Summation of Findings
Natural Water Quality Committee
2006-2009

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Southern California Coastal Water Research Project

Technical Report 625 - September 2010

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PREFACE

The Committee's Definition of Natural Water Quality

Natural ocean water quality: That water quality (based on selected physical chemical and biological characteristics) that is required to sustain marine ecosystems, and which is without apparent human influence, *i.e.*, an absence of significant amounts of:

a) man-made constituents (e.g., DDT),
b) other chemical (e.g., trace metals), physical (temperature/thermal pollution, sediment burial) and biological (e.g., bacteria) constituents at levels that have been elevated due to man's activities above those resulting from the naturally occurring processes that affect the area in question, and
c) non-indigenous biota (e.g., invasive algal bloom species) that have been introduced either deliberately or accidentally by man.

Natural ocean water would be expected to vary noticeably both from place to place, and from time to time. For example, there are significant variations in the composition of minor constituents of seawater (e.g., nutrients, oxygen, trace metals) with depth in the ocean, as well as with distance from land and even between ocean basins. Furthermore, significant ocean properties such as salinity, temperature, and pH vary appreciably with location, season, and year to year due to natural oceanographic processes.

Even within California's coastal ocean, spatial differences exist as a result of regional differences in solar radiation, precipitation, and naturally occurring fresh water. Coastal seawater will differ measurably in trace element composition as a consequence of local watershed geology. Various places on the California shelf have naturally occurring hydrocarbon and groundwater seepage. In near-shore seawater, temporal and seasonal differences in suspended sediments result from variations in wave action. Naturally occurring marine life itself also alters water quality by various processes. For example, seawater near a sea lion haul-out may be high in fecal bacteria levels.

In addition, there are naturally occurring large-scale ocean cycles that dramatically influence the physical, chemical and biological components that support marine life along the California coast. For example, El Niño and La Niña oceanographic events can significantly alter the surface water temperature along the California coast thus extending or diminishing the range and abundance of cold versus warm water species. Rainfall during such El Niño events can also exert large influences on coastal water quality due to significant flood events that deliver (natural) sediments from undeveloped watersheds. Turbidity events associated with California river systems during large flood events have been observed from space.

However, the reality is that vast areas of the ocean are no longer pristine. Truly natural water quality probably does not now exist in California's coastal ocean, and may be rare throughout the world. For example, plastic debris can be found in remote areas of the ocean thousands of miles from continents, and persistent organic pollutants may be found in marine life inhabiting equally remote regions. Even if anthropogenic land-based waste discharges were to be completely eliminated from a section of coastline, there is no guarantee that natural water quality would be reestablished there. Aerial deposition, pollutants carried by oceanic currents from distant sources, and vessel discharges may influence water quality conditions.

As a result, it is not practical to identify a unique seawater composition as exhibiting *natural water quality*. Nevertheless, the committee believes that it is practical to define an *operational natural water quality for an ASBS*, and that such a definition must satisfy the following criteria:

- it should be possible to define a *reference* area or areas for each ASBS that currently approximate *natural water quality* and that are expected to exhibit the likely natural variability that would be found in that ASBS,
- any detectable human influence on the water quality must not hinder the ability of marine life to respond to natural cycles and processes.

Such criteria will ensure that the beneficial uses identified by the Ocean Plan are protected for future generations.

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EXECUTIVE SUMMARY

In response to the regulatory concerns about Areas of Special Biological Significance (ASBS), the California State Water Resources Control Board (State Water Board) empanelled eight experts from different scientific disciplines to develop a functional definition of "natural water quality." It is the work of this Natural Water Quality Committee (NWQC) that is the focus of this report.

The NWQC had a three-year mission to advise State Water Board staff regarding impacts of Scripps Institution of Oceanography's (SIO) discharges into an adjoining ASBS. While the committee focused on SIO and other relevant data in the SIO vicinity, they also recognized the importance of their work in the context of the greater ASBS, Ocean Plan, and stormwater issues. In response, the NWQC agreed that their recommendations may provide guidance for assessing impacts to water quality in any ASBS in the State. To that end, the NWQC addressed three primary questions:

1) Are water quality objectives and permit limits being met?
2) What are impacts of waste discharges to marine species and communities?
3) What would ambient marine water quality be like without waste discharges?

With regard to question 1, SIO has performed extensive monitoring of its waste seawater discharges, stormwater discharges, and marine receiving water. On the whole, the NWQC agreed that SIO was meeting the water quality objectives and permit limits in their permit. In fact, reasonable potential analysis indicated that many constituents were not a threat to ASBS water quality. The NWQC identified three issues of concern in SIO discharges: a) when constituent concentrations did exceed permit concentration limits, this occurred more frequently in stormwater than seawater discharges; b) ubiquitous constituents, such as dioxin, are not introduced at SIO, but were recorded in SIO seawater intake and discharge waters indicating inputs from external sources; and c) methodological issues raised concerns about potential false positive results for measurements including total residual chlorine and toxicity. Of particular concern was chronic stormwater toxicity as recorded in giant kelp (germination and fertilization) and purple sea urchin (fertilization) bioassays.

With regard to question 2, groundbreaking work has been performed in terms of biological monitoring at southern California ASBS, focusing on the rocky intertidal and subtidal communities. The NWQC felt it was too soon to identify the impacts of waste discharges on biological communities, but preliminary data show promise and warrant further assessment as well as continued monitoring for biological status and impacts.

With regard to question 3, the NWQC felt that it was practical to approximate what ambient marine water quality would be like in the absence of (or minimally influenced by) waste discharges by comparing water quality parameters in ASBS to water quality parameters at reference sites. In fact, based on recent studies at targeted reference sites in southern California, average water quality in ASBS was very similar to reference sites. Poor water quality in southern California ASBS was observed, but typically limited to a

small number of discharges and/or constituents. The NWQC observed that, at times, concentrations of certain constituents at reference sites were higher than concentrations in Table B water quality objectives listed in the California Ocean Plan.

The NWQC identified four recommendations that regulatory agencies should consider. First, further work needs to occur for quantifying natural variability. While the reference site approach was successfully applied in southern California, insufficient information was collected to have certainty in assigning natural water quality ranges throughout the State (i.e., reference sites need to be sampled in central and northern California). Second, effort should be spent identifying the most appropriate monitoring indicators. Not all indicators need to be measured at all times and adaptive strategies that trigger more (or less) monitoring are a practical and cost-efficient mechanism for ASBS stakeholders. The NWQC emphasized that biological monitoring is considered to be an important addition to monitoring of individual chemical constituents, in order to assess impacts on receiving biological populations and communities. Third, the NWQC recommended that regulators revise Table C of the California Ocean Plan to reflect nearshore, near-surface post-storm reference site water quality. The existing Table C was developed over 30 years ago from open ocean sites, using now out-of-date laboratory methods, for use with plume modeling data to calculate effluent limits at offshore submarine outfalls. Fourth, the NWQC urged regulatory agencies to identify strategies to account for shifting baselines. One flaw of the reference site approach is that, as a practical matter, natural water quality is defined as “the best of what’s left.” As future development occurs, this may lead to a steady decline in overall water quality.

BACKGROUND

The coastal environment of California is an important ecological and economic resource. It is home to diverse and abundant marine life and has some of the richest habitats on earth including forests of the giant kelp, *Macrocystis pyrifera.* The State Water Resources Control Board (State Water Board) has created 34 Areas of Biological Significance (ASBS) in order to preserve and protect these especially valuable biological communities.

California's coasts are also a repository for waste discharges from the State's ever-increasing population. Treated municipal and industrial wastewaters, urban runoff, and power generating station discharges all represent a number of threats to marine life from human activities. As a result, the State Water Board, in the California Ocean Plan, has prohibited the discharge of waste to ASBS, with certain exceptions. All ASBS are State Water Quality Protection Areas that require special protection under state law.

Despite the prohibition against waste discharges to ASBS, a recent survey has observed approximately 1,658 outfalls to these marine water quality protected areas (SCCWRP 2003). As a result, the State Water Board has initiated regulatory actions, establishing special protections through the Ocean Plan's exception process. The intent of these regulatory actions is to achieve natural water quality of the ocean receiving water in the ASBS. One of the first regulatory actions was taken in San Diego at the ASBS adjacent to the Scripps Institution of Oceanography (SIO). The SIO, which owns and maintains the discharge outfalls to the La Jolla ASBS, was issued an Ocean Plan exception and a National Pollutant Discharge Elimination System (NPDES) Permit. As part of this regulatory action, State Water Board staff was asked to create a panel of experts from different scientific disciplines to help develop a functional definition of "natural water quality." It is the work of the Natural Water Quality Committee (NWQC) that is the focus of this report.

The NWQC includes eight members (Table 1). The NWQC has the mission to evaluate the SIO monitoring data and to advise the San Diego Regional Water Quality Control Board (RWQCB) regarding impacts of SIO's discharges to ASBS. While the committee focused on SIO and other relevant La Jolla data, they also recognized the importance of their work in the context of the greater ASBS, Ocean Plan, and stormwater issues. In response, the NWQC agreed that their work may provide guidance for assessing impacts to water quality in any ASBS in the State. To that end, the NWQC is addressing three primary questions:

1) Are water quality objectives and permit limits being met?
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The NWQC created a three-year timeline to achieve milestones that help to answer these three questions. The first question, which is focused almost entirely on the SIO permit and site specific issues, was addressed in the first year. The second question, which has both site specific and regional spatial scale issues, was addressed in the second year. The increase in spatial scale is necessary because biological impacts at the SIO ASBS can only be interpreted in response to species and communities outside of the SIO ASBS. The third question, which is almost entirely exclusive of the SIO ASBS, was addressed in the third year. The increase in spatial scale for question three is a reflection of the need to select appropriate regional or statewide reference conditions, which by definition excludes areas with discharges.

Table 1. Members of the Natural Water Quality Committee.

Members	Affiliation
Andrew Dickson	Scripps Institution of Oceanography
Rich Gossett	California State University Long Beach
Dominic Gregorio	State Water Resources Control Board
Burt Jones	University of Southern California
Steve Murray	California State University Fullerton
Bruce Posthumus	San Diego Regional Water Quality Control Board
Kenneth Schiff	Southern California Coastal Water Research Project

DEFINITION OF NATURAL WATER QUALITY

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SPECIFIC FINIDINGS

Q1: Are water quality objectives and permit limits being met?

The NWQC met 20 times between October 2005 and August 2010. At several of those meetings the monitoring and conditions specific to the SIO NPDES permit were considered. Both effluent and receiving waters had been sampled by SIO since 2005 and the following general conclusions were drawn:

1) waste seawater system effluent measurements had identified some constituents of concern such as copper, suspended solids, settleable solids, acute toxicity (topsmelt), chronic toxicity (kelp) and dioxins. Notably, copper concentrations in waste seawater have generally declined over the permit period;
2) runoff generally had more constituents with concentrations greater than those specified in Ocean Plan Tables A and B compared with the waste seawater system. These constituents included copper, turbidity, oil and grease, settleable solids, PAHs, indicator bacteria, chronic toxicity (urchins, topsmelt and kelp) and dioxins;
3) chromium, lead, and zinc in the runoff were also elevated above the Ocean Plan Table B six month median levels on more than one occasion during wet weather;
4) receiving water in the ASBS was elevated above water quality objectives on at least one occasion for chronic toxicity (kelp) and/or dioxin during wet and dry weather sampling;
5) dioxins appear to be ubiquitous in the environment and are likely not a direct result of SIO activities (see Attachment B);
6) one sampling period coincided with a red tide event (June 2005) that may have had a confounding or synergistic effect with regard to the toxicity tests;

7) water quality measurements also revealed some technical shortcomings of EPA and State approved test methods, such as elevated total residual chlorine measurements in seawater matrix (see Attachment C), and acute toxicity interpretations; and
8) most other Table B constituents were not detected, or were present in small amounts that represented no reasonable potential (RP) to cause impacts based on RP analysis using State Water Board developed software.

A receiving water study for bacterial contamination was conducted by SIO examining more than 10 sites plus outfall discharges at multiple time intervals during dry weather. The results indicated that bacterial concentrations were routinely low and below water quality standards. In general, the NWQC determined that bacterial monitoring was an inappropriate indicator for assessing potential impacts to aquatic life for this ASBS than other water quality measures. Given that SIO and the County Health Department routinely monitors this beach for the protection of human health, the NWQC recommended against future non-routine bacterial monitoring and that efforts should be reinvested into other monitoring elements.

Finally, SIO had developed a dilution and dispersion computer model for their discharges into the nearshore coastal zone of the ASBS. The model had been previously calibrated and validated at the mouth of the Santa Margarita River that discharges into the littoral zone near Oceanside. Based on model runs at La Jolla conducted by SIO, results indicated that dilution of SIO discharges could be very large due to turbulent mixing and advection by wave action and longshore currents. Model output illustrated dilution factors ranging three orders of magnitude. The NWQC agreed that a 7:1 dilution factor was appropriate. While the model input parameters (i.e., tide, wave height and direction, etc.) were some of the best available, there was some concern that little model validation at the La Jolla ASBS had been conducted.

Q2: What are impacts of waste discharges to marine species and communities?

Quantifying the chemical components of an effluent only partially assesses the potential of waste discharge to ASBS. Ultimately, the biological integrity of marine communities residing in ASBS also need to be assessed to determine if the human influence on water quality is hindering the ability of marine life to respond to natural cycles and processes. To this end, several ASBS stakeholders and the State Water Board utilized scientists at the University of California Santa Cruz to compile data from existing intertidal biological monitoring programs from ASBS statewide. The goal was to assess if historical data were sufficient to make statements about the integrity of ASBS intertidal marine communities (Raimondi 2009).

Raimondi (2009) evaluated the historical data from 12 ASBS intertidal monitoring programs and summarized five features that hindered an independent, integrated assessment of biological impacts in ASBS. First, the methods used in the monitoring programs differed dramatically, ranging from careful designs developed from specific questions to almost naturalist perspectives of sites. Second, all of the monitoring programs were done either by the dischargers or their consultants. Third, the basis for determining if a discharge is causing an impact differed dramatically among monitoring programs. Fourth, and most important, most monitoring programs were not clear about the basis for determining impacts. One strong recommendation for an integrated assessment was that there should be a general basis for determining impact that is consistently applied. There should also be a general assessment design that would yield information sufficient to produce a rigorous determination of impact. Finally, the reporting requirements for assessments should be standardized including data and metadata reporting, transfer, and storage.

In part to overcome the limitations addressed by Raimondi (2009), a regional ASBS biological monitoring program was implemented in southern California. Twenty one rocky intertidal sites were quantitatively sampled for habitat quality, invertebrate and algal abundance, and composition by Raimondi's UC Santa Cruz Coastal Biodiversity research team. The monitoring question focused on differences between reference and ASBS discharge sites. Preliminary results indicated that: 1) there were no significant differences in macro-invertebrate or algal species richness based on geographic grouping or type of site (discharge vs. reference); 2) there were large geographic differences in algal and sessile invertebrate species composition, likely reflecting natural biogeography, but no statistically significant differences between reference sites and ASBS discharge sites; and 3) there were large geographic differences in mobile invertebrate species composition, once again reflecting natural biogeography, but no statistically significant differences between reference sites and ASBS discharge sites. However, the answers differed when sessile and mobile species were jointly considered. Not only were geographic differences observed, but differences were also observed at two discharge sites relative to reference condition (one of which was in La Jolla). While more work is needed to investigate the relationship of these differences to water quality impacts, it demonstrates that biological data can be used, and the NWQC suggested that there is sufficient data to warrant further investigation.

Because of the value of biological information, ASBS stakeholders in southern California supported monitoring of 70 subtidal rocky reef sites. Quantitative sampling for habitat quality, vertebrate, invertebrate and algal abundance, and composition was coordinated by Dr. Dan Pondella at Occidental College with collaborators at UC Santa Barbara and San Diego State University. Similar to the intertidal monitoring, the monitoring question focused on differences between reference and ASBS discharge sites. Data analysis for the subtidal rocky reefs has not progressed as far as the intertidal monitoring. Initial data examination has identified clear differences in community composition based on habitat characteristics (i.e., rock relief), but large differences in biological community characteristics between ASBS and reference sites have yet to be determined.

One last piece of biological monitoring was conducted by SIO, who performed a bioaccumulation study in receiving waters. This monitoring, which used both mussels and sand crabs, occurred in the vicinity of localized reference and ASBS discharge sites. The results indicated that:

1) most organic constituents were present at statistically nonsignificant levels relative to a reference site during the study period;
2) certain pollutants were elevated in transplanted mussels near the SIO pier (Cr, Ni, Fe, and Mn) and at the south end of the adjoining La Jolla ASBS (As) where the City of San Diego storm outfalls are located relative to other sites within the study area;
3) certain pollutants were elevated in transplanted mussels near the SIO pier (Cr and Ni) relative to historical statewide Mussel Watch results; and
4) large relative variability in tissue concentrations from sand crabs due to age/reproductive status precluded an assessment of spatial scale gradients and an evaluation of potential effects.

Q3: What would ambient marine water quality be like without waste discharges?

The State Water Board funded a pilot project during the winter of 2007-08 to evaluate selection of, and sampling methods in, potential reference sites. Proposed reference sampling was determined in collaboration with stakeholders and included surf zone samples at the mouth of a watershed with limited anthropogenic influences, defined as a minimum of 95% open space. The pilot project included a minimal number of sample sites in southern, central and northern California. The pilot project found no detectable levels of the synthetic pollutants DDT and PCB in the samples, and mean values for ammonia and metals were below Ocean Plan six-month medians objectives. The only trace metals with maximum values slightly above the six-month medians were chromium and lead. Notably, mean concentrations of PAHs were approximately an order of magnitude greater than the Table B 30-day average objective.

The State Water Board funded a statewide monitoring program during the winter of 2008-09 specifically to assess the water quality in ASBS near and far from regulated discharge sites. More than 100 chemical constituents and toxicity were measured from 62 sites using a probabilistic study design; roughly half of sites were sampled in the ocean directly in front of a regulated discharge and the other half were located in the ocean >500 m from a regulated discharge. It is important to point out that the sample sites >500 m from direct discharges may have been influenced by other watershed drainages into or adjacent to the ASBS, and therefore may represent background, but not necessarily natural, conditions. Samples at each site were collected <24 hr prior to rainfall and again <24 hr following rainfall. At least one ocean receiving water site was sampled within most mainland ASBS in California.

The statewide survey illustrated generally good chemical water quality in mainland ASBS sites (Table 2). None of the constituents measured exceeded the instantaneous maximum objective listed in the California Ocean Plan (SWRCB 2003). Seven out of 15 constituents did not exceed the Ocean Plan's most stringent objectives (six-month median or 30-day average, depending on the specific constituent) including strictly anthropogenic chemicals such as DDTs or PCBs. Of the eight parameters that did exceed the most stringent Ocean Plan objectives, six (arsenic, cadmium, copper, lead, nickel and zinc) exceeded the objective for relatively small (<15%) portions of ASBS shoreline. Many of these constituents are common in urban stormwater, but have natural sources as well.

Two constituents exceeded Ocean Plan objectives over relatively large proportions of ASBS shoreline including chromium (50%) and polycyclic aromatic hydrocarbons (PAH; 87%) (Table 2). Sources of chromium and PAH can be either natural or anthropogenic. The extent of Ocean Plan exceedence for chromium and PAH was similar near and far from discharge sites following storm events. Similarly, the extent to which chromium and PAH exceeded Ocean Plan standards was similar between pre-storm and post-storm conditions near discharges. It is important to note that the chromium standard is based on the more toxic form, hexavalent chromium, but that total chromium was analyzed for this study. The lack of excessive chemical contamination in ASBS receiving waters was supported by infrequent (<5% of ASBS shoreline) chronic toxicity to a California endemic species (the purple sea urchin, *Strongylocentrotus purpuratus*).

Table 2. Percent of ASBS shoreline with constituent concentrations that exceeded State Water Board Ocean Plan objectives following storm events.

	Ocean Plan Objective	% Shoreline Greater Than OP Objective		
		All ASBS	<500 m from Discharge	>500 m from Discharge
Ammonia-N[1]	0.6 mg/L	--	--	--
Arsenic[1]	8 ug/L	1.6	2.7	--
Cadmium[1]	1 ug/L	2.1	3.6	--
Chromium[1]	2 ug/L	50	61	35
Copper[1]	3 ug/L	6.9	4.8	9.8
Lead[1]	2 ug/L	4.8	--	11.5
Nickel[1]	5 ug/L	15	24	3
Silver[1]	0.7 ug/L	--	--	--
Zinc[1]	20 ug/L	3.8	6.5	--
HCH-lindanes[2]	8.0 ng/L	--	--	--
Chlordane[2]	0.023 ng/L	--	--	--
DDTs[2]	0.17 ng/L	--	--	--
Dieldrin[2]	0.04 ng/L	--	--	--
PAHs[2]	8.8 ng/L	87	85	89
PCBs[2]	0.019 ng/L	--	--	--

[1] 6-month median

[2] 30-day average

While the statewide survey provided valuable estimates of overall chemical condition in ASBS, it lacked an assessment of natural water quality. To address this data gap, the regulated dischargers and Regional Water Quality Control Boards (RWQCBs) initiated a collaborative ASBS regional monitoring program in the Southern California Bight (Bight'08). One goal of Bight'08 was to identify and sample reference sites to determine natural water quality. The dischargers and regulators agreed on reference site criteria that tried to simulate ASBS discharge sites with respect to most factors except one; lack of anthropogenic sources (e.g., <10% watershed development in the contributing catchment). A second goal was to compare these reference site concentrations to concentrations measured near ASBS discharges. Similar to the statewide survey, Bight'08 focused on wet weather conditions.

Regional reference condition was typified by low concentrations and lack of toxicity (Table 3). However, the range of reference site concentrations exceeded Ocean Plan objectives for 8 out of 10 parameters, including chromium and PAH. Intriguingly, the ASBS discharge sites behaved very similarly to reference sites. In fact, average chromium and PAH concentrations at ASBS discharge sites following storm events were not significantly different from average reference site concentrations for all constituents. While there were individual discharges and constituents that were dissimilar from reference concentrations, these appeared to be isolated events rather than the typical condition at southern California ASBS.

For comparing discharge sites to a measure of natural water quality, a threshold level equivalent to the 85^{th} percentile of the reference site post-storm concentrations was used. This 85^{th} percentile level was chosen to represent natural water quality to eliminate uncertainty associated with outliers, thereby being protective of water quality. Exceedence of natural water quality conditions was relatively infrequent at ASBS discharge sites; general constituents, nutrients, and trace metals were the most frequent groups of constituents to exceed natural water quality conditions identified in this study.

Table 3. Minimum, maximum, median, and mean (±95% confidence interval; CI) of post-storm constituent concentrations at reference sites in the Southern California Bight during 2009.

Constituent	Reference Site Concentrations							Ocean Plan Objective
	Units	%ND	Min	Median	Max	Mean	(±)95% CI	
TSS	mg/L	8	Nd	7.7	1692	140	171	-
Ammonia-N	mg/L	64	Nd	nd	0.05	0.01	0.01	0.6
Nitrate-N	mg/L	24	Nd	0.04	0.10	0.05	0.01	-
Nitrite-N	mg/L	88	Nd	nd	0.010	0.002	0.002	-
Total-P	mg/L	44	nd	0.05	0.59	0.08	0.05	-
Total-N	mg/L	65	nd	nd	7.0	0.9	0.7	-
Arsenic	ug/L	0	0.5	1.5	5.0	1.8	0.4	8
Cadmium	ug/L	4	nd	1.5	4.5	1.8	0.5	1
Chromium	ug/L	0	0.2	0.5	16.9	1.9	1.4	2
Copper	ug/L	0	0.05	0.5	6.1	1.1	0.6	3
Lead	ug/L	0	0.1	0.6	9.5	2.4	1.2	2
Nickel	ug/L	0	0.2	0.5	19	2.0	1.8	5
Silver	ug/L	76	nd	nd	6.0	0.7	0.8	0.7
Zinc	ug/L	24	nd	3.3	29	5.2	2.6	20
Total PAH	ng/L	16	nd	6.5	318	22	24	8.8

nd = not detected

95% CI = confidence interval

- = no objectives exist for this parameter

THE NEED FOR ADDITIONAL GUIDANCE

Consistent with the NWQC's desire to provide guidance to the State Water Board not only for SIO, but for all ASBS, the Committee delved into several issues in more detail. These included:

1) Interactions with the Coastal Ocean Observing System,
2) ASBS grant monitoring,
3) Suggested goals and approaches for protection of ASBS,
4) TCDD measurement, and
5) Total residual chlorine measurements.

The findings and recommendations for each of these issues are summarized below. Further details are captured in a series of white papers presented in Attachments A through C of this report.

Interactions with the Coastal Ocean Observing System

One concern related to the management and regulation of a specific ASBS is that the conditions of the ambient receiving waters may be influenced as much, or more, by discharges outside of the ASBS. These external ASBS discharges, if large enough, may overwhelm discharges inside the ASBS.

For the southern California region, the Southern California Coastal Ocean Observing System (SCCOOS) maintains an active set of ocean observing and modeling resources. One of SCCOOS comprehensive resources is the surface current mapping network that spans the entire California coastline (in collaboration with the Central California Coastal Ocean Observing System [CENCOOS]). Surface current mapping provides the capability of producing connectivity matrices and probability maps illustrating the likely regions of influence from discharges outside of the ASBS boundaries. A demonstration project was conducted to evaluate the probability of Los Penasquitos Lagoon discharge interacting with the San Diego-Scripps ASBS.

Los Penasquitos Lagoon is located approximately 7 km north of the San Diego-Scripps ASBS. Depending on the direction, speed and duration of coastal currents, it is possible that outflow from the Los Penasquitos Lagoon enters the region of that the San Diego-Scripps ASBS and its neighboring La Jolla ASBS. A statistical analysis using hourly data from surface currents measured by SCCOOS was used to estimate the percentage of time the Los Penasquitos outflow would enter the ASBS. Based on a complete year of data, it appeared that water from the lagoon entered the ASBS 10 to 25% of the time. Two years of precipitation data (62 days with measurable rainfall) were examined for wet weather contributions to the ASBS from Los Penasquitos Lagoon and its watershed. Within three days following each rain event, SCCOOS scientists predicted the wet weather plume would enter the ASBS 5 to 10% of the time.

This preliminary analysis indicated that it is possible for distant, non-ASBS regulated discharges to be transported into ASBS jurisdiction. While significant additional work needs to be completed to assess the extent of this problem, SCCOOS and CeNCOOS desire to continue their relationship with the state and regulated parties. Additional work could include: a) dilution and degradation of discharge constituents in addition to transport; b) targeted time scales to evaluate critical conditions; c) producing probability maps for other ASBS of concern; and d) interaction with other water quality issues such as harmful algal blooms.

ASBS Grant Monitoring

The voters of California have approved bond measures for Proposition 84 that provides funding to assist responsible parties to comply with the discharges prohibition into ASBS. The State Water Board is planning on distributing approximately $32,000,000 from Proposition 84 specifically to remove waste from discharges that drain directly to ASBS. Approximately $1,000,000 from Proposition 84 may be set aside to provide for coordinated effectiveness monitoring for the suite of projects recommended for funding. As a result, the NWQC was encouraged by State Water Board staff to address monitoring issues related to Proposition 84 grant funded projects. The NWQC addressed this issue in three steps: 1) determine the success (or failure) of monitoring programs associated with other grant programs; 2) assess what factors would be important for grant funded monitoring for ASBS; and 3) provide recommendations to the Proposition 84 Task Force, the body that evaluates Proposition 84 grant proposals, including monitoring.

Ultimately, the NWQC made three recommendations to the Proposition 84 Task Force to enhance the grant program monitoring components (*see NWQC White Paper*, Attachment A). These recommendations included: 1) a cohesive, question-driven monitoring program; 2) a unified monitoring design that ensures comparability in sampling, data analysis, and information management; and 3) a single person or group responsible for coordinating, collating, assessing and reporting on the Proposition 84 monitoring effort.

Suggested Goals and Approaches for Protection of ASBS

Recommendation

The State Water Board should consider a broader goal for protection of Areas of Special Biological Significance (ASBS) and different approaches for achieving that goal.

Background

The Ocean Plan establishes requirements that apply to discharges of waste to California ocean waters in general, with the intent of protecting the beneficial uses of those waters. The Ocean Plan also establishes a higher level of protection for ASBS by prohibiting discharges of waste to ASBS (with certain exceptions). The Ocean Plan specifies that waste discharges are to be located a sufficient distance from ASBS "to assure maintenance of natural water quality conditions" in ASBS.

Although "maintenance of natural water quality conditions" in ASBS would be desirable, such a goal may not always be realistic. Considering the definition of "natural water quality" (see *NWQC Definition* above), and considering the nature, extent, and magnitude of anthropogenic influences on California coastal waters (and their ecosystems) and on the watersheds and stream systems that drain to the coast, it seems unlikely that "natural water quality conditions" (or, for that matter, natural biological conditions) are or can be consistently achieved and maintained in all ASBS at all times. For example, substances such as mercury or dioxins are ubiquitous in the ocean at low levels and are not always from natural sources.

Although "maintenance of natural water quality conditions" in ASBS is probably not always an achievable goal, a goal to "minimize anthropogenic influence on water quality" in ASBS is realistic and provides a direction forward for continuing improvement.

Existing and Suggested Approaches

Completely stopping all existing waste discharges directly into ASBS would result in improved, more nearly natural, less anthropogenically influenced water quality conditions in ASBS. In some cases (e.g., certain smaller storm drainages and nonpoint runoff sources), such improvements may be insignificant yet the cost of terminating such discharges may be substantial. In fact, stopping and re-routing storm runoff potentially harms the ecosystem by altering the hydrologic cycle.

The State Water Board approach to regulating direct discharges to ASBS has been the inclusion of prohibitions and special conditions in Ocean Plan exceptions, referred to as "Special Protections," with permits implementing those conditions. Those conditions generally require the elimination of dry weather runoff, ensure that wet weather runoff and marine laboratory waste seawater does not alter natural water quality in the ASBS, and that adequate monitoring be conducted to determine if natural water quality and the marine life beneficial use is protected. Compliance for storm water runoff has generally been determined or proposed to be determined in receiving water.

However, stopping discharges directly into ASBS cannot ensure absolute protection of water quality in ASBS, if only because other discharges (including distant sources and aerial deposition) can influence water quality conditions in ASBS. The degree to which a discharge might influence an ASBS is a function of a number of factors, including but not limited to the proximity of the discharge to the ASBS and the characteristics of the discharge. Consequently, larger, "more polluted" discharges outside of or further away from an ASBS could have a greater influence on that ASBS than smaller, "less polluted" discharges directly into or closer to the same ASBS. Although the Ocean Plan calls for discharge locations to be kept away from ASBS, in many cases the locations where anthropogenically influenced land runoff (e.g., via streams and rivers) enters the ocean cannot readily be changed. Even if such locations could be changed, doing so could have significant adverse effects on beneficial uses of waters outside of ASBS (e.g., in estuaries).

In order to avoid significant expenditures that do little to protect ASBS, an assessment of existing and potential anthropogenic influences on each ASBS should be conducted. Those influences should be ranked as posing a high, medium, or low threat to the ASBS. Priority should be given to reducing and minimizing the anthropogenic influences that pose greater threats, regardless of their proximity to the ASBS.

In order to provide a higher level of protection to ASBS, a higher level of protection should be provided to California coastal waters as a whole. ASBS exist within the larger context of California coastal waters as a whole. ASBS are not separate from or isolated from those waters. Water, biota, and substances move between ASBS and surrounding coastal waters. Therefore, providing a higher level of protection to California coastal waters as a whole would also provide a higher level of protection to ASBS. This might be accomplished using various combinations of requirements, including requirements that would limit the total mass of specified pollutants that can be discharged into California coastal waters or segments thereof.

Dioxins

Dioxins (also known as TCDD) are toxic compounds that have both anthropogenic (e.g., combustion byproducts) and natural (e.g., forest fires) sources. Atmospheric deposition is a major source of dioxin in soil and water and national background soil levels are 1 to 6 ng/kg TEQ (TCDD Equivalents) in rural areas and 7 to 20 ng/kg TEQ in urban areas. In the California Ocean Plan, the objective for TCDD Equivalents addresses the human health beneficial use via consumption of seafood. The objective for TCDD Equivalents is 0.0039 picograms per liter, the lowest objective for any of the constituents in the Ocean Plan.

The Scripps Institute of Oceanography (SIO) ASBS Monitoring Program measures dioxins in their effluent and receiving water during dry weather and wet weather conditions. SIO Dioxin TEQ results were consistently above permit limits, but all of the sample concentrations (with one exception) were below the range detected in stormwater from the San Francisco Bay and the Santa Monica Bay areas. Since Scripps has no source of dioxin in their seawater system, the NWQC assumes that the TCDD in SIO discharges is most likely from regional sources such as stormwater runoff and/or aerial fallout (*See Attachment B*). This is supported by the results of their monitoring data where seawater discharge concentrations and congener profiles were similar to the concentrations measured in ambient seawater samples. Stormwater discharge samples routinely had greater TCDD concentrations than seawater discharge results. In particular, stormwater discharge (Outfall 002) sampled on 11/30/2007 had noticeably greater concentrations and a different congener profile than previous samples. This sample was collected just after a major forest fire in the San Diego area upland from SIO.

Total Residual Chlorine

Many NDPES Permit holders discharging estuarine or marine water into the coastal waters of California are required to monitor their effluent and/or receiving water for Total Residual Chlorine (TRC), even if they are not chlorinating their effluent. Chlorine is toxic to marine aquatic life and therefore Table B of the California Ocean Plan (SWRCB, 2005) lists 6-month median, daily maximum, and instantaneous maximum of 2, 8, and 60 µg/L, respectively. SIO does not add chlorine to its seawater or stormwater discharges.

At present, it is difficult to accurately quantify the amounts of residual or free chlorine in marine systems due to matrix interference introduced by naturally occurring salts of iodide and bromide. Two matrix-associated interferences were noted by the NWQC (*See Attachment C*). First, free chlorine reacts almost instantaneously with salt in seawater, so that any free chlorine has essentially reacted before the sampler can cap the sample bottle. Second, interferences by other oxidizing compounds such as bromide and iodide will cross-react with method reagents leading to a potential false negative. In the case of SIO, nearly every sample of seawater discharge exceeded permit limits. Since SIO does not chlorinate its discharge, the NWQC assumes that the permit limit exceedences for TRC are false positives. In addition, the NWQC recommends that the State Water Board either change the required method for TRC and/or allow for altering the interpretation of results (i.e., total residual oxidants).

CONCLUSIONS

- **On the whole, the Scripps Institution of Oceanography is meeting effluent limitations and water quality objectives in their permit.**

  The SIO consistently meets effluent limitations listed in their NPDES permit for the vast majority of monitored constituents and concentrations of constituents in excess of Ocean Plan objectives in receiving water was rare. In fact, the discharge monitoring requirements were eased in 2008 when reasonable potential analysis indicated that many constituents were unlikely to be a threat to ASBS receiving waters. However, not all constituents were within regulatory limits at all times. The NWQC identified three issues that regulators should be aware of. The first issue was the difference between seawater discharges (from once through use in aquaria and holding tanks) and stormwater discharges (from surface runoff generated both on- and off-campus). Stormwater discharges from SIO exceeded permit limits more frequently than seawater discharges, and often for known stormwater constituents such as copper and chronic toxicity (kelp, urchins). The second issue was ubiquitous constituents. Perhaps the best example of this issue was the frequent exceedence of permit limits for dioxins, which SIO does not add to its process stream, but is found routinely in receiving waters and stormwater discharges from southern California. The third issue was methodology. Two examples of methodology arose in our survey of SIO results including total residual chlorine (TRC) and toxicity testing. The NWQC observed many examples of permit limit exceedences for TRC, but after further investigation, identified that the method currently approved by the NPDES permit is prone to false positives in a seawater matrix. The NWQ prepared a white paper in this report that provides regulators and other ASBS stakeholders potential options for resolving this issue. The NWQC also observed several examples of acute toxicity, particularly for fish. While certain toxicity results were statistically significant, other toxicity exceedences did not have a significantly different response relative to controls (i.e., <5% effect). This is a known issue to regulators, but makes it difficult to identify when true toxic events occur that regulators should care about.

- **It is too soon to tell if there are impacts of waste discharge to marine species and communities**

  Examining biological impacts in ASBS is a worthwhile endeavor and SIO, as well as the other ASBS stakeholders in southern California, should be commended for undertaking biological monitoring. Collaboratively, these 14 entities have partnered with universities to conduct intensive biological surveys of communities in rocky intertidal and rocky subtidal habitats. While the final data analysis has not been completed, it is clear from preliminary results that a regional reference condition approach is necessary to define "natural" in ASBS. The NWQC agreed that comparing an ASBS to a minimal number of isolated reference sites is inadequate to describe these complex and dynamic habitats. The NWQC also recognizes that, while the current surveys are focused on spatial comparisons (many sites), examining temporal trends (individual sites over time) is necessary to assess how sites respond to both natural and anthropogenic stresses. Attributing causes and sources of impact to biological systems is not an easy task, particularly in intertidal and rocky subtidal reef systems where natural perturbations (waves, tidal exposure, etc.) and human-induced (fishing, trampling, kelp harvesting, etc.) stressors can be significant influences in addition to water quality. Yet, these are areas of special *biological* significance and minimum monitoring requirements could be used to trigger more detailed exploration when impacts are observed. One avenue currently being explored, and one that the NWQC endorses, is investing effort into identifying key indicator species, species groups, or assessment indices that can provide simple and effective answers to questions about water quality (and perhaps other) impacts.

- **It is practical to quantitatively define ambient water quality without (or with minimal) waste discharges.**

The definition of natural water quality supplied by the NWQC is an achievable goal. The collaborative southern California monitoring program (Bight'08) is currently the best illustration of this success. Bight'08 proxied natural water quality by examining the chemical and toxicological properties of ambient ocean water at reference sites. Results indicated no detectable trace synthetic organic compounds (i.e., DDT, PCB) or toxicity, and generally low concentrations of naturally occurring constituents (trace metals, PAH). With one minor exception, all of the constituents had median values below the strictest Ocean Plan objectives. However, there were times at reference stations when maximum concentrations of several naturally occurring constituents exceeded current Ocean Plan Table B thresholds. More importantly, values for many constituents in the reference data set exceeded Table C ("Background Seawater Concentrations") in the Ocean Plan. One positive outcome, and with few exceptions, most southern California ASBS discharge sites and monitored parameters behaved similarly to reference site conditions. While the reference site criteria used in Bight'08 could be altered, or alternative criteria could be developed, the fact that regulated parties and regulatory agencies could come together and agree on currently existing reference sites is a powerful statement.

It is important to note that the NWQC did discuss other approaches that could work, including tracers of waste discharge or reference condition normalizers, which could also be further explored. In addition, the reference area approach may have its limitations as in the case of widespread anthropogenic influences (i.e., PAHs, TCDDs) or the situation where distant sources impinge on reference site water quality. (i.e., transport of large stormwater plumes)

RECOMMENDATIONS

- **Further work needs to occur for quantitatively defining natural water quality.**

  While the definition of natural water quality supplied by the NWQC is an achievable goal, quantifying natural water quality is not concluded. It is important that the true range of natural variability be encompassed. Having too broad a reference site characterization will provide insufficient protection for ASBS. Having too narrow a reference site characterization will promote unrealistic or unachievable goals for regulated entities. The work initiated by Bight'08 represents the first such attempt in California to determine natural water quality characteristics in the nearshore following storm events. The NWQC felt that although the Bight'08 program provided sufficient information for the SWRCB to move forward, prudent management would also seek additional information. For example, Bight'08 quantified intra-annual (storm-to-storm) variability, but lacked inter-annual or even decadal scale variability known to produce natural alterations in ocean water composition and biological communities. Similarly, additional reference sites in central and northern California would be a sensible next step. Finally, the NWQC recognized that, for some instances, the reference site approach can be problematic. For example, the reference site approach may be limited in the case of widespread anthropogenic influence (i.e., PAHs, TCDDs) or the situation where distant sources impinge on reference site water quality. (i.e., transport of large stormwater plumes from outside the ASBS). All of these causes of natural variability, and impacts from unanticipated anthropogenic contributions, should be investigated before final natural water quality ranges can be ascertained. In addition, further collaboration between the ocean observing systems, regulators, and responsible parties can assist with identifying contributions from distant sources.

- **Effort should be spent identifying the most appropriate monitoring indicators**

  The NWQC strongly recommends that biological monitoring occur in addition to the required chemical or toxicological monitoring. Biological monitoring provides an integrative measure over time that chemical and toxicological measures do not. Biological monitoring also measures the effects of unmeasured constituents and/or cumulative effects of constituents. Regardless of chemical, toxicological or biological measures, the most informative indicators within each class should be selected. Minimizing the indicator list to the most informative measures will reduce per-event costs, enabling more locations or time periods to be monitored. If this approach is taken, the NWQC strongly urges that adaptive monitoring triggers be established *apriori* that can be used to increase (or decrease) monitoring effort should problems (or lack of problems) be identified. If the chemical constituent list is reduced, the utility of integrative measures such as toxicity also become more valuable. The NWQC suggests that multiple species and endpoints be considered for toxicity testing and, if sufficient toxicity is observed, dischargers be required to conduct toxicity identification evaluations (TIEs) to determine the problematic constituents.

- **Improvements should be made to the Ocean Plan**

  Table C in the California Ocean Plan (Seawater Background Concentrations) was first adopted in 1983 and based on relatively sparse data over 30 years old collected far from shore. Perhaps this was appropriate since the information was intended to be used with plume modeling data to calculate effluent limits for relatively consistent discharges of effluents from publicly owned treatment works (POTW) through offshore submarine outfalls. The current emphasis on stormwater runoff is incongruous with this application. Stormwater is highly unpredictable, where flows and concentrations can change by orders of magnitude over short time scales (sometimes within minutes) and is discharged at the surface. Table C values should be altered to reflect current needs, including values for nearshore, post-storm water quality.

  Other changes to the Ocean Plan that should be considered include addressing: a) new or revised methods for measuring total residual chlorine , b) improving trace metal sample extraction to eliminate interferences with seawater (such as using EPA Method 1640), and revise the acute toxicity equation in cases when survival in undiluted effluent is greater than control survival.

- **Regulatory agencies need to identify strategies to account for shifting baselines**

  Based largely on verbal accounts, it is suspected that increases in human population and development since the mid-1970's have resulted in degradation of water quality and biological communities. This may or may not be true, but scant little data is available to inform us. If true, then the water quality conditions at reference sites we identify today may be significantly different than they were 35 years ago when the ASBS were first designated. The NWQC is concerned that operational definitions of natural water quality years from now might be significantly different from today's conditions. In order to account for the potential shifting baseline where natural water quality is, as a practical matter, defined as the best of what's left, the NWQC recommends that the State Water Board identify how they plan to deal with future increases in human population and development and the potential for water quality degradation in and near ASBS and present day reference sites.

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ATTACHMENT A

Natural Water Quality Committee Initial Recommendations for Monitoring ASBS Implementation Projects

The Natural Water Quality Committee (NWQC) was formed at the direction of the State Water Resources Control Board (SWRCB, resolution 2004-052, Section 3.a.). The charge of the NWQC was to define natural water quality based on a review of monitoring data and to advise the Water Boards regarding the attainment of natural water quality relative to waste discharges in Areas of Special Biological Significance (ASBS). Some of these recommendations have focused on monitoring as one approach to assessing the attainment of natural water quality.

The voters of California have approved Bond measures for Proposition 84 that provides funding to assist responsible parties to comply with the discharge prohibition into ASBS. The SWRCB is planning on distributing approximately $32,000,000 from Proposition 84 specifically to remove waste from discharges to ASBS. Approximately $1,000,000 from Proposition 84 may be set aside to provide for coordinated effectiveness monitoring for the suite of projects recommended for funding. As a result, the NWQC was encouraged by State Water Board staff to address monitoring issues related to Proposition 84 funded projects. The NWQC addressed this issue in three steps: 1) determine the success (or failure) of monitoring programs associated with other grant programs; 2) assess what factors would be important for grant funded monitoring for ASBS; and 3) provide recommendations to the Proposition 84 Task Force, the body that evaluates Proposition 84 Grant proposals, including monitoring.

After discussions with RWQCB and SWRCB staff, task force members from other grant programs (i.e., Proposition 50), and the grantees themselves, the NWQC came to three conclusions regarding the successes and failures of previous grant programs. Frequently in the past, grant programs were incapable of assessing the success/failure of their program for either removal of pollutants or improvements to receiving waters. Inadequate guidance was provided to the grantees on the specific goals of the monitoring programs employed, especially to those grantees that lacked capabilities and experience with monitoring. Specifically, grantees rarely had a vision of the State's monitoring objectives such as cumulative pollutant removal. Even for those grantees with experience and capability, the timeline of the grant programs (typically two to three years) were inconsistent with adequately quantifying the goal of measuring pollutant reductions.

The NWQC discussed several important elements to enhance the Proposition 84 grant program monitoring components. These elements included: 1) a cohesive, question-driven monitoring program; 2) a unified monitoring design that ensures comparability in sampling, data analysis, and information management; and 3) a person or group responsible for coordinating, collating, assessing and reporting on the Proposition 84 monitoring effort. A clear statement of objectives needs to be composed so as to provide a vision for the Proposition 84 monitoring program. Monitoring experts universally agree that this is best achieved through the use of a well-formed and unambiguous monitoring question, much akin to a hypothesis for testing. This question should be crafted with care and agreed to by the Proposition 84 Task Force or other governing body.

A centralized monitoring design should be created with sufficient scientific rigor that the monitoring question can be answered with a specified level of confidence. It is impossible to describe what this design may look like until the monitoring question is created, but there are certain elements that must be included. The first element should be some level of standardized sampling. Standardized sampling approaches ensure representativeness and reduce bias in data collection. For example, flow weighted composite sampling during wet weather runoff can produce very different results than grab sampling, even during the same storm event at the same site. Comparing data from different sampling approaches is inappropriate and could lead to faulty conclusions. Similarly, standardized quality assurance should be achieved through the laboratory analysis portion of a large-scale monitoring program. Comparability is paramount and several large-scale monitoring programs use performance-based quality assurance guidelines to ensure comparability for laboratory analysis. Finally, a centralized data management system is necessary for collating the reams of information generated by multiple monitoring programs. Grantees will focus on the monitoring data associated with the management actions specific to their project and these individual data sets will be, for the most part, relatively small and easy to manage. Combining data sets from numerous individual grant projects *post hoc*, however, would be daunting to impossible and could cost hundreds of thousands of dollars unless a well-conceived information management system is implemented before data collection. Thankfully, several systems exist within the state that could be used as a vehicle for data management.

Finally, a person or group must be tasked from the beginning with the responsibility for coordinating the Proposition 84 ASBS monitoring program. Deriving monitoring questions, ensuring comparability and quality assurance/training cannot be done as a sideline to one's daily activities. It is a full-time job. The larger the program, the more likely it will require additional personnel to accomplish all of the integration necessary to address the monitoring question. It will be this entity that shall be responsible for communicating with grantees on monitoring and eventually for writing a summary report of the program's success at reducing pollutant loads and/or concentrations.

The NWQC had four recommendations to the ASBS Task Force on a structure for the statewide grant monitoring program to achieve the three goals of monitoring question(s), comparability, and organization. The first recommendation stated the singular monitoring question of utmost importance, "How much pollutant (i.e., in kg) was removed as a result of the grant-funded BMP?" Several additional questions are feasible and perhaps warranted, but this single question must be answered. The second recommendation addressed who should coordinate the Proposition 84 monitoring. The NWQC felt that the SWRCB should coordinate this monitoring, perhaps through one of their statewide programs such as the Surface Water Ambient Monitoring Program (SWAMP). Third, the NWQC felt that at least 10% of each grant should be allocated to monitoring activities. Each grantee can conduct this coordinated monitoring themselves or, if they prefer, return 10% of the grant back to the SWRCB to arrange for the coordinator to conduct this monitoring. Regardless of who implements the monitoring, the SWRCB must use the $1 million set aside from Proposition 84 to conduct the coordination, quality assurance, and data management to ensure comparability. Finally, the NWQC recommended that grantees be allowed a 1-year, no-cost extension to conduct post-construction monitoring. The extra time will provide invaluable monitoring information, particularly in the drier parts of the state where rainfall is limited to a short window of time during the year.

ATTACHMENT B

Dioxin White Paper
State Water Resource Control Board- Natural Water Quality Committee
August 2010

Dioxin is a general term for a group of chemicals that are highly persistent in the environment. Dioxins and a related group, the furans, are among the most toxic pollutants known to science. The US Environmental Protection Agency, in a draft report in September 1994, describes dioxin as a serious public health threat. According to their report, there does not appear to be a "safe" level of exposure to dioxin, and dioxins have been found in the general US population "at or near levels associated with adverse health effects." The most toxic dioxin compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).[1]

TCDD is the prototype for a class of halogenated aromatic hydrocarbons, which appear to have a common mechanism of action and to produce similar effects, although they differ in potency. TCDD achieved notoriety in the 1970's when it was discovered to be a contaminant in the herbicide Agent Orange and was shown to produce birth defects in rodents. It continues to generate concern because of its widespread distribution as an environmental contaminant, its persistence within the food chain, and its toxic potency.[2] TCDD is the most toxic polychlorinated dibenzo-p-dioxin (PCDD) to fish.[3]

Dioxins originate as combustion byproducts, from impurities during the manufacture of wood preservatives and herbicides, and as a byproduct of wood pulp bleaching. New research suggests that forest fires are also a major source of dioxins.[4] The estimated distribution of Dioxin sources for 2004 were; backyard trash burning (25%), societal, e.g. residential wood combustion, gasoline and diesel use, etc (5%), industrial (15%), and natural forest fires (54%).[4] Atmospheric deposition is a major source of dioxin in soil and water and US background soil levels are 1-6 ng/kg TEQ (TCDD Equivalents) in rural areas and 7-20 ng/kg TEQ in urban areas. San Francisco Bay Area stormwater contains 0.2 – 65 pg/L and Santa Monica Bay Watershed concentrations range from 1 – 53 pg/L.

<u>TCDD Equivalents</u>
In the California Ocean Plan TCDD Equivalents are defined as “the sum of the concentrations of chlorinated dibenzodioxins (2,3,7,8-CDDs) and chlorinated dibenzofurans (2,3,7,8-CDFs) multiplied by their respective toxicity factors…” The objective for TCDD Equivalents is for the human health beneficial use, through consumption of seafood, based on the fact that it is a carcinogen. The objective for TCDD Equivalents is 0.0039 picograms per liter, the lowest objective for any of the constituents in the Ocean Plan.

The California Toxics Rule has an objective for TCDD (but not equivalents), set at 0.0013 picograms per liter.

Recently the San Francisco Regional Board used a different definition for TCDD Equivalents based on new information: TCDD Equivalents means the sum of the concentrations of chlorinated dibenzodioxins and chlorinated dibenzofurans multiplied by their Toxicity Equivalency Factor (TEF) and their Bioaccumulation Equivalency Factor (BEF).[5]

$(TEC)_{TCDD}$= The sum of $(C)_x(TEF)_x(BEF)_x$

Where $(TEC)_{TCDD}$ = TCDD Equivalents concentration in effluent

$(C)_x$ = concentration of total congener x in effluent

$(TEF)_x$ =TCDD toxicity equivalency factor for congener x

$(BEF)_x$ = TCDD bioaccumulation equivalency factor for congener x

Toxicity Equivalency Factor and Bioaccumulative Equivalency Factors are listed in the table below.

The Scripps Institute of Oceanography (SIO) ASBS Monitoring Program measures dioxins in their effluent and receiving water during dry weather and wet weather conditions. A synopsis of the TEQ (pg/L) results are presented in the following table.

Outfall 001- Seawater Discharge		Outfall 002- Stormwater Discharge Wet Weather		Receiving Water- Dry Weather	
Sample Date	**TEQ (pg/L)**	**Sample Date**	**TEQ (pg/L)**	**Sample Date**	**TEQ (pg/L)**
9/30/2005	0.00587	2/27/2006	0.105		
10/13/2005	0.00876	11/30/2007	2.12		
11/16/2005	0.00930	1/5/2008	0.663		
8/21/2006	0.00222	2/6/2009	0.524	8/21/2006	0.00134
5/14/2007	0.00172	3/7/2010	0.601	5/14/2007	0.00227
10/14/2008	0.00703			10/14/2008	0.00251
7/28/2009	0.00355			7/28/2009	0.00331

SIO Dioxin TEQ results were almost all (with one exception) below the range detected in both the San Francisco Bay Area Stormwater and the Santa Monica Watershed. Since Scripps has no likely source of dioxin in their water system, the source of these compounds is most likely from particles present in the local coastal zone from runoff and/or aerial fallout which is supported by the following points:

- The results for the stormwater discharge (Outfall 002) are 2 orders of magnitude higher than the seawater
- The results for the seawater discharge (Outfall 001) are similar to the receiving water

- The result for the stormwater discharge (Outfall 002) sampled on 11/30/2007 are higher than the other sample dates. This sample was collected following a large forest fire upland from SIO. Moreover, the dioxin composition (not shown here) of this sample is also significantly different from all the other samples collected.

Toxicity Equivalent Factors by dioxin congener. OCDD was the primary congener found in SIO discharge.

Congener	Toxicity Equivalency Factor (TEF)	Bioaccumulation Equivalency Factors (BEF)
2,3,7,8-TCDD	1.0	1.0
1,2,3,7,8-Pe-CDD	0.5	0.9
1,2,3,4,7,8-HxCDD	0.1	0.3
1,2,3.6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.05
OCDD	0.0003	0.01
2,3,7,8-TCDF	0.1	0.8
1,2,3,7,8-PeCDF	0.03	0.2
2,3,4,7,8-PeCDF	0.3	1.6
1,2,3,4,7,8-HxCDF	0.1	0.08
1,2,3,6,7,8-HxCDF	0.1	0.2
2,3,4,6,7,8-HxCDF	0.1	0.7
1,2,3,7,8,9-HxCDF	0.1	0.6
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.4
OCDF	0.0003	0.02

[1] Web Resources for Environmental Justice Activists, website http://www.ejnet.org/dioxin/

[2] Stanford University Dept of Molecular Pharmacology website http://www.stanford.edu/group/whitlock/dioxin.html

[3] Walker and Peterson, Chapter 11 Aquatic Toxicity of Dioxins and related Chemicals, Dioxins and Health, Schecter 1994 http://books.google.com/books?hl=en&lr=&id=I7JoGkn3DI8C&oi=fnd&pg=PA347&dq=%22Walker%22+%22Aquatic+toxicity+of+dioxins+and+related+chemicals%22+&ots=nsMtfzop_d&sig=kTX2dSxIP0Jqe_qpn4_nw45_X7I#v=onepage&q=%22Walker%22%

20%22Aquatic%20toxicity%20of%20dioxins%20and%20related%20chemicals%22&f=false

[4] DioxinFacts.Org web site. Forest Fires: A Major Source of Dioxins. http://www.dioxinfacts.org/sources_trends/forest_fires2.html

[5] *San Francisco RWQCB 2009. NPDES NO. CA0037681 ORDER NO. R2-2009-0062*

ATTACHMENT C

Issues Related To Measuring Residual Chlorine
In Non-chlorinated Estuarine and Marine Water
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Background

Many NDPES Permit holders discharging estuarine or marine water into the coastal waters of California are required to monitor their effluent and/or receiving water for Residual Chlorine, even if they are not chlorinating their effluent. Chlorine is toxic to marine aquatic life and therefore Table B of the California Ocean Plan (SWRCB, 2005) lists 6-month median, daily maximum, and instantaneous maximum of 2, 8, and 60 µg/L, respectively. The USEPA 304(a) water quality criteria for chlorine are in terms of Total Residual Chlorine (TRC) in fresh water, which includes free chlorine and chloramines, and in seawater are for chlorine-produced oxidants (CPO), which includes the oxidative products of chlorine (hypobromous acid (HOBr), hypobromous ion (OBr-), and bromamines). The one hour average criteria is 19 µg/L for TRC and 13 µg/L for CPO, and the four day average criteria is 11 µg/L for TRC and 7.5 µg/L for CPO. However, the analytical methods typically used for Residual Chlorine (Standard Methods for the Examination of Water and Wastewater- 19th Edition, 1995) have detection limits around 10 µg/L or higher which exceeds the 6-month median and daily maximum values.

Sources of Chlorine

There are many potential sources of chlorine. Chlorine is used as a disinfectant in sewage wastewater treatment and in marine laboratories. Chlorination is also performed at power generating facilities using once-through cooling, and may be present in power plant discharges. Chlorine and other oxidants are being considered for treatment of ballast water in oceangoing vessels prior to discharge. There are various technologies for dechlorination, including the application of sulfite or sulfite compounds. Other discharges of free chlorine include may be due to the drainage of swimming pools, illicit laundry discharges, the use of chlorine bleach as a cleaning agent in waterfront activities, and industrial spills.

Chlorine and Chlorination Byproducts in Seawater

The issue of monitoring the release of chlorine into the marine environment is of great importance. While chloride ions are the most abundant ions in seawater, free chlorine is highly reactive and not a natural component in marine water. The formation of potentially dangerous byproducts as a result of chlorination can lead to negative consequences for ecologically important areas along our coast. Once introduced into a solution, whether seawater or freshwater, chlorine is generally present as either hypochlorous acid or hypochlorite which are both regarded as free chlorine. These compounds quickly react with the surrounding constituents, such as bromide, iodide, ammonia, and manganese through oxidation reactions to form a variety of products. Exposure to sunlight or any agitation of the solution increases the rates of these reactions. Any free chlorine that is left over is labeled as residual chlorine and quantified.

However, at present it is difficult to accurately quantify the amounts of residual chlorine in marine waters due to the complex nature of seawater. Unfortunately, the higher salt content makes the methodologies currently being used to quantify residual chlorine in fresh water unreliable for use with seawater samples (Johnson, 1977).

Seawater naturally contains approximately 67ppm of bromide and 64ppb of iodide, which are both quickly oxidized to bromine and iodine when they come into contact with chlorine. Seawater also contains variable amounts of ammonia, which in the presence of chlorine can lead to the formation of haloamines (e.g., chloramines and bromamine). As a result of these reactions, the free chlorine is reduced to chloride, while the bromine and iodine form hypobromous and hypoiodic acids, both potent oxidants, and the ammonia is oxidized to bromamine or chloramine, which are toxic to aquatic life. The rates of these reactions are quite rapid, to the point that they are almost instantaneous. For example, the oxidation of bromide by chlorine can use up one-half of the free chlorine in less than one second. These newly formed oxidants will continue to react with nearby compounds and eventually be reduced back to bromide, iodide, and ammonia.

Trihalomethanes (THM) are also formed as a result of chlorination in the presence of organic matter. The formation of these compounds is a function of precursor concentration, contact time, chlorine dose and pH. Typically, only four THM compounds are normally found and analyzed in the lab. They include chloroform (CHCl3), bromodichloromethane (CHBrCl2), dibromochloromethane (CHBr2Cl), and bromoform (CHBr3). Polyhalomethanes are naturally found in low concentrations in marine waters. Some species of marine algae are sources of polyhalomethanes including but not limited to bromoform (CHBr3), brodichlormethane (dichlorobromomethane, CHBrCl2), chloroform (trichloromethane, CHCl3), and dibromochloromethane (CHBr2Cl). Rock pool and shallow subtidal seaweeds in the genera *Laminaria, Fucus, Pelvetia, Gigartina, Polysiphonia, Enteromorpha, Chaetomorpha, Ulva, and Cladophora,* have been specifically identified as trihalomethane producers (Nightingale et al. 1995; Moore, 2003). Productive coastal waters are enriched with bromoform due in part to their production by marine macroalgae and possibly by marine microbes (Manley, Goodwin and North 1992). Seaweeds appear to be the dominant natural oceanic source of bromoform and methylene bromide. The marine coastal zone is a major source of bromoform produced by cyanobacteria (blue green algae), and other microalgae including phytoplankton and benthic forms. A major environmental source of chloromethane is also the decomposition of seaweeds. Salt marsh flowering plants also produce methyl halides (Murray et al. 2002). Toxicological studies suggest that chloroform is a potential human carcinogen (Standard Methods 19th Ed. 2005). The Ocean Plan defines halomethanes as the sum of bromoform, bromomethane (methyl bromide) and chloromethane (methyl chloride). The Ocean Plan's 30-day average water quality objective is 130 µg /l for total trihalomethanes (TTHM) and is based on protection of human health; the 2005 Ocean Plan does not provide an objective for the protection of marine aquatic life.

Measuring Chlorine in Seawater

It is because chloride, bromide and iodide are present in such high amounts that the determination of residual chlorine in seawater is so problematic (Johnson, 1977). By the time the analysis of seawater is initiated, the majority of the free chlorine will have reacted with something and been reduced to harmless chloride ions. Unfortunately, the methods used to measure the concentration of residual chlorine are not specific to that element. Rather, they measure the total concentration of oxidizing agents in the solution. Consequently, the oxidized bromine, iodine, and bromamine compounds would register as residual chlorine, even though they are something completely different (Eaton, 1995), and a more appropriate measurement may be for chlorine-produced oxidants. For this reason, it is important to be cautious when reviewing residual chlorine data for seawater samples. According to the 19th Edition of Standard Methods for the Examination of Water and Wastewater, as well as a paper published in the journal Chesapeake Science by Dr. J. Donald Johnson, iodide based residual chlorine methods, including colorimetric, amperometric monitors, and amperometric titrations, are inappropriate for the quantification of residual chlorine in estuarine and marine samples. Amperometric and continuous monitoring systems have been used successfully for chlorine-produced oxidants but do require additional expertise and care when making these measurements.

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