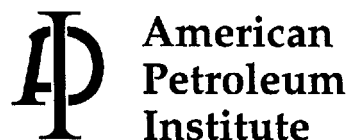


# Natural Attenuation Processes

API PUBLICATION 1628A  
FIRST EDITION, JULY 1996





One of the most significant long-term trends affecting the future vitality of the petroleum industry is the public's concerns about the environment. Recognizing this trend, API member companies have developed a positive, forward looking strategy called STEP: Strategies for Today's Environmental Partnership. This program aims to address public concerns by improving industry's environmental, health and safety performance; documenting performance improvements; and communicating them to the public. The foundation of STEP is the API Environmental Mission and Guiding Environmental Principles. API standards, by promoting the use of sound engineering and operational practices, are an important means of implementing API's STEP program.

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- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emissions and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.



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**Manufacturing, Distribution and Marketing Department**

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# Natural Attenuation Processes

## SECTION 1—INTRODUCTION

### 1.1 Purpose and Scope

This publication describes the physical, chemical, and biological processes that decrease the concentrations and ultimately limit the extent of the dissolved plume migrating from a hydrocarbon release. It is primarily focused on the more soluble hydrocarbon fraction that makes up the dissolved plume. Emphasis is given to the biological processes that can play a major role in the attenuation of a dissolved plume.

### 1.2 LNAPL Migration

After being released into the subsurface, petroleum hydrocarbons can be affected by the physical, chemical, and biological processes in the immediate vicinity. Initially, the hydrocarbons migrate through the vadose zone as a separate light non-aqueous phase liquid (LNAPL), moving downward in response to gravity, and laterally in response to changes in permeabilities encountered. This migration continues until (a) the migrating volume is immobilized by capillary forces and held within the pores of the soil in a residual state, (b) the liquid reaches an impermeable layer and perches upon it, or (c) the capillary fringe of the water table is encountered where the liquid begins to migrate laterally downgradient. When the hydrocarbons reach the capillary fringe, they can migrate laterally because they are lighter, and less dense than water. The fluctuations of the water table and capillary fringe cause this LNAPL layer to rise and fall accordingly. This coats the soils encountering the LNAPL and, in time, creates a smear zone marking the

range in fluctuation of the LNAPL. The LNAPL eventually ceases movement when the lateral and vertical spreading has disseminated it to the extent that the forces driving its movement are overcome by capillary forces in both the vadose and saturated zones. These hydrocarbons are then trapped as a residual saturation of LNAPL in these soils and are a source for continued migration in the vapor phase or in the dissolved phase.

### 1.3 Vapor and Dissolved Phase Migration

Once immobilized, the hydrocarbon compounds can migrate further as vapors or dissolved in water. Those compounds that can transfer by volatilization into the air in the vadose zone can eventually migrate as a *vapor phase* through the land surface and discharge into the atmosphere. The compounds in contact with water transfer into the aqueous phase and are transported as a *dissolved phase*.

The transfer into the vapor and dissolved phases provides the means for the hydrocarbon compounds to potentially migrate away from the hydrocarbon source area. Once released from the source area, the concentrations of the hydrocarbon compounds are decreased by several physical, chemical, and biological processes. Given sufficient flow distances and times, these processes can ultimately result in the complete attenuation of the dissolved hydrocarbon compounds. These processes are described in this publication.

## SECTION 2—PHYSICOCHEMICAL PROCESSES

### 2.1 General

The physicochemical processes in general decrease dissolved hydrocarbon concentrations by redistributing the hydrocarbon mass. In doing so, however, these processes can render the petroleum hydrocarbon compounds more bioavailable and hasten their attenuation by biodegradation. Several major physicochemical processes are discussed in this section. For further overview of these processes, refer to the book by Domenico and Schwartz [1].

### 2.2 Adsorption and Retardation

Because petroleum hydrocarbon molecules are to some degree nonpolar, there is a finite limit to their solubility in a more polar substance such as water. This results in low

(<10<sup>-3</sup> mg/L) to moderate (10<sup>3</sup> mg/L) aqueous solubility limits for the petroleum hydrocarbon compounds, as well as their tendency to partition to other forms of organic carbon in the subsurface. This characteristic can cause their migration in the dissolved plume as *micelles*, that is “packs” of organic molecules with the more hydrophilic compounds or the more hydrophilic portions of each molecule on the outer surface of the micelle. It also leads to adsorption of the petroleum hydrocarbon compounds to the organic coatings of the soil particles.

The tendency to adsorb to the subsurface material is different for each of the petroleum hydrocarbon compounds; the compounds that sorb strongly tend to migrate downgradient more slowly than those that sorb less strongly. This leads to a “chromatographic” effect within a migrating dissolved plume, with the more mobile compounds arriving at