The Use of Deuterated Monitoring Compounds to Monitor Method Performance by the USEPA Contract Laboratory Program

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USEPA Office of Superfund Remediation and Technology Innovation

Analytical Services Branch

National Environmental Monitoring Conference

2015

DMC and the USEPA CLP

- Purpose
  - ✓ To demonstrate that (DMCs) should replace matrix spikes across EPA.
    - ✓ We have the means of obtaining all the information that the MS and MSD offer and more, with accuracy and precision data that are more statistically robust, more representative of the chemistry of all analytes, and less subject to interferences than the MS/MSD. Yet the historical attachment to MS/MSD data keeps them as a part of project planning in some EPA Regions and several states.
- Discussion Topics
  - ✓ CLP Overview, Benefits, Quality Assurance, and Innovation
  - ✓ DMC Development in the CLP
  - ✓ Initial DMC Studies
  - ✓ DMC and Matrix Spike Compound Correlation Studies
  - ✓ DMC and MSC Precision Studies

USEPA Contract Laboratory Program (CLP)

- Overview
  - High volume, cost effective analytical services
  - Managed by EPA with experienced contractor support
  - Detailed SOWs and thorough documentation of data quality
  - Scalable operations, automated scheduling and invoicing,
  - Flexible products from enhanced EXES
  - Headquarters funding
  - Laboratories qualified through acquisition process
  - Comprehensive QA program

Innovation in the CLP

- Innovative analytical and data management initiatives by CLP and OSRTI:

  - ✓ Statements of Work (SOWs)
  - ✓ Uniform data and QC reporting forms
  - ✓ Comprehensive QA program
  - ✓ National Functional Guidelines for Data Review and Validation
  - ✓ Staged Electronic Data Deliverables – SEDD
  - ✓ Environmental Data Management System (SCRIBE)
  - ✓ On-line sample management tools in CLPSS
  - ✓ Deuterated Monitoring Compounds

Observations about MS/MSD

- MS/MSD intended to measure method accuracy and precision.
- MS/MSD assumed to represent SDG
- No guarantee that original sample, MS, and MSD are homogenous, and in fact they often are not.
- MS/MSD samples results interpreted inconsistently, ranging from no qualification to qualifying entire project.
- Over $200,000 per year cost to the CLP for analysis and reporting.
- MS/MSD currently an option for CLP customers (not a default).
    - What we need is an indicator of accuracy and precision for all samples in the SDG, and that requires a broadly applicable indicator of chemical similarity, and more data so we don't have to rely solely on the homogeneity of the MS and MSD samples.

DMC Development in the CLP

- Started in 1996 with Mike Wilson of the AOC tasking EPA's Quality Assurance Technical Support (QATS) contractor to propose DMCs for the GC/MS SOWs.
  - Hypothesis:
    - Typically elute on the GC column just prior to native target analytes, and present higher quantitation masses based on the degree of deuteration.
    - Are not naturally found in environmental samples, whereas some of the MSCs or SCs could be present.
    - Significant cost savings.

DMC Development in the CLP

- The DMCs were proposed and selected based on:
  - ✓ Cost and availability
    - ➢ All suppliers of DMCs were researched.
    - ➢ All levels of deuteration for each target analyte were investigated.
    - ➢ Stability and/or potential for deuterium/hydrogen exchange was evaluated.
    - ➢ Costs of DMC solutions and/or neat DMC compounds from all potential sources were assessed.
  - ✓ Representativeness of chemical classifications of target analytes
    - ➢ VOC target analytes were classified into 5 chemical groups.
    - ➢ SVOC target analytes were classified into 16 chemical groups.
    - ➢ Selected VOC DMCs represent all 5 VOC chemical groups.
    - ➢ Selected SVOC DMCs represent 13 of 16 SVOC chemical groups, with no DMC available, or was cost-prohibitive for remaining 3 groups.

DMC Development in the CLP

- The DMCs were proposed and selected based on:
  - ✓ Toxicity
    - ➢ When possible, toxicity of the DMCs was considered, with the higher toxicity compounds preferred. Deviation from this approach occurred for prohibitive cost, non-availability, or when more performance data were available for lower toxicity DMCs.
  - ✓ DMC performance based on native compound accuracy and precision characteristics
    - ➢ Analyte performance of DMCs was assumed to closely mimic the analytical behavior of the associated target compounds.
  - ✓ Cost estimate of a revised QC system versus continued use of SMCs and SCs
    - ➢ Preparing DMC spiking solutions from neat compounds results in a cost of pennies/VOC sample, and approximately $1.40/SVOC sample.
    - ➢ Other costs were required to change the QC system to accommodate the use of DMCs, such as rewriting the SOW.

DMC Development in the CLP

14 volatile DMCs

Vinyl chloride-d_3
Chloroethane-d_5
1,1-Dichloroethene-d_2
2-Butanone-d_5
Chloroform-d
1,2-Dichloroethane-d_4
Bromoform-d^1
Benzene-d_6
1,2-Dichloropropane-d_6
Toluene-d_8
trans-1,3-Dichloropropene-d_4
2-Hexanone-d_5
1,1,2,2-Tetrachloroethane-d_2
1,2-Dichlorobenzene-d_4

1Bromoform eliminated due to deuterium/ hydrogen exchange

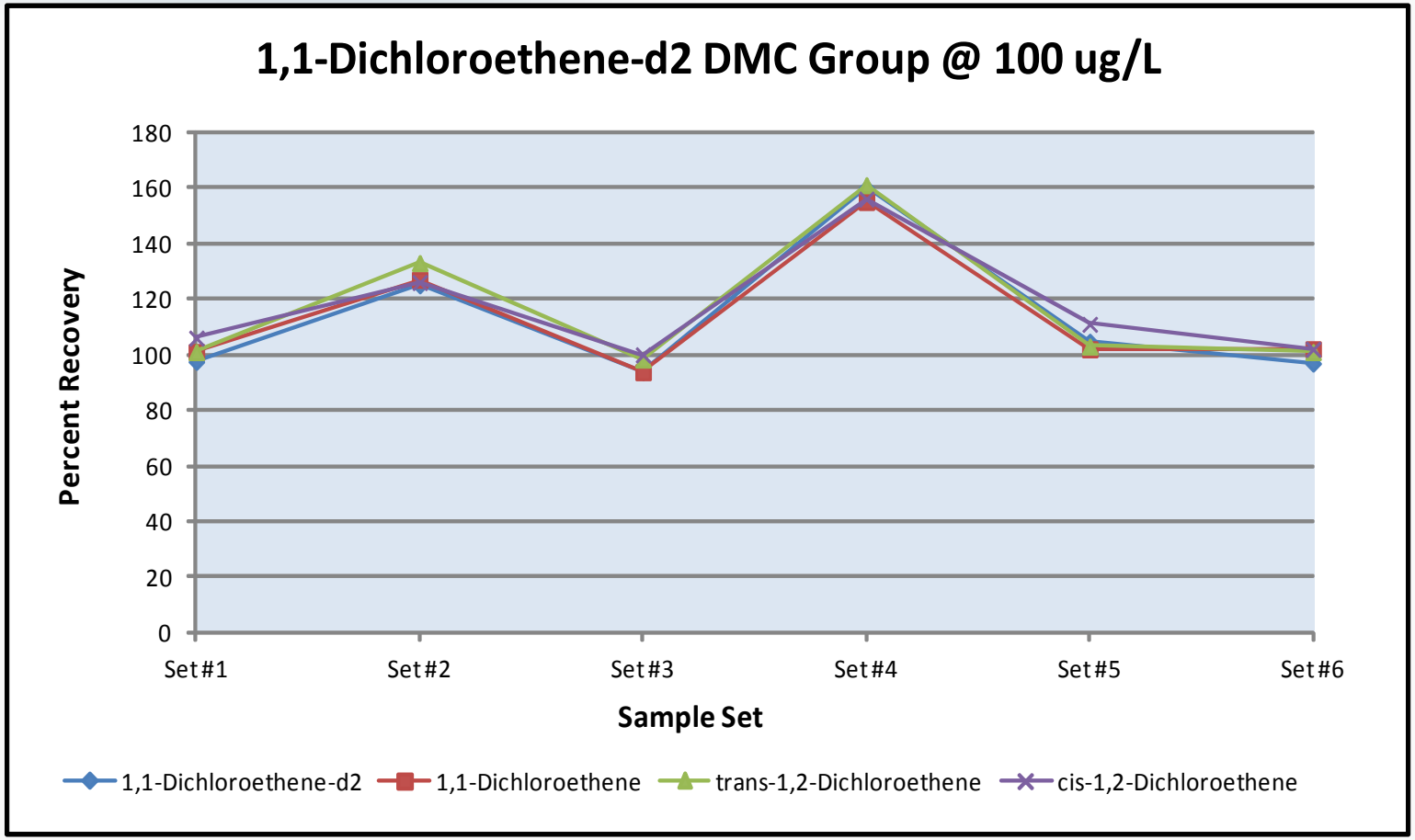
16 semivolatile DMCs

Phenol-d_5
Bis-(2-chloroethyl)ether-d_8
2-Chlorophenol-d_4
4-Methylphenol-d_8
4-Chloroaniline-d_4
Nitrobenzene-d_5
2-Nitrophenol-d_4
2,4-Dichlorophenol-d_3
Dimethylphthalate-d_6
Acenaphthylene-d_8
4-Nitrophenol-d_4
Fluorene-d_{10}
4,6-Dinitro-2-methylphenol-d_2
Anthracene-d_{10}
Pyrene-d_{10}
Benzo(a)pyrene-d_{12}

Initial DMC Development Studies

- In 1997, the QATS Lab was tasked to conduct single laboratory studies to evaluate the analytical behavior and ruggedness of the selected VOC and SVOC DMCs.
- VOC DMC single laboratory study analyzed initial calibration sets and spiked water sets (5-replicates) under 6 different instrument conditions to assess DMC and target analyte recovery and precision correlation, as well as ruggedness.
  - ✓ Sample Set #1 = Normal Purge/Normal GC/MS
  - ✓ Sample Set #2 = Low Purge Flow/Normal GC/MS
  - ✓ Sample Set #3 = High Purge Flow/Normal GC/MS
  - ✓ Sample Set #4 = Purge Tube Leak/Normal GC/MS
  - ✓ Sample Set #5 = Spent Purge Trap/Normal GC/MS
  - ✓ Sample Set #6 = Normal Purge Trap/Spent GC Column

Initial DMC Development Studies



Sample Set #1 = Normal Purge/Normal Analysis
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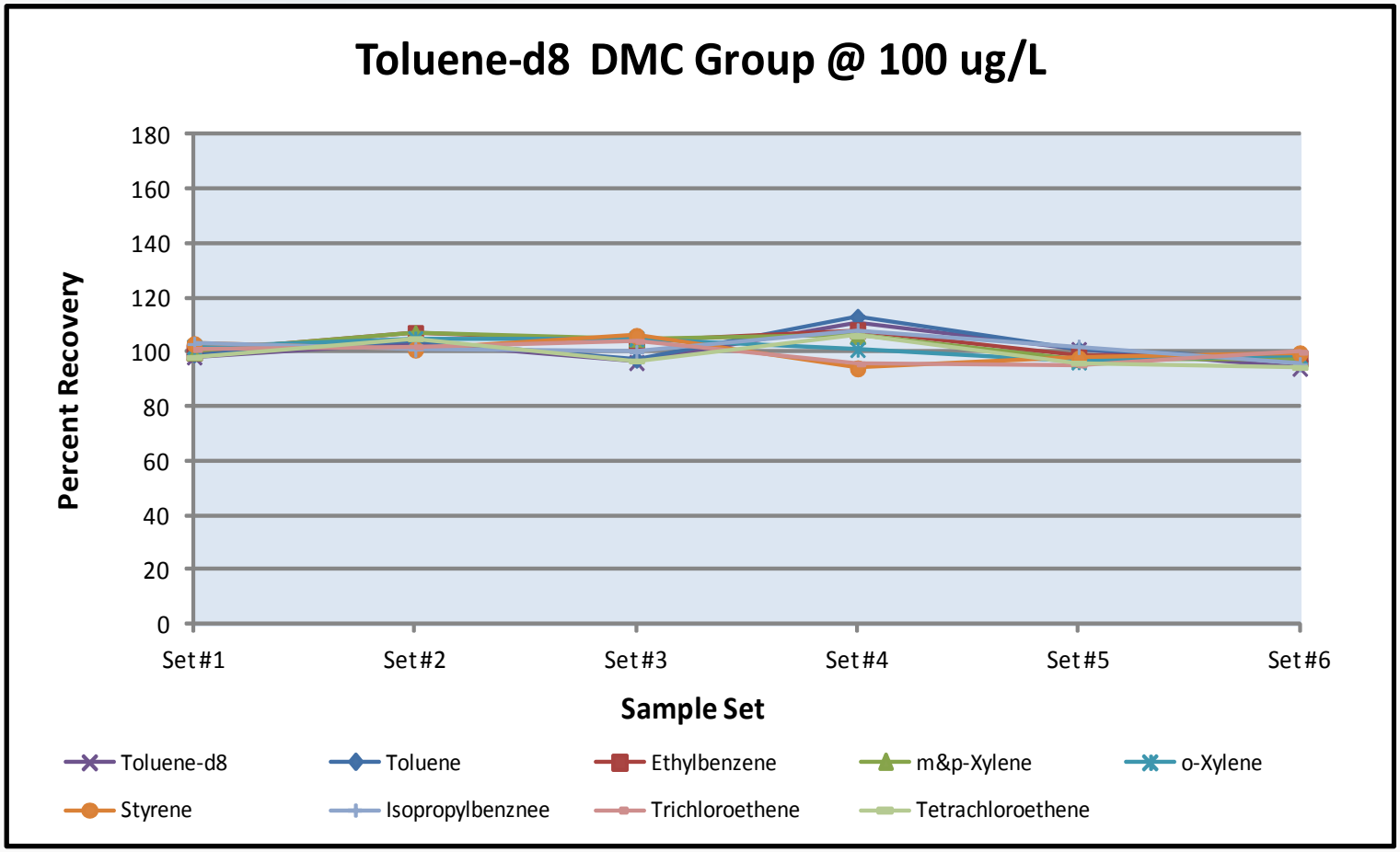

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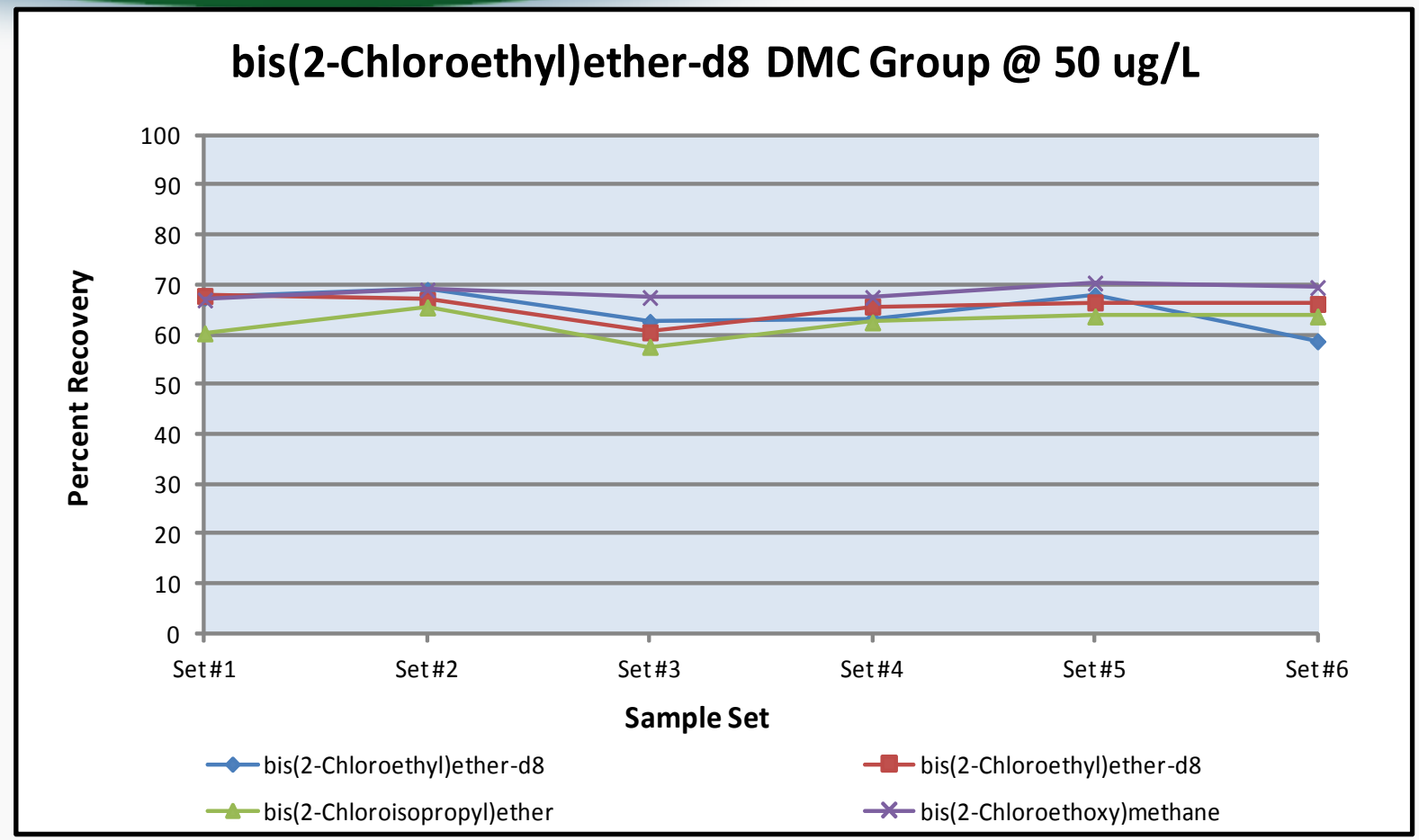
Sample Set #6 = Normal Purge/Spent GC Column

Initial DMC Development Studies

- SVOC DMC replicates for this study incorporated the following instrument conditions:

  - ✓ Sample Set #1 = Normal Extraction/Normal GC/MS
  - ✓ Sample Set #2 = 6 Hour Extraction/Normal GC/MS
  - ✓ Sample Set #3 = Boiled Dry Extraction/Normal GC/MS
  - ✓ Sample Set #4 = Evaporated Extraction/Normal GC/MS
  - ✓ Sample Set #5 = Normal Extraction/Dirty Injection Liner
  - ✓ Sample Set #6 = Normal Extraction/Spent GC Column

Initial DMC Development Studies



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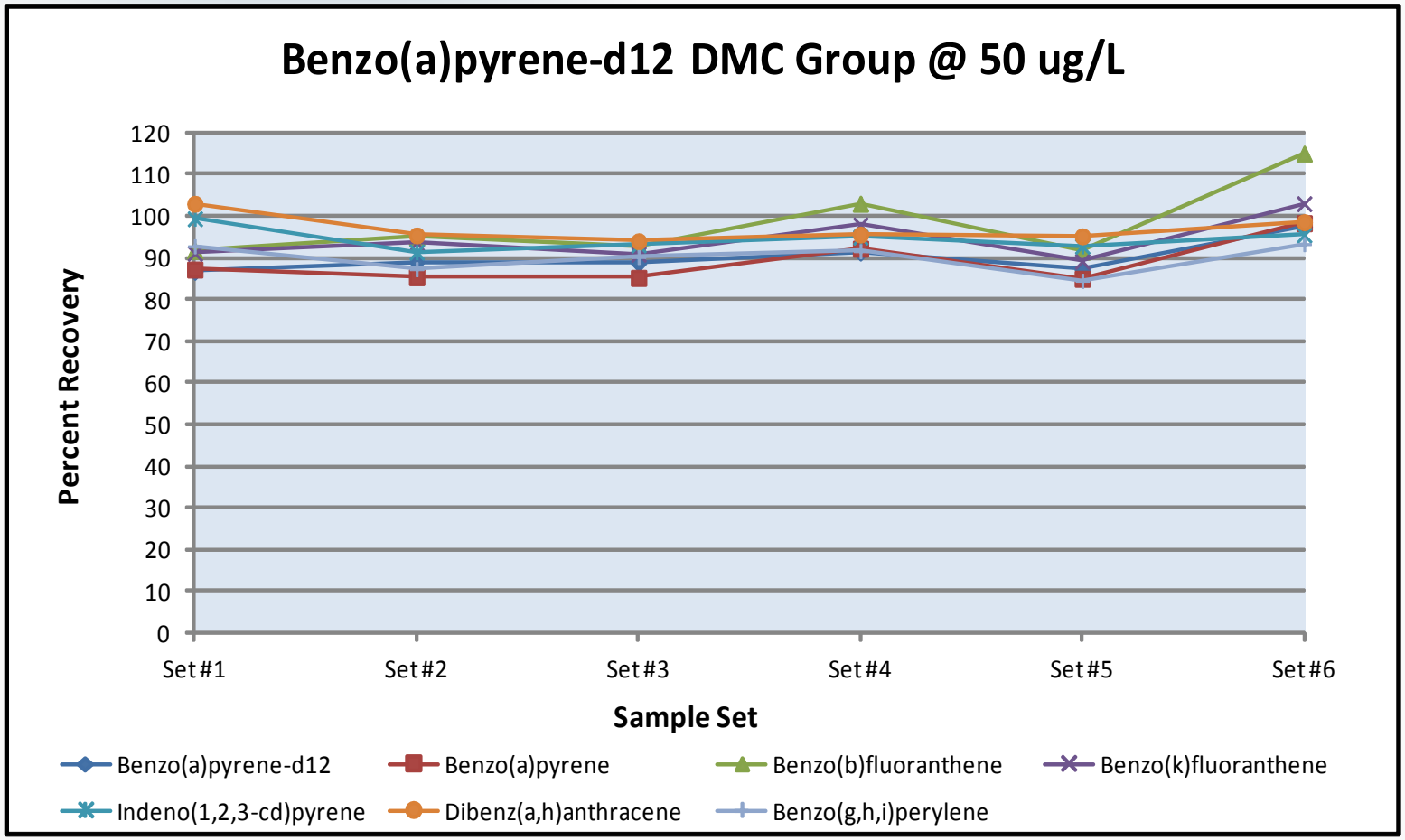
Initial DMC Development Studies



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Sample Set #4 = Evaporated Extraction/Normal Analysis
Sample Set #5 = Normal Extraction/Dirty Injection Liner
Sample Set #6 = Normal Extraction/Spent GC Column

Initial DMC Development Studies

- Conclusions and recommendations from the VOC and SVOC DMC single laboratory studies:
  - ✓ DMCs provide excellent recovery and precision correlation with corresponding native target compounds, and with most of the other target analytes within a DMC group.
  - ✓ The 14 VOC and 16 SVOC DMCs provide a group of QC compounds that better represent the classes of compounds in the target analyte lists and retention time groups than using the initial SMCs and SCs.
  - ✓ Initial advisory QC Recovery Limits for the DMCs were recommended using the 90% confidence intervals calculated from a historical database of native compound recovery data.
  - ✓ A revised SOW was prepared incorporating the use of VOC and SVOC DMCs.
  - ✓ Multi-laboratory studies were recommended as the next phase in DMC development.

Initial DMC Development Studies

- Subsequent QATS Studies Conducted:
  - ✓ 1997 Interlaboratory study for CLP's Mike Wilson on DMC recovery and precision.
  - ✓ 1997 Multi-laboratory study for CLP's Ed Messer on SPE, SPME, accelerated solvent extraction, and automated soxhlet extraction.
  - ✓ 2000 Multi-laboratory study for CLP's Eric Reynolds on potential new VOC and SVOC analytes.
  - ✓ 2000 Multi-laboratory study for CLP's Terry Smith on the effects of preservation and temperature on volatile VOC samples.
  - ✓ 2002 DMC/MSC study for CLP's Terry Smith on recovery and precision, including 312 volatile MS/MSD and 116 semivolatile MS/MSD analyses.
  - ✓ 2003 Multi-laboratory study for CLP's Terry Smith on recovery and precision of DMCs in soil samples, to establish acceptance limits for soils.
  - ✓ 2008 DMC Recovery Precision and Acceptance Limit Survey for CLP's Phil Cocuzza and John Nebelsick.

DMC and MSC Correlation Study

- The objective of the 2002 correlation study was to evaluate the statistical correlation between the DMC recovery and associated MSC recovery to determine the continued need for MS/MSD analysis.
- DMC and MSC recoveries evaluated from 312 volatile MS/MSD analyses and 116 semivolatile MS/MSD analyses.
- Data used in this study was derived from aqueous sample analytical results from CLP laboratories.
- Six VOC DMC/MSC pairs were identified for the study.
- Nine SVOC DMC/MSC pairs were identified for the study.
- DMC recoveries were evaluated against associated MSC recoveries.

DMC and MSC Correlation Study

- Linear regression analysis and numerical correlation analysis was performed on each data set after pre-processing data into nine subsets:
  - ✓ Unprocessed Raw Data
  - ✓ Data Set With Outliers Removed
  - ✓ Data Set Which Lies Within 95% Confidence Intervals
  - ✓ Data Set Which Lies Within 99% Confidence Intervals
  - ✓ Data Set With DMC/MSC Recovery Differences < 10%
  - ✓ Data Set With DMC/MSC Recovery Differences < 20%
  - ✓ Data Set Which Exhibits Only a Negative DMC/MSC Correlation
  - ✓ Data Set Which Exhibits Only a Positive DMC/MSC Correlation
  - ✓ Data Set Which Demonstrates a Correlation Value r > 0.900
- DMC/MSC correlation of each data set was measured through calculation of average r-Values.

DMC and MSC Correlation Study

- Data was processed as subsets to offset variables in data sets due to:
  - ✓ Sample results from different sites with matrix variation.
  - ✓ Sample results from up to eight different laboratories.
  - ✓ Samples spiked with standard solutions from different sources.
  - ✓ Samples spiked with several different standard solutions (TCL standards, DMC calibration standards, DMC spiking solutions, MS/MSD spiking standards) prepared by different individuals.
  - ✓ Samples prepared and analyzed under different conditions, facilities, and instrumentation.
- Additional statistics used to evaluate DMC/MSC recovery correlation included average % recoveries, standard deviation, and relative standard deviation.

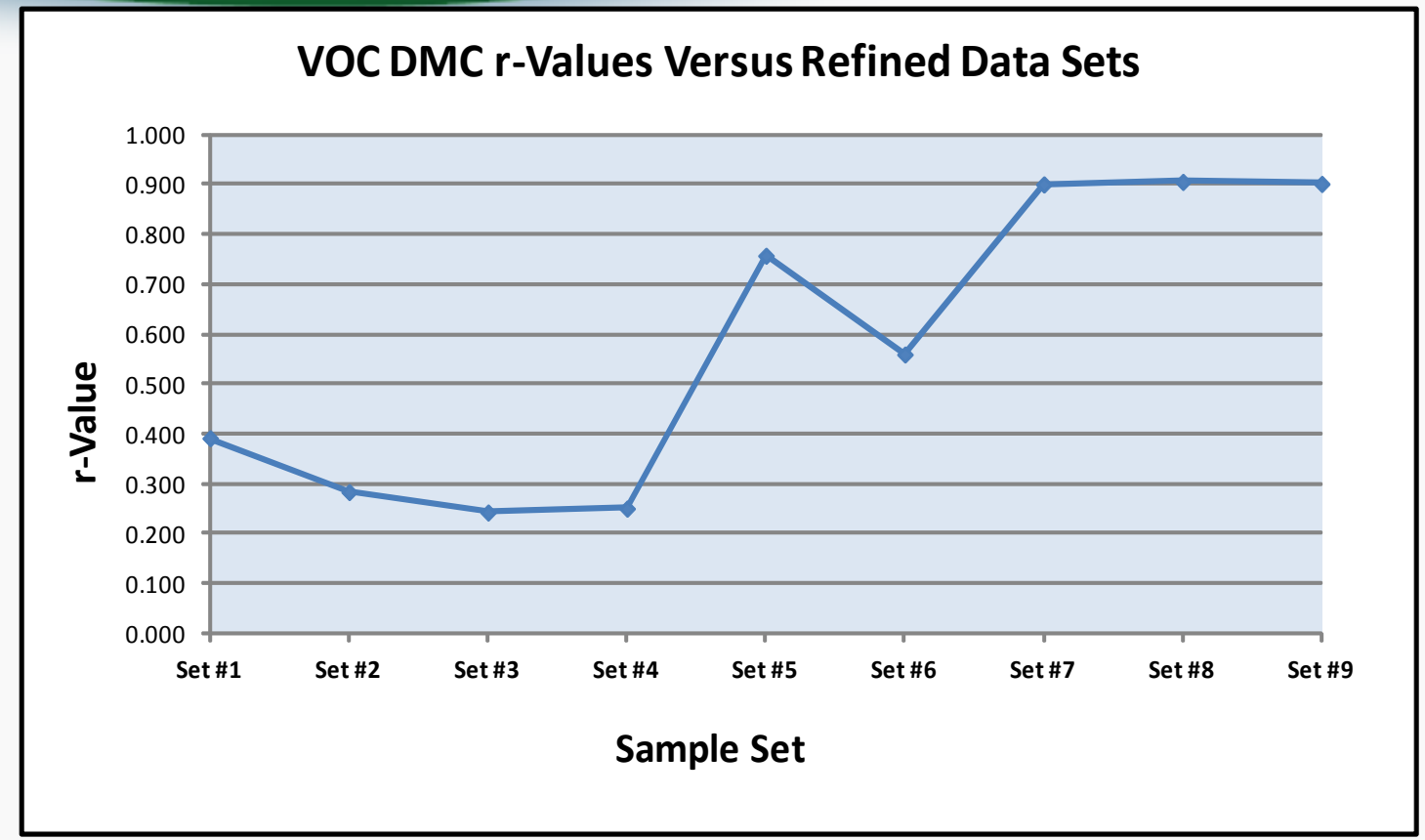
DMC and MSC Correlation Study

DMC/MSC PAIR #	*VOLATILE DMC*	*ASSOCIATED VOA SMC*
1	1,1-Dichloroethene-d2	1,1-Dichloroethene
2	1,2-Dichloroethane-d4	1,1-Dichloroethene
3	Benzene-d6	Benzene
4	Toluene-d8	Trichloroethene
5	Toluene-d8	Toluene
6	1,2-Dichlorobenzene-d4	Chlorobenzene

DMC and MSC Correlation Study

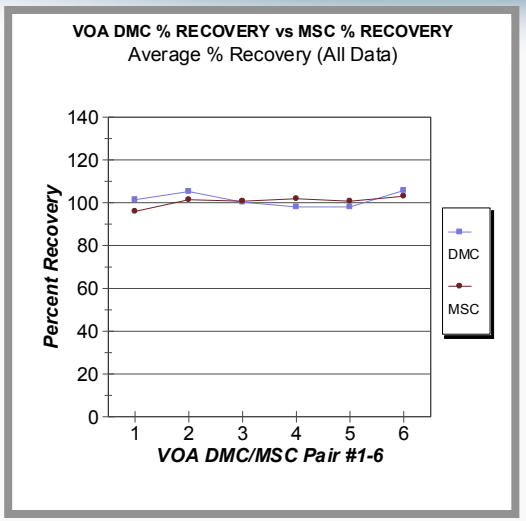
VOA DMC/MSC DATA SET AVERAGE r-VALUES			
DATA SET	***AVG. r-VALUE***	***% OF TOTAL SET***	***r-VALUE RANGE***
Raw Data Set	0.392	100	0.135 – 0.521
Outliers Removed	0.284	96	0.052 – 0.565
95% CI Data	0.243	86	0.015 – 0.454
99% CI Data	0.251	94	0.023 – 0.527
< 10% Difference Set	0.758	61	0.629 – 0.910
< 20% Difference Set	0.560	79	0.319 – 0.738
Neg. Corr. Data Set	0.901	78	0.900 – 0.903
Pos. Corr. Data Set	0.906	77	0.901 – 0.913
r > 0.900 Data Set	0.902	41	0.900 – 0.906

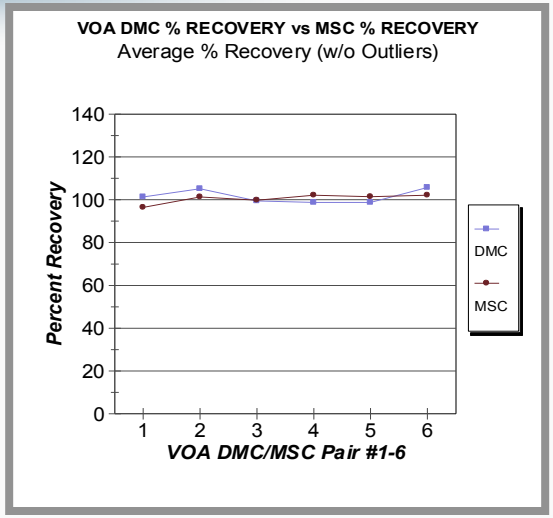
DMC and MSC Correlation Study

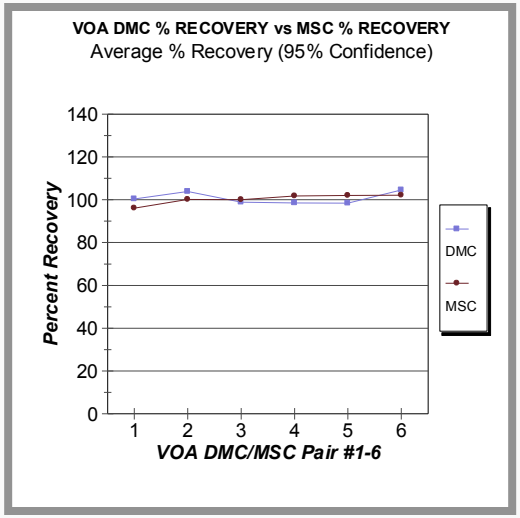


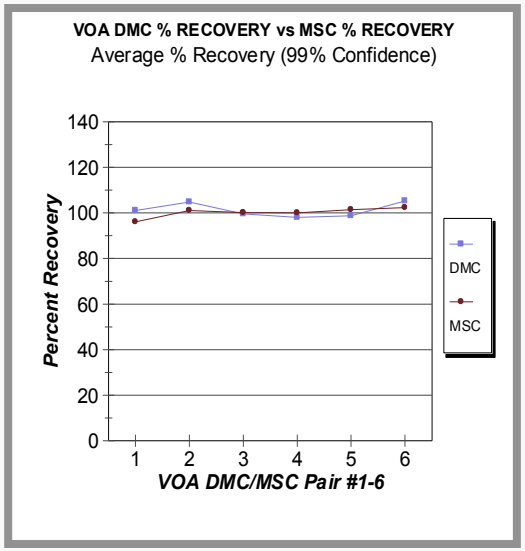
Set #1 =	Raw Data Set	Set #6 =	>20% Difference Data Set
Set #2 =	Outliers Removed Data Set	Set #7 =	Negative Correlation Data Set
Set #3 =	95% Confidence Interval Data Set	Set #8 =	Positive Correlation Data Set
Set #4 =	99% Confidence Interval Data Set	Set #9 =	r > 0.900 Correlation Data Set
Set #5 =	>10% Difference data Set		

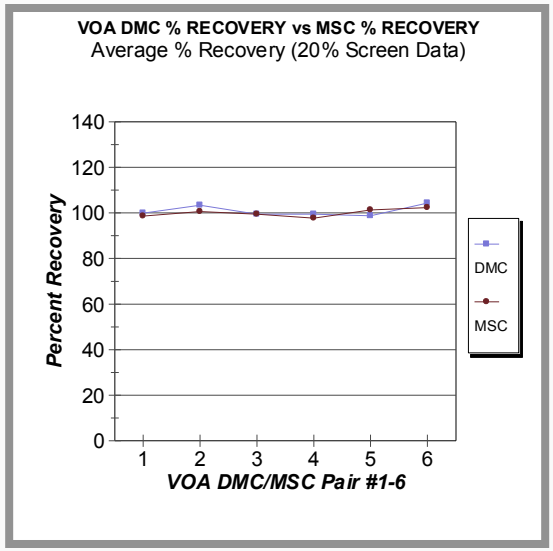
DMC and MSC Correlation Study

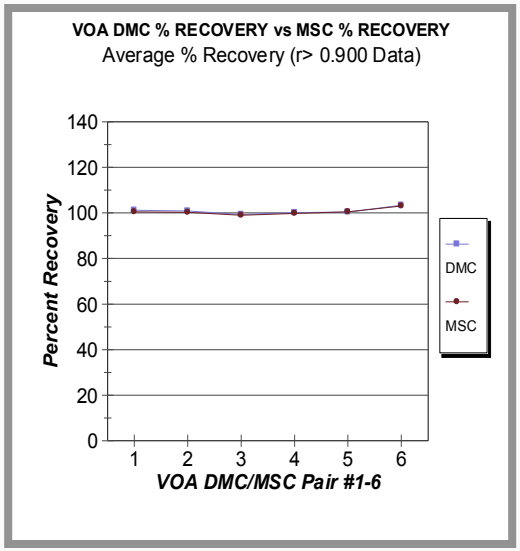












DMC and MSC Correlation Study

VOA DMC/ MSC Pair	Average % Recovery		RSD	
	DMC	MSC	DMC	MSC
#1	101	96	15.7	23.2
#2	105	101	12.1	15.7
#3	100	101	13.6	15.0
#4	98	102	12.8	18.7
#5	98	101	12.8	14.6
#6	106	103	11.1	13.2

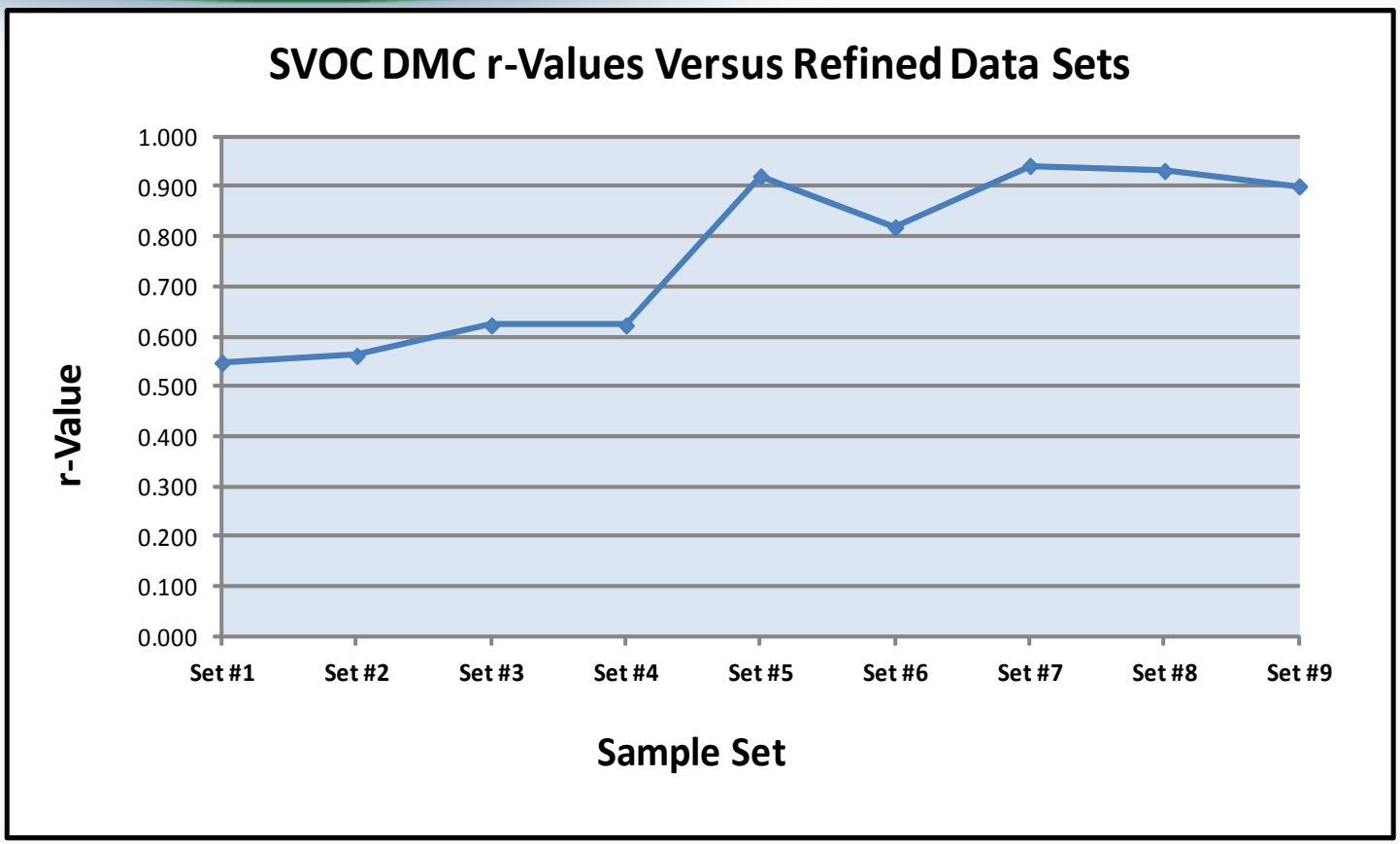
DMC and MSC Correlation Study

DMC/MSC PAIR #	*SEMIVOLATILE DMC*	*ASSOCIATED SVOA MSC*
1	Phenol-d5	Phenol
2	2-Chlorophenol-d4	2-Chlorophenol
3	Nitrobenzene-d5	N-Nitroso-di-n-Propylamine
4	Nitrobenzene-d5	2,4-Dinitrotoluene
5	2,4-Dichlorophenol-d3	4-Chloro-3-Methylphenol
6	2,4-Dichlorophenol-d3	Pentachlorophenol
7	Pyrene-d10	Pyrene
8	Acenaphthylene-d8	Acenaphthene
9	4-Nitrophenol-d4	4-Nitrophenol

DMC and MSC Correlation Study

SVOA DMC/MSC DATA SET AVERAGE r-VALUES			
DATA SET	***AVG. r-VALUE***	***% OF TOTAL SET***	***r-VALUE RANGE***
Raw Data Set	0.548	100	0.289 – 0.711
Outliers Removed	0.562	97	0.389 – 0.674
95% CI Data	0.623	88	0.318 – 0.768
99% CI Data	0.623	92	0.345 – 0.793
< 10% Difference Set	0.921	57	0.852 – 0.990
< 20% Difference Set	0.819	76	0.691 – 0.893
Neg. Corr. Data Set	0.942	87	0.902 – 0.977
Pos. Corr. Data Set	0.932	84	0.901 – 0.963
r > 0.900 Data Set	0.901	65	0.900 – 0.903

DMC and MSC Correlation Study



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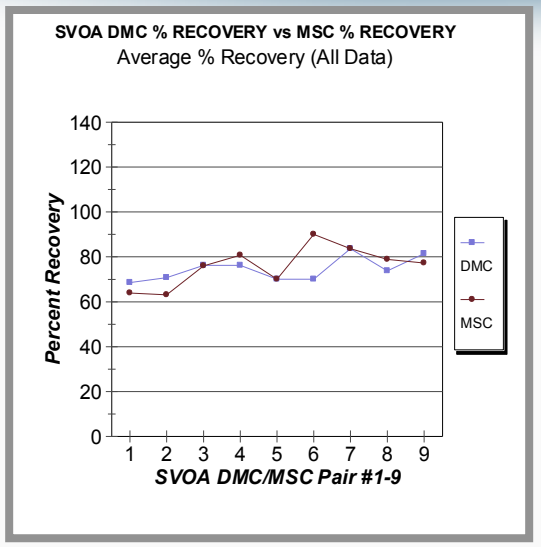
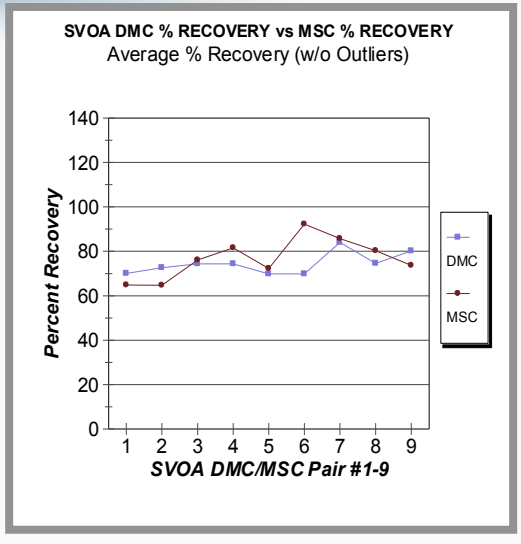
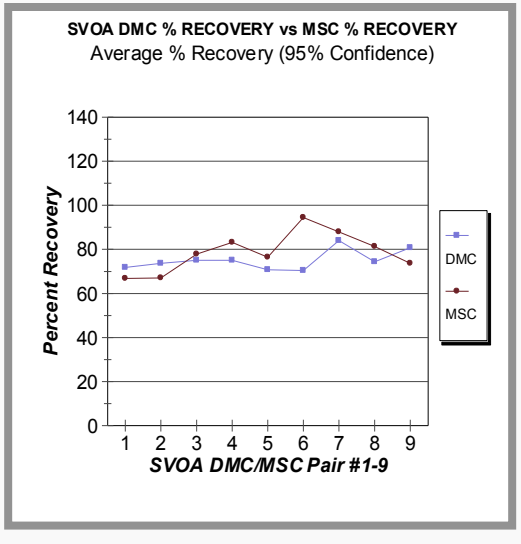
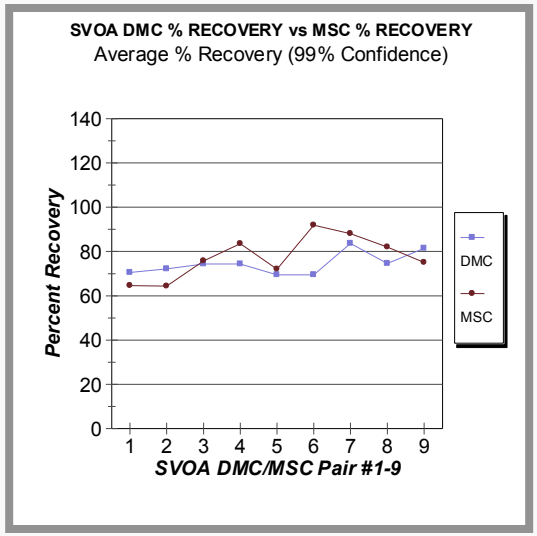
Set #5 =	>10% Difference data Set		

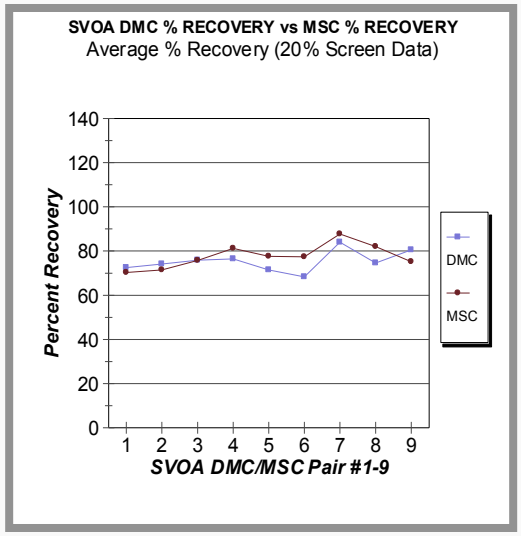
DMC and MSC Correlation Study

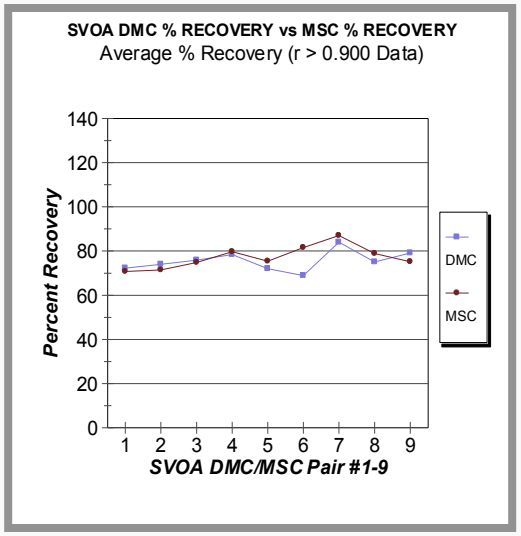












DMC and MSC Correlation Study

SVOA DMC/ MSC PAIR	Average % Recovery		RSD	
	DMC	MSC	DMC	MSC
#1	69	64	25.3	32.5
#2	71	63	23.6	33.2
#3	76	76	24.4	27.9
#4	76	81	24.4	23.3
#5	70	70	26.0	31.6
#6	70	90	26.0	34.8
#7	84	84	21.3	27.7
#8	74	79	18.1	29.6
#9	82	77	19.4	33.2

DMC and MSC Precision Study

- In 2008, under the direction of EPA's Mr. John Nebelsick and Mr. Phil Cocuzza, the QATS Laboratory conducted a DMC Recovery Precision and Acceptance Limit Evaluation Study.
- Objective of the study was to evaluate if DMC recovery accuracy and precision data can be use to replace the MS/MSD recovery and precision data.
- DMC data from 105 CLP SOM organic fraction SDGs were statistically evaluated to determine recovery accuracy and precision within an SDG.
- Recovery precision within an SDG was evaluated against a predetermined baseline of acceptable precision, adopted from the SOM SOW initial calibration precision criteria.

DMC and MSC Precision Study

- DMC statistical information evaluated within each SDG included:
  - ✓ Average percent recovery
  - ✓ Standard deviation
  - ✓ Relative standard deviation
  - ✓ Low and high DMC recoveries within the data set
  - ✓ Number of DMC recoveries exceeding the established QC Limits
  - ✓ Number of data points
- If DMC recovery precision indicators within an SDG exceeded the baseline limit of acceptable precision, further processing of DMC data was performed to determine the cause of the anomalous results.
- MS/MSD recovery and precision statistics were also determined for each SDG, provided that MS/MSD analyses were performed.

DMC and MSC Precision Study

- Five different organic fractions/matrices were examined from the 105 SDGs.
  - ✓ Trace concentration aqueous volatile organics (5,889 DMC data points)
  - ✓ Low/Medium Concentration Aqueous Volatile Organics (4,914 DMC data points)
  - ✓ Low/Medium Concentration Volatile Organics in Soil (4,550 DMC data points)
  - ✓ Aqueous Semivolatile Organics (3,232 DMC data points)
  - ✓ Low/Medium Concentration Semivolatile Organics in Soil (4,240 DMC data points)
- The following slides provide example data processing and narrative assessment from Trace Aqueous Volatile Organics SDG Y2F69

DMC and MSC Precision Study

- SDG Y2F69 Summary
  - ✓ SDG consisted of 30 sample analyses: 16 field samples, 4 field blanks, 1 MS/MSD set, 5 method blanks, 1 storage blank, and 2 field sample dilutions.
  - ✓ There were 390 DMC data points in the SDG, with only 1 DMC recovery outlier (1,1-DCE-d_2 biased high due to native 1,1-DCE in the sample).
  - ✓ 6 of the 10 MS/MSD results exceeded the recovery limits.
  - ✓ RSD values for all DMCs across the sample set are <20%, most <10%.
  - ✓ Most of the sample were relatively clean with no indication of matrix interference.
  - ✓ High level (outside calibration range) of trichloroethene in the sample used for MS/MSD.
  - ✓ No difference in RSD values when blanks are included in the sample set.

DMC and MSC Precision Study

SDG Number Y2F69

This SDG consists of thirty (30) sample analyses including sixteen (16) field samples, four (4) field blanks, an MS/MSD set, five (5) method blanks, one (1) storage blank, and two (2) field sample dilutions. The RSD values for the DMC recoveries in this sample set are all less than 20 percent (most less than 10 percent) indicating good precision. Two (2) of the field samples required dilution due to the high levels of trichloroethene reported in the original analyses. In addition to the trichloroethene detected in these samples, lower levels of additional chlorinated hydrocarbons were detected in several of the other samples. Most of the samples in this set were relatively clean with no indication of potential for matrix interference. One (1) of the 390 DMC recovery values in this sample set exceeded the current SOM01.2 QC acceptance limits. This high recovery was for 1,1-dichloroethene-d_2 in sample Y2F83 which contained a moderate amount of native 1,1-dichloroethene, contributing to a high bias result for the DMC. There are no substantial differences in the RSD values for the DMC recoveries when the blanks or the MS/MSD samples are excluded from the statistical data set. The recoveries for benzene, trichloroethene, and toluene in both the MS and MSD analyses exceeded the advisory QC limits, although the low RPD values for these compounds indicate good precision between the duplicate analyses. There was a high level of native trichloroethene in the sample used for the MS/MSD analysis, and the laboratory performed the MS/MSD analyses using a five-fold dilution of the sample.

DMC and MSC Precision Study

#	DMC/SMC Name	Avg %Rec	RSD	(n)	Low Value	High Value	Low Limit	High Limit	# Out
1	Vinyl Chloride-d3	95	9.5	30	79	120	65	131	0
2	Chloroethane-d5	97	9.2	30	80	118	71	131	0
3	1,1-Dichloroethene-d2	82	11.2	30	64	106	55	104	1
4	2-Butanone-d5	90	10.1	30	71	111	49	155	0
5	Chloroform-d	99	5.9	30	84	107	78	121	0
6	1,2-Dichloroethane-d4	97	5.8	30	86	109	78	129	0
7	Benzene-d6	111	6.3	30	87	120	77	124	0
8	1,2-Dichloropropane-d6	98	5.9	30	82	106	79	124	0
9	Toluene-d8	110	5.7	30	96	120	77	121	0
10	t-1,3-Dichloropropene-d4	96	5.5	30	82	103	73	121	0
11	2-Hexanone-d5	109	7.9	30	90	122	28	135	0
12	1,1,2,2-Tetrachloroethane-d2	94	5.7	30	82	103	73	125	0
13	1,2-Dichlorobenzene-d4	116	6.2	30	101	131	80	131	0
	Total DMC Values in SDG Exceeding Percent Recovery Limits								1

	MSC Name	MS %REC	MSD %REC	QC Limits	RPD	QC Limits
1	1,1-Dichloroethene	113	113	61-145	0	0-14
2	Benzene	128*	128*	76-127	0	0-11
3	Trichloroethene	128*	132*	71-120	3	0-14
4	Toluene	136*	136*	76-125	0	0-13
5	Chlorobenzene	120	116	75-130	3	0-13
	Total Outside Limits	3	3		0	

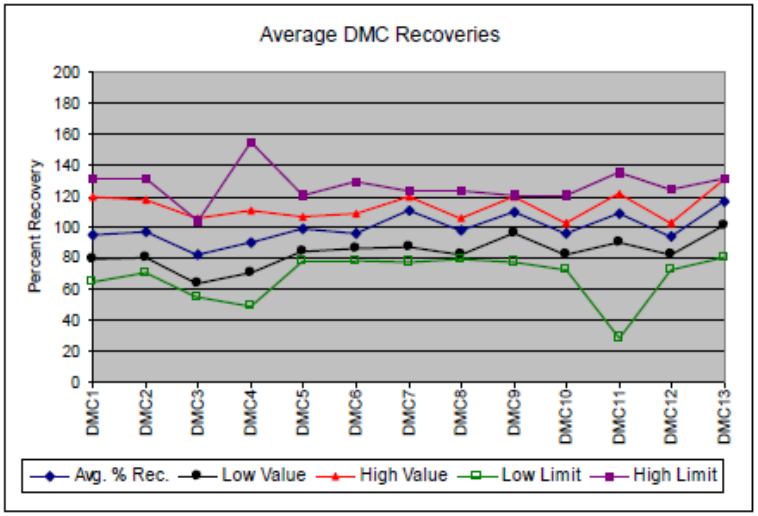
DMC and MSC Precision Study

SDG: Y2F69 Trace Concentration Aqueous Volatile Organics															
DMC Recoveries By Analysis															
Type	FB	FS	FS	FS	FB	FS	FS	FS	FS	FB	FS	FS	FS	FS	FS
Sam. #	Y2F69	Y2F70	Y2F70 DL	Y2F71	Y2F72	Y2F73	Y2F74	Y2F75	Y2F76	Y2F77	Y2F78	Y2F79	Y2F80	Y2F81	Y2F82
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
DMC1	99	94	86	93	95	88	92	92	93	99	99	98	95	112	109
DMC2	102	98	88	95	98	95	98	97	95	100	100	99	100	113	109
DMC3	84	80	73	81	81	77	80	79	80	84	100	82	82	87	103
DMC4	72	84	85	71	87	89	88	88	86	89	85	95	95	98	98
DMC5	97	97	92	95	99	99	97	98	99	100	101	104	102	107	103
DMC6	90	94	91	90	92	95	93	95	94	99	95	100	101	106	100
DMC7	113	115	102	113	111	111	111	110	107	114	116	116	116	114	113
DMC8	96	101	95	95	96	104	97	99	98	98	105	102	104	100	104
DMC9	112	115	102	110	110	111	111	110	107	112	115	115	114	114	114
DMC10	89	100	90	89	93	97	96	97	94	96	101	103	100	100	101
DMC11	90	106	106	90	99	110	107	111	102	110	109	116	119	111	121
DMC12	86	93	91	86	89	94	93	94	92	96	95	97	99	96	98
DMC13	110	115	111	114	117	116	113	115	112	105	121	116	121	113	117
DMC Recoveries By Analysis															
Type	FS	FS	FB	FS	FS-MS	FS-MSD	FS	FS	FS	MB	MB	MB	MB	MB	SB
Sam. #	Y2F83	Y2F85	Y2F86	Y2F89	Y2F89MS	Y2F89MSD	Y2F89DL	Y2F88	Y2F87	8032403	8032013	8031404	8032104	8032509	VHBLKZO
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
DMC1	106	95	97	82	79	81	97	93	85	120	102	89	87	99	101
DMC2	107	98	101	80	83	82	99	97	81	118	103	91	89	98	87
DMC3	106	81	83	67	93	91	82	79	64	85	84	76	72	74	79
DMC4	103	93	86	95	77	79	89	87	85	105	97	93	91	111	103
DMC5	106	104	103	84	92	91	107	101	85	107	101	103	97	95	101
DMC6	107	101	100	86	92	88	102	97	91	109	98	100	94	98	98
DMC7	114	120	118	100	103	101	119	110	87	116	116	114	111	107	103
DMC8	106	103	104	85	91	90	105	95	82	104	99	101	95	97	97
DMC9	112	116	117	99	100	96	120	112	102	115	116	111	112	101	99
DMC10	102	102	102	90	89	90	100	95	82	99	97	93	93	102	96
DMC11	122	117	109	106	97	101	115	107	100	121	118	118	109	116	114
DMC12	103	99	97	86	86	88	100	94	82	101	94	101	90	94	100
DMC13	125	126	113	101	118	114	126	113	104	124	128	125	131	109	121

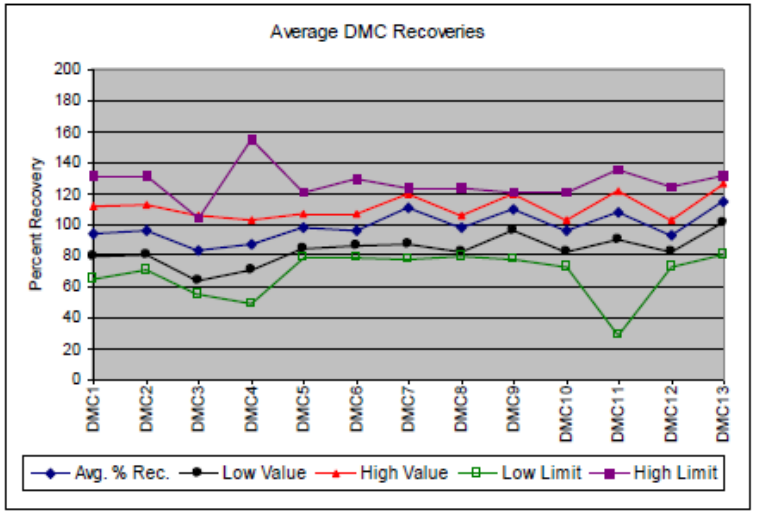
DMC and MSC Precision Study

SDG: Y2F69 Trace Concentration Aqueous Volatile Organics (Continued)

SDG Average DMC Recoveries Including Blanks



SDG Average DMC Recoveries Excluding Blanks

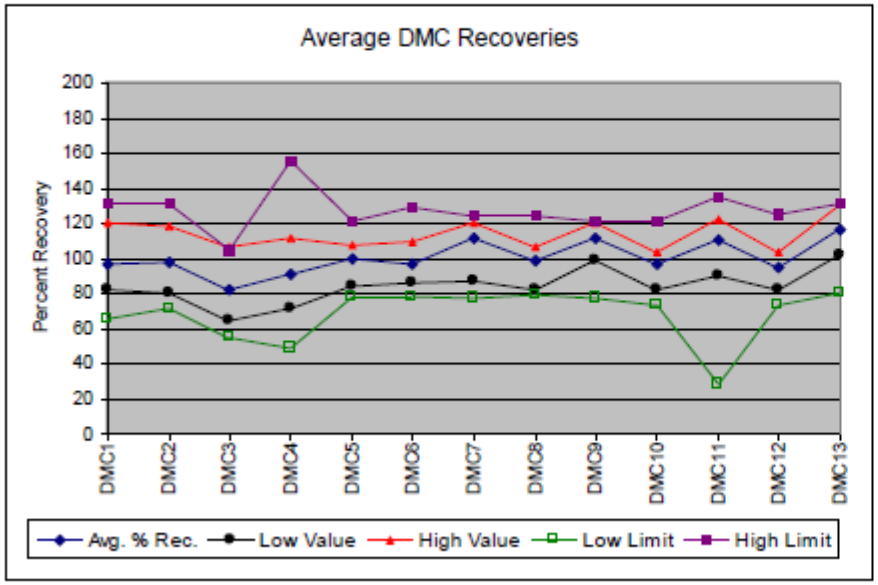


SDG Statistics Including Blanks							SDG Statistics Excluding Blanks						
	Average	SD	RSD	Low	High	(n)		Average	SD	RSD	Low	High	(n)
DMC1	95	9.05	9.5	79	120	30	DMC1	94	8.17	8.7	79	112	24
DMC2	97	8.93	9.2	80	118	30	DMC2	96	8.42	8.7	80	113	24
DMC3	82	9.26	11.2	64	106	30	DMC3	83	9.84	11.8	64	106	24
DMC4	90	9.14	10.1	71	111	30	DMC4	88	7.79	8.9	71	103	24
DMC5	99	5.86	5.9	84	107	30	DMC5	98	6.19	6.3	84	107	24
DMC6	97	5.56	5.8	86	109	30	DMC6	96	5.52	5.8	86	107	24
DMC7	111	7.00	6.3	87	120	30	DMC7	111	7.46	6.7	87	120	24
DMC8	98	5.84	5.9	82	106	30	DMC8	98	6.37	6.5	82	106	24
DMC9	110	6.29	5.7	96	120	30	DMC9	110	6.18	5.6	96	120	24
DMC10	96	5.26	5.5	82	103	30	DMC10	96	5.66	5.9	82	103	24
DMC11	109	8.60	7.9	90	122	30	DMC11	108	8.64	8.0	90	122	24
DMC12	94	5.37	5.7	82	103	30	DMC12	93	5.38	5.8	82	103	24
DMC13	116	7.27	6.2	101	131	30	DMC13	115	6.32	5.5	101	126	24

DMC and MSC Precision Study

SDG: Y2F69 Trace Concentration Aqueous Volatile Organics (Continued)

SDG Average DMC Recoveries Including Blanks/Excluding MS/MSD



SDG Statistics Including Blanks/Excluding MS/MSD

	Average	SD	RSD	Low	High	(n)
DMC1	96	8.34	8.7	82	120	28
DMC2	98	8.35	8.5	80	118	28
DMC3	82	9.19	11.3	64	106	28
DMC4	91	8.83	9.7	71	111	28
DMC5	99	5.71	5.7	84	107	28
DMC6	97	5.43	5.6	86	109	28
DMC7	111	6.82	6.1	87	120	28
DMC8	99	5.64	5.7	82	106	28
DMC9	111	5.55	5.0	99	120	28
DMC10	96	5.14	5.3	82	103	28
DMC11	110	8.42	7.7	90	122	28
DMC12	94	5.21	5.5	82	103	28
DMC13	117	7.51	6.4	101	131	28

DMC and MSC Precision Study

DMC Precision Study Analytical Fraction Summary						
Fraction	No. of DMC Data Points from 105 SDGs	No. DMCs Exceeding QC Limits	% of Data Set	% of SDGs with MS/ MSD	% of MS/ MSD Analytes Outside Criteria	% of RPD Results Outside Criteria
Trace Aqueous VOCs	5,889	83	1.4	42	11	2
L/M Aqueous VOC	4,634	88	1.9	52	5.5	3.6
L/M VOCs in Soil	4,550	472	10.4	45	7.3	18.2
Aqueous SVOC	3,232	108	3.3	60	9.3	0.0
SVOCs in SOil	4,224	114	2.7	65	3.4	0.9

DMC Development Studies
Summary of Findings

1) DMC recoveries correlate well with MSC recoveries.
2) The DMCs mimic the chemistry of the native compounds,
3) Chemical class representation
4) DMCs indicate matrix effects in every sample,
5) Precision can be assessed across an entire SDG.
6) Results more statistically significant, due to the number of DMCs used,
7) Quantitation bias is not observed for DMCs,
8) Further study possible of similar matrices
9) Eliminating MS/MSD saves solvent and other waste, and reduces resource consumption by labs
10) Substantial cost savings for CLP program as well.

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