

Chapter 3. Synthetic Organic Chemicals: Plastics:

Plastics: In Our Environment and in our Bodies

Background. A vast majority of synthesized chemicals are also organic. Plastics, are all synthetic organic compounds. Synthetic organic compounds are those that are derived from either coal or from petroleum and are, by and large, petrochemicals. Coal is from dead plants; petroleum is from dead animals (Animals are oily).^{i ii}

The annual production of plastics has increased from half a million tons in 1950 to over 260 million tons in 2009. The quantity of plastics synthesized in the 1st decade of the 21st century, approaches the total production of the entire 100 years that preceded it. No category of synthetic chemicals has increased its rate of production faster than plastics. Plastic now consumes 8% of the world's oil production.ⁱⁱⁱ

In this exercise we will explore the concept that synthetic organic chemicals are similar enough to naturally occurring chemicals to react with us, but are different enough to not easily go away.



Directions for Exercises 1 – 4.: In this exercise you will be researching one of the following categories of plastic products: **1.**

Polyvinylchloride (PVC), 2. Phthalates, 3. Bisphenol-A, or 4. Formaldehyde.

1. Name some other products, not mentioned that contain these plastic formulations. What are/were the benefits to society of the plastic product that you have selected for study?
2. What is the life span of the product and how is it disposed (Cradle to Grave)?
3. What happens to it after disposal? Discuss the break-down product(s).
4. What happens to the plastic product when it is burned? Are there any health hazards as a result of burning?
5. Discuss studies that have been conducted on health effects of these products, especially for infant and children's exposure.
6. Conduct a Risk/ Benefit analysis of this chemical: What are health and economic benefits, weighed against health and environmental risks or hazards.
7. Look at the body burden of these chemicals in both human and animal species. What does this tell you about the persistence and potential danger of these plastics?
8. Are there alternatives to these products in the marketplace? If so, are they cost effective?
9. What can be done to reduce exposure to the by-products of these compounds? What can you do personally?



Exercise #1. Polyvinylchloride (PVC)

Polyvinyl chloride (PVC), is a thermoplastic, vinyl polymer. constructed of repeating vinyl groups (ethenyls) having one of their hydrogens replaced with a chloride group. Polyvinyl chloride is the third most widely produced plastic in the world, after polyethylene and polypropylene.^{iv} PVC is widely used in construction because it is cheap, durable, and easy to assemble. PVC production is expected to exceed 40 million tons by 2016.^v

By the addition of plasticizers, such as phthalates, PVC can be made softer and more flexible. In this form, it is used in clothing, upholstery, flexible hoses and tubing, flooring, roofing membranes, and electrical cable insulation. PVC and its basic compound, vinyl chloride, are everywhere: in children's toys, garden hoses, wall paper, in office supplies and in the shrink-wrap that supermarkets use. It is also commonly used in inflatable products such as waterbeds, pool toys, and other inflatable structures.

PVC is fabricated from petroleum on a base of chlorine, embellished with various toxic additives, including lead. Undegradable substances like vinyl, including PVC, are quite inert in the middle of their life span, however, In the beginning the vinylchloride (VC) is a highly reactive synthetic chemical, a powerful liver carcinogen and violently explosive. In the presence of moisture, the chlorine molecules will disassociate from the compound, attach to hydrogen, forming hydrochloric acid, liquefying your lungs if inhaled.^{vi}



PVC cannot be recycled with other plastics, or it will contaminate the entire batch. That means that PVC items wind up in landfills or are dumped from barges into the sea. We see the presence of these PVC products every time we go to the beach. From the tropics to the poles, it is ubiquitous.

These chlorine-based products present hazards in landfills, because when vinyl chloride breaks down in a land fill, it transmutes into other toxic substances, such as TCE, easily poisoning water supplies. Whenever elemental chlorine is present, the natural environment will synthesize additional organochlorine molecules. When water containing decayed leaves is chlorinated, organochlorines are produced, the most common example of this process occurs when plastics are burned (in fires) or incinerated in power plants.^{vii} If PVC is burned, it becomes dioxin.

The manufacture of PVC products annually releases thousands of pounds of carcinogenic vinyl chloride gas into the air and into the water supply of communities, endangering families in surrounding neighborhoods.^{viii}

Questions: Refer to questions on previous page and adapt to PVC.



Exercise #2: Phthalates

Phthalates are what gives PVC plastic products their flexibility and are responsible for the smell of new car interiors or a new vinyl shower curtain. They are used to carry fragrance in perfumes and lotions. Phthalates are also found in foods, especially those with high fat content, such as eggs, milk, cheese, margarine and seafood. (Phthalates, like flame retardants, disrupt the body's hormones.^{ix})



A CDC body burden survey found near ubiquitous exposure to phthalates among all ages with the highest levels in children.^x School age children carry a burden of about 1 ½ x more phthalates than adults.^{xi} Women of child bearing age have a higher level of phthalates, suspected of disrupting the fetal hormone system.^{xii} Prenatal exposure to phthalates is associated with altered development of the male reproductive tract.^{xiii} Phthalates can also alter gender-specific behavior in boys.^{xiv} Studies have shown that the higher the concentration of phthalates in children's urine, the worse the ADHD and test scores.^{xv}

The National Toxicology Program's Center for the Evaluation of Risks to Human Reproduction concluded that the evidence of harm to adults was inconclusive, however, there is concern about infants and toddler exposure. The most recent CDC survey of Americans body burden showed that 11 of 12 phthalates were higher in children than adults.^{xvi}



How are we exposed to Phthalates? Babies chewing on some brands of teething rings are ingesting some phthalate molecules.^{xvii} Bath toys, including the rubber ducky are also made of phthalates. Barbie dolls are made of PVC and phthalates.

In the bathroom, the distinctive odor of a new vinyl shower curtain, means that it is outgassing both phthalates and 108 other chemicals.^{xviii} The new car smell is actually the odor of leaching

phthalates and other volatile chemicals.^{xix}

Phthalates are regulated as toxic substances under the major US law controlling industrial chemicals, but "companies are free to use unlimited amounts in cosmetics". (Env. Working Group study)^{xx} Much make-up, perfume and shave lotions contain phthalates that are absorbed into the skin, pollute the air and after a few hours, are found in the urine.^{xxi} 37 popular Nail products: polishes, top coats, and hardeners, contain phthalates, solvents and formaldehyde. Manufacturers include L'Oreal, Maybelene, Oil of Olay, Cover Girl. Many lipsticks (Revlon) contain phthalates.^{xxii} (Avon products do not contain phthalates).



Plastic food containers are often made of PVC with phthalates, as is plastic wrap. Microwaving meals in these containers, or with plastic wrap exposes all people to phthalates via ingestion. (Glad Cling Wrap and S.C. Johnson's Saran Wrap contain no phthalates).^{xxiii xxiv}

The problem is that phthalates can easily leach out of plastic products because they are not chemically bonded to the PVC plastic polymer. Phthalates are not just absorbed into the human body, in fact they have even been found in deep sea jellyfish more than 3,000 ft below the surface of the Atlantic Ocean.^{xxv}

Questions: Refer to questions on Plastics Background page and adapt to Phthalates.

Exercise #3: Bisphenol-A

Background. Chemicals like bisphenol A (BPA) and phthalates, key ingredients in modern plastics, may disrupt the endocrine system, leading to a plethora of developmental problems or illnesses such as obesity, diabetes, autism, and ADHD.

Bisphenol-A (BPA), was originally invented in 1936 as synthetic estrogen. This plastic is used in many plastic water bottles, polycarbonate baby bottles, in Sippy cups, teething toys and in many re-useable and microwavable food and drink containers.^{xxvi} Bisphenol-A is also found in the plastic resins used in dental materials, and the linings of metal food and infant formula cans, soft drink cans, water supply pipes and dental sealants used on children's teeth to prevent cavities.



Today, 6.4 billion pounds (2.7 billion kg) of Bisphenol-A is produced each year generating \$6 million / day for manufacturers in the US, Japan and Europe.^{xxvii}

The problem with plastics containing BPA, is that the chemical bonds that create the polycarbonate polymer in plastics are not stable. They degrade in water and heat, when exposed to alcohol, soaps or acids, and simply with age. As they break-up, Bisphenol-A leaches out into food and water that enters the human body.^{xxviii}



The CDC has found BPA in the urine of 93% of surveyed Americans over the age of 6. If you do not have BPA in you, you are not living in the modern world. The levels of BPA are below the federal safety threshold of 50 micrograms per kg of body weight per day, but that tolerance level was set 22 years ago, and scientists have since discovered the damage that even a tiny bit of BPA can cause. As scientists are getting better at detecting the chemicals in our bodies, they are discovering that even tiny quantities of BPA can have a potentially serious impact on both our and our children's health.

Hundreds of published studies have found that laboratory animals exposed to low levels of BPA have elevated rates diabetes, mammary and prostate cancers, decreased sperm count, reproductive problems, early puberty, obesity, and neurological problems. In animal laboratory studies, even at very low doses of bisphenol-A, rats turn hyperactive and aggressive.^{xxix} Some scientists believe that humans, especially infants, are currently exposed to levels that are known to cause harm in laboratory animals. In body burden studies, BPA remains far longer in the bodies of babies because they lack a crucial liver enzyme that would break down and excrete it. In some babies, BPA has accumulated to levels up to 11x higher than in adults.^{xxx}

The US FDA and the chemical industry maintain that BPA is safe, but the US Congress took steps to restrict the use of bisphenol A and asked the FDA to reexamine it. In August of 2008, the FDA issued a draft reassessment, reconfirming their initial opinion that, based on scientific evidence, it is safe,^{xxxi} however by October, the FDA's advisory Science Board sent FDA back to the drawing board, concluding that the Agency's assessment was "flawed" and hadn't proven the chemical to be safe for formula-fed infants.^{xxxii} Canada has been phasing out the use of bisphenol A in baby bottles and metal formula cans^{xxxiii} and Nalgene, Playtex, and Wal-Mart had removed BPA from their products by 2009.^{xxxiv}

Questions: Refer to questions on Plastics Background page and adapt to BPA.

Exercise #4: Formaldehyde

Formaldehyde is a colorless, flammable, strong-smelling chemical that is used in building materials and to produce many household products. It is used in pressed-wood products, such as particleboard, plywood, and fiberboard; glues and adhesives; permanent-press fabrics; paper product coatings; and certain insulation materials. In addition, formaldehyde is commonly used as an industrial fungicide, germicide, and disinfectant, and as a preservative in mortuaries and medical laboratories.

Prior to the development of formaldehyde, wood glue was derived from soybeans. After WWII soybeans were replaced by formaldehyde for adhesives. Formaldehyde has been classified as a probable carcinogen by the EPA and is listed as a known carcinogen by the International Agency for Research on Cancer.

If your babies' furniture is made of pressed wood, it is most likely glued together with formaldehyde. In addition, some baby shampoo contains formaldehyde, and some air fresheners contain multiple volatile organic compounds, such as formaldehyde, and phthalates, further exposing infants and adults to this probable carcinogen.^{xxxv}

Formaldehyde ranks among the top 50 chemicals with highest US production rates. In 2000, 11.3 billion gallons were produced. According to a 1997 report by the U.S. Consumer Product Safety Commission, formaldehyde is normally present in both indoor and outdoor air at low levels, usually less than 0.03 parts of formaldehyde parts per million (ppm) of air. Materials containing formaldehyde can release formaldehyde gas or vapor into the air. Pressed-wood products containing formaldehyde resins are often a significant source of formaldehyde in homes. Its subsequent evaporation from construction materials and furniture makes this chemical a significant contributor of indoor air pollution.^{xxxvi}

When formaldehyde is present in the air at levels exceeding 0.1 ppm, some individuals may experience adverse effects such as watery eyes; burning sensations in the eyes, nose, and throat; coughing; wheezing; nausea; and skin irritation. Some people are very sensitive to formaldehyde, whereas others have no reaction to the same level of exposure.

In 1980, laboratory studies showed that exposure to formaldehyde could cause nasal cancer in rats. This finding raised the question of whether formaldehyde exposure could also cause

cancer in humans. In 1987, the US EPA classified formaldehyde as a probable human carcinogen under high or prolonged exposure.^{xxxvii} Since then, studies of humans have suggested that formaldehyde exposure is associated with certain types of cancer such as nasopharyngeal cancer, leukemia, lymphatic cancers and brain tumors. The International Agency for Research on Cancer (IARC) classifies formaldehyde as a human carcinogen.^{xxxviii}

Questions: Refer to questions on the Plastics Background page and adapt to formaldehyde.



Exercise 5. Dioxin

Not all organochlorines are produced in factories. Whenever elemental chlorine is present, the natural environment will synthesize additional organochlorine molecules. When water containing decayed leaves is chlorinated, organochlorines are produced, the most common example of this process occurs when plastics are burned (in fires) or incinerated in power plants.^{xxxix}

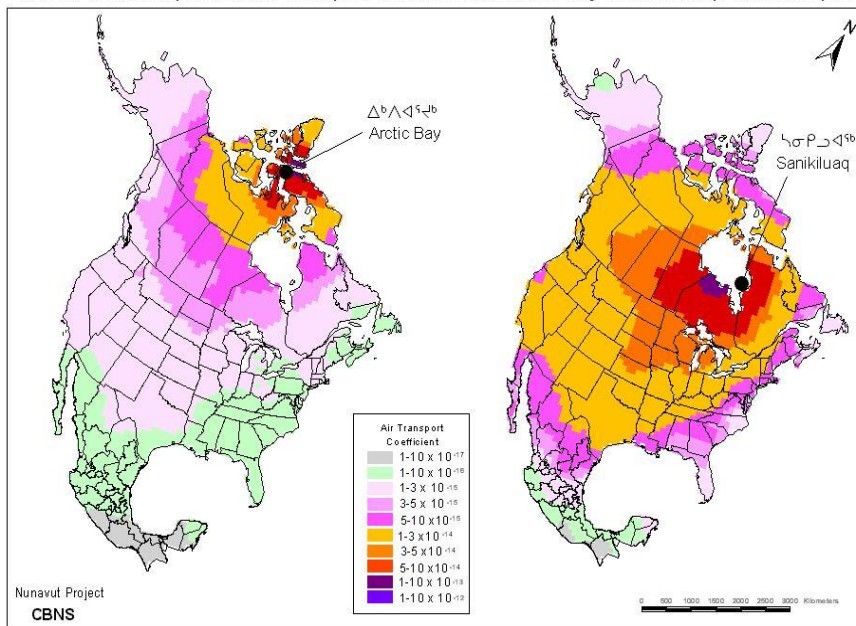


Dioxin is a chemical of no usefulness, has never been intentionally produced, is linked to a variety of cancers and is now believed to inhabit the body of every person living in the United States. The production of 2,4,5-T, the burning of plastic and some paper bleaching processes all contribute to the growing environmental burden of dioxin. Dioxin consists of two chlorinated carbon rings, held together by a double bridge of oxygen atoms, and like most other synthetic organochlorines, is extremely persistent in the environment.^{xl}

Emerging environmental research documents that trash incinerators routinely releases troubling amounts of toxic and carcinogenic pollutants, including dioxin. Several studies published in 1994 have demonstrated that dioxin is harmful at far lower exposures than anyone ever suspected. Even at a few ppt, dioxin was capable of profoundly altering biological processes. In 1994, the EPA released a 3,000-page draft reassessment of dioxin and was soliciting public comment and reaction. Three years in the making, the study reaffirmed dioxin's classification as a probable human carcinogen.^{xli}

Figure 3.12

Annual Dioxin Deposition Air Transport Coefficients to Arctic Bay & Sanikiluaq Land Receptors

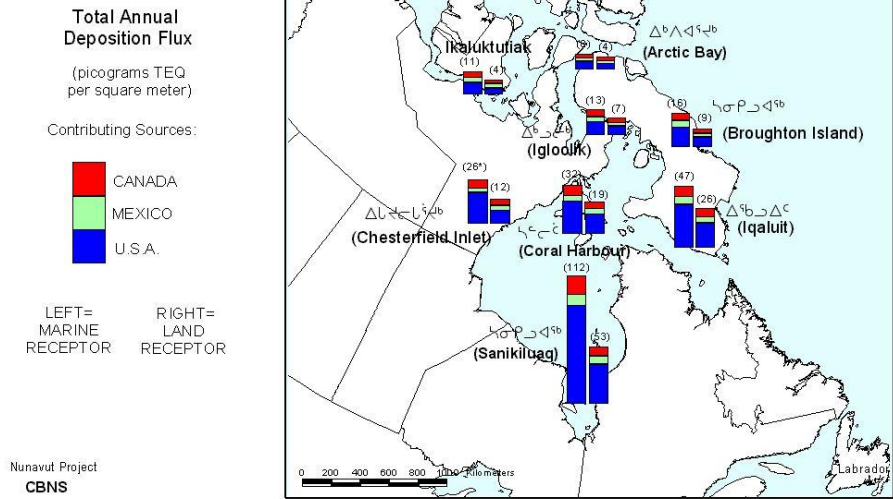


The EPA report announced dioxin has significant effects on the immune and reproduction systems and infant development. Second, there is no safe dose below which dioxin causes no biological effect. Third, quantities of dioxin and dioxin-like chemicals present in most people's bodies are already at or near levels shown to cause problems in animals. The report also identified incineration of both medical waste and common human garbage as a leading sources of dioxin emissions in the US. Food (meat, dairy and fish) is the other immediate sources of most of the dioxin found in the

bodies of the general population.^{xlii}

As a known endocrine disruptor, dioxin now appears on the Stockholm Convention's list of chemicals slated for worldwide abolition. The International Agency for Research on Cancer upgraded dioxin from a probable to a known human carcinogen in 1997. The most potent carcinogen ever known, dioxin is the only substance in the Toxics Release Inventory whose annual emissions are tallied in grams rather than in pounds..^{xliii}

Figure 3.1
Dioxin Deposition
at Nunavut Receptors



Questions.

1. Conduct extensive research on Dioxins in the environment.
2. Discuss toxicological effects on humans and in the environment.
3. Report on the fate and transport of dioxins in the air, and water around the globe.
4. Report on recent research being conducted on human body burden and bioaccumulation in mammals and other species.
5. What can we do to reduce the amount of dioxin that is released into the environment?
6. How can we avoid personal exposure to dioxins?
7. What can we do to reduce the amount of dioxins for future generations?

Exercise 6.

Plastic Pollution: A Ubiquitous Problem

Plastic pollution is found everywhere on Earth, from the coasts, to remote islands, to the poles. Unlike other litter, plastics are more than just an unsightly trash problem; they also have serious physical, biochemical and chemical issues of concern.

What are plastics? Plastics are synthetic organic compounds, mostly derived from petroleum. Today there are hundreds of plastics available, with over 300 types of plasticizer additives.^{xiv} We will be looking at a few of these in this study.

One of the major physical components of plastic pollution is that of sheer volume. The annual production of plastic has risen from half a million tons in 1950 to over 260 million tons in 2009. The quantity of plastic that has been synthesized in the last decade is close to the amount produced over the entire 20th century.^{xv} One reason for this is that plastic does not readily biodegrade. Except for the small amount that's been incinerated, every bit of plastic ever made still exists.^{xvi} Six-pack rings take 450 years to break down, a plastic milk jug takes 1 thousand years to break down, and a plastic cup takes 50-80 years to break down, resulting in almost every piece of plastic ever made is still around today.

Another component of plastic pollution is the disposal of plastic materials such as bags, bottles, and six-pack rings into the sea and other areas. Ocean pollution has occurred since the time of the Phoenicians, 3500 years ago, however, plastic pollution has only been around for about 50 years. Every year 14 billion pounds of trash (mostly plastic) is put into the oceans. Much of this debris is periodically washed up onto shorelines, resulting in more than 90% of debris on the beaches containing plastic.



Where does all of the plastic in the water come from? People not disposing of plastic properly, such as littering along roadsides or improperly disposing of trash. Storm sewers and drainage outflows that wash debris into rivers which eventually transport land pollution into the oceans. The rising tides sweep up the trash left on the beach, and along waterways and carry that into the oceans. Marine debris may enter the ocean from land and from merchant shipping and fishing fleets, cruise lines and recreational vessel. Through both accidental and intentional marine dumping, about 639,000 plastic containers are dumped into the ocean every day. Winds

and water currents, especially during storms, carry this debris out to sea. Since plastic does not biodegrade or decompose, all of the plastic that has ever entered the ocean is still there, unless it has washed up onto the shore.

What is Marine debris? Marine debris is any solid, manufactured or processed material that persists in the marine environment. This debris may consist of glass, metal plastic, bags, bottles, cans, packaging and cigarette butts. Debris with a density greater than the density of sea water ($\sim 1.026 \text{ km/m}^3$) will sink to the bottom. Debris with a density greater than the density of sea water will sink to the bottom, such as metal, glass, or dense, hard plastic. The most common materials observed floating at the ocean surface are high and low density polyethylene (HDPE #2, LDPE #4) and polypropylene (PP#5). Examples of these floatables are grocery bags, milk bottles, dairy containers, and drinking straws.



Physical Dangers of Plastic Marine Debris.

Why is plastic marine debris harmful? It affects all marine life, especially, marine mammals, marine birds, sea turtles, and fish.. More than 100,000 animals are found dead every year from plastic marine debris. Marine animals become entangled and die in 3 ways: (1) Drowning by becoming entangled in big debris. Sea turtles and marine mammals can drown or suffocate when they become entangled because they cannot get to the surface to breathe. (2) Exhaustion, depletion, starvation from either being entangled in medium debris. Marine critters slip into loops or holes in debris, often when they are young, and then grow into the loop over several months. Fur, skin, blubber, muscle, and vital organs become constricted. They can die from starvation, organ failure, or infection. (3) Starvation from ingestion of plastic debris. Sea turtles often mistake plastic bags for jellyfish and eat them. The bags do not pass through the turtles' gut and block their intestines. They die of starvation. Studies on dead turtles have found that more than 50% have plastic in their stomachs. Seabirds and fish often mistake small pieces of plastic for food, of which some gets caught in the gut, making the animal feel full. Eating enough plastic can cause numerous internal problems, leading to exhaustion, starvation and eventual death.



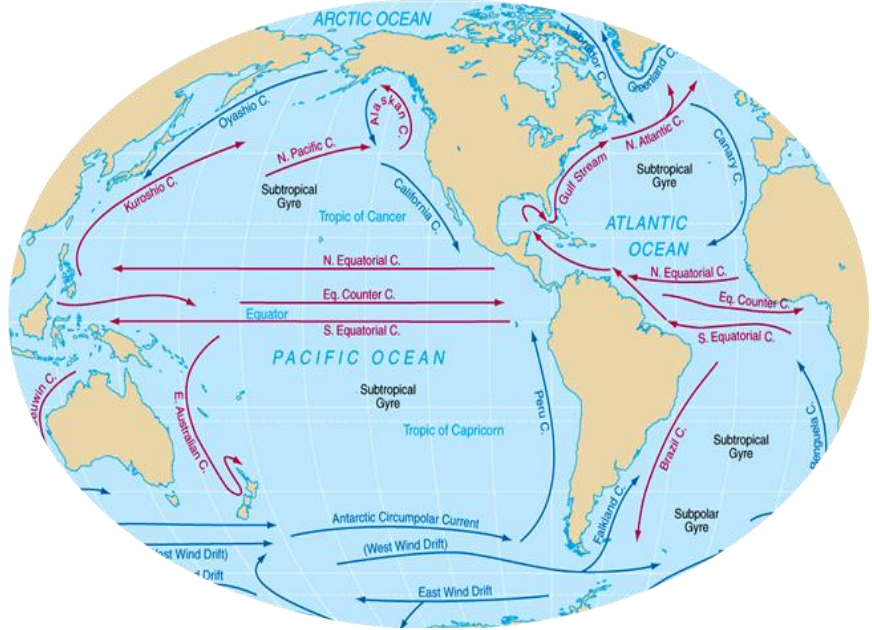
Plastic transport: Where does this marine plastic go? A vast swath of the ocean, larger than Texas, is full of a plastic stew that is entering the food chain. Wind driven currents transport the marine debris. Pushed along by winds, the ocean currents move in a circular pattern called a gyre transporting the plastic debris with them. Floating debris accumulates where surface ocean currents converge.

Plastic Fate.

Unlike debris, which biodegrades, photodegraded plastic disintegrates into ever smaller pieces while still staying a plastic. The process of disintegration means that many of the plastic particulates are too small to be seen. This process continues down to the molecular level. As it disintegrates, the plastic becomes small enough to be ingested by tiny aquatic organisms which reside near the ocean's surface.

Some plastics breakdown within a year of entering the water, leaching potentially toxic additives to plastic, such as plasticizers and chlorine, and derivatives of polystyrene. Of all plastic additives, phthalates and bisphenol-A are the most widely studied due to their potential effects on human and environmental health.^{xlvii}

Besides the particles' danger to wildlife, and leaching of plasticizers and chloride, the floating debris can adsorb persistent organic pollutants (POPs) from seawater, including PCBs, DDT, dioxin, and PAHs.^[29] Aside from toxic effects, when ingested, some of these chemicals are mistaken by the endocrine system as estradiol, causing hormone disruption in the affected animal.^[28] These toxin-containing plastic pieces are also eaten by plankton, small fish and jellyfish, which are then eaten by larger fish or other marine animals. Many of these fish are then consumed by humans, resulting in their ingestion of both leached and adsorbed toxic chemicals.



Questions.

1. Identify the 5 major oceanic gyres: location and the currents that drive them. Choose two gyres to examine in more detail. Explain why is so difficult to measure the size of the marine debris patches.
2. Examine the concentration of marine debris within the gyres. What research is being conducted on the marine debris? Can we identify the source of the marine debris?
3. Explain how photodegradation breaks down plastics. How long does this process take? How tiny can the particles become?
4. What is the cost to marine life of all of this plastic? What is ghost fishing? Are there any effects of marine debris on humans?
5. How are dioxins directly related to plastics and plastic pollution?
6. Next discuss how persistent organic pollutants (POPs) such as PCBs, DDT, Dioxins, and PAHs which are transported in the water and in the air, are adsorbed onto the bits of plastic floating in the water.
7. How do these POPs enter the food chain? Trace the path of bioaccumulation.
8. How do they affect the health of top predators? What systems in the body do they effect and how?
9. What can you do in your neighborhood to stop plastic pollution at the source.

End Notes for Plastics

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