San Francisco Estuary Regional Monitoring Program for Trace Substances

A Review of Urban Runoff Processes in the Bay Area:

Existing Knowledge, Conceptual Models, and Monitoring Recommendations

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Existing knowledge, conceptual models, and monitoring recommendations

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A report prepared for the Sources Pathways and Loadings Workgroup (SPLWG)

San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP)

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History

The Sources Pathways and Loadings Workgroup (SPLWG) of the Regional Monitoring Program (RMP) was formed in 1999 in response to recommendations from an external Review Panel (Bernstein and O'Connor, 1997). Recommendations also led to a new RMP objective to "describe general sources and loadings of contamination to the Estuary". In 1999, the SPLWG carried out a review of information on sources and loadings of PCBs, PAHs, registered pesticides, mercury, selenium, and other trace metals (copper, nickel, silver, and cadmium) (Davis et al. 1999). Except in the cases of trace metals and selenium, the report concluded that the greatest information gap was an understanding of local watershed sources and loads. Davis et al. (1999) asserted that information reviews and conceptual model development were necessary precursors to field studies that would quantify sources, pathways, and loadings. These concepts were further refined in subsequent reports (Davis et al., 2000; Leatherbarrow et al., 2002). The following were the main recommendations from a series of reports that relate to tributary characterization.

Davis, Abu-Saba, and Gunther (1999). Technical report of the SPLWG.

a. Review chemical use to assist in the prioritization of watersheds for study	PCBs only Not done
b. Conduct studies to evaluate individual drainages and prioritize creeks for further study	On going
c. Conduct a literature review and develop a conceptual model of watershed processes	This report [except PAHs] Done
d. Conduct loading studies to assess the prioritized watersheds	Not done

Davis, McKee, Leatherbarrow, and Daum (2000). Contaminant loads from stormwater to coastal waters in the San Francisco Bay Region: Comparison to other pathways and recommended approach for future evaluation.

a. Watershed Characterization: Characterize and classify the watersheds in the region with regard to factors that control stormwater transport of priority contaminants.	On going
b. Conceptual Model Development: Develop conceptual models for the generation, distribution, transformation, transport, and effects of classes of priority contaminants.	This report [except PAHs] Done
c. Develop Evaluation Strategies: Design and implement appropriate evaluation strategies for classes of contaminants with similar properties.	This report [except PAHs] Ongoing

d. Establish Regional Network of "Observation Watersheds": Carefully select representative "Observation Watersheds" for detailed, long-term evaluation of stormwater loading and related function.	Not done
e. Extrapolate to Other Watersheds: As appropriate, extrapolate results from the Observation Watersheds to other watersheds with similar characteristics.	Not done

Leatherbarrow, Hoenicke, and McKee (2002). Results of the Estuary Interface Pilot Study, 1996-1999.

a. Develop a methodology to accurately monitor contaminant loads from local tributaries by relating continuous monitoring of sediment and stream flow with discrete measurements of contaminant concentrations in the water column at frequent time intervals during the wet season.	See below
b. Prioritize monitoring locations in local tributaries based on contaminant data from recent and historic sediment studies in the Bay margins and watersheds, watershed characteristics (*e.g.*, land use, size, and hydrology), and ongoing or future studies focused on filling data gaps in the local tributaries that may drain watersheds with potentially significant sources of contamination.	On going
c. Explore and develop the application of alternative load indicators for determining trends in contaminant loading in the tributaries.	Not done
d. Develop a network of tributary monitoring locations in selected watersheds for long-term characterization of sources and loadings from selected watersheds with the general objectives of estimating contaminant loading from local tributaries and comparing tributary loading to other pathways of contamination to the Bay.	Not done
e. Coordinate future tributary monitoring with developing and continuing watershed management efforts (*e.g.*, BASMAA) to relate changes in contaminant concentration and loading at the lower end of the watersheds to the combined effects of potential sources in the watersheds, watershed characteristics and hydrology, and management actions.	Not done

Rationale

There are a number of management questions and uncertainties that have emerged through the work of the SPLWG which have implications for planning and development of TMDLs in the Bay and its watersheds by the San Francisco Bay Regional Water Quality Control Board (Regional Board). These questions have helped guide the

efforts of the SPLWG and the literature review developed and presented in this report. Examples of these questions are described below.

(1) Should control measures for a particular contaminant or group of contaminants be implemented to reduce contaminant loads entering the Bay from local tributaries, or should the focus of implementation be on in-place deposits in the Bay?

A small tributaries loading study in a key contaminated watershed would help to answer this question. If a significant load is measured in one such watershed (i.e., 5-10 kg y^{-1} PCBs), this would guide TMDL implementation toward management solutions that included watershed remediation. It might also suggest that further loadings studies should be conducted to quantify other contaminated watersheds. Alternatively, if a contaminated tributary were found to be only a small contributor to the contaminant budget of the Bay, management would need to focus on other solutions for attainment of water quality standards.

(2) Are local tributaries a more important source of some contaminants than the Central Valley?

Presently there is much uncertainty associated with the ratio of non-point source mass loads of mercury and PCBs entering the Bay from the Central Valley through the Sacramento and San Joaquin Rivers (the largest tributaries) versus loads from small tributaries that surround the Bay. If the estimates are too high from one or other of these two pathways, managers may expend much time and money on remediation without a concomitant improvement in water quality in the Bay. A better assessment of loads from small tributaries in combination with a loading assessment presently being conducted by the RMP at the head of the Bay at Mallard Island (contact Lester McKee, lester@sfei.org or Jon Leatherbarrow jon@sfei.org, for information) will help resolve this uncertainty and guide implementation of strategies for water quality attainment.

(3) How will we determine if actions taken to reduce contaminant discharge from the known local sources are effective?

It is expected that the TMDLs will identify implementation actions to reduce contaminant discharge from the watersheds around the Bay Area. A small tributaries loadings study will establish an accurate baseline load estimate that can be used as a benchmark for future comparisons once management actions have been taken to reduce discharge from the watershed sources. Trend indicators are an important component of any adaptive management process. A watershed loads study will provide a metric by which success can be measured.

(4) How accurate are estimates of urban runoff loads from local watersheds?

We cannot afford to measure the load from every local watershed; most load estimates will have to be produced by modeling. Model estimates will be more accurate if the

models are validated against actual load measurements. A watershed loadings study will provide actual load measurements from a watershed that can be used to validate models.

Objectives of this literature review

The primary aim of this literature review was to develop the information necessary to design a small tributaries monitoring study that would implement a new field sampling phase of investigation focused on water quality and loads monitoring in key contaminated watersheds around the Bay Area. Specifically the objectives were as follows:

1. Review information from the literature and local data where they exist on climate and hydrology, suspended sediment, polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), and mercury. Use this information to describe the chemistry and runoff process of each of these substances under the types of environmental and climatic conditions that are found in the Bay Area.

2. Make recommendations on how best to sample small tributaries in the Bay Area for accurate determination of temporal changes in water quality and determination of loads of contaminants of concern.

Report structure

This report is written with each section building progressively off the previous one. Water and sediment are the major vectors for source activation, transport and transmission of contaminants from the watersheds to the receiving waters in the Bay Area. The report begins with a review of climate and hydrology and suspended sediment processes using literature and local data. These sections are followed by sections that describe the physical and chemical properties of PCBs, OCs, and mercury that are of particular relevance to monitoring design in the context of accurately estimating loads. The final section is a synthesis of pertinent points from the other sections and includes recommendations for monitoring small tributaries in the Bay Area. Each section contains references specific to that section.

References

Bernstein, B., and O'Connor, J., 1997. Five-Year Program Review Regional Monitoring Program for Trace Substances in the San Francisco Estuary. Report to the Technical Review Committee of the Regional Monitoring Program for Trace Substances, San Francisco Estuary Institute, Richmond, CA.

Davis, J.A., Abu Saba, K., and Gunther, A.J. 1999. Technical report of the Sources Pathways and Loadings Workgroup. San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, September 1999. 55pp.

Davis, J.A., McKee, L.J., Leatherbarrow, J.E., and Daum, T.H., 2000. Contaminant loads from stormwater to coastal waters in the San Francisco Bay region: Comparison to other pathways and recommended approach for future evaluation. San Francisco Estuary Institute, September 2000. 77pp.

Leatherbarrow, J.E., Hoenicke, R., and McKee, L.J., 2002. Results of the Estuary Interface Pilot Study, 1996-1999. A Technical Report of the Sources Pathways and Loadings Work Group. San Francisco Estuary Regional Monitoring Program for Trace Substances, San Francisco Estuary Institute, Oakland CA.

Part 2: Climate and hydrology

Lester McKee

Introduction

PROBLEM STATEMENT

A detailed understanding of climate and hydrology of Bay Area small tributaries is essential to understanding contaminant loading from this pathway. The way in which climate and hydrological properties of each watershed interact with sources of contaminants is an important precursor to developing contaminant-loading studies. Water discharge from small watersheds directly tributary to San Francisco Bay is known to carry contaminants derived from watershed disturbances associated with urban development, industrialization, agriculture, and atmospheric pathways (Davis et al., 1999; 2000). Contaminant sources may be distributed across watershed surfaces (diffuse sources) or confined to contemporary or legacy point locations (point sources). As such, surface runoff associated with climatic processes interacts differently with each contaminant depending on such factors as the magnitude of the rain event, antecedent moisture conditions, the time since the last event, spatial distribution of the contaminant, and the chemical properties of the contaminant. Under the influence of gravity and water flow, contaminants are transported to the Bay during runoff events. Chemical concentrations will change during runoff resulting in a chemograph (concentration versus time relation) that, when combined with the discharge hydrograph, can be used to estimate the contaminant load entering the Bay.

IMPORTANCE OF RUNOFF FROM LOCAL WATERSHEDS

It is likely that local watersheds contribute a significant fraction of the loads of many contaminants even though runoff from local tributaries accounts for a small fraction of the total freshwater flow to the Bay. Average annual runoff from the combined area of small tributaries has been estimated to be about 890 Mm^3 (Russell et al., 1980). This result is similar to a more recent estimate of 1,049 Mm^3 (Davis et al., 2000). This equates to ~0.138 Mm^3 km^{-2} (equivalent to 138 mm of runoff). Annual average discharge of water from the Central Valley via the Delta over the period 1971 to 2000 was 25,000 Mm^3 (0.162 Mm^3 km^{-2} or 162 mm of runoff). Therefore local watersheds are only responsible for about 4% of the total surface runoff entering the Bay from its entire drainage basin. Given the small size of local watersheds and their close proximity to the Bay, and the fact that maritime Pacific storms tend to track west to east, water derived from local tributaries during intense storms is likely to enter the Bay prior to water from the Central Valley, a time when freshwater flushing is relatively minimal. Dense urbanization in the Bay Area helps to increase contaminant sources, urban drains provide good pathways for contaminants leading to higher concentrations and loads of sediments and related contaminants in urban waterways (see later chapters on contaminants). Soil disturbances associated with development of local tributaries along with highly erosive soils in many local tributaries leads to relatively high but regionally variable sediment loads (see next section on sediment processes). Sediment export from local small tributaries averages ~100 t km^{-2} whereas sediment export from the central valley averages ~14 t km^{-2}. Water from small tributaries that enters at literally hundreds of points on the Bay margin, has higher concentrations of some contaminants, and is less voluminous than

flow from the Central Valley and therefore less likely to flush to the ocean during a rain event. In contrast, water from the Central Valley enters the upstream end of the Bay, and during very large events, a portion of its total volume may flush directly off shore forming a plume of sediment and contaminant-laden water. Clearly, management of the Bay needs to consider not only volumes of water and masses of sediments and contaminants derived from these two primary sources, but also the timing of discharge and its chronic and acute effects on estuarine biota.

Watershed characteristics

AREA

San Francisco Bay is a tidal embayment that receives runoff, sediments and pollutant loads from the Central Valley and local Bay Area watersheds. The watershed upstream of Suisun Bay has an area of 154,000 km^2 or ~37% of the land area of California (411,000 km^2) (McKee et al. 2001). In addition, the Bay also receives runoff, sediment and associated pollutant loads from the urban and agricultural watersheds of the nine adjacent counties (Marin, Sonoma, Napa, Solano, Contra Costa, Alameda, Santa Clara, San Mateo, and San Francisco). Together the small tributaries of the local counties that drain directly to the Bay cover an area of about 7,600 km^2 (Davis et al 2000) or 5% of the total San Francisco Bay Area watershed (Figure 2.1). The ten largest local small tributary watersheds comprise about 4,951 km^2 (Table 2.1). A portion (approximately 950 km^2) of the land area surrounding the Bay is tidal Baylands (Goals Project, 1999). This area should not be considered to be part of the watersheds because of quite different physical, biological and chemical processes and vastly different management goals. Once the wetland area is discounted, the 10 largest watersheds comprise 74% of the total non-tidal watershed area. Of note, the Petaluma River watershed is the 11th largest and RMP data indicate the possibility of contaminant sources in that watershed.

LAND USE AND POPULATION

Runoff, pollutant supply, distribution, and transport are all affected by intensity of land use, land and water management, and history and changes in loading over time (e.g., Collins, 2001). Climatic influences on water and sediment loads are occurring in concert with the changing influences of human population and development. In 1769, the mission era began in California, and by the year 1800, 18 missions had been established along the coast of California including four in the Bay Area. There were missions in Sonoma, San Rafael, San Jose, and San Francisco. The primary land use during the mission era was grazing of cattle, sheep and horses with the addition of fruit and vegetables for subsistence. In the late 1700s as the population began to rise in California; San Francisco was developed as a port for the export of hides to New England (San Francisco Estuary Project, 1991). The discovery of gold in 1848 heralded a rapid growth in population. From 1848 to 1850, the population of California increased from 15,000 to 93,000 and most of it was centered in the gold districts of the western Sierra Nevada and San Francisco. Increased agricultural production was needed to fuel the rising population.

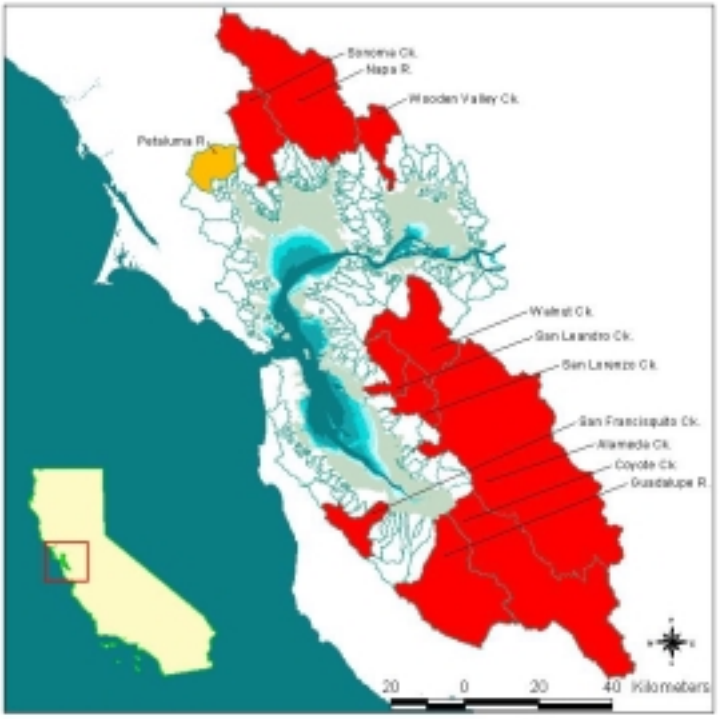


Figure 2.1. Discounting the Central Valley, the 10 largest small tributaries to San Francisco Bay (Red area). Petaluma is the 11th largest. The map also includes many smaller, poorly defined, drainage boundaries extracted using the USGS 10 m DEM (Areas not shaded). Better definition of many of these smaller drainage areas will require the addition of storm drain mapping or higher resolution topography (Wittner and McKee, 2002).

Table 2.1. The 10 largest watersheds of the Bay Area. Areas quoted exclude wetland or tidal areas adjacent to the Bay.

County	Watershed	Rank	Area (km^2)	Percentage of total area of local tributaries
Alameda	Alameda Creek	1	1,662	25.0
Santa Clara	Coyote Creek	2	914	13.7
Napa	Napa River	3	737	11.1
Santa Clara	Guadalupe River	4	556	8.4
Contra Costa	Walnut Creek	5	331	5.0
Sonoma	Sonoma Creek	6	241	3.6
Solano	Green Valley Creek	7	134	2.0
Alameda	San Leandro Creek	8	128	1.9
Alameda	San Lorenzo Creek	9	125	1.9
Santa Clara / San Mateo	San Francisquito Creek	10	123	1.8
			4,951	74.4

For example, dairying, viniculture, fruit and vegetable growing had begun in Sonoma by the 1850s, and scows were actively navigating Sonoma Creek bringing produce to San Francisco (Emanuals and Emanuals, 1998; SSCRCD 1997). In the East Bay, farmers began to plant grain on the flatlands, some of the fertile bottomlands along the creeks were developed into apricot, pear, and cherry orchards, and cattle grazing occurred on the hills (Brewster and Grossinger, 2001). In 1860, as the gold rush era began to draw to a close, the population of the Bay Area rose as displaced gold workers from the Sierra Nevada began to seek a new life. During the last 40 years of the 19th century, population and agriculture continued to expand and by 1900, the population had reached 700,000 (Figure 2.2).

In the early 1900s industry was beginning to boom. The petroleum industry was established (for example, Standard Oil established its west coast refinery in Richmond; Collins, 2001) and rail transportation improved the transmission of goods and services throughout the Bay Area, and connected San Francisco to the eastern United States. By 1915, the population of the nine counties had surpassed 1,000,000 and by 1945 2,000,000 people lived around the Bay (Figure 2.2). In addition to industrialization, this period also saw some remarkable changes in agriculture with increased mechanization and capital investment and the change from small family units to large conglomerates (San Francisco Estuary Project, 1991). The population more than doubled between 1950 and 1970 during the post war "baby boom" and flat areas around the Bay (previously in agriculture) were converted to suburban land use. Since 1970, population growth has leveled, averaging about 11% per decade. Population projections made by the Association of Bay Area Governments (ABAG) suggest a continued increase of between 7 and 8% through to 2020.

This brief review of land use and population trends in the Bay Area has important implications for conceptual model development and implementation of a watershed monitoring program. Monitoring, loads analysis, and subsequent management actions will be carried out in a rapidly changing environment. It will be important to interpret scientific information in this context using recent evaluations of watershed characteristics such as land use, populations, and storm drainage systems.

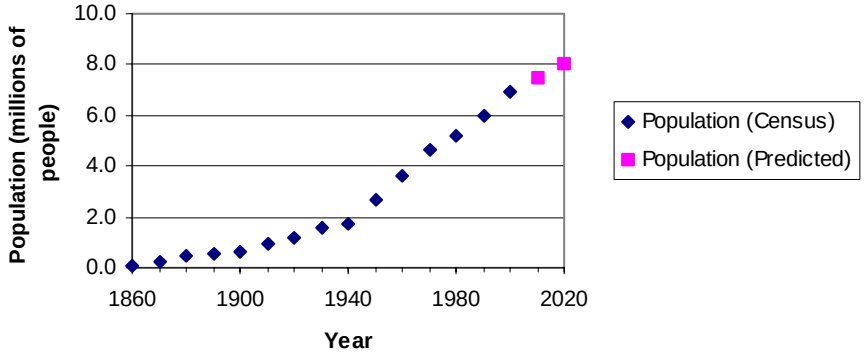


Figure 2.2. Total population in the nine counties of the Bay Area (ABAG, 2002).

TEMPERATURE AND CLIMATE

The residents of the Bay Area enjoy a mild Mediterranean style (dry summer sub-tropical) climate typified by dry, warm summers and cool, wet winters. Official temperature records in San Francisco were begun in 1871 by the U.S. Government, Army Signal Service (Null 2002a), although individuals for two decades prior collected unofficial records. Temperatures in the Bay Area may exceed 40ºC and lows may reach several degrees below freezing. On average, the coolest temperatures typically occur in January, however, the warmest month of the year is dependent upon location (Figure 2.3). In areas that are strongly influenced by wind and fog moving onto the Bay through the Golden Gate and from the Pacific coastline, the maximum average temperature occurs in September. In other areas maximum temperatures typically occur in July.

The high variability of temperature and development of multiple microclimates around the Bay Area has implications for estimation of runoff from ungauged watersheds. Evapotranspiration will vary considerably month-to-month and place-to-place, affecting the rainfall excess available for runoff. This is especially important in rural watersheds where impervious surfaces are at a minimum and soil moisture conditions play a larger role in runoff production.

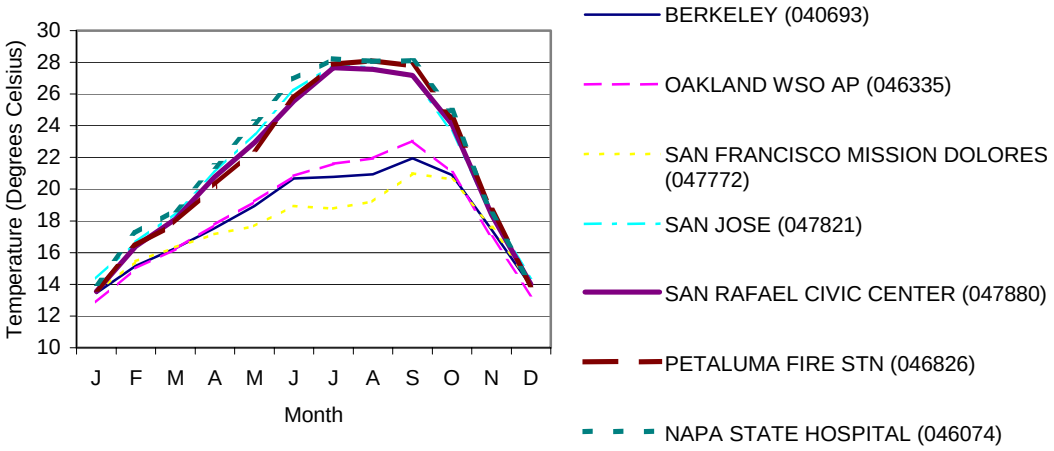


Figure 2.3. Monthly average maximum temperatures around the Bay Area. Data extracted from the climate averages for the Bay region (NWS, 2002).

Rainfall

GAUGING HISTORY, SEASONAL AND SPATIAL DISTRIBUTION

An understanding of the monthly and annual variability, and distribution of rainfall is an essential precursor to monitoring runoff and pollutant loads in small

tributaries. In areas where no measurement is made, models and extrapolation methods for estimating loads are likely to be driven at least in part by rainfall distribution.

Thomas Tennent, an instrument maker, began continuous rainfall statistics for San Francisco on August 14, 1849 (Null, 2002a). Rainfall records were begun in San Rafael in 1878, Berkeley in 1889, Napa and Calistoga in 1897, and in San Jose and Oakland in 1898. Most other locations in the Bay Area have less than 70 years of data. Rainfall in the Bay Area is predominantly maritime, with regional-scale weather systems moving on shore in response to the position of the Pacific high-pressure zone and westerly winds that bring moist air from the Pacific Ocean. In general, higher rainfall occurs on westerly and southerly facing slopes and on topographically higher areas. Rainfall decreases with distance from the coast and most storm tracks pass further to the north, resulting in a general increase in annual rainfall towards the north (Rantz, 1971). As such, annual average rainfall (July – June) varies from <300 mm (~12 inches) in low-lying areas or areas in a rain shadow (e.g. parts of Santa Clara Valley) to 1,400 mm (55 inches) on mountaintops (Figure 2.4). The maximum measured climatic year rainfall occurred in the 1982-83 season at Kentfield, Marin, where as the minimum measure rainfall occurred in Livermore during the 1975-76 season. On a regional scale, the map of mean annual precipitation developed by Rantz depicts the rainfall distribution well, however, recent analysis of the map for the purposes of modeling landslides and indications from vegetation distributions suggest that rainfall may have been underestimated in some areas such as the East Bay hills (Ray Wilson, USGS, personal communication February 2002). Further, although average annual rainfall has increased by about 50 mm in the past 30 years (discussed later), the map developed by Rantz remains a good approximate representation of the rainfall distribution in the Bay Area. About 90% of the annual precipitation occurs during the period November through April (Table 2.2) and the bulk of that occurs as a series of storms that generally affect the whole region to varying degrees (Rantz, 1971).

DRY VERSUS WET PERIODS

The large inter-annual variability in climate will have profound effects on the collection of representative watershed data and will make it more difficult, but not impossible, to interpret the data gathered. Annual rainfall in the Bay Area varies considerably from year to year. For example, rainfall recorded in San Francisco over the past 150 years has varied from 188 mm (7.4 inches) to 1251 mm (49.3 inches) (Figure 2.5). In addition to the large variation, the Bay Area typically undergoes successive periods of drier than average years and successive periods of wetter than average years, illustrated by positive and negative slopes on a graph of cumulative deviation from the mean (Figure 2.6). Dry years can be defined as those with rainfall less than the 30th percentile and wet years as those with rainfall greater than the 70th percentile based on the period of record (Jan Null personal communication). Notable dry periods occurred from climatic year 1929-34, 1946-50, 1960-66, 1975-77, and 1987-92. Notable wet periods have occurred from climatic year 1865-68, 1878-81, 1914-16, 1940-43, 1982 and 1983 (fifth and sixth wettest years on record) and 1995-00. There also appear to have been

longer climatic shifts as well but it is impossible to predict if the Bay Area is moving towards a drier or wetter period.

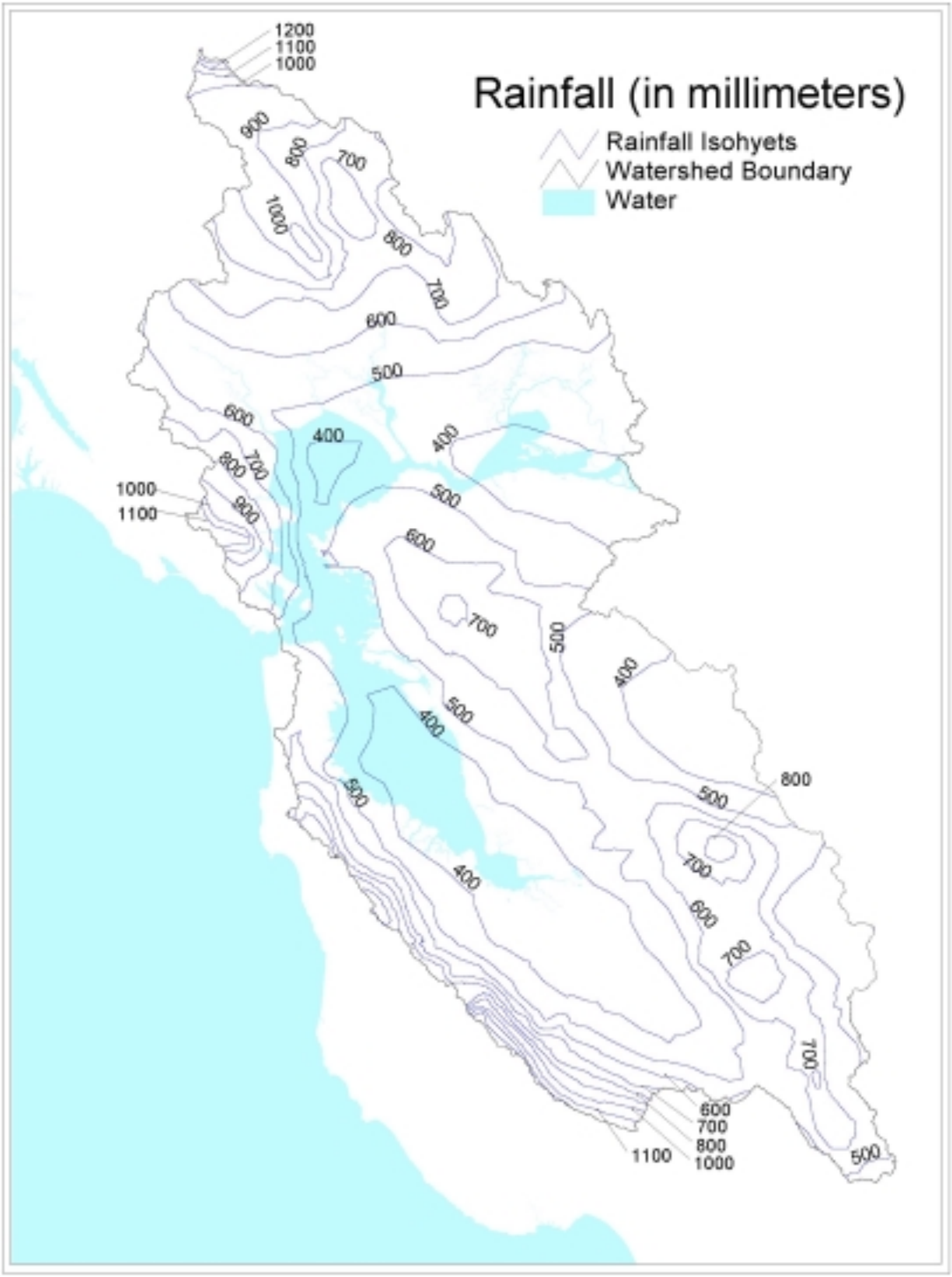


Figure 2.4. Distribution of rainfall (mm) in the Bay Area (After Rantz, 1971)

Table 2.2. Monthly rainfall (mm) at selected locations around the Bay Area. Extracted from the climate summaries provided by the Western Region Climate Center (WRCC, 2002a).

	Berkeley	Cumulative	SF Mission Dolore	Cumulative	San Jose	Cumulative	San Rafael	Cumulative	Livermore	Cumulative	Petaluma FS	Cumulative	Napa SP	Cumulative
	1919-2000	% annual	1914-2000	% annual	1948-2000	% annual	1948-2000	% annual	1930-2000	% annual	1948-2000	% annual	1917-1997	% annual
N	73	12	66	12	44	12	112	12	44	12	86	13	77	12
D	102	30	95	30	58	28	163	30	63	29	106	30	114	31
J	123	50	114	52	78	49	218	54	76	50	145	53	124	51
F	106	68	96	70	63	66	173	73	66	68	117	71	109	68
M	82	82	72	84	59	82	113	86	54	82	87	84	86	82
A	44	89	35	90	27	89	52	91	27	90	40	90	41	89
M	16	92	14	93	10	92	17	93	11	93	13	92	17	92
J	5	93	4	93	2	93	6	94	3	94	5	93	5	93
J	1	93	1	94	1	93	1	94	1	94	1	93	1	93
A	2	93	1	94	2	94	2	94	1	94	2	94	2	93
S	7	95	6	95	5	95	8	95	4	95	6	95	7	94
O	33	100	27	100	19	100	45	100	18	100	34	100	36	100
	593		*530*		*368*		*911*		*368*		*641*		*620*	

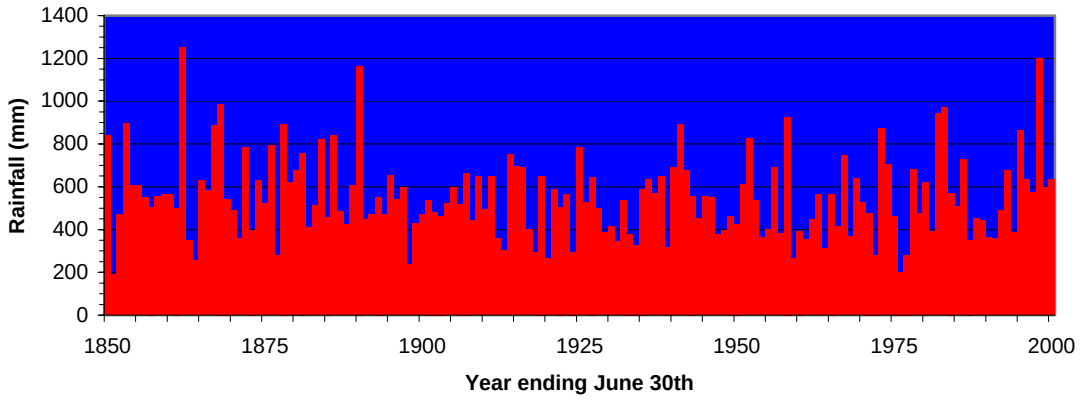


Figure 2.5. Annual rainfall for San Francisco. Data plotted with permission from Jan Null, Golden Gate Weather services (Null, 2002b).

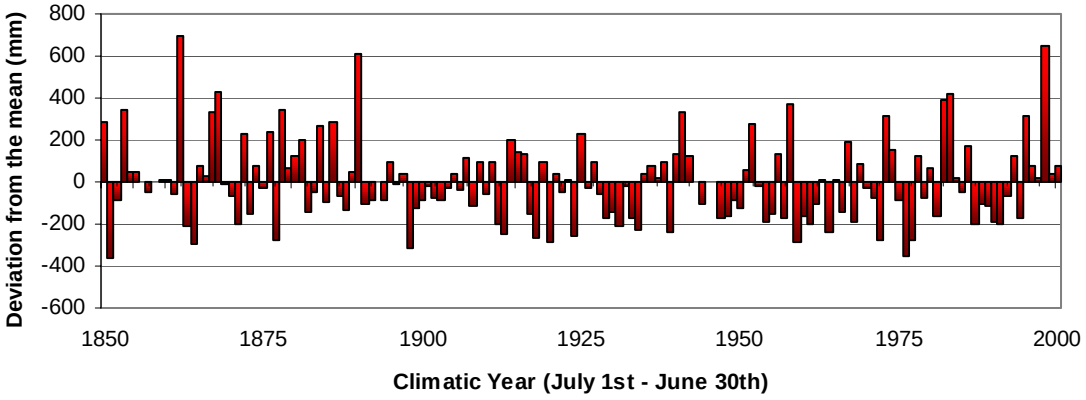


Figure 2.6. Annual rainfall for San Francisco. Graph shows an analysis of annual deviation from the long-term mean rainfall (554 mm), an indicator of periodic climatic change in the Bay Area.

This large variability in climate has strong influences on stream channel formation and channel stability. Channels in the western United States may go though periods of active erosion, instability, and states of healing (Leopold, 1994). Inman and Jenkins (1999) describe decadal variations in sediment fluxes in California watersheds associated with a dominantly dry period (1944-68) and a dominantly wet period (1969-95) (see sediment chapter for more details). Special care is needed to develop hydrological and contaminant models that take into account monthly and inter-annual climatic conditions and the effects of erosion and depositional processes and sequences in the watersheds on overall sediment and contaminant transport.

RAINFALL AS A DRIVER FOR SEDIMENT TRANSPORT

Antecedent moisture conditions, annual rainfall, rainfall intensity, and the number of rain-days are important predictors of the risk of landsliding in the Bay Area (Wilson, 2000; 2001). In general, as these soil and climatic attributes increase, the risk of slope failure increases and colluvium is an important supply of sediment to streams in the Bay Area (see sediment chapter for more details). Therefore, an understanding of rainfall distribution throughout the year is an important precursor to understanding sources, transport, and loads of sediment and related pollutants. In addition, changes in climate will affect stream sediment supply from colluvial sources on event, to annual and decadal time scales.

During the first rains of the year, significant runoff is not produced from a given rain event until the soils become saturated. For example, this seems to occur after about 100-200 mm of rain has accumulated at the St. Helena gauge (climatic year beginning October 1st) in the Napa River watershed (Figure 2.7). This phenomenon is modified from the natural state in urban areas by impervious surfaces. In urban areas that are almost 100% impervious, runoff will occur when the catch basins and drop boxes and other low points are full such that urban runoff is proportional to event magnitude rather than antecedent moisture conditions.

The average number of rain-days varies considerably around the Bay Area (Table 2.3). Angwin near Napa has recorded the highest average number of raindays ina year of 77. Return frequencies of rainfall of a given intensity and duration have been described by Rantz (1971). Typically, locations with higher mean annual rainfall have greater rainfall intensity during storms. Average rainfall was greater in the last 30 years (1971-2000) in comparison to 1941-1970 mostly because the latter time period included 4 El Nino events. Annual rainfall in San Francisco was 51 mm (2 inches) greater and annual rainfall at Napa State hospital was 56 mm (2.2 inches) greater in the latter period. Given that rainfall intensity is correlated to annual rainfall, it seems likely that there may have been a corresponding rainfall intensity increase (Ray Wilson, USGS, personal communication, February 2002).

Data available for San Francisco were tested for the two time periods (1941-1970 and 1971-2000). The average number of rain days increased from 68 to 71 and the average rainfall increased by 7.6 mm to 8.0 mm in a 24-hour period. Monthly distributions of rainfall have also shifted slightly with remarkable similarity across the region (Figure 2.8). These observed slight climatic shifts present the possibility that sediment supply and transport as well as natural loads of contaminants may have increased in the last 30 years relative to the earlier period.

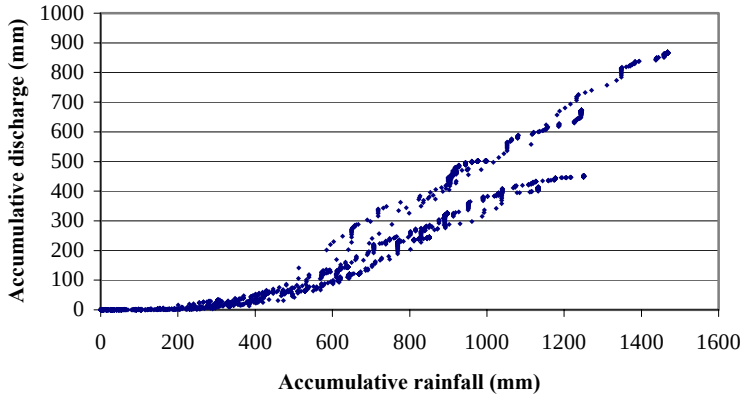


Figure 2.7. Response of the Napa River watershed to first winter rains of the year (water year beginning October 1st). Rain data are from St. Helena and runoff data are from Napa River at Napa for the period 1991 water year to 2000 water year.

Table 2.3. Number of rain days at a selection of locations in the Bay Area (WRCC, 2002b).

	Berkeley (040693) 1919-2000	Livermore (044997) 1930-2000	San Jose (047821) 1948-2000	San Rafael Civic Center (047880) 1948-2000	Sonoma (048351) 1952-2000	Calistoga (041312) 1948-2000
Precipitation	**Number of days**	**Number of days**	**Number of days**	**Number of days**	**Number of days**	**Number of days**
≥ 0.01 in (0.254mm)	63	59	58	66	66	67
≥0.10 in (2.54mm)	42	34	33	44	46	49
≥0.50 in (12.7mm)	16	9	9	23	21	25
≥1.00 in (25.4mm)	6	2	2	12	9	12

Runoff

GAUGING HISTORY AND VARIABILITY

Using the records available for the largest of the small tributaries in the Bay Area it is possible to gain a good understanding of daily, monthly, spatial and inter-annual runoff processes. Discharge gauging began on Alameda Creek at Niles in April 1891 and reliable data collection has continued through to the present. Also in Alameda County, San Lorenzo Creek has a record from October 1946 to present. Gauging began on Coyote Creek in 1903 and reliable statistics are available from 1907 to 1986 with a break

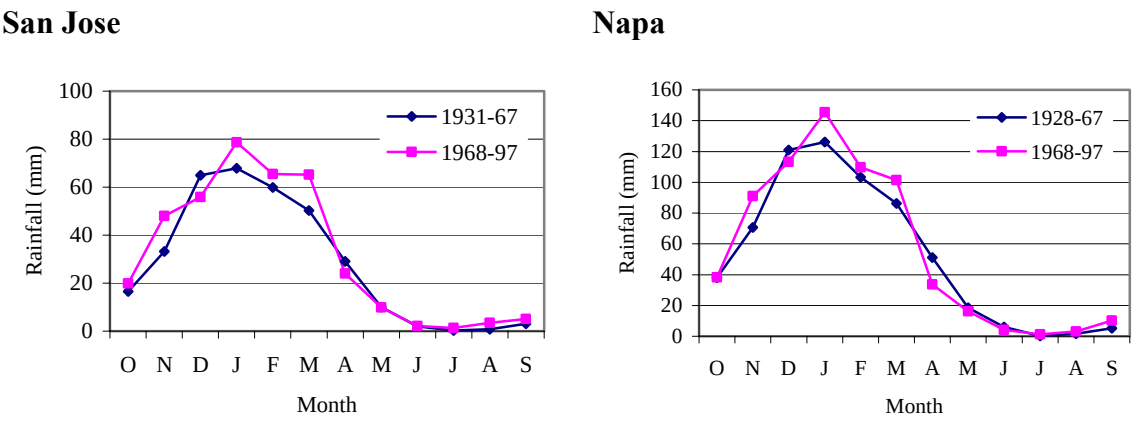


Figure 2.8. Changes in monthly rainfall distribution for two locations in the Bay Area.

between 1912 and 1916. The USGS resumed gauging on Coyote Creek in 1999 at the highway 237 downstream from the original location. Reliable data are available for Guadalupe River from 1930 to present and on San Francisquito Creek from 1931 to present. Of the largest watersheds in the Bay Area, Petaluma River and Sonoma Creek have the shortest records of only 14 years from 1949 to 1962 and 25 year from 1955 to 1981 for Petaluma and Sonoma respectively. These short records may not completely describe long-term inter-annual variation in runoff. Gauging on the Napa River began in October 1929 but was discontinued September 1932. Gauging resumed again in 1959 and continued to the present. Walnut Creek has a continuous record at two locations (Walnut Creek at Walnut Creek and Walnut Creek at Concord) from 1952 to 1992.

Runoff follows the same spatial trends as rainfall, however variation within a year is affected by soil moisture storage and evapotranspiration. Watershed runoff in the Bay Area may be perennial or intermittent though commonly one stream may have reaches that have flow all year round and other reaches that flow only during storms. Between 87% and 99% of the runoff in the Bay Area occurs during the six months of November through April (Table 2.4). An example of an exception is Coyote Creek that has only 56% of it annual runoff during November to April. This watershed has been impounded for flood control since 1936. During the pre-impoundment period of 1907 to 1935 total annual runoff was virtually the same but an average of 96% of the annual runoff occurred during the 6-month wet season, illustrating the deliberate effects of flow regulation on runoff perhaps typical of other regulated watersheds in the Bay Area.

Annual runoff varies spatially mainly in response to rainfall, although evapotranspiration, geology, slope, and basin area play a minor role as well. For a selection of watersheds, Table 2.4 demonstrates spatial variation in annual runoff of between 69 mm (2.7 inches) and 412 mm (16.2 inches). The majority of the Bay Area can be classified as semiarid (10-20 inches [254-508 mm] of rainfall and 0.3-5 inches

Table 2.4. Monthly runoff in a selection of the largest Bay Area watersheds (USGS, 2002). Annual averages are calculated for the water year ending September 30th.

Month	Alameda Creek At Niles 1891-2000	Cumulative % of annual	Coyote Creek Nr. Madrone 1936-1987	Cumulative % of annual	Coyote Creek Nr. Madrone Pre-regulation 1907-1935	Cumulative % of annual	Guadalupe River at San Jose 1930-2000	Cumulative % of annual	San Francisquito Creek at Stanford 1931-2000	Cumulative % of annual
N	1.7	2.5	4.9	4.4	0.4	0.4	3.1	2.8	4.5	2.3
D	5.4	10.3	5.2	9.2	8.5	7.7	8.0	10.2	18.9	11.8
J	15.5	32.6	5.7	14.3	27.3	31.4	20.9	29.3	49.9	37.1
F	18.6	59.5	14.5	27.4	35.0	61.7	29.9	56.8	57.4	66.2
M	15.7	82.2	17.2	42.9	30.9	88.5	27.7	82.2	42.0	87.5
A	6.5	91.6	14.0	55.6	9.1	96.4	12.8	93.9	19.3	97.3
M	2.0	94.4	9.8	64.4	2.1	98.2	2.4	96.1	3.0	98.8
J	1.0	95.9	9.5	72.9	1.0	99.1	0.9	96.9	0.9	99.2
J	0.8	97.1	8.8	80.9	0.5	99.4	0.7	97.6	0.4	99.4
A	0.7	98.2	7.9	88.0	0.2	99.7	0.7	98.2	0.2	99.5
S	0.6	99.1	6.9	94.3	0.2	99.8	0.7	98.8	0.2	99.6
O	0.6	100.0	6.3	100.0	0.2	100.0	1.3	100.0	0.7	100.0
Annual (mm)	*69*		*110*		*118*		*109*		*197*	
Annual (in)	*2.7*		*4.3*		*4.6*		*4.3*		*7.8*	
	Petaluma River at Petaluma 1948-1963	**Cumulative % of annual**	**Sonoma Creek at Agua Caliente 1955-1981**	**Cumulative % of annual**	**Napa River nr Napa 1929-2000**	**Cumulative % of annual**	**Walnut Creek at Concord 1952-1992**	**Cumulative % of annual**	**San Lorenzo Creek at Hayward 1940-2000**	**Cumulative % of annual**
N	2.1	1.1	13.2	3.2	9.5	2.9	7.6	4.7	2.7	1.7
D	35.7	19.9	58.7	17.6	36.8	14.4	18.0	15.8	16.2	11.7
J	55.6	49.3	128.9	49.1	92.3	43.0	35.5	37.7	42.8	38.3
F	55.0	78.3	102.9	74.2	85.9	69.7	34.2	58.9	39.6	62.9
M	26.9	92.5	59.7	88.8	63.3	89.4	27.9	76.1	29.8	81.4
A	12.8	99.3	31.9	96.6	22.7	96.4	18.2	87.4	18.9	93.1
M	0.5	99.5	6.3	98.2	6.5	98.4	5.6	90.9	4.5	95.9
J	0.0	99.5	2.1	98.7	2.2	99.1	3.3	92.9	1.8	97.1
J	0.0	99.5	0.8	98.9	0.7	99.3	2.4	94.4	0.8	97.6
A	0.0	99.5	0.5	99.0	0.3	99.5	2.0	95.6	0.6	97.9
S	0.0	99.5	0.4	99.1	0.3	99.5	2.1	96.9	0.5	98.2
O	0.9	100.0	3.7	100.0	1.5	100.0	5.0	100.0	2.9	100.0
Annual (mm)	*189*		*412*		*322*		*162*		*152*	
Annual (in)	*7.5*		*16.2*		*12.7*		*6.4*		*6.0*	

[7.6-127 mm] of runoff) to subhumid (20-40 inches [508-1,016 mm] of rainfall and 3-20 inches [76.2-508 mm] of runoff). However there are small, topographically higher, and western facing areas that are humid (>40 inches of rainfall and >10 inches of runoff) (Rantz, 1971, 1972).

Spatial runoff distribution maps for the Bay Area have been developed using data from 1931 to 1970 (Rantz, 1974a). Data presented by Rantz for watersheds in near natural condition show a spatial variation in the Bay Area of <25.4 mm (1 inch) in small watersheds near Livermore to more than 457 mm (18 inches) in mountainous watersheds of Marin County. The proportion of rainfall that maintains stream flow (the runoff coefficient) varies greatly from year to year and from place to place. For example, during the drought years of 1976 and 1977, many of the watersheds in the Bay Area had virtually no runoff whereas during wet years such as 1983, up to 70% or more of the rainfall can runoff. Rantz (1974a) developed a series of rainfall / runoff relations for four sub-regions, three of which are relevant to this review (Table 2.5 and Figure 2.9). Runoff coefficients can vary from 0% to 75% of the annual rainfall depending on the magnitude of the annual rainfall, the proximity to the Pacific coast and the steepness of the terrain.

Table 2.5. Expected runoff for various amount of rainfall in regions in the Bay Area. Data extracted from Rantz (1974a).

North Bay				Peninsula and South Bay				East Bay			
Precipitation		Runoff		Precipitation		Runoff		Precipitation		Runoff	
(mm)	(in)	(mm)	(in)	(mm)	(in)	(mm)	(in)	(mm)	(in)	(mm)	(in)
356	14	41	1.6	305	12	5	0.2	330	13	0.0	0.0
432	17	86	3.4	406	16	66	2.6	356	14	2.5	0.1
660	26	201	7.9	483	19	104	4.1	381	15	5.1	0.2
711	28	231	9.1	889	35	267	10.5	406	16	12.7	0.5
737	29	249	9.8	1,067	42	356	14.0	432	17	22.9	0.9
787	31	290	11.4	1,118	44	386	15.2	457	18	35.6	1.4
889	35	381	15.0	1,168	46	422	16.6	610	24	127.0	5.0
2,032	80	1,524	60.0	1,219	48	462	18.2	762	30	203.2	8.0
				1,270	50	508	20.0	889	35	254.0	10.0
				1,524	60	762	30.0	940	37	279.4	11.0
								1,118	44	386.1	15.2
								1,168	46	421.6	16.6
								1,219	48	462.3	18.2
								1,270	50	508.0	20.0

Runoff variability in Bay Area watersheds is among the highest in the world. High inter-annual variability of annual runoff in the Mediterranean climatic settings such as the Bay Area poses greater challenges for data collection and modeling relative to other parts of the world. Watersheds in the Bay Area show a coefficient of variation (CV,

standard deviation divided by the mean x 100) between 78% and 117% (Table 2.6). Sonoma Creek shows a lower inter-annual variation compared to other watersheds (CV =

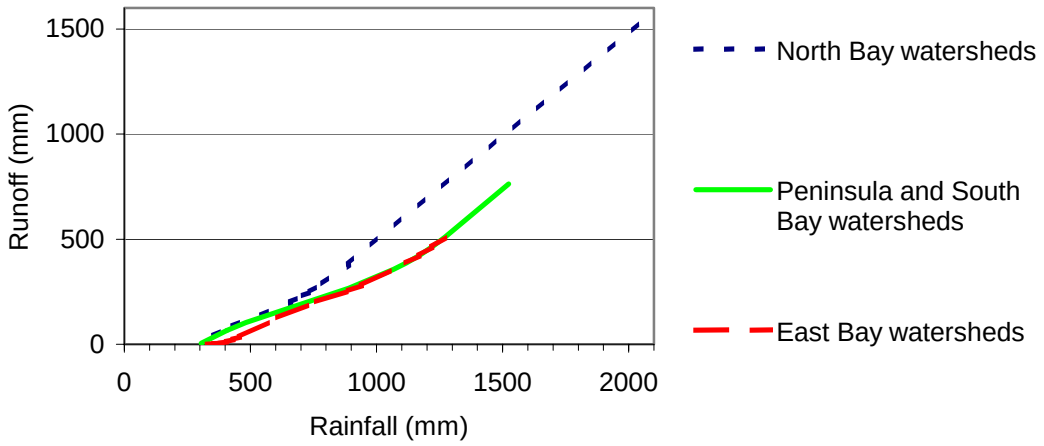


Figure 2.9. Regional rainfall runoff relationships for the Bay Area. After Rantz (1974a).

Table 2.6. Runoff variation in the larger watersheds of the Bay Area calculated for the period of record. All statistics are calculated for the water year ending September 30th.

Annual runoff (mm)	Alameda Creek near Niles 1892-2000	Coyote Creek near Madrone	Guadalupe River at San Jose	San Francisquito Creek at Stanford	Petaluma River at Petaluma	Sonoma Creek at Agua Caliente	Napa River near Napa	Walnut Creek at Concord	San Lorenzo Creek at Hayward
Min	0	2	1	0	25	8	1	20	6
Max	338	514	638	769	503	921	926	679	519
Mean	69	113	109	197	189	412	322	162	152
Standard deviation	70	100	127	190	158	269	250	146	142
Coefficient of variation	101	89	117	96	84	65	78	90	94

65%) perhaps indicative of the short period of record. The average CV for discharge in an analysis of 974 watersheds from around the world was computed as 43% (Finlayson and McMahon, 1988). The average for North America was found to be 31%. The most variable watersheds were found in Australia and South Africa, a runoff response to Mediterranean, sub-tropical and tropical climatic zones.

As noted for long term rainfall records in San Francisco, analysis of annual runoff demonstrates flood and drought periods and longer term climatic trends (Figure 2.10). Although Alameda Creek runoff compares closely to rainfall variation in San Francisco (Figure 2.6), there are notable differences between 1905 and 1925. This may be

indicative of slight spatial climatic differences between San Francisco and Alameda or more likely that runoff is a better indicator of and more sensitive to flood and drought conditions because each year of runoff is not entirely independent of the previous year. Leopold (1994) suggested that channels in western United States were in a state of erosion and instability during the first quarter of the 20th century and then changed to a state of healing by vegetation through to the middle of the 20th century. These observations may provide evidence of the influence of drought conditions on sediment transport and depositional processes in watersheds of the western US, and the Bay Area.

Pollutant response to these climatic processes can be variable. For example, a year of moderate flow that follows several years of drought may produce greater loads of contaminants than a year of extreme high flow that follows other years of greater than average flow. Scientists, engineers and managers in the Bay Area are used to dealing with the issue of variability. Designs of data collection and modeling programs will need to be focused on data and calibration for the wet season floods and need to span a range of wet years and dry years. It is highly possible that a scientist or manager may initiate a study that aims to characterize flood runoff and then end up waiting for several years before event of sufficient magnitude occur.

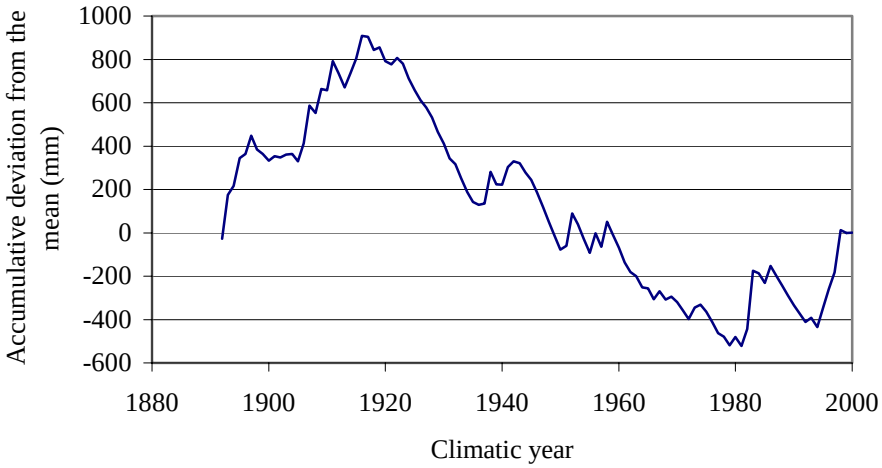


Figure 2.10. Runoff variability for Alameda Creek at Niles over the past 110 years. A negative slope is indicative of successive years of lower than average rainfall whereas a positive slope indicates successive years of above average annual rainfall.

RESPONSE TIME

The speed with which a watershed responds to rainfall (response time) is important for determining the timing of contaminant transport and for designing watershed monitoring that aims to capture variability during floods. Response time is

dependent on factors such as watershed size, slope, soil type and geology, rainfall intensity, and antecedent moisture conditions. Soil moisture plays a dominant role in the water budget during the first rains of the wet season in November. During this period, 1 in (25.4 mm) or more of rainfall may not cause any significant surface runoff in areas where there are pervious watershed surfaces, though soil moisture will increase and ground water recharge will occur that may result in a base flow over the days and weeks that follow. Later in the runoff year when soils are moist, response time varies mainly with watershed size (Figure 2.11). The scatter on this graph is indicative of the other factors such as rainfall volume and intensity and watershed slope.

Rantz (1971) discussed response time for urbanized watersheds and related it to degree of urbanization. Watersheds that are completely urbanized in the Bay Area are likely to peak in 25% of the time of their original non-urban state. Those that are 50% urbanized would be expected to peak in 62% of the time in a natural condition. A prediction of response time is necessary for improving initial sampling design if the scientist is trying to capture concentration variability during floods, however usually the initial hypotheses are modified after the first year of empirical data collection.

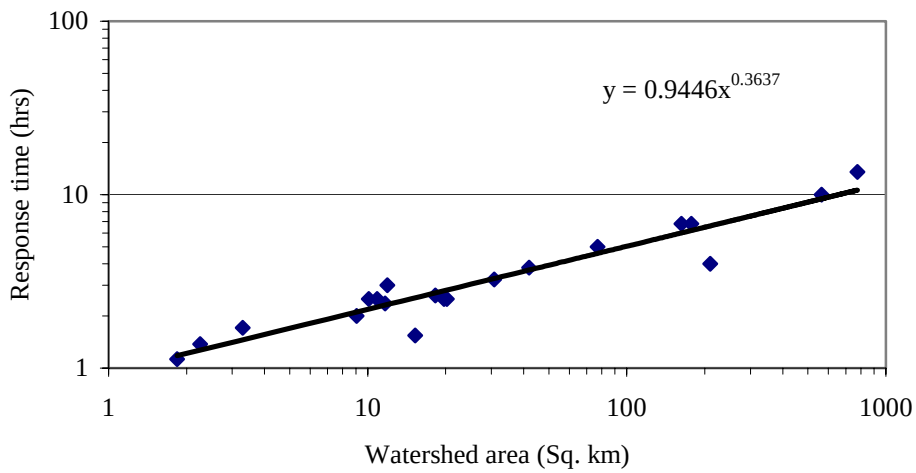


Figure 2.11. Response time of peak runoff to rainfall in watersheds of varying size for the San Francisco region. Data extracted from USACE, 1963, Anon., Late 1950s, and Rantz, 1974b.

IMPACTS OF URBANIZATION

The impacts of the urban environment on hydrology of streams can be divided into three main categories:

1. Impacts to the flood discharge peaks and the lag time from peak rain mass to peak runoff;

2. Increases in the total discharge volume;
3. Changes in the monthly runoff distribution.

The principal impact of urbanization is on the peak discharge (Waananen et al., 1977). In urban areas, runoff volumes are transmitted to receiving waters much more quickly (lag time decreases) because of increased velocities on catchment surfaces, increased velocities in hydraulically more efficient drainage channels and storm sewer networks, and because floodplains in the lower parts of the watersheds are often deliberately isolated from the channel network by structural controls. The magnitude of the effects of urbanization is also influenced by the spatial distribution of urbanization in a watershed. Urbanization in the lower parts of Bay Area drainage basins may cause short sharp peaks that are routed to the stream network and precede flow from the upper drainage basin. Alternatively, increased flow resulting from urbanization in the upper parts of watersheds may arrive in the lower watershed at the same time as flow from lower watershed tributaries. Thus peak flows may be reduced or increased depending on the basin configuration and patterns of urbanization (Waananen et al., 1977).

The amount of runoff relative to the size of a rainstorm generally increases as the wet season progresses in response to a general increase in soil moisture. An increase in soil moisture is effectively the same as an increase in imperviousness. In cases where there is an increase in peak flow, the magnitude of the increase will typically be greater for smaller floods (Figure 2.12). This phenomenon is best illustrated by considering a low rainfall year of 300 mm. If this rainfall is distributed over three or four storms, areas of agricultural and open space will produce virtually no runoff, whereas in a 100% urbanized area, runoff is likely to be 70 to 90% of the rainfall.

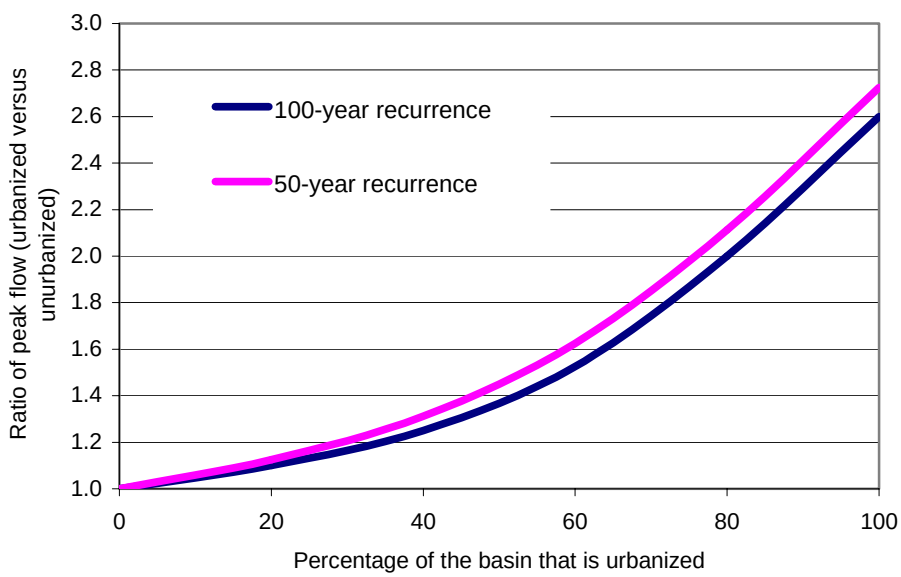


Figure 2.12. Impacts of urbanization on peak discharge in hypothetical Bay Area streams. After Waananen et al., 1977.

In the urban setting, annual runoff volumes are significantly increased because of a decrease in infiltration associated with impervious urban surfaces (roofs, roads, and parking lots). During pre-urban conditions, runoff during the dry season, during early wet season floods and during drier years and successive dry years would have been minimal. This is because soil infiltration during these dry times exceeds rainfall intensity. Therefore, most of this volume increase associated with urbanization occurs during drier times and during smaller floods, not only changing the total annual volume of runoff but changing the monthly distribution as well. Decreases in infiltration impact ground water recharge with subsequent effects on base flow during times when there is no rainfall. Dams and managed releases, retention basins, and withdrawal for irrigation also deliberately impact the monthly distribution. Less deliberate hydrological changes include legal or illegal point source release, return flows from irrigation, watering lawns, and washing cars.

Given the steadily urbanizing environment in the Bay Area, it seems likely that the runoff from local watersheds may have changed to more or less confined to a few months in the wet season depending on the types of watershed modifications, and that the total annual runoff volume from local watersheds is increasing over time. Even if BMPs ensure that contaminant concentrations in watersheds remain constant, contaminant loads entering San Francisco Bay might still increase because runoff volume will continue to increase with increasing impervious surfaces.

At first glance, in the case of Alameda Creek at Niles and Guadalupe River at San Jose, this appears to be true (Figure 2.13). Annual runoff at Niles on Alameda Creek has increased from 51 to 80 mm and at San Jose on the Guadalupe River from 83 to 147 mm. Given that rainfall has increased by about 50 mm over the same period, an analysis was done to test if rainfall alone could have caused the increase in runoff. This was done using relationships between annual rainfall and annual runoff developed by Rantz (1974a) and reproduced in Tables 2.5 and Figure 2.9 of this report. Annual average rainfall for Alameda Ck basin was about 480 mm (19 inches). If this were increased by 50 mm, an increase in runoff from 51 mm to 83 mm would be expected. In the case of Guadalupe River at San Jose, annual average rainfall for the basin was about 530 mm (21 inches). If this were increased by 50 mm, using the Rantz relationships, an increase in runoff from 83 to 134 mm would be expected. It appears that all of the increase in runoff from Alameda Creek (about 30% urbanized) can be accounted for by climatic changes alone, however, in the Guadalupe watershed, there appears to be an effect associated with urbanization (70% urbanized).

Increased flow peaks, annual runoff volume, and a decrease in response time have implications for contaminant loads entering the Bay. The process of mobilization of contaminants at source may be more efficient, there may be less chance for deposition and storage during transport, and loads may delivered over a shorter time span potentially worsening an acute impact to the receiving water body. Estimates of increasing runoff have been made previously. For example, urbanization of Colma Creek, South San

Francisco caused flooding problems during the 1960s (Hydrocomp INC. 1973). A study completed in 1980 suggested that runoff had increased by 47% from 1800 to 1980 and would increase a further 2% by 2000 (Russell et al., 1980).

Alameda Creek at Niles **Guadalupe River at San Jose**

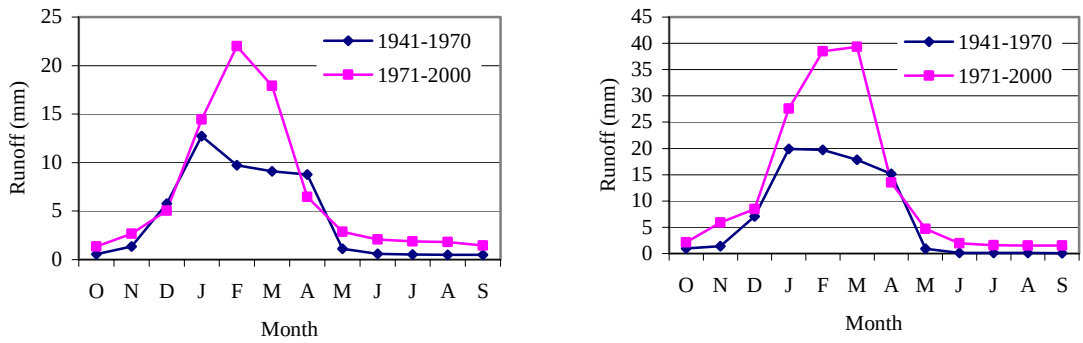


Figure 2.13. Changes in monthly runoff distribution for two locations in the Bay Area.

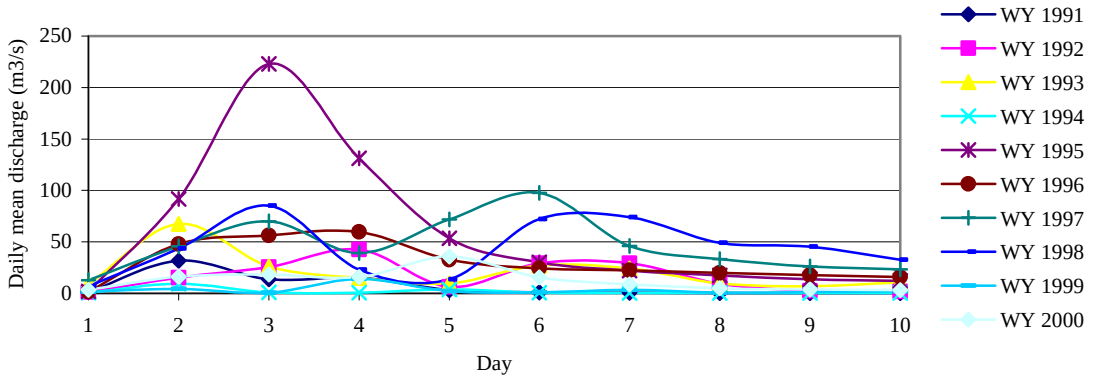
STORM RUNOFF CHARACTERISTICS IN THE BAY AREA

Analyses of storm runoff character have important implications for flood sampling for suspended sediment and trace contaminants. Sampling teams will need to be responsive to weather forecasts and be willing to remobilize for subsequent peaks that commonly occur less than 7-10 days apart especially later in the wet season.

An analysis of storm characteristics was carried out for the Guadalupe River at San Jose and the Napa River at Napa. Guadalupe is a low rainfall highly urbanized watershed with an area of 378 km^2 at the gauge that contrasts with Napa, a high rainfall watershed with mainly agricultural and open land use and an area of 565 km^2 at the gauge. In both watersheds, the 1995 flood was the largest in the past decade (Figure 2.14). In the case of Guadalupe, discharge peaked at 17.4 feet (5.3 m), 11,000 cfs (311 m^3s^{-1}) with a mean daily discharge of 7,870 cfs (223 m^3s^{-1}). In contrast, the Napa River watershed with an area at the gauge of 1.5 times that of Guadalupe and a greater rainfall peaked at 30.5 feet (9.3 m), 32,600 cfs (923 m^3s^{-1}) with a mean daily discharge of 19,100 cfs (541 m^3s^{-1}). The Guadalupe River averaged seven floods per year with an average daily discharge in excess of an arbitrarily chosen discharge of 200 cfs (5.7 m^3s^{-1}). On average, five of these were single peak events and two were events with three to five peaks less then seven days apart. Napa River on average had nine flood peaks greater than an arbitrarily chosen discharge of 300 cfs (8.5 m^3s^{-1}) per year; on average three of these floods were single peak events. Using these arbitrary flood definitions, on average, there is a 17% chance that the first flood will occur in September or October, a 45% chance of the first flood being before November 30th and a 76% change that the flood season will begin prior to New Year. A sampling protocol that aims to begin collection in

October and uses real-time rainfall, runoff, and turbidity data served up via the Internet to inform field participants will have the best chance of success.

Guadalupe River at San Jose



Napa River at Napa

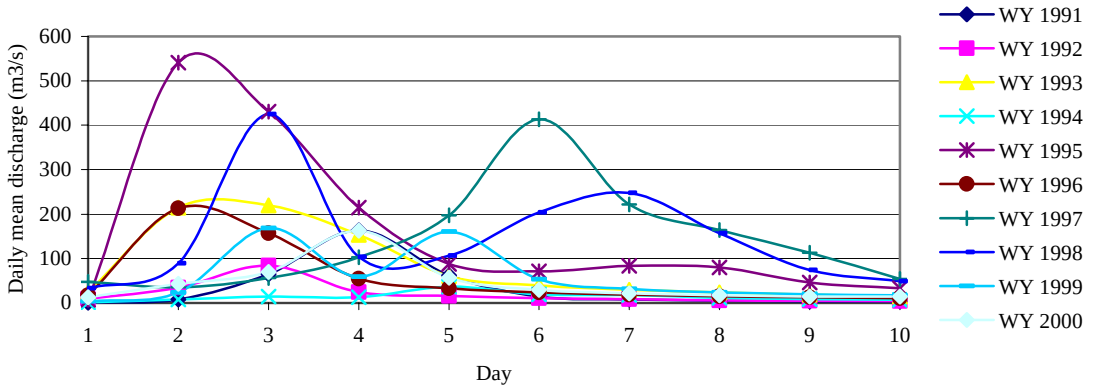


Figure 2.14. Analysis of the largest storms that occurred for each water year in the last decade for two contrasting locations in the Bay Area.

Water budget

The review of urban runoff process for the Bay Area is a necessary precursor to the development of conceptual models for pollutants that enter the Bay from local watersheds. Atmospheric input and the mobilization of sources, subsequent transport, and loadings of pollutants will be affected by timing and magnitude of rainfall and runoff. Urban runoff processes vary greatly from year to year and from watershed to watershed around the Bay Area largely depending on rainfall input but impervious surfaces also play a role. However, in the context of development of conceptual understanding of the most important pollutant pathways and inter-annual variability in loads, a hydrological conceptual model will be developed for three scenarios:

1. The wettest year between 1971 and 2000
2. The driest year between 1971 and 2000
3. The "average" year (average for the period 1971-2000)

The conceptual model will be presented for each scenario using unit runoff (mm) and volume (Mm^3) assuming a watershed area of 6,650 x 10^6 m^2 (the area of small tributaries in the Bay Area that are upstream from tidal influence).

RAINFALL INPUT

The average rainfall input was estimated by reworking estimates from Davis et al. (2000). An area-weighted mean was calculated by using the rainfall for each hydrologic area that drains directly to the Bay and its area. This calculation suggests an average rainfall of 648 mm (25.5 inches). Using data contained in Rantz (1974a), an area-weighted average of 627 mm (24.7 inches) was calculated. Given that rainfall has increased over the past 30 years by about 51 mm (2 inches), the estimate using figures from Davis et al. (2000) was chosen. Rainfall at locations around the Bay Area can vary from 200% of normal to 40% of normal (average of Berkeley, SF Mission, San Jose, San Rafael, Livermore, Petaluma, Napa). The maximum and minimum spatially averaged rainfall was calculated by multiplying the average (648 mm) by 200% and 40% respectively to give 1,296 mm and 259 mm (Table 2.7).

Table 2.7. Water budget for the Bay Area (the area of the nine counties that are directly tributary to the Bay).

	Average	Wet	Dry		Average	Wet	Dry
	(mm)	(mm)	(mm)		(Mm^3)	(Mm^3)	(Mm^3)
Rainfall	648	1246	259		4309	8286	1722
Runoff	138	591	27		918	3930	180
Groundwater	1.6	1.6	1.6		11	11	11
Evapotranspitation	374	374	374		2487	2487	2487
Change in groundwater storage	134	279	-144		894	1858	-955

RUNOFF

Like rainfall, runoff varies greatly between locations and between years as discussed above (Tables 2.4 and 2.5, Figure 2.9). Using data provided by Davis et al. (2000), the average runoff coefficient was estimated to be 31% of mean annual rainfall. Using a regression between rainfall and runoff derived from data provided by Rantz (1974a) (Table 2.5), the average runoff for the Bay Area is estimated as 138 mm or 21% of annual rainfall. The model developed by Rantz (1974a) was specifically aimed at predicting runoff from non-urban watersheds so it seems likely that the model developed by Davis et al. (2000) gave a better estimate since it incorporated the effects of

urbanization. Runoff during the wettest and driest year was estimated as 591 mm and 27 mm, respectively, or (10 % and 46 % of precipitation) using the regression developed with data from Rantz (1974a) (Table 2.5). The minimum runoff may be an underestimate given impervious surfaces whereas the estimate of maximum runoff should be reasonable given that during very large rain events soils will be saturated and act more like impervious urban area (Table 2.7).

EVAPOTRANSPIRATION, GROUNDWATER FLOW AND SOIL MOISTURE

The residual of rainfall input minus surface flow output must be accounted for by evapotranspiration, groundwater flow and changes in soil moisture. Analysis carried out in Tomales Bay (Oberdorfer et al. 1990) suggests that groundwater flow for that basin was of a similar magnitude to dry season surface flow. Dry season runoff in non-regulated watersheds of the Bay Area range between 0.2 and 3.4 mm and average 1.6 mm.

During the driest years it has been suggested that evapotranspiration and stream flow will account for all losses (Fischer et al., 1996). Using linear regression on the data presented in Figure 2.9 and assuming all rainfall that falls during the hypothetical dry year (y=0 of the graph) will be lost through evapotranspiration, annual average evapotranspiration is 335 mm in the East Bay, 374 mm in the South Bay and 414 mm in the North Bay (for this analysis 374 mm is used as the average). This method (the land-area water balance) is the most common method for estimation of actual evapotranspiration (Dingman, 1994; Dunne and Leopold, 1978). The assumption of negligible change in soil moisture storage typically leads to only small errors in the estimate of evapotranspiration especially when data are summed for a water year or over many successive years (Dingman, 1994). Water budgets constructed for the watersheds of Tomales Bay include estimates of evapotranspiration using this technique (Fisher et al. 1996). Change in groundwater storage for each scenario is then estimated as the residual of rainfall – runoff – groundwater flow – evapotranspiration assuming the change in soil moisture is negligible in the overall annual budget.

Budgets are a powerful tool in environmental analysis because they force the investigator to estimate the relative magnitude of each parameter and thereby help to prioritize data collection. In addition, when developing a closed budget, the investigator is forced to reconcile errors and determine the sensitivity of each budget parameter to those errors. Developing budgets under a range of scenarios (e.g., the wettest and driest years) is necessary to test how the importance of each parameter changes under the range of expected conditions. Finally, budgets provide a framework for data analysis during and after empirical data collection. As with any model (or hypothesis of the way the environment works), there will usually be an iterative process of refining the model or the data collection processes as a study proceeds. Thus conceptual models, such as the Bay Area water budget developed here, are a necessary precursor and companion to empirical observation.

Summary

- The discharge of water from small tributaries is about 4% of the total runoff entering the Bay (about the same as the area ratio).
- The area of small tributaries that is non-tidal is 6,550 km^2.
- The ten largest watersheds (ranging in size from 105 to 1,662 km^2) make up 74% of this area (Alameda, Coyote, Guadalupe, San Francisquito, Sonoma, Napa, Wooden Valley, Walnut, San Leandro, and San Lorenzo).
- Rainfall in the region varies from about 125 mm (Livermore 1975-76) to 2,250 mm (Kentfield 1982-83 year).
- About 90% of the annual precipitation falls between November and April.
- There are an average of 58 - 67 rain days per year (Maximum of 77 at Angwin).
- Annual rainfall varies from 200% of normal to 40% of normal.
- The region undergoes dry and wet periods that can last 4 to 8 years.
- There are also longer-term wetter and drier periods that can last for several decades or more.
- Between 87 and 98% of the annual runoff occurs from November to April.
- Runoff can vary from 0% of annual rainfall during drought years to 75% of annual rainfall during wet years.
- Inter-annual runoff variation is amongst the highest in the world and urbanization further increases the "flashiness" of runoff response, adding to the difficulties of field monitoring and subsequent modeling an extrapolation.
- The response time of small tributaries ranges from about 5 hours (e.g., Petaluma River [105 km^2] to 12 hours for Alameda Creek (1,662 km^2).
- Urbanization increases flow volume, peak flow, and decreases the response time, although there are complexities associated with basin configuration.
- A regional scale water budget was constructed using the last 30 years of data and shows that annual runoff volume varies from 180 to 3,930 Mm^3 and averages 918 Mm^3.

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Part 3: Sediment processes

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Sarah Pearce

Introduction

PROBLEM STATEMENT

There is a strong relationship between sediment loads and transfer of certain contaminants to the Bay, such as mercury (Hg) and other trace metals, PCBs, PAHs and chlorinated pesticides (Davis et al., 1999). Sediment and contaminant loads enter the Bay from the Central Valley watershed via the Delta and from local tributaries via natural and modified river channels and hundreds of constructed channels and storm drains. New estimates have been made recently for suspended sediment loads entering the Bay from the Delta (McKee et al., 2002). The best estimate for sediment loads from local tributaries is thought to be that of Krone (1979) although more recently Davis et al. (2000) made an estimate using the SIMPLE model and locally available data. Although there are limited or no sediment data on most of the tributaries that enter the Bay, the sediment data set does far exceed the data available on contaminants and therefore represents a powerful tool for making improved contaminant loads estimates.

IMPORTANCE OF RUNOFF FROM LOCAL WATERSHEDS

A review carried out by the Sources Pathways and Loading Work Group (SPLWG) of the Regional Monitoring Program (RMP) outlined the influence of local tributaries on water quality of the Bay (Davis et al., 1999, 2000). If we make the assumption that sediment loads from local urbanizing watersheds are unlikely to be decreasing over time, and given that there is evidence that loads passing through the Delta from the Central Valley are decreasing over time, it appears that the contribution of sediment (and related contaminants) from local tributaries to the overall sediment and contaminant budgets of the Bay may be increasing over time (McKee et al., 2002).

In that context, gaining an improved understanding of spatial and temporal variation in the sources, pathways and loadings of sediment that enters the Bay from local small tributaries will be essential in the design of a small tributaries sampling plan. Such a plan will lead to better estimates of contaminant loadings and greater confidence in management initiatives brought about through the TMDL process.

GENERAL WATERSHED SEDIMENT PROCESSES

Streams are delicately adjusted to the amount of discharge and sediment supplied to them from their watershed. During periods of drought, a natural river channel adjusts to a decrease in flow and a decreased sediment supply associated with decreased erosive forces by reducing its cross-section area. During successive years of high flow associated with short or longer-term changes in climate, the streambed and banks may erode, increasing the cross-section area and improving the capacity of the channel to transport sediment and water. Human influences such as dams, revetments, and realignment or constraint of channel systems may also increase or decrease sediment loads and water discharge. Human induced changes are analogous to climatic effects, however human induced changes tend to be more permanent or bias the natural variability of the system

in one direction causing a trend over time. In this way, stream channel morphology and its sediment and water transporting capacity change at scales of months to decades in response to human and natural influences.

Streams in the Bay Area receive sediment from landslides, rills and sheetwash, soil erosion, headward extension of channels, and bed and bank erosion (Figure 3.1). This sediment is stored in sinks such as bars, floodplain deposits, alluvial fans, wetlands, and a portion of it is ultimately deposited in the San Francisco Bay or the ocean. The sources, sinks, and processes occurring in any individual watershed vary considerably due to current and past land use practices, urbanization, bedrock geology and soils, tectonics, watershed area, physiography, and climate. The sediment flux also varies monthly and annually, mainly responding to changes in climate (wet season versus dry season, ENSO El Nino Southern Oscillation years versus drought years). Considering these processes, a conceptual understanding of sediment transport in the Bay Area will be developed to assist in design of watershed monitoring and sources, transport, and fate of sediment-related contaminants.

Sources of sediment

LANDSLIDES

Given the active tectonic geology and the prevalence of landslides in the Bay Area, a portion of sediment that is transported to the Bay via local rivers, creeks, constructed drainage channels, and storm drains is derived from landsliding. The factors that influence the magnitude, distribution, and temporal variability of landsliding will also influence sediment loads and related contaminants entering the Bay. For example, relatively “clean sediment” derived from landslides in upslope areas may dilute relatively contaminated sediment that is sources from urban and industrial areas nearer the Bay margin. Landslides, debris flows, and earthflows are common throughout the nine-county Bay Area. Landslides occurring in the Bay Area in 1997-1998 alone caused over $150 million in damage (Godt, 1999). Although landslides occur regionally, the eastern half of Marin County, the central and western portions of Contra Costa County, Alameda County, and portions of the Coast Ranges in San Mateo County are most susceptible (Figure 3.2).

The USGS conducted studies of landslides occurring in the Bay Area during the wet years of 1968-1969, 1972-1973, 1982-1983, and 1997-1998 (Nilsen and Turner, 1975; Nilsen et al., 1976, Cannon and Ellen, 1985, Godt, 1999, Ellen et al., 2000, Coe and Godt, 2001). Ancient landslide deposits, slope, bedrock geology and rainfall are the major factors controlling natural landslide activity (Nilsen and Turner, 1975; Nilsen et al., 1976). During the winter seasons of 1968-1969 and 1972-1973, 50% of landslides occurred in locations of ancient landslides, 74% occurred in areas with slopes steeper than 15%, and 60% occurred on rock units that were considered to be susceptible to slope failures. Thus it appears that landsliding will persist at one location over long periods of time. In addition to geology and slope, the duration of the storm period, the intensity of the storm period, and antecedent rainfall are critical factors that determine the magnitude

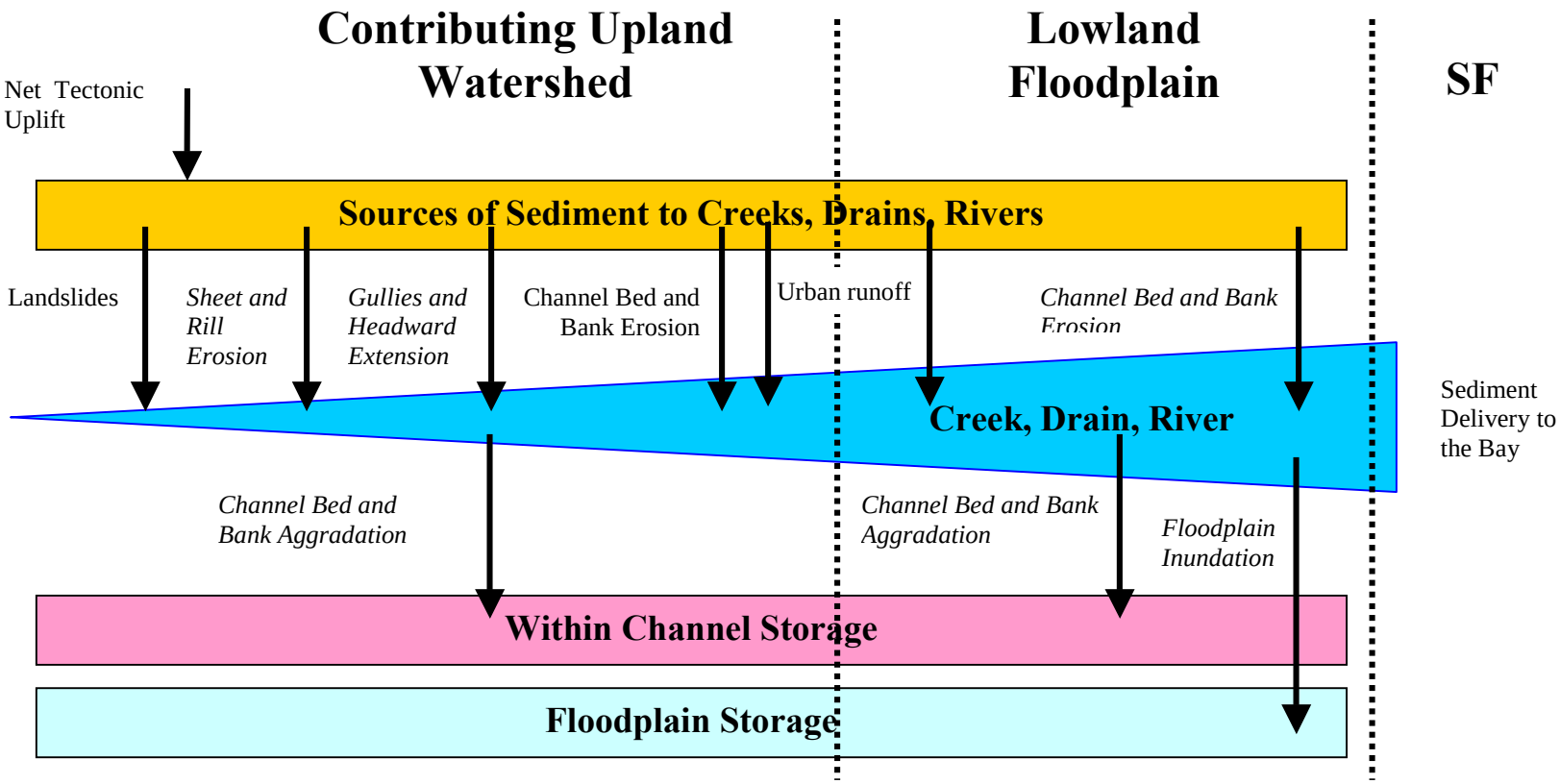

Figure 3.1. Conceptual sediment budget model for small tributaries in the Bay Area.

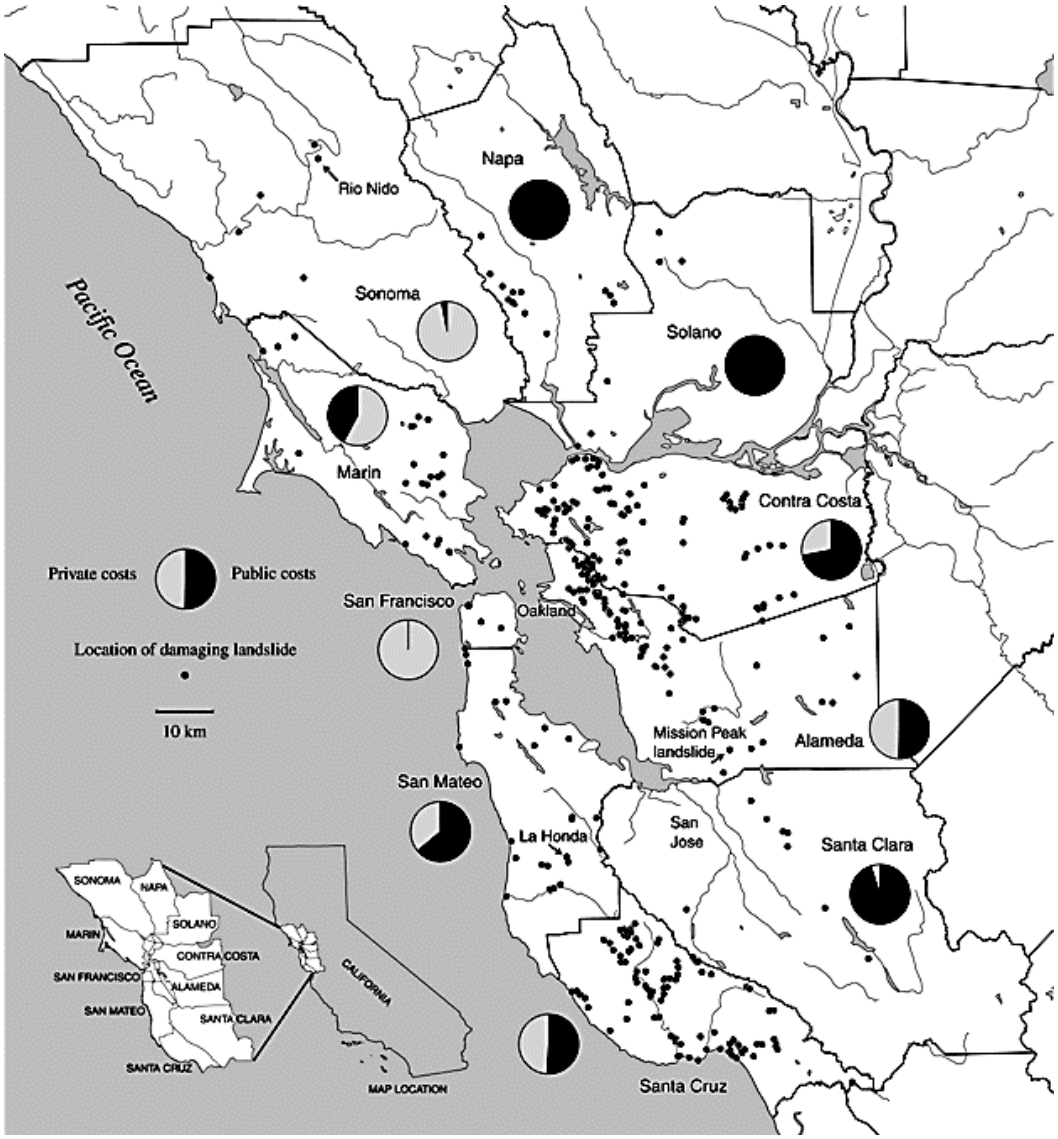

Figure 3.2. Landslide distribution in the Bay Area during the 1997-98 El Nino year (Godt, 1999).

and distribution of landslides. Large numbers of landslides are triggered during storm periods in which more than 150-200 mm (6-8 in) of rain falls in areas where 250-380 mm (10-15 in) of rain has already fallen during a rainy season (Nilsen et al., 1976). Coe and Godt (2001) analyzed 531 debris flows in Alameda County that occurred as a result of the February 1998 storm that dropped up to 150 mm of rain in 30 hours. Most (94%) debris flows were initiated on hillsides with gradients between 10° and 45°, and 80% of flows occurred in areas that had rainfall intensities of 15 - 20 mm hr^{-1} (0.6 - 0.8 in hr^{-1}).

Major sources of sediment do not always coincide with rainfall-induced landsliding. Work conducted recently by the USGS has demonstrated that hillslopes with

similar slope geometry and soil type may exhibit different rainfall thresholds for significant debris flow activity (Wilson, 2001). In drought years many of the watersheds in the Bay Area are susceptible to wildfires (Booker et al., 1993). After a wildfire, the hillslopes become vulnerable to erosion problems, especially if the following rainy season begins abruptly or is unusually intense. However, Booker et al. (1993) found that soil erosion in the Oakland hills after the 1991 wildfire was not significant; sediment control measures and post-fire reconstruction activities actually posed the largest threat for increased erosion and increased shallow landsliding hazards.

Sediment supplied by landslides can be a significant factor in the total amount of sediment transported from a watershed. Lehre (1981) conducted a 3-year (1971-1974) sediment budget study on Lone Tree Creek, a small basin in Marin County. Over three years, 2,068 t km^{-2} of sediment was discharged from the basin. Debris slides and flows from colluvium-filled swales were the most important erosional agent in this basin, and accounted for most (53%) of the long-term sediment yield from the basin. A study on Olema Creek, Marin County provides constraints on sediment delivery from a 32.6 km^2 (12.6 mi^2) rural watershed in the North Bay (Questa Eng. Corp., 1990). The 3-year study (1986-1989) found total annual sediment discharges of 8,606, 5,567, and 11,760 tons (7,807, 5,050, and 10,668 metric tonnes) for water years 1987, 1988, and 1989, respectively, similar to fluxes from neighboring watersheds (Lagunitas and Walker Creeks). A single landslide that impinged on the creek was the most significant point source of erosion, providing 50 tons y^{-1} (45.4 tonnes y^{-1}) of sediment to the creek. About 38% of the estimated annual sediment yield was attributed to gullying, landslides and other forms of hillslope erosion in the watershed.

Collins (2001) conducted a detailed study of Wildcat Creek, a 22.5 km^2 (8.7 mi^2) drainage in Contra Costa County. The Wildcat watershed is dominated by earthflows controlled by the bedrock lithology and increased runoff due to grazing and urban development. A total of 3,631 yd^3 y^{-1} (2,772 m^3 y^{-1}) of sediment supply was calculated and measured for the lower canyon segment of Wildcat Canyon over the last 167 years. Of this 3,631 yd^3 y^{-1}, the amount of erosion directly related to hillslope land use and landslides was 150 yd^3 y^{-1} (114 m^3 y^{-1}), whereas landsliding determined to be natural and/ or indirectly related to land use was about 591 yd^3 y^{-1} (451 m^3 y^{-1}). Approximately 64% of the sediment supply from the sub-watersheds was found to be associated with soil and landslide creep. These observations agree with earlier work by Leopold (1994) who measured a suspended load at bankfull discharge in Wildcat Creek of 1,793 tons mi^{-2} y^{-1} (828 tonnes $km^{-2}y^{-1}$), to which he attributed the cause to landslides.

In summary, it appears that for a few studies that have related sediment supply to sediment loads from watersheds in the Bay Area, between 38% and 64% of the sediment transported to the Bay may be derived from landsliding. This is consistent with a study of 61 watersheds in California (Anderson, 1981). Anderson (1981), through the use of principal components analysis using eight potential contributing variables, found that landslide activity accounted for 31% of the model variance and concluded that in areas of steep terrain and high rainfall, landslides will be the largest contributor to sedimentation. This implies that quantity and quality of sediment loads in Bay Area streams will be in

part controlled by soil, climatic, and anthropogenic factors that influence landslide occurrence, distribution and temporal variability. At the regional scale hillslope processes are responsible for a significant portion of sediment that enters the Bay over a decadal time scale, but it will remain difficult to assess the hillslope contributions at the watershed scale without detailed geomorphic assessments. For some contaminated watersheds geomorphic study may be necessary to design load reduction methods.

CHANNEL BED AND BANK EROSION

Sediment derived from erosion of the channel bed and banks, as well as reworking of in-channel features may comprise a large proportion of total sediment loads in Bay Area small tributaries. Many Bay Area streams are highly entrenched, suggesting a process (downcutting) from which sediment was recently, or is still actively being eroded. Increased urbanization and changes in land use throughout the Bay Area are likely to be accelerating streambed erosion in response to the greater frequency and magnitude of peak stream flow and stream power caused by runoff from impervious urban surfaces in some watersheds (Inman and Jenkins 1999; Collins 2001).

Studies of various watersheds in the region illustrate the magnitude of sediment supply from the channel bed and banks. Questa Eng. Corp. (1990) reported that 62% of the annual sediment yield from Olema Creek is due to the remobilization and erosion of sediment stored within the channel boundaries. Streambank erosion of the Napa River is considered to be a major source of the excessive sediment deposition observed in the lower river system (Stillwater Sci. 2002).

A 1985 inventory of streambank erosion of Napa County streams (excluding the Napa River) showed that 49.2 miles (79.2 km) were eroding severely, and 6.9 miles (11.1 km) were eroding very severely (Whyte et al. 1992). A similar conclusion was reached in recent work by Stillwater Sciences, who also observed between 6 and 8 feet (1.8 and 2.4 m) of bed incision in the mainstem of Napa River from the City of Napa to Calistoga (Stillwater Sci. 2002). In Lone Tree Creek from 1971-1974, headcut erosion, bank and bed erosion comprised 8% of the total sediment discharged from the basin (Lehre, 1981). Presently, the Watershed Program at SFEI is researching the character and spatial and temporal variability of channel morphology in the Napa River watershed with the objective of understanding the relationships between climatic and anthropogenic influences and change in watershed and stream character over time. A series of reports are anticipated during 2002 and 2003. In Wildcat Creek, 50% of the total bank length of the channel is eroding, 32% is stable, and 17% is revetted (Collins 2001). The volume of sediment supplied from the banks is 41 $ft^3\ ft^{-1}$ (3.8 $m^3\ m^{-1}$), the volume supplied from the bed is 124 $ft^3\ ft^{-1}$ (11.5 $m^3\ m^{-1}$), and the total sediment volume from bank and bed supply is 152 $yd^3\ mi^{-1}\ y^{-1}$ (72 $m^3\ km^{-1}\ y^{-1}$). The total estimated long-term supply of sediment to the channel network from 1832 - 1999 was 18,146 $yd^3\ y^{-1}$ (13,851 $m^3\ y^{-1}$), with approximately 60% of this total directly attributed to landuse practices since European settlement.

Collins et al. (2001) looked at the amount of sediment supplied by the channel bed and banks from 8 other streams in the Bay Area. Sediment supply from the channel bed per linear foot of channel ranged from 118 - 187 ft^3 ft^{-1} (10.9 - 17.4 m^3 m^{-1}), whereas sediment supply from the channel banks per linear foot of channel ranged from 15 - 155 ft^3 ft^{-1} (1.4 - 14.4 m^3 m^{-1}). In 4 out of 5 streams, the volume of sediment supplied from the channel bed was greater than that supplied from the banks. In four channels that had total sediment volume from the bank and bed supply calculated; estimates ranged from 148 - 308 yd^3 mi y^{-1} (70.2 - 146.0 m^3 km^{-1} y^{-1}).

In summary, a large mass of sediment that is discharged from local tributaries to the Bay is derived from channels and banks of streams. The causes and spatial and temporal variability of sediment supply from bed and bank erosion will influence the variability of suspended sediment concentrations and loads (and associated contaminants) entering the Bay from local tributaries. Contaminants that are stored within channel, bed, and bank deposits may erode and be transported at a later time in response to climatic or human induced changes in discharge (see for example Steuer et al., 1999 on PCBs). One consequence is that models such as the SIMPLE model that relate sediment loads to land use alone without accounting for processes such as landsliding and channel erosion and storage will fail to provide accurate estimates of loads. Ideally, the design of small tributary monitoring should employ components of geomorphic analysis of sources, channel processes, and short and long time scale variability of sediment concentration and loads near the Bay margin.

SEDIMENT EROSION FROM URBAN AND AGRICULTURAL AREAS

Urban sources

Sediment load derived from urban areas is of particular significance because it is often associated with the transport of particle bound contaminants such as trace metals, trace organic chemicals, and phosphorus (e.g., AWRC, 1981; Lau et al., 2002). In addition, urban runoff can contain significant amounts of organic particles derived from lawn clippings, leaf matter associated with vegetated strips, gardens and parks, and organic trash and it is known that dissolved and particulate organic carbon influence the processes of contaminant transport (see sections of this report on mercury, PCBs, and OC pesticides).

Sediment transported from urban areas is derived from a number of sources within the urban environment. Land surface sources include building and roadway construction sites where there is ineffective mitigation to prevent sediment erosion, roadway median strips and edges where there is often limited or no vegetation cover, shaded areas (e.g., on the lee side of industrial buildings or under bridges) where vegetation does not grow, and industrial yards where heavy vehicles may damage the structure of the soil making it more susceptible to erosion. Dust particles on impervious surfaces (e.g., roads, driveways, parking lots and other paved areas, and roofs of houses, commercial buildings, factories and warehouses) derived from the bottoms of vehicles and wind blown loess will also be transported easily during rain events. In addition,

private yards, parks, golf courses and cemeteries where chemicals such as pesticides and herbicides are used may also exhibit areas of eroding soils. Instream sources include failing banks and revetments (perhaps associated with increased peak discharge or water velocity in channels [see climate and hydrology section of this report]), bed erosion, and illegal dumping of inorganic or organic waste off bridges and in the near stream environment may also occur. All, or a combination of sources and processes such as these contribute to a typical sediment export from urban areas of between 160 and 1,000 t $km^{-2}y^{-1}$ (e.g., Letcher et al., 1999).

Agricultural sources

Sediment derived from erosion in agricultural parts of Bay Area watersheds is a concern for at least three reasons. From the land manger's point of view, sediment erosion often equates to loss of farm productivity because it is the fine organic rich topsoil that is lost most easily during heavy rainstorms. Farmers in the Bay Area implement a range of preventative measures such as avoiding tillage prior to the wet season, adopting no-till technologies, actively planting ground cover crops during the wet season, and contouring or plumbing the land to reduce down slope runoff and increase the travel path of water and reduce runoff velocities (e.g., Napa River Watershed Owners Manual, NRCD, 1994). In addition, some farmers may associate loss of soil to a loss of trace elements and nutrients such as nitrogen and phosphorus that are actively applied to augment crop growth.

Napa, Sonoma, and Petaluma watersheds are on the Clean Water Act 303(d) list of impaired water bodies for sediment. From the environmental manager's standpoint, fine sediments derived from sediment erosion in dominantly agricultural and open space watersheds is of great concern because it can impact the quality of spawning and rearing habitat for anadromous fishes (e.g., Stillwater Sci., 2002; Pearce et al., 2002). In addition, transport of fine sediment during floods is an important vector for the transport and loading of sediment-associated contaminants such as mercury, PCBs, PAHs, and organochlorine pesticides (see other sections of this review).

Sources of sediment in the agricultural environment include erosion from tilled fields, erosion from areas of intensive concentration of animals such as yards and laneways, areas of limited vegetation cover due to over grazing or drought, bank erosion associated with damage by animals in the near-stream environment, or loss or removal of riparian vegetation associated with agricultural land management. In addition to these more obvious sediment sources, there is typically an overall increase in sediment erosion associated with the change from perennial to annual non-native grasses, and the clearing of forest for timber harvest or to make way for agriculture. When considering sediment sources, it is important to take into account land use and land management change over time. Today's land and environmental managers may be inheriting legacy sediment erosion sources from past activities.

Pathways of sediment

STORAGE

Sediment from its various sources can be stored temporarily or permanently in various sinks within the fluvial system. The magnitude and distribution of sediment (and related contaminant) storage will vary from reach-to-reach within a creek and also between watersheds depending on factors such as stream slope, valley confinement, geology, soils, land use, the presence of reservoirs, and climate. These factors, in turn, affect the temporal and spatial sediment discharge from local tributaries to the Bay.

Over the long term, streams will transport almost all sediment that is supplied; however, over the short term, streams will use the sediment that is supplied to construct a path within the channel and valley confines. The storage of sediment by a stream contributes to channel morphology, including features such as bars, riffles and dunes, the floodplain, and terraces. Thus, not all sediment supplied by hillslope processes and bank and bed erosion is immediately transported from the basin. Additionally, a large amount of sediment is stored in alluvial fans built by the channels as they spill from canyons cut in the uplands onto a valley floor. For example, during the Pleistocene and Holocene, tributary streams to the Napa River built alluvial fans on the Napa River valley floor that are still visible in the topography and soils today. Where Soda Creek, an eastern tributary to the Napa River, exits the uplands, it has deposited an early to middle Pleistocene alluvial fan approximately 1.3 km^2 (0.5 mi^2) in area (Sowers, et al., 1998). The surface of this fan has developed a Coombs gravelly loam soil, which has been described in a soil survey for Napa County as a gently sloping soil on old terraces and old alluvial fans (Lambert and Kashiwagi, 1978).

In-channel sediment storage will vary on monthly, annual, and decadal timescales depending mainly on climate but also on human influences. Sediment storage in channels can be quite significant, especially the volume of deposition that occurs during and on the waning stages of high discharge events. In natural stream systems, bars formed by various mechanisms comprise the largest volumetric in-channel locations of sediment storage. In Soda Creek, bars ranging from 0.03 - 171 m^3 (1.1 - 6,038.8 ft^3) have been measured throughout the length of the channel (SFEI, unpublished data). In Lone Tree Creek, Lehre (1981) found that 47% of sediment mobilized remained in the basin, and was stored in slide scars, on footslopes, and in gully and channel banks and beds. Unpublished observations on San Francisquito Creek, San Mateo County suggest that sediment supplied to the stream during the 1997-98 ENSO event is still being discharged from the watershed four years later. This being the case, the sediment must currently be stored in bars, channels deposits, in the floodplain or in alluvial fans. In some river channels, the grain size of bars may be dominantly coarse sand or larger particles whereas in other systems particles stored in bars may be finer (e.g., Sulphur Creek, tributary to Napa River, SFEI Watershed Program unpublished data) and may be a more important storage mechanism for contaminants that are usually attached to fine sands, silts, and clays.

Sediment storage is known to occur when reservoirs change the hydrology of a watershed. Sediment typically deposits in the upstream portion of a reservoir lake forming a delta consisting mainly of sands and larger particles but also silts and clays. The trapping efficiency of a dam for silt and clay particles is dependant on factors such as the flashiness of the watershed, the capacity of the reservoir relative to the volume supplied by flood water, the geometry and depth of the reservoir lake, the operation of the dam, and the design of the spillway. Reservoirs by definition have a significant influence on the hydrology in reaches downstream that again varies depending of the design purpose and operation of the dam. Without exception, the hydrograph is attenuated and in most cases the total volume of discharge in decreased. This can have varying impacts on sediment process downstream. Sediment starvation in downstream reaches can cause bed armoring when the "hungry" water strips away the fines and leaves mainly coarse particles. Sediments from other tributaries entering the mainstem further downstream from a reservoir may deposit due to lack of sufficient flood peaks to transport sediments to the mouth. The impacts of a reservoir on a watershed sediment budget are unique for each given situation but as a general rule, sediment transport is usually decreased. In the Bay Area reservoirs capture a combined area of about 1,600 km^2.

Modified channels, especially flood control channels that have been re-graded and widened can fill with large volumes of sediment, as the channel tries to return to equilibrium. This filling process has been observed in many modified channels in California. For example, in 1959 the San Lorenzo River, Santa Cruz County was modified as part of a flood control project by the Army Corps of Engineers (Griggs and Paris, 1982). The channel was widened and dredged to increase the slope and capacity of the river, however this modification drastically increased the channel's gradient by 32%. In an effort to return to its original gradient, the river deposited large amounts of sediment in the channel, raising the channel bottom 0.9 - 1.2 m (3 - 4 ft) above the original channel bed. In 1982 it was estimated that 350,000 m^3 (450,000 yds^3) of sediment must be removed in order to restore the channel to its original flood control design (Griggs and Paris, 1982).

Sediment storage also occurs in floodplain deposits during floods when the discharge is greater than the channel can convey. The channel uses the floodplain to disperse excess flow, resulting in decreased velocity and power. Because the flow spreads and slows, sediment settles out of suspension, forming a floodplain deposit that generally decreases in grain size with distance from the channel. However, these natural processes pose a natural hazard to urban and agricultural communities that utilize the flat rich soils of the floodplains. As such, channels that have been deepened, widened, or leveed are most often disconnected from the floodplain. Because discharge is retained in the banks, the stream will have more power, which results in erosion of banks, undermining or complete failure of revetments, or flood and erosion problems further downstream (e.g., Collins, 2001). A decrease in stream access to the floodplain and the increase in erosive power potentially result in greater sediment (and contaminant) discharge from local small tributaries in the Bay Area.

Wetlands are another location of sediment storage around the Bay. Over the past 200 years, tidal marsh and tidal flats in the Bay Area have reduced in area from about 235,000 acres (950 km^2) to about 68,000 acres (275 km^2) largely as a result of conversion to agriculture, diked wetlands, and salt ponds, but more recently by urban encroachment (Goals Project, 1999). Sediment storage acts as a buffer of sediment and related pollutants. Many small tributaries in the Bay Area never reached the Bay margin historically, instead ending in finger like distributaries on the upstream of swamps and wetlands (Robin Grossinger, SFEI unpublished data). Thus, in their natural condition, many small streams only rarely deposited their sediment loads to the Bay and wetlands were the receiving ecosystem for sediments and related nutrients and trace substances. Today, creeks on the Bay margin have been channelized and in most cases connected to the Bay in an effort to increase flood conveyance and predictability. This has probably led to a decrease in wetland sediment deposition and an increase in sediment discharge to the Bay.

In summary, sediment storage in rivers, creeks, modified or constructed channels and storm drains, and wetlands will have an influence on the spatial and temporal variability of sediment and contaminant concentrations and loads entering the Bay. During small storms, much of the sediment and contaminants entering the Bay may be eroded from temporary storage in channels. During larger events, a greater proportion of sediment and contaminant loads will be derived from source areas outside of the near channel environment and perhaps anywhere within the drainage basin.

DELIVERY OF SEDIMENT – AVERAGING ON DECADAL TIME SCALES

As discussed, for any given watershed, only part of the sediment (and related contaminants) eroded on the hill slopes or supplied to the stream will end up reaching the receiving waterbody. The remainder will be stored in various locations on the valley slopes, near and in channels, and on the floodplain. Novotny and Chesters (1989) describe methods of calculating soil loss and sediment delivery in the context of non-point source effects upon water quality. The “delivery ratio” describes the relation between basin sediment yield and upland erosion generation potential; $Y=DR(A)$, where Y is the basin sediment yield, A is the upland erosion generation potential, and DR is the delivery ratio. The delivery ratio captures the different physical sediment storage processes occurring in a watershed, and ideally represents processes occurring on a 5 - 10 year time period. It is necessary to use some ratio between upland erosion and downstream sediment delivery and transport, but problems arise when estimating a single delivery ratio for a watershed, including: the time span considered; the spatially lumped character of the delivery ratio over an entire watershed; and the seasonality and hydrological variability of the parameter (Novotny and Chesters, 1989).

Problems with seasonality arise because of the intermittent nature of sediment movement and the variable correlation between individual runoff events and sediment delivery. Although modeling of sediment has been researched extensively, the models do a poor job of representing the transport of clays and other fine material, especially with the deposition and re-entrainment of these particles, which tend to only have temporary

in-channel storage. Novotny and Chesters (1989) conclude that more research must be completed to understand the processes involved with sediment delivery and to more accurately estimate delivery ratios representative of the highly variable nature of the delivery process, so models representing sediment transport and storage can be used.

Despite the lumped nature of the sediment delivery ratio there is a relationship between delivery ratio and watershed size. Larger watersheds retain a greater proportion of eroded sediment than smaller ones (Figure 3.3). Watersheds draining into the San Francisco Bay vary in size from essentially <1 km^2 up to 1662 km^2 (0.4 - 642 mi^2), although the 10 largest watersheds have an area greater than 105 km^2 and comprise about 75% of the total watershed area around the Bay. Although watersheds in the Bay Area vary in slope, geology, intensity of tectonic deformation, and rainfall, as a first approximation, sediment delivery ratios for the 10 largest watersheds are likely to range from 55% - 7% for the smallest and largest basins, respectively. The relationship has some scatter, but on average, the sediment delivery ratio may be approximately 20%.

In summary, about 80% of sediment (and related contaminants) in local watersheds derived from hillslopes, channel erosion, and temporary storage areas is likely to be retained in watersheds over timescales of decades. This retention (or buffering capacity) will vary spatially and temporally between watersheds, and over longer timeframes depending on climate, and will undoubtedly contribute to the variability of concentrations and loads of sediment and related contaminants entering the Bay from

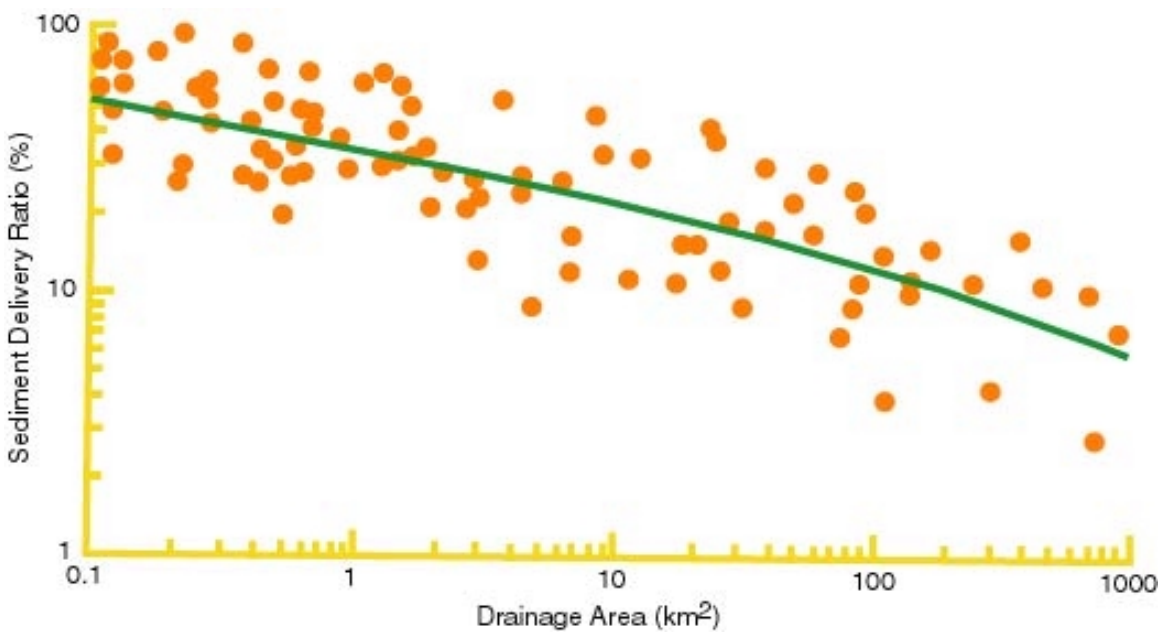

Figure 3.3. Drainage area versus sediment delivery ratio in watersheds from around the world after Novotny and Chesters (1989). The dashed lines represent the range of scatter around the regression line.

local tributaries. In the case of urban areas, sediments derived from locations of erosion or from impervious surfaces are less likely to be stored because modified channels and storm drains are designed to pass sediment and water quickly and because the channels are usually disconnected from the floodplain or wetlands.

Sediment loads

SUSPENDED SEDIMENT CONCENTRATIONS

Variation of suspended sediment concentration (SSC) (and associated contaminants) in relation to discharge variation will have a bearing on the contaminant loads study sampling design. Greater variability will require a more detailed sampling design aimed to characterize short interval changes in concentrations. In addition to requiring careful sampling of the water column, high variability can cause greater difficulty during laboratory analysis, and may negate the use of surrogate measuring techniques such as turbidity probes if maximum SSC exceed the probes design capabilities.

Turbidity probes have been used to improve the understanding of extremely dynamic suspended sediment transport processes in watersheds all over the world (Buchanan and Schoellhamer, 1999; Walling et al., 1997; McKee et al 2002). The method relies on a strong relationship between suspended sediment concentration and turbidity (the attenuation of light by organic and inorganic particles). There are confounding factors such as variation in grainsize (most important), organic matter content of suspended sediment (e.g., Madej et al., 2002), and color (e.g., Pavelich, 2002). However, under most circumstances, the use of surrogate techniques for extrapolation of temporally limited data sets has improved the accuracy of suspended sediment loads estimates. The optimal condition is considered to be low variation in grainsize during flood events in rivers and creeks where grainsizes are dominantly (>60-80%) finer than 0.062 mm. Given differences in the optical detectors and instrument configurations, as well as different sediment properties between watersheds or in different places in a single watershed, turbidity itself cannot be used as a surrogate without site specific calibration with water samples analyzed for suspended sediment concentration (e.g., Riley, 1998).

Redwood Sciences Laboratory may be considered one of the leaders on the west coast of the US in the development of methods and deployment of optical sensors for the estimation of suspended sediment loads (Eads, 1991; Lewis and Eads, 1996; Eads and Lewis, 2001). They have developed a method called “turbidity threshold sampling” that combines optical sensor technology with software driven automatic pump sampling technology. The objective of turbidity threshold sampling is to automatically obtain samples for analysis of suspended sediment either when the range for the optical sensor is exceeded (2,000 NTU or about 3,000 – 4,000 mg l^{-1} suspended sediment) or when the equipment malfunctions. These technologies, combined with manual depth and cross-

section integrated sampling, ensure the highest quality data set for improved understanding of transport processes and sediment loads estimation.

The USGS has measured suspended sediment concentrations in streams within the nine-county Bay Area over the past 40 years at 26 locations (Table 3.1). Periods of record range from a few days to more than 15 years at three locations in Alameda County (Table 3.1). Peak concentrations can be remarkably high at some locations during storm events; six locations recorded in excess of 10,000 mg l^{-1} and a further six locations recorded between 5,000 and 9,999 mg l^{-1}. Only 18 out the 26 locations had at least one full wet season of record. Flow-weighted mean concentrations at many locations were in excess of 1000 mg l^{-1} perhaps indicative of both a tectonically active erosive terrain coupled with a storm dominated rainfall regime and an anthropogenically modified landscape.

Suspended sediment concentrations were measured in urban areas in the Contra Costa, Alameda, and Santa Clara Counties during the late 1980s and early 1990s (BASMAA, 1996). These same data were summarized and used as input data for the SIMPLE model to estimate sediment loads from local tributaries (Davis et al., 2000). Concentrations chosen for the model ranged between 90 and 157 mg l^{-1} for urban land uses, 2,068 mg l^{-1} for agricultural land use and 85 mg l^{-1} for open space land use (Davis et al., 2000). A comparison of data collected by the USGS over the past decades (Table 3.1) with concentrations collected by BASMAA agencies and used in the development of the SIMPLE model (Davis et al. 2000) suggests that the data collected during the drought of the late 1980s and early 1990s may be atypical of long term averages and that consequently, Davis et al. are likely to have underestimated sediment loads entering the Bay from local tributaries.

Daily suspended sediment concentrations typically vary by 3 orders of magnitude, however, some stations show a variation of more than 4 orders of magnitude (Figure 3.4). Discharge at the locations with the longest SSC records varies by 4 - 5 orders of magnitude, except on Colma Creek where discharge only varies by 4,700 times perhaps because it is so highly urbanized. Given that discharge varies more than SSC, the accuracy of loads estimates will be very reliant on accurate estimates of discharge.

Table 3.1. A summary of suspended sediment concentration measured in local tributaries of (or near) San Francisco Bay by the USGS and calculated flow-weighted mean concentration (FWMC). * represents locations with ongoing data collection.

Location	Station Number	Years with part or full record	Watershed area (km^2)	Number of non-zero data points	Minimum concentration ($mg\ l^{-1}$)	Maximum concentration ($mg\ l^{-1}$)	FWMC ($mg\ l^{-1}$)
*ALAMEDA C AT NILES	11179000	1959-73 1999-00	1,639	3,962	2	5,050	809
*CULL C AB CULL C RES NR CASTRO VALLEY	11180960	1978-89 1991-92 1994-00	15	2,778	1	22,400	4,472
*SAN LORENZO C AB DON CASTRO RES NR CASTRO V	11180825	1980-89 1991-92 1993-94 1997-00	47	2,593	2	15,300	2,610
COLMA C A SOUTH SAN FRANCISCO	11162720	1965-76	28	2,507	2	19,400	2,442
ARROYO VALLE BL LANG CN NR LIVERMORE	11176400	1973-79	337	1,359	1	2,670	502
PINE C A BOLINAS	11460170	1967-70	20	1,145	1	5,370	837
WILDCAT C AT VALE ROAD AT RICHMOND	11181390	1977-80	20	1,093	1	13,400	2,329
CORTE MADERA C A ROSS	11460000	1977-80	47	1,065	1	1,240	374
PERMANENTE C NR MONTE VISTA	11166575	1985-87	10	810	1	5,800	560
ARROYO VALLE NR LIVERMORE	11176500	1963-67	381	502	1	6,390	1,329
NAPA R NR NAPA	11458000	1977-78	565	444	1	1,750	541
NAPA RIVER NEAR ST. HELENA	11456000	1961-62	211	390	1	2,260	436
WEST FORK PERMANENTE CR NR MONTE VISTA	11166578	1985-86	7.7	347	2	1,850	491
PESCADERO C NR PESCADERO	11162500	1980	119	305	1	2,980	683
*ARROYO DE LA LAGUNA NR PLEASANTON	11177000	1999-00	1,049	214	8	1,860	525
* CREEK BELOW WELCH CREEK, NEAR SUNOL	11173575	1999-00	375	214	1	1,180	219
*CROW CREEK NEAR HAYWARD	11180900	1999-00	27	214	12	11,200	3,369
SAN LORENZO C AT SAN LORENZO	11181040	1991-92	116	213	1	1,230	424
CULL C BL CULL C DAM NR CASTRO VALLEY	11180965	1978-79	16	192	8	256	124
SPRUCE BRANCH AT SOUTH SAN FRANCISCO	11162722	1966-67	1.8?	84	24	6,350	2,490
AGUA FRIA C AT WARM SPRINGS ROAD AT FREMONT	11172300	2000	4.6	2	78	124	-
TOROGES C AT WARM SPRINGS ROAD AT FREMONT	11172360	2000	3.2	3	138	8,130	5,139?
ZONE 6 LINE B AT WARM SPRINGS BOULEVARD AT FREMONT	11172365	2000	2.15	7	506	73,500	55,548?
SAN ANTONIO C NR SUNOL 1 KM BL LAKE SAN ANTONIO	11174000	2000	96	6	1	11	-
ALAMEDA C AT HIGHWAY 680 NR SUNOL	11174060	2000	495	6	4	272	-
ARROYO MOCHO AT HOPYARD RD AT PLEASANTON	11176325	2000	440	2	246	414	-

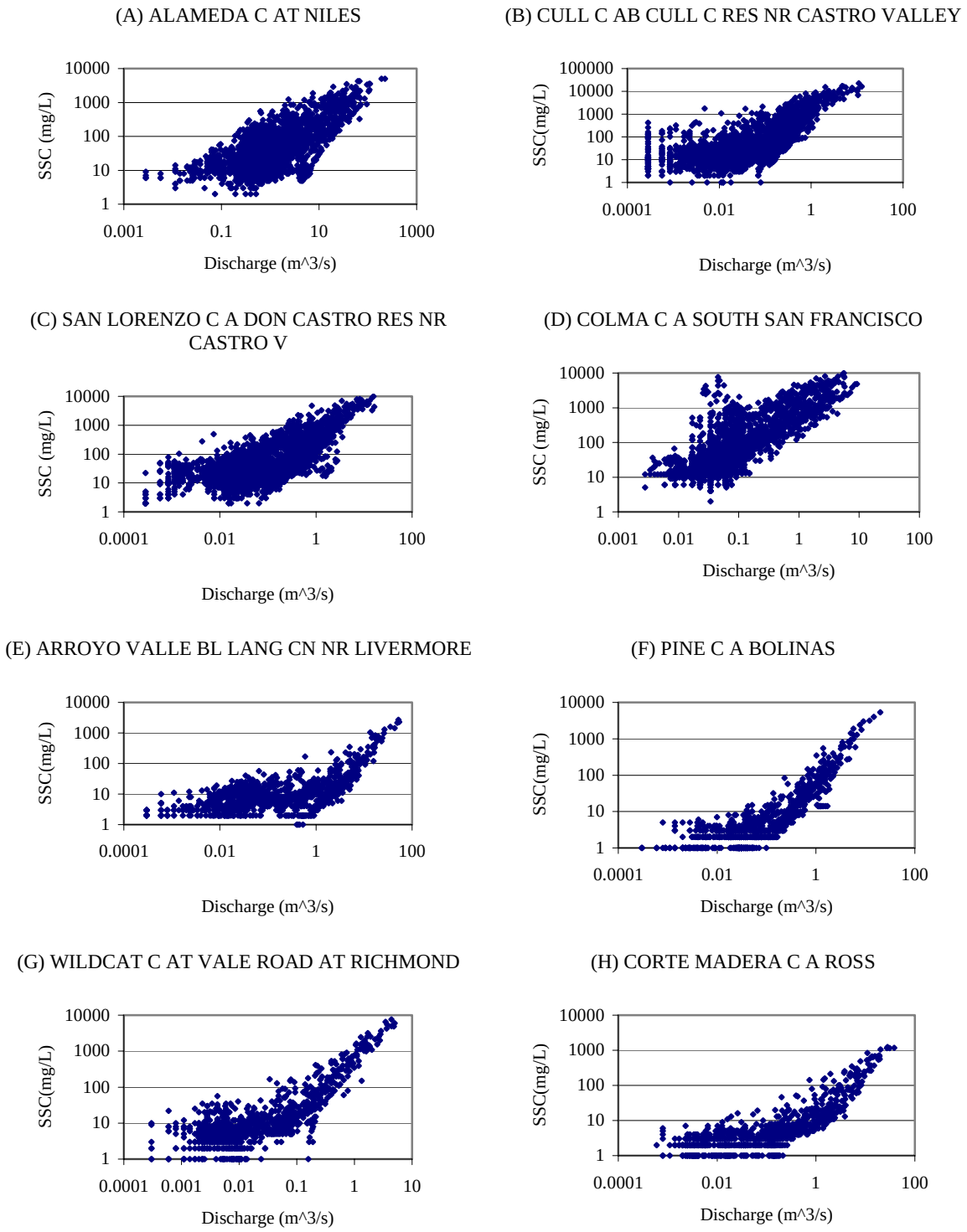

Figure 3.4. Discharge versus suspended sediment concentrations at Bay Area locations with long concentration records. For the periods of record, see Table 3.1.

SUSPENDED SEDIMENT GRAIN SIZE

Grain size may vary between watersheds and between events due to differences in source geology and soil texture, rainfall intensity, event recurrence interval, sediment sources (landslide, sheet and rill erosion, instream erosion, road dust), watershed size, and the time period since the last flood event. Some watersheds may exhibit remarkably constant grain size regardless of the magnitude of the event and stream power, while others typically show vast variations between events and between years. In order to estimate suspended sediment concentrations using surrogate techniques such as optical back scatter (OBS), grain size must be predominantly silt and clay size particles and grain size must not vary greatly in size and composition (inorganic versus organic particles). Thus grain size and compositional variability may confound the results generated by continuous monitoring probes by changing the calibration curve.

Grain size of suspended particles has been measured in a number of watersheds in the Bay Area by the USGS (Figure 3.5). The number of samples available for analysis in each watershed varies from just 12 samples in Wildcat Creek at Vale Road to 96 in Cull Creek above Cull Creek Reservoir. The median percentage of grains that are <0.062 mm (fines) ranges from 67% in West Fork Permanente Creek near Monte Vista to 100% at Alameda Creek near Niles. There appears to be a weak relationship between watershed size and grain size in Bay Area watersheds (Figure 3.6), however the scatter about the regression is probably a result of variation in geology and land use and differences in sampling period and event magnitude between watersheds. The trend of decreasing particle size with increasing watershed size is probably associated with a general decrease in average channel slope as watershed size increases.

Grain size also appears to vary with discharge (Figure 3.7). The relationships for four stations of contrasting land use and watershed area seems to be poor but generally grains transported during floods are larger due to higher bed stress and turbulence. Napa appears to be the exception to the rule but data for Napa does not cover a full range of discharge conditions that occur in that watershed. It is suspected that at higher discharge the Napa River reacts similarly to the other watersheds even though it displays more scatter at lower discharges.

SUSPENDED SEDIMENT TRANSPORT

Intra-annual variation

The seasonality of sediment transport (and related contaminants) will impact the seasonality of water quality in stream environments and receiving water bodies. In streams that have intermittent or extremely low dry season flows, a greater emphasis is usually placed on quantifying variability over the time scales of floods when concentrations change rapidly. Sediment

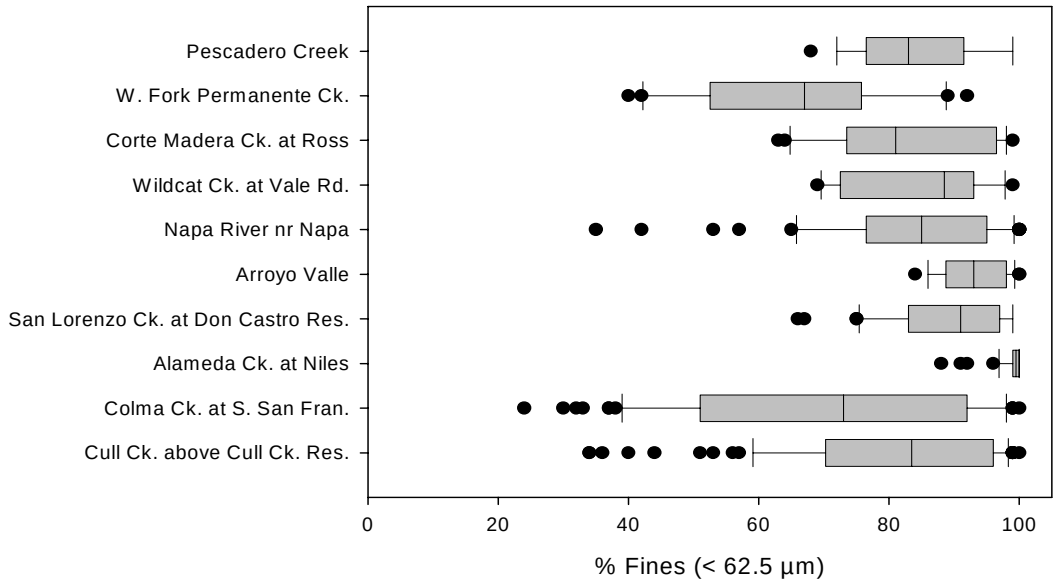

Figure 3.5. Percentage of particle size less than 0.0625 mm in watersheds where there are sufficient data for analysis. Data collected by the USGS.

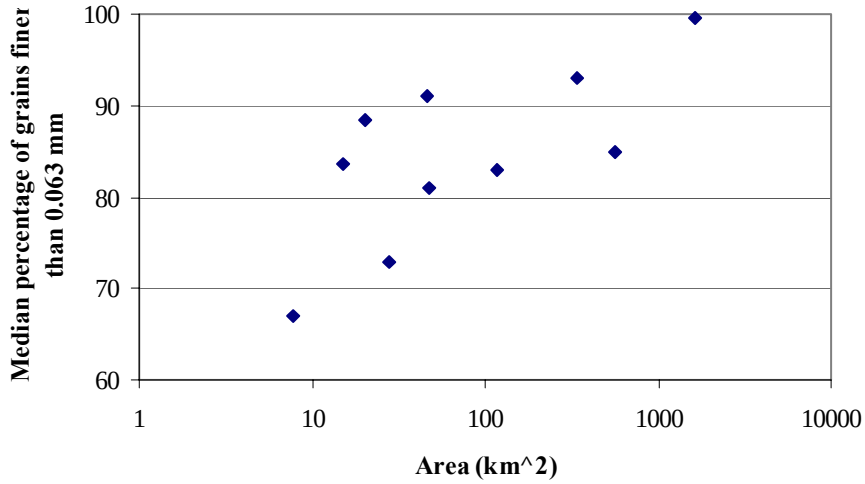

Figure 3.6. Grain size variation in response to watershed area in watersheds of the Bay Area with suitable records. Data collected by the USGS.

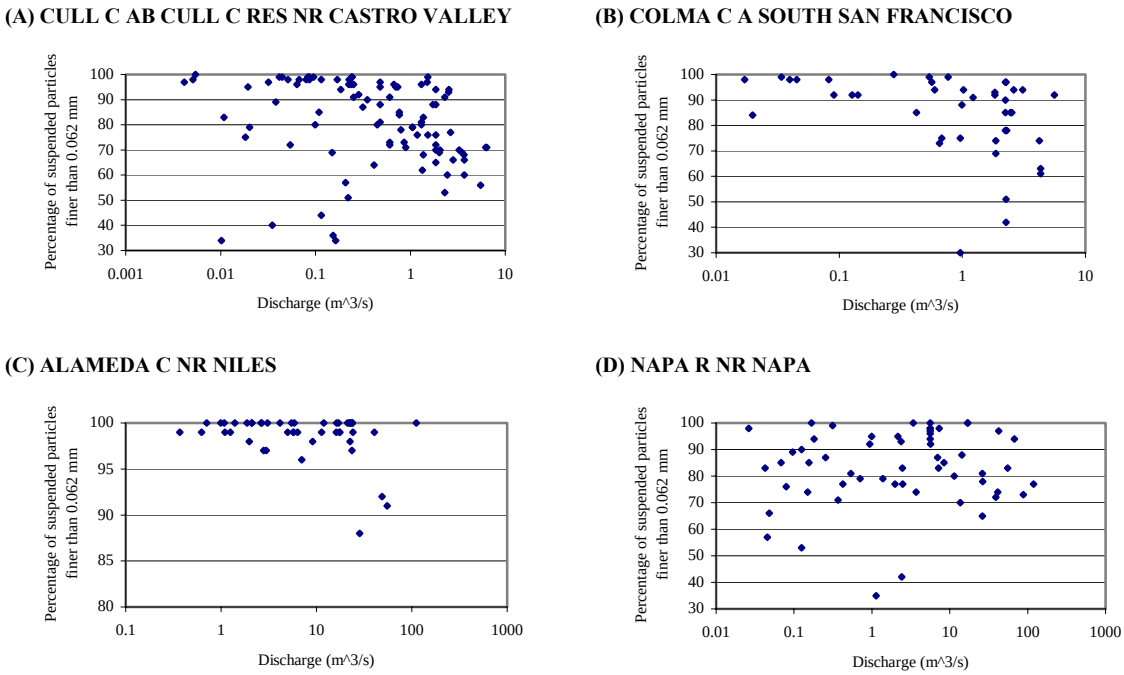

Figure 3.7. Grain size variation in relation to discharge in selected watersheds of the Bay Area where there are sufficient data collected for this type of analysis. Data collected by the USGS.

output from watersheds in the Bay Area varies intra-annually; 90% of the region's precipitation falls between November and April, and increased sediment output typically is correlated with the winter increase in precipitation and runoff. Data from Olema Creek, Marin County, show that >90% of sediment transported from the basin occurs between December and March (Questa Eng. Corp. 1990). Data collected by the USGS in watersheds of the Bay Area suggest that closer to 99% of the sediment transport occurs during the three or four wettest months (Table 3.2).

In terms of intra-annual, Bay Area watersheds appear to transport loads similarly to sub-tropical systems (Figure 3.8), mainly because the climatic variability of the annual cycle is similarly variable. In contrast, local watersheds transport much greater percentages of the annual load in less time than temperate systems (e.g., river systems in southwest England) (Figure 3.8). Local small tributaries also differ in monthly load transport in comparison to loads from the Central Valley. Local tributaries transport over 90% of the load in approximately two months whereas it takes about five months for 90% of the loads transport from the Central Valley. Variation in both the timing and composition of the loads from each of these pathways have implications for toxicity and intra-annual water quality. Given that small tributaries enter the Bay around virtually the whole perimeter of the Bay, the concentrations and loads that are delivered

Table 3.2. Monthly percentage of suspended sediment load for three Bay Area watersheds. (Data extracted from USGS data reports).

	Cull Creek (wet season 1996-2000) (%)	Napa River (WY 1979) (%)	Wildcat Creek (WY 1978-1979)
October	0	0	0
November	0.1	3.1	0.3
December	4.2	7.4	2.4
January	53.1	76.7	40.8
February	96.4	89.5	74.9
March	99.8	99.6	96.7
April	100	99.9	99.99
May		99.92	99.995
June		99.95	99.997
July		99.97	99.998
August		99.99	99.999
September		100	100

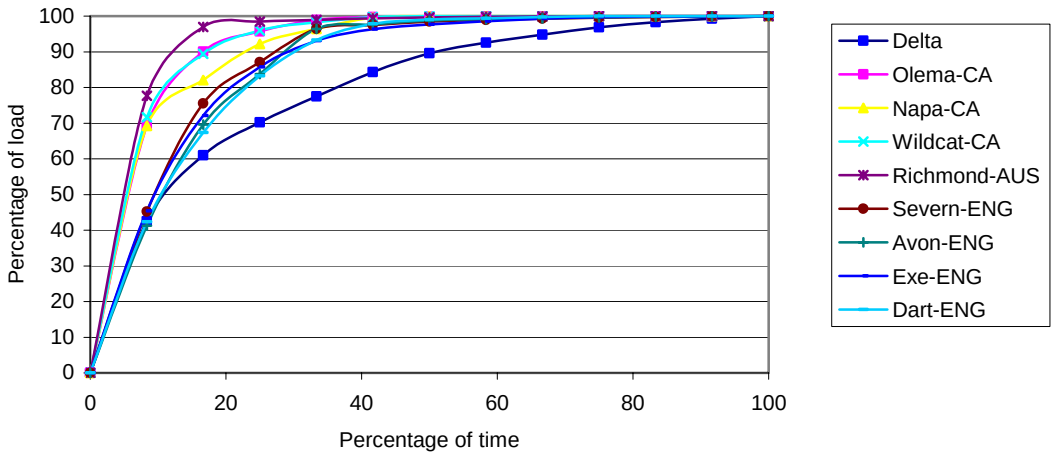

Figure 3.8. A comparison of intra-annual loads transport in a selection of local streams and systems in other parts of the world.

must travel across wetlands and mud flats. In addition, the loads will typically be transported to the Bay prior to the arrival of loads from the Central Valley during any given regional scale rainstorm.

In terms of developing monitoring programs in the Bay Area to accurately estimate loads, monitoring need only occur during the wet season and during storm events because of the intra-annual nature of water and sediment runoff. Given that tributaries to the Bay are relatively small and respond to rainfall events in less than 12

hours (in many cases in less than 2 hours), the use of surrogate techniques (such as turbidity probes and optical back-scatterance) and automatic-pumping samplers may be necessary.

Inter-annual variation

Because sediment load is typically correlated with discharge, inter-annual variation in precipitation totals will cause the sediment output to vary also. Variation from the average annual precipitation totals can be quite drastic in ENSO or drought years, as discussed in the rainfall section of this report and demonstrated by downtown San Francisco receiving 240% of normal precipitation during the 1997-1998 ENSO event (Godt, 1999). The large fluctuation of sediment load carried by streams on an annual basis has been documented for many watersheds in California. For example, the January 4-6 1982 storm caused a total sediment transport of 944,000 metric tonnes in the San Lorenzo River, Santa Cruz Mountains, or 5.8 times the average annual total-sediment load for the period 1973-1980 (Nolan and Marron, 1988). Inman and Jenkins (1999) also document suspended sediment fluxes for ENSO years (1969 and 1983) up to 27 times larger than the average annual flux for the drier years 1944-1968 in southern California rivers.

Annual sediment loads can vary in Bay Area watersheds from 2 - 4 orders of magnitude between dry and wet years (Table 3.3). Colma Creek shows low variability relative to the other four stations in Table 3.3. Discharge on Colma Creek is less variable than other small watersheds where there is a comparable record. For the period WY 1979 - 1993, annual average discharge on Colma Creek varied by only 4 times compared to San Francisquito Creek (41 times) and Cull Creek above Cull Creek reservoir (202 times). Low annual discharge and sediment loads variability is likely a result of predominantly urban land use in the Colma Creek watershed. Variation in sediment flux is also observed on the multi-decadal timescale as the climate changes from slightly drier decades to slightly wetter decades. This climate change and the associated sediment flux response of the rivers is recorded by Inman and Jenkins (1999); data collected shows sediment fluxes 5 times greater for the dominantly wet period of 1969-1999 than for the dominantly dry period of 1944-1968.

In conclusion, given the highly variable nature of suspended sediment transport in Bay Area streams, watershed monitoring programs will need to focus on data collection during the wet season (November to April) when the majority of the sediment (and contaminant) transport occurs. Because inter-annual variation is also high, studies that select for a certain time (perhaps 1, 2, or 3 years) may fail to sample the range of watershed response to climatic variation and therefore fail to estimate the average or range of annual loads. An alternative sampling design might allow for a certain number of samples and preference only sampling floods of a minimum specified size or those early in the wet season when the first flush of suspended sediments and related contaminants occurs. Ideally sampling should occur over 7 - 10 years in selected watersheds. Data from long-term studies such as these could then be used to help to extrapolate more limited data sets in other watersheds.

Table 3.3. Inter-annual variation of suspended sediment loads (metric tonnes) entering San Francisco Bay from a range of small tributaries for which there are long term data records. (Data extracted from USGS Water Resources publications).

	ALAMEDA C AT NILES		CULL C AB CULL C RES NR CASTRO VALLEY		SAN LORENZO C AB DON CASTRO RES NR CASTRO VALLEY		COLMA C A SOUTH SAN FRANCISCO		ARROYO VALLE BL LANG CN NR LIVERMORE	
Area (km^2)	1,639		15		47		28		337	
	Year	Load (t)	Year	Load (t)	Year	Load (t)	Year	Load (t)	Year	Load (t)
	1960	14,674	1979	8,475	1981	548	1966	29,242	1974	8,037
	1961	9	1980	43,038	1982	66,828	1967	110,823	1975	10,752
	1962	36,784	1981	1,282	1983	80,469	1968	32,423	1976	6
	1963	163,405	1982	93,217	1984	10,714	1969	59,053	1977	2
	1964	6,431	1983	87,180	1985	3,034	1970	22,571	1978	65,356
	1965	99,569	1984	19,508	1986	47,243	1971	25,074	1979	2,641
	1966	5,745	1985	4,186	1987	3,226	1972	5,614		
	1967	260,780	1986	48,908	1988	1,040	1973	52,937		
	1968	8,344	1987	2,359	1989	453	1974	23,411		
	1969	146,757	1988	98	1992	4,852	1975	3,753		
	1970	79,417	1989	280	1994	589	1976	2,068		
	1971	24,999	1992	1,328	1998	151,514				
	1972	2,766	1995	15,826	1999	21,328				
	1973	209,652	1996	12,560	2000	27,032				
	2000	35,413	1997	35,701						
			1998	45,291						
			1999	7,081						
			2000	8,116						
Average		72,983		24,135		29,919		33,361		14,466
Variation (Max / Min)		28,746		951		335		54		31,573

Max = maximum; Min = minimum

Suspended sediment exports

The term export (or export coefficient) refers to a load of a substance that has been normalized to watershed area (metric tonnes per square kilometer per year [t $km^{-2}y^{-1}$]). Export coefficients allow watershed areas of differing size to be compared with each other in the context of other watershed characteristics such as rainfall, land use, or landslide susceptibility. USGS stream flow and daily suspended sediment records can be used to estimate average annual suspended sediment loads and average annual suspended sediment exports from a number of Bay Area watersheds (Table 3.4). In addition, there are several published estimates available (Anderson, 1981; Collins, 2001; USACE 2001). Estimates of annual average loads may differ by a factor of 2 depending on the method of

calculation. There will be no attempt here to reconcile this issue as it is lengthy subject to test and discuss. It is recommended that critiquing loads estimation methods should be the subject of a future literature review. The emphasis in the current analysis is to demonstrate the variation in loads and unit area exports in Bay Area watersheds.

Table 3.4. Loads (metric tonnes) and exports (metric tonnes per square kilometer per year) of sediment in Bay Area streams with suitable suspended sediment concentration and flow records or published estimates. Dark shading represents ongoing data collection in 2002.

Location	Station Number	Area (km^2)	FWMC ($mg\ l^{-1}$)	Annual average load (t)	Export ($t\ km^{-2}\ y^{-1}$)
ALAMEDA C AT NILES	11179000	1,639	809	[A] 72,983 [D] 91,947	[F] 45
CULL C AB CULL C RES NR CASTRO VALLEY	11180960	15	4,472	[A] 24,135 [D] 13,684	[F] 1,609
SAN LORENZO C AB DON CASTRO RES NR CASTRO V	11180825	47	2,610	[A] 29,919 [D] 17,664	[F] 637
COLMA C A SOUTH SAN FRANCISCO	11162720	28	2,442	[A] 33,361 [D] 16,547	[F] 1,191
ARROYO VALLE BL LANG CN NR LIVERMORE	11176400	337	502	[A] 14,466 [D] 17,389	[F] 43
PINE C A BOLINAS	11460170	20	837	[B] 12,508	[G] 619
WILDCAT C AT VALE ROAD AT RICHMOND	11181390	22.5 20	- 2,329	[C] 23,803 [D] 10,363	[C] 1,190 [F] 518
CORTE MADERA C A ROSS	11460000	47	374	[D] 8,829	[F] 188
PERMANENTE C NR MONTE VISTA	11166575	10	560	[B] 16,385	[G] 1,639
ARROYO VALLE NR LIVERMORE	11176500	381	1,329	[D] 30,023	[F] 79
NAPA R NR NAPA	11458000	565	541	[D] 98,317	[F] 174
NAPA RIVER NEAR ST. HELENA	11456000	211	436	[E] 45,150 [D] 35,602	[E] 215 [F] 169
PESCADERO C NR PESCADERO	11162500	119	683	[D] 26,026	[F] 219
ARROYO DE LA LAGUNA NR PLEASANTON	11177000	1,049	525	[D] 27,829	[F] 27
ALAMEDA CREEK BELOW WELCH CREEK, NEAR SUNOL	11173575	375	219	Insufficient stream flow record to estimate long term average loads, data collection is ongoing	
CROW CREEK NEAR HAYWARD	11180900	27	3,369		
SAN LORENZO C AT SAN LORENZO	11181040	116	424	[D] 8,185	[F] 71
SONOMA C A AGUA CALIENTE	11458500	161	-	[E] 26,082	[E] 162
GUADALUPE RIVER	-	378	-	[H] 91,044	[H] 702
WALNUT C AT WALNUT C	11183500	205	-	[I] 75,479	[I] 368
COYOTE C AT GILROY	11169800	282	-	[J] 44,575	[J] 158
SAN FRANCISQUITO C AT STANFORD	11164500	97	-	[J] 13,693	[J] 141
WEST FORK PERMANENTE C NR MONTA VISTA	11166578	8	-	[K] 868	[K] 109

[A] Average of USGS multi year annual suspended sediment load record
[B] Average of 3 year USGS annual suspended sediment load record
[C] Collins 2001
[D] FWMC * annual average watershed flow
[E] Anderson, 1981. Data converted from U.S. units to metric
[F] Average of USGS multi year annual suspended sediment load record divided by watershed area
[G] Average of 3 year USGS annual suspended sediment load record divided by watershed area
[H] USACE, 2001. Data converted from U.S. units to metric
[I] Porterfield, 1972. Data converted from U.S. units to metric
[J] Brown III and Jackson Jr. 1973. Data converted from U.S. units to metric
[K] Nolan and Hill, 1989. Data converted from U.S. units to metric

Unit exports (loads normalized to watershed area) vary from 27-1,639 t km^{-2} y^{-1} in Bay Area watersheds. The lowest unit export of sediment occurs in watersheds in Alameda County that drain eastern low rainfall areas. The highest unit export occurs in small watersheds with eroding soils (Cull Creek), the west facing steep Permanente Creek watershed, and the highly urbanized Colma Creek watershed in South San Francisco. The agricultural watersheds of Sonoma and Napa appear to export moderate unit sediment loads when compared to estimates for other Bay Area watersheds. Suspended sediment exports have been previously estimated using the SIMPLE model (Davis et al., 2000). Three of the drainage areas delineated by Davis et al. (2000) (Alameda, Sonoma, and Napa) are comparable to estimates presented in the current work (Table 3.4). Estimates presented in Table 3.4 for Alameda Creek (45 t km^{-2} y^{-1}), Sonoma Creek (162 t km^{-2} y^{-1}), and Napa River near Napa (174 t km^{-2} y^{-1}) are 2 - 3 times greater than estimates using the SIMPLE model (26, 66, and 55 t km^{-2} y^{-1} for each watershed, respectively).

Suspended sediment exports from 81 watersheds in California have been previously estimated (Anderson, 1981; Inman and Jenkins, 1999). One of the primary objectives of Inman and Jenkins (1999) was to test for differences in sediment yields associated with multi-decadal climate changes related to ENSO. They found that the predominantly wet period of 1969 - 1995 caused unit sediment exports 3 times greater than for the dry period from 1944 - 1968.

Long-term estimates of exports in California watersheds by Anderson (1981) and Inman and Jenkins (1999) suggest a range from 3 - 2,650 t km^{-2} y^{-1} with an average of 460 t km^{-2} y^{-1} (Figure 3.9). The range of exports from Bay Area watersheds is similar in magnitude to other watersheds of California. Both Anderson (1981) and Inman and Jenkins (1999) attributed most of the variation between watersheds of California to the influence of rainfall and geology on soil erosivity and slope stability. In addition, Inman and Jenkins (1999) found that the urban rivers of Los Angeles (Ballona Creek, Los Angeles River, and San Gabriel River) with its hard covered streets and river channels had relatively low yields (60, 110, 32 t km^{-2} y^{-1} respectively).

Although watershed characteristics undoubtedly affect yields in Bay Area watersheds, watershed area also appears to influence sediment exports (Figure 3.9) either because of its likely correlation with topography and mean stream slope or because larger watersheds tend to have greater sediment retention (lower sediment delivery ratios) (Novotny and Chesters, 1989). Milliman and Syvitski (1992) gathered sediment data from 280 watersheds around the world including a number from the continental USA and California. The data were stratified according to maximum headwater elevation and showed that runoff and watershed area were the best variables for predicting sediment export on a global basis.

In summary, sediment loads normalized to area (t km^{-2} y^{-1}) vary greatly between watersheds of the Bay Area, a similar conclusion to previous studies in California. Exports are influenced by watershed characteristics including rainfall, slope, topography, area, land use, geology and soil erosivity. The magnitude of suspended sediment export

estimated in the present study from data collected by the USGS over the past 40 years appears to be greater by 2 - 3 times than estimates made using the SIMPLE model (Davis et al. 2000). The difference is primarily associated with the sediment concentration data that were available for input into the SIMPLE model. The consequence is that recent estimates of contaminant loads made using the sediment load estimates provided by Davis et al. (2000) are likely to be an underestimate also (e.g., KLI, 2002).

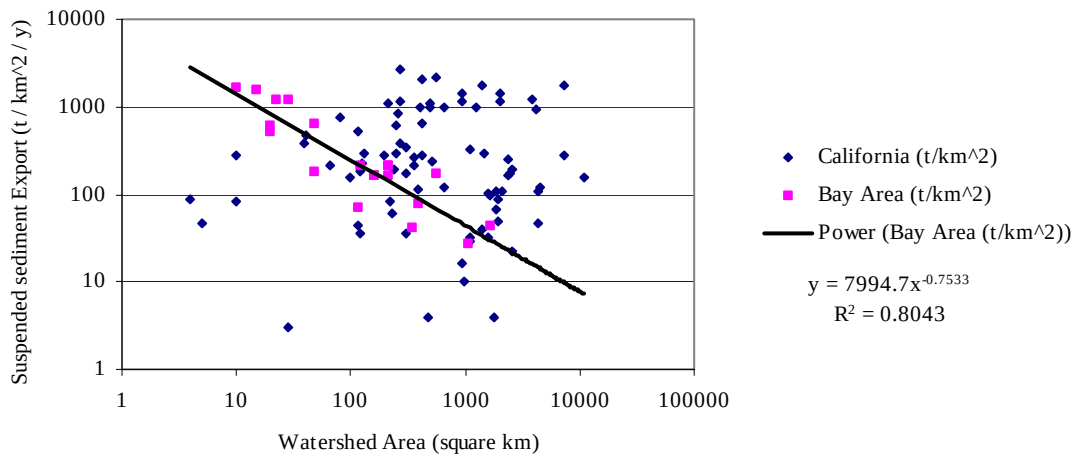

Figure 3.9. Suspended sediment exports in watersheds of California. Data extracted from Anderson (1981), Inman and Jenkins (1999), Collins (2001), and Table 3.4, this study.

Estimates of sediment loads from local small tributaries

Sediment loads to the Bay from local small tributaries have been estimated by several authors (Table 3.5). The most reasonable estimates of total overall suspended sediment loads appear to be between 744,000 and 1,000,000 t y^{-1}. As discussed previously, the estimate using the SIMPLE model is believed to be an underestimate. This is further supported by the summation of loads from watersheds totaling 3,541 km^2 (53% of the total area of local tributaries) where measurements have been made (Table 3.4). Although there is no basis for suggesting that the area covered by the analysis in Table 3.4 is representative, if the estimates are extrapolated to the non-gauged areas by dividing by 0.53, an estimate of 738-795 thousand metric tonnes per year is generated.

If it were assumed that all suspended sediment derived from areas upstream from dams is impounded, then this estimate would form an upper bound. The area upstream from dams was estimated by Davis et al. (2000). Excluding an area of 1,600 km^2 and performing the area extrapolation again yields 561-604 thousand metric tonnes per year. Given that the majority of impoundment (by area) occurs in Alameda Creek and Coyote Creek watersheds (two naturally low runoff watersheds) and that not all sediment will be

trapped, it seems likely that this estimate should be considered a low boundary. In addition, erosion can intensify in stream channels below dams as a result of sediment starvation, therefore the net result may not be an immediate reduction in sediment load from the watershed, rather a change in source. In any case, it seems reasonable to assume that the best estimate of suspended sediment loads from small tributaries in the Bay Area is between 561,000 and 1,000,000 t y^{-1}.

Sediment bed load, although not the subject of this report, was estimated at 8% of the total load in Bay Area tributaries when the sediment budget was being developed for the Bay (Ogden Beeman and Associates, Inc., 1992). USACE (2001) estimated average bed load for Guadalupe to be approximately 12% of the total load in that watershed. USGS data reported by Griggs and Paris (1982) suggests bed load makes up on average 3.4% of the total load for the San Lorenzo River watershed, Santa Cruz; however, bed loads may vary from <1 - 11% depending on the year. Inman and Jenkins (1999) suggested that for southern California coastal rivers, basins of <500 km^2 may be expected to yield >15% of their total load as bed load and for river basins >500 km^2, bed load is < 10% of total load. Milliman and Meade (1983) used an estimate of 7 -14% when estimating sediment bed loads transported by rivers to the world oceans. Therefore it is suggested that the ratio of bed load to total sediment load in Bay Area streams may be expected to vary depending on storm magnitude and watershed size, but a general estimate can be assumed to be 10 - 15% on average. Typically the concentration of trace contaminants associated with larger particles is less that concentrations found in the smaller particle sizes. This occurs because the surface area to volume / mass ratio is greater as particle size decreases, because smaller particles tend to have a greater organic content and because clays and colloids have a complex structural surface and polar charge characteristics that increase their affinity for trace compounds and ions.

Table 3.5. Loads of sediment (thousand metric tonnes) entering San Francisco Bay from local small tributaries (excluding the loads derived from the Central Valley).

Author	Suspended load	Bed load	Total load	Comment
Krone (1979)	934	-	-	Author's review of Smith (1965), and Porterfield et al., 1961 converted to metric tonnes
Ogden Beeman and Associates, Inc. (1992)	744	63 (8%)	807	Authors review of Porterfield (1980) converted to metric tonnes
Russell et al. (1980)	1000	-	-	No explanation by the author on the origin of the numbers
Davis et al. (2000)	320	-	-	SIMPLE model using local data collected during drought
This study [A]	394	-	-	Sum of loads estimates (low) from Table 3.4 without double counting any area.
This study [A]	424	-	-	Sum of loads estimates (high) from Table 3.4 without double counting any area.

[A] Area included is 2,964 km^2 or about 45% of the Bay Area watersheds.

In summary, the best estimate of suspended sediment loads entering the Bay from local tributaries appears to be between 561,000 and 1,000,000 t y^{-1}, which is similar to

estimates by Krone (1979). Bed loads are likely to supply an additional 10 - 15% of sediment mass to the Bay. Given that contaminants are typically associated with fine sediments, silts, clays, colloidal materials, and organic carbon (see contaminant sections of this review), it seems unlikely that bed loads will be a major vector for the transport of contaminants to the Bay.

Summary

- Local tributaries currently contribute up to 40% of the sediment load that enters the Bay annually. Regardless of the absolute proportion, it seems likely that local tributaries may be increasing in their importance.
- Suspended sediment transports contaminants, such as mercury, PCBs and OC pesticides.
- Unit sediment export from the Central Valley is currently about 14 t $km^{-2}y^{-1}$ whereas unit sediment exports from Bay Area local small tributaries averages about 100 t $km^{-2}y^{-1}$.
- Sediment is supplied to Bay Area streams by landslide erosion (38-64%), channel bed and bank erosion (8-60%), urban runoff, and agriculture.
- Given the size of local tributaries, between 7 and 55% of the sediment mobilized from sources within the watersheds will be retained on hillslopes, in channels, or on floodplains.
- Urbanization reduces the buffering capacity of these storage areas (for sediment and contaminants) because of channelization, increased velocity, increased peak flow, and disconnection from the floodplain and wetlands.
- Suspended sediment concentrations have been recorded in excess of 5,000 mg l^{-1} at 12 locations in the Bay Area. This will make the use of surrogate techniques more difficult given that turbidity probes usually only record up to about 3,000 mg l^{-1}.
- Daily suspended sediment concentrations vary from 3-4 orders of magnitude between low and high flow periods.
- Daily discharge varies from 4-5 orders of magnitude at the sample locations between low and highest flow periods.
- There are six (6) locations in the Bay Area (all in Alameda County) where suspended sediment is currently being measured. These would be ideal locations to measure contaminant concentrations.
- At locations where there have been sufficient measurements, sediment grains in suspension are between 67 and 100% finer than 0.062 mm (silts and clays). Surrogate technologies are likely to work well for these grain sizes.
- In general larger watersheds show finer median grain sizes in suspension.
- Greater than 99% of the suspended sediment loads are transported between November and April. Monitoring designs for sediments and related contaminants should be focused on the wet season only.
- Inter-annual variation of loads is high and can vary by 3-4 orders of magnitude in less urbanized watersheds but may be much less in urbanized areas (1-2 orders).

- Because inter-annual variation is also high, studies that select for a certain time (for example 3 years) may fail to sample the range of sediment and contaminant response to climatic variation and therefore fail to estimate the average or range of annual loads. An alternative sampling design might budget for a certain number of samples and preference only sampling floods of a minimum specified size or those early in the wet season when the first flush of suspended sediments and related contaminants occurs. Ideally sampling should occur over 7-10 years in selected watersheds. Data from long-term studies such as these could then be used to help to extrapolate more limited data sets in other watersheds.
- Sediment export varies from 27-1,639 t $km^{-2}y^{-1}$. Of the watersheds with sufficient data, the highest exports occur from Cull Creek, Colma Creek, and Wildcat Creek. The lowest occur in eastern parts of Alameda County and Alameda Creek at Niles.
- Total suspended sediment load entering SF Bay from local tributaries is estimated to be between 561,000 and 1000,000 t y^{-1}. This is about 3 times greater than estimates made using the Simple Model and therefore any other estimate of contaminant loads that rely on the sediment load generated by the SIMPLE Model will also be biased low.
- Bed loads are likely to supply an additional 10 - 15% of sediment mass to the Bay. Given that contaminants are typically associated with fine sediments, silts, clays, colloidal materials, and organic carbon (see contaminant sections of this review), it seems likely that bed loads will be a minor vector for the transport of contaminants to the Bay.

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Part 4: Polychlorinated biphenyls (PCBs)

Jon Leatherbarrow

Introduction

PROBLEM STATEMENT

Polychlorinated biphenyls (PCBs) are synthetic organic compounds that are toxic to humans and wildlife, highly persistent in the environment, and bioaccumulative in the food chain. PCBs were manufactured between 1929 and 1979 for uses in various industrial and commercial applications. The most toxic PCB congeners (*e.g.* PCB 77, 126, and 169) are those that mimic the effects of 2,3,7,8-tetrachlorodibenzo-p-dioxin, commonly referred to as dioxin. Chronic exposure to these PCB congeners is known to cause developmental abnormalities, growth suppression, endocrine disruption, impairment of immune functions, and promotion of cancer (Ahlborg *et al.*, 1994).

Although production of PCBs has been banned for decades, they are still ubiquitous in watershed soils, estuarine sediment, and biota of San Francisco Bay. The RMP has consistently measured concentrations of PCBs that exceed water quality criteria and screening values in water and fish samples collected from the Estuary. In the most recent sampling (July, 2001), 15 out of 18 water samples had total PCB concentrations that exceeded the water quality criterion of 170 pg l^{-1} for PCBs (SFEI, 2003; detection limits ~ 1 pg l^{-1} for individual congeners), established by the USEPA California Toxics Rule (CTR) (USEPA, 2000). In response to health concerns over human exposure to PCBs and other bioaccumulative contaminants, including methyl mercury, dioxins, and organochlorine (OC) pesticides, the Office of Environmental Health and Hazard Assessment (OEHHA) issued an advisory with detailed recommendations for limiting human consumption of fish caught in the Bay (OEHHA, 1994). Due to the interim advisory, PCBs were placed on the 303(d) list for all San Francisco Bay segments in 1998 spurring the current development of a PCB TMDL for San Francisco Bay (Hetzel, 2000).

IMPORTANCE OF RUNOFF FROM LOCAL WATERSHEDS

The recent state of knowledge about sources and pathways of PCBs in the San Francisco Estuary has been summarized by the RMP through the Chlorinated Hydrocarbon Workgroup (CHCWG; Davis and Yoon, 1999) and Sources Pathways and Loadings Workgroup (SPLWG; Davis *et al.*, 1999), which led to the development of a PCB mass budget for the Bay (Davis, 2002). These reviews concluded that small tributaries and storm drains probably contribute significant loads of PCBs to the Bay. Given that PCBs have a strong affinity to sediment particles, it is assumed that sediment and stormwater are the main vectors of transport from these pathways. Furthermore, Davis (2002) concluded from the PCB mass budget model of the Bay that an annual load of 10 kg per year of PCBs would be sufficient to significantly delay declines of PCB concentrations in Bay fish. Model results stress the importance of developing and implementing monitoring strategies that accurately account for PCB loading from Bay Area watersheds to determine whether local tributaries are significant contributors of PCBs in relation to other major inputs.

To understand the contribution of PCBs and other contaminants of concern from small tributaries and storm drains, the SPLWG emphasized the need to develop conceptual models that describe contaminant transport in urban runoff and the variability associated with hydrologic and sediment processes in the urban landscape. In addition, SFEI began a review of digital storm drain information (Wittner and McKee, 2002), and the local stormwater agencies began monitoring PCBs in bed sediments of local tributaries and storm drains to characterize concentration ranges and distribution in areas of specific land uses in Bay Area watersheds. This chapter will provide a basis for identifying and developing monitoring strategies for capturing spatial and temporal variability in PCB concentrations and loading from local watersheds.

PCB properties and analytical limitations

PROPERTIES

The chemical and physical properties of individual PCB congeners vary according to the extent of chlorination and arrangement of chlorine atoms around the molecule. For example, the most chlorinated PCB is decachlorobiphenyl (PCB 209), which has 10 chlorine atoms around the biphenyl group (Figure 4.1). The hydrophobic nature of PCBs gives them characteristic properties of low water solubility, low vapor pressure, and a relatively high octanol-water coefficient (K_{OW}) indicative of preferential sorption to organic matter (Table 4.1). PCB congeners with higher numbers of chlorine atoms are less water soluble, less volatile, and have higher affinities for sorption to organic phases (*i.e.*, higher K_{OW}) compared to less-chlorinated PCBs. Therefore, highly chlorinated PCB residues have a greater tendency to partition into organic matter, persist in soil and sediment in the environment, and bioaccumulate in lipids of wildlife and humans.

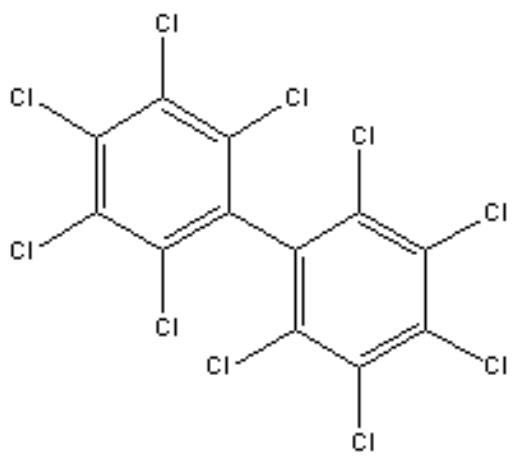

Figure 4.1. Chemical structure of decachlorobiphenyl, PCB 209. PCB 209 is the most chlorinated PCB congener with molecular formula of $C_{12}Cl_{10}$ and molecular weight 498.7 g mol^{-1}**.**

Table 4.1. Chemical properties of selected PCB compounds. Data summarized by Schwarzenbach *et al.* (1993) from references therein.

	Number of Chlorine Atoms	Mol-Wgt g mol^{-1}	Vapor Pressure Po atm	Solubility Cw mol l^{-1}	Henry's Law Constant K_H atm l mol^{-1}	Oct-Water Coeff (Kow) Log Kow (mol*l^{-1} octanol)* (mol*l^{-1} water)$^{-1}$
PCB 015	2	223.1	0.14	0.15	0.16	5.33
PCB 066	4	292	0.12	0.13	0.31	6.31
PCB 153	6	360.9	0.11	0.13	0.071	7.15
PCB 209	10	498.7	0.081	0.095	0.019	8.23

ANALYTICAL LIMITATIONS

PCBs are often measured by methods employing filtration and analysis of dissolved and particulate fractions. This approach tends to underestimate the actual concentrations of PCBs associated with particles in the water column. In the RMP, PCBs in water are measured as individual congeners separated into particulate and dissolved concentrations (operationally defined as the fraction of the sample that will pass through a filter of pore size 1 µm). Of note, this contrasts to suspended sediment concentration (SSC) that is operationally defined as those particles that do not pass through a 0.45 µm filter (*e.g.*, Gray *et al.*, 2000).

Studies of PCB partitioning in natural waters have indicated that a large portion of PCBs and other nonionic organic compounds may be associated with colloids (*e.g.*, Baker *et al.*, 1986; Rostad *et al.*, 1995; Burgess *et al.*, 1996), which are solids that have very low water solubility and diameters of approximately 0.01-10 µm (Sposito, 1989). Because much of the colloid-associated fraction of PCBs passes through commonly used filters, the 'apparent' solubility of PCBs increases with increased concentrations of humic substances and colloids (Chiou *et al.*, 1986). Given that colloids have greater surface area per volume and organic carbon content for sorption of PCBs (Rostad *et al.*, 1995), this leads to an underestimate of actual particle-associated PCB concentrations.

Another limitation to using PCB concentrations in estimating loads is that total PCB concentrations are typically calculated by summing a representative list of congeners that often underestimate the actual PCB concentrations. For example, the RMP measures 40 congeners, which comprise an estimated 80% by mass of all PCB congeners (Jay Davis, SFEI, personal communication). Adding an additional 30 congeners to the list would only account for a 12% increase in PCB mass for 75% more congeners. Accordingly, a balance between costs and benefits usually results in analysis of an incomplete, yet representative list of PCB congeners to determine the total mass of PCBs in a sample. This may not pose a significant problem for studies in Bay Area watersheds since recent and ongoing studies of PCBs in storm drains (Gunther et al., 2001; KLI,

2001; KLI 2002) and tributaries (Leatherbarrow et al., 2002), as well as PCB mass budget modeling exercises in the Bay (Davis, 2002), have used consistent lists of PCB congeners to represent total PCB concentrations. Furthermore, transport modeling of PCBs is often conducted on an individual congener basis since transport processes (e.g., volatilization, partitioning) are unique to the congener. Thus, transport modeling on a congener basis is not dependent on the sum of PCBs and is expected to be more successful than on a total basis.

Insensitive analytical methods are another potential limitation in studies of PCBs in stormwater. As with other organic contaminants, analytical techniques for PCBs have become increasingly more sensitive in recent years, with method detection limits (MDLs) for individual PCB congeners in RMP water samples at approximately 1 pg l^{-1} (1 ppq). Given that PCB residues exist at trace levels in tributaries of San Francisco Bay (Leatherbarrow *et al.* 2002), concentrations of many PCB congeners may be below detection, potentially leading to underestimation of the total PCB mass in water. However, concentrations of the predominant PCB congeners (*e.g.*, 110, 118, 153) typically exceed this concentration, sometimes by 2 to 3 orders of magnitude. The extent to which method detection limits prevent accurate accounting of PCB congener concentrations will be less important in samples collected from contaminated locations compared to 'cleaner' samples. For this reason, watersheds in the Bay Area that have had high PCB use in the past and that currently have high concentrations in sediments either on the adjacent Bay margin or within drainage lines will likely have water column concentrations much higher than detection limits during floods.

Historic and current sources

PCBs were commercially produced from 1929 to 1979 and primarily used as insulating fluids in transformers, capacitors, and electromagnets. PCBs were also used for various purposes in heat exchanger fluids, chemical stabilizers, plasticizers, adhesives, insulating materials, flame-retardants, lubricants, and other products (Wong et al, 2000; Davis, 2000; Walker *et al.*, 1999). Most of these uses were associated with industrial applications; however, some uses occurred in residential and commercial areas (*e.g.*, electrical transformers, appliances) and even non-urban regions (*e.g.*, hydroelectric power).

Aroclor was the most widely produced and used trade name of PCBs in the United States, with an estimated total production of 610 x 10^6 to 635 x 10^6 kg (Hetzel, 2000). Aroclors are mixtures of PCB congeners named according to the number of carbon atoms and the mass percentage of chlorine atoms associated with the mixture. For example, Aroclor 1248 has 12 carbon atoms and is approximately 48% chlorine by weight. Approximately 65% of the Aroclors produced were relatively low-molecular weight mixtures, Aroclor 1242 and Aroclor 1016 (Erickson, 1997), which are comprised of approximately 42% chlorine by mass. The highly chlorinated mixtures Aroclor 1254 (54% chlorine) and 1260 (60% chlorine), which are more persistent in the environment, comprised 16% and 12% of the Aroclors produced, respectively (Erickson, 1997).

Similar to varying properties of individual PCB congeners, hydrophobic properties of Aroclors increase with increasing percent contribution of chlorine.

The USEPA banned the production and use of PCBs in 1979, with exceptions for totally enclosed applications, which are responsible for an undetermined amount of PCBs that are still in use (Rice and O'Keefe, 1995). The amount is difficult to quantify; however, some estimates are as high as 50-60% of the original stock of PCBs, with an additional 20-30% of PCBs as residues in the environment (Steuer *et al.*, 1999a).

The USEPA maintains a database that lists an inventory of current PCB use in the San Francisco Bay region based on information voluntarily provided by local agencies and organizations (http://www.epa.gov/opptintr/pcb/data.html). According to this inventory, as of 1999, at least 200,000 kg of PCBs were being used in transformers throughout the Bay Area. One of the primary historical users of PCBs in the Bay Area, Pacific Gas and Electric (PG&E), still has large supplies of equipment that contain PCB residual contamination from earlier PCB use (Davis *et al.*, 1999). Due to widespread use of PCBs in industrial applications and potential leaks and/or spills and the persistence of PCBs in soil and sediment, urbanized drainage areas throughout the Bay Area are persistent ongoing sources of PCBs (Gunther *et al.*, 2001; KLI, 2001; KLI, 2002).

Sediment studies conducted in the San Francisco Estuary and its watersheds have consistently measured higher PCB concentrations in areas of urban development compared to regions of open space or non-urban land uses (Hunt *et al.*, 1998; Daum *et al.*, 2000; KLI, 2001; Gunther *et al.*, 2001) (Figure 4.2). However, PCB concentrations in bed sediment of urban conveyances are not necessarily evenly distributed throughout urban regions of the Bay Area watersheds (Gunther *et al.*, 2001). This indicates that variability exists between Bay Area watersheds in their capacity to supply and transport PCB residues to the Bay.

To determine the extent to which urban watersheds contribute PCB loading to the overall budget of the Bay, monitoring should be conducted downstream from drainage areas with known PCB sources. These areas are commonly associated with industrial activity, but might also include non-urban areas of past and current PCB use (*e.g.*, hydroelectric plants). Data from the various sediment studies, combined with information about watershed characteristics (*e.g.*, known locations of past use, land use, and hydrology), provide a useful gauge for identifying watersheds with potential PCB sources and prioritizing watersheds for implementation of source reduction activities and monitoring techniques designed to detect long-term changes in PCB loading to the Bay.

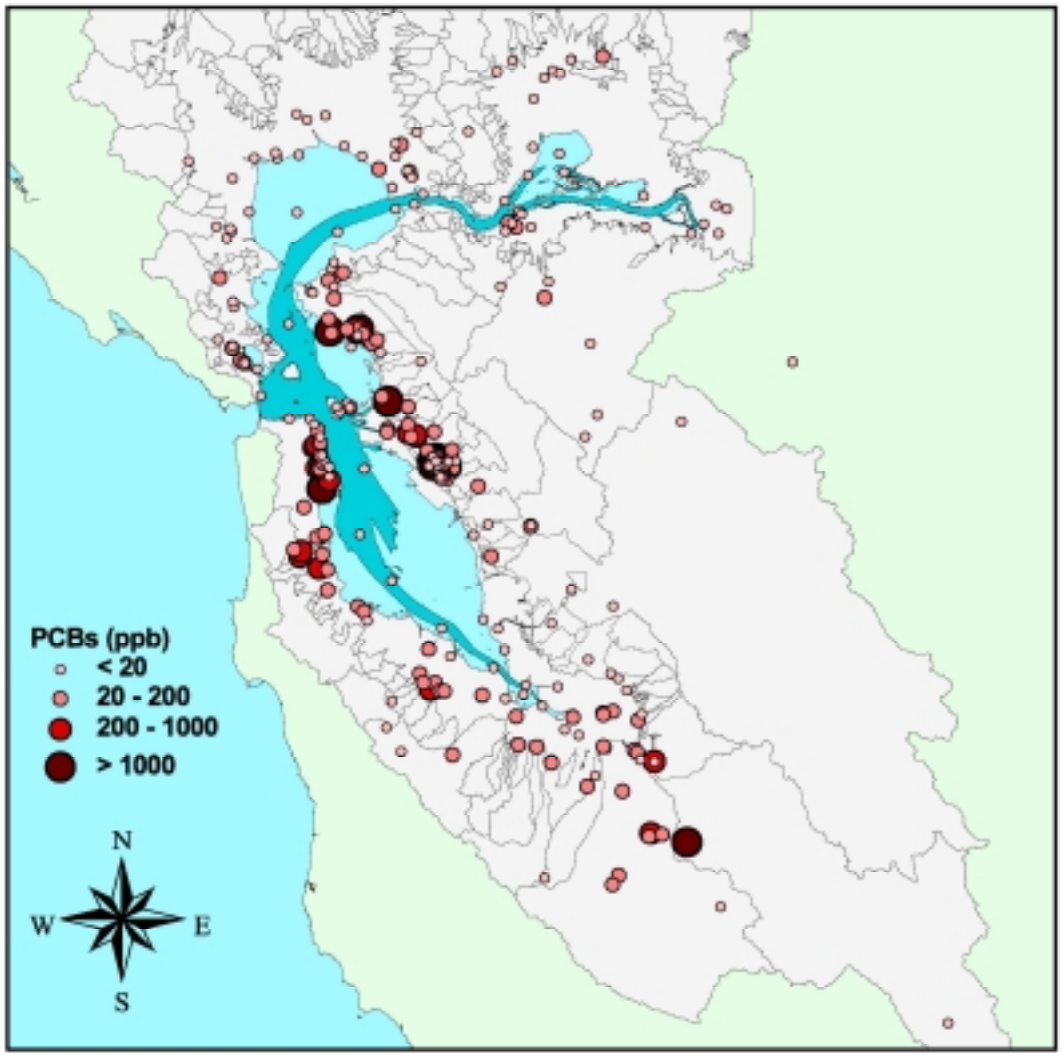

Figure 4.2. Average PCB concentrations in Bay Area sediment. Data compiled from RMP monitoring (*e.g.*, SFEI 2002), Hunt *et al.* (1998), Flegal *et al*. (1994), Daum *et al.* (2000), KLI (2001), and Gunther *et al.* (2001).

PCB transport in tributaries

The following discussion addresses issues of partitioning behavior and the spatial and temporal variability of PCB concentrations and loading. It will be discussed in relation to watershed processes and characteristics as a basis for understanding PCB transport through Bay Area watersheds and recommending strategies for monitoring PCB concentrations and loading. The discussion focuses on important pathways of PCB transport through Bay Area watersheds, including tributaries, storm drains, and atmospheric deposition (in the following section) (Davis *et al.*, 1999). Compared to these

pathways, transport through biota and groundwater flow is assumed to be minor and were not discussed within the current scope of this literature review.

As previously noted, small tributaries and storm drain systems in Bay Area watersheds are known pathways of PCB contamination to San Francisco Bay (Davis *et al.*, 1999; KLI, 2001; Gunther *et al.*, 2001). The physico-chemical behavior of PCBs in urban runoff is influenced by a complex array of factors: existence of sources, sediment and organic carbon supply and transport, watershed characteristics (*e.g.*, land use, impervious cover, waterway modifications), hydrologic factors (*e.g.*, rainfall amount and intensity) and the degree of weathering (*i.e.*, time since the release of PCBs to the environment). Limited data is available from local studies of PCB transport through the water column of tributaries and storm drains. To improve our understanding of watershed processes and their influence on spatial and temporal variability in PCB loading, data from studies in other river systems are discussed in the following section.

PCB PARTITIONING AND CONCENTRATIONS IN TRIBUTARIES

PCB Partitioning in Tributaries

An effective tributary monitoring strategy should take into consideration the high affinity and sorption of PCBs and other hydrophobic organic compounds to material in river systems, such as organic matter dissolved in the water column and associated with suspended sediment. In tributaries and stormdrains of watersheds contaminated by PCBs, mobilization of PCB residues by erosion and leaching of particulate material is often the dominant transport mechanism (Table 4.2; Steuer *et al.*, 1999a; Foster *et al.*, 2000a, 2000b; Verbrugge *et al.*, 1995; Marti and Armstrong, 1990; Quemerais *et al.*, 1994a). For example, particulate PCB concentrations in water samples collected during flood-flow conditions from the tidal reaches of the Guadalupe River (556 km^2) and Coyote Creek (914 km^2), which drain into the Lower South San Francisco Bay, comprised approximately 87 ± 2.3% and 90 ± 6.4% of total PCB concentrations measured, respectively (SFEI Annual Results, *e.g.*, SFEI, 2002). Furthermore, samples from these locations have PCB congener patterns indicative of Aroclor 1260 (Leatherbarrow *et al.*, 2002), which sorbs to particulate phases more readily than lower-molecular weight Aroclors.

Several studies have determined that significant correlations exist between PCB concentrations and POC (Butcher *et al.*, 1998; Teil *et al.*, 1998), suspended particulate matter (SPM) (Quemerais *et al.*, 1994b), and total suspended solids (TSS) (Steuer *et al.* 1999a, 1999b). The linear relationship between PCB concentrations and TSS, among other variables such as discharge and soil loss coefficients, allowed Steuer *et al.* (1999a, 1999b) to use linear regression to successfully estimate PCB loading in several tributaries. In a similar manner, surrogate techniques that use continuous monitoring of turbidity may provide a cost-effective means of recording fluctuations in suspended sediment concentrations (McKee *et al.*, 2002), which can, to a large extent, be related to variation in concentrations of particle-associated contaminants, such as PCBs.

In contrast to the expected preferential sorption of PCBs to particulate phases, several studies have measured higher proportions in the dissolved fraction in water samples with low suspended particulate concentrations (Chevreuil *et al.*, 1990; Marti and Armstrong, 1990) and low organic carbon content (Jiang *et al.*, 2000). Marti and Armstrong (1990) determined that in 15 samples collected from nine tributaries of Lake Michigan, samples with suspended particulate material (SPM) less than 10 mg l^{-1} had higher proportions of dissolved PCBs than particulate PCBs. Above 35 mg l^{-1} SPM, particulate PCBs comprised greater than 85% of total PCBs (Marti and Armstrong, 1990). Marti and Armstrong (1990) also determined that samples with PCB homolog patterns similar to Aroclor 1242/1248 were predominantly in the dissolved phase, while Aroclor 1254/1260 samples were mostly associated with the particulate phase. Similarly, Chevreuil *et al.* (1990) consistently measured greater proportions of dissolved PCBs in the Seine River during high flows, but attributed this to low sorption capacity (log K_d ~ 4-5) and low concentrations of suspended material (mean = 25 mg l^{-1}) and/or organic carbon. These studies indicate that tributaries with low suspended sediment concentrations and organic carbon, as well as relatively low-molecular weight PCBs in the water column are not necessarily suitable for monitoring techniques that rely on particle-associated transport of PCBs. In such cases, alternative methods of monitoring must be employed to record the variability in concentrations and loading associated with the dissolved phase.

Table 4.2. Proportion of PCBs in particulate phase in selected river systems.

River	Land Use	Basin Size (km^2)	Percent Particulate PCBs (%)
Guadalupe River - SF Bay [1]	Urban, Historic Mining, Ag	556	87 ± 2.6
Coyote Creek - SF Bay [1]	Urban, Ag	914	90 ± 6.4
Sacramento River - SF Bay [1]	Ag, Open, Urban	154,000	48 ± 31
San Joaquin River - SF Bay [1]	Ag, Open, Urban		53 ± 24
Anacostia River - Ches. Bay [2]	Urban	440	89-95
Susquehanna River - Ches Bay [3]	Forest, Ag, Urban	70,160	41
Saginaw River – Michigan [4]	Urban, Ag	15,695	69 ± 6
Milwaukee River – Milwaukee [5]	Ag, Open, Urban	2,200	61-74
Seine River – Paris [6]	Urban, Ag	78,900	27
St. Lawrence River – Canada [7]	Industrial, Municipal	1,300,000	89 ± 12
Yangtse River – China [8]	Mixed	?	22-39

[1] RMP wet-season samples, Delta Outflow Index > 100,000 cfs, salinity <0.5‰, conductivity < 1,000 µmho, TSS = 15-318 mg l^{-1}.
[2] Foster *et al.* (2000a)
[3] Foster *et al.* (2000b)
[4] Verbrugge *et al.* (1995)
[5] Steuer *et al.* (1999a)
[6] Chevreuil *et al.* (1990)
[7] Quemerais *et al.* (1994b) – May sampling
[8] Jiang *et al.* (2000)

One factor that may account for greater proportions of PCBs in the operationally-defined dissolved phase is an artificial increase of apparently soluble PCBs associated

with colloids (Baker *et al.*, 1986; Rostad *et al.*, 1995; Jiang *et al.*, 2000). Colloidal material that passes through commonly used filters during separation of the sample between the operationally defined 'dissolved' and particulate phases typically has greater surface area and organic carbon content, and may have PCB concentrations 2 to 3 times greater than concentrations on suspended silts (Rostad *et al.* 1995). Furthermore, dissolved and colloidal loads of PCBs pass through the watershed once those masses are mobilized, while particulate PCB loading and deposition are influenced more by hydrologic factors, such as rainfall intensity, shear stress, stream velocity, turbulence and residence time. Although the magnitude of PCB loading associated with colloids can be 3 to 5 times less than PCB loads associated with suspended silts (Rostad *et al.*, 1995), this is still a potentially significant portion of the load. For this reason, total concentrations of PCBs should be measured to account for loading of PCBs in the truly dissolved fraction and PCBs associated with particles of all sizes.

The accuracy of a PCB load monitoring design that is based on defining the variability in suspended sediment is dependent on the supply of suspended sediment and the affinity of PCBs for particulate material in the water column. As noted previously, in tributaries that transport low concentrations of suspended sediment and/or organic matter and low-molecular weight residues of PCBs, PCBs may occur primarily in the dissolved phase. In Bay Area watersheds, however, surface runoff that occurs during high flow conditions typically contains flow-weighted suspended sediment concentrations ranging between 374 and 4,472 mg l^{-1} (see Table 3.1 in section on Sediment Processes). At stations with multi-year data and discrete concentrations, some locations have suspended sediment concentrations greater than 20,000 mg l^{-1}. Furthermore, samples collected from the water column and bed sediment of contaminated tributaries and storm drains of Bay Area watersheds typically have PCB congener patterns indicative of high-molecular weight Aroclors 1254 and 1260 (KLI 2001, Johnson *et al.*, 2000, Leatherbarrow *et al.*, 2002). For these reasons, PCBs residues in surface runoff and resuspended bank and bed sediment in local tributaries and stormwater conveyance systems that drain heavily impacted watersheds are expected to be primarily associated with suspended particulate material transported during large storm events.

Accordingly, a tributary monitoring component for local tributaries should (1) explore the use of continuous monitoring of turbidity as a surrogate for concentrations of suspended sediment and particle-associated contaminants, such as PCBs; (2) measure total PCB concentrations in the water column to account for the entire PCB mass associated with the particulate and dissolved fractions; and (3) measure ancillary water quality parameters that influence partitioning, transport, and fate of PCBs, including particulate organic carbon (POC), dissolved organic carbon (DOC), and suspended sediment concentrations (SSC).

Spatial Variability of PCB Concentrations in Tributaries

To improve our understanding of the extent to which urbanized watersheds contribute to total inputs of PCBs to the Bay, watershed monitoring locations should be prioritized based on known regions of PCB contamination and potential for

remobilization of PCB residues (Figure 4.2). Tributaries and storm drains in watersheds with extensive urban development generally have higher concentrations of PCBs compared to non-urban drainage areas (KLI, 2001; Gunther *et al.*, 2001; Steuer *et al.*, 1999a; Foster *et al.*, 2000a; Rostad *et al.*, 1993, 1995, 1999). In a recent characterization study of PCBs in bed sediments of urban storm drains, the Bay Area storm water management agencies determined that PCB concentrations in urban drainage areas were significantly higher (median = 44 $\mu g\ kg^{-1}$) than concentrations in sediment from non-urban drainage areas (median = 1.1 $\mu g\ kg^{-1}$) (Gunther *et al.*, 2001; KLI, 2001). Furthermore, the maximum concentration measured at an industrial site in the Coyote Creek watershed of the Santa Clara Valley (26,000 $\mu g\ kg^{-1}$) was approximately 3 orders of magnitude greater than the maximum concentration measured in open space locations (29 $\mu g\ kg^{-1}$). It follows then that monitoring in relatively large watersheds that drain highly contaminated areas and export large supplies of sediment to the Bay, such as Coyote Creek or Guadalupe River, will provide important information for the purpose of estimating the total contribution of PCBs from local urban watersheds.

Monitoring should also be conducted downstream of potential sediment storages of PCBs within the watershed to integrate total PCB exports from local tributaries to the Bay. Downstream effects of urban land use often include increased PCB concentrations in the water column (Steuer *et al.*, 1999a; Verbrugge *et al.*, 1995), channel bed and bank sediments, and floodplain deposits (Owens *et al.*, 2001). However, repeated deposition and resuspension of contaminated bed sediment along reaches of tributaries may result in more homogeneous PCB concentrations that blur distinct linkages between PCB contamination and specific sources in the watershed (Rostad *et al.*, 1995). Therefore, monitoring locations should be located far enough downstream to account for PCBs associated with locally resuspended bed sediments as well as PCB residues entrained in runoff from watershed surfaces.

Urbanized portions of Bay Area watersheds are typically located in the downstream sections of the watersheds. Monitoring of PCB loading to the Bay should, therefore, be conducted in the freshwater reaches of tributaries directly upstream from the zone of tidal influence. Furthermore, given that the tidal reaches are also substantial deposits of PCB residues (Leatherbarrow *et al.*, 2002), studies of contaminant fate in tidal reaches downstream of monitored tributaries will further improve our understanding of the impact of local tributaries on PCB contamination in the Bay.

Temporal Variability of PCB Concentrations in Tributaries

Accurate estimates of PCB loading from local tributaries must account for the short- and long-term variability of PCB concentrations and transport in response to episodic and seasonal changes in rainfall, streamflow, and sediment discharge. In relatively contaminated watersheds, stormwater discharge may increase PCB concentrations in the water column from remobilization of PCB residues by surface runoff or resuspension of contaminated channel bed and bank sediments (Chevreuil *et al.* 1991; Steuer *et al.*, 1999a, 1999b; Foster *et al.*, 2000a, 2000b; Quemerais *et al.*, 1994b). Conversely, water bodies with primarily internal PCB sources, such as eroding channel

bed deposits, or point source discharges may have decreasing PCB concentrations in response to greater rainfall and streamflow due to the diluting effects from less-contaminated runoff and sediment from upstream (Bremle and Larsson, 1997). As discussed previously, Bay Area watersheds have known areas of contamination where PCB residues are still transported through storm drains and tributaries to the Bay (Gunther *et al.*, 2001; KLI, 2001; KLI, 2002; Leatherbarrow *et al.*, 2002). As an effect of increased sediment supply and runoff during storm events in Bay Area watersheds (see Figure 3.4 in section on Sediment Processes), a plausible hypothesis is that PCB concentrations and loading will also increase in response to large storm events and wet-season conditions.

First flush effects are especially important in Mediterranean climates, such as that of the Bay Area, and cause an even greater increase in PCB concentrations during the initial stages of the wet season (Froese *et al.*, 1997; Chevreuil *et al.*, 1991). This occurs due to sudden pulses of surface runoff and resuspension of channel bed sediments that entrain PCB loads that deposited and accumulated during the preceding dry period. For example, Chevreuil and Granier (1991) measured maximum PCB concentration (> 2,700 ng l^{-1}) in an urban storm drain within hours of peak rainfall, which preceded flood discharge. PCB concentrations decreased to 400 ng l^{-1} by the time discharge peaked (~ 0.60 m^3s^{-1} [21 cfs]) and eventually decreased over 100-fold to ambient levels (< 20 ng l^{-1}) as storm flow attenuated back to low flow conditions (Chevreuil and Granier, 1991). This commonly observed pattern in urban drainage areas was attributed to surface runoff of accumulated PCB residues from dry deposition combined with washing out of atmospherically derived PCBs (Chevreuil and Granier, 1991). The source of the high range of PCB concentrations was not identified in the study; however, first-flush patterns of PCB transport are expected in urbanized watersheds in the San Francisco Bay region given the quick response times to rainfall events and the Mediterranean climate (see section on Climate and Hydrology).

Less distinct increases in PCB concentrations have been measured on longer time scales of days and months during wet-season conditions (Froese *et al.*, 1997; Foster *et al.*, 2000a, 2000b). Foster *et al.* (2000a) measured a 25-fold (0.5 ng l^{-1} to 13 ng l^{-1}) increase in total PCB concentrations between base and storm flow conditions over a four-day period in a branch of the Anacostia River. Dissolved phase concentrations, however, remained relatively constant throughout different flow regimes. In the relatively small River Orge (mean annual discharge = 3.4 m^3 s^{-1} (120 cfs) mixed land use), Chevreuil and Granier (1991) measured PCB concentrations during the winter storm season (maximum = 400 ng l^{-1}) that were at least 8-fold greater than typical concentrations measured during summer and autumn sampling (50 ng l^{-1}). Similar patterns were observed in the larger less urbanized watershed of the Susquehanna River throughout the duration of a storm on a monthly time scale (Foster *et al.* 2000b).

Although particulate and total PCB concentrations typically increase during storm events, dissolved PCB concentrations and PCB concentrations on particles (mass PCBs/mass sediment) often decrease due to dilution from increased streamflow and the transport and mixing of sediment from less contaminated upstream areas (Steuer *et al.*,

1999b; Foster *et al.*, 2000a; Verbrugge *et al.*, 1995). At the confluence of two tributaries, one of which received discharge from a sewage treatment plant, Steuer *et al.* (1999b) measured a 30-fold decrease in PCB concentrations on suspended sediment from 10.7 to 0.3 ug g^{-1}, which coincided with greater than a 100-fold increase in streamflow (<6 to 644 cfs (0.17 to 18.2 m^3s^{-1}). Dissolved concentrations were also at a minimum of 5.7 ng l^{-1} during peak flow conditions. This decrease in PCB concentrations may have occurred due to dilution by upstream runoff and sediment from the less-contaminated tributary during high flow conditions. In other cases, PCB concentrations in water and sediment in urban regions that lie downstream of agricultural fields or rangelands may be diluted by eroded material from the upper watershed (Owens *et al.*, 2001; Steuer *et al.* 1999b). Furthermore, contaminated flood plains may not erode as readily as less contaminated steep-sloped regions of some upper watershed regions (Owens *et al.* 2001, Steuer *et al.* 1999b).

To summarize, monitoring of PCB loading from local tributaries should characterize the short-term variability in water-column PCB concentrations and loading that occurs in response to storm events, including first-flush effects. Peak contaminant concentrations in the water column occur in response to rainfall and runoff in urbanized portions of Bay Area watersheds on the order of minutes to hours. The logistical and practical limitations of sampling such events give reason for exploring the applicability of continuous monitoring of surrogate parameters, such as turbidity. As previously noted, local watersheds that are heavily impacted by PCB contamination are expected to release PCB residues in surface runoff that are primarily associated with suspended sediment. In some watersheds, however, variation in PCB concentrations in suspended sediment may occur downstream due to dilution by 'cleaner' sediment from upstream. Therefore, the application of surrogate techniques is most appropriate for watersheds with widespread PCB contamination and consistent supplies of suspended sediment.

Temporal Variability of PCB Partitioning in Tributaries

The accuracy of surrogate techniques as a means for measuring PCB loading depends on how partitioning of PCBs to the particulate phase changes over the time of sampling. In the Saginaw River (15,600 km^2), which receives drainage from urban runoff and domestic sewage effluent, Verbrugge *et al.* (1995) measured a relatively consistent distribution of PCBs between particulate and dissolved phases (~ 66% particulate PCBs) during several storm events. This was attributed, in part, to continuous inputs from the surrounding watershed as opposed to episodic pulses from point source discharges.

In contrast, severe storm events that mobilize relatively coarse-grained sediment loads, which typically have lower concentrations of organic carbon than fine-grained sediment and less sorption capacity for contaminants, may cause inconsistent PCB partitioning in the water column (Chevreuil and Granier, 1991; Teil *et al.*, 1998; Foster *et al.* 2000b). In the Seine River (78,900 km^2), Chevreuil and Granier (1991) determined that the percentage of PCBs adsorbed to particulate matter decreased from approximately 52% to near zero when streamflow increased from approximately 450 m^3s^{-1} (15,892 cfs) to greater than 700 m^3s^{-1} (24,721 cfs) over the course of 3 to 4 days. With mean

concentration of suspended matter (SM) of approximately 160 mg l^{-1}, Chevreuil and Granier (1991) attributed this to poor sorption capacity of the SM and low organic matter in flows greater than 600 m^3 s^{-1}. Similar results were found in the Susquehanna River (70,160 km^2) where log K_d (4.0-5.5) was inversely correlated to discharge (795-10,000 m^3s^{-1} [28,075-353,150 cfs]) (Foster *et al.* 2000b).

The literature suggests that partitioning of PCBs to particulate phases varies over time scales of storm events in response to changes in sorption capacity of particulate material in the water column and sediment characteristics. With limited empirical data and information available on the partitioning of PCBs in local tributaries, it is difficult to determine whether partitioning of PCBs to the particulate phase remains constant during storm events. However, as discussed earlier, local tributaries in highly contaminated watersheds typically transport highly chlorinated PCB residues with high sorption affinities to particulate material from ongoing sources in contaminated watersheds. Furthermore, the fine-grained sediment fraction dominates the suspended sediment load in local tributaries under varying flow regimes (see Figure 3.7 in section on Sediment Processes). These characteristics of local tributaries support the exploration of suspended sediment-based monitoring to characterize temporal variability of PCB concentrations and loading in tributaries and storm drains of contaminated Bay Area watersheds.

PCB LOADING IN TRIBUTARIES

Previous estimates of PCB loading from local tributaries have been derived in only a few studies using simple modeling approaches and best estimates for input parameters (Gunther *et al.*, 1987; Gunther *et al.*, 2001; KLI 2002). To estimate PCB loading from local watersheds, KLI (2002) used bed sediment concentrations of PCBs normalized to the percentage of fine-grained material (*i.e.*, percent of sediment sample with grains <62.5 µm in diameter), and estimates of suspended sediment loads derived from the SIMPLE model (Davis *et al.*, 2000). KLI (2002) estimated that local tributaries and storm drains contribute approximately 0.18 to 63 kg y^{-1} to the Bay with a median load of 31 kg y^{-1}. This loading estimate is less than the range presented previously by Gunther *et al.* (1987), which used very limited available data to estimate that 6 to 400 kg y^{-1} of PCBs entered the Bay from urban runoff.

The range of estimates associated with both desktop studies encompasses approximately two orders of magnitude and are very sensitive to estimates of suspended sediment loads. For example, KLI (2002) used the SIMPLE model to estimate suspended sediment loads following the work of Davis *et al.* (2000). More recent evidence (see section on Sediment Processes) suggests that the SIMPLE Model may underestimate actual loads by a factor of 2 to 3. It follows then that PCB loads may be underestimated by the same amount. As discussed in other sections of this review, however, bed sediment concentrations may not be a good estimator for flow-weighted mean water column concentrations of organic contaminants (see section on OC Pesticides). The mass budget model of PCBs in San Francisco Bay (Davis, 2002) indicates that the time it will take for the Bay to attain an acceptable water quality standard is highly sensitive to the accuracy of PCB loading from external pathways. Therefore, achieving more accurate

estimates of PCB loading from local tributaries will assist in validating the mass budget model and determining the long-term implications of continued PCB loading from Bay Area watersheds.

Spatial Variability in Loading

Effective management strategies for source control and reduction in the Bay require accurate estimates of PCB loading from watersheds with PCB sources that continue to contribute to increased PCB concentrations in Bay sediment. To evaluate potential spatial differences in loading from different watersheds in Alameda County, Gunther *et al.* (2001) used bed sediment PCB concentrations and previous estimates of TSS loading to estimate that PCB loading from eight watersheds ranged from 0.1 g y^{-1} from Dry Creek to 260 g y^{-1} at the Ettie Street Pump Station. Although the Ettie Steet Pump Station (3.86 km^2) is approximately 7 times smaller than the Dry Creek drainage basin (24.4 km^2) and has an estimated TSS load approximately 4 times lower, annual PCB loading was estimated to be approximately 2,600 times greater from Ettie Street (Gunther *et al.* 2001). Furthermore, PCB load estimates normalized to watershed area for Alameda County tributaries indicate that watershed exports may be approximately 4 to 5 orders of magnitude greater in completely urbanized watersheds (*e.g.*, Ettie Street and Codornices Creek) compared to predominantly non-urban drainage areas, such as Dry Creek (Figure 4.3). Similar findings were reported by Foster *et al.* (2000a) where flow-weighted mean concentrations were used to estimate that PCB loads per unit area in the heavily urbanized Anacostia River (9-10 g $km^{-2}y^{-1}$; 440 km^2, 60% urban) were at least 3 times greater than estimated basin yields in the Susquehanna River (2.7 g $km^{-2}y^{-1}$: 70,160 km^2, 5% urban).

These studies indicate that, while large watersheds may export large supplies of sediment and PCBs, small highly contaminated watersheds in the Bay Area with a great extent of urban development may also cause significant loading of PCBs to the Bay. In terms of PCB contamination of the Bay, continued loading of highly contaminated sediment from these smaller urban watersheds could sustain increased concentrations of PCBs in Bay sediment and have greater impacts on biota than larger watersheds with greater sediment loads. High sediment delivery from large watersheds could, in fact, dilute PCB concentrations in downstream Bay sediment. Following this rationale, a tributary monitoring component should incorporate a loading study on a smaller completely urbanized watershed for further understanding of the expected range of contributions and impacts of PCB loading from Bay Area watersheds that range in size and characteristics.

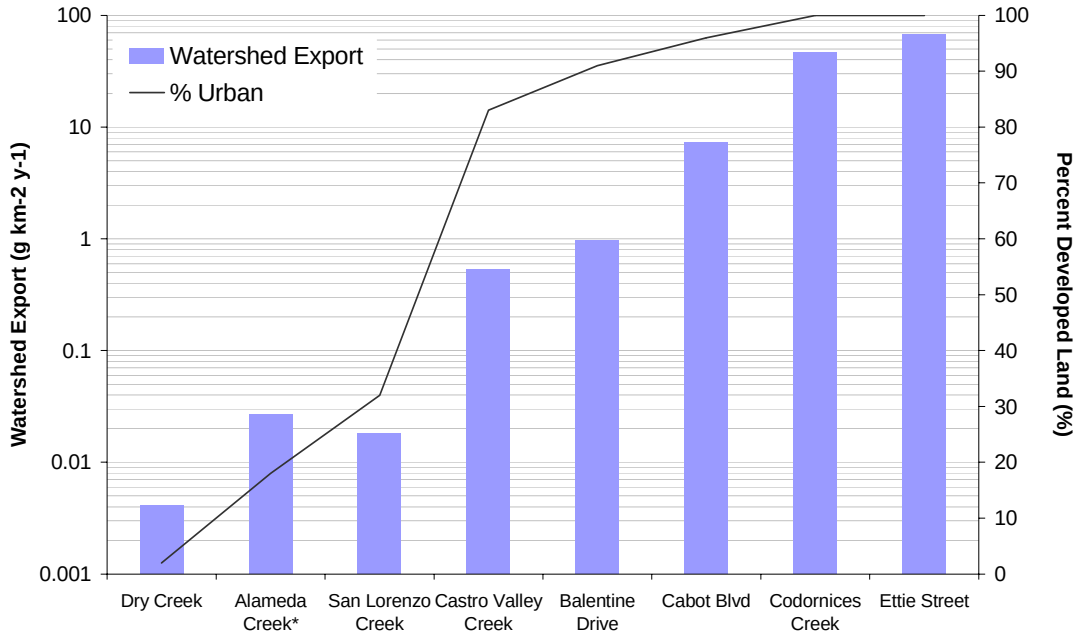

Figure 4.3. Estimates of PCB loading normalized to watershed area from selected tributaries in Alameda County. Data adapted from Gunther *et al.* (2001). *Urban land use data for Alameda Creek from Davis *et al.* (2000).

Temporal Variability in Loading

Temporal variability in PCB loading closely follows the variability associated with hydrologic conditions and sediment discharge. As discussed earlier, Chevreuil and Granier (1991) measured PCB concentrations and streamflow in 15-minute intervals in an urban storm drain immediately following a rainfall event. Within one hour of rainfall and preceding peak discharge, instantaneous PCB loads reached a maximum (> 600 µg s^{-1}) that was over 2 orders of magnitude greater than instantaneous loads measured over the duration of a few hours after storm flow attenuated (<10 µg s^{-1}) (Chevreuil and Granier, 1991). On much larger spatial scales, a wet-season swell on the Seine River caused a peak in PCB loads that preceded peak discharge during the spring of 1991 (Teil *et al.*, 1998) (Figure 4.4). Approximately three days before a peak discharge of 498 m^3s^{-1} (17,587 cfs), daily loads of PCB 101, 138, and 180 peaked at 400, 4,219, and 6,439 g d^{-1}, respectively (Teil *et al.*, 1998). Compared to the previous day, calculated daily loads had increased by 3, 10, and 23 times, respectively, for the three PCB congeners. Greater increases in loading for higher-molecular weight congeners may have occurred due to greater loading of suspended material in surface runoff and resuspension of bed sediments during the initial stages of the storm event.

In Bay Area watersheds, rapid transport of sediment and associated contaminants across the urban landscape presumably results in peak tributary loads of sediment and

PCBs on time scales of minutes to hours in response to rainfall events (see section on Climate and Hydrology). Thus, an appropriate monitoring strategy for measuring PCB loading from local tributaries in the Bay Area must account for the variability in PCB concentrations in the water column during the beginning stages of a storm event. Due to logistical and practical limitations to collecting samples within response times of minutes to hours, the use of surrogate techniques should be explored to relate continuous monitoring of turbidity to discrete measurements of PCBs and suspended sediment collected under conditions of varying flow regimes on the rising limb, peak, and falling limb of the storm hydrograph.

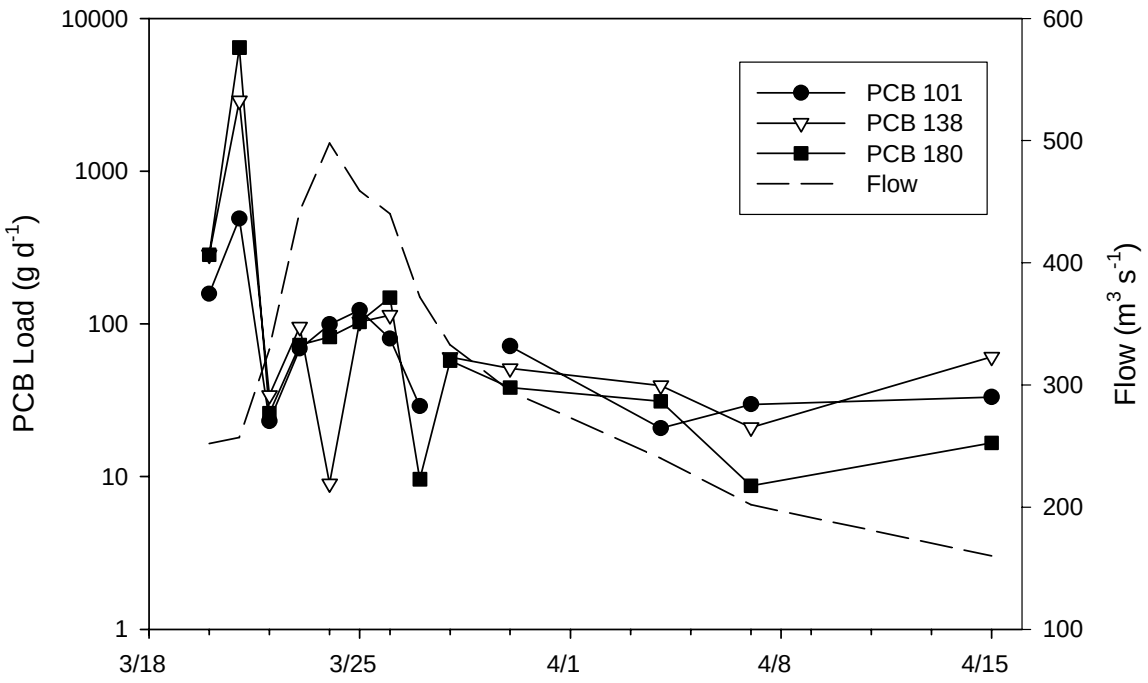

Figure 4.4. PCB loading on the Seine River on a daily time scale. Data from Teil *et al.* (1998).

Atmospheric transport of PCBs

A tributary monitoring design should consider the effects of atmospheric loading of PCBs to watershed surfaces on downstream monitoring results. PCB residues that enter the atmosphere through volatilization or wind-induced erosion of particles from contaminated regions of local watersheds may be locally deposited onto watershed surfaces and washed through the system during the wet season. As part of the RMP Atmospheric Deposition Pilot Study, Tsai *et al.* (2001) determined that the Estuary is probably a net source of PCBs to the atmosphere, which may result in local redeposition to Bay Area watersheds during wet and dry season conditions.

PCB CONCENTRATIONS IN THE ATMOSPHERE

Spatial Variability of PCB Concentrations in the Atmosphere

Regional variability exists between San Francisco Bay Area watersheds as evidenced by several studies in the U.S. that have measured higher PCB concentrations in urban air samples compared to samples collected from rural locations (Offenberg and Baker 1999, Pirrone *et al.* 1995, Miller *et al.* 2001). For example, Offenberg and Baker (1999) in the Chesapeake Bay region measured higher gaseous PCB concentrations at an urban site (0.38-3.4 ng m^{-3}) that spanned an order of magnitude compared to concentrations measured in samples from a rural site (less than 0.34 ng m^{-3}) in the Chesapeake Bay region. Therefore, urbanized regions of Bay Area watersheds presumably have higher concentrations of PCBs compared to open spaces or non-urban land uses, and therefore, probably have higher magnitudes of atmospheric loading of PCBs.

In the San Francisco Bay region, highly urbanized portions of watersheds are situated at lower elevations, where less annual rainfall occurs compared to the upper watershed. Although less rainfall occurs on an annual basis at lower elevations, impervious cover in urban regions reduces the natural retention capacity of the watershed. This, along with modified flow channels, decreases the transport time for runoff and associated contaminants (see sections on Climate and Hydrology and Sediment Processes). Chevreuil and Granier (1991) contend that most of the mass of organic contaminants deposited onto urban surfaces is eventually transported through the watershed system into the receiving waters. Although less rainfall may occur in urban watersheds of the Bay Area, increased impervious cover and modified flow channels may transmit greater loads of PCBs derived from the atmosphere.

Temporal Variability of PCB Concentrations in the Atmosphere

Distinct hydrologic and meteorological differences between wet and dry seasons drive a large extent of the variability in atmospheric concentrations and loading of PCBs to watershed surfaces. Approximately 90% of the rainfall in the Bay Area occurs between November and April when air temperatures are cooler, reducing the concentrations of PCBs in the atmosphere due to scavenging of the atmospheric PCBs by rainfall and lower volatility from decreased temperatures. In suburban Minnesota, Franz and Eisenreich (1998) measured a decrease in concentration between the beginning of rainfall (0.35 ng m^{-3}) and after (0.12 ng m^{-3}). Furthermore, the percentage of PCBs in the gaseous phase increased from approximately 90% to 100% (Franz and Eisenreich, 1998), suggesting that particulate phase PCBs are essentially washed out of the atmosphere early during rainfall events. Although gaseous phase PCB concentrations may comprise the largest fraction of air samples (compared to particulate phase) (Tsai *et al.* 2001, Holsen *et al.* 1991), PCBs associated with particles often represent the largest fraction of total wet and dry deposition (Park *et al.* 2001, Holsen *et al.* 1991). To effectively capture the atmospheric contribution of PCBs to Bay Area watershed budgets, monitoring should be

conducted during the initial rainfall events of the season and the rising stages of runoff that mobilize accumulated PCB residues from watershed surfaces to local tributaries.

PCB LOADING FROM THE ATMOSPHERE

Comparisons of depositional fluxes of PCBs from the atmosphere to overall watershed mass budgets indicates that atmospherically derived PCBs comprise a potentially significant portion of loading from non-urban watersheds. Tsai *et al.* (2001) estimated that dry deposition of particulate PCBs at a sampling site in the East Bay city of Concord was approximately 0.35 to 2.0 ng $m^{-2}d^{-1}$ (0.13 to 0.73 g $km^{-2}y^{-1}$). Although PCBs were not measured in rainfall during the study, which precluded estimating wet depositional fluxes, a companion study by Tsai and Hoenicke (2001) estimated that approximately 80% of the total daily flux of mercury occurred as dry deposition. Assuming similar proportions exist for PCBs and other particle-associated contaminants, the total depositional flux (wet + dry deposition) would be approximately 0.16 to 0.91 g $km^{-2}y^{-1}$. This assumption is consistent with an estimate by Park *et al.* (2001), which concluded that dry deposition (4.86 g $km^{-2}y^{-1}$) comprised approximately 76% of the total deposition (6.40 g $km^{-2}y^{-1}$) of PCBs to Galveston Bay, Texas.

Despite the uncertainties associated with the estimates of atmospheric deposition and tributary loading of PCBs, a comparison of depositional fluxes to the range of watershed yields derived for Alameda County tributaries (0.004 to 67 g $km^{-2}y^{-1}$; Figure 4.3) leads to the hypothesis that the atmospheric contribution of PCBs comprises a significant portion of overall PCB budgets for some of the less-urbanized watersheds, while it represents only a fraction of the watershed budgets for highly contaminated urban watersheds, such as those of the Ettie Street Pump Station and Codornices Creek.

Summary

Sources

- PCBs were commercially produced from 1929 to 1979 and primarily used in urban regions of Bay Area watersheds. PCBs were used primarily as dielectric fluids in transformers, capacitors, and electromagnets, and were also used for various purposes in heat exchanger fluids, chemical stabilizers, plasticizers, adhesives, insulating materials, flame-retardants, lubricants, and other products.

Partitioning

- PCBs are hydrophobic organic contaminants that partition into organic matter found in soils, sediments, and water, and are also slightly soluble in water.
- Partitioning of PCBs to the dissolved or particulate fractions in the water column is influenced by concentrations of suspended sediment and organic matter, as well as the affinity of PCBs for particulate material. In tributaries with low concentrations of suspended sediment organic matter and low-molecular weight PCBs, PCBs are primarily in the dissolved phase. In contrast, the presence of high-suspended sediment concentrations and high-molecular weight PCBs in the water column supports preferential sorption to particulate material.

- In water samples collected during flood conditions from RMP stations near the mouths of the Guadalupe River and Coyote Creek, particulate concentrations of PCBs comprised approximately 90% of total PCBs. Furthermore, these samples had PCB congener profiles that were indicative of the high-molecular weight Aroclor 1260, which has higher affinities for particulate matter than lower-molecular weight Aroclors.
- In a bed sediment survey of tributaries and storm drains in Bay Area watersheds samples with PCB concentrations greater than 300 µg kg^{-1} had PCB congener spectra that were indicative of high-molecular weight Aroclors, 1254 and 1260, further supporting the hypothesis that PCBs are primarily associated with the particulate fraction in the water column of local tributaries.
- Colloids (particles with diameters of 0.01-10 µm) may have PCB concentrations that are 2 to 3 times greater than suspended silts and comprise a large portion of total PCB loading in tributaries. Therefore, measurement of total PCBs is necessary to account for the mass of PCBs associated with truly dissolved, colloidal, and particulate fractions.
- The expected high affinity of PCBs and other particle-associated contaminants for particulate fractions (including colloids) in local tributaries that drain highly contaminated watersheds supports the development of a monitoring strategy for measuring PCB loading from local tributaries based on defining the variability of suspended sediment concentrations.

Spatial Variability of PCBs

- The historic and current use of PCBs, primarily in urban regions of Bay Area watersheds, combined with their persistence in soil and sediment, suggest that concentrations and loading of PCBs are expected to be highest in tributaries that drain urbanized watersheds in the Bay Area.
- The recent investigation of bed sediment in Bay Area tributaries and storm drains determined that PCB concentrations differ by at least 3 orders of magnitude between industrial and open space land use areas.
- Load estimates from the local sediment survey also indicate that PCB loading from small highly polluted watersheds with extensive urban development may be orders of magnitude greater than loading from much larger non-urban drainage areas. Furthermore, watershed exports (load per unit area) may be 4 to 5 orders of magnitude greater in urbanized watersheds compared to non-urban watersheds.
- Locations for monitoring PCB loading from local tributaries should be selected in tributaries with the greatest potential for contaminant loading to the Bay in the context of other pathways of contamination. In the case of PCBs, priority should be given to tributaries that drain highly urbanized watersheds with a high magnitude of suspended sediment export.

Temporal Variability of PCBs

- In Bay Area tributaries, increased PCB concentrations and loading are expected to occur in response to increased sediment discharge and runoff during storm events. First flush effects in urban areas are expected to cause even greater increases due to

increased impervious surface cover and modified channel flow, which hastens contaminant transport from sources to receiving waters.

- First flush effects may increase total PCB concentrations in urban storm drains by 2 orders of magnitude in minutes to hours during storm events. On longer time scales, PCB concentrations undergo less distinct increases on daily (25-fold) and seasonal (8-fold) time scales in response to storms and resulting wet-season conditions.
- Due to the logistical difficulties of sampling on time scales of minutes to hours, the use of continuous monitoring of turbidity with optical backscatter (OBS) as a surrogate should be explored to relate short-term fluctuations in suspended sediment to variability in concentrations and loading of PCBs and other particle-associated contaminants.

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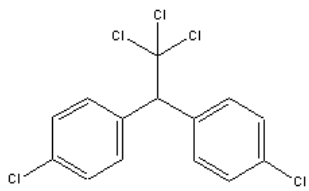
Part 5: Organochlorine pesticides: DDT, chlordane, and dieldrin

Jon Leatherbarrow

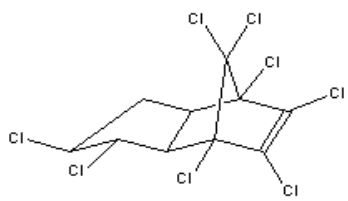
Introduction

PROBLEM STATEMENT

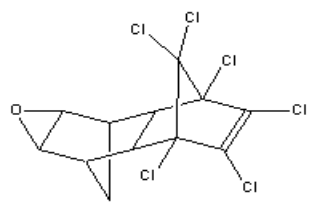
Organochlorine (OC) pesticides are persistent organic chemicals of current environmental concern in San Francisco Bay due to their lengthy persistence in the ecosystem and their potential deleterious effects on wildlife and human health. The OC pesticides of specific concern for regulation and management in the Bay are Σ DDT (the sum of o,p'- and p,p'-isomers of DDT, DDE, and DDD), Σ Chlordane, and dieldrin (Figure 5.1). The main components of Σ Chlordane include alpha-Chlordane, gamma-Chlordane, cis-Nonachlor, trans-Nonachlor, oxychlordane, heptachlor, and heptachlor epoxide. All of the discussed pesticides are known neurotoxicants that affect reproductive development and are classified by the U.S. EPA as probable carcinogens (USEPA, 2000). These pesticides have also been implicated as endocrine disruptors (Arnold *et al.*, 1996; Soto *et al.* 1995).



DDT
$C_{14}H_9Cl_5$
354.5 g mol^{-1}



Chlordane
$C_{10}H_6Cl_8$
409.8 g mol^{-1}



Dieldrin
$C_{12}H_8Cl_6O$
380.9 g mol^{-1}

Figure 5.1. Molecular structures and weights of DDT (p,p'-DDT), chlordane (gamma-chlordane), and dieldrin.

Concentrations of OC pesticides in the San Francisco Estuary have often exceeded water quality guidelines and fish screening values in RMP samples. Due to high concentrations of OC pesticides and other bioaccumulative contaminants in Bay fish, the Office of Environmental Health and Hazard Assessment (OEHHA) issued an advisory with recommendations to limit human consumption of fish caught in the Bay (OEHHA, 1994). Consequently, DDT, chlordane, and dieldrin were placed on the 303(d) list for all San Francisco Bay segments.

IMPORTANCE OF RUNOFF FROM LOCAL WATERSHEDS

In 1999, the RMP Chlorinated Hydrocarbon Workgroup (CHCWG) summarized the various sources and pathways of OC pesticides in the San Francisco Estuary and determined that there were probably continuing inputs of these contaminants from local tributaries (Davis and Yoon, 1999). The CHCWG provided several recommendations for a phased approach to evaluate CHC loading from local tributaries and storm drains: (1) review existing information to identify drainages with greatest potential for continuing inputs; (2) survey local watersheds to determine potential continuing sources; (3) sample sediments upstream in the tributaries; and (4) measure loads from the largest potential sources.

In 2001, the storm water management agencies in the Bay Area began to characterize the distribution and concentration ranges of OC pesticides in bed sediment of storm drains and local tributaries to assist the San Francisco Bay Regional Water Quality Control Board (Regional Board) in developing TMDLs for these contaminants (KLI, 2002). To meet the RMP objective of characterizing contaminant loads to the Bay and further assist the TMDL process, information from those sediment studies and this literature review will assist in designing an effective monitoring strategy for characterizing OC pesticide concentrations and loading from local watersheds.

OC pesticide properties

Similar to other CHCs of concern for the San Francisco Estuary, OC pesticides generally have relatively low water solubility and high octanol-water partitioning coefficients (K_{OW}) that favor partitioning to organic material (Table 5.1). OC pesticides are also relatively resistant to biotic and chemical transformations, which make them very persistent in the environment. Because of their hydrophobic and persistent nature, OC pesticides tend to partition into soils, sediment, and water and bioaccumulate in lipids of biota and humans.

DDT and chlordane were primarily developed as technical mixtures of individual compounds manufactured in relatively constant proportions. Technical DDT was comprised of greater than 90% p,p'-DDT and o,p'-DDT, while technical chlordane was comprised of greater than 60% cis- and gamma-chlordane and cis-nonachlor (Mischke *et al.,* 1985; Dearth and Hites, 1991; Wong *et al.,* 2000). Of the individual DDT and chlordane compounds, the most refractory compounds are typically p,p'-DDE, trans-nonachlor and gamma-chlordane (Wong *et al.,* 2000; Rostad *et al.,* 1995). Due to the relatively long half-lives of OC pesticides and the persistence of the more refractory compounds, higher proportions of p,p'-DDE, trans-nonachlor, and gamma-chlordane have been measured in RMP water and sediment samples collected from the Bay (*e.g.,* SFEI 2002). For purposes of this document, DDT and chlordane will refer to the sum of all constituents (listed in Table 5.1) for each pesticide type.

Table 5.1. Chemical properties of selected OC pesticides and metabolites. Data from Nowell *et al.* (1999).

	Compound	Water Solubility ($mg\ l^{-1}$)	log K_{OW}	Estimated Half-Life in Soil (days)
DDT [1]	o,p'-DDD	0.1	5.1-6.2	730-5,700
	p,p'-DDD	0.05	5.1-6.2	730-5,700
	o,p'-DDE	0.065	5.7-7.0	730-5,700
	p,p'-DDE	0.065	5.7-7.0	730-5,700
	o,p'-DDT	-	6	2,400
	p,p'-DDT	0.0077	6	110-5,500
Chlordane [1]	cis-Chlordane	0.06	6	365
	trans-Chlordane	0.06	6	365
	cis-Nonachlor	0.06	5.7	-
	trans-Nonachlor	0.06	5.7	-
	Oxychlordane	200	2.6	-
	Heptachlor	0.056	4.4-5.5	250
	Heptachlor Epoxide	0.3	3.6	5-79
Dieldrin	-	0.14	3.7-6.2	1,000

[1] DDT and chlordane are mixtures of individual compounds.

Historic and current sources

OC pesticides were used as insecticides beginning in the 1940s primarily for agricultural applications on crops, such as cotton, corn, and citrus, and also to a large extent for pest control and mosquito abatement in urban areas (Table 5.2) (Davis, 1999; Mischke *et al.*, 1985; Rinella *et al.*, 1999; Wong *et al.*, 2000). Forestry, transportation, and various other industries also used OC pesticides (Nowell, 1999).

In California, watersheds of the Sacramento and San Joaquin Rivers were regions of widespread use of OC pesticides in the 1950s and 1960s (Kratzer, 1998), which resulted in the San Joaquin River and its tributaries having some of the highest concentrations of DDT and dieldrin in bed sediments compared to other river systems in the United States (Gilliom and Clifton, 1990). In 1970, approximately 2 million kg of DDT was used throughout California compared to less than 91 kg y^{-1} between 1975-1980 (Mischke *et al.*, 1985). Although agricultural use of DDT was restricted beginning in 1963 and banned nearly a decade later (Mischke *et al.*, 1985), residual DDT in the agricultural watersheds of California continue to get transported to aquatic ecosystems via surface runoff (Mischke *et al.*, 1985, Gilliom and Clifton, 1990) and atmospheric transport (Spencer *et al.*, 1996).

Similar restrictions on agricultural use of chlordane and dieldrin were implemented in 1978 and 1974, respectively; however, domestic and industrial use continued in some capacity until the late 1980s (USDHHS, 1994; USDHHS, 2002b). Although peak usage of OC pesticides preceded the implementation of pesticide-use

reporting to the California Department of Pesticide Regulation (CDPR), it is assumed that historic use of OC pesticides for agricultural and urban applications was extensive and widespread throughout Bay Area watersheds.

Table 5.2. Uses, history, and toxicity of selected OC pesticides.

Compound	Uses	History	Toxicity
DDT	Extensive use in agriculture and urban settings[4]; DDD and DDE are breakdown products of DDT and impurities in the insecticide dicofol; DDD was also manufactured as an insecticide[1].	Use in California began in 1944[4]. EPA banned use in 1973, except for public health emergencies[1].	Neurotoxin and probable human carcinogen; Effects on development and reproduction in wildlife[1].
Chlordane	Agricultural uses on variety of crops, such as corn, grapes, and strawberries; Urban uses for termite and ant control, and for dipping nonfood roots and tops[2].	Registered as pesticide in 1948. All uses cancelled in 1987, except for subsurface termite control; Production was discontinued voluntarily in July 1987, and commercial use stopped in 1988[2].	Neurotoxin and probable human carcinogen[2].
Dieldrin	Agricultural uses on corn and citrus crops, soil-dwelling insects; Urban uses for controlling insects associated with public health issues, and termites; Dieldrin is also a transformation product of Aldrin, an insecticide used heavily on corn crops[3].	EPA banned production of dieldrin and aldrin and use of dieldrin on food products in 1974; All uses were banned in 1985, except for subsurface termite control, dipping of nonfood roots and tops, and moth proofing; Industry voluntarily cancelled all uses in 1987[3].	Neurotoxin and probable human carcinogen[3].

[1]USDHHS, 2002a
[2]USDHHS, 1994
[3]USDHHS, 2002b
[4]Mischke *et al.*, 1985

Contamination of the Bay by OC pesticides may still occur from more recent and unintentional applications or activities. For example, DDD and DDE have been created as impurities in the production process for the insecticide, dicofol, with proportions as high as 0.5% in 1992 (USDHHS, 2002a). According to the CDPR, the nine Bay Area counties reported using approximately 1,140 kg of dicofol in 2000 (CDPR, 2002), which suggests that areas of more recent applications of dicofol may contribute to some amount of DDT contamination of the Bay. An additional potential source of contamination from local watersheds are agricultural and residential users whom may still be in possession of and use old stocks of OC pesticides.

Recent studies have determined that OC pesticide residues are currently transported to the Bay through local tributaries and storm drains (Daum *et al.*, 2000; Leatherbarrow *et al.*, 2002; KLI, 2002). A recent survey of contaminants in bed sediment of local tributaries and storm drains found that median concentrations of DDT and chlordane in urban regions were at least 2 orders of magnitude greater than concentrations measured in samples collected from non-urban sampling locations (KLI,

2002). Other studies have found that urbanized regions of the Bay margins tend to have high concentrations of DDT (Figure 5.2) and chlordane (Figure 5.3) in sediment (Hunt *et al.*, 1998; Daum *et al.*, 2000; Leatherbarrow *et al.*, 2002). Existing data from various studies may be used in conjunction with information on potential sources or locations of past usage, hydrology, and sediment discharge to prioritize and select Bay Area watersheds for monitoring OC pesticide concentrations and loadings.

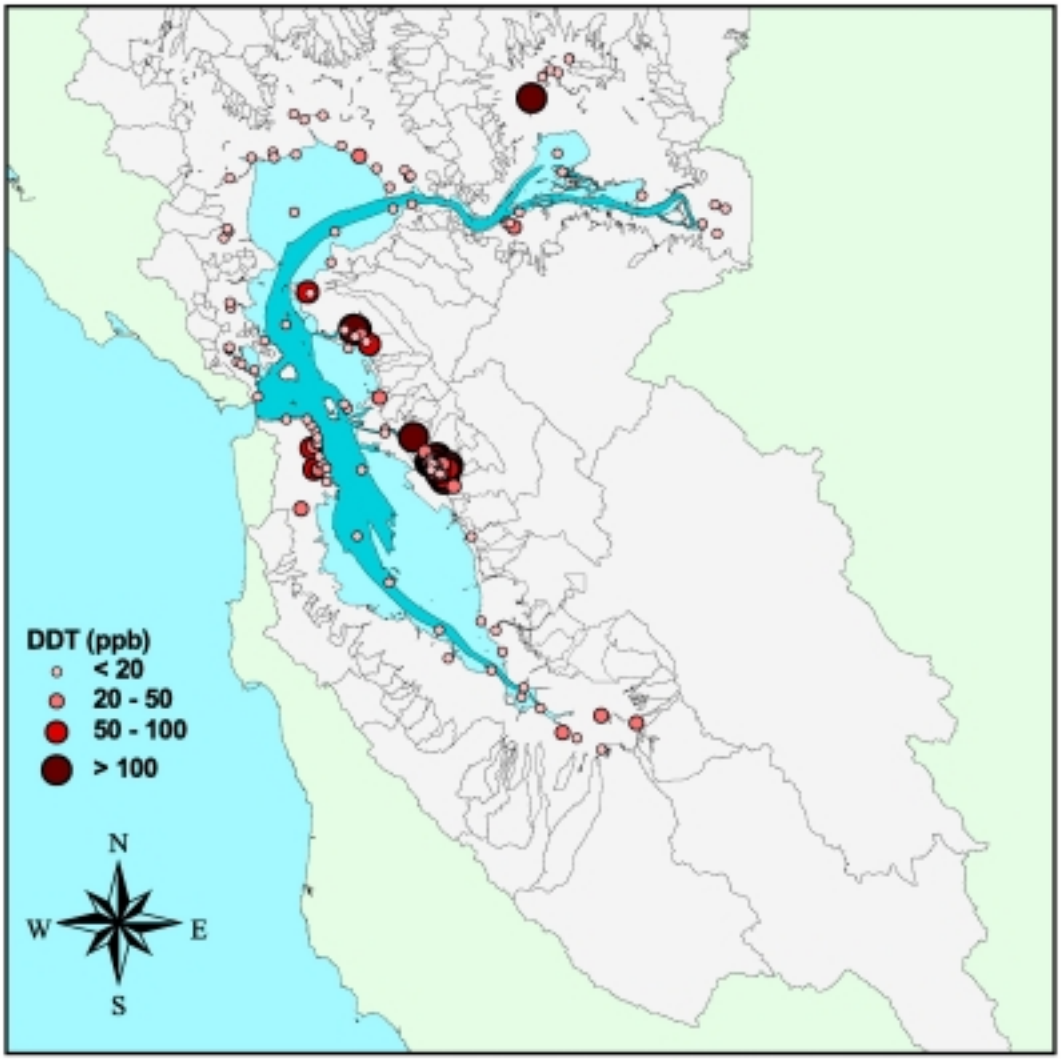


Figure 5.2. Average DDT concentrations in Bay Area sediment. Data compiled from RMP monitoring (*e.g.*, SFEI, 2002), Flegal *et al.* (1994), Hunt *et al.* (1998), and Daum *et al.* (2000).

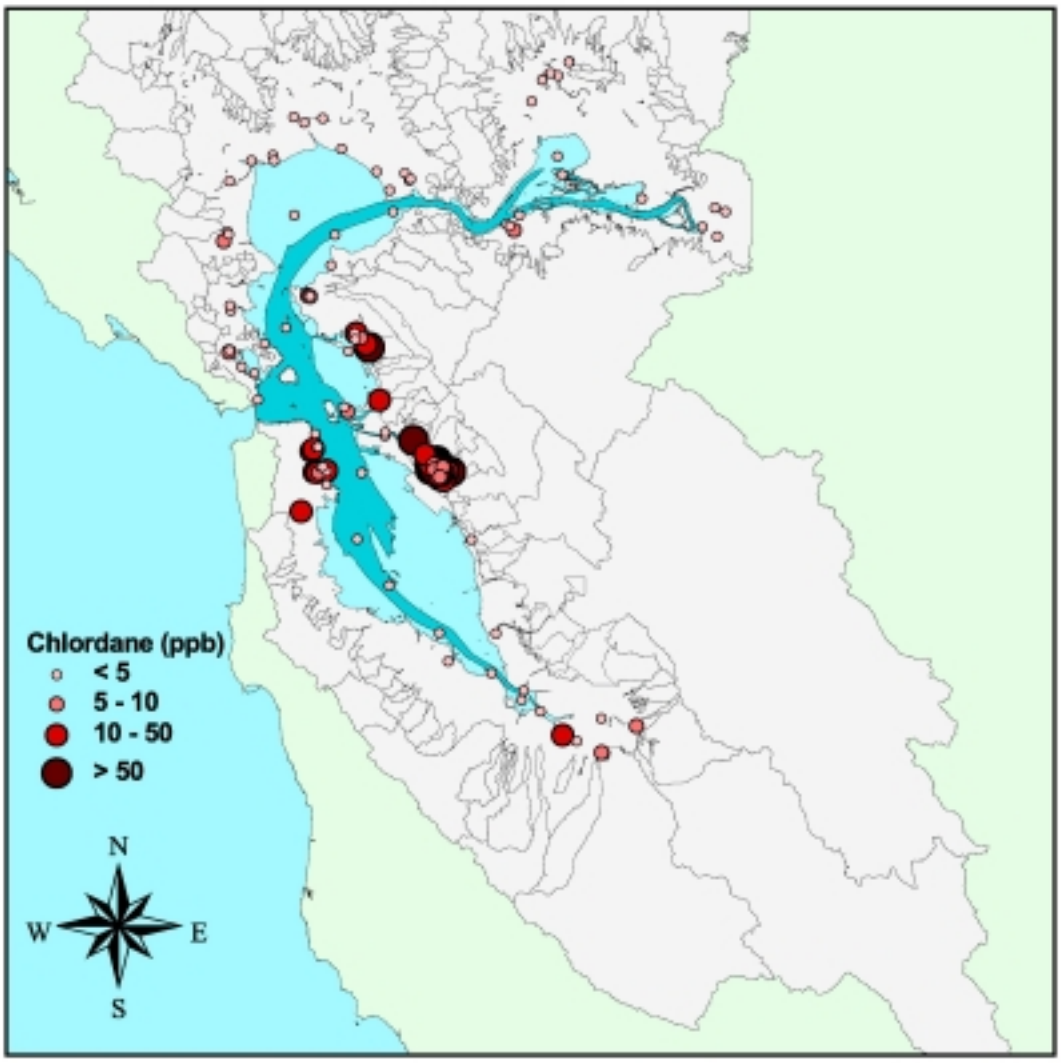


Figure 5.3. Average chlordane concentrations in Bay Area sediment. Data compiled from RMP monitoring (*e.g.*, SFEI, 2002), Flegal *et al.* (1994), Hunt *et al.* (1998), and Daum *et al.* (2000).

OC pesticide transport in tributaries

Important pathways of OC pesticide contamination to downstream surface waters include surface runoff from agricultural and urban areas (Larson *et al.*, 1997; Pereira *et al.*, 1996), as well as atmospheric deposition directly onto watershed surfaces followed by washing of OC pesticides into surface water bodies (Nowell *et al.*, 1999). Limited research has been conducted on the transport of OC pesticides through Bay Area watersheds via surface runoff and atmospheric deposition; however, studies conducted in other major river systems in the U.S. provide information on general watershed processes

that mobilize OC pesticides. These concepts are likely to provide us with a better understanding of the processes of source activation, transport and loading of OC pesticides in local watersheds of the San Francisco Bay.

OC PESTICIDE PARTITIONING AND CONCENTRATIONS IN TRIBUTARIES

OC Pesticide Partitioning

Effective monitoring of OC pesticide loading in tributaries should take into account the influence of the particulate fraction as a transport mechanism for particle-associated contaminants and their predicted responses to hydrology and sediment transport. Nonionic organic contaminants, such as OC pesticides, tend to partition into organic material on suspended and bed sediment (Chiou *et al.*, 1983), including colloidal material. Therefore, OC pesticides are often primarily associated with the particulate fraction of the water column in tributaries (Kratzer, 1998; Foster *et al.*, 2000a, 2000b).

In water samples collected during wet-season RMP monitoring near the mouth of the Guadalupe River (556 km^2) and Coyote Creek (914 km^2), in Lower South Bay, concentrations of OC pesticides were primarily associated with the particulate phase (RMP Annual Results, *e.g.*, SFEI 2002) (Figure 5.4). This was consistent with partitioning in water samples from two branches of the heavily urbanized Anacostia River in the Chesapeake Bay system (Foster *et al.*, 2000a). Relatively high proportions of particulate concentrations were observed for more recalcitrant compounds, such as p,p'-DDE, alpha- and gamma-chlordane, and trans-nonachlor. These compounds comprise greater than approximately 70% of the total concentrations of DDT and chlordane in water samples collected from these stations. Lower proportions were associated with dieldrin concentrations in all four rivers. The data suggest that concentrations and loadings of DDT and chlordane, and to a lesser extent, dieldrin, in surface runoff from Bay Area watersheds will most likely be comprised of a larger percentage of particle-associated concentrations. Accordingly, a sampling scheme that defines the variability of suspended sediment during floods will most likely be suitable for characterizing concentrations and loads of these pesticides.

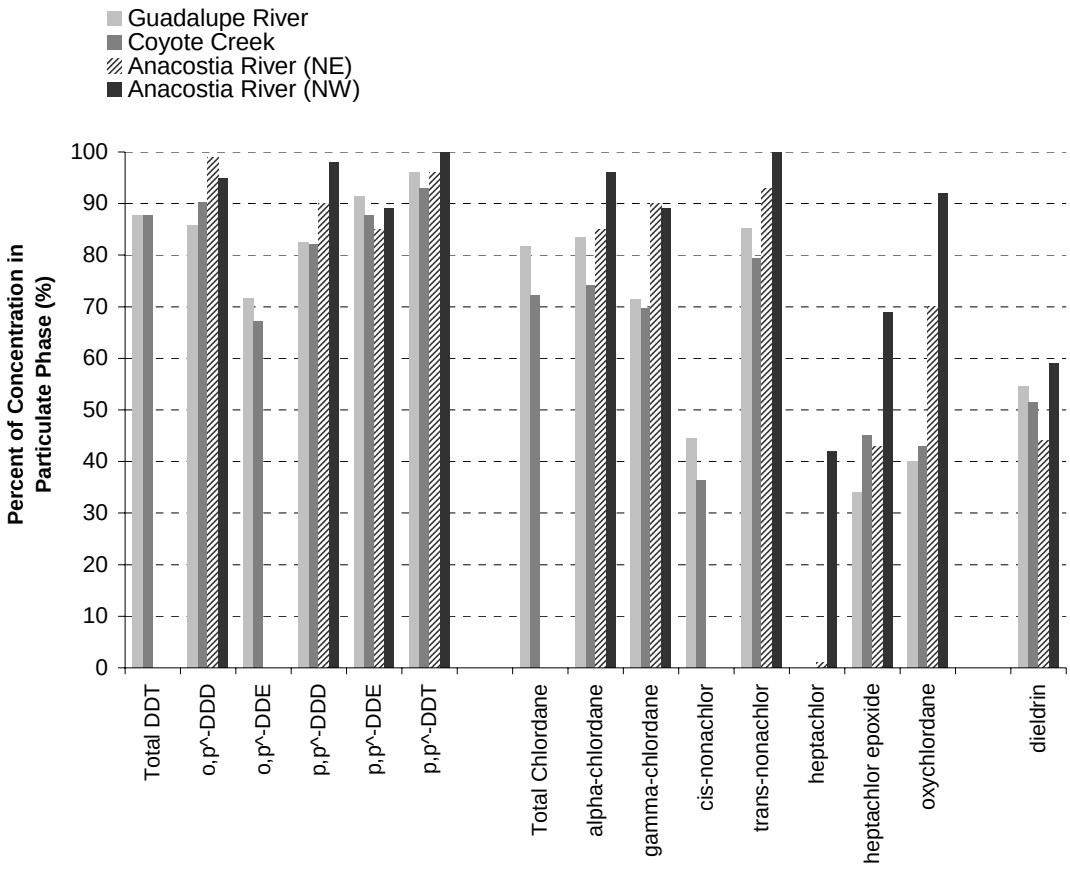


Figure 5.4. Percentage of total OC pesticide concentrations associated with the particulate phase in water samples collected from four urbanized tributaries. Guadalupe River and Coyote Creek samples were collected during wet season RMP sampling events. Anacostia River data were adapted from Foster et al. (2000a).

In contrast, several studies have measured higher proportions of dieldrin and chlordane in the dissolved phase (Kratzer, 1998; Foster *et al.*, 2000b). For example, Kratzer (1998) measured particulate concentrations of total chlordane, total DDT, and dieldrin that comprised approximately 14-17%, 87%, and 43% of total concentrations, respectively, during the irrigation season (June 1994) in tributaries of the San Joaquin River. These proportions were much lower than proportions measured during a storm event in January 1995, in which particulate concentrations of total chlordane, total DDT, and dieldrin comprised approximately 52-57%, 98%, and 78% of the total concentrations, respectively (Kratzer, 1998). This decrease in particulate proportions probably occurred due to lower SSC in the summer and possible desorption during longer residence times of agricultural return flow. Similar particulate proportions were measured in the Susquehanna River (70,160 km^2, 62% forested, 31% agricultural, and 5% urban) by Foster *et al.* (2000b) for dieldrin (28%), chlordane (17-38%), and DDT (61-73%) under conditions of low stream discharge and low total suspended particulates (< 132 mg l^{-1}).

Given that Bay Area watersheds typically have high TSS concentrations and induce rapid transport of suspended sediment and particle-associated contaminants in response to peak rainfall and runoff, samples collected during flood flow conditions will most likely have the highest proportions of OC pesticides in the particulate phase. This association of OC pesticides with suspended particulate matter in the water column provides a basis for exploring the use of surrogate techniques, such as continuous measurement of turbidity using optical backscatter (OBS), to relate short-term fluctuations in suspended particulate matter to changes in OC pesticide concentrations.

Spatial Variability in OC Pesticide Concentrations

Selection and prioritization of tributary monitoring locations in Bay Area watersheds depends largely on the spatial variability of OC pesticide contamination throughout the watersheds and the potential for mobilizing and transporting pesticide residues to the Bay. Spatial variability in concentrations and loading of OC pesticides in Bay Area watersheds exists due to varied historic usage in both urban and agricultural regions and the degree to which OC pesticide residues have moved through the system since application.

A recent sediment study by the stormwater management agencies in the Bay Area (KLI, 2002) measured maximum concentrations of DDT (4,010 µg kg^{-1}), chlordane (11.3 µg kg^{-1}), and dieldrin (28 µg kg^{-1}) in drainage areas of industrial sites in Bay Area watersheds. Maximum concentrations of DDT and chlordane were greater by 3 and 2 orders of magnitude, respectively, than maximum concentrations measured in open space sites. Although only four samples were collected in non-urban locations, and not necessarily in areas affected by agricultural inputs, the findings suggest that urban areas of past applications and manufacturing continue to contribute to contamination of the Bay from local tributaries and storm drains. Similar results for dieldrin and chlordane were found in nationwide sampling of streambed sediment by the USGS as part of their National Water-Quality Assessment Program (NAWQA) from 1992 to 1995 (Wong *et al.,* 2000). Maximum concentrations of chlordane (> 50 µg kg^{-1}) and dieldrin (> 10 µg kg^{-1}) were measured in urban locations (Wong *et al.,* 2000), while DDT concentrations were much higher in cropland sites (maximum ~ 500 µg kg^{-1}) than in urban locations (maximum = 50 µg kg^{-1}).

In studies of OC pesticide distribution in other river systems, maximum concentrations of DDT and dieldrin have been measured in agricultural regions (Rinella *et al.,* 1999; Pereira *et al.,* 1996), which result from heavy historic usage, frequent tillage, and increased erosion of suspended particulate matter that transport residues to receiving waters (Rinella *et al.,* 1999). Pereira *et al.* (1996) measured highest concentrations of DDT and dieldrin in suspended and bed sediment collected from Orestimba Creek, which drains a predominantly agricultural watershed on the western side of the San Joaquin River (Table 5.3). Conversely, the highest concentrations of chlordane compounds were measured in Dry Creek, which receives urban runoff from Modesto (Pereira *et al.,* 1996).

Sources of technical chlordane have been associated with more industrialized areas in other regions of the U.S. (Rostad *et al.*, 1993; 1999; Rostad, 1997), including watersheds with significant past usage of chlordane for agriculture (Arruda, 1987). Bay Area watersheds typically have both regions of current or past agricultural activity and urban development, which suggests that variation in concentrations and loading of OC pesticides may depend on the distribution of pesticides and hydrologic influences from both types of land use. Conceptually, regions of Bay Area watersheds that were historically agricultural may have undergone urban development or expansion and required OC pesticide application for control of mosquitoes, termites, and ants. These watersheds, therefore, contain areas of OC pesticide contamination from both agricultural and urban sources that contribute to OC pesticide loading to the Bay.

Table 5.3. Concentrations of DDT, chlordane, and dieldrin in bed sediment and suspended sediment from four selected tributaries of the San Joaquin River. Data from Pereira *et al.* (1996).

Concentrations (ng g^{-1})	Salt Slough		Orestimba Creek		Dry Creek		SJ River at Patterson	
	Bed	Susp.	Bed	Susp.	Bed	Susp.	Bed	Susp.
DDE	3.5	17	115	212	2	59	1.4	61
DDD	1	4	14	32	0.7	9.6	0.4	10
DDT	0.4	3.3	39	59	0.8	6.3	0.4	4.4
Total DDT	4.9	24	170	303	3.5	75	2.2	75
gamma-chlordane	0.8	< 0.5	1.2	2.1	1.6	50	0.7	5.2
alpha-chlordane	0.7	7.8	0.9	2.9	1	55	0.7	< 0.5
trans-nonachlor	1	< 0.5	1.2	2.6	1.6	38	< 0.5	7.1
cis-nonachlor	< 0.5	5.7	0.8	2.1	1.1	17	0.7	5.8
Total chlordane	2.5	14	4.1	9.7	5.3	160	2.1	18
dieldrin	< 0.5	< 0.5	4.6	10	< 0.5	< 0.5	< 0.5	< 0.5

Concentrations of OC pesticides measured on suspended sediment provide further evidence of the linkage between chlordane contamination and urban sources (Figure 5.5) and DDT contamination and agricultural sources (Figure 5.6). The maximum concentration of chlordane from five reviewed studies was measured by Pereira *et al.* (1996) at Dry Creek (160 ng g^{-1}), which was an order of magnitude greater than the concentration measured at the agricultural site, Orestimba Creek (9.7 ng g^{-1}), from the same study. This concentration was also 160 times greater than the chlordane concentration measured by Kratzer (1998) at a reference site, Del Puerto Creek near Patterson, which only receives drainage from the eastern slope of the Coast Range Mountains.

In contrast to the patterns of chlordane distribution, concentrations of DDT were generally higher at agricultural sites compared to urban and reference sites (Figure 5.6). The maximum concentration of DDT measured by Kratzer (1998) at the agricultural site,

Anderson Road Drain, in the San Joaquin River system was approximately 4 to 5 times greater than concentrations measured in urban locations and 100 times greater than concentrations measured at two reference sites located on the eastern side of the Coast Range Mountains. These patterns further illustrate the importance of both urban and agricultural sources on OC pesticide contamination in tributaries.

The widespread use of DDT, chlordane, and dieldrin throughout Bay Area watersheds, combined with their persistence in soil and sediment, has resulted in continued mobilization and transport of OC pesticide residues through tributaries and storm drains (Daum *et al.*, 2000; Leatherbarrow *et al.*, 2002; KLI, 2002). The extent of contamination and loading to the Bay at the bottom of the watershed depends on such heterogeneous influences as past usage in both urban and agricultural regions, organic carbon content of soils, discharge, and suspended sediment export. Although the bulk of OC pesticides were historically used for agriculture, the proximity of concentrated urban development and more recent use of chlordane and dieldrin increase the likelihood of urban influences on downstream water quality for these contaminants. In this context, consideration must be given to the historic land use configuration throughout the Bay Area during peak usage of these pesticides when choosing monitoring locations in tributaries that are potentially significant pathways of contamination to the Bay.

Temporal Variability in OC Pesticide Concentrations

A methodology for accurately estimating loading of particle-associated contaminants, including OC pesticides, must account for episodic and seasonal fluctuations in concentrations of suspended sediment and contaminants in the water column. In urban and agricultural areas of past OC pesticide application, storm events mobilize contaminated source sediments from adjacent fields, hillsides, floodplains and the beds and banks of channels and storm drains. The initial storms of the wet season may cause greater increases in OC pesticide concentrations due to ‘first flush’ effects that ‘wash’ watershed surfaces of sediment and contaminants that were atmospherically deposited during a preceding dry period or that settled out during the waning stages of the previous wet season. First flush effects may be even more drastic in urban areas of Bay Area watersheds due to increased impervious cover and modified flow channels, which hasten the transport of contaminants from sources to receiving waters; however these effects are also evident in non-urban watersheds of the Bay Area (see section on Climate and Hydrology).

Short-term variability in runoff, sediment discharge, and OC pesticide concentrations may occur on time scales of minutes to hours in response to the onset of a storm event. For example, Kratzer (1998) collected water column samples during a winter storm (January 10, 1995) on Orestimba Creek, a predominately agricultural watershed in the Central Valley, to evaluate short-term variability of OC pesticide concentrations in the water column. Particulate DDT and chlordane concentrations were positively correlated to SSC in the five samples collected during the storm, with a significant linear relationship found for DDT (Figure 5.7). Similar linear relationships were determined with DDT and dieldrin in relation to SSC and TOC by Rinella *et al.*

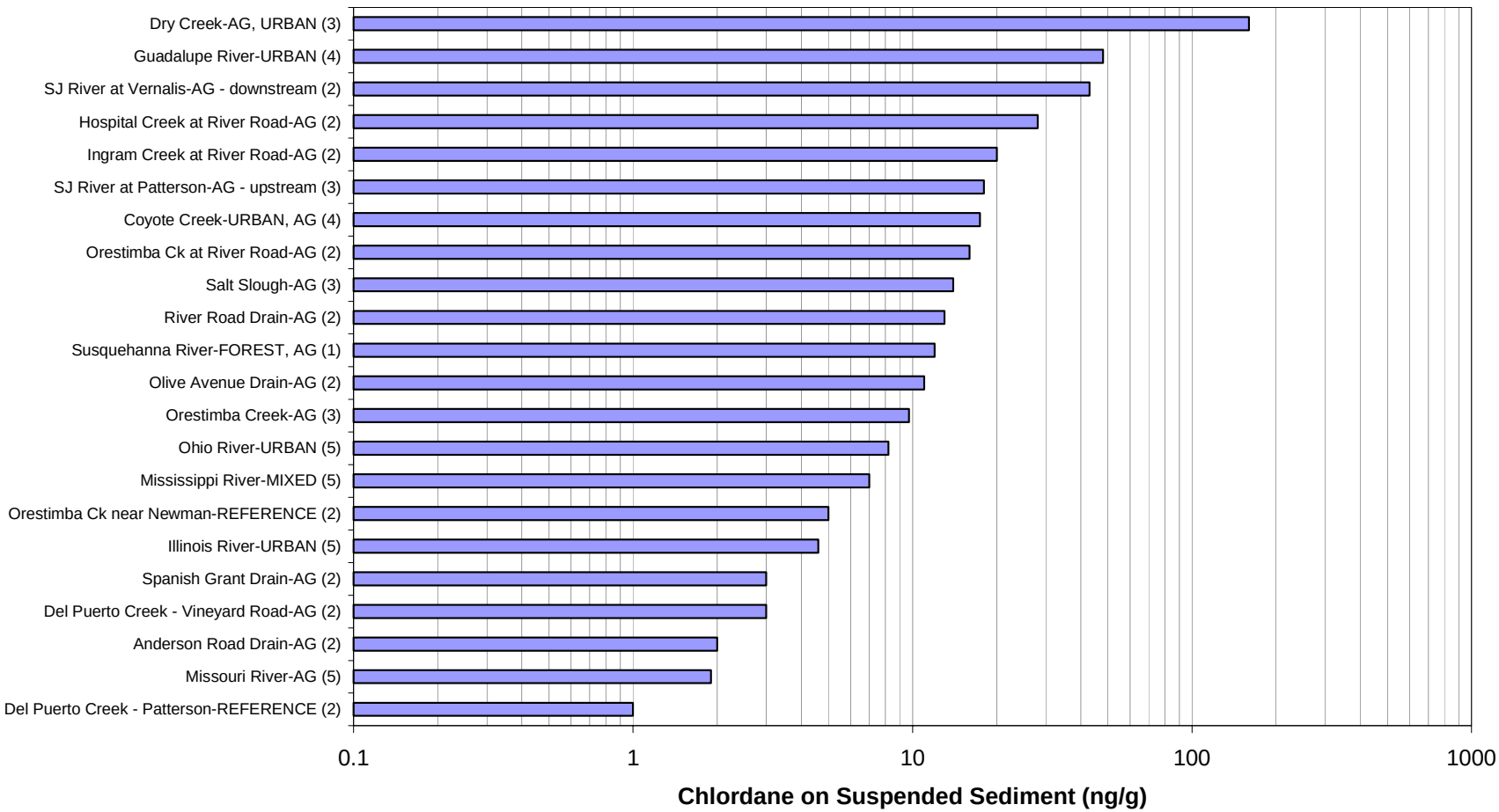


Figure 5.5. Maximum chlordane concentrations in suspended sediment from various studies. Study locations were designated as agricultural (AG), urban, forest, mixed, or reference sites based on predominate land uses. Data from (1) Foster *et al.* (2000b), (2) Kratzer (1998), (3) Pereira *et al.* (1996), (4) Leatherbarrow *et al.* (2002), and (5) Rostad *et al.* (1999).

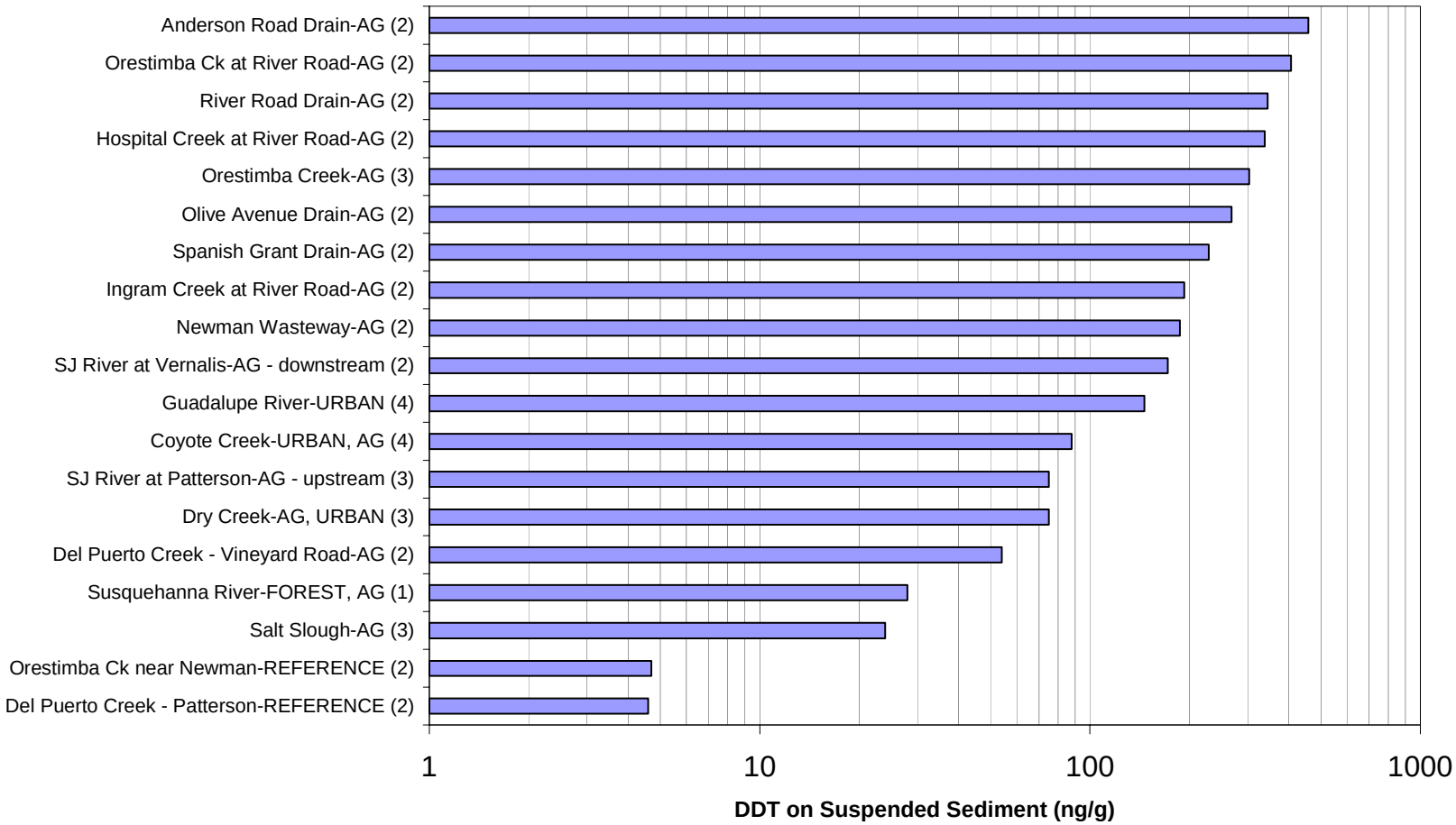


Figure 5.6. Maximum DDT concentrations in suspended sediment from various studies. Study locations were designated as agricultural (AG), urban, forest, or reference sites based on predominate land uses. Data from (1) Foster *et al.* (2000b), (2) Kratzer (1998), (3) Pereira *et al.* (1996), and (4) Leatherbarrow *et al.* (2002).

(1999) in the Yakima River Basin. OC pesticide concentrations were not measured in the sample with maximum SSC (13,800 mg l^{-1}); however, assuming that a consistent relationship between DDT and SSC existed throughout the duration of the flood, extrapolation of DDT concentrations using the given linear relationship would result in a peak DDT concentration of 4.1 µg l^{-1}. The range of SSC and DDT concentrations suggest that order of magnitude increases in OC pesticide concentrations may occur on hourly time scales during floods. The fact that SSC typically varies in Bay Area watersheds by 3 to 4 orders of magnitude (see Figure 3.4 in section on Sediment Processes) adds further support for the hypothesis that OC pesticide variation in local tributaries are at least an order of magnitude on hourly time scales.

Similar variation in OC pesticides has been measured on monthly and seasonal time scales with increasing concentrations associated with periods of high-suspended sediment concentrations and organic carbon content in storm runoff (Rinella *et al.,* 1999; Pham *et al.,* 1996; Rostad *et al.,* 1999; Foster *et al.,* 2000a). Rinella *et al.* (1999) measured total DDT concentrations in water samples that were 14 times greater during a storm event (14 ng l^{-1}) compared to baseflow conditions in the summer (1 ng l^{-1}). This coincided with an approximate 10-fold increase in suspended sediment concentrations from 10 to 103 mg l^{-1}. Similar increases are expected in Bay Area watersheds on seasonal time scales due to distinct hydrologic conditions created by increased precipitation, surface runoff, and sediment discharge during the wet season.

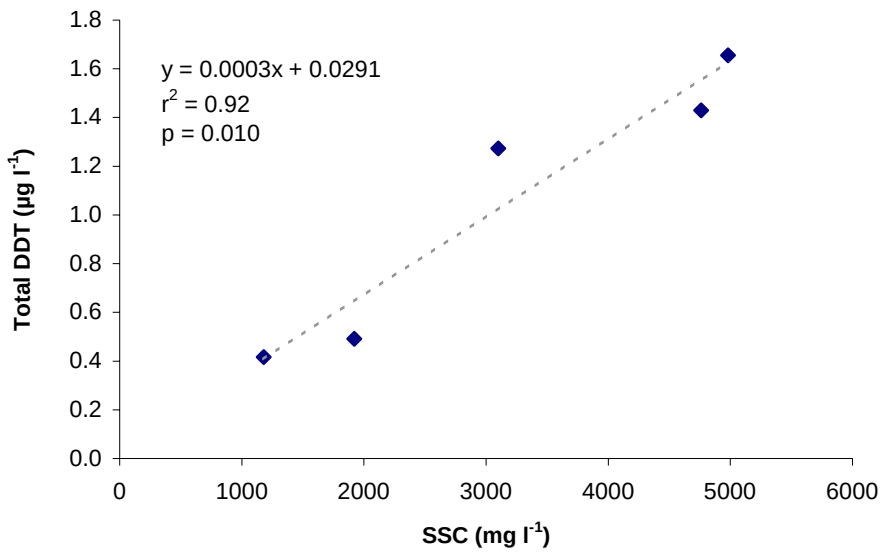


Figure 5.7. Linear regression of concentrations of total DDT (µg l-1) and SSC (mg l-1) during a storm event on Orestimba Creek. Data from Kratzer (1998).

While particulate and total concentrations of OC pesticides in the water column tend to mirror changing patterns of sediment discharge, concentrations of OC pesticides adsorbed on suspended sediment do not necessarily follow any pattern with streamflow or suspended sediment. Kratzer (1998) found that DDT concentrations measured directly on suspended sediment showed little variation (316 ± 58 µg kg^{-1}) over the duration of the storm on Orestimba Creek; dieldrin concentrations, however, gradually decreased from 8.2 to 1.4-1.8 µg kg^{-1}. This was attributed to varying sources of sediment and organic matter supply from adjacent floodplains, channel banks and bed, and upper watershed loading (Kratzer, 1998). To directly relate variable influences of sediment discharge and runoff in the wet season to changes in OC pesticide loading, total OC pesticide concentrations should be measured along with continuous measurement of streamflow and suspended sediment transport.

Bay Area watersheds typically have high flow-weighted mean concentrations of TSS and rapid response of runoff and sediment discharge to storm events, which likely result in order of magnitude increases in OC pesticide concentrations on time scales of minutes or hours. Due to the logistical difficulties of sampling within minutes or hours of the onset of a storm event, an effective monitoring design should explore the use of surrogate techniques, such as continuous measurement of turbidity, to relate sediment transport to loading of particle-associated contaminants, such as OC pesticides.

OC PESTICIDE LOADING IN TRIBUTARIES

OC pesticide loads from Bay Area watersheds have been estimated by two recent studies (KLI, 2002; Leatherbarrow *et al.*, 2002); however, limitations of the methods of data collection and estimation precluded defining the accuracy and uncertainties associated with these estimates. Leatherbarrow *et al.* (2002) provided lower bound estimates of OC pesticide loading from Guadalupe River and Coyote Creek using limited seasonal data collected for the RMP Estuary Interface Pilot Study. Flow-weighted mean concentrations and local hydrologic data yielded estimated loads on the order of 0.6 kg y^{-1} DDT, 0.4 kg y^{-1} chlordane, and 0.02 kg y^{-1} dieldrin from the two watersheds. It should be noted that these are lower bound estimates based on data collected in conjunction with RMP Status and Trends monitoring, which were not necessarily representative of conditions of peak flow and sediment transport.

The local storm water management agencies also estimated a range of loads for DDT and chlordane using bed sediment concentrations normalized to the percentage of fine grained material (< 62.5 µm in diameter), total suspended solids (TSS) concentrations and runoff coefficients for specific land uses (KLI, 2002). Loads from local tributaries were estimated to be 0.02 to 1.8 kg y^{-1} of DDT and 0.5 to 14 kg y^{-1} of chlordane, resulting in variability of 1 to 2 orders of magnitude. However, for reasons discussed in the section on suspended sediment loads in this report (see Chapter 3: Sediment Processes), these estimates are likely to be biased low by a factor of 2 to 3. In addition, the extent to which loads from the two studies were inaccurate was uncertain, which emphasizes the need to collect data for the purpose of quantifying OC pesticide

loading from Bay Area watersheds for comparison to loads from other pathways of contamination to the Bay.

Another limitation to using bed sediment concentrations for estimating contaminant loads is that differing physical and chemical processes and characteristics between suspended and bed sediment often result in higher contaminant concentrations in the suspended sediment. For example, Pereira *et al.* (1996) determined that OC pesticide concentrations were generally higher in the suspended sediment compared to bed sediment in four tributaries of the San Joaquin River. This was attributed to higher organic carbon content of the suspended sediment. The extent to which OC pesticide concentrations differed between suspended and bed sediment varied among tributaries, as depicted by ratios of concentrations on suspended sediment to bed sediment (Figure 5.8). Concentrations of most pesticides in suspended sediment were at least twice as high as concentrations in bed sediment. This finding was consistent with previous studies of suspended and bed sediment where OC pesticide concentrations on suspended sediment were 2.5 to 5 times greater than concentrations in bed sediment (summarized by Gilliom and Clifton, 1990).

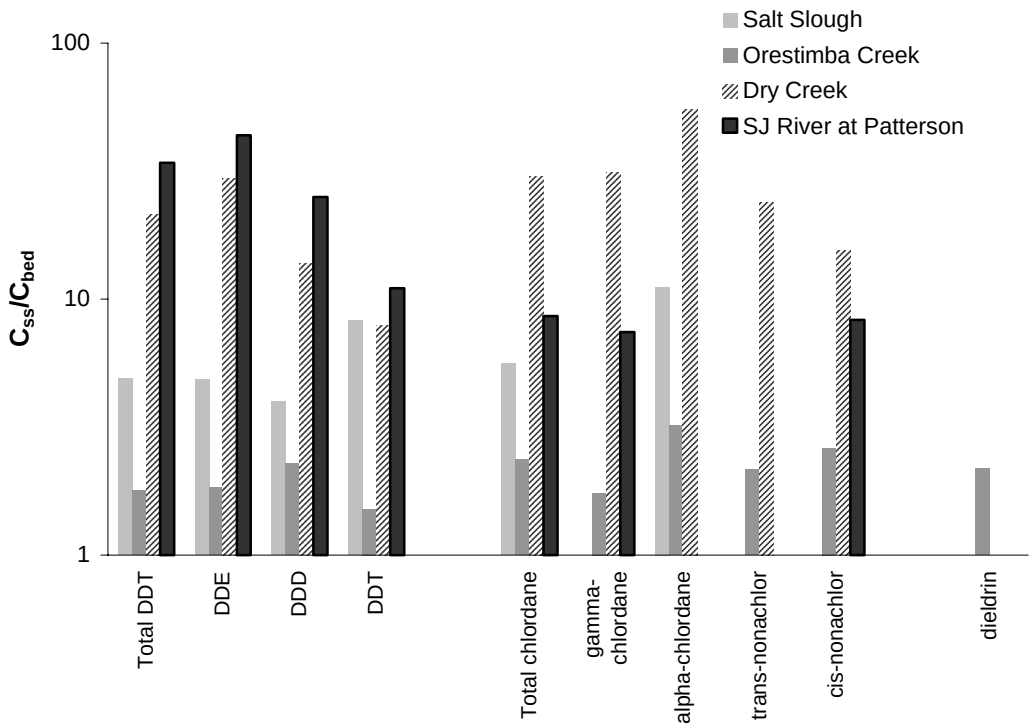


Figure 5.8. Ratios of OC pesticide concentrations in suspended sediment (C_{ss}) to concentrations in bed sediment (C_{bed}) in four tributaries of the San Joaquin River. Data from Pereira *et al.* (1996).

The relatively consistent relationship between OC pesticide concentrations in bed and suspended sediment in the agricultural Orestimba Creek was attributed to resuspension of bed sediment to the water column (Pereira *et al.,* 1996). Samples from other sites did not follow a similar pattern and may have been affected by varying sources of sediment to the water column. The greatest differences occurred in samples from Dry Creek, which had OC pesticide concentrations in suspended sediment that were 8 to 55 times greater than concentrations in bed sediment. This site also had the highest concentration of TOC (18.6%). As mentioned previously, this site receives urban runoff from Modesto, which may explain such high concentrations of chlordane in the water column compared to bed sediment (Pereira *et al.,* 1996).

At the same time, the San Joaquin River site at Patterson, which receives drainage from extensive agricultural lands, had the highest ratios of DDT in suspended sediment to bed sediment compared to other sites. The analysis suggests that local tributaries may differ in water column concentrations and loading of OC pesticides based on the varying sources of sediment (*e.g.*, resuspension, runoff) and contamination. Furthermore, locations that differ in bed sediment concentrations within an order of magnitude may, in fact, show similar suspended sediment concentrations and loading. Therefore, prioritization of watersheds for monitoring based on bed sediment concentrations may only be appropriate in areas where OC pesticide concentrations are 2 to 3 orders of magnitude greater than other locations. Even further consideration must be given to using bed sediment concentrations for prioritization since watersheds in the Bay Area show widely varying SSC and export widely varying suspended sediment loads (27 to 1,639 t $km^{-2}y^{-1}$).

Spatial Variability in Loading

Watershed exports (load per unit area) of OC pesticides from selected tributaries provide insight into expected loading from Bay Area watersheds with different watershed characteristics, such as land use and potential source activation (Table 5.4). Foster *et al.,* (2000a) used flow-weighted mean concentrations to determine that watershed exports in the heavily urbanized Anacostia River (440 km^2, 60% urban) in the Chesapeake Bay region were approximately 4 to 5 times greater for DDT and dieldrin than in the Susquehanna River (Foster *et al*., 2000b). Although the Susquehanna River watershed contains agricultural and urban land uses, this large watershed also contains non-impacted areas, such as forests, that diluted contaminated runoff and sediment resulting in smaller yields than the Anacostia River. As expected, exports for chlordane were much greater (approximately 40 times) in the Anacostia River.

DDT exports in the Susquehanna River were consistent with those estimated for four agricultural tributaries to the St. Lawrence River (Tham *et al.,* 1996). These estimates indicate that smaller urbanized watersheds provide greater exports of OC pesticides to the Bay compared to larger agricultural or non-urban watersheds. As stated previously, the process of prioritizing and selecting watersheds for monitoring OC pesticide loading should utilize existing contaminant data in conjunction with watershed

characteristics, such as hydrology, sediment transport, and land use, to determine which watersheds may contribute the greatest loads of OC pesticides to the Bay.

Table 5.4. Watershed exports from selected tributaries (g $km^{-2}y^{-1}$).

Study Site	Basin Size (km^2)	DDT	Chlordane	Dieldrin
		(g km^{-2} y^{-1})	(g km^{-2} y^{-1})	(g km^{-2} y^{-1})
Anacostia River [1]	440	2.87	17.8	0.67
Susquehanna River[2]	70,160	0.58	0.44	0.17
Richelieu[3]	23,700	0.75	-	-
Yamaska[3]	4,840	0.81	-	-
St. Francois[3]	10,230	0.40	-	-
Nicolet[3]	3,420	0.40	-	-

[1]Foster *et al.* 2000a – includes NE and NW branches
[2]Foster *et al.* 2000b
[3]Tham *et al.* 1996

Temporal Variability in Loading

Temporal variability in OC pesticide loadings is primarily influenced by changes in suspended sediment loads and streamflow associated with erosion and runoff during wet-season conditions. Tham *et al.* (1996) estimated that seasonal loading of DDT from four agricultural tributaries to the St. Lawrence River was generally highest during periods of rainfall in autumn and snowmelt in the spring. Between the four tributaries, DDT loading in the autumn 1990 and spring 1991 were between 2 to 7 times greater than loading in summer 1991. Similarly, Kratzer (1998) calculated instantaneous loads of chlordane, dieldrin, and DDT from seven tributaries of the San Joaquin River that were greater than dry season loads by approximately 14, 33, and 16 times, respectively. Given that variability of a similar or greater scale probably occurs in Bay Area tributaries, monitoring should be conducted at more frequent intervals and in conjunction with continuous monitoring of suspended sediment and streamflow during storm events and resulting high flow conditions.

Atmospheric transport of OC pesticides

OC PESTICIDE CONCENTRATIONS IN THE ATMOSPHERE

A tributary monitoring design must consider the contribution of atmospherically derived OC pesticides to overall watershed budgets. Atmospheric deposition of OC pesticides contributes to watershed budgets to the extent that OC pesticides enter the atmosphere from urban and agricultural regions of historic use through volatilization and wind-induced erosion of contaminated particles. Subsequent removal of contaminants from the atmosphere involves dissolution into rainfall and sorption onto particulate

matter followed by wet and dry deposition onto watershed surfaces. Wet season runoff and dry season irrigation may then mobilize and transport accumulated OC pesticides through the watershed. Atmospheric transport studies in the Bay Area have yet to attempt to characterize the transport and fate of atmospherically derived OC pesticides in relation to watershed processes; however, findings from studies in other regions provide insight into potential contributions of atmospheric contributions to Bay Area watershed budgets.

Spatial Variability of OC Pesticides in the Atmosphere

Due to the persistence of OC pesticides in soils, concentrations and transport of OC pesticides in the atmosphere are largely influenced by patterns of historic application and the meteorological factors associated with volatilization and deposition. For example, Spencer *et al.* (1996) measured DDT concentrations in air ranging from 6.1 to 23.8 ng m^{-3} at a site in Coachella Valley, California, where large-scale DDT applications occurred decades before. In the Mississippi River Valley, p,p'-DDE, which is the most volatile metabolite of DDT, was measured in 100% of air samples from an agricultural site, while approximately 50% of the urban samples had detectable levels (Coupe *et al.*, 2000). In a companion study, approximately 84% of air samples from the urban site had detectable concentrations of dieldrin, while only 26% of samples from the agricultural site had detectable concentrations (Foreman *et al.*, 2000).

High concentrations of dieldrin have also been measured in air samples collected in areas of low dieldrin use, but high aldrin use (Kutz *et al.*, 1976), showing that breakdown products of pesticides, such as dieldrin from aldrin, may also exist in high concentrations in areas related to past usage of parent products. Assuming that the historic use of OC pesticides in Bay Area watersheds was widespread in urban and agricultural regions, concentrations and loading of OC pesticides are expected to be highest in watersheds with high densities of both land-use types.

Temporal Variability of OC Pesticides in the Atmosphere

Seasonal variability in OC pesticide concentrations in the atmosphere is influenced to a large extent by the distinct differences in precipitation and temperature between wet and dry season conditions. Spencer *et al.* (1996) measured higher concentrations of DDT in warmer air in late summer compared to winter sampling in February. Similar seasonal patterns have been observed for dieldrin and chlordanes in other regions of the U.S. (Park *et al.*, 2001; Jantunen *et al.*, 2000) due to increasing volatility of OC pesticides with increasing temperatures.

Agricultural activities and practices may also have a significant effect on the amount of OC pesticides that volatilize into the air and resulting atmospheric concentrations. On an hourly time scale, Spencer *et al.* (1996) measured a 40-fold increase in volatilization fluxes of p,p'-DDE (from 0.42 to 16 µg m^{-2} h^{-1}) from agricultural soil immediately following irrigation. Furthermore, fluxes for all DDT compounds were greater in late summer compared to winter, which was attributed to higher temperatures and more frequent irrigation (Spencer *et al.*, 1996). Although the

study did not account for volatilization in urban areas, the findings indicate that these processes may also be occurring on irrigated urban areas such as parks, lawns, cemeteries and golf courses. For this reason, it is expected that volatilization of OC pesticides from regions of historic use in urban and agricultural portions of the Bay Area may be locally redeposited onto watershed surfaces and washed through the system during the wet season.

OC PESTICIDE LOADING FROM THE ATMOSPHERE

The extent to which atmospheric loading of OC pesticides contributes to watershed budgets was evaluated with comparisons of depositional fluxes to overall watershed exports. In Galveston Bay, Texas, Park *et al.* (2001) measured depositional fluxes for DDT, chlordane, and cyclodienes, a group of pesticides that includes dieldrin, and determined that wet deposition was responsible for the greatest fraction of deposition for DDT and chlordane (Table 5.5). Dry deposition, however, was more important for cyclodienes. For all OC pesticides, particulate phase deposition was responsible for greater than 84% of total deposition (Park *et al.*, 2001). Chan *et al.* (1994) reported similar wet deposition rates at three locations around the Great Lakes region.

In comparison to watershed exports derived from reviewed studies (Table 5.4), it is plausible that atmospheric loading of DDT and dieldrin may be of the same order of magnitude as watershed exports from non-urban and urban watersheds, while deposition rates of chlordane may represent only a fraction of the overall budget in urban watersheds. It should be noted that differences between discussed sampling locations preclude making conclusive statements about the atmospheric contribution to total OC pesticide loading from watersheds. Nonetheless, it is likely that similar deposition rates are recycling and supplying inputs to Bay Area watersheds and that atmospheric OC pesticides may be responsible for some extent of concentration variation in wet season runoff.

Table 5.5. Estimated depositional fluxes of OC pesticides (g $km^{-2}y^{-1}$).

Flux (g km^{-2} y^{-1})	Type of Deposition	DDT	Chlordane	Dieldrin
Wolfe Island[1]	wet	0.32	.	0.46
Pelee Island[1]	wet	0.34	.	1.3
Sibley[1]	wet	0.12	.	0.45
Galveston Bay[2]	wet	1.51	0.52	0.25[3]
Galveston Bay[2]	dry	0.43	0.23	0.54[3]
Galveston Bay[2]	total (wet + dry)	1.94	0.75	0.79[3]

[1]Chan *et al.*, 1994; averaged from 1986-1991.
[2]Park *et al.*, 2001
[3]Estimated flux for cyclodienes, which included aldrin, dieldrin, and endrin.

Summary

Sources

- OC pesticides were used extensively from the 1940s to the late 1980s for agricultural applications on various crops and for pest control, mosquito abatement, and residential use in urban areas.

Partitioning

- OC pesticides preferentially sorb to particulate matter, such as sediment and organic matter in soil, sediment, and water.
- In water samples collected during flood conditions from RMP stations near the mouths of the Guadalupe River and Coyote Creek, particulate concentrations of DDT, chlordane, and dieldrin comprised greater than 80%, 70%, and 50% of total concentrations.
- The high affinity of OC pesticides to particulate phases supports the development of a monitoring strategy for measuring OC pesticide loading from local tributaries based on defining the variability of suspended sediment concentrations.

Spatial Variability of OC Pesticides

- The historic use of OC pesticides for urban and agricultural applications, combined with their persistence in soil and sediment, suggest that concentrations and loadings are expected to be high in Bay Area watersheds with both land use types.
- In a bed sediment survey of Bay Area tributaries and storm drains, concentrations of DDT and chlordane were at least 2 orders of magnitude higher in samples from industrial sites compared to samples from non-urban sites.
- In tributaries of the San Joaquin River in the Central Valley, the maximum concentration of chlordane in suspended sediment (160 ng g^{-1}) collected from an urban site was 16 times greater than concentrations at an agricultural site sampled in the same study. Furthermore, this concentration was 160 times greater than concentrations measured at a reference site with no known urban or agricultural influences. In a similar manner, DDT concentrations in suspended sediment from an agricultural site were 4 to 5 times greater than concentrations at urban sites and approximately 100 times greater than concentrations at reference sites.
- In the reviewed literature, watershed exports (loads per unit area) of DDT and dieldrin were approximately 4 to 5 times greater from the tributary of an urbanized watershed compared to a predominately non-urban influenced tributary. Moreover, chlordane exports were 40 times greater in the urbanized tributary.
- Locations for monitoring OC pesticide loading from local tributaries should be selected in tributaries with the greatest potential for contaminant loading to the Bay. In the case of OC pesticides, priority should be given to watersheds that still contain highly contaminated deposits from historic agricultural or urban applications and export large amounts of suspended sediment.

Temporal Variability of OC Pesticides

- In tributaries of the Bay Area, increased concentrations and loading of OC pesticides are expected in response to increased sediment discharge and runoff during wet-

season storm events. First flush effects are expected to cause even greater increases in both urban areas and non-urban watersheds.

- In the reviewed literature, order of magnitude increases of DDT concentrations and loading in tributaries have occurred on time scales of minutes to hours and between seasons. These increases corresponded to an approximate order of magnitude increase in suspended sediment concentrations.
- Tributaries in the Bay Area may show even greater variability in OC pesticide concentrations and loading considering that suspended sediment concentrations actually vary by 3 to 4 orders of magnitude in some tributaries.
- Due to practical and logistical difficulties of sampling within minutes to hours of the onset of a storm event, a tributary monitoring design should explore the use of surrogate techniques, such as continuous monitoring of turbidity with optical backscatter (OBS), to relate suspended sediment loading to loading of OC pesticides and other particle-associated contaminants.

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Part 6: Mercury

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Introduction

PROBLEM STATEMENT

Sampling conducted in the San Francisco Bay by the Regional Monitoring Program for Trace Substances (RMP) since 1993 has indicated concentrations of mercury (Hg) in water, sediment, and fish tissue posing human and ecological health risk. Mercury is a principal concern to local environmental managers because of the way that it bioaccumulates in tissue and biomagnifies in higher levels of the food web. Mercury may contribute to an increase in hatching failures in aquatic bird species and is a developmental neurotoxin that can lead to birth defects, infant mortality, and learning disorders in humans. In relation to human risks, a recent study found that the majority of people who catch and eat fish from the Bay do so safely; however about 10% do consume more than recommended daily amounts of contaminated fish, and Asian anglers appear to be most at risk due to large numbers of individuals, rate of consumption, and methods of preparation (CDHS & SFEI, 2001).

IMPORTANCE OF RUNOFF FROM LOCAL WATERSHEDS

Much of the mercury contamination in the Bay is linked to historic mining (e.g., Alpers and Hunerlach, 2000; Abu-Saba and Tang, 2000; Abu-Saba, 2001); however, there are ongoing inputs associated with both natural processes and human activities that are either disturbing historic deposits or continuing to provide allochthonous inputs from contemporary uses. Davis et al. (1999) suggested that the mercury load from local small tributaries is probably a significant source of contamination to the Bay, recommended accurate measurement of stormwater loadings, and suggested the use of turbidity as a surrogate measure to assist in calculating loads. Presently estimates of mercury loads entering the Bay from local tributaries (Abu-Saba and Tang, 2000; Abu-Saba, 2001; Leatherbarrow et al., 2002; KLI, 2002) and from the Central Valley (Davis et al., 2000; McKee and Foe, 2002) have a high degree of uncertainty. This uncertainty may result in implementation of less successful mercury control measures. For example, if estimates of mercury loads entering the Bay from local tributaries are estimated too low, environmental managers may focus efforts on the reduction of other sources and pathways such as the loads from the Central Valley, point sources, or internal recycling. Clearly, improving mercury load estimates from the Central Valley and from local tributaries will increase the certainty of sound management decisions. The Sources, Pathways, and Loading Workgroup have initiated a study at Mallard Island to improve estimates from the Central Valley. Studies to improve estimates of mercury loads in small tributaries have not been initiated (except in the Guadalupe River), yet small tributaries are pathways that significantly influence mercury processes in the Bay.

Types and properties

CHEMICAL PROPERTIES AND SPECIATION

Mercury, with an atomic number of 80 and an atomic mass of 200.6 g mol^{-1}, is the only metal that is liquid at room temperature. Mercury readily forms solutions with other metals, and it is this property that led to its widespread use for amalgamation and extraction of gold. Mercury in natural streams occurs in a range of different forms. Elemental mercury can be found in ores, mine sites, and in close proximity to mines (Gray et al., 2000). Given its modern uses in the urban environment, elemental mercury (Hg^o) and compounds containing mercury can be present in urban streams associated with illegal or accidental dumping of devices that contain mercury such as fluorescent tubes (Abu-Saba and Tang, 2000; Abu-Saba, 2001). Cinnabar (HgS) is usually found in association with mining areas and is found in Bay Area streams downstream from abandoned mine sites such as the Guadalupe River (Abu-Saba and Tang, 2000; Abu-Saba, 2001). Under slightly alkaline conditions, cinnabar has a very low solubility. Other common forms of mercury in the environment are insoluble. Generally, the dissolved phase comprises only a small portion of the total mercury in natural waters, largely because natural waters have a pH range from slightly acidic to slightly alkaline that favors Hg complexation to organic carbon and sediment particles.

Methylation is the process by which Hg^{2+} is converted to organic methyl mercury species (CH_3Hg^+ and $(CH_3)_2Hg$) by sulfate reducing bacteria in anoxic environments (Jones and Slotten, 1996; Alpers and Hunerlach, 2000). Organic forms such as mono-methyl mercury (MMHg) and di-methyl-mercury (DMHg) are more easily taken up by organisms and stored in their tissues. Therefore the methylation process strongly impacts the effect of mercury in the environment. Methylation often occurs in wetland areas on the margins of estuaries where there is a source of sulfate from seawater, an abundance of organic carbon, and a low or fluctuating concentration of dissolved oxygen. This is because methylation is dependent on environmental factors such as dissolved oxygen, dissolved inorganic carbon, temperature, salinity, pH, redox, and the forms and concentrations of sulfur and mercury (Jones and Slotten, 1996; Alpers and Hunerlach, 2000). The relative availability for methylation of new mercury loads versus the mass that is already present due to historic loads is a key management concern in the Bay area (Davis et al. 1999).

Only a small portion of mercury released into the environment through human activities is in the methylated forms. Given that San Francisco Bay is surrounded by wetland systems, it seems likely that the margins of the Bay may be supplying methyl mercury to the food chain (perhaps a greater supply than from allochthonous inputs). Because of the continuous degradation of methyl mercury species in natural oxic environments (Oremland, 1995) such as San Francisco Bay, water column concentrations of methylated mercury often more closely mirror concentrations in adjacent sediments rather than upstream waters (Benoit et al., 1998). Although factors controlling the rates of methyl mercury production and degradation are not yet well understood, an order of

magnitude assessment of the relative contributions of mercury that is methylated locally and upstream of the Bay could be made.

PARTITIONING

Mercury is transported from naturally occurring deposits and contaminated locations in dissolved, colloidal, and particulate forms. The distribution and transport of mercury among these phases affects the toxicity and bio-uptake of mercury in surface waters (Babiarz et al., 2001). Particulate mercury is commonly reported as the fraction of mercury that is retained on a filter paper with pore sizes of 0.4 or 0.45µm (e.g., Balogh et al., 1998; Whyte and Kirchner, 2000). Colloidal forms may be considered those particles that pass through a 0.45µm filter paper that are not dissolved (Davis et al. 1999), but practically the technology to partition the dissolved and colloidal phases has only recently been developed (Babiarz et al., 2001). They describe an ultra-filtration technique that partitions out colloidal particles and the dissolved phase at a 0.0015µm cutoff. This contrasts with Roth et al. (2001) who used ultra-filtration techniques to partition the dissolved phase as <0.005µm.

In order to help compare the distribution of mercury among phases and between systems, partition coefficients can be calculated. Typically partition coefficients (log k_d) for mercury range between 3.7 and 6.6 for natural fresh waters (Benoit et al., 1998; Mason and Sullivan, 1998; Ganguli et al., 2000; Babiarz et al., 2001; Lawson et al., 2001). Similar log k_d have been reported for MMHg (e.g., Babiarz et al., 2001), but often log k_d for MMHg are a little lower (e.g., Ganguli et al., 2000). Metals and other substances exhibit high log k_d when they are dominantly bound to particles in the laboratory environment. However, other factors such as the concentration of suspended sediments can influence partitioning in the natural environment (Figure 6.1a). For mercury, a log k_d >5 indicates that the particulate phase will dominate even in waters of relatively low suspended sediment concentrations (10 mg l^{-1}). A k_d of 4 would require a suspended sediment concentration in excess of 100 mg l^{-1} before particulate forms of mercury would dominate (Lawson et al., 2001).

A relationship between partitioning and organic carbon has also been observed in natural environments associated with the ability for organic carbon to form strong complexes with mercury (Mason and Sullivan, 1998). As the percentage of organic carbon in particles increases, the k_d increases (Figure 6.1b). The lack of any relationship between dissolved organic carbon and dissolved mercury seems to suggest that even low DOC concentrations can cause the binding of both inorganic and organic dissolved mercury into metal-organic complexes (Mason and Sullivan, 1998) that act like particles.

In summary, mercury is transported in a range of forms, and the distribution between these forms is largely controlled by the presence of suspended particles and organic carbon either associated with these particles or in solution within the water column. In situation where suspended sediment concentrations are in excess of 100 mg l^{-1} or when even small concentrations of organic carbon are present, mercury will tend to bind with the particles or form particle like organo-complexes with DOC. It is inferred

that transport of mercury in small tributaries of the Bay Area will likely occur dominantly as particulate mercury. The expense and measurement of the full suit of mercury species in water samples collected for estimation of mercury loads may be unnecessary, unless the data are to be used for other purposes such as modeling fate in the receiving waters.

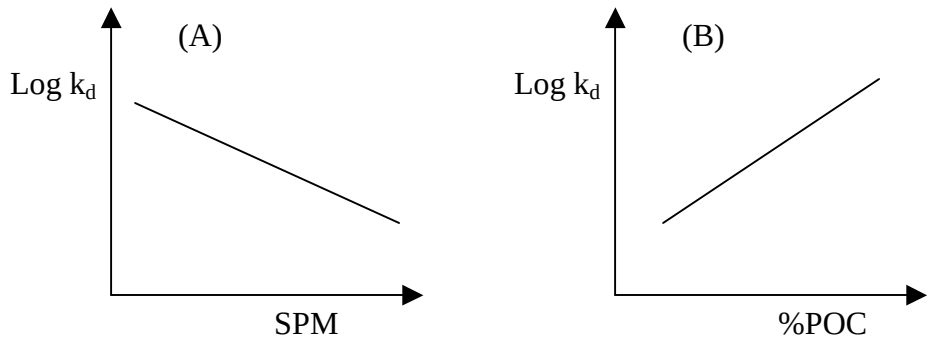

Figure 6.1. Relationships between (A) log k^d and suspended particulate matter concentration (sediments and colloids) and (B) log k^d and %POC.

ANALYTICAL CONCERNS

Determining the concentration of mercury in water is not straightforward and requires ultra-clean sampling and laboratory techniques (e.g., Gill and Fitzgerald, 1985; USEPA, 1996). Roth et al. (2001) demonstrated the difficulties associated with incomplete digestion of the whole sample during laboratory analysis. They found that the sum of the dissolved and particulate fractions was usually greater than the concentration determined by whole water analysis alone. Mason and Sullivan (1998) had similar results in an urban watershed in Washington D.C. and attributed the problem to sub-sampling whole water samples and incomplete oxidation due to high organic content in the water samples. Detection limits for total mercury are around 0.04 to 0.39 ng l^{-1} (e.g., Whyte and Kirchner, 2000; Ganguli et al., 2000; Domagalski, 2001). Detection limits for MMHg are about 0.02 to 0.025 ng l^{-1} e.g., Domagalski, 2001; Babiarz et al., 2001). Although these analytical concerns exist, they do not pose a problem for mercury sampling in the water columns of the small tributaries in the Bay Area if the aim is to determine total mercury loads and detection limits will not pose a problem given that land management and urbanization in the Bay Area as well as historic mining activities have led to concentrations that are much above background (e.g., Leatherbarrow et al., 2002).

IMPLICATIONS FOR LOAD MEASUREMENT

Suspended sediment concentrations in urban and rural streams of the Bay Area increase to well in excess of 100 mg l^{-1} during high flow. Flow-weighted mean concentrations are in excess of 374 mg l^{-1} in 14 Bay Area small tributaries where data

have been collected over two or more years (see the section on sediment processes). Although there is no corresponding dataset on the concentration of either organic carbon or mercury for local tributaries, it seems reasonable to hypothesize that mercury transport in Bay Area streams will be dominantly associated with particles. If this is the case, studies developed to determine total loads of mercury that enter the Bay annually should focus on measuring total mercury. Surrogate techniques such as continuous measurement of turbidity would also seem an appropriate methodology for extrapolation between samples. In addition, data on the forms of organic carbon (DOC, POC, and TOC) are likely to provide a useful tool for accounting for some of the variance that is not explained by variation in suspended sediment concentrations.

Speciation studies that determine the proportions of mercury transported in methyl forms would provide a better understanding of the immediate impact of the receiving ecosystem. Although loading studies should focus resources on the measurement of total mercury concentrations, a small allocation of funds should also be applied for the determination of methylated forms.

Sources

SPATIAL DISTRIBUTION IN THE WATERSHED

Mercury is a naturally occurring element in the Earth's crust, although elemental mercury (Hg^0) is rarely found in nature. The chief ore is cinnabar, HgS. Spain and Italy presently produce about 50% of the world's supply of the metal and the California Coast Range was a world-class mercury deposit. The average concentration in the Earths crust is about 67 ppb (mg t^{-1}) (Cox, 1989). Mercury naturally occurs in the Coast Ranges of California and is associated with Cenozoic hydrothermal deposits (Domagalski, 1998). These deposits were the result of the spread of silica-carbonate alteration of serpentinite by low-temperature (<120 ºC) CO_2-CH_4-H_2S-rich fluids derived from connate waters in Great Valley forearc sedimentary rocks (Rytuba and Enderlin, 1999).

Silica-carbonate-alteration zones bearing mercury, nickel, zinc, copper, chromium, and cobalt in varying quantities are found in sedimentary rocks of the Great Valley Sequence and Franciscan Complex in all nine counties of the Bay Area. The ore bearing deposits of mercury occur in areas where antiformal structures trapped and concentrated hydrothermal fluids. Excluding the watersheds that drain to Tomales Bay, there are 16 historic mercury mine sites in the Bay Area (RWQCB, 1995). The majority of these occur in the New Almaden mining district, Santa Clara County, within the Guadalupe River watershed. The was the highest producing mercury mining area of North America (Rytuba and Enderlin, 1999); however there are abandoned mines in Napa River watershed, Petaluma River watershed, in the small watersheds that drain the country north of Carquinez, and Bay side San Mateo County (Figure 6.2).

Mercury occurs in soils as a natural weathering product of parent lithology and derived from atmospheric redistribution and deposition. Typical concentrations in California soils range from 0.2 mg kg^{-1} to 0.9 mg kg^{-1} (Bradford et al., 1996). This

implies that natural or anthropogenically enhanced sediment erosion and supply to streams will impart a background load of mercury, and this can be estimated using estimates of natural sediment load assuming there is no enrichment or depletion of mercury on particles during transport.

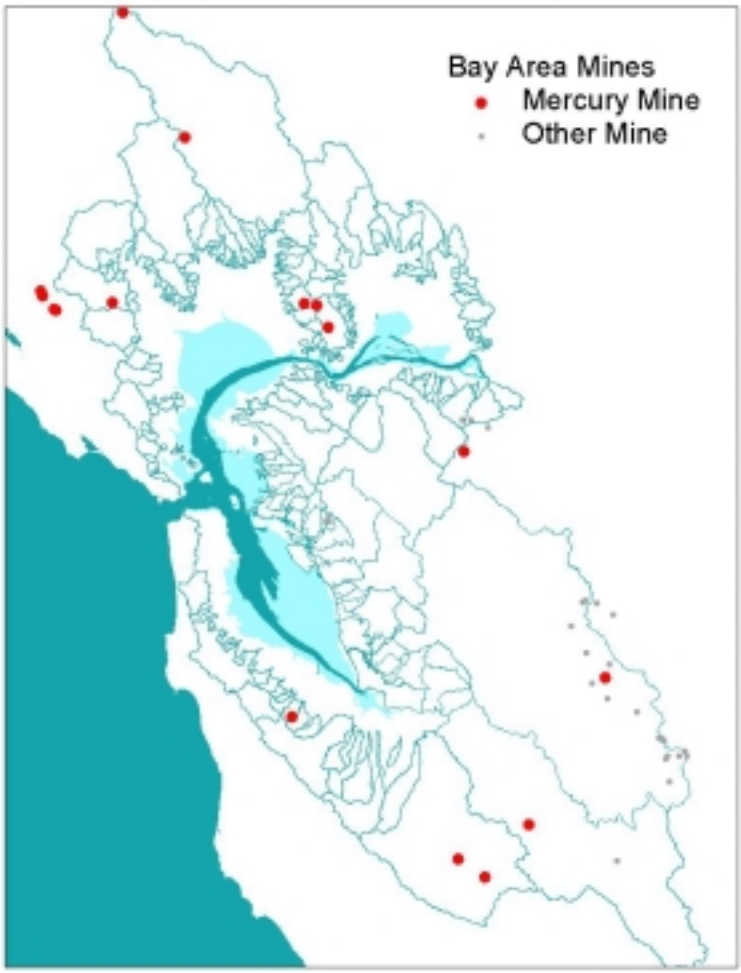

Figure 6.2. The distribution of mercury mines in Bay Area watersheds. Data provided by RWQCB. Map developed by Eric Wittner, SFEI.

There are two important implications relating to sources of mercury in Bay Area watersheds. It will be important to concentrate on quantifying the impact from large sources such as the abandoned mercury mines of the New Almaden mining district. Loading studies should be sensitive enough to allow an analysis of trend over time as a tool for determining effectiveness of any remediation. Another important implication is that there is a natural background concentration and load that is associated with mercury

in Bay Area soils. It is important to use this as a reasonable baseline limit in efforts to attain water quality standards.

LONG TERM TRENDS IN USE OR ABUNDANCE

Mercury is used for a variety of applications totaling about 3,000 separate uses (MSU, 2002). Anthropogenic uses include commercial manufacturing, production of munitions, thermometers, barometers, diffusion pumps, and many other instruments, electrodes in laboratory experiments, batteries, dental amalgams, contact lens solutions and other health care products, fluorescent lights and advertising signs, switches and other electronic devices, pesticides and antifouling paints. In 1976, EPA banned most pesticide uses of mercury - with the exceptions of fungicidal uses in paints and outdoor fabrics, and for control of Dutch elm disease. In 1990, the EPA halted mercury use as a fungicide in interior latex paint. This action stemmed from requests by Michigan officials after a child was poisoned from over-formulated mercury-containing paint used in his home. More recently, the use of mercury compounds in exterior latex paint has also been halted.

In the Bay Area, the most important sources of mercury in each watershed will vary depending on industrial and commercial mercury uses, population density and traffic density, natural background geological sources (and disturbance of these caused by land management practices), and historical mining sources. Motor vehicles are likely to be an important source in urbanized areas. On average, motorists in the Bay Area drive 125,000,000 miles (~200,000,000 km) each workday. If each vehicle averages 25 miles per gallon (~10 km l^{-1}) of fuel this would equate to 20,000,000 l d^{-1} or approximately 5.2 x 10^9 liters of fuel per year. Concentrations of mercury in gasoline range between 0.22 and 3.3 ppb depending on the geological origin of the fuel (Center for Air Toxic Metals 2002). Therefore, on an annual basis, vehicles in the Bay Area could supply between 1 and 17 kg per year to the air/ watershed. The average daily distance driven has been increasing by about 3% annually, but this is partly offset by improving vehicle fuel efficiency.

It would seem likely that urban sources might decrease over time given several influential factors: the ban of certain uses of mercury, the reduction in the use of mercury in the dental industry, the growing community awareness to avoid certain products that contain mercury, ongoing improvements in recycling and disposal of products containing mercury, and the ongoing pressure on the gasoline industry to reduce concentrations in fossil fuels. In addition, mercury loads entering the Bay from local watersheds may further decline if local efforts to remediate historic mine deposits are successful. What is unknown, is how much mercury is mobilized from mercury bearing soils and rocks in Bay Area watersheds through natural processes such as landslide failures and sheet erosion and how that is being modified by disturbances associated with urban, industrial, and agricultural development.

Pathways

IMPORTANT PATHWAYS

Mercury can be transported through the terrestrial environment via four pathways:

1. Riverine and stormwater urban drainage transport in dissolved form or attached to sediment particles either suspended or as bedload;
2. To and from the atmosphere either in rainfall, gaseous forms, or attached to windblown dust particles;
3. Tissue of host organisms such as anadromous fishes or other migratory creatures that spend part of their lives in freshwaters;
4. Wastewater from municipal and industrial sources.

Mercury transport via movement of host organisms is unlikely to be significant relative to the other pathways and will not be discussed further. Movement of mercury through the waste streams will not be discussed further because treated waste is predominantly discharged to tidal water bodies in the Bay Area and therefore does not influence concentration and loads variability in streams and urban drainages.

SMALL TRIBUTARIES AND STORM DRAINS

In many watersheds, total mercury in creeks is dominated by particulate forms (those that do not pass through a 0.4 or 0.45 µm filter paper). For example, in a study on San Carlos Creek, New Idria, Ganguli et al. (2000) found that particulate mercury comprised between 69 and 99% of total mercury in the water column, and Blum et al. (2001) found that 88 to 96% of the mercury in the water column was in particulate form in Steamboat Creek, Nevada. In addition, if it is taken into account that much of the "dissolved" fraction can be associated with colloids, virtually all mercury in some watersheds is associated with particles in sizes greater than 0.0015µm (Roth et al., 2001; Babiarz, 2001). In watersheds where there is a strong association of mercury with particles, factors that influence the magnitude and location of areas of active soil erosion will cause the majority of variability of concentration and loads entering downstream environments (e.g., Balogh et al., 1998).

In contrast, however, the mercury load in other watersheds is transported predominantly in dissolved forms and there is only a poor correlation with suspended sediments. For example, the Croix River in the head of the Mississippi is 37% agriculture, 47% open space, and 1% urban. In this watershed, total mercury mobility was dominated by the dissolved phase and it was hypothesized that DOC may have played a more important role in transport. Similarly, mercury transport was about 50% dissolved loads in the upper St. Lawrence River, and the Ottawa River (Quémerais et al., 1999). These rivers have predominantly vegetated non-urban watersheds and mercury is probably stabilized by complexation or sorption with dissolved and / or colloidal humic-hydrous oxide associations (Quémerais et al., 1999).

It follows that watersheds in which mercury is transported dominantly in particulate forms, mercury may be stored in depositional zones on beds, banks and floodplains, whereas watersheds dominated by dissolved transport will have little storage capacity once mercury is mobilized and transmitted to the receiving water body. The implication is that a successful strategy for minimizing loads from local small tributaries in the Bay Area will need to take into account the specific transport mechanisms and consider the need to apply different strategies in different watersheds.

Question: Do both types of transport occur in different types of watersheds in the Bay Area (agricultural, urban, mine-impacted) or is mercury dominantly transported in either dissolved or particulate phase in all Bay Area watersheds?

Given the high suspended sediment concentrations found in Bay Area watersheds (see section on sediment processes), it seems likely that the transport of mercury in Bay Area watersheds is dominated by particle transport. However, pilot studies initiated might determine both dissolved and particulate concentration at least during the first season of data collection to determine the importance of each vector.

ATMOSPHERIC TRANSPORT

Mercury is delivered to both watershed surfaces and water bodies via the atmosphere. Atmospheric mercury is ultimately derived from natural sources through the processes of wind suspension of dust particles, volcanoes, sea salt spray, biogenic sources, and forest fires (Nriagu, 1990). On a global scale these natural sources amount to 2.5 M kg y^{-1}. Anthropogenic inputs to the atmospheric include energy production, smelting and refining, manufacturing processes, and waste incineration and amount to a further 3.6 M kg y^{-1} (Nriagu, 1990). These combined inputs to the atmosphere lead to a global background air concentration of about 1 ng m^{-3} (Shannon and Voldner, 1995). The consequence of this global background is that even remote watersheds and lakes can become contaminated through wet and dry deposition from the atmosphere.

Research on Hg concentration in rainfall suggests the long-range transport of Hg across the Pacific may be having an influence on the deposition of mercury on coastal California watersheds (Steding and Flegal, 2002). A recent study of atmospheric mercury contributions in the Bay Area (Tsai and Hoenicke, 2001) estimated an average net dry deposition of 19 µg m^{-2} y^{-1} and an average wet deposition of 4.2 µg m^{-2} y^{-1}. The authors suggest errors of ±25% for wet deposition and as great as five-fold for dry deposition. If we combine these estimates with the watershed area tributary to San Francisco Bay (6,650 x 10^6 m^2), the annual average mercury input to watershed surfaces of the Bay would be approximately 150 kg y^{-1}.

Although the atmospheric pathway has little implication for how concentrations and loads should be measured at the downstream point of a watershed, it has major implications for the concentrations that may be encountered. For example, during small

rain events, most of the mercury derived from the atmosphere is likely to be retained on watershed surfaces, and in channels. This newly deposited mercury is likely to remain available for transport during subsequent larger events. In addition, similar to watersheds surfaces, small rain events and the initial showers during a rainstorm will tend to have higher concentrations than larger rainstorms, and subsequent showers or days of rain. In this way, rainfall "cleanses" the atmosphere of mercury and other substances and intensity and duration contribute to the "first flush" seen in chemographs of urban and rural watersheds.

Retention of atmospheric mercury deposition has been discussed by a number of workers (Balogh et al., 1997; Mason and Sullivan, 1998; Quémerais et al., 1999; Lawson et al., 2001; Tsai and Hoenicke, 2001). Lake watersheds in Minnesota have been shown to export approximately 25% of atmospherically derived mercury (Balogh et al., 1997). Mason and Sullivan (1998) compared mercury exports with atmospheric inputs in two urban areas and found less than 37% retention, although they suggest that there may be other unaccounted inputs. Quémerais et al. (1999) developed a more inclusive budget for the St. Lawrence River watershed and estimated that about 88% of the total inputs are retained in the watershed. In watersheds of varying land use and size tributary to Chesapeake Bay, exports were found to be typically less than 30% of inputs and for the Herring Run watershed (100% urban), the export was 18% of the atmospheric input (Lawson et al., 2001). Given that most workers have not included mercury input from sources other than the atmosphere, is seems likely that retention of mercury from diffuse sources in watersheds is greater than 80%, even in urbanized systems. In watersheds where point sources dominate or where bank or bed erosion is a large source, export of mercury will be greater and retention will be diminished.

As a first approximation for Bay Area watersheds, Tsai and Hoenicke (2001) made the assumption that mercury retention from atmospherically derived inputs would approximately equal the proportion of rainfall that becomes runoff (about 32% was assumed for the Bay Area). It follows, using that logic, that urban areas with a greater proportion of impervious surfaces and therefore greater runoff coefficients (the proportion of rainfall that is manifested as runoff) will retain less atmospheric mercury than less dense urban areas, agricultural and open space areas.

Loadings

TRANSPORT PROCESSES

As discussed previously, mercury can be derived from a number of areas within a watershed depending on the watershed's history, social, and physical characteristics, and can be temporarily stored in channel or storm drain sediment deposits. During rainstorms, mercury stored in source and storage areas can be mobilized and entrained in overland flow on hillslopes, in more concentrated flow lines in gullies and swales, and in creeks, drains, and rivers. If the rainstorm is short-lived or of low intensity, the mercury that is in dissolved form may adsorb to soil particles as water percolates back into the watershed surface. Mercury that is mobilized and associated with sediments will likely settle

somewhere within the watershed either on the hillslope near the source or in channel lags, bars, low banks and floodplains, or within the urban drainage system in a myriad of areas capable of trapping sediment. If the rainstorm is large, the majority of dissolved mercury and a lesser fraction but significant amount of particulate mercury that is mobilized in the various source areas will be transported out of the watershed to the receiving water body.

These facets of the transport process for mercury are true for other dissolved and particle associated substances. It is these processes that lead to a number of recognized transport phenomena for sediment and trace substances. For example, intra-annual transport is more temporally restricted for mercury than water flow. If 90% of the annual water flow occurs in 6 months in Bay Area watersheds (see the section on climate and hydrology), we would expect that greater than 90% of the mercury load would occur in the same 6 months. In the case of mercury, if most of it is associated with sediment particles, then we might expect closer to 99% of the mercury load to be transported in 6 months (see the section of sediment processes). Another recognized transport phenomenon is the first flush effect. Mercury that is mobilized from sources but not transported out of a watershed either during small floods or during dry years remains available for transport during later events. This process leads to higher concentrations in early wet season events than in events later in the wet season when there is less stored mercury in the watershed. As such it will be important to quantify loads from early wet season flows and larger events later in the wet season, and we might expect there to be seasonally specific relationships between parameters (mercury, suspended sediment, organic carbon).

CATASTROPHIC EVENTS AND INTER-ANNUAL VARIATION

Different source areas and temporary storage areas will respond differently depending on their character, antecedent climatic conditions, and the intensity and duration of the storm event. Tailing dams at historical mining sites are known to be massive storage areas for both inorganic and methyl mercury (Rytuba and Enderlin, 1999). These tailing dams may be relatively stable during most rain events and release only minor amounts of mercury to the downstream environment. However, as an example, during the intense rainstorms of 1982 when antecedent soil moisture conditions were high, the Gambonini Mine tailings dam failed, introducing a large load of particulate mercury into a tributary of Walker Creek, Marin County (Rytuba and Enderlin, 1999; Whyte and Kirchner, 2000). Landslides occurred on the mine waste pile during the winter of 1998 and supplied another slug of mercury-contaminated sediment to the Creek, which further illustrates the triggering influence of climate on some source areas.

At the other end of the spectrum with small rain events, only easily mobilized mercury stored in channels lags and bars, storm drain systems, or accumulated on impervious surfaces (Fergusson and Kim, 1991; Tiefenthaler et al., 2001) will form the majority of the fluxes moving down stream. The ultimate source or storage areas, the type of rainfall event, and the period of time since the last rainfall event work in concert to

influence the magnitude and variability of mercury concentrations at a down stream sampling location.

In order to capture all catastrophic kinds of variation, studies should be designed to capture a wide range of event magnitudes focusing on the wet seasons. For mine-impacted areas, the largest events might trigger catastrophic supply and only if the largest events are captured, could we be sure that a complete picture of process and loads has been achieved. In the case of urban areas, it should be adequate to focus in first flush and a range of flood sizes over a 3 or 4-year period.

VARIATION AMONG WET AND DRY SEASONS AND STORMS

Seasonal and event mercury concentrations in the water column of streams and storm drains have been measured on a number of watershed scales and land use environments, such as downstream of mine-impacted source areas (Balogh et al., 1997; Balogh et al., 1998; Foe and Croyle, 1998; Domagalski, 1998; Mason and Sullivan, 1998; Quémerais et al., 1999; Alpers et al. 2000; Whyte and Kirchner, 2000; Blum et al., 2001; Domagalski, 2001; Ganguli et al., 2001; Lawson et al., 2001; Roth et al., 2001; Bariarz et al., 2001; Thomas et al., 2002). Concentrations in some watersheds can vary by about 80 times between low flow and high flow conditions (e.g., Balogh et al., 1998) and in some extreme cases by three orders of magnitude at mine contaminated locations (e.g., Whyte and Kirchner, 2000; Domagalski and Dileanis, 2000). Typically, the highest concentrations of total mercury occur during floods in both rural and urban watersheds (e.g., Balogh et al., 1998; Mason et al., 1998; Lawson et al., 2001; Thomas et al., 2002) indicating that the process of mobilization is associated with rainfall impact and surface water flow. Dissolved concentrations also peak during floods (e.g., Quémerais et al., 1999) as do MMHg concentrations in most rural watersheds (e.g., Domagalski, 2001) and urban watersheds (Mason and Sullivan, 1998; Lawson et al., 2001).

The first flush effect, whereby concentrations are highest during the first floods of the water year and lower during later floods regardless of flood magnitude, is a phenomenon commonly reported in urbanized watersheds. It is now recognized that this process also occurs in larger watersheds in rural areas. For example, in the Minnesota River (44,000 km^2) that is dominated by agriculture, early wet season events can have higher concentrations of mercury than later larger events (Balogh et al., 1998). First flush of mercury is also observed in the Elbe River in Europe (148,268 km^2) (Wilkin and Wallschläger, 1996). As suggested previously, it will be important to capture the first flush process when studying both urban and rural watersheds in the Bay Area because higher concentrations during early wet season events might contribute higher loads than might be expected from the magnitude of the discharge alone.

VARIATION AMONG WATERSHEDS

It should be no surprise that watersheds that have ongoing impact through human development or that have legacy point sources show higher water column concentrations of total mercury than other less impacted watersheds (Figure 6.3). Higher

concentrations are mostly caused by a combination of both greater mass of mercury stored in source areas and available for transport, and secondly a greater load of sediment and perhaps organic carbon, both of which are known vectors that influence mercury transport. Impacted watersheds usually exhibit greater variability in concentration (Figure 6.4). Thus in most cases, even impacted watersheds typically have better water quality during low flow periods when the mechanisms for mobilizing sources and storage areas are not operating. It is suggested here that intra-annual variation in water column concentration may be a good indicator of relative water quality between watersheds and could be used in the Bay Area for prioritization for management. The same data could also be used for estimating loads if coupled with monthly estimates of discharge. Measuring monthly or bimonthly concentrations throughout the year for watershed characterization and load estimates is currently being used by the USGS in the Central Valley as a precursor to detailed studies in identified areas of concern (Alpers et al., 2000; Domagalski and Dileanis, 2000; Roth et al., 2001; Domagalski, 2001). It is recommended that sampling programs in the Bay begin to focus on water column measurements of concentration.

RELATION OF MERCURY CONCENTRATIONS IN SEDIMENT TO LOADS

Mercury and methyl mercury concentrations have been measured in bed sediments in a range of fluvial systems (Gray et al., 2000; Domagalski, 1998, 2001; Blum et al., 2001; Gunther et al., 2001; KLI 2001; Lawson et al., 2001). Mercury concentrations in bed sediment finer than 63 µm were between about 0.01 to 0.4 µg g^{-1} dry-weight in Sacramento Valley sampling locations, excluding the mine-impacted area of Cache Creek (Domagalski, 1998, 2001). Average sediment mercury concentrations in watersheds with mainly non-urban mixed land use tributary to Chesapeake Bay range from 1.54 to 3.98 nmol g^{-1} (0.31 to 0.8 µg g^{-1}) (Lawson et al., 2001). Mercury concentrations in sediments in non-urban areas of the Bay Area have been measured during 2000 and 2001 (KLI 2001, 2002) (Figure 6.5). Concentrations from 21 samples ranged from 0.051 to 1.15 ppm (µg g^{-1}) and averaged 0.3 µg g^{-1}. These concentrations appear to be similar to non-urban environments near Chesapeake Bay and in the Central Valley of California.

In urban systems, the average mercury sediment concentrations may be similar or a little higher than in non-urban systems. For example, in Arcade Creek, an urbanized watershed with about 79% urban land use in the greater Sacramento metropolitan area, mercury in sediment was 0.13 mg g^{-1} (Domagalski, 2001). Concentrations in Herring Run, a 100% urbanized watershed tributary to Chesapeake Bay averaged 4.5 nmol g^{-1} (0.9 µg g^{-1}) (Lawson et al., 2001). Mercury concentrations at locations in Alameda County were measured during 2000 (Gunther et al., 2001) (Figure 6.5). Concentrations of Mercury ranged between 44 ppb dry-weight (0.044 µg g^{-1}) and 800 ppb (0.8 µg g^{-1}) and averaged 0.2 µg g^{-1}. Urban drainages of Santa Clara, Contra Costa, San Mateo, and Marin Counties and Vallejo and Suisun during 2000 and 2001 showed concentrations ranging between 0.073 and 40 µg g^{-1} with an average of 2.66 µg g^{-1} (KLI 2002) (Figure 6.5).

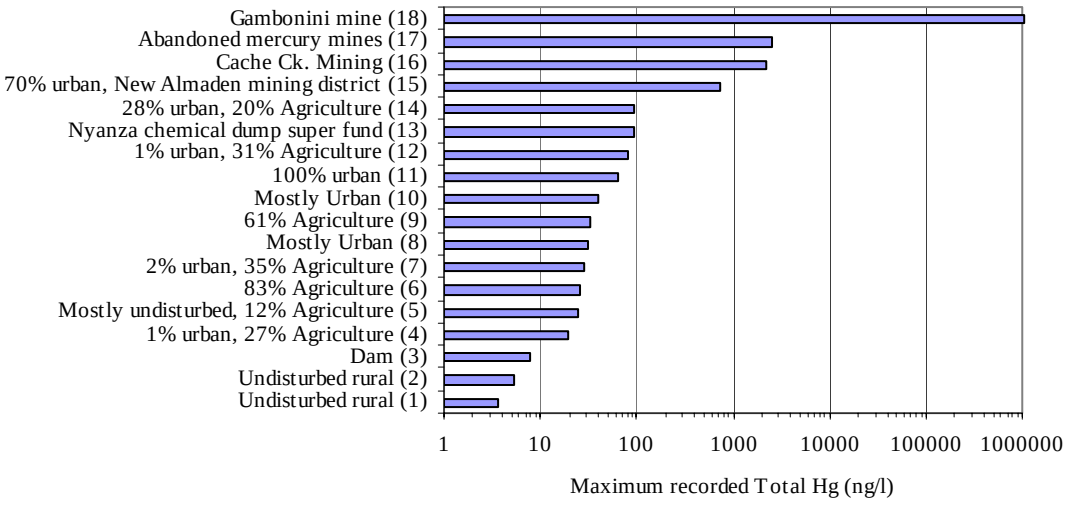

Figure 6.3. Total mercury in a selection of watersheds with different types of impact.

1: Site B2 Sudbury River, Massachusetts (Waldron et al., 2000); 2: Site B1 Sudbury River, Massachusetts (Waldron et al., 2000); 3: Below Keswick Dam, Sacramento Basin (Domagalski and Dileanis, 2000; Roth et al., 2001); 4: Above Bend Bridge, Sacramento Basin (Domagalski and Dileanis, 2000; Roth et al., 2001); 5: Rappahannock River, Chesapeake (Lawson et al., 2001); 6: Choptank River, Chesapeake (Lawson et al., 2001); 7: At Freeport, Sacramento Basin (Domagalski and Dileanis, 2000; Roth et al., 2001); 8: Anacostia River NW. Branch (Mason and Sullivan, 1998); 9: Susquehanna River, Chesapeake (Lawson et al., 2001); 10: Anacostia River NE. Branch (Mason and Sullivan, 1998); 11: Herring Run River, Chesapeake (Lawson et al., 2001); 12: At Colusa, Sacramento Basin (Domagalski and Dileanis, 2000; Roth et al., 2001); 13: Site M1 Sudbury River, Massachusetts (Waldron et al., 2000); 14: Potomac River, Chesapeake (Lawson et al., 2001); 15: Guadalupe River, Bay Area (Leatherbarrow et al., 2002); 16: Cache Creek, Sacramento Basin (Domagalski and Dileanis, 2000); 17: Kuskakwim River Basin, SW Alaska (Gray et al., 2000); 18: Walker Creek Marin County, California (Whyte and Kirchner, 2000).

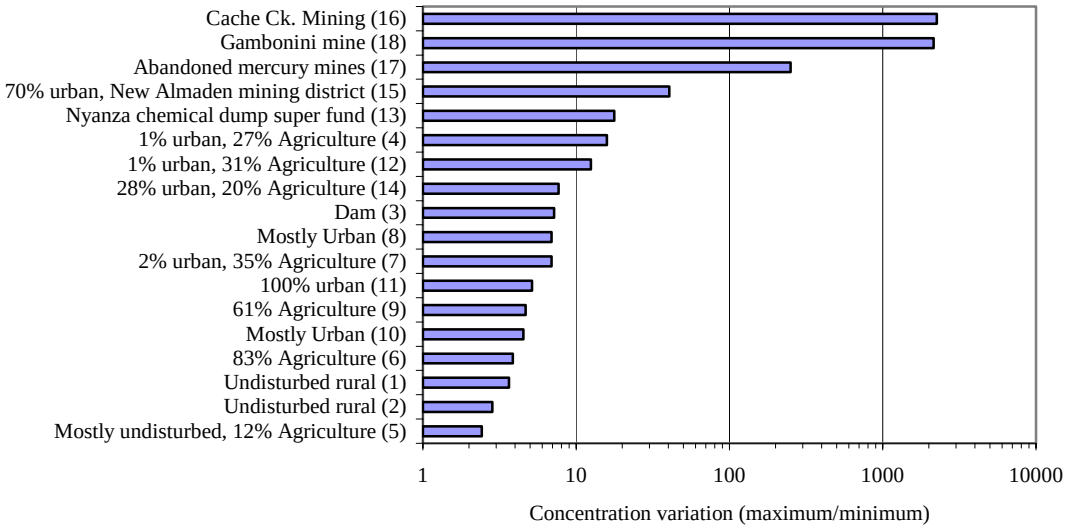

Figure 6.4. Variation of total mercury in watersheds with different types of impact (See Figure 6.3 for data sources).

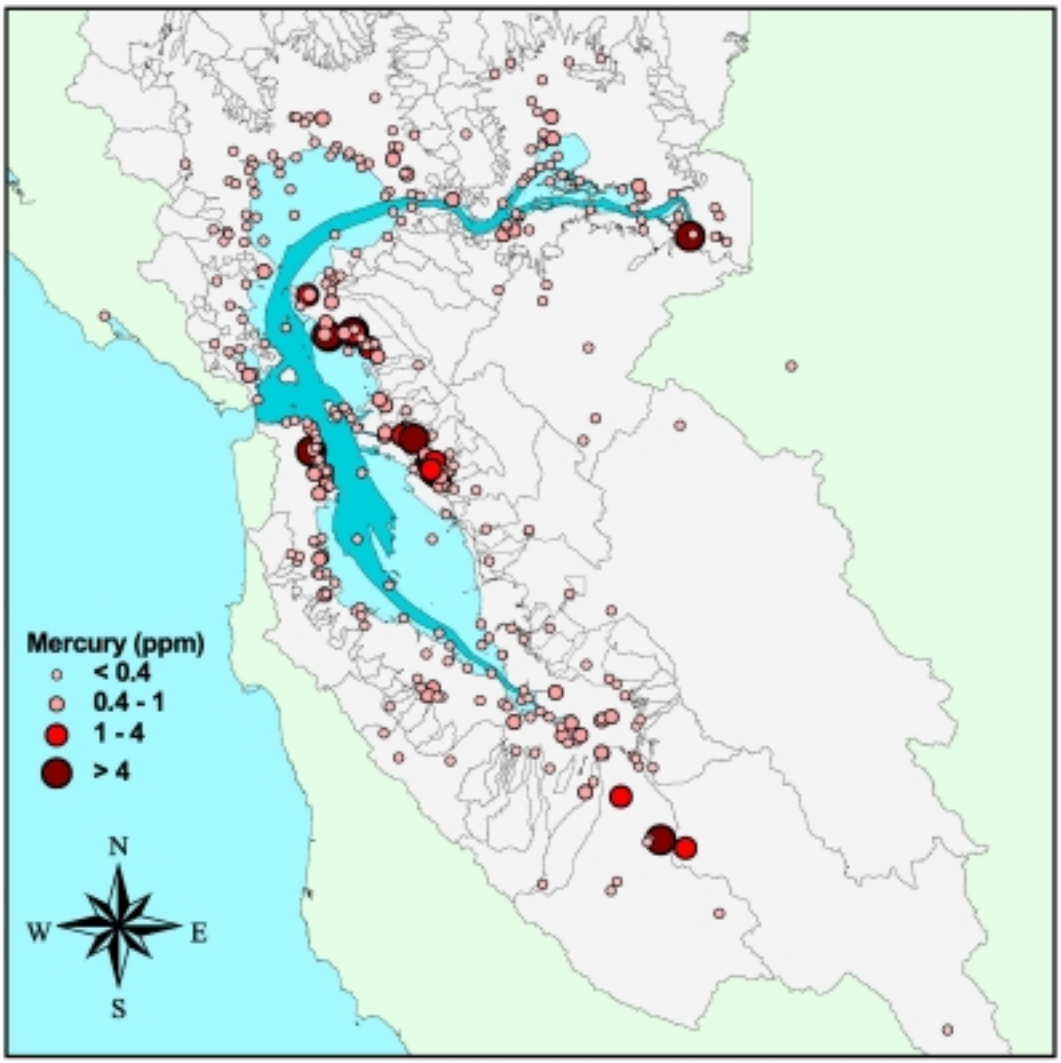

Figure 6.5. Average mercury concentrations in Bay Area sediment Data were compiled from Flegal et al. (1994), Hunt et al. (1998), Daum et al. (2000), Gunther et al. (2001), KLI (2001), and Heim (2002).

Concentrations measured in Bay Area urban bed sediments appear to be similar to those measured in creek sediments downstream from some mine sites. For example, mercury sediment concentrations were measured in Cache Creek, Sacramento Basin (0.45 µg g^{-1}, Domagalski, 2001) and Steamboat Creek, Truckee River (<0.01 to 7.13 µg g^{-1}, Blum et al., 2001). However, in extreme cases abandoned mines can exhibit much higher bed sediment concentration such as in southwestern Alaska (typically 1000 µg g^{-1} but up to 5500 µg g^{-1} in Red Devil mine, Gray et al., 2000). These observations beg the question:

> Is bed sediment a good indicator of contamination given that watersheds with known sources of contamination do not always exhibit high bed sediment concentrations relative to other relative unimpacted watersheds?

To answer this question conceptually, the commonly understood watershed sediment processes must be considered. Sediment particles eroded from a source or temporary storage area within a watershed are mobilized during a rainstorm. Mercury adsorbed to such particles travels down slope, and may enter a stream, and travel out of the system. At any point on the way, the particle may be deposited if the velocity of the water that carries it decreases to a point where it is no longer able to supply enough energy for transport. Subsequent rainstorms may pick the particles up again and move them further towards the outlet of the watershed. Thus particles travel in a start stop motion and usually spend more time stopped than in motion (Novotnoy and Chesters, 1989).

Typically sediment grainsize decreases in a downstream direction (e.g., Leopold et al., 1964) and given that mercury concentration is higher on smaller particles, the point of measurement may influence the characterization of that watershed as either contaminated or uncontaminated relative to other watersheds unless grain size effects are taken into account. The process of fining downstream leads to “enrichment” of particle concentrations in bed sediments relative to the source sediments (coined an enrichment ratio). In the case of phosphorous, a substance not dissimilar to mercury in terms of its strong association with particles, the enrichment ratio can be up to 9 times (Sharpley and Menzel, 1987). A similar process of enrichment occurs between soil and street dust in urban environments due to selective winnowing and deposition by wind and water that may cause enrichment factors for mercury of around 3 (Fergusson and Kim, 1991).

Some watersheds may store a lot of sediment within the stream channels in bars and low floodplains, whereas others will store little sediment. In this way, some watersheds with large contaminated source areas may not exhibit high concentrations in bed sediments if most of the load is transported out of the system during floods. Furthermore, deposition may vary between years or between floods for a particular system. This mechanism was suggested in the Sacramento Basin studies as a reason why Cache Creek (a known mine-contaminated watershed) exhibits similar bed sediment concentrations to the urban site (Arcade Creek) (Domagalski, 1998). Watersheds may go through periods of storage in bars and floodplain formation during droughts and periods of down cutting and bank erosion during periods of successive flood (Leopold 1994). This process has been noted as an important factor in the periodicity of mercury transport in Steamboat Creek, Nevada. Higher concentrations of mercury in 1999 compared to 1993 were attributed to adjustment of the stream to a change in climate and associated erosion of the bed and banks where legacy mercury are stored (Blum et al., 2001).

Another reason why bed sediment mercury may bear little relation to suspended sediment mercury may relate to heterogeneous activation of source areas. For example, water column mercury particle concentrations in Harley Gulch in Cache Creek vary between rainstorms by 25 times depending on the size and distribution of the rain event

relative to source areas (Joe Domagalski, unpublished data, pers. comm. April, 2002). The ratio of mercury to total suspended solids (ppm) was found to vary at locations on the Sacramento River depending on the origin of water from tributaries (Foe and Croyle, 1998). For example, mercury varied between 0.17 and 0.35 ppm at Greene's Landing and 0.12 and 0.4 ppm at Prospect Slough. This phenomenon has also been noted in predominantly urban areas in greater Washington (Mason and Sullivan, 1998). They found that on a per gram basis, concentration of mercury in the water column did not change in a predictable way with flow, sometimes being lower under high flow conditions and vice versa. However they did not suggest a reason.

The timing of deposition and post-deposition leaching may also cause the difference between mercury concentrations in bed sediment and the water column. In terms of loads measurement, it is well established that the most accurate estimates of loads of any material are derived from the combination of flow rate and an accurate measurement or estimate of concentration during the peak of the hydrograph when the majority of discharge occurs (e.g., Walling and Webb, 1985). However, sediment deposition in stream channels occurs on the falling limb of the hydrograph as flow competence decreases and mercury concentration on particles that are deposited on the falling limb of the hydrograph may or may not be representative of either a flow-weighted mean concentration or an event peak concentration. Furthermore, mercury may desorb or degas from bed sediments after deposition during dry periods that follow thus reducing sediment concentrations over time.

In order to test these issues further, a review of bed-sediment concentrations in comparison to concentrations found on particles in the water column was conducted using published literature (Table 6.1). It was surprisingly difficult to find studies that had concurrently measured bed sediment mercury, water column mercury and suspended sediment concentration as single locations. The two studies demonstrate that there is no reliable relationship between total mercury in the water column suspended sediments ($\mu g\ g^{-1}$) and total mercury in bed sediments ($\mu g\ g^{-1}$), however, the two studies that were found did not sieve for specific size fractions, therefore comparisons may not be reliable. Vasiliev et al. (1996) found there was an inverse relationship between the size of suspended particles and mercury concentration on those particles. Unless all particles in the water column deposit at a similar rate independent of size and organic carbon content, it would seem unlikely that concentrations of mercury would be consistent between bed and suspended sediments.

This review and discussion, although not exhaustive, suggests that bed sediment mercury concentrations do not show a reliable relationship to concentrations of mercury of suspended particles. Given the variety of chemical and geomorphic processes that may occur during the source activation, transport, deposition, and period of time since deposition it is suggested that the use of bed sediment concentrations for watershed characterization will have a low sensitivity and differences may only be significant at the order of magnitude level. As such, it seems unlikely that comparisons of bed sediment mercury concentrations over time will yield trends except in the unusual situation when a

Table 6.1. A comparison between bed sediment mercury concentrations and suspended sediment mercury concentrations.

Author	Sample	Bed sediment Hg_T (µg/g)	Suspended sediment Hg_T (µg/g)	Ratio (Suspended/ Bed)
John Gray, Pers. Comm., USGS Denver	98RD9	0.77	2.65	3.4
	98RD10	2400	373	0.2
	98RD11	280	126	0.5
	98RD12	1100	182	0.2
	98RD13	170	294	1.7
Vasiliev et al., 1996	Yariy Amry, mouth	157	153	1.0
	Chibitka, mouth	90	142	1.6
	Chuya, mouth	0.5	15.7	31.4
	Katun Inya	0.21	1.1	5.2
	Katun Anos	0.14	<1.3	<9.3

management action completely abates the supply of mercury to a previously polluted stream. The use of bed sediment data for loads calculations is not recommended. There are a whole variety of geomorphic processes and chemical processes that the method of data collection is not sensitive to. As such, there is no way of determining the bias and error associated with performing loads calculations.

VARIATION OBSERVED IN OTHER SYSTEMS

Mercury loads vary between watersheds in response to the magnitudes of sources, land use and land management, and climatic factors. For example, loads in the Sacramento River Basin vary intra-annually based on monthly sampling by up to 292 times (Table 6.2). Daily loads, in systems where continuous monitoring has been carried out, can vary by over 1000 times (Balogh et al., 1997). Exports from different land uses have been reported and typically exports are lower from less impacted watersheds and more pristine uplands. For example, Waldron et al. (2000) estimated exports from upland reference locations on the Sudbury River, eastern Massachusetts of 3.2 mg km^{-2} d^{-1} (1.2 g km^{-2} y^{-1}) contrasting 5-fold with 16 mg km^{-2} d^{-1} (5.8 g km^{-2} y^{-1}) at the river location downstream of the Nyanza chemical waste dump superfund site. Exports from large watersheds (>20,000 km^2) in the Upper Mississippi with varying influence of agriculture range from an average of 0.47 g km^{-2} y^{-1} in the Croix River (37% Ag, 0.9% Urb) to 0.49 g km^{-2} y^{-1} in the head water Mississippi River (44% Ag, 2.6% Urb) to 1.2 g km^{-2} y^{-1} (92% Ag, 1.8% Urb) and the variation was attributed to differences in artificial drainages patterns, soils, land use and vegetation cover (Balogh et al., 1998).

Table 6.2. Monthly total mercury loads variation in selected watersheds of the Sacramento Valley (extracted from Roth et al., 2001).

Location	Land use	Minimum ($g\ d^{-1}$)	Maximum ($g\ d^{-1}$)	Monthly variation (Maximum/minimum)
Below Keswick, Sacramento River Basin	Dam	6.3	810	129
Above Bend Bridge, Sacramento River Basin	1% urban, 27% Agriculture	30	4216	141
At Colusa, Sacramento River Basin	1% urban, 31% Agriculture	34	9925	292
At Freeport, Sacramento River Basin	2% urban, 35% Agriculture	50	6700	134

INDIRECT ESTIMATION OF LOADS

Loading of mercury from watersheds in the Bay Area has been estimated using several linear models (the SIMPLE model: KLI, 2002, and the "SIMPLEST" model: Gunther et al., 2001; Abu-Saba and Tang, 2000; Abu-Saba, 2001). The SIMPLE model assumes that runoff and contaminant concentration are proportional to land use, negating accepted hydrological principles that runoff will not only vary with rainfall, but will also vary with slope, soils, and vegetation cover, and antecedent soil water budget conditions (Dunne and Leopold, 1978). True runoff coefficients will vary between years from near zero to near 100% depending on watershed characteristics, and this variability will be greater for open space and agricultural areas and less for impervious urbanized areas. Furthermore concentrations will vary between events and between years within each land use depending on build up of source material and the dilution effects of flow volume. Therefore the best use of the SIMPLE model (and what it was designed for) is as a planning tool for educational purposes and determining likely changes over time given land use changes and BMP implementation, and as a framework for assessment of data quality. Without comparisons to other more accurately derived loads, there is no way of knowing how well the SIMPLE model estimates the magnitude of loads or relative loads between different watershed areas.

The "SIMPLEST" model (e.g., Abu-Saba and Tang, 2000) uses an estimate of sediment load (kg) from a given area and combines that with a contaminant concentration of a pollutant of concern ($\mu g\ kg^{-1}$). The "SIMPLEST" model has similar problems in that it assumes that particulate mercury concentrations do not vary during storms or between storms, or between years depending on recent antecedent history. Secondly, the model data available in the Bay Area are for bed sediments. Workers have made the assumption that bed sediment concentration taken during low flow periods will be the same as a flow-weighted mean concentration in the water column. However, there has been no effort in the Bay Area to test this assumption, and data from other watersheds do not support this assumption (see discussion above). One redeeming factor of the model is the possibility of improving contaminant load estimates through improving estimates of sediment loads.

In the absence of better tools, loads of mercury to San Francisco Bay from local watersheds has been estimated as 58 to 278 kg for the watershed background load during "average" years and an additional 49 kg from the mine-impacted Guadalupe River watershed (Abu-Saba and Tang, 2000). More recently, KLI (2002) estimated mercury loads from local watersheds using the SIMPLE model as 10 to 452 lbs (4.5 to 205 kg) with an average during an "average" year of 93 kg. There is now quantitative evidence that the SIMPLE model estimates developed by Davis et al. (2000) underestimated suspended sediment loads from local small tributaries by 2-3 times, therefore the loads estimates made by KLI (2002) are also likely to be biased low by 2-3 times. Given the discussion above on the weak relationship between bed and suspended sediment mercury concentrations, there is no way of knowing the accuracy of the KLI (2002) loads estimates. Both of these load estimates (Abu-Saba and Tang, 2000; KLI, 2002) represent first order hypotheses of actual loads and should be used as a starting point prior to application of more accurate small tributaries load estimation techniques.

Summary

- Mercury is transported from naturally occurring deposits and contaminated locations in dissolved, colloidal, and particulate forms.
- Particulate mercury is conventionally reported as the mass that does not pass through a 0.4 or 0.45µm filter paper. The colloidal fraction can be partitioned out using ultra-filtration leaving the truly dissolved fraction that passes through 0.0015-0.005 µm pore size.
- Field and laboratory techniques need to follow "clean techniques". These issues will pose a challenge or potential barrier to the use of automated field sampling for mercury but this will not matter if loads are computed using grab samples taken with clean techniques and relationships with suspended sediment or turbidity for extrapolation of data.
- There are 16 historic mine locations in the Bay Area distributed across all nine counties. Mercury loads should be quantified in watersheds where there are historic mines and mercury bearing rocks.
- There are many anthropogenic uses of mercury that are concentrated in urban areas. This suggests that urban areas with high population will also be likely to have high mercury loads.
- Based on studies in other parts of the US, particulate mercury is between 69 and 99% of total mercury in the water column of contaminated streams. In agricultural watersheds, particulate mercury may only form 37-50% of the total mercury load, and organic carbon seems to play a role in transport. Given that colloidal transport make up part of the "dissolved phase" and colloidal material is detectable using optical sensors, surrogate techniques are likely to be applicable to loading studies for mercury under most circumstances.
- Mercury is often transported from contaminated sources in the watersheds following catastrophic events such as large rainstorms, and landslides or tailings dam failures. These "rare events" may cause the majority of loads.

- Total mercury concentration can be expected to vary by 2-3 orders of magnitude during storm events but variation tend to be less in watersheds that have lower mercury loadings.
- Based on literature, total mercury concentrations in undisturbed rural watersheds are likely to be 3-10 ng l^{-1}. Mercury concentration is likely to be 30 times greater in urban and mixed urban and agricultural watersheds and more than 500 times greater at historic mine sites.
- It appears that upwards of 63% of atmospherically derived mercury is retained in watersheds. This may be diminished in Bay Area watersheds if bed, bank and landslides play are role in mercury supply to the stream

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Part 7: Synthesis and recommendations for loads monitoring

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Problem statement

Loads of suspended sediments and associated trace substances such as PCBs, OC pesticides, and mercury are difficult to measure given a myriad of factors that influence concentrations between different watersheds and rapid changes in concentrations during floods. Yet accurate estimates of loads, or at least the relative magnitude of loads from different pathways (point sources, atmospheric deposition, the Central Valley, and dredging and resuspension of legacy contaminants already in the Bay) are needed for effective environmental management. If the relative magnitude estimate for a particular contaminant is wrong, emphasis may be placed on remediation actions that do not result in the greatest possible improvement in water quality over subsequent years or decades. There are no recent suitable data on priority contaminants to estimate loads for a single watershed, let alone from all the small tributaries entering the Bay. Modeling efforts in the Bay Area to date have used simple planning level models that are not designed for calibration (e.g. Davis et al., 2000). In any case, there are presently no water column concentration data available in the watersheds to test or verify model performance.

KEY FINDINGS FROM THIS LITERATURE AND LOCAL DATA REVIEW

Finding 1. Sediment loads from local tributaries may be up to 40% of the total inputs to the estuary when averaged over the longer term.

Sediment loads from the Central Valley are estimated to be an average of approximately 1,000,000 metric tonnes (t) for the period Water Year 1971-2000 (McKee et al., 2002). Our present best estimates for small tributaries range from 561,000 – 1,000,000 t or an average of ~780,000 t. Thus it appears that small tributaries might be supplying about 40% of the total annual average sediment load to the Bay. At a first glance, this might be somewhat surprising given that local small tributaries only comprise approximately 5% of the watershed areas of the Bay and contribute approximately 4% of the annual average total surface runoff entering the Bay from its entire drainage basin. Local tributaries have a small area that probably helps to support a greater delivery ratio, are prone to intense and variable rainfall, have an active tectonic geology, and are prone to landslides on hillslopes. These factors, in addition to soil and watershed perturbations associated with land management activities practiced for approximately 150 years of post-European contact help to contribute to an annual average export of 100 t km^{-2}. This is approximately seven times greater than Central Valley exports (14 t km^{-2}). Dense urbanization in the Bay Area along with a history of mercury mining helps to increase contaminant sources. Urban drains provide efficient pathways for contaminant transport leading to higher concentrations and loads of sediments and related contaminants in urban waterways. Water from small tributaries that enters at literally hundreds of points on the Bay margin has higher concentrations of some contaminants and is less voluminous than flow from the Central Valley. Therefore, it is less likely to flush to the ocean during a rain event. In contrast, water from the Central Valley enters the upstream end of the Bay, and during very large events, a portion of its total volume may flush directly off shore forming a plume of sediment and contaminant-laden water.

Finding 2. Concentrations of sediment and related contaminants, exports, and loadings vary greatly from one small tributary to another.

Flow-weighted mean concentrations of suspended sediments vary from ~100 – 4,500 mg L^{-1} between watersheds in the Bay Area where the USGS has made measurements over the past 40 years. Average annual runoff in the local small tributaries varies greatly [e.g., Alameda Creek at Niles (69 mm or ~2 L s^{-1} km^{-2}) and Sonoma Creek and Agua Caliente (412 mm or ~13 L s^{-1} km^{-2})]. Taking discharge and watershed area into account, unit sediment exports vary from approximately 30 - 1,650 t km^{-2} y^{-1}. These observations exemplify the wide variation in supply and transport processes operating in local small tributaries. Although little data exist on water column Hg, PCB, and OC pesticide concentrations in local tributaries, literature from other parts of the world suggest that contaminant concentrations, exports, and loadings will also vary greatly between watersheds partly associated with variation in sediment processes but also in relation to the mass and distribution of sources. Based on our literature search, we would anticipate the following concentrations of Hg in Bay Area watersheds: open space (3-6 ng L^{-1}), mostly agriculture (20-30 ng L^{-1}), mostly urban (40-100 ng L^{-1}), mining (100-2,000,000 ng L^{-1}). It remains difficult to build a similar conceptual model for PCBs and OC pesticides because there are vastly less literature data available.

Finding 3. Concentrations and loads of sediment and related contaminants show large temporal variations between storm events and between years.

For the purposes of standardization we defined the wet season as November to April inclusive. In small tributaries in the Bay Area, during this six month winter period, greater than 89% of the rainfall, 91% of the water discharge, and 99% of the sediment transport occurs. On average, about 7-9 major storm events occur each climatic year that account for the majority of the rainfall, runoff and sediment transport. The ratio of rainfall to runoff typically increases as a single winter storm season progresses due to the increase in soil moisture (this process is less important in urban areas with a lot of impervious surfaces). In contrast, concentrations of sediments tend to be greater in the runoff from the first storms of the winter season (called the first flush), and this phenomenon can also occur after long drought periods. In terms of inter-annual variation, runoff in local small tributaries varies about 2-3 orders of magnitude and sediment annual sediment loads can vary by 2-5 orders of magnitude. Although there are little data available for the Bay Area, our literature review shows that similar kinds of process operate for PCBs, OC pesticides and Hg in watersheds in other parts of the world. Therefore we suggest that similar processes will occur in local tributaries of the Bay although we would expect the inter-annual variation of contaminant loads would be less than for sediments, in most cases, given a portion of the contaminant load is transported in dissolved form and the supply to stream may be more consistent.

Finding 4. Concentrations of sediment and related contaminants show large temporal variations during storms.

Suspended sediment concentrations in all watersheds of the Bay Area where USGS data exist increase during storms and typically peak during the rising stage or about the same time as the peak storm discharge. Concentrations during a single storm peak can vary by 2-3 orders of magnitude. The period of time between peak rainfall and peak stage varies mainly in response to watershed size; for small tributaries in the Bay Area, a watershed of 10 km^2 would have a response time of about 2 hours, whereas a watershed of 500 km^2 would likely take about 9 hours to peak. The discharge associated with these relatively fast, high-energy watersheds quickly remobilizes fine sediments stored in channels in bars and stream bank deposits in addition to new sediment supplied from watershed surfaces. As the channel water velocity increases on the rising stage of a flood event, greater concentrations and sizes of particle can be entrained in the water column. The reverse process usually operates during the falling stage, there is less sediment available for transport because of washout during the rising stage and larger particles that were entrained at higher energies tend to deposit. Our review of literature on PCBs, OC pesticides and Hg from other parts of the world suggests a similar kind of runoff hysteresis pattern probably occurs for these sediment-associated contaminants.

Finding 5. Sediment is the main vector for the transport of Hg, PCBs, and OC pesticides during storms and over the longer term.

The partitioning of PCBs, OC pesticides and Hg in natural fresh waters is influenced by a number of factors including the time period of transport that influences equilibrium, particulate and dissolved organic carbon concentrations, suspended sediment concentrations and particle size. A review of PCB data from 11 river systems throughout the world suggests that the particulate fraction of total PCBs (sum of congeners) can vary from 22 to 100%, but in most cased it is greater than 50% Given the high concentrations of suspended sediments found in Bay Area streams during floods (>>100 mg L^{-1}) we suggest that in Bay Area stream the transport of PCBs will be dominated by the particulate fraction. The literature also suggests that OC pesticides are dominantly transported in the particulate phase and this will again likely be accentuated by high concentrations of suspended sediments. Local data from Guadalupe during a single small storm event suggests that greater than 90% of the mercury in that system is transported in particulate form, a result that is consistent with much of the world literature for urban or mine-impacted watersheds.

General recommendations

1) **Characterization of probable sources.** PCBs are unique compared to PAHs, OC pesticides, mercury, and other trace metals in that they are more likely to be associated with legacy point sources such as electrical storage yards or industrial sites of high electricity use. It is recommended that a review be done of all existing information on the historic distribution of contaminated sites in the Bay

Area. This information should be placed on GIS maps and compared to the sediment data already collected (Gunther et al., 2001, KLI, 2001, 2002).

2) **Determine Loadings.** Sampling should be carried out in at least two watersheds (ideally six watersheds: urban, mixed, and rural in high and low runoff areas of the Bay) to determine the loads of key contaminants. This recommendation would fulfill some key objectives:

    a) Accept or reject the hypothesis that small tributaries form a significant proportion of the input of contaminants of concern in the Bay relative to other pathways;
    b) Determine if the loads of PCBs from urban runoff will be sufficient to impact the recovery time of the Bay (see Davis, 2002);
    c) Provide new information that can be used to determine the best management solutions for mercury in the Bay;
    d) Test methodologies for application in other tributaries;
    e) Verify or reject the use of simple planning level models for determination of loads and guiding management;

Specific recommendations

a) Where to measure

There are a number of criteria that will help determine where future small tributary loading studies might be best implemented. The criteria include known sources of contamination such as historic mercury mines, power generation or distribution facilities where PCBs were in common use, or urban and agricultural areas where OC pesticides were applied for pest control. In addition, indicators such as known contamination in water or sediment on the Bay margin or in sediments in the watersheds are currently being used to characterize and prioritize watersheds for study and management. Other characteristics might include watershed size, rainfall, discharge, erosion potential, sediment load, number of cars, road density, and major highway usage. At present, these kinds of information have not been compiled into a single GIS database (although SFEI is working on improving regional mapping piecemeal and without funding: see Wittner and McKee, 2002). In some cases the data are not available or not in a suitable format to assist management.

In spite of an incomplete knowledge of sources, there are some watersheds that are known to contain problem areas for contaminants of concern. PCBs are known to be in high concentrations in bed sediment in certain locations within Coyote Creek and Guadalupe River watersheds and at the Ettie Street pump station. The Bay margins adjacent to these watersheds also show high concentrations. DDT, dieldrin and chlordane was used in both rural and urban applications, but more typically the literature suggests we would find higher loads associated with urban areas. In that regard, areas that were urbanizing during the time of peak usage would be good candidate watersheds to test.

These would include watersheds in Alameda, Santa Clara and, to a lesser extent, Contra Costa (Figure 7.1).

Mercury contamination in small tributaries in the Bay Area is derived from urban uses (in commercial products and the burning of fossil fuels), natural loads from mercury bearing rocks and soils, and loads from disturbed areas associated with inactive mercury mine sites. The review of studies of mercury in watersheds in other parts of the world suggests that we might expect local tributaries of the Bay Area that are not directly impacted by mercury mining to have concentrations ranging from 4-100 ng l^{-1} depending on the degree of urbanization (0-100%). Based on the Estuary Interface Pilot Study (Leatherbarrow et al., 2002) and other studies in the Central Valley, it is hypothesized that the Guadalupe River watershed near its tidal interface with the Bay might display concentrations during peak flow in excess of 2000 ng l^{-1} associated with mercury mines and urbanization. Given historical mining operations in Napa and Petaluma River watersheds, it would be informative to consider monitoring to determine their impact on the mercury budget of San Pablo Bay.

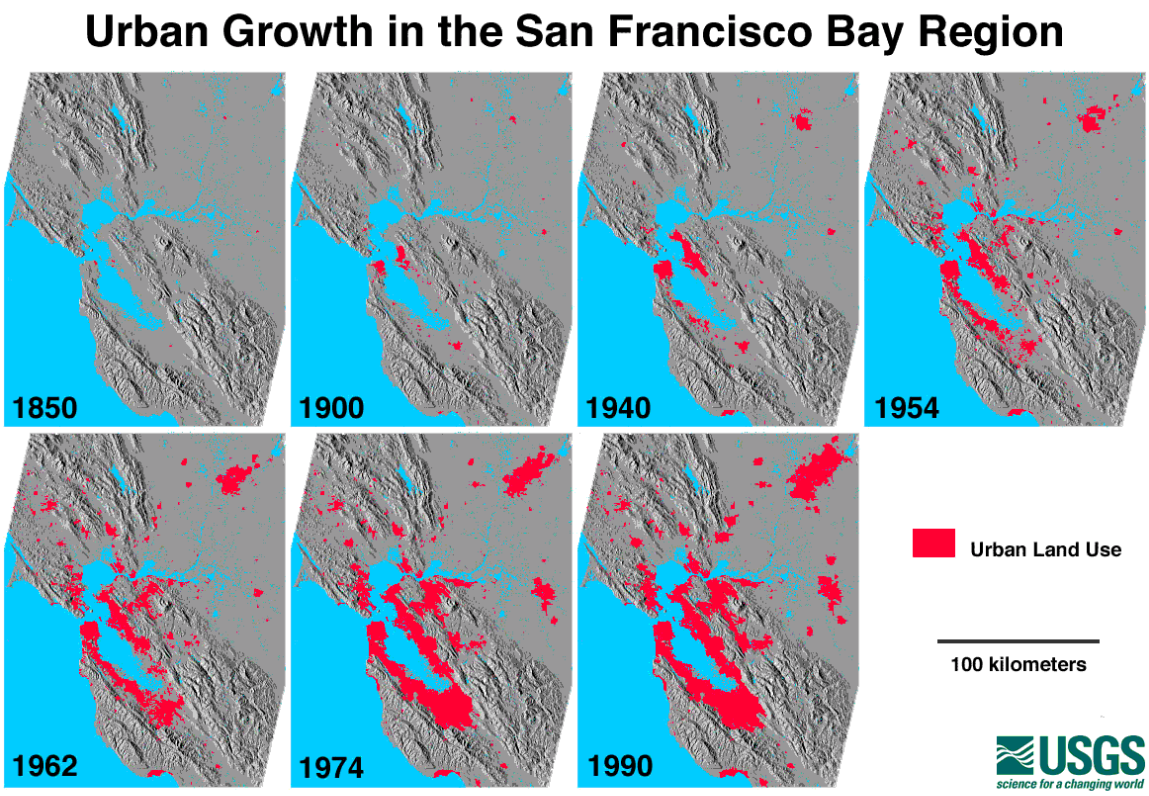

Figure 7.1. Urban growth in the Bay Area (USGS 2002).

Given the distribution of mercury sources, the likely distributions of PCBs and OC pesticides, and taking into account climatic variation and potential impact on source activation, it is recommended that watershed studies for loads concentrate on:

1. Guadalupe River (for Hg mining impacts and urban loads characterization of Hg, PCBs and OCs)
2. Napa River (for Hg mining impacts and rural / background loads characterization of Hg, PCBs, and OCs)

Should resources be available, further studies should be initiated in:

3. Petaluma (for Hg mining impacts and rural / background loads characterization of Hg, PCBs and OCs)
4. Fairfield and Carquinez (for Hg mining loads characterization, agricultural pesticides under low rainfall / irrigated conditions, and rural / background loads characterization of Hg, PCBs, and OCs)
5. San Mateo (for Hg mining impacts, urban loads of Hg, PCBs, and OCs)
6. Alameda (for urban and historic pesticide loads characterization under low rainfall conditions)

b) When to measure

Given that about 90% of the water and greater than 99% of the sediment is discharged from local tributaries during the wet season, water sampling for determination of concentrations for loads estimation should be focused between November and April when most of the loads are predicted to occur. On average, Bay Area watersheds experience high flow about 7-9 times per year in response to rain storms passing over the region from the Pacific Ocean. There is less than 20% chance of the first flood occurring before November 1st of any given year and a 75% change of the first flood occurring before December 31st. Studies should be designed to be ready in the event of unusually early rains occurring in October. It will be important to capture the first flush process when studying both urban and rural watersheds because higher concentrations during early wet season events might contribute to higher loads than might otherwise be estimated from the magnitude of the discharge alone. Studies should be designed to be reactive given that watersheds in the Bay Area are “flashy” and can exhibit peak discharge within a few hours after intense rainfall.

In order to characterize rapid changes in concentrations that are likely to occur over the rising and falling stages of a flood hydrograph, sampling will need to occur frequently during the rain event. Given the high probability of strong relationships between sediment related contaminants such as Hg, PCBs, and OCs, surrogate data such as turbidity and suspended sediment concentrations may be used to extrapolate a temporally limited contaminant dataset and improve load estimates. It is recommended that 5-10 samples be collected at a sampling location during an event and that turbidity be collected continuously to improve the interpretation of the contaminant data. Collecting

10's to 100's of water samples for laboratory analysis would be logistically more difficult and more expensive than the use of surrogate measures.

c) What to measure

PCBs, OC pesticides, and mercury appear to be dominantly transported in particulate forms in urban point source contaminated settings. In agricultural settings, dissolved organic carbon can play a more important role. PCB, OC pesticides and mercury partitioning vary in response to organic carbon and suspended sediment concentrations. At suspended sediment concentrations above 100 mg l^{-1} partitioning tends toward particulate forms for these contaminants. Flow-weighted mean suspended sediment concentrations are in excess of 374 mg l^{-1} in 14 streams of the Bay Area small tributaries where there are USGS data collected over 2 or more years (see the section on sediment processes). Therefore, it seems likely that particles will be the dominant vector for transport of PCBs, OC pesticides, and mercury.

Given these factors, it is recommended that the following parameters be measured in river water samples for urban runoff studies that aim to determine water column transport processes and loads:

1. Total PCBs, OCs, and Hg
2. Suspended sediment concentration (SSC)
3. Turbidity
4. Organic carbon (DOC, POC)

d) How to measure

The small watersheds that are directly tributary to the Bay have fast response times between peak rainfall and peak runoff. For example, the Napa River, with an area of 737 km^2 rises to peak discharge within 10.5 hours of peak rainfall. The Guadalupe, with an area of 556 km^2 is likely to reach a peak within 9.5 hours and its lower watershed urbanized area will provide discharge to the mainstem Guadalupe within several hours. Although these are simplistic estimates that do not take into account the variation associated with both the overall size of the rain event, antecedent soil moisture conditions, or rainfall intensity, they do illustrate the difficulty associated with field sampling.

Methods for field sampling generally fall into two categories: Automated pumping sampler technologies and manual sampling. Automated pumping samplers have been criticized for the manner in which samples are lumped together during sampling and prior to analysis and also for lack of reliability associated with malfunction or physical damage from river-born debris or vandalism. There has also been discussion on the problems associated with the rate of pumping relative to the velocity in the water column. Disparities between rate and velocity can lead to unrepresentative samples because sediment particles entrained in the water column may not be captured properly. There have been questions raised on what depth to draw the point samples from and on

potential contamination problems associated with the period between storms when a film of sediment or biological fouling can form. The positive side of using such devices is the ability to catch small or rapid events that manual sampling is likely to miss and the ability to catch events overnight when field personnel may be unavailable.

Manual sampling on the other hand enables the use of isokinetic samplers, depth and cross-section integrated sampling, and collection of numerous samples without lumping. This enables an analysis of process and the most accurate and precise estimate of loads. Samples for analysis of trace contaminants can be processed on-site using clean sampling techniques and preserved for transportation to the laboratory for analysis. The disadvantage with manual sampling is the difficulty associated with catching small or flashy events, events that occur overnight, and discomfort to workers who may have to collect samples in the rain.

These difficulties can be overcome by careful collection and analysis of surrogate parameters at a smaller interval than the interval for sampling for trace chemistries. The valid use of time continuous surrogates such as turbidity or suspended sediment concentration to estimate contaminant concentrations and loads relies on the hypothesis that there is a strong correlation between the surrogate and the contaminant of concern. Our review of the literature supports this hypothesis, although we recognize that the relation may change depending on season and source activation. We recommend that:

1. Sampling for trace contaminants coupled with time-continuous measurement of turbidity and suspended sediment concentration following the USGS seasonal suspended sediment daily loads protocol.
2. Turbidity information be made available real-time on the Internet to inform the sampling teams on the best times to sample, thus maximizing the use of a limited laboratory budget.
3. Analysis of the loads of contaminants of concern be assisted by extrapolation between time limited sample points using the surrogate data and organic carbon.

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