

California Regional Water Quality Control Board
North Coast Region

MONITORING & REPORTING PROGRAM R1-2001-9

For

DISCHARGES OF HIGHLY-TREATED GROUNDWATER TO SURFACE WATERS
FOLLOWING EXTRACTION AND CLEANUP OF GROUNDWATER POLLUTED WITH
PETROLEUM HYDROCARBONS AND VOLATILE ORGANIC COMPOUNDS

NORTH COAST REGION

MONITORING

A. RECEIVING WATER MONITORING

Samples shall be collected from the receiving waters, within 50 feet upstream of the discharge, and immediately downstream of the point of discharge. The flow rate of the receiving water shall be measured at the time of sampling (if a river or creek). These samples shall be analyzed as follows:

<u>Constituent</u>	<u>Units</u>	<u>Type of Sample</u>	<u>Sampling Frequency</u>
Temperature	°C	Field Monitor	Monthly
pH		Field Monitor	Monthly
Salinity	mg/l	Grab	Semi-Annually
Hardness (as CaCO ₃)	mg/l	Grab	Semi-Annually
Metals ¹	ug/l	Grab	Semi-Annually
Total Petroleum Hydrocarbons	ug/l	Grab	Semi-Annually
Benzene	ug/l	Grab	Semi-Annually
Toluene	ug/l	Grab	Semi-Annually
Ethylbenzene	ug/l	Grab	Semi-Annually
Total Xylenes	ug/l	Grab	Semi-Annually
1,2-Dichloroethane	ug/l	Grab	Semi-Annually
1,2 Dibromomethane (EDB)	ug/l	Grab	Semi-Annually
Methyl tertiary-butyl ether (MtBE) ²	ug/l	Grab	Semi-Annually
Di-Isopropyl ether (DIPE) ²	ug/l	Grab	Semi-Annually
Ethyl tertiary-butyl ether (ETBE) ²	ug/l	Grab	Semi-Annually
Tertiary-amyl methyl ether (TAME) ²	ug/l	Grab	Semi-Annually
Tertiary-butyl alcohol (TBA) ²	ug/l	Grab	Semi-Annually
Methanol	ug/l	Grab	Semi-Annually
Ethanol ²	ug/l	Grab	Semi-Annually
Volatile Organic Compounds ³	ug/l	Grab	Semi-Annually

1. Metals to include California Action Metals list (CAM 17).

2. All fuel oxygenates are to be analyzed using EPA Method 8260 (except methanol).

3. Volatile organic compounds includes other 8021/8260 compounds that are not listed in this table.

B. INFLUENT & EFFLUENT MONITORING

Samples of influent to the groundwater treatment plant and effluent from the treatment plant shall be collected and analyzed as follows:

<u>Constituent</u>	<u>Units</u>	<u>Type of Sample</u>	<u>Sampling Frequency</u>
pH		Grab	Monthly
Hardness (as CaCO ₃)	mg/l	Grab	Monthly
Metals ⁵	ug/l	Grab	Monthly
Total Petroleum Hydrocarbons	ug/l	Grab	Monthly
Benzene	ug/l	Grab	Monthly
Toluene	ug/l	Grab	Monthly
Ethylbenzene	ug/l	Grab	Monthly
Total Xylenes	ug/l	Grab	Monthly
1,2-Dichloroethane	ug/l	Grab	Monthly
1,2 Dibromomethane (EDB)	ug/l	Grab	Monthly
Methyl tertiary-butyl ether (MtBE) ¹	ug/l	Grab	Monthly
Di-Isopropyl ether (DIPE) ¹	ug/l	Grab	Monthly
Ethyl tertiary-butyl ether (ETBE) ¹	ug/l	Grab	Monthly
Tertiary-amyl methyl ether (TAME) ¹	ug/l	Grab	Monthly
Tertiary-butyl alcohol (TBA) ¹	ug/l	Grab	Monthly
Methanol	ug/l	Grab	Monthly
Ethanol ¹	ug/l	Grab	Monthly
Volatile Organic Compounds ²	ug/l	Grab	Monthly
Fish Bioassay (Chronic Toxicity)	TUc ³	--	Annually
Effluent Flow Rate	gal/min	--	Monthly Average
Dioxin/Furan Study	Varies	Grab	First year ⁴

1. All fuel oxygenates are to be analyzed using EPA Method 8260 (except methanol).
2. Volatile organic compounds includes other 8021/8260 compounds that are not listed in this table.
3. TUc = Chronic Toxicity Units, as defined in part C of this Monitoring & Reporting Program.
4. Dioxin/Furan study is to only be conducted during the first year, unless otherwise directed by the Executive Officer.
5. Metals to include California Action Metals list (CAM 17).

All data reporting under this monitoring and reporting program shall conform to the requirements as outlined in the "Reporting Protocols" in Appendix A of this Order.

C. TOXICITY MONITORING

1. Compliance with Toxicity objective

The permittee shall monitor and evaluate effluent for chronic toxicity in order to demonstrate compliance with the Basin Plan narrative toxicity objective. Compliance with this requirement shall be achieved in accordance with the following:

- a) The permittee shall perform an initial "screening phase" of chronic toxicity monitoring, which is to be submitted with the report of waste discharge. All chronic toxicity monitoring thereafter shall be in accordance with the schedule outlined in 3.c of this Monitoring and Reporting Program.

2. Screening Phase Chronic Toxicity Monitoring Requirements

- a) The permittee shall submit a screening phase proposal to the Executive Officer for approval prior to conducting the chronic toxicity testing. The proposals shall address each of the elements listed below in 2.b. Upon approval of the proposal by the Executive Officer, the permittee shall perform the screening phase monitoring of the effluent and submit it with the report of waste discharge.
- b) Design of the screening phase shall, at a minimum, consist of the following elements:
 - i. At least three test species with approved test protocols shall be used to measure compliance with the toxicity objective;
 - ii. If possible, the test species shall include a vertebrate, an invertebrate, and an aquatic plant;
 - iii. Use of test species specified in Tables 1 and 2, and use of the protocols referenced in those tables, or as approved by the Executive Officer;
 - iv. Appropriate controls; and
 - v. Concurrent reference toxicant tests.
- c) Chronic toxicity evaluation parameters:
 - i. A three sample median value of 1 TU_c; and
 - ii. A single sample maximum value of 2 TU_c.
- d) If data from the toxicity monitoring exceed either of the evaluation parameters shown in 2.c.i and 2.c.ii above, then the permittee shall immediately conduct a second chronic toxicity test. If the second chronic toxicity test indicates toxicity in excess of the evaluation parameters, the permittee shall immediately cease the discharge to surface waters (if applicable) and submit an evaluation to the Regional Water Board on the cause of the toxicity, alternate disposal methods, or treatment system modifications that are proposed to correct the effluent toxicity. The permittee shall correct the toxicity to the satisfaction of the Executive Officer prior to resuming or beginning discharge to surface waters.

3. Annual Chronic Toxicity Monitoring

- a) Sampling: The permittee shall collect 8-hour composite or 24-hour composite samples of effluent for critical life stage toxicity as indicated below. For toxicity tests requiring renewals, 8-hour composite samples collected on consecutive days are required. Grab sampling may be considered on a case-by-case basis by the Executive Officer.
- b) Test Species: Chronic toxicity shall be monitored by using critical life stage test(s) and the most sensitive test specie(s) identified during the screening phase testing done for the report of waste discharge. Test specie(s) shall be those indicated in Tables 1 & 2 of this Monitoring & Reporting Program, or as approved by the Executive Officer. Two test species may be required if test data indicate that there is alternating sensitivity between the two species.
- c) Frequency:
 - i. **Routine Monitoring**: Annually on date of Order issuance to permittee, or as necessary.
 - ii. **Accelerated Monitoring**: Within 7 days of discovery of toxicity exceedance.
- d) Conditions for Routine Monitoring: Annual monitoring reports for chronic toxicity testing shall be submitted no later than 60 calendar days following the anniversary of the permittees coverage under this permit. Toxicity testing may be required subsequent to any significant change in the nature of the effluent discharged through changes in sources or treatment, except those changes resulting from reductions in pollution concentrations due to pretreatment, source control, and waste minimization efforts. The Executive Officer may also request additional toxicity testing following significant system modifications or as deemed appropriate or necessary.
- e) Conditions for Accelerated Monitoring: The permittee shall immediately conduct accelerated monitoring (chronic toxicity retest) when either of the following conditions are exceeded:
 - i. Three-sample median value of 1 TUc.
 - ii. Single-sample median maximum value of 2 TUc.

If data from accelerated monitoring tests are found to be in compliance with the evaluation parameters, then routine monitoring shall be resumed. However, if a second toxicity test continues to exceed either evaluation parameter, then the permittee shall immediately cease discharge and submit an evaluation to the

Executive Officer on the cause of the toxicity, alternate disposal methods, or treatment system modifications that are proposed to correct the effluent toxicity.

- f) Methodology: Sample collection, handling and preservation shall be done in accordance with EPA protocols. The test methodology used shall be in accordance with the references cited in this Order, or as approved by the Executive Officer. A concurrent reference toxicant test shall be performed for each test.
- g) Dilution Series: The permittee shall conduct tests at 100%, 85%, 70%, 50%, and 25%. The “%” represents percent effluent as discharged. Dilution and control waters shall be obtained from an area unaffected by the discharge in the receiving waters. Standard dilution water may be used if the above sources exhibit toxicity or if approved by the Executive Officer.

4. Chronic Toxicity Reporting Requirements

- a) Routine Reporting: Toxicity test results for the reporting period shall include, at a minimum, for each test:
 - i. Sample date(s)
 - ii. Test initiation date
 - iii. Test specie(s)
 - iv. End point values for each dilution (e.g. number of young, growth rate, percent survival)
 - v. NOEC value(s) in percent effluent
 - vi. IC₁₅, IC₂₅, IC₄₀, and IC₅₀ values (or EC₁₅, EC₂₅...etc.) in percent effluent
 - vii. TUC values (100/NOEC, 100/IC₂₅, and 100/EC₂₅)
 - viii. Mean percent mortality (\pm standard deviation) after 96 hours in 100% effluent (if applicable)
 - ix. NOEC and LOEC values for reference toxicant test(s)
 - x. IC₅₀ or EC₅₀ value(s) for reference toxicant test(s)
 - xi. Available water quality measurements for each test (e.g. pH, dissolved oxygen, temperature, conductivity, hardness (as CaCO₃), salinity, ammonia)
- b) Compliance Summary: The results of the chronic toxicity testing shall be provided in the most recent self-monitoring report and shall include a table of chronic toxicity data from at least eleven of the most recent samples. The information in the table shall include the items listed above under 4.a, item numbers i, iii, v, vi (IC₂₅ or EC₂₅), vii, and viii.
- c) After at least four (4) test rounds, the permittee may request the Executive Officer to decrease the required number of test species to one. Such a request may be considered only if toxicity exceeding the TUC values specified in the effluent limitations was never observed using that test specie.

D. DEFINITION OF TERMS

1. Three-sample median: A test sample showing chronic toxicity greater than 1 TU_c represents an exceedance of this parameter, if one of the past two tests also show chronic toxicity greater than 1 TU_c .
2. TU_c (chronic toxicity unit): A TU_c equals $100/NOEL$ (e.g., If $NOEL = 100$, then toxicity = 1 TU_c). $NOEL$ is the maximum percent test water that causes no observable effects on a test organism.
3. No observed effect level (NOEL) for compliance determination is equal to IC_{25} or EC_{25} . If the IC_{25} or EC_{25} cannot be statistically determined, the $NOEL$ shall be equal to the $NOEC$ derived using hypothesis testing.
4. Effective concentration (EC) is a point estimate of the toxicant concentration that would cause an adverse effect on a quantal, "all or nothing," response (such as death, immobilization, or serious incapacitation) in a given percent of the test organisms. If the effect is death or immobility, the term lethal concentration (LC) may be used. EC values may be calculated using point estimation techniques such as probit, logit, and Spearman-Kärber. EC_{25} is the concentration of toxicant (in percent effluent) that causes a response in 25% of the test organisms.
5. Inhibition Concentration (IC) is a point estimate of the toxicant concentration that would cause a given percent reduction in a non-lethal, non-quantal biological measurement, such as growth. For example, an IC_{25} is the estimated concentration of toxicant that would cause a 25% reduction in average young per female or growth. IC values may be calculated using a linear interpolation method such as EPA's Bootstrap Procedure.
6. No observed effect concentration (NOEC) is the highest tested concentration of an effluent or a toxicant at which no adverse effects are observed on the aquatic test organisms at a specific time of observation. It is determined using hypothesis testing.

TABLE 1
Short-term Methods for Estimating Chronic Toxicity- Saltwater¹

<u>Species</u>	<u>Scientific Name</u>	<u>Effect</u>	<u>Tier²</u>	<u>Reference</u>
giant kelp	<i>Macrocystis pyrifera</i>	percent germination; germ tube length	1	1, 3
red abalone	<i>Haliotis rufescens</i>	abnormal shell development	1	1, 3
oyster	<i>Crassostrea gigas</i>	abnormal shell development; percent survival	1	1, 3
mussels	<i>Mytilus spp.</i>	abnormal shell development; percent survival	1	1, 3
urchin sand dollar	<i>Strongylocentrotus purpuratus</i> <i>Dendraster excentricus</i>	percent normal development	1	1, 3
urchin sand dollar	<i>Strongylocentrotus purpuratus</i> <i>Dendraster excentricus</i>	percent fertilization	1	1, 3
shrimp	<i>Holmesimysis costata</i>	percent survival; growth	1	1, 3
shrimp	<i>Mysidopsis bahia</i>	percent survival; growth; fecundity	2	2, 4
topsmelt	<i>Antherinops affinis</i>	larval growth rate; percent survival	1	1, 3
silversides	<i>Menidia beryllina</i>	larval growth rate; percent survival	2	2, 4

Toxicity Test References:

1. Chapman, G.A., D.L. Denton, and J.M. Lazorchak. 1995. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. U.S. EPA Report No. EPA/600/R-95/136.
2. Klemm, D.J., G.E. Morrison, T.J. Norberg-King, W.J. Peltier, and M.A. Heber. 1994. Short-term methods for estimating the chronic toxicity of effluents and receiving water to marine and estuarine organisms. U.S. EPA Report No. EPA-600-4-91-003.
3. SWRCB 1996. Procedures Manual for Conducting Toxicity Tests Developed by the Marine Bioassay Project. 96-1WQ.
4. Weber, C.I., W.B. Horning, I.I., D.J. Klemm, T.W. Nieheisel, P.A. Lewis, E.L. Robinson, J. Menkedick and F. Kessler (eds). 1988. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. EPA/600/4-87/028. National Information Service, Springfield, VA.

¹ For waters in which the salinity is equal to or greater than 10 parts per thousand 95% or more of the time, the applicable criteria are the saltwater criteria in the CTR.

² The first tier test methods are the preferred toxicity tests for compliance monitoring. The Executive Officer may approve the use of a second tier test method for waste discharges if first tier organisms are not available.

TABLE 2
Short-term Methods for Estimating Chronic Toxicity – Fresh Water³

<u>Species</u>	<u>Scientific Name</u>	<u>Effect</u>	<u>Test Duration</u>	<u>Reference</u>
fathead minnow	<i>Pimephales promelas</i>	larval survival; growth	7 days	5
water flea	<i>Ceriodaphnia dubia</i>	survival; number of young	6 to 8 days	5
alga	<i>Selenastrum capricornutum</i>	growth rate	4 days	5

Toxicity Test Reference:

5. U.S. EPA. 1994. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. Third edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio. EPA/600/4-91-00
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³ For waters in which the salinity is equal to or less than 1 part per thousand 95% or more of the time, the applicable criteria are the freshwater criteria in the CTR. For waters in which the salinity is between 1 and 10 parts per thousand, the applicable criteria are the more stringent of the freshwater or saltwater criteria. In this case, the species chosen for compliance with the chronic toxicity control provision shall be based on the biology of the receiving water.

E. Dioxin/Furan Study of the Effluent

The Policy for Implementation of Toxics Standards for Inland Surface Water, Enclosed Bays, and Estuaries of California includes criteria for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). In addition to this compound, there are many congeners (a compound of the same class or kind) of chlorinated dibenzodioxins (2,3,7,8-CDDs) and chlorinated dibenzofurans (2,3,7,8-CDFs) that exhibit toxic effects similar to those of 2,3,7,8-TCDD. The US EPA has published toxic equivalency factors (TEFs) for 17 of the congeners. The TEFs express the relative toxicities of the congeners compared to 2,3,7,8-TCDD (whose TEF is 1.0). The current TEFs for the 17 congeners are shown in the following table.

Congener ^a	Chemical Abstract Service (CAS) Number	TEF ^b
2,3,7,8-TetraCDD	1746-01-6	1.0
1,2,3,7,8-PentaCDD	40321-76-4	1.0
1,2,3,4,7,8-HexaCDD	39227-28-6	0.1
1,2,3,6,7,8-HexaCDD	57653-85-7	0.1
1,2,3,7,8,9-HexaCDD	19408-74-3	0.1
1,2,3,4,6,7,8-HeptaCDD	35822-39-4	0.01
OctaCDD	3268-87-9	0.0001
2,3,7,8-TetraCDF	51207-31-9	0.1
1,2,3,7,8-PentaCDF	57117-41-6	0.05
2,3,4,7,8-PentaCDF	57117-31-4	0.5
1,2,3,4,7,8-HexaCDF	70648-26-9	0.1
1,2,3,6,7,8-HexaCDF	57117-44-9	0.1
1,2,3,7,8,9-HexaCDF	72918-21-9	0.1
2,3,4,6,7,8-HexaCDF	70648-26-9	0.1
1,2,3,4,6,7,8-HeptaCDF	70648-26-9	0.01
1,2,3,4,7,8,9-HeptaCDF	55673-89-7	0.01
OctaCDF	39001-02-0	0.0001

Reference: "Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California", March 2, 2000. Page 27.

- a. It is recommended that all listed CDD and CDF congeners be quantified using EPA method 8280A or 8290.
- b. TEF = Toxicity Equivalency Factor

The permittee must monitor the effluent for the presence of the 17 congeners once during the dry weather and once during wet weather for one year. Following the initial screening submitted with the report of waste discharge, one (1) additional dioxin/furan congener study must be conducted during the next season. For example, if a dry weather study is submitted with the report of waste discharge, a wet weather study must be submitted during the following wet weather season (or vice versa).

The permittee shall submit the analytical results of the effluent monitoring, including the quantifiable limit and the method detection limit, and the measured or estimated concentrations.

In addition, the permittee shall multiply each measured or estimated congener concentration by its respective TEF value (presented in the table above) and report the sum of these values. Based on the monitoring results, the Executive Officer may increase the monitoring requirement to further investigate frequent or significant detections of any congener, as deemed necessary.

F. Reporting

Monitoring reports shall be submitted to the Regional Water Board monthly. These reports are due by the 15th day of following month. All analytical data shall be submitted in clear, concise tables and shall also be included in an electronic format that is compatible with MS Access or MS Excel.

Ordered by _____

Lee A. Michlin
Executive Officer

January 26, 2001

(M&R Pro1)

(*Number will be assigned after adoption)