CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD LOS ANGELES REGION

ORDER NO. R4-2004-0180

WASTE DISCHARGE REQUIREMENTS FOR CONOCOPHILLIPS COMPANY 76 STATION NO. 6923 (OZONE INJECTION FOR GROUNDWATER CLEANUP) (FILE NO. 04-133)

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

PURPOSE OF ORDER

- The ConocoPhillips Company (hereafter Discharger) owns the 76 Station No. 6923 (hereinafter Site) located at 2383 Sycamore Drive, Simi Valley, California (Figure 1). The Site, an active 76 Service Station, is located at the southwest corner of the intersection of Sycamore Drive and Cochran Streets in Simi Valley at latitude 34⁰16'42" and longitude 118⁰44'35".
- 2. On September 25, 2003, the Discharger filed a Report of Waste Discharge for injecting gaseous ozone into the shallow aquifer to remediate contaminated groundwater at the Site.

FACILITY DESCRIPTION

- 3. Unocal operated the Site until 1997 when the ownership was transferred to Tosco. ConocoPhillips acquired Tosco in 2001 and has been operating the Site as a retail motor vehicle fuel service station. Currently, there are two 12,000-gallon gasoline underground storage tanks (USTs), one 10,000-gallon diesel UST, three fuel dispenser islands, and a station kiosk building at the Site.
- 4. Petroleum hydrocarbon contaminated soil was first detected at the Site in 1990 in conjunction with UST removal activities. Maximum concentrations of 7,000 milligrams per kilograms (mg/kg) total petroleum hydrocarbons as gasoline (TPH_G) and 51 mg/kg benzene were detected in the soil samples collected under each of the three gasoline USTs. Petroleum hydrocarbon contaminated soil was also identified adjacent to the central dispenser island at concentrations of 22 mg/kg as TPH_G, 6,700 mg/kg total petroleum hydrocarbons as diesel (TPH_D) and 0.08 mg/kg of benzene. Based on these findings, approximately 360 cubic yards of contaminated soil were removed from the Site.
- 5. Subsequent onsite and offsite assessment activities have resulted in the installation of seventeen groundwater monitoring wells (MW-1 through MW-17), three soil vapor extraction (SVE) wells (B-3 through B-5), and two nested air sparge (AS) wells (AS/SVE-1 and AS/SVE-2) (Figure 2). In the wells installed adjacent to the southern dispenser island and to the northwest of the former gasoline USTs, maximum concentrations of 4,400 mg/kg TPH_G, 20 mg/kg

benzene, and 3.7 mg/kg methyl tertiary butyl ether (MTBE) were detected in the soil.

- 6. In June 1997, a soil vapor extraction (SVE) pilot test was conducted at the site. TPH_G concentrations reported in soil vapor samples collected at the beginning and end of the SVE test were 7,100 parts per million by volume (ppmv) and 8,100 ppmv, respectively. In addition, a radius of influence (ROI) of approximately 38 feet was estimated based on the test results.
- 7. In September and October 2002, additional site assessments were conducted including the installation of two clustered wells (SVE-4S and SVE-4D) and the abandonment and replacement of well B-3 with new well SVE-3 (Figure 2A). Results of the investigation indicated that detectable concentrations of petroleum hydrocarbon were present in soil beneath the site in depths ranging from 41 feet to 120.5 feet below ground surface (bgs).
- 8. Results of the monitoring and sampling event conducted at the Site during the second quarter of 2003 indicated that dissolved-phase petroleum hydrocarbons extend offsite to the west. Maximum dissolved-phase petroleum hydrocarbon concentrations of 190,000 micrograms per liter (μ g/L) of TPH_G, 32,000 μ g/L benzene and 44,000 μ g/L MTBE were reported in groundwater samples collected from well AS/SVE-2. An earlier sampling event also showed the same contaminants present in SVE-4D.
- 9. Based on an evaluation of current site conditions and the results of SVE pilot testing activities, the Discharger proposed to remediate the petroleum hydrocarbon contaminated soil within the vadose zone and capillary fringe using SVE and the dissolved-phase petroleum hydrocarbon impacted groundwater using C-Sparge[™] technology.

SITE HYDROGEOLOGY

- 10. The Site is located within the Simi Valley Groundwater Basin. Two active municipal water supply wells are located within one-half mile of the site according to the records of Southern California Water Company (SCWC). The first well, known as Sycamore Well #3, is located approximately 1,056 feet south of the site and the second well, known as Niles Well is located approximately 1,584 feet south of the site. Groundwater quality in the Simi Valley Groundwater Basin is generally poor due to high concentrations of total dissolved solids. Based on historic groundwater data, the groundwater flow direction observed beneath the site has been to the west-southwest making the SCWC production wells appear to be located cross-gradient to the Site. The groundwater gradient at the site does not appear to be influenced by groundwater production from the SCWC wells.
- 11. Depth to groundwater at the Site, measured during the groundwater sampling event for the fourth quarter of 2002, ranged from 71.92 feet to 80.5 feet below ground surface (bgs). Groundwater flow direction was to the west with a hydraulic gradient of approximately 0.004 foot per foot (ft/ft).

REMEDIATION DESCRIPTION

- 12. On August 29, 2003, the Discharger submitted to the Ventura County Environmental Health Division (VCEHD) a revised Remedial Action Plan (RAP) proposing to use C-Sparge[™] ozone injection technology to remediate the dissolved-phase petroleum hydrocarbon plume beneath the site. The revised RAP was approved on November 25, 2003.
- 13. Because of the sustained presence of elevated dissolved phase hydrocarbons in the monitoring wells located northwest of the former USTs and in the adjacent property, soil and groundwater remediation were considered for the site. SVE/high vacuum dual-phase extraction and ozone sparging using the C-Sparge[™] system were chosen as the cost-effective and feasible technologies to remediate the petroleum hydrocarbon-affected soil and groundwater beneath the site. The SVE system will utilize vertical extraction wells and lateral subsurface conveyance piping to transport petroleum hydrocarbon-affected soil vapor to a thermal/catalytic oxidizer for treatment.
- 14. The C-Sparge[™] system will utilize five sparge wells (CS-1 through CS-5), installed onsite within the dissolved-phase plume (Figure 3). The C-Sparge™ technology combines low-flow [3 to 5 cubic feet per minute (cfm)] air sparging with ozonation to oxidize petroleum hydrocarbons into benign byproducts, carbon dioxide and water. Ozone is generated onsite using a control panel with a builtin compressor and ozone generator. Using perforated sparge points, microbubbles [10 to 50 micrometer (µm)] of encapsulated ozone are introduced below the water table, where the oxidation reactions take place. Five C-Sparge points will be installed onsite within and around the dissolved-phase plume, where highest concentrations of dissolved-phase benzene and TPH_G are detected, and down gradient from the former USTs and dispenser island (Figure 3). The C-Sparge[™] wells will be installed so that the bottom of the 30-inch long spare tips are set at depths between 76.5 and 79 feet. During sparging, no groundwater or vapors will be extracted. Sparging will be performed on a cycled basis.
- 15. 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
МТВЕ	TBA (tertiary butyl alcohol), TBF (tertiary butyl formate), formate, oxygen, hydrogen peroxide
ETBE	TBA, TBF, acetate, oxygen, hydrogen peroxide
ТВА	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.

16. Prior to initiating the C-Sparge[™] technology, baseline samples will be collected from monitoring wells AS/SVE-2, SVE-4D, MW-1, MW-3, MW-10, MW-11 and MW-13 and analyzed for the following parameters: TPH_G, TPH_D, BTEX, MTBE, TBA, tertiary amyl methyl ether (TAME), di-isopropyl ether (DIPE), ethyl tertiary butyl ether (ETBE), ethanol, pH, temperature, dissolved oxygen (DO), oxidation-reduction potential (ORP), and dissolved ferrous iron. In addition, groundwater samples from wells MW-2, SVE-2, MW-10 and MW-13 will be analyzed for total chromium and chromium 6. After the ozone injections, groundwater samples will be collected bi-weekly during the first month of system operation and analyzed according to a groundwater monitoring program required by the Regional Board. Data collected during the testing period will be used to evaluate the C-SpargeTM effectiveness at this site.

APPLICABLE LAWS, PLANS, POLICIES AND REGULATIONS

- 17. 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 project implements the plans, policies and provisions of the Regional Board's Basin Plan.
- 18. The Basin Plan designates beneficial uses and water quality objectives for groundwater within the Simi Valley Groundwater Basin as follows:

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

- 19. 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.
- 20. The permitted discharge is consistent with the anti-degradation provisions of State Water Resources Control 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 Simi Valley Groundwater Basin.
- 21. This Regional Board has assumed lead-agency role for this project under the California Environmental Quality Act (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.
- 22. 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.
- 23. Pursuant to California Water Code section 13320, any aggrieved party may seek review of this Order by filing a petition with the State Board. A petition must be received by the State Water Resources Control Board, P.O. Box 100, Sacramento, California, 95812, within 30 days of the date this Order is adopted

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 Specifications

- 1. The discharge (injection) of ozone into the groundwater shall be only performed according to the C-Sparge[™] system operations described in the August 29, 2003 revised RAP.
- 2. The Discharger shall provide hydraulic control, if required by the Executive Officer, that provides full and complete containment of any released materials or by-products of chemical processes, for the duration of the C-Sparge[™] system operations.
- 3. During the C-Sparge[™] 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 Prohibitions

- 1. The Discharger shall not allow the by-products of the chemical reduction process to migrate offsite.
- 2. The Discharger shall not cause the groundwater outside of the remediation area to exceed background concentrations of total dissolved solids, sulfate, chloride, and boron established prior to start of the C-Sparge[™] 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 (MRP) No. CI-8842 which is incorporated herein by reference. If there is any conflict between provisions stated in the MRP and the Standard Provisions, those provisions stated in the MRP 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 selfmonitoring work performed according to the detailed specifications contained in MRP No. CI-8842 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 MRP 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 of wastes 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 by-products 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 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:
 - 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).
- 20. After the ozone injections, groundwater samples will be collected bi-weekly during the first month of system operation and analyzed according to a groundwater monitoring program required by the Regional Board. Data collected during the testing period will be used to evaluate the C-Sparge[™] effectiveness at this site. Upon completion of the test, a determination will be made whether to continue with the C-Sparge[™] technology or whether any alternate technologies, including monitored natural attenuation, may be more viable.

D. Expiration Date:

This Order expires on December 13, 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, 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 December13, 2004.

Jonathan S. Bishop, Executive Officer