

STORMWATER MONITORING COALITION
LABORATORY GUIDANCE DOCUMENT
Third Edition

*Richard Gossett
and
Kenneth Schiff*



Southern California Coastal Water Research Project

Technical Report 615 - April 2010

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(Third Edition)

Richard Gossett

California State University Long Beach
Institute for Integrated Research on Materials, Environment and
Society

and

Kenneth Schiff

Southern California Coastal Water Research Project

www.sccwrp.org

April 2010

Technical Report 615

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1 INTRODUCTION

Municipal stormwater monitoring programs in southern California are different than most other monitoring programs around the United States. The southern California monitoring programs differ because stormwater managers have invested in the Stormwater Monitoring Coalition (SMC), a consortium of all the primary regulated and regulatory stormwater agencies overseeing more than 5,000 stream miles (Table 1). Although the consortium consists of at least seven distinct local monitoring programs, the SMC has established a continuing goal to compile local monitoring data to make region-wide assessments.

In order to compile local monitoring programs into regional assessments, the SMC has expended considerable effort to design monitoring programs with similar goals and objectives, integrated sampling efforts, establish standardized data protocols, and focused training opportunities (Bernstein and Schiff 2003, Cooper et al. 2004). However, none of the SMC agencies have their own chemistry laboratories, and a review of regional contract laboratories indicated differences in laboratory methods, reporting levels (detection limits), and levels of quality control including internal requirements for accuracy and precision. Therefore, the SMC has established periodic laboratory intercalibration studies to ensure comparability in chemistry measurements.

In 2003, the SMC launched their first laboratory intercalibration study to help ensure comparability for chemistry measurements (Gossett et al. 2003). The 2003 intercalibration study established common reporting levels and target analytes, and utilized iterative round robin exercises to minimize interlaboratory variation. The success of the 2003 exercise was primarily due to three factors: 1) communication and commitment among laboratory personnel; 2) setting performance-based criteria for establishing standards of success; and 3) using locally derived reference materials including using a stormwater matrix. The outcome was a performance-based chemistry guidance manual to be used for SMC monitoring programs. The SMC's second laboratory intercalibration in 2006 focused on the same constituents (total suspended solids, nutrients, total trace metals) and included more laboratories (Gossett and Schiff 2007). The success of the 2006 intercalibration rivaled the 2003 intercalibration, which indicated some residual memory in the system. This is especially good news because system memory would result in consistently high quality data during the intervening years.

This document is the third edition of the SMC's Laboratory Guidance Document. Not long after the completion of the first study, the SMC recognized that periodic intercalibrations are a necessity to ensure ongoing performance. This edition builds on the previous editions by adding more laboratories, more constituents, and varying the types of reference materials. Eighteen laboratories participated in the current 2009 study (Table 2), more laboratories than ever before. While the same constituents used in previous intercalibrations were once again evaluated, this edition marks the addition of several new inorganic constituents (chloride, silica, ortho-phosphate, and total nitrogen), dissolved as well as total trace metals, and three classes of organic constituents (chlorinated pesticides, pyrethroid pesticides, and polychlorinated biphenyls).

1.1 Objectives and Goals of this Document

The objective of this guidance manual is to update and present the performance-based guidelines established during the SMC interlaboratory studies of 2003 and 2007. This document sets the minimum standards of sensitivity, precision, and accuracy across laboratories so that individual data sets can be combined with estimated levels of confidence for making regional assessments of stormwater quality. The philosophy of performance-based guidelines is key to achieving this comparability. Although nearly every laboratory involved in the stormwater intercalibration study was certified by the State of California Environmental Laboratory Accreditation Program (ELAP), inventories of existing methods demonstrated that most analytes are not analyzed in exactly the same manner. This will continue as new laboratories, or new equipment at existing laboratories continues to proliferate. Rather than mandate specific methods that are inflexible and discourage existing laboratories from achieving faster, more sensitive, and more cost-effective methods, this document merely sets minimum levels of comparability so that data sets can be combined regardless of current technology.

This guidance manual is a living document. It should be revisited each time an intercalibration exercise is conducted and can be expanded to include additional constituents, additional laboratories, or to refine the recommended performance-based sensitivity, accuracy, and precision requirements as new information becomes available.

This document and laboratory intercalibration study is not a certification program. The guidelines set by this document merely express the desired needs of stormwater agencies throughout the southern California region. Therefore, these stormwater agencies can use these guidelines in establishing specifications for work assignments or requesting proposals to conduct stormwater analyses. Alternatively, or in combination, stormwater regulatory agencies may use these specifications in the development of regulatory expectations for laboratory performance by monitoring agencies.

Table 1. Members of the Southern California Stormwater Monitoring Coalition.

| Agency |
|---|
| Los Angeles County Flood Control District |
| County of Orange, OC Public Works |
| County of San Diego, Department of Public Works |
| Riverside County Flood Control and Water Conservation District |
| San Bernardino County Flood Control District |
| Ventura County Watershed Protection District |
| City of Long Beach Public Works Department |
| City of Los Angeles, Department of Public Works |
| California Regional Water Quality Control Board, Santa Ana Region |
| California Regional Water Quality Control Board, Los Angeles Region |
| California Regional Water Quality Control Board, San Diego Region |
| State Water Resources Control Board |
| California Department of Transportation |
| Southern California Coastal Water Research Project |

Table 2. Participating Laboratories in the 2009 SMC Intercalibration.

| Laboratory Name | Contact |
|--|--------------------|
| Advanced Technology Laboratories | Bing Roura |
| Associated Laboratories | Jim McCall |
| California Department of Fish and Game | Dave Crane |
| California State University Long Beach | Rich Gossett |
| CalScience Environmental Laboratories | Larry Lem |
| City of Los Angeles- EMD | Mahesh Pujari |
| CRG Marine Laboratories | Michele Chamberlin |
| Enviromatrix Analytical Laboratories | Dan Verdon |
| E.S. Babcock & Sons | Cyndi Moore |
| FGL Environmental | David Terz |
| Los Angeles County- ACWM | Wai Leung |
| MWH Laboratories | Andrew Eaton |
| Soil Control Laboratories | Mike Galloway |
| Southern California Coastal Water Research | Keith Maruya |
| TestAmerica, Irvine | David Dawes |
| Truesdail Laboratories | Norm Hester |
| UC Santa Barbara MSI | George Paradis |
| Weck Laboratories | Alan Ching |

2 GUIDANCE INFORMATION

This document consists of four elements. First is a list of target analytes and minimum levels of sensitivity (reporting levels). Second are minimum levels of accuracy and precision. Third are recommended protocols for method specific comparability. Fourth are participation requirements for intercalibration studies and the laboratory evaluation criteria and results.

2.1 Analytes and Reporting Levels

2.1.1 Target Analytes

More than 100 analytes were targeted for intercalibration (Table 3). This list includes total suspended solids (TSS), total organic carbon (TOC), nutrients, total and dissolved trace metals, chlorinated pesticides, pyrethroid pesticides, and polychlorinated biphenyls (PCBs). Approximately 80% of the target analytes are new to the SMC intercalibration (Table 3). The list of target analytes is not meant to be an exhaustive list of all constituents that could or should be measured in individual programs. For example, there are no organophosphorus pesticides, herbicides, or polynuclear aromatic hydrocarbons on the list of target analytes. Any or all of these target analytes may be the focus of individual monitoring programs. At this point in time, however, there has not been an intercalibration study conducted for these constituents to make performance-based recommendations for stormwater laboratories.

2.1.2 Reporting Levels

Targeted reporting levels (RLs) are provided in Table 3. The targeted reporting levels were lower for this intercalibration relative to previous intercalibrations. The rationale for lowering targeted RLs was to achieve target RLs listed in most SMC member agency NPDES permits and align more closely with the State Water Resources Control Board (SWRCB) Surface Water Ambient Monitoring Program (SWAMP). All of these target RLs are below water quality thresholds of concern established in the California Toxics Rule (CTR). For a participating laboratory to achieve these reporting levels, it should include a calibration standard at or below this level (the RL is a quantitation level and not the minimum detection limit or MDL).

Table 3. Target analytes and Reporting Levels (RL) for the Stormwater Monitoring Coalition Monitoring Program.

| TARGET GROUP | TARGET ANALYTE | UNITS | RL |
|----------------------------------|-----------------------------|---------------------------|------|
| Conventional | TSS | mg/L | 5 |
| | Hardness* | mg/L as CaCO ₃ | 5 |
| Major Ions | Chloride* | mg/L | 1 |
| | Sulfate* | mg/L | 1 |
| | Silica* | mg/L | 1 |
| Nutrients | Nitrate+nitrite | mg/L as N | 0.1 |
| | ammonia | mg/L as N | 0.1 |
| | total N* | mg/L | 0.2 |
| | total P | mg/L | 0.05 |
| | ortho P* | mg/L as P | 0.05 |
| Metals (Dissolved* and Total) | Arsenic | ug/L | 1 |
| | Cadmium | ug/L | 0.2 |
| | Chromium | ug/L | 0.5 |
| | Copper | ug/L | 0.5 |
| | Lead | ug/L | 0.5 |
| | Nickel | ug/L | 1 |
| | Selenium | ug/L | 1 |
| | Zinc | ug/L | 1 |
| Chlorinated Hydrocarbons | PCB Congeners ^{1*} | ug/L | 0.10 |
| | DDT ^{2*} | ug/L | 0.05 |
| | alpha-Chlordane* | ug/L | 0.01 |
| | gamma-Chlordane* | ug/L | 0.01 |
| Pyrethroid Pesticides | Bifenthrin* | ug/L | 0.01 |
| | Cyfluthrin* | ug/L | 0.01 |
| | Cyhalothrin-lambda* | ug/L | 0.01 |
| | Cypermethrin* | ug/L | 0.01 |
| | Deltamethrin* | ug/L | 0.01 |
| | Esfenvalerate* | ug/L | 0.01 |
| | Fenvalerate* | ug/L | 0.01 |
| | Permethrin* | ug/L | 0.01 |

* Indicates new target analyte for the SMC intercalibration

¹ PCB Congeners: 8, 18, 27, 28, 29, 31, 33, 37, 44, 49, 52, 56, 60, 61, 64, 66, 70, 74, 77, 81, 87, 95, 128, 138, 141, 146, 149, 151, 153, 156, 157, 158, 167, 168, 169, 170, 174, 177, 180, 183, 187, 189, 194, 198/199, 200, 201, 203, 206, 209

² DDTs: 2,4'-DDD, 4,4'-DDD, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT,

2.2 Accuracy and Precision

Analysis of spiked samples or reference materials provides a mechanism for assessing within laboratory accuracy. Reproducibility among replicate sample analyses provides a determination of within laboratory precision. General guidance provided by ELAP and the United States Environmental Protection Agency (USEPA; 40 CFR Part 136) is recommended for assessing within-laboratory accuracy and precision by analyzing two replicate sample matrix spikes per batch of 20 or less samples. Matrix spike concentrations of approximately 10 times the laboratory RLs are recommended for most meaningful spike recovery measurements. As general guidance, matrix spike concentrations should be in the same general range as relevant regulatory limits to truly represent accuracy and precision at these concentrations. It is also recommended that a set of laboratory replicate samples be analyzed with each batch of samples to indicate precision using actual sample matrices, which are typically larger than MSD due to natural variation of sample homogeneity. The relative percent difference (RPD) between replicate spikes for the general, nutrient, and trace metal parameters listed in Table 3 should be less than 20%. The RPD between replicate spikes for the chlorinated hydrocarbons and pyrethroid pesticides should be less than 40%. Accuracy limits for matrix spiked (MS) and matrix spiked double (MSD) are provided in Table 4. These SMC recommended accuracy limits mimic ELAP and USEPA guidelines. Accuracy limits for Certified Reference Materials (CRM) are provided by the supplier.

Additional quality assurance/quality control (QA/QC) requirements in the methods referenced by each laboratory should conform to the requirements listed within that method by Standard Methods or the US EPA (i.e. Blank Spikes). Project specific QA/QC requirements may also be listed in the Quality Assurance Project Plan (QAPP). Because spiked samples can be complicated by matrix interferences, this can confound assessments of accuracy. Therefore, the analysis of Certified Materials, when available, is also a recommended (but not required) option for the monitoring agency.

Intercalibration studies evaluate the accuracy and precision of analysis among laboratories. For this document, interlaboratory precision guidelines were developed by analyzing two reference materials and two runoff samples using 18 different laboratories (Table 1). The reference materials included a commercially available performance evaluation (PE) sample or a calibration standard. The runoff samples included one dry-weather and one wet-weather matrix. All samples were delivered “blind”, so the identity of each sample was unknown to all of the laboratories.

For each of the matrices, the grand mean and standard deviation were calculated using the pooled results from all 18 laboratories (Table 5). A Grubb’s test was used to identify outliers that were removed along with the “not detected” values from the data set prior to calculating the grand means and standard deviations. It should be noted that not all laboratories analyzed every target analyte; consequently, the number of results varied by parameter. Upper and lower “Warning” limits were based on two standard deviations within the grand mean, and upper and lower “Control” limits were based on three standard deviations within the grand mean.

Using the same data set as the grand means and standard deviations, the overall relative standard deviation (RSD) for each matrix was calculated; RSDs are presented in Table 6. Precision within a laboratory is expected to be less than 20% for those analytes that are present at concentrations at least 10 times the MDL. In this intercalibration exercise, the RSD for 39 of 48 analyte-sample combinations were all less than requisite 20% indicating that the between laboratory precision was at least as good as within laboratory precision. The remaining nine analyte-sample combinations were less than 10 times the MDL.

The accuracy and precision of organic analytes by SMC laboratories were evaluated for the first time during this intercalibration exercise. As a first step towards comparability evaluation, laboratories analyzed a calibration standard with the project analytes for organochlorine pesticides, PCBs, and pyrethroid pesticides. The quantity of each analyte in the calibration standard was unknown to each laboratory. The recovery of each group of analytes is given in Figures 1 through 3.

Table 4. Laboratory accuracy and precision guidelines for concentrations greater than 10 times the reporting limits for ongoing analysis of stormwater samples.

| Target Analyte | Precision (RPD of Duplicate Samples) | Accuracy (Percent Recovery of MS or MSD ^a) |
|-----------------------------|--|--|
| General Constituents | | |
| Hardness | 0 – 20 | 80 - 120 |
| TSS | 0 – 20 | _ ^b |
| Chloride | 0 – 20 | 80 - 120 |
| Sulfate | 0 – 20 | 80 - 120 |
| Silica | 0 – 20 | 80 - 120 |
| Ammonia | 0 – 20 | 80 - 120 |
| Nitrate+Nitrite | 0 – 20 | 80 - 120 |
| Total N | 0 – 20 | 80 - 120 |
| Total P | 0 – 20 | 80 – 120 |
| Ortho-Phosphate | 0 – 20 | 80 – 120 |
| Trace Metals | | |
| Arsenic | 0 – 20 | 80 – 120 |
| Cadmium | 0 – 20 | 80 – 120 |
| Chromium | 0 – 20 | 80 – 120 |
| Copper | 0 – 20 | 80 – 120 |
| Lead | 0 – 20 | 80 – 120 |
| Nickel | 0 – 20 | 80 – 120 |
| Selenium | 0 – 20 | 80 – 120 |
| Silver | 0 – 20 | 80 – 120 |
| Zinc | 0 – 20 | 80 – 120 |
| Organics | | |
| PCBs | 0 – 40 | 60 – 140 |
| DDTs | 0 – 40 | 60 – 140 |
| Chlordanes | 0 – 40 | 60 – 140 |
| Pyrethroids | 0 – 40 | 60 – 140 |

^{a-} For certified reference materials, use supplier recommendations

^{b-} Defined by supplier

Table 5. Grand mean, warning limits, and control limits of each matrix from the combined results of all laboratories participating in the intercalibration. Warning limits and control limits are indicated as difference from the mean (e.g. TSS for Dry Weather control limits are 43 to 63 mg/L).

| Target Analyte | Units | Dry Weather Runoff | | | Wet Weather Runoff | | | CRM | | |
|-----------------------------|---------------------------|--------------------|--------------------------|--------------------------|--------------------|--------------------------|--------------------------|-------|--------------------------|--------------------------|
| | | Mean | Warning Limit (+2 SD) | Control Limit (+3 SD) | Mean | Warning Limit (+2 SD) | Control Limit (+3 SD) | Mean | Warning Limit (+2 SD) | Control Limit (+3 SD) |
| General Constituents | | | | | | | | | | |
| Hardness | mg/L as CaCO ₃ | 441 | 130 | 195 | 246 | 84 | 126 | 142 | 31 | 47 |
| TSS | mg/L | 53 | 7 | 10 | 221 | 36 | 55 | 2163* | 1329 | 1994 |
| Chloride | mg/L | 149 | 8.7 | 13.1 | 90.7 | 8.7 | 13.1 | 12.5 | 1.5 | 2.3 |
| Sulfate | mg/L | 297 | 27 | 40 | 121 | 16 | 25 | 36 | 3 | 5 |
| Silica | mg/L | 29 | 8 | 12 | 24 | 8 | 12 | 2.6 | 0.5 | 0.7 |
| Ammonia | mg/L as N | 1.27 | 0.32 | 0.49 | 3.29 | 1.35 | 2.02 | 0.40 | 0.09 | 0.14 |
| Nitrate+Nitrite | mg/L as N | 3.22 | 0.48 | 0.72 | 3.76 | 0.37 | 0.55 | 0.22 | 0.22 | 0.33 |
| Total N | mg/L | 6.1 | 1.5 | 2.3 | 11.0 | 3.4 | 5.1 | 0.7 | 1.0 | 1.5 |
| Total P | mg/L | 0.97 | 0.33 | 0.50 | 0.64 | 0.43 | 0.65 | 0.14 | 0.51 | 0.76 |
| Ortho-Phosphate | mg/L as P | 0.80 | 0.12 | 0.18 | 0.37 | 0.44 | 0.66 | 0.01 | - | - |
| Trace Metals | | | | | | | | | | |
| Arsenic | µg/L | 4.5 | 1.4 | 2.1 | 3.2 | 1.3 | 1.9 | 6.2 | 1.5 | 2.3 |
| Cadmium | µg/L | 0.29 | 0.25 | 0.38 | 0.77 | 0.45 | 0.68 | 1.95 | 0.91 | 1.37 |
| Chromium | µg/L | 2.0 | 1.6 | 2.4 | 5.8 | 2.6 | 3.9 | 5.0 | 1.5 | 2.2 |
| Copper | µg/L | 14.2 | 5.6 | 8.4 | 209.7 | 31.2 | 46.8 | 8.0 | 2.2 | 3.3 |
| Lead | µg/L | 1.01 | 0.40 | 0.60 | 6.76 | 1.14 | 1.72 | 3.84 | 1.13 | 1.69 |
| Nickel | µg/L | 5.2 | 3.6 | 5.4 | 35.3 | 4.7 | 7.1 | 9.7 | 2.1 | 3.2 |
| Selenium | µg/L | 3.6 | 1.5 | 2.3 | 2.3 | 0.8 | 1.3 | 4.4 | 1.5 | 2.2 |
| Zinc | µg/L | 40 | 13 | 19 | 634 | 135 | 203 | 35 | 9 | 13 |

- Limit not quantified

* Spiked sediment sample in dry-weather runoff

Table 6. Relative standard deviation results for each matrix for the combined results from all laboratories.

| Target Analyte | Relative Standard Deviation (%) | | |
|-----------------------------|---------------------------------|-----------------------|-----------------|
| | Dry Weather Runoff | Wet Weather Runoff | CRM |
| General Constituents | | | |
| Hardness | 15 | 17 | 11 |
| TSS | 6 | 8 | 31 |
| Chloride | 3 | 5 | 6 |
| Sulfate | 5 | 7 | 4 |
| Silica | 14 | 17 | 9 |
| Ammonia | 13 | 20 | 11 |
| Nitrate+Nitrite | 7 | 5 | 33 ^a |
| Total N | 12 | 16 | 72 ^a |
| Total P | 17 | 34 | - |
| Ortho-Phosphate | 8 | 60 ^a | - |
| Trace Metals | | | |
| Arsenic | 15 | 20 | 12 |
| Cadmium | 44 ^a | 29 ^a | 23 ^a |
| Chromium | 40 ^a | 22 | 15 |
| Copper | 20 | 7 | 14 |
| Lead | 20 | 8 | 15 |
| Nickel | 34 | 7 | 11 |
| Selenium | 21 | 19 | 17 |
| Zinc | 16 | 11 | 13 |

^a grand mean less than 10x the detection limit

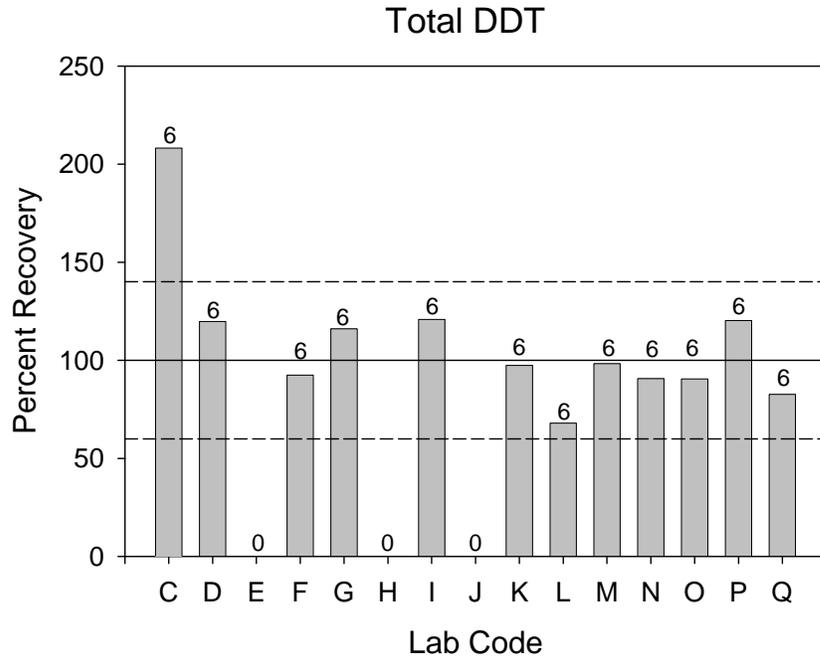


Figure 1. Percent recovery of a calibration standard fortified with six isomers and metabolites of DDT. Number of above bar represents number of target analytes quantified by each lab.

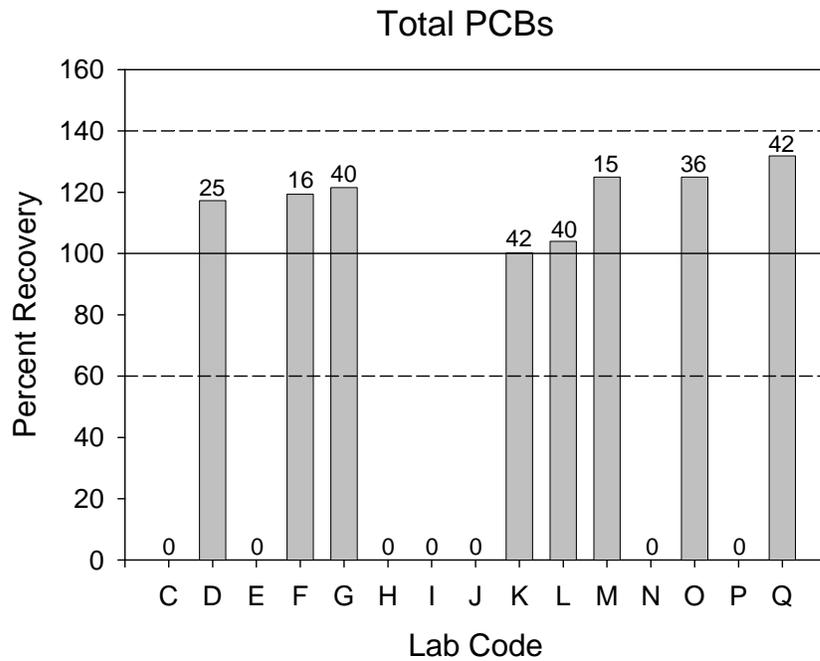


Figure 2. Percent recovery of a calibration standard fortified with 42 PCB congeners. Number of above bar represents number of target analytes quantified by each lab.

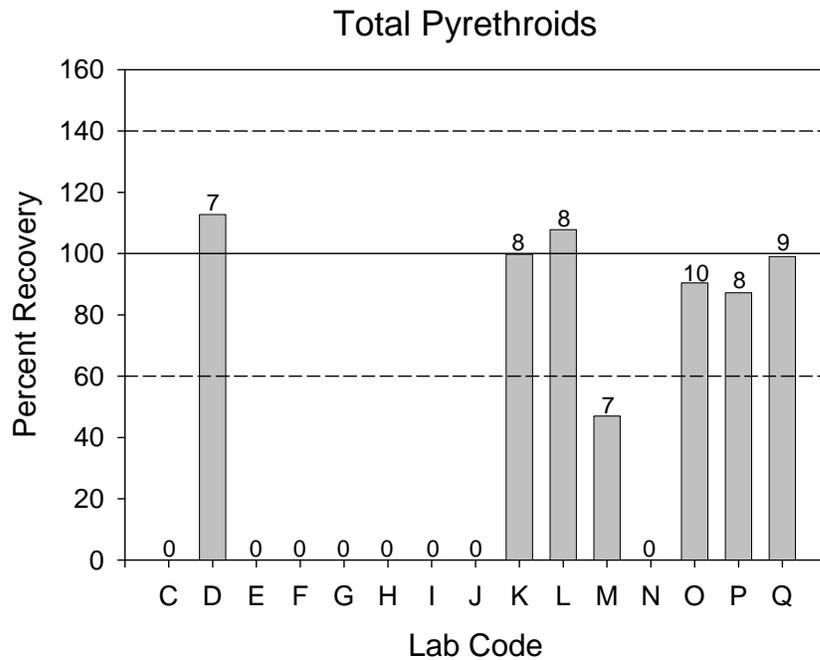


Figure 3. Percent recovery of a calibration standard fortified with eight pyrethroid pesticides. Number of above bar represents number of target analytes quantified by each lab.

2.3 Standardization

Although this document is founded on performance-based guidelines enabling flexibility within each laboratory to achieve consistency, the laboratory intercalibration studies have identified four protocols whereby recommended standardization can dramatically increase comparability. This standardization includes sub-sampling, Total Phosphorus digestion, TKN digestion, and trace metal digestion techniques.

2.3.1 Sub-Sampling Techniques

Sub-sampling techniques are an important component of both within and among laboratory variability. This was especially true for particle-laden samples, such as those from more rural catchments with unlined channels. Particle-bound constituents have the potential to be dramatically biased if sub-sampling techniques selectively target or avoid particles within samples. To this end, standardized laboratory techniques for sub-sampling were developed for splitting large volume stormwater samples collected in the field into smaller bottles for distribution to the laboratory and for subsequent sampling of smaller aliquots in the laboratory at the time of analysis.

2.3.1.1 Sub-sampling of large-volume composite containers

In order to ensure that sample containers destined for an analytical laboratory all contain water that is similar and representative of the original composite sample, it is important to maintain a well-mixed composite sample during sub-sampling and to prevent stratification and the settling out of heavier particles. This is accomplished by the use of a large-capacity stirrer and a 2- to 3-inch, pre-cleaned, Teflon-coated stir bar; larger stir bars can be used for larger volume containers. Adjustment of stirring speed is important. Speeds that are too fast will create a large vortex within the composite bottle that can actually concentrate heavier particles and should be avoided. Speed should be based on a visual assessment of the most even mixing throughout the composite bottle.

Sub-sampling from the homogenized composite bottle is accomplished using a peristaltic pump and pre-cleaned (inside and outside) sub-sampling hose. Filling sample containers by pumping from the composite bottle is best performed by two people. One person is responsible for filling individual sample containers, and one person is responsible for constantly moving the intake tubing up and down in the water column of the composite sample. Based on experimental evidence, this up and down movement of the intake is a procedure that helps obtain a more representative sub-sample. This is because there can still be some stratification of heavier particles in the composite sample despite the mixing created by the stirrer. The up and down movement of the intake tubing should be limited to approximately 80 to 90% of the depth of the water column and should never touch the bottom of the composite bottle.

2.3.1.2 Sub-sampling of sample containers for analysis

The goal of sub-sampling bottles in the laboratory for analysis is similar to field sampling techniques: to maintain homogeneous particle distribution. Analysis of particle-associated constituents will be biased if non-representative particle suspensions are used for analysis. In order to maintain homogeneous particle distributions, we recommend the use of sub-sampling techniques described by the US Geological Survey (Charles J. Patton, USGS National Water Quality Laboratory, Denver, CO). Appropriately, a similar technique for large-composite container sub-sampling is used. Briefly, a “+” shaped magnetic stirring bar is placed into the sample container, and the sample is stirred while a sub-sample is aspirated and dispensed into the processing container.

2.3.2 Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen analysis was affected by the digestion technique during the current laboratory intercalibration exercise. This was due to the influence caused by particle content and size distribution. Therefore, minimum standardization of the digestion procedure for stormwater samples is recommended. Either micro- or macro-TKN digestions are acceptable. However, the length of time of digestion should be set at a minimum of 1 hour at 380°C, until copious fumes are generated and the digestion solution turns yellow, and then for an additional 30 minutes (to ensure adequate recovery) prior to analysis.

2.3.3 Total Phosphorus

Total Phosphorus analysis was also affected by the digestion technique during the laboratory intercalibration exercise. Therefore, we recommend that the standardization of the digestion procedure include the use of an acid persulfate digestion.

2.3.4 Trace Metals

Trace metal analysis was also affected by the digestion technique during the current laboratory intercalibration exercise. This is because trace metal concentration may be influenced by particle content and size distribution. Therefore, minimum standardization of trace metal digestion is recommended for stormwater samples. Trace metals should be digested using a nitric/hydrochloric acid digestion at 95°C for 2 to 4 hours until the sample has evaporated from 50 mL down to 10 mL.

Dissolved metals analysis should be performed on filtered samples and does not require digestion if the turbidity is <1. Sample spiking for the Matrix Spike should be done prior to filtering. Filtration is a common source of contamination, when measuring dissolved metals. All other criteria for trace metals in this guidance document are applicable to both total and dissolved metals.

2.4 Participation Requirements

2.4.1 Proficiency Testing

Laboratories performing analyses for SMC Stormwater Monitoring Programs should pass a SMC performance evaluation (PE) sample and participate successfully in SMC intercalibration exercises. The PE and intercalibration exercises are strongly recommended to be performed on a bi-annual basis. This frequency is recommended because: 1) new laboratories may wish to participate; 2) existing laboratories need to evaluate new personnel; and 3) new and existing laboratories with new equipment or altered laboratory techniques need to be evaluated. Intercalibrations should occur within the first six months of the calendar year to ensure evaluations prior to the following wet season that typically begins on October 15th.

For minimum proficiency, SMC PE samples should be spiked between 1 and 10 times established RLs (Table 2) for analytes of concern. To evaluate accuracy, all sample results should meet the criteria provided by the commercial supplier of the sample. The PE samples are to be coordinated through the SMC, or their representatives on a Chemistry subcommittee, and can be purchased from private companies such as Environmental Resource Associates, Inc. (ERA), Wibby Environmental, APG, or other NELAC approved proficiency testing sample providers.

Intercalibration studies require laboratories to analyze one PE sample and three replicates of two runoff samples (from different locations). Additional sample types could include

blanks, spiked runoff samples, or laboratory control samples. Each intercalibration study should be performed with one or more iterations to evaluate consistency and allow for laboratory corrective actions if deficient analysis resulted from the first iteration.

2.4.2 *New Laboratories*

New laboratories that have not participated in previous intercalibration exercises may still be able to analyze stormwater samples during the present wet season. These labs, however, will need to provide resources to purchase a PE sample with the same requirements described in Section 3.1 (i.e., samples will be spiked at 1 to 10 times the established reporting limits in Table 2). These samples should be delivered to the new laboratory blind and as whole volume samples. All new laboratories are required to participate in the next intercalibration exercise to remain qualified for the SMC program.

2.4.3 *Laboratory Intercalibration Exercise Evaluation Criteria*

Laboratories participating in the intercalibration exercise will be evaluated to determine if their results are within acceptable accuracy and precision, thereby insuring comparability of data between the different SMC stormwater monitoring programs. For the current study, a scoring system was used to assign a numeric value and letter grade to each laboratory indicating the quality of their performance in the exercise. A grade of “C” or better is recommended for a laboratory to be eligible to perform analyses for SMC programs.

2.4.3.1 *Scoring system and results*

Based on the combined results from all fourteen laboratories participating in the exercise, a Grubb’s test was performed to identify outlier data points. After removal of the outlier data, the “not detected” results were removed and the grand mean and standard deviation were calculated for each analyte. Upper and lower warning and control limits were based on 2 and 3 times the standard deviation, respectively (see table 4).

A scoring system was established to rate each laboratory’s performance. Each replicate analysis by a laboratory was given three points if the result for that sample-analyte combination was within the warning limit and two points if the result was within the control limit (Figure 4). Zero points were given if the result was outside the control limit. For example, if a laboratory got all three replicate results within 2 SD, it received nine points for that analyte. If two results were within 2 SD and one was within 3 SD, then the laboratory was given eight out of nine points. The Relative Standard Deviation (RSD) was also calculated for each parameter, and one point was given for each analyte/matrix with an RSD of < 20%. The total points awarded to each laboratory were combined for the General Constituents (TSS, Ammonia-N, Nitrate-N + Nitrite-N, TKN, TOC, Total P, hardness, chloride, sulfate, and ortho-phosphate), and then divided by the total possible points, then multiplied by 100 for the final score. Trace metals were all combined as a separate score using the same criteria.

Laboratories that did not analyze a particular analyte were not given a score for that parameter so that they were not penalized. The omitted analyte was listed in the scoring results summary so that SMC programs managers have the option of using another laboratory for that specific analysis. A letter grade was assigned based on 90-100% being an "A", 80-89% being a "B", 70-79% being a "C", and below 70% being an "F".

The results from the 2009 laboratory intercalibration exercise are presented in Tables 7a and 7b. Because this is a public document and participation in this exercise is intended to be kept anonymous, the laboratories are listed by randomly assigned numbers. The SMC member agencies will be given the key to the laboratory names upon request.

All but one of the laboratories scored an "A" on analysis of general constituents including TSS, nutrients, and several major ions. The only non-"A" scored a "B". A similar pattern was observed for analysis of trace metals with all "A" grades, except for one "B". This high level of quality and comparability indicates that SMC member agencies can have confidence in several laboratories for analysis of their wet- and dry-weather samples. The SMC member agencies can also feel comfortable combining data sets from each of these participating laboratories.

There was no grading system used for organic analytes. Grades were not issued because the intercalibration for organic constituents was not yet complete. A calibration standard was used for preliminary evaluation in the current study (Figures 1-3). Most laboratories were able to achieve recoveries within 40% of the true value, and the majority of these laboratories were within 20%. However, a calibration standard was the easiest of matrices; no sample extraction was required. Moreover, additional work is still required to standardize the list of target analytes for organic parameters. Virtually none of the laboratories measured the exact same list of PCB congeners or pyrethroid pesticides. To quantify both within and among-laboratory variability, a more thorough intercalibration for quality and comparability must utilize multiple samples with replication. Preferably, some of the samples used for additional intercalibration will include a runoff matrix.

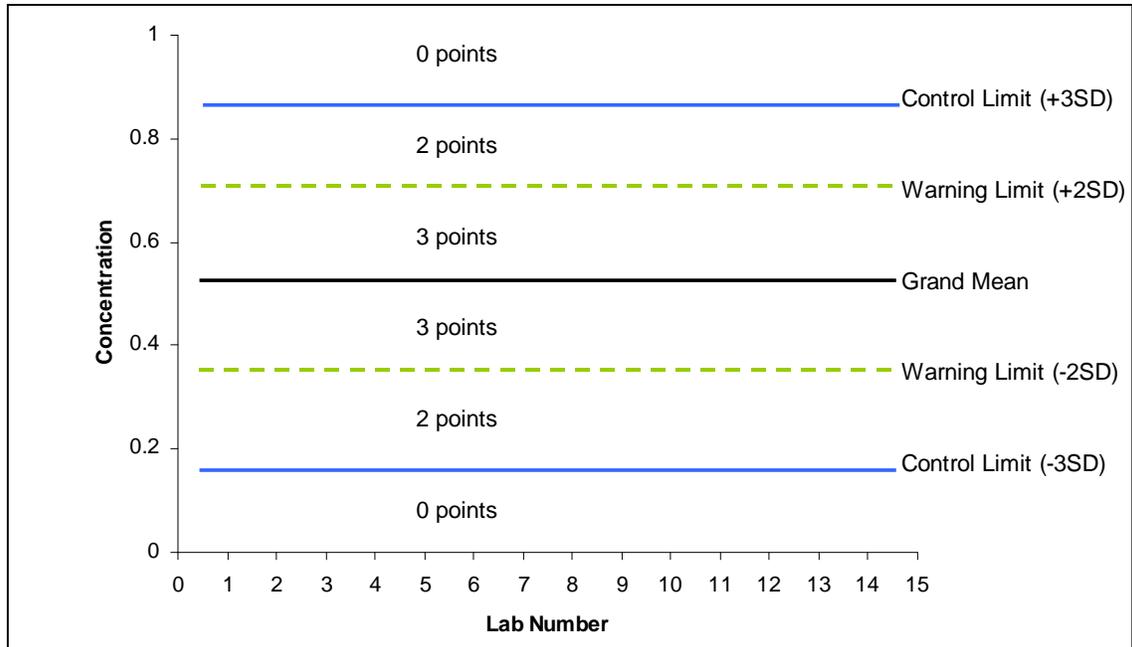


Figure 4. Example of scoring system for SMC intercalibration studies without any specific data shown.

Table 7a. Scoring results for General Constituents in the 2009 Laboratory Intercalibration Exercise.

| Laboratory Code | Analytical Result Score | RSD Score | Percent Success | Letter Grade |
|------------------------------------|-------------------------|--------------|-----------------|--------------|
| A | 216 out of 216 | 21 out of 21 | 100% | A |
| C (did not analyze Si) | 202 out of 209 | 20 out of 21 | 97% | A |
| D | 210 out of 216 | 21 out of 21 | 97% | A |
| E | 204 out of 216 | 21 out of 21 | 95% | A |
| F | 202 out of 216 | 20 out of 21 | 94% | A |
| G | 216 out of 216 | 21 out of 21 | 100% | A+ |
| H | 213 out of 216 | 21 out of 21 | 99% | A |
| I | 206 out of 216 | 21 out of 21 | 96% | A |
| J | 212 out of 216 | 21 out of 21 | 98% | A |
| L | 206 out of 216 | 21 out of 21 | 96% | A |
| M | 212 out of 216 | 21 out of 21 | 98% | A |
| N | 216 out of 216 | 21 out of 21 | 100% | A+ |
| P (did not analyze Si) | 187 out of 209 | 19 out of 21 | 90% | A |
| Q (only analyzed TSS, hardness) | 47 out of 48 | 7 out of 7 | 98% | A |
| R (did not analyze Si) | 180 out of 209 | 17 out of 21 | 86% | B |

Table 7b. Scoring results for Trace Metals in the 2009 Laboratory Intercalibration Exercise.

| Laboratory Code | Analytical Result Score | RSD Score | Percent Success | Letter Grade |
|-----------------|-------------------------|--------------|-----------------|--------------|
| A | 167 out of 168 | 16 out of 16 | 99% | A |
| C | 168 out of 168 | 16 out of 16 | 100% | A+ |
| D | 168 out of 168 | 15 out of 16 | 99% | A |
| E | 163 out of 168 | 16 out of 16 | 97% | A |
| F | 168 out of 168 | 16 out of 16 | 100% | A+ |
| G | 166 out of 168 | 16 out of 16 | 99% | A |
| H | 166 out of 168 | 16 out of 16 | 99% | A |
| I | 167 out of 168 | 16 out of 16 | 99% | A |
| J | 161 out of 168 | 15 out of 16 | 96% | A |
| L | 167 out of 168 | 16 out of 16 | 99% | A |
| M | 165 out of 168 | 15 out of 16 | 98% | A |
| N | 139 out of 168 | 16 out of 16 | 84% | B |
| P | 167 out of 168 | 16 out of 16 | 99% | A |
| Q | 165 out of 168 | 16 out of 16 | 98% | A |
| R | 154 out of 168 | 14 out of 16 | 91 | A |

3 DEFINITIONS

Batch – An analytical batch consists of 20 or fewer client samples.

Method Blank (MB) – Analyte free water that is carried through the entire analytical process. The method blank is used to evaluate contamination contributed from the method. Analyte detections in the method blank must be less than 10x the analyte result for a client sample to be considered usable without flagging.

Duplicate – A client sample analyzed in duplicate. Duplicate RPD should be summarized in the report.

Blank Spike/Blank Spike Duplicate – A blank spike (laboratory control sample) is a certified standard reference material that is spiked into a reagent blank. It is carried through all steps of sample preparation to demonstrate method performance inclusive of sample preparation steps. The blank spike should be spiked near the midpoint of the calibration curve.

Matrix Spike/Matrix Spike Duplicate – A matrix spike is a regular sample that is split into three sub-samples. Two of the replicates are spiked with analyte solution at the same concentration and are defined as the matrix spike and matrix spike duplicate (MS/MSD). The MS/MSD samples are carried through the sample preparation and analysis procedure with each batch of 20 or less samples. The MS/MSD results provide information regarding laboratory precision, sample matrix effects, and method efficiency.

RPD – Relative Percent Difference is calculated using the following formula:

$$RPD = \frac{(\text{Result1} - \text{Result2})}{(\text{Result1} + \text{Result2})/2} * 100$$

RSD – Relative Standard Deviation is calculated using the following formula:

$$RSD = \frac{(\text{Standard Deviation})}{(\text{Mean})} * 100$$

4 REFERENCES

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