

# RMP

## THE TRANSPORT OF CONTAMINANTS TO SAN FRANCISCO BAY BY STORMWATER

by Lester McKee and Jay Davis

In 1998 the Regional Monitoring Program (RMP) adopted an objective that established a new direction for the Program: to describe general sources and loading of contamination to the Estuary. Stormwater runoff is considered to be a potentially significant pathway for the entry of many contaminants that are currently of great concern, such as PCBs, PAHs, registered pesticides (e.g., diazinon and chlorpyrifos), mercury, copper, and nickel. At present, contaminant inputs from stormwater are relatively poorly characterized.

The San Francisco Estuary Institute (SFEI) has prepared a report (currently in review) estimating the quantity of contaminants entering coastal waters in the San Francisco Bay region from local stormwater runoff. Due to improvements in municipal wastewa-

ter treatment, the masses of some contaminants transported to the Bay from urban and rural landscapes via rivers and drains are now greater than from sewage treatment plants. With these ideas in mind, it seems likely that achieving high water quality in San Francisco Bay may require the treatment of stormwater, or the reduction of these contaminants at their source in the landscape.

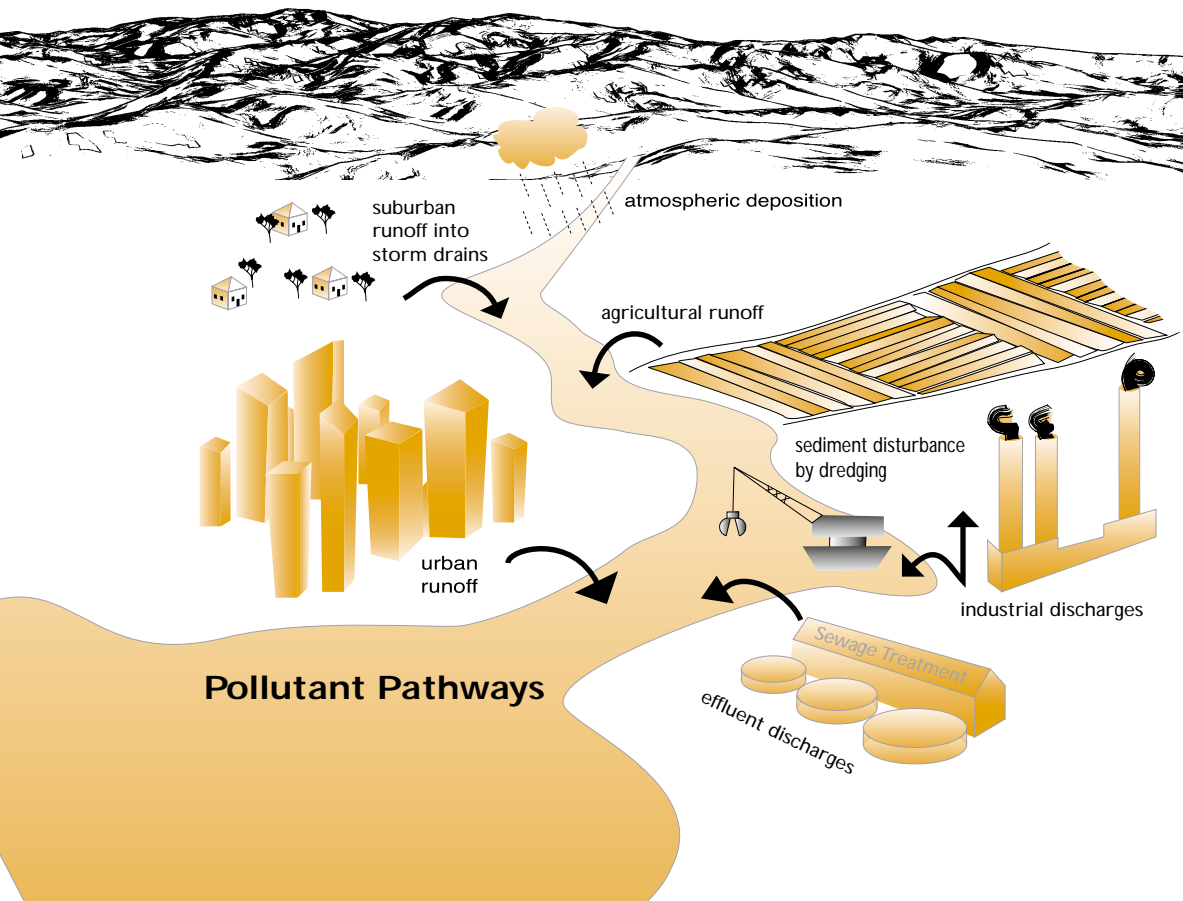
The analysis was conducted using a simplified model for calculating local stormwater contaminant loads. The study didn't take into account well known complex nonlinear processes such as the transfer of rainfall to runoff, of contaminant mobilization during storms, and contaminant fate and transport during stormwater runoff. In spite of simplifications, this desktop study successfully identified data gaps and brought to-

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### ESTUARY MONITORING

- This insert briefs ESTUARY readers on current developments in an ongoing effort to gauge and understand contamination in the Estuary. This effort, funded by government and local industry, is known as the Regional Monitoring Program for Trace Substances (RMP). The RMP began in 1993 and analyzes samples from throughout the Estuary.

- For additional information about the RMP, or to receive the RMP News, contact the San Francisco Estuary Institute (SFEI) at 510•231•9539 or visit the RMP website at <http://www.sfei.org/rmp>.



**Pollutant Pathways**

gether a group of local stormwater experts to develop recommendations for future evaluation of stormwater emissions in the San Francisco Bay region.

A number of high priority contaminants have not been quantified using existing local data (i.e., mercury, selenium, PCB's, PAH's, DDT, chlordane, dieldrin, diazinon, and dioxins). In some cases the data that exist are unreliable, and in other cases no data exist at all. This lack of reliable data for some key contaminants is a critical information gap.

The recommendations from the study reflected limitations in the current estimation methods, and the data quality and quantity for key contaminants. The report recommended the need for improving communication to the public and stormwater managers. There are some key questions that are not yet answered because of a previous lack of funding and coordinated effort. The following tasks were identified during consultation with local stormwater managers and agencies.

**1. Characterize Watersheds.** At a given scale, how many discrete watersheds are there in the Bay Area? How do storm drains influence the definition of such watershed boundaries? What are the key land uses within these boundaries and where are the sources of key contaminants? What is the condition of the banks of the streams and the riparian and in-stream habitats in these watersheds?

**2. Develop Conceptual Models.** What are the most important sources, flows, and processes of a given contaminant in the landscape, and how do these interact with the people and biology of the bay? Conceptual graphic diagrams should be developed that include key sources, flows, and environmental processes of each individual contaminant. These would improve communication to the public and to stormwater managers, help to prioritize data collection, and are necessary prior to the design of data collection and evaluation strategies.

**3. Develop evaluation strategies.** Is the source of a particular contaminant historical or contemporary, is it from a point or is it diffuse in nature, and how is it dominantly

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## UNKNOWN CONTAMINANTS IN SF BAY

by Patricia Chambers

*Thirty-five years ago they were considered unidentified contaminants; today they're commonly known as PCBs and are among the pollutants of greatest concern to scientists monitoring the fate of toxics in the environment. Now, with the help of chromatography and mass spectrometry, "new" contaminants have been detected in San Francisco Bay.*

The tools of identification, mass spectrometry and gas chromatography, have been detecting unknown pollutants in Bay Area water and wildlife for decades. Unfortunately, many of the detected compounds remain unidentified. Recently, one group of "unknown suspects" with bioaccumulative properties was identified as brominated diphenyl ethers (BDEs), a class of compounds widely used in fire retardants.

For some environmental scientists, the discovery of BDEs in water and wildlife samples in the Bay Area is a sign that the need to identify "unknown" contaminants is long overdue. Using BDEs as a model, the Regional Monitoring Program intends to conduct a special study to expand the identification and quantification of organic contaminants for which enough early warning signals have been raised to warrant attention.

Using an existing database of mass spectrometry from Bay samples collected over several decades, the RMP hopes to determine the history of environmental distribution of BDEs in the Bay. "This information, considered with data on toxicology, could then be used in a preliminary assessment of the need to regulate or end their use," cites the draft scope of the project.

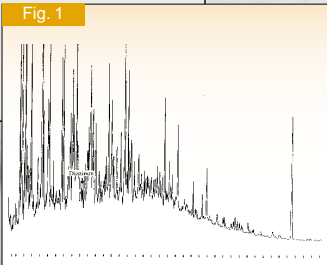
In addition to quantifying BDEs, the study intends to identify other currently unidentified contaminants

### Fingerprinting Unknown Contaminants

*Illustration based on an Interpretation of "Observations of Similarities Between Bird-Watching in Amazonian Peru with a California Checklist" by Robert W. Risebrough.*

**1. Problem**

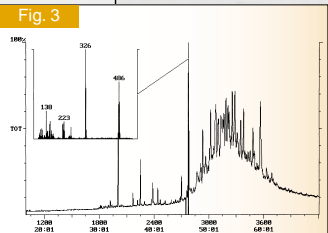
- Hundreds of organic compounds are observed by GC/MS but are not identified
- Electron capture chromatograms alone provide little assistance in compound identification, but identification can be aided by existing databases of mass spectra
- Occasionally current libraries of mass spectra are useful, but most of the compounds in a sample are not represented in the current libraries



**Fig. 1**

**3. Authentic Standard Obtained**

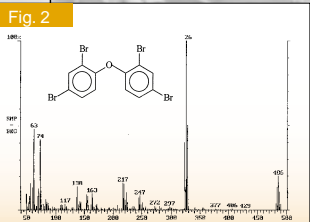
- After a compound is identified by mass spectrometry, an authentic standard is obtained
- The standard is then associated with one of the previously unidentified peaks on the electron capture gas chromatograms



**Fig. 3**

**2. Cataloging**

- A chemist systematically goes through the mass spectral runs, characterizing each spectrum by its principal ions, their intensity, and the relative retention time of the compound
- This data is entered into a data management system
- Comparisons with this database allows the chemist to identify unknown compounds



**Fig. 2**

**4. Retroactive Identification**

- Routine quantitation of previous unknowns would become possible
- Once a new compound represented by a chromatogram peak is quantified, peaks for that compound on previous chromatograms can be compared and quantified

**Fig 1.** chromatogram showing many "Unknowns"  
**Fig 2.** mass spectrum of a BDE and its molecular structure  
**Fig 3.** \*Indicates the retention time of the BDE peak  
 \*Data from a double-crested cormorant egg from San Francisco Bay. J.A. Davis, unpublished data.

in the database of mass spectra and assess if links exist between the newly identified compounds and adverse impacts.

Exactly how BDEs affect ecological and human health is still unknown. "We know they're bioaccumulative. If something bioaccumulates, it usually spells trouble," notes Rainer Hoenicke, director of the Regional Monitoring Program. Hoenicke recalls the brown pelican that was placed on the endangered species list due to the effects of DDT bioaccumulation on eggshell thinning.

"In Europe, many flame retardant compounds are already regulated or banned," observes Hoenicke. Leading European companies in the electric and electronic industry have adopted an official policy of no longer using brominated diphenyl ethers in their products. In Denmark, brominated flame retardants have

been put on the Danish List of Undesirable Substances, and in Austria their production has been banned.

### NEW CONTAMINANTS RECEIVING ATTENTION

While unidentified contaminants haven't received as much attention as the "legacy pollutants" in this country, researchers nationwide are finding the problem worthy of investigation.

Do we really know what the undesirable effects on the ecosystem and human health might be as we manufacture and release new synthetic chemicals? Can we learn from past mistakes and prevent potential pollutants from becoming serious concerns? These are some of the questions now being raised by environmental researchers in the attempt to identify responsible management practices.

"Countless synthetic compounds are completely harmless and break down into simple molecules that occur naturally," says Hoenicke. "Others, however, enter the food web, are not broken down easily, or may have unsuspected side effects that are not immediately recognizable but may be chronic and insidious over the long term—such as the long list of suspected endocrine disruptors," Hoenicke adds.

In an attempt to better manage the chemical industry's testing efforts, 62 of the nation's largest chemical companies have recently volunteered to screen commonly used chemicals for basic toxicity. Despite their wide use, these chemicals have escaped basic testing requirements due to a loophole in the Toxic Substances Control Act of 1976. At present, studies have indicated

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transported? Some contaminants are predominantly associated with sewage disposal or industrial effluents, have a broad spatial distribution, or have natural sources. Some are predominantly transported associated with sediment particles or organic material, and others are in dissolved form. In some cases, land use based models that determine loads may be appropriate. For others, PCBs for example, land use based models are inappropriate due to very localized sources. The evaluation strategies will be pollutant specific.

**4. Establish a regional network of "observation watersheds."** What are the concentrations of pollutants arising from key land uses in the San Francisco Bay Area? Are best management practices designed to reduce contaminants working? These watersheds should be strategically selected to fill data gaps for priority contaminants, and specific land use areas such as farming and open lands for which data are sparse. Observation watersheds could be laboratories for testing the effectiveness of best management practices and determining for which landscapes selected best management practices (BMPs) are likely to be effective.

**5. Extrapolate to other watersheds.** What are the key processes occurring in a San Francisco Bay Area watershed where there is little or no information? What are the likely concentrations of key contaminants in less studied watersheds, and what are the likely impacts? Can we use knowledge of contaminant processes in other Bay Area watersheds to make a hypothesis about an area of interest where there are no data? Extrapolation of existing local data from one watershed to another using reliable conceptual or statistical models would further facilitate interim management, help to determine priority of data collection and preemptive BMPs, provide hypotheses which would improve the design and implementation of data collection, and potentially decrease the cost of data collection while increasing the information gained.

Further information: Jay Davis or Lester McKee at the San Francisco Estuary Institute ([www.sfei.org](http://www.sfei.org)).





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that toxicity data exists for only 10% of the chemicals in use.

The USGS and the EPA are currently in the early stages of investigating unknown or "emerging contaminants" in the waterways of America. What are they discovering so far? A potpourri of synthetic organic compounds downstream from sewage treatment plants—caffeine, animal feed additives, fragrances, sunscreen lotions, hormones, antibiotics and other pharmaceuticals.

Though these emerging contaminants have been detected at very minute levels, the concern arises that a slow but continuous accumulation of such a diverse mix may cause problems whose consequences we're unable to predict.

"Effects on aquatic organisms are particularly worrisome because effects could accumulate so slowly that major change goes undetected until the cumulative level of these effects finally cascades to irreversible change," writes EPA researcher Chris Daughton in a special report on these new pollutants.

According to Daughton and other scientists, "priority pollutants" first identified and regulated thirty years ago, "are only one piece of the larger risk puzzle."

In an attempt to fill in some of the unknown pieces of this puzzle, the Regional Monitoring Program will begin, in December of this year, to identify unknown organic contaminants monitored in SF Bay. The study is expected to generate a final report 18 months later.

"It doesn't make much sense to continue to focus our monitoring efforts on chlorinated hydrocarbons banned 30 years ago," says Hoenicke. "We need to identify compounds that may pose environmental risks in the future. Nobody in the San Francisco Bay Area has systematically related the peaks on the chromatograms with adverse environmental effects. This needs to be done."

What happens when these unknown contaminants are identified and matched up with environmental effects studies? Among the obvious benefits of identification and quantification, is the possibility for a more proactive model for identifying pollutants and anticipating potential problem contaminants.



#### For Further Reading:

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- Raloff, J., More Water Test Positive for Drugs: Science News Online, Apr. 1, 2000.
- Bowman, C. Medicines, Chemicals Taint Water: Contaminants Pass Through Sewage Plants: Sacbee News Search, March 28, 2000.
- Mansur, M., Martellaro, J., Traces of Drugs Found in U.S. Water Sources: Contra Costa Times, May 30, 2000.
- Hall, C.T., Makeup, Medication May Pollute Waterways, SF Gate Science, March 28, 2000.
- USGS, SF Bay Estuary Toxic Contaminants Project, <<http://water.wr.usgs.gov/toxics/intro.html>>
- USGS, National Reconnaissance of Emerging Contaminants in US Streams, <<http://toxics.usgs.gov/regional/contaminants.html>>
- American Chemical Society, Pharmaceuticals and Personal Care Products, March 27, 2000. <<http://www.acs.org>>
- Jobling, S., et al., Widespread Sexual Disruption in Wild Fish, Environmental Science & Technology, Vol. 32, No. 17, 1998.



## SAN FRANCISCO BAY SEAFOOD CONSUMPTION STUDY

The Regional Monitoring Program for Trace Substances (RMP) sponsored the San Francisco Bay Seafood Consumption Study, contracting with the California Department of Health Services and Impact Assessment, Inc. The RMP participants—74 public and private entities that discharge treated wastewater, cooling water, dispose of dredged material, and manage stormwater discharges—recognized that seafood consumption data for the San Francisco Bay Area were insufficient and decided to contribute funding to this study effort.

### WHAT ARE THE GOALS OF THIS STUDY?

- To gather data in order to assess exposures of the fishing population of San Francisco Bay to chemical contaminants from consumption of Bay-caught fish and shellfish
- To identify people who may be highly exposed to chemicals from consuming Bay fish
- To gather information needed to develop educational messages

### WHEN WILL THE STUDY RESULTS BE READY?

Angler interviews at selected fishing sites through out the Bay have been completed. A preliminary draft is currently being revised and is expected to be ready for public distribution by autumn of 2000.

For more information, please contact Rainer Hoenicke via e-mail at [rainer@sfei.org](mailto:rainer@sfei.org)

## AIR MONITORING FOR DIOXINS IN THE SF BAY AREA

Thanks in part to the RMP Air Deposition Pilot Study and the visibility it has received nationwide, EPA Region 9, the Bay Area Air Quality Management District, and the California Air Resources Board are collaborating in using \$100,000 of Persistent Bioaccumulative Toxics Initiative (PBTI) to support ambient air monitoring to measure average air dioxin concentrations in the Bay Area.

This air monitoring effort is part of a multimedia dioxins reduction and outreach strategy for the Bay Area. Key components of the strategy include multimedia monitoring, including fish tissue and sediment sampling and emissions research.

In 1994, the California Office of Health Hazard Assessment issued a public health advisory due to the presence of pollutants, including dioxins, in SF Bay fish. As a result, the Bay has been listed under the Federal Water Pollution Control Act as failing to meet water quality standards for dioxins.

Such listing requires EPA and the California Water Quality Control Board to establish a total maximum daily pollutant load (TMDL) to maintain water quality. This will be one of the first multimedia TMDLs to address a full suite of dioxins and dioxin-like compounds.

The effort represents a model for engaging state and local governments and the public on the emerging dioxin issue and augments the RMP's air monitoring of trace metals, PAHs and PCBs. Dioxin data collection is scheduled to begin in April 2001 and will result in a final report in late 2002. For more information, contact Catherine Brown and Carol Bohnenkamp in the EPA Air Division at 415-744-1298.



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