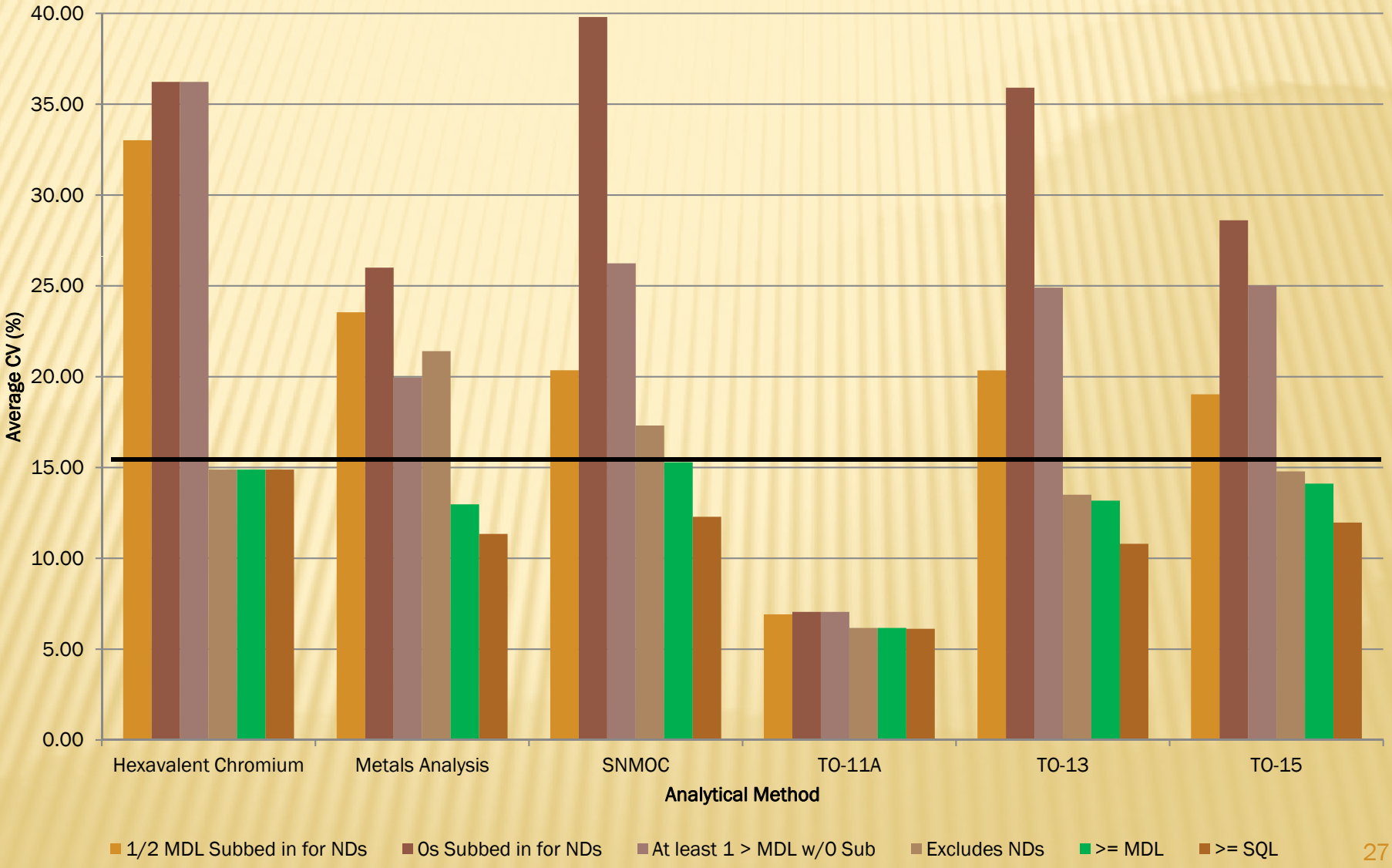
Method	Average CV (%)	Count of Pairs	
Hexavalent Chromium	14.89	112	112
Metals Analysis	11.34	860	1178
SNMOC	12.28	672	1191
TO-11A	6.13	1201	1209
TO-13	10.80	282	378
TO-15	11.97	2054	2935

*Program MQO is 15%

COMPARISON

Method	½ MDL	0 Sub	1>MDL, 0 Sub	Exclude NDs	>MDL	>SQL
Cr6+	**33.01**	**36.23**	**36.23**	14.89	14.89	14.89
Metals	**23.54**	**26.00**	**19.96**	**21.40**	12.97	11.34
SNMOC	**20.35**	**39.80**	**26.24**	**17.31**	**15.29**	12.28
TO-11A	6.91	7.05	7.05	6.17	6.17	6.13
TO-13	**20.35**	**35.91**	**24.90**	13.50	13.18	10.80
TO-15	**19.03**	**28.61**	**25.02**	14.79	14.11	11.97

COMPARISON


40.00
35.00
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25.00
20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs
At least 1 > MDL w/0 Sub
Excludes NDs
>= MDL
>= SQL

ITERATION #6 (EXCLUDES <5XMDL)

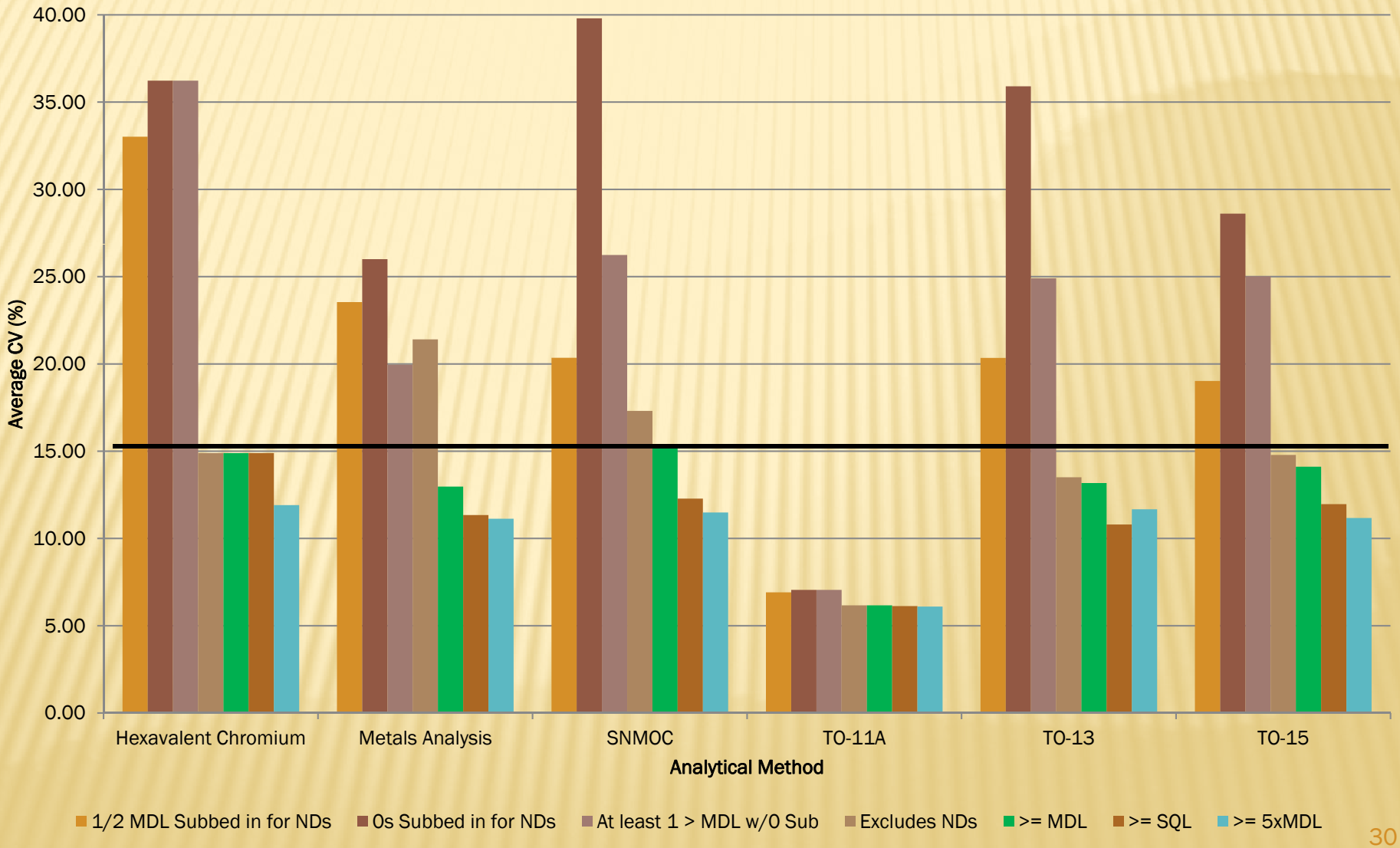
Method	Average CV (%)	Count of Pairs	
Hexavalent Chromium	11.91	95	112
Metals Analysis	11.13	707	860
SNMOC	11.49	498	672
TO-11A	6.10	1163	1201
TO-13	11.67	254	282
TO-15	11.17	1659	2054

*Program MQO is 15%

COMPARISON

Method	½ MDL	0 Sub	1>MDL, 0 Sub	Exclude NDs	>MDL	>SQL	>5xMDL
Cr6+	**33.01**	**36.23**	**36.23**	14.89	14.89	14.89	11.91 ↓
Metals	**23.54**	**26.00**	**19.96**	**21.40**	12.97	11.34	11.13 ↓
SNMOC	**20.35**	**39.80**	**26.24**	**17.31**	**15.29**	12.28	11.49 ↓
TO-11A	6.91	7.05	7.05	6.17	6.17	6.13	6.10 ↓
TO-13	**20.35**	**35.91**	**24.90**	13.50	13.18	10.80	11.67 ↑
TO-15	**19.03**	**28.61**	**25.02**	14.79	14.11	11.97	11.17 ↓

COMPARISON


40.00
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25.00
20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs
At least 1 > MDL w/0 Sub
Excludes NDs
>= MDL
>= SQL
>= 5xMDL

ITERATION #7 (EXCLUDES <CAL)

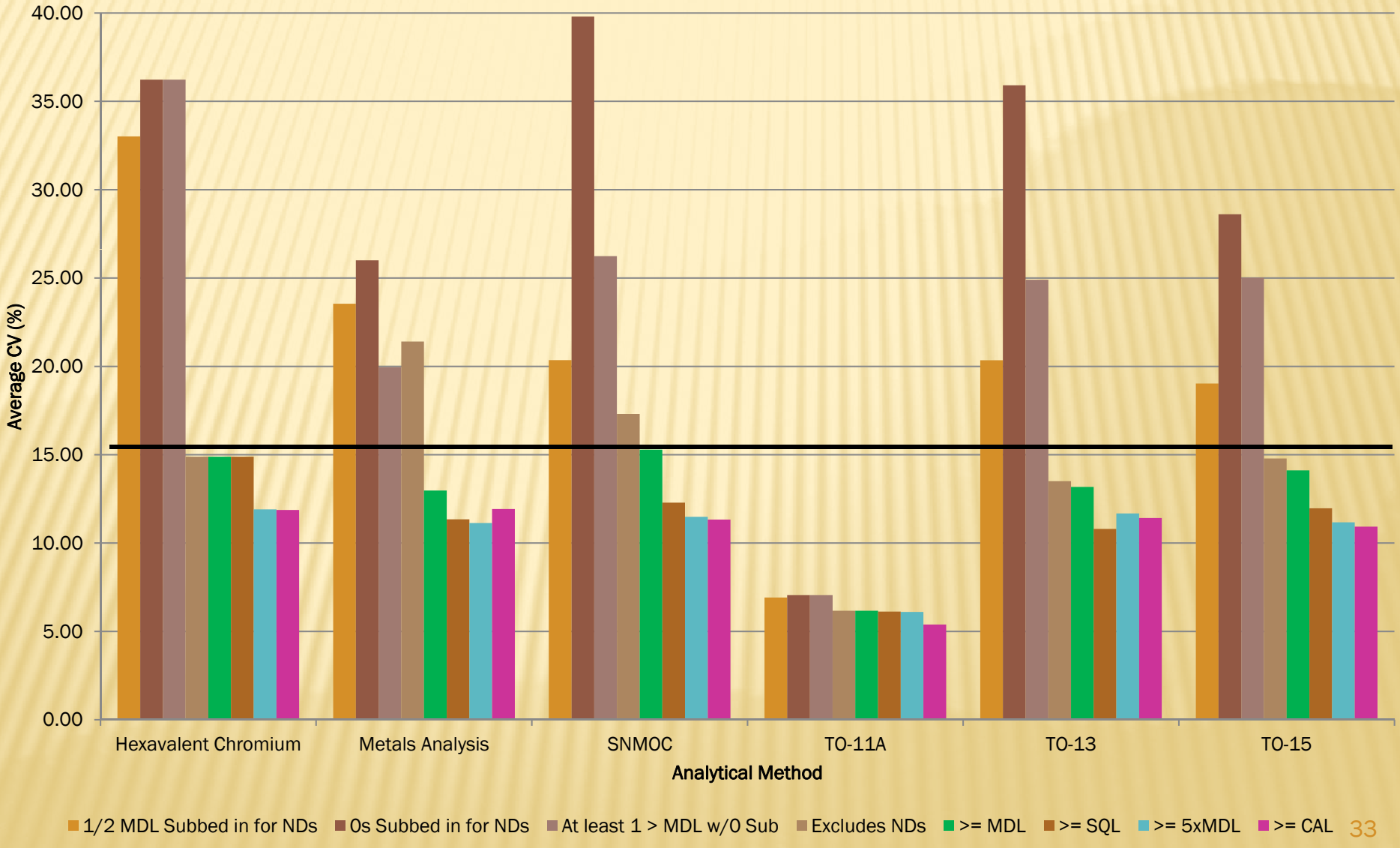
Method	Average CV (%)	Count of Pairs	
Hexavalent Chromium	11.87	61	95
Metals Analysis	11.93	1118	707
SNMOC	11.33	130	498
TO-11A	5.39	740	1163
TO-13	11.42	290	254
TO-15	10.93	886	1659

*Program MQO is 15%

COMPARISON

Method	½ MDL	0 Sub	1>MDL, Exclude 0 Sub	NDs	>MDL	>SQL	>5xMDL	<CAL
Cr6+	**33.01**	**36.23**	**36.23**	14.89	14.89	14.89	11.91	11.87
Metals	**23.54**	**26.00**	**19.96**	**21.40**	12.97	11.34	11.13	11.93
SNMOC	**20.35**	**39.80**	**26.24**	**17.31**	**15.29**	12.28	11.49	11.33
TO-11A	6.91	7.05	7.05	6.17	6.17	6.13	6.10	5.39
TO-13	**20.35**	**35.91**	**24.90**	13.50	13.18	10.80	11.67	11.42
TO-15	**19.03**	**28.61**	**25.02**	14.79	14.11	11.97	11.17	10.93

COMPARISON


40.00
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25.00
20.00
15.00
10.00
5.00
0.00
Average CV (%)
Hexavalent Chromium
Metals Analysis
SNMOC
TO-11A
TO-13
TO-15
Analytical Method
1/2 MDL Subbed in for NDs
0s Subbed in for NDs
At least 1 > MDL w/0 Sub
Excludes NDs
>= MDL
>= SQL
>= 5xMDL
>= CAL

CONCLUSION

Method	½ MDL	0 Sub	1>MDL, Exclude 0 Sub	NDs	>MDL	>SQL	>5xMDL	< CAL
Cr6+	**33.01**	**36.23**	**36.23**	14.89	14.89	14.89	11.91	11.87
Metals	**23.54**	**26.00**	**19.96**	**21.40**	12.97	11.34	11.13	11.93
SNMOC	**20.35**	**39.80**	**26.24**	**17.31**	**15.29**	12.28	11.49	11.33
TO-11A	6.91	7.05	7.05	6.17	6.17	6.13	6.10	5.39
TO-13	**20.35**	**35.91**	**24.90**	13.50	13.18	10.80	11.67	11.42
TO-15	**19.03**	**28.61**	**25.02**	14.79	14.11	11.97	11.17	10.93

CONCLUSION

Method	½ MDL	0 Sub	1>MDL, 0 Sub	Exclude NDs	>MDL	>SQL	>5xMDL	>CAL
Cr6+	**33.01**	**36.23**	**36.23**	14.89	14.89	14.89	11.91	11.87
Metals	**23.54**	**26.00**	**19.96**	**21.40**	12.97	11.34	11.13	11.93
SNMOC	**20.35**	**39.80**	**26.24**	**17.31**	**15.29**	12.28	11.49	11.33
TO-11A	6.91	7.05	7.05	6.17	6.17	6.13	6.10	5.39
TO-13	**20.35**	**35.91**	**24.90**	13.50	13.18	10.80	11.67	11.42
TO-15	**19.03**	**28.61**	**25.02**	14.79	14.11	11.97	11.17	10.93

Keeps the highest number of pairs in the precision calculations while excluding two of the three things that we know introduce uncertainty (non-detects and substitutions as well as reported values below the MDL)

ACKNOWLEDGEMENTS

- Dave Dayton, ERG
- Julie Swift, ERG
- Donna Tedder, ERG
- Regi Oommen, ERG

A CASE STUDY IN PRECISION

Thank you.

Questions?

NUMBER OF PAIRS IN EACH CALCULATION

Method	½ MDL	0 Sub	1>MDL, Exclude 0 Sub	NDs	>MDL	>SQL	>5xMDL	<CAL
Cr6+	121	121	121	112	112	112	95	61
Metals	1538	1538	1240	1523	1178	860	707	1118
SNMOC	1819	1819	1356	1627	1191	672	498	130
TO-11A	1212	1212	1212	1209	1209	1201	1163	740
TO-13	477	477	403	439	378	282	254	290
TO-15	3393	3393	3116	3246	2935	2054	1659	886