Information Paper 3.8.4
A Citizen Monitor's Guide to Hydrocarbons

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1.0 About this Information Paper

(This section is essentially common to all DQM Information Papers. If you have seen it already, please skip to Section 2 below). This Information Paper is a new type of guidance. It has been created for our new integrated system of guidance and tools for water quality monitoring called "the Data Quality Management (DQM) System". DQM is implemented by the Clean Water Team (CWT) where needed to support collection of reliable data of known quality in a fully documented, scientifically defensible manner. Most DQM materials are delivered in Parameter-Specific Folders, which provide both the traditional "protocol" materials and new, expanded guidance in three types of inter-related documents: Fact Sheet, Information Paper, and Standard Operation Procedures. Background information on the ecological significance of each parameter and the regulatory benchmarks that have been developed for it is summarized in the FACT SHEET. The technical information on measurement methodology provided in this IP with its method-menu. Then there are several detailed standard operating procedures (SOPs) that provide step-by-step instructions for each instrument or kit, as well as instrument-specific Quality Assurance/Quality Control and CCRR directions and data validation checklists.

This Information Paper (IP), a part of the Parameter-Specific Folder for hydro carbons (DO), provides "big picture" technical information on hydrocarbons. If you are a Trainer or a Technical Leader of any monitoring project, this may help you select a good method to measure hydrocarbons in your water body.

2.0 Hydrocarbons

What are Hydrocarbons?

Hydrocarbons are organic chemical compounds made up of carbon and hydrogen. They have a carbon backbone with hydrogen bases (Hydrocarbons and Chlorinated Solvents, 1). They can be straight-chain, branched, or cyclic in form. They are naturally found on earth, but are also altered and reformed through chemical reactions, such as combustion via the burning of fuel.

Where are they found?

Hydrocarbons can be found in nature and outside of nature:

Naturally Occurring Hydrocarbons

Hydrocarbons are found naturally on earth in both liquid (oil) and gas form. They are found in crude oil reservoirs both underground and underwater and in natural crude oil, tar, and gas seeps. They allow hydrocarbons to naturally come into contact with surface waters. Underground hydrocarbons can escape through rock fractures and reach underground water or rise unto the surface of land and be washed away. In California, crude that seeps out of the ground can be found at the La Brea Tar Pits in Los Angeles, and crude that seeps out of rock fractures under the sea and washes onto the shore can be found off the coast of Santa Barbara. These oil residues that wash onto the shores and create sheens over the ocean water add to water pollution concerns. Natural gas seeps are also found along the Southern California coast, where methane gas can be seen bubbling on the water surface.

Anthropogenic Hydrocarbons
Hydrocarbons that are affected by human activities (altered or moved from their natural state by humans) can be considered anthropogenic hydrocarbons. For example, crude oil is initially found underground, however; for human use it is continuously pumped and transported by ships or trucks to other areas to be refined (altered). In general, for human use, hydrocarbons tend to undergo a process of pumping, transportation, refinement, and distribution. Therefore, throughout this process, hydrocarbons can be found almost everywhere, from ships, to storage tanks, to trucks, to gasoline stations, to stores, to homes. They are in crude oils (for refining), fuels like gasoline and diesel, automobile oils, lubricating oils like Vaseline, plastics, pesticides, and dyes.

3.0 Types of Hydrocarbons

Hydrocarbons fall under one of the following categories: Paraffins, Olefins, Naphthenes, Aromatics, and Polycyclic aromatics.

Paraffins
Paraffins are characterized as molecules whose carbon atoms are connected by a single bond and whose remaining bonds are completely saturated with hydrogen atoms. For example, these include ethane, propane, normal butane, and isobutene (Figure 1). These saturated hydrocarbons follow the formula CnH2n+2 (Gary and Handwerk, 20-21).

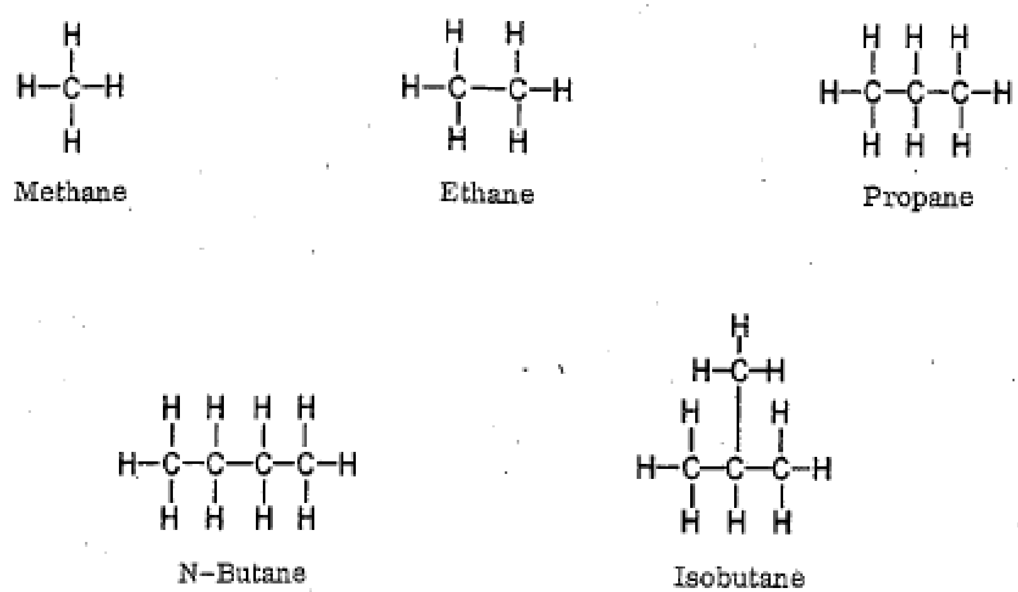

Figure 1: Examples of Paraffins (Gary and Handwerk, 21)

Olefins

Olefins are similar to paraffins, except that at least two of the carbon atoms are joined by double bonds. The double bond makes these molecules more reactive and more likely to polymerize (form high molecular weight unsaturated molecules). The general formula is CnH2n. Olefins do not occur naturally in crude oils but are formed during refining processes. In the process, diolefins (containing two double bonds) also form, but react fairly quickly to form polymers (Gary and Handwerk, 21).

Naphthenes

Naphthenes are cycloparaffin hydrocarbons (cyclic structure/form), in which the remaining carbon atoms are saturated with hydrogen. Examples of naphthenes are shown in Figure 2. Notice that like paraffins, napthenes have single bonds and are saturated with hydrogen atoms, but are in a cyclic form (Gary and Handwerk, 21).

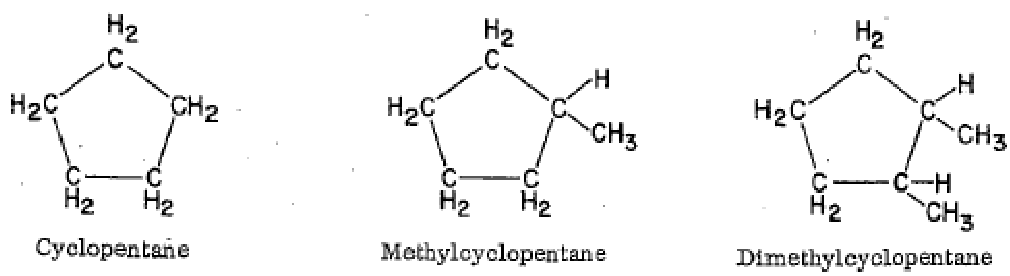

Figure 2: Examples of Naphthenes (Gary and Handwerk, 22)

Aromatics-

Aromatic hydrocarbons contain a benzene ring (refer to Figure 3), which is unsaturated, but relatively stable. Aromatics are chemically and physically very different from paraffins, olefins, and napthenes, primarily due to the benzene ring (Gary and Handwerk, 22). Examples of aromatics, including benzene, are shown in Figure 3.

Polycyclic Aromatic Hydrocarbons (PAHs):

Polycyclic aromatic hydrocarbons (PAHs) consist of merged aromatic rings. They are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. PAHs are usually found as a mixture containing two or more of these compounds, such as soot (Agency for Toxic Substances, 1). Examples of PAHs, including pericondensed (three or more rings share common carbon atom) and catacondensed (no more than two rings have a single carbon atom in common) PAH structures, are shown in Figure 4

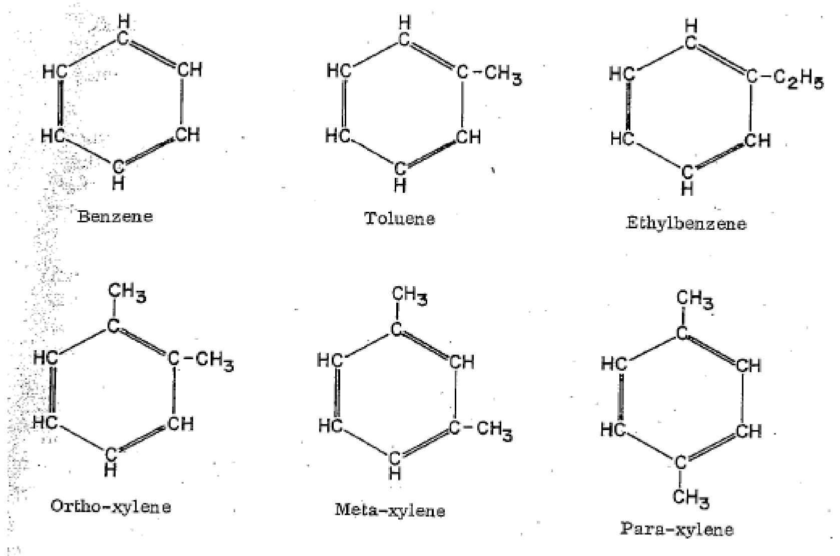

Figure 3: Examples of Aromatics (Gary and Handwerk, 23)

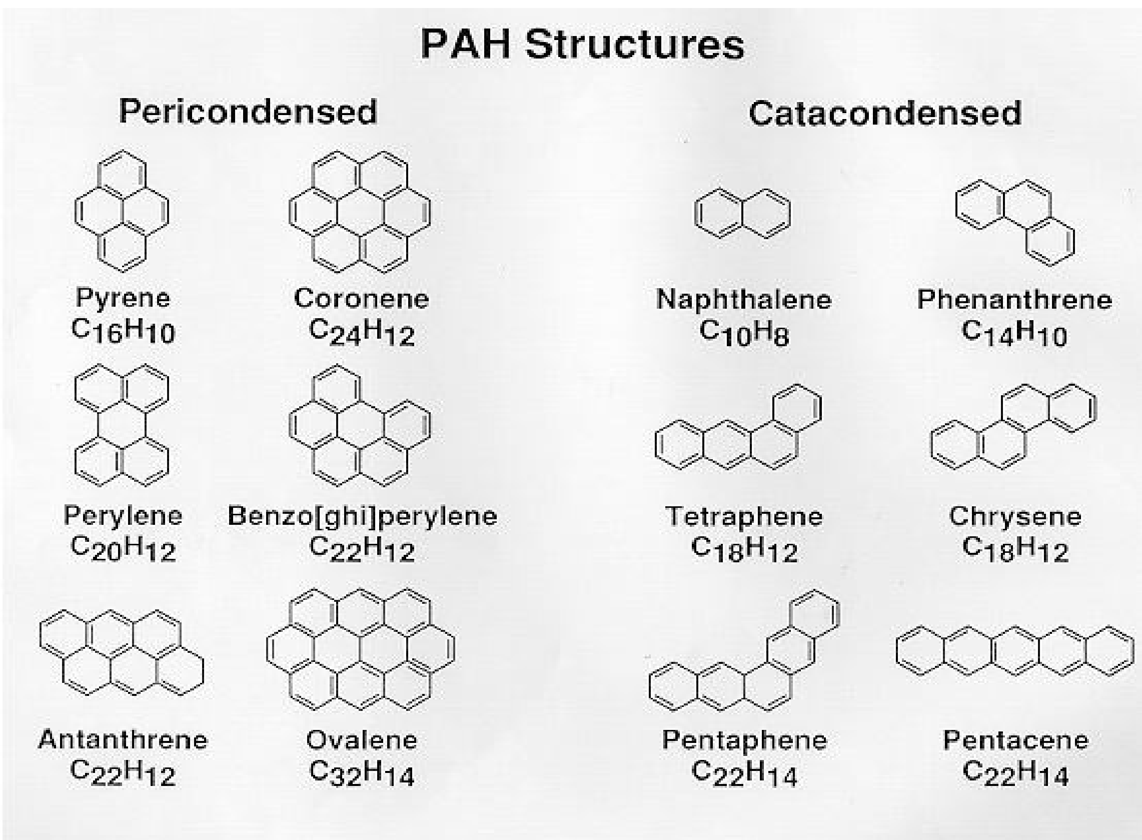

Figure 4: Examples of PAHs (Diffuse Interstellar Bands, 1)

Some PAHs are manufactured. These pure PAHs usually exist as colorless, white, or pale yellow-green solids. PAHs are found in coal tar, crude oil, creosote, and roofing tar, but a few are used in medicines or to make dyes, plastics, and pesticides (Agency for Toxic Substances, 1).

They are the most lethal hydrocarbon, and therefore more research work is done on PAHs than on other hydrocarbons.

In general, to help compare these hydrocarbons we know the following: Molecules with a larger carbon backbone have a larger molecular weight than those containing less carbon atoms. In addition, molecules with single bonds have weaker bonds than those with double bonds. This is because double bonds hold the atoms closer together than single bonds do. However, molecules with double bonds are generally more reactive than those with single bonds. Likewise, molecules with triple bonds are generally more reactive than those with double bonds.

4.0 Physical Properties of Hydrocarbons

Table 1 contains the main properties and uses for some of the single-chain hydrocarbons. This Properties Table only lists a few of the possible hydrocarbons. There are more hydrocarbons that have different forms and atom compositions, and, therefore, will have different properties. The different types of hydrocarbons were discussed in the previous section.

Table 1: Properties

Name	Molecular Formula	Molecular Mass	Melting Point (oC)	Boiling Point (oC)	State (25oC, 101.3 kPa)	Density (liquid g cm-3, 20oC)	Density (gas Kg/m3)	Solubility in Water (g/100ml water)	Uses
methane	CH4	16	-182	-162	gas		0.717	0.0035 (17◦C)	major component of natural gas (fuel)
ethane	C2H6	30	-183	-88.6	gas		1.212	4.7	component of natural gas (fuel)
propane	C3H8	44	-188	-42.1	gas		1.83	10 (37.8◦ C)	component of liquefied petroleum gas (LPG), bottled gas (fuel)
butane	C4H10	58	-138	-0.5	gas		2.48	0.0061 (20◦ C)	component of liquefied petroleum gas (LPG), cigarette lighters (fuel)
pentane	C5H12	72	-130	36.1	liquid	0.626		0.01 (20◦ C)	component of petrol (fuel)
hexane	C6H14	86	-95.3	68.7	liquid	0.659		Immiscible	component of petrol

									(fuel)
heptane	C7H16	100	-90.6	98.4	liquid	0.684		Immiscible	component of petrol (fuel)
octane	C8H18	114	-56.8	126	liquid	0.703		Immiscible	major component of petrol (fuel)
nonane	C9H20	128				0.718		Immiscible	component of petrol (fuel)
decane	C10H22	142	-30	174	liquid	0.730		Immiscible	component of petrol (fuel)
hexadecane	C16H34	226	18.5	288	liquid	0.775		insoluble	component of diesel fuel & heating oil
eicosane	C20H42	282	36	343	solid			insoluble	

Edited from: Summary Tables for Properties and Uses of Hydrocarbons and Pure Component Properties

Properties of Gas and Liquid Mixtures
The properties of a hydrocarbon gas or liquid mixture will depend on the properties of the hydrocarbon molecules in the mixture. For example, petroleum fuels contain different amounts of hydrocarbons since crude oils (which are refined to create petroleum fuels) naturally contain different compositions of hydrocarbons. Once the crude is refined for petroleum fuels and byproducts, these will contain different compositions of hydrocarbons depending on their purpose: jet fuel, automobile fuel, diesel fuel, or lubrication (oils).

Note: Hydrocarbons are highly flammable. Safety precautions must be taken when handling or storing hydrocarbons. The flashpoint is important when handling hydrocarbons, because it determines the minimum temperature at which the vapor pressure of a liquid is high enough for an explosive mixture to form with air.

Other Basic Properties: Color, Odor, and Feel
Hydrocarbon Gas: Generally colorless and odorless.

Petroleum Crude: The color varies from black to light amber. The odor of crude petroleum oils depends on their sulfur content. Those with higher sulfur content have a more intense "rotten egg" smell than oils with less sulfur content. The thick feeling of petroleum oils vary according to their viscosity (or thickness), and they have a waxy feeling depending on their content of paraffin wax.

How do hydrocarbon physical properties affect water quality?
The molecular weight, temperature ranges, and water solubilities of hydrocarbons are important because if hydrocarbons are present in water these properties will affect the impact they will have on water quality.

Molecular Weight & Density
In water, light hydrocarbons are expected to float to the surface and heavier ones are expected to sink. This will affect the range of depth that hydrocarbons could reach in various water bodies. At room temperature (about 25°C) water density is 1 g/cm3. Those hydrocarbons less dense than water (<1 g/cm3) will float and those denser than water (>1 g/cm3) will sink.

Temperature Range
The melting and boiling temperatures of hydrocarbons affect how easily hydrocarbons can spread. If the melting temperature for a hydrocarbon is met then the hydrocarbon can spread more easily in water, and if the boiling temperature of the hydrocarbon is met, it can emit fumes that can also spread in the air.

Water Solubility
Soluble, immiscible, and insoluble hydrocarbons will all affect water quality. Their solubility in water will affect hydrocarbon spread and flow. The more soluble hydrocarbons will spread more easily by dissolving, the immiscible hydrocarbons will separate from water and either sink or float, and the insoluble hydrocarbons will also separate from water.

5.0 Causes of Hydrocarbon Pollution

Indirect Water Pollution (through air pollution, atmospheric deposition)
Hydrocarbon pollution affects both air and water quality. Air pollution affects water quality by introducing air pollution particles into surface waters through wet deposition (washing away particles from the air with water, usually by rain) and dry deposition (settlement of particles into the water).

Wet and dry deposition refers to deposited material from the atmosphere containing higher than normal amounts of nitric and sulfuric acids. Wet and dry deposition is also referred to as acid rain. The precursors of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO2) and nitrogen oxides (NOx) resulting from fossil fuel combustion. In the United States, roughly 2/3 of all SO2 and 1/4 of all NOx come from electric power generation from burning fossil fuels, like coal. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid. When sulfur dioxide and nitrogen oxides are released from power plants and other sources, prevailing winds blow these compounds across state and national borders, sometimes over hundreds of miles (What is Acid Rain, pars. 1).

Wet Deposition
Wet deposition refers to acidic rain, fog, and snow. If the acid chemicals in the air are blown into areas where the weather is wet, the acids can fall to the ground in the form of rain, snow, fog, or mist. As this acidic water flows over and through the ground, it affects a variety of plants and animals. The strength of the effects depends on several factors including the acidity of the water, the chemistry and buffering (alkalinity) capacity of the soils involved, and the types of fish, trees, and other living things that rely on the water (What is Acid Rain, pars. 2).

Dry Deposition
In areas where the weather is dry, the acid chemicals may become incorporated into dust or smoke and fall to the ground through dry deposition, sticking to the ground, buildings, homes, cars, and trees. Dry deposited gases and particles can be washed from these surfaces by rainstorms, leading to increased runoff that can end up in surface waters. Runoff water makes the resulting mixture more acidic. About half of the acidity in the atmosphere falls back to earth through dry deposition. The dry deposited particles can also settle down on their own into surface waters (What is Acid Rain, pars. 3). Figure 5 shows how gases and particles in the air descend onto land and water through wet and dry deposition.

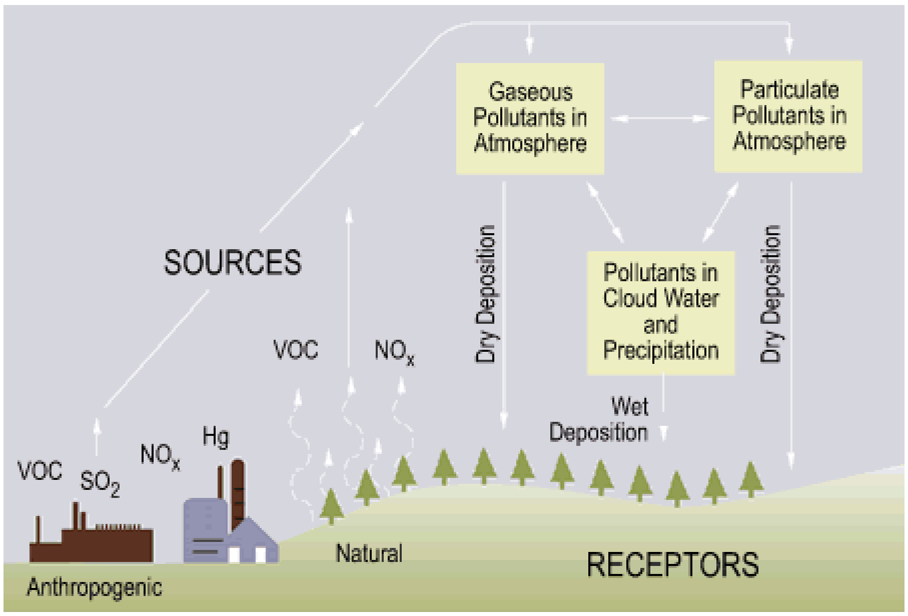

Figure 5: Sources and Receptors (What is Acid Rain, 1)

Direct Water Pollution
Direct water pollution can occur through natural or anthropogenic factors. As mentioned in the introduction, naturally occurring hydrocarbons are found in gas and oil seeps both underground and underwater. In the ocean, natural oil that seeps from rock fractures under the sea can harm marine creatures. It can harm marine birds by sticking onto their feathers and preventing them from properly flying away. Also, oil that seeps from underground can reach surface water and pollute it, harming or killing other creatures, and possible even affecting drinking water. Natural gas bubbles from gas seeps will also pollute water because the gas, mostly methane, is soluble in water.

Although there are natural causes of hydrocarbon water pollution, the most notable pollution is caused through anthropogenic hydrocarbons. Main causes of anthropogenic hydrocarbon pollution in water are from marine crude oil spills, oil field operation explosions from exploratory oil wells at sea, gasoline underground storage tank leaks, and human misuse of hydrocarbons.

Oil Spills

Oil spills are the most severe problem associated with hydrocarbon pollution. This is because it is the most catastrophic; it has the most noticeable effects immediately. They occur when a liquid petroleum hydrocarbon (crude oil) is released from a tanker (the ship that transports the crude oil) into the ocean or coastal waters. The released oil spreads in the water affecting the natural wild life present. A historical example of an oil spill is the 11,000,000 gallon Exxon Valdez Oil Spill in Prince William Sound, Alaska on March 24, 1989 that caused the worse oil spill in U.S. history. The tanker struck a reef in Prince William Sound. Within two months the oil spread over 470 miles southwest from the spill area (Events Mark Oil-spill date, pars. 1). More recently, on November 7, 2007, a South Korea-bound ship struck a tower supporting the San Francisco-Oakland Bay Bridge in dense fog, releasing 58,000 gallons of oil in San Francisco Bay (Oil Spill, pars. 1-5).

Exploratory Well Explosions
Explosions of oil wells at sea also release hydrocarbons into the water. In 1979 an exploratory oil well, Ixtoc 1, blew up, spilling an estimated 140 million gallons of crude oil into the open sea (Oils Spills and Disasters, pars. 5).

Underground Storage Tanks
The majority of underground storage tanks (USTs) contain hydrocarbon fuels and are most common in gasoline stations. Hydrocarbons can leak out of gaps or corroded areas in the UST. They penetrate underground soils and reach underground water and contaminate it. The major hydrocarbon contaminants from USTs at gasoline stations are benzene, toluene, ethylbenzene, xylenes, methyl tertiary butyl ether (MTBE), and tertiary butyl alcohol (TBA) (Boulder Area, pars. 2). Previously, USTs were made of steel or concrete, but current specifications require them to be of fiberglass in order to prevent leakage from corrosion.

Note: MTBE is no longer used in petroleum fuels, but current underground water contamination from this hydrocarbon is present due to past UST leaks.

Misuse of Hydrocarbons
Fuels that leak from cars or are spilled on the ground can be washed away with water, into the soil, and into waterways. This will reach and contaminate underground and surface waters. Incorrectly disposing of used fuels and oils down the sewage system will also reach and contaminate surface water.

6.0 Environmental Impacts

Animals and plants can be impacted by direct physical contact with the oil. For example, filter feeding shellfish and bird eggs can be smothered by oil. The feathers of birds or the fur of seals lose their insulating properties when coated with oil, leading to the danger of death from the cold. Birds can also drown when their feathers become matted with oil. Oil can destroy food resources, directly killing prey species and also tainting the way they taste and smell and making them unacceptable as food. If ingested, oil can damage the digestive system. Oil vapors have the potential to damage the nervous system of animals, as well as damaging their lungs and liver (Casco Bay, 1).

Concentrations of hydrocarbons, especially PAHs, can prove toxic to marine fauna. A study conducted using caged mussels to determine the toxicity of the Exxon Valdez Oil Spill indicated that hydrocarbons were available to subsurface marine fauna, such as fish and invertebrates during the summer after the spill. At these trophic levels, marine fauna would be affected through the ingestion of hydrocarbons (American Fisheries Society, 29). In addition, after an oil spill, oil can travel from oiled beaches to adjacent shallow subtidal sediment, and also reach benthic surface and core sediment (Figure 6) (American Fisheries Society, 40). Toxicity at these depths will affect the benthos, the organisms living in this zone, which include sea stars, oysters, clams, and sea cucumbers.

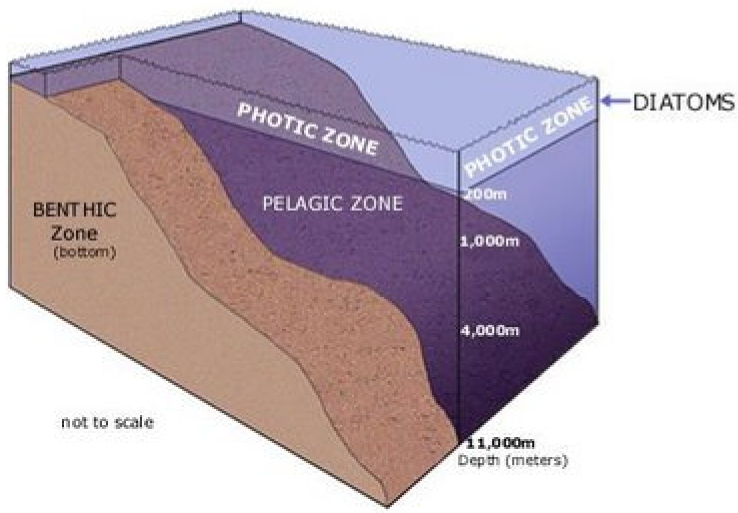

Figure 6: Benthic Zone (Marine Biology: Habitat, 1)

As far as water pollution goes, the PAHs are the type of hydrocarbons that are causing very serious problems. PAHs enter the air mostly as releases from volcanoes, forest fires, burning coal, and automobile exhaust, and can occur in air attached to dust particles. Some PAH particles can readily evaporate into the air from soil or surface waters. PAHs enter water through discharges from industrial and wastewater treatment plants and most of them do not dissolve easily in water. They stick to solid particles and settle to the bottoms of lakes or rivers. Microorganisms can break down PAHs in soil or water after a period of weeks to months. In soils, PAHs are most likely to stick tightly to particles; certain PAHs move through soil to contaminate underground water (Agency for Toxic Substances, 1).

PAHs are mutagenic (cause body mutations), morphogenic (cause deformities), carcinogenic (cause cancer), and teratogenic (cause fetal mutations). Recently there has been an effort in stopping hydrocarbon water pollution, but still each year 157,500,000 gallons of oil and hydrocarbon emissions are being dumped into oceans and lakes and seep into our ground water. Added to this number is the amount of hydrocarbons that reach water from atmospheric fall out. Another prominent problem is hydrocarbons contaminating our ground water. If underground water near a water well is contaminated, the water well can also become contaminated. This can adversely affect drinking water (Hydrocarbons and Chlorinated Solvents, 1).

Hydrocarbon contaminations also have secondary impacts such as one in the Suez geographic region. The Suez petroleum geographic region, which is shared by several oil companies, had a massive fire incident in August 2000, which killed 8 people. The primary reason contributing to this environmental hazard was the petroleum hydrocarbon release to subsurface water (Afifi).

7.0 Exposure and Health Impacts

As mentioned in the previous section, hydrocarbons are a concern because some compounds have been identified as carcinogenic (cancer causing), mutagenic (can increase frequency of mutation), and teratogenic (able to disturb the development of an embryo). They can also damage the nervous system, lungs, and liver.

PAHs can enter human body through breathing air containing PAHs in the workplace of coking, coal-tar, and asphalt production plants, smokehouses, and municipal trash incineration facilities. It can also enter by breathing air containing PAHs from cigarette smoke, wood smoke, vehicle exhausts, asphalt roads, or agricultural burn smoke. People can also become toxicated by eating grilled or charred meats; contaminated cereals, flour, bread, vegetables, fruits, meats; and processed or pickled foods and by drinking contaminated water or cow's milk (Agency for Toxic Substances, 1).

The toxic effect of PAHs on human health has not been confirmed yet. However harmful effects such as birth defects, problems with pregnancies and the ability to fight disease have been experienced in laboratory animals. Mice that were fed high levels of one PAH during pregnancy had difficulty reproducing and so did their offspring. These offspring also had higher rates of birth defects and lower body weights. It is not known whether these effects occur in people. Animal studies have also shown that PAHs can cause harmful effects on the skin, body fluids, and ability to fight disease after both short- and long-term exposure. But these effects have not been seen in people (Agency for Toxic Substances, 1).

The Department of Health and Human Services (DHHS) has determined that some PAHs may reasonably be expected to be carcinogens. People who have breathed or touched mixtures of PAHs and other chemicals for long periods of time have developed cancer. Some PAHs have caused cancer in laboratory animals: lung cancer from inhalation, stomach cancer from ingestion, and skin cancer from contact or application to the skin (Agency for Toxic Substances, 1).

8.0 Hydrocarbon Identification and Measurement

Visual

A quick look at water can help identify the presence of oil hydrocarbons. Primarily, as seen in Figure 7, oil hydrocarbons will create sheen that appears on the surface of water. The presence of sheen is an indication of the presence of hydrocarbons.

Figure 7: Oil sheen on Water (Oil Sheen, 1)

Quantitative
Analyzers, such as a portable infrared analyzer, can be used to measure hydrocarbon contamination in water. Water samples can also be examined in a lab to detect hydrocarbon contamination.

9.0 Water Quality Benchmarks and Typical Ranges

The Occupational Safety and Health Administration (OSHA) has set a limit of 0.2 milligrams of PAHs per cubic meter of air (0.2 mg/m3). The OSHA Permissible Exposure Limit (PEL) for mineral oil mist that contains PAHs is 5 mg/m3 averaged over an 8-hour exposure period.

The National Institute for Occupational Safety and Health (NIOSH) recommends that the average workplace air levels for coal tar products not exceed 0.1 mg/m3 for a 10-hour workday, within a 40-hour workweek. There are other limits for workplace exposure for things that contain PAHs, such as coal, coal tar, and mineral oil (Agency for Toxic Substances, 1).

In addition there are limits for contamination of underground water from hydrocarbons. The party responsible for the contamination (for example, gasoline stations) is also responsible for the cleanup and remediation and for keeping contamination below allowed maximum levels. The EPA Maximum contaminant Level (MCL) for benzene is 5 parts per billion (ppb). Higher levels of benzene increase the risk of cancer. As for toluene and ehtylbenzene, which are not considered carcinogenic, their MCLs are higher: 1.0 and 0.7 parts per million (ppm), respectively. Nevertheless, overtime, toluene and ehtylbenzene are harmful to the liver, kidneys, and central nervous system, and therefore need to be monitored. Xylenes (ortho-, meta-, and para-xylene) are also considered harmful to the liver, kidneys, and central nervous system, and their MCL for total xylenes is 10 ppm.

10.0 Preventative Anti-Pollution Measures

Preventative measures can be taken by commerce, industry, and governments. Federal and state regulations limit the amount of hydrocarbon emissions to prevent hydrocarbon contamination in water. Regulations can also require industries to implement best management practices (effective, practical structural or nonstructural methods to prevent movement of pollutants to surface or ground water) to prevent future water contamination due to industrial activities. In addition, citizens can also take preventative measures to avoid water contamination. Organizations, such as Heal the Bay, encourage citizens to recycle used oils or to dispose of them in appropriate waste disposal facilities instead of throwing them down the drain, as it was customary in the past. The best preventative practice is to avoid the use of hydrocarbon oils and to completely eliminate hydrocarbon emission. However, this is not realistically possible, the next best measure is to follow best management practices when utilizing hydrocarbons and to dispose of the used hydrocarbons appropriately at waste management facilities.

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