PRINCIPLES AND RELEVANCE OF MEASUREMENT UNCERTAINTY

All types of measurement have some inaccuracy due to bias and imprecision and therefore measurement results can be only estimates of the values of the quantities being measured. To properly use such results environmental laboratories and their users need some knowledge of the accuracy of such estimates. Traditionally, this has been by using the concept of error, but the difficulty with this approach is that the term ‘error’ implies that the difference between the true value and a test result can be determined and the result corrected which is rarely the case. In contrast, the more recent concept of measurement uncertainty (MU) assumes that significant measurement bias is either eliminated, corrected or ignored, evaluates the random effects on a measurement result, and estimates an interval within which the value of the quantity being measured is believed to lie with a stated level of confidence.

Estimates of MU provide a quantitative indication of the level of confidence that a laboratory has in each measurement and are therefore a key element of an analytical quality system for environmental laboratories. The principles of measurement uncertainty contribute to ensuring test results are fit-for-purpose by:

- defining the quantity intended to be measured (measurand)
- indicating the level of confidence a laboratory has in a given measurement
- providing information essential for the meaningful interpretation of measurement results and their comparison over space and time
- identifying significant sources of MU and opportunities for their reduction

Reporting Measurement Uncertainty of Chemical Test Results

In metrology, measurement uncertainty is a non-negative parameter characterising the dispersion of the values attributed to a measured quantity. All measurements are subject to uncertainty and a measurement result is complete only when it is accompanied by a statement of the associated uncertainty. By international agreement, this uncertainty has a probabilistic basis and reflects incomplete knowledge of the quantity value. Measurement uncertainty has been calculated from the respective laboratory control samples (LCS) conducted in each batch of samples (one in every batch of 20 samples) using a minimum of 25 data points according to ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques. A coverage factor of 2 has been used.

Measurand	**Matrix**	
	Soil	**Aqueous**
Per- and Polyfluorinated Alkyl Substances (PFASs)		
Perfluorobutanoic acid (PFBA)	24%	29%
Perfluorobutanesulfonic acid (PFBS)	29%	18%
Perfluoro-n-pentanoic acid (PFPeA)	32%	22%
Perfluorohexanoic acid (PFHxA)	22%	22%
Perfluorohexanesulfonic acid (PFHxS)	30%	17%
Perfluoroheptanoic acid (PFHpA)	30%	19%
Perfluorooctanesulfonic acid (PFOS)	19%	10%
Perfluorooctanoic acid (PFOA)	14%	21%
Perfluorononanoic acid (PFNA)	32%	18%
Perfluorodecanoic acid (PFDA)	25%	22%
Perfluorodecanesulfonic acid (PFDS)	30%	38%
Perfluorododecanoic acid (PFDoA)	29%	31%
Perfluoroundecanoic acid (PFUnA)	31%	25%
Perfluorotridecanoic acid (PFTrDA)	36%	40%
Perfluorotetradecanoic acid (PFTeDA)	29%	40%
Perfluorooctanesulfonamide (PFOSA)	32%	26%
1H.1H.2H.2H-perfluorohexanesulfonic acid (4:2 FTS)	34%	31%
1H.1H.2H.2H-perfluorooctansulfonic acid (6:2 FTS)	22%	24%
1H.1H.2H.2H-perfluorodecanesulfonic acid (8:2 FTS)	31%	19%
N-ethyl-perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	32%	28%
N-methyl-perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	27%	27%
Polycyclic Aromatic Hydrocarbons		
Acenaphthene	25%	26%
Acenaphthylene	27%	32%
Anthracene	26%	27%
Benz(a)anthracene	29%	33%
Benzo(a)pyrene	30%	29%
Benzo(b&j)fluoranthene	29%	36%
Benzo(g.h.i)perylene	40%	32%
Benzo(k)fluoranthene	27%	29%
Chrysene	25%	24%
Dibenz(a.h)anthracene	31%	26%
Fluoranthene	31%	27%
Fluorene	24%	31%
Indeno(1.2.3-cd)pyrene	33%	29%

Measurand	Matrix	
	Soil	Aqueous
Naphthalene	25%	27%
Phenanthrene	26%	24%
Pyrene	28%	29%
Phenols (Halogenated)		
2.4.5-Trichlorophenol	29%	41%
2.4.6-Trichlorophenol	33%	41%
2.4-Dichlorophenol	29%	40%
2.6-Dichlorophenol	26%	39%
2-Chlorophenol	26%	40%
4-Chloro-3-methylphenol	30%	42%
Pentachlorophenol	39%	47%
Tetrachlorophenols - Total	33%	42%
Phenols (non-Halogenated)		
2.4-Dimethylphenol	26%	41%
2.4-Dinitrophenol	41%	56%
2-Cyclohexyl-4.6-dinitrophenol	44%	56%
2-Methyl-4.6-dinitrophenol	39%	49%
2-Methylphenol (o-Cresol)	25%	34%
2-Nitrophenol	32%	42%
4-Nitrophenol	42%	40%
Dinoseb	37%	54%
Phenol	27%	33%
Total Recoverable Hydrocarbons - 2013 NEPM Fractions		
TRH >C10-C16	20%	28%
TRH C6-C10	26%	23%
Polychlorinated Biphenyls		
Aroclor-1260	33%	34%
BTEX		
Benzene	26%	16%
Ethylbenzene	23%	20%
m & p-Xylenes	20%	23%
o-Xylene	19%	24%
Toluene	19%	19%

Measurand	Matrix	
	Soil	Aqueous
Naphthalene	31%	24%
Inorganics		
Biochemical Oxygen Demand (BOD-5 Day)	N/A	14%
Suspended Solids	N/A	5%
Total Dissolved Solids	N/A	9%
Total Kjeldahl Nitrogen (as N)	20%	21%
Heavy Metals		
Arsenic	20%	20%
Cadmium	15%	15%
Chromium	15%	15%
Cobalt	15%	15%
Copper	15%	15%
Lead	15%	15%
Manganese	20%	15%
Mercury	15%	20%
Nickel	15%	15%
Zinc	15%	15%
Alkali Metals		
Magnesium	17%	15%
Sodium	11%	15%
Potassium	15%	13%
Calcium	23%	15%
Chromium Suite		
Acid Neutralising Capacity - acidity (ANCbt)	7%	N/A
Acid trail - Titratable Actual Acidity	14%	N/A
Chromium Reducible Sulfur	11%	N/A
HCl Extractable Sulfur	24%	N/A
pH-KCL	2%	N/A
Sulfur - KCl Extractable	20%	N/A

Reporting Measurement Uncertainty of Microbiology Test Results

The American Association for Laboratory Accreditation provides a technical note G108 - Guidelines for Estimating Uncertainty for Microbiological Counting Methods that is used for the estimation of measurement uncertainty for methods that use counting for determining the number of colonies in a test sample. The data has been applied for all quantitative microbiological methods, including plate count and MPN. The data below are based on 20 data points each but larger datasets when available produce more reliable estimates and smaller data sets may be used with caution. The coverage factor used is obtained from the Student t-tables to estimate expanded uncertainty for smaller datasets.

Reproducibility Replicates for Laboratory Control Samples

This procedure illustrates the use of "reproducibility replicates" to estimate uncertainty for the same type of sample matrix analysed. This technique captures various sources of uncertainty that can affect routine samples by having "replicates" produced independently under as many different conditions as possible that are received routinely. This procedure presents the techniques recommended in ISO TS19036: *Microbiology of foods and animal feeding stuffs – Guidelines for the estimation of measurement uncertainty for quantitative determinations.* The results are from control samples which have been analysed through all of the steps of the test method and were set up on different days, in duplicate, by different analysts, using different equipment (e.g. balances, pipettors) and also using different batches of media/reagents.

Measurand	**Water Matrix**	
	Low range	**Upper range**
Microbiology		
Legionella by AS3896: 2008	-33%	+50%
Total Coliforms by filtration (MF)	-22%	+28%
Thermotolerant Coliforms by filtration	-22%	+28%
E.coli by filtration (MF)	-17%	+21%
Enterococci by filtration (MF)	-18%	+22%
Pseudomonas aeruginosa by MF	-30%	+42%
Clostridium perfringens by MF	-14%	+16%
E.coli by Defined Substrate Technology	-20%	+25%
Total Coliforms by Defined Substrate#	-22%	+29%
Enterococci by Defined Substrate	-14%	+16%
Standard Plate Count (TPC-2)	-20%	+25%
Cooling Towers Plate Count (TPC-4)	-27%	+36%
Somatic Coliphages (100mL)	-13%	+15%
Male-specific or fRNA Coliphages*	-27%	+36%

- Defined Substrate Technologies (DST) include enzyme detection methods such as Colilert™, Enterolert™, Colitag™