1.0 SAMPLES AND FACTORS AFFECTING SAMPLING

1.1 INTRODUCTION

There are two important steps in the process of investigating environmental problems: environmental sampling and subsequent chemical analysis. Chemical analysis is often done in the laboratory where the spill responder would not be involved, and will not be discussed in depth here. With regard to environmental sampling, attention will be concentrated on the introduction of the physical, chemical, and biological dynamics of the contaminant within the environment under investigation, and on sampling plans. The sampling plans include sampling location, procedures, materials, sampling devices, sample size or number, sampling frequency, and handling operation. Useful criteria for determining representative samples include physical, chemical, and biological variables, and those which should meet quality assurance/quality control requirements.

1.2 FREE PRODUCTS

Spill responders have to be generally familiar with a variety of petroleum and hazardous materials when responding to a call. There is a vast number of different materials in today's market, and no one is capable of knowing them all. But, there is a certain number of properties, such as flammability, health and environmental impacts, and reactivity which have been used for classification.

The U.S. Department of Transportation (US DOT) has been assigned the responsibility of regulating the transportation of hazardous materials, and its rules and regulations have been adopted by all industries. The US DOT classification system and related labels are as follows:

1.2.1 Class I - Explosives

The US DOT defines an explosive as any chemical compound, mixture or devices with the primary or common purpose of exploding and instantaneously releasing substantial amount of gas and heat. Under the DOT regulations, explosives are further divided into four sub-classes:

Sub-Class	Characteristics	Example	Labeling	
Class A	capable of detonation. (most dangerous)	black powder,dynamite, desensitized nitroglycerin, lead azide,urea nitrate,etc.		with dark orange color base and inscription in black.
Class B	rapid combustion rather than detonation. (2nd most dangerous)	flash powders for special fireworks, some pyrotechnic signal devices, some liquid or solid propellant explosives.		with dark orange color base and inscription in black.
Class C	compounds containing restricted quantity of Class A and Class B explosives. will not normally mass detonate under fire.(3rd most dangerous)	detonative cords or fuses, explosive rivets, explosive pest control devices, etc..		with dark orange color base and inscription in black.

Blasting Agent	requires devices to cause initiation of detonation. (least danger within class-I)	blasting agents.		with dark orange color base and inscription in black.

1.2.2 Class II - Gases

A compressed gas is defined as any material or mixture having, in a container, an absolute pressure exceeding 40 psi at 70°F or, regardless of the pressure at 70°F, having an absolute pressure exceeding 104 psi at 130°F; or any flammable liquid material having a vapor pressure exceeding 40 psi absolute at 100°F as determined by ASTM Test D-323. Included in this class are poison gases, flammable, and non-flammable gases.

Sub-Class	Characteristics	Example	Labeling	
Poison Gas	extremely dangerous and maximum hazard to emergency personnel.	hydrocyanic acid,phosgene, cyanogen,bromoacetone,etc..		white color base and inscription in black.
Flammable Compressed gas	once released, it will return to gaseous state.	acetylene,liquid petrogas, compressed natural gas, vinyl flouride,etc..		red color base and inscription in white.
Non Flammable compressed gas	least fire problem, major health concerns.	carbon dioxide,argon, nitrogen,helium, etc..		green color base and inscription in white.

1.2.3 Class III - Flammable Liquids

A flammable liquid is any liquid that has a flash point below 100°F (37.8°C). A combustible liquid is any liquid that has a flash point at or above 100°F (37.8°C) and below 200°F (93.3°C). The National Fire Protection Association (NFPA) defines a flammable liquid as one having a flash point below 200°F. And the flammable and combustible liquids are further divided into five categories according to the various ranges of flash and boiling points.

Flash points (FP) of aviation fuels are : -50°F for aviation gasoline; -36°F, 100 octane gas; 100°F, JP-1 jet fuel; 110°F to 150°F, JP-3; -10°F to +30°F (closed cup), JP-4; 140°F (min.) (closed cup), JP-5. Kerosene (sometimes, synonymous with JP-1 or Fuel Oil No. 1) has a FP of 100°F to 185°F. For diesel fuel oils: FP 100°F (minimum) for Diesel No. 1-D; 125°F(min.), Diesel No. 2-D; 130°F (min.), Diesel No. 3-D. For fuel oils: FP 100°F to 162°F (closed cup) for Fuel Oil No. 1; 126°F to 204°F, No. 2; 142°F to 240°F, No. 4; 156°F to 336°F, No. 5; 140°F minimum and up, No. 6 (Bunker oil)(no hazard label required).

Both have red color base with the inscription in white color.

The labels for flammable and combustible liquid are basically identical to flammable gas--a red color base with the inscription in white.

1.2.4 Class IV - Flammable Solids

Flammable solids include materials other than explosives which are likely to cause fire by self-ignition through friction, adsorption of moisture, or spontaneous chemical changes, or as a result of retained heat from manufacturing or processing. They can be ignited readily, and when ignited burn so vigorously and persistently as to create a serious transportation hazard. Charcoal and matches are examples of this category.

The labels for flammable solids consist of a set of red stripes placed vertically to the words "Flammable Solid" on a white background. The inscription, border, and symbol are in black color.
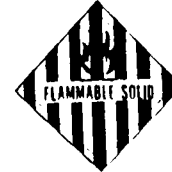
In addition to the above classified solids, there is an additional sub-classification for those materials that can create a special hazard if they become wet. These include calcium carbide, sodium, and potassium. The labeling for such materials is white color inscription on a blue background.

1.2.5 Class V - Oxidizing Substances (Oxidizers)

An oxidizing substance, as the US DOT defines it, is a substance that yields oxygen readily to stimulate the combustion of organic matter. These substances tend to be very unstable, and the combustion can be so vigorous or explosive, that they cannot be controlled by depriving (air) oxygen, smothering with water, or using normal fire fighting techniques. Substances such as benzoyl peroxide, ammonium nitrate and calcium hypochlorite (bleaching powder) are examples of this category.

The labeling is black inscriptions on a yellow color background.

1.2.6 Class VI - Poisonous Materials and Etiologic Agents

The poisonous materials are sub-divided into three major classes: Class A, Class B, and irritants. Both Class A and Class B poison need to be considered extremely dangerous to human health. Poisons may be found as liquids or solids in these classifications. Gases are found listed in Class II substances.

| Sub-Class	Characteristics	Example	Labeling
Class A Poison	gases or liquids of such nature that a small amount of gas, or vapor of the liquid, when mixed with air, is dangerous to life (extremely dangerous)	nitrogen peroxide (tetroxide),phosegene, cyanogen,bromoacetone, etc..	white color background and inscription in black.
Class B Poison	liquids or solids, (including pastes and semi-solids) which are known to be so toxic as to afford a hazard to health during transportation, storage, or use. Key dangers are external contact with body or intake, as of contaminated food.(very dangerous)	pesticides,herbicides, arsenic acid, hydrocyanic acid, etc..	white color background and inscription in black.

| Irritants | liquid or solid substances which upon contact with fire or when exposed to air gives off dangerous or intensely irritating fumes. | bromobenzylcyanide, chloracetophenone, tear gas, diphenyl-chlorarsine, etc.. | | white color background, red wording, and black borderline. |

Etiologic Agents - An etiologic agent is a viable micro-organism, or its toxin, which causes, or may cause, human disease. The materials in this class present a danger of disease, or even an epidemic upon exposure to it. The labeling is a white color background, red inscription, and red and white wording. For more information see 42 CFR 72.3.
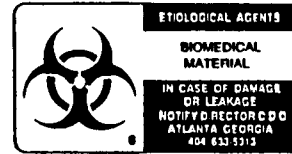
1.2.7 Class VII - Radioactive Substances

These materials spontaneously disintegrate and emit ionizing radiation of alpha or beta particles, or gamma rays or any combination of the three. The biological damage from radioactive substances depend on the type of radiation emitted and the amount of radiation to which a person is exposed. Time, distance, and shield are the control factors of the exposure. With a fixed distance and time, the amount of exposure caused by any radioactive material is proportional to the radioactivity of the material. The US DOT has three labels for identifying of radioactivity involved in surface and air transportation.

Sub-Class	Level of Radiation	Labeling
Class 1 (Radioactive White I)	A maximum of 0.5 mr/hr. at the surface of the package and a zero dose rate at 3 feet from its surface.	on white color background with black trefoil and wording containing a single red vertical bar overprinted
Class 2 (Radioactive Yellow II)	Not greater than 10 mr/hr. at the surface and not more than 0.5 mr/hr. at 3 feet from the package.	yellow in the upper half of the label and white in the lower half with black trefoil and wording containing two red vertical bars overprinted.
Class 3 (Radioactive Yellow III)	Not greater than 200 mr/hr. at the surface and not more than 10 mr/hr. at 3 feet from the surface.	similar to the label of Class 2, but with 3 red, instead of 2, vertical bars overprinted for Class 3.

If the dose rate exceeds 200 mr/hr at the surface, or 10 mr/hr at 3 feet from the surface of the package, the radioactive material may not be transported in any carrier but a sole use vehicle.

1.2.8 Class VIII - Corrosives

A corrosive material can be either an acid or a base. It is a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact, such as sulfuric acid, nitric acid, sodium and potassium hydroxide. In the case of leakage from its container, it is the liquid that has a severe corrosion rate on other materials such as steel or aluminum.

The label for materials of this class is white in the upper half of the label with

a figure depicting corrosive effect on another material and on a hand, and black in the lower bottom half with white "corrosive" lettering.

1.2.9 Class IX - Miscellaneous Dangerous Substances

Materials which are not covered by any of the other classes, but are regulated by US DOT, are considered to be in the category of "Other Regulated Material (ORM)". The materials in this category are further divided into five sub-classes as follows:

Sub-Class	Characteristics	Example
ORM-A	Materials which have an anesthetic, irritating, noxious, toxic, or other similar property and which can cause extreme annoyance or discomfort to passengers and crews in the event of leakage during transportation.	Ammonium hydrosulfide solution, camphene, chloroform, solid dry ice (CO_2), etc..
ORM-B	Materials (including a solid that has become wet) capable of causing significant damage to a transport vehicle from leakage during transportation. A liquid substance that has a corrosion rate exceeding 0.250 inches per year on aluminum at a test temperature of 130°F is also considered to be in this category.	Ammonium hydrogen sulfate, barium oxide, lead chloride, calcium oxide, etc..
ORM-C	Materials which have other inherent characteristics not described as an ORM-A or ORM-B but which make it unsuitable for shipment, unless properly identified and prepared for transportation.	Ammonium sulfate nitrate, exhausted and unwashed battery parts, bleaching powder containing less than 39% available chlorine, etc..
ORM-D	Materials such as a consumer commodity which, though otherwise subject to the regulations, present a limited hazard during transportation due to its form, quantity and packaging.	Flammable liquid inside metal containers containing 1 quart or less, or oxidizers inside containers having a rated capacity of 1 pint or less.
ORM-E	Materials that are not included in any other hazard class, but are subject to the DOT requirements.	Hazardous waste and hazardous substances, solid or liquid.

In classifying materials for transportation, the US DOT classes each material according to its major hazard, although many materials present more than one hazard. In the event that a material has more than one hazard classification, the container must be labeled for each hazard. When two or more hazardous materials of different classes are packed within the same packaging, the package must be labeled for each material it contains.

1.3 SOILS

There is a variety of definitions and classification of soils. The discussion in this section is primarily based on the parameters that affect groundwater and its associated matters.

1.3.1 Soils, Soil Horizons, and Soil Profile

Soils are natural bodies having characteristics resulting from a unique combination of soil-forming factors such as climate, parent materials, relief, age, and organisms. Examination of a vertical section of soil, called soil profile, in the field shows the presence of more or less distinct horizontal layers called horizons. Above bedrock some unconsolidated material is almost universally present. This material, known as regolith, may be negligibly shallow or hundreds of feet in thickness. Further examination of the regolith shows that the upper material differs

from the one below. The upper and biochemically weathered portion of the regolith can be distinguished from the material below by (a) a relatively high organic matter content, (b) an abundance of the roots of high plants and of soil organisms, (c) more intense weathering, and (d) the presence of characteristic horizontal layers. As might be expected, the regolith varies in composition from place to place, and is predominantly mineral or inorganic in composition.

Physically, soil is a porous mixture of inorganic materials, decaying organic matter, and air and water. The larger mineral fragments usually are embedded in and coated over with colloidal and other fine materials. In some cases, the larger mineral particles predominate and a gravelly or sandy soil results. In other cases, the mineral colloids are more prevalent, which gives the soil clayey characteristics. All gradations between these extremes exist in nature. Organic matter acts as a binding agent to stimulate the individual particles to cluster into clumps or aggregates.

Some important properties of soil that need to be considered are its texture, structure, and chemical makeup. Soil texture has to do with the size of mineral particles. Specifically, it refers to the relative proportion of particles of various sizes in a given soil. Equally important is the soil structure, which is the arrangement of soil particles into groups or aggregates. Together with soil chemical composition, these properties substantially affect or determine not only the groundwater flow and quality, but also the interaction between the soil and pollutant when they come in contact with each other. The interaction includes adsorption, retention, reaction, and component exchange, etc. of a pollutant in the soil.

1.3.2 Soil Classification and Associated Physical Properties

There are a number of different classifications of soil by soil texture or by the size of mineral particles. Figure S-1 shows seven systems.

Figure S-1   Soil Classification by Particle Size (mm)

System	Date	Gravel	Sand	Silt	Clay
Bureau of Soils	1890	1-100	0.05-1	0.005-0.05	0.005
Atterberg	1905	2-100	0.2--2	0.002-0.2	0.002
MIT	1931	2-100	0.06-2	0.002-0.06	0.002
USDA	1938	2-100	0.05-2	0.002-0.05	0.002
Unified	1953	4.75-75	0.075-4.75	0.075	
ASTM	1967	4.75-75	0.075-4.75	0.075	
AASHTO	1970	2-75	0.075-2	0.002-0.075	0.001-0.002

Stone and gravel range in size from 2 mm upward and may be more or less round, irregularly angular, or even flat. The distinction between gravel and stone is technically based on size. Gravel, chert, and slate are considered to range from 2 mm to 3 inches along their greatest diameter. Stones, cobbles, and boulders, on the other hand, exceed 3 inches.

Sand grains may be round or quite irregular, depending on the amount of abrasion that they have received. When not coated with clay and silt, such particles are not sticky even when wet. They do not possess the plasticity as clay does. Their water holding capacity is low, and because of the large size of the spaces between the separate particles, the passage of percolating water is rapid. Hence, they facilitate drainage and encourage good air movement.

Further down in size are silt and clay. Surface area is the characteristic most affected by small size and fine division of silt and especially of clay. A grain of fine colloidal clay has about 1000 times as much surface area as the same weight of medium-sized sand. The specific surface (area per unit weight) of colloidal clay ranges from about 10 to 1,000 square meters per gram. The specific surfaces for the smallest silt particles and for fine sand are 1.0 and 0.1 square meter per gram respectively. Since the adsorption, absorption, and retention of water, gas,

and chemical, and the attraction of particles for each other are all surface phenomena, the significance of the very high specific surface for clay is obvious. Clay particles are highly plastic and tend to be sticky when wet. The silt separates, because they have an adhering film of clay, possess some plasticity, cohesion (stickiness), and adsorption, but to a much lesser degree than the clay separates themself. Figure S-2 shows the relationship of surface area, adsorbing power, swelling, plasticity, and cohesion heat of wetting with various soils.
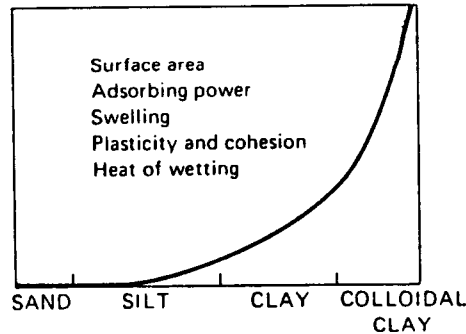

Figure S-2 The finer the texture of a soil, the greater is the effective surface exposed by its particles. Note that adsorption, swelling, and the physical properties cited follow the general trend and that their intensities go up rapidly as the colloidal size is approached.

Structurally there are four primary types of soil which are recognized. They are plat-like, prism-like, block-like, and spheroidal. An area may be dominated by a single structural pattern. More often, a number of types of aggregation are encountered as progress is made from horizon to horizon. The soil conditions and characteristics, which reflect on parameters such as water movement, heat transfer, aeration, bulk density, and porosity (pore space), are much influenced by structure.

MAXIMUM 10 PERCENT GRADE SIZE IN MILLIMETERS
(THE GRADE SIZE IN WHICH THE CUMULATIVE TOTAL BEGINNING WITH THE
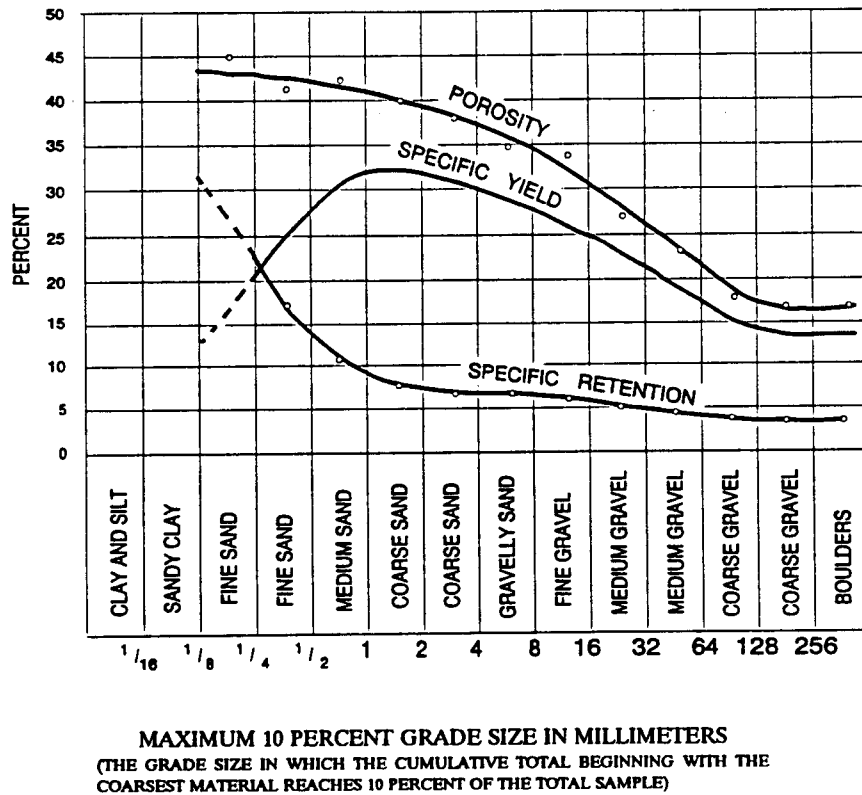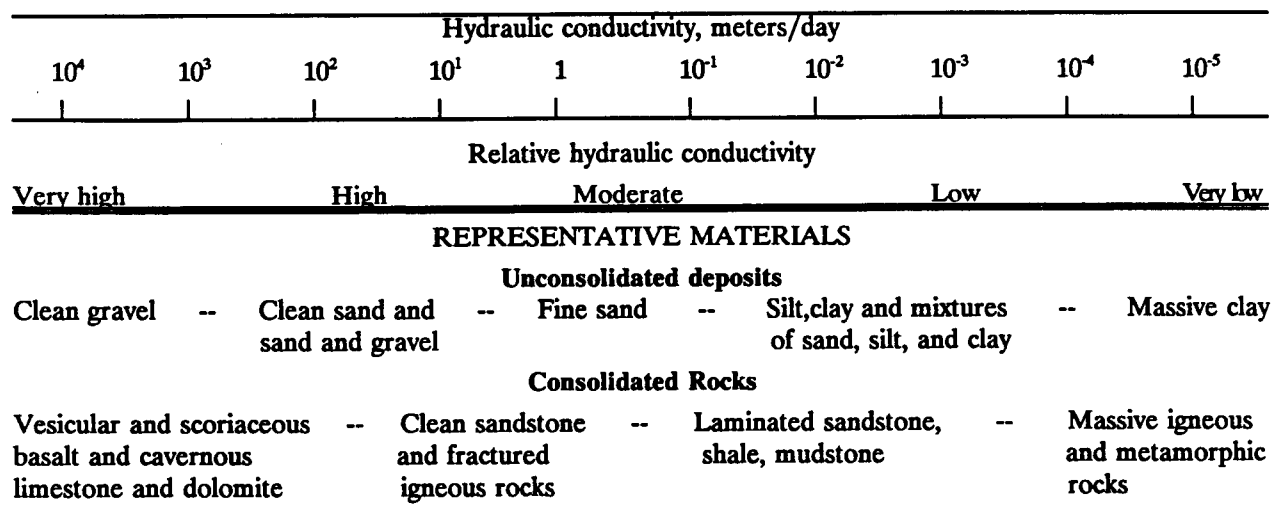COARSEST MATERIAL REACHES 10 PERCENT OF THE TOTAL SAMPLE)

Figure S-3—Porosity, specific retention, and specific yield for sediments of the South Coastal Basin, Cal. (After Eckis 1984)

1-7

An important element of soil is the pore space that is not only occupied by an air and water, but that also provides a channel for air or water movement. The amount of pore space varies considerably, depending on soil conditions, and decreases with depth. This accounts, in part, for the inadequate aeration of deeper horizons. Figure S-3 demonstrates the relationship of porosity, specific yield, and specific retention with various soils. Specific yield is the ratio of the volume of water that a saturated soil or rock will yield by gravity to the total volume of the soil or rock. Specific retention is the ratio of the volume of water a soil or rock can retain against gravity drainage to the total volume of the soil or rock. Figure S-4 exhibits the relationship of hydraulic conductivity with different soils.

Figure S-4

Hydraulic conductivity, meters/day									
10^4	10^3	10^2	10^1	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}

Relative hydraulic conductivity

Very high	High	Moderate	Low	Very low

REPRESENTATIVE MATERIALS

Unconsolidated deposits

| Clean gravel | -- | Clean sand and sand and gravel | -- | Fine sand | -- | Silt,clay and mixtures of sand, silt, and clay | -- | Massive clay |

Consolidated Rocks

| Vesicular and scoriaceous basalt and cavernous limestone and dolomite | -- | Clean sandstone and fractured igneous rocks | -- | Laminated sandstone, shale, mudstone | -- | Massive igneous and metamorphic rocks |

Hydraulic conductivities for various classes of geologic materials(after Bureau of Reclamation).

1.3.3   Chemical Components of Soil

As indicated before, soils consist of four major components: mineral (inorganic) materials, organic matter, water, and air. Organic matter can be subdivided into organic chemicals and biological substances. These components exist mostly in a fine state of subdivision and are so intimately mixed that satisfactory separation is rather difficult.

1.3.3.1   Mineral (Inorganic) Soil Components--Mineralogically, the coarsest sand particles are often fragments of rocks as well as minerals. Quartz commonly dominates the sand and coarse silt fraction. Primary silicates, such as feldspars, hornblendes, and micas, are present in the sands but tend to disappear as one moves to the silt fraction. Secondary silicates, such as kaolinite, illite, and montmorillonite, dominate the fine colloidal clay. Other secondary minerals, such as the oxides of iron and aluminum, are prominent in the fine silt and coarse clay fractions.

Chemically, sand and silt are predominantly quartz and generally quite inactive, but the other soils may be different depending upon what they are and what environments they are exposed to. Some clay particles, especially those in the coarser clay fractions, are composed of minerals such as quartz and the hydrous oxides of iron and aluminum. Another is the complex aluminosilicates. In well-weathered soils, especially those in the hot, humid areas, oxides of iron and aluminum are prominent if not dominant, even in the clay-size fraction. Thus, climate can have a profound effect on the chemical and mineralogical composition of soil separates.

In other words, inorganic soils are composed predominantly of minerals very high in silicates, especially aluminosilicates and oxides. Many elements, including metals, substitute in varying degrees for aluminum, iron,

and silicon in these silicate and oxide structures. These isomorphous substitutions result in many complex series of minerals in soils differing in composition only slightly from next, or one end of a mineral crystal differing in composition from the other end. In the silicate minerals, substitutions of ions by other ions having the same approximate size and chemical properties (isomorphism) are so common that probably no two samples of the mineral can be found that would have exactly the same composition. The oxides of these minerals always contain at least traces of other ions.

Trace elements which support plant and micro-organism growth or other functions are also found sparingly in most soils. These elements have both good and bad effects to the environment.

1.3.3.2   Organic Soil Components--Organic matter in soil usually contains a range of substances, from easily degradable biological products to extremely stable polymers. Higher plants, micro-organisms and animals, polysaccharides, proteins, lignin, mercapto-compounds, nucleic acid derivatives, and other phosphoacids, when disposed to soils, are partially and quickly decomposed by enzyme systems of organisms in the soils. The monomers or simpler polymers of the substrate plus large amounts of energy derived from the oxidation of many of the monomeric compounds are released. Some of the monomers or simple polymers are reused by plants or other organisms growing in or on the soils, or they may recopolymerize with each other to form the stable humic substances of soil organic matter. These reactions result in various amino acids, sugars, bases, organic phosphorus compounds, and organic sulfur compounds found in soil. Also, numerous fats, waxes, and resins are found in soils. These chemicals can be broadly classified as hydrocarbons, alcohols, long-chain acids, sterols, terpenes, pigments, heterocyclics, and phospholipids.

Enzymes are proteins, that are synthesized by living cells, that are catalysts in biological reactions. Like all catalysts, they are effective in very small concentrations, speed up a reaction until equilibrium is reached, are unchanged by the reaction, and exhibit specificity for certain limited reactions.

1.3.3.3   Biological Soil Components--A vast number of organisms live in the soil. Those that have a significant effect on chemical degradation or that exist in significant numbers in soil are nematodes, protozoa, algae, fungi, actinomycetes and bacteria.

Nematodes are found in almost all soils, and are often present in large numbers. Some nematodes live on decaying organic matter; some on other nematodes, small earthworms, and the like; and others are parasitic, attacking the roots of high plants.

Protozoa depend on organic matter as a source of food. They are the most varied and numerous in the micro-animal population of soils. Usually, the numbers of protozoa is highest in the spring and autumn.

Most algae are chlorophyll bearing organisms and must live at or near the surface of the soil. All of the ordinary types of algae are greatly stimulated by the application of sludge, manures, and other organics.

Fungi play a very important part in the transformation of soil constituents. Fungi depend on organic matter for energy and carbon. Molds, one form of fungi, will grow vigorously in acidic, neutral, or alkaline soils. This is especially important in the decomposition of organics in acidic soils, where organic matter is ample and aeration adequate.

Actinomycetes are important in the dissolution of soil organics and liberation of nutrients. They can reduce even more resistant compounds to simpler forms . Actinomycetes develop best in moist, well aerated soil. But in times of drought, they remain active to a degree not generally exhibited by either bacteria or molds.

Bacteria are single-cell organisms, one of the simplest and smallest forms of life known. They can increase their number at a tremendous rate within a short period of time under favorable conditions. Bacteria transform matter via autotroph and heterotroph. The autotroph obtain their energy from the oxidation of simple mineral and inorganic constituents, such as ammonium, sulfur, iron, and get most of their carbon from carbon dioxide. Most soil bacteria are heterotrophic--that is, their energy and carbon both come directly from complex soil

organic matter. Among the most important conditions affecting bacteria growth in soil are the supplies of oxygen and moisture, the temperature, the amount and nature of the soil organic matter, the pH value, and the amount of exchangeable calcium present. Bioreclamation uses these organisms by providing the conditions necessary for them to degrade the organic contaminants in the soil.

1.4   WATER

1.4.1   Hydrologic Cycle

The endless circulation of water between ocean, atmosphere, and land can be schematically represented in Figure W-1, although the process is much more complicated. Inflow to the hydrologic system comes as precipitation, in the form
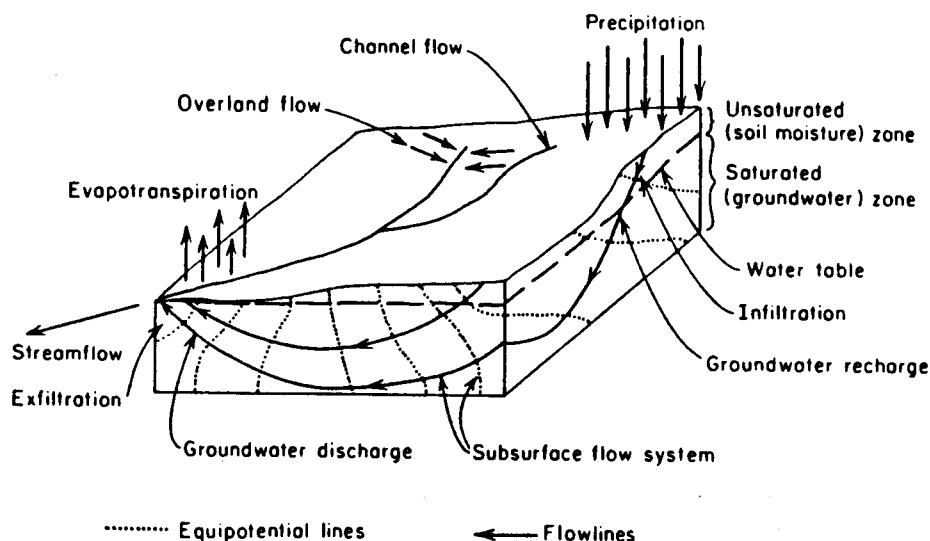

Figure W-1 Schematic reprsentation of the hydrologic cycle.

of rainfall or snowfall. Outflow takes place as streamflow, or runoff, and as evapotranspiration. The evapotranspiration is a combination of evaporation from open bodies of water, evaporation from soil surfaces, and transpiration from the soil by plants. Precipitation is delivered to streams both on the land surface, as overland flow to tributary channels; and by subsurface flow routes, as interflow and baseflow following infiltration into the soil. A watershed must be envisaged as a combination of both the surface drainage area and the parcel of subsurface soils and geologic formations that underlie it. As the hydrologic cycle continues, so does the evolution of chemicals in natural water.

1.4.2   Evaluation of Chemicals in Natural Waters

The chemistry of most surface waters and groundwaters is the result of interaction between rain, or snow, and rocks near the earth's surface. Much of this interaction takes place in the soil zone.

1.4.2.1   In Atmosphere--Atmospheric gases such as SO_2, NH_3, N_2O, NO_2, HCl, CO, and CO_2 are produced in substantial amounts by the burning of fuels, by metallurgical processes, by other anthropogenic activities, by biochemical processes in soil and water, and by volcanic or geothermal activity. Elements such as Ca, Mg, Pb, Na, Cl, etc. are also found in the atmosphere. As rainfall starts, water in the atmosphere would come in contact with these substances in the air. The amount of each substance in solution is proportional to the solubility and

the partial pressure of each and is dependent on the temperature and the atmospheric pressure. In an area with SO_2, NO_2, HCl, CO_2, etc. in the atmosphere, this leads to increased concentrations of H^+ and SO_4^{-2}, CO_3^{-2}, NO_3^{-1}, etc. in rain and snow and the formation of what is referred to as acid rain.

The composition of rain or snow will differ in different locations, and it may vary greatly with time at any one location. Among the various solutes in rainwater, the most important of these substances may be oxygen (O_2) because it imparts an appreciable oxidizing capability to the water.

In conclusion, rain and snowmelt are extremely dilute and slightly to moderately acidic oxidizing solutions that can cause chemical alteration in soil or in geologic materials into which they infiltrate.

1.4.2.2   On Soils--Here the term "soil" means the layer at the surface of the earth that has been sufficiently weathered physically, chemically, and biologically to provide for the growth of rooted plants. Almost all water that infiltrates into natural groundwater flow systems passes through the soil zone. The soil has a capability to generate relatively large amounts of acid and to consume much or all of the available dissolved oxygen in the water that infiltrates it.

Geochemically, the most important acid produced in the soil zone is H_2CO_3, which is derived from the reaction of CO_2 and H_2O. The CO_2 is generated by the decay of organic matters and by respiration of plant roots. Anaerobic reactions, such as the reduction of sulfate and nitrate, also generate CO_2 in a small amount. Carbon dioxide-charged water infiltrating through the soil zone commonly encounters minerals that is dissolvable, under the influence of H_2CO_3, and the mineral is consumed by the mineral-water reaction. As H_2CO_3 is consumed in the soil zone, oxidation of organic matter and respiration of plant roots continue the replenishment of CO_2 to the soil air. Other reactions, such as that from free oxygen reacting with reduced iron minerals, e.g. pyrite (FeS_2), also produce acidity.

In addition to the inorganic acids, there are many organic acids produced in the soil zone by biochemical processes. These substances, such as humic acid and fulvic acids, can play a major role in the development of soil profiles and in the transport of dissolved constituents downward toward the water table.

As groundwater moves along its flow paths in the saturated zone, total dissolved solids and most of the major ions normally increase. As would be expected from this generalization, it has been observed in the groundwater investigations in many parts of the world that shallow groundwater in recharge areas has less dissolved solids than the water deeper in the same system and less than the water in the shallow zones in the discharge areas.

1.4.3   Surface Water - Groundwater Relationship

The interrelationships between surface water and groundwater are of great importance in both regional and local hydrologic situations, and a wide variety of information can be obtained by analyzing streamflow data. Streamflow may consist of several components, including surface runoff, groundwater runoff, waste effluent, and precipitation that falls directly into the channel. The amount of water which falls directly onto the surface of lakes and reservoirs can be considerable, but the volume of water that is added by precipitation directly into the channel is relatively small compared to the stream's total flow. The contribution by waste effluent may or may not be significant, since waste effluent depends on the activities that are occurring in the basin.

1.4.3.1   Surface Runoff to Streamflow and Groundwater--Surface runoff, including interflow or stormflow, is the only source of water in ephemeral streams and intermittent streams during part of the year. It is the major cause of flooding. An ephemeral stream owes its entire flow to surface runoff. It may not have a well-defined channel, and the water table consistently remains below the bottom of the channel. Water leaks from the channel into the ground, recharging the underlying strata. Intermittent streams flow only part of the year, generally from spring to midsummer, as well as during wet periods. During a major surface runoff, the stage in the stream would be higher than the adjacent water table, and water would migrate from the stream into the ground. The stream would continue to lose water until the water table and river stage were equal. As water infiltrates in a recharge area, the mineral content or dissolved solids are relatively low, but will increase along

the flow path and with increasing distances.

1.4.3.2   Groundwater Runoff to Streamflow and Surface Water--When the stage of surface runoff is below the water table, groundwater runoff would begin. During dry season groundwater runoff may account for a stream's entire flow. It is the major source of water to streams from later summer to winter; at this time streams are also most highly mineralized under natural conditions.

In order to fully appreciate the origin and significance of groundwater runoff, it is necessary to first examine the groundwater flow system. Groundwater flow systems may be local, intermediate, or regional. And its flow paths may be short or long, amounting to a few yards on the local level to many miles in the regional level. Individual flow lines are, of course, influenced by the stratigraphy and, in particular, are controlled by hydraulic conductivity. In humid and semi-arid regions, the water table generally conforms to the surface topography. Consequently, the hydraulic gradient or water table slopes away from divides and topographically high areas toward adjacent low areas, such as streams and rivers. Topographic highs and lows, therefore, serve as recharge and discharge areas, respectively.

As water moves through the hydrologic cycle, its quality changes in response to differences in the physical, chemical, and biological environments through which it passes. The changes may be either natural or man-made; sometimes it is difficult to determine the origin (man-made or natural) of many water quality problems.

The chemical quality of water in surficial or shallow aquifers may range within fairly wide limits from one time to the next. Surficial or shallow aquifers, however, are not well protected from chemical changes brought about by natural events occurring on the land surface or from man-induced pollution, and are the most susceptible to rapid and sometimes dramatic changes in quality. Deeper or confined aquifers are generally characterized by nearly constant physical properties and chemical qualities that, at any particular site, reflect the geochemical reactions that occurred as the water migrated through confining layers and aquifers from its recharge area to the point of collection or discharge, at least on a local scale where the aquifer is unstressed by pumping. As mentioned before, the dissolved-solids content increases with depth and with the time and distance the water has traveled in the ground. A few uncommon water quality situations exist throughout the country, reflecting unusual geologic and hydrologic conditions. These situations include, among others, thermal areas and regions characterized by high concentrations of certain elements, some of which may be health hazards. This further implies that in any hydrologic study, the investigation should begin with or include an examination of geologic conditions.

1.4.4   Indicators of Water Quality and their Significance

The parameters in Table W-1 (on next page) are the important factors which are often used to measure and indicate the quality of natural water.

1.5   AIR

1.5.1   Background-Pollutants in Air

There are two sources of air pollution : natural and man-made. Sources of natural air pollution include wind blown dust, pollen, and other aero-allergens, sea-salt nuclei, smoke and flyash and gases from forest fires, microorganisms, gases and odors from swamps and marshes, fog, volcanic ash and gases, natural radioactivity, ozone from lightning and other natural processes, meteoritic dust and natural hazes, etc. Sources of man-made air pollutant include dust-producing processes such as crushing, grinding and demolition; combustion processes such as fuel burning and refuse incineration; manufacturing processes such as those in metallurgical plants and chemical plants; agricultural activities such as pesticides or herbicides spraying, crop dusting, plowing and field burning; and spills of various substances or chemicals.

By broad chemical categories, the major air pollutants and pollution sources can be found in Table A-1. Transportation, primarily automobile, contributed more pollution than all other sources together; and carbon

Table W-1 Indicators of Water Quality and their Significance

Parameters	Principal Cause	Significance	Remarks
1. Temperature	Weather-seasons, locations, geological condition.	Temperature affects: solubility, reactivity, physical and chemical balance, biochemical and biological activities.	
2. Dissolved oxygen (DO)	Temperature, pressure, other chemical components in water.	Higher forms of aquatic life and abiotic chemical reactions require oxygen for continuation.	
3. Redox Potential (Eh)	Temperature and the oxidation-reduction reaction of the involved species.	Also called as the oxidation potential of an aqueous solution. A transfer of electrons at chemical reaction is an electrical current, therefore, a redox equation has an electrical potential. The sign of the potential is positive if the reaction is oxidizing and negative if it is reducing.	
4. Hardness	Calcium and magnesium dissolved in the water.	Calcium and magnesium combine with soap to form insoluble precipitate (curd) and thus hamper the formation of the lather. Hardness also affects the suitability of water for use in the textile and paper industries and certain others and in steam boilers and water heaters.	USGS classification of hardness (mg/l as CaCO$_3$): 0-60: Soft; 61-120: Moderately hard; 121-180: Hard; More than 180: very hard.
5. pH (or hydrogen ion activity)	Dissociation of water molecules and of acids and bases dissolved in water.	The pH of water is a measure of its reactive characteristics. Low values of pH, particularly below pH 4, indicate a corrosive water that will tend to dissolve metals and other substances that it contacts. High values of pH, particularly above pH 8.5, indicate alkaline water that, on heating, will tend to form scale. the pH significantly affects the treatment and use of water.	pH values: less than 7, water is acidic; value of 7, water is neutral; more than 7, water is basic.
6. Specific electrical conductance	Substances that forms ions when dissolved in water.	Most substances dissolved in water dissociate into ions that can conduct an electrical current. Consequently, specific electrical conductance is a valuable indicator of the amount of material dissolved in water. The larger the conductance, the more minerals in the water.	Conductance values indicate the electrical conductivity, in micromhos, of 1 cm^2 of water at a temperature of 25° C.
7. Total dissolved solids	Mineral substances dissolved in water.	Total dissolved solids is a measure of the total amount of minerals dissolved in water and is, therefore, a very useful parameter in the evaluation of water quality. Water containing less than 500 mg/l is prefered for domestic use and for many industrial processes.	USGS classification of water based on dissolved solids (mg/l): Less than 1,000: Fresh; 1,000-3,000: slightly saline; 3,000-10,000: moderately saline; 10,000-35,000: very saline; More than 35,000: Briny.

Table A-1 ESTIMATED EMISSION OF AIR POLLUTANTS BY WEIGHT, NATIONWIDE, 1969 (in millions of tons per year)

Pollution Source	CO	Parti-culates	SO$_x$	HC	NO$_x$	Total	Change,% 1968-1969[a]
					Pollutant		
Transportation	111.5	0.8	1.1	19.8	11.2	144.4	-1.0
Fuel combustion in stationary sources	1.8	7.2	24.4	0.9	10.0	44.3	+2.5
Industrial processes	12.0	14.4	7.5	5.5	0.2	39.6	+7.3
Solid waste disposal	7.9	1.4	0.2	2.0	0.4	11.9	-1.0
Miscellaneous	18.2	11.4	0.2	9.2	2.0	41.0	+18.5
Total	151.4	35.2	33.4	37.4	23.8	281.2	+3.2
Change, % (1968-1969)	+1.3	+10.7	+5.7	+1.1	+4.8		

[a]Computed by the 1969 method from the difference between 1969 estimates and 1968 estimates. The new method results in higher values for 1968 than those computed by EPA for 1968.
SOURCE: The Mitre Corp. MTR-6013. Based on Environmental Protection Agency data.

monoxide alone outweighed the other four major pollutants combined.

As for hydrocarbons, most of the volatile hydrocarbons observed in natural gas, liquified petroleum gas, gasoline or other petroleum products have also been observed in ambient air. The most abundant ones are methane, ethane, propane, and higher alkanes, and their concentrations decrease more or less as the molecular weight increases. Of the components of automobile exhaust, ethylene and acetylene are the two largest hydrocarbon components. Of the members of the aromatic class, benzene is the most volatile substance, but is less abundant than toluene and m-xylene in most full-range petroleum fractions or products. Benzene levels in the atmosphere at selective sites are shown in Table A-2. Table A-3, from EPA Toxic Air Monitoring System (TAMS), shows various organics in the air for sites at Houston, Boston, and Chicago.

Table A-2. ATMOSPHERIC BENZENE LEVELS IN SELECTED SITES

Location	Average/Range(ppb)	Location	Average/Range(ppb)
Denver	3-30	Hartford, Conn.	6.9
Toronto	13-98	Waltham, Mass.	6.9
New Jersey (Collective sites)	Trace-94	Washington, D.C.	6.9
		Peoria, Ill.	5.3
Staten Island	0.7	Springfield, Ill.	3.1
Los Angeles	5.5	Oakbrook, Ill.	5.6
Long Beach	7.1	Remote sites,nationwide	0.3-1.1
St. Louis	18.9	Batelle, Ohio	1.6 Suburb
Baton Rouge	1.0		3.7 Downtown
Columbus, Ohio	2.4-5.1 Downtown		7.3 Near Highway
	2.2-8.6 Near Downtown		
	1.3-2.0 Suburb		

from: Indoor Air Petroleum Sampling and Analysis Protocol of NY DOH, October 1986.

Parameters that effect the movement and distribution of pollutants in outdoor air are vertical temperature structure, wind structure, topographic effects, and pollutant characteristics. The processes and interactions of these elements are quite complex and beyond our intended introduction here.

1.5.2 Indoor Air Quality

Indoor air quality also depends on many factors. These factors are indoor generating sources, outdoor air quality, indoor and outdoor air exchange rates, and the mixing of indoor air and pollutant characteristics. The

Table A-3   1986 TAMS TENAX DATA

Compound	Houston[a] Obs.[b]	Range,ppbv	Boston[c] Obs.[b]	Range,ppbv	Chicago[d] Obs.[b]	Range,ppbv
Benzene	9	0.56 - 2.48	23	0.39 - 2.57	25	0.48 - 2.51
Carbon tetrachloride	1	0.33			1	0.17
Cumene	12	0.02 - 0.13	2	0.02 - 0.03	7	0.03 - 0.38
Ethyl benzene	26	0.15 - 1.46	17	0.16 - 0.71	27	0.09 - 1.14
Methylene Chloride			1	0.52	2	0.40 - 0.41
Perchloroethylene	8	0.08 - 0.17	25	0.09 - 0.63	14	0.16 - 0.66
Styrene	6	0.30 - 0.72	4	0.02 - 0.38	4	0.25 - 0.28
Tetrahydrofuran			3	0.28 - 0.61	1	0.03
Toluene	26	0.39 - 9.56	25	0.38 - 4.96	27	0.92 - 6.54
1,1,1-Trichloroethane	2	0.26 - 0.50	8	0.23 - 1.11	19	0.16 - 1.00
Trichloroethylene			2	0.25 - 0.29	5	0.28 - 0.67
1,3,5-Trimethylbenzene	3	0.22 - 0.64	4	0.07 - 0.21	2	0.11 - 0.24
m &/or p-Xylene	20	0.22 - 2.96	19	0.27 - 2.19	24	0.12 - 3.67
o-Xylene	22	0.24 - 1.84	18	0.13 - 0.86	23	0.13 - 0.88

(a) 33 Sampling days - Data from 1/2/86 through 11/16/86 - Site 1
(b) Number of observations
(c) 37 Sampling days - Data from 1/2/86 through 9/17/86 - Site 1
(d) 34 Sampling days - Data from 1/9/86 through 11/16/86 - Site 1

indoor pollutants include asbestos from insulation materials; formaldehyde from particleboard, plywood, and foam insulation; carbon monoxide, nitrogen dioxide,and sulfur dioxide from kerosene and gas heaters, gas or wood stoves, and other fuel combustion sources; pesticides and semivolatile organics from spray and stripping operations; volatile organics from cooking, solvents, paints, wood burning, etc.; ozone from electrostatic air cleaners and radioactive radon and its progeny; and, many others.

Outdoor air contaminants affect indoor air quality primarily through indoor and outdoor air exchanges. Studies indicate that the indoor concentration of carbon monoxide (CO) increases, but at slower rates, as the outdoor concentration of CO rises, which would primarily be due to local traffic vehicles. The air exchange by the infiltration of air into a building with closed windows and doors, known as stack effect, prevails in the winter. During the summer, natural ventilation of air flowing into and out of a building through open windows and doors occurs more dominantly.

The characteristics of a pollutant are important in determining indoor concentrations. To illustrate, carbon monoxide (CO) and nitrogen dioxide (NO_2) that result from the same combustion sources behave differently even though they are released at the same time and are under the same conditions of air exchange rates. Reduction in NO_2 concentration is due not only to indoor air leaving the building through air exchange, as in the case of CO, but also to a chemical reaction that NO_2 undergoes, probably with various available indoor surfaces. Thus, NO_2 concentration decreases much more rapidly than CO.

Therefore, in determining indoor air quality the items to be considered are:

● Monitoring Objectives
● Pollution Sources and Pollutant Characteristics

- Monitoring Equipments-Methods
- Outdoor Conditions - Background
- Season and Weather
- Type of Building Structure and Materials
- Measuring Location
- Sampling Size and Numbers

1.5.3 Soil Air-Gas or Vapor

In the soils, the most abundant gases, which can also exist as dissolved gases in groundwater, are N_2, O_2, CO_2, CH_4 (methane), H_2S, and N_2O. The first three make up the earth's atmosphere, and are brought down with precipitation, and are found in subsurface water. CH_4, H_2S, and N_2O often can be found in groundwater in significant concentrations because they are the product of biogeochemical processes that occur in nonaerated subsurface zones. The gas production in the subsurface occurs by chemical or biochemical reactions involving the groundwater, minerals, organic matter, and bacterial activity. Hence, the concentrations of these gases can serve as indicators of geochemical conditions in groundwater.

The movement of gases in the subsurface primarily occurs by diffusion and advection, and is affected by the pore space of soil, soil moisture content, pore air pressure, gas vapor pressure gradient, temperature, and gas or vapor density. Diffusion is the mass transport that results from the random motion of vapor or gas molecules and is generally away from areas of high concentration toward areas of low concentration. Advection results from changes in the total pressure gradient and is the net downgradient migration of gases.

1.5.4 Points and Effects on the Measurement and Interpretation of Soil- Gas or Vapor

- Soil-gas measurements are an approximation of the parameter of interest, i.e., contamination in the underlying soils and/or groundwater.

- Soil-gas techniques are applicable to contaminated soils and water table aquifers but are relatively ineffective for confined acquifers or soils overlain by strata that are impermeable to gas diffusion.

- The applicability of soil-gas sampling to individual sites depends, largely, on the various sampling and analytical techniques that are used.

- Generally, soil-gas sampling is most applicable to sites at which the vadose zone is characterized by dry, coarse-grained soils containing a minimal organic carbon fraction. Organic material can act as a sink for volatile organic compounds (VOCs) diffusing vertically from the water table.

- Soil-gas sampling is probably more applicable to sites with water tables at 15 feet or greater than to sites with very shallow groundwater. Because the chemical concentration gradient can be very steep in soil gas in shallow groundwater conditions (e.g.,several orders-of-magnitude difference over a very short vertical distance), and slight variations in the groundwater elevation or water table depth can result in large variations in VOCs concentrations.

- Soil-gas sampling results are most reliable when the predominant transport mechanism is molecular diffusion rather than bulk gas flow.

- The most common site-specific interference to the mapping of groundwater contamination plumes using soil-gas techniques is the presence of barriers to gas diffusion in the vadose zone. These barriers include perched water, clay lenses, buried foundations, and irrigated or recently disturbed soils.

- The general rule of thumb for determining the applicability of soil-gas sampling to specific groundwater contaminants is that they should have a Henry's law constant of at least 0.05 kPa m^3/mol. and a vapor pressure of 1 mm Hg (at 20°C) or greater.

- Some compounds may be present in soil-gas but not in the underlying groundwater. Because these compounds can either partition predominantly into gaseous phase (e.g., chlorofluorocarbons) or are retarded during their migration in groundwater relative to their diffusion through soil gas (e.g., aliphatic hydrocarbons). Also gaseous compounds can be introduced directly to the soil gas through cracks or joints in underground sewer or natural gas lines.

- Certain compounds appear and disappear over time at the same sampling location because of changing conditions in the subsurface. For example, if the soil gas contains equal concentrations of tetrachloroethane (PCE) and methylene chloride, the latter can disappear, after a heavy rainfall, in two orders of magnitude relative to PCE as a result of methylene chloride's higher solubility. Similarly, conditions such as pH and redox potentials can change over time periods short enough to affect the relative concentrations of VOCs. Therefore, the mapping of a gasoline plume in groundwater using soil gas concentrations of butane and isooctane is recommended because aliphatic hydrocarbons are less susceptible to oxidation at the plume boundaries than are aromatic compounds such as benzene and toluene.

- Using soil gas contours to define the boundary of a contaminant plume in groundwater is rarely successful because compounds possessing low to moderate air/water partitioning coefficients are not present at high enough concentrations in soil gas to be detected and because compounds possessing high partitioning coefficients have usually diffused in soil gas beyond the groundwater plume.

- Reducing the soil-gas sampling interval will not necessarily provide better resolution of the mapping of the groundwater plume. As a rule of thumb, soil-gas probes that are sampled on centers less than two to three times the depth to groundwater are probably more indicative of small-scale heterogeneities in the vadose zone than of changes in the parameter of interest (e.g., VOC concentrations in the underlying groundwater).

In conclusion, the successful use of soil-gas surveying to assist in detecting and searching for VOC plumes in groundwater is as much dependent on interpretation and planning as on sample collection and analysis. The decision to conduct soil-gas investigation should be based on the probability of successfully interpreting data, not on the feasibility of collecting data.

1.5.5 Screening Techniques for Organics in Air

Typical commercially available screening techniques for organics in air as well as manufacturers, compounds detected, and approximate detection limits are listed in Table A-4.

Table A-4 TYPICAL COMMERCIALLY AVAILABLE SCREENING TECHNIQUES FOR ORGANICS IN AIR

Technique	Manufacturer	Compounds Detected	Approximate Detection Limit	Comments
Gas Detection Tubes	Draeger Matheson (Kitagawa)	Various organics and inorganics	0.1 to 1 ppmv	Sensitivity and selectivity highly dependent on componenet of interest
Continuous Flow Colorimeter	CEA Instruments, Inc.	Acrylonitrile, For-maldehyde, Phosgene, and various organics	0.05 to 0.5 ppmv	Sensitivity and selectivity similar to detector tubes
Colorimetric Tape Monitor	MDA Scientific	Toluene, diisocyanate, dinitrotoluene,Phosgene, and various inorganics	0.05 - 0.5 ppmv	Same as above
Infrared Analysis	Foxboro/Wilkes	Most organics	1 - 10 ppmv	Some inorganic gases (H_2O, CO) will be detected and therefore are potential interferences
FID (Total Hydrocarbon Analyzer)	Beckman; MSA. Inc.; AID, Inc.	Most organics	0.5 ppmvC	Responds uniformly to most organic compounds on a carbon basis
GC/FID (portable)	Foxboro/Century; AID, Inc.	Same as above except that polar compounds may not elute from the column	0.5 ppmvC	Qualitative as well as quantitative information obtained
PID and GC/PID (portable)	HNU, Inc.; AID, Inc.; Photovac, Inc.	Most organic compounds can be detected with the exception of methane	0.1 to 100 ppbv	Selectivity can be adjusted by selection of lamp energy. Aromatics most readily detected
GC/ECD (portable)	AID, Inc.	Halogenated and nitro substituted compounds	0.1 to 100 ppbv	Response varies widely from compound to compound
GC/FPD (portable)	AID, Inc.	Sulfur or phosphorus-containing compounds	10 to 100 ppbv	Both inorganic and organic sulfur or phosphorus compounds will be detected
Chemiluminescent Nitrogen Detector	Antek, Inc.	Nitrogen-containing compounds	0.1 ppmv (as N)	Inorganic nitrogen compounds will interfere

Source: Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air. EPA 600/4-83-027.