

**An Assessment of The Loading
of Toxic Contaminants to
The San Francisco-Bay Delta:**

Executive Summary

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August 26, 1987



EXECUTIVE SUMMARY

INTRODUCTION

The Aquatic Habitat Institute is required under the terms of contracts with the Environmental Protection Agency and the State Water Resources Control Board to review available data on the sources of toxic contaminants (trace elements, chlorinated hydrocarbons, and petroleum-derived hydrocarbons) to the San Francisco Bay-Delta. This report has been prepared in response to such a requirement.

The San Francisco Bay-Delta is a large and complex estuary, draining a significant proportion of the land area of California. As a result, the calculation of contaminant loading to the estuary is a complex task. The available data on toxicant concentrations and flows to the Bay-Delta vary in quality with respect to their usefulness in calculating contaminant loadings. In many cases, assumptions are required in computing mass emissions, or data from estuaries elsewhere must be employed due to the lack of reliable local information. In such instances, the calculations and assumptions employed are clearly enumerated in the report, such that improved loading estimates may be easily computed at a future time, when more reliable local data are available.

Contaminant loads to the estuary are derived from a number of distinct sources. These are dealt with individually in the main report; the method of calculation of



loadings is described briefly below. It is notable here that decisions were required at the commencement of the project on whether to attempt to provide a historical perspective to loadings, or to focus efforts on identifying current time-averaged loadings of contaminants as accurately as possible. It was argued that the more recent data were generally more abundant and of higher quality with respect to analytical accuracy and precision, and to quality assurance and control. In addition, difficulties were faced with the previous historical estimates of contaminant loadings to the Bay-Delta, in that the data sources and assumptions used in their computation were often not stated. As a result of these concerns, it was agreed between the contracting parties that the present report should focus on more recent data (1984 to 1986 inclusive) and should attempt to define best estimates of current time-averaged loadings of contaminants to the Bay-Delta.

CONTAMINANT SOURCES TO THE BAY-DELTA

Point Sources: Data employed in this report on toxicant loadings from point sources (publicly owned treatment works [POTWs] and industrial discharges) are mainly derived from self-monitoring required by permits issued under the National Pollution Discharge Elimination System (NPDES) program. This monitoring provides a substantive database for computing contaminant loads to the estuary from the major point source



discharges; as a result, the estimates of loadings from these sources are among the most precise. In general, three-year average loadings are employed to characterize each source. It was found that eight discharges generally dominate mass emissions of toxicants from POTWs to the estuary, and that POTWs as a whole provide the majority of loads of most trace metals to the estuary. Among industrial discharges, petroleum refineries contribute significant flows and amounts of certain contaminants to the Bay-Delta, including selenium, chromium, nickel, lead, copper, and zinc. Other large industrial concerns have generally less significant impacts on overall mass emissions of toxicants to the estuary, although the U.S. Steel plant in Pittsburg discharges large amounts of chromium, and the effluent from the Chevron Chemical facility in Richmond also contains high trace element concentrations on occasion. It is also notable that much less is known of the mass emissions of organic contaminants to the Bay-Delta from point sources than of trace metal loadings. This is largely due to analytical problems and inadequate quality control of analysis.

Urban Runoff: The local database required to calculate mass emissions of toxicants from urban runoff to the Bay-Delta is of very poor quality. Runoff volumes may be reasonably accurately predicted by employing estimates of urbanized land area, precipitation, and runoff coefficients. However, the



calculation of mass loads depends on a thorough knowledge of contaminant concentrations in runoff from these areas, and local information on this aspect is inadequate. Data from studies elsewhere have thus been employed to estimate probable loads to the Bay-Delta from this source. These estimates should be improved by the acquisition of reliable data on local runoff characteristics.

Nonurban Runoff: The calculation of contaminant loadings to the Bay-Delta from nonurban runoff in this report relies upon methods developed by the National Oceanic and Atmospheric Administration for this purpose. The basic technique involves the computation of trace element loadings through assessments of soil yield from nonurban land, coupled with estimates of average metal concentrations in soils. Mass emissions of chlorinated hydrocarbon pesticides are calculated in a different fashion, however, employing data on their rate of utilization in the Bay-Delta catchment and an assumed value for their release to the estuary in runoff. Estimates in this category in the present report are relevant only to the nonurban land draining directly to the Bay-Delta; loads in runoff derived from the Central Valley are incorporated in riverine inputs.

Riverine Inputs: The mass emissions of contaminants to the Bay-Delta in riverine inputs are calculated based on water quality and flow data for the major rivers entering the



Sacramento-San Joaquin Delta. The sites of sampling operationally define the upstream limit of the Bay-Delta (at Sacramento, Stockton, and Vernalis). Problems relating to infrequent sampling and analytical detection limits constrain the accuracy of these mass loading estimates. In particular, no loading data for organic contaminants from this source can be derived.

Dredging and Dredged Material Disposal: The remobilization and release of contaminants by dredging and dumping activities in the Bay-Delta do not truly represent de novo loads of contaminants, but are more a function of the redistribution of historically-introduced toxicants. However, this process may nevertheless give rise to elevated concentrations of contaminants in certain portions of the estuary, and is therefore considered here. While the theory relevant to toxicant remobilization during dredging and dredged material disposal operations is reasonably well-established, no reliable data exist to define the quantities or rates of contaminant release in such activities locally. Generic release rate estimates are therefore employed to provide an assessment of the possible impacts of this process on the overall abundance of contaminants in the Bay-Delta.

Atmospheric Deposition: The estimates of toxicant loading to the Bay-Delta through atmospheric deposition are calculated here only on the basis of the water surface area of the estuary (1240 km²), as contaminants originally from the



atmosphere entering the estuary after their deposition on the surrounding land mass are accounted for in urban and nonurban runoff and in riverine inputs. As the local database is not adequate to permit estimation of contaminant loads from this source, information from the Great Lakes region (where extensive studies of this nature have been undertaken) is employed. There is a need for further investigations locally to refine these estimates.

Spills: Contrary to popular opinion, spills are generally found to be a relatively minor source of contaminants to estuaries, at least in the absence of single massive accidents. The available data on spills in the Bay-Delta are collected by the U.S. Coast Guard. This database is inadequate in two major respects. Firstly, little information is available on the precise contaminants spilled in an incident. Secondly, not all spills listed actually occurred; some were "potential spills" or were otherwise of an uncertain nature. The present synthesis employs the 1984-1986 data to derive generic estimates of loads of petroleum hydrocarbons to the Bay-Delta from this source.

Hazardous Waste Sites: No quantitative estimates of contaminant loadings from hazardous waste sites can be made, due to a paucity of data.



MASS LOADING ESTIMATES

The marked uncertainties in loading estimates from each of the sources of contaminants considered in this report are significant, in that they emphasize the inadequacies inherent in the local database. Until monitoring of flows and (especially) contaminant concentrations in discharges entering the Bay-Delta is improved, mass loading estimates will continue to be uncertain. This situation is unsatisfactory, as the management of Bay-Delta water quality (and its impact on beneficial uses in the estuary) depends at least to some degree on an understanding of the sources of toxicants in the estuary.

The uncertainties inherent in present loading calculations also render conclusions as to precise absolute mass emissions scientifically indefensible. As a result, loadings of toxicants are presented here as ranges, rather than single absolute values. It is considered that the true loads are most likely to lie within the ranges between the probable minimum and possible maximum values reported for each contaminant and source.

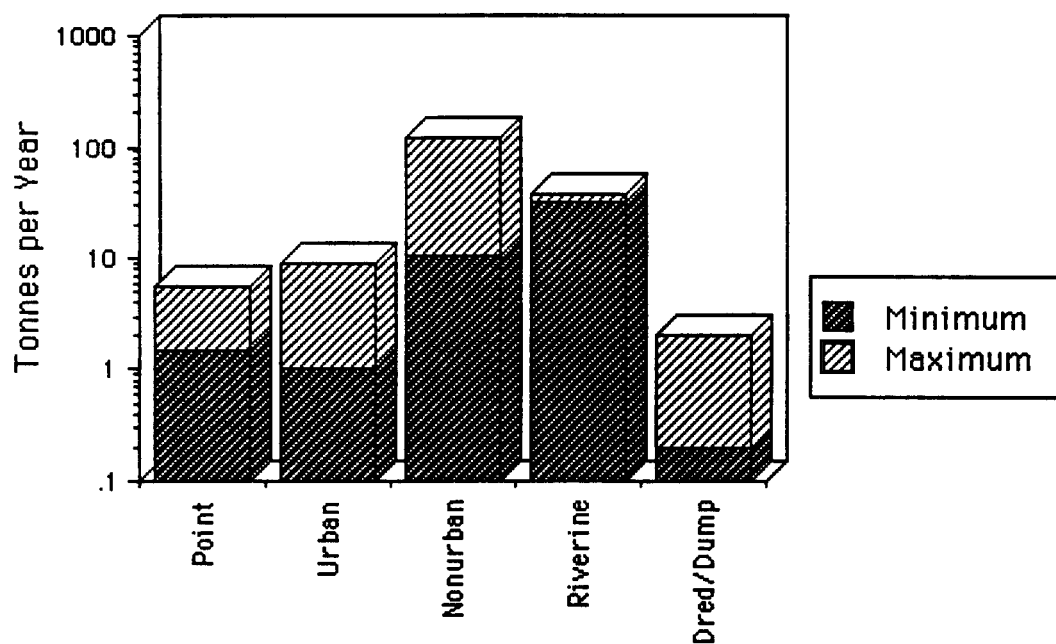
In some instances, the paucity of data is so great that even a range in mass loading cannot be derived for particular sources and contaminants. It follows that the overall loads of some toxicants are better characterized than those of others.



Estimated mass emissions of individual toxicants are presented in Figures ES1 to ES13, which are also shown in Section III of the main report. The relative ranking of sources for each contaminant is given in Table ES1. Detailed discussion of these data is presented in the main report for each toxicant; generic conclusions only are included in this summary. It is evident from Table ES1 that most trace elements are derived predominantly from riverine inputs and nonurban runoff. Point sources and urban runoff are generally more minor sources of metal loadings to the estuary, at least with the exception of lead (which is present at significant levels in urban runoff). Atmospheric sources and the release of trace elements from dredging and dredged material disposal operations are negligible in their contribution to overall trace element loadings to the Bay-Delta. The mass emissions of three elements (nickel, selenium, and silver) are computed only on the basis of three quantified sources, data for other sources being unavailable. In two of these three cases (selenium and silver), point sources provide significant proportions of overall loadings to the estuary. In the case of selenium, such loads largely arise from refineries, whereas silver is derived mainly from POTWs, particularly in the South Bay.

Atmospheric deposition is far more important as a source of organic contaminants to the Bay-Delta than as a source of trace elements. Large quantities of polychlorinated

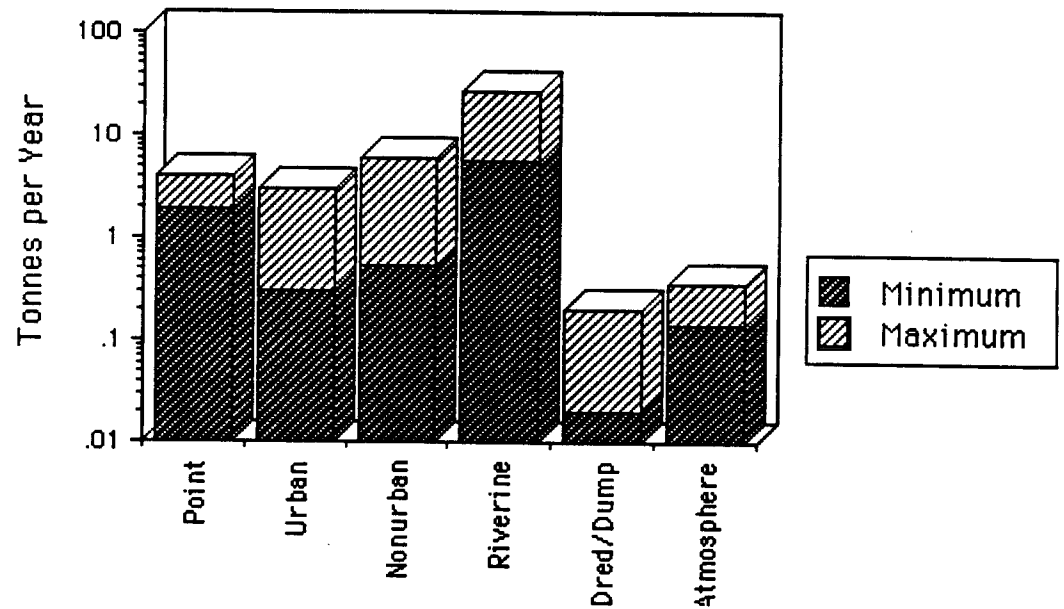




Maximum	5.7	9	119	37	2
Minimum	1.5	1	10.3	32	0.2

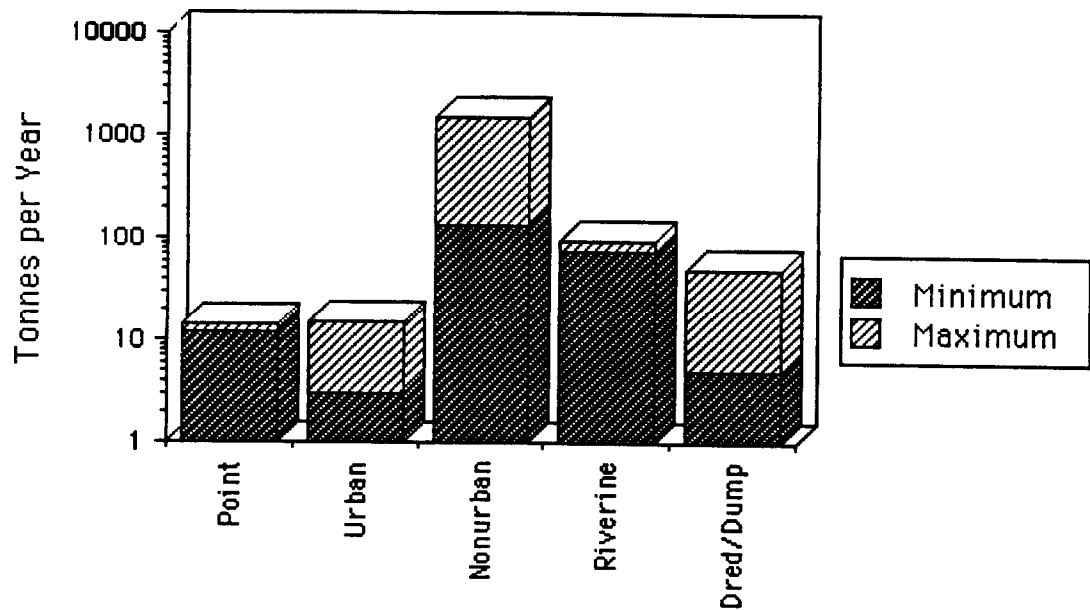
Fig. ES1. Estimated range for the mass loading of arsenic to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.





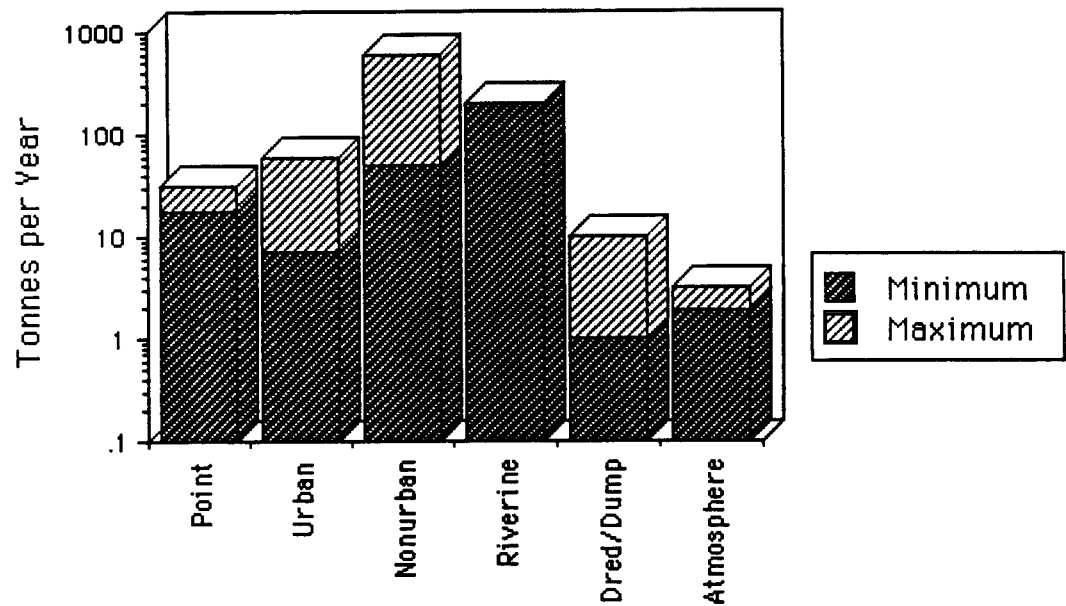
Maximum	4.0	3	6	27	0.2	0.35
Minimum	1.9	0.3	0.52	5.5	0.02	0.14

Fig. ES2. Estimated range for the mass loading of cadmium to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.



Maximum	14	15	1537	92	50
Minimum	12	3	134	77	5

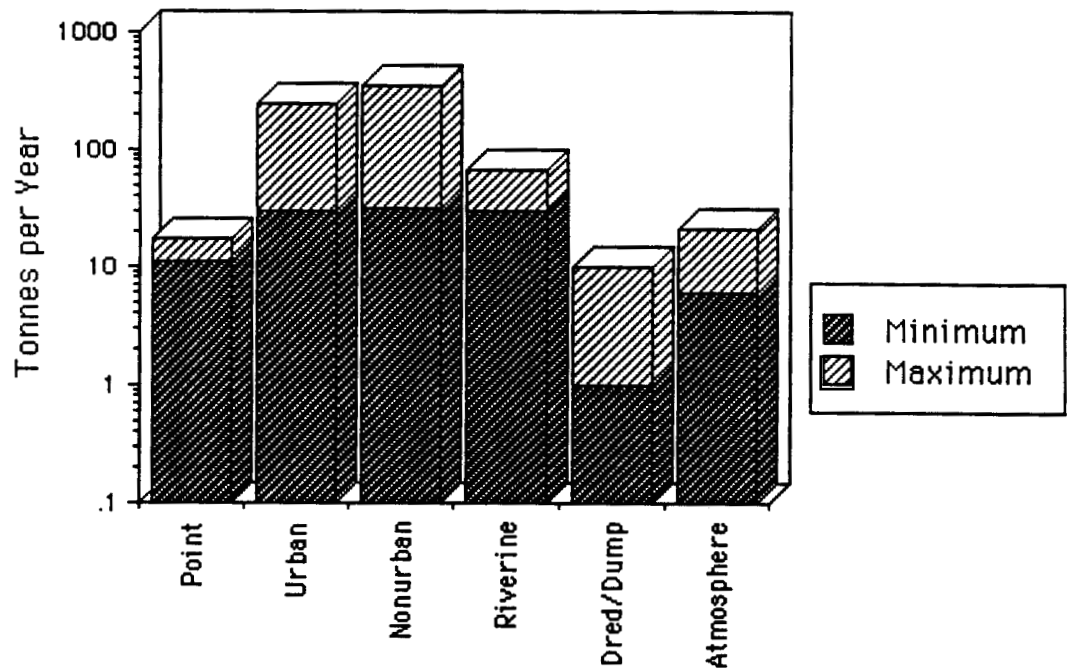
Fig. ES3. Estimated range for the mass loading of chromium to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.



Maximum	31	59	581	203	10	3.1
Minimum	18	7	51	203	1	1.9

Fig. ES4. Estimated range for the mass loading of copper to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

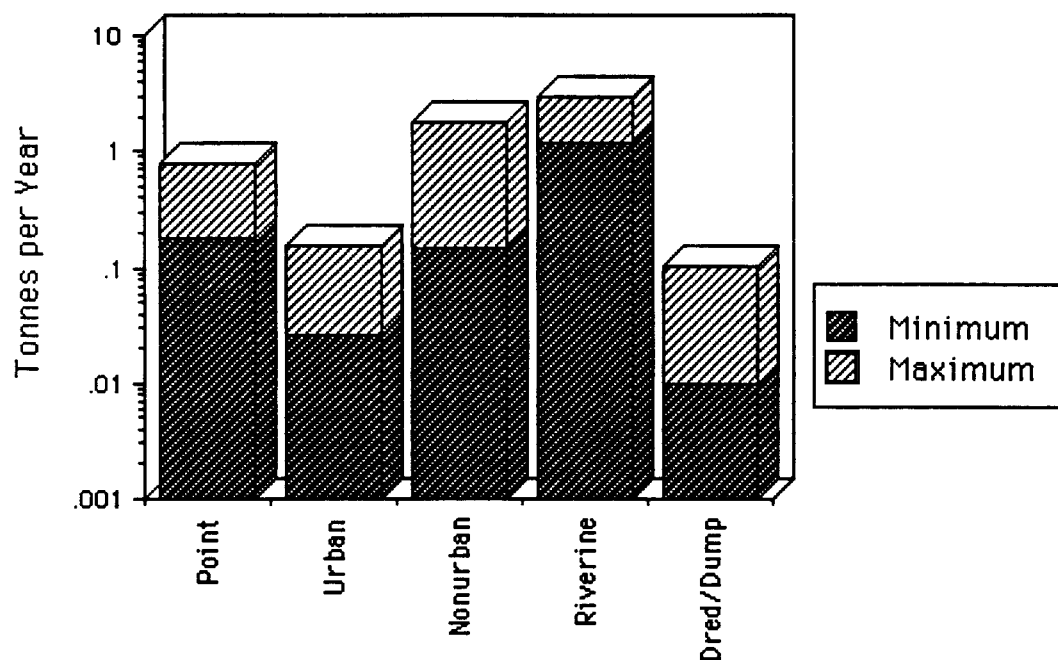




Maximum	17	250	358	66	10	21
Minimum	11	30	31	30	1	6

Fig. ES5. Estimated range for the mass loading of lead to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

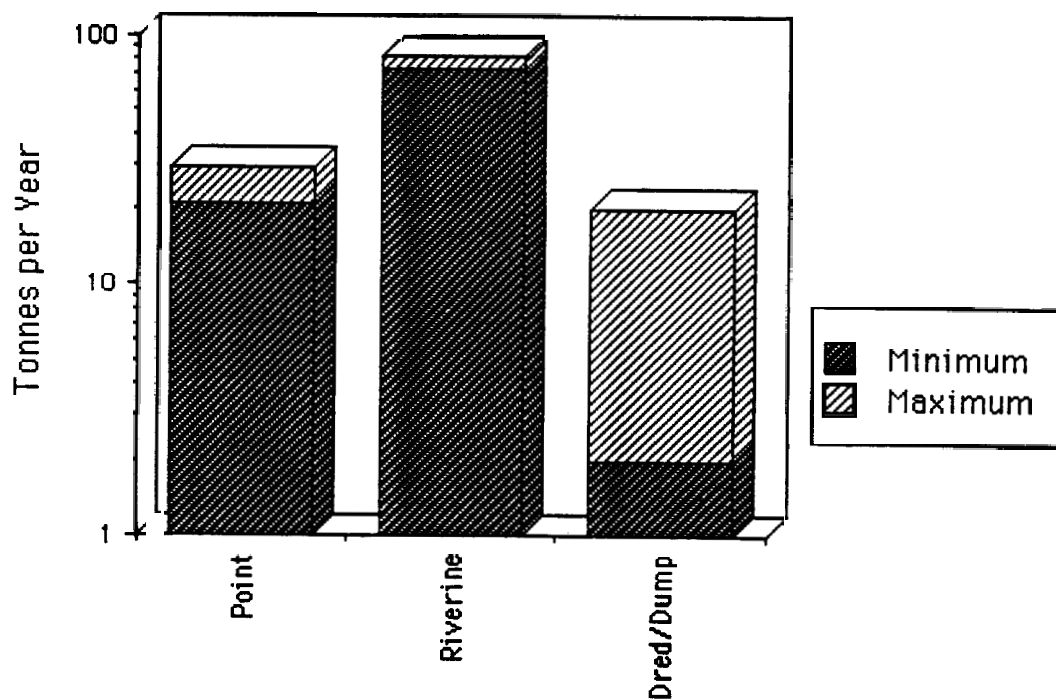




Maximum	0.8	0.15	1.7	3	0.1
Minimum	0.18	0.026	0.15	1.2	0.01

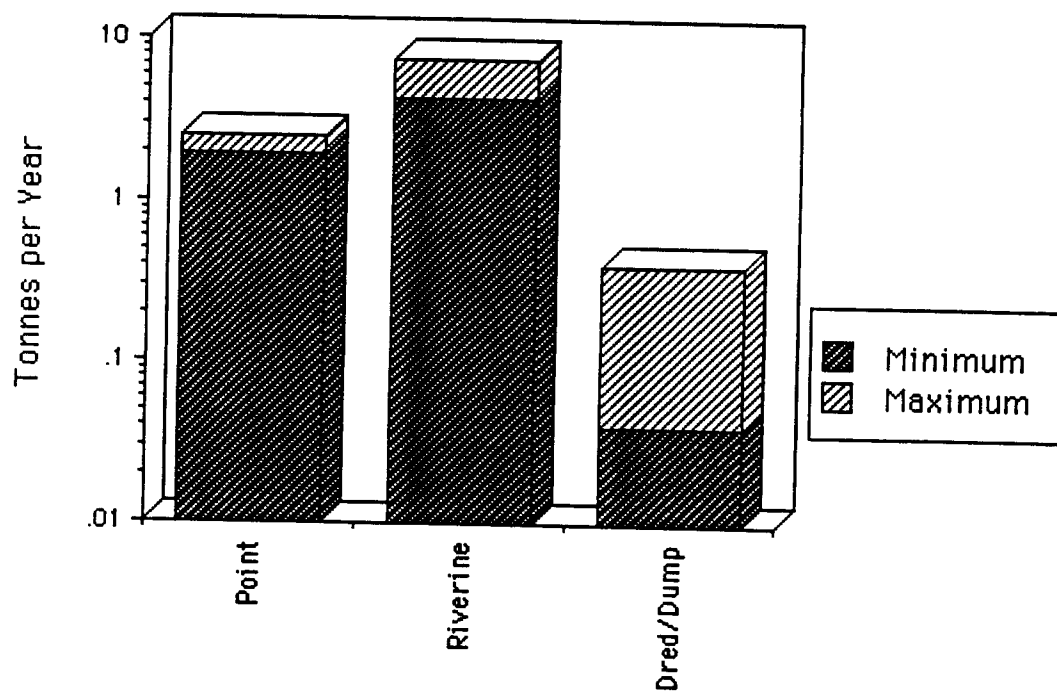
Fig. ES6. Estimated range for the mass loading of mercury to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.





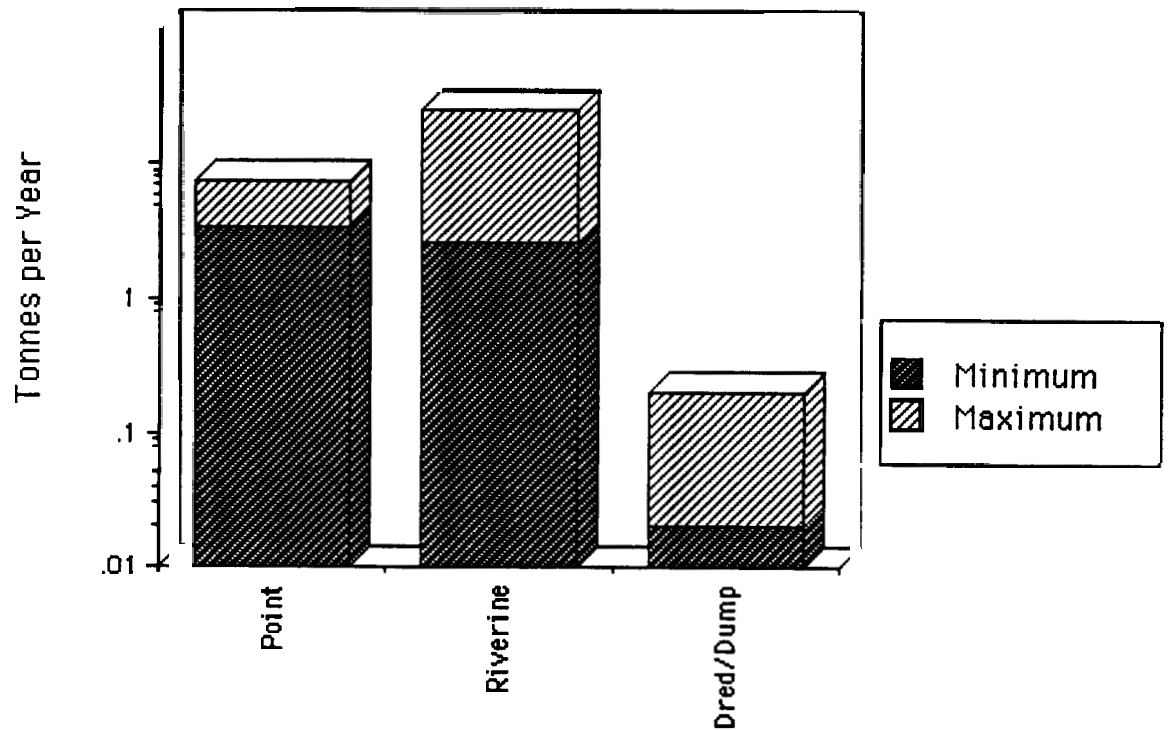
Maximum	29	82	20
Minimum	21	74	2

Fig. ES7. Estimated range for the mass loading of nickel to the San Francisco Bay-Delta from point sources, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.



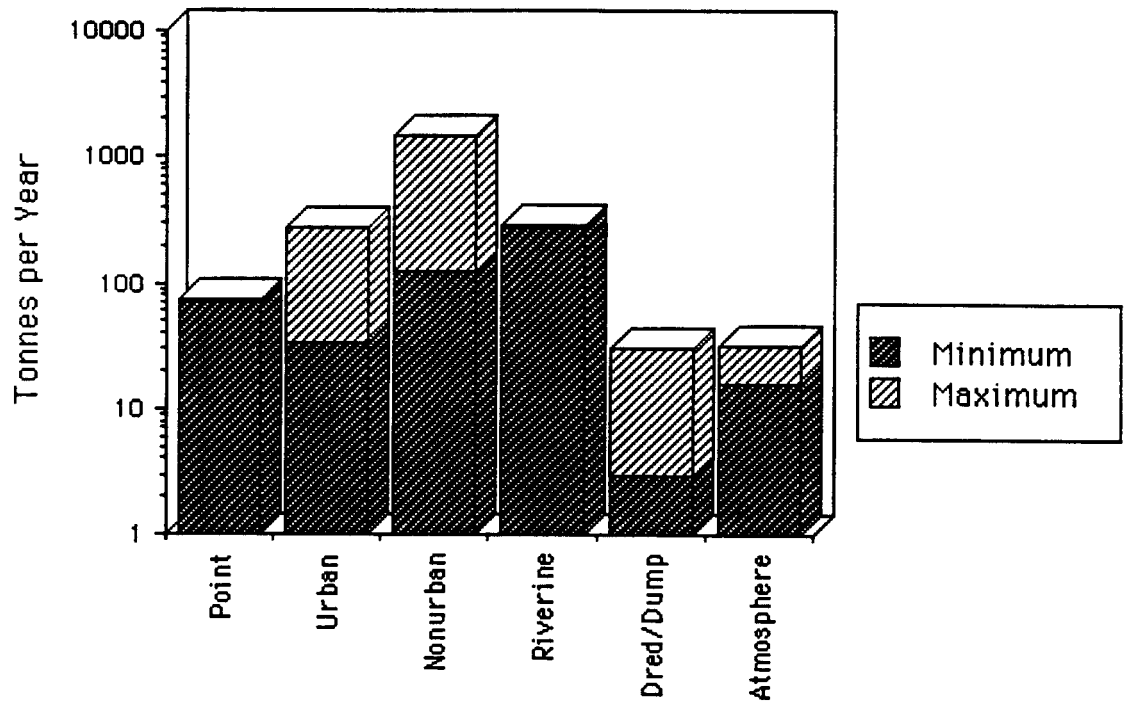
Maximum	2.5	7.4	0.4
Minimum	1.9	4.3	0.04

Fig. ES8. Estimated range for the mass loading of selenium to the San Francisco Bay-Delta from point sources, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.



Maximum	7.5	26	0.2
Minimum	3.3	2.6	0.02

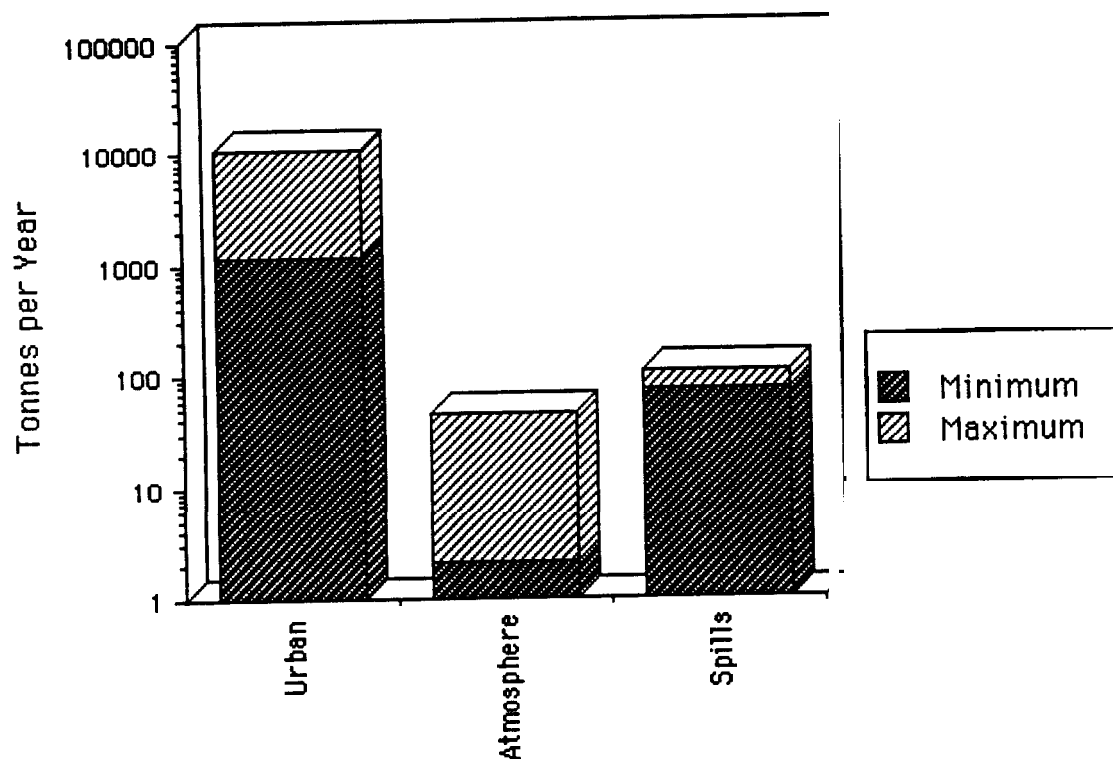
Fig. ES9. Estimated range for the mass loading of silver to the San Francisco Bay-Delta from point sources, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.



Maximum	74	268	1453	288	30	32
Minimum	70	34	126	272	3	16

Fig. ES10. Estimated range for the mass loading of zinc to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.





Maximum	11016	45	110
Minimum	1143	2.1	72

Fig. ES11. Estimated range for the mass loading of total hydrocarbons to the San Francisco Bay-Delta from urban runoff, atmospheric₁ deposition, and spills. All values in tonnes yr.



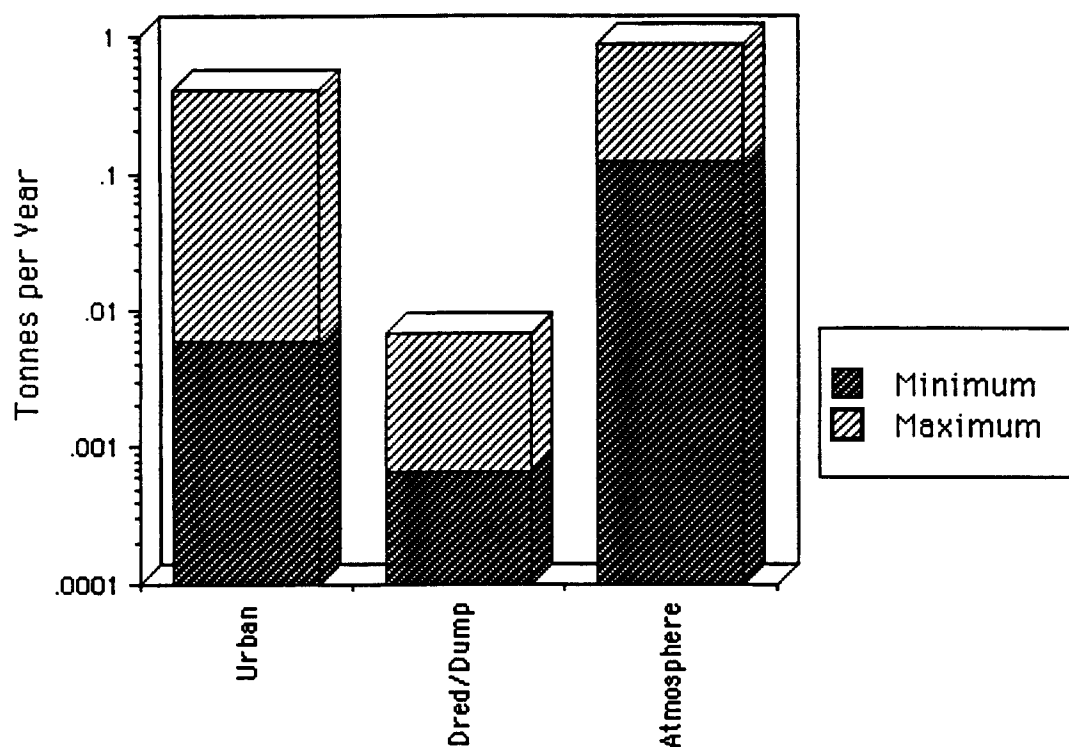
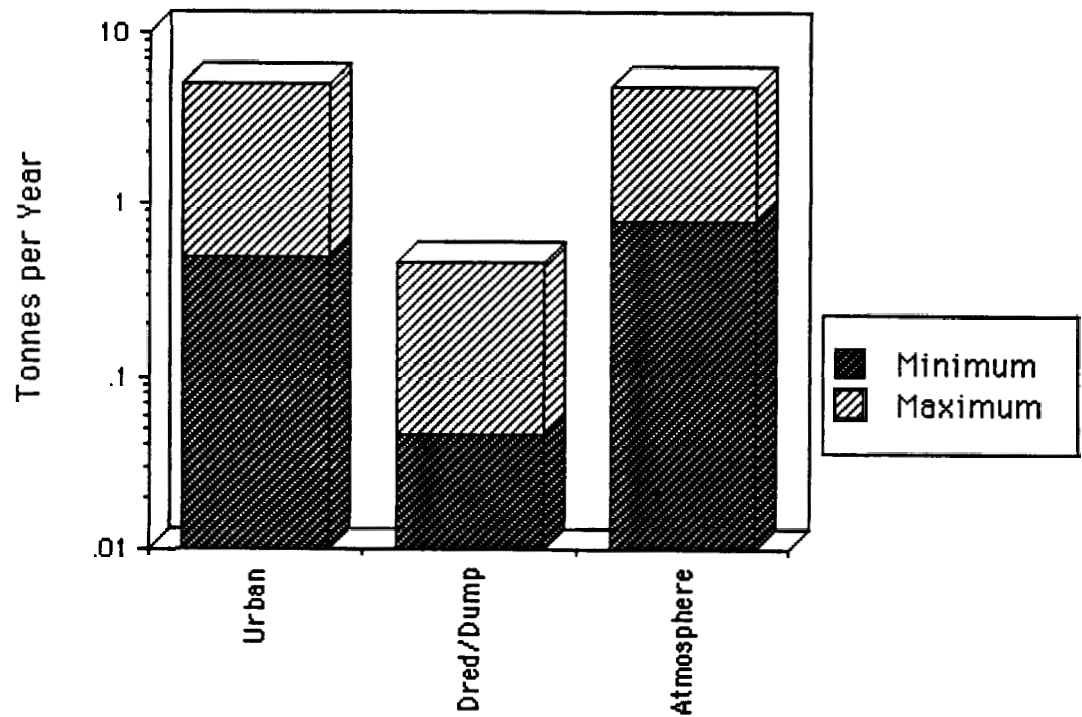


Fig. ES12. Estimated range for the mass loading of PCBs to the San Francisco Bay-Delta from urban runoff, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.





Maximum	5	0.47	4.8
Minimum	0.5	0.05	0.8

Fig. ES13. Estimated range for the mass loading of PAHs to the San Francisco Bay-Delta from urban runoff, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

TABLE ES1. Ranking of loading estimates for various contaminants and sources in the San Francisco Bay-Delta. Ranks for each contaminant are given based on minimum and maximum loading estimates, from greatest (1) to least.

		P O I N T S O U R C E S	U R B A N R U N O F F	N O N U R B A N R U N O F F	R I V E R I N E I N P U T S	D R E D G I N G / D I S P O S A L	A T M O S P H E R E	S P I L L S
ARSENIC	Minimum	4	3	2	1	5	-	-
	Maximum	4	3	1	2	5	-	-
CADMIUM	Minimum	2	4	3	1	6	5	-
	Maximum	3	4	2	1	6	5	-
CHROMIUM	Minimum	3	5	1	2	4	-	-
	Maximum	5	4	1	2	3	-	-
COPPER	Minimum	3	4	2	1	6	5	-
	Maximum	4	3	1	2	5	6	-
LEAD	Minimum	4	2.5	1	2.5	6	5	-
	Maximum	5	2	1	3	6	4	-
MERCURY	Minimum	2	4	3	1	5	-	-
	Maximum	3	4	2	1	5	-	-
NICKEL	Minimum	2	-	-	1	3	-	-
	Maximum	2	-	-	1	3	-	-
SELENIUM	Minimum	2	-	-	1	3	-	-
	Maximum	2	-	-	1	3	-	-
SILVER	Minimum	1.5	-	-	1.5	3	-	-
	Maximum	2	-	-	1	3	-	-
ZINC	Minimum	3	4	2	1	6	5	-
	Maximum	4	3	1	2	6	5	-
TOTAL HYDROCARBONS	Minimum	-	1	-	-	-	3	2
	Maximum	-	1	-	-	-	3	2
PCBs	Minimum	-	2	-	-	3	1	-
	Maximum	-	2	-	-	3	1	-
PAHs	Minimum	-	2	-	-	3	1	-
	Maximum	-	1	-	-	3	2	-

biphenyls and polyaromatic hydrocarbons enter the estuary through this route; this is in keeping with the known propensity of such contaminants to be transported aerially. However, caution is required in the interpretation of such data, as the loadings from several sources have not been quantified as yet.

CONCLUSIONS

Considerable uncertainty surrounds any estimates of the mass loading of contaminants to the Bay-Delta which may be derived using presently-available data. This is due to inadequate monitoring, imprecision of analysis, and many other factors.

In addition, it is important to note that contaminant loading to the estuary (and the flux of toxicants through estuarine components) is a dynamic phenomenon, and is not fully described by annually-averaged estimates. For example, runoff and riverine inputs will undoubtedly provide the majority of trace element loadings to the estuary in periods of heavy rainfall (particularly considering their time-averaged importance as sources of metals to the Bay-Delta, as outlined here). However, in dry seasons, point sources may be significant with respect to trace metal loadings. Similarly, the impact of both atmospheric deposition and urban runoff on hydrocarbon delivery to the estuary varies seasonally. Thus, the actual importance of each contaminant source may alter markedly with time and season. Only one of



the sources considered here (dredging and dredged material disposal) can be identified as a truly minor source of contaminants to the estuary under all conditions. Even in this case, it is possible that local impacts may occur if contaminants are fractionated into fine suspended material during dredging and disposal operations and preferentially deposited in particular parts of the Bay-Delta.

Further studies are clearly required to improve the present understanding of contaminant loads (and their fluxes) in the estuary. To be successful, such future investigations should be cognizant of both the inadequacies of the existing database and the reasons for such problems. It is to be hoped that the present report provides much data relevant to such matters, and will aid in future improvements.



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ACKNOWLEDGEMENTS

Many individuals provided assistance to the authors in the collection of data used in this report, and in the production of the report itself.

Thanks are due to Susan Anderson of the San Francisco Bay Regional Water Quality Control Board in her untiring role as contract officer and for her contributions to data collection and discussions.

Jeremy Johnstone and Mike Monroe of the U.S. EPA Region IX office also provided much help in their roles as contract officers. Financial support from the State Water Resources Control Board and the U.S. EPA is gratefully acknowledged.

Staff of SCI Data Systems (Jerry Oglesby, Larry Moritz and Bob Gerzoff) expended much effort in the computerization of data used in this report, and in its initial analysis. Tom Johansen was also of assistance.

Technical input to the report was provided by Doug Segar (dredging and dumping) and Don Baumgartner. The acquisition of data was made possible through the efforts of Daniel Basta, Forest Arnold, Bob Gilliom, John Bader, Dave Carlson, Jerry Bruns and his staff, Ed Long, Kris Lindstrom, Marv Jung, Mike Carlin, and several other staff members of the San Francisco Bay Regional Water Quality Control Board (particularly Theresa Rumjahn, Tom Mumley, Phil Mellan, Randy Lee and Rick Chan).

A grant of a Macintosh Plus Computer and peripherals from Apple Computer, Inc., allowed for the incorporation of high quality graphics into the report.

The actual production of the report was made possible by the hard work of staff under the direction of Susan Prather of AHI, who contributed much to the report herself. Thanks are due to Susan for all phases of production, to Melissa Blanton for copy editing, to Paul Moreson for administrative aid, and to Emilia Martins, Lori Duncan, Renee Ragucci and Ginny Goodwind for word processing.

Reviewers of the draft of this report are acknowledged for their efforts. The contributions of Susan Anderson, Karen Garrison, Jim McCarthy, Bob Spies, and Daphne Clifton were particularly useful in this respect.

Members of the AHI Board of Directors are also owed our thanks for their contributions of support, votes of confidence, and technical assistance.

Finally, the authors wish to thank Teresa Gunther, Ellyn Miller, and Lee Phillips for their support and patience.

I. INTRODUCTION

A. General

The San Francisco Bay-Delta is the largest estuary on the Pacific coast of the USA, and has been exposed to massive anthropogenic influence over the last 200 years (Nichols et al., 1986). Many of the major historical changes in the estuary and its catchment have given rise to the increased disposal of contaminants to the Bay-Delta ecosystem. In recent times, however, attempts have been made to control the discharge of pollutants to the estuary. Several authors have commented on historical water quality changes in the estuary (e.g. Luoma and Cloern, 1982). Present concerns center around the so-called "toxics" in the Bay-Delta. These include trace metals, chlorinated hydrocarbons, and petroleum-derived or other types of hydrocarbons. It is these contaminants which are addressed in the present report.

The identification of sources of toxicants in the Bay-Delta is a vital step towards understanding their mechanisms of transport through the estuary, their fates, and their possible effects on biological resources of the Bay-Delta. In addition, the introduction of further controls on contaminant sources to the estuary cannot be successful or cost-effective unless a full understanding of the relative magnitudes of toxicant sources in the Bay-Delta exists.

As a result of these needs, the Aquatic Habitat Institute has been requested by the California State Water Resources Control Board and the U.S. Environmental Protection Agency to collect and review available data on the sources of toxic contaminants to the Bay-Delta. The present report has been produced in response to these requests.

It is of relevance here that, while very considerable amounts of data exist on contaminants entering the estuary, the database is incomplete in many respects. Certain sources of contaminants (such as urban and non-urban runoff) have received little study locally. In other cases, toxicant levels are frequently reported as being "below detection limits", and have therefore been inadequately quantified. Many studies also do not report details of quality control or quality assurance (QA/QC) procedures, rendering the assessment of data exceptionally difficult. QA/QC concerns are particularly relevant to the quality of data reported here, and to the use of these data to derive contaminant loading estimates.

These problems were identified in the early phase of data acquisition and assessment in this project. It was also noted that the more recent data are generally of higher quality with respect to both detection limit values and (sometimes) quality control and assurance. As a result, it was agreed between the contracting parties that data from the most recent three full calendar years (1984-1986) should, when available, be considered as a basis for the calculations of contaminant loading to the Bay-Delta. This report thus concentrates on data produced between 1984 and 1986.

Because of the inadequacies in the existing database, it has been necessary to use a variety of assumptions in generating estimates of contaminant loadings for the present report. In some cases, data from studies of other estuaries exist which may be applicable to the Bay-Delta; these are identified and discussed where relevant in each section of the report. In other instances, so little is known about the contaminant loading from

a particular source that best estimates have to be made, sometimes on a partially subjective basis. In all such cases, the calculations employed to derive estimates for mass loading of contaminants are clearly enumerated. As a result, the estimates herein may be improved or altered with ease in the future, when additional data become available.

B. The Conceptual Model

Estuaries receive contaminants from a wide variety of sources, and this gives rise to difficulties in computing overall loads, particularly in such a large and complex estuary as San Francisco Bay-Delta. The contaminant loadings from all major sources and geographical areas must be calculated using best available data, and summed to provide an estimate of overall loads per unit time. Decisions must be made on how to deal with temporal averaging of loads, and care must be taken to avoid the double-counting of contaminants.

The concept of pollutant loading to the estuary must be clearly separated from contaminant fluxes or transport within the Bay-Delta (the area of which is defined below). This report takes no account of the transport or fate of such contaminants in the estuary. Thus, for example, no estimate is made of the fate of toxicants introduced to the estuary through Delta outflows. Such contaminants may be distributed and retained within the estuary in water, sediments, or biota, or may be lost from the system by their transport to oceanic waters outside the Golden Gate, or by volatilization and aerial transport away from the estuary. Such matters are of great importance in determining the amounts of contaminants present in estuarine components at any one time, and their distribution within the system. This is

obviously highly relevant to regulatory controls of a wasteload allocation nature, needed to maintain acceptable water quality conditions in portions of the estuary. However, contaminant fluxes and fates are outside the scope of the present report; if information of this type is required, its synthesis would follow the estimation of contaminant loads (as presented here) as an additional task, requiring further assumptions and data treatment.

Because the present report takes no account of the fluxes or fates of toxicants, several items are not included in the presentation. There is no attempt to allocate contaminant loads to different sectors or portions of the estuary. This is because such treatment is meaningless unless it is combined with estimates of contaminant transport and flux (through tidal action or other mechanisms), thus permitting estimates of the likely degree of overall pollution of sectors of the Bay-Delta. It should also be noted here that seasonal factors would intrude upon such a synthesis of data. For example, the impacts of Delta outflows on the water quality in parts of the northern reach of the estuary (and probably also the entire Bay-Delta, at least to some extent) will vary markedly with season, depending principally on runoff rates in the Central Valley catchment. Additional comments on seasonal variations (in contaminant loads, not fluxes) are given below.

The flux of contaminants through the Golden Gate is also not included as a load to the estuary in the present document. There is a clear distinction between toxicants entering the Bay-Delta (and remaining therein or passing through the estuary) from Delta flows, effluent discharges, or other such sources, and

contaminants brought into the estuary on a rising tide through the Golden Gate. The latter can only be considered to be a load to the estuary in a time-averaged sense if a net transport of pollutants occurs to the Bay through multiple tidal exchanges. The available evidence shows that the estuary is generally a net source of contaminants to offshore oceanic water (i.e. that almost all toxicants are present at higher levels within the Bay-Delta than in marine waters of the Pacific). Thus, the net transport of contaminants over multiple tidal cycles will consist of an export of pollutants through the Golden Gate, from the Bay-Delta to the Pacific Ocean. This net export is not quantified herein, as it concerns contaminant fluxes, not loads to the estuary.

The sources of toxicants considered in the present report are enumerated below, in the order in which they appear in the document. Various issues related to the calculation of contaminant loading from each source are discussed, in order to fully explain the conceptual model employed for computation of total mass emissions.

* Point Sources: Toxic contaminant loadings from point sources in the estuary are largely computed from data in NPDES self-monitoring reports. Discharge rates (flow and concentrations of contaminants) may vary from such sources throughout the year and between years, as a result of variations in influent loads (sewage treatment plants), industrial processes, or the degree of treatment of effluents. The estimates employed here to compute mass emissions of toxicants are based upon three-year (1984-1986) averages, which employ all available data points to enhance the characterization of mean loadings. It may be noted that in a few

cases, the use of three-year averages may either underestimate or overestimate present contaminant loadings from individual sources, depending on whether an overall trend towards higher or lower loading with time exists. Where such trends are thought to be significant, they are discussed in the text. Most data used are available from AHI in computer-generated form. Details will be published in an Appendix to the final report.

* Urban Runoff: The section on urban runoff is the first of three sections (urban runoff, nonurban runoff, and riverine inputs) dealing with contaminant loadings in forms of runoff entering the estuary and its catchment. As described in detail in each section, the entire Bay-Delta catchment land area (including the Central Valley) was assigned in portions to either an "urban" or "nonurban" category based upon land use, or was covered by mass emissions calculated for riverine inputs (see below). The details of land use, runoff coefficients, and contaminant concentrations employed to calculate toxicant loadings from urban runoff are described in full in the text.

* Nonurban Runoff: Contaminant loadings in this category were computed based on the estimates by the National Oceanic and Atmospheric Administration, in their National Coastal Pollutant Discharge Inventory (NOAA, 1987a, c, d). These employ calculations of sediment yield and trace element levels in soils to derive metal loadings; chlorinated hydrocarbon pesticide loadings are computed based on data for their utilization. Care was taken to avoid overlap between the area employed in this category and the regions covered either by the urban runoff category or the riverine inputs. Thus, only the nonurban land draining directly to the Bay-Delta was included in the

calculations of nonurban runoff; contaminants from the area above the operationally-defined Delta (see below) were included as part of the riverine inputs.

* Riverine Inputs: It is not possible to calculate contaminant loadings arising in the Central Valley from such databases as NPDES self-monitoring reports for point sources therein, as this assumes that any toxicant discharged to a river in the catchment reaches the Bay-Delta. Contaminant loadings were therefore calculated directly, employing monitoring data on water quality. The sites at which such data are available thus served to operationally define the upstream limits of the Bay-Delta (at Sacramento, Stockton, and Vernalis).

Two factors deserve mention here concerning these data. The first is that no attempt has been made to define anthropogenic loadings of contaminants, as opposed to total mass emissions. Thus, no assumptions are employed as to likely "background" concentrations of contaminants in the riverine inputs to the Bay-Delta. It is of course self-evident that any river contains some background load of toxicants, which may be elevated by anthropogenic impact in its catchment. However, the computation of total contaminant emissions to an estuary need take no account of this, just as such "background levels" are not subtracted from point source emissions. It is recognized that the relatively large loading estimates as derived in fact represent low concentrations of toxicants in very large volumes of water or great total masses of suspended particulates. Indeed, the point is made that this represents one of the shortcomings of the dataset on riverine inputs; a small difference in observed contaminant concentrations (many of which are close to analytical

detection limits, and therefore somewhat unreliable) generates a considerable change in computed mass loadings. Nevertheless, these data are deemed to be the best available basis for estimating the mass loading of contaminants from the Central Valley catchment.

The second factor of note is that water diversions occur within the Delta region downstream of the operationally-defined Bay-Delta area. These water diversions serve to distribute water to the southern portion of the Central Valley (from whence some may eventually return via the San Joaquin River to the Delta) and to southern California (in which case it is lost from the Bay-Delta, with its associated contaminant loads). A portion of the flows of both the Sacramento and the San Joaquin Rivers is taken out of the Bay-Delta ecosystem in this fashion, and this amount varies considerably with season and between years. The riverine loads computed and presented here are thus a legitimate mass emission to the Bay-Delta region, but only a proportion of these loads actually enters the Bay itself in the final Delta outflow. The amounts entering the Bay itself may be computed using additional assumptions and flow data available from the Department of Water Resources, Sacramento, CA. No attempt is made to compute these loads entering the Bay here, as the topic of this report concerns loadings of toxicants to the Bay-Delta, which by definition includes the entire flows of the rivers passing through Sacramento and Vernalis. It may be noted, however, that water diversions are of least importance at times of high runoff and high river flow, and these are the periods in which the greatest loads of contaminants are transported to the Bay-Delta by the inflowing rivers. On a time-averaged basis, it

is unlikely that contaminant loadings entering the Bay itself (after water diversions) will be more than 20% lower than those calculated here. Given the assumptions inherent in the calculations and the generally poor quality of the existing database, this distinction is largely considered meaningless.

* Dredging and Dredged Material Disposal: The introduction of contaminants to the Bay-Delta through dredging and the disposal of dredged material is not strictly a de novo load to the estuary, but more of a remobilization and redistribution of toxicants. This source cannot therefore be considered as strictly analogous to loadings from the other sources addressed in this report. However, the potential for contaminant release from such activities is included to attempt to place such loadings into the context of overall toxicant sources in the Bay-Delta. This is of particular relevance if decisions were to be required on how to reduce the overall abundance of contaminants in the system and hence improve water quality in the estuary.

* Atmospheric Deposition: As noted for dredging and dredged material disposal, there is potential for double-counting of toxicants with respect to atmospheric deposition. All possible attempts to avoid this were made. Thus, estimates for the loading of contaminants through this route were computed only for the Bay surface area, on the assumption that atmospheric deposition of toxicants on the surrounding land mass would be included in loading estimates for urban and nonurban runoff or riverine inputs. It is of course possible that double-counting could occur through contaminants volatilizing from the surface of the Bay and being redeposited; however, little can be done to account for such a scenario (which is in any event unlikely to

represent a significant proportion of overall rates of contaminant loading to the estuary through this route).

Spills: It is notable that this is the sole category in which the oceanic area outside the Golden Gate was included as a potential source of contaminants to the Bay. However, no significant spills in the offshore marine area occurred in the three years covered by this report.

* Hazardous Waste Sites: These sources of contaminants are briefly discussed, but no mass emissions of toxicants may be derived from the limited data available.

C. Mass Loading Estimates

Computed mass loads of toxicants presented in this report are quoted as ranges in values, from a probable minimum to a possible maximum loading. This treatment differs from many previous assessments of contaminant loading to the estuary (e.g. see Risebrough et al., 1978; Russell et al., 1982; CBE, 1983), which generally provided absolute estimates. Ranges are preferred for the present synthesis, as these impart significant information as to the uncertainty surrounding each estimate of mass loading. The need for further studies to refine individual estimates is also defined by the magnitude of such ranges in loading. Conclusions relating to requirements for additional data or other improvements are presented in the final section of this report.

II. CONTAMINANT SOURCES TO THE BAY-DELTA

1. POINT SOURCES

A. Introduction

This section discusses point source emissions of toxic pollutants into the Bay-Delta ecosystem. As the term is commonly used, "point source" connotes more than the fact that a waste stream enters the environment at a discrete point. The term also signifies that the parties responsible for managing the levels of contaminants in a waste stream can be readily identified.

Point sources of water pollution in general receive far greater attention from regulatory bodies than non-point sources for two reasons that follow from this definition. First, it is straightforward to assess the composition of such a waste stream and relatively easy to define its immediate environmental impacts. Second, it is possible to require dischargers responsible for the impacts to reduce or eliminate them.

In this section, average long-term loadings based on data collected for January 1984 through December 1986 are presented for different categories of point source dischargers. These estimates are based on measured average concentrations and flows provided in discharger self-monitoring reports (SMRs). For some pollutants, the concentration measurements are not sufficiently frequent or statistically conclusive to allow a confident estimate of mass loading. In these cases, the data and their limitations are presented and discussed.

B. General Methods

Description of Data

All data presented in this section were generated as a result of State and Federal regulation of point sources of surface water pollution through the National Pollutant Discharge Elimination System (NPDES) program. The NPDES program was established by the Federal Water Pollution Control Act Amendments (known as the Clean Water Act) of 1972 (P.L. 92-500). California was the first state to obtain approval from EPA to administer its own NPDES program. This program is coordinated by the State Water Resources Control Board (SWRCB).

Under the program, the State issues NPDES permits to public and private dischargers of waste to surface waters. Each permit requires that a discharger maintain concentrations of specified pollutants in its waste stream below certain limits and that concentrations of the regulated pollutants be measured according to a designated schedule. Reports of the findings of this self-monitoring are submitted, typically on a monthly basis, to the Regional Water Quality Control Boards of the State of California. Dischargers in the basin of the Bay-Delta submit reports to the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) and the Central Valley Regional Water Quality Control Board (CVRWQCB).

This discussion is based upon actual measurements of the volume and chemical composition of wastewater flows. Every permitted discharger in the Bay region was reviewed for this study, except those that discharge directly to the Pacific Ocean. In the Central Valley Region, every permitted point source inside the legal boundaries of the Delta was reviewed. Inputs from point and non-point sources beyond the boundaries of the Delta

were assumed to be accounted for by monitoring at the entry points of river flows into the Delta, as described in detail in section II.4 below. Discharge volumes discussed below range from 50 L d^{-1} to 38 billion L d^{-1} .

The NPDES self-monitoring data presented here were generated using standard methodologies for sampling and analysis prescribed by the U.S. Environmental Protection Agency (EPA, 1984). Any one method usually applies to a group of substances with similar chemical properties. Table 1 shows some EPA methods that are referred to in the following discussion and the contaminants which can be detected by each test. Most of the methods that are sophisticated or capital-intensive, such as those requiring gas chromatography/mass spectrometry (GC/MS), are performed by commercial laboratories.

Data Acquisition

The following discussion of data acquisition applies to all categories of point source dischargers which are characterized in this section. Data on public and private point sources were primarily acquired from files at the two Regional Boards. Monthly average flows and concentrations were taken, where possible, from annual reports. Annual reports are submitted by many of the larger dischargers and summarize a year's measurements in tabular form. Data in this format were photocopied and are on file at the Aquatic Habitat Institute (AHI). Data from dischargers which did not submit such summaries, or those which simply did not monitor many parameters, were manually compiled from monthly monitoring reports.

Self-monitoring reports are filed in a central location at both Regional Boards. NPDES permits and general correspondence

Table 1. EPA methods for analysis of contaminants mentioned in this report.

<u>Method</u>	<u>Classes of Compounds Detected</u>	<u>Reference</u>
608	Pesticides and PCBs	EPA, 1982
612	Chlorinated Hydrocarbons	EPA, 1982
624	Volatile Organics	EPA, 1984
625	Semi-Volatile Organics	EPA, 1984
202-289	Trace Elements	EPA, 1983

pertaining to each permit are also centrally filed. Current permits on each discharger were obtained for this study. All of the pertinent reports that could be found in the central files at either Regional Board were also collected.

Annual and monthly reports that cannot be found in the central files are likely to be in the office of the staff person that handles each particular discharger's case. These filing practices make it difficult to access the data upon which this section is based. Many meetings were arranged with individual staff members at both Regional Boards in order to locate and discuss reports submitted by most dischargers. In several instances at both Regional Boards, SMRs could not be located, even with the assistance of the staff. Some reports submitted in the 1984-86 period could not be included in this analysis because tracing them would have been too time-consuming. An inventory of data included in this report is provided in the Appendix.

Some of the data that could not be found at the Regional Boards were obtained directly from the dischargers. The SFBRWQCB requested all permitted dischargers in the Bay Region to send 1986 annual reports to AHI, and this yielded some of the needed information. In the Central Valley Region, the Sacramento County Regional Wastewater Treatment Plant provided a printout of their monitoring results.

Inconsistencies in reporting on the part of the dischargers posed additional obstacles to obtaining the data required for this study. One problem encountered was that some dischargers do not present their monthly average data in a usable form. Another difficulty was that minor dischargers often do not submit all of the required reports.

At the end of 1986 the SFBRWQCB listed a total of 205 NPDES permits, and 51 were listed in the Delta. Data on 95% of the permitted dischargers were obtained for this study. Many of the listed permits are inactive or do not require flow and chemical monitoring. Less than 20 minor permits are not included because the appropriate SMRs were not centrally filed and the staff responsible for the cases could not be contacted. No major sources of contaminant loadings were omitted from review.

Data Processing

Monthly average concentrations and flows for all point sources were entered on EPA's National Computing Center computer in Research Triangle Park, North Carolina. As described above, the majority of this information was initially photocopied and filed at AHI.

Two types of photocopied material are on file. The first type, tabular summaries for most of the non-priority pollutants, was photocopied from annual reports. The second type, priority pollutant data, was photocopied from the most concise tables or laboratory report sheets that could be found. Most of the priority pollutant data were reported using a standard form distributed by the SFBRWQCB.

The monthly data were then entered into Statistical Analysis System (SAS) datasets. The presentation of data by different dischargers in annual reports is neither homogeneous nor always concise. This information consequently was manually condensed into tables with a uniform format before it was keypunched. Smaller dischargers frequently do not submit annual reports, so their data were put into this same format after extraction from

monthly SMRs. Priority pollutant data were keypunched directly from the photocopied tables or lab sheets.

One portion of the data presented in this section was transferred directly into SAS from diskettes obtained from the SFBRWQCB. Priority pollutant raw data from municipal wastewater treatment plants for the period between mid-1984 and mid-1985 had been entered into spreadsheet files on diskette as part of a staff analysis.

Evaluation of the Data

The mass loading of any contaminant from a discharge into a receiving water is calculated by multiplying the rate of flow of the waste stream by the concentration of the given substance. This straightforward procedure, however, only produces a valid estimate of mass loading if it is based upon statistically meaningful data. Three major criteria which water quality monitoring data should meet if they are to be used for estimating monthly mass loading are discussed below.

First, monitoring data should be collected frequently enough to provide an accurate estimate of the temporal variation in the composition and volume of a discharge. Infrequent sampling may miss periodic flushes of highly contaminated waters. To illustrate, weekly analyses of trace elements in refinery process effluents in 1986 comprise perhaps the most informative dataset discussed in this section. This testing shows that measured trace element concentrations can vary two- or three-fold each month, at concentrations well above the limit of detection. Pollutant concentrations in waste streams with washdown, storm runoff, or other intermittent components are even more variable than refinery process effluents. Publicly Owned Treatment Works

(POTWs) which receive indirect industrial discharges can similarly be expected to produce effluents with fluctuating composition.

In general, frequent sampling allows better estimation of all sources of variation that influence the measurement of a chemical concentration in water. This includes variation in the composition of the waste stream itself, in addition to variation associated with sample collection and analysis. When a discharge is sampled quarterly or less often, it is difficult to make strong quantitative conclusions about annual or seasonal mass loading.

A second criterion that monitoring data should meet in order to serve as a basis for quantitative statements about monthly average mass loading is that measured concentrations of contaminants should be significantly larger than their detection limits. This criterion severely restricts the utility of a large proportion of analyses of synthetic organic chemicals and trace elements in wastewater discharges, where results often fall near or below the limit of detection.

The limit of detection of a method is defined as the lowest concentration that can be stated with 99% confidence to be greater than zero (EPA, 1984). Analytical measurements of concentrations in a sample that are at or near the limit of detection are not meaningful in a quantitative sense because they have large uncertainties associated with them. This uncertainty can approach or even equal the reported value (Keith et al., 1983). Quantitative treatment of a result is only justified at a level that is roughly three times as large as the limit of detection (Keith et al., 1983; Kirchmer, 1983). This level is

known as the limit of quantitation. Measurements at the limit of quantitation are still only within 30% of the real value at the 99% confidence level (Keith et al., 1983). The uncertainty associated with a measurement decreases as its magnitude relative to the detection limit increases. The strongest statement that can be made about a single measurement near the detection limit is that the substance is present in the sample, but the actual amount is not precisely known. When such a result is multiplied by a large flow to obtain an estimated average mass loading, the estimate is uncertain and has limited meaning.

Values reported as being below the detection limit (BDL) provide limited information concerning the concentration of a substance in a sample. A BDL result means that the true concentration may be anywhere in the interval including zero and the detection limit. In estimating mass loading, this information can only be used to specify a range of possible values.

The third criterion against which monitoring data should be assessed is the availability of the results of quality control testing. A large number of factors in the collection, transport, storage, and analysis of samples can invalidate analytical results. Quality control results provide evidence of the reliability of a given set of data. Quality control data are reviewed below where they were available. Unfortunately, these data were generally not cited by dischargers, so this criterion could not be strictly applied to the datasets reviewed below.

Evaluation of the self-monitoring data collected for this report against these three criteria provides the framework in which the data are presented. Primary emphasis is placed on data

that rate highly in this assessment. Shortcomings of data that do not satisfy the criteria are also discussed.

Estimated average loadings for point sources are presented throughout this section. These averages usually are presented as a range, with a minimum and maximum. The minimum average was calculated assuming that a BDL value represented an actual concentration (and thus a mass loading) of zero. The maximum average was calculated assuming that each BDL value represented an effluent concentration equal to the detection limit, with a corresponding finite mass loading. True average loadings are most likely to fall between the calculated minima and maxima. Contaminants which are rarely detected have a mass loading range that is large relative to the estimated minimum. Contaminants detected frequently, or at high concentrations relative to the limit of detection, exhibit comparatively small ranges of mass loading. The ratio of the minimum average to the range indicates the degree to which a contaminant is quantified analytically, summarizing information regarding both the frequency of detection and the magnitude of detected values relative to detection limits.

C. Emissions Data for Point Sources

Point source dischargers are separated into several categories in the following analysis. These groupings are made to allow general discussion of dischargers that engage in similar economic and/or monitoring activities.

Publicly Owned Treatment Works

Publicly Owned Treatment Works (POTWs) receive and treat a variety of wastewater from the communities they serve, including residential, commercial, and industrial flows. Table 2 lists the POTWs which are addressed in this report.

Table 2. POTWs in the Bay-Delta included in this study.

	Segment of estuary receiving waste	Ave. Flow, 1984-1986 (millions L d ⁻¹)
Delta POTWs	Sacramento RWT	North Delta 508 ^b
	Walnut Grove WTP	North Delta 0.4 ^b
	Davis STP	North Delta 12
	West Sacramento STP	North Delta 14
	Lodi White Slough WPCP	North Delta 19
	Rio Vista WTP	Central Delta 2
	Stockton STP	Central Delta 109
	Central CCSD #19	Central Delta 1
	Tracy	South Delta 14
Bay Area POTWs	Delta Diablo SD	Suisun Bay 36
	Fairfield-Suisun SD	Suisun Bay 36
	Benicia WTP	Suisun Bay 9
	Central Contra Costa SD	Suisun Bay 146
	Mountain View SD	Suisun Bay 5
	Yountville WTP	San Pablo Bay 2 ^b
	Napa SD	San Pablo Bay 29 ^b
	Vallejo SD	San Pablo Bay 42
	Calistoga	San Pablo Bay 2
	Rodeo WTP	San Pablo Bay 4
	Pinole-Hercules WTP	San Pablo Bay 7
	Sonoma Valley WTP	San Pablo Bay 14 ^b
	Petaluma WTP	San Pablo Bay 14 ^b
	Novato-Ignacio SD	San Pablo Bay 19
	Las Gallinas STP	San Pablo Bay 12
	West County Agency	Central Bay 59
	Central Marin SA	Central Bay 39
	Marin: Paradise Cove	Central Bay <.1
	Marin: Tiburon	Central Bay 4
	SA of Southern Marin	Central Bay 6
	Sausalito-Marin SP	Central Bay 6
	East Bay MUD	Central Bay 329
	San Leandro WTP	South Bay 21
	Livermore	South Bay 171
	Dublin-San Ramon SD	South Bay 32
	Oro Loma SD	South Bay 59
	Hayward WTP	South Bay 48
	Union SD	South Bay 81
	SF:Southeast	South Bay 279
	SF:North Point	South Bay 19
	Millbrae WTP	South Bay 51
	Burlingame WTP	South Bay 181
	San Mateo WTP	South Bay 51
	South Bayside SA	South Bay 81
	Palo Alto WTP	South Bay 104
	Sunnyvale WTP	South Bay 67
	San Jose/Santa Clara WTP	South Bay 492

^a POTWs not on this list (St. Helena, Vacaville, SSF-SB, and SFIA) will be included in the Final version of this Report.

^b Reclaims wastewater in the summer. Wet season flows averaged over the entire year.

Municipal effluent is a significant source of freshwater to the Bay-Delta, especially in the South Bay. During the dry season, wastewater effluent makes up the greatest volume of freshwater entering the South Bay (Russell et al., 1982), and most of this effluent is discharged by POTWs. The mean total rate of discharge by POTWs into the Bay-Delta in 1984-1986 was approximately 2.9 billion L d⁻¹.

A range of toxic contaminants is typically found in municipal wastewater (e.g. Schafer 1982; 1984). Certain pollutants, such as some trace elements and ammonia-nitrogen, are components of domestic sewage. Synthetic organic chemicals (including pesticides, solvents, and plastics) and petroleum hydrocarbons can also enter a waste stream as a result of household and commercial activities. Industrial discharges to sewer systems, sometimes called "indirect" industrial discharges, can contribute a variety of contaminants as waste products of manufacturing activities. Most of the pollutants in treatment plant influents are removed from the wastewater to some degree by the treatment process. Nevertheless, as will be shown below, significant quantities of certain pollutants pass through the treatment plants and into Bay-Delta waters.

Effluent Monitoring. Self-monitoring data from POTWs make up the largest uniform record of information on point source discharges. Monitoring of the group of toxic pollutants listed in Table 3 has been carried out since the early 1970s. The monitoring frequencies for these pollutants vary from once a week to once a year, depending on the volume and composition of wastewater produced by a discharger. Monthly average concentrations and flows were generally found in annual reports.

Table 3. Conventional monitoring parameters for POTWs, 1984-1986.

Silver	Mercury	Cyanide
Arsenic	Nickel	Oil and Grease
Cadmium	Lead	Phenols
Chromium	Zinc	TICH ^a
Copper		

^a Total identifiable chlorinated hydrocarbons

Analyses for these contaminants are conducted as prescribed by EPA (1984). Quality control data for these analyses do not appear in annual reports.

The 1972 Amendments to the Federal Water Pollution Control Act called for the development of industrial "pretreatment" programs to control indirect industrial discharges. Little progress was made towards that end until the 1979 Amendments to the Act called for EPA to begin the Pretreatment Program by establishing pretreatment standards for a list of priority toxic pollutants. Table 4 presents selected groupings from the current list of 126 priority pollutants which are discussed in this report.

Monitoring of the 126 priority pollutants and other toxic organics began in the Bay-Delta region in 1984. In May of that year, the SFBWRQCB started a special one-year study to characterize toxic pollution from 32 wastewater treatment plants that had EPA-approved Pretreatment Programs. The study also included two POTWs receiving no industrial wastewaters. Table 5 lists the POTWs participating in the Board's priority pollutant monitoring program that are included in this review. Two of the plants which are part of the Pretreatment Program, the San Francisco Richmond-Sunset Plant and North San Mateo County Sanitation District, are not included here because they discharge to the Pacific Ocean.

The SFBWRQCB study actually preceded EPA's action to implement a priority pollutant monitoring program in August 1984, and was one of the first programs of its kind. This was an ambitious project that involved complex quality assurance techniques that had not previously been used on a large scale for NPDES monitoring. Analytical costs during the Board's study ranged from \$900 to \$1,500 per sample.

Table 4. Priority pollutants commonly analyzed by POTWS participating in the Pretreatment Program.

VOLATILES

(EPA Method 624)

Acrolein
Acrylonitrile
Benzene
Bromodichloromethane
Bromoform
Bromomethane
Carbon tetrachloride
Chlorobenzene
Chloroethane
2-Chloroethylvinyl ether
Chloroform
Chloromethane
Dibromochloromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
trans-1,2-Dichloroethene
Dichloromethane
1,2-Dichloropropane
1,3-Dichloropropene
Ethyl benzene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Vinyl chloride

ACID EXTRACTABLES

(EPA Method 625)

p-Chloro-M-Cresol
2-Chlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
4,6-Dinitro-O-Cresol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
Phenol
2,4,6-Trichlorophenol

BASE/NEUTRAL EXTRACTABLES

(EPA Method 625)

Acenaphthene
Acenaphthylene
Anthracene
Benzidine
Benzo (a) anthracene
Benzo (b) fluoranthene
Benzo (k) fluoranthene
Benzo (a) pyrene
Benzo (g,h,i) perylene
Butyl benzyl phthalate
Bis (2-chloroethyl) ether
Bis (2-chloroethoxy) methane
Bis (2-chloroisopropyl) ether
Bis (2-ethylhexyl) phthalate
4-Bromophenyl phenyl ether
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Chrysene
Dibenzo (a,h) anthracene
Di-n-butylphthalate
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
Diethyl phthalate
Dimethyl phthalate
2,4-Dinitrotoluene

2,6-Dinitrotoluene
Di-n-octylphthalate
1,2-Diphenylhydrazine
Fluoranthene
Fluorene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Indeno (1,2,3-cd) pyrene
Isophorone
Naphthalene
Nitrobenzene
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine
Phenanthrene
Pyrene
1,2,4-Trichlorobenzene
Trichlorofluoromethane

METALS

Antimony
Arsenic
Beryllium
Cadmium
Chromium, Total
Copper
Cyanide
Lead
Mercury
Nickel
Selenium
Silver
Thallium
Zinc

Table 5. POTWs participating in the Pretreatment Program and reviewed in this report. Data were obtained for 1984-1986.

Benicia	Petaluma
Burlingame	Richmond
Central Contra Costa SD	Sacramento Regional WTP
Delta-Diablo SD	San Francisco Southeast
Dublin San Ramon SD	East Bay MUD
East Bay Dischargers Auth.	San Jose-Santa Clara
Fairfield-Suisun	San Leandro
Hayward	South Bayside SA
Millbrae	South SF/San Bruno
Napa	Stockton
North Bayside SU	Sunnyvale
Oro Loma	Union SD
Palo Alto	Vallejo

Quality control techniques and reporting were an integral part of the special study. Sampling, handling, and analytical procedures were specified (Rumjahn, 1986). Table 6 shows the contaminants measured and sampling frequencies required. Analytical methods prescribed by EPA (1983, 1984) were employed. Quality control information to be submitted in SMRs included replicate effluent sample results (required once in the first year), field blank results, and recovery percentages for internal and surrogate standards. Most of the POTWs retained commercial laboratories to perform the necessary chemical analysis.

After the one-year study concluded in the latter half of 1985, priority pollutant monitoring as prescribed by EPA and the State Water Resources Control Board began. In the first year, effluent samples generally had been taken quarterly. Subsequent monitoring schedules were adjusted based on the first year's results, with many plants changing to semi-annual sampling. Reports under both programs were submitted as often as samples were analyzed, and annual reports were produced to summarize each year's sampling.

Further modifications were also made after the first year. No explicit requirements were given for analyzing duplicates or field blanks, or for reporting such information. Recovery percentages, however, are still reported by most POTWs. Results of analyses of blanks and duplicates are rarely reported.

Findings. This report is based on a comprehensive review of available data for each of the parameters listed in Tables 3 and 4. The availability of POTW self-monitoring data at the time this study was conducted is summarized in the Appendix to this report, available from AHI. Loading data for each of the

Table 6. Sampling requirements for the SFBRWQCB priority pollutant study.

Parameter	STATION LOCATION			Test Method	Compositing (24-hr. composite)
	Influent (Annual Test)	Effluent (quarterly Test)	Effluent Duplicate (Annual Test)		
-----	-----	-----	-----	-----	-----
Volatile Organic Compounds	x	x	x	EPA 624	8 grab samples collected at 3-hr. intervals; composited by analytical laboratory as a single flow-proportioned sample.
Semi-Volatile Organic Compounds (Base/Neutral Acid Extractable Organic Compounds)	x	x	x	EPA 625	8 grab samples collected at 3-hr. intervals; composited by plant or analytical lab as a single flow-proportioned sample.
Organochlorine Pesticides	x	x	x	EPA 608	Flow-proportioned composite collected by automatic sampler.
Organophosphate Pesticides	x	x	x	EPA 614	Flow-proportioned composite collected by automatic sampler.
Carbanate Pesticides	x	x	x	EPA 632	Flow-proportioned composite collected by automatic sampler.
Trace Metals, Cyanide and Phenolics	x	x	x	Atomic absorption Spectrophotometry	Flow-proportioned composite collected by automatic sampler.

parameters included in Table 3 and statistical summaries of analytical results for POTW priority pollutant analyses also appear in the Appendix.

The following discussion is divided into two sections. The first section focuses on loadings of selected parameters from Table 3 which are of particular biological significance in the estuary. This is followed by an analysis of concentration data for synthetic organic chemicals (Table 4) detected in POTW effluents in 1984-1986. Load estimates are not presented for organic pollutants because concentration data do not provide a sound basis for such calculations, as discussed in detail below.

Figure 1 presents ranges of average mass loading for trace elements in POTW effluents from 1984 to 1986. Three-year average loadings for all of the POTWs which performed analyses for the contaminants are summed in this Figure. The solid bars for each contaminant represent minimum average loadings, calculated with values reported below the detection limit (BDL) set equal to zero. The lightly shaded, taller bars represent maximum average loadings, calculated with BDL values set equal to the detection limit. Actual average loadings probably lie somewhere in the ranges indicated for each contaminant.

Frequently-occurring BDL values were reported for contaminants with maxima that are conspicuously larger than minima in Figure 1(a). All of the trace elements in Figure 1(a) (mercury, arsenic, cadmium, and silver) have long-term average loadings which are characterized poorly because concentrations in POTW effluents are near or below analytical limits of detection. Trace elements grouped in Figure 1(b) (chromium, lead, copper, nickel, and zinc) are present in POTW effluents in amounts that

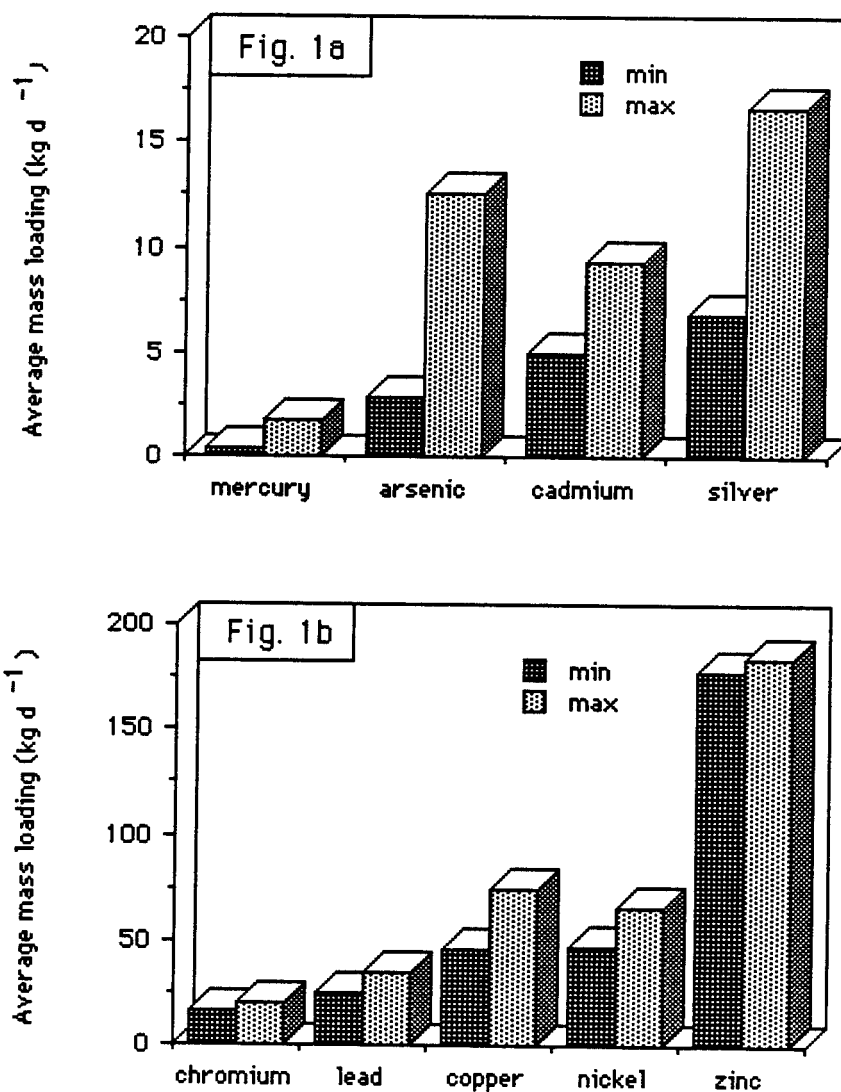


Figure 1. Ranges of average mass loading of trace elements from POTWs (Table 2), 1984-1986. Solid bars represent minima (calculated with BDL values set to zero). Lightly shaded bars represent maxima (BDL values set at the detection limit).

typically are above the limits of detection. These trace elements consequently have relatively narrow ranges of long-term average mass loading and are known to be released into the estuary in significant amounts.

Total contaminant loadings from POTWs are primarily determined by the amounts released from the eight largest plants. These POTWs, their outfall locations, and their average flows for 1984-1986 are listed in Table 7. Figure 2 illustrates the relative contributions of each plant to the total volume of wastewater discharged to the estuary from POTWs. Flow from these facilities accounts for 70% of the total from POTWs. The Sacramento Regional Wastewater Treatment Plant and the San Jose-Santa Clara Water Pollution Control Plant alone discharge 34% of the total flow from POTWs. Spatial and temporal trends in contaminant releases from these eight plants dictate overall patterns of point source loadings of most contaminants in the estuary.

POTW mass loadings of all nine trace elements in Figure 1 are better defined than those from any other source. Each of the nine elements, therefore, is addressed individually below.

* Silver. The largest single point sources of silver in the estuary are the Sacramento RWTP and San Francisco's Southeast Water Pollution Control Plant (SF Southeast) (Table 8). SF Southeast was a consistent source of silver in 1984 and 1985. Silver was detected in 20 of 24 months in those years, with a minimum average concentration of $9.2 \mu\text{g L}^{-1}$. In 1986, however, silver was detected only once in 12 analyses, with a median detection limit of $7 \mu\text{g L}^{-1}$. The Sacramento RWTP showed a different pattern. In 1984, silver was not detected in any month

Table 7. The eight largest POTWs in the Bay-Delta Region, and average flows, 1984-1986. Segments after Gunther (1987).

	Segment of estuary receiving effluent -----	Flow 10 ⁶ Liters day ⁻¹ -----
Sacramento Regional	Sacramento River	508
Central Contra Costa Sanitary District (CCCSD)	Suisun Bay	146
East Bay Municipal Utility District (EBMUD)	Central Bay	329
San Francisco: Southeast Water Pollution Control Plant (SWPCP)	South Bay	279
Union Sanitary District (USD)	South Bay	81
South Bayside System Authority (SBSA)	South Bay	81
Palo Alto Sub-regional Water Quality Control Plant	South Bay	104
San Jose-Santa Clara Water Pollution Control Plant	South Bay	448

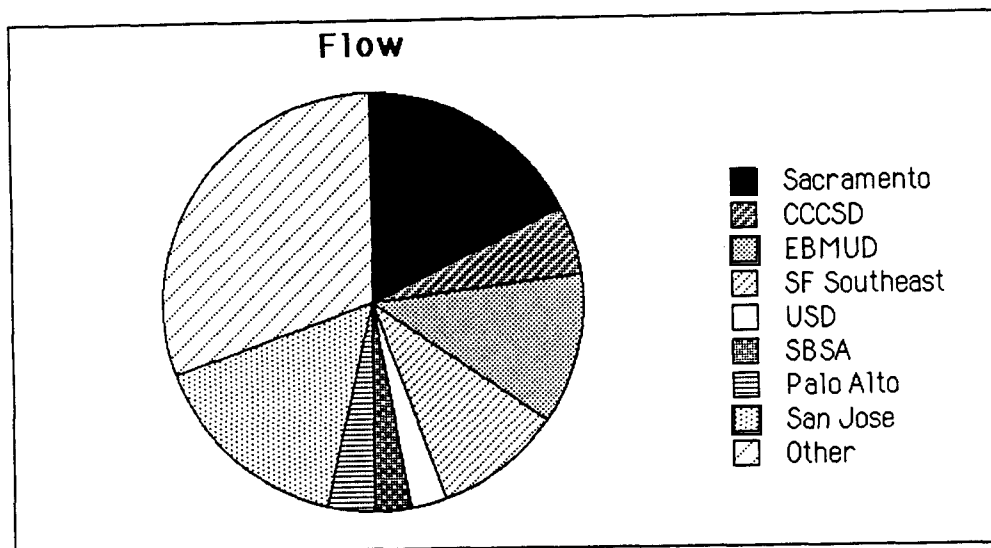
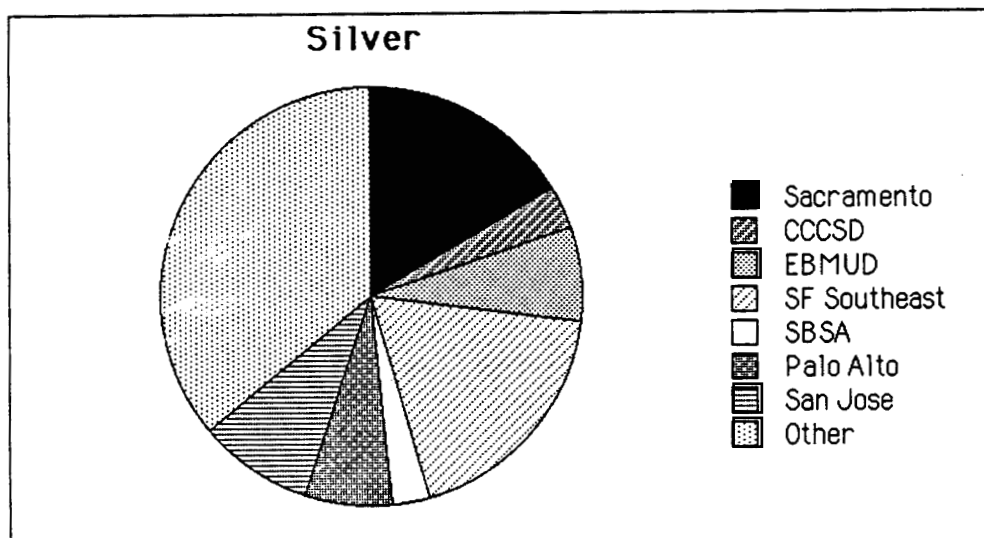


Figure 2. Average flows from the eight largest POTWs in the Bay-Delta, 1984-1986. "Other" includes all other treatment plants.

Table 8. Average loadings (kg d^{-1}) of silver from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	1.50	3.50
CCCSD	0.27	0.70
SF: Southeast	1.67	2.53
EBMUD	0.65	0.68
Union SD	0	1.38
SBSA	0.25	0.25
Palo Alto	0.59	0.62
San Jose	0.79	0.79
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Total	5.72	10.45
% of all POTWs	64%	53%



(detection limit = $5 \mu\text{g L}^{-1}$), while in 1985 and 1986 it was detected in 12 of 24 analyses with a minimum average concentration of $5.1 \mu\text{g L}^{-1}$.

Napa Sanitation District (Napa SD) appears to be a potentially major source of silver. Concentrations above $100 \mu\text{g L}^{-1}$ were reported on two occasions in 1984-1986, while wet season concentrations averaged $52 \mu\text{g L}^{-1}$. Few data are available for Napa SD, however, partially because wastewater is reclaimed during the dry season. Available data suggest an average loading of 2.84 kg d^{-1} , but the actual long-term average may be significantly lower than this.

The data from SF Southeast and Sacramento RWTP do not necessarily indicate that large spatial and temporal variation in silver loadings occurred in the estuary in 1984-1986. A more likely explanation for the observed discontinuities in concentrations (and thus loadings) is that actual levels of silver in these effluents are very near the limit of detection. Small variations in silver concentrations at that level can make the qualitative difference between their being reported as detected or as below detection limits. This qualitative difference then translates into extreme variation in calculated mass loading, which is probably largely illusory.

Studies of biological accumulation of silver in the South Bay have implicated the Palo Alto sewage treatment plant as a major source (Thomson et al., 1984). Palo Alto released significant amounts of silver in 1984-1986 (0.59 kg d^{-1}) but the largest source in the extreme South Bay was the San Jose-Santa Clara (SJSC) plant (0.79 kg d^{-1}). South Bayside System Authority (SBSA) and Hayward also contributed significant amounts of silver to the

South Bay.

* Copper. Copper loadings are distributed relatively evenly among the major POTWs (Table 9). These eight plants account for 57-78% of the total copper input to the estuary from POTWs. The largest single sources were SF Southeast, East Bay Municipal Utility District (EBMUD), SJSC, and the Sacramento RWTP. Major sources of copper, therefore, are found throughout the estuary.

Copper concentrations, and thus loadings, are relatively well quantified. Out of 195 analyses for copper by the eight major POTWs in 1984-1986, 173 detected the element. Much of the uncertainty in the range of average loading of copper is attributable to several results reported as BDL at the relatively high detection limit of $100 \mu\text{g L}^{-1}$ by Union Sanitary District (USD) in 1985 and 1986 (Table 9).

* Mercury. Mercury loadings from POTWs are not well quantified. A predominance of BDL values produces a broad range in the calculated average loading from POTWs in 1984-1986 (Table 10). Three of the major POTWs (Central Costa Sanitary District [CCCS], USD, and SJSC) failed to detect mercury in 28 total analyses.

SF Southeast consistently detected mercury in its effluent in 1984-1986 and was by far the largest quantified point source of this element. Thirty-nine percent of the minimum average total input from POTWs originated from this plant. SF North Point, which receives overflows from San Francisco's combined sewer system, also emitted as much as 0.15 kg d^{-1} (March 1985) during the wet season. Sixty-three percent of the minimum average loading to the estuary was released into the southern reach.

* Cadmium. The San Francisco Southeast plant was the

Table 9. Average loadings (kg d^{-1}) of copper from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	5.75	6.78
CCCSD	2.66	2.66
SF: Southeast	7.80	8.37
EBMUD	6.82	7.28
Union SD	2.92	7.93
SBSA	2.92	2.92
Palo Alto	3.14	3.14
San Jose	5.91	5.91
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Total	37.92	44.99
% of all POTWs	78%	57%

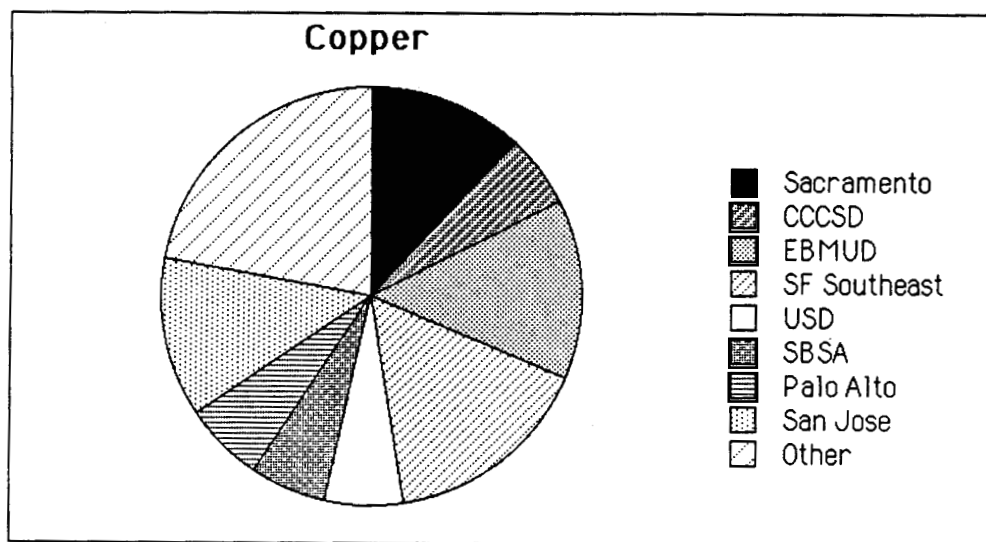
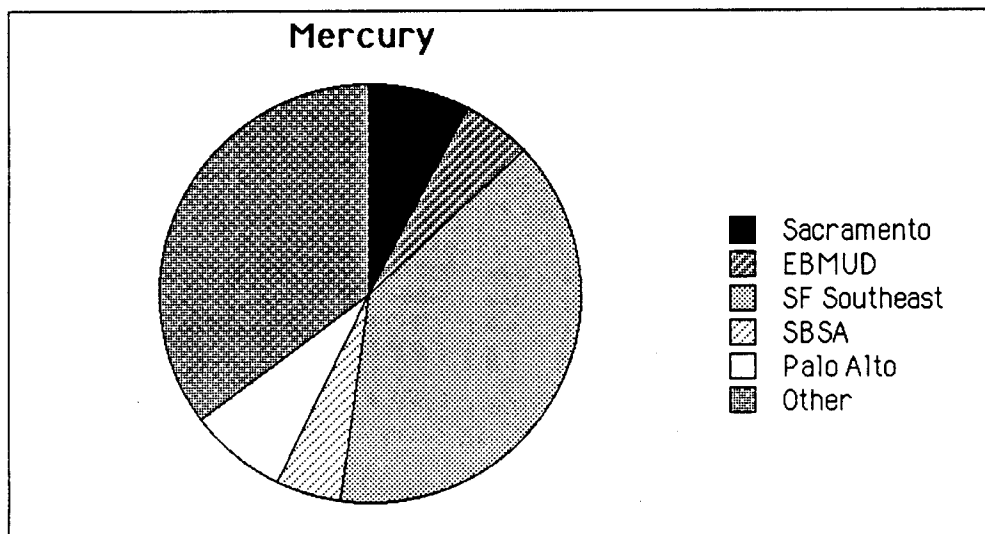


Table 10. Average loadings (kg d^{-1}) of mercury from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	0.035	0.121
CCCSD	0	0.150
SF: Southeast	0.177	0.195
EBMUD	0.024	0.088
Union SD	0	0.084
SBSA	0.023	0.577
Palo Alto	0.034	0.034
San Jose	0	0.090
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Total	0.293	1.339
% of all POTWs	65%	71%



largest single source of cadmium among the POTWs, contributing 17-28% of the total loading (Table 11). Other major sources were also concentrated in the South Bay, including SJSC, SBSA, and Palo Alto. The South Bay received 65% of the cadmium released from POTWs. The eight plants accounted for 83% of the total minimum mass loading of cadmium by POTWs.

Cadmium emissions from POTWs were characterized moderately well, as indicated by the comparatively small ranges of the average values presented in Table 11. Seven of eight results reported by USD in 1985 and 1986 as below a $10 \mu\text{g L}^{-1}$ limit of detection account for much of the difference between the minimum and maximum average loadings for this element.

* Lead. Once again, the SF Southeast plant released the greatest amount of this element of any POTW, a minimum average of 6.79 kg d^{-1} (Table 12). Much of the total mass loading of lead from this plant occurred in 1984. The minimum average loading of lead in that year was 15.7 kg d^{-1} . This quantity fell to 2.0 kg d^{-1} and 2.7 kg d^{-1} in 1985 and 1986, respectively. SJSC in 1984-1986 discharged an average of 6.01 kg d^{-1} , an amount comparable to the three-year average for SF Southeast. Together, these two plants contributed 49% of the minimum average loading of lead from POTWs. The southern reach received 69% of the lead that entered the estuary in 1984-1986.

Lead concentrations in POTW effluents were relatively well quantified, indicated by a small range of average mass loading (Table 12). Infrequent detection by the Sacramento RWTP (9 of 36 analyses, detection limit of $5 \mu\text{g L}^{-1}$) and high detection levels reported by the SF Southeast plant account for much of the

Table 11. Average loadings (kg d^{-1}) of cadmium from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	0.23	0.64
CCCSD	0.65	0.90
SF: Southeast	1.46	1.67
EBMUD	0.26	0.33
Union SD	0.07	0.81
SBSA	0.41	0.41
Palo Alto	0.30	0.37
San Jose	0.90	0.90
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Total	4.28	6.03
% of all POTWs	83%	60%

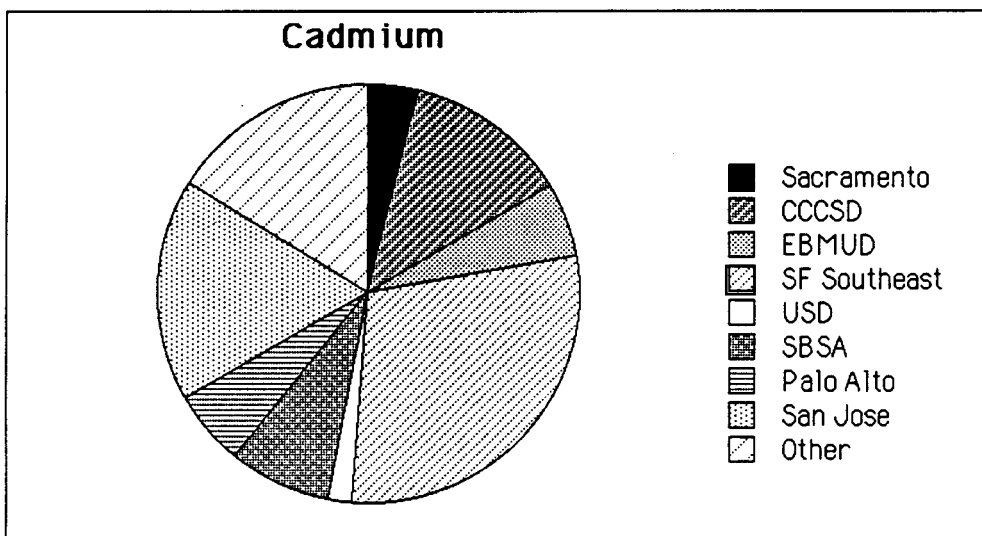
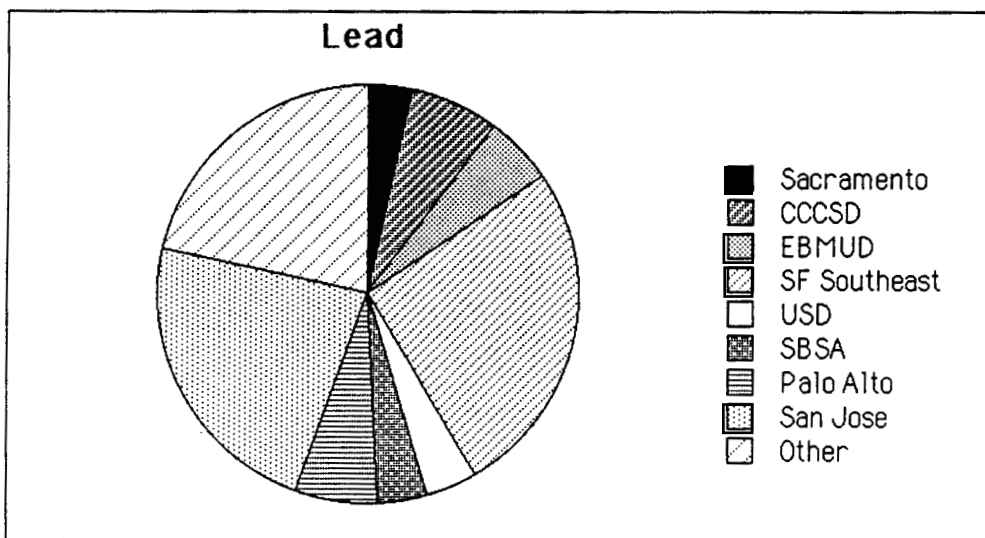


Table 12. Average loadings (kg d^{-1}) of lead from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	0.85	2.88
CCCSD	1.78	2.38
SF: Southeast	6.79	8.80
EBMUD	1.44	2.00
Union SD	1.00	1.10
SBSA	1.04	1.19
Palo Alto	1.68	1.71
San Jose	6.01	6.01
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Total	20.59	26.07
% of all POTWs	78%	66%



uncertainty in the final average.

* Zinc. Zinc showed a different spatial pattern than that seen for most elements discussed previously. The largest source of zinc among the POTWs was the Sacramento RWTP, which released an average of 44.7 kg d^{-1} into the northern Delta in 1984-1986 (Table 13). The eight major treatment plants discharged 73-76% of the total quantity of zinc from POTWs. Major sources in the Bay were EBMUD, SJSC, and SF Southeast.

Zinc is the best quantified of the trace elements monitored by POTWs, with a very narrow range associated with its long-term average mass loading (Figure 1).

* Chromium. The eight major treatment plants released 84-89% of the total amount of chromium from POTWs. Chromium also showed a different spatial pattern from many of the other elements, with the greatest input taking place in the Central Bay (Table 14). EBMUD was the greatest single source (5.07 kg d^{-1}), followed by SF Southeast, Sacramento RWTP, and SJSC. Most of the mass emission of chromium by EBMUD occurred in 1984. A particularly high loading in September 1984, 37 kg d^{-1} (based on a concentration of $130 \mu\text{g L}^{-1}$), had a strong influence on average loading in that year.

Chromium was detected in most analyses by the eight POTWs over the three-year period. The average mass loading estimate therefore has a narrow range of 15.2 to 17.6 kg d^{-1} .

* Nickel. Nickel loadings are distributed quite evenly among the major POTWs that discharge into the Bay, with only a minor contribution by Sacramento RWTP in the Delta (Table 15). SJSC is the largest single source, followed by EBMUD and SF Southeast. These eight plants discharge 70-82% of the total from

Table 13. Average loadings (kg d^{-1}) of zinc from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	44.7	44.7
CCCSD	6.6	6.6
SF: Southeast	22.1	22.2
EBMUD	24.1	24.1
SD	7.9	7.9
SBSA	6.6	6.6
Palo Alto	6.9	6.9
San Jose	22.2	22.2
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Total	141.1	141.2
% of all POTWs	76%	73%

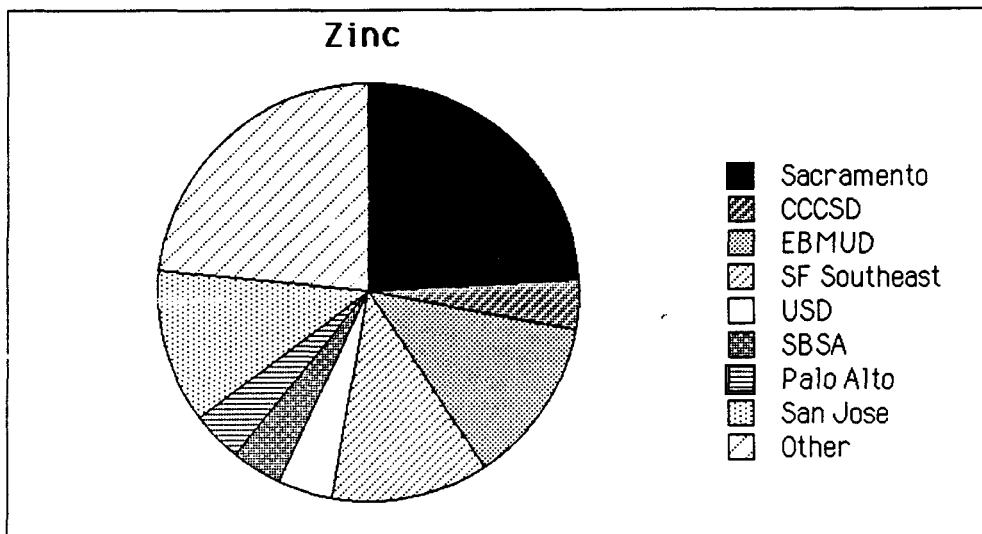


Table 14. Average loadings (kg d^{-1}) of chromium from the eight largest POTWs in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	2.75	3.84
CCCSD	0.14	0.77
SF: Southeast	3.46	3.46
EBMUD	5.07	5.29
Union SD	0.13	0.59
SBSA	0.66	0.66
Palo Alto	0.97	0.97
San Jose	2.06	2.06
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Total	15.25	17.64
% of all POTWs	89%	84%

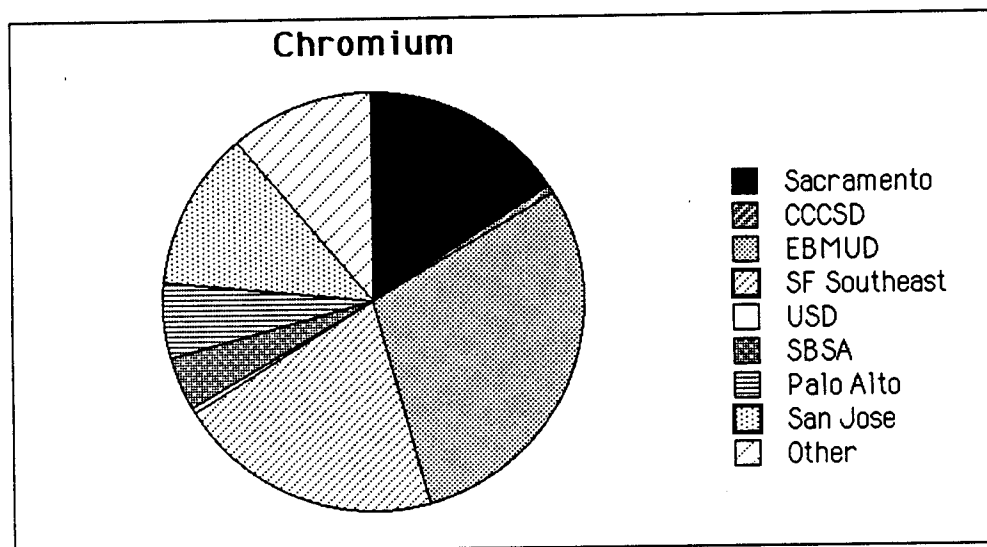
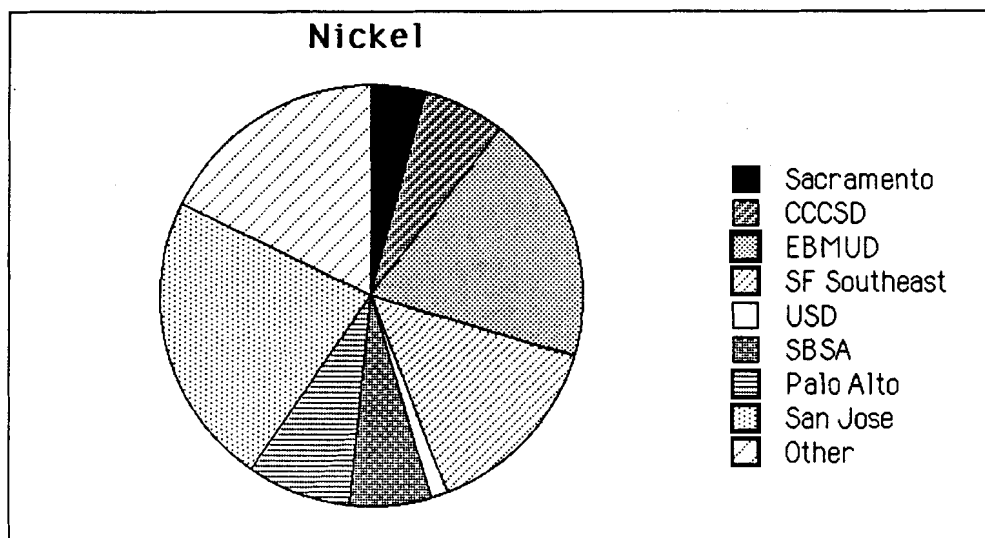


Table 15. Average loadings (kg d^{-1}) of nickel from the eight largest POTWS in the Bay-Delta, 1984-1986. Chart depicts minimum average loadings.

	<u>Min</u>	<u>Max</u>
Sacramento Regional	1.99	3.77
CCCSD	3.13	3.13
SF: Southeast	7.19	10.45
EBMUD	9.46	9.46
Union SD	0.52	3.67
SBSA	3.23	3.23
Palo Alto	3.76	3.76
San Jose	11.19	11.19
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Total	40.47	48.66
% of all POTWS	82%	70%



all POTWS.

Nickel is moderately well quantified, as most POTWS detect nickel with great consistency. High detection limits for analytical methods employed by SF Southeast and USD (up to $56 \mu\text{g L}^{-1}$ and $50 \mu\text{g L}^{-1}$, respectively) account for much of the range of average loading calculated for this element.

* Arsenic. Arsenic concentrations in municipal effluents are poorly characterized. SJSC releases most of the total from the eight major POTWS into the extreme South Bay. Four of the major POTWS (Sacramento RWTP, CCCSD, USD, and SBSA) did not detect arsenic at all in 37 total analyses. Detection limits for the above four plants in general ranged from 5 to $10 \mu\text{g L}^{-1}$. Average concentrations detected by SJSC and other plants are below $5 \mu\text{g L}^{-1}$; thus it is not surprising that the POTWS cited above did not detect the element.

* Priority Pollutants. Accurate analysis of concentrations of synthetic organic chemicals in wastewater is a demanding task. Actual concentrations in wastewater typically are near or below the detection limits of the methods employed in analysis and results can be affected significantly by contamination of samples, analytical interferences, and other factors. Quality control is therefore a crucial component of reported priority pollutant data.

The SFBRWQCB requires quality control testing of the POTWS that conduct priority pollutant analyses. Although a few POTWS report quality control results on analyses of pesticides and trace elements, this testing focuses mainly on volatile and semi-volatile organics. As mentioned above, quality control testing was somewhat more comprehensive in the initial year of priority

pollutant monitoring. Most POTWs conducted analyses of duplicate samples at least once that year, and many had at least one travel blank analyzed. Analyses of duplicates and travel blanks are no longer explicitly required, though several POTWs still perform them. Recovery rates for analyses of volatile and semi-volatile organics, however, have been reported regularly since the program began in 1984.

Infrequent analyses of travel blanks from 1984-1986 detected several compounds which were often reported as being present in POTW effluent samples. Phthalates were the main class of compound detected in blanks analyzed for semi-volatile organics. Also detected in travel blanks analyzed for semi-volatiles were 1,2-diphenyl hydrazine, n-nitrosodiphenylamine, and phenol. Travel blanks analyzed for volatile organics were found to contain chloroform and dichloromethane.

Analyses of method blanks in 1986 detected many of the same compounds detected in travel blanks. Method blanks analyzed for semi-volatile organics often contained concentrations of phthalates, particularly bis(2-ethylhexyl)phthalate. On one occasion the potent carcinogen benzo[a]pyrene was detected. Method blanks analyzed for volatiles have frequently shown positive results for dichloromethane, toluene, and chloroform.

EPA's presentation of Method 624 (volatiles) includes a discussion of potential interferences in the analysis. Volatile organics, especially dichloromethane, can diffuse through the seals of sample containers during transport of samples. Travel blanks can identify this source of contamination. Other potential sources for contamination of samples are impurities in the purge gas, outgassing from plumbing, and solvent vapors in

the laboratory.

Specific substances that were common contaminants for Method 625 (semi-volatiles) are not discussed in EPA (1984). It is stated, however, that contamination may arise from impurities in solvents and reagents, and from substances present on sample processing hardware. Phthalate esters, which were detected regularly in blanks analyzed by POTWs, are common interferents in analyses of plastics and are easily extracted from plastic products when these are used in the processing of samples.

Effluent concentrations reported for the organics that were detected in blanks should be interpreted with great caution. Analytical results for most effluent samples are not accompanied by results for travel or method blanks. In general it is therefore not possible to distinguish positive results that reflect concentrations in wastewater from those that reflect contamination of the sample.

Recovery rates reported for analyses of volatile and semi-volatile organics cast further doubt on the accuracy of concentrations measured in effluents. A summary of the largest and most comprehensive set of recovery data is shown in Table 16. These data are for analyses of semi-volatiles (Method 625) and were all reported in 1986. Average recoveries for the method as stated by EPA (1982) are included in the Table for comparison. Recoveries of 16 compounds were an average of 18% lower (based on 151 individual observations) than those reported by EPA (1982). Recoveries for Method 624 were also reviewed, but few observations were available for each compound tested. Recovery rates for 19 volatile organics (based on 102 observations) were an average of 11% lower than those in EPA (1982).

Table 16. Spike recoveries for semi-volatile organics (EPA Method 625), 1986

											EPA 1982			
Compound Name			% recoveries								Mean	SD	Mean	SD
Phenol	19	--	78	53	68	57	105	65	36	60	48.6	25.0	36	21
2- Chlorophenol	19	77	98	53	75	98	55	63	53	41	63.2	24.7	71	25
N- Nitroso-di-n-propylamine	25	43	45	75	30	125	21	54	38	96	55.2	33.7	76	45
Hexachloroethane	17	35	31	18	13	21	--	49	10	39	25.9	13.2	52	26
Isophorone	29	43	59	73	--	96	125	31	38	92	65.1	33.6	77	42
2,4-Dimethylphenol	18	45	65	69	68	128	105	49	37	47	63.3	32.4	58	26
2,4-Dichlorophenol	21	15	70	62	60	135	57	67	48	26	56.1	34.1	80	21
1,2,4-Trichlorobenzene	21	30	38	27	29	33	58	59	18	46	35.9	14.3	69	26
4-Chloro-3-Methylphenol	26	--	75	63	52	33	58	73	63	55	55.3	6.6	75	21
2,4,6-Trichlorophenol	24	40	74	64	56	44	42	49	59	49	49.7	14.1	81	20
2-Chloronaphthalene	6	19	56	32	33	75	46	75	12	16	37.0	25.2	79	27
2-Methyl-4, 6-Dinitrophenol	13	94	65	6	80	10	80	79	95	59	53.1	35.3	90	35
Pentachlorophenol	21	103	95	48	75	3	43	90	88	29	59.5	35.2	66	36
Phenanthrene	38	43	75	48	46	100	42	50	50	92	58.4	22.3	76	22
Fluoranthene	34	48	69	98	63	81	42	53	55	108	65.1	24.1	80	26
Butylbenzylphthalate	28	38	69	--	--	56	--	--	--	71	52.4	19.0	74	43

Of the 84 volatile (Method 624) and semi-volatile organics listed in Table 4 (page 25), just 15 were detected in greater than 10% of the analyses by POTWs in 1984-1986. Only chloroform was detected in greater than 50% of the analyses, with a detection frequency of 87% (153 of 176 analyses). The mean concentration of chloroform (based only on detected results) was $18 \mu\text{g L}^{-1}$. Other compounds detected nearly 50% of the time were bromodichloromethane (47.7%), dichloromethane (45.9%), and tetrachloroethene (45.6%). Mean detected concentrations of these three compounds were between 13 and $16 \mu\text{g L}^{-1}$.

Compounds discussed above as being common contaminants found in field and method blanks were among the most frequently detected organic priority pollutants. Chloroform, dichloromethane, toluene, phenol, and a number of phthalates comprised 8 of the 15 most frequently detected compounds. Clearly, comprehensive reporting of quality control testing is required in order to distinguish results for these compounds that reflect concentrations in treatment plant effluents from those produced by sample contamination in the field or in the laboratory.

Chlorinated and brominated compounds were also frequently detected in POTW effluents in 1984-1986, and make up most of the remainder of the 15 compounds detected in more than 10% of the analyses. Some of these which have not already been mentioned are bromodichloromethane, bromoform, dibromochloromethane, trans-1,2-dichloroethene, trichloroethene, 1,1,1-trichloroethane, 1,2-dichlorobenzene, and 1,4-dichlorobenzene. Chlorinated compounds can be created during the chlorination step in the wastewater treatment process, as evidenced by a comparison of

influent and effluent results from the SFBRWQCB one-year study (Rumjahn, 1986). It was speculated in Rumjahn (1986: Attachment D) that humic or fulvic material in treatment plant influents may supply bromine ions that react with other organic molecules to form organobromines.

The remaining 69 compounds listed in Table 4 were detected in less than 10% of the analyses. Forty nine compounds were detected only once or not at all. The total number of analyses for these organics from 1984 to 1986 averaged approximately 150. Detection limits were typically $1 \mu\text{g L}^{-1}$, with some variation occurring between laboratories and within laboratories over time.

Most of the trace elements which POTWs monitor under the pretreatment program (Table 4) are also analyzed on a more routine basis as required by NPDES permits issued by the Regional Boards. The pretreatment program, however, is the sole source of data on concentrations of antimony, beryllium, selenium, and thallium in POTW effluents. Selenium is an important toxicant in the Bay-Delta basin, and data for this element are discussed below.

Selenium was detected in 30 of 189 analyses in 1984-1986, a detection frequency of 16%. The mean concentration detected was $5.4 \mu\text{g L}^{-1}$. These analytical results were mostly generated using EPA Method 270.2 (EPA, 1983), an atomic absorption technique which is unreliable for selenium analysis, particularly when actual concentrations are near the method detection limit. This topic is discussed further under "Petroleum Refineries".

Detected concentrations of selenium were generally in the range of $1 - 5 \mu\text{g L}^{-1}$, although some higher values were reported. The highest concentration, $40 \mu\text{g L}^{-1}$, was reported by SF Southeast, and was an average of duplicate observations.

Fourteen plants scattered throughout the estuary detected selenium at least once in their effluent. However, only Benicia, Palo Alto, SJSC, and Sunnyvale detected the element more than once.

The data suggest that selenium is usually present in POTW effluents at concentrations in the range of $1 \mu\text{g L}^{-1}$. Even at that concentration, POTW effluents could be a major source of selenium in the estuary because of their large discharge volumes. For example, the SJSC plant, at an average concentration of $1 \mu\text{g L}^{-1}$ (which is not unlikely based on available data), would release an average of 0.5 kg d^{-1} . More accurate methods with lower detection limits and more frequent sampling are needed to determine the actual loadings of selenium from POTWs.

Analytical results for all of the priority pollutants (including the organics and trace elements mentioned above, as well as pesticides and PCBs) are presented in the Appendix to this report, available from AHI.

Summary. POTWs discharged an average of approximately 2.9 billion L d^{-1} of wastewater effluent into the Bay-Delta in 1984-1986. Seventy percent of this flow, and a comparable amount of the loading of toxic contaminants from POTWs, originated from eight major plants. Five of these eight plants discharge into the South Bay. POTWs release substantial amounts of nine trace elements that are of biological significance in the estuary. Loadings of copper, lead, zinc, chromium, and nickel are relatively well quantified in analytical terms. Silver, mercury, cadmium, and arsenic loadings are not well characterized because the detection limits of methods employed in their analysis approach or exceed actual concentrations in POTW effluents.

Petroleum Refineries

Petroleum refining is one of the major economic activities in the Bay-Delta region. In 1977, petroleum traffic in the Bay accounted for between three and four percent of the total volume of crude oil transported yearly by tankers throughout the world (Risebrough et al., 1978). The six refineries discussed here currently process approximately 671,000 barrels of crude oil per day into fuels, lubricants, asphalt, and other hydrocarbon products (SFBRWQCB, 1987). Chevron's Richmond Refinery is the largest of the six, processing an average of 256,000 barrels per day (SFBRWQCB, 1987) into over 300 different products (Jefferson Associates, 1987). Table 17 lists the refineries and describes the location of their outfalls.

Refineries produce several types of wastewater which vary in volume and quality. NPDES permit requirements focus on treatment and monitoring of "process" wastewater, which contains significant quantities of waterborne contaminants. The average rate of process wastewater discharge for these refineries in 1986 totaled 114 million L d⁻¹.

Other types of wastewater released from these facilities which receive less regulatory scrutiny are cooling water and stormwater runoff. Large volumes of cooling water are discharged from some refineries, but usually do not come into contact with sources of toxicants. Only Chevron and Union have separate discharges of cooling water. Stormwater runoff from refinery properties is also regulated in each NPDES permit. The refineries analyze stormwater runoff for only one of the parameters considered in this report, oil and grease. Refinery analytical results for oil and grease are not included in this

Table 17. Petroleum refineries in the Bay-Delta and average process effluent flows, 1984-1986.

Refinery	Segment of estuary receiving effluent	Average process ₁ flow (millions L d ⁻¹), 1984-1986
Exxon	Suisun Bay	8.2
Tosco	Suisun Bay	16.5
Shell Oil	Carquinez Strait	16.4
Union Oil	San Pablo Bay	9.3
Pacific Refining	San Pablo Bay	0.8
Chevron USA	San Pablo Bay	63

report because they are not presented in annual summaries, and review of monthly reports for this information was considered a relatively unproductive task. Furthermore, stormwater runoff from these facilities is a component of urban runoff, discussed in Section II.2 below.

Contaminants present in process wastewater partially reflect the composition of the crude oil being refined. Diverse classes of hydrocarbons are obvious components of crude oil. Also present are certain trace elements, including selenium (Kallio, 1976; Posthuma, 1977). Additional substances can enter the waste stream at different stages in the separation and chemical conversion of the crude oil.

Effluent Monitoring. Data on the parameters listed in Table 18 have been collected by Bay Area refineries for several years. In recognition of the fact that a number of potentially important contaminants were not included this list, the SFBRWQCB in February, 1985, initiated a program to determine effluent concentrations of additional trace elements and organics. These so-called "constituents of concern" are listed in Table 19. Starting in March 1985, samples were tested for trace elements once a month and for volatile (Method 624) and semi-volatile (Method 625) organics once every two months. In March 1986, trace element sampling was stepped up to once a week because of findings in the first year's monitoring of significant and consistent concentrations. Results of these analyses are submitted to the Regional Board along with normal monthly self-monitoring data.

Table 18. Standard parameters monitored by petroleum refineries,
1984-1986.

Total Chromium	Ammonia-nitrogen
Hexavalent Chromium	Oil and Grease
Zinc	Phenols
	Sulfides

Table 19. The "constituents of concern" monitored by petroleum refineries in 1985 and 1986.

Aluminum	Mercury
Arsenic	Nickel
Cadmium	Selenium
Cobalt	Vanadium
Copper	Cyanide
Lead	Volatile Organics (EPA 624)
	Semi-volatile Organics (EPA 625)

Chemical analyses for trace toxic contaminants are primarily performed by commercial laboratories, while other analyses are conducted by the dischargers. Standard methods (EPA, 1983, 1984) are used in sampling and analysis of trace elements, organics, and other parameters. Individual methods are mentioned below where necessary. Quality control data for the analyses are not regularly submitted. One set of quality control results was provided by each refinery as part of a special five week study in April and May of 1986 on analyses of trace elements and organics.

Findings. Ranges of average loadings of all of the contaminants listed in Tables 18 and 19, except the organic priority pollutants, are presented for each refinery in the Appendix to this report, available from AHI. Statistical summaries of data collected on the organic priority pollutants also appear in the Appendix. Toxic contaminants with the greatest potential biological significance in the estuary are discussed here.

Fig. 3 summarizes the ranges of average mass loading for selected contaminants in refinery process effluents from 1984-1986. Three-year average loadings for individual refineries are summed. The solid bars for each contaminant represent means calculated with values reported as below the detection limit (BDL) set equal to zero. These solid bars can be considered a minimum average loading based on reported concentrations. The taller, lightly shaded bars show maximum mean loadings, calculated with BDL values set equal to the detection limit. Actual average loadings are most likely to lie somewhere between the minima and maxima indicated.

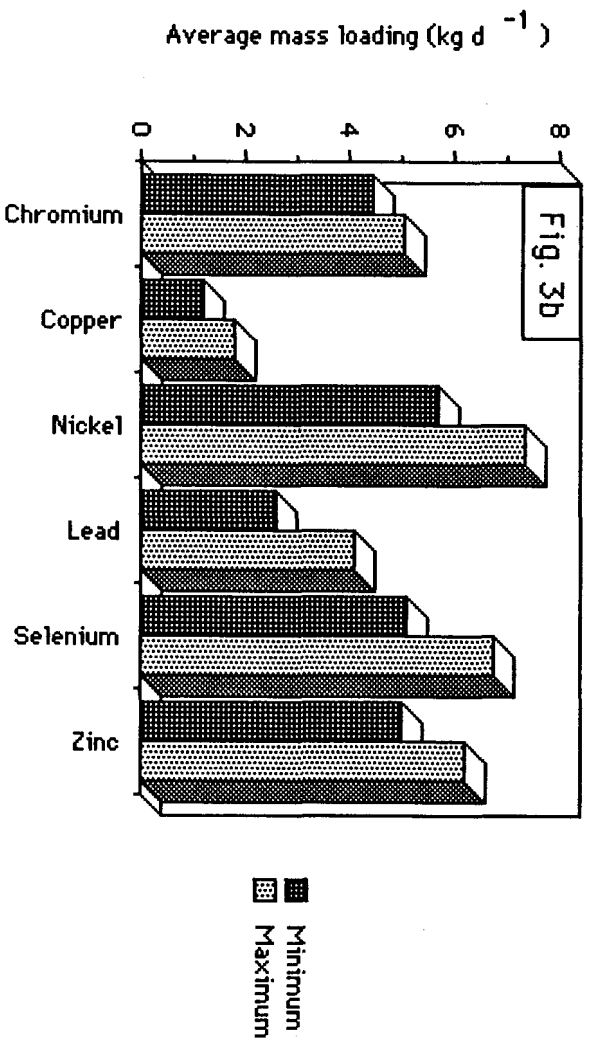
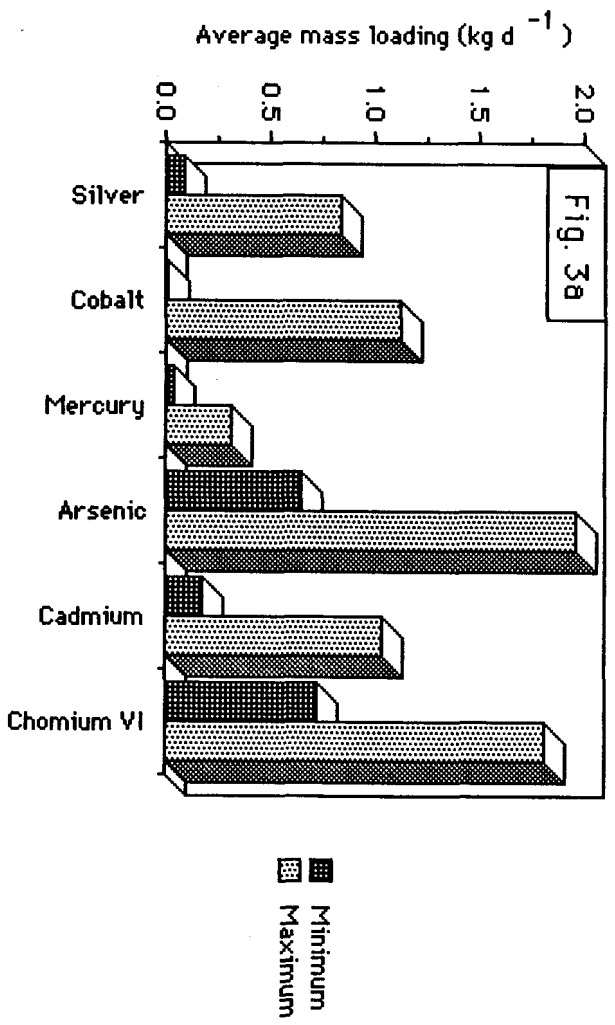


Fig. 3. Summary of ranges of average mass loading for selected contaminants in refinery process effluents, 1984 to 1986.

Relatively large and/or frequently occurring BDL values were reported for the contaminants with maxima that are markedly elevated above the minima. Silver, for example, was reported as BDL in 56 out of 78 samples. The maximum possible average loading for silver, as a consequence, is much greater than the average based on detected concentrations alone. Other contaminants with poorly quantified average loadings, as seen in Fig. 3(a), are cobalt, mercury, arsenic, cadmium, and hexavalent chromium.

Contaminants with relatively small differences between minimum and maximum loadings in Fig. 3(b) are detected frequently in refinery effluents and are being released into the estuary in significant amounts. Included in this category are chromium (total), copper, nickel, lead, selenium, and zinc. Table 20 presents three-year average ranges of mass loadings for each of these trace elements. Flow data are also included in Table 20, with flow from each refinery expressed as a percentage of the total from the group.

Chevron USA accounts for 55% of the process wastewater flow for the refineries, as well as a large proportion of the mass loading for each element. Broad ranges for trace element loadings from Chevron are largely responsible for the size of ranges seen in the refinery totals and are a result of unusual reporting by Chevron of analytical results in 1986. In mid-1986, Chevron began reporting all results below the level of quantitation as "below practical quantitation level (PQL)." Chevron's PQLs are several times greater than detection limit levels. Initially, the PQLs reported for some elements were quite high (Pb $65 \mu\text{g L}^{-1}$; Ni $111 \mu\text{g L}^{-1}$; and Se $48 \mu\text{g L}^{-1}$).

Table 20. Ranges of average loading of selected
contaminants (kg d⁻¹) from refinery process effluents,
1984-1986.

Process	Chevron		Exxon		Pacific		Shell		Tosco		Union		Totals	
Effluent	55%		7%		1%		14%		14%		8%			
(% of total)														
	Min ^a	Max ^b	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
=====														
Chromium	.86	1.39	.63	.63	.05	.05	1.39	1.41	.93	.99	.58	.58	4.44	5.05
Copper	.53	.97	.06	.08	.03	.03	.34	.38	.18	.24	.08	.11	1.21	1.79
Lead	1.71	2.72	.04	.09	.03	.03	0	.09	.32	.37	.52	.83	2.61	4.12
Nickel	3.45	4.97	.09	.12	.06	.07	1.26	1.32	.63	.65	.18	.20	5.68	7.33
Selenium	.92	2.20	.32	.35	.04	.05	1.67	1.99	.60	.64	1.53	1.53	5.09	6.76
Zinc	2.59	3.04	.46	.46	.09	.09	1.08	1.10	.38	.43	.39	.40	4.99	6.20
=====														

- a) Minium average loading calculated with bdl values set equal to zero.
b) Maximum average loading calculated with bdl values set
equal to the detection limit.

These PQLs were reduced appreciably (Pb $11 \mu\text{g L}^{-1}$; Ni $6 \mu\text{g L}^{-1}$; and Se $1.8 \mu\text{g L}^{-1}$) by the end of 1986. The temporarily high PQLs, however, significantly influenced the ranges of mass loading presented in Table 20.

The range of average loading of selenium from refinery discharges is comparable to the amounts which enter the estuary via the Sacramento and San Joaquin Rivers (see section II.4, below). Of the minimum average loading of selenium (Table 20), Shell, Union, and Chevron contributed 33%, 30%, and 18%, respectively.

Relatively high average concentrations of selenium reported for process effluents from Shell and Union explain the large contributions of those two refineries. Selenium was detected in Shell's effluent in 11 of 13 months, with a minimum average concentration of $112 \mu\text{g L}^{-1}$. Mass loading from Shell's effluent increased sharply in late 1986 (see Fig. 4). The average loading (based on 4 samples) in September was 4.84 kg d^{-1} , and the average for October (5 samples) was 4.68 kg d^{-1} . One sample measured at $480 \mu\text{g L}^{-1}$ in October indicates a loading of 6.83 kg d^{-1} .

Selenium in Union's process effluent was detected in all 16 months in which it was analyzed, at an average of $173 \mu\text{g L}^{-1}$. Loadings from Union were relatively constant in 1986, with a maximum monthly average of 2.40 kg d^{-1} in May. The minimum average loading for Chevron, 0.92 kg d^{-1} , is heavily influenced by a single observation in May 1985 (the first month of Chevron's selenium monitoring). The reported concentration, if accurate, translates into a mass loading of 8.58 kg d^{-1} . Selenium was measured above detection limits in Chevron's effluent in just 6 of 18 monthly average concentrations.

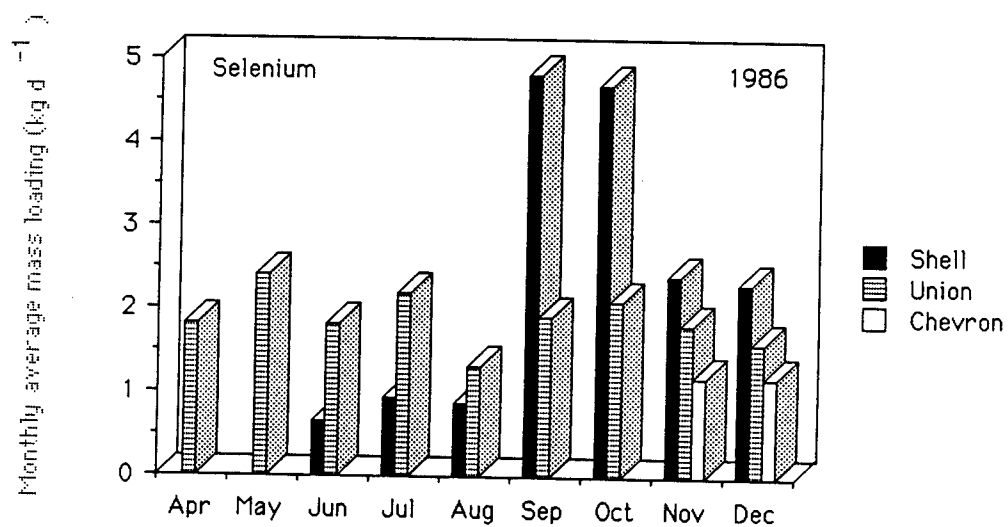


Fig. 4. Monthly average selenium loadings from Shell, Chevron, Union refineries (1986).

There is reason to be skeptical about Chevron's May 1985 result, as well as of selenium analyses by other refineries before late 1986. In September 1986, the SFBRWQCB requested the refineries to adopt a hydride generation analytical technique (Method 270.3 in EPA, 1983), instead of the graphite furnace/atomic absorption (GF/AA) (Method 270.2 in EPA, 1983) and inductively coupled plasma (ICP) (Method 200.7 in EPA, 1984) techniques which had been employed previously. The hydride generation method is the most accurate method for determination of selenium (Cutter, 1978). Limited quality control data submitted by the refineries for selenium analyses verify the inaccuracy of the GF/AA and ICP methods. Average spike recovery rates for the GF/AA technique, which was employed most of the time, were around 50%. The discontinuity in Shell's monthly average loadings at the end of 1986 (Fig. 4) are probably explained to some degree by the change in analytical methods at that time.

Cutter (1987) measured selenium concentrations in refinery effluents in samples taken on 24 February 1987, employing an extremely sensitive hydride generation method with detection limits in the ng L^{-1} range. These observations are compared with ranges of long-term average concentrations generated from NPDES self-monitoring data in Table 21. Cutter's data provide evidence that the long-term averages are probably reasonably accurate. The refineries also contribute significant loadings of chromium, lead, and nickel to the estuary (Table 20). Chevron releases 66% of the minimum average loading of lead from refineries, and 61% of the minimum average loading of nickel. Weekly analyses of trace elements by Chevron in late 1986 yielded few positive

Table 21. Results of analyses for selenium in refinery effluents: Long-term averages based on NPDES self-monitoring and a single analysis by Cutter, 1987.

Selenium concentrations, $\mu\text{g L}^{-1}$		
Refinery	Average concentrations from NPDES monitoring, 1985-198	Cutter February 1986 Dissolved Selenium
Chevron	18.5 - 43.4	13.0
Exxon	38.7 - 42.7	65.0
Pacific	48.1 - 58.2	6.6
Shell	112.2 - 133.7	132.0
Tosco	45.6 - 50.4	21.8
Union Oil	173.2	156.3

results for lead (1 detection in 22 analyses from September to December, with a detection limit of $11 \mu\text{g L}^{-1}$). These results suggest that loadings were declining in late 1986, but the actual levels at that time were poorly characterized. The frequent occurrence of BDL values for lead is reflected by a broad range of Chevron's average mass loading, $1.71 - 2.72 \mu\text{g d}^{-1}$ (Table 20). Nickel, on the other hand, was consistently detected by Chevron in September to December 1986, with an average concentration of $90 \mu\text{g L}^{-1}$. Chevron, therefore, continued to be a significant source of nickel at the end of 1986.

The largest single average loading of chromium, $1.39 \mu\text{g d}^{-1}$, is released into the Carquinez Straits by Shell (Table 20). Contributions to the total chromium loading, however, are distributed rather evenly among the six refineries. The estimated loading for chromium has a relatively small range (Fig. 3) because of its very high frequency of detection by all six refineries. Copper and zinc loadings from the refineries (Table 20) are relatively minor compared to the total loadings from other sources, including POTWs and the tributaries of the Delta.

All of the refineries discharge their process effluent in the portion of the Bay stretching from the lower Suisun Bay to Richmond. Total loadings for each of the contaminants listed in Table 20, therefore, are of potential significance on a local scale.

Summary. The six petroleum refineries discussed above contribute significant loadings of selenium, chromium, nickel, lead, copper, and zinc to the estuary. Selenium loadings, in particular, are substantial and are comparable to inputs from each of the San Joaquin and Sacramento Rivers. Reliable analytical

methods for selenium adopted in October 1986 confirm the presence of elevated levels of selenium in process effluents. Long term average loadings for arsenic, cadmium, cobalt, hexavalent chromium, and mercury are uncertain because of a prevalence of results below the limit of detection.

Large Industrial Dischargers

This is a miscellaneous group of dischargers that are potentially significant sources (relative to other point sources) of toxic contaminants to the estuary. Those included in this category discharge more than 400,000 L d⁻¹, and each monitors its effluent for several toxic pollutants. The facilities are listed in Table 22. This category will not be treated as a homogeneous source of pollution. The grouping is intended only to aid organization of the information presented in this report.

Trace elements, organic chemicals, and inorganic chemicals are found in wastewaters from these facilities. These substances originate from activities related to the manufacture of diverse products, including agricultural pesticides and fertilizers, chlorinated solvents, steel, paper, sugar, and others. Effluents produced which are monitored for pollutants consist of process wastes, usually in combination with various blowdowns, washdowns, and storm runoff. The total flow from these facilities in 1984-1986 averaged 109 million L d⁻¹.

These dischargers monitor for specific pollutants associated with each different manufacturing process. No special monitoring programs have been initiated for these dischargers by the Regional Boards. Some unusual analyses, however, are regularly performed by the plants which produce agricultural chemicals and organic solvents. These include analyses for individual chemical

Table 22. Dischargers treated in the "large industrial dischargers" category in this report, their siting and average discharge flows.

Company (outfalls) -----	Segment of the estuary receiving waste -----	Average flow, 1984- 1986 (million L d ⁻¹) -----
Libbey-Owens-Ford	San Joaquin River	0.8
McCormick and Baxter (E001, E002)	San Joaquin River	0.8
Dow Chemical	Suisun Bay	1.5
General Chemical	Suisun Bay	4.2
United States Steel	Suisun Bay	75.7
Stauffer Chemical, Martinez	Carquinez Straits	0.4
C & H Sugar (E002)	Carquinez Straits	3.8
Mare Island Naval Shipyard	San Pablo Bay	1.9
Chevron Chemical	San Pablo Bay	0.8
Stauffer Chemical, Richmond	Central Bay	0.4
San Francisco Int'l Airport (E001, E002, E004)	South Bay	15.1
New United Motors	South Bay	3.4

	Total	108.8

end-products (e.g. Ro-Neet, produced by Stauffer Chemical in Richmond) and general scans for priority pollutants. Quality control results for these measurements are not submitted in routine self-monitoring reporting.

Findings. U.S. Steel in Pittsburgh is the only facility in this group which had an appreciable influence on the overall mass loading of contaminants in the estuary. All of the other dischargers in this group, and in all of the point source categories yet to be discussed, released amounts of contaminants that are noteworthy only on a small spatial or temporal scale.

U.S. Steel discharged a remarkable amount of chromium into Suisun Bay in 1984-1986. An average of 10.5 kg d^{-1} was released, one-third of the total from all point sources. Concentrations of chromium in U.S. Steel effluent often rose well above $100 \text{ } \mu\text{g L}^{-1}$, to a level as high as $890 \text{ } \mu\text{g L}^{-1}$ in September 1984. This concentration corresponds to a mass loading of 68 kg d^{-1} , more than twice the long-term average for all point sources. In the following month, another 59 kg d^{-1} were released. Although loadings in these two months were exceptionally high, average loading in other months was consistently in the range of 5 kg d^{-1} , still a significant input. Hexavalent chromium also was released in considerable amounts, with a three-year average of 6.7 kg d^{-1} . Copper, lead, nickel, and zinc were also present in this wastewater, but each contributed less than 1% of the total from point sources.

Chevron Chemical monitors its wastewater for a wide variety of toxic trace elements and organic chemicals. Extraordinary concentrations of trace elements were often measured in this effluent. Arsenic, chromium, copper, lead, nickel, selenium, and

zinc each were detected near or above $1,000 \mu\text{g L}^{-1}$ in 1984-1986. One extremely high result for selenium of $2,400 \mu\text{g L}^{-1}$ (suggesting a mass loading of 1.2 kg d^{-1}), was recorded in March 1985. Although selenium was not detected at all in most other analyses, this single value accounts for nearly 1% of the total calculated average loading of selenium from point sources in 1984-1986. In the absence of quality control information, it is not possible to be certain whether this unusual result represents a real peak in loading or analytical error.

Ultimate mass loadings of the other elements mentioned are minor in terms of overall estuarine inputs because of the small volume of this discharge. Chevron Chemical manufactures synthetic organic pesticides, and thus is required to monitor its effluent for many different products and intermediaries. Of these, only difolatan was detected in any analyses. Detected concentrations of difolatan were in the range of $0.2 \mu\text{g L}^{-1}$, which indicate a mass loading of 0.13 g d^{-1} at the time these samples were collected.

Data for U.S. Steel, Chevron Chemical, and the other dischargers included in this category are presented in the Appendix to this report, available from AHI. None of these other facilities released quantities of contaminants that approached 1% of the average total input to the estuary.

Groundwater Treatment Effluents

At the end of 1986 a total of 19 permits had been issued for facilities in the South Bay that extract and treat groundwater contaminated with organic solvents, and release the effluent to surface waters of the estuary. Many additional investigations of groundwater contamination are being conducted at other sites in

the South Bay. The total number of these permits may increase by around 75% in the near future (Olivieri et al., 1987). Facilities with these permits are manufacturers of computer products (Table 23). Groundwater contamination on their properties typically occurred by leakage of organic solvents from underground pipes or storage tanks.

Chlorinated organics--such as trichloroethane, trichloroethene, Freon, and chloroform--are the most common pollutants, and can be present in groundwater plumes well above the part per million level. Contaminated groundwater is extracted from wells and treated by carbon adsorption or air stripping. Available data are insufficient to allow an estimate of total average flows to the Bay from these operations.

Effluent Monitoring. Cleanup of these sites, directed by the SFBRWQCB, is a complicated task. The amounts of effort expended and data generated in characterizing the contamination and movement of groundwater in each case are enormous. Once the treatment system is in place at these sites, the most challenging regulatory work has been finished. Monitoring of the treatment system effluent does not receive primary emphasis, and the data consequently are usually not presented in a very useful format. Reported data typically are unsummarized and immersed in a profusion of monitoring data from groundwater testing wells. Furthermore, some dischargers do not measure flow of their final consolidated effluent, or present flow data in a concise form.

Locating and reviewing all of this diffuse information was beyond the scope of this study. Where feasible, however, unsummarized data for 1986 were extracted and summarized. The

Table 23. Facilities treating groundwater contaminated with synthetic organics, 1984-1986.

Facility -----	Outfall Location in the South Bay -----
Advanced Micro Devices	Calabazas Creek
Hewlett Packard (E. Arques)	Calabazas Creek
Intel (Magnetics)	Calabazas Creek
Magnetic Peripherals	Calabazas Creek
National Semiconductor	Calabazas Creek
Signetics (#28665)	Calabazas Creek
Signetics (#28720)	Calabazas Creek
TRW	Calabazas Creek
Fairchild Camera	Guadalupe River
IBM (#27961)	Guadalupe River
IBM (#28738)	Guadalupe River
Memorex	Guadalupe River
Precision Monolithics	Guadalupe River
Varian Associates	Guadalupe River
Teledyne	Permanente Creek
Applied Materials	San Tomas Aquino Creek
Intel (SC.III)	San Tomas Aquino Creek

majority of these discharges began after 1985; thus, although an exhaustive review was not carried out, the data are at least reasonably complete. Groundwater cleanup permittees are required to analyze for various groupings of volatile organics.

Findings. A comprehensive review of self-monitoring data from groundwater treatment facilities was not possible for this study, as discussed previously. This section will therefore characterize variation in the data reviewed, but will not estimate loadings from an exhaustive list of groundwater cleanup sites.

Table 24 summarizes data reviewed on these facilities. Compounds included in the Table had monthly average concentrations above detection limits at least twice in 1986 (data were collected for 1986 only, for reasons described above). Although analyses of many compounds are conducted by groundwater cleanup facilities, the cursory screening for this Table produced only a short list of compounds proven to be present in these effluents. Compounds analyzed but not appearing in the Table in general are present at less than $1 \mu\text{g L}^{-1}$ in the wastewaters, and would have very small and highly uncertain calculated mass loadings because actual concentrations are below the limit of detection. Loadings from this category of dischargers on the whole are poorly quantified.

The chemical composition of wastewaters from facilities included in Table 24 varied somewhat. The highest concentrations of organics were observed in effluent from two outfalls of National Semiconductor. Outfall E-3 released a monthly average of $63 \mu\text{g L}^{-1}$ of trichloroethene, the highest mean concentration for any of the monitored organics. This concentration implies a

Table 24. Minimum average mass loading of synthetic organic chemicals from groundwater cleanup sites, 1986.

<u>Discharger</u>	<u>Compound</u>	<u>Frequency of Detection</u>	<u>Mass Loading Average for Months Reviewed (bdl=0)</u>
Advanced Micro Devices	trichloro-ethylene	3/6	1.1-1.2
	1,1,1-trichloroethane	2/8	0.1-0.3
	1,2-dichloro-ethene	2/4	5.2-5.4
Applied Materials	1,1,1-trichloroethane	8/12	0.1
National Semiconductor:			
Outfall E-2	trichloroethane	9/10	4.0
	trichloroethene	9/10	1.9
	1,1-dichloro-ethene	9/10	1.0
	1,2-dichloro-ethene	9/10	6.7
	Total Volatiles	10/10	1 14.7
	acetone	3/10	1.5-3.4
Outfall E-3	trichloroethane	5/8	0.3
	trichloroethene	6/8	8.6
	1,2-dichloro-ethene	2/8	0.3-0.4
	Total volatiles	6/8	9.5
	acetone	2/8	0.9-3.0
Precision Monolithics	trichloroethene	3/11	0.2-0.6
	1,2-dichloro-ethene	8/11	0.7-0.9
Signetics:			
740 Kifer Rd.	trichloro-ethylene	11/11	0.1
	1,1,1-trichloroethane	11/11	0.1
811/440	trichloroethylene	11/11	6.1
	1,1,1-trichloroethane	9/10	3.4

maximum monthly average loading of any particular compound of 8.6 g d^{-1} (Table 24).

The average total loading of organic solvents detected in effluents at individual sites in this group (including Magnetic Peripherals and Varian, which are not included in Table 24 because neither detected a compound more than once in 1986), was approximately 6.4 g d^{-1} . If this figure is representative of quantified loadings for groundwater treatment facilities in general, then a crude estimate of the average total emission at 33 sites in the South Bay would be 211 g d^{-1} . Once again, this estimate does not account in any way for parameters which are not detected in these effluents often enough to be considered adequately quantified. Estimates of loadings for unquantified compounds can not be generated with any degree of confidence in their accuracy.

Minor Point Sources

This final category is made up of a very heterogeneous group of dischargers that have at least one of two things in common. Either they discharge small volumes of wastewater, or they perform very limited monitoring for toxic substances in their effluents. The magnitudes of toxic loadings from these sources therefore are generally small and not well characterized. The possibility should not be excluded, however, that these facilities could introduce locally significant loads of particular toxic pollutants into the estuary.

Table 25 lists the minor dischargers which performed any monitoring for the parameters reviewed in this report, and describes the locations of their outfalls. Dischargers involved in similar business activities are grouped together in the Table.

Table 25. Minor dischargers which monitored for at least one toxic parameter during 1984-1986. Industrial categories are descriptive only. Segments after Gunther (1987).

Discharger	Industry	Segment of estuary receiving waste
Mare Island Naval Shipyard	Power Plant	San Pablo Bay
PGE: Avon	Power Plant	Suisun Bay
PGE: Contra Costa	Power Plant	Central Delta
PGE: Hunter's Point	Power Plant	Central Bay
PGE: Martinez	Power Plant	Suisun Bay
PGE: Oleum	Power Plant	San Pablo Bay
PGE: Pittsburg	Power Plant	Suisun Bay
PGE: Potrero	Power Plant	Central Bay
Atlantic Richfield	Oil Terminal	Central Bay
Burmah-Castrol	Oil Terminal	Central Bay
Pennzoil	Oil Terminal	Central Bay
PGE: Oakland	Oil Terminal	Central Bay
Shell Oil (South SF)	Oil Terminal	Central Bay
Shell Oil (West Sacto.)	Oil Terminal	North Delta
Simmons Terminal	Oil Terminal	Central Bay
Texaco Inc.	Oil Terminal	Central Bay
Time Oil	Oil Terminal	Central Bay
Tosco Corp.	Oil Terminal	North Delta
Union Oil	Oil Terminal	Central Bay
Unitank	Oil Terminal	Central Bay
Wickland Oil	Oil Terminal	Carquinez Strait
Amchem	Chemical	South Bay
Shell Oil Co.	Chemical	Suisun Bay
Union Carbide: Solvent	Chemical	Central Bay
AAA Machine Shop	Dry Dock	Central Bay
Kaiser Steel	Dry Dock	San Pablo Bay
American Can (San Jose)	Metal	South Bay
American Can (Oakland)	Metal	Central Bay
Campbell Chain	Metal	South Bay
Kaiser Aluminum	Metal	South Bay
Allied Energy	Oil Production	Central Delta
Int'l Oil and Gas	Oil Production	Central Delta
John Pestana Family	Oil Production	Central Delta
Termo	Oil Production	Central Delta
Crown Zellerbach	Paper	Central Delta
Fibreboard	Paper	Central Delta
Pacific Paperboard	Paper	Central Delta
C & H Sugar	Sugar	Carquinez Strait
Discovery Bay	Lagoon	Central Delta
General Electric: Vallecitos	Nuclear Power	South Bay
Hysol/Dexter	Adhesives	Suisun Bay
IT Corporation	Hazardous Waste	Suisun Bay
Kaiser Aerotech	Rockets	South Bay
Lone Star	Cement	South Bay
Mohawk Rubber	Rubber	Central Delta
Owens-Illinois	Glass	Central Bay
Petromark	Cooking Oil	Central Bay
Sacramento River Water TP	Water Treatment	North Delta
Sharpe Army Depot	Depot	South Delta
Siliconix	Semiconductors	South Bay
Union Carbide: Linde Div.	Gases	Central Delta

Loadings from these sources are assessed in detail in the Appendix to this report. Two of these categories, power plants and oil terminals, have participated in special monitoring programs for toxic contaminants and are discussed briefly below. As the term is used here, "minor" refers only to the magnitude of documented loadings in 1984-1986, and does not correspond to the regulatory classification used by EPA.

Oil Terminals. The large amount of petroleum transported in the Bay-Delta region is stored and handled at many facilities. Most of these oil terminals are concentrated on the shore of Contra Costa County. These facilities blend, package, store, and transfer petroleum products. Shipping occurs via trucks, trains, and barges. Wastewater discharges from these operations consist of storm runoff and washdown from rinsing of grounds and equipment. This runoff can contain quantities of hydrocarbons that have spilled or leaked onto exposed surfaces. Flows from these dischargers occur mostly during the wet season.

In light of a suggested correlation between tissue concentrations of monocyclic aromatic hydrocarbons (MAHs) and the condition of striped bass in the Bay (Whipple et al., 1983), the SFBRWQCB and the U.S. Bureau of Reclamation (USBR) initiated a study to examine levels of MAHs in runoff from facilities that store and handle petroleum. Oil terminals were requested to analyze for MAHs (Method 602: EPA, 1984) on a monthly basis in 1985 and 1986. The compounds analyzed are listed in Table 26, and the dischargers participating are listed in Table 27. As detailed in the Appendix, sampling regimes for these analyses do not provide an adequate basis for mass loading estimation. In any case, mass transport in runoff from urban areas is

Table 26: Monocyclic aromatic hydrocarbons analyzed
by oil terminals, 1985 and 1986.

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Ethylbenzene
Toluene
Total Xylene

Table 27. Oil terminals analyzing MAHs in their discharges to the estuary, 1985 and 1986.

Facility -----	Segment of estuary receiving discharge -----
Atlantic Richfield	Central Bay
Burman Castrol	Central Bay
GATX Terminals	Central Bay
Shell Oil Company	Central Bay
Texaco	Central Bay
Time Oil Company	Central Bay
Union Oil	Central Bay
Wickland Oil	Carquinez Strait

generically treated in Section II.2 below; estimation of loadings based on this MAH monitoring would result in counting storm runoff from these facilities twice.

Power Plants. Power plants that generate electricity from the combustion of fossil fuels produce several types of wastewater. Tremendous quantities of water are withdrawn from the Bay by several types of industries, used for cooling, then released. Power plants are the principal users of Bay water for this purpose. Releases of "once-through cooling water" by power plants alone average over 6 billion L d⁻¹ (SFBRWQCB 1987, CVRWQCB 1987). This volume equals the average flow of the San Joaquin River in 1985.

Even though the volume of these releases far outweighs the volumes of other anthropogenic waste streams that enter the estuary, monitoring for toxic contaminants is not required for discharges that consist solely of cooling water. Sources of toxicants to these waste streams are thought to be absent. If toxic maintenance chemicals are added to the cooling towers, then monitoring is required. In practice, the addition of toxic chemicals rarely took place in the three year period. Toxic loadings from cooling water releases have been mishandled in the past (see Discussion below). No data were collected in 1984-1986 to provide a basis for loading estimates from this source. Fossil fuels used to generate electricity are stored and handled at these facilities. Storm runoff from these properties consequently contains contamination similar to that found in runoff from bulk oil terminals. Most of the power plants analyze storm runoff for oil and grease. MAH analyses (Method 602 in EPA, 1984) were also carried out by some plants in 1985 and 1986.

These plants are listed in Table 28.

The same problems encountered in interpreting the MAH data from oil terminals apply to hydrocarbon data from the power plants. The data collected are summarized and discussed in the Appendix to this report.

Other Minor Point Sources. Monitoring requirements for this group vary somewhat from discharger to discharger, but in general are minimal. Samples are typically taken quarterly or less often. Self-monitoring data for these facilities are summarized and discussed in the Appendix. As a whole, this group contributes insignificant quantities of the contaminants characterized in this report. Some of these facilities generate large discharges of cooling water, for which no data on toxic pollutants are collected. Many of these monitored flows are comprised of stormwater runoff or other intermittent waste streams.

D. Discussion

Table 29 summarizes the total average mass loading of trace elements from point sources in 1984-1986. POTWs were the principal source of most of these elements. The notable exceptions to this pattern were selenium and chromium. The petroleum refineries released selenium in quantities comparable to those from any other source category. These loadings are concentrated in the area between the Carquinez Straits and Richmond. The greatest single point source of chromium was the U.S. Steel plant in Pittsburgh.

Table 28. Power plants and other PG&E facilities analyzing MAH concentrations in runoff from their properties, 1984-1986.

Facility -----	Segment of estuary receiving waste -----
PG&E: Avon	Suisun Bay
PG&E: Martinez	Suisun Bay
PG&E: Pittsburg	Suisun Bay
PG&E: Oakland	Central Bay

Table 29. Ranges of average mass loading (kg d^{-1}) of trace elements from point sources, 1984-1986.

	Ag		Cu		Se		Hg		Cd	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
POTWs	6.8	16.6	45	74	*	*	.42	1.7	5.0	9.3
Refineries	0.1	0.8	1.2	1.8	5.1	6.8	.04	.31	0.2	1.0
Other	0	0.1	0.7	2.5	0.1	0.1	.01	.01	0	0
Totals	6.9	17.5	47	78			0.47	2.0	5.2	10.3

	Pb		Zn		Cr		Ni		As	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
POTWs	24	34	178	184	17	20	47	66	2.8	12.5
Refineries	2.6	4.1	5.0	6.2	4.4	5.1	5.7	7.3	0.6	2.0
Other	0.8	4.5	3.0	3.2	11	12	1.3	3.4	0.2	0.3
Totals	27	43	186	193	32	37	54	76	3.6	14.8

* Available data are an insufficient basis for a quantitative estimate.

The ranges presented for average loadings of these elements are indications of the degree to which concentrations in point source effluents are characterized in a quantitative analytical sense. Broad ranges (in terms of the ratio of the minimum to the maximum) result from the reporting of a high proportion of values below the limit of detection. Copper, selenium, lead, zinc, chromium, and nickel were more accurately described than the other elements in Table 29.

Comparison With Other Studies

Several assessments of toxic loadings to the estuary have been conducted in the last 10 years. Estimates generated by other researchers should not be compared directly to those presented in this report, however, until the different methods and scopes of the other studies are recognized. The following paragraphs outline some basic differences between this analysis and other frequently-cited studies.

Risebrough et al. (1978) presented estimates of average mass emissions of several trace elements into the Bay from 1975-1977. The Delta was not included in this analysis. Self-monitoring data were provided to the authors by the SFBRWQCB. Little is said of the original source of the data except that "many of the data are estimates only and are subject to revision." This statement leaves some doubt as to whether the estimates are based on reported data, or are derived in some other way. Estimates presented in that study, therefore, may not be directly comparable to those given in this report. Loading estimates in Risebrough et al. (1978) for refineries are presented only for oil and grease, chromium, and zinc. Oil and grease is the only parameter listed for other industrial sources.

Citizens for a Better Environment (CBE) conducted an analysis of toxic pollutant loadings to the Bay in 1982 (CBE, 1983). As in this study, data were obtained from self monitoring reports on file at the SFBRWQCB. Estimated loadings from POTWs were derived solely from data submitted in annual reports, and appear reliable on the whole. However, CBE presents estimates of total loadings to the Bay which are heavily influenced by estimated loadings from discharges of cooling water by power plants. As mentioned previously, power plants discharge immense volumes of cooling waters which are not monitored for contaminants. Contaminant loadings attributable to cooling water discharges are not addressed in this report because of the lack of data.

CBE's estimates of toxic loadings from these cooling waters were based on single analyses of contaminant concentrations in influent and effluent, conducted in the process of application for NPDES permits. Net loadings were estimated based on the differences between effluent and influent concentrations. These differences, however, are more likely to indicate analytical imprecision and contamination of samples rather than the presence of toxicant sources in the power plants. To illustrate, 40 $\mu\text{g L}^{-1}$ of thallium were found in the influent of the PG&E Pittsburg Power Plant, and the element was not detected in the effluent. This concentration difference translates (when multiplied by nearly 4 billion L d^{-1}) into a net removal of 52,000 kg yr^{-1} of thallium from the waters passing through the power plant. CBE ignored these apparent net removals in their calculation of net loadings. This example demonstrates how uncertainty in chemical analyses can lead to gross inaccuracy when loadings from large-

volume discharges are assessed.

The National Oceanic and Atmospheric Administration (NOAA) generated estimates of point source contaminant loadings to the Bay-Delta as part of an appraisal of pollutant discharges in the coastal areas of the entire continental U.S. (NOAA, 1987a). Their National Coastal Pollutant Discharge Inventory (NCPDI) is discussed in detail in Section II.2 below. The extensive scope of that project necessitated the use of generic information on categories of dischargers. Estimates for the Bay-Delta were based on generic concentrations of toxic contaminants in both POTW and industrial effluents (NOAA, 1987a). Flow data, however, were collected from the Regional Water Quality Control Boards. NOAA, like CBE, estimated loadings for 1982.

In Table 30, loading estimates from these three studies are compared with those presented in this report. Only data on POTWs are presented because monitoring data for these facilities discussed by Risebrough et al. included most of the same contaminants for which estimates were made in later studies, and CBE's treatment of these dischargers appears to be generally accurate.

Estimates by NOAA are substantially higher for most elements than those presented by CBE and in this report. The generic effluent concentrations employed by NOAA (1987a) apparently are higher than actual average concentrations for Bay-Delta POTWs. The data from Risebrough et al. (1978) and CBE (1983) include only discharges to the Bay. The significant loadings of contaminants from the Sacramento RWTP consequently were not included in either of those studies. CBE calculated their averages with values below detection limits set to zero; those loadings are comparable in terms of their method of calculation

Table 30. Comparison of average mass loading from POTWs with estimates by other researchers (kg d^{-1}).

	This study Preliminary data 1984-1986	Risebrough 1975-1977	CBE 1982	NOAA 1982
Ag	6.8-16.6	*	*	*
Cu	45-74	306	82	137
Hg	0.4-1.7	<20	0.7	1.0
Cd	5-9	24.5	8	47
Pb	24-34	131	49	110
Zn	178-184	453	38	533
Cr	17-20	182	26	120
Ni	47-66	106	72	*
As	3-12	13	6.5	77

* No estimate was made.

to the minima presented in this report. Risebrough et al. (1978) did not specify how values below detection limits were treated.

Despite the exclusion of the Sacramento RWTP, CBE and Risebrough et al. both tended to estimate higher average loadings than those in this report. The data suggest an apparent decline in loadings of these trace elements from POTWs in the last decade. In the absence of full documentation by Risebrough et al. (1978), however, it is difficult to discuss with confidence the significance of this apparent decline.

Other evidence, however, also suggests that the trend seen in the data does reflect actual decreases in loadings to the estuary over the last decade. Secondary or advanced treatment and pretreatment source control programs were adopted at many plants during this period, combining to reduce effluent contaminant concentrations. As an example, EBMUD (the third largest discharger in 1984-1986) has documented a sharp reduction in effluent loadings of a group of trace elements (including cadmium, chromium, copper, lead, nickel, and zinc) from a total of 790 kg d^{-1} in 1974 to 54 kg d^{-1} in 1986 (EBMUD 1985; 1986). Influent loadings to the treatment plant of these same metals have fallen from 1170 kg d^{-1} in 1974 to 160 kg d^{-1} in 1986.

The only discrepancy in the overall pattern suggested by the data in Table 30 is an unusually low loading estimated for zinc by CBE (1983). Typical zinc concentrations in Bay-Delta POTW effluents are significantly higher than those of all other trace elements, yet the zinc loading estimated by CBE was lower than those they computed for both nickel and lead. The reason for this discrepancy is unknown.

E. Conclusions

POTWs contributed 75% or more of the total point source loading of silver, copper, mercury, cadmium, lead, zinc, nickel, and arsenic to the estuary in 1984-1986. Petroleum refineries released most of the selenium that originated from point sources, in amounts that were on the same order of magnitude as inputs from the San Joaquin and Sacramento Rivers. Large loadings of chromium from a single discharger, U.S. Steel, accounted for a third of the total for this element from point sources.

The eight largest POTWs contributed most of the flow and contaminant loading from point sources in the estuary. Five of these eight plants are located in the South Bay.

Several of the trace elements and nearly all of the synthetic organic contaminants which were monitored by point source dischargers were not well quantified analytically. Detection limits of the methods employed in determining concentrations of these substances approach or exceed the actual levels present in effluents. Data generated for these contaminants are of limited value in an assessment of long-term trends in mass loading. Toxic contaminants with poorly characterized mass loadings that are of potential biological significance in the estuary would be better described by analytical methods with lower limits of detection. One notable inadequacy of the present database is the lack of meaningful data on selenium levels in POTW effluents.

The general absence of results of quality control testing for chemical analyses in 1984-1986 further constrains interpretation of these data. Quality control results should

accompany any reported measurements of contaminant concentrations, particularly if the concentration data are to be of value in assessments of historical trends in mass loading. Considering the expense involved in producing these data, it is unfortunate that more definitive interpretation of monitoring results from 1984-1986 is not possible.

Requirements for quality control testing and the presentation of these results need to be further developed. A considerable improvement in the database would result if such requirements focused in particular on the few major plants which contribute most of the point source contaminant mass loading to the estuary.

2. URBAN RUNOFF

A. Introduction

This section presents an estimate of the flow of toxic contaminants into the Bay-Delta ecosystem due to runoff from urban areas. In contrast to discharges from point sources, the chemical composition of urban runoff is poorly understood. Relatively few studies of urban stormwaters as a source of pollution have been undertaken, and only a very small subset of these have occurred in the Bay-Delta region. Consequently, the estimates of pollutant loads associated with urban runoff must be generated using acceptable mathematical relationships based in part on data collected in other parts of the country.

This section first briefly discusses the physical phenomenon of urban runoff and then describes the basic method used by most investigators to develop estimates of pollutant loads from urban stormwaters. This is followed by a discussion of data needs and availability, including strengths and weaknesses of the existing database. Previous loading estimates are summarized, including those of the National Oceanic and Atmospheric Administration National Coastal Pollution Discharge Inventory (NCPDI), which has been used to develop an assessment of the discharge of several toxic chemicals into the Bay-Delta estuarine system. Through the use of existing data, the assumptions underlying the NCPDI are examined and refined to produce a more accurate and complete estimate of the loading of contaminants to the Bay-Delta ecosystem from urban runoff.

B. Background

Upon reaching the ground, rainfall enters two hydrologic pathways. Some of the water is stored in the receiving ecosystem, where it is either returned to the atmosphere by evapotranspiration or slowly released into watercourses. The remainder of the precipitation flows out of the system, both above and below the surface of the ground, as runoff. The amount of runoff is influenced by many factors, including soil characteristics, topography, and rainfall volume.

Urban development can drastically alter the characteristic runoff patterns of a given region. Impervious surfaces, such as pavement, are substituted for permeable ones, reducing the ability of a region to store precipitation. Consequently, the volume and rate of runoff increase dramatically. A significant amount of public investment has gone into managing urban drainage through the development of systems of channels and conduits to collect and move urban stormwaters.

With the development of urban drainage systems has come growing awareness of the potential adverse impact of urban stormwater on receiving water quality. Pollutants deposited on urban surfaces are dissolved in runoff and carried into rivers, estuaries, and coastal ocean waters. The U.S. Public Health Service began to investigate this problem in the early 1960s after several investigators had reported significant levels of BOD, fecal coliforms, nitrogen, and phosphorus in urban runoff (Weibel et al., 1964). More recent research has demonstrated that urban stormwaters contain toxic pollutants, including trace metals, petroleum hydrocarbons, and synthetic organic chemicals. Atmospheric deposition, spills, deliberate dumping of wastes,

crankcase drippings from vehicles, and tire wear are among the sources of these substances.

With the institution of more complete control on pollutant discharges from point sources, greater attention is being focused upon urban runoff as an uncontrolled source of water pollution. An assessment of pollution from urban runoff was included by the U.S. EPA as a requirement of the Areawide Waste Management Plans funded under Section 208 of the Water Pollution Control Act Amendments of 1972. With Section 208 funding, local agencies were to identify important nonpoint sources of pollution and develop regulations or land use measures termed "best management practices" to control these sources. In practice, nonpoint pollution has not been accorded high priority in most areas, for a variety of technical, economic, and political reasons (Barton, 1978). In the San Francisco Bay Basin Plan, the Regional Water Quality Control Board identifies urban runoff as a significant source of pollution to San Francisco Bay (SFBRWQCB, 1982). Citing data from the Association of Bay Area Governments (ABAG, presumably Russell et al., 1982) that heavy metal loadings to the Bay from urban runoff represent about 32% of total annual loadings, the Basin Plan calls for the development and adoption of measures (including land use controls) to control urban runoff.

It has thus become imperative that existing estimates of the loading of toxic contaminants into the Bay-Delta ecosystem be further critiqued and refined. It is vital to develop a better understanding of the strengths and weaknesses of available methods and data in order to make informed assessments of the importance of urban runoff as a source of contaminants to the

estuary. This need is recognized in the San Francisco Bay Basin Plan (SFBRWQCB, 1982). The current state of knowledge, particularly with respect to the concentrations of toxic pollutants in urban stormwaters, makes it exceedingly difficult to derive accurate estimates of loadings by this pathway. The following section describes and analyzes a basic method used by many researchers to estimate the loading of pollutants in urban runoff.

C. Methods for Estimating the Loading of Contaminants from Urban Runoff

The most accurate method of estimating the load of toxic chemicals from urban runoff would be to measure the stormwater flow and constituent concentrations from each urban drainage basin in the estuarine catchment for each storm over several years. These statistics could then be combined to produce an estimate of loading for each storm, and this could be summed across all storms and drainages to derive a loading estimate for the entire estuary. Such a study has never been attempted for any system of the size of the Bay-Delta and has only rarely been performed on smaller watersheds. This is undoubtedly due to the expense of such an intensive monitoring effort.

Without such a comprehensive database, it is necessary to use the more limited available data to make generalizations for the entire estuary. By obtaining appropriate information to characterize runoff from a few representative watersheds, it is possible to construct a mathematical model that can be used to predict the loading of contaminants from watersheds that have not been monitored.

Investigators often choose relatively simple mathematical models to estimate the loading of toxic chemicals from urban runoff, for two major reasons. First, the primary objective is usually to ascertain only an order of magnitude measure of the importance of urban stormwaters as a source of toxic chemicals on an annually-averaged basis. In other words, using reasonable assumptions, what is the order of magnitude of a specific flow? Second, the lack of available data precludes the development of a more complex, and potentially more accurate, mathematical model. A more complex model could require, depending on its formulation, details of surface characteristics, rate constants for chemical reactions, and a large quantity of data on the temporal and spatial variation of the concentrations of contaminants in stormwaters. While such models have been applied to agricultural areas to predict erosion and sediment yield from runoff (see Section II.3 below on nonurban runoff), they have generally not been applied to large urban areas.

The basic method used is to derive an estimate of runoff volume by combining precipitation data and runoff coefficients, the latter being an estimate of the percentage of rainfall that becomes runoff. This is a standard method for estimating runoff volume and is often referred to as "The Rational Method" (Te Chow, 1964) or "The Rational Formula" (Jens and McPherson, 1964). A mean pollutant concentration is then assigned to runoff volume, and by summing over a year, an annual loading for the contaminants of interest is obtained. This method has been adopted by the majority of studies of pollutant loading through urban runoff (see, for example, Hunter et al., 1979; Hoffman et al., 1982; U.S. EPA, 1983; Stenstrom et al., 1984). This

mathematical model can be represented by the algebraic expression

$$Q_i = (\sum_{j=1-n} [C_j (P-D)] A_j X_{j,i})$$

where:

Q_i = annual load of contaminant i

C_j = runoff coefficient for each land use j

P = annual precipitation

D = depression storage

A_j = area of catchment devoted to land use j

$X_{j,i}$ = concentration of contaminant i from land use j

Thus, for each land use j , a fraction of the precipitation that is not captured in surface depressions becomes runoff that is assumed to contain a certain concentration of the contaminants of interest. In this formulation, both the runoff coefficients and the pollutant concentrations are linked to specific land uses. Applying this method to estimate urban runoff thus requires four sets of data: precipitation, land use, runoff coefficients (including depression storage), and pollutant concentrations. This section examines potential sources for each of these datasets, and the important assumptions that are inherent in their application in the model described above.

Precipitation

Of the four datasets, precipitation data are the easiest to obtain and the most accurate. The National Climatic Data Center collects weather information, including precipitation, for all areas of the country. This database can be supplemented by other local sources of information. Precipitation data used to estimate urban runoff must reflect the fact that average rainfall

in the Bay-Delta region can vary by a factor of four (from 25 cm yr⁻¹ in parts of San Joaquin County to over 100 cm yr⁻¹ in portions of Marin County; see Metcalf and Eddy, Inc., 1978). The treatment of precipitation data for the Bay-Delta region is simplified by not including snowfall, which has very different runoff characteristics from rainfall.

Depression storage represents that portion of incident rainfall that is captured in the small depressions present on almost every surface. The difficulty in obtaining meaningful data for depression storage from field measurements means that estimates for this factor must be developed. One such method is to observe the quantity of rainfall necessary to initiate runoff, although this type of estimate can be confounded by infiltration and thus soil moisture conditions (Jens and McPherson, 1964). Only storms which deposit rainfall in excess of this quantity would be considered in runoff calculations. Hoffman et al. (1983), for example, determined this value to be 0.025 cm, while Hunter et al. (1979) assumed a value of 0.25 cm.

Land Use

Land use data are necessary because urban land uses influence both the runoff coefficient and the estimates of some pollutant concentrations in stormwaters. Land use data for the Bay-Delta region are collected and compiled by several government agencies, including the U.S. Bureau of the Census, U.S. Geological Survey (USGS), and ABAG. Inventories of general land uses are available, with the general categories usually divided into more specific sub-categories. Thus, urban land might be separated into residential, commercial, industrial, and open sub-categories.

Classification of land use by category over large regions unavoidably ignores highly specific local variation. Usually, a standard-sized land area is used to develop the database, and each parcel of land is assigned to a category based upon the predominant land use within that parcel. While this ignores minor land uses within areas, these errors should average out across all parts in a region.

Another significant issue regarding the accuracy of land use inventories involves the date of their preparation. In fast-growing urban areas, open lands are being converted to urban uses at a significant rate. Thus, an older inventory would underestimate runoff volumes by not reflecting the degree to which permeable areas in a region have been replaced by impervious surfaces.

Runoff Coefficients

Given data on precipitation and land use, the above method for calculating loads requires the estimation of runoff coefficients for the different land use categories. This coefficient is determined in large part by the degree of permeability of the land surface. For example, up to 90% of the rainfall on a parking lot will become runoff ($C = 0.9$), while for a park the runoff coefficient would be between 10 and 25% (Te Chow, 1964).

Assigning a runoff coefficient based upon land use alone ignores several other factors that influence the quantity of runoff from a given watershed. One of the most important of these is slope. Runoff is basically a gravity-driven process, and for a given land use, steeper sections will have a higher

runoff coefficient. For example, a sandy soil with a 2% slope will have a runoff coefficient between 0.05 and 0.1, while the same soil with a 7% slope will have a runoff coefficient of 0.15-0.2. Surface roughness can also affect the amount of runoff (Te Chow, 1964).

Runoff will also vary with season, as during warmer months there is greater evapotranspiration and interception of precipitation by leaves. Antecedent moisture conditions influence runoff coefficients, because a greater fraction of the incident precipitation will become runoff if soils or surfaces are already wet. Pitt and Shawley (1981), working in an undeveloped region of Alameda County, noted that the first storms of the winter season produced no runoff as the dry, permeable ground absorbed all the rainfall. Thus, annual average runoff coefficients underestimate runoff in wet years and overestimate runoff in dry years.

Consequently, assigning a runoff coefficient based upon land use implicitly averages across these interfering factors. For annual estimates of runoff, the seasonal factors cited above are included in this averaging. The averaging is less valid as one develops runoff estimates on a more detailed level. It therefore must be emphasized that the use of the rational method to estimate runoff does not provide useful results on a small spatial or temporal scale, unless carefully measured site-specific data are provided as input to the calculation.

Pollutant Concentrations

The final dataset required for estimating annual contaminant loads is that concerning concentrations of pollutants in urban runoff. Obtaining such measurements is not an easy task, because

pollutant concentrations and runoff flow rates can vary independently by orders of magnitude during a complete storm event. Thus, to obtain meaningful information, careful attention must be paid to sampling design, as simply taking a single sample during a storm event will undoubtedly lead to erroneous conclusions. Indeed, variations of up to five orders of magnitude in discharge rates of contaminants (the product of concentration and flow) led Hoffman et al. (1983) to conclude soon after the outset of their study "...that there was no such thing as a 'representative' grab sample for urban runoff" (p.44 in Hoffman et al., 1983).

Despite this unpredictable variability, it is often the case that the early portion of a runoff event contains the highest concentration of pollutants. This phenomenon, called the "first flush," has been documented by several investigators and requires that sampling commence at the beginning of a storm event to accurately characterize pollutant concentrations. Secondary flushes, related to changes in rainfall intensity during storms, can also be very important in determining total loadings, especially for toxic chemicals. This is because most toxic organic and inorganic constituents are associated with particulates which are only suspended in (and carried by) runoff at higher rainfall intensities (Hoffman et al., 1982; Brown and Caldwell, Inc., 1984).

Consequently, one must rely upon automatic sampling equipment or have a field crew standing by to travel to the sampling sites at the prospect of rain. In regions where rainfall occurs in fast-moving and often short-lived events (such

as thunderstorms), automated equipment is required. This equipment must be maintained in good working order, especially in semi-arid regions where one has the opportunity to sample only a few storm events (Pitt and Shawley, 1981, their Appendix B; Sonnen, 1984). Several measurements of flow and concentration must be taken during each storm and combined into a flow-weighted statistic, such as an event mean concentration [$\Sigma(\text{flow} \times \text{concentration for each sample}) / \text{total flow}$]. These necessities significantly boost the cost of sampling urban stormwaters for contaminants, which is a reason often cited for the relative lack of water quality data for urban stormwaters (Metcalf and Eddy, Inc., 1978; Whipple and Hunter, 1979).

It is thus not surprising that there is very little information on urban runoff quality for the Bay-Delta ecosystem. Only a few studies have been conducted in specific drainage areas, and researchers have attempted to generalize from these measurements to the Bay system as a whole using mathematical models (Metcalf and Eddy, Inc., 1978; Russell et al., 1982; Silverman et al., 1985; NOAA, 1987a). Given the extent of existing land use data, one attractive alternative is to assign concentrations of pollutants to unmeasured watersheds based upon prevailing land uses. Studies have demonstrated that the loading of oil and grease (Stenstrom et al., 1984; Brown and Caldwell, Inc., 1984), petroleum hydrocarbons (Hoffman et al., 1983), and many polycyclic aromatic hydrocarbons or PAHs (Hoffman et al., 1984) are correlated with land use, with industrial sites exhibiting significantly higher loadings and concentrations than residential areas. Working at an industrial site in Fresno, the USGS found that runoff concentrations of most trace metals were

significantly higher than nearby residential or commercial sites, especially for zinc and arsenic (Brown and Caldwell, Inc., 1984). Use of such relationships, if valid, would allow for the more accurate prediction of pollutant concentrations in urban stormwaters.

While correlations with land use have been demonstrated for composite organic parameters, there is also evidence that the loading of individual toxicants can be very site-specific. When specific organic constituents in runoff from four land uses in Fresno were examined, there was no discernible trend (Brown and Caldwell, Inc., 1984). The priority pollutant monitoring project that was part of the Nationwide Urban Runoff Program (NURP) also supports the notion of site-specificity. The priority pollutant project monitored for 127 priority pollutants in runoff from 61 sites across the country (none in California). It was discovered, for example, that the majority of detected levels for the trace metals antimony, beryllium, mercury, nickel, selenium, and thallium were in samples from Washington, D.C. The NURP program included a rigorous QA/QC element, which was used to explain that this result could not be assigned to analytical or sampling error. Similarly, eight of the halogenated aliphatics detected were found only in runoff from Eugene, Oregon (Cole et al, 1983). Data from the main portion of the NURP program (U.S. EPA, 1983) indicate that there is no statistical basis for concluding that land use can be used to predict the concentrations of lead, zinc, or copper in urban runoff.

While utilizing land use to predict pollutant concentrations is not supported by these results from the NURP program, the

findings may be influenced by the study design. No heavy industrial sites were included in the study, as the "industrial" category actually consists of industrial parks that more closely resemble commercial land uses. Similarly, the industrial site used by Brown and Caldwell (1984) contained a significant amount of undeveloped land. Inclusion of true industrial sites could have produced a more significant correlation between land use and pollutant concentration for some substances, as industrial sites (and highways) demonstrate significantly higher concentrations of oil and grease (Stenstrom et al., 1984), petroleum hydrocarbons (Hoffman et al., 1983), and PAHs (Hoffman et al., 1984). In the latter study, the loading of 12 out of 14 individual PAHs monitored was significantly greater at the industrial and highway sites than at the residential site. Commercial and residential sites, however, did not show a significant trend.

It is also interesting to note that the sites included in the NURP residential land use category varied from 6 to 76% coverage by impervious surfaces (U.S. EPA, 1983, their Tables 6-8). This would indicate a high degree of variation in the nature of the residential sites included in the study. It is possible that more detailed specification of land uses would result in more significant correlations with pollutant concentrations and loadings.

Pollutant concentrations based upon land use may be more accurate for composite parameters, such as total hydrocarbons or oil and grease, as opposed to studies of specific pollutants. While the concentrations of some specific substances in runoff may be correlated to land use, others appear to show no such

relationship. After careful review, NOAA (1987b) decided to abandon concentrations specific to land use for their loading study in favor of a single average concentration for all pollutants except oil and grease. This decision was based largely upon the results from the NURP study cited above.

Even in studies in which oil and grease concentrations show significant correlation with land use, much of the variation in the concentration measurements remains unexplained. Silverman et al. (1985), working in the San Francisco Bay area, found statistically significant relationships between total or particulate oil and grease levels in stormwaters and land use, but this relationship explained only one third of the observed variation. Thus, even for the composite hydrocarbon measurements, predicted concentrations based upon land use are still highly uncertain numbers. This is due in part to the fact that different investigators use different methods to develop composite hydrocarbon data. Oil and grease data can be generated by extraction with hexane, freon 113 (Stenstrom et al., 1982), or dichloromethane (Silverman et al., 1985). Petroleum hydrocarbon measurements generally involve further isolation of aliphatic and aromatic fractions, yet the components from such further extractions are often termed total hydrocarbons.

A significant degree of uncertainty is therefore connected with any estimate of the loading of toxic chemicals from urban runoff that attempts to predict concentrations of specific substances in runoff, based upon land use. However, in many studies, runoff from industrial sites clearly produces greater loadings of hydrocarbons. Similar data are not available for

trace metals. Although the NURP program found no correlation between land use and pollutant concentrations, true industrial sites were not included in this study. Even in investigations where significant correlations were found between hydrocarbon loadings and land use, however, there remained a large amount of unexplained variation. Given the lack of conclusive data on the effects of land use on contaminant levels of stormwaters, the simple sensitivity analysis employed here does not attempt to quantify such effects.

Rainfall-Loading Relationship

In addition to the problems associated with selecting average runoff coefficients and pollutant concentrations for use in modeling the loading of toxic chemicals in urban runoff, this modeling method has a further notable weakness. The model assumes that loading is directly proportional to rainfall. A linear relationship between rainfall and loading of hydrocarbons has been demonstrated for data aggregated from several storms for oil and grease (Stenstrom et al., 1982), petroleum hydrocarbons (Hoffman et al., (1983), and aromatic hydrocarbons (Hoffman et al., 1984), but this is not always the case. Heavy rainfall will produce high pollutant concentrations initially, and thus high loadings; however, in long storms, concentrations can decrease as accumulated particles are scoured from urban surfaces.

Hoffman et al. (1983) noted that in their study, the relationship between hydrocarbon loading and rainfall volume varied with land use. The scouring effect was clearly present for residential land uses, as in larger storms hydrocarbon mass loadings per unit rainfall were much smaller. However, at their industrial site (a 0.8 km² area including metal finishers, oil

distributors, and scrap metal dealers), the relationship between hydrocarbon loading and rainfall volume remained linear even at high rainfall volumes. Runoff from highways and commercial sites (see also Hoffman et al., 1982) demonstrated a pattern similar to the industrial site, as there was only a small decrease in loading with increased rainfall volume. This result seems intuitively understandable; the hydrocarbons available to be suspended in stormwaters are more quickly exhausted at less polluted sites.

It is not clear whether this relationship is true for individual toxic substances, although the high degree of particulate-association of most toxic chemicals would support this hypothesis. However, Hoffman et al. (1984) could not detect a linear relationship between loading and total rainfall for any of the 14 PAHs examined in their study. Data also indicate that residential sites are more important than industrial sites as sources of some compounds, such as lead (U.S. EPA, 1983; Brown and Caldwell, Inc., 1984), further complicating the rainfall-loading relationship by land use for individual substances.

Addressing this problem adequately would require incorporating into the model polynomial expressions reflecting the non-linear relationships between rainfall volume and loads for less polluted sites. Yet in order for these new components of the model to have a meaningful impact, they would have to be calibrated by comparing model predictions to measured local data and adjusting the polynomial coefficients to minimize the difference between measurements and predictions. The model would then have to be validated by comparing its predictions to

monitored data from subsequent storms. As this is not possible in the current study (and has not been attempted by local investigations), the linear relationship is used here with the proviso that it is a simplification that could lead to inaccuracies in estimation of loads.

While the model does have weaknesses, it also has three important strengths when used in the current application. First, the model covers the basic physical parameters influencing contaminant loading from urban runoff, including land use, runoff coefficients, precipitation, and pollutant concentrations. Second, its simplicity allows for estimates to be developed with relative ease, and the sensitivity of these predictions to the different input parameters can be determined quickly. Simple models can often be particularly useful in obtaining a basic understanding of a phenomenon averaged over time and space. Finally, the formulation of the model is very appropriate given the nature of the existing database. It would not be wise to include additional physical or chemical parameters without the ability to more carefully calibrate and verify the performance of the model.

Summary

The difficulty in obtaining data regarding urban stormwater quality, the problematic nature of accurately predicting contaminant concentrations, and the other problems discussed above, mean that the loading of toxic substances into the San Francisco Bay-Delta ecosystem by urban runoff can only be estimated in a rudimentary fashion. While a simple model can be used to attempt to estimate contaminant loadings throughout the region, averages must be made across large variations in loadings

between storms and between sites. The ability to estimate loadings on a local scale, which could be vitally important when considering the potential acute effects on estuarine biota of high concentration runoff events, is virtually nil. While it appears that correlation of composite hydrocarbon measurements with land use will allow loading statistics for these substances to be the most accurate, even for these measurements there are large and unpredictable variations in loads from the same land use. Moreover, these composite measures are of little use in understanding the effects on the estuary of the individual contaminants present in urban runoff.

D. Data Availability

As was stated at the beginning of this section, relatively little research has been performed regarding the loading of toxic substances into receiving waters by urban runoff. Of these studies, fewer than ten have investigated sites in California, and less than five have occurred in the Bay Area. This section will examine the data provided in these and other studies to develop the database available for estimating contaminant loadings to the estuary.

To review, there are four categories of data needed to make an estimate of the loading of toxic chemicals into the Bay-Delta by urban runoff: precipitation, land use, runoff coefficients, and pollutant concentrations. For the loading estimate to provide information that could be reasonably applied to the estuary, the precipitation and land use data must be specific to the region, rather than derived from national or state-wide averages. Clearly, it would also be desirable to use a locally-generated database for runoff coefficients and pollutant

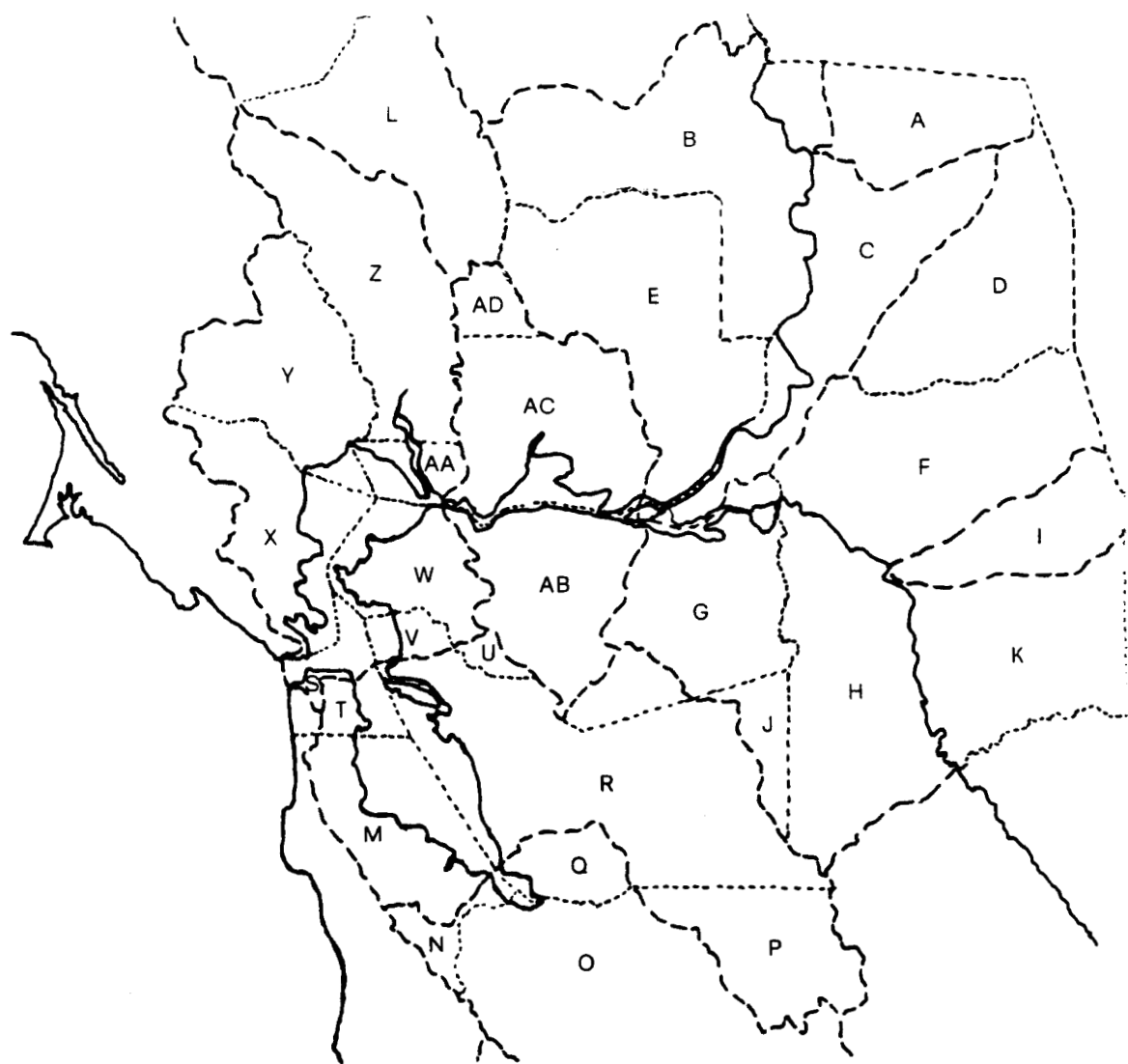
concentrations to achieve the most accurate loading estimate for the Bay-Delta estuary. Unfortunately, this is not possible, as few local data of high quality are available for these parameters, particularly with respect to trace metal concentrations. This section will examine the quality of the information available.

The data on precipitation and land use taken from the recent work of NOAA (1987a) are organized by a special modeling unit called a "HUCO," which is the geographical intersection of counties and USGS hydrologic cataloging units (Seaber et al., 1984). The organization of data allows for predicted loads to be reported by county or by hydrologic cataloging unit. The HUCOs in the Bay-Delta region are presented in Figure 5.

Precipitation

NOAA (1987a) has summarized precipitation data in the Bay-Delta region for the years 1981-1982 for use in the National Coastal Pollutant Discharge Inventory (NCPDI). The information was derived from records of the National Climatic Data Center, which is considered the definitive source of precipitation data in the nation. Local weather stations were assigned to NOAA's modeling units, or "HUCOs," based upon several criteria. For example, stations must have been collecting data for at least 30 years and have fewer than ten days of data missing for the period under study. Missing data were provided by using the average of two or three neighboring stations (Dalton, Dalton, and Newport, Inc., 1985).

While reasonably accurate, the database suffers from the fact that the density of acceptable weather stations by NOAA's criteria cannot capture the regional meteorological variation in



SEGMENT	KEY	HUCO	SEGMENT	KEY	HUCO
DELTA	A	0606718020111	CENTRAL/ SAN PABLO BAY	S	0607518050002
	B	0611318020109		T	0607518050004
	C	0606718020109		U	0601318050004
	D	0606718040003		V	0600118050002
	E	0609518020109		W	0601318050002
	F	0607718040005		X	0604118050002
	G	0601318040003		Y	0609718050002
	H	0607718040003		Z	0605518050002
	I	0607718040004		AA	0609518050002
	J	0600118040003	SUISUN BAY	AB	0601318050001
	K	0607718040005		AC	0609518050001
	L	0605518020117		AD	0605518050001
SOUTH BAY	M	0608118050004			
	N	0608118050003			
	O	0608518050003			
	P	0608518050004			
	Q	0600118050003			
	R	0600118050004			

- - - - - USGS Hydrologic Units
 County Lines

Fig. 5: HUCOs for the Bay-Delta Region. HUCOs are defined as the geographical intersection of counties and U.S. Geological Survey hydrologic cataloging units, and are used in the National Coastal Pollutant Discharge Inventory (NDPDI). After NOAA (1987a and F. Arnold 1987, personal communication).

detail. As Table 31 demonstrates, there are basic regional differences in rainfall in the Bay-Delta. While certain local variation is undoubtedly lost due to necessary spatial averaging, this weakness in the database is less important when only annual average precipitation is being considered, rather than precipitation over shorter time periods.

It should be noted that 1982 (the modeling year chosen by NOAA) exhibited the highest precipitation of any year between 1975 and 1983. As precipitation is the driving variable in estimates of contaminant loading using the Rational Method, loading estimates for 1982 are higher than normal. This is examined in more detail in the section below on findings.

Land Use

Land use within the Bay-Delta catchment must be identified to determine the extent of urban area to include in the urban runoff loading estimate. As runoff coefficients, and possibly pollutant concentrations, vary between different urban land uses, knowledge regarding the amount of land under particular land uses is also needed. Developing such a database is clearly a time-consuming process that is beyond the scope of this study, and, consequently, it is necessary to look to existing land use compilations for the Bay-Delta region. Data on land use are collected by the U.S. Bureau of Census, the USGS, and local governments. Land use data on the Bay area, exclusive of the Delta, are compiled by the Association of Bay Area Governments (ABAG) from both the U.S. national census data and local sources.

In implementing the NCPDI, the Strategic Assessments Branch of NOAA developed a land use inventory for the Bay-Delta catchment. As discussed above, the NCPDI aggregates pollution

Table 31: Annual precipitation for 1977, 1981 and 1982 in the Bay-Delta region by HUCO. Values are given as depth in meters. HUCOs, the geographical intersection of counties and U.S. Geological Survey hydrologic cataloging unit, are mapped in Figure 1. 1981 and 1982 data from NOAA (1987a); 1977 data from NOAA (1978).

COUNTY	HUCO	1977	1981	1982
Alameda	0600118040003	0.20308	0.32741	0.57074
	0600118050004	0.22641	0.42875	1.03683
	0600118050003	0.23359	0.37795	0.55728
	0600118050002	0.40769	0.73381	0.63652
Contra Costa	0601318040003	0.41974	0.65075	0.91609
	0601318050001	0.33667	0.56261	0.8189
	0601318050002	0.40769	0.73381	1.03683
	0601318050004	0.41974	0.65075	0.91609
Marin	0604118050002	1.05026	1.48048	1.9972
Napa	0605518020117	0.69923	1.30708	1.52946
	0605518050001	0.47385	0.59969	0.85903
	0605518050002	0.57795	0.76708	1.08788
Sacramento	0606718020109	0.30026	0.56718	0.80264
	0606718020111	0.33231	0.80975	1.0541
	0606718040003	0.31692	0.52527	0.81178
	0606718040005	0.30026	0.56718	0.80264
	0606718040013	0.33231	0.80975	1.0541
San Francisco	0607518050004	0.32154	0.49835	0.81763
San Joaquin	0607718040002	0.19718	0.36398	0.52095
	0607718040003	0.20308	0.32741	0.57074
	0607718040004	0.19923	0.40742	0.63568
	0607718040005	0.31692	0.52527	0.81178
San Mateo	0608118050003	0.31359	0.7427	0.92939
	0608118050004	0.29487	0.59614	0.88417
Santa Clara	0608518050003	0.35718	0.54381	0.9078
	0608518050004	0.39949	0.60405	0.85446
Solano	0609518020109	0.49359	0.68047	1.06629
	0609518050001	0.47385	0.59969	0.85903
	0609518050002	0.40769	0.73381	1.03683
Sonoma	0609718050002	0.60436	0.88849	1.19863
Yolo	0611318020109	0.32949	0.48489	0.86411

information based upon either coastal county or USGS hydrologic cataloging unit, and data are stored based upon regions called HUCOs.

The NCPDI has two major sources of land use information: the U.S. 1980 Census and the USGS Land Use Data Analysis (LUDA) system. LUDA is a national land use database developed from aerial photographs of the entire country taken between 1972 and 1975. Ten-acre land parcels are identified according to the land use classifications listed in Table 32 and stored on computer with associated information, such as the county or hydrologic cataloging unit that contains the parcel. Given this structure, NOAA was able to assemble these parcels into HUCOs, and thus obtain the breakdown of urban land uses as an input to the NCPDI program. As a quality assurance procedure, the estimates of total county land area assembled in this manner from LUDA were compared to the U.S. Bureau of Census 1980 assessments of county area. The two estimates, which were prepared by different methods, rarely varied by more than 5% (Dalton, Dalton and Newport, Inc., 1985).

As the U.S. Census data is more up to date than the LUDA estimates, census data were used to define the extent of major and minor urban areas within each HUCO. These areas were defined based upon population or population density and were apportioned to different HUCOs using a variety of maps. This procedure often required making subjective decisions regarding how to apportion an urban area between HUCOs, as cities and towns often cross hydrologic cataloging unit boundaries.

These estimates of total urban land within each HUCO for major and minor urban areas were then divided into urban land use

Table 32. Land use classifications of the Land Use Data Analysis System for Urban or Built-up Land (U.S.Geological Survey), the NCPDI, and the land use inventory of the Association of Bay Area Governments. After NOAA (1987a) for USGS and NCPDI classifications, and ABAG (1985). Groupings indicate how the LUDA classifications were condensed in the NCPDI.

<u>LUDA</u>		
USGS	NCPDI	ABAG
Residential	Residential	Residential
Commercial and Services Transportation, Communication and Services	Commercial	Commercial and Industrial
Industrial Industrial and Commercial Complexes	Industrial	Streets and Highways
Mixed Urban or Built-up	Mixed	Available for Development
Other Urban or Built-up	Open	Unavailable for Development

classifications, based upon the proportions for that HUCO from the LUDA database. Thus, the total urban area for a given HUCO from the 1980 census was split into the different urban land use classifications based upon the proportions observed for that HUCO in the 1972-75 period in LUDA. If only major or only minor urban areas were contained in a given HUCO, the land use classifications from LUDA for that HUCO were applied to each urban area. However, the amount of land in the different classifications varies between big cities (major urban areas) and small towns (minor urban areas). Thus, if a HUCO contains both, it was not possible to use the proportions of land in each of the LUDA classifications in assigning land uses.

This problem was addressed by calculating regional average distributions of land use for HUCOs with only major urban areas and for those with only minor urban areas. These average distributions were then used to assign land uses to the appropriate portions of those HUCOs that contain both major and minor urban areas.

ABAG developed a land use inventory for the Bay Area based upon 1980 census data modified by local surveys performed during 1982-1983. The data are stored by census tract, of which there are about 1000 in the Bay Area, and the land use categories included in the database are also listed in Table 32. Silverman et al (1985) established 110 hydrologic modeling regions in the Bay catchment and used the ABAG database for land use inputs to their model. This required some subjective judgment, because census tract and modeling unit boundaries did not coincide.

As Table 32 demonstrates, different land use inventories summarize land uses in different ways, making it difficult to

compare summaries for individual land uses among inventories. The existence of different land use categories also complicates the assignment of runoff coefficients and pollutant concentrations for urban runoff modeling purposes. Research sites in stormwater quality investigations may have yet another set of land use categories, or may use very general or very specific identifiers.

Thus, assembling the land use database for estimating the loading of toxic chemicals in urban runoff requires assumptions about how to compile land uses and match these categories to those associated with data on runoff coefficients or stormwater pollutant concentrations. For example, Table 32 also indicates how the USGS land use classifications were further condensed by NOAA for use in the NCPDI (F. Arnold, personal communication). The NOAA land use database was used to estimate toxic chemical loads from nonpoint sources in this study as it covers the entire Bay-Delta region. The strength of this inventory due to its geographical extent is balanced by the weakness that it depends on LUDA data from 1975. As part of the sensitivity analysis, an effort was made to examine how land use changes in the Bay-Delta region since 1975 might affect loading estimates.

Runoff Coefficients

Runoff coefficients, representing the percentage of rainfall incident upon a drainage basin that becomes runoff, are obtained in two ways. The majority of investigators utilize "generic" runoff coefficients that have been measured for specific land use types. These values are assigned to the study area based upon measured (or assumed) land uses, and runoff volumes are estimated from precipitation records. Alternatively, some researchers have

measured runoff volume and precipitation depth for a series of storms and, utilizing the area of the study site to calculate precipitation volume, have determined a runoff coefficient empirically (Hoffman et al., 1982; Brown and Caldwell, Inc., 1984).

Table 33 presents runoff coefficients for a variety of land uses from several sources. The table indicates that the two methods for obtaining runoff coefficients for use in loading analyses can produce very different values. For example, although industrial sites can be expected to have relatively large runoff coefficients (0.5-0.9), the empirical value determined by Brown and Caldwell, Inc. (1984) for their industrial site in Fresno was only 0.18. This is apparently because this site had significant amounts of undeveloped land. Similarly, the commercial drainage area studied by Hoffman et al. (1982), 90% of which was a parking lot, exhibited an unusually low empirical runoff coefficient of only 0.59. These results underscore the earlier discussion regarding the site-specific nature of runoff coefficients.

As it was not possible to empirically determine runoff coefficients for each urban portion of the Bay-Delta catchment in this study, it was necessary to assign values to the major land use classifications in the NCPDI inventory. The runoff coefficient values utilized by NOAA (1987b) are listed in Table 33. It can be seen that, of the five major land use classifications (residential, industrial, commercial, mixed, and open), estimated values vary the least for the commercial and open land uses and vary the most for residential areas. In the simple sensitivity analysis presented in the next section, the runoff coefficients

Table 33. Runoff coefficients by land use measured or utilized in various studies of urban runoff.

SOURCE	LAND USE TYPE					
	RESIDENTIAL		INDUSTRIAL	COMMERCIAL	MIXED	OPEN
	Single Family	Multi-Family				
Hoffman et al. (1982)			0.59			
Stenstrom et al. (1984)	0.19		0.76	1.00		0.02
Brown and Caldwell (1984)	0.21	0.39	0.18	0.93		
NOAA (1987b)	0.2		0.3	0.65	0.23	0.06
Ven te Chow (1964)	0.3-0.5	0.5-0.7	0.5-0.8			0.1-0.3
			0.6-0.9			
Metcalf and Eddy (1978)	0.3	0.4	0.6	0.7		0.2
EPA (1983)	0.3	0.8	0.8			
Range	0.19-0.5	0.39-0.7	0.18-0.9	0.6-1.00	0.23	.02-0.3

assigned by NOAA (1987b) were varied within the range indicated in Table 33 to develop a range of estimates of urban runoff volumes in the Bay-Delta region.

Pollutant Concentrations

As previously discussed, the concentrations of toxicants in urban stormwaters can vary significantly, both between storms and during the same storm. Of the four required datasets, it would thus be most beneficial to have a large pollutant concentration database for the Bay-Delta region. The database could then be used to derive estimates of average pollutant concentrations for use in modeling.

Unfortunately, the data on toxic chemicals in urban stormwaters of the Bay-Delta region are limited. Very few studies of urban runoff quality have been undertaken, and many of these examine conventional constituents (BOD, nutrients, etc.) rather than the toxic pollutants of concern in this report. Consequently, it is necessary to utilize stormwater quality data from other parts of the country to estimate probable pollutant concentrations in urban runoff in the Bay-Delta region. The local and national data of interest are summarized in this section. As discussed in Sections I and III of this report, the existence of quality control and quality assurance (QA/QC) programs is vital for determining the reliability of any dataset.

Local Studies. In the Bay-Delta region, seven studies that included the monitoring of urban runoff have been identified. Four of these have been carried out by the Association of Bay Area Governments (ABAG), one by the California Department of Transportation (Caltrans), one by the East Bay Municipal Utility District (EBMUD), and one by the Alameda County Flood Control

District as part of the NURP.

The Association of Bay Area Governments, along with local counties in the Bay Area, conducted the Surface Runoff Program as part of the development of the Bay region's Section 208 study (Environmental Management Plan). ABAG contracted with the USGS to assist in training local agency personnel. ABAG synthesized and analyzed the data generated by this monitoring effort, focusing primarily on the relationship between land uses and stormwater quality (Litwin and Miller, 1977; Litwin et al., 1977).

Most of the data collected on stormwater quality was for BOD, suspended solids, total nitrogen, and total phosphorus. Data from samples analyzed for trace metals and oil and grease are presented in Tables 34 and 35. Of the 24 watersheds examined, 13 were classified as residential in nature.

It is necessary to treat these data with caution when using them to derive loading estimates. Analysis of the variability of the data is difficult, as the number of samples is not reported and several mean values are reported without standard deviations. Limited data are available from commercial and industrial areas, which are important regions for urban runoff studies due to the extent of impervious land in these areas. Reported flow-weighted mean concentrations varied between storm events by an order of magnitude for lead, cadmium, nickel, and copper; by two orders of magnitude for zinc, and by three orders of magnitude for mercury and arsenic (Litwin et al., 1977). As no results of QA/QC work during this research were reported (Litwin and Miller, 1977; Litwin et al., 1977; Metcalf & Eddy, Inc., 1978), it is not possible to discount methodological problems as the cause of the

Table 34. Concentration of trace metals in urban stormwaters in the Bay-Delta region. Values are flow-weighted means in $\mu\text{g L}^{-1}$ unless otherwise noted. Values in parentheses are standard errors of the mean.

Metal ₁ ($\mu\text{g L}^{-1}$)	Pitt and Shawley (1981) ^a Knox Station (1982a)	Litwin <u>et al.</u> ^b (1977)	Racin <u>et al.</u> ^c (1982)
Arsenic	0.4(0.5)	210	1(1)
Cadmium	3(0.9)	10	--
Chromium	13(3.8)	20	--
Copper	100(36)	150	--
Iron (mg/l)	9.3(1.1)	--	--
Lead	490(122)	610	603(132)
Mercury	0.4(.14)	10	--
Nickel	37(10.6)	90	--
Zinc	310(71.2)	580	239(44)

^a Their Appendix E

^b Their Appendix B

^c Samples from Interstate Highway 680 in Walnut Creek, flow weighted mean calculated from Tables 4A and 4B in Racin et al. (1982).

Table 35. Measurements of oil and grease in urban stormwaters in the Bay-Delta region. Data are flow-weighted means for Stenstrom et al. (1977). Data from Silverman et al. (1985) are for grab samples from different storm events in creeks discharging to the Bay-Delta. All data shown as $\mu\text{g L}^{-1}$. (Numbers in parentheses are standard errors).

Source	Land Use	Oil and Grease	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
Stenstrom <u>et al.</u> (1984)	residential commercial industrial open ^a	3.89 13.13 7.1 0		
Litwin <u>et al.</u> (1977)	residential commercial industrial	6 28 25		
Silverman <u>et al.</u> (1985)	See note ^b	6.71(.86)	3.77(1.2)	.92(.15)

^a This value was assumed, not measured.

^b Not related to land uses in creek catchments.

extremely large variation. Finally, there is no discussion of the methods of analysis or the treatment of sample values below analytical detection limits, a common occurrence in trace-metal research.

This monitoring program was carried out during the winter season of 1976-1977, when Northern California experienced its worst two-year drought in history. Consequently, runoff volumes were well below normal, which could lead to relatively high and variable estimates of flow-weighted concentrations. Supplemental monitoring under non-drought conditions was identified as an important element in future studies (Metcalf and Eddy, Inc., 1978).

Stenstrom et al. (1982) measured the concentration of oil and grease in urban stormwaters in Richmond from five sites, representing a variety of land uses, during the winter of 1981-1982 (this study is summarized in Stenstrom et al., 1984). Flow-weighted mean values for each station were derived, and based upon the proportion of land use types within each station drainage area, land-use specific concentrations of oil and grease were estimated (Table 35). In this study, careful attention was paid to describing methods, presenting raw data, and deriving relevant statistics. A significant effort was made to review possible correlations between oil and grease concentration or loading and factors such as land use, runoff or rainfall volume, rainfall rate, or days since the beginning of a storm. Oil and grease concentrations were found to be correlated to sampling station (and thus land use), and total oil and grease loads were correlated with total rainfall.

Unfortunately, Stenstrom et al. (1982, 1984) report no

results from or discussion of a QA/QC program. During one storm, duplicate samples were taken, but the data from this experiment were not presented. Controls for the retention of oil and grease on laboratory glassware were included (Stenstrom et al., 1982, their p. 160), however, and analytical methods were carefully selected following Standard Methods for the Analysis of Water and Wastewater (APHA, 1975) to minimize sample loss and methodological bias due to the loss of semi-volatile oil and grease components.

The study was followed by an effort to estimate the loading of oil and grease from runoff into the entire Bay through sampling in 15 separate watersheds throughout the region (Silverman et al., 1985). ABAG's land use database was applied to 110 drainage areas throughout the Bay catchment to develop estimates for residential, industrial/commercial, and undeveloped land, and the Rational Method to estimate runoff was combined with empirically derived oil and grease concentrations to estimate loads.

An important part of the study concerned a review of the techniques used to measure hydrocarbon concentrations in an effort to develop a more accurate (yet still practical) method. The method adopted, which involved extracting samples in different solvents to separate hydrocarbon fractions, was verified experimentally by testing the recovery of solutions of known concentration. The results of this QA/QC procedure are presented (Silverman et al., 1985). However, no other QA/QC procedures or results are discussed.

Based upon the results of Stenstrom et al. (1984), which did

not demonstrate a significant relationship between storm phase and oil and grease concentration, the Silverman et al. (1985) sampling scheme involved single grab samples from many locations throughout the Bay Area rather than intensive sampling of flow and concentration from a few sites at several times during storm events, the latter permitting flow-weighted concentration data to be calculated. The authors acknowledge that Hoffman et al. (1982) (and to a lesser extent, Stenstrom et al., 1984) documented a "first flush" of hydrocarbons at the beginning of storm events, which their sampling program would miss. They do not discuss the existence of secondary flushes (increases in concentrations corresponding to changes in rainfall intensity during a storm), which their sampling program also would have been unable to identify.

Indeed, in their analysis, the estimates of oil and grease concentration for runoff from commercial/industrial sites appeared to be influenced by a few, relatively high measured values which could have been related to very short-lived flushes rather than being characteristic concentrations at the sites sampled. Eliminating two measurements from Temescal Creek that were greater than 40 mg L^{-1} reduced their estimate for oil and grease concentration from commercial/industrial land uses from 21.64 mg L^{-1} to 16.67 mg L^{-1} . Data from gas chromatographic analyses indicated that these high concentrations were due to a significant quantity of diesel fuel in the sample, probably from a bus repair yard and other industrial establishments near the sampling site.

Consequently, Silverman et al. (1985) used both their concentration estimates and the flow-weighted concentrations of

Stenstrom et al. (1984) to estimate oil and grease loadings to the Bay. This decision was made because the authors correctly recognized that the high concentrations they recorded were a realistic reflection of the large variation in the quality of urban stormwaters. The estimates of oil and grease loading made using their data, however, were 85% higher than similar estimates made by Stenstrom et al. (1984). Without flow-weighted measurements of concentration, it is not possible to obtain accurate estimates of oil and grease loadings to the Bay-Delta. It would thus appear that the concentration data of Stenstrom et al. (1984) are the more appropriate values to use in estimating such loadings.

Meorin (1986) tested the efficacy of treating urban stormwater using a wetland created specifically for this purpose. Urban stormwater was diverted through the Demonstration Urban Stormwater Treatment (DUST) marsh at Coyote Hills Regional Park in Fremont, and pollutant concentrations were monitored at various points throughout the system. This included monitoring the concentration of oil and grease and several trace metals in the urban runoff prior to its entering the marsh. The study clearly describes a strong QA/QC program that was ongoing during the project.

Unfortunately, Meorin (1986) only monitored the concentration of pollutants in the storm channel outside the marsh four times, and on one of these occasions trace metal samples were not taken during the first six hours of the storm (November 13, 1984). Most of the monitoring occurred after stormwater passed through a debris basin in the marsh, where many

particulates (and adsorbed contaminants) would be likely to settle out. As flow measurements were only reported for this latter station, it is not possible to estimate flow-weighted mean concentrations for the stormwater measurements taken in the drainage channel. Consequently, the concentration data in the study are of no use for estimating the loading of toxicants into the Bay-Delta ecosystem from urban runoff.

Urban runoff was monitored in the drainage of Castro Creek in Alameda County as part of a NURP project to correlate street cleaning with urban runoff quality (Pitt and Shawley, 1981). Several trace metals were monitored at two stations along Castro Creek. The Seaview station drained an area of open and undeveloped land, while the downstream Knox station drained an urban area. The concentrations at the Knox station thus represent a combination of the stormwater runoff from both of these drainages; these are presented in Table 34.

The USGS trained Alameda County Flood Control District personnel to collect samples, which were sent to U.S. Geological Survey facilities in Denver for analysis. The method used by Pitt and Shawley (1981) for collecting samples followed QA/QC procedures described in Standard Methods for the Analysis of Water and Wastewater (APHA, 1975) and utilized automatic flow measuring and sampling equipment to collect composite (flow-weighted) samples. The samples were stored in the field in a 55-gallon stainless steel drum into which bottles with ice had been inserted to keep samples cold.

Unfortunately, no discussion of contamination blanks is presented; however, with such a system, the consistent collection of blanks is essential. Scientists undertaking trace metal work

prepare polyethylene sample containers in a "clean room" by soaking them in successive solutions of acid and quartz distilled water (see, for example, Moody and Lindstrom, 1977). Without such preparation, it is highly probable that samples were contaminated, and no data to the contrary are presented in the study. The trace metal data from this study must therefore be treated with caution if they are used to generate loading estimates.

Caltrans monitored the chemical quality of runoff from various sections of highway in different parts of California. During the winter of 1975-1977, two to five storms were monitored at three sites for oil and grease and a variety of trace metals (Howell, 1978). As this effort coincided with the drought in California, and because of problems encountered in sampling techniques, a second runoff monitoring program was initiated (Racin et al., 1982) that included sampling in Los Angeles (I-405), Walnut Creek (I-680), and Sacramento (I-50).

One of the major sampling problems in the earlier study was that the beginning of the runoff event was missed in the majority of cases, thus failing to collect data on any "first flush" pollutant concentrations. In the subsequent study, results for the levels of cadmium, copper, and zinc for various portions of the hydrograph are reported with their corresponding flow volumes, allowing for the calculation of flow-weighted mean concentrations (Racin et al., 1982). These values appear in Table 34. While the authors described quality assurance problems with the earlier dataset (Howell, 1978), there is no discussion in their report of QA/QC procedures used in the later studies.

The Caltrans Laboratory indicated that blanks and recovery determinations were utilized in the analytical portion of the work, but no field QA/QC efforts were undertaken (J. Giddley, personal communication).

As part of their ongoing local effects monitoring program, EBMUD monitors the concentration of oil and grease and several trace metals in urban runoff at three sites in the East Bay. Due to a lack of precision in flow measurements, however, they were unable to calculate flow-weighted means (EBMUD, 1986, their Appendix A). Consequently, this data is not useful for calculating contaminant loads from urban runoff.

Other Studies. With the possible exception of the oil and grease data from Stenstrom et al. (1984), there are few high quality data available from local studies for use in estimating the loading of toxicants to the Bay-Delta ecosystem by urban stormwaters. Either studies were not designed to measure stormwaters prior to settling (Meorin, 1986), did not measure flow-weighted mean values (Silverman et al., 1985), or certain sampling techniques were questionable (particularly for trace metals; Litwin et al., 1977; Pitt and Shawley, 1981). A general lack of attention to QA/QC procedures is disappointing and raises questions regarding the reliability of the database.

Consequently, to develop an estimate of toxic chemical loading in urban runoff, it is necessary to also utilize research conducted outside of the Bay-Delta region. This work includes the Nationwide Urban Runoff Program (NURP) and a variety of independent research efforts concerning hydrocarbons in runoff.

In generalizing the results from other urban regions of the country to the Bay-Delta area, one must acknowledge certain

limitations. For example, differences in population densities, climate, traffic patterns, and local sources of contaminants could result in differences in urban stormwater quality between regions. The site-specificity of certain pollutant concentrations (discussed previously) is evidence to support this assertion. Consequently, the use of data from other regions to calculate the loading of toxicants to the Bay-Delta could introduce inaccuracies that would be very difficult to identify.

The NURP was established to gather information that would contribute to an understanding of the impact of urban runoff on receiving water quality. Data were collected over several years from projects in 22 cities around the country, including sites on Castro Creek (see above) and in Fresno. Data from over 2300 storm events at 81 sites were compiled and analyzed, including measurements for zinc, lead, and copper (conventional constituents examined included BOD, TSS, COD, total phosphorus, soluble phosphorus, total Kjeldahl nitrogen, and nitrite plus nitrate; (see U.S. EPA, 1983). In addition, a priority pollutant project was instituted to monitor for 127 of the EPA priority pollutants (see Table 4, Section II.1 above). More than \$27 million of federal and local funds were expended for the NURP studies (Brown and Caldwell, Inc., 1984).

The NURP required that all the projects throughout the country include a QA/QC element as an integral part of their program. Projects were required to designate a QA/QC coordinator, guidance was provided for data collection in the field, and a laboratory manual containing analytical quality control information was supplied to all projects. While this

would give the appearance of careful attention to QA/QC, it must be kept in mind that the studies of Pitt and Shawley (1981) were part of the NURP project, and did not include details of their QA/QC procedures. The NURP final report (U.S. EPA, 1983) contains no results or detailed discussion of QA/QC concerns.

The NURP priority pollutant project, however, contained a very detailed and rigorous QA/QC program. Of all the urban runoff studies reviewed in this report, the NURP priority pollutant project is the only one that clearly describes a sophisticated QA/QC program. Aspects of the program included holding time restrictions, field and method blanks, replicate samples, performance evaluation samples (analyzing samples of known concentrations), and samples spiked with priority pollutants or surrogate compounds (Cole et al. 1983). As pointed out in the introduction, utilizing results of these QA/QC tests, 2,006 of 11,008 observations (18.2%) were withdrawn from the database prior to its statistical analysis (Cole et al., 1984).

The large NURP database was examined in a statistically sophisticated manner. A probability distribution of the median event mean concentrations (EMC) was prepared for most pollutants at each site, and the Kolmogorov-Smirnoff D test was used to demonstrate that the data were lognormally distributed, and thus geometric rather than arithmetic means were used to describe the data. It should be noted that individual investigators have difficulty utilizing such a test for lognormality as a large number of samples are necessary. Even in the NURP database, there were not enough data points for copper to demonstrate a lognormal distribution for this element (U.S. EPA, 1983).

The geometric mean values for the trace metals analyzed in

the NURP priority pollutant project and their frequencies of detection are presented in Table 36. Two sets of mean values appear, depending upon the treatment of samples below analytical detection limits (BDL). High means are calculated by assuming BDL samples have concentrations equal to the detection limit, while low means assume that BDL values equal one-tenth the detection limit. (Values of zero were not used for the low estimates, as this interferes with the calculation of geometric means).

The trace metals were the most prevalent priority pollutants found in urban runoff by the NURP. Copper, lead, and zinc were found in over 91% of the samples, with arsenic, chromium, cadmium, nickel, and cyanides also frequently detected. Elements detected in greater than 10% of the samples were antimony (13%), beryllium (12%), and selenium (11%). Mean values were calculated only for those substances detected in greater than 20% of the samples. The only two organic constituents detected with that frequency were bis(2-ethylhexyl)phthalate (22%) and alpha-hexachlorocyclohexane (20%).

Also included in Table 36 are the means for copper, lead, and zinc from the general NURP database, as these elements were sampled in both the priority pollutant project and the general NURP program. As can be seen, the means from the general NURP program are approximately twice the values of the high means from the priority pollutant monitoring. In noting this disparity, NOAA (1987b) stated that there was no obvious reason for this result. Given the strength of the QA/QC program in the priority pollutant project and the uncertainty regarding the QA/QC element in the general program (in light of the critique of the Castro

Table 36. Trace metal concentrations in urban runoff from the Nationwide Urban Runoff Program. All values are geometric means in $\mu\text{g L}^{-1}$. High means are calculated assuming samples below detection limits [BDL] equal detection limit; low means assume BDL samples equal one-tenth of detection limit. After Cole *et al.*, (1983) and U.S. EPA (1983).

Trace Metal	Geometric mean ($\mu\text{g L}^{-1}$)		Occurrence (%)
	Low	High	
Priority Pollutant Project			
Arsenic	2.18	6.63	52
Cadmium	0.54	1.84	48
Chromium	3.49	9.18	58
Copper	15.8	19.5	91
Cyanide	2.78	17.09	23
Lead	70.8	81.7	94
Nickel	5.3	19.8	43
Zinc	89.7	103.9	94
General NURP Database			
Copper		43	
Lead		182	
Zinc		202	

Creek study cited above), it might be that the more stringent QA/QC program led to the withdrawal of enough artificially high values (due presumably to problems with contamination) to reduce the calculated means.

Several studies of hydrocarbons in urban runoff have been conducted outside California. These studies, which appear either in peer-reviewed scientific journals or the NURP priority pollutant project, examine quantitative and qualitative aspects of hydrocarbons in stormwaters, including the concentrations of aliphatic and aromatic fractions, and loading by land use. This research has used more sophisticated laboratory methods to separate petroleum hydrocarbons from the other constituents included in standard oil and grease analyses. The estimates of hydrocarbon concentrations from these studies, which will be discussed below, are presented in Table 37.

Hoffman et al. (1982) examined the loading of hydrocarbons from a shopping center complex in Warwick, Rhode Island. Analysis involved filtering to separate particulate and soluble fractions; extraction of the particulate phase in methanolic potassium hydroxide and the soluble phase in dichloromethane. Particulates were isolated by further extraction in petroleum ether, and hydrocarbons were further separated in both fractions by silica gel chromatography. Total hydrocarbon concentrations were determined by glass capillary gas chromatography. (QA/QC procedures described in Hoffman et al. [1983] included the use of contamination blanks and replicate samples, the latter showing their technique to be accurate to about $\pm 15\%$.)

Table 37. Hydrocarbon concentrations in urban runoff found by various studies outside the Bay-Delta region. Data are flow-weighted means in mg L^{-1} . (Numbers in parentheses are standard errors).

SOURCE	STUDY-SITE	LAND USE (n=# of samples)	Oil and Grease	Pet HC	Aliphatic Hydro- carbons	Aromatic Hydro- carbons
Hoffman et al. (1982)	Shopping Center: 90% parking lot	(n=6)		1.44(.24)		
Hunter et al (1979)	Storm drain, mostly residential	(n=5)		3.69(.57)	2.5(.43)	1.12(.17)
Whipple and Hunter (1979)	4 storm drains, diff land uses	residential (n=5)		3.78		
		industrial (n=2)		5.9		
		res/ind (n=3)		2.5		
		overall average		3.3		
Brown and Caldwell, Inc., 1984	Fresno	single family	3			
		multi-family	1.5			
		commercial	4.2			
		industrial	11			
Eganhouse and Kaplan (1981)	Los Angeles River	(n=11)		13.1	11.5	1.6

This procedure separates substances such as petroleum hydrocarbons from the vegetable and animal oils (triglycerides) that are included in standard oil and grease measurements (Hoffman et al., 1982). The distinction is important when examining the ecological effects of urban runoff on the estuary, as the triglycerides included in oil and grease measurements should not be considered as toxic contaminants. By contrast, the local studies of hydrocarbons measured oil and grease through extraction in Freon 113 followed by infrared spectrophotometry (Stenstrom et al., 1984) or extraction in dichloromethane followed by gravimetric determination (Silverman et al., 1985). The latter study also developed a procedure similar to Hoffman et al. (1982) to isolate specific hydrocarbon fractions. These data are presented in a rather unclear format (Silverman et al., 1985, their Tables IV-1 and IV-2), however, making it difficult to determine the amount of material in the various fractions.

It is important to note that, from their commercial site, Hoffman et al. (1982) measured only an average of 1.44 mg L^{-1} total hydrocarbons, which were predominantly petroleum hydrocarbons. This compares to the commercial oil and grease measurement of Stenstrom et al. (1984) of 13.13 mg L^{-1} . It is not possible to determine whether the latter measurement is higher due to the additional materials isolated in the oil and grease measurement or if higher concentrations of petroleum hydrocarbons were indeed present in the Richmond runoff. Eganhouse and Kaplan (1981), who used thin layer silica gel chromatography in methylene chloride to separate total hydrocarbons, found 13.1 mg L^{-1} of total hydrocarbons and 24.2 mg L^{-1} of total extractable organics in the Los Angeles River, again

indicating that simple extractions will overestimate petroleum hydrocarbon concentrations.

Hunter et al. (1979) studied hydrocarbons in runoff from a residential area in Philadelphia. After separating the particulate fraction by centrifugation, they extracted each fraction in hexane, benzene, and chloroform/methanol, and evaporated the extracts onto a silica gel column. The column was then eluted with hexane to obtain the aliphatics and with benzene to obtain the aromatics, with the sum of these fractions (quantified gravimetrically) being reported as total hydrocarbons. QA/QC procedures included using infrared spectrophotometry to judge the efficiency of silica gel separation. As can be seen in Table 37, the average petroleum hydrocarbon concentration from this predominantly (75%) residential site was 3.69 mg L^{-1} , similar to the residential oil and grease estimate (3.89 mg L^{-1}) of Stenstrom et al. (1984); see Table 35 in this report. While this might suggest that oil and grease estimates are not always higher than more sophisticated hydrocarbon measurements for a given land use, the result could also simply represent a difference in the level of pollution at the two residential sampling sites. Whipple and Hunter (1979) utilizing a method similar to Hunter et al. (1979), found comparable levels of total hydrocarbons (Table 37).

Data for specific toxic hydrocarbon groups are even rarer than total hydrocarbon measurements. The NURP priority pollutant project and others have sampled for synthetic hydrocarbons in urban stormwaters, including monocyclic aromatic hydrocarbons (MAHs), polycyclic aromatic hydrocarbons (PAHs), chlorinated

hydrocarbon pesticides (CHPs), and polychlorinated biphenyls (PCBs). The NURP program detected PCBs only once in all of the samples included in their analysis. PCB-1260 was detected at a concentration of $0.03 \mu\text{g L}^{-1}$ in Lake Quinsigamond, Massachusetts (Cole et al., 1983). This low frequency led NOAA (1987b) to conclude that the concentration of PCBs in urban runoff should be taken as zero when calculating loads. The Southern California Coastal Water Research Project (SCCWRP) detected PCBs at $0.31 \mu\text{g L}^{-1}$ as a flow-weighted mean for three storms monitored in 1979-1980 in the Los Angeles river (Young et al., 1980). QA/QC procedures included the construction of special, noncontaminating glass and metal samplers, and the research methods of the SCCWRP are considered reliable (Risebrough et al., 1978).

The loading of MAHs to the Bay-Delta is of particular interest due to the correlation of MAH tissue concentrations with lesions in striped bass (Whipple et al., 1983). The existing database for MAHs in urban runoff comes from the NURP priority pollutant project, which detected four MAHs in urban runoff around the country. Table 38 lists the MAHs and PAHs detected in urban runoff and their concentrations and frequency of detection, where these are available. Although MAHs were rarely found by the NURP (four compounds detected 5% of the time or less; see Table 38), many reported detections of benzene and toluene were removed from the database due to contamination problems (Cole et al., 1984).

At least 16 different PAHs have been detected in urban runoff around the country (Table 38). Hoffman et al. (1984) estimated PAH loadings to Narragansett Bay, Rhode Island, and concluded that urban runoff is the major source of high molecular

Table 38. Monocyclic and Polycyclic Aromatic Hydrocarbons
 Detected in Urban Runoff. Concentration ranges are those of Cole et al. (1984), as others did not report quantitative concentrations. Sources: 1. Cole et al. (1984); 2. Hoffman et al. (1984); 3. Whipple and Hunter (1979); 4. Eganhouse et al. (1981).

Hydrocarbon	Frequency of Detection ^a %	Concentration Range ($\mu\text{g L}^{-1}$)	Source
MAHs			
Benzene	5	3.5-13	1
Chlorobenzene	5	1-10	1
Ethylbenzene	4	1-2	1
Toluene	2	9	1
PAHs			
<u>Low molecular weight</u> ^a			
n-naphthalene	11	.8-2.3	1, 2, 3, 4
2-methyl naphthalene	-	-	2, 4
1-methyl naphthalene	-	-	2, 4
biphenyl	-	-	2, 4
2-ethyl naphthalene	-	-	2
fluorene	1	1	1, 2
dibenzothiophene	-	.04-.06	2, 3
<u>High molecular weight</u> ^b			
phenanthrene	12	0.3-10	1, 2, 4
fluoranthene	10	0.3-12	1, 2, 3, 4
pyrene	11	0.3-10	1, 2, 3, 4
benzo[a]anthracene	8	1.0-10	1, 2
chrysene	7	0.6-10	1, 2, 3, 4
benzo[e]pyrene	-	-	2
benzo[a]pyrene	4	1-10	1, 2, 3, 4
benzo[b]fluoranthene	1	2	1
benzo[k]fluoranthene	2	4-10	1
xanthene	-	-	4

^a From Cole et al. (1984).

^b After Hoffman et al. (1984).

weight PAHs (Table 38) to that estuary. Low molecular weight PAH loadings were dominated by point sources, as these compounds are probably weathered from urban surfaces and thus are found at lower concentrations in urban stormwaters. They found the precision of their methods to be 11-25%, except for benzo[a]pyrene (41%), based upon analysis of National Bureau of Standards Urban Dust (Standard Reference Material 1649; see NBS, 1986). The paucity of data regarding the concentrations of these compounds in urban runoff makes any analysis of a range of PAH (or MAH) loadings to the Bay-Delta ecosystem extremely preliminary. In the next section, some of the values in Table 38 for PAHs will be combined with land use, precipitation, and runoff coefficient data to estimate a potential (but highly uncertain value) for the loading of these toxic substances to the estuary in urban stormwaters.

Of the 17 CHPs included in the NURP program (Cole et al., 1984), 12 were detected, but only three were found in greater than 10% of the samples. These were alpha-hexachlorocyclohexane (20%), gamma-hexachlorocyclohexane or Lindane (11%), and alpha-endosulfan (13%). By summing the highest or lowest observed concentration for each compound and accounting for its frequency of detection, NOAA (1987b) estimated a reasonable CHP concentration range to be 0.01-0.28 $\mu\text{g L}^{-1}$ for CHPs in urban runoff. This calculation eliminates one chlordane measurement of 10 $\mu\text{g L}^{-1}$ as an outlier. A value of 0.1 $\mu\text{g L}^{-1}$ was selected as a typical concentration. (NOAA [1987b] acknowledged this selection as an arbitrary procedure and noted that a value of 0.05 $\mu\text{g L}^{-1}$ would also be reasonable. In the sensitivity analysis to follow, both of these estimates are utilized.)

Summary

It appears that the NURP priority pollutant monitoring project provides the highest quality database for trace metal concentrations and many synthetic hydrocarbons in urban stormwaters. This finding is based upon the strength of their QA/QC program and the relatively large size of the database. For organics, particularly total hydrocarbons, measurements have been made in several studies from outside the Bay Area although each used slightly different methods. While it is of interest to estimate the input of particular toxic organic constituents such as PCBs, MAHs, PAHs or other chlorinated hydrocarbons, the limited nature of the available database makes such estimates extremely uncertain. Although some local studies have estimated oil and grease concentrations in urban runoff, this measurement is known to include a variety of compounds that are not considered toxic chemicals. Estimates of petroleum hydrocarbon concentrations in stormwaters from other regions indicate values that tend to be lower than the local oil and grease data.

E. Findings

Utilizing data presented in the previous section, an estimate of the loading of toxic chemicals into the Bay-Delta system is now presented. Previous estimates of stormwater loading of toxic substances to San Francisco Bay will first be examined, including the work of Risebrough et al. (1978), Russell et al. (1982), Silverman et al. (1985), and NOAA (1987a). Particular attention will be paid to the latter study, as it is the most comprehensive and ambitious attempt in the field to date. By utilizing the land use and precipitation data of NOAA (1987a) for the Bay-Delta region, along with data from other

investigators on runoff coefficients and pollutant concentrations, a sensitivity analysis of NOAA's loading estimates will be conducted to identify the reasonable ranges of uncertainty which bound estimates of the loading of toxic chemicals into the Bay and Delta by urban stormwaters.

Previous Loading Studies

The Association of Bay Area Governments (ABAG) has investigated the nature and magnitude of pollution flow to the estuary by urban runoff, due to the role of ABAG as the lead agency for the Bay Area's 208 study. The major studies sponsored by ABAG include the work of Risebrough et al. (1978), Russell et al. (1982), and Silverman et al. (1985).

Risebrough et al. (1978) were among the first to present an estimate of the input of toxic chemicals into the Bay-Delta estuary by urban runoff. The study focused upon the fate and effects of toxic substances in the estuarine ecosystem and only briefly examined the sources of these materials. By assuming a volume of urban runoff equal to one-tenth of delta outflow, they calculated the loading of eight trace metals to San Francisco Bay (Table 39). The authors, however, state that the values used in their calculations are "suspect" and "little credence" should be given to the loading estimates until a detailed review of sampling and analytical methods is conducted. Consequently, the work of Risebrough et al. (1978) provides no data that may be used to develop more refined estimates of the loading of toxic substances into the estuary by urban runoff.

Russell et al. (1982) present an estimate for the loading of trace metals by surface runoff into San Francisco Bay of 1,200

Table 39. Previous estimates by the Association of Bay Area Governments of the loading of toxic chemicals to San Francisco Bay. All values in tonnes yr⁻¹.

Pollutant	Risebrough <u>et al.</u> (1978)	Silverman <u>et al.</u> (1985)
Arsenic	111	
Cadmium	8.5	
Chromium	1.2	
Copper	89	
Lead	590	
Mercury	6.2	
Nickel	51	
Zinc	330	
Oil and Grease		
low rainfall		1690
mean rainfall		3446
high rainfall		5293

tonnes yr^{-1} , in which the load for all metals is converted to chromium equivalents based upon the relative toxicities of these elements compared to chromium. While it is not clear from their paper, their estimate is evidently derived from trace metal concentrations presented by Metcalf and Eddy, Inc. (1978), who in turn cite the trace metal analysis of Litwin et al. (1977). As discussed in the previous section, the problems associated with this dataset limit its usefulness for estimating trace metal loads in urban runoff.

Following the work of Stenstrom et al. (1984), Silverman et al. (1985) developed an estimate of the loading of oil and grease into the Bay by urban runoff (Table 39). Estimates of the concentration of many hydrocarbons in urban runoff were provided. As discussed previously, however, their sampling scheme might lead one to question the utility of their concentration data for loading estimates.

The most recent effort to estimate the loading of toxic substances to the Bay-Delta ecosystem is the National Coastal Pollutant Discharge Inventory (NCPDI), which has been developed by the National Oceanic and Atmospheric Administration. This study is the only one that has examined the discharge of several toxic chemicals into the entire Bay-Delta ecosystem from urban runoff, as the ABAG studies focused only upon the Bay and did not include the Delta.

The NCPDI is a database and computer model that approximates the discharge of pollutants into estuarine and coastal waters of the nation for the year 1982. The program covers three distinct geographic regions: the East Coast, the Gulf Coast, and the West

Coast. The goal of the program, which was developed by the Strategic Assessment Branch of NOAA, is to assist in the identification and evaluation of present and future conflicts regarding the use of coastal and oceanic resources. Of great interest is the relative contributions to the nation's estuarine and coastal waters of different sources of pollution. Particular attention has been paid to documenting all methods and assumptions used to develop the database and computer model, and \$2 million has been spent over the last four years in program development and implementation.

The nine pollutant categories covered are oxygen-demanding materials, particulate matter, nutrients, heavy trace metals, petroleum hydrocarbons, chlorinated hydrocarbon pesticides, pathogens, sludges, and wastewater. The source categories included are streamflows, point sources, urban runoff, nonurban runoff, irrigation return flows, oil and gas operations, marine transportation operations, accidental spills, and dredging operations. The toxic pollutants included in the NCPDI are arsenic, cadmium, chromium, copper, iron, lead, mercury, petroleum hydrocarbons, chlorinated hydrocarbon pesticides, and PCBs (Basta et al., 1985).

The NCPDI calculates stormwater runoff using the Rational Method based upon runoff coefficients derived from the NURP. Runoff is estimated for different land use classifications included in their land use inventory (see Table 32). Urban areas identified are then cataloged based upon the existence of separate or combined sewers, and pollutant concentrations are estimated utilizing data from the NURP and from Stenstrom et al. (1984), with separate data used to estimate concentrations for

combined sewer overflows. Overflow volumes are estimated for each half hour of each storm using characteristics of sewage treatment plants in different urban areas, such as detention basin size and hydraulic capacity (including factors for pump wear; NOAA, 1987**b**).

NCPDI output is available in a variety of formats, including various spatial scales such as county, USGS hydrologic cataloging unit, or offshore grid cells. NOAA has prepared a special summary of NCPDI output for the San Francisco Bay area that includes the Delta (see Fig. 5 above).

NCPDI loading estimates for 1982 are presented in Table 40. The data have been edited to remove those hydrologic units included in the NOAA regional summary (NOAA, 1987**a**) that do not drain into the estuary (USGS cataloging units 18050005 and 18050006). Even a cursory comparison of the data in Table 39 with those in Table 40 reveals great disparities in the estimates of the loading of toxic chemicals into the Bay and Delta due to urban runoff. The estimates of Risebrough et al. (1978) for the loading of arsenic, cadmium, mercury, lead, and zinc are from 2 to 50 times greater than the estimates of NOAA (1987**a**), while the estimate for chromium by Risebrough et al. (1978) is an order of magnitude less than the NOAA estimate. It should be noted that Risebrough et al. (1978) stated that "little credence" should be placed in their urban runoff estimates pending further investigation of sampling methods.

The estimate of oil and grease loading to San Francisco Bay by NOAA (1987**a**) of almost 7,500 tonnes is about 2 to 4 times the values presented by Silverman et al. (1985). This might seem

Table 40. Loading of toxic chemicals into the Bay-Delta for 1982 from urban runoff as calculated by the National Coastal Pollutant Discharge Inventory (NOAA, 1987a). Results for USGS hydrologic cataloging units 18050005 and 18050006 have been removed from this summary, as these units do not drain into the Bay-Delta ecosystem. Values in tonnes unless otherwise noted.

Pollutant	Total Delta	Total S.F. Bay	Total Bay-Delta
Arsenic	2	5	7
Cadmium	<1	2	2
Chromium	4	11	14
Copper	12	39	51
Lead	49	166	215
Mercury (kg)	30	3	3
Zinc	53	177	230
Oil and Grease	2,294	7,457	9,751
PCB (kg)	3	12	15
CHP ^a (kg)	13	44	57

^aCHP = chlorinated hydrocarbon pesticides

remarkable, in that the total San Francisco Bay urban land use used by NOAA (1987a) is approximately 2,500 km², while Silverman et al. (1985) estimated total oil and grease input from all Bay land uses (12,265 km²). Silverman et al. (1985) assumed, however, that oil and grease loadings from non-urban land uses were equal to zero.

Although NOAA presents their estimate as a value for petroleum hydrocarbon loading in urban stormwaters, their method utilizes the pollutant concentrations of Stenstrom et al. (1984). As the latter investigators measured oil and grease rather than petroleum hydrocarbons, the estimates included in the NCPDI for petroleum hydrocarbons are in fact estimates of oil and grease loadings.

Two important aspects of the estimates by NOAA (1987a) must be kept in mind. First, the estimates presented in Table 40 utilize precipitation data for the year 1982, one of the wettest years in the last decade. For a dry year, the estimates of NOAA (1987a) could be lower by an order of magnitude, and combined sewer overflow volumes (affecting loading estimates for Sacramento and San Francisco) could be reduced by an even greater proportion.

Second, in making assumptions regarding pollutant loadings, NOAA (1987b) adopted a policy of erring on the side of "worst case" values when faced with relatively arbitrary decisions. Thus, in addition to the high precipitation values, other components of the NCPDI assessments tend to overestimate loadings. An example of this is NOAA's estimate for the chlorinated hydrocarbon pesticide concentration in urban runoff (NOAA 1987b).

Sensitivity Analysis

As a result of the above factors, it is considered most appropriate to conduct a sensitivity analysis of the NCPDI loading estimates. In such an analysis, the assumptions underlying a model are varied to determine the sensitivity of the model's predictions to different parameters. Even though the NCPDI is the most thorough, sophisticated, and well-documented analysis performed to date, the information presented throughout this chapter clearly indicates that the uncertainty of urban stormwater loading estimates is very large. It is not considered appropriate to simply provide a "best estimate" of the loading of toxic chemicals to the Bay-Delta ecosystem from urban runoff. Instead, sensitivity analysis is employed to provide a range of possible values that may then be rendered more accurate through continued research.

In this section, some parameters in the NCPDI will be varied based upon data from other studies (for runoff coefficients and pollutant concentrations) or time periods (for precipitation). A "base case scenario" will be generated, reflecting the existing assumptions of NOAA (1987a, b). Reasonable values from other studies will then be substituted into the model to establish "high," "low," and "lowest" cases, the latter using the parameters from the low case and the precipitation data from the drought year of 1977. The estimated loadings from "high" and "lowest" cases will serve as the upper and lower bounds for the estimated range of contaminant loading to the San Francisco Bay-Delta ecosystem from urban runoff.

With the cooperation of the Strategic Assessments Branch of NOAA (F. Arnold, personal communication), the data on land use

and precipitation used as input for the NCPDI were obtained. The land use information is included in the Appendix to this report (available from AHI); and precipitation data are presented in Table 31. The runoff coefficients and pollutant concentrations utilized by NOAA (Table 41) were then combined with the data on precipitation and land use to generate loading estimates, using the spreadsheet program Excel (Microsoft, Inc.).

As both Sacramento and San Francisco employ combined sewers, loading estimates for these regions were prepared by multiplying overflow volumes by estimated pollutant concentrations.

Pollutant concentrations in combined sewer overflows are higher than for stormwater runoff (see Table 41). Overflow volumes were calculated as described earlier (see NOAA, 1987b). Information about the acreage served by the combined sewer in Sacramento was necessary, as only a portion of the HUCO (hydrologic unit/county) containing Sacramento is served by the combined sewer. This area of 27.5 km² (6800 acres) (NOAA value confirmed by Montoya [1987]) was subtracted from the land use data for the Sacramento HUCO (#0606718020109) by assuming that the land uses represented in the combined sewer acreage were divided in the same proportions as for the entire HUCO. For example, as this HUCO contained 63% residential land, 63% of combined sewer area was subtracted from the residential land use category.

The loading estimates generated by this method are presented in Table 42. As the estimates were calculated based upon the HUCO scheme, it was possible to compile estimates by estuarine segment in a gross manner (see Figure 5 above and Table 42). Comparison of Table 42 with the estimates of NOAA (1987a) in Table 40 indicates that the base case loading estimates for urban

Table 41. Summary of pollutant concentrations and runoff coefficients utilized by NOAA (1987a) in the National Coastal Pollutant Discharge Inventory for the West Coast. After NOAA (1987b). All concentration values in $\mu\text{g L}^{-1}$, except as noted.

Pollutant	urban runoff	combined sewer overflows	runoff coefficients
Arsenic	6.63	9.82	
Cadmium	1.84	8.09	
Chromium	9.18	103	
Copper	43	100	
Lead	182	474	
Mercury	0.1	0.673	
Zinc	202	264	
PCB	0.0	0.416	
CHP ^a	0.05	0.069	
Oil and Grease (mg L^{-1})			
Residential	3.89	13.8	0.2
Industrial	13.13	13.8	0.3
Commercial	7.1	13.8	0.65
Mixed	6.23	13.8	0.23
Open	0.0	13.8	0.06

^a CHP = chlorinated hydrocarbon pesticides.

Table 42. AHI Base case loading estimates utilizing the data of NOAA (1987a,b). The above estimates differ from the data in Table 10 due to differences in land use inputs. Data in metric tonnes for 1982, except for mercury, PCBs and CHP, which are in kg for 1982.

SEGMENT					POLLUTANT LOADS			Hydro-			runoff
	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Zinc	carbons	PCB	CHP	volume
						(KG)			(KG)	(KG)	m3
DELTA	2	0	3	11	46	28	49	2251	3	12	2.3E+08
SOUTH BAY	3	1	4	17	71	39	78	3323	0	19	3.9E+08
CENTRAL/SAN PABLO BAY	2	1	5	11	48	38	46	1993	12	12	2.2E+08
SUISUN BAY	1	0	1	3	15	8	16	726	0	4	8.0E+07
Total SF Bay	5	1	9	31	134	85	141	6043	12	35	6.9E+08
Total Bay-Delta	6	2	12	42	179	113	189	8293	15	47	9.2E+08

runoff used in this report are 14-18% lower than the values from the NCPDI. This bias is due to the fact that the land use data readily available from the Strategic Assessment Branch of NOAA are LUDA data from USGS for the 1972-75 period that are not corrected by the 1980 census as described earlier. This is demonstrated by the fact that the estimates for PCB loadings in the base case in this report and the NCPDI are identical (Tables 40 and 42; 15 kg for the Bay-Delta system in 1982). As the NCPDI assumed that only combined sewer overflow resulted in PCB loadings (Table 41), the estimates of PCB loadings are based solely on estimated overflow volumes and not on land use. As only the PCB estimates match, it would appear that the differences are due to the difference in land use inputs. (Although the estimates for cadmium [approximately two tonnes] only differ by 3%, this is probably an artifact of rounding the small loading estimate). It should be noted that, as a quality assurance check, all data inputs to the spreadsheet program were checked against the original hardcopy.

The variation between the loading estimates of NOAA (1987a) and the base case scenario in this report provides some insight into the sensitivity of the loading estimates to land use assumptions. In essence, the base case utilizes land use data that are 5 to 8 years older than the NOAA (1987a) data, and the base case loading estimates are 14-18% less. Without the details of the two sets of data, it is not possible to fully identify the influence of land use. However, it appears that utilizing current land use information could possibly increase the loading estimates by up to 20%, demonstrating the impact of increasing urbanization.

Table 43 presents the assumptions used to create the "high", "low", and "lowest" loading scenarios. The "high" case was generated by (1) substituting larger runoff coefficients for all land uses based upon the values in Table 33, and (2) utilizing the data of Young et al. (1980) regarding PCBs in runoff in Los Angeles. Utilizing these data on PCBs results in a loading estimate for the Bay-Delta that could be too high, given the documented PCB contamination in the Los Angeles region. As the goal of this analysis is to present a high and low estimate, however, and as there are no local data available, the value of Young et al. (1980) is used.

The "low" case was generated by using the "low mean" concentrations of trace metals from the NURP priority pollutant project (Table 36) and total hydrocarbon estimates (Table 37), rather than values for oil and grease. As mercury was detected in only 4% of the samples, the NURP priority pollutant program reported no value (Cole et al., 1983). For the "low" case, the mercury concentration was arbitrarily reduced by half. As there are so few measurements of total hydrocarbons in urban runoff, approximate values were assigned by land use as follows: residential (2 mg L^{-1}), commercial (3 mg L^{-1}), mixed (3 mg L^{-1}), industrial (5 mg L^{-1}), and open (0 mg L^{-1}). Although somewhat arbitrary, these lower concentrations reflect the important need to separate toxic hydrocarbons from the larger suite of substances isolated in traditional oil and grease measurements. As NOAA (1987b) indicated that the lowest reasonable value for CHP concentration based upon the NURP priority pollutant data would be $0.01 \text{ } \mu\text{g L}^{-1}$, this value was used in the "low" case.

Table 43. Conditions for "high," "low," and "lowest" loading scenarios calculated in the sensitivity analysis.

"High"

- (1) Increase runoff coefficients for open (0.15); residential (0.3); commercial (0.8); industrial (0.6); and mixed (0.3).
- (2) Use data on PCBs in Los Angeles River stormwater runoff, after Young et al. (1980).

"Low"

- (1) Use "low mean" trace metal concentrations from NURP Priority Pollutant Project (Table 36).
- (2) Substitute estimated total hydrocarbon concentrations for oil and grease concentrations as: residential (2 mg L^{-1}); industrial (5 mg L^{-1}); commercial (3 mg L^{-1}); mixed (3 mg L^{-1}); and open (0 mg L^{-1}).
- (3) Use intermediate year precipitation data (1981).
- (4) Use base case runoff coefficients.

"Lowest"

- (1) Pollutant concentrations set as in low case.
- (2) Use drought year precipitation data (1977).
- (3) Reduce runoff coefficients for open land use to 0.02 and mixed land use to 0.15.

The final condition in the low scenario is to utilize a drier year than 1982 for precipitation, as in a dry year, total runoff and thus total loads are significantly reduced. As mentioned previously, precipitation during 1982 was greater than any other year between 1975 and 1983. Clearly, contaminant loading from urban runoff will vary between years according to overall precipitation. This variation exists whatever the precise effects of pollutant concentrations and runoff coefficients may be, and is thus worthy of modeling here.

Consequently, it was decided that the "low" case should use a year of intermediate precipitation (such as 1981), while a "lowest" case should also be included, to reflect precipitation conditions during the drought in 1977. This helps to separate the influence on loading estimates of precipitation variation from changes due to varying other modeling parameters. In this analysis, runoff coefficients for open and mixed land uses were slightly lowered to reflect drier soil conditions.

It should be noted that the combined sewer overflow (CSO) volumes from 1982 were not recalculated based upon the lower precipitation input in the "low" and "lowest" cases, because the values included for CSO volumes were calculated by NOAA (1987b) in a complex manner, as previously described. In an effort to reduce these volumes in keeping with the "low" and "lowest" scenarios, CSO volumes were adjusted based upon the ratio between 1982 and 1981 precipitation ("low" case) or 1982 and 1977 precipitation ("lowest" case) for the appropriate HUCOs. These ratios were calculated from the data in Table 31 for Sacramento and San Francisco (the only regions in the Bay-Delta employing combined sewers).

The results of these sensitivity analyses are presented in Tables 44 ("high"), 45 ("low"), and 46 ("lowest"). The tables indicate that the range for loading estimates from the "high" to the "lowest" case is approximately 800%. (Note in these tables that some estimates are in kilograms and some in metric tonnes). The highest loadings for any trace metal are those for zinc (34 to 268 tonnes yr^{-1}), followed closely by lead (30 to 250 tonnes yr^{-1}). The lowest trace metal loadings are for mercury (26 to 152 kg yr^{-1}) and cadmium (0.3 to 3 tonnes yr^{-1}).

As would be expected, the greatest loading estimated for any category is that for oil and grease, which in the "low" and "lowest" cases is more accurately identified as total hydrocarbons (1,143 to 11,016 tonnes yr^{-1}). The greatest variation for any single constituent is for PCBs (6 to 399 kg yr^{-1}). As mentioned previously, this is due to the use of a concentration range from zero to 0.3 $\mu\text{g L}^{-1}$, and the high estimate is considered to be a maximum PCB load for the Bay-Delta that is rather unlikely.

Of the four portions of the estuary identified, the South Bay receives the largest loadings in all cases, with the Delta and Central/San Pablo Bay receiving intermediate loadings and Suisun Bay receiving the least. This follows the pattern of urban land distribution; the South Bay catchment contains 42% of the urban land, followed by the Delta (27%), Central/San Pablo Bay (20%), and Suisun Bay (11%). It must be re-emphasized, however, that the method and data used in these calculations become less valid as one attempts to apply them on a finer scale. Moreover, as urban growth is not evenly distributed throughout

Table 44: Pollutant Loadings as Predicted in the "High" scenario.
 All values in metric tonnes except where noted.
 Case parameters are described in Table 40 and text.

SEGMENT	POLLUTANT LOADS										Runoff Volume
	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury (KG)	Zinc	Hydro- Carbons	PCB (KG)	CHP (KG)	
<i>DELTA</i>	2	1	4	15	62	37	67	2921	100	17	3E+08
<i>SOUTH BAY</i>	4	1	5	24	103	57	115	4567	170	28	6E+08
<i>CENTRAL/SAN PABLO BAY</i>	2	1	6	15	64	47	64	2571	95	16	3E+08
<i>SUISUN BAY</i>	1	0	1	5	20	11	23	957	34	6	1E+08
Total SF Bay	7	2	12	44	188	115	201	8095	299	50	1E+09
Total Bay-Delta	9	3	15	59	250	152	268	11016	399	67	2E+09

Table 45: Pollutant Loadings as Predicted in the "Low" scenario Case. All values in metric tonnes except where noted. Case parameters are described in Table 40 and text.

SEGMENT	POLLUTANT LOADS										runoff
	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Zinc	Hydro-carbons	PCB	CHP	volume
						(KG)			(KG)	(KG)	m3
<i>DELTA</i>	2	0	3	11	46	28	49	2251	3	12	2.3E+08
<i>SOUTH BAY</i>	3	1	4	17	71	39	78	3323	0	19	3.9E+08
<i>CENTRAL/SAN PABLO BAY</i>	2	1	5	11	48	38	46	1993	12	12	2.2E+08
<i>SUISUN BAY</i>	1	0	1	3	15	8	16	726	0	4	8.0E+07
Total SF Bay	5	1	9	31	134	85	141	6043	12	35	6.9E+08
Total Bay-Delta	6	2	12	42	179	113	189	8293	15	47	9.2E+08

Table 46: Pollutant Loadings as Predicted in the "Lowest" scenario. All values in metric tonnes except where noted. Case parameters are described in Table 40 and text.

SEGMENT					POLLUTANT LOADS			Hydro-			Runoff
	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Zinc	Carbons	PCB	CHP	Volume
		(KG)				(KG)			(KG)	(KG)	m3
DELTA	<1	64	1	2	7	6	8	266	1	1	8.3E+07
SOUTH BAY	<1	66	<1	2	9	6	11	359	0	1	1.2E+08
CENTRAL/SAN PABLO BAY	<1	142	1	3	12	12	11	418	5	2	1E+08
SUISUN BAY	<1	19	<1	1	3	2	3	100	0	<1	3.6E+07
Total SF Bay	1.0	228	2	5	23	20	26	877	5	3	2.6E+08
Total Bay-Delta	1.0	292	3	7	30	26	34	1143	6	4	6.1E+08

the catchment, more recent land use data may alter this assessment somewhat. Consequently, this prediction of stormwater loadings by segment must be considered of the most preliminary nature. Given the site-specific nature of urban runoff phenomena and the potential for acute effects of high-concentration flushes, the further refinement of loading estimates for different portions of the estuary would be a valuable exercise.

Tables 45 and 46 demonstrate that calculating loads based upon the drought year conditions of 1977 reduces loading estimates by approximately 50% when compared to the values generated using precipitation data for the more normal year of 1981. This indicates that differences in stormwater loadings between years can easily vary by a factor of two based solely upon changes in precipitation. These changes are reflected in the runoff volumes also presented in Tables 45 and 46.

Given the fact that Hoffman et al. (1984) determined urban runoff to be the most important source of high molecular weight PAHs (see Table 38) to Narragansett Bay, Rhode Island, it is considered important to develop an approximate estimate of the loading of these substances to the Bay-Delta system. As mentioned previously, such an estimate is extremely uncertain due to the small database that exists on PAH concentrations in urban stormwaters.

Utilizing the base case scenario for precipitation, land use, and runoff coefficients, and including a concentration estimate of $5 \mu\text{g L}^{-1}$ for high molecular weight PAHs in urban runoff, a preliminary estimate of 4 tonnes yr^{-1} for the Bay-Delta is estimated. The concentration data used represent the approximate sum of high molecular weight PAHs shown in Table 38,

using the lower concentrations reported therein. Based upon the ratio between high and low molecular weight PAHs in urban runoff found by Hoffman et al. (1984), a loading estimate for low molecular weight PAHs for the Bay-Delta would be about 1 tonne yr^{-1} . Given the range of variation determined for other toxic substances, these values must be considered to be of a very preliminary nature.

Hoffman et al. (1984) estimate a total PAH discharge rate of 1.0 g per capita. It is most interesting to note that, assuming a population in the Bay-Delta region of five million, the above preliminary loading estimates also produce a per capita loading factor of 1.0 g. As the Bay-Delta loading for total PAHs could also be 0.5 tonnes yr^{-1} (0.1 g per capita), little importance should be attached to the correspondence of these two estimates without further study.

F. Conclusions

This section presents an estimate of the annual loading of various contaminants into the Bay-Delta ecosystem through urban stormwater runoff. The basic method employed involves predicting runoff volumes for various land uses, and multiplying these volumes by reasonable estimates of pollutant concentrations. Much uncertainty is associated with this method, and the results are only valid when averaging over relatively large ranges of space and time.

Precipitation and land use data compiled by NOAA for the Bay-Delta as part of the National Coastal Pollutant Discharge Inventory were combined with various estimates of runoff coefficients and pollutant concentrations to develop ranges for the loading of contaminants into the Bay-Delta. These estimates

utilize concentrations measured for the most part in the Priority Pollutant Monitoring Project of the Nationwide Urban Runoff Program, as these data are considered to be the most reliable. Due to a disappointing lack of attention to QA/QC procedures in most local studies, data from the Bay-Delta itself were considered too unreliable to be used in deriving loading estimates for the estuary.

The estimated ranges in annual loads for the Bay-Delta are summarized in Figure 6. Note that these Figures include a logarithmic scale on the vertical axis. Ranges are presented, rather than means because the level of uncertainty in these estimates is simply too great to identify a "best estimate". Most estimates vary by a factor of 8 to 10, with estimates of PCB loads varying by an even greater amount.

It is clear that urban stormwater runoff is a significant source of toxicants to the Bay-Delta estuary. Estimates of the loading of trace metals vary from 0.3 to 3 tonnes yr^{-1} of cadmium, to 34 to 268 tonnes yr^{-1} of zinc. The range of total hydrocarbon inputs to the ecosystem is 1,100 to 11,000 tonnes yr^{-1} . This latter range encompasses the previous estimates of oil and grease inputs to the Bay of Silverman et al. (1985).

The most important conclusions that can be made from the information presented in this section, however, concern recommendations for reducing the uncertainty inherent in estimating stormwater loads by improving the database. Without such an effort, it will not be possible to more precisely determine the loading of contaminants into the Bay-Delta ecosystem by urban runoff.

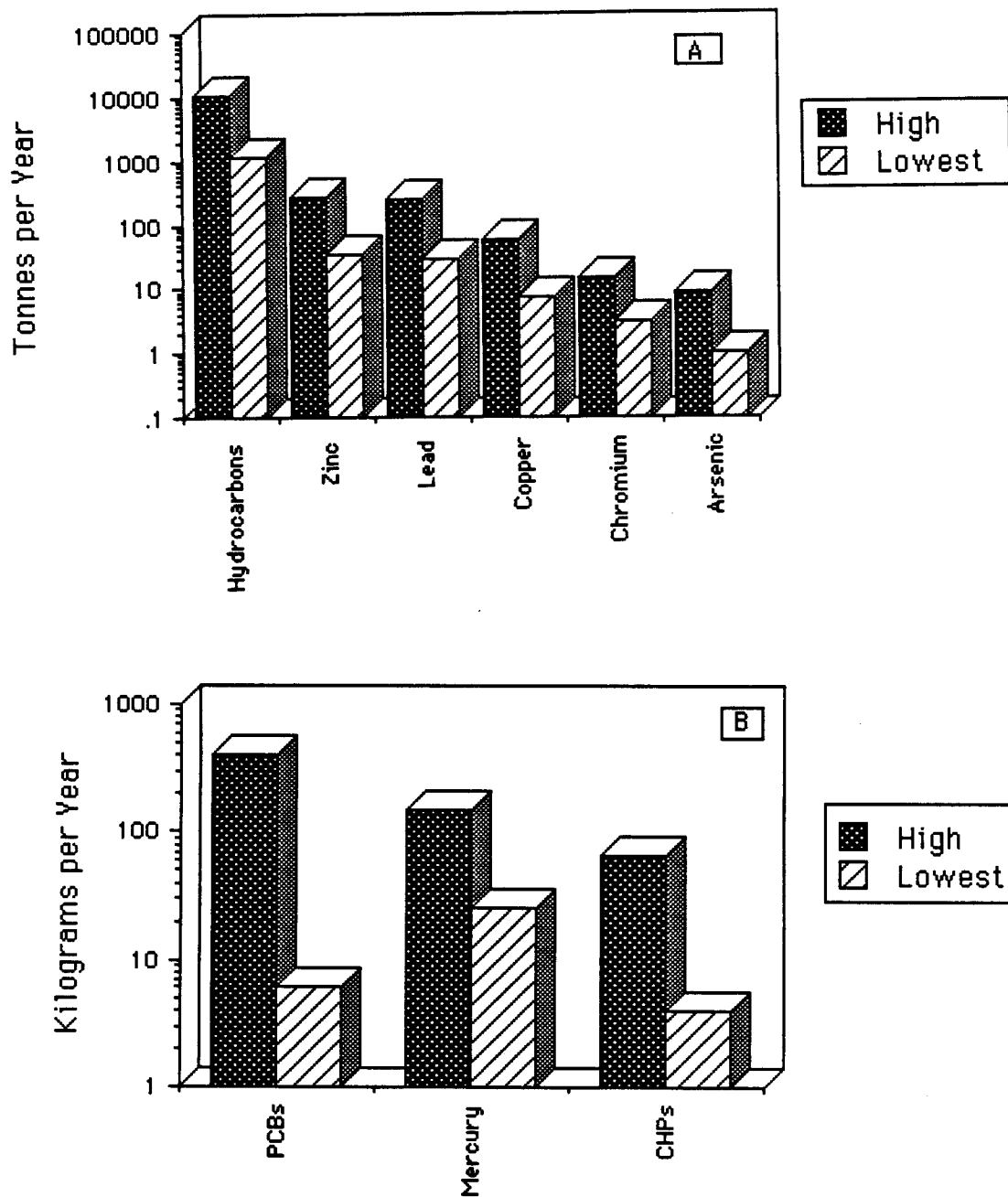


Fig. 6: Ranges for the Loading of Contaminants into the Bay-Delta Ecosystem from Urban Runoff. (A) Values in tonnes yr⁻¹ for hydrocarbons, (high estimate is calculated as oil and grease, low estimate as total hydrocarbons); (B) Values in kilograms yr⁻¹. CHPs = chlorinated hydrocarbon pesticides.

Of particular concern in this regard are measurements of the concentrations of contaminants in stormwaters of the region. In order to utilize the best available data, the estimates presented above were based upon concentration estimates from other parts of the country. Due to variations in such factors as climate, land use, topography, and traffic patterns, concentration data from the Bay-Delta region may be significantly different in reality from the ranges discussed in this section.

Contaminant measurements must utilize rigorous QA/QC procedures to assure the quality of the database, and must estimate flow-weighted concentrations to ensure the production of accurate loading estimates. QA/QC procedures should include the use of blanks and standards throughout the sampling and analytical phases of a project, plans to monitor for transcription and labelling errors, analysis of National Bureau of Standards Reference Materials, and intercalibration among analytical laboratories.

In order to truly understand the potential impact of urban runoff on the estuary, intensive sampling of regions both in time and space will be necessary. The loading of contaminants from urban runoff is controlled by a variety of factors that can vary tremendously among sites, or among storms at the same site. Thus, certain portions of the estuary are likely to receive greater loads than would be predicted from basin-wide averages. The demonstration of high concentration flushes of pollutants during storms means that receiving water monitoring must also be conducted on an intensive scale in order to develop an understanding of the potential acute impacts of runoff events on estuarine biota.

3. NONURBAN RUNOFF

A. Introduction

This section reviews the loading of toxic pollutants to the Bay-Delta ecosystem in runoff from nonurban areas. This source includes runoff from agricultural lands (including irrigation return flows), pastureland, and forests within the Bay-Delta area. Nonurban runoff into the Sacramento and San Joaquin Rivers beyond the boundaries of the Delta is considered in section II.4 on riverine inputs. Toxic substances in nonurban runoff are derived from the erosion of soils and leaching of trace elements and introduced synthetic compounds, such as pesticides. While erosion and runoff are natural processes, anthropogenic alterations of terrestrial ecosystems can lead to large increases in the quantity of substances discharged to receiving waters.

Concern over the flow of toxic chemicals into the estuary in nonurban runoff has been heightened by the detection of agricultural chemicals in water, sediment, and biota throughout the Delta and by the leaching of selenium into the Kesterson National Wildlife Refuge from farmlands in the western San Joaquin Valley. Particularly well-studied have been the rice herbicides molinate and thiobencarb, marketed under the trade names Ordram and Bolero, respectively (Cornacchia et al., 1984; California Department of Food and Agriculture [DFA], 1986). One third of the flow of the Sacramento River between Knight's Landing and Sacramento during the rice growing season can be water draining from rice fields, and rice herbicide residues have been measured in portions of the Sacramento River used by striped bass, American shad, and white sturgeon as spawning areas (Cornacchia et al., 1984). According to the Department of Water

Resources (DWR), agricultural drainage is the predominant source of water in the San Joaquin river during the summer (DWR, 1986**b**).

The complexity of estimating loads from nonurban regions, combined with the lack of readily available data for parameters of interest, means that the development of an independent estimate of the loading of toxic chemicals to the estuary is beyond the scope of this study. Instead, existing estimates of the loads of toxic substances to the estuary from nonurban runoff will be reviewed and critiqued. Analysis of the methods and assumptions used in existing analyses will help in understanding the level of uncertainty associated with these estimates and how their accuracy can be improved.

There has been only one estimate of the loading of toxic substances into the Bay-Delta ecosystem from nonurban runoff. This estimate has been made by (NOAA, 1987**a**) as part of the National Coastal Pollutant Discharge Inventory (NCPDI), a nationwide assessment of the loading of pollutants into estuaries and coastal ocean waters from several different sources. (For a more detailed description of the NCPDI, see section 2 on Urban Runoff [see also Basta et al., 1983]). Consequently, this section reviews the methods and results of NOAA (1987**a**, **c**) in order to describe the complexity of nonurban runoff phenomena, the potential magnitude of the problem, and the major sources of uncertainty in loading estimates. (It should be noted that, while DFA [1986] has estimated the loadings of molinate and thiobencarb to the Sacramento River, their study area lies outside the Bay-Delta. This is also true of the estimates of selenium discharge to the San Joaquin river developed by the State Water Resources Control Board, [SWRCB 1987]).

B. Methods for Estimating Nonurban Runoff

Runoff from nonurban lands is a highly complex phenomenon involving physical, biological, and cultural factors. Physical factors include precipitation duration and intensity, soil characteristics such as permeability and erodability, and topography. Biological factors are particularly in evidence with respect to type of crops planted and degree of vegetative cover, and cultural factors include various agricultural practices such as method and amount of irrigation, tillage, and terracing. The concentration of toxic substances in runoff from nonurban lands is also influenced by a similar suite of factors. These include soil composition, the stability and solubility of various contaminants, the rate of application of agricultural chemicals, and the methods for handling and releasing drain water.

One way to measure the loading of toxic substances in nonurban runoff is to combine pollutant concentration measurements with river flow data from agricultural regions. By subtracting similar data from an upstream station, loads from a particular agricultural region can be estimated. Unfortunately, river concentrations are often so low, and monitoring so infrequent, that it is not possible to calculate loads in this manner (see section on riverine inputs for discussion of this topic in more detail).

Moreover, toxic pollutants from agricultural lands are often associated with suspended particulates that may settle out of the water column into creek and river sediments. During periods of high and turbulent flow, these particles will be resuspended and carried downstream. Evidence for this fact can be seen in the elevated concentrations of DDT and its derivatives still found in

Bay-Delta species many years after the use of these substances has been prohibited by law. While there may be some illegal use of these materials, (they can also be found as contaminants in other pesticides [Harte et al., 1987]), their continued detection is undoubtedly due to their resistance to degradation and their episodic movement through the estuary during high flow periods.

Another way to estimate the loading of toxic chemicals from nonurban lands is to actually measure flows and pollutant concentrations from many sites in the Bay-Delta region. By correlating such data with factors such as precipitation, irrigation, and pesticide application, loading factors can be developed to allow the prediction of pollutant loads, given certain levels of precipitation and irrigation. As was alluded to above, however, there are many additional factors that will influence loads from nonurban runoff, including crop type, topography, and soil characteristics. The collection, compilation, and analysis of such a volume of data is a challenging and expensive proposition that has yet to be undertaken.

Some data on agricultural drainage water quality do exist, mostly for regions outside the Bay-Delta (Cornacchia et al., 1984; Department of Water Resources, 1986a, b; DFA, 1986). The Interagency Delta Health Aspects Monitoring Program (initiated in 1983) is in the process of identifying and mapping agricultural drains in the Delta and is also monitoring the concentration on a monthly basis of selenium, certain pesticides, trihalomethane precursors, and several conventional constituents in drainage water from the Empire Tract, Tyler Island, and Grand Island. The program includes a strong QA/QC element. These data will be combined with estimates of flow (derived from electricity use and

pump efficiencies) to estimate loads to the Delta from these agricultural drains (DWR, 1986c).

Loads calculated from these data will be highly uncertain due to several factors. The concentrations of toxic contaminants are often at or below limits of detection, and the monthly sampling scheme could miss discharges of higher concentration related to specific storms, irrigation events, or pesticide applications. In addition, many pumping stations are probably poorly maintained, making pumping efficiencies quite inaccurate (DWR, 1986c).

An alternate method that could be used to estimate pollutant loadings from nonurban runoff would be to estimate total suspended sediment delivered to receiving waters from nonurban runoff ("sediment yield") and combine this estimate with typical concentrations of toxic substances in the soils of interest. When used to calculate loadings for an estuary, such a method provides an estimate of the soil-derived toxic substances eventually delivered to the system as discussed above. Another method, however, must be used to estimate discharge of applied chemicals.

Given the importance of soil erosion in agriculture and silviculture and the adverse impacts in aquatic ecosystems of soil erosion through habitat destruction, a significant amount of research has been conducted in an effort to understand the important factors and processes involved in sediment loss from nonurban lands. Much of this research has focused upon developing models that can assist in predicting sediment loss from nonurban lands. The loading estimate of NOAA (1987a) mentioned above uses such a model, termed "Simulator for Water

Resources in Rural Basins" (SWRRB), to generate estimates for sediment yield from a variety of land use types. These estimates are combined with average trace metal concentrations in soils to calculate loads for these substances.

As discussed below, sediment loss models such as SWRRB are relatively complex and require a significant amount of data as input. Since the development or use of such a model is beyond the scope of this study, the paragraphs below describe the methods of NOAA (1987a, c) and present their results.

Methods Used in the NCPDI

NOAA (1987a) has estimated the loading of several trace metals and chlorinated hydrocarbon pesticides (CHPs) to the Bay-Delta ecosystem from nonurban runoff. Trace metal loadings were calculated from sediment yields derived using the SWRRB model and a nationwide survey of trace metals in soils. CHP loadings were calculated using data on pesticide use in each Bay-Delta county in combination with a loss factor that estimated the fraction of applied CHPs included in runoff. Loads of trace-metals and CHPs were estimated separately for irrigation return flows. These methods are summarized briefly below; a more detailed treatment is available in NOAA (1987c).

Nonurban Runoff. The SWRRB model was developed by scientists from the Agricultural Research Service, U.S. Department of Agriculture, in Texas. As the model is relatively new, there is very little published information regarding its development, formulation, or use. The model was selected for use in the NCPDI because it: (1) includes the processes most important in determining sediment yield, such as event-based precipitation

data and daily soil moisture conditions; (2) is rationally based and thus does not require re-calibration for each region being simulated; and (3) uses readily available data as input.

There are 29 separate input parameters for the SWRRB model (Table 47), including data on soils, topography, climate, hydrology, and agricultural practices. The data are used by the model to compute daily sediment and water budgets for a given basin by simulating rainfall, percolation, evapotranspiration, subsurface return flow, crop growth, surface runoff, sheet and rill erosion, and sediment transport. As this model has been applied to individual watersheds using specific data collected in the field, the use of the SWRRB by NOAA represents a new application of the model. Consequently, NOAA (1987c) had to adapt the model for use on a much wider geographic scale and assemble data from this larger region in a format suitable for input to the model.

The basic method used was to develop the necessary data on the basis of HUCOs, the geographical intersection of counties and U.S. Geological Survey (USGS) hydrologic cataloging units used as the basic modeling unit by the NCPDI. General nonurban land uses by HUCO were obtained from the Land Use Data Analysis (LUDA) System of the USGS (for more detail on this program see the discussion of land use in section 2 on urban runoff) and are presented in Table 48. Climatological data were obtained from the National Climatic Data Center. Information on soil and crop types, agricultural practices, watershed slopes and Soil Conservation Service runoff curve number were all obtained from the National Resource Inventory, a regularly updated national soils survey conducted by the Soils Conservation Service (SCS).

Table 47. Input parameters used by the simulator for Water Resources in Rural Basins model. Parameters are grouped according to the sensitivity of the model to each parameter (F. Arnold, personal communication). Source: NOAA (1987c, Table III-4). SCS = Soil Conservation Service, USLE = Universal Soil Loss Equation.

Most Sensitive

Drainage area
Daily precipitation
Daily temperature (maximum and minimum)
SCS runoff curve number (CNII)
Number of soil layers
USLE K factor
USLE C factor
For each soil layer:
 Depth to bottom of layer
 Bulk density
 Available water capacity
 Saturated conductivity
 Clay content

Moderately Sensitive

Mean solar radiation
Standard dev. solar rad.
Main channel length
Main channel slope
Manning's "n" - overland
Manning's "n" - channel
Average land slope
Average land slope length
USLE P factor
Planting date
Harvesting date
Tillage practice

Least Sensitive

Basin latitude
Maximum 1/2 hour rain intensity expected
in 10 year interval
Maximum 6 hour rain intensity expected
in 10 year interval
Number of years of record for 1/2 hour rainfall
Monthly probabilities of having a wet day
following a dry day, and a wet day following
a wet day

Table 48. Nonurban land use by HUCO (Hydrologic Unit-County for the Bay-Delta Region as compiled by NOAA [1987a]). For description of methods, see text. All values in km².

COUNTY	HYDROLOGIC UNIT	HUCO (LUDA Categories) =>	Total Ag Land 21-24	Total Rangeland 31-33	Forest Land 41-43
Alameda	18040003	0600118040003	13.2	144.5	30.5
	18050004	0600118050004	135.4	443.2	456.9
	18050003	0600118050003	33.9	46.6	3.9
	18050002	0600118050002	0.0	0.0	5.2
	County Total		182.5	634.3	496.5
Contra Costa	18040003	0601318040003	288.9	256.3	104.6
	18050001	0601318050001	50.0	182.5	115.5
	18050002	0601318050002	2.1	81.3	85.4
	18050004	0601318050004	19.7	124.5	41.7
	County Total		360.6	644.6	347.2
Marin	18050002	0604118050002	79.0	73.3	150.7
Napa	18020117	0605518020117	26.9	277.3	473.5
	18050001	0605518050001	7.2	15.5	96.0
	18050002	0605518050002	226.5	111.6	513.9
	County Total		260.7	404.4	1083.4
Sacramento	18020109	0606718020109	831.8	27.2	0.0
	18020111	0606718020111	142.6	18.1	11.6
	18040003	0606718040003	28.7	4.1	0.0
	18040005	0606718040005	709.6	59.3	25.9
	18040013	0606718040013	54.4	0.0	22.5
	County Total		1767.1	108.7	60.1
San Francisco	18050002	0607518050002	0.0	0.0	0.0
	18050004	0607518050004	0.0	0.5	0.0
	County Total		0.0	0.5	0.0
San Joaquin	18040002	0607718040002	708.6	96.8	0.0
	18040003	0607718040003	1200.4	156.4	57.0
	18040004	0607718040004	365.8	18.9	0.5
	18040005	0607718040005	657.8	17.3	2.1
	County Total		2932.6	289.4	59.5
San Mateo	18050003	0608118050003	1.6	9.1	48.2
	18050004	0608118050004	0.5	75.9	26.4
	County Total		2.1	84.9	74.6
Santa Clara	18050003	0608518050003	124.0	406.4	689.7
	18050004	0608518050004	1.3	190.5	369.7
	County Total		125.3	597.0	1059.3
Solano	18020109	0609518020109	1045.9	24.9	141.1
	18050001	0609518050001	271.0	172.4	85.2
	18050002	0609518050002	0.0	9.6	0.0
	County Total		1316.9	206.8	226.3
Sonoma	18050002	0609718050002	240.0	187.7	149.9
Yolo	18020109	0611318020109	1144.8	23.0	143.2
Total Bay-Delta			8411.5	3254.6	3850.6

The NRI is a random survey designed to provide statistically valid results at a scale of "Major Land Use Areas," of which there are about five in the Bay-Delta region. Thus, by utilizing NRI survey points at the level of HUCOs (portions of counties), NOAA (1987c) indicates that the NCPDI is applying this database on a more detailed level than that for which it was designed.

Data from the NRI were used to separate the general land use classifications in LUDA into 17 various land use types, including six crop types, orchards and vineyards, hayland, rangeland, and well- or poorly-covered forest land. Basically, this was accomplished by assuming that the total agricultural, range, or forest land in a given HUCO (as obtained from LUDA) was divided among the specific land uses based upon the proportion of these various factors in the NRI sample points in that HUCO. Thus, if half the agricultural NRI points in a HUCO are in corn fields, 50% of the agricultural acreage in that HUCO is assumed to be in corn production. These estimates were verified by comparison to the 1982 Census of Agriculture. Soil types and other NRI parameters were assigned to a crop type in a HUCO based upon the most prevalent soil type represented in the relevant NRI data points. Normally, a certain soil was clearly dominant for a given crop type (F. Arnold, personal communication). Given the large number of parameters, a variety of other assumptions were necessary as described in NOAA (1987c). The model was run for each land use type in each HUCO, or a total of 235 runs for the Bay-Delta region.

The SWRRB model is most sensitive to certain of the 29 input parameters, according to the groupings in Table 48. Of note is the fact that precipitation is among the most sensitive

parameters, as the modeling year chosen (1982) had the highest precipitation of any year between 1975 and 1983. Another important factor is soil hydrologic type, a classification that runs from A to D, with A being the most permeable soil. Substituting a type C for a type D soil will reduce predicted sediment yield by about 50%, while substituting type A for type D will reduce sediment yield by about 150% (F. Arnold, personal communication). Of the 235 runs for the Bay-Delta region, 88 used type D, 84 used type C, 62 used type B, and only once was type A utilized (NOAA, 1987a). Although NOAA believes they have the most accurate data for the parameters to which the model is most sensitive (F. Arnold, personal communication), the model has not been subjected to a rigorous sensitivity analysis (NOAA, 1987c).

The trace metal loads for each HUCO were calculated by multiplying the predicted sediment yield by a typical soil concentration for the elements arsenic, chromium, copper, mercury, lead, zinc, and cadmium. For all elements except cadmium, the soil concentrations were taken from the national soil survey of Shacklette and Boerngen (1984). In that study, the authors summarized data from samples collected by many different investigators at over 1,300 sites around the country. All samples were collected at 20 cm depth, and the database includes seven sample sites in the Bay-Delta region. For cadmium, which was not included in the work of Shacklette and Boerngen (1984), an average value for nonurban lands of 0.4 g g^{-1} was derived from summaries of cadmium concentrations in nonurban soils worldwide (NOAA 1987c).

The concentrations of metals in soils used in the NCPDI are

presented in Table 49. These values, except that for cadmium, were derived from the national frequency distribution for elements in soils developed by Shacklette and Boerngen (1984). First, the same point closest to each county in the Bay-Delta region was determined, and the location of that sample in the histograms of Shacklette and Boerngen (1984) was identified. The most frequently occurring concentration in that portion of the histogram was used as the typical soil concentration. It should be noted that Shacklette and Boerngen (1984) identify ranges in their histograms as a percentage of the samples taken, and it appears that these designations are somewhat arbitrary. In any event, the concentrations obtained in this manner by NOAA (1987c) are thus an average from data collected around the country and are not specific to the Bay-Delta region.

As an alternative, represented in Table 50, it is possible to utilize the site-specific concentrations of Shacklette and Boerngen (1984) for their Bay-Delta sites, rather than data points selected from national frequency distributions, as these site-specific data appear in an earlier publication (Boerngen and Shacklette, 1981). The data from the seven Bay-Delta sites which appear in Table 50 clearly demonstrate a much larger variation than the values in Table 49 adopted by NOAA (1987c). For example, the site-specific data for chromium and lead vary by at least an order of magnitude, while the values for arsenic, copper, and mercury vary by a factor of four or five. It is also apparent from Table 50 that the selected sites might not even be representative of the counties in which they are located, as the soil sample used to characterize Marin County came from Muir Woods.

Table 49. Concentrations of metals in soils used to estimate trace metal loads in The National Coastal Pollutant Discharge Inventory. All values in $\mu\text{g g}^{-1}$.
Source: NOAA (1987c, d).

<u>County</u>	<u>Arsenic</u>	<u>Chromium</u>	<u>Copper</u>	<u>Lead</u>	<u>Mercury</u>	<u>Zinc</u>	<u>Cadmium</u>
Alameda	6.5	100	50	30	0.2	120	0.4
Contra Costa	10	100	50	30	0.1	120	0.4
Marin	16	100	50	30	0.1	120	0.4
Napa	4.1	100	30	20	0.1	74	0.4
Sacra- mento	10	100	50	15	0.2	120	0.4
San Francisco	10	100	50	30	0.2	120	0.4
San Joaquin	4.1	50	20	15	0.1	74	0.4
San Mateo	6.5	100	30	30	0.1	120	0.4
Santa Clara	10	100	30	15	0.1	120	0.4
Solano	10	70	30	15	0.1	74	0.4
Sonoma	4.1	100	50	20	0.1	74	0.4
Yolo	10	100	50	15	0.2	120	0.4

Table 50. Concentration of selected elements in soils from seven sites in the Bay-Delta Region. All values in $\mu\text{g g}^{-1}$.
Source: Boerngen and Shacklette (1981).

USGS Sample No.	County	Arsenic	Chromium	Copper	Mercury	Nickel	Lead	Selenium	Zinc
GC023350	Marin	13.2	150	100	0.11	100	50	0.5	113
GC062450	San Joaquin	3.2	50	20	0.04	20	15	0.1	62
GC077650	Solano	10.8	70	30	0.04	20	15	<0.1	70
GC242950	Solano	6.7	70	30	0.13	15	30	0.3	100
GC074350	San Mateo	9.2	200	100	0.23	70	300	<0.1	212
GC077550	Sonoma	3.3	700	30	0.07	150	20	0.1	58
GC242850	Yolo	11	150	70	0.24	150	15	0.3	130

Perhaps most importantly, seven samples represent an extremely limited data base from which to estimate typical concentrations of trace metals in the soils of the Bay-Delta region. This fact, combined with the significant variability in the available data, means that the trace metal loadings estimated by NOAA (1987a) must be considered of the most preliminary nature.

Loads of chlorinated hydrocarbon pesticides (CHPs) from nonurban lands were estimated by calculating the total amount applied to a given land use and then utilizing a loss coefficient representing the percent of applied CHPs lost in runoff. The data on the annual use of CHPs in Bay-Delta counties were obtained from the DFA and are presented in Table 51. Note that these data are only for that portion of the county that is within the study area of NOAA (1987a).

Given the data on total CHP use by county, this information was then distributed to each HUCO in the county according to which crop types CHPs were applied to most heavily. If 90% of the CHPs were applied to orchards, for example, CHP use was assumed to be distributed throughout the HUCOs in the county based upon the distribution of horticultural lands. If neither horticultural nor agricultural lands received a minimum of 90% of applied CHPs, then the distribution of CHP use to each HUCO in the county was based upon the distribution of all croplands in the county.

The actual load of CHP in runoff was then estimated as a percentage of applied material, using a runoff coefficient of one percent. This number was derived from the review of experimental literature for CHPs by Wauchope (1978) and is acknowledged as a relatively uncertain value (F. Arnold, personal communication).

Table 51. The use of Chlorinated Hydrocarbon Pesticides in the Bay-Delta Region in 1982. Data for Yolo and San Joaquin counties are only for the portion of these counties within the study area of NOAA (1987a). All values in kilograms. Source: NOAA (1987c).

COUNTY	PESTICIDE					Total
	Lindane	Toxaphene	Endrin	Endosulfan	Methoxychlor	
Alameda	295	0	0	12	0	307
Contra Costa	767	7523	0	284	58	8632
Marin	21	0	0	0	16	37
Napa	16	0	0	3	13	32
Sacramento	506	11183	0	1057	553	13299
San Francisco	31	0	0	2	0	34
San Joaquin	428	910	0	1066	954	3359
San Mateo	57	141	0	929	0	1128
Santa Clara	0	3599	0	391	36	4027
Solano	119	4834	0	5777	314	11043
Sonoma	23	0	0	66	1	90
Yolo	57	1747	0	7485	424	9714
Total Bay-Delta	2321	29937	0	17073	2370	51700

Several factors contribute to this uncertainty. First, the research reported by Wauchope (1978) is based almost exclusively on data from the central and southeastern parts of the country, where a climate different than that present in California would be likely to lead to different runoff characteristics for CHPs. Second, the database shows significant variation in loss rates of up to an order of magnitude for identical pesticide applications. This is due at least in part to the timing and intensity of rainfall in relation to times of pesticide application, as heavy rainfall (or irrigation) directly after pesticide application can lead to larger runoff losses. Finally, pesticides of differing solubilities can be lost from fields at different rates, and soil conservation practices can significantly reduce the loss of sediment-bound residues (Wauchope, 1978). Seiber (1987) points out, however, that even with the knowledge of physical properties of pesticides, not enough is known of important environmental processes (such as leaching) to allow prediction of losses.

Irrigation Return Flows. NOAA (1987d) calculated irrigation return flows (IRFs) as a separate source of nonurban runoff in 12 HUCOs identified as having significant potential for return flows (Table 52; see also Fig. 5 in Section 2 above). Estimates of irrigated acreage and rate of irrigation (acre feet/acre) were obtained from the 1982 and 1978 Census of Agriculture, respectively. An average return flow coefficient of 16% was applied to total irrigation volume to represent IRF volume, based upon the flow measurements of Merrill et al. (1979), for several districts in the Central Valley. NOAA (1987d) notes that this coefficient can vary from 1 to 24% based upon crop type and irrigation method. A reduction in the return flow volume was

Table 52. HUCOs in the Bay-Delta region identified as having potential significant irrigation return flows.
Source: NOAA (1987d).

<u>County</u>	<u>USGS Hydrologic Cataloging Unit</u>	<u>HUCO</u>
Napa	18050002	0605518050002
Yolo	18020109	0611318020109*
Solano	18050001 18020109	0609518050001* 0609518020109*
Sacramento	18020109 18040003	0606718020109 0606718040003
San Joaquin	18040003	0607718040003*
Contra Costa	18040003 18050001 18050004	0601318040003* 0601318050001 0601318050004
Alameda	18050004	0600118050004
Santa Clara	18050004	0608518050004

* Reductions in irrigation return flow (IRF) estimates made to reflect pumping of IRF away from Delta or channeling to wetlands.

made for four of the twelve HUCOs (see Table 52) as IRFs from these regions are pumped away from the Delta or channeled to wetlands, and are thus not loads to the estuary.

Concentrations of total suspended solids were taken from the data of Merrill et al. (1979) and were used as before to estimate trace metal loads. CHP concentration in IRF was estimated as the geometric mean of detected values from the San Joaquin Drainage Monitoring Program for 1979-1982 ($0.3 \mu\text{g L}^{-1}$).

As with any method for estimating the loading of toxic substances from IRF, there are significant uncertainties associated with the procedure described above, most of which are recognized by the authors (NOAA, 1987d). The data for irrigation volumes from the 1978 Census of Agriculture are out of date, and it is not clear how data were accumulated for Delta lowlands that are irrigated using portable, unmetered siphons (Harte et al., 1987). The flow data of Merril et al. (1979) were sometimes only estimates by local water managers rather than actual measurements. Upstream IRF is clearly reused by downstream farms, confounding estimates of actual (or net) IRF volumes.

The method for estimating trace metal loads suffers from the problems described above relating to the restricted number of soil samples on which typical concentration estimates are based. As Merrill et al. (1979) sampled for suspended sediments only weekly or monthly, it is not known if their data adequately represent average concentrations of suspended soils. Finally, CHP loads are clearly overestimated, as CHP concentration estimates are based solely on detected values. An important characteristic of pesticide concentrations in surface waters of the Bay-Delta region is the low frequency with which they exceed

standard detection limits (see DWR 1986c, for example) and it is clearly inappropriate to ignore this phenomenon.

C. Contaminant Loads From Nonurban Runoff

Using the methods described above, NOAA (1987a) estimated loads to the San Francisco Bay-Delta from nonurban runoff for the year 1982 (Table 53). The table demonstrates that nonurban runoff is potentially an extremely important source of toxic pollutants to the estuary, particularly for chromium, mercury, zinc, and arsenic. Of the three nonurban classifications, "other nonurban land" contributes from 62 to 83% of the total load for each trace metal, significantly more than cropland or forest land. This is undoubtedly due to estimates of high erosion from rangelands and pasturelands which comprise the other nonurban category. In Napa County, for example, NOAA (1987a) estimates that 85% of the sediment yield for all land uses is from rangeland. Irrigation return flows, however, represent a minor contribution of toxic substances to the Bay-Delta according to NOAA (1987a). (It is important to note that this refers only to the IRF within the Bay-Delta region, and not IRF entering the Delta in boundary rivers.)

These loading estimates of NOAA (1987a) are for 1982, a year of high precipitation, and the potential for sediment yield to vary in a non-linear fashion with rainfall means that a more average rainfall year could result in much lower predicted loadings of toxic chemicals. Indeed, the loading estimates presented in Table 53 are probably at the high end of the range of potential loads in nonurban runoff. Unfortunately, identifying the boundaries of this range is beyond the scope of this study.

Table 53. Loading from nonurban runoff of selected trace metals and chlorinated hydrocarbon pesticides (CHPs) to the San Francisco Bay-Delta for 1982. All values in metric tonnes except for mercury and CHPs, which are in kilograms. Totals not exact due to rounding errors.

	<u>Arsenic</u>	<u>Chromium</u>	<u>Copper</u>	<u>Lead</u>	<u>Mercury(kg)</u>	<u>Zinc</u>	<u>Cadmium</u>	<u>CHP(kg)</u>
Cropland								
Delta	20	159	72	32	253	176	1	373
SFBay	14	110	50	29	126	117	1	49
Total								
Bay-Delta	34	269	122	61	379	293	2	422
Forest land								
Delta	3	39	15	8	50	35	0	0
SFBay	8	94	35	25	114	100	0	0
Total								
Bay-Delta	11	133	49	33	164	135	0	0
Other								
Nonurban land								
Delta	34	728	231	152	745	572	3	0
SFBay	41	406	179	113	439	451	2	0
Total								
Bay-Delta	74	1134	410	265	1184	1023	5	0
Total Irrigation								
Return Flows								
Delta	0	2	0	0	2	2	0	69
SFBay	0	0	0	0	0	0	0	7
Total								
Bay-Delta	0	2	0	0	2	2	0	76
Total								
Nonurban								
Land and IRF								
Delta	56	928	317	192	1050	783	4	442
SFBay	63	609	263	167	679	668	3	56
Total	119	1537	581	358	1729	1453	6	498

The significant uncertainties associated with these estimates means that these values must be considered to be of the most preliminary nature. These uncertainties are found in the input data to the model and the model itself. In addition, there are a variety of toxic organic chemicals applied to nonurban lands in the Bay-Delta region that are not considered by NOAA (1987a).

Several uncertainties in the application of the SWRRB model and the data used as input to the model are identified by NOAA (1987c). The document points out that the data from the NRI, which are used to obtain much agricultural and soils information utilized as model input, are designed to be representative of much larger regions than the portions of HUCOs used for modeling purposes. Thus, if an NRI point happened to be located in an uncharacteristic site within a HUCO (such as a land area with poor vegetative cover, for example), sediment yields calculated for that HUCO could be very inaccurate. This is especially true for those HUCOs without NRI sampling sites, where average values from neighboring HUCOs had to be used. The investigators suggest that results for HUCOs should be reviewed on an individual basis and input data verified by consulting county extension agents or local soil conservation service personnel (NOAA, 1987c). This is especially important given the sensitivity of the SWRRB model to assumed soil characteristics.

Also pointed out by NOAA investigators (NOAA, 1987c) is the fact that the performance of the SWRRB model has not been verified for forested areas. This is an essential step in determining the accuracy of the model's predictions of surface runoff from forests. Moreover, the model has not been subjected to a rigorous sensitivity analysis to positively identify the

parameters to which it is most sensitive.

Performing a sensitivity analysis is vital for a model of this complexity, especially as many of the calculations used by the model to predict sediment yield involve non-linear mathematical relationships. For example, surface runoff is calculated using an algorithm involving the square of a measure of soil moisture content (the soil retention parameter). This would indicate that prediction of surface runoff volumes by the model might be particularly sensitive to estimates of soil moisture. Similarly, evapotranspiration is proportional to the square of mean daily temperature. There are many other examples of nonlinear algorithms in the computational framework of the model (NOAA, 1987c), and variation of the appropriate input parameters within the bounds of their uncertainty is necessary to judge the concomitant uncertainty in the model's predictions.

As pointed out previously, significant uncertainty surrounds the estimates of pollutant loads in addition to that associated with the predictions of sediment yield by the SWRRB model. The typical soil concentrations of trace metals used in the analysis are based upon an unacceptably small sample of soils in the Bay-Delta region. For CHPs, the assumption of 1% loss of applied material ignores significant variation in losses based upon storm timing and various agricultural practices. The estimate of CHP loading from IRF is overestimated, as measurements below detection limits were ignored in developing typical concentrations.

In addition, it is essential to remember that the use of CHPs in the United States is declining steadily as many of these substances have been banned or restricted. There are, however,

many other pesticides, herbicides, and fungicides applied within the Bay-Delta region. (In 1982, about 500 different pesticide chemicals were applied in the San Joaquin Valley, representing almost 10% of the total used on major crops in the U.S. [Clifton and Gilliom, 1986].) These substances, often designed to be much less persistent in the environment than CHPs, tend to be more soluble in water and thus more mobile. A variety of physical and chemical processes will influence the fate of these toxic chemicals, including volatilization (Spencer, 1987), chemical reactions (Farmer and Aochi, 1987), photolysis (Miller and Herbert, 1987), and microbial metabolism (Kearny and Karns, 1987). For example, the rice herbicide molinate (marketed as Ordram) is quite volatile, and by retaining treated water for several days prior to discharge, farmers can dramatically lower loss of this chemical from their fields to surface waters (DFA, 1986). A significant amount of research will be needed on specific chemicals and specific sites before enough is known to begin to assign loss or runoff coefficients for many of these toxic chemicals.

It will also be difficult to estimate the use of many of these substances, as the DFA only collects information on the use of certain restricted chemicals (approximately 50-60 substances) applied by licensed commercial applicators. Application of unrestricted chemicals is not monitored by DFA.

Finally, it should be noted that, while most attention is given to the active ingredients, agricultural chemical mixtures contain large quantities of carriers or solvents listed only as "inert" ingredients. By weight, inert ingredients can be the

majority of the mixture (Table 54), and these substances include chemicals known to be toxic. The identity of these substances, although registered with the government, is considered proprietary information and is not made public.

D. Conclusions

Runoff from nonurban lands carries toxic chemicals into receiving waters. These include trace metals leached or eroded from soils and synthetic chemicals applied in agricultural, horticultural, or silvicultural activities. The only estimate of the loading of some toxic substances in nonurban runoff has been made by NOAA (1987a, c, d) as part of the National Coastal Pollutant Discharge Inventory. This study utilized a model to estimate sediment yield from nonurban lands using 29 separate input parameters, and typical trace metal concentrations in soil were used to derive loading estimates from sediment yield data. Chlorinated hydrocarbon pesticide (CHP) loads were estimated from data on CHP use, assuming 1% of applied pesticides entered runoff. Loads of trace metals and CHPs were also estimated for irrigation return flows.

Although the estimates of NOAA (1987a) indicate that nonurban runoff could be an important source of toxic substances to the estuary, significant uncertainty surrounds these estimates for several reasons (many of which are explained by NOAA (1987c)). The model used to predict sediment yields has not been subjected to a rigorous sensitivity analysis that would help quantify the uncertainty. Many of the input parameters were derived from the National Resource Inventory of the Soil

Table 54: Proportions of inert and active ingredients in six fungicides and two rice herbicides. Data are percent by weight. Source: Ogawa et al. (1981), for fungicides; Cornacchia et al. (1984), for rice herbicides.

<u>Product Name</u>	<u>Active Ingredients</u>	<u>Inert Ingredients</u>
C-O-C-S wettable	50	50
Kolodust	84	16
Dithane M-45	80	20
Captan 50-WP	50	50
Benlate	50	50
Funginex	18.2	81.8
Ordram 10G	10	90
Bolero 10G	10	90

Conservation Service, which was designed to provide representative data on soils and land uses only when averaged over much larger scales. The estimates derived are also for 1982, a year of very high precipitation and runoff, and in a more average precipitation year, loading estimates could be significantly lower.

The metal concentrations in soils used to estimate loads are based on very few samples, but the few available data indicate that metal concentrations in soils are quite variable. There is also significant uncertainty associated with the estimate of the runoff of CHPs from fields. The value of 1%, which is based upon a review of research from the central and southeastern United States, can vary significantly among sites and storms. Moreover, CHP use is declining in the U.S., and many other agricultural chemicals are used in the Bay-Delta region. Data on the use of these chemicals are limited, as is knowledge of their fate in the environment. There is also uncertainty associated with the estimate of trace metal and CHP loadings in irrigation return flows.

In particular, CHP loadings are significantly overestimated. It is clear, however, that trace metal loadings due to irrigation return flows are inconsequential when compared to other nonurban sources. This is also probably true for CHPs, but additional research is necessary for the many other pesticides in use in the Bay-Delta region.

As these estimates of NOAA (1987a) are for 1982, a year of high precipitation in the Bay-Delta region, they probably are near the high end of the range of uncertainty associated with the loading of toxic contaminants to the estuary. The simplest way

to generate a lower bound on this range would be to divide the loading estimates by a ratio of Delta inflow between a high and low runoff year. For example, the ratio of Delta inflow for 1982-83 to that for 1976-77 as predicted by the DAYFLOW model of DWR (DWR 1986d) is 11.5 (68,856 divided by 5,956 trillion acre feet). Thus, a first approximation of the lower bound on the range of contaminant loads from nonurban runoff would be obtained by dividing the data in Table 27 by a factor of 11.5.

Clearly, the loading estimates of NOAA (1987a) for nonurban runoff must be considered of the most preliminary nature. Significant research to refine the modeling scheme and the quality of input data is necessary before a reasonably precise range for the loading of toxic chemicals to the Bay-Delta by this potentially important pathway is available.

4. RIVERINE INPUTS

A. Introduction

Riverborne loadings of toxic contaminants into the Bay-Delta are characterized in this section. These riverine inputs are assumed to integrate loadings to the estuary from all point and non-point sources of aquatic pollution outside the region of study. The study region is therefore partially defined by the location of sites where the most comprehensive data on river flows and pollutant concentrations are recorded. Table 55 describes the sampling sites. Primary emphasis in the following discussion is on the San Joaquin and Sacramento Rivers. Data on the Mokelumne and other minor tributaries are also presented.

Water quality data on the rivers are collected by several independent agencies. This report is based on a compilation of information available from those agencies. In order to supplement the limited information available at the chosen sampling points, some data from locations near the sites listed in Table 55 are also discussed. For each sampling program, the data and their limitations are discussed. Ranges of average mass loading from January 1984 through September 1986, based on the best set of concentration data available for each contaminant analyzed, are presented for the San Joaquin, Sacramento, and Mokelumne Rivers.

B. Description of the Basin

The basin which drains into the Bay-Delta estuary contains many waterways which have individually and collectively been radically altered from their natural state. The basin is dominated by the Sacramento and San Joaquin Rivers, which drain approximately 40% of the land area of the State. Before they

Table 56. Characteristics of Delta tributaries. Adapted from USGS (1985).

Location	USGS Station number	Drainage Area ² (km ²)	Total Discharge, Oct 83 - Sept 84 (km ³)	Long Term Average Annual Discharge, 10 ⁹ L (no. of years included)
Calaveras River below New Hogan Dam	11308900	929	0.37	0.63 (23)
Cosumnes River at Michigan Bar	11335000	1,372	0.74	1.24 (77)
Dry Creek near Galt	11329500	829	0.22	0.33 (47)
Mokelumne River at Woodbridge	44658800	1,692	0.95	1.55 (55)
Sacramento River at Freeport	11447650	69,670	27.77	60.6 (36)
Sacramento Weir Spill to Yolo Bypass	11426000	Not applicable	0.5	0.62 (45)
San Joaquin River near Vernalis	11303500	34,652	7.78	11.7 (56)
Yolo bypass near Woodland	11453000	Not applicable	5.00	9.22 (38)
Putah Creek ² near Winters	11454000	1,469	0.64	1.35 (54)
Total ³			43.97	86.8

¹ From SWRCB 1986.

² In 1984, 49.9% of the flow of Putah Creek was diverted before it reached the Delta.

³ Putah Creek flow not included.

empty into the Delta, these rivers flow through a series of dams and vast areas of land devoted mainly to agriculture. Activities in both the Sacramento and San Joaquin Valleys influence the composition of Bay-Delta waters. Table 56 summarizes basic hydrologic information on each of the major Delta tributaries.

The Sacramento River carries the great majority (about 70% on average) of the freshwater that flows into the Bay-Delta estuary. The River also is a major source of water for irrigation in the Central Valley and for 16 million people in Southern California. The average flow of the Sacramento River in water year (WY) 1986 (October 1985 through September 1986) was 64.9 billion L d⁻¹. In the same year, 45% of the total flow occurred during February and March. During May and June, agricultural drainage in the Sacramento Valley may contribute over 30% of the total river flow (Cornacchia et al., 1984) and has a significant influence on the chemical composition of water entering the estuary.

Rice is the major crop grown on the floor of the Sacramento Valley. In 1980, more than 500,000 acres of rice were grown, producing over 90% of the total crop of rice in California (SWRCB, 1986). Hundreds of different pesticides are applied to rice and other crops grown in the Sacramento Valley (SWRCB, 1986).

The herbicides molinate and thiobencarb are used extensively in the Sacramento Valley to prevent the invasion of wetland plants into the expanses of artificial wetlands created for rice culture. These compounds are of particular importance in the Bay-Delta catchment because of their toxicity to aquatic organisms and high concentrations in segments of the Sacramento

applied there; this amount is almost 10% of the total applied to major crops in the U.S.A. (Clifton and Gilliom, 1986). Measurable amounts of some of these chemicals are washed into the river in drainage from croplands.

Agricultural drainage in the San Joaquin Valley also contains elevated levels of some trace elements. The most notorious of these is selenium. Selenium naturally occurs in soils of the Valley, and irrigated farming concentrates the element in agricultural drainage. Drainage from these irrigated lands carried selenium into the Kesterson National Wildlife Refuge, where it is the probable cause of reproductive failure in aquatic birds (Ohlendorf et al., 1986). Dilute amounts of some contaminants present in this agricultural drainage are detected many miles downstream, where the River enters the Bay-Delta.

Water quality monitoring efforts in the Delta focus mainly on the large flows of the Sacramento and San Joaquin Rivers. Of the remaining Delta tributaries, only the Mokelumne is analyzed for its chemical composition as it enters the estuary. The transport of contaminants by the Sacramento, San Joaquin, and Mokelumne Rivers is discussed below. Little can be said about potential contaminant loadings from other (minor) tributaries. As shown in Table 56, the largest of the tributaries without chemical monitoring is the Yolo Bypass, which diverts excessively high flows from the Sacramento River in the wet season. Potential loadings from the remaining minor tributaries are probably on the order of those presented below for the Mokelumne River, which contributes less than 2% of overall flows to the Delta.

River. Molinate concentrations in the Colusa Basin Drain were elevated sufficiently to cause annual fish kills in the late 1970s and early 1980s (Cornacchia et al., 1984). Thiobencarb, in addition to being toxic to aquatic life, can impart an unpleasant taste to the City of Sacramento's drinking water when concentrations peak in May and June of each year (DFA, 1987). In 1986, 272,822 acres in the Valley were treated with molinate, and 81,121 acres were treated with thiobencarb (DFA, 1987). In 1984, 695,000 kg of molinate and 159,000 kg of thiobencarb were applied to rice fields (CVRWQCB, 1986).

River flows through the arid San Joaquin Valley are much smaller than those in the Sacramento Valley. During the dry season, the flow in 132 miles of the San Joaquin River between Friant Dam and Stevinson is intermittent. Flows become perennial in the 60 mile reach between Stevinson and Vernalis due to the contributions of three major rivers from the Sierras. Agricultural drainage comprises more than 20% of the total time-averaged flow in the San Joaquin River (Nichols et al., 1986), and most of the flow in the summer (DWR, 1986c). The mean daily flow of the San Joaquin in water year 1986 was 17.7 billion $L\ d^{-1}$. Fifty-two percent of the flow in WY1986 occurred during March and April.

Agricultural activity in the Valley is intense. Fresno County, at the southern end of the Valley, has consistently ranked first in the nation in total annual agricultural production, and is considered the most productive agricultural area in the world (SWRCB, 1978). The Valley is also a world leader in pesticide application. In 1982, a total of nearly 23 million kilograms of about 500 different pesticide chemicals was

surface runoff is at a maximum. The U.S. Geological Survey (USGS) (Clifton and Gilliom, 1986) conducted frequent sampling on the San Joaquin River near Vernalis during a high-flow period in 1986. Large proportions of the total annual riverine transport of certain contaminants occurred during a two-month period. The duration of these pulses of contaminant transport appear to be on the order of days. Sampling less than once a month provides essentially no possibility of characterizing the long-term importance of such events, and is inherently inaccurate as a method of estimating contaminant loadings to the Bay-Delta.

The second criterion is that measured contaminant concentrations should be significantly larger than the detection limits of the method used in their analysis for reliable data to be produced. As discussed in Section II.1, analytical results at or near the limit of detection have large uncertainties associated with them. The uncertainty of a result at the detection limit can approach or equal the reported value (Keith et al., 1983). Quantitative treatment of an analytical result is only justified when the result is equal to or greater than three times the limit of detection (Keith et al., 1983; Kirchmer, 1983).

An example will illustrate the effect of the uncertainty associated with a result near the detection limit on a mass loading estimate. In September 1986, a grab sample from the San Joaquin River at Vernalis was analyzed for dissolved copper (DWR, 1986a). Monthly mean flow for September was $10.23 \text{ billion L d}^{-1}$. The analytical result was $10 \mu\text{g L}^{-1}$, and the detection limit was also $10 \mu\text{g L}^{-1}$. The calculated mass loading based on the reported concentration is 102 kg d^{-1} . Taking the uncertainty of the analytical result into account, the range for this loading

C. Framework for Evaluation of Monitoring Data

Estimates of mass transport by Delta tributaries based on existing water quality data should be interpreted with caution. Riverine flows into the estuary are vastly larger in volume than any other freshwater inflows, and small differences in measured concentrations translate into tremendously divergent absolute mass loadings. Accurate estimates of mass transport in rivers are particularly dependent upon accurate measurements of chemical concentrations in water.

Three criteria which should be addressed before any water quality monitoring data are used as a basis for valid long-term estimates of seasonal trends in mass loading are presented in Section II.1. These criteria relate to the frequency of sampling, the ratio of measured concentrations to detection limits, and quality control testing. These criteria are discussed here as they apply to monitoring on the Delta tributaries.

First, sampling should be frequent enough to portray the temporal variation in a river's chemical composition. As shown below, the sampling frequency for the Delta tributaries from 1984 through 1986 was in general less than one per month. Exceptions to this rule (where several samples per month were analyzed) provide evidence that contaminant transport in the rivers may occur in pulses. These pulses are sometimes related to very specific activities in the basin. For example, monitoring for rice herbicides in the Sacramento River (DFA, 1986) has provided a detailed record of concentration trends in the River that can be traced back to specific episodes of pesticide application and releases of irrigation water in the Sacramento Valley. Other pulses of mass transport occur during high-flow periods, when

allows greater confidence in its accuracy. As an example, 9 consecutive monthly average concentrations of total arsenic, based on about 30 samples collected by the USGS in 1986 (USGS, unpublished data), were all between the limit of detection and the limit of accurate quantitation. In cases like this, the parameter is included in the category receiving quantitative treatment.

The third criterion for assessment of analytical results is the availability of quality control data. Many factors in the handling and analysis of samples can introduce additional variation in the final results. Unfortunately, strict application of this criterion would make for a very brief discussion of riverine mass transport. Quality control results are mentioned for each set of data where they are available. Where quality control information is not available, conclusions drawn from a set of data may be refuted if subsequent review of such information indicates faulty analytical procedures.

Mass transport in this section is calculated as the product of monthly average concentrations and monthly average flows. Where a number of observations of concentration and flow were available for a single month, monthly averages of each were calculated prior to computation of a monthly average mass loading.

D. Mass Transport Estimates for Delta Tributaries

The following subsections discuss mass transport of contaminants in individual rivers that empty into the Delta. Chemical data from 1984-1986 are available only for the San Joaquin, Sacramento, and Mokelumne Rivers. Most of the sampling on the three rivers was performed under four major programs.

estimate is approximately 0 kg d^{-1} to 200 kg d^{-1} . Clearly this estimate is not very informative. Larger flows than 10.23 billion L d^{-1} , which are not uncommon in the San Joaquin River, would produce an even broader range for the estimate. Flows in the Sacramento River at Freeport averaged 64.9 billion L d^{-1} in WY1986. Using the same analytical result for dissolved copper discussed above and average flow in the Sacramento as a hypothetical (but not unrealistic) example of available information, the estimated mass transport of dissolved copper in the Sacramento River would be 649 kg d^{-1} , with a range of 0 to 1200 kg d^{-1} .

Values reported as being below the limit of detection are also of limited use in quantifying mass transport. These values can only strictly be interpreted as a range, stretching from zero to the limit of detection, in which the actual concentration might lie.

In the following analysis, three individual categories of analytical results are treated separately: 1) quantitative assessment of monthly trends in mass loading is reserved for parameters whose concentrations consistently exceed the limit of detection by a factor of three; 2) individual values between the limit of detection and the limit of quantitation are treated as qualitative evidence of long-term mass transport of a contaminant; and 3) values below the limit of detection are treated as ranges (which include the possibility that mass transport is negligible).

For some parameters, highly consistent positive results between the limit of detection and the limit of accurate quantitation are observed. Repeated observation of such a result

The San Joaquin River

Water quality monitoring on the San Joaquin River at Vernalis has been more extensive than on any other Delta tributary, largely because of the SJRS. Table 57 lists the agencies which sample the River, and provides information on their sampling programs.

The SJRS (Clifton and Gilliom, 1986) was initiated in part to assess riverine mass transport of contaminants to the Bay-Delta and is the most useful set of data available for that purpose. Table 57 shows the parameters analyzed and the frequency of sampling for the study. Samples were collected twice monthly, except during February - April 1986 when more frequent sampling was performed to document a high-flow period. In February 1986, up to 11 samples were collected for the analysis of certain trace elements. Standard USGS sampling and analytical methods were employed (Gilliom, 1986). The majority of these data are unpublished, so quality control information is not yet available. Data collected in 1986 are preliminary and were obtained from WATSTORE, the data retrieval system of the USGS. Despite the preliminary nature of the data, the SJRS provides a basis for the most meaningful discussion of mass transport trends in any of the Delta tributaries.

In general, the other agencies listed in Table 57 sampled four or fewer times per year. The lone exception was the IDHAMP, where selenium was sampled monthly from July 1984 through September 1986. Sampling under these other programs was generally too sporadic to provide a suitable basis for confident estimates of long-term mass transport. Some of the information is useful, however, in a qualitative sense and is discussed

These programs are introduced briefly here because they each apply to more than one of the rivers.

Data on the San Joaquin River are being generated primarily under the San Joaquin River Study (SJRS), a cooperative effort between USGS and the U.S. Bureau of Reclamation (USBR) (Gilliom, 1986). This study is examining water quality of the San Joaquin River and its tributaries. Sampling commenced in June 1985. Under a separate program, the USGS also performs chemical analyses on all three rivers under an ongoing national program. This is entitled the National Stream Quality Accounting Network (NASQAN).

DWR also assesses water quality under two separate programs. The Interagency Delta Health Aspects Monitoring Program (IDHAMP) was initiated in 1983 (DWR, 1986c). This program focuses on factors that affect the quality and quantity of water exported from the Delta for human consumption. Trace elements and pesticides, and certain other parameters, are analyzed in samples collected at locations throughout the Delta. DWR also analyzes water quality in accordance with Water Right Decision 1485, which sets terms for the operation of the State Water Project (DWR, 1984). The monitoring called for by Decision 1485 includes semi-annual sampling of trace elements and chlorinated organics.

All flow data presented here were measured by the USGS (1986; and unpublished data). Data on flow in the San Joaquin and Sacramento Rivers for October to December 1986 are not yet available. Discussion of loadings from the major tributaries in 1986 is limited therefore to the period from January through September. Flow data on the Mokelumne River and other minor tributaries are available only through September 1984.

where appropriate.

Parameters analyzed for the San Joaquin River Study are separated into the three categories of results described above. The first category consists of accurately quantified parameters (those detected consistently at levels significantly greater than their limit of detection). Analytical results for these parameters are considered to be adequately representative of actual trends in contaminant concentrations and worthy of quantitative treatment.

Tables 58 and 59 list monthly average mass loadings for the parameters detected at accurately quantifiable levels in the SJRS in 1985 and 1986, respectively. Figure 7 depicts trends in river flow at Vernalis over the three year period (1984-1986). Hydrologic conditions in 1985 and 1986 were unusual and very different from each other. Flows were consistently low throughout the entire 1985 calendar year, never exceeding 10 billion L d^{-1} . In February 1986, a high-flow period began, with monthly average discharge peaking at over 60 billion L d^{-1} in March. These two years provide an interesting context for discussing trends in water quality.

In 1985, the levels of one group of elements (including arsenic, chromium, copper, and zinc) showed similar trends (Table 58). Mass transport of "total" forms of each of these elements peaked in July and gradually declined through November. Dissolved forms did not show as strong a trend. The peaks are probably related to increased sediment discharge in July. Dissolved and total boron and dissolved ammonia-N exhibited peak loadings in December. The remaining elements showed no distinct temporal trends in 1985.

Table 57. Summary of chemical monitoring on the San Joaquin River at Vernalis.

Agency	Toxic Contaminants Analyzed ^a	Study Period	Sampling Frequency	Source
USGS: San Joaquin River Study	NH ₃ -N-d, NH ₃ -N-t, As-d, As-t, Ba-d, Ba-t, Be-d, Be-t, B-d, B-t, Cd-d, Cd-t, Cr-d, Cr-t, Cu-d, Cu-t, Fl-d, Pb-d, Pb-t, Li-d, Li-t, Mn-d, Mn-t, Hg-d, Mo-d, Mo-t, Ni-d, Ni-t, Se-d, Se-t, Ag-d, Ag-t, Zn-d, Zn-t	June 1985 -September 1986	Twice monthly, roughly 10 per month for some forms in Feb. and March 1986.	Gilliom, 1986; USGS unpublished data. (1986 data are preliminary.)
USGS: NASQAN	NH ₃ -N-d, As-d, Ba-d, Be-d, Cd-d, Cr-d, Co-d, Cu-d, Pb-d, Li-d, Mn-d, Hg-d, Mo-d, Ni-d, Se-d, Ag-d, Sr-d, V-d, Zn-d	January 1984-June 1985	Four per year	USGS, 1985; and USGS unpublished data
DWR: Decision 1485	As-d, As-t, Cd-d, Cd-t, Cr-d, Cr-t, Cu-d, Cu-t, Pb-d, Pb-t, Mn-d, Mn-t, Hg-t, Zn-d, Zn-t, chlorinated hydrocarbons, PCBs	1984-1986	Twice per year	DWR 1985 _a , 1986 _a . (1986 data obtained from DWR.)
DWR: IDHAMP	Se-t, 2,4-D, atrazine/simazine, bentazon bis (2-ethylhexyl) phthalate, carbofuran, chloropicrin, dacthal, diazinon, MCPA, metalaxyl, methamidophos, methyl bromide, methyl parathion, molinate, paraquat dichloride, thiobencarb, 1,1,1-trichloroethane, trichloroethylene,	1984-1986	Se: Monthly since 10/84. Others less than quarterly	DWR 1985 _b , 1985 _c , 1986 _b , 1986 _c , 1987.
USBR: Cutter	Se-d	1984-1986	Approx. 3 per year	Cutter, 1987.

^a suffix -d indicates dissolved concentrations; suffix-t indicates total concentrations.

Table 59. Monthly average mass transport (kg d^{-1}) of selected contaminants by the San Joaquin River at Vernalis from January through September, 1986. Data from the USGS San Joaquin River Study and the NASQAN program.

	jan	feb	mar	apr	may	jun	jul	aug	sep	Annual Summary		
										n	ave	sd
NH3	2319	8344	4902	2397	2144	458	283	389	409	9	2405	2537
As-d	10	43	61	48	21	15	7	16	10	9	26	19
As-t	13	49	116	81	43	31	18		26	8	47	33
Ba-d	282	856	1777	1055	708	412				6	848	489
B-d	2394	5777	7659	5033	2573	1983	2337	2375	2046	9	3575	1941
B-t	2394	3338	7965	5656	2895	1754	2549	2259	1944	9	3417	1945
Cr-t	25	513	1409	815	172	153	113	62	72	9	370	441
Cu-d	10	43	306	0	64	76	14	16	10	9	60	91
Cu-t	20	257	980	431	322	107	85	78	61	9	260	286
Mn-d	383	663	1777	1007	515	137	120	117	72	9	532	530
Mn-t	756	4193	6678	3355	2681	1906	1452	1012	1228	9	2585	1806
Ni-t	35	364	735	479	86	107	50	164	113	9	237	226
Zn-d	25	235	1103	575	86	168	71	78	0	9	260	340
Zn-t	0	1048	3247	1198	429	153	106	156	153	9	721	981

Table 58. Monthly average mass transport (kg d^{-1}) of selected contaminants by the San Joaquin River at Vernalis from June through December, 1985. Data from the USGS San Joaquin River Study and the NASQAN program.

	jun	jul	aug	sep	oct	nov	dec	Annual Summary		
								n	ave	sd
NH3	599	688	509	518	406	1558	2590	7	981	748
As-d	9	19	13	9	10	9	11	7	11	3
As-t	13	25	16	14	13	9	16	7	15	5
Ba-d	287	300	261	254	248	264	281	7	271	17
B-d	1668	1064	1432	801	887	1227	2374	7	1350	503
B-t	1839	1001	1877	942	963	1463	2266	7	1479	491
Cr-t	60	144	89	47	51	38	59	7	70	34
Cu-d	9	16	10	12	8	5	5	7	9	3
Cu-t	34	88	45	38	23	24	27	7	40	21
Mn-d	222	213	127	160	162	208	318	7	202	57
Mn-t	898	1032	1082	801	710	543	809	7	839	172
Ni-t	86	113	140	66	132	61	27	7	89	38
Zn-d	0	38	0	26	35	28	38	7	24	15
Zn-t	257	375	127	118	76	0	81	7	148	117

Fig. 8 summarizes monthly average transport data for contaminants in the San Joaquin River at Vernalis for June through December 1985. Arsenic and boron were transported predominantly in dissolved form. By contrast, copper, manganese, and zinc were largely carried on suspended particles.

Massive flows in early 1986 had an overriding effect on the mass transport of contaminants in that year (Figs. 9 and 10). Transport of every pollutant, with the lone exception of ammonia-nitrogen, showed pronounced peaks in March. Contaminants which are particle-associated (including chromium, copper, manganese, nickel, and zinc) exhibited especially prominent peaks during this period. Comparison of trends in transport between dissolved and total forms, as shown in Figs. 9 and 10, illustrates the predominance of particle-associated transport in high-flow periods for copper and zinc. Maximum concentrations for 1986 of total chromium, total copper, and total zinc coincided with the extreme high-flow period. In March, concentrations were reported as high as $42 \mu\text{g L}^{-1}$ for total chromium (March 2) and $54 \mu\text{g L}^{-1}$ for total copper (March 17; $50 \mu\text{g L}^{-1}$ for total lead was recorded on this same day, indicating the presence of an unusually contaminated mixture of suspended sediment). On each date that these high values were observed, the discharge of suspended sediment was also extremely high.

Arsenic was present in the San Joaquin River primarily in dissolved form during 1985. High flows in 1986, however, resulted in the movement of relatively large quantities of arsenic bound to suspended material (Fig. 9A). Concentrations of barium, boron, and ammonia-nitrogen, which normally are transported in solution, declined in March from previous months

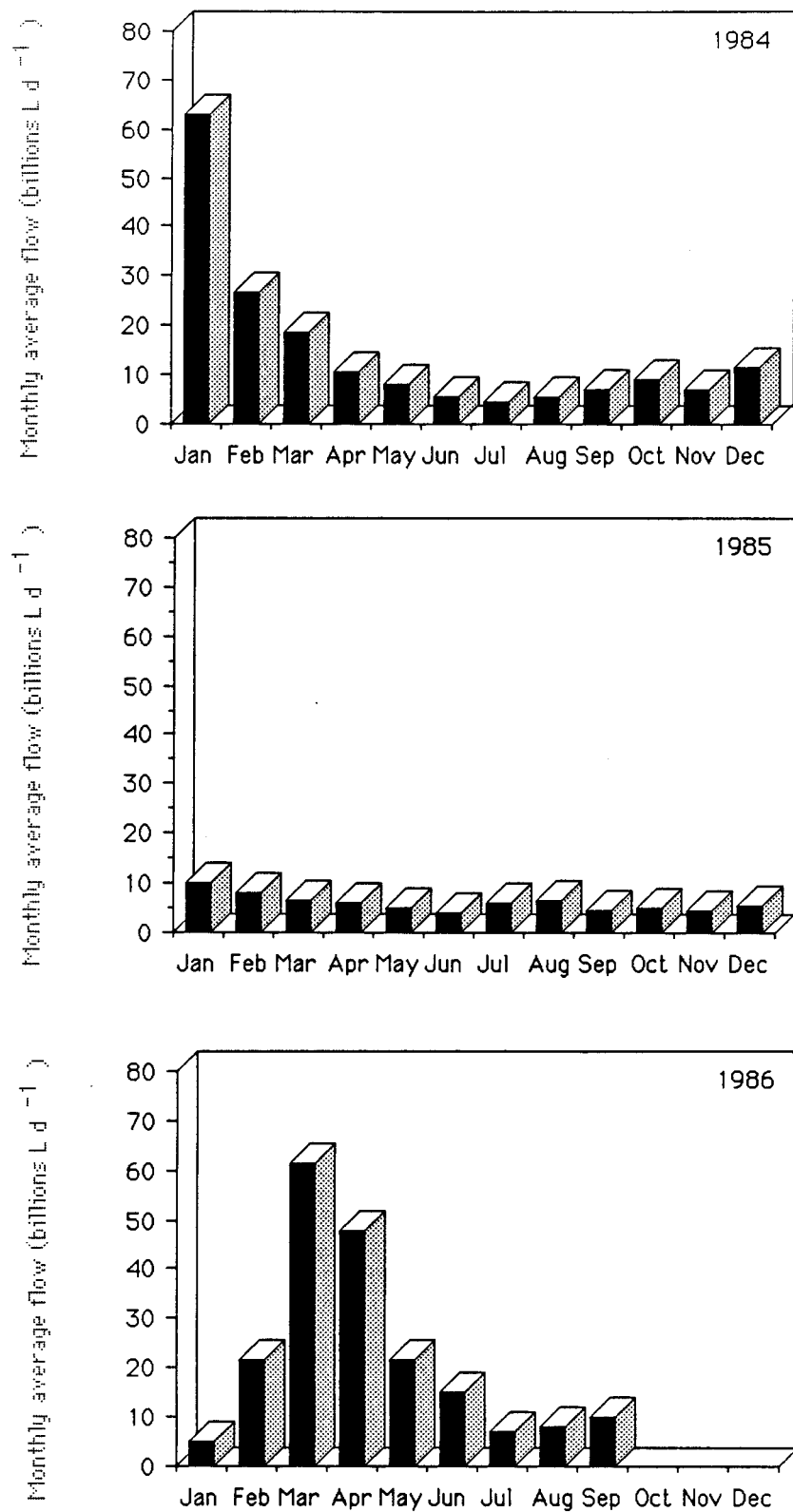


Fig. 7. Monthly average flow (billion L d⁻¹) of the San Joaquin River at Vernalis, 1984-1986. Data from USGS (1986) and USGS, unpublished data.

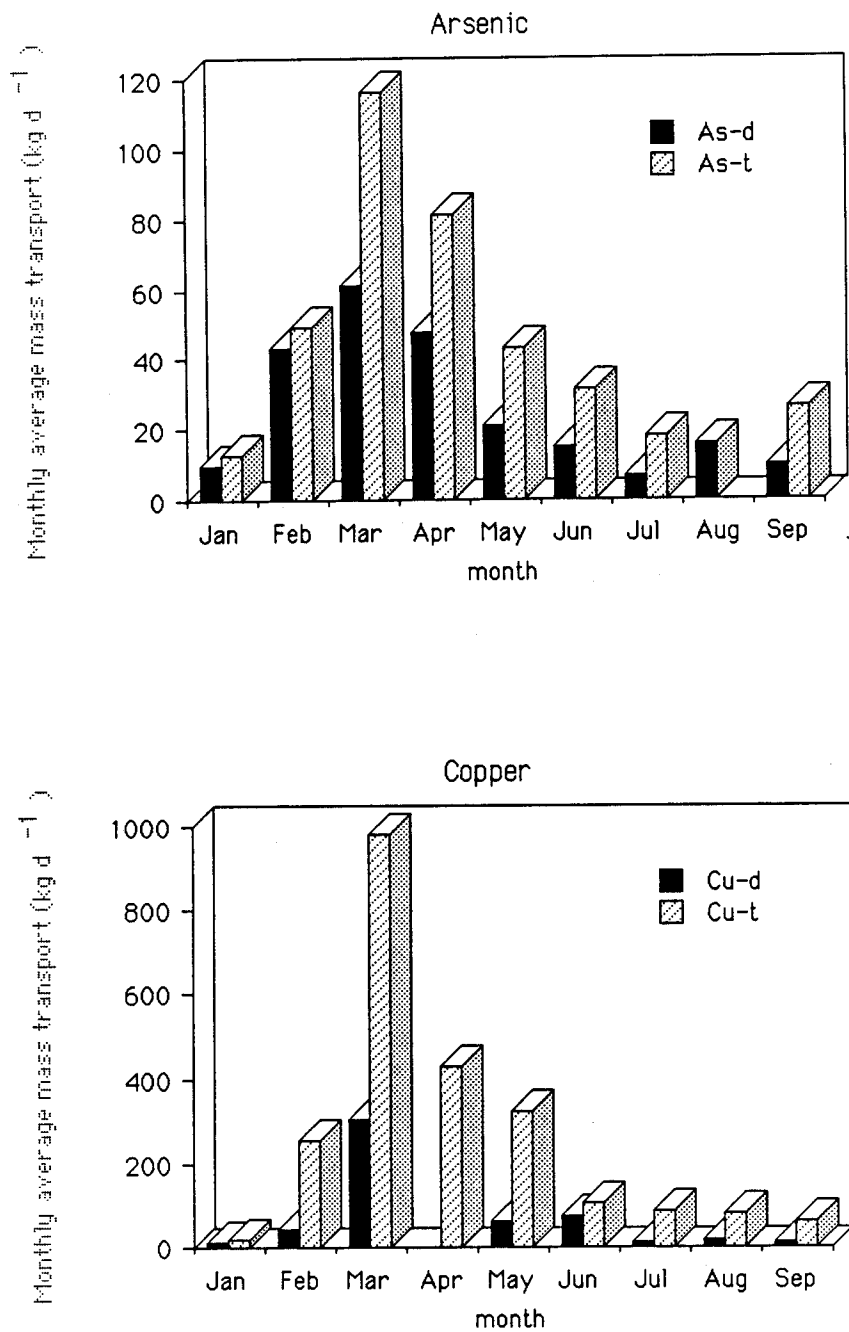


Fig. 9. Monthly average mass transport for arsenic (A) and copper (B) in the San Joaquin River at Vernalis, 1986. Mass transport shown for both dissolved and total forms of each element. Data from USGS studies (SJRS and NASQAN).

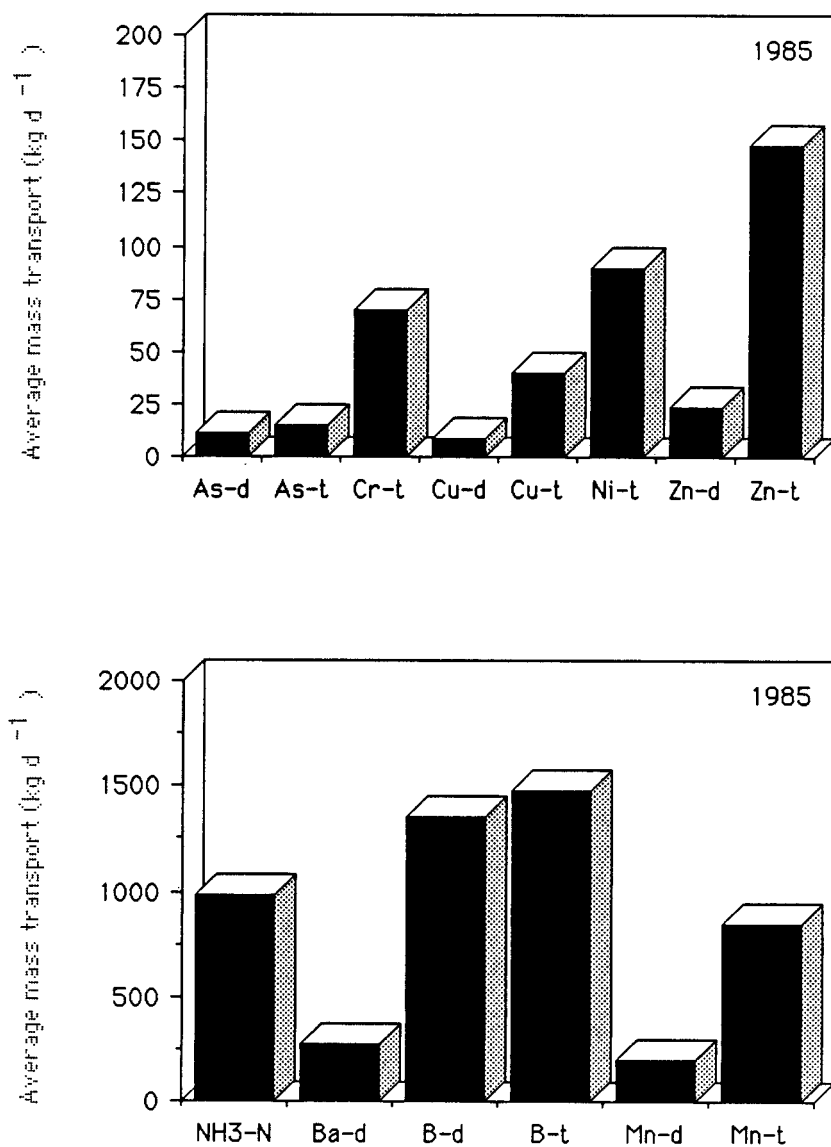


Fig. 8. Average transport of selected contaminants in the San Joaquin River at Vernalis, June to December, 1985. Computed from USGS data from the San Joaquin River Study and the NASQAN program.

due to the diluting effect of large flows. For example, ammonia-nitrogen concentrations fell by 80% from February to March.

The 1986 high-flow period had a tremendous influence on annual transport. In nine months from January through September, 62% of the total flow occurred in February and March alone. Of the mass transport of total chromium in the nine months, 66% occurred during February and March. Similarly, 42% of the loading of total copper, 56% of total nickel, and 68% of total zinc, occurred during these two months. Fig. 11 portrays average mass transport for each of the quantified parameters from January to September 1986.

As might be expected, selenium has received a great deal of attention at the Vernalis sampling station. Table 60 presents a summary of all concentration data generated from January 1984 through September 1986. Data reported by Cutter (1987) are informative, in spite of his relatively infrequent sampling. Cutter developed an improved method of selenium analysis, with a detection limit of 5 ng L^{-1} (Cutter, 1978). Cutter's selenium analyses on the San Joaquin River are supported by rigid quality control testing and are considered reliable. Cutter reports a range of concentrations from $0.136 \text{ } \mu\text{g L}^{-1}$ to $2.259 \text{ } \mu\text{g L}^{-1}$, with most values falling just below $1 \text{ } \mu\text{g L}^{-1}$. The USGS (Gilliom, 1986) and DWR (1986c) both employ methods with $1 \text{ } \mu\text{g L}^{-1}$ limits of detection. Since actual concentrations in the river at Vernalis are below or very near $1 \text{ } \mu\text{g L}^{-1}$, the USGS and DWR datasets for selenium must be regarded as quantitatively inexact, relative to the data of Cutter (1987). Monthly trends in selenium mass transport are not presented here because Cutter's sampling was too infrequent, and the other programs did not precisely quantify

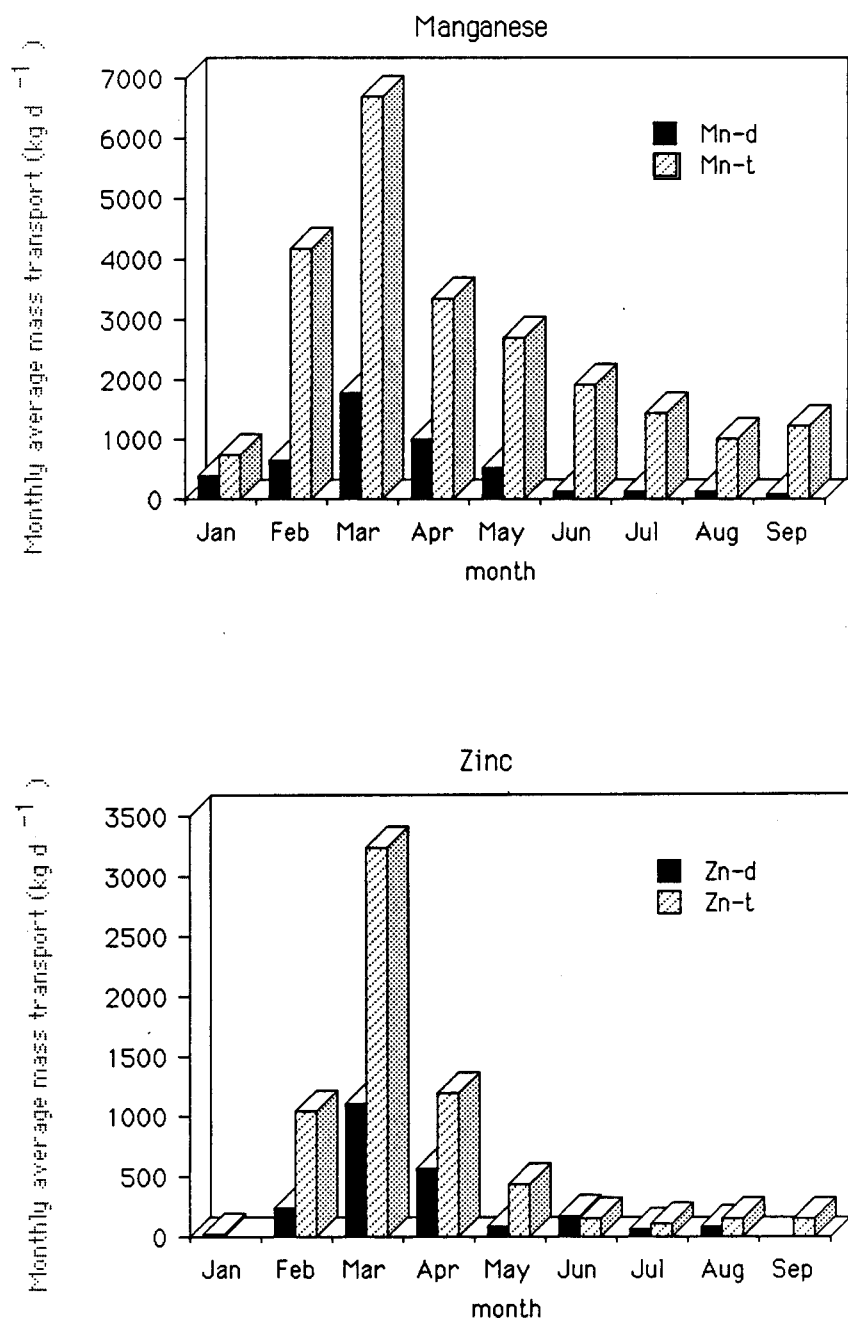


Fig. 10. Monthly average mass transport of manganese (A) and zinc (B) in the San Joaquin River at Vernalis, 1986. Mass transport shown for both dissolved and total forms of each element. Data from USGS studies (SJRS and NASQAN).

Table 60. Summary of selenium analyses on the San Joaquin River at Vernalis.
All data as $\mu\text{g L}^{-1}$.

Agency	Form ^a	No. detected	No. of analyses	Summary of detected values		Det. Limit
				Mean	S.D.	
USGS: SJRS	Se-d	9	25	1.2	0.3	1
	Se-t	7	19	1.1	0.2	1
DWR: IDHAMP	Se-t	16	26	1.3	0.5	1
USBR: Cutter	Se-d	9	9	0.077	0.025	0.005

^a Se-d: dissolved selenium. Se-t: total selenium.

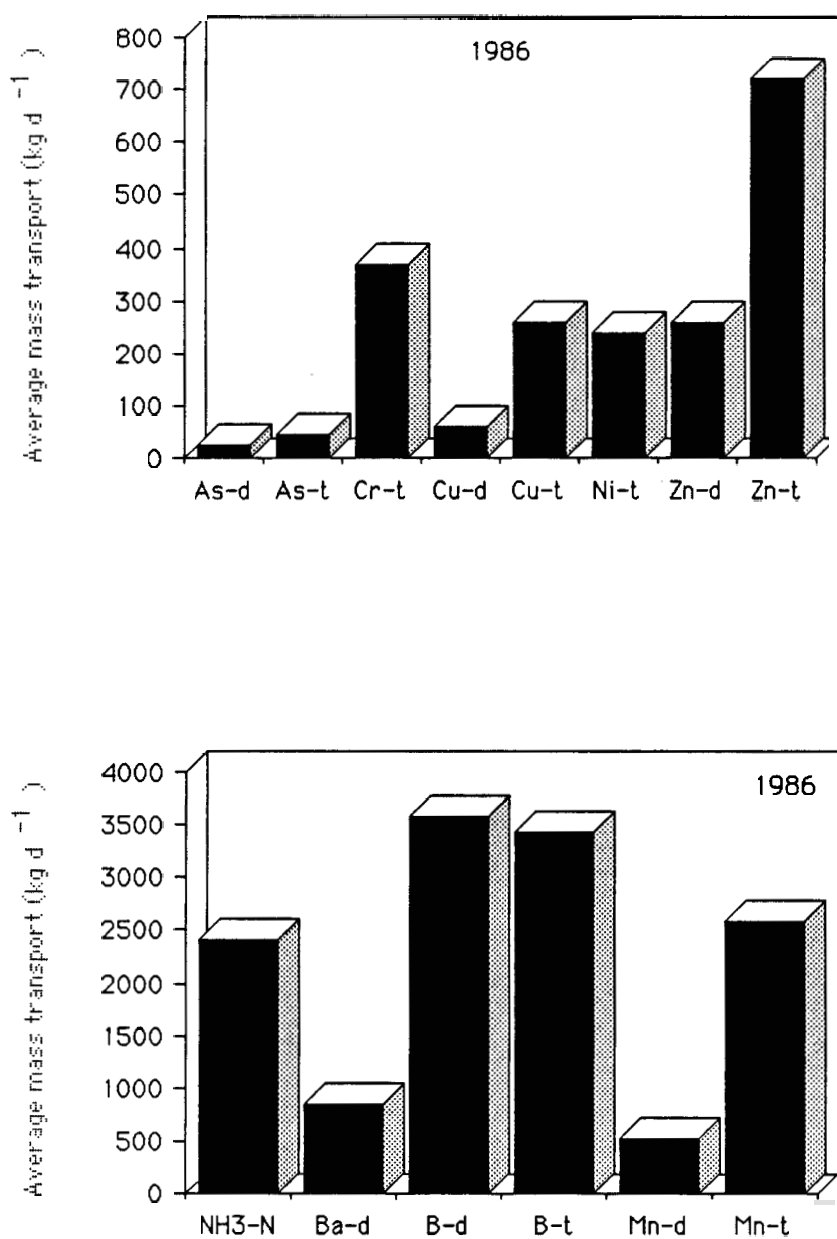


Fig. 11. Average transport of selected contaminants in the San Joaquin River at Vernalis, January to September, 1986. Computed from USGS data from the SJRS and the NASQAN program.

Table 61. Summary of contaminant data and average mass transport based on best available data, San Joaquin River at Vernalis, January 1984 - December 1986. Concentrations in $\mu\text{g L}^{-1}$, except for $\text{NH}_3\text{-N}$ which is in mg L^{-1} .

Parameter	#months selected/ #months analyzed	Agencies Analyzing	Lowest Monthly	Highest Monthly	Likely Average Concentration For 1/84-12/86	Likely Average Mass Loading, kg d^{-1} (Based on flows 1/84-9/86)	
			Average Concentration	Average Concentration		Low Flow	High Flow
$\text{NH}_3\text{-N-d}$	27/28	1,2	<.2	1.4	280	2201	5477
As-d	22/25	1,2	<1	3	1.5-1.6	11.8-12.6	29.3-31.3
As-t	18/18	1	1.5	4	2.4	18.9	46.9
Ba-d	20/20	1,2	22	67	46	362	900
Ba-t	6/16	1	<100	150	42-104	330-817	822-2034
Be-d	0/20	1,2	<.5	<1	0-.55	0-4.3	0-10.8
Be-t	0/16	1	<10	<10	0-10	0-78.6	0-196
B-d	19/19	1	105	475	236	1855	4616
B-t	19/19	1	115	475	242	1902	4734
Cd-d	5/20	1,2	<1	2	.36-1.1	2.8-8.6	7.0-21.5
Cd-t	2/16	1	<1	4	.31-1.2	2.4-9.4	6.1-23.0
Cr-d	2/20	1,2	<1	1	.1-1.0	.8-7.8	2.0-19.6
Cr-t	17/17	1	<1	24	12.3	97	241
Co-d	0/11	1,2	<3	<3	0-3	0-23.6	0-58.7
Cu-d	22/25	1,2	<1	5	3.2-3.3	25.2-25.9	62.6-64.5
Cu-t	19/19	1	4	16	9.1	71.5	178
Fl-d	12/28	1,2	<100	200	49-106	385-833	958-2073
Pb-d	6/20	1,2	<1	4	.6-1.8	4.7-14.1	11.7-35.2
Pb-t	9/18	1	<1	20	2.8-4.6	22.0-36.2	54.8-90.0
Mn-d	31/31	1,2,3	7	76	31	244	606
Mn-t	25/25	1,3	70	210	131	1030	2562
Mo-d	13/25	1,2	<1	<10	1.9-6.3	14.9-49.5	37.2-123
Mo-t	14/18	1	<1	<10	2.2-3.7	17.3-29.1	43.0-72.4
Ni-d	20/25	1,2	<1	8	1.7-2.3	13.4-18.1	33.3-45.0
Ni-t	19/19	1	2	26	12	94.3	235
Se-d	9/9	3	.136	2.259	.777	6.1	15.2
Se-t	23/45	1,4	<1	2	.6-1.1	4.7-8.6	
Ag-d	1/20	1,2	<1	<2	.05-1.1	.39-8.6	1.0-21.5
Ag-t	2/16	1	<1	2	.1-1.1	.8-8.6	2.0-21.5
Sr-d	10/10	1,2	140	460	317	2492	6201
V-d	0/11	1,2	<6	<6	0-6	0-47.1	0-117
Zn-d	20/25	1,2	<3	26	8.7-9.3	68.4-73.1	170-182
Zn-t	15/18	1	<10	60	22.5-24.2	177-190	440-473
Li-d	23/25	1,2	<4	17	8.4-8.9	66.0-70.0	164-174
Li-t	5/19	1	<10	20	3.2-10.5	25.2-82.5	62.6-205
Hg-d	0/21	1,2	<.1	<.1	0-.1	0-.8	0-2.0
Hg-t	4/18	1	<.1	.24	.04-.11	.3-.86	.8-2.2

1. USGS: SJRS
2. USGS: NASQAN
3. Cutter: (1987)
4. DWR: IDHAMP

the levels of selenium present.

Analytical results from other monitoring programs on the San Joaquin River at Vernalis are of little use in assessing the monthly average mass transport of contaminants. Trace element analyses from the NASQAN program (USGS, 1986; and unpublished data) and DWR's Decision 1485 monitoring (DWR, 1985a, 1986a, and unpublished data) are consistent with data from the SJRS. Methods with detection limits of $10 \mu\text{g L}^{-1}$, used by DWR, yielded few quantified results. Although sampling is infrequent, IDHAMP analyses (DWR, 1986c; 1987) for some pesticides (including 2,4-D, atrazine/simazine, dacthal, and diazinon) have shown consistently positive results. Most of these analyses were of samples taken in February-April 1985. However, quality control testing for 2,4-D and dacthal uncovered problems in detection of spikes by the contracted laboratory (DWR, 1986a). Without such testing, these analytical problems could not have been addressed.

Table 61 presents likely ranges of mass transport for selected parameters measured in the San Joaquin River at Vernalis. Datasets with the best combination of low detection limits and large numbers of observations from January 1984 through December 1986 are included in the table. Each parameter listed was analyzed on at least nine occasions. Likely average concentrations for the three year period are presented as ranges if results below the limit of detection are a significant proportion of the total number of observations. Mass transport estimates based on these concentrations are calculated for average high flows (average of flows in November through April) and average low flows (May through December). These estimates are made using the assumption that concentrations remain constant

Table 62. Summary of chemical monitoring on the Sacramento River.

Sampling Location	Agency	Toxic Contaminants Analyzed	Study Period	Sampling Frequency	Source
Freeport	CVRWQCB	Molinate, thiobencarb	May and June, 1984-1986	One to several per month	DFA, 1986
	USBR: Cutter	Se-d	1984-1986	Approx. three per year	Cutter, 1987
	USGS: NASQAN	NH ₃ -N-d, Ba-d, Be-d, Cd-d, Cr-d, Co-d, Cu-d, Pb-d, Li-d, Mn-d, Hg-d, Mo-d, Ni-d, Se-d, Ag-d, Sr-d, V-d, Zn-d	1984-1986	Four per year	USGS, 1985; and unpublished data
Greene's Landing	DWR: Decision 1485	As-d, As-t, Cd-d, Cd-t, Cr-d, Cr-t, Cu-d, Cu-t, Pb-d, Pb-t, Mn-d, Mn-t, Hg-t, Zn-d, Zn-t, chlorinated hydrocarbons, PCBs	1984-1986	Two per year	DWR 1985 _a and 1986 _a . 1986 data obtained from DWR.
	DWR: IDHAMP	Se-t, 2,4-D, atrazine/simazine, bentazon, bis(2-ethylhexyl) phthalate, carbofuran, chloropicrin, dacthal, diazinon, MCPA, metalaxyl, methamidophos, methyl bromide, methyl parathion, molinate, paraquat dichloride, thiobencarb, 1,1,1-trichloroethane, trichloroethylene, thiobencarb	1984-1986	Se: Monthly since 10/84. others less than quarterly	DWR 1985 _b ; 1985 _c ; 1986 _b ; 1987.
Hood	CVRWQCB	Sb, As-d, As-t, B-t, Cd-d, Cd-t, Cr-d, Cr-t, Cu-d, Cu-t, Hg-d, Hg-t, Mn-t, Ni-d, Ni-t, Se, Sn, Zn-d, Zn-t	May-December 1985	8 obs. for Cu, fewer for others	SWRCB, 1986; CVRWQCB, unpublished data
Sacramento	City of Sacramento	molinate thiobencarb	May and June, 1984-1986	32 or more in 2 months	DFA, 1986.

at all flow rates. Ranges of estimated average transport are broadest where undetected values form a large fraction of the total number of observations. The Table indicates that even the SJRS, which is the best contaminant monitoring effort to date on any of the Delta tributaries, provides a somewhat uncertain basis for mass transport calculation. Pesticides are not listed in the Table because they were not analyzed the minimum of nine times through the three year period.

The estimates in Table 61 are intended only to indicate the likely average range of amounts of contaminants actually transported by the San Joaquin River, and to provide a crude basis for comparison with loadings attributable to other sources of toxic contaminants to the estuary. As discussed previously, riverine mass transport is a dynamic phenomenon which is not completely described by long-term averages.

The Sacramento River

Water quality monitoring on the Sacramento River as it flows into the northern Delta has been less extensive than monitoring on the San Joaquin River at Vernalis. No study comparable to the SJRS took place on the Sacramento between 1984 and 1986. Table 62 lists the agencies which sampled from January 1984 to September 1986, and provides information on each sampling program. Sampling on the Sacramento, as seen in Table 62, is complicated by the lack of a common sampling location. Results presented here are based on sampling at four different locations. Comprehensive monitoring to assess long-term trends in contaminant transport is not performed on the Sacramento River. Sampling on a monthly or more frequent schedule has only been performed on a regular basis for a few specific pollutants, including selenium, and the rice

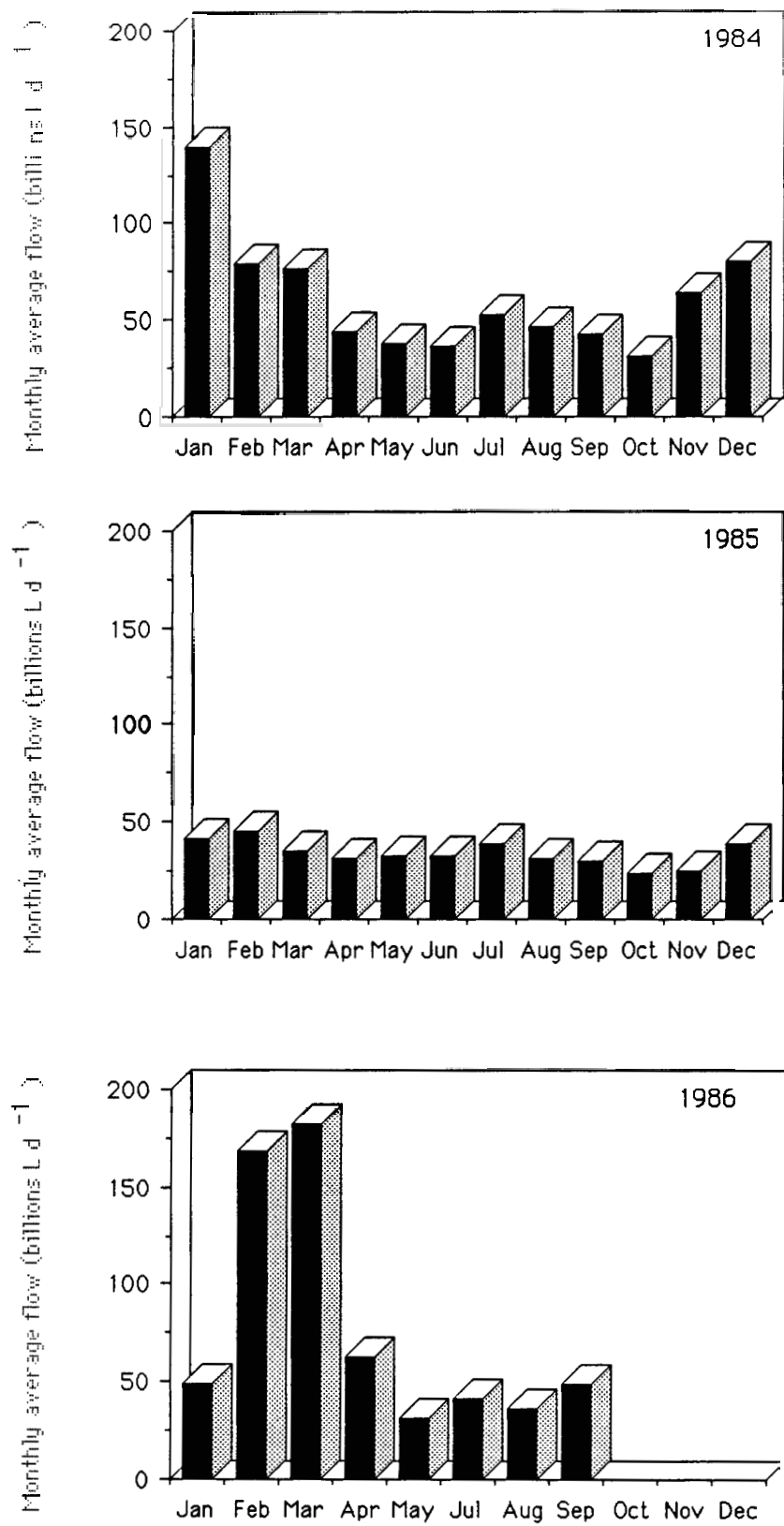


Fig. 12. Monthly average flows (billion $L\ d^{-1}$) of the Sacramento River at Freeport, 1984-1986. Data from USGS (1986) and USGS, unpublished data.

herbicides molinate and thiobencarb. Sampling under the San Joaquin River Study on the Sacramento River at Freeport began in October 1986, and should improve the present database considerably.

Fig. 12 depicts the average daily flow of the Sacramento River at Freeport from January 1984 to September 1986 by month. Flows in the Sacramento at this location are an average of five times greater than those in the San Joaquin River at Vernalis. There is general agreement between the flow regimes of the two rivers, however (compare Figs. 8 and 12). During the high-flow period in 1986, monthly average discharge peaked in March at over 180 billion $L\ d^{-1}$. Clearly, there is a potential for minute concentrations of contaminants in the Sacramento River to be translated into significant mass loadings to the estuary.

Contamination by molinate and thiobencarb in the Sacramento Valley has been well documented, beginning with studies in the early 1980s (summarized in Cornacchia et al., 1984), and continuing to the present (DFA, 1986). Monitoring data discussed here were generated by the City of Sacramento and the CVRWQCB (the data are presented in DFA, 1986).

The City of Sacramento analyzes water taken from the River at a point just downstream of the confluence with the American River, at the intake to the City's water treatment plant. Sampling is performed on almost a daily basis in May and June in the Sacramento Valley. Table 63 presents average herbicide mass loadings based on the City's analyses for April through July,

1984-1986. Application and transport of these herbicides are documented well enough to be able to trace peak concentrations at the City intake on 26 May 1986 back to peak application of herbicides onto flooded fields in the Valley on May 17 of that year. Data collected by the CVRWQCB further downstream at Freeport support trends seen in the City of Sacramento's data.

Selenium was the only other contaminant analyzed monthly for a significant portion of the three year period. Selenium was measured monthly from September 1984 through June 1986 under the IDHAMP (DWR, 1986c, 1987). The data are summarized in Table 64, along with supplemental data collected by Cutter (1987) and USGS (1986; and unpublished data). As was the case with monitoring on the San Joaquin River, monthly data generated by DWR at Freeport are of limited use in a quantitative assessment of mass transport. Actual concentrations of selenium in the River, as indicated by reliable analyses by Cutter (1987), are generally at least an order of magnitude below the detection limits of the methods employed by DWR and USGS.

The CVRWQCB conducted a special study on the Sacramento River at Hood during a seven month period in 1985. Many elements were analyzed, but problems were encountered with quality control in two commercial laboratories contracted for the analyses, making some of the data unusable (CVRWQCB, unpublished data). Reported detection limits varied widely for some elements, and split samples sent to two contracted laboratories produced widely disparate results. Data for copper, however, appear reliable. The copper data are reported in SWRCB (1986). Quality control data are also reported, including results for duplicates, and

Table 63. Mass transport of molinate and thiobencarb on the Sacramento River, April-June, 1984-1986 (date from DFA, 1984; 1985; 1986). BDL values set to zero.

		Mass transport in kg d ⁻¹ (no. of samples taken)			
Year	Herbicide	April	May	June	July
City of Sacramento at City Intake					
1986	molinate	0 (1)	164 (10)	*	4.5 (1)
	thiobencarb	0 (1)	21.9 (10)	*	0 (1)
1985	molinate	0 (1)	163 (20)	123 (14)	-
	thiobencarb	0 (1)	46.7 (20)	46.6 (14)	-
1984	molinate	0 (1)	250 (21)	65 (14)	0 (1)
	thiobencarb	0 (1)	17.7 (21)	8.8 (14)	0 (1)
CVRWQCB: Freeport					
1986	molinate	-	162 (3)	*	-
	thiobencarb	-	0 (3)	*	-
1985	molinate	-	427 (1)	261 (1)	-
	thiobencarb	-	29.6 (1)	42.3 (1)	-
1984	molinate	-	528 (1)	326 (1)	-
	thiobencarb	-	0 (1)	44.0 (1)	-

* No flow data available.

recoveries from standard solutions and spiked samples. Reported monthly average concentrations are shown in Table 65. Flows during 1985 were low and relatively constant (Fig. 12); thus, trends in mass transport of copper based on these data would parallel trends in the reported concentrations.

Contaminant concentrations measured on a quarterly or less frequent basis in the Sacramento are reported by USGS under the NASQAN program (USGS, 1985; and unpublished data), DWR under Decision 1485 monitoring (DWR, 1985a, 1986a), and DWR's IDHAMP (DWR, 1985b, 1985c, 1986b, 1986c, 1987). The data indicate that the River carries dissolved forms of arsenic, copper, lead, mercury, nickel, zinc, and other elements during at least some portions of the year. Pesticides have also been detected occasionally in sampling under the IDHAMP. Only bentazon, diazinon, and molinate have been detected on more than one date, however.

One final set of data requiring mention was based on a sample taken at Rio Vista in September 1986 as part of the environmental impact study on the relocation of Chevron USA's Richmond outfall (Stukas, 1986). Although only one sample was analyzed, extremely low detection limits (of the order of pg L^{-1}) and strict quality control lend significance to the results. Only total zinc, total nickel, total chromium, and soluble and total copper were present at concentrations above 1 ng L^{-1} (Table 66). Soluble and total cadmium, soluble and total lead, soluble zinc, soluble nickel, and soluble and total selenium were all present at concentrations well below 1 ng L^{-1} . These data confirm that actual contaminant levels in the Sacramento River, as in the San Joaquin River, are often well below the detection limits of methods commonly used.

Table 64. Summary of selenium analyses on the Sacramento River₁ in the northern Delta, 1984-1986, All data as $\mu\text{g L}^{-1}$.

Agency	Form ^a	# detected # analyses	Summary of detected values		Detection limit
			Mean	SD	
USGS: NASQAN (Freeport)	Se-d	0/12	-	-	1
DWR: IDHAMP (Greene's Landing)	Se-t	2/21	1	0	1
USBR: Cutter	Se-d	9/9	.78	.67	.005

^aSe-d: dissolved form. Se-t: total selenium.

Table 66. Trace element concentrations ($\mu\text{g L}^{-1}$) in the Sacramento River at Rio Vista in September 1986 (data from Stukas, 1986).

Form	Cd	Cr	Cu	Pb	Ni	Se	Zn
Soluble	.001	-	1.340	.054	.670	<.010	.547
Total	.020	1.757	2.807	.463	2.033	<.012	2.630

Table 65. Copper concentrations ($\mu\text{g L}^{-1}$) on the Sacramento River at Hood from May - Dec. 1985 (data from SWRCB, 1986).

	<u>May</u>	<u>Jun</u>	<u>Jul</u>	<u>Aug</u>	<u>Oct</u>	<u>Nov</u>	<u>Dec</u>
Cu-d	6	4	2	2	3	9 ^a	3
Cu-t	8	7	4	7	5	11 ^a	13

^a Based on two samples.

Table 67. Summary of contaminant data and average mass transport based on best available data, Sacramento River in the northern Delta, 1984-1986. Concentrations in $\mu\text{g L}^{-1}$, except for $\text{NH}_3\text{-N}$ which is in mg L^{-1} .

Parameter	#months delected/ #months analyzed	Agencies Analyzing	Lowest Monthly Average Concentration	Highest Monthly Average Concentration	Likely Average for 1/84-12/86	Likely Average Mass Loading (Based on flows 1/84-9/86)	
						Low Flow	High Flow
NH ₃ -N-d	9/12	1	<100	100	22-24	824-899	1600-1745
As-d	9/12	1	<1	2	1-.25	37.4-46.8	72.7-90.9
Ba-d	12/12	1	21	62	30	1124	2181
Be-d	2/12	1	<.5	.8	.1-.6	3.7-22.5	7.3-43.6
Cd-d	4/13	1,2	.011	1	.2-1.0	7.5-37.4	14.5-72.7
Cr-d	4/13	1,2	<1	6	.8-1.5	30.0-56.2	58.2-109
Cu-d	21/21	1,2,3	1	11	3.1	116	225
Pb-d	5/12	1,2	.054	4	.8-2.1	30.0-78.6	58.2-153
Li-d	6/12	1	<4	8	2.8-4.8	105-180	204-349
Mn-d	17/18	1,5	2	10	6.5	243	473
Hg-d	4/12	1	<.1	.3	.05-.12	1.9-4.5	3.6-8.7
Mo-d	0/12	1	<10	<10	0-10	0-374	0-727
Ni-d	8/13	1,2	.67	2	.7-1.1	26.2-41.2	50.9-80.0
Se-d	9/10	2,4	<.01	.111	.069	2.6	5.0
Ag-d	1/12	1	<1	1	.1-1	3.7-37.4	7.3-72.7
V-d	0/12	1	<6	<6	0-6	0-225	0-436
Zn-d	11/13	1,2	.547	19	7.7-8.1	288-303	560-589
Fl-d	1/12	1	<100	100	10-100	374-3745	727-7271
Cu-t	9/9	2,3	2.8	16	7.6	285	553

1. USGS: NASQAN
2. Stukas (1986)
3. SWRCB (1986)
4. Cutter (1987)
5. DWR: 1485 Monitoring

Table 67 presents likely ranges of mass transport for selected parameters measured in the Sacramento River in the northern Delta. The same procedures for selecting the data presented in the table and for calculating likely ranges of average mass transport used in Table 61, which summarized mass loading on the San Joaquin River, were followed. Datasets with the best combination of low detection limits and large numbers of observations from January 1984 through December 1986 are included in the table. Molinate and thiobencarb are not included in the table because significant mass transport of these herbicides occurs almost exclusively in May and June of each year.

The estimates in Table 67 are intended only to indicate the likely average range of amounts of contaminants actually transported by the Sacramento River, and to provide a crude basis for comparison with loadings attributable to other sources of toxic contaminants to the estuary. As discussed previously, riverine mass transport is a dynamic phenomenon which is not completely described by long-term averages.

The Mokelumne River

The only sampling performed on a regular basis on any of the minor tributaries to the Delta is undertaken by the USGS on the Mokelumne River at Woodbridge (Table 68). This sampling site is one of the national network of NASQAN stations. Flows of the Mokelumne comprise only an average of 1.8% of the total volume entering the Delta each year (Table 56). Flow data are only available through September 1984. Barium, copper, manganese, and strontium were detected in each sample collected over the three year period.

Table 69 presents estimated ranges of mass loading based on average concentrations from January 1984 to September 1986. The same format used for Table 61 and Table 67 is employed here. The table is based exclusively on data collected by the USGS NASQAN program. Average high and low flows were calculated using flow data for January through September, 1984.

E. Conclusions

Few toxic contaminants which are carried into the estuary by the Delta tributaries are characterized adequately in terms of monthly trends in mass transport. Water quality sampling programs on the rivers have been deficient in two principal areas. The first of these is that sampling has in general been too infrequent. Pulses of contaminant transport related to rainfall or discrete releases of wastewater in the basin are likely to pass into the estuary unrecorded. The other deficiency is that methods employed in analyzing contaminant concentrations often exhibit detection limits which are above or close to the actual levels present in the rivers. Quantitatively uncertain results obtained for such contaminants are of limited use in describing monthly trends, and (as seen in Tables 61 and 67) make for uncertain estimates of long-term average mass transport of contaminants. Recent analyses using methods with improved sensitivity, on both the Sacramento and San Joaquin Rivers, have been revealing. Use of these methods should be expanded for contaminants of concern that are present in the Rivers at or below $1 \mu\text{g L}^{-1}$. Stringent quality control procedures must also be adopted in such studies if useful data are to be provided.

Table 68. Summary of chemical monitoring on the Mokelumne River at Woodbridge.

Agency	Toxic Contaminants Analyzed	Study Period	Sampling Frequency	Source
USGS: NASQAN	NH ₃ -N-d, As-d, Ba-d, Be-d, Cd-d, Cr-d Co-d, Cu-d, Fl-d, Pb-d Li-d, Mn-d, Hg-d, Mo-d, Ni-d, Se-d, Ag-d, Sr-d, V-d, Zn-d	1984-1986	4 per year	USGS, 1986 and WATSTORE unpublished data.

These deficiencies are particularly apparent for the Sacramento River. Although approximately 80% of the flow that entered the estuary in 1984-1986 was carried by the Sacramento, consistent water quality monitoring in that time was only quarterly in frequency and only examined dissolved forms of trace elements. Minute concentrations of toxic contaminants in the Sacramento River can contribute highly significant total loadings to the estuary, and these certainly need to be more accurately described.

Table 69. Summary of contaminant data and average mass transport based on best available data, Mokelumne River at Woodbridge, 1984. Data₁ from USGS NASQAN program. Concentrations in $\mu\text{g L}^{-1}$, except for $\text{NH}_3\text{-N}$ which is in mg L^{-1} .

Parameter	#months detected/ #months analyzed	Lowest Monthly	Highest Monthly	Likely Average	Loading (Based on flows	
		Average Concentration	Average Concentration	for 1/84-12/86	1/84-9/86) Low Flow	High Flow
=====						
NH ₃ -N-(mg/L)	9/12	<.01	.04	.02	23.6	57
As-d (µg/L)	12/12	<1	<1	0-1	0-1.2	0-2.8
Ba-d	12/12	15	54	23	27.1	65.6
Be-d	3/12	<.5	.9	.22-.64	26-.76	.6-1.8
Cd-d	2/12	<1	1	.17	.20-1.2	.5-2.8
Cr-d	1/12	<1	2	.17-1.1	.20-1.3	.5-3.1
Co-d	0/12	<3	<3	0-3	0-3.5	0-8.6
Cu-d	12/12	1	3	1.7	2.0	8.1
Li-d	3/12	<4	6	1.2-4.2	1.4-5.0	3.4-12.0
Mn-d	12/12	3	10	6.1	7.2	17.4
Hg-d	2/11	<.1	.2	.04-.12	.05-.14	.1-.34
Mo-d	0/12	<10	<10	0-10	0-11.8	0-28.5
Ni-d	6/12	<1	3	.7-1.2	.83-1.4	2.0-3.4
Se-d	0/12	<1	<1	0-1	0-1.2	0-2.8
Ag-d	1/12	<1	1	.1-1	.1-1.2	.3-2.8
Sr-d	12/12	42	52	47	55.5	134
V-d	0/12	<6	<6	0-6	0-7.1	0-17.1
Zn-d	12/12	4	22	11	13.0	31
Fl-d	0/12	<.1	<.1	0-.1	0-.1	0-.3

biologically available than they were at the dredging site. This is particularly true of contaminants in more deeply buried sediments from a dredged site, which may be effectively occluded from equilibrium with the biota of the ecosystem by the overlying sediment. Particularly in new dredging or in maintenance dredging of infrequently dredged areas, these more deeply buried sediments may contain toxic contaminants introduced to the Bay-Delta years or even decades ago. Therefore, while toxicants introduced at dredged material disposal sites in the Bay-Delta are not strictly inputs of new contaminants, they must be considered as potential point sources of newly biologically-available contaminants.

As the proportions of contaminants in disposed dredged material which are derived from current or historical inputs are unknown, any assessment of contaminant loads from this source faces difficulty with the "double counting" problem. Thus, recent contaminants which reside in sediment which is dredged have been accounted for in estimates of loads from other sources, and are simply redistributed in the Bay-Delta by their dredging and dumping. In calculating total contaminant loads to the ecosystem for a given year it is, therefore, not possible to add dredged material inputs to other sources estimated in this report, since some unknown proportions of the dredged material contaminant load would be counted twice (or possibly more than twice where maintenance dredging occurs more than once a year).

There are currently three dredged material disposal sites designated and used in the Bay-Delta, at Alcatraz, Carquinez Strait, and in San Pablo Bay (Fig. 13). At these sites, material

5. DREDGING AND DREDGED MATERIAL DISPOSAL

A. Introduction

Several beneficial uses of the San Francisco Bay-Delta rely on the ability of a variety of vessels to navigate and dock within the Bay-Delta itself. Recreational boating, national defense, and commerce all rely on navigability of the Bay-Delta. The depth and shoreline configuration of the Bay-Delta in equilibrium with river sediment load and natural sediment redistribution processes are, in places, not optimal to navigation needs. Therefore, channels and harbors must be dredged to provide for these needs. Dredging is needed where bigger vessels require deeper channels or docks or where new port or marina facilities are to be created. In addition, maintenance dredging of existing channels, ports, and marinas is necessary on a continuing basis to remove accumulating sediments brought into the dredged areas from river transport or by the dynamic redistribution of Bay-Delta sediments.

Contaminants entering the Bay-Delta ecosystem from point discharges, atmospheric fallout, urban and non-urban runoff, spills and other sources are distributed within the estuary by physical mixing and enter a complex set of dynamic equilibria among dissolved, colloidal, particulate, sedimentary, and biological components of the ecosystem. For many pollutants, these equilibria favor association of a large fraction of the contaminant load with particulate material and the sediments. Therefore, when sediments are dredged from channels and harbors they contain concentrations of a variety of toxic contaminants.

Upon disposal into an aquatic dredged material disposal site, some of these contaminants may become more readily

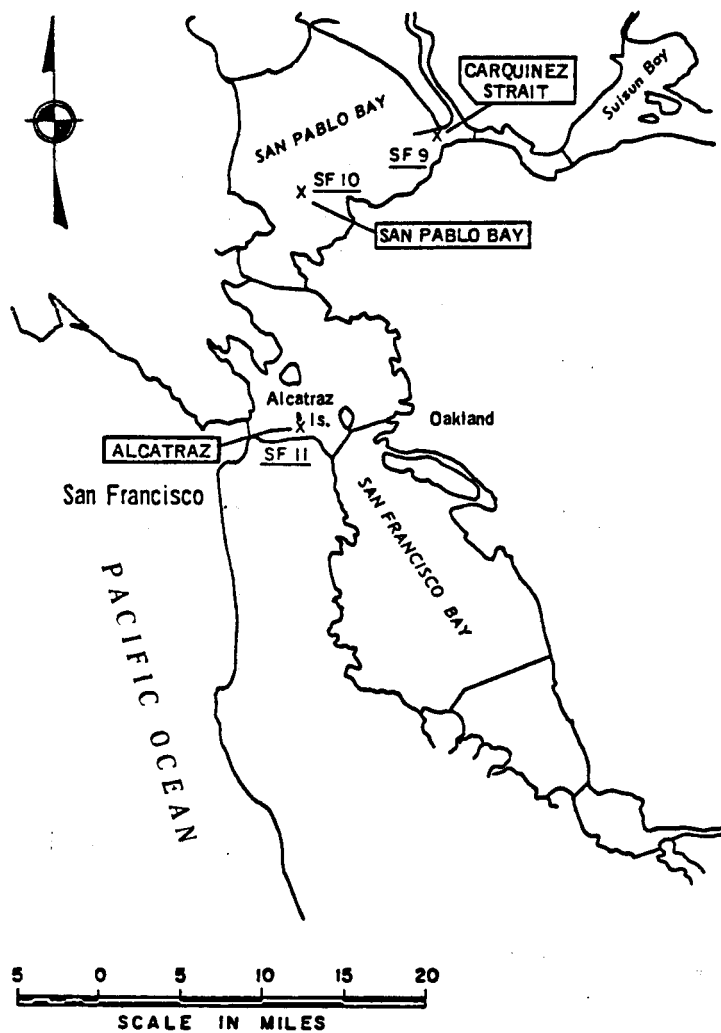
dredged from multiple locations in the Bay-Delta is disposed. It is often argued that the contaminants associated with dredged material disposed at these sites do not represent a potential or actual significant source of bio-available contaminants because they are bound to the sediments (and stay bound upon disposal), and the dredged material does not accumulate but is dispersed and diluted in the natural sediments. While each of these arguments has some merit, the true situation is more complex.

Accordingly, this section attempts to derive estimates of the fraction of each of the studied dredged material contaminants that is potentially biologically available. In order for the rationale behind these estimates to be better understood, a brief review is presented of the behavior of dredged material and associated contaminants disposed in marine and estuarine waters in general and in the San Francisco Bay-Delta, specifically. The derived loading estimates should be interpreted with this information in mind.

B. Processes Occurring During Aquatic Disposal of Dredged Material

When dredged material is released into the water column at an aquatic disposal site, several physical and chemical processes occur before the material reaches a resting place on the Bay floor or is transported from the Bay. These include physical fractionation and dispersion, the release of pore fluids, adsorption and desorption reactions, ion exchange processes, and chemical oxidation. The dredged material has several potential effects on the biosphere during the initial settling period: (1) contaminants released to solution may be taken up by and may affect organisms in the dispersion zone; (2) contaminants associated with the sediments may become biologically available

Fig. 13. Locations and details of open-water disposal sites for dredged material in the Bay-Delta. After Fong et al. (1982).



DESIGNATED SITES

SF 9 CARQUINEZ STRAIT	38° 03' 50"N, 122° 15' 55"W
SF 10 SAN PABLO BAY	38° 00' 28"N, 122° 24' 55"W
SF 11 ALCATRAZ ISLAND	37° 49' 17"N, 122° 25' 23W

The solid fraction of dredged material is itself heterogeneous and also fractionates. The sand or minerals of larger grain size and higher density sink more rapidly than the finer particles, which are predominantly authigenic and organic matter. The extent of fractionation of solids is dependent upon the water depth at the dumpsite. The shallower the depth, the less fractionation occurs before initial impact of the density plume on the bottom sediments. If the water is sufficiently deep, the density plume dissipates before reaching the substrate and becomes a collection of individual particles, each settling at their characteristic velocity. The depth necessary to dissipate the density plume is a function of dredged material composition, nature of the dumping process, water column density and stratification, and other factors. The water column at the designated dredged material dumpsites in the San Francisco Bay-Delta is relatively shallow. Therefore, it is likely that: (1) any dumping of dredged material at these locations results in an impact of the density plume with the bottom sediments; (2) the quantity of pore water released during the downward advective phase is small; and (3) the fractionation of the solids in the dredged material during the downward advective phase is minimal. However, the requirement that dredged material be released as a slurry of high water content would tend to enhance pore water loss and fractionation during advective descent of the dumped material.

When a density plume impacts bottom sediments, the kinetic energy of the plume is partially dissipated by resuspension of the upper layers of sediments at the impact site, and partially translated into a horizontal plume which disperses near and along

the bottom, away from the initial impact site. During resuspension of the upper layers of sediment at the impact site, the pore waters of these sediments are released to the water column. Following initial impact and resuspension, the suspended matter, which is dispersed over a large area of the sea floor (typically tens to hundreds of thousands of square meters), settles out at its characteristic velocity. Dense mineral grains such as coarse sands will settle out very rapidly, while the lighter fractions (including organic matter) will remain suspended for a longer period. Therefore, the lighter material is preferentially dispersed and advected away from the disposal site compared to the denser material.

The less dense authigenic and organic fractions of dredged sediments contain proportionately larger quantities of the trace metal and organic contaminants introduced to the environment by human activity than do the coarser mineral fractions (e.g. U.S. COE, 1975). Therefore, the net effect of the physical processes occurring during and after the dredged material dumping event is to fractionate these contaminants preferentially to the surface sediment layer and the water column. Any material permanently buried by continued dumping is enriched in coarse sands compared to the original dredged material. The dumping process thus fractionates fine materials containing higher contaminant levels to the surface of sediments at the dumpsite itself and in nearby areas. Given the rapid currents at the San Francisco Bay disposal sites, it is likely that the transport of fine material away from these area is considerable.

Release of Pore Waters

During the initial dispersal and settling out of the dredged material after dumping, the pore waters dredged with the sediments from their original site, and the water entrained with the sediments during dredging, are dispersed and diluted with disposal site water. The mixed pore waters and entrained dredging site water (hereafter the mixture is referred to as pore fluids) are often of lower salinity (and density) than the water at the disposal site. Therefore, some of the pore fluids will disperse in the surface waters at the dump site. The remainder of these fluids is entrained with the initial convective descent of the dredged material mass and will be mixed upwards into the water column when the dredged material mass impacts upon the Bay floor.

The dispersal of pore fluids during dredging has not been studied extensively in the field. However, the available evidence suggests that the major fraction of the pore fluids is entrained with the solids during convective descent and disperses in the deeper waters, particularly at sites as shallow as those in San Francisco Bay. Acoustic studies suggest that rising convective plumes of pore fluids containing fine-grained suspended solids are formed after the breakup of the dredged material mass upon its impact with the sea floor. It would appear that the dredged material pore fluids are dispersed throughout the water column at the dumpsite. However, the dispersal is not uniform vertically, and it is probable that the major fraction of the dissolved components of the pore fluids is dispersed into the near-bottom waters at the shallow San Francisco Bay disposal sites.

The pore waters of dredged material may have significant concentrations of both trace metals and organic compounds. Some trace metals may accumulate in the pore waters of sediments to concentrations in excess of those in the overlying water. The available data show that, with the exception of manganese and iron, the concentrations of trace metals in sedimentary pore waters are generally less than ten times higher than the concentrations of the same metal found in coastal sea water. However, the variability of metal concentration in pore waters at different locations is large, and sediments dredged from any particular region may have anomalously high pore water concentrations of one or more metals. Nevertheless, dilution factors of greater than ten times, which should be achieved within minutes in all dumping situations, will usually effectively reduce the concentration of the released pore water trace metals to close to the ambient background.

The levels of organic contaminants in pore waters of sediments are less well-documented than those of trace elements in general. Most of the highly persistent (and toxic) organic pollutants exhibit very low solubilities in water, and it is likely that their partitioning to solution will be less than that of most trace metals. However, their preferential association with fine particulate material may nevertheless permit uptake of such compounds by biota (especially filter feeders) following the disturbance of sediments by dredging and dumping activities.

Chemical Processes Occurring During Initial Dispersal of Dredged Material After Dumping

When dredged material is introduced to marine waters, a variety of chemical reactions occurs. The dredged material is

under the influence of one set of physicochemical conditions (pH, redox potential, ionic strength, temperature) at the dredging site. These conditions are altered during the dredging process and then again upon entry of the dredged material into the disposal environment. Most commonly, the dredged material is subjected to higher pH, redox potential, and ionic strength, and lower temperature at the dumpsite than at the dredging site, as such materials are generally dredged from low-salinity areas up estuaries and dumped at sites of a more marine nature. One effect of the increased ionic strength is to cause the flocculation of colloidal particles (the so-called "salting out" effect). Upon mixing following the dump, colloidal organic and inorganic material in the dredged material pore waters will aggregate, if the ionic strength of the pore waters is small compared to that of the disposal site water. The aggregates may contain significant quantities of organic and inorganic contaminants, and they may be used as a food source by planktonic and benthic animals. Therefore, the formation of such aggregates constitutes a mechanism whereby contaminants may be transferred from the dredged material into the food chain. However, very little information exists to permit an assessment of the significance of such a pathway close to disposal sites.

The altered physicochemical conditions experienced by the dredged material at the disposal site have significant effects on the equilibria between solid and solution phases of the dredged material and mixing water, and as a consequence, various chemical reactions take place.

Some of these reactions can have the effect of introducing

chemical species to solution, while the reverse (removal of dissolved species) will be the effect of others. The transfers of chemical species between dissolved and solid phases is not instantaneous, but can continue during and after the dispersion and settling of particles to the sediments.

Five different reactions that occur during dispersal of sediments in saline waters are described below:

Ion exchange processes. Sediment particles have many ion exchange sites on their surfaces. The metals bound at these exchange sites are determined by the chemical composition of the aqueous phase surrounding them and the species present. As the chemical composition of the water at a dumpsite is different from the water at the dredging site, ion exchanges take place when the sediment particles are subjected to the new environment. These basically depend upon the relationship between the salinities at the dredging and dumping sites.

Adsorption-desorption reactions. In addition to ion-exchange sites on the surfaces of sediment particles, there are adsorption sites which can bind inorganic species. Exchanges similar to those occurring at ion exchange sites will occur at these binding sites during the disposal of sediments.

Complexation reactions. Organic compounds and metals, particularly transition metals, form complexes with each other, usually in ring compounds termed chelates. The complexes can be of diverse strengths and solubilities according to the nature of the organic compound involved. Some of these complexes may be dissociated, releasing

contaminants of toxicological concern, when sediments and associated pore water are subject to dredging and dumping and alterations in the ambient chemical environment occur. However, very little is known regarding this process.

Redox reactions and precipitation. The altered physicochemical conditions at the disposal site usually include an increase in both the redox potential and the pH. These changes favor the oxidation of sulfide and reduced metal ions and the formation and precipitation of hydroxides. Anoxic dredged material may contain large concentrations of sulfides and reduced metal ions in solution in the pore waters. Oxidation of these is initiated during dredging and transport to the disposal site, and may be completed during the dumping process. The oxidation of iron and manganese is of particular importance, as hydrated oxides of these elements are formed. These are colloidal in nature and tend to adsorb to particulate material; this process leads to the scavenging of metals from solution (see below).

Coprecipitation. Colloidal hydroxide precipitates are, under appropriate conditions, extremely effective scavengers for many of the dissolved trace components of seawater, including several important trace elements. Trace quantities of various elements and organic compounds are adsorbed and occluded in the hydroxide lattice during its precipitation; this phenomenon is termed coprecipitation. Hydrated ferric oxide is a particularly effective coprecipitating agent. Hydrated manganese oxide will similarly coprecipitate many elements and organic compounds.

In view of the diversity of, and complex relationships among, chemical and physical reactions taking place during the initial dispersal of dredged material in the marine environment, it is not surprising that the resulting distribution of chemical contaminants between waters and sediments cannot be predicted at present with confidence. Field studies of the fate of contaminants during San Francisco Bay disposal operations have been carried out (U.S. COE, 1977). The data from these studies are limited by the logistic problems of sampling a transient event using currently available techniques. Laboratory studies of net chemical transfers occurring between sediments and water during dispersal and settling of the sediments in sea water cannot reproduce field conditions. However, these studies may be useful to indicate (qualitatively) the types of processes which may be present in the field. In brief, these include:

- * The initial oxygen demand (first hour) of dredged material after its disposal is significant. If dilution is not rapid and if the ambient water column oxygen concentration is low, the potential exists for the creation of regions of anoxic water at the bottom, which will persist until relieved through mixing and dispersion. In general, mixing rates are high enough to preclude the persistence of anoxia for periods in excess of an hour or more, especially in high-energy environments such as the San Francisco disposal sites.
- * Substantial quantities of ammonium ion are released to solution. The concentration of ammonium ion in the disposal site water may reach toxic levels if dilution is not efficient. Phosphate is not normally released to solution, but can be released from certain sediments

(particularly if anoxic conditions persist).

- * Manganese is released to solution in significant quantities. The behavior of other metals depends upon the physical and chemical conditions of the mixing water and the nature of the dredged sediment. In general, other metals are not released to solution in substantial quantities if the dispersion water remains oxygenated. Some metals (particularly zinc) may actually be removed from the dilution water. These data are consistent with the hydrated ferric oxide precipitation effectively and immediately removing metals released by other chemical reactions. Cadmium appears to be released slowly (but in significant quantities) from dredged material solids after the initial dispersion, if oxygenated conditions persist.
- * Chlorinated insecticides and PCBs are not released to solution when dredged material solids are dispersed in seawater. However, these compounds are preferentially fractionated into the slowly-settling residual suspended particles during deposition. The quantity of the chlorinated compounds in the residual suspended particles increases with increasing concentrations of hydrocarbon contaminants in the original sediments.
- * Significant quantities of organic compounds as yet unidentified are released to solution during the initial dispersion of dredged material.
- * Differential settling of particulates tends to accumulate the more contaminated fractions of the sediments at the sediment-water interface, and to bury the coarse sand or mineral grains more deeply.

C. San Francisco Bay Dredged Material Disposal Sites

General Description

There are three currently designated and actively utilized dredged material aquatic disposal sites in San Francisco Bay. These are at Alcatraz, Carquinez Strait, and San Pablo Bay. The locations of these three sites are shown in Fig. 13. The principal site used to dispose dredged materials is the Alcatraz site. This is a circular area of 609 meters diameter, located immediately south of Alcatraz Island; geographic coordinates for the center of the site are 37 49'17"N and 122 25'23"W. Water depths within the area range from about 12 to 34 meters. Circulation at the site is dominated by tidally-driven oscillatory currents with principal flow directions of east and west.

The Carquinez Strait is a rectangular area (305 x 609 meters), located at the north side of the seaward end of Carquinez Strait, off the south western tip of Mare Island (38 03'50"N, 122 15'55"W). On the edge of the site lies the deep natural channel which has depths ranging from 8 to 17 meters. Current velocities at the site are generally high and are dominated by tidally- oscillating flows during low river flow, but by river flow during periods of high runoff.

The San Pablo Bay site is the least used of the three disposal sites, being devoted almost exclusively to materials dredged from harbors and channels of the northern part of San Pablo Bay. The site is rectangular (457 x 914 meters) and is located in the natural deep channel crossing San Pablo Bay from Carquinez Strait to the Point San Pablo - Point San Pedro narrows (38 00'28"N, 122 24'55"W); water depths at this site are about 12 meters. Currents in the area are normally dominated by

oscillating tidal flows except at high Delta flow rates, when the main flow component is from the northeast to the southwest.

Special Characteristics of San Francisco Bay Sites

The San Francisco Bay dredged material dumping sites differ from the majority of aquatic (especially ocean) disposal sites in the USA in one extremely important fundamental characteristic. Thus, the San Francisco Bay sites are specifically selected because of their high current energy regime. The sites are, therefore, dispersive in nature. Most other such disposal sites around the USA are located in areas where bottom currents are slow, so that material may be accumulated and buried within a mound of accumulating material at the site. This accumulative strategy using low energy sites has been adopted in many instances as a means to ensure that toxic contaminants in the dredged material are buried and thereby removed from contact with the biosphere. At several sites, this strategy has been further developed by using relatively clean material to "cap" or bury more contaminated material placed at a disposal site. The dispersive nature of the San Francisco Bay sites has both advantages and disadvantages. Long term use of these sites, if they are sufficiently dispersive, should not result in shoaling (and the consequent hazard to navigation); thus such sites may be used continuously for an indefinite period. On the other hand, because the dredged material disposed at a dispersive site is subject to dispersion within the water column and surficial sediments (where it is in contact with the biosphere), previously buried contaminants in the dredged material may be rendered biologically available by the dumping and dispersal

process. Since contaminants in dredged material are preferentially concentrated in fine-grained, lower-density particles which are easily resuspended and transported, the use of a dispersive site guarantees that the dredged material will be transported and spread over a wide area, diluting the contaminants and possibly minimizing their potential impact through this dilution. However, this dilution effect may be offset by the greater proportion of contaminants which become biologically available, and the accumulation of toxicants derived from dumped materials in quiescent areas of the system, where particulates settle out. Although the Alcatraz site is highly dispersive, some accumulation of dredged material (or "mounding") has occurred when extremely cohesive, coarse-grained, or rubble-containing material has been disposed (BCDC, 1987). In order to avoid future mounding, the U.S. Corps of Engineers (who retain jurisdiction over all San Francisco Bay open water dredged material disposal) have introduced a requirement that future disposal at Alcatraz will be restricted to dredged materials with densities less than 1.3 grams per cubic centimeter and with sand contents of less than 80%. With some Bay-Delta sediments, the density requirement is met by mixing water with the dredged sediments before disposal, by utilizing appropriate dredging techniques.

For a major portion of the year, the flow of freshwater through San Francisco Bay is limited. In this condition, the movement of water and suspended sediments within the Bay is controlled primarily by oscillating tidal currents and wind-driven mixing. Since tidal currents are strong throughout much of the Bay, and since wind mixing is effective particularly in

shallower areas, dissolved contaminants and suspended particulates with which these contaminants are associated are dispersed very efficiently and widely throughout the Bay. This highly dispersive character of the Bay reduces the potential for accumulation of toxicants close to point sources, or "hot-spots." This high dispersivity has caused San Francisco Bay to have in general fewer, less contaminated hot-spots than other estuaries (e.g. Puget Sound), but higher background concentrations of toxics throughout the Bay sediments and probably the water column.

The high degree of dispersion of contaminants (and dredged material) achieved within San Francisco Bay should not be confused with flushing. High dispersion effectively reduces toxicant concentrations around point source inputs, but also increases the background concentrations of these contaminants throughout the Bay.

Contaminants can only be removed from the San Francisco Bay ecosystem by three physical routes: permanent transport through the Golden Gate to the ocean; permanent burial in accumulating sediments; and permanent removal to upland sites. Organic toxicants can also be removed by chemical or biochemical destruction or decomposition. Of the three physical mechanisms, transport to the ocean may be the dominant process in San Francisco Bay, since there are few areas of continuous sediment deposition. This combination of high dispersion driven by fast tidal currents, poor flushing, and vigorous sediment resuspension and reworking tends to ensure that contaminants introduced in dredged material (or other sources) are not rapidly removed from contact with the Bay biosphere, but are diluted and

distributed throughout the Bay.

The transport of dissolved and suspended materials in and out of the Bay through the Golden Gate is controlled by a complex array of physical transport mechanisms that are poorly quantified. Material moving out of the Golden Gate on a falling tide may be brought back into the Bay on the next rising tide. Conceptually, it should be possible to measure concentrations of dissolved or suspended constituents and current velocity profiles at the Golden Gate, and calculate the mean transport from the Bay- Delta by the difference between flux estimates for outgoing and incoming tides. However, the distribution of concentrations and velocities within the Golden Gate is extremely complex. Therefore, the uncertainties in both the incoming and outgoing flux calculated by direct measurement would be larger than the difference between these estimates, and the potential errors in the resultant calculated mean flux would almost certainly be larger than the flux itself.

The behavior of suspended particulates (from dredging and dumping activities or other sources) during their transport through the Golden Gate is more complex than that of dissolved components, since these particles tend to be deposited during quiescent periods (slack tide) and resuspended as current velocities rise. Since a weak two-layer flow (fresh water flowing out at the surface, more saline water flowing in at depth) exists at the Golden Gate during low river flow, suspended particulates may tend to be preferentially retained in the Bay. Qualitatively, the net effect of these complex mechanisms is that contaminants associated with suspended sediment will not be flushed out of the Bay as fast as dissolved contaminants.

In summary, the complexity of the physical, chemical and hydrological events incorporated in the dredging of bottom sediments at any one location in the Bay-Delta and their transport to and disposal at one of the three disposal sites confounds any attempt at quantitatively understanding contaminant fluxes. Although it is intuitively evident that material dumped at the Carquinez Strait or San Pablo Bay sites is less likely to be transported from the Bay than that disposed at the Alcatraz site, no strict quantitation is defensible. Similarly, there have been no reliable studies of contaminant remobilization rates from dredging and dumping activities in the Bay-Delta.

As a result of this general lack of quantitative information, the impact of dredging and dumping operations on contaminant levels in the estuary can only be estimated by considering the total amounts of material dumped, and the potential for remobilization of contaminants therefrom. The following section employs such a rationale.

D. Estimates of Potential Loadings of Contaminants From Dredging and Dumping

As noted above, no reliable quantitative estimates of the release of contaminants to the Bay-Delta ecosystem from dredging and dumping activities are available. However, it is certain that some proportion of the contaminants present in dredged sediments is remobilized during these activities. The available evidence is sufficient only to suggest that the proportion remobilized is relatively minor compared to the total amounts of contaminants in dredged materials. Estimates vary widely, but are generally considered to range from less than 1% to about

10%; these are thus employed here as lower and upper bounds to the possible release rates for contaminants in the estuary from dredging and dumping processes.

Giari (1982) reports that some 320 million m^3 of material is dredged from the coastal waterways of the USA annually. The amounts dredged in the San Francisco estuary have been estimated to range from about 5 to 10 million m^3 (e.g. Eaton, 1979; U.S. Department of the Navy, 1987). The most recent estimate suggests a figure of just greater than 6 million m^3 (U.S. Department of the Navy, 1987), and this estimate is used as a basis for calculations here.

Several authors have reported data concerning the concentrations of toxicants in sediments of the Bay-Delta (for a more complete review, see Bradford and Luoma, 1980; Phillips, 1987). As discussed above, the degree of enrichment of contaminants in local sediments varies somewhat according to location, but such variation is less marked in the Bay-Delta than in most estuaries, probably because of the large tidal prism and high rates of sediment transport in the Bay-Delta. As material is dredged from many locations in the estuary (and contaminant distributions in local sediments have been insufficiently characterized in either dredged materials themselves or the sites from which they are derived), it is not possible to provide precise estimates of contaminant levels in dredged material. This report thus uses generic estimates of such concentrations, derived from a number of sources (reviewed by Phillips, 1987). The levels of trace elements in Bay-Delta sediments are better documented in general than those of organic contaminants. For estimates of the latter, more recent

publications are preferred (see Chapman et al., 1986; NOAA, 1987f; Baumgartner et al. unpublished manuscript), as these generally include improved quality control procedures and more reliable quantification of parameters.

Table 70 presents data for average contaminant levels in Bay-Delta sediments (based on data considered to be the most reliable currently available), and for calculated possible release rates of such contaminants due to dredging and dumping activities. The latter are calculated based upon: a water content of 75% for dredged material (applied to transform contaminant concentrations quoted by dry weight of sediments to those by wet weight); an annual dumping rate of 6.36 million m³ (U.S. Department of the Navy, 1987), taken as 8.3 million metric tonnes; and potential release rates of 1%, 5% and 10% of the total amounts of contaminants present in the dredged material. It is considered that the state of the current knowledge on the extent of (and factors influencing) contaminant remobilization from dredged/dumped sediment does not permit a more precise estimate to be made of this parameter than that employed herein.

Given these generic assumptions, it is clear from Table 70 that potential release rates of contaminants vary directly according to their average concentrations in Bay Delta sediments. It is fully appreciated that this estimate is crude at best; however, it permits the comparison of potential releases of contaminants from dredging and dumping activities with loadings of the same pollutants from other sources. Such comparative data are further discussed in section III of this report.

Table 70.

Estimates of average concentrations ($\mu\text{g g}^{-1}$ dry weight) of contaminants in Bay Delta sediments, and their potential release by dredging and dumping activities in the Bay-Delta. See text for assumptions employed. Amounts released are in tonnes per year for trace elements but in kilograms per year for organic contaminants.

<u>Contaminant</u>	<u>Average Concentrations in Sediment</u>	<u>Amount Released</u>		
		<u>1%</u>	<u>5%</u>	<u>10%</u>
Silver (Ag)	1.0	0.02	0.10	0.20
Arsenic (As)	10.0	0.2	1.0	2.0
Cadmium (Cd)	1.0	0.02	0.10	0.20
Chromium (Cr)	250.0	5.0	25.0	50.0
Copper (Cu)	50.0	1.0	5.0	10.0
Mercury (Hg)	0.5	0.01	0.05	0.10
Nickel (Ni)	100.0	2.0	10.0	20.0
Lead (Pb)	50.0	1.0	5.0	10.0
Selenium (Se)	2.0	0.04	0.20	0.40
Zinc (Zn)	150.0	3.0	15.0	30.0
PCBs ^a	0.03	0.67	3.3	6.7
EDDT ^a	0.001	0.02	0.1	0.2
PAHs ^a , LMW ^b	0.3	6.7	33.0	67.0
PAHs ^a , HMW ^b	2.0	40.0	200.0	400.0

^aIn kilograms per year

^bLow molecular weight and high molecular weight

6. ATMOSPHERIC DEPOSITION

A. Introduction

This section examines the loading of toxic chemicals into the Bay-Delta due to their deposition from the atmosphere. Through a variety of pathways, including combustion, evaporation, and suspension of dust, toxic substances enter the air in the Bay-Delta region. These materials can then be directly deposited into the waters of the Bay and Delta. Although atmospheric deposition is often assumed to be a small contributor of toxic substances when compared to runoff or point source discharges, this may not always be the case. Webber (1983) concluded that atmospheric deposition of hydrocarbons to Chesapeake Bay is of the same order of magnitude as hydrocarbon discharge from municipal wastewater treatment plants. Atmospheric deposition may supply as much as 90% of the total input of PCBs to Lakes Superior and Michigan (Eisenreich et al., 1981).

The loading of toxic substances to the Bay-Delta by atmospheric deposition has been estimated only twice previously and only for a few trace metals (SFBRWQCB, 1975; Eaton, 1979). Although atmospheric deposition was mentioned by Riseborough et al. (1978) as a source of toxic substances worth exploring, existing data were considered too unreliable for use in developing an estimate. Today there are still very few data on the atmospheric deposition of toxic chemicals in the Bay-Delta region. A major reason for this is the difficulty of measuring dry deposition of these materials; the uncertainty of loading estimates based on the measurements cannot be overemphasized.

This section: (1) presents a brief discussion of the nature of toxic contaminants in the atmosphere and their movement to

aquatic environments; (2) reviews existing data available to estimate loads; and (3) uses data from other regions of the country to derive preliminary estimates for the loading of some contaminants to the estuary.

B. Toxic Substances in the Atmosphere

Toxic substances in the atmosphere exist in the vapor phase, as vapors adsorbed on the surface of particles and as aerosols. Although trace metals have been long considered to exist in the atmosphere almost exclusively as aerosols, there is a growing body of evidence to suggest that this may not be the case, at least for certain elements. Harrison and Laxen (1978), for example, have measured significant concentrations of tetraalkyl lead at Morecombe Bay, United Kingdom, in patterns that suggest a source distinct from neighboring urban areas. It would appear that the source is bioalkylation of lead by bacteria in intertidal mudflats.

Organic substances are found in the atmosphere in the vapor phase (both free and adsorbed to particulates) and as aerosols. Factors influencing the partitioning between vapor and particulate phases include the vapor pressure of the substance and the size, surface area, and organic content of the particulates. The size of the particulates in question ranges from sub-micron levels to greater than 5 microns, although particulates in the latter class tend to settle rather quickly and are thus only important components of deposition close to sources. While some investigators have found up to 70% of the mass of organic particulates in the sub-micron fraction, high molecular weight species are detected in significant quantities associated with particles greater than one micron in diameter

(Eisenreich et al., 1981).

The physical state of toxic substances in the atmosphere exerts a profound influence upon their transport into aquatic environments. Atmospheric contaminants can enter aquatic environments in wet and dry deposition. Although gaseous molecules will diffuse into raindrops, this process is thought to be relatively unimportant compared to the removal of atmospheric particulates by rainfall (Eisenreich et al., 1981). Standardized methods for collection and analysis of precipitation allow for accurate determination of contaminant concentrations (see, for example, Galloway et al., 1982).

By contrast, measuring the movement of gases and particulate contaminants from the atmosphere to aquatic ecosystems by dry deposition is a much more difficult task. Contaminants in the gaseous phase will diffuse across the air-water interface until a chemical equilibrium is established between atmospheric and dissolved concentrations of the contaminant, and the equilibrium concentration in water can be calculated from atmospheric levels using Henry's Law. In practice, however, it is extremely difficult to measure dissolved concentrations of trace organics with the accuracy necessary to determine whether equilibrium concentrations have been achieved. This effort is further complicated by the constant removal of substances from the dissolved state in the aquatic environment.

The dry deposition of particles to aquatic environments is no less difficult to determine, despite extensive research into the topic in an effort to quantify the deposition of acidic particulates to ecosystems (Kerr, 1981). The mechanism of particle deposition is influenced by particle size (diameter) and

includes Brownian diffusion ($<0.3 \mu\text{m}$), interception-impaction ($0.5\text{--}5 \mu\text{m}$), and gravitational settling ($>5 \mu\text{m}$). In practice, particle fluxes can be estimated as the product of atmospheric concentration and deposition velocity, but the latter term is influenced by the deposition surface, particle size distribution, and wind speed. Attempts to measure deposition velocity in the field are often confounded by gaseous diffusion and can easily vary by a factor of six (Eisenreich et al., 1981).

Atmospheric deposition of contaminants is often estimated by measuring bulk deposition (the combination of wet and dry deposition to a collector). A prewashed container is placed at a site, often for a month at a time, and the contents assumed to represent wet and dry deposition of contaminants. This method is thought to underestimate total deposition to aquatic ecosystems by factors between 2 to 10 through inadequately measuring dry deposition (Eisenreich, 1980). This is due in part to the effects of different surfaces on deposition, and also to the influence of particle size and micro-meteorology (Eisenreich et al., 1981).

C. Loading Estimates

Estimates of the flux of toxic contaminants into the Bay-Delta ecosystem due to atmospheric deposition, which are the basic component of loading calculations, can thus be determined in two ways. One method is to use measurements of the concentration of various particulates in the atmosphere of the region in combination with a reasonable estimate of deposition velocities to determine the flux from dry deposition. These are then added to wet deposition measurements to determine total flux. This method is subject to the uncertainty of the values

used in the calculation, which can be significant. A second method is to use direct measurements of wet and dry deposition, such as bulk deposition monitoring, to determine contaminant flux to the estuary. As mentioned above, however, bulk deposition monitoring can significantly underestimate dry deposition.

In both instances, the flux estimate is multiplied by the water surface area of the Bay-Delta to estimate loads, as atmospheric deposition to the rest of the catchment is accounted for in estimates of runoff and river inputs. Both methods need to be supplemented by a calculation of the molecular diffusion of gaseous contaminants, which is very important for certain chemical species. Eisenreich et al. (1981) point out that, theoretically, 90% of the atmospheric burden of PCBs should be in the vapor phase, and field measurements basically confirm this calculation. Despite the potential for other substances to diffuse into the aquatic environment, even Eisenreich et al. (1981) simplify their loading calculations by combining gaseous and particulate concentrations of all substances except PCBs. Part of the reason for doing this is the difficulty in actually measuring the particulate and gaseous fractions for different organic substances in the atmosphere.

Eaton (1979) estimated the loading of zinc, copper, and nickel to the estuary using a method of approximation that is claimed to be roughly equivalent to direct deposition measurements. He utilized the concentration data of John et al. (1973), taken for a single day from nine sites around San Francisco Bay, and assumed that this atmospheric burden to a height of five kilometers is deposited on the Bay by each of 40 storms annually (Table 71). Although this procedure is driven by

Table 71. Previous Estimates of Atmospheric Deposition of Toxic Substances to San Francisco Bay. All values in metric tons yr⁻¹.

	Eaton (1979)	SFBRWQCB (1975) ^c
Copper	10	12.2
Nickel	1	2.5 ^b
Zinc	30	63 ^b
Mercury		0.24 ^b
Lead		282 ^a
DDT Compounds		0.32 ^a
PCBs		0.32 ^a

a: wet and dry deposition

b: wet deposition only

c: Table 15-15 in SFBRWQCB (1975)

wet deposition, the loading estimate is assumed to represent total deposition. (Table 71 also contains deposition estimates of the Regional Water Quality Control Board [SFBRWQCB, 1975]. Unfortunately, the methods used to calculate these estimates are not described.)

It would be most advantageous to obtain measurements of direct deposition to determine how well this approximation, which the author (Eaton, 1979) acknowledges as somewhat arbitrary, actually matches deposition in the Bay Area. Of course, given the uncertainty of direct deposition measurements, even such verification would still leave much unresolved uncertainty. In addition, the data of John et al. (1973) vary up to a factor of 20 between stations for zinc, indicating that additional sampling is advisable to establish appropriate mean values to use in such calculations. It also should be noted that, while cited as such by Eaton (1979), the data of John et al. (1973) contain no measurement of nickel concentrations in the atmosphere of the Bay Area.

Estimates of the loading of hydrocarbons from the atmosphere have been made for the Hudson Raritan estuary in New York (Connell, 1982), Chesapeake Bay (Webber, 1983), and the Great Lakes (Eisenreich et al., 1981). Although the uncertainties are recognized, this report applies the deposition rates from these studies to provide a preliminary estimate for the Bay-Delta region for hydrocarbons (Table 72) and trace metals (Table 73). These estimates assume a surface area for the Bay of $1,240 \text{ km}^2$ (Conomos et al., 1985), and the flux for the hydrocarbon species in the Great Lakes as derived from Table 7 of Eisenreich et al.

Table 72. Preliminary Estimates for Atmospheric Depositions of Hydrocarbons to San Francisco Bay. Bay Surface Area = 1,240 km² (Conomos et al., 1985).

Source/Site	Substance	Flux (kg km ⁻² yr ⁻¹)	SF Bay Loading (tonnes yr ⁻¹)
Webber (1983) Chesapeake Bay	total hydrocarbons	36.5 ^a	45
Connell (1982) Hudson Raritan Estuary	Petroleum hydrocarbons	1.7 ^b	2.1
Eisenreich <u>et al.</u> (1981) Great Lakes	total PAHs	0.65-3.9	0.80-4.8
	PCBs	0.1-0.7	0.12-0.87

a: average of rural and urban sites (100 µg m⁻² d⁻¹)

b: derived from 6x10⁵ tonnes yr⁻¹ of petroleum hydrocarbons to world's oceans (NAS, 1975)

Table 73. Preliminary Estimates of Atmospheric Deposition of Trace Metals to San Francisco Bay Through Application of Fluxes for Lake Michigan. Flux values in $\text{kg km}^{-2} \text{yr}^{-1}$, loads in tonnes yr^{-1} . Calculations assume surface area of Lake Michigan = $58,000 \text{ km}^2$, with area of North and South Basins equaling one-half this total. Source: Eisenreich (1980) Table II. SF Bay surface = $1,240 \text{ km}^2$ (Conomos et al., 1985)

	LOW ^a		HIGH ^b	
	Flux	Load	Flux	Load
Cadmium	0.11	0.14	.28	.35
Copper	1.5	1.9	2.5	3.1
Lead	4.8	6.0	17.2	21.3
Zinc	12.8	15.9	25.5	31.6

a: Calculated using data from the north (rural) basin of Lake Michigan

b: Calculated using data from the south (urban) basin of Lake Michigan

(1981) by assuming a surface area for the Great Lakes of 246,000 km² (Nalco Chemical Company, 1979). It is assumed that the water surface area of the Delta is sufficiently small relative to the Bay to be safely disregarded.

The estimates derived in Table 72 are, as expected, quite variable. Connell (1982) utilized a deposition estimate developed by the National Academy of Science (NAS) of 600,000 tonnes yr⁻¹ of petroleum hydrocarbons to the world's oceans (NAS, 1975) to derive a flux of 1.7 kg km⁻² yr⁻¹. The loading estimate of 2.1 tonnes yr⁻¹ generated utilizing this flux is substantially less than the 45 tonnes yr⁻¹ estimated using the data of Webber (1983). Contributing to this difference is the fact that a global average deposition rate would undoubtedly underestimate the deposition in urbanized estuaries. In addition, the total hydrocarbon flux of Webber (1983) includes biogenic hydrocarbons, which have been shown to be a significant fraction of hydrocarbon deposition in several studies (Wakeham, 1977; Matsumoto and Hanya, 1980; Webber, 1983). It might seem reasonable to assume that the actual input of toxic organic substances to the San Francisco Bay-Delta by atmospheric deposition is within the range defined by those two estimates (2.1-45 tonnes yr⁻¹). Given the uncertainty in dry deposition estimates, however, it is possible that the high end of this range could still be underestimated.

The estimates of PCBs and PAHs in atmospheric deposition derived for this report from Eisenreich et al. (1981) are worthy of comment. The estimated range for PCB loading was derived using the range for PCB fluxes in urban areas of the Great Lakes region provided by the authors (0.1-0.7 kg km⁻² yr⁻¹). (It should be noted that, unlike the other estimates in Table 72, the

figure for PCBs includes gaseous diffusion of PCBs from the atmosphere into the water column.) This number is of the same order of magnitude as the estimate of SFBRWQCB (1975), which appears in Table 71. The estimated range for mass loads of PAHs to the estuary from atmospheric deposition was obtained by first calculating the flux for PAHs used by Eisenreich et al. (1981). The authors state that this flux, $1.96 \text{ kg km}^{-2} \text{ yr}^{-1}$, was derived by selecting a deposition velocity of 0.3 cm sec^{-1} from a possible range of 0.1 to 0.6 cm sec^{-1} . The range for loading in Table 72 was thus derived by recalculating the flux of $1.96 \text{ kg km}^{-2} \text{ yr}^{-1}$ using the above range for deposition velocities. The estimate of 0.8 - $4.8 \text{ tonnes yr}^{-1}$ of PAHs is relatively large given the magnitude of other sources of these substances to the estuary. This suggests, when considered with the estimate of 5 tonnes yr^{-1} of PAHs in urban runoff (Section II.2 above), that atmospheric deposition as a source of PAHs to the estuary merits further investigation. The estimates for PAH mass loading from both of these sources, however, are highly uncertain.

Table 73 presents estimates for atmospheric deposition of trace metals to San Francisco Bay using fluxes derived from the work of Eisenreich (1980) on Lake Michigan. A range is presented based upon data from the rural northern basin and the more urbanized southern basin of the Lake. It is most interesting that the estimates so derived for deposition of copper and zinc to San Francisco Bay are rather less than the approximations of Eaton (1979), particularly for copper (Table 71). The loading estimate for lead derived from the Lake Michigan data is much less than the previous estimate (SFBRWQCB, 1975). As the data

from Lake Michigan are from 1975-1976, it would be expected that these data would give rise to an overestimation of current lead deposition, given the reduction in the lead content of gasoline over the last decade.

The loading estimates for copper, cadmium, zinc, and lead (Table 73) and total hydrocarbons (Table 72) are certainly smaller than the estimated loads of these contaminants from point sources, runoff, and rivers discussed in Sections 1 to 4 above. Although there is significant uncertainty associated with many of these loading estimates, it seems reasonable to assume that atmospheric deposition is a relatively unimportant source of total hydrocarbons and trace metals to the estuary.

The uncertainty of these estimates for atmospheric deposition of toxic contaminants to San Francisco Bay cannot however, be overemphasized. Deriving data from the respected work of Eisenreich (1980) and Eisenreich et al. (1981) in the Great Lakes area is of interest in judging the potential magnitude of this source in the Bay Area. Due to the uncertainty in these calculations, however, such data must be considered extremely preliminary. The difference in climates between the Bay-Delta region and the Great Lakes means that the proportion of contaminant loads delivered in wet and dry deposition will vary between the two regions. Given the difficulty of estimating dry deposition, utilizing deposition estimates from the Great Lakes could lead to inaccurate data for the Bay-Delta region. Differences in regional fuel sources and the coastal location of the Bay-Delta could also lead to differences in contaminant concentrations in the atmosphere.

D. Conclusions

Toxic chemicals are present in the atmosphere in the Bay-Delta region and reach the waters of the estuary in both wet and dry deposition. As atmospheric concentrations vary considerably and dry deposition is extremely difficult to measure accurately, a significant degree of uncertainty is associated with estimates of the loading of toxic substances to the estuary by atmospheric deposition.

Loading estimates for San Francisco Bay have been made in the past for a few toxic substances using relatively arbitrary assumptions regarding deposition velocities. These estimates indicate that atmospheric deposition is a relatively small source of toxic contaminants to the Bay-Delta ecosystem. As a comparison to previous loading estimates, a new range of values for atmospheric loading was generated for this report using fluxes for toxic contaminants derived from extensive research in the Great Lakes region. These new estimates are somewhat lower than the earlier values, but differences in climate and possibly atmospheric composition in the two regions limit the accuracy of estimates for San Francisco Bay based upon data from the Great Lakes. These new estimates reinforce the concept that atmospheric deposition is a relatively unimportant source of toxic substances to the estuary, with the possible exception of PAHs and PCBs.

7. SPILLS

A. Introduction

This section reviews spills as a source of contaminants to the San Francisco Bay-Delta. Included herein are only spills of toxic substances from vessels or shoreline facilities that directly enter the estuary, as spills at other land-based sites within the catchment are covered in this report under urban and nonurban runoff and riverine inputs. Accidental spills, particularly of petroleum hydrocarbons, are often referred to as an important source of toxicants to marine and estuarine waters. This is due in part to the great public attention that has been focused upon large spills of crude oil such as the Ixtoc oil well blowout in Mexico (520 million liters) or the break up of the tanker Amoco Cadiz (250 million liters) off the coast of France (Herz and Kopec, 1985).

While no spills of this magnitude have occurred into the Bay-Delta, there have been two major spills in the region. On January 18, 1971, a collision of two tankers at the entrance to the Bay spilled 3.18 million liters of bunker C fuel oil. Most of this oil was moved out of the Bay by tides and currents, and it spread along the coast from Point Reyes southward almost to Point Ano Nuevo (Smail et al., 1972). More recently, on October 31, 1984, the tanker Puerto Rican exploded and caught fire 13.7 kilometers west of the Golden Gate Bridge. Although the fire was controlled, the vessel broke in two after three days, while under tow in the waters of the Point Reyes-Farallone Islands Marine Sanctuary. The stern portion of the vessel sank, releasing between 3.9 and 5.6 million liters of refined petroleum products and bunker C fuel oil (Herz and Kopec, 1985).

B. Data Availability

The definitive source of data on spills in the San Francisco Bay-Delta is the United States Coast Guard (USCG). The USCG compiles data on spills from around the nation through its Pollution Incident Reporting System, and this computerized database is available for review. Searches of the database can be made by latitude and longitude, water body into which material was spilled, or other identifying characteristics.

All spills into the Bay that are identified by the USCG or brought to their attention are written up by the 12th District office in Alameda and transmitted to Washington for inclusion in the database. Data are collected on spills and potential spills of all substances including inorganic chemicals, crude oil, refined petroleum products, animal and plant oils, and other miscellaneous organic liquids. Unfortunately, for many of the spills in the database, the substance involved is undefined, and the USCG cannot be sure how many spills go undetected. It is extremely unlikely, however, that the USCG would be unaware of a spill of any significant size.

At least two reviews of oil spills in the Bay-Delta have been conducted in the past using data from the USCG. Whipple et al. (1983) and Lawrence Berkeley Laboratory (LBL, 1981) summarized data on spills in the Bay-Delta during the period 1978-1980. As LBL (1981) studied only the northern reach of the estuary, their data will not be summarized in this report. Whipple et al. (1983) reported the USCG spill data for five sections of the estuary: the lower Bay (South of the San Mateo Bridge), the South Bay (Hunters Point to the San Mateo Bridge), Central Bay (from near Hunters Point to near Point Richmond), San Pablo Bay (from Point

Richmond to Carquinez Strait), and the West Delta (from Carquinez Strait into the Central Delta, to the mouth of the Mokelumne River).

The data indicate that oil and chemical spills in the estuary vary significantly among years and segments (Table 74). This would be expected, as the total spilled in any given region or year can easily be dominated by a few large events. This is reflected in the annual average volume per spill in each segment, as calculated by Whipple et al. (1983). For example, in the Delta region the average volume per spill in 1978 was 3,776 liters, but was only 202 liters in 1979.

It is not clear if Whipple et al. (1983) removed from the USCG database the many potential spills that did not actually deliver spilled material to the estuary (see below). In addition, the current review of the database raises serious questions about the quality assurance procedures in force; thus, the data used by Whipple et al. (1983) from the USCG may have been inaccurate.

C. Findings

As in this report loads were calculated for the years 1984-1986 when practical, a new search of the USCG database was conducted for these years for the entire estuary, including the Delta region from Sacramento on the north to Vernalis on the south, and the region west of the Golden Gate (as spills in this area can enter the estuary). Many spills are included in the USCG database that did not result in release of materials to estuarine waters, and these values were removed prior to summarizing the data. In addition, many spills of "undefined" or "not elsewhere specified" materials are listed. The vast

Table 74. Oil and Chemical spills in San Francisco Bay for 1978-1980. All values in liters. Source: Whipple et al. (1983).

Bay-Delta Segment ^a	Volume Spilled		
	<u>1978</u>	<u>1979</u>	<u>1980</u>
Lower Bay	5,712	19,782	4,770
South Bay	8,491	9,740	20,018
Central Bay	31,839	34,898	147,645
San Pablo Bay	6,495	165,140	135,302
West Delta	117,058	6,858	166,449
Total	169,595	236,418	447,185

^a See text for explanation of segments

majority of materials spilled into the Bay are petroleum hydrocarbons, and the totals for petroleum hydrocarbons and undefined materials are displayed in Table 75.

These data indicate that the loading (by volume) of petroleum hydrocarbons into the estuary due to spills varies between years by 50-100%, depending upon the identity of undefined substances. These latter compounds can comprise a significant fraction of the total material spilled in a single year (e.g. 58% in 1984). To calculate a mass loading of petroleum hydrocarbons to the Bay, assumptions must be made regarding the density of spilled materials. The densities of gasoline, kerosene (The Chemical Rubber Company 1971, their table F-3), and crude oil (Harte 1985, his Appendix, Table VII-4) are approximately 0.6, 0.8, and 0.9 kg L⁻¹, respectively. If an average density of 0.8 kg L⁻¹ is assumed for petroleum hydrocarbons spilled into the Bay-Delta, the mass loading estimates presented in Table 76 are obtained. It is not possible to estimate a mass loading for the undefined substances, as the densities of these materials are unknown.

There are significant problems, however, with the data from the USCG on spills to the estuary. There appear to have been no quality assurance procedures for checking the accuracy of data input to the database before October, 1985. Consequently, specific spill events are reported in an erroneous fashion that could lead to serious misinterpretation of the USCG database. On at least two occasions in the current study, "potential" spills were included in the data obtained from the Coast Guard as actual spills to the estuary. These potential spills can be very large, thus influencing any summary data.

Table 75. Spills of Petroleum Hydrocarbons and other Undefined Substances in the Bay Delta during 1984-1986. All values in thousands of liters. Source: USCG (1987).

Year	Total Petroleum Hydrocarbons	Undefined Substances ^a
1984	134.3 ^b	77.8
1985	126.4 ^c	28.6
1986	90.9	10.4
Total	352	117

^a Sum of USCG categories "undefined" and "not elsewhere specified".

^b Listed spill of 3.2 million liters removed as this event was a "potential" spill.

^c Listed spill of 151,416 liters removed as this event was a "potential" spill.

Table 76. Approximate Mass Loading of Petroleum Hydrocarbons to the San Francisco Bay-Delta from spills in 1984-1986. Values calculated from volumes listed in Table 75, assuming an average density of 0.8 kg L^{-1} .

Year	Mass Load of Petroleum Hydrocarbons (Tonnes yr^{-1})
1984	107
1985	101
1986	72.7

For example, on May 2, 1984, a tanker-barge carrying 3.2 million liters of jet fuel ran aground in Guadalupe Slough. Although this vessel was refloated without the loss of cargo, this event (USCG case number MP84900874) was listed as a spill in the data obtained for this study. Similarly, on April 2, 1985, about 150,000 liters of aviation gasoline were reported missing from a storage tank on Treasure Island. As this material may have leaked from the tank into the Bay, the local USCG district reported this as a potential spill. (It is possible the material was reported missing due to a reading error when checking the level of the storage tank.) This event was also erroneously included in the database for the current study (with the month listed as March instead of April). As it was not possible to review all of the data received from the USCG on a case by case basis, the mass loadings estimated in Table 76 must be considered preliminary. This is especially the case as the volume of potential spills is very large; the tanker-barge incident described above exceeds the three-year totals in Table 75 by a factor of almost ten.

It should be noted that in October, 1985, the USCG changed its method of collecting, reviewing, and entering data into their system in an effort to reduce errors of this kind. Rather than having information coded by hand and then sent to another office for keypunching, information is now entered directly into a computer and reviewed in hard copy prior to transfer to the central database (Lt. M. Moore, personal communication). This should improve the quality of the database, and may also indicate that the data reported here for 1986 are more reliable than information from earlier years.

8. HAZARDOUS WASTE SITES

This section summarizes the current state of knowledge concerning contaminant loadings to the estuary from hazardous waste sites. Loadings to the Bay-Delta from this source category are poorly understood, and have not been investigated in detail to date. Although it is likely that overall loadings from this source are minor relative to the other categories discussed in this report, contaminated runoff and leachates from such sites may be significant inputs to local environments. Furthermore, hazardous waste sites often contain contaminants (such as organochlorines) which bioaccumulate, are extremely persistent in the environment, or are toxic at very low concentrations. As existing data are not sufficient to allow the estimation of mass loading from this source category, this discussion only defines their potential significance.

Many sites in the Bay-Delta region are known to be contaminated with a broad variety of toxic substances. The Department of Health Services (DHS) regulates cleanup activities at hazardous waste sites throughout California. DHS (1987) summarizes the history of contamination and budgets for cleanup at 356 sites in California. More than 100 of these are located in the Bay-Delta region, with many situated along the margins of the estuary. Migration to the estuary of contaminated surface or groundwater is noted as a proven or potential concern in approximately 40 of these sites. Contaminated waters may enter the estuary directly, or may discharge into creeks which empty into the Bay-Delta.

Trace elements are common contaminants at sites listed in DHS (1987), released as waste products from various industrial activities. Pesticides (including DDT and its metabolites, and other chlorinated organics) are present at many locations where agricultural chemicals were manufactured or stored. PCBs are found at several sites where the manufacture, repair, or salvage of transformers and other electrical power equipment occurred. PAHs, MAHs, and other categories of organics are also present at many sites. Extremely toxic compounds such as dioxin and ethylene dibromide are present at several locations.

The Regional Water Quality Control Boards also regulate hazardous waste sites, in cases where the quality of waters is threatened. The SFBRWQCB lists hundreds of cases throughout the Bay Area which are being investigated. Some of these cases are partially regulated under the NPDES program and were discussed in the subsection on groundwater cleanup effluents in Section II.1 above. No compilation of background information on sites regulated by the SFBRWQCB was available for this review, and production of such a compilation is beyond the scope of this report.

Only a few cases exist where the movement of contaminants from hazardous waste sites directly to the estuary has been investigated sufficiently to document their transport in even a qualitative sense. Information on many cases is on file at the SFBRWQCB. Four of these cases are reviewed below to serve as examples of situations where hazardous waste sites are thought to contribute toxicant loadings to the Bay-Delta. These four cases

are representative of the best information available on any individual sites. In most other cases, the issue of transport to the estuary is not addressed in any detail.

Selby Slag Site

This site lies on the shoreline of Contra Costa County at the western end of the Carquinez Strait. Slag is a waste residue from smelting operations, and was deposited at this location from 1886 through 1970 (IT Corporation, 1985). The slag covers 66 acres of shoreline and marsh and is approximately 3 to 13 meters thick. This slag contains high concentrations of trace elements, including arsenic, cadmium, chromium, lead, and zinc.

One of the few attempts at quantifying mass loading from a hazardous waste site was performed in this case (IT Corporation, 1985). This example demonstrates the complex nature of contaminant movement from such sites. The first component of a mass loading determination is characterization of water movement. A water balance for the site was formulated, which required measurement of volumes of rainfall, evaporation, surface runoff during storm events, groundwater movement towards the Bay, and the influence of tidal fluctuations. The primary flow off the site, accounting for 95% of the total water budget, was base flow seeping towards the Bay. Infiltration of rainwater accounted for an average of 5% of the total budget. Average groundwater flow from the site was $2,600 \text{ L d}^{-1}$.

The highest dissolved trace element concentrations in monitoring wells were found for arsenic, and a mass load was estimated for this element based on a mean concentration and average flow. The authors erroneously reported a loading of 3.5

kg d⁻¹ (which would be quite significant if it were valid); the actual loading based on their data would be 0.0035 kg d⁻¹. The actual loading is small compared to overall inputs of the element to the estuary.

Point Isabel

Another shoreline site at Point Isabel in Contra Costa County was shown to be a source of trace elements to the local estuarine environment (Levine Fricke, 1985). Placement of fill material on approximately 20 acres of tidal marsh occurred in the late 1960s. During this activity large quantities of crushed battery casings were dumped without the knowledge or consent of the landowners. The battery casings were a source of trace elements, particularly lead and zinc, to the local environment. Although this site was cleaned up in 1986, it serves as an example of the types of contamination and transport that can occur.

An investigation of the site (Levine Fricke, 1985) examined groundwater flow and quality and trace element concentrations in sediment and shellfish. Groundwater samples were collected from nine wells on two dates for analysis of lead and zinc. Dissolved lead concentrations were above detection limits in only two wells on just one of the sampling dates, with a maximum of 39 µg L⁻¹. Based on this information the authors concluded that groundwater transport was insignificant, and suggested that sediment transport was the dominant mechanism of lead movement to the estuary. Zinc levels in the groundwater were higher, and concentrations in offshore water samples averaged approximately 10 µg L⁻¹. Apparently, zinc was moving off the site in

groundwater. Offshore sediments and shellfish in Point Isabel Cove and Hoffman Channel exhibited elevated concentrations of both lead and zinc.

Travis Air Force Base

Travis Air Force Base occupies 5000 acres in Solano County, north of Suisun Bay (Weston Inc., 1986). Military operations have resulted in the development of a number of areas suspected of releasing toxic contaminants to the environment.

Weston Inc. (1986) describes an investigation into contamination at several areas on the property. Groundwater, soil, surface water and storm drains, and sediments from creeks receiving flows from the facility were all sampled at numerous locations. Toxic contaminants analyzed included volatile organics, petroleum hydrocarbons, trace elements, pesticides, and herbicides. Groundwater and surface water hydrology were also evaluated. Union Creek was found to contain sediments with elevated levels of petroleum hydrocarbons and volatile organics (a maximum of 3.4 mg kg^{-1} of ethylbenzene). Volatile organics were detected at elevated concentrations in storm drains and Union Creek waters. The shallow aquifer beneath the property was contaminated with volatile organics and pesticides, and was thought to be contributing to contamination of Union Creek. Although samples were only analyzed on at most two occasions, contaminant levels were consistently elevated at most of the different locations tested. In summary, the data suggested that several toxic contaminants were probably being transported from the Base into local surface waters, which flow into the estuary.

Concord Naval Weapons Station

The final example quoted here concerns the Naval Weapons Station on the south shore of Suisun Bay. The Station covers nearly 13,000 acres, including extensive areas of tidal marsh, which have been contaminated with several trace elements. A very thorough study of contaminant levels and mobility was performed by the Army Corps of Engineers Waterways Experiment Station (Lee et al., 1986).

Extensive analysis of both abiotic and biotic components of the contaminated marsh was performed (Lee et al., 1986). Major pathways of trace metal transport considered included soil, water, air, and biotic uptake. Soils on the site were found to exhibit elevated arsenic, cadmium, lead, selenium, zinc, and copper concentrations. An evaluation of the hydrology of the area indicated that substantial movement of contaminants from the site occurred during storm events and high tides. Sediments deposited in the marsh are gradually distributed into Suisun Bay by tidal and wave action. Clam analyses indicated that lead, cadmium, and zinc were moving into local surface waters.

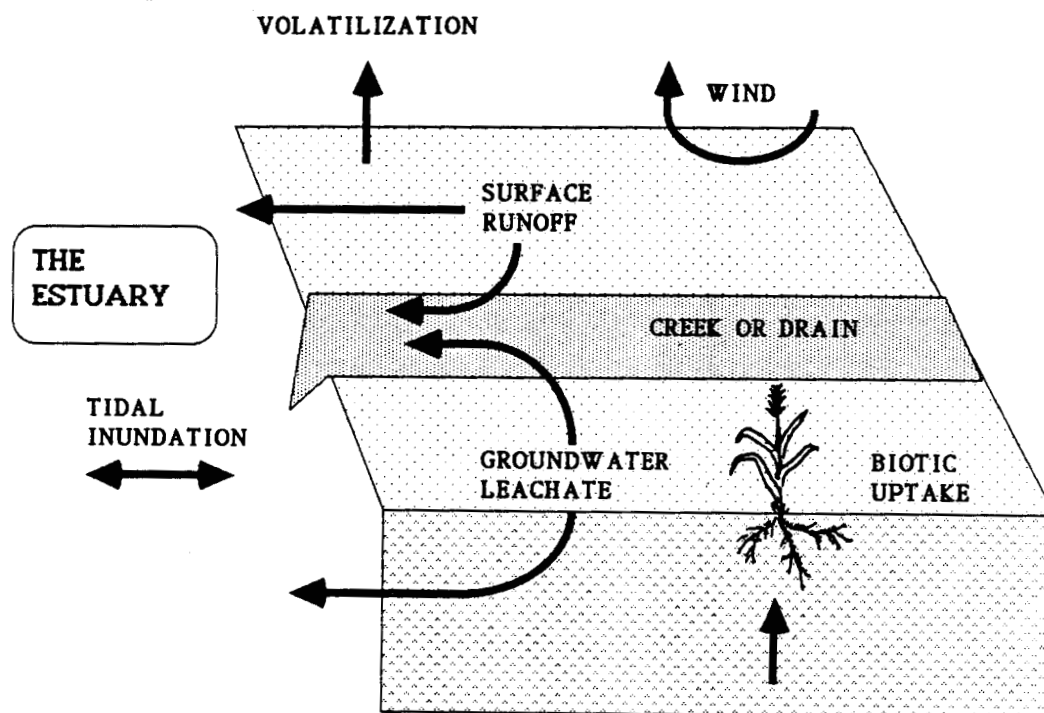
Lee et al. (1986) provided a model that describes basic pathways for contaminant transport from the contaminated site. An adaptation of their model is shown in Figure 14. High flows during storm events can lead to the movement of contaminants bound to soil particles. Particle-associated substances then gradually reach the marsh and are dispersed by tidal and wave action. Biological uptake, volatilization, and wind erosion are other mechanisms by which contaminants may ultimately be transported to the estuary.

The model of Lee et al. (1986) has been adapted in Figure 14 to apply to hazardous waste sites around the estuary in general. Water that infiltrates the soil on the site may transport dissolved forms into ground water. Although Lee et al. (1986) do not discuss groundwater movement off the site, this may be a significant transport pathway in sites near the estuary or adjacent to creeks that empty into the estuary. Base flows may carry contaminants directly to the estuary (e.g. Selby Slag Site), and groundwater discharges to creeks may also transport substances that eventually reach the Bay-Delta (e.g. Travis Air Force Base).

Summary

These four examples demonstrate that hazardous waste sites can be significant sources of contaminant loadings to the Bay-Delta. Such loadings are difficult to quantify in most cases because of the many routes by which transport may occur. Although loads from such sources are probably minor compared to other categories of inputs, they may affect local populations in the estuary. A potential exists for many persistent and/or bioaccumulated toxic substances to enter the estuary from at least some of the hundreds of hazardous waste sites in the Bay-Delta region. Both surface water and groundwater transport of contaminants from these sites are complex and difficult to accurately quantify. Where a site is suspected to be a source of contamination, the most cost-effective means of determining whether loads are entering the estuary may be the monitoring of contaminants in biota or sediment in the local area.

Figure 14. Pathways of contaminant transport from hazardous waste sites to the estuary. Adapted from Lee et al. (1986).



III. MASS LOADINGS OF TOXIC CONTAMINANTS TO THE BAY-DELTA

A. Introduction

This section summarizes and compares the mass loading from each of the major quantified sources of toxic contaminants to the estuary. These sources are point discharges, urban runoff, nonurban runoff, riverine inputs, dredging and dredged material disposal, atmospheric deposition, and spills. Contaminant sources not fully reviewed or quantified in this report include leaching of landfills and hazardous waste sites, vessel wastes, and biotic remobilization of contaminants from sediments. For a discussion of the methods and data used to derive mass loading estimates, the reader is referred to section II. A range of mass loadings is presented for each contaminant by source, and this is followed by conclusions and recommendations arising from the present studies.

Ranges of mass loading are presented here (rather than means or best estimates) due to the significant degree of uncertainty associated with any estimate for the loading of contaminants to the estuary. It is vital that any discussion of mass loading reflect this uncertainty, which has several distinct origins. Some of the mass loading estimates have been produced utilizing average contaminant concentrations from monitoring in the Bay-Delta region or other parts of the country, and sampled concentrations are often below the analytical detection limit (BDL). Treatment of these data points will affect the calculation of average concentrations, particularly if BDL values are a large fraction of the dataset. There is no standard procedure for mathematically incorporating these values; some investigators set BDL values equal to the detection limit, while

others assume these values to be equal to zero. In this report, two sets of average concentrations are calculated by alternately setting BDL values equal to the detection limit, and to zero. The resulting averages are employed as ranges (or for calculating ranges) of mass loading estimates.

An additional source of uncertainty is the fact that many parameters used to estimate mass loads from non-point sources are highly variable. These parameters (such as runoff coefficients, soil moisture conditions, or atmospheric particulate deposition velocities) are often highly site-specific, yet are poorly quantified in the Bay-Delta region at present. As a consequence, it is most appropriate to utilize a reasonable range of variation for each of these parameters to generate minimum and maximum estimates for mass loadings from these sources.

For nonurban runoff, a further source of uncertainty is incorporated in the model used by NOAA (1987c) to generate mass loading estimates. This model employs 29 separate input parameters that are utilized in many nonlinear algorithms to predict sediment yield from nonurban lands, but the model has yet to be subjected to a rigorous sensitivity analysis. It is thus not clear how the uncertainty in the input parameters influences the predictions of the model, introducing a real (yet currently non-quantifiable) range of uncertainty in predicted mass loadings from nonurban runoff.

The data presented here for mass loadings of contaminants to the Bay-Delta from riverine inputs also merit discussion. As stated in Section II.4 of the report, these estimates are derived from water quality monitoring data, principally at Sacramento and Vernalis. Certain inconsistencies in the results from these

water quality monitoring programs affect the final estimates as shown in Figs. 15 to 24 below. Thus, monitoring data for the San Joaquin River include estimates of both metals in solution and total metals (those in solution and suspension). However, in all cases but one, data for the Sacramento River represent only elements in solution, as total metals are not measured in the monitoring program for this river. The sole exception is copper; both soluble and total amounts of this element are available for the Sacramento River samples.

Where estimates for total metals are available, these were employed to calculate the mass emissions shown in Figs. 15 to 24. The loading shown for copper in Fig. 18 thus reflects total emissions in both soluble and particulate phases from both the Sacramento and San Joaquin Rivers. All loading estimates other than that for copper are based upon total measured loads in the San Joaquin River and soluble loads in the Sacramento River. As a result, these data underestimate total riverine mass emissions to the Bay-Delta, as the metals in suspension in the Sacramento River are not quantified and cannot therefore be included.

For some elements, the omission of suspended loads in the Sacramento River will affect the total loading estimate only marginally. Thus, for example, selenium is present mostly in solution (Cutter, 1987), and loadings calculated using soluble concentrations will approximate total mass emissions. However, for elements which are significantly associated with suspended particulates, the omission of data of this type for the Sacramento River may influence mass loading estimates substantially, particularly as the Sacramento River flow carries the majority of suspended material to the Bay-Delta from upstream sources.

Crude estimates of total loadings may be made for the Sacramento River if it is assumed that soluble:particulate ratios of metals in this river and in the San Joaquin flow are comparable. Applying such an assumption to the calculation of total mass emissions (in both soluble and suspended phases) increases the estimates shown for arsenic by 2-fold; for chromium by 15-fold; for lead by 2-fold; for nickel by 6-fold; and for zinc by 3-fold. Estimates cannot be produced for the other elements, as insufficient data exist to characterize soluble:particulate ratios in San Joaquin River samples.

The treatment of mass emission data as described above is not reflected in the estimates shown in Figs. 15-17 and 19-24, as the assumption inherent in such calculations is not considered strictly defensible. However, it should be noted that the riverine loadings shown for elements other than copper do not include metals in suspension in the Sacramento River flow.

This discussion of soluble and total loads of contaminants in riverine inputs to the Bay-Delta is relevant not only to the accurate computation of mass emissions from this source, but also to any comparisons between trace element loadings from riverine inputs and from nonurban runoff. Because metal emissions from the latter source are derived from estimates of total concentrations in soils deposited in the Bay-Delta by runoff, they represent total metal loadings (not loads in solution).

Superimposed upon the uncertainties described above is the natural variability in the loading of toxic contaminants to the Bay-Delta. Climatic variations, particularly in precipitation, will cause significant temporal variation in mass loads to the estuary from riverine and runoff sources. Moreover, such changes

in loading cannot be simply related to variations in annual average precipitation, as these two functions exhibit a complex rather than a linear relationship. For example, temporal variation in precipitation on a short time scale can have a profound influence on the transport of particulate matter containing toxic contaminants. The stochastic nature of the factors driving such pulses of contaminants to and through the estuary limits the precision with which the mass loading of contaminants can be determined for the Bay-Delta.

The spatial variation in mass loading to different segments of the estuary is extremely important when evaluating the impact of contaminants, but is not considered in this report. Considerable additional work would be required to assign toxicant loads (especially those from non-point sources) to different sectors of the estuary. Such a wasteload allocation, and the ensuing logical step of matching contaminant loads to water quality (existing or desired) is outside the scope of the present study. Nevertheless, the overall loading estimates for contaminants provided in this report are considered adequate as a basis for such further studies.

B. Mass Loads to the Bay-Delta by Contaminant

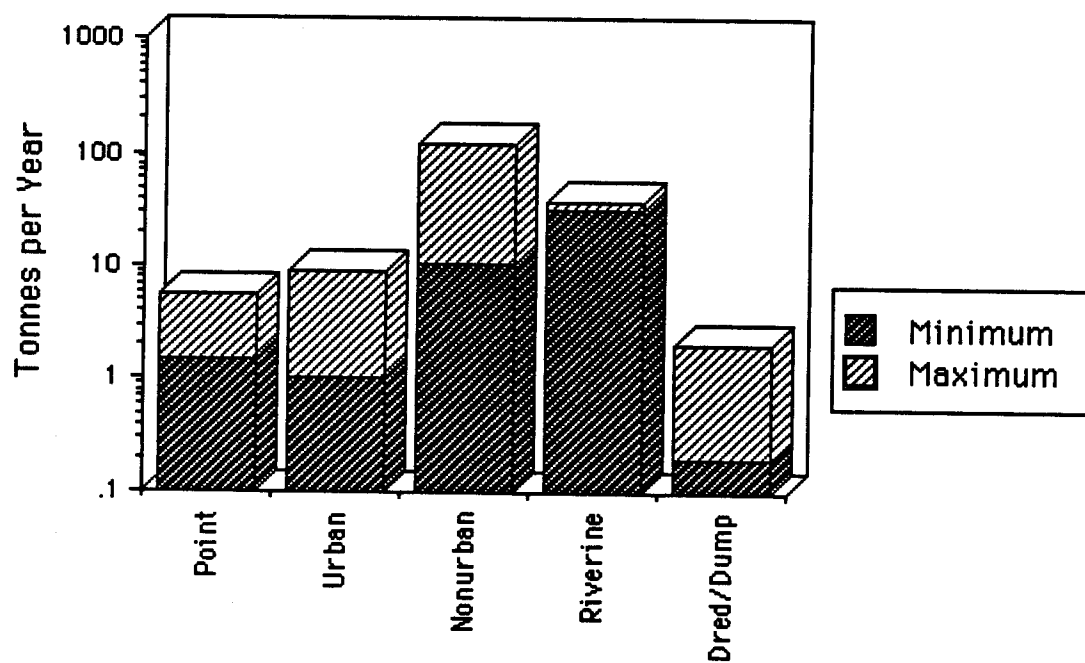
While much is unknown, the estimates developed in this report provide some insight into the magnitudes of the mass loading of different toxic contaminants to the estuary and the relative contribution of each major source. In the following discussion, there are three factors that should be kept in mind. With regard to Figs. 15 through 27, the reader should note that the ordinate is presented on a logarithmic scale to allow for the comparison of all sources in one figure. The "minimum" portion

of each column is the minimum load estimate in tonnes yr^{-1} , while the maximum load estimate is represented by the total height of each column. Thus, the size of the upper section of a column relative to the total height of that column is a visual description of the degree of uncertainty associated with the estimated load for the corresponding source. Absolute estimates of minimum and maximum loads are given on each figure to aid in interpretation of the logarithmic scale.

As it was not possible to estimate the contribution of each contaminant by all sources, in several figures only a few sources appear. Thus, if a source does not appear in a figure, this implies only that an estimate for that source was not made in this report. (The only exception to this is for spills, which is considered an inconsequential source of all contaminants except petroleum hydrocarbons). Conclusions as to the relative importance of each source of a contaminant must be tempered by this consideration.

Trace Metals

Arsenic. Riverine inputs ($32\text{--}37 \text{ tonnes yr}^{-1}$), and nonurban runoff ($10\text{--}119 \text{ tonnes yr}^{-1}$) appear to be the major contributors of arsenic to the estuary (Fig. 15). The small range of uncertainty for riverine inputs indicates that arsenic is almost always detected in river samples. Urban runoff and point sources contribute less than $10 \text{ tonnes yr}^{-1}$ of arsenic to the estuary, while dredging and dumping mobilizes less than two tonnes of this element annually.



Maximum	5.7	9	119	37	2
Minimum	1.5	1	10.3	32	0.2

Fig. 15. Estimated range for the mass loading of arsenic to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.

Cadmium. The riverine input of cadmium, in the range of 5 to 27 tonnes yr^{-1} , is the dominant source of this trace metal to the estuary (Fig. 16). Urban runoff (0.3-3 tonnes yr^{-1}) and nonurban runoff (0.5-6 tonnes yr^{-1}) contribute similar amounts of cadmium, while the range for point sources is from about 2 to 4 tonnes yr^{-1} . It appears probable that the mass loading rate from atmospheric deposition of cadmium (0.14-0.35 tonnes yr^{-1}) exceeds the loading due to dredging and dumping (0.02-0.2 tonnes yr^{-1}), but these estimates are too uncertain to be dogmatic in respect to their relative magnitudes. Both of these sources are insignificant when compared to riverine input.

Chromium. Nonurban runoff appears to be the dominant source of chromium to the Bay-Delta, potentially contributing over 1,500 tonnes yr^{-1} of this element (Fig. 17). At the lower end of their range, the estimated mass loading from nonurban runoff (134 tonnes yr^{-1}) is similar to chromium emissions from riverine inputs (77-92 tonnes yr^{-1}). Estimates of riverine and point source mass loadings exhibit a small range of uncertainty, as chromium is frequently detected in local monitoring programs. Point sources (12-14 tonnes yr^{-1}) probably contribute more chromium to the Bay-Delta than urban runoff (3-15 tonnes yr^{-1}). Dredging and dredged material disposal loads are estimated to be from 5 to 50 tonnes yr^{-1} .

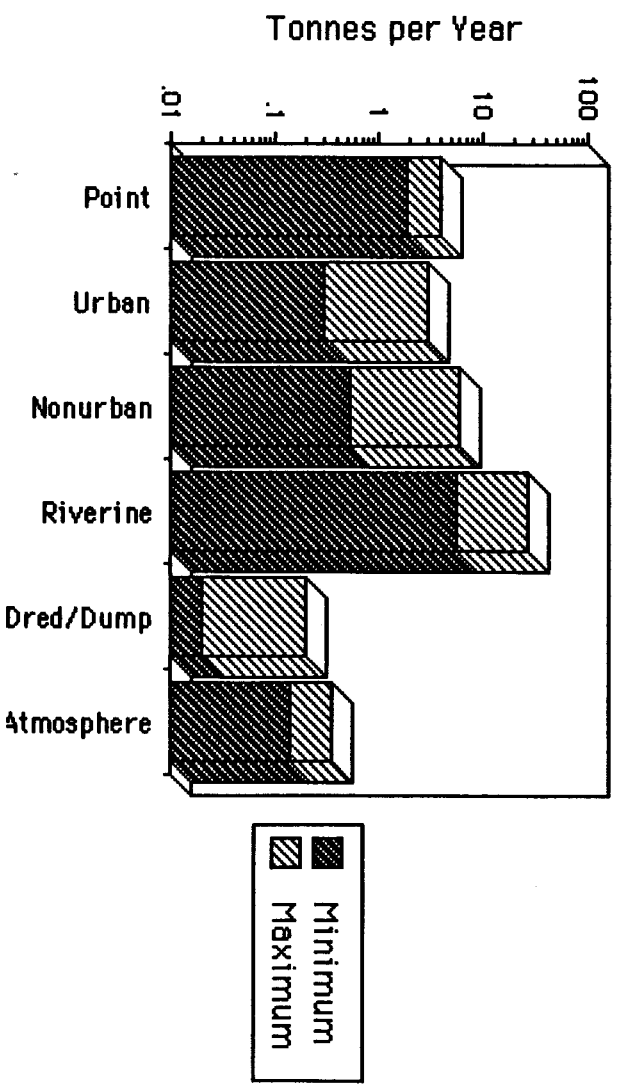
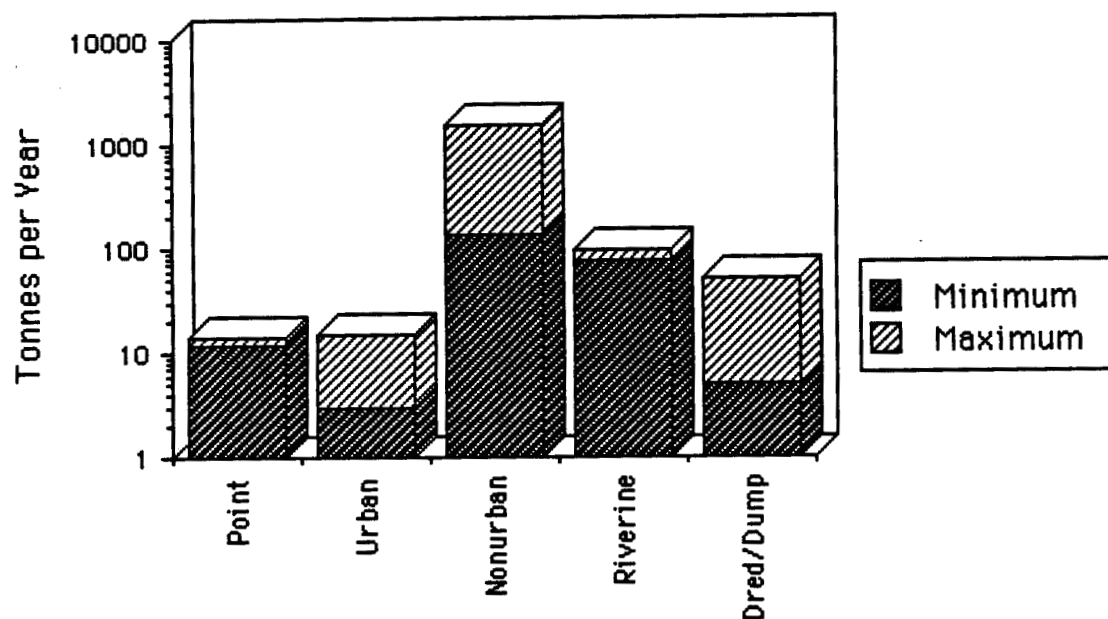


Fig. 16. Estimated range for the mass loading of cadmium to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

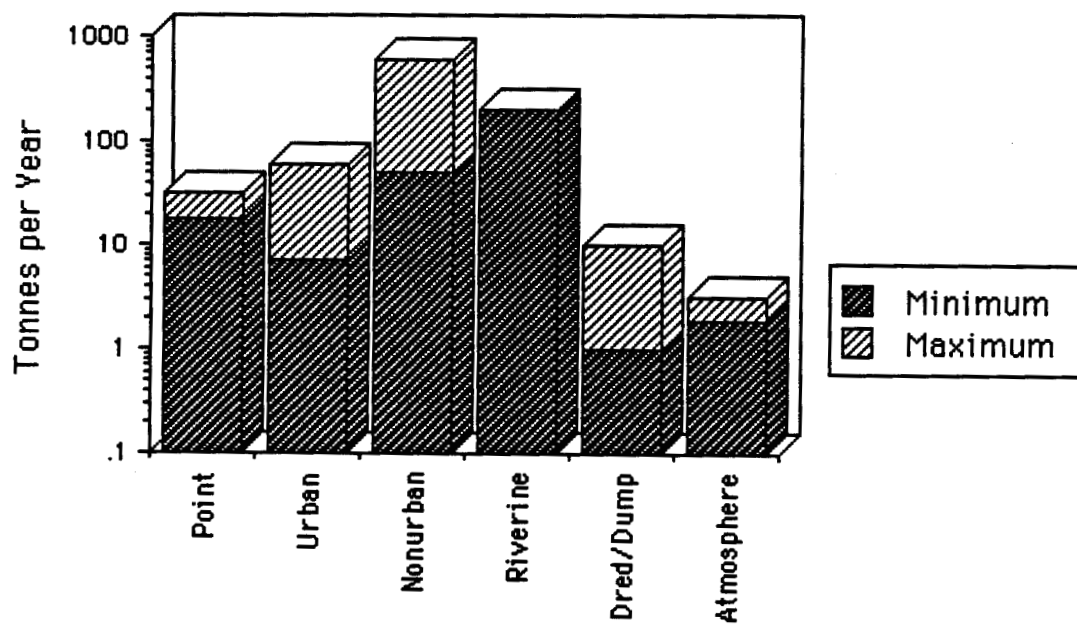


Maximum	14	15	1537	92	50
Minimum	12	3	134	77	5

Fig. 17. Estimated range for the mass loading of chromium to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, and dredging and dumping. All values in tonnes yr^{-1} .

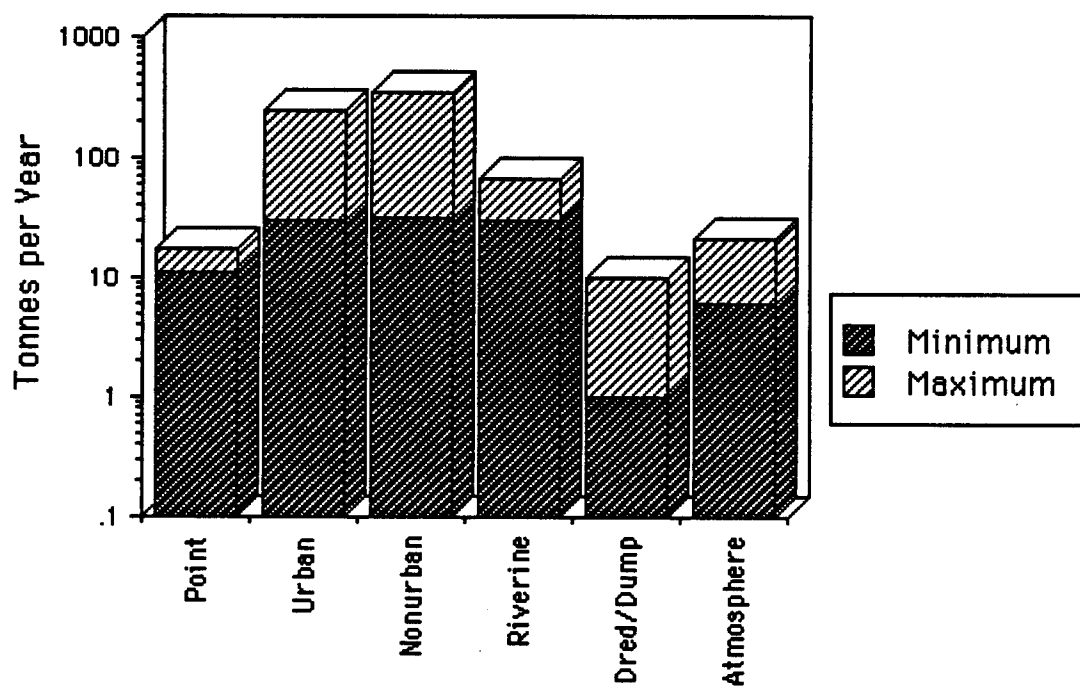
Copper. As noted for arsenic and chromium, nonurban runoff and riverine inputs are the major sources of copper to the estuary (Fig. 18). The range for mass loadings from nonurban runoff is 50-580 tonnes yr^{-1} , while riverine loadings are about 200 tonnes yr^{-1} . (There is no range for riverine loadings of copper, as no monitoring samples were below the limit of analytical detection.) The estimated range for copper loads in urban runoff (7-59 tonnes yr^{-1}) encompasses the more precise estimate for point sources (18-31 tonnes yr^{-1}). Similarly, the estimate for dredging and disposal (1-10 tonnes yr^{-1}) encompasses the estimate for atmospheric deposition (2-3 tonnes yr^{-1}). Both these latter sources of copper are inconsequential on an estuary-wide basis when compared to riverine inputs.

Lead. As might be expected given the automotive and industrial nature of the sources of lead in the environment, the estimated mass loadings of lead to the estuary from urban runoff (30-250 tonnes yr^{-1}) suggest this to be an important source of lead in the Bay-Delta (Fig. 19). The estimated range of mass loading is slightly larger than this for nonurban runoff (31-358 tonnes yr^{-1}), but is considerably smaller for riverine inputs (30-66 tonnes yr^{-1}), although the minimum contribution by these three sources is similar. The contribution of lead from point sources (11-17 tonnes yr^{-1}) is of a similar magnitude to that from atmospheric loadings (6-21 tonnes yr^{-1}). Dredging and disposal (1-10 tonnes yr^{-1}) is probably the smallest source of lead to the estuary.



Maximum	31	59	581	203	10	3.1
Minimum	18	7	51	203	1	1.9

Fig. 18. Estimated range for the mass loading of copper to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.



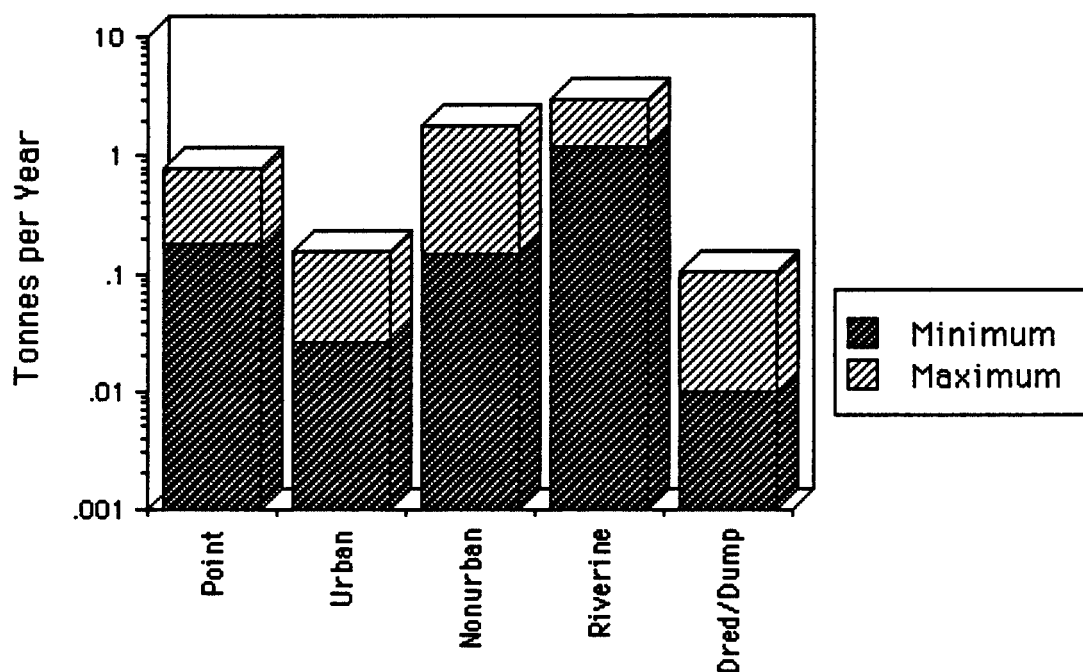
Maximum	17	250	358	66	10	21
Minimum	11	30	31	30	1	6

Fig. 19. Estimated range for the mass loading of lead to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

Mercury. As documented for many of the trace metals, riverine inputs are probably the largest source of mercury to the estuary, ranging between 1.2 and 3 tonnes yr^{-1} (Fig. 20). Mass loads from point sources (0.18-0.80 tonnes yr^{-1}) may be somewhat smaller than loads from nonurban runoff (0.15-1.73 tonnes yr^{-1}), and both of these sources exceed inputs of mercury to the estuary from urban runoff (0.026-0.15 tonnes yr^{-1}). Mass loads of mercury from dredging and dumping (0.01-0.1 tonnes yr^{-1}) indicate this is probably the least important source of this element to the Bay-Delta. No data are available to permit estimation of the atmospheric deposition of mercury to the Bay-Delta receiving waters.

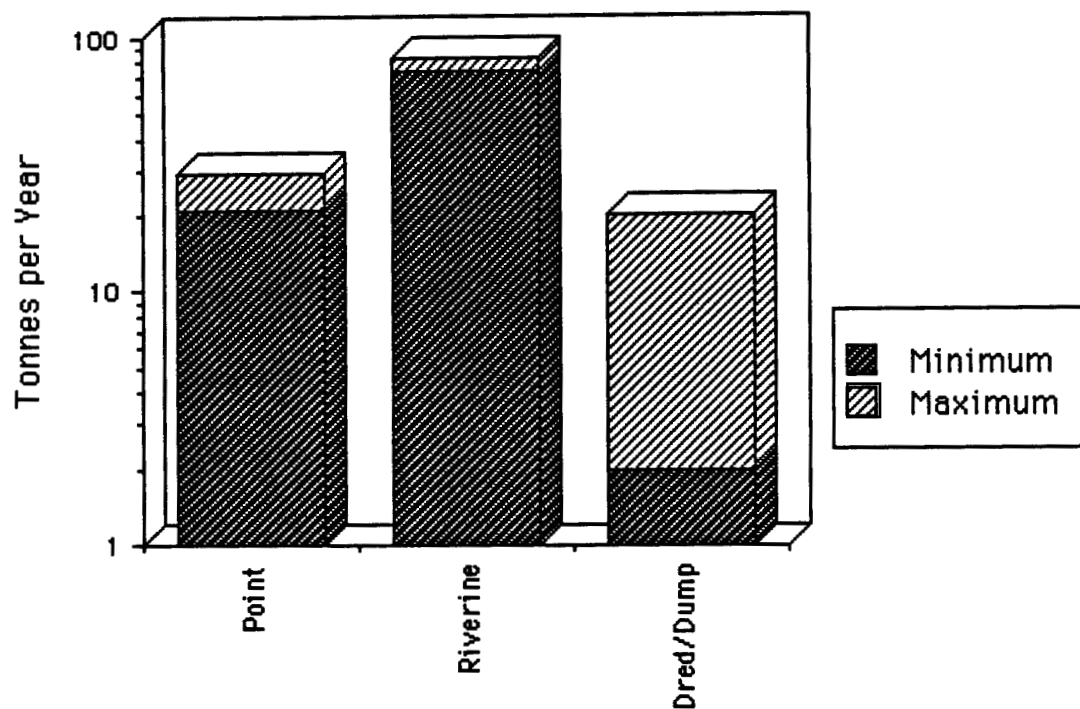
Nickel. Only three sources could be quantified for this element. Among these sources, riverine inputs again appear to be the dominant source (Fig. 21). Thus, estimates of riverine inputs of nickel (74-82 tonnes yr^{-1}) significantly outweigh those for either point sources (21-29 tonnes yr^{-1}) or dredging and dredged material disposal (2-20 tonnes yr^{-1}).

Selenium. As for nickel, selenium loads could be quantified from only three sources. The pattern for mass loads of selenium to the estuary is very similar to that of nickel, except that selenium is delivered to the estuary in much smaller quantities (Fig. 22). The estimated mass loads from riverine inputs of selenium (4.3-7.4 tonnes yr^{-1}) are about double those from point sources (1.9-2.5 tonnes yr^{-1}). It is notable here that



Maximum	0.8	0.15	1.7	3	0.1
Minimum	0.18	0.026	0.15	1.2	0.01

Fig. 20. Estimated range for the mass loading of mercury to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, and dredging and dumping. All values in tonnes yr^{-1} .



Maximum	29	82	20
Minimum	21	74	2

Fig. 21. Estimated range for the mass loading of nickel to the San Francisco Bay-Delta from point sources, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.

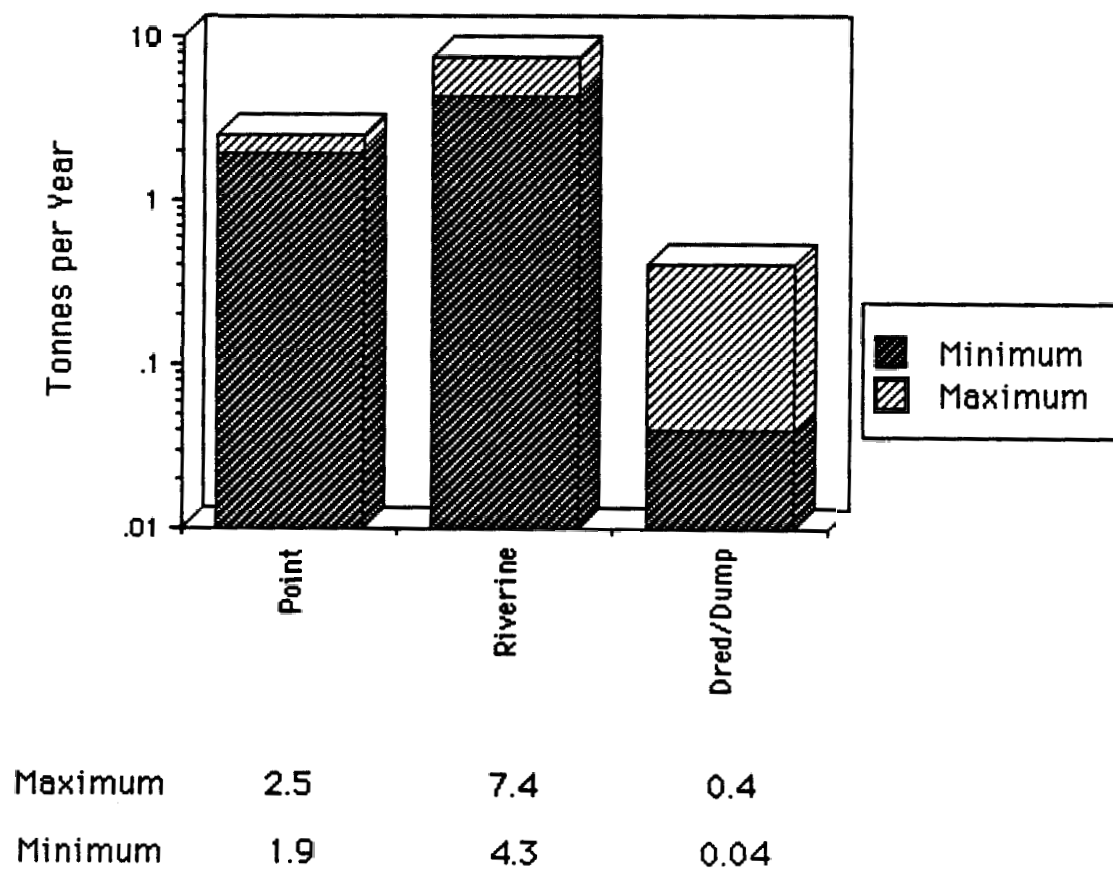
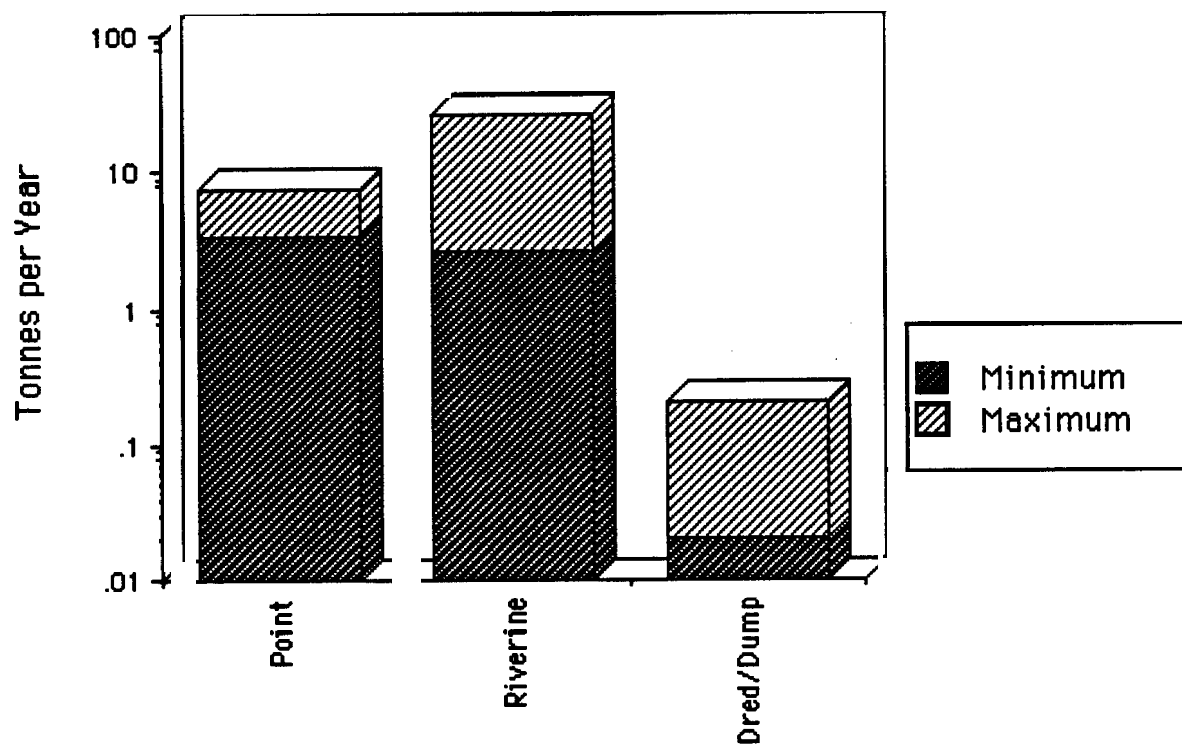


Fig. 22. Estimated range for the mass loading of selenium to the San Francisco Bay-Delta from point sources, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.

a recent review of selenium in the estuary (Cutter, 1987) concluded that in periods of low Delta flow, point source loads of the element would rival riverine inputs. If the effects of season were overlain on the estimates in Fig. 22, this would seem to agree with the present conclusions. Dredging and dredged material disposal probably contribute only modest amounts of selenium to the Bay-Delta (0.04-0.4 tonnes yr^{-1}).

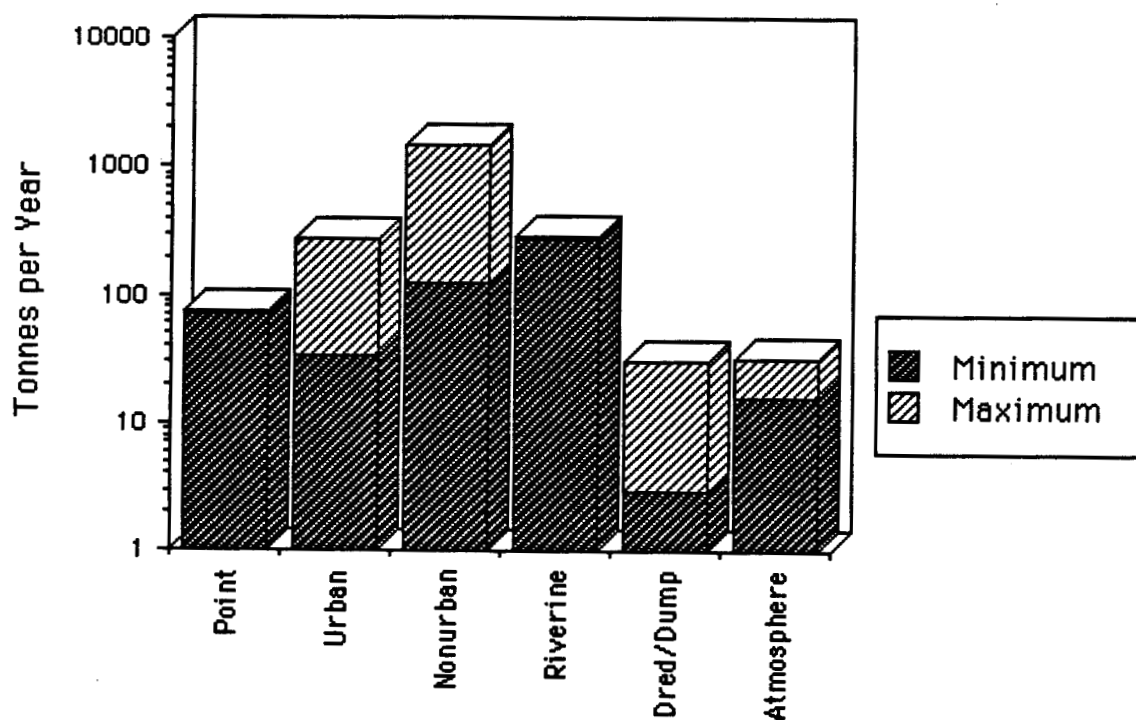
Silver. Only three sources of silver to the Bay-Delta could be quantified (Fig. 23). The estimated load from riverine inputs (2.6-26 tonnes yr^{-1}) is similar at its lower extreme to that for point sources (3.3-7.5 tonnes yr^{-1}). POTWs are responsible for over 94% of the mass loading of silver from point sources. Mass emissions of silver from dredging and disposal operations (0.02-0.2 tonnes yr^{-1}) are probably inconsequential when compared to riverine and point source loads.

Zinc. Nonurban runoff and riverine inputs are probably the most important sources of zinc to the San Francisco Bay-Delta (Fig. 24). As zinc is only rarely found to be below detection limits in riverine and point source monitoring programs, the uncertainty in loading estimates for these sources is small (272-288 and 70-74 tonnes yr^{-1} , respectively). This compares with the much greater uncertainty associated with estimates of zinc loads from nonurban runoff (126-1,453 tonnes yr^{-1}) and urban runoff (34-268 tonnes yr^{-1}). Atmospheric deposition (16-32 tonnes yr^{-1}) and dredging and disposal (3-30 tonnes yr^{-1}) are probably less important than any of the



Maximum	7.5	26	0.2
Minimum	3.3	2.6	0.02

Fig. 23. Estimated range for the mass loading of silver to the San Francisco Bay-Delta from point sources, riverine inputs, and dredging and dumping. All values in tonnes yr⁻¹.



Maximum	74	268	1453	288	30	32
Minimum	70	34	126	272	3	16

Fig. 24. Estimated range for the mass loading of zinc to the San Francisco Bay-Delta from point sources, urban runoff, nonurban runoff, riverine inputs, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

above sources, although the maximum estimates for these two sources are similar to the minimum mass loading of zinc estimated for urban runoff.

Summary of trace metal loadings. In cases where metal loadings from most sources could be quantified, the overall mass emissions appear to be dominated by riverine inputs of metals and by nonurban runoff. Both the leaching of trace elements to solution from soils in the catchment and the washdown of intact soil particles are significant sources of metals to the Bay-Delta.

It is important to note here that, despite the predominance of riverine and nonurban runoff sources for most trace element loads, this does not imply that toxic effects of metals (should they exist) would be necessarily most evident in the Delta. The trace elements introduced to the estuary from those sources are largely in adsorbed forms, attached in relatively low concentration to a huge sediment load (or alternatively, exist at very low levels in solution, in massive inflow volumes). The effects of contaminants are thus completely distinct from their mass loadings. The present report is restricted to mass loading estimates only.

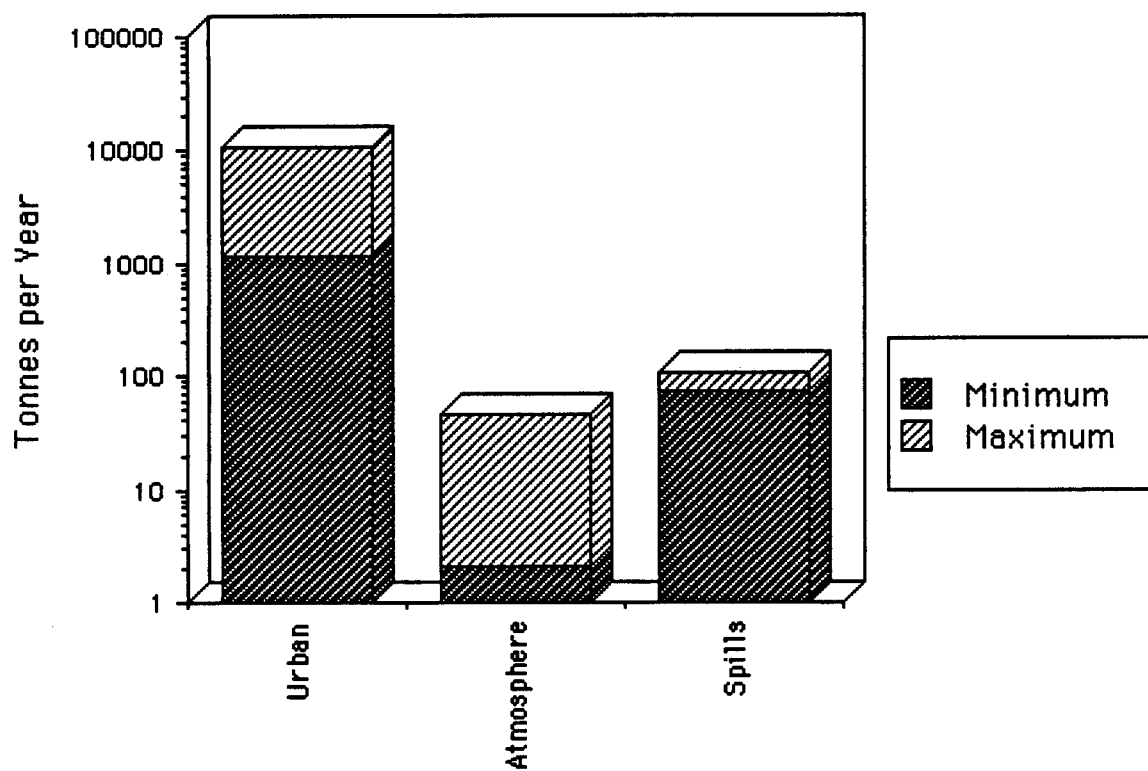
Mass loadings from point sources appear more important for certain elements, especially silver, cadmium, and selenium, although riverine inputs of these elements probably still exceed point source contributions on an annually-averaged basis. However, the mass loadings of silver or selenium from urban and nonurban runoff could not be estimated, and conclusions as to total mass loads of these elements cannot therefore be derived. For the trace metals reviewed, urban runoff appears to be an

important source only for lead and (possibly) zinc. Both urban and nonurban runoff probably contribute more lead to the estuary than riverine inputs. However, it should be kept in mind that the ban on the use of lead additives in gasoline is thought to be altering the rate at which lead is mobilized. The mass loading estimates for lead from urban runoff (and atmospheric deposition) depend upon concentration measurements from the late 1970s and early 1980s, and reduction in the use of leaded gasoline would be expected to reduce the loadings of lead from urban runoff.

Organics

Fewer mass loading estimates were developed for organic contaminants, due mostly to the paucity of monitoring data for these substances. When sampling has occurred, different investigators have measured different substances, and contaminant concentrations in the great majority of samples are often reported to be below analytical detection limits. The absence of mass estimates of the loads of organic contaminants from riverine sources is particularly notable. Mass loading estimates are presented below for total hydrocarbons, PCBs, and PAHs from urban runoff, dredging and dumping, and atmospheric deposition. Point source loadings of hydrocarbons are not presented, as most of these measurements are actually for "oil and grease" and thus include a variety of non-toxic contaminants.

Hydrocarbons. Urban runoff is clearly the most important source of hydrocarbons among those reviewed in this report (Fig. 25). Even the low end of the range estimated for urban runoff ($1,140 \text{ tonnes yr}^{-1}$) exceeds the loading from spills by greater than an



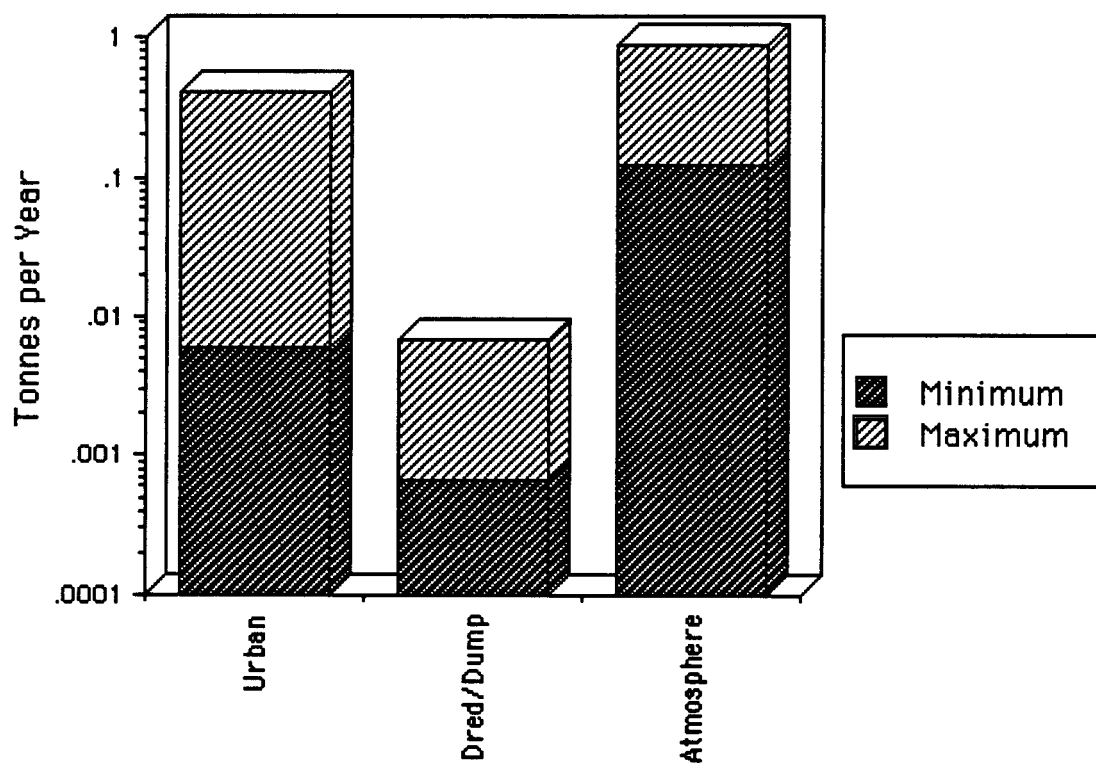
Maximum	11016	45	110
Minimum	1143	2.1	72

Fig. 25. Estimated range for the mass loading of total hydrocarbons to the San Francisco Bay-Delta from urban runoff, atmospheric deposition, and spills. All values in tonnes yr⁻¹.

order of magnitude. Atmospheric deposition of hydrocarbons appears to be the least important of the three sources analyzed. It is clearly appropriate to develop more precise estimates of total hydrocarbon loads to the estuary from point sources. (It should be noted that the upper bound of the range for urban runoff may contain some non-toxic hydrocarbons due to the use of some oil and grease data in the mass loading calculations.)

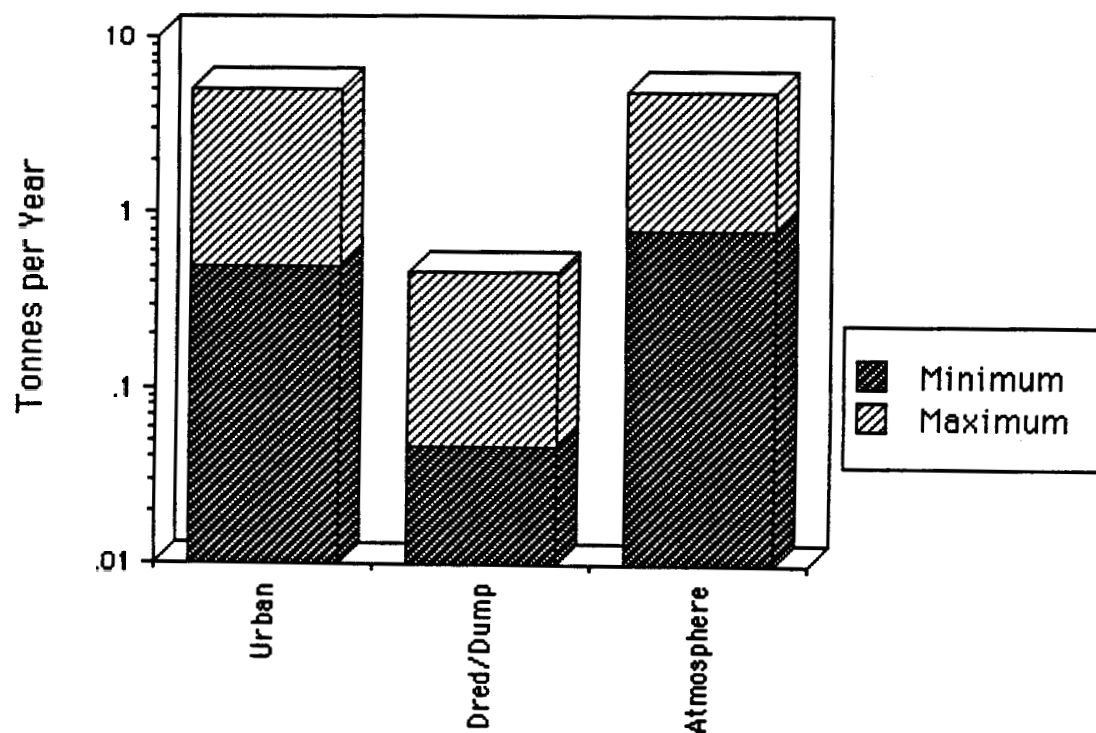
PCBs. The use of measurements from the Great Lakes region leads to the conclusion that atmospheric deposition is the predominant source of PCBs to the estuary among the three sources quantified herein, with mass loading estimates for this pathway ranging from 0.12 to 0.75 tonnes yr^{-1} (Fig. 26). PCB loads from urban runoff are of great uncertainty, but are probably less than those from atmospheric deposition. Dredging and dredged material disposal (contributing only 0.67 to 6.7 kilograms yr^{-1} of PCBs) appears to be an insignificant source of these contaminants to the estuary. However, it must be emphasized that the mass loading estimates for PCBs are based upon measurements from other parts of the USA and are therefore of uncertain application to the Bay-Delta.

PAHs. Mass loadings of PAHs from urban runoff (0.5-5.0 tonnes yr^{-1}) and atmospheric deposition (0.8-4.8 tonnes yr^{-1}) are similar in magnitude in the Bay-Delta (Fig. 27). These nearly identical ranges exceed the estimated range for dredging and dredged material disposal



Maximum	0.4	0.0067	0.75
Minimum	0.006	0.00067	0.12

Fig. 26. Estimated range for the mass loading of PCBs to the San Francisco Bay-Delta from urban runoff, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.



Maximum	5	0.47	4.8
Minimum	0.5	0.05	0.8

Fig. 27. Estimated range for the mass loading of PAHs to the San Francisco Bay-Delta from urban runoff, dredging and dumping, and atmospheric deposition. All values in tonnes yr⁻¹.

(0.05-0.47 tonnes yr^{-1}) by almost exactly an order of magnitude. The paucity of data on PAHs in the Bay-Delta means that these estimates, which are based upon data from other regions, are of the most preliminary nature. PAH concentrations in other sources are needed to fully define overall loads of these compounds to the Bay-Delta.

C. Conclusions

1. There is significant uncertainty associated with estimates of mass loading of toxic contaminants to the San Francisco Bay-Delta. This uncertainty is derived from many sources, including natural climatic variability, imprecision in the estimates of parameters used to calculate nonpoint mass loadings, and the treatment of values below analytical detection limits when calculating average contaminant concentrations. Consequently, it is only possible to estimate ranges for the mass loading of toxic contaminants to the estuary from the various sources.

2. The estimated annual average mass loadings of toxic contaminants to the entire Bay-Delta presented in this report do not fully address the temporal and spatial variation inherent in these loads. Although a certain source category may not contribute a significant amount of a specific contaminant to the estuary on an annually-averaged basis, this finding may not be valid on a different spatial or temporal scale. For example, while rivers are a predominant source of many trace metals for the estuary, the vast majority of this mass loading occurs during high-flow periods. During the summer in a year of low precipitation, the relative importance of riverine inputs will be

significantly reduced. Similarly, on an annually-averaged basis, the mass loading of toxic contaminants from dredging and dredged material disposal activities appears to be insignificant. The disposal of dredged materials occurs, however, only in certain locations in the Bay-Delta. The dispersion of the fine-grained sediments containing elevated levels of toxicants through the estuary may nevertheless give rise to significant contamination of locations where these settle out, such as in quiescent waters in harbors and marinas.

3. For most trace metals, riverine inputs and nonurban runoff are the dominant sources of mass loadings to the estuary. This is particularly the case for arsenic, chromium, copper, mercury, and zinc. Riverine inputs are also a major source of cadmium to the Bay-Delta.

4. Although riverine inputs are the major quantified source of silver and selenium to the estuary, point source discharges of these two elements appear to be important, particularly in the case of silver. POTWs discharge over 94% of the silver from point sources, while refineries produce the majority of the point source loadings of selenium. As no estimates of the mass loading of silver or selenium from urban and nonurban runoff are available, however, the precise importance of sources of these elements relative to overall loads remains uncertain.

5. Urban runoff is an important source of lead to the estuary, and possibly of zinc. Mass loadings of other trace elements from this source are probably not significant when compared to riverine inputs, nonurban runoff, or (in certain instances), point sources. As lead concentrations in the environment are declining due to the decreased use of leaded

gasoline, contributions of this element from urban runoff are expected to decrease.

6. Among the sources quantified here, urban runoff is the the major source of hydrocarbons to the estuary, contributing amounts at least an order of magnitude greater than the mass loading of hydrocarbons from spills. Urban runoff is also a major source of high molecular weight PAHs. Data for total hydrocarbons (as opposed to oil and grease) in point source discharges are needed before an adequate estimate of hydrocarbon mass loadings from point sources can be made.

7. While not a significant source of trace metals to the estuary, atmospheric deposition appears to be an important source of both PCBs and PAHs. This conclusion, however, is based upon data from the Great Lakes region that may be of limited applicability in the Bay-Delta due to regional differences in climate and levels of atmospheric contamination. The mass loading of these contaminants to the estuary by atmospheric deposition merits further investigation.

8. Dredging and the disposal of dredged material appear to be a relatively insignificant source of contaminants to the Bay-Delta. Only if one assumes that 10% of the contaminants contained in dredged sediments are released upon disposal might the calculated mass loadings be significant, and then only for chromium. As discussed above, however, the uneven spatial distribution of dredging and disposal activities and the fate of remobilized contaminants are significant factors in determining the possible impacts of toxicants from such operations in the Bay-Delta.

D. Recommendations for Improving Mass Loading Estimates

Given the need to identify the important sources of toxic contaminants to the estuary, and the large uncertainty that is currently associated with mass loading estimates, there is a clear need to improve the precision of these estimates for the San Francisco Bay-Delta. Several steps can be taken in this regard, and these are enumerated below.

1. Additional monitoring to characterize the chemical composition of flows to the estuary is clearly necessary. Carefully-designed monitoring of urban and nonurban runoff is needed, as is more frequent examination of contaminant concentrations in the Sacramento and San Joaquin Rivers. Reliable data on organic constituents are sparse at present.

2. Oil and grease measurements should be augmented or replaced by procedures to measure total hydrocarbons, which exclude the triglycerides and other non-toxic species included in measurements of oil and grease. This is particularly important for point sources, as analyses of total hydrocarbons in point source effluents are lacking.

3. For contaminant sources which characteristically demonstrate large variations in flow and concentration, such as urban runoff, several measurements of flow and concentration must be taken during each event and flow-weighted statistics must be used to interpret the data.

4. It is of highest priority that all future monitoring for contaminants in flows to the estuary and in the estuary itself take place within the context of a formal and coordinated program of quality assurance and quality control (QA/QC). QA/QC is a vital aspect of any scientific enterprise, especially when

samples of very low concentration are collected in the field and transported to a laboratory for analysis. Verification of equipment function and all methods of sampling, storage, transport, and analysis should be obtained through the use of standard solutions, field and laboratory blanks, spikes, and the blind testing of samples. A rigorous QA/QC program assumes that data generated as part of the investigation are invalid unless all predetermined QA/QC objectives have been met. When samples of extremely low concentration are being collected and analyzed by different groups for constituents that are ubiquitous in urban environments, the importance of a QA/QC program cannot be overemphasized. It would be most appropriate for all laboratories to participate in a coordinated program, as this would allow for the intercalibration of results from different establishments. Such a program could be modeled after the QA/QC element in the National Status and Trends Program of the National Oceanographic and Atmospheric Administration. Any QA/QC program should include the analysis of Standard Reference Materials from the National Bureau of Standards.

5. Nonurban runoff appears to be an important source of many toxic contaminants to the estuary, yet very little review of this source category has occurred in the Bay-Delta region. A detailed assessment of the methods available to estimate mass loadings from this source is clearly warranted.

6. Review of the fate of contaminants in the estuary is essential to place the findings of this report in appropriate perspective. As discussed above, annually-averaged mass loading estimates do not account for important spatial and temporal variability in the loading of contaminants to the estuary.

7. Given the potential importance of atmospheric deposition as a source of PCBs and PAHs to the estuary, monitoring of the concentrations of these substances in the atmosphere of the Bay-Delta region is needed.

8. Data generated by various entities in the Bay-Delta region are currently stored in different formats and locations, making compilation and analysis of this information exceptionally difficult. It can be the case that an organization has a significant amount of data without the resources to properly review and compile this information in a manner that would make it useful for others. It would thus appear that a centralized database for the Bay-Delta ecosystem, if properly organized and maintained, could be an important step toward developing an improved understanding of the structure and function of this complex estuary.

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