RMP Watershed Pilot Study: An Information Review with Emphasis on Contaminant Loading, Sources, and Effects

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TABLE OF CONTENTS

BACKGROUND AND INTRODUCTION

"Why do we see exceedances of water quality objectives in the Estuary?" was one of the questions posed as early as the second year of the Regional Monitoring Program (RMP), after the first year's data had been evaluated. Other questions were: "What can environmental managers do to reduce pollutant inputs into the Estuary? How are they best controlled?" Many Program Participants came to the realization that the Estuary represents a mixing bowl whose pollutant profile is reflected by inflow of the two large rivers, local runoff contributions, wastewater discharges, complex sediment resuspension and distribution processes, and atmospheric deposition. In order to take the next step from describing the pollutant profile in the Estuary to drawing conclusions about general source categories, and getting from there to pollutant control actions, Pilot Studies would have to be undertaken.

The Watershed Pilot Study is the first one of these studies with the general goal of describing how the pollutant spectrum in surface runoff attenuates and influences that of nearby RMP stations in the main channel of the South Bay. In addition to any sampling effort, it was decided that more specific assessment questions should be selected which could then guide a targeted review of existing information that could serve, together with new data at the watershed-Estuary interface, to better interpret pollutant data and identify knowledge gaps.

This report represents the companion document to the Watershed Pilot Study chapter in *the 1996 Annual Report* of the Regional Monitoring Program for Trace Substances and is the result of a targeted information review that attempted to summarize the current state of knowledge pertaining to questions posed by an *ad hoc* committee. The efforts of this committee preceded those of the Santa Clara Basin Watershed Management Initiative and its various subgroups but may prove useful in the development of the *State of the Watershed Report*.

SUMMARY OF APRIL 24, 1996, PRIORITIZATION OF ISSUES RELATED TO CONTAMINANTS

The RMP Watershed Pilot Study was overseen by various agency and public representatives with an interest in finalizing the scope of work and directing the following information review. The issues that were brought up during several brainstorming session of the *ad hoc* committee overseeing the RMP Watershed Pilot Study are summarized and prioritized in the following table. The questions listed as “high priority” were used in reviewing available information sources to discover gaps in knowledge and to help develop a fact-finding framework for inclusion in the Santa Clara Basin Watershed Management Initiative stakeholder process.

The subsequent information review lists the pertinent questions in this matrix and attempts to identify uncertainties and data gaps related to each. The review is by no means exhaustive but at a minimum provides some sense of where future activities could be focused to obtain a better sense of watersheds as landward extensions of the Estuary. We hope that this review will assist the stakeholders who are shaping the Watershed Management Initiative in the Santa Clara Valley in planning and implementing cost-effective actions that are geared toward measurable environmental improvement objectives.

A. LOADING

1. Stream (tributary) loading to the Bay (non-storm event).	Data exist in various NPS Program reports. To be reviewed under task 3 of CCWS Pilot Study	High Priority
2. Stormwater loading to the South Bay.	To be reviewed under task 3	High Priority
3. Why don't we do a mass audit study on the Bay?	Falls outside the scope of this study and needs to include aerial deposition estimates.	Beyond Scope
4. Could the data collected be used in establishing TMDLs? (e.g., testing hydrodynamic models).	Probably. Question should be referred to Regional Board.	Beyond Scope, but part of long-term goal
5. Differentiate between wet and dry weather flows and loadings.	To be done under task 3	High Priority
6. To what degree does urban (man-caused) erosion contribute to metals loadings?	May be answered as part of metals enrichment study.	Medium Priority

B. COMMUNICATION

1. How do we educate the public about the results of our studies, and the direction that our future studies are going in?	Is "the public" interested at this point, or primarily decision-makers?	
2. How do we share what we know with each other?	How about setting up an e-mail network?	
3. How do we coordinate our efforts?	The CC Watershed Club meeting provides a good forum. Any other ideas?	
4. How do we convince political entities that we are spending our resources on those issues that will give us the most benefit?	Are we sure at this point that we spend resources in the most efficient way?	
5. How do we get public support for, and involvement in, this effort?	CCRS has a large membership base; existing newsletters and other venues could be used to disseminate relevant messages.	

C. POLLUTANTS OF CONCERN

1. Are we measuring the right parameters? Biological criteria.	Probably more than enough chemical parameters and not enough integrative biological measures (e.g. invertebrate indices, fish community composition, etc.)	High Priority
2. Are nickel and copper the proper focus of concern?	They are two contaminants "of concern" for several reasons.	High Priority
3. What pollutant should we focus on first?	Part of prioritization exercise.	High Priority
4. What pollutants have the worst impact on the Bay?	The "metals control project" of the NPS Program is looking at this right now, and so is SFEI as follow-up to the Indicator Workshop.	High Priority
5. How to integrate non-pollutant watershed problems with pollutant-specific problems.	Usually, watershed problems not directly related to pollutants (e.g. bank failure, riparian vegetation removal) aggravate pollution-related problems or are indirectly linked. Developing a watershed inventory of physical, biological, and chemical characteristics will clearly help in integration.	High Priority

D. PRIORITIZATION

1. What are some potential pollutant reduction efforts that may be successfully implemented with the limited data available?	Ongoing efforts outside the scope of this study.	Beyond Scope
2. When will we assign tasks?	Unclear question. Tasks with respect to what?	
3. What is our timeline?	The timeline for this phase of the study is until December 1996, with the possibility of extension.	See Scope of Work
4. Why are we doing this?	To inform pollution prevention managers and other watershed stakeholders.	Done
5. Are sediments a bad thing?	It depends. Where they impair beneficial uses, they are.	Beyond Scope

6. How can we make connections between implementation of control measures and protection of beneficial uses?	By choosing the correct quantifiable environmental indicators for measuring the success of control measures.	Beyond Scope
7. What is the definition of "the health of the Bay"?	SFEI, EPA, IEP, CalFed and others are currently working on this question.	Beyond Scope
8. What are our goals?	For general goals see Scope of Work. For specific goals (e.g. reduce pollutant x by amount y), we need to see the outcome of this study.	Done
9. What are some potential pollutant reduction efforts that may be successfully implemented with the limited available data?	The RWQCB and EPA can answer this question.	Redundant
10. Are there any problems in the South Bay?	It depends how you define problem. If the question relates to beneficial use impairment, the answer is yes.	Beyond Scope
11. What criteria do we use to prioritize?	That's a task for the CC Watershed Club. A strawdog is attached.	Redundant
12. How can we get a complete database to start prioritization?	We are making a start with this study and as part of the RMP as a whole.	High Priority

E. FATE AND TRANSPORT

1. How do the pollutant levels upstream of urban areas compare with the levels downstream?	Existing data to be reviewed as part of task 3.	High Priority
2. What data exist on heavy metals moving through the environment and the changes they take on?	Incomplete picture	High Priority
3. How do pollutant signatures in suspended sediments in runoff compare to Bay suspended and benthic sediments?	Is being investigated now, as part of task 2.	High Priority
4. Pollutant movement through water column versus sediments.	Question unclear.	High Priority
5. Fates of pollutants in Bay.	Dynamic process; incomplete picture.	High Priority
6. What are the concentrations of trace contaminants and other parameter values (toxicity) measured by the RMP	Will find out very soon. Part of task 2. Toxicity measurements at Standish Dam are not included,	High Priority

at the interface of Coyote Creek and the Estuary?	however, and are available only in the South Bay for three distinct sampling events (snapshots only).	
7. Determine the source of contaminant and transport of it.	This is where the watershed inventory comes into play. There really is no such thing as nonpoint source pollution.	Beyond Scope
8. What happens to metals in stormwater when they reach the Bay? (Saline versus freshwater).	Incomplete picture.	High Priority
9. Do we have any data on mixing of Bay via osmotic pressure or diffusion?	To be included in task 3.	High to Medium Priority
10. How does contaminant profile compare between TSS-associated trace elements and organics in creek water and South Bay water?	Similar question as 3 and same answer.	Redundant
11. How is water/sediment quality in creeks related to water/sediment quality of the Bay?	Part of task 2.	Redundant

F. POLLUTANT TRADING

1. How are our resources best spent to reduce impact on the Bay?	This Pilot Study will provide part of the answer.	Beyond Scope
2. How do we quantify pollutant reductions due to nonpoint source control measures?	The correct monitoring design should provide unambiguous answers.	Beyond Scope
3. Which pollutants can be controlled more cost effectively by nonpoint source pollution prevention than by point source controls?	Part of this study effort under task 3.	Beyond Scope
4. How can we combine the requirements of point and nonpoint source to maximize use of resources?	Dialogue with RWQCB and EPA needed. Should be part of Watershed Mgt. Initiative.	Beyond Scope

G. BIO ASSESSMENT

1. How does toxicity testing of freshwater and freshwater species relate to toxicity testing of Bay/saltwater species? How can freshwater be evaluated for saltwater effects?	May be outside scope of this study. Can be delegated to RMP Indicator component. Special effort proposed for 1997 RMP	Beyond Scope, but high priority for mention in report
2. Are pollutants being removed by new species of bivalves in the Bay?	The South Bay can be considered a black box in this context. Even if bivalves take up pollutants, unless they are removed from the system, they will eventually release them again.	Beyond Scope
3. When will the Regional Board accept the concept of bioavailability instead of mass loading. Or do they accept it now? If not, why not?	Delegated to RWQCB.	Beyond Scope
4. Are there apparent biological effects in Coyote Creek? In the Bay? How do we measure this?	Part of task 3; RMP is dealing with this question as part of Indicator Development project.	High Priority
5. What is at risk? (i.e., what human and natural resources occur along Coyote Creek that are potentially at risk?).	Common theme throughout: Watershed inventory is needed!	Medium Priority
6. Toxicity of loading events?	Part of task 3.	High Priority
7. What species are best for toxicity testing?	RMP Indicator Development process.	Beyond, but high priority for mention in report

H. SOURCE

1. Are the metals entering the Bay through stormwater runoff originating in lower urbanized streambeds or upper non-urbanized streambeds?	Part of task 3.	Medium Priority
2. In watershed inputs of trace contaminants, what fraction is from anthropogenic sources ("pollution") and what fraction is from natural sources ("background geology")? Of anthropogenic, how much is aerial deposition?	Special study need.	Medium Priority
3. What is the primary source (point or nonpoint) of each pollutant concern? What is secondary source (location of input)?	Here's the watershed inventory again!	Medium Priority

4. Do we have enough data to begin making determinations of relative loading sources (to be used in trading scenarios between point and nonpoint sources)?	Part of task 3.	High Priority
5. What information can we get on fallout pollutants? What "air flow" data is available?	Big data gaps, but investigations are planned.	Beyond Scope

I. DATA AND DESIGN ANALYSIS

1. Is the current data quality in the nonpoint source program comparable with the RMP data quality? Are the datasets integratable?	As long as data quality objectives are known and the analytical performance standards are met, the data are integratable.	High Priority
2. What are the appropriate sampling design, monitoring protocols, and data management plans for a watershed assessment, and what components can be compiled by volunteer monitors?	To be answered by task 5.	High Priority
3. How do we develop and agree upon data collection and data distribution?	Task for the CC Watershed Task Force.	High Priority
4. How to standardize the methods of sampling and analysis of contaminants?	Methods don't have to be standardized in most cases. Only performance standards have to be agreed upon.	High Priority
6. What additional information is needed to develop pollutant source signatures on fingerprints?	Part of task 3.	High Priority
7. Do we have any baseline data on pollutants in the Bay prior to the 1980's?	Yes. Sam Luoma's core data may come in handy.	High Priority
8. Is there value to the transitional station versus other methods?	Yes, but adjustments may be made at the end of Phase 1 of this study.	High Priority

J. FUNDING

1. How do we find other funding sources?	Isn't the funding source the tax and rate payer anyway? Are there any other sources than that?	Beyond Scope

1.0 POLLUTION HISTORY

1.1 Natural geology and background levels of chemical constituents.

The San Francisco Bay-Delta Estuary was created by a combination of mountain forming geological processes and global climate change. Its origins extend back 10 to 12 million years to the early Pliocene Epoch, although the Estuary in its current form has existed for only about 5,000 years (Atwater, 1979). The Estuary can be split into two distinct hydrologic systems. The Northern Reach encompasses the Sacramento-San Joaquin Delta, Suisun, San Pablo, and Central Bays, and the Southern Reach encompasses the area from the Golden Gate to the far South Bay. The Southern Reach receives only about one tenth as much freshwater as the Northern Reach, and as a result is essentially a tidal lagoon with relatively constant salinity.

Before the arrival of Europeans the input, or loading, of trace elements and organic chemical constituents to the Estuary came from natural sources such as the weathering of rocks, oil seeps, atmospheric deposition from fires, and from the settlements of Native Americans along the shoreline (SFEP, 1991; SFEP, 1992a). The effects of these inputs were probably small and localized (SFEP, 1992a). Observations based on sediment core analysis (LWA and MW, 1996) suggest that silver, mercury, copper, chromium, and selenium have been anthropogenically enriched in the Estuary, as their pre-European concentrations were lower. Nickel was present in sediments as far back as 1840 at levels similar to those found today, indicating that sediment concentrations of this element are most likely of natural origin.

1.2 Gold Rush Era

In 1848 gold was discovered in the Sierra Nevada foothills, and within two years San Francisco grew from an isolated trading post of about 400 people to a city of 25,000. The resulting gold mining, farming and land development which accompanied this population boom resulted in profound effects on the Estuary. These included massive changes in sedimentation processes, elimination of most tidal marsh areas, and mobilization of chemicals in excess of that from natural sources (Nichols *et al.,* 1986). For instance, the process of hydraulic mining for gold, which occurred from 1853 until it was outlawed in 1884, deposited tens of millions of cubic meters of rock and sediment and added increased levels of mercury to the Estuary (Phillips, 1987).

1.3 1940's through 1970's

Beginning in the 1940's, major developments occurred which affected the abundance and fate of pollutants in the Bay-Delta. These were massive water development projects, increased pollutant loading or input including industrial effluent, inadequately treated sewage, and nonpoint source input including the use of then new synthetic organic pesticides (SFEP, 1992a). These occurrences were related to agricultural development and expanding human population centers. The alteration of the freshwater flow regime has affected hydrodynamics, and therefore pollutant fate and transport, and the use of organic pesticides in the Central Valley has resulted in their transport to the Estuary (SFEP, 1991).

Beginning efforts to control the effects of sewage began in the early 1950's with the implementation of primary treatment facilities, and continued in the mid-1960's with secondary treatment. In 1969 California implemented the Porter-Cologne Water Quality Act, and in 1972 the Federal Clean Water Act was passed, both of which led to greatly reduced pollutant loading from municipal and industrial effluent, and corresponding improvements in San Francisco Estuary water quality. Although loading from these sources has decreased, analyses of sediment and biota have not shown many corresponding decreases in toxicant concentrations in the Estuary, and these may threaten its biological health (Luoma and Cloern, 1982; Phillips, 1987). There is a need to investigate the causes and effects of these toxic chemicals of concern in the Estuary. The 1996 Basin Plan (SFBRWQCB, 1996) and the Comprehensive Conservation and Management Plan (SFEP, 1994) provide frameworks with which to begin these investigations.

2.0 POLLUTANT LOADING ESTIMATES

Estuary pollutant loading estimates for point sources have been based upon actual measurements of the volume and chemical composition of wastewater flows from National Pollutant Discharge Elimination System (NPDES) permit holders throughout the Bay (Gunther *et al.,* 1987). More recent point source estimates (SCVRPPP, 1997) use measurements from three wastewater treatment plants discharging to the South Bay for five pollutants of concern (see section 4.1). Data used in these estimates are based on measured average concentrations and flows contained in the Self Monitoring Reports which are required of NPDES permit holders.

Ideally, pollutant loadings from non-point stormwater sources would be estimated by measuring the stormwater flow and chemical constituents from each drainage in all Bay-Delta watersheds, for every storm. The summation of these measurements for all storms and for all drainages would give an accurate estimate of pollutant loadings from surface runoff. Because of the prohibitive expense of implementing this approach, generalizations must be made for the Estuary using available data, and models constructed.

Both statistically based empirical models (Gunther *et al.,* 1987; SFEP 1992b) and physically based hydrologic models SCVNSS (1991) have been used to estimate contaminant loading in the Estuary. These approaches can be combined. For instance, SCVNSS (1991) used an empirical model for contaminant concentrations and a physically based model for runoff volume. The Stormwater Management Model (SWMM) was calibrated and verified on the 5.5 square mile Castro Valley watershed in Alameda County. The model simulated the hydrological processes of precipitation, evapo-transpiration, surface storage, infiltration, soil moisture, surface runoff, and channel flow from the upstream to the downstream hydrologic units. It also simulated pollutant accumulation, wash-off, and decay (Alameda County, 1994).

The underlying framework for these models is the same. Runoff volume is derived by multiplying total precipitation with a runoff coefficient, e.g., an estimate of the percentage of rainfall which becomes surface runoff. Contaminant loads are calculated as a product of runoff volume and a flow-weighted contaminant concentration for a particular storm or storms, extrapolated to the entire wet season (Gunther *et al.,* 1991).

Assumptions which introduce some uncertainties are required for these models. One is that pollutant concentration data from one part of the Estuary are extrapolated to other parts of the Estuary based on generalized land use classifications, not taking into account the potential differences within a classification from one area to another. Another is that locally based variations in the amount of impervious surface associated with different land uses may be concealed. This is due to the fact that estimated runoff coefficients are based on mean values from U.S. Soil Conservation Studies on urban hydrology (SCS, 1986), or the assignment of runoff coefficients to general land use types (Gunther *et al.,* 1987). For many watersheds around the Bay Area, however, data exist that would make calculations of realistic runoff coefficients possible. Another assumption is that although pollutant concentrations in the runoff are calculated, the percentage of pollutants actually reaching the Bay is not. This last assumption may be offset by the view that eventually a steady-state will be reached, where the outflow of pollutants from the drainage system will be equal to the inflow, with temporary storage in the system (SFEP, 1992b).

Do we have enough data to begin making determinations of relative loading sources? (matrix question H4)

2.1 Pollutant loadings from surface runoff and point sources

Sources of pollutant loading to the Estuary include both non-point surface runoff from urban and non-urban areas (particularly agricultural areas) including dry and wet deposition of pollutants on land surfaces, riverine inputs, direct aerial deposition, and point sources including industrial and municipal dischargers and dredging operations.

A 1992 Santa Clara Valley Nonpoint Source Pollution Control Program (SCVNSPCP, 1992a) report found the major source classes of copper and mercury to be atmospheric emissions including industrial and tail-pipe emissions; automotive sources including spills, leaks, and dumping of automobile fluids, and wear and tear of automotive parts; industrial sources such as mining and point source discharges both regulated and unregulated; residential sources such as household product disposal, soil erosion from new developments, and corrosion of down spouts and gutters; and water supply sources such as corrosion and algae inhibitors (SCVNSPCP, 1992a).

In general, nonpoint source loads for chromium, copper, lead, nickel, and zinc are at least twice the point source loads, whereas point source loads for nutrients are much higher. It should be noted that these estimates have great variability and uncertainty associated with them, since runoff loadings depend greatly on runoff amounts and precipitation. Biochemical oxygen demand from both sources are comparable, and total suspended solids loads are almost exclusively from nonpoint sources. Point source loading estimates for the extreme South Bay based on Self Monitoring Reports from 1987 and 1988 were compared with non-point source estimates for the same area averaged over a 12 year period from 1978–1989. The following average annual loads, in 1,000 pound units, were reported (point source/nonpoint source): chromium 2/10; copper 8/15; lead 8/15; nickel 12/21; zinc 28/50; nitrate 8,700/206; total Kjeldahl nitrogen 1,500/378; phosphate 8,700/161; biochemical oxygen demand 2,000/2,100; total suspended solids 1,300/69,000 (SCVNSS, 1991). A more recent study (SCVRPPP, 1997) found the following average annual loads (in 1,000 pound units, point source/nonpoint source) from South Bay sources: copper 2.5/6.4; nickel 4.5/12.1; mercury 0.002/0.07; silver 0.42/0.065.

The San Francisco Regional Water Quality Control Board is close to finalizing a point source dischargers database based on Regional Board and EPA required Self Monitoring Reports. This database, when implemented, will provide more up-to-date data for calculation of point source loading estimates for the entire Bay (Johnson Lam, San Francisco Bay Regional Water Quality Control Board, personal communication).

There has been no detailed source inventory of polychlorinated biphenyls (PCBs) for the San Francisco Estuary, but in general, sources have included industrial sites, direct emissions in times with less stringent emission guidelines than we now have, and landfills with improperly placed PCB-contaminated waste. Although new inputs are likely to be negligible due to the ban on PCB production and use restrictions in the 1970's, a current major source of PCBs to surface water is remobilization or re-deposition of residues in soils, sediment, or the atmosphere (SFEI, 1995). Unquantified current sources may still exist through accidental releases.

The major sources of polycyclic aromatic hydrocarbon (PAHs) loads appear to be from fossil fuel combustion, where vehicle exhaust containing the compounds reaches the Estuary either through wet (rainfall) or dry (dust and soot settling) deposition, or through stormwater runoff of PAH-laden particles. The spatial distribution of PAH concentrations at RMP stations and the relative abundance of individual PAH compounds suggests that street runoff is a primary source of these compounds (SFEI, 1996b).

Little information exists on the specific sources of organophosphate pesticides (which include diazinon and chlorpyrifos). Because of widespread farm and residential use of these compounds, loading occurs from both agricultural and urban runoff. Several subcatchments within several watersheds in Alameda County were sampled to characterize the spatial and temporal variability of diazinon (Scanlin *et al.,* 1997). It was found to be prevalent in stormwater runoff throughout the County but with wide variation in subcatchment concentration. In a 1994 sampling program, the Central Contra Costa Sanitary District identified the following sources:

residential areas, pet groomers, kennels, and commercial pest control operators. More sampling will be necessary in order to more accurately estimate the mass loading contributions of each of these sources (SFEI, 1996b). It is estimated that the load reduction potential of these compounds in the local watersheds surrounding the Estuary is large, because residential use is estimated to be ten times higher per acre than agricultural use (Lindsay Museum, 1995). The implication is that non-agricultural users do not apply these pesticides according to instructions.

Stream (tributary) loading to the Bay (non-storm) (matrix question A1)

For arsenic, cadmium, chromium, copper, lead, mercury, and nickel riverine and nonpoint inputs are the dominant sources of mass loadings to the Estuary, while for silver and selenium dominant sources are riverine and point source inputs. Nonpoint inputs are probably the major sources for hydrocarbons (Gunther *et al.,* 1987), and contributions of both organophosphate and chlorinated pesticides are probably higher in surface runoff as well.

Differentiate between wet and dry weather flows and loadings (matrix question A5)

Dry-weather flow consists primarily of natural base flow (e.g., stream loading), discharges from NPDES permit holders, and managed releases of reservoir water. In the South Bay, point source flows are greater than natural stream flows during the dry season. In the Santa Clara Valley Nonpoint Source Pollution Control Program 1991 Loads Assessment Report (SCVNSS, 1991), data suggested that dry weather loads are typically a minor component of the total annual loads to the Bay, and that a substantial portion of the flow and pollutants in this component does not reach the Bay during dry weather periods. The following average annual loads (in 1,000 pound units) were reported for the far South Bay (wet weather/dry weather): cadmium 0.5/0.01; chromium 8.7/0.08; copper 13.6/0.16; lead 14.3/0.03; nickel 19.4/0.04; zinc 48.6/0.29.

Stormwater loading to the South Bay (matrix question A2)

Pollutant concentrations in runoff tend to be higher during the first storm of the season compared to later storms, possibly due to the resuspension of bottom sediment which contain pollutants deposited during the extended summer dry-weather period (SCVNSS, 1991). In a study designed to determine if relationships exist between hydrology and toxicity intensity, all monitoring data collected in Castro Valley Creek during 1990–1995 were analyzed. The study found that the relationship between rainfall volume and toxicity is nonlinear, with toxicity being low for small and large storms, but greater for intermediate storms. It was surprising that during small storms there may not be enough runoff from toxic sources to create a toxic environment, while the increased runoff during large storms may dilute the toxic substances (ACCWP, 1996).

For samples collected on the Guadalupe River, exceedance for total metals occurred only during times when stormwater flow was highest. Dissolved metal concentrations did not vary significantly throughout the storm event. Flow-weighted sampling was shown to be a reliable method to evaluate compliance of stormwater discharges in waterways with established Water Quality Objectives. Analysis for total metals showed that copper, lead, and zinc concentrations were lower in post-storm versus during-storm samples. Post-storm samples did not exceed Water Quality Objectives. Results indicated elevated concentrations of total metals do not persist after storms and dissolved metal concentrations are generally very low during and after storm events (SCVNSPCP, 1994).

An evaluation of the concentrations of PAHs at three stormwater monitoring stations, to ascertain their risks from storms, showed no Water Quality Objective exceedances for any storm for four non-carcinogenic PAHs. For seven carcinogenic PAHs, total concentrations exceeded Water Quality Objectives for consumption by organisms (ACCWP, 1994).

Some trace metals transported in streams are deposited in the stream bed as a result of settling before reaching the Bay. Estimating that fraction is difficult because of several factors, including 1) turbulent stream flow during storms making estimation of the settling velocities difficult; 2) possible resuspension of sediments in subsequent storms if not removed during maintenance operations; 3) possible release of sediments back to the stream if significant base flow occurs during dry weather; 4) processes occurring at the freshwater saltwater interface which are not fully understood and which are difficult to estimate (ACCWP, 1994). This study recommended that records of county flood districts be reviewed and compared to estimated loads for a given creek to estimate what fractions of the metal loads are removed by settling and by dredging of channels. This information will be important for efforts to refine existing loading estimates and fate and transport models.

RMP watershed pilot study (matrix questions A1, A2, A5, E1, E3, E4, E5)

The Watershed Pilot Study is a Regional Monitoring Program for Trace Substances (RMP) Pilot Study with the general goal of determining if the pollutant spectrum in runoff can be differentiated from that of nearby RMP stations in the South Bay. A station at Standish Dam at the watershed-Estuary interface was selected for water and sediment sampling beginning in 1996. Samples were taken at the same time as were the water and sediment samples for the regular RMP stations e.g., wet season (February); period of declining Delta outflow (late April); and dry season (August). Together, the City of San Jose and the Santa Clara Valley Nonpoint Source Pollution Control Program made available half of the necessary funds to conduct this Pilot Study, while the RMP provided the other half. At the same time, the City of San Jose also decided to expand the monitoring parameter list at their Local Effects Monitoring (LEM) station to include trace organic contaminants in water and sediment.

The goals of the Watershed Pilot Study were to:

1) Link contaminant patterns found in the Estuary with those in an adjacent watershed to test if runoff and sediment taken at the lower end of Coyote Creek differs from water and sediment in the South Bay, including the LEM stations maintained by the San Jose-Santa Clara Wastewater Treatment Plant and the Sunnyvale Treatment Plant;
2) Explore what kinds of ancillary water quality parameters and watershed characteristics should be measured or described to explain some of the patterns found, improve sampling design, and fine-tune testing methodology.

The following results are from a very limited dataset (the first year of the Pilot Study), and should not be interpreted as a definitive assessment of Coyote Creek watershed contributions to the Estuary. Results are included in the *1996 Annual Report* (SFEI, 1997).

For water metals, arsenic and cadmium (both dissolved and total) were consistently lower at Standish Dam than at adjacent RMP and LEM stations for all three sampling events, while selenium (both dissolved and total) showed pronounced elevated signals compared to the South Bay stations at the spring and summer sampling events. Total mercury at Standish Dam was slightly higher than at the South Bay stations for all three sampling events. Total nickel was appreciably higher at the Standish Dam site during the wet season than in the South Bay, suggesting transport of nickel out of the watershed. Total copper, lead, silver, and zinc concentrations were comparable at the Standish Dam site and in South Bay water. Pronounced seasonal differences between the watershed site at Standish Dam and the RMP South Bay stations were not recognizable, with the exception of total/near-total selenium and nickel. Seasonal differences between Standish Dam, the closest LEM station (San Jose), and the closest Estuary station (Coyote Creek) are very apparent for most chlorinated hydrocarbons. Although data points from one year are not necessarily representative, it appears as though during high runoff periods, contaminant concentrations at the watershed station are distinctly different from the South Bay RMP sites for dissolved and total PCBs, DDTs, and chlordanes.

Metals data from the first year show that contaminant concentrations in sediment carried down the watershed and deposited where the creek meets the Bay may not be very different from what we find in the Bay itself. In contrast, the Santa Clara Valley and the Alameda County urban runoff programs have found in their sampling studies that stream sediments were higher in lead, copper, zinc, cadmium, nickel, and chromium than Bay sediments. Possibly because the sediments sampled at Standish Dam represent a mixture of Bay and creek sediments, the urban runoff program findings were not corroborated. It should also be noted that prior to sampling, several major storms had caused high runoff events with associated creek-bed scouring. Based on the predominance of coarse grain sizes in the sediment sample collected in the wet season, it is fair to assume that much of the previous year's accumulated sediment at the site had been washed away. If contaminant concentrations were normalized to grain size, Standish Dam sediment concentrations would likely be higher than Bay sediment concentrations, since smaller particles can adsorb more pollutants than large ones due to their greater surface area per unit mass of sediment.

As with water samples, spatial differences appear to be quite pronounced for trace organic contaminants, with the Standish Dam site having the highest DDT and chlordane concentrations during the wet season when high flows mobilize sediment in the watershed and carry down particle-associated pollutants with them. The Santa Clara Valley was prime agricultural land during the time these pesticides were still in use, and residual pesticides seem to get mobilized during the rainy season and washed down the creek. For DDT compounds, the South Bay stations were consistently low relative to the San Jose and Standish Dam sites. PCBs showed pronounced seasonal and spatial differences: they were highest near the San Jose LEM station, intermediate at Standish Dam, and lowest in the Bay. PCB concentrations at Standish Dam, although not as high as at the San Jose LEM station, were considerably higher than anywhere in the Estuary itself. Sediment PAH concentrations, on the other hand, were lower at Standish Dam than most stations in the Estuary.

2.2 Pollutant Loading Data Gaps

Current loading estimates rely on a number of assumptions which introduce a fairly high level of uncertainty to predictive models. Stormwater management models could benefit from watershed-specific rainfall and runoff data and incorporation of more specific land use information. Pollutant concentrations, as well as loads, are also heavily influenced by the sediment supply in any given watershed. In order to improve the sensitivity of comparisons of metals concentrations in sediments, enrichment factors can be used to normalize concentrations in stream sediments relative to the earths crust (Luoma, 1990). An enrichment factor can be defined as the ratio of a metal pollutant to a normalizing crustal metal such as Al, at a given location, to the same ratio at a corresponding location that represents the background or naturally occurring concentration (Luoma, 1990). Enrichment factors for many pollutants, as water flows through urbanized areas, are expected to be higher in watersheds with a high sediment yield. Consequently, it is important to assess a number of basic physical watershed characteristics that influence directly or indirectly pollutant load estimates. Pollution reduction efforts will be most cost-effective and successful, if at least some rudimentary knowledge exists about these physical watershed characteristics prior to implementing alternative management practices.

3.0 BIOLOGICAL EFFECTS

Are there apparent biological effects in Coyote Creek? In the Bay? How do we measure this? (matrix question G4)

Between 1977 and 1981 Pitt and Bozeman (1982) investigated the effects of urban runoff on water quality, sediment quality and biota in Coyote Creek. Extensive biological studies consisting of fish, benthic macroinvertebrate, and insect sampling were conducted to assess relative abundance and diversity. The studies, designed to differentiate between the non-urbanized upper reach and more urbanized lower reach, found a significant decrease in the abundance and diversity of biota in urban reaches compared to non-urban. This could be related to both water quality and physical factors associated with hydrological modifications, such as channelization, of the lower reaches of Coyote Creek.

The 1991 Santa Clara Valley Nonpoint Source Pollution Control Program (SCVNSS, 1991) conducted toxicity tests at stream and land use stations including Coyote Creek. Using EPA 3 species test protocols with *Ceriodaphnia dubia* (a cladoceran), *Pimephales promelas* (fathead minnow), and *Selenastrum capricornutum* (a green alga), results showed that during dry weather, only 14% of the tests showed toxicity. However, during wet weather, samples from these sites were frequently toxic. The results suggested that runoff from these urban areas can adversely affect biota under laboratory conditions and, by extrapolation, biota in the receiving streams.

Aquatic bioassay results for the 1995 Regional Monitoring Program for Trace Substances showed no toxic effects for *Mysidopsis bahia* (a mysid shrimp) or larval *Mytilus edulis* (mussel) at any station except the San Joaquin River, which had low *Mysidopsis* survival (although many tests did not produce usable results due to poor survival or reproduction in the laboratory). The current RMP sampling design is not conducive to "tracking" episodic pollutant pulses associated with first-flush effects. The 1997 RMP Implementation Plan contains a Special Study to investigate episodic toxicity events, and preliminary results indicate that episodic toxicity does occur in South Bay sloughs. Sediment bioassay results did show toxic effects for *Eohaustorius estuarius* at seven stations, including South Bay stations (SFEI, 1996c). How much the sediment toxicity was influenced by current sources of pollutant input versus historical deposits, is unknown at this time.

Toxicity of loading events (matrix question G6)

3.1 Stormwater Toxicity

Since the mid to late 1980's, Santa Clara and Alameda Counties have, through their stormwater monitoring programs, undertaken efforts to characterize stormwater toxicity

The 1993–94 Alameda County Urban Runoff Clean Water Program Annual Report (ACCWP, 1994) showed: Water Quality Objectives (WQOs) for maximum concentrations of the following metals were exceeded for the following (number of exceedances/total number of samples): Acute toxicity for total copper (5/6), lead (3/6) and zinc (6/6) at Castro Valley Creek. There were chronic exceedances at Castro Valley Creek for total and dissolved copper (6/6, 1/6), lead (6/6, 2/6), and mercury (2/2, 2/2), and total zinc (6/6). Chronic exceedances for Alameda Creek were for total lead (4/5) and total and dissolved mercury (2/2, 2/2). Bioassay toxicity testing showed most samples as being toxic, in particular Castro Valley Creek. Dissolved copper and zinc exceeded criteria at Castro Valley Creek. San Lorenzo Creek had exceedances of the chronic dissolved lead criterion. In a five year study of Castro Valley Creek (see "Stormwater loading to the South Bay" in section 2.1 of this paper), data indicated that antecedent hydrologic conditions explain 50% of the observed variability in total copper concentrations. New dissolved pollutant criteria (40 CFR 131 May 4, EPA 1995) suggest that previous comparisons may over estimate the toxicity impact of metal loads to small watersheds, due to lower exposure times for stormwater. No conclusions could be drawn from these data as to whether levels of mercury and PAHs were above water quality guidelines long enough to bioaccumulate in fish. In other Program studies, the use of adequate detention basins was shown to reduce copper by 30% and lead by 50% in stormwater, and vegetated swales and channels offer even more effective treatment (ACCWP, 1994).

Ceriodaphnia dubia toxicity tests were used to quantify the toxicity of urban runoff at Crandall Creek and the downstream DUST (Demonstration Urban Stormwater Treatment) Marsh near Fremont, California in the winters of 1991–92 and 1992–93 (ACURCWP, 1994c). Acute toxicity, expressed as median time to lethality (LT_{50}) for *C. dubia* was used to compare intensities of toxicity in this system. Results showed: 1) that toxic stormwater generated by small to medium sized storms (5 to 25 mm. precipitation) was contained in the marsh; 2) toxicity was greatly reduced upon dilution of stormwater runoff with pre existing marsh water; 3) mixing of the water column in the marsh increased the rate of toxicity decline; 4) toxicity reduction, above and beyond that attributable to dilution, was evident in the marsh. This study demonstrated the potential use of toxicity assessments as an integral component of marsh design and management (Katznelson *et al.,* 1995). It also points out that without the marsh and its toxicity reducing function, runoff which enters the Bay may cause toxicity.

Two stations, one on Rheem Creek and one on Walnut Creek, were established by the Contra Costa Clean Water Program for long-term monitoring to provide information on trends in intensity and frequency of detection of toxicity. Although these stations may not be representative of South Bay conditions, they serve to illustrate aspects of the toxicity of loading events. Monitoring efforts in 1994–95 included *Ceriodaphnia dubia* chronic seven day toxicity tests during five storms using EPA protocol 600/4-89/001 (USEPA, 1989). The results showed that three out of the 10 test events were lethal to *C. dubia*. Six out of the ten showed enhanced reproduction compared to laboratory control water. Diazinon concentrations in the streams can explain only two of the toxicity results. In a separate protocol, new water samples were collected from the creeks on each of the seven days after the storm event. In these results, the *C. dubia* survived, but reproduction was slightly impaired (CCCWP, 1995).

Exceedances of acute EPA WQOs for metals at the Alameda County Urban Runoff Clean Water Program stream stations did not result in toxicity to *Pimephales* or *Selenastrum*. Toxicity occurred in *Ceriodaphnia* after 4 days, which is longer than typical exposures in the environment. Toxicity corresponded to the WQO exceedances only at the industrial site, where these exceedances were very high. These data suggest that EPA WQOs are overprotective when applied to total metals concentrations (ACURCWP, 1992a).

A 1993–94 Alameda County Urban Runoff Clean Water Program special study, utilizing Toxicity Identification Evaluations for the Demonstration Urban Stormwater Runoff (DUST) Marsh system in Fremont, found that diazinon was consistently the toxic agent. There was little evidence of elevation or accumulation of copper, lead, or zinc in the creek or marsh over time (ACURCWP, 1994a).

The Santa Clara Valley Nonpoint Source Pollution Control Program 1994–95 stormwater monitoring effort showed the following WQO exceedances (exceedances/total number of samples). For acute toxicity: total copper (7/19), dissolved copper (1/19), total lead (2/19), total zinc (4/19). For chronic toxicity: total copper (13/19), dissolved copper (1/19), total lead (19/19), dissolved lead (2/19), total zinc (4/19) (SCVNSPCP, 1995b).

3.2 Biological Effects Data Gaps

Toxicity tests in the laboratory on non-indigenous "surrogate" species have been shown to reflect the potential of adverse biological effects on natural aquatic systems in many cases (deFlaming, 1995). However, pollutant impacts on natural resources or other valued ecosystem components within any given watershed or receiving water are not readily established unless these resources are known. Frequently, pollutant impacts interact with physical disturbances to generate chronic effects that are not immediately recognizable.

4.0 SELECTION CRITERIA FOR "POLLUTANTS OF CONCERN" (WATER QUALITY OBJECTIVES, SEDIMENT GUIDELINES, TOXICITY EVENTS, AND HUMAN HEALTH EFFECTS)

The interim dissolved water quality criteria promulgated by the EPA and Basin Plan WQOs based on total metals were used for comparison of water sample data for the ranking of metals in South San Francisco Bay and stream environments (WCC, 1996).

The San Francisco Bay Regional Water Quality Control Board has developed interim sediment screening criteria for wetland creation and upland reuse, in lieu of regulatory standards. These values are based on a study by Long *et al.* (1995) which compiled biological effects and corresponding sediment chemistry data from numerous studies, and they take into account the higher naturally occurring concentrations of chromium and nickel in soils surrounding San Francisco Bay and within its sediments (WCC, 1996).

A study was conducted for the Alameda County Clean Water Program from 1992–94, in order to learn what the levels, spatial and temporal patterns, causes and sources of toxicity in stormwater are and what threat they pose to impacted water bodies. Procedures were recommended for increasing the effectiveness of Phase I and Phase II Toxicity Identification Evaluations, and control strategies were outlined for prevention of toxicity from diazinon, which was shown by the study to be a pollutant of concern (ACURCWP, 1995).

4.1 Trace Elements

What pollutants have the worst impact on the Bay? (matrix question C4)

Past studies in the San Francisco Bay suggest that the trace elements of greatest concern are silver, copper, selenium, cadmium, and mercury (Luoma and Phillips, 1988). Silver is highly bioavailable, and because of its low naturally occurring concentrations, anthropogenic contamination in estuarine waters can result in concentrations 100–300 times higher than natural background levels. Furthermore, it is one of the three most toxic trace metals (along with copper and mercury) to invertebrates and algae in marine and estuarine environments (Luoma *et al.,* 1995).

Conclusions similar to those in Luoma and Phillips were found in the Santa Clara Valley Nonpoint Source Metals Control Measures Plan, where trace metals were ranked into three classes as follows: Problem metals are those for which the weight of evidence suggests an impact is likely occurring or has the potential to occur if sources are not controlled. Metals of concern are those for which an impact is suspected but there is less confidence in the monitoring data, evaluation criteria, or severity of the impact. Metals likely not of concern are those for which there is no compelling evidence of impact. The ranking is as follows: Problem metals: copper, nickel, mercury, silver, selenium; metals of concern: cadmium, lead, zinc; metals likely not of concern: chromium (WCC, 1996).

Are nickel and copper the proper focus of concern? (matrix question C2)

A recent report (WCC, 1996) stated that exceedances of water quality criteria for copper and nickel in the Bay should be weighted heavily because they represent a potentially widespread problem. The toxicity of copper to aquatic biota is considerable (Phillips, 1987), and there have been recent increases in copper concentrations in resident mussels compared to drought year concentrations in mudflat sediments off the Palo Alto Water Quality Control Plant. Studies utilizing Palo Alto bivalve (*Macoma balthica*) data (Luoma and Phillips, 1988) showed stresses from elevated levels of copper and other metals occurring on several trophic levels, including 1) sub-cellular, with the shift in the intracellular protein level; 2) whole organism, where production of biomass was lower; 3) population, where reappearance of *M. balthica* after a decline may have necessitated physiological adaptation or selection for a genetically metal-tolerant sub-population; and 4) absence of other species less tolerant to elevated metals including copper.

The tendency for nickel to be accumulated into the food chain through phytoplankton bioaccumulation is well documented (Phillips, 1980), thus the bioaccumulation potential for nickel is high. Nickel is abundant in Bay sediments, and studies have suggested high toxicity to nickel in single-celled organisms (USEPA, 1986). Spencer and Nichols (1983) found algal growth to be inversely related to free divalent nickel, and Patrick *et al.* (1975) found that nickel decreased diatom diversity and caused a shift to green and blue-green algae. However, other reports (City of San Jose, 1996) showed inconclusive toxicity results in the Bay from nickel.

4.2 Trace organics

Recent discoveries of widespread organophosphate pesticide impacts on aquatic biota in local streams, the large rivers, and the Estuary itself have focused attention on compounds previously believed to have too short a half life or little effect beyond the immediate area of application. Particularly diazinon and chlorpyrifos have been identified in both treatment plant effluent and streams at levels toxic to bioassay organisms. Often, it is difficult with current analytical methods to quantify concentrations of these pesticides.

Certain trace organic endocrine disruptors found in the San Francisco Estuary that are individually innocuous at ambient concentrations can be synergistically activated when combined (Simons, 1996). Arnold *et al.* (1996) found that combinations of weak environmental estrogens such as dieldrin, endosulfan, or toxaphene, were 1000 times as potent as any one chemical alone. Similarly, the results of toxicity identification evaluations for diazinon and chlorpyrifos (Bailey, *et al.,* 1996) suggested cumulative toxicity when present together.

PAHs can evoke a wide variety of toxic effects in aquatic species, particularly benthic species, since these compounds tend to accumulate in sediments. Survival, growth, metabolism, reproduction, photosynthesis, and immune function can be affected by PAHs. Regional Monitoring Program (RMP) data indicate that background concentrations of PAHs in sediment approach or exceed levels where toxic effects are possible in biota (SFEI, 1996c).

RMP results from 1994 and 1995 showed PCB concentrations in Estuary waters to be orders of magnitude greater than the EPA water quality criterion, and a study conducted by the Regional Water Quality Control Board found that PCB concentrations in fish collected throughout the Bay exceeded screening values for protection of human health, resulting in an advisory on consumption of Bay fish. Although PCBs are not particularly toxic in acute exposures, certain PCBs are extremely toxic in chronic exposures, and can cause symptoms similar to those caused by dioxin exposure, including developmental abnormalities, disruption of the endocrine system, impairment of the immune system and promotion of cancer. Data indicate that due to their persistent nature in the environment, current levels of PCB contamination in the food web is likely to persist for some time (SFEI, 1995), although new inputs are likely to be negligible due to the ban on PCB production and use in the 1970’s.

4.3 Uncertainties in Organic Pollutants

Only a small percentage of organic compounds present in the Estuary are measured (Risebrough, 1996). It is quite possible that some of those unknown compounds may have toxic effects on estuarine biota, either individually or in combinations. The US EPA is currently working on a computer model that would be able to identify likely organic compounds that disrupt the endocrine system. Laboratory experiments have shown that a number of compounds commonly used in detergents, emulsifiers, lubricants, and other applications, have effects on the endocrine system and are present in the aquatic environment at levels that could subject organisms exposed to discharges of these compounds to endocrine disruption and reproductive abnormalities (Lye *et al*., 1997; Bennie *et al.,* 1997). Samples were analyzed for alkylphenol polyethoxylate metabolites in Canadian sewage treatment plant waste streams, and measurable quantities of these substances were found (Bennie *et al.,* 1997).

4.4 Uncertainties associated with selecting "pollutants of concern"

Although widespread toxicity in Bay sediments has been observed throughout the Estuary, adverse effects on test organisms has not yet been linked to any particular agent or suite of pollutants. Probably many more pollutants of concern exist than are currently monitored, and this is probably the case in stream environments as well. Numerical objectives set by the regulatory agencies have been shown to be both over- as well as under-protective and frequently do not take site-specific conditions into account that may influence adverse biological effects. For example, sediment guidelines for nickel are almost certainly not applicable for the San Francisco Estuary, and water quality objectives appear to be considerably lower than any toxic effects thresholds. Nickel inputs into the Estuary from surrounding serpentine soils may outweigh any anthropogenic inputs, which has expensive implications for source control measures.

How can we get a complete database to start prioritization? (matrix question D12)

With the many programs and projects in the Estuary all collecting data on thousands of parameters and having differing goals, objectives, and database designs, it will be virtually impossible to get a complete database. Instead, the creation of an index, or metadata database, which will describe in some detail and “point” to the many disparate datasets which are needed for prioritization, must occur. This effort was undertaken by SFEI in 1989 with the resulting Estuarine Data Index (EDI) addressing this need at that time. Its update and enhancement with the Internet technology which has been developed in the ensuing years would go a long way towards creation of a comprehensive metadata index to be used in prioritization of parameters. On a smaller scale, the Bay Area Stormwater Management Association (BASMAA) recently completed a comprehensive summary of special studies up to the spring of 1996, and serves as a resource to a wide variety of information users.

5.0 NONPOINT POLLUTANT SOURCE CATEGORIES

5.1 Atmospheric Deposition

Of anthropogenic deposition, how much is aerial? (matrix question H2)

Some studies show that atmospheric deposition (both wet and dry) is the major source of contamination in arid and semi-arid climates, such as that which exist in the South Bay. Although inconclusive, data indicate that depending on the metal, over half of the contamination in stormwater could be accounted for by atmospheric deposition (ACURCWP, 1992b), and atmospheric deposition appears to be an important source of both PCBs and PAHs (Gunther *et al.,* 1987). Dry deposition is probably more important than wet deposition. Chromium, nickel, copper, and lead rainfall concentrations are about equal to background levels. Zinc concentrations in rainfall are about equal to concentrations measured in streams. However, the prevailing westerly winds in the Bay Area may reduce the effects of atmospheric deposition by moving the pollutants away from the Estuary watersheds. Starting in 1997 an RMP aerial deposition pilot project is being implemented, with the goal of adding information needed to more accurately estimate inputs from this source.

5.2 Runoff

Are the metals entering the Bay through stormwater runoff originating in lower urbanized stream beds or upper non-urbanized stream beds? (matrix question H1)

In watershed inputs of trace contaminants, what fraction is from anthropogenic sources ("pollution") and what fraction is from natural sources ("background geology") (matrix question H2)

As part of the monitoring program conducted for the Alameda County Clean Water Program, source identification studies included a literature review of natural and anthropogenic sources of nonpoint source pollution that is compared to Alameda County water quality data to determine which pollutants have mainly anthropogenic sources. These studies suggested that lead and zinc are primary metals contributed by urban activities, copper to a lesser degree, and nickel and chromium are primarily due to erosion. The enrichment factor for a background station on Strawberry Creek was calculated from a study by Shacklette and Boerngen (1984), and these concentrations were applied to other sites in Alameda County. The results were consistent with those above. Lead and zinc were significantly enriched above soil concentrations, copper less so and nickel and chromium even less. Cadmium found in stormwater runoff may be primarily a result of association with zinc (ACURCWP, 1992b).

Results from a 1995 Contra Costa Clean Water Program study established that the Mt. Diablo mercury mine site is an overwhelming and ongoing mercury source to the Marsh Creek watershed. Eighty eight percent of total mercury input was traceable specifically to exposed tailings piles at the mine. Data indicate that mercury from the tailings mobilizes in a dissolved state that partitions on to particulates as it moves downstream (CCCWP, 1996).

Brake pad wear was identified as a significant source of lead, zinc, and particularly copper to stormwater loads into the South Bay (SCVNSPCP, 1992a). In a 1994 Santa Clara Valley Nonpoint Source Pollution Control Project report, a model was used to estimate the loading of these metals into the South Bay from disc brake pads of seven auto manufacturers. Loads model conclusions showed disc brake pads a significant source of copper to stormwater in Santa Clara Valley (ACURCWP, 1992e).

Results from an Alameda County Urban Runoff Clean Water Program 1994 study showed that most roofing materials have substances that release pollutants to stormwater. Asphalt is commonly used for water proofing. It contains metals and organics that may release or dissolve in wet weather and enter roof runoff. Galvanized metal used in rain gutters and down spouts can contribute high zinc levels in runoff, as an EPA study (USEPA, 1978) showed. In Alameda County much of the roof runoff in residential areas is allowed to infiltrate into the soil or run over vegetated surfaces, while most roof drainage in commercial and industrial areas drains directly into storm drain systems. Because of this, the percentage of commercial and industrial pollutant input to the Bay is likely higher than that of residential input, even though commercial and industrial runoff is a minor portion compared to total residential area runoff. And since current local policies encourage direct connection of roof drains to storm drains, pollutant contributions from roofing materials will likely grow (ACURCWP, 1994b).

The results of a 1994 Santa Clara Valley Nonpoint Source Pollution Control Program study showed that background water supply is a relatively minimal source of copper to wastewater treatment influent, accounting for only 3 to 6 percent of the load. Results of selenium monitoring at water supply sources and influents indicated that most of the selenium in the water supply is from groundwater sources (SCVWD, 1994).

Results from a 1995 Santa Clara Valley Nonpoint Source Pollution Control Program report on characterization of runoff water quality from parking lots showed that metals concentrations are lower than concentrations from industrial, residential and transportation land use areas sampled, but, except for chromium, higher than concentrations from open space land use samples. This study concludes the pollutants in stormwater runoff from parking lots are mainly in a dissolved, not particulate phase (SCVNPSCP, 1995a).

5.3 Stream Sediments Versus Bay Sediments

How do pollutant signatures in suspended sediments in runoff compare to Bay suspended and benthic sediments? (matrix question E3)

Results in the Alameda County Urban Runoff Clean Water Program 1991–1992 Annual Report showed that suspended stream sediments were enriched in cadmium, copper, lead, and zinc compared to Bay benthic sediments. This suggests that surface runoff, rather than Bay sediment resuspension, supplied these pollutants to the Bay (ACURCWP, 1992c), and that sediment enrichment of these metals continues to exist despite the implementation of major point source control measures.

Similar results from the Santa Clara Valley Nonpoint Source Pollution Control Program 1992 Annual Report indicated that suspended stream sediments are enriched compared to suspended and benthic sediments in the South Bay for chromium, cadmium, copper, lead, nickel, and zinc. This suggests that there may be additional input of metals, probably from surface runoff. Somewhat elevated nickel and chromium levels are likely from erosion of localized soil sources rather than from urban sources (SCVNPSCP, 1995a).

5.4 Nonpoint Pollutant Source Categories Data Gaps

More information is needed on atmospheric deposition as a source of pollutants to the Bay, and whether information gleaned from studies of comparable land use types in other areas are comparable to the Bay Area with the prevailing westerly wind effect.

More information is needed on the sources of pollutant loads in stream sediments to the Bay, including possible sources from erosion.

6.0 CONTAMINANT TRANSPORT AND FATE

6.1 Transport in Streams

What data exist on pollutants moving through the environment and the changes they take on? (matrix question E2)

In a 1994 vegetated channels study for Alameda County Urban Runoff Clean Water Program, results showed concentrations of copper, lead, zinc and PAHs in control plants and sediments to be significantly lower than plants and sediment in channels exposed to stormwater runoff. There also was a decrease in PAH concentrations along a gradient from upstream to downstream in Crandall Creek (ACURCWP, 1994b). This demonstrates active uptake by the plants. A review of related studies supports the conclusion that vegetated flood control channels trap sediments that would otherwise enter the Bay. However, sediment resuspension (see Matrix E3, section 5.3) is a factor in the remobilization of pollutants.

As part of the Alameda County Urban Runoff Clean Water Program Stormwater Management Plan for 1992–93 monitoring and analysis, a geochemical equilibrium model (MINTEQA2 Version 3.d) was utilized and assessed for its potential to predict chemical behavior of heavy metals in a stream discharging into San Francisco Bay. A station on Alameda Creek was selected as a representative site, and copper was the test metal. The model simulated copper percent in solution as a function of Total Suspended Solids and pH. Complexation of copper with natural dissolved organic matter was also computed. Results showed the model simulated the distribution between dissolved and adsorbed copper species. It can predict the chemical fate and speciation of copper from total copper concentrations measured during storm events. This may help more precisely evaluate the impact of copper in the receiving water body as bioavailability and toxicity are linked to speciation. The study suggested that copper can be used as a surrogate for other metals found in the Bay, and that the model in was effective in simulating their chemical behavior (ACURCWP, 1992d).

Pollutant movement through water column versus sediments (matrix question E4)

Diagenic remobilization of metals from Bay benthic sediments is important to some trace element cycles, and appears to be most pronounced in the southern reach of the Estuary (Flegal, 1994). However, results from the Santa Clara Valley Nonpoint Source Pollution Control Project 1992 Annual Report suggest that the majority of suspended sediment metals concentrations in streams during storms are not solely explained by remobilization of previously deposited sediments, but may be due to additional input from surface runoff. Comparison of stream suspended sediment metals with those in the South Bay show that the stream particulates have greater metals concentrations during storms than either suspended or benthic particulates in the South Bay (SCVNSPCP, 1992b).

Fates of pollutants in the Bay (matrix question E5)

In the 1991 Alameda County Urban Runoff Clean Water Program report, partition coefficients were calculated for metals in streams and in the South Bay to determine their fate. Cadmium and chromium appeared to remain attached to particles when discharged into the Bay. Copper, nickel, and zinc appear to be released. Stream particles appear to remove dissolved lead from the water column in the Bay (ACURCWP, 1992e).

Monitoring data from the Santa Clara Valley Nonpoint Source Pollution Control Program (SCVNSPCP, 1992b) were used to calculate apparent partition coefficients for the trace elements chromium, cadmium, copper, lead, nickel, and zinc. The higher the partition coefficient, the stronger is the sorption of the compound to solids (e.g., sediments). Santa Clara Valley streams have higher partition coefficients than the Bay for copper, chromium, and nickel. This result suggests that some of these suspended sediment-bound elements are solubilized upon discharge to the Bay. Comparison with Alameda County results show higher nickel and chromium coefficients in the Santa Clara Valley. This suggests an erosional source of these metals in the Guadalupe River and Coyote Creek watersheds.

6.2 Contaminant Transport and Fate Data Gaps

Partition coefficient models have not been validated for the South Bay. The bioavailability of contaminants associated with particulates is not known, and little information exists on contaminant fate at the fresh-saltwater interface. Current data suggest that particulates carried into the Bay from surrounding watersheds are comparable in concentrations of some metals to Bay sediments, once they become "enriched" in urban areas. This is a troubling conclusion, given the considerable anthropogenic Bay sediment enrichment by many contaminants that has occurred over the past 150 years.

Are we measuring the right parameters? Biological criteria. (matrix question C1)

Since the passage of the Clean Water Act, significant improvements in water and sediment quality have been made. These improvements were not only reflected in reduced loads of pollutants from point sources to receiving water bodies nation-wide, but also in dramatic recoveries of benthic communities and other ecosystem health indicators. After the re-classification of urban runoff as a point source and its inclusion into the NPDES (National Pollution Discharge Elimination System) program, the initial approach to monitoring the performance of pollution reduction efforts was similar and focused primarily on chemical characterization of runoff and comparisons to water quality objectives. However, the complex interactions between chemical and physical factors impairing valued watershed resources and the lack of knowledge about watershed processes are slowly being recognized. New indicators are required that are sensitive to change, reflect societal values within a watershed, and are geared more directly toward the resources of concern or impacted by human operations. Efforts in this direction have recently been started to select more appropriate indicators of progress (or regress) toward very specific and quantifiable objectives (e.g., RMP 1995 Annual Report).

How to integrate non-pollutant watershed problems with pollutant-specific problems. (matrix question C5)

Local watersheds are inadequately described to cost-effectively reduce impacts from various kinds of pollution sources and land development. Best Management Practices (BMPs) are being implemented, while their ultimate goal and desired outcome is often not well defined. Too many factors controlling pollutant inputs, transport, storage, and transformation processes are unknown, yet relatively easily obtained through straight-forward reconnaissance work. Habitat restoration plans and mitigation projects are drafted and implemented without sufficient information on habitat controls, such as water and sediment supply, resulting in less than optimal outcomes.

Both pollution prevention and natural resource managers have basic information needs in common that can be assembled through watershed inventories that include determination of watershed boundaries and area, rainfall patterns, historical and current natural resources, changes in the distribution and abundance of surface water and alluvial sediment, land development history and present land use, soils and geology, and hill slope processes. Watershed inventories are the foundation upon which quantitative goals can be built, which subsequently serve to measure the degree of success of management actions.

Science-based goals and objectives are essential for the protection of watershed and estuarine resources through pollution prevention and mitigation activities. Goals and objectives should be based upon an understanding of the environmental past, an understanding of the present, and an understanding of environmental change. Parameters collected as part of watershed inventories could be spatially integrated in a geographical information system (GIS), such that spatial analyses can be performed which will: a) help in assessing the relative influence of natural processes and human operations on pollutant loading; b) assist in determining the best locations for monitoring stations within any given watershed and in the Estuary itself; and c) determine the appropriate mix of BMPs, land use decisions, and restoration or mitigation sites.

7.0 METHODS OF STANDARDIZATION

7.1 Runoff Sampling Design

In the long-term Contra Costa Clean Water Program effort mentioned in Section 3.1, a study was conducted to compare event mean concentrations of metals from an automatic sampler vs. an Equal Discharge Increment method. Results showed samples collected by the Equal Discharge Increment method have lower total and dissolved metals concentrations than samples collected by the automatic sampler method. Recommendations from this study for the 1995–96 wet weather season are based on the above findings: 1) continue the same sampling schedule and locations; 2) submit samples for analysis but discontinue chlorinated organics analysis; 3) analyze for mercury at the low level detection limit; 4) continue the two special studies at the Walnut Creek station for three storms for the effect of daily stormwater renewal on *C. dubia* survival, and sampling by both the automatic sampler and the Equal Discharge Increment methods (CCCWP, 1995).

7.2 Quality Assurance

How to standardize the methods of sampling and analysis of contaminants. (matrix question I4)

A portion of the Amended Monitoring Plan requested by the San Francisco Bay Regional Water Quality Control Board in 1991 for their NPDES permit was prepared by Woodward Clyde. In this report, design and implementation of a strict Quality Assurance/Quality Control (QA/QC) plan was outlined to quantify data accurately and to provide a mechanism for control and evaluation of procedures in the monitoring program. The plan includes established Standard Operating Procedures (SOPs) to be followed by field personnel and laboratory personnel, blind equipment blanks and sample duplicates to assess contamination potential, and duplicate field samples. Sample custody and transfer procedures are based on EPA recommended procedures. Laboratory analysis methods must meet precision and accuracy objectives by use of duplicates and blind standard reference samples analysis. Contamination is assessed by analysis of laboratory blanks and equipment blanks. Detection limits are reported in the final report summary. Water quality constituents include the metals arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc; organics like oil and PAHs; and cognates such as hardness, total suspended solids, and pH. Reporting of these QA/QC data will be part of the Annual Report (SCVNSPCP, 1991).

As part of the continuing Santa Clara Valley Nonpoint Source Pollution Control Program, quality assurance data were collected to determine if sampling analysis methods are adequate to measure metals concentrations in stormwater runoff, and if Water Quality Objectives (WQOs), especially those that protect freshwater aquatic life, were achieved during storms. Results showed 1) laboratory and field procedures are adequate to compare stormwater quality with acute water quality objectives; 2) laboratory and field procedures were not adequate to compare all samples to chronic objectives for all metals. Specifically most of the total and dissolved mercury, most of the total and dissolved cadmium, and significant parts of the total and dissolved lead samples could not be compared; 3) laboratory and field procedures are adequate for determining long-term trends for total copper, lead, and zinc; 4) laboratory and field procedures are not optimal to determine long-term trends for other total metals (arsenic, cadmium, chromium, mercury, nickel, selenium, silver) and for all dissolved metals; 5) selenium concentrations were successfully quantified using modified selenium analysis for low concentrations; 6) laboratory and field procedures were modified to enable quantification of mercury concentrations in streams during storms (SCVNSPCP, 1993).

Regionally standardized collection and analysis protocols for stormwater monitoring that meet NPDES permit requirements were prepared for the BASMAA Monitoring Committee. A first step is to set laboratory performance standards. QA/QC procedures must meet the objectives for water quality, even though techniques and procedures may not be completely identical among participating county monitoring programs. New ways of organizing and managing data are necessary to find the pertinent highlights in large data sets. A flexible and adjustable information management system and protocols for entering data from the stormwater monitoring programs was recommended. The following specific recommendations are made to create sensible standardization in the stormwater monitoring procedures: 1) field blanks should be collected. Pre-deployment QA/QC is advised. Develop a field blank collection method using auto samplers; 2) the laboratory minimum performance level should be one fifth of the WQO. Practical Quantitation Limit (PQL; this equals 3 times the Method Detection Limit) for laboratories should be determined; 3) set frequency goals for analysis of field and laboratory duplicates, spikes and reference materials analysis. Determine a reasonable frequency for QA/QC; 4) standardize QA nomenclature. Adopt the definitions listed in this report; 5) establish a baseline parameter list for all programs. Watershed-specific parameters could be added later. Analyze existing data to determine data needs; 6) collect all data necessary to perform data analysis and reporting. Agree on what hydrologic data should be reported; 7) detect 40% change in pollutant concentrations. Conduct power analysis using existing data; 8) use EPA guidance and clean equipment and techniques to measure dissolved metals. Determine if field filtration is necessary; 9) for toxicity protocols, calculate % survival, LT_{50}, and reproductive success per day and per female; 10) standardize data formats whenever possible. (BASMAA, 1995)

7.3 Methods of Standardization Data Gaps

Existing programs provide a general characterization of stormwater chemical composition, but current protocols are unable to account for sporadic events. As management goals and questions become more specific, more rigorous and focused measurements and sampling programs must be designed.

8.0 CONCLUSIONS

Chemical characterization of runoff from various land uses and various effects studies have been able to provide information on problem pollutants and made comparisons to quantitative goals (i.e. water quality objectives) possible. So far, however, this approach of identifying single problems without taking into account the complex interactions of multiple causes of environmental degradation has not always resulted in tangible environmental improvement. Integrative and quantitative measures of watershed "health" derived from societal values and environmental resources promise to result in more effective management decisions than tinkering with individual parts of a watershed system. Obtaining a "systems" picture is the first step toward setting goals and identifying management objectives. Many of the questions listed in the "Issue Matrix" that this report is based on could be answered more exhaustively if a picture of basic watershed form and structure existed.

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