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Ohio Environmental Protection Agency

Surface Water Field Sampling Manual - Appendix IV

Data Management

Photo Courtesy of Russ Gibson, Ohio EPA, DSW

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Next Revision Due: April 22, 2021

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Revision History

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions are maintained by the OEPA Division of Surface Water Modeling, Assessment and TMDL Section Manager.

History	Effective Date
Ohio EPA Surface Water Quality Sampling Manual version 7.0 **Appendix IV: Data Management** Section B: Removed text; section will be reserved for future use. Older version available upon request. Section C: Removed text; section will be reserved for future use. Older version available upon request. Section D: Removed text; section will be reserved for future use. Older version available upon request.	**April 22, 2019**

Surface Water Field Sampling Manual

Appendix IV

APPENDIX IV – SECTION A. DATA MANAGEMENT

Subsection A1. Data Validation Guidelines for QC and Field Samples

For most DSW chemical water quality data, data validation is generally confined to evaluation of Blank results, Duplicate results, sample holding times, paired parameter results (defined below) and confirming that samples were properly preserved/prepared (including filtration, etc. - if indicated by the method). Standards for evaluation of analytical results of those QC sample types and general field samples are described below.

Data can be qualified using the standard qualifiers available as defined by DES (in their field handbook) such as "J" for an estimated concentration or "R" for rejected result as well as one additional qualifier, "Trend." Some results may be too uncertain for some data uses but potentially useful for more general data trend applications.

Data qualifiers should be added by samplers to EA3 as part of their data review process. This will ensure the qualifier remains with the sample result. We want to be sure that valid conclusions can be made using our data for any current and future data uses.

Data Qualifiers

All sample results have some amount of uncertainty surrounding the quantification of analyte in a given sample. Data qualifiers are used to indicate that extra uncertainty is present surrounding a given result (e.g., "J" for estimated or "Trend" to indicate more uncertainty). The data qualifier "R", Rejected, is used to indicate that too much uncertainty is present to consider the result quantitatively (for most data applications). "Trend" is a qualifier used by DSW to indicate when data is considered to have less quantitative significance but enough for assessing data trends.

Blanks – Blank contamination can result in qualification of other results that were in the same field batch as that blank. In some cases, these other results may still be useable and other times the sample results should not be considered valid, largely depending on the concentration in the sample vs. the concentration in the blank.

Laboratories often use a factor of three to differentiate a detected compound from background "noise" present in the system (analytical instrument, etc.). When a result exceeds three times the background noise, it is considered to be positively identified in the sample. We can consider blank contamination as extra "noise" in the system, since we don't know the source of the contamination, and use this factor of three to help us assess our data. To do so, the sample concentration must be at least three times the blank concentration for us to be confident that analyte is truly present in the sample.

Sample Result	**Interpretation**
Blank > Sample	The result is "J" for system uncertainty
Sample ≤ 3x Blank	Reject sample results in this range as insufficiently different from blank results
3x Blank < Sample ≤ 5x Blank	Likely indication that the analyte is present but poor confidence in the numerical result - generally limit data use to data "trend" applications
< 5x Blank < Sample ≤ 10x Blank	Consider the sample result to be an estimated concentration (qualified "J") but still suitable for most data uses
> 10x Blank	Do not qualify data (blank contamination does not significantly change the result within the uncertainty of the value reported)

Blank qualification examples:

Blank Result	Detect. Level	Sample Result	Qualifier	Reason
8	5	7	"R"	Result ≤ 3x Blank
8	5	16	"R"	Result ≤ 3x Blank
8	5	29	"Trend"	< 3x Result ≤ 5x Blank
8	5	79	"J"	< 5x Result ≤10x Blank
8	5	81	No qualifier	Result > 10x Blank
8	5	Non-detect	"J"	System uncertainty

Note: If Data Quality Objectives for a parameter are well above (>5x) blank contamination and field sample results use of only a "J" qualifier, instead of "Trend" or "R", may be warranted.

Field Duplicates – Laboratories analyze and evaluate duplicates for their own internal procedures but DSW staff collect field duplicates to evaluate variability regarding sampling precision for field QC. Duplicates must be submitted "blind" to the laboratory in order to properly assess precision. The duplicate sample results are compared using a statistic called Relative Percent Difference (RPD).

RPD - Relative Percent Difference: $$\% \, Diff. = \left| \frac{x_1 - x_2}{\left[\frac{(x_1 + x_2)}{2}\right]} \right| x \; 100$$

In the %RPD example below one sample result/ concentration is substituted in the equation for x_1 (6) and the other for x_2 (10 - it doesn't matter which is which in this equation - but traditionally the duplicate will be x_2).
Example RPD calculation:

$$\frac{|\,(6-10)\,|}{|((6+10)/2)|} \quad x\ 100 \;=\; \frac{|-4|}{|8|} \; x\ 100 = 0.5 \; x\ 100$$

(positive since it's an absolute value)

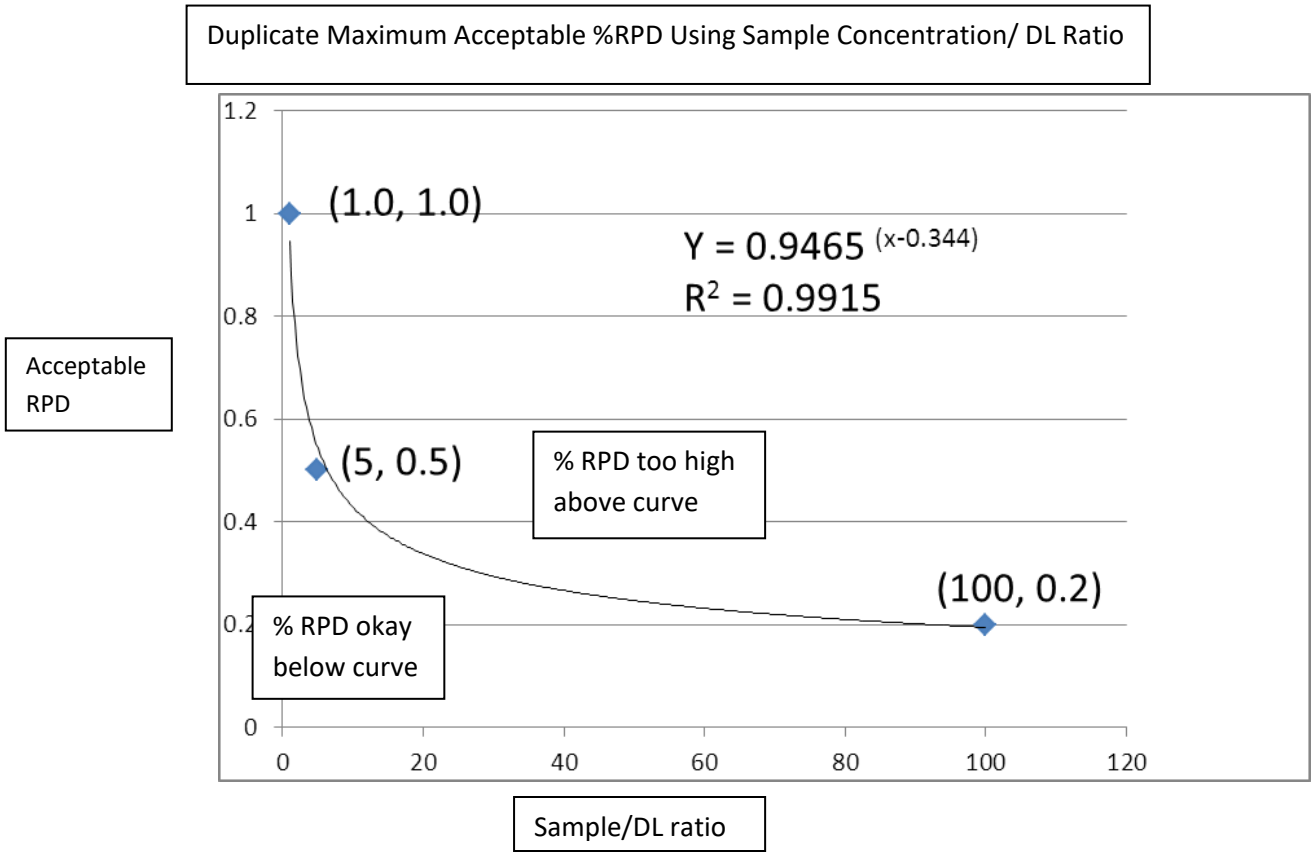
RPD = 50%

We allow a higher %RPD at lower concentrations, since there is a greater percent uncertainty closer to the detection level, and allow a lower %RPD at higher concentrations, since analytical results should be more consistent at higher concentrations. To account for this varying acceptable %RPD, we assess our duplicate samples using a curved line.

By starting with three points based on the ratio of the sample concentration to the detection limit and the %RPD we are willing to accept, we can use Excel to generate the equation of a line. The three points used were:

(1, 1.0) – At the minimum detection limit, we are willing to accept approximately 100% RPD
(5, 0.5) – at 5x the detection limit (often near the RL), we are willing to accept approximately 50% RPD
(100, 0.2) – at 100x the detection limit, we are willing to accept approximately 20% RPD

The graph (taken from Excel, using the "Power" option from the "Trendline" function) shown below illustrates the curve of best fit for these three points. The resulting R^2 value confirms a good fit of our line to our points.



Using "Trendline" in Excel we are able to generate an equation with a very good fit to these three points. With additional tweaking of the equation (adding 5% to each result,) we get a result that gives us almost exactly 100% RPD when the sample concentration equals the detection limit and puts us back up above 10% RPD for high concentration samples (see the table below).

The resulting final equation is $Y = [(0.9465x^{-0.344}) * 100] + 5$

where x = Sample/DL ratio and y = acceptable %RPD

At first take, this approach might seem somewhat arbitrary, but we have to remember that all approaches have some arbitrary component and what we need is to be consistent and to define an approach that we are comfortable with. Using the above equation, we get acceptable %RPDs at the following levels:

Determine Maximum Acceptable %RPD (based on sample concentration to DL ratio)

Sample* Conc./DL (x)	"Trendline" equation from Excel $Y = (0.9465x^{-0.344}) *100$	$y' = [(0.9465x^{-0.344}) *100] +5$ (add 5% to baseline eqn.)
1	94.65	99.65
2	74.57	79.57
5	54.41	59.41
10	42.87	47.87
50	24.64	29.64
100	20.41	24.41
200	15.30	20.30
1000	8.79	13.79

*Not the duplicate sample concentration. For sample results below the minimum detection limit (and the duplicate is above the MDL), use the MDL in the Duplicate Maximum %RPD calculations (otherwise there is insufficient latitude for variability at low concentrations).

This leaves us with a two-tiered system for duplicates. If our %RPD is below the values from our equation (i.e., below the curve), we accept both data points as valid. If the %RPD exceeds the %RPD from the equation, we don't know which value to believe is correct, the sample or the duplicate value, so we must reject ("R" qualify) both data points. At that point, particularly if multiple duplicate pairs have been rejected, the sampler(s) should look into possible causes for the disagreement and work to minimize those causes for future sampling.

Paired Parameters – There are some parameter pairings that DES evaluates (using %RPD) in tandem, since they are related. We can make use of these assessments too. Some parameters are fractions or subsets of others, such as nitrate being part of nitrate/nitrite, so that the one parameter should, in theory, never have a higher concentration than the other parameter. Examples of paired parameters are below:

TOC ≥ DOC
Nitrate/Nitrite ≥ Nitrate
Total P ≥ orthophosphate (or dissolved reactive phosphorus)
Total Cr ≥ Hexavalent Cr
TKN ≥ Ammonia
BOD ≥ Dissolved BOD (or other dissolved parameter pairings)

It's theoretically possible that the subset analyte could be 100% of the total (or larger) analyte, but any result where that compound exceeds the total (or larger compound) should be considered an estimated concentration (qualified with a "J"). Results that are quite close may be essentially the same number and valid for most data uses. Similar to

how we evaluated duplicate samples above, we will use the same equation to determine the acceptable %RPD for "Paired Parameters" analytical results within the same sample.

For "Paired Parameters" with a %RPD less than the equation amount (using an average Detection Limit this time, since they may be different), we will simply acknowledge the difference with a "J" qualifier, leaving both data points as useable for most applications. However, when the %RPD exceeds the amount from the equation, we will generally not use the two data points and reject (qualify with an "R") the results. In this situation we don't know which result to believe and they are too different for us to be comfortable with `the variability present. This all applies only when the subset parameter has a higher concentration than the expected larger/parent parameter. If the subset parameter has a lower concentration, then no evaluation/qualifiers are needed.

Example data for "Paired Parameters" assessed using the maximum %RPD equation:
$Y = [(0.9465x^{-0.344}) * 100] + 5$ (where x is the "parent" sample concentration/DL and Y is the max. %RPD).

Subset parameter – example concentration	Parent (larger) parameter –example concentrations	Subset DL (DES webpage*)	Parent DL (DES webpage*)	Average DL	%RPD (Parent and Subset)	Max. Allowed %RPD (from the eqn.)	Data Qualifier
Cr^{+6} – 3.6	Tot. Cr – 3.5	3.4 ug/L	0.28 ug/L	1.8 ug/L	2.82	75.87	"J"
Cr^{+6} – 7.5	Tot. Cr – 3.5	3.4 ug/L	0.28 ug/L	1.8 ug/L	72.73	75.87	"J"
Cr^{+6} – 7.8	Tot. Cr – 3.5	3.4 ug/L	0.28 ug/L	1.8 ug/L	76.11	75.87	"R"
Cr^{+6} – 24	Tot. Cr – 16	3.4 ug/L	0.28 ug/L	1.8 ug/L	40.0	44.98	"J"
Cr^{+6} – 26	Tot. Cr – 16	3.4 ug/L	0.28 ug/L	1.8 ug/L	47.62	44.98	"R"
Cr^{+6} – 16	Tot. Cr - 26	3.4 ug/L	0.28 ug/L	1.8 ug/L	47.62	38.06	None (par>sub)

** Detections limits may change – make sure that you are using the MDL associated with your data from that day's DES analysis. For results below the detection limit, the minimum detection limit in the Paired Parameter Maximum %RPD calculations.*

Sample Holding Time – This is an important QC item that is easily checked on any data set. Generally, DES will note any holding time discrepancy but it's still worth some discussion. With some parameters, like a total result for a metal, slightly exceeding the holding time may make little or no difference (and would likely result in only a "J" qualifier being added to the result in the reported concentration. But for other parameters missing the holding time would generally lead to complete rejection ("R") of that data.

The amount of the holding time exceedance can be evaluated relative to the total holding time, shorter times lead to lower tolerance of exceedances (as a result of less stable analytes). It can also be situation dependent – in some cases a one-day exceedance for a 28 day holding time may be acceptable and other times, not so. Alternately a one-day exceedance for a metals sample would likely make no difference (but we'd likely "J" qualify it as an acknowledgement of the exceedance – and for most situations we will use "J" qualified data anyway).

Subsection A2. Reserved for other Data Management Topics in the future.

APPENDIX IV –SECTION B. *RESERVED - EA3 STATION MODULE MANUAL*

Older version available upon request.

APPENDIX IV – SECTION C. *RESERVED - EA3 MANUAL*

Older version available upon request.

APPENDIX IV – SECTION D. *RESERVED - SAMPLE MASTER® INSTRUCTION MANUAL*

Older version available upon request.