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**A STUDY OF POLLUTANTS FROM THE BALLONA CREEK
WATERSHED AND MARINA DEL REY DURING WET WEATHER FLOW**

**Part 1. Pollutants Associated With Suspended Solids From The Ballona
Creek Watershed And Marina Del Rey**

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EXECUTIVE SUMMARY

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	A.2
TABLE OF CONTENTS	A.3-A.6
APPENDICES	A.6
LIST OF TBLES	A.7
LIST OF FIGURES	A.8-A.13
PROJECT ORGANIZATION AND RESPONSIBILITIES	1
1.0 INTRODUCTION	2
2.0 DESCRIPTION OF SAMPLING SITES	6
2.1 Upstream Sites	6
2.1.1 Ballona Creek	6
2.1.2 Sepulveda Channel	6
2.1.3 Centinela Channel	6
2.2 Downstream Sites	7
2.2.1 Ballona Creek	7
2.2.2 Marina Del Rey	7
3.0 EXPERIMENTAL METHODS	7
3.1 Sampling Methodology	7
3.2 Analytical Methods	7
3.2.1 Filtration and Storage	7
3.2.2 Water Quality	12
3.2.3 Total Organic Carbon (TOC)	13
3.2.4 Trace Organic Analyses	13
3.2.4.1. Isolation of Acid/Base Neutral Compounds from Aqueous Phase	17
3.2.4.2. Supercritical Fluid Extraction (SFE) of Suspended Solids	17
3.2.4.3. Analysis of Semi-Volatile Extracts by GC/MS, EPA Method 525/625*	17

3.2.4.4.	Chlorinated Pesticides and PCB Analysis By EPA Method 608	20
3.2.4.5	Screening of the Aqueous Phase for Hydro- phobic Organics	21
3.2.5	Metals Analyses	24
3.2.5.1	Digestion of Suspended Solids	24
3.2.5.2	ICP/AE Analysis	26
3.2.5.3	Metals Recovery Experiments	26
3.2.6	Facilities and Equipment	27
4.0	RESULTS AND DISCUSSION	29
4.1	Stormwater Runoff Flow Data	29
4.2	Summary of Stormwater Sampling	30
4.3	Water Quality Results	30
4.3.1	General Water Quality Data	30
4.3.2	Dissolved Organic Carbon Results	31
4.3.3	Suspended Solids Data	38
4.4	Screening of Water Phase for PAHs	43
4.5	Organic Pollutants Associated of Suspended Solids from Upstream Sites: Ballona Creek, Sepulveda Channel and Centinela Channel	46
4.5.1	Analytical Recovery Data - Quality Assurance	46
4.5.2	Identification of Target Base-Neutral Semivolatile Organic Compounds in Wet Weather Flow	47
4.5.3	Relative Contribution of Organic Pollutants from Ballona Creek, Sepulveda Channel and Centinela Channel	48
4.5.4	Estimated Total Mass of PAHs and Phthalates Transported by Ballona Creek During Selected Storm Events	67
4.5.5	Comparison of PAH, Phthalate, and Suspended Solid Loads in Stormwater Runoff as a Function of Sampling Times	73

4.5.6	Analyses of Suspended Solids for Organochlorine Compounds	79
4.6	Tidal Influence on Stormwater Runoff Flow	81
4.6.1	Ballona Creek - Marina Del Rey Hydrodynamics	81
4.6.2	Tidal Influence on Conductivity	86
4.7	Organic Pollutants Associated with Suspended Solids in Stormwater from the Downstream Locations	86
4.7.1	Marina Del Rey vs. Ballona Creek at Pacific Ave Bridge	86
4.8	Results of Metals Analysis	98
4.8.1	Overview	98
4.8.2	Zinc Data	99
4.8.3	Concentrations of Metals in Stormwater Runoff	102
4.8.3.1	Aqueous Phase	102
4.8.3.2	Suspended Solids	105
4.8.3.3	Relative Total Metals Contributions at the Upstream Sites - Sepulveda Channel, Centinela Channel and Ballona Creek	115
4.8.4	Relative Total Metals Concentrations at the Downstream Sites - Ballona Creek vs. Marina Del Rey	126
4.8.5	Mass Transport Estimates for Lead in Stormwater	126
4.8.6	General Discussion	133
5.0	CONCLUSIONS	135
5.1	Conclusions: Stormwater Runoff Flow Data	136
5.2	Conclusions: General Water Quality Data	136
5.3	Conclusions: Trace Organics Data - Upstream Sites	136
5.4	Conclusions: Trace Organics Data - Downstream Sites	136
5.5	Conclusions: Metals Data - Upstream Sites	137
5.6	Conclusions: Metals Data - Downstream Sites	137
6.0	Future Considerations	137
7.0	REFERENCES	138

**A STUDY OF POLLUTANTS FROM THE BALLONA CREEK
WATERSHED AND MARINA DEL REY DURING WET WEATHER FLOW**

**Part 1. Pollutants Associated With Suspended Solids From The Ballona
Creek Watershed And Marina Del Rey**

APPENDICES

Appendix A. Stormflow Data From the Ballona Creek Monitoring Station

**Appendix B. Organic Target Compound Sampling Data for Upstream
Sampling Performed in the Ballona Creek Watershed**

**Appendix C. Data of the Metals in Stormwater From the Ballona Creek
Watershed.**

**A STUDY OF POLLUTANTS FROM THE BALLONA CREEK
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**Part 1. Pollutants Associated With Suspended Solids From The Ballona
Creek Watershed And Marina Del Rey**

LIST OF TABLES

	<u>Page</u>
1. Field and Sampling Parameters	9
2. Laboratory Analysis Parameters	10
3. Minimum Detection Limit (MDLs) and Standards for Drinking Water and the California Ocean Plan and ERLs and ERMs for Target Acid/Base Neutral and Organochlorine Compounds by the Upgraded EPA Method 608/625*	14-16
4. The 16 Polynuclear Aromatic Hydrocarbons (PAHs) Screened for in the stormwater aqueous phase using EPA Method 550.1.	23
5. A List of the Regulated and Non-Regulated Metal Analytes in this Study. Included Are Their Respective Wavelength Used for Quantitation MDLs, ERLs, ERMs, MCLs and CTLs.	25
6. Suspended Solids and Sediments Metals Recovery Data (EPA Method 3050b)	28
7. Relative Mass Loads on a Per Volume Basis of PAHs and Phthalates in Stormwater From Selected Storms During The 1995-96 Wet Weather Season.	46
8. A Comparison of Suspended Solid, PAH and Phthalates Concentration in Stormwater Samples as a Function of Sampling Time	74
9. Concentration of Metals in Suspended Solid Evaluated in Terms of Potential for Toxicity to aquatic Biota Bases on sediment ERMs and ERLs (Long et al., 1995)	100
10. A Comparison Among Some of the Results from this Study, the Water Quality Objectives in the California Ocean Plan, and Equivalent Pollution Contributions from the Effluent of a Major Point-Source Discharger to the Santa Monica Bay.	134

WATERSHED AND MARINA DEL REY DURING WET WEATHER FLOW

Part 1. Pollutants Associated With Suspended Solids From The Ballona Creek Watershed And Marina Del Rey

LIST OF FIGURES

	<u>Page</u>
1. A Map showing the location of the upstream sampling sites: (1) Sepulveda Channel at Culver Blv'd., (2) Ballona Creek at Sawtelle and (3) Centinela Channel at Centinela Ave. (US-ACE Marina Del Rey and Ballona Creek, Final Reconnaissance Report, 1995).	3
2. A map showing the locations of the downstream sampling sites: Pacific Ave Bridge and Marina Del Rey, Front and Back (US-ACE Marina Del Rey and Ballona Creek, Final Reconnaissance Report, 1995).	4
3a. Aqueous phase dissolved organic carbon data for filtered stormwater samples from the Ballona Creek watershed. Data is for November 1995 through January 1996.	34
3b. Aqueous phase dissolved organic carbon data for filtered stormwater samples from the Ballona Creek watershed. Data is for February and March 1996.	35
4a. Total organic carbon data for the suspended solids phase from stormwater samples collected during the January 1996 storm event.	36
4b. Total organic carbon data for the suspended solids phase from stormwater samples collected during the March 1996 storm event.	37
5a. Total suspended solids data for stormwater samples collected in the Ballona Creek Watershed. Samples from various sites for storms from December 1995 through January 1996.	39
5b. Total suspended solids data for stormwater samples collected in the Ballona Creek Watershed. Samples from various sites for storms from December 1995 through January 1996.	40
6a. Stormwater flow for the January 31, 1996 storm by the Ballona Creek monitoring station and suspended sediment load from the upstream samples at the locations specified.	41
6b. Stormwater flow for the March 4-5, 1996 storm by the Ballona Creek monitoring station and suspended sediment load from the upstream samples at the locations specified.	42
7.a. HPLC chromatogram of a standard solution of the 16 PAHs screened for in the aqueous phase.	44
7.b. HPLC chromatogram of a representative aqueous phase extract of a stormwater sample from the 12/13/95 storm event.	45

8. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.	49
9. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total PAH mass concentration from upstream samples at the locations specified.	50
10. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.	51
11. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate mass concentration from upstream samples at the locations specified.	52
12. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.	53
13. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from upstream samples at the locations specified.	54
14. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.	55
15. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate mass concentration from upstream samples at the locations specified.	56
16. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.	57
17. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from upstream samples at the locations specified.	58
18. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.	59
19. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total phthalate mass load concentration from upstream samples at the locations specified.	60
20. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.	61
21. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration	

from upstream samples at the locations specified.	62
22. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.	63
23. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total phthalate mass load concentration from upstream samples at the locations specified.	64
24. Diagram illustrating the methodology utilized to estimate total PAH transport at Ballona Creek at Sawtelle Blvd during the storm which occurred January 31, 1996.	69
25. Diagram illustrating the methodology utilized to estimate total phthalate transport at Ballona Creek at Sawtelle Blvd during the storm which occurred January 31, 1996.	70
26. Diagram illustrating the methodology utilized to estimate total PAH transport at Ballona Creek at Sawtelle Blvd during the storm which occurred March 4-5, 1996.	71
27. Diagram illustrating the methodology utilized to estimate total phthalate transport at Ballona Creek at Sawtelle Blvd during the storm which occurred March 4-5, 1996.	72
28. A plot of the PAH concentration in suspended solids from the three upstream sites as a function of sampling time for the storm events sampled during the 1995-96 wet season.	75
29. A plot of the PAH concentration in stormwater from the three upstream sites as a function of sampling time for the storm events sampled during the 1995-96 wet season.	76
30. A plot of the Phthalates concentration in suspended solids from the three upstream sites as a function of sampling time for the storm events sampled during the 1995-96 wet season.	77
31. A plot of the Phthalates concentration in stormwater from the three upstream sites as a function of sampling time for the storm events sampled during the 1995-96 wet season.	78
32. Plot of total organochlorine pesticides and PCBs in suspended solids from stormwater runoff samples collected at various sites in the Ballona Creek Watershed.	80
33. Stormwater flow stagnation at Ballona Creek under high tide conditions.	83
34. Stormwater flow from Ballona Creek under low tide conditions.	84
35. Stormwater flow from Ballona Creek during maximum flow and flood tide conditions.	85

36. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and conductivity of samples taken in Ballona Creek at Pacific Ave.	87
37. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and conductivity of samples taken in Ballona Creek at Pacific Ave.	88
38. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	90
39. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	91
40. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	92
41. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	93
42. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	94
43. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	95
44. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	96
45. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marin Del Rey Harbor.	97
46. A plot of aqueous lead concentration and conductivity vs. time for samples collected from Ballona Creek at Pacific Ave bridge during the December 12-13, 1995 Storm event.	103
47. A plot of aqueous lead concentration and conductivity vs. time for samples collected from Ballona Creek at Pacific Ave bridge during the	

February 19-22, 1996 Storm event.	104
48. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Sawtelle Blvd. during the January, 1996 storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	106
49. Lead concentrations in stormwater suspended solids for samples collected from Sepulveda Channel at Culver Blvd. during the January, 1996 storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	107
50. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave. during the January, 1996 storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	108
51. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Sawtelle Blvd. during the February 1996. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	109
52. Lead concentrations in stormwater suspended solids for samples collected from Sepulveda Channel at Culver Blvd. during the February, 1996. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	110
53. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the February, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	111
54. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	112
55. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	113
56. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	114
57. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Pacific Ave bridge during the January, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM's, and CTLs to assist in data evaluation.	116
58. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Front) during the January, 1996 Storm. Also plotted	

are the runoff hydrograph for Ballona Creek, the ERLs, ERM, and CTLs to assist in data evaluation.	117
59. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Back) during the January, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM, and CTLs to assist in data evaluation.	118
60. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Pacific Ave bridge during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM, and CTLs to assist in data evaluation.	119
61. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Front) during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM, and CTLs to assist in data evaluation.	120
62. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Back) during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM, and CTLs to assist in data evaluation.	121
63. Streamflow data from January 31, 1996 as measured at Ballona Creek metering station. Total lead concentration for all the upstream sites including chronic toxicity and drinking water standards are plotted against time.	122
64. Streamflow data from February 19-21, 1996 as measured at Ballona Creek metering station. Total lead concentration for all the upstream sites including chronic toxicity and drinking water standards are plotted against time.	123
65. Streamflow data from March 4-5, 1996 as measured at Ballona Creek metering station. Total lead concentration for all the upstream sites including chronic toxicity and drinking water standards are plotted against time.	124
66. Total lead concentration and conductivity of water samples collected from Ballona Creek at the Pacific Ave Bridge during the January 1996 storm event.	127
67. Total lead concentration in water samples collected from Marina Del Rey (Front) during the January, 1996 storm event.	128
68. Total lead concentration in water samples collected from Marina Del Rey (Back) during the January, 1996 storm event.	129
69. Total lead concentration and conductivity of water samples collected from Ballona Creek at the Pacific Ave Bridge during the March 1996 storm event.	130
70. Total lead concentration in water samples collected from Marina Del Rey (Front) during the March, 1996 storm event.	131
71. Total lead concentration in water samples collected from Marina Del Rey (Back) during the March, 1996 storm event.	132

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PROJECT ORGANIZATION AND RESPONSIBILITY

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1.0 INTRODUCTION

During the 1995-1996 rainy season a study of the pollutants associated with suspended solids in stormwater runoff was conducted in an effort to understand the types and quantity of pollutants entering Santa Monica Bay via wet weather flow. It has become clear in recent years that urban stormwater runoff is a major contributor of non-point source pollution to the Santa Monica Bay.

This study focused on the Ballona Creek and its two major tributaries, Centinela Channel and Sepulveda Channel. (Figure 1; ~~US-ACE Marina Del Rey and Ballona Creek, Final Reconnaissance Report, 1995~~). The Ballona Creek Watershed is the largest watershed in the region, ~ 127 square miles, and it is extensively developed. Moreover, it is thought to be the most significant source of non-point source pollution to the Santa Monica Bay. Ballona Creek is concrete lined upstream of Centinela Avenue, and all of its tributaries are either concrete channels or covered culverts. Thus, the vast majority of the precipitation within the watershed is conveyed to the ocean along with its entrained load of trash and pollutants.

Two other locations in Marina Del Rey were also selected for study. Marina Del Rey was evaluated to ascertain the relative role of the Marina itself as a source of pollutants to Santa Monica Bay. The Marina sites were compared with samples collected from the Ballona Creek Estuary at the Pacific Avenue Bridge (see Figure 2). The overall goal of this study is to understand whether Ballona Creek is the primary source the contaminants in the sediments which accumulate at the south entrance of Marina Del Rey/Mouth of Ballona Creek. To accomplish this goal, the specific objectives of this project are as follows:

1. To determine the types and concentrations of organic pollutants and heavy metals associated with suspended solids emanating from Ballona Creek and its tributaries.
2. To estimate the relative contributions of pollutants emanating from Sepulveda Channel, and Centinela Channel and Ballona Creek before Sepulveda Channel, and Centinela Channel empty into Ballona Creek during wet weather flow.
3. To compare the types and concentrations of pollutants associated with suspended solids emanating from Ballona Creek and its tributaries with those pollutants associated with suspended solids in Marina Del Rey.

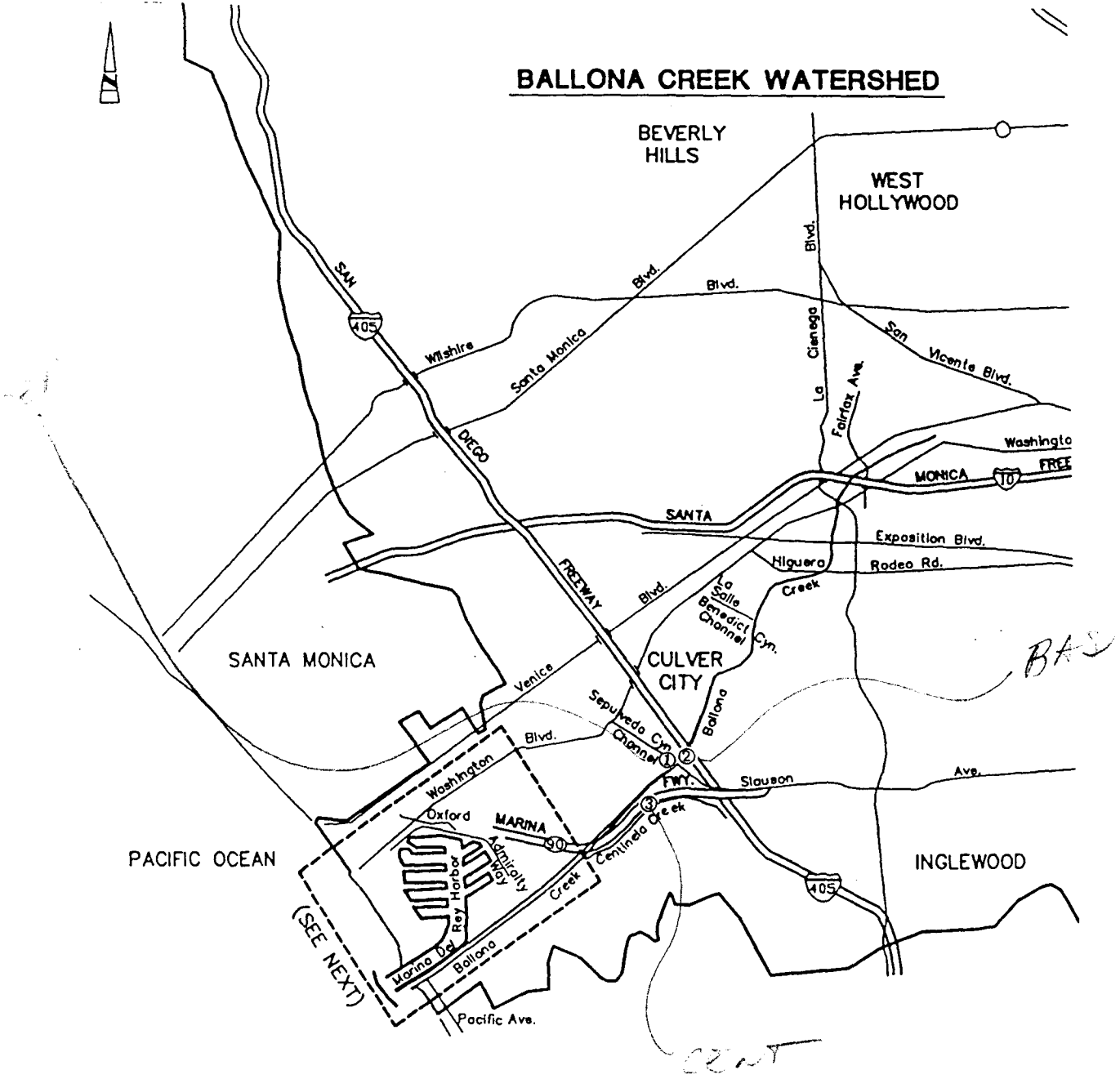


Figure 1. A map showing the location of the upstream sampling sites: ① Sepulveda Channel at Culver Blvd., ② Ballona Creek at Sawtelle Blvd., and ③ Centinela Channel at Centinela Ave.

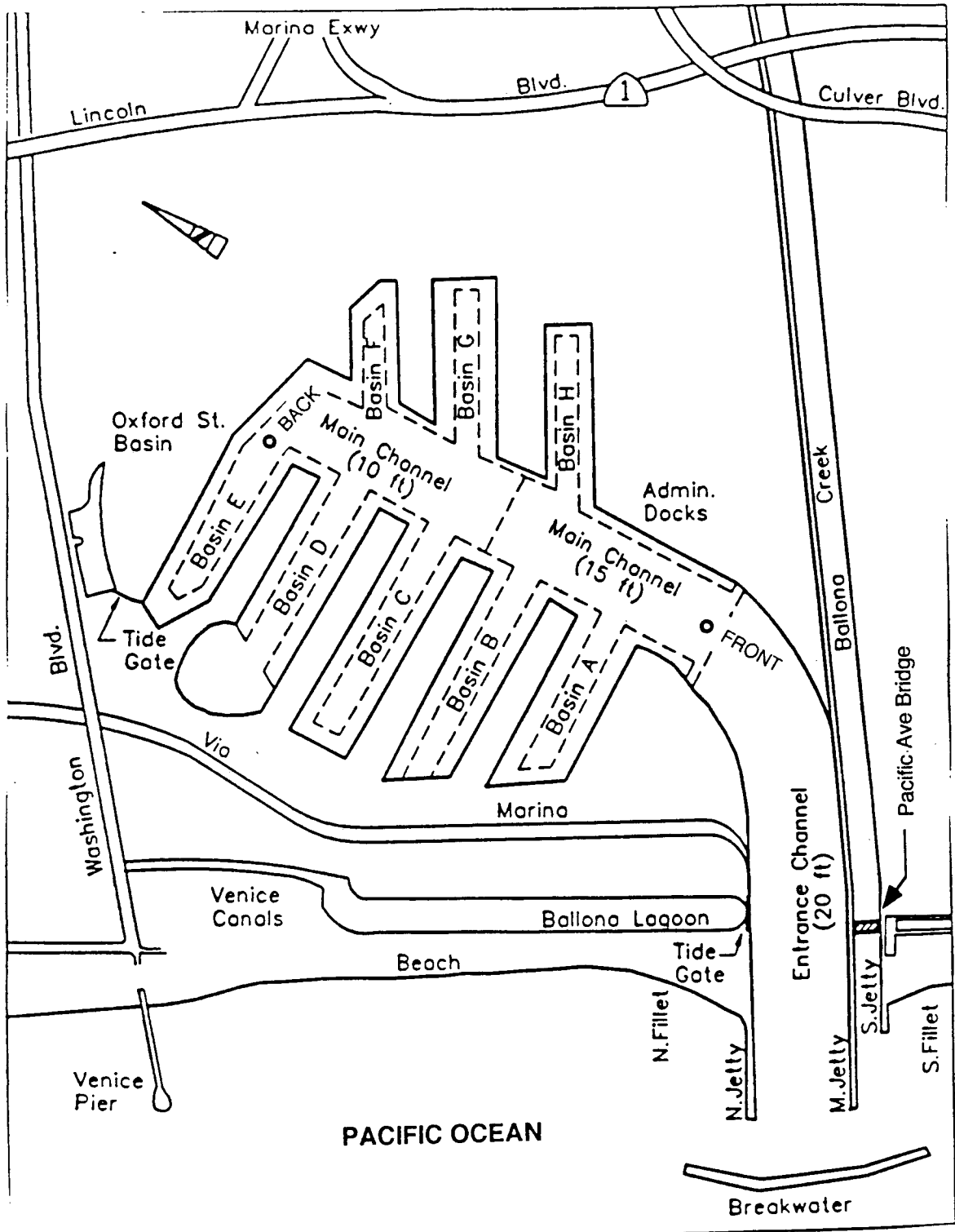


Figure 2. A map showing the location of the downstream sampling sites: Pacific Ave Bridge, and Marina Del Rey, Front and Back (●).

To achieve these objectives, six rainfall events were sampled between November 1, 1995 and March 5, 1996. The storms varied in duration from a few hours to several days. Rainfall intensities also varied greatly during each storm event. Since there is no way to know a priori the duration or intensity of an individual storm event, decisions regarding when and where to take samples, was determined in the field, based on observations and weather forecasts. Because of the logistical problems associated with sampling an unpredictable event, the number of samples taken at each location was not consistent between storms.

The focus of the study is on the suspended solids because this is the phase which most likely is responsible for the contamination in the sediments which accumulate at the south entrance of Marina Del Rey/Mouth of Ballona Creek. Moreover, it is well established that suspended solids are the medium most important for the transport of hydrophobic organic pollutants and heavy metals in aquatic systems. Sediment quality criteria are currently under development by the EPA. (Ankley et al. 1996 a,b; DiToro et al. 1991). In addition, screening of the water phase for the first two storm events confirmed that the concentration of hydrophobic organics (e.g., PAHs) was insignificant in comparison to the suspended solid phase.

Sixty-eight target semi-volatile organic compounds were analyzed for by an updated EPA procedure and capillary GC/MS. Some of the chemical classes included in this method were polynuclear aromatic hydrocarbons, N-nitrosoamines, chlorinated aromatics, and phenols. Nineteen Chlorinated Pesticide, PCBs and Toxaphene were analysed by dual capillary GC - electron capture detector (ECD) with two different GC phases. Finally, 28 inorganic elements were determined by inductively coupled plasma (ICP) - atomic emission spectroscopy (AES).

2.0 DESCRIPTION OF SAMPLING SITES

2.1 Upstream Sites

2.1.1 Ballona Creek

Several sites were used for the upstream sampling on Ballona Creek depending on the storm event, and the extent of the sampling. The primary sampling location was at the Sawtelle Blvd. bridge. The Sawtelle site was selected because it was the first location upstream of the where the two large tributaries, Sepulveda and Centinela Channels, merge with Ballona Creek. Thus, Sawtelle Blvd. is the farthest location downstream which contains flow solely from Ballona Creek. Two other sites were also used for specific samples. The Ballona Creek sample taken during the November 1, 1995 storm was taken at Sepulveda Blvd. The sample for the December 23, 1995 storm was taken at Centinela Ave. Figure 1 shows these sampling sites.

2.1.2 Sepulveda Channel

Sepulveda Channel was sampled at only one location for all storms during the 1995-96 rainy season. The samples were collected where Sepulveda Channel emerges after passing underneath Culver Blvd., on the south (i.e., downstream) side of the street. The sampling point is approximately a quarter-mile upstream of the confluence of Sepulveda Channel and Ballona Creek. This location was selected because it is the nearest point upstream of where Sepulveda Channel and Ballona Creek merge, which is easily accessible.

2.1.3 Centinela Channel

Centinela Channel was also sampled at only a single location. All samples were collected from the west side of the bridge at Centinela Ave. This site is approximately one half-mile upstream of the confluence of Centinela Channel with Ballona Creek. Again, the site was selected because it is the first location upstream of the confluence which is readily accessible.

2.2 Downstream Sites

2.2.1 Ballona Creek

The downstream sampling location for Ballona Creek was at the Pacific Avenue Bridge, which is located several hundred yards upstream of the outlet to the ocean and the confluence with the south entrance to Marina Del Rey (See Figure 2). Samples were collected at this site in order to compare the total mass emissions from the Ballona Creek watershed with the pollutants emanating from Marina Del Rey.

2.2.2 Marina Del Rey

Two sampling locations were selected in Marina Del Rey (Figure 2; US-ACE Marina Del Rey and Ballona Creek, Final Reconnaissance Report, 1995). One location was chosen to be near the front of the main channel in order to sample the possible influx of pollutant in the stormwater from Ballona Creek. The location selected was at the bend where entrance channel becomes the main channel. Samples were collected from a boat at the approximate middle of the channel.

The second sampling location was near the back of the main channel at the entrance to Basin E. This site was chosen to sample the input of stormwater and the associated pollutants from drains which empty into the back of Basin E, and other areas near the back of the main channel.

3.0 EXPERIMENTAL METHODS

3.1 Sampling Methodology

Suspended solids were collected by taking 5 -10 liter grab samples at various times during the given storm events. The sampling times were determined in the field based on observations, and weather forecasts. The grab samples were taken by dropping a bucket attached to a nylon rope into the flow, allowing the bucket to sink into the water, and then retrieving it. Stainless steel buckets were used for collection of samples for organic analyses and toxicity testing. Polypropylene buckets were used in the collection of

samples for metals analyses.

Inside Marina Del Rey and at the upstream sites - Ballona Creek at Sawtelle Blvd., Sepulveda Channel at Culver Blvd., and Centinela Channel at Centinela Ave.- 2 x 4 liter grab samples were collected in pre-cleaned amber glass bottles with Teflon-lined closures at each time interval: one bottle each for organic and metals analyses. Samples from inside the Marina were collected using the same buckets from a Sheriff's Department boat. The buckets were thrown as far away from the boat as possible to minimize any contamination from the boat itself.

Typically, for the downstream site - Ballona Creek at Pacific Ave- 4 x 4 liter samples were collected in pre-cleaned amber glass bottles with Teflon-lined closures at each site, for each time, during each storm event: two bottles for organic analyses, one bottle for metals analyses, and one bottle for toxicity testing. Each of the bottles were filled from a separate grab sample.

In addition, during the January 31, 1996 sampling in Marina Del Rey, Deputy Fred Pausch, Marina Del Rey Station, Sheriff Department, County of Los Angeles, Marina Del Rey, CA, 90292 videotaped the suspended solids plume entering the Marina from Ballona Creek.

3.2 Analytical Methods

3.2.1 Filtration and Storage

After collection, all samples were transported back to UCLA for filtration. Samples were stored at 4°C until filtered. Samples were filtered as soon as possible so as to minimize any alteration or redistribution of contaminants between the dissolved and aqueous phases. Samples of the whole water were filtered through 142 mm, 0.7 µm pure glass (no binder) TCLP filters (MSI, Inc.) These filters are manufactured specifically to be extremely low in metals. In addition, they were found to give the lowest background concentration of organic impurities upon subsequent supercritical fluid extraction. Justification for the use of these filters, and the filter preparation and cleaning procedure is

described in Capangpangan et al., (1996a). The filters to be used for organic analyses were pre-cleaned by baking at 175-200° overnight, then allowed to cool to room temperature in a desiccator. The filters were then weighed to the nearest 0.1 mg, and placed in order into a glass petri dish for storage. The filters to be used for metals analyses were used directly from the box.

The apparatus used was a stainless steel, Teflon-lined Millipore 142 mm Hazardous Waste Filtration System with an integral 1.5 liter reservoir. The system was pressurized up to 100 psi by zero grade nitrogen. Between 2 and 4 liters of whole water sample was through each filter depending upon the suspended solids load. Samples were filtered in one liter increments until the filter became clogged. A new filter was then used, and filtration resumed until each sample was consumed. The filtrates were retained for water quality analyses and preliminary evaluation of the dissolved phase.

After each sample, the filtration apparatus was disassembled, and the filter was carefully removed, folded in half, then in quarter to enclose the solids, and placed into a pre-cleaned 125 or 250 ml glass jar with a Teflon-lined closure. The samples for organic analysis were stored in a freezer until needed. The samples for metals analysis were stored at 4°C until digested. Filter blanks were prepared by filtering equal volumes of Milli-Q water through filters, and then treating them the same as actual samples in all subsequent procedures.

In general, 4.0 - 8.0 liters of sample were collected at each site for each time interval. The concentration of suspended solids in a particular sample determined the number of replicate samples obtained from a certain volume of stormwater. Typically, for samples with a high suspended solids concentration, only 2.0 liters of sample could be passed through a single filter before clogging occurred. Samples with low suspended solids concentration, an entire 8.0 liter sample was passed through a single filter. Thus, a single collected stormwater sample resulted in one to four replicate suspended solids sub-samples depending on the volume collected and the suspended solids concentration.

Table 1. Field and Sampling Parameters

Parameter	Sample Volume	Sample Containers	Processing & Storage
Field			
pH	25 ml	plastic, glass	determine on site, record to the nearest 0.1 unit
Conductivity	100 ml	plastic, glass	determine on site, record to the nearest 0.1 μ mho
Velocity	---	---	determine on site, record as M/S
Laboratory			
Total suspended solids (TSS)	100-1000 ml	glass only	refrigerate at 4°C (analyzed within 7 days)
Total dissolved solids (TDS)	100-1000 ml	glass only	refrigerate at 4°C (analyzed within 7 days)
Dissolved organic carbon (DOC)	10 ml	Amber glass bottle with TFE-lined cap	refrigerate at 4°C (analyzed within 3 days)
Percent organic carbon of suspended solids (% OC)	10-25 mg	vial -- pellets	freeze, store in the dark (analyze in 30 days)
Ultraviolet absorption	100 ml	glass only	refrigerate at 4°C (analyzed within 3 days)
Acid/Base-Neutral organics in aqueous filtrate, EPA Method 608/625* (Liquid-Liquid Extraction with Capillary GC/MS) [@]	2 - 8 liters	Amber solvent bottle (filled to the top; no air bubble; no head space)	store in the dark; refrigerate at 4°C (extract within 7 days; analyze within 40 days)
Semivolatile organics on Suspended Solids collected on filters and Supercritical Fluid Extraction of filters with Capillary GC/MS [@]	2 - 8 liters	Water sample -amber solvent bottle (filled to the top; no air bubble; no head space)	store in the dark; refrigerate at 4°C (extract within 7 days; analyze within 40 days)
Heavy Metals in aqueous filtrate, Standard Method 3120B (ICP)	1-8 liters	Amber solvent bottle (filled to the top; no air bubble; no head space)	store in the dark; refrigerate at 4°C (extract within 7 days; analyze within 40 days)
Heavy Metals from Suspended Solids collected on filters and prepared by Standard Method 3120B (ICP)	1-8 liters	Water sample -amber solvent bottle (filled to the top; no air bubble; no head space)	store in the dark; refrigerate at 4°C (extract within 7 days; analyze within 40 days)
PAHs in aqueous filtrate, EPA Method 550.1 (Liquid-Liquid Extraction - LC/UV diode detector)	2 - 8 liters	Amber solvent bottle (filled to the top; no air bubble; no head space)	store in the dark; refrigerate at 4°C (extract within 7 days; analyze within 40 days)

[@]This method also isolates chlorinated hydrocarbon pesticides, and PCBs which are analyzed by dual column capillary GC with an electron capture detector. See Capangpangan et al., 1996a and 1996b.

Table 2. Laboratory Analysis Parameters

Parameter	Matrix	Units	Modified Methods (1)	Maximum Holding Time	Preservation
Total suspended solids (TSS)	water	mg/L	2540.D	7 days	refrigerate at 4°C
Total dissolved solids (TDS)	water	mgC/L	2540.C	7 days	refrigerate at 4°C
Percent organic carbon of suspended solids	solid	% OC	Centrifuge (Described in text) & analysis by 5310.C	7 days	freeze
Dissolved Organic Carbon	water	mg/L	5310.C	7 days	refrigerate at 4°C keep in dark
Ultraviolet absorption	water	Absorbance	5910.B	3 days	refrigerate at 4°C
Acid/Base-Neutral Organic Compounds	water	ng/L	EPA SW-846 Method 3520.A - Liquid-Liquid Extraction (2) Isolation & EPA608/625* Analysis)	7 days before extraction ----- 40 days after extraction	refrigerate at 4°C protect from light
Semivolatile Organic Compounds	Solids on 0.45u filter from filtered water sample	ng/g	Supercritical Fluid Extraction Method (3) (Described in text) & EPA 608/625* Analysis)	7 days before extraction ----- 40 days after extraction	refrigerate at 4°C protect from light
Heavy Metals	water	ug/l	Preparation Method: EPA 3120.B	60 days	refrigerate at 4°C protect from light
Heavy Metals Suspended Solids collected on filters and prepared for EPA Method 3120.B (ICP)	Solids on 0.45u filter from filtered water sample	ug/g	Preparation Method: EPA Method 3050B (Acid digestion for metals from solids)	60 days	refrigerate at 4°C protect from light

(1) Standard Methods for the Examination of Water and Wastewater 18th Edition, 1995.

(2) Modified Standard Methods of Water and Wastewater Research: One-Step™ extractor/concentrator - Fowler, H., "Applications of a "One-step" Extractor/concentrator in Environmental Testing", American Laboratory, 39, 1991.

(3) Capangapangan, et al., 1996a and 1996b.

3.2.2 Water Quality

Table 1 shows the field and laboratory sampling parameters. The sample volume, sample container and processing and storage information is presented in the table. Table 2 shows the laboratory analysis parameters. The filtered stormwater samples were analyzed for pH, conductivity, total dissolved solids, and total suspended solids. The pH measurements were performed using a Fisher Accumet 925 pH meter, with a glass combination electrode and two-point calibration. Conductivity was measured with an Horizon Ecology Co. Model 1484 conductivity meter. Total dissolved solids and total suspended solids were measured using the procedures 2540 C and D, respectively, described in *Standard Methods for the Examination of Water and Waste Water* (AWWA, 1995).

3.2.3 Total Organic Carbon (TOC)

The organic carbon concentration of both the water and suspended solids phases was measured using a Dohrmann DC-80 TOC Analyzer. The 0.7 μm filtered water samples were analyzed using UV-persulfate oxidation method described in section 5310 C of *Standard Methods for the Examination of Water and Waste Water* (AWWA, 1995).

Suspended solids were isolated by repeated centrifugation of whole water samples in 50 ml Teflon Oak Ridge centrifuge tubes (Nalgene) until a sufficient mass of solids was obtained. The tubes were centrifuged at approximately 27,500 x g in a Sorvall RC-5B Superspeed Centrifuge (DuPont). The suspended solids pellet obtained was then washed into a pre-cleaned aluminum pan, and allowed to air-dry in a fume hood. The dried suspended solids were placed into a vials and refrigerated until analyzed. Some water samples were so low in suspended solids that a sufficient quantity could not be obtained from a reasonable volume of water (< 1 liter).

The TOC of the dried suspended solids was determined using the sludge/sediment

analyzing unit of the TOC instrument. The sample is weighed into a small platinum boat, placed into a quartz-tube furnace at ~800°C in a pure oxygen atmosphere, in the presence of a cobalt oxide catalyst. All of the organic matter in the sample is converted to carbon dioxide which is subsequently measured by an infrared gas analyzer.

3.2.4 Trace Organic Analyses

The suspended solids and the filtered water extracts were analyzed by capillary gas chromatography/mass spectrometry (GC/MS) following EPA 525/625* methodology as modified in USEPA Contract Laboratory Program (CLP) August 1991 Statement of Work. Organic compounds analyzed by this procedure are listed in Table 3. Table 3 shows the Method Detection Limits (MDLs) were compound dependent and varied. Analytes that were inefficiently extracted from water or suspended sediment could not be detected at low concentrations, but could be measured when present in sufficient amounts. Co-eluting compounds with very similar mass spectra, e.g., structural isomers, were reported as a group.

Some samples of suspended solids extracts also were analyzed for chlorinated pesticides and PCBs by dual column capillary gas chromatography following EPA 608 methodology. The Organochlorine compounds analyzed by this procedure are also given in Table 3, along with their associated MDLs.

Table 3 also shows the MDLs, Drinking Water Maximum Contaminant Levels (MCLs), California Ocean Plan Chronic Toxicity Levels for Aquatic Life in Water and the Effective Range Low (ERLs) and Effective Range Median (ERMs) for sediment toxicity evaluation. The ERLs and the ERMs were developed by the U.S. National Oceanographic and Atmospheric Administration (NOAA) by Long et al., (1995) to evaluate the quality of marine and estuarine sediments. The data to develop ERLs and ERMs came from throughout the US where chemical concentration and effects data had been correlated. The ERL is the 10th percentile of the ranked data and represented the point below which adverse effects are not expected to occur. The ERM is the 50th percentile of the ranked data

Table 3 Minimum Detection Limits (MDLs) and Standards for Drinking Water, the California Ocean Plan, and ERLs and ERM for Target Base-Neutral and Organochlorine Compounds by the Upgraded EPA Method 608/625.^(a)

CHEMICAL NAME:	CALIFORNIA OCEAN PLAN ^(c)							
	Water	S.S.	Drinking	HUMAN HEALTH		MARINE		
	MDL (ng/l)	MDL (ng/l)	Water MCLs ^(b) (ng/l)	CARCINOGEN (ng/l)	NON-CARCINOGEN (ng/l)	AQUATIC LIFE (ng/l)	ERLs (ug/kg dry weight)	ERMs (ug/kg dry weight)
Base-Neutral Organic Target Compounds								
acenaphthene	64	0.064					16	500
acenaphthylene	56	0.056		8.8 ^(e)			44	640
aniline	2100	2.10						
anthracene	70	0.070		8.8 ^(e)			85.3	1,100
azobenzene	63	0.063						
benzidine	51400	51.4		0.069				
benzo[a]anthracene	62	0.062					261	1,600
benzo[b]fluoranthene	137	0.137						
benzo[k]fluoranthene	145	0.145		8.8 ^(e)				
benzo[g,h,i]perylene	370	0.37						
benzo[a]pyrene	73	0.073	0.2	8.8 ^(e)			430	1,600
benzylalcohol	808	0.808						
bis(2-chloroethyl)ether	345	0.345		45				
bis(2-chloroisopropyl)ether	83	0.083			1,200,000			
bis(2-chloroethoxy)methane	328	0.328			4,400			
bis(2-ethylhexyl)phthalate	48	0.048	6	3,500				
4-bromophenyl-phenyl ether	619	0.619						
butyl benzyl phthalate	300	0.300						
carbazole	370	0.37						
4-chloroaniline	1270	1.27						
2-chloronaphthalene	126	0.126						
4-chlorophenyl ether	346	0.346						
2-chlorophenol	330	0.33				(f)		
chrysene	68	0.068		8.8 ^(e)			384	2,800
dibenzo[a,h]anthracene	395	0.395		8.8 ^(e)			63.4	260
dibenzofuran	57	0.057						
1,2-dichlorobenzene	80	0.080	600		5,100,000 ^(d)			
1,3-dichlorobenzene	84	0.084			5,100,000 ^(d)			
1,4-dichlorobenzene	84	0.084	75	18,000				
3,3-dichlorobenzidine	1340	1.34		8.1				
diethyl phthalate	60	0.060			33,000,000			
dimethyl phthalate	64	0.064			820,000,000			
di-n-butyl phthalate	60	0.060			3,500,000			
2,4-dinitrotoluene	1160	1.16		2,600	4,000			
2,6-dinitrotoluene	1170	1.17						
di-n-octyl phthalate	64	0.064						
fluoranthene	61	0.061			15,000		600	5,100

Table 3 Minimum Detection Limits (MDLs) and Standards for Drinking Water, the California Ocean Plan, and ERLs and ERM for Target Base-Neutral and Organochlorine Compounds by the Upgraded EPA Method 608/625.⁽⁴⁾

CHEMICAL NAME:	CALIFORNIA OCEAN PLAN ^(c)							
	Water	S.S.	Drinking	HUMAN HEALTH		MARINE	ERLs (ug/kg dry weight)	ERMs (ug/kg dry weight)
	MDL (ng/l)	MDL (ng/l)	Water MCLs ^(b) (ng/l)	CARCINOGEN (ng/l)	NON-CARCINOGEN (ng/l)	AQUATIC LIFE (ng/l)		
fluorene	62	0.062		8.8 ^(e)			19	540
hexachlorobenzene	602	0.602	1					
hexachlorobutadiene	791	0.791						
hexachlorocyclopentadiene	2430	2.43	50		58,000			
hexachloroethane	167	0.167		2,500				
indeno[1,2,3,4-cd]pyrene	374	0.374		8.8 ^(e)				
isophorone	123	0.123			150,000,000			
2-methylnaphthalene	125	0.125						
naphthalene	68	0.068					160	2,100
2-nitroaniline	1240	1.24						
3-nitroaniline	943	0.943						
4-nitroaniline	1320	1.32						
nitrobenzene	666	0.666			4,900			
N-nitrosodimethylamine	828	0.828						
N-nitrosodi-N-propylamine	329	0.329						
N-nitrosodiphenylamine	206	0.206		2,500				
phenanthrene	64	0.064		8.8 ^(e)			240	1,500
pyrene	69	0.069		8.8 ^(e)			665	2,600
1,2,4-trichlorobenzene	0		70					
benzoic acid	4000	4.0						
4-chloro-3-methylphenol	548	0.548				(f)		
2,4-dichlorophenol	608	0.608				(f)		
2,4-dimethylphenol	404	0.404				(g)		
2,4-dinitrophenol	4100	4.1				(g)		
2-methyl-4,6-dinitrophenol	2700	2.7			220,000	(g)		
2-methylphenol	443	0.443				(g)		
4-methylphenol	491	0.491				(g)		
2-nitrophenol	639	0.639				(g)		
4-nitrophenol	6200	6.2				(g)		
pentachlorophenol	3100	3.1				(f)		
phenol	1510	1.51				(g)		
2,4,5-trichlorophenol	2100	2.1				(f)		
2,4,6-trichlorophenol	579	0.579		290		(f)		
Total PAHs							4,022	44,792
Low M.W. PAHs							552	3,160
High M.W. PAHs							1,700	9,600

Table 3 Minimum Detection Limits (MDLs) and Standards for Drinking Water, the California Ocean Plan, and ERLs and ERM for Target Base-Neutral and Organochlorine Compounds by the Upgraded EPA Method 608/625.^(a)

CHEMICAL NAME:	CALIFORNIA OCEAN PLAN ^(c)							
	Water	S.S.	Drinking	HUMAN HEALTH		MARINE		
	MDL (ng/l)	MDL (ng/l)	Water MCLs ^(b) (ng/l)	CARCINOGEN (ng/l)	NON-CARCINOGEN (ng/l)	AQUATIC LIFE (ng/l)	ERLs (ug/kg dry weight)	ERMs (ug/kg dry weight)
Organochlorine Compounds								
Aldrin					0.022			
α-BHC								
β-BHC								
γ-BHC								
Δ-BHC								
Chlordane ^(h)			2000	0.023				
ODT ⁽ⁱ⁾				0.17				
Dieldrin				0.040				
Endosulfan ^(j)								
Endrin			2000			27		
Endrin aldehyde								
Heptachlor			400 ^(k)	0.72 ^(k)				
Heptachlor epoxide			200					
Methoxychlor			40,000					
Mirex								
Toxaphene			5,000	0.21				
PCB ^(l)				0.0039				
^(a) The EPA Method 608/625 was upgraded by use of a capillary GC column and more analytes were added to the quantification list.								
^(b) USEPA Drinking Water Standards reported by the AWWA Journal, Feb. 1993, p. 48.								
^(c) California Ocean Plan, 1990, State of California, State Water Resources Control Board, Resolution No. 90-27, Adopted and Effective March 22, 1990.								
^(d) Sum of 1,2- and 1,3-dichlorobenzenes.								
^(e) Sum of Polynuclear Aromatic Hydrocarbons (PAHs) including all PAHs listed and 1,2-benzanthracene and 3,4-benzfluoranthene = <8.8 ng/l.								
^(f) Phenolic compounds, chlorinated- 6 month median = 1 ug/l; daily maximum = 4 ug/l; instantaneous maximum = 10 ug/l.								
^(g) Phenolic compounds, nonchlorinated- 6 month median = 30 ug/l; daily maximum = 120 ug/l; instantaneous maximum = 300 ug/l.								
^(h) Chlordane shall mean the sum of α-chlordane, γ-chlordane, α-chlordene, γ-chlordene, α-nonachlor, γ-nonachlor, and oxychlordane.								
⁽ⁱ⁾ DDT shall mean the sum of 4,4'-DDT, 2,4'-DDT, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD.								
^(j) Endosulfan shall mean the sum of α-endosulfan, β-endosulfan, and endosulfan sulfate.								
^(k) Heptachlor shall mean the sum of heptachlor and heptachlor epoxide.								
^(l) PCBs shall mean the sum of chlorinated biphenyls whose analytical characteristics resemble those of Aroclor-1016, Aroclor-1232, Aroclor-1242, Aroclor-1248, Aroclor-1254, and Aroclor-1260.								

and represent the point above which adverse effects are expected. A direct cause and effect link in the field was not a requirement for inclusion in the analysis. Therefore, adverse effects at a pollution site could be attributed to both a high concentration of one chemical and a low concentration of another chemical if both chemicals were measured at the site. Also, neither could be the cause of the problem as combination of chemicals could be the true cause.

3.2.4.1. Isolation of Acid/Base Neutral Compounds from Aqueous Phase

The Pyrex Accelerated One-Step Liquid/Liquid Extractor/Concentrator, which is recognized as an allowed variation for use in the EPA SW-846 Method 3520A was used in the acid/base neutral extractions. A water bath was used as a heating source for all of the extractions. To the water phase, 5 μ l of base-neutral surrogate (1000 ppm) was added. The extracts were dried in a column of sodium sulfate and further concentrated by Kuderna-Danish evaporation in a Kontes tube heater to 1.0 ml.

3.2.4.2. Supercritical Fluid Extraction (SFE) of Suspended Solids

Filters and suspended solids for organic analysis by supercritical fluid extraction (SFE) were dried before extraction as described in Capnagpangan et al., 1996a. Briefly, the filters were placed in prepared drying jars for 24 hour drying, with anhydrous calcium chloride, 8 mesh (Spectrum Chemicals Mfg. Corp., Gardena, CA), as desiccant. The frozen or wet filter to be dried was positioned to rest on top of two tubes, with the "X" position providing support. The glass support was needed to prevent the wet filter from coming into contact with the desiccant, otherwise the filter would stick to the desiccant due to caking. The dry filters with suspended sediments were then weighed to enable the determination of the weight of suspended sediments. After weighing, the samples were ready for SFE.

Supercritical Fluid Extraction (SFE) consists of a Model SFX™ 2-10 Supercritical Fluid Extractor (ISCO, Inc., Lincoln, NE), a 100D Syringe Pump with Controller

(ISCO, Inc.), and SFC/SFE Grade CO₂ (Air Products and Chemicals, Inc., Allentown, PA). The system was upgraded by the addition of a Restrictor Temperature Controller from ISCO. The entire study was limited to the use of supercritical carbon dioxide as the extraction solvent.

The SFE of the samples was done using the optimum Pressure-Temperature-Modifier combination, comprised of a pressure of 355 atm, a temperature of 120°C, and a modifier mixture consisting of 250 µl each of water, methanol, and methylene chloride (Capanagpangan et al. 1996b). 2.0 grams of fine granular copper metal (Mallinkrodt, Cat. No. 4649-03) were placed at the bottom of a 10 ml sample cartridge, to trap any sulfur (from the sample), which could plug the restrictor if allowed to pass through the exit end of the sample cartridge during extraction. The dry sample to be extracted was rolled to fit the 10 ml sample cartridge, then compacted inside the cartridge. The modifiers were then spiked onto the sample inside the cartridge. 20 µl of surrogate standards (EPA Method 8270 Surrogate Standard, Supelco, Inc., Catalog No. 4-7960, diluted to 2000 ppm level with methylene chloride), was also spiked onto the compacted sample to monitor the consistency of the extraction. (Another 20 µl of the same surrogate stock mixture was spiked directly into 1.0 ml of methylene chloride as reference, and sealed in a vial for subsequent GC-MS analysis). The restrictor temperature was set at 120°C which was within the range (100-150°C) recommended in EPA Method 3561 for SFE of PAHs using fixed restrictor and liquid trapping. Each sample was extracted sequentially two times at the same P-T-M combination, each for 5 minutes static and 20 minutes dynamic extraction, adding the modifiers before each extraction sequence. The extracts were collected using the optimized analyte collection technique developed for this study, i.e., by liquid trapping (using 10 ml of pre-chilled methylene chloride) and with a C₁₈ vent trap (C-18 SPE cartridges, Part #51910, Waters Corp., Milford, MA) of the off gas from the liquid trap. The C₁₈ vent trap was eluted with 2 ml methylene chloride and the eluent was also added into the combined extract. The resulting extract was then concentrated to a final volume of 1.0 ml, then stored in a sealed vial for subsequent GC-MS analysis. After extraction, the final volume was adjusted to exactly 0.5 ml, followed by spiking of the internal

standard mixture at a ratio of 5 μl per 0.5 ml sample.

Table B-2, Appendix B shows the percent recovery of surrogate standards in different samples calculated by a standard curve procedure using the GC/MS analyzer. The grand mean average was 67.8 % with average values for the 6 surrogates ranging from 47 to 95 % .

3.2.4.3. Analysis of Semi-Volatile Extracts by GC/MS, EPA Method 525/625*

All extracts were in methylene chloride and delivered in 1.5 ml glass vials. While in the custody of the GC/MS facility, sample extracts were protected from light and stored in a refrigerator at 4°C away from potential contaminants in a room adjacent to the laboratory. Standards were stored in a separate refrigerator. Just prior to analysis the extract was allowed to warm to room temperature and the appropriate volume of internal standard mixture at 200 $\mu\text{g}/\text{ml}$ added to the vial. Five μl was used in the 250 μl extract and 10 μl was used for the 500 μl extract to give a final concentration in the vial of 40 $\text{ng}/\mu\text{l}$. Using a 10 μl syringe, 1-1.2 μl of extract was injected splitless on the Finnigan 9610 gas chromatograph (GC) initiating the GC temperature program and the data acquisition on the Finnigan 4000 mass spectrometer (MS).

Data were acquired (Superincos Data System, Finnigan) and stored over the mass range m/z 35-500 with a total scan cycle time of one second. Five or more spectra were measured during the elution of each GC peak. The gas chromatograph used a 30 meter narrow bore (0.25 mm) DB-5MS (J&W Scientific) fused silica capillary column. The helium carrier gas flow rate was 40 cm/sec . The initial column temperature was 30°C and held for 4 minutes, programmed at 6°C/min to 300°C, and held at that temperature for 30 minutes.

Compounds eluting from the GC column were identified by comparing their measured mass spectra and retention times to reference spectra and retention times to reference spectra and retention times in a data base compiled by the user from the measurement of authentic standard compounds under the same conditions used for samples. Calibration standards were measured at five concentration levels (5, 10, 20, 50 and 80 $\text{ng}/\mu\text{l}$) and response factors calculated for each compound quantitation ion using linear regression analysis. The concentration of each identified

compound was measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that was used as an internal standard. Calculation of the target analyte concentrations was made by the Autoquan Software package (Finnigan Corp.) using a linear fit of the three closest points in the multi-point response list for each analyte from the plot of area of unknown/area of standard versus amount of standard. For a compound to be quantitated, its spectra must match the library spectra by exceeding the fit threshold value of 900 out of 1000 and it must occur within the specified 10 second retention time window. Surrogate analytes, whose concentrations were known, were measured with the same internal standard calibration procedure.

Many of the compounds elucidated by GC/MS are not on either the volatile or semi-volatile target analyte list. These non-target analytes are tentatively identified using several techniques such as a) matching the unknown spectra to spectra in the 40,000 compound EPA/NIH Mass Spectral Data Base and b) interpretation of mass spectra by the mass spectroscopist and finally confirmation by co-injection of authentic compound standards. Determining chromatographic peaks on which identifications will be attempted can either be selected manually by the operator or be selected by using a modified Biller-Biemann type peak detection algorithm to search for compounds. The algorithm assumes that a compound is present whenever it finds the elution of more than three simultaneous masses which maximize within a single scan. Scans that are flagged as peaks are then searched against the EPA/NIH Mass Spectral Data Base and if the fit threshold is greater than 850 out of 1000, the spectra and tentative identification are presented to the spectroscopist for evaluation. All identifications are tentative until authentic compounds have been analyzed or co-injected under the same analytical conditions as the unknown.

3.2.4.4. Chlorinated Pesticides and PCB Analysis By EPA Method 608

Chlorinated Pesticides and PCB were isolated by the same method for suspended sediments extracts as described above for EPA Method 525/625*(See Table 3). The

methylene chloride extracts from the EPA Method 525/625* was solvent-exchanged with hexane. The hexane extracts were analyzed by EPA Method 608, with a Varian 3500 GC equipped with a Dual Electron Capture Detector (ECD). A detector temperature of 330°C was used with a splitless injector at 280°C. The programming temperature used was 1 min at 60°C, 15°C/min to 150°C, 2°C/min to 200°C, 5°C/min to 280°C hold 10 min. A 1 µl sample in hexane was injected into a single injector and then split using a 1 meter 0.32 mm fused silica retention gap and glass Y connector to two analytical columns. Column 1 was connected to channel A Electron Capture Detector J&W 30 meter DB-5 0.032 mm diameter and Column 2 was connected to channel B ECD J&W 30 meter DB-5 0.032 mm. diameter. A Varian Star Integrator/ Workstation Ver. A2 was used for data collection and processing. Quantitation from Channel A with confirmation from Channel B were used with an external calibration:

$$M_x = M_{STD} \times A_x / A_{STD}$$

M_x = amount compound in unknown run; A_x = area compound in unknown run

M_{STD} = amount compound in standard run; A_{STD} = area compound in standard run

Sample concentration was reported as ng/l of water sample. The surrogate standard used was 4-Tetraphenyl d-14 which is the least polar surrogate used as a recovery standard.

Recovery was 93 % (See Appendix B., Table B-2).

3.2.4.5 Screening of the Aqueous Phase for Hydrophobic Organics

The filtrate from stormwater samples taken during the first two storms of the 1995-1996 rainy season (i.e., 11/1/96 and 12/13/96) were extracted and screened for polynuclear aromatic hydrocarbons (PAHs) using EPA Method 550.1. The extraction was performed using 47 mm Empore™ C18 solid phase extraction disks. The eluate from the extraction step was concentrated using Kuderna-Danish tubes with nitrogen blowdown. The extracts were analyzed by HPLC with multiple wavelength UV detection (Hewlett-Packard 1090

Liquid Chromatograph w/ a 9543A diode array detector). Recoveries were determined from samples spiked with deuterated fluorene and pyrene, followed by GC/MS quantitation.

Using this instrument and methodology, the MDL's for all 16 PAHs was less than 1 µg/l.

Table 4 shows the list of the 16 polynuclear aromatic hydrocarbons (PAHs) analytes using EPA Method 550.1. The recoveries for the surrogate PAHs (deuterated fluorene and pyrene) spiked into the filtered stormwater sample matrix for the first two storm events were 50 - 79%. In contrast, the recoveries for the 16 PAHs from spiked Milli-Q water were all > 95%. The lower recoveries for the actual field samples is due to the complex organic materials in the sample matrix.

Table 4. The 16 polycyclic aromatic hydrocarbons screened for in the stormwater aqueous phase using EPA method 550.1.

Naphthalene	Benzo(a)anthracene
Acenaphthene	Chrysene
Acenaphthylene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Benzo(a)pyrene
Anthracene	Dibenz(a,h)anthracene
Fluoranthene	Benzo(g,h,i)perylene
Pyrene	Indeno(1,2,3-c,d)pyrene

3.2.5 Metals Analyses

The suspended solids and the filtered aqueous phase were analyzed by EPA Method 3120.B, an Inductive Coupled Plasma/ Atomic Emission (ICP/AE) method. Metals analyzed by this procedure are shown in Table 5. In addition, Table 5 shows the MDLs, Drinking Water Maximum Contaminant Levels (MCLs), California Ocean Plan Chronic Toxicity Levels for Aquatic Life in Water and the ERLs and ERMs for sediment toxicity evaluation. The ERL and ERM have been described in the trace organic chemical section of the report.

3.2.5.1 Digestion of Suspended Solids

The filters containing the suspended solids were digested using a slightly modified version of EPA Method 3050B. The particular digestion procedure used was the one specified for subsequent analysis ICP/AE. The only modification was a doubling of the acid volumes to account for the presence of filter. The filters containing the suspended solids were cut into small pieces using surgical scissors. The samples (suspended solids + plus filter) were then placed into 250 ml glass beakers. Next, 20 ml of concentrated hydrochloric acid, and 5 ml concentrated nitric acid were added to each beaker. This volume was sufficient to completely immerse the sample. Only Fisher Scientific trace metal grade acids were used for these digestions. After any initial reaction had subsided, the beakers were placed on a hot plate, covered with a ribbed watch glass, and refluxed at 90-95° C. The samples were digested until the no further reaction was observed. Because the filters had a tendency to swell during the digestion, a Teflon spatula was used to periodically mash down filters and stir the sample so that complete reaction with the suspended solids was ensured. The remainder of the procedure was exactly as described in method 3050B. The final diluted and submitted for analysis by ICP-AES.

Table 5. A list of the regulated and non-regulated metal analytes in this study. Included are their respective wavelength used for quantitation, MDLs, ERLs, ERM, MCLs, and CTLs.

Element Analyzed /Wavelength (λ)	Water MDL ^(d) ($\mu\text{g/l}$)	S.S. MDL ($\mu\text{g/g}$)	Drinking Water MCL ($\mu\text{g/l}$) ^(c)	ERL (mg/kg dry wgt.) ^(b)	ERM (mg/kg-dry wgt.) ^(b)	Chronic Toxicity to Aquatic Life ($\mu\text{g/l}$) ^(a)
Regulated metals						
Arsenic/(188.979,193.696,197.197,228.812)	7.38	0.007	50	8.2	70	19
Cadmium/(226.502)	0.99	0.001	5	1.2	9.6	8
Chromium/(205.552)	3.19	0.003	-	81	370	18
Copper/(213.598, 222.700)	4.96	0.005	1300 (MCLG)	34	270	5
Lead/(216.999,220.353,224.688)	19.50	0.019	0 (MCLG)	46.7	218	22
Nickel/(231.604,232.003)	2.24	0.002	100	20.9	51.6	48
Silver	-	-	-	1	3.7	3
Zinc/(202.548 or 206.200)	3.02	0.003	-	150	410	51
Non-regulated Elements						
Aluminum/(237.312)	14.14	0.014	-	-	-	-
Barium/(230.424)	3.74	0.004	2000	-	-	-
Beryllium/(313.042)	3.39	0.003	4	-	-	-
Boron/(182.527)	50.54	0.051	-	-	-	-
Iron/(238.204)	5.00	0.005	-	-	-	-
Lanthanum/(384.902)	8.26	0.008	-	-	-	-
Selenium/(196.026)	11.96	0.012	50	-	-	-
Tin	-	-	-	-	-	-
Titanium	-	-	-	-	-	-
Vanadium/(270.094)	3.97	0.004	-	-	-	-

(a) California Ocean Plan 1990

(b) Long et al. 1995

(c) National Primary Drinking Water Standards. *Fed. Reg.*, 59:126:34320-34321 (July 1994).

(d) Several wavelengths were used for analysis of each metal due to possible sample matrix interferences.

The MDL's are the averaged values when more than one wavelength was used. Wavelength selection was based on minimization of relative standard deviations within samples.

3.2.5.2 ICP/AE Analysis

Analysis of the filter and suspended solids digestates, and the 0.7 μm -filtered water phase samples was performed on a Perkin-Elmer Optima 3000 DA ICP-AES Spectrometer. Analyses were performed by Mr. David Kimbrough at the Castaic Lake Water Agency. The samples were analyzed using three characteristic wavelengths for each metal. In each case, the wavelength which gave the lowest standard deviation was chosen for quantitation. In the cases where more than one wavelength showed sufficiently low standard deviations, the final concentration value was obtained by averaging the results from multiple wavelengths. A list of all the metal analytes and their respective wavelengths, MDLs, etc., are given in Table 5 and Appendix C, Table C.1.

3.2.5.3 Metals Recovery Experiments

As the procedures described above is a slight modification of the standard method (3050B), recovery experiments were performed to determine if the inclusion of the filters had any adverse impact on the recoveries or the background levels of the metals of interest. An EPA approved CLP plasma emission spectroscopy spike sample analysis Standard # 3 (for soils; traceable to NIST) was obtained from Radian Corporation. This standard contained all of the metals of interest in this study.

To determine the recovery and background concentration of the metals, method blanks were run using no sample (acids + Milli-Q water), filters alone (no solids), and "clean" sediments from Marina Del Rey and Malibu Lagoon. The sediments were chosen from areas which were thought to be relatively free of metals contamination so that some idea of the natural metals concentrations derived from the sediments using this digestion procedure could be obtained.

The recoveries of the metals using method 3050B for both suspended sediments and bottom sediments is given in Table 6. The table shows that the recoveries for most of the compounds were good, 75-89% for the suspended solids and 82-110% for the

bottomsediments. However, two of the metals, Zn and Ba, were at very high concentrations in the filter control digestates. The levels of these metals in the Milli-Q water blanks, Reagent Blanks (acids + water), and the sediment control samples were all low. Thus, the high levels of Zn and Ba must have been derived from the filters themselves. This result was unexpected since the filters used in this study (0.7 μm pure glass TCLP filters, MSI, Inc.) were chosen specifically because they are manufactured to be extremely low in trace metals.

In fact, these filters are specified for hazardous waste evaluation by the EPA. Given the time constraints due to the approaching wet weather season, the decision was made to proceed as planned with the chosen filters, rather than embarking on a new study to identify a more appropriate filter. This was considered a practical compromise since the filters did show low background levels of the eight regulated toxic heavy metals.

3.2.6 Facilities and Equipment

The analytical facilities were located at the University of California, Los Angeles. Specific analyses were performed at three locations on the campus and one off-campus location. The wet laboratory, total organic carbon analysis and preparation of all sample extracts were completed in the School of Public Health, Environmental Health Department Laboratories of Dr. Suffet, The Laboratory of Mr. David Kimbrough of the Castaic Water Company, a Ph.D. student under Dr. Suffet's direction performed the majority of the ICP-AES analyses. Supplementary metals analyses were performed by The Laboratory of Biomedical and Environmental Sciences (LBES), Room 1-4-184, Warren Hall at UCLA. The GC/MS for base-neutrals and the GC-ECD for pesticide/ PCB/ Toxaphene analysis were completed in Edward Ruth's laboratory in Environmental and Civil Engineering in Building: Engineering I Room 4502. Organic samples were stored there prior to their analysis. An adjacent room was used for long-term storage of methylene chloride extracts.

Table 6. Suspended Solids and Sediment Metals Recovery Data (EPA Method 3050B).														
Sample	Metals Concentrations (ppm)													
	Zn	Cu	Mn	V	Co	Ni	Cr	Pb	Ba	As	Se	Cd	Ag	Sn
Water Blank	0.002	0.002	0.001	0.002	<MDL	0.003	0.001	0.007	0.001	0.003	0.008	0.0082	0.001	0.008
Reagent Blank	0.003	0.004	0.003	0.002	0.005	0.005	0.002	0.004	0.005	0.023	<MDL	0.003	0.004	<MDL
Filter Control #1	65.5	0.006	0.031	<MDL	<MDL	0.065	0.057	<MDL	88.1	<MDL	<MDL	<MDL	<MDL	10.40
Filter Control #2	3.58	0.033	0.018	0.001	<MDL	0.059	0.159	<MDL	2.48	0.002	0.010	0.002	<MDL	0.612
Filter Control #3	74.3	0.066	0.039	0.037	0.135	0.124	0.093	0.224	98.4	0.319	0.283	0.022	0.069	12.00
Filter Spike #1	120	0.865	1.73	1.70	1.80	1.77	0.815	1.92	166	7.98	6.81	0.19	0.197	19.1
Filter Spike #2	119	0.882	1.73	1.72	1.80	1.76	0.819	1.83	164	7.63	6.84	0.185	0.24	18.8
Filter Spike #3	110	0.813	1.58	1.57	1.66	1.62	0.757	1.78	150	7.30	6.44	0.177	0.201	17.4
Sediment Control #1	0.898	0.243	5.11	0.88	0.024	0.424	0.525	0.183	0.980	<MDL	1.08	<MDL	0.012	0.866
Sediment Control #2	1.22	0.413	11.0	1.36	0.092	0.871	0.802	0.028	2.11	<MDL	0.409	0.012	0.018	1.25
Sediment Control #3	0.644	0.069	1.69	0.374	0.02	0.188	0.262	0.189	0.359	0.114	<MDL	<MDL	<MDL	0.38
Sediment Spike #1	2.75	1.2	6.15	2.77	1.86	2.30	1.34	2.05	9.24	8.16	8.42	0.188	0.202	1.00
Sediment Spike #2	2.81	1.28	10.7	2.97	1.81	2.50	1.49	1.83	9.83	7.97	8.56	0.198	0.187	1.28
Sediment Spike #3	2.51	1.04	3.47	2.28	2.00	2.08	1.10	2.11	8.82	8.72	7.88	0.202	0.218	0.624
100% Recovery Std.	2.15	1.09	2.14	2.10	2.14	2.14	0.925	2.13	9.09	9.04	7.02	0.214	0.213	0.00
Sus. Solids Recov. #1	*	78.81	79.39	80.95	84.11	79.67	81.95	90.14	*	88.27	97.01	88.79	92.49	**
Sus. Solids Recov. #2	*	77.89	80.00	81.86	84.11	79.49	71.35	85.92	*	84.38	97.29	85.51	112.68	**
Sus. Solids Recov. #3	*	68.53	72.01	73.00	71.26	69.91	71.78	73.05	*	77.22	87.71	72.43	61.97	**
Avg. Recovery	*	75.08	77.13	78.60	79.83	76.36	75.03	83.04	*	83.29	94.00	82.24	89.05	**
CV (%)		7.57	5.77	6.20	9.29	7.32	7.99	10.72		6.73	5.80	10.52	28.67	
Sediment Recov. #1	86.14	87.80	48.60	90.00	85.79	87.66	88.11	87.65	90.87	90.27	104.56	87.85	89.20	**
Sediment Recov. #2	73.95	79.54	65.73	76.67	80.28	76.12	74.38	84.60	84.93	88.16	116.11	86.92	79.34	**
Sediment Recov. #3	86.79	89.08	83.18	90.76	92.52	88.41	90.59	90.19	93.08	95.20	112.25	94.39	102.35	**
Avg. Recovery	82.29	85.47	65.89	85.81	86.20	84.07	84.36	87.48	89.63	91.21	110.97	89.72	90.30	**
CV (%)	8.79	6.06	26.24	9.24	7.11	8.20	10.35	3.20	4.70	3.96	5.30	4.54	12.78	
* Recoveries not determined due to high levels of metal in filter control samples														
** Recoveries not determined because Sn was not present in the Recovery Standard #3														

4.0 RESULTS AND DISCUSSION

Ante...

4.1 Stormwater Runoff Flow Data

The available stormwater runoff flow data for the storm event during the 1995-96 season were compiled and are presented in Appendix A. Storm durations and intensities were highly variable, and thus each storm was unique~~X~~ sampled. Peak flows in Ballona Creek (at Sawtelle Blvd.) for the 1995-96 storm season ranged from a low of 150 cfs for the November 1, 1995 event, to nearly 10,000 cfs for the January 31, 1996 event. It was also visually observed that the relative flow in the three major channels varied greatly from storm to storm. Flow data was only available from the LA County gauging station located on Ballona Creek, just east of Sawtelle Blvd.

In order to provide some indication of the variability for stormwater flows in Centinela and Sepulveda channels, pollutant concentrations measured in samples taken from these two channels were compared to the flows measured in Ballona Creek. However, due to variability in rainfall patterns, and the varying size and topography of each sub-watershed, flows in Sepulveda and Centinela Channels are not expected to be the same as the flows which occurred in Ballona Creek. Therefore, any interpretations of data for samples taken from Sepulveda and Centinela channels should be considered as estimates given that the actual flows in these channels are not known.

Stormwater flow hydrographs constructed from data taken at the Ballona Creek monitoring station for the entire 1995-1996 storm season are shown in Figure A.1, Appendix A. During this storm season, eleven storms produced flows in Ballona Creek which exceeded 1000 cubic feet per second (cfs). The project was scheduled to sample only 2 storm~~X~~ events. Of the eleven storms, upstream sampling was performed for the six largest storms. More detailed hydrographs of each of these storms are shown in Figures A.2 through A.6. It was intended that samples be taken at similar times for each storm; early in the storm flow, during the storm peak flow, and late in the storm flow. However,

each storm exhibited a unique flow pattern which could not be predicted. Therefore, the sampling times were determined in real time based upon observation in the field.

4.2 Summary of Stormwater Sampling

For the first three storms for which upstream sampling was performed, the sampling was limited. For the November 1, 1995 storm, samples were taken 4 hours after peak flow from Ballona Creek at Sepulveda Boulevard, and from Sepulveda Channel at Culver Boulevard. For the December 12-13 storm, samples were taken only from Ballona Creek at Sawtelle Avenue approximately 3 hours after peak flow. For the December 23, 1995 storm, samples were taken from all three locations less than 1 hour prior to peak flows. For both the January 31, 1996 and March 4-5, 1996 storms, samples were taken at three different times at all three locations. However, due to accidental laboratory breakage, two of the samples from Centinela Channel for the January 31, 1996 were lost. Therefore, only one sampling time was reported for Centinela Channel during that Storm event. In total, 62 samples were taken and analyzed for six different storms. A complete list of the upstream sampling locations and times is given in Appendix B, Table B.1 for the organic analyses and Appendix C, Table C.1 for metals. Please note that for the upstream sampling locations, only samples for organic analyses were taken for the November 1, 1995 storm, and only metals samples were taken from the February 19-22, 1996 storm.

4.3 Water Quality Results

4.3.1 General Water Quality Data

The water quality data for the samples collected from upstream sites at Ballona Creek, Sepulveda Channel and Centinela Channel are presented in Appendix A, Table A-1. Data are given for pH, conductivity, total dissolved solids (TDS), total suspended solids (TSS), total organic carbon (TOC), and turbidity. There were no obvious trends observed in the pH, conductivity, TDS, or turbidity data. The pH values varied from 5.30 to 8.00,

and were consistent with the observed TDS values. The lower pH values occur when the TDS is very low, and probably reflect an unbuffered system in equilibrium with the atmospheric carbon dioxide (pH = 5.7), and the scavenging of acidic species from the atmosphere by the precipitation.

In contrast, the TOC and TSS data did seem to show trends both over the season and the course of a single storm. Because of the importance of these parameters in the transport and fate of pollutants in aquatic systems, the results will be discussed in detail in the following sections.

} TSS

4.3.2 Dissolved Organic Carbon Results

The organic carbon concentration data for the filtered dissolved phase, the so-called dissolved organic carbon (DOC) is presented in Appendix A, Table A-1. A plot of the DOC data for Stormwater runoff from Ballona Creek, Sepulveda Channel, and Centinela Channel during the 1995-96 rainy season are shown on Figures 3a and 3b. The runoff from the first rain event of the season carried the highest DOC (> 40 mg/l). The DOC values tended to decrease with subsequent storm events. Also, within a single storm event, the DOC appears to decrease over the course of the storm. Inspection of the plots shows that in nearly every case, the first sampling interval (i.e., T1, i.e. the so-called first flush) showed the highest DOC concentration. The DOC concentrations dropped dramatically for following sample intervals.

The organic carbon data for the suspended solids is given in Appendix A, Table A-2. Plots of the organic carbon data for the suspended solids are shown in Figures 4a and 4b for two storm events. The suspended solids in the samples from Ballona Creek collected at the Pacific Avenue Bridge (BAP) showed 8 to 10 % organic carbon for both the January 31 and March 4, 1996 storms. This is a very high organic carbon load in comparison to typical bottom sediments. The organic carbon content of suspended solids collected in Marina Del Rey (MDR) during the January storm were ≤ 3 %. Suspended

solids could not be collected for the March 4, 1996 storm in MDR because of the low turbidity in the water (see Appendix A, Table A-1).

The organic carbon content of the suspended solids from samples collected from the upstream site at Centinela Channel were between 6 and 14 % for both storm events. The ~~organic carbon content of the suspended solids from~~ samples collected from the upstream site at Ballona at Sawtelle (BAS) were between 8 and 13 % for both storm events.

The organic carbon content of the suspended solids samples collected from Sepulveda Channel were substantially lower at between 4 and 5 %. This difference in organic carbon content of the suspended solids reflects the different land uses with the respective drainage areas. For example, Sepulveda Channel drains primarily residential areas, whereas Ballona Creek and Centinela Channel drain heavily industrialized areas. The load of hydrophobic organics on the suspended solids probably will not be effected by these differences in organic carbon content as they all contain sufficient organic carbon to be the controlling factor in the sorption and transport of pollutants.

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Dissolved Organic Carbon in Stormwater Runoff from the Ballona Creek Watershed from November 1995 through January 1996

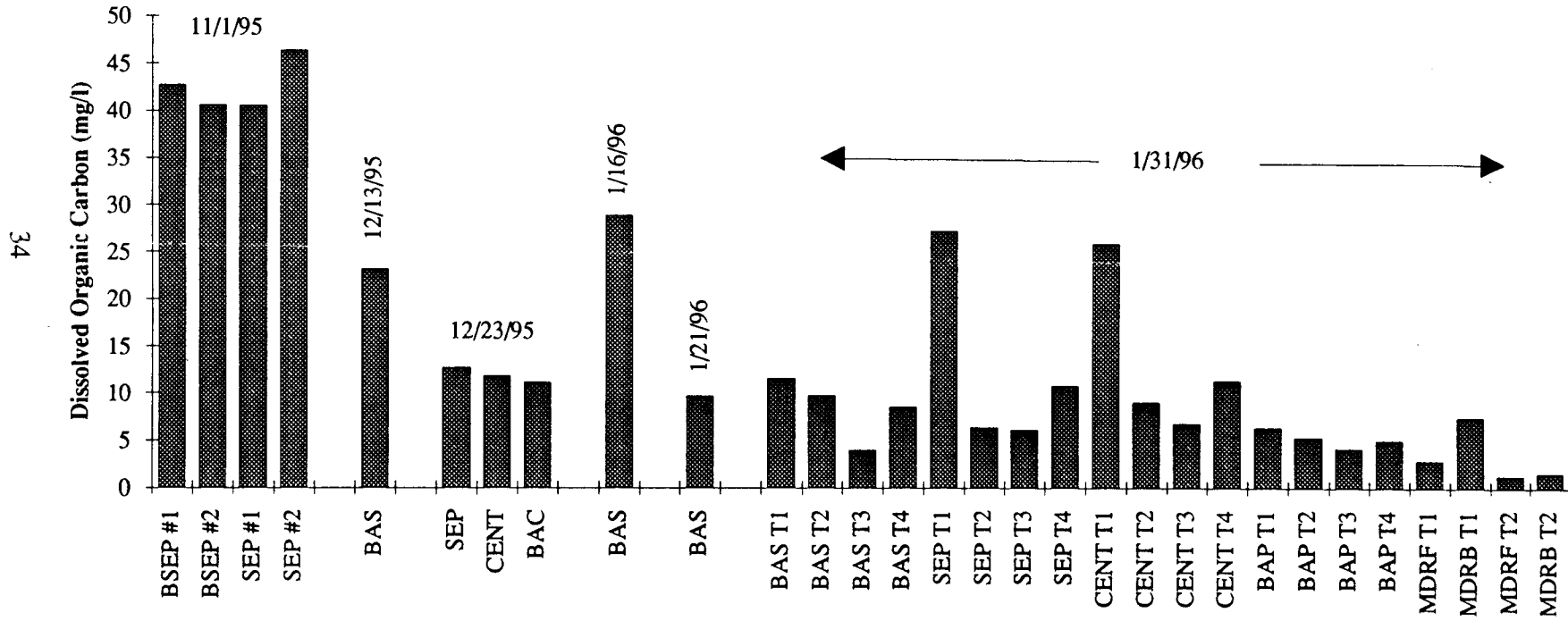


Figure 3a. Aqueous phase dissolved organic carbon data for filtered stormwater samples from the Ballona Creek watershed. Data is for November 1995 through January 1996.

Dissolved Organic Carbon in Stormwater Runoff from the Ballona Creek Watershed from February and March 1996

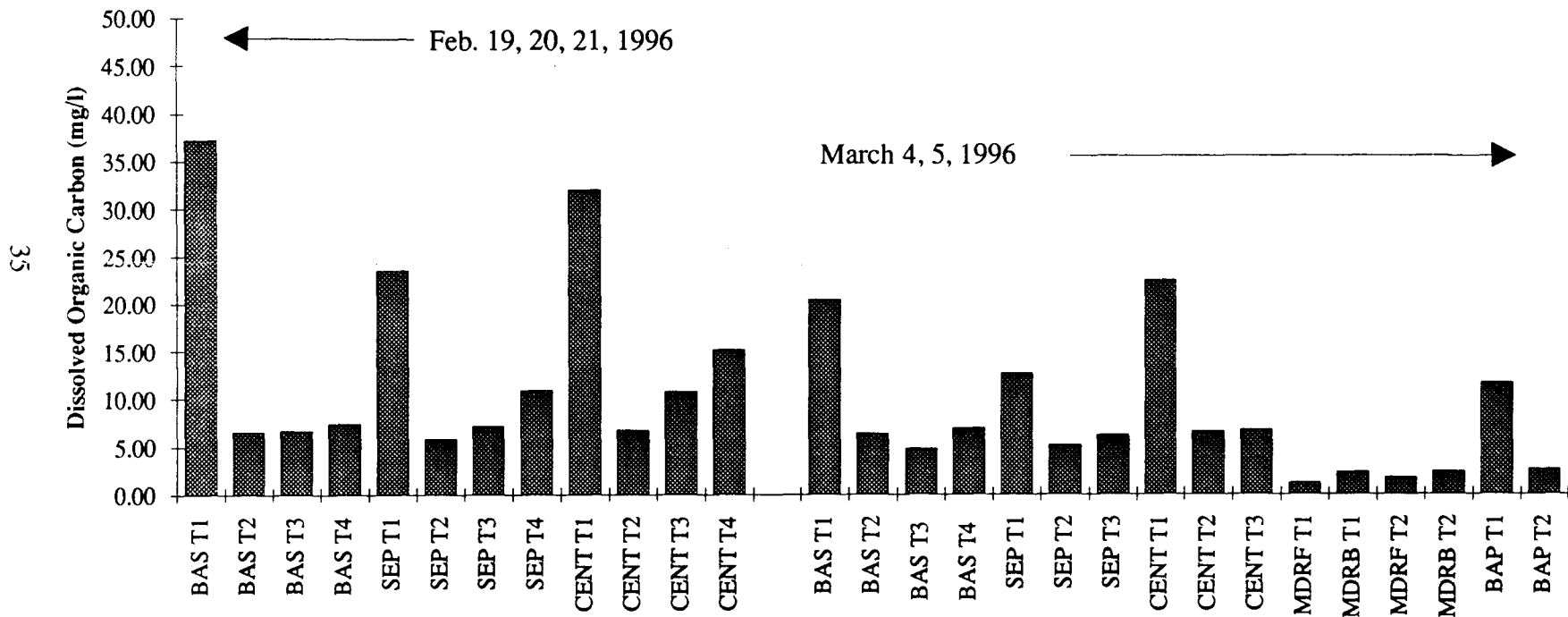


Figure 3b. Aqueous phase dissolved organic carbon data for filtered stormwater samples from the Ballona Creek watershed. Data is for February and March 1996.

Total Organic Carbon Data for Suspended Solids from Selected Sites and Times for the January 31, 1996 Storm

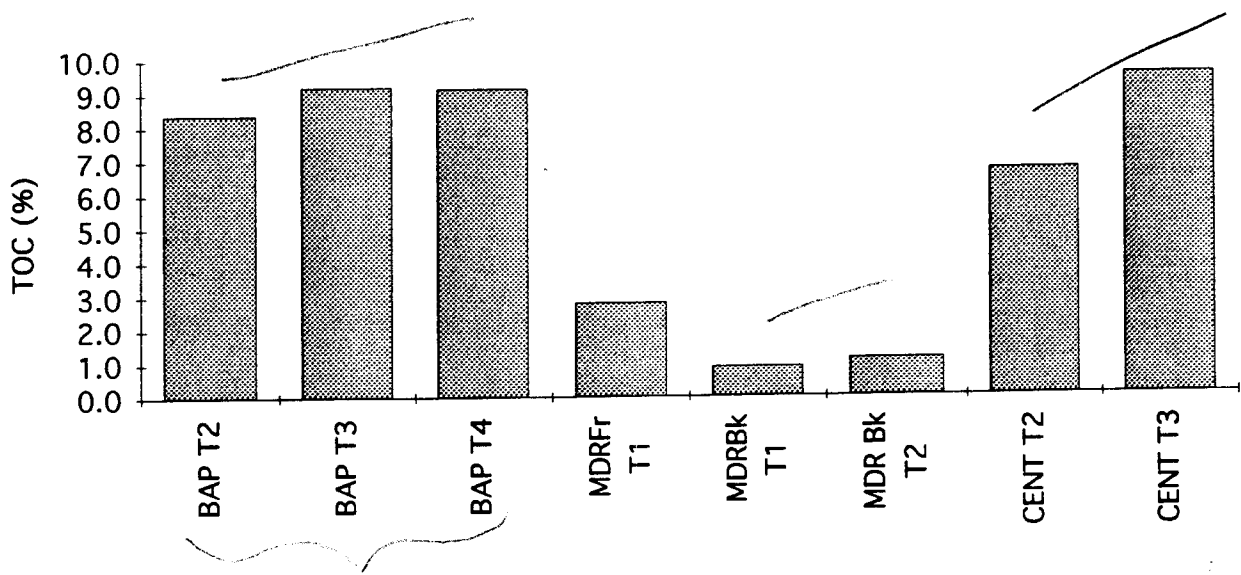


Figure 4a. Total organic carbon data for the suspended solids phase from stormwater samples collected during the January 1996 storm event.

Total Organic Carbon Data for Suspended Solids from Selected Sites and Times for the March 4, 1996 Storm

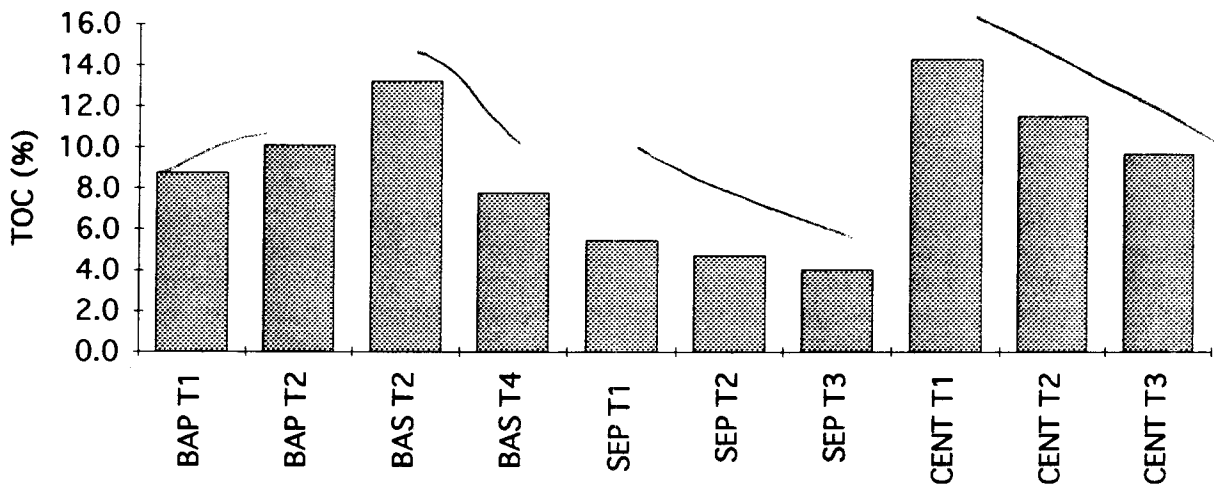


Figure 4b. Total organic carbon data for the suspended solids phase from stormwater samples collected during the March 1996 storm event.

4.3.3 Suspended Solids Data

The data for the suspended solids concentration in the stormwater runoff collected at the upstream sites is given in Appendix A, Table A-1 and plotted on Figures 5a and 5b.

The suspended solids loads do tend to decrease over the course of the rainy season.

~~As~~ However, within a single storm event there is no trend observed. The suspended solids load should be related to flow, and thus the variability of the suspended solids data reflects the variability in the precipitation and the corresponding changes in runoff flow.

The suspended solids load as a function of flow was investigated for the January 31 and March 4-5, 1996 storms. The data are shown in Figures 6a and 6b, and Appendix B, Figures B.31 and B.44. During the January 31, 1996 storm, suspended solids loads never exceed 180 mg/L, with a peak flow of nearly 10,000 cfs. In contrast, the maximum suspended solids concentrations for the March 4-5, 1996 storm were between 300 and 750 mg/L, with a peak flow of less than 6,000 cfs. These data infer that high flow rates may lead to lower suspended solids concentrations. Apparently, once there is sufficient runoff flow to entrain the available particulates, any further flow results in dilution rather than more suspended solids transport.

→ the load

→ not true
can't say
not enough
data pts
load
vs []

antecedent dry days?
? yes
but what
RE frands
throughout storm → that's what is imp.

Total Suspended Solids in Stormwater Runoff from the Ballona Creek Watershed from November 1995 through January 1996

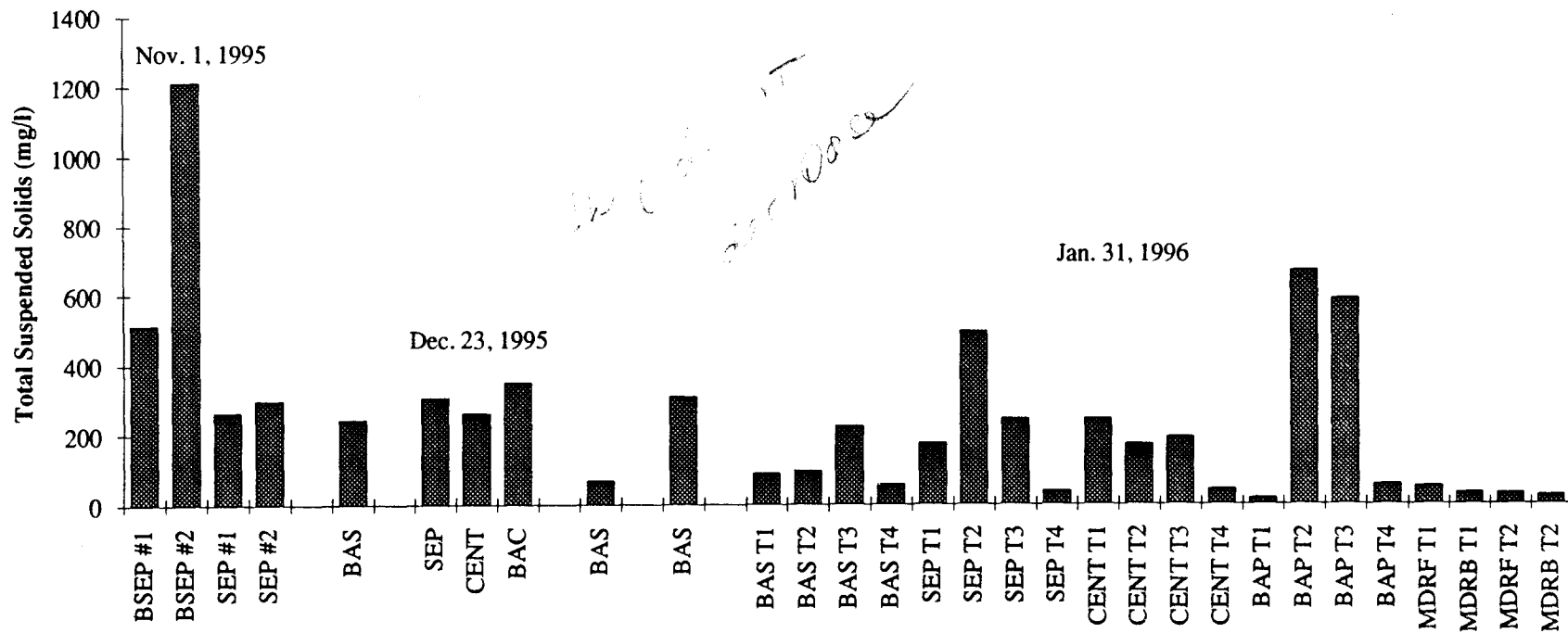


Figure 5a. Total suspended solids data for stormwater samples collected in the Ballona Creek Watershed. Samples from various sites for storms from December 1995 through January 1996.

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Total Suspended Solids in Stormwater Runoff from the Ballona Creek Watershed from February and March 1996

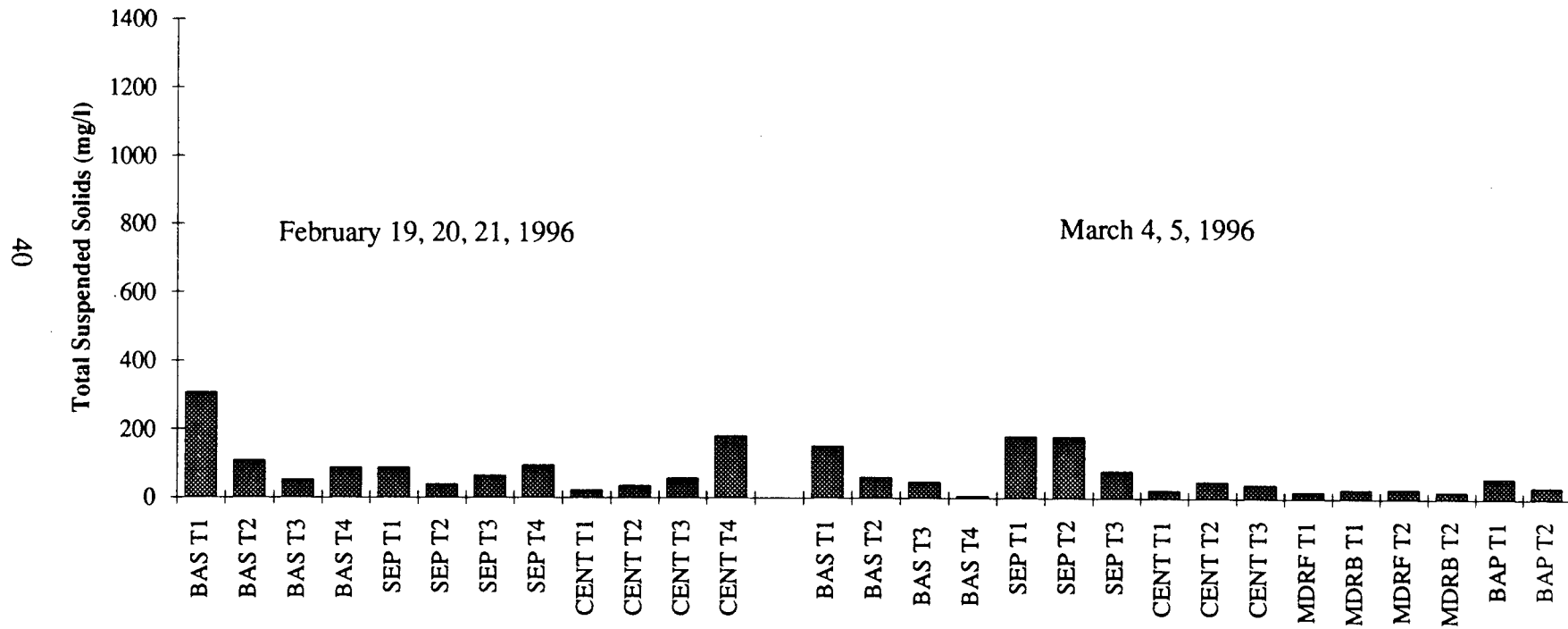


Figure 5b. Total suspended solids data for stormwater samples collected in the Ballona Creek Watershed. Samples from various sites for storms from December 1995 through January 1996.

Suspended Sediment Load

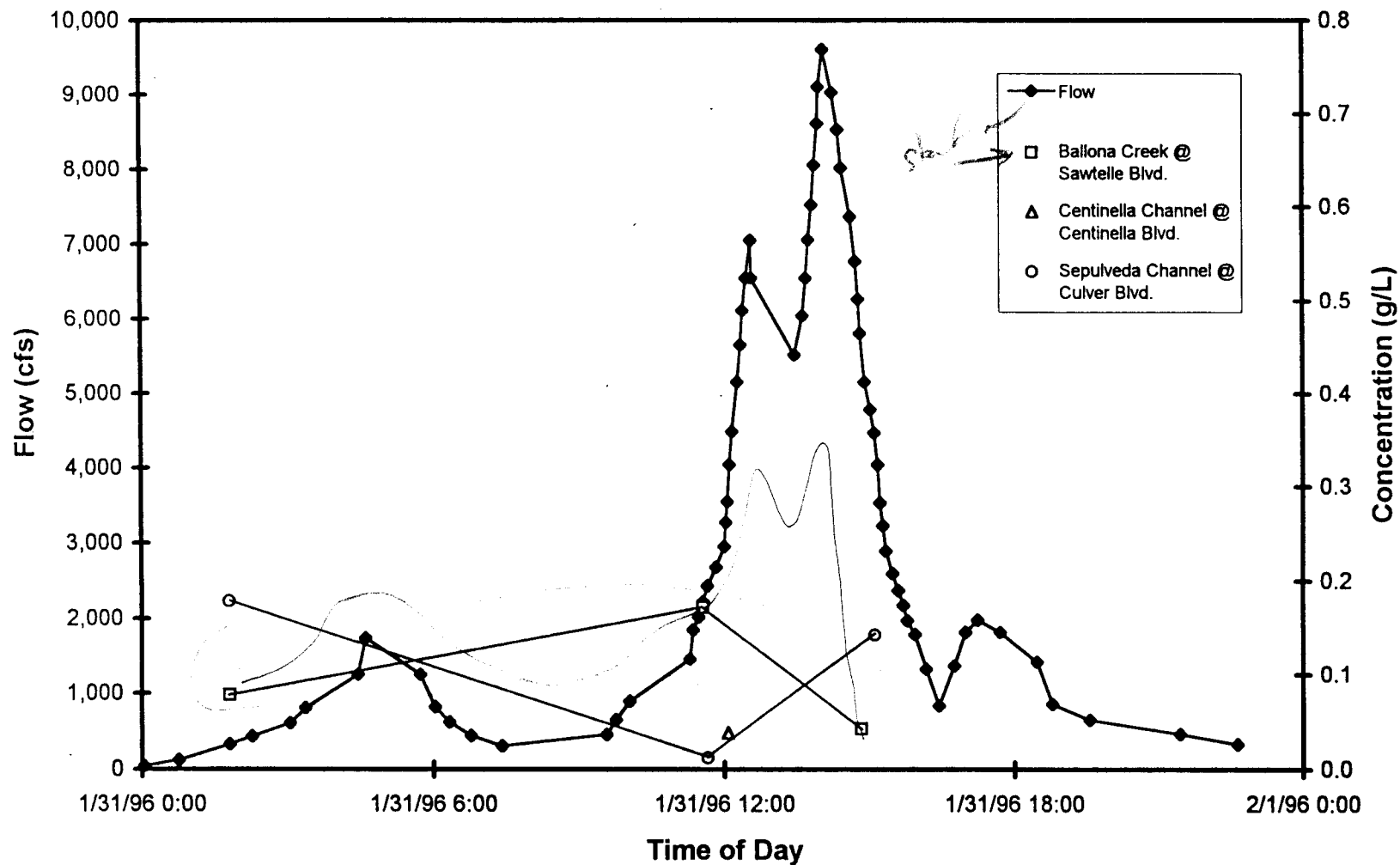


Figure 6a. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and suspended sediment loads from upstream samples at the locations specified.

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Suspended Sediment Load

42

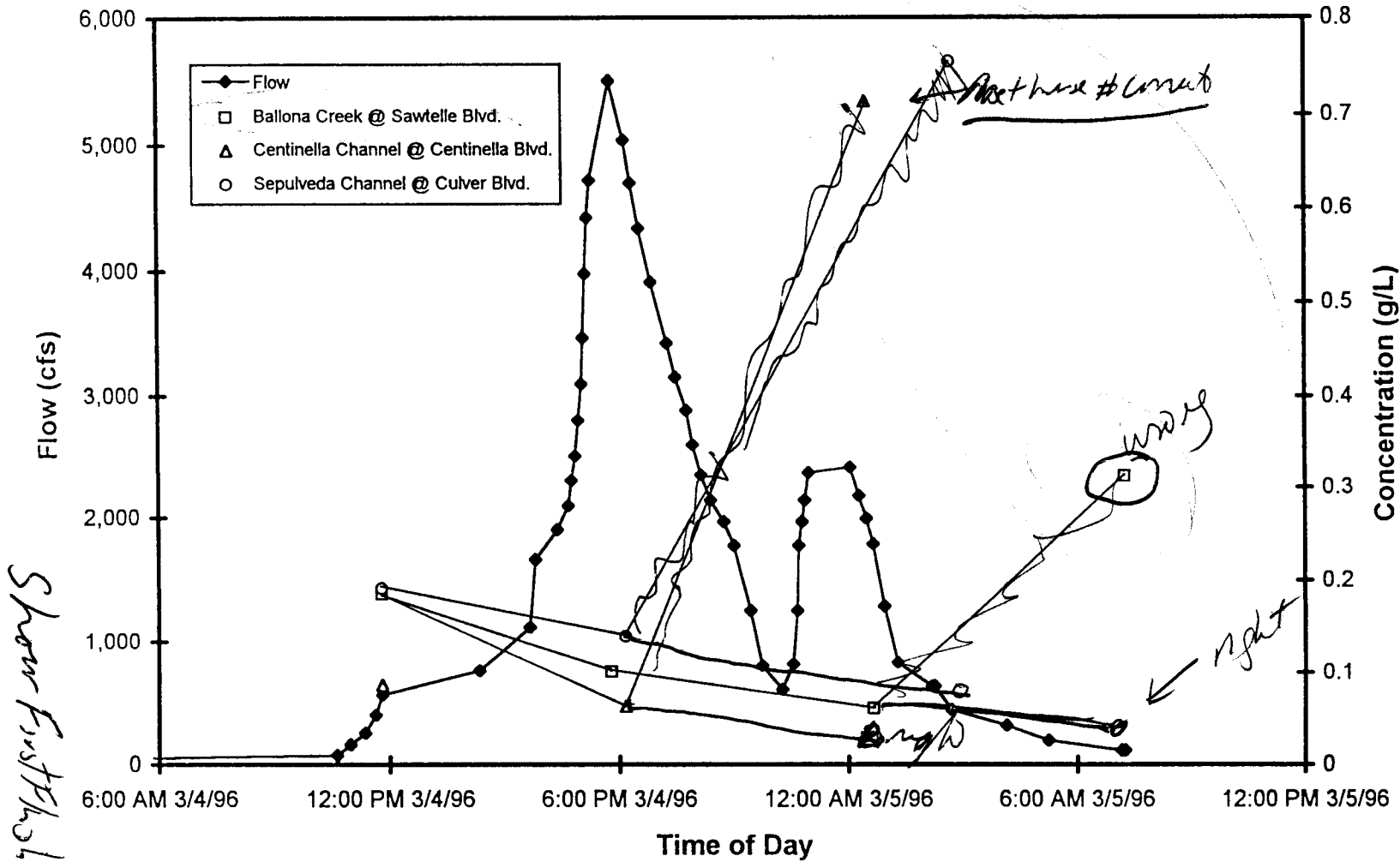
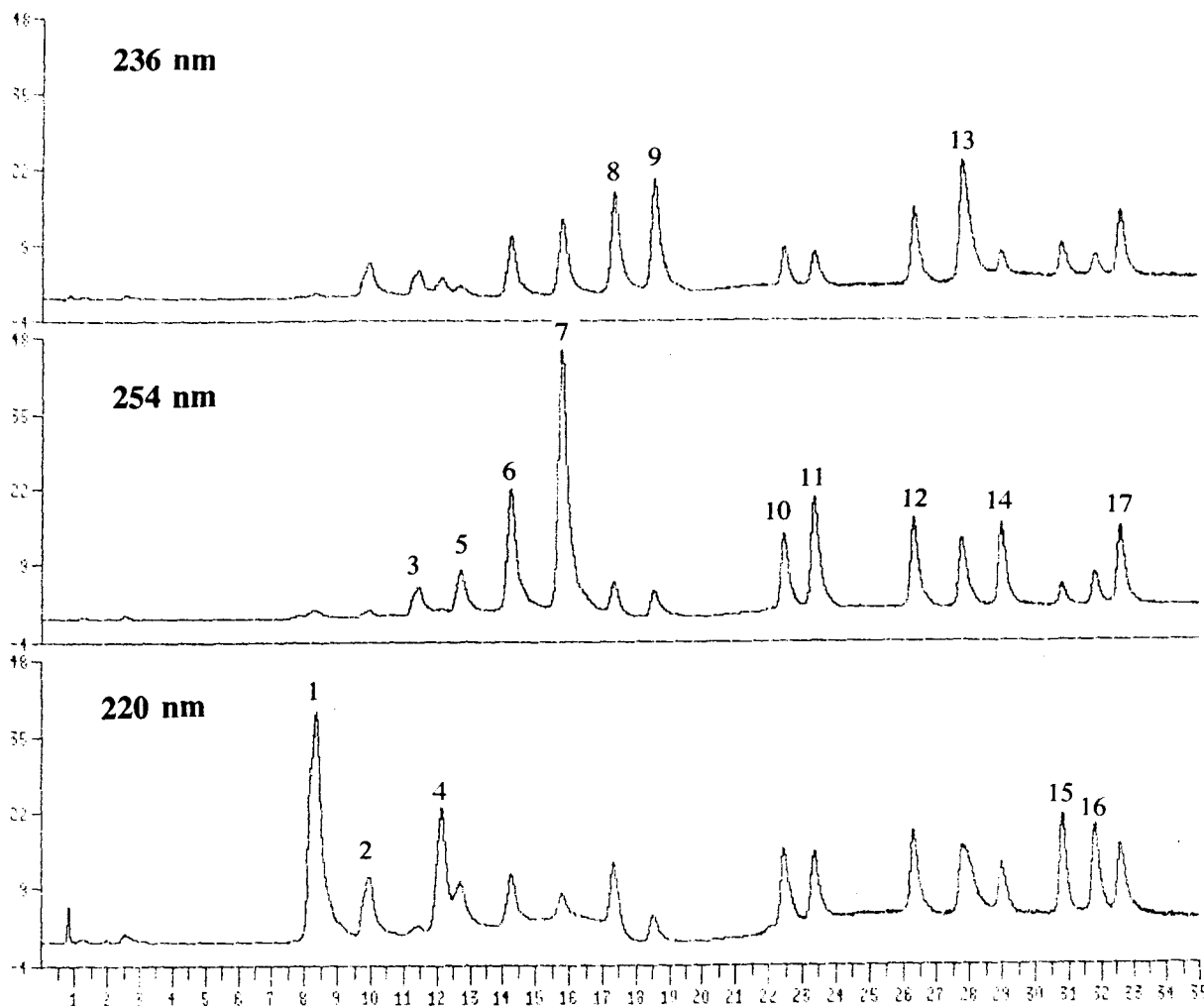


Figure 6b. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and suspended sediment loads from upstream samples at the locations specified.

4.4 Screening of Water Phase for PAHs

Table 4 shows the PAH compounds analyzed at the 0.5 to 5 ppb concentration level. Surrogate recoveries in Milli-Q water were > 95%. Recoveries from actual stormwater samples were between 50-70%. This is probably due to poorer recoveries when natural organic matter is present (Fish et al., 1995). Five sample from the first two storms were analyzed for PAHs by HPLC using EPA Method 550.1. Figures 7a and 7b show an analysis of the PAH standards in contrast to a typical stormwater extract. The stormwater extract is from the December 12-13, 1995 storm event. This was the first big storm of the season, and as such should contain the highest levels of contaminants. None of the water extracts screen showed detectable levels of any of the PAHs. In addition to the recovery standards, there were a few other peaks observed in the chromatograms. However, the UV spectrum of the small peaks indicated that they were not PAH's. Since the water phase extracts showed little indication of any compounds above detection limits, and since the focus of the project was on the contamination of sediments near the mouth of Ballona Creek, and based upon these results, no further analyses of the aqueous filtrates was performed.



- | | | |
|----------------------------|--------------------------|-----------------------------|
| 1. Naphthalene | 7. Anthracene | 13. Benzo(k)fluoranthene |
| 2. Acenaphthylene | 8. Fluoranthene | 14. Benzo(a)pyrene |
| 3. 4, 4'-difluorobiphenyl* | 9. Pyrene | 15. Dibenz(a,h)anthracene |
| 4. Acenaphthene | 10. Benzo(a)anthracene | 16. Benzo(g,h,i)perylene |
| 5. Fluorene | 11. Chrysene | 17. Indeno(1,2,3-c,d)pyrene |
| 6. Phenanthrene | 12. Benzo(b)fluoranthene | * Internal Standard |

Figure 7a. HPLC Chromatograms of a standard solution of the 16 PAHs screened for in the aqueous phase. Three different wavelengths were used in order to maximize the sensitivity to all PAHs. The chromatogram was generated using a 250 x 4.6 mm Whatman PAH column, gradient elution (CH₃CN and H₂O), and a 50 μl injection. The concentration of the solution is approximately 2 ppm.

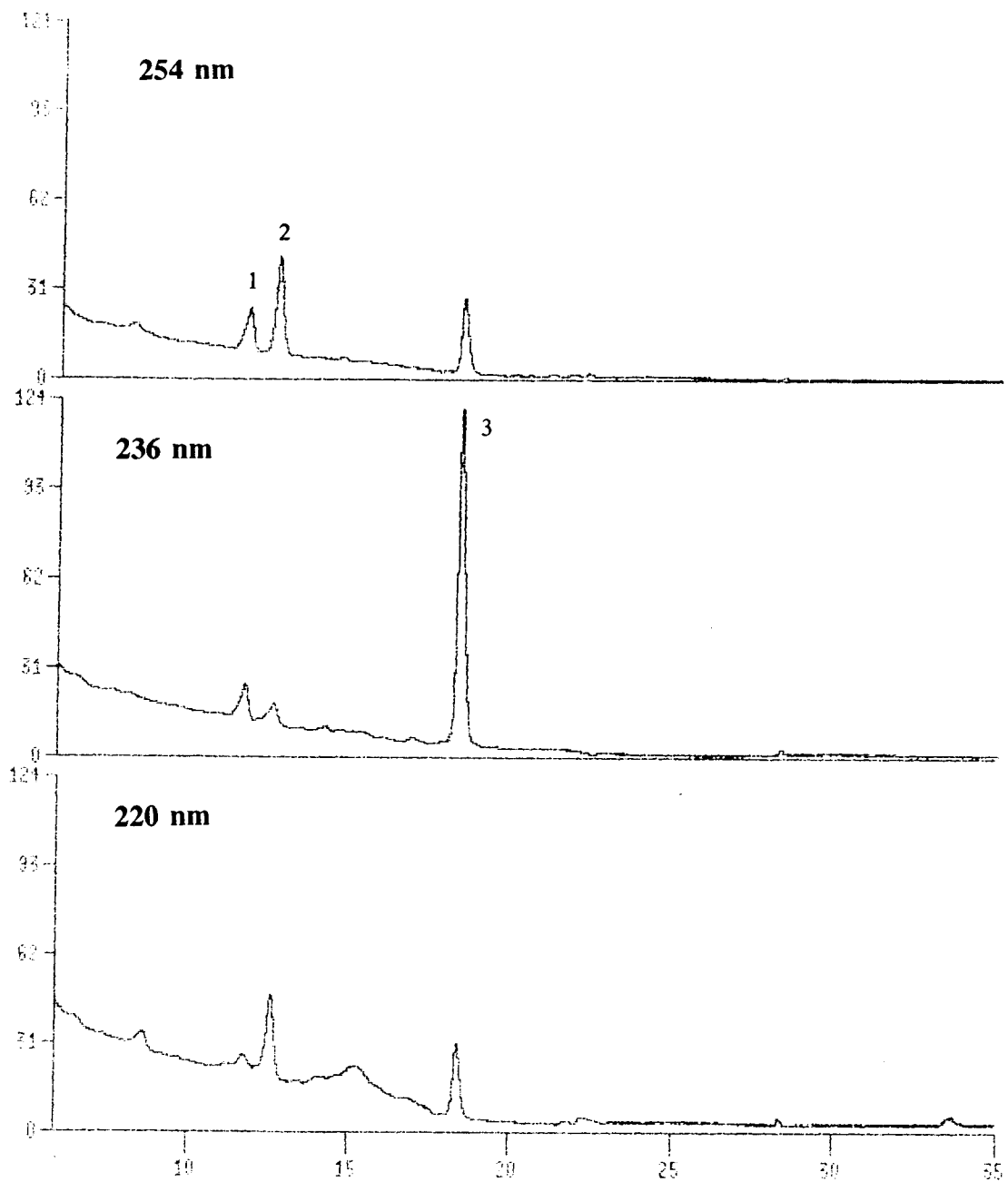


Figure 7b. HPLC chromatograms of a representative aqueous phase extract of a stormwater sample from the 12/13/96 storm event. The sample was taken from Ballona Creek at the Pacific Ave bridge (T3). The three prominent peaks are the internal standard and two deuterated recovery surrogates: 1. 4,4'-difluorobiphenyl, 2. D10-Fluorene and 3. D10-Pyrene.

4.5 Organic Pollutants Associated of Suspended Solids from Upstream Sites: Ballona Creek, Sepulveda Channel and Centinela Channel

A complete list of the results from the base/neutral target compound analyses for each storm event sampled are presented in Appendix B (Tables B.4 through B.7 and B.9). The results reported were obtained from the analyses of suspended solids in stormwater collected in the Ballona Creek Watershed during the 1995-1996 storm season. Specifically, the suspended solids analyzed were from Sepulveda Channel, Centinela Channel and Ballona Creek (See Figures 1). The isolated suspended solids were analyzed for semivolatile organic compounds. A list of the acid/base neutral target compounds is shown in Table 3 and Appendix B, Table B.3. In this section of the results, data will be presented which attempts to address the main objectives of the study, namely to determine the types and concentrations of organic pollutants associated with suspended solids emanating from Ballona Creek and its two major tributaries, and to estimate their relative contributions.

4.5.1 Analytical Recovery Data - Quality Assurance

Recovery factors for the base neutral organics were determined by measuring the recoveries of surrogate compounds spiked into various samples. Surrogates represent a broad spectrum of the types of organics isolated by the base neutral analytical procedure. The fraction of surrogate recovered was determined for each of the samples. The surrogate which exhibited the greatest recovery was 4-terphenyl-D14 (overall average recovery of 99.9 %) while the surrogate which showed the least recovery was nitrobenzene-D5 (overall average recovery of 41.8 %). The average recovery of all surrogates for each sample was determined and used to adjust the concentration of each base-neutral compound detected in the analysis by dividing the concentration determined by GC analysis by the recovery factor. However, not all samples were spiked with recovery surrogate compounds so as to permit the subsequent analysis of the same extract for organochlorine compounds by GC/ECD (EPA Method 608). In order to adjust the concentrations of base-neutral

compounds in these samples, an overall surrogate recovery factor was determined using the average recovery factor for all of the samples which were spiked with surrogates. Since the upstream sampling efforts reported here were only a portion of a larger study which included samples taken from Ballona Creek at Pacific Avenue Bridge, surrogate recovery factors obtained from these samples were also included in the average in order to provide a more robust data set. As shown at the bottom of Table B.2, the overall recovery factor was determined to be 67.8 % (with a range of 41 to 99%). The grand mean was within EPA guidelines of EPA Method for surrogate analysis (33 - >100%). This overall recovery factor was then applied as described above.

4.5.2 Identification of Target Base-Neutral Semivolatile Organic Compounds in Wet Weather Flow

Based on the results obtained in this study, the primary classes of target compounds detected in the stormwater suspended solids were Polynuclear Aromatic Hydrocarbons (PAH's) and phthalates (see Appendix B). PAH's are known to be formed from the incomplete combustion of fossil fuels, with the greatest contribution stemming from the burning of gasoline and diesel fuels in automobiles and trucks. Of the 17 target PAH's, pyrene was consistently found in greatest concentration. Other PAH's which were consistently found in stormwater samples included benzo[a]pyrene, benzo[k]fluoranthene, chrysene, fluoranthene, and phenanthrene. Phthalates are derived from plastics and are known to be common pollutants in estuarine environments (Libes, 1992). The phthalate found in the greatest concentrations was bis(2-ethylhexyl)phthalate. Other phthalates found in most samples but in lesser quantities were butylbenzylphthalate, di-n-butylphthalate, and di-n-octylphthalate. Blank control samples showed insignificant levels of phthalates in comparison to the actual samples, with exception of di-n-butylphthalate (see Appendix B, Table B.4). Therefore, the blank values for di-n-butyl phthalate were subtracted prior to evaluation for all the quantitative data.

In addition to PAH's and phthalates, other target compounds were detected such as

aniline, benzoic acid, 4-chloro-3-methyl phenol, dibenzofuran, and 2,4-dinitrotoluene. However, occurrences of these other target compounds were few, and in low concentrations. Numerous non-target compounds were detected. However, these consisted mostly of long chained branched hydrocarbons (C₁₀-C₃₀), which are common constituents of oil and grease. These types of compounds have been reported in other studies and are derived mostly from automobiles.

Calculations of individual and total PAH concentrations on suspended sediment and in the total sample fraction for each sample at each location for each storm was performed and graphed (Appendix B, Tables B5 through B.15, and Figures B.1 through B.55). Selected Figures from Appendix B will be included in later sections to address the objectives of this study. Since it was impractical to graph all individual PAH's, only the ones which were found most consistently, and in highest concentrations were included.

4.5.3 Relative Contribution of Organic Pollutants from Ballona Creek, Sepulveda Channel and Centinela Channel

The primary objective of this study was to determine the relative contribution of semivolatile organic and heavy metal pollutants from each storm drain to Santa Monica Bay. To achieve part of this objective we have determined the concentrations of semivolatile organic compounds in the runoff from each of the three storm drains on both mass ($\mu\text{g/g}$) and volume ($\mu\text{g/L}$) basis. Reasonable estimates of mass emissions of pollutants can only be determined for Ballona Creek since that was the only location for which flow data were available. The relative mass emissions from Sepulveda and Centinela Channels can be qualitatively described based upon field observations of the flow, and the known concentration of pollutants in the suspended solids samples derived from these drains.

Figures 8 through 23 show the total PAH and phthalate suspended sediment concentrations ($\mu\text{g/g}$), and the mass loads per unit volume ($\mu\text{g/L}$), plotted versus times of day. Superimposed on each plot is the corresponding hydrograph from the Ballona Creek

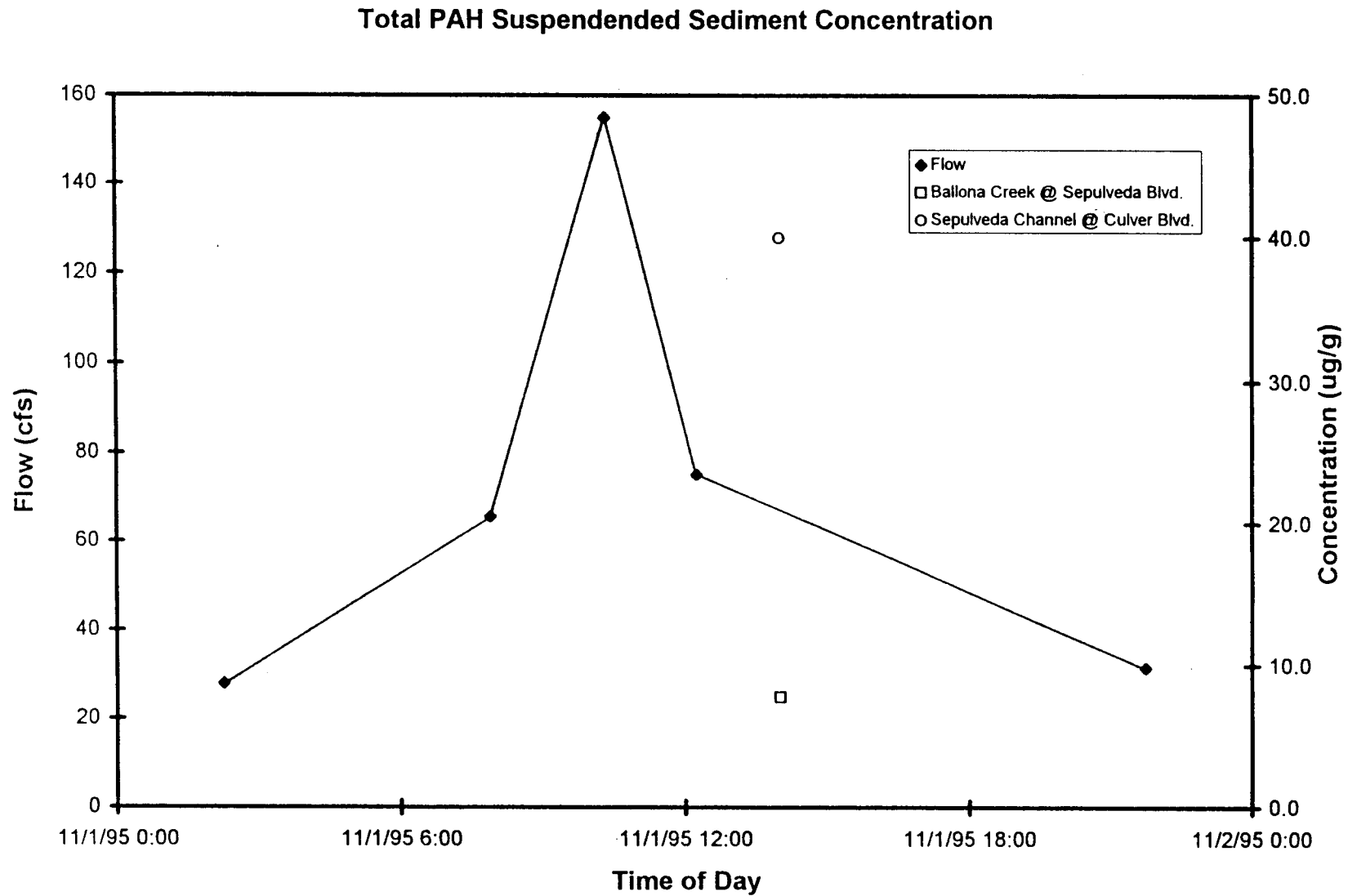


Figure 8. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.

Total PAH Mass Load Concentration

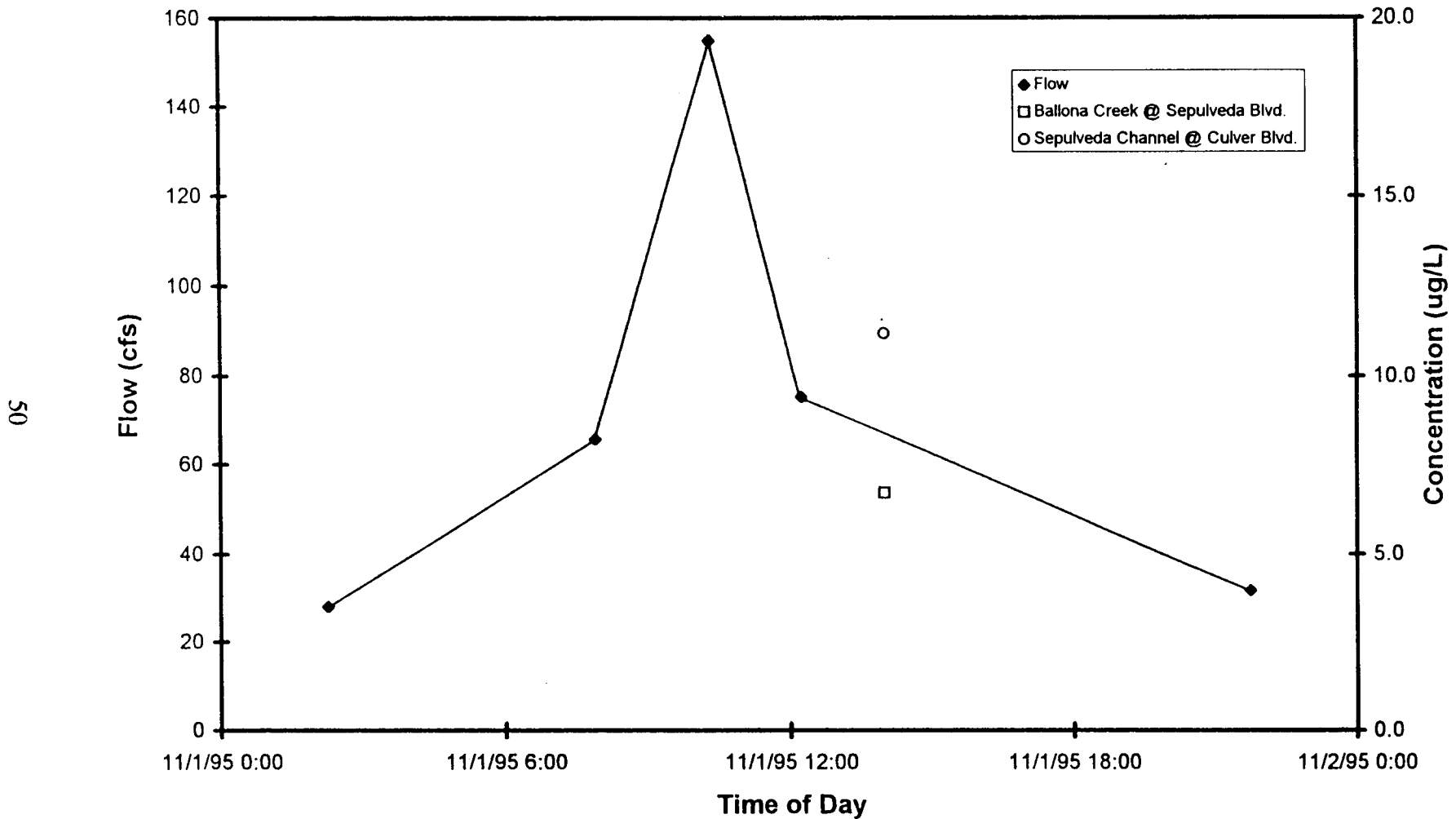


Figure 9. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from upstream samples at the locations specified.

Total Phthalates Suspended Sediment Concentration

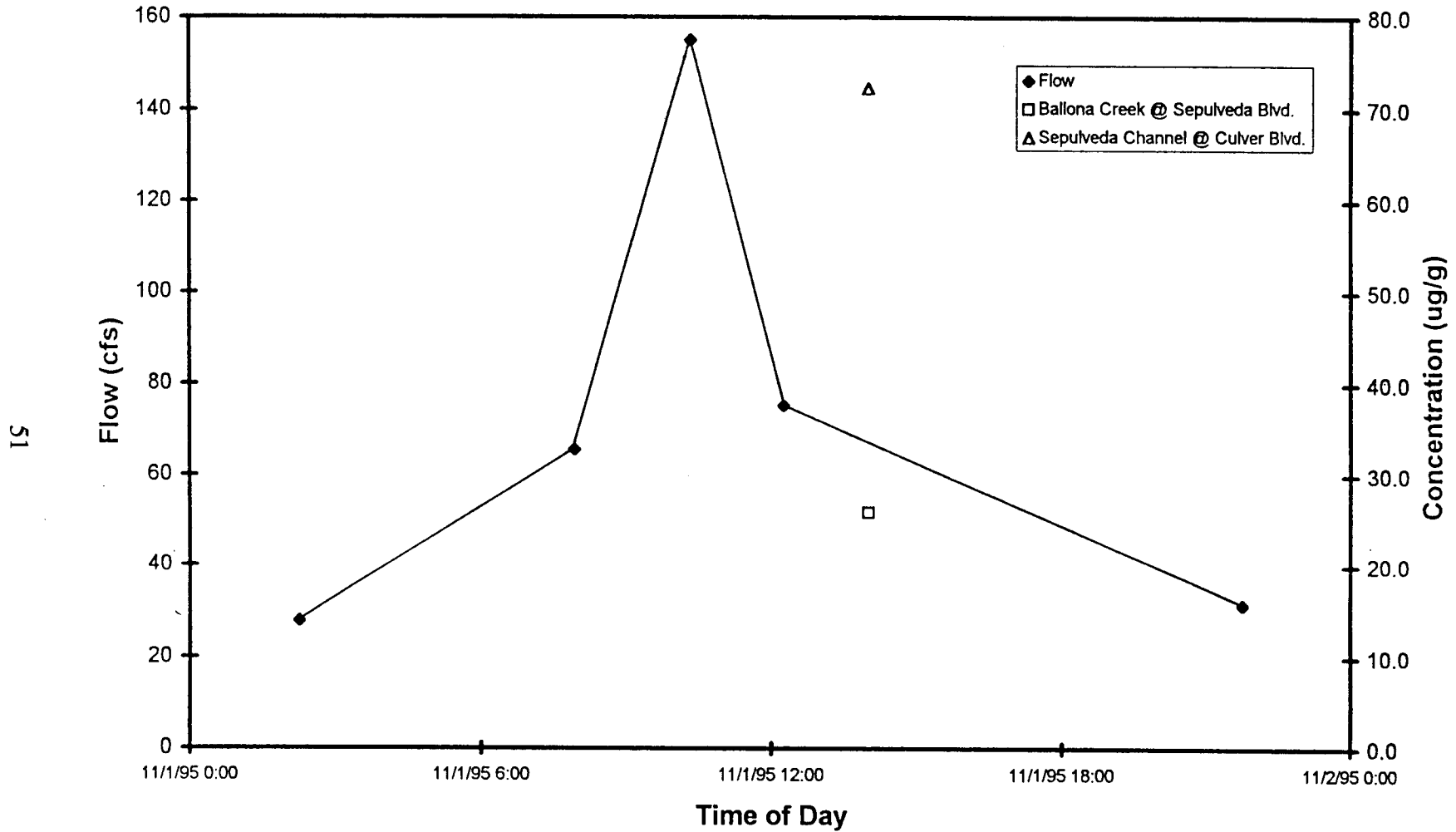


Figure 10. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.

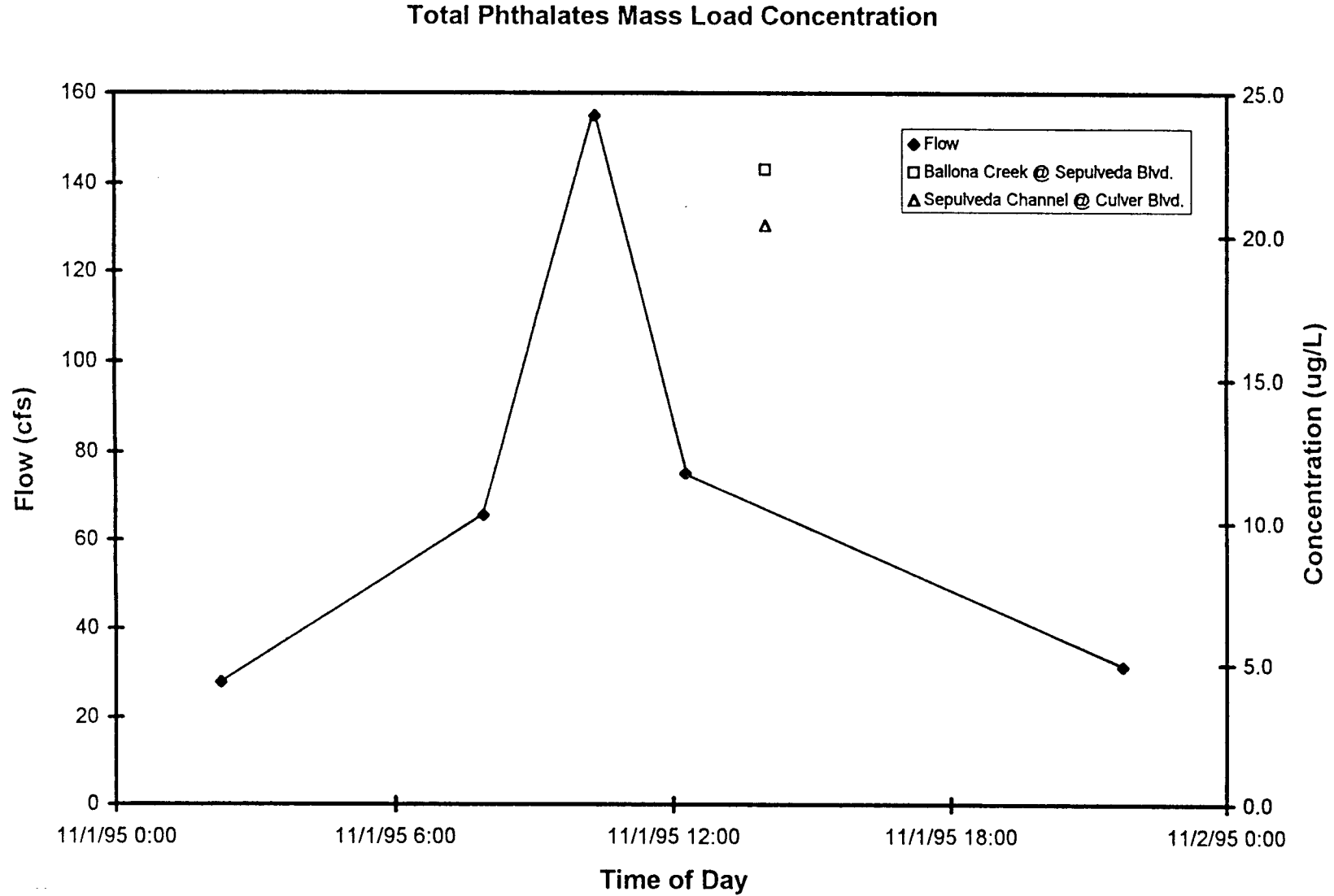


Figure 11. Stormwater flow for the November 1, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate mass load concentration from upstream samples at the locations specified.

Total PAH Suspended Sediment Concentration

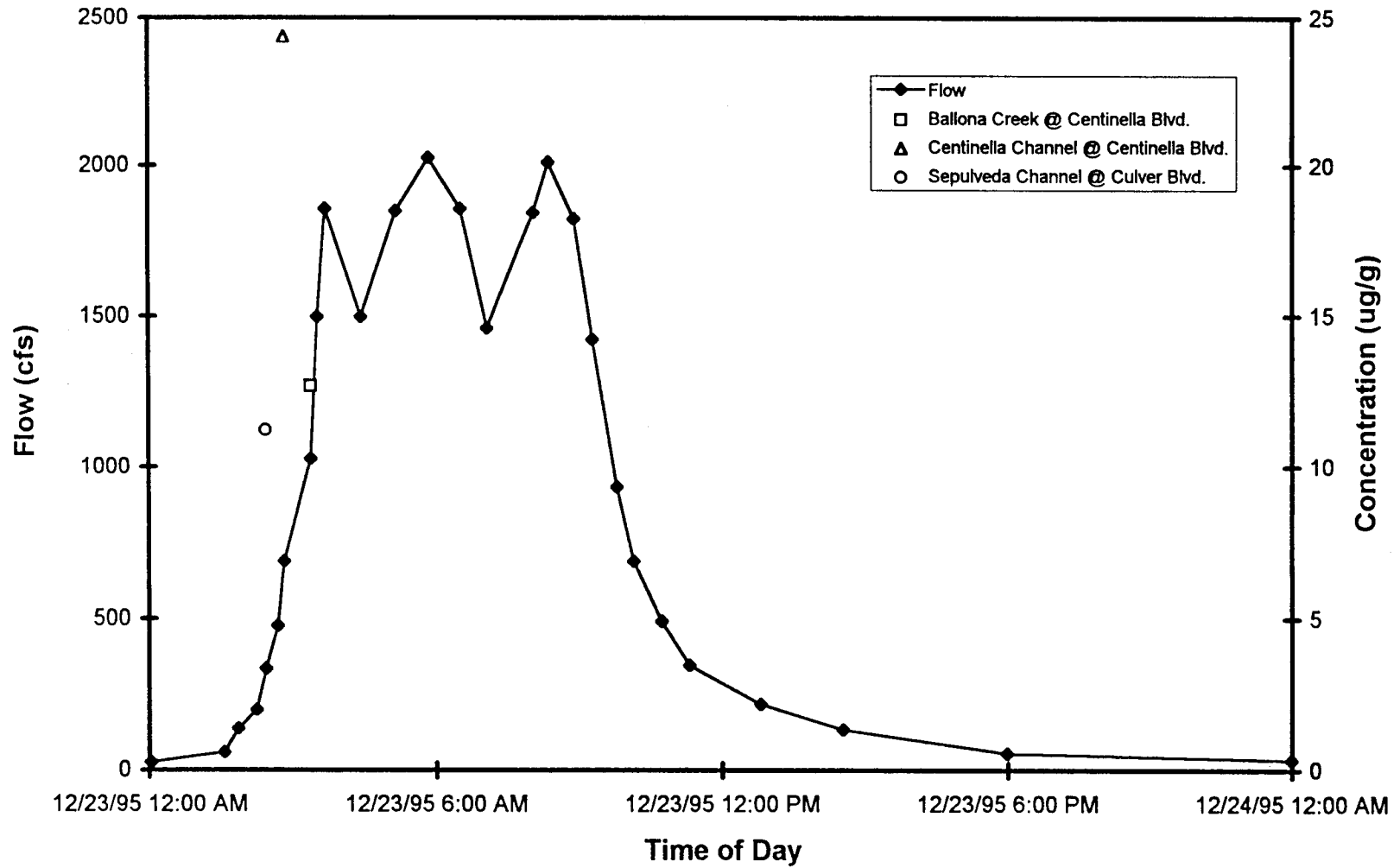


Figure 12. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.

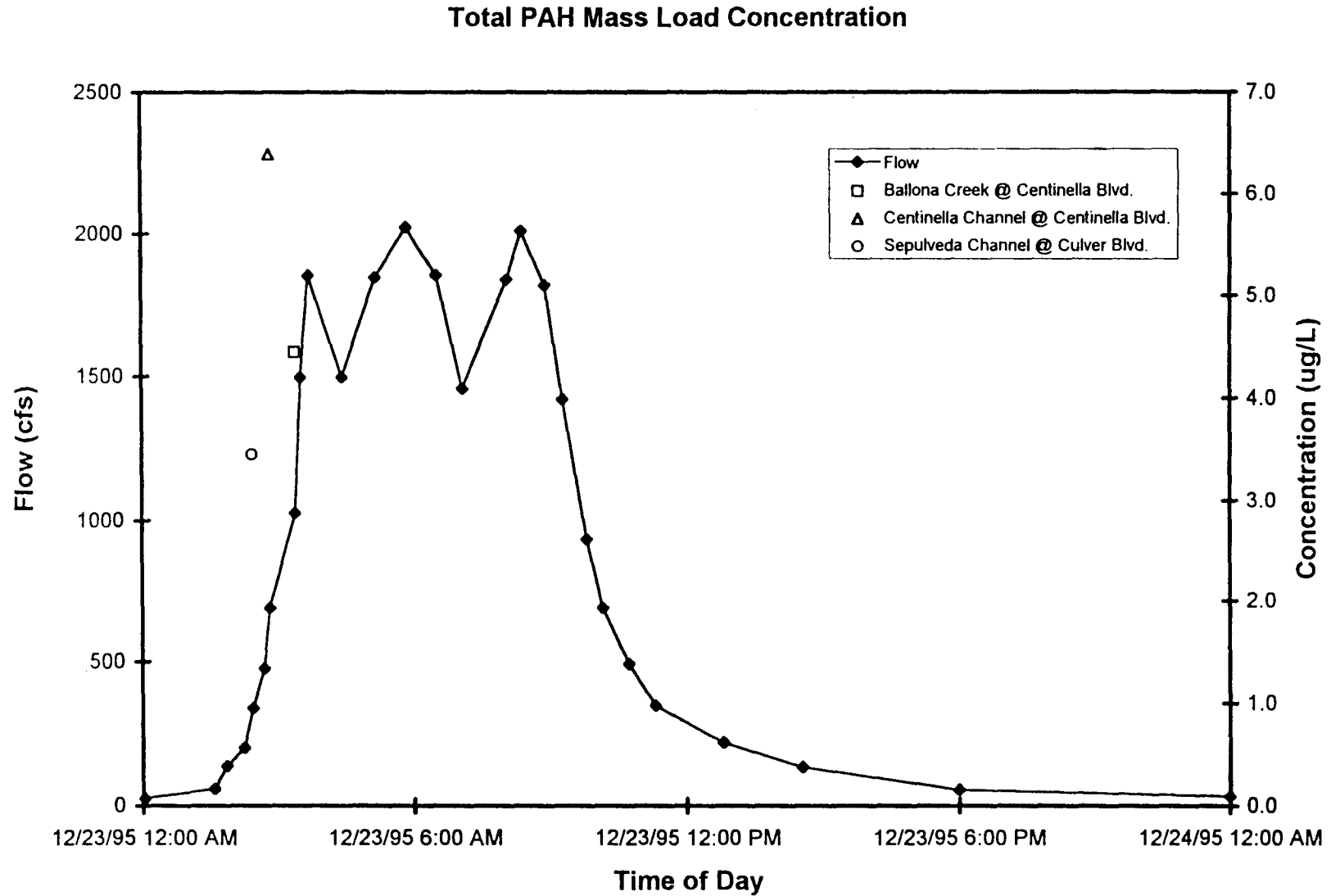


Figure 13. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from upstream samples at the locations specified.

Total Phthalate Suspended Sediment Concentration

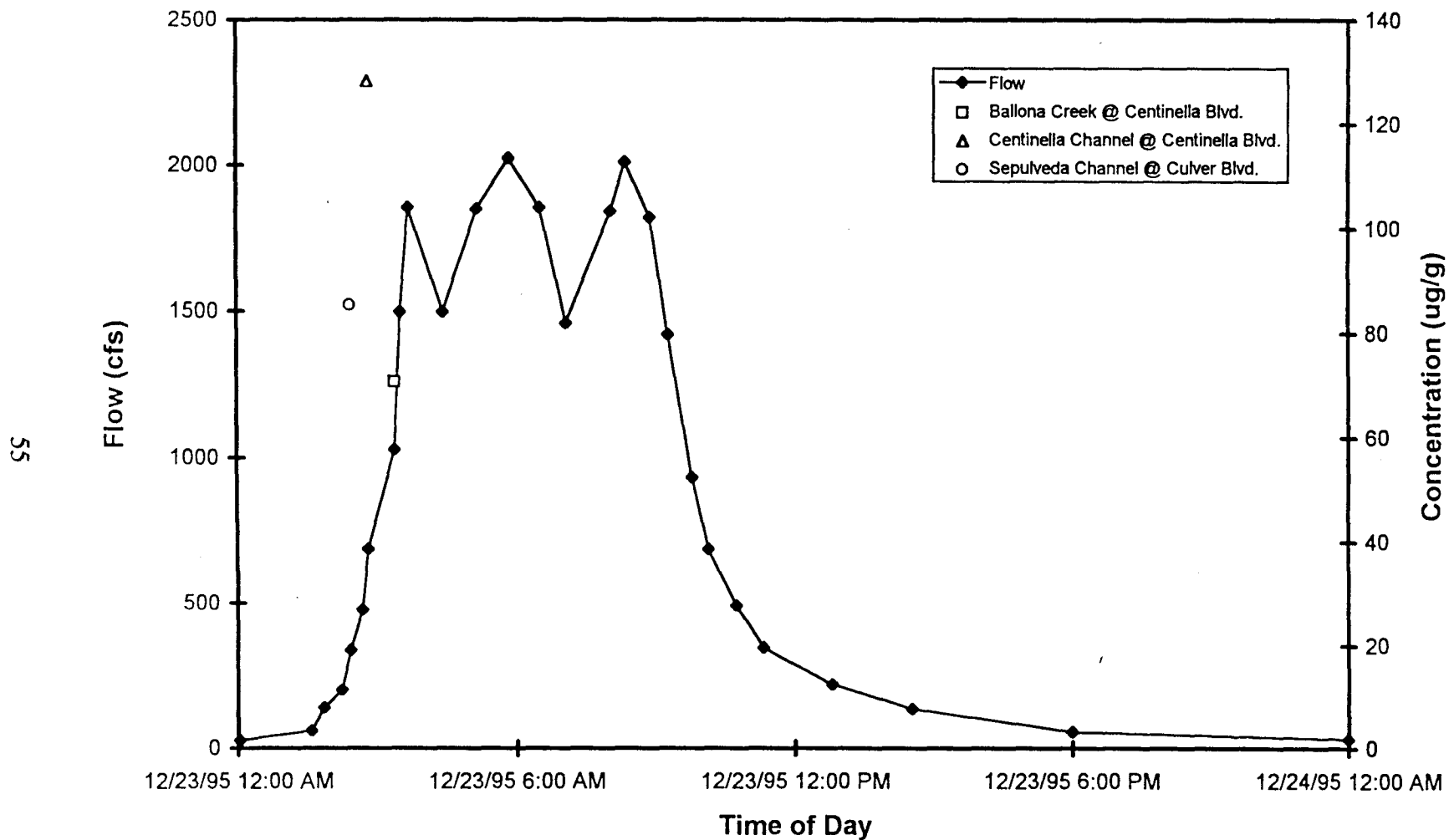


Figure 14. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.

Total Phthalate Mass Load Concentration

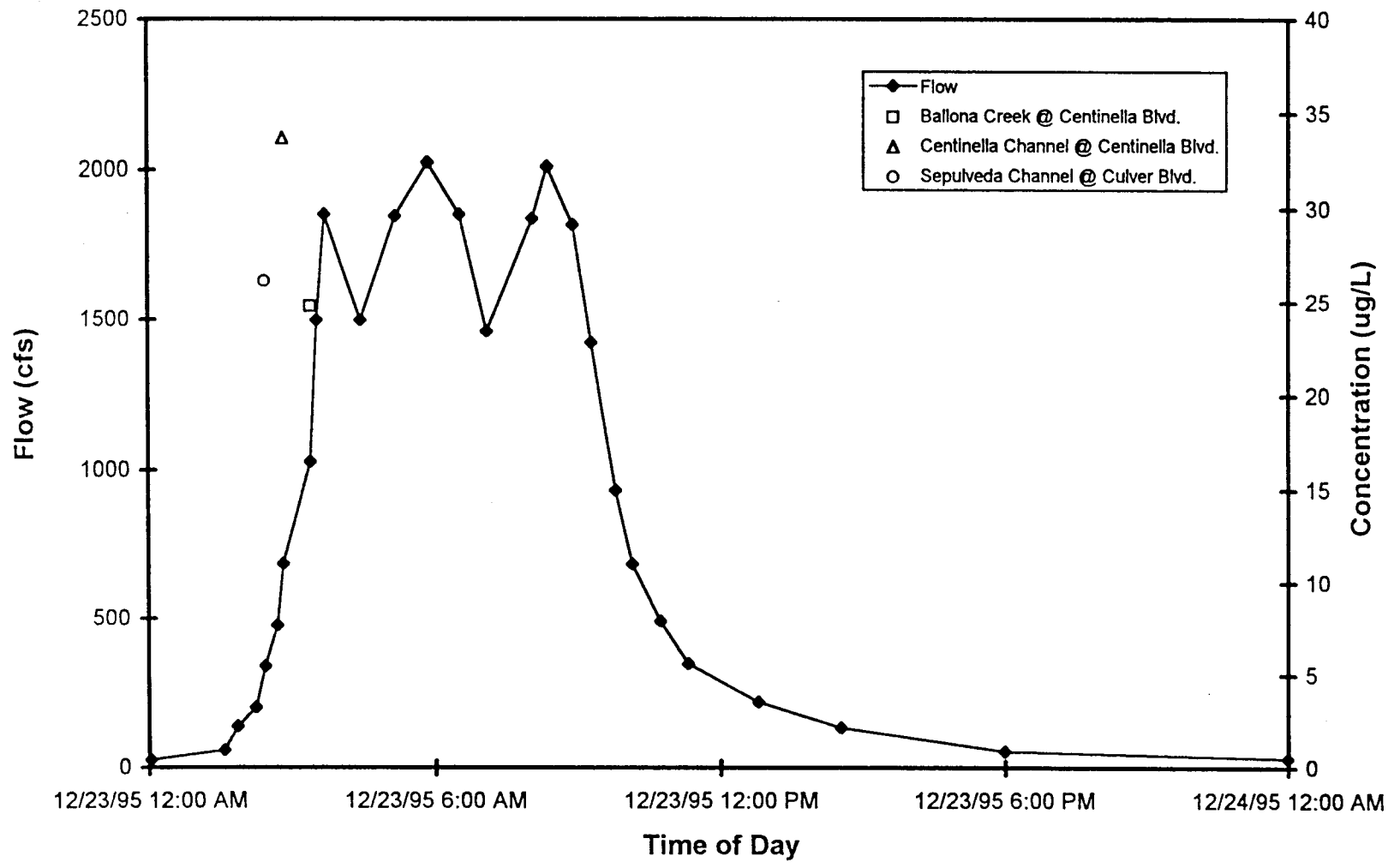


Figure 15. Stormwater flow for the December 23, 1995 storm as measured by the Ballona Creek monitoring station and total phthalate mass load concentration from upstream samples at the locations specified.

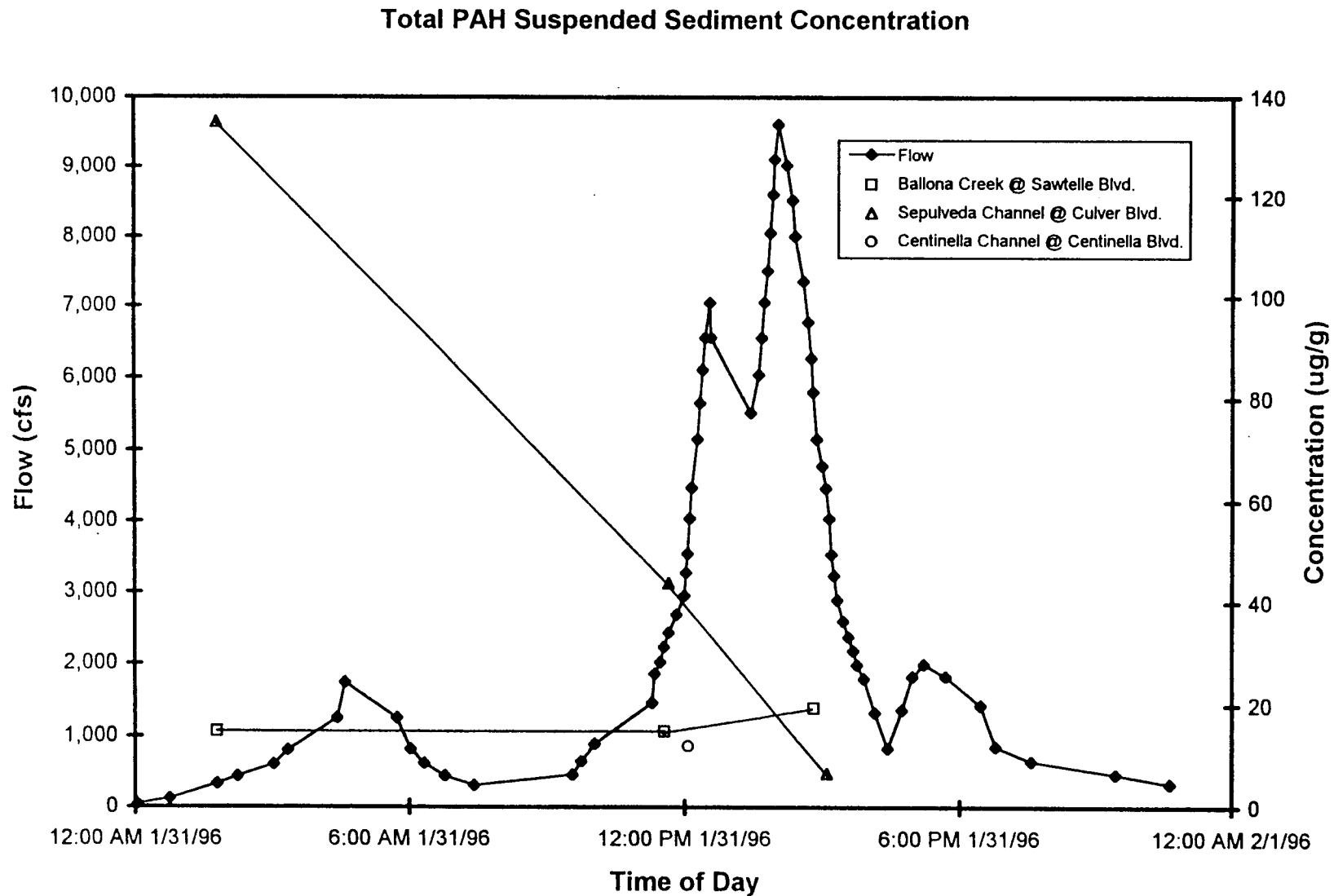


Figure 16. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.

Total PAH Mass Load Concentration

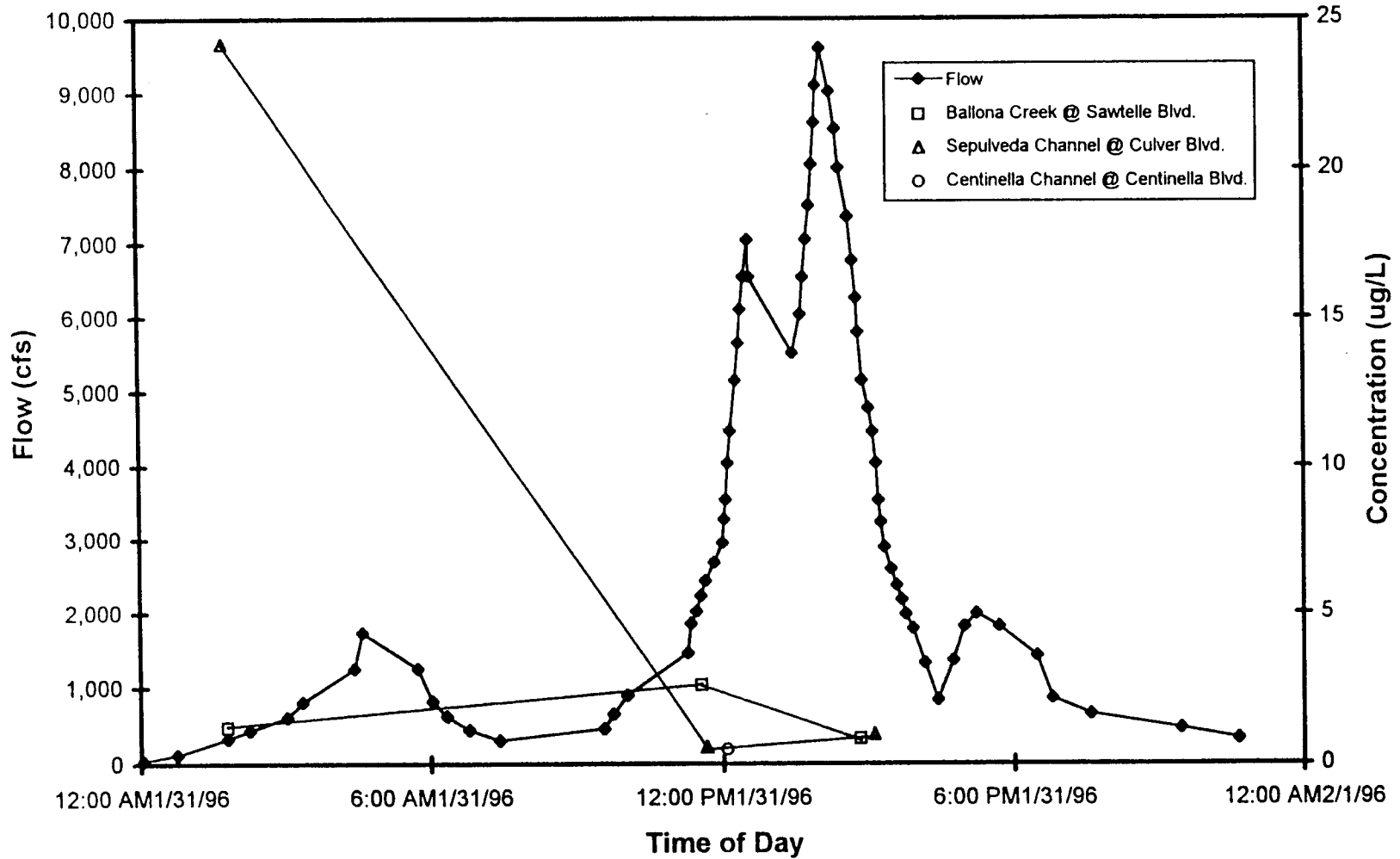


Figure 17. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from upstream samples at the locations specified.

Total Phthalate Suspended Sediment Concentration

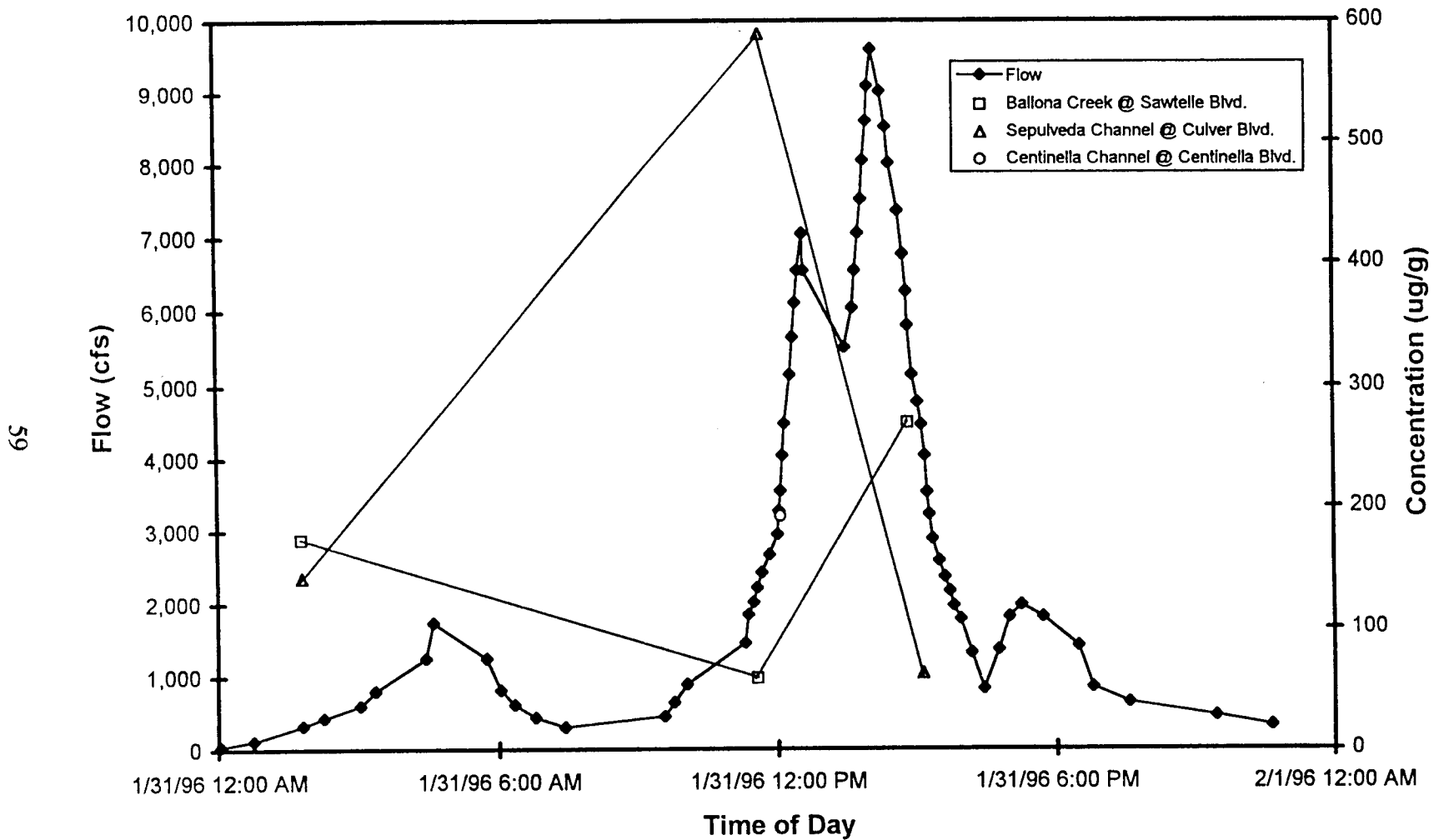
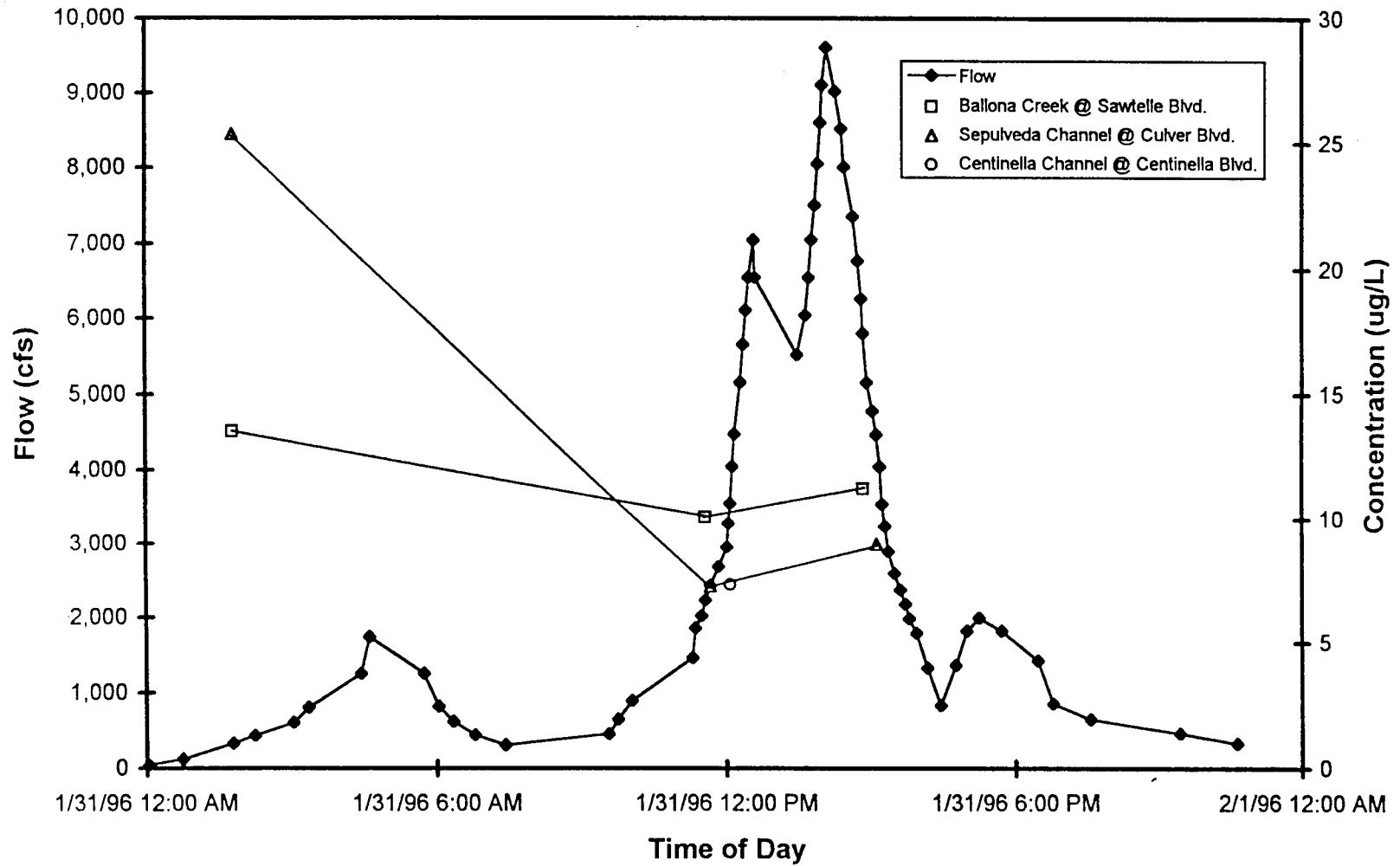


Figure 18. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total phthalate suspended sediment concentration from upstream samples at the locations specified.

Total Phthalates Mass Load Concentration



09

Figure 19. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total phthalate mass load concentration from upstream samples at the locations specified.

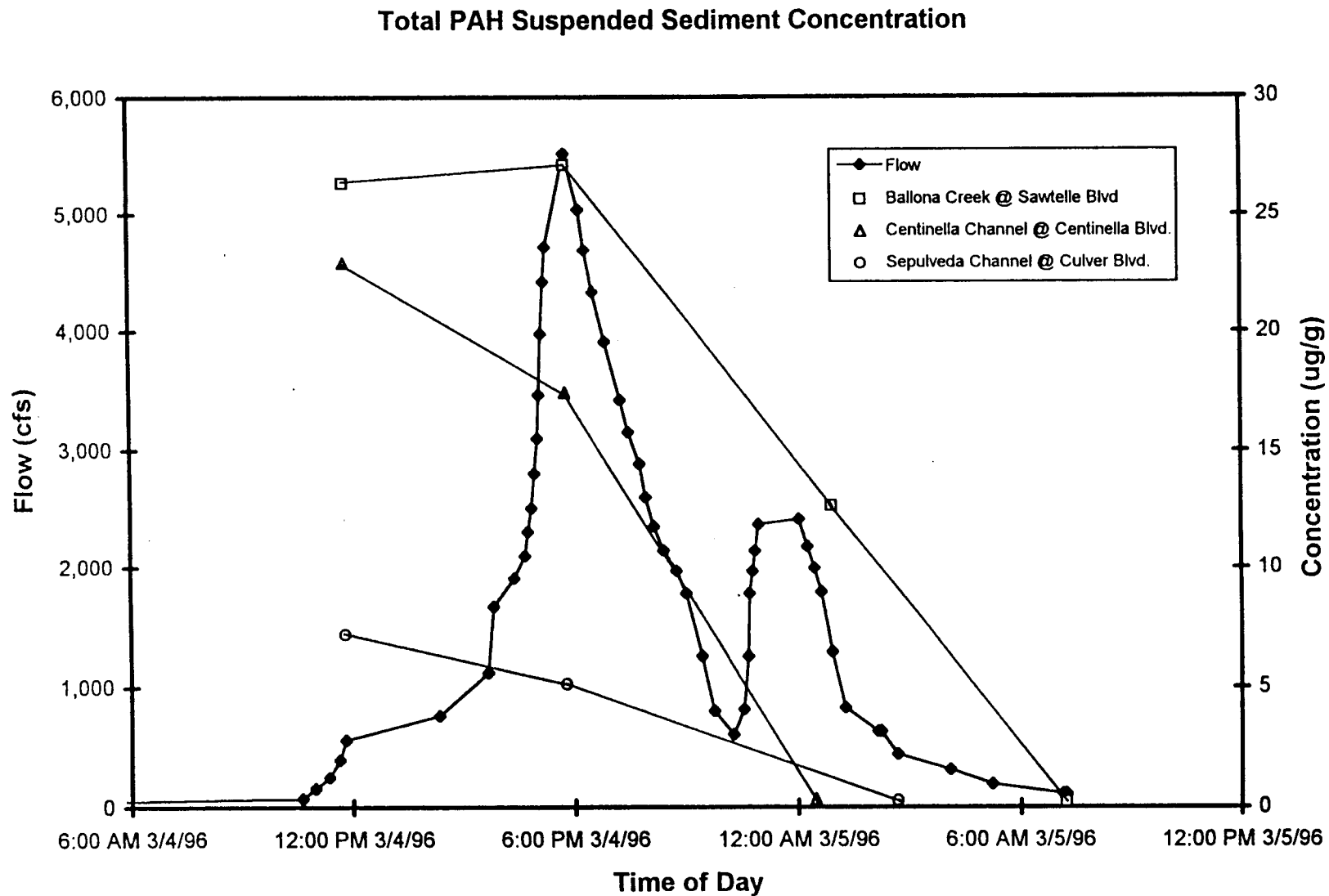


Figure 20. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from upstream samples at the locations specified.

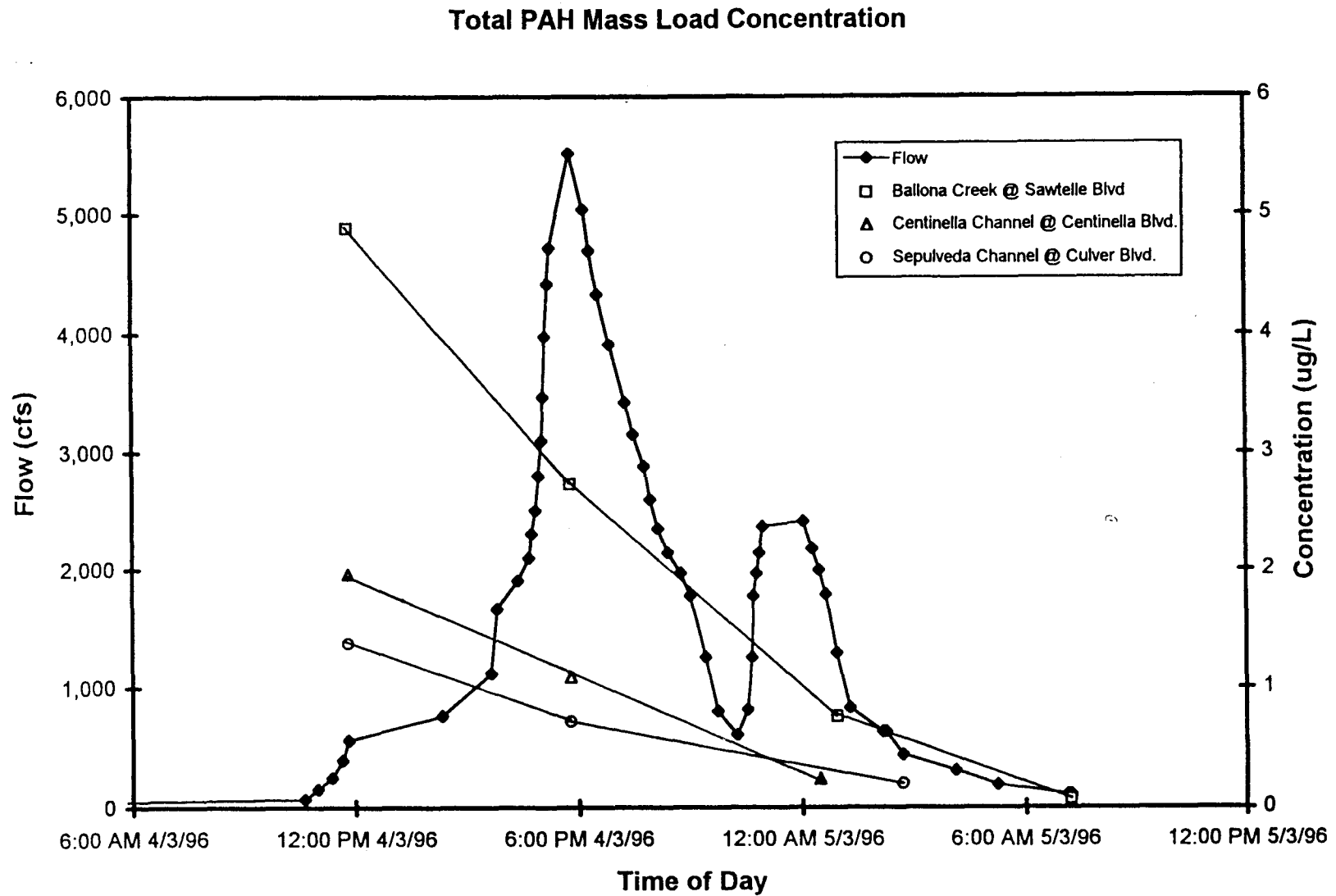


Figure 21. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from upstream samples at the locations specified.

Total Phthalate Suspended Sediment Concentration

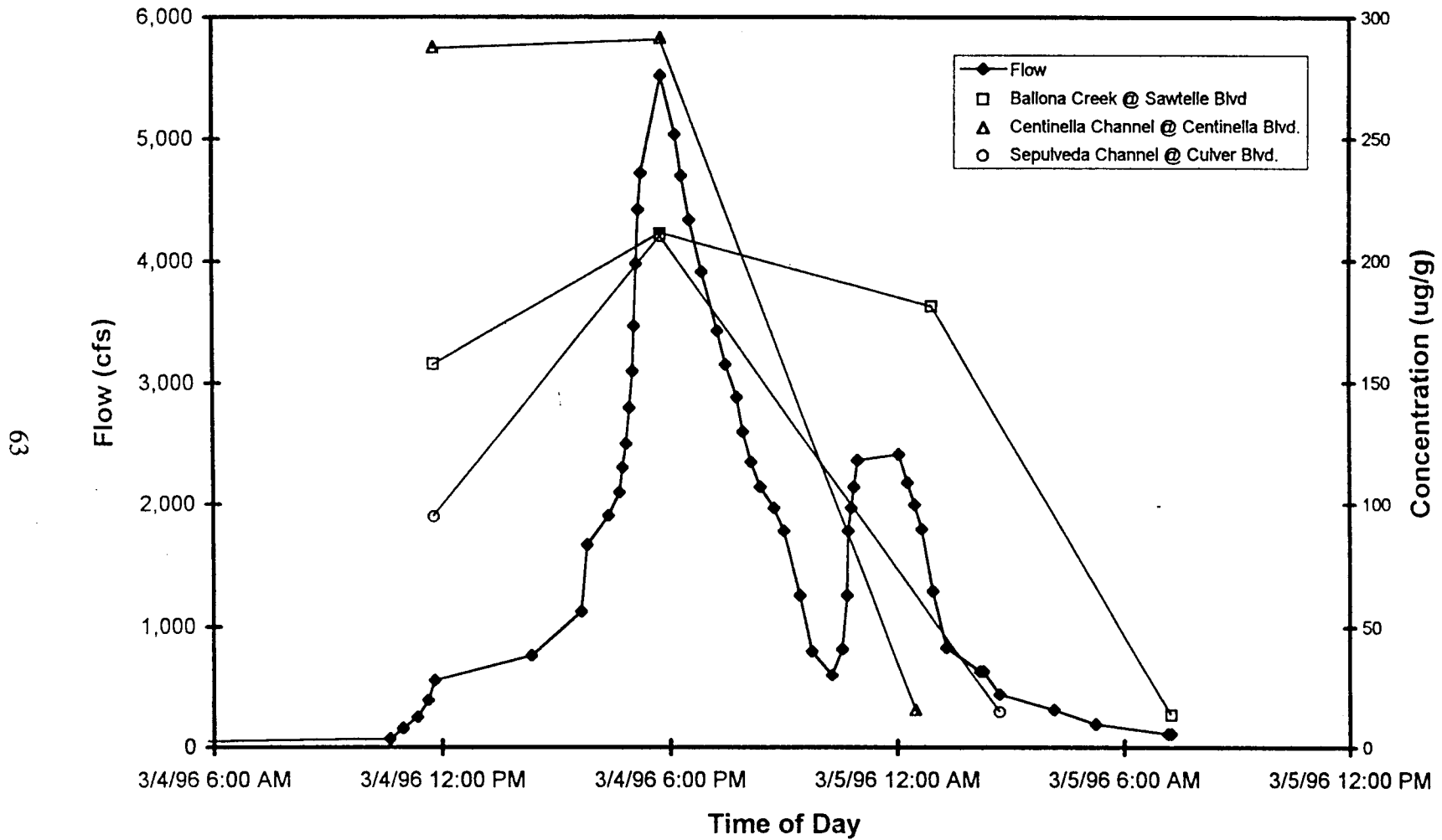


Figure 22. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate suspended sediment concentration from upstream samples at the locations specified.

Total Phthalate Mass Load Concentration

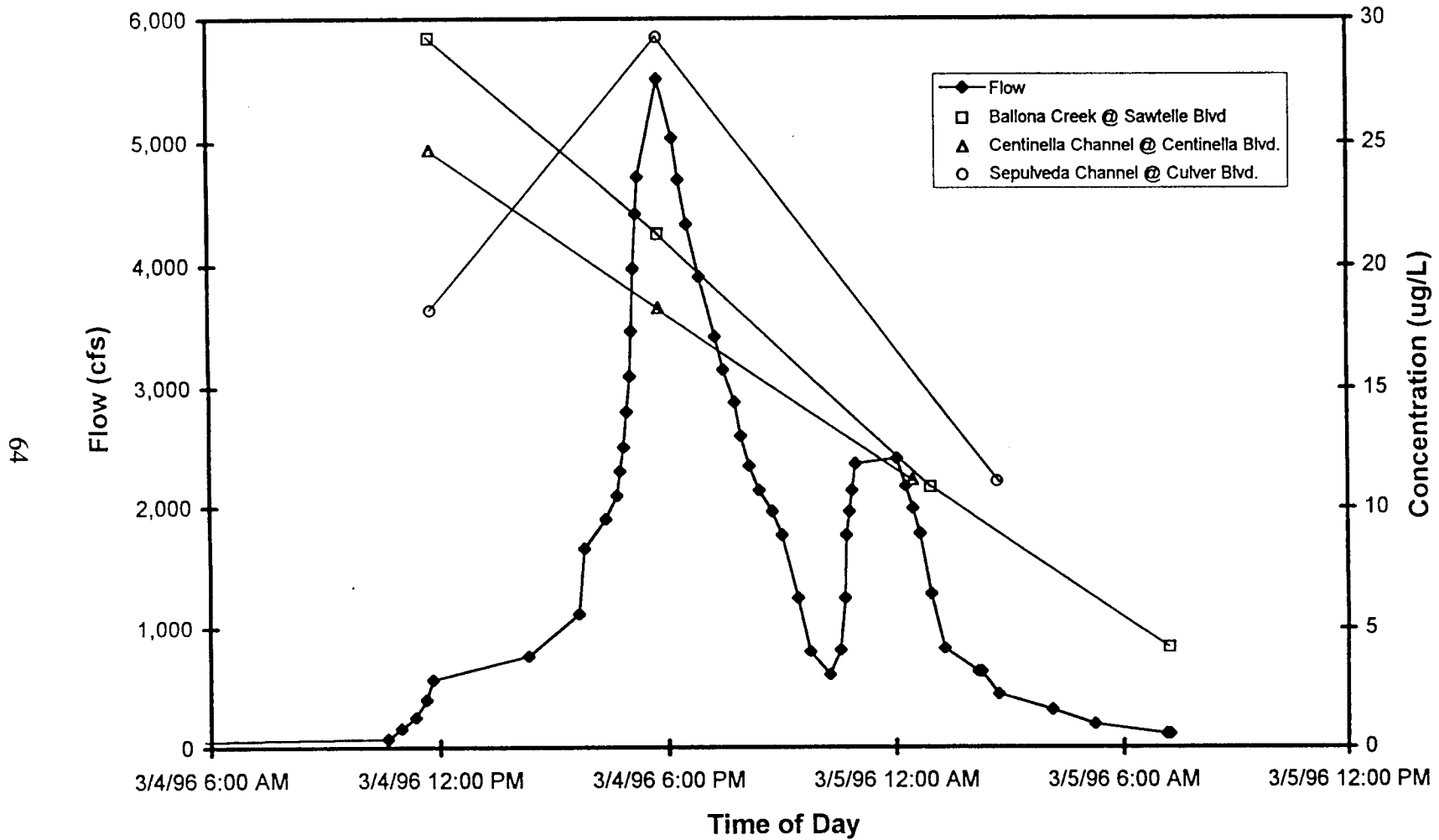


Figure 23. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate mass load concentration from upstream samples at the locations specified.

Monitoring station. This was done to provide a reference between the sampling time and the stage of the storm runoff. Note that single grab samples were collected for the November 1, December 12-13, and December 23, 1995 storms, whereas multiple samples were collected for the January 31, and March 4-5, 1996 storms.

In order to determine the relative contributions of the three storm drains, the total mass of pollutants on a per volume basis (i.e. mass loading) must be considered. Recall that based on the PAHs screening study of the filtered stormwater, it was determined that few of these compounds exist dissolved in the water column at detectable levels, and virtually all of the pollutant mass is associated with the suspended solids phase. Therefore, the mass loadings discussed herein were derived by considering only the concentration of pollutants on the solid phase (i.e., water concentrations were assumed to be negligible).

In general, the data show that the highest concentrations of organic contaminants (primarily PAH's and phthalates) are found early in the runoff hydrograph, prior peak flow. This is the so-called "First Flush" of the rainfall event. As time progressed in the storm, the concentrations of the organic compounds often gradually diminished until many of the PAH's were below the analytical detection limits.

Table 7. Relative mass loads on a volume basis ($\mu\text{g/L}$) of PAHs and Phthalates in stormwater samples from the three major storm drains of the Ballona Creek Watershed for selected storms during the 1995-96 wet weather season.

Compound	11/1/95 Storm* (After peak Flow)	12/23/95 Storm (First Flush)	1/31/96 Storm (First Flush)	3/4-5/96 Storm (First Flush)
PAHs	S>B	C>B>S	S>B>C	B>C>S
Phthalates	B>S	C>S>B	S>B>C	B>C>S

Legend: B= Ballona Creek , S=Sepulveda Channel, C=Centinela Channel

* Only Ballona Creek and Sepulveda Channel were sampled for the 11/1/95 storm.

For two of the storms (Nov. 1, 1995 and Jan. 31, 1996), Sepulveda Channel contained the highest concentration (per volume) of PAHs, followed by Ballona Creek and then Centinela Channel. However, for the December 23 storm, Centinela Channel was found to have the highest PAH concentration followed by Ballona Creek and then Sepulveda Channel. For the March 4-5 storm, Ballona Creek was found to have the highest PAH concentration followed by Centinela Channel and then Sepulveda Channel. Interestingly, the single highest total PAH concentration was found in a sample from Ballona Creek during the December 12-13, 1995 storm; unfortunately no samples were taken from the other two channels for comparison. The contributions of phthalates parallels the results for the PAHs for the 1996 storms, but differs for the 1995 storms.

It is not possible from these data to make any definitive statements regarding the relative contributions of pollutants from each of the three major storm drains. It is true however, that for every storm during the 1995-96 wet weather season, Ballona Creek had consistently higher flow than either Sepulveda and Centinela Channels. The relative volume of flow in the three drains was qualitatively observed to be in the order Ballona Creek > Sepulveda Channel > Centinela Channel. The flow in a particular drain is obviously a function of the size of the drainage area, and the intensity and duration of the precipitation therein. However, based on the observations made during sampling, the general conclusion can be made that the flows in Sepulveda and Centinela Channels were both lower and more variable than those in Ballona Creek. Thus, although the relative concentrations of pollutants in the suspended solids varied for different storms, the larger volume of flow from Ballona Creek suggests that it contributes the largest share of the contaminant load.

Accurate quantitative determination of the relative pollutant contributions could only be accomplished if accurate flow data were available on all three drains. Thus, future studies should include the placement of flow meters on both Sepulveda and Centinela

Channels. Also, since flows could be monitored in real time, this would facilitate the taking of stormwater samples at pertinent stages of the runoff.

4.5.4 Estimated Total Mass of PAHs and Phthalates Transported by Ballona Creek During Selected Storm Events

An estimate of the total mass of PAHs and phthalates transported in stormwater runoff via Ballona Creek was calculated for the January 31 and March 4-5, 1996 storm events. This was possible due to the availability of both the total PAH and phthalate concentrations determined in this study, and storm flow data obtained from the Ballona Creek monitoring station. The methodology used to estimate the total PAH and phthalate mass transport is illustrated in Figures 24 through 27, and also in Appendix B, Tables B.9, and B.10, and Figures B.32 and B.33 for the January 31, 1996 storm; and Tables B.12 and B.13, and Figures B.45 and B.46 for the March 4-5, 1996 storm.

The method entailed first determining the amount of stormwater passing the monitoring station between each measured reading. This was accomplished by multiplying the amount of time between each reading (in seconds) by the average flow (cfs or ft^3/sec) which occurred between these readings. Then, using the concentration data obtained in this study a line was drawn between each data point and the equation for the line determined. It was assumed that the pollutant concentration was 0 $\mu\text{g}/\text{L}$ at base flow both prior to and after the storm. Using this equation, the concentration of pollutants at the mid-point between each time reading was determined. This value was taken to be the average total pollutant concentration during each time interval. Then, the pollutant concentration for each time interval (in $\mu\text{g}/\text{L}$) was multiplied by the volume of stormwater flow (in liters), resulting in an estimated mass of the specific pollutants transported during the time interval. Finally, the masses of contaminants so determined for each time interval were summed over the entire storm event. It should be noted again here, that the concentrations used in these calculations represent only the contribution of contaminants associated with the suspended solids phase (aqueous concentrations are neglected). Moreover, these estimates are only

for Ballona Creek upstream of Sepulveda and Centinela Channels. Thus, these calculations represent a very conservative estimate of the total mass of PAHs and phthalates transported into Santa Monica Bay via Ballona Creek during the specified storm event.

The results of the calculations indicate that the January 31, 1996 storm transported an estimated 5.44 Kg of PAHs via Ballona Creek along with some 4.05×10^9 liters stormwater. This translates into an average concentration of 1.34 $\mu\text{g/L}$ of total PAH. For the March 4-5, 1996 storm, a estimated total of 6.79 Kg of PAHs were transported via Ballona Creek along with about 3.00×10^9 liters of stormwater, translating into an average concentration of 2.26 $\mu\text{g/L}$ of total PAH.

It is typically thought that the total amount of pollutant transport in a given channel would be dependent upon the time since the previous storm. If a storm which results in flows in Ballona Creek of at least 1000 cfs is assumed be significant, then the results obtained here did not appear to support that general conclusion. The January 31, 1996 storm occurred approximately 10 days after the previous storm (January 21st), and had both a lower average PAH concentration and total mass transport than the March 4-5, 1996 storm which followed only about 6 days after the previous significant storm (February 27th). In addition, for the 30 days prior to the March 4-5, 1996 storm, at least four storms, one of which lasted for 3 days, produced flows in Ballona Creek which were considered significant while for the 30 days prior to the January 31 storm, only two storm occurred which were considered significant. Therefore, it is not possible, based on the limited data, to make any general conclusions regarding the total contaminant mass loads transported via Ballona Creek. Future studies, including analyses of all storm events for a given season and with data from all three major drains, would be needed in order to provide a better understanding of the total mass of pollutants transported into Santa Monica Bay during storm events.

Total PAH Transport Estimation Methodology Ballona Creek @ Sawtelle Blvd.

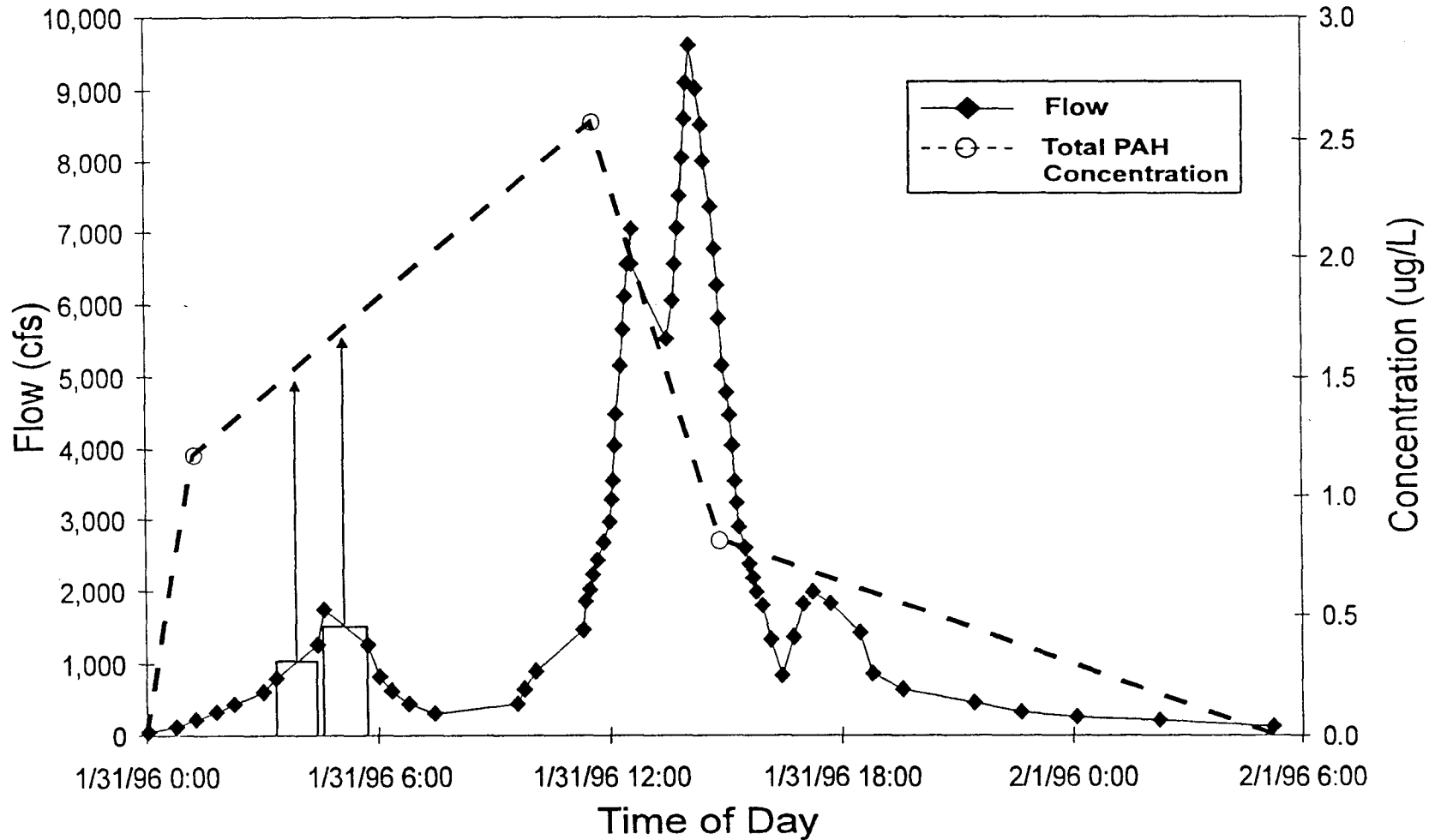


Figure 24. Diagram illustrating the methodology utilized to estimate total PAH transport at Ballona Creek at Sawtelle Blvd. during the storm which occurred January 31, 1996. Stormwater flow is indicated by triangles (◆) and total PAH concentration is indicated by open circles (○). Rectangles indicate method used to estimate flow between two time points. Arrow indicate the total PAH concentration used for each time interval.

Total Phthalate Transport Estimation Methodology Ballona Creek @ Sawtelle Blvd.

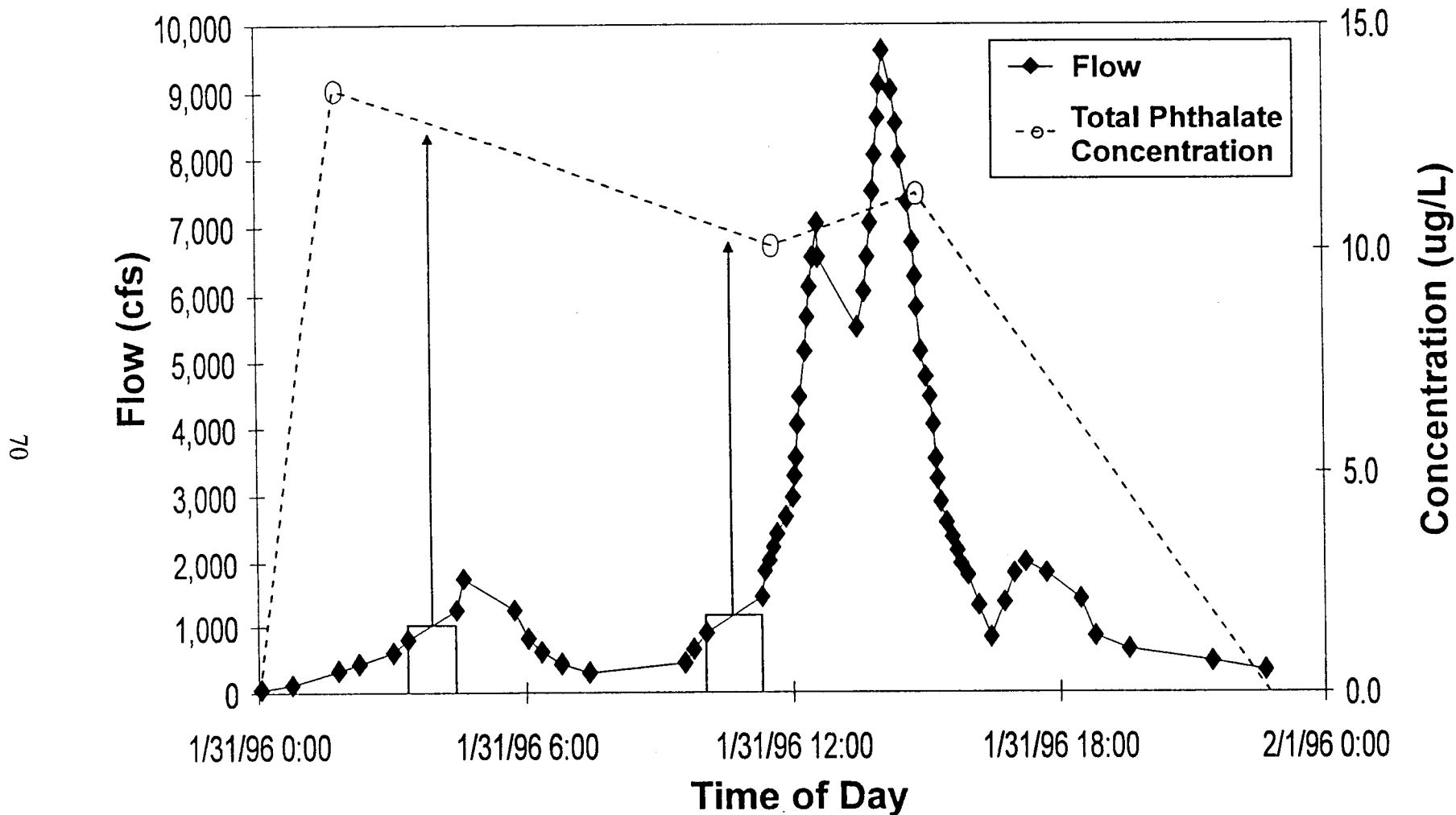


Figure 25. Diagram illustrating the methodology utilized to estimate total Phthalate transport at Ballona Creek at Sawtelle Blvd. during the storm which occurred January 31, 1996. Stormwater flow is indicated by triangles (◆) and total Phthalate concentration is indicated by open circles (○). Rectangles indicate method used to estimate flow between two time points. Arrows indicate the total Phthalate concentration used for each time interval.

Total PAH Transport Estimation Methodology
Ballona Creek @ Sawtelle Blvd.

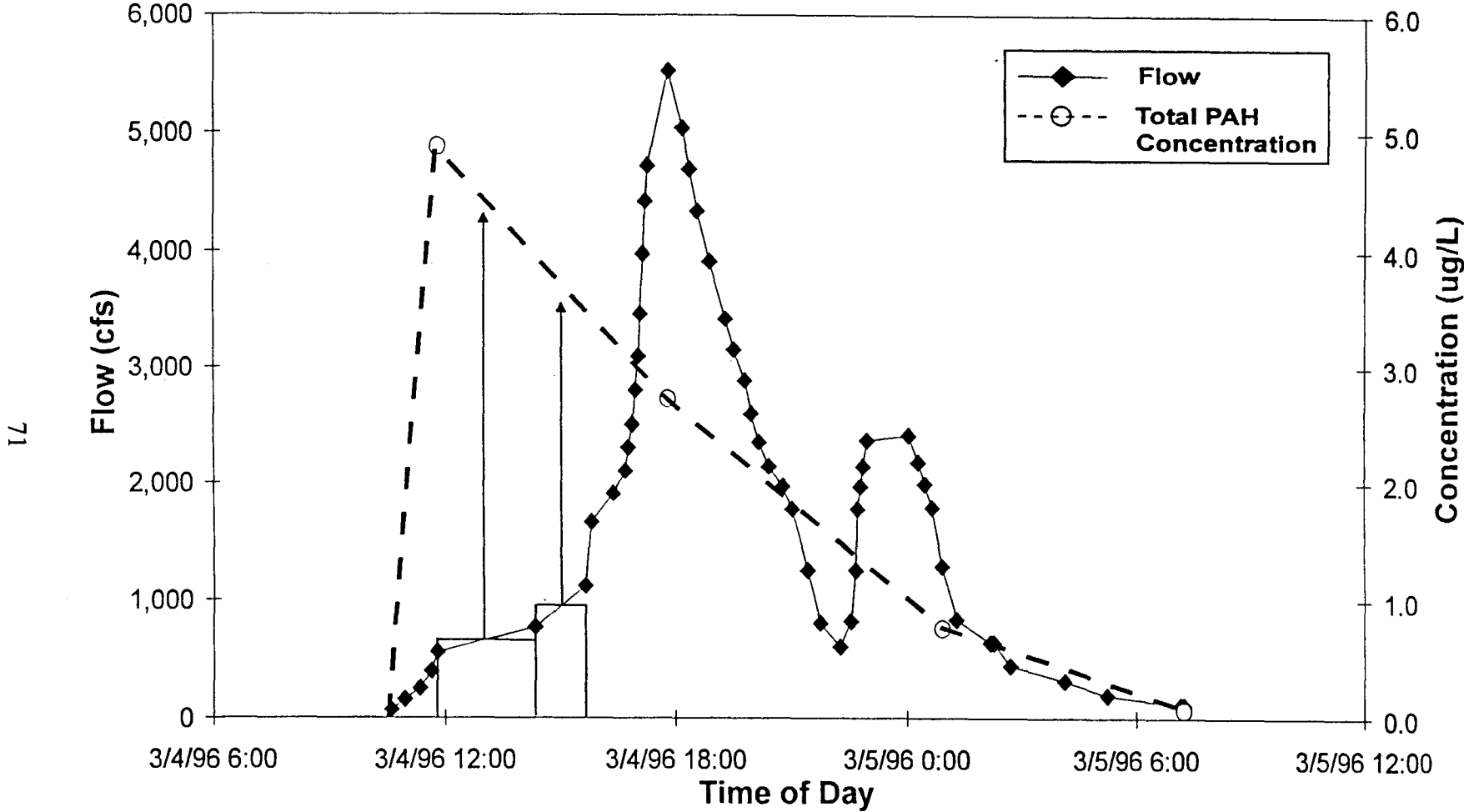
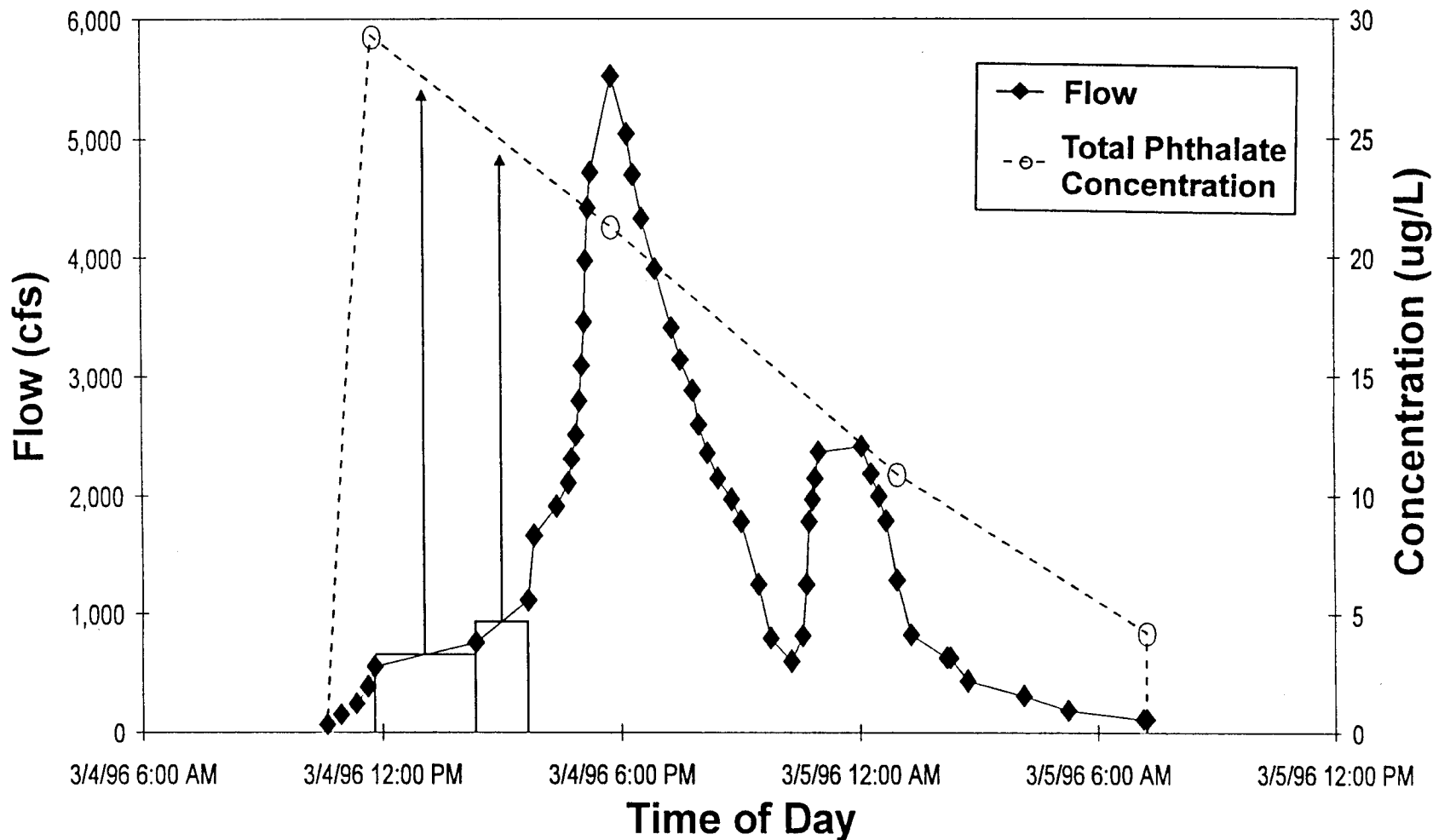


Figure 26. Diagram illustrating the methodology utilized to estimate total PAH transport at Ballona Creek at Sawtelle Blvd. during the storm which occurred March 4-5, 1996. Stormwater flow is indicated by triangles (◆) and total PAH concentration is indicated by open circles (○). Rectangles indicate method used to estimate flow between two time points. Arrow indicate the total PAH concentration used for each time interval.

Total Phthalate Transport Estimation Methodology

Ballona Creek @ Sawtelle Blvd.



72

Figure 27. Diagram illustrating the methodology utilized to estimate total phthalate transport at Ballona Creek at Sawtelle Blvd. during the storm which occurred March 4-5, 1996. Stormwater flow is indicated by triangles (◆) and total phthalate concentration is indicated by open circles (○). Rectangles indicate method used to estimate flow between two time points. Arrow indicate the total phthalate concentration used for each time interval.

4.5.5 Comparison of PAH, Phthalate, and Suspended Solid Loads in Stormwater Runoff as a Function of Sampling Times

As previously stated, the sampling times were determined in the field based upon observations of the stormwater flow, and the most recent weather forecasts. Thus, although we endeavored to collect samples at an early, middle and late stage of a storm event, this was not always achieved. In order to understand the impact of when a sample was taken on the resulting analytical data, a comparison was made of the concentrations of various constituents in stormwater runoff as a function of the point in the storm event when the samples were taken. Table 8 (also Table B.17, Appendix B) shows the suspended solids, PAH, and phthalate concentrations in samples from the five storms for which upstream sampling was performed. For each date, location and time, a particular sampling is designated as being from the early, early middle, middle, late middle or late part of the given storm event. The designation was made according to where the sampling time fell on the runoff hydrograph from the Ballona Creek Monitoring station. In order to show any trends more clearly, the data for the PAHs and phthalates are plotted on Figures 28 to 31.

The plots of the data for the PAHs do show a so-called "first flush" pattern, where the concentrations tend to be higher in samples taken in the early to middle part of the storm events. The trend is observed in both the suspended solids phase and the whole water concentrations, although the effect is more pronounced for the data presented on a volume basis (i.e., $\mu\text{g/L}$). The phthalates show a similar trend, although it is more subtle. The data actually show an increase for concentrations of phthalates in the suspended solids phase for samples taken in the middle part of the storm. However, when the data is presented on a volume basis (i.e., normalized to the amount of suspended solids in a sample) the trend is restored.

These results make intuitive sense in that the concentrations should drop as the storm progresses due to flushing of the system. In addition, as flows subside the capacity of the runoff to carry of suspended solids also decreases, and thus the concentrations on a

Table 8. A comparison of suspended solids, PAH and phthalate concentrations in stormwater samples as a function of sampling time.

Storm	Sampling Location	Time	Suspended Sediment Load (g/L)	Total PAH		Total Phthalate	
				Susp. Sed. Conc. (ug/g)	Mass Load Conc. (ug/L)	Susp. Sed. Conc. (ug/g)	Mass Load Conc. (ug/L)
Nov. 1	Ballona Sepulveda	Late	0.83	7.76	6.70	25.90	22.35
		Late	0.28	39.96	11.19	72.73	20.38
Dec. 12-13	Ballona	Middle	0.17	81.68	13.51	491.04	81.22
Dec. 23	Ballona	Early	0.35	12.70	4.44	70.66	24.71
	Sepulveda	Early	0.31	11.25	3.45	85.11	26.10
	Centinella	Early	0.26	24.36	6.39	128.23	33.64
Jan. 31	Ballona	--	--	--	--	--	--
	T1	Early	0.08	14.92	1.17	172.79	13.54
	T2	Early Middle	0.17	14.96	2.57	58.57	10.08
	T3	Late Middle	0.04	19.45	0.81	269.20	22.24
	Sepulveda	--	--	--	--	--	--
	T1	Early	0.18	134.98	24.17	141.55	25.35
	T2	Early Middle	0.01	43.75	0.54	589.06	7.26
	T3	Late Middle	0.14	6.66	0.95	62.67	8.98
	Centinella	--	--	--	--	--	--
T1	Early Middle	0.04	12.13	0.46	192.31	7.32	
Mar. 4-5	Ballona	--	--	--	--	--	--
	T1	Early	0.19	26.32	4.88	157.60	29.22
	T2	Early Middle	0.10	27.10	2.73	210.84	21.27
	T3	Late Middle	0.06	12.64	0.76	181.07	10.85
	T4	Late	0.31	0.23	0.07	13.45	4.20
	Sepulveda	--	--	--	--	--	--
	T1	Early	0.19	7.17	1.37	95.02	18.17
	T2	Early Middle	0.14	5.13	0.72	209.97	29.27
	T3	Late Middle	0.76	0.27	0.20	14.70	11.10
	Centinella	--	--	--	--	--	--
	T1	Early	0.09	22.90	1.96	287.77	24.68
	T2	Early Middle	0.06	17.40	1.09	291.47	18.28
	T3	Late Middle	0.71	0.34	0.24	15.66	11.17

"Early" = sampling occurred prior to the start of high flows in Ballona Creek.
 "Early Middle" = Sampling occurred at the beginning of high flows in Ballona Creek.
 "Middle" = Sampling occurred near the time of high flows in Ballona Creek.
 "Late Middle" = Sampling occurred near the ending of high flows in Ballona Creek.
 "Late" = Sampling occurred subsequent to the high flows in Ballona Creek.

Note: Due to the methods employed to calculate Average Mass Load Concentrations from multiple samples, multiplying Suspended Sediment Load by Suspended Sediment Concentration will not equal Mass Load Concentration.

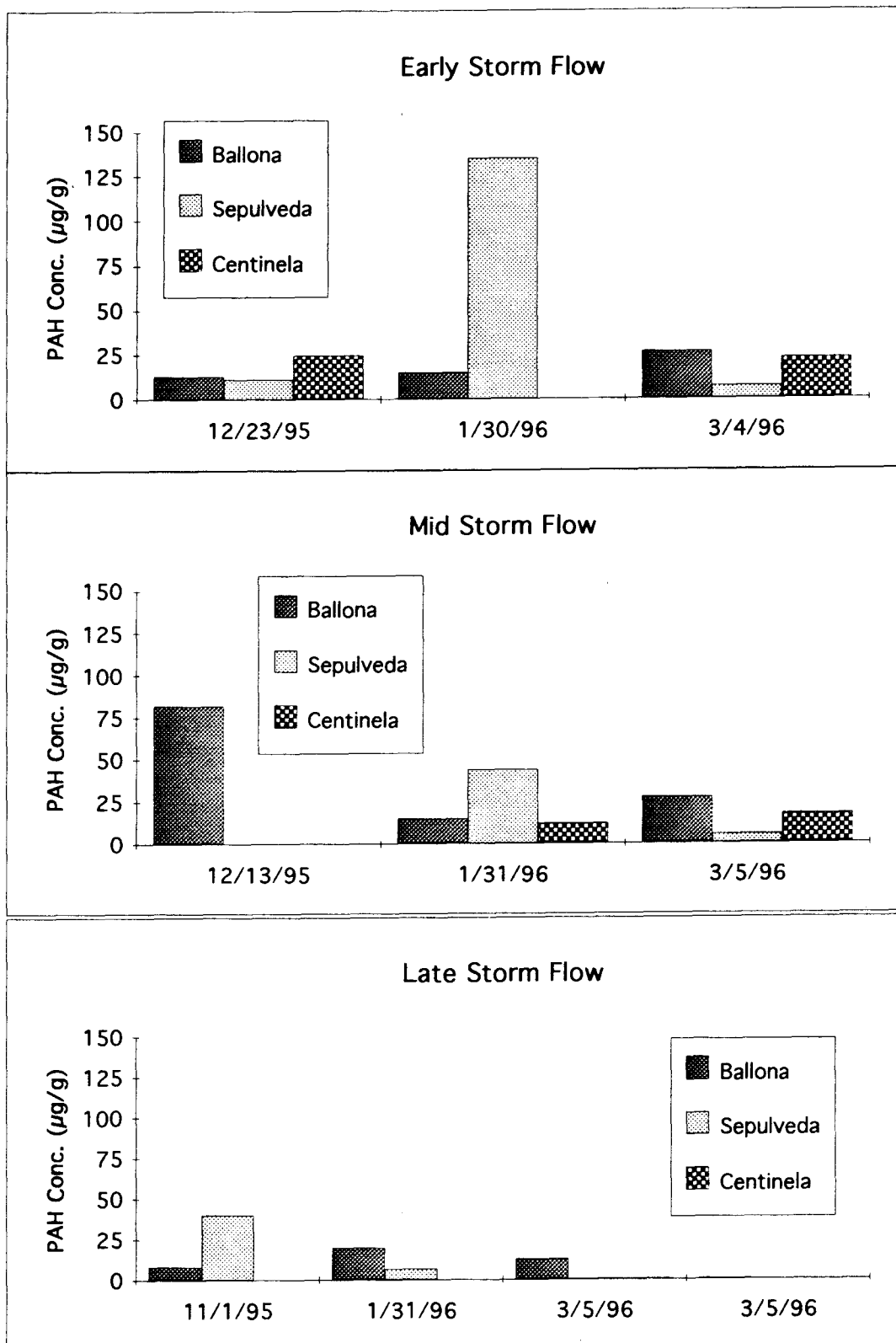


Figure 28. A plot of the PAH concentrations in suspended solids from the three upstream sites as a function of sampling time for the storm events sampled during the 1995-96 wet season.

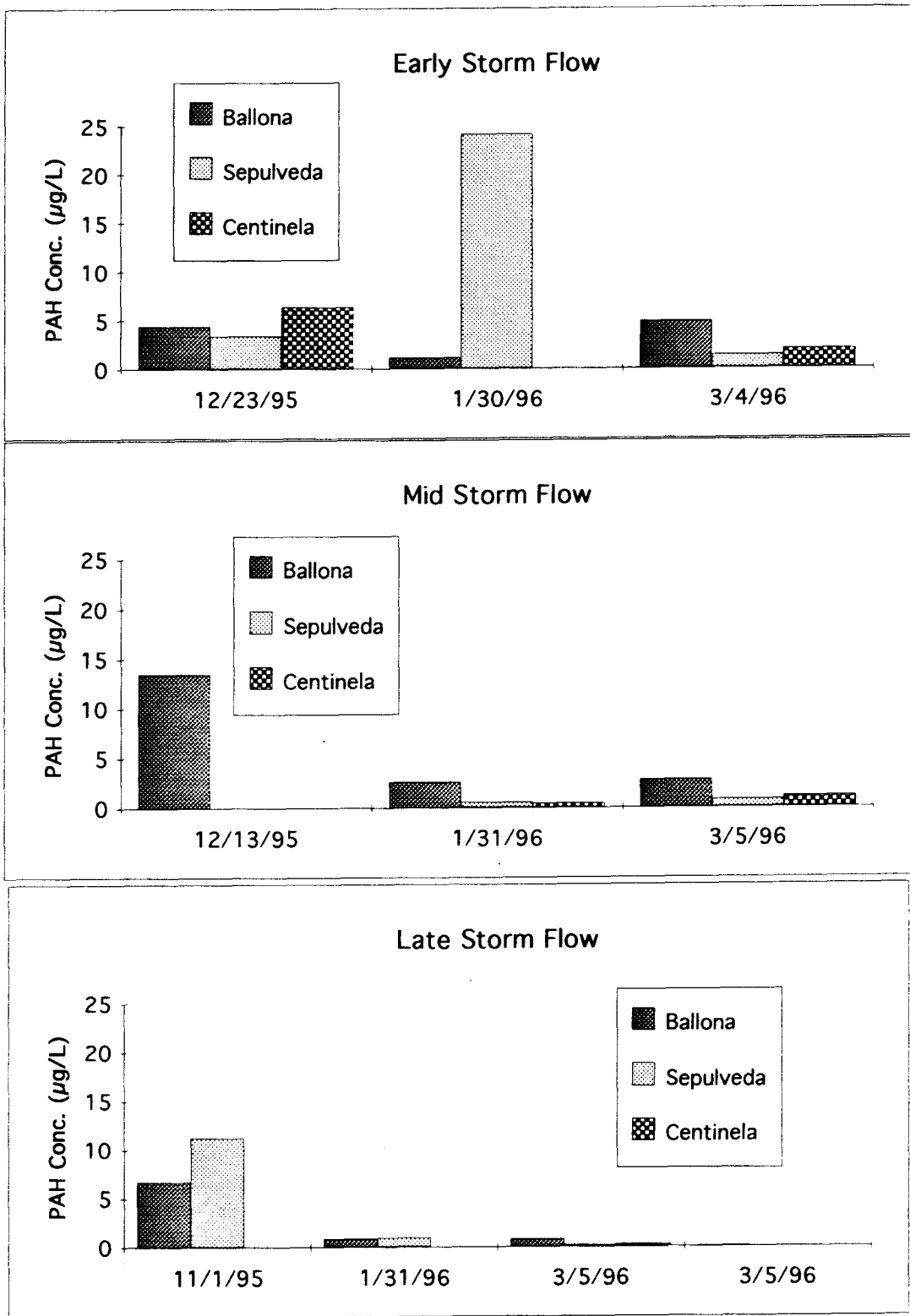


Figure 29. A plot of the PAH concentrations in stormwater from the three upstream sites as a function sampling time for the storm events sampled during the 1995-96 wet season.

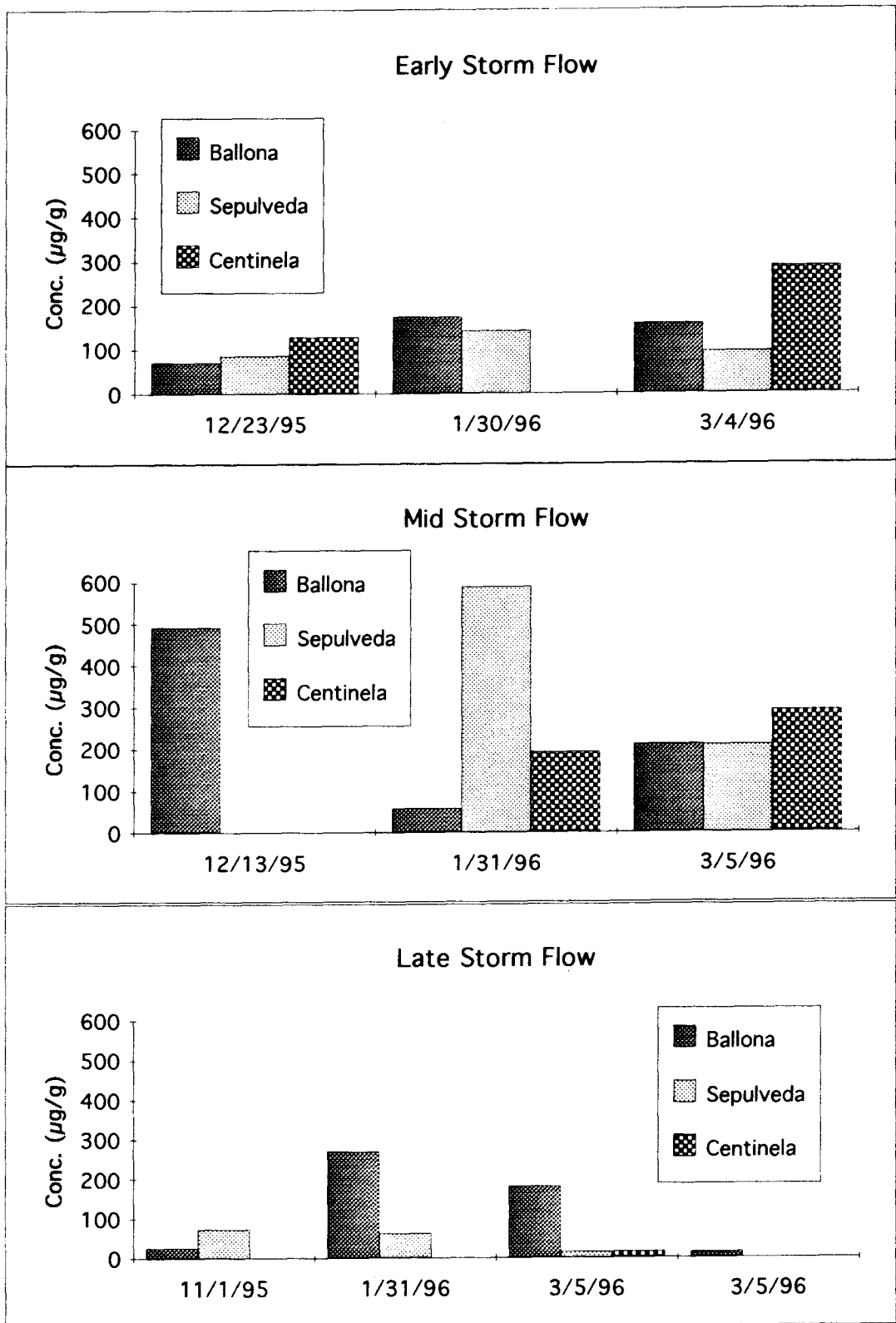


Figure 30. Aplot of the phalate concentrations in suspended solids from the three upstream sites as a function of sampling times for the storm events sampled during the 1995-96 wet season

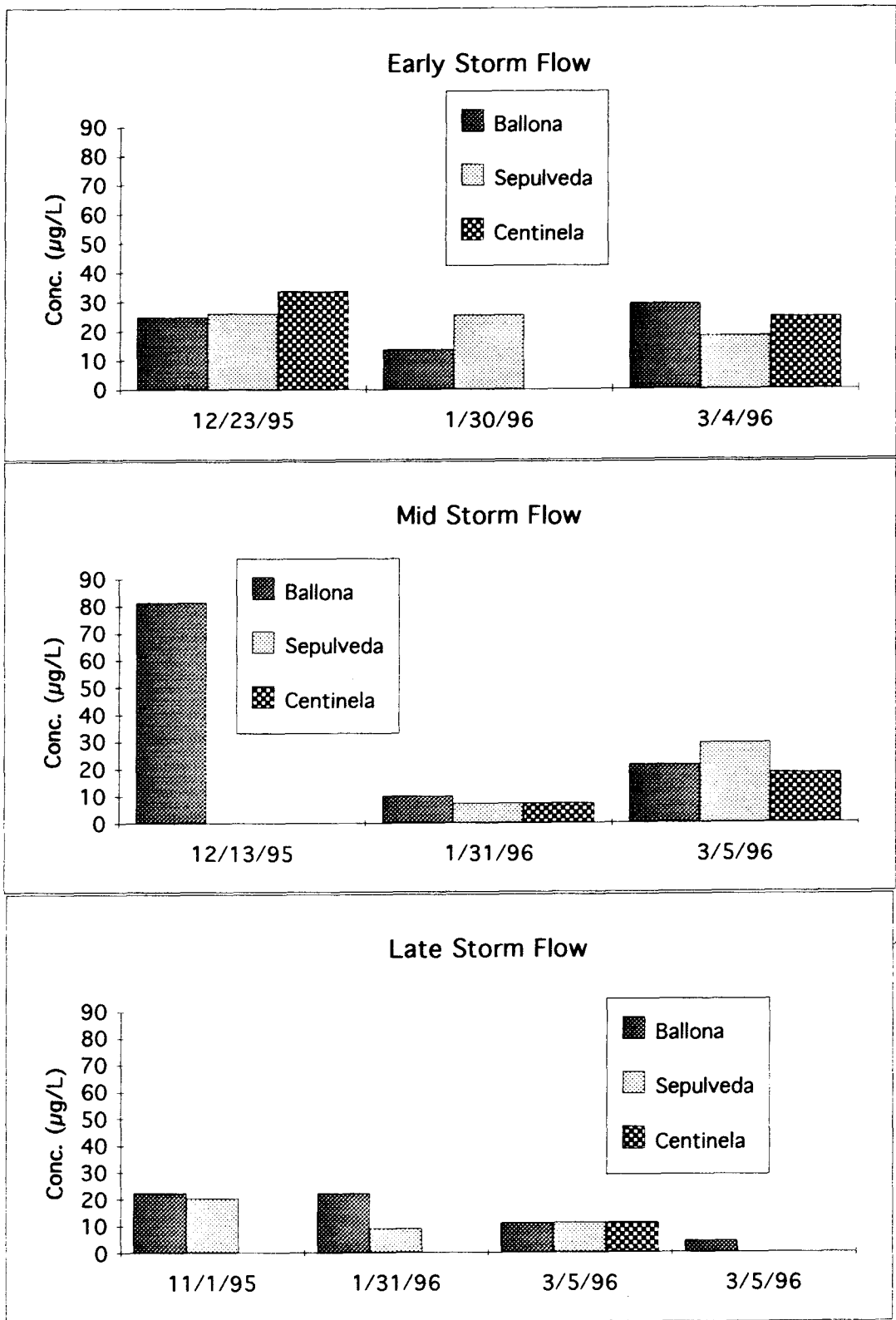


Figure 31. Aplot of the phalate concentrations in stormwater from the three upstream sites as a function of sampling times for the storm events sampled during the 1995-96 wet season.

volume basis would also decrease. Thus, the concentration on a volume basis ($\mu\text{g}/\text{L}$) of pollutants that are primarily associated the suspended solids phase would decrease faster than the concentrations on a mass basis ($\mu\text{g}/\text{g}$) because the system is both getting cleaner and the suspended solids load is decreasing.

4.5.6 Analyses of Suspended Solids for Organochlorine Compounds

As mentioned previously, halogenated recovery surrogates were not added to all suspended sediment samples obtained from the upstream sites. This was done so that splits from these samples could be analyzed for organochlorine compounds. The data obtained from these analyses are tabulated in Appendix B, Table B.16. The organochlorine target analytes fall into two general classes of compounds; 1) pesticides, such as DDT and dieldrin, and 2) polychlorinated biphenyls (PCBs). The resulting data from the organochlorine analyses are summarized graphically in Figure 32. In order to simplify the presentation, the data were summed and plotted total pesticides and total PCBs. The data are presented on both a mass ($\mu\text{g}/\text{g}$) and a volume basis ($\mu\text{g}/\text{L}$). Again the concentrations reported on a volume basis represent the contribution of the suspended solids only, i.e. the water phase concentration of the organochlorine compounds is assumed to be negligible. This is a good assumption given the hydrophobicity of the target compounds. Also indicated in Figure 32 are the approximate stages within the storm at which the samples were taken.

The most striking aspect of Figure 32 is the extremely high concentration of PCBs in the sample from the December 13, 1995 storm. However, it must be emphasized that this was a single sample, and thus confirmation of these results by other samples was not possible. If accurate, the very high concentration of PCBs in the sample could be related to the fact that it was the first big storm of the season. Another factor for consideration is that the sample was collected just after peak flow. The samples from Sepulveda Channel for the January 1996 storm do appear to suggest a relationship between PCB concentration

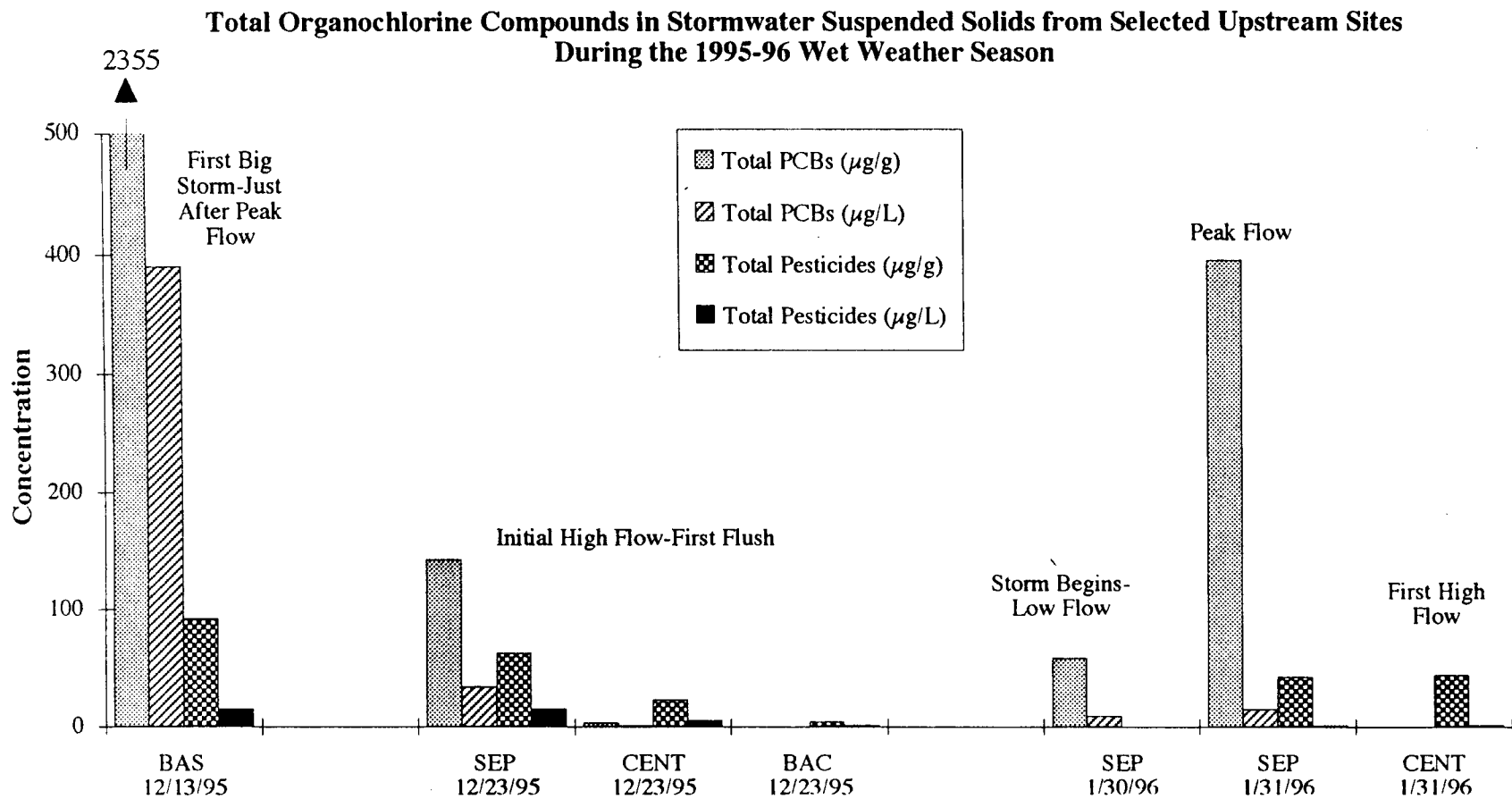


Figure 32. Plot of total organochlorine pesticides and PCBs in suspended solids from stormwater runoff samples collected at various sites in the Ballona Creek Watershed.

and flow.

The data also show that for this small set of samples, the PCB concentrations are both higher and more variable than the pesticide data. In contrast to the PCBs, the maximum pesticide concentrations seem to fairly constant over the three storms. However, during a single storm event the concentration of both PCBs and pesticides varies significantly by location.

4.6 Tidal Influence on Stormwater Runoff Flow

4.6.1 Ballona Creek - Marina Del Rey Hydrodynamics

One of the most interesting observations made during the course of this study was the profound influence of the tidal cycle on the flow of runoff from Ballona Creek, and the effect on the suspended solids plume. As it turns out, the flow of urban runoff from Ballona Creek is, in all but the heaviest precipitation, controlled to a large extent by the tides. Under dry weather conditions, the salt water lens at high tide extends up Ballona Creek as far as Centinela Ave. During wet weather flow, the high tide can hold back the flow of runoff from entering the bay. During sampling, it was commonplace to observed very high flow rates in all three channels upstream, and virtually no flow at the Pacific Ave Bridge. Then, a large surge of stormwater would follow sometime after the ebb tide. Thus, in retrospect, Pacific Ave Bridge is a poor choice of location for monitoring flow from Ballona Creek. The fact that the flow occurs as a series of stagnations and surges makes predicting mass loading problematic.

It well known that Marina Del Rey is awash in trash and debris after a storm event. In fact the County has special boats whose sole purpose is to skim floating trash from the surface of the water after storms. Ballona Creek has long been thought to be the source of the vast majority of the debris, but this had not been proven. However, during the January 31, 1996 sampling in Marina Del Rey, Deputy Pausch of the L.A. County Sheriff's Department videotaped the suspended solids plume, with its entrained debris, entering the

Marina from Ballona Creek.

The mechanism by which the effluent from Ballona Creek enters the Marina is interesting and was observed by our sampling crews on several occasions. It was noted during our sampling efforts that the maximum flow at Pacific Ave Bridge did not occur until approximately one-half to one hour after low tide. Apparently, there is a delay of up to an hour between when the tide recedes, and the maximum stormwater surge occurs. Thus, just when the maximum amount of runoff is flowing from the mouth of Ballona Creek, a new flood tide has already begun. The incoming tide opposes the flow from Ballona Creek, and causes a some of the flow to go northward toward the entrance to the Marina. Meanwhile, tide is also coming in through the north entrance to the Marina, which forces the flow from Ballona to "wrap-around" the jetty separating Ballona Creek from the Marina Del Rey entrance channel. The end results is that some of the flow is turned 180° into the Marina, and the trash and suspended solids are entrained with the incoming tide.

However, it was observed during sampling, and supported by the suspended solids data, that the water inside the marina is quite clear (i.e., low turbidity). Thus, although there is an abundance of trash and floating debris, the suspended solids load is low. Thus, much of the suspended solids must be removed by some mechanism prior to reaching the main channel of the marina. It is well known that high ionic strength water (e.g., seawater) facilitates the coagulation and precipitation of fine suspended solids. Therefore, it is probable that much of the solids are precipitated upon encountering the incoming tide. It is very likely that this is the mechanism responsible for the notorious shoaling problem at the south entrance of the marina. A generalized depiction of the Ballona Creek-Marina Del Rey stormwater hydrodynamics are shown in Figures 33, 34 and 35.

Some of the flow from Ballona Creek is also turned toward the south by the incoming tide, and creates a large eddy just south of the outlet from Ballona Creek. The L.A. County Department of Beaches and Harbor reports that there is frequently a large

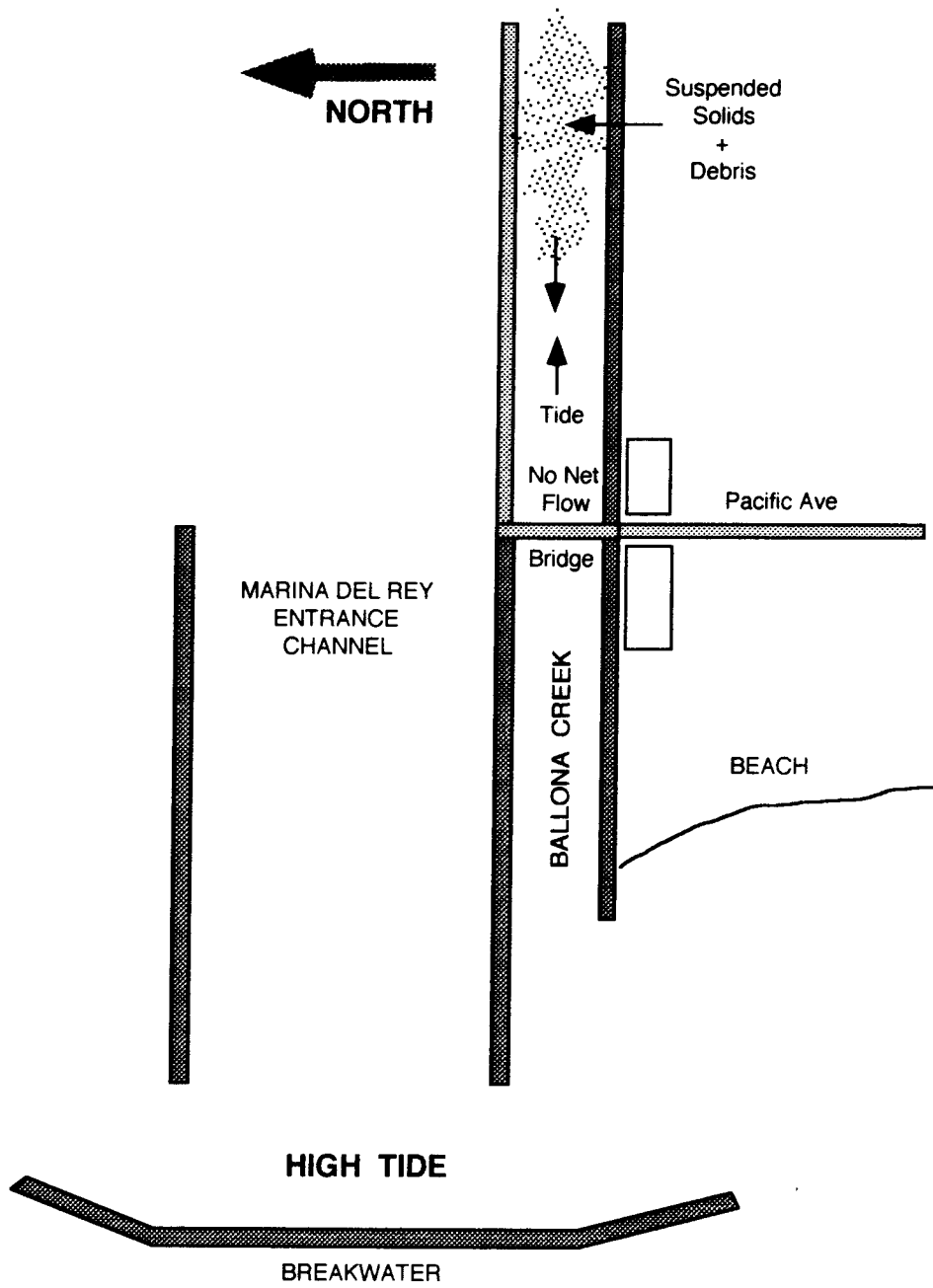


Figure 33. Stormwater flow stagnation at Ballona Creek under high tide conditions.

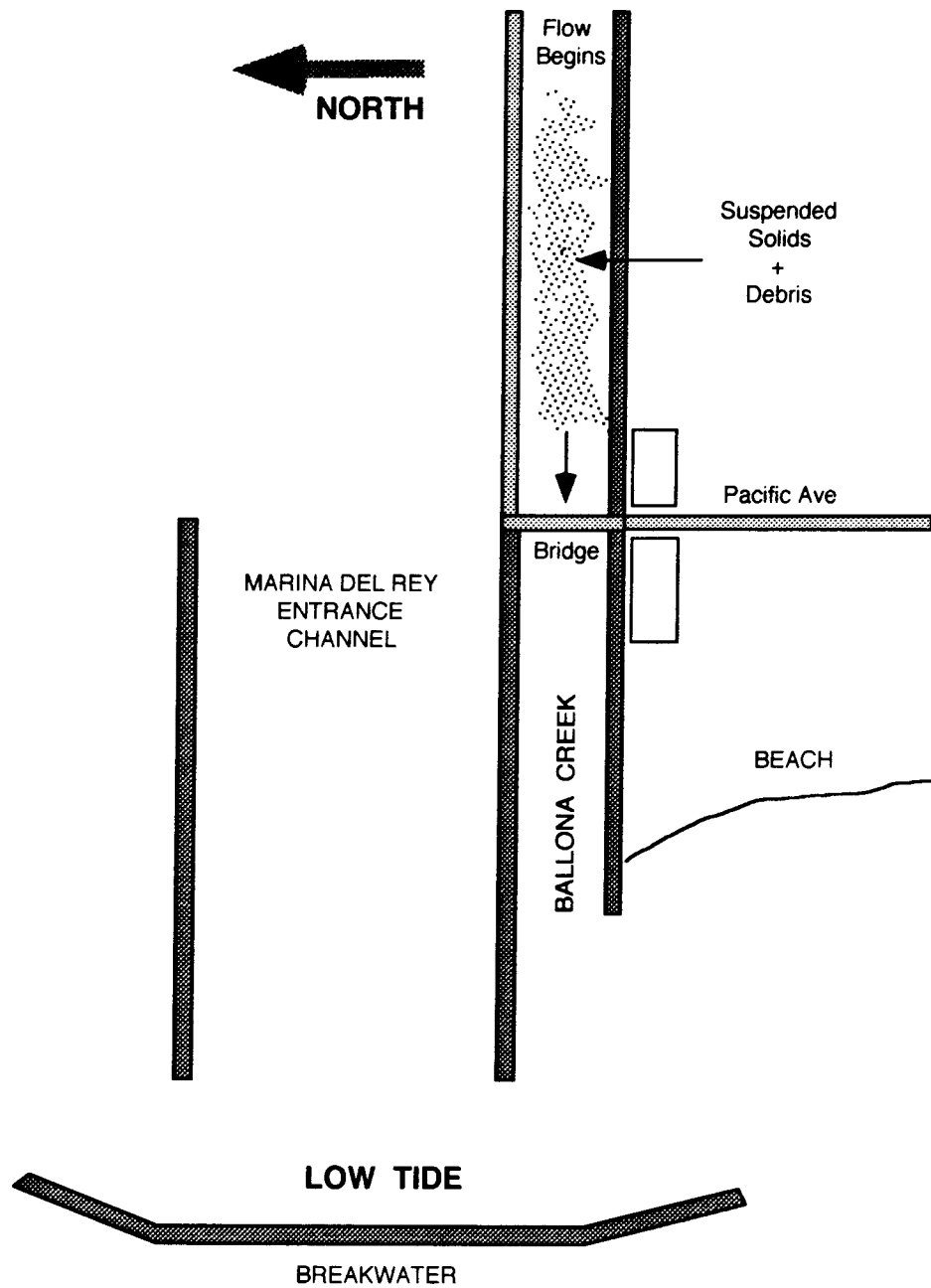


Figure 34. Stormwater flow from Ballona Creek under low tide conditions

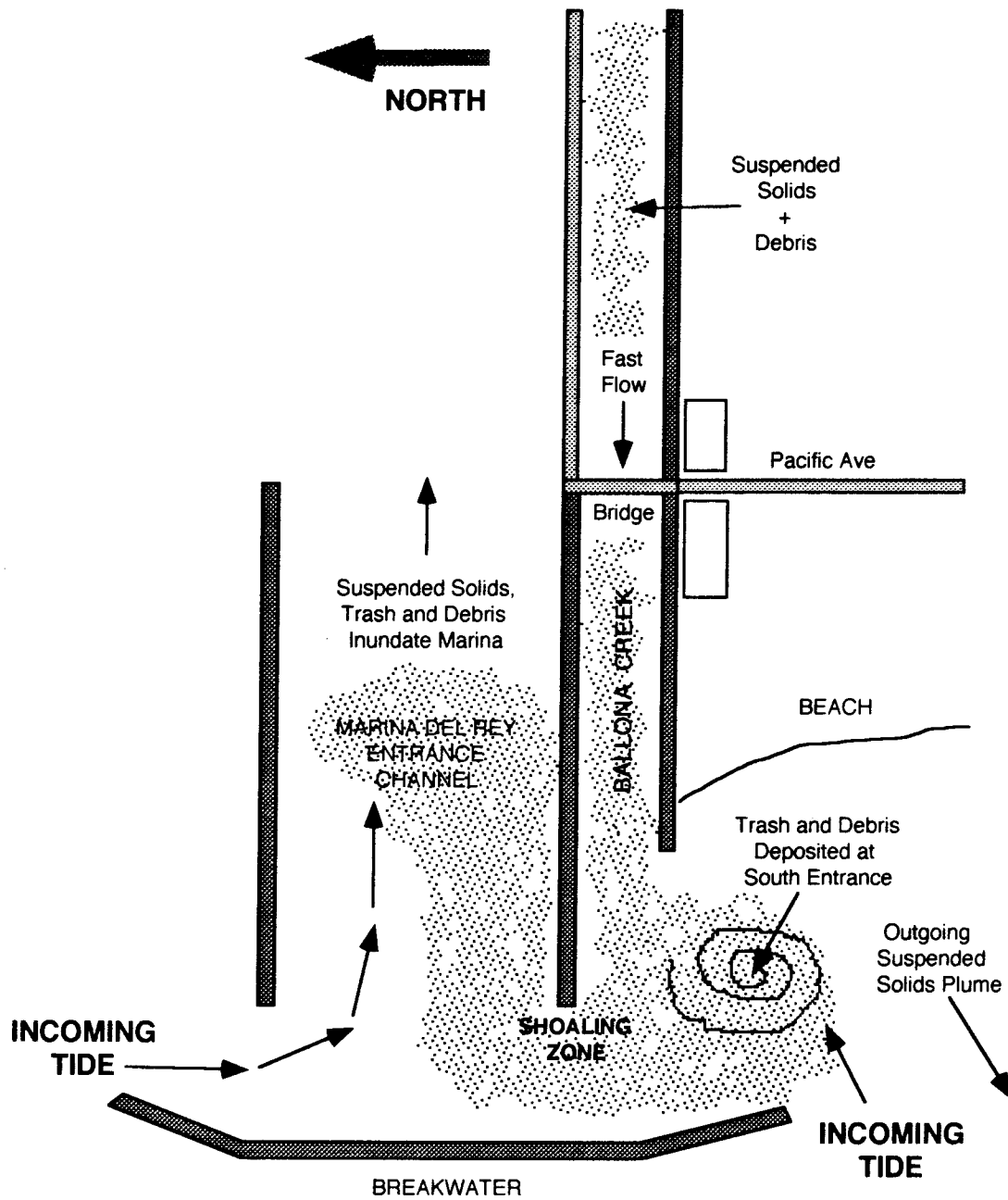


Figure 35. Storwater flow from Ballona Creek during maximum flow and flood tide conditions.

amount of floating debris accumulated in this area after a storm event. One of the authors (J. Noblet) has been SCUBA diving in the area, and observed large amount of trash and debris on the bottom. So much in fact that the bottom has the appearance of an "underwater landfill." In addition, recent sediment sampling has shown that the sediments in the that area have the highest levels of contaminants.

4.6.2 Tidal Influence on Conductivity

Conductivity is related to the ionic strength or the salinity of the water, and thus the conductivity can be used to estimate the relative proportions of seawater and freshwater in a particular sample. This is important because the ionic strength can significantly affect the partitioning behavior of hydrophobic organic pollutants between the solid and the aqueous phases. Figures 36 and 37 show the conductivity of samples taken from Ballona Creek at the Pacific Ave Bridge in relation to the tidal cycle, for the January 31, 1996 and March 4-5, 1996 storms, respectively. Superimposed on each plot is the flow data from the Ballona Creek monitoring station at Sawtelle Blvd. Because the flow monitoring station is more than two miles upstream of Pacific Ave Bridge, and because the flow hydrograph does not include the inputs from Sepulveda and Centinela Channels, the flow data is included only to give an estimate of storm's progress. Nevertheless, Figures 36 and 37 do show a significant relationship between the tide, flow upstream, and the conductivity. The dramatic drops in conductivity occur around low tide, which is consistent with the observations discussed above.

4.7 Organic Pollutants Associated with Suspended Solids in Stormwater from the Downstream Locations

4.7.1 Marina Del Rey vs. Ballona Creek at Pacific Ave Bridge

In addition to upstream sites, samples were taken during the January 31 and March 4-5, 1996 storm events at two downstream locations, Ballona Creek at the Pacific Ave Bridge (BAP) and inside Marina Del Rey (MDR), front and back of the main channel (see

**Conductivity of Water Samples vs. Tidal Height
Ballona Creek at Pacific Ave.**

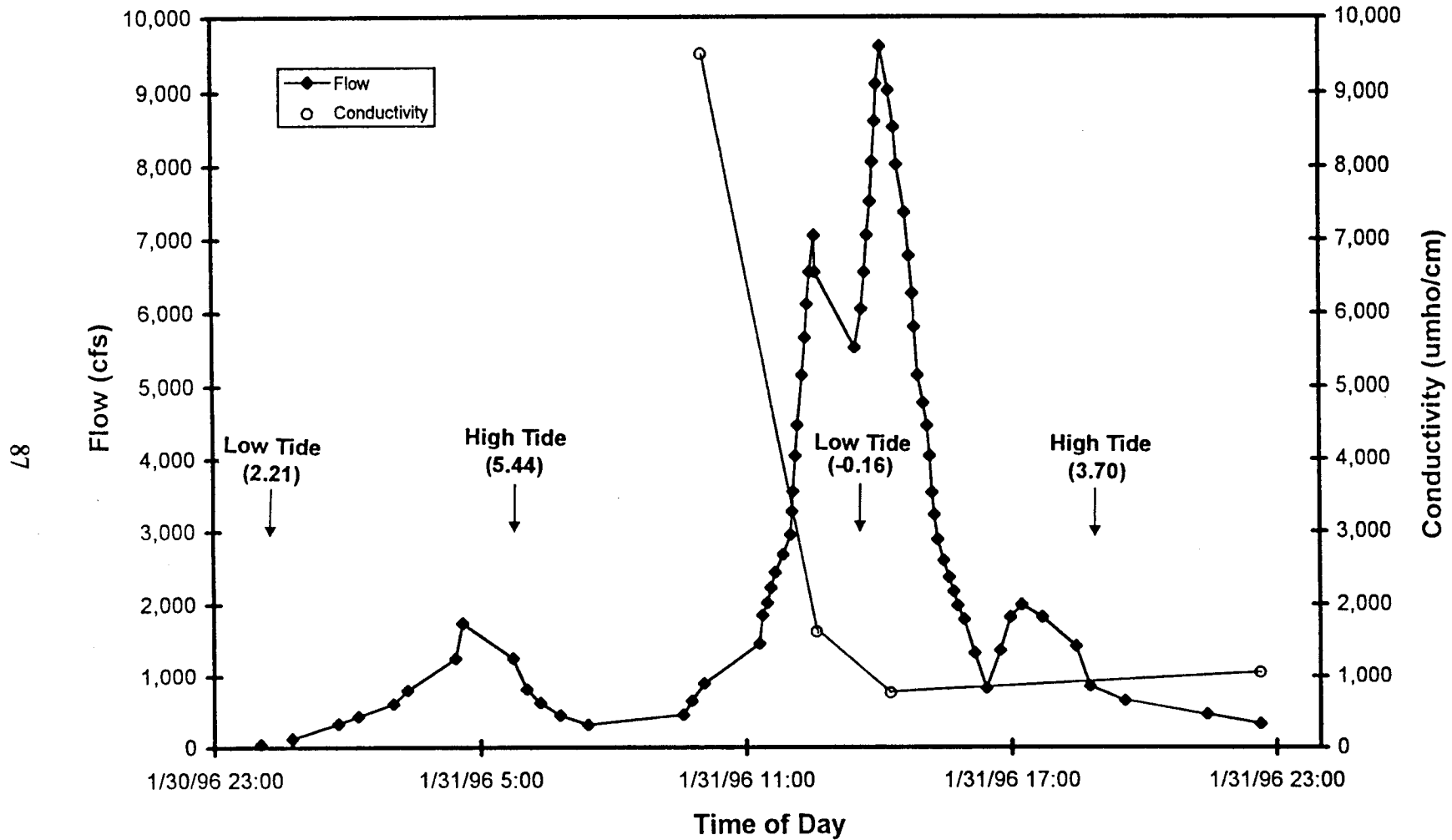


Figure 36. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and conductivity of samples taken in Ballona Creek at Pacific Ave.. Graph includes times and heights of tidal highs and lows.

Conductivity of Water Samples vs. Tidal Height Ballona Creek at Pacific Ave.

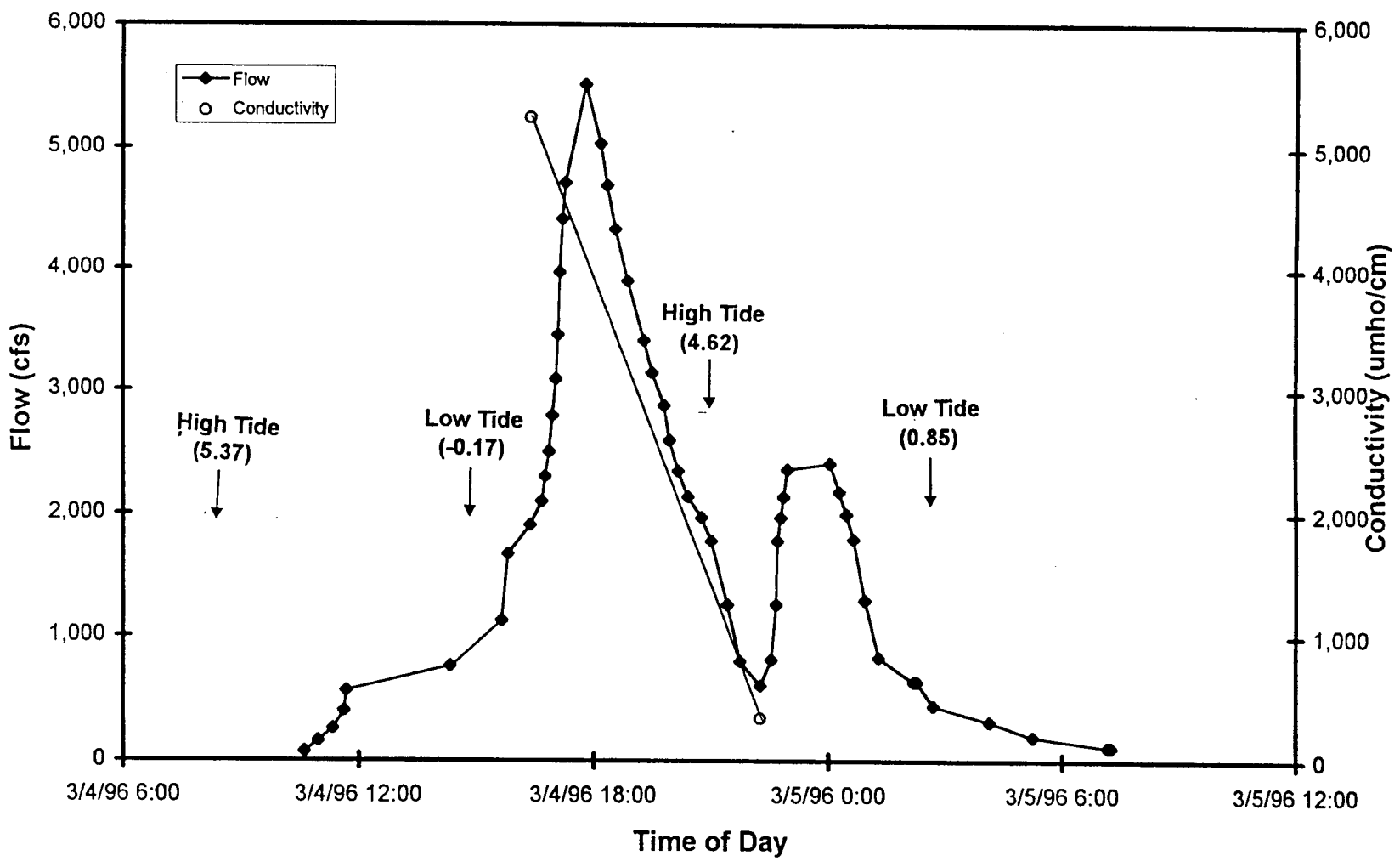


Figure 37. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and conductivity of samples taken in Ballona Creek at Pacific Ave.. Graph includes times and heights of tidal highs and lows.

Figure 2). The BAP site was chosen because it is the last convenient sampling location downstream before Ballona Creek empties into the bay, and thus includes all possible contributions of stormwater runoff to Ballona Creek. In addition, it provides a point of reference for the juxtaposition of Ballona Creek and Marina Del Rey as potential sources of pollution to the Santa Monica Bay.

The results from the organic analyses of the suspended solids from these samples is given in Appendix B, Tables B.14 and B.15. The total PAH and total phthalate concentration data are shown graphically in Figures 38-41 and Figures 42-45 (also Appendix B, Figure B.47-50 and B.52-55) for the January 31 and March 4-5, 1996 storms, respectively. These data show that the concentration of PAHs in the suspended solids from BAP are consistently and significantly higher than those from MDR. The difference is even greater when the data are plotted on a volume basis ($\mu\text{g/L}$). This is due to the very low suspended solids concentrations in the samples from MDR. The data for the phthalates mirrors the PAHs, although the absolute differences are much less. The concentrations of PAHs and phthalates in the suspended solids were similar for the front and back of the Marina during both storm events. Also, for both storm events, T1 and T2 samples were taken before and after the peak flow, respectively, as measured at the Ballona Creek monitoring station at Sawtelle Blvd.

Given the distance upstream to the monitoring station (> 2 miles), and the time delay involved in the runoff reaching the mouth of Ballona Creek, and the hydrodynamic barriers discussed above, it is unlikely that any significant amount of the flow from Ballona Creek had entered MDR by the time the T2 samples were taken. Therefore, both the T1 and T2 samples probably represent the inherent pollutant concentrations due to runoff contributed directly to the respective water bodies. These results clearly indicate that Ballona Creek is a much more significant source of organic pollutants to the Santa Monica Bay in comparison to Marina Del Rey. This is especially true given the much greater runoff flows from Ballona Creek relative to Marina Del Rey.

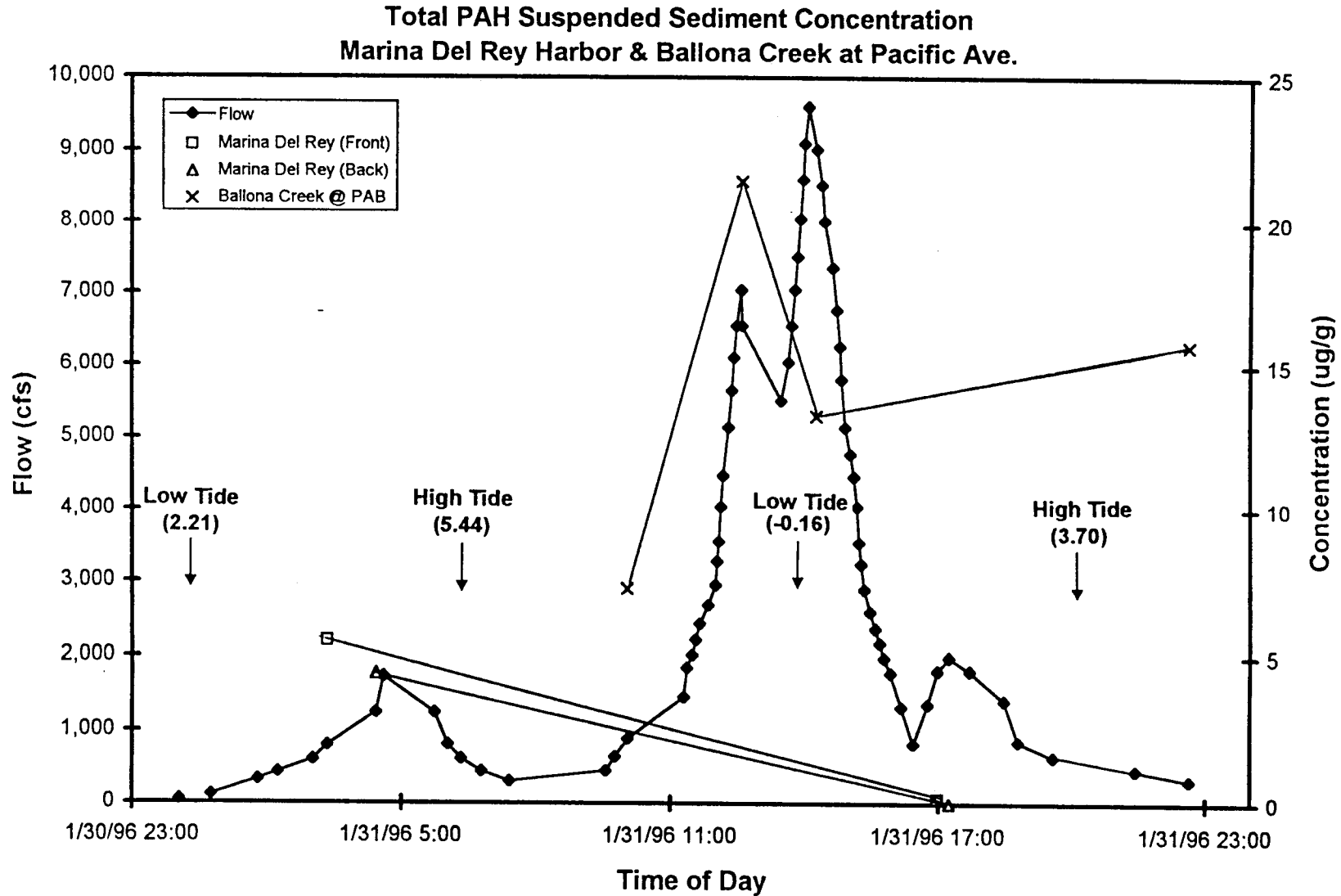


Figure 38. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

Total PAH Mass Load Concentration Marina Del Rey Harbor & Ballona Creek at Pacific Ave.

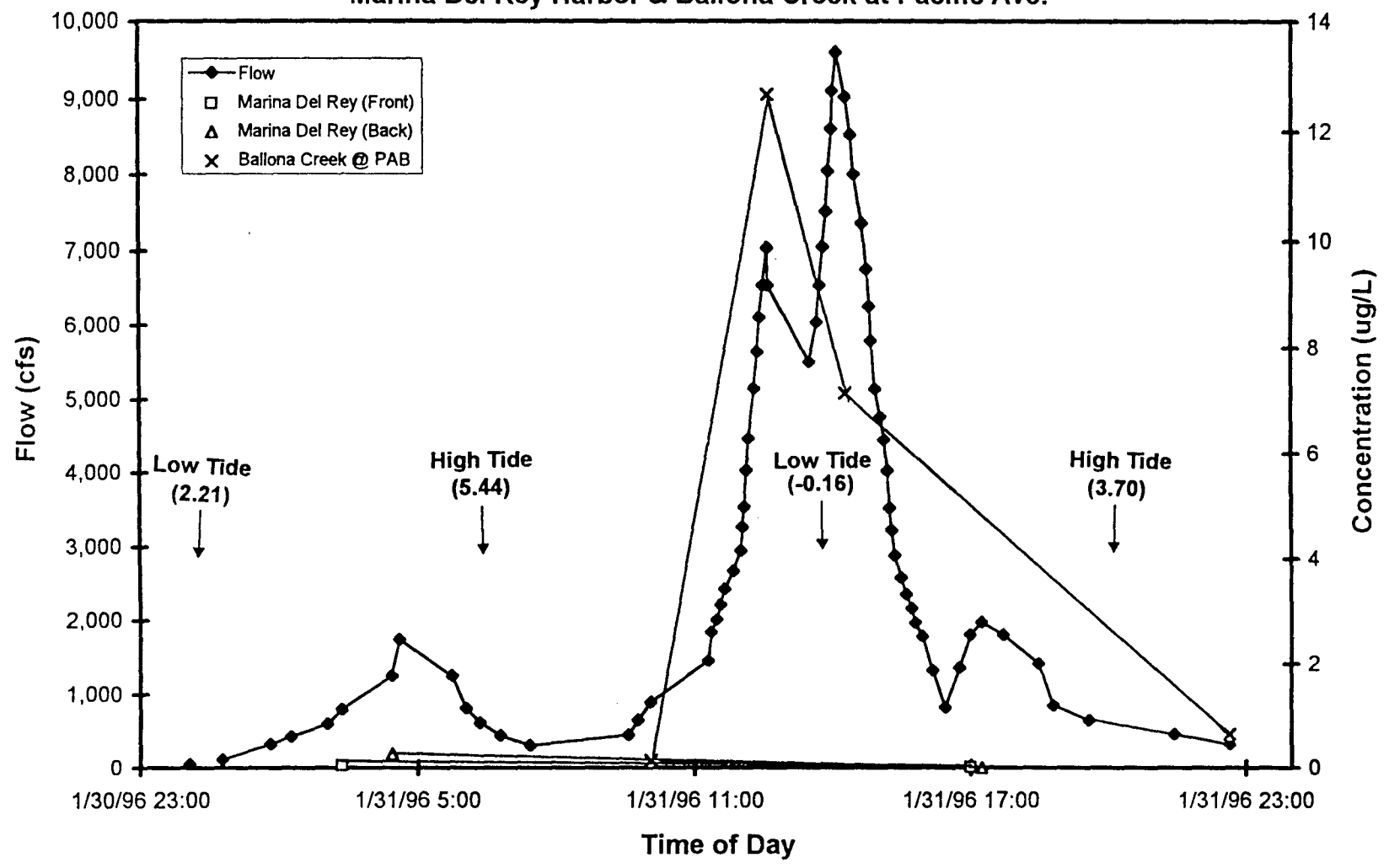


Figure 39. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

**Total Phthalate Suspended Sediment Concentration
Marina Del Rey Harbor & Ballona Creek at Pacific Ave.**

92

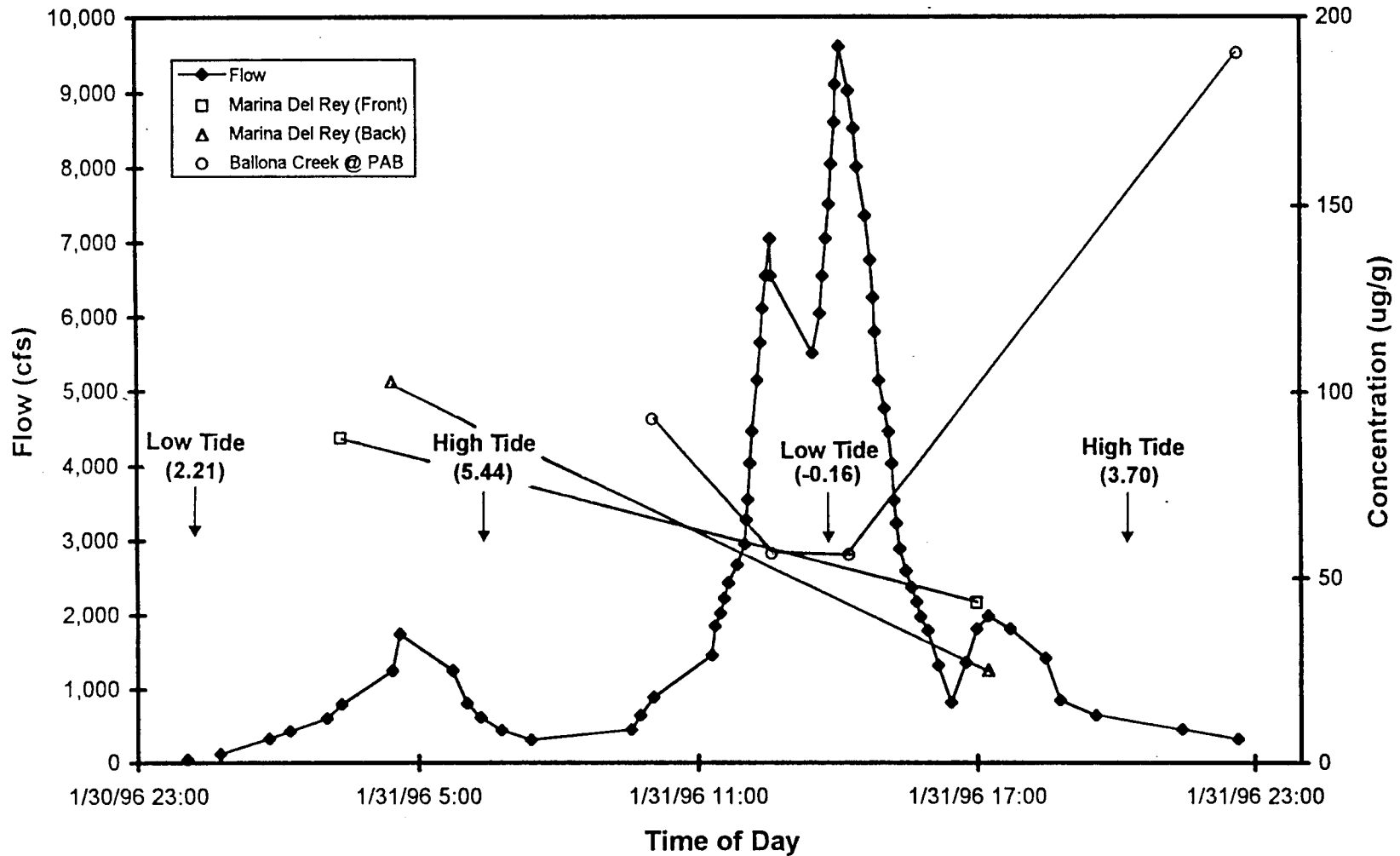


Figure 40. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

**Total Phthalate Mass Load Concentration
Marina Del Rey Harbor & Ballona Creek at Pacific Ave.**

96

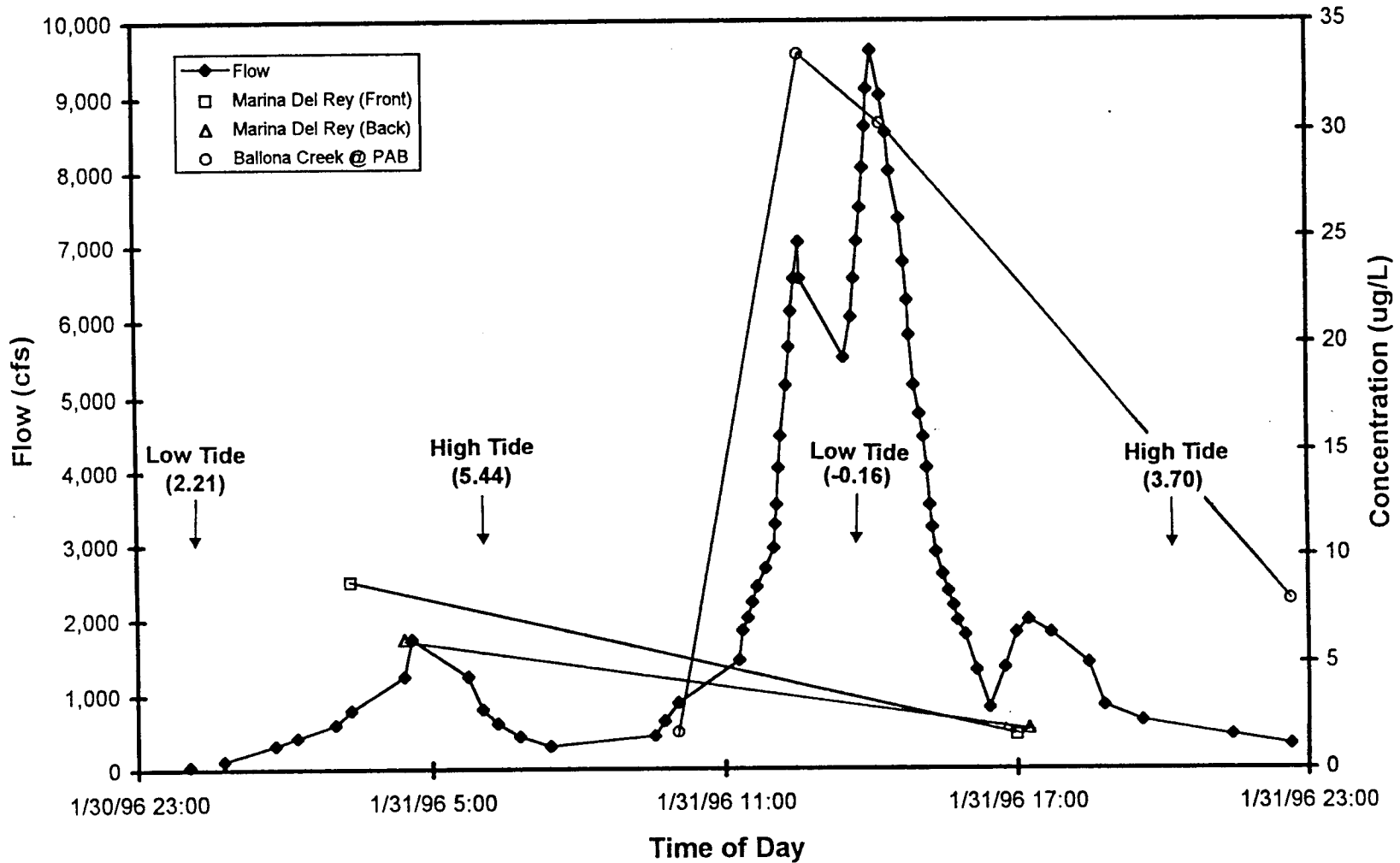


Figure 41. Stormwater flow for the January 31, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

**Total PAH Suspended Sediment Concentration
Marina Del Rey Harbor & Ballona Creek at Pacific Ave.**

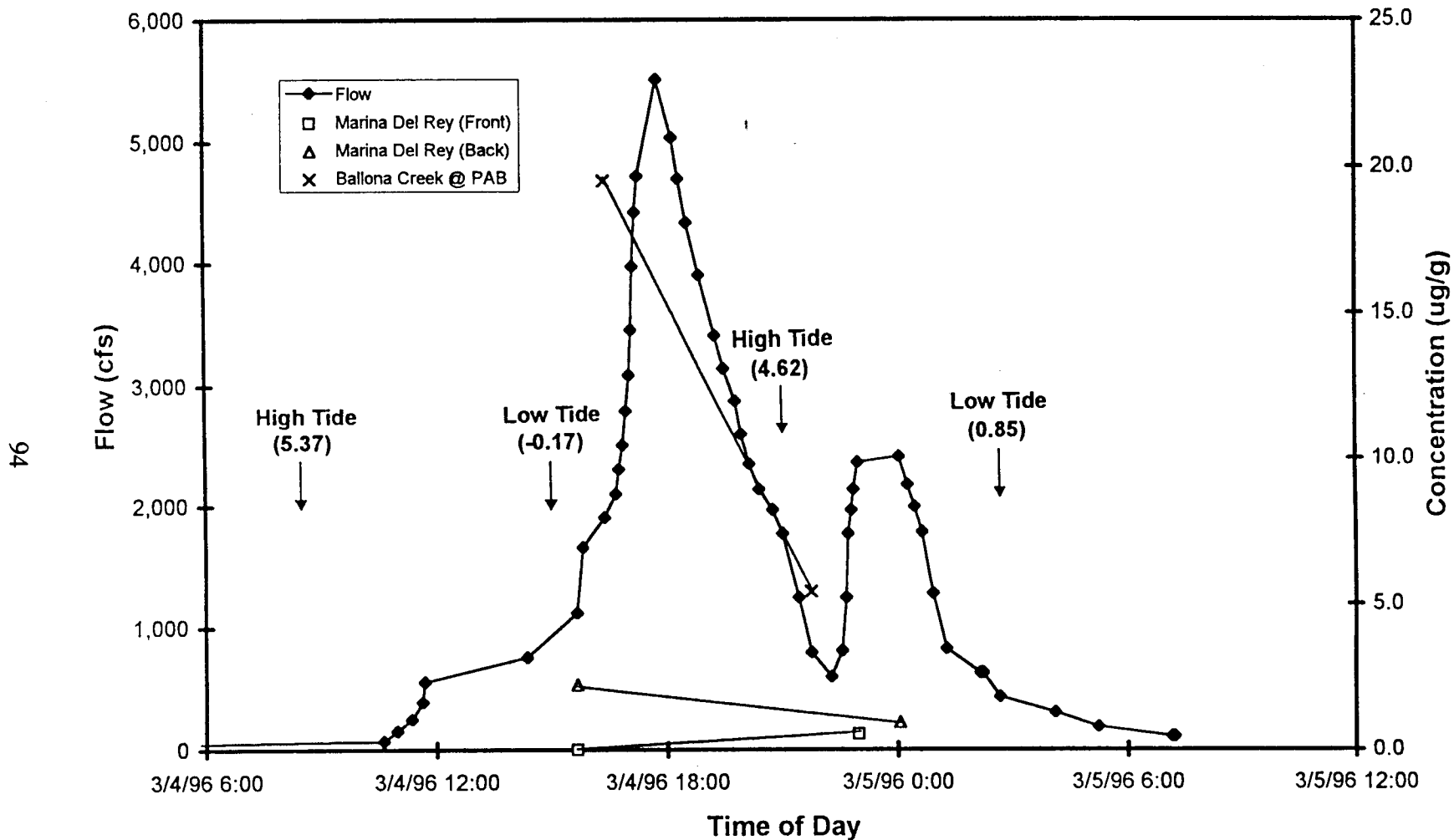


Figure 42. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

**Total PAH Mass Load Concentration
Marina Del Rey Harbor & Ballona Creek at Pacific Ave.**

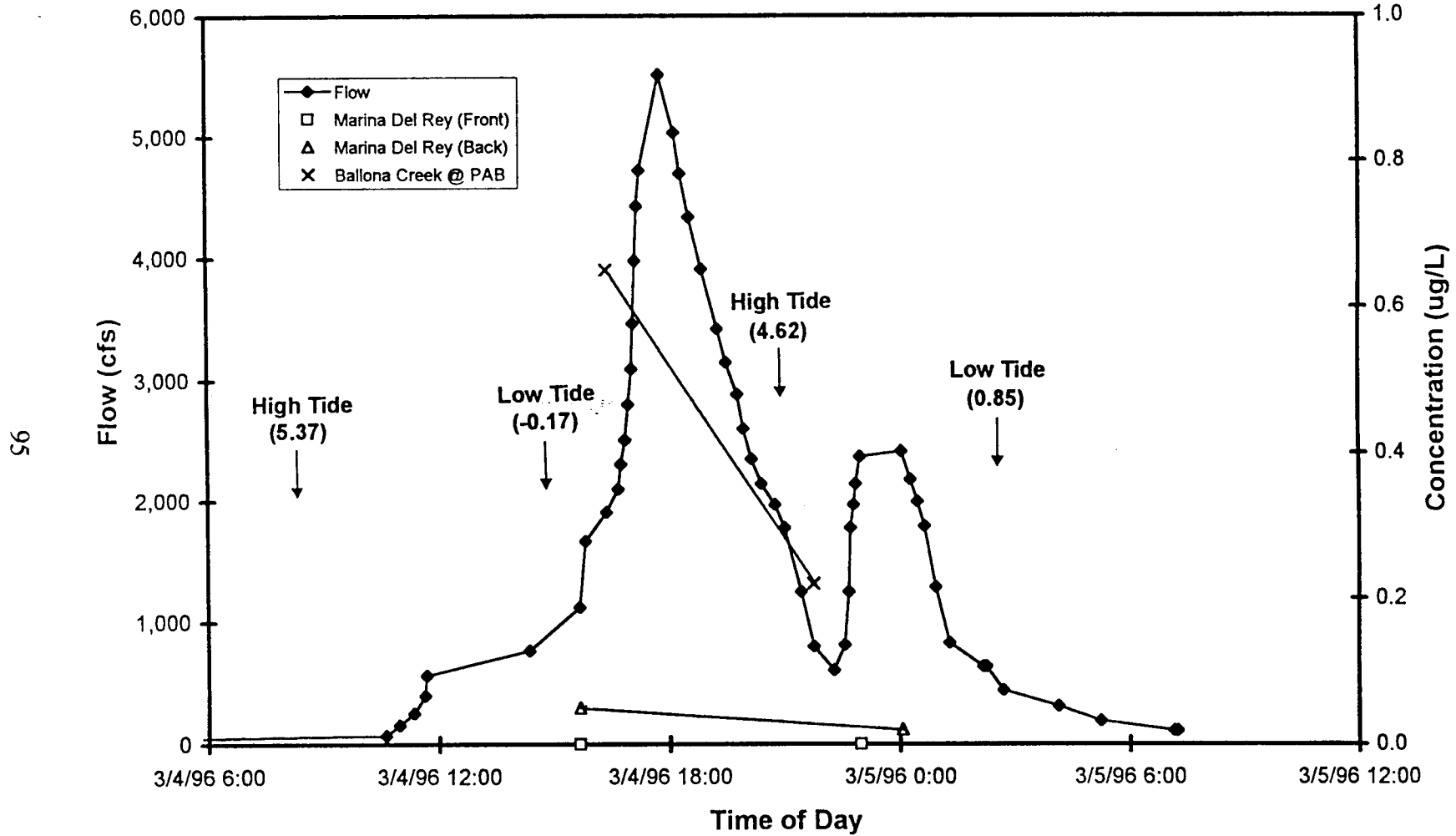


Figure 43. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total PAH mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

Total Phthalate Suspended Sediment Concentration Marina Del Rey Harbor & Ballona Creek at Pacific Ave.

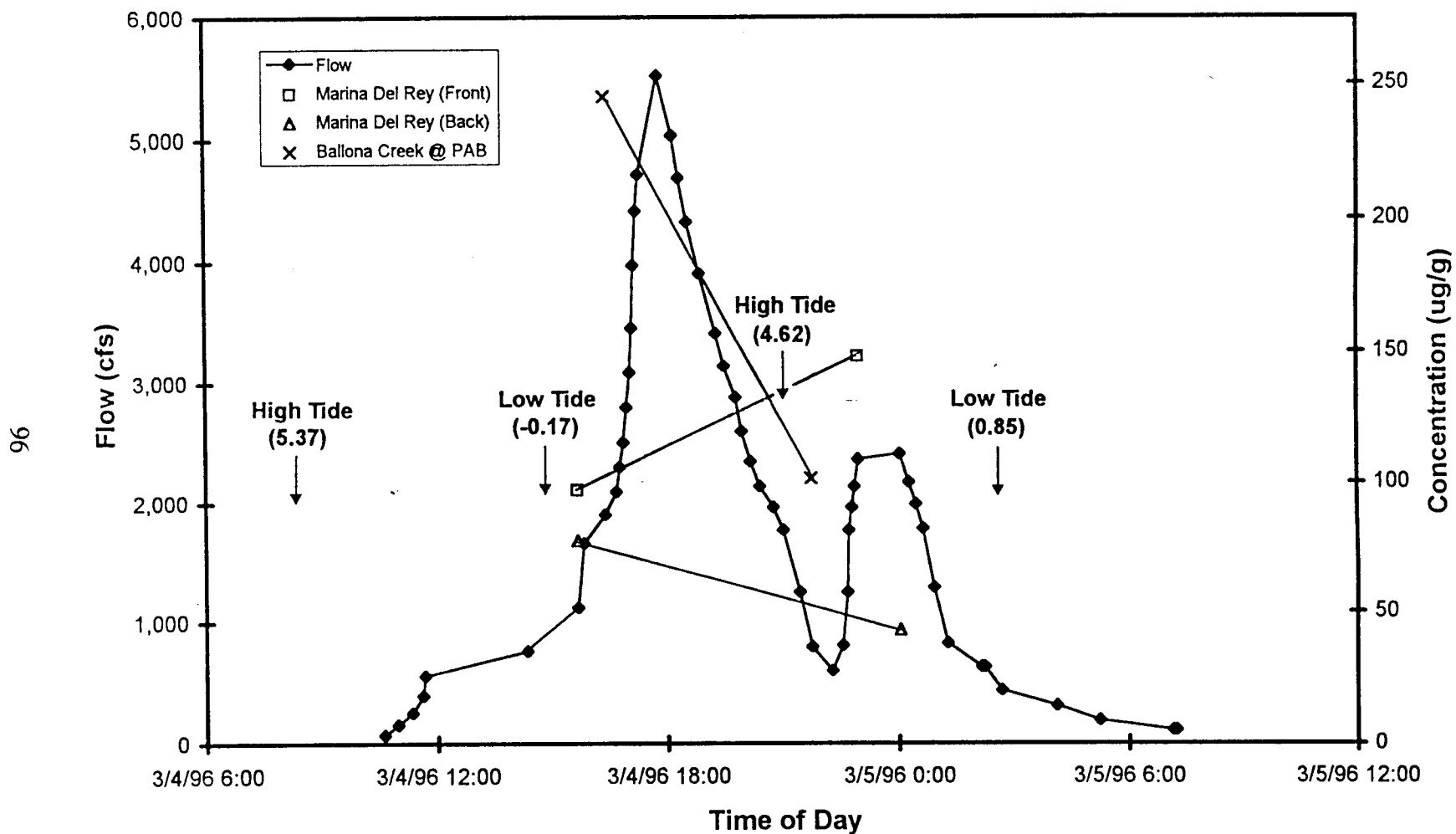


Figure 44. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate suspended sediment concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

**Total Phthalate Mass Load Concentration
Marina Del Rey Harbor & Ballona Creek at Pacific Ave.**

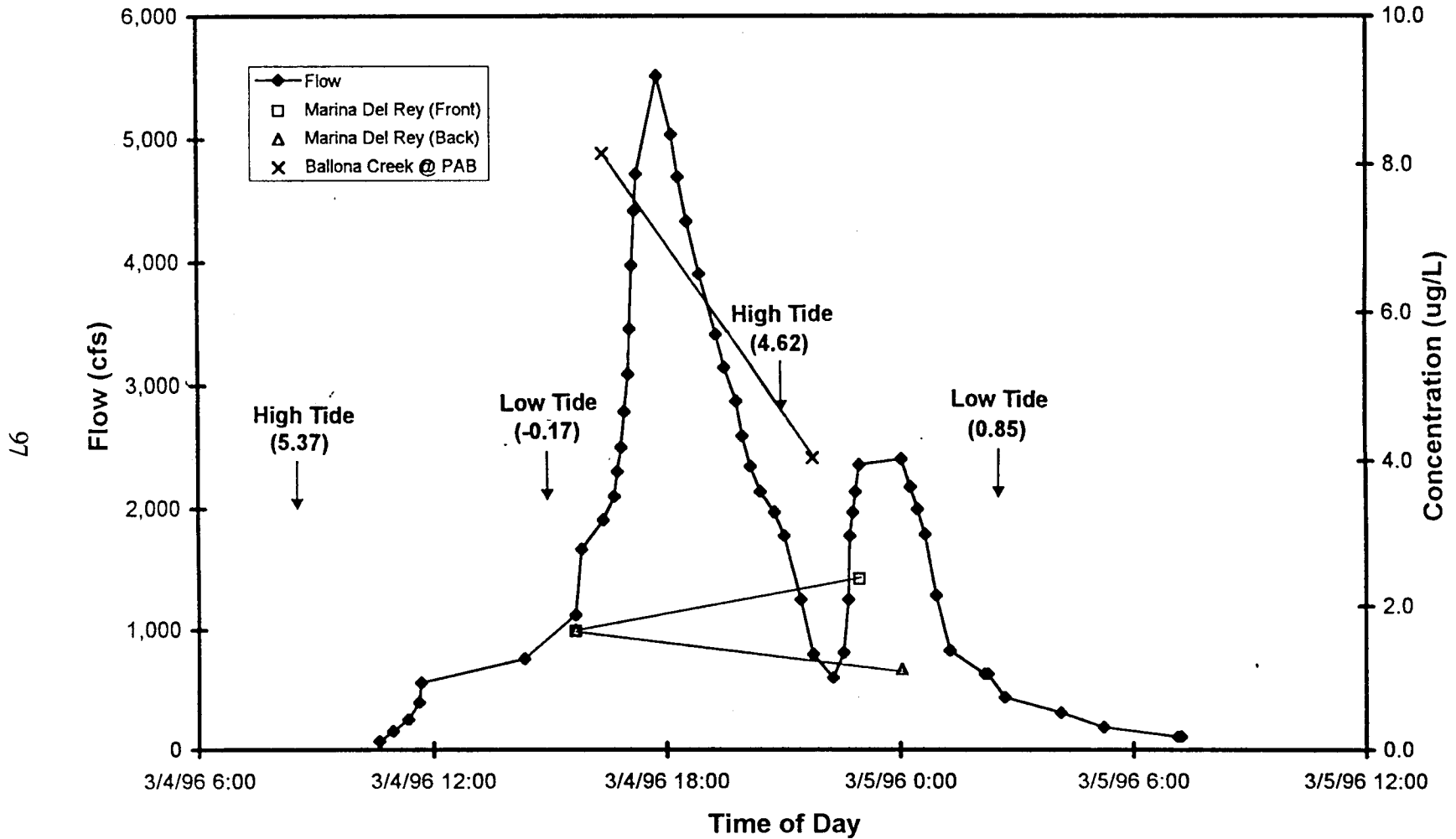


Figure 45. Stormwater flow for the March 4-5, 1996 storm as measured by the Ballona Creek monitoring station and total Phthalate mass load concentration from samples taken in Ballona Creek at Pacific Ave. and Marina Del Rey Harbor. Graph includes times and heights of tidal highs and lows.

4.8 Results of Metals Analyses

4.8.1 Overview

Table 5 (see experimental section) shows the regulated and non-regulated metals studied in this project, and compares the water MDLs with the drinking water MCLs, and the California Ocean Plan (1990) aqueous chronic toxicity to aquatic life (CTL). In addition, Table 5 also shows the suspended solid MDLs, and the NOAA Criteria for effects range medium (ERM-the 50th percentile of toxic biological response) and the NOAA criteria for effects range low (ERL-the 10th percentile of toxic biological response). All of the resulting metals data for both the dissolved and suspended solids phases in the stormwater samples collected during this study are presented in Appendix C, Tables C.1 and C.2, respectively.

As stated in the organics section of this report, the one of the primary objectives of this study was to estimate the relative contributions of pollutants to Santa Monica Bay from each of the three major storm drains in the Ballona Creek watershed. Figures C.1 - C.80 in Appendix C present the suspended solid metals concentrations on a per mass basis ($\mu\text{g/g}$) for each of the upstream sampling sites - Sepulveda Channel at Culver Blvd., Centinela Channel at Centinela Ave., and Ballona Creek at Sawtelle Blvd.- for the January 30-31, February 19-22, and March 4-5, 1996 storms. Note that metals data is presented for an additional storm event, the February 19-22, 1996 storm, for the upstream sites. No samples were collected for organic analyses at the upstream sites during this storm. Data is also reported for three downstream sites - Ballona Creek at Pacific Ave. Bridge, and Marina Del Rey (front and back) - for the January 30 - 31 and March 4 -5, 1996 storms.

To facilitate evaluation of the large amount of data, the suspended solids concentrations of the toxic metals for samples from the upstream sites were plotted versus time, along with corresponding ERM and ERL values plotted as a horizontal lines. In addition, superimposed on each plot is the runoff hydrograph from the Ballona Creek monitoring station.

The NOAA ERL and ERM values were developed as guidelines for assessing the potential for biological impacts from bottom sediments, and their appropriate application is currently the subject of much debate in the toxicological literature (Long et al., 1995; MacDonald, et al., 1996a and 1996b; Sampson et al., 1996; Lee and Jones-Lee, 1996). They are used here as an aid in the evaluation of the suspended solids metals data, and as an indicator of the potential for biological impacts due to stormwater runoff. Again, since accurate runoff flow data was available only for Ballona Creek, the flow data is overlain on the metals concentration plots to give a qualitative indication of the stage of the storm.

A summary of the analytical results for the eight toxic regulated metals in suspended solids, relative to their respective individual ERMs and ERLs, for all the storm events sampled, at each location is presented in Table 9. Evaluation of the data obtained in this study has indicated that lead is the metal pollutant of consistently the highest concentration. Lead is of environmental importance with regard to both human health effects and toxicity to aquatic organisms. Table 9 shows that lead was the only one of the eight toxic metals whose concentration in the suspended solids was consistently above the ERM. Due to its ubiquitous nature and high concentrations, lead was used as the focus of the discussions to follow. Representative plots of the lead data for each storm and location will be presented as examples of the types of plots to be found in Appendix C. The other seven metals (As, Cd, Cr, Cu, Ni, Ag, Zn) will be discussed as dictated by their concentrations.

4.8.2 Zinc Data

The metals recovery data, as well as the control, and reagent data were given in Table 6. Two of the three filter blanks, and all three spiked filter recovery samples showed extremely high zinc levels. Analyses of duplicate samples were performed in another laboratory, on a different instrument to test the validity of the results similar results were obtained. Since the other control samples did not have exhibit the high

Table 9. Concentration of metals in suspended solids evaluated in terms of potential for toxicity to aquatic biota based on sediment ERLs and ERMs (Long et al., 1995). Where numbers are given, they represent the factor by which the ERM must be multiplied to give the measured metal concentration in the suspended solids.

Location & Date	As	Cd	Cr	Cu	Pb	Ni	Ag	Zn*
Sepulveda								
1/31/96								
Initial flow	>ERL <ERM	1 x	1 x	>ERL <ERM	3 x	1 x	1 x	8 x
High flow	10 x	9 x	>ERL <ERM	>ERL <ERM	16 x	7 x	6 x	172 x
2/19,22/96								
Initial flow	2 x	3 x	>ERL <ERM	4 x	7 x	4 x	Int.	<ERL
High flow	3 x	11 x	4 x	3 x	18 x	14 x	Int.	<ERL
3/4/96								
Initial flow	1.5 x	2.5 x	=ERL	>ERL <ERM	3 x	5 x	Int.	21 x
High flow	2 x	2.5 x	>ERL <ERM	>ERL <ERM	3 x	6 x	Int.	43 x
Centinela								
1/31/96								
Initial flow	1 x	>ERL <ERM	<ERL	<ERL	2 x	>ERL <ERM	Int.	26 x
High flow	2 x	4 x	>ERL <ERM	6 x	10 x	4 x	Int.	<ERL
2/19,22/96								
Initial flow	6 x	<ERL	4 x	>ERL <ERM	11 x	19 x	>ERL <ERM	97 x
High flow	1 x	<ERL	1.5 x	>ERL <ERM	8 x	6 x	<ERL	<ERL
3/4/96								
Initial flow	<ERL	3 x	>ERL <ERM	1.5 x	5 x	5 x	<ERL	<ERL
High flow	<ERL	1.5 x	>ERL <ERM	2 x	4 x	6 x	<ERL	<ERL
Ballona								
1/31/96								
Initial flow	>ERL <ERM	>ERL <ERM	<ERL	>ERL <ERM	3 x	1 x	2 x	<ERL
High flow	>ERL <ERM	>ERL <ERM	<ERL	>ERL <ERM	4.5 x	1 x	>ERL <ERM	<ERL
2/19,22/96								
Initial flow	>ERL <ERM	1.5 x	<ERL	2 x	3 x	<ERL	1 x	6 x
High flow	>ERL <ERM	>ERL <ERM	<ERL*	>ERL <ERM	3 x	<ERL	>ERL <ERM	8 x
3/4/96								
Initial flow	>ERL <ERM	>ERL <ERM	>ERL <ERM	>ERL <ERM	3 x	4 x	4.5 x	<ERL
High flow	>ERL <ERM	>ERL <ERM	>ERL <ERM	>ERL <ERM	5 x	2 x	1.5 x	<ERL

Int. = Interference precluded quantitation

* The zinc data are approximate and represent the residual concentration after subtraction of the very high levels observed in the control samples.

zinc levels, the zinc had to be from the digestion of the TCLP filters used to collect the suspended solids. This was disturbing since these filters are supposed to be free of toxic compounds, specifically trace metals.

The high zinc concentrations in our controls samples is unfortunate given that zinc is a major pollutant in urban runoff. Moreover, we observed extremely high zinc levels in all over our samples. Thus, it was decided that rather than discard the zinc data entirely, an attempt would be made to subtract out the zinc contributions from the filters, and report the data with the appropriate caveat. A conservative concentration estimate of 100 ppm in the final digestates was chosen as being due to the TCLP filters. Since the final volume of all the digestates was 100.0 ml, this means that 10 mg of zinc was leached from the filters during the digestion procedure. Thus, 10 mg was subtracted from the mass of zinc present in all of the suspended solids digestates. Only the mass in excess of 10 mg was considered to have come from the sample and was subsequently used for calculating the zinc concentration in the suspended solids.

Even after subtracting the 10 mg of zinc from every digestate, about half of the suspended solids samples exceeded the ERM value of 410 ppm. In fact, two samples had zinc concentrations which exceeded the ERM by the greatest margins of any metals in all of the samples analyzed, namely 172 times and 97 times the ERM for samples from Sepulveda (1/31/96) and Centinela (2/20/96) Channels, respectively.

The aqueous phase data for zinc appears to be suspect as well. The filter digest blanks showed high levels for two metals, zinc and barium. The dissolved phase metals data (Table C.1) also shows consistently high levels of these two metals in all samples both upstream and downstream. Moreover, the range of concentrations of barium was similar at all sampling locations, suggesting that the barium was derived from the filters and not from the sample itself. Thus, since the zinc and barium data seem to correlate, this brings the validity of both into question.

4.8.3 Concentrations of Metals in Stormwater Runoff

4.8.3.1 Aqueous Phase

In contrast to hydrophobic organic compounds, the aqueous phase (i.e. freely dissolved) concentration of metals in stormwater can be significant. Table C.1, Appendix C shows the aqueous phase concentrations of the metals investigated in this study. Several of the metals such as tin, zinc, nickel, and copper. The aqueous phase data for lead is particularly interesting. Table C1 shows that the dissolved phase lead concentrations were below the detection limits for all the samples from the upstream sites. These data show that virtually all of the lead in the stormwater runoff is sorbed to the solids phase, since Table C.2 shows that there was significant lead in the suspended solids collected at the upstream sites.

In contrast, high aqueous lead concentrations were measured in the samples from Ballona Creek at Pacific Ave Bridge, and Marina Del Rey. The samples from Marina Del Rey exhibited consistently high levels of lead in the dissolved phase (2730 - 3450 ppb), whereas those from Ballona Creek at Pacific Ave Bridge showed variable lead concentrations (130 - 3350 ppb). In comparing the times that the individual samples were taken with the water quality data and the dissolved phase lead concentration data, it was noted that the lead concentrations appeared to correlate with the conductivity. Figures 46 and 47 show the dissolved phase lead concentration and the conductivity data for the December 12-13, 1995 and February 19-22, 1996 storms, respectively.

Excellent correlation was observed between the Aqueous lead concentrations and the water conductivity. These data suggested one two possibilities: The lead associated with the suspended solids was desorbing into the aqueous phase as the conductivity increased, or the seawater was already highly contaminated with lead and the concentrations simply reflected the proportion of seawater in the sample.

The desorption of trace metals from solid phases upon mixing with seawater in estuaries is a well-established phenomenon (Libes, 1992). However, this does not appear

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12-13

Correlation Between Aqueous Lead Concentration and Conductivity for the Dec. 12-13, 1995 Storm

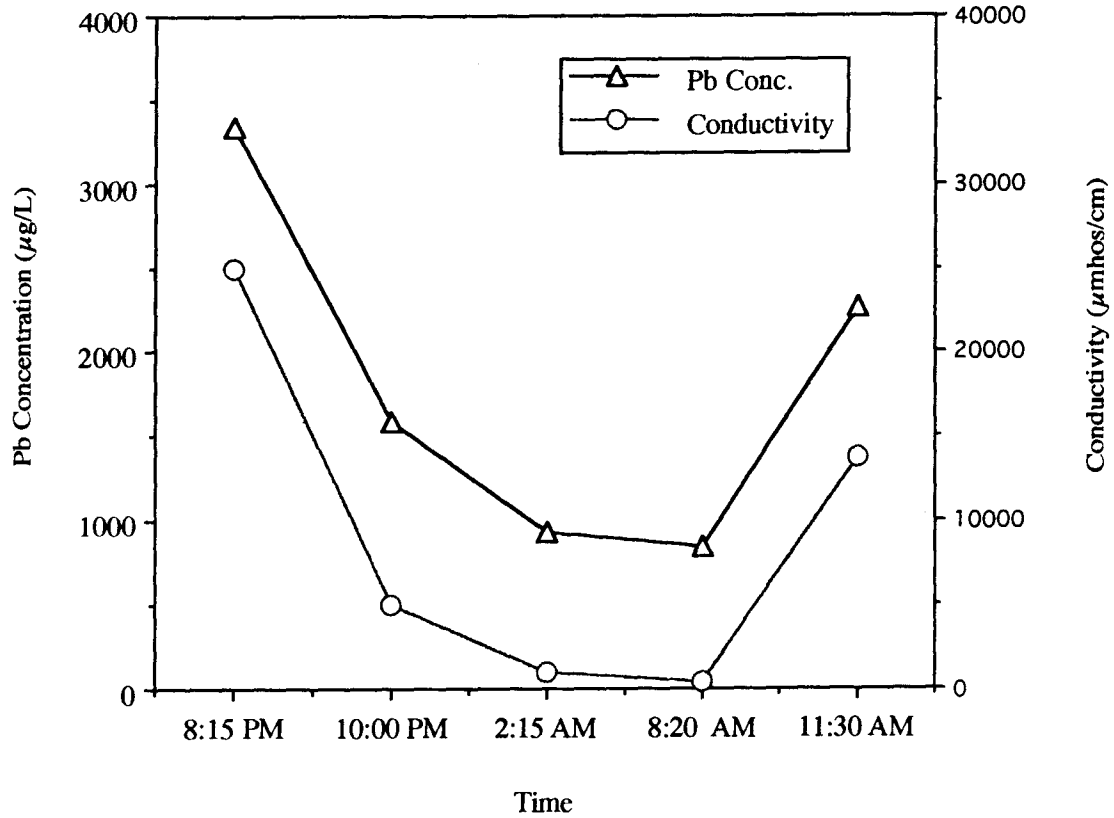


Figure 46. A plot of aqueous lead concentration and conductivity vs. time for samples collected from Ballona Creek at Pacific Ave bridge during the December 12-13, 1995 Storm event.

Correlation Between Aqueous Pb Concentration and Conductivity for the Feb. 19-22, 1996 Storm

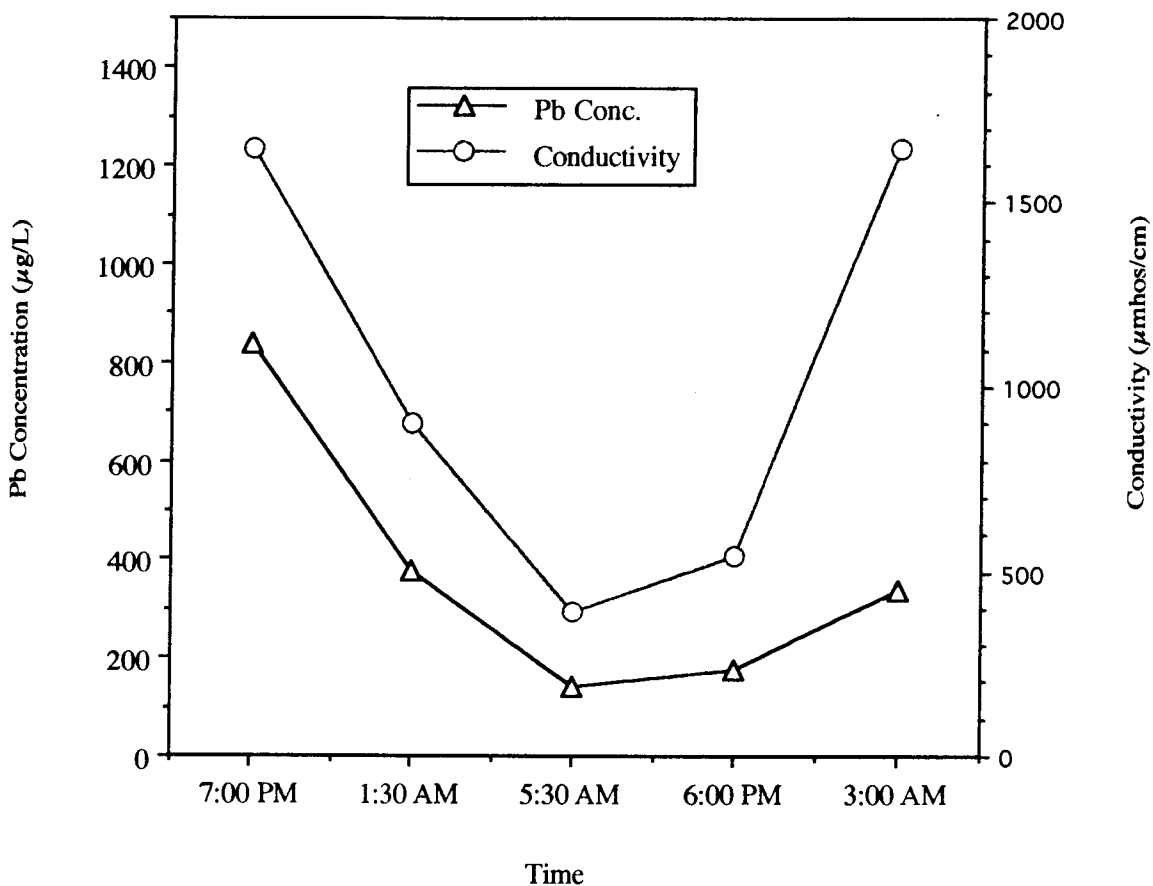


Figure 47. A plot of aqueous lead concentration and conductivity vs. time for samples collected from Ballona Creek at Pacific Ave bridge during the February 19-22, 1996 Storm event.

to the operative mechanism in this case. Unfortunately, there are no suspended solids phase metals data for the December 12-13, 1995 storm, for comparison. There are, however, suspended solids data for the February storm and no corresponding variation in the suspended solids lead concentration is observed. Moreover, if the lead in all of the upstream suspended solids samples and their respective suspended solids concentration is considered, then the potential contribution of lead to the aqueous phase via desorption can be estimated. Even if it is assumed that all of the lead on the suspended solids desorbed, it could not account for the observed changes in the water concentrations of lead.

These data show, although some desorption is certainly occurring as evidenced by changes in suspended solids lead concentrations between the upstream sites and Pacific Ave Bridge, the vast majority of the aqueous lead was already present in the receiving waters. Moreover, the consistently high lead concentrations observed in Marina Del Rey suggests that the marina is the probable source of the extremely high aqueous lead concentration in the seawater around the mouth of Ballona Creek.

4.8.3.2 Suspended Solids

As previously mentioned, Table 9 summarizes the suspended solids metals data for each storm at the three upstream sites relative to the respective ERLs and ERMs for each metal. The actual concentration data is given in Appendix C, Table C.2. Also presented in Appendix C are a series of plots of the metals concentration data for each storm event. The plots for each metal and location include the concentrations at each sampling time, the respective ERL and ERM, and the storm runoff hydrograph at the Ballona Creek gauging station. Representative plots for lead are shown in Figures 48-50, Figures 51-53 and Figures 54-56 for the January, February, and March, 1996 storms, respectively.

Table 9 shows that Sepulveda and Centinela Channels generally had higher suspended solids concentrations of the eight regulated metals than did Ballona Creek. Approximately half of all the upstream samples showed suspended solids metals

*reflecting
diff. land uses
what are
they?*

Ballona Creek @ Sawtelle Ave. Suspended Solids Filter Digest Data 1/31/96

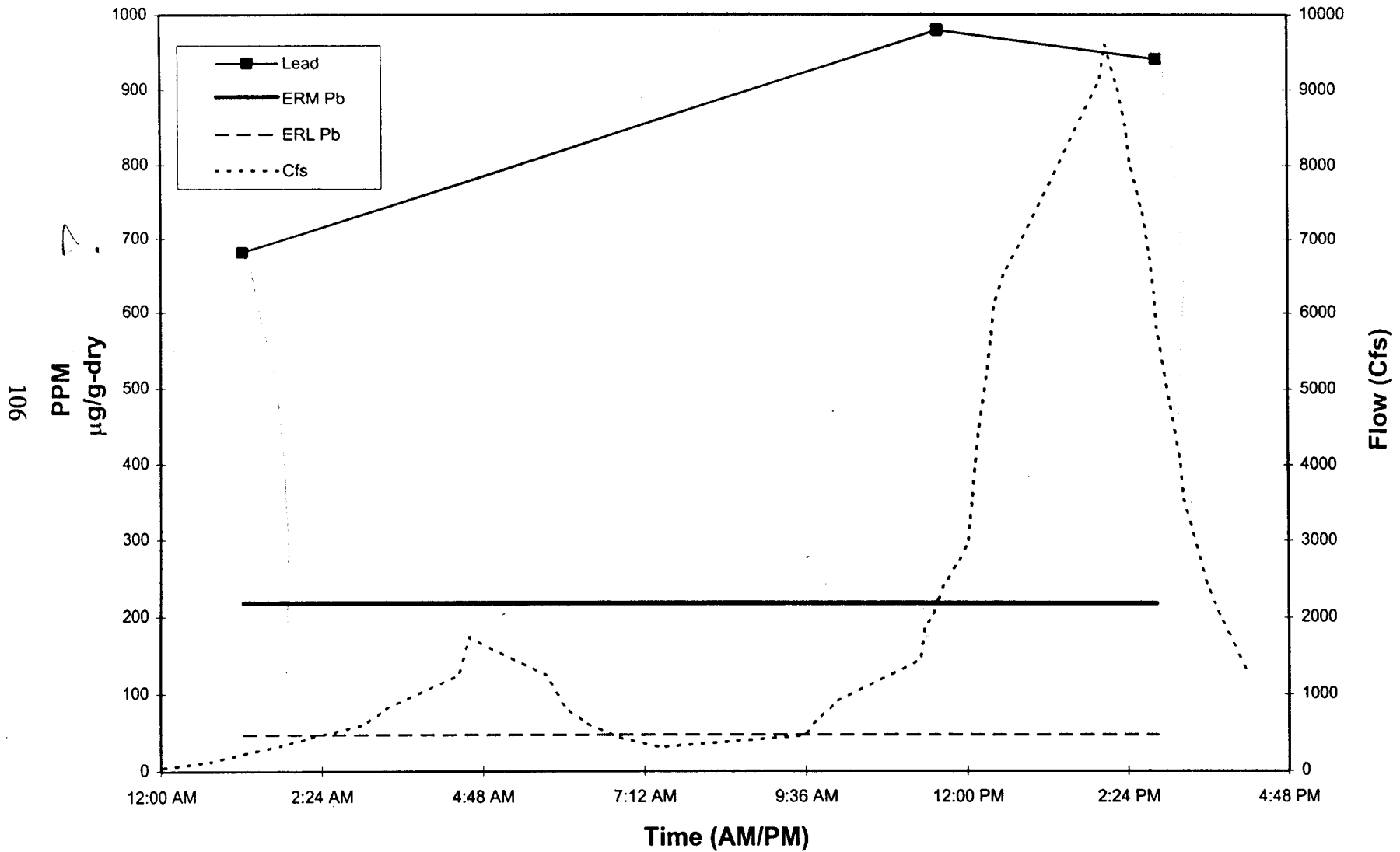


Figure 48. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Sawtelle Blvd. during the January, 1996 storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Sepulveda Channel @ Culver Ave. Suspended Solids Filter Digest Data 1/31/96

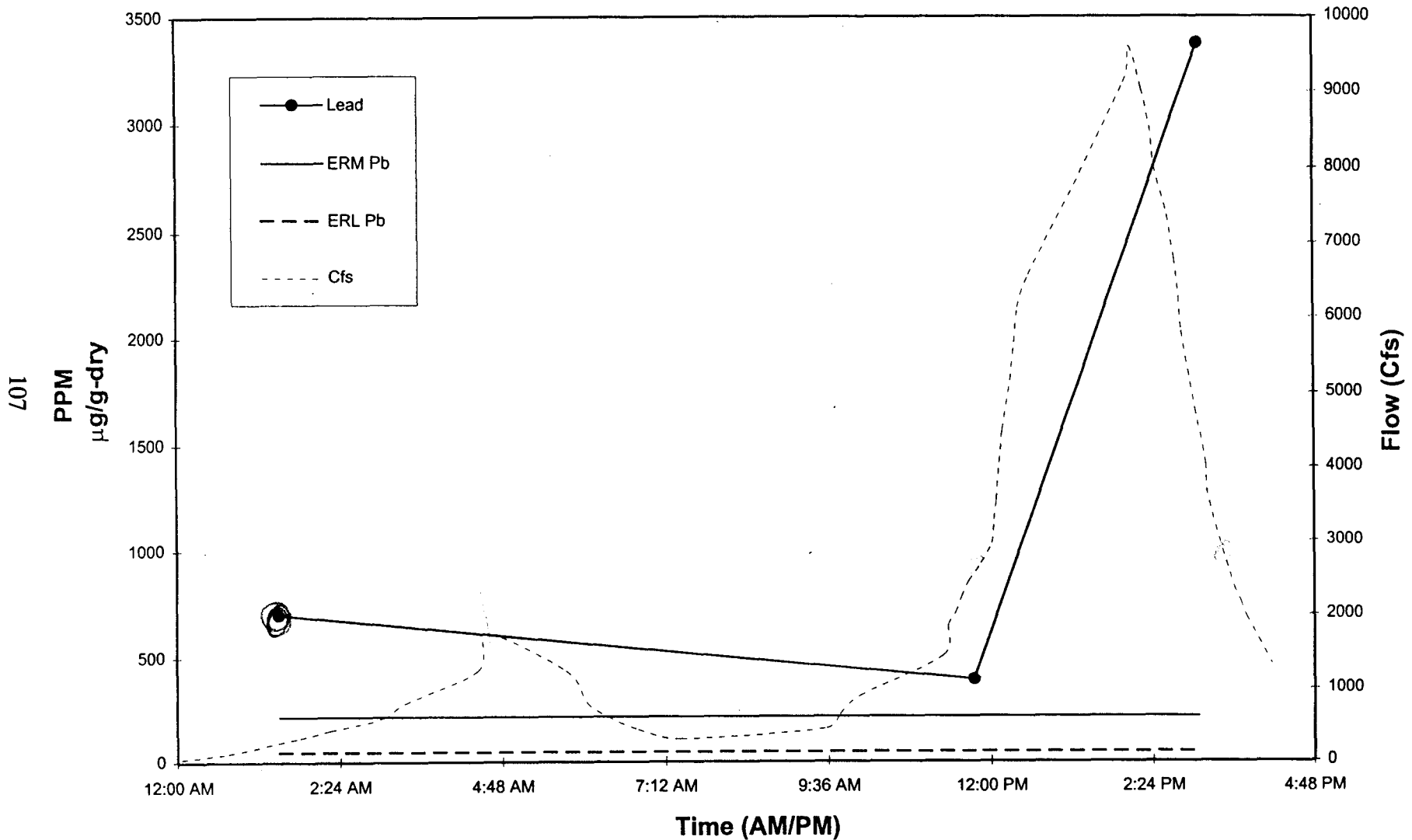


Figure 49. Lead concentrations in stormwater suspended solids for samples collected from Sepulveda Channel at Culver Blvd. during the January, 1996 storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Centinela Channel @ Centinela Ave. Suspended Solids Filter Digest Data 1/31/96

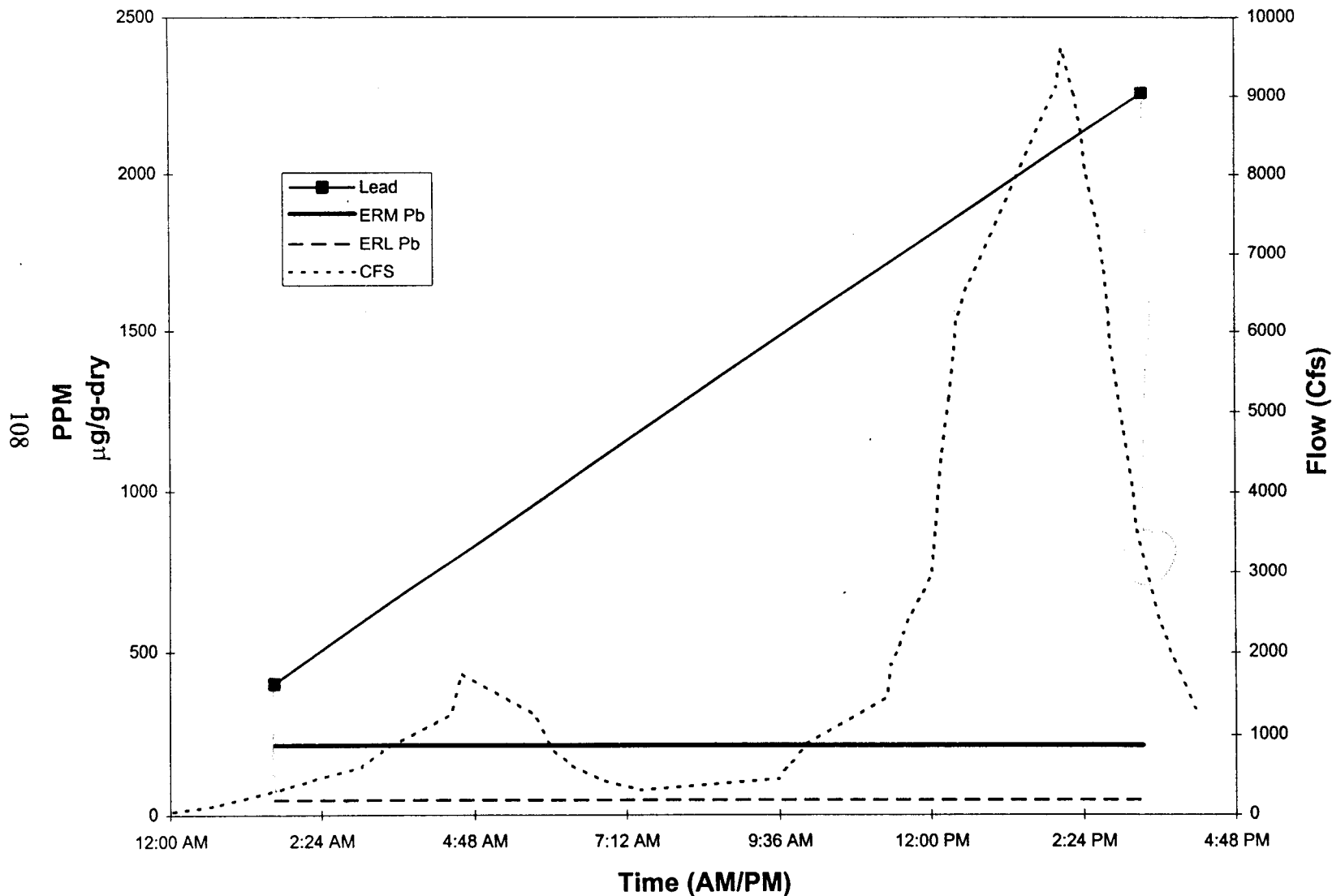


Figure 50. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave. during the January, 1996 storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Ballona Creek @ Sawtelle Ave. Suspended Solids Filter Digest Data 2/19/96-
2/21/96 Feb

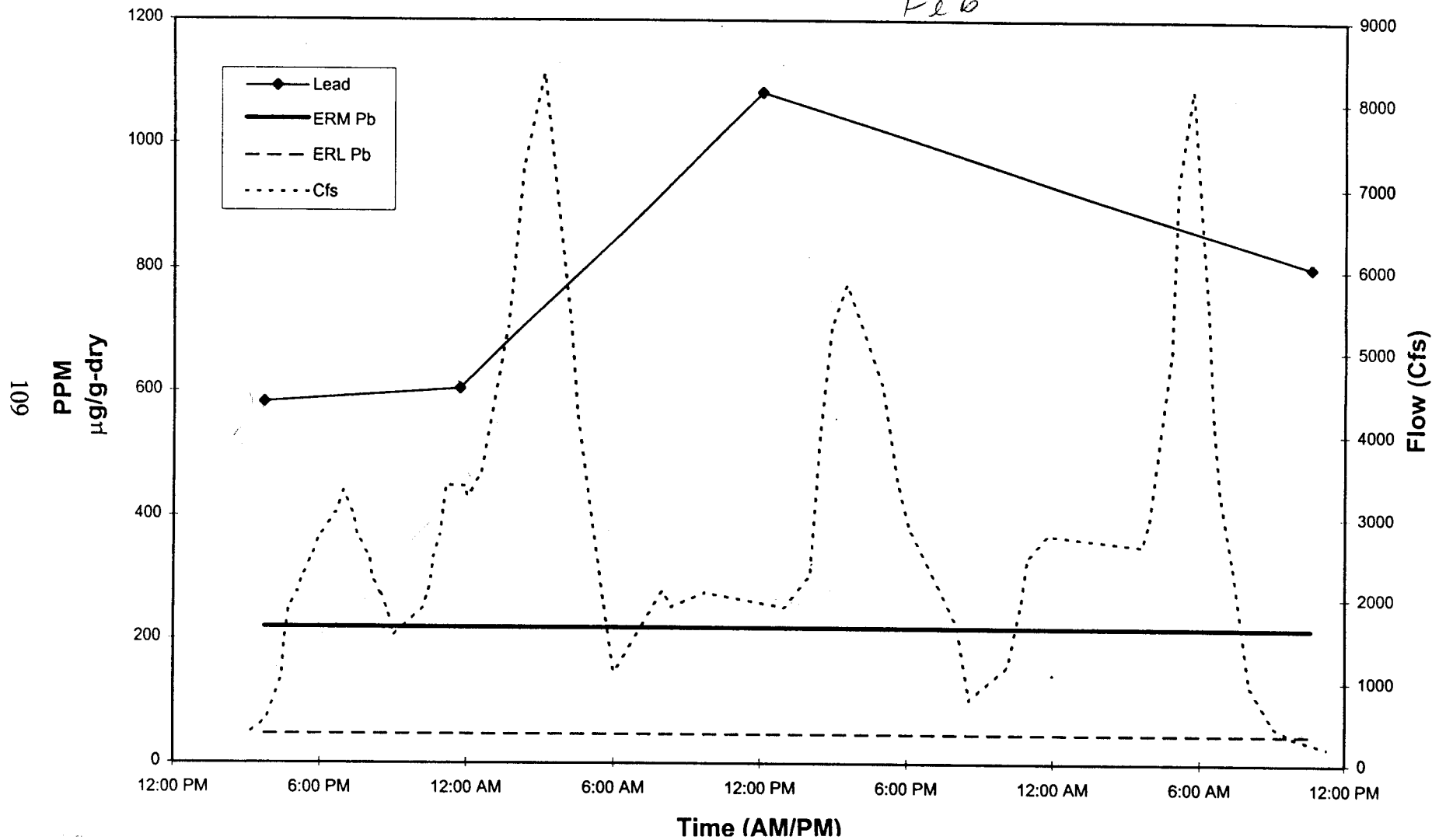


Figure 51. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Sawtelle Blvd. during the February 1996. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Sepulveda Channel @ Culver Ave. Suspended Solids Filter Digest Data 2/19/96-2/21/96

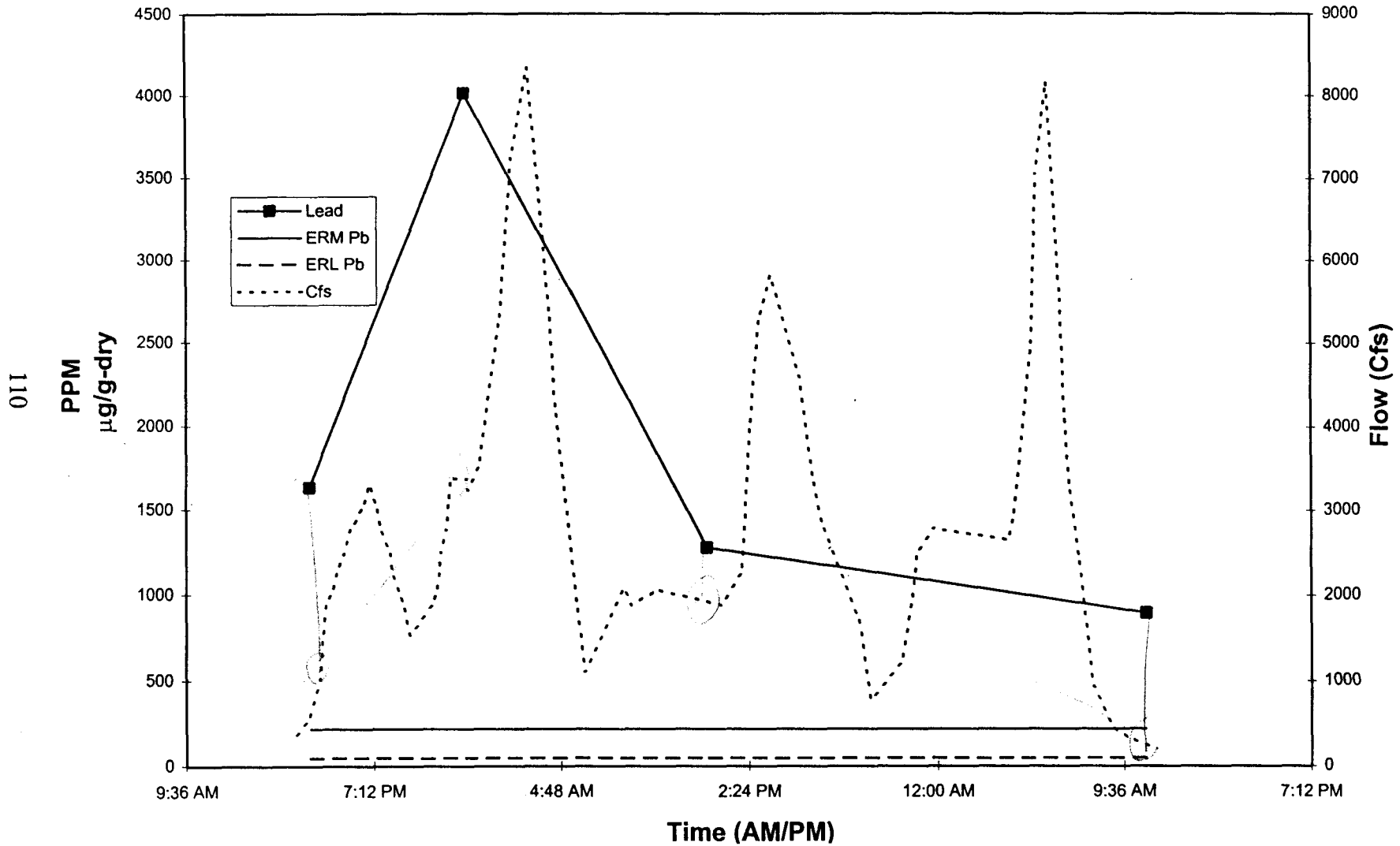


Figure 52. Lead concentrations in stormwater suspended solids for samples collected from Sepulveda Channel at Culver Blvd. during the February, 1996. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Centinela @ Centinela Ave. Suspended Solids Filter Digest Data 2/19-2/21/96

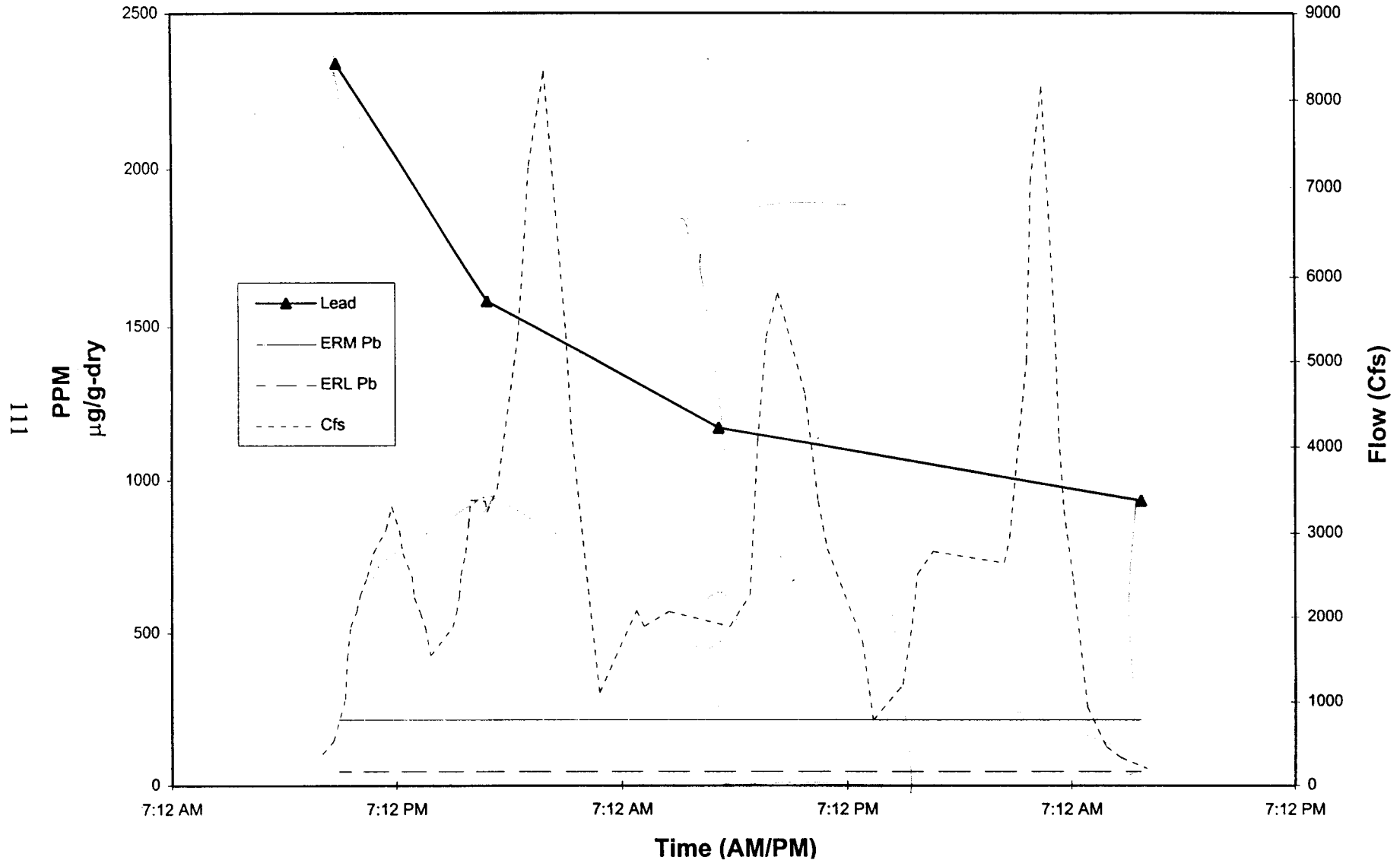


Figure 53. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the February, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Ballona Creek @ Sawtelle Ave. Suspended Solids Filter Digest Data 3/4/96-3/5/96

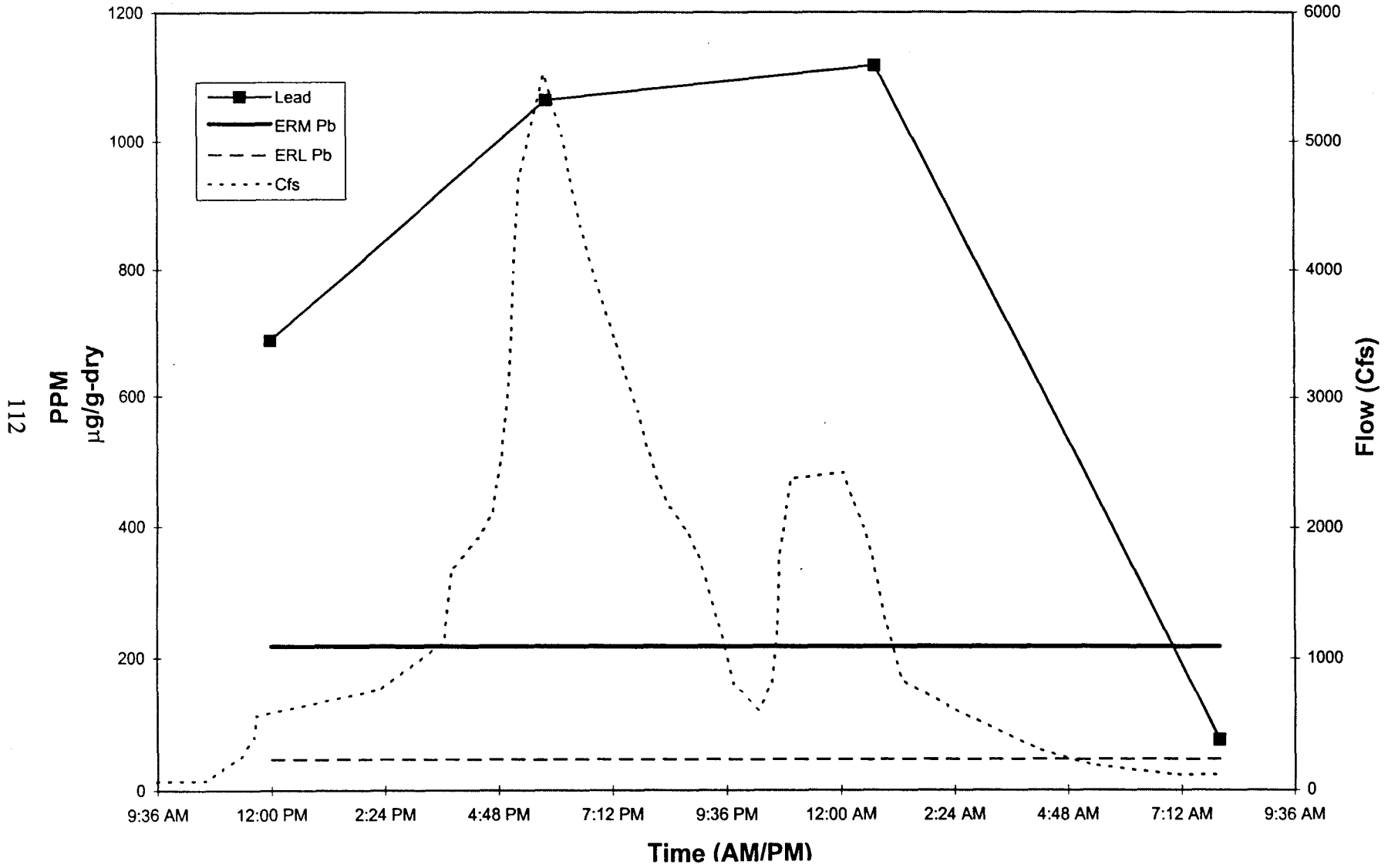


Figure 54. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Sepulveda Channel @ Culver Ave. Suspended Solids Filter Digest Data 3/4/96

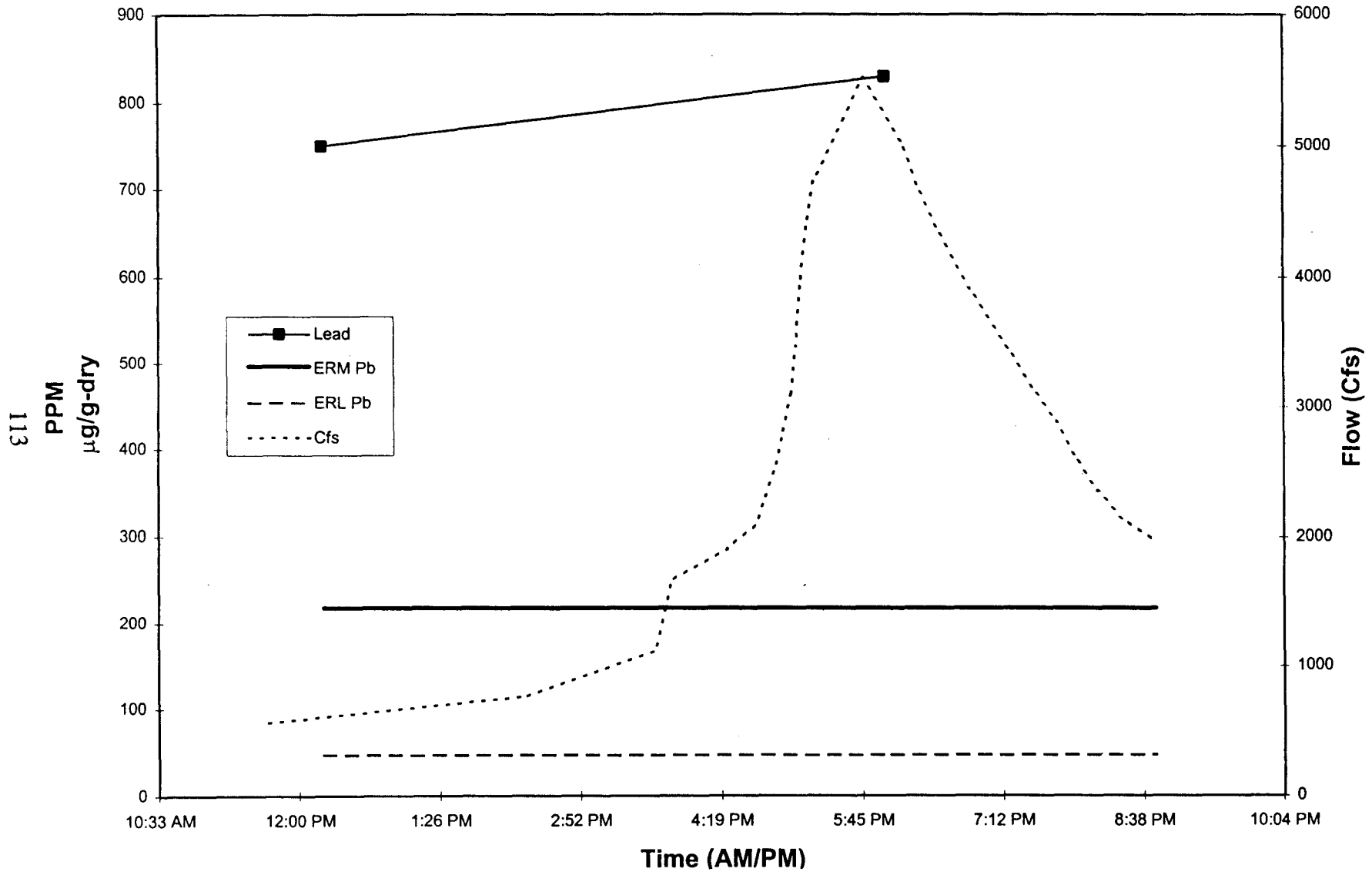


Figure 55. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Centinela Channel @ Centinela Ave. Suspended Solids Filter Digest Data 3/4/96-3/5/96

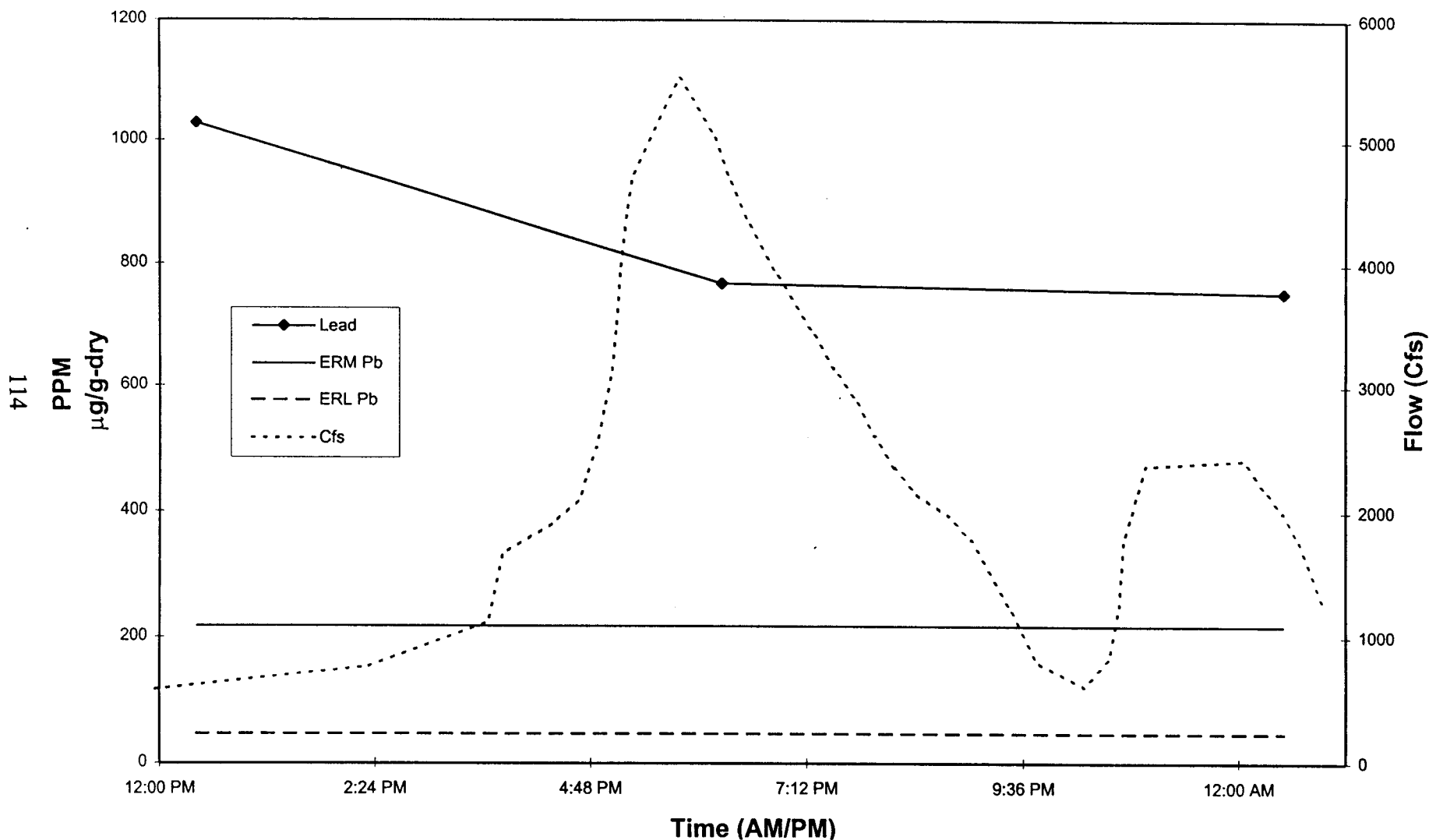


Figure 56. Lead concentrations in stormwater suspended solids for samples collected from Centinela Channel at Centinela Ave during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

concentrations above the ERMs. This indicates a potential for adverse biological impacts when these suspended solids ultimately become bottom sediments.

The suspended solids metals concentrations for the downstream locations are also given in Appendix C. Representative plots of the lead concentration data for Ballona Creek and Marina Del Rey are shown in Figures 57-59 and 60-62 for the January 30-31 and March 4-5, 1996 storms, respectively. Several aspects these data are noteworthy. Figures 57 and 60 include the corresponding conductivity data for the samples collected from Ballona Creek at Pacific Ave Bridge. These figures both show the inverse relationship between the suspended sediment lead concentrations and the conductivity. This indicates that desorption of was in fact occurring to some extent in the mixing zone. However, as pointed out above, the desorption from the solid phase could not account for the high lead concentrations in the aqueous phase. All of the suspended solids samples downstream had lead concentrations above the ERM. The suspended solids in the marina had lead concentrations 2-3 times higher than those from Ballona Creek at Pacific Ave. This supports the assertion that Marina Del Rey is a significant source of lead contamination to the receiving waters. However, the concentration of suspended solids (i.e., the turbidity) in the samples taken from Marina Del Rey were so low that their contribution to the total metals concentration in the water column was negligible.

conclusion

4.8.3.3 Relative Total Metals Contributions at the Upstream Sites- Sepulveda Channel, Centinela Channel and Ballona Creek

The total metals concentrations in the runoff for the each storm event and each sampling site are also given in Appendix C. The total metals concentrations reported are the sum of the aqueous and suspended solids phase concentrations, and thus represent the actual total mass of each metal in a particular volume of water. Figures 63-65 show the relative total lead concentrations among Ballona Creek, Sepulveda and Channels for the January 30-31, February 19-22, and the March 4-5, 1996 storms respectively.

Ballona Creek @ Pacific Ave. Suspended Solids Filter Digest Data 1/31/96

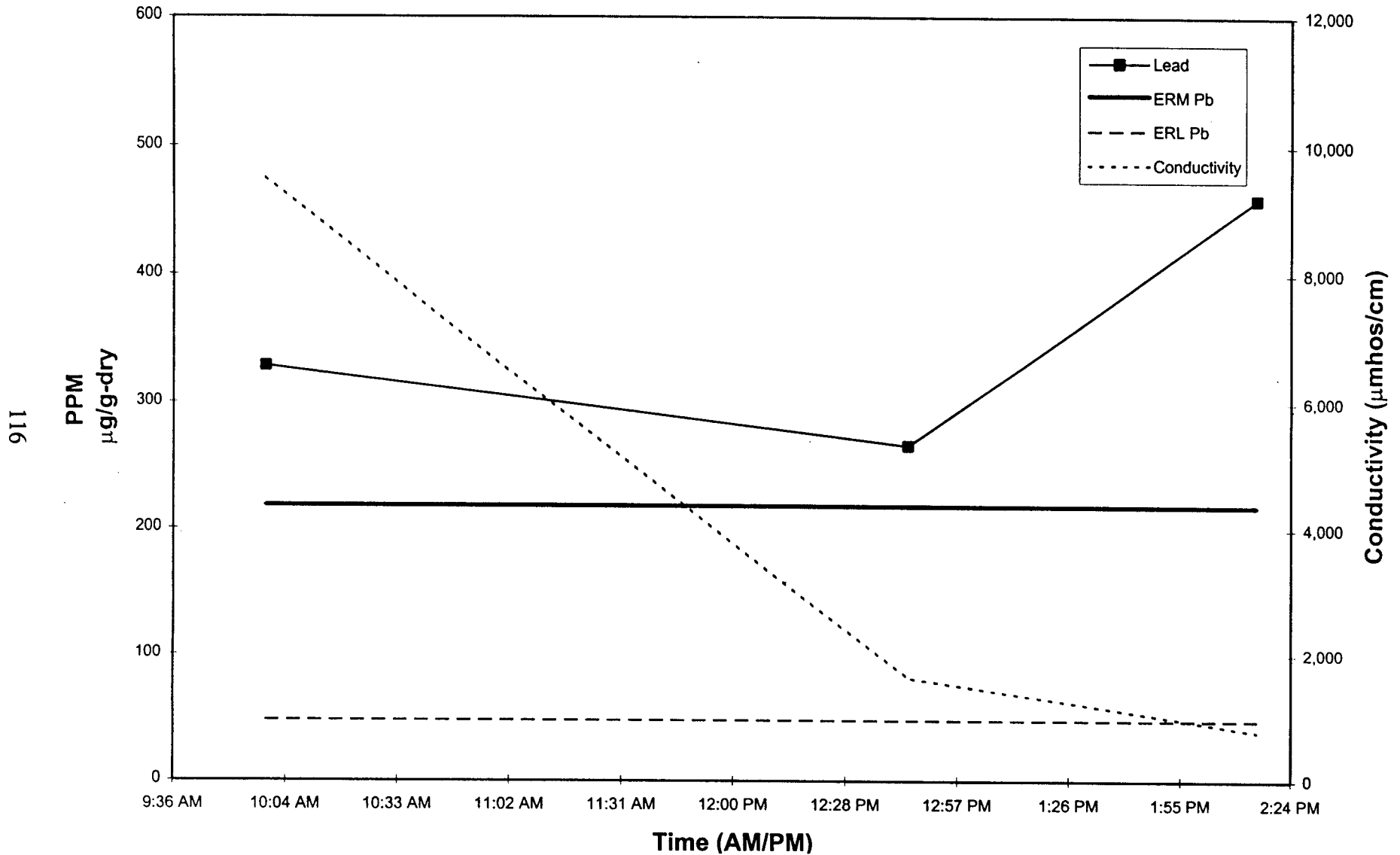


Figure 57. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Pacific Ave bridge during the January, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Marina Del Rey (Front) Suspended Solids Filter Digest Data 1/31/96

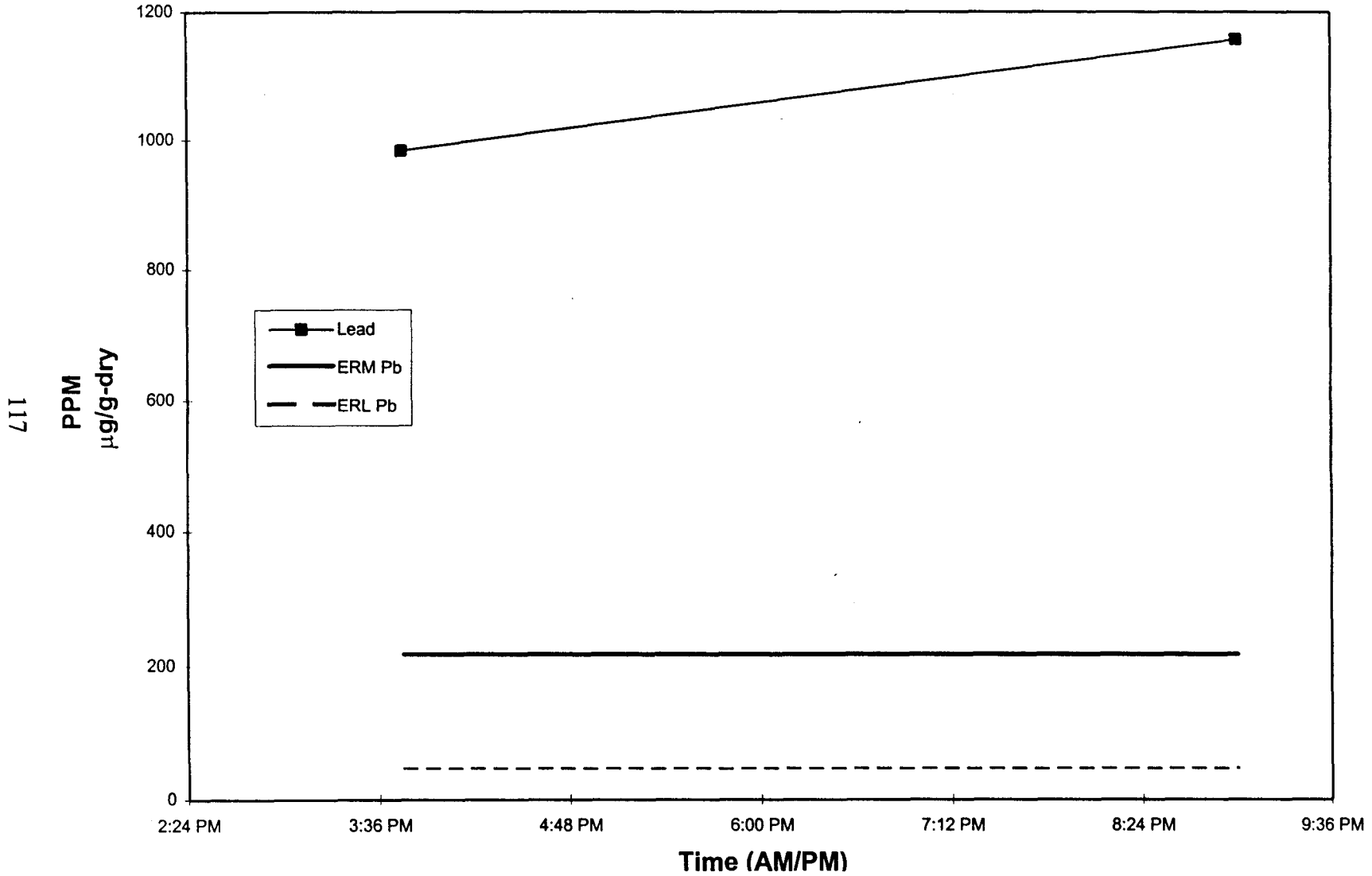


Figure 58. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Front) during the January, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Marina Del Rey (Back) Suspended Solids Filter Digest Data 1/31/96

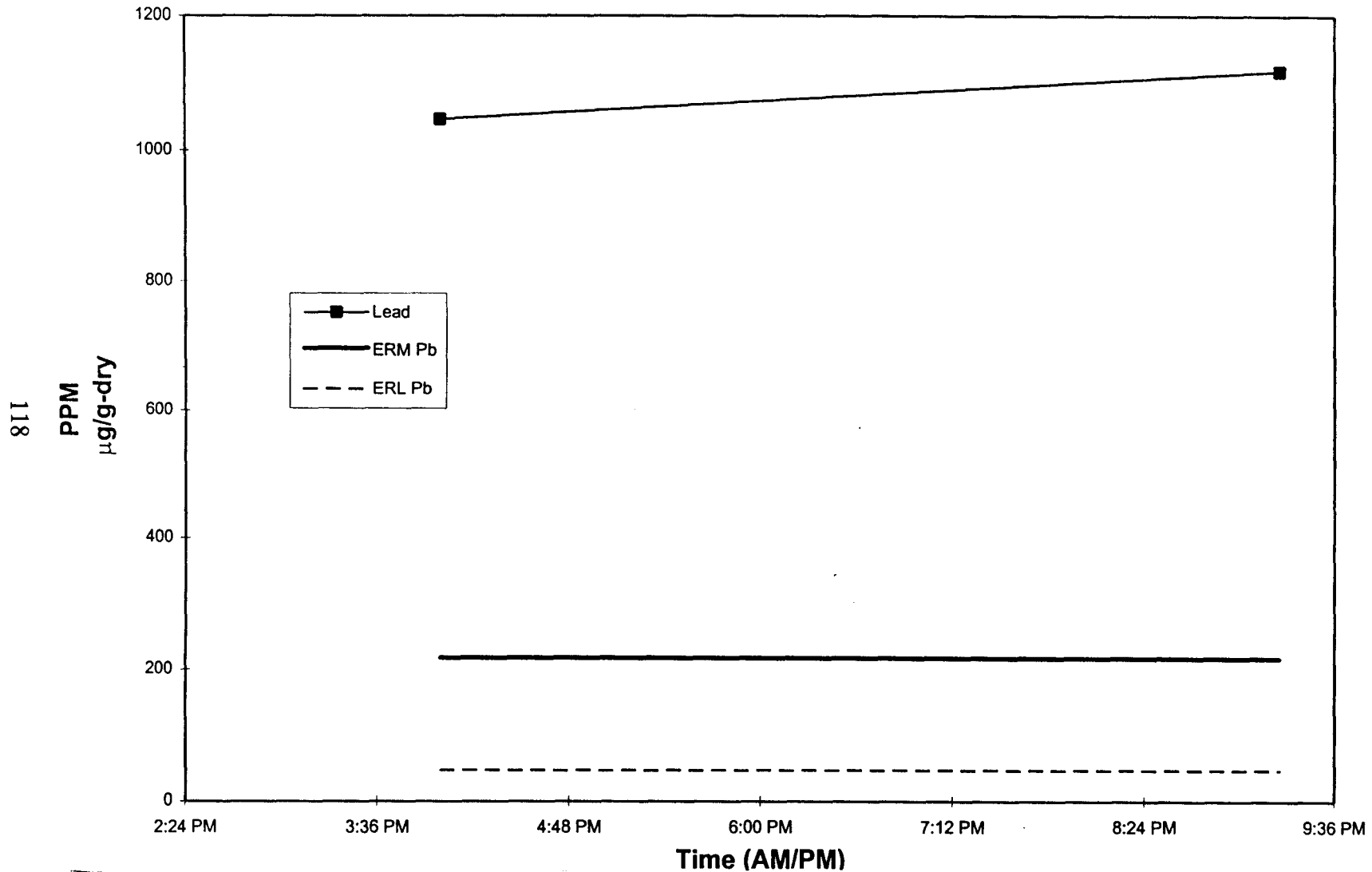


Figure 59. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Back) during the January, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Ballona Creek @ Pacific Ave Suspended Solids Filter Digest Data 3/4/96

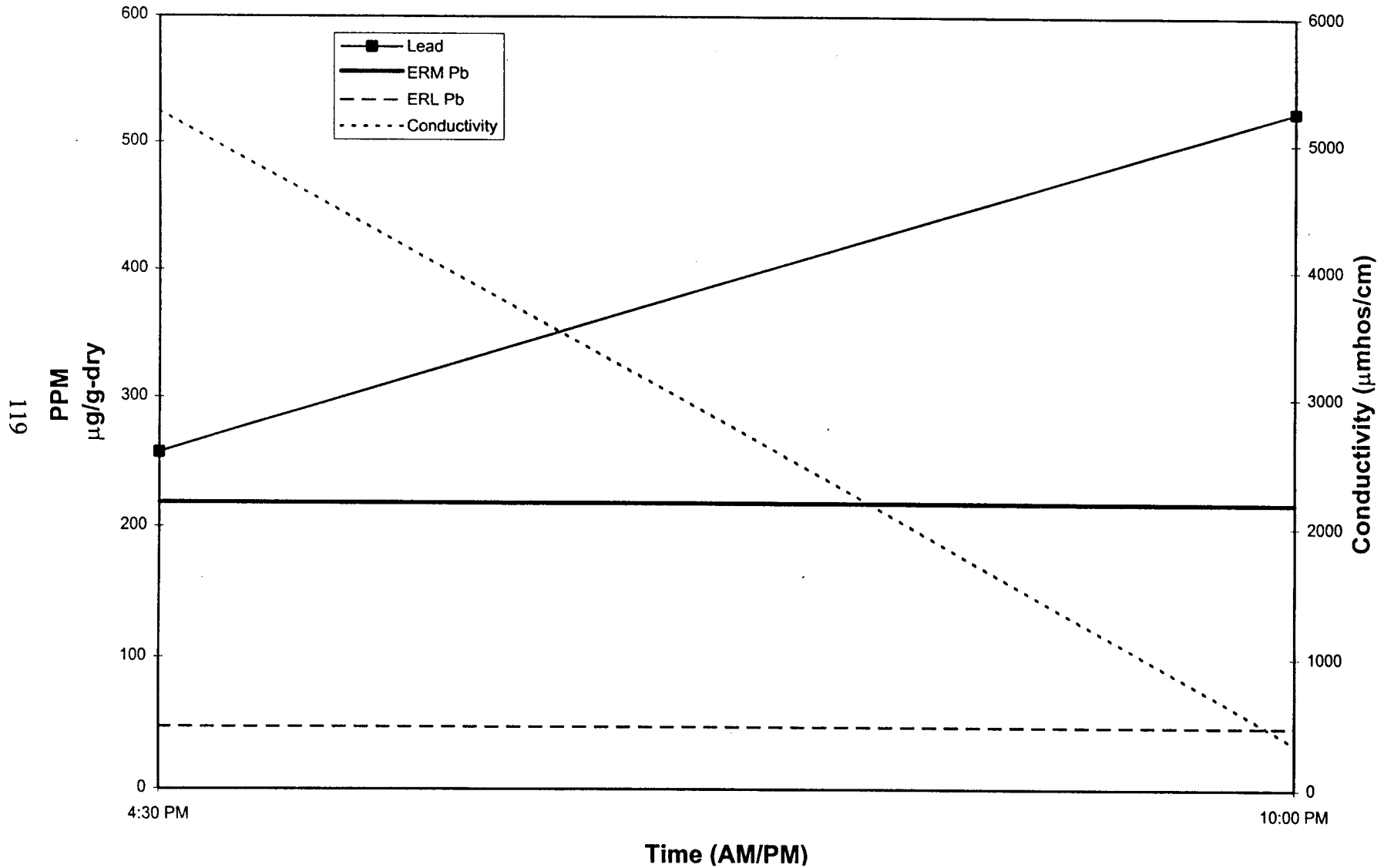


Figure 60. Lead concentrations in stormwater suspended solids for samples collected from Ballona Creek at Pacific Ave bridge during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Marina Del Rey (Front) Suspended Solids Filter Digest Data 3/4/96

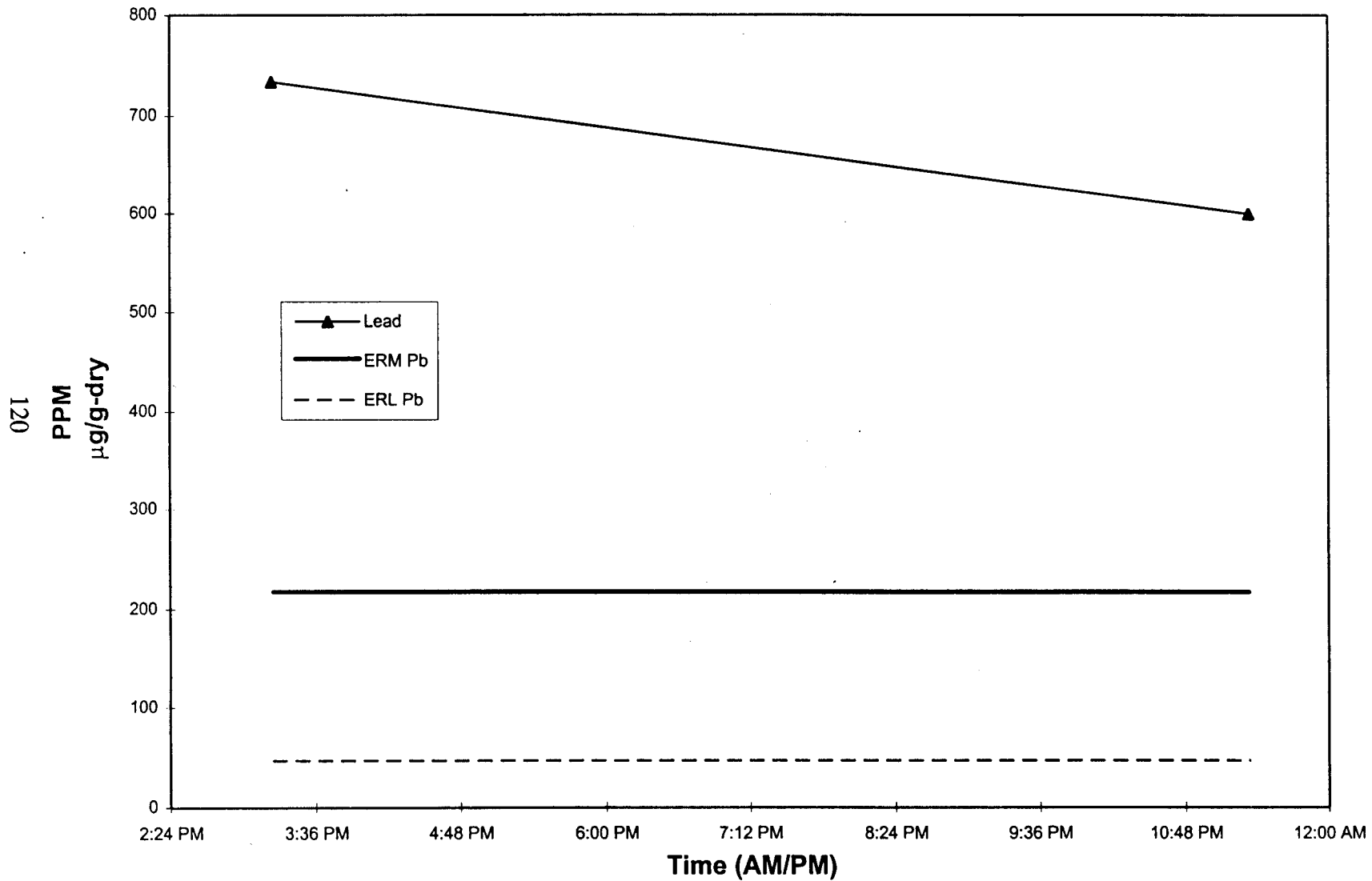


Figure 61. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Front) during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERMs, and CTLs to assist in data evaluation.

Marina Del Rey (Back) Suspended Solids Filter Digest Data 3/4/96

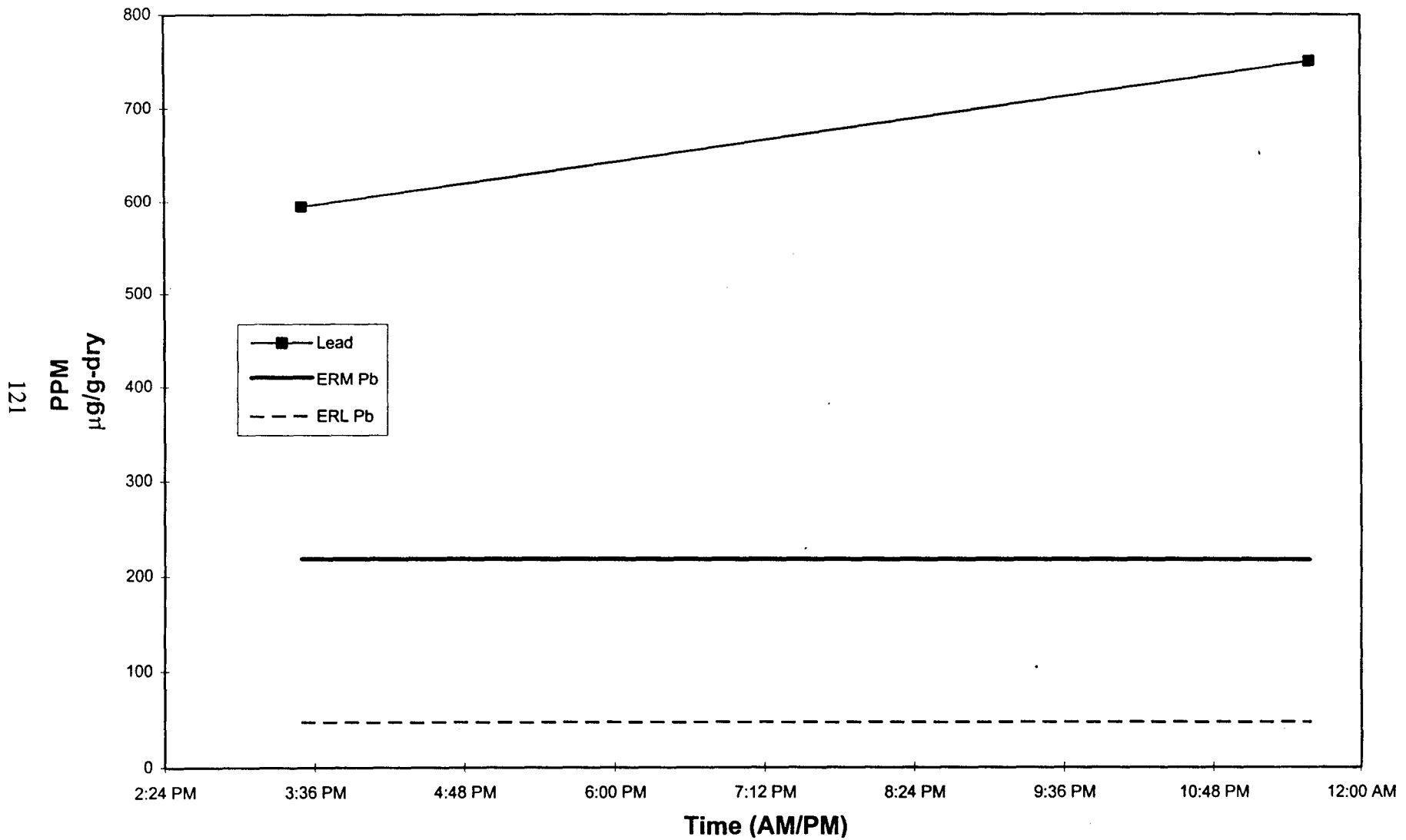


Figure 62. Lead concentrations in stormwater suspended solids for samples collected from Marina Del Rey (Back) during the March, 1996 Storm. Also plotted are the runoff hydrograph for Ballona Creek, the ERLs, ERM, and CTLs to assist in data evaluation.

Upstream Locations: Total Lead Concentration 1/31/96

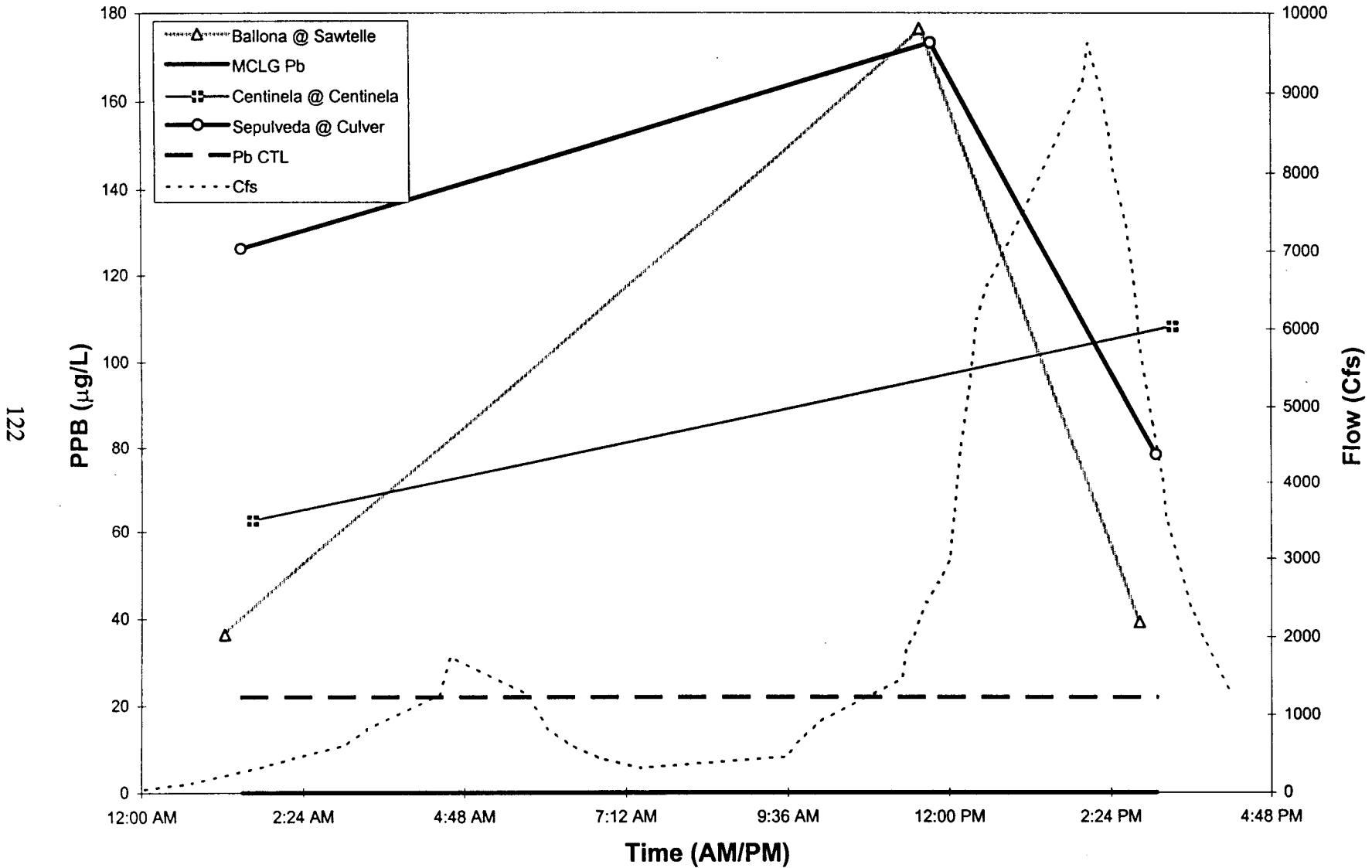


Figure 63. Streamflow data for January 31, 1996 as measured at Ballona Creek metering station. Total lead concentrations for all upstream sites including chronic toxicity and drinking water standards are plotted against time.

Upstream Locations: Total Lead Concentrations 2/19-2/21/96

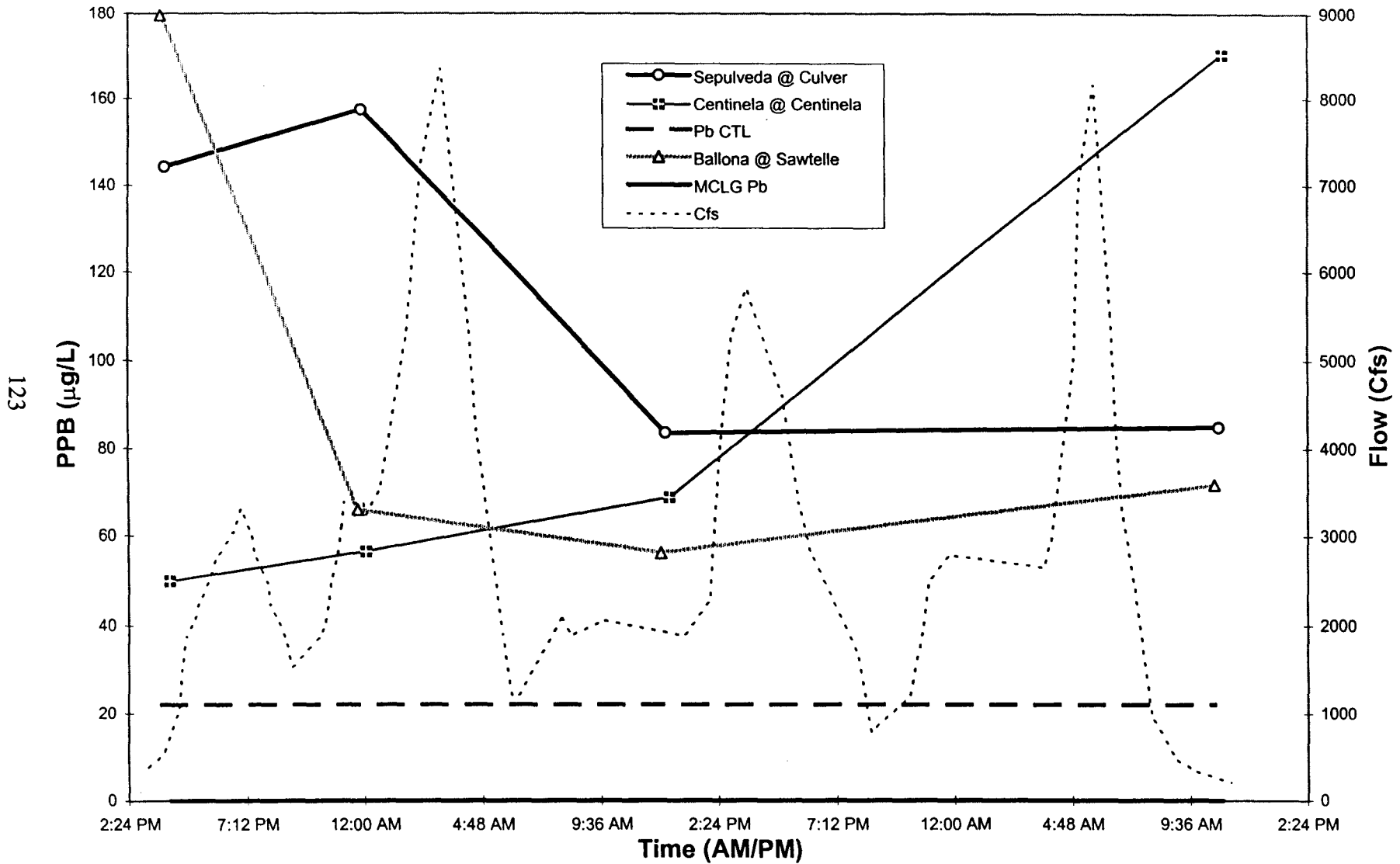


Figure 64. Streamflow data for February 19-21, 1996 as measured at Ballona Creek metering station. Total lead concentrations for all upstream sites including the chronic toxicity and drinking water standards are plotted against time.

Upstream Locations: Total Lead Concentration 3/4-3/5/96

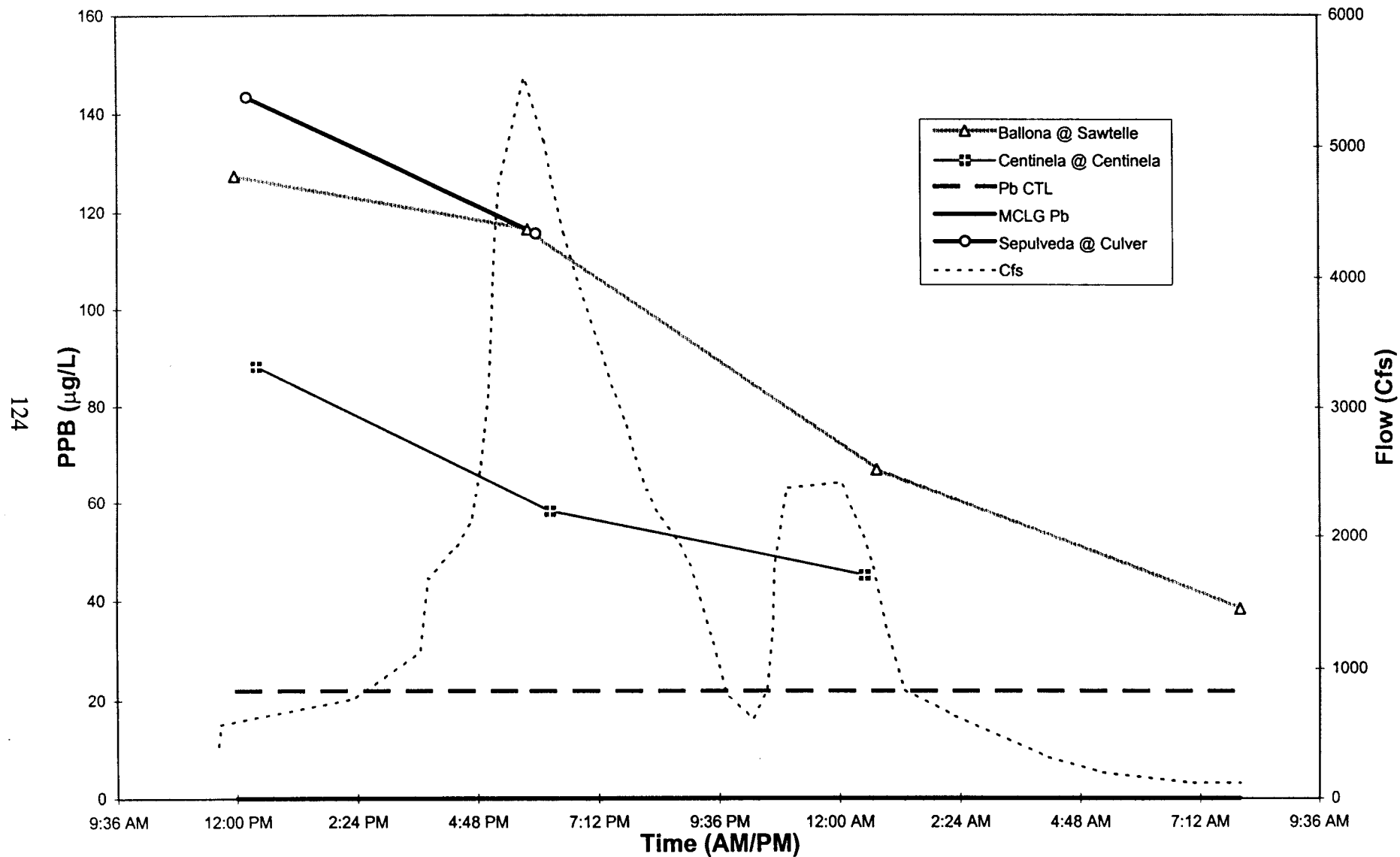


Figure 65. Streamflow data for March 4-5, 1996 as measured at Ballona Creek metering station. Total lead concentrations for all the upstream sites including the chronic toxicity and drinking water standards are plotted against time.

The relative total lead concentration in the stormwater for the January 30-31 and March 4-5, 1996 storms is in the order Sepulveda>Ballona>Centinela. For the February 19-22, 1996 storm the concentration of lead in stormwater is in the order

Sepulveda>Ballona=Centinela. The total lead concentration among the different storm events was fairly consistent. The total lead concentrations varied from 50-200 $\mu\text{g/L}$ for the January and February storms, and 50-150 $\mu\text{g/L}$ for the March storm. However, the total lead concentrations within a storm event varied by location and sampling time. The

variations in total lead concentrations appear to be related to the runoff hydrograph. Low concentrations are observed near the beginning of the storm, prior to any significant flow. The highest total lead concentrations are observed at or near initial onset of significant flow. Low concentrations are again observed near peak flow, and generally thereafter.

The relative contributions of metals cannot truly be determined because of the lack of accurate flow data from Sepulveda and Centinela Channels. However, given that the concentrations of metals in the stormwater from all three drainage areas were of a similar range and magnitude, some generalizations can be made.

Since the concentrations of metals in the three drain are similar, then the relative contribution will be directly proportional to the runoff flow in each drain. Although, the total concentration of lead in Sepulveda Channel was clearly higher than the other two drain for two of the three storm events, it was not so much higher as to make up for the difference in runoff volumes. It was qualitatively observed in the field that the total stormwater flows in the three channels were consistently in the order

Ballona>Sepulveda>Centinela regardless of the intensity or duration of the storm event.

This suggests that the relative contribution of metals to the Santa Monica Bay from these three drains should follow that order as well. However, it should be emphasized all three drains contribute a significant portion of the total metals load, and thus all three sub-watersheds need to be considered by any stormwater pollution management plans.

why does [] matter?

→ this is first flush?

4.8.4 Relative Total Metals Concentrations at the Downstream Sites - Ballona Creek vs. Marina Del Rey

Plots of the total metals concentrations for samples collected at the downstream sampling sites-Ballona Creek at Pacific Ave Bridge and Marina Del Rey (front and back)- for the January 30-31 and March 4-5, 1996 storms, are also presented in Appendix C. Representative plots of the total lead concentrations in stormwater from Ballona Creek at Pacific Ave and Marina Del Rey presented in Figures 66-68 and 69-71 for the January and March storms, respectively.

The data from both storms clearly shows that Marina Del Rey has extremely high concentrations in the water column. The total lead concentrations in the marina are 5-10 times the concentrations observed at Ballona Creek. Moreover, the lead concentrations that are measured at Ballona Creek at Pacific Ave are primarily due to mixing with the already highly contaminated receiving water. This is evidenced by the fact that, like the dissolved phase data, the total lead data is strongly correlated to the conductivity. Figures 66 and 69 show how the conductivity and total lead concentration lines mirror each other.

The concentration of lead in the samples from both the January and March storms far exceeds the water quality objectives of outlined in the California Ocean Plan (1997). The plan sets for a six month median objective for lead of $2 \mu\text{g/L}$, and suggests a conservative estimate for chronic toxicity to marine aquatic life () of $22 \mu\text{g/L}$. In the case of Marina Del Rey, the total lead concentrations were fairly consistent, and over 1000 and 100 times higher than the above water quality objectives, respectively.

4.8.5 Mass Transport Estimates for Lead in Stormwater

The total mass of lead transported by the January 30-31, February 19-22 and March 4-5, 1996 storms via Ballona Creek was estimated by the same method described in section

4.5.4. Again, mass transport could only be estimated for Ballona Creek because flow data were only available for that drain. The raw data for these calculations are given in

Appendix C. To summarize the results, the January storm transported an estimated

→ read it. you relate it so sub basin size.

Ballona Creek @ Pacific Ave. Total Lead Concentration 1/31/96

127

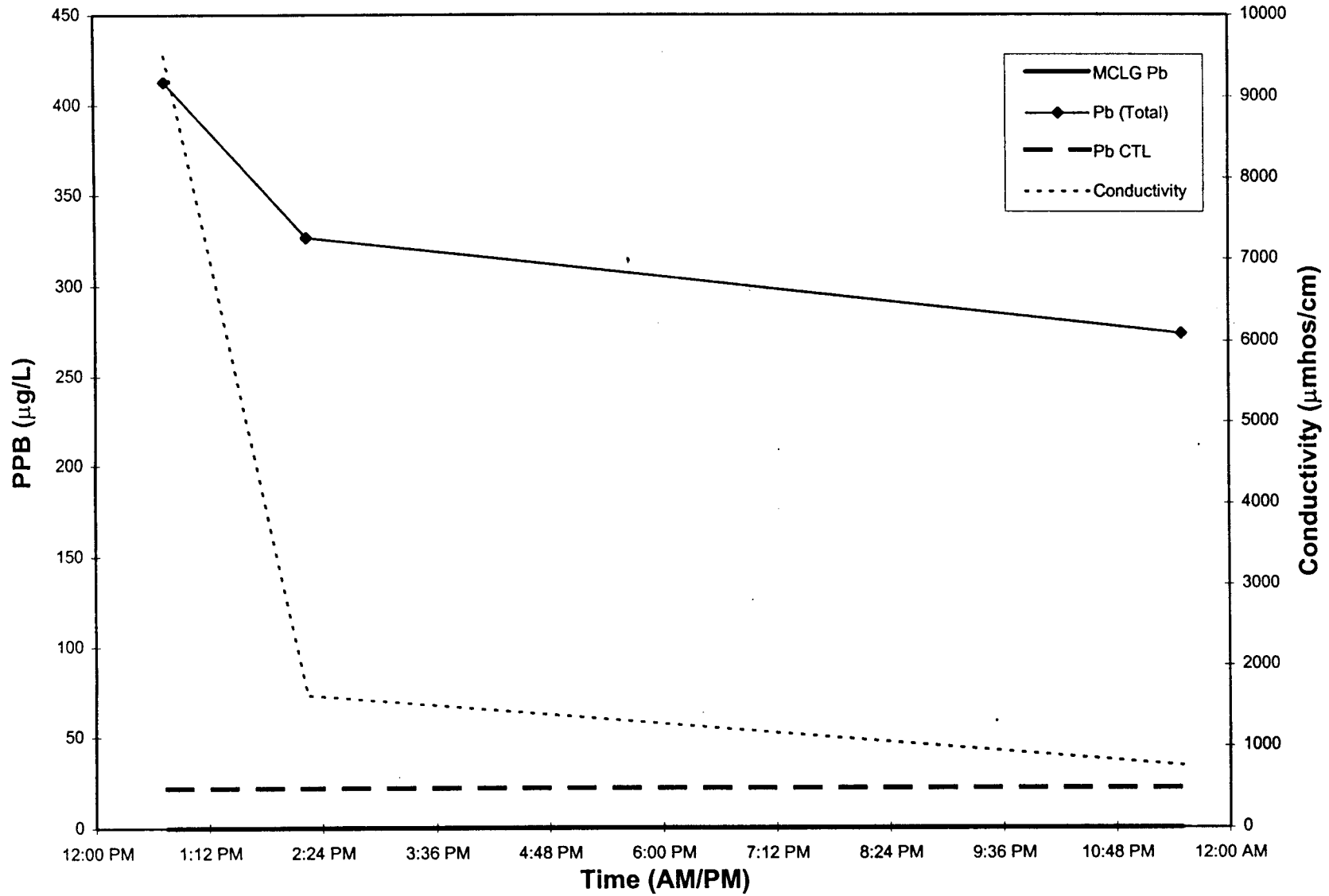


Figure 66. Total lead concentration and conductivity of water samples collected from Ballona Creek at the Pacific Ave Bridge during the January 1996 storm event.

Marina Del Rey (Front) 1/31/96 Total Lead Concentrations

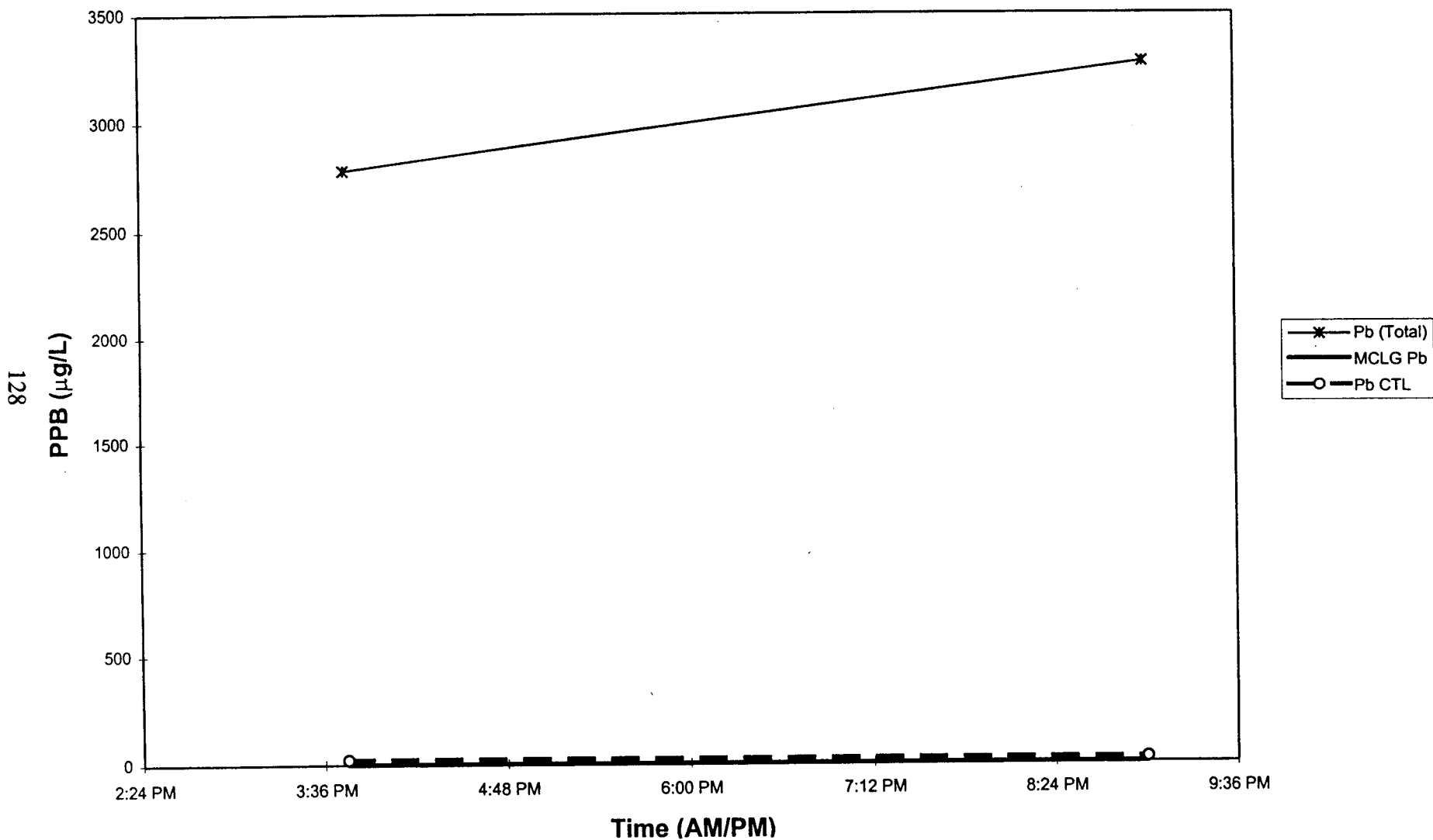


Figure 67. Total lead concentration in water samples collected from Marina Del Rey (Front) during the January, 1996 storm event.

Marina Del Rey (Back) 1/31/96 Total Lead Concentration

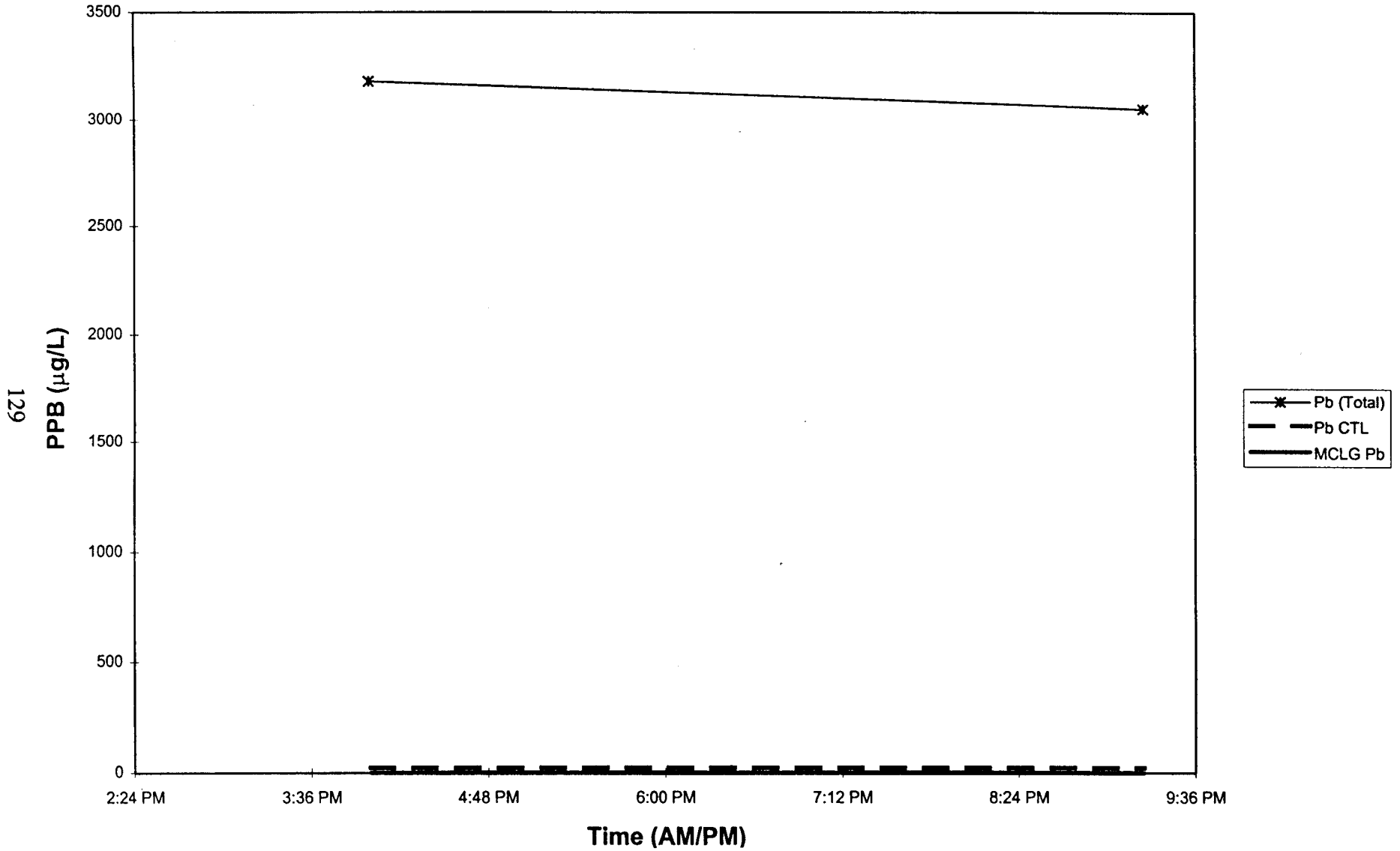


Figure 68. Total lead concentration in water samples collected from Marina Del Rey (Back) during the January, 1996 storm event.

Ballona Creek @ Pacific Ave. Total Lead Concentration 3/4/95

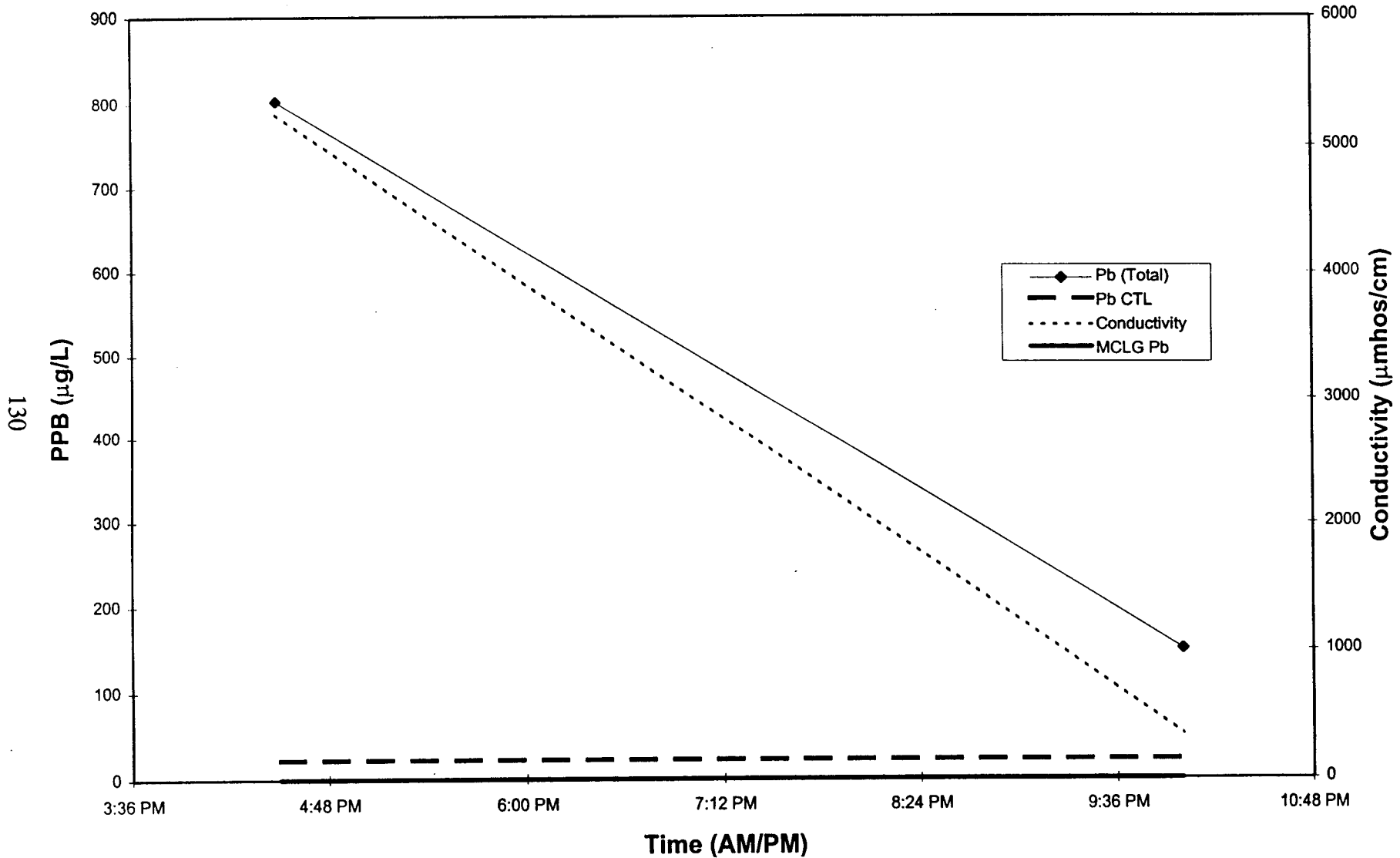


Figure 69. Total lead concentration and conductivity of water samples collected from Ballona Creek at the Pacific Ave Bridge during the March 1996 storm event.

Marina Del Rey (Front) 3/4/96 Total Lead Concentration

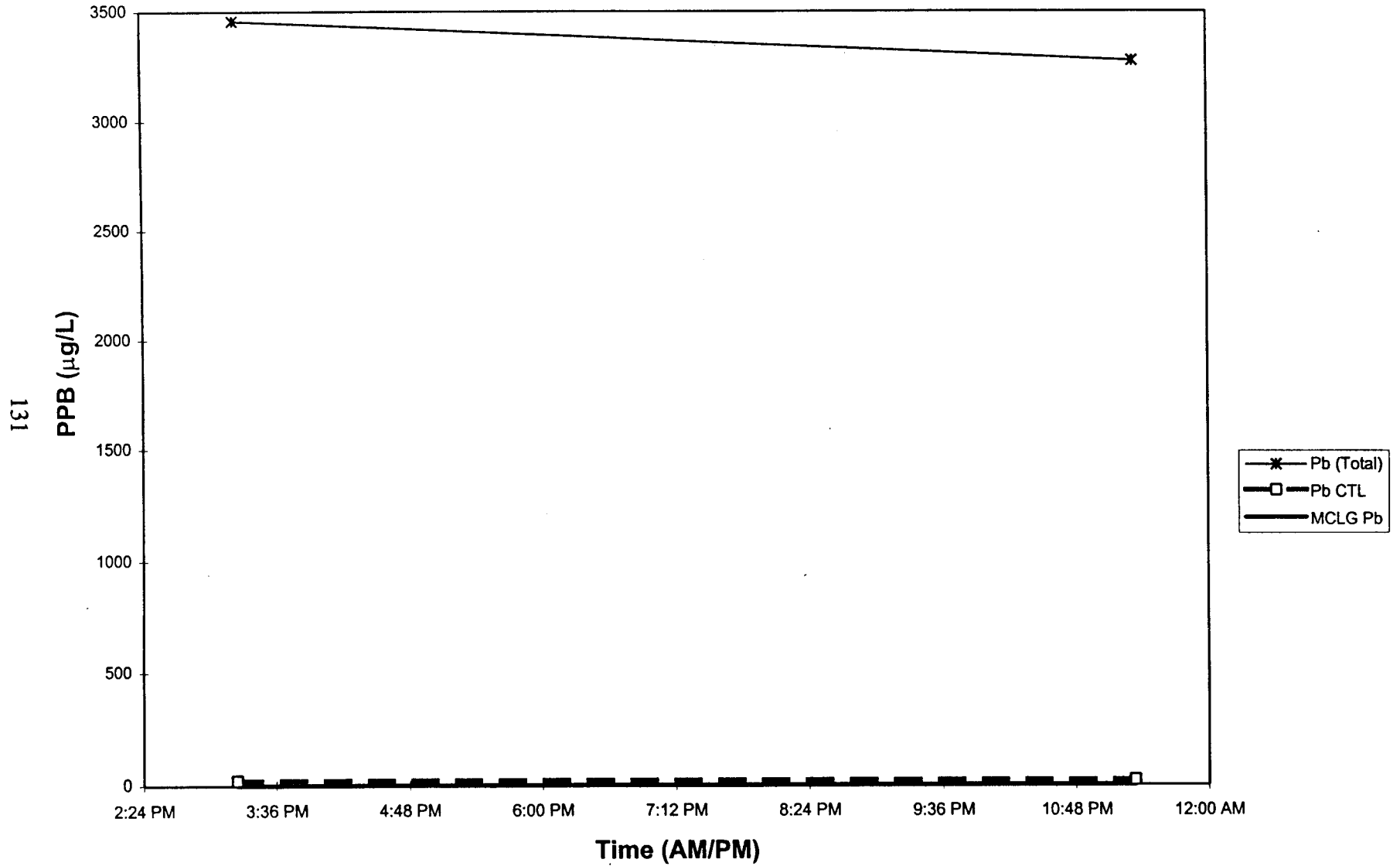


Figure 70. Total lead concentration in water samples collected from Marina Del Rey (Front) during the March, 1996 storm event. 71

Marina Del Rey (Back) 3/4/96 Total Lead Concentration

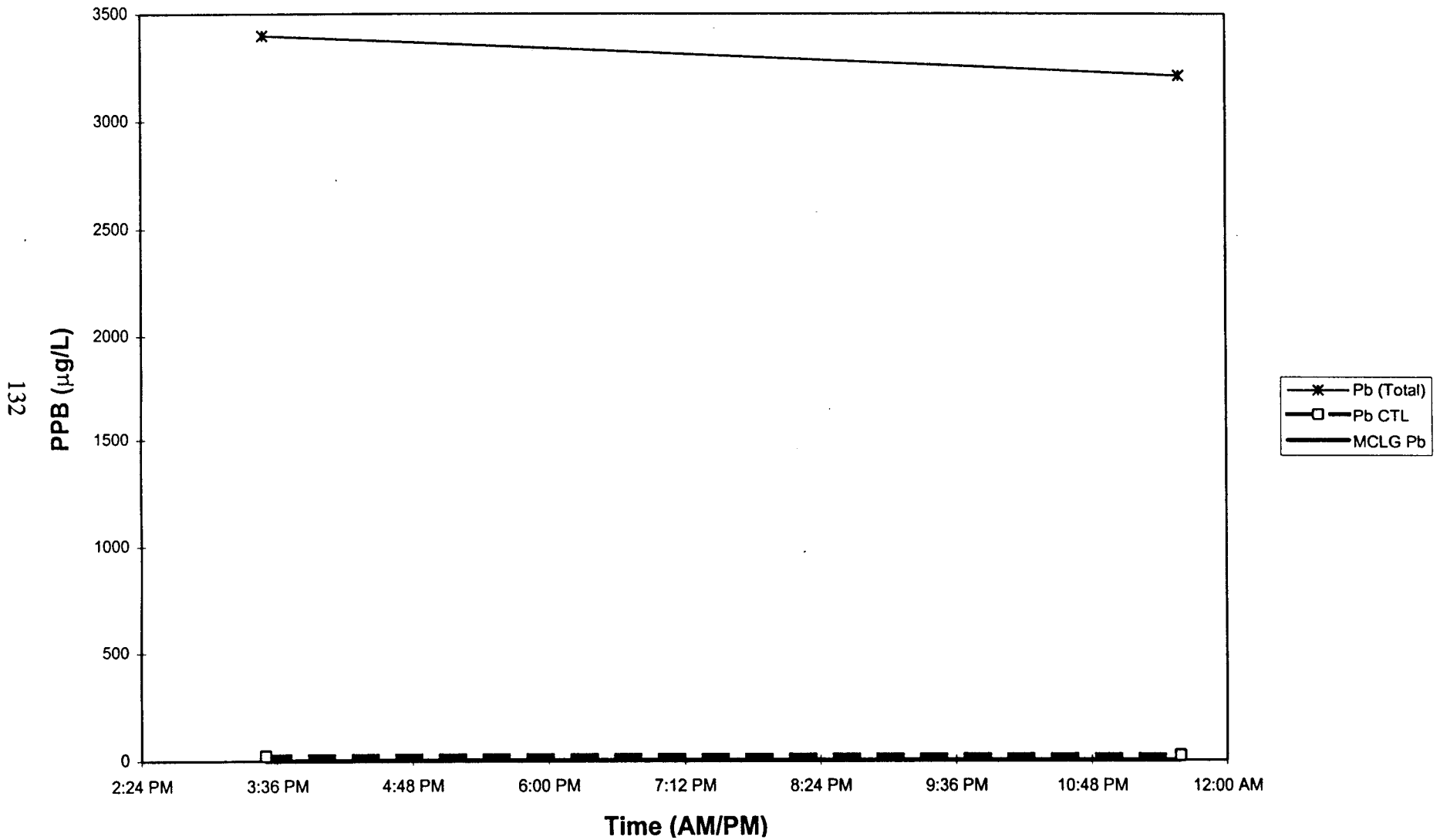


Figure 71. Total lead concentration in water samples collected from Marina Del Rey (Back) during the March, 1996 storm event.

298.37 Kg of lead, in about 4.05×10^9 liters of runoff. The February storm was larger and of longer duration, and carried an estimated 894.21 Kg of lead via Ballona Creek along with approximately, 1.24×10^{10} liters of runoff. Lastly, the March storm transported an estimated 302.45 Kg of lead along with 3.0×10^9 liters of stormwater.

4.8.6 General Discussion

A very large amount of data was generated in this study and presented in this report. The authors have attempted to present the data in a clear and concise manner, and emphasize key points where appropriate. However, it is difficult to assimilate such a large quantity data, and to draw meaningful conclusions that pertain to the objectives of project. In an effort to give the data a sense of perspective, a table was prepared which summarizes the major results of this study relative to water quality objectives and another significant source of pollution to the Santa Monica Bay.

Table 10 presents the concentrations and/or estimates of pollutant mass emissions determined in this study in juxtaposition to the water quality objectives in the California Ocean Plan (1997), and the equivalent duration of effluent at the maximum allowable concentrations from Chevron USA, Inc. refinery, El Segundo, CA. Also given in Table 10 are the dilution ratios which would be necessary to achieve the respective water quality objectives.

The data for the phthalates are not included in Table 10 for two reasons. First, the mass emissions estimated in this study were for total phthalates. However the phthalates are regulated individually. Thus, the mass emissions would need to be performed separately for each compound in order to interpret the data properly. Second, even when the regulated allowable concentrations are summed and compared to the estimated stormwater mass emissions, the results are not nearly as striking as for the PAH's and lead. The estimated total phthalate mass emissions from Ballona Creek are equivalent to 3.5 days and 4.7 days of Chevron effluent for the January and March 1996 storms,

Table 10. A comparison among some of the results from this study, the Water Quality Objectives in the California Ocean Plan, and equivalent pollution contributions from the effluent of a major point-source discharger to the Santa Monica Bay.

Pollutants/ Storm Event	Site ^a	Average Conc. in Stormwater ^b (µg/l)	Water Quality Objective ^c (µg/l)	Required Dilution Factor ^d (Dm)	Estimated Mass Emission from Storm ^e (kg)	Chevron USA Effluent Equivalent ^f (time)
PAHs						
1/30-31/96	BAS	1.34	8.8×10^{-3}	152	5.44	8.5 months
3/4-5/96	BAS	2.26	8.8×10^{-3}	257	6.79	10.5 months
PCBs						
12/13/95	BAS	390	1.9×10^{-5}	2.1×10^7	N/A	N/A
12/23/96	SEP	34.5	1.9×10^{-5}	1.8×10^6		
1/31/96	SEP	15.1	1.9×10^{-5}	7.9×10^5		
Lead						
1/30-31/96	BAS	73.7	8.0	9.2	298.4	2 months
2/19-22/96	BAS	72.1	8.0	9.0	894.2	6 months
3/4-5/96	BAS	100.1	8.0	12.5	302.5	2 months

^a BAS = Ballona Creek at Sawtelle Blvd; SEP = Sepulveda Channel at Culver Blvd.

^b Where only a single sample was taken, that value was used.

^c As specified in the Draft California Ocean Plan, March 1997. For PAHs and PCBs the 30-day avg. was used; For lead the Daily Maximum of 8.0 µg/L was used.

^d The dilution factor Dm, necessary to achieve the stated water quality objective. Dm is expressed as parts seawater per part wastewater as specified in the Draft California Ocean Plan, March 1997, and is required for the calculation of effluent limitations from the water quality objectives.

^e Estimated mass of pollutant discharged to Santa Monica Bay during the specified storm event using the methodology described in Section 4.5.4. Flow data was only available for Ballona Creek, and thus these are very conservative estimates of the mass emissions of the specified pollutants from the Ballona Creek Watershed.

^f Derived from the NPDES Permit for Chevron USA, Inc., El Segundo CA., assuming the maximum allowable effluent concentrations for the duration specified. For PAHs and PCBs, the 30-day average discharge limitations in µg/L were used, and an average discharge of 7.9 MGD was assumed. For lead, the 30-day average in kg/day was used to calculate the time required for Chevron to discharge an equivalent mass of lead.

respectively.

The information in Table 10 allows the data from this study to be put in perspective relative to other sources of pollution to Santa Monica Bay. The data clearly show that stormwater is a major source of both organic and inorganic pollutants. It must be emphasized that the mass emission estimates given in Table 10 are only for Ballona Creek at Sawtelle Blvd., and thus they do not include the contributions of pollutants from Sepulveda and Centinela Channels. Thus, the total mass contribution of pollutants to Santa Monica Bay due to stormwater runoff from the Ballona Creek Watershed is at least comparable to having another point source discharger the size of Chevron.

However, the stormwater will have a greater impact on the coastal marine environment since all of the pollutant load is discharged to the bay in a relatively short period of time. For example, the February 19-22, 1996 storm event, contributed some 3.3 billion gallons of stormwater via Ballona Creek alone (not including Sepulveda and Centinela Channels). This corresponds to an average discharge of about 815 MGD, or over 100 times the Chevron's average discharge rate 7.9 MGD. With such a high rate of discharge, the stormwater runoff may overwhelm the ability of the natural systems to dissipate and degrade the entrained pollutants. Therefore, for the same total pollutant load, stormwater may have a more adverse impact on the coastal marine environment.

5.0 CONCLUSIONS



Project Goal: The overall goal of this study is to understand whether Ballona Creek is the primary source the contaminants in the sediments which accumulate at the south entrance Marina Del Rey/Mouth of Ballona Creek.

Project Specific Objectives:

1. To determine the types and concentrations of organic pollutants and heavy metals associated with suspended solids emanating from Ballona Creek and its tributaries.
2. To estimate the relative contributions of pollutants emanating from Sepulveda Channel, and Centinela Channel and Ballona Creek before Sepulveda Channel, and Centinela

Channel empty into Ballona Creek during wet weather flow.

3. To compare the types and concentrations of pollutants associated with suspended solids emanating from Ballona Creek and its tributaries with those pollutants associated with suspended solids in Marina Del Rey.

5.1 Conclusions: Stormwater Runoff Flow Data

- Varying flow patterns were observed during different storms. Each storm appears unique. Modeling the system is very difficult.
- Upstream the first flush contains the highest concentration of trace organics.
- Storm flow from the end of Ballona Creek is highly influenced by tidal action. Storm flow/tidal interactions are complex.

5.2 Conclusions: General Water Quality Data

- The TOC in the aqueous phase decreased as the storm season progressed. TOC is a rough estimate for oil and grease.

5.3 Conclusions: Trace Organics Data - Upstream Sites

- The suspended solids and aqueous phase concentrations were evaluated separately. The suspended solids phase carries the primary load of organic chemicals to Santa Monica Bay.
- The trace organics mass load on the suspended solids contributed by each channel is proportional to their flow, i.e. Ballona > Sepulveda > Centinela. However, the load from each channel is a significant contributor to the overall pollution load to Santa Monica Bay.
- PAHs were the primary target organic pollutant detected on the suspended phase in all the storm drains. Of the 17 target PAHs, pyrene was consistently found in greatest concentration. Other PAHs which were consistently found include benzo[a] pyrene, benzo[k]fluoranthrene, chrysene, fluoranthene and phenanthrene.
- Many PAH's in the water column are primarily associated with suspended solids and were much greater than ERM's and the California Ocean Plan objectives.
- The estimated mass load calculated for total PAHs for Ballona Creek are 5.4 and 6.8 kg for the January and March storms, respectively. The mass loading is equivalent to 8.5 months and 10.5 months discharge of the maximum amount allowed by the NPDS permit of a major oil refinery that discharges to Santa Monica Bay.
- Phthalates were detected at a lower rate than PAHs on the suspended phase. Other target compounds were found sporadically on the solid phase. The phthalate found in greatest concentration was bis(2-ethylhexyl) phthalate.

5.4 Conclusions: Trace Organics Data - Downstream Sites

- The flow out of Ballona Creek to the bay and Marina Del Rey primarily occurs during low

tide cycles.

- The suspended solids carrying the target organic pollutants (primarily PAHs and Phthalates) in Ballona Creek enter Marina Del Rey after low tide condition during wet weather flow.

5.5 Conclusions: Metals Data - Upstream Sites

- The metals mass load contributed by each channel is proportional to their flow, i.e. Ballona > Sepulveda > Centinela. However, the load from each channel is a significant contributor to the overall pollution load to Santa Monica Bay.
- The aqueous phase metal concentrations were generally 100 times less than the solid phase metal concentrations. The solid phase metal concentrations are in ppm range. The eight regulated metal concentrations (Ag, As, Cd, Cu, Cr, Ni, Pb, Zn) in the suspended sediment load are primarily above the ERLs with some above the ERM.
- Lead was the primary target metal that was detected at the highest concentration in the runoff. The concentration of lead on the suspended solids was always > ERM. The other metals in a relative fashion generally followed the lead levels, but the absolute concentrations were lower. The relative order of the concentration of metals that was found was Pb > (Zn?) > Ni > Cd > As > Cu. Zinc vs also in high concentration but an artifact in the filtration step interfered with its evaluation. This is why zinc is listed as (Zn?)

5.6 Conclusions: Metals Data - Downstream Sites

- Although the Ballona Creek is a significant source of non-point source runoff of lead to Santa Monica Bay, the receiving waters are already highly contaminated with lead apparently from Marina Del Rey. Ambient lead concentrations in the water column in Marina Del Rey is about 3,000 - 350,000 ug./L.
- Estimated mass load calculated for total Pb for Ballona Creek are 30 to 900 Kg for the January and March storm, respectively. The lead level is equivalent to 2 month and 6 month discharge of the maximum amount allowed by the NPDS permit of an oil refinery that dumps into Santa Monica Bay.

6.0 Future Considerations

7.0 REFERENCES

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