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## Characterization of Heavy Metals in Santa Clara Valley

Attershed monitoring efforts have traditionally focused on water chemistry. Watershed managers attempt to use this data to quantify temporal and spatial differences in pollutant concentrations, and by extrapolation, improvements (or declines) in water quality conditions. However, the variability of water quality monitoring data and differences in station conditions often compromise the statistical validity of observed data trends. The total cost associated with use of traditional water quality monitoring then incurs a large, and often neglected, additional expense: statistical analysis to separate actual trends from masking variations attributable to background sources, hydrologic events, and sampling frequency.

Since 1986, the San Francisco Regional Water Quality Board has required that stormwater discharges into the southern end of San Francisco Bay be characterized and controlled (see Figure 1). In response, 13 munici-



palities situated along the southern end of San Francisco Bay, Santa Clara County, and the Santa Clara Valley Water District joined together to form the Santa Clara Valley Nonpoint Source Pollution Control Program. The Program implemented a proactive watershed management effort targeting heavy metal pollution in the 700 square mile watershed, particularly in the southern end of San Francisco Bay which, in 1989, was declared an impaired water body due to frequent exceedance of heavy metal water quality standards.

The monitoring portion of the watershed management effort is built on traditional stormwater monitoring and toxicity testing. The objectives of the monitoring program include evaluation of spatial and temporal trends, land use impacts, examination of urban versus erosional sources, and comparison of automatic versus grab sampling methods.

Four years of monitoring data, representing approximately 200 station-events, were examined. Statistical analysis was used to examine differences in water quality between monitoring stations and monitoring years using analysis of variance (ANOVA) and analysis of covariance (ANACOVA). Power analysis was used to determine the number of stations and the sampling frequency required to ensure detection of long-term trends in heavy metal concentrations.

Sampling was conducted at 15 stations (see Table 1). Eleven land use stations, situated in small streams or storm drain pipes, represent relatively small catchments (12 to 8,500 acres) with one predominant land use. Water quality data from the land use stations are used to characterize urban runoff water quality. The remaining four stations, waterway stations, represent larger drainage basins (15,000 to 80,000 acres). The waterway stations are used to characterize local receiving water quality, collect compliance data, characterize upstream and non-urban metal inputs, and examine stream sediment contributions.

Automated set-ups, consisting of an automatic sampler, data logger and controller, and pressure transducer, were used to collect most of the stormwater data. Flow was rated using established flow rating curves or a weir and weir equations. Samples were analyzed for ten heavy metals (dissolved and total fraction). Various organic, inorganic, and physical parameters were also examined (see Table 2).

Heavy metal concentrations were correlated with land use using two years of data from nine of the land use stations. Data from open land use stations were also included for comparison (see Figure 2). Land use impacts were only statistically significant when land uses were grouped into three broad categories: residential/ commercial, industrial (heavy and light). (Open land use was also examined for comparison purposes.) Not unexpectedly, the highest median concentrations for total zinc, cadmium, nickel, lead, and copper were associated with industrial land uses. (The heavy industrial station, which included a metal plating operation, exhibited the highest total zinc and cadmium levels.) High total nickel and lead concentrations (pollutants associated with brake line wearing, car deterioration, and automobile emissions) were also noted at the transportation stations.

The relative importance of urban versus erosional, upland sources was assessed through an enrichment analysis. Assuming that erosional sources are the only heavy metal source, enrichment analysis suggests that suspended metal concentrations would equal upland surficial concentrations and the *enrichment factor* (see Table 3) would be one. The South Bay Area, characterized by various mineral formations, contains natural erosional sources of nickel, copper, chromium, mercury, and other metals. Most of the chromium derives from these erosional sources.

The enrichment analysis results indicate that urban land uses (residential/commercial, industrial, and transportation) are the most significant sources of cadmium, lead, and zinc. Both erosional sources and urban land uses are significant sources of copper and nickel. Apparent spatial and temporal trends in the water quality data were verified using two-way analyses of variance (ANOVA) and covariance (ANACOVA). The ANOVA analysis, using total cooper as a representative trace metal, focused on apparent spatial trends (differences between stations). The ANOVA analysis results indicate that stormwater runoff from the smaller, more urbanized watersheds in the South Bay area have higher total metal concentrations than the larger, less urbanized watersheds.

The ANACOVA analysis focused on differences in total metal concentrations not attributable to variations in TSS. (Much of the total metal load is associated with TSS.) It was assumed that differences in concentrations that were corrected for TSS variations were the best indicators of spatial and temporal trends. The ANACOVA results indicate that TSS concentrations are lower at stations located in constructed channels. The minimal streambank erosion results in lower TSS concentrations, which, in turn, lead to lower total metals concentrations.

A second ANACOVA analysis was performed to investigate temporal trends. Once again, copper was used as the representative metal. Copper concentrations were significantly lower in 1992 as compared to

## **Table 1: Station Descriptions**

		Drainage Area
Location	Land Use	(acres)
Junction Ave.	Industrial park	22
Walsh Ave.	Heavy industrial	28
Frances & Beamer Streets	Commercial	265
Hale Creek	Low-density SFR	1,633
Sunnyvale E. Channel	SFR	2,080
Pasetta and Williams	MFR	85
Stevens Creek	Open (forest)	8,410
Packwood Creek	Open (ranch land)	6,464
W. San Carlos Ave.	Industrial	40
Montague Expressway	Transportation	12
Interstate 280	Transportation	35
Calabazas Creek	Mixed	9,216
Sunnyvale E. Channel	Mixed	3,437
Guadalupe River	Mixed	15,904
Coyote Creek	Mixed	79,552

Table 2: Monitoring Parameters		
Total metals	Dissolved metals	
arsenic	cadmium	
mercury	copper	
cadmium	lead	
nickel	mercury	
chromium	silver	
selenium	zinc	
copper		
silver	Inorganic / Physical	
lead		
zinc	hardness	
Organics	turbidity total suspended solids	
PAH		
total organic carbon		
total oil and grease		

## **Table 3: Enrichment Analysis**

Analysis to assess the relative importance of urban versus erosional pollutant sources.

Particulate Metal Concentration (g/L): total metal concentration minus the dissolved metal concentration.

**Suspended Metal Concentration (g/g):** the ratio of particulate metal concentration (g/L) to TSS concentration (g/L).

**Enrichment Factor**: the ratio of suspended metal concentration (g/g) in urban stormwater runoff sample to surficial soils concentrations (g/kg) in upland areas of watershed.



Figure 2: Median Metal Concentration in Stormwater Runoff in Santa Clara Valley, 1987-1989 (Cooke, 1995)

1990 and 1991. The ANCOVA analysis, which used station and years as the effects to be tested, indicates that the observed differences are probably attributable torainfall. Rainfall was significantly higher in 1992 than in the other two years.

Stormwater data from waterways stations (which are used to evaluate compliance) were analyzed to determine the duration, frequency, and severity of water quality objectives (WQOs) violations. Four years of data were compared to water quality objectives listed in the California Inland Surface Waters Plan (April 1991). Acknowledging the relatively short, pulse-like loading associated with stormwater pollutants, the storm data were compared to one-hour and four-day freshwater criteria. (The average storm duration in the Santa Clara Valley is 36 hours.) The one-hour ("acute") objective was indicative of potential toxicity problems. The four-day objective was used to observe "chronic" conditions.

Dissolved metal concentration did not exceed the acute, one-hour limit. Furthermore, less than 5% of the samples exceeded the lower, four-day, chronic limit. Although this finding suggests that metal toxicity was not a problem, other more traditional toxic tests indicated otherwise. The traditional toxicity tests were performed to characterize toxicity with respect to land use and to provide a basis for assessing long-term toxicity frequency and intensity at the waterways stations. Chronic, seven-day toxicity tests using *Ceriodaphnia dubia* and toxicity identification evaluations (TIE) protocols were used.

The toxicity tests suggest that stormwater runoff from heavy industrial, commercial, and residential land uses in the Santa Clara Valley impairs aquatic health. All of the samples from the heavy industrial station were extremely toxic (i.e., 50 % of the test organisms died within 24 hours). The residential/commercial station samples were extremely to moderately toxic (50% mortality within four to seven days). In comparison, less than one-quarter of the transportation station samples were extremely or moderately toxic.

The causes of the observed toxicity were investigated using TIEs. The TIE results suggest that dissolved metals account for the extremely toxic conditions at the heavy industrial station. Additional TIE results indicate that non-polar organics such as pesticides and hydrocarbons are the most significant causes of toxicity in the mixed land use, waterways stations.

It should be noted that because non-native organisms and a laboratory testing environment were used in the toxicity tests, the test results may not accurately represent stormwater impacts on aquatic health. In-situ testing with native species has been proposed as a more accurate assessment methodology.

The watershed monitoring effort represents a tremendous expenditure of time, manpower, and finances. A power analysis was conducted to examine if the watershed monitoring effort could be reduced while providing sufficient data to detect potential long-term trends in water quality. The ability to detect statistically significant long-term trends is influenced by the magnitude of the difference to be observed, the data availability, the number of observations, and the targeted confidence level. In general, the probability of detecting a long-term trend decreases with data variability and increases with the number of observations.

The power analysis focused on the number of observations and stations analyzed. If all four waterway stations are included in the monitoring effort, an average of seven storms per year at each station would be required to confirm a 40% change in heavy metal concentrations over a 10-year period at the 80% confidence level (see Figure 3). Assuming that it is possible to achieve a 40% reduction in total metals concentrations in one decade, it is unlikely that the resources needed to collect the required stormwater data will remain available.

Continued dependence upon traditional water quality monitoring and toxicity testing should be reconsidered. Although the Program collected data from 200 station-events, no unexpected trends were revealed. The spatial and temporal trends detected using the traditional monitoring approach were not unanticipated: higher pollutant levels are generally associated with urbanized areas, runoff from industrial and transportation land uses usually contain elevated heavy metal levels, and metal concentrations are generally lower during rainy years.

An alternative indicator monitoring program could provide the data required to assess the efficacy of the watershed program control efforts. The toxicity test results suggest that aquatic health is endangered. Incorporation of biological monitoring based on native species and in-situ testing would confirm (or negate) the toxicity result. In addition, trends in fish and/or macro-invertebrate health and abundance can be extrapolated to assess overall aquatic health.

At this time, the Program plans to continue traditional stormwater monitoring in the two major watersheds. Five storms per year will be monitored to evaluate long-term trends and to assess compliance with WQOs and toxicity objectives. The two smaller subwatersheds will be monitored every other year to provide comparative data and to assess compliance. Special stations will also be used to evaluate the effectiveness of pollution control measures.

Although the Program has placed greater emphasis on expansion of the stormwater monitoring program as part of the overall management effort, public education and participation have also been incorporated into the monitoring effort. One such example is their support of citizen efforts such as the Coyote Creek Riparian Station (CCRS). CCRS sponsors a volunteer biological monitoring effort, Community Creek Watch. This effort, which focuses on birds, amphibians, and reptiles, provides data on riparian habitat and, to a lesser extent, water quality in the streams. **See also article 16.** 

## References

Cooke, T., D. Drury, R. Katznelson, C. Lee, P. Mangarella, K. Whitman. 1995. "Storm Water NPDES Monitoring in Santa Clara Valley." *Proceed From Stormwater NPDES Related Monitoring Needs*. Crested Butte, CO. Aug. 7-12, 1994.



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