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Date: October 19, 2009 **To**: Phil Lauri, P.E

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Subject: Stormwater and Marine Biotoxin Monitoring – Final Report

Table of Contents

SECTION 1 - EXECUTIVE SUMMARY	1
SECTION 2 - INTRODUCTION	7
2.1 Project Information	7
2.1.1 IDENTIFICATION OF IMPORTANT BIOTOXINS	7
SECTION 3 - STORMWATER MONITORING	11
3.1 Introduction	11
3.1.1 STORM DEFINITION	11
3.1.2 SCHEMATIC OF EL SEGUNDO PILOT PLANT AND SAMPLING POINTS	13
3.1.3 REGULATORY ASPECTS	14
3.1.4 MONITORING APPROACH	15
3.2 BASELINE COMPARISON OF WATER QUALITY AT INTAKE SITE	16
3.3 EL SEGUNDO DESALINATION PILOT PLANT STORMWATER MONITORING	25
3.3.1 RAW WATER QUALITY	25
3.3.2 Granular Media and Arkal Disc Filtrates	28
3.3.3 PALL MICROFILTRATION 1 AND 2	29
3.3.4 REVERSE OSMOSIS 1 AND 2	30
3.3.5 SECOND PASS REVERSE OSMOSIS	32
3.4 FINDINGS/RECOMMENDATIONS	35
SECTION 4 - MARINE BIOTOXIN MONITORING	36
4.1 Introduction	36
4.1.1 Procedure Summary	36
4.2 WATER QUALITY AND NUTRIENT MONITORING RESULTS	37
4.3 CHARACTERIZATION OF PHYTOPLANKTON TAXONOMY	39
4.4 EL SEGUNDO DESALINATION PILOT PLANT RESULTS	40
4.5 BENCH-SCALE REVERSE OSMOSIS RESULTS	45
4.6 FINDINGS/RECOMMENDATIONS	49
REFERENCES	51
APPENDIX A – STORMWATER AND MARINE BIOTOXIN MONITORING PROJECT	
ASSESSMENT PLAN (PAP)	A-1
APPENDIX B - STORMWATER AND MARINE BIOTOXIN MONITORING QUALITY	
ASSURANCE AND QUALITY CONTROL PLAN	B-1
APPENDIX C - STORMWATER MONITORING EXPERIMENTAL PLAN	C-1
APPENDIX D - MARINE BIOTOXIN MONITORING EXPERIMENTAL PLAN	D-1
APPENDIX E – SUBMITTED MANUSCRIPT TO WATER RESEARCH	_
AFFENDIA E - SUDMITTED MANUSCRIPT TO WATER RESEARCH	<u>E-1</u>
APPENDIX F - ENTEROLERT DISCUSSION	F-1

APPENDIX G - TIME SERIES PLOTS OF STORM AND NON-STORM EVENTS	G-1
APPENDIX H - CONSTITUENTS WITH MCLS AND NLS DURING STORM EVENTS	H-1
APPENDIX I – SUMMARY STATISTICS OF ALL DETECTED CONSTITUENTS FOR STO)RM
EVENTS	I-1
list of Tobles	
List of Tables	
Table 1. Summary of detected constituents during storm events	3
Table 2. Marine biotoxin species of concern for southern California	
Table 3. Ballona Creek (above Sawtelle Blvd) storm events summary for 2003-2008	
Table 4. Process train pathogen removal/inactivation for SWTR compliance (WBMWD, 2006)	
Table 5. Possible MF/RO process train to meet maximum pathogen removal/inactivation requirer (WBMWD, 2006)	
Table 6. Possible UF/RO process train to meet maximum pathogen removal/inactivation requiren	
(WBMWD, 2006)(WBMWD, 2006)	
Table 7. Summary of detected raw water quality parameters during storm events	
Table 8. Microbiological quality of raw water intake and Pall microfiltrate	
Table 9. Summary statistics for raw water intake and reverse osmosis (RO) 1 and 2 permeate	
Table 10. Summary of detected finished water quality parameters during storm events	
Table 11. Biotoxin analysis summary statistics for El Segundo desalination pilot plant intakea	
Table 12. Salt Rejections for each Biotoxin Challenge Test RO Membrane	46
Figure 1. Ballona Creek Watershed with rain gauges, WBMWD intakes and buoy mooring location (map adapted from Google Earth 2009)	12
Figure 2. Schematic of the El Segundo Pilot Desalination Facility treatment process	
Figure 3. Probability plot of storm and baseline total coliform data Figure 4. Probability plot of storm and baseline fecal coliform data	
Figure 5. Comparison of total coliform and E. coli concentrations	
Figure 6. Various E. coli detection methods for comparison and validation of improved methods di	
storms 3 and 4	_
Figure 7. Probability plot of storm and baseline E. coli data	
Figure 8. Probability plot of composite bacteriological data	
Figure 9. Probability plot of turbidity data	
Figure 10. Probability plot of fluorescence data	
Figure 11. Comparison of boron data from two laboratories for storm and non-storm events	
Figure 12. Routine WBMWD monitoring during storm and non-storm events ^a	
Figure 13. Surface water quality data from Redondo Beach buoy, March-May 2009	
Figure 14. Surface water quality data from El Segundo buoy, May-August 2009	
Figure 15. Bottom water quality data from El Segundo buoy, May-June 2009	
Figure 16. Domoic acid concentrations of El Segundo desalination pilot plant intake and RO perm	
Biosense ELISA method: a) particulate and b) dissolved	
Figure 17. Domoic acid concentrations of El Segundo desalination pilot plant intake and RO perm. Marcury Science El ISA Method: a) Particulate and b) Dissolved	
Mercury Science ELISA Method: a) Particulate and b) DissolvedFigure 18. Dissolved saxitoxin concentration of El Segundo desalination pilot plant intake and RO	
permeate	
Figure 19. Specific flux for bench scale experiments	
Figure 20. Bench-scale reverse osmosis performance – brevetoxin	
Figure 21. Bench-scale reverse osmosis performance – domic acid	
Figure 22. Bench-scale reverse osmosis performance – saxitoxin	

Section 1 – Executive Summary

1.1 Background

This report provides the objectives, results and recommendations from stormwater and marine biotoxin monitoring conducted by West Basin Municipal Water District (WBMWD) as part of a program partially funded by the California Department of Water Resources under Proposition 50. Prior to this specific monitoring program, WBMWD developed integrated membrane seawater desalination systems, established a pilot desalination facility at El Segundo and conducted preliminary research, all for the purpose of investigating the operational and water quality implications of these treatment processes. Monitoring activities for this monitoring program focused on the effects of stormwater inputs and harmful algal blooms (HABs) on the desalination process at the El Segundo pilot plant.

1.2 Project Goals

The goals for the project are summarized as follows:

- Identify baseline water quality data via on-going water quality monitoring and data collection proximal to ocean intakes at El Segundo and Redondo Beach
- Characterize phytoplankton taxonomy present in raw water samples from the El Segundo ocean intake
- Monitor key water quality parameters during stormwater runoff events, with regular sampling and analysis of raw ocean intake water and locations throughout the desalination treatment train at El Segundo.
- Identify water quality constituents that are impacted by storm events
- Sample and analyze raw and RO permeate water from the El Segundo pilot plant for select marine biotoxins
- Conduct bench-scale experiments for testing RO membrane performance in removing known quantities of select marine biotoxins from ocean water samples
- Correlate water quality parameters with algal blooms and the production of marine biotoxins, to the extent possible.

1.3 Stormwater Monitoring

The WBMWD project team monitored water quality parameters and desalination treatment implications associated with four storms that occurred near the El Segundo pilot intake between November 2008 and February 2009. A storm event was defined as a precipitation event in which at least 0.5 inches were recorded during a 24-hour period, using nearby online rain gauges in the Ballona Creek watershed. Monitoring encompassed a broad range of water quality parameters affected by urban runoff, including inorganic and organic compounds, pathogens and indicators of pathogens, nutrients and metals. The concentrations of these constituents were assessed in the raw water ocean intake, as well as according to sampling locations throughout the stages of the El Segundo pilot treatment train.

Results from the stormwater monitoring confirmed that the WBMWD treatment process effectively removed or inactivated water quality constituents (e.g., total coliform, fecal coliform and turbidity) to meet or exceed requirements promulgated by the United States Environmental Protection Agency (USEPA) Surface Water Treatment Rule (SWTR). It is important to note that using the current microfiltration and reverse osmosis treatment process train, a disinfection step to achieve 3.5-log virus removal will still be required. The microbiological quality and turbidity levels of the raw ocean intake water are such that, even considering the adverse impacts of storm events, the source water would be exempt from USEPA SWTR filtration requirements. During the four storm events, only two samples exceeded the 100 MPN/100 mL total coliform and 20 MPN/100 mL fecal coliform target levels. More than 98% of the samples from this period were below the total and fecal coliform target levels, thereby meeting the requirement of 95% or greater compliance. Using daily averages of the 15minute interval turbidity data, the turbidity levels are consistent with the SWTR turbidity requirement of less than 5 NTU promulgated by EPA SWTR for exemption from filtration.

Correlation of storm and baseline water quality data revealed that storm events resulted in levels of total and fecal coliform, *E. coli* and turbidity that were slightly elevated from non-storm levels. Conversely, relative fluorescence levels were reduced during storm events as compared with non-storm conditions. The reduction was likely due to the related weather conditions (e.g., reduced light and colder temperatures). Analysis of microbiological concentrations and turbidity levels measured throughout the treatment process during the storm events revealed that these constituents were effectively removed during the microfiltration stage.

The treatment process train included two pre-straining alternatives, a high-rate granular media filter (GMF) operated at 23 gpm/ft² and an Arkal disc filter, arranged in parallel configuration for the purpose of comparison. During stormwater monitoring, the average 1.22 NTU turbidity in the raw ocean water was reduced to averages of 0.74 NTU and 0.38 NTU, respectively, in the Arkal disc and GMF filtrates. At these levels, GMF produced water quality that approached compliance levels for USEPA drinking water regulations (e.g., 0.3 NTU or less in 95% of filtered water samples) without the addition of coagulant. Additionally, the GMF was demonstrated to be more effective in reducing biofouling in downstream microfilter membranes than the Arkal disc filter.

A comprehensive summary table of all stormwater monitoring constituents detected in the raw water intake and second pass RO permeates is included in Table 1.

Table 1. Summary of detected constituents during storm events

Water Quality Parameter	Units	Meanª	Standard Deviation ^a	Median⁵	Minimum⁵	Maximum	Number of Observations		Reporting Limit ^b
				WATER					
Aluminum total	110/1	NA	NA NA	ganic para	<50	200	56	44	50
Aluminum, total Arsenic, total	μg/l	NA NA	NA NA	<4	<4	4	56	55	4
	μg/l	NA NA	NA NA	6	6	8	14	1	
Barium, total ^d	μg/l	4.18	0.44	4.20	2.50	5.10	56		5;10 0.01;0.02
Boron, total	mg/L							0	
Chromium, total	μg/l	NA	NA	<2	<2	55	56	55	2
Copper, total	μg/l	NA	NA	<5	<5	9	56	55	5
Iron, total	μg/l	NA NA	NA NA	<200 <2	<200 <2	6000 42	56 56	52 28	200
Manganese, total	μg/l								
Molybdenum, total	μg/l	11	2	10	9	22	56	0	1
Selenium, total	μg/l	NA 7470	NA 070	6	<4	9	56 14	13	4
Strontium, totald	μg/l	7179	278	7100	6900	8000		0	2
Tin, total	μg/l	NA	NA	<2	<2	2	56	55	2;4
Titanium, total	μg/l	NA	NA	<20	<20	31	56	53	20
Uranium rad ^d	μg/l	NA	NA	3	<2	3	14	2	2;4
Vanadium, total	μg/l	NA	NA	<5	<5	8	56	37	5
Zinc, total	μg/l	NA	NA	<50	<50	71	56	55	50
				anic para					
Bis(2-ethylhexyl) phthalate	μg/l	NA	NA	<3	<3	4	56	55	3
Caffeine	μg/l	NA	NA	<0.1	<0.1	0.3	56	55	0.1
				sical para					
Ammonia as N	mg/l	NA	NA	<0.1	<0.1	0.1	56	55	0.1
Conductivity ^f	mS/cm	49.17	0.90	49.32	44.33	49.87	32	0	0.01
Nitrate as N	mg/l	NA	NA	<0.1	<0.1	550.0	56	54	0.1
Phosphorus, total as P	μg/l	35	7	35	22	59	56	0	10
Fluorescence ⁹	RFU	1.39	0.63	1.39	0.25	5.48	388	0	0.1
рН ^f	pH units	8.18	0.35	8.10	7.47	9.33	35	0	0.01
Temperature ^f	ů	15.31	1.52	14.85	12.50	18.10	32	0	NA
Turbidity ⁹	NTU	1.22	1.05	0.84	0.26	7.33	1599	0	0.001
UV 254	1/cm	NA	NA	0.013	<0.009	0.042	56	5	0.009
			Microbi	ological p	arameters ^h				
E.coli ⁱ	MPN/100 ml	NA	NA	<2	<2	13	30	22	2
Enterococcus	MPN/100 ml	NA	NA	<10	<1	21	59	49	1;10
Fecal coliform	MPN/100 ml	NA	NA	<2	<2	30	76	44	2
Total coliform	MPN/100 ml	NA	NA	4	<2	170	72	23	2
		SECO	D PASS RI	EVERSE (OSMOSIS P	ERMEATE			
				ganic par					
Aluminum, total	μg/l	NA	NA	<5	<5	8	38	26	5
Boron, total	mg/L	0.86	0.57	0.56	0.37	2.20	38	0	0.001;0.01
Copper, total	μg/l	NA	NA	<0.5	<0.5	1.5	38	37	0.5
Manganese, total	μg/l	NA	NA	<0.2	<0.2	18.0	38	28	0.2
Molybdenum, total	μg/l	NA	NA NA	<0.1	<0.1	0.2	38	37	0.1
Strontium, total ^d	µg/l	NA	NA	<0.2	<0.2	5.8	10	9	0.2
Tin, total	µg/l	NA	NA	<0.2	<0.2	0.3	38	36	0.2
Vanadium, total	µg/l	NA	NA.	<0.5	<0.5	1.8	38	34	0.5
	ra,,			anic para					
Bis(2-ethylhexyl) phthalate	μg/l	NA	NA NA	<3	<3	69	38	37	3
			Phy	sical para	meters				
Ammonia as N	mg/l	NA	NA	<0.1	<0.1	1.5	38	25	0.1
Conductivity ^f	μS/cm	41.48	39.77	13.43	1.59	100.06	1439	0	0.01
Nitrate as N	mg/l	NA	NA	<0.1	<0.1	55.0	38	37	0.1
pH	pH units	8.65	0.93	8.93	5.96	9.62	21	0	0.01
Temperature ^f	оС	21.84	1.35	21.10	20.70	23.80	5	0	NA
Turbidity	NTU	0.07	0.02	0.08	0.05	0.09	5.00	0.00	0.001
UV 254	1/cm	NA	NA	<0.009	<0.009	0.046	38	27	0.009
3. 23.					parameters	0.0.0			
	MPN/100 ml	NA	NA NA	NA	<1	10	38	34	

"Mean and standard deviations were only computed for those analytes that were detected in all samples analyzed; For those analytes that resulted in at least one non-detect, the mean and standard deviation are reported as NA (not applicable)

"Use of different dilution factors resulted in multiple reporting limits for some constituents; Median values for constituents having multiple reporting limits and detected values above

and below the reporting limits are reported as NA (not applicable) to avoid ambiguity. The minimum values is reported as the lowest detected value or< lowest detection limit, which ever value is lower

^{&#}x27;All samples analyzed for the following inorganic parameters were below the detection or reporting limit: nitrite, cadmium, beryllium, antimony, cobalt, mercury, nickel, silver, thallium, tungsten and zirconium

Data only available for storm event 1

[&]quot;Data only available for storm event 1
"All samples analyzed for the following organic parameters were below the detection or reporting limit: 2,4-Dinitrotoluene, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Acenaphthene,
Acenaphthylene, Acetochlor, Alachior, Aldrin, alpha-BHC, Benzo (g,h,i) perylene, Captan, Dieldrin, Endosulfan sulfate, gamma-BHC (Lindane), Metolachlor, Prometryn, Benzo (k)
fluoranthene, Chloropropham, Diethyl phthalate, Endrin, gamma-Chlordane, Metribuzin, Propachlor, alpha-Chlordane, beta-BHC, Chrysene, Dimethoste, Endrin aldehyde, Heptachlor,
Molinate, Pyrene, Anthracene, Cyanazine, Dimethyl phthalate, Endrin ketone, Heptachlor epoxide, Naphthae, Simazine, Atrazine, Bromacil, detta-BHC, Diphenamid, EPTC,
Hexachlorobenzene, PCNB, Terbacil, Benzo (a) anthracene, Butachlor, Di-n-octyl phthalate, Disulfoton, Ethion, Hexachlorocyclopentadiene, Pentachlorophenol, Thiobencarb, Benzo
(a) pyrene, Butyl benzyl phthalate, Diaziuno, Endosulfan I, Fluoranthene, Indeno (1,2,3-db) pyrene, Phenathere, Trifluralin, Benzo (b) fluoranthene, Caffeine, Dibenzo (ah),
anthracene, Endosulfan II, Fluorene, Methoxychlor, Prometon, Trithion, 1,1-Dichloroethane, 1,2,4-Trichlorobenzene, 2-Chlorotoluene, Bromochloromethane, Chloroform,
Dichlorodifluoromethane, Greno 12, mp-Xylene, P-Dichlorobenzene, 10-Lindicorethane, 1,1-1-Tertachloroethane, 1,3 Dichloropropene, 1,2-Dichloropropane,
Bromoform, 6:1-2-Dichloroethene, Ethylene chloride, see-Butylbenzene, Ethylene chloride, see-Butylbenzene,

Data only available for storm events 1-3

Data only available for storm events 2 and 3

All samples analyzed for the following microbiological parameters were below the detection or reporting limit: F-specific coliphage, human adenoviruses and human enteroviruses 'Data only available for storm event 4

Overall, Table 1 reveals that the desalination treatment process was successful at removing most of the contaminants identified during the storm events, as evident from comparison between the raw and finished water qualities. Furthermore, all samples were non-detect for F-specific coliphage and human pathogens, suggesting little impact from urban runoff on the West Basin El Segundo seawater intake.

1.4 Marine Biotoxin Monitoring

Phytoplankton blooms, commonly referred to as 'red tides' or harmful algae blooms (HABs), are capable of producing toxic metabolic byproducts exhibiting a variety of size, structure and reactivity characteristics. Although scientific research has identified specific marine biotoxins produced by various phytoplankton species, the underlying conditions and mechanisms contributing to the biotoxin production are poorly understood. In order to enhance understanding of biotoxin production and its impacts on seawater desalination, the WBMWD project team implemented a marine biotoxin monitoring program.

Marine biotoxins associated with HABs in southern California were identified by a comprehensive literature review conducted for this project by Dr. David Caron and his lab group at the University of Southern California. This literature review identified domoic acid, saxitoxin, brevetoxin, okadaic acid and yessotoxin as the biotoxins of concern for southern California. David Caron and the project team used the literature review as the basis for a journal article entitled "Harmful algae and their potential impacts on desalination operations off southern California", which was accepted for publication in *Water Research* (2009) as an additional project outcome. The marine biotoxins considered in the monitoring portion of the study were selected based on of the likelihood of their presence in southern California waters as discussed in the literature review and because of the availability of enzyme-linked immunosorbent assay (ELISA) methods for their analysis.

In order to improve understanding of the dynamics between water quality parameters and both the occurrence of HABs and the production of marine biotoxins, the project team established buoy systems with water quality sensors (e.g., temperature, chlorophyll a, turbidity and dissolved oxygen) for monitoring conditions near the WBMWD pilot and potential demonstration facilities at El Segundo and near the possible site of the demonstration facility at Redondo Beach. An additional goal was to attempt to correlate phytoplankton taxonomy with marine conditions indicating the potential for HABs using samples taken proximal to the buoy and intake sites. It was envisioned that correlating the occurrence of specific taxa with water quality parameters from the buoy data, as well as detections of associated marine biotoxins in the El Segundo raw ocean intake water would provide an indication of the conditions related to the production of marine biotoxins by those phytoplankton taxa. Unforeseen difficulties delayed the buoy monitoring set-up; as a result, limited data was

available for providing the envisioned correlations between water quality parameters and the occurrence of both phytoplankton taxonomy and associated biotoxins. As discussed in the literature review, the presence of phytoplankton taxa that are known to produce specific marine biotoxins does not indicate that they will produce the marine biotoxins under all circumstances. In many cases, no marine biotoxins are observed despite the presence of phytoplankton taxa known to produce them.

Another objective of the project was to study the implications of the marine biotoxins on the WBMWD desalination treatment process. In order to accomplish this, a two-phase marine biotoxin monitoring program was devised, based on available analytical methods. Weekly samples were collected from the raw and RO permeate waters at the El Segundo pilot plant, then analyzed for domoic acid and brevetoxin in dissolved and particulate forms, particulate okadaic acid and dissolved saxitoxin. Of the raw water samples, only domoic acid (dissolved and particulate) and dissolved saxitoxin were detected. *No biotoxins were detected in the RO permeate water, providing a strong indication of the effectiveness of biotoxin removal through the RO desalination treatment process.*

In order to conclusively test for the removal of the identified marine biotoxins via the RO membrane treatment process, bench-scale RO experiments were conducted. The bench-scale experiments utilized waters challenged with dissolved domoic acid, saxitoxin and brevetoxin to test for removal efficacy using RO. Yessotoxin was excluded from the analyses because no ELISA testing method was available. The marine biotoxin concentrations used in the RO bench-scale tests were chosen to be representative of levels exceeding the maximum concentrations expected to be observed in the raw seawater in the area of study, as identified by the Caron research group at USC. All of the tested biotoxins were successfully removed during the bench-scale experiments, providing further support to the findings from the pilot-scale sampling in which all detected marine biotoxins in the raw ocean intake at El Segundo (domoic acid and saxitoxin) were shown to be completely removed by the RO desalination process.

1.5 Recommendations and Conclusions

- The current desalination treatment process train is expected to meet the maximum pathogen removal/inactivation requirements from the SWTR, provided a disinfection step is included.
- The microbiological quality is good during both storm and non-storm events, however storms do have a slightly negative impact on the raw water quality at the intake.
- Turbidity levels were slightly less for non-storm samples, as compared with stormwater samples, however the overall levels are consistent with the SWTR turbidity requirement of less than 5 NTU promulgated by EPA SWTR for exemption from filtration.

- During the stormwater sampling period (November 2008 February 2009), the total coliform, fecal coliform and turbidity levels never exceeded the requirements promulgated by EPA SWTR for exemption from filtration.
- It is envisioned that the buoy monitoring system be used as a tool for correlating water quality parameters with the occurrence of specific phytoplankton and their associated biotoxins. This may improve understanding of the conditions and mechanisms related to biotoxin production, as well as appropriate treatment responses.
- No biotoxins were detected in the RO permeate water in both the pilot and bench scale studies, providing a strong indication of the effectiveness of biotoxin removal through the RO desalination treatment process. Of the biotoxins monitored at the pilot plant facility, dissolved and particulate domoic acid, as well as dissolved saxitoxin were detected in the raw seawater and subsequently removed by the treatment process. Further validation of the removal of biotoxins by RO treatment was warranted considering infrequent and unpredictable occurrence of biotoxins in seawater, thus bench-scale experiments were conducted. Dissolved domoic acid, brevetoxin and saxitoxin were all successfully removed by the bench-scale RO process. If future monitoring of the southern California bight indicates the possible presence of additional unidentified biotoxins in the area proposed for the desalination facility, additional bench-scale experiments would be recommended to demonstrate the effectiveness of RO treatment in removing the newly identified biotoxins.
- Blending desalination product water with conventional water supplies offers a potential solution to meet the ideal water quality goal for boron (< 0.5 mg/L).
- The recommendation that a high-rate granular media filter (GMF) be used as a more efficient pre-straining treatment stage alternative to the Arkal disc filter is supported by the stormwater sampling data collected on this project. Additionally, GMF was demonstrated to be more effective in reducing biofouling in downstream microfilter membranes than the Arkal disc filter (Lauri et al., 2009). It is recommended that during algal blooms a coagulant be added upstream of the GMF to provide further protection for downstream membranes.

Section 2 – Introduction 2.1 Project Information

This project investigates critical raw water quality issues unique to seawater that may have an impact on the West Basin Municipal Water District (WBMWD) desalination processes. The scope of the study is outlined in the project assessment plan (PAP), included in Appendix A – Stormwater and Marine Biotoxin Monitoring Project Assessment Plan (PAP), and includes monitoring of source water quality associated with both urban stormwater runoff and 'red tides' caused by phytoplankton blooms, and the implications of these events on the desalination processes. A quality assurance and quality control plan, provided in Appendix B – Stormwater and Marine Biotoxin Monitoring Quality Assurance and Quality Control Plan, complements the PAP to ensure the success of the identified tasks.

As part of the comprehensive pilot testing program, WBMWD funded research to examine the effects of stormwater runoff on ocean intake and reverse osmosis (RO) permeate water quality at the El Segundo desalination pilot plant. Within this final report, the methods used in conjunction with each phase of the project are summarized, followed by a presentation and discussion of the results. Experimental plans with detailed descriptions of the testing parameters and associated methods are included in relevant appendices. The experimental plan for the stormwater monitoring research is presented in Appendix C – Stormwater Monitoring Experimental Plan. Additionally, the WBMWD pilot-testing program studied the dynamics of phytoplankton blooms and associated production of marine biotoxins, specifically as these phenomena impact the desalination treatment process.

The study included: 1) characterization of phytoplankton taxonomy present in raw water samples from the El Segundo ocean intake, 2) on-going water quality monitoring and data collection proximal to ocean intakes at El Segundo and Redondo Beach, 3) sampling and analysis of various water quality constituents at each stage of the pilot treatment process, 4) sampling and analysis of raw and RO permeate water from the El Segundo pilot plant for select marine biotoxins, as well as 5) bench-scale experiments for testing RO membrane performance in removing known quantities of select marine biotoxins from ocean water samples. The details of this study are provided in the experimental plan in Appendix D – Marine Biotoxin Monitoring Experimental Plan.

2.1.1 Identification of important biotoxins

Phytoplankton blooms can produce a complex array of toxic metabolic byproducts collectively referred to as marine biotoxins, which exhibit varying size, structure and reactivity characteristics. A lack of previous research related to the treatment behavior and human health effects of marine biotoxins prompted the WBMWD to investigate biotoxins and the related treatment implications. The aims of this investigation were to not only assess the removal of select marine biotoxins using the RO membrane treatment process, but to also enhance

preliminary understanding of the underlying phytoplankton bloom dynamics and water quality parameters affecting marine biotoxin production. In order to accomplish the latter, WBMWD proposed correlating data from water quality monitoring sensors located near the pilot plant intake with marine biotoxin analyses from raw ocean water samples.

Dr. David Caron and his lab group at the University of Southern California (USC) identified marine biotoxins of concern for this project through a comprehensive literature review of harmful algal blooms (HABs). The identified marine biotoxins of primary concern for southern California were domoic acid, saxitoxin, brevetoxin, okadaic acid and yessotoxin. Information about these toxins is outlined in Table 2.

Table 2. Marine biotoxin species of concern for southern California

Toxin	Formula	MW	Structure	Microalgae	Poison Effects	References
Domoic acid (DA)	C ₁₅ H ₂₁ NO ₆	311.14	HO OH OH	Diatoms Pseudo-nitzschia spp. P. australis P. cuspidata P. delicatissima P. fraudulenta P. multiseries P. pungens P. pseudodelicatissima P. seriata	Amnesic Shellfish Poisoning (ASP) Human effects -Gastro-intestinal symptoms -Neurological symptoms -Death Ecosystem effects -Marine mammal mortalities -Bird mortalities	Hallegraeff et al. (2004), Litaker et al. (2008), Caron et al. (2009)
Saxitoxins (STXs)	$C_{10}H_{17}N_7O_4$	299.3	H ₂ N O H NH NH NH OH OH	Dinoflagellates Alexandrium spp. A. acatenella A. catenella A. fundyense A. hiranoi A. ostenfeldii A. tamarense	Paralytic Shellfish Poisoning (PSP) Human effects -Gastro-intestinal symptoms -Paralysis -Death Ecosystem effects -Marine mammal mortalities	Hallegraeff et al. (2004), Lefebvre et al. (2008), Caron et al. (2009)
Brevetoxins (PbTxs) Brevetoxin 2 Brevetoxin 3 Brevetoxin 9	$C_{50}H_{70}O_{14}$ $C_{50}H_{72}O_{15}$ $C_{50}H_{74}O_{14}$	895.1 897.1 899.1	Constitution S	Raphidophytes Chattonella marina Fibrocapsa japonica Heterosigma akashiwo	Neurotoxic Shellfish Poisoning (NSP) Human effects -Gastroenteritis -Neurological symptoms -Respiratory irritation and/or failure Ecosystem effects -Marine mammal mortalities -Fish mortality events	Hallegraeff et al. (2004), Caron et al. (2009)
Okadaic acid (OA)	C ₄₄ H ₆₈ O ₁₃ 805		Dinoflagellates Dinophysis spp. D. acuminata D. acuta D. caudate D. fortii D. norvegica D. rotundata D. tripos Prorocentrum spp.	Diarrhetic Shellfish Poisoning (DSP) Human effects -Gastro-intestinal symptoms Ecosystem effects -None reported	Hallegraeff et al. (2004), Caron et al. (2009)	
Yessotoxins (YTXs)	$C_{55}H_{80}O_{21}S_2Na_2$	1187.3	10 to	P. micans P. minimum Dinoflagellates Lingulodinium polyedrum Gonyaulax spinifera Protoceratium reticulatum	Human and ecosystem effects -None reported	Hallegraeff et al. (2004), Caron et al. (2009)

A journal article based on the literature review of marine biotoxins was produced by David Caron and the project team. This article, entitled "Harmful algae and their potential impacts on desalination operations off southern California", was accepted for publication in *Water Research* (2009) as an additional project outcome. The manuscript submitted to *Water Research* is included in Appendix E – Submitted Manuscript to *Water Research*.

The most important marine biotoxins identified in conjunction with the literature review as to possible presence in Southern California were incorporated into a two-phase monitoring program provided there were available analytical methods. Pilot-scale testing of raw and RO permeate waters was conducted for domoic acid, saxitoxin, brevetoxin and okadaic acid. Bench-scale experiments utilized challenge water to test for the removal of domoic acid, saxitoxin and brevetoxin. Yessotoxin was excluded from these analyses because the ELISA testing method was not available.

Section 3 – Stormwater Monitoring 3.1 Introduction

One of the major concerns for a desalination treatment plant is the adverse impact of urban stormwater runoff on ocean intake source water quality. Contaminants such as sediments, nutrients, organic matter, pathogens, oil and grease, toxic substances and high metal concentrations accumulate during the dry seasons, and are transported to coastal water via runoff from storm events. The runoff from four storm events was monitored in conjunction with preliminary WBMWD seawater desalination treatment pilot studies at the El Segundo site in 2003 and 2004, however no notable water quality impacts were indicated. A comprehensive experimental plan was developed from the previous stormwater monitoring studies at the El Segundo pilot site, including evaluation of the ability of the overall desalting process to remove select constituents detected as a result of stormwater influences. The experimental plan and quality assurance and quality control documents are included in Appendix C – Stormwater Monitoring Experimental Plan and Appendix B – Stormwater and Marine Biotoxin Monitoring Quality Assurance and Quality Control Plan, respectively.

3.1.1 Storm Definition

Stormwater monitoring was conducted during four storm events. A storm was defined as a local precipitation event with a total of at least 0.5 inches recorded for a 24-hour period, as determined using online rain gauges. Beginning within 24-hours of the storm event declaration, water samples were collected twice each day for 7 days from each of the sampling sites indicated on Figure 1.

The intake of the West Basin El Segundo pilot facility is located near the Santa Monica Bay, and mainly receives flows from Ballona Creek. Figure 1 depicts the Ballona Creek watershed, and indicates the location of the WBMWD facilities at El Segundo.



Figure 1. Ballona Creek Watershed with rain gauges, WBMWD intakes and buoy mooring locations (map adapted from Google Earth 2009)

Historical precipitation data from October 2003 to September 2008 were evaluated in order to correlate rainfall precipitation with the flow discharge to Ballona Creek. Rain gauges from within the Ballona Creek drainage area that were included as part of this evaluation were located at the Hollywood Dam, Los Angeles-Ducommun St. and the University of Southern California, as indicated on Figure 1. Additionally, the rain gauge located at the LAX International Airport was included, as it is located between the El Segundo Pilot facility and the Santa Monica Bay outlet.

Table 3 summarizes storm events from the past 5 years, according to two parameters: (1) daily precipitation of 0.5 inches or more, as well as (2) daily discharge flow rates from Ballona Creek of at least 1000 cfs, occurring on the same day as a rain event.

Table 3. Ballona Creek (above Sawtelle Blvd) storm events summary for 2003-2008

	Oct 2003 - 3	Sept 2004	Oct 2004 - 3	Sept 2005	Oct 2005- S	Sept 2006	Oct 2006- S	Sept 2007	Oct 2007- Sept 2008		
Rain Gauge	No. Rainfall ≥ 0.5 in	No. Flow ≥ 1000 cfs	No. Rainfall ≥ 0.5 in	No. Flow ≥ 1000 cfs		No. Flow ≥ 1000 cfs	No. Rainfall ≥ 0.5 in	No. Flow ≥ 1000 cfs		No. Flow ≥ 1000 cfs	
Hollywood Dam	7	3	22	13	8	3	1	0	12	1	
LA-USC	5	2	21	14	8	4	1	0	9	2	
LAX	7	4	19	15	6	5	0	0	8	4	
LA-Ducommun St	7	2	21	13	7	2	1	0	9	2	
Total No. Flow ≥ 1000 cfs		4		16		7		0		4	

As detailed in Table 3, the number of annual precipitation events varies considerably from year to year, both according to rainfall (≥ 0.5 inches/24-hours) and flow (≥ 1000 cfs recorded over a 24-hour period with a rain event) for the Ballona Creek area. The incidence of the required flow discharge parameter was less frequent than that for rainfall. Correlation between discharge flow data for individual rain gauges and the total number of annual qualifying discharge flow events for the Ballona Creek area was closest for the LAX rain gauge, as highlighted in bold within Figure 1. This factor, combined with distance proximity to Ballona Creek resulted in the selection of the LAX rain gauge as the most appropriate indicator for storm events affecting the El Segundo pilot facility. An official storm event was thus declared for the WBMWD stormwater monitoring program if the LAX rain gauge reported ≥ 0.5 inches of precipitation within a 24-hour period.

Using these criteria, four storm events were declared on 26 November 2008, 15 December 2008, 24 January 2009 and 6 February 2009. Each storm was then monitored for 7 days.

3.1.2 Schematic of El Segundo Pilot Plant and Sampling Points

As part of the evaluation of the impacts of stormwater runoff on each stage of the pilot treatment process, the following sampling locations were selected for the stormwater sampling, as shown in Figure 2.

- 1. The ocean intake (point "1" on Fig. 2)
- 2. The Arkal Disc Filter effluent (point "2" on Fig. 2)
- 3. Granular Media Filter (GMF) effluent (point "3" on Fig. 2)
- 4. Pall MF 1 effluent (point "4" on Fig. 2)
- 5. Pall MF 2 effluent (point "5" on Fig. 2)
- 6. The RO 1 effluent (point "6" on Fig. 2)
- 7. The RO 2 effluent (point "7" on Fig. 2)
- 8. The 2nd Pass RO effluent (point "8" on Fig. 2)

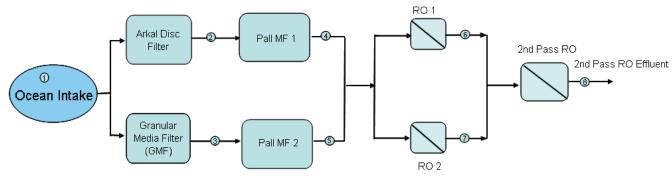


Figure 2. Schematic of the El Segundo Pilot Desalination Facility treatment process

3.1.3 Regulatory Aspects

Regulatory requirements have been established by the United States Environmental Protection Agency (USEPA) and the California Department of Public Health (CDPH) for surface water intakes such as the West Basin desalination facilities. Pathogen removal/inactivation requirements under the USEPA's Surface Water Treatment Rule (SWTR) were outlined as part of the preliminary design development for the WBMWD Temporary Ocean Water Desalination Demonstration Project. The minimum and maximum applicable pathogen removal requirements are summarized in Table 4.

Table 4. Process train pathogen removal/inactivation for SWTR compliance (WBMWD, 2006)

Pathogon	Log Removal							
Pathogen	Minimum	Maximum						
Giardia	3	5						
Virus	4	6						
Cryptosporidium	2	5.5						

In addition to identifying the USEPA regulations, this previous work analyzed the pathogen removal/inactivation provided by potential process trains for desalination treatment. Two of these treatment trains are provided in Tables 5 and 6, involving MF/RO+Disinfection and UF/RO+Disinfection, respectively.

Table 5. Possible MF/RO process train to meet maximum pathogen removal/inactivation requirements (WBMWD, 2006)

Dothogon	Log Removal										
Pathogen	Objective	MF ¹	RO	Disinfection							
Giardia	5	4	2	0							
Virus	6	0.5	2	3.5							
Cryptosporidium	5.5	4	2	0							

¹Maximum credit that can be earned by the MF process for the given pathogen. Actual credit is determined based on challenge testing.

Table 6. Possible UF/RO process train to meet maximum pathogen removal/inactivation requirements (WBMWD. 2006)

5 41	Log Removal										
Pathogen	Objective	UF ¹	RO	Disinfection							
Giardia	5	4	2	0							
Virus	6	4	2	0							
Cryptosporidium	5.5	4	2	0							

¹Maximum credit that can be earned by the UF process for the given pathogen. Actual credit is determined based on challenge testing.

Both of the above desalination treatment process trains would be expected to meet the maximum pathogen removal/inactivation requirements from the SWTR, but would require challenge testing. In Table 5, the log removal shown for MF represents the *highest* log removal that can be credited for MF. The actual credit must be determined based on challenge testing of the MF unit with male-specific (also known as MS2 or F+) coliphage and may be less than the credit shown in Table 5. The same holds true for the credits shown for UF in Table 6. The male-specific coliphage is used as an indicator for fecal pollution, and has previously been found in seawater meeting bacteriological standards for open ocean recreation (Jiang et al., 2001). Thus, in order to verify the expected log-removal credit compliance for MF and UF and to provide an indicator for enteric viruses, F-specific coliphage were included within the scope of the stormwater monitoring. However, *Cryptosporidium* was not measured because the desalination treatment process is expected to provide 6-log reduction, based on the treatment trains and associated log-removal credits previously outlined in Tables 5 and 6.

3.1.4 Monitoring Approach

The scope of the stormwater monitoring experimental plan includes a broad range of water quality parameters, such as inorganic and organic compounds, pathogens and indicators of pathogens, nutrients and metals. F-specific coliphage and human pathogens were analyzed by UCI Professor Jiang's Laboratory; all other analyses were performed by Weck Laboratory.

Dr. Jiang used sampling and methods adapted from Jiang et al (2007), including coliphage detection by plaque assay method from Adams (1959), human viruses detection by Polymerase Chain Reaction (PCR) and detection of infectious human viruses by cell culture. The use of F-specific coliphage as an indicator, is

not as well established as bacterial indicators, however it has been demonstrated as an effective method by He and Jiang (2005), Jiang and Chu (2004), Jiang et al. (2001) and Ahn et al. (2005). Polymerase chain reaction (PCR) was used as the method for detection of human viruses, using primers specific to human adenoviruses and enteroviruses. Human adenoviruses and enteroviruses are generally indicators of sewage contamination in surface water. *Human adenovirus* frequently cause acute upper respiratory tract (URT) infections (i.e. "colds"). Adenoviruses are readily inactivated by most chemical disinfectants routinely used in drinking water treatment, including free chlorine, chlorine dioxide, and ozone, however this species is more resistant to UV than the viruses traditionally considered to be significant waterborne disease indicators (Yates et al, 2006). *Human enteroviruses* (family Picornaviridae) are the major cause of a wide range of acute illnesses.

Considering the broad water quality monitoring scope, the stormwater sample analysis results were non-detect for a large percentage of constituents. In order to interpret the stormwater monitoring data, time-series and probability plots were developed. All non-detected data values were plotted at the detection limit for these analyses.

3.2 Baseline Comparison of Water Quality at Intake Site

This section provides a baseline comparison of water quality constituents for which both non-storm and storm data were available. The following constituents are presented and discussed below: total coliform, fecal coliform, *E. coli*, enterococcus, turbidity, fluorescence and boron.

Considering the large volume of water quality data that was generated as part of the WBMWD pilot study, probability plots were constructed to improve analysis of key water quality constituents. Probability plots for total coliform and fecal coliform are presented in Figures 3-4.

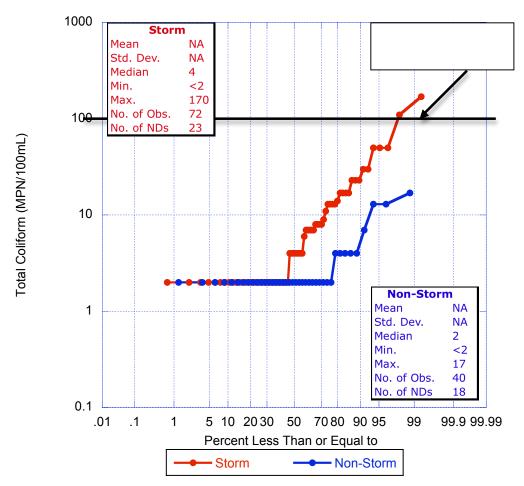


Figure 3. Probability plot of storm and baseline total coliform data SWTR = Surface Water Treatment Rule

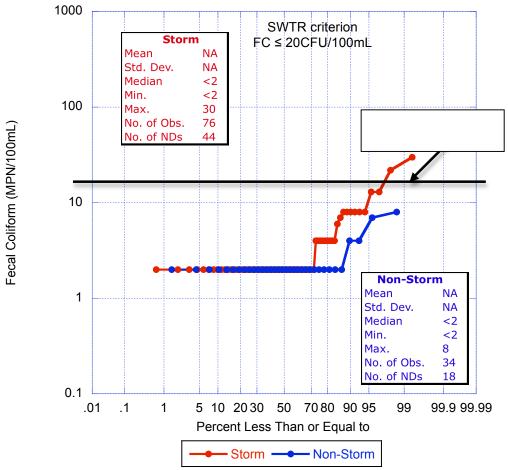


Figure 4. Probability plot of storm and baseline fecal coliform data SWTR = Surface Water Treatment Rule

As shown in Figures 3-4, the microbiological quality is good during both non-storm and storm events, however storms do have a slightly negative impact on the microbial quality of the raw water intake. All non-storm total and fecal coliform concentrations are below the SWTR criterion for exemption from filtration treatment. During the four storm events, only two samples exceeded the 100 MPN/100 mL total coliform and 20 MPN/100 mL fecal coliform target levels. More than 98% of the samples during this period were below the total and fecal coliform target levels, thereby meeting the requirement of 95% or greater compliance. These results indicate that the West Basin El Segundo intake source water is relatively clean and would be exempt from the filtration requirement.

The results for *E. coli* were problematic for storms 1 and 2, as it was observed that *E. coli* levels were occasionally higher than total coliform levels, as evident in Figure 5.

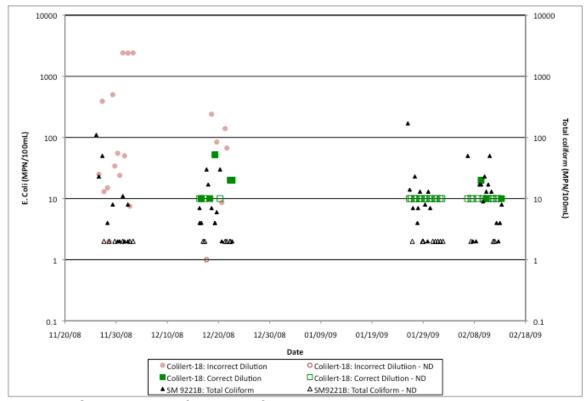


Figure 5. Comparison of total coliform and *E. coli* concentrations

Further investigation revealed incorrect application of the Colilert-18 method (also referred to as SM 9223B) for *E. coli* enumeration in raw ocean intake, specifically use of an inappropriate dilution factor. Previous research by Palmer and colleagues (1993) found that, at a minimum, a dilution factor of 10 is necessary to reduce the number of false positives resulting from the growth of *Vibrio* spp. using Colilert. Because *Vibrio* spp. thrive in saline waters, it is more competitive than coliform bacteria at high salinities. Utilization of the Colilert-18 method for the detection of *E. coli* requires a dilution of the salinity to provide a competitive advantage to the targeted *E. coli* bacteria. This problem with the dilution was identified during storm 2 and appropriately resolved prior to storms 3 and 4. In an effort to validate that a dilution of 10 was appropriate, after consultation with Weck Laboratories, the project Team directed Weck to utilize SM 9221F in addition to Colilert-18for Storm 4. Additional validation was available, using corresponding pilot intake samples from storms 1 and 2 associated with another WBMWD project, as presented in Figure 6.

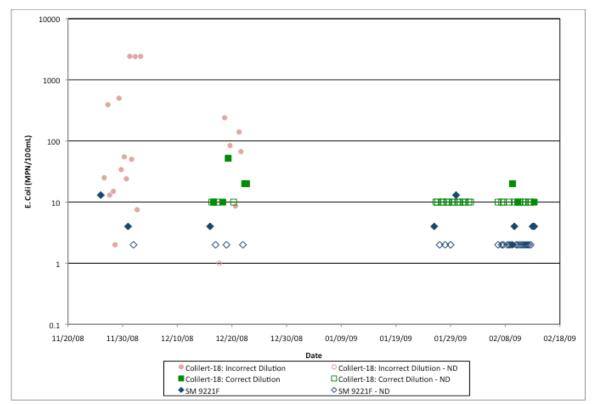


Figure 6. Various *E. coli* detection methods for comparison and validation of improved methods during storms 3 and 4

E. coli levels analyzed using SM9221F were consistent with the results from the corresponding project. Using the correct dilution factor of 10, Colilert-18 results associated with storms 3 and 4 were more consistent with expected findings. In Figure 5, *E. coli* was present at a lower concentration than total coliform for given samples. In addition to the multiple tube fermentation methods, the University of California, Irvine, analyzed 14 raw ocean intake samples during storm 4 using the membrane filtration technique (EPA 1103.1). The range of concentrations observed was 0 to 8 CFU/100mL in the raw water intake. It is important to note that all plates were counted outside of the recommended counting range of 20 to 80 colonies.

A probability plot of *E. coli* levels is presented in Figure 7, using only the data from SM 9221F. This includes data from the corresponding WBMWD project, as well as storms 3 and 4.

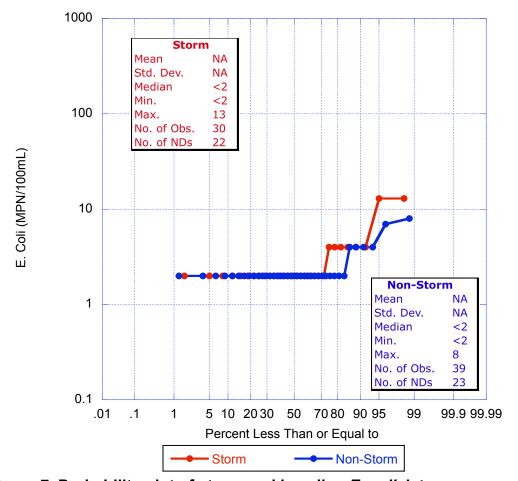


Figure 7. Probability plot of storm and baseline *E. coli* data

All data points, storm and non-storm, are combined for total coliform, fecal coliform and *E. coli* in Figure 8.

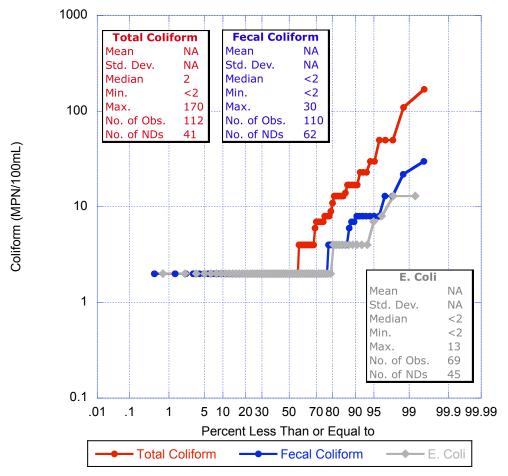


Figure 8. Probability plot of composite bacteriological data

As expected, Figure 8 depicts *E. coli* as a subset of fecal coliform, which is a subset of total coliform. The composite results are also consistent with the plots of storm and non-storm data, since total coliform levels are below 100 MPN/100mL and fecal coliform levels are below 20 MPN/100mL for almost all samples.

There was regular occurrence of coliform bacteria in the raw water samples, with 63%, 43% and 34% detects for total coliform, fecal coliform and *E. coli*, respectively including all samples. This number is slightly elevated for total coliform during storm events, with 68% detects, however detected fecal coliform and *E.coli* samples dropped to 42% and 29%, respectively during storm events.

Enterococcus bacteria were also monitored as an indicator of fecal contamination in the source water, using the USEPA-approved Enterolert method. Overall, 83% of the samples taken during storm events were below the detection limit, whereas 92% of corresponding samples taken during non-storm events were below the detection limit. The non-storm data was available from another WBMWD project, which also utilized the same Enterolert detection method. Comparison of the two enterococcus data sets and consultation with Enterolert's

manufacturer (IDEXX Laboratories Inc.) served to identify the use of inappropriate dilution factors, similar to the aforementioned problematic *E. coli* results. This investigation is described in detail within Appendix F – Enterolert Discussion.

Time-series graphs for the main bacteriological indicators, as well as physical parameters such as relative fluorescence and turbidity are available in Appendix G – Time Series Plots of Storm and Non-Storm Events. Figures 9 and 10 depict probability plots of turbidity and relative fluorescence data taken at 15-minute and 1-hour intervals, respectively, using online meters.

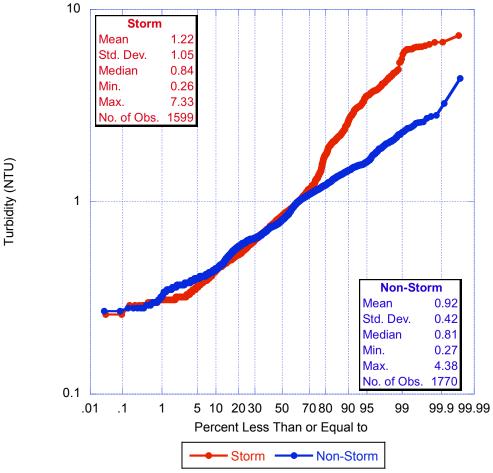


Figure 9. Probability plot of turbidity data

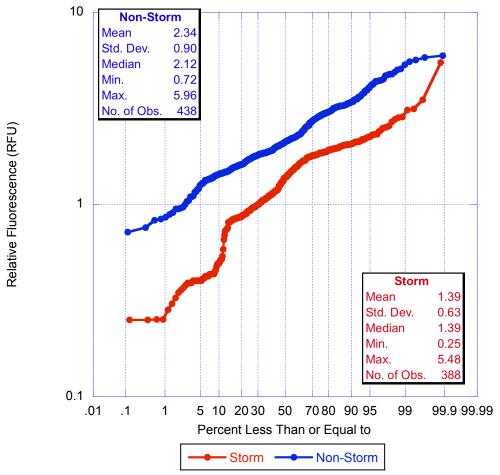


Figure 10. Probability plot of fluorescence data

Note: All values < 6 RFU were removed for the plot because the elevated values represented the presence of bubbles or biofilm growth on the probe.

Turbidity levels depicted in Figure 9 were slightly less in non-storm readings as compared with readings made in conjunction with storm events. Less than 1% of all turbidity values exceeded 5 NTU, each of which correlated with storm events. Using daily averages of the 15-minute interval turbidity data, the turbidity levels are consistent with the SWTR turbidity requirement of less than 5 NTU promulgated by EPA SWTR for exemption from filtration.

From Figure 10, it is apparent that relative fluorescence was reduced during storm events. Since relative fluorescence is typically an indicator of phytoplankton, it can be concluded from the plot in Figure 10 that storm events correspond to decreased levels of algae growth. The storm events produced condition with reduced light and colder weather from which reduced algal growth would be expected.

During the time period of interest (16 November 2008 (10 days before storm 1) to 23 February 2009 (10 days after storm 4)), storm event boron data are available from this study. For the same time period, corresponding boron data (storm and

non-storm) are available related to routine WBMWD monitoring. Weck Laboratory was contracted to assist with the data analysis for the stormwater monitoring study, whereas United Water Laboratory was contracted for the routine WBMWD monitoring. Both laboratories utilized the ICP-MS method (EPA 200.8). As evident in Figure 11, some discrepancies were identified in the boron data reported by Weck Laboratory.

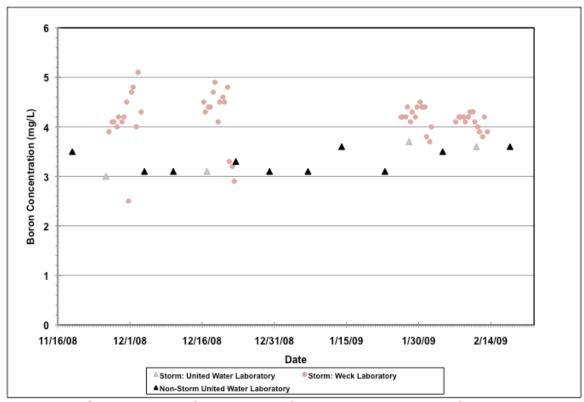


Figure 11. Comparison of boron data from two laboratories for storm and non-storm events

During storm events, the range of the boron data produced by Weck Laboratory is greater (2.5-5.1 mg/L), as compared to the boron data produced by United Water Laboratory (3.0-3.7 mg/L). The degree of fluctuations observed between storm and non-storm events were not expected, because stormwater runoff does not constitute a significant source of boron in seawater. It was expected that stormwater runoff would dilute the boron in the seawater, thus resulting in slightly lower concentrations during storm events. Given these concerns, the Weck Laboratory boron results were dismissed and only data from United Water Laboratory are presented herein.

3.3 El Segundo Desalination Pilot Plant Stormwater Monitoring 3.3.1 Raw Water Quality

Several of the constituents that were monitored have primary and secondary maximum contaminant levels (MCLs) that are regulated by the Safe Drinking Water Act (SDWA). In addition to the national guidelines, some contaminants are

regulated by the CDPH with notification levels (NLs). Appendix H – Constituents with MCLs and NLs During Storm Events features a table quantifying the constituents from the stormwater monitoring in terms of corresponding MCLs and NLs.

Summary statistics of all constituents detected in the raw water are provided in Table 7. An additional summary of the comprehensive statistics through each stage of the treatment process for these detected constituents is provided in Appendix I – Summary Statistics of all Detected Constituents for Storm Events.

Table 7. Summary of detected raw water quality parameters during storm events

Water Quality Parameter	Units	Meanª	Standard Deviation ^a	Median ^b	Minimum ^b	Maximum	Number of Observations	Number of Non-Detects	Reporting Limit ^b
			Inorg	anic para	ameters°				
Aluminum, total	μg/l	NA	NA NA	<50	<50	200	56	44	50
Arsenic, total	µg/l	NA	NA	<4	<4	4	56	55	4
Barium, total ^d	μg/l	NA	NA	6	6	8	14	1	5;10
Boron, total	mg/L	4.18	0.44	4.20	2.50	5.10	56	0	0.01;0.02
Chromium, total	μg/l	NA	NA	<2	<2	55	56	55	2
Copper, total	μg/l	NA	NA	<5	<5	9	56	55	5
Iron, total	μg/l	NA	NA	<200	<200	6000	56	52	200
Manganese, total	μg/l	NA	NA	<2	<2	42	56	28	2
Molybdenum, total	μg/l	11	2	10	9	22	56	0	1
Selenium, total	μg/l	NA	NA	6	<4	9	56	13	4
Strontium, totald	μg/l	7179	278	7100	6900	8000	14	0	2
Tin, total	μg/l	NA	NA	<2	<2	2	56	55	2;4
Titanium, total µg/l		NA	NA	<20	<20	31	56	53	20
Uranium rad ^d	μg/l	NA	NA	3	<2	3	14	2	2;4
Vanadium, total	μg/l	NA	NA	<5	<5 8		56	37	5
Zinc, total	μg/l	NA	NA	<50	<50	71	56	55	50
			Org	anic para	meters ^e				
Bis(2-ethylhexyl) phthalate	μg/l	NA	NA	<3	<3	4	56	55	3
Caffeine	μg/l	NA	NA	<0.1	<0.1	0.3	56	55	0.1
			Phy	sical para	ameters				
Ammonia as N	mg/l	NA	NA	<0.1	<0.1	0.1	56	55	0.1
Conductivity ^f	mS/cm	49.17	0.90	49.32	44.33	49.87	32	0	0.01
Nitrate as N	mg/l	NA	NA	<0.1	<0.1	550.0	56	54	0.1
Phosphorus, total as P	μg/l	35	7	35	22	59	56	0	10
Fluorescence ⁹	RFU	1.39	0.63	1.39	0.25	5.48	388	0	0.1
pН ^f	pH units	8.18	0.35	8.10	7.47	9.33	35	0	0.01
Temperature ^f	°C	15.31	1.52	14.85	12.50	18.10	32	0	NA
Turbidity ⁹	NTU	1.22	1.05	0.84	0.26	7.33	1599	0	0.001
UV 254	1/cm	NA	NA	0.013	<0.009	0.042	56	5	0.009
					parameters ^t				
E.coli ⁱ	MPN/100 ml	NA	NA	<2	<2	13	30	22	2
Enterococcus	MPN/100 ml	NA	NA	<10	<1	21	59	49	1;10
Fecal coliform	MPN/100 ml	NA	NA	<2	<2	30	76	44	2
Total coliform	MPN/100 ml	NA	NA	4	<2	170	72	23	2

[&]quot;Mean and standard deviations were only computed for those analytes that were detected in all samples analyzed; For those analytes that resulted in at least one non-detect, the mean and standard deviation are reported as NA (not applicable)

"All samples analyzed for the following organic parameters were below the detection or reporting limit: 2,4-Dinitrotoluene, 4,4'-DDD, 4,4'-DDT, Acenaphthene, Acenaphthylene, Acetochlor, Alachlor, Aldrin, alpha-BHC, Benzo (g,h.) perylene, Captan, Dieldrin, Endosulfan sulfate, gamma-BHC (Lindane), Metolachlor, Prometryn, Benzo (k) fluoranthene, Chloropropham, Diethyl phthalate, Endrin (apma-Chlordane, Metribuzin, Propachlor, alpha-Chlordane, beta-BHC, Chrysene, Dimethodate, Endrin aldehyde, Heptachlor, Molinate, Pyrene, Anthracene, Cyanazine, Dimethyl phthalate, Endrin ketone, Heptachlor epoxide, Naphthalene, Simazine, Atrazine, Bromacil, delta-BHC, Diphenamid, EPTC, Hexachlorobenzene, PCNB, Terbacil, Benzo (a) anthracene, Butachlor, Di-n-octyl phthalate, Disuffoton, Ethion, Hexachlorocyclopentadiene, Pentachlorophenol, Thiobencarb, Benzo (a) pyrene, Butyl benzyl phthalate, Disuffoton, Ethion, Hexachlorocyclopentadiene, Pentachlorophenol, Thiobencarb, Benzo (a) pyrene, Butyl benzyl phthalate, Disuffoton, Ethion, Hexachlorocyclopentadiene, Pentachlorophenol, Thiobencarb, Benzo (a) pyrene, Butyl benzyl phthalate, Diszinon, Endosulfan II, Fluorene, Methoxychlor, Prometon, Trithion, 1,1-Dichlorochane, 1,2,4-Trichlorobenzene, 2-Chlorotoluene, Bromochloromethane, Chloroform, Dichlorodifluoromethane (Freon 12), m.p-Xylene, p-Dichlorobenzene, Tollene, 1,1,1-Trichlorochane, 1,3-Dichloropropene, Bromodichloromethane, Chlorochane, 1,3-Dichloropropene, Methyl tert-butyl ether, Romenon, Fron 113, n-Propylbenzene, Styrene, Trichlorochane, 1,1,2-Trichlorochane, 1,3-Dichloropropane, 4-Chlorotoluene, Bromomethane, cis-1,3-Dichloropropane, Freon 113, n-Propylbenzene, Styrene, Trichlorochane, 1,1,2-Trichlorochane, 1,3-Dichlorochane, A-Methyl-2-pentanone, Carbon tetrachlorothane, Bopropylbenzene, O-Dichlorobenzene, Errabutylbenzene, Myllylenzene, Myllylenzene, Myllylense, Myllylense, B

Twenty-seven inorganic constituents were tested, and sixteen were detected in the raw water. Of these, only seven were detected in the finished water.

Of seventy-four semi-volatile organics tested, only caffeine and bis(2-ethylhexyl) phthalate were detected in the raw water. Each of these contaminants was only

bUse of different dilution factors resulted in multiple reporting limits for some constituents; Median values for constituents having multiple reporting limits and detected values above and below the reporting limits are reported as NA (not applicable) to avoid ambiguity; The minimum values is reported as the lowest detected value or< lowest detection limit, which ever value is lower

[°]All samples analyzed for the following inorganic parameters were below the detection or reporting limit: nitrite, cadmium, beryllium, antimony, cobalt, mercury, nickel, silver, thallium, tungsten and zirconium

Data only available for storm event 1

Data only available for storm events 1-3

⁹Data only available for storm events 2 and 3

^hAll samples analyzed for the following microbiological parameters were below the detection or reporting limit: F-specific coliphage, human adenoviruses and human enteroviruses Data only available for storm event 4

detected once, with values near the reporting limit. This demonstrates a lack of anthropogenic semi-volatiles. It is important to recognize that bis(2-ethylhexyl) phthalate is ubiquitous and often found as a contaminant in laboratories and in sample collection vessels.

All samples were non-detect for male-specific coliphage and human pathogens, suggesting little impact from urban runoff on the West Basin El Segundo seawater intake. The viral detection limit for this study was approximately one virus per liter of sample water. Although a larger sample size may have produced some positive results, the concentrations would still be expected to be far below that of polluted coastal seawater.

3.3.2 Granular Media and Arkal Disc Filtrates

Previous research has demonstrated that larger particulates from open-intake seawater sources, such as shell fragments, compromise downstream microfilters. Pre-straining filtration using a 100-micron disc filter has been successfully employed by WBMWD and others in order to protect the integrity of downstream microfilters. An alternate pre-straining approach using a high-rate granular media filter (GMF) was investigated at the WBMWD pilot plant treatment, with the goal of developing a more robust pretreatment process at a reduced total water cost. The WBMWD pilot plant process configuration thus included the two different pre-straining systems, high-rate GMF and Arkal disc filters, operating in parallel on pre-screened raw ocean water followed by identical microfiltration (MF) systems.

Lauri et al. (2009) used water quality data generated during testing of the pilot plant to assess operating performances and compare the two pre-straining systems. It was noted that with average seawater turbidity and quality, the GMF produced water quality that approached compliance levels for USEPA drinking water regulations (e.g., 0.3 NTU or less in 95% of filtered water samples) without the addition of coagulant. Comparison of the filtrate from the identical Pall microfilters provided an additional measure of the feedwater quality from the parallel GMF and Arkal disc filters located upstream. The transmembrane pressure (TMP) downstream of the GMF was consistently less than the corresponding TMP downstream of the disc filter system, indicating higher quality feedwater and improved performance from the GMF.

During the period from April 20 to May 19, 2009, Lauri et al. (2009) cited elevated phytoplankton levels and increased biological activity in the seawater proximal to the El Segundo pilot plant, indicating an algal bloom. This bloom event resulted in slightly elevated feed water turbidity levels of 1.5 to 2 NTU and differential pressure increase from 5 psi to 10-12 psi over a 48-hour run time, however the GMF produced a consistent filtrate turbidity range of 0.2 to 0.5 NTU (Lauri et al., 2009). This demonstrated the ability of the GMF to perform with reduced capital costs and a smaller footprint. Following these results, loading rates were readjusted to match the pilot design specifications (lowered from 23 to 20

gpm/ft.²) and test the corresponding differential pressure for the GMF. By lowering the loading rate 15%, the differential pressure rise was reduced by 50%, thereby reducing energy consumption and operating costs. Further life-cycle cost evaluation is required to fully weigh the advantages of providing reduced capital costs and space requirements (elevated loading rate) against the benefits of reduced operational and energy costs (lower loading rate).

Following storm events, urban runoff supplies nutrients into the waters proximal to the WBMWD pilot intake. The nutrient loading increases the potential for biological activity, particularly algal blooms, and often contributes to membrane biofouling. One indicator of membrane biofouling is increased TMP. Lauri et al. (2009) collected TMP data at the EI Segundo pilot plant from the identical Pall microfilters operating in parallel downstream of GMF and disc filters during the period from November 10 to December 14, 2008. Storm event 1 occurred on November 25, and the previously consistent TMP values downstream of both Pall microfilters increased steadily during the subsequent two-week period. This increase in TMP was likely caused by biofouling related to the storm event. Although the TMP increased on both microfiltration systems, the Pall 1 – Disc Filter TMP rose more rapidly than the Pall 2 – GMF TMP. Ultimately, the Pall 1 – Disc Filter reached a terminal TMP of 40 psi, requiring that the unit be shutdown for cleaning. The Pall 2 – GMF system was also shutdown for cleaning three days later (TMP of 30 psi), however it never attained the terminal TMP of 40 psi.

Some inorganic parameters were detected at concentrations near the detection limit in the GMF and Arkal disc filtrates, but never detected in the raw water intake. Antimony, silver, and thallium were detected once and cobalt was detected twice in the GMF filtrate. Cobalt was detected once in the Arkal filtrate. These detects are suspect and most likely attributed to laboratory error.

3.3.3 Pall Microfiltration 1 and 2

Microfiltration units are typically utilized to remove particulates, such as insoluble metals and turbidity, and microbes. A summary of the microbiological data is presented in Table 8.

Table 8. Microbiological quality of raw water intake and Pall microfiltrate

	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	4. 9.											
Water Quality		Mean	Standard	Median ^b	Minimum ^b		Number of	Number of	Reporting				
Parameter	Units	Wicaii	Deviationa	Wedian	William	Maximum	Observations	Non-Detects	Limit ^b				
Raw water intake													
E.coli ^c	MPN/100 ml	NA	NA	<2	<2	13	30	22	2				
Enterococcus	MPN/100 ml	NA	NA	<10	<1	21	59	49	1;10				
Fecal coliform	MPN/100 ml	NA	NA	<2	<2	30	76	44	2				
Total coliform	MPN/100 ml	NA	NA	4	<2	170	72	23	2				
Turbidity	NTU	1.22	1.05	0.84	0.26	7.33	1599	0	0.001				
Pall microfiltrates ^d													
E.coli ^c	MPN/100 ml	ND	ND	ND	ND	ND	17	17	2				
Enterococcus	MPN/100 ml	NA	NA	<10	<1	10	28	26	1;10				
Fecal coliform	MPN/100 ml	ND	ND	ND	ND	ND	28	28	2				
Total coliform	MPN/100 ml	ND	ND	ND	ND	ND	28	28	2				
Turbidity ^e	NTU	0.03	0.04	0.03	0.02	0.92	1233	0	0.001				

^{*}Mean and standard deviations were only computed for those analytes that were detected in all samples analyzed; Otherwise, ND (non-detect) is utilized to represent scenarios who be of different dilution factors resulted in multiple reporting limits for some constituents; Median values for constituents having multiple reporting limits and detected values above and below the reporting limits are reported as NA (not applicable) to avoid ambiguity; The minimum values is reported as the lowest detected value or < lowest detection limit, which ever value is lower

All effluent samples from the microfiltration unit were free of total coliform, fecal coliform and *E. Coli*. Of the 28 samples from the microfiltration unit that were analyzed for *enterococcus*, 26 samples were below the detection limit and 2 samples were detected at the detection limit. The detection of *enterococci* in the MF filtrate is problematic, because it is inconsistent with known removal efficiency of bacteria the size of *enterococci* via microfiltration. These data are suspect, because the application of the method was questionable. Additional discussion of these results is available in Appendix F – Enterolert Discussion.

Thallium was detected once in the Pall 1 filtrate at a concentration near the detection limit, but was never detected in the raw water intake. This detect is suspect and most likely attributed to laboratory error.

3.3.4 Reverse Osmosis 1 and 2

The purpose of the RO treatment stage is to reduce the concentration of dissolved solids. Table 9 provides a summary of the water quality constituents detected in the permeates from the parallel RO1 and 2 treatment units. The raw water intake quality is also provided for comparison purposes.

[°]Data only available for storm event 4

dStatistics are based on composite Pall microfiltrates 1 and 2

^{*}Data only available for storm event 1

Table 9. Summary statistics for raw water intake and reverse osmosis (RO) 1 and 2 permeate

abio di daiii	<u>,</u>											 ,			P011110				
		Inorganic Parameters								Organic Physical Parameters							Microbiological Parameters		
Water Quality Parameter	Aluminum, total	Boron, total	Copper, total	Iron, total	Manganese, total	Strontium, total ^a	Tin, total	Vanadium, total	Zinc, total	Bis(2-ethylhexyl) phthalate	Ammonia as N	Conductivity ^b	Nitrate as N	pН	Temperature ^b	Turbidity	UV 254	Enterococcus	Total colifor
Units	μg/l	mg/L	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	mg/l	mS/cm	mg/l	pH units	°C	NTU	1/cm	MPN/100 ml	MPN/100 m
Raw water intake																			
Mean ^c	NA	4.18	NA	NA	NA	7179	NA	NA	NA	NA	NA	49.17	NA	8.18	15.31	1.22	NA	NA	NA
Standard deviation ^c	NA	0.44	NA	NA	NA	278	NA	NA	NA	NA	NA	0.90	NA	0.35	1.52	1.05	NA	NA	NA
Median ^d	<50	4.20	<5	<200	<2	7100	<2	<5	<50	<3	<0.1	49.32	<0.1	8.10	14.85	0.84	0.013	<10	4
Minimum ^d	<50	2.50	<5	<200	<2	6900	<2	<5	<50	<3	<0.1	44.33	<0.1	7.47	12.50	0.26	<0.009	<1	<2
Maximum	200	5.10	9	6000	42	8000	2	8	71	4	0.1	49.9	550.0	9.3	18.10	7.33	0.042	21	170
Number of observations	56	56	56	56	56	14	56	56	56	56	56	32	56	35	32	1599	56	59	72
Number of non-detects	44	0	55	52	28	0	55	37	55	55	55	0	54	0	0	0	5	49	23
Reporting limit ^d	50	0.01;0.02	5	200	2	2	2;4	5	50	3	0.1	0.01	0.1	0.01	NA	0.001	0.009	1;10	2
RO1 permeate																			
Mean ^c	NA	1.24	NA	NA	NA	6.1	NA	NA	NA	NA	NA	0.65	ND	8.67	17.30	0.09	NA	ND	NA
Standard deviation ^c	NA	0.66	NA	NA	NA	0.2	NA	NA	NA	NA	NA	0.49	ND	0.35	1.26	0.03	NA	ND	NA
Median ^d	<5	0.89	<0.5	<20	<0.2	6.2	<0.2	<0.5	<5	<3	<0.1	0.37	ND	8.76	16.90	0.08	<0.009	ND	<2
Minimum ^d	<5	0.60	<0.5	<20	<0.2	5.7	<0.2	<0.5	<5	<3	<0.1	0.003	ND	7.71	16.10	0.05	<0.009	ND	<2
Maximum	7	2.40	1.3	96	2.3	6.4	0.7	1.7	10	240	0.8	2.00	ND	9.3	19.80	0.13	0.034	ND	2
Number of observations	48	48	48	48	48	14	48	48	48	47	48	1436	48	27	9	9	48	48	48
Number of non-detects	39	0	45	47	35	0	46	45	43	30	37	0	48	0	0	0	37	48	47
Reporting limit ^d	5	0.001;0.01	0.5	20	0.2	0.2	0.2	0.5	5	3	0.1	0.0001	0.1	0.01	NA	0.001	0.009	1	2
RO2 permeate																			
Mean°	NA	1.32	NA	ND	NA	NA	NA	NA	NA	NA	NA	0.90	NA	8.35	17.66	0.08	NA	NA	ND
Standard deviation ^c	NA	0.73	NA	ND	NA	NA	NA	NA	NA	NA	NA	0.70	NA	0.44	1.12	0.02	NA	NA	ND
Median ^d	<5	0.83	<0.5	ND	<0.2	5.6	<0.2	<0.5	<5	<3	<0.1	0.34	<0.1	8.36	17.60	0.07	<0.009	<1	ND
Minimum ^d	<5	0.59	<0.5	ND	<0.2	<0.2	<0.2	<0.5	<5	<3	<0.1	0.17	<0.1	7.23	16.20	0.04	<0.009	<1	ND
Maximum	10	2.50	0.6	ND	4.7	6.6	0.7	0.6	15	94	0.3	2.00	55.0	9.2	19.20	0.13	0.009	1	ND
Number of observations	38	38	38	38	38	14	38	38	38	38	38	1437	38	20	9	9	38	38	38
Number of non-detects	32	0	37	38	26	1	37	36	35	22	37	0	37	0	0	0	37	36	38
Reporting limit ^d	5	0.001;0.01	0.5	20	0.2	0.2	0.2	0.5	5	3	0.1	0.0001	0.1	0.01	NA	0.001	0.009	1;10	2

Data only available for storm event 1

Data only available for storm events 1-3

^{&#}x27;Mean and standard deviations were only computed for those analytes that were detected in all samples analyzed; Otherwise, ND (non-detect) is utilized to represent scenarios where all samples were below the reporting limit and NA (not applicable) is utilized for constituents detected in at least one sample

⁴Use of different dilution factors resulted in multiple reporting limits are reported as NA (not applicable) to avoid ambiguity, The minimum values is reported as the lowest detected value or < lowest detection limit, which ever value is lower

The RO effectively addressed constituents found in the raw seawater. It is important to note that the median concentrations of bis(2-ethylhexyl) phthalate and ammonia were below the detection limit in both raw seawater and RO 1 and 2 permeates, however the maximum values exceeded the raw seawater concentration. Bis(2-ethylhexyl) phthalate (DEHP) is likely present in the permeate due to its introduction during water quality analysis, as it is important to recognize DEHP is ubiquitous and often found as a contaminant in laboratories and in sample collection vessels. The presence of ammonia can be attributed to the use of preformed chloramines during experimental work with chlorine as a disinfectant. RO process shutdowns with chloramines exposed to seawater in the pressure vessels may have caused membrane oxidation, which likely contributed to more variable results than typically observed. The detection of UV 254 was not expected in the RO permeates and likely indicates biofouling on the RO membrane. Enterococcus was detected in the RO 2 permeate, but these data are problematic and there is doubt surrounding the proper implementation of the method. The suspect *enterococcus* results are discussed in detail in Appendix F – Enterolert Discussion.

Some inorganic parameters were detected at concentrations near the detection limit in the RO 1 and 2 permeates, but were never detected in the raw water intake. Silver and lead were detected twice in the RO 1 permeate and thorium was detected once in the RO 2 permeate. These detects are suspect and most likely attributed to laboratory error.

3.3.5 Second Pass Reverse Osmosis

Classically, in addition to the first pass of RO membranes, the second pass RO has been utilized in seawater desalination to ensure proper removal of boron, sodium and chloride. These monovalent sodium and chloride ions are present at high concentrations in seawater, thus desalination plants often utilize a second pass RO as a polishing step. Boron is a low molecular weight compound poorly rejected by SWRO membranes, further necessitating the second pass to achieve the CDPH NL of 1 mg/L.

With respect to boron removal by the RO membranes during storm events, limited conclusions can be drawn due to concerns surrounding the application of the boron detection method by Weck Laboratory and the minimal data availability from the routine WBMWD monitoring. As depicted in Figure 12, the routine WBMWD monitoring data suggest that the first set of RO membranes (RO1 and RO2 from the treatment train) are capable of reducing the boron concentration to meet the 1 mg/L NL determined by the CDPH.

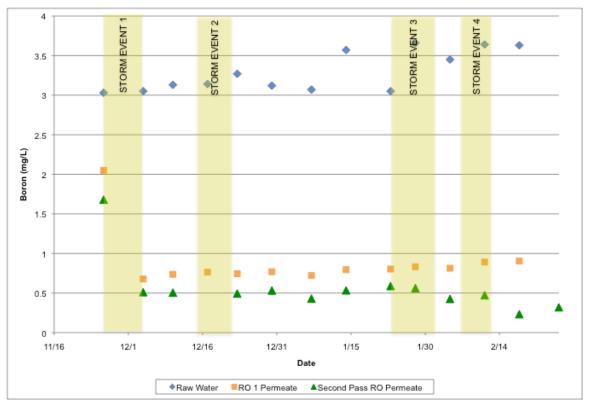


Figure 12. Routine WBMWD monitoring during storm and non-storm events^a

^alt is important to note that the elevated boron in RO permeates in late November 2008 is attributed to experimental work with chloramines. The chloramines used during the experimental work caused membrane oxidation, which likely compromised membrane performance and required the replacement of the RO membranes on December 3rd, 2008.

Although limited data are available, the results in Figure 12 suggest that storm events did not affect RO performance for the removal of boron. An ideal water quality goal (as defined in TM 1 from Phase A – Preliminary Design Development, Oct. 2006) for boron is less than or equal to 0.5 mg/L. This reduced concentration is recommended, because the 1 mg/L NL for boron is considered toxic to various plant species. As visible in Figure 12, the mean boron concentration following second pass RO is still greater than the ideal water quality goal, and indicates a potential limitation in the application of the finished water. One possible approach to achieve boron levels that are consistent with the ideal water quality goal would be to blend the desalination product water with conventional water supplies that have much lower boron concentrations.

As presented in Table 10, UV 254 was also detected in the second pass RO permeate, most likely indicating biofouling of the membrane.

Table 10. Summary of detected finished water quality parameters during storm events

Storin events									
Water Quality	Units	Meana	Standard	Medianb	Minimum ^b	Mavimum	Number of	Number of	Reporting
Parameter	Onits	Wicaii	Deviation	Wedian	William	Waxiiiiuiii	Observations	Non-Detects	Limit ^b
			İr	norganic _l	parameters				
Aluminum, total	μg/l	NA	NA	<5	<5	8	38	26	5
Boron, total	mg/L	0.86	0.57	0.56	0.37	2.20	38	0	0.001;0.01
Copper, total	μg/l	NA	NA	<0.5	<0.5	1.5	38	37	0.5
Manganese, total	μg/l	NA	NA	<0.2	<0.2	18.0	38	28	0.2
Molybdenum, total	μg/l	NA	NA	<0.1	<0.1	0.2	38	37	0.1
Strontium, total ^c	μg/l	NA	NA	<0.2	<0.2	5.8	10	9	0.2
Tin, total	μg/l	NA	NA	<0.2	<0.2	0.3	38	36	0.2
Vanadium, total	μg/l	NA	NA	<0.5	<0.5	1.8	38	34	0.5
				Organic p	arameters				
Bis(2-ethylhexyl) phthalate	μg/l	NA	NA	<3	<3	69	38	37	3
			F	hysical p	arameters				
Ammonia as N	mg/l	NA	NA	<0.1	<0.1	1.5	38	25	0.1
Conductivity ^d	μS/cm	41.48	39.77	13.43	1.59	100.06	1439	0	0.01
Nitrate as N	mg/l	NA	NA	<0.1	<0.1	55.0	38	37	0.1
pН	pH units	8.65	0.93	8.93	5.96	9.62	21	0	0.01
Temperature ^d	°C	21.84	1.35	21.10	20.70	23.80	5	0	NA
Turbidity ^c	NTU	0.07	0.02	0.08	0.05	0.09	5.00	0.00	0.001
UV 254	1/cm	NA	NA	<0.009	<0.009	0.046	38	27	0.009
			Micı	obiologic	al paramete	ers			
Enterococcus	MPN/100 ml	NA	NA	NA	<1	10	38	34	1;10

^{*}Mean and standard deviations were only computed for those analytes that were detected in all samples analyzed; Otherwise, ND (non-detect) is utilized to represent scenarios where all samples were below the reporting limit and NA (not applicable) is utilized for constituents detected in at least one sample

Again, maximum values for bis(2-ethylhexyl) phthalate and ammonia in the second pass RO permeate exceeded the maximum values observed for raw seawater. Bis(2-ethylhexyl) phthalate is likely present in the permeate due to its introduction during water quality analysis as discussed above. The presence of ammonia can be attributed to the use of preformed chloramines during experimental work with chlorine as a disinfectant. As mentioned previously, a shutdown during the experimental work with preformed chloramines may have caused membrane oxidation, which likely contributed to more variable results than typically observed.

Enterococcus was observed four times in the second pass RO permeate. Of the 4 instances listed in Table 10 where enterococcus was detected in the second pass RO permeate, 3 of the samples were incorrectly diluted by a factor of 10. On the date when enterococcus was detected in the second pass RO permeate using the correct dilution factor (a dilution factor of 1), the lab reports found no detection of enterococcus in the raw water and RO1 permeate. These unexpected results, combined with the inconsistencies in analysis identified for enterococcus, as well as those found in conjunction with the E. coli, raises doubt surrounding the proper implementation of the method. The validity of the data is discussed further in Appendix F – Enterolert Discussion.

Lead was detected once in the second pass RO permeate at a concentration that was approximately ten times the detection limit, but was never detected in the raw water intake. This detect is suspect and most likely attributed to laboratory error.

bUse of different dilution factors resulted in multiple reporting limits for some constituents; Median values for constituents having multiple reporting limits and detected values above and below the reporting limits are reported as NA (not applicable) to avoid ambiguity; The minimum values is reported as the lowest detected value or < lowest detection limit, which ever value is lower

[°]Data only available for storm event 1

Data only available for storm events 1-3

3.4 Findings/Recommendations

- Overall, the desalination treatment process was successful at removing most of the contaminants identified during the storm events, as evident from comparison between the raw and finished water qualities.
- The current desalination treatment process train is expected to meet the maximum pathogen removal/inactivation requirements from the SWTR, provided a disinfection step is included.
- The microbiological quality is good during both storm and non-storm events, however storms do have a slightly negative impact on the raw water quality at the intake.
- All samples were non-detect for F-specific coliphage and human pathogens, suggesting little impact from urban runoff on the West Basin El Segundo seawater intake.
- Turbidity levels were slightly less for non-storm samples, as compared with stormwater samples, however the overall levels in the raw ocean water are consistent with the SWTR turbidity requirement of less than 5 NTU promulgated by EPA SWTR for exemption from filtration.
- During the stormwater sampling period (November 2008 February 2009), the total coliform, fecal coliform and turbidity levels met the requirements promulgated by EPA SWTR for exemption from filtration.
- It was observed that storm events result in reduced levels of relative fluorescence as compared with non-storm conditions. The reduction is likely due to the related weather conditions (e.g., reduced light and colder temperatures).
- Twenty-seven inorganic constituents were tested, and 16 were detected in the raw water.
- Seventy-four semi-volatile organics were tested, and only caffeine and bis(2-ethylhexyl) phthalate were detected in the raw water. Each of these was only detected once, with values near the reporting limit, and the DEHP levels are suspect for reasons stated above.
- The recommendation that a high-rate granular media filter (GMF) be used as a more efficient pre-straining treatment stage alternative to the Arkal disc filter is supported by the stormwater sampling data collected on this project. Additionally, GMF was demonstrated to be more effective in reducing biofouling in downstream microfilter membranes than the Arkal disc filter (Lauri et al., 2009). It is recommended that during algal blooms a coagulant be added upstream of the GMF to provide further protection for downstream membranes
- Blending desalination product water with conventional water supplies offers a potential solution to consistently meet the ideal water quality goal for boron.

Section 4 – Marine Biotoxin Monitoring 4.1 Introduction

HABs and their associated marine biotoxins have been identified as a concern for West Basin's full-scale desalination treatment plant. In addition to health concerns related to toxins in permeate water, dense aggregation of these phytoplankton, algae or cyanobacteria can reduce the efficiency of desalination pretreatment processes and contribute to biofouling of reverse osmosis (RO) membranes themselves. WBMWD has proposed to investigate the causes and implications of HABs by the approach described in the experimental plan in Appendix D – Marine Biotoxin Monitoring Experimental Plan. A quality assurance and quality control plan for the marine biotoxin monitoring is outlined in Appendix B – Stormwater and Marine Biotoxin Monitoring Quality Assurance and Quality Control Plan.

4.1.1 Procedure Summary

Marine biotoxins associated with HABs in southern California were identified by a comprehensive literature review conducted for this project by Dr. David Caron and his lab group at the University of Southern California. This literature review identified domoic acid, saxitoxin, brevetoxin, okadaic acid and yessotoxin as the biotoxins of concern for southern California. David Caron and the project team used the literature review as the basis for a journal article entitled "Harmful algae and their potential impacts on desalination operations off southern California", which was accepted for publication in *Water Research* (2009) as an additional project outcome. The marine biotoxins considered in the monitoring portion of the study were selected based on of the likelihood of their presence in southern California waters as discussed in the literature review and because of the availability of enzyme-linked immunosorbent assay (ELISA) methods for their analysis.

During the timeline of this study, the majority of the raw water intake samples from the El Segundo pilot plant were non-detect for marine biotoxins. Only domoic acid and saxitoxin were detected in raw water samples, and both toxins were successfully removed by the RO treatment process. To better demonstrate RO biotoxin removal performance, bench-scale testing was conducted, using challenge water with controlled biotoxin concentrations.

The decision to analyze particulate and/or dissolved concentrations of specific biotoxins was based on the relevance of the toxins to southern California, as well as the available detection methods. Domoic acid and brevetoxin were evaluated in both particulate and dissolved forms at the pilot plant because detection methods were available. Due to limited established protocols, however, only particulate okadaic acid and dissolved saxitoxin were evaluated. While the marine organism capable of producing okadaic acid is present in southern California, significant blooms have not been observed and the presence of dissolved okadaic acid has not been documented in the environment.

4.2 Water Quality and Nutrient Monitoring Results

Water quality parameters (e.g., temperature, chlorophyll *a*, fluorescence, turbidity and dissolved oxygen) are being monitored using buoy mooring sensors located at El Segundo and Redondo Beach. Each buoy has sensors attached at the surface and bottom of the ocean. The buoy monitoring system was envisioned as a tool for assisting with the correlation of water quality parameters and both phytoplankton occurrence and biotoxin production. The ability to predict algal blooms and biotoxin production would be valuable for indicating appropriate treatment response. Due to difficulties in buoy monitoring system set-up, limited data are currently available. The currently fully-functioning buoy monitoring systems have the potential to facilitate future work to solve scientific goals relating phytoplankton impact and the desalination treatment process. Results of initial water quality monitoring from buoys moored near El Segundo and Redondo Beach are presented in Figures 13-15.



Figure 13. Surface water quality data from Redondo Beach buoy, March-May 2009

Elevated phytoplankton levels and increased biological activity indicated an algal bloom during the period from April 20 to May 19, 2009, as cited by Lauri et al. (2009). Water quality data from sensors located at the surface of the Redondo Beach mooring system are presented in Figure 13. The data is incomplete for portions of the algal bloom period, however no marked changes were measured in surface water temperature or average turbidity from the available data. As

seen in Figure 13, the beginning of the algal bloom (April 20) corresponded with slightly elevated average dissolved oxygen and chlorophyll *a* levels.

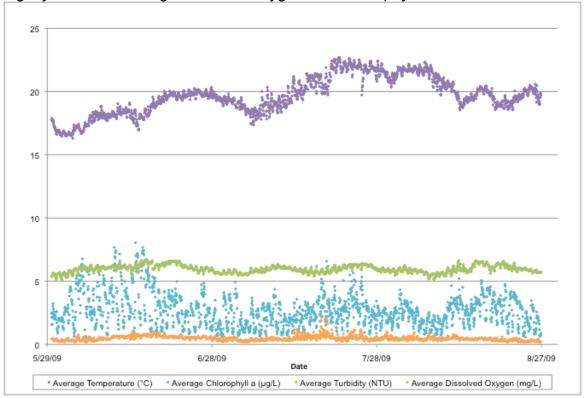


Figure 14. Surface water quality data from El Segundo buoy, May-August 2009

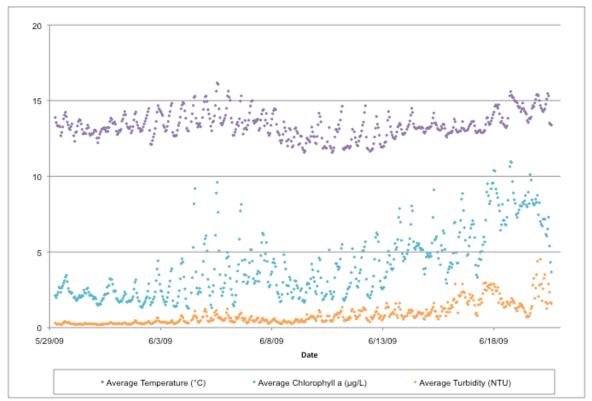


Figure 15. Bottom water quality data from El Segundo buoy, May-June 2009

Sample water quality data presented in Figure 15 serves to characterize conditions at the bottom of the ocean near the El Segundo intake. Increasing levels of chlorophyll *a* and turbidity may indicate a phytoplankton bloom. The oxygen sensor anchored to the ocean floor attached to the El Segundo buoy was damaged, limiting data availability.

4.3 Characterization of Phytoplankton Taxonomy

One of the goals outlined within the project assessment plan was to conduct testing of phytoplankton taxonomy on raw water samples from the El Segundo pilot plant. The desired outcome was to establish the occurrence of phytoplankton taxonomy and marine biotoxins in intake water, as well as the ability of the RO membrane treatment process to remove marine biotoxins. While the results from the bench and pilot experiments demonstrated the efficacy of the RO treatment process in successfully removing marine biotoxins, future correlation of phytoplankton taxonomy and biotoxin production are recommended. Future raw water samples can be tested for regionally specific biotoxins, as well as the presence of the phytoplankton known to produce the target toxins. Using additional water quality information provided by the buoy monitoring systems, it may be possible to develop a more complete understanding of the factors contributing to biotoxin production. If so, warning systems can be developed, based on monitoring of the relevant water quality parameters.

4.4 El Segundo Desalination Pilot Plant Results

Biotoxins produced during harmful algal blooms may pose a challenge to desalination treatment plants. Four biotoxins of potential concern among southern California ocean water, namely brevetoxin, domoic acid, okadaic acid and saxitoxin, were measured at the El Segundo desalination pilot plant raw water intake (point "1" on Figure 2) and the reverse osmosis effluent (point "6" on Figure 2). The purpose of this effort was to determine if these biotoxins are a viable concern and the efficacy of the RO system to remove detected biotoxins.

Of the four biotoxins examined, only domoic acid and saxitoxin were detected in the raw ocean water intake. Summary statistics are provided in Table 11. Table 11. Biotoxin analysis summary statistics for El Segundo desalination pilot plant intake^a

Marine Biotoxin	Detection Method	Units	Median ^b	Minimum ^b	Maximum	Number of Observations	Number of Non-Detects	Detection Limit
Brevetoxin, Particulate ^c	Abraxis ELISAs	μg/l	ND	ND	ND	12	12	0.0008
Brevetoxin, Dissolved ^c	Abraxis ELISAs	μg/l	ND	ND	ND	13	13	0.1
Domoic Acid, Particulate	Biosense ELISAs	μg/l	<0.0025	<0.0025	3.96	97	73	0.0025
Domoic Acid, Particulate	Mercury Science ELISAs	μg/l	<0.007	<0.007	2.40	31	23	0.007
Domoic Acid, Dissolved	Biosense ELISAs	μg/l	<0.01	<0.01	10.1	96	70	0.1
Domoic Acid, Dissolved	Mercury Science ELISAs	μg/l	<0.2	<0.2	3.0	32	27	0.2
Okadaic Acid, Particulate ^c	Abraxis ELISAs	μg/l	ND	NA	NA	12	12	0.008
Saxitoxin, Dissolved	Abraxis ELISAs	μg/l	<0.2	<0.2	0.3	24	20	0.2

^aMean and standard deviations were not computed because all analytes had at least one non-detect among all samples analyzed

^bAll analytes with medians below the detection limit are reported as '<DL'

^cAll samples below the detection limit

The median, minimum and maximum values are the only statistics provided in Table 11, because all biotoxins had at least one non-detect. The presence of biotoxins in the pilot plant intake samples indicates that biotoxins are a potential threat to the public, thus the desalination plant must address these contaminants appropriately. Saxitoxin is known to be the most potent marine toxin, and toxic conditions can exist even when *Alexandrium* is present at levels that do not significantly discolor the water (e.g., in the absence of a bloom). This demonstrates the importance of correlating water quality parameters with the production and/or direct measurement of marine biotoxins to ensure public safety.

The unforeseen difficulties with the buoy set-up hampered the ability to relate results from pilot studies with water quality parameters in the raw water. Overall, only saxitoxin and domoic acid were detected in the raw water samples. Of these detections, few occurred within the dates of the available fluorescence and turbidity data collected from an online meter (see Appendix G – Time Series Plots of Storm and Non-Storm Events). Further study of the correlation between raw water quality parameters and marine biotoxin detection is necessary in order to make any meaningful conclusions.

The results from the pilot studies demonstrate that the RO system completely removed all biotoxins detected in the raw water, as shown in Figures 16-18.

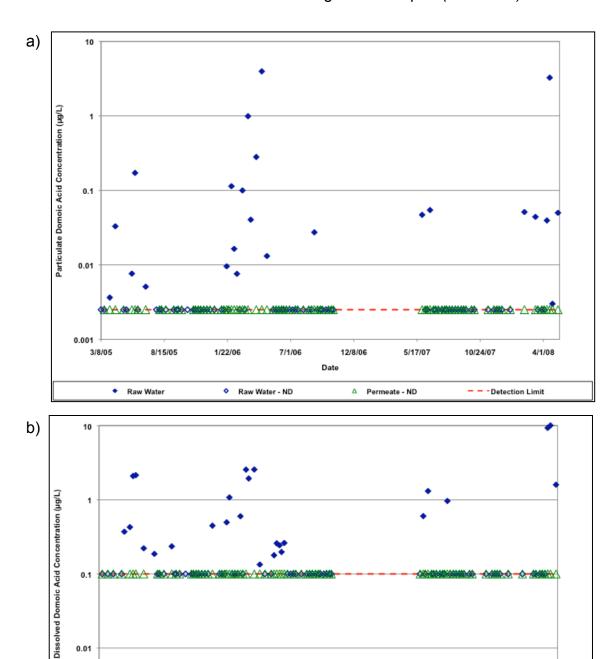


Figure 16. Domoic acid concentrations of El Segundo desalination pilot plant intake and RO permeate - Biosense ELISA method: a) particulate and b) dissolved

Date

12/8/06

△ Permeate - ND

5/17/07

10/24/07

4/1/08

7/1/06

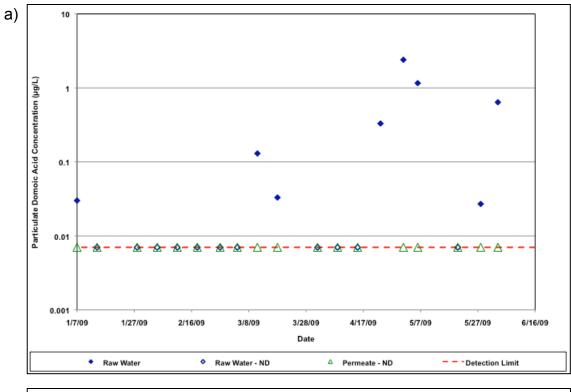
1/22/06

Raw Water - ND

8/15/05

0.01

0.001 3/8/05



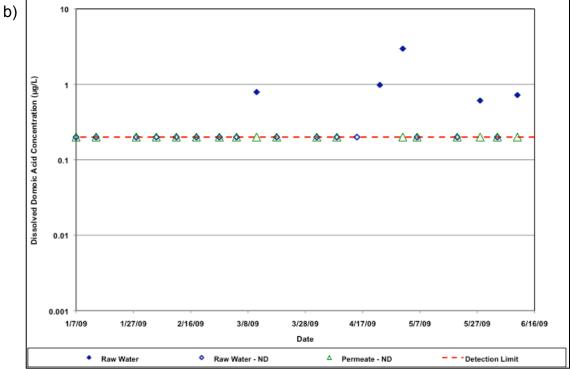


Figure 17. Domoic acid concentrations of El Segundo desalination pilot plant intake and RO permeate – Mercury Science ELISA Method: a) Particulate and b) Dissolved

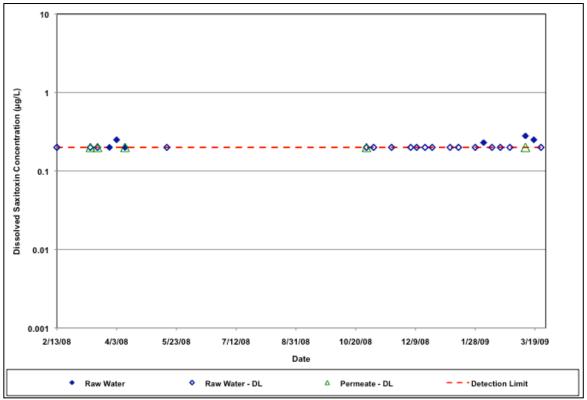


Figure 18. Dissolved saxitoxin concentration of El Segundo desalination pilot plant intake and RO permeate

Although specific to the southern California region, these results demonstrate that marine biotoxins are indeed present in source waters, and need to be addressed via appropriate measures by desalination facilities. These preliminary results indicate that RO treatment is efficient in removing the detected biotoxins.

4.5 Bench-Scale Reverse Osmosis Results

Bench-scale challenge tests were conducted to determine the efficacy of RO membranes for the removal of marine biotoxins under a controlled laboratory setting. Hydranautics SCW4+ RO membranes were challenged with dissolved domoic acid, saxitoxin and brevetoxin, which represent the most relevant biotoxins to southern California, for which ELISA methods were available at the time of study. The biotoxin concentrations used for the bench-scale RO challenge were derived to exceed typical concentrations of dissolved biotoxins found in west coast seawater (Caron et al., 2009). In an effort to consider the worst-case scenario, challenge concentrations used for the bench-scale RO were much higher than typically observed. For example, during the course of this study, the maximum raw seawater saxitoxin and domoic acid concentrations observed were 0.3 and 3.0 μ g/L, respectively, and the average concentrations of saxitoxin and domoic acid used for the bench scale RO experiments were 2.8 and 52.9 μ g/L, respectively.

The RO membranes used for each experiment maintained salt rejections of greater than 99% throughout the challenge tests. As shown in Table 12, all experiments utilized RO membranes with similar salt rejection capabilities.

Table 12. Salt Rejections for each Biotoxin Challenge Test RO Membrane

Biotoxin Challenge	Percent Salt Rejection					
Test Experiment	Mean	Range				
Domoic Acid	99.4	0.06	99.3–99.5			
Saxitoxin	99.5	0.07	99.3–99.6			
Brevetoxin	99.5	0.02	99.4–99.5			

The bench scale RO apparatus was maintained at approximately 9 gfd, in order to match the flux at which the pilot plant is operated. Using the specific flux as an indication of membrane fouling, Figure 19 shows there was initially some fouling (reduced specific flux), but equilibrium was reached approximately 10 hours into the experiments. Once equilibrium was established, the membranes did not exhibit further fouling; this is evidenced by a relatively constant specific flux during the remainder of the bench-scale experiment time period in Figure 19.

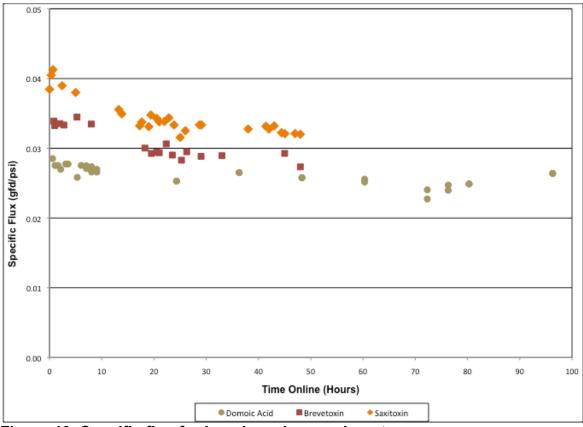


Figure 19. Specific flux for bench scale experiments

Bench-scale results are presented in Figures 20-22 for brevetoxin, domoic acid and saxitoxin.

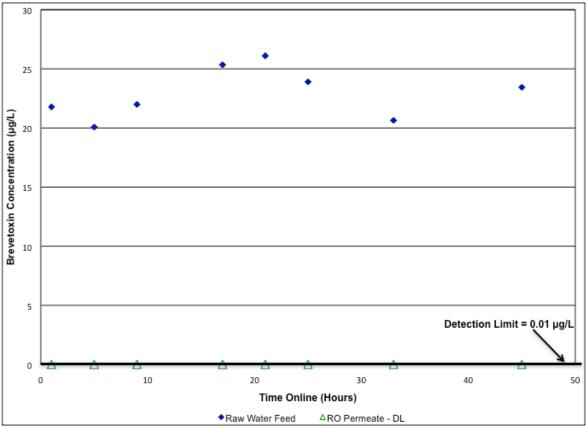


Figure 20. Bench-scale reverse osmosis performance – brevetoxin

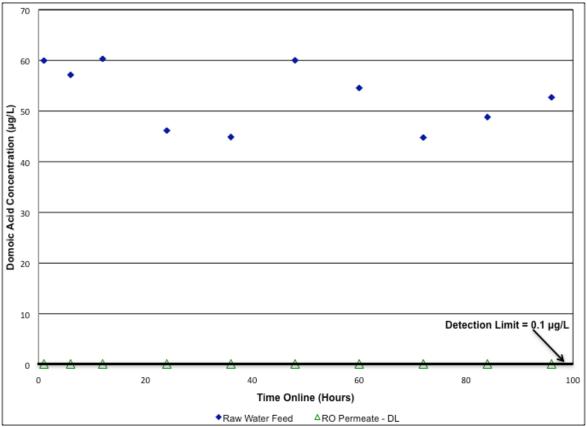


Figure 21. Bench-scale reverse osmosis performance – domic acid

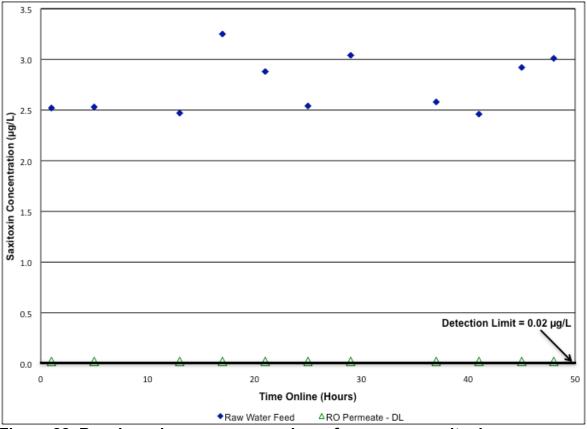


Figure 22. Bench-scale reverse osmosis performance – saxitoxin

As visible in Figures 20-22, dissolved brevetoxin, domoic acid and saxitoxin were all successfully removed by the bench-scale RO process. This supports the results from pilot-scale testing, in which all detected marine biotoxins (domoic acid and saxitoxin) in the raw water were shown to be completely removed through the desalination pilot plant process. The infrequent and unpredictable occurrence of biotoxins in the pilot plant intake water warranted the use of challenge feedwaters with bench-scale experiments. For example, since brevetoxin was not detected in the raw water samples from the pilot study, RO efficacy was inconclusive. To provide further assurance of the RO treatment efficiency for the removal of brevetoxin, bench-scale RO systems were challenged with known concentrations of brevetoxin. If additional marine biotoxins are identified as significant to Southern California waters and associated analytical methods become available, future studies can utilize the RO bench-scale apparatus to test the removal of additional marine biotoxins.

4.6 Findings/Recommendations

The buoy monitoring system is now in proper operating condition. It is
envisioned that the system be used as a tool for correlating water quality
parameters with phytoplankton occurrence and biotoxin production, in
order to develop appropriate treatment response.

- Future correlation of phytoplankton taxonomy and biotoxin production are recommended, particularly in conjunction with physical water quality parameters from the buoy monitoring systems.
- No biotoxins were detected in the RO permeate water in both the pilot and bench scale studies, providing a strong indication of the effectiveness of biotoxin removal through the RO desalination treatment process.
- Of the four biotoxins examined, only domic acid and saxitoxin were detected in the raw water ocean intake. The pilot plant studies demonstrated complete removal of the biotoxins detected in the raw water.
- Further validation of the removal of biotoxins by RO treatment, beyond the pilot testing, was warranted considering infrequent and unpredictable occurrence of biotoxins in seawater, thus bench-scale experiments were conducted. Dissolved domoic acid, brevetoxin and saxitoxin were all successfully removed by the bench-scale RO process to non-detect levels. If future monitoring of the southern California bight indicates the possible presence of additional, currently unidentified biotoxins in the area proposed for the desalination facility, additional bench-scale experiments would be recommended to demonstrate the effectiveness of RO treatment in removing the newly identified biotoxins.

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Appendix A – Stormwater and Marine Biotoxin Monitoring Project Assessment Plan (PAP)

Date: June 30, 2009 **To**: Phil Lauri, P.E

Authors: David R. Hokanson, Ph.D., P.E.

Joanne Chiu Emily Owens

Reviewer: R. Rhodes Trussell, Ph.D., P.E.

R. Shane Trussell, Ph.D., P.E.

Subject: Project Assessment Plan - Critical Raw Water Quality Issues

Unique to Seawater: Marine Phytoplankton Blooms, their

Associated Biotoxins, and Transient Urban Stormwater Inputs¹

I. <u>Project Summary</u>

A. Funding Program: *Proposition 50 Clean Drinking Water,*Coastal and Beach Protection Act of 2002

B. Project Description: This project encompasses four primary tasks: 1) Stormwater Monitoring, 2) Marine Biotoxin Monitoring, 3) Pilot Plant Operations, and 4) Project Workshops. This assessment plan will address tasks 1 and 2.

Comprehensive experimental plans were developed to monitor the influence of stormwater and marine biotoxins on influent and effluent water quality at the West Basin Municipal Water District (WBMWD) El

¹ Note: This draft Project Assessment plan was prepared by Trussell Tech in collaboration with the USC research groups of Dr. David Caron and Dr. Burton Jones.

Segundo pilot site. The pilot facility utilizes seawater from an open ocean intake as its source water for experimental desalination investigation. The treatment process includes two Arkal pretreatment strainer units, a Granular Media Filter (GMF) system, two Pall Microfiltration systems, two first pass Reverse Osmosis (RO) system, and one 2nd pass RO system.

An extensive stormwater sampling event will start and continue for 7 consecutive days once rainfall has exceeded a minimum precipitation of 0.5 inches in 24 hours. A total of 4 events are anticipated. Evaluation of the ability of the overall desalting process to remove the pollutants being assessed will follow each storm event.

In addition to the stormwater sampling discussed above, marine biotoxins will be analyzed in both raw and RO Train 1 permeate waters from the WBMWD EI Segundo pilot plant using phytoplankton taxonomy paired with ELISA method testing for Domoic Acid, Saxitoxin, Brevetoxin, and/or Okadaic Acid over various time periods. Removal of domoic acid, saxitoxin, and brevetoxin will be also be tested at the bench-scale in RO experiments to be conducted at USC under guidance from Trussell Tech with participation of Separation Processes, Inc.

Additionally, buoys equipped with water quality monitor (WQM) sensors will be moored in proximity to WBMWD facilities at El Segundo and Redondo Beach. The WQM will provide measurements of temperature, salinity, dissolved oxygen, depth, chlorophyll a fluorescence, turbidity, and optical backscattering. These additional water quality parameters will be monitored in tandem with marine biotoxin analysis to improve assessment of 'red tide' events and the impacts on the desalination process.

A quality assurance and quality control plan (QA/QC) for these monitoring activities will complement this project assessment plan to ensure the success of these tasks.

II. Stormwater Monitoring

A. Problem Statement: The potential for urban stormwater to deliver pollutants and increase flows to receiving waters over short period of time is well recognized as a problem that must be addressed. Urban stormwater runoff is a major source of contaminants to southern California's coastal waters. Stormwater runoff usually carries sediments, nutrients, organic matter, pathogen, oil and grease, toxic substance and high metal concentrations; these have been accumulating during the dry seasons. West Basin Municipal Water

District (WBMWD) has been researching and developing integrated membrane seawater desalination systems and investigating the operational and water quality implications of these treatment processes for several years. One of the major concerns full-scale desalination treatment plant must manage is the adverse impact of stormwater runoff to the source water fed to the treatment plant. Pilot studies have been conducted to monitor these stormwater impacts to the pilot desalination treatment processes.

i. Identify or characterize baseline data

To-date, WBMWD has monitored four storms. A comprehensive experimental plan has been developed building upon the experience gained from previous studies monitoring the influence of stormwater on the influent water quality at the El Segundo pilot site. The pilot site has been monitored on a regular basis to provide baseline data for evaluation during the stormwater events.

- ii. Identify Pollution source categories
 - Stormwater runoff is generated by precipitation and runoff from land, building rooftops, streets, and other open surface areas, and it usually carries sediments, nutrients, organic matter, pathogen, oil and grease, toxic substance and high metal concentrations which lead to very poor surf zone water quality.
- iii. Identify and describe current restoration activities; Best Management Practices (BMP's); Load reduction activities; Prevention activities West Basin Municipal Water District (WBMWD) has been researching and developing integrated membrane seawater desalination systems and investigating the operational and water quality implications of these treatment processes for several years. A desalination pilot plant was built for these stormwater monitoring programs.
- iv. Describe the manner in which the proposed best management practices or management measures will be implemented. Project team will meet with staff at WBMWD and others, as appropriate, during preparation of experimental plan for stormwater monitoring. Get quotes from laboratories for appropriate analytical work.
- v. Summarize how the effectiveness of the proposed practices or measures in preventing or reducing pollution will be determined. Testing will include evaluation of the ability of the overall desalting process to remove any constituents detected as a result of stormwater influences. A more complete water quality profile will be developed from this project.

- vi. Determine "changes in flow pattern" in affected water bodies

 Part of this stormwater monitoring program is to monitor the influence
 of stormwater runoff on the intake to the desalination pilot plant.
- vii. Determine economic benefits of implementing the project

 A more complete water quality profile will be developed from this project to understand the impacts of stormwater to the influent water quality and the desalination process. Results will be a valuable reference for full-scale plant design development in the future.
- B. Project Activities or Tasks: This stormwater-monitoring program encompasses six sub-tasks described below.

Task 1 – Stormwater Monitoring

Developed a comprehensive experimental plan to monitor the influence of stormwater on the influent water quality at the El Segundo pilot site. For any constituents detected as a result of stormwater influences, testing will include evaluation of the ability of the overall desalting process to remove them. Quality constituents to be addressed in the monitoring program include metals, organics and pathogens and/or indicators of pathogens.

Task 1.1 - Experimental Plan

Task 1.1a – Prepared a draft experimental plan for stormwater monitoring which specified the number of storms to be sampled each year, the samples to be taken during each storm, the analyses to be conducted on the samples and the criteria for evaluating the data obtained.

Task 1.1b – Finalized experimental plan for stormwater monitoring based in input from CDHS and other parties at Workshop No. 1.

Task 1.2 - Quality Assurance/Quality Control Plan

The purpose of this task is to provide a protocol for guaranteeing the accuracy and validity of the data collected during stormwater monitoring. The plan will detail analytical methods, sampling methods, sample handling, shipment and storage methods and sampling logistics. It will also specify the level of duplicate sampling. This plan will be reviewed by a member of the TAP.

Task 1.2a – Prepare a draft QA/QC plan in concert with the preparation of the draft experimental plan for stormwater monitoring. Task 1.2b –Finalize QA/QC plan for stormwater monitoring based in input from CDHS and other parties at Workshop No. 1.

Task 1.3 – Project Assessment Plan

This document. Project Assessment Plans are combined for both Stormwater and Marine Biotoxin Monitoring.

Task 1.4 – Monitoring Coordination and Intermediate Meetings Monitoring has been conducted according to the experimental plan and the QA/QC plan that supports it. Nevertheless necessity usually leads to a few changes as the project goes forward. These changes will be made in a coordinated way involving project staff and project advisors as appropriate.

Task 1.4a – Meet with staff at WBMWD and others, as appropriate, during preparation of experimental plan for stormwater monitoring. Get quotes from laboratories for appropriate analytical work.

Task 1.4b – Coordinated to gather information to finalize experimental plan for stormwater monitoring based in input from CDPH and other parties at Workshop No. 1.

Task 1.5 - Analyze Data and Intermediate Reports

Data from the stormwater monitoring effort will be collected, stored, and checked and the results will be communicated to all parties in the form of quarterly data summaries accompanied by limited discussion.

Task 1.6 - Draft and Final Report

A draft final report that includes stormwater monitoring results will be prepared and, following its review, a final report will be issued.

Task 1.6a – After all data is in and its meaning and interpretation have been discussed at Workshop 2, a draft report on stormwater influences will be prepared for review by the project team and the TAP.

Task 1.6b – Upon receipt of comments on the draft, the final report will be prepared that addresses all comments received.

C. Category of Project Activities or Tasks:

Tasks	Category
Experimental Plan	Planning, Research, Monitoring and Assessment
2. QA/QC Plan	Planning, Research, Monitoring and Assessment
3. Assessment Plan	Planning, Research, Monitoring and Assessment
4. Monitoring Coordination and Intermediate Meetings	Planning, Research, Monitoring and Assessment
5. Analyze Data and Intermediate Reports	Planning, Research, Monitoring and Assessment
4. Draft and Final Report	Planning, Research, Monitoring and Assessment

III. Marine Biotoxin Monitoring

Α. Problem Statement: 'Red Tides' and harmful algal blooms (HABs) containing microalgal species capable of producing toxic compounds are well recognized as a marine water quality problem. In terms of the desalination process, HABs and the marine biotoxins they produce introduce major health concerns, can reduce the efficiency of desalination pretreatment processes, and contribute to biofouling of reverse osmosis (RO) membranes. As such, HABs and marine biotoxins must be addressed as part of a comprehensive assessment of the desalination treatment process by WBMWD. Bench and pilot scale studies are being conducted to monitor the impacts of HABs and marine biotoxins on the pilot desalination treatment processes. Assessment methods include analysis of raw and RO Train 1 permeate waters using phytoplankton taxonomy and ELISA techniques for Domoic Acid, Saxitoxin, Brevetoxin, and/or Okadaic Acid over various time periods, as well as water quality monitoring data from sensors attached to buoy systems located proximally to potential ocean intakes at El Segundo and Redondo Beach.

i. Identify or characterize baseline data

To-date, WBMWD has conducted pilot scale monitoring of Domoic Acid in raw and RO Train 1 permeate waters since March 2005. A comprehensive experimental plan has been developed, building upon the experience gained from a literature review and bench scale studies monitoring the influence of marine biotoxins on influent and effluent water quality at the El Segundo pilot site.

- ii. Identify pollution source categories
 - Marine biotoxins are produced by microalgal species related to 'red tides' and HABs. Algal blooms are associated with changes in nutrient availability, however the mechanisms of toxin production are not well understood. In addition to potentially introducing toxins, algal blooms are composed of dense aggregates of phytoplankton, algae, or Cyanobacteria, and can reduce dissolved oxygen levels in the water.
- iii. Identify and describe current restoration activities; Best Management Practices (BMP's); Load reduction activities; Prevention activities West Basin Municipal Water District (WBMWD) has been researching and developing integrated membrane seawater desalination systems and investigating the operational and water quality implications of these treatment processes for several years. A desalination pilot plant was built in order to conduct extensive marine biotoxin and related water quality monitoring programs.
- iv. Describe the manner in which the proposed best management practices or management measures will be implemented. The project team will meet with staff at WBMWD and others, as appropriate, during preparation of experimental plan for marine biotoxin monitoring. Analytical work will be performed at David Caron's and Burton Jones's laboratories at USC.
- v. Summarize how the effectiveness of the proposed practices or measures in preventing or reducing pollution will be determined Testing will include evaluation of the impact of HABs on the desalination treatment process, in particular the ability of the overall desalting process to remove marine biotoxins. Analysis of toxin test results will be paired with WQM data, to the extent possible, to assist in characterizing the conditions and mechanisms associated with the production and release of marine biotoxins. Together, the results of these monitoring activities will provide a more complete water quality profile.
- vi. Determine "changes in flow pattern" in affected water bodies

 One aspect of the marine biotoxin monitoring program is, to the extent possible, to examine the influence of HABs on the open ocean intake for the desalination pilot plant.
- vii. Determine economic benefits of implementing the project

 A more complete water quality profile will be developed from this project to understand the impacts of HABs and associated marine biotoxins on influent and effluent water quality, as well as the desalination treatment process itself. Results will be a valuable reference for full-scale plant design development in the future.

B. Project Activities or Tasks: This marine biotoxin-monitoring program encompasses six sub-tasks described below.

Task 2 - Marine Biotoxin Monitoring

A comprehensive experimental plan will be developed to monitor the dynamics of marine phytoplankton blooms and biotoxins in the Pacific Ocean in the general vicinity of the El Segundo pilot project. Monitoring will be limited to marine biotoxins for which ELISA analytical kits are available. To the extent feasible, testing will include evaluation of the RO desalting process to remove any toxins detected. The budget allows for samples to be collected and analyzed mainly at USC; USC will do the bulk of the work for this task, with fairly extensive guidance and coordination by Trussell Technologies, Inc.

Task 2.1 – Experimental Plan

Task 2.1a – A draft experimental plan for marine biotoxin monitoring will be prepared in concert with the Caron and Jones Labs at USC. The plan will specify the intensity and frequency of sampling, as well as the target analytes.

Task 2.1b – Finalize experimental plan for marine biotoxin monitoring based on input from CDPH and/or other parties.

Task 2.2 - Quality Assurance/Quality Control Plan

Quality Assurance/Quality Control Plans are combined for both Stormwater and Marine Biotoxin Monitoring.

The purpose of this task is to provide a protocol for guaranteeing the accuracy and validity of the data collected in the marine biotoxin monitoring program. The plan will detail analytical methods, sampling methods, sample handling, shipment and storage methods and sampling logistics. It will also specify the level of duplicate sampling. A member of the TAP will also review this plan.

Task 2.2a – Working with the Caron and Jones Labs at USC, prepare a draft QA/QC plan in concert with the preparation of the draft experimental plan for marine biotoxin monitoring.

Task 2.2b – Finalize QA/QC plan for marine biotoxin monitoring based on input from CDPH and/or other parties.

Task 2.3 – Project Assessment Plan

This document. Project Assessment Plans are combined for both Stormwater and Marine Biotoxin Monitoring.

Task 2.4 – Monitoring Coordination and Intermediate Meetings

Task 2.4a – Meet with staff at WBMWD and others, as appropriate, during the preparation of an experimental plan for marine biotoxin monitoring. Work with the USC lab to get prices for the required analytical work.

Task 2.4b – Gather information to finalize experimental plan for marine biotoxin monitoring based in input from CDPH and/or other parties.

Task 2.5 – Analyze Data and Intermediate Reports

This task includes collection and dissemination of data from biotoxin sampling, as well as benchtop testing support for USC to demonstrate biotoxin removal.

Task 2.5a – Data collection and dissemination - Data from the marine biotoxin monitoring effort will be collected, stored, and checked. The results will be communicated to all parties.

Task 2.5b – Benchtop RO testing – Trussell Technologies will oversee the benchtop RO testing. They will send an engineer affiliated with Separation Processes, Inc. (SPI) to the Caron Laboratory at USC to assist in testing of biotoxin removal.

Task 2.6 - Draft and Final Report

A draft report on marine biotoxin monitoring results will be prepared and, following its review, a final report will be issued.

Task 2.6a – After all data has been compiled and its meaning and interpretation have been discussed, a draft final report that includes marine biotoxin influences will be prepared for review by the project team and the TAP.

Task 2.6b – Upon receipt of comments on the draft, the final report will be prepared that addresses all comments received.

C. Category of Project Activities or Tasks:

Tasks	Category
Experimental Plan	Planning, Research, Monitoring and Assessment
2. QA/QC Plan	Planning, Research, Monitoring and Assessment
3. Assessment Plan	Planning, Research, Monitoring and Assessment
4. Monitoring Coordination and Intermediate Meetings	Planning, Research, Monitoring and Assessment
5. Analyze Data and Intermediate Reports	Planning, Research, Monitoring and Assessment

4. Draft and Final Report	Planning, Research, Monitoring and Assessment
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IV. Project Goals & Desired Outcomes

The goals of this project:

- 1. Develop a stormwater sampling plan.
- 2. Perform sampling at various sampling locations at the El Segundo pilot site for 7 days after rainfall has produced a minimum precipitation of 0.5 inches in a 24-hour period.
- 3. Create a plan for marine biotoxin sampling.
- 4. Conduct testing for phytoplankton taxonomy on the raw water at the El Segundo pilot plant. Conduct testing for Domoic Acid, Saxitoxin, Brevetoxin, and/or Okadaic Acid on samples of raw and RO Train 1 permeate waters at the El Segundo pilot plant.
- 5. Deploy buoys with WQM and nutrient sensors in proximity to potential intake locations at El Segundo and Redondo Beach.
- 6. Produce a water quality profile for future full-scale desalination plant design purpose.

The desired outcomes of this project:

- 1. Development of a comprehensive stormwater sampling plan that enables the success of the sampling process during the stormwater events.
- 2. Understand the impacts of stormwater runoff on the El Segundo pilot intake, identify any potential human pathogens, and monitor the treatment and removal of these components through the RO membrane treatment process.
- Development of a comprehensive marine biotoxin sampling plan that enables successful analysis of raw water at the El Segundo pilot for phytoplankton taxa, as well as raw and RO Train 1 permeate waters for the presence and removal of specific biotoxins.
- 4. Establish the occurrence of phytoplankton taxonomy and marine biotoxins in intake water, as well as the ability of the RO membrane treatment process to remove marine biotoxins.
- 5. To the extent possible, correlate the results of marine biotoxin testing with WQM and nutrient sensing data in order to increase understanding of the conditions and mechanisms related to marine biotoxin release.
- 6. Obtain sufficient water quality data for evaluation of desalination treatment processes.

V. Project Performance Measures Table







Appendix B – Stormwater and Marine Biotoxin Monitoring Quality Assurance and Quality Control Plan

Date: December 30, 2008

Revised: June 30, 2009 **To**: Phil Lauri, P.E

Authors: David R. Hokanson, Ph.D., P.E.

Joanne Chiu Emily Owens

Reviewer: R. Rhodes Trussell, Ph.D., P.E.

R. Shane Trussell, Ph.D., P.E.

Subject: QA/QC Plan - Critical Raw Water Quality Issues Unique to

Seawater: Marine Phytoplankton Blooms, their Associated

Biotoxins, and Transient Urban Stormwater Inputs¹

A - PROJECT MANAGEMENT

A.1 Distribution List

The following is a list of the individuals and their organizations, with titles, who will receive copies of the approved QA QC Plan and any subsequent revisions.

West Basin Municipal Water District

17140 S. Avalon Blvd., Suite 210

Carson CA 90746

Project Title	Name	Phone Number	Email
Project Manager	Phil Lauri	310-660-6238	phill@westbasin.org

¹ Note: This draft QA/QC plan was prepared by Trussell Tech in collaboration with the USC research groups of Dr. David Caron and Dr. Burton Jones.

MWH

618 Michillinda Av., Suite 200

Arcadia, CA 91007

Project Title	Name	Phone Number	Email
			John.Robinson@us.mwhglobal.co
Project Manager	John Robinson	(626)568-6369	m

Trussell Technologies, Inc.

232 N. Lake Ave., STE. 300

Pasadena, CA 91101

Project Title	Name	Phone Number	Email
Project Manager	Shane Trussell	(858)458-1030	shane.trussell@trusselltech.com
Project Advisor	Rhodes Trussell	(626)486-0560	rhodes.trussell@trusselltech.com
Project Engineer	David Hokanson	(626)486-0560	david.hokanson@trusselltech.com

California Department of Public Health

1180 Eugenia Place, Suite 200

Carpinteria CA 93013-2000

Title	Name	Phone Number	Email
Chief Regional Sanitary Engineer	Kurt Souza	805-566-1326	kurt.souza@cdph.ca.gov

A.2 Project Organization and Responsibility

WBMWD's project manager, Mr. Phil Lauri, will supervise day-to-day activities regarding project tasks to ensure adequate progress. MWH's project manager, John Robinson, will do the same with respect to the consultant team. Dr. R. Shane Trussell of Trussell Technologies will provide overall leadership of technical team. The project managers will provide direction to task leaders and keep track of tasks to ensure that they are completed in a timely manner. Careful coordination among members of the project management team will ensure that appropriate resources are employed both within the District and among its contracted resources. Regular progress reports will also be provided, including progress reports, budget status and other communications. A Technical Advisory Panel, Drs. Caron, Trussell and Eaton, will provide guidance on the direction of the project. Project team responsibilities are described in more detail below:

Integration of results and activities

Coordinate among members of the project management team to ensure that appropriate resources are employed both within the District and among its contracted resources.

Communication

General Communication - PMs will provide direction to task leaders and keep track of tasks to ensure that they are completed in a timely manner.

Mid-course Teleconference - A conference call will take place among key participants near the end of the first year of data collection to review and confirm changes in the sampling and analysis program.

Budget Tracking

All participants will chart costs monthly and the MWH project manager will maintain an ISBM chart on the project.

Quarterly Reporting

Quarterly progress reports will also be provided, including budget status.

A.3 Problem Definition / Background

Urban stormwater is well recognized as a problem because of its ability to deliver pollutants and increase flows to receiving waters over a short period of time. The runoff from urban stormwater is a major source of contaminants to southern California's coastal waters. Stormwater runoff usually carries sediments, nutrients, organic matter, pathogens, oil and grease, toxic substances and high metal concentrations which have been accumulating during the dry seasons. The West Basin Municipal Water District (WBMWD) has been researching and integrated membrane seawater desalination developing systems investigating the operational and water quality implications of these treatment processes for more than three years. One concern for a full-scale desalination treatment plant is the adverse impact of stormwater runoff on the sourcewater supply for the treatment plant. Pilot studies have been conducted to monitor these stormwater impacts on the pilot desalination treatment processes. Another concern is the possibility for harmful algal blooms ("red tide" events) and their associated marine biotoxins impacting the desalination system at WBMWD. This study will identify the important marine biotoxins that may occur in the area of the desalination system, demonstrate the removal of the toxins identified by RO at the bench-scale, and conduct monitoring of important biotoxins and water quality parameters associated with red tide events in raw seawater and at the WBMWD pilot facility.

The WBMWD pilot facility includes a prescreening/pretreatment process consisting of an Arkal pretreatment strainer unit, operating in tandem with a high-rate granular media filter (GMF), followed by two parallel Pall microfiltration (MF) units. The filtrate from the Pall MF units. The filtrate from the Pall MF units is subsequently fed into two seawater reverse osmosis (SWRO) trains followed by a second pass brackish RO train.

A previous study conducted by WBMWD in 2005-2006 involved the monitoring of four storms. The results from stormwater monitoring in Fall 2005 showed no notable water quality impact at the El Segundo seawater desalination pilot plant intake.

A.4 Project Objectives

The major objective of the stormwater monitoring program is to effectively determine the potential negative impact of transient stormwater runoff on seawater water quality at the El Segundo intake. The objective of the marine biotoxin program is to identify the important biotoxins, demonstrate their removal by RO, and, to the extent possible, monitor them in raw seawater and treated water from the desalination pilot facility at El Segundo.

A.5 Project / Task Description

This project encompasses four overarching tasks. Each task includes several subtasks, which are described in detail below. The main focus of this QA/QC plan is the stormwater monitoring program for the El Segundo pilot site.

Task 0- Project Management

Mr. Paul Shoenberger, WBMWD's project manager will supervise project activities to ensure adequate progress. The project management tasks includes providing directions to the task leaders; keeping track of the tasks; ensure the usage of appropriate resources within and outside the district; and producing progress reports, communication with DWR, and tracking budget status.

Task 1 – Stormwater Monitoring

A comprehensive experimental plan will be developed to monitor the possible influence of stormwater on the influent water quality at the El Segundo pilot site. Testing will include evaluation of the ability of the overall desalting process to remove constituents of stormwater which may adversely impact water quality. Elements of particular concern include metals and organics, as well as pathogens and/or indicators of pathogens. The budget assumes samples will be collected and analyzed by outside laboratories.

Task 1.1 – Experimental Plan

- Task 1.1a A draft experimental plan for stormwater monitoring will be prepared which specifies the number of storms to be sampled each year, the samples to be taken during each storm, the analyses to be conducted on the samples and the criteria for evaluating the data obtained.
- Task 1.1b Finalize experimental plan for stormwater monitoring based on input from CDPH and other parties at Workshop No. 1.

Task 1.2 – Quality Assurance/Quality Control Plan

This document. Quality Assurance/Quality Control Plans are combined for both Stormwater and Marine Biotoxin Monitoring.

Task 1.3 – Project Assessment Plan

Prepare a Project Assessment Plan whose purpose is to define project goals and objectives, specify how results will be used and goals and objectives achieved, and assure that valid and useful results are obtained and reported.

Task 1.4 – Monitoring Coordination and Intermediate Meetings

Monitoring will be conducted according to the experimental plan and the QA/QC plan that supports it. Nevertheless, it is typically necessary to accommodate a few changes as the project proceeds. Such changes will be made in a coordinated way involving project staff and project advisors, as appropriate.

- Task 1.4a Meet with staff at WBMWD and others, as appropriate, during preparation of experimental plan for stormwater monitoring. Get quotes from laboratories for appropriate analytical work.
- Task 1.4b Gather information to finalize experimental plan for stormwater monitoring based in input from CDPH and other parties at Workshop No. 1.

Task 1.5 – Analyze Data and Intermediate Reports

Data from the stormwater monitoring effort will be collected, stored, and checked. The results will be communicated to all parties in the form of data summaries accompanied by limited discussion.

Task 1.6 – Draft and Final Report

A draft report on stormwater monitoring results will be prepared and, following its review, a final report will be issued.

- Task 1.6a After all data is compiled and its meaning and interpretation have been discussed at Workshop 4, a draft report on stormwater influences will be prepared for review by the project team and the TAP.
- Task 1.6b Upon receipt of comments on the draft, the final report will be prepared that addresses all comments received.

Task 2 – Marine Biotoxin Monitoring

A comprehensive experimental plan will be developed to monitor the dynamics of marine phytoplankton blooms and biotoxins in the Pacific Ocean in the general vicinity of the El Segundo pilot project. Monitoring will be limited to marine biotoxins for which ELISA analytical kits are available. To the extent feasible, testing will include evaluation of the RO desalting process to remove any toxins detected. The budget allows for samples to be collected and analyzed by others; USC will do the bulk of the work for this task, with fairly extensive guidance and coordination by Trussell Technologies, Inc.

Task 2.1 – Experimental Plan

Task 2.1a – A draft experimental plan for marine biotoxin monitoring will be prepared in concert with the Caron Lab at USC. The plan will specify the intensity and frequency of sampling, as well as the target analytes. Task 2.1b – Finalize experimental plan for marine biotoxin monitoring based on input from CDPH and other parties at Workshop No. 1.

Task 2.2 – Quality Assurance/Quality Control Plan

This document. Quality Assurance/Quality Control Plans are combined for both Marine Phytoplankton and Marine Biotoxin Monitoring.

Task 2.3 – Project Assessment Plan

Prepare a Project Assessment Plan with the purpose of defining project goals and objectives, specifying how results will be used and goals and objectives achieved, and assuring that valid and useful results are obtained and reported.

Task 2.4 – Monitoring Coordination and Intermediate Meetings

- Task 2.4a Meet with staff at WBMWD and others, as appropriate, during the preparation of an experimental plan for marine biotoxin monitoring. Work with the USC lab to get prices for the required analytical work.
- Task 2.4b Gather information to finalize experimental plan for marine biotoxin monitoring based in input from CDPH and other parties at Workshop No. 1.

Task 2.5 – Analyze Data and Intermediate Reports

This task includes collection and dissemination of data from biotoxin sampling, as well as benchtop testing support for USC to demonstrate biotoxin removal.

- Task 2.5a Data collection and dissemination Data from the marine biotoxin monitoring effort will be collected, stored, and checked. The results will be communicated to all parties in the form of data summaries, accompanied by limited discussion.
- Task 2.5b Benchtop RO testing Trussell Technologies will oversee the benchtop RO testing. They will send an engineer affiliated with Separation Processes, Inc. (SPI) to the Caron Laboratory at USC to assist in testing of biotoxin removal.

Task 2.6 – Draft and Final Report

A draft report on marine biotoxin monitoring results will be prepared and, following its review, a final report will be issued.

- Task 2.6a After all data has been compiled and its meaning and interpretation have been discussed, a draft report on marine biotoxin influences will be prepared for review by the project team and the TAP.
- Task 2.6b Upon receipt of comments on the draft, the final report will be prepared that addresses all comments received.

Task 3 – Pilot Plant Operations

WBMWD will operate their existing SWRO pilot plant throughout the duration of this monitoring project, in order to demonstrate the impacts of stormwater and marine biotoxins on the treatment process, as well as to allow determination of RO rejection of constituents of concern and acceptable permeate water quality.

Task 3.1 - Operational Guidance

Provide operational guidance to the contract operators on the operation of the seawater desalination pilot plant. Such guidance will include operating conditions, clean-in-place frequency, cleaning-in-place chemical formulations, and advice on equipment and control issues.

Task 3.2 – Pilot Plant Operations

WBMWD will provide for operations of their desalination pilot plant through their contract operators. Operations will include staff on site to operate the pilot, conduct membrane cleaning, and conduct repairs.

Task 4.0 - Project Workshops

There will be two workshops held during the course of the project. These workshops will be held at key decision-making points where input from a variety of parties is a requirement for success. Each workshop and its objectives are described below.

Task 4.1 – Workshop 1 – CDPH Workshop

This is a workshop to discuss with CDPH how stormwater and marine biotoxin issues will be addressed. *The objective of the workshop* is to present research approach to CDPH and get feedback on the program.

Task 4.2 – Workshop 2 – Final Data Review Workshop

This will be a one-day workshop following the completion of the research, but preceding the completion of the draft report summarizing and interpreting the results. Participants will include WBMWD, MWH, Trussell Technologies, Inc., USC, CDPH and TAP. The objective of the workshop is to present research results and preliminary interpretations to principal project team members, as well as to CDPH, in order to get further insight into the data and in order to better understand the elements that CDPH would like to see addressed in the discussion of the final report.

A.6 Quality Objective and Criteria

The data collected from this storm-monitoring program will be compared to the previous studies available. All analytical procedures will meet criteria specified in EPA analytical procedures. The data collected for the marine biotoxin monitoring program via ELISA methods, discussed below, will follow guidance established in previous studies.

A.7 Special Training/Certification

There are no special training or certification requirements for this project.

A.8 Documentation and Records

A standard labeling and recording system will be in place for sampling. A set of procedures including calibration will be available for all instruments. All field data sheets, laboratory data, and reports written will be stored in an appropriate data storage system maintained by the project team. Data will be collected and stored electronically, with backup copies made routinely. All hard copies of original bench sheets will be stored and made available upon written request.

B – DATA GENERATION AND ACQUISITION

B.1 Stormwater Monitoring

B.1.1 Sample Process Design

This study will evaluate the water quality at the following locations as shown in Figure B1.

- 1. Raw Water (point "1" on Fig. B1)
- 2. Arkal Filtrate (point "2" on Fig. B1)
- 3. Granular Media Filter (GMF) Filtrate (point "3" on Fig. B1)
- 4. Pall MF 1 Filtrate (point "4" on Fig. B1)
- 5. Pall MF 2 Filtrate (point "5" on Fig. B1)
- 6. RO 1 Permeate (point "6" on Fig. B1)
- 7. RO 2 Permeate (point "7" on Fig. B1)
- 8. 2nd Pass RO Permeate (point "8" on Fig. B1)

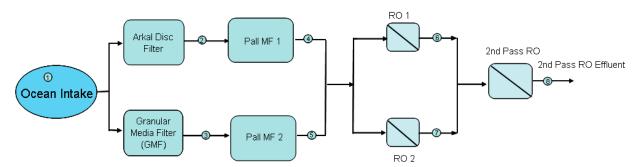


Figure B1. Simplified Schematic of the El Segundo Pilot Desalination Facility Treatment Process

Sampling will begin within 24 hours after a 0.5-inch storm has been identified. Two rounds of sampling will be conducted per sampling location in each 24-hr period for 7 days after sampling begins. The ideal sampling interval is 12 hours. Samples will be analyzed or monitored for the parameters listed in Table B1. Closely following operational procedures will be a particular concern during the stormwater sampling period, and any irregularities in the processes will be recorded.

Real time data loggers or portable measuring devices will be used for temperature, conductivity, chlorophyll a, pH, and turbidity measurements, as shown in Table B2. All instruments will be deployed at each selected sampling location before the first storm.

Laboratory-prepared sample bottles will be obtained from the labs before each storm event. Sample bottles provided by the labs will be labeled and contain any preservatives necessary.

Trussell Technologies will have responsibility for determining whether 0.5 inches of rain has fallen and declaring each storm event. Weather forecast information will be obtained online from the National Weather Service AccuWeather.com (http://www.nwsla.noaa.gov/) and (http://www.accuweather.com/us/ca/el-segundo/90245/city-weatherforecast.asp?partner=accuweather&traveler=0&u=1). real-time precipitation records will be obtained from LA County Department of Public Work (http://dpw.lacounty.gov/wrd/precip/index.cfm). precipitation records may be obtained from the National Weather Service for Los Angeles International Airport (LAX), a site near the El Segundo pilot plant facility (http://www.weather.gov/climate/index.php?wfo=lox).

B.1.2 Sampling Methods

Before sampling, one to two liters of water will be flushed from the sample port to minimize potential contamination. The sample bottle will then be carefully filled from the sampling port, without touching any of the internal parts of the bottles. This procedure is very critical, especially for pathogen samples. Once samples are collected, sample containers will be capped. Samples will be stored on ice or refrigerated prior to packaging for shipment within the allowable holding time (see Table B1 for holding time requirements).

B.1.3 Sample Handling and Custody

All water samples will be stored in coolers and delivered by courier to the labs. The samples will have custody forms attached that identify the date and time of collection, sample locations (sample numbers), analyses to be performed, and the initials of the sample collector. The courier from University of California at Irvine (UCI) will pick up samples for F-specific phage and human pathogens analyses. All other samples will be picked up by the courier affiliated with the commercial lab retained for the laboratory analyses.

B.1.4. Analytical Methods

Table B1 summarizes the monitoring parameters with analytical methods, the amount of sample needed, sample bottle type, holding time, sampling locations, and total number of samples per storm event.

Table B1. Stormwater Monitoring Parameters, Analysis Methods, and Sampling Locations

Parameters	Method	Sample Amount Needed	Bottle Type	Preservative	Holding Time	Sampling Locations	# of Samples/ event
Organic Parameters							
UV ₂₅₄	SM5910B	250 mL	Poly	<6°C	2 days	1,6,7,8	56
Volatile organic compounds (VOCs)	EPA 524.2	120 mL	40 mL VOA	<6°C, Ascorbic (If Chlorinated), HCI	14 days	1,6,7,8	56
Synthetic organic compounds (SOCs)	EPA 525.2	2000 mL	1 L Amber	<6°C, Sulfite (If Chlorinated), HCl	14 days	1,6,7,8	56
Pathogen Parameters							
Total Coliform	SM 9221B	125 mL	Sterile plastic	'<10°C, Na2S2O3 (If	6 hrs	1,6,7,8	56
Fecal Coliform	SM 9221E	120 1112	Otorno piaotio	Chlorinated)	6 hrs	1,6,7,8	56
Enterocci	Enterolert	125 mL	Sterile plastic	'<10°C, Na2S2O3 (If Chlorinated)	24 hrs	1,6,7,8	56
E. Coli	SM 9223	125 mL	Sterile plastic	'<10°C, Na2S2O3 (If Chlorinated)	6 hrs	1,6,7,8	56
F-specific Coliphage (5-tube MPN)	EPA 1602	see human pathogen	see human pathogen	4 - 10 deg. C	24 hrs	1,6,7	42
Human pathogens							
Quantitative adenovirus	RT-QPCR		1 gal Sterile				42
Quantitative enteroviruses	Q-RT-PCR	1 gal	plastic	4 - 10 deg. C	24 hrs	1,6,7	42
Infectivity adenovirus	ICC-PCR						42
Nutrient Parameters							
NH ₄ ⁺	EPA 353.2	250 mL	'250 mL Poly	<6°C, H2SO4	28 days	1,6,7,8	56
NO ₃ -	EPA 353.2	250 mL	'250 mL Poly	<6°C	2 days	1,6,7,8	56
NO ₂ -	EPA 350.1				2 days	1,6,7,8	56
Phosphorus Phosphate (PO ₄ ³⁻)	EPA 365.1 EPA 365.1	250 mL	'250 mL Poly	<6°C, H2SO4	28 days	1,6,7,8 1,6,7,8	56 56
Metal Parameters	EFA 303.1					1,0,7,0	30
Al	EPA 200.8					1,2,3,4,5,6,7,8	112
Sb	EPA 200.8					1,2,3,4,5,6,7,8	112
As	EPA 200.8					1,2,3,4,5,6,7,8	112
Ве	EPA 200.8					1,2,3,4,5,6,7,8	112
В	EPA 200.8					1,2,3,4,5,6,7,8	112
Cd	EPA 200.8					1,2,3,4,5,6,7,8	112
Cr(T)	EPA 200.8					1,2,3,4,5,6,7,8	112
Co	EPA 200.8 EPA 200.8					1,2,3,4,5,6,7,8	112 112
Cu Fe	EPA 200.8 EPA 200.8					1,2,3,4,5,6,7,8 1,2,3,4,5,6,7,8	112
Pb	EPA 200.8		l		180 days	1,2,3,4,5,6,7,8	112
Mn	EPA 200.8	250 mL	plastic	HNO3	,5	1,2,3,4,5,6,7,8	112
Mo	EPA 200.8					1,2,3,4,5,6,7,8	112
Ni	EPA 200.8					1,2,3,4,5,6,7,8	112
Se	EPA 200.8					1,2,3,4,5,6,7,8	112
Ag	EPA 200.8					1,2,3,4,5,6,7,8	112
TI Sn	EPA 200.8 EPA 200.8					1,2,3,4,5,6,7,8 1,2,3,4,5,6,7,8	112 112
Sil Ti	EPA 200.8					1,2,3,4,5,6,7,8	112
V	EPA 200.8					1,2,3,4,5,6,7,8	112
Zn	EPA 200.8					1,2,3,4,5,6,7,8	112
Hg	EPA 245.1				28 days	1,2,3,4,5,6,7,8	112

B.1.5 Quality Control

All samples will be carefully collected, to avoid any contamination, and to ensure collection of a representative sample. Proper QA/QC will be conducted by the labs on all instruments used for analyses. All samples will be refrigerated and analyzed within the allowable holding time. A copy of the results of each analysis will be sent to the project team including the QA/QC reports for each analysis.

Laboratory methods for quality control will include the use of method blanks, laboratory control spikes, and matrix spikes and matrix spike duplicates, as appropriate. Details are provided below.

Method Blanks

Method blanks will be prepared by the laboratory using blank water, and then analyzed for every batch of samples analyzed. Any detected concentration in a method blank will be an indication of contamination in the analytical process.

Laboratory Control Spikes

Laboratory control spike (LCS) analyses will be used to test the accuracy of the entire laboratory analytical process. LCS samples are standards prepared internally by the laboratory using a known amount of analyte. The laboratory will perform these LCS analyses to demonstrate that the instrumentation and laboratory procedures are accurate and compliant with typical laboratory performance standards.

Matrix Spikes and Matrix Spike Duplicates

A matrix spike (MS) will be used to determine the efficiency of the analytical process in recovering the analyte in the sample matrix. This will be determined by observing how much of the spike is detected through the analytical process. In this process, a sample taken from the flow stream in question is spiked by the laboratory with a known amount of the constituent being analyzed. The amount of the spike recovered will show as the "% recovery" of the target analyte. A matrix spike duplicate (MSD) is a duplicate of the matrix spike analysis to determine how closely the lab is able to duplicate the results of the initial MS. The MS result will be used to confirm that the laboratory's instrumentation and procedures are accurate and the MSD result will be used to confirm that the laboratory's instrumentation and procedures are precise. Both are required to demonstrate compliance with typical laboratory performance standards.

B.1.6 Instrument/Equipment Testing, Inspection and Maintenance

The equipment used at the pilot site requires maintenance. Pumps will be checked daily to make sure they are in operation. If a pump fails, it will be replaced or fixed immediately. Table B2 summarizes on-line meter and portable meters required for the project. All the on-line instruments should be in-place, and portable meters should be available before the first storm event. Spare parts will be on-hand when feasible, and operation manuals will be kept for each instrument and available as needed.

Table B2. Online meter and portable meter summary table

Table B2. Offine meter and portable meter summary table									
	Equipments used at the pilot	Model#	Equipment Type						
	Chlorophyll-a	Turner Designs AlgaeWatch Online Fluorometer	Online meter						
Raw Water (1)	pН	Cole Palmer	Portable						
	Conductivity Temperature	Myron L Ultrameter	Portable						
	Turbidity Hach 1720E		Online meter						
Arkal Disc Filter (2)	Turbidity	Hach 1720 E (at the Feed to UF)	Online meter						
GMF (3)	Turbidity	Hach 1720E	Online meter						
Pall MF (4,5)	Turbidity,	Hach FilterTrak 660 sc Laser Trubidimeter	Online meter						
Fall WIF (4,3)	Temperature	Endress Hauser Temperature Transmitter	Online meter						
RO Trains (6,7,8)	Conductivity Temperature	Rosemount 54e	Online meter						
	рН	Cole Palmer	Portable						

B.1.7 Instrument/Equipment Calibration and Frequency

All of the on-line instruments will be calibrated and ready to be in service before the first storm event. These instruments (Table B2) will require periodical calibration as detailed in the instrument operation manuals. Calibration frequency depends on the individual instrument requirements.

B.1.8 Inspection/Acceptance of Supplies and Consumables

All supplies used in conjunction with stormwater sampling and testing will be acceptable in compliance with standard laboratory procedures.

B.1.9 Non-direct Measurements

A preliminary literature review was conducted in order to identify the relevant monitoring parameters and water quality indicators associated with stormwater events.

B.1.10 Data Management

All on-line measurements will be downloaded after the storm event and saved to a stormwater monitoring data logsheet for evaluation. Lab results will be sent to the project team and will be input to the stormwater monitoring data logsheet as well.

B.2 Marine Biotoxin Monitoring B.2.1 Sample Process Design

This study will evaluate water quality parameters related to 'red tides', using sensors mounted to buoys moored in proximity to the possible in-take areas for the El Segundo and Redondo Beach potential desalination plant locations, as shown in Figure B2. Additionally, samples of raw water (point "1" on Figure B2) and RO 1 permeate water (point "6" on Figure B2) will be taken from the El Segundo desalination pilot plant and analyzed for marine biotoxins.

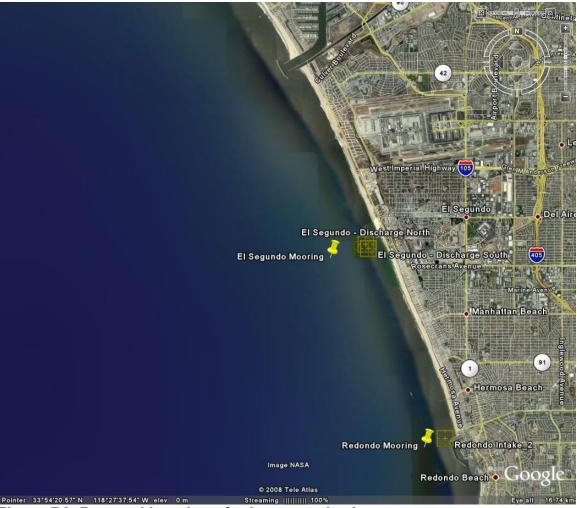


Figure B2. Protocol locations for buoy monitoring system

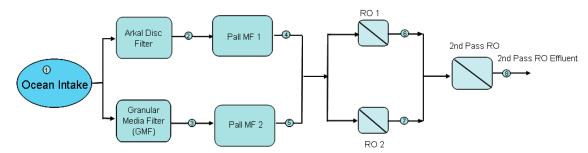


Figure B3. Simplified Schematic of the El Segundo Pilot Desalination Facility Treatment Process

B.2.2 Sampling Methods

Before sampling, one to two liters of water will be flushed from the sample port to minimize potential contamination. The sample bottles will then be carefully filled from the sampling port, without touching any of the internal parts of the bottles. This procedure is very critical, especially for pathogen samples. Once samples are collected, sample containers will be capped. Samples will be stored on ice or refrigerated prior to packaging for shipment within the allowable holding time.

B.2.3 Sample Handling and Custody

All water samples will be stored in coolers and delivered by courier to the cooperating labs at USC. The samples will have custody forms attached that identify the date and time of collection, sample locations (sample numbers), analyses to be performed, and the initials of the sample collector

B.2.4 Analytical Methods

The analytical methods, analysis methods and sampling locations for the marine biotoxins and associated water quality parameters are summarized in Table B3.

Table B3. Marine Biotoxin Monitoring Parameters, Analysis Methods, and Sampling Locations

Parameters	Method	Sample Amount Needed	Bottle Type	Preserv- ative	Sampling Locations	Sampling Frequency
Phytoplankton	Taxonomy					
Micro- phytoplankton cells	Sedi- mentation	250 mL raw*	plastic	Lugo's iodine soultion	1	1/week
Nano- phytoplankton cells	Sedi- mentation	250 mL raw*	plastic	Lugo's iodine soultion	1	1/week
Nutrient Param	eters					
Phosphate (PO ₄ ³⁻)	phosphate sensor	N/A	N/A	N/A	buoys	continuous
Biotoxin Param	neters					
Domoic Acid	ELISA	2 L raw, 2 L permeate	plastic	freezing	1, 6	1/week
Saxitoxin	ELISA	1 L raw. 1 L permeate	plastic	freezing	1, 6	1/week
Brevetoxin	ELISA	250 mL raw, 25 mL permeate	glass	N/A	1, 6	14 x 1/day
Okadaic Acid	ELISA	1 L raw. 1 L permeate	plastic	freezing	1, 6	1/week
Other Paramete	ers	•				
chlorophyll a	WET Labs backscatter/ fluorometer	N/A	N/A	N/A	buoys	continuous
turbidity	WET Labs backscatter/ turbidity sensor	N/A	N/A	N/A	buoys	continuous
temperature	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous
salinity	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous
dissolved oxygen	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous
conductivity	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous
depth	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous

^{*} Weekly samples of 250mL (raw) for phytoplankton taxonomy and 1L raw, 1 L permeate for biotoxin analysis are used for test for multiple parameters

Phytoplankton taxonomy

Dr. Burton Jones' research team from USC is responsible for phytoplankton characterization. The phytoplankton composition analysis has been conducted using a raw water sample (250 mL) collected each week by West Basin from the ocean intake (point "1" on Figure B1) at the El Segundo desalination pilot plant. The raw water sample is preserved with acid Lugo's iodine solution (~5% final solution), as it is the recommended method for prolonged preservation and storage of the samples (Anderson et al. 2001: Throndsen 1978). After sedimentation for 24 h, a 50 mL subsample is analyzed, and cell counts are obtained using the inverted microscope method (Utermohl 1958). Microphytoplankton cells (longer than 20 µm) are counted at magnifications of 200 and 400x. Nanophytoplankton cells (2-20 µm) are counted in 20 randomly selected fields of vision, under magnification of 400 and 1000x. Morphological identification will be conducted based on the published literature (Cetinic, 2009).

Bench Scale Marine Biotoxin Monitoring

A bench-scale apparatus for RO desalination will be established at USC to test RO membrane performance in removing known quantities of marine biotoxins most relevant to Southern California, extracellular materials, and diverse phytoplankton taxa. Procedures for sampling and testing of the specific marine biotoxins targeted in the bench-scale RO operations will be laid out in detail in the marine biotoxin experimental plan.

ELISA (enzyme-linked immunosorbent assay)

Marine biotoxin analysis is conducted by Dr. David Caron's research team at USC. Throughout the pilot scale phase of the project, two one-liter samples of raw water and RO 1 permeate have been collected by West Basin each week and sent to USC. Portions of these fresh samples have been analyzed for Domoic Acid, while the rest were passed through a 0.2micron glass fiber filter, in which approximately 10 mL was dissolved. The resulting particulate was frozen and preserved for retrospective analysis of Saxitoxin and Okadaic Acid during the pilot scale phase of the project. Samples that have been frozen or stored in plastic are unacceptable for Brevetoxin analysis, thus USC has developed an alternative approach. Concurrent with the retrospective analyses, West Basin will collect daily samples of 250 mL of raw water and 25 mL of permeate water in glass bottles for 14 days. These samples will be delivered to USC and analyzed for Brevetoxin in one batch, in order to minimize the cost for use of the expensive ELISA kit. Bench-scale RO experiments will be conducted for domoic acid, saxitoxin, and brevetoxin, as discussed in more detail in the marine biotoxin experimental plan.

All marine biotoxin analysis by USC utilizes the ELISA method, a biochemical technique used mainly in immunology to detect the presence of an antibody or an antigen in a sample. The ELISA method works by affixing an unknown amount of antigen to a surface, and then washing a specific antibody over the surface so that it can bind to the antigen. Next, a second antibody (conjugate) linked to an enzyme is added to the solution to bind to the primary antibody. In the final step, a specific substrate (chromogen) is added to the plate. The enzyme changes color through a reaction with the substrate, and based on this color, the concentration can be determined. Discussion of the ELISA method for domoic acid is included in Litaker et al. (2008) and for saxitoxin is included in Lefebvre et al. (2008). Two different kits (Mercury Science, Biosense) were used for Domoic Acid during the project. Separate Abraxis LLC kits were used for saxitoxin, brevetoxin, and okadaic acid as described below.

Domoic Acid Screening Test Kit (Mercury Science Inc.)

Domoic Acid is measured using a solid phase colorimetric immunoassay, as illustrated in Figure B4. This ELISA is based on competition between Domoic Acid and an enzyme-labeled Domoic Acid (DA-Tracer) for anti-Domoic Acid antibody. Both the Ab-Domoic Acid and Ab-DA-Tracer complexes are captured on the surface of the microtiter plate wells, but any of the samples containing Domoic Acid inhibit the binding of the DA-Tracer to the antibody molecules. The microtiter plate is subjected to a washing step, followed by the addition of an enzyme substrate (TMB) that forms a color proportional to the amount of DA-Tracer in the well. The amount of color measured is inversely proportional to the concentration of Domoic Acid in the sample (Mercury Science Inc., 2007).

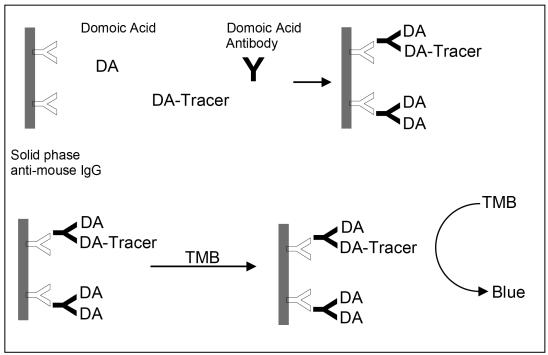


Figure B4. Schematic of the reaction of Domoic Acid kit (Mercury Science Inc., 2007)

Domoic Acid Screening Test Kit (Biosense)

This ELISA is based on competition between free Domoic Acid and the DA-conjugated protein, coated on plastic wells for binding to anti-DA antibodies free in the solution. This is shown in figure 5 below. The anti-DA antibodies are conjugated to a horseradish peroxidase (HRP). Samples are then incubated in the wells with the anti-DA-antibody-HRP conjugate. The well is subjected to a washing step, the remaining conjugate that is bounded to the wells are then measured with a substrate (TMB) that forms a color proportional to the amount of DA-Tracer in the well. The amount of color measured is inversely proportional to the concentration of Domoic Acid in the sample.

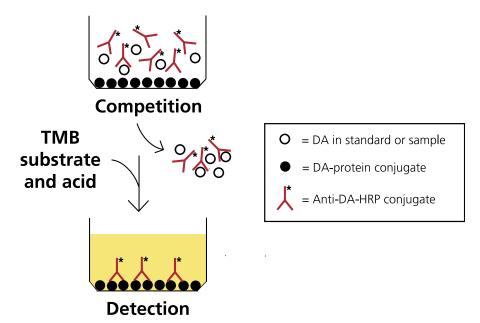


Figure B5. Schematic of the reaction of Domoic Acid kit (Biosense)

Saxitoxin (PSP) ELISA, Microtiter Plate (Abraxis LLC)

The Saxitoxin test is a direct competitive ELISA based on competition between Saxitoxin and a Saxitoxin enzyme-conjugate for the binding sites of rabbit anti-saxitoxin antibodies in solution. The saxitoxin antibodies bind to a second antibody (sheep anti-rabbit) immobilized on the plate, then following a washing step, a substrate solution is added, producing a color signal. After a specified time, the color reaction is stopped, and the color is evaluated using an ELISA reader. The blue color is associated with the Saxitoxin enzyme-conjugate, thus its intensity is inversely proportional to the concentration of the Saxitoxin present in the sample. The test kit constructs a standard curve with each run, from which Saxitoxin concentrations of the samples are determined (Abraxis LLC, manual for Saxitoxin ELISA).

Brevetoxin (NSP) ELISA, Microtiter Plate (Abraxis LLC)

The test for Brevetoxin is a direct competitive ELISA based on competition between Brevetoxin and a Brevetoxin enzyme-conjugate for the binding sites of sheep anti-brevetoxin antibodies that have been immobilized in the wells of a microtiter plate. Following a washing step, a substrate solution is added, producing a color signal. After a specified time, the color reaction is stopped, and the color is evaluated using an ELISA reader. The blue color is associated with the Brevetoxin enzyme-conjugate, thus its intensity is inversely proportional to the concentration of Brevetoxin present in the sample. The test kit constructs a standard curve with each run, from which Brevetoxin concentrations of the samples are determined (Abraxis LLC, manual for Brevetoxin ELISA).

Okadaic Acid (DSP) ELISA, Microtiter Plate (Abraxis LLC)

The test for OkadAic Acid is a direct competitive ELISA based on competition between okadaic and a okadaic acid-enzyme-conjugate for the binding sites of rabbit anti- okadaic acid antibodies that have been immobilized in the wells of a microtiter plate. Following a washing step and addition of a substrate solution, a color signal is produced. After a specified time, the color reaction is stopped, and the color is evaluated using an ELISA reader. The blue color is associated with the okadaic acid enzyme-conjugate, thus its intensity is inversely proportional to the concentration of okadaic acid present in the sample. The test kit constructs a standard curve with each run, from which okadaic acid concentrations of the samples are determined (Abraxis LLC, manual for Okadaic Acid ELISA.

Water Quality and Nutrient Sensors

Extensive water quality monitoring will be conducted in conjunction with WBMWD efforts to investigate the causes and implications of HABs proximal to the possible ocean intakes at El Segundo and Redondo Beach. Four water quality monitor (WQM) units manufactured by WET Labs will be installed on two Watchmate buoys from AXYS Technologies Inc. near these facilities. The WQM combines WET Labs' fluorometer-turbidity sensor with Seabird's CTD sensors, to provide measurements of temperature, salinity, dissolved oxygen, depth, chlorophyll a fluorescence, turbidity, and optical backscattering. CDOM (colored dissolved organic matters) will not be monitored. Data from the sensors will be transferred via antennas to an computer stationed at AES power plant in Redondo Beach, and transmitted to USC for analysis. This data will be monitored in tandem with marine biotoxin and other water quality results from on-going sampling of both raw and permeate water from the pilot plant.

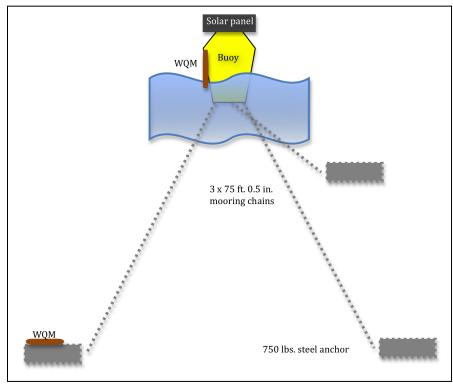


Figure B5. Schematic of buoy and mooring configuration

In the summer, algal blooms are typically in the subsurface (20-30 m depth), whereas in the spring they are more likely to occur near the water surface. Two of the WQMs will be attached to each buoy in order to provide water quality data from the ocean surface, as well as from a depth of 15 m. The WQM located at the bottom of the ocean will allow for the monitoring of algal blooms in deeper water, which are typically caused by internal tides. It will be attached to the top of one of the three mooring wheels, and will be powered by a WET Labs battery pack (BPA-50). The aluminum superstructure of each buoy is fitted with three Solar Module Shell ST20 panels and AXYS Watchman sensor processor module battery storage unit. These will power the WQM attached to the buoy, the WatchMan500 data acquisition and processing system, as well as the Freewave wireless data transceiver. Data from the WQM will be transmitted to an antenna and radio transmitters at AES power generation station in Redondo Beach. This data will be accessed directly by the USC lab group, through their server.

It is expected that nutrient loading in the in-take water will be observed prior to the occurrence of algal blooms. Nutrient monitoring will thus be included as an important component of the overall marine biotoxin monitoring project. The Watchmate buoys will initially be moored without the nutrient sensors, but there is additional space to accommodate phosphate sensors at a later time. Purchasing the nutrient sensors was outside the scope of the project budget, however Dr. Burton Jones has an

established relationship with WET Labs, and has arranged to be a beta tester in order to use the nutrient sensors without cost to the project. As a beta tester, it will be possible to obtain phosphate data from the nutrient sensors. It is important to monitor phosphate because it is likely to be present for algal blooms associated with deep water, runoff, or sewage effluent. Another potential future addition would be instrumentation to upgrade the buoys as a weather station.

B.2.5 Quality Control

All samples will be carefully collected to avoid any contamination and to ensure collection of a representative sample. Proper QA/QC techniques will be implemented by the labs with all instruments used in analyses. All samples will be refrigerated and analyzed within the allowable holding time. A copy of the results of each analysis will be sent to the project team including the QA/QC reports for each analysis.

As appropriate for the ELISA technique, quality control for laboratory methods will include the use of method blanks, laboratory control spikes, and matrix spikes and matrix spike duplicates. Details are provided below.

Method Blanks

Method blanks will be prepared by the laboratory using blank water, and then analyzed for every batch of samples analyzed. Any detected concentration in a method blank will be an indication of contamination in the analytical process.

Laboratory Control Spikes

Laboratory control spike (LCS) analyses will be used to test the accuracy of the entire laboratory analytical process. LCS samples are standards prepared internally by the laboratory using a known amount of analyte. The laboratory will perform these LCS analyses to demonstrate that the instrumentation and laboratory procedures are accurate and compliant with typical laboratory performance standards.

Matrix Spikes and Matrix Spike Duplicates

A matrix spike (MS) will be used to determine the efficiency of the analytical process in recovering the analyte in the sample matrix. This will be determined by observing how much of the spike is detected through the analytical process. In this process, a sample taken from the flow stream in question is spiked by the laboratory with a known amount of the constituent being analyzed. The amount of the spike recovered will show as the "% recovery" of the target analyte. A matrix spike duplicate (MSD) is a duplicate of the matrix spike analysis to determine how closely the lab is able to duplicate the results of the initial MS. The MS result will be used to confirm that the laboratory's instrumentation and procedures are accurate and the MSD result will be used to confirm that the laboratory's instrumentation and procedures are precise. Both are required to demonstrate compliance with typical laboratory performance standards.

B.2.6 Instrument/Equipment Testing, Inspection and Maintenance

The equipment used for the phytoplankton taxonomy and marine biotoxin assays of domoic acid, saxitoxin, okadaic acid, and brevetoxin will be provided by the lab groups of Dr. Burton Jones and Dr. David Caron at USC. The lab groups will conduct routine tests of the instruments and equipment used in their analyses. The sensors and buoy mooring systems will be tested upon installation at both El Segundo and Redondo Beach by WET Labs and Dr. Burton Jones' lab group from USC. The buoys will be monitored remotely via antennas at AES power generation station in Redondo Beach and maintained as necessary. Operation manuals will be kept for each instrument and available as needed.

B.2.7 Instrument/Equipment Calibration and Frequency

All of the laboratory instruments used in marine biotoxin analysis will be calibrated and ready to be in service prior to testing. These instruments will require periodic calibration as detailed in the instrument operation manuals. Calibration frequency depends on the individual instrument requirements.

B.2.8 Inspection/Acceptance of Supplies and Consumables

All supplies used in conjunction with marine biotoxin sampling and testing will be acceptable in compliance with standard laboratory procedures.

B.2.9 Non-direct Measurements

USC will conduct a comprehensive literature review of phytoplankton taxonomy and marine biotoxins associated with 'red tide' events. This body of research will provide baseline information for analytical methods, related studies, and recommendations for future research.

B.2.10 Data Management

All water quality measurement data collected at the buoys will be transmitted from the buoy sensors to an AES plant computer and accessed directly by USC via server for evaluation. Marine biotoxin lab results will be sent to the project team and will be included in the final report.

C. Assessment and Oversight

C.1 Assessments and Response Actions

WBMWD's project manager, Mr. Phil Lauri, will supervise day-to-day activities regarding project tasks to ensure adequate progress. MWH's project manager, John Robinson, will do the same with respect to the consultant team. Dr. R. Shane Trussell of Trussell Technologies will provide overall leadership of technical team. Trussell Technologies project team members will be responsible for reviewing the data.

C.2 Reports to Management

After all data have been compiled and the meaning and interpretations have been discussed at Workshop #2, a draft report on stormwater influences and

marine biotoxins will be prepared by Trussell Technologies, Inc. Upon receipt of comments on the draft, the final report will be prepared that addresses the comments received.

D. Data Validation and Usability

D.1 Data Review, Verification, and Validation

All data will be reviewed upon receipt and will be managed through the use of computer spreadsheet software, including manually recorded operational parameters. Manually recorded operational observations will be entered into computer spreadsheets on a daily basis. All hard copies will be kept in a binder. Trussell Technologies project staff will conduct data review. Results will be summarized in graphical format as well as tabular format. All data will be included in the report.

D.2 Verification and Validation Methods

Verification and validation methods include identifying gaps in the data, examining raw data for outliers, checking calculations, and reviewing equipment calibrations. Outliers and inconsistencies will be flagged for further review. Supplemental sampling or analysis may be called for as required.

D.3 Reconciliation with User Requirements

All data collected and validated by the project team will be made available to the project managers. Conclusions drawn from these data will undergo peer review before publication.

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Appendix C – Stormwater Monitoring Experimental Plan

Date: November 25, 2008

To: Phil Lauri, P.E.

Authors: Joanne Chiu

David R. Hokanson, Ph.D., P.E. R. Rhodes Trussell, Ph.D., P.E.

Reviewer: R. Shane Trussell, Ph.D., P.E.

Subject: Stormwater Monitoring Experimental Plan for West Basin

Municipal Water District (WBMWD) El Segundo Pilot Facility¹

1. INTRODUCTION

West Basin Municipal Water District (WBMWD) has been researching and developina integrated membrane seawater desalination systems investigating the operational and water quality implications of these treatment processes for over three years. The WBMWD pilot facility includes a Arkal pretreatment strainer unit, a high-rate granular media filter (GMF), serving as prescreening/pretreatment process prior to two parallel Pall microfiltration (MF) units. The filtrate from the Pall MF units is then fed to two seawater reverse osmosis (SWRO) trains followed by a second pass brackish RO train. One of the major concerns for a full scale desalination treatment plant is the adverse impact of stormwater runoff to the sourcewater fed to the treatment plant. stormwater runoff is a source of contaminants to southern California's coastal waters, which has high visibility in the public eye. Stormwater runoff usually carries sediments, nutrients, organic matter, pathogen, oil and grease, toxic substance and high metal concentrations which have been accumulating during the dry seasons. Therefore, pilot studies have been conducted to monitor these stormwater impacts to the pilot desalination treatment processes. To date, WBMWD has monitored four storms. The previous stormwater monitoring results from fall 2005 showed no notable water quality impact at the El Segundo seawater desalination pilot plant intake. However, it is important to continue to identify and assess the sourcewater quality and treatment issues. A

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¹ Note: The experimental plan is subject to change due to input from parties including, but not limited to, the District, CDPH, and the authors.

comprehensive experimental plan has been developed building upon the experience gained from the previous studies of monitoring the influence of stormwater on the influent water quality at the El Segundo pilot site. Testing will include evaluation of the ability of the overall desalting process to remove any constituents detected as a result of stormwater influences. Quality constituents to be monitored in this experimental plan include inorganic and organic matters, pathogens and/or indicators of pathogens, nutrients, and metals.

2. STORMWATER RUNOFF

Stormwater results from precipitation following rainfall or as a result of snowmelt. Stormwater runoff is generated by precipitation and runoff from land, building rooftops, streets, and other open surface areas, and it usually carries sediments, nutrients, organic matter, pathogen, oil and grease, toxic substance and high metal concentrations which lead to very poor surf zone water quality. A rainfall defined as a storm is when the rainfall has produced a minimum precipitation of 0.5 inches.

3. PARAMETERS TO BE MEASURED

The current monitoring program has been monitoring the surrogate water quality parameters, indicator bacteria, and regulated organics as shown below.

- Conductivity
- pH
- Turbidity
- UV₂₅₄
- Total coliforms
- Fecal coliforms
- Enterococcus
- Volatile organic compounds (VOCs)
- Synthetic organic compounds (SOCs)
- Metals
- Inorganic cations and anions
- General physical and mineral constituents

There are 22 metals that have been analyzed and that include: aluminum (AI), antimony (Sb), arsenic (As), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr(T)), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), thallium (TI), tin (Sn), titanium (Ti), Vanadium (V,) and zinc (Zn). The same metals will be monitored in this experimental plan.

In order to ensure a more complete water quality profile based upon the existing monitoring program, additional monitoring parameters that are proposed include temperature, amount of stormwater precipitation, particle counts, chlorophyll, oil and grease (O&G), additional coliform bacteria, and human pathogens.

Furthermore, stormwater runoff may add nutrients that contribute to phytoplankton growth; therefore, this project will also monitor nutrients, which include ammonia, nitrate, nitrite, total Kjehldahl nitrogen (TKN), and phosphorus. It is important to understand the impacts of the stormwater to the pilot plant in terms of its nutrient removal capability.

Aside from trash on the beach, microbial contamination of beaches is probably the stormflow impact which is most visible to the public. It is essential that the West Basin monitoring program do an excellent job of characterizing any increase in microbial threat resulting from stormflow. As a result, monitoring to understand the potential for pathogens in the seawater intake will also be extended. Two additions to the existing program are being made. First the monitoring of bacterial indicators will be extended to include *Escherichia coli* (*E. coli*) in addition to total coliforms, fecal coliforms, and enterococcus. *E. coli* is one of the four bacteria types that are commonly used as microbial indicators of water quality (APHA, 1998). Culture methods specific for *E. coli* and Enterococcus bacteria are thought by the EPA to more accurately identify fecally contaminated waters (USEPA, 1986) and monitoring for *E. coli* is recognized the most specific method available indicate the presence of human fecal contamination (Yates, 2007).

Monitoring for indicators has several advantages over directly monitoring for the pathogens themselves (NRC, 2004). Among them: The logic of protecting against the potential for contamination vs. monitoring for actual contamination, the fact that there are so many pathogens that could be monitored, the fact that there are so many pathogens for which methods are not available and, the fact that most direct monitoring methods have poor sensitivity. Thus monitoring of bacterial indicators is all well and good, but it is also widely recognized that some pathogens, particularly certain protozoa and viruses, are more persistent in the environment, particularly the seawater environment, than the bacterial indicators are. The membrane processes being employed in the West Basin treatment are effective with both, but particularly where the protozoa are concerned. As a result there is a need to understand the potential for the presence of viral pathogens. Thus a second addition has been made to the monitoring program to address this need. First F-specific phage will be monitored. These viruses, which prev on the coliform organisms, have size, chemistry and environmental persistence similar to the enteric viruses for which humans are the host. Thus they can have the potential to serve as a supplemental indicator organism. Another attractive feature is that suitable culture methods are available for their determination (APHA 2008).

Nevertheless, the use of F-specific phage as an indicator is not as well established as the bacterial indicators; questions have been raised about their suitability as an indicator of human viral pathogens. In an attempt to address this issue, Ahn, et al used F-specific phage as well as PCR methods for human adenovirus and enteroviruses to examine the impacts of stormwater runoff from

the Santa Ana River to the coastal water quality, both in the surf zone and offshore (Ahn, 2005). Human adenovirus is a frequent cause of acute upper respiratory tract (URT) infections, i.e. "colds". Adenoviruses are readily inactivated by most chemical disinfectants in routine use to treat drinking water, including free chlorine, chlorine dioxide, and ozone (Yates et al. 2006). Also, adenoviruses are more resistant to UV than the viruses traditionally considered of significant waterborne indicators (Yates et al, 2006). Human enteroviruses (family Picornaviridae) are the major cause of aseptic meningitis and also cause a wide range of other acute illnesses, including neonatal sepsis-like disease. acute flaccid paralysis, and acute hemorrhagic conjunctivitis. As a result the use of PCR methods (Jiang et al, 2007) to monitor human adenoviruses and enteroviruses will also be employed to assess the potential for the presence of pathogens in the seawater as a result of stormflows. Thus microbiological sampling will include culture methods for total coliform, fecal coliform, enterocci, E. coli, and F-specific phage, as well as PCR methods for human adenovirus and enteroviruses.

4. SAMPLING LOCATIONS

In order to evaluate the impact of stormwater to each stage of the pilot treatment process, the following locations have been selected for the stormwater sampling as shown in Figure C1.

- 1. The ocean intake (point "1" on Fig. C1)
- 2. The Arkal Disc Filter effluent (point "2" on Fig. C1)
- 3. Granular Media Filter (GMF) effluent (point "3" on Fig. C1)
- 4. Pall MF 1 effluent (point "4" on Fig. C1)
- 5. Pall MF 2 effluent (point "5" on Fig. C1)
- 6. The RO 1 effluent (point "6" on Fig. C1)
- 7. The RO 2 effluent (point "7" on Fig. C1)
- 8. The 2nd Pass RO effluent (point "8" on Fig. C1)

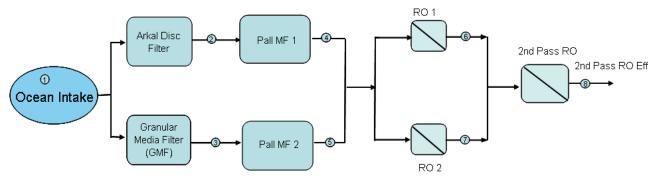


Figure C1 – Simplified Schematic of the El Segundo Pilot Desalination Facility Treatment Process

Results from these locations will provide a complete evaluation of the ability of each treatment stage to remove any constituents detected as a result of

stormwater influence. Comparisons between the different feedwater pretreatment technologies also will be assessed.

5. SAMPLING FREQUENCY AND ANALYTICAL TECHNIQUES

It is important to sample the ocean intake and treated water at the locations shown on Figure C1 at times when they are impacted by storm events. Because the stormwater discharge to the ocean is located at some distance from the sampling locations and the timing of when the storm events will impact the El Segundo intake is also affected by various factors such as ocean currents, it is necessary to sample over a long enough time period that allows for capturing the storm event in the face of this uncertainty. Therefore, grab samples are recommended to be collected every 12 hours up to 7 days to start. The sampling frequency may be fine-tuned for subsequent storm events based on the results of prior events as appropriate. Samples will be analyzed for the parameters listed in Section 3 except conductivity, pH, turbidity, amount of stormwater precipitation, particle counts, chlorophyll-a (which will be monitored as described in Table C 2 below). The following table summarizes the sampling parameters, methods, and locations. F-specific Coliphage and human pathogens will be analyzed by UCI Professor Jiang's Laboratory; all other analyses will be performed by Weck Laboratory.

Table C1 – Stormwater Monitoring Parameters, Analysis Methods^{*}, and Sampling Locations

Parameters	Method	Sample Amount Needed	Bottle Type	Preservative	Holding Time	Sampling Locations	# of Samples/event
Inorganic Parameters							
Conductivity	Rosemount 54e / Myron L Ultrameter	NA	NA	NA	NA	1,6,7,8	Continusouly/Hourly
pH		NA	NA	NA	NA	1,6,7,8	Hourly
Turbidity	Hach 1720E Low Range Process and Hach FilterTrak 660 sc Laser Trubidimeter	NA	NA	NA	NA	1,4,5,6,7,8	Continusouly
Temperature	Rosemount 54e / Myron L Ultrameter	NA	NA	NA	NA	1	Continusouly/Hourly
Storm precipitation	http://www.nwsla.no	NA	NA	NA	NA	1	-
Particle counts	aa.gov Met One GT-321	NA	NA	NA	NA	1	Hourly
Organic Parameters	Wet One G1-321	INA	INA	INA	INA	'	riouny
UV ₂₅₄	SM5910B	250 mL	Poly	<6°C	2 days	1,6,7,8	56
	Turner Designs AlgaeWatch Online Fluorometer	NA	NA	NA	NA	1	Continusouly
Volatile organic compounds (VOCs)	EPA 524.2	120 mL	40 mL VOA	<6°C, Ascorbic (If Chlorinated), HCl	14 days	1,6,7,8	56
Synthetic organic compounds (SOCs)	EPA 525.2	2000 mL	1 L Amber	<6°C, Sulfite (If Chlorinated), HCl	14 days	1,6,7,8	56
Pathogen Parameters							
Total Coliform	SM 9221B	125 mL	Sterile plastic	'<10°C, Na2S2O3 (If Chlorinated)	6 hrs	1,6,7,8	56
Fecal Coliform Enterocci	SM 9221E Enterolert	125 mL	Sterile plastic	'<10°C, Na2S2O3 (If Chlorinated)	6 hrs 24 hrs	1,6,7,8 1,6,7,8	56 56
E. Coli	SM 9223	125 mL	Sterile plastic	'<10°C, Na2S2O3 (If Chlorinated)	6 hrs	1,6,7,8	56
F-specific Coliphage (5-tube	EPA 1602	see human pathogen	see human	4 - 10 deg. C	24 hrs	1,6,7	42
MPN) Human pathogens			pathogen				
Quantitative adenovirus	RT-QPCR						42
Quantitative enteroviruses	Q-RT-PCR	4 L	4 L Sterile	4 - 10 deg. C	24 hrs	1,6,7	42
Infectivity adenovirus	ICC-PCR		plastic	. To dog. o	211110	1,0,7	42
Nutrient Parameters	100 1 011						
NH ₄ ⁺	EPA 353.2					1,6,7,8	56
NO ₃	EPA 353.2	250 mL	'250 mL Poly	none	48 hrs	1,6,7,8	56
NO ₂	EPA 350.1					1,6,7,8	56
Phosphorus	EPA 365.1	250 mL	'250 mL Poly	<6°C, H2SO4	28 days	1,6,7,8	56
Phosphate (PO ₄ ³⁻)	EPA 365.1	2002		,	20 00,0	1,6,7,8	56
Metal Parameters						,-, ,-	
Al	EPA 200.8					1,2,3,4,5,6,7,8	112
Sb	EPA 200.8					1,2,3,4,5,6,7,8	112
As	EPA 200.8					1,2,3,4,5,6,7,8	112
Be						1,2,3,4,5,6,7,8	112
B Cd	EPA 200.8 EPA 200.8					1,2,3,4,5,6,7,8	112
Cr(T)	EPA 200.8					1,2,3,4,5,6,7,8	112 112
Ci(1)	EPA 200.8					1,2,3,4,5,6,7,8	112
Cu	EPA 200.8					1,2,3,4,5,6,7,8	112
Fe	EPA 200.8					1,2,3,4,5,6,7,8	112
Pb	EPA 200.8	500 mL	plastic	HNO3	180 days	1,2,3,4,5,6,7,8	112
Mn		JOO IIIL	piadilo	111400		1,2,3,4,5,6,7,8	112
Mo						1,2,3,4,5,6,7,8	112
Ni So						1,2,3,4,5,6,7,8	112
Se						1,2,3,4,5,6,7,8	112 112
Ag Ti						1,2,3,4,5,6,7,8	112
Sn						1,2,3,4,5,6,7,8	112
Ti						1,2,3,4,5,6,7,8	112
V	EPA 200.8					1,2,3,4,5,6,7,8	112
Zn						1,2,3,4,5,6,7,8	112
Hg	EPA 245.1				28 days	1,2,3,4,5,6,7,8	112

^{*}F-specific Coliphage and human pathogens sampling and analyses methods are adapted from Jiang et al (Jiang et al, 2007). The other sampling and analyses methods are obtained from Weck Laboratories.

Real time data loggers and potable measuring devices will be deployed at each selected sampling location before the coming of the first storm as shown in Table C2.

Table C2 - Online meters and potable meters summary list

	Equipments used at the pilot	Model#	Equipment Type	Equipemt needed	
	Chlorophyll-a	Turner Designs AlgaeWatch Online Fluorometer	Online meter	-	
	Storm precipitation	http://www.nwsla.noaa.gov	NA	-	
Raw (1)	Particle counter	-	Portable	Met One GT-321	
Raw (1)	pН	Cole Palmer	Portable	-	
	Conductivity Temperature	Myron L Ultrameter	Portable	-	
	Turbidity	-	Online meter	Hach 1720E	
GMF (2)	Turbidity	Hach 1720E	Online meter	-	
Arkal Disc Filter (3)	Turbidity	Hach 1720 E (at the Feed to UF)	Online meter	-	
Pall MF (4,5)	Turbidity,	Hach FilterTrak 660 sc Laser Trubidimeter	Online meter	-	
Fail IVIF (4,5)	Temperature	Endress Hauser Temperature Transmitter	Online meter	-	
	Conductivity	Rosemount 54e	Online meter	-	
RO Trains (6,7,8)	Temperature	Nosemburit 54e	Offiliale fileter	-	
NO TIAITIS (0,7,6)	pН	Cole Palmer	Portable	-	
	Turbidity	-	Online meter	Hach 1720E	

Sampling bottles and all required sampling equipment should be ready before a storm comes. Weather forecasts can be obtained online (e.g., from the National Weather Service at http://www.nwsla.noaa.gov/) as can precipitation records. Online precipitation records will be used to determine if a 0.5-inch storm has occurred (e.g., National Weather Service for Los Angeles Airport, which is near the sampling site, available online at http://www.weather.gov/climate/index.php?wfo=lox and/or LA Department of Public Works rain gage data for El Segundo available online at http://ladpw.org/wrd/precip/index.cfm). Trussell Tech will identify when a 0.5-inch storm has occurred and notify SPI, United Water Services, and WBMWD. Sampling should begin within 24-hrs after notification by Trussell Tech that a storm 0.5-inch storm has occurred. Two samplings, one AM and one PM, will be conducted during each 24-hr period for a total of 7 days (14 total samplings).

Table C3 shows a summary of the number of sample bottles at each sampling location.

Table C3 – Summary of Sample Bottles Required at Each Sample Location

					Samplin	g Locations				
	Bottle Type	Raw Water (1)	Arkal Filtrate (2)	GMF Filtrate (3)	Pall 1 Filtrate (4)	Pall 2 Filtrate (5)	RO 1 Permeate (6)	RO 2 Permeate (7)	2nd Pass RO Permeate (8)	Total # of Bottles
	250 ml Poly	3					3	3	3	12
	40 mL VOA	3					3	3	3	12
No. of	1 L Amber	2					2	2	2	8
bottles per	125 mL Sterile plastic	1					1	1	1	4
sampling	1 Gal Sterile Plastic	1					1	1		3
	250 mL plastic	1	1	1	1	1	1	1	1	8
	250 ml Poly	42					42	42	42	168
	40 mL VOA	42					42	42	42	168
No. of	1 L Amber	28					28	28	28	112
bottles per	125 mL Sterile plastic	14					14	14	14	56
event	1 Gal Sterile Plastic	14					14	14		42
	250 mL plastic	14	14	14	14	14	14	14	14	112

Trussell Tech will coordinate with the couriers at the labs for pickup of the samplings in consideration of the holding times shown in Table C1 once confirmation of the time of the first sampling is received from SPI/United Water Services. Given the large number of sample bottles involved as shown in Table C3, the labs will provide bottles for the first several days prior to a storm event and then provide additional bottles during the the storm events. For each individual sampling (AM/PM on a given day), the sample bottles will be separated into coolers for each location (1-8) and for each sampling (AM/PM).

Special attention will be paid to the operational processes during the stormwater sampling period any irregular processes will be recorded. Table C4 is the field logsheet template.

Table C4 – Stormwater sampling field logsheet template

Date and	Time Rainfa	all Begins						
Date	Time	Sampling Locations	Particle Count	Temperature	Conductivity	Please Check here if all the samples are taken for lab analyses	Comments/Observation	Operator Initial

Once samples are collected and preserved, sample containers should be capped, labeled and stored on ice or refrigerated until shipped to the laboratory (see Table C1 for preservation requirements).

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Appendix D – Marine Biotoxin Monitoring Experimental Plan

Date: June 30, 2009 **To**: Phil Lauri, P.E

Authors: David R. Hokanson, Ph.D., P.E.

Emily L. Owens Jay S. Wang

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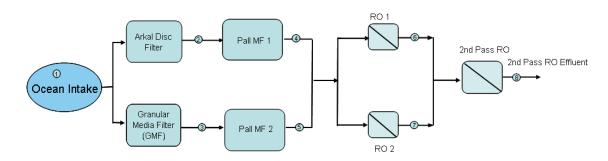
R. Shane Trussell, Ph.D., P.E.

Subject: Marine Biotoxin Monitoring Experimental Plan for West Basin

Municipal Water District (WBMWD) El Segundo Pilot Facility¹

1. INTRODUCTION

West Basin Municipal Water District (WBMWD) has been researching and developing integrated membrane seawater desalination systems and investigating the operational and water quality implications of these treatment processes for more than seven years. As outlined in Figure D1, the WBMWD pilot facility includes a prescreening/pretreatment process consisting of an Arkal pretreatment strainer unit, operating in tandem with a high-rate granular media filter (GMF) followed by two parallel Pall microfiltration (MF) units. The filtrate from the Pall MF units is subsequently fed into two seawater reverse osmosis (SWRO) trains followed by a second pass brackish RO train.



¹ Note: This draft experimental plan was prepared by Trussell Tech in collaboration with the USC research groups of Dr. David Caron and Dr. Burton Jones.

Figure D1. Simplified Schematic of the El Segundo Pilot Desalination Facility **Treatment Process**

One aspect of the WBMWD investigation involves the implications of source water quality (open ocean intake) on the operation of desalination treatment processes. 'Red Tides' are a phenomenon caused by algal blooms associated with changes in nutrient availability, and can indicate the relative abundance of major nutrient elements such as nitrogen and phosphorus. A small proportion of the microalgal species related to 'red tides' are capable of producing toxic compounds. Blooms of such algae are referred to as harmful algal blooms (HABs), and can cause illness or death in humans and other species. Human activities have been implicated in increasing both the intensity and global distribution of HABs (Hallegraeff et al., 2004). This increase in frequency of HABs has been paired with rising public health and economic impacts related to these events during the past two decades (Hallegraeff et al., 2004).

HABs and their associated marine biotoxins have been identified as a concern for West Basin's full-scale desalination treatment plant. In addition to health concerns related to toxins in permeate water, dense aggregation of these phytoplankton, algae, or cyanobacteria HABs can reduce the efficiency of desalination pretreatment processes and contribute to biofouling of reverse osmosis (RO) membranes themselves. WBMWD has proposed to investigate the causes and implications of HABs by the approach described in this experimental plan.

The approach involves (1) a literature review to identify important marine biotoxins to consider in this study; (2) bench-scale experiments to demonstrate the removal of select marine biotoxins by SWRO membranes; characterization of phytoplankton taxonomy in the raw water intake for WBMWD's SWRO pilot facility at El Segundo; (4) collecting water quality data from sensors attached to buoy systems located proximally to possible ocean intakes at El Segundo and Redondo Beach; (5) sampling and testing both raw water and permeate for marine biotoxins; and (6) analysis of marine biotoxins with enzyme-linked immunosorbent assay (ELISA) methods.

Identification of Important Toxins

Dr. David Caron and his lab group at USC conducted a comprehensive literature review of marine biotoxins, and identified contaminants of concern to this project (Caron et al., 2009). The biotoxins of concern include domoic acid, saxitoxin, brevetoxin, okadaic acid, and yessotoxin, and are discussed below.

1. Domoic acid (DA) has been identified as a potent neuroexcitant that can cause amnesic shellfish poisoning (ASP) in humans. Symptoms of ASP may include vomiting, diarrhea, potential confusion, memory loss, disorientation, and sometimes coma

or death (Litaker et al., 2008). DA is a secondary amino acid from the

kainoid class of compounds produced by several marine diatoms belonging to the genus *Pseudo-nitzschia* (Hallegraeff et al., 2004). The main toxin producing species that have been documented on the U.S. west coast include: *P. australis*, *P. delicatissima*, *P. fraudulenta*, *P. multiseries*, *P. pungens*, *P. multistriata*, *P. pseudodelicatissima* and *P. seriata* (Hallegraeff et al., 2004).

2. Saxitoxin has more than 30 analogues in the natural environment, and is produced by Dinoflagellates in marine ecosystems from the genus Alexandrium, as well as from some freshwater Cyanobacteria. It is the most potent marine toxin currently known (Lefebvre et al, 2008), and toxic conditions can be caused by abundant Alexandrium, even without full 'algal bloom' conditions. Consumption of seafood made of filter-

feeding organisms containing saxitoxin by humans can cause paralytic shellfish poisoning (PSP), with symptoms including burning or tingling, dizziness, vomiting, diarrhea, and in extreme cases muscle paralysis or death (Hallegraeff et al., 2004).

3. Brevetoxin is a ladder-shaped polycyclic ether compound that can bind to sodium channels in neurons, disrupting the initiation of action potentials and nerve function in humans. This condition, neurotoxic

shellfish poisoning (NSP), can produce symptoms such as chills, headache, diarrhea, muscle weakness, nausea, and vomiting (Hallegraeff et al., 2004). Brevetoxin is produced by the dinoflagellate species *Karenia brevis, K. bicuneiformis, K. brevisulcata, K. papilionacea,* and *K. selliformis* (Hallegraeff et al., 2004), as well as a few raphidophyte species, including *Heterosigma akashiwo, Chattonella marina,* and *Fibrocapsa japonica*. Along the western coast of Florida, red tides caused by *Karenia brevis* occur on an almost annual basis. Wave activity releases large amounts of brevetoxin into the air and can affect respiratory function in humans (Hallegraeff et al., 2004).

 Okadaic acid and its analogues are long chain compounds with transfused or spiro-linked cyclic polyether rings. They are produced by

the *Dinophysis* and *Prorocentrum* species, and can cause diarrheic shellfish poisoning (DSP), which is similar to food poisoning (Hallegraeff et al, 2004). Okadaic acid and its derivative dinophysistoxins have been confirmed in *D. acuminata*, *D. acuta*, *D. mitra*, *D. fortii*, *D. norvegica*, *D.*

rotundata, D. tripos, and are suspected in D. caudate, D. hastate, and D. sacculus (Hallegraeff et al, 2004).

5. Yessotoxin is another ladder-shaped polycyclic ether compound, but it is produced by the dinoflagellate *Protoceratium* reticulatum (Hallegraeff et al., 2004). Several analogues of yessotoxin have been identified, and they are produced by

three Dinoflagellates, *Protoceratium reticulatum* (Claparede and Lachmann) Buetschi, *Lingulodinium polyedrum* (Stein) Dodge, and *Gonyaulax spinifera* (Claparede et Lachmann) Diesing. All three of these dinoflagellates are present on the U.S. west coast, however toxin production among strains within each species appears to be highly variable, and conflicting reports have been published regarding the toxicity of yessotoxin. Some studies have shown that yessotoxin targets the immune system, while other reports have shown yessotoxin-caused damage to the central nervous system.

Algal blooms may adversely impact desalination by contributing large amounts of phytoplankton material to intake water; this may significantly reduce the efficiency of pretreatment processes and contribute to fouling of RO membranes. It is reasonable to expect that phytoplankton cells will be removed during pretreatment, however the phytoplankton may release toxins extracellularly or due to cell rupture during RO treatment. These toxins may be capable of passage into the RO permeate.

The potential impacts of these biotoxins on human and marine mammal health have been examined in studies involving the consumption of shellfish and other lower marine organisms. Current data is limited to domoic acid and phytoplankton speciation, thus the proposed work regarding marine biotoxins and their implications on the SWRO treatment process and public health will focus on the other toxins.

Bench Scale Marine Biotoxin Monitoring

A bench-scale apparatus for RO desalination was established at USC to test RO membrane performance in removing known quantities of marine biotoxins most relevant to Southern California, extracellular materials, and diverse phytoplankton taxa. Procedures for sampling and testing of the specific marine biotoxins targeted in the bench-scale RO operations are outlined in Appendix I. The Osmonics SEPA® CF II Membrane Cell System was used for the bench-scale testing. Some initial problems were encountered in achieving the expected salt rejection, prompting some changes in the protocol. A new, unproven

membrane had been used, and was switched in favor of an industry standard, the Hydranautics SCW4+ membrane. Another change involved eliminating the use of deionized water in the feed. Photos of the bench-scale apparatus are provided in Appendix II. In the bench-scale testing, feed biotoxin concentrations will be used representative of the highest biotoxin concentration expected in seawater and accounting for the RO recovery typical of seawater desalination.

Characterization of Phytoplankton Taxonomy

Dr. Burton Jones' research team from USC is responsible for phytoplankton characterization and they describe their phytoplankton taxonomy characterization technique as follows (Cetinic, 2009). The phytoplankton composition analysis has been conducted using a raw water sample (250 mL) collected each week by West Basin from the ocean intake (point "1" on Figure D1) at the El Segundo desalination pilot plant. The raw water sample is preserved with acid Lugo's iodine solution (~5% final solution), as it is the recommended method for prolonged preservation and storage of the samples (Anderson et al. 2001; Throndsen 1978). After sedimentation for 24 h, a 50 mL subsample is analyzed, and cell counts are obtained using the inverted microscope method (Utermohl 1958). Microphytoplankton cells (longer than 20 µm) are counted at magnifications of 200 and 400x. Nanophytoplankton cells (2-20 µm) are counted in 20 randomly selected fields of vision, under magnification of 400 and 1000x. Morphological determination will be conducted based on published literature, including the following citations and many others: Horner, 2002; Steidinger and Tangen, 1995; Throndsen, 1993.

Pilot Scale Marine Biotoxin Monitoring

Phytoplankton taxonomy and domoic acid analysis will continue throughout the bench-scale and pilot phases of the West Basin desalination project. During the pilot scale phase, USC will expand the scope of marine biotoxins analysis. The following algal toxins will be analyzed using the ELISA method, if indicated by phytoplankton taxonomy:

- Saxitoxin
- Brevetoxin
- Okadaic Acid

Dr. David Caron's research team at USC is responsible for marine biotoxin analysis. For the bench-scale work, they have been given one-liter samples of both raw water (point "1" on Figure D1) and RO 1 permeate (point "6" on Figure D1), collected each week by West Basin. These samples were analyzed for domoic acid. Extra raw water and RO 1 permeate samples were collected and passed through a 0.2-micron glass fiber filter, in which approximately 10 mL were dissolved. The resulting sample was frozen and preserved for possible retrospective analysis of additional algal toxins at a future date.

During the pilot scale phase of operations, West Basin will continue with weekly sampling of both raw and RO 1 permeate water. The procedure for

phytoplankton characterization will remain the same as the bench-scale monitoring approach. For the marine biotoxin analysis, there will be a change in sampling volumes from 1 L to 2 L for raw water and RO Train 1 permeate collected for Domoic acid analysis by the David Caron research team. A 'retrospective' analysis for saxitoxin and okadaic acid will be conducted, using the frozen samples of raw water that were collected during weekly sampling at El Segundo in 2008.

Samples that have been frozen or stored in plastic are unacceptable for brevetoxin, thus the retrospective analysis is not possible due to the nature of sample preservation (frozen in plastic containers). Instead, West Basin will use glass bottles to collect daily samples of 250 mL of raw water and 25 mL of permeate water for 14 days. These samples will be delivered to USC and analyzed for brevetoxin in one batch, to minimize the cost for use of the expensive ELISA kit.

Yessotoxin was originally identified as a marine biotoxin for possible inclusion within this analysis. Testing for yessotoxin has proven problematic, however, because the ELISA analysis kits are no longer made, and the LCMS analysis method is prohibitively expensive. The research team at USC will be unable to test for yessotoxin.

Water Quality and Nutrient Monitoring

Extensive water quality monitoring will be conducted in conjunction with WBMWD efforts to investigate the causes and implications of HABs proximal to the ocean intakes at their El Segundo and Redondo Beach facilities. Four water quality monitor (WQM) units manufactured by WET Labs will be installed on two Watchmate buoys from AXYS Technologies Inc. near these facilities. The WQM combines WET Labs' fluorometer-turbidity sensor with Seabird's CTD sensors, to provide measurements of temperature, salinity, dissolved oxygen, depth, chlorophyll a fluorescence, turbidity, and optical backscattering. CDOM (colored dissolved organic matters) will not be monitored. Data from the sensors will be transferred via radio antennas to a computer stationed at AES power plant in Redondo Beach, and transmitted to USC for analysis. This data will be monitored in tandem with marine biotoxin and other water quality results from on-going sampling of both raw and permeate water from the pilot plant.

Buoy and Mooring System

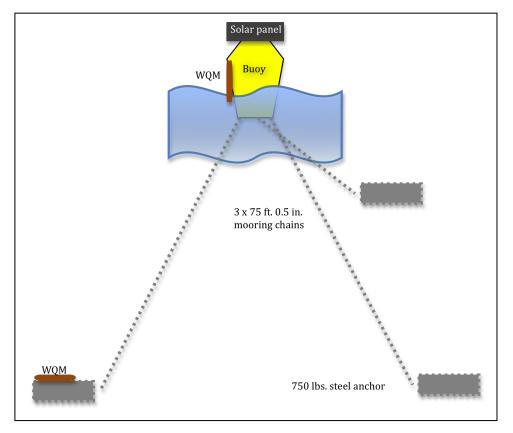


Figure D2. Schematic of buoy and mooring configuration

A schematic of the buoy and mooring system is pictured in Figure D2, featuring a 3-point mooring system that was designed and built at USC to accommodate the Watchmate buoys and WQM with AXYS data management system that will be located at the surface and bottom of the ocean. Each buoy will be moored by three 75 ft.-long ½" galvanized shackle chains hooked onto wheels with a minimum of 750 lbs. steel anchor, and placed in a triangular configuration on the bottom of the ocean. This design will allow for additional stability and to protect the monitoring instruments.

Water Quality Monitoring Sensors



Figure D3. WQM submerged in water for testing

In the summer, algal blooms are typically in the subsurface (20-30 m depth), whereas in the spring they are more likely to occur near the water surface. Two of the WQMs from Figure D3 will be attached to each buoy in order to provide water quality data from the ocean surface, as well as from a depth of 15 m. The WQM located at the bottom of the ocean will allow for the monitoring of algal blooms in deeper water, which are typically caused by internal tides. It will be attached to the top of one of the three mooring wheels, and will be powered by a WET Labs battery pack (BPA-50), as depicted in Figure D4.



Figure D4. Battery for WQM located at ocean bottom (15 m depth)

The buoys will be equipped with a WQM attached to a cage at the water surface, as shown in Figure D5. Data will be collected by the WQMs on the buoys using a WatchMan500 data acquisition and processing system, and will be transmitted via Freewave wireless data transceiver (pictured in Figure D6) to an antenna and radio transmitters at the AES power generation station in Redondo Beach. This data will be accessed directly by the USC lab group, through their server.



Figure D5. Buoy with cage for WQM



Figure D6. Computer stationed at AES with wireless data transceiver

Solar Panels and Power Generation

Figures 7 and 8 feature the three Solar Module Shell ST20 panels and AXYS Watchman sensor processor module battery storage unit with associated connections which will power the WQM and data transmission systems on each buoy. According to members of the Dr. Burton Jones lab group at USC, the frequency of data transmissions from the WQM and to the AES computer will depend on the weather conditions and power generated by the solar panels, since radio transmission of stored data collected by the WQM will be the biggest drain on the solar-powered battery packs. The current plan is to transmit data once per hour, for 5 minutes.



Figure D7. Buoy with solar panels and battery power connections



Figure D8. Solar panels on top of buoy

Protection and Maintenance

In order to protect the WQM from the movements of the heavy mooring chain that is hooked to a ring next to the sensor cage (visible in Figures 9 and 10), the protective cover in Figure D10 has been made using improvised plastic milk crates. This will be modified with a more permanent and sophisticated anti-chain cover in the future.



Figure D9. RR Wheel Anchor and mounting for WQM at depth (15 m)



Figure D10. RR Wheel Anchor with plastic cover for WQM cage and ring for chain mooring

In addition to the metal cages and plastic covers for the WQM equipment, the orange plastic fencing in Figure D11 will be wrapped around the buoy to deter seals, as seen in Figure D12. Seals are notorious for climbing onto buoys, and would harm the WQM surface mounts, as well as the solar power and transmission connections. This is demonstrated in Figure D13, one of many shots available on the internet.



Figure D11. Orange plastic fencing for seal-control



Figure D12. Buoy with anti-seal protection, prior to deployment (photo by Phil Lauri)



Figure D13. Seals camping out on a similar buoy off San Pedro (from internet)

Though rugged by normal standards, the WQM will require routine cleaning and maintenance, replacing the battery for the submerged WQM, verifying all of the connections, and calibrating the instruments.

Buoy Deployment

The first buoy was launched at Redondo Beach on Thursday, March 19, 2009. Figures 13-15 depict the deployment and mooring of the buoy. Due to the weight of the buoy and mooring, the sensitivity of the instrumentation, as well as the time involved in securing the buoy and mooring systems, only one buoy was launched. The remaining buoy was moored at El Segundo on May 29, 2009.



Figure D13. March 19, 2009 buoy launch at Redondo Beach (photo by Phil Lauri)



Figure D14. Lower buoy into the water at Redondo Beach (photo by Phil Lauri)



Figure D15. Buoy moored at Redondo Beach (photo by Phil Lauri)

Future Additions

It is expected that increased nutrient loading in the intake water will be observed prior to the occurrence of algal blooms. Nutrient monitoring will thus be included as an important component of the overall marine biotoxin monitoring project. The Watchmate buoys will initially be moored without the nutrient sensors, but there is additional space to accommodate nutrient sensors at a later time. Purchasing the required nutrient sensors was outside the scope of the project budget, however Dr. Burton Jones has an established relationship with WET Labs, and has arranged to be a beta tester in order to use the nutrient sensors without cost to the project. As a beta tester, it will be possible to obtain phosphate data from the nutrient sensors at each mooring. Nutrient monitoring is important, as phosphate will be present for algal blooms associated with deep water, runoff, or sewage effluent. Another potential future addition would be instrumentation to upgrade the buoys as a weather station.

Buoys – Locations

Sensors mounted to buoys will be moored in proximity to the intake areas for the El Segundo and Redondo Beach desalination pilot plants, as shown in Figure D16.

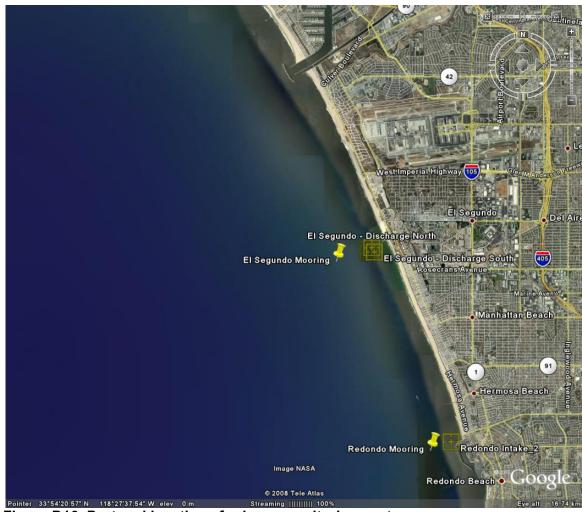


Figure D16. Protocol locations for buoy monitoring system

Monitoring Parameters

Specific parameters measured as part of the marine biotoxin monitoring are outlined in Table D1, along with the analysis method, sampling location, and other details.

Table D1. Marine Biotoxin Monitoring Parameters, Analysis Methods, and Sampling Locations

Parameters	Method	Sample Amount Needed	Bottle Type	Preserv- ative	Sampling Locations	Sampling Frequency	
Phytoplankton	Taxonomy						
Micro- phytoplankton cells	- Sedi-		plastic	Lugo's iodine soultion	1	1/week	
Nano- phytoplankton cells	Sedi- mentation	250 mL raw*	plastic	Lugo's iodine soultion	1	1/week	
Nutrient Param	eters		•	•	•		
Phosphate (PO ₄ ³⁻)	phosphate sensor	N/A	N/A	N/A	buoys	continuous	
Biotoxin Param	neters						
Domoic Acid	ELISA	2 L raw, 2 L permeate	plastic	freezing	1, 6	1/week	
Saxitoxin	ELISA	1 L raw. 1 L permeate	plastic	freezing	1, 6	1/week	
Brevetoxin	ELISA	250 mL raw, 25 mL permeate	glass	N/A	1, 6	14 x 1/day	
Okadaic Acid	ELISA	1 L raw. 1 L permeate	plastic	freezing	1, 6	1/week	
Other Paramete							
chlorophyll a	WET Labs backscatter/ fluorometer	N/A	N/A	N/A	buoys	continuous	
turbidity	WET Labs backscatter/ turbidity sensor	N/A	N/A	N/A	buoys	continuous	
temperature	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous	
salinity	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous	
dissolved oxygen	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous	
conductivity	Seabird CTD sensor	N/A	N/A	A N/A buoys co		continuous	
depth	Seabird CTD sensor	N/A	N/A	N/A	buoys	continuous	

^{*} Weekly samples of 250mL (raw) for phytoplankton taxonomy and 1L raw, 1 L permeate for biotoxin analysis are used for test for multiple parameters

Analytical Methods

All marine biotoxin testing will be conducted by Dr. David Caron's lab group at USC, using ELISA test kits. This method has been selected based on availability, cost, and accuracy.

Enzyme-linked immunosorbent assay (ELISA) Overview

Enzyme-linked immunosorbent assay (ELISA), a common marine biotoxins detection technology, is a biochemical technique used mainly in immunology to detect the presence of an antibody or an antigen in a sample. The ELISA method works by affixing an unknown amount of antigen to a surface, and then washing a specific antibody over the surface so that it can bind to the antigen. Next, a second antibody (conjugate) linked to an enzyme is added to the solution to bind to the primary antibody. In the final step, a specific substrate (chromogen) is added to the plate. The enzyme changes color through a reaction with the substrate, and based on this color, the concentration can be determined.

Domoic Acid Screening Test Kit (Mercury Science Inc.)

Domoic acid is measured using a solid phase colorimetric immunoassay, as illustrated in Figure D17. This ELISA method is based on competition between domoic acid and an enzyme-labeled domoic acid (DA-Tracer) for anti-domoic acid antibody. Both the Ab-domoic acid and Ab-DA-Tracer complexes are captured on the surface of the microtiter plate wells, but any of the samples containing domoic acid inhibit the binding of the DA-Tracer to the antibody molecules. The microtiter plate is subjected to a washing step, followed by the addition of an enzyme substrate (TMB) that forms a color proportional to the amount of DA-Tracer in the well. The amount of color measured is inversely proportional to the concentration of domoic acid in the sample (Mercury Science Inc., 2007).

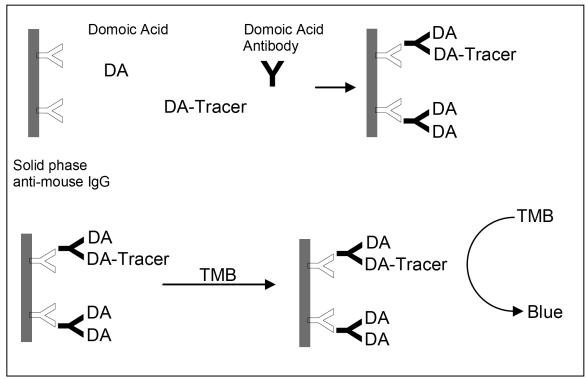


Figure D17. Schematic of the reaction of Domoic acid kit (Mercury Science Inc. 2007)

Domoic Acid Screening Test Kit (Biosense)

This ELISA is based on competition between free Domoic Acid and the DA-conjugated protein, coated on plastic wells for binding to anti-DA antibodies free in the solution. This is shown in Figure D5 below. The anti-DA antibodies are conjugated to horseradish peroxidase (HRP). Samples are then incubated in the wells with the anti-DA-antibody-HRP conjugate. The well is subjected to a washing step, the remaining conjugate that is bounded to the wells is then measured with a substrate (TMB) that forms a color proportional to the amount of DA-Tracer in the well. The amount of color measured is inversely proportional to the concentration of Domoic Acid in the sample (Biosense, 2006).

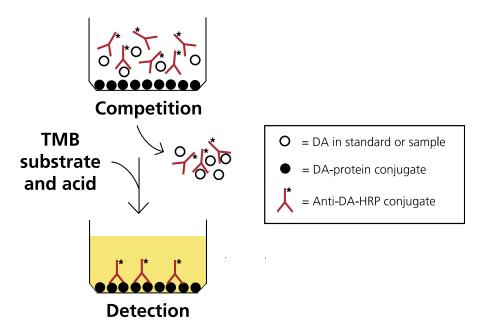


Figure D5. Schematic of the reaction of Domoic Acid kit (Biosense, 2006)

Saxitoxin (PSP) ELISA, Microtiter Plate (Abraxis LLC)

The saxitoxin test is a direct competitive ELISA based on competition between saxitoxin and a saxitoxin enzyme-conjugate for the binding sites of rabbit antisaxitoxin antibodies in solution. The saxitoxin antibodies bind to a second antibody (sheep anti-rabbit) immobilized on the plate, then after a washing step, a substrate solution is added, and a color signal is produced. After a specified time, the color reaction is stopped, and the color is evaluated using an ELISA reader. The blue color is associated with the saxitoxin enzyme-conjugate, thus its intensity is inversely proportional to the concentration of the saxitoxin present in the sample. The test kit constructs a standard curve with each run, from which saxitoxin concentrations of the samples are determined (Abraxis LLC, Saxitoxin ELISA manual).

Brevetoxin (NSP) ELISA, Microtiter Plate (Abraxis LLC)

The test for brevetoxin is a direct competitive ELISA based on competition between brevetoxin and a brevetoxin enzyme-conjugate for the binding sites of sheep anti-brevetoxin antibodies that have been immobilized in the wells of a microtiter plate. Following a washing step, a substrate solution is added, producing a color signal. After a specified time, the color reaction is stopped, and the color is evaluated using an ELISA reader. The blue color is associated with the brevetoxin enzyme-conjugate, thus its intensity is inversely proportional to the concentration of brevetoxin present in the sample. The test kit constructs a standard curve with each run, from which brevetoxin concentrations of the samples are determined (Abraxis LLC, Brevetoxin ELISA manual).

Okadaic Acid (DSP) ELISA, Microtiter Plate (Abraxis LLC)

The okadaic acid test is a direct competitive ELISA based on competition between okadaic acid and an okadaic acid-enzyme-conjugate for the binding sites of rabbit anti- okadaic acid antibodies in solution. The okadaic acid antibodies bind to a second antibody (goat anti-rabbit) immobilized on the plate, and following a washing step and addition of a substrate solution, a color signal is produced. After a specified time, the color reaction is stopped, and the color is evaluated using an ELISA reader. The blue color is associated with the okadaic acid enzyme-conjugate, thus its intensity is inversely proportional to the concentration of the okadaic acid present in the sample. The test kit constructs a standard curve with each run, from which okadaic acid concentrations of the samples are determined (Abraxis LLC, Okadaic Acid ELISA manual).

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APPENDIX I: RO Bench Scale Draft Experimental Plan

Prepared by E. Seubert, J. Eagleton, S. Chiu, D. Caron, S. Trussell

<u>Testing of Algal Toxins Rejection by RO membranes using Sepa Cell CFII</u> <u>Testing Procedure</u>

This procedure will outline the operation of the Sepa Cell particular to the testing of the algal toxins and not contained in the Sepa Cell instructional manual. The different sections describe the set points and how to set up the system.

1. Set Points

These are the various set points for the different step during start-up and running the test.

1.1 General (applicable to all operating modes):

Temperature: To be maintained between 23°C and 24°C

Feed/Concentrate Flow: 2.2 L/min Cell Holder Pressure: 900 psi

1.2 Membrane Conditioning

The membrane need to be flush and base-lined using tap water and a solution made with tap water and NaCl.

1.2.1 Tap Water Flush and Base-line Flux Measurement

Permeate Flow Rate: 25 ml in 7 min or 3.6 mL/min Operating pressure during de-chlorinated tap water conditioning: approximately 260 psi

1.2.2 Base-line Rejection measurement

NaCl solution for Membrane Conditioning: 47 g/L (added to de-chlorinated tap water)

Permeate Flow with 47 g/L NaCl feed: 25 ml in 7 min or 3.6 mL/min

Feed conductivity at 47 g/L: ≈75 mS/cm

Operating pressure during NaCl conditioning: ≈800 psi

Permeate conductivity: less than 500 µS/cm

1.3 Normal Seawater Operation: A 50/50 mixture of El Segundo Pilot Feed and Concentrate streams

Permeate Flow Rate: 25 ml in 7 min or 3.6 mL/min

Feed Conductivity: ≈75 mS/cm Operating Pressure: ≈800 psi

Permeate Conductivity: less than 500 µS/cm

2. Replacing the RO membrane

At the beginning of every test run the membrane will need to be replaced. A test run is defined as system set-up, membrane conditioning, a 24 hour stabilization period, toxin injection and a seven day toxin sampling period.

2.1 Placing Membrane into Cell:

- See Sections 3 and 4 of the Sepa CFII Manual for general operation of the Sepa Cell
- Cut the membrane carefully using the cardboard template
- Rinse the membrane and the open cell with plenty of DI water using a wash bottle
- Place the membrane into the cell in between the four guidepost (pins) making sure that both the feed spacer (cell body top) and the permeate carrier (cell body bottom) are not displaced from their recesses. The shiny side of the membrane should face down. Use more DI water if needed as it will help the membrane, the spacer and the permeate carrier to stay in place
- Place the cell in the holder and increase the holder pressure as described below using the hand pump. If the pressure does not increase after more than 10-15 pump strokes, tighten the pressure relief valve located on the hand pump (on the opposite end of the pump handle).

3 Membrane Conditioning and Characterization

Membrane conditioning and characterization is required any time a new piece of membrane is used. Membranes need to be replaced if they are damaged (which can occur from handling i.e. scratches etc), become fouled or have reached the end of a particular test run (see Section 4). Each coupon is cut from the large membrane sheet and there is a possibility of slight defects between different coupons. Sometimes these defects can present significant differences in their characteristics (salt rejection and permeate flux). It is important that each membrane coupon is consistent with the other membrane coupons used in the test so that the data can be compared. Therefore, membrane conditioning and characterization steps represent a trial and error method and are critical to find representative coupons before starting a new test.

- 3.1 Tap water conditioning of the membrane coupon
 - 3.1.1 De-chlorinate the tap Water by adding metabisulfite (SMBS) powder to the tap water. The concentration of SMBS needed to de-chlorinate is 1.5 mg/l per 1 mg/l Cl₂. (10 liters of tap water requires 30 mg of SMBS assuming 2 ppm Cl₂).

- 3.1.2 Adjust the system operating pressure and holder pressure as described below.
 - o Pump the cell holder to 200 psi
 - o Make sure the concentrate valve is completely open
 - Turn on the feed pump
 - Slowly close the concentrate valve to a pressure of 200 psi and then open it completely up. Do this 3 times. (To remove any trapped air)
 - Let the system run for one minute at 200 psi.
 - o Then pump the cell holder to 400 psi.
 - Slowly increase the concentrate pressure to 400 psi by slowly closing the concentrate valve.
 - Let the system run at 400 psi for one minute.
 - o Then pump the cell holder to 600 psi.
 - Slowly increase the concentrate pressure to 600 psi by slowly closing the concentrate valve.
 - Let the system run at 600 psi for one hour.
- 3.1.3 Decrease the operating pressure to 300 psi. Allow the system to stabilize for ten minutes. Take the required instrument readings and flow measurement (see Table D1). Reduce the pressure to 200 psi. Allow 10 minutes for system to stabilize and take another data point. Reduce the pressure to 100 psi. Allow 10 minutes for system to stabilize and take another data point. Take at least two permeate flow measurements for each sample and take the average.

The normalized permeate flow is obtained by dividing the permeate flow by the operating pressure. This parameter does not depend on pressure and should not vary by more than 5-7%, assuming constant feed temperature. Confirm that the normalized permeate flux is within 10% of the set point defined in Section 1. If the differences are larger, discard the membrane and start again with Section 2.1.

3.2: NaCl solution conditioning

- 3.2.1 Prepare feed solution by dissolving 2.7 mg/l of SMBS and 47 g/L of NaCl in tap water. 10 liters of tap water requires 27 mg of SMBS and 470 g NaCl. Make sure that all salt has been dissolved by visual inspection and by checking the conductivity against the set point defined in Section 1.
 - o Pump the cell holder to 200 psi
 - Make sure the concentrate valve is completely open
 - Turn on the feed pump
 - Close the concentrate valve to a pressure of 200 psi then open it completely. Do this 3 times. (To remove any trapped air)
 - Let the system run for one minute at 200 psi.

- o Then pump the cell holder to 400 psi.
- Slowly increase the concentrate pressure to 400 psi by slowly closing the concentrate valve.
- Let the system run at 400 psi for one minute.
- o Then pump the cell holder to 600 psi.
- Slowly increase the concentrate pressure to 600 psi by slowly closing the concentrate valve.
- Let the system run at 600 psi for one minute.
- o Then pump the cell holder to 800 psi.
- Slowly increase the concentrate pressure to 800 psi by slowly closing the concentrate valve.
- Let the system run at 800 psi for one minute.
- o Then pump the cell holder to 900 psi.
- O Make sure the system is stable (no fluxuasions in the feed pressure).
- 3.2.2 Take all of the required readings hourly for the first five hours. Calculate the rejection and normalized flow rate. The rejection should be above 99% and the normalized flow rate should be within +/- 10% of the set point defined in section 1 after five hours. If the rejection is not above 99% or the normalized flow is off specification, there is a high possibility of membrane having a defect and the test should be restarted.

4 Normal Operation

The test solution is a mixture of the feed and concentrate streams from the West Basin Ocean-water Desalination Pilot Program in El Segundo. The mixture is made by adding 10 liter of the feed stream to 10 liter of the concentrate stream. Verify that the conductivity matches the set point defined in Section 1.

Slowly increase the system pressure to its set point outline in Section 1.3. Verify the feed temperature is between 23-24°C. If not, adjust the temperature accordingly. Take a permeate sample and measure conductivity and flow every hour for the first 5-8 hours. Allow the system to run for at least 24 hours. After 24 hours, take two data readings one hour apart to verify that the system is stable. If there is more than 2% difference between those readings, additional run time must be added to stabilize the system. Once the system is stable the contaminants can be added. It is important that the system is stable and operating at set points before toxin sampling begins.

Sampling of the toxin level in the concentrate and permeate will take place over a 7 day period on the following time points:

Day 1 T0, T1, T6, T12, T24

Day 2 T36, T48

Day 3 T60, T72

Day 4 T84, T96

```
Day 5 T108, T120
Day 6 T132, T144
Day 7 T156, T168
```

The "T" is the total amount of time in hours that a particular toxin has been flowing through the test cell.

At each time point the sample size will be 1mL.

Toxin Calculations to determine the amount of toxin to be placed in the reservoir:

Domoic Acid

```
Target: 25\mu g/L

5mg 90% DA dissolved into 1L Milli-Q = 4500\mu g/L

(4500\mu g/L) x = (25\mu g/L)(20L)

x = 0.111L \rightarrow 111mL of 1° Stock into 19.9L 50/50

Concentrate/Feed Mix
```

Saxitoxin

```
Target: 1µg/L
0.5mL ampoule of 65µM STX in 0.003M HCI
Molecular Weight STX = 299.3g/mol
65µM * 299.3g/mol = 19454.5µg/L → comes in 0.5mL
ampoules, therefore 9.727µg in ampoule
(9.727µg)/(0.5mL) = (20µg)/x mL
x = 1.03mL of STX (2.06 ampoules) into 19.9L 50/50
Concentrate/Feed Mix
```

Brevetoxin

```
Target: 60\mu g/L

1mg PbTx 2 dissolved into 100mL EtOH \rightarrow 10000\mu g/L

(10000\mu g/L) x = (60\mu g/L)(20L)

x = 0.12L \rightarrow 120mL of 1° Stock into 19.88L 50/50

Concentrate/Feed Mix
```

5 When to replace the membrane

A new piece of membrane will be required as soon as any of the following circumstances occur:

- The permeate flow at constant operating pressure and temperature changes by more than
 - +/-10% OR
- The permeate conductivity at constant operating pressure and temperature increases by more than 10% OR
- A new test run is initiated.

6 Shut Down

If the system is shut down for longer then eight hours it should be flushed with de-chlorinated tap water. This will slow down any biological growth and rusting of the system.

West Basin Red Tide Experiment (USC)

Date	Time	Feed Pressure Feed Conductivity		Permeate Conductivity	Tank Temperature	Bath Temperature	Time per 25 ml
Date	Tille	(psi)	(mS/cm)	(mS/cm)	(°C)	(°C)	(sec)

Table D1. Required data to be taken

APPENDIX II: Photos of RO Bench-scale Experimental Setup



Figure D2.1 – Portion of RO Bench-Scale Cell showing inlet, concentrate outlet, pressure gauge, and flow control valve (FCV). RO membrane is not in place.



Figure D2.2 - Portion of RO Bench-Scale Cell showing inlet, concentrate outlet, pressure gauge, and flow control valve (FCV). RO membrane is in place.



Figure D2.3 – RO Bench-scale Cell showing RO permeate flow into the beaker



Figure D2.4 – RO bench-scale skid showing high-pressure pump (bottom middle)

Appendix E – Submitted Manuscript to *Water Research*

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3	HARMFUL ALGAE AND THEIR POTENTIAL IMPACTS ON
4	DESALINATION OPERATIONS OFF SOUTHERN CALIFORNIA
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23	Key Words: Harmful Algal Blooms, Desalination, Red Tides, Phytoplankton, Phytotoxins

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ABSTRACT

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Seawater desalination by reverse osmosis (RO) is a reliable method for augmenting drinking water supplies. In recent years, the number and size of these water projects have increased dramatically. As freshwater resources become limited due to global climate change, rising demand, and exhausted local water supplies, seawater desalination will play an important role in the world's future water supply, reaching far beyond its deep roots in the Middle East. Emerging contaminants have been widely discussed with respect to wastewater and fresh water sources, but also must be considered for seawater desalination facilities to ensure the long-term safety and suitability of this emerging water supply. Harmful algal blooms, frequently referred to as 'red tides' due to their vibrant colors, are a concern for desalination plants due to the high biomass of microalgae present in ocean waters during these events, and a variety of substances that some of these algae produce. These compounds range from noxious substances to powerful neurotoxins that constitute significant public health risks if they are not effectively and completely removed by the RO membranes. Algal blooms can cause significant operational issues that result in increased chemical consumption, increased membrane fouling rates, and in extreme cases, a plant to be taken off-line. Early algal bloom detection by desalination facilities is essential so that operational adjustments can be made to ensure that production capacity remains unaffected. This review identifies the toxic substances, their known producers, and our present state of knowledge regarding the causes of toxic episodes, with a special focus on the Southern California Bight.

TABLE OF CONTENTS

44

45	Abstra	ct	2
46	1 Int	roduction	5
47	1.1	General overview of harmful algal blooms: a growing global concern	5
48	1.2	Regional HAB issues along U.S. coastlines	6
49	1.3	Desalination, plankton and water quality issues	7
50	2 To	xin producers and toxin concentrations of the west coast	8
51	2.1	Domoic acid	10
52	2.1.1	Toxin description and activity	10
53	2.1.2	Producers	11
54	2.2	Saxitoxins	13
55	2.2.1	Toxin description and activity	13
56	2.2.2	Producers	14
57	2.3	Brevetoxins	15
58	2.3.1	Toxin description and activity	15
59	2.3.2	Producers	16
60	2.4	Diarrhetic shellfish toxins	16
61	2.4.1	Toxin description and activity	16
62	2.4.2	Producers	17
63	2.5	Yessotoxin	18
64	2.5.1	Toxin Description	18
65	2.5.2	Producers	19
66	2.6	Toxin detection and quantification	20
67	2.7	Other potentially toxic, noxious and nuisance organisms	21
68	3 Sp	atial and temporal patterns of harmful algae	22
69	3.1	Temporal variability	23
70	3.2	Spatial variability	27

For: Water Research

71	3.3 Environmental driving factors	30
72	4 Desalination operations and HAB events	33
73	4.1 Concern with harmful algal blooms and their toxin production	33
74	4.2 Addressing spatiotemporal variability in HAB abundance and early detection	34
75	5 Conclusions	36
76	5.1 Potential impacts, unresolved issues and research prospectus	36
77	6 Acknowlegements	39
78	7 References	39
79		
80		

For: Water Research

1 INTRODUCTION

1.1 General overview of harmful algal blooms: a growing global concern

Microscopic algae constitute an essential component of all aquatic foodwebs. Photosynthetic production of organic material by this diverse group of species comprises the primary source of nutrition for all heterotrophic forms of life in much of the world's ocean and freshwater ecosystems. Microalgae can reach high abundances in the plankton during periods of optimal growth and reduced grazing pressure by herbivores. Such localized mass proliferations are known as algal (or phytoplankton) blooms. In addition, a small proportion of microalgal species are capable of producing a number of noxious or toxic compounds that cause a variety of adverse effects on ecosystem structure and function. These substances pose the potential for ecosystem damage, food web disruption and marine animal mortality, and present a significant human health risk through the consumption of contaminated seafood and, in at least one case, direct exposure to water or aerosols containing these toxic compounds. Additionally, the algal biomass and the associated organic load cause significant desalination operational issues, impacting the pretreament system and possibly forcing the treatment plant to be taken off-line (Petry et al., 2007).

Countless human deaths have been avoided through rigorous monitoring programs, but sea life has not been so fortunate. Approximately one half of all unusual marine mammal mortality incidents are now attributable to the ingestion of food or prey contaminated by harmful algal blooms (Ramsdell et al., 2005). Losses in revenue due to the direct contamination of seafood products and indirect effects on tourism and other uses of coastal areas have been estimated in the tens of millions of dollars annually in the U.S. states along the Pacific coast (Trainer et al., 2002).

There is now convincing evidence that harmful algal bloom (HAB) events are increasing at local, regional and global scales worldwide (Smayda, 1990; Hallegraeff, 1993; Anderson et al., 2002; Hallegraeff, 2003; Glibert et al., 2005a) and along the North American west coast in particular (Horner et al., 1997; Trainer et al., 2003). This increased occurrence may be due in part to better detection of HAB episodes and species identification in the recent years or the dispersion of toxic algal species through the transport of resting spores in ships' ballast waters

For: Water Research

110 (Hallegraeff and Bolch, 1992; Burkholder et al., 2007), but another very likely cause is the 111 increasing impact of anthropogenic activities on coastal ecosystems (Smayda, 1990; Anderson et 112 al., 2002; Glibert et al., 2005b; Glibert et al., 2006; Howard et al., 2007; Cochlan et al., 2008; 113 Kudela et al., 2008a). Recent reports reveal extensive and, in some cases, newly emerging 114 occurrences of HABs along the coasts of the U.S. (Fig. 1). These incidents engender a variety of 115 noxious impacts on ecosystems and public health, including direct effects on organisms due to 116 the production of acutely toxic substances, and indirect effects such as reduced availability of 117 dissolved oxygen in the water column resulting from the decomposition of the extensive amounts 118 of organic substances usually produced during such blooms. The dramatic increases in biomass 119 and organic load that accompany these events pose a significant threat to seawater desalination 120 facilities (Gaid and Treal, 2007).

1.2 Regional HAB issues along U.S. coastlines

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Harmful algae are present throughout U.S. coastal waters, but not all species are of equal concern in all regions (Fig. 1). For example, toxic species of the dinoflagellate genus Alexandrium are common over vast stretches of the U.S. coastline, but areas of the northeastern and northwestern U.S. coasts appear to experience particularly high rates of occurrence of toxic 'red tides' caused by these species. The neurotoxins produced by *Alexandrium*, called saxitoxins, cause paralytic shellfish poisoning (PSP) in humans when ingested through contaminated seafood (particularly filter-feeding shellfish). Similarly, several toxic species of the diatom genus *Pseudo-nitzschia* occur along the entire U.S. coastline but significant concentrations of the neurotoxin, domoic acid, produced by these species have historically constituted a health threat primarily in the northeastern and northwestern U.S. (Bates et al., 1989). However, high concentrations of domoic acid in the plankton and in diverse planktivorous organisms have been recently documented along the entire Pacific coast of the U.S. (Scholin et al., 2000; Trainer et al., 2002; Schnetzer et al., 2007), as well as in the Gulf of Mexico (Pan et al., 1998). Domoic acid has been attributed to numerous marine animal mortalities along the U.S. west coast, and is the cause of amnesic shellfish poisoning (ASP) in humans. In the Gulf of Mexico, primarily along the west coast of Florida, extensive and recurrent blooms of the dinoflagellate *Karenia brevis* produce a suite of toxins, known as brevetoxins, that can be aerosolized by breaking waves and induce neurotoxic shellfish

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poisoning (NSP) in people inhaling the aerosols (see review of Kirkpatrick et al., 2004). The Tampa Bay seawater desalination facility is the only operating treatment plant of significant size in the United States. It is located along the west coast of Florida and is likely to encounter algal blooms that contain brevetoxin.

Less toxic blooms also take place with regional specificity. The pelagophyte *Aureococcus* anophagefferens causes 'brown tides' in coastal waters of Rhode Island, near Long Island (NY) and southward along the mid-Atlantic coast of the U.S. since 1985. No specific toxins have been identified for *A. anophagefferens*, and no human fatalities have been directly attributed to these blooms. Nevertheless, this species appears to be unpalatable or inhibitory to many filter-feeding mollusks and has caused substantial mortality among these populations, including commercially valuable species (Bricelj and Lonsdale, 1997).

Other microalgal species can disrupt food webs or cause reductions in water quality without producing acutely toxic conditions. Among these are the 'colorful' red tides of the dinoflagellate *Lingulodinium polyedrum*, a yessotoxin producer, that have occurred periodically throughout several decades along the south and central California coasts (Horner et al., 1997; Gregorio and Pieper, 2000). However, these blooms have so far been found to be relatively innocuous in these waters. Massive accumulations of these cells could have significant impact on desalination plants because of increased turbidity, high suspended solids and organic loading of influent water. Furthermore, accumulations of cells in protected harbors can cause fish mortality by depleting oxygen dissolved in the water, further challenging influent screening and pretreatment systems at desalination plants. Other taxa, such as species of the prymnesiophyte genus *Phaeocystis*, produce substances that can lead to enormous buildups of sea foam along coasts (Armonies, 1989).

1.3 Desalination, plankton and water quality issues

Large research programs have developed within different geographic areas around the U.S. to address regional HAB issues. These programs are designed to study the species, toxins and environmental causes of HAB outbreaks. These efforts, as well as local, county, state and federal monitoring programs provide basic information for marine resource use and seafood consumption vis-à-vis the presence of microalgal toxins. Unfortunately, few if any of these

For: Water Research

programs provide sufficient information on appropriate temporal and spatial resolution for assessing the potential impact of HAB events on reverse osmosis desalination operations.

There are two potential impacts that HABs may have on seawater desalination facilities: (1) algal toxins in ocean water pose a significant treatment challenge for the reverse osmosis system to ensure that these molecules are effectively removed and (2) increased turbidity, total suspended solids and total organic content resulting from algal biomass and growth challenge the entire desalination facilities treatment train. The signficance of these issues will depend on the specific algae forming a bloom and the toxin(s) or other substances they produce, as well as the magnitude and duration of the blooms. Therefore, a thorough understanding of HAB episodes in terms of incidence and seasonality, vertical and horizontal spatial distribution, as well as biological aspects and algal composition within a geographical region could help optimize the efficiency of desalination plant operations.

This paper provides an overview of HABs occurring along the continental U.S. coastline with special emphasis on the southwestern U.S., and provides some insight on the potential impacts that these events may have on the seawater desalination process. In recent years, this geographical area has become a focal point of discussions regarding desalination (Cooley et al., 2006) because of its sizable population and the particularly tenuous nature of the water supply to this region. Although numerous issues involving the desalination process are now being examined (Separation Processes Inc., 2005; Gaid and Treal, 2007; Pankratz, 2008, 2009), very limited information exists on the risks that algal blooms pose to seawater desalination facilities. A review of the major species producing harmful blooms, the substances they produce, and information on the spatial and temporal distributions of blooms are presented along with some conclusions on their potential impacts. This paper also provides some general guidelines on how early detection may help prevent or minimize the impact of HABs on a desalination facility's production capacity or quality.

2 TOXIN PRODUCERS AND TOXIN CONCENTRATIONS OF THE WEST COAST

A variety of toxins including several powerful neurotoxins are produced by planktonic microalgae, and several of these toxins and numerous potentially toxic algal species have been

For: Water Research

197 detected on the U.S. west coast (Table 1). The ability to rapidly detect and quantify toxic algae 198 in natural water samples is problematic at this time. Many of these species are difficult to 199 identify using light microscopy. For this reason, new genetic and immunological methods for 200 species identification and enumeration have been appearing rapidly in the literature (Miller and 201 Scholin, 1998; Bowers et al., 2000; Coyne et al., 2001; Caron et al., 2003; Galluzzi et al., 2004; 202 Anderson et al., 2005; Mikulski et al., 2005; Ahn et al., 2006; Bowers et al., 2006; Handy et al., 203 2006; Moorthi et al., 2006; Iwataki et al., 2007; Demir et al., 2008; Iwataki et al., 2008; 204 Matsuoka et al., 2008; Mikulski et al., 2008). Moreover, many toxin-producing algal species 205 exhibit variable toxin production in response to environmental conditions, and among different 206 strains of the same species even when isolated from the same geographic region (Smith et al., 207 2001a; Smith et al., 2001b; Trainer et al., 2001; Kudela et al., 2004b).

Laboratory experiments have revealed a wide range of physico-chemical factors that increase or decrease toxin production by many harmful species of algae and appear to be speciesspecific (see review of Granéli and Flynn, 2006). Reports of factors inducing toxin production have sometimes been conflicting, presumably indicating that multiple factors, or perhaps generally stressful conditions, may stimulate toxin production. Factors affecting toxin production include: (1) temperature (Ono et al., 2000); (2) light intensity (Ono et al., 2000); (3) salinity (Haque and Onoue, 2002a, b); (4) trace metal availability, especially iron (Ladizinsky and Smith, 2000; Rue and Bruland, 2001; Maldonado et al., 2002; Wells et al., 2005; Sunda, 2006) but also copper (Maldonado et al., 2002) and selenium (Mitrovic et al., 2004; Mitrovic et al., 2005); (5) macronutrient availability including silicate (Pan et al., 1996b; Fehling et al., 2004; Kudela et al., 2004a), phosphate (Pan et al., 1996a; Pan et al., 1998; Fehling et al., 2004), nitrogen (Bates et al., 1991; Pan et al., 1998; Kudela et al., 2004a) and combinations of nutrient limitation (Anderson et al., 1990; Flynn et al., 1994; John and Flynn, 2000); (6) cellular elemental ratios of nutrients and physiological stress (Granéli and Flynn, 2006; Schnetzer et al., 2007); and (7) growth phase (Anderson et al., 1990; Bates et al., 1991; Flynn et al., 1994; Johansson et al., 1996; Maldonado et al., 2002; Mitrovic et al., 2004). The precise combination(s) of environmental factors that select for population growth of particular algal species within diverse natural assemblages, and the specific conditions that induce toxin production, are poorly understood for most harmful algae. This present state of knowledge

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For: Water Research

makes it difficult to predict the timing, duration or spatial extent of the vast majority of HAB events and the toxic events resulting from them.

Our ability to thoroughly characterize HABs is also complicated by the complex array of toxins produced by algae. Marine algal species produce a suite of toxic components (Yasumoto and Murata, 1993), and unidentified toxins undoubtedly remain to be described. Additionally, most toxins are actually composed of families of closely related compounds. Slightly different forms of a toxin can exhibit very different levels of toxicity, or may be characterized differently by some detection methods and analytic approaches (Garthwaite et al., 2001; Lefebvre et al., 2008). Such variability can sometimes yield vague or contradictory conclusions regarding the exact source of toxicity in a natural sample (Bates et al., 1978; Paz et al., 2004; Paz et al., 2007).

Finally, characterization of HAB events is complicated by inherent difficulties associated with linking specific toxins measured in natural water samples to a specific algal species in a complex, natural phytoplankton assemblage and, as noted above, the presence of toxic species in a water sample does not necessarily indicate the presence of toxins. Despite these shortcomings, there is considerable knowledge of many of the major algal toxins and their producers in U.S. coastal waters that constitute the most important potential concerns for desalination activities because they are the most likely to be encountered in ocean water intakes.

2.1 Domoic acid

2.1.1 Toxin description and activity

Domoic acid (DA; Fig. 2; Table 3) is an amino acid derivative belonging to the kainoid class of compounds containing three carboxyl groups and one secondary amino group (Wright et al., 1990; Jeffery et al., 2004). All four groups are charged at neutral pH, and the carboxyl groups become successively protonated as pH decreases, yielding five possible protonated forms of domoic acid (Quilliam, 2003; Jeffery et al., 2004). There are currently ten known isomers of domoic acid, including the isodomoic acids A through H and the domoic acid 5' diestereomer (Jeffery et al., 2004).

For: Water Research

Domoic acid and other members of the kainoid class are glutamate analogues that interfere with the normal neurochemical transmissions by binding to glutamate receptors of brain neurons (Wright et al., 1990; Quilliam, 2003). The resulting effect of these neuroexcitants, or excitotoxins, is a continuous stimulation of the neurons, which can lead to rupture and/or eventual formation of lesions (Wright et al., 1990). Depolarized neurons result in short-term memory loss (Clayden et al., 2005), which has led to the common name for the illness related to the consumption of seafood contaminated with domoic acid: Amnesic Shellfish Poisoning (ASP). Symptoms of ASP include gastroenteritis (vomiting, diarrhea, abdominal cramps) that can be experienced in humans within 24 hours after ingestion, and neurological symptoms of confusion, memory loss, disorientation, seizures, coma and/or cranial nerve palsies that are typically experienced within 48 hours (Perl et al., 1990; Wright et al., 1990). The number of human illnesses resulting from domoic acid poisoning have been few (Horner et al., 1997), likely due to active monitoring of fisheries. However, cultured blue mussels (*Mytilus edilus*) contaminated with domoic acid poisoned 107 people and killed three during the first major ASP outbreak in 1987 on Prince Edward Island, Canada (Perl et al., 1990).

ASP poses a serious threat to marine wildlife, and the deaths of thousands of marine mammals and sea birds have been attributed to domoic acid intoxication (Bates et al., 1989; Scholin et al., 2000; Gulland et al., 2002; Caron et al., unpubl. data). The first documented poisoning episode of marine animals related to domoic acid on the U.S. west coast was attributed to *Pseudo-nitzschia australis* and occurred in September 1991 off central California (Table 2; Buck et al., 1992; Fritz et al., 1992). High concentrations of domoic acid were also detected in Washington and Oregon in the 1990s (Wekell et al., 1994; Adams et al., 2000; Trainer et al., 2002), and a decade later in coastal waters off southern California (Schnetzer et al., 2007). The frequency and severity of these toxic events appears to be increasing (Trainer et al., 2007).

2.1.2 Producers

The production of domoic acid and its isomers is confined to approximately a dozen chain-forming marine pennate diatom species within the genus *Pseudo-nitzschia* (Bates and Trainer, 2006), a pennate diatom that forms long chains of cells attached at their ends (Fig. 3a,b). The main toxin producing species that have been documented on the U.S. west coast include: *P*.

For: Water Research

australis, P. delicatissima, P. fraudulenta, P. multiseries, P. pungens, P. pseudodelicatissima, P. seriata and P. cuspidata (Tables 1, 2). These species are distinguished based on fine morphological features of their silica frustules (Fig. 3a,b). These distinctions are subtle and require careful electron microscopical analysis and elaborate taxonomic training. As a consequence, historical misidentifications are not unusual and debates regarding some species descriptions are still unresolved.

It is surprising that the first reports of ASP on the west coast of the U.S. were not recorded until the 1990s, even though *Pseudo-nitzschia* species have been recorded in surveys of phytoplankton species in the Southern California Bight since 1917 (Allen, 1922; Allen, 1924, 1928, 1936, 1940, 1941; Reid et al., 1970; Reid et al., 1985; Lange et al., 1994; Fryxell et al., 1997; Thomas et al., 2001). Given that these species generally comprise a significant portion of the total diatom assemblage in these waters, it can be surmised that either toxin production has increased in these west coast species, or that poisoning events prior to the 1990s have occurred but have not been attributed to these diatoms. Historical accounts of 'unusual animal mortality events' along the U.S. west coast tend to support the latter hypothesis.

Recently, there have been an increasing number of toxic events recorded along U.S. west coast (Table 2), notably in Puget Sound (Trainer et al., 2003; Trainer et al., 2007), Monterey Bay (Vigilant and Silver, 2007; R. Kudela, unpubl. data), Santa Barbara Barbara (Trainer et al., 2000; Anderson et al., 2006; Mengelt, 2006), Los Angeles harbor and San Pedro Channel (Busse et al., 2006; Schnetzer et al., 2007), Newport Beach (Busse et al., 2006) and San Diego (Lange et al., 1994; Busse et al., 2006). Most recently, toxic blooms of *Pseudo-nitzschia* in the Long Beach-Los Angeles Harbor and San Pedro Channel have been particularly toxic, with some of the highest domoic acid concentrations recorded for the U.S. west coast (Caron et al., unpublished data). The increased incidence and severity of these toxic episodes off the western U.S. coast parallels the increase in frequency and intensity of harmful algal blooms observed globally (Smayda, 1990; Hallegraeff, 1993; Anderson et al., 2002; Hallegraeff, 2003; Glibert et al., 2005b).

For: Water Research

2.2 Saxitoxins

2.2.1 Toxin description and activity

Saxitoxin is a complex guanidine-based alkaloid that exists as more than 30 identified analogues in the natural environment (Llewellyn, 2006). It is the most powerful marine toxin currently known, and among the most dangerous poisons on Earth, except for some venoms and bacterial toxins (Schantz et al., 1957). Due to its acute toxicity, saxitoxin is currently listed as a chemical weapon in Schedule 1 of the Chemical Weapons Convention (Llewellyn, 2006). Saxitoxins display a rigid tricyclic core (Fig. 2; Table 3) and are very stable in biological and physiological solutions (Rogers and Rapoport, 1980). This nitrogen-rich molecule and its chemical relatives are polar and have a positive charge at pH 7.7 (Shimizu et al., 1981). Consequently, they are soluble in water and lower alcohols and insoluble in organic solvents (Schantz et al., 1957).

Saxitoxins are known to disrupt the flow of sodium ions through voltage gate sodium channels (Catterall, 1992; Cestele and Catterall, 2000). It has also been recently discovered that they have the ability to bind to calcium (Su et al., 2004) and potassium channels (Wang et al., 2003) and to be a weak inhibitor of neuronal nitric oxide synthase (reviewed in Llewellyn, 2006). These activities directly affect the nervous system, and the consumption of seafood containing saxitoxin can result in serious human illness and death, commonly referred to as Paralytic Shellfish Poisoning (PSP).

Minor symptoms of PSP, such as burning or tingling sensation of the lips and face, dizziness, headache, salivation, intense thirst and perspiration, vomiting, diarrhea and stomach cramps, can be experienced within 30 minutes after the consumption of contaminated seafood (Llewellyn, 2006). The consumption of a lethal dose can result in death within hours due to muscular paralysis and respiratory difficulty followed by complete respiratory arrest. PSP outbreaks result in more than 2000 illnesses worldwide each year, with a 5-10% mortality rate (Hallegraeff, 2003). PSP toxins also have adverse effects on marine wildlife that can cause mortalities among fish, marine mammal and seabird populations (Geraci et al., 1989; Montoya et al., 1996; Shumway et al., 2003). There are presently no records of unusual animal mortality events along the California coast that are attributable to saxitoxin poisoning (Jester et al., 2009b),

For: Water Research

but occurrence of the toxins in species consumed by humans is sufficient to warrant year-round monitoring.

2.2.2 Producers

Saxitoxins are biosynthesized by dinoflagellates in marine ecosystems, most notably species within the genus *Alexandrium* (Fig. 3c), as well as *Gymnodinium catenatum*, *Pyrodinium bahamense* var. *copressum*, and by some cyanobacteria in freshwater ecosystems (Hallegraeff, 2003). Blooms of toxic and noxious dinoflagellates are often referred to as 'red tides' because of the red discoloration of water created by the accessory pigments of the cells. However, toxic levels of saxitoxins can be attained at dinoflagellate abundances that do not significantly discolor the water because of the exceptionally high potency of saxitoxins (Burkholder et al., 2006). This situation exists for *Alexandrium* in that it does not typically reach 'bloom' abundances on the U.S. west coast, and constant toxin monitoring is necessary to identify toxic conditions (Langlois, 2007; IOC HAB Programme, 2008; Jester et al., 2009a).

Alexandrium species and measurable saxitoxin concentrations are common along the U.S. west coast (Table 1), although concentrations reported for this toxin typically have not been as high as noted along the U.S. east coast (Table 2). Thus, few west coast studies have contributed to our understanding the dynamics of Alexandrium abundances and saxitoxin production while a recent study in the Gulf of Maine represents the most comprehensive regional study of this HAB (Anderson et al., 2005; McGillicuddy et al., 2005). Combined field observations, laboratory studies and modeling effort have led to a scenario for toxic events along the northeastern coast of the U.S. that involve an interplay between river runoff, resuspension of dinoflagellate cysts from coastal sediments, favorable offshore growth conditions, and winds that generate onshore flow into coastal shellfish areas. A monitoring study of PSP in Puget Sound (WA) from 1993 to 2007 underscores that the timing and location of PSP outbreaks and high Alexandrium abundances are highly variable and not easily predicted from local or large-scale climate data (Moore et al., 2009). However, the study points out that periods of warm air and low stream flow may favor saxitoxin accumulation in sentinel mussels (Moore et al., 2009).

For: Water Research

2.3 Brevetoxins

2.3.1 Toxin description and activity

Brevetoxins are polyether, non-polar compounds that depolarize cell membranes by opening voltage gate sodium ion channels and induce enhancing inward flux of sodium ions into cells (Lin et al., 1981; Baden, 1983, 1989; Purkerson et al., 1999). Brevetoxins exist as two structural types and multiple analogs possessing various levels of potency (Baden, 1989; Cembella, 2003; Kirkpatrick et al., 2004). The types differ in their ladder-frame polycyclic ether structural backbones and are designated type A and type B (Fig. 2). The brevetoxin derivatives found in the marine environment (PbTx-2, PbTx-3 and PbTx-9; Table 3) are produced most commonly by dinoflagellate and raphidophyte algae and are of the structural type B (Baden, 1989; Baden et al., 2005).

Brevetoxins bind to site 5 of the voltage-sensitive sodium channel in neurons, causing these channels to remain open and fire repeatedly (Catterall, 1992; Cestele and Catterall, 2000). Brevetoxin poisoning in humans is referred to as Neurotoxic Shellfish Poisoning (NSP), and includes gastrointestinal symptoms of nausea, diarrhea and abdominal pain, neurologic symptoms of paresthesias, and respiratory irritation and/or failure (Kirkpatrick et al., 2004).

The effects of brevetoxins on human health are well documented along the western coast of Florida where severe, nearly annual red tides caused by the dinoflagellate *Karenia brevis* release large amounts of brevetoxins into the air when the fragile cells are broken in breaking waves at the water edge (Kusek et al., 1999; Kirkpatrick et al., 2004). The aerosolized toxins constitute a significant health risk when they are inhaled and, as a result, *K. brevis* blooms are one of the most intensively studied and best-understood regional HABs. Red tides caused by *K. brevis* have been implicated in marine mammal fatalities, fish kills and human illnesses.

Brevetoxins have not been reported from the U.S. west coast, and therefore no known human fatalities or health issues have been attributed to brevetoxins from that region.

For: Water Research

2.3.2 Producers

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Several dinoflagellate species and a few raphidophyte species produce a suite of brevetoxins (Baden, 1989). K. brevis, the most notorious brevetoxin producer within the Gulf of Mexico, has not been observed on the west coast of the U.S., but several species of raphidophytes that are potential brevetoxin producers have been documented (Tables 1; 2). Heterosigma akashiwo (Fig. 3e), Chattonella marina, and Fibrocapsa japonica (Fig. 3f) have been isolated and cultured from coastal waters off southern California. In general there are few reports of significant blooms of these species on the west coast, although blooms of raphidophytes in San Francisco Bay and Delaware Inland Bays have been observed with cell abundances in excess of 10⁸ cells L⁻¹ (Herndon et al., 2003; Covne et al., 2005). In part, this lack of information is a consequence of the fact that raphidophyte species are notoriously difficult to identify using traditional microscopical techniques because they preserve poorly (Hallegraef and Hara, 1995; Throndsen, 1997). Recently developed genetic approaches for the identification and quantification of some raphidophytes are beginning to provide much-needed tools for studying the distributions and ecology of these HAB species (Handy et al., 2006; Demir et al., 2008). Despite the difficulties of characterizing these blooms, fish kills have been attributed to raphidophyte blooms on the west coast of the U.S. although these studies have not quantified brevetoxins (Hershberger et al., 1997; Hard et al., 2000).

2.4 Diarrhetic shellfish toxins

2.4.1 Toxin description and activity

Toxins that cause Diarrhetic Shellfish Poisoning (DSP) include okadaic acid, dinophysistoxins and pectenotoxins (Ramsdell et al., 2005). Okadaic acid is a monocarboxylic acid named for the marine sponge *Halichondria okadai* from which it was first isolated (Tachibana et al., 1981). Okadaic acid can also be found in natural water samples in polar and non-polar esteric forms (Prassopoulou et al., 2009). The first dinophysistoxin described was isolated from the mussel *M. edilus* and was found to be a methyl form of okadaic acid (Murata et al., 1982). Okadaic acid and dinophysistoxins are linear polyethers (Fig. 2) and the mode of action is the inhibition of protein phosphatases (Takai et al., 1987; Bialojan and Takai, 1988; Haystead et al., 1989), enzymes that play a key role in dephosphorylation in many biological

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processes including cell cycle regulation. The pectenotoxins are lipid soluble and differ structurally from other diarrhetic toxins in that they possess a lactone ring (Fig. 2), are not considered to be protein phosphatase inhibitors, but have a high actin-depolarizating action (Hori et al., 1999). There is speculation that pectenotoxins may not produce diarrhetic effects (Cembella, 2003).

DSP toxins (Table 3) were named for the human symptoms resulting from the ingestion of contaminated shellfish, including inflammation of the intestinal tract, diarrhea, abdominal cramps, vomiting and nausea beginning 30 min to a few hours after ingestion (Hallegraeff, 2003). In addition to the symptoms listed above, okadaic acid known to be a strong tumor promoter (Suganuma et al., 1988), although the potential health implications of this activity due to the ingestion of contaminated seafood is unknown. There are presently no documented cases of DSP resuling from okadaic acid, dinophysistoxins or pectenotoxins on the U.S. west coast, and thus these toxins are not regularly monitored in the marine environment. DSP toxins have been detected in mussels and water samples from California (Sutherland, 2008), so it is possible that DSP has occurred on the U.S. west coast but has been attributed to food poisoning and gone unreported.

2.4.2 Producers

Okadaic acid and dinophysistoxins are produced by a few species of the dinoflagellate genus *Prorocentrum* (Cembella, 2003) and most commonly by species of the genus *Dinophysis*. *Dinophysis* species present on the western U.S coast include *D. acuminata*, *D. acuta*, *D. caudata*, *D. fortii*, *D. norvegica*, *D. rotundata*, *D. tripos* (Table 2). *D. acuminata* and *D. fortii* have been documented in California for many years (Bigelow and Leslie, 1930). *D. acuminata* produces okadaic acid (Yasumoto et al., 1985), *D. fortii* produces okadaic acid, dinophysistoxins and pectenotoxins (Yasumoto et al., 1980; Murata et al., 1982) and *D. rotundata*, and *D. tripos* produce dinophysistoxin-1 (Lee et al., 1989).

Dinophysis species are technically not phytoplankton, but heterotrophic protists that retain chloroplasts acquired from their prey. *Dinophysis* acquires its chloroplasts by preying on ciliates, which in turn prey on cryptophyte algae. This complex trophic relationship has made the culture of these species unsuccessful until recently (Park et al., 2006), and therefore no

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information on the environmental conditions that influence toxin production by these species presently exists. However, genus members are easily distinguished by light microscopy because they possess a pronounced 'keel' and other unique morphological aspects (Fig. 3d). These species are commonly encountered in plankton samples. Abundances of a 10³ cells L⁻¹ are commonly encountered (Nishitani et al., 2005), and occasionally they may reach abundances in excess of 10⁵ L⁻¹ (Carpenter et al., 1995).

2.5 Yessotoxin

2.5.1 Toxin Description

Yessotoxin (Fig. 2; Table 3) is a chiral molecule of high polarity due to the presence of two sulfate groups. The molecule consists of fused polyether rings organized into a ladder shaped skeleton (Yasumoto and Murata, 1993; Wright and Cembella, 1998), a structure similar to other ladder-like polyether toxins such as the ciguatera toxin complex (ciguatoxins and maitotoxin), gambieric acids and brevetoxins (Yasumoto and Murata, 1993; Wright and Cembella, 1998). There are nearly 100 analogs of yessotoxin that have been identified to date (Satake et al., 1997; Ciminiello et al., 1998; Daiguji et al., 1998; Satake et al., 1999; Ciminiello et al., 2000; Ciminiello et al., 2001; Miles et al., 2004; Miles et al., 2005b; Miles et al., 2005a; Miles et al., 2006; Paz et al., 2006).

The yessotoxin class was named for the species of scallop, *Patinopecten yessoensis*, in which yessotoxin was initially detected (Murata et al., 1987). Yessotoxin was originally classified in the DSP-toxin class because it was detected with other DSP toxins, but it appears that it does not induce diarrhetic effects (Ogino et al., 1997). Accordingly, the regulation of the European Commission on marine biotoxins now considers yessotoxins separately from DSP toxins (European Commission, 2002). The great number of yessotoxin analogs complicates toxicity studies, and may explain the sometimes contradictory reports of its mode of action. Studies have shown that lysosomes, the immune system and the thymus (with tumorigenic implications) are the biological targets of yessotoxin (Franchini et al., 2004; Malagoli et al., 2006), while other reports have indicated cardiotoxic effects (Terao et al., 1990; Ogino et al., 1997; Aune et al., 2002). The cardiotoxicity of yessotoxin might be attributed to phosphodiesterase activation in the presence of external Ca²⁺ (Alfonso et al., 2003). Unlike the

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other marine toxins, there have been no reported human health issues or marine mammal deaths associated with yessotoxin.

2.5.2 Producers

There are three known yessotoxin-producing dinoflagellates, *Protoceratium reticulatum*, *Lingulodinium polyedrum*, and *Gonyaulax spinifera*, and they have all been observed in coastal waters off the western U.S. (Table 1). According to phylogenetic analyses of available rRNA gene sequences, the capacity for yessotoxin production appears to be restricted to the order Gonyaulacales (Howard et al., 2009). However, toxin production among strains within each species appears to be highly variable.

Yessotoxin has been detected in *L. polyedrum* isolates cultured from around the globe (Tubaro et al., 1998; Draisci et al., 1999a; Strom et al., 2003; Paz et al., 2004), including isolates from Californian coastal waters (Armstrong and Kudela, 2006). The reported cellular concentrations in the latter cells ranged from below detection to 1.5 pg cell⁻¹, indicating that *L. polyedrum* is significantly less toxic than *P. reticulatum* or *G. spinifera*. Yessotoxin has been recorded in blue mussels at low concentrations along the U.S. west coast (Table 2) during red tides caused by *L. polyedrum*, as well as during non-bloom conditions, but yessotoxin production by this dinoflagellate appears to be less than toxin levels produced by isolates from other geographical regions (see Table 2 in Howard et al. (2008)). Expansive and dense blooms of *L. polyedrum* (Fig. 3h) have been reported in California since 1901, but there have only been anecdotal reports of health problems associated with the red tides caused by *L. polyedrum* (Kudela and Cochlan, 2000).

Yessotoxin production by isolates of *P. reticulatum* has been confirmed (Satake et al., 1997; Boni et al., 2002; Miles et al., 2002; Riobo et al., 2002; Stobo et al., 2003; Samdal et al., 2004; Eiki et al., 2005), but concentrations ranging from below detection to 79 pg cell⁻¹ have been reported for isolates from Washington, California and Florida (Paz et al., 2004; Paz et al., 2007). Isolates of G. spinifera appear to be the most prolific yessotoxin producers. Concentrations in New Zealand isolates ranged from below detection to 200 pg cell⁻¹ (Rhodes et al., 2006), more than 20-fold higher than the per-cell toxicity of P. reticulatum and 600-fold higher than L. polyedrum. G. spinifera species does not generally bloom in high densities on the U.S. west coast, but it has been frequently observed at low abundances (Howard et al., 2008; M. Silver, pers. comm.) but has reached blooms in Tomales Bay, north of San Francisco (G. Langlois pers. comm.). Yessotoxins are monitored in New Zealand, Europe and Japan but they are not routinely measured on the U.S. west coast. Howard et al. (2008) was the first study to confirm yessotoxins in California and Washington coastal waters albeit at very low concentrations.

2.6 Toxin detection and quantification

A wide variety of methodologies and technologies exist to detect, characterize and quantify the major toxins produced by microalgae. These approaches can be broadly divided into approaches used to characterize biological activity (toxicity assays) and those used to identify specific chemical structure(s) (immunological, various analytical techniques). Because of the highly variable approaches employed, and in most cases the highly diverse set of compounds comprising a toxin class, the methods provide somewhat different estimates of absolute toxin concentrations or presumed toxicity.

Domoic acid has been detected and quantified in seawater, plankton, shellfish extract and homogenate, as well as sea bird and mammalian body fluid (e.g. blood, urine, amniotic fluid, cerebral spinal fluid). Analytical approaches for these measurements include commercially available immunological techniques (enzyme-linked immunosorbent assay; ELISA) (Garthwaite et al., 1998; Garthwaite et al., 2001), high pressure liquid chromatography (HPLC) with ultraviolet (UV) diode array detection (DAD; HPLC-UV-DAD) (Quilliam et al., 1989; Quilliam, 2003), receptor binding assay (RBA) (Van Dolah et al., 1994), mouse bioassy (MBA) or liquid chromatography-mass spectrometry (LC-MS). The results obtained by these various approaches are not yet completely compatible or comparable, and therefore comparisons across studies using different analytical methods can be problematic. In general, the choice of an approach is a compromise between cost of analysis (or access to costly equipment), sample throughput, sensitivity and analytical goal (e.g. thorough chemical characterization versus overall toxicity).

Saxitoxins can be rapidly detected and quantified with commercial ELISA kits, but the high specificity of these tests precludes the recognition of certain members of the saxitoxin family, especially the neo-saxitoxin (Garthwaite et al., 2001). Saxitoxin detection and

For: Water Research

quantification is often accomplished by HPLC, RBA, LC-MS, and mouse bioassays. Regulatory programs for seafood consumption are still based on 'lethal mouse dosage'.

Rapid detection and quantification of brevetoxin and its derivatives in seawater, shellfish, and mammalian body fluids can be accomplished using commercially available ELISA kits (Naar et al., 2002), by HPLC, RBA (Van Dolah et al., 1994), LC-MS and mouse bioassays. A comparative study also quantified brevetoxins by radioimmunoassay (RIA) and neuroblastoma (N2A) cytotoxicity assay (Twiner et al., 2007).

Detection and quantification of the DSP toxin suite can be underestimated by ELISA because commercial ELISA assays are usually optimized to detect okadaic acid and not the dinophysistoxins (Garthwaite et al., 2001). High performance liquid chromatography with fluorimetric detection (HPLC-FLD) has been commonly used to detect and quantify okadaic acid, its polar and non-polar esters, as well as dinophysistoxins (Lee et al., 1987). The mouse bioassay method has also been routinely used for the detection of DSP toxins.

The detection and quantification of yessotoxin is problematic because of the extensive suite of derivatives that may exist. HPLC-FLD analysis (Yasumoto and Takizawa, 1997), mouse bioassay and LC-MS (Draisci et al., 1999b; Paz et al., 2006; Paz et al., 2008) and ELISA (Samdal et al., 2004; Samdal et al., 2005) have been employed.

2.7 Other potentially toxic, noxious and nuisance organisms

Reports of newly occurring HAB species, or recognition of extant issues that have gone previously undocumented, are increasing our awareness of other potentially harmful bloomforming algae along the U.S. west coast. For example, blooms of an emerging potentially toxic organism, *Cochlodinium* sp. (Fig.3g) off central California have recently been reported (Curtiss et al., 2008; Iwataki et al., 2008; Kudela et al., 2008b). This species is difficult to identify using light microscopy, and therefore researchers have begun to use gene sequences to provide accurate identification (Iwataki et al., 2007; Iwataki et al., 2008; Matsuoka et al., 2008). While this organism has only recently reached sufficient abundances to discolor Californian waters, there has already been one reported abalone loss in central California that appears to be associated with a bloom of *Cochlodinium*.

For: Water Research

Species of the dinoflagellate *Prorocentrum* (Fig. 3k-m) occasionally bloom in California coastal waters where they can attain very high abundances periodically, causing discolorations of the water and nuisance accumulations of algae (Holmes et al., 1967; Shipe et al., 2008). The *Prorocentrum* species known to occur in Californian waters have not yet demonstrated DSP toxin production, but species from elsewhere in the world are know to produce theses toxins (Table 1). Similarly, massive blooms of the dinoflagellate *Akashiwo sanguinea* are common in coastal waters of southern and central California and have recently been the cause of seabird mortality due to surfactant-like proteins (Jessup et al., 2009). Although they may not be overtly toxic, these blooms can cause animal mortalities, deplete oxygen, and result in an increased organic and biomass loading to a seawater desalination facility.

The prymnesiophyte *Phaeocystis globosa* infrequently attains high abundances off the California coast (Armonies, 1989). This species produces single cells that are <10 µm in size, but it also forms fluid-filled colonies several millimeters in diameter in which individual cells are embedded in the polysaccharide skin of the colony (Fig. 3i). Single cells of *Phaeocystis* are consumed by many zooplankton species but the colonies are typically a poor food source. Selective feeding on single cells appears to favor colony formation and the accumulation of colonies in the water column (Netjstgaard et al., 2007). When released via colony destruction or algal life cycle events, the colony matrix material is easily worked into a 'sea foam' that can form layers many centimeters (even meters) thick at the ocean surface or along the coastline over fairly extensive regions (Fig. 3j).

3 SPATIAL AND TEMPORAL PATTERNS OF HARMFUL ALGAE

A fundamental aspect of the biology of harmful algal blooms, and of vital importance for desalination operations, is the tendency for rapid and dramatic changes in the spatial and temporal distributions of these species. These changes can occur rapidly across a wide range of scales, and pose significant challenges for documenting and predicting these distributions. Numerous approaches and instruments have been developed to characterize the dynamics of phytoplankton communities. Although these approaches have major limitations on their abilities to identify species composition of a bloom, they provide crucial information on the emergence and longevity of bloom events as well as their vertical and geographical extent. In turn, this

information can help seawater desalination facilities adjust operations to ensure reliable production for the duration of the bloom.

3.1 Temporal variability

Significant temporal variations in the abundances of phytoplankton take place on time scales ranging from hours to decades. Short-term temporal variability (hours to a few weeks) can be a consequence of rapid population growth or consumption by herbivores, sinking of senescent populations, diel vertical migration, tidal advection, and aggregation or dispersal by physical processes such as water mass convergences or divergences.

Diel vertical migration of several dinoflagellates has been attributed to geotaxis, phototaxis and nutrient sufficiency (Eppley et al., 1968; Blasco, 1978; Cullen and Horrigan, 1981; Levandowsky and Kaneta, 1987). A classic behavior involves nighttime sinking out of surface waters to deeper water where nutrient concentrations are greater, and returning to surface waters for photosynthesis during daytime. Shifts in nutrient cell quotas that accompany these migrations may have significant implications for toxin production if cell toxicity is related to nutrient status of the cells. For example, limitation of population growth by nitrogen and phosphorus led to increased toxin production in *Alexandrium* (Anderson et al., 1990; Flynn et al., 1994; John and Flynn, 2000; Flynn, 2002).

Diel-to-weekly variations in phytoplankton abundance, and concomitant changes in chemical/physical environmental parameters can be routinely characterized using self-contained or wirelessly networked sensor packages. Data collected in King Harbor of the City of Redondo Beach, CA (Fig. 4) demonstrate the efficacy of these instruments for providing high temporal resolution of chlorophyll *a* fluorescence (which correlates roughly with phytoplankton biomass) and pertinent environmental factors (e.g. dissolved oxygen and temperature) that provide first insights into the factors driving the observed pattern. These data reveal a 4-fold variation in phytoplankton standing stock over a two-day period. In addition, changes in water quality criteria were easily and rapidly identified (e.g. the slight decrease in dissolved oxygen concentration in Figure 4 near noontime on September 13). Daily variations in the latter parameter can be extreme during noxious or excessive algal blooms. High resolution, short-term

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monitoring approaches allow rapid detection of sentinel parameters, and in turn provide information for the construction of predictive models of HAB events.

Chlorophyll *a* fluorescence sensors provide useful short-term temporal patterns of algal abundance, yet these values yield only an approximation of total phytoplankton abundance. Most commonly available instruments cannot identify noxious algal species within a phytoplankton assemblage, although more sophisticated instruments now coming online offer that possibility. For example, the Environmental Sample Processor (http://www.mbari.org/ESP) is an *in situ* instrument capable of performing real-time identifications of HAB and other microbial species, as well as toxin analyses such as domoic acid using on-board molecular analyses (Greenfield et al., 2006). Similarly, handheld devices now exist for the detection of some HAB species and toxins in the field (Casper et al., 2007). These rapid and highly specific analyses are becoming valuable tools for quick determinations of toxin presence posed by algal blooms. These more costly instruments can be used to significantly improve the information available on bloom composition once the cheaper and more readily available sensors identify an emerging bloom event.

Seasonal variability in phytoplankton community composition and abundance in coastal ecosystems is also substantial. Seasonality of HAB species and their toxins along the California coast can be gleaned from the records of the Marine Biotoxin Monitoring Program (MBMP) of the California Department of Public Health (CDPH), a program started after a major domoic acid outbreak in fall 1991. At present, the annual effort involves the analysis of approximately 300 shellfish samples for domoic acid and >1000 samples for PSP toxins from all fifteen California coastal counties (CDPH, 2007). Shellfish toxin information provides a reasonable representation of toxins in the upper water column over seasonal and annual scales such as demonstrated in studies on toxic dinoflagellates (Montojo et al., 2006; Jester et al., 2009a; Moore et al., 2009). Detailed information on the sampling effort is provided in the MBMP annual reports (Langlois, 2007).

Distributions of domoic acid and PSP occurring along the California coast during the period 2002-2007 based on the MBMP data reveal seasonal and geographical trends in these toxins (Figs. 5 and 6). Monthly averages for the 6-year period (histograms) and maximal

For: Water Research

concentrations (triangles) showed detectable concentrations of PSP toxins and domoic acid in shellfish in nearly all months for all California coastal counties (Fig. 5). Domoic acid concentrations showed pronounced seasonality, with very high peaks during spring and much smaller peaks during fall. This temporal trend is concordant with previous observations along southern California coast (Lange et al., 1994; Walz et al., 1994; Schnetzer et al., 2007; Shipe et al., 2008). Fall domoic acid peaks correspond to late blooms of toxic *Pseudo-nitzschia* spp. commonly noted on the west coast of the U.S. (Bolin and Abbott, 1960; Buck et al., 1992; Walz et al., 1994; Trainer et al., 2002; Schnetzer et al., 2007).

Seasonal peaks in domoic acid along the U.S. west coast differ along a latitudinal gradient. Highest domoic acid concentrations in Washington have been observed during the fall (Trainer, 2002; Protection, 2008; Moore et al., 2009) compared to spring blooms that are common in southern California (Schnetzer et al., 2007). This north-south trend in seasonality is also evident on a more local scale. Blooms along the California coast have been more frequently observed later in the year in northern counties (Fig. 6). The time lag between bloom periods observed from south to north may be related to the timing of the California Current System (CCS) upwelling maximum, which brings nutrients into surface waters and promotes phytoplankton growth. The CCS upwelling occurs in early spring in southern California, in June offshore Washington, and throughout summer in northern California and Oregon (Reid et al., 1958; Landry, 1989).

Monthly averages as well as maximal PSP toxin concentrations showed less seasonal variability than seasonality for domoic acid during the period 2002-2007. Highest saxitoxin concentrations during the 6-year period, however, were recorded from July to September. The seasonal pattern of maximal toxin levels in late summer/fall is in agreement with the last 25 year of monitoring results (Langlois, 2007). It is also consistent with the 1927-1989 observations on the California coast indicating that most significant concentrations of the toxin take place between May and October (Price et al., 1991). The highest PSP toxins in shellfish have also been observed in summer and fall periods off the Washington and Oregon coasts (Trainer et al., 2002). Monitoring in Puget Sound (WA) since the 1930s revealed that PSP events occurred April through October, resulting in the closure shellfish beds (Determan, 2003).

For: Water Research

Diel to seasonal temporal patterns in ASP and PSP outbreaks off the U.S. west coast are augmented by large inter-annual variability in the intensity and frequency of HABs. Inter-annual variations in HABs presumably are related, at least in part, to changes in atmospheric and hydrographic features modulated by the 3-7 year cycles of El Niño-southern Oscillations (ENSOs) (Price et al., 1991; Horner et al., 1997), but the exact relationship between HABs and these climatic events is not clear because there are still relatively few observations. Warming off California during El Niño episodes reduces seasonal upwelling, enhances physical stratification in the CCS and lowers the nutricline in the water column (the depth of rapidly increasing nutrient concentrations). It is clear that these changes in water stability and nutrient availability have significant impacts on plankton productivity and community structure, but the specific responses of the phytoplankton communities vis-à-vis HAB events are not yet predictable (Barber and Chavez, 1983).

ASP outbreaks occurred during El Niño episodes of 1991 and of 1997-98 along the coasts of Oregon, Washington and California (Table 2; Moore et al., 2008). The 1991 El Niño event resulted in unusually warm weather followed by significant rainfall, and was speculated to have promoted blooms of *Pseudo-nitzschia* observed at that time, but no clear conclusions have been reached (Horner and Postel, 1993). Similarly, the 1997-98 El Niño resulted in reduced seasonal upwelling, but the specific factors contributing to toxic *Pseudo-nitzschia* blooms in June 1998 could not be discerned (Trainer et al., 2000). Interannual variability in ASP and PSP concentrations in coastal waters along the California coast was evident in the MBMP dataset during the period 2002-2007 (Fig. 6). ASP and PSP outbreaks were frequent, but they varied in intensity and the timing of peak concentrations between years within a single geographical location, and between southern and northern California counties in the same year and season. The magnitude of this variability is at least on the same order of magnitude as the variability observed on short-term (daily) or seasonal time scales.

Little is known regarding the longer time scale fluctuations in HABs along the U.S. west coast. Multi-decadal fluctuations in ocean temperature are known to provoke shifts in the biological regime (Chavez et al., 2003), and it is anticipated that climatic shifts would affect the timing, intensity or frequency of HABs. Long-term regime shifts were thought to have impacted occurrence of blooms of *L. polyedrum*, a producer of yessotoxin, along the coast of southern

For: Water Research

California (Tables 1, 2). The Pacific Ocean was cooler in the years preceding 1976, and red tides dominated by *L. polyedrum* commonly developed along the Southern California Bight during fall (Gregorio and Pieper, 2000). During a recent warm regime (1976-mid 1990s), red tides occurred during winter and spring and persisted until summer in the region of the Los Angeles River mouth (Gregorio and Pieper, 2000). Recent massive blooms of *L. polyedrum* may indicate a return to the pre-1976 conditions (Moorthi et al., 2006).

The generality surmised from data depicting short- to long-term temporal variability in phytotoxin dynamics is that variability can be high at all scales. Given our present state of understanding regarding the specific combination of forcing factors that give rise to this high variability, it is difficult to accurately predict the timing and magnitude of toxic blooms. For these reasons, monitoring at multiple temporal scales is necessary to adequately characterize plankton dynamics.

3.2 Spatial variability

Spatial variability of harmful algal blooms is considerable at multiple scales, analogous (and strongly related) to the temporal variability described above. Blooms can be highly localized (10s of meters) or tremendously expansive (100s of kilometers), and distributions vertically within the water column are typically heterogeneous over scales of centimeters to meters. Moreover, the geographical extent and heterogeneous nature of the U.S. west coast results in considerable differences local hydrography that are manifested in small- and large-scale differences in spatial patterns of toxic blooms.

Regional-scale variations in HAB distributions are illustrated by MBMP data during 2002-2007 for ASP and PSP concentrations observed along the coasts of counties in northern and central California (Fig. 6). ASP events (frequency and toxicity) were lower in northerly Humboldt County during this period relative to Santa Barbara County nearly 1000 km to the south. More recently, high domoic acid concentrations have been observed within the Southern California Bight, presumably indicating a continuing southward movement of the *Pseudo-nitzschia* spring blooms (Langlois, 2007; Schnetzer et al., 2007). On the other hand, Marin County (north of San Francisco) exhibited higher monthly PSP averages during most months than San Luis Obispo County which is located at nearly 500 km to the south. This general

For: Water Research

latitudinal trend in PSP events is consistent with findings that the three southernmost counties (Los Angeles, Orange and San Diego) generally experience low concentrations of PSP relative to northern California (Price et al., 1991; Langlois, 2007). Regional-scale, geographical differences in ASP and PSP events have also been reported along the coastline of Oregon State (Trainer et al., 2002).

Regional-scale differences in HAB distributions might be expected along a coastline as extensive as the U.S. west coast, but small-scale variability (horizontally and vertically) can be dramatic. HAB events can be highly restricted geographically (e.g. relegated to a protected embayment). Even within spatially extensive blooms, phytoplankton biomass is often highly discontinuous over very small spatial scales because of differences in local circulation, and wind or wave forcing. For example, considerable spatial variability was observed in the abundance of *P. australis* within Monterey Bay, a phenomenon that has been attributed to advective forces (Buck et al., 1992). Physical vertical discontinuities in the water column, such as thermoclines, haloclines, nutriclines and light partitioning, also can lead to the establishment of subsurface microlayers where phytoplankton biomass can be many-fold elevated relative to algal standing stocks only meters (or even centimeters) above or below (Dekshenieks et al., 2001; Rines et al., 2002). These heterogeneities make the characterization of small-scale spatial distributions of phytoplankton challenging.

Approaches for characterizing phytoplankton spatial distributions include a wide range of methods including sampling from small boats and oceanographic ships as well as shore-based sampling and remote sensing of large-scale patterns using satellite imagery. Vertical profiling of phytoplankton assemblages can be accomplished using over-the-side, ship-based instrument packages and more recently autonomous vehicles equipped with a variety of sensor packages. The use of autonomous vehicles to provide synoptic measurements of phytoplankton biomass from chlorophyll *a* fluorescence and pertinent chemical/physical parameters is rapidly becoming state-of-the-art for obtaining two-dimensional cross-sections or three-dimensional patterns in the water column (Fig. 7).

Autonomous vehicles provide time- and depth-synchronized measurements of a variety of parameters that can be optimized for a specific mission. Such an instrument deployed off

Newport Beach, CA (blue line in Fig. 7f) during May-June 2008 yielded detailed patterns of chemical/biological parameters that provided information on the extent and vertical distribution of phytoplankton biomass and, potentially, harmful bloom events (Fig. 7a-e). Evidence of upwelling in this spring deployment was shown by the upward-pointing isotherms (temperature) and isopycnals (density) on the shoreward end of the transect (left sides of Fig. 7a, e). This was particularly evident in the temperature plot between 5 and 10 km from shore, and between the surface and 20 meters (Fig. 7a, red circle). Nutrients (not shown) were generally depleted in surface waters, and increased with decreasing temperature. This physico-chemical structure is concordant with a significant subsurface maximum in chlorophyll *a* concentration, suggestive of a response of the phytoplankton assemblage to elevated nutrient concentrations at this depth (red circle on left in Fig. 7b), as previously observed (Jones et al., 2002). The cross-sectional picture provided by the autonomous vehicle indicated that the chlorophyll maximum had a patchy structure on the scale of meters (vertically) and kilometers (horizontally). Two major horizontal patches were observed at 6-12 km from shore and at 15-21 km from shore (red circles in Fig. 7b).

Chlorophyll *a* fluorescence provides information on total algal pigment (which roughly correlates with phytoplankton biomass), but it does not indicate the species of phytoplankton that are present in the assemblage. Other measurements can add information on the observed general patterns such as particle size distributions derived from the optical backscatter spectrum. For example, the backscatter profile obtained at a wavelength of 532 nm indicated a patch of particles that are not of algal nature (Fig. 7d). The wavelength-dependent slope of the backscatter, which is dependent on the particle size distribution, can also be mapped to indicate the size-class of phytoplankton particles that dominate the chlorophyll maxima. This information is particularly important for a seawater desalination facility, where the incoming particle size distribution is known to impact the source water filterability.

Although presently beyond the budgets of many coastal monitoring projects, autonomous vehicles allow nearly synoptic measurements of the spatial distribution of phytoplankton and ancillary parameters. Many of these instruments can operate for significant periods of time (weeks) and thereby supply some degree of temporal as well as spatial coverage. Knowledge of the temporal evolution and spatial organization of coastal marine systems enables a better

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understanding of the linkages between physical processes and the biological responses that contribute to the formation of harmful algal blooms. Data from these instruments can be telemetered to the laboratory in real time or near-real time. The information can then be used to direct costly and logistically difficult efforts such as shipboard sampling, or plan operations for land-based activities and measurements.

Broad-scale, horizontal distributions can also be acquired via shipboard sampling programs (Fig. 8). Such sampling conducted in April 2008 in the Long Beach-Los Angeles harbor area and the adjacent San Pedro Channel demonstrated considerable spatial variability in the distribution of HAB species and/or their toxins within this relatively small area (approximately 500 km²). Results indicated a patchy distribution of domoic acid in particulate material (i.e. phytoplankton cells) collected near the surface with highest concentrations in the vicinity of the harbor breakwater and at several offshore locations (Fig. 8). Intermediate regions exhibited toxin concentrations that were more than an order of magnitude less than these maxima. Although shipboard work cannot provide synoptic coverage over very large spatial scales and is time and labor intensive, onboard sample processing can often enable more sophisticated analyses than autonomous vehicles are presently capable of providing. Moreover, ships permit time series studies at a single study site.

3.3 Environmental driving factors

Characterizing the factors that lead to the stimulation of harmful algae and the production of toxins by these algae has been an area of very active research for decades. These studies have encompassed, and continue to involve, field observations to document the spatiotemporal extent of blooms and toxin concentrations in plankton and marine life, and laboratory experiments aimed at understanding the key environmental factors leading to HAB events. The latter work has typically been accomplished by examining those chemical and physical parameters that might specifically elicit the growth of toxic species and toxin production. The overall results gleaned from many years of work group into three basic categories: (1) factors and conditions leading to phytoplankton blooms in general, (2) factors leading specifically to growth of HAB species, and (3) factors leading to toxin production.

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For: Water Research

Numerous factors have been implicated as contributors to the observed global expansion of HABs (Smayda, 1990; Hallegraeff, 1993; Anderson et al., 2002; Hallegraeff, 2003; Glibert et al., 2005b). Phytoplankton blooms occur naturally as a consequence of mixing deep, nutrient-rich waters in lighted surface waters. This process occurs seasonally in temperate environments due to winter storm events, and due to coastal upwelling events caused by appropriate regional wind conditions. There is no a priori reason why these 'natural' sources of nutrients cannot lead to HAB events, but the global increase in frequency and severity of HABs implies that human activities may be an underlying reason for this escalation.

Eutrophication of coastal ecosystems is a growing global concern that has clear implications for blooms of nearshore algal populations (Anderson et al., 2008; Heisler et al., 2008; Howarth, 2008). Nutrient enrichment has been clearly implicated in a number of localized harmful blooms (e.g. protected bays with restricted water exchange and high rates of nutrient loading), but the linkage between nutrient discharges mediated by human activities and many HAB events is still unclear. For example, field studies have shown that coastal upwelling of nitrate-rich waters might be a dominant driving factor leading to toxigenic *Pseudo-nitzschia* blooms along the U.S. west coast (Horner et al., 2000; Scholin et al., 2000; Anderson et al., 2006) but evidence that river/coastal runoffs promote domoic acid production have been inconclusive (Scholin et al., 2000; Schnetzer et al., 2007). The importance of nutrient discharge into coastal waters is, of course, dependent on the amount of nutrients available for phytoplankton growth from natural sources. The latter term is poorly defined in most situations, therefore constructing nutrient budgets of coastal ecosystems is an area ripe for future work. Nevertheless, it has been speculated that anthropogenic nutrient sources, such as elevated nutrient concentrations in river discharge, coastal runoff from agricultural land, and sewage discharge may significantly increase the total amounts of nutrients available for the growth of coastal phytoplankton (Scholin et al., 2000; Glibert et al., 2005a; Glibert et al., 2005b; Glibert et al., 2006; Howard et al., 2007; Kudela et al., 2008a).

It is fair to conclude that there is now a basic understanding of the general conditions that are necessary to favor the growth of phytoplankton per se (Allen et al., 2008). Despite this basic understanding, there is still only rudimentary information on the specific conditions that selectively stimulate the growth of harmful algal bloom-forming species of phytoplankton. As a

For: Water Research

result, mathematical models that attempt to predict HAB events are few, and these models tend to be more correlative than deterministic (i.e., they identify the conditions that *may* promote a HAB, rather than the conditions that *will* promote a bloom). One conclusion arising from several decades of field and laboratory studies of harmful species is that rarely can one identify a 'silver bullet', a single parameter or set of circumstances that provide a true predictive understanding of the occurrence of a particular HAB species. The environmental circumstances leading to the dominance of a HAB population over all other species of algae in a given locale are comprised of a complex set of physical, chemical and biological conditions with poorly known variances, and these conditions appear to be species-specific. The latter situation (different conditions favor different HAB species) is logical because one would expect that different algal species would possess different autoecologies.

Conditions conducive to HAB formation are critically dependent on hydrographic and nutrient conditions. In addition, however, biological factors (co-occurring phytoplankton, consumers, possibly bacteria and viruses) contribute to the success or demise of individual taxa. These latter features are still poorly understood, but allelopathy among competing phytoplankton, mixotrophy by HAB species, and deterrence of potential consumers via the production of noxious or toxic compounds may all play roles in establishing or maintaining dominance of HAB species (Strom et al., 2003; Burkholder et al., 2008; Buskey, 2008; Flynn, 2008; Smayda, 2008). These biological interactions seem to presuppose a stable set of environmental conditions for some period of time in order that the scenarios of allelopathy, grazer deterrence or phagotrophic activity of HAB species can play themselves out. This requirement may explain why stable water mass formation appears to play a role in the formation of some HAB events (Scholin et al., 2000).

Models predicting the population growth of potentially toxic algae are necessary for understanding bloom dynamics, but these models must also integrate information on toxin induction. Many toxins do not appear to be constitutively produced by algae, but are induced by a variety of specific, not completely understood, environmental conditions. Silica, phosphorus, nitrogen and trace metal limitations, and nutrient or elemental ratios (in addition to or instead of absolute concentrations) have all been implicated in the toxin induction (Pan et al., 1996a; Pan et al., 1998; Rue and Bruland, 2001; Fehling et al., 2004; Wells et al., 2005; Granéli and Flynn,

For: Water Research

2006; Schnetzer et al., 2007). Again, species-specific differences (and perhaps strain-specific differences) may exist in the factors promoting toxin production. Physical aspects such as temperature and light intensity may stimulate toxin production by some harmful algae (Ono et al., 2000).

4 DESALINATION OPERATIONS AND HAB EVENTS

A thorough understanding of the specific factors and conditions giving rise to harmful algal blooms and toxin production in coastal waters will require a great deal of additional research before accurate models for predicting these toxic events will be readily available. Until then, appropriate monitoring strategies to detect imminent bloom events and the ability to track the evolution of an active bloom, coupled with an understanding of the potential toxins being produced, the toxin chemistry, and their rejection by seawater reverse osmosis membranes, provide a full-scale seawater desalination facility with the best strategy for making operational adjustments to ensure that the treatment plant capacity or product water quality remains unaffected.

4.1 Concern with harmful algal blooms and their toxin production

As seawater desalination has continued to become more cost-effective and less energy intensive (Al-Sahlawi, 1999), many communities are planning or implementing seawater desalination facilities (Al-Sahlawi, 1999; Burbano et al., 2007). The selected pretreatment procedures and the process engineering that determines the ultimate facility design is entirely dependent upon the source water quality (e.g. suspended solids, turbidity, organic material content, algal cell content, etc.) and its variations, particularly for facilities incorporating open intakes (Bonnelye et al., 2004b; Gaid and Treal, 2007). Although the seawater desalination process is performed by reverse osmosis membranes, the selection and proper operation of a pretreatment system is paramount to the success of the downstream desalination process (Tenzer et al., 1999; Bonnelye et al., 2004b; Separation Processes Inc., 2005; Gaid and Treal, 2007; Petry et al., 2007).

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Algal blooms are known to have significantly negative impacts on reverse osmosis desalination facilities. A variety of pretreatment trains have been considered to address the difficult source water quality associated with algal blooms, where the organic and biomass load increase dramatically (Adin and Klein-Banay, 1986; Al Arrayedhy, 1987; Hasan Al-Sheikh, 1997; Montgomery Watson Applied Research Department, 1997; Abdul Azis et al., 2000; Bonnelye et al., 2004b; Bonnelye et al., 2004a; Burbano et al., 2007; Gaid and Treal, 2007; Petry et al., 2007; Peleka and Matis, 2008). Recently, microfiltration and ultrafiltration membrane pretreatment has been identified as a component of a preferred pretreatment train due to the consistent, high quality water produced by membrane filtration, especially when compared to conventional processes (Wilf and Schierach, 2001). However, one significant drawback to implementation of these modern pretreatment technologies is that they are as susceptible, or possibly more so, to significant algal blooms (Bonnelye et al., 2004a).

Hence, there is a clear need for an early warning system to provide information to the seawater desalination facility so that functional changes can be made to efficiently maintain operations even as source water quality deteriorates. Chemical additions can be made, additional pretreatment equipment can be put on-line, and additional staff preparations (e.g. maintenance activities, guaranteeing all membranes and filters are clean in preparation for an event) can be preformed to continuously deliver a high quality feedwater to the reverse osmosis system that will produce the desalinated drinking water. Additionally, it is important for the seawater desalination industry to understand potential toxic source water contaminants to ensure that the overall treatment process provides an effective barrier to potential public health impacts.

4.2 Addressing spatiotemporal variability in HAB abundance and early detection

As detailed above, it is essential that a desalination facility incorporate a means of rapid algal bloom detection so that, when necessary, proper process changes can be made to maintain the production capacity. Sensors for detecting an eminent algal bloom can be located at the desalination facility to inform personnel regarding changes in water quality that are directly observed on the source water. Figure 9 presents the transmembrane pressure (TMP) of a microfiltration system that serves as pretreatment to a pilot-scale reverse osmosis desalination system along with the levels of chlorophyll *a* fluorescence observed in the feedwater. It is clear

For: Water Research

from this figure that increased membrane fouling rates (e.g. faster daily rise in the TMP) were associated with increasing chlorophyll *a* fluorescence (i.e. increased algal biomass in the source water) in the source water.

It is well known that higher concentrations of algae cause increased membrane fouling rates in microfiltration systems that are frequently incorporated, or considered, in today's desalination facilities (Gijsbertsen-Abrahamse et al., 2006; Lee and Walker, 2006; Reiss et al., 2006). A more complete approach might include a monitoring system located offshore that measures some of the primary factors influencing algal blooms, such as nutrient monitoring in near-real time using new *in situ* sensor technology (Glibert et al., 2008). Such information would be useful to both the desalination facility and HAB researchers who are continually improving their understanding of the causative factors that produce HABs and their associated toxins. Using the information provided by offshore sensors, the desalination facility personnel could note trends and shifts in driving factors that generate algal blooms and make any chemical orders or perform maintenance procedures that have significant lead times. The same offshore sensor might also incorporate real-time monitors of sentinel parameters for changes in algal biomass, such as turbidity and chlorophyll *a*, allowing facility to prepare for changes in chemical additions and redundant equipment service.

Monitoring of basic chemical parameters of seawater (e.g. chlorophyll *a* concentrations) will provide valuable information for facility operations, but this activity is not sufficient to fully assess potentially toxic conditions that might arise from algae that do not require high standing stocks to constitute a significant toxic threat, such as *Alexandrium* species. Species-specific approaches, such as automated *in situ* instruments or laboratory-based methods, as well as chemical/immunological analyses that identify and quantify specific algal toxins are necessary to more thoroughly characterize the potential hazards posed by HAB species. The consistent removal of these potentially toxic substances through the reverse osmosis process is both a function of size (e.g. molecular weight) and charge (e.g. zeta potential)(Amy et al., 2005). Depending on the size and charge of the contaminant of concern, the rejection, or removal, by the reverse osmosis process will differ. It is important that we continue to broaden our knowledge on potentially toxic substances excreted by algal stock and their associated blooms.

For: Water Research

The approach for obtaining this information would be best complemented with knowledge of the species that are present regionally, the potential problems they pose (e.g. specific toxins and the amounts of soluble microbial products and extracellular polymeric substances excreted), the spatial extent of HAB episodes, and their seasonality. The seasonality of *Pseudo-nitzschia* spp. and domoic acid near the intake of a pilot desalination plant in El Segundo (CA) exemplifies the usefulness of routine monitoring for identifying potentially toxic conditions in coastal waters adjacent to a plant (Fig. 10). Abundances of *Pseudo-nitzschia* spp. and concentrations of particulate and dissolved domoic acid in intake water exhibited a springtime peak. Knowledge of the seasonality of this toxic bloom-forming species allows intensive sampling of coastal waters during spring when toxic events are more common, improving the overall effectiveness of the monitoring effort and making it more cost effective.

Historical and real-time information on the spatial distribution of HABs can provide information vital for optimizing design and performance of desalination operations.

Local/regional hydrography, and resultant algal blooms can differ dramatically. When constructing a new intake pipeline, the selection of its location (e.g. depth and distance from shore) can be greatly enhanced throught the use of offshore monitoring devices and efforts to take into account the presence of any local accumulations of algal biomass due to currents, water mass convergences/divergences or internal waves, and also subsurface maxima in algal abundance. Properly locating offshore monitoring can provide significant information that will allow optimal location of a new intake pipeline or identificatification of issues that might affect an existing one, thereby significantly reducing the organic and suspended solid loads present in the feedwater during algal bloom events. These considerations will ease pretreatment operations, reduce the cost of water production, and help improve the facility's longevity.

5 CONCLUSIONS

5.1 Potential impacts, unresolved issues and research prospectus

The presence of harmful algae in coastal waters that might be employed in reverse osmosis desalination pose potential problems for these operations that have been known to even cause desalination facilities to temporarily cease production (Tenzer et al., 1999; Pankratz, 2008). As

For: Water Research

the number of seawater desalination facilities continues to grow with lower costs and increasing demand, it is essential that these operating facilities develop the tools necessary to allow process changes and ensure capacity objectives continue to be met. Regardless of the pretreatment configuration, changes in source water quality require adjustments and these changes need to carefully coordinate to ensure that the reverse osmosis membranes are not irreversible fouled or damaged in the process.

Benchmark work is required to establish the effectiveness of the seawater reverse osmosis process in dealing with HAB toxins and other phytoplankton-derived substances. Even if advanced pretreatment technologies such as microfiltration is implemented upstream of the reverse osmosis process, passage of transparent extracellular material produced by the algal bloom (Alldredge et al., 1993; Hong et al., 1997) may affect reverse osmosis membrane performance. Additionally, the physical durability of phytoplankton varies greatly and the pretreatment process might disrupt cells and create significantly higher concentrations of dissolved organic substances, including toxins, than were originally present in the source water. Therefore, it is important that the international desalination community carefully characterize these potential contaminants and their removal to improve treatment approaches in seawater desalination.

HABs on the U.S. west coast exhibit significant generalities across geographical and temporal scales (e.g. many of the same species occur throughout the region), but the details of bloom dynamics differ with geographic location, depth and season (and perhaps on interannual and decadal scales). The high degree of variability associated with these events makes constant monitoring of HABs in intake water for desalination a vital issue. Regional HAB programs and regulatory agencies along the U.S. west coast presently provide useful information for some known potential problems (e.g. ASP and PSP toxins) for end users that need information on coastal water quality. Awareness (and augmentation) of this information could improve planning and safe operation of desalination facilities. Monitoring of newly emerging HAB concerns (e.g. *Cochlodinium* spp.), or HABs and toxins that are presently poorly characterized (e.g. neurological shellfish poisoning, diarrhetic shellfish poisoning, and yessotoxin poisoning) should also be implemented in the future to allow evaluation of their potential impacts on desalination processes.

For: Water Research

New technologies for toxin detection and quantification, and <i>in situ</i> monitoring of biological
and chemical parameters are rapidly improving our ability to monitor coastal ecosystems and
identify potentially problematic situations involving HABs. Advances in in situ observing
technologies (sensor networks, autonomous sensor-equipped vehicles) provide the capability for
obtaining unprecedented resolution in the spatial and temporal distributions of chemical and
physical parameters, and some biologically important features (Sukhatme et al., 2007). New
approaches and instruments for toxin detection help identify contaminated seafood products, and
constitute sentinels for the threats of HABs to marine animal populations. Future uses of coastal
waters for desalination will also benefit from, and contribute to, these activities.

6 ACKNOWLEGEMENTS

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The authors are grateful to Mr. Mark Donovan at Separation Processing, Inc. for providing the data for Figure 9. The preparation of this manuscript was supported in part by funding from a contract between the West Basin Municipal Water District, Department of Water Resources and the University of Southern California, National Oceanic and Atmospheric Administration grants NA05NOS4781228 and NA07OAR4170008, Sea Grant NA07OAR4170008, National Science Foundation grants CCR-0120778 (Center for Embedded Networked Sensing; CENS), DDDAS-0540420, MCB-0703159, and a NASA Earth and Space Science Fellowship Grant NNX06AF88H.References

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Table 1. Planktonic species occurring along the west coast of the U.S. that are potential concerns for reverse osmosis operations.

Microalgae	Toxin(s)	Poisoning Event	References
Diatoms Pseudo-nitzschia spp. P. australis [§] P. cuspidata [§] P. delicatissima [§] P. fraudulenta [§] P. multiseries [§] P. pungens [§] P. pseudodelicatissima [§] P. seriata [*]	Domoic acid (DA)	Amnesic Shellfish Poisoning (ASP) Human effects	(Subba Rao et al., 1988; Bates et al., 1989; Martin et al., 1990; Buck et al., 1992; Garrison et al., 1992; Rhodes et al., 1996; Horner et al., 1997; Lundholm et al., 1997; Rhodes et al., 1998; Trainer et al., 2000; Trainer et al., 2001; Baugh et al., 2006)
Dinoflagellates Alexandrium spp. A. acatenella* A. catenella\$ A. fundyense* A. hiranoi* A. ostenfeldii* A. tamarense*	Saxitoxins (STXs)	Paralytic Shellfish Poisoning (PSP) Human effects	(Sommer and Meyer, 1937; Gaines and Taylor, 1985; Steidinger, 1993; Scholin et al., 1994; Taylor and Horner, 1994; Jester, 2008)
Dinoflagellates Lingulodinium polyedrum [§] Gonyaulax spinifera [*] Protoceratium reticulatum ^{*†}	Yessotoxins (YTXs)	Human and ecosystem effects None reported	(Holmes et al., 1967; Satake et al., 1997; Draisci et al., 1999a; Satake et al., 1999; Paz et al., 2004; Armstrong and Kudela, 2006; Rhodes et al., 2006; Howard et al., 2007; Paz et al., 2007)
Dinoflagellates Dinophysis spp. D. acuminata*	Okadaic acid (OA) Dinophysistoxins (DTXs) Pectenotoxins (PTXs)	Diarrhetic Shellfish Poisoning (DSP) Human effects • Gastro-intestinal symptoms 1	(Holmes et al., 1967; Yasumoto et al., 1980; Murata et al., 1982; Yasumoto et al., 1985; Cembella, 1989; Lee et al., 1989; Horner et al.,

Stormwater and Marine Biotoxin Monitoring – Final Report (continued)_{Water Research}

D. acuta*

D. caudate

D. fortii*

D. norvegica*

D. rotundata*

D. tripos*

Prorocentrum spp.

P. micans

P. minimum*[⋄]

Raphidophytes

Chattonella marina* Fibrocapsa japonica* Heterosigma akashiwo Ecosystem effects

• None reported

1997; Cembella, 2003; Miles et al., 2004; Shipe et al., 2008; Sutherland, 2008)

Brevetoxins (PbTxs)

Neurotoxic Shellfish Poisonining (NSP)

Human effects

- Gastroenteritis
- Neurologic symptoms
- Respiratory irritation and/or failure

Ecosystem effects

- Marine mammal mortalities
- Fish mortality events

(Loeblich III and Fine, 1977; Hershberger et al., 1997; Gregorio and Connell, 2000; Hard et al., 2000; Tyrell et al., 2002; O'Halloran et al., 2006)

^{*}Reported to produce toxin; § Reported to produce toxin on the west coast of the United States; †Conflicting reports on toxicity of *P. reticulatum* cultures isolated from California, Washington and Florida.; ♦ Reported to be present on the west coast of Mexico

Stormwater and Marine Biotoxin Monitoring – Final Report (continued) Water Research

Table 2. Distribution and concentrations of marine toxins in plankton of confirmed toxin producers in U.S. west coast waters. * Toxin concentration from cells in culture; b.d.: below detection limit.

Toxin(s)	Location and year	Causative species	Particulate μg L ⁻¹ (nmol L ⁻¹)	Cellular pg cell ⁻¹	Dissolved pg ml ⁻¹ (nmolL ⁻¹)	References
Domoic acid	Washington coast and Juan de Fuca Eddy, WA (1997, 1998)	P. pseudodelicatissima Pseudo-nitzschia spp.	b.d2.7 3.6-8.7	b.d4.6		(Adams et al., 2000; Trainer et al., 2001; Trainer et al., 2002)
	Penn Cove, WA (1997)	P. pungens P. multiseries P. australis P. pseudodelicatissima	b.d0.8			(Trainer et al., 1998)
	Washington coast, WA (2001)	P. australis	b.d0.03			(Marchetti et al., 2004)
	Washington coast, WA (2003)	Pseudo-nitzschia spp.	(0.4-15)	2x10 ⁻⁴ - 0.3* 0.1-94.4	(n.d4.3)* (1-5)	(Baugh et al., 2006)
	Puget Sound, WA (2005)	P. pseudodelicatissima Pseudo-nitzschia spp.	b.d14			(Trainer et al., 2007)
	Central Oregon coast, OR (1998)	P. australis	0.5	35		(Trainer et al., 2001)
	Pt. Año Nuevo, San Francisco, CA (1998)	P. pungens P. multiseries	0.1-0.7	0.3-6.3		(Trainer et al., 2000)
	Bolinas Bay, San Francisco, CA (2003)	P. australis	0.15-9.4			(Howard et al., 2007)
	Monterey Bay, CA (1991, 1998)	P. australis	b.d12.3 0.1-6.7	3-37 7.2-75		(Buck et al., 1992; Garrison et al., 1992; Walz et al., 1994; Scholin et al., 2000)
	Monterey Bay, CA (1998)	P. pseudodelicatissima P. multiseries	0.1-0.4 0.67	0.8-1.2 6		(Trainer et al., 2000; Trainer et al., 2001)
	Monterey Bay, CA (2000)	Pseudo-nitzschia spp. P. australis		b.d24	b.d8491	(Bargu et al., 2002; Bargu et al., 2008)

$Stormwater\ and\ Marine\ Biotoxin\ Monitoring-Final\ Report\ (continued)_{Water\ Research}$

	Monterey Bay, CA (2002-2003)	Pseudo-nitzschia spp.	24			(Vigilant and Silver, 2007)
	Morro Bay, CA (1998)	P. australis	1.3-7.4	37-78		(Trainer et al., 2000; Trainer et al., 2001)
	San Luis Obispo, CA (2003-2005)	P. australis P. multiseries	1.5-7.6	9-38		(Mengelt, 2006)
	Point Conception, CA (1998)	P. australis	2.2-6.3	15-22		(Trainer et al., 2000)
	Santa Barbara, CA (1998)	P. australis P. pungens P. pseudodelicatissima	0.5-1.2	0.1-0.9		(Trainer et al., 2000)
	Santa Barbara Channel, CA (2003)	P. australis	0.03-1.7	0.14-2.1		(Anderson et al., 2006)
	Santa Barbara (Santa Rosa Island and north San Miguel) (2004)	P. australis P. multiseries	6-12	b.d 80		(Mengelt, 2006)
	Southern California Bight, CA (2003, 2004)	Pseudo-nitzschia spp. P. australis, P. cuspidata	5.6-12.7	0-117		(Schnetzer et al., 2007)
	San Diego and Orange counties, CA (2004)	P. australis P. multiseries	0-2.33			(Busse et al., 2006)
Saxitoxins	Sequim Bay, WA (2004-2007)	Alexandrium spp.	0.02-0.5		150-800	(Lefebvre et al., 2008)
	Oregon coast, OR (2004)	Alexandrium spp.	0.004-0.028			Jester, Howard, Silver and Kudela, unpublished data
	Humboldt Bay, CA (2004)	A .catenella		1.6-19*		(Jester, 2008)
	San Mateo County coast, CA (2004)	A .catenella		2.1-62.6*		(Jester, 2008)
	Monterey Bay, CA (2004)	A. catenella		0.6-31.3*		(Jester, 2008)
	Monterey Bay, CA (2003-2005)	A. catenella	b.d0.962			(Jester et al., 2009b)
	Morro Bay, CA (2004)	A .catenella		1.4-16.6*		(Jester, 2008)
Yessotoxin	La Jolla, CA (1993 isolates)	Lingulodinium polyedrum		0.002-0.02* 0-0.05*		(Armstrong and Kudela, 2006; Howard et al., 2008)

$Stormwater\ and\ Marine\ Biotoxin\ Monitoring-Final\ Report\ (continued)_{Water\ Research}$

Brevetoxins					
	Indian Inlet, Bald Eagle Creek and Torque Canal, DE (2000)	Chattonella cf. verruculosa	0.008-<0.2	6	(Bourdelais et al., 2002)

Table 3. Summary of toxins that can be present in Southern California waters. MW: molecular weight.

Toxin	Properties	Formula	MW	Mode of action	References	
Domoic acid (DA)	Hydrosoluble At pH 7: DA ³⁻	C ₁₅ H ₂₁ NO ₆	311.14	Binds to glutamate receptors in the brain disrupting normal neurochemical transmission	(Wright et al., 1990; Quilliam, 2003)	
Saxitoxins (STXs)	Hydrosoluble pH ≤7: Stable	C ₁₀ H ₁₇ N ₇ O ₄	299.3	Bind to site 1 of voltage-sensitive sodium channels and block sodium conductance; Bind to calcium and potassium channels	(Wong et al., 1971; Wang et al., 2003; Su et al., 2004){Catterall, 1992 #58;Cestele, 2000 #62}	
Brevetoxins (PbTxs) Brevetoxin 2 (PbTx 2) Brevetoxin 3 (PbTx 3) Brevetoxin 9 (PbTx 9)	Liposoluble	$C_{50}H_{70}O_{14} \ C_{50}H_{72}O_{15} \ C_{50}H_{74}O_{14}$	895.1 897.1 899.1	Bind to site 5 of voltage-sensitive sodium channels, shifting activation to more negative membrane potentials and block channel activation	(Lin et al., 1981; Baden, 1983, 1989; Purkerson et al., 1999)	
Diarrhetic shellfish toxins Okadaic acid (OA) Dinophysistoxins (DTXs) Pectenotoxins (PTXs)	Liposoluble	C ₄₄ H ₆₈ O ₁₃	805	Inhibits protein phosphatases, inhibits dephosphorylation of proteins High actin-depolarizaing action	(Tachibana et al., 1981; Murata et al., 1982; Yasumoto et al., 1985; Takai et al., 1987; Bialojan and Takai, 1988; Haystead et al., 1989; Hori et al., 1999)	
Yessotoxins (YTXs)	Hydrosoluble	C ₅₅ H ₈₀ O ₂₁ S ₂ Na ₂	1,187.3	Activation of phosphodiesterase in presence of external Ca ²⁺ ; Disruption of the E-cadherin-catenin system in epithelial cells and potentially disrupting its tumour suppressive functions	(Murata et al., 1987; Takahashi et al., 1996; Alfonso et al., 2003; Ronzitti et al., 2004)	

Figure Legends

Figure 1. Distribution of some well-known regional HAB issues along U.S. shores, including a) Alaska and b) Hawaii. Causes and impacts of these poisoning events are defined in Tables 1-3.

Figure. 2. Chemical structures of commonly encountered toxins produced by microalgae in U.S. coastal waters.

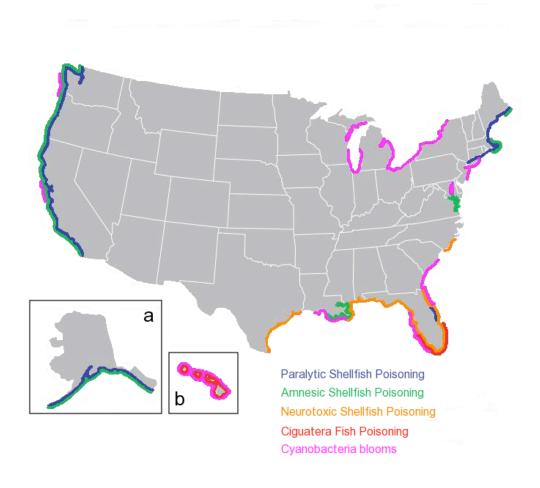
Figure 3. Major algal toxin producers occurring along the U.S. west coast. a) *Pseudo-nitzschia australis* producer of domoic acid; b) Scanning electron micrograph of *Pseudo-nitzschia australis*; c) *Alexandrium catenella*, a producer of saxitoxin; d) *Dinophysis* sp., producer of okadaic acid;; e) *Heterosigma akashiwo*, a potential source of brevetoxin; f) *Chattonella marina*, a potential source of brevetoxin); j) *Cochlodinium* sp.; h) *Lingulodinium polyedrum*, a source of yessotoxin; i) *Phaeocytis antarctica* colony; g) foam produced by the prymnesiophyte, *Phaeocystis* accumulating along the shore; k) Unconcentrated seawater from King Harbor, City of Redondo Beach, with significant discoloration due to an algal bloom; l) *Prorocentrum* sp., the dominant organism in (k); m) Higher magnification of *Prorocentrum* sp. from (l). Scale bars = 10 μm. Photo (c) courtesy of Carmelo Tomas, (j) courtesy of Cindi Heslin.

Figure 4. Time series of chlorophyll *a* fluorescence (Chlorophyll *a*), temperature and dissolved oxygen in King Harbor, City of Redondo Beach, CA. Note the short-term temporal fluctuations in these parameters that are a result of tide, wind and biological interactions. These measurements were collected using autonomously recording sensors that provide high resolution observations of chemical and physical properties that might indicate an algal bloom, or environmental factors that might stimulate a bloom.

Figure 5. Seasonal variability of domoic acid (upper panel) and PSP toxin (lower panel) concentrations along the California coast. Monthly averages of data collected from 2002 and 2007 in fifteen Californian coastal counties are shown as histograms. Also shown are the maximal values recorded during each month over the entire study period (triangles and solid

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1869 lines). Toxin concentrations were derived from shellfish tissue. Data from CDPH (Langlois, 1870 2007). 1871 Figure 6. Interannual variation in toxin concentration in four California coastal counties 1872 from 2002 to 2007 during three months exhibiting high concentrations of domoic acid (April, 1873 May, June) and saxitoxin (July, August, September). Toxin concentrations were measured from 1874 shellfish tissues. Data from CDPH (Langlois, 2007). *Not detected. 1875 Figure 7. Two-dimensional presentations of chemical and physical data collected by an 1876 autonomous vehicle (Webb Slocum glider, bottom picture) along a nearshore-offshore transect at 1877 Newport Beach, CA (indicated on map by the blue line in lower right panel). Contour plots are 1878 shown for temperature, chlorophyll a fluorescence (Chlor. Fluor.), salinity, backscattered light 1879 (b_b) and water density (Sigma-ø). The Webb Slocum glider (g) is an autonomous vehicle 1880 commonly employed in coastal ecosystems. This buoyancy-driven underwater vehicle generates 1881 horizontal motion by ascending and descending with pitched wings (Schofield et al., 2007). A 1882 rudder directs heading while buoyancy is controlled by pumping seawater into and out of the 1883 nose of the vehicle. This long-lived, low-power glider achieves horizontal velocities of approximately 25-30 cm s⁻¹ with vertical velocities of 10-15 cm s⁻¹. 1884 1885 Figure 8. Spatial variability in particulate domoic acid concentrations in surface waters 1886 within the San Pedro Bay area including the San Pedro/Long Beach harbor area. Data were 1887 collected at 20 sampling stations (locations indicated by filled circles). 1888 Figure 9. Correlation between chlorophyll a fluorescence (open squares, in relative 1889 fluorescence units) and transmembrane pressure (filled circles) in a pilot-scale reverse osmosis 1890 desalination system. Increased loading of phytoplankton biomass resulted in greater 1891 transmembrane pressure. 1892 Figure 10. Time-series of abundances of *Pseudo-nitzschia* spp. cells (top), domoic acid 1893 concentrations in particulate material (middle) and dissolved in seawater (bottom) at a coastal 1894 monitoring site in El Segundo, CA.



Stormwater and Marine Biotoxin Monitoring – Final Report (continued)

Domoic acid

Saxitoxin

Brevetoxin (type B)

Okadaic acid

Dinophysistoxin

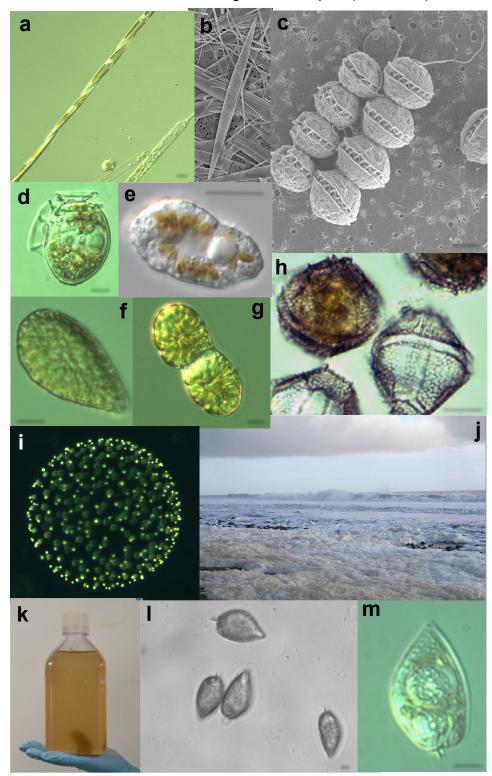
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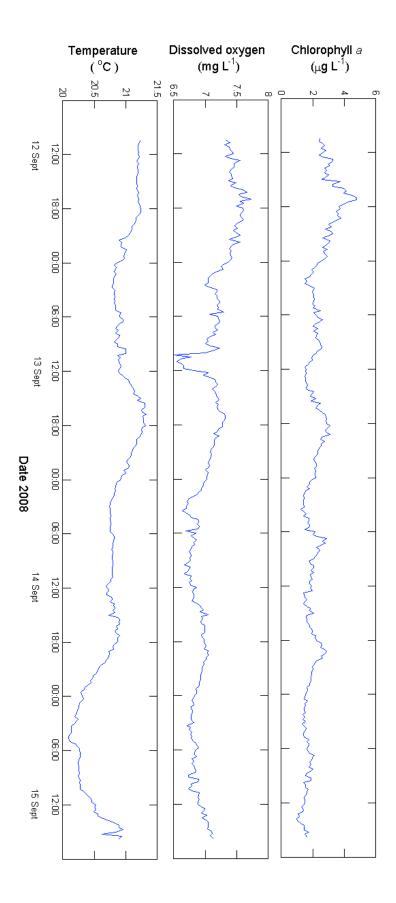
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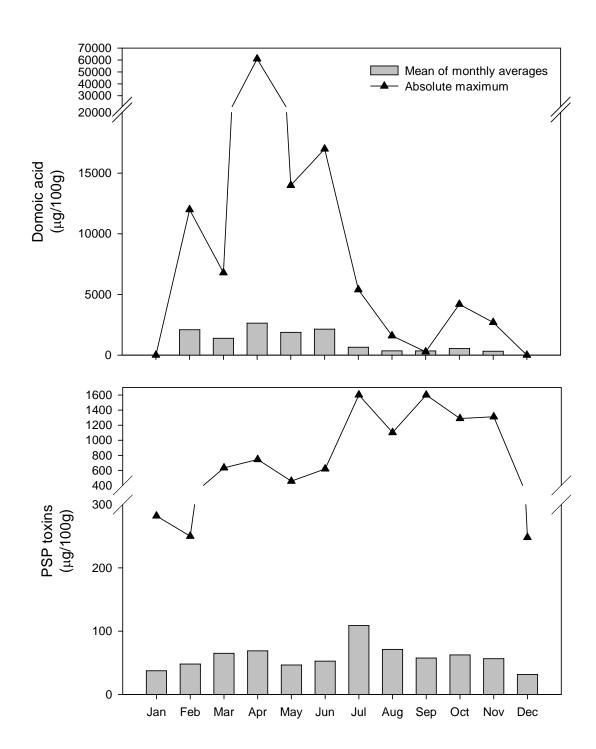
Yessotoxin

Pectenotoxin

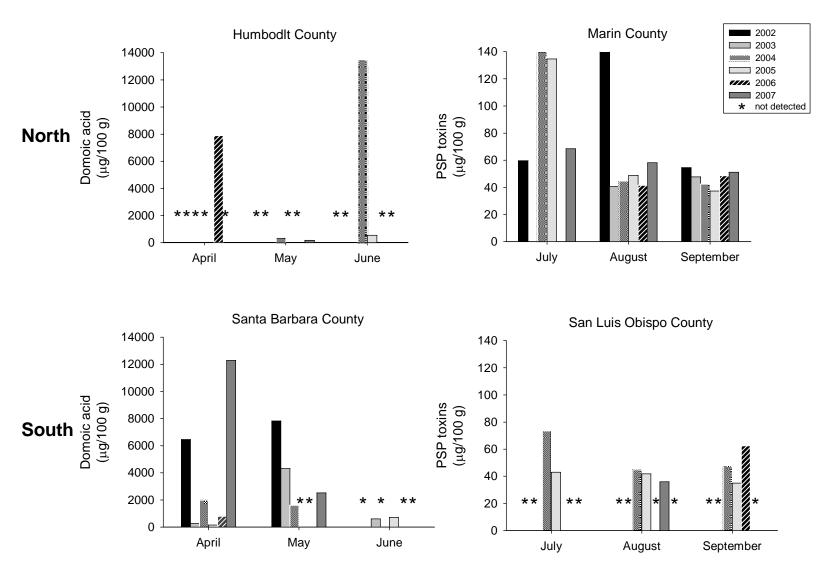
Stormwater and Marine Biotoxin Monitoring – Final Report (continued)

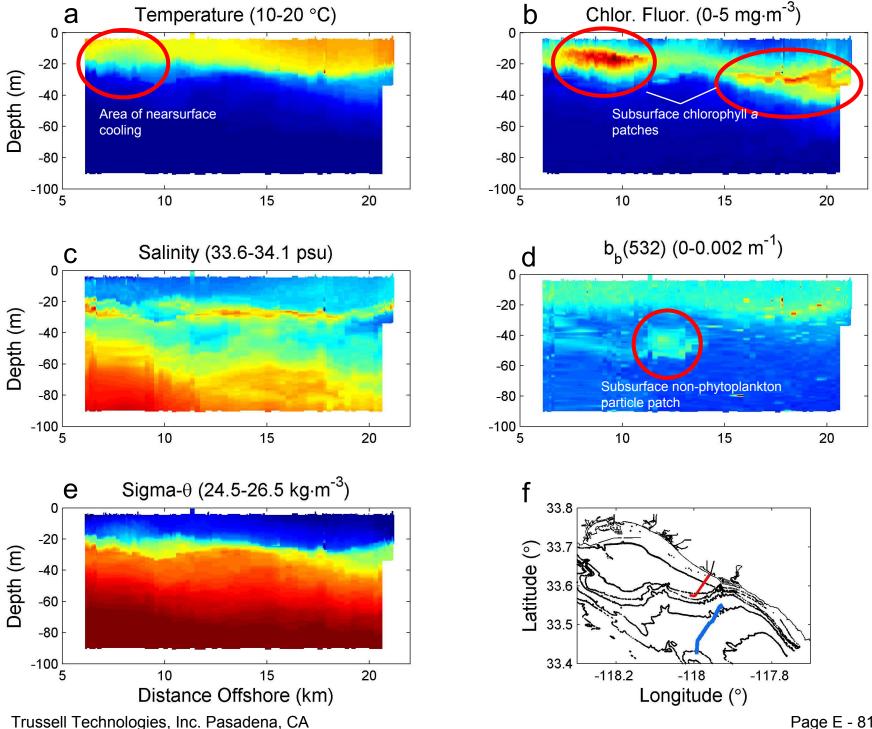




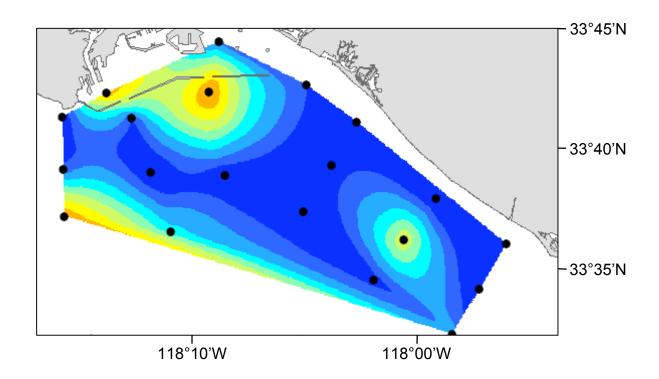


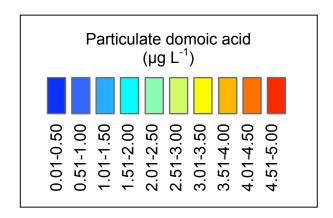
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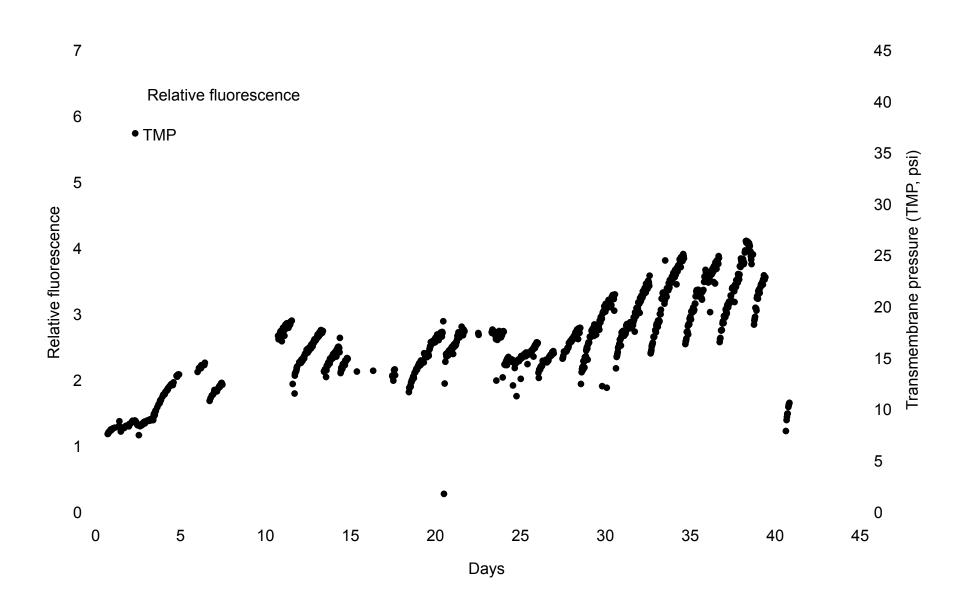


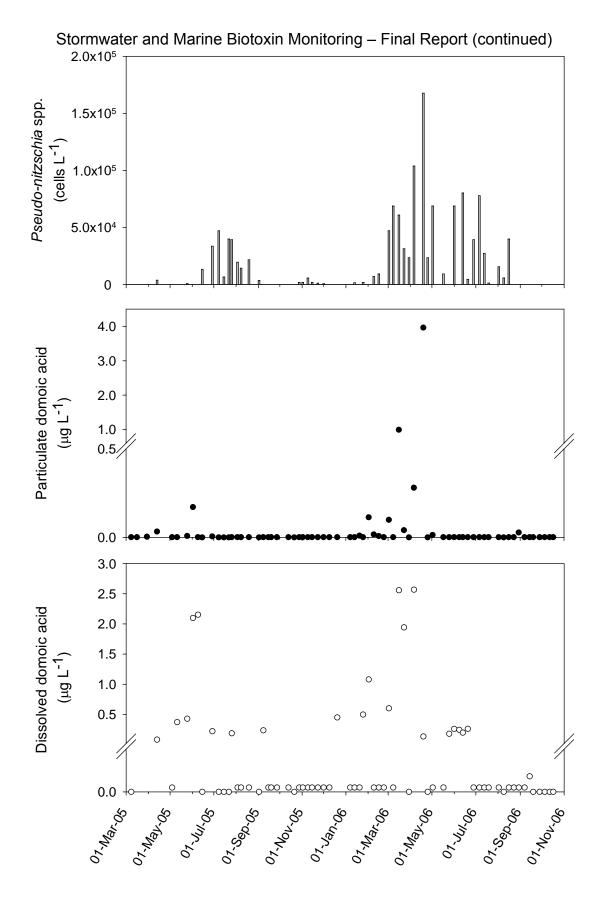
Page E - 81





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Appendix F – Enterolert Discussion

Enterococcus bacteria were monitored as an indicator of fecal contamination in the source water. Weck Laboratories analyzed water samples for *enterococcus*, using the USEPA-approved Enterolert method. Table F1 presents the detected *enterococci* data associated with stormwater monitoring.

Table F1. Detected enterococcus data from stormwater monitoring

Sample Date	Sample Source	Units	Result	Reporting Limits ^a
11/26/08 PM	Raw water	MPN/100 mL	21	1
11/30/08 AM	Raw water	MPN/100 mL	10	10
11/30/08 PM	Raw water	MPN/100 mL	10	10
12/1/08 AM	Raw water	MPN/100 mL	10	10
12/2/08 AM		MPN/100 mL	10	10
12/22/08 PM	Raw water	MPN/100 mL	10⁵	10
1/30/09 AM	Raw water	MPN/100 mL	10	10
1/31/09 AM	Raw water	MPN/100 mL	10	10
2/10/09 AM	Raw water	MPN/100 mL	10	10
1/30/09 AM	GMF filtrate	MPN/100 mL	10	10
2/10/09 AM	GMF filtrate	MPN/100 mL	10	10
1/26/09 PM	Arkal filtrate	MPN/100 mL	10	10
2/9/09 AM	Arkal filtrate	MPN/100 mL	10	10
2/9/09 PM	Arkal filtrate	MPN/100 mL	10	10
2/10/09 AM	Arkal filtrate	MPN/100 mL	20	10
1/31/09 AM	Pall 1 filtrate	MPN/100 mL	10	10
2/9/09 AM	Pall 1 filtrate	MPN/100 mL	10	10
2/10/09 AM	RO2 permeate	MPN/100 mL	1	1
2/11/09 PM	RO2 permeate	MPN/100 mL	1	1
12/19/08 AM	2nd pass RO permeate	MPN/100 mL	2	1
1/30/09 PM	2nd pass RO permeate	MPN/100 mL	10	10
1/31/09 AM	2nd pass RO permeate	MPN/100 mL	10	10
2/10/09 AM	2nd pass RO permeate	MPN/100 mL	10	10

^aUse of different dilution factors resulted in multiple reporting limits; According to manufacturer procedures, the appropriate dilution factor for use with marine waters should be 10, and drinking water samples do not need to be diluted.

According to Table F1, *enterococci* were detected in 9 raw water storm samples, 8 of which were detected at the detection limit. The sample with the highest detected value was associated with a dilution factor of 1, whereas the other values were detected using a dilution factor of 10. In addition to the use of more than one dilution factors, Weck Laboratories qualified one of the detected values from the raw water with a high bias, due to prolonged incubation of the sample that may have introduced interference caused by slower-growing organisms.

Upon further investigation and consultation with the manufacturer of Enterolert (IDEXX Laboratories Inc.) and Weck Laboratories, it was discovered that in several cases dilution factors were incorrectly applied. Much like the case of *E. coli*, manufacturer protocols require marine water samples to be diluted by a

^bThis result was qualified with a "high bias" by Weck Laboratories, due to prolonged incubation.

Stormwater and Marine Biotoxin Monitoring – Final Report *(continued)*

factor of 10. The concentration of salts in marine waters provides favorable conditions for additional bacteria whose presence can cause interference with the media used in Enterolert and result in false-positive detections. If the marine samples are diluted, the media can suppress these bacteria and eliminate the interference with *enterococcus* detection (IDEXX Laboratories Inc., 2009).

Given the interference of salinity, a dilution factor of 10 should have been applied to the samples from the raw water ocean intake, as well as the filtrate from the Arkal disc filters, GMF, Pall 1 and Pall 2 microfilters (sampling points 1-5 from Figure 2). All results detected using a dilution factor of 1 with samples from these treatment stages are thus inconclusive due to potential false-positives. Likewise, the samples from the RO1, RO2 and second pass RO permeates should not have been diluted.

Table F1 reveals that *enterococci* were detected in the Pall microfiltrate, as well as in the permeates from both the RO1 and second pass RO treatment stages. These results are inconsistent with established literature addressing the removal of bacteria the size of *enterococci* via microfiltration and reverse osmosis treatment. Of the 4 instances listed in Table F1 where *enterococcus* was detected in the second pass RO permeate, 3 of the samples were incorrectly diluted by a factor of 10. On the date when *enterococcus* was detected in the second pass RO permeate using the correct dilution factor (no dilution), the lab reports found no detection of *enterococcus* in the raw water and RO1 permeate. These unexpected results, combined with the inconsistencies in analysis identified for *enterococcus* as well as in conjunction with the *E. coli*, raise questions about the validity of the data.

Corresponding baseline data from sampling locations within the El Segundo pilot desalination treatment train are more in-line with expected results from the stormwater monitoring. The baseline *enterococcus* data was also analyzed by Weck Laborabories, using the Enterolert detection method. Table E2 displays results from the analysis of periodic baseline samples of *enterococcus* collected between March 2008 and May 2009.

Table F2. Summary of baseline enterococcus results

Treatment Stage	Units	Min.	Max.	Number of Observations	Number of Non-Detects	Number of Detected Observations	Reporting Limits ^a
Raw Water	MPN/100 mL	ND	ND	2	2	0	1
Raw Water	MPN/100 mL	<10	20	36	32	4	10
Arkal disc	MPN/100 mL	2	13	4	0	4	1
Arkal disc	MPN/100 mL	<10	>2419.6 ^b	6	5	1	10
GMF	MPN/100 mL	52	52	1	0	1	1
GMF	MPN/100 mL	ND	ND	6	6	0	10
Pall 1	MPN/100 mL	ND	ND	4	4	0	1
Pall 1	MPN/100 mL	ND	ND	6	6	0	10
Pall 2	MPN/100 mL	ND	ND	1	1	0	1
Pall 2	MPN/100 mL	ND	ND	5	5	0	10
RO1	MPN/100 mL	ND	ND	10	10	0	1
RO1	MPN/100 mL	ND	ND	1	1	0	10
RO2	MPN/100 mL	ND	ND	9	9	0	1
RO2	MPN/100 mL	ND	ND	1	1	0	10

^aUse of different dilution factors resulted in multiple reporting limits; According to manufacturer procedures, the appropriate dilution factor for use with marine waters should be 10, and drinking water samples do not need to be diluted. Results from Weck Labs had dilutions of 1 and 10 for all treatment stages in 2008. The data from 2009 was consistent with the appropriate dilution factors.

As displayed in Table F2, *enterococcus* was non-detect in 100% of the baseline samples from the filtrates of the Pall 1&2 MFs, as well as in those from the permeates of the RO 1&2 membrane treatment stages. Again, a few of the initial samples were analyzed using incorrect dilution factors (e.g., the reporting limit used with 2 of the raw water samples was 1 MPN/100 mL and 2 of the RO permeate samples were analyzed with a reporting limit of 10 MPN/100 mL), however data from subsequent dates was analyzed using correct dilution factors.

Another important factor in the discussion of the *enterococci* results is the fact that there are multiple species of these bacteria. Some *enterococcus* species can regrow or colonize in marine and estuarine waters, particularly if seaweed is an available substrate. In these cases, *enterococci* are not fecal specific. Methods exist for distinguishing among the species (e.g., biochemical speciation, PCR and nucleotide sequencing), however these can be complicated, time-consuming and expensive (Sobsey, 2009). Often, concurrent measurements of *E. coli* and *enterococci* are used as an indicator of consistent response to treatment. Measurements of male-specific (F+) coliphages can provide additional verification of treatment performance, as these species do not regrow.

The stormwater monitoring included measurements of both *E. coli* and male-specific coliphage. *E. coli*, when analyzed correctly, was demonstrated to be present in 34% of the raw water storm samples, but was successfully removed from 100% of the samples from the Pall filtrates and RO permeates. This suggests that *enterococcus* should likewise be removed, and the detections from Table E1 should be attributed to laboratory error. Although male-specific coliphage was sampled and analyzed as part of the stormwater monitoring

^bNote: It is expected that unusually elevated results from this sample may be due to the detection of a clump of bacteria that had accumulated on the Arkal disc filter and was included within the sample. On the day when the reading from the Arkal disc filtrate was >2419, the value in the raw water was 10.

Stormwater and Marine Biotoxin Monitoring – Final Report *(continued)*

program, a lack of detected values in the raw intake water preclude the ability to correlate this data with the expected results from *enterococci* data.

Appendix G - Time Series Plots of Storm and Non-Storm Events

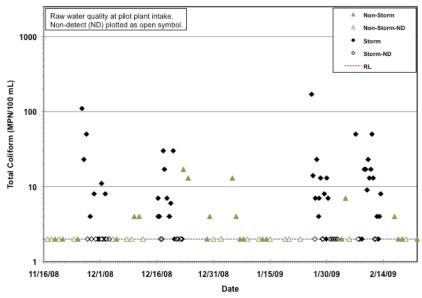


Figure G1. Time-series total coliform data

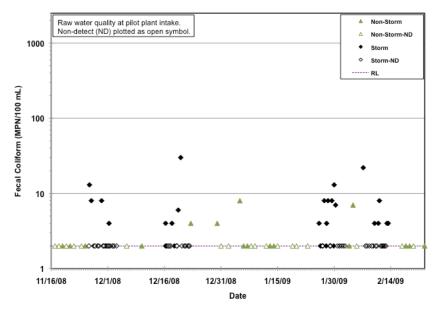


Figure G2. Time-series fecal coliform data

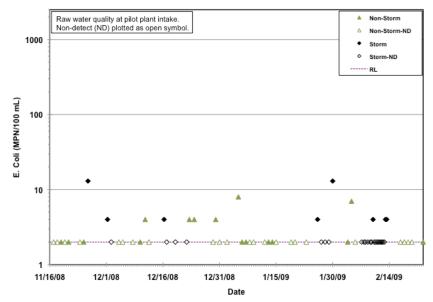


Figure G3. Time-series E. coli data

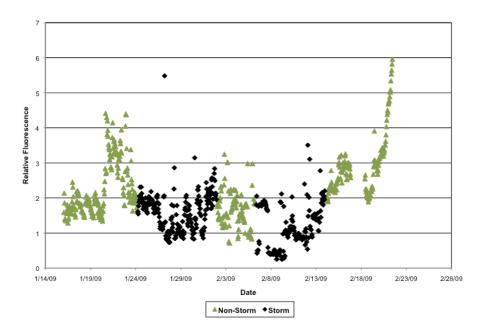


Figure G4. Time-series relative fluorescence data

Stormwater and Marine Biotoxin Monitoring – Final Report (continued)

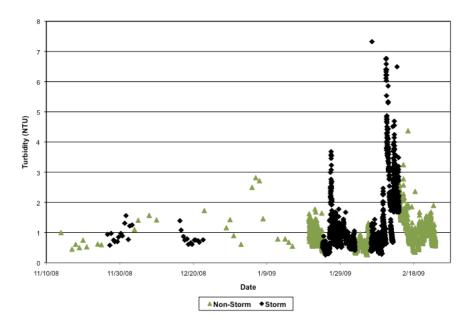


Figure G5. Time-series turbidity data

Appendix H – Constituents with MCLs and NLs During Storm Events

Table H1. Incidence of raw water constituents with MCLs and NLs during storm events

	WATE	ER MATRIX: F	Raw Ocean In	take at El Segundo	
Chemicals with MC	CLs ^a in SDWA ^b or I	VLs ^c	Chemicals w	No. of Chemicals	
Constituent	Туре	No. of Constituents	No. of Constituents	List of Constituents	Not Detected
Inorganic Chemicals	Primary MCLs	8	0	-	3
Organic Chemicals Primary MCLs 2		23	0	-	23
Physical Parameters	Primary MCLs	3	1	turbidity	1
Microbiological Parameters	Primary MCLs	3	3	E. Coli, fecal coliform, total coliform	0
Various Constituents Secondary MCLs 7		7	3 alumimum, iron, pH		1
Various Constituents	NLs	14	1	boron	11

^{*}MCL=Maximum Contaminant Level (determined by United States Environmental Protection Agency Primary and Secondary Drinking Water Treatment Regulations)
*SDWA=Safe Drinking Water Act

Table H2. Incidence of finished water constituents with MCLs and NLs during storm events

<u> </u>				505 () (510)	
	WATER MATRIX	C: Finished Wa	ater (2nd Pass	RO Permeate) at El Segundo	
Chemicals with MC	Ls in SDWA or NL	_S	Chemicals wi	th Exceedances of MCLs or NLs	No. of Chemicals
Constituent	Туре	No. of Constituents	No. of Constituents	List of Constituents	Not Detected
Inorganic Chemicals	Primary MCLs	8	0	-	7
Organic Chemicals	Primary MCLs	23	0	-	23
Physical Parameters	Primary MCLs	3	0	-	1
Microbiological Parameters	Primary MCLs	3	0	-	3
Various Constituents	Secondary MCLs	7	1	рН	3
Various Constituents	NLs	14	1	boron	11

[°]NL=Notification Limit (determined by the California Department of Public Health)

pendix I – Summary Statistics of all Detected Constituents for Storm Events
le I1. Desalination treatment process summary statistics for all constituents detected in raw water^a

	ole I1. Desalinat	ion treatment pro	cess sur	nmar	ry statistics for all constituents detected in raw water ^a							
Aluminum, total	ter Quality Parameter	Sampling Point	Units	Mean⁵		Median ^c	Minimum ^c	Maximum			I	
Alumnum, total	Aluminum, total	Raw water	μg/l	NA	NA	<50			56	44		
Aluminum, total Pall filtrate ygg ND ND ND ND ND ND S1 51 550;	Aluminum, total	Arkal filtrate	μg/l	NA	NA	<50	<50	220	54	47		
Aluminum, total	Aluminum, total		μg/l	NA	NA	<50	<50		54	50		
Aluminum, total	Aluminum, total		μg/l									
Alaminum, total	Aluminum, total	Pall 2 filtrate	μg/l								5;5	
Aluminum, total 2nd pass RQ permeate 1961 NA NA <5 <5 <5 <5 <5 <5 <5 <	Aluminum, total		μg/l									
Ammonia as N	Aluminum, total	RO 2 permeate	μg/l			_						
Ammonia as N		2nd pass RO permeate	μg/l								5	
Ammonia as N RO 2 permeate mg/l NA NA <0,1 <0,1 <0,3 38 37 <0.7			mg/l									
Ammonia as N 2nd pass RO permeate mg/l NA NA <0.1 <0.1 <0.1 <1.5 38 25 0.		·										
Arsenic, total Raw water μg/l NA NA 4 4 4 56 55 4												
Arsenic, total Arkal filtrate μg/l ND ND ND ND 54 54 4 Arsenic, total Pell 1 filtrate μg/l ND ND ND ND ND 55 54 4 Arsenic, total Pell 2 filtrate μg/l ND ND ND ND ND 51 51 0.4% Arsenic, total Pell 2 filtrate μg/l ND ND ND ND ND 48 48 0.4 Arsenic, total RO 2 permeate μg/l ND ND ND ND ND 38 38 0.9 Arsenic, total Zed pass RO permeate μg/l ND ND ND ND ND 38 38 0.9 Arsenic, total Road Arkal filtrate μg/l 6 0.4 6 6 8 14 1 5.5 Barium, total* Arkal filtrate μg/l 6 0.4 6 6		' '										
Arsenic, total GMF fittrate μg/l ND ND ND ND ND S4 54 44												
Arsenic, total												
Arsenic, total												
Arsenic, total RO 1 permeate μg/l ND ND ND NB 48 48 0_0 Arsenic, total 2 Oz permeate μg/l ND ND ND ND 38 38 0_0 Arsenic, total 2nd pass RO permeate μg/l ND ND ND ND 38 38 0_0 Barium, total** Raverage μg/l NA NA 6 6 8 14 1 5.1 Barium, total** GMF litrate μg/l NA NA 6 6 7 14 0 5 Barium, total** Pall 2 litrate μg/l 6 0.4 6 6 7 11 0 5 Barium, total** Pall 2 litrate μg/l ND ND ND ND ND ND 14 14 0.1 2-ethylhexyl) phthasite Ro2 permeate μg/l ND ND ND ND 10 10 0.2<												
Arsenic, total												
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Barium, total* Raw water µg/l NA NA 6 6 8 14 1 5-11												
Barium, total Arkal filtrate μg/l 6 0.4 6 5 7 14 0 5												
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Barium, total Pall 2 filtrate µg/l 6 0.4 6 6 7 11 0 5					1			_		·		
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Barium, total						_		·		_		
Barium, total 2nd pass RO permeate μg/l ND ND ND ND 10 10 0.8		·										
2-ethylhexyl) phthalate Raw water μg/l NA NA <3 <3 4 56 55 3 2-ethylhexyl) phthalate RO 1 permeate μg/l NA NA <3		·										
2-ethylnexyl) phthalate												
2-ethylhexyl) phthalate RO 2 permeate μg/l NA NA <3 <3 94 38 22 3 2-ethylhexyl) phthalate 2nd pass RO permeate μg/l NA NA <3												
2-ethylhexyl) phthalate 2nd pass RO permeate μg/l NA NA <3 <3 69 38 37 3												
Boron, total Raw water mg/L 4.18 0.44 4.20 2.50 5.10 56 0 0.01;		2nd pass RO permeate	<u>. </u>		NA	<3	<3	69	38	37		
Boron, total GMF filtrate mg/L 4.24 0.34 4.30 3.20 4.90 54 0 0.01;			mg/L	4.18	0.44	4.20	2.50	5.10	56	0	0.01;(
Boron, total Pall 1 filtrate mg/L 4.19 0.50 4.20 1.60 4.80 51 0 0.01;	Boron, total	Arkal filtrate	mg/L	4.22	0.31	4.20	3.00	4.90	54	0	0.01;(
Boron, total Pall 2 filtrate mg/L 4.11 0.82 4.40 0.84 4.80 23 0 0.01;	Boron, total	GMF filtrate	mg/L	4.24	0.34	4.30	3.20	4.90	54	0	0.01;(
Boron, total RO 1 permeate mg/L 1.24 0.66 0.89 0.60 2.40 48 0 0.001;	Boron, total	Pall 1 filtrate	mg/L	4.19	0.50	4.20	1.60	4.80	51	0		
Boron, total RO 2 permeate mg/L 1.32 0.73 0.83 0.59 2.50 38 0 0.001;			mg/L									
Boron, total 2nd pass RO permeate mg/L 0.86 0.57 0.56 0.37 2.20 38 0 0.001;	· · · · · · · · · · · · · · · · · · ·	-										
Caffeine Raw water μg/l NA NA < 0.1 < 0.1 0.3 56 55 0.3 Caffeine RO 1 permeate μg/l ND ND ND ND ND AVA 47 0.3 Caffeine RO 2 permeate μg/l ND ND ND ND ND ND 38 38 0.3 Caffeine 2nd pass RO permeate μg/l ND		•										
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Chromium, total Raw water μg/l NA NA <2 <2 55 56 55 2 Chromium, total Arkal filtrate μg/l ND ND ND ND ND 54 54 2 Chromium, total GMF filtrate μg/l ND ND ND ND ND 54 54 2 Chromium, total Pall 2 filtrate μg/l ND ND ND ND ND 54 54 2 Chromium, total Pall 2 filtrate μg/l ND ND ND ND ND ND 23 23 0.2 Chromium, total RO 1 permeate μg/l ND ND ND ND ND ND 48 48 0.2 Chromium, total RO 2 permeate μg/l ND ND ND ND ND ND 38 38 0.2 Chromium, total Raw water μg/l ND ND <td></td>												
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Chromium, total GMF filtrate μg/l ND ND ND ND ND 54 54 2 Chromium, total Pall 1 filtrate μg/l ND ND ND ND ND 51 51 0.2; Chromium, total Pall 2 filtrate μg/l ND ND ND ND ND ND 23 23 0.2 Chromium, total RO 1 permeate μg/l ND ND ND ND ND ND 48 48 0.2 Chromium, total RO 2 permeate μg/l ND ND ND ND ND ND 38 38 0.2 Chromium, total 2nd pass RO permeate μg/l ND ND ND ND ND ND ND ND 38 38 0.2 Chromium, total 2nd pass RO permeate μg/l ND ND </td <td></td>												
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Chromium, total 2nd pass RO permeate μg/l ND ND ND ND ND 38 38 0.2 Copper, total Raw water μg/l NA NA <5		·										
Copper, total Raw water μg/l NA NA <5 <5 9 56 55 5 Copper, total Arkal filtrate μg/l ND ND ND ND ND 54 54 5 Copper, total GMF filtrate μg/l NA NA <5		·										
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Copper, total GMF filtrate μg/l NA NA <5 <5 9 54 53 5 Copper, total Pall 1 filtrate μg/l NA NA <5												
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Copper, total Pall 2 filtrate μg/l ND ND ND ND ND 23 23 0.5 Copper, total RO 1 permeate μg/l NA NA <0.5												
Copper, total RO 1 permeate μg/l NA NA <0.5 <0.5 1.3 48 45 0.8 Copper, total RO 2 permeate μg/l NA NA <0.5												
Copper, total RO 2 permeate μg/l NA NA <0.5 <0.5 0.6 38 37 0.8 Copper, total 2nd pass RO permeate μg/l NA NA <0.5												
Copper, total 2nd pass RO permeate μg/l NA NA <0.5 <0.5 1.5 38 37 0.4 Conductivitye Raw water mS/cm 49.17 0.90 49.32 44.33 49.87 32 0 0.0												
Conductivitye Raw water mS/cm 49.17 0.90 49.32 44.33 49.87 32 0 0.0												
	Conductivitye	RO 1 permeate	mS/cm	0.65	0.49	0.37	0.00	2.00	1436	0	0.00	

ple I1. Desalination treatment process summary statistics for all constituents detected in raw water ntinued)

er Quality Parameter	Sampling Point	Units	Mean⁵	Standard Deviation ^b	Median ^c	Minimum ^c	Maximum	Number of Observations	Number of Non-Detects	Repor Limi
Iron, total	Raw water	μg/l	NA	NA	<200	<200	6000	56	52	200
Iron, total	Arkal filtrate	μg/l	NA	NA	<200	<200	360	54	52	200
Iron, total	GMF filtrate	μg/l	NA	NA	<200	<200	290	54	53	200
Iron, total	Pall 1 filtrate	μg/l	ND	ND	ND	ND	ND	51	51	20;200
Iron, total	Pall 2 filtrate	μg/l	ND	ND	ND	ND	ND	23	23	20;20
Iron, total	RO 1 permeate	μg/l	NA	NA	<20	<20	96	48	47	20
Iron, total	RO 2 permeate	μg/l	ND	ND	ND	ND	ND	38	38	20
Iron, total	2nd pass RO permeate	μg/l	ND	ND	ND	ND	ND	38	38	20
Manganese, total	Raw water	μg/l	NA	NA	<2	<2	42	56	28	2
Manganese, total	Arkal filtrate	μg/l	NA	NA	<2	<2	38	54	29	2
Manganese, total	GMF filtrate	μg/l	NA	NA	<2	<2	5	54	46	2
Manganese, total	Pall 1 filtrate	μg/l	NA	NA	<2	0.3	6	51	41	0.2;2
Manganese, total	Pall 2 filtrate	μg/l	NA	NA	<2	<0.2	3	23	21	0.2;
Manganese, total	RO 1 permeate	μg/l	NA	NA	<0.2	<0.2	2.3	48	35	0.2
Manganese, total	RO 2 permeate	μg/l	NA	NA	<0.2	<0.2	4.7	38	26	0.2
Manganese, total	2nd pass RO permeate	μg/l	NA	NA	<0.2	<0.2	18.0	38	28	0.2
Molybdenum, total	Raw water	μg/l	11	2	10	9	22	56	0	1
Molybdenum, total	Arkal filtrate	μg/l	10	1	10	9	13	54	0	1
Molybdenum, total	GMF filtrate	μg/l	10	1	10	9	18	54	0	1;2
Molybdenum, total	Pall 1 filtrate	μg/l	10	2	10	1	15	51	0	0.1;1
Molybdenum, total	Pall 2 filtrate	μg/l	NA	NA	10	<0.1	13	23	1	0.1;1
Molybdenum, total	RO 1 permeate	μg/l	ND	ND	ND	ND	ND	48	48	0.1
Molybdenum, total	RO 2 permeate	μg/l	ND	ND	ND	ND	ND	38	38	0.1
Molybdenum, total	2nd pass RO permeate	μg/l	NA	NA	<0.1	<0.1	0.2	38	37	0.1
Nitrate as N	Raw water	mg/l	NA	NA	<0.1	<0.1	550.0	56	54	0.1
Nitrate as N	RO 1 permeate	mg/l	ND	ND	ND	ND	ND	48	48	0.1
Nitrate as N	RO 2 permeate	mg/l	NA	NA	<0.1	<0.1	55.0	38	37	0.1
Nitrate as N	2nd pass RO permeate	mg/l	NA	NA	<0.1	<0.1	55.0	38	37	0.1
pН	Raw water	pH units	8.18	0.35	8.10	7.47	9.33	35	0	0.0
pH	RO 1 permeate	pH units	8.67	0.35	8.76	7.71	9.34	27	0	0.0
pH	RO 2 permeate	pH units	8.35	0.44	8.36	7.23	9.21	20	0	0.0
pH	2nd pass RO permeate	pH units	8.65	0.93	8.93	5.96	9.62	21	0	0.0
osphorus, total as P	Raw water	µg/l	35	7	35	22	59	56	0	10
osphorus, total as P	RO 1 permeate	µg/l	ND	ND	ND	ND	ND	48	48	10
osphorus, total as P	RO 2 permeate	μg/l	ND	ND	ND	ND	ND	38	38	10
osphorus, total as P	2nd pass RO permeate	μg/l	ND	ND	ND	ND	ND	38	38	10
Selenium, total	Raw water	μg/l	NA	NA	6	<4	9	56	13	4
Selenium, total	Arkal filtrate	μg/l	NA	NA	6	<4	9	54	11	4
Selenium, total	GMF filtrate	μg/l	NA	NA	6	<4	8	54	10	4
Selenium, total	Pall 1 filtrate	μg/l	NA	NA	6	0.4	9	51	10	0.4;4
Selenium, total	Pall 2 filtrate	μg/l	NA	NA	5	<0.4	9	23	7	0.4;
Selenium, total	RO 1 permeate	μg/l	ND	ND	ND	ND	ND	48	48	0.4
Selenium, total	RO 2 permeate	µg/l	ND	ND	ND	ND	ND	38	38	0.4
Selenium, total	2nd pass RO permeate	µg/l	ND	ND	ND	ND	ND	38	38	0.4
Strontium, totald	Raw water	µg/l	7179	278	7100	6900	8000	14	0	2
Strontium, totald	Arkal filtrate	μg/l	7079	176	7050	6900	7400	14	0	2
Strontium, totald	GMF filtrate	µg/l	7129	164	7150	6900	7500	14	0	2
Strontium, totald	Pall 1 filtrate	µg/l	6650	1720	7100	700	7500	14	0	0.2;
Strontium, totald	Pall 2 filtrate	µg/l	7118	194	7100	6800	7400	11	0	2
Strontium, totald	RO 1 permeate	μg/l	6.1	0.2	6.2	5.7	6.4	14	0	0.2
Strontium, totald	RO 2 permeate	µg/l	NA	NA	5.6	<0.2	6.6	14	1	0.2
Strontium, totald	2nd pass RO permeate	μg/l	NA	NA	<0.2	<0.2	5.8	10	9	0.2
Temperature	Raw water	°C	15.31	1.52	14.85	12.50	18.10	32	0	NA
Temperature ^e	RO 1 permeate	°C	17.30	1.26	16.90	16.10	19.80	9	0	NA
Temperature ^e	RO 2 permeate	°C	17.66	1.12	17.60	16.20	19.20	9	0	NA
Temperature ^e	2nd pass RO permeate	°C	21.84	1.35	21.10	20.70	23.80	5	0	NA
Tin, total	Raw water	μg/l	NA	NA	<2	<2	2	56	55	2;4
Tin, total	Arkal filtrate	µg/l	NA	NA	<2	<2	4	54	53	2;4
Tin, total	GMF filtrate	µg/l	NA	NA	<2	<2	5	54	53	2;4
Tin, total	Pall 1 filtrate	μg/l	NA	NA	<2	<0.2	8	51	50	0.2;2
Tin, total	Pall 2 filtrate	μg/l	NA	NA	<2	<0.2	2	23	22	0.2;2
Tip total	PO 1 permente	110/1	NΙΛ	NΙΛ	-O 2	ZO 2	0.7	10	16	0.1

rmwater and Marine Biotoxin Monitoring – Final Report (continued)

ple I1. Desalination treatment process summary statistics for all constituents detected in raw water ntinued)

ter Quality Parameter	Sampling Point	Units	Mean ^b	Standard	Median ^c	Minimum°	Maximum	Number of	Number of	
				Deviation ^b				Observations		Limi
Turbidity	Raw water	NTU	1.22	1.05	0.84	0.26	7.33	1599	0	0.00
Turbidity	Arkal filtrate	NTU	0.74	0.42	0.58	0.31	3.53	787	0	0.00
Turbidity	GMF filtrate	NTU	0.38	0.37	0.30	0.10	11.57	1318	0	0.00
Turbidity	Pall 1 filtrate	NTU	0.03	0.05	0.03	0.02	0.92	775	0	0.00
Turbidity ^g	Pall 2 filtrate	NTU	0.03	0.02	0.02	0.02	0.21	458	0	0.00
Turbidity ^d	RO 1 permeate	NTU	0.09	0.03	0.08	0.05	0.13	9	0	0.00
Turbidity ^d	RO 2 permeate	NTU	0.08	0.02	0.07	0.04	0.13	9	0	0.00
Turbidityd	2nd pass RO permeate	NTU	0.07	0.02	0.08	0.05	0.09	5	0	0.00
Uranium rad ^d	Raw water	μg/l	NA	NA	3	<2	3	14	2	2;4
Uranium rad ^d	Arkal filtrate	μg/l	NA	NA	3	2	3	14	1	2;4
Uranium rad ^d	GMF filtrate	μg/l	NA	NA	3	<2	3	14	3	2;4
Uranium rad ^d	Pall 1 filtrate	μg/l	NA	NA	2	2	3	14	1	2;4
Uranium rad ^d	Pall 2 filtrate	μg/l	NA	NA	3	2	3	11	1	2;4
Uranium rad ^d	RO 1 permeate	μg/l	ND	ND	ND	ND	ND	14	14	0.2
Uranium rad ^d	RO 2 permeate	μg/l	ND	ND	ND	ND	ND	14	14	0.2
Uranium rad ^d	2nd pass RO permeate	μg/l	ND	ND	ND	ND	ND	10	10	0.2
UV 254	Raw water	1/cm	NA	NA	0.013	<0.009	0.042	56	5	0.00
UV 254	RO 1 permeate	1/cm	NA	NA	<0.009	<0.009	0.034	48	37	0.00
UV 254	RO 2 permeate	1/cm	NA	NA	<0.009	<0.009	0.009	38	37	0.00
UV 254	2nd pass RO permeate	1/cm	NA	NA	<0.009	<0.009	0.046	38	27	0.00
Vanadium, total	Raw water	μg/l	NA	NA	<5	<5	8	56	37	5
Vanadium, total	Arkal filtrate	μg/l	NA	NA	<5	<5	8	54	35	5
Vanadium, total	GMF filtrate	μg/l	NA	NA	<5	<5	7	54	36	5
Vanadium, total	Pall 1 filtrate	μg/l	NA	NA	<5	<0.5	8	51	38	0.5;
Vanadium, total	Pall 2 filtrate	μg/l	NA	NA	<5	2.6	7	23	16	0.5;
Vanadium, total	RO 1 permeate	μg/l	NA	NA	<0.5	<0.5	1.7	48	45	0.5
Vanadium, total	RO 2 permeate	μg/l	NA	NA	<0.5	<0.5	0.6	38	36	0.5
Vanadium, total	2nd pass RO permeate	μg/l	NA	NA	<0.5	<0.5	1.8	38	34	0.5
Zinc, total	Raw water	μg/l	NA	NA	<50	<50	71	56	55	50
Zinc, total	Arkal filtrate	μg/l	NA	NA	<50	<50	70	54	53	50
Zinc, total	GMF filtrate	μg/l	NA	NA	<50	<50	52	54	53	50
Zinc, total	Pall 1 filtrate	μg/l	ND	ND	ND	ND	ND	51	51	5;50;1
Zinc, total	Pall 2 filtrate	μg/l	NA	NA	<50	<5	64	23	22	5;50
Zinc, total	RO 1 permeate	μg/l	NA	NA	<5	<5	10	48	43	5
Zinc, total	RO 2 permeate	μg/l	NA	NA	<5	<5	15	38	35	5
Zinc, total	2nd pass RO permeate	µg/l	ND	ND	ND	ND	ND	38	38	5

available data for all constituents detected in raw water are included

n and standard deviations were only computed for those analytes that were detected in all samples analyzed; Otherwise, ND (non-detect) is utilized to represent scenarios where all samples were below the ting limit and NA (not applicable) is utilized for constituents detected in at least one sample

of different dilution factors resulted in multiple reporting limits for some constituents; Median values for constituents having multiple reporting limits and detected values above and below the reporting limits a ted as NA (not applicable) to avoid ambiguity; The minimum values is reported as the lowest detected value or < lowest detection limit, which ever value is lower

only available for storm event 1

only available for storm events 1-3

only available for storm event 4

only available for storm events1, 2 and 4