Executive Summary

Characteristics of Effluents from Large Municipal Wastewater Treatment Facilities in 1993

Effluents from the Hyperion Treatment Plant (HTP; City of Los Angeles), the Joint Water Pollution Control Plant (JWPCP; County Sanitation Districts of Los Angeles County), County Sanitation Districts of Orange County (CSDOC), and Point Loma Wastewater Treatment Plant (PLWTP; San Diego) comprise 90% of municipal wastewater discharged directly to the Southern California Bight. We summarized the concentrations of effluent constituents and estimated the mass emissions for these agencies for 1993, and we present the trends in mass emissions from 1971 through 1993.

In 1993, the four facilities discharged 1,075 million gallons per day (4,069 x 10^6 L/day) of treated effluent into the bight. From 1992 to 1993, the combined daily volume of effluent discharged from the four facilities increased 3% while the proportion of effluent receiving secondary treatment decreased from 46% to 44%. During this period, the concentrations of 58% of the effluent constituents declined, 24% were unchanged, and 18% increased. The combined emissions of suspended solids and oil and grease decreased 5%. The combined emissions of trace metals decreased 13%. The greatest decreases were for lead (47%), chromium (38%), and mercury (33%). The annual mean DDT concentrations were below method detection limits in both years, but concentrations were measurable in some months. The concentrations of PCBs were below detection limits in 1992 and 1993.

From 1971 to 1993, the combined flow from the four facilities increased 16%. The volume of wastewater discharged by CSDOC and PLWTP doubled while the volume decreased 12% at JWPCP and 1% at HTP. During this period, the combined emissions of suspended solids declined 74%, BOD declined 52%, and oil and grease declined 71%. The combined emissions of trace metals declined 95%. Cadmium, chromium, mercury and lead declined 99%; zinc, copper, and nickel declined 90-96%; and arsenic declined 71%. The combined emissions of chlorinated hydrocarbons declined more than 99%. The declines in constituent concentrations and mass emissions were the result of improved primary treatment, increased secondary treatment, and improved source control.

Characteristics of Effluents from Small Municipal Wastewater Treatment Facilities in 1993

The 15 small municipal wastewater facilities discharge effluent to the Southern California Bight through relatively short, shallow-water outfalls and treat the sewage to a greater degree prior to discharge than the large municipal wastewater facilities. We summarized the concentrations of effluent constituents and estimated the mass emissions for the small municipal wastewater facilities for 1993, and we present the trends in mass emissions from 1971 through 1993.

In 1993, the 15 small facilities discharged 135 million gallons per day (mgd) (511 x 10^6 L/day) of treated effluent into the bight. They accounted for 11% of the total volume of municipal wastewater discharged to the bight, but only 2-3% of the suspended solids, oil and grease, and BOD. The small facilities contributed a disproportionately low share of ammonia, arsenic, copper, silver, and DDT, but they contributed most of the inputs of lead and cadmium, and a disproportionately high share of cyanide, chromium, mercury, nickel, and zinc.

The contribution of the small facilities to the combined municipal wastewater discharge of the large and small facilities was about the same from 1989 (10%) to 1993 (11%), and their contribution of suspended solids, BOD, and oil and grease was about 2-3%. However, the cyanide contribution from the small facilities increased from 6% of the total discharged in 1989 to 20% in 1993, and the total metals contribution increased from 7% in 1989 to 14% in 1993. Contributions of cadmium increased from 22% to 67%, chromium from 4% to 18%, and lead from 10% to 72%.

The annual combined volume of effluent discharged from the small facilities nearly doubled from 1971 to 1993. Ammonia increased 129%, but oil and grease decreased 90%, BOD decreased 79%, suspended solids decreased 72%, and cyanide decreased 55%. Estimated mass emissions for other contaminants are not available for 1971.

Extraction of Hydrophobic Organics from Aqueous Samples with 90-MM C-18 Bonded Disks

Technological advances in hardware, software, and computing have reduced the price of sophisticated analytical instruments and automated their use. By contrast, sample extraction methods still require significant amounts of manpower and time. The conventional liquid-liquid extraction (LLE) method widely used for extracting semi- or non-volatile organic pollutants from aqueous samples is labor intensive and requires a large quantity of hazardous organic solvents. The solid phase extraction (SPE) technique requires less organic solvent and less labor than LLE while providing similar extraction efficiencies.

We examined the efficiency and precision of the relatively new 90-mm Empore^{TM} C-18 bonded disks (3M Company, St. Paul, MN) for extracting several groups of hydrophobic organics from municipal wastewater effluents. We focused on polycyclic aromatic hydrocarbons (PAHs), linear alkylbenzenes (LABs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (DDTs). For comparison, LLE was used simultaneously with SPE on some samples.

Extraction of hydrophobic organic compounds from municipal wastewater effluent by the 90-mm Empore^{TM} C-18 bonded disks was as effective as LLE. The condensed packing structure of SPE disks allowed better extraction of hydrophobic organic compounds from municipal wastewater enriched with dissolved organic matter. The large diameter SPE disks were well suited for extracting large sample volumes. SPE was superior to LLE because it used less solvent and labor. The SPE technique will find extensive applications in analyses of aqueous samples with low levels of hydrophobic organic compounds.

Measurements of Linear Alkylbenzenes by GC/MS and GC/FID

Linear alkylbenzenes (LABs) have been used since the early 1960s to synthesize linear alkylbenzenesulfonate (LAS) surfactants, the raw materials used in the manufacture of commercial detergents. LABs eventually replaced the tetraproplene-based alkylbenzenes (TABs) that had been used previously as precursors for detergents. The LASs are synthesized by sulfonation of LABs; incomplete sulfonation introduces LABs into detergents with LASs. LABs were first discovered in coastal sediments of Tokyo Bay and Southern California; the source is the disposal of domestic wastes containing unsulfonated residues of LABs.

There is no standard analytical method available for analysis of LABs, probably because their residues are not considered a major environmental concern. However, LABs are useful as indicators of domestic wastes. The objective of this study was to develop an analytical procedure for analysis of LABs. Since there are only a few individual LAB standards available commercially, we quantified a pure LAB mixture (secondary standard) by individual LAB standards (primary standards). The characterized LAB mixture was used as a calibration standard for measuring LABs in municipal wastewater effluent and marine sediments.

TABs in historically deposited sediments near sewage outfalls can complicate measurements of LABs. Analysis by GC/MS minimized the interference when the appropriate ion fragments were chosen for quantitation. TABs were not detected in effluent from the Point Loma Wastewater Treatment Plant, but they were detected in sediments from the bottom of a core from Santa Monica Bay. With the methods developed here, we can now measure LABs in complex samples and use them as an indicator of domestic waste inputs in the coastal marine environment.

Post-Depositional Distribution of Organic Contaminants Near the Hyperion 7-Mile Outfall in Santa Monica Bay

To evaluate the impact of contaminated sediments, we need to understand the fate of contaminants after deposition, including transport mechanisms within the sediment column and across the sediment/water interface. The City of Los Angeles discharged sewage sludge into Santa Monica Bay through a 7-mile outfall from 1957 through 1987. We investigated the distributions of polychlorinated biphenyls (PCBs), chlorinated pesticides (DDTs), linear alkylbenzenes (LABs), total organic carbon (TOC), and total nitrogen (TN) in sediment cores collected near the 7-mile outfall. We characterized the distribution of organic compounds in the sediment column and reconstruct their depositional histories.

Four sediment cores were collected from the Santa Monica Bay. The profiles of LABs, PCBs, and TOC concentrations in the core nearest the 7-mile outfall corresponded to historical events associated with sludge discharge and the use of LABs and PCBs. Based on this dating, the accumulation rate of carbon from 1957 to 1994 was approximately 50-350 $mg/cm^2/yr$ — two to three orders of magnitude higher than the accumulation rate in the nearby basins. Systematic variation in LABs, PCBs, and TOC was not as pronounced in the three other cores because of low particle deposition rates and large core subsampling intervals.

Detectable amounts of PCBs and DDTs were present in the surface sediments near the 7-mile outfall, even though their discharge was banned in the early 1970s and concentrations in the effluent have been undetectable since 1990. It is likely that historically deposited PCBs and DDTs have been mixed upward in the sediment column by sediment resuspension and reworking processes. Extrapolating the trends of the concentration profiles, PCBs and DDTs compounds will be present in surface sediments in Santa Monica Bay for years to come.

Seafood Consumption Habits of Recreational Anglers in Santa Monica Bay

We investigated the demographic and consumption characteristics of recreational anglers in and around Santa Monica Bay, identified groups with high consumption rates, and identified the species most abundantly caught and consumed. The study area extended from Point Dume to Cabrillo Pier in Los Angeles Harbor. Recreational anglers were interviewed at 11 piers and jetties, five party boat landings, three private-boat launches, and 11 beach and intertidal sites in 1991 and 1992.

The majority of Santa Monica Bay anglers were male (93%), 21-40 years old (54%), white (43%), with an annual household income of $25,000-$50,000 (39%). The next most abundant ethnic groups among the Santa Monica Bay anglers were Hispanics, Asians, and blacks. Hispanics were the most abundant group on piers and jetties, while whites were the most abundant group on party boats and private boats. Most anglers fished throughout the year, but 19% fished only during the summer.

Interviewers identified 67 species of fish, two crustaceans, two mollusks, and one echinoderm that were taken by recreational anglers. The most abundant species caught were chub (=Pacific) mackerel, barred sand bass, kelp bass, white croaker, Pacific barracuda, and Pacific bonito. The species consumed at the highest rates were barred sand bass, kelp bass, rockfish, Pacific barracuda, and California halibut. Thirty-nine percent of the respondents had eaten fish from the study area in the four weeks prior to the interview, and most anglers had caught fish on the day of the interview.

The median consumption rate was 21 g/individual/day; the 90th percentile rate was 107 g/ind/day. The median consumption rate among Santa Monica Bay anglers was 70% of the national median consumption rate (30 g/ind/day). Median consumption rates were highest for blacks (24 g/individual/day) while the 90th percentile rate was highest for Asians (116 g/individual/day). Anglers with annual household incomes less than $5,000 had the highest median consumption rates (32 g/individual/day), but those with incomes greater than $50,000 had the highest 90th percentile rates (129 g/individual/day).

Most of the anglers (77%) were aware of health warnings about consumption of fish from Santa Monica Bay and cited television and newspaper or magazine articles as the major source of information. About half of the anglers that were aware of the warnings had altered their seafood consumption habits.

Sediment Grain Size: Results of an Interlaboratory Intercalibration Experiment

SCCWRP hosted a workshop in 1993 that brought together participants from marine monitoring programs in Southern California to discuss techniques for measuring sediment grain size. It was apparent during the workshop that there were significant differences in instrumentation and sample preparation among the participants. The group decided to conduct an interlaboratory intercalibration experiment that compared pipette/sieve, hydrometer/sieve, and laser techniques.

The sediment intercalibration experiment was designed to determine measurement precision among techniques and laboratories, and the effect of sample digestion on the grain size distributions. The precision within a laboratory was good; the maximum standard deviation for replicates was 2.9% for pipette/sieve, 5.4% for hydrometer/sieve, and 0.5% for laser analysis. The variation between laboratories was also good; the differences between laboratory size class measurements was 2-8% for laser analysis and 6-18% for pipette analysis. Only one laboratory used hydrometers.

Interlaboratory comparisons were complicated by the varying number of size intervals measured by the laboratories, which affected the shape of the size distributions. As the number of intervals increased, the size distributions became better defined and the proportionate error of each size class decreased. Between-laboratory variation based on the percent of gravel, sand, and silt and clay was 6-10% for sandy samples and 16-18% for silty samples. The interlaboratory comparison for laser analysis was based on one-phi intervals, and the results were generally within 2%. The results for sand-sized particles, however, varied by 6-8%.

Sample digestion had little effect on the size distributions. The size distributions for the digested and undigested coarser samples were virtually identical. Digestion had more effect on the sample with the most organic material and generally increased the amount of material in the smallest class by 3-9%. The standard deviations were generally higher for digested samples than for undigested samples.

Overall, laser analysis was preferable to pipette analysis because precision was higher within- and between-laboratories, sample analysis was faster and less labor-intensive, and the method produced a well-defined sediment grain size distribution curve.

A Conceptual Model of Pollutant Flux Through the Coastal Ecosystem off Los Angeles

Contaminants that are released into the marine environment become distributed among the water, sediments, and biota as a result of complex physical, chemical, and biological processes. A conceptual model of the flux of pollutants through the coastal ecosystem off Los Angeles was developed at an interdisciplinary workshop. The model traces the pollutants from their sources through ecosystem processes to their ultimate physical and biological fates.

The framework for the conceptual model was based on vertical stratification of the water column and sediments, which is determined by biological and physical processes. The water column was divided into the sea-surface microlayer, euphotic zone, underlying water, and nepheloid layer. The sediments were divided into surface sediments, bioturbated sediments, and deep sediments. The thickness of these water and sediment layers varies on time scales of days and longer. The compartments containing anthropogenic contaminants are the particulate phase within the water column and sediments; the dissolved phase within the water column and sediment pore water; and the biota in the benthic, demersal, and pelagic food webs.

The conceptual model was divided into three submodels: physical transport, animal-sediment relations, and food web transfers. Physical transport and the physico-chemical transformations of material account for contaminant concentrations in the dissolved and particulate phases in the water column. Animal-sediment relations are the biological and chemical processes within and at the surface of the sediments that account for contaminant concentrations in the sediments and biota. Food web transfers are the processes that account for contaminant concentrations in the biota.

The gaps in our knowledge and information were identified during model development. Some of the biological and physical processes of the conceptual model are poorly understood and are candidates for research. Other aspects of the model are reasonably well understood, but data for Southern California are lacking; these are candidates for data collection and monitoring programs.

Toxicity of Sediments on the Palos Verdes Shelf

The Palos Verdes Shelf has one of the largest municipal wastewater outfall systems in Southern California. Over the past two decades, the biological and chemical conditions on the Palos Verdes Shelf have improved in response to increased and improved treatment of the municipal wastewaters that are discharged to the shelf. However, benthic communities near the outfalls remain altered relative to reference areas. The most obvious biological impacts are changes in the composition and abundance of invertebrate populations living in and on the sediments. This study measured the toxicity of sediments and interstitial water from 12 stations on the Palos Verdes Shelf in the laboratory to amphipods, which live in the sediments, and sea urchins, which live on the sediments.

Acute toxicity (amphipod survival with *Rhepoxynius abronius*) was not observed in the sediment tests. However, chronic toxicity was observed in the sediment tests (sea urchin growth with *Lytechinus pictus*) and in the interstitial water tests (sea urchin fertilization with *Strongylocentrotus purpuratus*) for stations nearest the municipal wastewater outfalls. The spatial pattern of interstitial water toxicity was consistent with the spatial pattern of sediment contamination. Sea urchin growth was also affected by exposure to sediments with low contaminant levels from areas away from the outfalls. Trace metals (Ag, Cd, Cr, Cu, Ni, Pb, Zn) were not accumulated by sea urchins during the experiment, but trace organics (∑DDT, ∑PCB, ∑PAH) were accumulated. DDTs and PCBs were accumulated to a greater extent than PAHs. Statistical analyses identified significant correlations between biological effects and most of the contaminants measured, including hydrogen sulfide.

Structure of the *Amphiodia urtica* Population Near a Municipal Wastewater Outfall off Orange County

The causes of the reduced abundance of the red brittlestar *Amphiodia urtica* in sediments near municipal wastewater outfalls in Southern California has interested SCCWRP scientists for several years. We measured the population structure and recruitment of *A. urtica* over a gradient of sediments affected by the municipal wastewater outfall off Huntington Beach during 1990 and 1991.

The abundance of *A. urtica* was lowest at the station closest to the outfall and increased with increasing distance from the outfall. The trend in abundance over the gradient was non-linear; brittlestar abundance increased from 0 to 4.8 km from the outfall and then decreased to 8.7 km. The proportion of juveniles was highest at the station closest to the outfall and decreased linearly with distance away from the outfall. At the station closest to the outfall, no *A. urtica* were collected with an oral width greater than about 1 mm, about half the size of the largest brittlestars collected at the remaining stations.

In the laboratory, the oral width of *A. urtica* increased an average of 0.03 mm per week. At a growth rate of 0.03 mm per week in the field, a recruiting brittlestar would reach adult size in 58 weeks and would grow to 2.0 mm oral width in 88 weeks. *Amphiodia urtica* may reach maturity in one year and have a life span of two to three years. However, since growth in the field is probably variable and may slow with age, larger *A. urtica* may be more than two to three years old.

Growth of Brittlestars Exposed to Sediments from a Municipal Wastewater Outfall Gradient off San Diego

The red brittlestar, *Amphiodia urtica*, is one of the most abundant sediment-dwelling organisms off Southern California. However, it is rare or absent in near municipal wastewater outfalls, which suggests that the brittlestar is responding to altered sediment quality. The reason for the decline in abundance is unknown. In this study, we measured the growth and reproductive condition of adult *A. urtica* exposed in the laboratory to sediments collected near the municipal wastewater outfall off Point Loma near San Diego.

The survival, growth, and reproductive condition of adult *Amphiodia urtica* were not affected by a 16-week exposure to sediments from the area influenced by the municipal wastewater outfall. This is consistent with the results of previous laboratory experiments with adult *Amphiodia urtica* exposed to sediments collected near other municipal wastewater outfalls off Southern California. During the experiment, there was some mortality in all treatments that may have been due to degradation of sediment quality. Renewing the sediments halfway through the experiment did not prevent this mortality. Growth rates were not constant and most of the growth occurred by the midpoint of the experiment. The decrease

in growth rate during the second half of the experiment may have been an artifact caused by deteriorating sediment quality.

The lack of effects on growth and reproduction of *Amphiodia urtica* suggests that either laboratory exposures do not simulate field conditions, or that something other than toxicity to adults is responsible for the reduced brittlestar abundances near municipal wastewater outfalls. Factors such as predation, sediment resuspension, or reduced juvenile survival may be responsible for reduced brittlestar abundances in moderately contaminated sediments.

Reproduction and Population Dynamics of *Grandidierella japonica* in Upper Newport Bay

Grandidierella japonica is a common gammarid amphipod in sandy intertidal and subtidal sediments of Newport Bay. It has been used to assess the toxicity of marine sediments off Southern California, and to monitor spatial and temporal changes in sediment toxicity in Santa Monica Bay. In this study, we measured the annual cycle of abundance and fecundity of *G. japonica* in Upper Newport Bay and identified relations between these data and characteristics of the physical environment.

The abundance of *G. japonica* was high throughout the summer of 1993, declined in the fall to a low in winter, and recovered by spring of 1994. Gravid females were collected each month during the study indicating that they reproduced throughout the year. However, brood size and size of the offspring decreased during the winter.

The annual cycle of abundance and fecundity in *G. japonica* followed the annual cycle of temperature and photoperiod in Upper Newport Bay. While temperature and photoperiod could directly affect reproduction, they probably also affect the availability of food. Brood size began to decrease before water temperatures started to drop indicating that either photoperiod or food supply could be important. The decrease in brood size and juvenile size during the winter indicated that less energy was expended on reproduction, perhaps because of reduced food availability. A reduction in food supplies coupled with lower water temperature and reduced salinity (due to freshwater runoff from storms) could decrease juvenile production and increase adult and juvenile mortality.

The monthly changes in brood size have important implications for development of life cycle bioassays with *G. japonica*. If temperature and/or photoperiod affect brood size, then higher temperatures and/or longer photoperiods during bioassays should increase the number of offspring obtained from healthy females. A higher number of offspring could increase the sensitivity of the bioassay.