Sampling and Analysis – Quality Assurance

Appendix F to Small Tributaries Loading Strategy Multi-Year Plan

Version 2011 PROGRESS

A major objective of the STLS is consistency between monitoring data from the stations operated by the RMP and those operated by Bay Area stormwater programs to comply with the Municipal Regional Stormwater Permit.

Table 8.4 in MRP Provision C.8.e describes a basic approach using autosamplers and minimum storm capture per 40 CFR 122.21(g)(7)(ii), and target Reporting Limits and Data Quality Objectives (DQOs) established by SWAMP. MRP Table 8.4 also specifies collection and analysis of methylmercury samples as grab samples to be collected and analyzed four times each year (two wet season and two dry season), However RMP monitoring on small tributaries through 2009 used different sampling methods and performance-based selection of laboratories. This Appendix presents some background information used to develop the MYP's sampling and analysis approach, and identifies further activities for assuring consistent practices and data quality. Updates in 2012 will describe Quality Assurance / one Quality Control (QA/QC) and Standard Operating Procedures (SOPs) in more detail

Sampling and Analysis

The MRP specifies that default standards for monitoring data quality be consistent with the latest version of the Quality Assurance Program Plan (QAPrP; SWAMP 2008) adopted by the Surface Water Ambient Monitoring Program (SWAMP). The QAPrP adopts a performance-based approach with target Reporting Limits (RL) for a large list of analytes in water and sediment, as well as other matrices.

The RMP has not specified target Reporting Limits for most analytes in its Status and Trends Program or Special Studies. In previous stormwater monitoring studies SFEI has utilized laboratory services that provide much lower method detection limits (MDL) for some analytes than those that would be associated with the SWAMP Target RLs.

The STLS team reviewed the differences between default SWAMP RLs and performance of labs in actual RMP monitoring.results for Zone 4 Line A, summarized in Table F-1. The RMP laboratories typically obtained much higher frequencies of detection with much lower detection levels for the organic compounds. The STLS Work Group agreed to continue using the laboratories with demonstrated consistency in low-range detection, but also reviewed considerations of costs of these analyses as well as logistical issues before agreeing on the sampling approach summarized in Table F-2.

Table F-1. Default SWAMP Reporting Limits for MRP analytes compared to RMP performance-based results for stormwater samples collected at Zone 4 Line A. See text for notes.

MRP Category (Table 8.4)	Analyte	SWAMP RL	Z4LA Concentration range	Fraction Z4LA data detected >RL using SWAMP RLs	Actual RL	Percent Z4LA data detected >RL using Actual RLs
1	Cu (T)	0.01 µg/L	2.26-50 µg/L	45/45	0.03-0.1 µg/L	100%
1	Cu (D)	0.01 µg/L	1.44-10.9 µg/L	11/11	0.1 µg/L	100%
1	Hg	0.0002 µg/L	0.00143-0.147 µg/L	112/112	0.0002 µg/L	100%
1	meHg	0.00005 µg/L	0.000032-0.00130 µg/L	55/56	0.00002 µg/L	99%
1	PCB congeners	0.02 µg/L[1]	0.000332-0.109336 µg/L	20/77	NA	
1	SSC	0.5 mg/L	1.415-2744 mg/L	392/392	0.6 mg/L	99%
1	TOC	0.6 mg/L	3.39-22.54 mg/L	40/40	0.3-2.4 mg/L	100%
1	Nitrate as N	0.01 mg/L	0.0043-0.656	10/12	NA	
1	Hardness (as CaCO3)	1 mg/L	-		NA	
2	Se (T)	0.3 µg/L	0.053-2.86 µg/L	15/30	0.045-1 µg/L	36%
2	Se (D)	0.3 µg/L	0.041-0.101 µg/L	0/5	0.045-0.053 µg/L	66%
2	PBDEs	NL (assume=PCB)	0.000348-0.141218 µg/L	18/36	NA	(75%)
2	PAHs (std list)	10 µg/L	0.01-23 µg/L	3/21	NA	(99%)
2	DDTs	0.002 µg/L[2]	0.000411-0.059480 µg/L	14/20	NA	(100%)
	Chlordane	0.002 µg/L[2]	0.000349-0.016400 µg/L	13/20	NA	(100%)
	Dieldrin	0.002 µg/L[2]	0.000276-0.004590 µg/L	3/20	NA	(100%)
2	Pyrethroids	NL			NA	
	Bifenthrin		0.183-46.3 ng/L	-	NA	
	Delta/Tralomethrin		0.464-5.49 ng/L	-	NA	
	Permethrin, total		1.57-285 ng/L	-	NA	
2	Carbaryl	NL	-		NA	
2	Fipronil	NL	-		NA	
2	Phosphorus (T)	NL	-	-	NA	
2	Phosphorus (D)	(mg/L)	0.0242-0.236	-	NA	
1	Aquatic Toxicity?	(Not sampled at Zone 4 Line A)-				

Notes:
[1] With exception of PCB 189, which has a target RL of 1µg/L. SWAMP congener list differs slightly from the 40-congener list used by the RMP.
[2] With exception of DDT (p,p'), which has a target RL of 0.005 µg/L

Table F-2. Target sampling design and configuration of ISCO autosamplers at each STLS watershed monitoring station.

MRP Category	Parameter	No. Storms/ year	Type	Recom-mended Lab[1]	avg. no. samples/ storm[2]	No. Duplicates /season	Field samples /season	Container Size (L)	ISCO unit no.
1	PCBs (40 congener)	4	Discrete	AXYS	4	1	17	1.8	1
1	Total Mercury	4	Discrete	MLML	4	1	17	0.35	2
1	Dissolved Cu	4	Composite	BRL	1	1	5	1.8	4
1	Total Cu	4	Composite	BRL	1	1	5	1.8	4
1	Hardness	4	Composite	BRL	1	1	5	1.8	4
1	SSC (GMA)	4	Discrete	EBMUD	8	2	34	0.35	2
1	Nitrate as N and Total Phosphorous	4	Discrete	EBMUD	4	1	17	0.35	2
2	Dissolved phosphorus	4	Discrete	EBMUD	4	1	17	0.35	2
1	TOC	4	Discrete	CAS?	2.5	1	11	0.35	2
1	Toxicity – water column	4	Composite	TBD	1	0	4	3.8	3
2	Pyrethroids	4	Composite	AXYS?	1	1	5	1.8	4
2	Carbaryl	4	Composite	DFG – WPCL?	1	1	5	1.8	4
2	Fipronil	4	Discrete	DFG – WPCL?	1	1	5	1.8	4
2	Chlordane, DDTs, Dieldrin	0	--	--	0	0	--	--	--
2	Dissolved Se (collect with Dissolved Cu)	4	Composite	BRL	(1)	(1)	(5)	--	(4)
2	Total Se (collect with Total Cu)	4	Composite	BRL	(1)	(1)	(5)	--	(4)
2	PBDE	2	Discrete	AXYS	1	1	3	1.8	1
2	PAH	2	Discrete	AXYS	1	1	3	1.8	1

[1] as of mid-July 2011; question marks indicate contacts to be followed up. [2]non- blank samples

Table F-1 shows preliminary results using available data. The RMP does not require laboratories to submit RLs, but some do provide them in which case the RLs are stored in database. For analytes reported without RL's, a percentage of detection is shown within parentheses, based on valid results greater than the sample-specific MDL.

Several of the analyses that were quantified by RMP labs would have been qualified or reported as non-detects by laboratories meeting but not exceeding SWAMP targets, especially PCBs and some of the other organic pollutants For some parameters (e.g. selenium, for which a few samples did not meet SWAMP RLs) different laboratories were used in different sampling seasons. Limited or no Zone 4 Line A data were available for pyrethroids, carbaryl or fipronil. Analytical methods for some of these pesticides have lagged behind their increasingly wide use in California, as indicated in reports prepared for the urban pesticides committee, e.g. TDC Environmental (2008) which recommends the following detection limits in water, based on available aquatic toxicity data:

- Each individual pyrethroid –as close to 1 nanograms/liter as available
- Carbaryl – 0.5 ug/liter
- Fipronil and degradates – 0.002 ug/liter

While improved water column methods have since been developed for fipronil (Hladik 2006, cited in TDC 2007), analytical capability to meet recommended detection limits has not been advertised by commercial laboratories. A few have informally indicated they would be able to provide these services given adequate market demand. SFEI is exploring agreements with these labs.

Key considerations in finalizing Table F2 included

- Obtaining the 16 samples per season recommended for loads estimation is a high priority for mercury PCBs and SSC. The design further increases the seasonal number of SSC samples since the turbidity surrogate is linked to SSC.
- Shifting to the lowest practicable detection limits is most important for PCBs PBDE and PAHs but also results in much higher laboratory analysis cost per sample.
- Sample volumes are constrained by available bottle configurations for the iSCO autosamplers; to make efficient use of no more than four samplers per station, analytes were grouped by container size and sample type, subject to the assignment of each sample bottle to a single analytical laboratory. Field duplicates can be collected wants per season for each analyte, rotating the assignment of duplicates among different events.
- Sampling for Category 2 pollutants was averaged out to be the same for each year, rather than being focused in alternating years.
- Tracking copper loads to the Bay is not a high priority in the near term[1], so the sampling effort for dissolved and total copper was kept at the MRP level of four composite samples

[1] Copper Site-Specific Objectives adopted for the Bay required a Copper Action Plan involving a variety of source control actions by dischargers. The largest source of copper to urban runoff, vehicle brake pads, is expected to be effectively phased out over the next 10-25 years as mandated by California SB 346, enacted in 2010.

per season, to allow consolidation into the same sampling containers as dissolved and total selenium.

For pesticides, sampling design was driven by priorities other than loads to San Francisco Bay:

- Recent data on organochlorine pesticides in the Bay suggest a recovery trajectory that will not require development of a TMDL. Load estimates from small tributaries are thus not a pressing priority and chlordane, DDTs and dieldrin were removed from the analyte list.
- The remaining Category 2 pesticides are primarily of concern as potential causes of toxicity in freshwater streams and water bodies. Thus the STLS will collect samples with the same type and frequency for these pesticides and for water column toxicity. Since toxicity effects are a function of integrated exposure over time,

Quality Assurance

A Quality Assurance Project Plan (QAPP) and Field Manual (FM) are being developed with BASMAA funding, concurrent with planning and setup for the WY 2011-12 monitoring season. The MRP does not require submission of a QAPP so for the purposes of the STLS the term "QAPP" is used in a flexible sense, not strictly tied to the rigid content and format in the templates generated by SWAMP. These documents will describe:

- Program management: roles and relationships between BASMAA programs and the RMP
- Data quality objectives.
- Standardized approaches to data management, quality assurance and reporting
- Coordination between the QAPP, the Field Manual and additional SOPs

The Field Manual for Watershed Stormwater Monitoring will describe all methods and procedures, with reference to existing SOPs and procedures already produced or in development by BASMAA or SFEI. Table F-3 provides a working outline of its contents.

Review of the first year's data may involve reexamination and updating of some aspects of the QAPP and Field Manual. Additional QA issues that may be reviewed in the future include:

- Comparison of different turbidity sensors. Past RMP monitoring has used one instrument type (Forest DTS-12), but a different model capable of reading higher turbidity levels will be deployed at STLS sites with high turbidity readings during WY2011-12. Raw turbidity readings from different types of probes may not be directly comparable due to differences in design features such as sensor type, wavelength of light and algorithm used to calculate turbidity.
- Suspended Sediment Concentration calibration. An articulated boom provides continuous depth integration for both the continuous turbidity sensor and SSC sample collection. WY2011-12 plans do not include calibration of the depth-integrated sample across the cross-section, assuming that the channels are sufficiently well-mixed at the sampling locations.

Table F-3. Main content of STLS Field Manual for Watershed Stormwater Monitoring, including additional Standard Operating Procedures (SOPs)

Section	Main contents
1. Introduction	• NPDES municipal permit to discharge storm water (CS / AF) • RMP STLS (SFEI / CS / AF) • MRP Requirements from Table 8.4 as adapted by STLS (PS / SFEI) • SOP background - application of manual and SOPs
2. References to existing SOPs (e.g. developed for other RMC or RMP programs	• Collection of grab samples • Clean hands grab sampling, • Data processing, analysis and interpretation • Development of stream rating curves by project-specific gauging methods • Flow measurement methods
3. Special Cautions and Considerations; Health and Safety	• Introduction • Hazard identification • Health and safety practices
4. Methods / Procedures	• Monitoring station description • Instrument programming, calibration and maintenance • Storm monitoring • Field data management • Field quality assurance and quality control • Equipment maintenance
5. Quality Assurance / Quality Control	• Training • Internal Reporting
6. References	
7 Additional SOPs	1. Cleaning procedure for sample intake tubing and intake strainers 2. Cleaning procedures for composite and discrete sample bottles 3. Determination of flow / turbidity-triggers for sampling or sample pacing 4. Station preparation for event sampling 5. Changing a composite bottle set during a storm 6. Discharge measurement procedures 7. Sample Container, Handling, and Hold Time

References

TDC Environmental (2007) Urban Use of the Insecticide Fipronil--Water Quality Implications, Memorandum to the Urban Pesticide Committee from Kelly D. Moran, TDC Environmental, June 18, 2007.

TDC Environmental (2008). Pesticides in urban surface water- annual review of new scientific findings 2008. Prepared for the San Francisco Estuary Project, April 2008.