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Technical Appendix 5 – Introduction

This technical appendix discusses the behavior of Key *contaminants of potential concern* (COPCs) in *groundwater* underlying the San Gabriel Valley Area 3 *Superfund* Site (Area 3). Physical and chemical properties of the *contaminant* and of the environment influence the rate of contaminant movement in groundwater.

Two important characteristics determine the probable behavior of a contaminant in the environment: the *mobility* and the *persistence of the contaminant*. Mobility is the potential for a contaminant to migrate from a source; persistence is the relative duration of how long a contaminant will remain in the environment.

Environmental factors that potentially affect the mobility and persistence of a contaminant include the *pH* of the groundwater, the presence and concentration of other chemicals, the *oxidation-reduction potential* and *geochemistry* of the groundwater, the *organic-matter content* of *aquifer* sediments (matrix), and the presence of *microorganisms*.

The primary mechanisms of contaminant transport in groundwater include *advection*, *dispersion*, and *diffusion*. The physical and hydraulic properties of the water-bearing units in contact with the contaminant during transport determine which mechanisms control movement of the contaminant.

Figure TA5-1 conceptually presents some of the potential contaminant *fate* and *transport* mechanisms.

TA5.1 Contaminant Transport in Vadose Zone

The transport pathway of primary focus for the *remedial investigation* (RI) is contaminant transport in groundwater. This report also considers transport within the *vadose zone* because *contamination* that migrates from the vadose zone is the main source of contamination in groundwater in Area 3.

As discussed in Section 4.4, the detection of Key COPCs in soil and *soil vapor* beneath numerous facilities in Area 3 indicates the occurrence of releases of contaminants to the vadose zone. Key COPCs released from a source at the ground surface could evaporate; dissolve in surface water and migrate in surface water runoff; infiltrate into the subsurface by migration through permeable layers; or undergo a combination of the three processes.

A contaminant that migrates downward through the vadose zone could remain in the form of a *free-phase liquid* or could dissolve in water. *Tetrachloroethene* (PCE), *trichloroethene* (TCE), *cis-1,2-dichloroethene* (*cis-1,2-DCE*), and carbon tetrachloride might volatilize within the vadose zone and migrate to the atmosphere.

Each section of this report provides a discussion of the subject, followed by any tables or figures cited in the text. In addition, exhibits and text boxes noted in the margins present key concepts, tables, and figures.

The glossary explains words presented in **bold, italicized** text.

Figure TA5-1 presents potential contaminant fate and transport mechanisms.

A contaminant that encounters perched groundwater or a fine-grained geologic unit, such as clay or silt, could migrate laterally from the source area. If conditions are favorable, such as the occurrence of shallow groundwater or a sufficient quantity of contamination, or both, contamination may continue to migrate downward through the vadose zone until reaching the groundwater table.

Residual soil contamination also can remain in the vadose zone. As recharge water infiltrates through residual contamination in soil, contaminants can dissolve into recharge water and cause concentrations of contaminants in the recharge water to increase.

TA5.2 Contaminant Transport in Groundwater

Three primary mechanisms drive contaminant migration in groundwater: advection, dispersion, and diffusion, as described below.

TA5.2.1 Advection

Advection is the transport of a dissolved contaminant by groundwater flow in a downgradient direction. In aquifers with relatively high *hydraulic conductivities*, such as the coarse-grained aquifers in Area 3, contaminant migration by advection is much greater than by the other transport mechanisms (Driscoll, 1986; Fetter, 1993). Advection is mostly responsible for the contamination currently found in groundwater at production wells in Area 3.

Groundwater flow patterns provide evidence of the significant influence of advection on the movement of contamination within Area 3 as shown in Figure 3-18. In the western portion of Area 3, groundwater flows generally southeastward to eastward. Groundwater flow follows the *bedrock* structural features, in particular the southeastward-eastward *plunging syncline*. The groundwater contours show a steep gradient away from the *anticline*, most likely due to the restriction of groundwater flow by the relatively fine-grained bedrock. The distribution of detected contaminants in the western portion of Area 3 is consistent with the effects of advective transport controlled by the groundwater flow patterns.

In the eastern portion of Area 3, pumping strongly influences the composite groundwater flow, as groundwater flows toward areas of high groundwater production. Groundwater flows radially to the Alhambra Pumping Hole in the south-central portion of Area 3, generally westward in the eastern portion of Area 3, and northward in the northeastern portion of Area 3 near the Raymond *Fault*. Contamination distribution in the eastern portion of Area 3 is consistent with the effects of advective transport toward historically active production wells. Contamination in groundwater is drawn to production wells due to the local depression of the water table caused by pumping and the corresponding influence of pumping on groundwater flow directions.

Contaminant migration generally occurs at a slower rate than groundwater flow due to contaminant sorption to the aquifer matrix. *Sorption* reduces the rate of contaminant migration because contamination continuously sorbs to and leaches from the aquifer matrix as the groundwater moves. This reduction in migration rate is referred to as *retardation*. Limited retardation likely occurs in Area 3 because Key COPCs are relatively soluble and, thus, less inclined to sorb to the aquifer matrix.

TA5.2.2 Dispersion

Dispersive migration of contamination occurs in conjunction with advective flow, and affects the shape of contaminant plumes. Data needs preclude the delineation of contaminant plumes in Area 3, and thus the significance of dispersion as a transport mechanism relative to advection remains undefined. *Longitudinal dispersion* is the elongation of a volume of contamination in an aquifer in the direction of groundwater flow. Longitudinal dispersion is caused by small differences in flow velocity throughout the aquifer.

Transverse dispersion is the elongation of a volume of contamination in an aquifer in a direction perpendicular to groundwater flow (Driscoll, 1986). Transverse dispersion is caused by the sinuosity of flow paths (from void to void, around the aquifer matrix) in a porous medium.

Both types of dispersive migration spread the mass of contaminant along the flow path with increasing distance from a contaminant source. The spread of the contaminant results in reduced contaminant concentrations within the groundwater and an increased volume of contaminated groundwater (Hounslow, 1995).

TA5.2.3 Diffusion

Contaminant concentration gradients drive the last type of migration, diffusive migration. A contaminant will tend to migrate from an area of high concentration to an area of lower concentration until equilibrium is maintained. Diffusion will cause a contaminant to migrate in all directions from an area of higher concentration. Because diffusion occurs slowly, diffusive migration in groundwater generally can be disregarded (Driscoll, 1986), especially in Area 3, where the aquifers with high conductivity facilitate advective transport.

TA5.2.4 Physical and Chemical Properties

The properties that affect the fate and migration of Key COPCs in groundwater include *solubility*, *vapor pressure*, *density*, and sorption. Exhibit TA5-1 presents the physical and chemical properties of Key COPCs. The following discussion describes each property.

Exhibit TA5-1 presents physical and chemical properties of Key COPCs.

EXHIBIT TA5-1**Physical and Chemical Properties of Key COPCs**

Area 3 Key COPC	Solubility at 25°C g/L	Vapor Pressure at 25°C mm Hg	Henry's Law Constant at 25°C atm-m ³ /mol	Density at 20°C g/cm ³	Log K _{oc} mL/g	References
PCE	0.15	18.47	0.018	1.62	2.32	EPA, 1994 EPA, 2006e WHO, 2003
TCE	1.1 – 1.4	57.8	0.01	1.465	2	EPA, 2006f WHO, 2005
cis-,1,2-DCE	3.5	273 (30°C)	0.00337	1.26	1.56	EPA, 2006c
1,2,3-TCP	1.75	3.1	0.000317	1.38	1.89 – 1.98 (sand/loam)	ASTDR, 1992 CICADs, 2003
Carbon tetrachloride	1.2	91.3 (20°C)	0.0304	1.59	1.85	EPA, 2006d
Perchlorate	200	Not volatile	Not volatile	1.95	Completely soluble in water	ITRC, 2005

Notes:

ASTDR – Agency for Toxic Substances and Disease Registry

atm-m³/mol – atmosphere-cubic meter per mole

°C – degrees Celsius

CICADs – Concise International Chemical Assessment Documents

cis-1,2-DCE – cis-1,2-dichloroethene

EPA – United States Environmental Protection Agency

g/cm³ – grams per cubic centimeter

g/L – grams per liter

ITRC – Interstate Technology and Regulatory Council

K_{oc} – organic carbon coefficient

mL/g – milliliters per gram

mm Hg – millimeters of mercury

PCE – tetrachloroethene

TCE – trichloroethene

1,2,3-TCP – 1,2,3-trichloropropane

WHO – World Health Organization

TA5.2.4.1 Water Solubility

The measured water solubility value is the maximum concentration of a chemical that can dissolve in water at a given temperature and pH. A highly soluble contaminant is more mobile in the environment because movement of water through the vadose zone or through groundwater in the *saturated zone* easily transports the contaminant. A contaminant with low solubility might occur in the vadose zone or the saturated zone or in both zones as pools or droplets of free-phase liquid.

Exhibit TA5-1 shows that perchlorate is completely soluble. PCE, TCE, cis-1,2-DCE, 1,2,3-TCP, and carbon tetrachloride are relatively soluble in water. A potential indication of the presence of a free-phase liquid is the presence of the dissolved contaminant at concentrations greater than one to 10 percent of the effective solubility (Pankow and Cherry, 1996). PCE concentrations ranging from 1,500 to 15,000 micrograms per liter (µg/L) or TCE concentrations ranging

from 11,000 to 110,000 µg/L would be indicative of free-phase liquid. Data for Area 3 show an absence of COPCs in the form of free-phase liquids as the maximum concentrations of PCE and TCE detected in Area 3 are 950 and 2,300 µg/L, respectively.

TA5.2.4.2 Vapor Pressure and Henry's Law Constant

Volatilization is a process of evaporation that occurs when contaminants present either as nonaqueous phase liquids or dissolved in water contact a gas phase, such as exposure to the atmosphere (Domenico and Schwartz, 1990). The vapor pressure of a chemical represents the relative tendency of that chemical to volatilize. Chemicals with higher vapor pressures generally enter the atmosphere much more readily than chemicals with lower vapor pressures.

Henry's Law describes the relative degree of volatilization of a dissolved organic contaminant from water, such as groundwater (Domenico and Schwartz, 1990). A Henry's Law Constant measures volatility, and indicates the relative tendency for a contaminant dissolved in water to volatilize. A Henry's Law Constant is considered more representative than vapor pressure for evaluating the tendency of a dissolved contaminant in groundwater to volatilize. Vapor pressure represents volatilization of a chemical not dissolved in water. Henry's Law Constant values higher than 10^{-3} atmosphere-cubic meter per mole (atm·m³/mol) indicate a greater tendency for a dissolved contaminant to partition into the vapor phase.

Exhibit TA5-1 presents the values of vapor pressure and Henry's Law Constant for Key COPCs under normal temperature and pressure conditions. Significant volatilization of PCE, TCE, cis-1,2-DCE, and carbon tetrachloride could occur from water to air; whereas 1,2,3-TCP is relatively nonvolatile and perchlorate does not volatilize.

Exhibit TA5-1 presents physical and chemical properties of Key COPCs.

TA5.2.4.3 Density

The density of a contaminant affects the vertical migration of a free-phase contaminant in groundwater. All Key COPCs are denser than water. Density has a lesser effect, if any, on the vertical migration of a dissolved contaminant (Kehew, 2001).

TA5.2.4.4 Sorption

Sorption is the tendency for a chemical to adsorb to and to desorb from the aquifer sediments. Typically, chemicals sorb to clays and organic materials. The *organic carbon partition coefficient* indicates the tendency of a chemical to adhere to soil particles containing organic carbon. Based on the low organic carbon partition coefficients of Key COPCs, sorption to soil particles in the saturated zone in Area 3 is likely minimal.

TA5.2.5 Biological Degradation

Biological degradation occurs as a biochemical oxidation-reduction reaction produced by microorganisms in the subsurface. Naturally occurring bacteria in

groundwater use organic chemicals as food sources and generate degradation products.

Biological degradation can reduce the concentrations of a contaminant but increase concentrations of other chemicals as degradation products. Biological degradation occurs most readily among organic compounds, such as chlorinated *volatile organic compounds* (VOCs) (Kehew, 2001). Figure TA5-2 presents biological degradation pathways for chlorinated VOCs.

Reductive dechlorination is the primary biological degradation process for chlorinated organic compounds, including Key COPCs. This process replaces chlorine atoms on an organic compound with hydrogen atoms, and thereby converts the chlorinated compound to another chemical. Reductive dechlorination occurs in anaerobic (low oxygen) environments (Kehew, 2001).

Under appropriate conditions, Key COPCs biodegrade fairly readily through the processes depicted on Figure TA5-2. Perchlorate might biodegrade to the chloride ion under certain environmental conditions, but the degradation of perchlorate occurs very slowly. Perchlorate can, however, degrade readily under strongly reducing conditions. 1,2,3-TCP biodegrades with difficulty (EPA, 2005a).

Groundwater underlying Area 3 contains degradation products of PCE and TCE. Table TA5-1 summarizes the concentrations of PCE, TCE, and cis-1,2-DCE in monitoring wells in Area 3. The data presented in Table TA5-1 show that TCE, a possible degradation product of PCE, occurs with detections of PCE in Area 3; however, TCE contamination and PCE contamination appear to originate mainly from separate sources in Area 3. cis-1,2-DCE contamination, commonly detected with TCE contamination in Area 3, appears to occur as a degradation product of TCE as shown in Table TA5-1.

Biodegradation of TCE to cis-1,2-DCE may be occurring in groundwater, based on detections of cis-1,2-DCE at concentrations lower than TCE in several wells over time. The concentration patterns for TCE and cis-1,2-DCE provide the only evidence of the occurrence of biodegradation.

The absence of detections of vinyl chloride potentially suggests that if biodegradation is occurring, it may not be proceeding beyond the cis-1,2-DCE step in the TCE biodegradation process. However, if conditions are sufficiently oxidizing, the degradation of vinyl chloride can be rapid compared to degradation of cis-1,2-DCE, such that vinyl chloride is not detected. The absence of the degradation product chloroform suggests biodegradation of carbon tetrachloride is not occurring.

Additional chemical data used to evaluate the viability of biodegradation in groundwater, such as oxidation-reduction potential and dissolved oxygen, are needed to better understand whether conditions in Area 3 groundwater are favorable for biodegradation.

Figure TA5-2 presents biological degradation pathways for chlorinated VOC compounds.

Acronyms and Glossary

Acronyms and Abbreviations

Area 3	San Gabriel Valley Area 3 Superfund Site
ASTDR	Agency for Toxic Substances and Disease Registry
atm-m ³ /mol	atmosphere in cubic meters per mole
° C	degrees Celsius
CICADs	Concise International Chemical Assessment Documents
cis-1,2-DCE	cis-1,2-dichloroethene
cm ³	cubic centimeter
COPC	contaminant of potential concern
EPA	United States Environmental Protection Agency
g	gram
g/cm ³	grams per cubic centimeter
g/L	grams per liter
ITRC	Interstate Technology and Regulatory Council
L	liter
log K _{ow}	octanol water partition coefficient
m ³	cubic meters
µg/L	micrograms per liter
mL/g	milliliters per gram
mm of Hg	millimeters of mercury
PCE	tetrachloroethene
RI	remedial investigation
TCE	trichloroethene
1,2,3-TCP	1,2,3-trichloropropane
VOC	volatile organic compound
WHO	World Health Organization

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Glossary

advection: The process by which chemicals are transported by the bulk motion of the flowing groundwater.

anticline: A convex upward series of folded geologic units that contains older rocks at its core.

aquifer: A saturated fine-grained geologic unit, often of sand or gravel, which contains and transmits significant quantities of water under normal conditions.

bedrock: The solid rock that underlies loose material, such as soil, sand, clay, or gravel.

biological degradation: The process by which organic substances are broken down by the enzymes produced by living organisms.

chlorinated volatile organic compound: Any volatile organic compound that contains a chlorine atom. Solvents commonly used in cleaning and degreasing applications often contain chlorinated volatile organic compounds.

contaminant: A substance not naturally present in the environment or present in unnatural concentrations that can, in sufficient concentration, adversely alter an environment.

contaminants of potential concern: Contaminants that potentially pose a risk to human health or the environment.

contamination: The presence of hazardous substances in the environment.

density: The mass per unit volume of a substance. Chemicals that are less dense than water tend to float and chemicals that are denser tend to sink.

diffusion: The process of spreading out or scattering of a chemical from areas of higher concentration to areas of lower concentration.

dispersion: The spreading of chemical constituents in the direction of groundwater flow

fate: The processes by which the contaminant moves through and is transformed in the environment.

free-phase liquid: Liquids that do not mix easily with water or readily separate from water or both.

geochemistry: The study of the distribution and amounts of the chemical elements in minerals, rocks, soils, water and the atmosphere, and chemical element circulation in nature.

groundwater: Water occurring underground, in the zone of saturation in an aquifer.

Henry's Law: A law that states the amount of a gas that will be absorbed by water increases as the gas pressure increases.

hydraulic conductivity: The ability of soil, sediment, or rock to transmit fluid, dependent on the properties of the soil, sediment, or rock and the fluid.

Key contaminants of potential concern: The contaminants detected multiple times in groundwater at production wells within Area 3 at concentrations that exceed evaluation criteria. Key COPCs identify regional groundwater contamination within Area 3.

longitudinal dispersion: The spreading of chemical constituents in the direction of groundwater flow due to the spatial differences in the flow characteristics of the aquifer material.

microorganisms: An extremely small organism, such as a bacterium or protozoan, that can not be seen without a microscope.

mobility of a contaminant: A measure of the potential for a contaminant to migrate from a source.

organic carbon partition coefficient: A number that represents chemical partitioning between organic carbon and water in soil.

organic-matter content: A measure of matter that has come from a once-living organism or is composed of organic compounds.

oxidation-reduction potential: The tendency of a chemical species to acquire electrons and thereby be reduced.

persistence of a contaminant: A term describing how long a contaminant will remain in the environment.

pH: The measure of the acidity or alkalinity of a solution. pH for water is 7.0. Solutions less than 7.0 are considered acidic and solutions greater than 7.0 are considered alkaline.

plunging: A term used to describe a folded geologic unit that is not horizontal. A fold will plunge in a particular direction.

reductive chlorination: Degradation process where hydrogen atoms are substituted for a chlorine atom in the contaminant molecules.

remedial investigation: Actions undertaken to characterize the full nature and extent of contamination, including characterization of hazardous substances, identification of contaminant sources, and assessment of human health and ecological risk.

retardation: The act of slowing down or a decrease in the rate of change.

- soil vapor:** Elements and compounds in a gaseous state in the small spaces between particles of soil. Such gases can be moved or driven out under pressure.
- solubility:** The ability of a substance to dissolve in a given amount of water.
- sorption:** A process in which something is taken up and held, usually a liquid or gas, into the body of another material. Chemicals in groundwater sorb to aquifer materials.
- Superfund:** The program operated under the legislative authority of CERCLA and SARA that funds and carries out EPA solid waste emergency and long-term response actions, including conducting or supervising cleanup actions.
- syncline:** A concave upward series of folded geologic units that contains younger rocks at its core.
- tetrachloroethene:** A volatile organic compound primarily used for dry cleaning clothing and in manufacturing processes as a solvent and metal degreaser.
- transport:** Movement from one location to another.
- transverse dispersion:** The spreading of chemical constituents perpendicular to the direction of groundwater flow.
- trichloroethene:** A volatile organic compound that is a colorless or blue organic liquid with a chloroform-like odor. TCE is primarily used in manufacturing processes as a solvent, metal degreaser, and textile degreaser.
- vadose zone:** The soil or rock between the earth's surface and the water table.
- vapor pressure:** A measure of a substance's propensity to evaporate; the relative measure of the volatility of a chemical.
- volatile organic compound:** An organic (carbon-containing) compound that evaporates readily at room temperature.

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Tables

Figures
