

**The Bioavailability of Toxic Contaminants
In the
San Francisco Bay-Delta
Proceedings of a Two-Day Seminar Series**

October, 1988

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<p>This volume presents the proceedings of a conference entitled "The Bioavailability of Toxic Contaminants in the San Francisco Bay-Delta," hosted by The San Francisco Bay-Delta Aquatic Habitat Institute (AHI) on October 26-27, 1988. AHI is a nonprofit corporation established at the request of the State of California to coordinate and evaluate research on pollution and its effects in the San Francisco Estuary. The conference was sponsored by the Bay Area Dischargers Association, and it was held at the University of California at Berkeley.</p> <p>The goal of this conference was to provide attendees with a more detailed exposure to the question of pollutant bioavailability, thereby building upon the general foundation provided in a conference held the previous year entitled "Toxic Contaminants and Their Biological Effects in the San Francisco Bay-Delta". Presentations at the 1988 meeting included studies of environmental factors influencing bioavailability, examinations of <i>in situ</i> bioaccumulation of contaminants in invertebrates, fish, and mammals, and studies of contaminant biomagnification and toxicity. Transcripts of introductory remarks made by representatives of the Bay Area Dischargers Association and California Assemblyman Robert Campbell (D-Richmond) are included.</p> <p>Eleven of the 16 speakers provided contributions to these proceedings. These contributions range from full-length articles to abstracts.</p>				
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**The Bioavailability of Toxic Contaminants
in the
San Francisco Bay-Delta
Proceedings of a Two Day Seminar Series**

Berkeley, California

October 26-27, 1988

Andrew J. Gunther, Editor

May, 1990

TABLE OF CONTENTS

EDITOR'S COMMENTS	1
SEMINAR SCHEDULE	2
INTRODUCTORY REMARKS	4
Walter Bishop	
KEYNOTE ADDRESS	8
Cindy Deacon Williams	
TRACE METAL ASSOCIATIONS IN THE WATER COLUMN OF SOUTH SAN FRANCISCO BAY CALIFORNIA	15
James S. Kuwabara, <i>et al</i>	
THE INFLUENCE OF AMBIENT CONDITIONS ON THE BIOAVAILABILITY AND TOXICITY OF COPPER	45
Anthony R. Carlson	
CONTAMINATION AND TOXICITY OF THE SEA-SURFACE MICROLAYER .	48
John T. Hardy	
Jeffrey N. Cross	
STUDIES EMPLOYING THE CLAM <i>MACOMA BALTHICA</i> TO IDENTIFY BIOAVAILABLE TRACE METALS IN SAN FRANCISCO BAY	55
Daniel J. Cain	
CHLORINATED HYDROCARBONS IN MARINE MAMMALS FROM PUGET SOUND AND THE NORTHEAST PACIFIC	70
John Calambokidis	
INNOVATIVE METHODS OF TRACING CONTAMINANTS IN COASTALWATERS: THE USE OF BACTERIOPHAGES AND BACTERIAL SPORES	91
A. F. Godfree	
CHEMICAL TRANSFORMATIONS OF CONTAMINANTS IN DREDGED MATERIAL AND IMPLICATIONS FOR BIOAVAILABILITY	107
Thomas H. Wakeman, <i>et al</i>	
SPATIAL AND TEMPORAL TRENDS OF TOXIC CONTAMINANTS IN SEDIMENTS AND MARINE LIFE OF THE SOUTHERN CALIFORNIA BIGHT	124
Alan J. Mearns	

BIOMAGNIFICATION IN SEAFOOD ORGANISMS AROUND A LARGE CALIFORNIA SUBMARINE WASTEWATER DISCHARGE	137
D. R. Young, <i>et al</i>	

CHARACTERISTICS AND EFFECTS OF CONTAMINATED SEDIMENTS FROM SOUTHERN CALIFORNIA	152
Jack W. Anderson, <i>et al</i>	

A PROPOSED PROGRAM FOR MONITORING TOXIC CONTAMINANTS IN THE SAN FRANCISCO BAY DELTA	162
David J.H. Phillips	

APPENDICES

APPENDIX A - AQUATIC HABITAT INSTITUTE182
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EDITOR'S COMMENTS

This volume presents the proceedings of a conference entitled "The Bioavailability of Toxic Contaminants in the San Francisco Bay-Delta," hosted by The San Francisco Bay-Delta Aquatic Habitat Institute (AHI) on October 26-27, 1988. The conference was sponsored by the Bay Area Dischargers Association, and it was held at the Clark Kerr Campus of the University of California at Berkeley.

In 1987, a more general conference entitled "Toxic Contaminants and Their Biological Effects in the San Francisco Bay-Delta" was hosted by AHI. Over 220 people attended this earlier conference, reflecting the significant interest within the Bay-Delta region regarding chemical pollution of the Estuary. Many attendees suggested that future conferences could be improved through the preparation of proceedings, and consequently this document was prepared for the 1988 meeting.

The goal of the 1988 conference was to provide attendees with a more detailed exposure to the question of pollutant bioavailability, thereby building upon the general foundation provided in the previous year regarding pollution in the Estuary. Presentations included studies of environmental factors influencing bioavailability, examinations of *in situ* bioaccumulation of contaminants in invertebrates, fish, and mammals, and studies of contaminant biomagnification and toxicity. The program of presentations is found on the next page. Introductory remarks were provided by representatives of the Bay Area Dischargers Association and Assemblyman Robert Campbell (D-Richmond).

Eleven of the 16 speakers provided contributions to these proceedings. These contributions range from full-length articles to abstracts. AHI is grateful to those speakers who took the time to prepare submissions to the proceedings. We also acknowledge the wordprocessing efforts of Elizabeth Hartman in the AHI offices.

SEMINAR SCHEDULE
Wednesday October 26, 1988

- 08.30 **Registration**
- 09.00 **Welcoming Address**
Walter Bishop, AHI Board of Directors
Bay Area Dischargers Association
- 09.15 **Opening Remarks**
Assemblyman Robert Campbell
11th District, Contra Costa County
- 09.30 **Concentrations of Trace Elements in the Waters of South Bay**
James Kuwabara, US Geological Survey, Menlo Park, CA
- 10.15 **The Influence of Ambient Conditions on the Bioavailability and Toxicity of Copper**
Anthony R. Carlson, U.S. EPA Environmental Research Lab, Duluth, MN
- 11.00 **Break**
- 11.15 **Contamination and Toxicity of the Sea-surface Microlayer near Urban Areas**
Jeffrey Cross, S. California Coastal Water Research Project, Long Beach CA
- 12.00 **Factors Affecting the Bioavailability of Sediment Bound Contaminants to Benthic Organisms**
Jay Means, Louisiana State University, Baton Rouge, LA
- 12.45 **Lunch**
- 14.00 **Studies Employing the Clam *Macoma balthica* to Identify Bioavailable Trace Metals in San Francisco Bay**
Daniel Cain, U.S. Geological Survey, Menlo Park, CA
- 14.45 **The Bioavailability of Trace Metals in the San Francisco Delta: Studies with the Clam *Corbicula fluminea***
Samuel Luoma, U.S. Geological Survey, Menlo Park, CA
- 15.30 **Break**
- 15.45 **Chlorinated Hydrocarbons in Marine Mammals from Puget Sound and the Northeast Pacific**
John Calambokidis, Cascadia Research, Olympia, WA
- 16.30 **The Relationship of Accumulated PCBs to P-450 Enzymes, their Activities, and to Reproduction of Starry Founder from San Francisco Bay and Nearby Coastal Areas**
Robert B. Spies, Lawrence Livermore National Laboratory, Livermore, CA

Seminar Schedule
Thursday, October 27, 1988

- 09.00 **Innovative Methods of Tracing Contaminants in Coastal Waters: the Use of Bacteriophages and Bacterial Spores**
Alan Godfree, Altwell Ltd, Warrington, UK
- 10.00 **Chemical Transformations of Contaminants in Dredged Material and the Implications for Bioavailability**
Thomas Wakeman, U.S. Army Corps of Engineers, Bay Model, Sausalito, CA
- 10.45 **Break**
- 11.00 **Spatial and Temporal Trends of Toxic Contaminants in Sediments and Marine Life of the Southern California Bight**
Alan Mearns, NOAA, Seattle, WA
- 11.45 **The Cs:K Index of Trophic Level Separation and Pollutant Biomagnification in Seafood Organisms Around a Large California Submarine Wastewater Discharge**
David Young, EPA, Newport OR
- 12.30 **Lunch**
- 13.45 **Bioavailability and Toxicity of Contaminants from Sediments in Southern California**
Jack Anderson, S. California Coastal Water Research Project, Long Beach, CA
- 14.30 **Acute DDT Toxicity: Pathways in Sediments**
Jack Word, Battelle Northwest Laboratories, Sequim, WA.
- 15.15 **Break**
- 15.30 **Identifying Contaminants of Concern by Application of Toxicity Identification/Reduction Evaluation (TI/RE) Techniques**
Steven Hansen, S.R. Hansen & Associates, Berkeley, CA
- 16.15 **A Proposed Program for Monitoring Toxic Contaminants in the San Francisco Bay Delta**
David J.H. Phillips, Aquatic Habitat Institute, Richmond, CA

INTRODUCTORY REMARKS

Walter Bishop

Manager of Wastewater

East Bay Municipal Utility District

My name is Walter Bishop, and as a member of the Board of Directors of the Aquatic Habitat Institute I would like to welcome you to what I hope will be two days of a very valuable seminar. This is the second of what we plan to be a long series of informative scientific seminars sponsored by the Aquatic Habitat Institute. This forum for the exchange of technical information will hopefully contribute to the improvement of the water quality of San Francisco Bay. After each of you has reviewed the list of speakers for this seminar, I know you will join with me in congratulating the staff of AHI for putting together a very distinguished group.

Before I go any further I would like to spend a moment to review the organization known as the Aquatic Habitat Institute, and explain a little bit about what we, as members of the Board, consider to be its goals. When I talk to different groups and discuss the Institute, I am first pleased that someone even has a light bulb go off and says "Yeah, I've heard of them". That is the first threshold we must cross. The second threshold we cross is presenting the Institute's goals and objectives. Depending on who we talk to, people might say, "Oh, yeah, the Institute, they're an environmental group, like the Sierra Club and Citizens for a Better Environment. They are an environmental advocacy group". I get some of that. When you talk to governmental organizations, get to the bowels of EPA or the State Board, AHI is often referred to as a consulting firm - "They're up here basically trying to get contracts to do work", and so on.

The Institute was formed in 1983 essentially as the step-child of the State Water Resources Control Board. For two years the State Board studied what was right and what was wrong with research and monitoring in San Francisco Bay. What was determined very quickly is that we spent millions and million of dollars doing research on the Bay. Many of those studies were very focused with very specific goals in mind, and some studies

overlapping. The programs were often not well coordinated, and in many cases millions of dollars worth of data were sitting in the basements of governmental entities because there was no staff to sort, analyze and synthesize it. So it quickly became clear we needed a permanent, independent, and credible organization to deal with scientific research and monitoring in San Francisco Bay, and so in 1983 the Institute was formed.

I should take a moment to discuss the composition of AHI's Board of Directors. There are ten members of the board; the University of California, EPA, California Department of Fish & Game, The Regional Water Control Board, three entities representing non-point, municipal and industrial dischargers, and three members of the public. That's as diverse a group as you are going to see. There are various other entities like AHI around the country, but none of them brings together as diverse a group as AHI. We believe this diversity will help us achieve the goals we have established for AHI. One of those goals is to foster educated public exchange regarding the water quality of the Estuary through disseminating scientific information. This is why the Institute is sponsoring today's seminar.

Now why is BADA involved in this conference? Many of you are probably wondering what exactly BADA is. BADA is comprised of the five largest municipal dischargers in the San Francisco Bay. It is clear to us that there are two significant things happening that keep us on the forefront on some water quality issues. The first is that no longer can municipal dischargers, or other point sources, go to the public and say - "you know the problems of the 60's and 70's; BOD, suspended solids and conventional pollutants? They have been solved, and so you should pat us on the back. The bay doesn't smell, it looks a lot better and therefore we've done our job." The public looks at you generally and says "what have you done for me lately?" And secondly, the problem we deal with today is toxics. The issues we're concerned about are: "what are you doing to lower my risk" due to what you're putting in the environment. Risk assessment, a common method that has been used in the Food and Drug administration for years, is something that we in the municipal discharge sector must familiarize ourselves with. What that means is bioavailability of toxics, uptake of toxics by biota, are issues we have to be

knowledgeable about. They are issues the public demands we understand, and we find the science relative to those issues is running to catch up with these public demands. Anybody who participated in the Bay Delta Hearing process knows the frustration of speaking to the public and speaking to the public policy makers, and saying "I have done ten years of research on the striped bass and I can't answer the question about what's happening to the striped bass." The public doesn't know how to handle that. From a research standpoint there is validity in that statement. But in terms of public policy, we're in a situation where the public is convinced that we, as municipal dischargers, the scientific community, or regulators, may not be able to protect their health. If you don't believe that then why did Prop 65 pass? The public has found they have to regulate themselves, regulate us to protect their health.

So today and the next two days as we deal with the issues of bioavailability of toxics, as a discharger and one of the sponsors of this particular seminar, I find that I am a) here to learn, b) hoping that the staff I have here and the staff from other agencies will go back and challenge some of the policies of their organizations, to make sure we are moving in the right direction.

And, finally from a dischargers standpoint, this a very historic year. The State Water Resource Control Board, which once every ten years looks at water rights, and water distribution throughout the state, finally held the same set of hearings this year on the Bay-Delta with a water quality element. For the first time they are now balancing the impact of water use in the state with impacts on water quality. The Bay-Delta Pollution Policy Document is due out in the next couple of weeks. This is a very significant document, and one of the cornerstones of that document as I see it is the issue we will deal with in the next couple of days. Understanding bioavailability, how toxics we discharge into the environment how they find their way into biota, into the food chain, is very important. More and more often, when I go and talk to the public, and I say "Do you realize that the toxic metals that are being discharged to the bay from point sources in some cases have been reduced by over 90 percent?" I get a blank stare. The public wants to know about the other 10 percent, and about the years of unregulated discharge into the Bay.

So on the behalf of the Bay Area Dischargers Association and the Aquatic Habitat Institute, I welcome you here today. When I look around the room I see a lot of people I know, but I also see many new faces. I do not know why all of you are here today: some of you are from the University some are from government entities, some of you are from utilities, some of you have been sent here with your way paid, some of you have paid on your own. I would just say this; I think all of us are here to learn. And, I challenge you to keep your minds open. The speakers are going to be presenting some very new data; please challenge them. Challenge them with ideas that you hold on what is happening in San Francisco Bay and I think all of us will come out better for it.

KEYNOTE ADDRESS

Cindy Deacon Williams

Chief of Staff

for

Assemblyman Robert Campbell

As Margaret indicated I am with the office of Assemblyman Campbell, who is a very strong supporter of the Institute. I am delighted to see the kind of turn-out that we have today, both as a statement of interest for the work of AHI as well as an indication of the level of interest in the protection of the Bay.

As you know, there has been a real significant change over the years in the concerns associated with the Bay. In the 1950's concerns with the health of the Bay focused literally with getting the trash out of the water. The floating garbage made it obvious that people needed to do something, and there was a big effort to clean up the Bay. That sort of gross element was fairly successful. It is not likely you are going to go out and see trash floating on the surface any longer. Today we are dealing with more exotic and less obvious items of contamination.

As the seminar's program illustrates, we are no longer concerned with the improper disposal of lawn clippings and rotten fruit. We are now concerned with things like trace metals, and TBT, and PCB's. We have all heard jokes and have probably told jokes about the necessity of becoming experts on alphabet soup. The sad thing is, there is a large degree of truth to those jokes. People in a position like mine and my boss' are heavily dependent upon you all interpreting the alphabet soup and letting us know what it means. Proposition 65 is an excellent example of the kind of general public concern for these strange things floating around in our water that we can't see or taste. As a decision makers, legislators are under extreme pressure daily to make sure our constituents have a

healthy place to live and good water to drink. As we have many other issues to deal with, we are heavily dependent on your interpretation of what's going on out in the Estuary.

Many people have dubbed the new problems in the Bay and Delta as sort of "silent killers" because to the uninformed eye the Bay and Delta couldn't look better than it does today. Seldom do we have the situation where we've got an obvious outrage that results in massive fish kills or destruction of bird colonies. The water glitters in the sun light, it smells good, it feels great when it brushes up against you in the wind. We are dealing with problems that are typically chronic in nature. You run into it when you pull up a lesioned striped bass. All of a sudden, the impression and the feel of the Bay and Delta changes dramatically.

Modern society without a doubt is slowly poisoning the Bay. Fortunately we are trying not to. I think prospects are pretty good that we are headed in the right direction at this point but, we can't give up. We have to keep working.

Numerous indicators of the problems and difficulties exist, with loss of wetlands acreage to the decline of the striped bass index. From most of the people we deal with in the legislative office, however the kind of indicators that come home the hardest are the warnings regarding fish in the Bay. And, it says, "because of elevated mercury levels no one should eat more than four meals a month of any striped bass from the San Francisco Bay Delta region. Women who are pregnant or who may become pregnant, nursing mothers and children under the age of six should not eat fish from the area. Because of possible ingestion of parasitic organisms no fish of any kind from the Bay Delta region should be eaten raw." Those are the kinds of things that our constituents come up against, and they are understandably concerned not only for the potential implication of them eating fish, but also because half of our district drinks the water from the Delta. If it is causing those kinds of warnings for fish consumption, they are really worried about what it is doing to them because they are drinking the water. The sad fact, of course, is that the San Francisco Bay Delta is not an anomaly, similar warnings, although they are for different contaminants, exist in the regulations for the Salton Sea, the Santa Monica Bay, LA Basin,

Grasslands, Clear Lake, Lake Nacimiento, Lake Berryessa, Lake Herman and the Guadalupe River Reservoir Region. Fortunately as indicated earlier, as a society, we are getting a handle, or think we are getting a handle on the situation. We can only hope that we are acting in time.

There are numerous sources of Bay and Delta contamination. Contaminants from agricultural drainage enter the Delta from the Sacramento and San Joaquin rivers and from the Delta itself. Industries along the margins of the water collectively add their share of the contaminants. Nonpoint source run off and non-source discharges also do their share. Much of the problem is exacerbated because of the phenomenal reduction in Bay and Delta marshes. I remember as a child growing up in Las Vegas hearing about the new information and new discoveries of how, if we really worked hard to preserve the marshes in the Las Vegas wash they would act as a natural clean up for the municipal discharge before it entered Lake Mead and this was considered to be a grand and wonderful discovery.

Unfortunately, in the Bay and Delta we have already lost many acres of wetlands and therefore significantly reduced the natural clean up ability of the region. It doesn't look like there is a whole lot of slow down or recovery or replacement of some of that lost acreage. Changing water patterns have also left their mark and that's probably one of the biggest issues that floats around the legislature with about a two-year regularity. The location of the salt water/fresh water mixing zone has been shifted, flushing flows have been reduced, all as an out-growth of water management decisions who's focus has been on the deliverance of the water rather than the health of the Bay. No one party is culpable. There is plenty to go around. However, from this point forward I believe, and more importantly Assemblyman Campbell believes, that we are obligated to critically examine all of our choices and all of our decisions with our eye firmly on protection and restoration of the Bay and Delta as a primary goal.

I am sure all of you are far more familiar with the technical data than I am and that perhaps explains some of the problems that you see in policy decision-making. There

is truthfully some disarray and illogic to some of the management decisions. Part of this is undoubtedly due to the fact that many of the decisions are made not by the technical experts, but by well-intentioned and well-to-moderately informed lay people. We do depend on you for interpretation and this process of governance saddles you with a very heavy obligation. You not only have to collect the data, analyze the data and come up with a recommendation, you then have to look at what you have collected, analyzed and recommended, delete all of the jargon, crunch it down into at most a five minute's worth presentation and get it across so that we have a full and total understanding of what the problem is and what we need to do from here. Now that is a pretty tall order and I have great sympathy for you, but from our perspective you have to understand that legislators have to deal with approximately 7,000 different bills every session. Those bills deal with everything imaginable, and there is absolutely no way that anyone can be an expert in everything that comes before you. What you have to do is to try very hard to get as informed as you can and make your best decision. More often than not, what happens is a legislator ends up casting a vote based on a fundamental philosophic approach in what they think they heard.

That is why it is so critical for you to make sure that what they hear is not only accurate but clear. There is not the kind of background to readily absorb a lot of the information you are trying to get across. Our office is probably unique to a certain extent because we have someone on staff, namely me, that had some training in biology. So at least most of the jargon doesn't run over the top and I have got some basic understanding on how it fits. My specialty was endangered species. So when you start talking to me about water quality I run into things I really don't have a whole lot of fundamental understanding about and background on. You have got to realize we are probably better off than most of the other offices up there. There are a lot of folks on staff up there that are very intelligent and have worked long and hard to educate themselves.

The problem is the integration of information. Whether it is new information that has to be integrated into what we think we already know or whether there is, from your perspective, integration of new information into a million reports that you know are already

out there that unfortunately were developed without any real strong eye to standard methodologies and procedures. It truly does at this point take an expert to be able to hazard a guess as to what has happened and what will likely happen despite the mountains of historical data that we have.

I know that is why the Aquatic Habitat Institute is so generally loved by the Legislature. From our view, their job is to tell us what it all means, integrate the information, come together and act as a repository of all the historical data, try to coordinate all of the ongoing research and let us know what the heck is going on. It has to happen, I think, in a single location like AHI so that there is some plan to what we are doing.

One of the most refreshing projects that has come down the line in a long time is the Institute's Critical Review of Monitoring Studies. I can guarantee you that Assemblyman Campbell will be looking closely at the recommendations that the Institute is going to come up with in that study. As you can guess, probably one of the things that is most frustrating to a legislator is not coming into an apparently unresolvable complex problem but being told by the expert that despite the millions of dollars spent on studying it that we've got to study it some more. It doesn't fly very well. Those sorts of situations are kinds of things that shorten legislative careers.

We can't tell our constituents that we don't know what the answer is. We have to take our best shot and hope we are right. We need to at least make an effort to get something accomplished, to solve what is generally accepted as a problem. I suspect, as well, that the focus of this conference on Bioavailability of Contaminants would be the preferred approach rather than just a straight concentration measurement because you have to set your priorities and obviously the top priority has to be on the effects to the biotic community. It is nice to know what we've got in the mud and it is nice to know what we've got in the water but unless you can tell me what they are actually doing to the biotic community it doesn't tell me anything. Unless you can tell me what we need to do to try to short circuit the magnification in the food chain it doesn't get me anywhere. The

Legislature is really not in the pure research mode, we're into the real hands-on problem solving, whether or not we have the information to solve the problem.

As I alluded to earlier and as you all undoubtedly know, human activity has made its mark on the Delta. Our influence began at least as early as the 1700's with the arrival of the Spanish soldiers and missionaries. Marked and deleterious changes have occurred in the contour of the Bay and its tributaries and these changes were accelerated, of course, during the Gold Rush with the hydraulic mining and silting over of spawning gravels, and the filling of channels that reduced the capacity of the system to carry heavy run-off. What that lead to was massive flooding. So we diked, dredged and drained and tried to reclaim the land so it was safe. This lead to the reduction of the once more than 500,000 acres of marsh land to just a fraction of that today. Also with the increase in population the area of valley farmland under irrigation saw a vast and dramatic increase, and that lead to not only increased agricultural run-off but increased diversions, and that has also had obvious and significant impacts on the Bay and Delta.

Precisely what? Many folks will disagree. The situation we find ourselves in the Legislature is that because no one can tell us for sure, precisely what was caused by what, we back into our corner, and depending on what areas of the state we represent, we claim that it is the result of agricultural run-off or it is all the result of urban run-off, or it was all the result of dredging, or it was all the result of upstream diversion. Until we get some good solid attempts to integrate information to gain an overall perspective, I don't personally think we are going to get the actions and solutions we want.

Along with urbanization and industrialization there has been degradation of the water. I am about to read a section from an old newspaper article that indicated in '86 there were at least 30 municipal and 40 industrial waste water management facilities. And despite the dramatic improvements that Walter alluded to earlier, where you've got a 90 percent clean up, at that time we were looking at about 330 tons of potentially toxic waste material finding its way into the Bay each year. That's why our constituents, and consequently my boss, is focused more on what is still going in the bay rather than on

what has already been removed. We read those kinds of things and can't imagine a mountain of toxic waste that size being dumped voluntarily into the Bay each year. There has got to be a better way. We are looking to you all to tell us what it is. It is evident, of course, that the Bay is sensitive to what we do and to the changes that we cause and whether we are intentional or not.

As I mentioned earlier I am truly glad to see all you here today to discuss the problems. I am hoping you are also going to be floating some potential solutions. That is what it comes down to. One of the things that I heard early on, from my father actually, was an observation that if what is unique on being human is the ability to know, then every time we cause an extinction we limit our ability to be human. I think extinction of an ecosystem is at least as critical, and probably more so, if for no other interest than an enlightened self interest and a call to our ability to be human, I think we need to devote ourselves very heavily to the cause of improving the quality and restoring of the ecosystem.

Surely the Bay and Delta system is worth it. I am obviously preaching to the converted, that is why you are here. But one thing you need to do is carry that message on and out and you need to understand how vital it is for us, either as staff or my boss in a decision-making position, to hear from you clearly and directly without the 90 percent probability. Just tell us what is going on because that is the only way we can work on it and deal with it in the Legislature. We can't pass a law that only works 95 percent of the time. We can't pass a law that only deals with the situation if that probability is true. Where passing a law or not passing a law is based on what our best guess is, and our best guess is uninformed unless you give us the information on which to base it.

Thanks very much.

TRACE METAL ASSOCIATIONS IN THE WATER COLUMN OF SOUTH SAN FRANCISCO BAY CALIFORNIA¹

by

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Abstract

Spatial distributions of copper (Cu), zinc (Zn) and cadmium (Cd) were followed along a longitudinal gradient of dissolved organic carbon (DOC) in South San Francisco Bay (herein referred to as the South Bay). Dissolved Cu, Zn and Cd concentrations ranged from 24 to 66 nM, from 20 to 107 nM and from 1.2 to 4.7 nM, respectively, in samples collected on five dates beginning with the spring phytoplankton bloom and continuing through summer, 1985. Dissolved Cu and Zn concentrations varied indirectly with salinity and directly with DOC concentration which ranged from 2.1 to 4.1 mg L⁻¹. Available thermodynamic data strongly support the hypothesis that Cu speciation may be dominated by association with dissolved organic matter. Analogous control of Zn speciation by organic complexation was, however, not indicated in our computations. Computed free ion activity estimates for Cu, Zn and Cd were of the order of 10⁻¹⁰, 10⁻⁸ and 10⁻¹⁰ M, respectively. The availability of these metals may be among the factors regulating the growth of certain phytoplankton species within this region of the Estuary. In contrast to dissolved Cu, dissolved Cd was directly related to the concentration of suspended

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particulate matter, suggesting a source of dissolved Cd coincident with elevated particle concentrations in the South Bay (e.g., runoff and solute desorption). Consistent with work in other estuaries, partitioning of all three trace metals onto suspended particulates was negatively correlated with salinity and positively correlated with increases in particulate organic carbon associated with the phytoplankton bloom. These results for the South Bay indicate that sorption processes influence dissolved concentrations of these trace metals, the degree of this influence varies among metals, and processes controlling metal distribution in this estuary appear to be more element-specific than spatially-or temporally-specific.

Introduction

Understanding the transport and distribution of solutes in estuaries is for many reasons a highly complicated task. This environmental complexity is very evident in studies of trace metal reactions in estuaries. Hydrodynamic processes affect sediment transport and, thus, metal sorption processes (Delfino and Otto, 1986; Helz and Sinex, 1986). Advective transport influences movement of certain metals from bottom sediment pore waters (Delfino and Otto, 1986). Coagulation of riverine particles may remove trace metals from solution, or particle-bound metals may be desorbed as salinity increases (Salomons, 1980; Li *et al.*, 1984; Ackroyd *et al.*, 1986). These sorbed metals may be associated with various mineral phases, e.g., clays (Gibbs, 1986), oxide coatings (Balls, 1986), or with particulate organic matter (Davis, 1984; Laxen, 1985; Wangersky, 1986). In the solution phase, speciation of metals may be affected by organic complexation (van den Berg *et al.*, 1987). The transport of degraded plant material and the influx of marine humic acids associated with algal blooms have been implicated as important sources of such organic complexing agents in estuaries (Delfino and Otto, 1986; Jones *et al.*, 1986). Although physical and chemical factors affect primary productivity, algae and other microbes may in turn alter trace element cycling. The biota may serve as a source of organic chelators (Lumsden and Florence, 1983), a sink for solute sorption (Boyle *et al.*, 1982; Froelich *et al.*, 1985; Kuwabara *et al.*, 1986) and a catalyst for particle flocculation and sedimentation (Sholkovitz, 1976; Avnimelech *et al.*, 1982).

As one of the large estuarine systems in the world to experience the effects of urban and industrial development, San Francisco Bay exemplifies the complexity of estuaries. It has been described as a three-component system: the northern reach (including the Suisun and San Pablo Bays), the Central Bay and the South Bay (Conomos, 1979). Temporal trends in primary productivity, biomass and species composition in the northern reach are significantly influenced by physical processes related to freshwater input from the Sacramento and San Joaquin Rivers. In comparison, phytoplankton biomass in the South Bay is more sensitive to grazing pressure as well as to the physical effects of tidal fluctuation and river discharge (Cloern *et al.*, 1985). Although the South Bay is typically well mixed, an algal bloom occurs each spring concurrent with the establishment of a vertical salinity gradient.

Several studies have examined the spatial and temporal distributions of dissolved trace metals within San Francisco Bay. In the northern reach, Eaton (1979a) observed that dissolved trace metal distributions reflected physical mixing, chemical removal and multiple inputs within the estuary. Gordon (1980) reported conservative mixing of dissolved trace metals in the northern reach and an undefined metal source in the upper estuary at low salinities. Girvin *et al.* (1978) observed a concentration gradient for dissolved Cd, Cu and Zn in the South Bay and a temporal increase in concentrations during the spring and summer during two drought years. In general, Cd was found to be predominantly partitioned in the dissolved phase, Cu was about equally associated with the solid and solution phases, and Zn was primarily particle-bound.

In this paper we assess potentially important mechanisms that control trace metal distribution in the water column of South San Francisco Bay. Chemical, biological and physical data are examined from five sampling surveys conducted between the spring algal bloom period of March 1985, and September 1985. Large climatic and hydrographic changes occur between sampling dates as a result of the well-defined wet and dry seasons, and dramatic changes in many chemical and physical parameters result, in part, from changes in phytoplankton density (Table 1). The data indicate that, 1) Cu speciation is regulated by complexation with dissolved organic matter (DOM), 2) elevated dissolved Cd

Table 1. Physical and chemical parameters collected from five sampling cruises in the South San Francisco Bay in 1985 including: suspended particulate mass in mg L^{-1} (SPM), chlorophyll-*a* in $\mu\text{g L}^{-1}$ (CHL-*a*), particulate organic carbon in $\mu\text{g L}^{-1}$ (POC), dissolved inorganic carbon in mg L^{-1} (DOC), salinity in g solid per g solution (SAL), and dissolved and particulate trace metal concentrations. Confidence intervals (95%, N=3) for trace metal concentrations about the mean are also presented. Station numbers refer to midchannel sampling sites as depicted in Figure 1, with increasing numbers corresponding to a southward direction away from the estuary mouth. The column for freshwater discharge data (DIS) represents in m^3s^{-1} the sum of freshwater inputs to the South Bay by local riverine and municipal sewage treatment sources. The percent DIS attributable to water treatment plant effluent is given in parentheses.

DATE	DIS	Station No.	SPM	CHL-a	POC	DOC	SAL	DISSOLVED (nM)			PARTICULATE ($\mu\text{g/g}^{-1}$)		
								Cu	Zn	Cd	Cu	Zn	Cd
29/3/85	17.4 (31)	27	11.3	21.5	1250	2.9	0.0250	47+3	32+3	1.2+0.4	45.3+0.5	43.2+3.2	0.36+0.01
		30	13.5	35.2	1720	3.6	0.0234	55+5	57+3	2.4+0.4	56.1+1.8	79.5+4.5	0.83+0.01
		32	16.1	32.4	1870	3.5	0.0220	53+6	61+3	2.8+0.4	54.1+2.9	87.6+1.0	0.87+0.01
		36	17.2	37.4	1180	4.0	0.0197	66+5	107+5	4.4+0.2	65.2+0.9	154.1+8.0	1.58+0.03
16/4/85	6.7 (79)	27	2.1	7.3	400	2.7	0.0271	55+2	43+8	2.3+0.2	51.1+2.0	54.8+3.8	0.59+0.01
		30	2.4	5.0	390	2.8	0.0261	58+3	49+5	2.8+0.5	50.9+2.9	63.7+2.6	0.69+0.02
		32	7.9	9.5	540	2.8	0.0250	53+9	50+5	2.8+0.4	48.8+3.5	65.7+0.8	0.81+0.02
		36	11.6	6.3	530	3.0	0.0223	58+6	62+8	4.3+0.4	53.3+1.2	85.0+2.4	1.41+0.05
29/4/85	6.3 (83)	27	3.5	2.9	230	2.6	0.0268	53+8	47+5	3.1+0.5	46.7+7.9	60.4+2.0	0.83+0.06
		30	2.1	2.8	250	2.6	0.0265	57+2	43+3	3.1+0.4	48.1+0.7	54.8+5.1	0.81+0.05
		32	9.0	3.6	370	2.4	0.0261	44+6	46+9	3.6+0.2	38.2+3.9	58.0+2.2	1.12+0.06
		36	8.5	1.7	300	2.6	0.0245	57+2	49+5	4.0+0.7	46.6+2.3	64.0+1.5	1.26+0.15
9/7/85	6.2 (88)	27	0.1	1.2	200	2.0	0.0301	46+2	20+6	2.1+0.3	39.6+1.0	21.5+2.7	0.51+0.01
		30	0.6	1.0	180	2.3	0.0295	49+3	31+8	2.3+0.4	41.0+1.7	36.3+4.4	0.54+0.02
		32	2.8	1.5	250	2.3	0.0290	46+2	34+3	2.4+0.1	41.2+2.2	39.6+4.1	0.65+0.03
		36	9.3	1.5	330	3.1	0.0271	49+2	37+1	3.6+0.1	44.2+2.0	45.0+4.0	1.06+0.03
10/9/85	5.3 (88)	27	1.9	1.9	200	2.1	0.0316	39+2	32+3	1.4+0.1	32.9+1.1	36.6+2.6	0.36+0.02
		30	2.0	1.2	200	2.1	0.0316	39+2	32+2	2.0+0.4	34.1+1.0	37.1+4.0	0.48+0.03
		32	4.5	2.4	250	2.1	0.0311	36+3	44+2	2.7+0.2	32.0+0.8	50.7+6.8	0.70+0.09
		36	20.7	7.2	400	2.4	0.0286	24+5	47+6	4.7+0.3	22.1+0.5	53.2+3.3	1.40+0.55

appears to be coincident with elevated suspended particulate mass concentrations, but less dissolved Cd is observed when particles with elevated POC are present, and 3) temporal and spatial variability in the chemical character of the DOM and mineralogical composition of the suspended sediment are not pronounced.

Materials and Methods

On each of five sampling dates, surface water (1 m depth) was collected from a small fiberglass boat at four mid-channel stations along the longitudinal axis of South San Francisco Bay for trace metal and organic carbon analyses. Subsequent reference to sampling sites in the text, tables and figures are in terms of U.S. Geological Survey sampling station numbers 27, 30, 32 and 36 (Fig. 1) with higher station numbers representing greater southward distance from the estuary mouth at the Golden Gate Bridge (31.2, 42.4, 48.9 and 57.0 km, respectively, along the center of the main channel). Mean lower low water depths for stations 27, 30, 32 and 36 were 11.0, 12.2, 13.1, and 7.0 m, respectively. Additional surface water samples were collected simultaneously from a research vessel positioned approximately 100 m downstream from the small boat. These samples were analyzed for salinity (Lewis, 1980) and concentrations of particulate organic carbon (POC), suspended particulate matter (SPM), and chlorophyll-a, using methods specified by Wienke and Cloern (1987).

Immediate initial processing of surface water samples for dissolved and suspended particulate analyses was done on board. Suspended particles were collected on acid-washed 142-mm diameter, 0.4 μm pore size polycarbonate filters (Nuclepore). Particulate-bound trace metals were extracted with 0.1N nitric acid (HNO_3) for 2 h. Quartz-distilled HNO_3 (6 M) contained $<2 \times 10^{-9}$ M total Cu or Zn and $<1 \times 10^{-10}$ M total Cd. After particles were separated from the extractant by filtration, the filtrate was refrigerated for subsequent trace element analysis. Samples for dissolved organic carbon (DOC) analysis were filtered through furnace-treated glassfiber filters (Whatman GF/D) and preserved by refrigeration and addition of *ca.* 50 μL of a saturated mercuric chloride solution per 20 mL sample. DOC was measured on a Dohrmann carbon analyzer by persulfate and ultra violet oxidation. Dissolved trace metal samples were filtered through acid-washed 47 mm

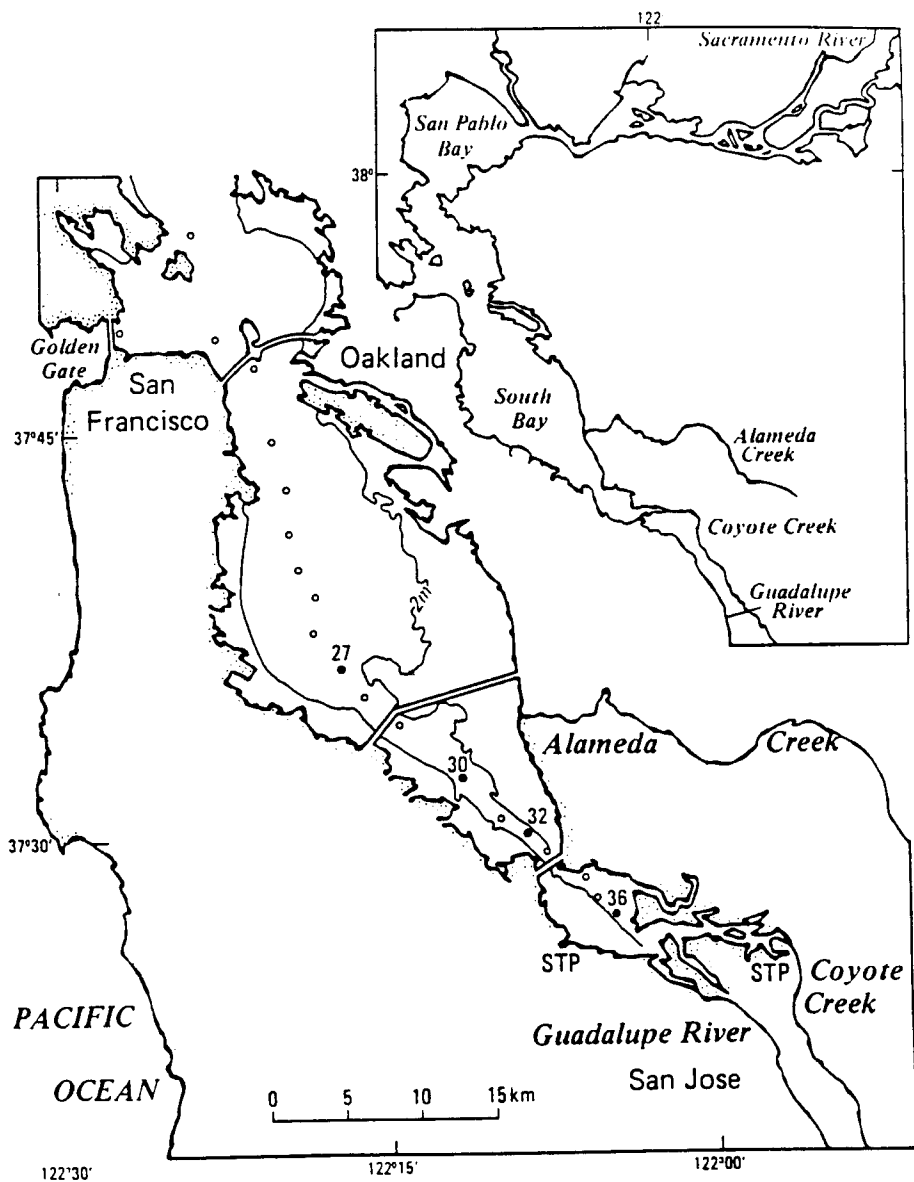


Figure 1. Mid-channel sites in South San Francisco Bay where surface water was sampled to examine processes affecting trace metal distributions. Major freshwater sources from riverine and sewage treatment plant (STP) inputs are also depicted. Longitude and latitude is shown for the South Bay and in the figure insert, which provides an overall view of the Bay.

diameter, 0.4 μm pore size polycarbonate membranes. A fluoroethylene polymer filter holder mounted on a resin kettle (Kuwabara, 1980) was used to minimize metal contamination during sample processing. After filtration, samples were acidified to pH 2 with HNO_3 and refrigerated. Dissolved trace metals were extracted and concentrated by a cobalt coprecipitation method (Bloom and Crecelius, 1984). Trace metal analyses were performed by stable platform graphite furnace atomic absorption spectroscopy with Zeeman correction. Confidence intervals (95%, $n=3$) for trace metal measurements were typically <10% of the mean concentration (Table 1). However, confidence intervals for dissolved Cd concentrations, with low mean concentrations relative to other metals, were as high as 33% of the mean.

Initial observations of dissolved and particulate trace metal distributions indicated a need to examine the spatial and temporal variability of the chemical composition of inorganic suspended particles and DOC. On three subsequent dates at Stations 27 and 32 (Fig. 1), gram quantities of suspended sediment were collected by hollow fiber tangential flow filtration (Kuwabara and Robinson, 1987) for major elemental analyses by lithium metaborate fusion after sequential extraction (Tessier 1979; Lichte *et al.*, 1987). Sediment samples (before extraction) were also analyzed by X-ray diffraction for mineralogy. As a crude indication of the spatial and temporal variability in the chemical character of the DOC in the South Bay, DOC was also extracted to determine concentrations of humic substances (Thurman and Malcolm, 1981) on these dates.

Results

The minimum salinity observed in the South Bay during any sampling was 0.0197 (expressed herein in terms of g solids per g solution, or 10^3 parts per thousand). Salinity increased with proximity to the mouth of the Bay in all five profiles, as expected in the main channel. Although the spring phytoplankton bloom in March was distinctively represented by elevated Chlorophyll-a and POC concentrations (Tables 1 and 2), spatial trends for both parameters were not consistent. Both chlorophyll-a and POC generally increased with decreasing salinity in individual profiles, but the concentrations sometimes

peaked at Station 32 rather than 36 (the southern-most sampling site) or decreased from Station 27 to 30.

Dissolved organic carbon concentrations usually increased away from the estuary mouth (i.e., going southward), mirroring salinity (Table 1). DOC concentrations generally decreased from spring through the summer. Spatial trends in dissolved Cu concentration were not pronounced and did not consistently follow SAL on any cruise (Fig. 2B). In March cruise, a weak increase in dissolved Cu occurred with distance away from the estuary mouth, and the September cruise showed the opposite trend. There was a slight southward increase in dissolved Zn concentration, which was most discernible during March (Fig. 2B). Dissolved Cd increased toward the south in all profiles, but in contrast to Cu and Zn, that increase was pronounced in September (Fig. 2C). Assessment of temporal changes in metal concentrations at individual sites must be interpreted carefully, because samples were not taken during the same tidal phase on different sampling dates.

Table 2. Correlation coefficients for parameters measured in South San Francisco Bay (underlined values are significant at the 0.01 level for N=20 per parameter).

	SPM	CHL-a	POC	DOC	Dissolved		Partitioning Coefficient			Zn
					SAL	Cu	Zn	Cd	Cu	
CHL-a	<u>0.68</u>									
POC	<u>0.67</u>	<u>0.95</u>								
DOC	<u>0.67</u>	<u>0.84</u>	<u>0.78</u>							
SAL	<u>-0.65</u>	<u>-0.73</u>	<u>-0.70</u>	<u>-0.91</u>						
Dissolved Cu	-0.01	0.40	0.34	<u>0.67</u>	<u>-0.73</u>					
Dissolved Zn	<u>0.64</u>	<u>0.69</u>	0.52	<u>0.81</u>	<u>-0.80</u>	0.54				
Dissolved Cd	<u>0.57</u>	0.05	-0.04	0.37	-0.47	0.14	<u>0.61</u>			
Cu Partitioning	<u>0.72</u>	<u>0.88</u>	<u>0.89</u>	<u>0.76</u>	<u>-0.62</u>	0.20	0.54	0.08		
Zn Partitioning	<u>0.52</u>	<u>0.78</u>	<u>0.78</u>	<u>0.90</u>	<u>-0.94</u>	<u>0.78</u>	0.72	0.23	<u>0.63</u>	
Cd Partitioning	<u>0.85</u>	<u>0.71</u>	<u>0.68</u>	<u>0.80</u>	<u>-0.83</u>	<u>0.35</u>	<u>0.73</u>	0.50	<u>0.66</u>	<u>0.74</u>

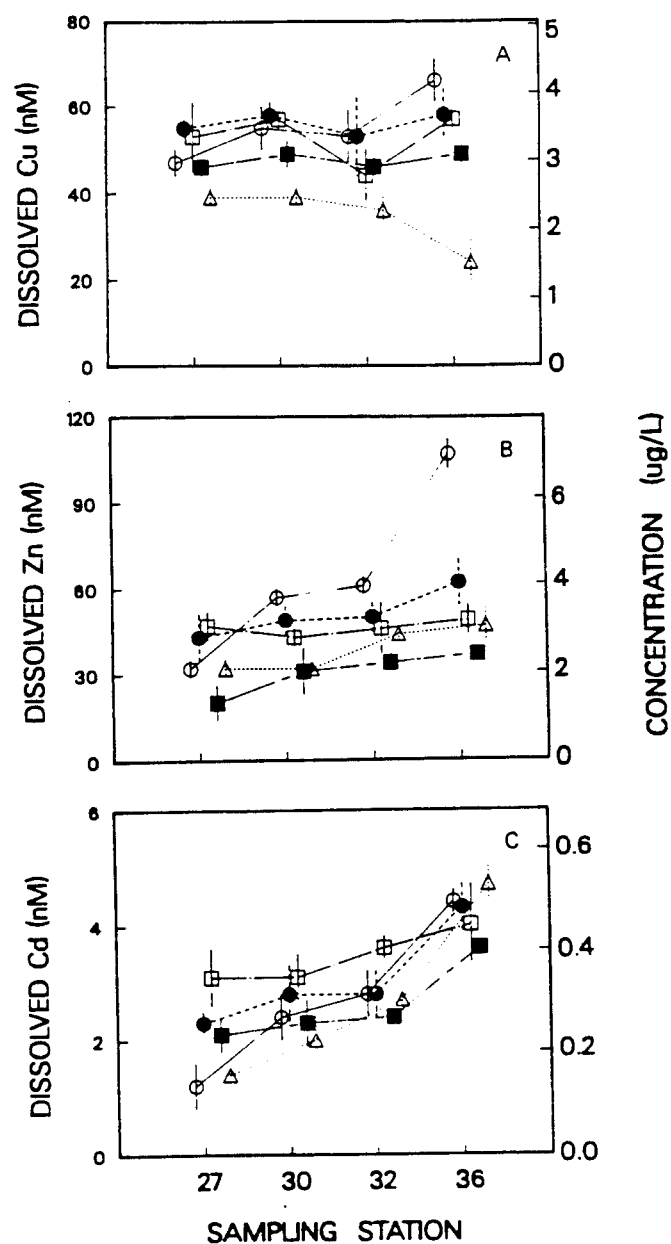


Figure 2. Spatial and temporal distributions of dissolved Cu, Zn and Cd (Fig. 2A, 2B and 2C, respectively) on each of five sampling dates beginning with the spring period of high phytoplankton biomass and high freshwater inflow, continuing through the summer period of low phytoplankton biomass and reduced freshwater inflow. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

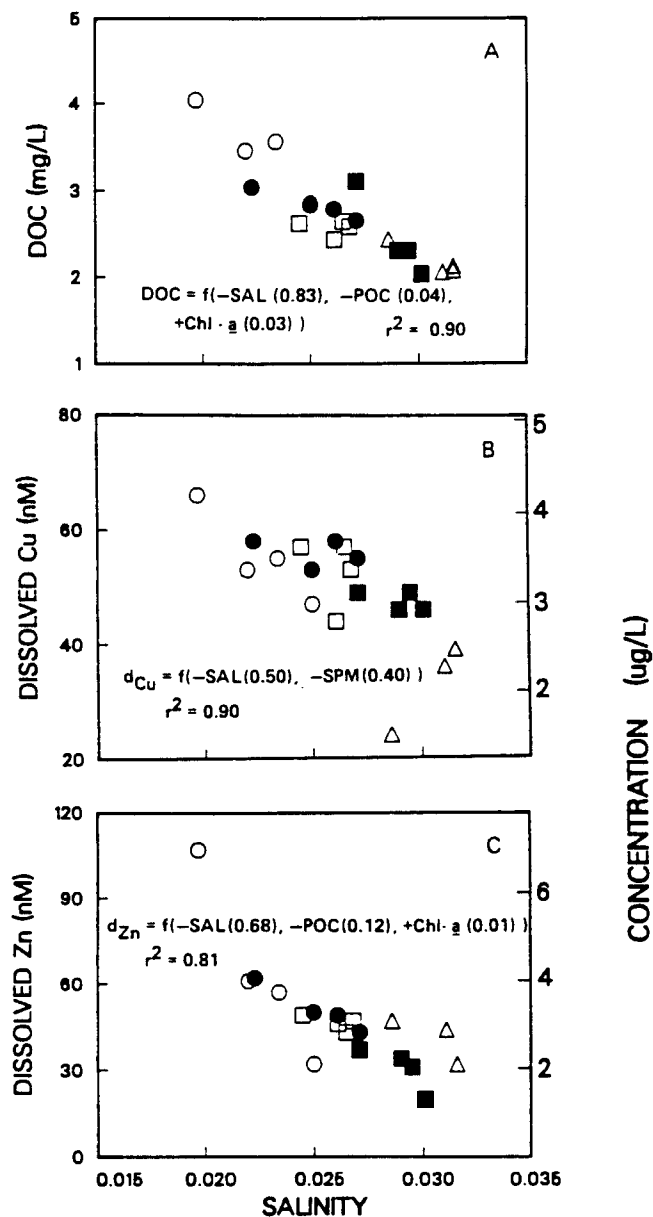


Figure 3. Coincident salinity correlation with DOC, dissolved Cu and Zn (Fig. 3A, 3B and 3C, respectively). Salinity measurements are expressed as g solid per g solution. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

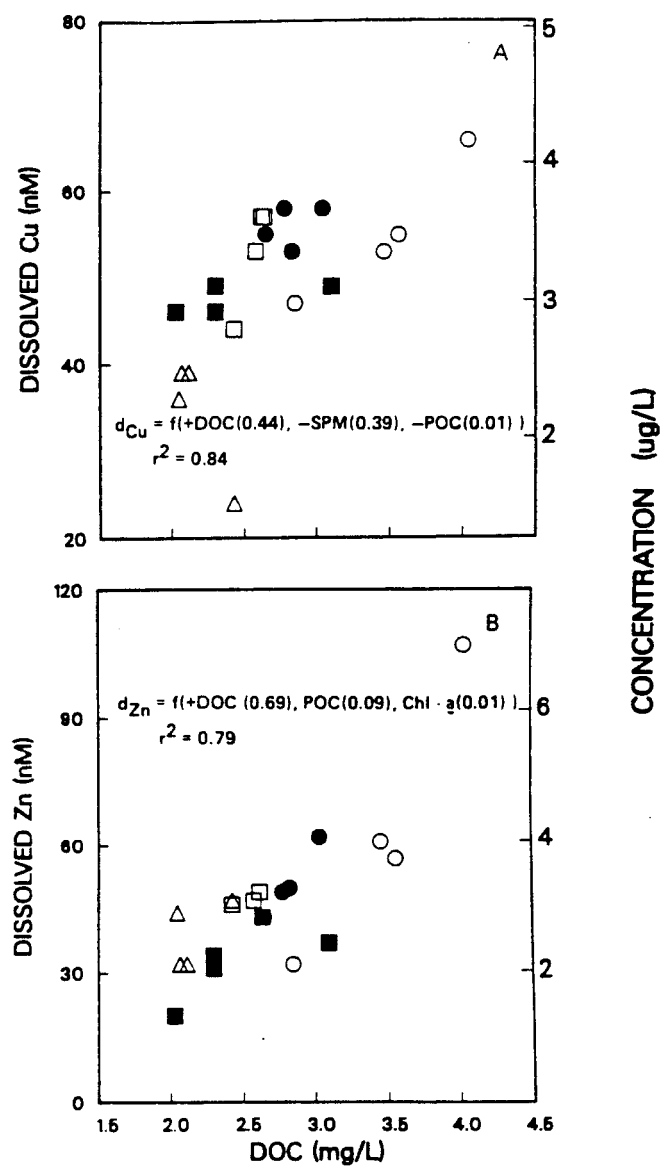


Figure 4. Relationship of dissolved Cu and Zn (Fig. 4A and 4B, respectively) with DOC. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

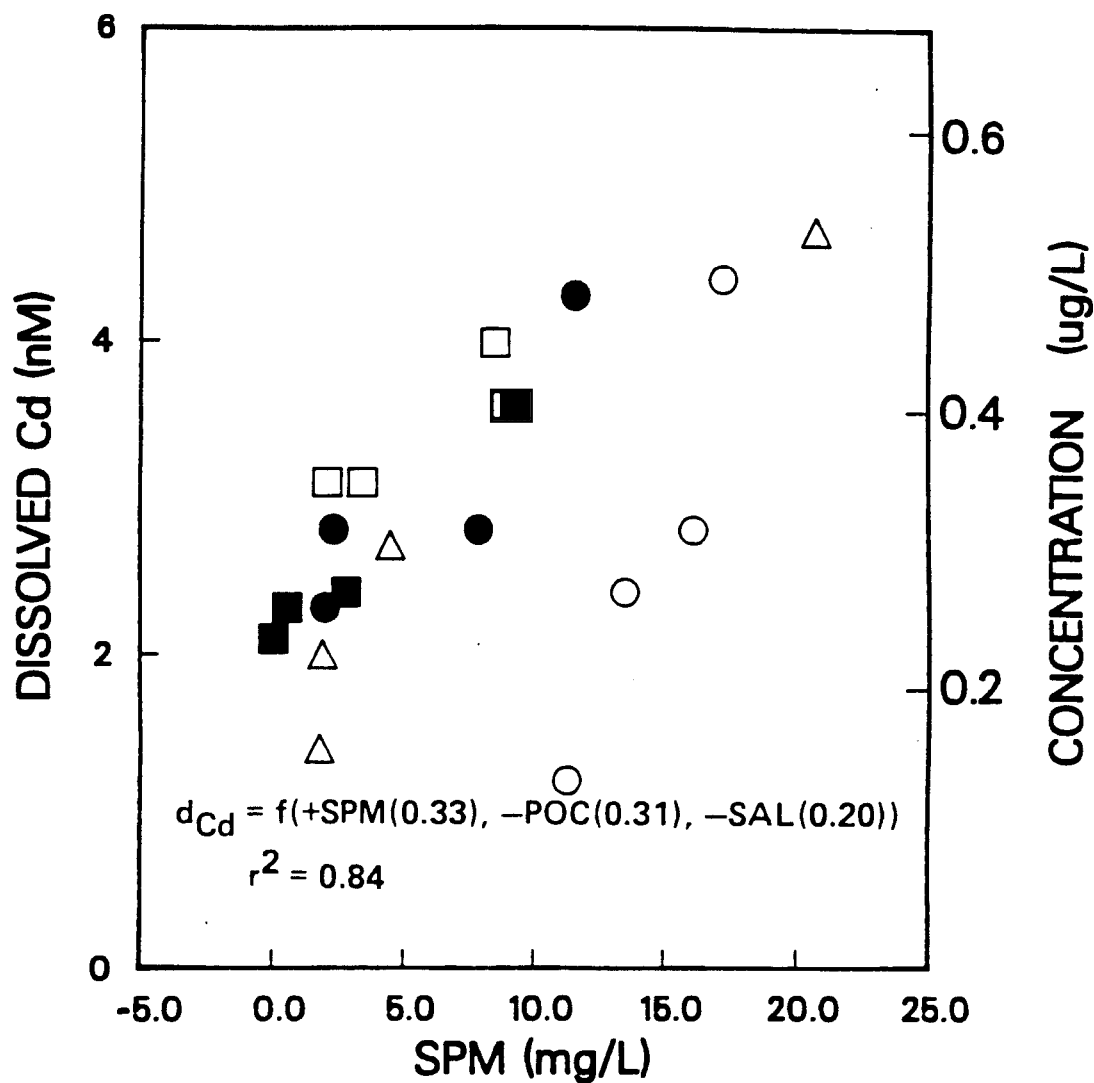


Figure 5. Regression analysis indicating a possible source of dissolved Cd from suspended sediments or undefined sources coincident with SPM (e.g., runoff). Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

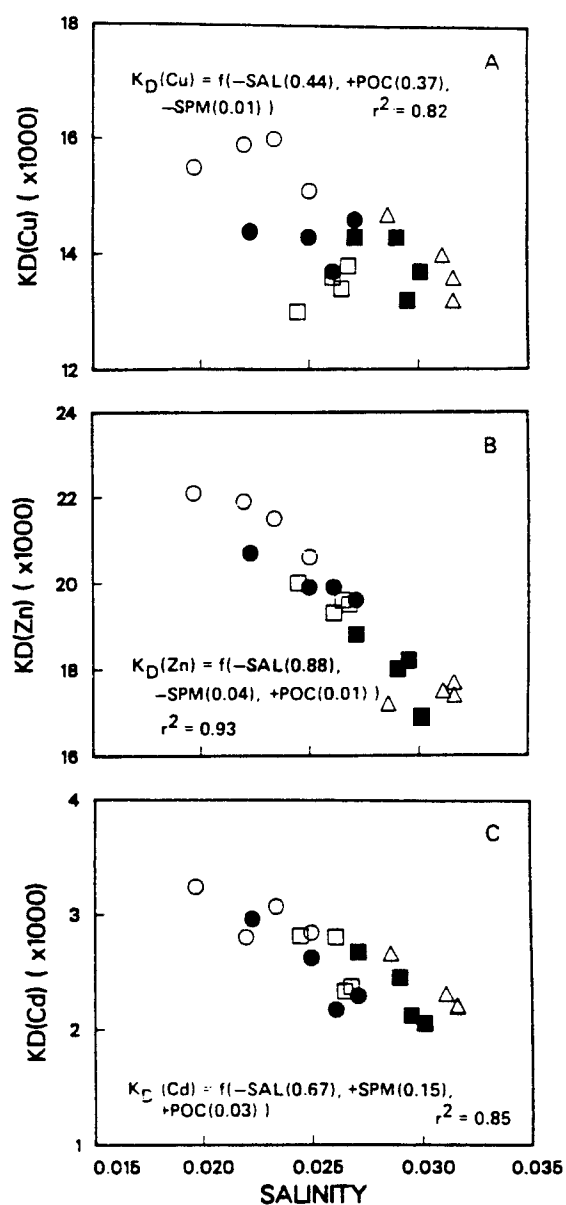


Figure 6. Partitioning of Cu, Zn and Cd (Fig. 6A, 6B and 6C, respectively) on suspended particles in South San Francisco Bay. Partitioning coefficients and salinity are presented in units of mL solution per g particles, and g solid per g solution, respectively. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

Linear regression on data aggregated from the five cruises indicated that approximately 83% of the DOC variance could be explained by changes in salinity (Fig. 3A). A similar negative correlation with SAL was observed for both dissolved Cu and Zn ($r^2=0.53$ and 0.64 respectively, Fig. 3B and 3C). Alternatively, concentrations of these metals correlated positively with DOC ($r^2=0.45$ and 0.66 for Cu and Zn respectively, Fig. 4). Dissolved Cd concentrations were also negatively correlated with SAL ($r^2 = 0.22$), but only weakly when compared to correlations of SAL with DOC, dissolved Cu or Zn (Fig. 3 and 5). Unlike Cu, dissolved Cd was positively correlated with SPM ($r^2 = 0.33$).

Partitioning coefficients (K_d) were calculated as the ratio of the mass of particulate-bound metal per unit particle mass ($\mu\text{g g}^{-1}$) over the dissolved solute mass per unit solvent volume ($\mu\text{g mL}^{-1}$). Values are expressed in units of mL solvent per g suspended particles. Partitioning of all three trace metals onto suspended particles decreased with increasing salinity ($r^2= 0.38$, 0.88 and 0.69 for Cu, Zn and Cd partitioning coefficients respectively, Fig. 6). Particle-bound copper also increased with particulate organic carbon ($r^2= 0.37$, Table 2), suggesting a transient effect on Cu partitioning due to the spring phytoplankton bloom. Particulate-bound metal concentrations in suspended sediment were higher than usually observed in surficial bottom sediment (Bradford and Luoma, 1980; Axtmann, personal communication). This may be due to differences in particle size distribution, since suspended particles typically have smaller mean particle diameters. Eaton (1979b) observed this particle size effect on metal concentrations of San Francisco Bay bottom sediment.

Results from subsequent cruises indicated that percent humic substance by carbon weight relative to total DOC was not statistically different between Stations 27 and 32 or between cruises (Table 3). The distribution of major cations in the suspended sediment was also similar, although spatial similarities appear more striking than temporal ones (Table 4). Analyses of suspended sediment by X-ray diffraction indicated that samples from both stations were mineralogically similar, with a predominance of illite and smaller amounts of chlorite and quartz.

Table 3 Results of subsequent sampling cruises to determine the humic substance fraction of the dissolved organic carbon at two stations in the South Bay. Mean values and 95% CI (N = 6) are presented for DOC and humic substance data.

Sample Station	Date	DOC (mgL ⁻¹)	%Humic substances
27	9/6/86	2.1 ± 0.5	44 ± 14
	15/7/86	2.5 ± 0.2	43 ± 4
32	9/6/86	3.0 ± 0.7	39 ± 12
	15/7/86	3.1 ± 0.4	40 ± 7

Table 4. Major elemental distribution of suspended sediment expressed in weight percent after sequential extraction, with 95% confidence intervals (N = 3). Sediment was initially analyzed in terms of oxide concentrations. Data were then normalized and transposed to the elemental state.

Element	Station 27 13/12/86	Station 27 15/7/86	Station 3 13/12/86	Station 32 15/7/86
Si	28.70 (0.99)	31.88 (0.99)	30.11 (1.50)	31.60 (0.42)
Ti	0.58 (0.02)	0.41 (0.01)	0.50 (0.02)	0.47 (0.02)
Al	10.91 (0.99)	8.89 (0.32)	9.69 (0.79)	9.00 (0.32)
Fe	6.29 (0.30)	4.55 (0.21)	5.94 (0.15)	5.10 (0.21)
Mn	0.05 (0.01)	0.04 (0.01)	0.05 (0.01)	0.04 (0.01)
Mg	2.11 (0.06)	1.63 (0.03)	2.11 (0.09)	1.75 (0.06)
Ca	0.65 (0.02)	0.70 (0.02)	0.62 (0.05)	0.62 (0.02)
Na	1.02 (0.07)	1.44 (0.04)	0.96 (0.07)	1.03 (0.06)
K	1.65 (0.09)	1.65 (0.09)	1.74 (0.12)	1.57 (0.19)
P	0.13 (0.02)	0.03 (0.01)	0.11 (0.01)	0.08 (0.06)

DISCUSSION

Cu and Zn

Although Cu and Zn profiles in the South Bay vary considerably between sampling dates (Table 1; Fig. 2), analysis of aggregated data from all cruises reveals a number of interesting correlations between measured parameters (Table 2). It is important to note that measured parameters (e.g., SPM, CHL-a, POC, DOC and SAL) are not all independent variables (Table 2). Given that particulate organic carbon dominated the suspended particles during the phytoplankton bloom, and that the annual phytoplankton bloom predictably occurs during prolonged salinity stratification (Cloern, 1984), correlations between these variables are not surprising. Thus, a regression approach cannot positively identify controlling mechanisms for trace metal distributions, but may serve as a useful exploratory tool to examine processes potentially significant among cruises.

The positive correlation of DOC and SAL with dissolved Cu and dissolved Zn raises the possibility that Cu and Zn are predominantly associated with SAL-dependent dissolved organic matter in the South Bay water column (Fig. 4). Previous studies have determined the presence and certain chemical properties of Cu-organic chelates in other estuarine environments (Sholkovitz and Copland, 1981; Mills *et al.*, 1982; Hanson and Quinn, 1983). DOC concentrations measured between 1979 and 1985 (Showalter, personal communication) also showed a positive correlation between dissolved metal and DOC concentrations near the mouth of the Guadalupe River (Fig. 1), a major freshwater source to the South Bay.

Chemical Simulations

Chemical speciation computations were employed to further examine the role of DOC in regulating metal speciation in the estuary. Using the computer program MINEQL (Westall *et al.*, 1976), Cu and Zn speciation in the South Bay were estimated using thermodynamic data of Mantoura *et al.* (1978) for dissolved organic complexation, and data of Hogfeldt (1983) for inorganic complexation. An exception was the constant for the

formation of aqueous $\text{Cu}(\text{OH})$, $\log^*\beta_2 = -16.2$, that was taken from a study that closely examined both inorganic and organic complexation of Cu (Sunda and Hanson, 1979).

A 3:1 ratio of seawater to riverine water [i.e., calculated mean salinity = 0.027, ionic strength (I) = 0.5 M] was assumed for determining major ion concentrations. End member concentrations for major ions in seawater and the Guadalupe River were taken from Brewer (1975) and Anderson *et al.* (1983), respectively. Activity coefficients for inorganic complexation were calculated using the Davies equation (Westall *et al.*, 1976). Seawater stability constants for dissolved organic complexation (Mantoura *et al.*, 1978) were used directly. Other fixed parameters for this calculation were: a) pH 8 compared to an observed range of 7.6 to 8.2, b) typical dissolved Cu and Zn concentrations of $3 \mu\text{g L}^{-1}$ (ca. 50 nM), c) a $1.2 \mu\text{M}$ concentration of dissolved organic ligand sites, based on measured humic substance concentrations and corresponding to 10^{-6} moles binding sites per mg-C in the humic substance (Mantoura and Riley, 1975; McKnight *et al.*, 1983; Davis, 1984).

Chemical equilibrium computations indicate that sites on humic materials should be primarily bound to Mg, but ca. 80% of the dissolved Cu would also be organically complexed. An alternative two-site binding model proposed by McKnight and Wershaw (1989) for Cu-organic complexation results in >90% of the total Cu complexed. Because the formation constants for Zn-humate complexes are typically orders of magnitude lower than for Cu-humate complexes (Mantoura *et al.*, 1978; van den Berg *et al.*, 1986), the calculation for Zn indicates that its speciation is controlled by inorganic complexation (primarily with chloride) with <10% of the dissolved Zn organically complexed. So although dissolved Zn concentrations correlated with DOC, our calculations do not indicate control of Zn speciation by organic complexation.

Limitations to the above metal speciation calculations bear close examination. First, chemical reactions with suspended particle surfaces were not considered in this computation. This limitation may have ecological implications, in that particle-bound metal

may increase metal bioavailability under conditions favorable for metal desorption (Kuwabara *et al.*, 1986).

Second, other values for $\log^*\beta_2$, the constant for the second hydrolysis equilibrium for Cu, have been reported and generally range between -13.7 and -17.3 (Vuceta and Morgan, 1977). Both of these $\log^*\beta_2$ values have little effect on Cu speciation with >90% of the total Cu still organically complexed. Computed Zn speciation was not discernably affected by these changes in the $\log^*\beta_2$ value for Cu. Similarly, a change of pH in our computation to either 7.6 or 8.2 (the lowest and highest measured value for our sampling period) does not alter the result that >90% and <5% of the dissolved Cu and dissolved Zn, respectively, are organically complexed.

Third, although the water column of San Francisco Bay is well-oxygenated (Smith and Herndon, 1980), dissolved sulfide could be present due to slow oxidation of sulfide diffusing from the bottom sediment. Speciation calculations suggest that over the range of sulfide concentrations observed by Vivit *et al.* (1984) during a drought year in the South Bay ($0.1\text{--}3.2 \times 10^{-7}$ M total sulfide), metal sulfide interactions could be important during times of high dissolved sulfide concentrations, but probably not important at lower concentrations.

Finally, variability in the chemical character of the dissolved organic matter could affect the applicability of the formation constants used here. McKnight *et al.* (1983) found that Cu associated with fulvic acids from 17 aquatic environments throughout the United States could be consistently modeled by 2 formation constants (i.e., for strong and weaker binding sites). Van den Berg *et al.* (1987) have, however, reported higher log stability constants for Cu-humate and Zn-humate complexes in the Scheldt Estuary of *ca.* 14 and 10, respectively. If these higher constants were used in our computations for the South Bay, both Zn and Cu speciation would be dominated by complexation with DOM. However, the log stability constants used in our calculations are conservative estimates relative to the range of published values and, in addition, do not reflect the potential for additional metal binding to dissolved organic material not efficiently isolated by

conventional methods like XAD-8 extraction. Ionic strength corrections were not made to the formation constants for metal-organic complexation due to a lack of thermodynamic data. At pH 8 the ionic strength effect is probably not pronounced due to conformational changes in the humic substances and because of additional complexation of hydrolyzed metal species by organic ligands (Cabaniss and Shuman, 1987). A conventional Davies correction, for example, would greatly over estimate the ionic strength effect on metal-EDTA formation constants (Anderegg, 1977). In summary, dissolved Cu is quite likely associated with DOM, except possibly during periods when dissolved sulfide is elevated in the water column. Correlation between Cu, DOC and SAL raises the possibility that organically bound Cu is transported through the South Bay without significant net interaction with particles. Zn association with DOC is supported only if relatively high formation constants like those reported by Van den Berg *et al.* (1987) are employed. However, the potential importance of such complexation cannot be excluded because of the observed Zn, DOC and SAL correlations.

Ecological Implications

It has been well demonstrated that the uncomplexed species of Cu and Zn control the bioavailability of these metals to phytoplankton (Sunda and Guillard, 1976; Anderson *et al.*, 1978), and that submicromolar activities of these metals can cause toxic effects on various algal species (Gavis *et al.*, 1981; Anderson *et al.*, 1978; Kuwabara, 1981).

Estimates for Cu, Zn and Cd free ion activities computed from our chemical simulation are of the order of 10^{-10} , 10^{-8} and 10^{-10} M, and are similar to threshold toxicity concentrations determined in the studies cited above. Using bacterial bioassays, Sunda (1987) estimated similar activity for the free cupric ion at similar total Cu in the marine plume of the Mississippi River.

The phytoplankton community structure in South San Francisco Bay is dominated by diatoms and small flagellates including cryptophytes (Wong and Cloern, 1981; 1982); dinoflagellates are rare. Phytoplankton communities in many other estuarine environments including Tomales Bay, a pristine estuary in close proximity to San Francisco Bay, are at

least periodically dominated by dinoflagellates (Graneli *et al.*, 1986; Cole, personal communication). Evidence exists that elevated free metal ion activities favor the dominance of diatoms over dinoflagellates (Mandelli, 1969; Brand *et al.*, 1986). Brand *et al.* (1986) found that Cu free ion activities between $10^{-10.4}$ and $10^{-11.1}$ M caused 50% inhibition of reproductive rates in four species of neritic dinoflagellates, while similar growth inhibition of eight neritic diatoms was observed between $10^{-9.5}$ and $10^{-10.5}$ M free Cu ion activity. Differences in Cd sensitivity between neritic dinoflagellates and diatoms were less pronounced, with 50% growth inhibition for dinoflagellates observed between $10^{-8.7}$ and $10^{-9.6}$ M free Cd ion activity versus a range of $10^{-8.1}$ and $10^{-9.4}$ M for diatoms. The order of magnitude of the free metal ion activities estimated for South San Francisco Bay combined with the small contribution of dinoflagellates to the phytoplankton community, raise the possibility that elevated free metal ion activities affect the phytoplankton community structure in favor of metal-tolerant species in the estuary.

Reactions with Particles

As a rule, our dissolved trace metal data do not show large deviation from a linear fit of metal concentration to salinity. Thus, trace metal removal is not detectable, except possibly with Cu during the final September cruise (Fig. 3B). On that date SPM was the highest observed in the study and Cu concentrations were the lowest (lower than suggested from the relationship with DOC) (Table 1; Fig. 4A). In the Tamar Estuary suspended particulate loads of 200 mg L^{-1} and salinities of <0.005 were accompanied by removal of dissolved Cu, Zn and Mn (Ackroyd *et al.*, 1986). Although these suspended loads and salinities are well outside the range of values observed in this study, they demonstrate that removal of metals from the dissolved phase by adsorption is feasible when suspended particulate loads are high (Morris, 1986; Ackroyd *et al.*, 1986). The apparent removal from solution at station 36 was more pronounced for Cu than for Zn during the September cruise in the present study (Fig. 2A and 2B). This observation is consistent with work by Mouvet and Bourg (1983), who showed that Cu has a greater affinity than Zn or Cd for adsorption sites on River Meuse bottom sediments (surface constants of $10^{-1.8}$, $10^{-3.6}$, $10^{-3.7}$ for Cu, Zn and Cd respectively).

In May 1984 (a dry year when an algal bloom was not detected in the South Bay), high dissolved Cu (14×10^{-8} M) at Station 36 accompanied high SPM (22 mg L^{-1}), but DOC (4.5 mg L^{-1}) concentrations were nearly twice those in September 1985. The interaction of Cu, DOC and particulate material is apparently complex in San Francisco Bay and may be characterized by some annual variability in the relative importance of processes affecting Cu speciation and distribution.

Partitioning coefficients for all three trace metals decreased with increased salinity. This trend is consistent with previous laboratory and field experiments (Van de Meent *et al.*, 1985). In laboratory experiments using iron hydroxides, trace metal adsorption is typically shifted to higher pH with increased chloride concentration (Davis and Leckie, 1978; Millward, 1980; Millward and Moore, 1982). This general behavior has been attributed to changes in metal speciation due to chloro-complex formation (particularly for Cd) and increased competition by major cations in the seawater matrix for adsorption sites.

An alternative explanation for the observed decrease in K_D with salinity would be a physical mixing of marine particles, characterized by a low K_D , with estuarine particles associated with a higher K_D . The inorganic composition of the suspended sediment does not vary greatly (Table 4), but the organic character of the particles do differ within the Bay (Table 1). In fact, elevated particulate organic carbon and Chlorophyll-a, a measure of phytoplankton biomass, were associated with elevated K_D values and lower salinities (Table 2). The importance of metal association with particle-bound organic matter has been well established in previous studies (Davis, 1984; Di Guilio and Scanlon, 1985). In modeling the effect of POC on trace metal sorption, others have estimated POC concentrations assuming that the relationship between POC and the ratio of DOC to SPM is linear (Mouvet and Bourg, 1983). The rationale for this assumption is that a scarcity of adsorption sites induces higher POC values at low SPM concentrations. This assumption is not appropriate for the South Bay. Even if the March data are omitted from the regression (the only sample date when phytoplankton constitute a significant POC fraction), the ratio of DOC to SPM explains only 9% of the total POC variance.

Cadmium

The distribution of dissolved Cd, relative to Cu and Zn, depicts a more complex relationship with: (1) a relatively weak dependence on salinity (Table 2), (2) a positive correlation with SPM, and (3) less dissolved Cd with the presence of elevated POC (Fig. 5). The correlation with SPM suggests that the suspended sediment could serve as a source of dissolved Cd if Cd associated with suspended particles is redistributed into solution as the particles enter high salinity bay waters. Although, there could be undefined sources of dissolved Cd coincident with SPM concentrations (i.e., runoff), the possibility of Cd desorption from SPM in the South Bay is also supported by the observed decrease in particulate Cd with increased salinity (Table 1). In the Amazon Plume, Boyle *et al.* (1982) observed evidence of Cd desorption from suspended sediment. Total Cd (dissolved and suspended) was <0.1 nM, i.e., an order of magnitude less than concentrations observed here. Laboratory observations show that Cd adsorption is depressed with increased salinity (Salomons, 1980). Cd desorption is enhanced by CdCl^+ and CdCl_2 formation, which are less likely to adsorb than Cd^{+2} (Benjamin and Leckie, 1982), and to Mg competition for Cd adsorption sites (Balistrieri and Murray, 1982), all of which occur as particles with adsorbed Cd move from freshwater into the Bay.

When particles were rich in POC in March 1985, less Cd was observed in solution than expected from measured SPM (Fig. 5). Enhanced Cd adsorption onto amorphous iron hydroxide in the presence of humic substances has been previously observed in laboratory experiments (Laxen, 1985) under conditions of low total iron (*ca.* 10^{-5} M). Others, however, have found that this affinity of Cd for POC is less significant under conditions of higher inorganic adsorption site densities (Davies-Colley *et al.*, 1984; Davis, 1984). Ten fold higher Cd partitioning coefficients in the Western Scheldt Estuary compared to the South Bay (POC concentration ranges of 1.3 to 5.5 mg L^{-1} and 0.2 to 1.9 mg L^{-1} , respectively) also are consistent with the notion of a Cd-POC association (Valenta *et al.*, 1986). This difference resulted from order of magnitude higher particulate Cd concentrations in the Western Scheldt relative to the South Bay (dissolved Cd concentrations were similar).

Although riverine sources represent a major freshwater input to the South Bay during the winter and spring (when virtually all precipitation for the year occurs), the major freshwater source to the South Bay during the summer dry season is effluent from municipal treatment plants (Table 1). With effluent concentration ranges for total Cu, Zn and Cd of 30-280 nM, 150-960 nM and *ca.* 20nM, respectively, treatment plant effluent represented a significant trace metal input to the South Bay during our sampling period. If the consistent correlations for dissolved Cd with SPM and dissolved Cu with DOC reflect geochemical associations, then the chemical character of the SPM and DOC may not have varied greatly over the spatial and temporal range of our sampling (despite large changes in the sources of freshwater). Major elemental analyses of the suspended sediment collected during subsequent cruises, and humic substance extractions of dissolved organic carbon, tend to support this hypothesis (Tables 3 and 4). Furthermore, X-ray diffraction of suspended sediment from these cruises indicates very similar mineralogy with samples dominated by illite and smaller amounts of quartz and chlorite.

It is clear from the previous discussion that many processes that affect trace metal distributions in South San Francisco Bay also operate in other estuaries. However, observations contrary to those discussed here have also been noted. For example, Villa and Pucci (1987), working in the anthropogenically-affected Blanca Bay, observed a positive correlation between dissolved Cd and POC and no correlation between dissolved Cd and SPM. Dissolved Zn was not significantly correlated with any of their measured parameters. Wangersky (1986) asserted that the principal routes of trace metal removal from solution in surface waters are physical and biological rather than strictly chemical. He based this statement on a review of the importance of chemical interactions of trace metals with dissolved and particulate organic matter, as well as biologically-mediated chemical reactions. In attempting to understand and predict trace metal behavior in aqueous environments, investigators should be wary of searching for generic answers to explain trends from one study site to another. Rather, a spatial and temporal description of the interdependence of chemical, physical and biological processes, unique to each system, is ultimately required.

Conclusions

Trace metal distributions in the water column were observed during and after a spring phytoplankton bloom in South San Francisco Bay. Strong positive correlations between dissolved Cu and DOC, and dissolved Zn and DOC, were observed. Control of Cu speciation by metal-humic material complexation in this part of the estuary is a process consistent with available elemental and thermodynamic data. However, analogous controls for Zn were not indicated by the speciation calculations. These computations also indicate that elevated free metal ion activities may be among the factors that control growth of certain phytoplankton species within the South Bay. Both Cu and Zn were significantly partitioned in solid and solution phases, whereas Cd was present primarily in solution. Results suggest a source for dissolved Cd coincident with elevated SPM. Interdependent processes that control the distribution of these metals were apparently element specific, but for the most part consistent over the temporal and spatial scales of this study.

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THE INFLUENCE OF AMBIENT CONDITIONS ON THE BIOAVAILABILITY AND TOXICITY OF COPPER

by

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Abstract

Comparative acute toxicity values for *Ceriodaphnia dubia*, *Scapholeberis* sp. and *Pimephales promelas* exposed to copper were used to calculate water effect ratios (e.g., site water LC₅₀ value/reference water LC₅₀ value), which reflect the difference in the biological availability and/or toxicity of copper between water from the Naugatuck River, Connecticut, and Lake Superior reference water. These ratios were used to modify U.S. Environmental Protection Agency (EPA) ambient aquatic life criteria for copper to site- and station-specific criteria, using the indicator procedure of the U.S. EPA guidelines for deriving site-specific water quality criteria. A water effect ratio of 1.0 was established using unpolluted upstream water, resulting in a site-specific criterion maximum concentration (CMC) and criterion continuous concentration (CCC) of 8.7 and 6.2 µg/L copper, respectively. Mean water effect ratios of 3.9 to 7.0, reflective of reduced biological availability and/or toxicity of copper, were determined for four successive downstream stations where the water continued copper and other industrial and domestic wastes. The resulting station-specific CMCs and CCCs ranged from 32 to 57 and 22 to 39 µg/L copper, respectively. These copper criteria were compared with effluent-contributed ambient copper concentrations and ecological survey data from each downstream station to ascertain impact on aquatic life. It was concluded that the national and site-specific criteria derived for copper would be protective of the river's aquatic life because a relatively healthy aquatic community existed where these criteria were exceeded slightly. Whether or not the station-specific criteria were protective could not be determined because these criteria were not exceeded at

stations with healthy communities; however, where they were exceeded, impaired aquatic communities were evident.

In general, *C. dubia* survival and young production data from receiving water tests and copper addition tests, conducted just prior to the acute toxicity tests, were also indicative of reduced copper biological availability and/or toxicity in the Naugatuck River at downstream stations.

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CONTAMINATION AND TOXICITY OF THE SEA-SURFACE MICROLAYER

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Introduction

The sea surface is a highly productive, metabolically-active interface, and a vital biological habitat for neuston such as surface dwelling bacteria, microalgae, protozoa, copepods and larger organisms (Zaitsev, 1971). Also, numerous species of fish, including, cod, sole, flounder, hake, anchovy, mullet, flying fish, greenling, saury, rockfish, halibut, and many others have surface-dwelling egg or larval stages (Ahlstrom & Stevens, 1975; Brewer, 1981; Kendall & Clark, 1982; Zaitsev, 1971).

Contaminants that have low water solubility or that associate with floatable particles concentrate in the surface microlayer (SMIC, upper 50 μm). Also, high concentrations of health-indicator bacteria have been found in surface microlayer samples (Dutka and Kwan, 1978).

Despite the demonstrated importance of the sea surface as both a vital habitat and a concentration point for contaminants, spatial distributions or temporal trends in surface contaminants, or their impacts on the reproduction of valuable marine species, remain largely unknown.

Stranding or beaching of materials represents a potentially serious, but unexamined problem. Limited evidence (see Word, in press) suggests that floatable material, both visible trash and less visible contaminated surface films, deposit on beaches as the tide recedes. This so-called "bath-tub ring effect" could lead to the introduction of high concentrations of both chemical and microbial contaminants into shellfish and other intertidal organisms. In the San Francisco Bay area, it was estimated that floatables, released from domestic sewage discharge, would accumulate at a rate of 1 percent/km south of the Golden Gate from Point Bonita to the Bolinas Peninsula (Norris *et al.*, 1973).

Methods

Details of methodology were described previously (Hardy *et al.*, 1986; Cross *et al.*, 1987; Hardy *et al.*, 1987a&b Hardy *et al.*, 1989). Areas examined have included Puget Sound, Chesapeake Bay and the Southern California Bight. In general, our approach has been to: 1) collect samples of the SMIC from selected field sites, 2) expose fertilized fish eggs or invertebrate larvae to the collected SMIC in the laboratory to determine toxicity, 3) chemically analyze the same SMIC samples, and 4) examine correlations between a number of toxic end-points (mortality, growth, chromosome aberrations) and the concentrations of major groups of contaminants. Also, a few *in situ* toxicity tests using sole eggs were conducted (Hardy *et al.*, 1987a).

More than 20 different techniques have been used for SMIC sampling (Hardy, 1982). Each has its own advantages and disadvantages (Carlson, 1982; Garrett and Duce, 1980; Huhnerfuss, 1981). We developed and tested a rotating teflon drum sampler (Hardy *et al.*, 1988). The drum collects a relatively thin layer (~34 μm), and is comparable in collection characteristics to the more time-consuming glass plate technique.

Results and Discussion

Details of analyses and results are described elsewhere (Hardy *et al.*, 1986; Cross *et al.*, 1987; Hardy *et al.*, 1987a&b Hardy *et al.*, 1989). In general, microlayer samples have much higher concentrations of contaminants, especially in visible slicks near urbanized coastal areas.

Many of our samples from Puget Sound, Chesapeake Bay, and Southern California were collected during Beaufort 3 or 4 conditions (10-16 knot winds with whitecaps) and yet showed high surface enrichments of contaminants and/or particles. This at first seems surprising, but several processes are at work to maintain the enrichments: 1) Strong interfacial forces exist and hydrophobic organic compounds create a static boundary layer between 50 and 190 μm in thickness, where turbulent mixing is much reduced (Huhnerfuss and Alpers, 1983; Hunter, 1980); 2) Adsorption on particles and complexation with surface active organics present near the interface helps to maintain enrichments of metals and other contaminants (Lion and Leckie, 1981); 3) In areas where whitecapping is present, surface enrichments are maintained by aeration of the upper water column (Wallace and Duce, 1978); 5) Even if well-mixed by wind forces, the surface enrichment re-forms within minutes. We have observed in Puget Sound the re-establishment of visible surface slicks within one hour after the wind decreased and laboratory experiments suggest film re-formation within minutes or seconds (Dragcevic and Pravdic, 1981).

In general, we found that toxicity was strongly correlated with the presence of natural biogenic organic slicks. In urban areas, toxic hydrophobic contaminants concentrate in natural films (Hardy, 1982). Wind and current patterns collapse the films into thicker visible slicks. Such slicks are not restricted to urban bays, but move from place to place. Contaminated surface films could be carried by wind and surface currents, deposit in intertidal beach areas, contaminate shellfish, and impact other species, such as herring, that deposit eggs intertidally.

Both stepwise regression and principal component analyses suggested a strong inverse relationship between the presence of contaminants in the sea-surface microlayer and the hatching success of neustonic fish eggs (see Hardy *et al.*, 1987b). Each of the measured major groups of contaminants (PAHs, PCBs, metals, pesticides) can contribute significantly to the overall decrease in the percentage of normal live larvae.

SMIC contamination originates from a variety of sources. High Pb concentrations near urban centers suggest a major source of surface contamination in these areas from gasoline combustion. Ratios of individual compounds (Prahl *et al.*, 1984) suggest that the high levels of PAHs in many of our samples result from runoff or direct deposition of fossil fuel combustion products. Carbon preference ratios (Barrick *et al.*, 1980) at some sites indicate the presence of uncombusted petroleum hydrocarbons. The presence of silver, a product of photographic processing, suggests inputs of domestic sewage, especially near West Point in Puget Sound. Thus, the water surface appears to be contaminated with a complex mixture originating from a large variety of sources.

The significance of surface contamination lies in the biological importance of the microlayer. Although eggs and larvae may be greater than 50 μm (the depth of the microlayer) in size they often float or come into contact with the microlayer. Also, as Liss (1975) suggested, solubilization of airborne particles at the sea surface will lead to their rapid introduction into marine food chains via the high concentrations of microorganisms found in the microlayer.

Benzo(a)pyrene (BaP) is strongly carcinogenic. Hose *et al.* (1982) found a 30% increase in mortality of floating embryos of the sand sole exposed to $0.1 \mu\text{g L}^{-1}$ BaP. BaP concentrations between 3 and $123 \mu\text{g L}^{-1}$ occurred in many of our samples. Metal concentrations in many of the SMIC samples exceed EPA water quality criteria by orders of magnitude. PCB concentrations in some samples were as much as 130 times greater than the Environmental Protection Agency Water Quality Criteria of 30 ng L^{-1} .

Contamination of the water surface is widespread and is not restricted to urban bays. Toxicity to floating fish eggs results from a complex mixture of anthropogenic contaminants arising from a variety of sources. Overall, these results raise considerable concern regarding the environmental quality of the sea surface as a habitat for the developmental stages of flatfish and other organisms. Our results strengthen the argument that maintenance of a healthy marine environment will require development of quality

standards and monitoring programs, not only for the water and the bottom sediments, but also for the sea surface.

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STUDIES USING THE CLAM *MACOMA BALTHICA* TO IDENTIFY BIOAVAILABLE TRACE METALS IN SAN FRANCISCO BAY

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Abstract

The availabilities of Cu and Ag to the clam *Macoma balthica* are described at eight stations in San Francisco Bay for periods ranging from three to ten years between 1977 and 1986. Copper and Ag displayed different patterns of distribution within the Bay. Areas of enhanced Cu availability occurred throughout the Bay, but the availability of Ag was several times to orders of magnitude higher in South Bay than in North Bay. Copper and Ag in the soft tissues of *M. balthica* were highest at a station near Palo Alto in South Bay. Changes in Cu availability over the ten years that that station has been studied were coupled to the discharge of Cu in effluent from a local municipal sewage treatment plant.

Regressions of yearly mean metal concentrations in surficial sediments and the metal content ($\mu\text{g}/\text{individual}$) of standard-size *Macoma balthica* were highly significant. The slope of the relation of Ag was much steeper than that for Cu, indicating the strong tendency of Ag to accumulate in the soft tissues of *M. balthica*. Copper content in *M. balthica* increased non-linearly at the highest Cu sediment concentrations suggesting that the biological availability of Cu increases disproportionately with increasing sediment contamination.

Introduction

Laboratory and field studies have established that metal concentrations in the tissues of some marine and estuarine bivalves generally reflect levels of metal contamination in sediments (Luoma and Jenne, 1977; Luoma and Bryan, 1978; 1982; Langston; 1986). In

1977, sampling was started in San Francisco Bay to study processes affecting the biological availability of sediment-bound trace metals to estuarine organisms. This paper summarizes published studies from this on-going effort (Luoma *et al.*, 1985; Thomson-Becker and Luoma, 1985; Cain and Luoma, 1986; Luoma and Cloern, 1982). Emphasis is given to describing temporal and spatial trends in the bioavailability of Cu and Ag observed in the Bay during the course of the study from collections of the clam *Macoma balthica*. The quantities of Cu and Ag in *M. balthica* are assessed relative to concentrations of these metals in Bay sediments. Evaluations are based on data from eight stations sampled regularly for periods ranging from three to ten years.

Materials and Methods

Oxidized sediments from the upper 1-2 cm and 20-30 specimens of *Macoma balthica* were collected simultaneously at low tide at near-monthly intervals from 8 intertidal mudflats in the Bay (Fig. 1). These stations were selected to represent the range of geochemical and hydrologic conditions in the Bay (Thomson-Becker and Luoma, 1985; Luoma *et al.*, 1985). Station 8 has been sampled continually since 1977. The other stations were sampled between 1977 and 1980. Sediments and clam tissues were prepared by methods previously described (Luoma and Cain, 1979; Thomson-Becker and Luoma, 1985; Cain and Luoma, 1986; Cain and Luoma, in press). Data for metal discharge from a municipal sewage treatment plant near station 8 were determined from the analysis of composited effluent samples by plant personnel.

Significant fluctuations in the concentrations of trace metals in the soft tissues of *Macoma balthica* can be caused by variation in tissue weight that characterizes the species' annual growth cycle (Cain and Luoma, 1986; Strong and Luoma, 1981). This source of biological variation was removed by calculating the total metal content of the soft tissues (Simpson, 1979; Cain and Luoma, in press). Metal content was standardized to shell length (25 mm unless otherwise stated) to account for its strong size (age) dependence (Boyden, 1974; Fisher, 1983). Data are reported as ug metal/individual. Cain and Luoma (in press) have shown that temporal variations in sediment metal concentrations were more closely matched by metal contents than by metal concentrations in *M. balthica*. These

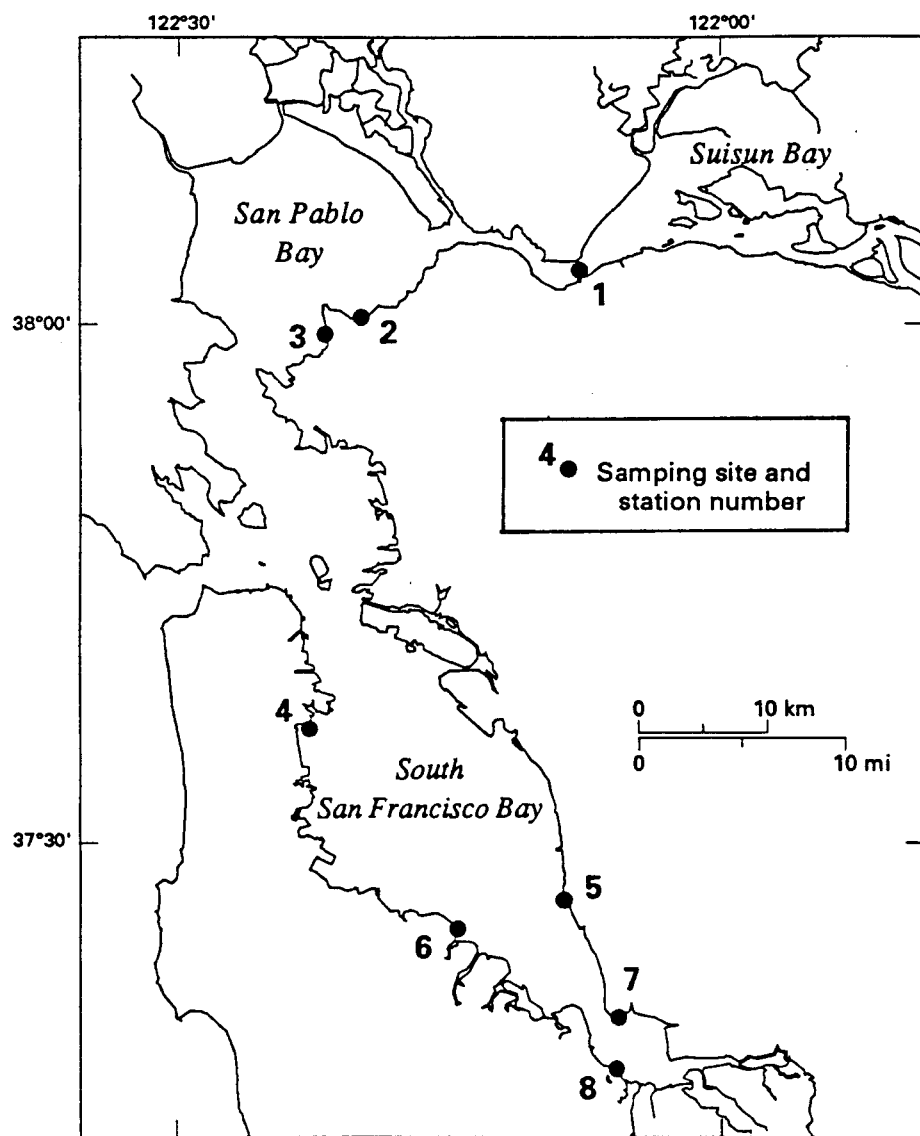


Figure 1. Location of intertidal sampling stations.

results demonstrated the benefit of using animal metal content to assess changes in bioavailable metal.

Results and Discussion

Luoma *et al.* (1985) and Cain and Luoma (1986; in press) showed that metal availability to *Macoma balthica* fluctuated at most stations within years. Short-term fluctuations in content occurred over periods of weeks to months within years (Cain and Luoma, in press). No consistent seasonal pattern of variation, however, was evident either among stations or from year to year within stations except at station 8 in the extreme South Bay. There Cu and especially Ag content were frequently highest between November and April and lowest between May and October (Fig. 2). This intra-annual pattern was superimposed upon the variability among years. The winter maximum/summer minimum in metal availability at station 8 did not appear to be directly related to seasonal changes in salinity (Luoma *et al.*, 1985). Correlations of metal content and salinity did not show any consistent relation within or among years (Cain and Luoma, unpublished data). At different times, metal content was inversely correlated with salinity, positively correlated with salinity, or varied independently of salinity. The absence of a consistent seasonal feature in the metal contents in *M. balthica* at other stations also indicated that there was no simple relation between salinity and the bioavailability of Cu and Ag in San Francisco Bay (Cain and Luoma, in press).

Processes within the estuary influence the distribution, abundance and bioavailability of trace metals. Flushing of South Bay during periods of high freshwater discharge into the estuary may affect fluctuations in metal content at station 8 by reducing the concentrations and residence times of contaminants in this segment of the Bay (Conomos, 1979; Luoma and Cain, 1979; Luoma *et al.*, 1985). Seasonally varying physical and chemical conditions in surficial sediments and in the water column affect the concentrations, chemical forms, and bioavailability of trace metals (Thomson-Becker and Luoma, 1985; Kuwabara *et al.*, 1989). Temporal patterns of metal accumulation in *M. balthica* also are complicated by the large number and variety of metal sources to the Bay (Luoma and Phillips, 1988; Luoma and Cloern, 1982; Gunther *et al.*, 1987).

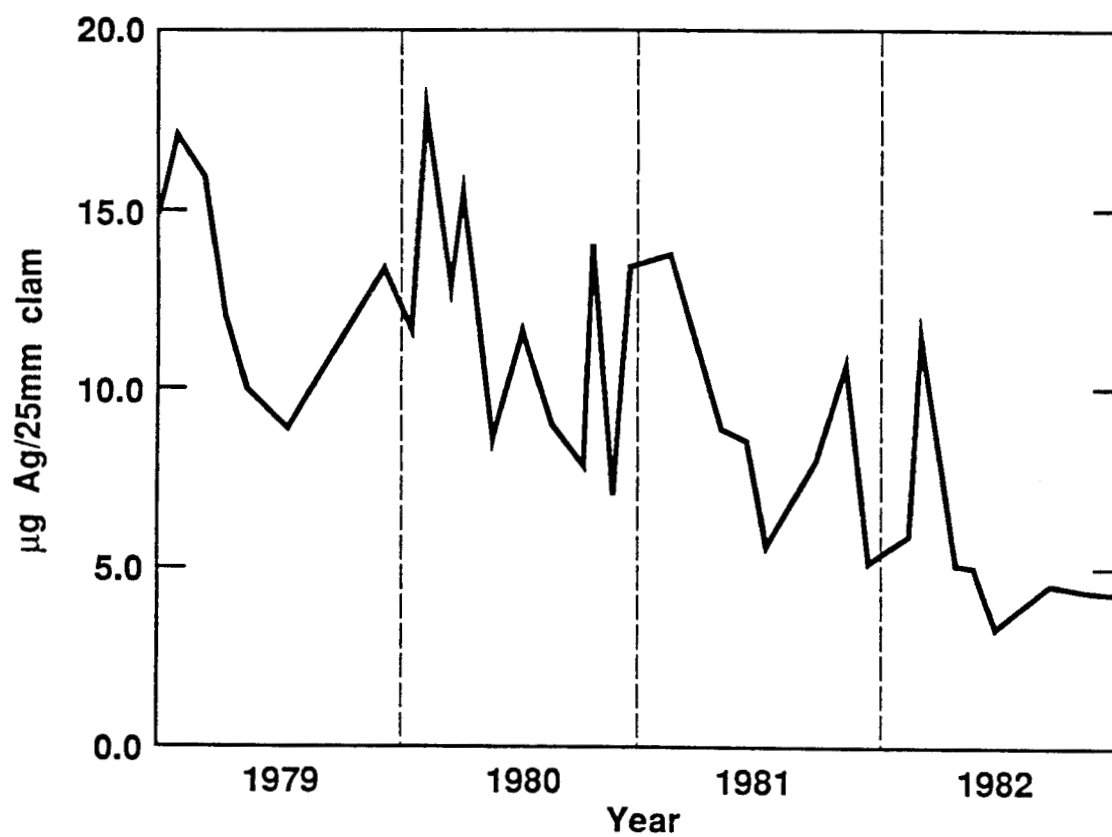


Figure 2. Silver content (ug/individual) in *Macoma balthica* from station 8 in South Bay. Content is standardized to a shell length of 25 mm.

Cain and Luoma (in press) reported that long term changes in metal bioavailability occurred at some stations and not at others. The year to year variation in Cu and Ag content was negligible in clams from North Bay (Fig. 3 and 4). Increases in metal availability, however, were evident at several stations in South Bay between 1977 and 1980. The annual mean Cu content increased significantly ($p < 0.05$; ANOVA) at stations 7 and 8, and Ag increased significantly at station 6. Increases in Cu at stations 4 and 7 and Ag at station 7 also were apparent although these were not significant. The 10-year record at station 8 over the period 1977-1986 was significantly correlated to sediment metal concentrations ($r^2 = 0.46$ and 0.42 for Cu and Ag, respectively; $p < 0.001$). Copper content in *M. balthica* and sediment Cu concentrations both followed trends in Cu discharged by a sewage treatment plant nearby (Cain and Luoma, in press). Plant records showed that Cu in effluent increased from about 7 kg d^{-1} in 1977 to 16 kg d^{-1} in 1979. Copper discharge began to decrease in 1981 after more advanced treatment processes were started. In 1986 Cu discharge was roughly 4 kg d^{-1} . The 10-year record at station 8 showed Cu content was highly correlated ($r^2 = 0.85$; $p < 0.001$) with Cu inputs from the plant (Fig. 5). Silver discharge displayed an erratic pattern that was not obviously related to trends observed in the clams or the sediments (Cain and Luoma, in press). Maximum peak discharges (exceeding 3 kg d^{-1}) were recorded in 1978 and 1981, but average Ag discharge between 1977 and 1981 when Ag content was highest (Fig. 4) was strikingly different than in 1982-86. The record for Ag discharge, however, may not reliably reflect Ag loading because the determinations of Ag in the effluent were often below or near the analytical detection limits (analysis by flame atomic absorption spectroscopy).

Spatial distributions of bioavailable Cu and Ag in the Bay were indicated by metal content in *Macoma balthica* collected during 1977-1980 (Fig. 3 and 4). Copper contents ranged over an order of magnitude throughout the Bay (Fig. 3) with areas of relatively high Cu availability were evident in both North and South Bay (stations 2 and 8). All studies to date indicate that, unlike Cu, the abundance of Ag is notably different in different segments of the Bay (Risebrough *et al.*, 1978; Goldberg *et al.*, 1983; Phillips,

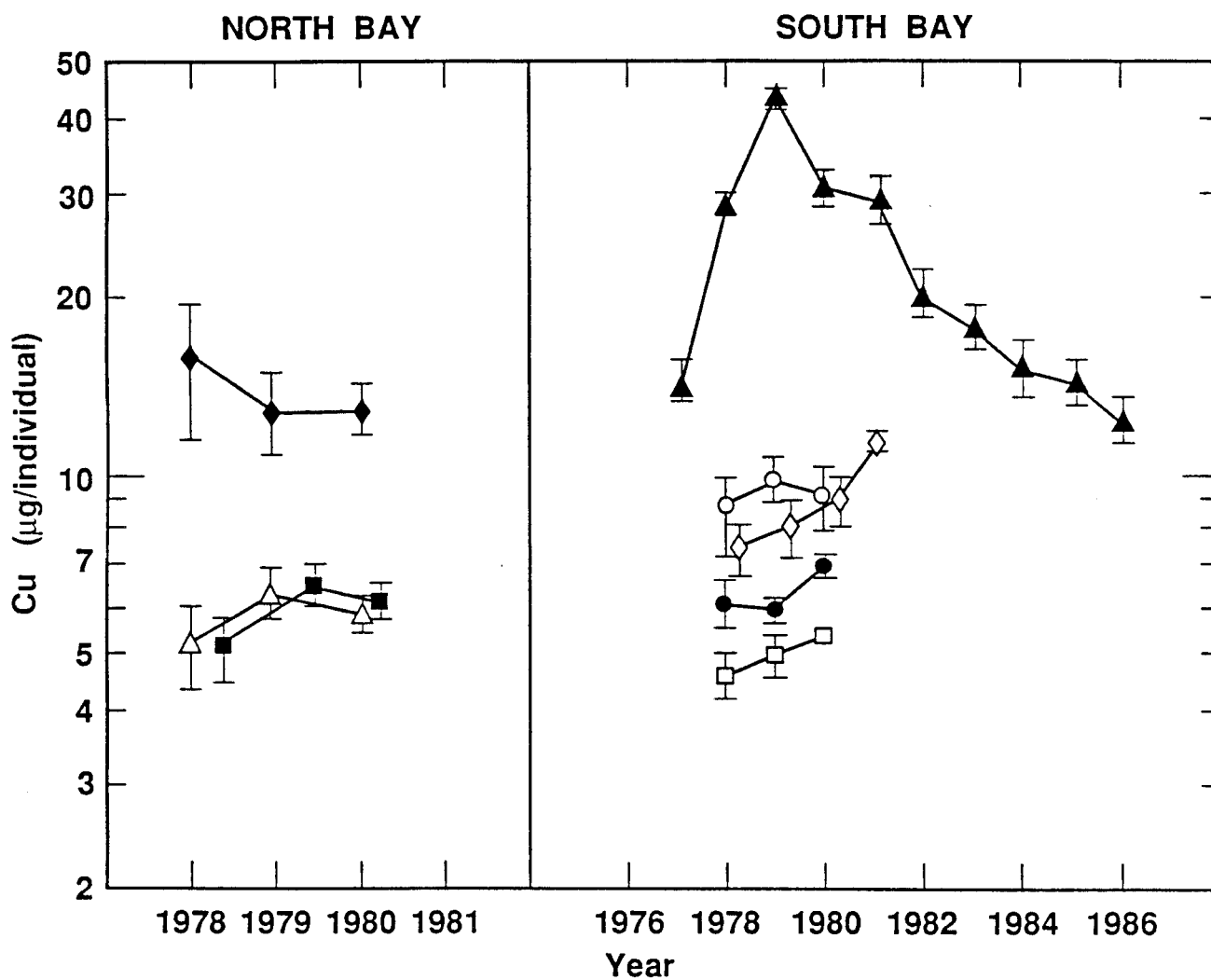


Figure 3. Yearly mean copper content (± 1 s.e.m.) in *Macoma balthica*. All data standardised to 25 mm shell length except station 2 (20 mm). Symbols identify stations: (□): 1; (△): 2; (◆): 3; (○): 4; (○): 5; (o): 6; (◇): 7; (△): 8.

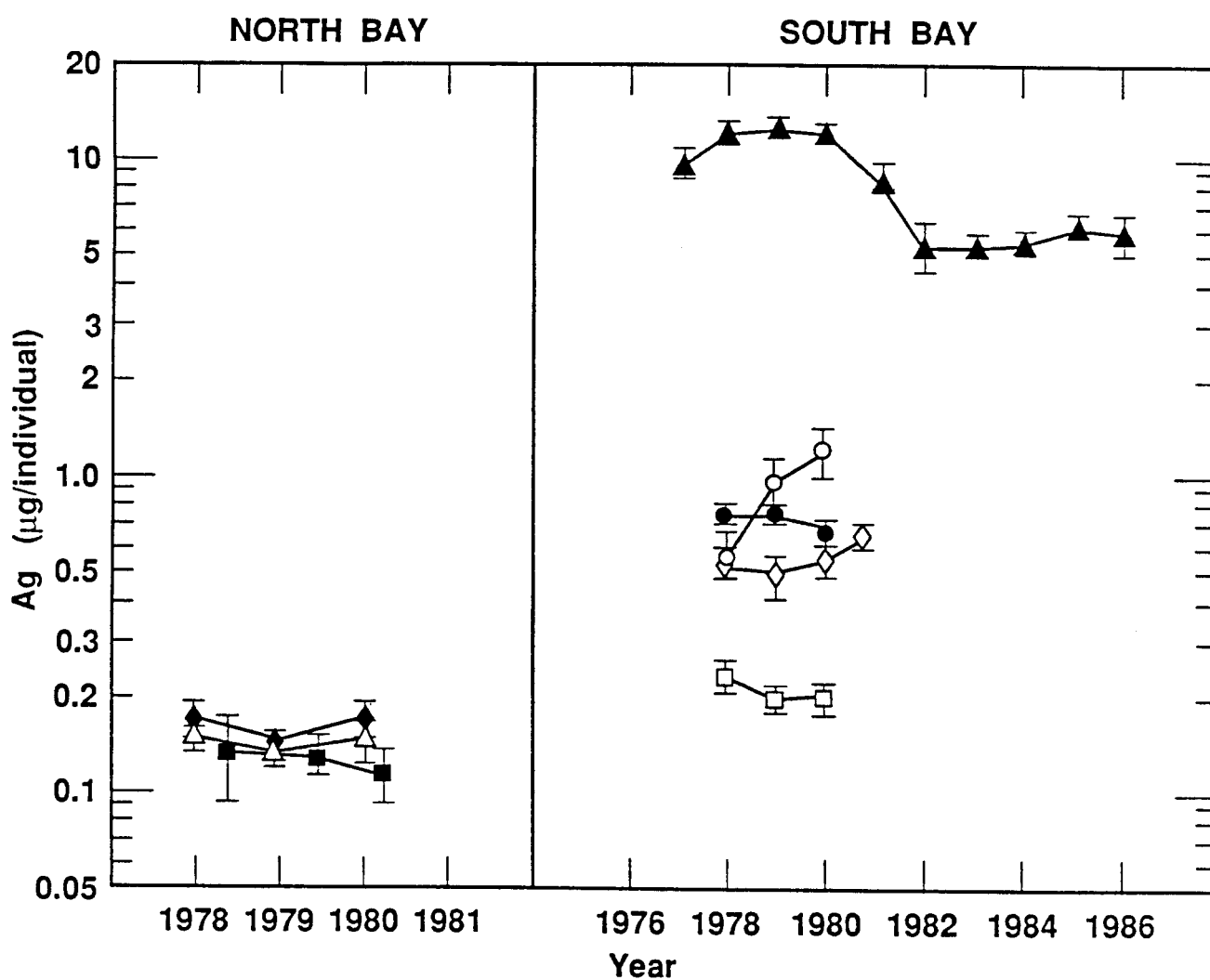


Figure 4. Yearly mean silver content (+1 s.e.m.) in *Macoma balthica*. All data standardized to 25 mm shell length. Symbol code same as Figure 3.

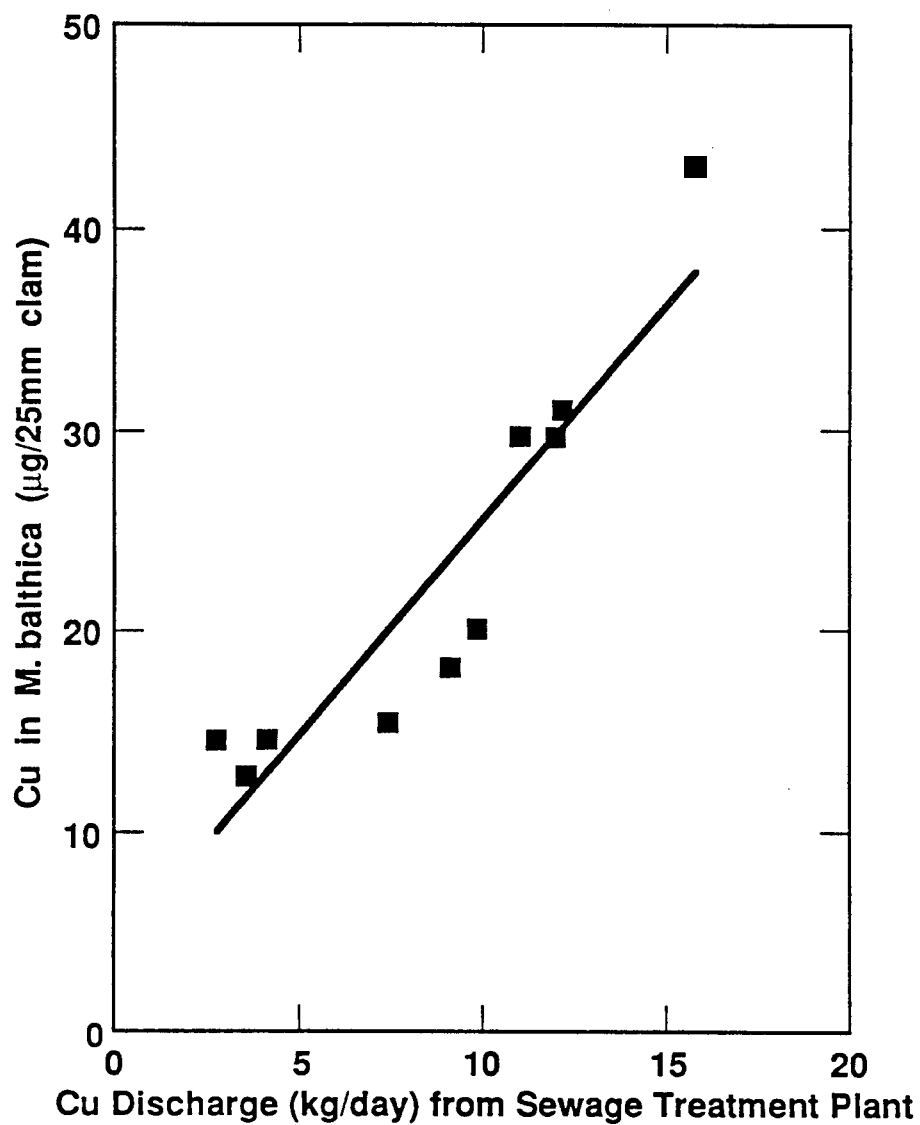


Figure 5. Correlation of log metal content in *Macoma balthica* and log metal concentrations in sediment extracted with 0.3N HCl. Data are the yearly means fitted by linear regression. Symbol code same as Figure 3. a: Ag b: Cu.

1987; Luoma and Phillips, 1988). Silver content was lowest in North Bay (Fig. 4). Direct comparisons of metal content in *M. balthica* from this study to other studies is difficult because of differences in animal sizes (ages) used to standardized the data. However, the range of Ag concentrations ($\mu\text{g/g}$) in *M. balthica* in North Bay was comparable to concentrations reported for specimens from uncontaminated sites (Luoma and Phillips, 1988; Bryan *et al.*, 1985; Langston 1986). Silver in *M. balthica* from South Bay was 2-100 times greater than in North Bay, reflecting the greater number of anthropogenic sources in this segment of the Bay (Conomos, 1979; Luoma and Cloern; 1982; Gunther *et al.*, 1987). Silver content at station 8 was an order of magnitude greater than at other South Bay stations.

Metal contents in *Macoma balthica* were highly correlated with sediment metal concentrations among stations (Cain *et al.*, 1987; Cain and Luoma, in press). Annual means integrated the short-term (within year) variability, and provided a simple but effective way of examining the relations (Fig. 6a and b). Residual variation in metal content in *M. balthica* fitted by linear regression appeared to be partially caused by differences in the ages of the standard 25 mm clams among the different populations. Thompson and Nichols (1988) showed that the growth rates of *M. balthica* varied within the Bay, and as a result, the ages of clams of similar size differed (Cain *et al.*, 1987). For example, the estimated ages of 25 mm clams at stations 1, 5, and 8 were 2, 4, and 4+ years. When metal content at these stations was standardized to age (4 years) rather than shell length, the correlation with Cu sediment concentrations was improved, and the influence of different Cu sediment concentrations on Cu content in clams from stations 1 and 5 was clearly evident (Cain *et al.*, 1987). Differences in the ages of standard-sized clams from stations 1, 5, and 8, however, had little effect on the correlation of Ag content and Ag sediment concentration (Cain and Luoma, in press).

In addition to age-related differences in metal content discussed above, residual variation in the relation between metal content in sediments and biota could result from differences in the composition of sediments (Luoma and Davis, 1983) and the availability

of metal-binding sites in sediments. The availability of Pb and As, for example, appears to be modified by the Fe content of the sediment (Luoma and Bryan, 1978; Lanston, 1980). The slope for the linear regression of the annual means of Cu sediment concentrations and Cu content had a value of less than 0.7 (Fig. 6b). At the highest sediment Cu concentrations, however, Cu content in *M. balthica* appeared to increase non-linearly. This type of behavior would be consistent with a progressive shift in metal partitioning within sediments from sites of high metal-binding intensity and low biological availability to sites of lower binding intensity and higher biological availability as metal contamination increases (Luoma and Davis, 1983).

Data for Ag (Fig. 6a) were fitted with a single linear regression model with a slope of 8. Relative to the respective sediment concentrations, Ag was accumulated in soft tissues at about 10 times higher levels than Cu.

Several conclusions can be drawn regarding the bioavailability of Cu and Ag to *Macoma balthica* in San Francisco Bay. The metal content in tissues of *M. balthica* generally reflect levels of metal enrichment in sediments (Cain and Luoma, in press). The 10-year record of data at station 8 demonstrated the link between long-term trends in metal contamination and point source inputs. Short-term variation (within years) in metal availability is superimposed upon base levels of contamination. Factors causing this variation have not been clearly identified, but periodic inputs of metals and geochemical changes in sediments likely are involved. Seasonal variation in salinity, however, does not appear to directly or dominantly influence short-term changes in bioavailability. The biological availability of Cu and Ag, relative to sediment concentrations, appears to differ. The relation between Cu content in *M. balthica* and sediment Cu concentrations suggested that extreme Cu contamination results in a disproportionate increase in Cu availability. In contrast, Ag increased proportionately over the range of sediment concentrations observed in the study, but the accumulation of Ag in *M. balthica*, relative to sediment concentrations, was much greater than Cu. Biota may be particularly vulnerable to Ag contamination in the Bay because of the high biological availability of this extremely toxic element.

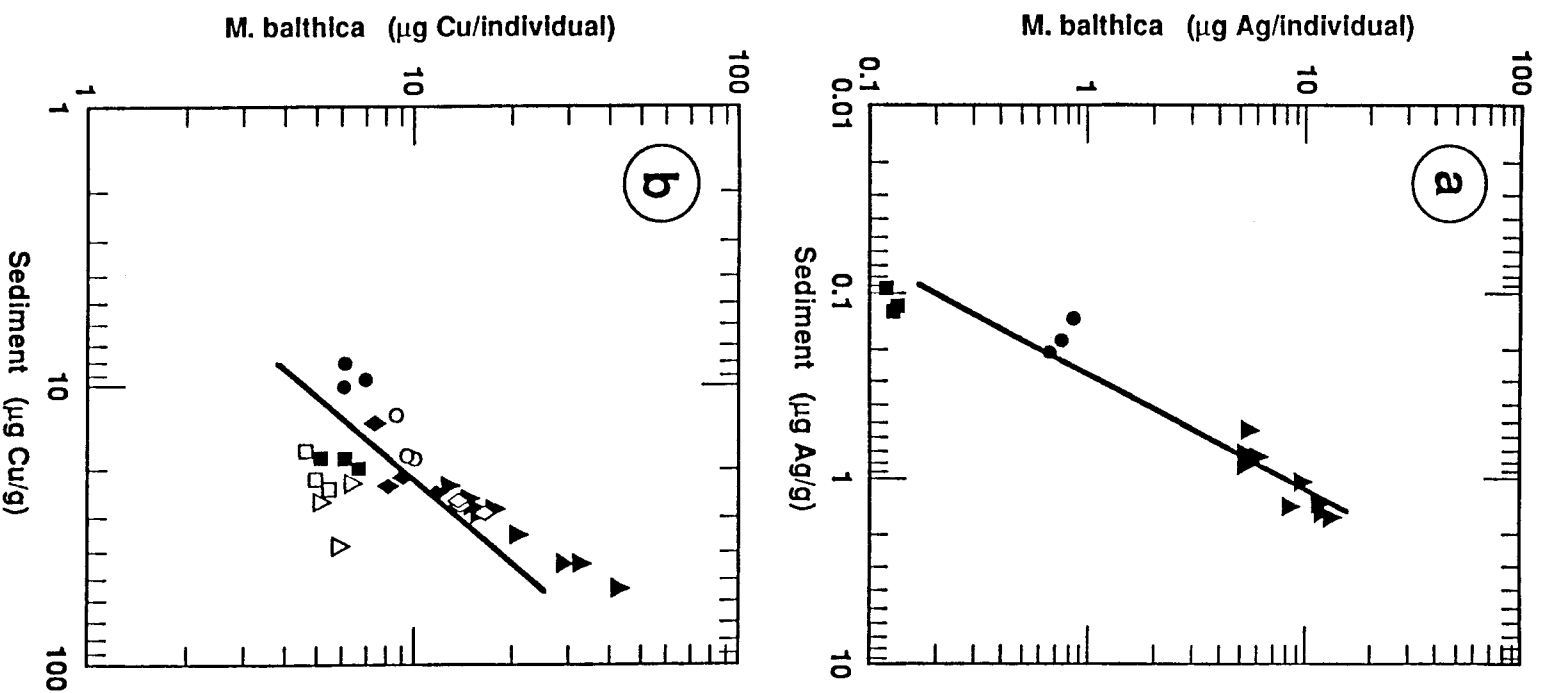


Figure 6. Correlation of log metal content in *Macoma balthica* and log metal concentrations in sediment extracted with 0.6N HCl. Data are the yearly means fitted by linear regression. Symbol code same as Figure 3. A: Ag; b: Cu.

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CHLORINATED HYDROCARBONS IN MARINE MAMMALS FROM PUGET SOUND AND THE NORTHEAST PACIFIC

by

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The objective of this talk is to review some of the information available on the impacts and dynamics of contaminants in marine mammals. I will also cover some of the research we have conducted on marine mammals in Puget Sound, Washington and along the California coast.

Background

Marine mammals have gained considerable public attention in recent years for a variety of reasons. One cause for this interest was the history of human exploitation of marine mammals that resulted in the extinction or near extinction of a number of species. Regulations protecting marine mammals have for the most part been instituted only in the last 30 years. Marine mammals are protected in the United States under the Marine Mammal Protection Act of 1972.

Current threats to marine mammals are often indirect and hard to quantify. Competition with commercial fishing, entanglement, pollution, and habitat loss are all potentially serious threats to marine mammals. The impact of contaminants on marine mammals has been an increasing concern. High levels of stable chlorinated hydrocarbons have been recovered from the tissues of marine mammals from different parts of the world, including Puget Sound (Calambokidis *et al.*, 1984; Risebrough, 1978) and San Francisco Bay (Risebrough *et al.*, 1979). These contaminants have been linked to reproductive problems in several pinniped populations (Reijnders, 1980; 1982a; DeLong *et al.*, 1973; Gilmartin *et al.*, 1976; Helle *et al.*, 1976a; 1976b; Helle, 1980) and reproductive failure

caused by ingestion of fish from contaminated areas has been demonstrated in a controlled experiment with harbor seals (Reijnders, 1986).

Marine mammals comprise a broad range of species which inhabit a variety of habitats. A number of factors influence the species of marine mammals that are most vulnerable to toxic contaminants. These include:

Trophic level/Food habits - Many marine mammals, including the pinnipeds and the odontocetes (toothed whales) feed high on the food chain on fish and cephalopods. These species are exposed to high concentrations of the stable contaminants such as PCBs that bioaccumulate through the food chain. Most baleen whales, however, feed lower on the food chain on copepods and euphausiids resulting in lower exposure to contaminants. The gray whale occupies an unusual position; it feeds low on the food chain but because it feeds directly off the bottom often ingesting sediments, it may be exposed to high concentrations of sediment-born contaminants.

Habitat - Marine mammal species occupy a variety of habitats including coastal marine waters, pelagic/open ocean, and freshwater lakes and rivers. Pelagic species, such as the sperm whale and the beaked whales inhabit regions where contaminant concentrations are relatively low. Species that inhabit coastal waters such as harbor seals, California sea lions, harbor porpoise, and bottlenose dolphin are more likely to be exposed to higher concentrations of contaminants. Consequently some of the highest contaminant concentrations have been found in these species near industrialized areas.

Length of life - Precise information on maximum lifespans on all marine mammals are not available, however, many species are fairly long-lived. Pinnipeds generally do not live past 30 years of age, and larger whale species may exceed 50 year lifespans. Long-lived species are potentially more vulnerable to contaminants that accumulate over time and are present in maximum concentrations in older animals.

Reported Impacts of Contaminants on Marine Mammals

The impact of contaminants on marine mammals has been difficult to study. Ethical and legal concerns limit the experimental research that can be conducted with captive animals. Research on contaminant impacts on marine mammals has relied on correlations and equivocal evidence. Potential or likely impacts have been reported in several cases and are reviewed below.

Premature births in California sea lions in the Channel Islands

A complex phenomenon has been documented in California sea lions giving birth to premature pups in the Channel Islands off southern California in the 1970s. Four factors have been identified in the females giving birth to premature pups, that singly or in combination, may be responsible for the premature births. These factors are: 1) significantly higher concentrations of PCBs and DDT in the females giving birth prematurely (DeLong *et al.*, 1973; Gilmartin *et al.*, 1976), 2) an imbalance of certain heavy metals (Martin *et al.*, 1976), 3) presence of the bacterium *Leptospira pomona* (Smith *et al.*, 1974a; 1974b; Vedros *et al.*, 1971; Gilmartin *et al.*, 1976) and 4) presence of San Miguel sea lion virus (Smith *et al.*, 1973; Gilmartin *et al.*, 1976). The most likely hypothesis was that high chlorinated hydrocarbon concentrations were making the animals more vulnerable to natural diseases (Gilmartin *et al.*, 1976). The incidence of premature births in California sea lions on San Miguel Island has declined through the 1980s (DeLong, Pers. Com.).

Population declines and low reproduction in Wadden Sea harbor seals

Reijnders (1981) and Reijnders *et al.* (1982a) document the decline of the harbor seal population of the Wadden Sea and cite PCBs as the cause of these declines. Harbor seals in the Wadden Sea show an increase in reproductive rate in a west to east gradient, with harbor seals in the Dutch Wadden Sea having the lowest reproductive rate (Reijnders *et al.*, 1982a; Drescher, 1979). Harbor seals in the Dutch Wadden Sea also have a higher mortality in the first weeks of life compared to seals from other parts of the Wadden Sea, though overall mortality appears to be of the same order after three months (Reijnders *et al.*, 1982a; Reijnders, 1982b). PCB concentrations in harbor seals from the Dutch Wadden Sea (an average of 700 ppm wet wt. in the blubber of eight adults) are among the highest

found anywhere, and are higher than the concentrations in other parts of the Wadden Sea (Reijnders 1980, 1982b). Reijnders (1980, 1982a) concludes that PCBs are responsible for the low reproductive rate of Dutch harbor seals, because: 1) the lower reproductive success in areas of higher PCB concentrations in the Wadden Sea, and 2) the demonstrated effect of PCBs on mammalian reproduction.

Experimental studies with harbor seals

Reijnders (1986) has provided the first experimental evidence of the impact of environmental concentrations of toxics on marine mammals. Captive harbor seals fed fish from contaminated areas of the Wadden Sea showed lower reproductive success than seals fed fish from less contaminated areas. Reijnders (1986) concluded PCBs were the most likely contaminant responsible for the observed reproductive failure.

Reproductive dysfunctions in Baltic seal populations

Three species of seals in the Baltic Sea area have experienced pathological changes of the uterus that appear to be related to pollutants. Helle *et al.* (1976a; 1976b) found a significantly higher concentration of PCBs and DDT in female ringed seals with the uterine occlusions than in pregnant females. They concluded PCBs and not DDT were directly or indirectly responsible for the ringed seal reproductive problems because: 1) the DDT levels in the blubber of Baltic ringed seals were equivalent to healthy non-aborting female California sea lions studied by DeLong *et al.*; (1973) and Gilmartin *et al.*; (1976), and 2) the PCB concentrations in Baltic ringed seals were equivalent to those shown to cause reproductive problems in mink (Jensen *et al.*, 1977). Helle *et al.*, (1976b) suggest that the occlusions and stenoses are either the direct effect of PCB intoxication or the result of an infection of the uterus in females weakened by PCBs. Reijnders (1980), in reviewing the Baltic ringed seal studies, concludes the hypothesis that PCBs are the cause of the pathological disorders should be viewed with caution.

Gulf of St. Lawrence beluga whales

High concentrations of contaminants and a high incidence of tumors have been reported in recent years in beluga whales from the Gulf of St. Lawrence, Canada

(Martineau *et al.*, 1987; 1988; 1987, Masse *et al.*, 1986). The authors suspected contaminants, specifically PCBs, DDT (and its metabolites), and benzo(a)pyrene, as being responsible for the pathologies observed. This conclusion was based on the high concentrations found and the reported effects of these chemicals. No direct proof of a cause and effect relationship, however, was reported.

Testosterone levels in Dall's porpoise and DDE

Subramanian *et al.* (1987) found a significant correlation between DDE and testosterone levels in male Dall's porpoise, and concluded contaminants were responsible for the lowered hormone levels. The study, however, appeared to be flawed in a number of respects. The authors make the leap from correlation to cause and effect without addressing other factors that could be responsible for the observed correlation. In particular, statistical testing of the data they present shows that both the testosterone levels and the contaminant concentrations were significantly correlated with the lengths of the individual porpoise. Increases with age in concentrations of PCBs and DDE in males has been demonstrated in a number of marine mammal species including: ringed seals (Addison and Smith, 1974), grey seals (Donkin *et al.*, 1981), harp seals (Addison *et al.*, 1973), harbor seals (Calambokidis *et al.*, 1984), pilot whales (Tanabe *et al.*, 1987), and harbor porpoise (Gaskin *et al.*, 1982; 1983). Conversely, declines in testosterone levels in older males has been reported in a number of species including humans (Gregerman and Bierman, 1981; Tenover *et al.*, 1987; Ottinger *et al.*, 1983). Therefore the correlation between DDE and declining testosterone in Dall's porpoise may merely be an incidental by-product of the relationship between age and each of these factors.

Research on Washington Harbor Seals

We have conducted research on the biology of marine mammals and the potential impact of contaminants in Puget Sound, Washington since 1976. This research has been funded primarily by the Ocean Assessments Division of NOAA and also by the National Science Foundation. Results of these studies have been reported elsewhere (Calambokidis *et al.*, 1978; 1979a; 1984; 1985; 1988) and are summarized below.

Contaminant concentrations

Concentrations of contaminants have been examined primarily in harbor seals from Puget Sound (Calambokidis *et al.*, 1978; 1984; 1988). Blubber tissues from over 100 harbor seals have been tested for concentrations of chlorinated hydrocarbons, primarily PCBs and DDT. Concentrations of PCBs were higher than concentrations of DDT in all harbor seals and ranged from less than 2 ppm to 750 ppm in blubber (mg/kg wet weight).

Concentrations of PCBs and DDT were found to vary by region, age class, sex, and with degree of emaciation (see Figure 1 for summary of relationships). Significantly higher concentrations were found in southern Puget Sound compared to other regions of Washington State; seals from the Pacific coast of Washington had the lowest concentrations. Concentrations increased with age/length in male harbor seals but not in females after they reached reproductive age. This reflects the ability of females to eliminate these stable contaminants through transplacental transfer and lactation. A significant correlation between blubber thickness and contaminant concentrations was not found; however, extremely emaciated animals had elevated concentrations.

Concentrations of PCB's and DDT in seals were substantially higher than in their prey. In two regions (southern Puget Sound and Hood Canal) the average concentrations in sampled prey were 50 to 100 times lower than in adult male seals from that area (concentrations compared on a lipid weight basis). Comparison of body burdens of PCBs in adult male seals and the estimated intake from prey indicated male seals absorb a majority of the PCBs present in their prey and retain most of it in their blubber. Selective metabolism of some specific PCB homologs was seen.

Concentrations of PCBs and DDE are declining in newborn harbor seals in several areas (Figure 1). The decline is dramatic in pups from southern Puget Sound, where the highest concentrations had been found. A significant decline was not seen in adult males, though sample size was smaller. Because adult males accumulate PCBs and DDT throughout their lives, there would be a delay before declines would be noticeable.

Limited data exist on concentrations of other contaminants in Puget Sound harbor seals (Calambokidis *et al.*, 1984). The available data indicates a wide variety of other organic and inorganic contaminants present in seal tissues; however, sample size does not allow evaluation of trends or significance of these contaminants.

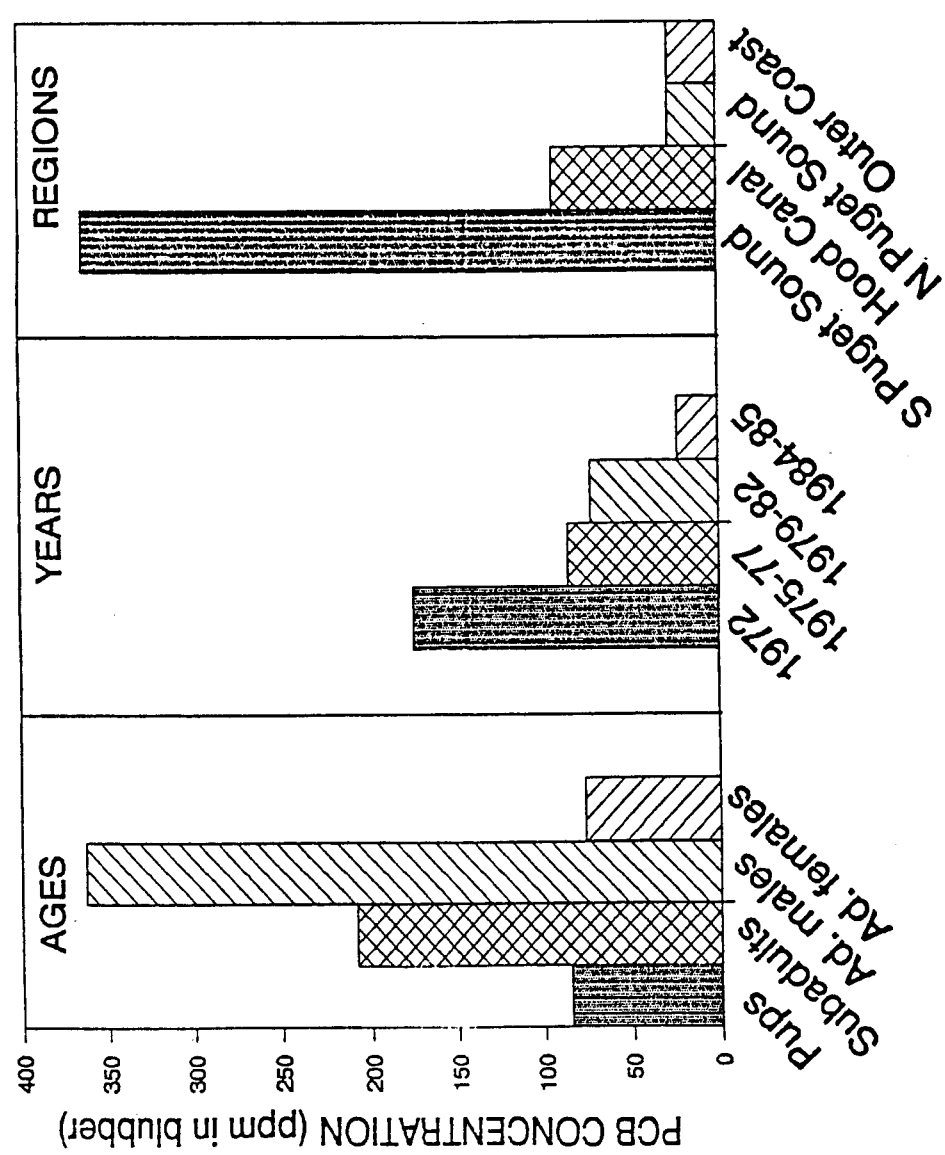


Figure 1. PCB concentrations in blubber of harbor seals from Washington State by age, year, and region. Age/sex class differences are for seals from southern Puget Sound collected in 1975-1959 (from Calambokidis *et al.*, 1984). Values by year are for harbor seals pups from southern Puget Sound (from Arndt, 1973; Calambokidis *et al.*, 1984; 1988). Values by region are for harbor seal pups 1975-1979 (Calambokidis *et al.*, 1984). Biological effects on Puget Sound harbor seals

Contaminants do not appear to be currently having a dramatic impact on harbor seal populations. Harbor seal numbers at sites throughout Puget Sound have increased significantly from the middle to late 1970s to the mid-1980s (Figure 2). Changes in numbers of seals were measured using three values: 1) the highest number of seals seen at any one time during the year, 2) the average of the daily high counts of seals, and 3) the number of pups born at the site. At all sites examined, all three of these indicators were higher in 1984 than in 1977-79. Average counts were significantly higher in 1984 compared to 1978-79 at 9 of the 10 areas (t-test, $p < 0.001$ in 7 cases and $p < 0.05$ in 2 cases). The annual rate of increase in seal numbers generally ranged from 5 to 20%.

Figure 3 summarizes the changes in the numbers of seals that have occurred at Gertrude Island, a site that has been monitored by a number of researchers since 1965. It is clear that increases in seal numbers at this site began in the late 1970s. Newby (1971; 1973a) reported a population estimate for seals in Washington State, but with the exception of Gertrude Island, these are based on very limited data. These data and anecdotal reports from people living near seal haul-out sites, however, suggest seals numbers at most other sites began increasing in the 1960s or early 1970s. This timing is consistent with the end to the bounty on harbor seals in the early 1960s and federal protection in 1972. The lack of an increase in seal numbers at Gertrude Island until the late 1970s indicates another factor may have been keeping the population low.

Reproductive problems in southern Puget Sound harbor seals, reported in the early 1970s, have not been observed in recent years in this region. High rates of pup mortality, premature births, and birth defects were reported in southern Puget Sound in the early 1970s (Newby, 1971; 1973b; Arndt, 1973). Research in Southern Puget Sound from 1975 to 1977 (Johnson and Jeffries, 1977; 1983; Calambokidis *et al.*, 1978) revealed occasional cases of premature births and birth defects. In 1984, however, pup mortality and the incidence of premature births was lower in southern Puget Sound than in other regions of Washington State exposed to lower contaminant concentrations (Calambokidis *et al.*, 1985, Steiger *et al.*, 1989).

CHANGES IN HARBOR SEAL NUMBERS BY SITE

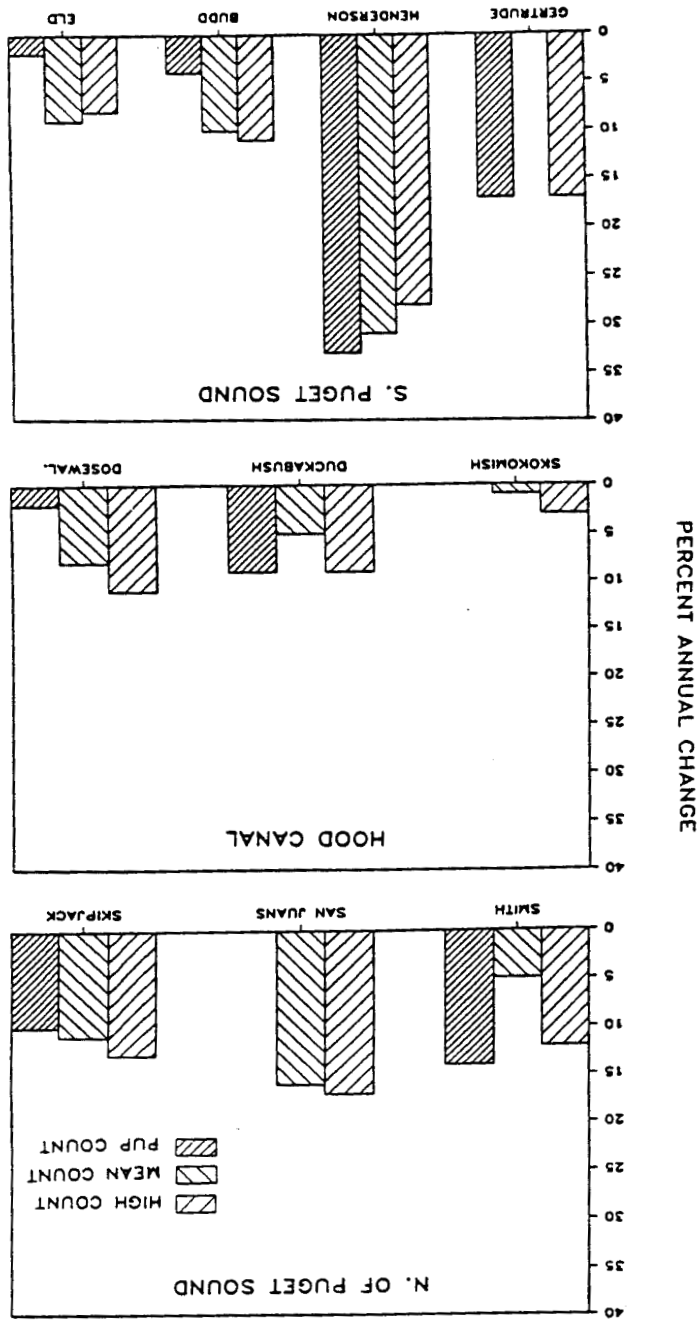


Figure 2. Percent annual increases in numbers of harbor seals at different haul-out sites based on comparison between counts made in 1977-79 and 1984. Figure from Calambokidis *et al.* (1985) using data from Calambokidis *et al.* (1978; 1985) except San Juan Island for 1978 (Everitt *et al.*, 1979) and Gertrude Island for 1979 (Skidmore and Babson, 1981).

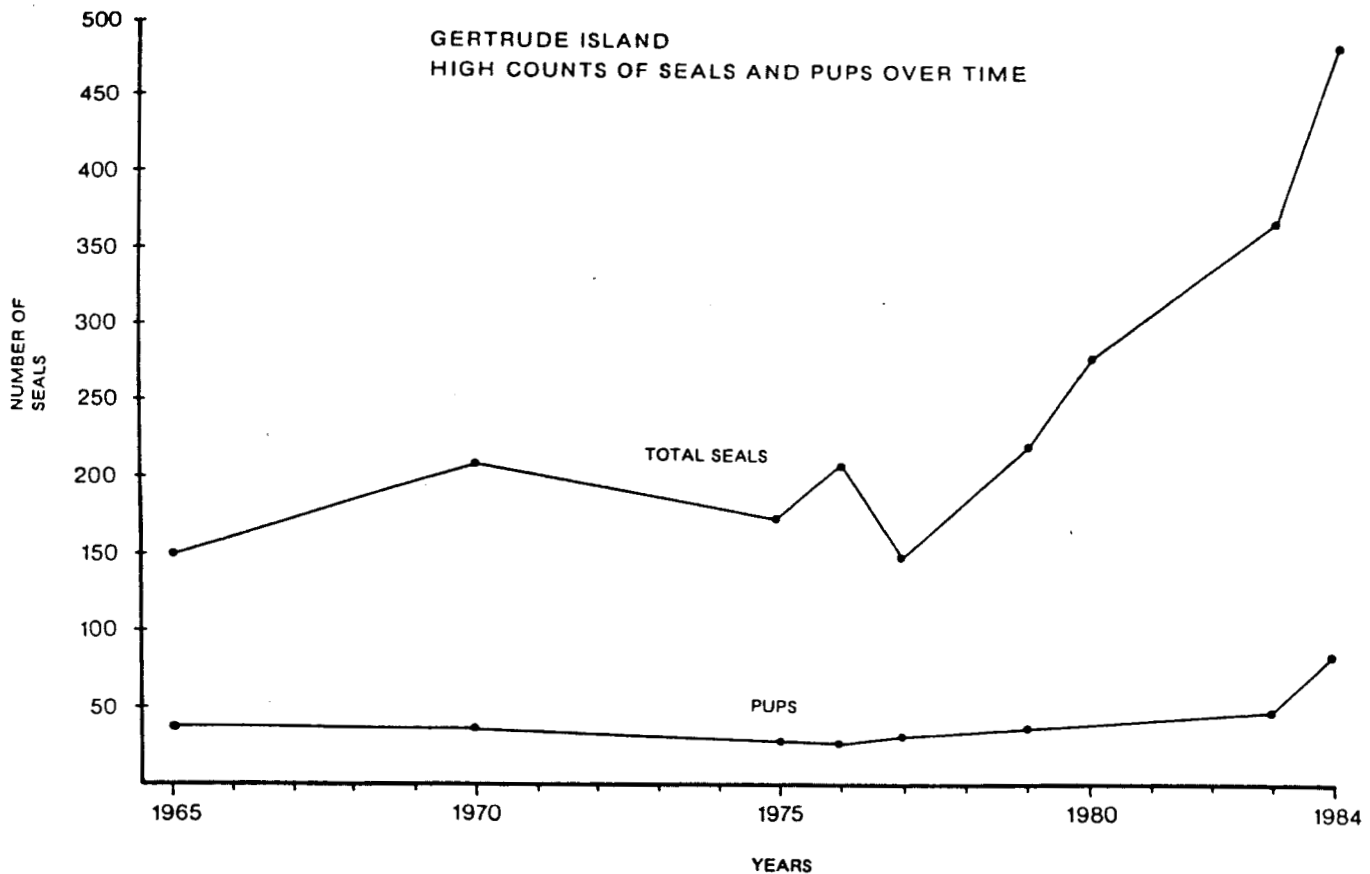


Figure 3. High counts of harbor seals and harbor seal pups at Gertrude Island, southern Puget Sound. Figure from Calambokidis *et al.* (1985) using data reported in Calambokidis *et al.* (1978; 1979; 1985), Arnold (1968), Newby (1971), Johnson and Jeffries (1983), Skidmore and Babson (1981), and Gearin and DeLong (1984).

Circumstantial evidence indicates PCBs probably had an impact on Puget Sound harbor seals in the 1970s. During this period: 1) concentrations of PCBs in southern Puget Sound harbor seals were similar to those reported to be impairing reproduction in seals in other areas, 2) reproductive problems were reported in the 1970s in this region and the population did not increase even with the legal protection enacted, and 3) seal numbers did not begin increasing in southern Puget Sound until the late 1970s when PCB concentrations were declining.

Contaminants in Other Species of Marine Mammals from Washington State

Only a few analyses have been conducted on Washington marine mammals species other than harbor seals. Table 1 summarizes the concentrations of PCB and DDE in some

of these samples. Killer whales and harbor porpoise had the highest concentrations. This is consistent with the food habits and habitats of these two species; both feed high on the food chain and inhabit contaminated coastal waters. One of the killer whales, an individual that had been photographically identified as O-1, is part of a pod that feeds on other marine mammals. This individual had the highest contaminant concentrations, a finding consistent with the high concentrations present in marine mammal prey.

Contaminant-related Research on California Marine Mammals

San Francisco Bay harbor seals

Only limited research has been conducted to date on the levels and impacts of contaminants on marine mammals in San Francisco Bay, though additional research is currently underway. A brief review of the past research is summarized here.

In 1971 five premature stillborn harbor seal pups were found on Strawberry Spit in San Francisco Bay, California (Paulbitsky, 1975), two more were found in January-February 1972 (Risebrough *et al.*, 1979). These findings prompted concern that pollutants in San Francisco Bay might be the cause of the reproductive failures. A study to examine the problem was funded by the Marine Mammal Commission (Risebrough *et al.*, 1979).

In 1975 and 1976 only one premature harbor seal pup was found each year. Risebrough *et al.* (1979) concluded that incidence of premature pupping was lower than in 1971. PCB concentrations in San Francisco Bay harbor seals were higher and DDE concentrations lower (an average of 195 and 56 ppm, respectively, lipid weight in blubber of two adults) than in California sea lions giving birth to premature pups in the Channel Islands (Risebrough *et al.*, 1979). Risebrough *et al.* (1979) concluded pollutants were not a current threat to San Francisco Bay harbor seals because of: 1) the low rate of premature pupping in 1975 and 1976, 2) the low concentration of DDE relative to the concentrations suspected to be the cause of premature births in California sea lions, and 3) the probable continued decline of DDE in the environment. The role of PCBs or DDT in the premature pupping that occurred in the early 1970s could not be determined, although Risebrough *et al.* (1979) suspected that DDT levels were higher during that time. The number of harbor

Table 1. Concentrations of PCB and DDE in the blubber of marine mammals (other than harbor seals) from Washington State (from Calambokidis *et al.*, 1984 and Unpubl. data).

Species	Date	Concentration (ppm)		Comment
		PCB	DDE	
Killer whale	Sept. 77	38	59	L-8
	Jan. 79	250	640	O-1
	Nov. 83	82	80	Calf
Harbor porpoise	Sept. 79	55	14	
	Aug. 77	1.7	1.4	Fetus
Dall's porpoise	Aug. 81	9.0	5.0	
Pygmy sperm whale	Oct. 77	0.15	1.3	
Calif. sea lion	June 77	2.6	4.8	
River otter	Sept. 81	6.7	0.6	
Minke whale	March 76	0.15	0.55	
Gray whale	June 84	3.1	0.62	

seals using Mowry Slough, the primary haul out site in San Francisco Bay, was generally stable with little change between 1972 and 1980 (Fancher and Alcorn, 1982).

Contaminants in marine mammals along the California coast

High concentrations of contaminants have been reported in a variety of marine mammals species along the California coast. Some of the highest concentrations of DDE reported anywhere have been seen in southern California pinnipeds (DeLong *et al.*, 1973; Gilmartin *et al.*, 1976; Le Boeuf and Bonnell, 1971) and small cetaceans (O'Shea *et al.*, 1980; Schafer *et al.*, 1984). The reported impacts of some of these contaminants in this region was discussed previously in this report.

We recently determined concentrations of PCBs, DDE, and HCB in harbor porpoise from different areas along the coasts of California, Oregon, and Washington (Calambokidis, 1986). All but one of the samples had been collected in the 1980s. The main objective of the research was to examine the population discreteness of harbor porpoise using ratios of contaminants as indicators of interchange between regions. DDE concentrations were highest in southern California and decreased with increasing latitude. Ratios of DDE to PCB varied significantly by region. Overall concentrations of both PCBs were lower than the high values reported in harbor seals from southern Puget Sound and San Francisco Bay and DDE concentrations were lower than reported previously in southern California pinnipeds and small cetaceans.

Conclusions

Marine mammals accumulate high concentrations of some contaminants such as PCBs and DDE. Proving cause and effect relationships between contaminants and dysfunctions in the wild has been difficult. A number of correlations suggest that contaminants have had impacts on marine mammals in some heavily contaminated regions. Concentrations of PCBs and DDE in marine mammals from some areas have declined in recent years as a result of the legal restrictions that have been placed on these contaminants.

Acknowledgments

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INNOVATIVE METHODS OF TRACING CONTAMINANTS IN COASTAL WATERS: THE USE OF BACTERIOPHAGES AND BACTERIAL SPORES

by

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Abstract

The monitoring and control of contaminants received by waters, including coastal waters, is constrained by a number of factors. Control policies are reliant upon reliable and accurate methods of identification and quantification. The fate of contaminants whether short-lived or persistent, is similarly of concern. Information regarding contaminant transport mechanisms may be extrapolated from data resulting from the use of sensitive and specific tracing systems. Biological markers, especially bacteriophages (bacterial viruses) and bacterial spores, can provide an environmentally acceptable, yet cost effective means of determining contaminant transport. Methods for the production, storage and recovery of these tracers are presented and illustrated by reference to case studies.

Introduction

Pollution of our aquatic environment can take many forms and have many consequences. It may be argued that not all pollution is deleterious (e.g., thermal discharges to receiving waters). Notwithstanding, many contaminants are capable of causing damage to the environment.

Pollution control policies can limit potentially harmful discharges to aquatic systems, and the effectiveness of such control procedures will be governed by a number of factors.

Implementation of such policies in the U.K. has led to the concepts of Environmental Quality Objectives (EQO's) and concomitantly Environmental Quality Standards (EQS's). Other European states favour the policy of Uniform Emission Standards for certain "Blacklist" substances (Bjerre and Hayward, 1984).

Irrespective of the philosophy behind a control policy, its effectiveness can be properly monitored only if regulatory authorities have the ability to measure pollutants. Equally important is knowledge regarding the fate of contaminants in aquatic ecosystems and their significance in terms of health and environmental impact. A number of techniques have been developed to gain data concerning the fate of pollutants in aquatic environments. These include the use of biological tracing systems.

The Nature of Potential Contaminants

The range of contaminants capable of being discharged to receiving waters is vast. They vary from inert materials to highly toxic or recalcitrant compounds such as PCB's (Table 1).

Table 1. Categories and sources of contaminants entering receiving waters.

Category	Sources
Particulates	<ul style="list-style-type: none"> . Dredging spoil . Fly ash . Incinerator residues . Mining spoil . Sewage sludge
Chemicals (organic/inorganic)	<ul style="list-style-type: none"> . Multi-point from manufacturing, use or disposal operations
Radioisotopes	<ul style="list-style-type: none"> . Medical facilities . Military and civil nuclear facilities
Biological (bacteria/algae/viruses)	<ul style="list-style-type: none"> . Agricultural practices . Sewage treatment facilities

Moreover the contaminants of concern may be represented in the aqueous or particulate phase, in both phases, or as a colloidal suspension.

Tracing Systems Available

Simple experiments to observe water movements were first carried out in the 19th century. The range of techniques available and their sophistication has increased since that time. Our experiences, reflected in this paper, have principally been concerned with the use of biological markers.

Before arriving at a decision as to which tracer to use, due account must be taken of the merits and demerits of the available techniques, bearing in mind the objectives of the study. Only then can the most suitable method be selected; this may not necessarily be a microbial system (Table 2).

Historical Application of Biological Tracers

The principle of using biological markers or tracers can hardly be described as innovative. In his excellent review of clinical aspects of *Serratia marcescens*, Yu (1979) recounts how, in 1906, Dr. M. H. Gordon after gargling a liquid culture of *S. marcescens*, proceeded to recite passages from Shakespeare to an empty House of Commons. He had been commissioned to study the atmospheric conditions of the House after an epidemic of influenza. By recovering colonies of the pigmented *S. marcescens* on agar plates spread around the House, he demonstrated that speech as well as coughing and sneezing could project bacteria into the air. He reportedly suffered no ill effects from the experiment.

The first reference to the use of biological tracers in aquatic environments was to two species of *Serratia*, *S. marcescens* and *S. indica*, being used to track water and effluent movement in marine locations (Putman *et al.*, 1956; Robson, 1956). The organism was used successfully in freshwater by Baaulsrud (1961) and Glenne and Simensen (1963). Further studies using *S. marcescens* were reported by Rippon *et al.*, (1961) and Rippon (1963), who used the bacterium to track water emanating from a power station discharge to

Table 2. Summary of tracing systems/tracers commonly used in aquatic situations.

Category	Examples
Physical/Mechanical	<ul style="list-style-type: none">. Floats. Drogues. Surface Radar. Modelling
Chemical	<ul style="list-style-type: none">. Coloured substances. Fluorescent dyestuffs. Ionic - LiCl, NaCl
Radiochemical	<ul style="list-style-type: none">. Aqueous phase - ^{82}Br, ^{60}Co, ^{36}Cl. Particulate phase - ^{110}Ag, ^{198}Au. Biphasic - ^{24}Na
Biological	<ul style="list-style-type: none">. Yeasts - <i>S. cerevisiae</i>. Bacterial (vegetative) - <i>Serratia indica</i>. Bacteria (spores) - <i>Bacillus globigii</i>, <i>B. stearothermophilus</i>. Bacteriophages - <i>Serratia marcescens</i>, <i>Bacillus</i> spp., <i>Enterobacter cloacae</i>, <i>Escherichia coli</i>

an estuary in southern England. The first reference to the use of a spore bearing bacterium as a marker was by Pike *et al.*, (1969) who compared *S. indica* and the spores of *Bacillus subtilis* var. *niger* with a radioisotope tracer (^{82}Br) for tracing sewage dispersion at sea.

At about this time workers in Finland successfully used a bacteriophage (bacterial virus) to measure river flows between three points (Niemela and Kinnunen, 1968). Bacteriophages have since become the tracer of choice in many situations, although the

spores of *Bacillus globigii* var. *niger* (formerly designated *B. subtilis* var. *niger*) is eminently suited for coastal studies. The conservative nature of the spore allows the long-term tracing of water movements. Survival in seawater is excellent, even under the most severe conditions (Godfree, 1985).

Biological Markers Available

A wide range of microorganisms possess characteristics which may make them suitable as tracers of water movements. Yeasts, fungal spores, bacteria, bacterial spores and bacteriophages have all been used (Keswick *et al.*, 1982). Many of these are unsuitable for marine studies due to their poor survival, low dilution capacity or natural occurrence. In our experience bacterial spores or bacteriophages are the only groups of biological tracers capable of providing meaningful results from coastal environments.

Production of Biological Markers

Bacterial Spores

Spores of *B. globigii* var. *niger* are commercially available. They can be grown in the laboratory by a highly selective sequential batch culture process (Evans and Harris-Smith, 1971). Optimisation of the cultural conditions to ensure good sporulation and the production of stable, well-pigmented, spore producing colonies is problematic. For this reason most workers tend to purchase the spore concentrates (1×10^{11} mL⁻¹) which may be held for several months at 4°C with no apparent loss of viability.

Bacteriophages

Yields of bacteriophage in the order of 10^{11} to 10^{13} pfu mL⁻¹ in whole lysed cultures have been reported (Sargeant and Yeo, 1966; Sargeant *et al.*, 1986). Using commercially available fermenters these yields can be routinely achieved in a reasonably well equipped laboratory.

We have used culture apparatus consisting of a two litre vessel stirred by means of a central drive shaft and two attached impellers. Associated controls allow the continuous

measurement and correction of pH, temperature and dissolved oxygen content of the culture (500 Series III Modular Fermenter, L. H. Engineering Co., Ltd., Stoke Poges, Bucks, U.K.).

In order to monitor the progress of the bacterial culture, the carbon dioxide content of the effluent gas is continually analysed and recorded. This is achieved by passing a proportion of the effluent gas stream through an infra-red gas analyser (carbon dioxide analyser type SS1, Analytical Development Co., Ltd., Hoddesdon, Herts. U.K.) linked to a standard flat bed recorder. The determination of carbon dioxide levels in the effluent gas allows an accurate and reliable estimation of the viable count of the culture at all times (Telling, *et al.*, 1958).

Using the equipment described, a number of different phages have been grown to high titres. These include phages of *Enterobacter cloacae*, *Serratia marcescens* and the coliphages lambda B2 and MS2. The bacterial hosts are maintained on nutrient agar slopes in screw-capped universal bottles held at 4°C. The cultures are renewed at four monthly intervals. Phage suspensions are stored in glycerol and held in a deep freeze at minus 18°C. Bacterial seeds, which are used to inoculate the fermentation vessel, are prepared as follows. Nutrient broth is added to a slope of the host bacterium sufficient to cover the agar surface. After incubation for 4 - 6 hours at 37°C, the broth is used to flood the surface of a nutrient agar slope within a 500 ml medical flat bottle. This is left to stand for about 30 minutes after which time excess liquid is drained from the slope, and the bottle incubated overnight at 37°C. Following incubation, 10 ml of sterile, quarter strength Ringers solution and a small number of sterile glass beads (8-9mm diameter) are added to the slope and gently agitated to remove the surface growth. The resulting suspension generally contains $1-2 \times 10^{10}$ viable organisms and may be stored at 4°C for at least two weeks without appreciable loss of viability. This may be used to inoculate the culture vessel at approximately 1×10^7 viable organisms mL^{-1} i.e., 1.5 - 2.0 ml of suspension.

The use of the equipment described previously allows a precise control of cultural conditions, enabling optimum growth of the bacterial host using a medium designed to maximise cell yields (Sargeant and Yeo, 1966). This comprises (gL^{-1}) casein hydrolysate

(Oxoid L41) 30.0, glycerol (Analar grade) 20.0, yeast extract (Difco) 1.0, KH_2PO_4 5.0 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 1.0. The pH is adjusted to 7.0 using 10N sodium hydroxide prior to sterilisation at 115°C for 20 minutes. All cultures are grown at 37°C. The dissolved oxygen concentration is controlled to ensure at least 70% saturation. Provided this can be maintained, no drop in the pH of the culture occurs, obviating the need for pH correction. As a result of the vigorous agitation, foam production will occur, and if excessive this will carry over from the vessel blocking filters (both air into and out of the vessel is passed through filters of 0.2 μm porosity to ensure a pure culture inside and no contamination outside the vessel). Foam is controlled by the manual addition of a sterile 25% (v/v) aqueous solution of polypropylene glycol.

A preliminary culture of each host bacterium is grown in order to obtain a correlation between the viable bacterial count and the carbon dioxide concentration in the effluent gas. During culture runs carried out subsequently, the measurement of carbon dioxide content is used to monitor the progress of the culture and determine the optimum stage for infection with phage. This is generally at a point where lysis of the host culture occurred immediately prior to the potential peak of carbon dioxide evolution. The ratio of host cells to phage particles at the time of infection is adjusted to give an excess of phage, usually at least five particles to every host cell. This is done in an attempt to ensure that all host cells are simultaneously infected and that only one cycle of infection ensues. In such a situation, lysis will be rapid and complete. In all cases the carbon dioxide evolution rate continues to rise after the addition of phage for a period of time consistent with the particular strain being produced, after which the rate will fall steadily, reaching a base level within 1.5-2 hours, indicating complete lysis. At this point the crude lysate is suitable for use as a tracer, if used within a short period (e.g. five days). However, if the suspension requires storage then a concentration step is recommended.

This is achieved by the use of a polyethylene glycol separation (Yamamoto *et al.*, 1970). Following lysis the culture is removed from the vessel. Sodium chloride is added to give a concentration of 0.5M and the culture allowed to cool overnight to 4°C. At this

stage a precipitate of cell debris will have formed which is discarded. To the supernatant is added polyethylene glycol having a molecular weight of approximately 6000 (Sigma Chemical Co., Ltd., Poole, U.K.) and stirred until fully dissolved. The rate of addition of polyethylene glycol is at 10% (w/v) except in the instance of the small RNA phage MS2, where the rate is increased to 12.5% (w/v). Allowing to stand again overnight at 4°C produces a dense sediment which contains up to 99.99% of the phage present in the original culture lysate. This lower layer is retained and following washing in tris buffer, (comprising NaCl, 0.15M; MgCl₂, 0.1M and tris hydrochloride 0.02M) is mixed with an equal amount of glycerol prior to storage at -18°C. Under these conditions the phage suspension can be stored for a considerable period (several years) with no detectable loss of viability.

ENUMERATION

Bacterial spores

The recovery technique involves a membrane filtration procedure. Colonies so arising have a typical appearance being bright orange in colour (Fig. 1).

The membranes and absorbent pads used are Gelman 0.45 µm (GN-6). The recovery medium consist of 2g tryptone (Oxoid L42), 0.5g sodium chloride (Oxoid L5), 90 ml distilled water, pH 6.8. This is autoclaved at 121°C for 15 mins and 10 ml of a filter sterilised solution of glucose and mannitol (10% w/v of each) is added before use.

The samples are heated at 63°C for 30 minutes in a waterbath to induce germination. This also serves to inactivate vegetative bacteria. A known volume, dependent on the circumstances of the investigation, is filtered through a membrane. Membranes are incubated on a pad soaked in the recovery medium for 18 hours at 30°C and characteristic orange colonies are counted.

Figure 1. FLOW DIAGRAM FOR RECOVERY OF B. GLOBIGII SPORES FROM AQUEOUS ENVIRONMENTS

HEAT AT 63°C FOR 30 MINS TO INDUCE GERMINATION



MEMBRANE FILTRATION (1-100ml)



PAD SOAKED IN B. GLOBIGII RECOVERY MEDIUM



INCUBATE @ 30°C FOR 18 HRS



EXAMINE AND ENUMERATE ORANGE COLONIES

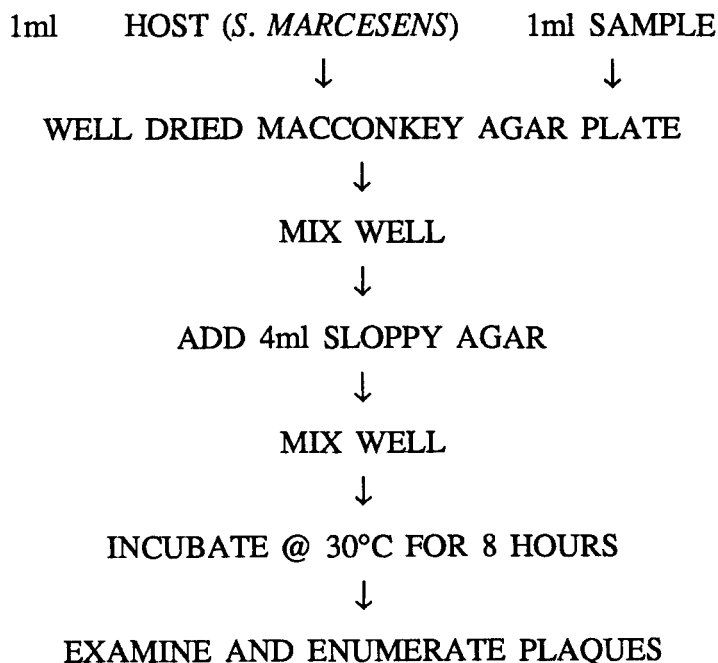
Bacteriophages

The bacteriophages are assayed by a selective sloppy agar overlay technique (Adams, 1959). If the samples are not to be examined immediately, it is advisable to put small amount of chloroform in the sample bottles to inhibit bacterial growth. The multiplication of phage gives rise to discrete plaques in the lawn of host bacterial (Fig. 2).

MacConkey agar (Oxoid CM7) is a standard preparation. The sloppy agar consists of (g/L) bacteriological agar (Oxoid L11) 9.1, nutrient broth (Oxoid CM76) 11.2, and sodium chloride (Oxoid L5) 7.0. This is distributed into 4 ml volumes and autoclaved at 121°C for 15 mins. The bacteriophage diluent comprises (g/L) bacteriological peptone (Oxoid L37) 1.0, sodium chloride (Oxoid L5) 0.3, 0.5M magnesium sulphate, tris hydrochloride 10ml, adjusted to pH 7.8 and autoclaved at 121°C for 15 minutes.

1 ml of the sample, either neat or diluted, is inoculated onto a well-dried MacConkey agar plate and 1 ml of a 12-18 hour nutrient broth culture of the host bacterium added. These are mixed well and 4 ml of molten sloppy agar held at 50°C is added. Immediate thorough mixing to ensure even-lawn plates then follows. Plates are allowed to set and incubated for at least 8 hours at 30°.

Figure. 2. FLOW DIAGRAM FOR RECOVERY OF BACTERIOPHAGE FROM AQUEOUS ENVIRONMENTS



FIELD STUDIES

Principally tracers have been used in coastal waters to model dispersion from submarine sewage outfalls. In such cases the contaminants of concern are microbiological or occasionally chemical. Existing discharges may also be investigated in order to differentiate the relative influence of adjacent outfalls.

During the period 1979-80 intensive investigations were carried out by North West Water Authority (NWWA) along the Fylde Coast area of NW England (Fig. 3). This section of coastline stretches for some 25km in an almost straight S - N direction. Rivers enter the sea at either extremity. Four major sewage outfalls and several stormwater discharges are located along this stretch of coast. Typical dry weather (DWF) flows are in the order of 102,000 m³ d⁻¹ of screened sewage. The resident population is 258,000 rising to an estimated 600,000 during the summer period. Day visitors during peak holiday

periods can result in total populations in excess of 1,000,000 on occasions. The coastal zone and associated coastal waters have considerable amenity and recreational value.

Routine monitoring of the coastal water zone was instigated during 1976 and continues to date. Using the requirements of the EC Directive on bathing water as a guide (Anon, 1975) sampling is conducted each year between May and September. Fifteen sampling stations along the entire length of the coast are monitored for a range of microbiological parameters; namely total coliforms, faecal coliforms and faecal streptococci. Figure 4 summarises a selection of the data resultant from this sampling programme. From these data, which are typical for the entire period, it is clearly evident that although counts vary along the coast they consistently exceed the requirements of the EC Directive (Table 3).

Table 3 - Summary of bacteriological quality requirements contained in the EC Directive concerning the quality of bathing water

Parameter (dL ⁻¹)	G		I	
Total coliforms	500	(80)	10,000	(95)
Faecal coliforms	100	(80)	2,000	(95)
Faecal streptococci	100	(80)	-	

Key

G = Guide value

I = Mandatory value

Figures in parenthesis shown percentile compliance

The development of a strategy designed to improve water quality in microbiological terms was undertaken. A prerequisite to the definition of treatment options was the identification of sources of faecal bacteria as revealed by routine monitoring.

Each outfall was investigated in turn on both neap and spring tides. A single discharge, occurring on the ebb tide, was labelled with *B. globigii* spores in proportion to the anticipated flows; typically one litre of spores to 5000 m³ effluent. Water samples were collected across an offshore sampling grid and along the shore at pre-determined intervals of 500 m. Sampling runs were carried out every three hours for the first day, progressively reducing to 12 hourly after 96 hours following discharge.

Figure 3. Location plan of study area.

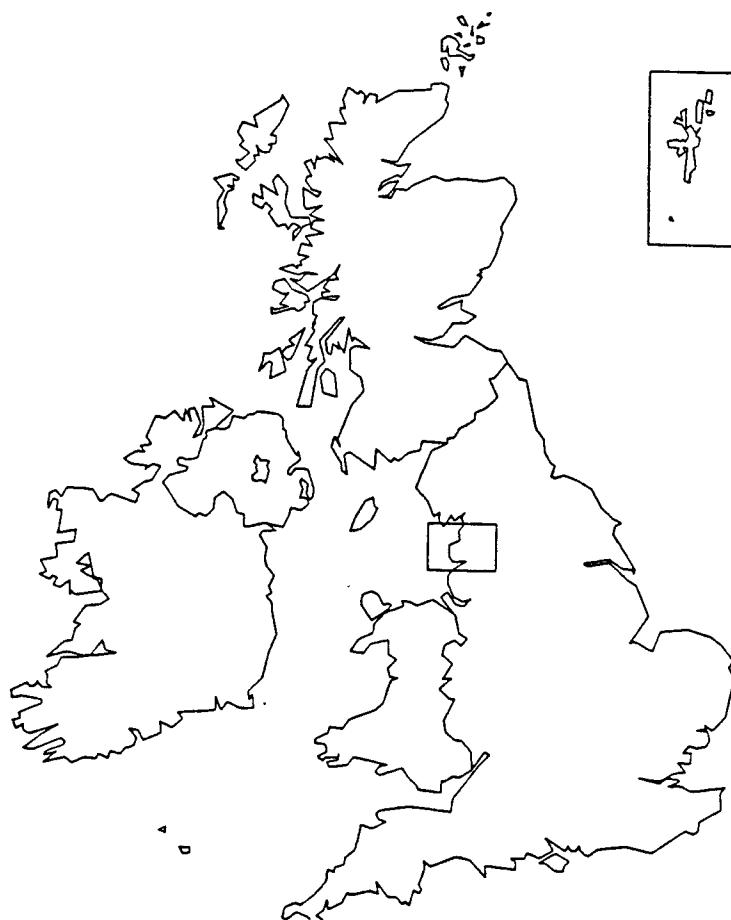
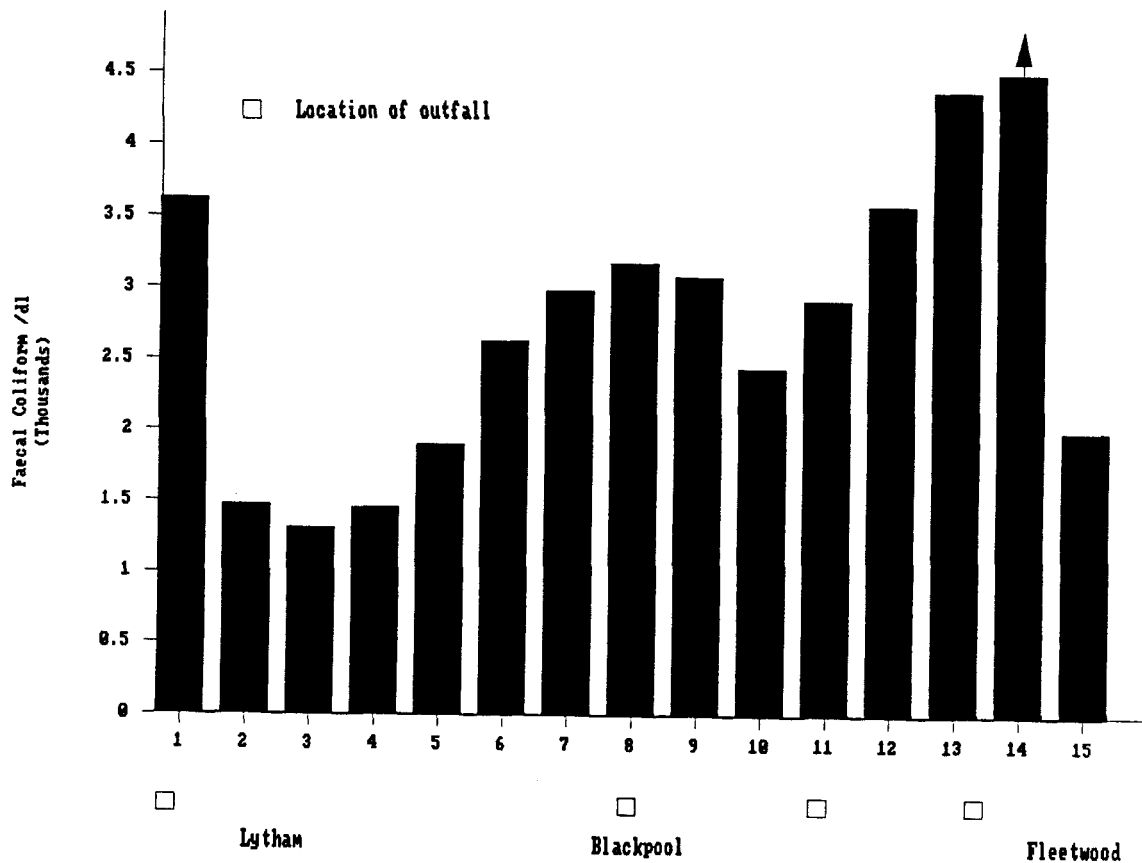


Figure 4. Mean faecal coliform counts at 15 sampling stations 1979-1982



The study showed that the central and northern sections of the coast were affected principally by sewage discharged from the three most northerly outfalls. The beaches at the southern extremity of the coastal strip appeared to be influenced by bacterial concentrations in the outflowing River Ribble in addition to an adjacent outfall.

It was clearly evident that in order to achieve the necessary water quality improvements required by the application of the EC Directive, considerable changes in the pattern of sewage discharge to the coastal zone was indicated. Computer modelling techniques were employed to define more closely the engineering options under consideration. Predicted dispersion patterns were validated by the continuous discharge of

B. globigii over several tidal cycles followed by field measurement of tracer concentration. The preferred engineering option involves the construction of a submarine outfall discharging screened sewage 5 km off the northerly end of the coastal strip. Flows from the three most northerly outfalls would be directed to this new outfall. Existing outfalls would remain and serve as emergency storm water overflows (Anon, 1988).

Future Developments

To date biological markers have found application in the tracing of water or effluent movements. Groundwaters, rivers, lakes and even treatment facilities can be studied with biological tracers. In principle, sediment transport mechanisms would be amenable to study by the use of bacteriophages. Certain strains of bacteriophage have been shown to be selectively bound to particulates (Adams, 1959).

Concern regarding the Public Health implications of consumption of shellfish contaminated with enteric viruses is increasing (Gerba, 1988). Bacteriophages, especially coliphages, are now being used in the UK to model enteric viruses in order to determine the accumulation and retention of viral particles by Shellfish (West, Pers. Comm).

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Appendix I is available from Aquatic Habitat Institute, Richmond, CA (415) 231-9539.

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CHEMICAL TRANSFORMATIONS OF CONTAMINANTS IN DREDGED MATERIAL AND IMPLICATIONS FOR BIOAVAILABILITY

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Introduction

San Francisco Bay is a shallow embayment that receives over eight million cubic meters of sediment annually from fourteen tributaries. In addition, spring/summer winds generate waves that resuspend approximately 160 million cubic meters of sediment from the local shallows. These suspended sediments are carried by freshet or tidal currents into navigation channels, where they settle into the low energy regions of the channels. Annual maintenance dredging is required in many of these channels to allow continued national defense and commercial traffic. When the draft of vessels is increased, new work dredging is necessary to provide added bottom clearance. Combined volume of both maintenance and new work dredging may exceed eight million cubic meters annually. These materials are presently discharged into the Bay at one of three aquatic disposal sites. The sites are located at Alcatraz, San Pablo Bay, and Carquinez Strait. Alcatraz is the primary site, receiving more than one-half of the disposed dredged material in San Francisco Bay.

Dredging and disposal operations have the potential of redistributing and releasing contaminants to the biota of the Estuary. Navigation channels receive contaminants from the atmosphere and from point and non-point sources adjacent to the waterway as well as from the vessels themselves. These contaminants are distributed among aquatic environmental compartments (sediments, water, suspended particulates, biota) according to their affinities for each. On a mass basis, by far the greatest proportion of chemical

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contaminants are accumulated in the sediments, which may be enriched several orders of magnitude over the contaminant concentrations found in overlying waters. Most contaminants become tightly bound in the sediments and are not readily available to organisms. Disturbance of the bottom by dredging equipment during the excavation process or subsequent release of dredged material back into the water has the potential of affecting sediment chemistry and increasing contaminant bioavailability. Chemical reactions may enhance bioavailability by changing the form of the contaminant or by simply releasing the contaminant back into the water from the sediment matrix.

The purpose of this paper is to review the chemical reactions that may occur during the dredging or disposal process and their implications for increased contaminant bioavailability in San Francisco Bay. Much of the discussion is drawn from research conducted during the mid-1970's in the bay. However, as indicated by more recent literature, many of the findings are still relevant. Bioavailability of organic chemical contaminants that are influenced more by physical processes than by chemical is also discussed. A numerical procedure is used to obtain a quantitative estimation of bioavailability of organic chemical contaminants in deposited sediment samples from the Alcatraz Disposal Site.

Sediment/Contaminant Reactions

The most accessible compartmental fractions of disturbed sediments to organisms are the organic carbon, the interstitial water, and the mineral surface ion exchange fractions. The organic carbon is almost exclusively the site for sorption of neutral organic chemicals such as polychlorinated biphenyls (PCB) or the polynuclear aromatic hydrocarbons (PAH); mineral surface adsorption sites for such compounds become important only when the sediment total organic carbon (TOC) is very low. The mineral surface ion exchange fraction and the interstitial water contain only a minor portion of the total heavy metal burden of the sediments (Serne and Mercer, 1975) but are probably the most significant in terms of bioavailability. Interstitial water metal concentrations are primarily dependent on the Eh and pH of the *in situ* sediment and the exchange reactions occurring under these conditions. When the sediments are resuspended during dredging operations, the interstitial

waters can be dispersed and diluted by the overlying waters almost immediately. Metal ions that may dissociate under these conditions, or other contaminants that are released, can complex with both inorganic and organic ligands or may be taken up by organisms. At the same time, dilution and dispersion reduce concentrations of chemicals that are locally bioavailable.

TOC consists primarily of humic matter and constitutes as much as 10-20% of harbor and channel sediments. Ranges for San Francisco Bay navigation channel sediments in general are on the order of 1-2%. Sediment organic carbon behaves as though it were an organic solvent in competition with the lipids of biota for distribution of any neutral organic chemicals that are present. However, many other factors operate to influence the rate at which a chemical dose is delivered to an organism, i.e., its "bioavailability." The maximum dose of neutral chemical an organism could receive from a sediment is indicated by the bioaccumulation potential of the sediment, a thermodynamic concept independent of rate.

For neutral organic chemicals, i.e., for those that do not dissociate, are not protonated, or do not interact electrostatically with solvents or substrates, the organic carbon content of the sediment is the primary determinant of bioaccumulation potential. Whether or not an organism would actually bioaccumulate to the calculated potential is determined by rate-affecting processes, or kinetics. For the same concentration of a neutral chemical on a whole sediment basis, high TOC content reduces bioaccumulation potential, and lower TOC proportionally increases it. TOC provides a basis for normalizing chemical concentration data among sediments of differing origin. For example, two sediments, one having 2 ppm DDT and 6% TOC, and the other having 1 ppm DDT and 3% TOC would both have 33 ppm DDT on an organic carbon-normalized basis, and would have the same bioaccumulation potential, but not necessarily the same bioavailability.

Metals also associate with the organic carbon fraction of sediments. However, the association is by electrostatic interaction with functional groups rather than by passive equilibration. Sediment organic carbon is predominantly associated with the fine-grained

(silt-clay) mineral fraction of sediments and it is this material that may be suspended during dredging operations. The TOC of the suspended sediment fraction is typically higher than the TOC of the *in situ* density sediment and may exceed 50%. Particulate organic materials in suspension can act as strong scavengers of metals and organic chemicals from the water column. In sea water the presence of divalent cations can cause particulate, colloidal, and soluble organic materials that are released by re-suspension to flocculate and settle out. Lower molecular weight organic acids under the same conditions can be precipitated as metal fulvates and humates with possible coprecipitation of trace elements (Williams *et al.*, 1974).

Ion-exchange sites, representing the ability of sediment particles to participate in exchange reactions, result because the particle surfaces, rather than being neutral, bear negative electrostatic charges. When a clay mineral with its negatively charged surface is immersed in salt or brackish water, there is a tendency for cations dissolved in the water to be attracted by electrostatic forces to the particle surface. Postma (1967) suggested this negative charge may be explained by: (1) residual valences (broken bonds at particle edges); (2) substitutions within crystalline lattice structure; (3) preferential adsorption of anions, especially hydroxyl ions, to the particle. The number of cations required to neutralize the surface charge is referred to as the "cation exchange capacity" of the mineral. Commonly the cation exchange capacity in San Francisco Bay sediments ranges from 10.6 to 35.2 meq/100g (Serne and Mercer, 1975).

Many factors, both physical and chemical, influence these ion-exchange reactions in the estuarine environment. The physical factors of the environment appear to be the major controlling component for the exchange reactions (Lee, 1970). These factors can be separated into the hydrodynamics of the system and the mixing of the sediments. In the San Francisco Estuary, the hydrodynamics are primarily affected by the tides but additionally freshwater inflow, atmospheric conditions, shipping, and to some extent pleasure boating can cause mixing of the water. These currents in the overlying waters tend to transport leached materials away from the sediments or an effluent outfall, allowing concentration-dependent exchange reactions to proceed. The amount of mixing that occurs

in the sediments can determine the rate of exchange as well as the depth of sediment that may ultimately become involved in ion-exchange reactions.

The chemical factors can be separated into the relative concentrations of the various ions, the concentration of positive charge possessed by the dissolved ion, the total ionic strength of the solution, and the specific interactions between certain ions and certain alumino-silicate clay minerals (Nelson, 1962).

Heavy metal cations participate in these exchange reactions to a greater or lesser extent, particularly during the transition of particles from freshwater to saline waters (Kharker *et al.*, 1968). Ion exchange-site extractions of selected Bay sediments indicated that 3.2 percent of the total copper, 1.8 percent of the total cadmium, 0.9 percent of the total lead, 1.4 percent of the total zinc and 19.3 percent of total manganese may be contained on these sites (Serne and Mercer, 1975). The possible release of these metals via replacement during resuspension in fresh water would elevate ambient water concentrations and thereby increase bioavailability of the metal for some period of time.

Chemical Transformations of Resuspended Sediments

Sorptive behavior and oxidation-reduction potential (redox) reactions of various chemical contaminants that occur with sediments during dredging and aquatic disposal and after redeposition, govern to a large extent the distribution of chemical constituents among various available and nonavailable forms. These contaminants may exist in various forms and reside in different fractions of the sediment, making them more or less available to the water column and to organisms. The heavy metals in the sediment may be found in the soluble form, exchangeable form, in the carbonate mineral phase, easily reducible form, or may be bound by interactions with organic and sulfide fractions, associated with a moderately reducible iron oxide or hydroxide, or present in the intricate lattice structure of clay and silicate minerals.

Among the metal species in various geochemical fractions of sediment, the fractions in the interstitial waters and water soluble phase can be immediately available for biological

uptake upon resuspension of sediments. However, these fractions represent only an extremely small part of the total metals present--the non-residual fraction. This non-residual fraction, consisting of trace metals from land source pollution and marine derivation, in contrast to that derived from crystalline structure of minerals, i.e., the residual fraction, has magnitudes ranging from a low of 1.4 percent for copper to a high of 98 percent for cadmium (Serne and Mercer, 1975). The residual phase, which contains the greatest percent of most trace metals, is probably not available for biological uptake.

During dredging and disposal activities, contaminants in the sediment are brought into direct contact with the water column for some period of time. Because the contaminants are found at much greater concentrations in the sediment than in the water column, the contact time during dispersion and settling could result in their release and availability for biological uptake. Depending on the water depth, mixing, and sediment characteristics, contact time between the disturbed sediments and water column will vary.

A sudden release of low levels of some trace metals into the water column upon addition of dredged material to seawater has been observed in laboratory studies (Chen *et al.*, 1975; Serne and Mercer, 1975). This is followed by a subsequent removal of metals from solution; either gradually, as would often be found in slightly reducing environments, or rapidly under oxidizing environments. The initial release of trace metals is most likely due to the dilution of interstitial waters, dissolution of the solid phase through complex formation, and release from the exchangeable phase (Chen *et al.*, 1975).

Turbulent mixing at any Bay disposal site during introduction and settling of the dredged material promotes the release and diffusion of metals from the enriched interstitial water found in reduced sediments. Upon release and exposure to oxygen many reactions occur. Metal species can be reabsorbed to organic matter, hydrous iron and manganese oxides; or form precipitates or complex compounds. The presence of active redox species such as carbon, nitrogen, oxygen, iron, manganese, and sulfur play predominant roles in regulating the soluble metal concentrations in the water column.

Oxidation-reduction potential, salinity, agitation time, solids-to-solution ratio, and type of sediment are considered to be the most important factors determining the release of trace metals to the water column during disposal of dredged material. During sorption-desorption laboratory experiments with dredged sediment from San Francisco Bay, oxidation-reduction potential was the factor demonstrated to have the greatest effect on the fate of trace metals (Serne and Mercer, 1975). The results of the experiments are summarized below.

Oxidizing Conditions

Under oxidizing conditions more copper, cadmium, lead, and zinc were released to the water column than under reducing conditions. However, more iron was released to the water column under reducing conditions. The release of mercury was not significantly affected by either oxidizing or reducing conditions.

Salinity

At higher salinities more cadmium, copper and zinc were released to the water column under oxidizing conditions and more iron under reducing conditions. The release of lead and mercury was not significantly affected by different salinity conditions either under oxidizing or reducing conditions.

Agitation Time

Under oxidizing conditions more cadmium, copper, and zinc were released during a longer duration in agitation time.

Solids-to-solution ratio

With an increase in the solids content in the sediment-seawater mixture, more zinc and iron were released under both oxidizing and reducing conditions.

Bioavailability of Metals in San Francisco Bay Sediments

To investigate bioavailability, dredging operations in Mare Island Strait in northern San Francisco Bay were examined between September 1973 and May 1974 to determine whether these operations release toxic heavy metals from the dredged sediments, resulting

in elevated concentrations of these metals in adjacent sediments and invertebrate populations (Anderlini *et al.*, 1975a).

Concentrations of silver, arsenic, cadmium, copper, mercury, nickel, lead, selenium and zinc were monitored prior to, during, and after two dredging periods. Metal concentrations were measured in sediments, several native invertebrates, and in mussels transplanted into Mare Island Strait from Tomales Bay, a relatively undisturbed area on the California coast. Samples were collected at stations established immediately adjacent to the dredge zone, and at stations located outside of the area exposed to dredging activity.

Changes in mean metal concentrations in sediments and invertebrates during the study period were relatively small, considerably less than an order of magnitude. Mean metal concentrations in sediments and native invertebrates increased by less than a factor of two and increases in metal levels in mussels were no greater than a factor of three.

The two dredging periods coincided with the two heaviest rainfalls of the year, and the resultant freshwater runoff caused significant changes in the salinity and particulate load in Mare Island Strait. It was therefore not possible to determine whether changes in metal concentration at stations within the dredge zone were caused by dredging or by rainfall phenomena. However, changes in metal levels at stations outside of the dredge zone were of comparable magnitude and direction to those exposed to dredging activity. If the observed increases had resulted from dredging, a gradient should have been apparent in the metal levels as distance from the area of intense activity increased. No such gradient was apparent. Thus, the observed increases could have been the result of rainfall washing pollutants into the channel from the adjacent town of Vallejo (URS, 1974).

Uptake and accumulation of the chloride salts of silver, cadmium, copper, lead and mercury by the clam *Macoma balthica* were examined in a laboratory study (Anderlini *et al.*, 1975a). Exposure to three environmentally realistic concentrations of these metals under three estuarine salinity regimes resulted in uptake above pre-exposure levels. The higher concentrations and lower salinities were associated with the highest

bioconcentrations. Based on these laboratory results, it seems that the uptake observed during the field operations could very well be the result of salinity reductions and metal concentration increases caused by urban runoff.

A second study (Anderlini *et al.*, 1975b) was conducted during a disposal operation to ascertain if chemical reactions resulting from the operation increased the availability of selected toxicants or in other ways caused significant adverse biological effects. The investigation was conducted during the release of 10,000 cubic meters of "polluted" sediments at an experimental disposal site in Central San Francisco Bay. Three inner stations were established 100 meters from the impact point of the release and three outer stations were established 300 meters from the center. The outer stations were situated at a sufficient distance to be used as reference stations receiving no or at most a diminished effect from the disposal. The concentrations of twelve trace elements (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn) were monitored in sediments, suspended and settled particulates, selected benthic invertebrates and transplanted mussels. Concentrations of chlorinated hydrocarbons (DDT, DDD, DDE and PCB as Aroclor 1254) were also monitored in sediment, water and mussels before, during, and after the releases.

The experimental disposal operation did not affect contaminant concentrations in the benthic invertebrates examined nor in mussels transplanted to the disposal area. Chlorinated hydrocarbon concentrations in disposal site mussels fluctuated slightly during the period of study and only DDE levels in mussels appear to have been affected by the disposal operation. DDE levels decreased significantly more in mussels at stations outside of the immediate disposal area and at other central bay locations than in mussels immediately adjacent to the disposal center. This effect was not apparent by the next sampling period, one month later. Subsequent analysis showed that the disposal operation had no effect on aromatic petroleum hydrocarbon levels in the mussels. Comparable results were obtained for the aliphatic fraction.

Based on these two field experiments, bay dredging and disposal activities were found, under the conditions of the experiments conducted, to redistribute contaminated sediments

without resulting in increased contaminant bioavailability. Fluctuations in the concentrations of the test elements were highly correlated with each other in sediment, invertebrates, and suspended and settled particulates, although element levels within any one component were not correlated with element levels in any other component. The high correlation among trace elements within each component suggests that only one or a few parameters may control trace element fluxes in San Francisco Bay.

Although some contaminants exhibit varying degrees of release to the water column during the discharge of dredged sediment, these releases are so small (parts per billion range) and of such short duration (minutes to a few hours) that their actual availability for direct biological uptake is highly localized. Outside of the zone being directly influenced by the operation, concentrations of the released contaminants are tremendously decreased because of dilution with uninfluenced waters. Dilution factors on the order of a thousand to ten thousand occur in a matter of a few hours. However, if the released constituents readsorb on organic or inorganic sinks from which biotransfer is possible, then increased contaminant availability may result in increased organism exposure on a long-term basis from the redeposited sediment (Lake *et al.*, 1988).

Bioavailability of Neutral Organics in Alcatraz Disposal Site Sediments

The bioaccumulation potential of conservative neutral organic chemicals in situations in which contaminated sediments provide the only source of contamination to exposed biota can be estimated by a simple calculation (McFarland and Clarke, 1986; 1987). The estimation is based on passive solubility partitioning of the chemicals and involves normalization of concentration data on the organic carbon fraction of sediments and on the lipid content of organisms. Application of a "preference factor" for equilibrium distribution of a chemical between the two phases (lipid and organic carbon) expresses the concentration of the chemical in lipid equivalents. The unitless preference factor was

calculated as 1.72 (McFarland and Clarke, 1986), and the lipid equivalent chemical concentration in a sediment has been termed the Thermodynamic Bioaccumulation Potential (TBP) (McFarland, 1984). TBP is calculated by equation (1):

$$\text{TBP} = 1.72 (C_s/\text{TOC}) \quad (1)$$

The concentration of a chemical in the sediment (C_s) and the total organic carbon content (TOC) are the input data.

TBP can be used to obtain an estimation of bioavailability if the steady-state concentration in the lipids (C_{ss}) of an organism exposed to the sediment is known or can be estimated. Equation (2) calculates C_{ss} based on a known whole organism chemical concentration (C_l), the lipid content of the organism, and known or estimated percentage of steady state tissue concentration achieved at the time of sampling:

$$C_{ss} = \frac{100(C_l/\text{lipid})}{\% \text{ steady state}} \quad (2)$$

Bioavailability (p) is the proportional difference between the steady state chemical concentration in an organism on a lipid basis and the bioaccumulation potential of the chemical in the sediment (TBP). Equation (3) expresses bioavailability as percent. The calculations require that TOC in equation (1) and lipid in equation (2) be expressed in the same units, e.g., percent or decimal fraction. C_l and C_s must also be in equivalent units.

$$p(\%) = 100 \frac{C_{ss}}{\text{TBP}} \quad (3)$$

Data were obtained in standard 10-day sediment bioassay/bioaccumulation exposures using Alcatraz Disposal Site sediments (McPherson and Chapman, 1983). The clam *Macoma nasuta*, and the sandworm, *Nephtys caecoides*, were analyzed for metals and

organic chemical contaminants after remaining in contact for ten days with sediments collected from several stations at the Alcatraz site. The chemical concentrations in the sediments and TOC of the sediments were also determined. The most complete tissue concentration data were obtained for the clam, and in all cases in which detectable concentrations of organic chemical contaminants were found both in the clams and in the sediments to which they were exposed, data are shown in Table 1. These data were used to calculate bioavailability (percent p) according to equation (3). Because lipid data were not obtained and exposures were not conducted to steady state, default values were used in the calculations. For lipid, a conservative value of 1% was used as the default. This was considered to be a probable normal lower limit for *M. nasuta* based on related species (Wenne and Styczynska-Jurewicz, 1987). Forty percent of steady state at the end of ten days exposure was chosen as a reasonable estimation representative of the chemicals listed in Table 1 based on the literature (Elder *et al.*, 1979; Foster *et al.*, 1987; Langston, 1978; Lohner and Collins, 1987).

Bioavailability as percent p is given in Table 1. The most bioavailable contaminant was DDE, ranging from about 50 to 100% in sediment from three out of four sites tested. DDE is the only organochlorine compound included in these analyses and is known to be highly bioaccumulating and persistent.

Measured concentrations in both sediment and clams were low and near the limits of detection. Variability in these measurements can be expected to have been greater than for the higher chemical mass concentrations and the estimations would have been affected accordingly. Of the PAHs listed, naphthalene showed highest percent bioavailability (31-37%) when present at low concentrations in the sediments (0.02 ppm), and much lower percent bioavailability when at high concentration (6.05 ppm). This observation is similar to observations of differential bioavailability of PCBs dependent on high or low sediment concentrations reported by Clarke *et al.* (1988) and independently by researchers at USEPA-ERL, Newport, OR and Narragansett, RI (manuscripts in preparation). Saturation

Table 1. Concentration of chemicals in sediment (C_s), concentrations in clams (*Macoma nasuta*) after ten days exposure (C_t), and calculated percentage bioavailability (p) at projected steady state (see Equation 3). Sediments collected at four stations at the Alcatraz Island Disposal Site. Concentrations given in wet weight for clams, dry weight for sediments.

Station	Parameter	C_s , ppm	C_t , ppm	p, (%)
A200 (TOC = 0.68%)	DDD	0.095	0.002	2.1
	DDE	0.002	0.001	49.
	Chrysene	0.12	0.002	1.7
	Fluoranthene	0.21	0.002	0.94
	Phenanthrene	0.14	0.001	0.71
	Pyrene	0.31	0.003	0.96
B200 (TOC = 0.99%)	DDE	0.002	0.001	72.
	Acenaphthene	0.27	0.005	2.7
	Acenaphthylene	2.49	0.112	6.5
	Anthracene	2.28	0.032	2.
	Benzo(a)anthracene	2.72	0.005	0.26
	Chrysene	2.95	0.006	0.29
	Fluoranthene	13	0.15	1.7
	Naphthalene	6.05	0.033	0.8
	Phenanthrene	14.2	0.412	4.2
	Pyrene	15.1	0.149	1.4
C200 (TOC = 0.73%)	DDE	0.001	0.001	106.
	Acenaphthylene	0.051	0.002	4.2
	Chrysene	0.57	0.002	0.37
	Fluoranthene	1.7	0.003	0.19
	Naphthalene	0.02	0.006	31.
	Phenanthrene	0.81	0.003	0.39
	Pyrene	1.95	0.004	0.22
D200 (TOC = 0.73%)	Acenaphthylene	0.022	0.003	14.
	Chrysene	0.23	0.002	0.92
	Fluoranthene	0.49	0.009	2.
	Fluorene	0.04	0.002	5.3
	Naphthalene	0.02	0.007	37.
	Phenanthrene	0.26	0.009	3.7
	Pyrene	0.06	0.011	19.

of the sediment interstitial water solubility capacity for hydrophobic organic chemicals has been suggested as a possible explanation for this phenomenon.

It can be seen that the highest sediment concentrations of the chemicals listed in Table 1 tend to produce somewhat higher tissue levels than do the lower sediment concentrations. However, the magnitude of increase in tissue concentrations is often much less than the magnitude of increase in the related sediment. This fact is reflected in percent p in Table 1, and the relationships are quite similar to those previously reported for PCBs (McFarland *et al.*, 1985). Fluoranthene and phenanthrene are exceptional in that bioavailability is roughly proportional to concentration in the sediment, although quite variable.

Implications

Uptake of various contaminants by marine organisms has been documented under a number of scenarios. The extent of contaminant mobilization and the effects on bioavailability produced by resuspension of contaminated sediments by dredging or disposal operations is still unclear (Lake *et al.*, 1988). Based on the work by Serne and Mercer (1975) and Chen *et al.* (1975), transfer via desorption to the water is insignificant compared to the loading induced by municipal-industrial effluents or urban runoff.

The possible importance of action of the highly acid chemical environment in the organism's stomach upon clay minerals or organic molecules that have chelated or complexed trace elements is uncertain. The selective extraction schemes used by Serne and Mercer (1975) and Chen *et al.* (1975) indicate that for the animal to free these elements from the atomic lattice of clay minerals, its gut would have to be made of materials more acid resistant than they are presently believed to be. However, gut acidity would probably be sufficient to hydrolyze and release trace metals bound to sediment organic matter. These organic complexes, sometimes partially broken down, are resuspended and again made available to various pelagic and filter-feeding organisms, and upon redeposition are available to the deposit-feeding organisms in the area influenced by disposal.

Effects that dredging activities may have on organic chemical bioavailabilities from sediments are largely unclear. The principle that governs neutral organic chemical

distribution between sediments and biota, namely passive solubility partitioning, most likely is the primary mechanism that also affects bioavailability under the conditions of resuspension and dispersion produced by dredging operations. The mass concentration of chemical in the water column can be calculated for any level of sediment suspension, and necessarily, will be substantially less than the mass concentration in *in situ* density sediment. The bioavailable fraction of chemical in the water column during resuspension could be expected to be correspondingly lower. Thus, it appears likely that bioavailability of sediment-sorbed neutral organic chemicals during periods of resuspension would be similar to the bioavailabilities described above, only of a lesser magnitude.

The magnitude of the effect of other factors is difficult to gauge. A particle interaction effect, for example, has been reported to reduce the partition coefficient for distribution of both metals and organic compounds between sediment particles and water at high concentrations of solids (O'Connor and Connolly, 1980; Horzempa and DiToro, 1983; Voice *et al.*, 1983). The particle interaction effect is still not fully explained or accepted in the scientific community. However, the existence of such an effect could have substantial implications for contaminant bioavailability during dredging operations. The production of high levels of contaminated suspended sediments, although transient, could conceivably increase the desorbed concentration, and therefore, the bioavailability of chemical contaminants associated with dredged material. There is presently very little reported research that sheds light on whether and to what extent such processes affect bioavailability under natural conditions.

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**SPATIAL AND TEMPORAL TRENDS OF TOXIC CONTAMINANTS IN
SEDIMENTS AND MARINE LIFE OF THE SOUTHERN
CALIFORNIA BIGHT**

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The Ocean Assessments Division (OAD) of the National Oceanic and Atmospheric Administration (NOAA) conducts the National Status and Trends (NS&T) Program, an annual survey of the U.S. coast to monitor temporal and geographic trends of contaminants in sediments, bivalves, and fish, and to document pollution-related diseases of fish. As a part of that Program, OAD's Pacific Office has been reviewing the long-term history of contamination nationally (Mearns *et al.*, 1988) and in specific coastal regions such as San Francisco Bay (Long *et al.*, 1988). The objectives of these historical assessments are to (1) help place the new data in a historical context, (2) identify data gaps (sites, species, chemicals) that might be filled by modifying the NS&T surveys or by conducting new intensive surveys, and (3) provide a data legacy for regional authorities including recommendations for goals of regional monitoring programs.

Currently, OAD is conducting a detailed review of contaminant trends in the Southern California Bight. The Bight is of particular interest because it is one of the few coastal areas in the United States where there has been an historical precedent for regionwide contaminant surveys that have been conducted in conjunction with pollution abatement and contaminant management actions (such as advanced waste treatment, industrial source control, pesticide use and production bans, and control of atmospheric pollutant emissions). Long-term trends of some contaminants such as DDT (dating back to the 1940s; MacGregor, 1974) and PCBs can be reconstructed for the entire region as well as for specific islands, bays, estuaries, and harbors. When coupled with trend data from

pollutant sources, the historical monitoring data can be used as a measure of the benefits and ecological responses of those management actions.

This brief paper reviews our progress in reconstructing the history and geography of contaminants in sediments, fish, and shellfish from the Southern California Bight. It provides an overview of the amount and kinds of data that exists and provides selected examples (mainly for cadmium, PCBs, and chlordane) of a few of the many charts and graphs that have been prepared for the final report.

Methods

Data on levels of trace metals, pesticides, PCBs, and PAHs were identified and acquired from any logical source including federal agencies (EPA IX, Minerals Management Service); state agencies (Regional Water Quality Control Boards, State Water Resources Control Board, California Department Fish and Game); local and regional authorities (Southern California Coastal Water Research Project, county environmental management agencies, sanitation districts, university professors, and student theses); and from scientific literature. Data were acquired in any reasonable form including hard copy and diskettes and digital tapes. In many cases, repeated contacts with contributing scientists and monitoring agencies were required to locate or develop missing information about sites, dates of sampling, species identification, tissues sampled, analytical methods, and other information needed for proper interpretation. All data and information on methods were extracted into a common computer format.

Historical data were acquired for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), chlorinated pesticides, and ten trace elements or metals (arsenic, cadmium, chromium, copper, lead, mercury, selenium, silver, tin, and zinc). The review identified data from over 10,000 samples including 5,000 samples of 132 species of fish and large invertebrates (shellfish) collected in at least 150 federal, regional, and local surveys. Data for contaminants in fish extends backwards in time for 45 years and in sediments (dated cores) several hundred years.

Summary of Results

With notable exceptions, sediments from bays and harbors were generally more contaminated than samples from open coastal sites including most sewage waste disposal areas. Table 1 shows an example of this comparison for cadmium. An exception was the Palos Verdes shelf (in Los Angeles County), which experienced among the highest sediment concentrations of PCBs, DDT, and trace metals and was an epicenter of 100- to 1,000-fold gradients of contamination along the coastal shelf of Los Angeles County. An example is shown for cadmium in Figure 1.

Intertidal mussels reflected regionwide sediment gradients for only a few chemicals: PCBs, DDTs, silver, chromium, lead, chlordane, and possibly tin. However, this does not mean their concentrations were controlled by sediment concentrations. Other trace metals in mussels either demonstrated no regionwide gradients (copper, mercury, selenium, and zinc) or gradients inverse of those in sediments (arsenic and cadmium). In addition, lead demonstrated an along-shore and onshore-offshore gradient indicative of aerial fallout. However, within bays and harbors contaminants in mussels appeared to identify point sources for most contaminants. An example for the regionwide distribution of cadmium is shown in Figure 2.

Large invertebrates such as lobster, crabs, prawns, and scallops did not experience excess metal contamination, except at Palos Verdes during the mid-1970s (mainly for chromium, lead, and silver; Young *et al.*, 1981).

Despite the occurrence of major chemical gradients in sediments, and, to some extent, mussels, there was no evidence of local or regionwide contamination of fish by any trace metal except tin; in the case of tin, there was evidence of higher concentrations in livers of fish collected near or in harbors. PCBs, DDT, and mercury were the only contaminants that appeared to undergo biomagnification (increase in concentration with trophic level; Young, 1984). Eight of the remaining metals experienced either no concentration increases with trophic level (arsenic and selenium) or significant decreases (cadmium, chromium, copper, lead, and zinc). Furthermore, cadmium and arsenic were

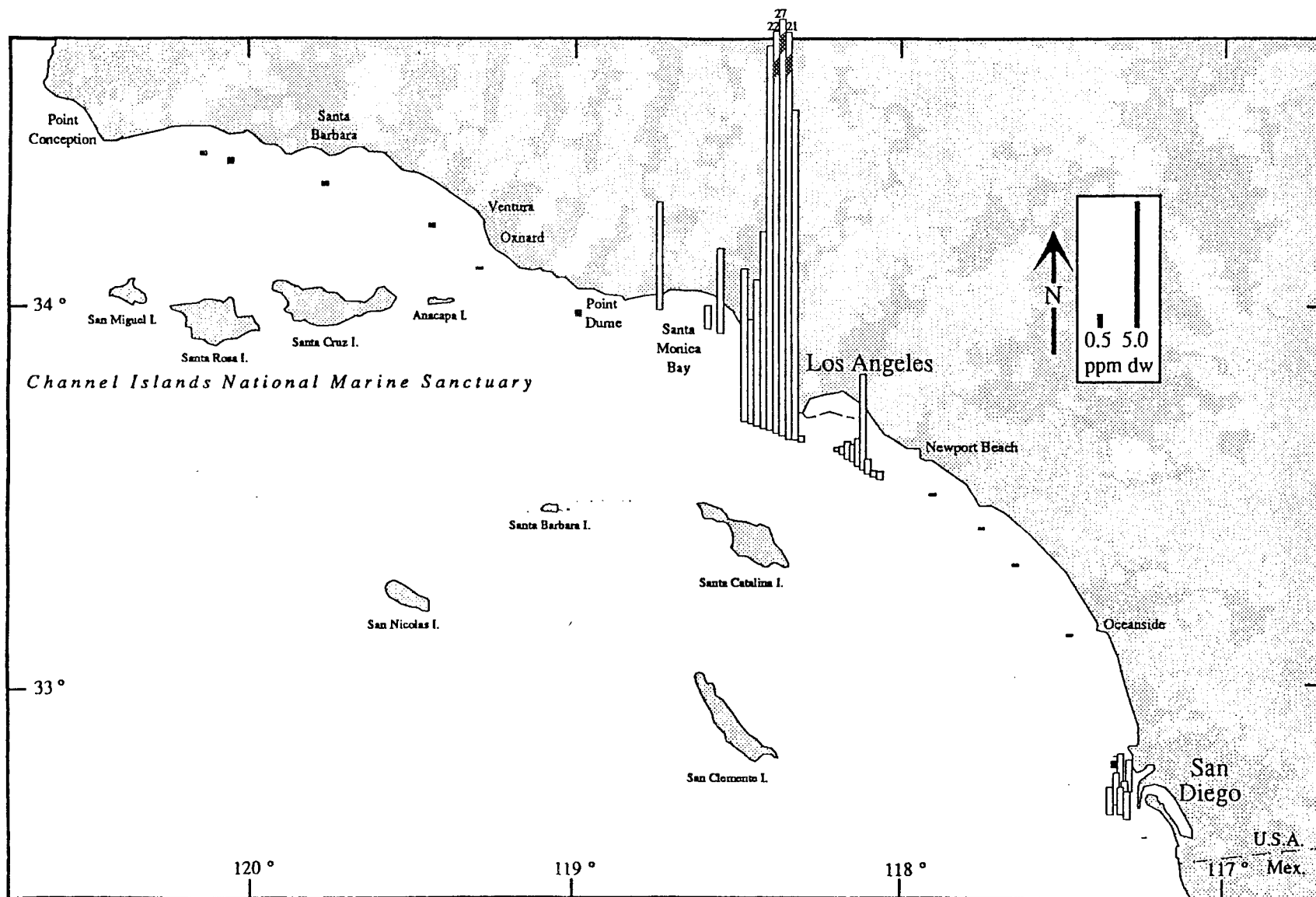


Figure 1. Cadmium concentrations in the surficial sediments of the Southern California Bight along the 60-m contour line for 1985; the black bars are based on data derived from Thompson *et al.*, 1987, while the white bars are based on data obtained from the various sanitation districts (City of Los Angeles, Los Angeles, Orange, and San Diego counties).

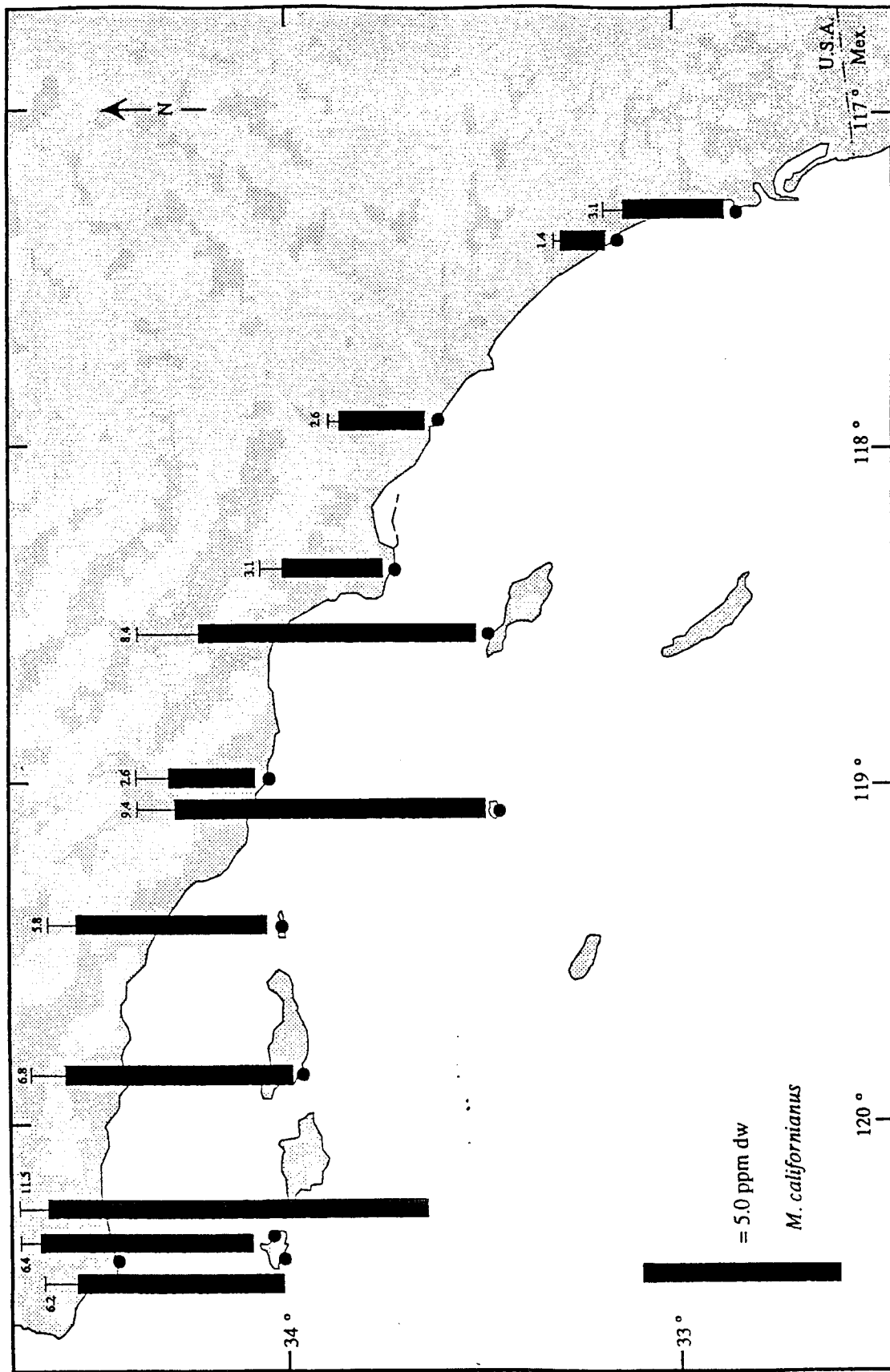


Figure 2. Cadmium in whole soft body tissue, less gonads, of mussels sampled in the Southern California Bight in 1977. Source: CMW Program, Phillips, 1988.

depressed in livers of fish taken from contaminated areas in contrast to those from adjacent or remote areas (de Goeij *et al.*, 1974). Examples for cadmium are shown in Figure 3.

Table 1: Median sediment cadmium concentrations and ratios to reference (0.4 ppm dw) concentration for most recent surveys in 16 coastal areas, bays, or harbors in the Southern California Bight. Data compiled from many sources to be cited in the forthcoming National Ocean Service Technical Memorandum.

Area	Year	Median	Ratio to Reference
Palos Verdes shelf ^a	1985	11.0	27.5
Santa Monica Bay ^a	1985	3.5	8.8
San Diego Harbor	1983	1.8	4.5
Lower Newport Bay	1985-88	1.1	2.7
Point Loma shelf ^a	1985	1.1	2.7
Upper Newport Bay	1980	0.84	2.1
Tijuana Estuary, south arm	1988	0.78	2.0
Los Angeles-Long Beach harbors	1978	0.62	1.5
Orange County shelf ^a	1985	0.60	1.5
Marina del Rey	1985	0.53	1.2
Bolsa Bay	1980	0.45	1.1
Santa Barbara shelf ^a	1985	0.20	0.51
Port Huneme to Point Dume, shelf ^a	1985	0.20	0.5
Tijuana Estuary, north arm	1988	0.17	0.43
Tiguana Estuary, mouth	1988	0.11	0.28
Newport to Dana Point, shelf ^a	1985	0.10	0.25

^a 60-m depth only; otherwise, all depths

In contrast to trace metals, there is abundant evidence of local and regionwide contamination of fish and shellfish by PCBs and the pesticides DDT, chlordane, and dieldrin. Although regionwide contamination gradients for these compounds center about the Palos Verdes Peninsula, there was evidence of independent localized centers of PCB, DDT, and chlordane contamination within San Diego Harbor (PCBs), Los Angeles-Long Beach harbors (PCBs and chlordane), Upper Newport Bay (DDT), and Marina del Rey (chlordane). An example is shown for PCBs in Figure 4 and for chlordane in Figure 5.

Long-term monitoring and analyses of dated sediment core samples do not indicate that any contaminant or contaminant class is increasing in concentration at or near past coastal contamination centers. On the contrary, there is strong evidence of moderate-to-major decade-long decreases of sediment contamination by trace metals, PCBs,

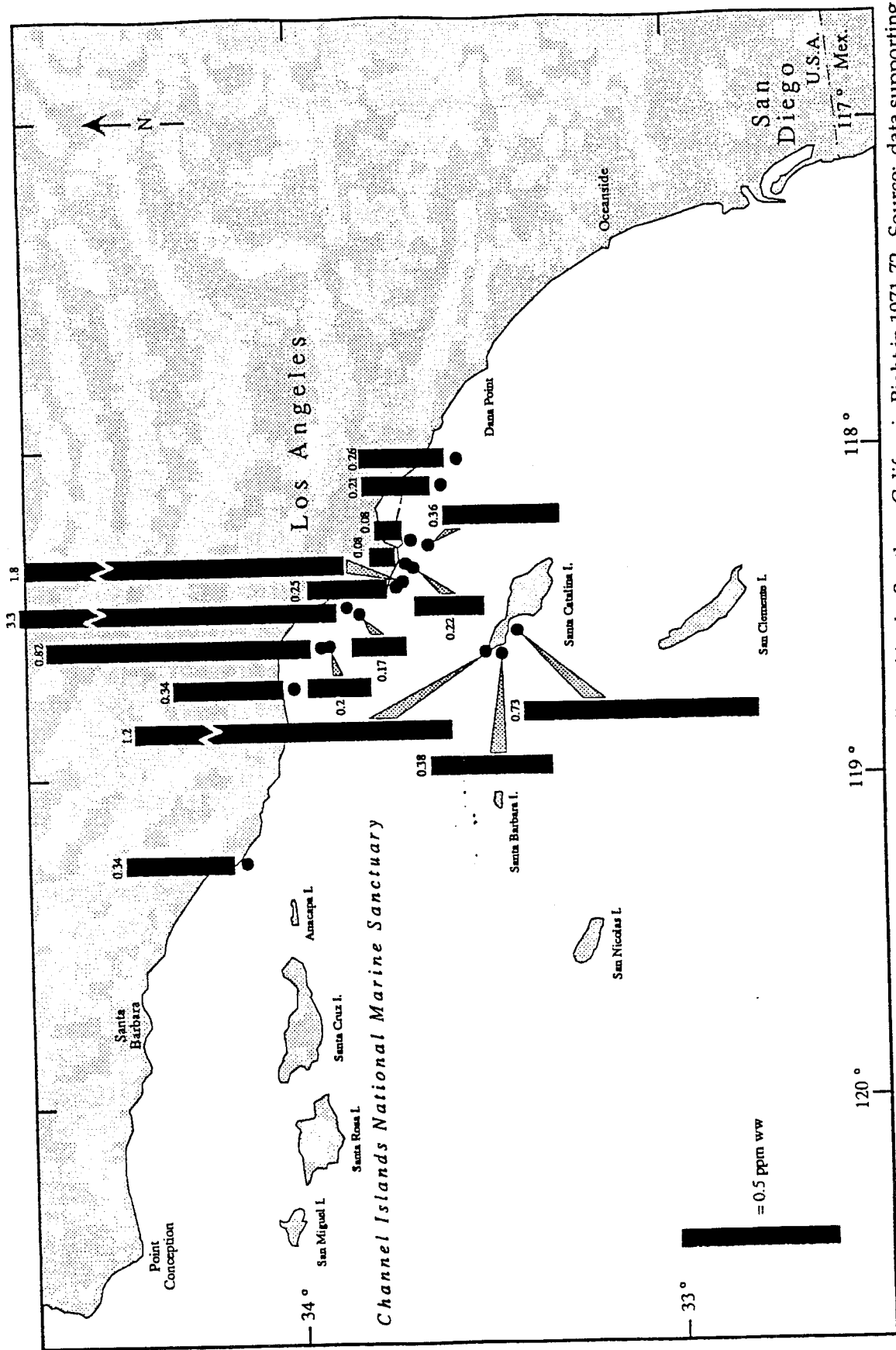


Figure 3. Cadmium concentrations in liver tissue of Dover sole collected in the Southern California Bight in 1971-72. Source: data supporting de Goeij et al., 1974.

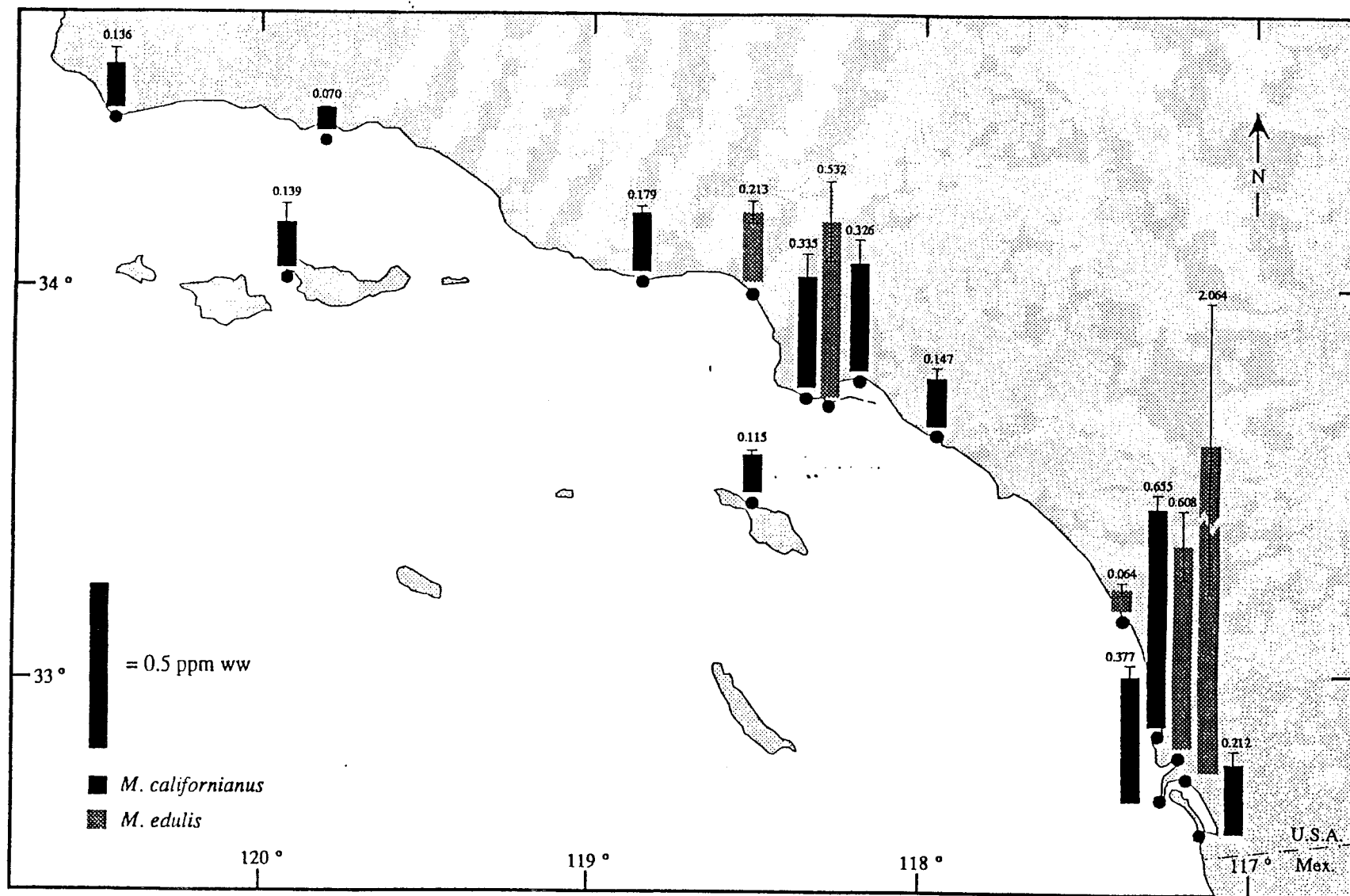


Figure 4. tPCB in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 30 individuals each. Source: NOAA NS&T Program (data supporting NOAA, 1987).

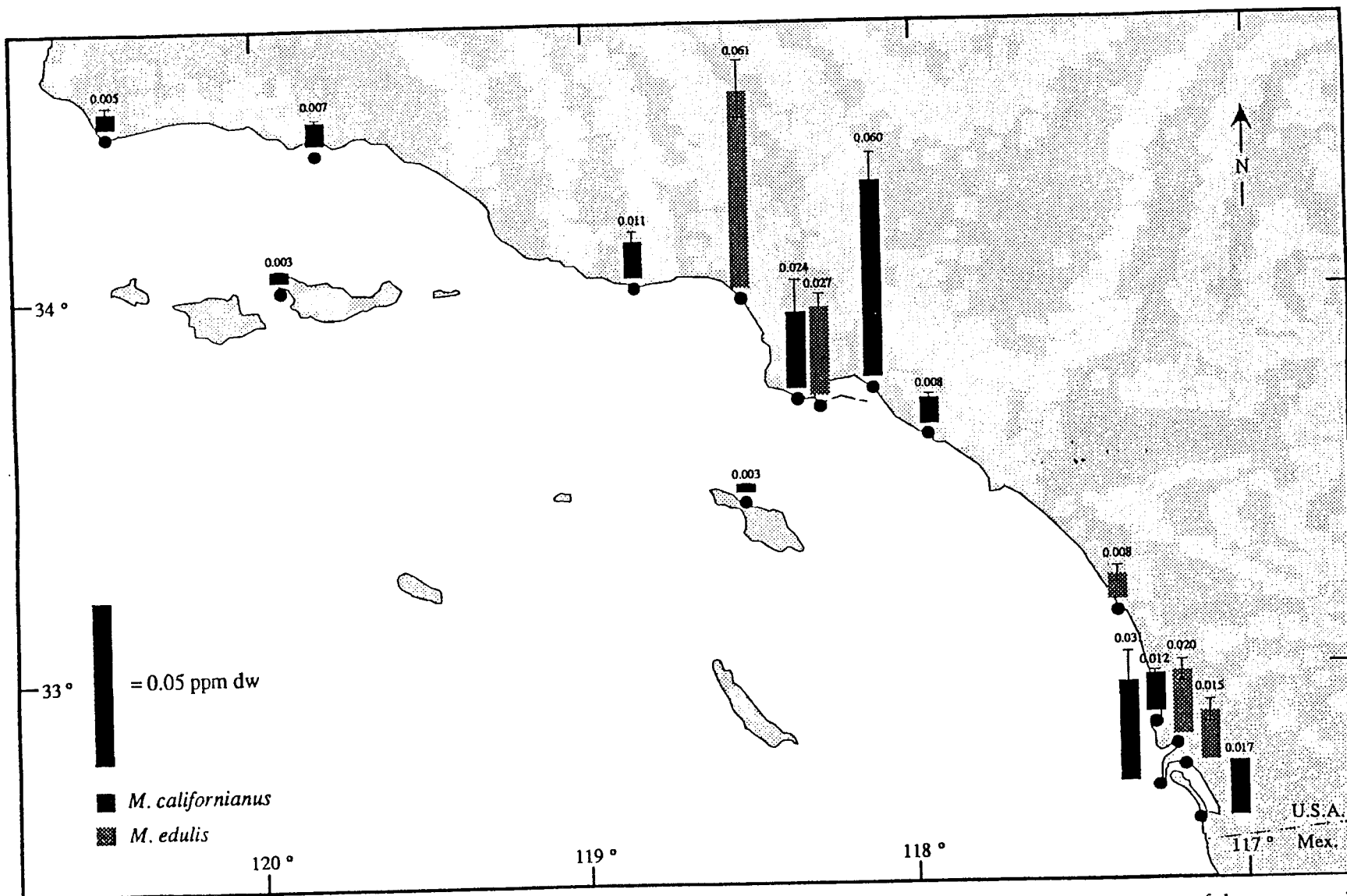


Figure 5. Chlordane in whole soft body tissue of mussels sampled in southern California in 1986. Values shown are means of three composites of 3 individuals each. Source: NOAA, NS&T Program (data supporting NOAA, 1987).

and DDT in surface sediments in Marina del Rey and near sewage discharge sites at Palos Verdes and off Orange County. An example for cadmium is shown in Figure 6. Further, there have been major order-of-magnitude declines of DDT contamination of fish and shellfish on both a regionwide and local basis over the past two decades (Mearns and O'Connor, 1984; Young *et al.*, 1988). However, sampling has been inadequate to confirm if such trends have also been occurring in Los Angeles-Long Beach harbors, San Diego Harbor, or Newport Bay. With one exception, data are also too limited to determine long-term trends in PAH contamination. However, cores from the San Pedro basin indicate that aromatic hydrocarbon concentrations have been decreasing there for over a decade (Venkatesan *et al.*, 1980).

Limited data indicate there have been no long-term unidirectional changes of concentrations of trace metals or PCBs in mussels or sediments from remote coastal or island reference areas in the Bight. However, there is some evidence that through the early 1980s there were slight increases of PCB contamination at a few coastal sites such as Oceanside. Finally, there is evidence of intriguing regionwide low-frequency fluctuations of cadmium, mercury, and silver in mussels that may reflect changing oceanographic or climatic conditions.

Implications

Although \$18 million is spent annually on ocean monitoring and research in the Bight, trend analysis is severely limited by incomparable sampling strategies. Species, tissues, and sites previously surveyed but once in the past need to be re-surveyed so that suspected trends can be verified for important resource species (such as scallops, lobster, prawns, and crabs) at historically sampled sites. Bays and harbors have been inadequately surveyed to determine contaminant levels and trends in fish and popular shellfish species other than mussels. The history of arsenic, selenium, silver, tin, chlordane, and dieldrin contamination needs to be determined, perhaps through analyses of dated cores or archived samples. A regionwide easily accessible data base could provide a strong basis for developing sampling and monitoring activities that would clearly determine the direction and rate of changing levels of contamination and for determining the extent to which local

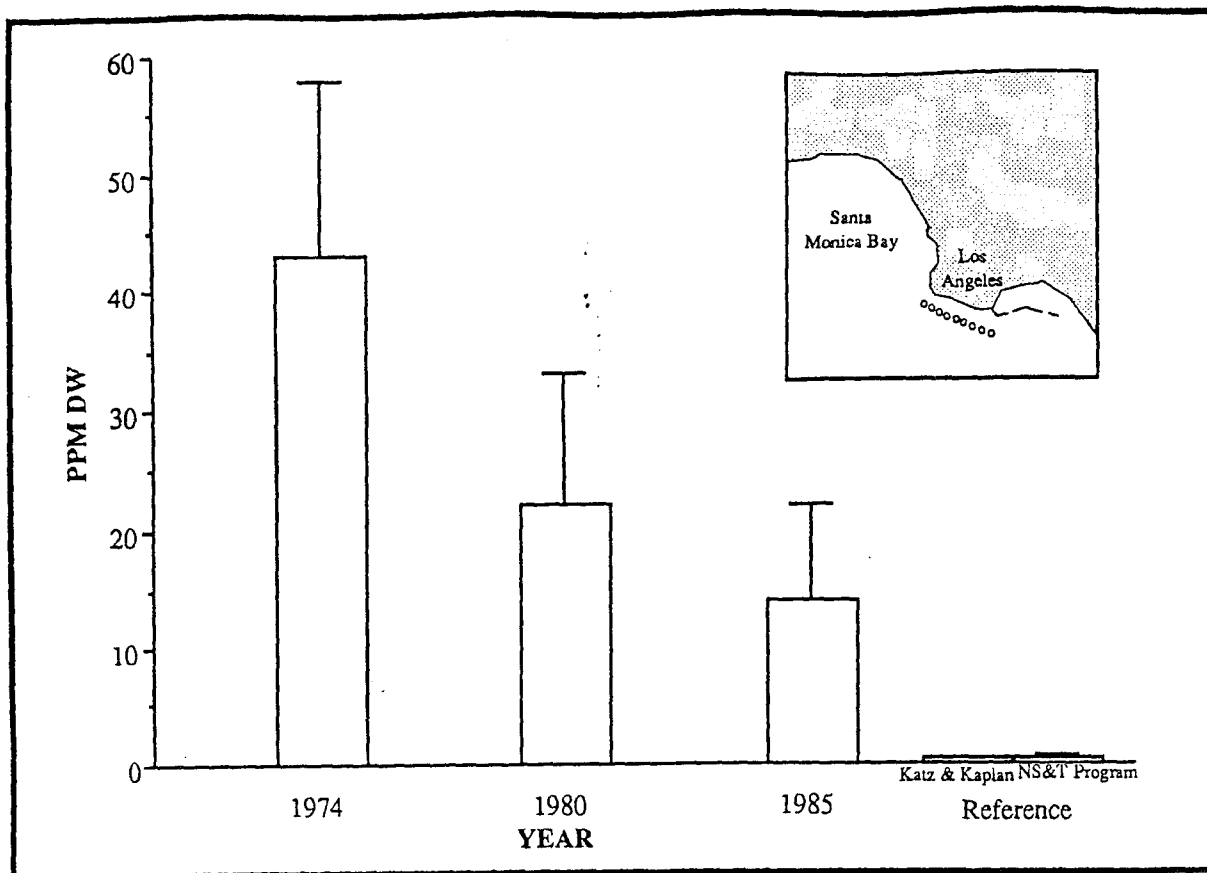


Figure 6. Mean cadmium concentrations in the sediment off Palos Verdes based on monitoring studies conducted by the CSDLAC (Stull and Baird, 1985 and unpublished data). The reference values are based on the value reported by Katz and Kaplan (1981) and the mean of four relatively isolated NOAA NS&T Program sites in the Southern California Bight sampled between 1984 and 1986. Inset shows approximate locations of sites sampled by CSDLAC.

and regional contamination has or has not been changing commensurate with waste management actions, source control, and clean-up activities.

The NOAA NS&T Program provides data that is comparable to, and in substantial agreement with, the magnitudes and spatial patterns of contamination evident from local and regional monitoring. Continued long-term surveillance at existing NS&T sites will provide an index to changes on a regionwide basis and for several bays and allow comparison with other coastal and estuarine regions in the United States.

The complete results of this assessment for 14 chemicals or chemical classes will appear in a forthcoming NOAA, National Ocean Service technical memorandum.

Acknowledgments

Many individuals from local, regional, state, and federal agencies provided data and helped answer numerous questions. A full account of contributors will appear in the forthcoming National Ocean Service Technical Memorandum. Special thanks to Pacific Office staff members Gary Shigenaka and Donald MacDonald for assistance in preparing data and graphics.

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BIOMAGNIFICATION IN SEAFOOD ORGANISMS AROUND A LARGE CALIFORNIA SUBMARINE WASTEWATER DISCHARGE

by

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Abstract

A chemical index (Cs:K ratio) of trophic level separation, or degree of food web structure, is described. The reliability of this index had been confirmed by a survey of the Salton Sea, a land-locked, quasi-marine ecosystem supporting a simple food web with well-established, distinct feeding relationships. Application of the index to seafood organisms collected from a highly-contaminated municipal wastewater coastal discharge zone indicated substantial structure. However, muscle tissue concentrations of the pollutant metals Ag, As, Cd, Cr, Cu, Se, and Zn did not increase with organism trophic level. In contrast, concentrations of Hg, which frequently occurs as an organometallic compound in tissues, and DDTs and PCBs generally did increase with trophic level. A conceptually-simple exponential biomagnification model often appears to be useful in describing such data.

Introduction

One of the potentially important processes counteracting man's efforts to disperse toxic constituents of wastewater in freshwater and marine ecosystems is reconcentration via food web biomagnification. However, (Isaacs, 1972; 1973) questioned the importance of this process for marine ecosystems, suggesting that marine food webs often are composed

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of omnivores, resulting in little distinction between feeding or trophic levels. He applied the term "unstructured" to such food webs. The objectives of the study described below were to determine the degree of trophic level separation or structure, and corresponding pollutant biomagnification, for a marine food web comprised of common seafood invertebrates and fishes collected off a major southern California municipal wastewater submarine outfall system.

Background

A Chemical Index of Structure. The Cs:K Index is based on the observation, first made from radioecological studies of terrestrial and freshwater ecosystems, that the ratio of cesium (Cs) to potassium (K) generally increases 2-3 fold per trophic step in linear food chains (Anderson, *et al.*, 1957; McNeill, *et al.*, 1960; Green, *et al.*, 1964; Hanson, *et al.*, 1964; Pendleton, *et al.*, 1965; Hanson, *et al.*, 1967). This agrees with laboratory study results showing that the biological half-life (tissue residence time) of Cs is two to three times that of K (Pendleton, 1964). To determine if this relationship for these intracellular alkali metals also pertained to marine organisms, Young (1970) conducted a year-long survey of the Salton Sea in Southern California's Imperial Desert. This site is a saline lake of freshwater origin with a salinity similar to that of seawater. It was chosen because a previous multi-year ecological survey of the transplanted marine species had clearly established the existence of feeding relationships constituting distinct trophic levels (Walker, 1961), and a much simpler food web than generally exists in coastal marine environments.

The results showed that the known trophic level separation was accurately reflected by tissue concentrations of Cs:K, which again generally increased 2-3 fold per trophic step (Young, 1970; 1984). The median predator:prey amplification factor based on stable element analyses was 2.6, and the average Trophic Step Amplification Factor determined from the Exponential Biomagnification Model (described below) was 2.4. These findings confirmed the utility of the Cs:K ratio as an index of average trophic level separation, and corresponding potential for pollutant biomagnification, in marine food webs.

Trophic Level Estimation. Biomagnification evaluations require an estimation of the average trophic level occupied by each species or taxa constituting the food web in question (Young, 1984). Mearns (1982) has described a method of making such estimates. Trophic levels first are assigned to basic prey items (e.g., diatoms are primary producers at Trophic Level 1.0; herbivores occupy Trophic Level 2.0). Assumptions based on observed or reported dietary data then are made about the feeding habits of the higher organisms constituting the sampled food web. Using this approach a weighted average trophic level for the diet of each of the constituent organisms is computed, and 1.0 is added to this value to obtain the estimated trophic level for that organism. This provides a method of obtaining a numerical assignment for an organism's position in the food web, which has termed the Trophic Level Assignment (TLA).

A Simplifying Model of Biomagnification. Owing to the complexity often encountered in summaries of biomagnification study results, Young and Mearns (1982) developed a procedure to approximate such results with a conceptually simple relationship termed the Exponential Biomagnification Model (EBM). The development of this model was stimulated by the observation, described above, that the tissue Cs:K concentration appears to increase by a relatively constant factor (Anderson *et al.*, 1957; Issacs, 1973) per trophic step in linear food chains. We call this value the average Trophic Step Amplification Factor (TSAF). This condition corresponds to a geometric or exponential increase in the tissue concentration (C) of an analyte with trophic level (TLA):

$$C = a'e^{b(TLA)} \quad (1)$$

where a' and b are constants. The Trophic Step Amplification Factor is defined as the ratio of tissue concentrations for organisms at trophic levels $(n + 1)$ and (n) :

$$TSAF = \frac{C_{(n+1)}}{C_{(n)}} \quad (2)$$

$$= \frac{a'eb^{(TLA)_{n+1}}}{a'eb^{(TLA)_n}} \quad (3)$$

$$= e^{b(TLA)_{n+1} - (TLA)_n} \quad (4)$$

But by definition of a trophic step:

$$(TLA)^{n+1} - (TLA)^n = 1.0 \quad (5)$$

Thus the average Trophic Step Amplification Factor is:

$$TSAF = e^b \quad (6)$$

where b is the regression coefficient for:

$$\ln C = \ln a' + b(TLA) \ln e \quad (7)$$

$$= a + b(TLA) \quad (8)$$

The test for the fit of a tissue concentration data set by the EBM is a significant linear regression of $\ln C$ against TLA , using the regression procedure of Sokal and Rohlf (1981) for multiple Y values ($\ln C$) per X value (TLA).

Two null hypotheses are tested:

$H[1]$: There is no significant linear regression of $\ln C$ against TLA .

$H[d]$: There are no significant deviations of the mean $\ln C$ values from linear regression.

The primary null hypothesis $H[1]$ is rejected if $p[1] < 0.05$. This indicates that the linear regression is significant, i.e.:

$$b \neq 0 \text{ and } TSAF \neq 1.$$

When this result is obtained we conclude that, in general, the data set is fit by the EBM. The secondary null hypothesis $H[d]$ is rejected if $p[d] < 0.05$. This indicates that, for one or more organisms, the mean tissue concentration deviates significantly from the regression (model). In this case, a corresponding caveat is attached to the conclusion that the EBM fits the data set.

It is important to note that, in general, the EBM is simply an empirical (as opposed to a mechanistic) model that conveniently describes the approximately exponential increase (or decrease) of tissue concentration C with increase in TLA sometimes observed for field data. Only for $Cs:K$ do we now have a physiological explanation for this relationship. In

this case, the Trophic Step Amplification Factors generally obtained for food chains or simple food webs (e.g., TSAF = 2.4 in the Salton Sea) are explained by laboratory observations that the tissue residence time of Cs generally is two to three times that of K. (To our knowledge the biochemical basis for these differences in residence times has not yet been described.) We also note that an acceptable fit of a data set by the EBM for a given tissue constituent and sampled food web is consistent with the hypothesis that there is an approximately constant tissue concentration amplification factor per trophic step. We may not yet have a biological explanation for an observed exponential relationship and constant TSAF that would lend confidence to its utility as a predictive tool. Nevertheless, such a relationship conceptually is simpler than a hypothesized linear relationship between C and TLA. A linear relationship may have the advantage of mathematical simplicity. However, it leads to a constant absolute increase (or decrease) in tissue concentration per trophic step over the TLA range; we submit this may well require a more complicated biological explanation than would a constant relative change in concentration (compared to that for the trophic level one step below), i.e., a constant TSAF.

Methods

Study Area. For this pollutant biomagnification investigation we selected one of the most contaminated regions in Southern California (Figure 1). This is the submarine outfall monitoring zone off Palos Verdes Peninsula, which in the early 1970's typically received a municipal wastewater discharge of about 365 million gallons per day ($1.38 \times 10^9 \text{ L d}^{-1}$) from the Los Angeles County Sanitation District's Joint Water Pollution Control Plant (JWPCP). Between 1971 and 1975 this discharge, which contained very high concentrations of trace elements and synthetic organics (Hershelman *et al.*, 1981; Young *et al.*, 1976; Stull *et al.*, 1986), yielded an annual suspended solids mass emission of 130-170 thousand metric tons ($\sim 1.5 \times 10^8 \text{ kg yr}^{-1}$). As a result, surficial (0-5 cm) sediments collected during the fall of 1975 from the monitoring zone were found to be highly contaminated with toxic trace metals, DDTs, and PCBs (Figure 1). Corresponding surficial sediment contamination factors (defined as the ratio of the median concentration in the outfall monitoring zone to the median baseline value for coastal southern California) were as follows: silver (Ag) - 27; cadmium (Cd) - 36; chromium (Cr) - 12; copper (Cu) - 20;

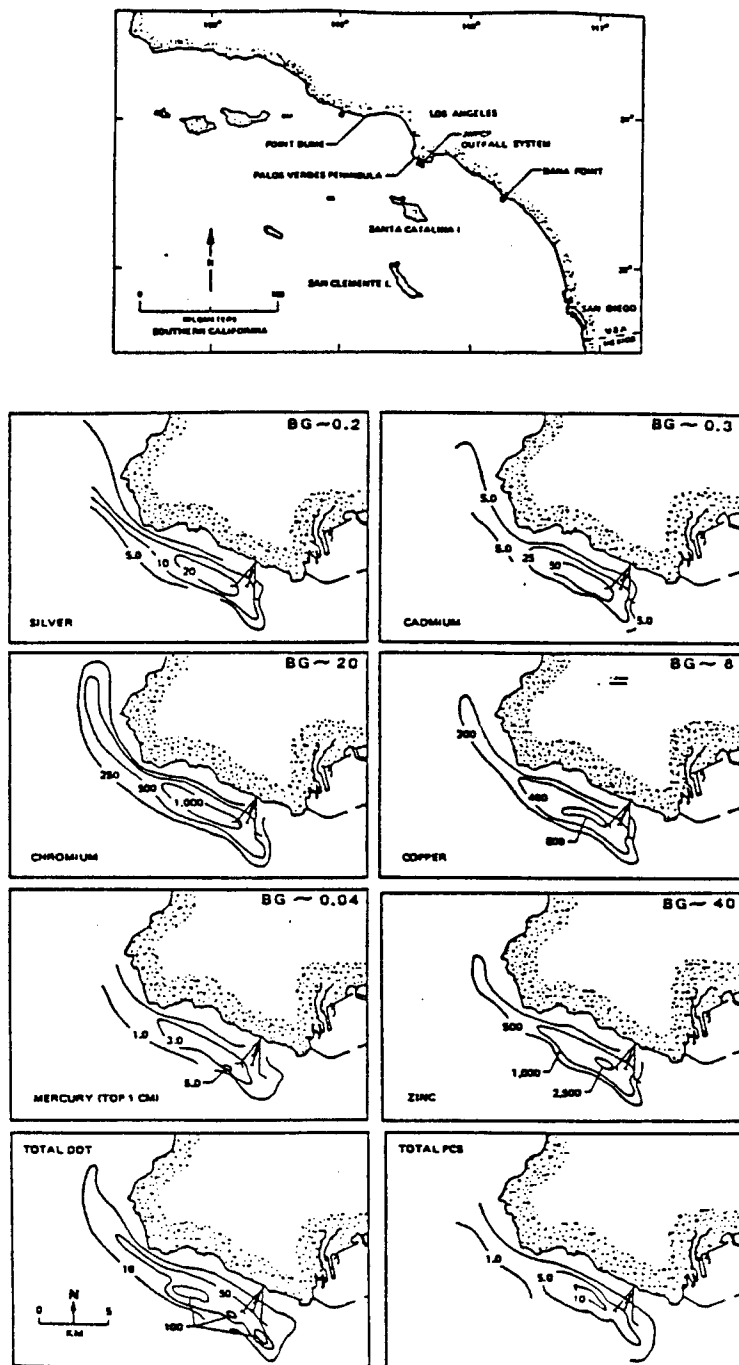


Figure 1. The study area: Location in the Southern California Bight (upper figure), and concentration isopleths (mg kg^{-1} dry wt) of pollutants in surficial sediments (0-5 cm) off Palos Verdes Peninsula, 1975, compared to background (BG) values.

mercury (Hg) - 23; nickel (Ni) - 5.4; lead (Pb) - 17; zinc (Zn) - 7.7 (Hershelman *et al.*, 1981).

Analyses of box cores collected during July 1971 about 4 km northwest (downcurrent) of the outfall diffusers yielded estimated contamination factors for arsenic (As) and selenium (Se) of 15 and 14, respectively (Young *et al.*, 1978). Further, the DDT and PCB residue concentrations measured in these surficial sediments in 1975 were among the highest ever reported for a coastal marine ecosystem (Young *et al.*, 1976; Stull, *et al.*, 1986; Young, *et al.*, 1978). (Improved source control and treatment begun in the 1970's has greatly reduced these loadings and surficial sediment concentrations [Stull *et al.*, 1986].

Sampling and Chemical Analysis. Ten species of common California sea food organisms (listed below) were collected by bottom trawl or scuba divers during 1975-77, from the JWPCP discharge zone (Young *et al.*, 1981). All the organisms were obtained within 4 km of the outfall diffusers, except for the prawns which were collected approximately 15 km down current near the northwest end of the contours shown in Figure 1 (Hershelman *et al.*, 1977). Upon collection, the specimens were rinsed free of adhering sediment in clean seawater; they were then placed in new polyethylene bags and frozen. In the laboratory, muscle tissue was carefully excised before the specimen was fully thawed; the dissections were performed on a clean Teflon sheet using carbon steel scalpels and Teflon-coated forceps that were frequently rinsed in deionized water. Care was taken not to introduce contamination from the surface of a specimen (such as the skin of a fish) or the digestive tract or other internal organs.

Tissue analyses for the alkali metals were conducted by digesting 5-10 wet grams in fuming nitric acid, filtering through Whatman No. 40 paper, withdrawing a small aliquot for potassium analysis (via air-propane flame emission spectrometry), splitting the sample for internal standardization, and concentrating the cesium on ammonium-12-molybdophosphate (AMP) which then was dissolved in 2N sodium hydroxide. Analysis for cesium (excluding lobster, croaker, and halibut samples, for which there was insufficient tissue) was conducted by graphite-furnace atomic absorption spectrometry, using alternate

injections of external standard, internal standard, and unspiked sample or procedural blank. This instrumentation also was used to analyze directly nitric/hydrochloric acid digestates for Ag, Cd, Cr, Cu, Ni, and Pb; Zn was analyzed by air-acetylene flame AAS (Young *et al.*, 1981). Total Hg was analyzed using a nitric/sulfuric acid tissue digestion followed by reduction to elemental Hg with analysis by cold-vapor atomic absorption spectrometry (Eganhouse *et al.*, 1978). S and Se were analyzed by neutron activation of wet tissue followed by radiochemical separation using sulfuric acid/hydrogen peroxide digestion, conversion to and capture of volatile bromides, and gamma ray spectrometry (Goeders, 1982).

Chlorinated hydrocarbon samples were blended with acetonitrile, extracted with hexane, passed through a Florisil clean-up column, and analyzed by packed column (1.5% OV-17 and 1.95% QF-1) electron-capture gas chromatography. Polychlorinated biphenyls (PCB) were quantified using Aroclor 1242 and 1254 external standard mixtures; the two major isomers (p,p' and o,p') of DDT, DDE, and DDD were quantified using external standards, following correction for PCB interferences (Young *et al.*, 1976). Tissue lipid content was determined using a chloroform/methanol extraction, drying, and weighing procedure (Bligh, *et al.* 1959).

Trophic Level Assignments. Based on various reports of dietary habits for the ten target seafood organisms (Young *et al.*, 1982), the following trophic level assignments were obtained. (When there was a range of TLAs for a dietary constituent, the median was used; when there were different TLA values for important food types, these were averaged to obtain the estimated TLA for the diet.) Owing to the limited and indirect nature of such dietary information the TLA values were estimated only to the nearest 0.25 unit. However, to distinguish between values for organisms with identical TLA values, prior to computer statistical analysis and graphics such values were adjusted by -0.05 or +0.05 TLA units (indicated by - or + symbols in the discussion below). The black abalone (*Haliotis cracherodii*) feeds principally on algae (I) and thus received a TLA of 2.0. The purple-hinged rock scallop (*Hinnites giganteus*) feeds on phytoplankton (I) and detritus (I-II) and was given a TLA of 2.25. The California spiny lobster (*Panulirus interruptus*)

feeds on invertebrates such as sea urchins (II) and was given a TLA of 3.0. The diet of the yellow crab (*Canceranthonyi*) is quite varied, including small invertebrates (II) and fishes (III); thus, its TLA was 3.5(-). The ridgeback prawn (*Sicyonia ingentis*) feeds on invertebrates such as ostracods, which appear to be somewhat higher in the food web (II-III); thus the TLA also was 3.5(+). Pacific sand dab (*Citharichthys sordidus*) and white croaker (*Genyonemus lineatus*) both feed on benthic and epibenthic crustaceans (II-III), and small fishes (III), and each were given TLAs of 3.75 (- and +, respectively). The California halibut (*Paralichthys californicus*), which feeds largely on anchovy (III) and benthic invertebrates and fish (III-IV), received a TLA of 4.25. Finally, California scorpion fish (*Scorpaena guttata*) and Bocaccio (*Sebastes paucispinis*) feed on various fishes, crustaceans, and mollusks occupying levels III-IV, and thus each were given TLAs of 4.5 (- and +, respectively).

Data Analysis. The linear regressions for $\ln C$ vs TLA and associated F tests were carried out using the Statistical Analysis System (SAS) program RSREG (SAS, 1985A), modified to conduct the F-tests as prescribed by Sokal and Rohlf (1981) and described above. The resultant best-fit exponential equations were plotted using SAS-GRAPH (SAS, 1985B). The output also included the average amplification factor per trophic step (TSAF = e^b), the probability $p[1]$ that this value was 1.0 (no linear regression), the probability $p[d]$ that none of the mean y values differed from the model (no deviation from linear regression), and the coefficient of determination (r^2) giving the proportion of the total variance explained by the model. Although for conciseness these statistics are included with the plots of mean C vs TLA (below), again it should be noted that said statistics were obtained from (and apply to) the linear regression of $\ln C$ vs TLA.

Results and Discussion

Food Web Structure. The linear regression of $\ln (Cs:K \times 10^6)$ vs. TLA (Figure 2) was significant ($p[1] < 0.01$). However, for one or more of the species mean values (e.g., yellow crab, TLA = 3.5), there also was significant deviation from linear regression ($p[d] < 0.001$). Nevertheless, the Exponential Biomagnification Model accounted for 72 percent of the total variance of the \ln -transformed $Cs:K$ values, and indicated measurable trophic level

separation (TSAF = 1.4). Therefore, this sampled food web of seafood organisms did exhibit potential for biomagnification of pollutants discharged from the JWPCP outfall system.

Trace Metals. The best-fit exponential curves generated by the EBM for the trace metals (or metalloids), and the mean (+ 1 std. error) muscle tissue concentrations of these analytes, are illustrated in Figure 3. (Ni and Pb generally were below detection and thus are not included here). These results show that, despite the established structure of this sampled food web, for most of the pollutant metals there was no systematic increase of muscle tissue concentration with organism Trophic Level Assignment value. Only for Hg was there an indication of such an increase (TSAF = 2.6), consistent with the hypothesis of biomagnification. However, similar muscle tissue concentrations and increases with trophic level, obtained from a corresponding survey conducted in a control zone (Young *et al.*, 1981), support the hypothesis that biomagnification of Hg is a natural phenomenon that was not measurably increased by the JWPCP discharge.

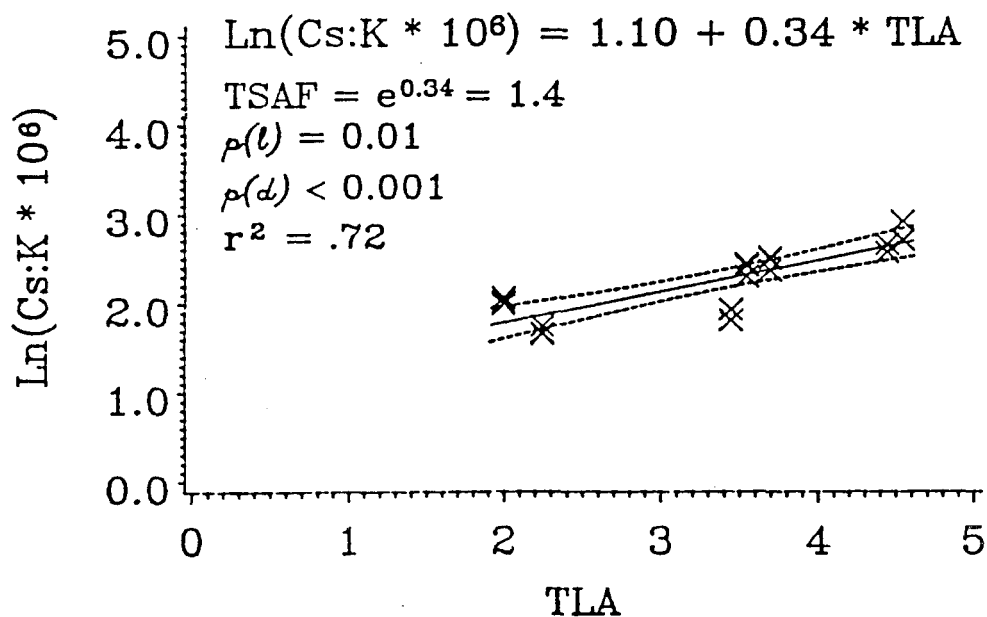


Figure 2. Linear regression between $\text{Ln}(\text{Cs:K} \times 10^6)$ and Trophic Level Assignment. Dotted lines indicate 95 percent confidence limits for predicted mean (Sokal and Rohlf, 1981).

In addition, for two of the trace metals of greatest concern (Cd and Cr), significant exponential decreases with TLA (although with significant deviations) were observed. The corresponding Trophic Step Amplification Factors were 0.09 and 0.25, respectively. This illustrates the utility of the EBM, in conjunction with the Cs:K index, in disproving the general biomagnification hypothesis for specific pollutants in sampled food webs. 3. Best-fit

Chlorinated Hydrocarbons. The results of the regression analyses for the principal residues of the DDTs (p,p'-DDE) and the PCBs (PCB 1254) are also illustrated in Figure 3. This figure shows that, on both wet-and-lipid weight bases, the data sets for these residues are fit by the EBM. However, in all cases there also are significant deviations of organism mean concentrations from the model, sometimes by as large as one order of magnitude. In contrast to our findings from other food web surveys, normalization to lipid weight does not improve the fit for either DDE or PCB. This suggests that heterogeneity of exposure, corresponding to the large gradients in surficial sediment concentrations shown in Figure 1, may be the cause of the large variation observed even after lipid normalization. These results illustrate the difficulties often experienced in attempting to generalize findings on bioaccumulation and biomagnification of pollutants near large point sources.

Conclusions

1. The Cs:K Index of food web structure indicated that the seafood organisms sampled from the JWPCP outfall monitoring zone during 1975-77 did represent trophic levels that were sufficiently separate to provide the potential for pollutant biomagnification.
2. Despite this structure, with the exception of Hg there were no systematic increases in muscle tissue concentration of measured trace metals (or metalloids) with increase in estimated trophic level (TLA). For Cd and Cr, significant exponential decreases occurred. These findings do not support the hypothesis that pollutant trace elements generally biomagnify in marine food webs.

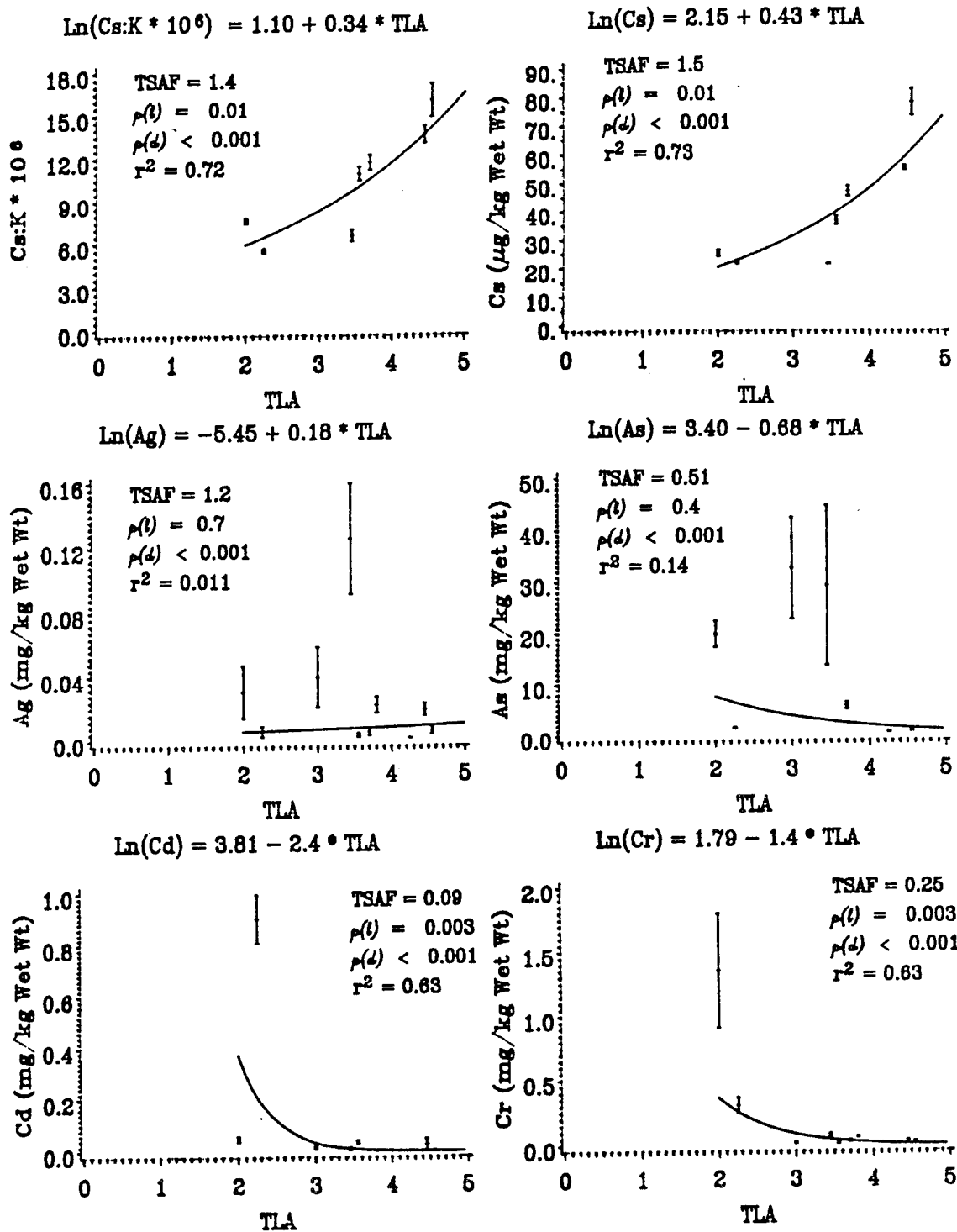


Figure 3. Best-fit exponential curves for analyte concentration vs. TLA and corresponding statistics from linear regressions, compared to mean (± 1 std. error) muscle tissue concentrations.

3. Muscle tissue concentrations of the persistent chlorinated hydrocarbons p,p'-DDE and PCB 1254 generally were fit by the EBM, with values for the higher level fishes often exceeding those in the lower invertebrates by 1 to 2 orders of magnitude. However, the high variability observed indicates the difficulty in modeling pollutant biomagnification near large point sources.

4. Nevertheless, for several of the target constituents the Exponential Biomagnification Model (EBM) appeared to be a useful tool for describing and summarizing field data on biomagnification.

5. The approach presented here, when applied to a variety of marine food webs, should assist environmental managers in determining whether tissue concentrations of specific pollutants typically increase or decrease, and by what factors, with increase in estimated trophic level.

Acknowledgements

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CHARACTERISTICS AND EFFECTS OF CONTAMINATED SEDIMENTS FROM SOUTHERN CALIFORNIA

by

Jack W. Anderson¹, Steven M. Bay, and Bruce E. Thompson

extracted from:

Anderson, J. W., S. M. Bay, and B. E. Thompson. 1988. Characteristics and effects of contaminated sediments from southern California. Final report to the California State Water Resources Control Board. Southern California Coastal Water Research Project, Long Beach, CA.

A multidisciplinary study of sediments from ten coastal sites in southern California was conducted in summer and fall of 1987. These sites included areas of high contamination near sewage outfalls and within harbors (Fig. 1). Measurements were made of metal, chlorinated hydrocarbon, polynuclear aromatic hydrocarbon, and dissolved sulfide concentrations in the sediment surface layer. These sediment samples were also examined for toxicity using three different test methods (Microtox, amphipod survival, and sea urchin growth). Sediment samples were also taken for examination of the benthic macrofauna resident at each site.

High concentrations of chlorinated hydrocarbons, polynuclear aromatic hydrocarbons, and trace metals were found in sediments from most stations. At open sea sites contamination was highest at the Santa Monica Bay sludge outfall (SMS) and the Palos Verdes outfall (PV). The Orange County outfall (OC) was relatively similar in contamination to our reference site at San Mateo Point (SMP). As expected from previous analyses, the harbor sites contained significant amounts of polynuclear aromatic hydrocarbons and metals. Tributyltin was found in sediments from the harbor stations and organotins of a different composition pattern were detected at the outfall sites.

Based on the relative concentrations of contaminant classes, macrofaunal communities, and toxicity for amphipods and urchins, the open sea and protected station

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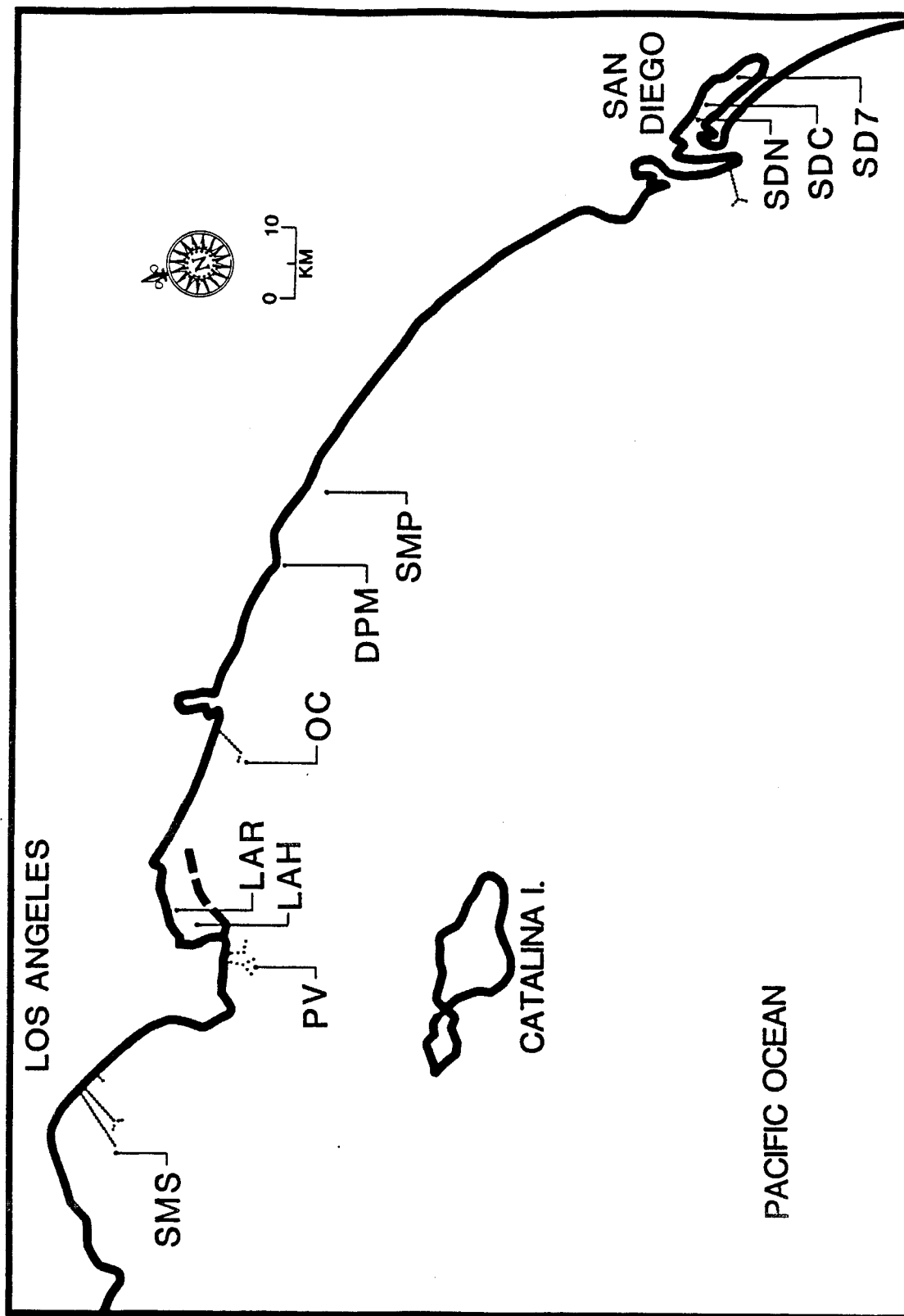


Figure 1. Location of test stations.

groups can be ranked from most to least affected (Table 1). While it is not surprising that the sludge outfall in Santa Monica Bay and the outfall at Palos Verdes are more impacted than the Orange County outfall and the reference station, it is gratifying that all analyses agree. Therefore, at the open sea sites, the two most contaminated outfall sites (SMS and PV) clearly separate themselves from the cleaner outfall at OC and the reference station. There is an obvious need to include more offshore stations in this type of ranking to aid in evaluating the sediment factors responsible for changes in macrofauna and toxicity in the laboratory.

Table 1. Objective rankings of sites based on sediment contamination, benthic macrofauna, and sediment toxicity measurements. (SMS - Santa Monica Bay Sludge Outfall; PV = Palos Verdes; OC - Orange County; SMP = San Mateo Point; SD7 = San Diego Bay, 7th Street; LAR = Los Angeles River Mouth; LAH = Los Angeles Harbor; SDN = San Diego Bay; SDC = San Diego Bay.

	Metals	Sediments		Macrofauna	Toxicity	
		PAH	CHC		Amphipod	Urchin
<u>Open sea</u>						
Most affected	SMS	SMS	PV	SMS	SMS	SMS
	PV	PV	SMS	PV	PV	PV
	OC	OC	OC	OC	OC	SMP
Least affected	SMP	SMP	SMP	SMP	SMP	OC
<u>Protected</u>						
Most affected	SD7	SD7	SD7	LAR	SDN	SD7
	SDN	LAR	LAR	LAH	SD7	LAH
	LAR	SDC	LAH	SD7	LAH	SDC
	SDC	LAH	SDN	SDC	DPM	SDN LAHSDN
SDC	DPM	SDC	DPM			
Least affected	DPM	DPM	DPM	SDN	LAR	LAR

At protected stations there was a better range of sediment types, leading to some differences in the ranking of stations. In most cases (4 of 6), the sediment from the Seventh Street channel in San Diego Bay (SD7) was the most affected. As described by Anderson and Gossett (1987), this location is in 6 meters of water near naval fuel dock

compared to the other metals (Fig. 2). The Los Angeles River mouth ranked high in impact for three of the six parameters measured. These sediments were high in all contaminants and they produced a different macrofaunal assemblage. However, they were not toxic to amphipods and urchins unlike the Seventh Street station.

The sediments from Los Angeles Harbor (LAH) and the two other stations in San Diego Bay (SDN and SDC) ranked next in relative effects. It is interesting that these three stations formed a group when lead and zinc content was plotted against other metals in sediments (Fig. 2). This may not necessarily indicate that lead and zinc are the significant toxic agents, but that these stations receive input from similar sources of contamination. These stations may represent locations receiving multiple inputs from storm runoff and numerous small spills. The types of aromatic hydrocarbons found at these three sites are also quite similar (Fig. 3). At protected sites, toxicity was the greatest at the four harbor (L.A. plus three San Diego) stations.

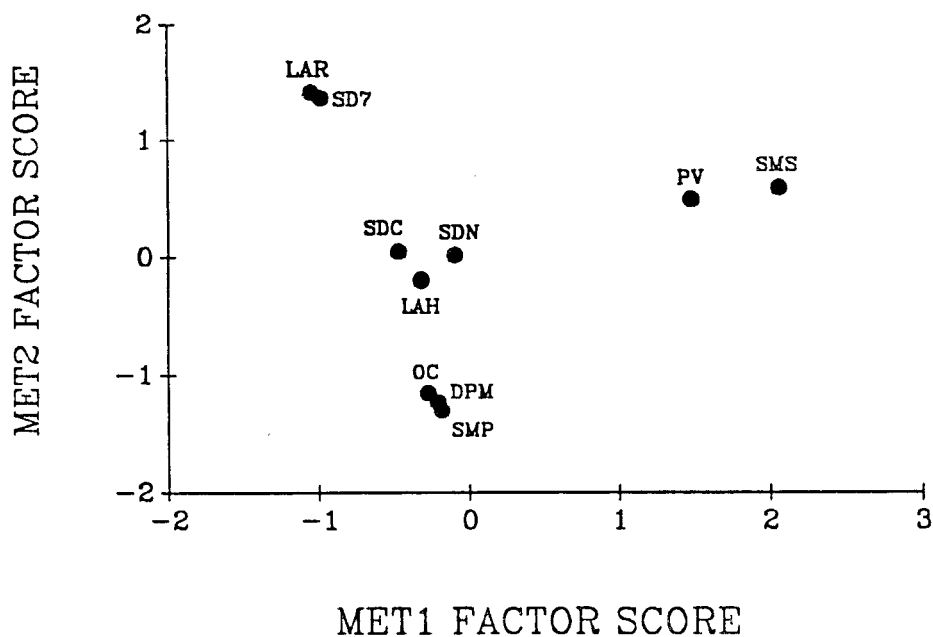


Figure 2. Plot of station scores for the two factors identified by principal components analysis of the sediment metals concentration data. Scores are standardized values with a mean of zero and a standard deviation of one unit. Increasing scores indicate higher metals concentrations. Factor MET1 was strongly correlated with the concentrations of Ag, As, Cd, Cr, Cu, Ni, and Sn. MET2 was strongly correlated with Pb and Zn.

While sediments from the Los Angeles River mouth showed high concentrations of sediment contaminants and effects on infaunal populations, these samples were the least toxic for both amphipods and sea urchins. For unknown reasons, even the sediments from the Dana Point Marina reference station (DPM) were more toxic than the Los Angeles River sediments. However, the contaminants measured were lowest in sediments from the Dana Point Marina, indicating factors not analyzed are responsible for the toxicity.

Principal components analysis (PCA) of the chemistry data was used to identify patterns in sediment contamination. This procedure manipulated the large number of individual chemical measurements which were often highly correlated with each other and produced a smaller number of uncorrelated factors. Each factor was a composite variable which was highly correlated with a subgroup of contaminants having similar distribution patterns between the ten study sites. Scores, representing the standardized relative concentrations for each group of contaminants, were calculated for the PCA factors. These scores were used like conventional concentration values in plots (Figures 2 & 3) and subsequent statistical analyses.

PCA identified two principal groups (factors for each of three major categories of contaminants. One of the two major PAH groups identified was composed primarily of low molecular weight compounds, while high molecular weight compounds predominated in the other; these groups represented hydrocarbons characteristic of petroleum and fossil fuel combustion, respectively. The remaining four contaminant groups identified were characteristic of PCB, DDT, lead and zinc, and other metals.

Further analysis of the contaminant data indicated that only four statistically independent patterns of contaminant distribution could be distinguished from the data. These patterns indicated associations between different groups of metal and hydrocarbon contaminants. One group represented the combined distribution pattern of PCB, petroleum PAH, most metals, and dissolved sulfide. This pattern was dominated by the contamination present at the sludge outfall (SMS) site. Fossil fuel PAH and lead and zinc were grouped together as having similar patterns, forming a group that characterized contamination

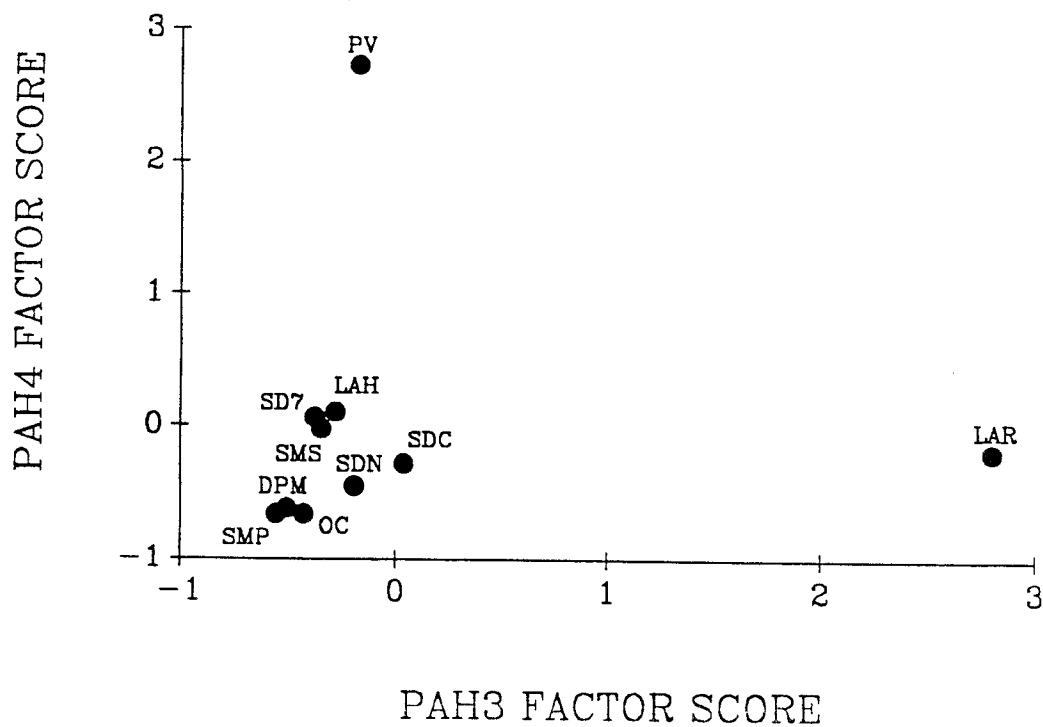
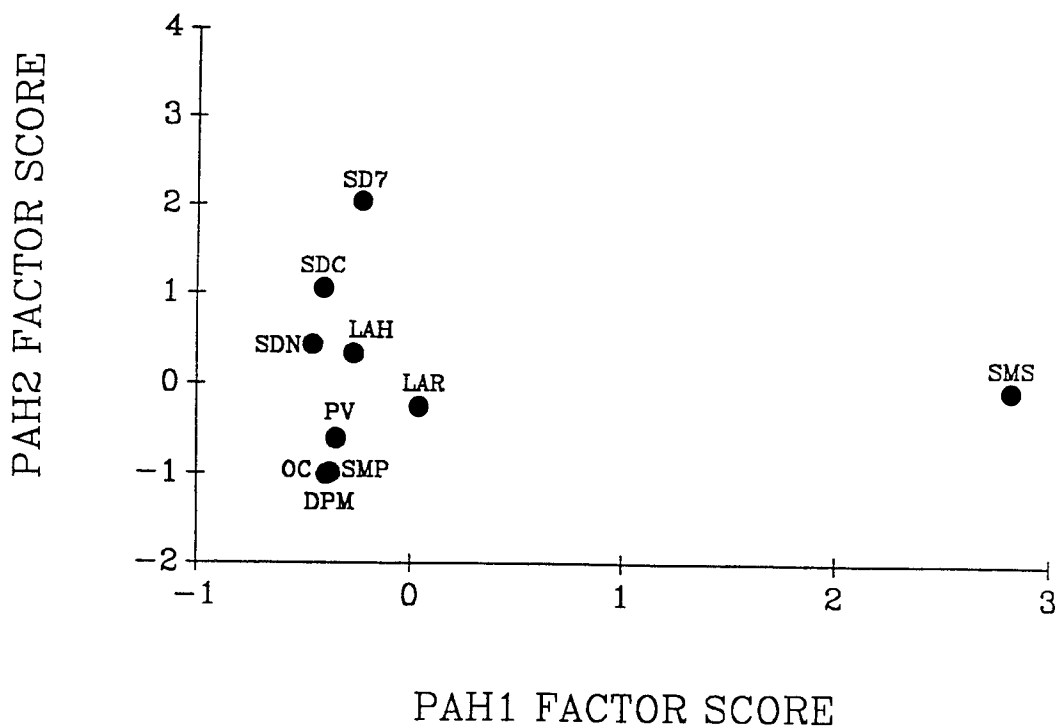


Figure 3. Plot of station scores for the factors identified by principal components analysis of the sediment PAH concentration data. The PAH1 factor was strongly correlated with petroleum compounds, while PAH2 was correlated with combustion compounds. PAH3 and PAH4 were minor factors correlated with relatively few compounds. Increasing scores indicate greater relative PAH concentrations.

patterns among most of the harbor stations. The remaining two groups represented contamination patterns that were characteristic of single stations. These stations were the Los Angeles County outfall, which had high DDT concentrations, and the Los Angeles River mouth, which had distinctive concentrations of several PAH.

Analysis of the benthic macrofauna data produced four groups of stations having similar species composition and abundance values. The sludge outfall site formed a group by itself and was most dissimilar in species composition and abundance when compared to the reference site. The Orange County outfall site was found to be most similar to the open water reference site. All but one of the harbor stations were grouped together with the protected reference site, even though these sites had high levels of some contaminants. The Los Angeles River mouth site was unusual in that this station's benthos were different from the other protected sites and most similar to the L.A. County Outfall site. This result was unexpected because of large differences in depth, contamination, and laboratory toxicity between these two sites. These two stations did have similar organic carbon and dissolved sulfide contents, however. It appears that the river station represents a transition between an organically enriched site and a site having toxic levels of contamination in addition to enrichment.

Multivariate analysis of the macrofauna data identified differences between the open water sites that corresponded to a gradient of contamination and organic enrichment. Similar results were also found when indicator taxa abundance or measures of assemblage structure and diversity were compared statistically. With the exception of the L.A. River mouth site, significant differences between the protected stations (including the protected reference site) were not found.

The laboratory toxicity tests usually identified more stations as being harmful than did macrofaunal analysis. There was generally good agreement among all three of the test methods in identifying the most toxic sites (SMS, PV, SD7). Strong evidence of chronic toxicity was found at the PV station. This finding contrasts with previous acute toxicity test results that indicated only slight toxicity at this station.

The sea urchin and amphipod test methods using moderate or long-term exposures to bulk sediment are well suited to future sediment assessment surveys in California. The results from this study indicate that each of the toxicity test methods used responded in a unique way to the sediment samples. This finding emphasizes the necessity of using multiple species and different test strategies in order to accurately assess sediment toxicity.

PCA was used to identify additional potential associations between chemical and biological (field and laboratory) measurements. Factor scores obtained from the multivariate analysis of each data set were combined and reexamined by PCA to identify similar patterns. A strong association was found between a dominant macrofauna ordination axis, Microtox results, and many contaminants (PCB, most metals, petroleum PAH, and sulfide). Amphipod survival was associated with organotin, combustion PAH, lead, and zinc. The macrofaunal pattern in the protected sites was best correlated with sea urchin growth.

Our analyses have shown that patterns in sediment contamination, macrofauna, and toxicity correlate well in some cases, but not all. Most notably, DDT concentration did not correlate with short-term toxicity or macrofaunal patterns. We believe a better gradient of chlorinated hydrocarbon concentrations (particularly DDT) will be required to accurately evaluate threshold levels of these contaminants in sediments.

This report has emphasized data expressed on a dry weight basis. Organic content is certainly an important modifier of contaminant partitioning, but a better understanding of this process is needed before normalization of concentrations from field samples can be made with confidence. Inconsistent results were obtained with organic carbon normalization in this study and suggest that this method may not be as useful for organic material derived from sewage. It is also possible that the range in sediment organic carbon found in this study was too great for accurate normalization.

We have presented empirically determined response concentration estimates (concentration at or above which significant biological effects were always found) for benthic macrofauna and toxicity test results. Estimated concentrations for many individual contaminants were not calculated because our analysis showed that we could not separate

patterns in greater detail than the contaminant groups listed. The small number of sites examined in this study was a major factor in preventing the determination of more specific and precise concentration estimates. Consequently, these values should be considered preliminary estimates and used with caution.

This study provided an initial evaluation of contaminated sediment effects in southern California. We were able to use these data to identify potential relationships between contaminant types and biological effects and also to estimate the range of effective concentrations of some sediment contaminants. Additional studies are needed, however, in order to better understand the interrelationships between specific sediment contaminants and biological response.

More extensive field studies of sediment toxicity and macrofaunal effects should be conducted. The small size of the present investigation was insufficient to determine the spatial extent of sediment toxicity within the study area. Field studies should also focus upon areas exhibiting gradients of DDT and PAH contamination. Such studies would improve upon the statistical relationships between contaminant type and biological effects identified in this study. Laboratory toxicity studies using spiked sediments are also needed to supplement and expand upon the information gained from the field surveys. These experiments provide the most straightforward method for determining the effects of specific contaminants.

Additional studies are also needed to better understand the relationship between changes in sediment characteristics and contaminant bioavailability. These studies should include measurements of interstitial water since strong correlations between contaminant concentrations in this phase and toxicity have been found by other investigators. Chemical analysis of both interstitial water and bulk natural sediments should be conducted to better understand the partitioning of contaminants between these two phases. Laboratory toxicity and bioaccumulation tests using interstitial water or water containing similar contaminant concentrations are also needed to provide a better understanding of effects resulting from exposure to contaminated environments.

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A PROPOSED PROGRAM FOR MONITORING TOXIC CONTAMINANTS IN THE SAN FRANCISCO BAY DELTA

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Introduction

The San Francisco Estuary has been subjected to tremendous change during the last two hundred years. Many of the present environmental concerns center around the existence of toxic contaminants in the Estuary, and their possible biological effects. It has been documented that several contaminants in particular are present in the Estuary and its catchment at elevated levels compared to more pristine locations on the Pacific coast. Among the contaminants of concern are trace elements such as copper, mercury, nickel, selenium; certain pesticides such as chlordane and toxaphene; polychlorinated biphenyls (PCBs); and polynuclear aromatic hydrocarbons (PAHs) (Phillips, 1987).

The Bay and Delta exhibit complex hydrodynamics, and the various toxic contaminants of concern arise from a variety of sources and locations. As a result, simple gradients in contamination of the Estuary are not generally found; rather, the Bay and Delta exhibit multiple "hot-spots" which are particularly polluted, overlaid upon a less elevated "background" level of contamination. The delineation of the abundances and distributions of contaminants in the Estuary is of great importance, as the control of pollution through regulatory initiatives is dependent upon a reliable database of this type. Such data are provided through monitoring programs, which quantify contaminants in both

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space and time in individual point source effluents (through NPDES self-monitoring efforts) and in the general aquatic environment.

This paper (a summary of Phillips [1988]) critically reviews the existing monitoring programs concerned with identifying the spatial and temporal abundances and distributions of contaminants in the Estuary. A new program is proposed for such monitoring, relying principally upon the use of biomonitors, and to a lesser degree on the analysis of receiving waters and sediments.

Monitoring Alternatives

The distributions of toxic contaminants in aquatic ecosystems may be defined through the analysis of water, sediments or organisms. Each of these approaches has its own particular advantages and disadvantages. The analysis of water is technically challenging because of the low concentrations of contaminants present; in addition, the concentrations of pollutants in solution or suspension change rapidly with time, and the delineation of average conditions is difficult as a result. However, perhaps the most important disadvantage of the analysis of aqueous samples for contaminants is that little information is imparted through this technique on the availability of contaminants to organisms (the "bioavailability" of pollutants). Due to these problems and others, there has been a general trend away from the analysis of aqueous samples for contaminants, although such methods remain the basis for regulatory control (through the use of water quality objectives, standards or criteria) of contaminants in discrete effluents and in receiving waters in many parts of the world (Phillips, 1988).

The use of sediments to define contaminant gradients or distributions may present certain advantages over the analysis of natural waters. Sediments generally exhibit much higher concentrations of pollutants than do the overlying waters (thus, the former are easier to analyze), and also provide a time-averaged picture of the levels of contamination in many cases. However, several factors influence the concentrations of toxicants in sediments; among the most important of these are grain size and total organic carbon

content of the sediments studied. In addition, the bioavailability of contaminants in sediments is once again unknown. Concentraations of contaminants in sediments can also vary on small spatial scales, frustrating comparisons between monitoring stations.

These and other reasons have contributed to the emergence of the use of organisms to monitor the abundance of toxic contaminants in aquatic environments. A substantial body of field and laboratory research shows that the availability of contaminants to aquatic biota may be measured directly by employing "sentinel" organisms (or "biomonitors") that accumulate the contaminants in question. Subsequent analysis of biomonitors indicates which contaminants are available to the biota for accumulation, and provides a measurement of time-integrated pollutant accumulation (Goldberg et al., 1979). Although no species can be the "ideal" biomonitor, a variety of bivalve molluscs have been shown to be effective indicators of pollutant loads in estuarine and marine waters around the world. Their effectiveness is due in large part to their sessile nature and their general inability to regulate the concentration of contaminants in their tissues (Phillips, 1976a, 1976b; Goldberg et al., 1979; Phillips, 1980; Luoma and Cloern, 1982; Phillips and Rainbow, 1988). In the San Francisco Bay region the Asiatic clam (*Corbicula fluminea*), the Pacific oyster (*Crassostrea gigas*), and the mussels (*Mytilus californianus* and *M. edulis*) have been used as biomonitors (Foe and Knight, 1985; Martin, 1985; Phillips, 1987; CDF&G, 1988).

Phillips (1988) concluded from a review of the international literature that the use of bio-monitors is the most appropriate technique for the monitoring of toxic contaminants in the Bay and Delta. Bivalve molluscs, which have been employed in many such monitoring programs throughout the world, are preferred as biomonitors in the local situation. However, the analysis of fish species should be continued, with the goal of protecting public health.

The Contaminants of Concern

Existing data on pollution of the San Francisco Estuary and its catchment have been reviewed to define the toxic contaminants of greatest concern (Phillips, 1988). Criteria were established to justify the selection of contaminants as being of concern in the Bay and Delta. On this basis, a list of contaminants which should be monitored in the local situation has been derived (Table 1). This list includes 13 trace metals (and their derivatives), 20 organochlorines and other pesticides, and a variety of hydrocarbons (including monocyclic aromatic hydrocarbons, cycloalkanes, and PAHs). Almost all of these are known to exhibit significant bioaccumulation, and would therefore be amenable to study using biomonitors. The few exceptions (the organophosphate pesticides, MAHs and cycloalkanes) are thought to be of less consequence as regional contaminants in the Estuary, and would have to be studied employing other techniques. It is noted that the list of the "contaminants of greatest concern" generated for the Estuary should not be considered fixed, but should be subject to amendment as new data are gathered, either through the monitoring program proposed here or otherwise.

The Regional Monitoring of Toxic Contaminants

The review of existing programs employed to monitor contaminants in the Estuary is sub-divided into regional and local programs. No routine program exists for the analysis of receiving waters for contaminants; organic contaminants (PCBs, pesticides, PAHs) have essentially never been quantified in the receiving waters of the Estuary, principally due to technical difficulties.

Several discrete studies have been completed that include useful and generally reliable data on trace metals in receiving waters of the Estuary. However, the extent of existing data on this topic are inadequate. Improved information on receiving water quality should be provided to support the regulatory control of contaminants in the Estuary through the use of water quality objectives. A new program which routinely quantifies the concentrations of particular contaminants (i.e., those for which

Table 1. 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. Phillips (1988).

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
Malthion
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-morpholynyl)benzthiazole
Naphthalene
Phenanthrene
Pyrene
2,3,5-Trimethylphenanthrene
Ideno(1,2,3-c,d)pyrene

objectives exist in the Basin Plan for the Estuary) in receiving waters of the Bay and Delta is required.

Existing data on contaminant levels in sediments in the Estuary have been reviewed by Long *et al.* (1988) and Gunther *et al.* (1989). The existing database is exceptionally fragmented, and data from different sources cannot be compared with confidence, because of differences in sampling and analytical methodologies. These data demonstrate the existence of spatial patchiness in contaminant concentrations in sediments of the Estuary, which presents a real problem for attempts to use sediments to monitor the abundances or distributions of contaminants on a regional scale in the Bay and Delta. The variation of contaminant concentrations in sediments over small distances in the Estuary creates a "background noise" that interferes with attempts to define larger-scale geographical variations in contaminant distributions. This fact means that sediment analysis should not be relied upon as a tool to define contaminant distributions on a regional scale in the Bay and Delta. However, the transport of contaminants within and through the Estuary undoubtedly depends to a large extent on fluxes of suspended particulates and the suspension/deposition cycle of sediments, and there is a need to better characterize these (see Gunther *et al.* [1989] and Davis *et al.* [1989]).

The principal regional monitoring programs which presently monitor contaminants in biomonitors in the Estuary are the State Mussel Watch Program (SMWP) and the Toxic Substances Monitoring Program (TSMP). There can be little doubt that the SMWP provides the most reliable database available at present on the distributions of contaminants in the Estuary. However, the program suffers from various problems, which degrade its overall value. The number of sites studied is not sufficient to properly characterize contaminant distributions in an Estuary of the size and complexity of the San Francisco Bay and Delta. Contaminants with rapid kinetics in the biomonitors used (mussels, *Mytilus californianus* and *M. edulis*) are not sufficiently well quantified. Hydrocarbons have not been included in the program in most years. There has been little consistency in the selection of study sites; this

severely degrades the value of the database for defining temporal trends in contaminant abundance. Opportunities for research and development of the techniques have been inadequate, as has financial commitment to the program.

The TSMP suffers from many of the same problems, in addition to certain others. Fish are generally preferred for analysis in this program, but these possess several disadvantages as biomonitors. In particular, the mobility of most fish species confounds their use to detect spatial trends for contaminants. Too few study sites exist to characterize contaminant distributions in the very large catchment (153,000 km² in area) of San Francisco Bay and Delta. Sampling occurs only once in each year, at different times at each study site; hence, the data do not provide a true "snapshot" of contaminant abundance at any period. Little consistency exists in the selection of either study sites or species; this severely restricts data comparability, rendering the synthesis of true spatial or temporal trend information virtually impossible. There has been little or no study of the chemical speciation of contaminants such as mercury or arsenic in the samples taken, despite the great impact of such speciation on the toxicity of these contaminants (both to the studied species and its predators). The SWRCB has undertaken the modification of both the SMWP and the TSMP programs.

The Local Monitoring of Toxic Contaminants

Point source dischargers are required to monitor the concentrations of contaminants in their effluents under NPDES permits; this is intended to provide indications of any likely toxic impact of discrete effluents, and also gives rise to data on contaminant loading to the Estuary (see Gunther et al., 1987). Similar studies are underway for a few non-point sources in the Estuary. In addition, direct bioassay studies of the toxic impacts of whole and diluted effluents have recently been introduced for certain of the major point source dischargers (the Effluent Characterization Program).

The self-monitoring requirements for contaminant concentrations in effluents generates a considerable amount of data, but only trace metals are regularly quantified. Organic contaminants are rarely detected in effluents. Thus, for example, the analysis of effluents for volatile organic contaminants (using EPA method 625) during calendar year 1987 gave rise to 5,273 results cited as "below detection limits" of a total of 5,337 analyses (98.8%) (Phillips, 1988). Several of the compounds that were detected in these effluents have also been found in blanks; it is therefore likely that contamination was responsible for at least some of the values cited above detection limits. The requirement for analysis for certain contaminants that are very rarely (if ever) detected in effluents is not cost-effective, and that funds devoted to this effort could better be expended on investigations of contaminants in biomonitors.

Few studies have been completed on the effects of individual outfalls in the Bay or Delta. However, those which have been undertaken have detected effects on the growth of aufwuchs or bivalves on occasion (Roth et al., 1983; Roth et al., 1984), and it appears that at least in some cases, effluents exert a measurable impact on biological resources in the near-field area. It is noted that, by contrast to effects-related monitoring, the use of biomonitors to measure contaminant abundance is well-established. It is therefore proposed that bio-accumulation should be monitored in such studies, rather than pollutant effects *per se*. If carefully designed, this would give rise to most useful data on the precise contaminants found in effluents and their bioavailabilities. Such studies would also provide a database which would enhance that from regional investigations using biomonitors. This approach is similar to that taken by studies of the U.S. Geological Survey on trace metals in the South Bay (Luoma and Cloern, 1982), and of the California Department of Fish & Game on selenium in the Estuary (CDF&G, 1988).

The Proposed Monitoring Program

The proposed monitoring program for toxic contaminants in the San Francisco Estuary and its catchment includes both regional and local components. The regional studies would replace the existing State Mussel Watch Program and would also

replace portions of the Toxic Substances Monitoring Program. The analysis of certain types of fish tissues should continue in the latter program, as this is relevant to the protection of public health and will provide useful comparative data to those from the studies of bivalves.

Regional monitoring

Water analysis: The collection and analysis of water samples is seen as necessary to ascertain compliance with receiving water quality objectives in the Estuary. A new routine program is proposed, involving the collection of water samples at 25 sites in the Bay (and three outside the Golden Gate, for comparative purposes) and 14 locations in the Delta.(Figures 1 and 2). Sampling should be undertaken at the same times as these stations are occupied for biomonitoring studies (see below), at monthly intervals between 01 January and 01 April, and between 01 July and 01 October (in each year). Samples should be taken for analysis of the contaminants for which water quality objectives are cited in the Basin Plan. Where possible, these samples should be collected employing time-integrating water samplers, such that the concentrations of contaminants may be quantified over a time period matching the period stated for the relevant objective in the Basin Plan. Concentrations of contaminants in solution and in suspension should be quantified.

Sediment analysis: No sediment analysis is recommended for the regional monitoring of spatial and temporal trends in the abundances and distributions of toxic contaminants in the Bay and Delta. This is because the spatial patchiness in the concentrations of contaminants found in sediments from the more open areas of the Estuary will confound any attempt to delineate spatial or temporal trends in contaminant abundance in these sediments. The impossibility of delineating trends in the regional abundance of contaminants through the use of sediment analyses does not imply that toxicants in sediments in the Estuary are of no concern, merely that their use is not scientifically justifiable for this particular goal.

Figure 1. Sampling locations for the regional component of the monitoring studies proposed on toxic contaminants in the San Francisco Bay. Phillips (1988).

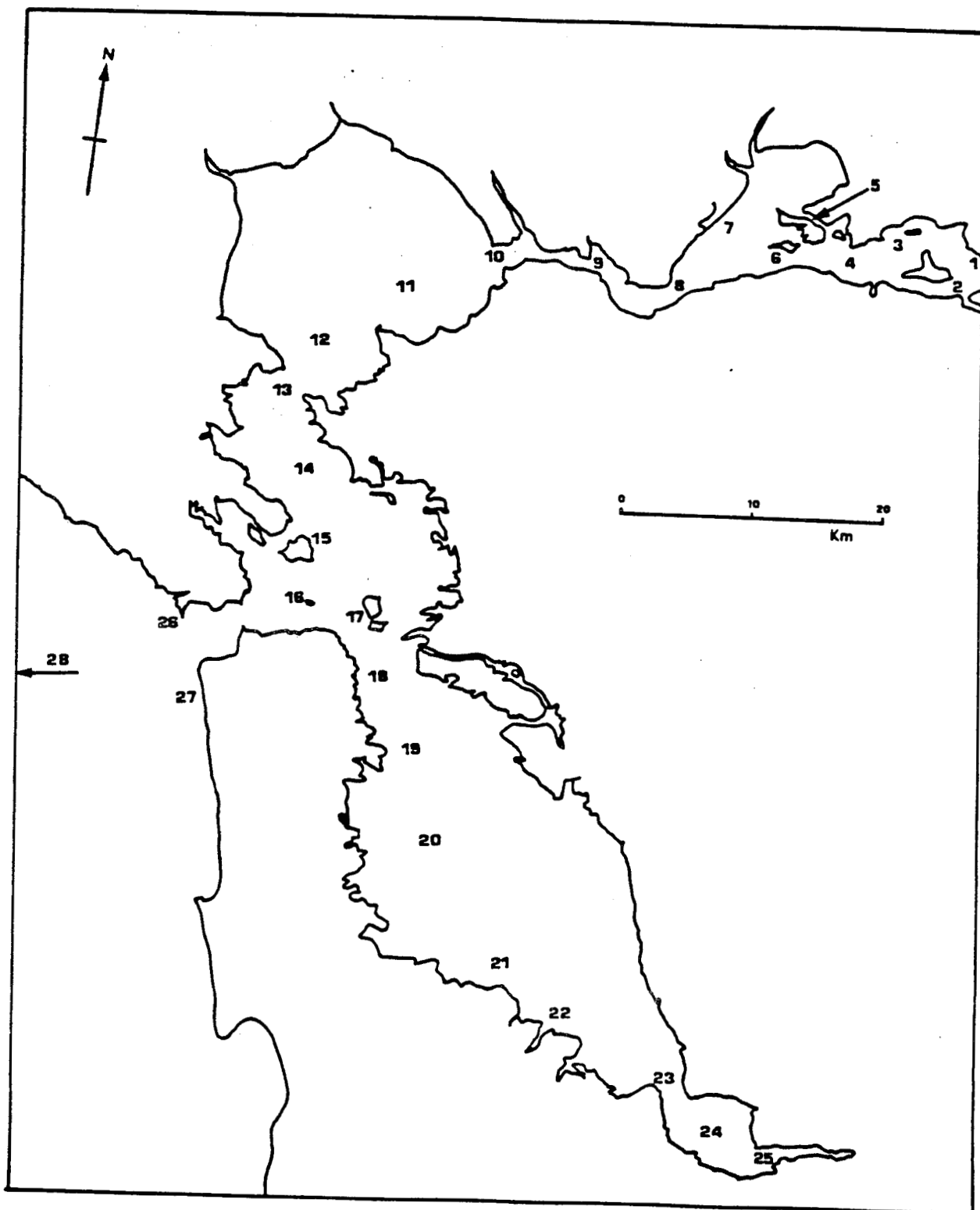
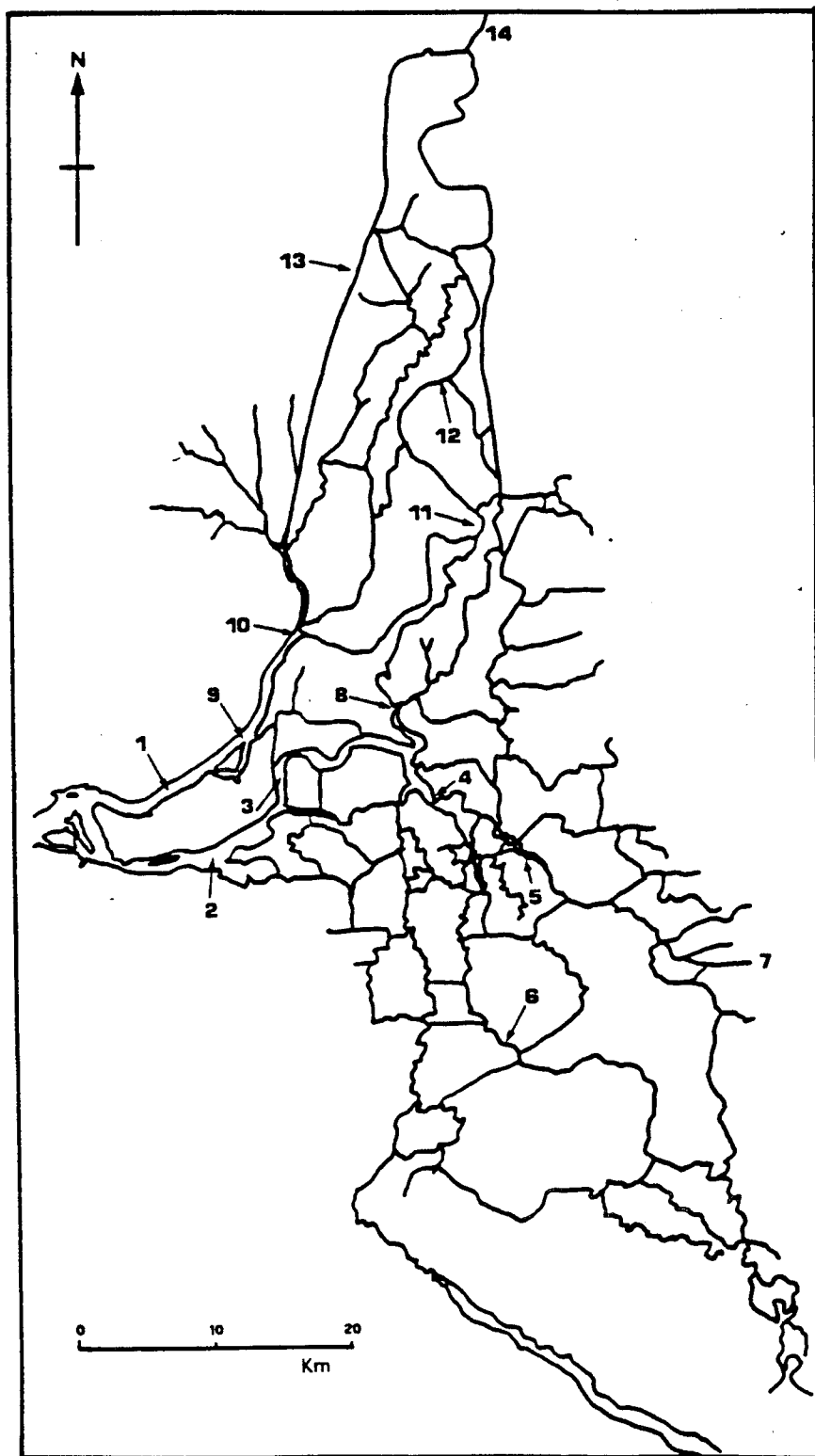


Figure 2. Sampling locations for the regional component of the monitoring studies proposed on toxic contaminants in the San Francisco Delta. Phillips (1988).



Biomonitors: It is proposed that biomonitors be transplanted into the Estuary from remote pristine locations elsewhere, as currently occurs in SMWP studies. Three species are proposed for use, to cover the range in salinity encountered through the Estuary: the Asiatic clam *Corbicula* sp. (from San Antonio Reservoir, for transplantation into freshwater regions); the Pacific oyster *Crassostrea gigas* (from Humboldt Bay, for transplantation into brackish areas); and the mussel *Mytilus californianus* (from Bodega Head, for transplantation into brackish/marine locations, as in the present SMWP studies). The same locations as those proposed for studies of receiving waters should be employed (25 in the Bay, 3 outside the Golden Gate, and 14 in the Delta [Figures 1 and 2]). Contaminants in *Corbicula* sp. should also be studied at additional sites in the catchment upstream of the Delta, these to be defined on the basis of a review of the TSMP data.

It is further recommended that studies employing biomonitors be undertaken over two periods in each year (contrasting to the single investigations presently undertaken annually by both the SMWP and the TSMP). These periods have been selected to represent wet and dry seasons in typical years, and are each three months in duration (01 January to 01 April, and 01 July to 01 October). It is likely that the contaminant distributions produced from such surveys will differ in any one year and between years, because of the temporal alterations in contaminant sources and the seasonally and annually varying impacts of freshwater inflows to the Estuary. It is proposed that biomonitors be sampled monthly for the analysis of contaminants other than trace metals, and either analysed as individual samples (representing monthly values) or bulked for analysis as one single sample (representing the entire 3-month period of transplantation) at the end of the transplantation period (Phillips and Segar, 1986). This recommendation is made because of the rapid uptake and excretion of organic contaminants in biomonitors. By contrast, samples of biomonitors to be analyzed for trace metals may be taken once only, at the end of the three-month transplantation period.

Costs of the regional program: Based upon the costs of the existing State Mussel Watch Program and those of commercial analyses of aqueous samples, the approximate costs of the regional monitoring program are suggested to be \$70,000 annually for the analyses of contaminants in receiving waters and \$200,000 annually for the biomonitoring component of the program. It should be noted, however, that the costs of managing the overall program (e.g. coordination; data management; production of annual reports, etc.) are not included in these estimates, and several assumptions are inherent in the costs provided (especially with respect to the costs of vessel time).

Local monitoring

Local monitoring studies of the abundances and distributions of contaminants should be undertaken at all major point source discharges in the Bay and Delta, and at selected non-point source discharges. Laboratory-based investigations are recommended as an initial stage for the characterization of contaminants in point source effluents; these would be followed by *in situ* field studies. However, non-point source effluents (being extremely variable in composition with time) do not lend themselves to a laboratory-based approach, and these should be studied using *in situ* field measurements only.

Water analysis: No recommendations are made concerning the need for water analysis in the local monitoring program. The existing NPDES self-monitoring of effluents (and in certain cases, receiving waters close to discharges) generally satisfies present requirements for such data. However, where the results of the regional monitoring of water quality suggest that problems of non-compliance with objectives occur in poorly-flushed areas of the Bay or Delta, there may be a case for additional local investigations.

Sediment analysis: In certain instances (where individual point source or non-point source effluents are found by the *in situ* field studies of biomonitors

described below to dominate the near-field abundances and distributions of contaminants), it may prove possible to employ the analysis of sediments on a local scale to demonstrate gradients in contaminant abundance. It may be that the spatial patchiness in contaminant abundance evident in more open areas of the Estuary would be lessened by the existence of a predominant local contaminant source. It is recommended that studies employing sediments be considered as a late stage in local monitoring, to follow the initial laboratory-based and/or field studies using biomonitors, described below. Where it appears that sediment analysis is warranted, both bulk sediment chemistry (including the determination of grain size and total organic carbon) and sediment bioassay techniques are recommended for use. The latter would best employ the amphipods *Rhepoxynius abronius* and *Ampelisca abdita*.

Biomonitors: It is recommended that the analysis of biomonitors constitute the principal effort in the local monitoring program. The local program has been designed to provide a database to match that from the regional monitoring effort. The same three species of bivalves as will be employed in the regional program (*Corbicula sp.*, *Crassostrea gigas* and *Mytilus californianus*) are proposed for use in local monitoring. All three species should be derived from the same locations as those proposed in regional monitoring. The particular species employed at each outfall will be defined by the salinity of the receiving waters during the period of study. All *in situ* field investigations should be undertaken at the same periods (01 January to 01 April; 01 July to 01 October) as those used in regional studies.

The laboratory studies proposed for point sources are intended to demonstrate the existence or otherwise of significant contaminant uptake by biomonitors maintained in whole or diluted effluents, and to identify those contaminants that are present in point source effluents (above background levels) in bioavailable form. Where the uptake of any contaminant of concern occurs to such a level as may be considered potentially detrimental to the biological resources of the Estuary, *in situ* field studies should be initiated. In the absence of alternative standards, it is proposed that the National Academy of Sciences limits for predator protection and the Food and Drug

Administration action levels for the protection of human health be employed to ascertain the need for further field studies. However, it is noted that these standards are incomplete and outdated, and should be reviewed. Certain details concerning the proposed laboratory-based studies (e.g. dilution rates for effluents; requirements for "salting-up" of test solutions) are discussed by Phillips (1988); additional details of this type may be provided on a case-by-case basis.

In situ field investigations for the local program will employ the same methods as those used in the regional monitoring of biomonitors and will seek to complement and expand the regional dataset, in addition to characterizing the near-field abundances and distributions of contaminants around specific outfalls. The general approach should be to select sampling locations on a transect or gradient away from the outfall towards a regional monitoring station, taking account of any available data on effluent dilution and the local hydrodynamics. Site selection for local studies will be necessary on a case-by-case basis.

Costs of the local program: It is difficult to estimate the costs of local studies, as these will vary substantially between individual dischargers, according to the volume and nature of the effluent produced and its discharge location. However, it is envisaged that individual laboratory-based studies of point source effluents would be likely to cost of the order of \$20,000. Discrete *in situ* field investigations would be unlikely to cost more than \$50,000, but would again vary substantially on a case-by-case basis. Managerial costs are not included in these estimates.

Contaminants to be analyzed; QA/QC; Sample archives

As noted previously, it is proposed that all receiving water samples should be analyzed for the contaminants for which objectives are cited in the Basin Plan for the Estuary (SFRWQCB, 1986). Samples of biomonitors from the regional and local monitoring programs (including both the laboratory-based and *in situ* field components

of the latter) should be analyzed for the "contaminants of concern" listed in Table 1.

Where several laboratory facilities are to undertake analysis of waters or bio-monitors for the proposed program, it is recommended that all studies be preceded by a comprehensive analytical quality assurance/quality control (QA/QC) program. This program should comprise the analysis of the "contaminants of concern" in reference or intercomparison materials, on a "blind" basis. Individual analytical facilities should be permitted to participate in the monitoring program only after achieving acceptable performance levels in such a QA/QC exercise. It is further recommended that regulatory authorities require the ongoing analysis of reference or intercomparison materials (results for which should be reported on a regular basis) during all monitoring studies.

It is recommended that the need for sample archival be further considered by regulatory authorities prior to the commencement of the proposed program. There are distinct advantages to the archiving of samples, but additional costs are attached to this approach. See O'Connor *et al.* (in press) for a more detailed treatment of QA/QC issues in contaminant analysis.

Other Recommendations

In addition to the proposed contaminant monitoring program, several other recommendations relative to contaminant monitoring in the Estuary can be made:

Contaminants in the microlayer: The abundance and toxicological effects of contaminants in the microlayer of the Bay and Delta deserve study. Investigations elsewhere, employing recently developed techniques, suggest that the microlayer is an important repository for certain toxicants, and that species or life-stages which come into physical contact with the microlayer may be affected by these contaminants (see Hardy and Cross, this volume).

Studies of other biomonitors: It is recommended that studies be undertaken to ascertain the potential usefulness of other types of biomonitors in the Estuary. The capacity of the newly-introduced clam (*Potamocorbula*) to act as an efficient biomonitor of conservative contaminants should be investigated. This species appears to possess a broad salinity tolerance, and may be a useful candidate as a biomonitor of contaminants in the Estuary. In addition, studies of macroalgae and barnacle species appear warranted, as these may complement any database provided by the use of bivalve molluscs as biomonitors.

Contaminants in "target species": Particular species in the Estuary are considered likely to be at risk from the toxic impacts of contaminants. Evidence exists that the reproduction of certain fish species (the striped bass, *Morone saxatilis*, and the starry flounder, *Platichthys stellatus*) may be affected by contaminants in the Estuary (Phillips, 1987). However, the results to date on striped bass are not thought adequate to support such a conclusion, and it is recommended that stratified sampling of this species be undertaken to attempt to reduce the sources of variance in the data. The research to date on starry flounder is considered to stop short of unequivocally demonstrating a cause-and-effect link between reproduction and PCB abundance in the Estuary; it is recommended that further work be undertaken in an attempt to establish such a link. Additional research on contaminant abundance and toxicological impacts in both birds (especially raptors) and harbor seals (*Phoca vitulina*) in the Bay and Delta is also recommended, as these species accumulate contaminants to high concentrations and are useful early indicators of the possible toxic impacts of pollutants.

Contaminants in food chains: Recent studies by the U.S. Fish and Wildlife Service and the California Department of Fish & Game have begun to define toxicant movements in food chains or food webs in the Estuary. These findings are relevant also to the definition of target species for contaminants in the Bay and Delta environments discussed above, and should receive further support.

The transport of contaminants and sediments: As noted above, the existing data on the transport of both sediments and their adsorbed contaminants are inadequate for the Bay and Delta. Further studies are needed, and these should attempt to define sediment fluxes through the system (and the associated fluxes of contaminants), relating the estuarine sediment dynamics to such factors as freshwater inflows, tidal exchange at the Golden Gate, and the impacts of dredging and disposal activities. The rates of within-Bay resuspension and deposition of sediments should be quantified also; existing estimates suggest that these are considerable (Gunther *et al.*, 1987).

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APPENDIX A

INFORMATION ON AHI

The Aquatic Habitat Institute is an independent non-profit corporation, directed by a board comprised of members from industry, environmental groups, municipal dischargers, State and Federal agencies, and The University of California at Berkeley. The Institute has a legislative mandate to coordinate and evaluate studies of the impacts of pollution on the beneficial uses of the San Francisco Bay/Delta Estuary. Data management is an integral part of this coordinating effort, as is the development of a master plan for monitoring and research on the Bay/Delta.

Recent products from AHI include reports on the principal environmental problems in the estuary, and a comprehensive review and critique of the monitoring of toxic contaminants in the Bay/Delta. In addition, two major reports on the loadings of toxic contaminants to the estuary and their biological effects were produced in August 1987 as exhibits for the State Water Resources Control Board's Bay-Delta Hearings. AHI served as an expert witness for the State in those proceedings.

The independent status of AHI and the composition of its Board of Directors provide a unique and constructive forum for analyzing the problems facing one of California's most valuable natural resources. Further information is available on request from the Institute.

**The Bioavailability of Toxic Contaminants
In the
San Francisco Bay-Delta
Proceedings of a Two-Day Seminar Series**

October, 1988

Report No.: AHI-90/01



**San Francisco Bay - Delta
Aquatic Habitat Institute**

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<p>This volume presents the proceedings of a conference entitled "The Bioavailability of Toxic Contaminants in the San Francisco Bay-Delta," hosted by The San Francisco Bay-Delta Aquatic Habitat Institute (AHI) on October 26-27, 1988. AHI is a nonprofit corporation established at the request of the State of California to coordinate and evaluate research on pollution and its effects in the San Francisco Estuary. The conference was sponsored by the Bay Area Dischargers Association, and it was held at the University of California at Berkeley.</p> <p>The goal of this conference was to provide attendees with a more detailed exposure to the question of pollutant bioavailability, thereby building upon the general foundation provided in a conference held the previous year entitled "Toxic Contaminants and Their Biological Effects in the San Francisco Bay-Delta". Presentations at the 1988 meeting included studies of environmental factors influencing bioavailability, examinations of <i>in situ</i> bioaccumulation of contaminants in invertebrates, fish, and mammals, and studies of contaminant biomagnification and toxicity. Transcripts of introductory remarks made by representatives of the Bay Area Dischargers Association and California Assemblyman Robert Campbell (D-Richmond) are included.</p> <p>Eleven of the 16 speakers provided contributions to these proceedings. These contributions range from full-length articles to abstracts.</p>				
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**The Bioavailability of Toxic Contaminants
in the
San Francisco Bay-Delta**

Proceedings of a Two Day Seminar Series

Berkeley, California

October 26-27, 1988

Andrew J. Gunther, Editor

May, 1990

TABLE OF CONTENTS

EDITOR'S COMMENTS	1
SEMINAR SCHEDULE	2
INTRODUCTORY REMARKS	4
Walter Bishop	
KEYNOTE ADDRESS	8
Cindy Deacon Williams	
TRACE METAL ASSOCIATIONS IN THE WATER COLUMN OF SOUTH SAN FRANCISCO BAY CALIFORNIA	15
James S. Kuwabara, <i>et al</i>	
THE INFLUENCE OF AMBIENT CONDITIONS ON THE BIOAVAILABILITY AND TOXICITY OF COPPER	45
Anthony R. Carlson	
CONTAMINATION AND TOXICITY OF THE SEA-SURFACE MICROLAYER .	48
John T. Hardy	
Jeffrey N. Cross	
STUDIES EMPLOYING THE CLAM <i>MACOMA BALTHICA</i> TO IDENTIFY BIOAVAILABLE TRACE METALS IN SAN FRANCISCO BAY	55
Daniel J. Cain	
CHLORINATED HYDROCARBONS IN MARINE MAMMALS FROM PUGET SOUND AND THE NORTHEAST PACIFIC	70
John Calambokidis	
INNOVATIVE METHODS OF TRACING CONTAMINANTS IN COASTALWATERS: THE USE OF BACTERIOPHAGES AND BACTERIAL SPORES	91
A. F. Godfree	
CHEMICAL TRANSFORMATIONS OF CONTAMINANTS IN DREDGED MATERIAL AND IMPLICATIONS FOR BIOAVAILABILITY	107
Thomas H. Wakeman, <i>et al</i>	
SPATIAL AND TEMPORAL TRENDS OF TOXIC CONTAMINANTS IN SEDIMENTS AND MARINE LIFE OF THE SOUTHERN CALIFORNIA BIGHT	124
Alan J. Mearns	

BIOMAGNIFICATION IN SEAFOOD ORGANISMS AROUND A LARGE CALIFORNIA SUBMARINE WASTEWATER DISCHARGE	137
D. R. Young, <i>et al</i>	

CHARACTERISTICS AND EFFECTS OF CONTAMINATED SEDIMENTS FROM SOUTHERN CALIFORNIA	152
Jack W. Anderson, <i>et al</i>	

A PROPOSED PROGRAM FOR MONITORING TOXIC CONTAMINANTS IN THE SAN FRANCISCO BAY DELTA	162
David J.H. Phillips	

APPENDICES

APPENDIX A - AQUATIC HABITAT INSTITUTE182
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EDITOR'S COMMENTS

This volume presents the proceedings of a conference entitled "The Bioavailability of Toxic Contaminants in the San Francisco Bay-Delta," hosted by The San Francisco Bay-Delta Aquatic Habitat Institute (AHI) on October 26-27, 1988. The conference was sponsored by the Bay Area Dischargers Association, and it was held at the Clark Kerr Campus of the University of California at Berkeley.

In 1987, a more general conference entitled "Toxic Contaminants and Their Biological Effects in the San Francisco Bay-Delta" was hosted by AHI. Over 220 people attended this earlier conference, reflecting the significant interest within the Bay-Delta region regarding chemical pollution of the Estuary. Many attendees suggested that future conferences could be improved through the preparation of proceedings, and consequently this document was prepared for the 1988 meeting.

The goal of the 1988 conference was to provide attendees with a more detailed exposure to the question of pollutant bioavailability, thereby building upon the general foundation provided in the previous year regarding pollution in the Estuary. Presentations included studies of environmental factors influencing bioavailability, examinations of *in situ* bioaccumulation of contaminants in invertebrates, fish, and mammals, and studies of contaminant biomagnification and toxicity. The program of presentations is found on the next page. Introductory remarks were provided by representatives of the Bay Area Dischargers Association and Assemblyman Robert Campbell (D-Richmond).

Eleven of the 16 speakers provided contributions to these proceedings. These contributions range from full-length articles to abstracts. AHI is grateful to those speakers who took the time to prepare submissions to the proceedings. We also acknowledge the wordprocessing efforts of Elizabeth Hartman in the AHI offices.

SEMINAR SCHEDULE
Wednesday October 26, 1988

- 08.30 **Registration**
- 09.00 **Welcoming Address**
Walter Bishop, AHI Board of Directors
Bay Area Dischargers Association
- 09.15 **Opening Remarks**
Assemblyman Robert Campbell
11th District, Contra Costa County
- 09.30 **Concentrations of Trace Elements in the Waters of South Bay**
James Kuwabara, US Geological Survey, Menlo Park, CA
- 10.15 **The Influence of Ambient Conditions on the Bioavailability and Toxicity of Copper**
Anthony R. Carlson, U.S. EPA Environmental Research Lab, Duluth, MN
- 11.00 **Break**
- 11.15 **Contamination and Toxicity of the Sea-surface Microlayer near Urban Areas**
Jeffrey Cross, S. California Coastal Water Research Project, Long Beach CA
- 12.00 **Factors Affecting the Bioavailability of Sediment Bound Contaminants to Benthic Organisms**
Jay Means, Louisiana State University, Baton Rouge, LA
- 12.45 **Lunch**
- 14.00 **Studies Employing the Clam *Macoma balthica* to Identify Bioavailable Trace Metals in San Francisco Bay**
Daniel Cain, U.S. Geological Survey, Menlo Park, CA
- 14.45 **The Bioavailability of Trace Metals in the San Francisco Delta: Studies with the Clam *Corbicula fluminea***
Samuel Luoma, U.S. Geological Survey, Menlo Park, CA
- 15.30 **Break**
- 15.45 **Chlorinated Hydrocarbons in Marine Mammals from Puget Sound and the Northeast Pacific**
John Calambokidis, Cascadia Research, Olympia, WA
- 16.30 **The Relationship of Accumulated PCBs to P-450 Enzymes, their Activities, and to Reproduction of Starry Founder from San Francisco Bay and Nearby Coastal Areas**
Robert B. Spies, Lawrence Livermore National Laboratory, Livermore, CA

Seminar Schedule
Thursday, October 27, 1988

- 09.00 **Innovative Methods of Tracing Contaminants in Coastal Waters: the Use of Bacteriophages and Bacterial Spores**
Alan Godfree, Altwell Ltd, Warrington, UK
- 10.00 **Chemical Transformations of Contaminants in Dredged Material and the Implications for Bioavailability**
Thomas Wakeman, U.S. Army Corps of Engineers, Bay Model, Sausalito, CA
- 10.45 **Break**
- 11.00 **Spatial and Temporal Trends of Toxic Contaminants in Sediments and Marine Life of the Southern California Bight**
Alan Mearns, NOAA, Seattle, WA
- 11.45 **The Cs:K Index of Trophic Level Separation and Pollutant Biomagnification in Seafood Organisms Around a Large California Submarine Wastewater Discharge**
David Young, EPA, Newport OR
- 12.30 **Lunch**
- 13.45 **Bioavailability and Toxicity of Contaminants from Sediments in Southern California**
Jack Anderson, S. California Coastal Water Research Project, Long Beach, CA
- 14.30 **Acute DDT Toxicity: Pathways in Sediments**
Jack Word, Battelle Northwest Laboratories, Sequim, WA.
- 15.15 **Break**
- 15.30 **Identifying Contaminants of Concern by Application of Toxicity Identification/Reduction Evaluation (TI/RE) Techniques**
Steven Hansen, S.R. Hansen & Associates, Berkeley, CA
- 16.15 **A Proposed Program for Monitoring Toxic Contaminants in the San Francisco Bay Delta**
David J.H. Phillips, Aquatic Habitat Institute, Richmond, CA

INTRODUCTORY REMARKS

Walter Bishop

Manager of Wastewater

East Bay Municipal Utility District

My name is Walter Bishop, and as a member of the Board of Directors of the Aquatic Habitat Institute I would like to welcome you to what I hope will be two days of a very valuable seminar. This is the second of what we plan to be a long series of informative scientific seminars sponsored by the Aquatic Habitat Institute. This forum for the exchange of technical information will hopefully contribute to the improvement of the water quality of San Francisco Bay. After each of you has reviewed the list of speakers for this seminar, I know you will join with me in congratulating the staff of AHI for putting together a very distinguished group.

Before I go any further I would like to spend a moment to review the organization known as the Aquatic Habitat Institute, and explain a little bit about what we, as members of the Board, consider to be its goals. When I talk to different groups and discuss the Institute, I am first pleased that someone even has a light bulb go off and says "Yeah, I've heard of them". That is the first threshold we must cross. The second threshold we cross is presenting the Institute's goals and objectives. Depending on who we talk to, people might say, "Oh, yeah, the Institute, they're an environmental group, like the Sierra Club and Citizens for a Better Environment. They are an environmental advocacy group". I get some of that. When you talk to governmental organizations, get to the bowels of EPA or the State Board, AHI is often referred to as a consulting firm - "They're up here basically trying to get contracts to do work", and so on.

The Institute was formed in 1983 essentially as the step-child of the State Water Resources Control Board. For two years the State Board studied what was right and what was wrong with research and monitoring in San Francisco Bay. What was determined very quickly is that we spent millions and million of dollars doing research on the Bay. Many of those studies were very focused with very specific goals in mind, and some studies

overlapping. The programs were often not well coordinated, and in many cases millions of dollars worth of data were sitting in the basements of governmental entities because there was no staff to sort, analyze and synthesize it. So it quickly became clear we needed a permanent, independent, and credible organization to deal with scientific research and monitoring in San Francisco Bay, and so in 1983 the Institute was formed.

I should take a moment to discuss the composition of AHI's Board of Directors. There are ten members of the board; the University of California, EPA, California Department of Fish & Game, The Regional Water Control Board, three entities representing non-point, municipal and industrial dischargers, and three members of the public. That's as diverse a group as you are going to see. There are various other entities like AHI around the country, but none of them brings together as diverse a group as AHI. We believe this diversity will help us achieve the goals we have established for AHI. One of those goals is to foster educated public exchange regarding the water quality of the Estuary through disseminating scientific information. This is why the Institute is sponsoring today's seminar.

Now why is BADA involved in this conference? Many of you are probably wondering what exactly BADA is. BADA is comprised of the five largest municipal dischargers in the San Francisco Bay. It is clear to us that there are two significant things happening that keep us on the forefront on some water quality issues. The first is that no longer can municipal dischargers, or other point sources, go to the public and say - "you know the problems of the 60's and 70's; BOD, suspended solids and conventional pollutants? They have been solved, and so you should pat us on the back. The bay doesn't smell, it looks a lot better and therefore we've done our job." The public looks at you generally and says "what have you done for me lately?" And secondly, the problem we deal with today is toxics. The issues we're concerned about are: "what are you doing to lower my risk" due to what you're putting in the environment. Risk assessment, a common method that has been used in the Food and Drug administration for years, is something that we in the municipal discharge sector must familiarize ourselves with. What that means is bioavailability of toxics, uptake of toxics by biota, are issues we have to be

knowledgeable about. They are issues the public demands we understand, and we find the science relative to those issues is running to catch up with these public demands. Anybody who participated in the Bay Delta Hearing process knows the frustration of speaking to the public and speaking to the public policy makers, and saying "I have done ten years of research on the striped bass and I can't answer the question about what's happening to the striped bass." The public doesn't know how to handle that. From a research standpoint there is validity in that statement. But in terms of public policy, we're in a situation where the public is convinced that we, as municipal dischargers, the scientific community, or regulators, may not be able to protect their health. If you don't believe that then why did Prop 65 pass? The public has found they have to regulate themselves, regulate us to protect their health.

So today and the next two days as we deal with the issues of bioavailability of toxics, as a discharger and one of the sponsors of this particular seminar, I find that I am a) here to learn, b) hoping that the staff I have here and the staff from other agencies will go back and challenge some of the policies of their organizations, to make sure we are moving in the right direction.

And, finally from a dischargers standpoint, this a very historic year. The State Water Resource Control Board, which once every ten years looks at water rights, and water distribution throughout the state, finally held the same set of hearings this year on the Bay-Delta with a water quality element. For the first time they are now balancing the impact of water use in the state with impacts on water quality. The Bay-Delta Pollution Policy Document is due out in the next couple of weeks. This is a very significant document, and one of the cornerstones of that document as I see it is the issue we will deal with in the next couple of days. Understanding bioavailability, how toxics we discharge into the environment how they find their way into biota, into the food chain, is very important. More and more often, when I go and talk to the public, and I say "Do you realize that the toxic metals that are being discharged to the bay from point sources in some cases have been reduced by over 90 percent?" I get a blank stare. The public wants to know about the other 10 percent, and about the years of unregulated discharge into the Bay.

So on the behalf of the Bay Area Dischargers Association and the Aquatic Habitat Institute, I welcome you here today. When I look around the room I see a lot of people I know, but I also see many new faces. I do not know why all of you are here today: some of you are from the University some are from government entities, some of you are from utilities, some of you have been sent here with your way paid, some of you have paid on your own. I would just say this; I think all of us are here to learn. And, I challenge you to keep your minds open. The speakers are going to be presenting some very new data; please challenge them. Challenge them with ideas that you hold on what is happening in San Francisco Bay and I think all of us will come out better for it.

KEYNOTE ADDRESS

Cindy Deacon Williams

Chief of Staff

for

Assemblyman Robert Campbell

As Margaret indicated I am with the office of Assemblyman Campbell, who is a very strong supporter of the Institute. I am delighted to see the kind of turn-out that we have today, both as a statement of interest for the work of AHI as well as an indication of the level of interest in the protection of the Bay.

As you know, there has been a real significant change over the years in the concerns associated with the Bay. In the 1950's concerns with the health of the Bay focused literally with getting the trash out of the water. The floating garbage made it obvious that people needed to do something, and there was a big effort to clean up the Bay. That sort of gross element was fairly successful. It is not likely you are going to go out and see trash floating on the surface any longer. Today we are dealing with more exotic and less obvious items of contamination.

As the seminar's program illustrates, we are no longer concerned with the improper disposal of lawn clippings and rotten fruit. We are now concerned with things like trace metals, and TBT, and PCB's. We have all heard jokes and have probably told jokes about the necessity of becoming experts on alphabet soup. The sad thing is, there is a large degree of truth to those jokes. People in a position like mine and my boss' are heavily dependent upon you all interpreting the alphabet soup and letting us know what it means. Proposition 65 is an excellent example of the kind of general public concern for these strange things floating around in our water that we can't see or taste. As a decision makers, legislators are under extreme pressure daily to make sure our constituents have a

healthy place to live and good water to drink. As we have many other issues to deal with, we are heavily dependent on your interpretation of what's going on out in the Estuary.

Many people have dubbed the new problems in the Bay and Delta as sort of "silent killers" because to the uninformed eye the Bay and Delta couldn't look better than it does today. Seldom do we have the situation where we've got an obvious outrage that results in massive fish kills or destruction of bird colonies. The water glitters in the sun light, it smells good, it feels great when it brushes up against you in the wind. We are dealing with problems that are typically chronic in nature. You run into it when you pull up a lesioned striped bass. All of a sudden, the impression and the feel of the Bay and Delta changes dramatically.

Modern society without a doubt is slowly poisoning the Bay. Fortunately we are trying not to. I think prospects are pretty good that we are headed in the right direction at this point but, we can't give up. We have to keep working.

Numerous indicators of the problems and difficulties exist, with loss of wetlands acreage to the decline of the striped bass index. From most of the people we deal with in the legislative office, however the kind of indicators that come home the hardest are the warnings regarding fish in the Bay. And, it says, "because of elevated mercury levels no one should eat more than four meals a month of any striped bass from the San Francisco Bay Delta region. Women who are pregnant or who may become pregnant, nursing mothers and children under the age of six should not eat fish from the area. Because of possible ingestion of parasitic organisms no fish of any kind from the Bay Delta region should be eaten raw." Those are the kinds of things that our constituents come up against, and they are understandably concerned not only for the potential implication of them eating fish, but also because half of our district drinks the water from the Delta. If it is causing those kinds of warnings for fish consumption, they are really worried about what it is doing to them because they are drinking the water. The sad fact, of course, is that the San Francisco Bay Delta is not an anomaly, similar warnings, although they are for different contaminants, exist in the regulations for the Salton Sea, the Santa Monica Bay, LA Basin,

Grasslands, Clear Lake, Lake Nacimiento, Lake Berryessa, Lake Herman and the Guadalupe River Reservoir Region. Fortunately as indicated earlier, as a society, we are getting a handle, or think we are getting a handle on the situation. We can only hope that we are acting in time.

There are numerous sources of Bay and Delta contamination. Contaminants from agricultural drainage enter the Delta from the Sacramento and San Joaquin rivers and from the Delta itself. Industries along the margins of the water collectively add their share of the contaminants. Nonpoint source run off and non-source discharges also do their share. Much of the problem is exacerbated because of the phenomenal reduction in Bay and Delta marshes. I remember as a child growing up in Las Vegas hearing about the new information and new discoveries of how, if we really worked hard to preserve the marshes in the Las Vegas wash they would act as a natural clean up for the municipal discharge before it entered Lake Mead and this was considered to be a grand and wonderful discovery.

Unfortunately, in the Bay and Delta we have already lost many acres of wetlands and therefore significantly reduced the natural clean up ability of the region. It doesn't look like there is a whole lot of slow down or recovery or replacement of some of that lost acreage. Changing water patterns have also left their mark and that's probably one of the biggest issues that floats around the legislature with about a two-year regularity. The location of the salt water/fresh water mixing zone has been shifted, flushing flows have been reduced, all as an out-growth of water management decisions who's focus has been on the deliverance of the water rather than the health of the Bay. No one party is culpable. There is plenty to go around. However, from this point forward I believe, and more importantly Assemblyman Campbell believes, that we are obligated to critically examine all of our choices and all of our decisions with our eye firmly on protection and restoration of the Bay and Delta as a primary goal.

I am sure all of you are far more familiar with the technical data than I am and that perhaps explains some of the problems that you see in policy decision-making. There

is truthfully some disarray and illogic to some of the management decisions. Part of this is undoubtedly due to the fact that many of the decisions are made not by the technical experts, but by well-intentioned and well-to-moderately informed lay people. We do depend on you for interpretation and this process of governance saddles you with a very heavy obligation. You not only have to collect the data, analyze the data and come up with a recommendation, you then have to look at what you have collected, analyzed and recommended, delete all of the jargon, crunch it down into at most a five minute's worth presentation and get it across so that we have a full and total understanding of what the problem is and what we need to do from here. Now that is a pretty tall order and I have great sympathy for you, but from our perspective you have to understand that legislators have to deal with approximately 7,000 different bills every session. Those bills deal with everything imaginable, and there is absolutely no way that anyone can be an expert in everything that comes before you. What you have to do is to try very hard to get as informed as you can and make your best decision. More often than not, what happens is a legislator ends up casting a vote based on a fundamental philosophic approach in what they think they heard.

That is why it is so critical for you to make sure that what they hear is not only accurate but clear. There is not the kind of background to readily absorb a lot of the information you are trying to get across. Our office is probably unique to a certain extent because we have someone on staff, namely me, that had some training in biology. So at least most of the jargon doesn't run over the top and I have got some basic understanding on how it fits. My specialty was endangered species. So when you start talking to me about water quality I run into things I really don't have a whole lot of fundamental understanding about and background on. You have got to realize we are probably better off than most of the other offices up there. There are a lot of folks on staff up there that are very intelligent and have worked long and hard to educate themselves.

The problem is the integration of information. Whether it is new information that has to be integrated into what we think we already know or whether there is, from your perspective, integration of new information into a million reports that you know are already

out there that unfortunately were developed without any real strong eye to standard methodologies and procedures. It truly does at this point take an expert to be able to hazard a guess as to what has happened and what will likely happen despite the mountains of historical data that we have.

I know that is why the Aquatic Habitat Institute is so generally loved by the Legislature. From our view, their job is to tell us what it all means, integrate the information, come together and act as a repository of all the historical data, try to coordinate all of the ongoing research and let us know what the heck is going on. It has to happen, I think, in a single location like AHI so that there is some plan to what we are doing.

One of the most refreshing projects that has come down the line in a long time is the Institute's Critical Review of Monitoring Studies. I can guarantee you that Assemblyman Campbell will be looking closely at the recommendations that the Institute is going to come up with in that study. As you can guess, probably one of the things that is most frustrating to a legislator is not coming into an apparently unresolvable complex problem but being told by the expert that despite the millions of dollars spent on studying it that we've got to study it some more. It doesn't fly very well. Those sorts of situations are kinds of things that shorten legislative careers.

We can't tell our constituents that we don't know what the answer is. We have to take our best shot and hope we are right. We need to at least make an effort to get something accomplished, to solve what is generally accepted as a problem. I suspect, as well, that the focus of this conference on Bioavailability of Contaminants would be the preferred approach rather than just a straight concentration measurement because you have to set your priorities and obviously the top priority has to be on the effects to the biotic community. It is nice to know what we've got in the mud and it is nice to know what we've got in the water but unless you can tell me what they are actually doing to the biotic community it doesn't tell me anything. Unless you can tell me what we need to do to try to short circuit the magnification in the food chain it doesn't get me anywhere. The

Legislature is really not in the pure research mode, we're into the real hands-on problem solving, whether or not we have the information to solve the problem.

As I alluded to earlier and as you all undoubtedly know, human activity has made its mark on the Delta. Our influence began at least as early as the 1700's with the arrival of the Spanish soldiers and missionaries. Marked and deleterious changes have occurred in the contour of the Bay and its tributaries and these changes were accelerated, of course, during the Gold Rush with the hydraulic mining and silting over of spawning gravels, and the filling of channels that reduced the capacity of the system to carry heavy run-off. What that lead to was massive flooding. So we diked, dredged and drained and tried to reclaim the land so it was safe. This lead to the reduction of the once more than 500,000 acres of marsh land to just a fraction of that today. Also with the increase in population the area of valley farmland under irrigation saw a vast and dramatic increase, and that lead to not only increased agricultural run-off but increased diversions, and that has also had obvious and significant impacts on the Bay and Delta.

Precisely what? Many folks will disagree. The situation we find ourselves in the Legislature is that because no one can tell us for sure, precisely what was caused by what, we back into our corner, and depending on what areas of the state we represent, we claim that it is the result of agricultural run-off or it is all the result of urban run-off, or it was all the result of dredging, or it was all the result of upstream diversion. Until we get some good solid attempts to integrate information to gain an overall perspective, I don't personally think we are going to get the actions and solutions we want.

Along with urbanization and industrialization there has been degradation of the water. I am about to read a section from an old newspaper article that indicated in '86 there were at least 30 municipal and 40 industrial waste water management facilities. And despite the dramatic improvements that Walter alluded to earlier, where you've got a 90 percent clean up, at that time we were looking at about 330 tons of potentially toxic waste material finding its way into the Bay each year. That's why our constituents, and consequently my boss, is focused more on what is still going in the bay rather than on

what has already been removed. We read those kinds of things and can't imagine a mountain of toxic waste that size being dumped voluntarily into the Bay each year. There has got to be a better way. We are looking to you all to tell us what it is. It is evident, of course, that the Bay is sensitive to what we do and to the changes that we cause and whether we are intentional or not.

As I mentioned earlier I am truly glad to see all you here today to discuss the problems. I am hoping you are also going to be floating some potential solutions. That is what it comes down to. One of the things that I heard early on, from my father actually, was an observation that if what is unique on being human is the ability to know, then every time we cause an extinction we limit our ability to be human. I think extinction of an ecosystem is at least as critical, and probably more so, if for no other interest than an enlightened self interest and a call to our ability to be human, I think we need to devote ourselves very heavily to the cause of improving the quality and restoring of the ecosystem.

Surely the Bay and Delta system is worth it. I am obviously preaching to the converted, that is why you are here. But one thing you need to do is carry that message on and out and you need to understand how vital it is for us, either as staff or my boss in a decision-making position, to hear from you clearly and directly without the 90 percent probability. Just tell us what is going on because that is the only way we can work on it and deal with it in the Legislature. We can't pass a law that only works 95 percent of the time. We can't pass a law that only deals with the situation if that probability is true. Where passing a law or not passing a law is based on what our best guess is, and our best guess is uninformed unless you give us the information on which to base it.

Thanks very much.

TRACE METAL ASSOCIATIONS IN THE WATER COLUMN OF SOUTH SAN FRANCISCO BAY CALIFORNIA¹

by

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Abstract

Spatial distributions of copper (Cu), zinc (Zn) and cadmium (Cd) were followed along a longitudinal gradient of dissolved organic carbon (DOC) in South San Francisco Bay (herein referred to as the South Bay). Dissolved Cu, Zn and Cd concentrations ranged from 24 to 66 nM, from 20 to 107 nM and from 1.2 to 4.7 nM, respectively, in samples collected on five dates beginning with the spring phytoplankton bloom and continuing through summer, 1985. Dissolved Cu and Zn concentrations varied indirectly with salinity and directly with DOC concentration which ranged from 2.1 to 4.1 mg L⁻¹. Available thermodynamic data strongly support the hypothesis that Cu speciation may be dominated by association with dissolved organic matter. Analogous control of Zn speciation by organic complexation was, however, not indicated in our computations. Computed free ion activity estimates for Cu, Zn and Cd were of the order of 10⁻¹⁰, 10⁻⁸ and 10⁻¹⁰ M, respectively. The availability of these metals may be among the factors regulating the growth of certain phytoplankton species within this region of the Estuary. In contrast to dissolved Cu, dissolved Cd was directly related to the concentration of suspended

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particulate matter, suggesting a source of dissolved Cd coincident with elevated particle concentrations in the South Bay (e.g., runoff and solute desorption). Consistent with work in other estuaries, partitioning of all three trace metals onto suspended particulates was negatively correlated with salinity and positively correlated with increases in particulate organic carbon associated with the phytoplankton bloom. These results for the South Bay indicate that sorption processes influence dissolved concentrations of these trace metals, the degree of this influence varies among metals, and processes controlling metal distribution in this estuary appear to be more element-specific than spatially-or temporally-specific.

Introduction

Understanding the transport and distribution of solutes in estuaries is for many reasons a highly complicated task. This environmental complexity is very evident in studies of trace metal reactions in estuaries. Hydrodynamic processes affect sediment transport and, thus, metal sorption processes (Delfino and Otto, 1986; Helz and Sinex, 1986). Advective transport influences movement of certain metals from bottom sediment pore waters (Delfino and Otto, 1986). Coagulation of riverine particles may remove trace metals from solution, or particle-bound metals may be desorbed as salinity increases (Salomons, 1980; Li *et al.*, 1984; Ackroyd *et al.*, 1986). These sorbed metals may be associated with various mineral phases, e.g., clays (Gibbs, 1986), oxide coatings (Balls, 1986), or with particulate organic matter (Davis, 1984; Laxen, 1985; Wangersky, 1986). In the solution phase, speciation of metals may be affected by organic complexation (van den Berg *et al.*, 1987). The transport of degraded plant material and the influx of marine humic acids associated with algal blooms have been implicated as important sources of such organic complexing agents in estuaries (Delfino and Otto, 1986; Jones *et al.*, 1986). Although physical and chemical factors affect primary productivity, algae and other microbes may in turn alter trace element cycling. The biota may serve as a source of organic chelators (Lumsden and Florence, 1983), a sink for solute sorption (Boyle *et al.*, 1982; Froelich *et al.*, 1985; Kuwabara *et al.*, 1986) and a catalyst for particle flocculation and sedimentation (Sholkovitz, 1976; Avnimelech *et al.*, 1982).

As one of the large estuarine systems in the world to experience the effects of urban and industrial development, San Francisco Bay exemplifies the complexity of estuaries. It has been described as a three-component system: the northern reach (including the Suisun and San Pablo Bays), the Central Bay and the South Bay (Conomos, 1979). Temporal trends in primary productivity, biomass and species composition in the northern reach are significantly influenced by physical processes related to freshwater input from the Sacramento and San Joaquin Rivers. In comparison, phytoplankton biomass in the South Bay is more sensitive to grazing pressure as well as to the physical effects of tidal fluctuation and river discharge (Cloern *et al.*, 1985). Although the South Bay is typically well mixed, an algal bloom occurs each spring concurrent with the establishment of a vertical salinity gradient.

Several studies have examined the spatial and temporal distributions of dissolved trace metals within San Francisco Bay. In the northern reach, Eaton (1979a) observed that dissolved trace metal distributions reflected physical mixing, chemical removal and multiple inputs within the estuary. Gordon (1980) reported conservative mixing of dissolved trace metals in the northern reach and an undefined metal source in the upper estuary at low salinities. Girvin *et al.* (1978) observed a concentration gradient for dissolved Cd, Cu and Zn in the South Bay and a temporal increase in concentrations during the spring and summer during two drought years. In general, Cd was found to be predominantly partitioned in the dissolved phase, Cu was about equally associated with the solid and solution phases, and Zn was primarily particle-bound.

In this paper we assess potentially important mechanisms that control trace metal distribution in the water column of South San Francisco Bay. Chemical, biological and physical data are examined from five sampling surveys conducted between the spring algal bloom period of March 1985, and September 1985. Large climatic and hydrographic changes occur between sampling dates as a result of the well-defined wet and dry seasons, and dramatic changes in many chemical and physical parameters result, in part, from changes in phytoplankton density (Table 1). The data indicate that, 1) Cu speciation is regulated by complexation with dissolved organic matter (DOM), 2) elevated dissolved Cd

Table 1. Physical and chemical parameters collected from five sampling cruises in the South San Francisco Bay in 1985 including: suspended particulate mass in mg L^{-1} (SPM), chlorophyll-*a* in $\mu\text{g L}^{-1}$ (CHL-*a*), particulate organic carbon in $\mu\text{g L}^{-1}$ (POC), dissolved inorganic carbon in mg L^{-1} (DOC), salinity in g solid per g solution (SAL), and dissolved and particulate trace metal concentrations. Confidence intervals (95%, N=3) for trace metal concentrations about the mean are also presented. Station numbers refer to midchannel sampling sites as depicted in Figure 1, with increasing numbers corresponding to a southward direction away from the estuary mouth. The column for freshwater discharge data (DIS) represents in m^3s^{-1} the sum of freshwater inputs to the South Bay by local riverine and municipal sewage treatment sources. The percent DIS attributable to water treatment plant effluent is given in parentheses.

DATE	DIS	Station No.	SPM	CHL-a	POC	DOC	SAL	DISSOLVED (nM)			PARTICULATE ($\mu\text{g/g}^{-1}$)		
								Cu	Zn	Cd	Cu	Zn	Cd
29/3/85	17.4 (31)	27	11.3	21.5	1250	2.9	0.0250	47+3	32+3	1.2+0.4	45.3+0.5	43.2+3.2	0.36+0.01
		30	13.5	35.2	1720	3.6	0.0234	55+5	57+3	2.4+0.4	56.1+1.8	79.5+4.5	0.83+0.01
		32	16.1	32.4	1870	3.5	0.0220	53+6	61+3	2.8+0.4	54.1+2.9	87.6+1.0	0.87+0.01
		36	17.2	37.4	1180	4.0	0.0197	66+5	107+5	4.4+0.2	65.2+0.9	154.1+8.0	1.58+0.03
16/4/85	6.7 (79)	27	2.1	7.3	400	2.7	0.0271	55+2	43+8	2.3+0.2	51.1+2.0	54.8+3.8	0.59+0.01
		30	2.4	5.0	390	2.8	0.0261	58+3	49+5	2.8+0.5	50.9+2.9	63.7+2.6	0.69+0.02
		32	7.9	9.5	540	2.8	0.0250	53+9	50+5	2.8+0.4	48.8+3.5	65.7+0.8	0.81+0.02
		36	11.6	6.3	530	3.0	0.0223	58+6	62+8	4.3+0.4	53.3+1.2	85.0+2.4	1.41+0.05
29/4/85	6.3 (83)	27	3.5	2.9	230	2.6	0.0268	53+8	47+5	3.1+0.5	46.7+7.9	60.4+2.0	0.83+0.06
		30	2.1	2.8	250	2.6	0.0265	57+2	43+3	3.1+0.4	48.1+0.7	54.8+5.1	0.81+0.05
		32	9.0	3.6	370	2.4	0.0261	44+6	46+9	3.6+0.2	38.2+3.9	58.0+2.2	1.12+0.06
		36	8.5	1.7	300	2.6	0.0245	57+2	49+5	4.0+0.7	46.6+2.3	64.0+1.5	1.26+0.15
9/7/85	6.2 (88)	27	0.1	1.2	200	2.0	0.0301	46+2	20+6	2.1+0.3	39.6+1.0	21.5+2.7	0.51+0.01
		30	0.6	1.0	180	2.3	0.0295	49+3	31+8	2.3+0.4	41.0+1.7	36.3+4.4	0.54+0.02
		32	2.8	1.5	250	2.3	0.0290	46+2	34+3	2.4+0.1	41.2+2.2	39.6+4.1	0.65+0.03
		36	9.3	1.5	330	3.1	0.0271	49+2	37+1	3.6+0.1	44.2+2.0	45.0+4.0	1.06+0.03
10/9/85	5.3 (88)	27	1.9	1.9	200	2.1	0.0316	39+2	32+3	1.4+0.1	32.9+1.1	36.6+2.6	0.36+0.02
		30	2.0	1.2	200	2.1	0.0316	39+2	32+2	2.0+0.4	34.1+1.0	37.1+4.0	0.48+0.03
		32	4.5	2.4	250	2.1	0.0311	36+3	44+2	2.7+0.2	32.0+0.8	50.7+6.8	0.70+0.09
		36	20.7	7.2	400	2.4	0.0286	24+5	47+6	4.7+0.3	22.1+0.5	53.2+3.3	1.40+0.55

appears to be coincident with elevated suspended particulate mass concentrations, but less dissolved Cd is observed when particles with elevated POC are present, and 3) temporal and spatial variability in the chemical character of the DOM and mineralogical composition of the suspended sediment are not pronounced.

Materials and Methods

On each of five sampling dates, surface water (1 m depth) was collected from a small fiberglass boat at four mid-channel stations along the longitudinal axis of South San Francisco Bay for trace metal and organic carbon analyses. Subsequent reference to sampling sites in the text, tables and figures are in terms of U.S. Geological Survey sampling station numbers 27, 30, 32 and 36 (Fig. 1) with higher station numbers representing greater southward distance from the estuary mouth at the Golden Gate Bridge (31.2, 42.4, 48.9 and 57.0 km, respectively, along the center of the main channel). Mean lower low water depths for stations 27, 30, 32 and 36 were 11.0, 12.2, 13.1, and 7.0 m, respectively. Additional surface water samples were collected simultaneously from a research vessel positioned approximately 100 m downstream from the small boat. These samples were analyzed for salinity (Lewis, 1980) and concentrations of particulate organic carbon (POC), suspended particulate matter (SPM), and chlorophyll-a, using methods specified by Wienke and Cloern (1987).

Immediate initial processing of surface water samples for dissolved and suspended particulate analyses was done on board. Suspended particles were collected on acid-washed 142-mm diameter, 0.4 μm pore size polycarbonate filters (Nuclepore). Particulate-bound trace metals were extracted with 0.1N nitric acid (HNO_3) for 2 h. Quartz-distilled HNO_3 (6 M) contained $<2 \times 10^{-9}$ M total Cu or Zn and $<1 \times 10^{-10}$ M total Cd. After particles were separated from the extractant by filtration, the filtrate was refrigerated for subsequent trace element analysis. Samples for dissolved organic carbon (DOC) analysis were filtered through furnace-treated glassfiber filters (Whatman GF/D) and preserved by refrigeration and addition of *ca.* 50 μL of a saturated mercuric chloride solution per 20 mL sample. DOC was measured on a Dohrmann carbon analyzer by persulfate and ultra violet oxidation. Dissolved trace metal samples were filtered through acid-washed 47 mm

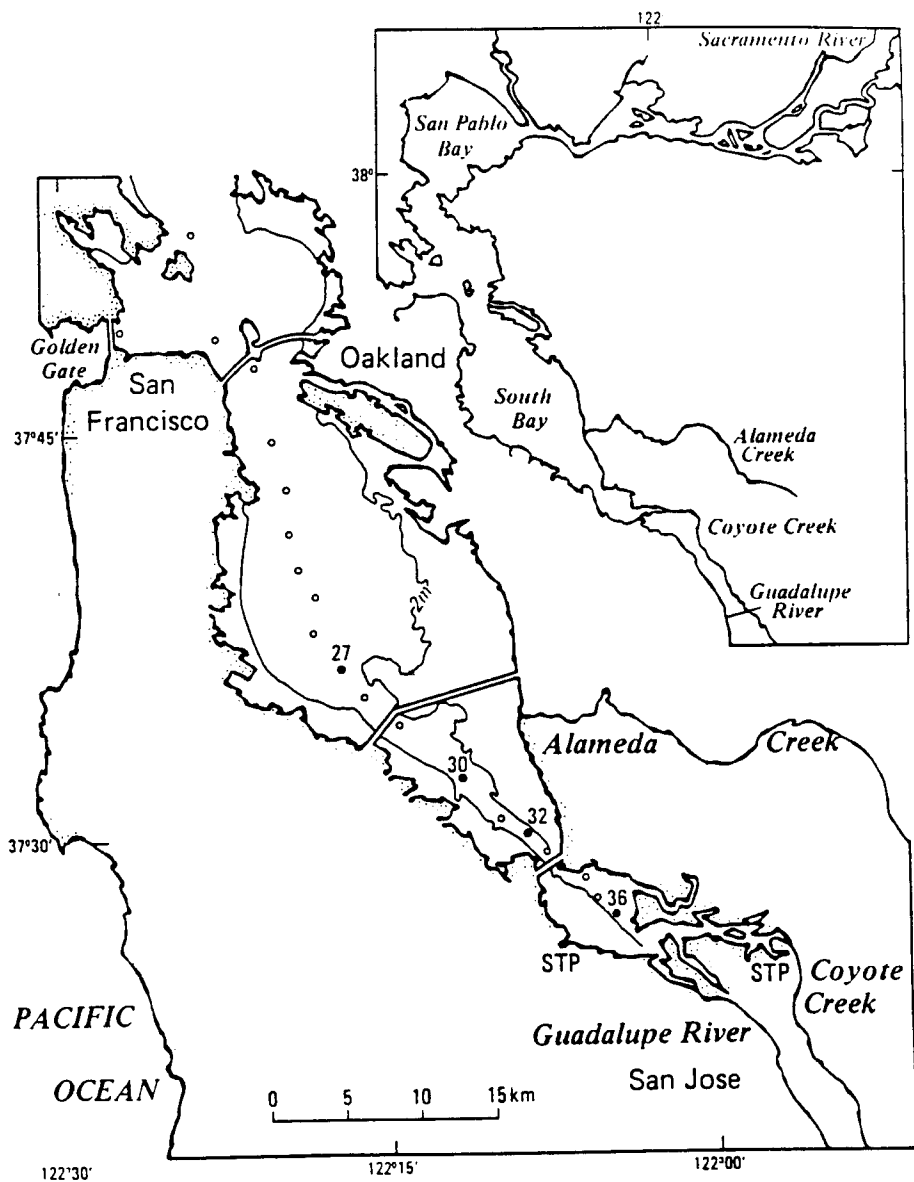


Figure 1. Mid-channel sites in South San Francisco Bay where surface water was sampled to examine processes affecting trace metal distributions. Major freshwater sources from riverine and sewage treatment plant (STP) inputs are also depicted. Longitude and latitude is shown for the South Bay and in the figure insert, which provides an overall view of the Bay.

diameter, 0.4 μm pore size polycarbonate membranes. A fluoroethylene polymer filter holder mounted on a resin kettle (Kuwabara, 1980) was used to minimize metal contamination during sample processing. After filtration, samples were acidified to pH 2 with HNO_3 and refrigerated. Dissolved trace metals were extracted and concentrated by a cobalt coprecipitation method (Bloom and Crecelius, 1984). Trace metal analyses were performed by stable platform graphite furnace atomic absorption spectroscopy with Zeeman correction. Confidence intervals (95%, $n=3$) for trace metal measurements were typically <10% of the mean concentration (Table 1). However, confidence intervals for dissolved Cd concentrations, with low mean concentrations relative to other metals, were as high as 33% of the mean.

Initial observations of dissolved and particulate trace metal distributions indicated a need to examine the spatial and temporal variability of the chemical composition of inorganic suspended particles and DOC. On three subsequent dates at Stations 27 and 32 (Fig. 1), gram quantities of suspended sediment were collected by hollow fiber tangential flow filtration (Kuwabara and Robinson, 1987) for major elemental analyses by lithium metaborate fusion after sequential extraction (Tessier 1979; Lichte *et al.*, 1987). Sediment samples (before extraction) were also analyzed by X-ray diffraction for mineralogy. As a crude indication of the spatial and temporal variability in the chemical character of the DOC in the South Bay, DOC was also extracted to determine concentrations of humic substances (Thurman and Malcolm, 1981) on these dates.

Results

The minimum salinity observed in the South Bay during any sampling was 0.0197 (expressed herein in terms of g solids per g solution, or 10^3 parts per thousand). Salinity increased with proximity to the mouth of the Bay in all five profiles, as expected in the main channel. Although the spring phytoplankton bloom in March was distinctively represented by elevated Chlorophyll-a and POC concentrations (Tables 1 and 2), spatial trends for both parameters were not consistent. Both chlorophyll-a and POC generally increased with decreasing salinity in individual profiles, but the concentrations sometimes

peaked at Station 32 rather than 36 (the southern-most sampling site) or decreased from Station 27 to 30.

Dissolved organic carbon concentrations usually increased away from the estuary mouth (i.e., going southward), mirroring salinity (Table 1). DOC concentrations generally decreased from spring through the summer. Spatial trends in dissolved Cu concentration were not pronounced and did not consistently follow SAL on any cruise (Fig. 2B). In March cruise, a weak increase in dissolved Cu occurred with distance away from the estuary mouth, and the September cruise showed the opposite trend. There was a slight southward increase in dissolved Zn concentration, which was most discernible during March (Fig. 2B). Dissolved Cd increased toward the south in all profiles, but in contrast to Cu and Zn, that increase was pronounced in September (Fig. 2C). Assessment of temporal changes in metal concentrations at individual sites must be interpreted carefully, because samples were not taken during the same tidal phase on different sampling dates.

Table 2. Correlation coefficients for parameters measured in South San Francisco Bay (underlined values are significant at the 0.01 level for N=20 per parameter).

	SPM	CHL-a	POC	DOC	Dissolved		Partitioning Coefficient			Zn
					SAL	Cu	Zn	Cd	Cu	
CHL-a	<u>0.68</u>									
POC	<u>0.67</u>	<u>0.95</u>								
DOC	<u>0.67</u>	<u>0.84</u>	<u>0.78</u>							
SAL	<u>-0.65</u>	<u>-0.73</u>	<u>-0.70</u>	<u>-0.91</u>						
Dissolved Cu	-0.01	0.40	0.34	<u>0.67</u>	<u>-0.73</u>					
Dissolved Zn	<u>0.64</u>	<u>0.69</u>	0.52	<u>0.81</u>	<u>-0.80</u>	0.54				
Dissolved Cd	<u>0.57</u>	0.05	-0.04	0.37	-0.47	0.14	<u>0.61</u>			
Cu Partitioning	<u>0.72</u>	<u>0.88</u>	<u>0.89</u>	<u>0.76</u>	<u>-0.62</u>	0.20	0.54	0.08		
Zn Partitioning	<u>0.52</u>	<u>0.78</u>	<u>0.78</u>	<u>0.90</u>	<u>-0.94</u>	<u>0.78</u>	0.72	0.23	<u>0.63</u>	
Cd Partitioning	<u>0.85</u>	<u>0.71</u>	<u>0.68</u>	<u>0.80</u>	<u>-0.83</u>	<u>0.35</u>	<u>0.73</u>	0.50	<u>0.66</u>	<u>0.74</u>

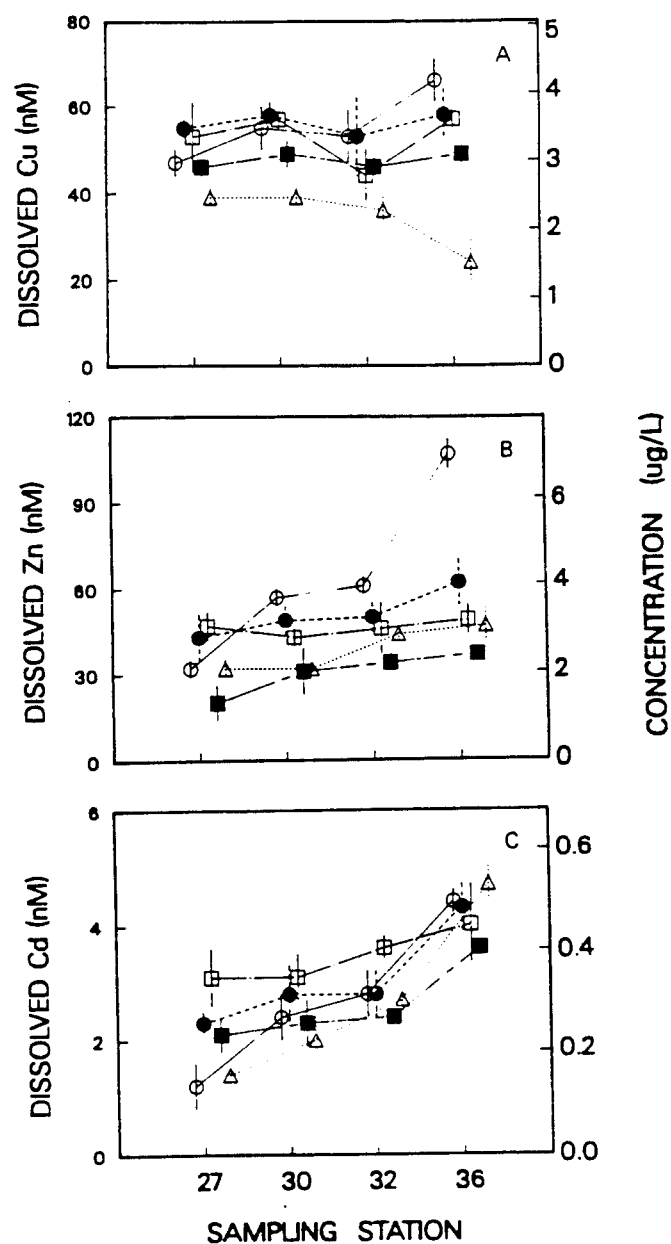


Figure 2. Spatial and temporal distributions of dissolved Cu, Zn and Cd (Fig. 2A, 2B and 2C, respectively) on each of five sampling dates beginning with the spring period of high phytoplankton biomass and high freshwater inflow, continuing through the summer period of low phytoplankton biomass and reduced freshwater inflow. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

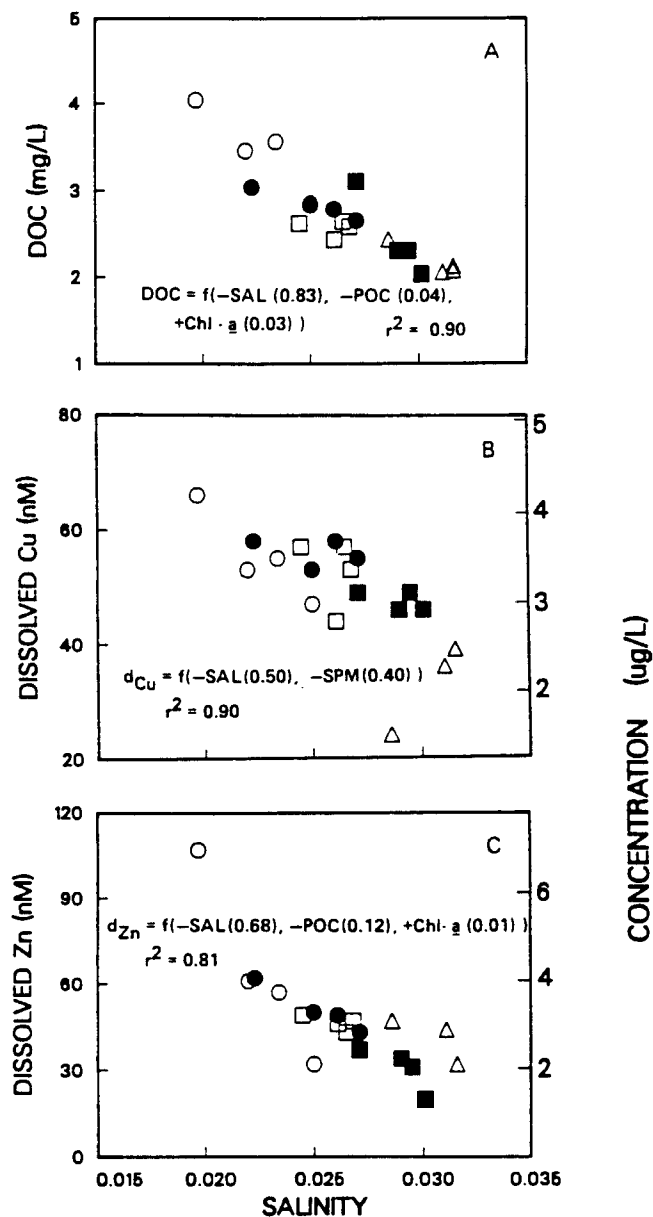


Figure 3. Coincident salinity correlation with DOC, dissolved Cu and Zn (Fig. 3A, 3B and 3C, respectively). Salinity measurements are expressed as g solid per g solution. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

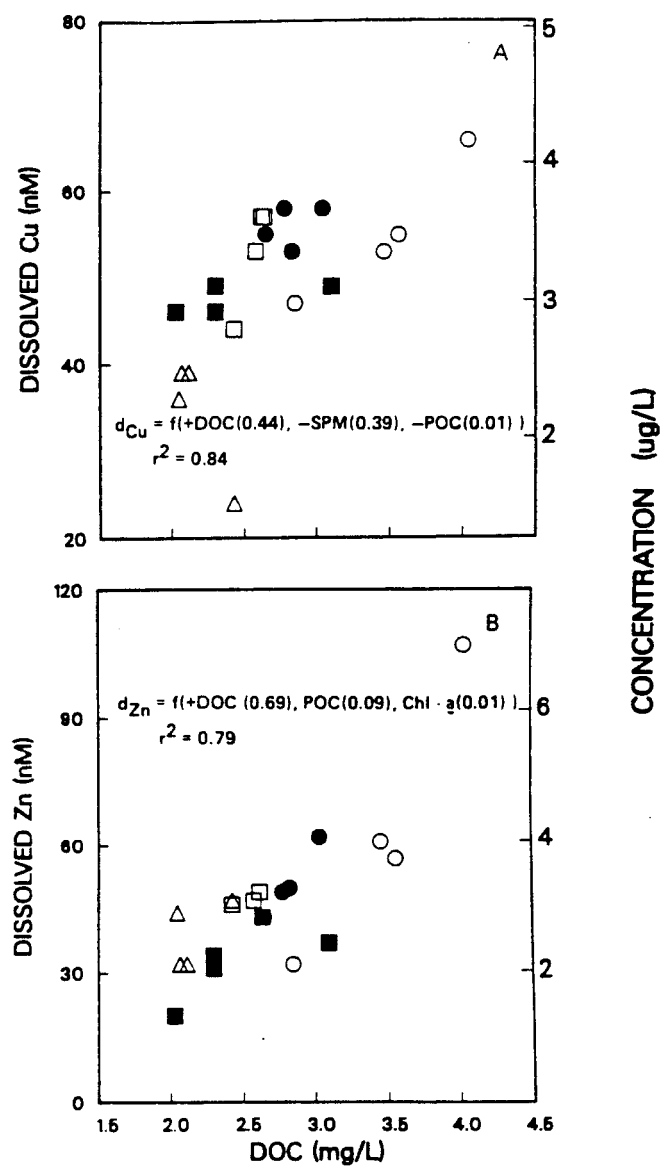


Figure 4. Relationship of dissolved Cu and Zn (Fig. 4A and 4B, respectively) with DOC. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

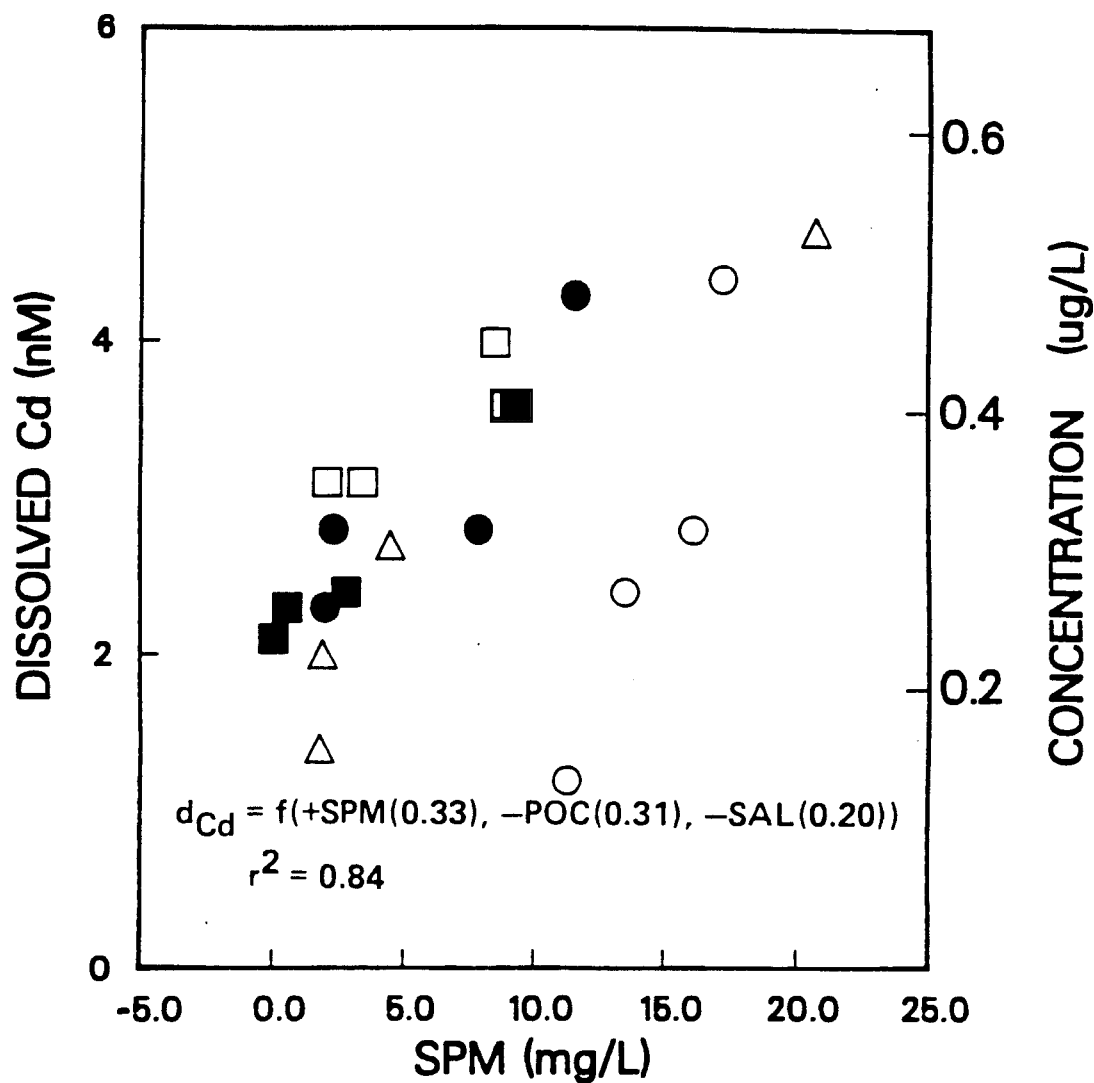


Figure 5. Regression analysis indicating a possible source of dissolved Cd from suspended sediments or undefined sources coincident with SPM (e.g., runoff). Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

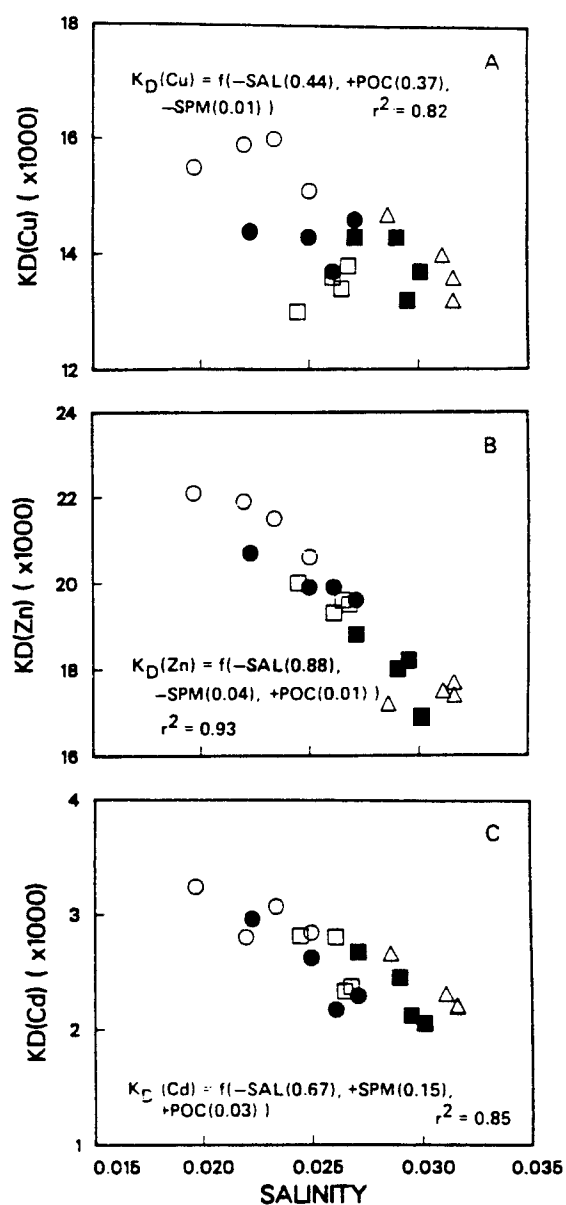


Figure 6. Partitioning of Cu, Zn and Cd (Fig. 6A, 6B and 6C, respectively) on suspended particles in South San Francisco Bay. Partitioning coefficients and salinity are presented in units of mL solution per g particles, and g solid per g solution, respectively. Data from the five sampling cruises on March 29, April 16, April 29, July 9 and September 10, 1985 are represented by open circles, shaded circles, open squares, shaded squares and triangles, respectively.

Linear regression on data aggregated from the five cruises indicated that approximately 83% of the DOC variance could be explained by changes in salinity (Fig. 3A). A similar negative correlation with SAL was observed for both dissolved Cu and Zn ($r^2=0.53$ and 0.64 respectively, Fig. 3B and 3C). Alternatively, concentrations of these metals correlated positively with DOC ($r^2=0.45$ and 0.66 for Cu and Zn respectively, Fig. 4). Dissolved Cd concentrations were also negatively correlated with SAL ($r^2 = 0.22$), but only weakly when compared to correlations of SAL with DOC, dissolved Cu or Zn (Fig. 3 and 5). Unlike Cu, dissolved Cd was positively correlated with SPM ($r^2 = 0.33$).

Partitioning coefficients (K_p) were calculated as the ratio of the mass of particulate-bound metal per unit particle mass ($\mu\text{g g}^{-1}$) over the dissolved solute mass per unit solvent volume ($\mu\text{g mL}^{-1}$). Values are expressed in units of mL solvent per g suspended particles. Partitioning of all three trace metals onto suspended particles decreased with increasing salinity ($r^2= 0.38$, 0.88 and 0.69 for Cu, Zn and Cd partitioning coefficients respectively, Fig. 6). Particle-bound copper also increased with particulate organic carbon ($r^2= 0.37$, Table 2), suggesting a transient effect on Cu partitioning due to the spring phytoplankton bloom. Particulate-bound metal concentrations in suspended sediment were higher than usually observed in surficial bottom sediment (Bradford and Luoma, 1980; Axtmann, personal communication). This may be due to differences in particle size distribution, since suspended particles typically have smaller mean particle diameters. Eaton (1979b) observed this particle size effect on metal concentrations of San Francisco Bay bottom sediment.

Results from subsequent cruises indicated that percent humic substance by carbon weight relative to total DOC was not statistically different between Stations 27 and 32 or between cruises (Table 3). The distribution of major cations in the suspended sediment was also similar, although spatial similarities appear more striking than temporal ones (Table 4). Analyses of suspended sediment by X-ray diffraction indicated that samples from both stations were mineralogically similar, with a predominance of illite and smaller amounts of chlorite and quartz.

Table 3 Results of subsequent sampling cruises to determine the humic substance fraction of the dissolved organic carbon at two stations in the South Bay. Mean values and 95% CI (N = 6) are presented for DOC and humic substance data.

Sample Station	Date	DOC (mgL ⁻¹)	%Humic substances
27	9/6/86	2.1 ± 0.5	44 ± 14
	15/7/86	2.5 ± 0.2	43 ± 4
32	9/6/86	3.0 ± 0.7	39 ± 12
	15/7/86	3.1 ± 0.4	40 ± 7

Table 4. Major elemental distribution of suspended sediment expressed in weight percent after sequential extraction, with 95% confidence intervals (N = 3). Sediment was initially analyzed in terms of oxide concentrations. Data were then normalized and transposed to the elemental state.

Element	Station 27 13/12/86	Station 27 15/7/86	Station 3 13/12/86	Station 32 15/7/86
Si	28.70 (0.99)	31.88 (0.99)	30.11 (1.50)	31.60 (0.42)
Ti	0.58 (0.02)	0.41 (0.01)	0.50 (0.02)	0.47 (0.02)
Al	10.91 (0.99)	8.89 (0.32)	9.69 (0.79)	9.00 (0.32)
Fe	6.29 (0.30)	4.55 (0.21)	5.94 (0.15)	5.10 (0.21)
Mn	0.05 (0.01)	0.04 (0.01)	0.05 (0.01)	0.04 (0.01)
Mg	2.11 (0.06)	1.63 (0.03)	2.11 (0.09)	1.75 (0.06)
Ca	0.65 (0.02)	0.70 (0.02)	0.62 (0.05)	0.62 (0.02)
Na	1.02 (0.07)	1.44 (0.04)	0.96 (0.07)	1.03 (0.06)
K	1.65 (0.09)	1.65 (0.09)	1.74 (0.12)	1.57 (0.19)
P	0.13 (0.02)	0.03 (0.01)	0.11 (0.01)	0.08 (0.06)

DISCUSSION

Cu and Zn

Although Cu and Zn profiles in the South Bay vary considerably between sampling dates (Table 1; Fig. 2), analysis of aggregated data from all cruises reveals a number of interesting correlations between measured parameters (Table 2). It is important to note that measured parameters (e.g., SPM, CHL-a, POC, DOC and SAL) are not all independent variables (Table 2). Given that particulate organic carbon dominated the suspended particles during the phytoplankton bloom, and that the annual phytoplankton bloom predictably occurs during prolonged salinity stratification (Cloern, 1984), correlations between these variables are not surprising. Thus, a regression approach cannot positively identify controlling mechanisms for trace metal distributions, but may serve as a useful exploratory tool to examine processes potentially significant among cruises.

The positive correlation of DOC and SAL with dissolved Cu and dissolved Zn raises the possibility that Cu and Zn are predominantly associated with SAL-dependent dissolved organic matter in the South Bay water column (Fig. 4). Previous studies have determined the presence and certain chemical properties of Cu-organic chelates in other estuarine environments (Sholkovitz and Copland, 1981; Mills *et al.*, 1982; Hanson and Quinn, 1983). DOC concentrations measured between 1979 and 1985 (Showalter, personal communication) also showed a positive correlation between dissolved metal and DOC concentrations near the mouth of the Guadalupe River (Fig. 1), a major freshwater source to the South Bay.

Chemical Simulations

Chemical speciation computations were employed to further examine the role of DOC in regulating metal speciation in the estuary. Using the computer program MINEQL (Westall *et al.*, 1976), Cu and Zn speciation in the South Bay were estimated using thermodynamic data of Mantoura *et al.* (1978) for dissolved organic complexation, and data of Hogfeldt (1983) for inorganic complexation. An exception was the constant for the

formation of aqueous Cu(OH), $\log^*\beta_2 = -16.2$, that was taken from a study that closely examined both inorganic and organic complexation of Cu (Sunda and Hanson, 1979).

A 3:1 ratio of seawater to riverine water [i.e., calculated mean salinity = 0.027, ionic strength (I) = 0.5 M] was assumed for determining major ion concentrations. End member concentrations for major ions in seawater and the Guadalupe River were taken from Brewer (1975) and Anderson *et al.* (1983), respectively. Activity coefficients for inorganic complexation were calculated using the Davies equation (Westall *et al.*, 1976). Seawater stability constants for dissolved organic complexation (Mantoura *et al.*, 1978) were used directly. Other fixed parameters for this calculation were: a) pH 8 compared to an observed range of 7.6 to 8.2, b) typical dissolved Cu and Zn concentrations of $3 \mu\text{g L}^{-1}$ (ca. 50 nM), c) a $1.2 \mu\text{M}$ concentration of dissolved organic ligand sites, based on measured humic substance concentrations and corresponding to 10^{-6} moles binding sites per mg-C in the humic substance (Mantoura and Riley, 1975; McKnight *et al.*, 1983; Davis, 1984).

Chemical equilibrium computations indicate that sites on humic materials should be primarily bound to Mg, but ca. 80% of the dissolved Cu would also be organically complexed. An alternative two-site binding model proposed by McKnight and Wershaw (1989) for Cu-organic complexation results in >90% of the total Cu complexed. Because the formation constants for Zn-humate complexes are typically orders of magnitude lower than for Cu-humate complexes (Mantoura *et al.*, 1978; van den Berg *et al.*, 1986), the calculation for Zn indicates that its speciation is controlled by inorganic complexation (primarily with chloride) with <10% of the dissolved Zn organically complexed. So although dissolved Zn concentrations correlated with DOC, our calculations do not indicate control of Zn speciation by organic complexation.

Limitations to the above metal speciation calculations bear close examination. First, chemical reactions with suspended particle surfaces were not considered in this computation. This limitation may have ecological implications, in that particle-bound metal

may increase metal bioavailability under conditions favorable for metal desorption (Kuwabara *et al.*, 1986).

Second, other values for $\log^*\beta_2$, the constant for the second hydrolysis equilibrium for Cu, have been reported and generally range between -13.7 and -17.3 (Vuceta and Morgan, 1977). Both of these $\log^*\beta_2$ values have little effect on Cu speciation with >90% of the total Cu still organically complexed. Computed Zn speciation was not discernably affected by these changes in the $\log^*\beta_2$ value for Cu. Similarly, a change of pH in our computation to either 7.6 or 8.2 (the lowest and highest measured value for our sampling period) does not alter the result that >90% and <5% of the dissolved Cu and dissolved Zn, respectively, are organically complexed.

Third, although the water column of San Francisco Bay is well-oxygenated (Smith and Herndon, 1980), dissolved sulfide could be present due to slow oxidation of sulfide diffusing from the bottom sediment. Speciation calculations suggest that over the range of sulfide concentrations observed by Vivit *et al.* (1984) during a drought year in the South Bay ($0.1\text{--}3.2 \times 10^{-7}$ M total sulfide), metal sulfide interactions could be important during times of high dissolved sulfide concentrations, but probably not important at lower concentrations.

Finally, variability in the chemical character of the dissolved organic matter could affect the applicability of the formation constants used here. McKnight *et al.* (1983) found that Cu associated with fulvic acids from 17 aquatic environments throughout the United States could be consistently modeled by 2 formation constants (i.e., for strong and weaker binding sites). Van den Berg *et al.* (1987) have, however, reported higher log stability constants for Cu-humate and Zn-humate complexes in the Scheldt Estuary of *ca.* 14 and 10, respectively. If these higher constants were used in our computations for the South Bay, both Zn and Cu speciation would be dominated by complexation with DOM. However, the log stability constants used in our calculations are conservative estimates relative to the range of published values and, in addition, do not reflect the potential for additional metal binding to dissolved organic material not efficiently isolated by

conventional methods like XAD-8 extraction. Ionic strength corrections were not made to the formation constants for metal-organic complexation due to a lack of thermodynamic data. At pH 8 the ionic strength effect is probably not pronounced due to conformational changes in the humic substances and because of additional complexation of hydrolyzed metal species by organic ligands (Cabaniss and Shuman, 1987). A conventional Davies correction, for example, would greatly over estimate the ionic strength effect on metal-EDTA formation constants (Anderegg, 1977). In summary, dissolved Cu is quite likely associated with DOM, except possibly during periods when dissolved sulfide is elevated in the water column. Correlation between Cu, DOC and SAL raises the possibility that organically bound Cu is transported through the South Bay without significant net interaction with particles. Zn association with DOC is supported only if relatively high formation constants like those reported by Van den Berg *et al.* (1987) are employed. However, the potential importance of such complexation cannot be excluded because of the observed Zn, DOC and SAL correlations.

Ecological Implications

It has been well demonstrated that the uncomplexed species of Cu and Zn control the bioavailability of these metals to phytoplankton (Sunda and Guillard, 1976; Anderson *et al.*, 1978), and that submicromolar activities of these metals can cause toxic effects on various algal species (Gavis *et al.*, 1981; Anderson *et al.*, 1978; Kuwabara, 1981).

Estimates for Cu, Zn and Cd free ion activities computed from our chemical simulation are of the order of 10^{-10} , 10^{-8} and 10^{-10} M, and are similar to threshold toxicity concentrations determined in the studies cited above. Using bacterial bioassays, Sunda (1987) estimated similar activity for the free cupric ion at similar total Cu in the marine plume of the Mississippi River.

The phytoplankton community structure in South San Francisco Bay is dominated by diatoms and small flagellates including cryptophytes (Wong and Cloern, 1981; 1982); dinoflagellates are rare. Phytoplankton communities in many other estuarine environments including Tomales Bay, a pristine estuary in close proximity to San Francisco Bay, are at

least periodically dominated by dinoflagellates (Graneli *et al.*, 1986; Cole, personal communication). Evidence exists that elevated free metal ion activities favor the dominance of diatoms over dinoflagellates (Mandelli, 1969; Brand *et al.*, 1986). Brand *et al.* (1986) found that Cu free ion activities between $10^{-10.4}$ and $10^{-11.1}$ M caused 50% inhibition of reproductive rates in four species of neritic dinoflagellates, while similar growth inhibition of eight neritic diatoms was observed between $10^{-9.5}$ and $10^{-10.5}$ M free Cu ion activity. Differences in Cd sensitivity between neritic dinoflagellates and diatoms were less pronounced, with 50% growth inhibition for dinoflagellates observed between $10^{-8.7}$ and $10^{-9.6}$ M free Cd ion activity versus a range of $10^{-8.1}$ and $10^{-9.4}$ M for diatoms. The order of magnitude of the free metal ion activities estimated for South San Francisco Bay combined with the small contribution of dinoflagellates to the phytoplankton community, raise the possibility that elevated free metal ion activities affect the phytoplankton community structure in favor of metal-tolerant species in the estuary.

Reactions with Particles

As a rule, our dissolved trace metal data do not show large deviation from a linear fit of metal concentration to salinity. Thus, trace metal removal is not detectable, except possibly with Cu during the final September cruise (Fig. 3B). On that date SPM was the highest observed in the study and Cu concentrations were the lowest (lower than suggested from the relationship with DOC) (Table 1; Fig. 4A). In the Tamar Estuary suspended particulate loads of 200 mg L^{-1} and salinities of <0.005 were accompanied by removal of dissolved Cu, Zn and Mn (Ackroyd *et al.*, 1986). Although these suspended loads and salinities are well outside the range of values observed in this study, they demonstrate that removal of metals from the dissolved phase by adsorption is feasible when suspended particulate loads are high (Morris, 1986; Ackroyd *et al.*, 1986). The apparent removal from solution at station 36 was more pronounced for Cu than for Zn during the September cruise in the present study (Fig. 2A and 2B). This observation is consistent with work by Mouvet and Bourg (1983), who showed that Cu has a greater affinity than Zn or Cd for adsorption sites on River Meuse bottom sediments (surface constants of $10^{-1.8}$, $10^{-3.6}$, $10^{-3.7}$ for Cu, Zn and Cd respectively).

In May 1984 (a dry year when an algal bloom was not detected in the South Bay), high dissolved Cu (14×10^{-8} M) at Station 36 accompanied high SPM (22 mg L^{-1}), but DOC (4.5 mg L^{-1}) concentrations were nearly twice those in September 1985. The interaction of Cu, DOC and particulate material is apparently complex in San Francisco Bay and may be characterized by some annual variability in the relative importance of processes affecting Cu speciation and distribution.

Partitioning coefficients for all three trace metals decreased with increased salinity. This trend is consistent with previous laboratory and field experiments (Van de Meent *et al.*, 1985). In laboratory experiments using iron hydroxides, trace metal adsorption is typically shifted to higher pH with increased chloride concentration (Davis and Leckie, 1978; Millward, 1980; Millward and Moore, 1982). This general behavior has been attributed to changes in metal speciation due to chloro-complex formation (particularly for Cd) and increased competition by major cations in the seawater matrix for adsorption sites.

An alternative explanation for the observed decrease in K_d with salinity would be a physical mixing of marine particles, characterized by a low K_d , with estuarine particles associated with a higher K_d . The inorganic composition of the suspended sediment does not vary greatly (Table 4), but the organic character of the particles do differ within the Bay (Table 1). In fact, elevated particulate organic carbon and Chlorophyll-a, a measure of phytoplankton biomass, were associated with elevated K_d values and lower salinities (Table 2). The importance of metal association with particle-bound organic matter has been well established in previous studies (Davis, 1984; Di Guilio and Scanlon, 1985). In modeling the effect of POC on trace metal sorption, others have estimated POC concentrations assuming that the relationship between POC and the ratio of DOC to SPM is linear (Mouvet and Bourg, 1983). The rationale for this assumption is that a scarcity of adsorption sites induces higher POC values at low SPM concentrations. This assumption is not appropriate for the South Bay. Even if the March data are omitted from the regression (the only sample date when phytoplankton constitute a significant POC fraction), the ratio of DOC to SPM explains only 9% of the total POC variance.

Cadmium

The distribution of dissolved Cd, relative to Cu and Zn, depicts a more complex relationship with: (1) a relatively weak dependence on salinity (Table 2), (2) a positive correlation with SPM, and (3) less dissolved Cd with the presence of elevated POC (Fig. 5). The correlation with SPM suggests that the suspended sediment could serve as a source of dissolved Cd if Cd associated with suspended particles is redistributed into solution as the particles enter high salinity bay waters. Although, there could be undefined sources of dissolved Cd coincident with SPM concentrations (i.e., runoff), the possibility of Cd desorption from SPM in the South Bay is also supported by the observed decrease in particulate Cd with increased salinity (Table 1). In the Amazon Plume, Boyle *et al.* (1982) observed evidence of Cd desorption from suspended sediment. Total Cd (dissolved and suspended) was <0.1 nM, i.e., an order of magnitude less than concentrations observed here. Laboratory observations show that Cd adsorption is depressed with increased salinity (Salomons, 1980). Cd desorption is enhanced by CdCl^+ and CdCl_2 formation, which are less likely to adsorb than Cd^{+2} (Benjamin and Leckie, 1982), and to Mg competition for Cd adsorption sites (Balistrieri and Murray, 1982), all of which occur as particles with adsorbed Cd move from freshwater into the Bay.

When particles were rich in POC in March 1985, less Cd was observed in solution than expected from measured SPM (Fig. 5). Enhanced Cd adsorption onto amorphous iron hydroxide in the presence of humic substances has been previously observed in laboratory experiments (Laxen, 1985) under conditions of low total iron (*ca.* 10^{-5} M). Others, however, have found that this affinity of Cd for POC is less significant under conditions of higher inorganic adsorption site densities (Davies-Colley *et al.*, 1984; Davis, 1984). Ten fold higher Cd partitioning coefficients in the Western Scheldt Estuary compared to the South Bay (POC concentration ranges of 1.3 to 5.5 mg L^{-1} and 0.2 to 1.9 mg L^{-1} , respectively) also are consistent with the notion of a Cd-POC association (Valenta *et al.*, 1986). This difference resulted from order of magnitude higher particulate Cd concentrations in the Western Scheldt relative to the South Bay (dissolved Cd concentrations were similar).

Although riverine sources represent a major freshwater input to the South Bay during the winter and spring (when virtually all precipitation for the year occurs), the major freshwater source to the South Bay during the summer dry season is effluent from municipal treatment plants (Table 1). With effluent concentration ranges for total Cu, Zn and Cd of 30-280 nM, 150-960 nM and *ca.* 20nM, respectively, treatment plant effluent represented a significant trace metal input to the South Bay during our sampling period. If the consistent correlations for dissolved Cd with SPM and dissolved Cu with DOC reflect geochemical associations, then the chemical character of the SPM and DOC may not have varied greatly over the spatial and temporal range of our sampling (despite large changes in the sources of freshwater). Major elemental analyses of the suspended sediment collected during subsequent cruises, and humic substance extractions of dissolved organic carbon, tend to support this hypothesis (Tables 3 and 4). Furthermore, X-ray diffraction of suspended sediment from these cruises indicates very similar mineralogy with samples dominated by illite and smaller amounts of quartz and chlorite.

It is clear from the previous discussion that many processes that affect trace metal distributions in South San Francisco Bay also operate in other estuaries. However, observations contrary to those discussed here have also been noted. For example, Villa and Pucci (1987), working in the anthropogenically-affected Blanca Bay, observed a positive correlation between dissolved Cd and POC and no correlation between dissolved Cd and SPM. Dissolved Zn was not significantly correlated with any of their measured parameters. Wangersky (1986) asserted that the principal routes of trace metal removal from solution in surface waters are physical and biological rather than strictly chemical. He based this statement on a review of the importance of chemical interactions of trace metals with dissolved and particulate organic matter, as well as biologically-mediated chemical reactions. In attempting to understand and predict trace metal behavior in aqueous environments, investigators should be wary of searching for generic answers to explain trends from one study site to another. Rather, a spatial and temporal description of the interdependence of chemical, physical and biological processes, unique to each system, is ultimately required.

Conclusions

Trace metal distributions in the water column were observed during and after a spring phytoplankton bloom in South San Francisco Bay. Strong positive correlations between dissolved Cu and DOC, and dissolved Zn and DOC, were observed. Control of Cu speciation by metal-humic material complexation in this part of the estuary is a process consistent with available elemental and thermodynamic data. However, analogous controls for Zn were not indicated by the speciation calculations. These computations also indicate that elevated free metal ion activities may be among the factors that control growth of certain phytoplankton species within the South Bay. Both Cu and Zn were significantly partitioned in solid and solution phases, whereas Cd was present primarily in solution. Results suggest a source for dissolved Cd coincident with elevated SPM. Interdependent processes that control the distribution of these metals were apparently element specific, but for the most part consistent over the temporal and spatial scales of this study.

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