

Microplastics in the Marine Environment – What’s the Harm?

A Long-term Field Experiment for St. Paul Island

Introduction

This lesson plan was inspired by a research article published in 2013. The original experiment took place in San Diego, California, and this lesson plan is a description of how the students at Seabird Summer Camp will attempt to replicate the original experiment. It will help us to better know the types of persistent organic pollutants (POPs) that might be contaminating the waters around St. Paul Island. Below you will find the title, authors, abstract, and conclusions of the article (for reference), followed by some background information and an outline of how to conduct the experiment:

Long-Term Field Measurement of Sorption of Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic Marine Debris

Authors: Chelsea M. Rochman, Eunha Hoh, Brian T. Hentschel, and Shawn Kaye

ABSTRACT: Concerns regarding marine plastic pollution and its affinity for chemical pollutants led us to quantify relationships between different types of mass-produced plastic and organic contaminants in an urban bay. At five locations in San Diego Bay, CA, we measured sorption of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) throughout a 12-month period to the five most common types of mass-produced plastic: polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), and polypropylene (PP). During this long-term field experiment, sorption rates and concentrations of PCBs and PAHs varied significantly among plastic types and among locations. Our data suggest that for PAHs and PCBs, PET and PVC reach equilibrium in the marine environment much faster than HDPE, LDPE, and PP. Most importantly, concentrations of PAHs and PCBs sorbed to HDPE, LDPE, and PP were consistently much greater than concentrations sorbed to PET and PVC. These data imply that products made from HDPE, LDPE, and PP pose a greater risk than products made from PET and PVC of concentrating these hazardous chemicals onto fragmented plastic debris ingested by marine animals.

Implications of This Study to Marine Plastic Debris: With escalating plastic production and poor policy enforcement, quantities of plastic debris in the marine environment will likely increase. In 2007, HDPE, LDPE, and PP accounted for 62% of all plastics produced globally, while PVC and PET represented only 19% and 7%, respectively. In accord with production trends, HDPE, LDPE, and PP are the most common plastic debris collected at sea. Our conclusion that HDPE, LDPE, and PP consistently sorbed greater concentrations of PCBs and PAHs than did PET and PVC implies that PET and PVC pose a reduced risk of concentrating these hazardous chemicals onto plastic debris ingested by animals (Figure 1). Although PVC sorbs

relatively small concentrations of PCBs and PAHs, its vinyl chloride monomer is classified as carcinogenic and toxic. In addition, PVC contains more hazardous additives than HDPE, LDPE, PP, and PET. Because PET requires fewer additives and degrades faster than other polymers, it has been suggested as one of the least hazardous plastics. These inherent properties in combination with the relatively low sorption of PCBs and PAHs we measured suggest that plastic products made from PET, especially items commonly encountered in marine debris such as plastic packaging and fishing gear, might have fewer chemical impacts on marine life than products made from other types of plastic. Testing this hypothesis will require measuring bioaccumulation and toxicity from different types of plastic marine debris, all containing a unique cocktail of chemicals which may act as a multiple stressor when ingested by marine animals.

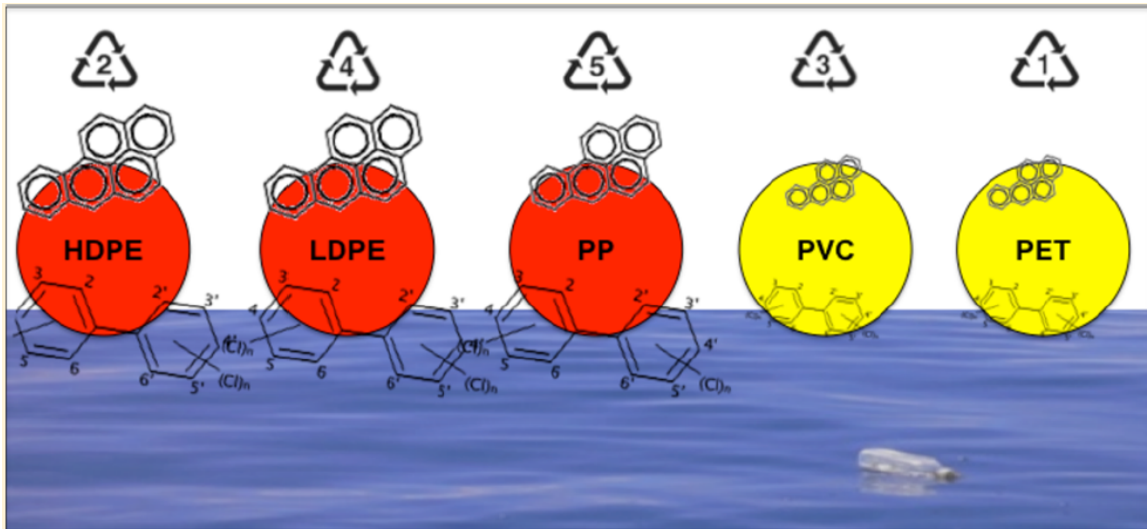


Figure 1: Graphic depicting the results of the Rochman et al. (2013) study. The circles represent the types of plastic resins used in the study, and the chemical structures represent persistent organic pollutants (POPs). The size of the chemical structure is proportional to the amount of POPs each type of plastic can absorb. For example, HDPE can absorb a high concentration of POPs, whereas PET cannot absorb as high a concentration of POPs.

Background Information

Types of Plastics (or Thermoplastics)

A **thermoplastic**, also called a **thermosoftening plastic** or **thermosetting plastic**, is a polymer, which becomes pliable or moldable above a specific temperature and returns to a solid state upon cooling. A **polymer** is a large molecule, or macromolecule, composed of many repeated subunits, known as monomers. Because of their broad range of properties,^[4] both synthetic and natural polymers play an essential and ubiquitous role in everyday life.^[5] Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals.

Most thermoplastics have a high molecular weight. The polymolecules chains associate through intermolecular forces, which permits thermoplastics to be remolded because the intermolecular interactions increase upon cooling and restore the bulk properties. In this way, thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process. Thermosets often do not melt, but break down and do not reform upon cooling.

Above its glass transition temperature, T_g , and below its melting point, T_m , the physical properties of a thermoplastic change drastically without an associated phase change. Within this temperature range, most thermoplastics are rubbery due to alternating rigid crystalline and elastic amorphous regions, approximating random coils. Some thermoplastics do not fully crystallize above glass transition temperature T_g , retaining some, or all of their amorphous characteristics. Amorphous and semi-amorphous plastics are used when high optical clarity is necessary, as light is scattered strongly by crystallites larger than its wavelength. Amorphous and semi-amorphous plastics are less resistant to chemical attack and environmental stress cracking because they lack a crystalline structure. Brittleness can be decreased with the addition of plasticizers, which increases the mobility of amorphous chain segments to effectively lower T_g . Modification of the polymer through copolymerization or through the addition of non-reactive side chains to monomers before polymerization can also lower T_g . Before these techniques were employed, plastic automobile parts would often crack when exposed to cold temperatures. Recently, thermoplastic elastomers have become available.

High-density polyethylene (HDPE) or polyethylene high-density (PEHD) is a polyethylene thermoplastic made from petroleum. Known for its large strength to density ratio, HDPE is commonly used in the production of plastic bottles, corrosion-resistant piping, geomembranes, and plastic lumber. HDPE is commonly recycled, and has the number "2" as its resin identification code (formerly known as recycling symbol).

Low-density polyethylene (LDPE) is a thermoplastic made from the monomer ethylene. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure process via free radical polymerization. Its manufacture employs the same method today. The EPA estimates 5.7% of LDPE (recycling number 4) is recycled. Despite competition from more modern polymers, LDPE continues to be an important plastic grade. LDPE has more branching (on about 2% of the carbon atoms) than HDPE, so its intermolecular forces (instantaneous-dipole induced-dipole attraction) are weaker, its tensile strength is lower, and its resilience is higher. Also, since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower. LDPE is defined by a density range of 0.910–0.940 g/cm³. LDPE contains the chemical elements carbon and hydrogen.

Polypropylene (PP) is useful for such diverse products as reusable plastic food containers i.e.) "microwave and dishwasher safe" plastic containers, diaper lining, sanitary pad lining and casing, ropes, carpets, plastic moldings, piping systems, car batteries, insulation for electrical cables and filters for gases and liquids. In medicine, it is used in hernia treatment and to make heat-resistant medical equipment. Polypropylene sheets are used for stationery folders and packaging and clear storage bins. Polypropylene is defined by the recyclable plastic number 5. Although relatively inert, it is vulnerable to ultraviolet radiation and can degrade considerably in direct sunlight. It may be worthy to note that (PP) is not as impact-resistant as the polyethylenes (HDPE, LDPE). PP is also somewhat permeable to highly volatile gases and liquids.

Polystyrene (PS) is manufactured in various forms that have different applications. Extruded polystyrene (PS) is used in the manufacture of disposable cutlery, CD and DVD cases, plastic models of cars and boats, and smoke detector housings. Expanded polystyrene foam (EPS) is used in making insulation and packaging materials, such as the "peanuts" and molded foam used to cushion fragile products. Extruded polystyrene foam (XPS), known by the trade name Styrofoam, is used to make architectural models and drinking cups for heated beverages. Polystyrene copolymers are used in the manufacture of toys and product casings.

Polyvinyl chloride (PVC) is a tough, lightweight material that is resistant to acids and bases. Much of it is used by the construction industry, such as for vinyl siding, drainpipes, gutters and roofing sheets. It is also converted to flexible forms with the addition of plasticizers, thereby making it useful for items such as hoses, tubing, electrical insulation, coats, jackets and upholstery. Flexible PVC is also used in inflatable products, such as water beds and pool toys.

Teflon (PTFE) is the brand name given by DuPont Corp. for a polymer called polytetrafluoroethylene (PTFE), which belongs to a class of thermoplastics known as fluoropolymers. It is famous as a coating for non-stick cookware. Being chemically inert, it is used in making containers and pipes that come in contact with reactive chemicals. It

is also used as a lubricant to reduce wear from friction between sliding parts, such as gears, bearings and bushings.

Chemicals Associated with Plastics

Phthalates

Phthalates, or **phthalate esters**, are esters of phthalic acid and are mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity). Phthalates are manufactured by reacting phthalic anhydride with alcohol(s) that range from methanol and ethanol (C1/C2) up to tridecyl alcohol (C13), either as a straight chain or with some branching. They are divided into two distinct groups, with very different applications, toxicological properties, and classification, based on the number of carbon atoms in their alcohol chain. They are used primarily to soften polyvinyl chloride (PVC). Lower-molecular-weight phthalates (3-6 carbon atoms in their backbone) are being gradually replaced in many products in the United States, Canada, and European Union over health concerns. They are replaced by high-molecular-weight phthalates (those with more than 6 carbons in their backbone, which gives them increased permanency and durability). In 2010, the market was still dominated by high-phthalate plasticizers; however, due to legal provisions and growing environmental awareness and perceptions, producers are increasingly forced to use non-phthalate plasticizers.

Phthalates are used in a large variety of products, from enteric coatings of pharmaceutical tablets and nutritional supplements to viscosity control agents, gelling agents, film formers, stabilizers, dispersants, lubricants, binders, emulsifying agents, and suspending agents. End-applications include adhesives and glues, electronics, agricultural adjuvants, building materials, personal-care products, medical devices, detergents and surfactants, packaging, children's toys, modeling clay, waxes, paints, printing inks and coatings, pharmaceuticals, food products, and textiles.

Phthalates are easily released into the environment. Although there is no covalent bond between the phthalates and plastics, they are physically bound into the plastic as a result of the heating process used to make PVC articles. They can be removed only by exposure to severe heat or using strong solvents. However, people are exposed to phthalates, and most Americans tested by the Centers for Disease Control and Prevention have metabolites of multiple phthalates in their urine. Phthalate exposure may be through direct use or by indirect means through leaching and general environmental contamination. Diet is believed to be the main source of di(2-ethylhexyl) phthalate (DEHP) and other phthalates in the general population. Fatty foods such as milk, butter, and meats are a major source.

Uses: Phthalates are used in a large variety of products, from enteric coatings of pharmaceutical pills and nutritional supplements to viscosity control agents, gelling agents, film formers, stabilizers, dispersants, lubricants, binders, emulsifying agents, and suspending agents. End-applications include adhesives and glues, agricultural adjuvants, building materials, personal-care products, medical devices, detergents and surfactants, packaging, children's toys, modelling clay, waxes, paints, printing inks and coatings, pharmaceuticals, food products, and textiles. Phthalates are also frequently used in soft plastic fishing lures, caulk, paint pigments, and sex toys made of so-called "jelly rubber". Phthalates are used in a variety of household applications such as shower curtains, vinyl upholstery, adhesives, floor tiles, food containers and wrappers, and cleaning materials. Personal-care items containing phthalates include perfume, eye shadow, moisturizer, nail polish, liquid soap, and hair spray.^[6] They are also found in modern electronics and medical applications such as catheters and blood transfusion devices. The most widely used phthalates are the di(2-ethylhexyl) phthalate (DEHP), the diisodecyl phthalate (DIDP), and the diisononyl phthalate (DINP). DEHP is the dominant plasticizer used in PVC due to its low cost. Benzylbutylphthalate (BBP) is used in the manufacture of foamed PVC, which is used mostly as a flooring material. Phthalates with small R and R' groups are used as solvents in perfumes and pesticides.

Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. Because of this, they have been observed to persist in the environment, to be capable of long-range transport, bioaccumulate in human and animal tissue, bioaccumulate in food chains, and to have potential significant impacts on human health and the environment.

Many POPs are currently or were in the past used as pesticides. Others are used in industrial processes and in the production of a range of goods such as solvents, polyvinyl chloride, and pharmaceuticals. There are a few natural sources of POPs, such as volcanic activity and vegetational fires, but most POPs are created by humans in industrial processes, either intentionally or as byproducts.

Public concern about contamination by POPs exists, due to the multitude of evidence showing the negative effects of POPs on human health and the environment. Several compounds have been identified as hormone disruptors which can alter normal function of endocrine and reproductive systems in humans and wildlife. Cardiovascular disease, cancer, obesity, and diabetes have also been linked to POPs. Exposure to POPs during pregnancy has been linked to developmental defects in the resulting offspring. There are many risks and effects of having these chemicals in our environment and none of them are a benefit to the Earth. After these pollutants are put into the environment, they are able to stay in the system for decades causing problems such as cancer, birth defects, learning disabilities, immunological, behavioral, neurological and reproductive disorders in humans and animals.

Bioaccumulation of Toxic Chemicals

Bioaccumulation refers to the accumulation of substances, such as pesticides, or other organic chemicals in an organism. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost. Thus, the longer the biological half-life of the substance the greater the risk of chronic poisoning, even if environmental levels of the toxin are not very high. Bioaccumulation of pollutants is typically associated with a compound's high lipid solubility and ability to accumulate in the fatty tissues of living organisms for long periods of time. Biotransformation can strongly modify bioaccumulation of chemicals in an organism. Persistent chemicals tend to have higher concentrations and are eliminated more slowly. Dietary accumulation or bioaccumulation is another hallmark characteristic of POPs, as POPs move up the food chain, they increase in concentration as they are processed and metabolized in certain tissues of organisms. The natural capacity for animals gastrointestinal tract concentrate ingested chemicals, along with poorly metabolized and hydrophobic nature of POPs makes such compounds highly susceptible to bioaccumulation. Thus POPs not only persist in the environment, but also as they are taken in by animals they bioaccumulate, increasing their concentration and toxicity in the environment.

Health effects: POP exposure may cause developmental defects, chronic illnesses, and death. Some are carcinogens per IARC, possibly including breast cancer. Many POPs are capable of endocrine disruption, within the reproductive system, the central nervous system or the immune system. People and animals are exposed to POPs mostly through their diet, occupationally, or while growing in the womb. For humans not exposed to POPs through accidental or occupational means, over 90% of exposure comes from animal product foods due to bioaccumulation in fat tissues and bioaccumulate through the food chain. In general, POP serum levels increase with age and tend to be higher in females than males.

Endocrine disruption: The majority of POPs are known to disrupt normal functioning of the endocrine system, for example all of the dirty dozen are endocrine disruptors. Low level exposure to POPs during critical developmental periods of fetus, newborn and child can have a lasting effect throughout its lifespan. A 2002 study synthesizes data on endocrine disruption and health complications from exposure to POPs during critical developmental stages in an organism's lifespan. The study aimed to answer the question whether or not chronic, low level exposure to POPs can have a health impact on the endocrine system and development of organisms from different species. The study found that exposure of POPs during a critical developmental time frame can produce a permanent changes in the organisms path of development. Exposure of POPs during non-critical developmental time frames may not lead to detectable diseases and health complications later in their life. In wildlife, the critical development time frames are in utero, in ovo, and during reproductive periods. In humans, the critical development timeframe is during fetal development.

Additive and synergistic effects: It is hard to predict specific effects and the potential for health problems in experiments and studies performed in labs on POPs. Laboratory experiments most often test individual compounds. In the environment, however, organisms are exposed to a mixture of multiple POP compounds at the same time. It is difficult to test mixtures of different POPs in controlled experiments due to the cost and the lack of resources. To approximate the toxicity of a mixture of compounds to an organism in nature, the effects are assumed to be additive. That is, the effects of each individual compound are added together to approximate the overall magnitude of effects of the mixture as a whole. Sometimes, however, this is not always the case. Mixtures of POPs, as with many other chemical mixtures, can sometimes produce synergistic effects. With synergistic effects, the toxicity of each compound is enhanced by the other compounds in the mixture. When put together, the effects can far exceed the approximated additive effects of the POP compound mixture. Thus, mixtures of POPs in nature can be more toxic to organisms than predicted in laboratory experiments.

Experimental Design

The students will attempt to replicate the first part of the Rochman et al. (2013) study, in which virgin plastic pellets will be closely examined, weighed out and separated into cotton bags, and those bags of plastic pellets will be deployed at several locations in the St. Paul Harbor. The bags will then be removed from the harbor during Bering Sea Days in the fall, closely examined for changes over time, and returned to Anchorage for chemical analyses at the University. Many of the materials will be supplied (I will send a package with one of the camp teachers, Trevor Haynes, when he flies out to St. Paul), however, you may want to consider having a backup of materials like gloves.

Materials

Nitrile gloves
 Forceps
 Dissecting scope
 Camera (a point-and-shoot that can take close-up, macro pictures)
 Aluminum foil
 Scientific scale
 Virgin plastic pellets of various types (HDPE, LDPE, PET, etc.)
 Small bags made with untreated cotton material
 Cotton cord
 Rocks
 GPS unit
 Data sheets

Methods

1. Examine the plastic pellets:
 - a. Virgin plastic pellets of various types will be supplied (INSERT PLASTIC TYPES)
 - b. Have students break into groups and put on gloves
 - c. Give each group a pellet of (PLASTIC TYPE) and allow them to examine the pellet up close
 - d. Have the groups list what they notice about the pellet of (PLASTIC TYPE). What color is it? Is the material very hard, soft, or somewhere in between? Is it smooth or jagged? The list can be shared on the blackboard or on a presentation, but make sure these characteristics are recorded on a data sheet
 - e. Repeat these examinations with the plastic pellets of other types (INSERT REMAINING PLASTIC TYPES)
2. Photograph the plastic pellets:
 - a. Take one more pellet of each plastic type and place under the dissecting scope
 - b. Using the macro setting on the point-and-shoot camera, take a picture of each pellet through the dissecting scope's lens (refer to Figure S10 at the end of this lesson plan to see what a close-up picture should look like)
 - c. Save these pictures with detailed descriptions: the type of plastic pellet, the date on which the picture was taken, and the fact that the pellet had not been deployed in the harbor

3. Prepare the plastic pellets inside the cotton bags:
 - a. Each cotton bag will contain 10g of only one type of plastic pellet
 - b. With students wearing gloves, give them a piece of aluminum foil to use as a “container” to weigh pellets out on the scale – there may be enough bags and pellets for each student to weigh out all 10g of pellets for one bag, however, if you think materials are limited, break students into groups to accomplish this task
 - c. Place the piece of aluminum foil on the scale and tare it so that the scale reads 0g
 - d. Using the forceps, have students place an individual pellet of (PLASTIC TYPE) on the aluminum foil that is resting on the scale, have them announce how much that one pellet weighs
 - e. You can use this moment for a little bit of math – if an individual pellets weighs x grams, and a bag needs 10g of pellets, approximately how many pellets will you need to reach 10g?
 - f. Once 10g of pellets have been weighed, transfer those pellets to a cotton bag
 - g. Also place a rock inside the bag – this will act as a sinker when the bag is deployed in the harbor
 - h. Clearly identify the type of plastic pellet stored in a particular bag, please identify the inside and outside of the bag (in case something on the outside gets washed away). Some things you might do: use different colors of duct tape to represent different plastic types and tape up the cotton cord; assign a specific color to each plastic type, and paint the rocks that you place inside the bag the color to represent what plastic type is inside the bag
 - i. Once the pellets and rock are inside the bag, fold the top of the bag over several times and securely tie the cotton cord around the bag – these bags will be in the water from July to October, so make sure everything is tightly closed so we don’t lose the plastic pellets!
4. Deploy the bags
 - a. Choose locations around the harbor where you will be able to securely tie the bags – dock posts may be good locations
 - b. Once a deployment site is selected, take one bag of each type of plastic and securely tie them to the site
 - c. Using the GPS unit, mark the latitude and longitude readings of your deployment site
 - d. Record the GPS point, date, and description of the deployment site on the data sheets
5. Wait and see!
 - a. The bags will be recovered during Bering Sea Days, where we will examine the plastic pellets for degradation
 - b. The pellets will be taken back to Anchorage for chemical analyses, and will be reported back to the students on St. Paul!

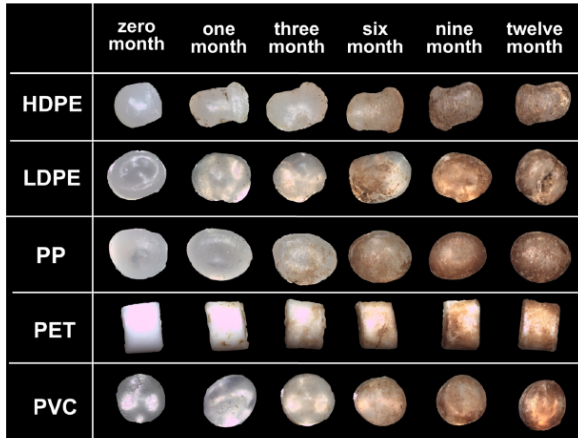


Figure S10. Photos of pre-production pellets (roughly 3 mm in diameter for HDPE, LDPE, PP and PVC and 2 mm in diameter for PET) of each polymer type taken through the lens of a dissecting microscope (16x) from 0-12 months (sampled from Harbor Excursion) showing the changes in color through time.

If you are interested in buying more plastic pellets for continuing experiments, affordable packages of plastic pellets can often be found on sites like ebay.com. Below are some results of searches I have performed on ebay.com. I thought they would be a good example with which to start.

<p>POLYPROPYLENE PLASTIC PELLETS 10 POUNDS</p>	<p>POLYPROPYLENE PLASTIC PELLETS 4 POUND BAG</p>
	
<p>POLYETHYLENE PLASTIC PELLETS 4 lbs</p>	<p>ENTEC POLYSTYRENE CLEAR PLASTIC PELLETS 4 lbs</p>
	