CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD LOS ANGELES REGION

ORDER NO. R4-2004-0110

WASTE DISCHARGE REQUIREMENTS FOR CONOCOPHILLIPS COMPANY 76 STATION NO. 6965 (OZONE INJECTION FOR GROUNDWATER CLEANUP) (FILE NO. 908080170, CUFID # 13344)

The California Regional Water Quality Control Board, Los Angeles Region, (hereafter Regional Board) finds that:

PURPOSE OF ORDER

1. The ConocoPhillips Company (hereafter Discharger) owns the 76 Station No. 6965 (Station) located at 3014 N. Studebaker Road, Long Beach, California (site) (Figure 1). On April 8, 2003, the Discharger filed with the Regional Board a Report of Waste Discharge for the injection of gaseous ozone/air mixture (ozone sparging) to remediate the petroleum hydrocarbon contaminated groundwater in the shallow aquifer at the site.

FACILITY DESCRIPTION

2. The Station is an active retail motor vehicle fuel service station consisting of two underground storage tanks (USTs) containing gasoline, one UST containing diesel, three dispenser islands, associated product distribution piping, and a station building. The in-place USTs are located in the same general locations as four 12,000 gallon USTs removed from the site in 1994. The area surrounding the Station includes a mixture of commercial and residential uses.

ASSESSMENT HISTORY

- 3. In a report prepared on behalf of the Discharger by SECOR International, Inc., dated November 15, 2001, the following assessment history information was reported.
- 4. In June 1994, four 12,000-gallon USTs, dispensers, and associated product piping were removed from the site. The USTs were reported as formerly containing gasoline and diesel. Soil samples were collected from the site. Total petroleum hydrocarbons as gasoline (TPH_G) concentrations in soil samples collected from the limits of the excavation ranged from 1.1 to 1,000 milligrams per kilogram (mg/kg), total petroleum hydrocarbons as diesel (TPH_D) concentrations ranged from below laboratory detection limits to 760 mg/kg, and benzene concentrations ranged from below laboratory detection limits to 4.4 mg/kg. All excavated material was transported offsite for disposal (Bechtel Environmental, Inc., 1994).

- 5. In September 1995, Tait Environmental Management (TEM) conducted additional assessment activities at the site. A total of ten soil borings were advanced around the perimeter of the dispenser islands and USTs to depths ranging from 20 to 35 feet below grade (fbg). Detectable concentrations of TPH_G and benzene were reported in soil samples collected from the vicinity of the USTs and northern dispenser island. TPH_D was not detected in any soil samples analyzed. Three of the soil borings were completed as nested monitoring wells screened within the vadose and saturated zones. The nested monitoring wells were screened from 3 to 18 fbg and from 25 to 35 fbg. Additionally, one soil boring (B-5) was completed as a vadose monitoring well screened from 3 to 17 fbg. Groundwater beneath the site was encountered during drilling at approximately 26 fbg, however the piezometric pressure elevated the static water level in the monitoring wells to approximately 17 fbg. Dissolved concentrations of TPH_G and benzene were detected as high as 5,200 micrograms per liter (ug/L) and 1,600 ug/L, respectively, in monitoring well B-1. TPH_D was not detected in groundwater (TEM, 1995).
- 6. No phase-separated hydrocarbon was observed in any of the groundwater monitoring wells. Dissolved benzene concentrations in groundwater samples ranged from below laboratory detection limits to 930 ug/L, dissolved MTBE concentrations ranged from below laboratory detection limits to 1,100 ug/L and dissolved TPH_G concentrations ranged from below laboratory detection limits to 6,600 ug/L (SECOR, 2001).

REMEDIATION ACTIVITIES

- 7. Initial cleanup activities began at the site in June 1994 when four 12,000 gallon USTs were removed. Approximately 700 tons of petroleum hydrocarbon contaminated soil were also removed from the site. Soil and assessment activities continued into May 2001, when the Regional Board approved the initial Interim Remedial Action Plan (IRAP) which proposed pilot testing for soil vapor extraction.
- 8. In November 2001, the Discharger submitted a revised IRAP proposing the use of high-vacuum dual phase extraction technologies (HVDPE) to improve remediation. Regional Board staff approved the revised IRAP in correspondence dated January 18, 2002. In July, 2002, the Discharger submitted a second revised IRAP which proposed HVDPE to remediate soil contamination and ozone sparging to remediate groundwater contamination. The Regional Board approved the July 2002 IRAP in correspondence dated November 15, 2002. In correspondence dated November 6, 2003, the Regional Board acknowledged the Discharger's request to change soil and groundwater remediation methodology from HVDPE to soil vapor extraction (SVE). The Discharger expects to initiate the operation of the SVE system by May 2005.

SITE GEOLOGY

- 9. The site is located approximately one-half mile west of the San Gabriel River and approximately 4 miles north of the Pacific Ocean. The site is located within the Dominguez Gap area of the Coastal Plain.
- 10. Based on previous investigations conducted at the site, the site is generally underlain by silts and silty sands to approximately 15 fbg, clayey-silt to silty-clay from approximately 15 to 25 fbg, and silty-sands to sands from approximately 25 to 35 fbg, the maximum depth explored (SECOR, April, 2002).

SITE HYDROGEOLOGY

- 11. The site is situated in the City of Long Beach at the southern boundary of the Central Basin of the Los Angeles Coastal Plain. The Central Basin has been divided into the Los Angeles Forebay, the Montebello Forebay, the La Brea subarea, and the Central Basin Pressure Area. The site is located within the Central Basin Pressure Area where groundwater used for municipal supply is under confined conditions. The Central Basin Pressure Area also has locally occurring perched or semi-perched water-bearing zones (Miller Brooks Environmental, Inc., July 2002). The groundwater cleanup operations proposed are for the plume in the local shallow groundwater zone.
- 12. Two production wells have been identified within one-half mile of the site. The nearest production wells, Wise 1A and Annex 201, are located about 500 feet southeast and 1,500 feet southwest of the site, respectively. These wells are reportedly owned and operated by the City of Long Beach Water Department and are used for drinking water production. Well Wise 1A is screened in water bearing zones located approximately 272-400 fbg and 403-1,078 fbg. Well Annex 201 is screened in multiple water bearing zones located from 507 fbg to 838 fbg (SECOR, April, 2002). Neither of the production wells are perforated in the shallow groundwater zone beneath the site.
- 13. Based on depth-to-groundwater measurements recorded on October 9, 2001, (SECOR, 2001), depth-to-groundwater ranged from approximately 16.40 to 18.30 fbg and groundwater is interpreted to be flowing toward the south-southeast with an approximate gradient of 0.0012 (feet/foot). Groundwater elevations have fluctuated between historic low and high elevations of approximately 4 and 10 feet above mean sea level, respectively (Miller Brooks Environmental, Inc., July 2002).

DESCRIPTION OF OZONE SPARGING SYSTEM

14. On July 15, 2002, Miller Brooks Environmental, Inc., on behalf of the Discharger, submitted an Updated Site Conceptual Model to the Regional Board proposing ozone sparging (injection of ozone to groundwater) by the use of a C-Sparge™

system (System) to remediate the dissolved-phase petroleum hydrocarbon plume beneath the site. The Regional Board approved the proposal in correspondence dated November 15, 2002.

- 15. The System consists of a control panel (which houses an ozone generator and a small compressor), the underground conveyance piping, and the sparge wells. The ozone generator consists of a corona discharge tube which ionizes di-atomic oxygen into ozone. The System can generate 3 to 6 standard cubic feet per minute (SCFM) of an ozone/air mixture at a maximum pressure of approximately 60 pounds per square inch (psi). The concentration of ozone in the system's output flow is adjustable from 100 to 300 parts per million by volume (ppmv) based on the concentration of oxygen input. The encapsulated ozone microbubbles sparged below the water table by the System are only 10 to 50 micrometers (μm) in diameter.
- 16. Four sparge point locations are proposed at this time for the operation of the System (Figure G01). There will be dual nested sparge well-points for each location. The shallow sparge well-point will be perforated along a depth of 23 feet to 25 fbg. The deeper sparge well-point will be perforated along a depth of 33 feet to 35 fbg.
- 17. Sparging will be performed on a cycled basis with each well cycled on for 5 to 15 minutes. Per manufacturer specifications, the System will inject approximately five grams per hour of ozone at a flow rate of 3 to 6 SCFM. The concentration of ozone injected into the subsurface during system operations will be approximately 0.59 milligrams per liter (mg/L)
- 18. During sparging, no other known constituents will be discharged to the subsurface during system operations.
- 19. Ozone will chemically react with hydrocarbons in the immediate vicinity of each injection point to form intermediate by-products of various smaller chain hydrocarbons and oxygenates. The following table shows the laboratory-isolated breakdown by-products that could be produced during the ozone oxidation process with the hydrocarbons:

Constituent	Breakdown Products		
TPH	acetate, butyrate, formate, propionate		
BTEX	Carboxylic acids		
MTBE	TBA (tertiary butyl alcohol), TBF (tertiary butyl formate), formate, oxygen, hydrogen peroxide		
ETBE	TBA, TBF, acetate, oxygen, hydrogen peroxide		
TBA	Formaldehyde, acetate, carbon dioxide, water		

Finally, the residual oxygen formed from the initial ozone reduction reaction encourages bioremediation which consumes the listed by-products and converts them to carbon dioxide and water, thereby completing the remediation process.

20. Ozone is toxic to life forms at high concentrations and can be corrosive to underground structures and piping conveyance systems. Therefore, these concerns must be addressed for any proposed ozone sparging system to insure that the operation will preclude fugitive emissions that could represent a health risk or a corrosion risk.

The System is designed to match the ozone supplied with the demand requirements of the contaminant. Furthermore, ozone has an expected half-life of only 20 minutes and reacts quickly with contaminants. Consequently, ozone would be expended quickly and would not be expected to migrate significantly downgradient or into the vadose zone.

- 21. Ozone sparging results in a low-exothermic reaction that involves no explosive risk. It has been reported that the process has been successfully and safely used in remediation efforts in over 32 states and in 22 counties in the state of California.
- 22. In locations where groundwater has excessive levels of tri-valent chromium or brominated hydrocarbons, an evaluation should be made to insure that toxic levels of hexavalent chromium or bromides/bromate compounds are not created. In this site, there are no known problems with tri-valent chromium or brominated hydrocarbons.
- 23. The permeabilities associated with the soils in the groundwater zones proposed for ozone sparging are estimated to be 10⁻⁶ centimeters per second or greater. This represents an optimal range for the success of the ozone perfusion process.
- 24. Prior to initiating the C-Sparge™ technology, groundwater samples will be collected from monitoring wells B-2, MW-10, MW-11, MW-13, and MW-14 for baseline measurements of depth to groundwater, TPH_G, benzene, toluene, ethylbenzene, xylenes, MTBE, TBA, tertiary amyl methyl ether (TAME), diisopropyl ether (DIPE), ethyl tertiary butyl ether (ETBE), ethanol, dissolved oxygen, and dissolved ferrous iron. These measurements/samples will also be collected bi-weekly during the first month of system operation. Data collected during the first month of system operation will be used to evaluate the C-Sparge™ effectiveness at this site.

APPLICABLE LAWS, PLANS, POLICIES AND REGULATIONS

25. On June 13, 1994, the Regional Board adopted a revised *Water Quality Control Plan for Coastal Watersheds of Los Angeles and Ventura Counties* (Basin Plan) which was amended on January 27, 1997 by Regional Board Resolution No. 97-02. The Basin Plan (i) designates beneficial uses for surface waters and groundwater, (ii) sets narrative and numerical objectives that must be attained or

maintained to protect the designated beneficial uses and conform to the State antidegradation policy (*Statement of Policy with Respect to Maintaining High Quality Waters in California*, State Water Resources Control Board (State Board) Resolution No. 68-16, October 28, 1968), and (iii) describes implementation programs to protect all waters in the Region. In addition, the Basin Plan incorporates by reference applicable State and Regional Board plans and policies and other pertinent water quality policies and regulations. The Regional Board prepared the 1994 update of the Basin Plan to be consistent with previously adopted State and Regional Board plans and policies. This Order implements the plans, policies and provisions of the Regional Board's Basin Plan.

26. The Basin Plan designates beneficial uses and water quality objectives for groundwater within the Central Groundwater Basin which underlies the Station as follows:

Existing: municipal and domestic supply; industrial service supply; industrial process supply; and agricultural supply.

- 27. The requirements contained in this Order are based on the *Basin Plan*, and, as they are met, will be in conformance with the goals of the aforementioned water quality control plans and will protect and maintain existing beneficial uses of the groundwater.
- 28. The permitted discharge is consistent with the anti-degradation provisions of State Board Resolution No. 68-16 (Anti-degradation Policy). The discharge may result in some localized temporary exceedance of background concentrations of dissolved oxygen, dissolved ferrous iron, total dissolved solids, sulfate, chloride, and boron. However, any parameter change resulting from the discharge:
 - a. will be consistent with maximum benefit to the people of the State,
 - b. will not unreasonably affect present and anticipated beneficial uses of such waters, and
 - c. will not result in water quality less than that prescribed in the Water Quality Control Plan for the Central Groundwater Basin.
- 29. This Regional Board has assumed lead-agency role for this project under the California Environmental Quality Act (CEQA) (Public Resources Code section 21000 et seq.) and has conducted an Initial Study in accordance with section 15063 of the "State CEQA Guidelines" at California Code of Regulations, title 14, section 15000 et seq. Based upon the Initial Study, the Regional Board staff prepared a Mitigated Negative Declaration that the project, as mitigated, will not have a significant adverse effect on the environment. The Regional Board is adopting the Mitigated Negative Declaration concurrently with its adoption of this Order.
- 30. The Regional Board has notified the Discharger and interested agencies and persons of its intent to prescribe Waste Discharge Requirements for this discharge and has provided them with an opportunity to submit their written views and recommendations. The Regional Board, in a public meeting, heard

and considered all comments pertaining to the discharge and to the tentative requirements.

IT IS HEREBY ORDERED that the Discharger, ConocoPhillips Company, in order to meet the provisions contained in Division 7 of the California Water Code and regulations and guidelines adopted thereunder, shall comply with the following:

A. Discharge Injection Specifications

- 1. The sparging discharge (injection) of ozone into the groundwater shall be performed only in accordance with the C-SpargeTM system operations described in the July 15, 2002, Updated Report prepared by Miller Brooks Environmental, Inc., on behalf of the Discharger and which is incorporated herein by reference.
- 2. The Discharger shall provide hydraulic controls, if required by the Regional Board Executive Officer (Executive Officer), that provide full and complete containment of any released materials or by-products of chemical processes for the duration of the C-SpargeTM system operations.
- 3. During the C-SpargeTM system operations, the discharge volume of ozone shall be approximately five grams per hour of ozone at a flow rate of 3 to 6 cubic foot per minute (cfm). In the event that additional ozone discharge is needed or additional injection locations are needed, written approval by the Executive Officer shall be obtained before such discharge is carried out.

B. Discharge Injection Prohibitions

- 1. The Discharger shall not allow excessive by-products of the chemical reduction process to migrate beyond the plume.
- 2. The Discharger shall not cause the groundwater outside of the remediation area plume to exceed the background concentrations of total dissolved solids, sulfate, chloride, and boron as established prior to the start of the C-SpargeTM system operations.
- 3. The discharge of ozone or any by-products into any surface water or surface water drainage course is prohibited.
- 4. The Discharger shall not cause the groundwater to contain taste, color, or odor producing substances in concentrations that cause nuisance or adversely affect beneficial uses outside the treatment area.
- 5. The Discharger shall not cause the groundwater to contain concentrations of chemical constituents, including ozone and its by-products, in amounts that may adversely affect municipal, domestic, industrial or agricultural uses.

C. Provisions

- 1. This Order includes the attached Monitoring and Reporting Program No. Cl-8773 which is incorporated herein by reference. If there is any conflict between provisions stated in the Monitoring and Reporting Program No. Cl-8773 and the Standard Provisions, those provisions stated in the Monitoring and Reporting Program prevail.
- 2. A copy of this Order shall be maintained at an on-site office and be available at all times to operating personnel.
- 3. In the event of any change in name, ownership, or control of this site, the Discharger shall notify the Regional Board in writing and shall notify any succeeding owner or operator of the existence of this Order by letter, a copy of which shall be forwarded to the Regional Board.
- 4. The Discharger shall file with the Regional Board technical reports on self-monitoring work performed according to the detailed specifications contained in Monitoring and Reporting Program No. CI-8773 as directed by the Executive Officer. The results of any monitoring done more frequently than required at the site and/or times specified in the Monitoring and Reporting Program shall also be reported to the Regional Board.
- 5. In accordance with section 13260(c) of the California Water Code, the Discharger shall file a report of any material change or proposed change in the character, location, or volume of the discharge.
- 6. Discharge to any point other than specifically described in this Order, or as approved by the Executive Officer, is prohibited and constitutes a violation thereof.
- 7. This Order includes the attached Standard Provisions Applicable to Waste Discharge Requirements which are incorporated herein by reference. If there is any conflict between provisions stated herein and the Standard Provisions Applicable to Waste Discharge Requirements, the provisions stated herein will prevail.
- 8. The Discharger shall notify Regional Board staff by telephone within 24 hours, followed by written notification within one week, in the event it is unable to comply with any of the conditions of this Order due to:
 - a) Breakdown of equipment;
 - b) Accident caused by human error or negligence, or other causes such as acts of nature: and
 - c) Site construction or development operations.

- 9. The Regional Board considers the Discharger to have continuing responsibility for correcting any problem that may arise in the future as a result of this discharge.
- 10. The Discharger shall submit quarterly Summary Reports detailing the results of the C-SpargeTM system operations. The report should include an evaluation of the effectiveness of using ozone to remediate petroleum hydrocarbons-impacted groundwater at the site, the impact of any byproducts on the receiving groundwater quality, and any other effects the insitu treatment may have caused.
- 11. All work must be performed by or under the direction of a California registered civil engineer, registered geologist, or certified engineering geologist, as provided in sections 6762, 7850, and 7842, respectively, of the California Business and Professions Code. A statement is required in all technical submittals that the registered professional in direct responsible charge actually supervised or personally conducted all the work associated with the project.
- 12. The application of ozone to groundwater may result in unintended adverse impacts to groundwater quality. Any potential adverse water quality impacts that may result shall be localized and short-term duration, and shall not impact any existing or prospective uses of groundwater. Groundwater quality shall be monitored before addition of ozone, during treatment, and after treatment is completed to verify no long-term adverse impact to water quality.
- 13. The Discharger shall cleanup and abate the effects of injecting ozone, including extraction of any by-products which adversely affect beneficial uses, and shall provide an alternate water supply source for municipal, domestic or other water use wells that become contaminated in exceedance of water quality objectives as a result of using ozone.
- 14. These requirements do not exempt the Discharger from compliance with any other laws, regulations, or ordinances which may be applicable. They do not legalize the waste treatment facility, and they leave unaffected any further restraints on the site that may be contained in other statutes and/or required by other agencies.
- 15. This Order does not relieve the Discharger from responsibility to obtain other necessary local, state, and federal permits to construct facilities necessary for compliance with this Order; nor does this Order prevent imposition of additional standards, requirements, or conditions by any other regulatory agency.
- 16. The Discharger shall furnish, within a reasonable time, any information the Regional Board may request to determine whether cause exists for modifying, revoking and reissuing, or terminating this Order. The

Discharger shall also furnish to the Regional Board, upon request, copies of records required to be kept by this Order.

- 17. After notice and opportunity for a hearing, this Order may be terminated or modified for cause including, but not limited to:
 - a) Violation of any term or condition contained in this Order;
 - b) Obtaining this Order by misrepresentation, or failure to disclose all relevant facts;
 - c) A change in any condition that requires either a temporary or permanent reduction or elimination of authorized discharge.
- 18. In accordance with California Water Code section 13263(g), these requirements shall not create a vested right to continue to discharge and are subject to rescission or modification. All discharges of waste into the waters of the State are privileges, not rights.
- 19. The Discharger shall allow the Regional Board, or an authorized representative upon the presentation of credentials and other documents as may be required by law, to:
 - (a) Enter upon the Discharger's premises where a regulated facility or activity is located or conducted, or where records must be kept under the conditions of this Order:
 - (b) Have access to and copy, at reasonable times, any records that must be kept under the conditions of this Order;
 - (c) Inspect at reasonable times any facilities, equipment (including monitoring and control equipment), practices, or operations regulated or required under this Order: and
 - (d) Sample or monitor at reasonable times, for the purposes of assuring compliance with this Order, or as otherwise authorized by the California Water Code, any substances or parameters at any location. [CWC section 13267]

File No. 908080170

D. Expiration Date:

This Order expires on June 4, 2009.

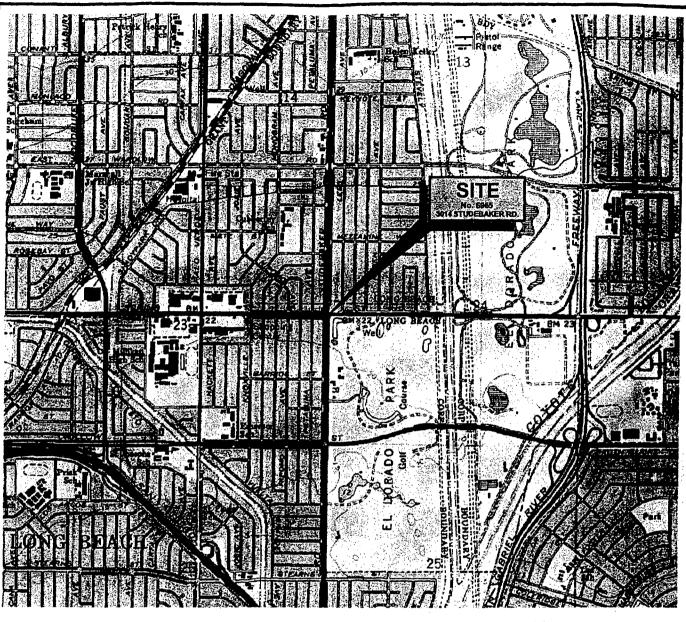
The Discharger must file a Report of Waste Discharge in accordance with sections 13260 and 13264 of the California Water Code not later than 180 days in advance of such date as application for issuance of new waste discharge requirements.

I, Jonathan Bishop, Interim Executive Officer, do hereby certify that the foregoing is a full, true, and correct copy of an Order adopted by the California Regional Water Quality Control Board, Los Angeles Region, on July 1, 2004.

Jonathan Bishop

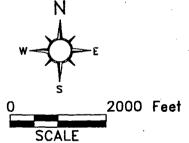
Interim Executive Officer

/GS



FROM: U.S. GEOLOGICAL SURVEY, 1981 QUADRANGLE: LONG BEACH COUNTY: LOS ANGELES SERIES: 7.5-MINUTE QUAD

NOTE: ALL BOUNDARIES AND LOCATIONS ARE APPROXIMATE



MILLER BROOKS Environmental, Inc.	DATE: 01/22/01 REVISED BY: AIL	SITE LOCATION MAP	FIGURE
2124 MAIN STREET, SUITE 200 HUNTINGTON BEACH, CA. 92648 (714) 960–4088	REVISED: 01/16/03 APPROVED BY: DES	76 STATION 6965 3014 STUDEBAKER ROAD LONG BEACH, CA.	
PROJECT NO. 01-495-6965	DATE: 01/16/03	FILE: K:\DWGS\C-P\LB .(3014 STUDEBAKER RD.)\VICI DATE PLC	NITY MAP OTTED: 01/16/03

