MONITORING OF TOXIC CONTAMINANTS IN THE SAN FRANCISCO BAY-DELTA: A CRITICAL REVIEW, EMPHASIZING SPATIAL AND TEMPORAL TREND MONITORING

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Preface

This report is produced in specific response to an agreement between the Aquatic Habitat Institute and the State Water Resources Control Board, with funding from the latter and the Bay Area Dischargers Association. It concerns principally one specific aspect of monitoring in the San Francisco Bay and Delta: the monitoring of the abundances, distributions and bio-availabilities of toxic contaminants.

The report should be read within the context of the broader issues facing the estuary and its protection. The State Hearing process presently underway will provide recommendations on the control of pollutants in the Bay and Delta, and perhaps on the control of any impacts of Delta inflows on pollutants. The San Francisco Estuary Project of the EPA National Estuary Program is also underway, and is in the process of reviewing the state of the estuary and its resources through the production of Status and Trends Reports and other documents.

AHI staff have been intimately involved in these projects. Every attempt has been made to reduce overlap between work undertaken by Institute staff for the various projects, and to build upon previous work. In this fashion, it is to be hoped that a cohesive program for the monitoring of contaminants and their effects can be implemented in the Bay and Delta (and its upstream catchment), and that this program can become part of a broader effort to protect the resources of the estuary. The monitoring program proposed here is not therefore a stand-alone product, but relates to these broader needs to protect the estuary. While it is hoped that the program proposed here will become the mainstay of studies of the abundance, distributions and bio-availabilities of toxic contaminants in the estuary, much remains to be done through the State Hearing process, the San Francisco Estuary Project, and other forums of this kind if the estuary is to be adequately protected in future.

I. INTRODUCTION

A. Contaminants in the Estuary: Historical and Existing Concerns

It is widely recognised that the San Francisco Bay-Delta Estuary has been radically altered by human activities (Nichols *et al.*, 1986; Wright and Phillips, 1988). The great majority of these impacts occurred subsequent to the arrival of the Spanish in 1769. Thus, for example, the increasing catchment population and industrialization of the margins of the Bay have caused problems with waste disposal, which began to impact resources in the estuary as early as the 1930s (Phillips, 1987). Large areas of historic marshland have been lost to agricultural, industrial and urban development, and the margins of the estuary have been extensively altered. Hydraulic mining in the Gold Rush period deposited huge quantities of sediment in the Bay, and also introduced trace metals such as mercury (Wright and Phillips, 1988). Exotic species have been introduced and have altered the ecological balance of the Estuary. Water diversions from the Delta for irrigation and potable use in central and southern California have affected estuarine hydrodynamics (Nichols *et al.*, 1986).

Several of these effects are relevant to concerns over pollution of the Bay and Delta. Early impacts due to the wash-down of sediments from the gold mining activities were accompanied by increases in mercury deposition in the estuary. The loss of wetlands and modifications of estuarine channels and margins have changed the hydrodynamics of the system, and may have exacerbated the impacts of introduced pollutants. Water diversions have reduced the potential assimilative capacity of the estuarine receiving waters and have affected flushing rates, altering residence times in the Bay and Delta. Increasing wastes disposed without adequate treatment to the estuary gave rise to organic enrichment in the early 1900s, which affected the use of the Bay waters for shellfish culture. In the 1960s, organic loads became sufficiently high to create hypoxia and anoxia in various portions of the estuary, South Bay being particularly affected. Improvements in industrial and municipal waste treatment were introduced in the late 1960s and 1970s to combat this problem, and total loads of both organic and inorganic contaminants were reduced considerably. It is now widely accepted that the estuary does not suffer from organic enrichment in general; indeed, there is concern that Bay and Delta waters may in fact be under-enriched, and that phytoplankton growth may be insufficient to support the local fishery populations at certain periods.

Despite these past improvements, pollution-related problems remain in the estuary. Phillips (1987) reviewed many of these problems, and they will not be exhaustively listed here. However, it must be noted that concerns over pollution of the estuary have shifted away from organic loading and the consequent impacts on primary productivity and dissolved oxygen levels, towards a belief that conservative toxic contaminants may be exerting unacceptable impacts on the beneficial uses of the estuary. Toxicants of particular concern at present (see Phillips, 1987) include the following:

- Mercury (derived both from historical gold mining activities and natural cinnabar deposits in the estuary catchment) is present at significant concentrations in sediments and fish in the estuary, and an advisory has been issued with respect to the eating of striped bass.

- Selenium enters the Bay both from the San Joaquin River (where seleniferous soils are present in certain areas) and from refineries on the margins of the Bay. This element is thought to have adversely affected bird populations at Kesterson National Wildlife Refuge, and selenium levels in the Bay and Delta may be high enough to exert detrimental effects on biological resources.

- The concentrations of several other trace metals in certain portions of the Estuary are thought to exceed federal and Basin Plan water quality objectives; both copper and nickel are included in this category.

- Discharges of silver in the South Bay are of concern, and the bioaccumulation of considerable amounts of silver by organisms close to point sources has been documented.

- Certain pesticides continue to be washed down into the lower estuary from agricultural areas in the Central Valley and elsewhere. Concentrations of DDT remain detectable in estuarine sediments and biota, although these have probably decreased substantially since the ban on DDT use in 1970 in California. Chlordane, dieldrin and toxaphene are all found in fish and sediments of the estuary and its catchment, as are several other persistent pesticides.

- Significant toxicity has been found to be present in ambient river waters of the upper catchment, presumably linked to pesticide usage. To date, the precise contaminants exerting this toxicity have not been positively identified, but studies are continuing.

- Polychlorinated biphenyls (PCBs) are present at elevated concentrations throughout the estuary, in both sediments and biota. The available data indicate the presence of multiple sources of PCBs, and there is also suggestive (but not yet conclusive) evidence of impacts on fish populations in the Bay. Few local data exist for dioxins and dibenzofurans, but the presence of elevated PCB levels might suggest that these contaminants are also of concern in the estuary. A very recent national survey (as yet unpublished) of dioxins in fish has found significant levels of these toxicants in samples from the San Francisco Estuary and its catchment. This is thought to be due to the chlorination of paper and pulp mill effluents, which is a source of dioxins; however, PCBs may also be implicated.

- Insufficient data exist to characterize the abundance and distributions of petroleum hydrocarbons in the Bay and Delta, but the presence of six major refineries on the Bay margins, the loading of certain hydrocarbons through urban runoff, and the potential for spills are all of concern. Monocyclic aromatic hydrocarbons (MAHs) were previously thought to be implicated in effects on striped bass (*Morone saxatilis*) populations in the estuary, but this evidence is equivocal. It is probable that polycyclic aromatic hydrocarbons (PAHs) are of greater impact in the Bay and Delta, but very little is known of the abundance and distribution of this class of contaminants in the estuary.

As a result of the complicated hydrodynamics of the Bay and Delta and the multiplicity of point and non-point sources of contaminants, the estuary exhibits a very complex patchwork of contamination (e.g. see reviews by Long *et al.*, 1988; Luoma and Phillips, 1988; Phillips and Spies, 1988). Some toxicants are concentrated in specific portions of the estuary and its catchment (e.g. silver in the South Bay; copper and nickel in the extreme southern portion of South Bay; mercury in Clear Lake and elsewhere), whereas others are more generally distributed (e.g. PCBs, DDT and metabolites). These differences relate both to the modes of contaminant transport (e.g. aerial transport of organochlorines; translocation of many metals adsorbed to suspended particulates) and to the fate of contaminants in the estuary, but neither of these factors is well understood. While we know that certain locations in the Bay and Delta ("hot-spots") are particularly

heavily polluted by one or more contaminant, very little is in fact known in detail (and even less is understood) about the abundance, distribution and bio-availability of contaminants in the estuary and its catchment.

There is thus a need to monitor for contaminants and their impacts in the San Francisco Bay, the Delta, and the upstream catchment. This report reviews one type of monitoring: that to delineate spatial and temporal trends in contaminant abundance, distribution, and bio-availability in the estuary. The following subsection discusses the importance of such monitoring in terms of management issues, and relates this to other types of monitoring and research needs involving contaminants in the estuary.

B. Management Issues Related to Contaminants

To be successful, any overall scheme for monitoring and research into contaminants in the San Francisco Estuary should relate specifically to management issues which require to be addressed. Management issues relating to the San Francisco Bay and Delta may be framed in many ways, ranging from the general to the highly specific. Most of these issues are referred to in the Water Quality Control Plan (the "Basin Plan") for the estuary (SWRCB, 1982c: SFRWQCB, 1986). Some 83 such issues were listed by the San Francisco Estuary Project in 1987 (Phillips and Baumgartner, 1987). The latter report is used here to provide a general framework for areas of concern which involve toxic contaminants.

The principal management issues listed by Phillips and Baumgartner (1987) and relating specifically to toxic contaminants in the San Francisco Bay and Delta are separated here into three categories, and are shown in Tables 1-3. Many of these could be further broken down to more specific management concerns; however, the issues as listed are thought to cover the majority of the contaminant-related issues and unknowns in the estuary. These management issues obviously relate directly to regulatory needs. There is a recognized need for monitoring to address both the management issues as a whole and the regulatory requirements in the estuary, i.e. to ensure compliance with effluent limitations and water quality objectives or standards.

The first category of management issues (Table 1) is derived generally from uncertainties in terms of the sources and distributions of contaminants in the estuary. Unknowns in this general area underpin much of the difficulty in providing acceptable management strategies to control contaminants in the estuary; more information is required on toxicant sources to support management decisions. Indeed, these issues are also basic to the understanding of contaminant effects in the estuary; if one does not know where contaminants are present at greatest concentration in the system and why, it is difficult to unequivocally relate observed impacts upon beneficial uses to the adverse effects of contaminants.

Table 1. Management issues relating to the sources, concentrations, and distributions of contaminants in the San Francisco Bay and Delta. Adapted from Phillips and Baumgartner (1987).

- What are the principal present and likely future sources of each contaminant of concern in the Bay and Delta, and how can the existing database on sources of toxicants be improved?

- In particular, how important is non-point runoff as a source of contaminants to the estuary?

- How do alterations in freshwater inflow rates and regimes affect the abundance and distribution of contaminants in the estuary?

- How important are particulate-adsorbed contaminants in riverine loads in defining toxicant distributions and abundance in the estuary?

- In which areas of the estuary are water quality objectives being violated, and what are the principal causes of this?

- What are the existing locations of hot-spots of contamination in the estuary?

- How important is dredging and dredged material disposal in defining contaminant distributions in the estuary? Should alternative disposal sites be considered?

- Is contamination of the surface microlayer of significant concern in the estuary?

- Is contaminant bio-availability in the estuary a critical issue, and how may the existing database on this topic be improved?

- What major temporal changes in the abundance and distributions of toxic contaminants have occurred and are occurring in the estuary?

- How does the export of contaminants from the estuary affect the offshore receiving waters of the Pacific?

Table 2. Management issues relating to the biological effects of contaminants in the San Francisco Bay and Delta. Adapted from Phillips and Baumgartner (1987).

- Are potable waters of adequate quality in the Bay and Delta?
- Is public health at risk from toxicants in fish and shellfish harvested from the estuary?
- What are the causes of observed toxicity in ambient receiving waters entering the Delta?
- What species and methods should be employed in bioassays to study the direct effects of toxicants in effluents discharged to the Bay and Delta?
- To what extent have toxic contaminants contributed to the decline of fish populations in the estuary?
- What are the impacts of sediment-borne toxicants on biological resources of the estuary? Can sediment-based regulatory criteria or standards be developed?
- Are wetland habitats and their associated wildlife at risk from toxicants in point source and non-point source effluents discharged directly to (or close to) wetlands?
- Will existing water quality objectives provide adequate protection for resident biota of the Bay and Delta?

Table 3. Management issues relating to methods employed to study contaminants in the San Francisco Bay and Delta. Adapted from Phillips and Baumgartner (1987).

- How may quality assurance and quality control of contaminant analysis be improved?
- Which methods can be introduced to improve the current detection limits of contaminant analysis?
- Can indices such as the striped bass health index be developed as a reliable tool for managing fish stocks in the Bay and Delta?
- How may cause-and-effect relationships between pollutants and their effects on biological resources of the estuary be unequivocally established?
- How may coordination between studies be improved in the estuary?
- What is the most appropriate data management system for information relating to the estuary, and how should improvements to current data management be made?

The present report is concerned principally with filling this area of uncertainty. It is argued that:

(i) Presently available methods for monitoring contaminants in aquatic ecosystems are adequate to provide a coherent picture of the abundance, distributions and bio-availabilities of toxic contaminants and their changes with time; such a knowledge will also inevitably define sources of contaminants and their relative importance.

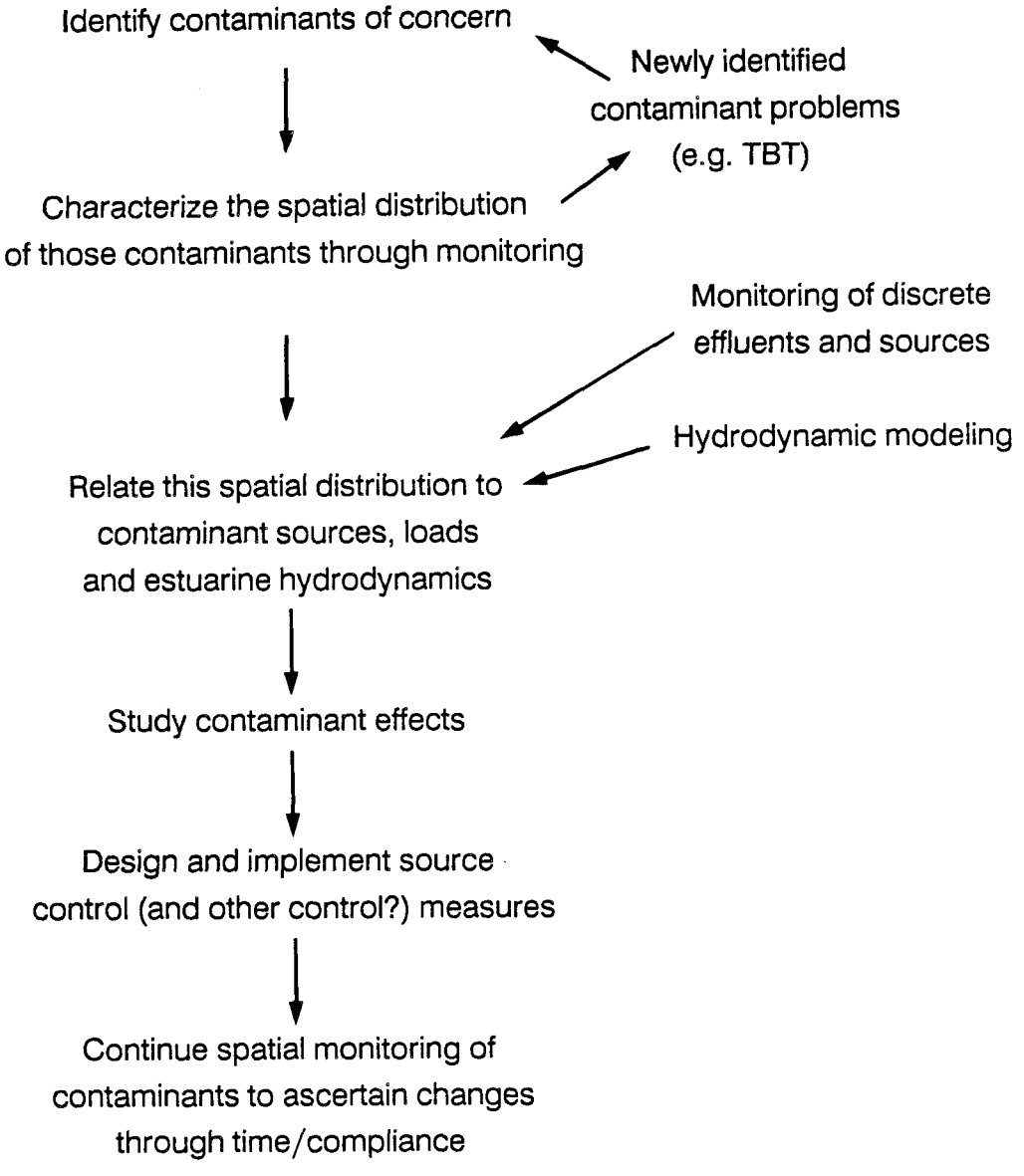
(ii) Existing monitoring programs in the San Francisco Bay-Delta and its catchment do not provide these needed data on the spatial and temporal trends in contaminant abundance, distributions or bio-availability; this is due to either their poor design, or their insufficient focusing on this specific and discrete goal.

A monitoring program which will provide these data on the spatial and temporal trends in the abundance of contaminants is therefore proposed (see section VII of this report). Monitoring to address regulatory and compliance issues is also proposed, where this is compatible with the overall bio-monitoring approach recommended here.

The other management issues in the estuary relating to toxic contaminants involve either unknowns concerning the impacts of contaminants on beneficial uses in the estuary (Table 2) or uncertainties concerning the methods of study of contaminants and their impacts in the estuary (Table 3). It must be emphasized that monitoring and research on these aspects is completely distinct from the monitoring of spatial and temporal trends in toxicant levels in the estuary. The latter is a pre-requisite for many of the effects-related types of studies, but is a stand-alone basic requirement in its own right. The present report does not address many of the effects-related issues in detail and also does not address the various topics relating to the methods of study of contaminants in the Bay and Delta; these aspects of the overall problem are not included in the scope of work for the production of the present report (Appendix 1).

Figure 1 provides a pictorial representation of a monitoring and management strategy for the control of contaminants in the estuary. It may be seen that the monitoring of spatial and temporal trends in contaminant distribution and abundance is central to the overall strategy. Thus, decisions to increase or decrease controls on the loading of contaminants to the estuary can only be legitimately made based upon a detailed

Figure 1. Pictorial representation of a monitoring and management strategy for the control of contaminants in the estuary.

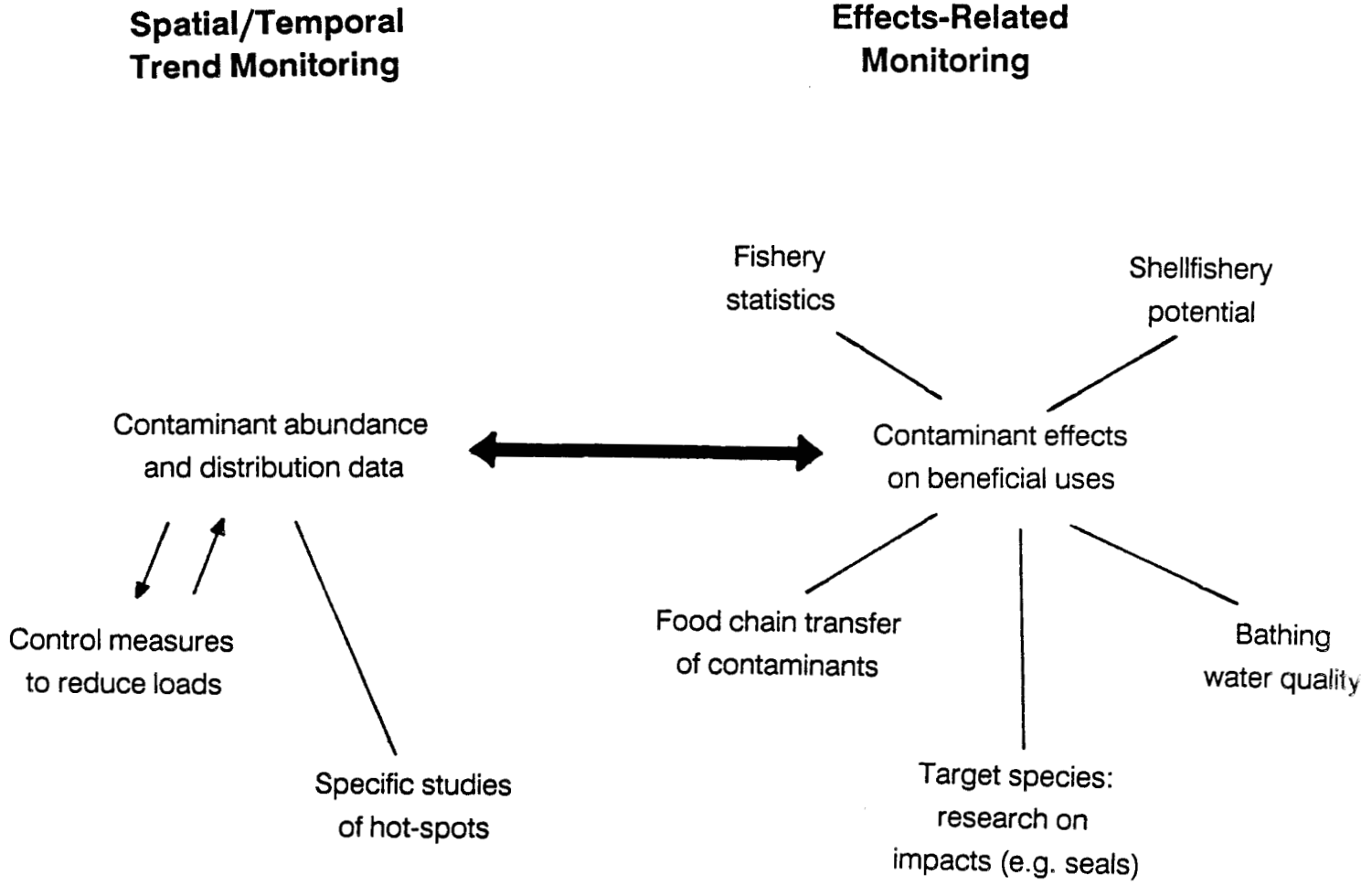


knowledge of the spatial and temporal distributions of contaminants in the Bay-Delta and its upstream catchment. Similarly, the success or otherwise of these controls can best be measured through the continued monitoring of the spatial distributions of contaminants in the system with time.

However, such monitoring does not in itself provide direct information on the adverse impacts of contaminants on beneficial uses, and in many cases this is also needed as an input to management decisions on the needs for further pollution controls. The relationship of these effects-related studies to spatial/temporal trend monitoring is depicted in Figure 2. It is important to understand that effects-related studies are only likely to be successful if a robust and consistent program to monitor spatial and temporal variations in contaminant abundance in the estuary exists. The need for spatial/temporal monitoring of contaminants in the estuary is thus seen as a critical first step in understanding and controlling the abundance and effects of toxic contaminants in the estuary and its catchment.

It is recommended that the spatial/temporal monitoring program proposed in this report be adopted as the basis for future work on the control of contaminants in the San Francisco Estuary and its catchment. In addition, however, it is recommended that further proposals be developed for effects-related studies in the estuary, with the principal goal of developing a monitoring/research program to study the impacts of contaminants on beneficial uses. This effects-related program should include those components shown in Figure 2, and should be designed to dovetail to the spatial/temporal monitoring program proposed herein.

Figure 2. Pictorial representation of the relationship between contaminant abundance, distribution and bio-availability (as monitored by spatial/temporal trend monitoring programs) and the adverse impacts of contaminants on beneficial uses in the Bay and Delta (as would be studied by effects-related monitoring programs).



C. Goals and Contents of This Report

Report Goals

The principal goals of this report are to:

- Provide recommendations on the most appropriate methods for spatial/temporal trend monitoring of contaminants in the San Francisco estuary, based upon a review of the international literature.

- Critically review the existing monitoring programs in the Estuary which attempt to delineate spatial and temporal trends in contaminants (either as a specific goal or as a spin-off). The principal existing programs of this type are the State Mussel Watch Program and the Toxic Substances Monitoring Program.

- Propose a new program for the elucidation of spatial and temporal trends in contaminant abundance, distribution and bio-availability in the San Francisco Bay-Delta and its catchment.

In addition, the report indicates areas of interface between the existing and proposed spatial/temporal trend monitoring scheme and other monitoring or research efforts.

Report Contents

This report consists of the following discrete but inter-related sections:

o Section II: A broad-based review of the international literature on the monitoring of toxic contaminants in estuaries is provided in section II. This review concentrates on the methods which have been employed internationally to date to define the spatial and temporal abundance and bio-availabilities of contaminants in coastal waters. The use of bio-monitors is emphasized, as this technique is generally thought to provide the most cost-effective and reliable data relating to contaminant abundance and bio-availabilities in coastal environments. The most appropriate bio-monitors for

use in estuaries are defined; the proposed program for the San Francisco Estuary (see below) relies upon this review to define the present state of the art in monitoring.

o Section III: The toxicants of greatest concern in the San Francisco Estuary and its catchment are delineated in section III, based upon the current knowledge of contaminant abundance and distributions in the Bay and Delta. This serves to provide a focus for the remainder of the report, in that the monitoring of these "contaminants of greatest concern" is emphasized in the later sections. However, it is relevant here that certain contaminants of considerable toxicity (e.g. the carcinogenic members of the PAHs) have received very little study to date in the estuary, and the list of contaminants of concern is likely to require amendment from time to time, as further data become available on the Bay and Delta.

o Section IV: This section reviews major programs undertaken presently to monitor the regional abundance, bio-availabilities and effects of toxic contaminants in the estuary. Data for water, sediment and biota are discussed separately. It is noted here that the separation of data points into those pertaining to "regional" conditions and those reflecting "local" environmental quality is largely arbitrary, particularly in situations where the link between pollutant sources and "background" levels in the estuary has been inadequately characterized by previous studies. In this review, data points on contaminant levels in water, sediments or biota at various sites are considered to reflect the "regional" abundance of such contaminants unless it has been clearly demonstrated that one or more specific known source of toxicants is responsible for locally elevated levels at those sites. It is acknowledged that this definition is restrictive. However, the general paucity of studies relating individual sources of toxicants to the "ambient" or "background" levels in the Bay and Delta does not permit a more rigorous definition at this time, at least in most instances.

o Section V: Schemes employed in the past, or those used presently, to monitor the abundance and bio-availabilities of toxic contaminants on a local scale in the estuary are covered in section V. Following the previous definition of "regional" toxicant levels, this section is restricted mainly to the monitoring of effluents themselves (both for contaminant concentrations and for their effects, the latter through bioassays). The current practice of "self-monitoring" of point source effluents is discussed, and the cost-effectiveness of this practice is examined. Studies which

have attempted to define the near-field abundance or effects of contaminants close to specific outfalls in the Bay and Delta are reviewed. Alternative approaches which should be considered in investigations of contaminants in effluents themselves or close to outfalls are also discussed. The use of bio-monitors to delineate contaminant abundance and bio-availabilities through their bioaccumulation of toxicants is addressed.

o Section VI: Certain species in the estuary may be at particular risk from the impacts of toxic contaminants, due to their high bio-accumulation of toxicants, or because of their innate sensitivities. The current monitoring of contaminant abundance in possible target species of this type and in food chains is addressed briefly in section VI of the present report, and this type of monitoring is contrasted to the use of bio-monitors to identify the abundance and distributions of contaminants in the estuary and their changes with time.

o Section VII: It is the central theme of this review that little real progress will be made on the cost-effective control of toxic contaminants in the San Francisco Estuary unless spatial and temporal trends in their abundance and bio-availabilities can be adequately defined, and these trends related to contaminant sources in the Bay and Delta. Further, it is considered that such trends are not sufficiently well defined by the existing monitoring programs. Proposals for a cohesive coordinated monitoring program to augment, alter or replace the existing programs and to provide a basis for the future control of pollutants in the estuary are presented in section VII of this report.

o Section VIII: Literature cited throughout the report is listed in section VIII.

II. AVAILABLE METHODS FOR MONITORING TOXIC CONTAMINANTS IN ESTUARIES

A. Alternative Approaches: Water, Sediment, Biota

Monitoring of the abundance and distributions of toxic contaminants in estuaries could rely upon the quantification of those toxicants in the estuarine waters themselves, in the underlying sediments, or in organisms. These alternatives have been considered by several authors (Phillips, 1977a, 1980; Förstner, 1980; Prosi, 1981; Thomson *et al.*, 1984).

The Analysis of Natural Waters

It is now generally held that the analysis of water for toxic contaminants such as trace metals, organochlorines or hydrocarbons suffers from several disadvantages, as follows:

- The concentrations of trace metals in coastal waters are generally very low, ranging from the ng L^{-1} (part per 10^{12}) to the low μg L^{-1} (part per 10^{9}) range, depending on the element concerned. This has caused great problems in the accurate quantification of elements in natural waters. The avoidance of extraneous contamination has been particularly problematical, and only in recent years have reliable data become available, through the use of "ultraclean" sampling and analytical techniques (Patterson and Settle, 1976; Bruland *et al.*, 1977, 1978a, 1978b; Burnett and Patterson, 1980; Gordon, 1980; Stukas, 1986).

- The concentrations of persistent organic contaminants in estuarine or coastal waters are frequently even lower than those of metals, ranging from considerably less than 1 ng L^{-1} to several hundred times this amount in particularly contaminated situations (Goldberg, 1975a; Phillips, 1986). Most such contaminants are not present at significant concentrations in the aqueous phase, but are predominantly adsorbed to suspended particulates (e.g. Duinker and Hillebrand, 1979; Pavlou and Dexter, 1979; Clark *et al.*, 1988). Very few researchers even attempt to quantify the levels of such

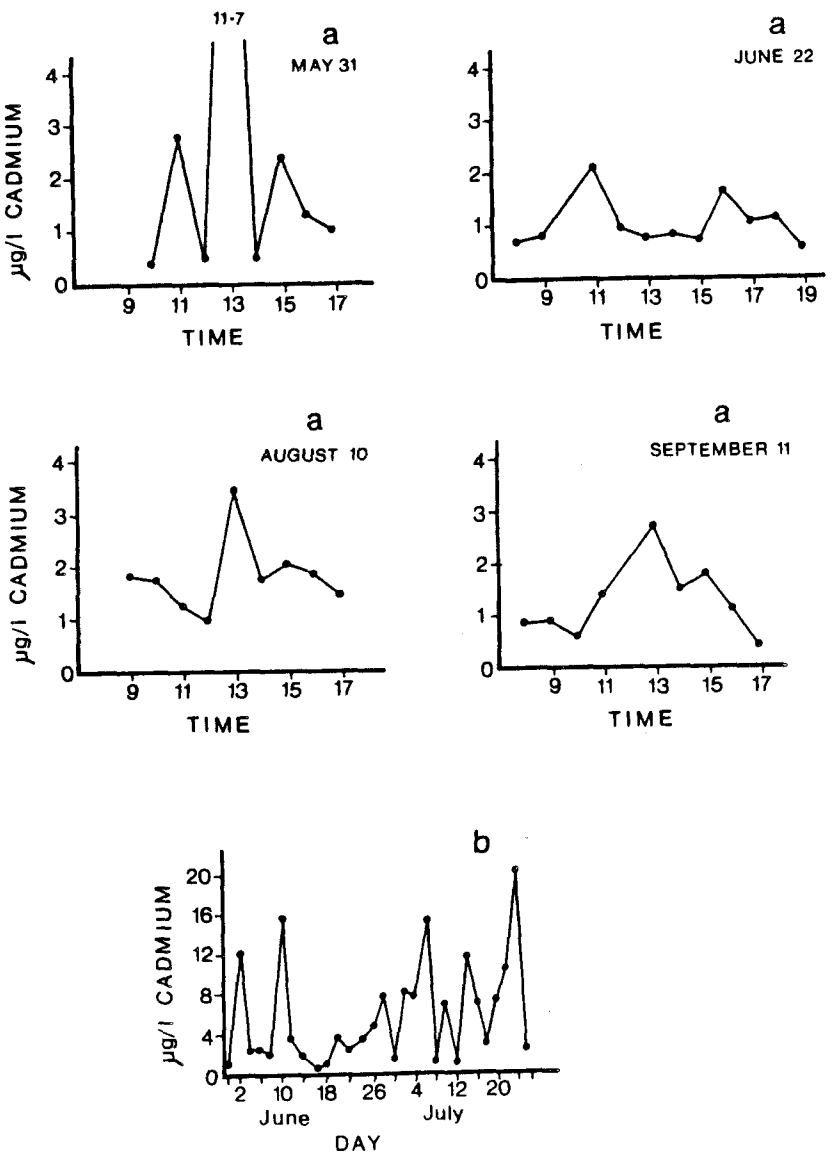
contaminants in natural waters because of the difficulties involved in the accurate analysis of such minute concentrations of toxicants.

- Even where these analytical problems can be solved, the concentrations of individual contaminants are usually found to be highly variable with time of sampling in coastal waters (Fukai *et al.*, 1975; Grimshaw *et al.*, 1976; Boyden *et al.*, 1979; Duinker and Hillebrand, 1979). An example of such temporal variability is shown in Figure 3. To adequately define average levels of metals, monitoring must account for this variability. This implies the use of time-integrating water samplers, or the extensive analysis of many samples, which is time-consuming and expensive.

- No definitive relationship exists between the levels of either "soluble" or "particulate" contaminants in natural waters (assigned to these categories empirically, through the use of a filtration step prior to analysis) and their availability to organisms (Phillips, 1980; Florence, 1982). Techniques to define the chemical speciation of contaminants such as metals in water and relate this to their bio-availability are in their infancy, and cannot be relied upon at present (Florence, 1982). Data on the relationship between the partitioning and speciation of organochlorines and hydrocarbons in water and their respective bio-availabilities are almost non-existent.

This creates problems not only for the use of waters to routinely define the distributions and abundance of contaminants, but also for the regulation of contaminant abundance in coastal waters through the use of water quality objectives. Such objectives have been developed by several regulatory agencies, generally through bioassay studies; the U.S. EPA has promulgated standards for both fresh and marine waters (EPA, 1986). The Basin Plan for the San Francisco Estuary (SFRWQCB, 1986) cites numerical objectives for several trace elements, although no such objectives are cited for persistent organic pollutants, with the exception of a 15 $\mu g\ L^{-1}$ objective (as a 24-hour average) for total PAHs in marine waters of the estuary. The direct monitoring of receiving waters for compliance with these objectives is an expensive practice. Relevant data of this type published to date for the estuary are reviewed later, in section IV of this report.

Figure 3. Examples of short-term and medium-term variation in the ambient concentration of a contaminant in the receiving waters of an estuarine system. (a) Concentrations of cadmium in solution and their variation with time of day on four different occasions in Poole Harbour, U.K. (b) Fluctuations in soluble cadmium levels over a two-month period at the same location, samples being taken every two days. Adapted from Boyden (1975), as shown by Phillips (1979a).



The Analysis of Sediments

Monitoring of toxic contaminants in coastal environments by the analysis of sediments offers several advantages over the use of water. Thus, sediments accumulate most or all such toxicants from the overlying water column and smooth out short-term variations, providing an improved measure of average contamination conditions. Sediment cores may also be useful in determining longer-term trends in contaminant abundance, although undisturbed areas of sediment are required for this purpose. However, problems exist in terms of several factors:

- Contaminant concentrations in sediments vary with particle sizes in the sediment sample. In some cases, this may be extreme. For example, Duinker and Hillebrand (1979) reported that the levels of PCBs in sediments from several locations in the Rhine-Meuse Estuary varied from <40 ng g^{-1} dry weight for the coarse fraction to between 2400 and 3400 ng g^{-1} dry weight for the fine fraction. Förstner (1980) discussed the effects of particle size on contaminant concentrations in sediments and also addressed techniques employed to circumvent this problem (none of which are ideal). While the use of sieved samples only partially overcomes the impact of particle size variations on concentration data, the use of corrections based on specific surface area shows greater promise (Mayer and Fink, 1980).

- Contaminant levels in sediments also covary with the organic carbon content of samples (Phillips, 1977a, 1980; Rice *et al.*, in press). Some authors have proposed that data for contaminants in sediments should be reported by reference to the amount of organic carbon present, rather than on the basis of sediment mass; however, there is no general consensus to the use of this approach, and some authors do not even quantify or report values for the organic carbon contents of sediments. The effects of organic carbon are thus difficult to eliminate from comparisons of data from different authors.

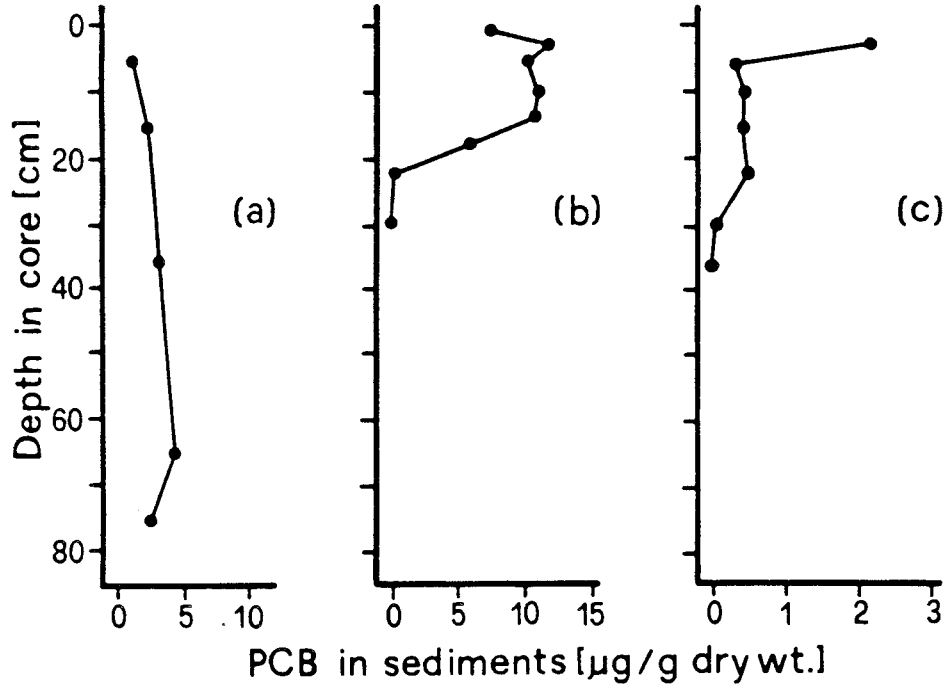
- Phillips (1977a, 1980) has argued that the concentrations of contaminants in sediments in coastal waters are a function not only of the ambient loads of contaminants themselves, but also of the rates of sedimentation. Unless the latter are known, the relative loading of pollutants to different portions of an estuary cannot be computed with accuracy.

- The concentrations of contaminants in sediments also commonly vary with depth of sampling of the sediment. This has been employed to provide a historical picture of contamination as noted above, but is also important in terms of its impacts on the sampling methods employed in sediment studies. Most methods of collecting sediments give rise to the loss of fine-grained surface material, which is often the most contaminated portion of the sample. The impacts of this (and of differences between studies in the depth of sediment taken for analysis) on data relating to sediment contamination may vary widely from site to site, as evidenced by the results shown in Figure 4. Long *et al.* (1988) considered this a significant factor influencing the interpretation of data on sediment contamination in San Francisco Bay (see section IV of this report).

- Sediments act as both sinks and sources of contaminants in aquatic environments (Ayling, 1974; Fowler *et al.*, 1978b; Luoma and Bryan, 1978; Elder *et al.*, 1979; Knezovich *et al.*, 1987). Although sequential leaching techniques recently introduced for the analysis of metals in sediments attempt to define the bio-availabilities of elements present in such materials (e.g. see Loring, 1981), there is no precise method to predict the degree of uptake of contaminants by biota from sediments.

It may be concluded here that the analysis of sediments is a useful tool to indicate the general abundance of contaminants in aquatic environments, and is particularly useful in local studies, where gradients of contamination may be investigated. However, the impacts of sampling methods, grain size and organic carbon, and the lack of any strict relationship between sediment-bound contaminants and their bio-availability are major drawbacks to the use of sediments (at least in isolation) for routine monitoring purposes. Pleas for the standardization of methods employed to study contaminants in sediments (e.g. de Groot *et al.*, 1982) have unfortunately fallen on deaf ears in most instances to date.

Figure 4. Examples of the variation in concentrations of a contaminant in sediments with depth of sampling. Data refer to PCBs in sediments of (a) New York Harbor; (b) the Hudson River, 83 miles upstream of Manhatten Island; (c) the Christaensen Basin in the New York Bight. Adapted from West and Hatcher (1980) and Bopp *et al.* (1981), as shown in Phillips (1986).



The Analysis of Biota

These problems with the use of water and sediments in monitoring contaminants in aquatic environments have given rise to a revolution in the field, involving an increased dominance of monitoring using biota. The uncertainties surrounding the chemical speciation of contaminants and the effects of this on bio-availability (Nelson and Donkin, 1985) are short-circuited by the use of organisms to quantify toxicants, as any contaminants present in the tissues of biota are by definition bio-available (Phillips, 1977a, 1978b, 1980). As Waldichuk (1985) stated:

"....there is no true substitute for chemical analysis of the tissues of exposed marine organisms for metal concentrations, if one wishes to determine the biological availability of metals at a given site."

Organisms employed to quantify pollutant abundance or bio-availability by virtue of their tissue concentrations of contaminants have been referred to in the literature by several generic terms. These include "bio-indicators" (also employed in other senses, to refer to species whose presence or absence in certain environments is indicative of the impacts of pollution or other factors), "sentinel organisms", and "bio-monitors". The latter term will be employed in the present report. The remainder of this section reviews the available literature on bio-monitors, and provides conclusions on the most appropriate organisms for study.

B. Bio-monitoring Techniques: Early Development

Organisms were first employed for routine monitoring of pollutants in coastal waters in the early 1960s, to study radionuclides. A need was identified to monitor isotopes released from the Hanford reactors to the Columbia River (in cooling water effluents), and those in coastal waters further afield, in California. The analysis of water samples for this purpose was exceptionally challenging and cumbersome, demanding huge sample volumes (up to 2000 litres for some nuclides) and often yielding barely detectable concentrations of the isotopes of interest (^{54}Mn, ^{60}Co and ^{65}Zn). However, the analysis of phytoplankton and euphausiids (Osterberg *et al.*, 1963, 1964) and of macroalgae, mussels, barnacles, and other species including fish (Folsom *et al.*, 1963; Folsom and Young, 1965) permitted the quantification of these radionuclides fairly simply. Later studies (Young and Folsom, 1973) favoured the use of mussels (*Mytilus edulis* and *M. californianus*) and barnacles (*Lepas anatifera* and *Pollicipes polymerus*) in particular, as these species heavily accumulated the isotopes of interest.

The mid- to late-1960s saw an increase in the use of biota (especially bivalve molluscs) in monitoring programmes. Butler (1966, 1969, 1973) headed an ambitious eight-year investigation in the USA, using several bivalve species to quantify pesticide contamination of coastal waters. In the United Kingdom, a bird kill incident in the Irish Sea in 1969 gave rise to the birth of monitoring programmes using shellfish and finfish species to quantify both pesticides and trace metals (Holden and Portmann, 1970; Portmann, 1971; Holden, 1973). Certain of these investigations have continued to date, and have been extended into international programs (Murray and Portmann, 1982).

Despite the commencement of such monitoring programmes, very little was then known about the mechanisms of uptake and excretion of the contaminants studied by the species used as bio-monitors. Such data became available slowly through the 1970s, and research continues to the present. This phase of the revolution in the monitoring of metals in aquatic environments has served to hone and improve the techniques employed, both in the sampling and analytical arenas.

C. Improvements and Important Concepts

The use of an aquatic organism as a bio-monitor of toxic contaminants in coastal waters is defensible only when it can be clearly shown that the resulting picture of environmental contamination (either in a spatial or temporal sense) is real, i.e. truly reflects ambient conditions, rather than depending on some physiological or other quirk of the species employed. Several authors have developed a list of pre-requisites for a species to be a useful bio-monitor (Butler *et al.*, 1971; Haug *et al.*, 1974; Phillips, 1977a, 1980). These pre-requisites may be summarised as follows:

- Bio-monitors should be sessile or sedentary, thus being representative of the study area.
- Bio-monitors should be hardy, tolerating high levels of pollutants and large ranges in salinity, and permitting laboratory studies of pollutant kinetics.
- Bio-monitors should be abundant in study areas, easy to sample, and provide sufficient tissue for analysis of the contaminants of interest.
- A simple correlation should exist between the pollutant concentration found in the tissues of a bio-monitor and the average ambient bio-available pollutant concentration. This correlation should be the same at all study sites.

It is unfortunate that many studies to date have lost sight of these basic essential pre-requisites. To generate an accurate estimate of environmental contamination using bio-monitors, it is not sufficient to simply collect and analyse previously-unstudied species, or to analyse any and all organisms available at a study site. Certain organisms offer particular advantages (because they conform well to the above pre-requisites), and it is these species which should be employed in bio-monitoring studies.

Perhaps the most important property of a bio-monitor is that it must not heavily regulate its accumulated tissue levels of pollutants. The propensity of species to regulate metals varies with the element concerned, and both between and within phyla. For example, decapod crustaceans are known to regulate their internal tissue concentrations of the metals copper, manganese and zinc (Bryan, 1964, 1967, 1968, 1971, 1976; White and Rainbow, 1982, 1984a; Rainbow, 1985a; Nugegoda and Rainbow, 1987, 1988). However, other elements such as cadmium are not subject to such regulation (Jennings and Rainbow, 1979b; White and Rainbow, 1982, 1986). The differences here may relate

to whether metals are essential in nature or otherwise, as this may define whether mechanisms to regulate metals in the tissues have evolved to ensure continued health of the organism.

By complete contrast to the decapod crustaceans, barnacles do not appear to metabolically regulate any of the metals (Walker *et al.*, 1975a, 1975b; Walker, 1977), and in fact accumulate many elements to very high absolute concentrations. Macroalgae are in general thought to be passive accumulators of metals, and most bivalve molluscs are also poor regulators of their body load of elements (Bryan, 1971, 1976; Phillips, 1977a, 1980; Simkiss *et al.*, 1982). However, even here, certain exceptions exist. Thus, a few bivalve species have been found to regulate their net uptake of zinc into soft tissues (Phillips and Yim, 1981; Klumpp and Burdon-Jones, 1982; Phillips, 1985; Chan, 1987).

These varying degrees of regulation of tissue metal levels undoubtedly relate closely to the evolution of metal sequestration strategies in different phyla (Walker *et al.*, 1975b; Roesijadi, 1980-81), which is a fascinating area for future research. However, the relevance here of such regulatory mechanisms is simply that their existence nullifies the possibility of employing certain species as efficient and accurate bio-monitors of metal contamination in aquatic environments.

Regulation *per se* (i.e. the metabolic restriction of concentrations to a defined range) of organochlorines and hydrocarbons by aquatic organisms is not thought to exist; rather, these contaminants are generally believed to be taken up passively by lipid-water partitioning (at least in lower organisms), their resulting concentrations being a direct function of their ambient levels in the environment and the amount of lipid in the tissues of the organism involved (Phillips, 1980). However, at least some of these contaminants are metabolized by organisms (generally in the liver), and this serves to reduce the body loads of such pollutants after their uptake in episodic exposure situations.

Phillips (1977a, 1978b, 1980) has also emphasized the importance of the *rates* of uptake and excretion of contaminants by bio-monitors, as these kinetics define the period over which such species reflect the ambient pollution conditions. If uptake and excretion rates are slow, the contaminant concentrations present in the tissues of bio-monitoring species will be indicative of the average bio-availability of those contaminants over a long period. By contrast, species which exhibit rapid turnover of

contaminants will reflect only recent pollution conditions. Surprisingly little information is available on contaminant kinetics in most bio-monitors, and those data which are published are frequently based on laboratory studies of pollutant uptake (mostly from solution). These often do not adequately mimic contaminant kinetics in the field (Fowler *et al.*, 1975, 1978a), presumably because the contaminants are taken up into different tissues and/or cellular sequestration sites (from which they are lost at different rates) in the two situations.

Despite this dearth of high-quality information, it is generally held true that metals exhibit relatively long half-lives in most bio-monitors compared to most organochlorines or hydrocarbons (Phillips, 1980; NAS, 1980; Phillips and Segar, 1986). This relatively slow excretion of metals by bio-monitors simplifies the design of monitoring studies for metals using such species, and reduces the need for multiple sampling with time (either by several discrete studies at different times, or using "time-bulking" methodology; see Phillips and Segar, 1986), which is required for studies of some other contaminants with much shorter half-lives (e.g. Tanabe *et al.*, 1987) This is also the case where seasonal fluctuations in metal concentrations in bio-monitors are minor (Goldberg *et al.*, 1978; NAS, 1980). However, in certain locations, large temporal fluctuations in metal uptake by bio-monitors may occur (e.g. Phillips, 1976a; Simpson, 1979; Satsmadjis and Voutsinou-Taliadouri, 1983; Luoma *et al.*, 1985), due to variations in ambient metal levels or to physiological changes in the species employed; in these instances, sampling must be particularly carefully designed if average metal bio-availabilities are to be measured accurately.

The movement or migration of a bio-monitor causes great problems for the interpretation of data in monitoring programmes. Thus, for example, contaminant levels in fish are a complex function of their exposure in space and time to pollutants, and these variables cannot be separated (Phillips, 1977a, 1978b, 1980). Many invertebrates move little, if at all, during their adult life, although some species of decapod crustaceans (and even certain bivalves, such as particular scallop species) may move considerable distances in estuarine and coastal waters. The use of species which exhibit significant movement or migration as bio-monitors is generally not defensible, at least in programs designed to establish spatial trends in contaminant abundance (Phillips and Segar, 1986).

Finally here, it should be noted that programmes employing bio-monitors to measure contaminant bio-availabilities in aquatic environments generally seek to identify significant differences in toxicant abundance between samples from different sites, or between those taken at the same location at different times. The identification of such spatial and/or temporal differences is only efficiently accomplished if the variation between the contaminant concentrations exhibited by the individuals sampled at any one site and time is minimized. The sources of variability and the residual "inherent variability" of contaminants within populations of bio-monitors have been analyzed and discussed by several authors (Stephenson *et al.*, 1978; Gordon *et al.*, 1980; NAS, 1980; Phillips, 1980; Phillips and Boyden, 1981; Wright *et al.*, 1985; Lobel, 1986). Sampling regimes to reduce within-site variability in metal concentrations in bio-monitors have been proposed (Phillips, 1976b), and the number of individuals required in any one sample for analysis has been discussed (Gordon *et al.*, 1980; NAS, 1980; Wright *et al.*, 1985). The data of Gordon *et al.* (1980) are particularly useful in the design of sampling programs, although it should be noted that the inherent variability of metals in bio-monitors varies between species, sites, and with the element concerned (Phillips, 1980; Wright *et al.*, 1985).

D. Review of Bio-monitoring Organisms

Macroalgae

Marine and estuarine macroalgae have long been known to concentrate metals to levels many times those found in the surrounding waters (Jones, 1922; Black, 1948a, 1948b, 1949; Black and Mitchell, 1952; Haug, 1959). This is believed now to be due to their accumulation of metals by both passive and active processes, involving ion exchange-types of binding to surface polysaccharides as well as metal sequestration within membrane-limited vacuoles rich in polyphenols (Haug and Smidsrød, 1965; Bryan, 1969; Skipnes *et al.*, 1975; Ragan *et al.*, 1979; Veroy *et al.*, 1980).

The binding of metals by macroalgae was shown by Bryan (1969) to be strong, with only minimal exchange between bound metals and ambient waters. Most metals were thought to be taken up in proportion to their external concentration (Bryan, 1969, 1971, 1976), and this lack of regulation gave rise to the possibility of the use of these seaweeds as bio-monitors.

Early studies of macroalgae as monitors of metals in coastal environments were mainly restricted to the United Kingdom (Butterworth *et al.*, 1972; Nickless *et al.*, 1972; Preston *et al.*, 1972; Bryan and Hummerstone, 1973a; Fuge and James, 1973, 1974). In a few instances in later studies in particular, direct comparisons between metal levels in waters and those in macroalgae were undertaken, and these generally provided encouraging results. Seeliger and Edwards (1977) found close correlations between dissolved levels of copper and lead in the waters of Raritan Bay near New York and concentrations of these elements in four species of algae. Morris and Bale (1975) produced similar data for cadmium, copper and zinc in solution and in *Fucus vesiculosus* from the Bristol Channel. However, the relationship for manganese in the latter studies was poor, and the alga was thought to partially regulate this element.

More recent studies have provided further insight into the extent of the usefulness of macroalgae to monitor metals in aquatic environments. These species essentially respond to metals present in solution in the ambient waters (Bryan, 1969; Phillips,

1977a). As a result, spatial trends in contamination provided by data on metal concentrations in macroalgae may not match those found for other species such as bivalve molluscs, which respond not only to metals in solution but also to those in suspension, adsorbed to inorganic particulates, or in phytoplankton food (Bryan and Hummerstone, 1977; Phillips, 1977b, 1978a, 1979b).

The details of sampling of macroalgae for metal studies are also important. Metal concentrations vary in different portions of the plant, generally being higher in older parts of the alga and least in fast-growing tips (Bryan, 1969, 1971; Haug *et al.*, 1974; Bryan and Hummerstone, 1973a; Fuge and James, 1973, 1974). This is believed to be a function of the strong binding of metals by macroalgae, giving rise to increased element concentrations with age (Bryan, 1971; Young, 1975; Phillips, 1980). Some authors have suggested that this may be advantageous, permitting the contamination history to be identified at any given location through the analysis of different portions of the alga, each of different age (Myklestad *et al.*, 1978; Eide *et al.*, 1980).

However, other authors (Phillips, 1977a, 1980; Rice and Lapointe, 1981) have proposed that the impacts of growth on metal levels in macroalgae are detrimental to the use of these species as efficient bio-monitors. Phillips (1977a, 1980) suggested that the known impacts of many variables [portion of the plant analysed, season, light intensity, temperature, possibly shore position (related to degree of submergence; see Schonbeck and Norton, 1979)] on metal concentrations in macroalgae were likely to be mediated at least in part through changes in the growth rates of the plants. Given this assumption, he proposed that any factor which tended to alter growth rates of macroalgae (light intensity, turbidity, nutrient availability, etc.) would interfere with the accuracy of inter-site comparisons of metal levels in these species, i.e. that concentrations of elements exhibited by macroalgae were a function not only of metal availability from solution, but also of plant growth rate at any particular site (Burdon-Jones *et al.*, 1982). Rice and Lapointe (1981) reached the same conclusion, based on laboratory studies of the net uptake of several trace elements by *Ulva fasciata*. This problem has not been solved to date, but is a potential major interference in the use of macroalgae as bio-monitors in coastal environments.

Other problems also exist in employing macroalgae to monitor trace metals in coastal waters. One practical problem concerns the surface contamination of algae by

metals associated with fine particulate material. Several authors have found that such material is difficult to eliminate by washing prior to analysis, and interferes with the quantification of metals actually present in the plant tissues (Bryan and Hummerstone, 1977; Romeril, 1977; Aulio, 1983; Barnett and Ashcroft, 1985). This problem is particularly prevalent for metals which are heavily associated with particulates in coastal waters, such as iron, lead and chromium.

Phillips (1977a, 1980) has reviewed published data on the existence of interactions between metals in macroalgae, and also discussed the impacts of such effects on the use of bio-monitors. Bryan (1969) showed that the uptake of ^{65}Zn by the brown alga *Laminaria digitata* in the laboratory could be reduced by additions of cadmium, copper, or manganese to the external medium. Foster (1976) found that the exceptionally heavy contamination of waters of Dulas Bay in Anglesey, Wales, was not reflected by metal levels in *Fucus vesiculosus* or *Ascophyllum nodosum* for all elements. It appeared that the uptake of large amounts of copper and zinc by these species at the polluted location reduced the accumulation of other elements, perhaps through the saturation of available binding sites. These two examples involve unusually high concentrations of metals in solution, much greater than those normally found in coastal waters. It is not known whether such metal interactions occur at lower ambient exposure concentrations.

The toxic effects of metals on macroalgae may also influence their ability to act as efficient bio-monitors in certain instances. Most elements are not significantly toxic to macroalgae at concentrations likely to be present in coastal waters (Markham *et al.*, 1980); however, copper is an exception to this general rule. Copper is unusually toxic to algae (Bryan, 1969; Strømgren, 1979) and in certain species, adaptive mechanisms have evolved to deal with this. Such mechanisms include the extracellular release of compounds which chelate copper ions, the use of particular storage sites within the tissues to detoxify accumulated copper, and the active exclusion of copper by the plant. The last of these mechanisms would clearly interfere with any attempt to employ these species as bio-monitors of copper in aquatic environments, and is effectively a case of metal regulation. Hall *et al.* (1979) have provided evidence for such an exclusion of copper in the marine fouling alga *Ectocarpus siliculosus*, which occurs in both copper-tolerant and copper-sensitive strains (only the former exhibiting the exclusion mechanism). By contrast, Reed and Moffat (1983) found that copper-tolerant isolates of

Enteromorpha compressa did not rely on exclusion of the metal, but on internal detoxification of copper subsequent to its normal uptake. These examples are extreme, in that the species concerned are fouling organisms found on vessels employing copper-based anti-fouling paints. There is no evidence to date that such adaptive mechanisms have evolved in macroalgae in more normal coastal environments.

It may be concluded that, despite the existence of significant unsolved problems concerning the use of macroalgae as bio-monitors of metals in estuaries and other coastal waters, these species continue to be of benefit for such purposes. Wide-ranging studies in Europe and elsewhere continue to be reported (e.g. Bradfield *et al.*, 1976; Cullinane and Whelan, 1982; Woolston *et al.*, 1982; Langston, 1986; Sawidis and Voulgaropoulos, 1986), and even deep-water species have been employed as bio-monitors of metals recently (Sears *et al.*, 1985). Interestingly, several relatively recent studies have also reported the use of macroalgae to monitor the abundance of rare types of radionuclides in coastal waters (Cross and Day, 1981; Jeanmaire *et al.*, 1981; Topcuoglu and Fowler, 1984; Guimaraes and Penna-Franca, 1985). This application is reminiscent of the early development of bio-monitors (see above), and the driving forces for such studies are no different today to those existing over two decades ago.

By contrast to the relatively widespread use of macroalgae as bio-monitors of trace elements in coastal waters, their use to monitor persistent organic contaminants has been very rare (Phillips, 1980). This is probably because macroalgae exhibit very low levels of lipid, and therefore do not accumulate large quantities of hydrophobic contaminants such as organochlorines or hydrocarbons.

Crustaceans

As noted previously, the metabolic handling of metals differs radically between decapod crustaceans and barnacles. These two groups will therefore be considered separately here.

Decapod Crustaceans: Early studies by Bryan (1964, 1967, 1968, 1971, 1976) were instrumental in demonstrating that the metals copper, manganese and zinc are subject to metabolic regulation in the tissues of decapod crustaceans, as well as by

amphipods. These investigations have been extended recently (Jennings and Rainbow, 1979a, 1979b; Jennings *et al.*, 1979; Rainbow and Scott, 1979; White and Rainbow, 1982, 1984a, 1984b, 1986, 1987; Rainbow, 1985a; Bryan *et al.*, 1986; Rainbow and Moore, 1986; Nugegoda and Rainbow, 1987, 1988). It is now accepted that although several factors (such as moulting, temperature and animal size) may interfere with the concentrations of these three elements in decapod crustaceans, there is no correlation between tissue concentrations of copper, manganese and zinc in these species and their levels in the ambient seawater (Phillips, 1980; Rainbow, 1985b). While the regulation of zinc can be overcome by exposure to very high concentrations of zinc in solution (100 $\mu g\ L^{-1}$ or greater), this is most unlikely to occur in the environment. As a result, decapod crustaceans cannot be employed as bio-monitors of these metals with useful results, despite attempts to the contrary (e.g. Balkas *et al.*, 1982; Satsmadjis and Voutsinou-Taliadouri, 1983; Sanders, 1984; Frenet and Alliot, 1985).

By contrast to this regulation of copper, manganese and zinc by decapod crustaceans, at least some other metals are accumulated in proportion to environmental exposure. Cadmium is one of these (see references cited above and O'Hara, 1973; Hutcheson, 1974; Fowler and Benayoun, 1974; Wright, 1977a,1977b,1977c; Chou *et al.*, 1978; Davies *et al.*, 1981; Brouwer *et al.*, 1984; Uthe *et al.*, 1986). Considerable attention has been given to cadmium in decapods because the element levels present in some species are sufficiently high to be potentially hazardous to human health (MAFF, UK, 1973; Friberg *et al.*, 1974; Uthe *et al.*, 1986). Other non-essential metals accumulated by decapods in proportion to external concentrations include lead (Hopkin and Nott, 1979), mercury (Ray and Tripp, 1976), and vanadium (Miramand *et al.*, 1981; Unsal, 1983).

Despite this, decapods have been little-used as bio-monitors of trace metals. This is largely due to the impacts of external variables on their uptake of metals. For example, the accumulation of cadmium by both crabs and prawns is heavily affected by salinity. Much of the metal taken up by these crustaceans is adsorbed to or bound in the exoskeleton, and moulting significantly affects the amounts of some metals present in the tissues. Animal size is also known to determine metal concentrations in at least some species. In addition, neither crabs nor prawns can be considered to be truly sedentary species; there is thus no guarantee that metal concentrations present in individuals taken from a given site accurately reflect the element bio-availability at that location. It is

concluded that decapod crustaceans are not suitable as bio-monitors of metals in coastal waters, at least in most instances.

Like macroalgae, decapods have been very little used as bio-monitors of persistent organic contaminants. However, Modin (1969) and Haughen (1983) analyzed Dungeness crabs (*Cancer magister*) from San Francisco Bay for organochlorines, and Guard *et al.* (1983) supplemented these results with data for hydrocarbons in the same species. Burnett (1971) and Heesen and McDermott (1974) used crabs to study organochlorine uptake in the Palos Verdes area of southern California. These limited investigations suggest that decapod species have potential as bio-monitors of such compounds, but further work is required to confirm this.

Barnacles: The accumulation and sequestration of metals by barnacles offers a direct contrast to the processes described above for decapod crustaceans (Phillips, 1980; Rainbow, 1985b, 1987). Early studies of radionuclide uptake by barnacles (cited above) showed these organisms to accumulate isotopes to high concentration, and later investigations of stable metals have confirmed this tendency. Ireland (1973, 1974) published some of the initial work on metals in barnacles, using *Balanus balanoides*. It was shown that this species accumulates greater amounts of zinc than those found in mussel (*Mytilus edulis*) tissues by at least an order of magnitude, and that concentrations of copper, lead, manganese and zinc vary considerably with season in *B. balanoides*.

Further studies by Walker *et al.* (1975a,1975b) and Walker (1977) on several species of barnacles (*B. balanoides*, *Elminius modestus* and *Lepas anatifera*) confirmed the unusually high accumulation of metals by these organisms, and showed that both copper and zinc were sequestered in granules in gut parenchyma cells (Brown, 1982); these studies were later extended by the use of X-ray microanalysis techniques (White and Walker, 1981). It was suggested on the basis of comparisons of contamination levels of barnacles at various sites with those of other species that barnacles might be useful bio-monitors of zinc in coastal environments (Walker *et al.*, 1975a).

While other studies have also generally concluded that barnacles exhibit many of the pre-requisites to act as efficient bio-monitors of metals in aquatic ecosystems (Barbaro *et al.*, 1978), surprisingly little use has been made of these species for such

purposes. Similarly, although some data are available on the uptake and depuration of metals in barnacles (Rainbow *et al.*, 1980; van Weerelt *et al.*, 1984), they have been largely ignored in laboratory investigations. This is unfortunate, and there is scope for further work on the use of barnacles as bio-monitors.

It is relevant here that Ireland (1973) reported differences between the profiles of contamination for zinc at several locations, based on either analyses of *B. balanoides* or mussels (*Mytilus edulis*). This suggests that the two bio-monitors respond to different portions of the total metal load in the environment, i.e. that the bio-availabilities of zinc in distinct forms in coastal waters differ to the two species. Recent studies (Chan *et al.*, in press; Phillips and Rainbow, in press) of three species of barnacles and the mussel *Perna viridis* in Hong Kong waters (in which well-defined gradients in metal pollution have been demonstrated) have generally not shown such subtleties; the contamination profiles exhibited by all four species matched well for most metals studied. Barnacles are thus thought to have considerable potential as bio-monitors of metals in coastal waters, and deserve further attention.

Gastropod Molluscs

Gastropod molluscs have been much less extensively studied as potential bio-monitors in aquatic ecosystems than have bivalve molluscs. Nevertheless, many gastropods conform well to at least some of the pre-requisites for a species to be a useful bio-monitor. Almost all data reported to the present concerns trace metals; very few studies on persistent organic contaminants have been reported.

The earliest monitoring studies using gastropods were undertaken in the Bristol Channel, UK, and employed both transplanted and native dog whelks (*Nucella lapillus*) and limpets (*Patella vulgata*); see Nickless *et al.*, 1972; Peden *et al.*, 1973; Stenner and Nickless, 1974. These investigations showed that gastropods steadily accumulated metals when transferred from relatively unpolluted locations to the contaminated study area, and that the subsequent excretion of metals was slow when the organisms were kept in clean water. Both animal size and the shore level at which the samples were taken were found to affect metal concentrations in the soft tissues. Later studies have also noted size to be an important variable influencing metal levels in gastropods (Boyden, 1974, 1977; Bryan *et al.*, 1977), and one interesting study of cadmium in the

land snail *Cepaea hortensis* has attempted to differentiate between the effects of size and age on levels of this element (Williamson, 1979).

While several authors have simply assumed that gastropod molluscs are efficient bio-monitors of metals in aquatic environments (e.g. Navrot *et al.*, 1974; Ramelow, 1985), there is evidence for at least partial regulation of certain metals in some species. Young (1975) postulated that the winkle *Littorina obtusata* was able to partially regulate its tissue content of zinc when fed macroalgae of differing degrees of contamination. Both Anderlini (1974) and Bryan *et al.* (1977) provided evidence for the regulation of zinc in abalone of the genus *Haliotis*. It might also be suspected that copper may be regulated in gastropods, given its central importance in the respiratory pigment haemocyanin. However, the evidence for this is equivocal. Betzer and Pilson (1974, 1975) considered that the channeled whelk *Busycon canaliculatum* regulated copper poorly, if at all, while Martoja *et al.* (1980) reported that the whelk *Littorina littorea* accumulated copper as its sulphide with age in the tissues, and that this was independent of environmental exposure to the metal. There is little evidence for the regulation of non-essential metals in gastropods (e.g. see Harrison *et al.*, 1987).

Studies of the uptake of zinc and iron by *Littorina obtusata* concluded that the accumulation of metals from food is important in determining their concentrations in gastropods (Young, 1975). Gastropod species differ considerably in their preferred diet, some being herbivorous (e.g. *L. littorea*, feeding mainly on species of *Fucus* and other algae) and others carnivorous (e.g. *Thais lapillus*, which feeds mostly on barnacles). In situations where comparative levels of metals in solution do not bear a consistent relationship to those associated with particulates at all locations, this introduces differences into the contamination profiles displayed by such species (Phillips, 1980). Thus, Ireland and Wootton (1977) noted that contaminant profiles generated from the analysis of *L. littorea* and *T. lapillus* at nine sites on the coast of Wales did not match. Other authors have reported similar data for other species (Bryan and Hummerstone, 1977; Langston, 1986). This is reminiscent of the differences between spatial trends in metal levels produced by studies of macroalgae and bivalve molluscs, discussed above. As noted by Phillips (1980), such differences do not negate the possibility of using these species as bio-monitors; rather, spatial trends in contamination should be compared with a knowledge of the dietary habits of species as a basis for interpretation.

Several extraneous factors (in addition to animal size, discussed above) are known to influence the concentrations of metals present in gastropod molluscs, and these should be considered if such species are to be employed as bio-monitors. Flegal and Martin (1977) have emphasized the importance of depuration of some species prior to analysis, as metals present in ingested sediment (or in particulates trapped in the mantle cavity) may interfere significantly with analytical data. Seasonal changes in metal concentration may also be considerable, and these variations may be due either to changes in the ambient concentrations of metals (Romeril, 1977) or to the effects of gametogenesis and spawning (Betzer and Pilson, 1974, 1975). Finally, a case of metal interactions has been reported by Nelson *et al.* (1983), in which the uptake of copper by slipper limpets (*Crepidula fornicata*) was enhanced by the co-presence of silver.

It may be concluded that the presently available information on the kinetics of contaminants in gastropod molluscs is sparse, and is generally insufficient to enthusiastically recommend such species for use as bio-monitors of toxicants in coastal waters. The existence of at least partial regulation of some of the essential metals is particularly notable, and to some extent parallels the situation in decapod crustaceans.

Bivalve Molluscs

Bivalve molluscs have been more frequently employed as bio-monitors of contaminants in aquatic environments than have species of any other family or phylum, and the available literature on their use for such purposes is considerable. Most studies have been carried out in temperate rather than tropical waters, although the latter areas have received greater attention recently, concomitant to the increased urbanization and industrialization of tropical nations, and their greater use of pesticides (all of which threaten the health of their coastal resources; see Goldberg, 1975a). Reviews of the use of bivalves as bio-monitors of aquatic pollutants have been produced by several authors (Phillips, 1980; Bryan *et al.*, 1980, 1985); the present paper largely concentrates upon more recent data, using these reviews as a basis to describe the older material.

Studies of the uptake, sequestration and excretion of contaminants in bivalves have been very extensive; selected data sources are listed in Table 4. These studies have provided a firm basis for the evaluation of the usefulness of bivalves as bio-monitors of toxicants in aquatic ecosystems. In general, the uptake of contaminants has

Table 4. Selected literature on studies of contaminant uptake, sequestration and excretion in bivalve molluscs. (See also references cited in the text).

Author(s)	Subject
George *et al.*, 1978	Cu and Zn in oysters, *Ostrea edulis*
Langston, 1978	PCBs in bivalves
D'Silva and Qasim, 1979	Cu in the oyster *Crassostrea cucullata*
Engel and Fowler, 1979	Review of Cd in bivalves
Zaroogian *et al.*, 1979	Pb in the oyster *Crassostrea virginica*
Carmichael *et al.*, 1980	Metals in the kidney of *Mercenaria mercenaria*
George and Pirie, 1980	Zn in the mussel *Mytilus edulis*
George *et al.*, 1980	Metals in the scallop *Pecten maximus*
Phillips, 1980	Review of bio-monitoring
Scholz, 1980	Cd in the mussel *Mytilus edulis*
Zaroogian, 1980	Cd in the oyster *Crassostrea virginica*
Burns and Smith, 1981	Hydrocarbons in mussels
Carmichael and Fowler, 1981	Cd in the scallop *Argopecten irradians*
Okazaki and Panietz, 1981	Metals in *Crassostrea gigas* and *C. virginica*
Beasley *et al.*, 1982	Technetium in *C. gigas* and *Mytilus californianus*
Brown, 1982	Review of sequestration of metals
Farrington *et al.*, 1982	Hydrocarbons in mussels, *Mytilus edulis*
Roesijadi *et al.*, 1982	Mercury in mussels
Simkiss *et al.*, 1982	Review of bioaccumulation and detoxification
Frazier and George, 1983	Cd in the oysters *C. gigas* and *Ostrea edulis*
Risebrough *et al.*, 1983	Hydrocarbons in mussels
Widdows *et al.*, 1983	Naphthalene in mussels, *Mytilus edulis*
Wilson, 1983	Ni in the cockle *Cerastoderma edule*
Pirie *et al.*, 1984	Metals in blood cells of oysters
Widdows *et al.*, 1984	Metals in mussels, *Mytilus edulis*
Harvey and Luoma, 1985	Metal uptake by *Macoma balthica*
Miller *et al.*, 1985	Mn and Zn in clams, *Mercenaria mercenaria*
Morse *et al.*, 1985	Cd in *M. mercenaria*
George *et al.*, 1986	Ag in mussels, *Mytilus edulis*
Tanabe *et al.*, 1987	PCBs in mussels, *Perna viridis*

been shown to be relatively rapid in bivalves and to reflect ambient exposure concentrations closely. Metals are sequestered both in granular form and bound to metallothioneins; the prevalence of each of these mechanisms of metal storage varies between elements and by species. The excretion of metals is thought to be generally slow, at least by comparison to most organochlorines or hydrocarbons (compare literature cited in Table 4 to Farrington *et al.*, 1982; Widdows *et al.*, 1983; Melzian and Lake, 1986/87; Tanabe *et al.*, 1987). It should be repeated here, however, that estimates of the half-lives of metals in biota generated from laboratory experiments are frequently unreliable indications of the situation in the field (Fowler *et al.*, 1975, 1978a). The best estimates of metal depuration rates are provided by transplantation of field populations of bivalves. Okazaki and Panietz (1981) provided an excellent example of this technique, and reported half-lives of 12 metals in *Crassostrea gigas* to range from 23 to 60 days, while the range for *C. virginica* was from 70 to 180 days. The rates of contaminant uptake and excretion by bivalves are important, as these define the period over which a species time-averages ambient concentrations of the contaminants (Phillips, 1977a, 1978b, 1980; NAS, 1980; Phillips and Segar, 1986). Certain authors have also provided insights into the effects of the chemical speciation of metals on their uptake by bivalves (e.g. Harrison, 1979; Crecelius *et al.*, 1982; Zamuda and Sunda, 1982; Zamuda *et al.*, 1985); however, these studies are in their infancy, and much remains to be discovered.

Most of the studies cited above on metal kinetics in bivalves have concluded that these species do not regulate elements in their tissues, but respond faithfully to changes in the ambient concentration of metals. However, a few isolated exceptions to this general rule are known; interestingly, these all involve zinc. Phillips and Yim (1981) reported that the mytilid *Septifer virgatus* (incorrectly named as *S. bilocularis* in the original paper) partially regulates its tissue concentrations of zinc in Hong Kong waters. Similar findings were later published for zinc in the hairy mussel *Trichomya hirsuta* from Australia (Klumpp and Burdon-Jones, 1982) and in green-lipped mussels (*Perna viridis*) from Hong Kong (Phillips, 1985; Chan, 1987; Chan *et al.*, in press; Phillips and Rainbow, in press). Unpublished data on *P. canaliculus* (which is closely related to *P. viridis*) from New Zealand waters also suggest the partial regulation of zinc (V. Anderlini, personal communication). It is not known why these few species have developed such a capacity for regulating their tissue levels of zinc; however, it is clear that this is a most exceptional

attribute among bivalves. There is no evidence for any regulation of organochlorines or hydrocarbons by bivalve molluscs.

Several species of bivalve molluscs exhibit broad geographical ranges (e.g. species of the genera *Mytilus*, *Perna*, and *Crassostrea*), which permits their use in large-scale studies of the distribution of contaminants (De Wolf, 1975; Phillips, 1977b, 1978a; Goldberg *et al.*, 1978, 1983; Farrington *et al.*, 1983) embodied by the "Mussel Watch" concept (Goldberg, 1975b; NAS, 1980). In addition, many bivalves are euryhaline in nature (allowing investigations of estuaries and purely marine environments using the same species), and most are highly tolerant of pollutant-induced stress.

Thus, few examples exist where pollutants are thought to potentially reduce the capacity of bivalves to reflect the ambient levels of contaminants. However, an important exception to this general rule concerns the toxic effects of copper on the blue mussel *Mytilus edulis* (probably the most widely used bio-monitor to date). Early indications that *M. edulis* might not accurately reflect copper bio-availabilities in all situations (Phillips, 1976a, 1976b) were followed by detailed investigations of the sublethal effects of copper on this species (Davenport, 1977, 1979; Davenport and Manley, 1978; Stromgren, 1982, 1986; Maung Myint and Tyler, 1982; Manley, 1983; Calabrese *et al.*, 1984; Davenport and Redpath, 1984; Howell *et al.*, 1984; Redpath, 1985). Copper has been documented to be of unusual toxicity to *M. edulis*, affecting filtration rates and growth rates, and eliciting a valve closure response at concentrations not dissimilar to those found in contaminated environments. The valve closure response effectively isolates the internal tissues of the mussel from the ambient seawater. In locations which are highly contaminated by copper, this may reduce the effectiveness of *M. edulis* as a bio-monitor. Other studies have suggested that the tolerance of *M. edulis* and other bivalves to copper may be either genetically-based or adaptive (Hvilsom, 1983; Luoma *et al.*, 1983).

Variables which affect the concentrations of contaminants in bivalves have been reviewed in detail elsewhere (Phillips, 1977a, 1978b, 1980). These include animal size, season (sexual condition), shore level of sampling, sex of the individuals sampled, and water salinity and temperature (Table 5). Most of the effects of such parameters can be eliminated or accounted for during sampling (NAS, 1980; Phillips, 1976b,1980) or in the interpretation of monitoring data.

Table 5. Selected literature sources describing the effects of variables on contaminant levels in bivalve molluscs. (See also references cited in the text).

Author(s)	Subject
Schulz-Baldes, 1973	Size effects, *Mytilus edulis*/lead.
Boyden, 1974, 1977	Size effects on metal levels, various species
Greig *et al.*, 1975	Season effects, *Crassostrea virginica*/metals
Jackim *et al.*, 1977	Salinity effects, various species/metals
Bryan and Hummerstone, 1978	Various, *Scrobicularia plana*/metals
Bryan and Uysal, 1978	Various, *S. plana*/metals
Davies and Pirie, 1978	Size effects, *Mytilus edulis*/metals
Cossa *et al.*, 1979	Season effects, *Mytilus edulis*/cadmium
Luoma and Cain, 1979	Season effects, *Macoma balthica*/metals
Romeril, 1979	Size effects, *Mercenaria mercenaria*/metals
Simpson, 1979	Season effects, *Mytilus edulis*/Pb and Zn
Orren *et al.*, 1980	Season effects, *Choromytilus meridionalis*/metals
Phillips, 1980	Review of all effects/metals and organochlorines
Zaroogian, 1980	Size and season effects, *C. virginica*/cadmium
Hornung and Oren, 1980-81	Size effects, *Donax trunculus*/metals
Burns and Smith, 1981	Season effects, *Mytilus edulis*/hydrocarbons
Phillips and Boyden, 1981	Season effects, *Crassostrea gigas*/metals
Strong and Luoma, 1981	Size effects, *Macoma balthica*/copper and silver
Langston, 1982	Size effects, various species/mercury
Lobel and Wright, 1982a, b, c	Size effects, *Mytilus edulis*/zinc
Fischer, 1983, 1986a, 1986b	Size effects, various species/cadmium
Gault *et al.*, 1983	Size and season effects, *Mytilus edulis*/metals
Marina and Enzo, 1983	Season effects, *Donax trunculus*/Mn and Zn
Meeus-Verdinne *et al.*, 1983	Season effects, *Mytilus edulis*/metals
Southgate *et al.*, 1983	Size effects, various species/metals
Graney *et al.*, 1984	Temperature effects, *Corbicula fluminea*/cadmium
Thomson *et al.*, 1984	Season effects, *Macoma balthica*/metals
Szefer and Szefer, 1985	Size effects, various species/metals
Purchase and Fergusson, 1986	Size and season effects, *Chione stuchburyi*/lead
Roberts *et al.*, 1986	Shore level, *Mytilus edulis*/cadmium

However, interactions between pollutants are difficult to account for, or even to recognize, in bio-monitoring studies (Phillips, 1977a, 1980). The existence of such interactions casts doubt upon the reliability of a species to accurately reflect the bio-availabilities of individual toxicants, and indeed, upon the very concept of bio-monitoring. Luckily, interactions between metals (or between metals and other contaminants) are rare among bivalves, although a few examples are known. Fowler *et al.* (1975) found that mercury displaced iron in the mantle fringes of the quahog, *Mercenaria mercenaria*. The uptake of copper by *Mytilus edulis* may be affected by the presence of other elements (Phillips, 1976a), and that of cadmium may be reduced by the co-presence of zinc (Jackim *et al.*, 1977), although these laboratory findings are based on high doses of metals and are of uncertain validity in field conditions. No evidence for such an interaction between cadmium and zinc was found for *M. galloprovincialis* (Fowler and Benayoun, 1974). Luoma and Bryan (1978) showed that lead uptake by the burrowing bivalve *Scrobicularia plana* was influenced by the co-presence of iron. However, this may be mediated by the scavenging of lead by hydrous oxides of iron in sediments externally to the animal, rather than through a *bona fide* interaction between the elements in the tissues of *S. plana*. It should also be noted that speculation by Young and Jan (1976) that the uptake of cadmium by the rock scallop *Hinites multirugosus* was reduced by the co-presence of high levels of DDE and PCBs in the heavily contaminated Palos Verdes area of California has not been resolved to date.

While several authors have reported that no interactions between elements could be observed in studies of metal uptake by various species of bivalves (Fowler and Benayoun, 1976; Frazier and George, 1983; George *et al.*, 1983; Robinson and Ryan, 1986), two recent reports have added further instances of metal interactions to those discussed above; coincidentally, these both involve silver. Luoma and Bryan (1982) found that levels of silver in *Scrobicularia plana* are low when copper concentrations are high in local sediments. However, as noted above for lead and iron in *S. plana*, this does not necessarily imply the existence of interactions within the tissues of the bivalve. Finally, Calabrese *et al.* (1984) found that mussels (*Mytilus edulis*) exposed to silver accumulated greater amounts of copper than did controls not exposed to silver. These data are reminiscent of the results cited previously for silver and copper uptake by slipper limpets, *Crepidula fornicata* (Nelson *et al.*, 1983).

Several authors have also considered the use of bivalve shells or even the byssus for monitoring trace metals (Sturesson, 1976, 1978; Bryan and Uysal, 1978; Carriker *et al.*, 1980; Miramand *et al.*, 1980; Coombs and Keller, 1981; Guary and Fowler, 1981; Koide *et al.*, 1982; Dermott and Lum, 1986; Purchase and Fergusson, 1986). However, metals vary in concentration in different regions of the shell and also with depth (and chemical composition) in the shell. In addition, the factors influencing the deposition of metals in shells or byssal threads are poorly understood. Although some elements (especially the transuranics) are heavily deposited in these tissues, this is no guarantee of their adequacy for bio-monitoring purposes. There is scope for additional work in this field.

In conclusion, most species of bivalves conform admirably to the requirements for an organism to be an effective bio-monitor of pollution. The use of these animals in national and regional monitoring programmes, such as those in the USA (Goldberg *et al.*, 1978, 1983; Flegal *et al.*, 1981; Farrington *et al.*, 1983; Martin *et al.*, 1984b; Martin and Castle, 1984, Martin, 1985; Smith *et al.*, 1986; NOAA, 1987) is clearly of great benefit, and there can be no doubt that this is an improvement over more traditional monitoring techniques employing water or sediment analysis. Where native bivalves of the required species are not present, transplantation techniques are readily available (e.g. Young *et al.*, 1976; Curran *et al.*, 1986). Some authors have stated that there are definite benefits to the use of transplants (Ritz *et al.*, 1982), and certain programs employ these routinely rather then using native animals, although occasional problems have been encountered with the interpretation of data from transplanted samples (Cain and Luoma, 1985). Whether native organisms or transplants are used, however, bivalve molluscs are in most cases a highly reliable and efficient tool for estimating the bio-availability of metals in coastal environments. This is particularly the case where the main sources of variance (see Phillips, 1980) are accounted for, and the necessary attention is paid to the choice of species used, the sampling regime, and the analytical methodology.

Other Invertebrate Species

Several aquatic species other than those described above have been considered for use as bio-monitors, and some have actually been employed in monitoring programs. However, in general, much less is known of the kinetics of contaminant uptake and

excretion in these species, and their use as bio-monitors has therefore not been shown to be legitimate as yet.

Henze (1911) first noted that ascidians accumulate large quantities of certain metals. Their uptake and sequestration of vanadium in particular has excited further work more recently (Bell *et al.*, 1982; Rowley, 1982; Pirie and Bell, 1984), and Papadopoulou and Kanias (1977) have suggested that certain ascidian species may be useful as bio-monitors. However, although species such as *Ciona intestinalis* exhibit widespread geographical distributions and may have potential for this purpose, almost nothing is known of contaminant kinetics in ascidians or the impacts of external variables upon these.

By contrast to the extensive studies on gastropod and (particularly) bivalve molluscs discussed above, relatively few data are available for metals in cephalopods. It is known that both squid and octopus accumulate elements to high levels (e.g. Martin and Flegal, 1975; Miramand and Guary, 1980; Smith *et al.*, 1984), but no attempts to employ these species as bio-monitors *per se* have been reported. Many cephalopod species exhibit significant movement, and this detracts from their likely usefulness as bio-monitors (Phillips, 1980).

More data are available on annelids (at least for metals), but these species do not appear to always be well-suited to a role in bio-monitoring programmes. At least some polychaete species are known to regulate certain elements such as zinc (Cross *et al.*, 1970; Bryan and Hummerstone, 1973b, 1973c; Bryan, 1976; Bryan and Gibbs, 1987) and the acquisition of tolerance to other metals (e.g. cadmium and copper) may be based upon a reduced net accumulation (Bryan and Hummerstone, 1973b; Pesch and Hoffman, 1982), which severely restricts the usefulness of such species as bio-monitors. The uptake of metals by polychaetes and other species is also affected by animal size (Bryan, 1976; Bryan and Hummerstone, 1973b; Packer *et al.*, 1980); by salinity in certain instances (Bryan and Hummerstone, 1973c); and by the reproductive cycle of the worm (Howard and Brown, 1983). Nevertheless, polychaetes such as *Nereis diversicolor* and *N. succinea* have been employed to monitor metals in coastal ecosystems by some authors (e.g. Luoma, 1977a; Langston, 1986), and studies of chromium uptake by *Neanthes arenaceodentata* suggest that this element is accumulated in proportion to environmental exposure levels (Oshida and Word, 1982). Investigations of metals in the

feather duster tube worm *Eudistylia vancouveri* (Young *et al.*, 1979; Popham and D'Auria, 1982; Young and Roesijadi, 1983) and in nematode species (Howell, 1982) are also informative, although little is known of element kinetics in these organisms.

Fish

Fish have been frequently employed as bio-monitors of contaminants in both freshwater and marine ecosystems. However, considerable problems are encountered by such studies, at least where the intent is to define the abundance and distributions of toxicants, rather than to investigate impacts of specific contaminants on the species studied. These problems involve both the regulation of metal levels in some fish tissues and the migratory habits of fish species.

The classical studies of Johnels *et al.* (1967) demonstrated that the axial muscle of pike (*Esox lucius*) could be employed to monitor levels of mercury in freshwater environments in Sweden. This discovery was followed by the widespread use of muscle tissues of fish for the bio-monitoring of metals; however, it became clear after some years that mercury was unusual, in that it was one of few metals which was not subject to metabolic regulation in the axial muscle of fish (see reviews by by Bryan, 1976; Phillips, 1977a, 1980; Bryan *et al.*, 1980, 1985). Thus, many trace elements of concern in aquatic environments (e.g. copper, zinc) are subject to metabolic regulation in the axial muscle tissues of finfish. This led researchers to use liver tissues of fish, rather than muscle, for bio-monitoring studies of metals other than mercury. While this is certainly an improvement, the site-to-site variation in metal levels in fish livers is not generally as extreme as that in the tissues of other bio-monitoring species such as bivalve molluscs (Bryan, 1976; Phillips, 1980).

Nevertheless, both liver tissues of fish (for metal studies) and axial muscle (for mercury and organochlorines) continue to be widely used for bio-monitoring purposes. The principal problem with this technique is the interference of fish movements in the interpretation of data (Phillips and Segar, 1986). While certain fish species, such as pike and some demersal fish (e.g. flathead; see Dix *et al.*, 1976) are effectively territorial or move little during their lifetime, many species migrate freely over large areas. This is particularly the case in estuarine regions, where many species exhibit spawning-dependent movements (reaching an extreme in the case of anadromous species). It is therefore impossible to differentiate between the effects of space and time in the

interpretation of data on toxicants in these species. For example, high concentrations of a contaminant in a particular fish could have been produced by a chronic exposure to relatively low levels of that toxicant, or by a much shorter exposure to very high ambient concentrations. In addition, there is no way of knowing whether either of these exposures occurred adjacent to the site of capture of the fish, or elsewhere.

It is therefore clear that if a fish species exhibits significant movement, its accumulated toxicant load cannot be considered to necessarily reflect the ambient contamination at the site of capture. It follows from this that fish which exhibit significant movement or migration in study areas cannot be justifiably employed as bio-monitors of spatial (or temporal) differences in the contamination of aquatic environments. While data on contaminant levels in fish are undoubtedly needed (e.g. to define any adverse impacts on individuals and populations due to the presence of toxicants; to protect public health), their use as bio-monitors to define spatial and temporal trends in the contamination of aquatic environments does not provide interpretable data.

E. Conclusions on Bio-monitoring Techniques

There can be no doubt that the trend towards the use of biota to monitor the abundance and distributions of contaminants in coastal waters has greatly improved our knowledge of the impacts of these pollutants in such areas. It has been argued that contaminants are of no consequence in aquatic ecosystems unless they are bio-available (or at least of direct toxicity to biota of such ecosystems, which probably equates to bio-availability in most cases). There is no true alternative at present to the use of bio-monitors, if the bio-availability of toxicants is the primary concern (Phillips, 1980; Waldichuk, 1985).

Nevertheless, it is certainly the case that this technique has been abused by many researchers. A lack of attention in establishing that a species possesses the necessary attributes to perform efficiently as a bio-monitor results in the compilation of data which are either meaningless or of very limited use in defining water quality. Such data are unfortunately not uncommon in the literature, and this debases the value of this powerful monitoring technique (Phillips and Segar, 1986).

The most basic requirement for a species to act as an accurate bio-monitor is that its tissue levels of contaminants should faithfully reflect the ambient bio-availability of those pollutants, which implies a lack of regulation of contaminant uptake. On this basis, the most appropriate bio-monitors include macroalgae, bivalve molluscs, and perhaps barnacles. This does not imply, however, that all species of these groups are equally useful bio-monitors in all situations. There is a need for continued research (which should emphasize the use of these types of organisms in particular) to further improve bio-monitoring techniques; this will require both laboratory and field investigations.

III. TOXIC CONTAMINANTS OF GREATEST CONCERN IN THE ESTUARY

While it is the central theme of this report that the abundance and distributions of toxic contaminants in the San Francisco Bay and Delta have not been adequately characterized to date, it is nevertheless the case that existing data permit preliminary judgements of the relative importance of at least some contaminants in the estuary. This is seen as a useful exercise, in that later sections of the present report may then concentrate upon the contaminants thought to be most likely to exert detrimental effects on the beneficial uses of the Bay and Delta. Clearly, it is these contaminants which must receive highest priority in any monitoring program designed for the estuary.

Staff of the San Francisco Estuary Project (part of the National Estuary Program of EPA) requested the author to prepare a list of toxic contaminants of concern in the estuary in March 1988. To provide some degree of objectivity to this exercise, criteria were established (Table 6) against which the existing data on contaminants in the San Francisco Estuary were compared.

Later work under the San Francisco Estuary Project expanded on the original criteria, and provided a more lengthy justification for the inclusion or exclusion of particular contaminants. The most recent matrix, presenting the grading of contaminants against the criteria employed, is shown as Appendix 2 to the present report.

The abundance and distributions of trace metals in the estuary have been subjected to more intensive study than have those of organochlorines or (particularly) hydrocarbons. It is therefore a relatively simple exercise to create a list of trace elements of greatest concern in the estuary, based upon the criteria discussed in Table 6 and the available published data from studies of metals in water, sediments and biota of the Bay and Delta. These data have been reviewed by several authors (e.g. Bradford and Luoma, 1980; Luoma and Phillips, 1988). However, the most comprehensive reviews are those of Phillips (1987) and Long *et al.* (1988).

For synthetic organic contaminants, this task is rather more difficult, as the available information on these compounds is much more restricted than that for trace elements (Phillips, 1987; Phillips and Spies, 1988). However, pesticides which are

Table 6. Criteria for the classification of toxic contaminants in the San Francisco Bay and Delta.

A. Contaminants thought to be of particular concern

(1) Contaminant is of widespread occurrence in the San Francisco Estuary and occurs at elevated concentrations in water, sediments or biota compared to other coastal areas;

and/or

(2) Contaminant is present at significantly elevated concentrations in local areas only of the Estuary;

and

(3) Contaminant is linked to detrimental biological effects on San Francsico Estuary biota through direct study, or is likely to be causing such effects based upon review of the international literature;

and/or

(4) Contaminant exhibits impacts on other beneficial uses of the Estuary.

B. Contaminants not thought to be of particular concern

(1) No evidence for widespread enrichment in the Estuary compared to other coastal waters;

and

(2) No evidence for significantly elevated local concentrations of contaminant in the Estuary;

and

(3) No evidence or presumptive evidence of likelihood of biological impacts from contaminant in the Estuary;

and

(4) No evidence for impacts of any type on other beneficial uses of the Estuary.

known to be employed presently in the Central Valley catchment are candidates for such a list, at least if these are of significant persistence in the environment. Organochlorines which were employed previously in the catchment (but are now banned or strictly regulated in use) may also be included, where monitoring data suggest a continuing problem from the wash-down of historically-applied residues; DDT and its metabolites are a case in point. Certain contaminants found to be present in the estuary in recent studies of the State Mussel Watch Program (M. Martin, personal communication) have also been included. Dioxins are included on the basis of their extreme toxicity and because of very recent findings of significant contamination of fish samples from the Central Valley catchment by dioxins (U.S. EPA, unpublished data); more data are clearly needed on these important compounds in particular.

The available database on the distribution of hydrocarbons in the estuary is very poor indeed, as discussed by Phillips (1987). It may be thought reasonable to list all hydrocarbons of concern in the environment as having possible impacts on the San Francisco Estuary, particularly in view of the magnitude of the transport of petroleum products (and their refining) in the Bay. However, current research suggests that certain of the PAHs may present the greatest threats to aquatic ecosystems, and it is principally these that are included in the list generated for San Francisco Bay and Delta.

Table 7 draws on the work performed for the San Francisco Estuary Project to present a proposed list of "contaminants of greatest concern" for the estuary. This list was generated by the author (based upon the criteria shown in Table 6 and Appendix 2), with the assistance of Dr. Robert Spies of the Lawrence Livermore National Laboratory. Contaminants are shown in both boldface and normal typeface. This denotes the level of significance of each contaminant in the estuary; those shown in boldface are thought to be particularly important because of their significantly elevated regional or local abundance, or for other reasons. The following points should be noted:

- The inclusion or exclusion of specific contaminants on this list is a function of inadequate data. More than 100,000 chemicals are employed by industry, and are thus potential environmental contaminants. Rather more than 100 of these have been recognized to date as significant contaminants in coastal waters (for example, the EPA "priority pollutant" list includes a total of 126 contaminants currently), and it is these that are most commonly measured. The database on the San Francisco Estuary is so poor, however, that judgements on the possible significance of specific

Table 7. List of toxic contaminants thought to be of concern in the San Francisco Bay and Delta. Contaminants shown in bold type are those thought to be of particular concern; all chemical species of named contaminants are deemed to be included.

Trace Metals

Cadmium
Copper
Mercury
Nickel
Selenium
Silver
Tin
Antimony
Arsenic
Chromium
Cobalt
Lead
Zinc

Organochlorines and other pesticides

Chlordane and its metabolites
DDT and its metabolites
Polychlorinated biphenyls
Toxaphene
Aldrin
Chlorbenside
Dacthal
Dieldrin
Dioxins
Endosulfan
Endrin
Heptachlor and its epoxide
Hexachlorobenzene (HCB)
Hexachlorobutadiene
Hexachlorocyclohexane (HCH)
Methoxychlor
Polychlorinated terphenyls
2,4,6-trichlorophenol
Malathion
Parathion

Hydrocarbons

(i) Monocyclic aromatic hydrocarbons (MAHs)

Benzene
Ethylbenzene
Toluene
Xylene

(ii) Cycloalkanes

(iii) Polycyclic aromatic hydrocarbons (PAHs)

Acenaphthene
Acenaphthylene
Anthracene
Benz(b)fluoranthene
Benz(k)fluoranthene
Benz(g,h,i,)perylene
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(a)anthracene
Benzthiazole
Chrysene
Dibenzo(a,h)anthracene
2,6-Dimethylnaphthalene
Fluoranthene
Fluorene
1-Methylnaphthalene
2-Methylnaphthalene
1-Methylphenanthrene
2-(4-morpholinyl)benzthiazole
Naphthalene
Phenanthrene
Pyrene
2,3,5-Trimethylphenanthrene
Indeno(1,2,3-c,d)pyrene

contaminants in the Bay and Delta must often be based on very little information. This is particularly the case with hydrocarbons (Phillips, 1987). The list shown in Table 7 includes a total of 24 polycyclic aromatic hydrocarbons (PAHs); these have mostly been included because they are the components of petroleum residues which are thought presently to be of greatest concern in coastal waters. There is a clear need for further studies on both these and other organic contaminants which are present in gas chromatograms generated from environmental samples taken from the estuary, but have not yet been identified.

- Some contaminants may exert effects in very localized areas only, and may not be included in the list as a result (particularly if these areas have not been heavily studied to date). Where known hot-spots exist exhibiting considerably elevated concentrations of contaminants in either sediment or biota (or both), such as the Lauritzen Canal, these contaminants have been included on the list shown in Table 7 if the levels seen are thought to be great enough to possibly exert detrimental effects locally on the biological resources of the estuary.

- As a result of the uncertainties noted above, the list shown in Table 7 should not be considered fixed, but should be updated periodically as more information becomes available.

Brief comment should be made here of some specific inclusions and omissions from the list in Table 7. As noted previously, data for metals in the estuary are more abundant than those for other contaminants. Trace elements which are found to be present in the estuary at concentrations close to or greater than established water quality objectives (e.g. EPA, 1986; SFRWQCB, 1986; see section IV of this report) are included in boldface, i.e. are thought to be of particular significance (Cu, Hg, Ni). Elements known to bioaccumulate heavily in parts or all of the estuary are also shown in boldface (Ag, Cd, Hg, Se). Tin is also included in this category, because of its extreme toxicity as tributyl tin, employed in antifouling agents. As noted by Phillips (1987), parts of the San Francisco Estuary exhibit high concentrations of tributyl tin (and less-butylated derivatives; see Goldberg, 1987). While this is not unusual compared to many other estuaries, the extreme toxicity of tributyl tin makes it likely that adverse effects exist in poorly-flushed areas such as harbors and marinas due to the presence of this compound. Among the elements of lesser concern, it should be noted that very few data exist for antimony,

arsenic or cobalt in particular. All of these may pose a significant threat to beneficial uses in the estuary (including public health for antimony and arsenic) under conditions of particular enrichment, however. There is a need for the differential analysis of arsenic in biota, to separate inorganic forms (which are highly toxic to consumers, including humans) from organic derivatives (which are much less toxic; see Phillips and Depledge, 1985, 1986; Phillips, 1987). Zinc has been included in Table 7, despite the fact that the levels of zinc in the estuary appear altogether unremarkable, and that water quality criteria for this element are not approached by receiving waters in the estuary. However, zinc is discharged to the Bay and Delta in considerable amounts from point and other sources (Gunther *et al.*, 1987).

The organochlorines of greatest importance in the Bay and Delta (shown in boldface in Table 7) are chlordane and its related compounds, DDT and its metabolites, and toxaphene among the pesticides. All of these are known to be present throughout the majority of the Bay and Delta (although levels are probably decreasing subsequent to the instigation of controls on their use). The other organochlorine pesticides shown in normal typeface may exert local effects, particularly in portions of the Central Valley catchment, close to areas of their current or previous application to crops. Polychlorinated biphenyls (PCBs) are of considerable importance in the estuary, being abundant throughout the system (Phillips, 1987; Phillips and Spies, 1988). There is a need for improvements in the analysis of these contaminants, to clearly identify the levels of the most toxic of the isomers and homologues (especially the coplanar PCBs; see Tanabe *et al.*, 1987a).

The reasons for the inclusion of the PAHs shown in Table 7 have been discussed above. The monocyclic aromatic hydrocarbons (MAHs) and cycloalkanes are included on the basis of evidence (reviewed by Phillips, 1987; see also section VI of this report) that these may have impacts on populations of striped bass (*Morone saxatilis*) in the estuary, although this evidence is controversial and requires further confirmation.

The following section reviews the present routine monitoring programs in the estuary which attempt to quantify the regional abundance of these contaminants in water, sediments and biota.

IV. REGIONAL MONITORING OF TOXIC CONTAMINANTS IN THE ESTUARY

A. Introduction

It is suggested here that the regional monitoring of toxic contaminants in ambient waters and biota of the estuary is required for the following purposes:

(i) Regulatory agencies employ water quality criteria, objectives or standards to attempt to control the general loading of toxicants to the estuary, and therefore need information on the level of attainment of such objectives in the receiving waters of the estuary. These objectives are relevant to all ambient waters of the estuary outside zones of initial dilution for point source effluents. Although a fully detailed wasteload allocation scenario for the estuary is yet to be developed, the regulation of toxicant sources through NPDES permitting and other methods is designed to dovetail to the eventual achievement and continued maintenance of objectives for ambient receiving waters; this provides a link between local toxicant sources and regional toxicant abundance. Thus, for example, concern over the "water quality-limited" nature of parts of South Bay for certain trace elements has given rise to discussions on the need to further regulate metal loads from point and perhaps non-point effluents in this area of the estuary.

(ii) Reliable data for toxicant levels in ambient receiving waters of the estuary are also required to provide information on the likely impacts of toxicants on biological resources if water quality objectives or criteria (which theoretically provide protection to all resident species) are not being met in all or part of the estuary. Sufficient data exist in the toxicological literature to permit at least preliminary judgements in some cases on the likely impacts of certain toxicants in the water column, if their levels are accurately defined. Thus, for example, the possible impacts of locally elevated concentrations of silver in ambient waters of the South Bay may be estimated through a concerted literature search of toxicological data relevant to this element. Such literature searches may be followed by the design and completion of specific studies to delineate the actual impacts of toxicants on individual species within the estuary (although no such specific studies have been completed to date; the best example of such work is the investigations of Spies and co-workers on PCBs and

starry flounder, but even this stops short of an unequivocal demonstration of cause-and-effect).

(iii) Because sediments act as both a sink and a source of contaminants in estuaries, their study theoretically provides information on both toxicant abundance within the system (spatially and perhaps also temporally) and potential sites of stress or toxicological effects from sediment-borne contaminants to resident biota. Data on sediment contamination may provide a picture of both regional and local pollution gradients, once again linking local toxicant sources to the regional abundance of these contaminants within the estuary. However, the impacts of extraneous parameters which affect the abundance of pollutants in sediments (principally grain size and organic carbon content, but perhaps also local sedimentation rates; see section II above) must be taken into account in either local or regional studies. In addition, it should be noted here that the use of sediments to study regional trends in contaminant abundance (spatially or temporally) is not always defensible. The contamination profiles of sediments in certain estuaries do not lend confidence to such an approach; this is considered in greater detail below.

(iv) Regional data on the abundance of toxicants in organisms of the estuary are required for several reasons, as follows:

- The protection of human health requires that organisms in the estuary which are subject to either commercial or recreational fisheries or other capture methods and which are consumed by humans in significant amounts should not pose a health hazard upon their ingestion. The Food and Drug Administration (FDA) promulgates federal standards (U.S. FDA, 1984) for allowable concentrations of toxicants in seafoods and other food products (although it is notable that few standards exist in the US for trace metals in seafoods, by contrast to other countries; see Nauen, 1983; SWRCB, 1986; Phillips, 1987).

- Just as human health must be protected in the estuary, so must the health of the resident aquatic species be safeguarded; the "limits for predator protection" prescribed to this end are frequently more stringent than the standards laid down by the FDA for the protection of public health. (This difference can hardly be considered surprising, in view of both the relatively infrequent exposure of humans to contaminants in seafoods and the differences in toxicological response

between humans and other lower organisms). The National Academy of Sciences has reviewed the available literature on the impacts of the ingestion of contaminated species upon predators, and has derived generic limits for the protection of predators in aquatic environments (NAS, 1973). It is notable that these limits were drawn up some 15 years ago; there is a clear need to update this work, employing the more recent toxicological literature. However, such an update is beyond the scope of the present report.

- Given the current technology and understanding of contaminants and their chemical speciation in aquatic ecosystems, the bio-availability of contaminants can only be accurately estimated through the direct analysis of organisms themselves, as discussed in detail in section II above. Thus, regional monitoring schemes of specific organisms may be employed not only to protect public health and natural predators, but also to provide data on the spatial and temporal variations in contaminant abundance and bio-availability in the estuary. This use of so-called "bio-indicators", "bio-monitors" or "sentinel organisms" has developed greatly over the last two decades, and is now generally considered to be the method of choice for the study of contaminant abundance in most aquatic ecosystems, for the reasons discussed in section II above.

These requirements are discussed in greater detail in the following sections, and the current monitoring programs and datasets produced through these programs are reviewed in each case.

B. Regional Monitoring of Toxic Contaminants in Ambient Waters

The Existing Database

General

The level of effort and expenditure on the frequent and detailed analysis of point source effluents for contaminants in the estuary through the NPDES self-monitoring requirements (helping to define local trends in pollutant abundance; see section V of this report) contrasts markedly with the paucity of data on the regional abundance of toxicants in ambient receiving waters of the Bay and Delta. While there may be several valid reasons for this (e.g. lack of designation of an organization with the overall responsibility to monitor ambient levels of toxicants; technical difficulties involved in trace analysis of many pollutants at ambient levels), the fact remains that reliable data on the concentrations of any of the persistent toxic contaminants of potential concern in the San Francisco Estuary are very sparse.

Organochlorines and Petroleum Hydrocarbons

No reliable recent data exist on the precise concentrations or even general abundance of most persistent organic contaminants (such as organochlorines or petroleum-derived hydrocarbons) in ambient receiving waters of the estuary. Anderlini *et al.* (1975) reported concentrations of PCBs of about 1 ng L^{-1} in eastern San Francisco Bay, but no data exist on spatial or temporal trends in the levels of these important pollutants in the estuary. de Vlaming (in draft, 1988) recently analyzed waters of the Delta and major upstream rivers to attempt to detect monocyclic aromatic hydrocarbons (MAHs), but could not detect any single MAH at concentrations greater than 0.5 $\mu g\ L^{-1}$. He noted that this agreed with most data from elsewhere, and concluded that the significant vapor pressures of the MAHs caused them to be lost rapidly from natural waters by volatilization; hence, their presence in such receiving waters was a transient phenomenon at best. This transient or episodic nature of contamination in receiving waters creates problems with the control of pollution through the analysis of these waters, as noted in previous sections.

This paucity of data on the concentrations of persistent organic contaminants in ambient waters is at least partly due to the extreme technical difficulties involved in the accurate measurement of the very low levels of such pollutants present in these natural waters [concentrations are in the part per trillion (ng L^{-1}) range or less for most compounds]. As a result, in all but the most contaminated situations, the use of receiving water analysis for the detection or control of such contaminants in aquatic ecosystems is generally not practiced. Indeed, it is rare for regulatory organizations to either cite or attempt to enforce water quality objectives for these compounds in receiving waters (either in solution or suspension). The environmental abundance of such contaminants is more usually monitored through the use of sediments or biota; the present document recommends the use of the latter techniques over any attempt to institute a routine monitoring system for persistent organic contaminants in ambient waters.

Trace Metals

By contrast to the extreme difficulties involved in the measurement of organochlorines and petroleum-derived hydrocarbons in ambient waters, the techniques for the measurement of trace metal concentrations in receiving waters are now quite well-developed. This is not to say, however, that the evolution of reliable methods for metal analysis in receiving waters has been either a simple or a rapid process. The accurate quantification of metals in coastal and open ocean waters in particular has only become possible in the last decade, as a result of the increased attention paid to extraneous sources of contamination, which are particularly problematical at both sampling and the post-sampling preparation and analysis of natural waters. The classic studies of Patterson and co-workers on the levels of lead in aquatic environments (Patterson and Settle, 1976; Burnett and Patterson, 1980) gave rise to later improvements in the analysis of several other trace metals in both natural waters and other media in which particularly low concentrations were present. Some of this original work was performed within California, by Bruland and co-workers (Bruland *et al.*, 1977, 1978a, 1978b).

The present state of the art permits the reliable analysis of natural waters for a wide range of trace metals at concentrations ranging from the ng L^{-1} (part per trillion) to the $\mu g\ L^{-1}$ (part per billion) level. The facilities required for such analyses are described in several of the original studies and will not be detailed exhaustively here. For work on open ocean waters in particular, ultra-clean sampling, preparative and analytical

techniques are required, generally employing custom-designed sampling equipment and laboratory facilities, and the use of ultra-pure chemicals. Such studies are expensive to perform because of these requirements; however, no lesser options exist if the analytical data are to be accepted as reliable. For studies of coastal environments (where the concentrations of metals encountered are generally rather higher than those found in open ocean waters), rather less sophisticated equipment and facilities may suffice, at least for some of the trace metals. However, even in these cases, sample contamination is an ever-present problem and must be carefully considered in any study plan. This is particularly the case for certain metals which are particularly abundant in natural or man-made materials or which may be significantly transported aerially, such as lead.

The following seven studies which relate to trace metal abundance in the San Francisco Estuary are believed to include generally reliable data:

(i) Girvin *et al.*, 1978. This study was restricted to the South Bay, and covered five sampling periods during 1976 and 1977. Filtered water samples (0.2 μm filters) were analyzed for six trace elements (Ag, Cd, Cu, Ni, Pb, and Zn). Problems were encountered with the contamination of samples by lead (Phillips, 1987), but the data for other metals appear reliable.

(ii) Eaton, 1979a. Waters of the northern reach of the estuary and the Gulf of the Farallones were included in this investigation; no sampling was undertaken in the South Bay. Samples were collected on three cruises in July and September 1975 and March 1976. Samples were filtered through 0.6 or 0.4 μm filters, and analyzed for Cd, Cu, Fe, Ni, and Zn.

(iii) Gordon, 1980. Filtered samples (0.4 μm) collected in 1979 and 1980 from San Pablo Bay, Central Bay and the Gulf of the Farallones were analyzed in this study. The precautions taken to avoid contamination were exemplary. Both chelex columns and organic extraction techniques were used to preconcentrate samples prior to analysis. The metals quantified in solution were Cd, Cu, Fe, Mn, Ni, Pb, and Zn.

(iv) Stukas, 1986. This investigation was performed under contract to the URS Corporation as part of the work covered by the Environmental Impact Report for the

Chevron USA Richmond Refinery Deep Water Outfall Study. Samples were taken from San Pablo Bay close to Point San Pablo and Pinole Point, and were filtered through 0.4 μm filters. Eight elements were quantified (Cd, Cr, Cu, Hg, Ni, Pb, Se [as Se_5], and Zn).

(v) Cutter, 1987. Data derived from the studies of Cutter (under contract to the U.S. Bureau of Reclamation) on selenium in the estuary have been reported in various documents (Ball and Arthur, 1986; Cutter, 1987; U.S. Bureau of Reclamation, 1987). These data refer to selenium levels only, in samples collected between 1984 and 1987, throughout the estuary. Various chemical species of the element were quantified.

(vi) Kuwabara *et al.*, in press. This study by U.S.Geological Survey personnel involved the analysis of filtered (0.4 μm) water samples taken on five dates from March to September 1986 from South Bay only, at 4 locations. These ranged from just north of the San Mateo Bridge to south of the Dumbarton Bridge. Samples were analyzed for Cd, Cu, and Zn, as well as for various other parameters.

(vii) Flegal and Gordon, unpublished data. These data cover seven sites in the South Bay (from Hunter's Point south to Palo Alto, all locations being identical to those occupied by State Mussel Watch studies). Filtered samples (0.4 μm) taken in October 1982 were analyzed for Ag and Pb only.

It is evident from the above compilation of the available reliable studies on trace elements in solution in the receiving waters of the estuary that relatively few studies have been undertaken, that those investigations which have been completed rarely covered the entire estuary, and that only eleven elements have been quantified (some in only one or a few studies). In addition, it is notable that controversy continues over the precise reliability of some of the data reported, especially for certain elements such as lead (e.g. see comments by Gordon, 1980). The available database is also heavily dominated by analyses of samples taken during drought periods (1976, 1977, 1979 and 1981), and by data for metals in solution rather than those in suspension.

This body of data can hardly be considered to be comprehensive. Information for each element is reviewed briefly in the following, particular attention being given to the level of agreement between authors. In all cases, concentrations of metals reported in

solution in the receiving waters of the estuary are emphasized, as these are considered to be of greatest toxicological significance. However, where relevant data exist, comments are also provided on metal levels in suspension. It should be noted here that although water quality objectives for trace metals are generally derived from bioassay studies employing metals *in solution* (presumably in highly bio-available forms), the derived objectives are treated as permissible *total* amounts of metals in receiving waters. This undoubtedly provides an added "safety margin" for the protection of aquatic biota, but as it is not possible to strictly relate laboratory-based bioassay data to field situations, the magnitude of this safety margin remains unknown.

Silver: Only two reports have dealt with silver concentrations in receiving waters of the estuary. Girvin *et al.* (1978) reported concentrations of dissolved silver of about 0.01 $\mu g\ L^{-1}$ in Central Bay, increasing to between 0.025 and 0.3 $\mu g\ L^{-1}$ in South Bay (Figure 5). Enrichment of the element was seen at some sites in South Bay by comparison to Central Bay, but no well-defined gradient in concentrations was present, observed levels varying considerably at the locations studied with time. Flegal and Gordon (unpublished data) found much lower concentrations than these in samples taken at seven sites in South Bay in 1982 (Figure 6). Dissolved concentrations of silver varied from 0.002 $\mu g\ L^{-1}$ at Hunter's Point to 0.006 $\mu g\ L^{-1}$ at Palo Alto, and a general increase with distance southwards in South Bay was observed. Concentrations of silver in particulates were approximately double those found in solution in these studies. It is not clear whether the differences between these two datasets reflect real temporal differences in silver levels in receiving waters of the estuary, or are a function of extraneous contamination of the earlier samples. There is some evidence from the analysis of biota that silver concentrations may have decreased in certain portions of the South Bay in the late 1970s (Phillips, 1987), and this may have been due to the improved control of industrial discharges containing silver. However, other authors have not found a temporal decrease in silver concentrations in biota from the South Bay (Luoma, personal communication), and the paucity of data permits no strong conclusions. The levels reported by either investigation are lower than the water quality objectives for silver cited in the Basin Plan (SFRWQCB, 1986); these require instantaneous maximum concentrations of the element to be below 2.3 $\mu g\ L^{-1}$ in marine waters, and 1.2 $\mu g\ L^{-1}$ in fresh waters.

Cadmium: Agreement between the five studies reporting data for cadmium in solution in the estuary is good. The concentrations of this element in Central Bay waters

Figure 5. Concentrations (ng L^{-1}) of dissolved silver at nine stations in South Bay. Bars represent mean concentrations from five curises (March 1976- July 1977). Error bars denote one standard error of the mean, data from Girvin *et al.* (1978).

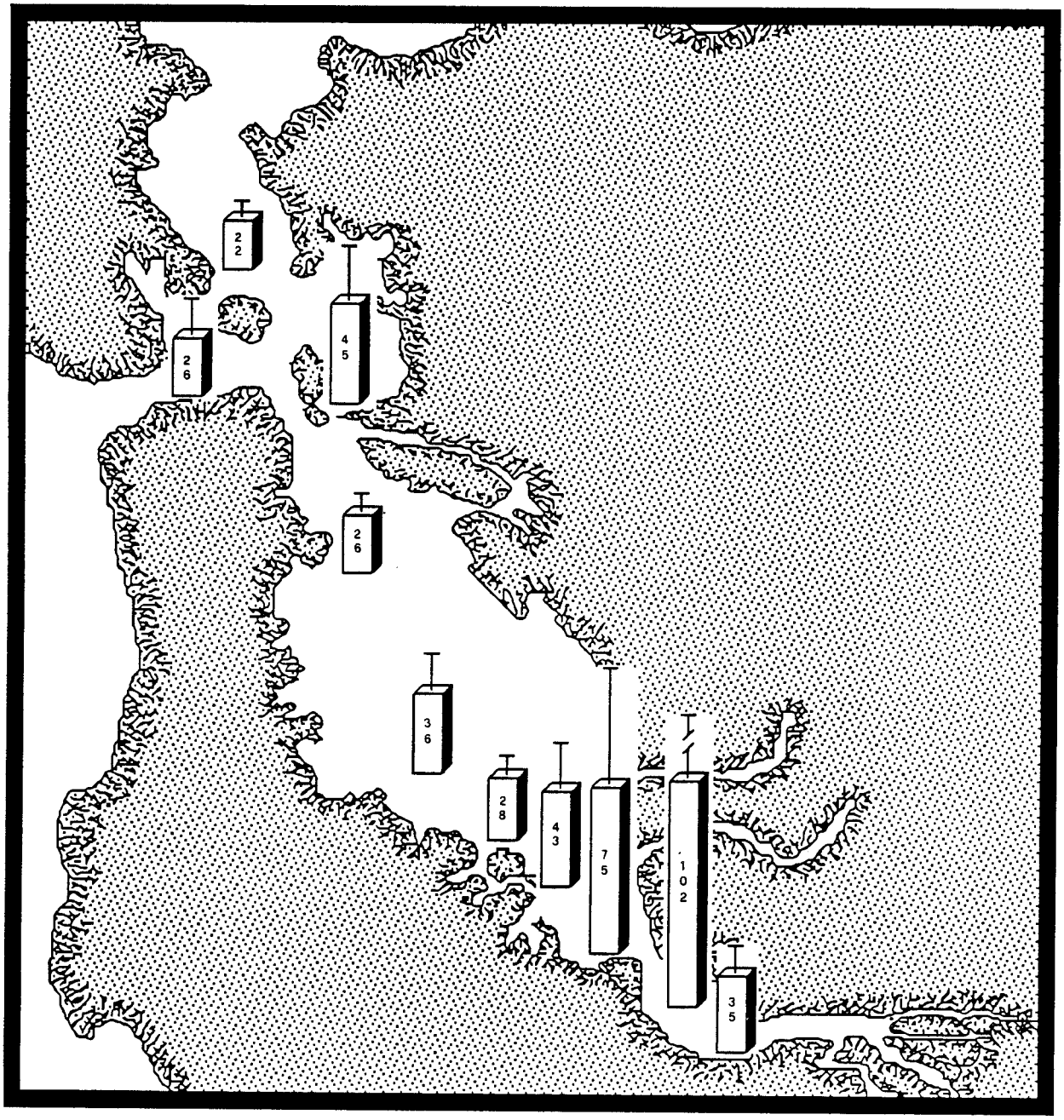
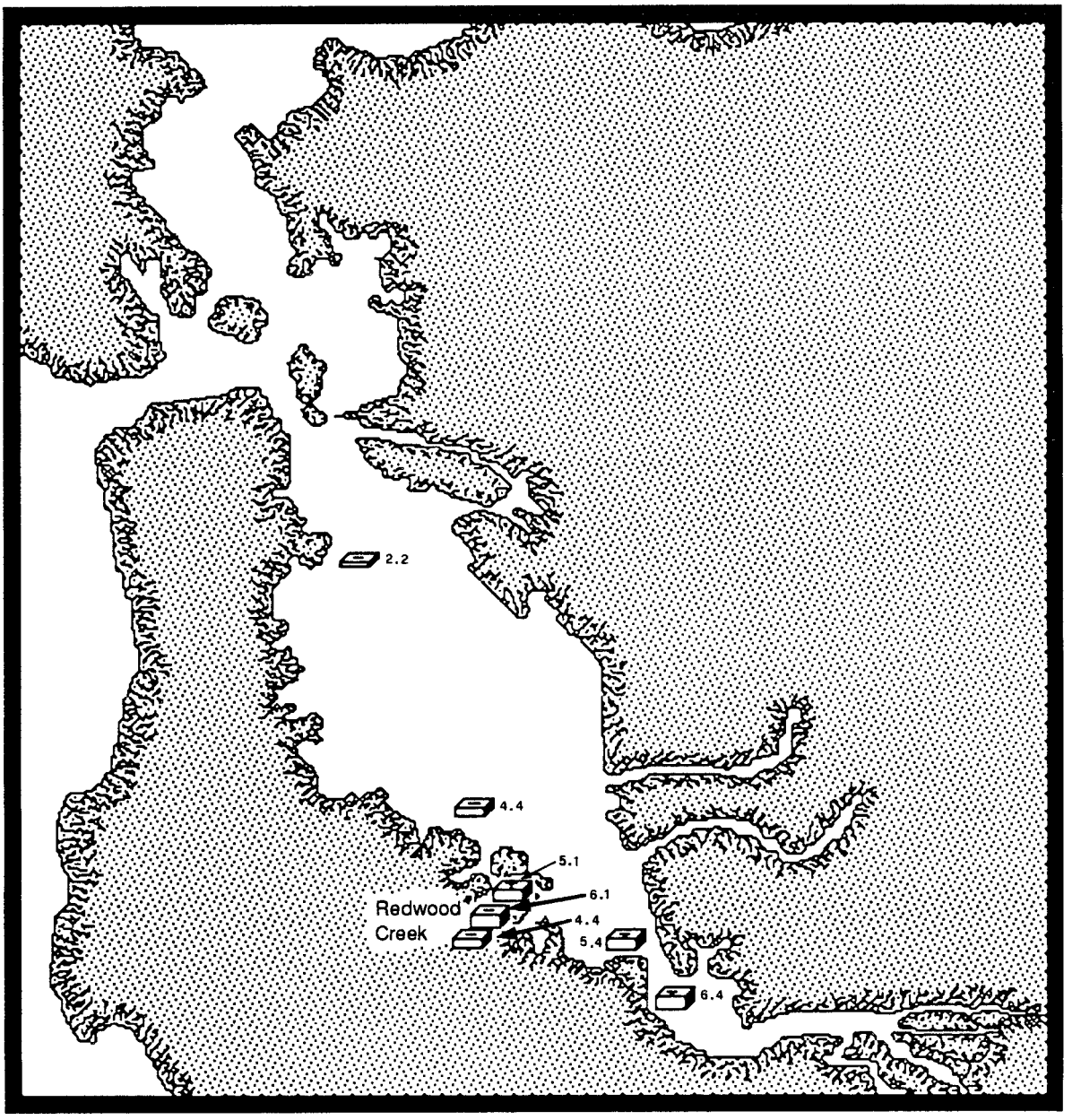


Figure 6. Concentrations (ng L^{-1}) of dissolved silver in the South Bay. Average of duplicate samples collected in 1982; error bar denotes one standard error of the mean. Data from Flegal and Gordon (unpublished).



appear to range from about 0.02 to 0.05 μg L^{-1}; levels in offshore waters of the Gulf of the Farallones are similar to these, or may be slightly higher in periods of upwelling (when cadmium-enriched water is brought up to the surface in offshore areas). In both the northern reach of the estuary and South Bay, the concentrations of dissolved cadmium are increased by comparison to Central Bay waters. Typical concentrations of dissolved cadmium in the northern reach are about 0.1 to 0.2 μg L^{-1}; in the South Bay, rather higher levels of 0.1 to 0.5 μg L^{-1} occur, and there is evidence of higher concentrations with distance south from the Golden Gate. Concentrations of cadmium in particulates are generally relatively low throughout the Bay, in keeping with the known tendency of this element to remain significantly in solution in marine and estuarine waters. None of these concentrations approaches the EPA water quality criterion for cadmium in marine waters (maximum of 9.3 μg L^{-1} as a four day average; see EPA, 1986), even when cadmium levels in particulates are accounted for in addition to concentrations of the element in solution. The EPA criterion for cadmium in freshwaters is dependent on water hardness; the four-day average criterion is 1.1 μg L^{-1} at a hardness of 100 mg L^{-1} as $CaCO_3$. Concentrations of cadmium in upstream areas of the estuary may be close to the criterion for freshwaters on some occasions, at least if cadmium in particulates is accounted for in addition to levels of the element in solution. The Basin Plan for San Francisco Bay has adopted objectives based upon these same EPA water quality criteria.

Chromium: Stukas (1986) reported that chromium levels in solution in San Pablo Bay ranged from 0.13 to 0.19 μg L^{-1}, with total levels of the element being considerably higher at 0.54 to 3.6 μg L^{-1}. The propensity for chromium to be found in significant amounts attached to particulate material in estuarine waters is documented also from other systems, although the toxicological importance of the particulate-associated forms of the element is difficult to ascertain. No other reliable data for chromium in the San Francisco Estuary exist. These levels are considerably lower than the Basin Plan objective or EPA ambient water quality criterion for hexavalent chromium (11 μg L^{-1} in freshwaters and 50 μg L^{-1} in marine waters, both as four-day averages).

Copper: Agreement between the various authors cited above on the concentrations of dissolved copper in the estuary is good (compare Figures 7 to 11). In general, it appears that the levels of copper in solution in waters offshore in the Gulf of the Farallones approximate 0.1 to 0.25 μg L^{-1}. Concentrations of dissolved copper are generally higher than this in the Bay, although different authors have reported rather

Figure 7. Concentrations (ng L^{-1}) of dissolved copper at nine stations in Central and South Bays. Bars represent mean concentrations from five cruises (March 1976-July 1977). Error bars denote one standard error of the mean. Data from Girvin *et al.* (1978).

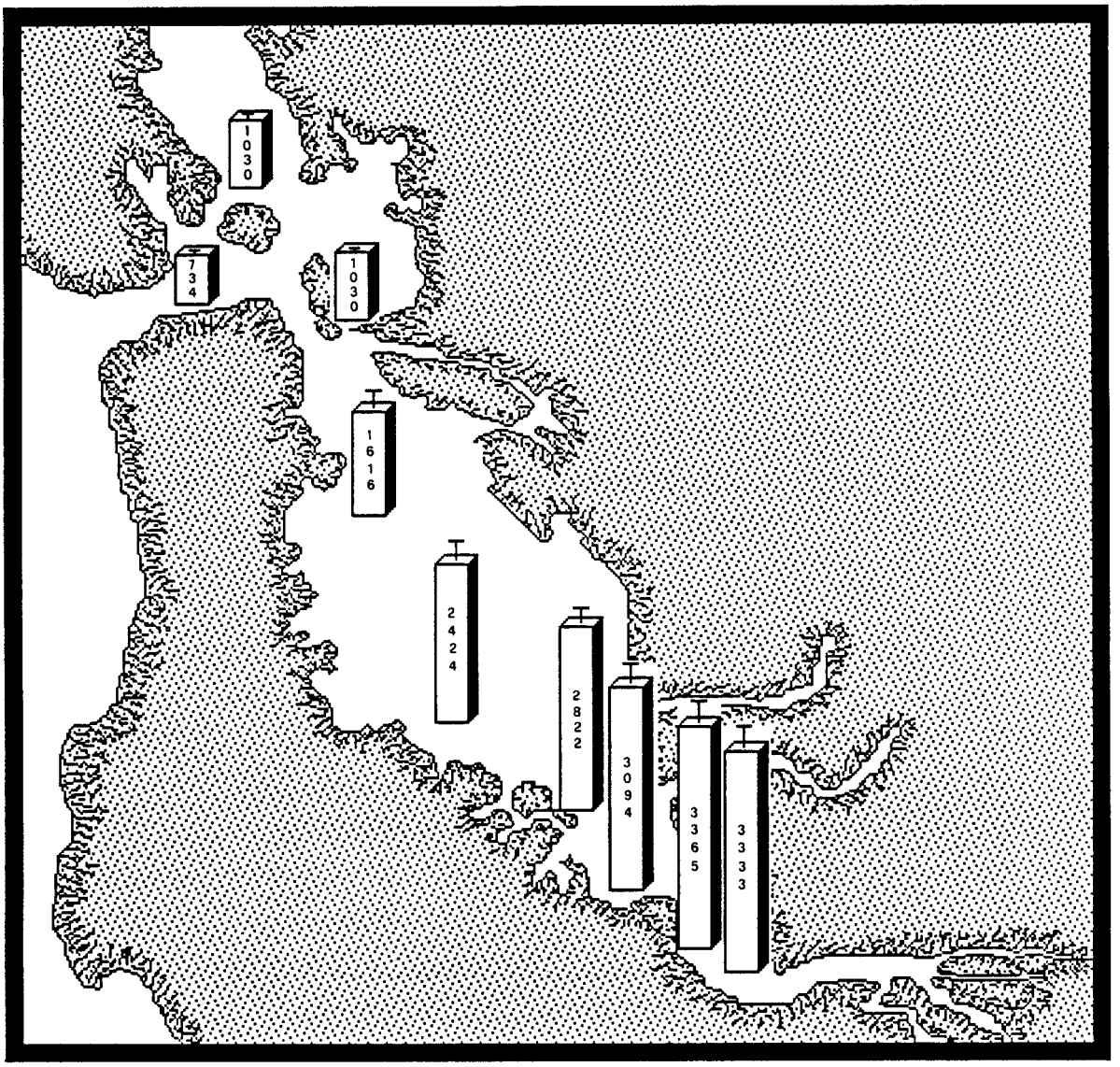


Figure 8. Concentrations (ng L^{-1}) of dissolved copper in the northern reach of the Estuary. Bars represent average of three cruises (1975-1976). Error bar denotes one standard error of the mean. Data from Eaton (1979).

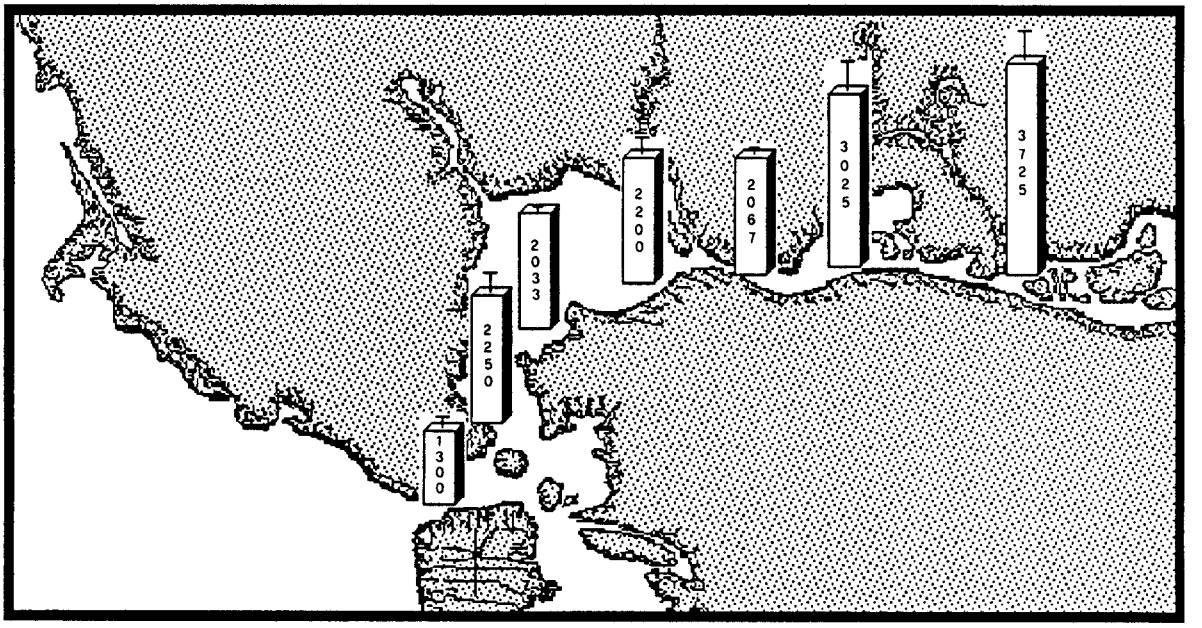


Figure 9. Concentrations (ng L^{-1}) of dissolved copper at nine stations in San Pablo and Central Bays. Bars represent single measurements, except for the Golden Gate (Gordon's station #10), which is a mean of single measurements from three cruises (March 1979-March 1980). Error bar in that case is one standard error of the mean. Data from Gordon (1980).

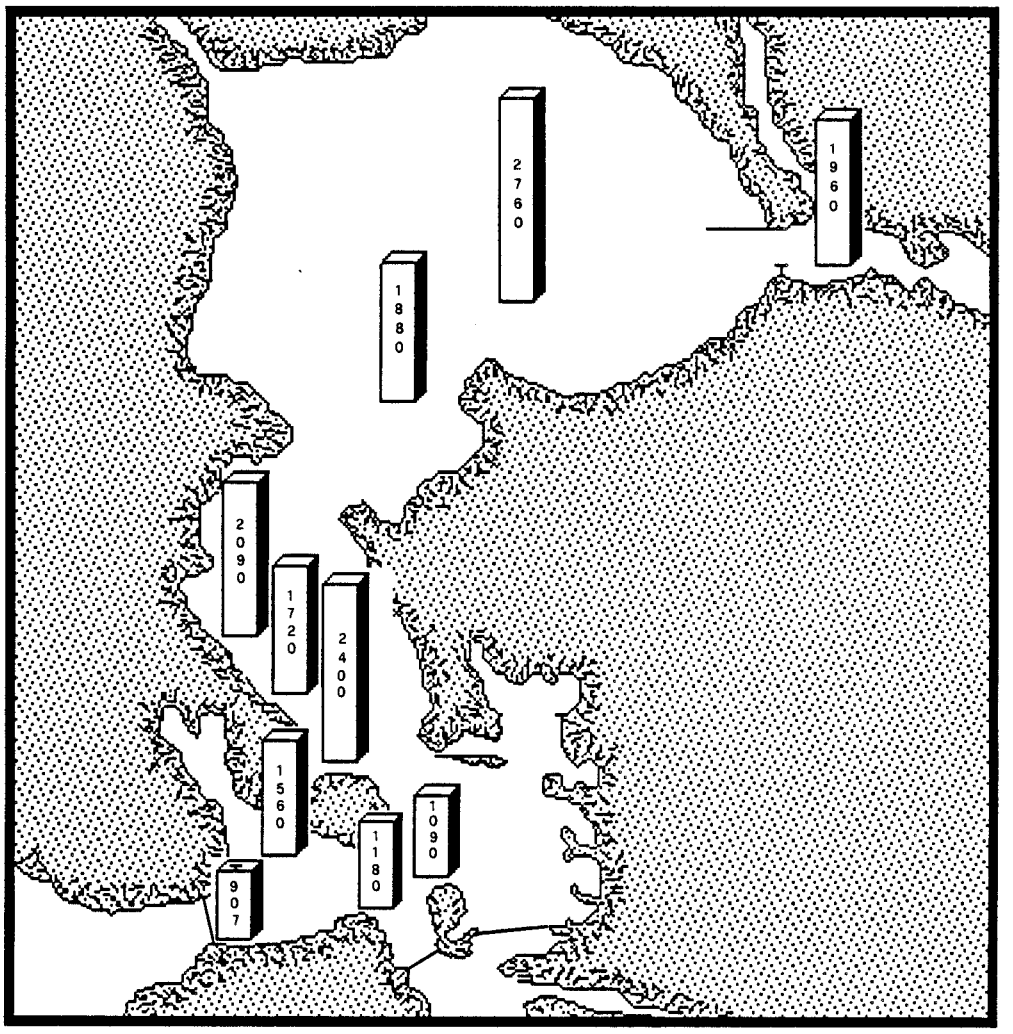


Figure 10. Concentrations (ng L^{-1}) of dissolved Copper in San Pablo Bay. Bars represent the mean of samples from several depths. Error bar is one standard error of the mean. Data from Stukas (1986).

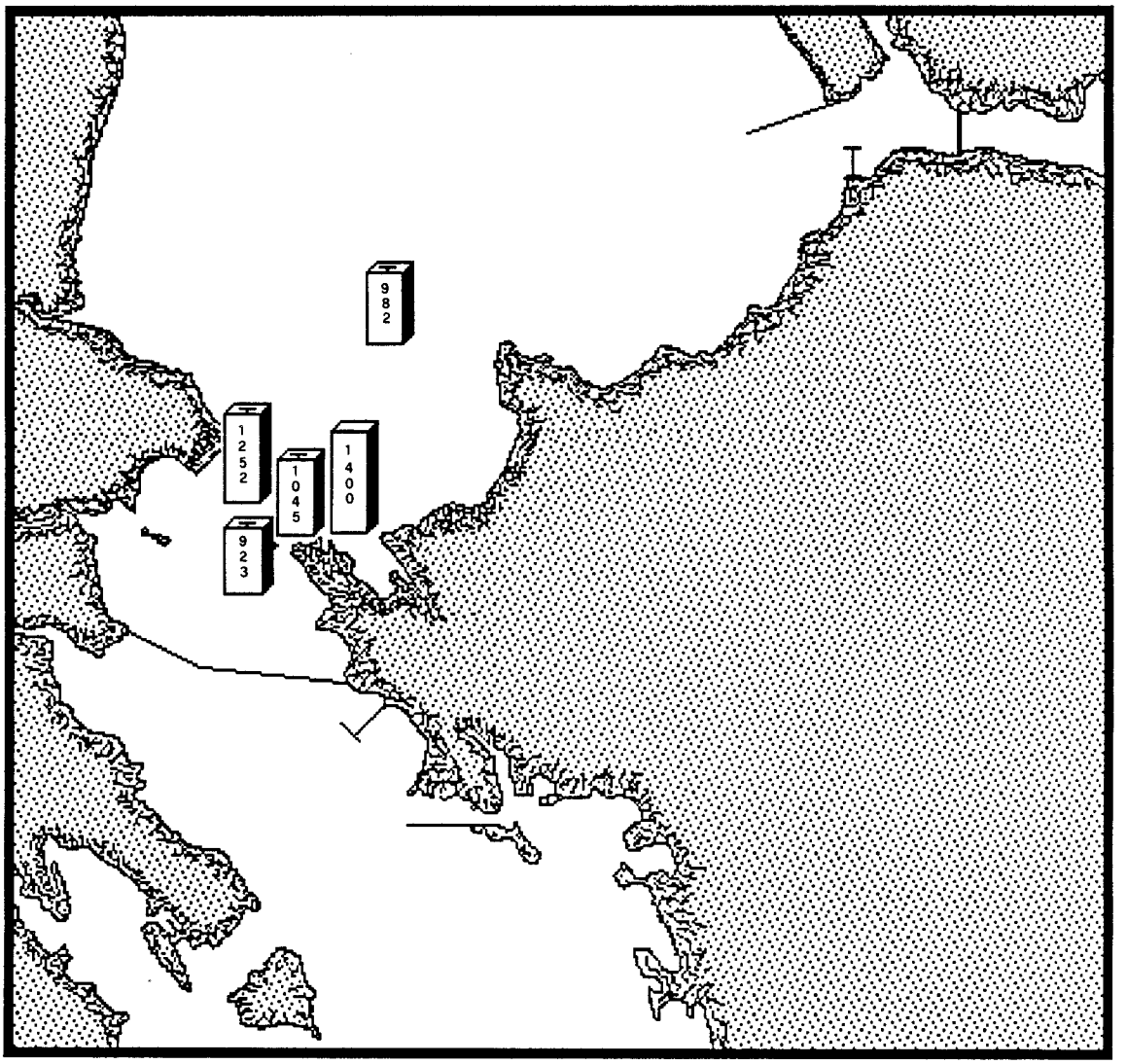
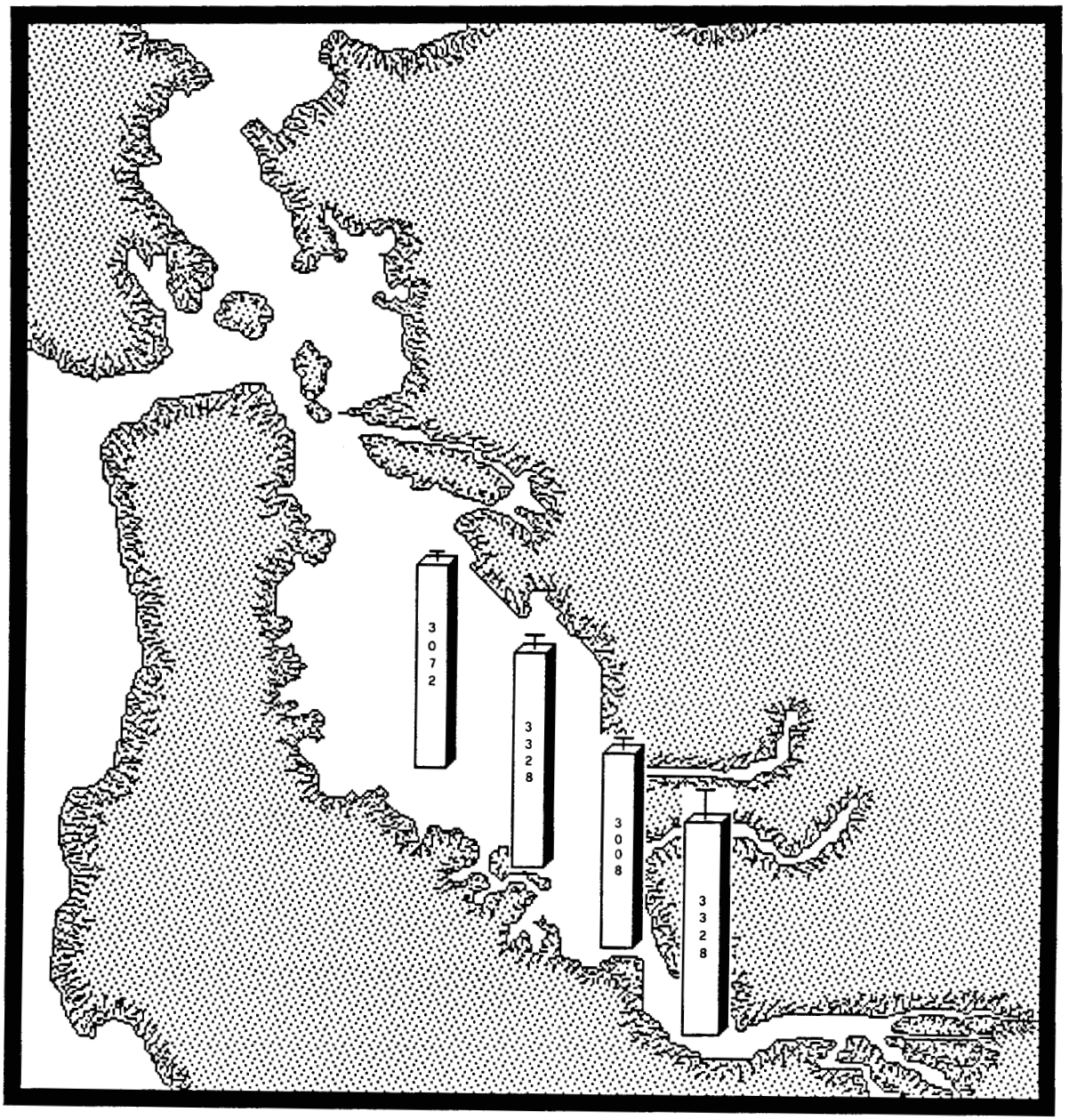


Figure 11. Concentrations (ng L^{-1}) of dissolved copper at four stations in the South Bay. Bars represent means over 5 cruises in 1985. Error bar denotes one standard error of the mean. Data from Kuwabara *et al.* (In Press).



divergent levels of the element, and this probably depends on the precise conditions of freshwater inflow and effluent discharges (as well as tides, etc.) at the time of sampling. In Central Bay and San Pablo Bay, dissolved copper concentrations may vary between about 0.1 and 4.0 $\mu g\ L^{-1}$. A general increase in copper levels in solution is commonly seen with distance away from the Golden Gate, both in the northern reach and the South Bay. [However, this is not always the case; Kuwabara *et al.* (in press) noted no well-defined gradient in the concentrations of dissolved copper with distance southwards in South Bay]. In areas of the Delta and close to the terminus of South Bay, receiving waters may contain as much as 4 or 5 $\mu g\ L^{-1}$ of dissolved copper on a regular basis. When copper present in particulates is taken into account (this would be likely to approximately double the levels cited above for the dissolved form of the element), these concentrations of copper in receiving waters of the estuary would commonly breach the ambient water quality criterion proposed by EPA for marine waters of 2.9 $\mu g\ L^{-1}$ as a one-hour average. The Basin Plan for the estuary (SFRWQCB, 1986) notes that the toxicity of copper varies with the complexing capacity of specific receiving waters, and that there is a need for the development of site-specific objectives for copper in the estuary. No decision on a suitable objective for copper in receiving waters of the estuary has yet been made.

Iron: Eaton (1979a) provided the only reliable data for iron in open waters of the estuary, citing values of about 0.01 $\mu g\ L^{-1}$ in the Gulf of the Farallones, increasing to seasonally-variable values of between 0.01 and 0.4 $\mu g\ L^{-1}$ in the northern reach of the estuary. The great majority of iron in coastal waters is present attached to particulates rather than in solution, and these concentrations are neither surprising nor particularly relevant to the protection of the estuary.

Manganese: Gordon (1980) found that dissolved concentrations of manganese varied from about 0.75 $\mu g\ L^{-1}$ in the Gulf of the Farallones to about 20 $\mu g\ L^{-1}$ in Central and San Pablo Bays. Like iron, manganese is highly particulate-associated in most receiving waters, and these concentrations are not of toxicological concern.

Mercury: Stukas (1986) found dissolved levels of mercury in San Pablo Bay to range from 0.006 to 0.011 $\mu g\ L^{-1}$, while total mercury concentrations varied between about 0.01 and 0.28 $\mu g\ L^{-1}$ (the latter maximum value ignores one outlier of 0.95 $\mu g\ L^{-1}$, which may have been due to sample contamination). These levels of mercury in solution are close to the Basin Plan objective for the estuary, even when concentrations of the

element in suspension are ignored in such a comparison (the Basin Plan objective calls for four-day average concentrations of total mercury of less than 0.025 $\mu g\ L^{-1}$ in both fresh and salt waters; SFRWQCB, 1986). The EPA ambient water quality criterion for mercury in fresh waters is 0.012 $\mu g\ L^{-1}$; the Basin Plan notes that this concentration would be desirable for adoption, but that 0.025 $\mu g\ L^{-1}$ was selected as the objective for fresh waters because of difficulties in detecting concentrations of mercury in waters below this concentration. It is probable that waters of the Delta would breach this criterion at least some of the time, given the mercury sources upstream in the Central Valley (CVRWQCB, 1987; Phillips, 1987). Other receiving waters of the lower estuary may also breach an objective of 0.025 $\mu g\ L^{-1}$ for total mercury, although no data are available to confirm this.

Nickel: The data of both Eaton (1979a) and Gordon (1980) show that nickel is present in dissolved form at concentrations between about 0.2 and 0.4 $\mu g\ L^{-1}$ in offshore waters of the Gulf of the Farallones. These levels increase within the Bay, to about 1 $\mu g\ L^{-1}$ in Central Bay, to as high as 4 $\mu g\ L^{-1}$ through the northern reach, and to between 3 and 8 $\mu g\ L^{-1}$ in South Bay. Although the data for the northern reach of the estuary suggest the presence of local sources of nickel, no well-defined geographical gradient in contamination for this portion of the Bay has been described. By contrast, Girvin *et al.* (1978) reported the existence of gradually increasing concentrations of dissolved nickel with distance southwards in South Bay. The Basin Plan (SFRWQCB, 1986) proposes a 24-hour average objective for nickel in receiving waters of 7.1 $\mu g\ L^{-1}$, which would be breached at least in some periods in the South Bay (particularly if nickel in particulates were taken into account). The concentrations of total nickel in the northern reach of the estuary might also occasionally breach such an objective.

Lead: As noted previously, lead is one of the most difficult elements to quantify reliably in natural waters, due to the problems caused by extraneous contamination of samples. Girvin *et al.* (1978) reported an increase in dissolved lead levels with distance southwards in South Bay, but also noted that the data were to be treated with caution, as sample contamination was suspected. Gordon (1980) found very low dissolved concentrations of lead in the Gulf of the Farallones; these ranged between 0.005 and 0.05 $\mu g\ L^{-1}$. Concentrations of lead in solution in Central and San Pablo Bays were variable, ranging between 0.01 and 0.12 $\mu g\ L^{-1}$. Stukas (1986) reported dissolved lead levels to be 0.001 to 0.04 $\mu g\ L^{-1}$ in San Pablo Bay. Flegal and Gordon (unpublished data) cited levels of 0.02 to 0.09 $\mu g\ L^{-1}$ for dissolved lead in the waters of South Bay. All

of these authors found much greater concentrations of lead in particulates than in solution, which is the normal situation for coastal waters. In most cases, the amounts of lead in solution were outweighed by those attached to suspended particulates by factors of 10-30. Even if the particulate-associated lead were taken into account, however, these levels do not approach water quality criteria or objectives for lead (5.6 $\mu g\ L^{-1}$ in marine waters and 3.2 $\mu g\ L^{-1}$ in fresh waters at a hardness of 100 mg L^{-1} as $CaCO_3$; see EPA, 1986; SFRWQCB, 1986).

Selenium: The available data for selenium in receiving waters of the estuary have been reviewed by Cutter (1987) and Phillips (1987), and will not be exhaustively detailed here. Selenium is known to be discharged from the San Joaquin River in periods of high flow; this input exists predominantly as selenate, and derives from the run-off (either natural or irrigation-induced) from areas of the Central Valley which exhibit naturally seleniferous soils, due to the presence of marine shales. In addition, oil refineries in the northern reach of the estuary are a known significant source of the element (Gunther *et al.*, 1987), and selenite predominates in these effluents. Total concentrations of the element (summing the various chemical species present in estuarine waters) increase with distance away from the Golden Gate in both the northern reach and South Bay. The principal sources of selenium in the South Bay have not yet been identified. The Basin Plan for the estuary (SFRWQCB, 1986) notes that objectives for selenium in the estuary should be set to control the levels of bio-accumulation of the element, rather than its direct toxicity in solution. No objective for this element has yet been set for the Bay and Delta.

Zinc: Concentrations of zinc in solution in the estuary have been studied by several authors, and agreement between authors is generally good. The levels found are unremarkable for an estuary of this type. Girvin *et al.* (1978) reported dissolved levels of zinc of about 0.3 $\mu g\ L^{-1}$ in Central Bay, increasing to 0.5 to 2.0 $\mu g\ L^{-1}$ in South Bay receiving waters. Eaton (1979a) found zinc concentrations in solution to be variable, both in the northern reach of the estuary and in the Gulf of the Farallones. The concentrations reported were generally less than 1.0 $\mu g\ L^{-1}$ in the offshore waters of the Gulf, increasing to 0.5 to 7.5 $\mu g\ L^{-1}$ in the northern reach. There was some indication of an increase in concentrations of dissolved zinc with distance away from the Golden Gate within the Bay, but the gradient was not well-defined. Gordon (1980) found dissolved zinc levels of 0.3 to 0.7 $\mu g\ L^{-1}$ in the Gulf of the Farallones, increasing to 0.6 to 4.2 $\mu g\ L^{-1}$ in Central and San Pablo Bays. Stukas (1986) reported dissolved concentrations of zinc

of 0.12 to 0.59 μg L^{-1} in San Pablo Bay. Kuwabara *et al.* (in press) found that dissolved zinc levels in South Bay varied between 2.1 and 7.0 μg L^{-1}, generally increasing with distance southwards. As noted above, these levels are unremarkable for a large estuary, and do not approach water quality objectives for this element (58 μg L^{-1} as a 24-hour average for both marine and fresh waters; see SFRWQCB, 1986).

Existing Problems

It is clear from the above compilation of the available data that considerable problems exist in attempting to introduce regulatory controls in the estuary based upon water quality objectives or ambient water quality criteria. These problems are broadly as follows:

(i) **Difficulties in measurement:** Concentrations of trace contaminants in receiving waters are difficult to measure accurately. "Clean laboratory" facilities are required, and these are not readily available in most of the Bay area. Controversy continues over the available data for lead in particular, because of the problems caused by the extraneous contamination of samples.

(ii) **Expense:** Because special facilities and equipment are required, and because sample preparation is labor-intensive, analyses of water for trace contaminants are expensive. A decision to regulate contaminant levels in the estuary through the imposition of receiving water quality objectives implies the continued monitoring of trace levels of contaminants in solution and suspension, and this in turn demands a significant financial commitment. Such a commitment has not been made to date.

(iii) **Paucity of data to date:** The general paucity of studies to date on contaminant levels in receiving waters of the estuary provides a very poor historical database. Any new program would be likely to be of a "stand-alone" nature, in that the use of previous data to generate conclusions on temporal changes in the concentrations of trace contaminants in solution would be suspect.

(iv) **Disagreement between studies performed to date:** As noted previously, there is disagreement between certain of the studies described above. There is therefore significant uncertainty concerning the real concentrations of trace elements

in receiving waters of the estuary. The oft-repeated conclusions concerning the "water quality-limited" nature of portions of the estuary for some contaminants are based on very little data.

(v) **Lack of coordinated approach or program:** Most importantly, there has been no attempt to introduce a coordinated approach to the elucidation of the levels of toxic contaminants in receiving waters of the estuary, notwithstanding the imposition of water quality objectives for trace metals and total PAHs in receiving waters through the Basin Plan (SFRWQCB, 1986). If these objectives are to be enforced, a new program is required to monitor trace metals and PAHs in receiving waters, and their changes with time.

(vi) **Lack of time-integrated water sampling:** Finally, it is notable that none of the studies performed to date employed time-integrating water samplers. All samples were therefore essentially grab samples. Any new program for the study of trace contaminants in receiving waters of the estuary should recognize the advantages of the use of time-integrating samplers. These serve to smooth out the short-term temporal fluctuations in contaminant concentrations, thus providing an improved estimate of average concentrations. In addition, the use of time-integrated samplers would permit sampling to match the water quality objectives themselves, as these are generally based on permitted maximum concentrations of metals over periods ranging from 24 hours to 4 days. Due to the known variability of trace metal concentrations in receiving waters with time (see section II of this report for examples), it is not strictly legitimate to compare the concentrations of trace elements found in grab samples with the time-averaged objectives to determine compliance levels.

Proposals for a Coordinated Program

There are definite benefits to dovetailing water sampling programs to those monitoring programs which sample sediments and biota in the estuary. This will not only reduce costs (e.g. by permitting all samples to be taken at the same times, from the same vessel) but will also provide a coordinated database in which concentrations of contaminants in the three types of media may be related to each other.

To avoid confusion and unnecessary repetition, all proposals for a coordinated monitoring program to be introduced to monitor toxic contaminants in the estuary are provided in section VII of this report.

C. Regional Monitoring of Toxic Contaminants in Sediments

The Existing Database

Existing data concerning toxic contaminants in sediments of the San Francisco Estuary have been comprehensively reviewed by Phillips (1987) and Long *et al.* (1988). As a result, these data will not be discussed in detail here, but information provided by these two reviews is summarized.

It is relevant here that the separation of sediment-related data for toxic contaminants into those reflecting "regional" trends and those indicative of "local" trends is rather more difficult and arbitrary than this categorization for water samples. In most cases, receiving waters from open portions of the Bay and Delta may be considered to be indicative of "regional" conditions, as these are remote from most local sources (although they undoubtedly reflect some integral of these sources). "Local" trends in the contamination of waters are evident in more enclosed portions of the Bay and Delta, and/or closer to sources. In many cases, it should be possible (given adequate sampling and sufficiently accurate analysis) to define spatial gradients in contaminant concentrations in water from known sources to "background" levels offshore, approximating regional conditions. In the case of sediments, it might be assumed simplistically that the same separation of regional and local trends should exist, and could be monitored. Thus, for example, nearshore sediments (close to sources of contaminants situated at the margins of the Bay and Delta) might be considered indicative of local trends only, while sediments from offshore regions could be argued to reflect regional trends. However, the impacts of extraneous parameters (including the rates of sedimentation, grain size, organic carbon content and other factors; see below) tend to confound this division, and to give rise to a general patchiness of contaminant levels in sediments throughout the estuary (Long *et al.*, 1988). Because of this, the following review of the available data for contaminants in sediments does not attempt to distinguish between samples or areas indicative of regional trends and those reflecting local patterns of contamination. The existence of patchiness in sediment contamination is of particular importance in defining the usefulness of sediments to monitor regional trends in toxicant abundance in the Bay and Delta, and will be returned to below.

Phillips (1987) discussed available data concerning both trace elements (principally Ag, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sn, and Zn) and organochlorines (principally DDT and metabolites and PCBs) in sediments of the estuary. He concluded that the database was fragmented, and suffered from inadequate information on quality control of analysis, as well as incomplete coverage (spatially or temporally) of the estuarine sediments. It is accepted that seasonal trends in metal levels in sediments (driven largely by temporal changes in grain size distribution) exist in at least parts of the estuary (e.g. Eaton, 1979b, Thomson-Becker and Luoma, 1985). Such trends would also be expected to exist for chorinated hydrocarbons, due to the effects of both grain size and the temporally-variable application of pesticides in the catchment of the Bay. However, no data exist to confirm the existence of seasonal trends in such contaminants in the estuary. Many authors have reported a covariance of contaminant concentrations in sediments with their organic carbon content, and this is also commonly observed elsewhere in coastal environments. Rice *et al.* (in press) have suggested that all data for sediment contamination should be reported normalized to the organic carbon content of samples, because of the over-riding importance of this parameter in determining the contamination levels observed in sediments. However, this approach has not yet been adopted for routine use, and many authors have not quantified or reported organic carbon contents of sediments in the past.

Long *et al.* (1988) reviewed data for nine contaminants (or groups of contaminants) in 20 studies of sediments, covering a total of 1232 sampling sites. Despite this considerable database, these authors suffered from the same problems as those noted above in attempting to synthesize a coherent picture of sediment contamination in the estuary. They discussed sources of variability, noting these to be the following:

- Differences in sampling protocols exist, especially with respect to the depth of sediments sampled. The latter varied widely, between truly surficial sediment sampling of the surface 1 cm or less, to bulk sampling involving sediment depths of several metres. This is important in defining both the precise levels of contaminants reported, and the degree of time-averaging which these values represent. These effects have been discussed in detail by Phillips (1986) in relation to PCBs in sediments; the principals are the same for all trace contaminants. It is particularly notable that certain types of sediment samplers tend to cause the loss of fine-grained

surface material; this will in many cases affect the analytical data (and the interpretation thereof) significantly.

- Differences in the analytical methods employed in various studies, and in their degree of sophistication and reliability are an important consideration, especially with respect to analyses of organic contaminants. Long *et al.* (1988) noted that: "...apparent [temporal] trends in concentrations of contaminants may merely reflect differences or changes in methods." No widely-accepted methods for the analysis of sediment-borne contaminants exist among the local scientific community, and each group of researchers tends to favor its own precise (or in some cases, imprecise) method. It is also notable that very few analyses of trace elements in sediments have differentiated between "residual" concentrations and metals bound in (theoretically) more bio-available forms to the surfaces of sediment particles.

- Grain size, minerology, organic carbon content, and various other parameters also affect the concentrations of metals found in sediments, as noted previously. Long *et al.* (1988) provided interesting data on these various relationships.

The concusions from these two reviews of the available data on sediment contamination within the estuary are provided in broad terms in Table 8.

Existing Problems

Several problems are encountered in an attempt to define an adequate regional monitoring program for toxic contaminants in sediments. These are as follows:

(i) **Poor historical database:** While the number of data points available on sediment contamination by trace metals in particular within the Bay and Delta is considerable, comparability is poor within the dataset. Different studies have employed distinct methodologies for sampling and analysis, and the results of these studies cannot be considered to be strictly comparable, as discussed by Long *et al.* (1988). Each study has attempted to address its own unique goals, without consideration of the remainder of the database and the comparability of new results to historical data. No concerted sampling regime has been used, either in terms of

Table 8. Conclusions concerning the degree of contamination of sediments of the San Francisco Estuary, based upon the reviews of Phillips (1987) and Long *et al.* (1988).

Contaminant	Degree of contamination	Remarks
Silver (Ag)	Minor/High	Considerable variation exists spatially in the estuary. The northern reach is generally not heavily enriched, but the South Bay sediments are heavily contaminated in some areas. Hot-spots exist close to some sewage outfalls.
Cadmium (Cd)	Minor	Apart from very localized hot-spots, cadmium concentrations in sediments of the estuary are unremarkable.
Chromium (Cr)	Uncertain	Very considerable differences exist between the data of different authors. It is possible that temporal decreases have occurred, explaining some of these differences. Inadequate QA/QC of early studies frustrates conclusions.
Copper (Cu)	Minor/Moderate	Concentrations are spatially very variable. Sediments of most of the estuary contain relatively little copper compared to polluted locations elsewhere; however, hot-spots exist, particularly close to certain sewage outfalls. Nearshore sediments tend to be more contaminated than offshore sediments.

Table 8 (continued). Conclusions concerning the degree of contamination of sediments of the San Francisco Estuary, based upon the reviews of Phillips (1987) and Long *et al.* (1988).

Contaminant	Degree of contamination	Remarks
Mercury (Hg)	Minor/High	Great spatial variability exists on a local scale, nearshore sediments often being much more contaminated than offshore samples. Multiple sources of Hg to the estuary clearly exist, in addition to natural and (historic) anthropogenic sources in the Central Valley.
Nickel (Ni)	Minor	Most reported concentrations are similar to those in average shale. Little spatial variation is evident from results to date; perhaps contaminated areas have not yet been studied (cf. data for water and biota).
Lead (Pb)	Minor/High	Considerable spatial variation exists, and contamination profiles are indicative of multiple sources. Urban runoff may be a significant source; nearshore sediments tend to be more contaminated than those offshore in the estuary.
Selenium (Se)	Uncertain	Very little information exists. Analytical problems are suspected for early data; additional work is required.

Table 8 (continued). Conclusions concerning the degree of contamination of sediments of the San Francisco Estuary, based upon the reviews of Phillips (1987) and Long *et al.* (1988).

Contaminant	Degree of contamination	Remarks
Tin (Sn)	Uncertain	Very little information exists. Organotins reside in sediments, and microbial activity degrades TBT to DBT and MBT. However, analytical techniques are still under development. TBT in paint chips in sediments may be a significant future source, despite impending bans on TBT use in antifouling compounds.
Zinc (Zn)	Minor	Little spatial variation exists, although a few hot-spots are known. In general, levels of zinc in sediments of the estuary are unremarkable.
DDT/DDE/DDD	Minor	Concentrations of DDT and metabolites are detectable in Bay sediments, but are present at much lower levels than those in sediments of contaminated areas of southern California. Hot-spots exist close to river mouths and other sources (e.g. Lauritzen Canal).

Table 8 (continued). Conclusions concerning the degree of contamination of sediments of the San Francisco Estuary, based upon the reviews of Phillips (1987) and Long *et al.* (1988).

Contaminant	Degree of contamination	Remarks
PCBs	Moderate/High	Little information exists. Spatial heterogeneity appears present over short distances. Some areas on the periphery of the estuary are highly contaminated. Recent studies of Rice *et al.* (in press) provide the most comprehensive picture, but more data are needed.
Chlordane/Other	Minor	Chlordane has been detected in sediments of the estuary, as has hexachlorobenzene. The levels found are not high by comparison to polluted locations.
Hydrocarbons	Uncertain	Very few studies conducted. Those which have been reported show significant levels of PAHs in sediments of the estuary, and considerable spatial variation. In general, sediments from the periphery of the estuary are more contaminated than those in offshore areas. More data are needed.

precise sampling method or with respect to decisions on sampling locations. No attempt prior to sampling has been made to account for the impacts of grain size and organic carbon content of sediments, although some authors have tried to account for these parameters in one fashion or another in sample preparation (e.g. by sieving) or in data interpretation. Relatively little information is available on the concentrations of chorinated hydrocarbons in sediments of the estuary. Those studies which have been published, notably by Spies and co-workers (Spies *et al.*, 1985b; Rice *et al.*, in press) have shown that considerable patchiness exists in sediment contamination, over short distances and even in the more open portions of the Bay. Finally, the database for hydrocarbons in sediments of the Bay and Delta (principally involving PAHs; MAHs are not expected to accumulate significantly in sediments - see de Vlaming, in draft 1988) is very poor indeed to date, being derived from only a few studies.

(ii) **Inadequate data on residual metals:** Very few studies (e.g. Eaton, 1979b) have reported data concerning the nature of the binding of metals to sediments. It is generally accepted that residual metals (those bound within the matrix of particulates) are less available to biota than are elements adsorbed to the surface of particulates. Differential extraction techniques are useful to broadly define the bio-availability of metals in sediments, and are now well-developed methodologically. This factor is not thought to be important with respect to organic pollutants, as these are not present within the matrix of sediment particles, generally being surface-adsorbed. However, it is possible that the precise method of binding of such contaminants as chlorinated hydrocarbons and PAHs to sediments affects their bio-availability, although there is little information on this topic in the open literature.

(iii) **Spatial patchiness:** The spatial patchiness in sediment contamination by metals and organic pollutants causes severe problems in attempting to devise a regional sampling program for sediments in the Bay and Delta, as noted above. Such a program should attempt to define "background" values of sediment-associated contaminants in the more open reaches of the estuary, such that these may be related to local trends in more contaminated areas. However, geographical small-scale heterogeneity in contaminant levels in the sediments in the open areas of the estuary confounds this goal. It is not possible to ensure that sediment samples are taken at *precisely* the same locations in offshore areas at all times of sampling in a long-term program, even with the use of sophisticated position-fixing methods. As

the causes of such patchiness in contaminant levels cannot be discerned and taken into account in program design and in sampling protocols, it seems impossible to rely upon sediment analysis as a means of characterizing background (regional) levels of toxic contaminants within the estuary. [It should also be noted here that almost nothing is known of the transport of sediments or suspended particulates in the estuary, which is undoubtedly of great importance in determining the fluxes of many contaminants through the system. There is a need to upgrade the existing mathematical models of hydrodynamics in the Bay and Delta to include the modeling of suspended particulate movements. However, this need is not comprehensively addressed here, being outside the scope of the present report.]

Proposals for a Coordinated Program

All proposals for a coordinated monitoring program involving water, sediments and biota in the estuary are provided in section VII below.

D. Regional Monitoring of Toxic Contaminants in Biota

The Existing Database

General

The use of organisms to monitor contaminant abundance and bio-availability in estuarine ecosystems has become extremely popular in the last two decades, for the reasons discussed in section II of this report. Most authors now consider this the method of choice for the regional monitoring of toxicants, and there are powerful arguments to support this viewpoint (Phillips, 1980; Bryan *et al.*, 1980; 1985; Waldichuk, 1985; Phillips and Segar, 1986). Organisms not only provide a time-averaged picture of contaminant abundance, but also a direct indication of the bio-availability of toxicants. This latter parameter cannot be ascertained through the analysis of water or sediments, yet is essential to any understanding of the impacts of pollutants in estuarine and coastal ecosystems.

While several authors have employed organisms to monitor toxic contaminants in the estuary (see review by Phillips, 1987), most of these studies were of a one-time or short-term nature, or covered a restricted range of contaminants; these have added relatively little to our present overall understanding of regional contamination in the estuary. Two long-term programs exist providing data on a range of toxic contaminants in bio-monitors, however; these studies, which have provided the basis for our present knowledge on toxicant abundance and bio-availability in the estuary, are reviewed below.

Researchers in California have contributed significantly to the historical development of bio-monitors for the assessment of contaminant levels in coastal waters, and long-term regional monitoring programs have resulted from these efforts . Both the national Mussel Watch program (initially funded through EPA; more recently subsumed within the National Status and Trends Program of NOAA) and the California State Mussel Watch Program (SMWP) have been instrumental in gaining widespread international acceptance of this technique as a monitoring tool in aquatic environments. However, such programs are only as reliable as their precise design permits, and the previous national program conducted through EPA was criticized for certain

inadequacies in its design (NAS, 1980; Phillips and Segar, 1986). These concerns are reviewed briefly in the present document, and the California SMWP is also critically reviewed herein.

The national and State Mussel Watch Programs employ mussels (native *Mytilus edulis* and transplanted *M. californianus*) to monitor contaminant levels in the San Francisco Bay. The salinity sensitivity of these species restricts their use within the estuary to the water mass west and south of the Carquinez Strait (San Pablo Bay, Central Bay, and South Bay, in addition to waters of the Pacific outside the Bay); neither native nor transplanted mussels of these species survive adequately in the low-salinity waters of Suisun Bay or the Delta.

In addition to these programs, Luoma and co-workers have amassed a long-term database for trace metals in the clam *Macoma balthica* in the South Bay, particularly for contaminated locations close to Palo Alto. This database will be considered in section V on local monitoring of contaminants in this report, as the conclusions therefrom are relevant more to the local impacts of effluent discharges than to regional monitoring efforts.

Freshwater areas in the Central Valley catchment are monitored through the Toxic Substances Monitoring Program (TSMP), funded by the State Water Resources Control Board. This program involves the collection and analysis of (mostly) freshwater and (some) anadromous fish species from the various tributaries of the Sacramento and San Joaquin River systems; certain invertebrate species have also been employed on occasion. The data on bivalves (especially *Corbicula fluminea)* are of particular interest, and these data have been expanded through additional studies by Luoma *et al.* (1984, and unpublished manuscript) and Johns and Luoma (in press). Just as the State Mussel Watch Program is an expanded Californian component of the national Mussel Watch studies, so the TSMP is an intensive version of a national program of this type run through the U.S. Fish and Wildlife Service. Emphasis will be given here to the local Californian components of these efforts, as these provide the great majority of the data relevant to the San Francisco Estuary and its catchment, and national programs do not add measurably to this database in most cases (because of the small number of sampling locations in the Bay or its catchment in national programs).

The State Mussel Watch Program

The SMWP commenced in 1977, although routine monitoring of toxic contaminants in the San Francisco Estuary through this program started in 1979. Data from these studies are published in annual reports (see Hayes *et al.*, 1985; Hayes and Phillips, 1986; Stephenson *et al.*, 1986; and Phillips, 1988 for the most recent reports). The initial objective of the program was to provide reliable data on spatial and temporal trends in contaminant abundance and bio-availability in the coastal waters of California. The initial design of the program, particularly with reference to the choice of sampling sites, reflected a desire to monitor "background" conditions in most areas. Thus, sampling sites in the San Francisco Estuary (and the majority of those elsewhere on the Californian coast) were generally located some distance from most known outfalls or other sources of contaminants, and were selected to represent the contamination levels in water masses, rather than those in local areas or "hot-spots". Thus, the initial objective of the SMWP in the San Francisco Estuary precisely matched that of regional monitoring programs for contaminants.

The techniques employed in the SMWP are in general exemplary. Much has been made of the importance of sampling design in such studies (e.g. Phillips, 1980), and it is an unfortunate fact that many monitoring programs employing bio-monitors fail to meet their objectives because of insufficient attention to detail in this respect. However, the sampling design employed by the SMWP is of a high calibre; indeed, several of the scientists involved in this program have forged international reputations on their publication of its results. Early research into the impacts of extraneous parameters such as shore level and size of sample employed (number of individuals analyzed; see Gordon *et al.*, 1980) was important in optimizing the techniques used. The analytical techniques employed reflected the state of the art, and have continued to be modified and improved since the inception of the program, permitting in more recent years the quantification of greater numbers of contaminants (especially chlorinated hydrocarbons).

The results of the national and State Mussel Watch Programs have been comprehensively reviewed by several authors (Goldberg *et al.*, 1978, 1983; Flegal *et al.*, 1981; Farrington *et al.*, 1983; Martin *et al.*, 1984b; Martin and Castle, 1984; Martin, 1985; Smith *et al.*, 1986; NOAA, 1987). In addition, Phillips (1987), Long *et al.* (1988) and Phillips and Spies (1988) have provided recent overviews of these data. The present

report does not seek to recap these results *per se*, but considers the broader question of the relevance of the historical and current programs within San Francisco Bay to addressing management questions on toxicant abundance and effects in the estuary.

Given the excellence of the work undertaken in the national and State mussel watch studies since their inception, it is a great pity that these programs have largely failed to provide a substantive database on temporal and spatial trends in contaminant abundance and bio-availablity in the San Francisco Estuary. The reasons for this are considered to be as follows:

(i) **Insufficient numbers of study sites:** It is generally recognized that the San Francisco Estuary is an exceptionally complex system. This complexity derives from its considerable size (water surface area of 1240 km^2, draining a catchment area of 153,000 km^2; see Conomos *et al.*, 1985), the asymmetry of freshwater inflows, and from anthropogenic impacts. Both the magnitude and locations of significant contaminant sources within the estuary have been very poorly defined to date (with the possible exception of point sources; see Gunther *et al.*, 1987), and an understanding of the hydrodynamics of the system is only beginning to emerge. Given this paucity of knowledge of the estuary, decisions on the required locations for sampling sites to characterize contaminant distributions within the system are largely relegated to the status of educated guesses.

Tables 9 and 10 show updated information from the SMWP on the observed concentrations of a trace metal (cadmium is employed as an example) and a chlorinated hydrocarbon (PCBs as an example) in mussels from the estuary, all data since the inception of the program being provided. It is evident that in most years, very few study sites have been employed. The numbers of sites studied in any one year for trace metals have varied from 5 (1983) to 23 (late 1982, including both transplanted and native mussels), and from 1 (1979) to 11(1986) for chlorinated organic contaminants. Given the great complexity and known heterogeneity of contaminant distributions over even small geographical areas of the estuary, this number of samples can hardly be considered to provide comprehensive coverage of the estuary, even in terms of attempts to define regional trends in contamination (i.e. ignoring local trends). National programs have not contributed significantly to this database in terms of station numbers. The original national Mussel Watch

Table 9. Mean concentrations of cadmium ($\mu g\ g^{-1}$ dry weight) in transplanted mussels (*Mytilus californianus*) or native Bay mussels (*M. edulis*, as shown[a]) from 33 sites in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes *et al.* (1985); Hayes and Phillips (1986); and Stephenson *et al.* (1986).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1986
MARE ISLAND	300.20							8.2a	5.0
DAVIS POINT	301.00	4.4a			11.7				
POINT PINOLE	302.00	4.3a	19.5	19.9	10.2b		11.8	10.8	5.5
RICHMOND BRIDGE	303.00	11.5	10.8	13.6	9.7b				
SANTA FE CH. MOUTH	303.10								7.5
RICHMOND INNER HARBOR	303.60							5.5	
STAUFFER'S	304.00			7.3					
ANGEL ISLAND	305.00	15.0	7.2	9.4	7.6b				
FORT BAKER	306.00		10.6		8.1c				
TREASURE ISLAND	307.00	12.5	9.4	8.3	8.6c		9.1	7.6	4.3
ALAMEDA YACHT HARBOR	307.20							14.3a	8.6
OAKLAND IN. HARBOR WEST	307.30								5.5
OAKLAND IN. HARBOR EMBC.	307.40								11.7
OAKLAND BACK HARBOR	307.60								4.7
HUNTER'S POINT	308.00		12.1	11.8	11.0c	6.8a			
SAN MATEO BRIDGE 8	309.00	11.3	18.9	12.1	10.9c	6.1a	13.0	9.5	9.9
SAN MATEO BRIDGE 8A	310.00			14.4					
SAN MATEO OLD BRIDGE	311.00			11.3					
BELMONT SLOUGH	312.00			17.2					
REDWOOD CREEK MOUTH	313.00		12.5	13.5	9.2c	6.4a	12.2	11.5	
REDWOOD CREEK 10	314.00			10.3					
REDWOOD CREEK TOWERS	315.00			10.6	7.6b	6.4a			
REDWOOD CREEK TRDWNDS	316.00	5.6a		7.7	7.2b	7.6a			
REDWOOD CREEK STP	317.00				8.2				
SF PETES	318.00				8.5				
SF PULGAS	319.00				9.1				
SF AIRPORT	320.00				7.8				
DUMBARTON BRIDGE 14	321.00	8.6a	16.0	9.9	8.9	8.5a	15.7	7.5	6.1
NEWARK SLOUGH	324.00			12.1					
CHANNEL 17	325.00			12.2					
PALO ALTO 8	326.00			10.4		9.2a			
PALO ALTO YACHT	327.00			10.8					
ALVISO SLOUGH	328.00			13.5					

J/F/O/N/D: January/February/October/November/December, all 1982

[a] Resident Mytilus edulis.

[b] Mean of two values.

[c] Mean of three values.

Table 10. Mean concentrations of PCBs (ng g^{-1} dry weight, as Aroclor 1254 with additional residues as noted) in transplanted mussels (*Mytilus californianus*) or native Bay mussels (*M. edulis*, as shown[a]) from 22 sites in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes *et al.* (1985); Hayes and Phillips (1986); and Stephenson *et al.* (1986).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985	1986
MARE ISLAND	300.20							100a	76
DAVIS POINT	301.00					230			
POINT PINOLE	302.00			690	140	330	180	78	56
RICHMOND BRIDGE	303.00		370	1100	220	280			
SANTA FE CH. MOUTH	303.10								540e
SANTA FE CH. L.C.	303.20							660b	500f
SANTA FE CH. L.C. END	303.30								970g
SANTA FE CH. END	303.40							860c	500h
RICHMOND INNER HARBOR	303.60								510
ANGEL ISLAND	305.00		770	830		230			
FORT BAKER	306.00			510		270			
TREASURE ISLAND	307.00	790	630	1500	220	300	280	200	
ALAMEDA YACHT HARBOR	307.20								600
OAKLAND IN. HARBOR WEST	307.30								180
OAKLAND IN. HARBOR EMBC.	307.40							880	700
OAKLAND BACK HARBOR	307.60							690d	540
HUNTER'S POINT	308.00			1800	230	340			
SAN MATEO BRIDGE 8	309.00			1300	180	430	180		
SAN MATEO BRIDGE 8A	310.00				140				
REDWOOD CREEK MOUTH	313.00			1200	200	390	210		
REDWOOD CREEK TRDWNDS	316.00		850a						
DUMBARTON BRIDGE 14	321.00			1300	250		180		

*J/F/D: January/February/December, all 1982.

[a]Native M. edulis

[b]Also 68 ng g^{-1} Aroclor 1248.

[c]Also 100 ng g^{-1} Aroclor 1248.

[d]Also 32 ng g^{-1} Aroclor 1260.

[e]Also 100 ng g^{-1} Aroclor 1248.

[f]Also 180 ng g^{-1} Aroclor 1248.

[g]Also 160 ng g^{-1} Aroclor 1248.

[h]Also 180 ng g^{-1} Aroclor 1248.

program, undertaken from 1976 to 1978, included only two samples each year from the San Francisco Estuary, which were composites from samples taken at several locations in the northern reach and the South Bay (Goldberg *et al.*, 1978, 1983). The present effort by NOAA under the umbrella of the National Status and Trends Program (NOAA, 1987) includes up to five sites for the analysis of toxicants in bivalves (Semple Point, Point San Pedro, Yerba Buena Island, the San Mateo Bridge, and the Dumbarton Bridge), but not each of these is sampled each year (in 1986, only the San Mateo Bridge and Dumbarton Bridge samples were taken for analysis). There is undoubtedly an argument for consolidating the State and Federal programs of this type in the Bay (despite minor differences in their methodologies); while this may be politically difficult, it should give rise to benefits both in terms of costs and coverage of the Bay.

(ii) **Insufficient temporal coverage for certain contaminants:** Different contaminants vary radically in half-lives in mussels of the genus *Mytilus*. In general, most trace metals exhibit relatively long half-lives in bivalve molluscs, varying from the order of months to perhaps a year or more in certain cases (NAS, 1980; Phillips, 1980; see also section II of this report). It is reasonable to assume that the use of annual sampling of transplanted mussels in the estuary sufficiently characterizes the ambient levels of trace metals in the system, at least over the period of transplantation (generally about 4 months in duration). It should be noted that virtually nothing can be concluded in terms of seasonal changes from the data provided from the current program, however. This is unfortunate, particularly in the sense that the impact of changes in Delta inflows on contaminant conditions within the estuary (which constitutes a major management question) cannot be ascertained.

By comparison to most trace metals, many organochlorines and petroleum-related hydrocarbons exhibit much shorter half-lives in mussels. The case of PCBs may be employed as an example; these contaminants consist of a mixture of biphenyls of varying degrees and positions of chlorine substitution, each homologue possessing its own unique kinetics in mussels. Tanabe *et al.* (1987b) investigated the kinetics of individual PCB homologues in green-lipped mussels (*Perna viridis*), using the transplantation and back-transplantation of field populations. Their results are shown in Figures 12 and 13 and Table 11. It is evident that the lower-chlorinated

Figure 12. Variations in the concentrations of individual and total isomers of dichlorobiphenyls (left), trichlorobiphenyls (center), and tetrachlorobiphenyls (right) in green-lipped mussels, *Perna viridis*. Mussels were transplanted from uncontaminated conditions to a polluted environment, and then back-transplanted to clean conditions. Open circles refer to transplants; filled circles to native mussels in the contaminated area, and half-filled circles to native mussels in the clean area. After Tanabe *et al*. (1987b).

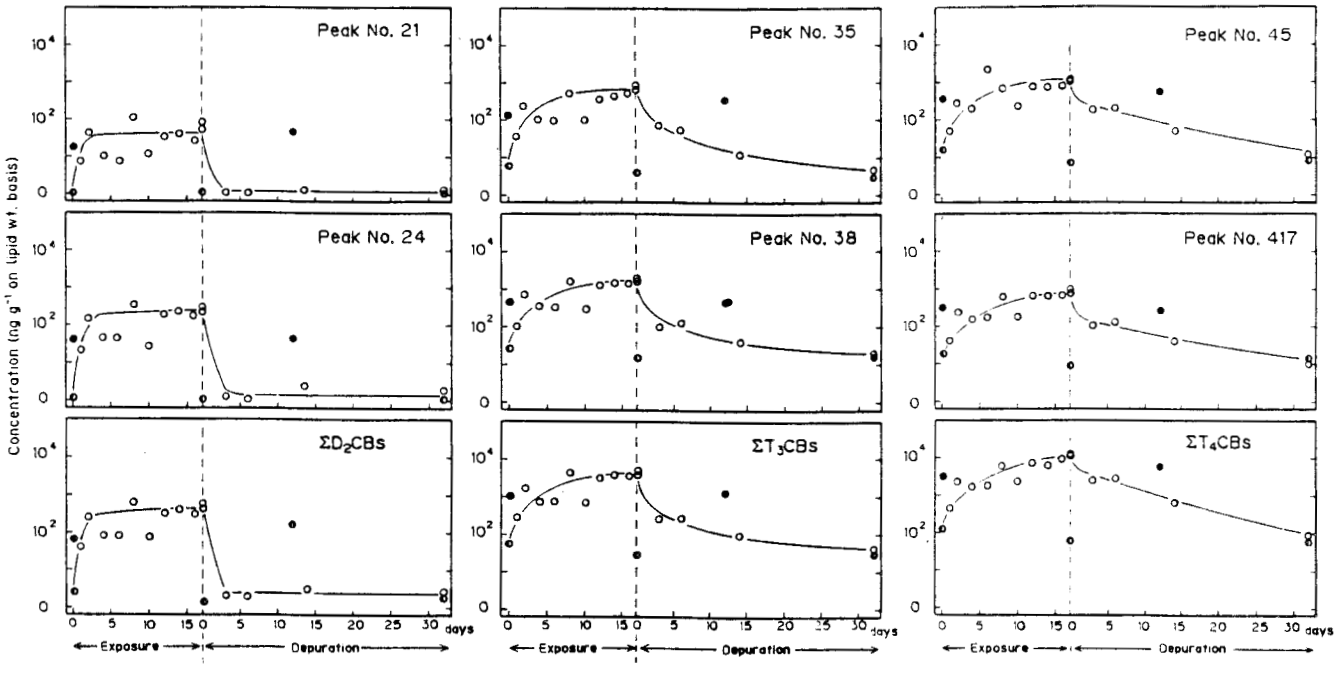


Figure 13. Variations in the concentrations of individual and total isomers of pentachlorobiphenyls (left), hexachlorobiphenyls (center), and heptachlorobiphenyls (right) in green-lipped mussels, *Perna viridis*. Mussels were transplanted from uncontaminated conditions to a polluted environment, and then back-transplanted to clean conditions. Open circles refer to transplants; filled circles to native mussels in the contaminated area, and half-filled circles to native mussels in the clean area. After Tanabe *et al*. (1987b).

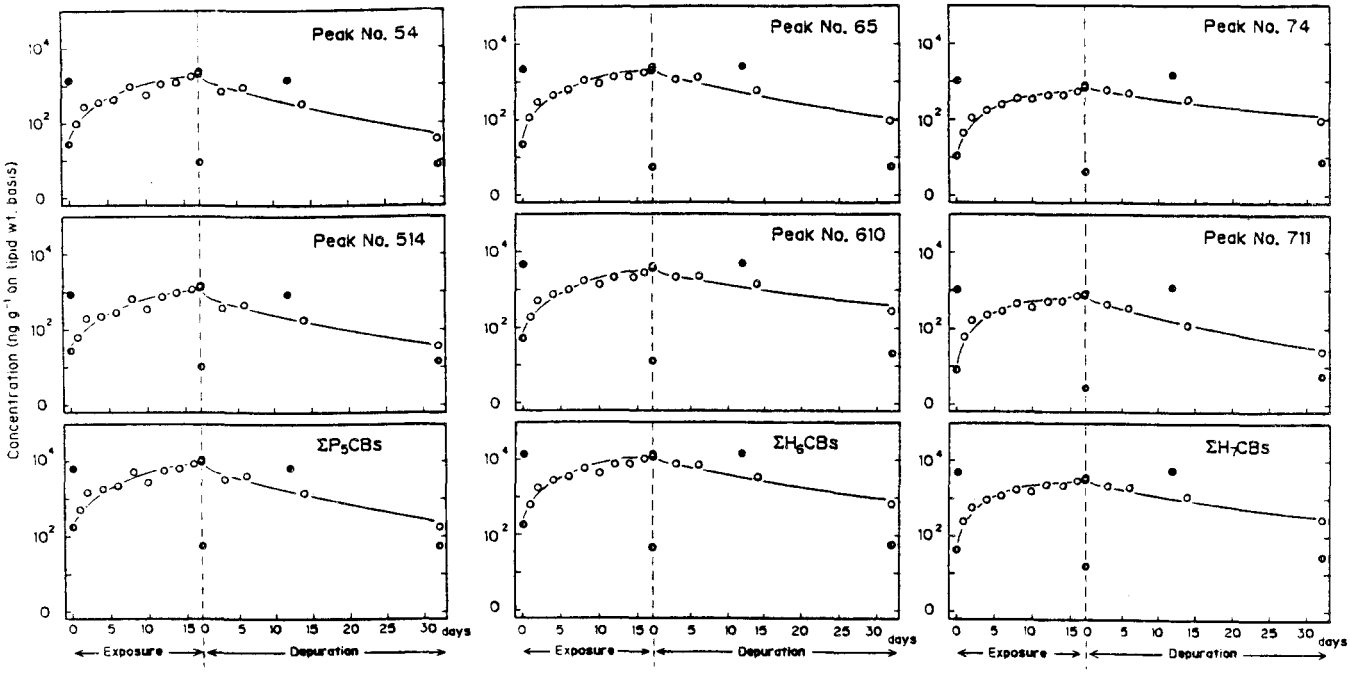


Table 11. Kinetic parameters describing the uptake and depuration of individual PCB components in green-lipped mussels (*Perna viridis*) transplanted in the field between contaminated and clean locations. Data are shown for clearance rates (k_2), biological half-life (*BHL*), and days to 90% uptake equilibrium (*t*). After Tanabe *et al.* (1987b).

Peak no.	k_2 (day^{-1})	r^a	*BHL* (*day*)	*t* (*day*)	*Peak no.*	k_2 (day^{-1})	r^a	*BHL* (*day*)	*t* (*day*)
21	>1·31		<0·5	<1·8	58	0·140	−0·98	5·0	16·4
22	>0·92		<0·8	<2·5	59	0·102	−0·97	6·8	22·6
23	>1·18		<0·6	<1·9	510	0·122	−0·98	5·7	18·9
24	>1·80		<0·4	<1·3	511	0·117	−0·95	5·9	19·7
25	>0·28		<2·5	<8·2	512	0·173	−0·94	4·0	13·3
26	>1·50		<0·5	<1·5	513	0·172	−0·94	4·0	13·4
					514	0·102	−0·96	6·8	22·6
31	>1·29		<0·5	<1·8	516	0·109	−0·96	6·4	21·1
32	0·108	−0·74	6·4	21·3					
34	>1·41		<0·5	<1·6	61	0·119	−0·99	5·8	19·3
35	0·131	−0·87	5·3	17·6	62	0·108	−0·99	6·4	21·3
36	>1·52		<0·5	<1·5	63, 64	0·098	−0·99	7·1	23·5
38	0·106	−0·79	6·5	21·7	65	0·097	−0·99	7·1	23·7
39	0·127	−0·87	5·5	18·1	66	0·111	−0·99	6·2	20·7
310	0·118	−0·86	5·9	19·5	68	0·080	−0·99	8·7	28·8
					69	0·106	−0·96	6·5	21·7
41	0·182	−0·98	3·8	12·6	610	0·079	−0·99	8·8	29·1
42	0·185	−0·99	3·7	12·4	611	0·176	−0·95	3·9	13·1
43	0·139	−0·88	5·0	16·6	612, 613	0·110	−0·98	6·3	20·9
44	0·142	−0·90	4·9	16·2	614	0·084	−0·99	8·3	27·4
45	0·125	−0·94	5·5	18·4	615	0·076	−0·99	9·1	30·3
46	0·149	−0·98	4·7	15·4	617	0·092	−0·99	7·5	25·0
47	0·147	−0·99	4·7	15·7	618	0·109	−0·99	6·4	21·1
48	0·148	−0·99	4·7	15·5	619	0·105	−0·98	6·6	21·9
49	0·119	−0·88	5·8	19·3					
410	0·123	−0·92	5·6	18·7	71	0·081	−0·99	8·6	28·4
411	0·131	−0·95	5·3	17·6	72	0·074	−0·97	9·4	31·1
412	0·159	−0·98	4·4	14·5	73	0·084	−0·99	8·3	27·4
416	0·105	−0·86	6·6	21·9	74	0·067	−0·99	10·3	34·3
417	0·115	−0·91	6·0	20·0	75	0·067	−0·99	10·3	34·3
418	0·119	−0·95	5·8	19·3	78	0·064	−0·99	10·8	35·9
420	0·118	−0·93	5·9	19·5	79	0·079	−0·99	8·8	29·1
					711	0·104	−0·99	6·7	22·1
51	0·141	−0·98	4·9	16·3	713	0·102	−0·98	6·8	22·6
52	0·125	−0·99	5·5	18·4	714	0·119	−0·98	5·8	19·3
53	0·124	−0·98	5·6	18·6					
54	0·118	−0·98	5·9	19·5	81	0·059	−0·98	11·7	39·0
55	0·112	−0·98	6·2	20·5	82	0·064	−0·95	10·8	35·9
56	0·084	−0·93	8·3	27·4					
57	0·130	−0·98	5·3	17·7	Total PCBs	0·102	−0·98	6·8	22·6

[a] Correlation coefficient in the equation used to obtain k_2.

biphenyls tend to be both taken up and lost from mussels much faster than the higher-chlorinated isomers. Superimposed upon this general tendency is a further effect due to the position of substitution of the biphenyl ring; for example, non-*ortho* chlorine substituted PCBs exhibit much slower uptake and depuration than do other homologues of the same degree of chlorination. There can be no doubt that such differences in isomer and homologue kinetics also exist in *M. edulis* and *M. californianus*, although studies as extensive as those of Tanabe *et al.* (1987b) have not been completed for these species as yet.

It may be concluded that the use of annual sampling for mussels to monitor contaminants which exhibit short half-lives in these species cannot hope to characterize the ambient concentrations of these contaminants over a significant period of time. It is clear from Table 11 that such sampling would characterize the ambient concentrations of some PCBs over a few days, and others over several weeks (i.e. half-lives vary from less than a day to about 12 days, depending on the degree and positions of chlorine substitution). This problem has been addressed by Phillips and Segar (1986), who proposed the use of "time-bulking" techniques to artificially improve the time-integrated values provided by the study of bivalves for contaminants of short half-life. This is discussed in further detail in section VII of the present report.

(iii) **Absence of study of some contaminants:** While the SMWP has increased the number of trace metals and chlorinated hydrocarbons for which mussels are analyzed in recent years (see Table 12), no petroleum-related hydrocarbons are included regularly in this program (although such analyses have been undertaken for mussel watch studies in the Monterey area; see Martin and Castle, 1984). The national program undertaken presently by NOAA analyzes samples for 18 PAHs, but the only available report to date (NOAA, 1987) includes data simply as "total PAHs", without citing the levels of individual contaminants.This lack of attention to petroleum-related hydrocarbons is most unfortunate, as these contaminants are of very considerable concern as potential pollutants in the San Francisco Estuary (see section III of this report), and the existing database from studies of water, sediments or biota describing their abundance and distribution is almost non-existent. This led Phillips (1987) to recommend that petroleum-related hydrocarbons should be

Table 12. Contaminants for which mussels are analyzed in State Mussel Watch Program studies at present. After Stephenson *et al.* (1986), and Phillips (1988).

Aldrin
Chlorbenside
Cis-chlordane
Trans-chlordane
Alpha-chlordene
Gamma-chlordene
Cis-nonachlor
Trans-nonachlor
Oxychlordane
Total chlordane
Chlorpyrifos
Dacthal
o,p' DDD
p,p' DDD
o,p' DDE
p,p' DDE
p,p' DDMS
p,p' DDMU
o,p' DDT
p,p' DDT
Total DDT
Methoxychlor
Diazinon
Dieldrin
Endosulfan 1
Endosulfan 2
Endosulfan sulfate
Total endosulfan
Endrin
Ethyl parathion
Alpha-HCH
Beta-HCH
Gamma-HCH
Delta-HCH

Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Methyl parathion
PCB (Aroclor) 1248
PCB (Aroclor) 1254
PCB (Aroclor) 1260
Total PCBs
Total phenol
Pentachlorophenol
Tetrachlorophenol
Tedion
Toxaphene
Ronnel
Tetradifon

Cadmium
Chromium
Copper
Mercury
Manganese
Lead
Zinc
Arsenic
Nickel
Selenium
Titanium
Barium
Cobalt
Silver
Tributyl tin
Aluminum

included in future analyses of the SMWP. This recommendation is repeated here, and will be covered in further detail in section VII of this report.

(iv) **Lack of consistency in sites studied with time:** It is also evident from Tables 10 and 11 that the study sites selected for the SMWP investigations in San Francisco Bay have varied extensively from year to year. There has been a marked tendency in recent years (1985 onwards) to conduct studies of local areas which exhibit particular contamination (e.g. Oakland and Richmond Harbors), and the numbers of samples taken at the more open sites in the Bay have decreased. As a result, very few locations have been consistently studied since the inception of the program (especially with respect to organochlorines). While the data from hot-spot areas are certainly useful in their contribution to our knowledge of contaminant distributions and sources in the Bay, the loss of the long-term database for the original study sites is most regrettable. This has degraded the overall value of the database considerably, as temporal trends in contaminant abundance and bio-availability cannot be distinguished for different areas of the estuary and inter-compared.

It is concluded that, while there is no doubt that information on the abundance and bio-availability of contaminants close to suspected or known point sources is critically required to improve our understanding of the overall distribution of contaminants in the estuary, this should not be permitted to dominate all decisions on the selection of study sites for the SMWP. If reliable and interpretable data on spatial and temporal trends in contaminant abundance and bio-availability in the estuary are to be produced, there must be a commitment to the long-term study of particular locations (selected to reflect either regional or local trends in pollutants) using the SMWP techniques. This has implications for program funding, which are considered below.

(v) **Inadequate opportunities for related research:** Insufficient research opportunities have existed within the SMWP, particularly in recent years. The use of bio-monitors such as mussels is a relatively new field, having developed significantly only over the last 15 years. As a result, there is a need for basic research to refine and extend these techniques. In particular, there is a growing body of evidence that mussels (and other bivalves; perhaps also certain species of other phyla) can be employed not only to quantify the abundance of toxic contaminants in aquatic

ecosystems, but also to study the biological effects of these (and/or other) contaminants (see Bayne, 1985). Attempts to this end in the San Francisco Estuary have been severely limited to date. Martin *et al.* (1984b) compared contaminant profiles to scope for growth measurements in mussels from San Francisco Bay, and noted a covariance between scope for growth and the levels of several toxicants. However, no conclusions on cause and effect relationships were possible because the observed gradients in contamination were similar for several toxicants. There is a need for the development of more techniques of this type, particularly those which may be pollutant-specific. It may also be possible to employ bio-monitors such as mussels to provide time-integrated data on the abundance of bacteria and viruses in the waters of the Bay; although this field is outside the scope of the present review, it is worthy of further consideration.

(vi) **Inadequate funding and commitment to the support of the program:** The principal reason for the deficiencies in the SMWP discussed above involves the level of financial support of this program (and commitment to the program by environmental managers), rather than the technical capabilities of the personnel involved in the program. It is the opinion of the present author that this program (altered and expanded as described in section VII of the present report) should constitute the backbone of the future monitoring of toxic contaminants in the San Francisco Bay itself. Such bio-monitoring programs have been introduced in many parts of the world (including the United States) as local, national and international efforts; there can be no doubt whatever of their value as monitoring tools. However, an expanded and continued long-term financial and political commitment to the State program is required if reliable estimates of the spatial and temporal trends in toxicant abundance and bio-availability in the estuary are to be provided in future. In the absence of such estimates, the interpretation of regional trends in contaminant abundance and distribution will continue to be restricted to the use of databases which are fragmented and offer no real chance of addressing the principal management issues concerning toxicants in the Bay.

The Toxic Substances Monitoring Program

The Toxic Substances Monitoring Program (TSMP) commenced in April 1976, having been set up by the State Water Resources Control Board in response to section 13001 of the Porter-Cologne Water Quality Control Act, which delegated the primary responsibility for coordination and control of water quality in Calfornia to the State Board. SWRCB staff established a "Primary Water Quality Monitoring Network" for the State, with the goals of providing a continuing assessment of water quality in California, and defining impacts of toxicants on beneficial uses of the freshwaters of the State (SWRCB, 1979a, 1979b). It was recognized that the analysis of water was not appropriate to this program, essentially for the reasons discussed in section II of the present report. A decision was therefore made to sample fish and invertebrates from 28 high-priority streams in the State in the initial stages of the TSMP. All sampling was conducted by the California Department of Fish & Game. The initial objectives of the program were stated as follows (SWRCB, 1979a):

- To develop statewide baseline data and to demonstrate trends in the occurrence of toxic elements and organic substances in the aquatic biota.

- To assess impacts of accumulated toxicants upon the usability of state waters by man.

- To assess impacts of accumulated toxicants upon the aquatic biota.

- Where problem concentrations of toxicants are detected, to attempt to identify sources of toxicants and to relate concentrations found in the biota to concentrations found in the water.

The reports on the TSMP provide a view of the historical evolution of this program, both in terms of its stated objectives and with respect to the methodologies employed. Salient points from the reports are as follows:

1976-77: The analysis of sediments was included in the initial stages of the TSMP, but was discontinued after the first sampling series (October 1976 to March 1977) because these data were not considered useful to the program (SWRCB, 1979a, 1979b).

Predator and forage fish and benthic invertebrates were sampled; whole fish (or cross-sections of large fish) were employed for analysis of both metals and pesticides or PCBs. These contaminants were also measured in whole soft parts of bivalve molluscs (principally the Asiatic clam, *Corbicula* sp.; species named variously as *C. fluminea* and *C. manilensis* in the later reports). Tail muscle of crayfish (*Procambarus clarkii* and *Pacifastacus leniusculus*) was also analyzed for trace elements, pesticides and PCBs. It is probable that these crayfish species regulate at least some metals in muscle tissues (see section II of this report). While certain common species were sampled at several locations, there was little effort in the initial stages of the program to design a sampling strategy based upon particular "indicator species"; the collection of large numbers of different species was preferred, in an attempt to define toxicant levels in various portions of the food web, and to provide a basis for later investigations. Concentrations of toxicants found in the various species were compared to the guidelines promulgated by the National Academy of Sciences (NAS, 1973) for predator protection, and to those of the Food and Drug Administration for the protection of public health (U.S. FDA, 1978a, 1978b).

1978: The elucidation of spatial and temporal trends in contamination of the freshwater areas studied was considered a primary objective of the program in the report on the third year of sampling (SWRCB, 1979b). Samples were collected from June to September. Some attempt was made at species standardization (which approximates the use of indicator species noted above), although this was frustrated on occasion by the unavailability of certain samples at some sites. The use of smaller (younger) fish was preferred at this stage of the program over the larger (older) fish employed at the outset, and samples were composited. This undoubtedly served to provide improved estimates of average toxicant concentrations in the sampled populations, which is important as the mobility of the fish species collected tends to create high variability in toxicant levels between individuals. Liver samples were preferred to whole fish for the analysis of trace metals other than mercury from 1978 onwards; this too is a significant improvement, as the concentrations of many trace elements are regulated in the axial muscle of finfish (Bryan, 1976; Phillips, 1980). Muscle tissues of fish were analyzed for mercury (which *does* accumulate in these tissues) and for pesticides, and these data were considered directly relevant to both human health and toxicant abundance at the sampled locations (SWRCB, 1979b). Analytical improvements were introduced to reduce the detection limits of the analyses (carbon rod atomic absorption spectrophotometry and high resolution glass capillary gas chromatography).

1979: The use of species collection goals and compositing of samples (6 individuals *per* composite) was continued in the 1979 collections, made from March to November (SWRCB, 1980). An attempt was made to standardize the sizes of the organisms collected, but this was noted to be contingent upon the availability of medium-sized animals at each location. The use of field replicates was introduced, and some samples were archived. Laboratory duplicates were analyzed for both metals and synthetic organic contaminants; results were good. Intercomparison exercises were undertaken for trace metal analysis, employing a reference mussel sample; the results indicated an acceptable degree of precision for the laboratory undertaking the analyses (Water Pollution Control Laboratory, CDF&G). In addition, GC-MS techniques were employed to confirm the identifications of Dachthal and toxaphene in samples.

1980: The 1980 TSMP collection covered the 28 Primary Network streams studied previously, but also sampled organisms from 58 other locations, employed to expand the database in general or to locate sources of toxicants in particular areas known from previous data to be contaminated (SWRCB, 1981). Samples were collected from April to November. Nine trace metals and 56 synthetic organic contaminants were quantified for most samples, although some were analyzed for only those toxicants thought to be likely to be present at high levels (from previous results). Analytical QA/QC procedures were similar to those employed in the 1979 program. The hepatopancreas of crayfish was preferred to tail muscle for trace metal analysis. The use of an adsorbent column sampler,designed to passively collect synthetic organic toxicants, was introduced. Improvements in analytical techniques permitted the detection of certain pesticides for the first time; among these were endrin, HCB and HCH, and at some sites the concentrations of these contaminants exceeded the NAS guidelines for predator protection. It was proposed that some of the Primary Network stations should be sampled less frequently in future phases of the program (perhaps at two or three year intervals), while known areas of contamination should be more intensively studied in future.

1981: The TSMP in 1981 sampled predator and forage fish in 32 streams and 8 lakes or reservoirs at a total of 44 sites (21 Primary network sites and 23 others), and analyzed samples for 10 trace metals and 66 synthetic organic toxicants (SWRCB, 1982b). Sampling covered the period from May to October 1981. Importantly, no benthic organisms were collected in 1981; it is not clear why this decision was made. Adsorptive water column analyses were continued, on selected streams only. New sampling station

codes were introduced, based on the hydrologic unit boundary system. It was recommended that increased sample consistency with respect to the species collected at the various sites be developed, to support the analysis of temporal trends in toxicant abundance. This recommendation is important, in that much of the TSMP database refers to different species collected in different years at the same locations. Temporal trends cannot be generated from such data with confidence, because of the effects of species-specificity in toxicant accumulation. Laboratory QA/QC procedures were similar to those employed previously.

1982: The TSMP investigations in 1982 involved the analysis of fish (but no benthic organisms) from a total of 44 locations (13 Primary Network sites; 29 supplemental sites; 2 archived samples from 1980); water analyses were performed at 4 of these locations and sediment analyses at 6 sites (SWRCB, 1983). Sampling was undertaken from April to November. It was recommended that adsorbent water column analyses should be discontinued, as these were considered not to be cost-effective. Attempts to increase consistency in the fish species collected at individual locations were again recommended. Of 2,580 analytical tests on 80 composite or individual fish species, only 482 (19%) measurable concentrations were recorded (i.e. 81% of the data points were reported as below detection limits), and NAS guidelines were surpassed by only 39 reported values.

1983: A total of 56 locations was employed in the 1983 TSMP, including 13 Primary Network sites, 29 supplemental stations, and 14 stations for intensive studies (SWRCB, 1985). Samples were taken between June and November (commencing later than usual because of high spring run-off). Fish, sediment and a few water samples were collected; no benthic species were studied. In total, some 179 tissue analyses were conducted, involving over 3,000 analyses. Special investigations were undertaken of mercury in Clear Lake and Lake Nacimiento, pesticides in the Moss Landing Harbor watershed and lower Salinas Valley, and toxicants in fish from three lakes near Los Angeles (to determine human health hazards). Improvements in data storage and analysis were introduced. The use was commenced of the "Elevated Toxic Pollutant Level" (ETPL) and median international standards for metals in fish, as benchmarks against which to compare observed levels of toxicants in the samples analyzed. It was recommended that later TSMP investigations employ lipid weights as a basis for the concentrations of synthetic organic toxicants, rather than wet tissue weights. This aids interpretation of data in many cases (e.g. see Phillips, 1980). The compositing and

analytical techniques (including QA/QC) in the 1983 investigations were similar to those of previous years.

1984: Some 70 sampling locations were included in the 1984 TSMP (SWRCB, 1986). Sixteen of these were Primary Network stations, the remaining 54 being supplemental or special study sites. Samples of fish (all sites) and sediments (11 sites only) were collected between April and October; no benthic species were collected or analyzed. In total, 204 fish tissue samples were analyzed. Details of sampling and analysis were essentially unchanged from previous years. The use of ETPL values (renamed elevated data levels, or EDL values) as a comparative benchmark for interpretation of analytical data was continued. Lipid weights were employed in addition to wet weights as bases for observed concentrations of synthetic organic toxicants. Data from previous years (1980 onwards; the quantification of total lipids was considered unreliable for years prior to 1980) were also recalculated on this basis. The calculation of "Chemical Group A Pesticides" was introduced to provide data on the summed levels of particular organochlorines.

1985: The number of locations sampled in the 1985 TSMP was 69; 9 of these were Primary Network stations, and a further 43 were locations which had not been previously sampled (SWRCB, 1987). Intensive monitoring was undertaken in the Monterey area and the New River catchment for pesticides, and in the Lake Berryessa catchment for mercury. Samples were collected between April and November. The program was restricted to the sampling of fish only; no sediments, water or benthic species were collected or analyzed. Details of sampling, compositing and analysis were similar to those of previous years.

1986: In total, 81 locations were sampled in the 1986 TSMP, samples being collected between April and December (SWRCB, 1988). Six locations were part of the Primary Network; all others constituted supplemental or intensive ("action plan") locations of study. Action plan-related investigations included the Guadalupe study of mercury contamination, Central Coast Mine Study streams, the U.S. Geological Survey San Joaquin Valley *Corbicula* study, the Lake Herman mercury evaluation, and the Huntington Harbor study of pollutant sources. The samples collected were fish in all cases, with the exception of 6 samples of Asiatic clam (named as *Corbicula manilensis* in the report). The reintroduction of investigations of clams followed a lag of six years,

since their previous use in the TSMP in 1980. Details of sampling, compositing and analysis were similar to those of previous years.

1987: The Data Report on the 1987 TSMP investigations has not yet been released by CDF&G; thus, no data can be included here for this year.

It is clear from the above that the TSMP has evolved significantly since its inception in 1976. The present program tends to concentrate on areas of particular contamination, rather than simply repeating studies on streams included in the original Primary Network. The aims of the program also appear to have changed from those noted at its inception; it is presently employed more to identify hot-spots of contamination, and the monitoring of long-term trends in contaminant levels is considered to be less important. There is little doubt that the program has been of value in defining the general level of contamination in the catchment of San Francisco Bay. However, the TSMP suffers from several general and specific problems, and some of these are similar to the problems faced by the State Mussel Watch Program (SMWP), discussed above. The existing problems with the TSMP are considered to include the following:

(i) **Inappropriate choice of species and/or tissue analyzed:** As noted above, some of the early work undertaken within the framework of the TSMP employed species and/or tissues which were inappropriate to the goals of the program, because at least some of the toxicants measured were subject to metabolic regulation in these species/tissues. The examples of zinc and copper in crayfish tail muscle and finfish axial muscle may be cited. However, the use of these species/tissues was discontinued quite early in the program (fish livers replaced axial muscle for metal analyses in 1978; crayfish hepatopancreas analyses replaced those of tail muscle for trace metals in 1980), and the present tissues employed by the program appear generally defensible as a basis for a bio-monitoring program. However, the lack of emphasis in the program as a whole on invertebrates as bio-monitors (rather than fish) is notable. As discussed in section II of this report, most authors consider invertebrates to be more appropriate than fish as bio-monitors (e.g. Bryan, 1976; Phillips, 1980), for a variety of reasons (greater accumulation of certain toxicants; less mobility, etc.). While it is recognized that the desire to protect both recreational fisheries and public health is central to the objectives of the TSMP, it is

considered that greater emphasis on the use of invertebrates in the program would be beneficial. This point is discussed further in section VII of the present report.

(ii) **Insufficient numbers of study sites:** Insufficient sites have been studied in the Central Valley catchment to fully characterize the abundance of trace elements and organic toxicants in this large area. The major rivers have been sampled at only a few sites in most cases, and some areas of the catchment have never been sampled. Because of the paucity of stations, sufficient comparative data often do not exist to show whether the stations sampled are indicative of regional trends (e.g. of the whole length of the river) or simply of local trends. In addition, the sampling sites employed in the TSMP do not extend significantly through the Delta, and it is therefore very difficult to relate this database to the results of the SMWP or other programs in the San Francisco Bay itself. This is particularly important, as the State Mussel Watch Program extends only to the western end of the Carquinez Straits; thus, contaminant levels in a large area of the lower Delta and Suisun Bay region are not characterized by either program.

(iii) **Insufficient temporal coverage for certain contaminants:** This problem is identical to that suffered in the SMWP, but in the case of the TSMP studies, additional concerns exist. The stations included in the TSMP are sampled once only in any year, and contaminants of short half-life may not be detected in the samples taken because of the precise timing of sampling. The program does not provide a true "snap shot" of toxicant abundance in any event, as sampling is carried out at different times in the various areas covered. The effects of the timing of sampling may be particularly important in riverine systems compared to the downstream estuary, as river flows (tending to dilute and disperse contaminants introduced to the individual rivers) are highly variable. The TSMP samples rivers at low-flow periods in general, and this may coincide with the greatest abundance of some contaminants (i.e. those of relatively constant loading, the levels of which will tend to be inversely related to flow rates in the river receiving waters). However, certain other toxicants (e.g. those derived from runoff) may not be present at their greatest annual levels during this period, and may therefore be underestimated by the sampling program. In addition, many pesticides of concern in the Central Valley are applied episodically, and these may not be detected by the TSMP studies if samples are not collected during or soon after such applications.

(iv) **Absence of study of some contaminants:** As in the SMWP, the TSMP does not include the analysis of petroleum-derived hydrocarbons. While MAHs and some organochlorines have been analyzed for in striped bass (see section VI of this report), no data on PAHs exist for biota of the Central Valley catchment and the Delta. This is a major omission, and should be rectified if our knowledge of these important toxicants is to improve.

(v) **Lack of consistency in sites studied with time:** Although certain sites on the original Primary Network have been studied over several years, it remains difficult to employ the TSMP data to provide long-term trend data for many locations. Such data would be particularly useful to discern changes in environmental contamination consequent to the banning or restriction in use of particular pesticides. For example, trend analysis of DDT levels in the Central Valley catchment rivers has provided equivocal results (partly due to alterations in sites with time and partly because of inconsistency in the species studied at individual locations; see below).

(vi) **Lack of consistency in species studied:** Subsequent to the initial two years of the TSMP, it was recognized that the analysis of trends in toxicant levels would require consistency in the sampling of species at the various sites studied. Thus, it is not scientifically defensible to generate and interpret either spatial or temporal trend data which involve different species at different locations and/or times of sampling. The literature is replete with examples of the variation in contaminant abundance with species, and it is widely accepted that multi-species comparisons do not provide reliable data on contaminant distributions or trends. It is, however, recognized that the sampling of the same species at all locations, or in all years of study at any one location, is possible only if that species is available. Table 13 shows information on sampled species from the 1984 TSMP report, which provided consolidated data for the program as a whole over the period 1978-84 (SWRCB, 1986). It is evident that 46 species were analyzed in total over these seven years of study, including 40 species of fish, 3 species of bivalve molluscs, and 2 species of crayfish. The most common fish species studied were largemouth bass (*Micropterus salmoides*) and channel catfish (*Ictalurus punctatus*); these two species accounted for 320 of a total of 916 samples taken (35%) during these seven years of the program. Figures 14 and 15 depict the distributions of these samples of *M. salmoides* and *I. punctatus* in the catchment of the Bay and Delta. It is clear that these two species occur

Table 13. Species sampled by the Toxic Substances Monitoring Program between 1978 and 1984, and frequency of their sampling. After SWRCB (1986).

GENUS	SPECIES	COMMON NAME	TOTAL NUMBER OF SAMPLES
Anodonta	californiensis	FRESHWATER MUSSEL	5
Bairdella	icistia	CROAKER	1
Carassius	auratus	GOLDFISH	14
Catostomus	occidentalis	SACRAMENTO SUCKER	6
Catostomus	rimiculus	SUCKER	2
Catostomus	sp	SUCKER	31
Corbicula	manilensis	ASIATIC CLAM	23
Cottus	sp	SCULPIN	54
Cynoscion	xanthulus	ORANGEMOUTH CORVINA	3
Cyprinus	carpio	CARP	66
Gambusia	affinis	MOSQUITO FISH	2
Gasterosteus	aculeatus	STICKLEBACK	2
Gillechthys	mirabilis	LONGJAW MUDSUCKER	3
Gonidia	angulata	FRESHWATER MUSSEL	3
Ictalurus	catus	WHITE CATFISH	66
Ictalurus	melas	BLACK BULLHEAD	1
Ictalurus	nebulosus	BROWN BULLHEAD	22
Ictalurus	punctatus	CHANNEL CATFISH	120
Lavinia	exilicauda	HITCH	4
Lepomis	cyanellus	GREEN SUNFISH	50
Lepomis	gulosus	WARMOUTH	1
Lepomis	macrochirus	BLUEGILL	10
Leptocottus	armatus	PACIFIC STAGHORN SCULPIN	3
Limnephilus	sp	CADDISFLY LARVAE	1
Micropterus	dolomieui	SMALLMOUTH BASS	23
Micropterus	punctulatus	NORTH SPOTTED BASS	5
Micropterus	salmoides	LARGEMOUTH BASS	200
Morone	chrysops	WHITE BASS	6
Morone	saxatilis	STRIPED BASS	6
Mugil	cephalus	STRIPED MULLET	6
Mylopharodon	conocephalus	HARDHEAD	2
Notropis	lutrensis	RED SHINER	2
Orthodon	microlepidotus	SACRAMENTO BLACKFISH	4
Pacifastacus	leniusculus	CRAYFISH	22
Perca	flavescens	YELLOW PERCH	2
Pomoxis	annularis	WHITE CRAPPIE	2
Pomoxis	nigromaculatus	BLACK CRAPPIE	5
Pomoxis	sp	CRAPPIE	5
Procambarus	clarkii	RED SWAMP CRAYFISH	18
Prosopium	williamsoni	MOUNTAIN WHITEFISH	2
Ptychocheilus	grandis	SACRAMENTO SQUAWFISH	10
Salmo	gairdneri	RAINBOW TROUT	47
Salmo	gairdneri gairdneri	STEELHEAD RAINBOW TROUT	16
Salmo	trutta	BROWN TROUT	33
Tilapia	mossambica	MOZAMBIQUE MOUTHBROODER	5
Tilapia	sp	TILAPIA	2

Figure 14. Locations of sampling (+) for largemouth bass (*Micropterus salmoides*) in the Toxic Substances Monitoring Program investigations between 1976 and 1986 inclusive. Plotted from data provided by Annual Reports of the TSMP.

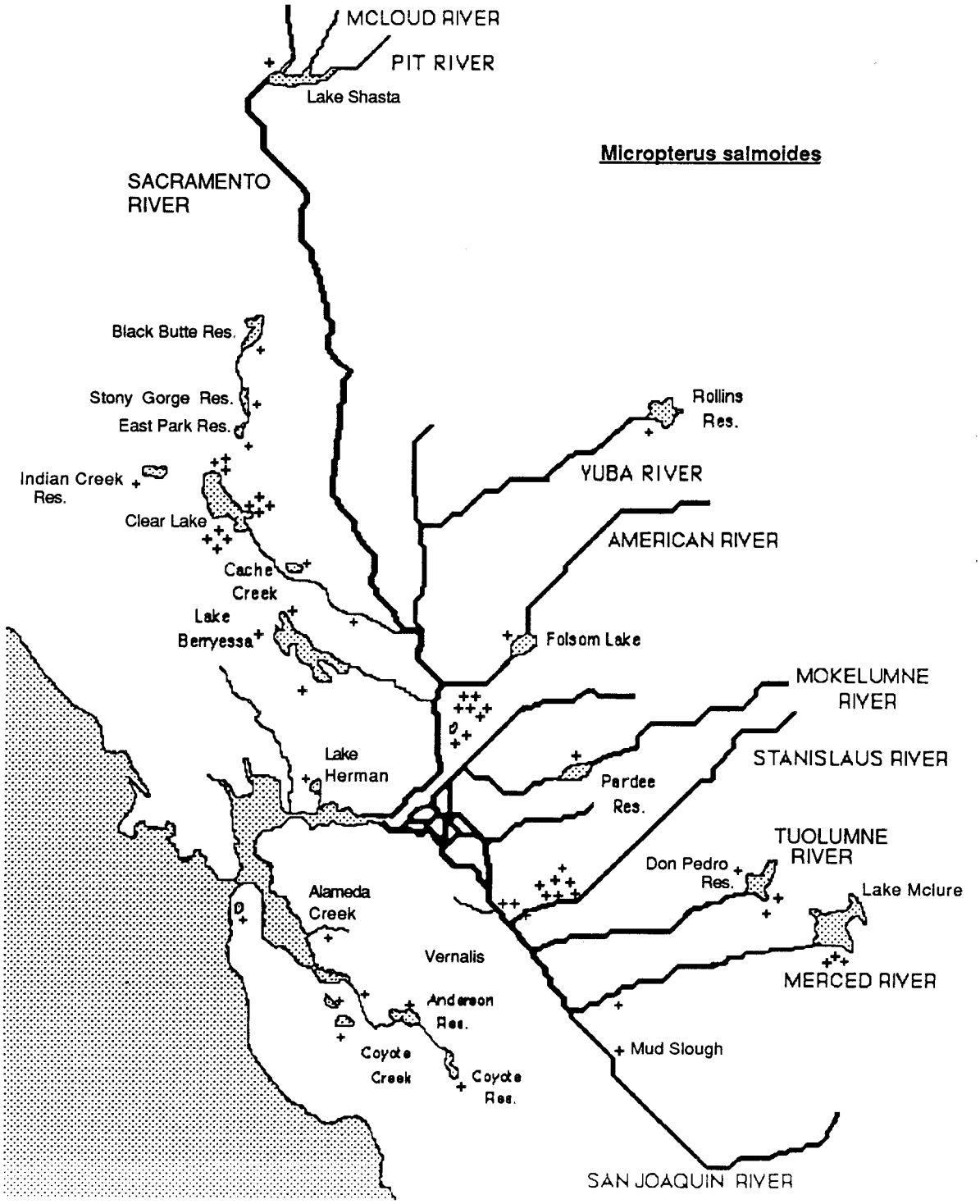
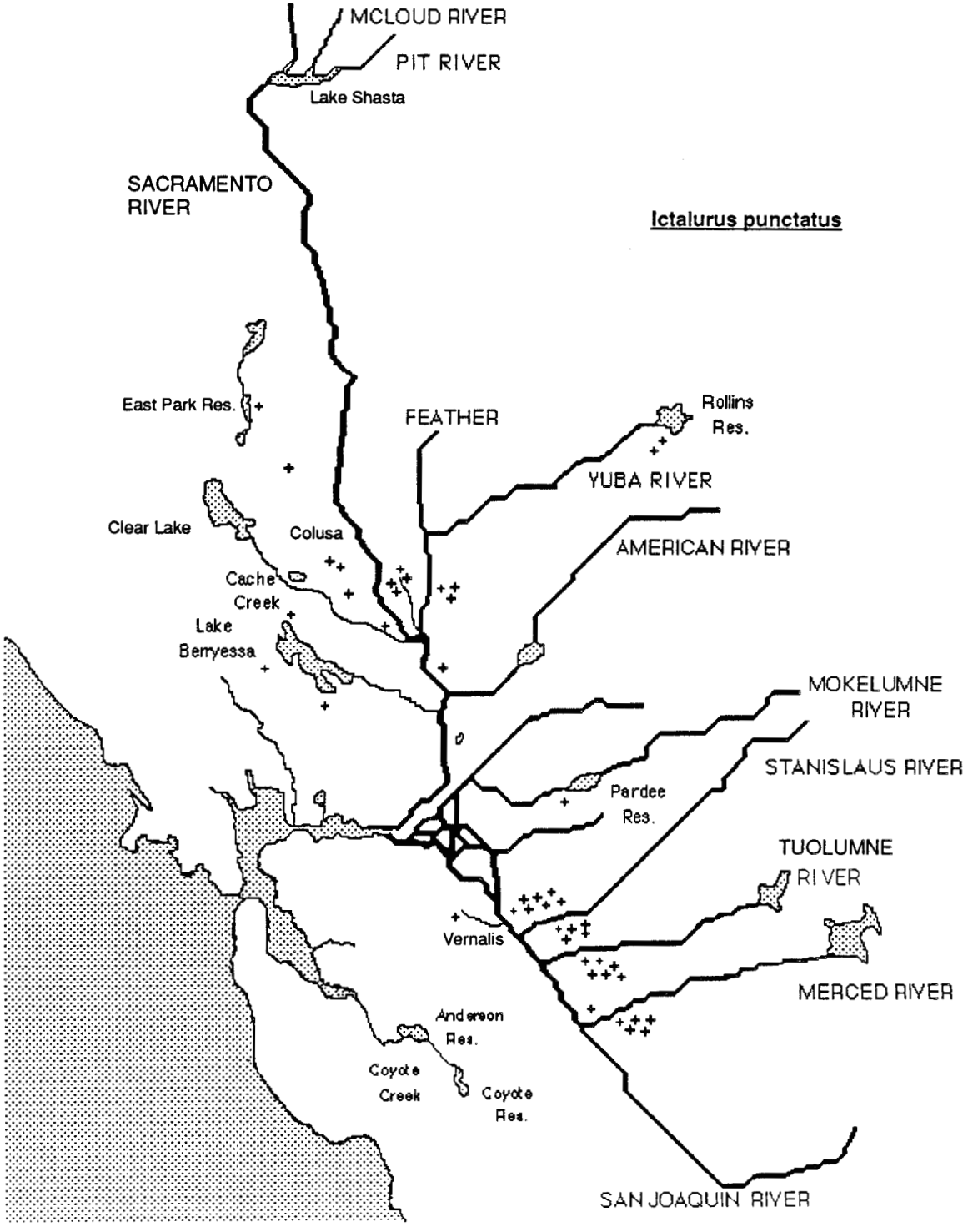


Figure 15. Locations of sampling (+) for channel catfish (*Ictalurus punctatus*) in the Toxic Substances Monitoring Program investigations between 1976 and 1986 inclusive. Plotted from data provided by Annual Reports of the TSMP.



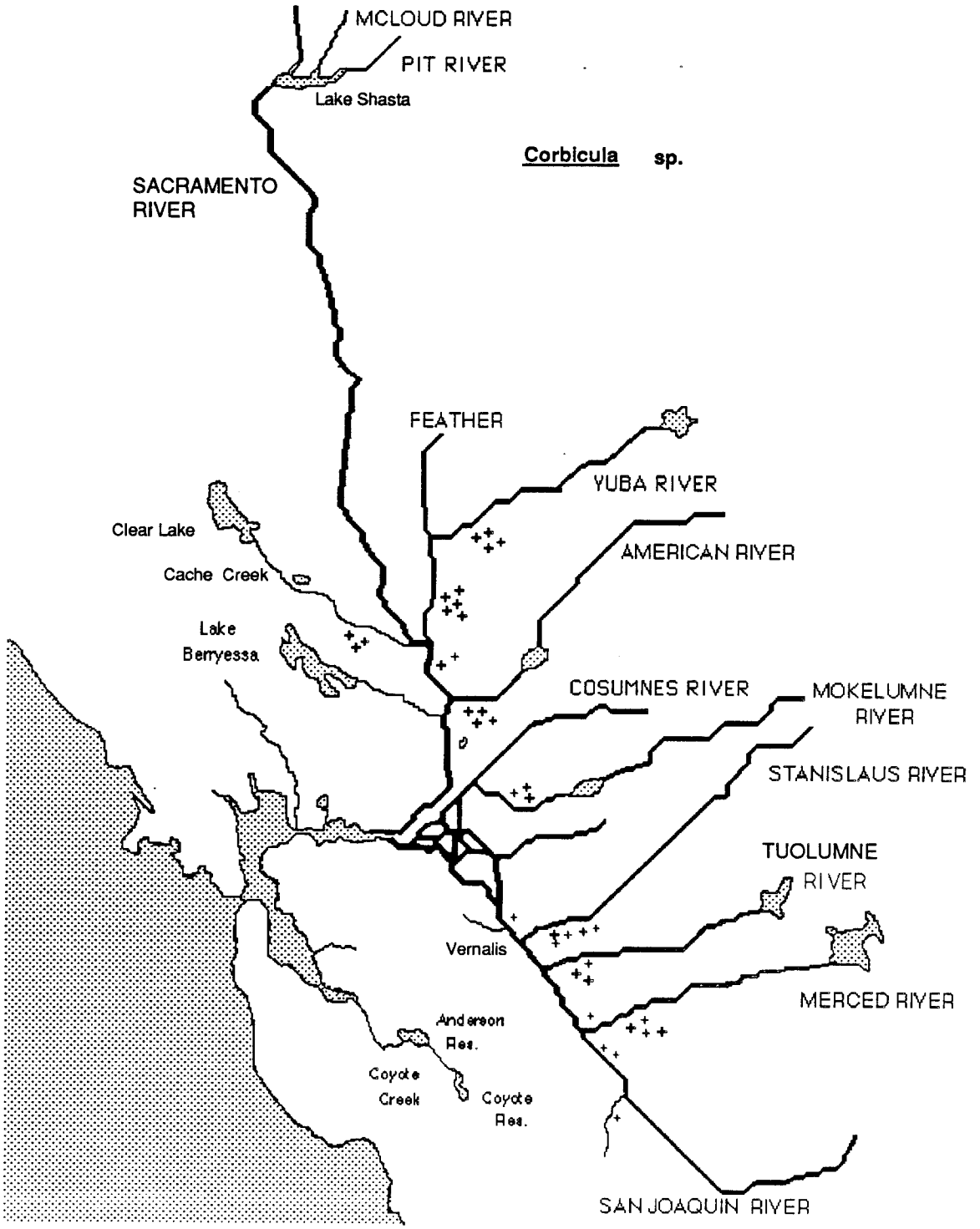
thoughout most parts of the Central Valley catchment. It would therefore appear that these two species might be particularly useful candidates for a consolidated program based upon the use of fish as bio-monitors of spatial and temporal trends in toxicant levels in this area. Figure 16 shows the distribution of the samples of Asiatic clam (*Corbicula* sp.) taken in the estuary catchment by TSMP studies. Once again, this species is found to be widespread in its distribution throughout the Central Valley region.

(vii) **Inadequate opportunities for related research:** Certain aspects of the overall objectives of the TSMP require additional research, which is not at present being undertaken through the program. The public health effects of some of the trace elements quantified through the TSMP studies are dependent largely upon the chemical speciation of the elements concerned. The best examples of this are mercury and arsenic.

Mercury can exist in several chemical forms in aquatic biota, but the most common forms are inorganic mercury and methylmercury. The latter is of much greater toxicity than the former, to both aquatic predators and to humans. Very few differential analyses of the two forms have been undertaken in the TSMP, although spot tests carried out as part of the 1984 studies suggested that the majority of the mercury present in the fish sampled was found as methylmercury (SWRCB, 1986). Given the large numbers of fish which exceed the NAS and/or FDA guidelines for mercury in their axial muscle, additional work on this aspect appears warranted.

Arsenic also exists in several forms in aquatic biota, being found in its organic forms, as arsenobetaine, as arsenosugars (in primary producers and tridacnid clams, containing zooxanthellae), and as arseno-lipids of various types (Phillips and Depledge, 1985). By direct contrast to mercury, the most toxic forms of arsenic are the inorganic forms; arsenobetaine, which is the most common form of the element in many aquatic species, is believed to be of insignificant toxicity to either aquatic predators or humans. No differential analyses of the chemical species of arsenic in fish sampled through the TSMP have been undertaken; the dry ashing technique employed for arsenic analysis is the method of choice for quantifying total arsenic in aquatic biota, but does not differentiate between the various chemical forms of the element.

Figure 16. Locations of sampling (+) for Asiatic clams (*Corbicula* sp., variously named as *C. fluminea* and *C. manilensis*) in the Toxic Substances Monitoring Program investigations between 1976 and 1986 inclusive. Plotted from data provided by Annual Reports of the TSMP.



Phillips (1987) recommended that additional work be undertaken to differentiate between the inorganic and organic forms of mercury and arsenic in the TSMP (and other) studies undertaken in the San Francisco Estuary and its catchment; this recommendation is repeated here.

It may be noted here in conclusion, that some at least of the above concerns have been reflected in the reports generated by the TSMP itself. The report on the 1982 studies (SWRCB, 1983: see page 11) stated the following:

"In some cases, toxic substances have been detected at relatively high concentrations every year. However, the specific significance of the changes in concentrations usually found from one year to the next is unclear. Normally, replicate samples are not taken and analyzed. A yearly change in a substance's concentration at a specific station may not, therefore, constitute an overall increase or decrease [in the abundance of that substance] in that body of water."

The same report contained the following statement (SWRCB, 1983; page 2):

"The reader is further cautioned that, because of limited program funding, the numbers of samples obtained and analyzed at each station are generally too small to provide a statistically sound basis for making definitive statements on toxic substance concentrations. The values reported herein should be accepted as indicators of relative levels of toxic pollution in water, not as absolute values."

Similar caveats have been included in all recent reports of the TSMP (e.g. SWRCB, 1986, page 1; SWRCB, 1987, page 1). It may be concluded that the principal purpose of the TSMP, stated as: ".....the acquisition of current, consistent data representing baseline and trend levels of toxic and other hazardous substances in the fresh waters of the state..." (SWRCB, 1987, page 1) is not being fully realized through the analyses undertaken. Section VII of this report provides proposals for a revised program, which is considered to offer a greater chance for the attainment of the objectives of the program, and is also designed to marry the studies in the catchment of San Francisco Bay to those downstream in the estuary itself.

Other Studies

Certain other studies have also been undertaken on contaminants in biota in the estuary or its catchment. However, many of these were of a one-time nature only, and cannot therefore be employed to delineate any general temporal trends in the levels of contaminants in the Bay and Delta, or the changes in the spatial distributions of contaminants with time. These cannot therefore be considered to be *bona fide* routine monitoring programs, and they are not reviewed herein as a result. Other monitoring programs are either relevant more to the local than the regional distributions of contaminants (and are therefore reviewed in section V of this report), or provide data relating to the accumulation and effects of contaminants in target species or food chains in the estuary (and are discussed briefly in section VI of the present report).

V. LOCAL MONITORING OF TOXIC CONTAMINANTS IN THE ESTUARY

A. Introduction

As noted in section I of this report, the distinction between the monitoring of regional and local contaminant abundance in the San Francisco Bay and Delta is somewhat arbitrary in many cases. This is principally due to the paucity of previous studies, and to their inability to define the precise contributions of individual toxicant sources in the estuary to the overall regional abundance of contaminants.

As employed here, the "local monitoring of toxic contaminants" includes studies on effluents themselves from both point and non-point sources, and on the receiving waters of the estuary close to outfalls, where it is clear that the quality of the latter is influenced primarily by specific nearby outfalls. In practice, this may equate to studies of effluents themselves and of the area of the "zone of initial dilution" of those effluents, or at least the highly localized area surrounding individual outfalls.

There are several reasons for the local monitoring of toxic contaminants in the San Francisco estuary, as follows:

(i) Regulatory agencies require information on both the concentrations and total loads of toxic contaminants entering the Bay and Delta from significant sources. Information on contaminant concentrations in effluents is required to ensure compliance with NPDES permits (see sub-section B below) and to provide insight into the potential for local effects close to outfalls (either in mixing zones or outside these). Similarly, data on contaminant levels in non-point effluents are required; these non-point sources will soon be subject to similar controls to those affecting point sources in the estuary. If the concentrations of individual toxicants in effluents are accurately characterized, preliminary judgements can be made as to the possibility of toxic effects on resident biota being seen in the area of the outfall. Such judgements commonly rely upon the international literature and on promulgated water quality objectives as a basis for ascertaining the likelihood of adverse effects, taking account of known initial dilutions of effluents by the receiving waters. It is

important to note that this process is by no means perfect. The effects of the chemical speciation of contaminants in effluents upon their bio-availability and toxic impact are of great importance, but chemical speciation cannot be accurately estimated and related directly to contaminant bio-availability at the present state of the art. Nevertheless, compliance with agreed water quality objectives is a reasonable starting point in attempts to control pollution in the estuary.

(ii) It is also not possible to predict the combined toxicological impacts of several contaminants present together in effluents. These impacts may differ from the effects of single toxicants in isolation, as contaminants may interact with each other in terms of their toxic effects. Such interactions vary with the contaminant mixtures concerned, and antagonistic, additive, or synergistic effects may be evident. This problem may be overcome by the direct study of the toxicities of whole effluents, employing a bioassay approach. Where significant toxicities are seen, several techniques exist for the fractionation of effluents to provide data on the toxic components of the discharge.

(iii) In addition to the need to consider concentration-based impacts of contaminant sources in the area close to outfalls, the total loads of toxicants discharged to the receiving waters of the estuary must be characterized. The regulation of water quality through the attainment of water quality objectives in receiving waters (as described in section IV of this report) requires a balancing of contaminant loading (from various sources) to the estuary with the overall assimilative capacity of the Bay and Delta. This is accomplished through a "wasteload allocation" approach, matching toxicant loads to the receptive capacities of different segments of the estuary. Such a wasteload allocation approach has not yet been fully developed in the Bay and Delta, but this will provide the basis for the future control of pollutants. Data on contaminant loads from point and non-point sources (and other significant sources) are therefore an integral part of attempts to control local and regional water quality in the estuary.

Present studies of a local monitoring nature in the San Francisco Estuary have until recently been restricted mainly to the direct analysis of contaminant concentrations in point source effluents (from municipal and industrial sources); these data are reviewed in sub-section B below. The database for contaminants in non-point effluents is essentially non-existent for the San Francisco Bay and Delta, although studies of this

type are presently underway in Santa Clara and Alameda Counties. There is a clear need to characterize both the amounts of contaminants discharged by non-point sources into the estuary and their impacts on the beneficial uses of the Bay and Delta.

Over the last year, the San Francisco Regional Water Quality Control Board has introduced a new study-based multi-species bioassay program, which is intended to define the direct toxicities of major point source effluents discharging to the Bay. This program, which is just commencing, is discussed briefly in sub-section C below. The relatively few attempts to date to delineate the near-field distributions of contaminants close to outfalls, or the toxicological impacts of discharges in the estuary around outfalls, are considered in sub-section D. The final portion of this section of the report discusses the potential use of studies of bio-accumulation as a basis for the local monitoring of toxicants in point and non-point effluents discharged to the estuary, and contrasts this approach with the present practices.

B. Monitoring of Contaminant Concentrations in Effluents

As noted above, the great majority of monitoring data on contaminants discharged in effluents to the San Francisco Estuary relates to municipal and industrial point sources. Very little is known about contaminants entering the Bay and Delta from non-point sources (Gunther *et al.*, 1987), although studies of the contributions of non-point sources to overall contaminant loading in the estuary have recently commenced in the Santa Clara Valley and in Alameda County. Because the results of the latter studies have not yet been released, this section will address data from point source monitoring programs only.

Point source dischargers are required to monitor their effluents under conditions attached to their National Pollutant Discharge Elimination System (NPDES) permits. The NPDES program was established initially as a federal program, under the Federal Water Pollution Control Act Amendments (the Clean Water Act) of 1972. In California, the NPDES program is administered by the Regional Boards on behalf of the EPA. Gunther *et al.* (1987) reviewed this database (and other sources of information relevant to point source discharges) for 1984-86 for the San Francisco Bay and Delta, and computed total loads of contaminants entering the estuary from these sources. The present report does not therefore seek to re-address these data in detail; rather, the existing requirements for monitoring, and the contribution of these data to the overall understanding of contaminant abundance and distributions in the estuary are discussed.

The self-monitoring required under NPDES permits varies between dischargers. Major effluents are required to be monitored relatively frequently (e.g. daily, weekly, or twice monthly) for flows, standard water quality parameters such as BOD_5, and trace metals; smaller-volume effluents are monitored less frequently (e.g. monthly, quarterly, half-yearly). Requirements for priority pollutant analyses also exist; major dischargers are required to analyze effluents for all 126 priority pollutants at various intervals. Analysis is performed using EPA standard methods (EPA, 1984).

Tables 14-18 provide a breakdown of data on analyses of trace metals and priority pollutants undertaken by major dischargers in the Bay and Delta during calendar year 1987. These data have been subjected to preliminary quality assurance procedures

Table 14. Data on trace element analyses conducted by POTWs, refineries and other industries during 1987 in self-monitoring programs required under NPDES permits.

CONTAMINANT	# DETECTED	TOTAL ANALYZED	FREQUENCY (%)
ANTIMONY	0	29	0
ARSENIC	136	402	33.8
BERYLLIUM	0	29	0.0
CADMIUM	160	504	31.7
CHROMIUM	682	1034	66.0
CHROMIUM, HEXAVALENT	8	52	15.4
COBALT	25	118	21.2
COPPER	643	827	77.8
LEAD	358	824	43.4
MERCURY	58	254	22.8
NICKEL	520	717	72.5
SELENIUM	408	505	80.8
SILVER	239	407	58.7
THALLIUM	0	29	0.0
VANADIUM	225	306	73.5
ZINC	813	960	84.7
**********	*****	*****	*****
SUM	4275	6997	61.1

Table 15. Data on analyses required during 1987 under NPDES permits of 38 volatile organic contaminants by POTWs and refineries, using EPA method 624.

CONTAMINANT	# DETECTED	TOTAL ANALYZED	FREQUENCY (%)
1,1,1-TRICHLOROETHANE	19	92	20.7
1,1,2,2-TETRACHLOROETHANE	0	93	0.0
1,1,2-TRICHLOROETHANE	0	93	0.0
1,1-DICHLOROETHANE	0	93	0.0
1,1-DICHLOROETHENE	0	69	0.0
1,1-DICHLOROETHYLENE	0	23	0.0
1,2-DICHLOROBENZENE	10	18	55.6
1,2-DICHLOROETHANE	1	93	1.1
1,2-DICHLOROPROPANE	0	93	0.0
1,3-DICHLOROBENZENE	5	14	35.7
1,3-DICHLOROPROPENE	0	81	0.0
1,4-DICHLOROBENZENE	5	13	38.5
2-CHLOROETHYLVINYL ETHER	0	93	0.0
ACROLEIN	0	69	0.0
ACRYLONITRILE	0	69	0.0
BENZENE	3	93	3.2
BROMODICHLOROMETHANE	38	93	40.9
BROMOFORM	12	92	13.0
BROMOMETHANE	0	93	0.0
CARBON TETRACHLORIDE	1	93	1.1
CHLOROBENZENE	1	93	1.1
CHLOROETHANE	0	92	0.0
CHLOROFORM	59	93	63.4
CHLOROMETHANE	3	93	3.2
CIS-1,3-DICHLOROPROPENE	0	12	0.0
DIBROMOCHLOROMETHANE	27	93	29.0
DICHLOROMETHANE	33	87	37.9
ETHYL BENZENE	4	93	4.3
TETRACHLOROETHENE	26	68	38.2
TETRACHLOROETHYLENE	3	23	13.0
TOLUENE	24	93	25.8
TRANS-1,2-DICHLOROETHENE	0	69	0.0
TRANS-1,2-DICHLOROETHYLENE	3	22	13.6
TRANS-1,3-DICHLOROPROPENE	0	33	0.0
TRICHLOROETHENE	10	68	14.7
TRICHLOROETHYLENE	2	23	8.7
TRICHLOROFLUOROMETHANE	0	36	0.0
VINYL CHLORIDE	0	93	0.0
**********	*****	*****	*****
SUM	289	2654	10.9

Table 16. Data on analyses required during 1987 under NPDES permits of 61 semi-volatile organic contaminants by POTWs and refineries, using EPA method 625.

CONTAMINANT	# DETECTED	TOTAL ANALYZED	FREQUENCY (%)
1,2,4-TRICHLOROBENZENE	0	92	0.0
1,2-DICHLOROBENZENE	17	93	18.3
1,2-DIPHENYLHYDRAZINE	0	77	0.0
1,3-DICHLOROBENZENE	3	93	3.2
1,4-DICHLOROBENZENE	11	93	11.8
2,3,7,8-TETRACHLORODIBENZO	0	33	0.0
2,4,6-TRICHLOROPHENOL	1	92	1.1
2,4-DICHLOROPHENOL	1	91	1.1
2,4-DIMETHYLPHENOL	1	93	1.1
2,4-DINITROPHENOL	0	93	0.0
2,4-DINITROTOLUENE	0	92	0.0
2,6-DINITROTOLUENE	0	91	0.0
2-CHLORONAPHTHALENE	0	93	0.0
2-CHLOROPHENOL	0	93	0.0
2-METHYL-4,6-DINITROPHENOL	0	36	0.0
2-NITROPHENOL	0	93	0.0
3,3'-DICHLOROBENZIDINE	0	93	0.0
4,6-DINITRO-O-CRESOL	0	51	0.0
4-BROMOPHENYL PHENYL ETHER	0	93	0.0
4-CHLORO-3-METHYLPHENOL	0	38	0.0
4-CHLOROPHENYL PHENYL ETHER	0	89	0.0
4-NITROPHENOL	0	93	0.0
ACENAPHTHENE	0	93	0.0
ACENAPHTHYLENE	0	93	0.0
ANTHRACENE	1	94	1.1
BENZIDINE	0	90	0.0
BENZO(A)ANTHRACENE	0	94	0.0
BENZO(A)PYRENE	0	94	0.0
BENZO(B)FLUORANTHENE	0	94	0.0
BENZO(G,H,I)PERYLENE	0	94	0.0
BENZO(K)FLUORANTHENE	0	94	0.0
BENZYL BUTYL PHTHALATE	0	94	0.0
BIS(2-CHLOROETHOXY)METHANE	0	94	0.0
BIS(2-CHLOROETHYL)ETHER	0	94	0.0
BIS(2-CHLOROISOPROPYL)ETHER	1	94	1.1
BIS(2-ETHYLHEXYL)PHTHALATE	3	94	3.2
CHRYSENE	0	94	0.0
DI-N-BUTYLPHTHALATE	2	93	2.2
DIBENZO(A,H)ANTHRACENE	0	93	0.0
DIETHYL PHTHALATE	1	94	1.1
DIMETHYL PHTHALATE	0	94	0.0
DIOCTYLPHTHALATE	0	92	0.0
FLUORANTHENE	1	94	1.1
FLUORENE	0	94	0.0
HEXACHLOROBENZENE	0	94	0.0
HEXACHLOROBUTADIENE	0	94	0.0
HEXACHLOROCYCLOPENTADIENE	0	94	0.0
HEXACHLOROETHANE	0	94	0.0
INDENO(1,2,3-C,D)PYRENE	0	94	0.0
ISOPHORONE	1	94	1.1
N-NITROSODI-N-PROPYLAMINE	0	94	0.0
N-NITROSODIMETHYLAMINE	0	78	0.0
N-NITROSODIPHENYLAMINE	0	87	0.0
NAPHTHALENE	10	94	10.6
NITROBENZENE	0	94	0.0
P-CHLORO-M-CRESOL	0	46	0.0
PENTACHLOROPHENOL	1	94	1.1
PHENANTHRENE	2	94	2.1
PHENOL	7	94	7.4
PYRENE	0	94	0.0
TRICHLOROFLUOROMETHANE	0	41	0.0
**********	*****	*****	*****
SUM	64	5337	1.2

Table 17. Data on analyses required during 1987 under NPDES permits of 26 pesticides and PCBs, primarily by POTWs using EPA method 608.

CONTAMINANT	# DETECTED	TOTAL ANALYZED	FREQUENCY (%)
p,p' DDD	0	52	0
p,p' DDE	0	53	0.0
p,p' DDT	0	52	0.0
Alpha-HCH	0	52	0.0
ALDRIN	0	53	0.0
Beta-HCH	0	53	0.0
CHLORDANE	0	49	0.0
Delta-HCH	0	52	0.0
DIELDRIN	0	53	0.0
ENDOSULFAN I	0	49	0.0
ENDOSULFAN II	0	50	0.0
ENDOSULFAN SULFATE	1	49	2.0
ENDRIN	0	53	0.0
ENDRIN ALDEHYDE	0	49	0.0
Gamma-HCH	1	52	1.9
HEPTACHLOR	0	52	0.0
HEPTACHLOR EPOXIDE	0	52	0.0
PCB-1016	0	48	0.0
PCB-1221	0	48	0.0
PCB-1232	0	48	0.0
PCB-1242	0	53	0.0
PCB-1248	0	48	0.0
PCB-1254	0	51	0.0
PCB-1260	0	51	0.0
PCB-1262	0	4	0.0
TOXAPHENE	0	49	0.0
**********	*****	*****	*****
SUM	2	1275	0.2

Table 18. Data on analyses required during 1987 under NPDES permits of 16 polyaromatic hydrocarbons, primarily by refineries using EPA method 610.

CONTAMINANT	# DETECTED	TOTAL ANALYZED	FREQUENCY (%)
ACENAPHTHENE	0	76	0.0
ACENAPHTHYLENE	0	76	0.0
ANTHRACENE	0	76	0.0
BENZO(A)ANTHRACENE	0	76	0.0
BENZO(A)PYRENE	0	76	0.0
BENZO(B)FLUORANTHENE	0	76	0.0
BENZO(G,H,I)PERYLENE	0	76	0.0
BENZO(K)FLUORANTHENE	0	76	0.0
CHRYSENE	0	76	0.0
DIBENZO(A,H)ANTHRACENE	0	76	0.0
FLUORANTHENE	1	76	1.3
FLUORENE	0	76	0.0
INDENO(1,2,3-C,D)PYRENE	0	76	0.0
NAPHTHALENE	2	76	2.6
PHENANTHRENE	1	76	1.3
PYRENE	2	75	2.7
**********	*****	*****	*****
SUM	6	1215	0.5

only in terms of computerized data entry and retrieval to date, and a further series of QA/QC checks are required before the precise data shown are fully confirmed as a correct summary of the self-monitoring analyses in 1987. However, the following conclusions may be noted, based upon these preliminary data:

- Data reported from the self-monitoring of effluents from POTWs, refineries and other industries for trace elements during 1987 are shown in Table 14. Of a total of almost 7,000 individual analyses, detectable levels of trace elements were reported in some 61%. Only three elements were never detected in effluents in 1987 (antimony, beryllium and thallium).

- Table 15 concerns the analysis of 38 volatile organic contaminants, analyzed by publicly-owned treatment works (POTWs) and refineries in the estuary using EPA method 624. Of 2,654 total analyses, some 2,365 results (89.1%) were reported as "below detection limits". Seventeen of the thirty eight compounds analyzed during 1987 were never detected in any effluent analyzed in that year. Some of the compounds detected in effluents (e.g. chloroform, dichloromethane, toluene) were also commonly found in blanks analyzed in that year or in previous years.

- Data for semi-volatile organic contaminants, analyzed using EPA method 625, are shown in Table 16. These data again refer to 1987, and are for effluents from POTWs and refineries. Of a total of 5,337 analyses, 5,273 reported results (98.8%) were below detection limits. Forty four of a total of sixty one compounds were never detected during 1987. Only four compounds were detected at a frequency greater than 5% of analyses (1,2-dichlorobenzene; 1,4-dichlorobenzene; naphthalene; phenol). The last two of these have also been detected in blanks analyzed to provide quality control.

- The results of analyses for pesticides and PCBs in effluents during 1987, primarily by POTWs, are shown in Table 17. These analyses are completed using EPA method 608. Of 1,275 analyses, only 2 datapoints (0.16%) were reported as above detection limits, while 99.94% of these analyses yielded data below detection limits.

- Table 18 provides data for PAHs, analyses of effluents for these contaminants being undertaken using EPA method 610 during 1987, primarily by refineries in the estuary.

Of a total of 1,215 analyses, only 6 results (0.49%) were positive, all others being reported as below detection limits (99.51%).

Some of the point source dischargers undertake their own analyses of effluents to provide data for the NPDES program. Others contract these analyses out to commercial laboratories. Total costs vary for such services. However, a conservative estimate of the costs to dischargers during 1987 to generate the data shown in Tables 14-18 is $300,000. These are of course by no means the only analyses performed; the routine analysis of influents and effluents to provide data on process and treatment efficiencies are extensive. Several of the major dischargers bear analytical costs easily exceeding $1 million annually.

It is suggested here that while the analysis of effluents for trace metals may be considered to be reasonably cost-effective, the requirement for the analysis of priority pollutants in point source effluents is not cost-effective, particularly when this is placed in the context of the very poor state of the existing knowledge on contaminant distributions and abundance in the estuary. The trace analysis of aqueous effluents for priority pollutants frequently fails to provide significant quantitative data on the abundance of these contaminants in such effluents, and also often fails to improve the current knowledge of contaminant loading to the Bay and Delta. Sub-section E below and section VII of the present report discuss alternatives to this testing.

C. Bioassays of Effluents

The Water Quality Control Plan, San Francisco Bay Basin (generally known simply as the "Basin Plan"; originally produced in 1975, and amended in 1982 and 1986) includes a requirement for an Effluent Toxicity Characterization Program (SWRCB, 1975, 1982c; SFRWQCB, 1986). The original version of the Aquatic Habitat Program Plan also proposed the inclusion of effluent bioassays in monitoring studies of the Bay and Delta (Horne *et al.*, 1982; SWRCB, 1982a). This program is required in order to protect the resources of the estuary from any direct toxic effects of contaminants discharged from point (or other) sources in the estuary. The toxicities of both effluents themselves (suitably diluted) and ambient receiving waters adjacent to discharge sites should be characterized in such a program.

Phillips (1987) reviewed the available data on effluent bioassays in the Bay and Delta to that time, and concluded that the historical use of species such as the stickleback (*Gasterosteus aculeatus*) in single-species bioassays of effluents was insufficiently sensitive, and could not be relied upon to adequately characterize the direct toxicities of effluents to resident species of the estuary. Multi-species testing (e.g. see EA Engineering, Science and Technology, 1986; Anatec Laboratories, 1987a, 1987b) was suggested to offer considerable improvements, and it was noted that the San Francisco Regional Water Quality Control Board was in the process of introducing a study-based bioassay approach to the multi-species testing of effluents in the estuary. This initiative has been developed in parallel to amendments to the Basin Pan for the estuary, noted above. The Regional Board promulgated Guidelines for a new effluent characterization program in mid-1987 (SFRWQCB, 1987). These Guidelines were developed from the EPA Technical Support Document for Water Quality Based Toxics Control (EPA, 1985), with some amendments to account for special circumstances thought to be present in the San Francisco Estuary.

The program proposed by the SFRWQCB has recently been approved by the State Water Resources Control Board, and is now in its early stages of implementation. The Guidelines for the Effluent Toxicity Characterization Program call for a study-based approach to the development and adoption of effluent bioassay techniques in the Estuary. This is intended to provide data on the most appropriate species for study in

local conditions, and also to develop much-needed information on the temporal variability of effluent toxicities in the estuary.

The Guidelines call for 21 of the largest dischargers in the Estuary to undertake effluent characterization studies which are outlined as follows:

- Each discharger must prepare an effluent toxicity study plan, based upon the approach given in the Guidelines, and defining the species to be used and the protocols for testing.

- Each of the dischargers (or their selected contractors undertaking the bioassays) must demonstrate their proficiency in the testing procedures by passing a quality assurance testing round. This involves the completion of three chronic bioassays (using the larval growth test on fathead minnows, the *Ceriodaphnia* reproduction test, and either the mollusc embryo development bioassay or the echinoderm fertilization test), to be run simultaneously.

- Each discharger must participate in a "screening phase", which is designed to delineate the comparative sensitivities of different test species to the various effluents. This screening phase involves the testing of six species in standard 96-hour acute toxicity bioassays, and a further five species in chronic or critical lifestage tests. The Guidelines provide lists of a range of species which may be employed in these tests.

- The results of the screening phase bioassays will be employed to determine the level of toxicity present in each individual effluent tested and in the ambient receiving waters close to the discharge sites. If the initial screening studies indicate no significant toxicity to be present for a given discharge, a partial study of effluent and ambient variability is required. If significant effluent toxicity is indicated, a complete study of effluent and ambient variability in toxicity will be required. Finally, if the initial data suggest that potential effluent toxicity exists outside the zone of initial dilution for an effluent, a program of "Toxicity Reduction Evaluation" is required. This program will seek to identify changes which can be made to the process by which the effluent is produced, or to the precise effluent composition, to attempt to reduce the toxic impact of the discharge.

- Each participating discharger will be required to submit a final report on the studies undertaken.

Testing by the first group of five dischargers is currently in progress; studies by other dischargers will follow. Because this program is only in its initial stages of implementation, no actual testing data are available for review here. However, general comments on the program content and approach are included here because of the relevance of this topic to the present report.

The proposed program is clearly a considerable improvement over previous bioassay testing requirements in the Bay and Delta. The use of a study-based approach is supported, as insufficient data currently exist on local species and local effluents to define the most appropriate test species and most cost-effective testing methods in the estuary. The use of multi-species testing involving (mostly locally-resident) organisms of several different trophic levels appears appropriate to the estuary, and the inclusion of both acute and chronic testing is also an important advance. The dependence in the testing program on static bioassays is open to debate, however; although the EPA Toxicity Support Document tends to support this approach (EPA, 1985), flow-through testing is preferred by many authors. Such preferences are based upon the reduced stress to test organisms in flow-through bioassays (less handling, reduced accumulation of metabolites and excretion products in test waters), and the improved testing of volatile or short-lived contaminants offered by flow-through bioassays. It is recommended that this aspect of the program be subjected to comparative testing if possible, and reconsidered on the basis of results from these.

In general, it is considered that the program content and approach is appropriate, and that the program promises to provide useful data relating the toxicities of point source effluents to their local impacts (if any) in the estuary and to their detailed chemical composition. Should the tests indicate the presence of significant toxicity of particular effluents discharged to the estuary, the causes of this observed toxicity will be defined through "toxicity reduction evaluation" studies. These investigations should theoretically define specific contaminants (or perhaps groups of toxicants) which exert significant local toxicity in the estuary; such contaminants may either be likely to accumulate in biota, or may be short-lived and unlikely to bio-accumulate. If significant effluent toxicity is observed which is due to contaminants which are likely to bio-accumulate, these

toxicants should be included in the regional monitoring program proposed for the estuary in section VII of the present report.

It may also be noted here that the existing testing program is dominated heavily by studies of point source effluents, with relatively little funding for studies on ambient toxicities or on the impacts of non-point sources of contaminants. Non-point sources of toxicants in the estuary have been very poorly-studied to date (Gunther *et al.*, 1987), and the existing database does not permit conclusions on the likely toxicological effects of such sources. However, it is known that significant toxicity is present in ambient waters of the Central Valley catchment on some occasions at least (perhaps due to the impacts of pesticides singly or in combination; see Shaner, 1986; Foe, 1987a, 1987b, 1988; Connor, 1988), and it is possible that similar impacts exist in the direct catchment of the Bay. The great variability in flow rates of natural streams entering the Bay, and in the hydraulics of the estuary, suggest that any testing to define the toxicological impacts of either ambient waters or non-point sources would require a comprehensive program of study. It is recommended that consideration be given to providing additional funding support for these investigations, such that the data from the testing of point source effluents may be placed into a wider context.

D. Studies Close to Effluent Outfalls

Study Design Problems in Identifying Local Impacts

In addition to a requirement for direct bioassays of effluents discussed above, the Aquatic Habitat Program Plan (AHPP) envisaged a need for "dilution field bioassays" to identify the biostimulatory or toxic impacts of effluents close to outfalls in the estuary (Horne *et al.*, 1982; SWRCB, 1982a). This element of the plan constituted an attempt to forge a link between the direct studies of effluents themselves, and investigations of the regional abundance and effects of contaminants in the receiving waters of the estuary. This link is of considerable importance, as it permits not only a greatly improved understanding of the individual and cumulative effects of discharges in the estuary, but also contributes to the development of equitable regulation of contaminant sources.

It should be noted here that techniques to directly test the toxicological or other impacts of contaminants in aquatic environments are still largely under development (and were in their infancy at the time of drafting of the AHPP), and are certainly not as advanced currently as methods employed to simply quantify toxicants in coastal ecosystems. While a variety of methods exist (see review by Bayne, 1985), many of these have not been sufficiently field-tested to be considered appropriate to all situations.

In addition, most of the methods which have been developed are not sufficiently pollutant-specific, i.e. similar end-points are evident from the effects of many different contaminants. An example of such a situation is the use of scope for growth measurements in bivalve molluscs (or other organisms) to define the impacts of pollutants. Unless the local environmental contamination is dominated by a particularly abundant toxicant, present at levels which can be directly correlated with observed effects on biota (which is an unusual occurrence in any estuary), a true cause-and-effect link to any specific contaminant can rarely be inferred.

This causes particular problems in the San Francisco Bay and Delta, as many contaminants co-vary in their distributions. For example, the northern reach of the estuary is generally more contaminated by several trace elements than is Central Bay; similar profiles are also evident between South Bay and Central Bay for many toxicants.

Unless a contaminant of concern exhibits a unique distribution (e.g. silver in the San Francisco Estuary, dominated by South Bay sources and exhibiting a gradient away from these sources throughout the estuary; see Phillips, 1987 for review), the demonstration of cause-and-effect for that toxicant will be likely to remain an elusive goal. Even in cases where an impact on biota can be linked to a specific contaminant of unique environmental distribution, the cause-and-effect link is not conclusively proven; other contaminants which are not measured may co-vary in distribution with the suspected cause of the observed impacts. As present studies of contaminants in aquatic ecosystems quantify only a fraction of the total number of toxicants actually present, incontrovertible evidence for cause-and-effect between a contaminant and an observed impact on biota is rare indeed. Attempting to define such effects in estuaries such as San Francisco Bay is tantamount to delineating the precise cause of death in an alcoholic overweight smoker, fond of butter and junk food, succumbing to heart disease after running his first marathon in a heatwave.

The studies of Martin *et al.* (1984b) provide an excellent example of this dilemma in the estuary. These authors demonstrated that the scope for growth of transplanted mussels (*Mytilus californianus*) declined significantly in the open waters of the South Bay, on a gradient from Fort Baker southwards to Redwood Creek. This effect is undoubtedly real, and reflects a considerable stress encountered by mussels in the South Bay; observations that transplanted mussels survive poorly and that no native mussels exist in the extremity of South Bay are most probably related to such findings. However, Martin *et al.* (1984b) found that the observed impacts on scope for growth of the transplanted mussels correlated to their bio-accumulation of a range of toxicants, including total chlordane, dieldrin, and several trace metals. It was therefore impossible to ascribe the effects seen to any one toxicant. This conclusion does not provide useful information to environmental managers, faced with decisions on the control of specific contaminants in the estuary, which may be derived from similar or divergent sources. However, in the absence of techniques to measure pollutant-specific effects, such conclusions are the only source of information available on the impacts of toxic contaminants.

Attempts to Date

The techniques proposed by Horne *et al.* (1982) in the AHPP to define the near-field impacts of effluent discharges acknowledged that such effects may be either

biostimulatory or toxic in nature. Thus, it was proposed that the growth of aufwuchs should be used to measure biostimulatory effects (which may most likely be ascribed to nutrients or other organic constituents present in outfalls), while the growth of mussels should be employed as an indication of toxic impacts.

Roth *et al.* (1983, 1984) undertook these investigations as pilot-scale "demonstration trials". Studies on the growth of aufwuchs (Roth *et al.*, 1983) were carried out at two sites: the East Bay Municipal Utility District (EBMUD) outfall close to the eastern arm of the Bay Bridge, and the Chevron USA Richmond refinery outfall in Castro Cove. These outfalls differed significantly from each other, the EBMUD discharge taking place in relatively deep well-mixed waters and therefore enjoying high initial dilution, and the Chevron effluent being discharged to a shallow cove with poor initial dilution and dispersion. Seven study sites were employed at each location; these are shown in Figures 17 and 18. The study design reflected an attempt to discern biostimulatory effects on a gradient from each outfall, decreasing towards more open waters as the effluents become more diluted and dispersed. Roughened tygon tubes were employed as a substrate for the growth of aufwuchs (which comprised a variety of fouling organisms, the principal component being diatoms). Figures 19 and 20 show data for photosynthesis and respiration rates, concentrations of chlorophyll-a, and dry weight for experiments undertaken at the two sites. The data shown are consistent with the presence of a significant biostimulatory impact from both of the discharges studied, at least in the near-field area.

Studies of the toxic impacts of effluents, utilizing the growth rates of mussels (*Mytilus edulis*) as an end-point, were performed only at the EBMUD outfall (Roth *et al.*, 1984). The study sites employed in preliminary investigations of mussel growth were identical to those used in the investigations of the growth of aufwuchs, discussed above (see Figure 17). Three separate studies were performed over two years (1982-83), and the later studies employed additional sites in the area close to the outfall. Transplanted mussels (from Berkeley Pier or Tomales Bay) were suspended close to the water surface for periods of between two and six weeks. In one of the three experiments, significant decreases in mussel growth rates (reductions of about 20% in shell length, wet flesh weight, and dry weight) were observed at locations close to the discharge; no such effects were found in the other two experiments. The authors speculated that the differences observed between the various experiments were due to alterations in effluent

Figure 17. Locations of study sites in the investigations of the growth of aufwuchs (Roth *et al.*, 1983) and the preliminary studies of mussel growth (Roth *et al.*, 1984; Martin *et al.*, 1984a) around the East Bay Municipal Utility District outfall. After Roth *et al.* (1983).

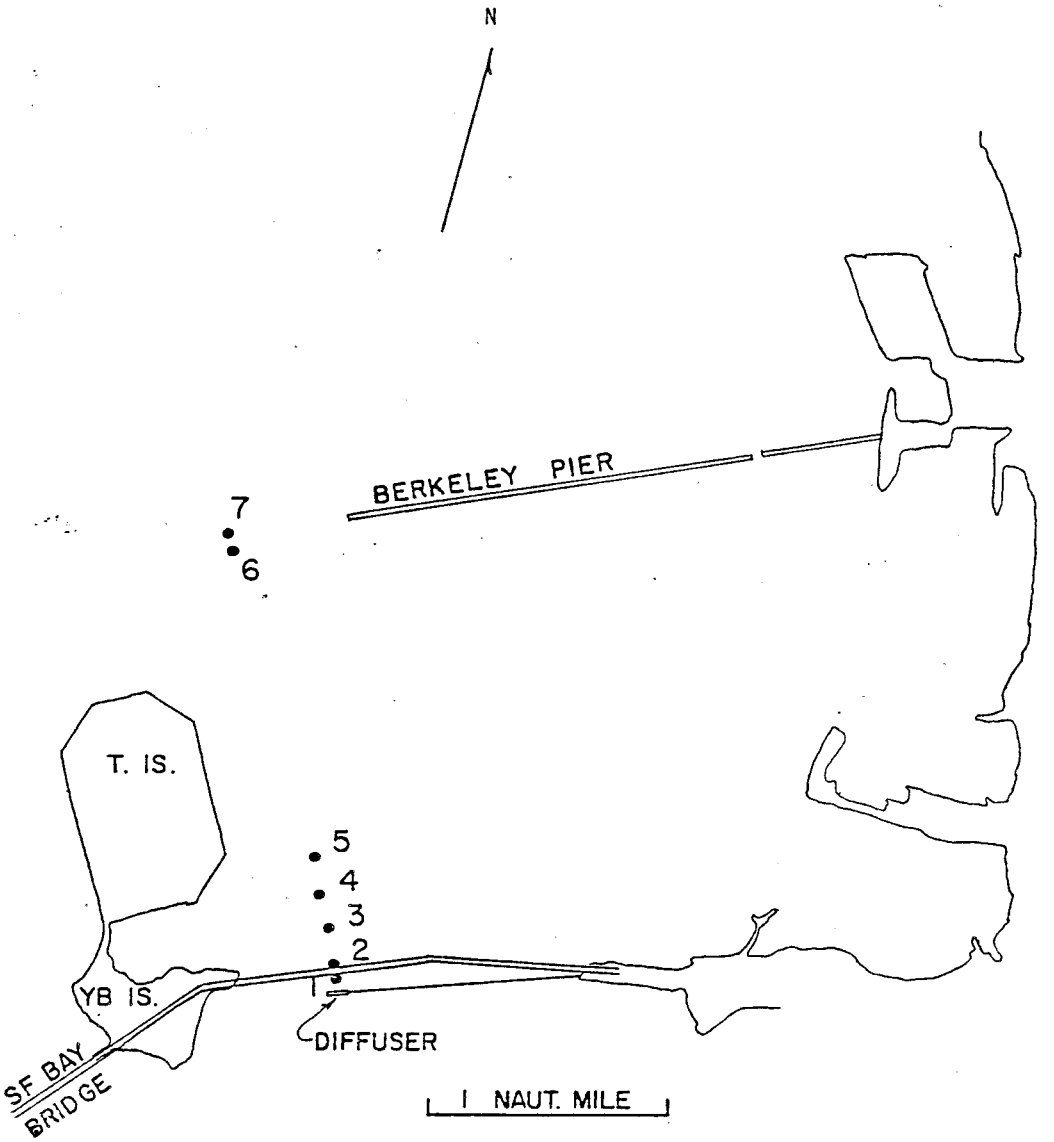


Figure 18. Locations of study sites in the investigations of the growth of aufwuchs around the Chevron USA Richmond refinery outfall. After Roth *et al.* (1983).

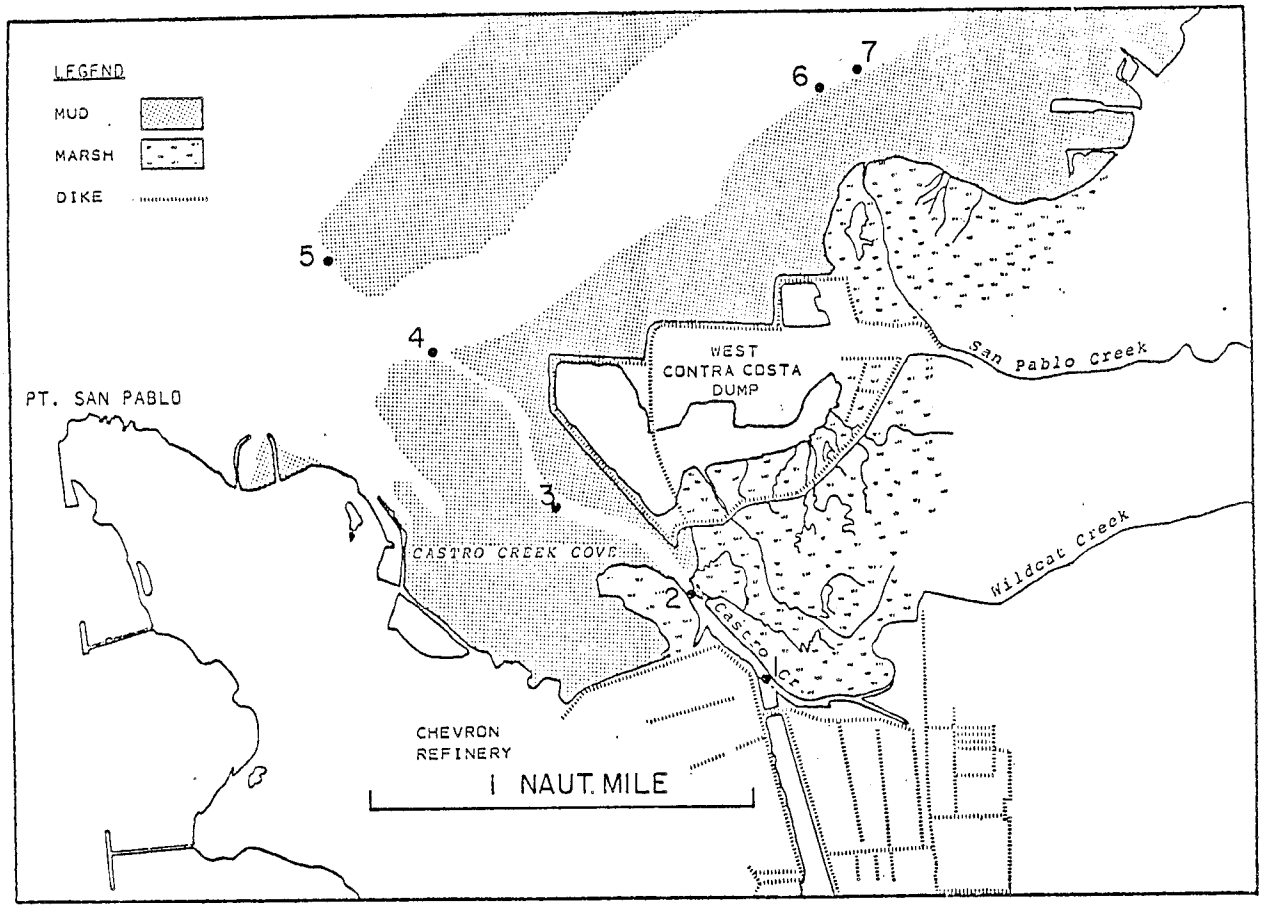


Figure 19. Example of biostimulatory impacts of the East Bay Municipal Utility District discharge on the growth of aufwuchs. Data from the fourth experiment at this site, showing trends between stations (see Figure 17) in photosynthesis (P), respiration (R), chlorophyll-a (CHL), and dry weight (DW) of aufwuchs. Error bars show standard deviations around the means for six replicates per site. Numbers below each point indicate station numbers which are significantly different from the marked station. After Roth *et al.* (1983).

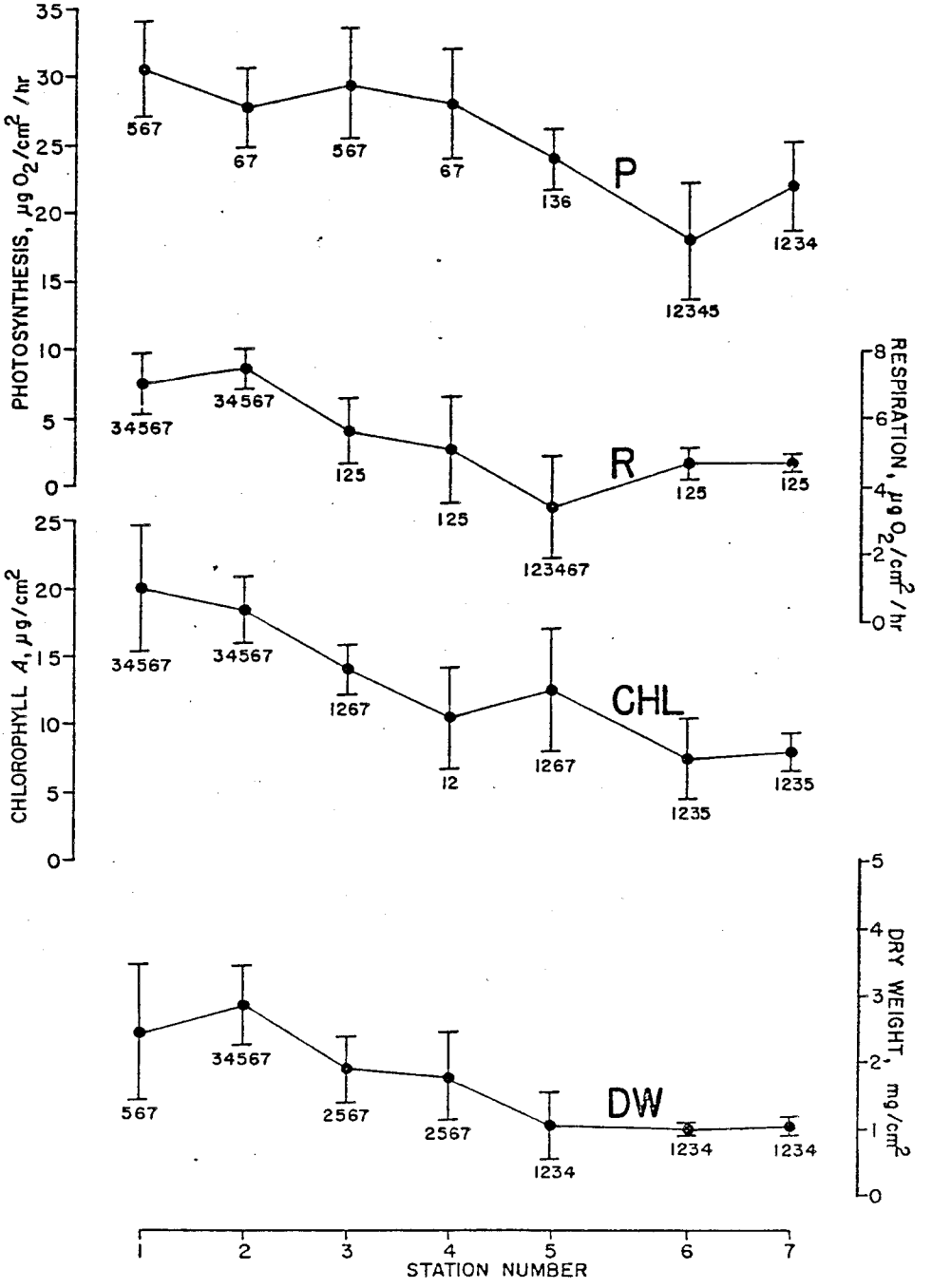
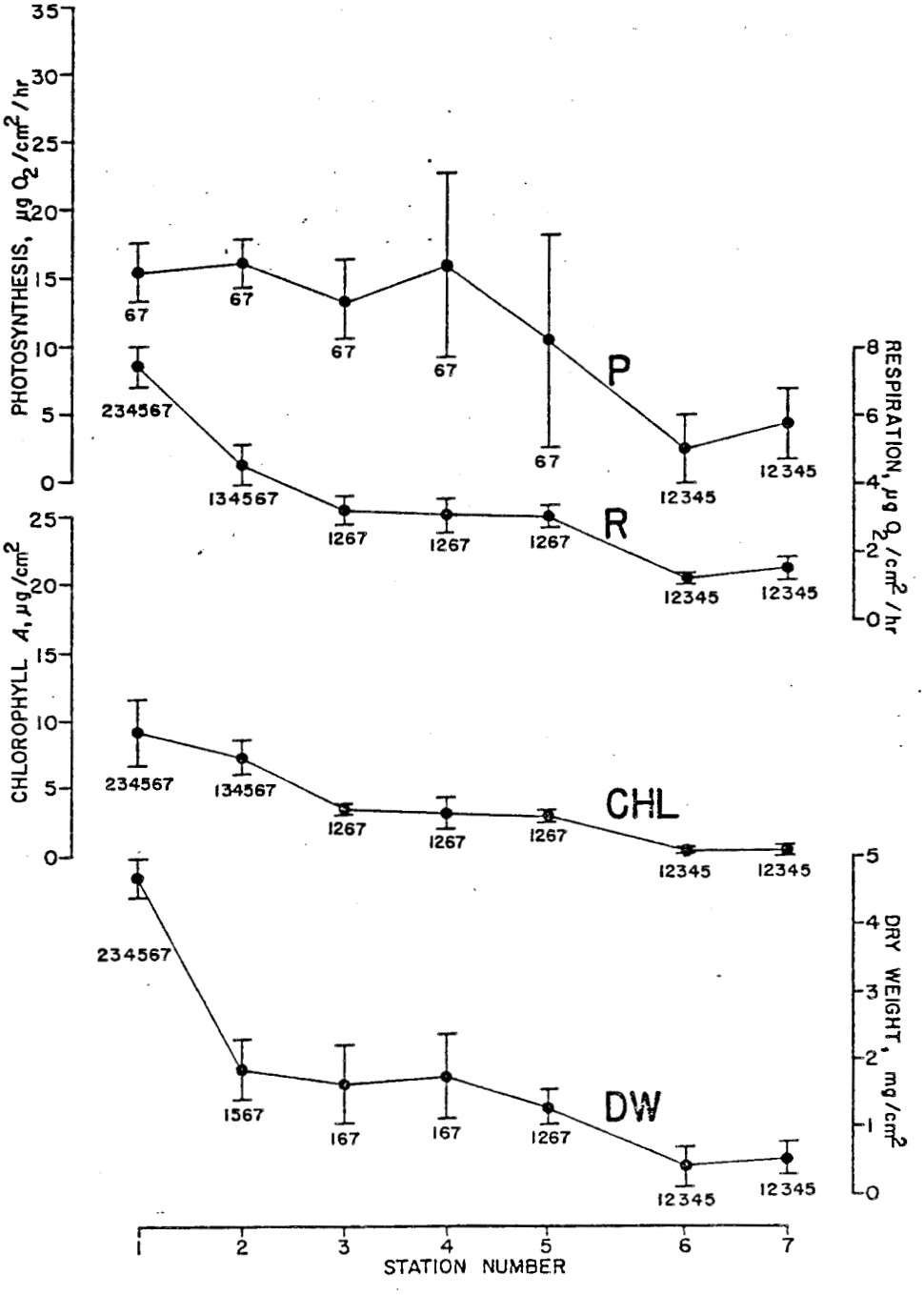


Figure 20. Example of biostimulatory impacts of the Chevron USA Richmond refinery discharge on the growth of aufwuchs. Station locations are shown in Figure 18; all symbols as in Figure 19. After Roth *et al.* (1983).



quality between the different study periods; self-monitoring data tended to support this, but were not conclusive.

Martin *et al.* (1984a) performed physiological measurements on duplicate samples taken by Roth *et al.* (1984) in two of their experiments on the impacts of the EBMUD discharge on mussels in the near-field area. The results of these investigations were mixed. In the first study, one sample of mussels from the location closest to the discharge point exhibited a statistically significant depression of scope for growth, and also a reduced assimilation efficiency compared to samples collected at greater distance from the outfall. However, this (presumed) impact from the discharge was not reflected by the other physiological measurements made. No statistically significant impacts of any kind related to distance from the outfall location were observed in the second study.

Several other studies have also been undertaken to attempt to define the near-field impacts of discharges in the estuary. CH2M Hill (1982) used shell growth of the ribbed horse mussel (*Ischadium demissum*) as an end-point in *in situ* studies of the effects of the Chevron USA Richmond refinery discharge. Kinnetic Laboratories (1984) employed mussel (*Mytilus edulis*) growth in pre-discharge and post-discharge investigations of the impacts of the East Bay Dischargers Authority outfall in South Bay; both flesh and gonad weights were measured. Also in the South Bay (but closer to the southern extremity), a five-year program of study included investigations of water and sediment chemistry, of fish food habits, of the incidence of avian botulism, and of the biology and contaminant status of the shrimp *Crangon franciscorum* (Larry Walker Associates/Kinnetic Laboratories, 1987a, 1987b). Data for contaminants in *C. franciscorum* suggested that certain trace elements (Cd, Hg, Pb) were enriched in the extreme South Bay compared to reference stations in the northern reach of the estuary; however, this could not be strictly correlated to the presence of major municipal outfalls in this area of the South Bay. PCBs and DDE were also found in these shrimp, PCBs being particularly abundant in 1984. It was suggested on the basis of data for samples from other areas of the estuary that this unusual enrichment of PCBs in 1984 was due to a spill in the northern reach of the estuary (see footnote 1). Few strong conclusions may

Footnote 1: Interestingly, data on PCBs in starry flounder (*Platichthys stellatus*) also suggest higher levels in 1984, consistent with the existence of a spill in that year (R.B. Spies, personal communication). However, no such conclusions may be drawn from the data of the State Mussel Watch Program (Phillips, 1987); possibly the mussels did not encounter PCBs from the spill, as they were transplanted into the estuary for only four months of the year.

be reached from this database on *C. franciscorum*. Some trace elements are certain to be regulated in the muscle of this species (see section II of this report), and the (salinity-dependent) movement of these shrimp in the estuary will have tended to reduce any inter-site differences in the levels of other contaminants that may have been present. Unfortunately, no data for contaminants in mussels were produced in this program of study.

Knight and Foe (1984) and Foe and Knight (1985, 1986) published extensive studies of the use of the Asiatic clam *Corbicula fluminea* in monitoring the sublethal impacts of point source discharges, involving investigations of the Contra Costa Sanitation District municipal outfall near New York Slough in the Delta, and the Pacific Gas & Electric cooling water outfall at Antioch. These data suggested the presence of significant near-field sublethal impacts (and at one site, lethal thermal effects) from the cooling water effluent, but no significant effects from the municipal outfall were noted. Shell and tissue growth, condition index, clam mortality, and scope for growth were all considered to be useful parameters for monitoring in the studies of *C. fluminea*, although Foe and Knight (1985) had reservations about the use of scope for growth measurements as a routine test in some situations. The latest paper (Foe and Knight, 1986) included data on copper and zinc levels in *C. fluminea* from the Delta. Transplanted clams appeared to match native clams in their accumulation of these metals, at least once the introduced animals had equilibrated to the new ambient conditions. Most samples exhibited higher concentrations of the two metals during the summer; this may be due to tissue weight changes (S.N. Luoma, personal communication). The zinc levels reported were similar to those in *Corbicula* sp. taken from upstream areas by the Toxic Substances Monitoring Program (see section IV of this report), but the copper levels found by Foe and Knight (1986) were greater than those from upstream areas. The latter difference was thought to be due to the industrial inputs of copper in the lower Delta region. Inter-site differences were evident for copper concentrations in these clams, but could not be ascribed to the effects of any specific outfall (due mostly to the placement of the sampling sites).

Hoffman and Meighan (1984) used several different methods to examine the impacts of combined sewer outfalls on the east side of the San Francisco Peninsula, at Islais and Mission Creeks. These data, and those of Chapman *et al.* (1986) on Islais Creek using sediment quality triad techniques, clearly indicate that the local area around

such outfalls is contaminated by a variety of toxicants, and that benthic infaunal diversities and distributions are affected (see review by Phillips, 1987). These studies are also among very few which have employed chemical analyses of sediments in areas local to specific outfalls to identify the impacts of individual effluent discharges in the estuary on the local abundance of contaminants. In local areas, such techniques sometimes provide more easily interpreted data than in regional monitoring, as grain size and organic carbon contents of samples are often less variable, and therefore have only minor impacts on analytical data.

In conclusion, near-field studies of the local impacts of point source effluents have been relatively rare to date in the estuary. Those studies which have been undertaken have mostly employed bivalves to monitor sublethal effects, with growth of mussels being the most popular technique. It may be noted here that it is probable that other more sensitive parameters exist, which could be employed for such effects-related monitoring. Thus, for example, recent work on the impacts of contamination on bivalves or other species has employed a wide variety of approaches, ranging from biochemical through physiological and histological techniques (Bayne, 1985; Bayne *et al.*, 1985).

Results from the local studies (mostly employing bivalve growth as an end-point, as noted above) have been mixed. Municipal outfalls have been found to have relatively minor or indistinguishable impacts in several cases, and this may reflect either the improvements in the qualities of such effluents in the last two decades, or the insensitivity of the monitoring technique (or both). Techniques to monitor pollutant-specific effects are generally not available as yet; it is therefore often impossible to ascribe any observed sublethal impact to the effects of particular contaminants.

In addition, the ecological significance of any observed sublethal effects is hard to define. Roth *et al.* (1983, 1984) felt that a doubling of the growth of aufwuchs was the minimum impact which should be considered ecologically significant as a biostimulatory effect due to an individual outfall, and a halving of bivalve growth should be deemed ecologically significant in terms of the toxic effects of outfalls. Such recommendations appear difficult to justify scientifically, as the selection of the degree of change thought to be significant to the biological resources of the estuary is basically arbitrary.

This dilemma can be solved only through the improvement of monitoring techniques designed to measure specific biological effects of toxic contaminants in estuaries, and to relate these to the overall health of aquatic environments as entire ecosystems. The present state of the art does not appear to permit this (Bayne, 1985). It is therefore suggested in the following sub-section that a more cost-effective approach under the present circumstances would involve the improved monitoring of the bio-accumulation of toxicants in local environments, as the technology and background understanding necessary to attain this goal are available now.

E. The Case for Local Bio-accumulation Studies

As noted previously in this report, the primary task of regulatory agencies in protecting water quality in the estuary involves the adjustment of contaminant loads from multiple sources to match receiving water quality objectives, the latter being selected to provide adequate protection to resident biota (either in terms of direct toxicity or with respect to the bio-accumulation of toxicants). This implies the existence of a reliable and extensive database on contaminant loading to the estuary, which does not presently exist (Gunther *et al.*, 1987). Even the monitoring of point sources in the estuary (which has been more extensive than that of any other toxicant source) has largely failed to provide sufficient quantitative data on at least some of the contaminants of concern in the Bay and Delta to date (see sub-section B above). Unless the available information can be radically improved, attempts at wasteload allocations for the estuary are likely to be seriously flawed.

One of the principal reasons for this situation is the difficulty encountered in accurately quantifying the trace levels of contaminants present in most aqueous effluents (hence the large numbers of values quoted as "below detection limits" in NPDES self-monitoring data). These very low concentrations may be inconsequential in individual effluents, but may nevertheless give rise in concert to unacceptable accumulations of toxicants in particular regions of the estuary (e.g. in sediments, as "hot spots"), or in particular "target species" resident in the Bay and Delta (see section VI below). It therefore appears vital that a monitoring system be found which provides accurate and reliable quantitative data on a local scale (i.e. for measuring contaminants in effluents themselves and in areas close to outfalls), and which also permits data from local studies to be viewed in a regional perspective. Monitoring of this type is required throughout the estuary, so that the contributions of toxicants from upstream sources may be related to those from within-Bay sources. The present monitoring programs for contaminants do not provide either the local-regional link or the Delta-Bay link in understanding.

The problems encountered in the direct analysis of effluents in the estuary are identical to those which acted as a driving force towards the use of bio-monitors for quantifying toxicants on a regional scale, in open receiving waters. Thus, as discussed in section II of this report, the use of bio-monitors is preferred to the direct analysis of

receiving waters because of the direct measurement of bio-availabilities of contaminants by bio-monitors, their time-averaging capacity, and their simpler analysis. These same advantages exist also with respect to the quantification of contaminants in effluents. Thus, bio-monitors may be exposed to effluents (whole, or diluted; in the laboratory or *in situ* in the field) to define not only the existence of significant concentrations of contaminants in such effluents, but also their bio-availabilities. This reliance upon bio-monitors for the local monitoring of toxicants would offer a range of advantages:

- The identification of the presence of contaminants in effluents would be improved radically (because of the bioaccumulation of such contaminants by the bio-monitor employed, to levels much greater than those seen in aqueous samples). Where bio-available toxicants are present in significant quantity in an effluent, the bio-monitor will reflect this, and will in general permit cheaper and simpler analysis than that required for the identification of contaminants in aqueous effluents themselves.

- Bio-availability would be measured directly. This is of considerable consequence for regulatory decisions; the introduction of controls on toxicant sources is clearly most cost-effective in situations where contaminants are highly bio-available (i.e. have the greatest impact on biological resources which are to be protected).

- The time-integrating facility provided by the use of bio-monitors would improve the characterization of temporally-variable effluents and receiving waters. Such improvements are of considerable importance, as they would provide greater cost-effectiveness in monitoring.

- "Local" data (e.g. on effluents themselves, and on the regions adjacent to discharges) could be related directly to "regional" data, through the matching of protocols employed in local and regional programs of study (use of same species and sampling times, etc.).

- Data relevant to the Delta could be related to that for the Bay if bio-monitoring species are selected which overlap or abut each other in their distributions.

It may be argued that data on the levels of contaminants in bio-monitors does not represent an "absolute" quantitative value of the concentration (and hence, loading) of contaminants in specific sources. However, this argument is flawed, in the sense that the

quantification of contaminant concentrations (and hence, loads) in aqueous solution in specific toxicant sources also fails to provide absolute quantitative data of any relevance; in particular, no measurement of the bio-availability of toxicants is afforded by the latter, and this is critical to any regulatory decision on the need for further pollution controls.

In many respects, the direct use of bio-monitors to quantify contaminant sources is paralleled by the use of effluent bioassays as a regulatory tool, and may also enhance the overall understanding of the impacts of contaminant sources derived from the use of bioassays to characterize effluents. Bioassay techniques rely upon a species response to a toxic impact, and the cause of the latter is often never fully identified, even through such methods as Toxicity Reduction Evaluations. The concerted study of the accumulation of toxicants by bio-monitors exposed to effluents would not only define the abundance of contaminants in effluents (and relate this to regional patterns in toxicant abundance and distributions), but would also provide data on the contaminants which might be responsible for any observed toxicity in bioassays. The use of biota in all stages of local and regional monitoring of toxicant abundance, distributions and effects would thus provide a cohesive, focused monitoring program in which each datapoint gathered could be related to all other data available on the estuary.

Certain of the previous studies of contaminant distributions and abundance in the estuary approximate the approach described here. The State Mussel Watch Program (SMWP) has recently investigated the local abundance of trace metals, pesticides and PCBs in mussels from Oakland and Richmond Harbors (Stephenson *et al.*, 1986; Phillips [D.J.H.], 1987; Phillips [P.T.], 1988). Although specific point sources were not directly studied in each of these areas, the investigations of contaminants in the Santa Fe Channel and Lauritzen Canal area of Richmond Inner Harbor are similar to the approach proposed here, as they characterize one principal source of contaminants (the highly-contaminated runoff from the banks of the Lauritzen Canal). In addition, the studies of Luoma and co-workers (see Luoma and Cain, 1979; Bradford and Luoma, 1980; Luoma and Cloern, 1982; Thomson *et al.*, 1984; Luoma *et al.*, 1985), employing analyses of the clam *Macoma balthica* at several sites in the South Bay, some of which are adjacent to point source discharges, are very similar to those proposed herein. These authors have sampled *M. balthica* close to outfalls in the South Bay (particularly the discharge site of the Palo Alto sewage treatment plant) over the last decade, and have provided a consistent database on the abundance of metals at these sites. Temporal fluctuations in metal concentrations have been related to local impacts (alterations in the loading of

metals such as copper with time) and to regional effects (possible effects of Delta inflows on silver levels in the South Bay). Although these data do not cover many points in the Bay, and do not extend out of the South Bay, this general approach is clearly of benefit in relating local to regional trends in contaminant abundance in the estuary.

Recent studies by the California Department of Fish & Game on selenium distributions in the estuary (CDF&G, 1988) also approximate the approach suggested here. In an effort to define sources of bio-available selenium in the Bay and Delta, mussels (*Mytilus californianus*) and oysters (*Crassostrea gigas*) were transplanted into several locations in the estuary, employing techniques developed by the State Mussel Watch Program studies. Some of the sites investigated were close to the discharges of refineries (thought to be a major source of selenite from the previous results of Cutter, 1987). Native samples of clams (*Corbicula* sp.) were also analyzed at some sites. It was necessary to use all three bivalve species because *M. californianus* does not survive well upstream of the Carquinez Strait, due to its salinity sensitivity. *C. gigas* was therefore employed in the area between Carquinez Strait and the Delta, and native *Corbicula* sp. in the Delta itself. Samples close to refinery discharges were found to accumulate higher levels of selenium than those from more distant sites, and a greater availability of selenium was noted in the northern reach compared to the South Bay. The level of sampling was not sufficient to delineate gradients in selenium bio-availability between the refinery outfalls and "background" levels in the northern reach, however, and no studies were performed on diluted effluents themselves.

It might also be noted here that the monitoring of sewage outfalls and their effects required under section 301(h) of the Clean Water Act frequently includes the use of bivalves to identify contaminants discharged at these outfalls, to define the near-field abundance of toxicants, and to relate these to background levels (EPA, 1987a, 1987b). The species recommended for use in bio-accumulation studies in this program in northern California include a variety of decapod crustaceans (see comments in section II of this report on the use of these as bio-monitors) and the mussels *Mytilus edulis* and *M. californianus* (EPA, 1987b). In addition, the use of the Pacific oyster (*Crassostrea gigas*) is considered acceptable, where these occur naturally at discharge sites, and clams (*Macoma balthica*) may be used where small invertebrates are thought to provide adequate tissue for analysis and sediment-associated contaminants are of concern (EPA, 1987b). Several documents have been produced to support this program, particularly with respect to the sampling and analytical techniques to be employed (e.g.

EPA, 1987c, 1987d). Although such monitoring techniques are now accepted practice in 301(h) monitoring programs, their inclusion in self-monitoring under the NPDES permitting system has not been introduced.

These investigations show that the analysis of bio-monitors in areas close to point sources provides data which constitute a great improvement over other monitoring techniques in areas adjacent to such sources of contaminants. If data of this type were available for each of the 200 point source discharges entering the Bay, for the 50 point source discharges entering the Delta, and for the many non-point source discharges in the estuary, our knowledge of contaminant sources in the system as a whole would be dramatically improved. Further, if such data in local areas could be compared to monitoring results on a regional scale (such as those from an expanded State Mussel Watch Program, supplemented by a similar program in freshwater and brackish-water reaches of the estuary), the sources, distributions and fates of contaminants in the entire estuary would be much better characterized. Section VII of this report provides proposals for such studies.

VI. THE MONITORING OF TOXICANTS IN TARGET SPECIES AND FOOD CHAINS

In any aquatic ecosystem, toxic contaminants will exert detrimental impacts on particular species at different levels of exposure. This is due to several factors, including the differences between species in cumulative exposure to individual contaminants (which may relate to habitat, diet, etc.), and differences in sensitivity between species (relating to innate factors or to acquired tolerance; see Luoma, 1977b; Luoma *et al.*, 1983). The protection of the resources of the estuary from the impacts of toxic contaminants should strive to recognize and predict such differences between species, and contaminant loadings should be reduced to such levels as may be required to protect the most sensitive species resident in the estuary from both the direct impacts of toxicants and from the bio-accumulation of contaminants through the food chain.

It follows from the above that certain species may be those at greatest risk from the toxic effects of contaminants in the estuary. These "target species" have not been fully identified to date, although the types of contaminants present in the estuary at elevated levels provide clues as to possible candidates for "target species" status. For example, particular types of organochlorines are known to exert impacts on the reproduction of specific seal and bird populations in various parts of the world, because of the accumulation of these pollutants to particularly high concentrations by such species of high trophic levels. Other contaminants present in aquatic ecosystems, such as certain of the trace elements, may constitute a particular threat to public health, and such effects on humans may be seen as the most significant problem due to elevated concentrations of these toxicants in aquatic environments.

The monitoring of contaminants and their effects in target species and food chains is distinct from monitoring programs which seek to identify spatial and temporal trends in contaminant abundance, using bio-monitors or other methods. The present report therefore considers data on toxicants in target species and food chains of the San Francisco Estuary only briefly. However, the close relationships between these two aspects of monitoring, and the importance in general of the monitoring of contaminants in various portions of food chains (as opposed to the use of bio-monitors in isolation), is

thought to be sufficient reason for the inclusion here of brief comments on such monitoring.

As noted above, present data are inadequate to provide an accurate picture of probable target species for toxicants in the San Francisco Bay and Delta. Insufficient information exists to delineate either the most sensitive species in the estuary to particular toxicants, or the probable pathways of contaminant transfer through food chains. Indeed, food chains or food webs have themselves been inadequately defined in the estuary to date; there is a need for further study of trophic relationships in the Bay and Delta, and methods involving the use of cesium/potassium ratios or isotopic carbon or nitrogen ratios are available for this. Studies to date have generally concerned species of particular economic importance in the estuary, or species which may be suspected to be exposed to high concentrations of contaminants, based on data from elsewhere.

Considerable work has been completed on the possible impacts of toxicants in the estuary on striped bass (*Morone saxatilis*), although this is driven more by the importance of this fishery and its recent decline than by any perception that *M. saxatilis* may be particularly sensitive to contaminants in the estuary. Data on contaminants in striped bass have been amassed through the Cooperative Striped Bass Studies (COSBS; see Whipple *et al.*, 1983, and Whipple, 1984) and by continuing work undertaken by the California Department of Fish & Game (Kohlhorst *et al.*, 1986; Knudsen and Kohlhorst, 1987; Urquhart and Knudsen, 1988a, 1988b). The monitoring of toxicants in this species presents some unusually difficult problems. Certain of the contaminants (in particular, certain monocyclic aromatic hydrocarbons) which have been suggested to exert detrimental effects on the reproduction of *M. saxatilis* are both ephemeral in the estuary and of short half-life in the fish themselves. This gives rise to possibilities for great variance in the levels of MAHs encountered in particular individuals, which in turn creates difficulty in data interpretation. Studies using power analysis techniques on data from both the COSBS program and the current CDF&G monitoring suggest that the present sample sizes (about 40 fish each year in total, half from the Sacramento River and the remainder from the San Joaquin River) are sufficient only to provide a very general indication of temporal changes in concentrations of individual MAHs between years. This is due to the existence of "outliers" in the population, which appear to exhibit particularly high concentrations of MAHs. The sampling of such outliers is basically a function of chance, although their inclusion in any

one year of sampling dramatically affects the data produced. Thus, despite protracted study over the last decade, no conclusion has been reached on the precise impacts of MAHs (or other contaminants, such as PCBs) on striped bass. The introduction of stratified sampling of this species throughout its spawning run in the estuary, and of intercomparative analyses by several laboratories for MAHs, have been proposed elsewhere as of value for future phases of this monitoring program. These recommendations are repeated here. Direct investigations of the effects of MAHs on egg resorption in female *M. saxatilis* under laboratory conditions also merit consideration.

The starry flounder (*Platichthys stellatus*) may be a more likely candidate as a target species for contaminants in the estuary. Its demersal habits and presence in areas of the Bay characterized by contaminated sediments argue that toxicants may exert adverse impacts on this species in areas of local contaminantion. Spies and co-workers have provided evidence for an adverse effect of PCBs on fertilization success of *P. stellatus* in the Bay (Spies *et al.*, 1984, 1985a, 1985b, 1988a, 1988b). However, this evidence stops short of conclusively showing that PCBs are interfering with the fertilization of starry flounders in the estuary, and there is a need for further work (Phillips and Spies, 1988). The laboratory-based dosing of *P. stellatus* females with PCBs through food and water exposure routes is required to confirm or refute the presence of significant impacts of contaminants in the field, and these studies have unfortunately not received funding to date.

It is now well-known that birds (and in particular, raptors) may accumulate high concentrations of organochlorines, creating reproductive problems through eggshell thinning and other mechanisms. Investigations of contaminant concentrations in birds have provided interesting data in the estuary (see Ohlendorf and Miller, 1984; Hoffman *et al.*, 1986; Ohlendorf *et al.*, 1986a, 1986b, 1986c, 1988). This topic is of considerable ecological importance because of the use of wetlands and other habitats in the Bay and Delta for the over-wintering of species on the Pacific flyway. These authors have shown that pesticides increase in concentration in birds during their stay locally, although the toxicological impacts of this are not known with certainty (Ohlendorf and Fleming, 1988). In addition, the impacts of selenium on birds at Kesterson National Wildlife Refuge (and most recently in the Tulare Lake basin) have generated controversy. Additional studies on selenium impacts on wildlife of the Bay and Delta are being continued by the California Department of Fish & Game (CDF&G, 1987b, 1988) and the U.S. Fish and Wildlife Service (Ohelndorf and Fleming, 1988). These investigations emphasize the

analysis of aquatic birds and fish for selenium, and these data are less useful for site-specific monitoring purposes (because of the significant movement of the organisms employed) than for their provision of insight into the food chain transfer of the element. The studies undertaken by CDF&G (1988) on selenium in bivalves in the estuary were discussed previously, in section V of this report.

Studies on contaminants in marine mammals resident in the estuary have been rare to date. Risebrough *et al.* (1978) cited data for organochlorine levels in harbor seals (*Phoca vitulina*) found dead in the Bay; as noted by Phillips (1987), these data are difficult to interpret with confidence, but are suggestive that PCBs in particular may possibly be exerting adverse effects on the reproduction of this species, at least in resident animals. Such effects have recently been confirmed in the same species from coasts of the Netherlands (Reijnders, 1986), and ringed seals (*Pusa hispida*) in the Baltic Sea and Bothnian Bay have long been known to be affected by organochlorines. There is a need for direct study of local seals in the Bay, emphasizing their migratory habits and their organochlorine levels. A recent proposal for such studies has received partial funding (D. Kopec, personal communication), and should be further supported.

VII. THE PROPOSED MONITORING PROGRAM

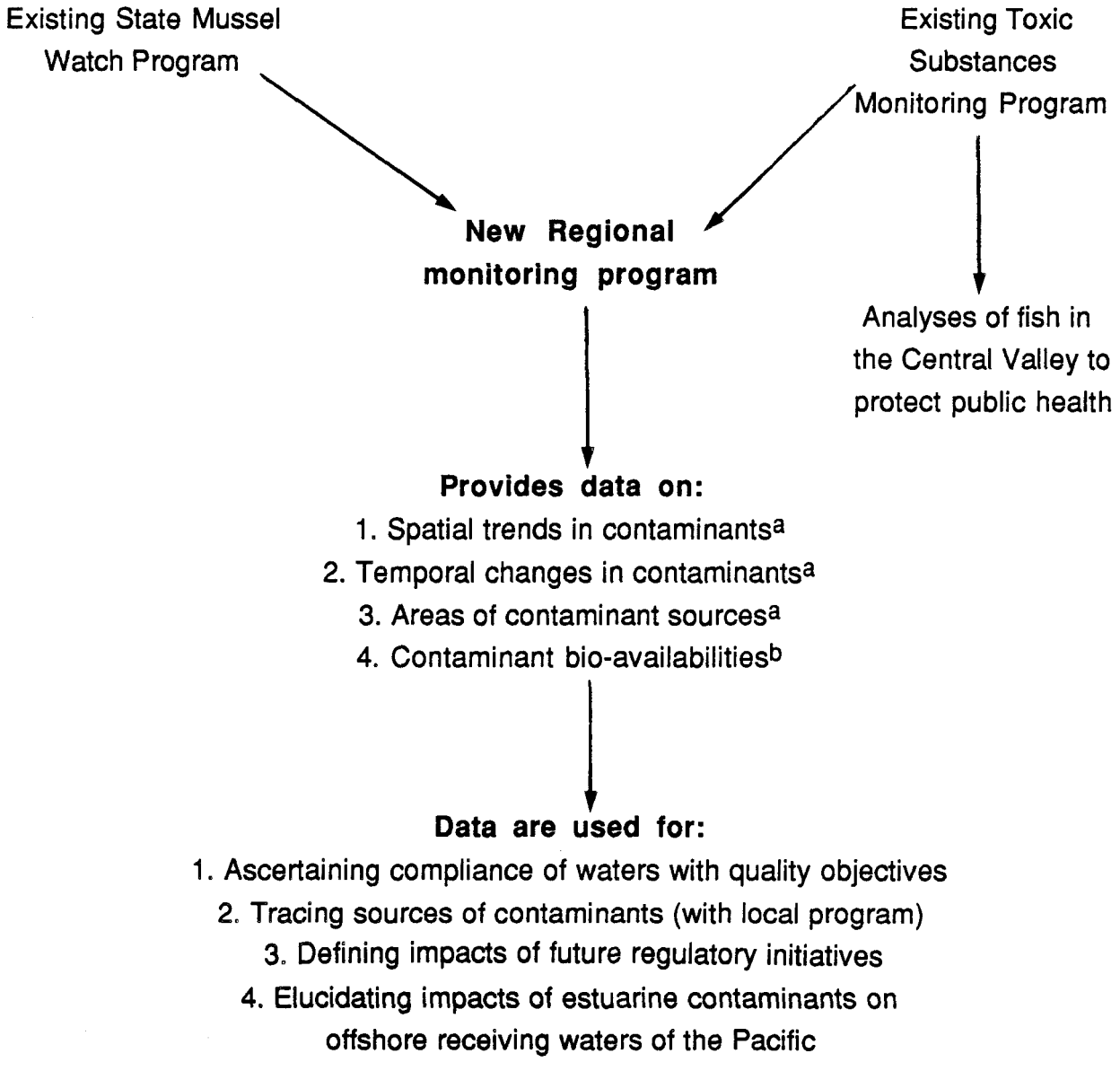
A. General Description of the Proposed Program

The Regional Monitoring Component

It is intended that the regional monitoring component of the program proposed here be the cornerstone of all future monitoring of the spatial and temporal changes in the abundance, distributions and bio-availabilities of toxic contaminants in the San Francisco Bay and Delta and the upstream Central Valley catchment (see schematic in Figure 21). The design of the proposed program reflects the needs identified in previous sections of this report to inter-relate contaminant concentrations and bio-availabilities in the various sections of the estuary and its catchment, on both local and regional scales. Thus, it is proposed that all future monitoring of spatial and temporal trends in contaminants on local scales or for special projects be designed to provide data which may be compared to the regional monitoring database.

The proposed regional program covers studies of contaminants in both water and bio-monitors. Data on toxicants in water are required for regulatory purposes, to ascertain compliance with water quality objectives for the estuary, cited in the Basin Plan (SFRWQCB, 1986). In addition, special studies are needed on contamination of the microlayer in the estuary; these are discussed in sub-section H below. With respect to bio-monitoring, the regional monitoring program outlined in the following sub-sections is intended to subsume the existing State Mussel Watch Program studies in the Bay (and the National Status and Trends studies of NOAA); the program proposed here is essentially an expanded and extended version of these existing investigations, with some design changes. The proposed program is also intended to replace much of the current work undertaken by the Toxic Substances Monitoring Program (TSMP) in the freshwater regions of the catchment. It is thus recommended here that the use of bivalve molluscs as bio-monitors of toxic contaminants (see sub-section C below) would be more appropriate to attain the original goals of the TSMP, which related principally to the production of a database on spatial and temporal trends in contaminant concentrations in the Central Valley catchment (see section IV D of this report). However, it is recommended that studies of toxicants in specific species of fish (largemouth bass,

Figure 21. The proposed regional monitoring program, and its relationships to existing programs and unknowns.



[a]Analyses of both water and bio-monitors

[b]Analyses of bio-monitors only

Micropterus salmoides and channel catfish, *Ictalurus punctatus*; see section IV D of this report) should be retained as part of the TSMP investigations, to provide a comparative database to the studies of bivalves proposed here.

The analysis of sediments is not included in the proposed regional program. This is because the spatial heterogeneity of contaminants in sediments over small distances in the Bay and Delta interferes with the use of this technique to identify meaningful spatial or temporal trends in contaminant abundance on a regional scale; in addition, sediment analyses do not provide data on contaminant bio-availability. However, sediments are included as part of the local studies proposed.

The Local Monitoring Component

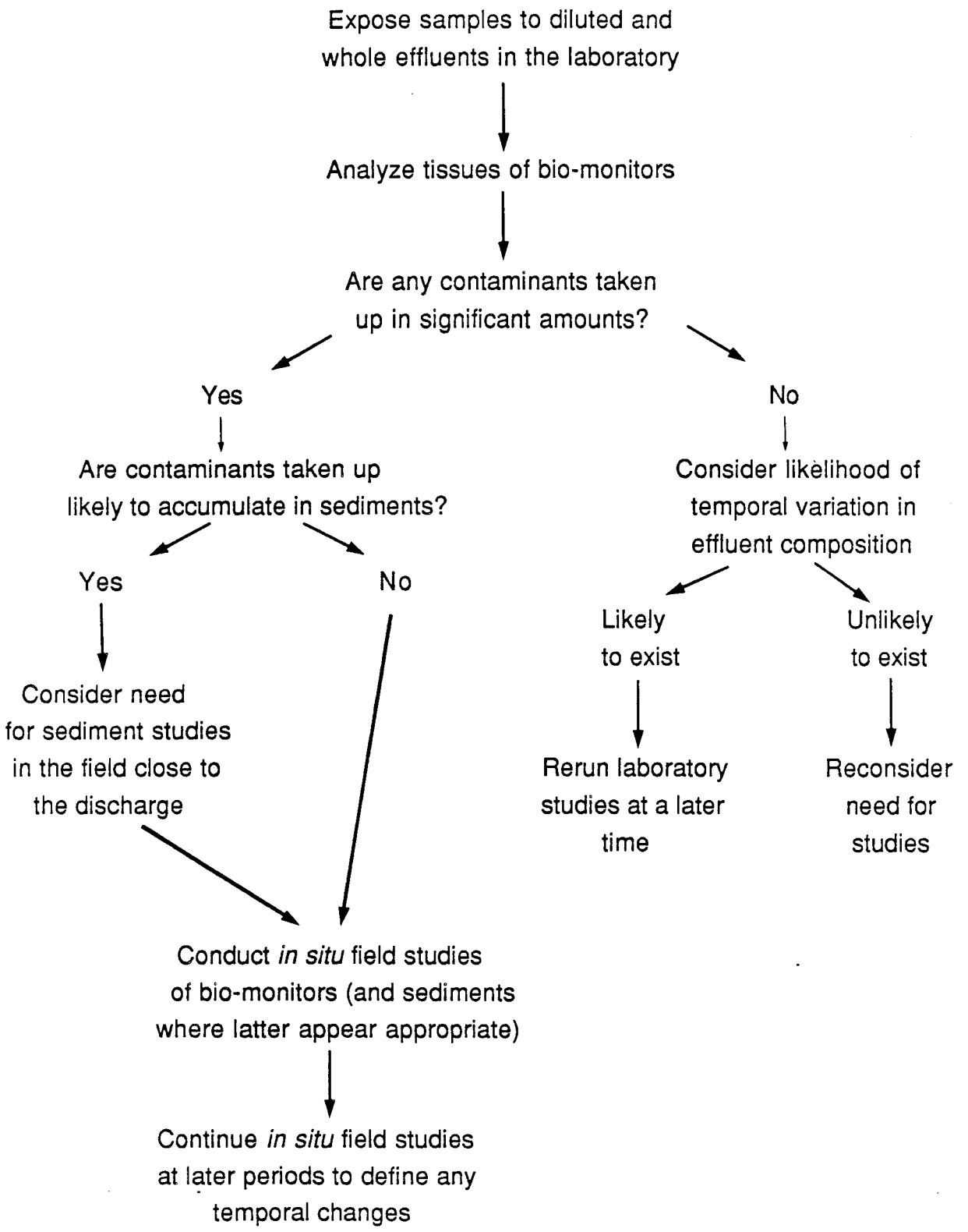
It is proposed that local monitoring studies should be undertaken for all major point discharges in the Bay and Delta, and also for selected non-point discharges in these areas. These studies should be based upon a combination of the laboratory-based bio-monitoring of contaminants in diluted effluents themselves (point sources only) and *in situ* at the discharge location (both point and non-point sources), supplemented in certain cases by the study of sediment contamination. A schematic of the proposed studies is shown in Figure 22.

The local monitoring studies are designed to complement the regional component of the proposed program. Thus, local monitoring will enhance the database provided by the regional program in terms of detail; the following data will be provided:

- Significant sources of bio-available contaminants will be identified, and their individual impacts on local and sub-regional contaminant abundances will be differentiated from each other.

- In particular, the comparative impacts of non-point and point sources on contaminant abundances and bio-availabilities in the estuary will be elucidated.

Figure 22. Design of the laboratory and field components of the proposed local monitoring program.



- Temporal changes in contaminant abundances and bio-availabilities in local areas will be discerned, and these may be related to both sub-regional trends and temporal changes in significant sources.

- The impacts of regulatory intiatives concerning both point sources and non-point sources will be identified.

Laboratory Studies (Point Source Discharges)

It is proposed that the monitoring of point source effluents themselves may be undertaken initially under laboratory conditions. The intention of this is to define:

- The existence or otherwise of contaminants at significant concentration in a bio-available form in point source effluents (and hence, the need or otherwise to conduct *in situ* field studies).

- The identity of those bio-available contaminants (and hence, the specific contaminants which should be monitored during *in situ* field studies).

The laboratory-based work would provide an initial stage in the investigations of the bio-availability of contaminants in effluents from point sources, such that dischargers are not required to initiate studies with full-scale investigations in the field (which are likely to be a significant expense). It is considered (on the basis of very limited data available from previous studies in the field, close to outfalls) that some point source effluents may not contain significant concentrations of bio-available contaminants, at least when the effluents are diluted by receiving waters in a fashion similar to that occurring at their actual discharge locations. In these cases, there is little argument for a requirement for full-scale field studies. In many cases, however, laboratory investigations of bio-accumulation are likely to indicate that significant uptake of particular contaminants does occur; in these cases, field studies would be initiated (see below).

The question of the level at which the uptake of contaminants in laboratory studies would be deemed sufficiently high to require point source dischargers to undertake field studies may be considered. The preliminary recommendation here is that this "trigger point" should be considered to have been attained where contaminant concentrations

are accumulated by bio-monitors (exposed to effluents diluted to match dilution rates at discharge locations) in excess of levels which are detrimental to human health (U.S. FDA, 1984) or levels which are prescribed for predator protection (NAS, 1973); these limits are shown in Table 19. However, as noted elsewhere in this report, these limits both have their drawbacks. The limits for public health (U.S. FDA, 1984) do not include data for most trace metals; this omission could perhaps be dealt with by selecting values for bio-accumulated metals from Nauen (1983). The limits for predator protection (NAS, 1973) were drawn up at a time when the toxicological literature was in its infancy, and require revision based on more recent work. However, such a revision is outside the scope of work for the present report, and the decision as to the magnitude of "trigger points" which would require field-based studies to be undertaken is one for regulatory bodies, rather than for the present report.

The techniques required for laboratory-based studies of contaminant bio-accumulation by bio-monitors are essentially similar to those involved in effluent bioassays, with which major dischargers in the estuary are now familiar. It is proposed that the relevant bio-monitoring species (defined by reference to the species employed at the closest regional monitoring point studied; see sub-section C below) be exposed to both whole effluents and diluted effluents. The degree of dilution of effluents employed in these studies should relate to the initial dilution of the effluent within its Zone of Initial Dilution (ZID) in the field, but studies should also be undertaken at greater and lesser dilutions. For example, if an effluent is diluted by a factor of 10 within its ZID, studies should employ whole effluents, and dilutions of 50%, 80%, 90%, 95%, 99% and 100% (control). It is recommended that dilution water be taken from local receiving waters outside the ZID of the discharge, rather than using reference waters as in the effluent bioassay program. The precise geographical source of dilution waters will vary from case to case, and cannot be covered in detail here. The use of local dilution waters rather than standard reference waters will give rise to laboratory data which are more indicative of the actual bio-accumulation of contaminants in field situations close to the various discharge locations studied.

This requirement for laboratory-based studies of bio-accumulation should take account of the temporal variability of point source effluents, just as the Effluent Toxicity Characterization Program takes account of this factor. It would appear logical to require dischargers to undertake both types of studies in parallel; however, the precise

Table 19. Concentrations of toxic contaminants in tissues of organisms prescribed as recommended guidelines for predator protection (NAS, 1973) or as action levels for the protection of public health (U.S. FDA, 1984). Additional values for trace metals are also shown, and are derived from median international standards for the protection of human health, from Nauen (1983). All data are shown as $\mu g\ g^{-1}$ wet weight of tissues.

Contaminant	Predator protection	Median International Health standard	FDA Action Level
Antimony	-	1.0	-
Arsenic	-	1.4[a]	-
Cadmium	-	0.3	-
Chromium	-	1.0	-
Copper	-	20[b]	-
Lead	-	2.0	-
Mercury	0.5	0.5	1.0[c]
Selenium	-	2.0	-
Zinc	-	45[b]	-
DDT[d]	1.0	-	5.0
PCBs[e]	0.5	-	2.0
Aldrin	0.1[f]	-	0.3
Dieldrin	0.1[f]	-	0.3
Endrin	0.1[f]	-	0.3
Heptachlor	0.1[f]	-	0.3[f]
Heptachlor epoxide	0.1[f]	-	0.1[f]
Hexachlorobenzene	0.1[f]	-	-
Chlordane	0.1[f]	-	0.3
Lindane (ɣ-HCH)	0.1[f]	-	-
Hexachlorocyclohexane	0.1[f]	-	-
Endosulfan	0.1[f]	-	-
Toxaphene	0.1[f]	-	5.0

[a]Refers to arsenic trioxide (equivalent to 1.0 $\mu g\ g^{-1}$ wet weight as the element)
[b]Will be exceeded by samples of Crassostrea gigas, which bio-accumulate copper and zinc heavily
[c]As methylmercury. CDHS employs a health advisory level of 0.5 $\mu g\ g^{-1}$ wet weight in edible tissues
[d]Total of all isomers present
[e]Termed a tolerance, rather than an action level
[f]Individually or in combination

requirements (number of discrete studies, time period covered by each, etc.) are a matter for the regulatory authorities to decide upon.

Such laboratory-based studies cannot be recommended for investigations of the impacts of non-point discharges, as non-point effluents are too variable in quality and quantity with time, and a representative sample is therefore too difficult to obtain. It is therefore recommended that non-point discharges should be studied by field-based investigations only, during periods of significant runoff.

Field Studies (Point and Non-point Discharges)

Where significant bio-accumulation of contaminants (i.e. accumulation above the "trigger point levels selected by the regulatory authorities; see above) is evident from the laboratory-based studies of diluted point source effluents discussed above, and the contaminant source appears sufficiently major to dominate or partially dominate the near-field distributions of particular toxicants of concern in the estuary, field investigations in the vicinity of the discharge site should be carried out. These would also be required for non-point source discharges.

Field investigations would employ the *in situ* use of bio-monitors, and in some instances the use of sediments also. Exhaustive detail obviously cannot be provided here on the precise design of studies around each individual point source outfall in the Bay and Delta. Detailed design work will be required with respect to each outfall to be studied if these investigations are to be undertaken. Such design work would define the study sites in the near-field area by consideration of the outfall location, the toxicants discharged and their loadings (data to be provided by both NPDES self-monitoring results and the results of the laboratory-based bio-accumulation studies), and the local hydrodynamics. The approach for the bio-monitoring studies proposed in the field close to outfalls would be generically similar to that of certain previous investigations of the near-field toxicological impacts of point sources (except that bio-accumulation is measured, rather than any toxic effect *per se*); the studies of Roth *et al.* (1983, 1984), Martin *et al.* (1984a), and Foe and Knight (1985, 1986) are relevant as examples. The last of these studies included investigations of bio-accumulation, and is particularly relevant to the approach proposed here. Field bio-monitoring investigations should be

extended away from outfalls, and should attempt to define gradients in contaminant abundance between the source and the nearest regional monitoring location. The results of these studies (and those of the bio-accumulation of contaminants from effluents in laboratory conditions) may be compared directly to the regional database, as well as to other local investigations and to limits for public health and predator protection (NAS, 1973; U.S. FDA, 1984).

In addition, it is recommended that sediment samples should be taken on transects or suspected gradients between point and non-point outfalls and regional monitoring stations, to be analyzed both for particular contaminants (those likely to accumulate in sediments; see Figure 22) and for toxic impact, the latter through sediment bioassays. The sediment chemistry analyses should include determinations of both grain size distributions and total organic carbon in all samples. The sediment bioassays employed should follow the methodology of Chapman and co-workers (Chapman *et al.*, 1986; Chapman, 1987). At present, the methods of choice would involve the use of the amphipods *Rhepoxynius abronius* and *Ampelisca abdita*. This requirement for sediment studies is not included to provide a comparative database to that from regional studies (no sediment studies are recommended in the latter case, because of the small-scale heterogeneity of sediments; see Long *et al.*, 1988 and section IV of this report). Rather, local investigations of sediments should simply attempt to define gradients in contamination and toxicity away from outfalls, such as those described by Hoffman and Meighan (1984) and Chapman *et al.* (1986) for combined sewage overflow discharges (Islais and Mission Creeks). Such gradients would indicate the degree to which individual (and sometimes multiple) outfalls contribute to the local and sub-regional pattern of sediment contamination in the estuary. The existence of local sediment contamination greater than sub-regional or regional "background levels" (which are themselves spatially variable, and hence difficult to accurately define in the estuary) could be considered as a further "trigger point" by regulatory authorities for the introduction of additional controls.

It should be noted that this local monitoring component of the proposed program has been designed specifically in order to complement the regional studies. Thus, the bio-monitoring portion of the local monitoring proposed is basically an extension of the regional bio-monitoring studies, on effluents themselves and in discrete areas close to known or suspected major sources of contaminants. In this fashion, local bio-monitoring

studies will contribute data which is directly comparable to those from regional investigations, and a cohesive database on the estuary as a whole will be provided.

In addition to extending the regional database, the local bio-monitoring studies proposed here will complement data produced through the existing Effluent Toxicity Characterization Program, being conducted through the San Francisco Regional Water Quality Control Board (SFRWQCB, 1987). Thus, the results of local studies on the bio-accumulation of contaminants by bio-monitors exposed to diluted and undiluted point source effluents will provide information on the possible causes of any observed toxic impacts of those effluents. This will be of particular benefit as an adjunct to toxicity reduction evaluations, where the latter are required as part of the effluent bioassay program studies.

The proposed regional and local components of the overall monitoring program will thus provide a cohesive and inter-relative database on spatial and temporal trends in the abundance, distributions and bio-availabilities of toxic contaminants throughout the estuary and its catchment. This database will delineate both spatial and temporal trends in contaminant abundance in the estuary, and will define the relative importance of various toxicant sources in the Bay and Delta.

B. Selection of Study Sites

Regional Monitoring

General considerations

The regional monitoring component of the proposed program seeks to define the "background" or "reference" abundance and distributions of toxic contaminants in the estuary and its catchment, and the changes in these with time. These would be employed both to provide reference data for local monitoring investigations, and to indicate the general level of contamination of the estuary as a whole. Such "background" levels of contamination are an integrated function of the toxicant loading from various sources and the dilution and dispersion characteristics of the estuary, the latter being defined principally by the hydraulics of the Bay and Delta. Although the presently available information on the distributions of toxicants in the estuary is not sufficient to fully delineate sites of "background" contaminant abundance, these are likely to be situated in areas of high flows (i.e. where contaminants are highly diluted and dispersed), distant from point sources. In most parts of the estuary, this equates to their location in the main water channels. However, the program proposed does not rely upon regional monitoring being necessarily reflective of "background" conditions in the estuary; rather, the use of the same techniques in both the regional and local components of the program will provide comparative data on both the channels and shallows in the estuary, and complete coverage of the Bay and Delta should result. In many instances, it is likely that the bio-monitoring data will indicate that no true "background" condition exists in the estuary for contaminants, but that concentrations of bio-available toxicants vary in a "complex mosaic" (Luoma and Phillips, 1988).

In the upstream freshwater catchment, hydraulic movements are rather simpler, at least in areas upstream of the tidal influence. The intention in this area would be to compare data from upstream and downstream segments of various sub-catchments (i.e., various rivers and streams draining to the Delta through the Sacramento and San Joaquin systems), to define toxicant sources between the sampling points employed. Studies of mercury distributions in the Central Valley (using sediments and fish; see CVRWQCB, 1987) and certain of the Toxic Substances Monitoring Program

investigations (see section IV of this report) have employed similar approaches to this in the past.

There is a clear benefit to the selection of study locations in the Bay and Delta which have been previously investigated, particularly if the historical studies have employed similar methods to those proposed here. However, previous studies of the regional abundance of toxicants in waters themselves downstream of the Delta (see section IV of this report for review) have varied widely with respect to the sampling locations employed, each author using different locations. With respect to any selection of study locations, therefore, the design of the investigations proposed here on toxicants in water is not constrained by previous work in the Bay. In the upstream areas, a long-term database exists for trace metals in water at sites at Sacramento and Vernalis; both the Department of Water Resources and the U.S. Geological Survey have undertaken monitoring in these locations. This is taken into account in the proposals discussed below.

Contaminants in bio-monitors have been quantified at a number of locations in the Bay in routine monitoring programs. Those employed at various times by the State Mussel Watch Program are tabulated in Tables 9 and 10 in section IV of the present report. As noted in that section, some of these locations may be considered to represent sites of "background" contaminant abundance (i.e. close to main channels, and distant from most point or other sources of contaminants), whereas others are clearly impacted by local sources of toxicants. Where sites exist in areas which are likely to reflect background levels of contaminants, these have been retained for the program proposed here.

Data from the Toxic Substances Monitoring Program have also defined areas of elevated local abundance of certain contaminants upstream of the Delta, and regions of "background" levels. A complete review of these data is outside the scope of this report, which concentrates specifically on the Bay and Delta regions, and provides proposals for sampling locations within those areas. It is recommended that the data from the TSMP investigations in areas of the Central Valley catchment upstream of the accepted limits of the Delta be comprehensively reviewed prior to any decisions on the siting of sampling locations to be employed in either regional or local studies of the type proposed here. Although study sites for these upstream areas are not identified as part of this report, it is nevertheless envisaged that the monitoring proposed here should be adopted in such

areas. Only in this fashion will a cohesive database relating contaminant levels in all parts of the estuary and its catchment be established.

Proposed study sites

The study sites proposed for regional investigations of toxic contaminants in the Bay (downstream of the Sacramento River/San Joaquin River confluence) could be selcted by a variety of means. Because the sites to be selected are supposed to reflect "background" conditions, the most important parameters which could define the locations of such study sites might be considered to be the existence of significant contaminant sources, and the hydraulics of the Bay. Thus, there would be an argument for siting greater numbers of stations in areas where sources are numerous (implying that contaminant concentrations may alter over short distances), and/or where currents are poor (implying that flushing is slow, and significant gradients in contamination may exist over small distances). However, it is felt that too little is known of existing contaminant gradients in the estuary to permit such sophistications. As a result, the locations proposed herein for regional monitoring of contaminants have been selected to simply cover the Bay in reasonable detail, to take account of previous studies, to avoid the majority of known contaminant sources, and to be approximately equidistant from each other.

The locations proposed for the study of toxic contaminants in the Bay (and just outside the Bay, in the Gulf of the Farallones) are shown in Figure 23; detailed location descriptions are provided in Table 20. In total, 28 sites are proposed for these studies, all close to or within channels. These sites would be employed for investigations of both toxicants in water (to ascertain compliance with water quality objectives) and contaminants in bio-monitors. Adjacent sites are approximately equi-distant from each other throughout the estuary, and all locations are in deep well-flushed regions of the estuary, distant from most point sources. Sites outside the Bay, in the area of the Gulf of the Farallones and further afield in California (not all shown on Figure 23; many are already studied by the SMWP), will provide "reference data" and will also indicate any impacts of toxicants derived from the Bay on the offshore waters of the Pacific. Of the sites proposed, a few have been employed previously by State Mussel Watch investigations, but most are new. The sites proposed are preferred to those employed in the current SMWP studies because they are more distant from the Bay margins, and more likely to reflect "background" conditions. It should be noted, however, that the

Figure 23. Sampling locations for the regional component of the monitoring studies proposed on toxic contaminants in the San Francisco Bay.

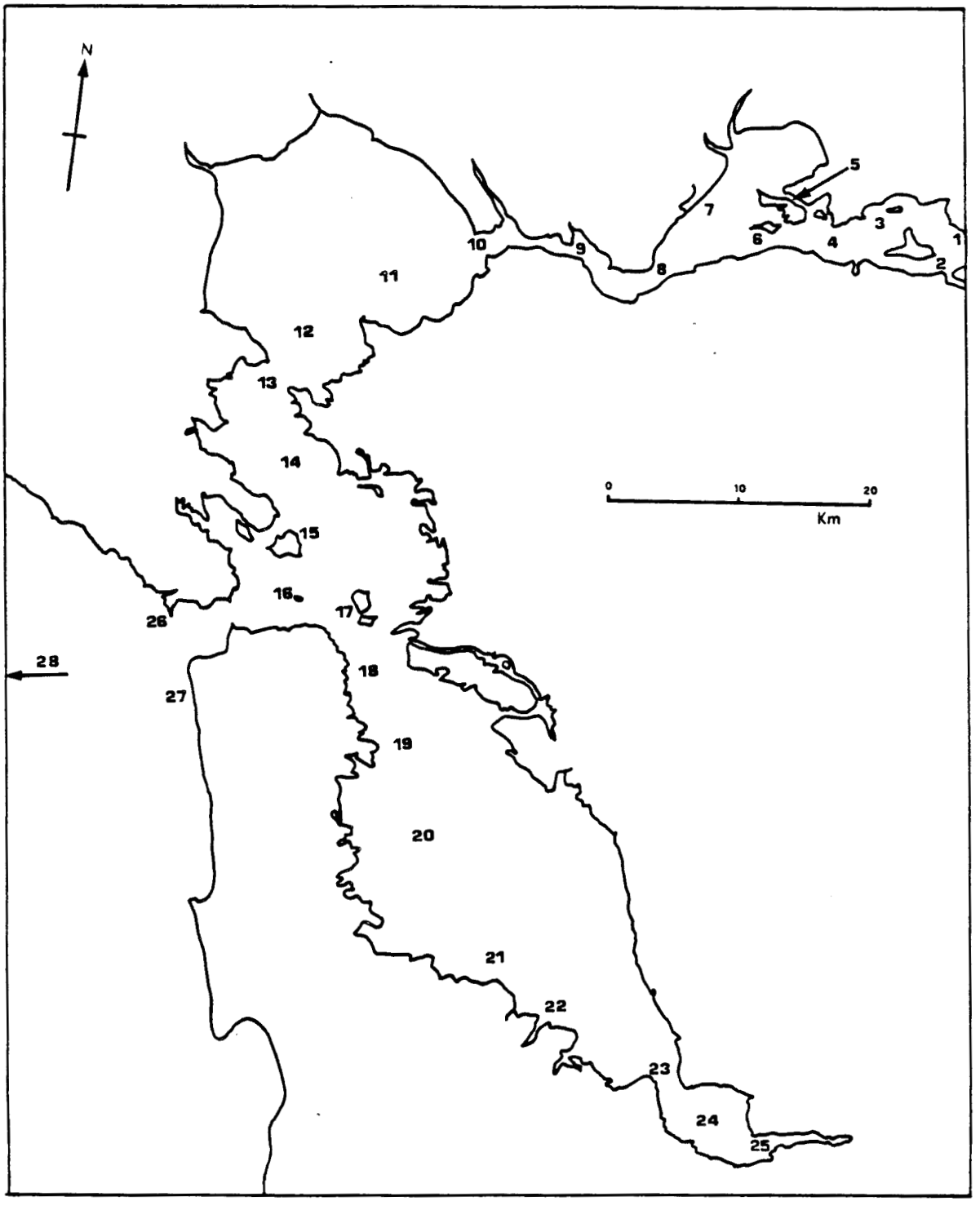


Table 20. Study sites proposed for investigations of toxic contaminants in water and bio-monitors in San Francisco Bay. Contaminants in water would be studied at all locations. For details of bio-monitor studies, see section VII C below.

Site	Location description
1	Lower Sacramento River, north of Sherman Island
2	East of Point Beenar, Winter Island
3	In channel between Van Sickle Island and Winter Island
4	South of Chipps Island, mid-channel
5	North of Ryer Island, mid-channel
6	Roe Island Channel
7	Due west of Roe Island, mid-channel
8	South of Benicia, mid-channel
9	South of Southampton Bay, mid-channel
10	South of Naval Anchorage #21, mid-channel
11	Pinole Shoal, south of main channel
12	North-west of Pinole Point
13	West of Point San Pablo (the Brothers)
14	Red Rock
15	East Angel Island
16	Alcatraz
17	West Treasure Island
18	East of Mission Rock Terminal, in channel
19	East of Hunter's Point, mid-channel
20	San Bruno Shoal
21	San Mateo Bridge, mid-channel
22	Channel due east of Redwood Creek
23	Dumbarton Bridge, mid-channel
24	North-east of Palo Alto, mid-channel
25	Coyote Creek channel
26	Point Bonita
27	Point Lobos
28	Farallon Islands

selection of such locations implies certain practical difficulties with transplantation in areas of high currents; these can be overcome by the redesign of transplantation equipment.

Study sites proposed for regional investigations of toxicants in the Delta are shown in Figure 24; location descriptions are provided in Table 21. In total, 14 sites are proposed for regional monitoring in the Delta. As in the studies proposed for the Bay, it is envisaged that both toxicants in water and contaminants in bio-monitors (*Corbicula fluminea*; see section VII C below) would be characterized at each of these locations. As noted above, these will be supplemented by additional sites in the upstream area of the Central Valley catchment, outside the accepted limits of the Delta (locations to be determined through a review of data from the TSMP studies over the last decade). All of the regional sites in the Delta will be impacted to some extent by upstream sources of contaminants (which would be defined by the upstream programs of study). Data from these locations in the Delta will of course be responsive to local contaminant sources where such exist, but will principally reflect the changes in contaminant abundance and bio-availability as the various upstream freshwater sources mix with each other *en route* to the Delta and the Bay.

Local Monitoring

As noted in section V of this report, it is proposed that all point source discharges of significant size in the estuary (numbering about 200 in the Bay, and a further 50 in the Delta) and selected non-point sources (the number to be defined by the relevant regulatory authorities) should undertake local studies of contaminants as part of the presently proposed program. This would provide an extensive database on contaminant abundance and bio-availability at the margins of the Bay, which would greatly amplify the data provided in the regional monitoring program, and relate conditions in the channels to those in the shallows of the Bay. An idea of the coverage which would result is provided by consideration of the distribution of major point source discharges in the Bay, shown in Figures 25 and 26; it should be noted that these Figures only show the sites of the largest point sources, and do not indicate smaller point sources or non-pont source locations. In the Delta, local monitoring investigations would serve to provide data for the river reaches between the regional sites of study.

Figure 24. Sampling locations for the regional component of the monitoring studies proposed on toxic contaminants in the San Francisco Delta.

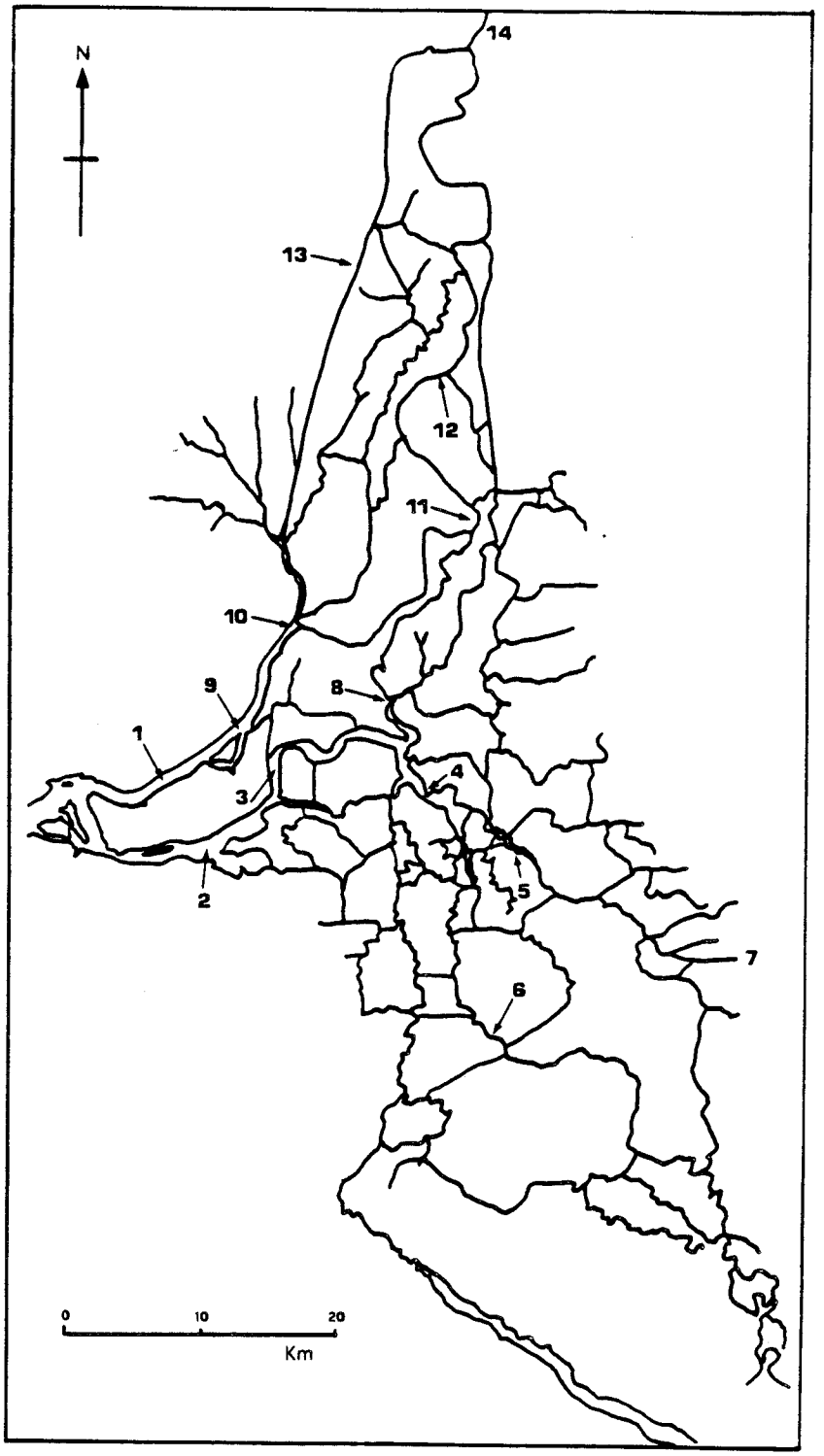


Table 21. Study sites proposed for investigations of toxic contaminants in water and bio-monitors in the San Francisco Delta. All sites would be studied for contaminants in water (see text) and in transplanted Asiatic clams, *Corbicula fluminea* (see sub-section C below).

Site	Location description
1	Toland Landing, Lower Sacramento River
2	West of Blind Point
3	West of Bradford Island
4	Prisoners Point, Venice Island
5	Medford Island
6	Mildred Island/Middle River
7	Stockton
8	Rancho Harbor, Mokelumne River
9	North of Decker Island
10	North of Rio Vista
11	Walnut Grove
12	Greens Landing
13	Sacramento Ship Channel
14	Sacramento

Figure 25. Distribution of the major municipal discharges to San Francisco Bay, and their magnitudes. After BCDC (1987).

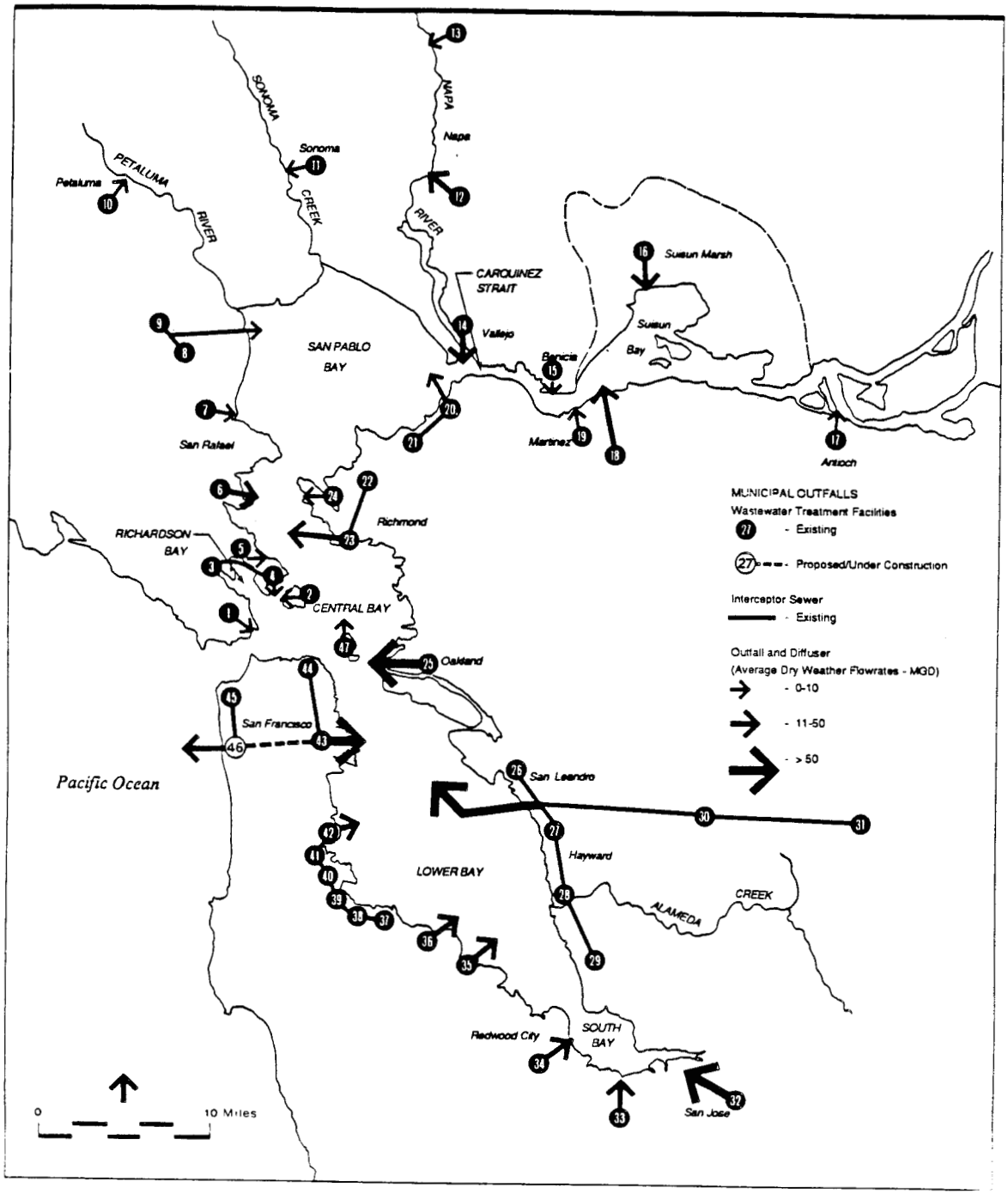
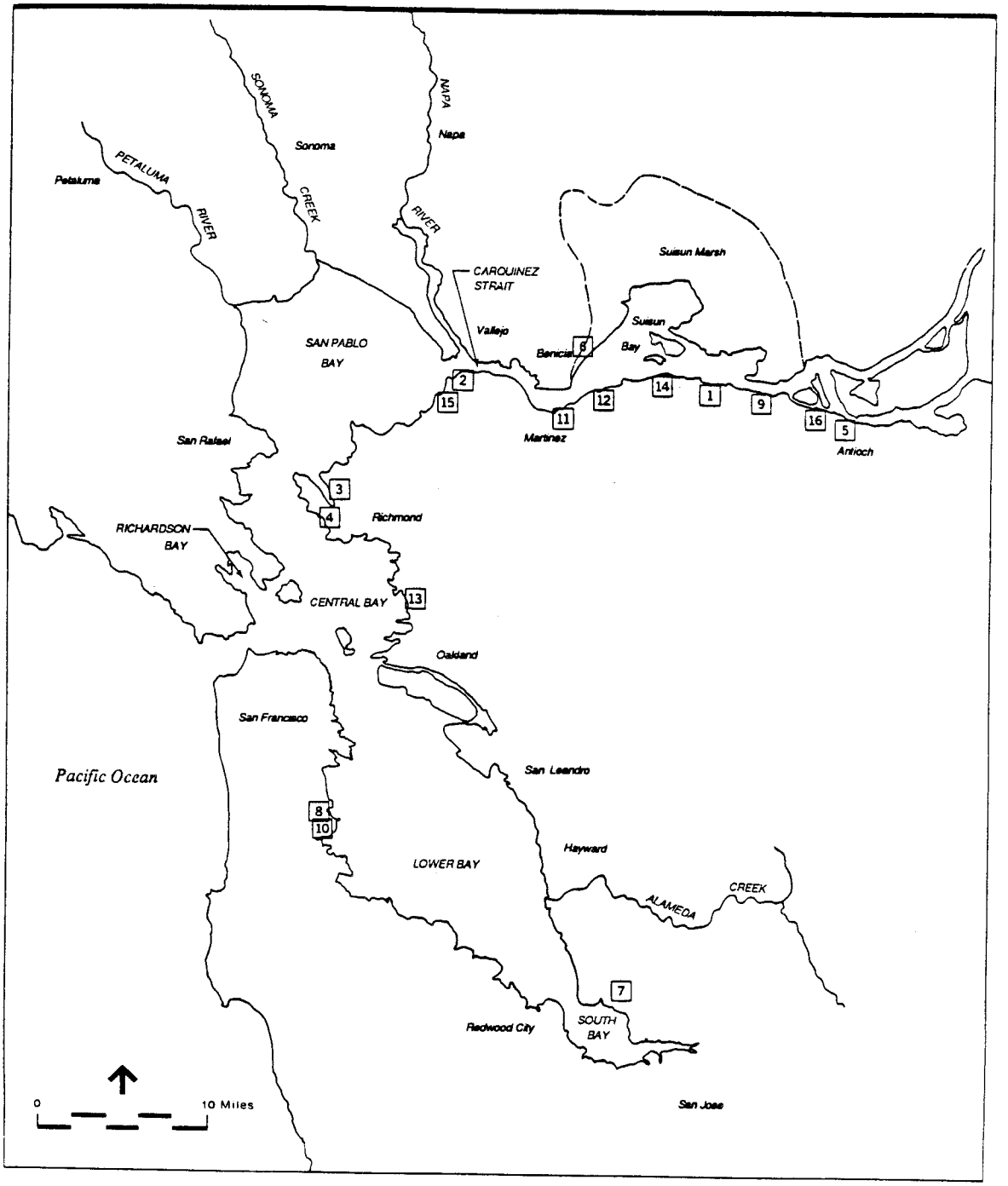


Figure 26. Distribution of the major industrial discharges to San Francisco Bay. After BCDC (1987).



C. Species to be Employed in Bio-monitoring Studies

The use of bio-monitoring techniques in the San Francisco Bay and Delta demands a multi-species approach if the entire estuary is to be studied. This is because no one species suitable for use as a bio-monitor exhibits the required distribution throughout the estuary, principally because of the salinity range encountered in the system (see footnote 2).

While macroalgae have been proposed recently as of possible use as bio-monitors in the Bay (Josselyn and Philips, 1988), the lack of previous studies on contaminants in these species locally suggests that their use should be regarded as developmental in the estuary, rather than suitable for a routine program of the magnitude described here. There is also an argument for research on the use of barnacle species as bio-monitors in the estuary (see section II of this report and sub-section H below), but this too is considered developmental in nature at present. There can be little argument that bivalve molluscs are the most appropriate bio-monitors for the routine monitoring of contaminants in the Bay and Delta, for both regional and local studies. Both the existence of a substantial historical database for contaminant levels in bivalves locally (on *Mytilus californianus* in particular; see Phillips, 1988) and the fact that these species conform particularly well to the requirements for a bio-monitor (see section II of this report) argue that bivalves must be the organism of choice for such programs. It is proposed that all bivalves employed in both regional and local bio-monitoring studies of toxicants in the estuary be transplanted into required study locations in the field. This is the same technique as that employed currently in the State Mussel Watch Program, and

Footnote 2. Recent regional monitoring studies and other investigations of benthic infauna in the Bay and Delta by staff of the U.S. Geological Survey (L.E. Schemel, F.H. Nichols) have noted the invasion (in 1987) of a new species of clam. This species has tentatively been identified as *Potamocorbula* sp., and is thought to have been brought into the estuary (probably in the ballast water of vessels) from the People's Republic of China. The new species has spread dramatically from its first area of occurrence in the northern reach of the estuary (deep waters of San Pablo Bay), and is now dominant in benthic infaunal communities throughout most of the estuary, apparently out-competing other species (L.E. Schemel, personal communication). It therefore appears to possess a considerable insensitivity to salinity, although no direct studies of its tolerance to salinity have been undertaken to date. Because of its salinity tolerance, this species may be considered a prime candidate for use as a bio-monitor in the estuary. However, nothing is known of its uptake of contaminants. It is recommended that studies to investigate the contaminant concentrations in this clam species be funded as a matter of high priority; even if *Potamocorbula* sp. is not found to be a useful bio-monitoring species, its emerging dominance in benthic infauna of the estuary is important with respect to the food-chain transfer of contaminants.

has been well-tested. The use of transplants rather than native animals has various advantages (independence of native population distributions; ability to transplant to any site and water depth; ability to define rates of uptake of contaminants in certain cases; see Young *et al.*, 1976; NAS, 1980; Phillips, 1980; Ritz *et al.*, 1982).

As recognized by State Mussel Watch Program studies, and recently confirmed by CDF&G (1988), neither transplanted *Mytilus californianus* nor native *M. edulis* survive well in the estuary upstream of the Carquinez Strait. This is due to the salinity sensitivities of these two species of mussels; the lowest salinity which can be tolerated for long periods is about 5‰, and fluctuations in salinity above this range can also be stressful to these species (e.g. see Bayne *et al.*, 1976). It is proposed here that *M. californianus* should be employed downstream of the western end of the Carquinez Strait for all regional and local bio-monitoring studies, effectively expanding and strengthening the database from the present State Mussel Watch Program investigations. However, in the extreme southern portion of South Bay, neither *M. edulis* nor *M. californianus* survive well over extended periods (M. Martin, personal communication). Problems of mortalities may therefore be encountered in this area, were these species to be employed exclusively in this location. In addition, the area close to the southern terminus of South Bay (near Coyote Creek) exhibits transient low salinities in periods of high runoff, compounding the stresses to such mussels. It is therefore recommended that both *M. californianus* and the oyster *Crassostrea gigas* be employed at locations 23, 24 and 25 (see Figure 23) of the regional studies. Any local monitoring studies in this area of the estuary should also be cognisant of this problem, and should be prepared to employ both species.

Upstream of the western end of the Carquinez Strait, salinities are particularly temporally variable, depending on Delta outflow rates. Low salinities can be encountered throughout the lower Delta and Suisun Bay, although the precise salinity regimes vary from year to year, depending on precipitation and runoff patterns. It is proposed that this area of the estuary should be studied employing clams (*Corbicula fluminea*) in the fresh and brackish waters of the upper estuary and the Delta, and both *Corbicula fluminea* and Pacific oysters (*Crassostrea gigas*) in the region between the lower Delta and the western end of the Carquinez Strait. *Corbicula fluminea* is tolerant of salinities in the range from 0 to at least 3‰ and possibly as great as 10‰ (Foe and Knight, 1986; S.N. Luoma, personal communication), and *Crassostrea gigas* will tolerate

salinities from about 2‰ to greater than 35‰; thus these two species can be employed to characterize all waters of the lower Delta and upper estuary (down to the western end of the Carquinez Strait). This is effectively the approach taken by the recent investigations of selenium in the Bay and Delta by CDF&G (1988), and permits the entire estuary to be studied employing three species of bivalves.

Theoretically, both the timing of transplantation/sampling of bio-monitors and the species to be employed at the northernmost and southernmost stations in the estuary should be selected on the basis of a knowledge of the hydrograph (i.e. the salinity distribution through the estuary for the period of transplantation). However, it is not possible to predict the salinity distribution through the estuary over the transplantation period in advance of the actual transplantation of the bio-monitoring samples. It is recommended that this problem be overcome by the pre-selection of times for transplantation and sampling based on previous experience of the hydrograph (see section D below), and by the transplantation of species of different salinity sensitivity into regions which exhibit large variations in ambient salinities. Thus, both *M. californianus* and *Crassostrea gigas* should be employed at the southern terminus of South Bay (stations 23, 24, and 25; see above), and both *Corbicula fluminea* and *Crassostrea gigas* should be employed between the lower Delta and the western end of the Carquinez Strait. At least one of these species will be likely to survive the transplantation period, whatever the salinity conditions. Where more than one species survives at any given location, both should be analyzed for accumulated contaminants, as the resulting data will be of use in interpreting the bio-accumulation data produced, and in comparing the species' response at other locations. The use of such "overlap samples" has been recommended elsewhere when multi-species programs are undertaken (NAS, 1980; Phillips and Segar, 1986).

Local bio-monitoring studies of both point and non-point effluents themselves and of the near-field distribution of contaminants around specific outfalls should employ the same (one or two) species as used in the closest regional monitoring site to the discharge. For laboratory studies of the bioaccumulation of contaminants using whole or partially diluted effluents, salinity adjustment of test solutions will be required in certain cases (for effluents of a low salinity discharged to a marine portion of the estuary, west of the Carquinez Strait), to permit the survival of the mussels used as bio-monitors. [Instances of high-salinity waters being discharged to very low-salinity receiving waters are not known, so the inverse problem does not appear to arise].

In such cases, it is proposed that the salinities of the effluents or diluted effluents should be adjusted upwards to 8‰, to permit the survival of *M. californianus* (which will be the bio-monitor of choice in these areas). This salinity adjustment may be achieved through the use of concentrated brine solutions, such as those available through the effluent bioassay program being conducted through the San Francisco Regional Water Quality Control Board. Salinity adjustments should only be carried out in cases where this is necessary to ensure the survival of the bio-monitor employed, as this adjustment will interfere with the uptake kinetics of certain contaminants such as cadmium (Phillips, 1979a, 1980). It is important to avoid such effects as far as possible if the real extents of contaminant bio-accumulation from effluents are to be gauged through the laboratory-based studies. In most cases, such adjustments should be required only for studies on whole (undiluted) effluents, as dilution using local receiving waters should give rise to acceptable salinities (i.e. 8‰ or greater) in test solutions of diluted effluents. In field studies close to discharges, it is likely that initial dilutions experienced by fresh effluents at their discharge will be sufficient to increase salinities close to outfalls to permit the survival of the bio-monitor employed. In local studies of effluents discharged to the southern terminus of South Bay, both *M. californianus* and *Crassostrea gigas* should be employed. Test solutions for laboratory-based studies of point source effluents using *C. gigas* should be salted-up to a salinity of 5‰ in a similar fashion to that proposed for studies of *M. californianus*.

Adherence to this methodology will ensure that all data from local studies may be related to those from the regional investigations, thus providing an integrated picture of the impacts of point sources of contaminants on both local and regional scales.

D. Sampling Details

General Timing of Sampling

Decisions as to the most appropriate timing of sampling for bio-monitoring and other studies must take account of several factors, as follows:

- Seasonal fluctuations in receiving water concentrations of contaminants: Although supporting data are generally too sparse to confirm the existence of seasonal trends in contaminant concentrations in receiving waters of the Bay and Delta (see section IV of this report), theoretical considerations suggest that such trends are likely to exist. In periods of high runoff, toxicants derived from the upper catchment (pesticides, certain of the trace metals) will be more efficiently washed down into the Delta and the Bay. This may dominate contaminant profiles in the estuary, at least in instances where upstream sources predominate over within-Bay sources of any particular toxicant (e.g. see copper profiles in Eaton, 1979a). Even where within-Bay sources of contaminants predominate over riverine inputs (e.g. silver, derived principally from certain of the point source inputs in the South Bay; see review by Phillips, 1987), changes in Delta inflow rates may give rise to seasonal fluctuations in abundances and/or bio-availabilities of such contaminants, through their effects on flushing rates in the Bay (see silver profiles in Luoma *et al.*, 1985). Alterations in toxicant loading from various sources within the Bay may also occur with time, and these too may cause seasonal fluctuations in contaminant levels in local or regional receiving waters, sediments or biota (e.g. data for copper in Luoma *et al.*, 1985).

- Temporal fluctuations in contaminant concentrations in bio-monitors: Contaminant concentrations in bio-monitors will also vary with time because of biological factors; this variation will be superimposed upon any seasonal fluctuations due to changes in contaminant loading to the estuary. The gametogenesis/spawning cycle of the bio-monitors employed is of particular importance, as the kinetics of many contaminants are affected by this reproductive cycle. Trace element levels in some populations of bivalves tend to be greatest following spawning, as these often vary inversely with the weights of whole soft parts of the individual organism (Simpson, 1979; NAS, 1980; Phillips, 1980; Luoma *et al.*, 1985). By contrast, synthetic organic contaminants

(which generally exhibit a highly lipophilic character) are often most concentrated in bivalves prior to spawning, as lipid levels are generally greatest at this time (NAS, 1980; Phillips, 1980, 1986). However, seasonality of contaminants in bio-monitors is a complex topic, and factors other than body weight play a part in many populations (see Phillips, 1980). It has been concluded that no universally acceptable period exists for sampling of bio-monitors, and that each case should be treated on its individual circumstances (NAS, 1980).

Relatively little is known of the local seasonal changes in contaminant levels of the bio-monitors proposed for use in this report in the San Francisco Estuary. Foe and Knight (1986) found that copper and zinc levels in *Corbicula fluminea* increased during summer in the Delta (perhaps due to changes in soft tissue weights; S.N. Luoma, personal communication), but these changes were not dramatic. Luoma and Cloern (1982) and Luoma *et al.* (1985) consistently observed winter maxima in the concentrations of several metals in clams (*Macoma balthica*) from the South Bay, although it is not known whether this pattern would also be reflected by *M. californianus*. It is probable that seasonal changes in contaminant levels in the bio-monitors proposed for use would vary at different sites in the estuary, depending on local factors.

Any sampling regime selected as the basis for studies of contaminants in either water or bio-monitors in the estuary should attempt to characterize both the average levels of contamination and the extremes in toxicant abundance, as both of these are of relevance toxicologically (and therefore in a regulatory sense). The lack of reliable information on the effects of freshwater inflows and other factors on contaminant abundance and bio-availabilities in the estuary eliminates the possibility of selecting "worst case" scenarios for monitoring (e.g. wet season only, or dry season only). Given the probable importance of freshwater inflow rates in affecting both contaminant loading and flushing in the estuary, the most appropriate monitoring approach for regional monitoring programs is suggested to involve discrete studies in the seasons of high and low runoff.

It is therefore recommended that regional monitoring for toxicants in both receiving waters of the estuary and bio-monitors should rely upon two discrete sampling periods in any year of study. These should reflect times of high runoff and low runoff. As noted previously, the hydrograph cannot be predicted in advance of transplantation of the bio-monitors employed; thus, past experience must be used to define the most

appropriate periods to characterize high and low runoff conditions in the estuary. Examination of average Delta inflow patterns suggests that the most appropriate study periods would be between 01 January and 01 April (high runoff) and between 01 July and 01 October (low runoff). Consideration of the biological aspects of the bio-monitors employed (spawning cycles and associated tissue weight fluctuations, lipid changes, etc.) suggests that these two periods may provide distinct data, useful for comparative purposes. Local monitoring investigations should also be undertaken at these two periods, providing data relevant not only to temporal changes in discharges themselves, but also to fluctuations in receiving water quality (which may have important effects on the bio-availabilities of discharged contaminants).

Sampling Frequencies and Time-bulking Needs

Sampling frequencies in monitoring programs should be defined by a consideration of the degree of variability within the monitored component of the system, coupled to decisions on the required accuracy of characterization of the mean values recorded. In most cases, however, existing data do not permit a complete assessment of variability of the monitored component, and programs are constrained by funding or other factors to given levels of effort.

This is effectively the case in the monitoring of contaminants in the San Francisco Estuary; previous data do not provide an adequate characterization of the temporal or spatial variability in contaminants within the system (in any medium), and funding is undoubtedly a significant constraint. The present report could legitimately propose the establishment of pilot studies to ascertain required levels of effort for monitoring programs based upon the variance encountered in contaminant concentrations in water and bio-monitors. However, it is considered that the funding agencies would prefer specific recommendations from this report.

It is proposed that regional studies of contaminants in water should be based upon monthly observations. This periodicity has been selected because many of the existing programs (monitoring of water quality parameters, fisheries, etc.) are also based upon monthly observations, and there is a clear benefit to the extension of such a database to contaminant-associated parameters. In addition, it is to be hoped that research vessels may be shared by the various study programs, thus reducing costs. The sampling of receiving waters for contaminant analysis at each of the regional monitoring

locations (Figures 23 and 24) should occur each month over the two seasonal phases of the monitoring program, providing a total of eight samples at each site in any one year (all samples taken on the first day of each month; total of eight cruises).

It is notable here that the sampling of receiving waters would most appropriately involve the collection of time-integrated samples, to smooth out short-term fluctuations and match sampling to the majority of the water quality objectives in the Basin Plan (based upon one-hour, one-day or four-day averages mostly; see SFRWQCB, 1986). This implies the deployment of time-integrating water samplers and their later collection, which is expensive in terms of staff and vessel time. This aspect of the program should be further considered by the regulatory agencies (against a background knowledge of the precise sampling regime to be employed), and every effort should be made to collect time-integrated samples rather than grab samples if possible. In this connection, it is notable that researchers at the Moss Landing Institute have developed a time-integrated water sampler which is very considerably less expensive than commercial versions (M. Stephenson, personal communication).

Bio-monitors provide a time-averaged value of contaminant bio-availability at a given location, as noted in section II of the present report. The degree of this time-averaging varies according to the kinetics of the toxicant in the species employed. Trace metals are generally taken up relatively slowly, and transplanted bio-monitors may take weeks or even months to equilibrate to new conditions in the field. State Mussel Watch Program studies have employed periods of about 3-4 months between transplantation and sampling. It is proposed here that the three-month periods recommended above (01 January to 01 April, and 01 July to 01 October) for monitoring studies are appropriate for trace metal investigations in the bio-monitors selected for monitoring in the estuary. Thus, bivalve samples for trace metal analysis should be transplanted into each location on 01 January and 01 July each year, and collected for analysis three months later.

However, this program of sampling will not permit the accurate characterization of the average bio-availabilities of contaminants of rapid kinetics in bio-monitors (most synthetic organic contaminants and hydrocarbons). As noted by Phillips and Segar (1986), such contaminants may best be studied using "time-bulking" techniques, which artificially increase the time-averaging capacity displayed by the bio-monitor employed. It is therefore recommended that three discrete samples of bio-monitors to be analyzed for organic contaminants should be transplanted into each study site at the outset of each

monitoring period (01 January and 01 July), and one sample should be recovered from each site on each of the three successive months (i.e. at one, two and three months after transplantation). These three samples may be analyzed separately (if funds permit), to provide a time series of data for contaminants of short half-life in bio-monitors at each study site. Alternatively, all three samples from each site may be composited and analyzed as a single sample, which would characterize the average ambient bio-availabilities of organic toxicants much more closely than a single sample taken for analysis after a three-month period subsequent to transplantation.

It should be noted that this design of sampling matches the frequency of studies of contaminants in water (monthly samples over three months at each site) to the needs for collection of bio-monitors at each site for the analysis of organic contaminants. Thus, all sites are visited for multiple purposes on all occasions. If such a program (presumably to be undertaken by the California Department of Fish & Game, who undertake the current State Mussel Watch Program studies and possess the necessary expertise for all sampling proposed here) could be "married" to existing cruises providing data on fisheries in the estuary, sampling costs would be dramatically reduced.

Studies of the local abundance and distributions of contaminants in near-field areas close to discharges in the Bay and Delta should be undertaken at precisely the same periods, using the same sampling methods and timing, as those proposed for regional investigations. Only in this fashion may truly intercomparative data be provided by both local and regional investigations. Clearly, considerable savings would accrue through the coordinated provision of bio-monitoring species to be transplanted into regional and local sites. All samples of each individual species should be derived from the same location of origin, selected because of its low level of natural contamination. The most appropriate locations from which to derive transplants may be selected based upon the results to date of the State Mussel Watch (and perhaps other) studies. For *Corbicula fluminea*, the San Antonio Reservoir may be an appropriate location (M. Martin, personal communication). Pacific oysters (*Crassostrea gigas*) may best be derived from Humboldt Bay (see CDF&G, 1988). Mussels (*Mytilus californianus*) should be derived from Bodega Head, as in most of the present State Mussel Watch investigations.

E. Contaminants to be Analyzed

The principal reason for the collection and analysis of samples of receiving waters in regional monitoring studies as proposed here is to investigate compliance with water quality objectives in the Basin Plan for the estuary (SFRWQCB, 1986). It is therefore recommended that those contaminants for which objectives are listed in the Basin Plan (or are pending for inclusion in the Plan) be included for analysis in these samples. This includes the following: arsenic; cadmium; chromium (VI); copper; cyanide; lead; mercury; nickel; selenium; silver; tributyl tin; zinc; and total PAHs. As noted in section IV of this report, the attempted quantification of organic contaminants other than total PAHs in receiving waters is not recommended.

Section III of the present report (Table 7, page 50) provides a list of "toxic contaminants of greatest concern" in the San Francisco Bay and Delta, generated by the author and Dr. Robert Spies of the Lawrence Livermore National Laboratory (as part of efforts required in the characterization phase of the San Francisco Estuary Project of the EPA National Estuary Program). As noted in that section, this list of high-priority contaminants in the estuary should not be considered fixed, but should be amended periodically as additional data become available.

It is recommended that all contaminants listed in Table 7 other than malathion, parathion, the MAHs and cycloalkanes should be quantified in all regional and local samples of bio-monitors employed in the monitoring program proposed herein. It is likely that malathion, parathion, and the MAHs and cycloalkanes will be rarely (if ever) encountered in significant quantities in bio-monitors, as these compounds are not highly bio-accumulative in nature. Their inclusion for analysis in bio-monitoring samples is not therefore considered to be warranted.

F. Sample Collection; Compositing; Archival; QA/QC

The scope of work covering the production and contents of the present report does not require the inclusion of exhaustive comments on matters such as sample collection, compositing, archiving, or analytical quality assurance and quality control. However, these topics are important, and brief comments are included here as a result.

As noted in section II of this report, the analysis of receiving waters for trace contaminants such as metals requires strict adherence to particular collection and analytical procedures which guarantee the absence of extraneous contamination of samples. Such methods are now well-developed; non-contaminating water samplers are available, and the requirements in terms of "clean laboratory" facilities have been extensively documented. The methods employed by authors such as Gordon (1980) and Stukas (1986) are considered to be excellent examples of this type of monitoring.

Several authors have considered needs for the compositing of samples in bio-monitoring programs (e.g. Gordon *et al.*, 1980; Boyden and Phillips, 1981; Wright *et al.*, 1985; EPA, 1987c). The use of power analysis techniques, as recommended by EPA (1987c) is particularly appropriate in the design of this aspect of monitoring programs. Decisions from the regulatory and management communities are required in terms of their needs for the differentiation of contaminant levels between sites or with time at any one site. Thus for example, should the program strive to identify differences in the concentrations of contaminants in bio-monitors from separate sites of 20%, 50%, 100%, or some other factor; should temporal changes of these or other magnitudes be detected at individual sites by the monitoring program? Only on the basis of these managerial decisions can the detailed sampling strategy (numbers of individuals required at each location; scheme for compositing samples) be designed to most efficiently and cost-effectively meet the required objectives.

The archival of bio-monitoring samples has been recommended by several authors (e.g. NAS, 1980) as a basis for the later analysis of samples for contaminants (which may or may not be currently monitored in aquatic biota), using newly developed or improved analytical techniques. For some contaminants, the archival of frozen or freeze-dried tissues of the bio-monitor may be adequate; for others, partial clean-up

techniques may be required prior to archival, to guarantee sample integrity during storage. It is recommended that the detailed design stage for the bio-monitoring program proposed herein consider the needs for sample archival, particularly in relation to the overall budget for the program.

With respect to analytical QA/QC concerns, it is likely that several analytical laboratories would be involved in the proposed local monitoring studies. Some point source dischargers possess in-house analytical capability for contaminants, and are likely to complete their own analysis of samples (as at present for their NPDES self-monitoring). However, other dischargers use commercial laboratories. It is recommended that all local monitoring investigations should be commenced only after an initial quality assurance/quality control testing round has been completed. This would involve the analysis of reference or intercomparison materials (on a "blind" basis) by all participating analytical facilities, in both regional and local monitoring programs. Both this initial QA/QC program and the ongoing quality control of analysis in the participating laboratories should be overseen by the relevant regulatory authorities. Only in this fashion is it envisaged that reliable information can be guaranteed from the monitoring program.

Considerable work has already been undertaken on QA/QC-related topics for 301(h) monitoring programs (e.g. see Taylor, 1986; EPA, 1987a, 1987d). This report does not seek to review such data, but notes the critical importance of this topic. There is a clear need for the improvement of analytical QA/QC in the Bay area, especially with respect to its overall coordination.

G. Approximate Program Costs

The costs provided herein are approximate in nature only (thought to be within 50% of actual costs), and are based upon information gathered on the costs of commercial analysis of aqueous samples and biota, and the experience of State Mussel Watch Program investigations. It should be noted that the costs quoted are for the conduct of the proposed program only (i.e. collection and analysis of water samples; collection and transplantation of bivalves; sampling and analysis of bivalves; interpretation of data), and do not include managerial cost elements (QA/QC programs, monitoring program oversight, data management, managerial report production, etc.). The latter may legitimately be considered a contributory cost of the overall program, but such costs are currently borne (for the State Mussel Watch and Toxic Substances Monitoring Programs) by State funding.

The Regional Monitoring Program

The proposed regional program involves the collection of water samples for the analysis of contaminants at 42 locations (28 in the Bay; 14 in the Delta) on eight occasions during the year (336 discrete samples). It is envisaged that the analysis of PAHs in all samples will be considered to be prohibitively expensive; these are not therefore included in the cost estimates given here, as it is thought unlikely that the program will include the monitoring of PAHs in aqueous samples simply to ascertain compliance with a "total PAH" objective in the Basin Plan. Analytical costs for this program, the primary objective of which is to monitor compliance of receiving waters with water quality objectives in the Basin Plan, are estimated at about $70,000 annually (costs of $15 per metal analysis used). Sampling costs are included in the calculation below on bio-monitoring costs, although the vessel time component is particularly uncertain (as it depends on cooperation between this program and other existing programs of study). It is notable that this sampling of receiving waters for contaminant analysis would effectively be a new program in the Bay and Delta, as routine monitoring of this type is not presently undertaken.

The proposed bio-monitoring program involves the study of three species of bio-monitors at the same 42 locations, except that overlaps in the species studied (at the

boundaries of their distributions, determined by ambient salinities) will be likely to increase the sample number to about 50 in any one period of study (depending on the precise salinity regimes encountered and the survival of transplanted samples). All sites would be sampled twice in any one year, producing a total of about 100 samples annually. The collection and analysis of these samples for the "toxic contaminants of concern" as shown in Table 7 of this report (excluding malathion, parathion, MAHs and cycloalkanes; see sub-section E above) is estimated to cost about $2,000 per sample, or a total of about $200,000 annually. These estimates are based upon data from the existing State Mussel Watch Program. The precise costs depend on such factors as vessel sharing, sample compositing strategy, overhead rates, etc.; however, it is considered that the estimates provided here are within 50% of actual costs.

It is therefore concluded that the regional component of the monitoring program proposed in the present report could be completed for less than $300,000 annually, at least if vessel sharing can be arranged (managerial costs are additional to this; see above). The expenditure of this relatively small amount (by comparison to the overall costs of the present monitoring undertaken in the estuary) would improve the current knowledge of the abundances and distributions of contaminants in the Bay and Delta immeasurably.

Local Monitoring

As noted elsewhere in this document, the detailed design of local monitoring studies at specific outfalls is outside the scope of the present work. However, sufficient detail is provided in a generic sense to permit very approximate costs to be calculated. It should be noted that these are likely to vary significantly according to the size of the discharge involved (volume, contaminant loading, extent of possible impacts) and its location (need for study of multiple species, etc.).

The monitoring scheme proposed for local studies in this report is tiered. It is proposed that initial studies relating to analytical QA/QC should be required prior to the commencement of any local monitoring (see above). Such studies would be likely to involve the analysis of up to 10 reference or intercomparison samples. Costs would be likely to approximate $1,500 to $2,000 per sample; hence, total costs for the QA/QC-related portion of the studies would approximate $15,000-$20,000 per discharger.

Following the QA/QC-related studies, it is proposed that point source dischargers would commence laboratory-based investigations. These would involve the exposure of bio-monitors to whole and diluted point source effluents, and would be followed (in cases where sufficient justification existed for suspecting significant impacts from individual outfalls) by *in situ* field investigations of contaminants in bio-monitors and sediments. Studies of non-point sources of contaminants would be initiated by similar field investigations, and would not employ laboratory-based studies as a preliminary step.

The laboratory-based studies are estimated to cost of the order of $2,000 per sample; total costs of perhaps $20,000 for each discharge might be anticipated annually, but these would depend on the requirements by the regulatory authority for studies over time (to characterize changes in effluent compositions). The costs of *in situ* field investigations would vary according to precise study design, but would be unlikely to exceed $50,000 for any individual investigation. As noted previously, managerial costs (program oversight, data management, production of managerial reports, etc.) are not included in this estimate.

H. Research Needs in Addition to the Proposed Program

The monitoring program proposed in this report will provide a substantive database concerning the spatial and temporal trends in the abundance, distributions and bio-availabilities of the toxic contaminants of greatest concern in the San Francisco Bay and Delta. However, additional monitoring and research studies are needed in the estuary if a complete understanding of toxicant distributions and effects is to be attained, and the depth of knowledge required as a basis for the appropriate protection of the estuary is to be acquired. These research needs are outlined briefly here.

Microlayer Studies

No studies have been completed to date on the quantification or significance of toxic contaminants in the microlayer of the estuary. This specialized aspect of receiving water chemistry is now open to study, as sampling equipment has been developed to permit the collection of significant volumes of the microlayer. It is recommended that a sampling program be established for such studies, employing some of the regional monitoring sites proposed in the current report, and selected local sites which are likely to be heavily contaminated (e.g. the Santa Fe Channel; Oakland inner harbor; the extreme southern end of South Bay). Samples of the microlayer collected in such a program should be analyzed for the contaminants of greatest concern in the estuary (shown in Table 7 of this report) and should also be employed in toxicity bioassays. The selection of species for the bioassay studies should take account of the organisms being used in the present effluent toxicity characterization investigations (SFRWQCB, 1987), and should also consider the use of species/life stages which contact the microlayer, such as the eggs of certain fish species.

Studies of other Bio-monitors

The proposals presented in this report rely heavily upon the use of bivalve molluscs as bio-monitors in the Bay and Delta. This is justified, in that these species have been consistently found to perform well in such studies. As noted in section VII, there is a need to investigate the potential of the newly-introduced species of clam (*Potamocorbula* sp.) in the estuary as a bio-monitor; the salinity tolerance of this species suggests that it may be of particular use as a bio-monitor locally, although nothing is

known of its bio-accumulation of contaminants. It is recommended that initial laboratory dosing experiments and field surveys be conducted to investigate the potential of this species to act as a bio-monitor of toxic contaminants in the estuary.

In addition, useful data would accrue from studies of other types of bio-monitors in the estuary, which may respond differently to the overall pollution loads encountered in the Bay and Delta. The most promising organisms for further study are considered to be species of macroalgae and barnacles. It is recommended that pilot-scale monitoring investigations be commenced employing such species, to provide a comparative database to that from the studies of bivalves. Where possible, such studies should employ the same monitoring locations as those proposed here for use with bivalve molluscs, so that direct comparisons may be made between the several sets of results.

Studies of Sediment Transport

Many toxic contaminants exhibit high affinities for binding to particulate material in aquatic ecosystems, due to their surface charge or their lipophilic character. It follows that the transport of suspended particulates and the resuspension/redeposition of sediments are important processes controlling the flux of contaminants through estuaries. In the local situation, it is believed that the sediments of the San Francisco Bay and Delta are unusually highly mobile, although very little information of an empirical nature exists on this topic. Schubel *et al.* (1988) suggested that sediment transport is a particularly important area for future research in the estuary, and this recommendation is supported here.

Monitoring of the Effects of Contaminants

As discussed in the introduction to this report, the establishment of a bio-monitoring program to accurately identify spatial and temporal trends in contaminant abundances, distributions and bio-availabilities in the Bay and Delta is considered the primary objective of this report, and the most urgent priority for the estuary. However, studies of the effects of contaminants should not be ignored, as the impacts of contaminants on beneficial uses are the primary driving force for the instigation of regulatory controls on contaminant loading to the estuary. Some information of this type will be provided through the bioassay studies of effluents (SFRWQCB, 1987), and investigations of the toxicity of the microlayer proposed above. However, there is a need

for developmental studies of methods to investigate contaminant effects in the Bay and Delta, particularly those which may be employed in concert with the bio-monitoring approach proposed here. Although most of the existing methods are not sufficiently pollutant-specific to provide unequivocal conclusions on the contaminants of greatest impact in the estuary, their use may nevertheless provide data of relevance to the overall "health" of the Bay and Delta. It is recommended that methods such as those reviewed by Bayne (1985) be considered for development in the estuary. Most such methods may be employed on bivalve molluscs which are also used in bio-accumulation studies, as proposed in this report. Investigations of scope for growth, organism growth and mortality, fecundity and other aspects would be useful adjuncts to the routine monitoring program proposed in this report.

In addition, there is a requirement for further studies on currently perceived problems in the estuary, to attempt to identify cause-and-effect phenomena. It is recommended that laboratory-based investigations be funded to study the impacts of PCBs and MAHs on striped bass (*Morone saxatilis*), and the effects of PCBs on starry flounder (*Platichthys stellatus*). Such studies should involve the dosing of fish with contaminants through water and food routes to attempt to mimic conditions seen in the field (egg resorption in female striped bass; reduction in fertilization success in starry flounder females).

There is also a need for further research and monitoring of the toxic impacts of contaminants on bird populations in the estuary and its catchment. Certain species of birds offer particular advantages as indicators of toxicant effects, partly due to their high trophic level position, and partly because of their innate sensitivity (especially with respect to reproduction). The studies of this type undertaken by the U.S. Fish and Wildlife Service and the California Department of Fish & Game should receive further funding and support.

Finally, research on harbor seals in the Bay is needed. Studies elsewhere have shown that seals are particularly sensitive to contaminants such as PCBs and DDE, suffering adverse effects on reproduction at levels which are not dissimilar to those found locally (e.g. see Reijnders, 1986). The problems being experienced presently in seal populations both in Europe and locally may or may not be related to their accumulation of toxicants, but merit study in any event.

I. Monitoring to Satisfy Management Needs

The present report does not represent the first attempt to initiate cohesive monitoring and research studies in the San Francisco Estuary on toxic contaminants and their impacts. ABAG (1978) proposed a five-point action plan to "guide water quality management decisions in the future" for the estuary, and several of these proposals related to the need for improved understanding of the transport, fate and effects of toxic contaminants in the Bay and Delta. The Aquatic Habitat Program Plan (Horne *et al.*, 1982; SWRCB, 1982a) was produced as a master plan for monitoring of the health of the estuary and the impacts of contaminants on beneficial uses in the Bay and Delta. Other attempts to introduce long-term monitoring include the Benthic Surveillance Project of the U.S. Geological Survey (recently stricken with a lack of funding, after only just over a year of monitoring), fisheries projects undertaken by the California Department of Fish & Game and the U.S. Fish and Wildlife Service, research on water quality and primary productivity by various State and Federal agencies, and the development of hydrodynamic models of the estuary by the U.S. Geological Survey and the University of California Berkeley.

However, many of these projects have either not been fully implemented, or have ceased after short periods due to the lack of committed funding. The result is a fragmented patchwork of existing and past monitoring and research programs which provide only a piecemeal understanding of the present health of the estuary and its resources, and of the abundances and impacts of toxic contaminants. A panel of international experts providing peer review on monitoring programs in the Bay and Delta recently concluded that the existing programs provide inadequate data to scientifically justify decisions on the future control of contaminants or on inflow-related questions (Schubel *et al.*, 1988). These authors considered that the management issues facing the regulatory agencies in the estuary were not being addressed by the present programs of monitoring and research, and that a completely new perspective was required if progress was to be made. This new perspective would involve the revision of existing fragmented studies into a cohesive program, designed specifically to meet stated management objectives, and with guaranteed long-term funding.

The present report provides proposals for one portion of such a cohesive program; that for the monitoring of the spatial and temporal abundances, distributions

and bio-availabilities of toxic contaminants in the Bay and Delta. Studies additional to those proposed here (involving both monitoring and research) are undoubtedly required to provide vital data on the impacts of contaminants on the resources and beneficial uses of the estuary, as noted in sub-section H above. However, it is considered that the monitoring of spatial and temporal trends is the most basic and pressing need in the estuary; if the principal sources of toxicants and areas of contaminant abundance are not adequately characterized, it is likely to prove impossible to undertake further studies on the specific impacts of contaminants in the system. The implementation of the monitoring program proposed here would begin to produce substantive insight into contaminant sources within a short period (less than a year after its inception), through data from the study of point and non-point sources of contaminants. These would immeasurably improve the present understanding of contaminant loading to the estuary (Gunther *et al.*, 1987), especially with respect to organic contaminants, which are very poorly characterized by the present NPDES self-monitoring of point source effluents (see section V of this report). Medium-term and longer-term benefits would also accrue, through the local and regional elements of the program indicating the overall abundances and bio-availabilities of contaminants in the estuary and its sub-catchments and their changes with time (due to alterations in land use, industrial practices, regulatory initiatives, and other factors).

It is recommended that the program of study proposed here be further developed as necessary, and be implemented in the Bay and Delta as soon as possible. This implies the alteration of several of the existing programs in the estuary and its catchment (the State Mussel Watch Program and the Toxic Substances Monitoring Program in particular; also the requirements of dischargers for monitoring contaminants). While the continuity of the existing database will be largely eliminated through these changes, it is argued that such continuity hardly exists at present, and that the current monitoring programs do not provide a sound basis for rational decisions on the control of pollution in the estuary and its catchment.

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APPENDIX 1

Scope of Work for State Board Contract Amendment:

Updating of the Aquatic Habitat Program Plan, and Monitoring of Contaminants in the San Francisco Bay-Delta.

Agreement 5-290-120-0 between the SWRCB and AHI is to be amended by the replacement of Task 1 and Task 4 by a broader scope of work. Funds available for this new work are those not yet committed under the original Tasks 1 and 4 of the agreement, an additional $20,000 (the latter constituting a amendment to the original contract), and matching funds from other sources, as required. This document provides a scope of work for the new task.

(a) Background

Task 1 of the original contract called for a general revision of the existing Aquatic Habitat Program Plan (AHPP). Task 4 of that contract required the development of a draft implementation plan for the program elements in the AHPP. The original level of funding by SWRCB of those tasks (totaling $12,500) did not permit a comprehensive review and redrafting of the AHPP. However, the addition of new funds consequent to the amendment of the contract will permit such a task to be completed.

(b) The Existing AHPP

The original AHPP was produced in 1982 under contract to the SWRCB. Overall goals of the AHPP were:

(i) To assess the health of the aquatic organisms in the Bay related to the effects of water pollutants.

(ii) To determine the specific causes of any adverse changes in the health of the Bay that appear to be pollutant-related.

(iii) To get the maximum use of funds by coordinating activities of this program with all other monitoring and research activities in the Bay.

Six program elements were proposed for inclusion in the original AHPP. These were: the Regional Effects Element; the Local Effects Element; the Effluent Assessment Element; the Hydrodynamic Element; the Coordination Element; and the Research and Special Studies Element.

Since 1982, some portions of the AHPP have been activated by the commencement of specific monitoring and/or research studies in the estuary. However, it is clear from the results of certain of these studies that revision of the program concepts is necessary. It is also clear from the proceedings of the State Hearings on the Bay-Delta that currently available knowledge does not permit strong conclusions on the present health of the Bay-Delta, or on factors relating to contaminants which may affect the biological resources of the estuary.

The improvements in available analytical and methodological techniques over the last 5 years provide a firmer basis for the design of a coordinated contaminant monitoring program in the Bay-Delta than was previously available (when the AHPP was drafted). A new perspective is therefore available, from which to redesign monitoring studies in the estuary.

(c) Scope of Work

Under the amended contract, AHI will address the inadequacies in the existing monitoring database for the Bay-Delta and will propose a new scheme for monitoring and research in the estuary. This new scheme will specifically address the following areas:

(i) Elucidation of the contaminants of greatest potential impact in the Bay-Delta (brief discussion, relying largely on previous work by AHI for the SWRCB).

(ii) Development of a monitoring scheme to distinguish spatial and temporal changes in the abundance and/or bio-availability of these contaminants on a regional level. This monitoring scheme will consider the use of water, sediments, and biota, and will recommend a coordinated monitoring strategy, complete with station locations, frequency of monitoring, and indicative costs.

(iii) Design of monitoring and research studies to relate the regional trends in toxic contaminant abundance and/or bio-availability to important local trends in these factors. These studies will take account of the location of major contaminant sources in the Bay-Delta and of the present knowledge of hydrodynamics in the estuary. The monitoring of effluents discharged directly or indirectly to the Bay-Delta, and the relationship of these effluents to local and regional trends in contaminant abundance and bio-availability will both be considered.

(iv) Production of recommendations on studies required to investigate specific contaminant impacts on individual target species. These studies will be designed to establish a cause-and-effect link between contaminant abundance and/or bioavailability and a documented or observable biological effect in resident estuarine biota.

In addition to the above, AHI will review the design of existing major State and Federal monitoring programs on the Bay-

Delta (State Mussel Watch, Toxic Substances Monitoring Program, fishery monitoring projects, etc.), and will consider how these may relate to the coordinated monitoring and research scheme developed as described above. Recommendations will be made on program changes, where these are thought to be necessary. Approximate costs of existing and proposed monitoring schemes will be included where appropriate.

The above scope of work is considered to be consistent with the general approach needed to attain the goals of the Aquatic Habitat Program Plan, cited above.

(d) Level of Effort/Personnel

The approximate percentages for effort devoted to the subtasks noted in section (c) above will be:

(i) Elucidation of contaminants of greatest impact: 10%

(ii) Development of regional monitoring scheme : 40%

(iii) Development of local monitoring schemes : 40%

(iv) Recommendations on target species studies : 10%

The studies will be completed by Dr. David Phillips (Senior Environmental Scientist), with minor assistance as required from other AHI staff.

(e) Reporting Requirements

AHI will provide the following products to the contracting officer:

1. Written progress reports at 2-monthly intervals from the start of the project to its completion.

2. Draft final report on the studies, by May 20, 1988.

3. Final report by June 30, 1988, or within 30 days of comments from the contracting officer on the draft final report.

APPENDIX 2

San Francisco Bay - Delta
Aquatic Habitat Institute

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09 October 1988

To: Members of SFEP Sub-Committee on Contaminant STR
From: David J.H. Phillips, AHI
Subject: Additional material on "contaminants of concern" in the Estuary

As requested at the last meeting of the sub-committee, a matrix has been prepared showing a variety of contaminants and their grading against criteria designed to identify contaminants of concern in the Estuary. This matrix, and associated notes, is attached.

I have worked from a number of lists of contaminants provided by Brian Melzian of EPA Region IX. These include lists from programs concerned with contaminants in foods because of public health concerns, those concerned with contaminants in sediments (Puget Sound and U.S. CoE programs), and others. The recommended inclusions reflect a compromise between "including the world" and attempting to focus the effort in the STR on those contaminants which are most likely to be affecting the beneficial uses of the Estuary.

This list and its recommendations will be discussed at the next meeting of the Pollutants sub-committee, on October 13, at the AHI offices. Please take the time to consider it prior to the meeting if possible.

GENERATION OF CONTAMINANT MATRIX: NOTES

CRITERIA EMPLOYED

(1) General significance of contaminants: This category is included because several of the contaminants listed are not considered "priority pollutants", either in the EPA sense or otherwise. It seems to make no sense to commit SFEP funds to the review of iron or manganese in the Estuary, for example, if these are not of significance (i.e. found to be toxic, or to affect beneficial uses) in estuarine ecosystems in general. General significance has been graded as H (high), M (moderate) or L (low).

(2) Extent of the database on the San Francisco Estuary: This category is self-explanatory. Where no (or very minor) data exist on particular contaminants, it is proposed that these areas be listed by the report as "datagaps" and their importance defined and discussed. The extent of the database for particular contaminants has been graded as E (extensive), S (significant), M (minor) or P (poor or non-existent).

(3) Whether the contaminant is widespread in the Estuary: Also self-explanatory. Responses to this category are graded Y (widespread) or N (not widespread).

(4) Whether the contaminant exhibits localized contamination ("hot-spots") in the Estuary: This is to some extent judgemental, depending on one's definition of a hot-spot. However, in most cases, responses are fairly clear-cut. Responses are graded Y (localized contamination exists) or N (no evidence for hot-spot existence).

(5) Whether the contaminant exerts detrimental effects on biological resources in the Estuary: Few definitive answers are possible in this category, and judgement calls are necessary in several cases. Responses are graded Y (adverse effects exist), P (effects may exist), or N (no evidence for effects, and the existence of such seems unlikely).

(6) Whether the contaminant affects other beneficial uses in the Estuary: In a few cases, contaminants probably affect beneficial uses other than biological resources; public health effects might be one example. Responses are graded Y (effects exist, or are likely to) or N (no evidence exists for effects and these seem unlikely).

GENERAL COMMENTS ON GROUPS OF CONTAMINANTS INCLUDED IN THE MATRIX

Metals

Most of the metals listed which are on the EPA Priority Pollutants list may be considered to be of potential toxicity in estuarine ecosystems. Other metals listed which do not appear on the EPA Priority Pollutants list are often rare in occurrence in estuaries, or of low toxicity.

Pesticides

Most of the pesticides listed are organochlorines and are therefore persistent in aquatic environments and potentially important contaminants. Only some of these are thought to be widespread or of significant localized contamination in the Estuary, however. A few additional compounds have been added to the EPA list here, these being compounds which are thought to be of local significance because of their use on crops in the Delta or the upstream catchment. Organotins are included elsewhere (under metals).

Organics- General

"Oil and grease" is suggested to be such a non-specific term that its consideration should be dropped from the STR. PAHs as a group are thought to be of importance in the Estuary, and several of these are listed individually elsewhere. "Persistent organohalogens" and "petroleum hydrocarbons" are generic terms also thought to be covered by the inclusion of specific contaminants elsewhere in the list.

Low and High Molecular Weight Aromatic Hydrocarbons

All the contaminants listed are PAHs; all are thought of potential significance in the Estuary, although the existing database is sparse. The EPA list has been slightly amended to produce a more concise listing of individual compounds in certain cases, but nothing has been dropped.

CONTAMINANT MATRIX

Criteria	1 Gen. Sig.	2 Data	3 Wide.	4 Local	5 Eff.1	6 Eff.2	Remarks
Metals							
Al	L	S	Y	?	N	N	
Sb	M	P	?	?	?	?	Datagap
As	M	S	I	Y	N	N	Include
Be	L	P	?	?	?	?	Datagap
Cd	H	E	Y	Y	P	Y	Include
Ca	L	S	Y	N	N	N	
Cr	M	S	Y	Y	?	?	Include
Cu	H	E	Y	Y	P	?	Include
Fe	L	S	Y	N	N	N	
Pb	M	S	Y	Y	N	N	Include
Mg	L	S	Y	N	N	N	
Mn	L	S	Y	N	N	N	
Hg	H	E	Y	Y	Y	Y	Include
Ni	M	S	Y	Y	?	?	Include
Se	H	E	Y	Y	Y	?	Include
Si	L	S	Y	N	N	N	
Ag	M	S	Y	Y	?	?	Include
Na	L	M	Y	N	N	N	
Th	M	P	?	?	?	?	Datagap
Sn	H	M	N	Y	Y	?	Include
Ti	M	P	?	?	?	?	Datagap
V	M	P	?	?	?	?	Datagap
Zn	M	E	Y	Y	N	N	Include

CONTAMINANT MATRIX (contd.)

Criteria	1 Gen. Sig.	2 Data	3 Wide.	4 Local	5 Eff.1	6 Eff.2	Remarks
Pesticides							
Aldrin	M	S	N	Y	?	?	Include
Dieldrin	M	S	N	Y	?	?	Include
Chlordane + derivatives	M	S	Y	Y	?	?	Include
Demeton	M	P	?	?	?	?	
DDT + derivatives	H	E	Y	Y	P	?	Include
Endosulfan + derivatives	M	S	N	Y	N	N	Include
Endrin + derivatives	M	S	N	Y	N	N	Include
Guthion	M	P	N	N	N	N	
Heptachlor + derivatives	M	S	N	Y	N	N	Include
HCH + derivatives	M	S	N	Y	N	N	Include
Malathion	M	S	N	Y	P	N	Include
Methoxychlor	M	S	N	N	N	N	
Mirex	M	M	N	N	N	N	
Parathion + derivatives	M	S	N	Y	N	N	Include
Toxaphene	M	S	N	Y	N	N	Include
HCB	M	S	N	Y	N	N	Include
Chlorbenside	M	S	N	Y	N	N	Include
Dacthal	M	S	N	Y	N	N	Include
Kepone	M	P	N	N	N	N	

CONTAMINANT MATRIX (contd.)

Criteria	1 Gen. Sig.	2 Data	3 Wide.	4 Local	5 Eff.1	6 Eff.2	Remarks
PAHs (Low and High Molecular Weight)							
Acenaphthene	M	M	Y	Y	P	?	Include
Acenaphthylene	M	M	Y	Y	P	?	Include
Anthracene	M	M	Y	Y	P	?	Include
Fluorene	M	M	Y	Y	P	?	Include
Naphthalene + derivatives	M	M	Y	Y	P	?	Include
Phenantherene + derivatives	M	M	Y	Y	P	?	Include
Benzo (a) anthracene	M	M	Y	Y	P	?	Include
Benzo (a) pyrene	M	M	Y	Y	P	?	Include
Benzofluoranthenes	M	M	Y	Y	P	?	Include
Benzo (g,h,i) perylene	M	M	Y	Y	P	?	Include
Chrysene	M	M	Y	Y	P	?	Include
Dibenzo (a,h) anthracene	M	M	Y	Y	P	?	Include
Fluoranthene	M	M	Y	Y	P	?	Include
Indeno (1,2,3-c,d) pyrene	M	M	Y	Y	P	?	Include
Pyrene	M	M	Y	Y	P	?	Include
Benzo (e) pyrene	M	M	Y	Y	P	?	Include
Miscellaneous							
Asbestos	L	P	N	N	N	N	
Cyanide	M	S	N	N	N	N	

OTHER GROUPS OF CONTAMINANTS IN EPA LIST

Phenols

All compounds listed generally only significant in conditions of direct exposure to high concentrations; all poorly characterized to date in the Estuary with the possible exception of effluents; none widespread; none likely to accumulate in sediments or biota significantly. **Conclude: Exclude from STR.**

Chlorinated Aromatic Hydrocarbons

Hexachlorobenzene (HCB) listed under pesticides above. All other compounds included in EPA list as noted for phenols above. **Conclude: Exclude from STR.**

Phthalates

All compounds listed poorly characterized to date in the Estuary; none likely to be toxicologically significant with respect to effects on beneficial uses. **Conclude: Exclude from STR.**

Polychlorinated Biphenyls

All mixtures of commercial products listed in EPA list are of extreme environmental concern. Most PCB profiles in the Estuary sediments and biota characteristic of Aroclor 1254, but a few exceptions exist. Database is extensive; PCBs are both widespread and present at high levels in particular hot-spots in the Estuary; adverse effects on biota are probable. **Conclude: Include in STR.**

Organonitrogen Compounds

All compounds listed poorly characterized to date in the Estuary; none likely to be toxicologically significant with respect to effects on beneficial uses. **Conclude: Exclude from STR.**

Chlorinated Aliphatic Hydrocarbons

All compounds listed poorly characterized to date in the Estuary; none likely to be toxicologically significant with respect to effects on beneficial uses. **Conclude: Exclude from STR.**

Halogenated Ethers

All compounds listed poorly characterized to date in the Estuary; none likely to be toxicologically significant with respect to effects on beneficial uses. **Conclude: Exclude from STR.**

Miscellaneous Oxygenated Compounds

Isophorene unlikely to be of toxicological significance in the Estuary. Data on dioxins are sparse for the Estuary, although these compounds are of extreme persistence and toxicity in the environment. **Conclude: Dioxins to be considered as a datagap.**

Volatile Halogenated Alkanes

All compounds listed generally only significant in conditions of direct exposure to high concentrations; all poorly characterized to date in the Estuary with the possible exception of effluents; none widespread; none likely to accumulate in sediments or biota significantly. **Conclude: Exclude from STR.**

Volatile Halogenated Alkenes

As noted above for alkanes.

Volatile Aromatic Hydrocarbons

These compounds (benzene, ethylbenzene, toluene, xylene, styrene) are thought to be of moderate significance generally as environmental contaminants. The database on these compounds in the Estuary is significant (at least in some respects). The first four of these compounds have been suggested to be implicated in the decline of striped bass

populations locally, although the evidence for this is controversial. **Conclude: Include in STR. Local styrene levels may be considered as a datagap.**

Volatile Chlorinated Aromatic Hydrocarbons, Volatile Unsaturated Carbonyl Compounds, Volatile Ethers

All compounds listed generally only significant in conditions of direct exposure to high concentrations; all poorly characterized to date in the Estuary with the possible exception of effluents; none widespread; none likely to accumulate in sediments or biota significantly. **Conclude: Exclude from STR.**

Miscellaneous Extractables

Compounds of significant volatility are covered by comments above. Coprostanol thought to be a useful indicator of sewage-derived pollution, although relatively few studies have been performed in the Estuary on this compound. Phenanthrene, naphthylene and perylene derivatives included in list of PAHs above. **Conclude: Exclude from STR, with exception of those compounds elsewhere listed as significant.**

Nutrients

These have been added here, not being shown in the EPA list. These contaminants may be considered to be of general significance because of their bio-stimulation of primary productivity in aquatic ecosystems. A considerable body of data exists on nutrients and related parameters in the Estuary, and it is thought that nutrient enrichment of the Estuary was a contributing factor to the dissolved oxygen sags experienced (particularly in the South Bay) in the 1960s and early 1970s. However, subsequent to the improvement of sewage treatment facilities at that time, there has been little evidence that nutrient enrichment leading to eutrophication is a significant problem, either on a regional or local scale. **AHI recommends that these contaminants not be included in the synthesis of data for the STR.**

Microbial Agents

Although not classical chemical contaminants *per se*, these have also been added to the EPA list. There is justified concern related to the microbial contamination of shellfisheries in the Estuary, and its possible impacts on public health. The database is moderate in quality only (including much data relating to total coliforms and other indicators not now thought to be of particular use), but we recommend that some resources be expended on this issue in the STR. We do not recommend that massive expenditure be incurred on computing loads/effects, however; rather, **we recommend that the present status of the microbial/shellfishery concerns be reviewed in a specific section of the STR, with management options for the future to be included.**