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Storm Water Metals-Issues and Historical Trends,Lawrence Livermore National Laboratory

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Storm Water Metals - Issues and Historical Trends, Lawrence Livermore National Laboratory

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Abstract

Lawrence Livermore National Laboratory (LLNL) is operated by the University of California under contract with the U.S. Department of Energy (DOE) under Waste Discharge Requirements (WDR) 95-174, allowing storm water discharges associated with industrial activities. Permit requirements include:

- Building drain tracking
- Non-storm water discharge tracking
- Dry and wet season observations
- Runoff sampling and analysis
- Development and application of a Storm Water Pollution Prevention Plan which includes detailed Best Management Practices (BMPs)

There are no chemical-specific limits for LLNL storm water effluent; the only limit applies to an annual fish toxicity test.

LLNL has over 10 years of storm water metals data. Recent data seem to indicate that concentrations of some metals are increasing in LLNL storm water effluent. If these trends can be attributed to LLNL, it may lead to increased and costly changes to infrastructure and BMPs. However, the trend may be due to changes in testing laboratories, and/or changes in procedures used at the laboratories (specifically, there may have been a shift from procedures which recover dissolved metals to procedures which recover total metal concentrations). It is also not clear how much of the trend is due to sediment loads, natural concentrations, or off-site contributions. During the 1997/1998 season, sampling at site influent and effluent locations included analysis for total suspended solids and analysis for metals in both filtered and unfiltered storm water. This study presents the preliminary conclusions of the 1997/1998 sampling. The comparison of filtered/unfiltered metals results, and comparison of these results with total suspended solids indicated that the source of increasing metals was naturally-occurring sediments being transported in storm water.

Introduction

LLNL serves as a national resource of scientific, technical, and engineering capabilities. The Laboratory's mission focuses on nuclear weapons and national security, and over the years has been broadened to include areas such as strategic defense, energy, the environment, biomedicine, technology transfer, the economy, and education. The Laboratory carries out this mission in compliance with local, state, and federal environmental regulatory requirements. It does so with the support of the Environmental Protection Department, which is responsible for environmental monitoring and analysis, hazardous waste management, environmental restoration, and assisting Laboratory organizations in ensuring compliance with environmental laws and regulations.

LLNL comprises two sites. The focus of this paper is the Livermore main site, which occupies an area of 3.28 square kilometers on the eastern edge of Livermore, California, approximately 80 kilometers southeast of San Francisco. Immediately to the south of the Livermore site is Sandia National Laboratories, operated by Lockheed-Martin under DOE contract. There are also some low-density residential areas and agricultural areas to the south of LLNL. Business parks are located to the southwest and north of the site, and a 200-hectare parcel of open space to the northeast has been rezoned to allow development of light industry. A small amount of low-density residential development lies to the east of the site, and agricultural land extends to the foothills that define the eastern margin of the Livermore Valley. Flow patterns at the site are such that storm water at sampling locations includes runoff components from these other sources, including agricultural land, industrial facilities, parking lots, and landscaped areas.

LLNL first monitored storm water runoff at the Livermore site in 1975. The original monitoring network, designed to detect pesticides, was expanded in 1990 to cover new locations and additional water quality parameters (including metals). Additional changes in 1993 complied with the National Pollutant Discharge Elimination System (NPDES) General Industrial Activities Storm Water Permit. It is important to show that LLNL is not contributing to storm water metals concentrations, in order to verify that provisions of the existing, BMP-based storm water permit are protective of storm water quality.

Methods

During the 1997/1998 wet season, source investigations were conducted to determine how much of the metals are present in the liquid (dissolved) and how much in sediments (suspended) being transported, for example, during high flow events. The study was also designed to evaluate how much of the loading in each fraction (dissolved and suspended) originates off site, and how much is contributed by on-site sources, and to relate concentrations of constituents in storm water from a particular storm and location to the concentration of total suspended solids from the same storm and location. To accomplish these goals, samples for applicable constituents were collected in duplicate. One sample was analyzed for total concentration (i.e., dissolved and suspended) of the constituents of interest. The second sample was passed through a 0.45 μm filter in order to evaluate the dissolved component. Although particles smaller than 0.45 μm (i.e., not dissolved) will of course pass through this filter, this removes the majority of the sediments, and is therefore adequate for evaluation of the dissolved fraction of the storm water. LLNL's contracts with the analytical laboratories are designed around collections or "suites" of analyses. Metals are included in two suites identified by "GENMIN" (general minerals) and "NPDESMETALS" (low reporting level drinking water metals under NPDES). Because there is some overlap in the metals specified in these two suites, some metals were subjected to duplicative analyses. In such cases, all analyses were utilized. Samples were also analyzed for concentration of total suspended solids (TSS).

Sample collection was by "grab sampling." In this method, technicians were dispatched to the field during rain events. When flow was observed, samples were collected by the technicians in one-liter bottles. Sample bottles, pre-labeled for the various analyses, were then shipped to off-site laboratories for analysis.

There are two main storm water flow pathways through the Livermore site (Figure 1). The majority of the site drains into Arroyo Las Positas. Arroyo Las Positas effluent is monitored at location WPDC, and influent to Arroyo Las Positas is monitored at locations ALPE, ALPO, and GRNE. Arroyo Seco crosses the southwest corner of the site. Influent and effluent monitoring locations for Arroyo Seco are ASS2 and ASW, respectively. During the 1997/1998 wet season, runoff samples from four storms were collected at these locations. For one sample set, the NPDESMETALS analyses reported as total metals were filtered. Because of this error by the analytical laboratory, this portion of the data was eliminated from the study.

Because there are no numerical criteria that limit concentrations of specific constituents in storm water effluent, various criteria were used to evaluate LLNL storm water quality. In the federal multisector permit, the Environmental Protection Agency (EPA) established benchmark values for

41 parameters but stressed that these concentrations were not intended to be interpreted as effluent limitations. Rather, they are levels that the EPA has used to determine if storm water discharged from any given facility merits further monitoring. Maximum Contaminant Levels (MCLs) for drinking water and Ambient Water Quality Criteria (AWQC) protective of fresh water organisms, developed by California and the federal government were also used as comparisons with LLNL storm water analytical results. However, these criteria are defined for other purposes, and are therefore not directly applicable to storm water effluent. Nevertheless, use of a broad range of criteria can help to evaluate LLNL's storm water management program and to allow LLNL to ensure high quality in its storm water effluent. Of greatest concern are constituents that exceeded comparison criteria at effluent points, but for which the influent concentrations were less than the corresponding effluent concentrations (indicating a possible on-site source). Each year, constituents identified by this screening process are subjected to detailed analysis, generally including evaluation of all historical data. It was this process that identified the apparent increasing trend in storm water metals. A review of data for the past five years identified four metals selected by this screening in multiple years, and with greater frequency of effluent values higher than influent values in recent years. The metals are chromium, copper, iron and zinc. These metals were therefore selected for detailed analysis in this study.

Data were evaluated in a variety of ways. First, dissolved concentrations were compared to total concentrations for each metal. Next, concentrations (both dissolved and total) were compared to total suspended solids concentrations. Finally, the dissolved and total concentrations were compared against the historical record. This last comparison was done on a location-specific basis, so that the apparent increases in influent and effluent concentrations for both pathways across the site could be evaluated for the relative contribution of total metals and dissolved metals.

Results

For every metal at every location, median total concentrations were greater than median dissolved concentrations (Table 1), generally by a factor of three or more. Dissolved concentrations of chromium and iron were almost all below their respective detection limits (0.001 and 0.05 mg/L, respectively). Median total iron concentrations ranged as high as 100 times the median dissolved concentrations. This provides the first clear indication that it is total metals that result in concentrations above the comparison criteria.

Plots of concentration and TSS (Figure 2) provide further evidence that suspended solids are at the root of the high concentrations. While there is a lot of variability in the data, all four metals show a clear relationship, with total concentrations increasing as TSS increases. As expected, dissolved concentrations do not increase with increasing TSS. For zinc, on the contrary, some of the highest dissolved concentrations occurred at low TSS levels.

Some of the observed variability may be due to between-sample variability. Separate sample bottles are submitted for each analysis (i.e. GENMIN filtered, GENMIN unfiltered, NPDESMETALS filtered, NPDESMETALS unfiltered, and TSS). The actual TSS level in the bottle submitted for GENMIN unfiltered analysis, for example, will not be identical to the TSS level in the bottle submitted for TSS analysis. Routine procedures exist at LLNL to collect duplicate samples at a frequency of approximately 1 out of every 10 samples. Duplicate samples are collected at the same location as the routine samples, immediately following collection of the routine sample. To evaluate the impact of between-sample variability, TSS in routine and duplicate samples from 1993 to present (25 data pairs) were compared. The average difference between duplicate and routine samples was 33%, and the difference ranged as high as 117%. Thus, between-sample variability may account for much of the variability observed, both in the relationship between total metal concentrations and TSS discussed above, and between dissolved and total metals concentrations (below).

Dissolved concentrations seem to be somewhat positively correlated to total concentrations for zinc, but again there is a lot of variability (Figure 3). No relationship is apparent for chromium, copper and iron (the two rows of points at dissolved copper concentrations of 0.01 and 0.001 mg/L are the result of differing reporting limits for the GENMIN and NPDESMETALS analyses, respectively). This provides strong evidence that the high concentrations observed in the historical record are due to metals bound up in the sediments, transported by turbulent storm flows, and not available for dissolution into the liquid phase.

The total and dissolved concentrations are compared to the historical record in Figure 4. In these historical trend figures, all available data for the influent and effluent locations of the two runoff pathways through the Livermore site have been aggregated. Also, data have been aggregated on a wet season basis—that is, October of one year through May of the next—rather than on a calendar year basis. Thus, data labeled 96/97 represent October 1996 through May 1997. For the 1997/1998 season, this was done separately for the total concentrations and dissolved concentrations. Because it is not certain *a priori* whether the historical data represent total concentrations, dissolved concentrations, or some combination, the lines connecting historical data points were not extended to the 1997/1998 data points. Also shown on each plot are the comparison criteria available for each constituent. To simplify interpretation of these complex plots, note that squares and diamonds were used to represent the Arroyo Seco pathway; and circles and triangles for the Arroyo Las Positas pathway. Also, solid shapes represent effluent, while open shapes represent influent.

The historical trends were compared to the historical trend in TSS concentrations (Figure 5). In the Arroyo Seco pathway, TSS at both influent and effluent locations increased up to the 1996/1997 season, and then decreased in the 1997/1998 season. In the Arroyo Las Positas pathway, TSS levels were relatively low during the most recent two years, and alternated between high and low values during the preceding 3 years. These trends were compared qualitatively to the trends for each of the metals, as summarized in Table 2. In general, metal concentrations corresponded to TSS concentrations, with only a few cases in which there was little or no correspondence. For example, the 1993/1994 high TSS in Arroyo Las Positas is generally not reflected in the metals data. This indicates that the historical record starting in 1994/1995 is primarily based on total concentrations, but that there may be some inconsistencies.

For the 1997/1998 data, chromium, copper and iron, median dissolved concentrations for both pathways at both influent and effluent locations were at or very near the reporting limits. Similarly, median dissolved zinc concentrations were generally much lower than median total zinc concentrations. Total concentrations are more consistent with the historical record, and generally correspond with the 1997/1998 TSS values, once again indicating that the historical trend is primarily due to total metals concentrations.

Discussion

An important lesson learned in this study is that it is essential that procedures at analytical laboratories be closely monitored in order to ensure that the correct data are being produced. Even during the course of this study, which required close, personal contact with laboratory personnel, not all analyses were done as specified. In the future, metals such as iron, for which there is a clear and consistent difference between dissolved and total concentrations, will be used to determine if the laboratory has used filtration on the appropriate analyses. Iron is a major component in aluminosilicate minerals that make up a major portion of sediment load.

The available data indicate that the apparent trend in increasing metals concentrations is due to a shift from analyses that recover the dissolved portion (i.e. filtered), to analyses that recover total metals. This is compounded by the observed increase in TSS in Arroyo Seco, due to the metals associated with the naturally-occurring sediments. There is a clear positive correlation between TSS and total metals concentrations, although there is notable variability. This variability could be reduced by homogenizing a large storm water sample volume and then separating it into the bottles submitted for the various analyses. Plans are underway to collect 1998/1999 samples in this manner. There is no relationship between dissolved concentrations and TSS. Only in the case of zinc was a relationship observed between dissolved concentrations and total concentrations. Where effluent metal concentrations were higher than influent concentrations, the data indicate that this is due to higher TSS levels.

While it is not completely clear how much of the historical record should be attributed to total metals analyses, it is clear that high metal concentrations are due to the suspended solids transported in the storm water. Because these high metal concentrations can be attributed to naturally-occurring sediments, costly changes to infrastructure and additional BMPs are not necessary. If reduction of storm water metal concentrations is needed, the appropriate response would be erosion control measures.

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Figures and Tables

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Table 1. Median influent and effluent concentrations, 1997/1998 wet season.

		Arroyo Seco		Arroyo Las Positas	
		Influent	**Effluent**	**Influent**	**Effluent**
TSS		55	306	139	121
Chromium	Dissolved	0.001	0.001	0.001	0.0014
	Total	0.0047	0.018	0.011	0.016
Copper	Dissolved	0.0048	0.0038	0.0044	0.0062
	Total	0.0175	0.023	0.015	0.017
Iron	Dissolved	0.05	0.05	0.05	0.05
	Total	1.45	6.1	5.2	3.3
Zinc	Dissolved	0.0505	0.0325	0.02	0.059
	Total	0.0785	0.185	0.061	0.205

Table 2. Qualitative comparison of agreement between historical TSS and metals concentrations.

	Arroyo Seco		Arroyo Las Positas	
	Influent	**Effluent**	**Influent**	**Effluent**
Chromium	medium	high	high	high
Copper	low	high	high	low
Iron	high	high	low	high
Zinc	high	medium	low	high

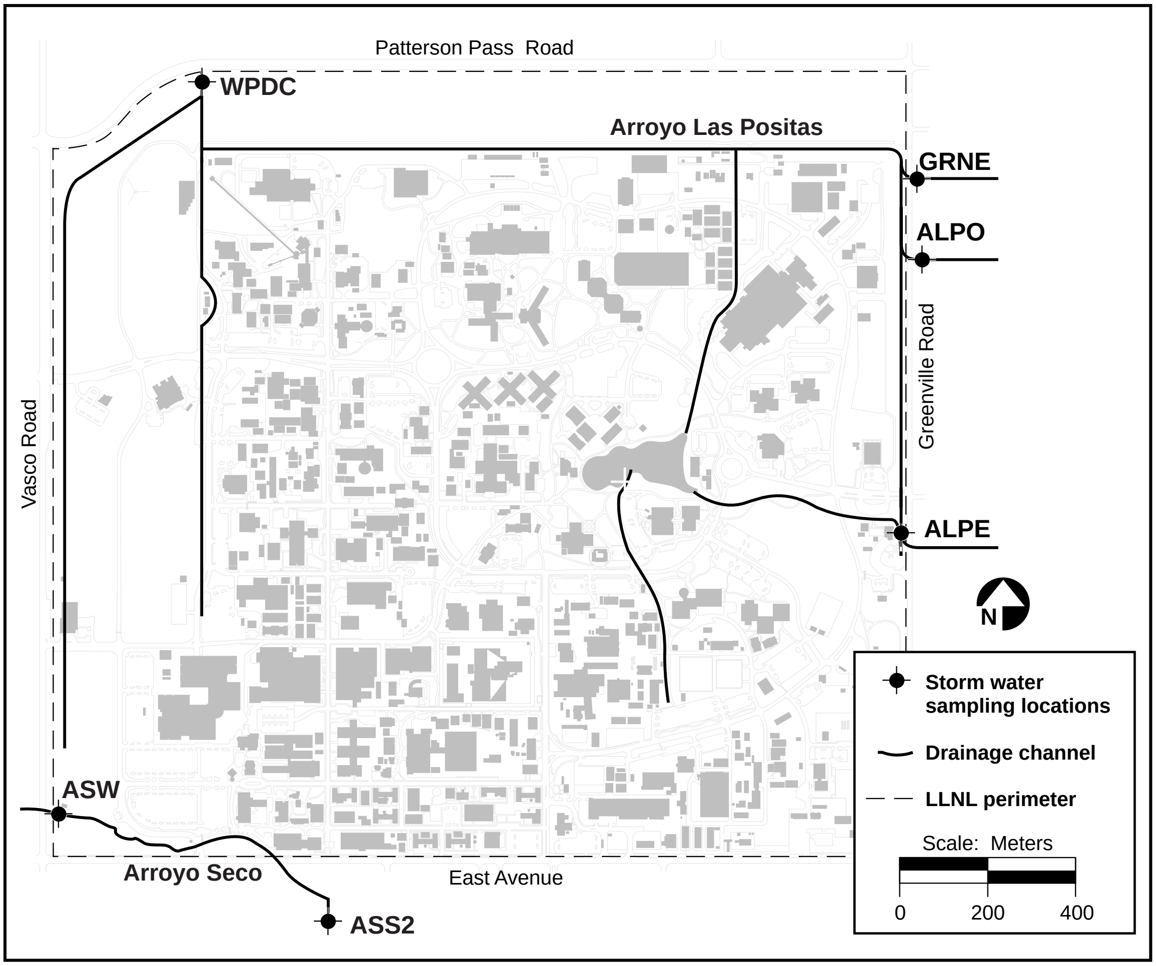

Figure 1. Livermore site storm water sampling locations.

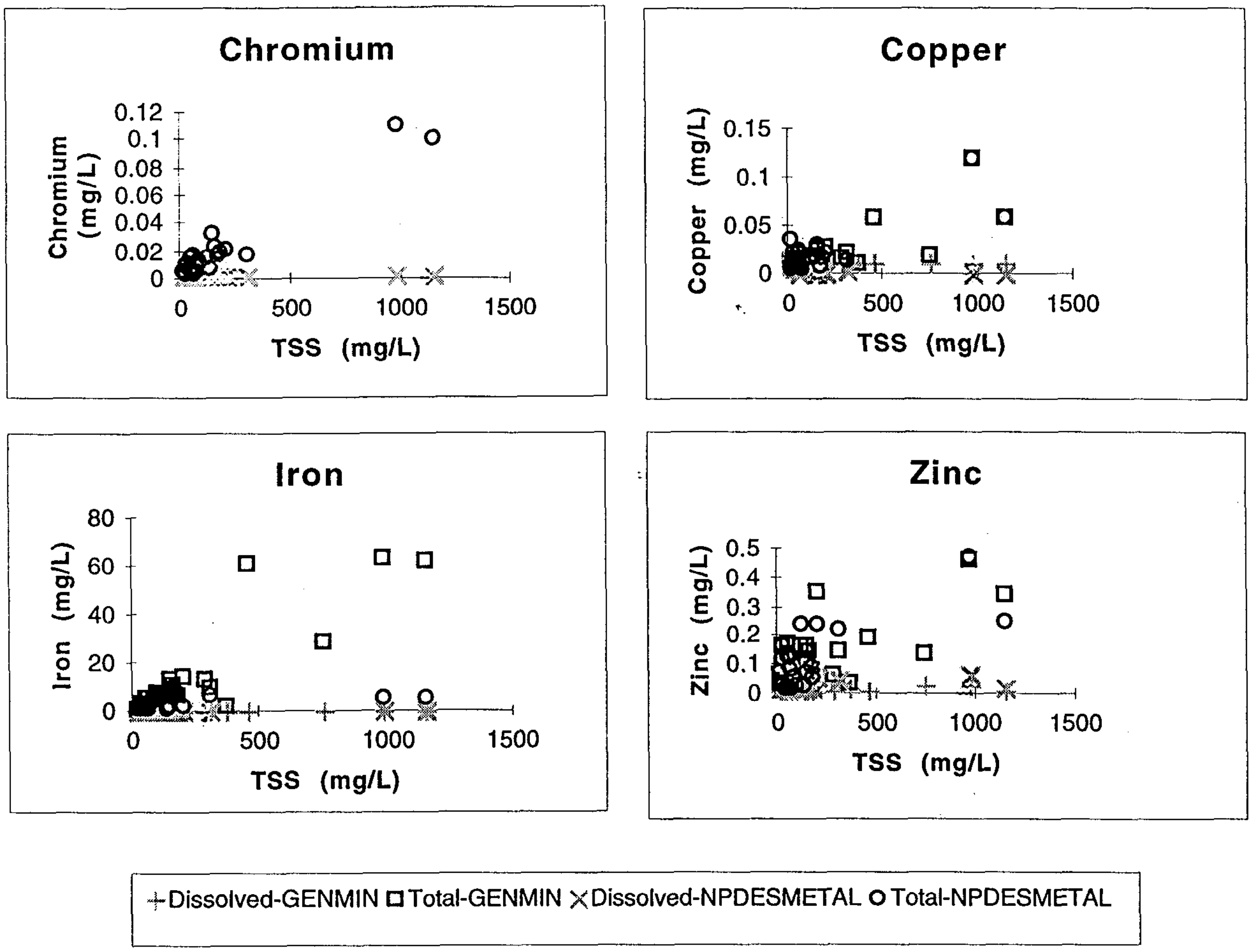

Figure 2. Relationship between metals concentrations and TSS.

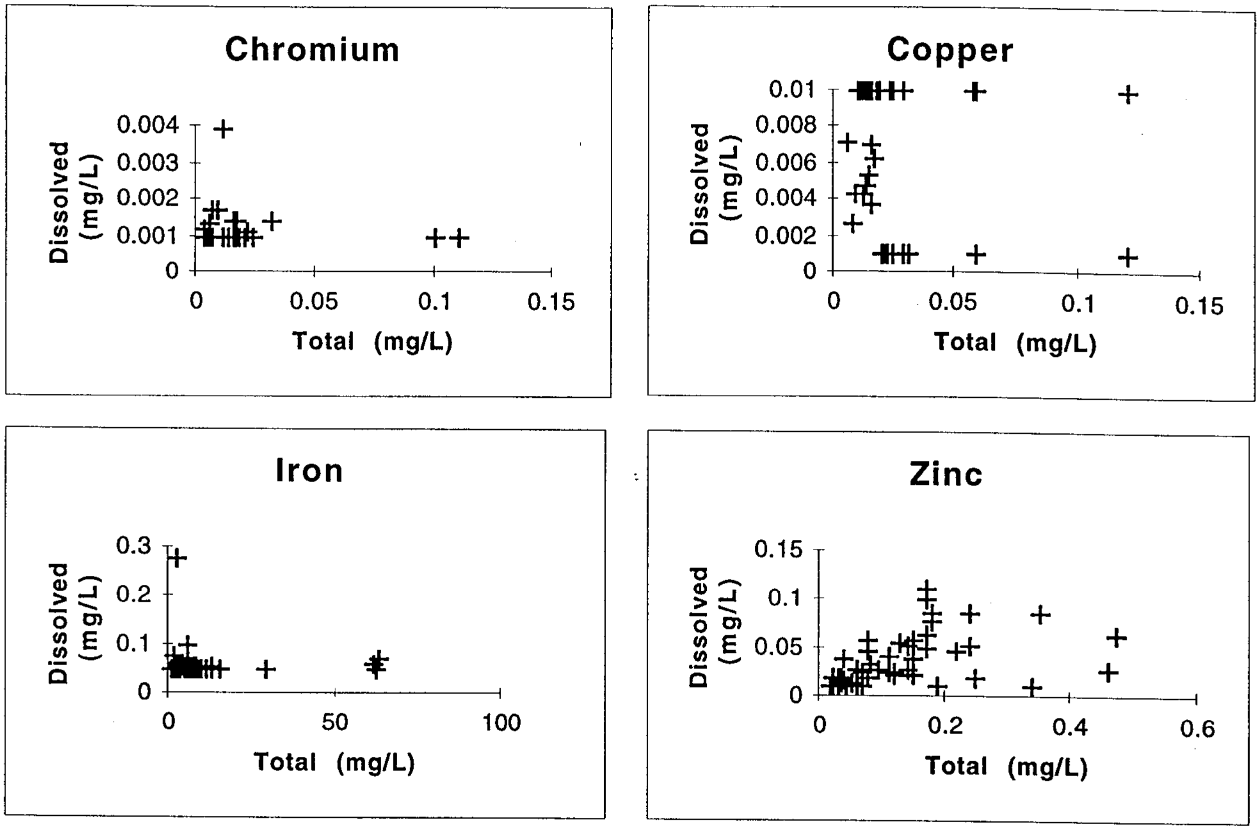

Figure 3. Relationship between dissolved and total metal concentrations.

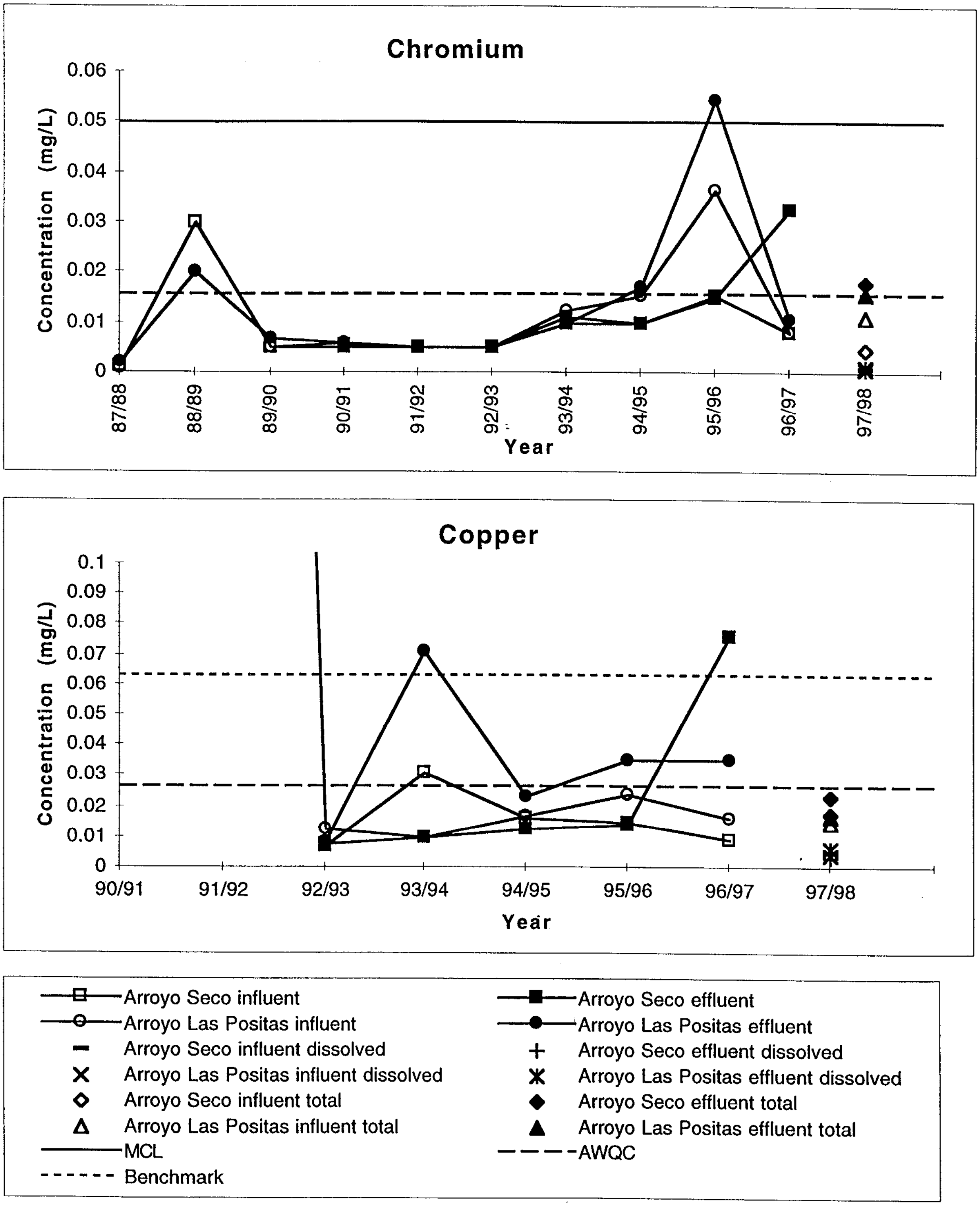

Figure 4. Annual median metal concentrations in LLNL storm water.

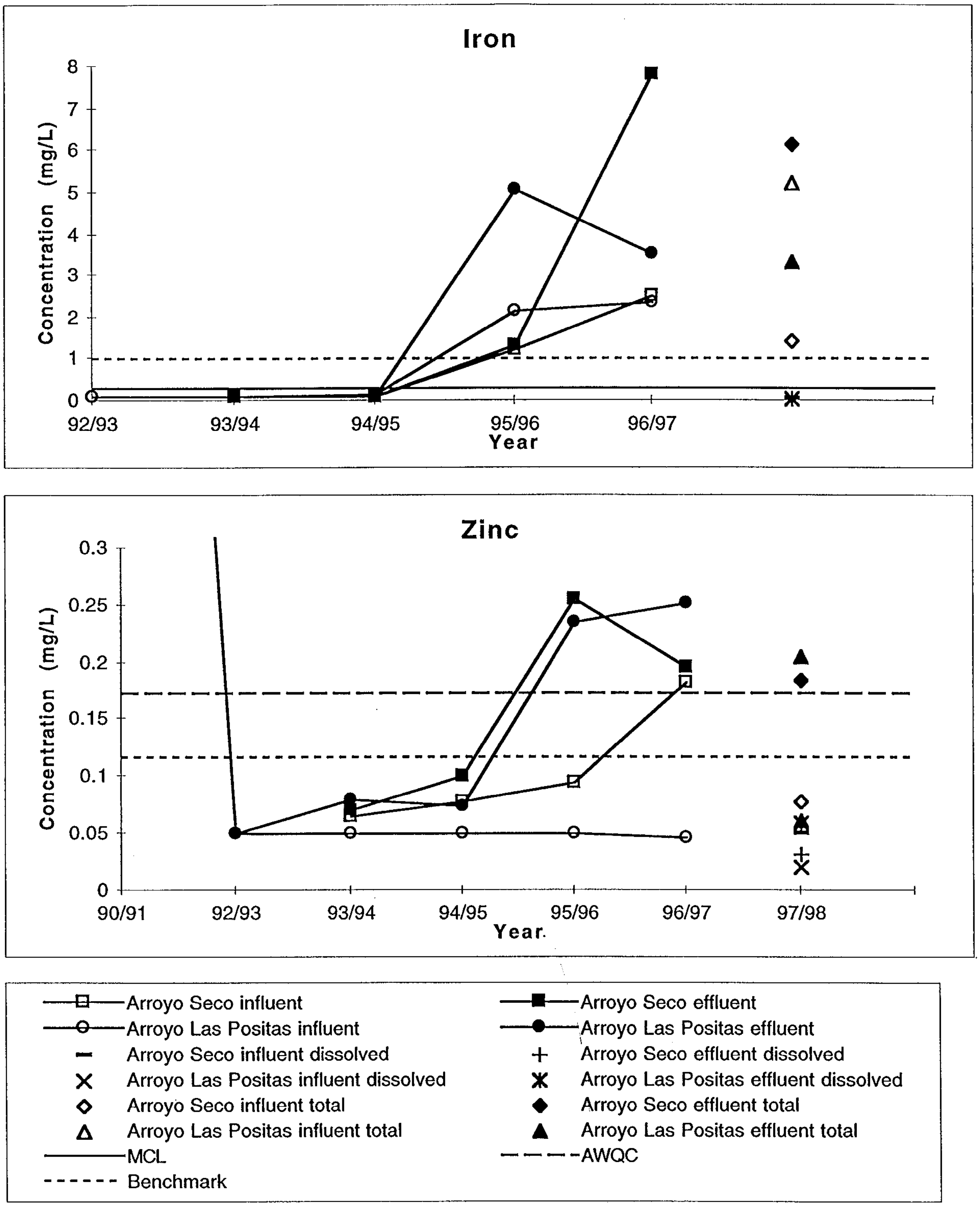

Figure 4 (continued). Annual median metal concentrations in LLNL storm water.

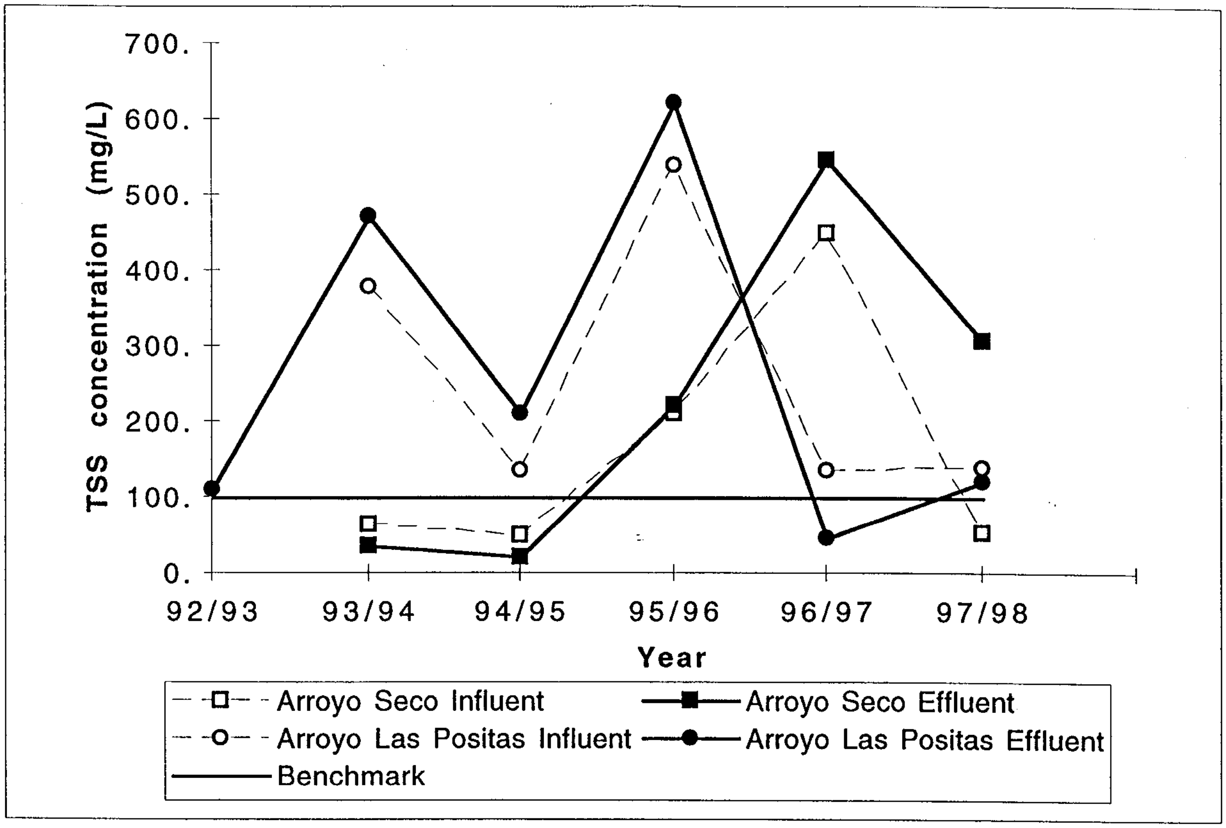

Figure 5. Annual median TSS concentrations in LLNL storm water.

Storm Water Metals -

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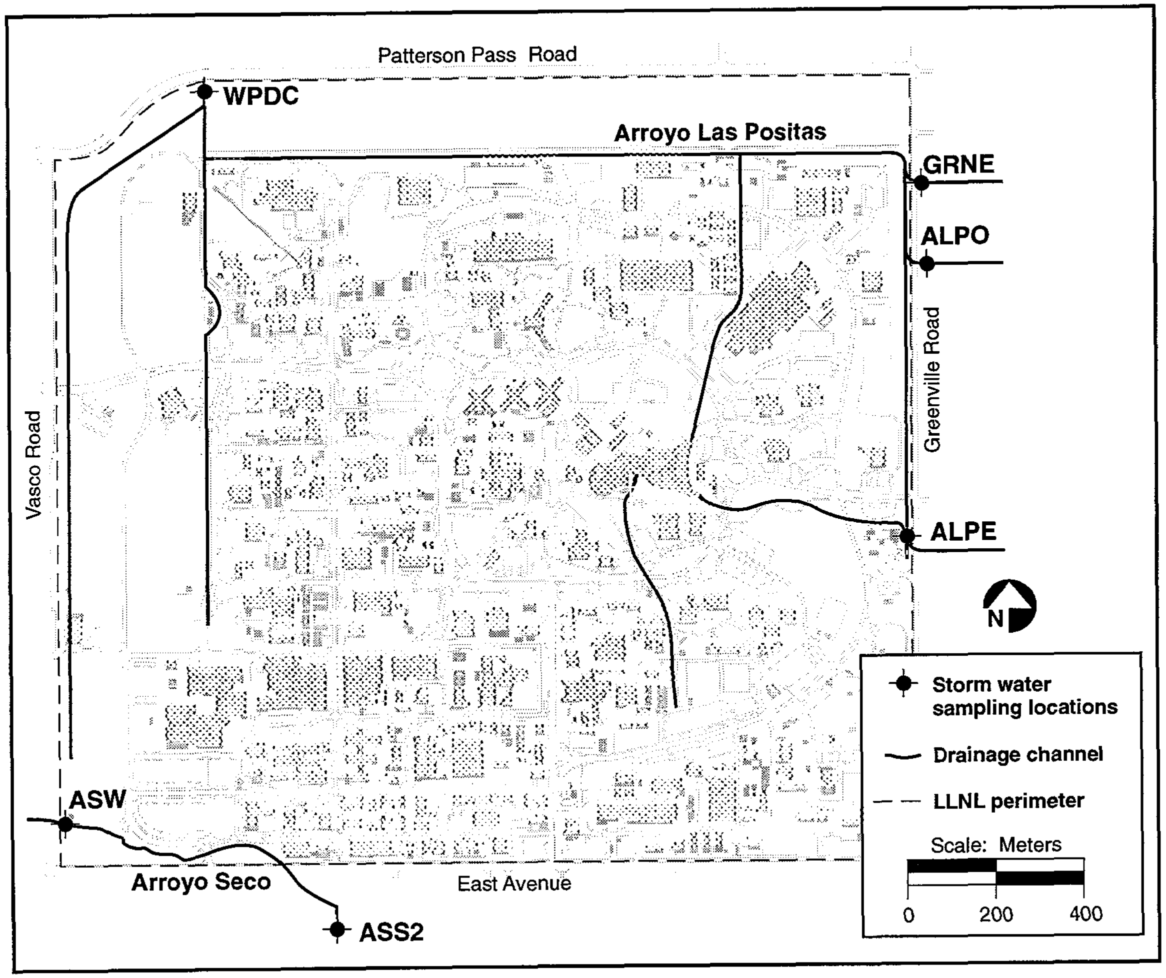
Storm Water Sampling Locations



(discussion of map; no viewgraph to go with this:

1 mile on a side (3.3 km2), east of SF
~10,000 employees
nearly 500 structures totalling almost 6 million square feet
surrounded by rural, industrial, residential, commercial
storm water flow paths

Introduction

- BMP-based storm water permit (no discharge limits).
- Up to 10 years of storm water metal data.
- Apparent upward trend in some metal concentrations.
- Source unclear:
  - Changes in laboratories
  - Changes in laboratory procedures
  - Natural sediments
  - Off-site or on-site
- If attributed to LLNL, increasing metals concentrations could lead to costly changes to infrastructure and BMPs, and to storm water effluent concentration limits.

1997/1998 Source Investigation

- Four samples at effluent and influent locations.
- Both dissolved (0.45 μm filter) and total (digested) analyses conducted.
- Grab sampling.

Screening Criteria

- EPA Benchmark values.
- San Francisco Bay Regional Water Quality Control Board Basin Plan.
- MCLs and AWQC.
- Higher concentrations in effluent than in influent.
- Identified chromium, copper, iron and zinc as key metals.

Data Evaluation

- Compared dissolved and total concentrations.
- Compared metals concentrations (dissolved and total) with total suspended solids (TSS)
- Compared metal concentrations with the historical record:
  - Location-specific.
  - Dissolved and total.
  - Compare with TSS historical record.

Data Summary

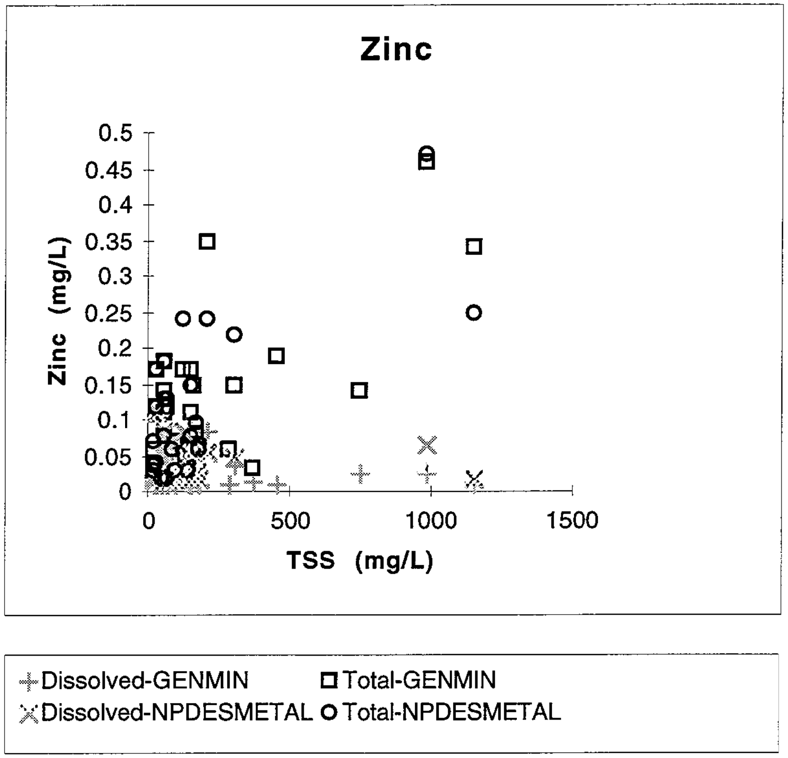
- Median total concentration always greater than median dissolved concentration.

- Total metals concentration high when TSS level high.

		Arroyo Seco	
		Influent	**Effluent**
TSS		55	306
Chromium	Dissolved	0.001	0.001
	Total	0.0047	0.018
Copper	Dissolved	0.0048	0.0038
	Total	0.0175	0.023
Iron	Dissolved	0.05	0.05
	Total	1.45	6.1
Zinc	Dissolved	0.0505	0.0325
	Total	0.0785	0.185

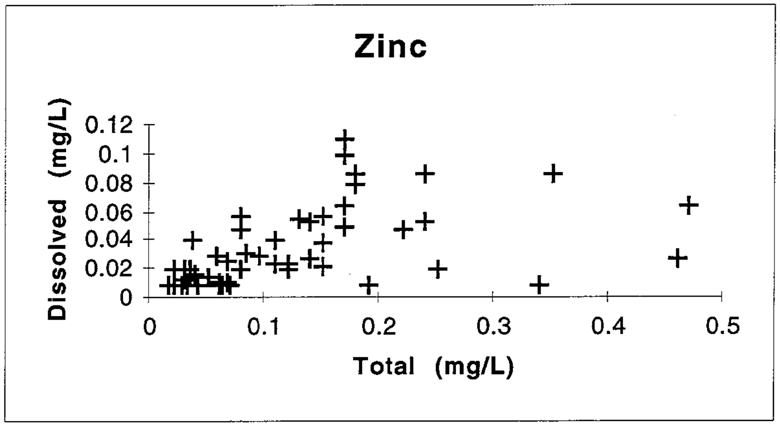
Metals and TSS

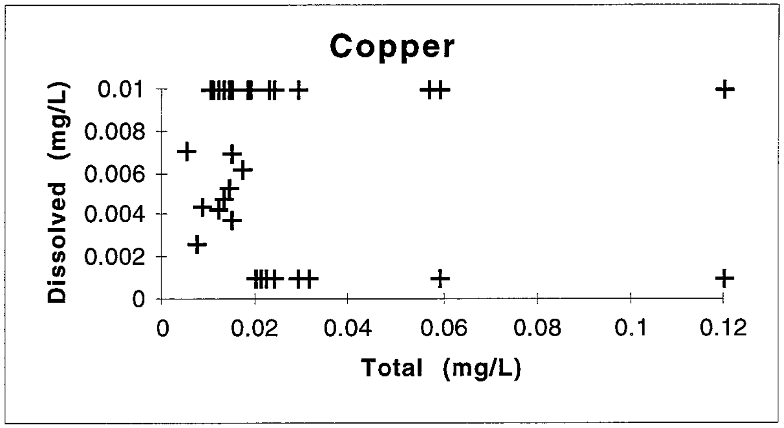
- Clear relationship of total concentration with TSS for all four metals.
- No relationship for dissolved concentration.
- High variability.



Dissolved and Total Concentrations

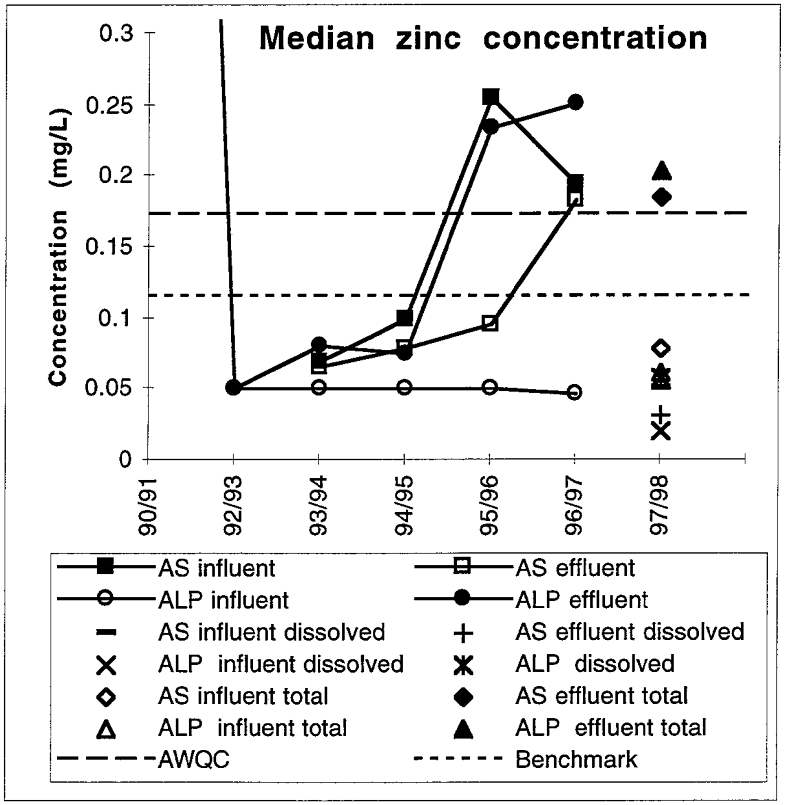
- Some correlation for zinc.
- No correlation for other chromium, copper or iron.
- Implies high concentrations are often bound in sediments.





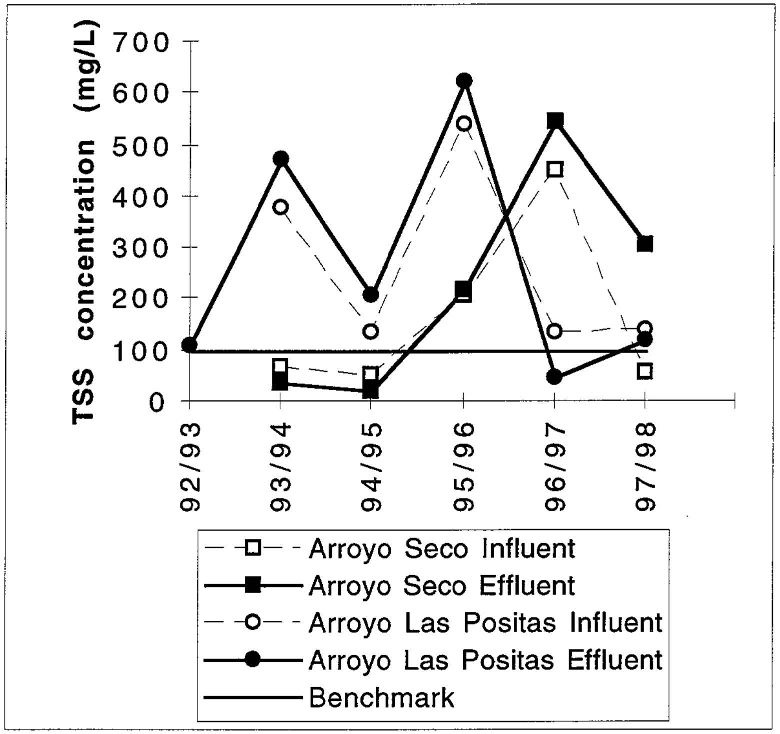
Historical Trend

- Medians by season and location.
- Total concentrations more consistent with recent increases.
- Historical concentrations tend to correspond to the historical trend in TSS.
- (in 1997/1998, total concentrations correspond to TSS)



Historical Trend in TSS

- Arroyo Seco increase.
- Arroyo Las Positas fluctuation.
- Zinc trend tracks TSS, except for Arroyo Las Positas effluent.
- 1993/1994 TSS peak not reflected in any of the metals evaluated.
- Indicative of shift from dissolved to total analysis.



Summary and Conclusions

- Laboratories must be closely monitored.
  - Even in LLNL "microcosm", consistent data difficult to obtain.
  - Even during this special study, not all analyses done as specified.
  - Implications for broader comparison studies.
  - Some metals have a clear "signature" that can be used to identify the analysis as dissolved or total.
- Indications that recent historical record can be attributed to total concentrations.
- High metals concentrations shown to be due to sediments transported in storm water.
- Sediment-based metals often do not result in higher dissolved concentrations.
- Costly changes to infrastructure or BMPs are not required.

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