

**FINAL**

ATTACHMENT

**■■■■■ EVALUATION OF  
ANALYTES AND  
QA/QC SPECIFICATIONS  
FOR MONITORING PROGRAM**

**December 1996**

Prepared for



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Following sixteen years of stormwater monitoring, two of which were under an NPDES permit (Permit), the Los Angeles County Department of Public Works (LACDPW) is evaluating the adequacy and appropriateness of its Monitoring Program. The purpose of this report is to provide a refined constituent list that reflects our current understanding of pollutants of concern in the receiving waters, and to specify the quality assurance and quality control (QA/QC) procedures required for reliable monitoring of these constituents.

The Monitoring Program was established with an overall goal to develop and support effective watershed stormwater quality management programs in order to reduce pollutants to the maximum extent practicable. There are seven major specific objectives listed in the Permit:

Track water quality status, pollutant trends and loads, and identify pollutants of concern.

- Monitor and assess pollutant loads from specific land uses and watersheds.
- Identify, monitor, and assess significant water quality problems related to stormwater discharges.

Identify pollutant sources in stormwater runoff.

- Identify and eliminate illicit discharges.
- Evaluate the effectiveness of management programs.

Assess the impacts of stormwater runoff on receiving waters.

To address this spectrum of objectives, initial permit monitoring in Los Angeles County included a broad analytical suite that provided detailed information on urban pollutants in the water as well as major ions, nutrients, and chemical and biological properties. Some of these water quality parameters are related to natural processes rather than to human activity. Furthermore, many constituents in the analytical suite are not thought to be posing any ecological risk or human health risk in the receiving waters. To focus future monitoring on relevant constituents, the data collected during the winters of 1994/95 and 1995/96 were reviewed with the following questions in mind:



- What are the pollutants of concern?
- What are the levels of concern (e.g., toxic concentrations) for each pollutant?

Are those pollutants found in stormwater runoff in Los Angeles County?

- Is the existing analytical methodology adequate for detecting pollutants at the levels of concern?

Should analysis for some constituents be done to achieve lower detection levels? For which constituents?

Are there analyses which could be discontinued?

- Are there other constituents that should be added?

Section 2 describes pollutants of concern in freshwater and marine receiving waters. Section 3 summarizes the findings of the last two years of stormwater monitoring in Los Angeles County and identifies the pollutants that have been detected consistently. Section 4 presents recommended constituents for chemical monitoring in stormwater, and provides a rationale for the recommendations. Section 5 describes recommended sampling and shipping procedures. Section 6 delineates recommended QA/QC procedures and Section 7 lists the references used in writing this report.

## SECTION TWO

## Pollutants Of Concern In Los Angeles County Water Bodies

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Stormwater runoff from urban catchments in Los Angeles County ultimately flows into rivers, lagoons, bays, and the ocean. Pollutants exhibit different impacts in the water column or the sediment, as well as in freshwater, brackish, or sea water. Some pollutants (e.g., silver) are very toxic, i.e., they may poison aquatic life at very low concentrations, whereas other pollutants (e.g., zinc) can be tolerated at relatively high concentrations without causing harm. Conservative elements, such as metals, do not degrade and may pose more long-term risks than non-conservative compounds, such as petroleum hydrocarbons that can be broken down by microorganisms.

Table 2-1 lists pollutants of concern for seven major receiving water bodies in the portion of Los Angeles County covered under the NPDES Permit and the corresponding USEPA Water Quality Criteria for the Protection of (1) Freshwater Aquatic Life and (2) Saltwater Aquatic Life. These water quality criteria are hereafter referred to collectively as criteria. Concentrations in the listed water bodies are uncertain and may not exceed the criteria given in the table. The constituents listed in Table 2-1 are pollutants of concern in local water bodies, however, they may not be present in stormwater, and if present, may not exceed the criteria.

The most obvious feature of Table 2-1 is the number of pollutants, both organic and inorganic, that are associated with past and present human activity in Los Angeles County watersheds. Some pollutants are typical of residential, industrial and commercial sources (e.g., copper, lead, and zinc), while others reflect special activities (e.g., tributyltin, which is used as an antifouling agent in boat hull paints). Some pollutants of concern may originate in one location and migrate to other watersheds. For example, it is conceivable that DDT found in sediments in the mouths of Los Angeles County rivers could have been washed in by ocean currents from Palos Verdes (B.H. Jones, personal communication).

The criteria (supplied for informational purposes only) vary in magnitude among pollutants and depend on whether the receiving water is fresh or marine. For some pollutants, the criteria are lower than the detection limits of the laboratory analytical methods used in previous years of the Monitoring Program. As a rule of thumb, it is typically recommended that laboratory analytical methods which have detection limits several times lower than the criteria be used to assure detection of potentially harmful substances at the criteria concentration.

**TABLE 2-1**  
**POLLUTANTS OF CONCERN IN LOCAL WATER BODIES**  
**AND WATER QUALITY CRITERIA FOR SELECTED CONSTITUENTS**

Pollutant	Ballona Creek and Wetlands	Los Angeles River	San Gabriel River	Malibu Creek	Malibu Lagoon	Marina del Rey	Santa Monica Bay	Freshwater EPA Criteria (1)	Saltwater EPA Criteria (2)	Units
Conventional Pollutants										
Oil & Grease	x	x					x	5.2 6.5 - 9	1 6.5 - 8.5	ug/l
Cyanide	x	x								
pH		x								
Bacteria and other Pathogens										
Coliform	x	x	x		x	x	x			
Enteric viruses					x					
General										
Phosphorus	x		x					2.2	0.44	mg/l
Turbidity		x								
TSS				x						
TDS		x			x					
TPH	x	x		x						
Ammonia	x	x	x	x						
Nitrogen	x		x							
Metals										
Arsenic	x	x	x	x				190	36	ug/l
Barium	x	x	x	x						
Beryllium		x						0.37	9.3	ug/l
Cadmium	x	x	x	x			x			
Chromium	x	x	x	x		x		57	50	ug/l
Copper	x	x	x	x		x	x	3.5	2.4	ug/l
Lead	x	x	x	x		x	x	0.54	8.1	ug/l
Mercury	x	x		x			x	0.012	0.025	ug/l
Nickel	x	x	x	x			x	49	8.2	ug/l
Selenium	x	x	x	x				5	71	ug/l
Silver	x		x					0.32	0.92	ug/l
Zinc	x	x	x	x			x	32	81	ug/l
Organics										
Bromodichloromethane			x					0.014		ug/l
Carbon tetrachloride			x							
Chloroform		x	x	x						
Dichlorobenzenes			x							
Methylene chloride		x	x							
PCBs	x						x			
Tetrachloroethene (PCE)			x							
Trichloroethene (TCE)		x						0.026		ug/l
Tributyl tin (TBT)	x					x				
Toluene		x								
Xylenes		x								

**TABLE 2-1**  
**POLLUTANTS OF CONCERN IN LOCAL WATER BODIES**  
**AND WATER QUALITY CRITERIA FOR SELECTED CONSTITUENTS**

Pollutant	Ballona Creek and Wetlands	Los Angeles River	San Gabriel River	Malibu Creek	Malibu Lagoon	Marina del Rey	Santa Monica Bay	Freshwater EPA Criteria (1)	Saltwater EPA Criteria (2)	Units
<b>Organics (continued)</b>										
PAHs	x						x			
Naphthalene		x								
Pesticides						x	x			
Aldrin		x						3		ug/l
Chlordane	x					x	x	0.0043		ug/l
DDT/DDE/DDD	x			x		x	x	0.001		ug/l
Priority Organics		x	x							

Data Source: RWQCB, Los Angeles Region, 1996.

**Notes:**

- (1) USEPA Water Quality Criteria for the Protection of Freshwater Aquatic Life  
Criteria are chronic except those marked with an asterisk, which denotes acute criteria.  
Hardness is assumed to be 25 mg/l for those metals whose WQC depends on hardness, specifically Cd, Cr, Cu, Pb, Ni, Ag, and Zn.  
All metals criteria are for the dissolved fraction with the exceptions of Hg and Se, which are total.  
Ammonia criteria assumes pH of 6.5 and temperature of 15 C for salmonid habitat.
  - (2) USEPA Water Quality Criteria for the Protection of Saltwater Aquatic Life (chronic)  
All metals criteria are for the dissolved fraction with the exception of Hg.  
Ammonia criteria assumes pH of 8.4, temperature of 20 C, and salinity of 20 g/kg.
- x Pollutant is present at unspecified concentration, not necessarily exceeding criteria.

## SECTION THREE

## Los Angeles County Stormwater Data Review

A data review was conducted which included historical data used for mass loading assessment (Stenstrom and Strecker, 1993), pathogen and indicators data reported by the Santa Monica Bay Restoration Project (Gold et al., 1992), LACDPW Monitoring Program data obtained during 1994/95 (Los Angeles County Department of Public Works, 1996), and raw data from the 1995/96 wet season as provided by the LACDPW. The LACDPW data were summarized in Table 3-1 as received, i.e., we did not perform any QA/QC evaluation of the data. The analytical suite, detection limits, and frequencies of detection at these limits are included in Table 3-1 for both the 1994/95 and 1995/96 data. The range of station means for 1994/95, and the maximum concentrations detected in the 1995/96 wet season were also included in Table 3-1. For the 1995/96 wet season, the data were pooled for all urban catchments and reported separately from the open space data.

### 3.1 CONVENTIONAL AND GENERAL WATER QUALITY PARAMETERS

Oil and grease and total petroleum hydrocarbons (TPH), were detected in more than 50% of the urban runoff samples and were not detected in runoff from open space catchments.

Total suspended solids (TSS) and turbidity were always detected in the stormwater runoff samples collected at all monitoring stations. However, TSS and turbidity values were generally higher in open space stations, indicating that a major source of solids could be soil erosion in the upper, open space portions of the watersheds. Cyanide was not detected in any of the samples at a detection limit of 50 µg/l; however, the criteria for cyanide are in the range of 1-5 µg/l (see Table 2-1) so there is no way to assess potential harmful effects of cyanide in the stormwater runoff samples analyzed.

Nutrients (nitrogen and phosphorous compounds) were detected in a high percentage or in all of the samples, both from urban and open space catchments, at levels that could support rapid growth of algae and aquatic plants. Maximum ammonia concentrations are not expected to cause toxicity at the maximum pH values reported.

**TABLE 3-1**  
**SUMMARY OF 1994/95 AND 1995/96 LACDPW STORMWATER MONITORING DATA**

				Mixed Urban Land Use			Open Space	
Class	Constituent	Detection Limit	Units	94/95	95/96		95/96	
				Range of Means	Maximum	% of Detects	Maximum	% of Detects
Conventional								
	O&G	1	mg/l	ND - 3.30	37.5	54.2	ND	0
	Total Phenols	0.1	mg/l		0.1	1.7	ND	0
	Cyanide	0.05	mg/l		ND	0	ND	0
	pH	NA	pH	6.88 - 8.19	8.4	100	8.43	100
Indicator Bacteria								
	Total Coliform	20	MPN/100 ml	9740 - 514,464	>1,600,000	100	1,600,000	100
	Fecal Coliform	20	MPN/100 ml	6640 - 166,692	>1,600,000	96.8	280,000	100
	Fecal Streptococcus	20	MPN/100 ml	2235 - 202,076	2,400,000	100	1,400,000	100
	Fecal Enterococcus	20	MPN/100 ml	688 - 109,476	>1,600,000	100	1,100,000	100
General								
	Phosphorus, dissolved	0.05	mg/l	ND - 0.307	1.95	88.1	0.44	60
	Phosphorous, total	0.05	mg/l	ND - 0.984	1.95	100	0.5	100
	Turbidity	0.1	NTU		90	100	1800	100
	TSS	1	mg/l	17 - 609	880	100	8728	100
	TDS	5	mg/l	16 - 910	1240	100	1160	100
	VSS	1	mg/l		300	100	600	100
	TOC	1	mg/l	11.1 - 31.3	102	100	13.1	100
	TPH	1	mg/l		37.5	52.5	ND	0
	BOD	1	mg/l	ND - 45.2	97.8	100	90.3	100
	COD	50	mg/l	ND - 63.1	140	17.1	ND	0
	Ammonium-N	0.1	mg/l	ND - 3.05	6.19	57.5	2.09	20
	NH3-N	0.1	mg/l		5.12	71.8	1.73	50
	TKN	0.03	mg/l	ND - 1.84	5.86	97.4	13.7	100
	Nitrate	0.1	mg/l		96.3	100	11.4	100
	Nitrate-N	0.03	mg/l		21.7	100	2.58	100
	Nitrite-N	0.03	mg/l		6.54	67.4	0.11	50
	Nitrate & Nitrite		mg/l	0.19 - 3.37				
	Alkalinity	4	mg/l		262.3	100	242.7	100
	Specific Conductivity	1	umhos/cm		1920	100	1660	100
	Hardness	5	mg/l		640	100	700	100
	Chloride	2	mg/l	1 - 105	218	100	52.4	100
	Fluoride	0.1	mg/l	0.103 - 0.428	0.66	100	0.38	100
	Sulfate	0.1	mg/l	2 - 382	452	100	518	100
	Bicarbonate	2	mg/l		273	100	232	100
	Carbonate	2	mg/l		10.7	4.8	10.7	20

**TABLE 3-1**  
**SUMMARY OF 1994/95 AND 1995/96 LACDPW STORMWATER MONITORING DATA**

Class	Constituent	Detection Limit	Units	Mixed Urban Land Use			Open Space	
				94/95 Range of Means	95/96 Maximum    % of Detects		95/96 Maximum    % of Detects	
Total Metals								
	Antimony	10	ug/l	ND - 16	49	6.3	ND	0
	Arsenic	10	ug/l	ND - 17	17	3.1	ND	0
	Barium	100	ug/l		126	4.7	723	22.2
	Beryllium	5	ug/l	ND	ND	0	7	11.1
	Boron	250	ug/l		510	27.1	45	20
	Cadmium	10	ug/l	ND - 15	ND	0	31	11.1
	Calcium	2	mg/l		156	100	158	100
	Chromium	10	ug/l	ND - 52	35	24.6	200	33.3
	Copper	10	ug/l	20 - 49	168	92.2	305	77.8
	Iron	100	ug/l	ND - 718	7280	83.6	187,000	77.8
	Lead	10	ug/l	ND - 504	188	48.4	42	33.3
	Manganese	30	ug/l		504	51.6	4550	66.7
	Magnesium	2	mg/l		68.3	83.7	60.8	90
	Mercury	1	ug/l	ND	1	1.6	ND	0
	Nickel	10	ug/l		47	43.8	226	55.6
	Potassium	1	mg/l		20.7	100	6.78	100
	Selenium	5	ug/l	ND	24	9.4	ND	0
	Silver	10	ug/l	ND	ND	0	19	11.1
	Sodium	5	mg/l		156	100	83.6	100
	Thallium	10	ug/l		ND	0	ND	0
	Zinc	50	ug/l	56 - 272	876	82.8	651	55.6
Dissoived Metals								
	Antimony	10	ug/l	ND	4	1.6	ND	0
	Arsenic	10	ug/l	ND	ND	0	ND	0
	Barium	100	ug/l		ND	0	ND	0
	Beryllium	5	ug/l	ND	ND	0	ND	0
	Boron	250	ug/l		400	17	450	14.3
	Cadmium	10	ug/l	ND	ND	0	ND	0
	Chromium	10	ug/l	ND - 10	10	1.6	ND	0
	Copper	10	ug/l	ND - 17	42	50.8	ND	0
	Iron	100	ug/l		1550	27.1	ND	0
	Lead	10	ug/l	ND - 17	100	10.8	ND	0
	Manganese	30	ug/l		70	17.2	32	11.1
	Mercury	1	ug/l	ND	ND	0	ND	0
	Nickel	10	ug/l		15	6.2	ND	0
	Selenium	5	ug/l	ND	24	4.6	ND	0
	Silver	10	ug/l	ND	ND	0	ND	0
	Thallium	10	ug/l		ND	0	ND	0
	Zinc	50	ug/l	ND - 116	600	56.9	ND	0
Organic Compounds								
	Volatile Organics (8240)	varies	ug/l			0.26		0
	Bis(2-ethylhexyl)phthalate (625)	3	ug/l	ND - 81.3	236	77.3	38.9	100
	Other Semi-Volatile Organics (625)	varies	ug/l			0.91		1.12
	Organochlorine Pesticides (608)	varies	ug/l			0		0
	Organonitrogen Herbicides (619)	varies	ug/l			0		0

Method used for analysis of organic constituents is in parentheses.

## **3.2 BACTERIA**

Indicator bacteria of fecal origin were detected in virtually all samples, sometimes at densities higher than were quantifiable by the dilution procedures employed. Opportunistic pathogens including coliforms and fecal coliforms, streptococci and enterococci were detected in runoff from open space stations as well as mixed land use stations.

## **METALS**

Of the metals of concern, arsenic, barium, beryllium, cadmium, mercury, and silver were below the detection limit in the dissolved fraction, and were sporadically detected in the total fraction. However, the detection limits used for cadmium, copper, lead, mercury, silver, and zinc are higher than the corresponding criteria (see Table 2-1), so it is not possible to assess the potential for harmful effects due to metal contamination of stormwater.

## **ORGANIC COMPOUNDS**

Volatile organic compounds (VOCs, EPA Method 8240), semivolatile organic compounds (SVOCs, EPA Method 625), organochlorine pesticides and PCBs (OCs, EPA Method 608), and organonitrogen herbicides (EPA Method 619) were not detected (with a few exceptions) at the detection limits attainable by these methods. The exceptions include bis(2-ethylhexyl)phthalate, which was detected in most samples at concentrations that were not correlated to any land use, and other plasticizers known as persistent lab and field equipment contaminants.



## SECTION FOUR

## Recommended Constituents For Monitoring

After reviewing the data collected by LACDPW over the past two years, recommended analytical suites for mass emission stations and land use stations were developed. Special studies may be developed using an additional analytical suite (referred to as the special studies suite) in conjunction with the mass emission and land use suites to choose appropriate analytes for the specific questions being asked. This section presents the three analytical suites and provides justification for the recommendation to lower detection limits.

The Permit requires that stormwater collected from mass emission and land use stations be analyzed for specific constituents which don't correspond to the analytical suites recommended in this report. Table 4-1 presents an overview of the analyses required by the Permit and the analyses recommended by this report for both mass emission and land use stations. Tables 4-2, 4-3, and 4-4 present the suggested analytical suites for the Monitoring Program. The major modifications from previous years are as follows:

Detection limits have been reduced for many constituents.

Analyses of VOCs (EPA Method 8240), SVOCs (EPA Method 625), organochlorine pesticides (OCs) and PCBs (EPA Method 608), and organonitrogen herbicides (EPA Method 619) at the detection limits attainable by these methods, are no longer recommended.

- Alternative methods for analyses of polycyclic aromatic hydrocarbons (PAHs) and selected organophosphorus pesticides have been added.

Use of the recommended analytical suites for mass emission and land use station monitoring would require negotiation with the Regional Water Quality Control Board (RWQCB) since the recommended analytical suites deviate from the analytical suites set forth in Attachment C (Monitoring Program Requirements) of the Permit.

### 4.1 DETECTION LIMITS

The concentrations of pollutants which can be detected are controlled by detection limits. When comparing pollutant concentrations to criteria, detection limits several times lower than the criteria are recommended. If inappropriate detection limits are chosen, analytes which are

**TABLE 4-1**  
**Comparison of Permit Requirements with Recommended Analyte Suites**  
**and Detection Limits**

Constituent	Units	Detection Limits		Analytical Suites			
		Permit	Recommended	Mass Emission Stations		Land Use Stations	
				Permit	Recommended	Permit	Recommended
<b>Conventional</b>							
O&G	mg/l	1	1	x	x		x
Total Phenols	mg/l	0.1		x			
Cyanide	mg/l	0.01	0.01	x	x		x
pH	pH	0 - 14	sens. $\pm$ 0.1 pH uni	x	x		x
Temperature	no units given	None	sens. $\pm$ 1 degree	x	x		x
Dissolved Oxygen	mg/l	5	0.5	x			
<b>Microbial</b>							
Total Coliform	MPN	< 20	< 20	x	x		x
Fecal Coliform	MPN	< 20	< 20	x	x		x
Fecal Streptococcus	MPN	< 20	< 20	x	x		x
<b>Inorganic</b>							
Phosphorus, dissolved	mg/l	0.05	0.05	x	x		
Phosphorus, total	mg/l	0.05	0.05	x	x	x	x
Turbidity	NTU	0.1	1	x	x		x
TSS	mg/l	2	2	x	x	x	x
TDS	mg/l	2	2	x	x		x
VSS	mg/l	2	10	x			
TOC	mg/l	1	1	x			
TPH	mg/l	1	1	x	x		x
BOD	mg/l	2	4	x	x		x
COD	mg/l	20-900	5	x	x		x
Ammonium-N	mg/l	0.1	0.1	x	x	x	x
TKN	mg/l	0.1	0.1	x	x	x	x
Nitrate-Nitrite	mg/l	0.1	0.1	x	x	x	x
Alkalinity	mg/l	2	2	x			
Specific Conductivity	umho/cm	1	10	x	x		x
Hardness	mg/l	2	2	x	x		x
MBAS	mg/l	0.5	0.5	x			
Chloride	mg/l	2	2	x			
Fluoride	mg/l	0.1	0.1	x			
Sulfate	mg/l	2	2	x			
<b>Inorganic (total and dissolved)</b>							
Aluminum	ug/l	100,000	1000	x			
Antimony	ug/l	10	10	x			
Arsenic	ug/l	10	1	x	x		x
Barium	ug/l	100	1	x	x		x
Beryllium	ug/l	5	1	x	x		x
Boron	ug/l	250	100	x			
Cadmium	ug/l	10	1	x	x	x	x
Calcium	ug/l	200	1000	x			
Chromium	ug/l	10	1	x	x	x	x
Copper	ug/l	10	1	x	x	x	x
Hex. Chromium	ug/l	< 10,000 *	1	x			
Iron	ug/l	100	100	x	x		
Lead	ug/l	10	1	x	x	x	x
Magnesium	ug/l	200	1000	x			
Manganese	ug/l	30	100	x			
Mercury	ug/l	1	0.1	x	x	x	x
Nickel	ug/l	10	1	x	x	x	x
Potassium	ug/l	1000	1000	x			
Selenium	ug/l	5	0.2	x	x	x	x
Silver	ug/l	10	0.2	x	x	x	x
Sodium	ug/l	5	1000	x			
Thallium	ug/l	10	10	x			
Zinc	ug/l	50	10	x	x	x	x
<b>Organic</b>							
volatile Organic Compounds	ug/l	< 0.5 to <5		x			
pesticides and PCBs	ug/l	< 0.02 to <5		x			
pesticides	ug/l	< 10 to < 2000		x			
pesticides	ng/l	no DL given	10		x		x
pesticides	ng/l	no DL given	50		x		x
Organic Compounds	no units given	< 0.01 to 10	10 - 50	x	x		x

**Detection Limit**

Permit limits required by the Permit are given in the "Permit" column under the heading "Detection Limits".

Recommended limits recommended in this report are given in the "Recommended" column under the heading "Detection Limits".

Permit limits required by the Permit for the mass emission and land use stations are indicated by x's in the corresponding "Permit" columns under the "Analytical Suites" headings.

Recommended limits recommended in this report for the mass emission and land use stations are indicated by x's in the corresponding "Recommended" columns under the "Analytical Suites" heading.

Detection limit for hexavalent chromium is listed in the Permit as < 10 mg/l.

**TABLE 4-2**  
**SUGGESTED ANALYTE SUITE FOR MASS EMISSION MONITORING STATIONS**

Class	Constituent	Method	Detection Limit	Units	Preservation	Holding Time	Sample Type
Conventional	O&G	413.2	1	mg/l	4°C	28 days	grab
	Cyanide	335.1	0.01	mg/l	4°C pH>12 NaOH 0.6 g ascorbic acid	14 days	grab
	pH			pH		ASAP	grab
	Temperature <sup>(1)</sup>			degrees C		Field	grab
Bacteria	Total Coliform	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
	Fecal Coliform	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
	Fecal Streptococcus	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
General	Phosphorus, dissolved	365.3	0.05	mg/l	filter	48 hours	composite
	Phosphorus, total	365.3	0.05	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	Turbidity	180.1	1	NTU	4°C	48 hours	composite
	TSS	160.2	2	mg/l	4°C	7 days	composite
	TDS	160.1	2	mg/l	4°C	7 days	composite
	TPH	418.1	1	mg/l	4°C	28 days	grab
	BOD	405.1	4	mg/l	4°C	48 hours	composite
	COD	410.4	5	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	Ammonia-N	350.3	0.1	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	TKN	351.4	0.1	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	Nitrate-N	4110 <sup>(2)</sup>	0.1	mg/l	4°C	48 hours	composite
	Nitrite-N	4110 <sup>(2)</sup>	0.1	mg/l	4°C	48 hours	composite
	Electrical Conductivity		10	umhos/cm	4°C	ASAP	composite
	Hardness	130.2	2	mg/l	4°C	6 months	composite
Metals (total and dissolved)	Arsenic	206.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Barium	208.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Beryllium	210.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Cadmium	213.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Chromium	218.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Copper	220.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Iron	236.1	100	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Lead	239.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Mercury	245.1	0.1	ug/l	pH<2 HNO <sub>3</sub>	28 days	composite
	Nickel	249.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Selenium	270.2	0.2	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Silver	272.2	0.2	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Zinc	289.1	10	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
Organics	Diazinon	507	10	ng/l	4°C	7 days	composite
	Chlorpyrifos	507	50	ng/l	4°C	7 days	composite
	PAHs	Texas A&M	10 - 50	ng/l	4°C	7 days	composite
Toxicity	Sea Urchin Fertilization				4°C	72 hours	composite

<sup>(1)</sup> Temperature must be measured in the field immediately after taking the sample

<sup>(2)</sup> Standard Methods for the Examination of Water and Wastewater, 19th ed.

**TABLE 4-3**  
**SUGGESTED ANALYTE SUITE FOR LAND USE MONITORING STATIONS**

Class	Constituent	Method	Detection Limit	Units	Preservation	Holding Time	Sample Type
Conventional	O&G	413.2	1	mg/l	4°C	28 days	grab
	Cyanide	335.1	0.01	mg/l	4°C pH>12 NaOH 0.6 g ascorbic acid	14 days	grab
	pH			pH		ASAP	grab
	Temperature <sup>(1)</sup>			degrees C		Field	grab
Bacteria	Total Coliform	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
	Fecal Coliform	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
	Fecal Streptococcus	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
General	Phosphorus, total	365.3	0.05	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	Turbidity	180.1	1	NTU		48 hours	composite
	TSS	160.2	2	mg/l	4°C	7 days	composite
	TDS	160.1	2	mg/l	4°C	7 days	composite
	TPH	418.1	1	mg/l	4°C	28 days	grab
	BOD	405.1	4	mg/l	4°C	48 hours	composite
	COD	410.4	5	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	Ammonia-N	350.3	0.1	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	TKN	351.4	0.1	mg/l	4°C pH<2 H <sub>2</sub> SO <sub>4</sub>	28 days	composite
	Nitrate-N	4110 <sup>(2)</sup>	0.1	mg/l	4°C	48 hours	composite
	Nitrite-N	4110 <sup>(2)</sup>	0.1	mg/l	4°C	48 hours	composite
	Electrical Conductivity		10	umhos/cm	4°C	ASAP	composite
	Hardness	130.2	2	mg/l	4°C	6 months	composite
Metals (total)	Arsenic	206.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Barium	208.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Beryllium	210.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Cadmium	213.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Chromium	218.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Copper	220.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Lead	239.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Mercury	245.1	0.1	ug/l	pH<2 HNO <sub>3</sub>	28 days	composite
	Nickel	249.2	1	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Selenium	270.2	0.2	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Silver	272.2	0.2	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Zinc	289.1	10	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
Organics	Diazinon	507	10	ng/l	4°C	7 days	composite
	Chlorpyrifos	507	50	ng/l	4°C	7 days	composite
	PAHs	Texas A&M	10 - 50	ng/l	4°C	7 days	composite
Toxicity	Sea Urchin Fertilization				4°C	72 hours	composite

Temperature must be measured in the field immediately after taking the sample.  
Standard Methods for the Examination of Water and Wastewater, 19th ed.

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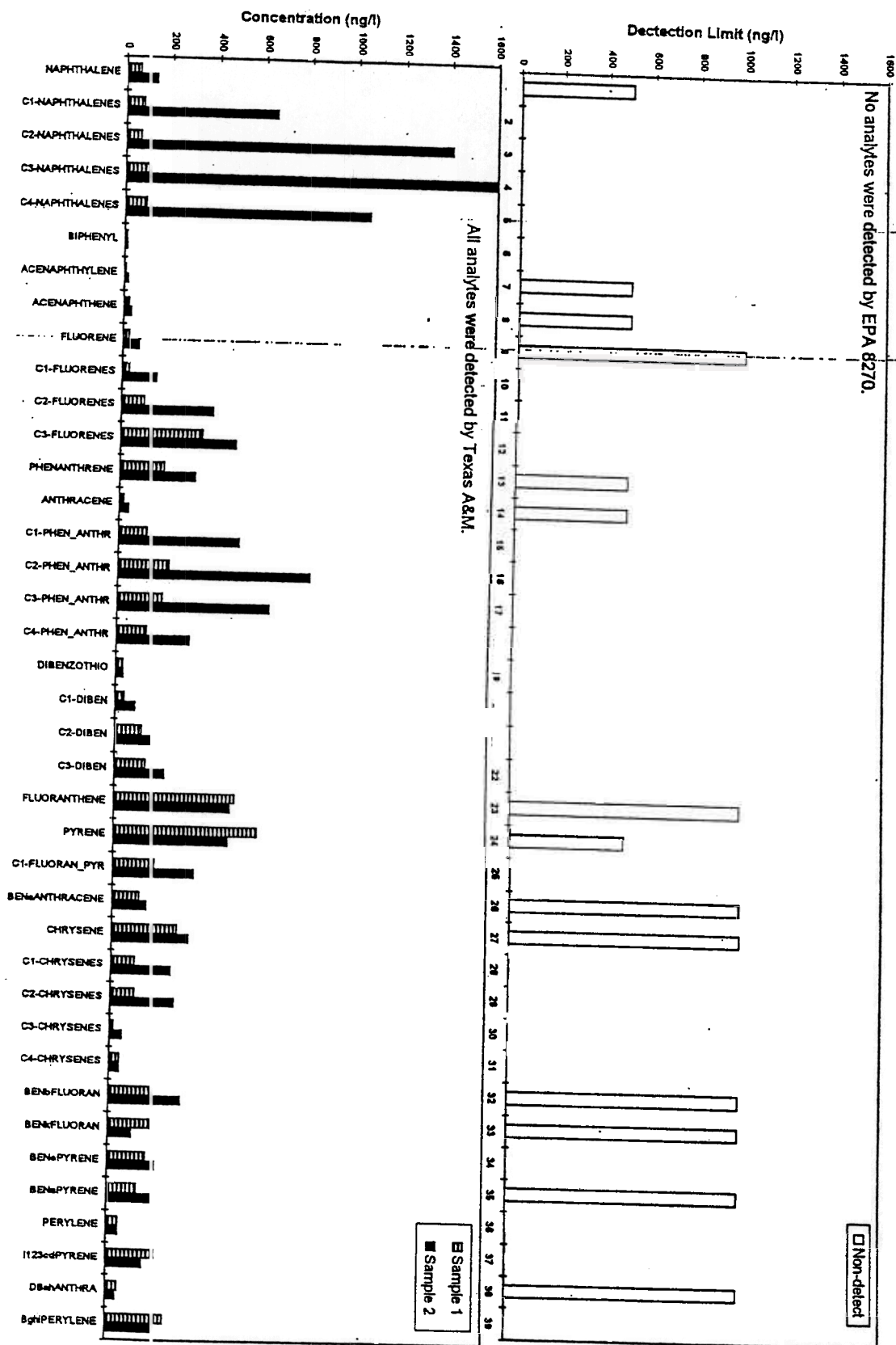
### 4.2.3 O&G, TPH, and PAHs

Oil and grease (O&G) compounds are operationally defined by the method of detecting them, that is the ability to detect and/or measure them by extracting them into an organic solvent, evaporating the solvent and measuring the number of carbon-hydrogen bonds using infra-red light (EPA Method 413.2) or weighing the residue (EPA Method 413.1). The O&G group is comprised of a variety of fatty compounds including petroleum hydrocarbons, vegetable oils, animal fats, etc. Total petroleum hydrocarbons (TPH) and total recoverable petroleum hydrocarbons (TRPH) are subsets of the O&G compounds (EPA Methods 8015M and 418.1, respectively). Polynuclear aromatic hydrocarbons (PAHs) are a specific group within the O&G class, which are dominated by ringed aromatic carbon structures. All PAHs have two or more rings, hence the name "polynuclear aromatic hydrocarbons". Potential sources of PAHs include petroleum products (raw and used motor oil, diesel, and gasoline) and combustion byproducts of petroleum hydrocarbons, wood, and other organic materials. Some PAHs, namely benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c)pyrene, and dibenzo(ah)anthracene, are known to be carcinogenic, and some exert outright toxicity, depending on their concentrations. The PAHs have been analyzed for by the SVOC method (EPA 625) in 1994/95 and 1995/96, but the SVOC method did not detect any.

Stormwater programs in Portland, Eugene, San Diego, and the San Francisco Bay Area have been utilizing a low-level detection method developed by Texas A&M. The peaks include both the parent molecules and the methylated molecules derived from them, which have similar environmental effects and are of similar concern. The Texas A&M method reports the concentrations of 39 individual compounds at detection levels of 0.01 - 0.05  $\mu\text{g/l}$  for each peak. The methylated PAH compounds currently are not regulated by the United States Environmental Protection Agency (EPA) or the San Francisco Basin Plan.

Figure 4-1 shows a plot presenting the concentrations for each of 39 individual compounds in two samples as measured by EPA Method 8270 (upper plot) and by the Texas A&M method (lower plot). The open bars represent the detection limits of EPA Method 8270 while the striped and solid bars represent the concentrations of specific PAHs as determined by the Texas A&M method. The relative abundance of the different compounds found in Sample #1 provides a "fingerprint" typical of urban runoff where the lighter, more volatile compounds (left of the plot) are present at very low concentrations due to weathering. This pattern was seen in most of the other samples collected in

FIGURE 4-1  
COMPARISON OF PAH DATA AVAILABLE FROM DIFFERENT METHODS



non-detect can not be dismissed as unimportant in the sample analyzed. Lower detection limits lead to greater accuracy at low concentrations, better estimates of mass emissions, and more accurate determination of risks to aquatic life and human health.

For many constituents (e.g., copper, lead, zinc) the laboratory currently utilized is capable of calibrating the instrument for the recommended detection limits using current EPA-approved analytical methods. However, for some organic constituents (e.g., PAHs, diazinon) the standard EPA approved methodology cannot achieve the recommended detection limits, even with modifications. There are laboratories which specialize in these low-level analytical techniques but the use of these methods would need to be negotiated with the RWQCB.

## **4.2 CHEMICAL AND PHYSICAL ANALYSES**

### **4.2.1 Metals, Anions, and Cations**

Metals that are considered pollutants of concern are recommended for analysis in mass emission stations (total and dissolved fractions) and land use stations (total fraction), at the detection limits specified (Tables 4-2 and 4-3). Other metals, anions, and cations that are neither toxic nor macronutrients are recommended only for special studies which require their analysis (Table 4-4). Iron, especially the fraction bound to particles, has an effect on the ratio between total and dissolved copper by providing binding sites for copper and decreasing the dissolved (toxic) fraction. It is recommended that iron be measured at mass emission stations and that "particulate iron" concentrations be calculated from total and dissolved data.

### **4.2.2 VOCs and SVOCs**

With the exception of bis(2-ethylhexyl)phthalate and other plasticizers, volatile and semivolatile organic compounds were not detected at the detection limits used in the past two years.

Continued monitoring of VOCs and SVOCs is not anticipated to yield any useful data. These methods may be appropriate for special studies or, in specified areas, in response to spills or mass discharges of organic constituents. Additionally, in accordance with the Permit, the LACDPW may exclude VOCs from the list of constituents [Attachment C, provision B(2)(b)] for mass emission monitoring sites.



**TABLE 4-4**  
**SUGGESTED ANALYTE SUITE FOR SPECIAL STUDIES**

Class	Constituent	Method	Detection Limit	Units	Preservation	Holding Time	Sample Type
Conventional	Total Phenols	420.1		mg/l	°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O	7 days	grab
	Dissolved Oxygen			mg/l	none required	immed.	grab
Bacteria and Viruses	Fecal Enterococcus	MTF	< 20	MPN/100 ml	4°C	6 hours	grab
	Enteric Viruses	9510 <sup>(1)</sup>	1	PFU	4°C	48 hours	grab
General	VSS	160.4		mg/l	4°C	7 days	
	TOC	415.1		mg/l	4°C pH<2 HCl or H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub>	28 days	
	MBAS	425.1		mg/l	4°C		
	Chloride	4110		mg/l	none required		
	Fluoride	4110		mg/l	none required	28 days	
	Sulfate	4110		mg/l	none required		
Metals (total and/or dissolved)	Aluminum	202.1	1000	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Antimony	204.2	10	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Boron	212.3	100	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Calcium	215.2	1000	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Iron	236.1	100	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Magnesium	3500 <sup>(1)</sup>	1000	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Manganese	243.1	100	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Potassium	258.1	1000	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Sodium	273.1	1000	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
	Thallium	279.1	10	ug/l	pH<2 HNO <sub>3</sub>	6 months	composite
Semivolatile Organic Compounds		8250	varies	ug/l	4°C	7 days	composite
Pesticides and PCBs		608	varies	ug/l	4°C	7 days	composite
		507	varies	ug/l	4°C	7 days	composite
Volatile Organic Compounds		8240	varies	ug/l	4°C	7 days	composite

<sup>(1)</sup> Standard Methods for the Examination of Water and Wastewater, 19th ed.



stormwater was consistently toxic to test organisms (*Ceriodaphnia dubia*, a small crustacean) and diazinon was identified as the cause, exhibiting toxicity at concentrations of 0.3 µg/l. Diazinon was detected in all samples tested from San Francisco Bay Area watersheds using LC/MS (a more sensitive method), sometimes at concentrations that are known to be toxic, while chlorpyrifos was detected less often. Diazinon is much more soluble (about 40 mg/l in water at 20° C) than chlorpyrifos (2 mg/l) and other pesticides used by homeowners.

#### **4.2.6 Bacteria**

The data reported previously does not specify the meaning of numbers reported as “higher than”, e.g., >1,600,000 MPN/100 ml. For all microbial parameters, it is recommended that stormwater samples be given sufficient decimal dilutions in the most probable number (MPN) method to provide definitive values. Results indicating the order of magnitude (e.g.,  $2.4 \times 10^3$ , or 2.4E+3) are easier to comprehend and use in statistical analysis where logarithmic transformations are desired. As for different species of human fecal indicators, it is recommended that the “traditional” indicators (total coliform, fecal coliform, and fecal streptococcus) be used in routine monitoring, and that other indicators be used in focused studies to answer specific questions, in coordination and possible collaboration with other agencies that conduct epidemiological studies. Specifically, coordination and consolidation with the Santa Monica Bay Restoration Project (SMBRP) Technical Advisory Committee beach testing may be beneficial to LACDPW.

#### **4.2.7 Toxicity Testing**

The sea urchin fertilization test specified in the Permit is a suitable toxicity test to predict the potential impact of stormwater runoff on marine receiving waters. The same test can also be used to predict problems associated with sediment contamination through the examination of sediment pore (interstitial) water samples.

### **4.3 SPECIAL STUDIES**

Special studies have been used to address a vast array of stormwater-related problems and questions, and in many situations have provided extremely valuable information at a relatively low cost. The most important features of special studies are their focused design and their being

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the San Francisco Bay Area in recent years. On the other hand, unusually high concentrations of naphthalene and its substituted derivatives (the original molecule with additional carbon sidechains) were seen at one of the monitoring stations (Sample #2) for one event. This may reflect fresh inputs of some light mixture such as diesel fuel, and could imply that a spill had occurred somewhere in the watershed. In comparison, the same data are plotted as if the sample had been analyzed by EPA Method 8270 at the detection limits previously used in the LACDPW Monitoring Program. This hypothetical analysis results in no detections for any PAHs.

Samples analyzed by EPA Method 8270 which are reported as non-detects may contain parent PAH molecules (e.g., naphthalene) at concentrations below the detection limit and/or substituted compounds at any concentration. For example, in Figure 4-1 compound 1 in the upper plot corresponds with naphthalene in the lower plot. Naphthalene, the parent molecule, is present at a concentration of about 150 ng/l in Sample #2 (lower plot), however it would go undetected if the sample had been analyzed by EPA Method 8270 with a detection limit of 500 ng/l (upper plot). Substituted naphthalene compounds, which have similar environmental effects as naphthalene, are present at concentrations ranging from about 650 ng/l to about 1600 ng/l in Sample #2 (lower plot). However, because EPA Method 8270 does not measure substituted PAHs, these naphthalene-derived compounds would go undetected in the hypothetical analysis pictured in the upper plot.

### 4.2.4 Chlorinated Pesticides and PCBs

Chlorinated pesticides and PCBs were not detected in any of the stormwater samples analyzed. Most of the compounds that this method (EPA 608) quantifies have been banned in the U.S. for years. They persist in the environment (very few bacteria have enzymes that can metabolize these synthetic molecules) and some can accumulate and bioconcentrate in the food chain. Although some of the banned chlorinated organics are retained in sediments, they are very insoluble and tend to stay attached to particles. If there is no massive resuspension of deep sediments in the watersheds, it is unlikely that these compounds will be detected in stormwater.

### 4.2.5 Organophosphorus Pesticides (OPs)

Organophosphorus pesticides have widely replaced chlorinated pesticides because they are broken down rather quickly in the environment and they are very effective (toxic to insects) at low concentrations. Unfortunately, these compounds are also very toxic to aquatic life, particularly to crustaceans and insect larvae. Routine analysis of stormwater in the San Francisco Bay Area using EPA Method 8140 at a detection limit of 1 µg/l consistently resulted in no detections. However,

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amenable to a tiered approach, in which each phase of the study is designed based on the conclusions drawn from the previous phase.

Table 4-4 includes the recommended methodology and detection limits for constituents that may be relevant to specific special studies. These constituents are not recommended for routine monitoring, either because they have not been detected in the past, or because it is not clear what the past detections actually meant and how such data could be used. Additional analytes could be chosen from Table 4-2 as desired.

For example, metals, anions, and cations that are not considered pollutants of concern have been quantified in the past and an extensive database has been compiled. If desired, the existing data could be analyzed and questions could be formulated based on that analysis. A special study could be designed, a limited study area selected, and new data analyzed to try to answer the formulated questions. Topics of interest may include ionic balance in stormwater, effects on speciation of trace metals, etc.

The background concentrations of trace metals within a watershed is of interest for many stormwater monitoring programs. For example, monitoring in the San Francisco Bay Area watershed indicated that peak concentrations of mercury and other metals were observed when the contribution of runoff and suspended solids from open land began, after the hills were saturated (Contra Costa Clean Water Program, 1995). An open space special study was designed to provide data that allowed comparison of metals concentrations in the runoff from open space, upper watershed areas with metals concentrations from the urban portion of the same watershed.

Plasticizers, particularly bis(2-ethylhexyl)phthalate, have typically been detected by stormwater monitoring programs that used EPA Method 8270. The plasticizers could be coming from the watershed, the sampling equipment, the laboratory reagents, or even from the laboratory distilled water. If deemed necessary, a focused, highly controlled special study could be conducted to identify the source of plasticizers, rather than extending monitoring resources to continue analyzing for plasticizers in all stormwater samples.

## Sampling Procedures

## 5.1 PREPARATION AND TRAINING

- be trained by experienced personnel in the use of all sampling equipment;  
maintain an adequate supply of sample bottles, coolers, ziplock bags, chain-of-custody forms, etc.;
- clean any equipment that will come into contact with the samples using laboratory grade soap (Alconox) and thoroughly rinse with distilled water;
- label all sample bottles prior to collection; and
- check all equipment to ensure that it is in proper working order.

## 5.2 SAMPLE COLLECTION

- Wear clean latex gloves and avoid contact with the inside of sample bottles, bottle caps, and sampling tubing.

Grab samples are collected for several analyses. The use of grab samples is intended to minimize the loss of PAHs and Oil and Grease (O&G) to the walls of the composite bottle and improve data quality. Bacterial samples must be collected directly into sterile sample containers. The *NPDES Storm Water Sampling Guidance Document* (EPA, July 1992) states:

“The regulations at 40 CFR 122.21(g)(7) identify certain pollutants for which grab sampling is required. Monitoring by grab sample must be conducted for pH, temperature, cyanide, total phenols, residual chlorine, O&G, fecal coliform, fecal streptococci. Composite samples are not appropriate for these parameters due to their tendency to transform to different substances or change in concentration after a short period of time. Such transformations may be particularly likely in the presence of other reactive pollutants.”

However, in accordance with the Permit, for land use monitoring sites the LACDPW may exclude constituents that require grab sampling [Attachment C, provision B(1)(d)].

All other recommended laboratory analyses are performed on aliquots of composite samples.

### **5.3 SAMPLE COMPOSITING AND DISPENSING**

The automatic samplers used by the LACDPW accommodate four bottles of 10 liters each that are filled in rounds during the storm event. This arrangement allows for collection of any volume up to 40 liters, and assures a good capture of the storm event even when it is not possible to accurately predict rainfall and storm duration. Moreover, it is not necessary to replace bottles during a storm event. Compositing is simple if the entire volume from each of the four bottles can be combined into one 10-liter bottle. However, if this is not the case, care must be taken to obtain representative subsamples for analysis.

Flow-weighted sampling results in larger volumes of sample being collected in high flow conditions as compared to low flow conditions. An accurate representation of the EMC can be obtained by combining equal percentages of the volume from each of the four bottles into one container. For example, if the four bottles contained 5L, 7L, 3L, and 4L, a representative sample

- Fill sample bottles directly from the stormwater discharge (if possible) or from the appropriate sample collection container. Dip the sample bottle or sample collection container into the center of flow with the opening facing upstream. Prevent the sample bottle or sample collection container from coming into contact with or collecting uncharacteristic floating debris or disturbed sediment.

Do not rinse or overfill sample bottles to prevent loss of any preservative (often an acid).

- Cap sample bottles tightly and place in a cooler for preservation.

Rinse sample collection containers with deionized water between sample collection sites and with local stormwater once immediately before beginning sample collection for the next site.

This process is intended to prevent cross-contamination between sites.

When it is not possible to collect a sample with the sample bottle, it is essential to use a sample collection container which will not contaminate the sample. In other words, do not use a metallic container to collect samples which will be analyzed for metals and don't use a plastic container to collect samples which will be analyzed for organics. Appropriate containers for the collection of organic samples include teflon bailers, bottles, or pump tubing; and metal buckets.

Some analyte concentrations will change over time unless the samples are preserved. Required sample containers, preservation techniques, and maximum holding times for various types of analytical parameters are provided in Tables 4-2, 4-3, and 4-4.

Samples must be tracked from the time of collection through laboratory analysis. All sample custody and transfer procedures will be based on EPA-recommended procedures for documenting sample collection and handling processes. Chain-of-custody forms will be used to document the relevant information for each sample bottle and the transfer of bottles to the laboratory.

Two types of samples are collected in stormwater monitoring programs: grab and composite. A grab sample represents a snapshot at one point in time during an event, while a flow-weighted composite sample provides the event mean concentration (EMC) for parameters analyzed and provides the best overall representation of analyte concentrations resulting from the storm event.

could be obtained by combining 50% of the sample from each bottle into a fifth 10-liter bottle. In this case, 2.5L, 3.5L, 1.5L, and 2L would be combined for a total composite sample of 9.5L.

Since most stormwater pollutants are known to be adsorbed to particulate matter to some extent, it is important to obtain a representative distribution of suspended solids when samples are composited and subsequently subsampled into different aliquots. Failure to do so may affect the observed ratio between dissolved and total metals, the toxicity of dissolved substances, and the observed relationships between various analytes. Representative subsamples can be obtained by siphoning each composite sample into the subsample containers in small, repetitive increments while constantly stirring the composite sample.

## **5.4 SHIPPING**

Samples must be properly packed to eliminate the possibility of breakage or contamination. The appropriate shipping or transport procedures are as follows:

Place blue ice (frozen) or regular ice (in ziplock bags) in the cooler to maintain sample temperature at 4°C.

- Wrap glass sample bottles in bubble wrap or similar protective material to eliminate movement and breakage during transport. Plastic bottles do not need to be wrapped. Make sure all caps are tightened.

Verify that filled sample bottles correspond to the completed chain-of-custody form.

- Place all sample bottles securely in the cooler. Enclose sampling records (including chain-of-custody forms) in a ziplock bag inside the cooler.
- Deliver samples to the laboratory immediately.

## SECTION SIX

## Quality Assurance/Quality Control Plan

A Quality Assurance/Quality Control (QA/QC) plan is an important component of a stormwater monitoring program involving field sampling and laboratory analyses. Because of the inherent variability in stormwater samples, it is important to minimize additional variability introduced by sample collection, handling, and analytical techniques. It is also important to minimize inaccuracy introduced by contamination or poor calibration of laboratory instruments. This section reviews current QA/QC practices and presents specific recommendations for QA/QC procedures to be performed as part of the Monitoring Program.

The objectives of a QA/QC plan are threefold: (1) to assure completeness, i.e., all elements of a stormwater monitoring program are conducted, (2) to help identify and minimize potential sources of introduced error in the stormwater sampling and analysis process, and (3) to assure that reported results meet data quality objectives of accuracy, precision, sensitivity, and detection limits. Implementation of a sound QA/QC plan ensures that the data collected are of high quality and defensible in regulatory proceedings.

### 6.1 FIELD QA/QC SAMPLES

Field QA/QC procedures include the collection and analysis of predeployment blanks, field blanks, and field duplicates.

*Predeployment Blanks:* Potential sample contamination due to sample collection equipment is assessed through the collection and analysis of predeployment blanks. At the beginning of the storm season, all sample collection tubing should be cleaned. A predeployment blank for each set of sample collection tubing (all tubing associated with one sampler or pump is a set) should be collected and analyzed. Clean reagent-grade laboratory water is pumped through the clean tubing, collected in sample bottles, labeled as "predeployment blanks", and analyzed. Results are checked prior to the deployment and if not clean, equipment is recleaned until acceptable blanks are achieved.

- *Field Blanks:* Potential sample contamination due to sample handling and storage methods is assessed through the collection and analysis of field blanks. Clean reagent-grade laboratory water is collected using the standard sampling procedure (where possible), labeled as "field blank", and analyzed. If the standard collection procedure at a site utilizes fixed intake lines, predeployment blanks rather than field blanks are collected and analyzed. One field blank should be collected for each storm event from one of the sites sampled during that event.



- *Field Duplicate:* Sample representativeness, accuracy, and precision are assessed through the collection and analysis of duplicate stormwater samples. Accuracy refers to how close the measured value is to the true value. Precision reflects the reproducibility of a measurement; how close repeated measurements are to one another. An additional set of grab sample bottles are collected at the chosen QA/QC site, labeled, and analyzed. All grab sample duplicates are treated as "blind field" duplicates and given a fictitious station identification and collection time. For those water quality parameters being analyzed with flow-weighted composites, sample duplicates are prepared by the laboratory by replicate subsampling of the composite bottle. Field duplicates should be collected from one site during one storm event of the season.

## **LABORATORY PROCEDURES**

In order to assure quality data, the laboratory must strictly adhere to QA/QC protocols conforming to or exceeding those set forth in EPA/DOHS guidelines. Specifically, the laboratory must follow all QA/QC procedures outlined in their QA/QC manual. This manual includes equipment calibration procedures, preventative maintenance, data validation procedures, and corrective actions. Required quality control procedures, as given in the laboratory QA/QC manual, are summarized in Tables 6-1a through 6-1d. Every effort to meet target detection limits, holding times, and sample preservation techniques must be made by the laboratory.

## **INDEPENDENT QA/QC EVALUATION**

The accuracy and precision of the stormwater data should be evaluated. The evaluation should include a review of the results of field QA/QC samples as well as the following aspects of laboratory procedures and analytical performance: holding times, method blanks, duplicates, matrix spikes and matrix spike duplicates, surrogate recoveries, laboratory control samples, and standard reference materials as required by the specific analytical method used.

- *Holding Time:* Analytical methods have an associated prescribed holding time, that is the maximum amount of time after collection that a sample may be held prior to extraction and/or analysis. Sample integrity becomes questionable for samples extracted and/or analyzed outside of the holding times due to physical and chemical changes to the sample (e.g. degradation or volatilization). The results of such analyses are suspect. Sample preparation

**TABLE 6-1a**  
**LABORATORY'S ANALYTICAL QUALITY CONTROL REQUIREMENTS FOR WASTEWATER**

Reference	MICROBIOLOGICAL ANALYSES	Sterility Control	Positive Control	Air Control	API 20E (for ≥5%)	Completed Test	Duplicate Samples
Frequency of Analyses						(Quarterly or all +)	(for 10% of samples)
	(OF WASTEWATER)						
BB9221B	Total Coliforms by MTF	✓	✓				✓
BB9221C	Fecal Coliforms by MTF	✓	✓				✓
BB9222B	Total Coliforms by MF	✓ (before and after each run)	✓ (before each run)				✓
BB9222D	Fecal Coliforms by MF	✓ (before and after each run)	✓ (before each run)				✓
BB9230B	Fecal Streptococci/Enterococci by MTF	✓	✓				✓
BB9230C	Fecal Streptococci/Enterococci by MF	✓	✓				✓

**TABLE 6-1d**  
**LABORATORY'S ANALYTICAL QUALITY CONTROL REQUIREMENTS FOR WASTEWATER**

Reference	ORGANIC ANALYSES	Calibration Curve <sup>14</sup>	Laboratory Blank <sup>15</sup>	Laboratory Fortified Blank <sup>16</sup>	Laboratory Fortified Matrix <sup>17</sup>	Laboratory Fortified Matrix Dup. <sup>18</sup>
Frequency of Analyses		Each Analyses	Each Analyses	Each Analyses	Each Analyses	Each Analyses
EPA 601	Volatile Halogenated Compounds	3-point	✓	✓	✓	✓
EPA 602	Volatile Aromatic Compounds	3-point	✓	✓	✓	✓
EPA 603	Acrolein, Acrylonitrile	3-point	✓	✓	✓	✓
EPA 604	Phenols	3-point	✓	✓	✓	✓
EPA 605	Benzidine	3-point	✓	✓	✓	✓
EPA 606	Phthalate esters	3-point	✓	✓	✓	✓
EPA 607	Nitrosamines	3-point	✓	✓	✓	✓
EPA 608	OrgAnochlorines/PCBs	3-point	✓	✓	✓	✓
EPA 609	Nitroaromatics and Cyclic Ketones	3-point	✓	✓	✓	✓
EPA 610	Polynuclear Aromatics	3-point	✓	✓	✓	✓
EPA 632	Carbamates	3-point	✓	✓	✓	✓
EPA 619	Triazine Pesticides	3-point	✓	✓	✓	✓
EPA 608	PCBs only	3-point	✓	✓	✓	✓
EPA 608	Pesticides Only	3-point	✓	✓	✓	✓
EPA 624	Volatile Organic Compounds by GCMS	3-point	✓	✓	✓	✓
EPA 625	BNA by GCMS	3-point	✓	✓	✓	✓

14. It is assumed that external standard calibration is performed. The number of calibration standards given is the minimum recommended by the specific method. Consult individual methods for recommended standard concentrations. Run a standard check every 15 samples and at the end of each run.

15. A laboratory blank is DI water processed the same way as an actual sample.

16. A laboratory fortified blank (LFB) is DI water spiked with the analyte of interest at 10 times the MDL (method detection limit) or at MCL (maximum contaminant level) whichever is less.

17. A laboratory fortified matrix (LFM) is an actual sample spiked with the analyte of interest at 10 times MDL or MCL concentrations whichever is less.

18. A laboratory fortified matrix duplicate (LFMD) is identical to the LFM.

**TABLE 6-1b**  
**LABORATORY'S ANALYTICAL QUALITY CONTROL REQUIREMENTS FOR WASTEWATER**

Reference	INORGANIC CHEMISTRY, NUTRIENTS, & DEMAND	Calibration Curve <sup>1</sup>	Method Standard <sup>2</sup>	Matrix Spike <sup>3</sup>	Matrix Spike Dup <sup>4</sup>	Duplicate Analyses <sup>5</sup>	Reagent Blank <sup>6</sup>	External Reference <sup>7</sup>
Frequency of Analyses		Each Analyses	Each Analyses	5% for WW 10% for DW		5% for WW 10% for DW	Each Analyses	Each Analyses
A310.1	Alkalinity					✓		
A350.3-3	Ammonia	✓		✓	*	✓		✓
A405.1	BOD			✓	*	✓		
A212.3	Boron	✓		✓	*	✓		✓
A215.2	Calcium				*	✓		
A410.4	COD	✓		✓	*	✓		✓
B429	Chloride	✓		✓	*	✓		✓
A335.2	Cyanide	✓	✓	✓	✓	✓	✓	✓
BB4110B	Fluoride	✓		✓	*	✓		✓
A130.2	Hardness				*	✓		
A351.3-4	Kjeldahl Nitrogen	✓	✓	✓	✓	✓	✓	✓
BB3500M	Magnesium				*	✓		
A425.1	MBAS	✓		✓	*	✓		✓
BB4110B	Nitrate	✓		✓	*	✓		✓
BB4110B	Nitrite	✓		✓	*	✓		✓
A413.1	Oil and Grease				*	✓	✓	
A415.1	Organic Carbon, Total	✓		✓	*	✓		✓
A150.1	pH	✓		✓	*	✓		✓
A420.1	Phenols	✓	✓	✓	✓	✓	✓	✓
BB4110B	Phosphate, Ortho	✓		✓	*	✓		✓
A365.2	Phosphorus, Total	✓		✓	*	✓		✓
A258.1	Potassium	✓		✓	*	✓		✓
A273.1	Sodium	✓		✓	*	✓		✓
A120.1	Specific Conductance	✓		✓	*	✓		✓
BB4110B	Sulfate	✓		✓	*	✓		✓
A160.1	Total Dissolved Solids (TDS)				*	✓	✓	
A160.5	Total Settleable Solids				*	✓		
A160.2	Total Suspended Solids				*	✓	✓	
A160.4	Volatile Suspended Solids				*	✓	✓	
A418.1	TPH	✓		✓	*	✓		✓
A180.1	Turbidity	✓		✓	*	✓		✓

1. A calibration curve is required for all spectrophotometric, ISE, IC, and automated wet chemical methods. See QA Manual for calibration curve requirements. Run a standard check every 15 samples or at the end of the run.
2. Two calibration standards (high and low concentration) must be taken through the complete analytical process to verify the reliability of the technique.
3. Matrix spike recovery analysis is not required for gravimetric or titrimetric methods. Spiked level should not exceed action level, if established, or should be at midrange standard.
4. For analyses with an asterisk (\*), duplicate matrix spike is recommended, not required.
5. Replicate analyses of actual sample is required for all analyses performed.
6. A reagent blank (method blank) is DI water processed the same way as an actual sample.
7. An external reference sample should be run with each sample batch.

**TABLE 6-1c**  
**LABORATORY'S ANALYTICAL QUALITY CONTROL REQUIREMENTS FOR WASTEWATER**

Reference	TOXIC CHEMICAL ELEMENTS	Calibration Curve <sup>8</sup>	Method Blank <sup>9</sup>	Duplicate Analyses <sup>10</sup>	Matrix Spike <sup>11</sup>	Matrix Spike Dup. <sup>12</sup>	External Reference <sup>13</sup>
Frequency of Analyses		Each Analyses	Each Analyses	5% for WW 10% for DW	5% for WW 10% for DW		Each Analyses
A202.2	Aluminum	✓	✓	✓	✓	See note 12	✓
A204.2	Antimony	✓	✓	✓	✓	See note 12	✓
A206.2	Arsenic	✓	✓	✓	✓	See note 12	✓
A208.2	Barium	✓	✓	✓	✓	See note 12	✓
A210.2	Beryllium	✓	✓	✓	✓	See note 12	✓
A213.2	Cadmium	✓	✓	✓	✓	See note 12	✓
A218.6	Chromium (VI)	✓	✓	✓	✓	See note 12	✓
A218.2	Chromium, Total	✓	✓	✓	✓	See note 12	✓
A219.2	Cobalt	✓	✓	✓	✓	See note 12	✓
A220.1	Copper	✓	✓	✓	✓	See note 12	✓
A236.1	Iron	✓	✓	✓	✓	See note 12	✓
A239.2	Lead	✓	✓	✓	✓	See note 12	✓
A243.1	Manganese	✓	✓	✓	✓	See note 12	✓
A245.1	Mercury	✓	✓	✓	✓	See note 12	✓
A246.2	Molybdenum	✓	✓	✓	✓	See note 12	✓
A249.2	Nickel	✓	✓	✓	✓	See note 12	✓
A270.2	Selenium	✓	✓	✓	✓	See note 12	✓
A272.2	Silver	✓	✓	✓	✓	See note 12	✓
B326A	Strontium	✓	✓	✓	✓	See note 12	✓
A279.2	Thallium	✓	✓	✓	✓	See note 12	✓
A282.2	Tin	✓	✓	✓	✓	See note 12	✓
A283.2	Titanium	✓	✓	✓	✓	See note 12	✓
A286.2	Vanadium	✓	✓	✓	✓	See note 12	✓
A289.1	Zinc	✓	✓	✓	✓	See note 12	✓

8. A calibration curve must be established for each analyses from a calibration blank and a minimum of three standards. A calibration blank is DI water with the same amount of acids or other reagents as the actual samples and standards. Run a standard check every 15 samples or at the end of the run.

9. A method blank is DI water processed the same way as an actual sample.

10. Replicate analyses of actual sample is required for all analyses performed.

11. Samples should be spiked at levels not exceeding the action level or maximum contaminant level (MCL) for the analyte. Spiking standard must be from a source separate from the calibration standard.

12. Duplicate matrix spike is recommended, not required.

13. An external reference sample should be run with each sample batch.

and holding times prior to analysis should be reviewed for exceedances of the method prescribed holding times. For composite samples, the holding time begins when the last portion of the sample is taken. For example, a composite sample which is collected from 8:00 am on Thursday to 6:00 pm on Friday has a holding time which begins on Friday at 6:00 pm.

*Method Blanks:* Potential sample contamination due to laboratory contamination (e.g. contaminated reagents, improperly cleaned laboratory equipment, or persistent contamination due to the presence of certain compounds in the ambient laboratory air) can be assessed through the analysis of method blanks. Method blanks consist of deionized, distilled water that is extracted and analyzed as a sample. Method blanks are also called laboratory blanks. One method blank should be analyzed per analytical batch per matrix type for the appropriate methods.

- *Duplicates:* An evaluation of analytical precision can be obtained through the analysis of duplicates. Duplicates are two aliquots of the same sample that are analyzed for the same constituent. The relative percent difference (RPD) between the duplicates is calculated by dividing the difference between the results by the average of the results as a percentage. Duplicate RPDs are reviewed to assure that they are below the control limit (20%). Duplicates should be analyzed on a 5% basis for the appropriate methods.

*Matrix Spike and Matrix Spike Duplicates (MS/MSD):* An evaluation of analytical accuracy and precision can be obtained through the analysis of matrix spikes and matrix spike duplicates. Matrix spikes are necessary because matrix interference (interference from the sample matrix - water, soil, or other) may have widely varying impacts on the accuracy and precision of the sample analysis. A sample aliquot is spiked with a known quantity of the analyte, then it is extracted and analyzed. The results of the analysis are compared with the known additions and a matrix spike recovery is calculated. The recovery gives an evaluation of the accuracy of the extraction and analysis procedures. Typically matrix spikes are performed in duplicate in order to also evaluate the precision of the methods. Matrix spike recoveries are reviewed to assure that they are within the acceptable range (80% to 120%). Matrix spike RPDs are reviewed to assure that they are below the control limit (20%). The frequency suggested is one MS/MSD pair per analytical batch for each analyte for the appropriate methods.

- *Surrogate Recoveries:* Surrogates of complex organics are added to samples to monitor the effect of the matrix on the accuracy of the analysis. Accuracy refers to how close the measured value is to the true value. Surrogate spikes are compounds very similar to target



analytes, but are not normally found in environmental samples. Surrogates should be spiked into every method blank, laboratory control sample, sample, and MS/MSD for the organic compounds for which they are used.

*Laboratory Fortified Matrices:* Laboratory Fortified Matrices can be used to monitor the accuracy of a given method. The laboratory fortified matrix is prepared similarly to the matrix spike, except a fortified matrix (contaminant free) is used in place of the sample matrix. The recovery of the laboratory fortified matrix spike gives an evaluation of laboratory accuracy independent of matrix interference. Laboratory fortified matrices are used to determine the overall performance of methods used. Laboratory fortified matrix recoveries are reviewed to assure that they are within the acceptable range (80% to 120%). Laboratory fortified matrices should be analyzed once per analytical batch for the appropriate methods.

- *External References:* External References are samples of known concentrations from a source external to the laboratory, and are used to provide a measure of the accuracy of the analytical methods used by the laboratory. External reference recoveries are reviewed to assure that they are within the acceptable range (80% to 120%). External references should be analyzed once per analytical batch for the appropriate methods.

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