

RMP

Regional
Monitoring
NewsDETERMINISTIC TO PROBABILISTIC:
CHANGING THE RMP'S SAMPLING DESIGN

by Cristina Grosso and Sarah Lowe

When the RMP was established in 1993 by the San Francisco Bay Regional Water Quality Control Board (Regional Board), its primary objectives were to collect baseline data on trace substances in the Estuary and to determine seasonal and long-term trends in contaminant concentrations. A deterministic monitoring design was established to characterize trends by sampling fixed sites located in the deeper shipping channels, primarily along the "spine" of the Estuary.

An external review of the program was conducted in 1997 to evaluate the Program's technical and administrative structure, function, and performance. One of the outcomes of this review process was the recommendation to develop a new sampling design that incorporated revised RMP objectives (see sidebar, next page) and knowledge acquired on contaminant trends in the Estuary to date.

Concurrently, meetings with Regional Board staff on regulatory issues, such as sediment cleanup and remediation plans, development of Total Maximum Daily Loads (TMDL), and the implementation of a state-wide surface water quality monitoring program, demonstrated that regulators needed the ability to draw conclusions about contaminant conditions in the Estuary's sub-regions, defined by segments characterized primarily from

hydrologic and sedimentological processes. As the implementing agency of the federal Clean Water Act and the State of California's Porter Cologne Water Quality Control Act, the Regional Board is also required to protect beneficial uses of the Estuary, for which numerical water quality objectives and narrative guidelines were defined.

However, the original RMP sampling design was not well-suited to evaluate contamination by segment or to describe what proportion of a segment might be impaired or exceed a contaminant guideline. This inability

to infer the average concentrations of contamination in a segment presented an obstacle to regulatory decision-making. Therefore, based on the Five-Year Review

Panel's recommendation for a revised monitoring design and the need to provide the Regional Board with information on the contaminant status within each segment and in the Estuary as a whole, SFEI assembled a work group of sampling experts to design a

**SPATIALLY-BALANCED,
RANDOMIZED MONITORING
WILL BE IMPLEMENTED
IN JULY 2002.**

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STABLE ISOTOPES
MAY HELP
EXPLAIN FISH
CONTAMINATION
PATTERNS IN THE
ESTUARY

by Ben Greenfield

One major objective of the Regional Monitoring Program is to describe patterns and trends in contaminant concentration in the San Francisco Estuary. In 2000, the RMP began measuring stable isotopes in fish and their prey because stable isotopes may help explain why some Estuary fish are more contaminated than others. Stable isotopes can provide information about the position of fish in the food web, and in many aquatic ecosystems, fish higher in the food web have elevated concentrations of mercury and organochlorine contaminants (Cabana and Rasmussen 1994).

Stable isotope analysis measures the relative abundance of different forms of an element in environmental samples. Elements such as nitrogen, carbon, and sulfur, naturally occur as a mixture of different isotopes. For nitrogen, the relative abundance of two isotopes (^{15}N and ^{14}N) is measured. Nitrogen isotope ratios are particularly useful for characterizing animal food web positions. When an animal digests food, the enzymatic processes preferentially absorb ^{15}N and the animal tends to excrete ^{14}N . Therefore, a predator will typically have a higher $^{15}\text{N}/^{14}\text{N}$ ratio than its prey. Because ^{15}N is heavier than ^{14}N ,

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Regional Monitoring Program for Trace Substances

A Cooperative Program Managed and Administered by the San Francisco Estuary Institute

Original RMP Objectives

To provide a framework for data collection, interpretation, and analysis during the Program's initial years, staff at the Regional Board and SFEI, along with representatives of RMP participating agencies, developed the Program's original objectives to:

- Obtain high quality baseline data describing the concentrations of toxic and potentially toxic trace elements and organic contaminants in the water and sediment of the San Francisco Estuary;
- Determine seasonal and annual trends in chemical and biological water quality in the San Francisco Estuary;
- Continue to develop a data set that can be used to determine long-term trends in the concentrations of toxic and potentially toxic trace elements and organic contaminants in the water and sediments of the San Francisco Estuary;
- Determine whether water and sediment quality in the Estuary at large are in compliance with objectives established by the Basin Plan;
- Provide a data base on water and sediment quality in the Estuary which is compatible with data being developed in other ongoing studies in the system, including, but not limited to, wasteload allocation studies and model development, sediment quality objectives development, in-bay studies of dredged material disposal, Interagency Ecological Program (IEP) water quality studies, primary productivity studies, local effects biomonitoring programs, and state and federal mussel watch programs.

Revised RMP Objectives

Based on the recommendation from the Program's Five-Year Review to identify objectives that could answer more specific management questions and better address the needs of the Regional Board and Program Participants, the following revised objectives were adopted in 1997:

- Describe patterns and trends in contaminant concentration and distribution;
- Describe general sources and loading of contamination to the Estuary;
- Measure contaminant effects on selected parts of the Estuary ecosystem;
- Compare monitoring information to relevant water quality objectives and other guidelines;
- Synthesize and distribute information from a range of sources to present a more complete picture of the sources, distribution, fates, and effects of contaminants in the Estuary ecosystem.

new monitoring scheme (see box, page 5).

This Work Group set about the task of devising a new sampling design by (1) developing a new segmentation scheme for the Estuary, (2) determining the number of samples to allocate per segment, (3) devising a new random sampling design, and (4) selecting sites throughout the geographic extent of the Estuary. The resulting spatially-balanced, randomized monitoring scheme, which will be implemented in July 2002, was designed to provide data representative of the Estuary's

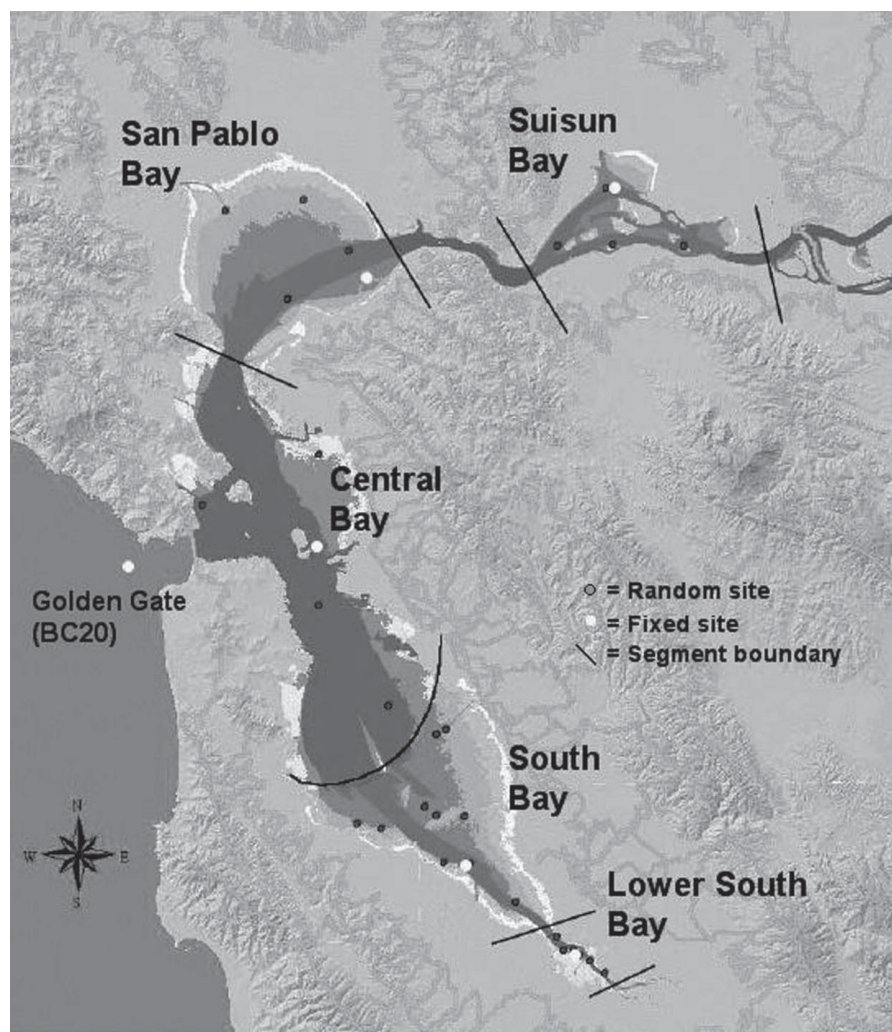
segments and allow for probabilistic analyses to be conducted.

SEGMENTING THE ESTUARY INTO HYDROGRAPHIC REGIONS

The Work Group questioned if the segments currently used by the Regional Board for regulatory purposes were representative of coherent hydrographic regions, and if sediment and water attributes in the Estuary follow a similar segmentation scheme.

Therefore, new segments were defined by reviewing and evaluating existing segmentation regimes; surveying local scientists for their expert opinions about the natural hydrologi-

FIGURE 1. RMP WATER SAMPLING SITES, 2002



Water sampling will be conducted at four to ten random sites (four in Suisun, San Pablo, and Central Bay; ten in South Bay, and six in Lower South Bay) and one historical fixed site per segment, as well as the Golden Gate for a relatively clean reference site.

cal and ecological boundaries within the Estuary; and performing cluster and partition analyses using water-quality and sediment-quality attributes from samples collected between 1989 and 1998.

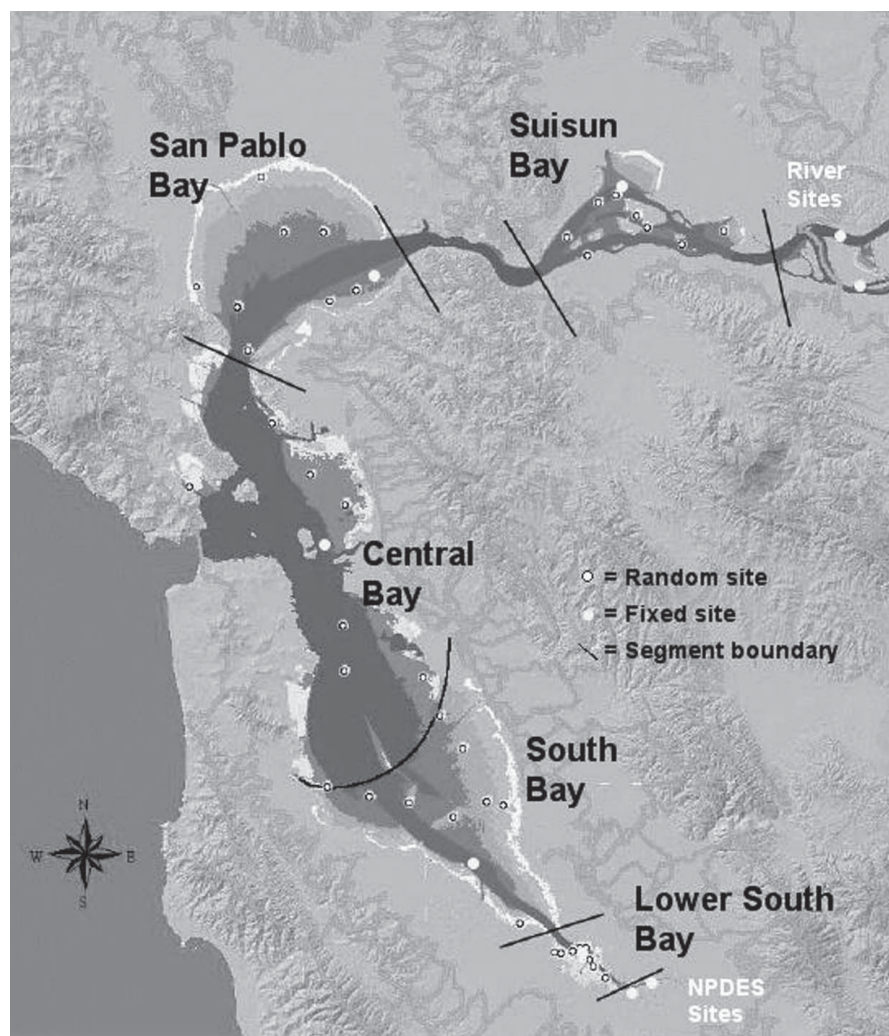
Results were displayed on maps and compared to identify the overlap or disconnection of segments, the extent of seasonal variability, and the differences in segmentation between the hydrology and the sediment characteristics.

The existing segmentation scheme used by the Regional Board for regulatory decisions, such as issuing National Pollutant Discharge Elimination System (NPDES) permits, divides the Estuary into seven hydrological planning segments, with boundaries defined by several major bridges (SFBRWQCB 1995).

Bay Area scientists with expertise on the Estuary's hydrologic processes were asked to review this scheme and to offer recommendations on new segmentation possibilities. During this process, several factors, including turbidity in the shallow regions from tidal influences, temporal variation from seasons and tides, and the influence of potential anthropogenic sources (e.g., outfalls and storm drains) were identified as important considerations in determining segments.

Numerical cluster and graphical analyses were performed using water and sediment data collected between 1989 and 1998 from the RMP, Department of Water Resources, and the Bay Protection and Toxic Cleanup Program. Cluster analyses were used to identify coherent, persistent Estuary segments using attributes for water-quality (salinity, dissolved oxygen, dissolved organic carbon, temperature, total suspended solids, and pH) and sediment-quality (percentage of fine sediments and total organic carbon). Contamination data were not considered, since these results are affected by source gradients, which may have confounded identification of hydrographic and sedimentological segments. Graphical analyses were conducted by first grouping samples with similar attributes, and then plotting them on a map. Water samples were grouped by temperature and salinity. Sediment samples were grouped by

FIGURE 2. RMP SEDIMENT SAMPLING SITES, 2002



Sediment sampling will be conducted at eight random sites and one historical fixed site per segment, the two historical river sites in the Delta, and the two NPDES sites in the Extreme Lower South Bay. Repeated measurements will be sampled at two sites per segment on a bi-annual, five-year, and ten-year cycle.

grain size and total organic carbon attributes.

With the emphasis on characterizing the Estuary for management purposes, a best approximation of the segments of the Estuary was recommended by compiling the number of times a segment boundary was identified by professional opinions, dry season water cluster analyses, and water and sediment graphical results.

Five major segments emerged from these results, and a new segmentation scheme consisting of Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay was proposed.

The most notable variations from the original segmentation were in the Central Bay segment, which was originally bounded by the Richmond and Bay bridges and now extended to Point San Pablo (in the north) and San Bruno Shoal (in the south), and in the South Bay where the geographical constriction at the Dumbarton Bridge was identified as the new segment boundary.

DETERMINING THE NUMBER OF SAMPLES PER SEGMENT

After establishing a new segmentation scheme for the Estuary, the Work Group needed to determine the number of samples to allocate within

each segment. Power analysis, a statistical tool, was conducted to evaluate the number of samples needed in any given segment of the Estuary to achieve an acceptable level of confidence that the mean concentration for key contaminants was above the Water Quality Criterion (WQC) or the Effects Range-Median (ERM) for water and sediment, respectively.

Both water and sediment power analyses showed that when contaminant concentrations varied widely within a given segment, or when the observed mean concentrations were close to a guideline value, an impractically large number of samples was needed to achieve adequate statistical power. Therefore, the power analyses were limited to a few key contaminants of concern to the Regional Board – dissolved copper for water, and copper, mercury, and total PAHs for sediment.

Based on areas of greater regulatory concern (e.g., South Bay and Lower South Bay), statistically adequate power for key contaminants, and funding constraints, water and sediment sample sizes for each segment were recommended.

DEVISING THE NEW RANDOM SAMPLING DESIGN

Based on almost ten years of trends monitoring data, the Work Group decided that long-term trends for many contaminants could be monitored on an annual or five-year basis and that seasonal fluctuations related to the sources, pathways, and loadings of contaminants to the Estuary could be addressed better through separate, focused special studies.

Numerous other issues were also considered during the development of the new sampling design and the allocation of samples. These included the type of random design (should a random, stratified random, or spatially-balanced random design be used); treatment of the shallows and channels (should samples be proportionally allocated between the two); tidal action (should water samples be collected at slack tide to minimize the amount and effect of total suspended solids); estuary margins (should estuary margins and sloughs be sampled in the Base Program); minimum depth for the sampling region; river mouths

TABLE 1. OVERVIEW OF 2002 RMP MONITORING DESIGN

Water Sampling

- Dry weather sampling at 33 sites, including random sites and a few fixed historical sites
- Sampling region delineated by the three-foot contour at MLLW
- Same analyte list as in previous years for cognates, trace elements, and trace organics
- New analytes include trace organic contaminants PBDEs, Phthalates, and p-Nonylphenol
- Aquatic toxicity sampling at 15 sites

Sediment Sampling

- Dry weather sampling at 49 sites, including random sites and a few historical sites
- Sampling region delineated by the one-foot contour at MLLW
- Same analyte list as in previous years for cognates, trace elements, and trace organics
- Pore-water sampling discontinued

- New analytes include trace organic contaminants PBDEs, Phthalates, and p-Nonylphenol
- Sediment toxicity sampling at 28 sites

Bivalve Bioaccumulation Sampling

- Dry weather deployment at 15 sites
- Only trace organics analyzed in 2002
- Trace elements will be analyzed on a five-year cycle (sampling scheduled in 2006)
- Same analyte list as in previous years for trace elements and trace organics
- Tributyltins analysis discontinued
- New analytes include trace organic contaminants PBDEs, Phthalates, and p-Nonylphenol

Episodic Toxicity Sampling

- Wet weather water sampling for 5 storm events at four tributaries and continued intensive study at Mallard Island
- Invertebrate and fish-larvae toxicity tests will be performed

(should samples be taken from sites located near the mouths of rivers, since these locations reflect sources of contamination and do not represent the general status of a segment); maintenance of historic sites (should the Base Program continue to sample historic sites per segment, including the sites located at the mouths of the San Joaquin and Sacramento rivers, to maintain the important historical dataset and to monitor contaminant inputs from the Estuary's largest rivers); and seasonality (should water and sediment sampling be conducted annually in the dry season, since long-term trends can be determined more easily when data are not influenced by high variability as during wet season flows).

Table 1 summarizes the new monitoring design and includes some of the outcomes from these discussions.

SELECTING SAMPLING SITES

With the sampling design and number of samples per segment defined, the next step was to select the sampling sites. Assisted by Don Stevens from the Oregon EPA, a sophisticated site selection framework developed for EMAP (the Generalized Random Tessellation Stratified [GRTS] sample design) was used to achieve a random, spatially-balanced distribution of sites (Stevens 1997; Stevens and Olsen 1999; Stevens and Olsen 2000).

While the potential advantage of co-locating certain water and sediment sampling sites was explored, an independent site selection scheme was adopted since co-location did not seem to add a significant amount of information without having to conduct sophisticated statistical calculations. Figures 1 and 2 display the random and historical fixed sites that will be sampled during the first year of the new sediment and water monitoring design.

For sediment sampling, the Work Group decided that it is important to incorporate repeat sampling at a subset of sites for long-term trends analyses. A rotating panel design was devised, including eight random sites and one historical site per segment, and repeated measurements at two sites per segment implemented on a bi-annual, five-year, and ten-year cycle. However, the advantage of repeated measurements potentially eliminating the component of within-population variation is only useful if a population element retains much of its identity through time. While this can be assumed to be true for sediment samples, it cannot for water due to the constantly moving water masses within the Estuary. The assumption was made that although the water parameters would exhibit a strong spatial pattern, returning to the same site would not enable the same characteristics of a previous sample to be captured. Therefore, the water sampling design incorporates a non-repeating, spatially-balanced, random site distribution, including four to ten random sites and one historical fixed site per segment, as well as the relatively clean reference site at Golden Gate (BC20). Trend descriptions for water attributes will be derived from estimates of population statistics (e.g., trend in mean value or in the proportion that meets a water quality criterion).

Sediment and aquatic toxicity evaluations and bivalve bioaccumulation sampling will also continue to be conducted in 2002. However, only trace organics will be analyzed in tissue samples; trace elements will be measured in bivalves on a five-year cycle beginning in 2006.

DISCUSSION AND CONCLUSION

The new spatially-balanced, random sampling design will allow the RMP to better address the new RMP objectives and to provide the Regional Board with statistically sound characterizations of contamination in each segment and the Estuary as a whole. From this new design, the RMP will be able to estimate the spatial and temporal distribution of water and sediment contamination in the Estuary, determine if the mean contaminant concentration within a segment is above a regulatory guideline, and estimate what proportion of the Estuary is toxic to laboratory test organisms.

Continued from page 1 – Stable Isotopes

this is referred to as having a "heavier" stable isotope ratio. The fact that predators have heavier nitrogen isotope ratios enables scientists to compare nitrogen isotope ratios among organisms in the same system to estimate relative food web position (Minagawa and Wada 1984; see figure on page 3).

The RMP will be using stable isotopes to better understand the relationship between contaminant concentrations and food web position. In general, mercury, PCBs, and other contaminants often reach high concentrations in organisms high in the food web; i.e., herbivores will have lower concentrations than the predators that eat the herbivores. For example, a striped bass

that has been eating jacksmelt for most of its life will ultimately accumulate greater mercury concentrations than the jacksmelt because the mercury tends to build up in the striped's body, rather than being efficiently excreted. Understanding the relationship between food web position and contaminant concentration in fish could have significant management implications for the Bay. If food web position is strongly related to contaminant concentration for fish in the San Francisco Estuary, people could lessen contaminant exposure by eating fish species lower in the food web. In certain species such as striped bass, individuals have a wide-range of mercury concentrations and stable isotopes will enable the RMP to understand if varia-

tions in food web position cause these variations in mercury concentrations. Because the nitrogen isotope ratio will be monitored along with contaminant concentrations every three years, it will also help determine whether long-term changes in fish contaminant concentration are related to changes in food web position.

The RMP is analyzing fish stable isotopes as part of the triennial fish sampling program. In addition to nitrogen isotope ratios, carbon isotope ratios will be measured. These fish will be compared to Bay mussels collected from the same sites. Because mussels are herbivores low in the food chain, they are useful baseline organisms in fish

RMP Design Integration Work Group

Khalil Abu-Saba, SFB RWQCB
Cindy Brown, US Geological Survey
Jay Davis, San Francisco Estuary Institute
Jim Delorey, US Army Corps of Engineers
Russ Flegal, University of California Santa Cruz
Andrew Gunther, Applied Marine Sciences
Rainer Hoenicke, San Francisco Estuary Institute
Michelle Hornberger, US Geological Survey
Wally Jarman, University of Utah
Sarah Lowe, San Francisco Estuary Institute
Jim McGrath, Port of Oakland
Alan Mearns, NOAA

Trish Mulvey, CLEAN South Bay
Tom Mumley, SFB RWQCB
Arleen Navarret, City & County of San Francisco
Tara Schraga, US Geological Survey
Robert Smith, Independent Contractor
Anke Mueller-Solger, CA Department of Water Resources
Don Stevens, DYNAMAC
Karen Taberski, SFB RWQCB
Kim Taylor, CALFED Bay-Delta Program
Bruce Thompson, SFEI
David Tucker, City of San Jose

Data collected can also be "back-stratified" according to the shallow and deep channels, delineated by the six-foot contour at mean lower low water (MLLW), to determine what proportion of the shallow versus deep channels is impaired. These types of inferences are not possible with the original, fixed-site RMP sampling design. However, a subset of these historical sampling sites will be maintained to assess long-term contaminant trends in the Estuary and to serve as a link between the two sampling designs.

Note: This brief overview of the new RMP Status and Trends sampling design has been summarized from the more thorough, preliminary technical report currently being prepared and which will be made available later in 2002.

Authors: Cristina Grosso: (510) 746-7371, cristina@sfei.org; Sarah Lowe: (510) 746-7384, sarah@sfei.org

REFERENCES

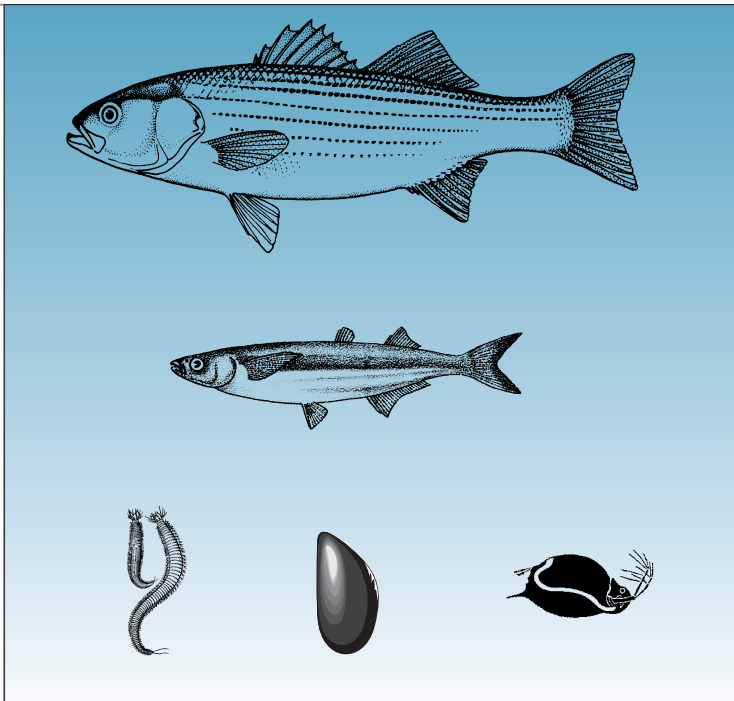
- SFB RWQCB. 1995. Water Quality Control Plan: San Francisco Bay Basin (Region 2). San Francisco Bay Regional Water Quality Control Board, Oakland, California.
- Stevens, Jr., D.L. 1997. Variable density grid-based sampling designs for continuous spatial populations. *Environmetrics* 8:167-195.
- Stevens, Jr., D. L. and A. R. Olsen. 1999. Spatially restricted surveys over time for aquatic resources. *Journal of Agricultural, Biological, and Environmental Statistics* 4:415-428.
- Stevens, Jr., D.L. and A. R. Olsen. 2000. Spatially-restricted random sampling designs for design-based and model-based estimation. In *Accuracy 2000: Proceedings of the 4th International Symposium on Spatial Accuracy Assessment in Natural Resources and Environmental Sciences*. Delft University Press, The Netherlands, pp. 609-616.

Continued on next page

High Food Web Position
High Nitrogen Isotope Ratio
High Contamination (?)



Low Food Web Position
Low Nitrogen Isotope Ratio
Low Contamination (?)



Stable nitrogen isotope ratios are indicators of food web position. The RMP is using stable nitrogen isotopes to determine whether fish higher in the food web have higher concentrations of contaminants in their tissues.

isotope studies (Cabana and Rasmussen 1996). Fish food web position is estimated by comparing the fish isotope ratios to the mussel isotope ratios.

Stable isotope analysis has also been incorporated into a Regional Board study that is designed to evaluate how PCBs become available to Bay sport fish. In this study, a food web model is being built to determine how sediment and water PCB concentrations affect concentrations in fish. For the study, stable isotope data will be used to help determine whether variation in prey choice among fish is causing variation in their PCB concentrations. This study complements the RMP fish sampling because data were collected at RMP sampling sites and will provide information on a variety of potential fish prey.

In addition to characterizing food web position, stable isotopes can sometimes help determine organism movement patterns and energy sources. For example, USGS researchers have demonstrated that the carbon in mussels collected from South Bay tends to be heavier than the carbon from mussels collected in North Bay (Canuel et al. 1995). In the Hudson River, fish movement patterns have been shown to influence contaminant concentrations (Zlokovitz and Secor 1999). Because the RMP is collecting stable carbon and nitrogen isotope data, it may be possible

to characterize fish movement patterns and determine whether they affect contaminant concentrations. However, isotope analysis of movement patterns is often complicated by other factors, such as whether a fish has significantly switched its diet within a given area.

A number of other research programs are also conducting stable isotope analysis to characterize food web position, movement patterns, and nutrient flow patterns throughout the Estuary. For example, Robin Stewart and colleagues at the USGS and IEP have been conducting food web studies in Suisun Bay to evaluate why selenium concentrations in white sturgeon appear to have increased (Stewart et al. 2001). For example, Robin Stewart and colleagues at the USGS and IEP have been conducting food web studies in Suisun Bay to evaluate why selenium concentrations in white sturgeon appear to have increased following the introduction of *Potamocorbula amurensis*. Additionally, carbon and nitrogen isotope data are being collected in the CALFED assessment of mercury in the Bay-Delta watershed, which will help determine whether food web position of Delta sport fish, such as largemouth bass, seems to be related to tissue mercury concentrations in the Delta (Greenfield et al. 2001). When the investigators on these studies share their findings and interpretations,

we should have a richer overall understanding of how food webs are structured in the San Francisco Estuary.

Author: Ben Greenfield (510) 746-7385;
ben@sfei.org

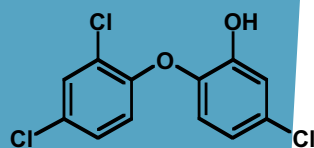
REFERENCES

- Cabana, G. and J. B. Rasmussen. 1994. Modeling food chain structure and contaminant bioaccumulation using stable nitrogen isotopes. *Nature*. 372:255-257.
- Cabana, G. and J. B. Rasmussen. 1996. Comparison of aquatic food chains using nitrogen isotopes. *Proc. Nat. Acad. Sci. USA*. 93:10844-10847.
- Canuel, E. A., J. E. Cloern, D. B. Ringelberg, J. B. Guckert, and G.H. Rau. 1995. Molecular and isotopic tracers used to examine sources of organic matter and its incorporation into the food webs of San Francisco Bay. *Limnology and Oceanography*. 40:67-81.
- Greenfield, B. K., J. A. Davis, G. Ichikawa, M. Stephenson, D. G. Slotton, S. Ayers, and W. Jarman. 2001. Mercury contamination of sport fish in the Delta and its tributaries. NorCal SETAC 11th Annual Meeting. Poster available for viewing at www.sfei.org/cmr/Mercury.pdf
- Minagawa, M. and E. Wada. 1984. Stepwise enrichment of ^{15}N along food chains: further evidence and the relation between delta ^{15}N and animal age. *Geochimica et Cosmochimica Acta*. 48:1135-1140.
- Stewart, R. et al. 2001. Applications of stable isotopes research in understanding complex ecological processes in the San Francisco Estuary. *IEP Newsletter*. 14(4):27-32.
- Zlokovitz, E. R. and D. H. Secor. 1999. Effect of habitat use on PCB body burden in Hudson River striped bass (*Morone saxatilis*). *Can. J. Fish. Aquat. Sci.* 56 (suppl.1):86-93.

RMP DETECTIVE WORK: IDENTIFYING NEW ORGANIC CONTAMINANTS IN THE ESTUARY

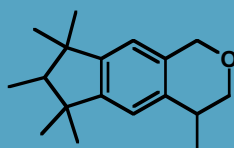
by Daniel R. Oros

ANTISEPTICS



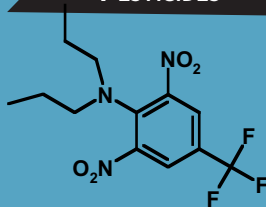
Triclosan

MUSKS



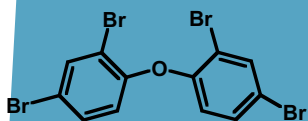
Galaxolide

PESTICIDES



Trifluralin

FLAME RETARDANTS



2,2',4,4'-Tetrabromodiphenyl ether

The recent addition of a surveillance component to the Regional Monitoring Program for Trace Substances (RMP) was prompted by a need to make the regulatory system more proactive in anticipating potential problem contaminants in the San Francisco Estuary. Our efforts have focused mainly on identifying as many as possible of the "unknown" organic compounds that were resolved by combined gas chromatography-mass spectrometry (GC-MS).

All samples were collected by the RMP and during the earlier SEDQUAL program from 1990 to the present year. Water samples were extracted in-situ with polyurethane foam or XAD resin. Foam plugs and biota tissue samples were each spiked with surrogate standards then extracted with organic solvents (MeOH and CH_2Cl_2). Sample extracts were combined and then subjected to Florisil column chromatography for separation into PCB/aliphatic (F1), pesticide/aromatic (F2) and polar fractions (F3). Fractions were analyzed by GC-MS.

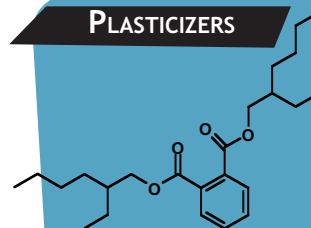
Preliminary findings show the presence of both natural (e.g., terrestrial and marine plants) and anthropogenic (e.g., biomass burning, meat cooking, petroleum, synthetics, etc.) organic compounds and their decomposition products in environmental samples.

The anthropogenic organic compounds that are of immediate concern to the RMP include antioxidants used as preservatives (butylated hydroxy toluene, butylated hydroxy anisole), flame retardants (tetra- and pentabromo diphenyl ethers), surfactants (nonylphenol and alkylbenzenes), organophosphate pesticides (oxadiazon, diazinon and chlorpyrifos), industrial polymer plasticizers (di-N-butyl phthalate, butyl benzy phthalate and bis(2-ethylhexyl) phthalate), a flame retardant plasticizer (triphenylphosphate), and fragrance compounds (musk ketone, galaxolide, and versalide).

Recent evidence suggests that some of these synthetic compounds and their metabolites may induce toxicity, disrupt endocrine systems, and accumulate in marine biota (fish, crabs, and bivalves) and in higher food chain consumers (birds, marine mammals, and humans). Herein, we demonstrate that a monitoring program can incorporate a surveillance component that is useful for identifying past, current, and potential problems in the environment. Studies to confirm contaminant spatial and temporal distributions, and link these newly identified compounds to adverse impacts in the Estuary are warranted to ensure these contaminants do not become the legacy pollutants of the future.

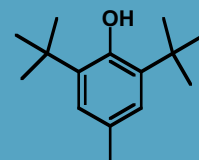
Author: Daniel Oros (510) 746-7386; daniel@sfei.org

PLASTICIZERS



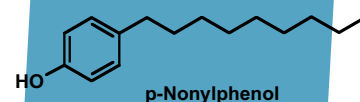
Bis(2-ethylhexyl)phthalate

ANTIOXIDANTS



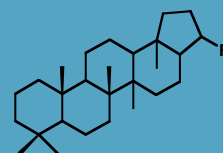
Butylated hydroxy toluene

SURFACTANTS



p-Nonylphenol

PETROLEUM BIOMARKERS



R = H, C_2H_5 , C_3H_7 - C_8H_{17}
Hopanes

TOXIC POLLUTANTS ROUTINELY TRANSFERED FROM BAY AREA AIR TO WATER

by John Ross and Pam Tsai*

Toxic pollutants are routinely emitted into the atmosphere naturally, such as through volcanoes and forest fires, and through human sources, such as industry and motor vehicles. Beginning in August 1999 and continuing through November 2000, the San Francisco Estuary Institute (SFEI), in collaboration with other state and local agencies, conducted a San Francisco Bay Atmospheric Deposition Pilot Study to estimate the input of selected trace metals and trace organic pollutants from the atmosphere to the San Francisco Estuary.

Through two different pathways — wet and dry deposition — pollutants can move from the atmosphere to surface waters. Wet deposition is the transfer of a substance within or on the surface of snow, hail, rain or fog, whereas dry deposition is the transfer of dry particles or the absorption of gases from the air. Pollutants can reach bodies of water by falling directly into the water (direct deposition), or by falling onto the land and washing into a body of water as runoff (indirect deposition).

Mercury, one of the trace metals evaluated in the study, has been found to impair the waters of the San Francisco Estuary, as well as some of the surrounding rivers, creeks, and reservoirs. Mercury at concentrations that may pose a threat to human health has been measured in fish caught in the Estuary <http://www.sfei.org/rmp/reports/fish_contamination.html>. The Atmospheric Deposition Pilot Study measured mercury concentrations in the air and rainfall of the San Francisco Bay Area that were comparable to other urban areas of the United

States. Direct atmospheric deposition (dry and wet) was estimated to contribute approximately 27 kg of mercury a year to the Estuary, with 18% of this being contributed by rainfall. Indirect inputs from atmospheric deposition via runoff from the watersheds of the San Francisco Estuary were estimated to constitute an additional 55 kg per year. Total mercury load to the Estuary from direct and indirect atmospheric deposition (82 kg per year) is almost seven times the amount attributable to wastewater discharges (12 kg per year; Ellgas 2001). The Pilot Study results suggest that atmospheric deposition of mercury may be a major factor influencing the water quality of the San Francisco Estuary, and represents a large enough contribution to the total mercury load to warrant further investigation.



Dry deposition sample collection using a greased surrogate surface plate. The Greased Mylar film was exposed to the ambient air for 24 hours. Duplicate samples, as well as one field blank, were collected at each site once every 14 days.



Wet deposition sample collection using the automatic Aerochem Metrics Precipitation Collector. One cumulative composite precipitation sample was collected every 14 days.

Direct atmospheric deposition (dry and wet) of copper, nickel, cadmium, and chromium to the Estuary was estimated to be approximately 1900, 930, 93, and 1600 kg/year, respectively. On an annual basis, indirect deposition onto land surfaces surrounding the Estuary and subsequent input into the Estuary through runoff from tributaries contributes approximately twice as much as the loads from direct atmospheric deposition. Total loads from direct and indirect atmospheric deposition to the San Francisco Estuary might contribute similar amounts of copper, half the amount of nickel, and as much as three times the loads of chromium attributable to wastewater discharges, but this constitutes less than 10% of the loadings of these trace metals from stormwater runoff (Davis *et al.* 2000).

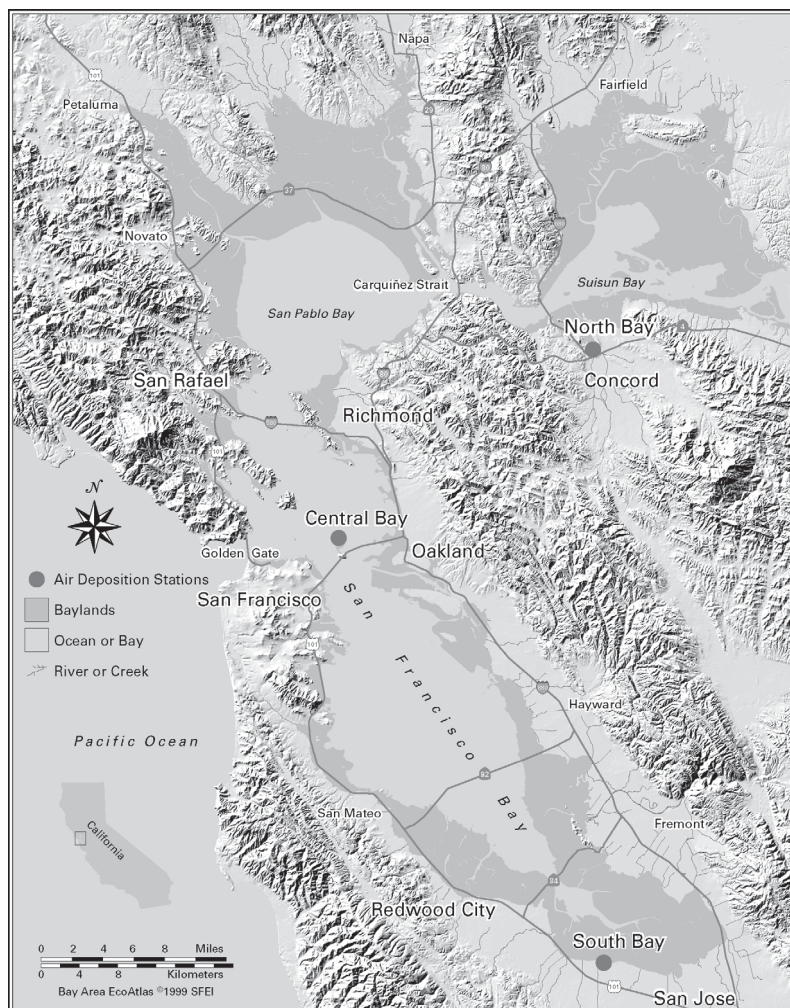
Trace organic pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) have been implicated in the impairment of beneficial uses of the San Francisco Estuary. The recognized beneficial uses of water bodies are: support of aquatic life; fish consump-

tion; shellfish harvesting; drinking water supply; swimming; boating; agriculture; ground water recharge; support land-based wildlife habitat; and cultural role (SFBRWQCB 1995). Fish caught in the Estuary have shown PCB concentrations at levels that may pose a potential threat to human health <http://www.sfei.org/rmp/reports/fish_contamination.html>. Observations of elevated PAH concentrations in bivalve tissues, and the suspected contribution of PAHs to sediment toxicity and altered benthic community structure have also warranted concern.

During June through November 2000, the SFEI Atmospheric Deposition Pilot Study found ambient air concentrations of PCBs were relatively consistent from month to month, ranging from 0.17 to 0.32 ng/m³. Concentrations of PCBs detected in the San Francisco Bay Area were two to five times higher than those measured in the Lake Tahoe basin (Datta *et al.* 1998) or the more pristine areas around the Great Lakes (Hoff *et al.* 1996), but lower than those measured in the urban Baltimore area (Offenberg and Baker 1999).

In contrast to PCBs, PAH concentrations exhibited large seasonal variation, with the highest concentrations measured in November (56 ng/m³) being almost ten times the concentrations detected in August (5.7 ng/m³). The dramatic increase in total PAHs in November may partially reflect an increase in residential wood-burning activities. Air concentrations of PAHs measured in the Bay Area were ten times lower than those detected in the urban Chicago area (Odabasi *et al.* 1999), but comparable to those found around the urbanized areas of Baltimore (Offenberg and Baker 1999) and New Jersey (Gigliotti *et al.* 2000).

Results of air-water flux modeling show a net deposition of PAHs from the atmosphere to the Estuary occurred during the six-month sampling period, suggesting that atmospheric deposition might be a significant pathway contributing to the total load of PAHs in the Estuary. The model results also suggest that the Estuary is a source for the emission of PCBs into the atmosphere.



Atmospheric Deposition Sampling Stations

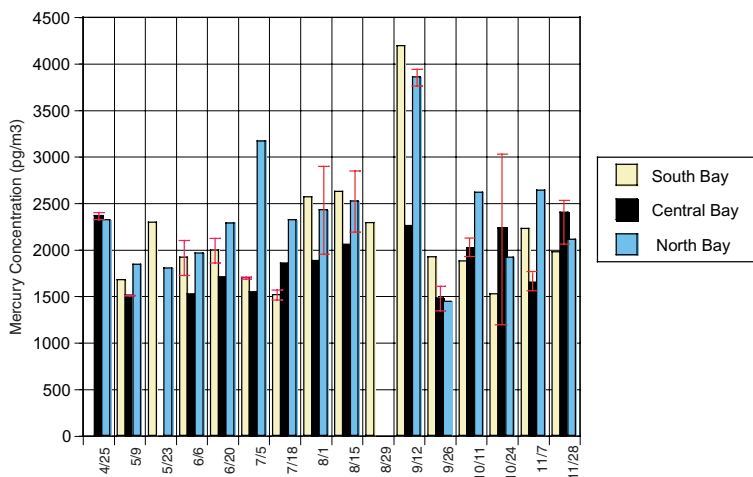
Atmospheric deposition, like watershed run-off and wastewater discharge, is an external conveyor of pollutants to the San Francisco Estuary. A suitable plan for minimizing the pollutant loads to the Estuary, therefore, should include an examination of strategies that could mitigate the sources and pathways contributing to releases of trace metals, including mercury, and PAHs to the atmosphere.

Copies of the complete technical reports for the first two parts of the San Francisco Bay Atmospheric Deposition Pilot Study covering mercury (Part I) and trace metals (Part II) are

available on request by contacting the San Francisco Estuary Institute. Trace organics (Part III) is currently in peer review.

Author: John Ross (510) 746-7382, jross@sfei.org

*Corresponding author. Present Address: US EPA Region IX (Air-6), 75 Hawthorne Street, San Francisco, CA 94105. Tel: (415) 947-4196; Fax: (415) 947-3583; E-mail: tsai.pam@epa.gov



Mercury concentration in the ambient air in the San Francisco Bay Area, Year 2000

REFERENCES

- Datta, S., L. L. McConnell, O. E. Baker, A. Lenoir and J. N. Seiber. 1998. Evidence for atmospheric transport and deposition of polychlorinated biphenyls to the Lake Tahoe Basin, California-Nevada. *Environmental Science and Technology* **32**(10): 1378-1385.
- Davis, J. A., L. J. McKee, J. E. Leatherbarrow and T. H. Daum. 2000. Contaminant loads from stormwater to coastal waters in the San Francisco Bay region: Comparison to other pathways and recommended approach for future evaluation (draft internal document). San Francisco Estuary Institute, Richmond, CA.
- Ellgas, B. 2001. Comparison of 1999-2000 POTW Hg Data, Methods and Special Studies. CWEA/BADA Mercury Workshop, San Jose, CA.
- Gigliotti, C. L., J. Dachs, E. D. Nelson, P. A. Bruniak, and S. J. Eisenreich. 2000. Polycyclic aromatic hydrocarbons in the New Jersey coastal atmosphere. *Environmental Science and Technology* **34**(17): 3547-3554.
- Hoff, R. M., W. M. J. Strachan, C. W. Sweet, C. H. Chan, M. Shackleton, T. F. Bidleman, K. A. Brice, D. A. Burniston, S. Cussion, D. F. Gatz, K. Harlin, and W. H. Schroeder. 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmospheric Environment* **30**(20): 3505-3527.

Odabasi, M., A. Sofuoglu, N. M. Vardar, Y. L. Tasdemir and T. M. Holsen. 1999. Measurement of dry deposition and air-water exchange of polycyclic aromatic hydrocarbons with the water surface sampler. *Environmental Science and Technology* **33**(3): 426-434.

Offenberg, J. H. and J. E. Baker. 1999. Influence of Baltimore's urban atmosphere on organic contaminants over the Northern Chesapeake Bay. *Journal of the Air & Waste Management Association* **49**: 959-965.

SFBRWQCB. 1995. Water Quality Control Plan: San Francisco Bay Basin (Region 2). San Francisco Regional Water Quality Control Board, Oakland, California.

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Editors: Patricia Chambers, Jay Davis, Cristina Grosso, Sarah Lowe, Mike May
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San Francisco Estuary Institute
7770 Pardee Lane, 2nd Floor
Oakland, CA 94621
(510) 746-7334

BIOINDICATORS, SENTINELS OF ECOLOGICAL EFFECTS

by Sarah Lowe

In keeping with the RMP objectives and the recommendations of several workgroups, the RMP is developing a new component to monitor biological exposure and effects of contaminants in the Estuary. The RMP is implementing a five-year Pilot Study to develop several ecological indicators to monitor contaminant exposure and effects at several trophic levels, at different levels of biological organization (biochemical, individual, population, and community levels), and at different spatial scales (locally and regionally).

A small workgroup was formed in 2001 to begin planning.

The objectives for 2001 were to develop management questions, review existing literature, solicit recommendations from the local scientific community (by using a survey), and come up with a preliminary outline for the Exposure and Effects Pilot Study.

As a first step in this effort, Regional Board staff defined their information needs by developing a set of management questions linked to beneficial uses pertaining to the accumulation and effects of contaminants in Bay biota. Survey responses and an extensive literature review were used to develop the list of general exposure and effects measurements outlined in Table 1. This initial design idea builds

on recommendations of the 1995 Indicator Workshop (SFEI 1997) and the Interagency Ecological Program (IEP).

Detailed work plans remain to be worked out, and more local and regional experts are being asked to join the Workgroup to provide guidance. The Exposure and Effects Workgroup will focus on specific measures each year, spending up to two years to develop and evaluate the efficacy of an indicator.

In 2002, bird and invertebrate measures will be evaluated. Bioaccumulation of specific contaminants in bird eggs and tissue for several avian species will be studied along with reproductive effects measures.



FAREWELL RAINER

In October 2001, the San Francisco Estuary Institute bid farewell to Regional Monitoring Program manager Dr. Rainer Hoenicke. After four years as the program's manager, Rainer opened a new chapter in his career with the California Continuing Resource Investment Strategy Project (CCRISP), where he is currently helping to develop the Resources Status Analysis and Trends (RSAT) component of the Resources Agency.

Rainer began his work with the RMP in 1994, beginning as QA officer and becoming the Program manager in 1998. He served as a guiding force behind the Program's early development, when in Rainer's words, "things were a guessing game, and we didn't know what specific purpose the data were going to be used for," to the RMP's current status as a complex technical program that has successfully generated an ever-expanding database of information that is



tailored to management needs and is used in a variety of environmental management decisions.

Rainer's charismatic leadership helped establish a climate of cooperation and commitment that had far-reaching implications for the RMP. Under his direction, the Program achieved notable successes fostering the "collective responsibility" of regulators, dischargers, industry representatives, and scientists to safeguard the well-being of the Estuary.

"Don't start mopping the floor without first turning the tap to the overflowing sink off!"

– "Rainerism" #235

Ever prolific, Rainer led the charge of the RMP through a host of committee and workgroup meetings, technical reports, pilot studies, special studies, annual reports, quality assurance/quality control issues, data analysis and study design issues, organizational partnerships, management and budgeting issues, and still had enough energy left over to motivate and organize RMP staff.

Rainer's position has since become a two-person job with Dr. Jay Davis and Sarah Lowe acting as Program manager and associate Program manager, respectively. Dr. Jay Davis, says, "After trying to fill Rainer's shoes for a few months, I now fully appreciate and marvel at the workload Rainer shouldered so well."

Invertebrate and fish larvae aquatic and sediment toxicity studies will evaluate the relative sensitivities of EPA laboratory test species vs. resident species to specific contaminants. In 2003, the Workgroup will develop an effects component that will augment the already scheduled Fish Contamination Study.

The goal of this pilot study is to arrive at a 'tool box' of locally tested and validated, biological exposure and effects indicators that can be used to monitor the Estuary at different temporal and spatial scales. These indicators will be developed over the next five years, and in the long-term will help inform the Regional Board on questions related to managing and protecting beneficial uses. An effort will be made to take advantage of other studies in the Estuary in order to obtain as much ancillary information as possible (for interpretive purposes) at minimal cost.

TABLE 1. THE GENERAL SUITE OF EXPOSURE AND EFFECTS INDICATORS TO BE EVALUATED DURING THE RMP'S EXPOSURE AND EFFECTS PILOT STUDY.

Exposure and Bioaccumulation Measures	Trophic Level	Description
Biomarkers: (e.g. cytochrome P450, vitellogenin, macrophage aggregates, acetylcholinesterase, Comet test)	low & high	These cellular tests help to evaluate possible cause of effects by providing information about exposure to specific contaminant groups. Could be studied in invertebrates, fish, birds and seals.
Bioaccumulation of contaminants in birds, bird eggs, fish tissue, benthic prey species, and seals	low & high	These tests help to evaluate possible cause of effects by providing information about exposure to specific contaminant groups.
Toxicity Identification Evaluations (TIEs)	low	This is an ancillary measure for toxicity testing that helps provide information about which contaminant groups are causing the observed toxicity.
Testing of Appropriate Effects Indicators		
Histopathology of fish	high	Liver and gonad evaluations in conjunction with fish bioaccumulation and biomarker studies provide a solid weight of evidence for biological effects of contamination.
Physiology of seals	high	Would evaluate overall health measures of a high trophic level animal. Would provide a regionally integrated ecological effects measure.
Toxicity (invertebrates)	low	Toxicity evaluations that include resident and important prey species would make these tests more ecologically relevant to the San Francisco Bay.
Toxicity (Fish larvae)	high	Menidia are currently proposed as part of the RMP Episodic Toxicity component. We would like to consider using a rare & endangered species to address beneficial use questions.
Bird egg hatchability and/or other reproductive measures	high	Birds integrate regional exposure to certain contaminant groups and based on their feeding and behavioral habits provide information about different modes of exposure within the food web.
Benthic Community	low	Benthic evaluations are a common monitoring tool for both site-specific and regionally integrated ecological effects.

CALENDAR OF EVENTS

Tuesday, Feb. 12, 2002

Gilles Tremblay will present a seminar on analysis of spatial and temporal patterns in fish mercury concentrations (location to be determined). (510) 746-7334

Wednesday, Feb. 27, 2002 (Noon)

Brown Bag seminar on the origin of San Francisco Bay by Dr. Ken Lajoie
San Francisco Estuary Institute
7770 Pardee lane, 2nd Floor
Oakland
(510) 746-7334

Friday, March 22, 2002

Regional Monitoring Program for Trace Substances' Annual Meeting
Elihu M. Harris State Building, 1515 Clay Street, Oakland
For more information: (510) 746-7334

Tuesday, April 2, 2002

Technical Review Committee Meeting
San Francisco Estuary Institute
(510)-746-7334

ANNOUNCEMENT

The new management team for the RMP consists of Dr. Jay Davis, RMP Manager (jay@sfei.org) and Sarah Lowe, Associate RMP Manager (sarah@sfei.org). Dr. Bruce Thompson (Interim Executive Director of SFEI and former RMP Manager) is helping to keep us headed in the right direction.

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