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# Capstone of Alydia Moorhead

Submitted in Partial Fulfillment of the Requirements for the Degree of

## Master of Science Marine Science

Nova Southeastern University Halmos College of Arts and Sciences

April 2022

Approved: Capstone Committee

Committee Chair: Dr. Amy Hirons

Committee Member: Dr. David Kerstetter

Committee Member: Dr. Dimitrios Giarikos

### HALMOS COLLEGE OF ARTS AND SCIENCES

## ACCUMULATION OF PERSISTENT ORGANIC POLLUTANTS IN MARINE MAMMALS: A CASE STUDY ON CETACEANS, PINNIPEDS, AND SIRENIANS

By

Alydia J Moorhead

Submitted to the Faculty of Halmos College of Arts and Sciences in partial fulfillment of the requirements for the degree of Master of Science with a specialty in:

Marine Biology

Nova Southeastern University April 2022

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Special thanks to my family, specifically my husband, who has continued to encourage and support me through this journey. I would also like to thank my peers, specifically those in the Charismatic Megafauna and Oceanography Lab, for their support and collaboration during the development of this capstone and the completion of my master's degree.

### Abstract

Persistent organic pollutants (POPs) are lipophilic semi-volatile organic chemicals that present a range of challenges to marine biota, specifically marine mammals that often occupy a high trophic position in the food web. POPs have become a global problem since they have been shown to cause immunologic, teratogenic, carcinogenic, neurological, and reproductive complications in living organisms due to their resistance to biodegradation and their lipophilic nature. Marine mammals can accumulate these toxic substances through direct ingestion, trophic transfer, adsorption, and maternal offloading. They are susceptible to both bioaccumulation and biomagnification of POPs. Accumulation of POPs is affected by many variables, including habitat, feeding strategy, age, sex, and physiology. This review looks at the trophic transfer and accumulation of persistent organic pollutants in three groups of marine mammals: cetaceans. pinnipeds, and sirenians. These groups are ecologically and physiologically diverse and occupy a large range of trophic positions and habitats; therefore, this diversity is expected to affect how POPs accumulate and magnify in marine mammals. Variations in rates of biomagnification and bioaccumulation of pollutants can help us to understand anthropogenic effects and their impacts on marine mammal trophic ecology. By evaluating data from several different marine mammal organic contaminant studies, we can conclude that POPs are having a direct impact on these animals and their aquatic environments. From the studies evaluated, the mean summed POP concentrations range from undetectable in certain herbivorous species, such as the manatee, to 457,000 ng/g lipid weight in apex predators, such as the California sea lion. There are also substantial differences in contaminant loads between mature male and female mammals, indicating maternal transfer of contaminants to offspring.

**Keywords:** Marine mammals, persistent organic pollutants, trophic ecology, biomagnification, bioaccumulation

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#### **Statement of Significance**

This study reviews and evaluates concentrations of POPs in marine mammals and compares differences across trophic positions. Differences in habitat, latitude, feeding ecology, morphology, and physiology present a range of challenges in understanding how organic contaminants accumulate and magnify in marine mammals (Bowen, 1997; Tsygankov et al., 2015; Nelms et al., 2018; Trites, 2019). Therefore, this review focuses on differences in trophic interactions and ecology and how these can impact bioaccumulation and biomagnification of POPs in three different groups: cetaceans, pinnipeds, and sirenians. Several methods of contaminant exposure are explored, including trophic transfer, direct consumption, and maternal offloading (Holden and Marsden, 1967; Pauly et al., 1998; Hoekstra et al., 2003; Krahn et al., 2009; Fair et al., 2010; Berta et al., 2015).

Marine mammals serve as important indicators of global pollution, and several species are declining or endangered due to both natural changes in their environment and anthropogenic impacts (Ross et al., 2000b; Tanabe and Subramanian, 2006). This study serves to represent the diversity in marine mammals, particularly focusing on routes of exposure to organic contaminants and comparing levels of organic contaminants, such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDTs), polybrominated diphenyl ethers (PBDEs), hexachlorocyclohexanes (HCHs), and polycyclic aromatic hydrocarbons (PAHs), across species. Specific attention is given to ten different marine mammal species, the bowhead whale (*Balaena mysticetus*), gray whale (*Eschrichtius robustus*), humpback whale (*Megaptera novaeangliae*), common bottlenose dolphin (*Tursiops truncatus*), killer whale (*Orcinus orca*), California sea lion (*Zalophus californianus*), Hawaiian monk seal (*Neomonachus schauinslandi*), walrus (*Odobenus rosmarus*), West Indian manatee (*Trichechus manatus*) and dugong (*Dugong dugon*). These species represent a broad range of diversity in terms of ecology, habitat, life-history parameters, and morphology.

While data on some marine mammal species is still limited regarding organic contaminant concentrations, new studies continue to shed light on the trophic interactions and ecology of marine species that help determine susceptibility to contaminant accumulation and magnification throughout the food web, which can ultimately affect survival rates, reproductive success, and overall population dynamics. Several marine mammals are also keystone species, meaning they have substantial impacts on the success and survival of the ecosystems they inhabit (Helle, 1980; Duggins, 1980; Berta et al. 2015; Desforges et al., 2016). Contaminant exposure in marine mammals could also have important implications for humans, as we are high order consumers and several indigenous communities rely on marine mammals, as well as other marine species, for subsistence and cultural purposes (O'Hara et al., 1999; Hoekstra et al., 2005; Bolton et al., 2020).

#### Background

#### Marine Mammals

Marine mammals are long-lived aquatic animals that rely on salt or freshwater ecosystems for their existence, including foraging, growth, and mating success (Andersen, 1969; Berta et al., 2015; NOAA, 2021d). They inhabit all the major bodies of water on Earth, occupy a wide range of habitats, feeding strategies, and physiologies, and span several trophic levels, making it difficult to form generalizations regarding their trophic ecologies and food web dynamics (Brookes, 1763; Andersen, 1969; Ross, 2000b; Trites, 2001; Berta et al., 2015; NOAA, 2021d). Being mammals that take to the sea for some period of their lives, these animals have numerous challenges that they must overcome. They must adapt to differences in pressure, temperature, salinity, light, sound, viscosity, and buoyancy in the marine environment (Scholander, 1940; Bowen, 1997; Ortiz et al, 1998; Ponganis, 2011; Berta et al., 2015). They are homeotherms and require a steady body temperature. Certain metabolic and circulatory mechanisms allow them to achieve this homeostasis, such as countercurrent heat exchange (CCHE). CCHE allows several marine mammals to conserve heat by maintaining a heat differential between areas of oppositely directed blood flow; this is especially important for circulation to the flippers, fins, and flukes (Husar, 1977; Caldwell and Caldwell, 1985). Other common adaptations for thermoregulation include large amounts of blubber or fur for insulation and a small surface area to volume ratio, both of which allow them to reduce heat loss (Whittow, 1987; Innes et al., 1990; Berta et al., 2015). They also have streamlined bodies and modified appendages to reduce drag while swimming, and most marine mammals have minimal air cavities and collapsible lungs and ribs, which allow for greater diving capabilities. Other important adaptations include higher red blood cell counts and greater myoglobin production, which allow for greater oxygen retention, endurance, and dive time (Scholander, 1940; Ridgway et al., 1966, 1979; Williams, 1999; Ponganis, 2011; Goldbogen et al., 2013).

Marine mammals are from the class Mammalia and occupy three orders: Cetacea, Carnivora, and Sirenia (Trites, 2001; Berta et al., 2010; NOAA, 2021d). Each order has specific adaptations based on its ecology, including diet, climate, and migratory patterns. These various adaptations rely heavily on what portion of their lives they spend in the water and what their range and habitat consist of (Brookes, 1763; Howell, 1930; Andersen, 1969; Ridgway, 1979; Whittow, 1987; Boyd, 1993; Evans et al., 2001; Trites, 2001; Boyd et al., 2010; Berta et al., 2015; NOAA, 2021d). Although marine mammals have adapted well to the marine environment, most are still listed as endangered, threatened, or depleted according to the International Union for Conservation of Nature (IUCN) Red List, Endangered Species Act, and the Marine Mammal Protection Act (Schipper et al., 2008; Laake et al., 2018; Muto et al., 2020; Lourenço et al., 2021; IUCN, 2021a).

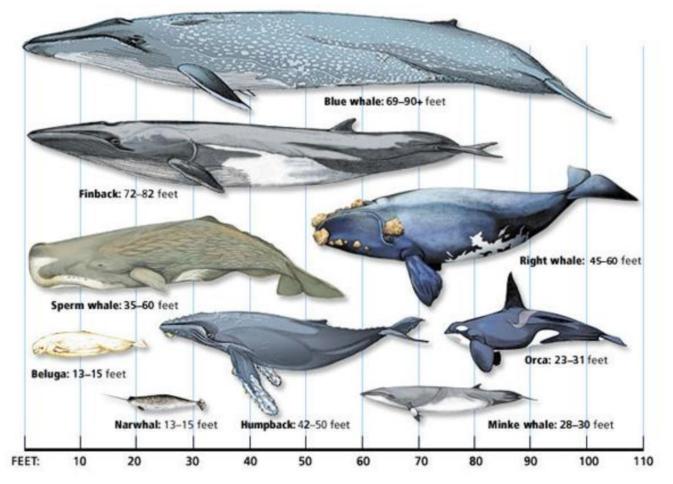
#### Cetacea

The order Cetacea is comprised of two suborders: Mysticeti (baleen whales) and Odontoceti (toothed whales). Cetaceans have specific adaptations that allow them to spend their whole lives in the water. They are generally streamlined and have great breath-holding capacity, which allow them to move throughout the water column for extended periods of time with little resistance (Irving, 1939; Scholander, 1940; Norris, 1966; Gaskin, 1982; Berta et al., 2015). They have specialized nostrils in the form of a blowhole that allow them to easily breathe while only exposing the dorsal surface of their heads. Cetaceans move through caudal propulsion primarily, and they can efficiently maintain sustained velocities using narrow, pointed, high-aspect-ratio flukes (Slijper, 1936; Yablokov et al., 1972; Fish, 1997; Berta et al., 2015).

Although all marine mammals have relatively dense blubber layers, cetaceans have more extensive amounts of blubber, which act as insulation and help them regulate their body temperature. The middle and deeper layers of blubber appear to be more metabolically active, while the superficial layer is likely targeted for roles of structuring, including streamlining (Struntz et al., 2004; Berta et al., 2015). The integument of some odontocetes has been reported to be composed of as much as 80-90 % blubber (Meyer et al., 1995; Berta et al., 2015). They are also distinguished from other marine mammals by their absence of hair and glands on their skin, except for vibrissae near the mouth (Irving, 1939; Scholander, 1940; Evans, 1987; Berta et al., 2015).

Baleen whales include some of the largest animals on earth, including the blue whale, fin whale, bowhead whale, right whale, humpback whale, gray whale, and minke whale (Figure 1). They lack teeth but are known for their distinct baleen plates, which are made of keratinous fibers that grow continuously throughout their lifetimes. These plates allow them to filter and trap prey, which mostly consists of plankton, krill, and small fish (Pfeiffer, 1993; Werth, 2013; Young et al., 2015). Whales belonging to the family Balaenopteridae, also referred to as Rorqual whales, feed vertically throughout the water column by ram filter feeding, a process by which they open their mouths while ascending and allow gravity to push down prey. Their jaw can disarticulate, allowing the mouth to expand to a greater volume for optimal prey consumption (Pyenson et al., 2012; Berta et al., 2015). Whales from the family Balaenidae have long and finely textured baleen and exhibit continuous ram filter feeding or skimming, where they move slowly in a horizontal direction near the surface, and water flows into the mouth continuously. They typically feed on slow-moving, nonevasive prey items, such as copepods (Lambertsen et al., 2005; Simon et al., 2009; Goldbogen et al., 2013; Berta et al., 2015). The gray whale, from family Eschrichtiidae, is unique among the baleen whales and feeds by using its tongue to draw in water and sediments along the seafloor and filters the sediments with its short, coarse baleen. The baleen retains the prey, which are typically bottom invertebrates, like small amphipod crustaceans. This is referred to as suction filter feeding (Nerini, 1984; Sumich, 2014; Berta et al., 2015).

Odontocetes, or toothed whales, make up over half of all marine mammals with 76 extant species, consisting of several species of whales, dolphins, and porpoises (Figure 1) (Berta et al., 2015). They have a single blowhole nostril and exhibit greater sexual dimorphism compared to the mysticetes. Odontocetes have teeth, which allow them to forage on a variety of prey items. Most of the toothed whales are carnivorous with homodont cone-shaped teeth to help them grasp or strain their prey (Rice, 1998; Struntz et al., 2004; Armfield et al., 2013). They have the most diverse diets of all marine mammals, feeding on fish, squid, large crustaceans, birds, and occasionally other marine mammals. Odontocetes also include some of the ocean's most dynamic apex predators, such as the killer whale (*Orcinus orca*) (Krahn et al., 2009; Reeves et al., 2017). Several odontocetes also use echolocation to detect prey; they can emit sound waves and listen for an echo that bounces off an object; this can allow them to determine prey distance and size (Kellogg et al., 1953; Au, 1993; Parker et al., 2013).

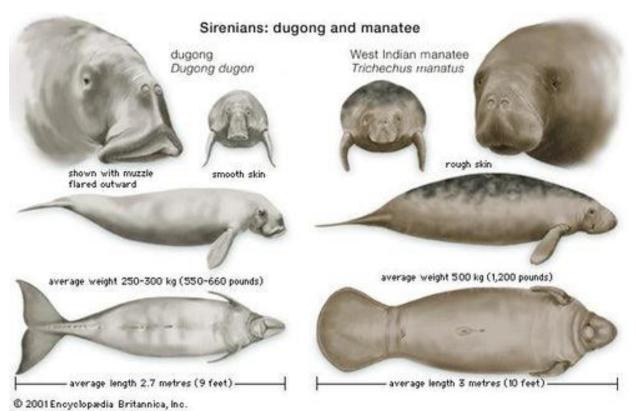


**Figure 1**. Size comparison of cetacean species, including baleen and toothed whales, ranging from 13 to 90+ feet in length (https://ocean.si.edu/ocean-life/marine-mammals/whales).

Sirenia

The order Sirenia is made up of two families: Trichechidae and Dugongidae. The trichechids are comprised of three species of manatees, and the dugongs make up the only extant member of the family Dugongidae (Reynolds III and Odell, 1991; Marsh et al., 2012; Berta et al., 2015). Like cetaceans, sirenians also spend their whole lives in water; however, they stay in shallower waters as they are not built for deep diving (Wells et al., 1999; Berta et al., 2015). They have large rotund bodies and modified front limbs that help steer them in the water. They are the only marine mammals that follow a strictly herbivorous diet and have specialized adaptations to help with the digestion of plant-based materials. They are non-ruminant herbivores that undergo a specialized hindgut fermentation, and they also have longer digestive tracts, which allow for a greater amount of time to break down cellulose and fibrous carbohydrates from plant compounds (Best, 1981; Lomolino and Ewel, 1984; Nishiwaki and Marsh, 1985; Bowen, 1997; Trites, 2001; Marsh et al., 2012). Horizontal tooth replacement is another specialized adaptation unique to the sirenians compared to other marine mammals; their teeth are continually being replaced in a "conveyor belt" mechanism due to abrasion from excessive amounts of sand and grit from their herbivorous diets (Hartman, 1979; Domning and Hayek, 1984; Beatty et al., 2012; Berta et al., 2015).

Sirenians move in a similar way to cetaceans, using caudal oscillation to propel them forward. Both dugongs and manatees tend to swim at a leisurely pace since they do not require speed in catching prey as other marine mammals do (Hartman, 1979; Nishiwaki and Marsh, 1985; Reynolds III and Odell, 1991; Berta et al., 2015). Manatees have more generalized features than dugongs (Figure 2); they are smaller in size, move slowly with a paddle-like tail, and feed throughout the water column (Hartman, 1979). However, dugongs have a fluke-like tail to accelerate them forward; this allows them to inhabit more open-water areas compared to manatees. They also exhibit a specialized rostral disc that is oriented downward towards the seafloor. They are obligate benthic foragers and use their expanded upper lip to feed along the benthic sediments. The degree of snout deflection in sirenians can be directly correlated with the degree of bottom feeding versus feeding throughout the water column (Hartman, 1979; Best, 1981; Berta et al., 2015).



**Figure 2**. A comparison in morphology between the dugong and manatee (https://dipndive.com/blogs/marine-life/manatee-vs-dugong-whats-the-difference).

#### Carnivora

The order Carnivora is comprised of marine mammals from five different families: Odobenidae, Otariidae, Phocidae, Ursidae, and Mustelidae. Most marine carnivores are considered semiaquatic, often depending on the ocean for food; these include the polar bear, marine otter, and most pinniped species. They often come to land or ice floes to bear their young, rest, or molt (Trites, 2001; Berta et al., 2015; NOAA, 2021d).

The suborder Pinnipedia is comprised of three of these families, including the odobenids (walrus), phocids (earless or "true" seals), and otariids (sea lions and fur seals) (Figure 3). Pinniped means "fin-footed" or "feather-footed," referring to the animal's webbed limbs that allow for movement on both land and at sea (Riedman, 1990; Berta et al., 2015). These front and back flippers allow pinnipeds to move on land in order to mate, give birth, and molt and allow for swimming and diving at sea to obtain food. Pinnipeds are primarily generalist feeders and mostly range from intermediate to apex predators (Laws, 1984; Lawson et al., 1994; Levermann et al., 2003; Berta et al., 2015). Their stomachs are similar in structure to that of other terrestrial carnivores, and they have heterodont teeth, like most terrestrial mammals, that allow them to grasp, puncture, shear, and crush varying prey items (King, 1983; Mårtenssen et al., 1998). Fish and cephalopods are the primary prey items of most pinniped species although several also consume significant quantities of krill and other crustaceans (Laws, 1984; Lawson et al., 1994). Walruses rely heavily on bivalve mollusks and forage by swimming along the seafloor with their snout, vibrissae, and foreflippers rooted and head down. They use their tongue as a piston to suck out the soft tissues of clams (Fay 1982; Levermann et al., 2003).

Marine mammals are necessary to maintain healthy trophic relationships within the food web, allowing for a balanced, healthy marine ecosystem. By observing trophic relationships, we can study evolving patterns of predator-prey interactions and understand the role competition plays among marine mammals and other species (Andersen, 1969; Moore, 2008; Berta et al., 2010; Nelms et al., 2018; Trites, 2019). Competition can affect the growth, reproduction, and survival rate of marine mammals. Since marine mammals generally have long lifespans and occupy a wide range of trophic positions, they serve an important role as bioindicators of global pollution, allowing us to monitor current ecological trends and anthropogenic effects to the biosphere (Ross, 2000b; Struntz et al., 2004; Tanabe and Subramanian, 2006; Moore, 2008;

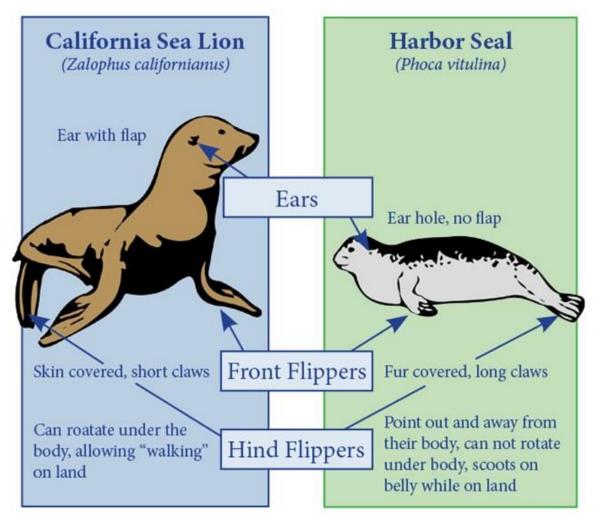


Figure 3. A comparison between otariids and phocids

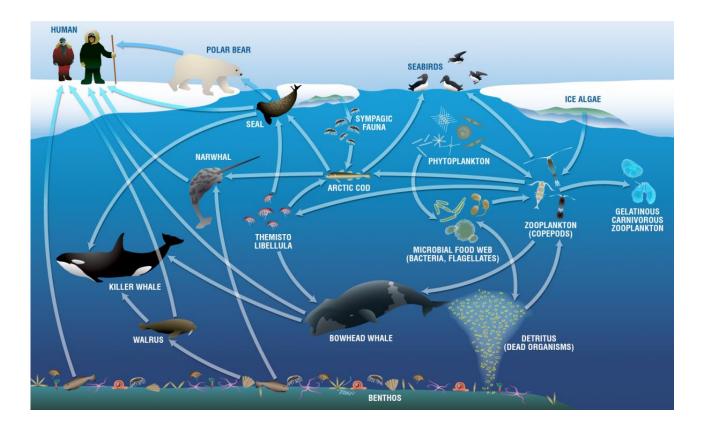
(https://www.nps.gov/redw/learn/nature/true-seals-versus-fur-seals-and-sea-lions.htm).

Lourenço et al., 2021). By better understanding these roles, we can implement management strategies to promote conservation of these species and protection of their marine habitats.

#### Marine Food Web

The marine food web is diverse and made up of both simple and complex food chains, with animals occupying a variety of trophic levels (Figure 4) (Briand and Cohen, 1987). Diets and foraging behaviors of marine mammals are influenced by a wide range of factors, including reproductive status, risk of predation, competitive interactions, and the distribution and abundance of prey (Berta et al., 2015). Consumer dynamics, such as type and length of food webs, can vary among taxa, and can impact how environmental contaminants are accumulated and assessed (Madgett et al., 2019). Due to this variation in trophic dynamics, individuals of the same species may not always occupy the same trophic level due to differences in age, sex, habitat, and seasonal and dietary differences (Frost and Lowry, 1986; Metcalfe et al., 2004; Kousteni et al., 2017). Both theoretical and assigned trophic levels can be used to model and estimate biomagnification of POPs in order to understand the diversity and complexity of the marine food web (Cardoso et al., 2013; Madgett et al., 2019)

Primary producers – the photoautotrophs such as phytoplankton, algae, and seagrasses – occupy the lowest trophic level. The next trophic level is made up of first order consumers, such as zooplankton and herbivorous feeders; this includes the manatees and dugongs (O'Shea et al., 2018; Trites, 2019). Second order consumers are made up primarily of filter feeders like mysticetes (baleen whales), which feed on first order consumers like zooplankton and larvae. Trophic levels continue up to intermediate and apex predators, such as odontocetes (toothed whales) and pinnipeds (seals, sea lions, and walruses); these species often feed on large fishes and even other marine mammals (Bowen, 1997; Nelms et al., 2018). Some of the highest trophic positions are held by those marine mammals that consume other marine mammals; these include species like the killer whale (*Orcinus orca*) and polar bear (*Ursus maritimus*) (Bowen, 1997; Reeves et al., 2017; Nelms et al., 2018). Many indigenous communities are also at risk of contaminant exposure due to subsistence feeding on several different marine mammal species (O'Hara et al., 1999; Hoekstra et al., 2005; Dehn et al., 2006; Moses et al., 2009). It is important to determine the trophic levels of organisms in order to better comprehend relationships between marine mammals and their surrounding environment and to also determine implications these



**Figure 4**. An example of a dynamic marine food web in the Arctic that could have human implications (https://askabiologist.asu.edu/plosable/marine-food-web-collapse).

interactions may have on human populations. There are several ways we can determine trophic relationships among marine mammals; diets can be assessed through stomach content analysis or by measuring isotopic ratios from marine mammal tissues (Lowry et al., 2005; Hernandez-Gonzalez et al., 2018; Trites, 2019).

#### Bioaccumulation and Biomagnification

Trophic levels are assigned to marine mammals based on their feeding relationships and metabolic functions within the marine ecosystem (Trites, 2001). Higher trophic level groups are at a higher risk of harm from POPs due to bioaccumulation and biomagnification processes (Bowen, 1997; Fair et al., 2010; Tsygankov et al., 2015; Nelms et al., 2018; Trites, 2019). Bioaccumulation refers to the process by which toxic chemicals accumulate in the tissue of a living organism, and biomagnification refers to the process by which the concentration of these toxins continues to increase as they move up the trophic levels of the food web (Kelly et al., 2007; Hernandez-Gonzalez, 2018; Nelms et al., 2018). Both processes can and do occur in marine mammals. Bioaccumulative pollutants are typically lipophilic and resistant to metabolic break-down, allowing them to persist in the environment and specifically accumulate in the lipidrich tissues found in marine mammals (Macdonald et al., 2002; Fair et al., 2010; Varanasi et al., 1992). Krahn et al. (2001) specifically evaluated the differences in contaminant concentrations of North Pacific gray whales (Eschrichtius robustus) and found that lipid content of tissues has a large impact on distribution and accumulation of organic contaminants. Since most marine mammals (minus the herbivorous Sirenia) are higher level trophic organisms and tend to have longer lifespans, they are much more vulnerable to the effects of bioaccumulation and biomagnification of organic contaminants (Ross, 2000b; Kelly et al., 2007; Pierce, 2008; Fair et al., 2010; Tsygankov et al., 2015). Both marine ecology and the life-history traits of marine mammals allow for greater occurrence of environmental contaminant accumulation, leading to greater disease susceptibility (Tanabe, 2002; Desforges, 2016).

An important method of determining biomagnification of organic compounds in top predators is by evaluating their food sources. A study by Borgå et al (2001) near Svalbard compared concentrations and patterns of organochlorines in several taxa within the arctic marine food web, including pelagic crustaceans, fishes, and seabirds. These taxa allowed for a diverse group of marine organisms that occupied both lower and higher trophic levels. The results of the study indicated that crustaceans and fishes, occupying lower trophic positions, generally had lower concentrations of organochlorines compared to the seabirds, which had concentrations one to three orders greater. This may be due in part to the lower ability of seabirds to metabolize foreign contaminants and greater elimination mechanisms of crustaceans and fishes, such as direct diffusion (Livingstone, 1992; Borgå et al, 2001, 2005; Walker et al., 2005).

Marine mammals occupying higher trophic levels accumulate pollutants in amounts that can have a toxic effect at several levels, including the cell, tissue, organism, and population. These effects can cause reproductive harm and irreversible damage to their immune systems, which leaves these animals at higher risk of obtaining life-threatening diseases and potentially endangering populations (**Reijnders**, 1986; Tanabe, 2002; Tsygankov et al., 2015; Desforges et al., 2016). Desforges et al. (2016) determined that both innate and adaptive immunity are affected by increasing concentrations of organic contaminants and found a correlation between lymphocyte proliferation and phagocytosis associated with greater contaminant exposure in marine mammals.

The field of immunotoxicology has continued to grow over the last several decades, starting with concerns of adverse effects of pollutants on human health and continuing to both domestic and wild animals (Tanabe et al., 1994; Newman and Unger, 2003). The "Baltic Seal Disease Complex" was investigated in the 1970-80s, linking higher POP concentrations in the Baltic grey seal (Haliocherus grypus) and the ringed seal (Pusa hispida) to greater disease susceptibility. Studies showed greater occurrence of lesions, osteoporosis, leiomyoma, stenosis, and occlusions of the uterus, which can affect reproductive success and survival of species (Helle, 1980; Reijnders, 1986; Olsson et al., 1994; Wang et al., 2007; Desforges et al., 2016; Nelms et al., 2018). Letcher et al. (2010) showed particular concern for top trophic level species in the Arctic, where climate change and seasonal changes in food intake may affect the level of POP concentrations. Toxicokinetic effects of POPs appear to have strong ties to temporal changes in bioenergetics, particularly during periods of fat accumulation and mobilization, which may correspond to higher POP sensitivity in Arctic marine mammal populations (Krahn et al., 2001; Tilbury et al., 2002; Letcher et al., 2010; Desforges et al., 2016). The accumulation of POPs in marine mammals could be related to greater disease susceptibility and several unusual mortality events (UMEs); further investigation can help us in determining trends of population

declines and patterns of marine ecosystem health and diversity (Tanabe, 2002; Struntz et al., 2004).

#### Persistent Organic Pollutants

Persistent organic pollutants (POPs) are a growing concern to both marine and freshwater environments due to their immunologic, carcinogenic, teratogenic, neurological, and reproductive effects (Tanaabe et al., 1983; Safe, 1992; Lahvis et al., 1995; Sarkar et al., 2012). POPs are harmful organic (carbon-based) compounds that are highly resistant to biodegradation, posing major threats to marine biota (Holden and Marsden, 1967; O'Shea, 1999; Ilyina et al., 2006; Cole et al., 2010). Residues of these pollutants have been found in all levels of marine biota, from phytoplankton to marine mammals (Muir et al., 1999; Svendsen et al., 2007; Struntz et al., 2004). Marine mammals, especially those that eat fish and reside in coastal regions with dense human populations and larger industrial and agricultural activities, have been shown to have higher concentrations of POPs (O'Shea, 1999; Aguilar et al., 2002; Fair et al., 2010). However, marine mammals are exposed to organic contaminants worldwide, including Arctic and Antarctic regions. Although these regions are further from sources of contamination, they are still susceptible to contaminant exposure due to transport of POPs over large distances by oceanic currents and atmospheric long-range transport, depositing POPs into sediments, ice, and soil (Letcher et al., 2010; Trumble et al., 2012; Kallenborn et al., 2015). Marine mammals are also some of the most susceptible animals to organic contaminant accumulation since they generally have high levels of fat to accommodate needs for insulation and energy reserves (Holden and Marsden, 1967; O'Shea, 1999; Sarkar et al., 2012; Berta et al., 2015).

Age, sex, and nutritive status are all important factors of contaminant accumulation in marine organisms. Juveniles of several marine mammals have been shown to have increasing concentrations of organic contaminants until sexual maturity is reached (Aguilar and Borrell, 1988; Kuehl and Haebler, 1995; Krahn et al., 1999; Tilbury et al., 1999). Although females generally have greater lipid reserves, the males are often more susceptible to organic contaminants once sexual maturity is reached since they do not eliminate them through lactation and gestation as females do (Wagemann and Muir, 1984; Subramanian et al. 1988; Beckmen et al., 1999; Tilbury et al., 2002). Several marine mammals, especially baleen whales, also have varying nutritional statuses and overall lipid content, which often change during migrations, based on breeding and feeding seasons (Mackintosh and Wheeler; 1929; Rice and Wolman, 1971; Aguilar and Borrell, 1990; Tilbury et al., 2002).

POPs have low solubility in water but can easily latch on to solid particles, where they are highly soluble in organic liquids, such as fats, fuels, and oils. Several studies have shown the affinity POPs have for marine sediments, especially those in coastal areas (Varanasi et al., 1992; Iwata et al., 1994; Brasher and Anthony, 2000; Sarkar et al., 2012). Most POPs originate from man-made sources, such as pesticides, pharmaceuticals, and industrial chemicals (Holden and Marsden, 1967; Tanabe et al., 1983; O'Shea, 1999; Tanabe, 2002; NOAA, 2020). They can bioaccumulate in living organisms and have toxic effects, leading to harmful and even fatal events (Jones and Voogt, 1999; Wang et al., 2007; Fair et al., 2010). With oceans acting as a natural sink for POPs, it is important to understand the slow but long-term transport of contaminants that occurs in the marine environment (Iwata et al., 1993). Atmospheric deposition and river runoff can deliver contaminants to oceans and pose threats to the marine environment, specifically in highly industrialized regions (Ilyina et al., 2006). Some of the most common POPs discovered and measured in marine mammal tissues include pesticides. dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs, used as flame retardants) (Holden and Marsden, 1967; Tanabe et al., 1983; Iwata et al., 1993; Svendsen et al., 2007; Fair et al., 2010; Yordy et al., 2010; Law et al., 2012; Sarkar et al., 2012; Winfield et al., 2020).

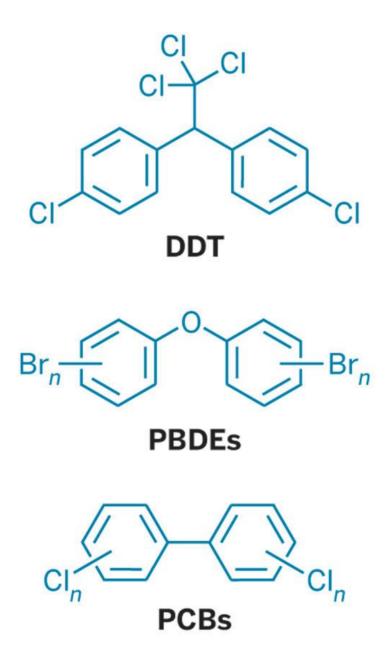
PCBs (polychlorinated biphenyls) are one of the most prominent and well-studied POPs in marine mammals. PCBs are industrial products or chemicals that contain carbon, hydrogen, and chlorine atoms; the configuration of these atoms has a large impact on both the physical and chemical properties of these contaminants and how they persist in the environment (Jensen, 1966; Tilbury et al., 2002; Sarkar et al., 2012; NOAA, 2020; EPA, 2020). Although commercial production of PCBs was banned in the United States in the late 1970's, they can still be introduced into the environment from materials produced before the ban and are often released due to poorly managed hazardous waste facilities, illegal or improper disposal of PCBs, leaking from electrical transformers, and burning of certain waste materials in industrial incinerators (Tanabe, 2002; Ilyina et al., 2006; Sarkar et al., 2012; EPA, 2020).

DDT (dichlorodiphenyltrichloroethane) was one of the first synthetic insecticides developed during the 1940s. It has been known to persist in the environment for long periods and

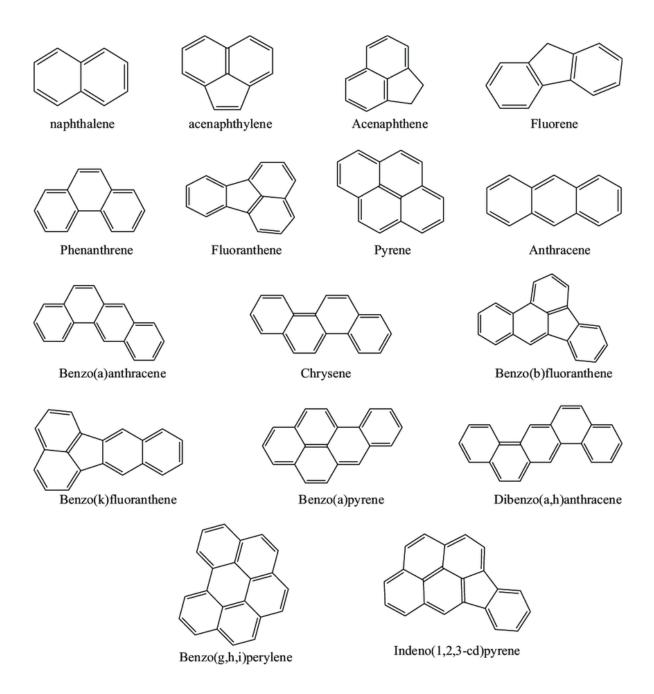
has a tendency of accumulating in fatty tissues of animals. DDT has no documented toxic effects while stored in fatty tissues, but it can become a major threat when fat stores are mobilized, allowing for harmful DDT metabolites to be released into the bloodstream and travel to other systems of the body (WHO, 1979; Tanabe et al., 1983; Sarkar et al., 2012). This can cause damage, specifically to the liver and the nervous system. DDT can persist in the environment for long periods. It has a half-life ranging from 2-15 years in soil; however, it can last approximately 150 years in aquatic environments. The EPA has labeled DDT as a B2 carcinogen, meaning it has been demonstrated to cause cancer in laboratory animals (Young et al., 1976; EPA, 2020).

Similar in structure to PCBs and DDTs (Figure 5), PBDEs are brominated flame retardants that are added to manufactured products, such as electronic enclosures, foam in upholstery, and industrial plastics, to prevent products from catching on fire. After being released from breakdown or leaking of products, these contaminants can travel throughout the air, water, and sediments where they pose threats to a variety of organisms (Sellström et al., 1993; Pijnenburg et al., 1995; Sarkar et al., 2012). PBDEs are an emerging concern in both coastal and pelagic waters and have been shown to bioaccumulate in several small cetaceans, such as the spinner, humpback, and Irrawaddy dolphin (Kannan et al., 2005; Kajiwara et al., 2006; Yordy et al., 2010). Based on different experimental exposure studies, PBDEs have been shown to induce a wide range of disorders, including cancer, disruption of endocrine and central nervous system functions, and developmental and reproductive toxicity (Eriksson et al., 1998; Hana et al., 2004; Birnbaum and Staskal, 2004; Fair et al., 2010).

PAHs are naturally occurring chemicals that consist of at least two benzene rings (Figure 6) and are often found in coal, gasoline, and crude oil (Neff, 1980; Lourenço et al., 2021). Anthropogenic activities, such as burning of coal, wood, tobacco, and fossil fuels and petroleum spills can also impact the concentration of PAHs in the environment, where they readily bind to small air particles (Neff, 1980; McCready et al., 2000; Fair et al., 2010; Lourenço et al., 2021). PAHs have become a growing concern as they are likely increasing in the environment due to higher demand for oil and gas industries (Svendsen et al., 2007). They are lipophilic and hydrophobic and have a high affinity for organic fractions, allowing them to readily adsorb to particulate organic matter and accumulate in both terrestrial and marine sediments (Bjørseth, 1985; McElroy, 1989; Skupinska et al., 2004; Lourenço et al., 2021). Once they are released into



**Figure 5**. General chemical structure of DDT, PBDE, and PCB, showing their similar overall structure (https://cen.acs.org/articles/93/i9/Persistence-Pays-Off-Studying-Persistent.html).



**Figure 6**. Examples of common PAH compounds, each consisting of at least two fused benzene rings (https://www.researchgate.net/figure/Molecular-structures-of-PAHs\_fig1\_323700398).

the marine environment, they partially evaporate and dissolve in the seawater, where the majority quickly adsorb suspended particles and sediments (Lourenço et al., 2016). Due to their extensive metabolism, PAHs are not easily quantified and analyzed in marine mammals; however, they do still pose threats to marine life as they are widespread and toxicologically significant (Varanasi et al., 1994).

Marine mammals can ingest POPs directly and indirectly (Desforges et al., 2016; Trites, 2019; Zantis et al., 2021). Several species ingest organic contaminants directly through filter feeding, while others ingest organic contaminants indirectly through prey consumption. Species that occupy a higher trophic level are at a greater risk for toxicity from increasing organic contaminant concentrations as they bioaccumulate and then biomagnify up the food web (Bowen, 1997; Trites, 2019). Feeding strategies have a major impact on how contaminants can be ingested. Some marine mammals are filter feeders that can uptake POPs directly from the ocean water, while others actively prey on food and ingest POPs indirectly from their food source (Pauly et al., 1998). Differences in life history traits, behaviors, morphologies, and physiologies among marine mammals can affect the rate at which they accumulate organic pollutants (Holden and Marsden, 1967; Fair et al., 2010; Trites, 2019).

In recent years there have been increasing reports of marine mammals infected by uncommon diseases. These diseases, which often lead to mortalities, have been largely attributed to exposure to man-made toxic contaminants (Tanabe, 2002; Desforges et al., 2016). Several of these contaminants can act as endocrine disruptors, affecting normal physiological functions of marine mammals (Ross et al., 2000; Krahn et al., 2001; Tanabe, 2002; Stockin et al., 2010; Yordy et al., 2010). Several unusual mortality and stranding events are also believed to be correlated with increasing organic contaminant concentrations (**Muir et al., 1988**; Tilbury et al., 1999; Tanabe, 2002; Struntz et al., 2004; Law et al., 2012). Various studies over the past several decades indicate that both natural and anthropogenic contaminants modulate the immune system of marine mammals (Desforges et al., 2016).

#### Maternal Offloading

Not only can organic contaminants be transferred through predator-prey interactions, but more recent research has shed light on the interactions between mother and offspring. Maternal transfer of contaminants, also referred to as maternal offloading, has been recorded and analyzed in several fish species, such as the mackerel sharks (Lyons et al., 2013), but it is becoming an increasing concern in marine mammals (Tilbury et al., 1999; Krahn et al., 2009). Several marine mammals have exhibited maternal transfer of contaminants to their offspring, with the offspring generally exhibiting higher concentrations than the mother. The killer whale, pilot whale, northern and Atlantic fur seals, harp seal, and grey seal have all exhibited some degree of maternal offloading; both lactation and *in utero* transfer of contaminants have been recorded as transfer methods (Beckmen et al., 1999; Tilbury et al., 1999; Sørmo et al., 2003; Wang et al., 2007; Schiavone et al., 2009; Krahn et al., 2009; Frouin et al., 2012; Taylor et al., 2018). Although embryonic transfer is important, it appears that lactational transfer of contaminants is of a greater significance quantitatively (Nakashima et al., 1997; Schiavone et al., 2009).

Krahn et al. (2009) found that juvenile Southern resident killer whales were at greater risk of obtaining adverse health effects, specifically related to immune and endocrine dysfunction, due to maternal transfer of contaminants during rapid development of their biological systems. Since the reproductive females transfer a large portion of their contaminant burden to their calves, they generally have less contaminants than their male counterparts (Ross et al., 2000; Ylitalo et al., 2001; Krahn et al., 2009). Phocid seals have lipid-rich milk, which serves as a medium through which persistent organic pollutants can travel from mother to pup during lactation (Lydersen and Kovacs, 1999; Sørmo et al., 2003; Wang et al., 2007). One study evaluated the partitioning of chlorinated organic contaminants in maternal blood, blubber, and milk as well as pup blubber, both early and late in the lactation period. The study concluded that more hydrophobic and highly chlorinated contaminants are passed less efficiently into the milk than more water soluble and lowly chlorinated contaminants (Sørmo et al., 2003). Another study used biomagnification factors to describe the transfer and accumulation of lipophilic contaminants from dams to pups in northern fur seals (otariids). Results from this study indicated a higher exposure of contaminants from primiparous milk ingestion, which is reflected in a much higher concentration of organic contaminants in the blood of first-born pups (Muir et al., 1988; Beckmen et al., 1999).

#### **Marine Mammal Contaminant Studies**

Given the diversity among marine mammals, the following species are selected to evaluate the impacts of organic pollutants on different trophic positions, morphologies, migration patterns, habitats, and life histories (Rice, 1998; Perrin, 2021). For the cetaceans, the bowhead whale (Balaena mysticetus), gray whale (Eschrichtius robustus), humpback whale (Megaptera novaeangliae), common bottlenose dolphin (Tursiops truncatus), and the killer whale (Orcinus orca) are chosen to represent differences in contaminant concentrations in different trophic positions and foraging and migration patterns, including a benthic suction feeder, ram filter feeder, and two apex predators. The California sea lion (Zalophus californianus), Hawaiian monk seal (Neomonachus schauinslandi), and walrus (Odobenus rosmarus) are chosen to represent the pinnipeds as they occupy three different families (Phocidae, Otariidae, and Odobenidae) with different habitats and feeding strategies. Although these three pinnipeds are all apex predators and generalist feeders, they occupy distinct regions, with the Hawaiian monk seal occupying subtropical waters, the California sea lion primarily occupying temperate to subtropical waters in shallow, coastal Pacific regions, and the walrus occupying Arctic waters (Littnan et al., 2015; Lowry, 2016). This can shed light on latitudinal and climate driven differences in contaminant accumulation. The sirenians make up the final group, including the West Indian manatee (Trichechus manatus) and the dugong (Dugong dugon); these two marine mammals hold the lowest trophic positions as they are herbivorous feeders. Although they have similar diets, the dugong feeds primarily on benthic seagrass, whereas the manatee feeds in surface waters. This could also impact how they accumulate POPs (Hartman, 1979; Marsh et al., 2012).

#### Cetaceans

Making up more than two-thirds of all marine mammals, the cetaceans are comprised of 86 extant species, including two suborders: the mysticetes (baleen whales) and odontocetes (toothed whales) (Rice, 1998; Perrin, 2021). These marine mammals have been shown to have strong effects on community structure and can be important indicators of marine ecosystem health (Bowen, 1997). This is the largest and most diverse of the marine mammals, and occupies the widest range of trophic positions, from filter feeders to apex predators (Rice, 1998; NOAA, 2021d). Several cetaceans are also migrators and have varying nutritive statuses over the course of their lives (Aguilar et al., 2002; Bolton et al., 2020). Due to large differences in trophic ecology and exposure route, mysticetes and odontocetes tend to have significantly different levels of organic contaminants (O'Hara et al., 1999; Krahn et al., 2001).

#### Bowhead Whale

The bowhead whale (*Balaena mysticetus*) (Figure 7) is a baleen whale from the suborder Mysticeti belonging to the family Balaenidae. As one of the longest living animals on Earth, often living well over 100 years, the bowhead whale has a higher risk for bioaccumulation of organic contaminants during its lifetime (Cooke and Reeves, 2018; Bolton et al., 2020). The bowhead whale is comprised of five stocks currently recognized by the International Whaling Commission (IWC): the Sea of Okhotsk, Davis Strait, Hudson Bay, the offshore waters of Spitsbergen, and the western Arctic stock (Cooke and Reeves, 2018). Commercial whaling, which occurred between the 16<sup>th</sup> and mid-19<sup>th</sup> centuries, led to a depletion in all the bowhead whale stocks (Bolton et al., 2020), although they are currently listed as least concern on a global scale (IUCN, 2021e). However, the western Arctic stock is currently listed as "endangered" according to the U.S. Endangered Species Act and also considered "depleted" according to the U.S. Marine Mammal Protection Act (Braham, 1980, 1984; Bolton et al., 2020; Muto et al., 2020). Some of the current threats to the bowhead whale are pollution, climate change, shipping lanes, oil and gas drilling, and commercial development (Cooke and Reeves, 2018).

Bowhead whales are categorized as continuous ram filter feeders, meaning they feed with their mouths open while swimming horizontally into a dense group of prey (Werth, 2001). They occupy a lower-level trophic position since they feed primarily on crustacean zooplankton (Schell et al., 1989; Lowry et al., 2005). Since the mid-1970s, researchers have collected stomach content samples from bowhead whales, indicating that copepods, euphausiids and amphipods, are some of their most prevalent prey items (Lowry et al., 1993, 2005).

Although the bowhead whales occupy a lower trophic level compared to other marine mammals, they live in the Arctic, where lipid-dependent food webs thrive. Their heavy blubber and muscle content allow for accumulation of lipophilic organic contaminants (O'Hara et al., 1999; Hoekstra et al., 2005). O'Hara et al. (1999) collected organochlorine levels from the blubber and liver of twenty bowhead whales during an Eskimo subsistence harvest in Barrow, Alaska between 1992 and 1993. They found that most of the organochlorines measured were greater in longer-lived whales. Some organochlorines, specifically DDT, increased in males with increasing size; however, females tended towards an opposite outcome, with levels decreasing or showing no change with increasing size. This trend has been observed in other marine mammals as well and likely indicates excretion of organic contaminants by the sexually mature females



Figure 7. A bowhead whale at the surface of the water (https://ocr.org/sounds/bowhead-whale/).

during lactation, offloading contaminants to the neonate (Addison et al., 1986; Muir et al., 1988; Boon et al., 1992).

Another study by Bolton et al. (2020) showed declining trends of POPs in the blubber and muscle of bowhead whales between 2006 to 2015 compared to previous years, which is likely due in part to international action (e.g., the Stockholm Convention) taken to restrict the use and production of several POPs. This study also indicated that seasonal migration may have an impact on contaminant concentrations; certain polychlorinated biphenyls (PCBs) and dichlorodiphenyl dichloroethene (DDE) had higher concentrations in the spring compared to the fall. These seasonal variations may be due to differences in sea water concentrations of POPs in winter and summer feeding zones and differences in lipid content, with bowheads exhibiting higher lipid reserves in the spring (Fisk et al., 2001; Hoekstra et al., 2002, 2005; Bolton et al., 2020). Overall, studies indicate a decline in POPs in Arctic organisms, like bowhead whales, since international measures (e.g., Stockholm Convention) were taken to limit production of POPs (AMAP, 2016; Bolton et al., 2020). These studies are vital to indigenous Inuit communities that rely on bowhead whales for nutritional, cultural, and spiritual subsistence (O'Hara et al., 1999; Moses et al., 2009; Bolton et al., 2020).

#### Gray Whale

The gray whale (*Eschrichtius robustus*) is a baleen whale from suborder Mysticeti and is the only living member of the family Eschritiidae (Rice and Wolman, 1971; Sumich, 2014; Berta et al., 2015). Gray whales primarily occupy coastal waters and are known migrators from tropical to high temperate waters during feeding and breeding seasons (Tilbury et al., 2002). Gray whales occupy continental shelf waters along the eastern margin of the North Pacific Ocean. They migrate annually between summer feeding grounds in waters off Alaska and British Columbia and then winter in the Gulf of California, where calving and breeding primarily occur (Rice and Wolman, 1971). This southbound migration allows for breeding in warmer waters that are relatively safer from predators (Blokhin, 1986). Although their population is stable according to the IUCN (IUCN, 2021d), threats to the populations are still present, primarily in the form of fishing and harvesting of aquatic resources and pollution (Cooke, 2018).

Gray whales are omnivorous feeders and differ from other baleen whales in their feeding ecology. They have a piston-like tongue for suction and short, coarse baleen to filter small

benthic organisms (Rice and Wolman, 1971; Nerini, 1984; Sumich, 2014; Berta et al., 2015). Given their unique feeding ecology, their baleen is constantly being abraded by the seafloor sediment, so the baleen continuously grows throughout the life of the whale (Rice and Wolman, 1971; Berta et al., 2015). Their primary prey items are ampeliscid amphipods (*Ampelisca macrocephala*) (Caraveo-Patiño and Hobson, 2007). These crustaceans dominate a large volume of the benthic community in the northern Bering and southern Chukchi seas (Nerini, 1984). However, recent studies evaluating the isotopic composition in the epidermis of eastern gray whales indicate contribution of prey outside their Arctic feeding grounds, specifically observing lactating females continuously feeding to satisfy their physiological needs during migration and breeding seasons. They found that benthic amphipods from the Bering Sea were not the eastern gray whale's primary food source, and each mother also exhibited a different feeding strategy (Walker, 1971; Caraveo-Patiño and Soto, 2005; Gelippi, 2022).

Although gray whales can filter sediments through their baleen plates, their unique feeding ecology still allows for some sediments and bottom materials to be ingested, increasing their exposure to sediment associated contaminants (Rice and Wolman, 1971; Nerini, 1984; Tilbury et al., 2002). One study found higher concentrations of certain trace elements, namely aluminum, were present in higher concentrations in the stomachs of gray whales, which may directly correspond with the ingestion of sediments as part of their natural feeding ecology (Haley, 1978; Nerini, 1984; Tilbury et al., 2002). This hypothesis is supported by differences in liver concentrations of aluminum between the gray whale and the bowhead whale; the bowhead whale feeds throughout the water column with little exposure to sediments, which corresponds with its considerably smaller concentration of aluminum in the liver (Lowry, 1993; Krone et al., 1999; Tilbury et al., 2002).

Between the years 1999 and 2000, there was a dramatic increase in fatal gray whale strandings (Figure 8); the number of gray whales involved increased from 50 to approximately 274 whales per year (Le Boeuf et al., 2000; Law et al., 2012; NOAA, 2021b). Concentrations of POPs, specifically in sediment-associated compounds, were proposed as potential causes for these increased mortality events (Varanasi et al., 1994; Le Boeuf et al., 2000; Dehn et al., 2006). Although gray whales generally have lower trace element and organic contaminant concentrations compared to other cetaceans due to their lower trophic ecology, they are still



**Figure 8**. A stranded gray whale located off Point Reyes National Seashore in northern California (NOAA, 2021b).

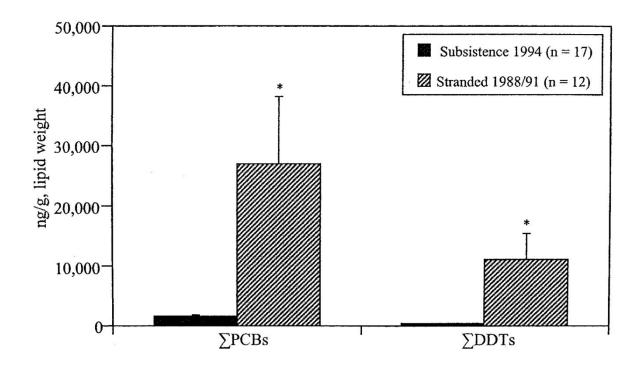
vulnerable to accumulation of contaminants and can have a large impact on Inuit communities that rely on gray whales for subsistence (Hoekstra et al., 2005; Dehn et al., 2006).

Tilbury et al. (2002) assessed the anthropogenic contaminants in tissues of juvenile gray whales and found that concentrations were low compared to other marine mammals feeding at higher trophic positions. They also found lower concentrations of organochlorines (OCs) in lipid-based tissues in juvenile subsistence whales than that of juvenile stranded whales from previous studies (Figure 9) (Varanasi et al., 1994). The higher concentrations in stranded whales are likely due to retention of OCs in the blubber of stranded whales since lipid stores are mobilized for energy, decreasing total lipid levels. This shows how the nutritive condition of an animal can affect the composition of blubber, specifically the lipid content and blubber thickness, and, therefore, affects how OCs are accumulated in lipid-rich tissues (O'Hara et al., 1999; Krahn et al., 2001; Tilbury et al., 2002).

Another study performed by Krahn et al. (2009) found biological factors, such as gender, age, and reproductive status, coupled with varying sampling methods, such as biopsy, subsistence hunts, and strandings, to be key components in determining contaminant load in gray whales. The study concluded that the blubber of subsistence animals contained greater lipid content compared to lipids of both biopsied and stranded gray whales. Subsistence whales were sampled after summer feeding took place in the Bering and Chukchi Seas. Stranded whales likely had lesser lipid levels due to poor health, reduced prey availability, reduced feeding during breeding season, or leaching of lipids from blubber postmortem. Also, similar in comparison to other marine mammal contaminant findings, this study indicated a trend of higher OC concentrations in males versus females, presumably due to maternal transfer of contaminants by sexually mature females during lactational and gestational periods, where contaminant burden was transferred to calves. However, the small sample size in this study did not yield statistically significant results between male and female gray whales. (Krahn et al., 2001).

## Humpback Whale

The humpback whale (*Megaptera novaeangliae*) (Figure 10) is a rorqual baleen whale from the suborder Mysticeti, belonging to the family Balaenopteridae. It is present in all oceans globally and has one of the longest migrations of any mammal (Rosenbaum and Collins, 2006; Berta et al., 2015; Clapham, 2018). Prior to the final moratorium on commercial whaling in 1985



**Figure 9**. Mean concentrations (ng/g, lipid weight) of  $\sum$ PCBs and  $\sum$ DDTs in blubber of subsistence 1994 and stranded 1988–1991 juvenile gray whales. Asterisk indicates that the mean concentration of organic contaminants in stranded whales is significantly higher ( $p \le 0.05$ ) than the corresponding value for subsistence whales of the same age class (juvenile) by student's *t*-test. (Varanasi et al., 1994; Tilbury et al., 2002).



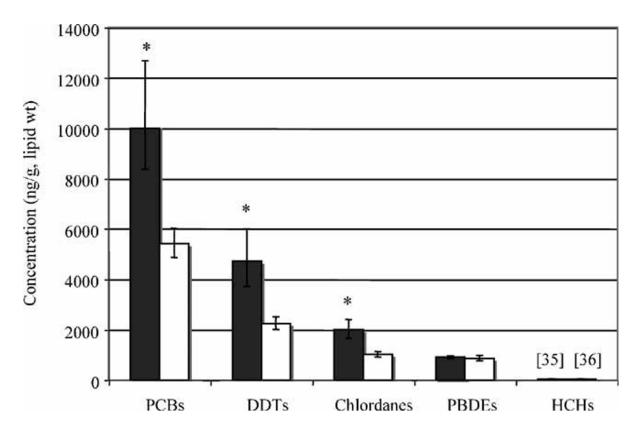
Figure 10. A humpback whale breaching at the surface of the water (NOAA, 2022).

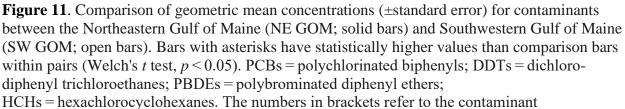
by the International Whaling Commission, populations of humpback whales drastically declined due to commercial whaling. Although two subpopulations are still endangered, the humpback whales as a species have been steadily recovering and are considered of least concern according to the IUCN Red List (IUCN, 2022). Their primary threats include vessel strikes, climate change, and entanglement in fishing gear (Clapham, 2018; NOAA, 2022).

Humpback whales are useful as bioindicators of regional contamination due to both their seasonal feeding behavior and high consistency to feeding grounds (Calambokidis et al., 2001; Elfes et al., 2010; Remili et al., 2020). Humpbacks spend most of the warmer months feeding in high latitude areas in order to build up their lipid reserves to sustain themselves through the winter. They can travel thousands of miles from their tropical breeding grounds to cooler, more productive waters for feeding (Chittleborough, 1958; Rosenbaum and Collins, 2006; NOAA, 2022). They primarily consume small crustaceans, particularly krill, and small fish through filter feeding, often employing coordinated bubble net feeding mechanisms to corral and condense prey (Chittleborough, 1965; D'Vincent et al., 1985; Wiley et al., 2011; Berta et al., 2015; NOAA, 2022).

A study by Elfes et al. (2010) evaluated the variation of POPs in the humpback whales of the North Pacific and North Atlantic (Figure 11). They found that North Atlantic Whales were more contaminated overall than their Pacific counterparts, having higher levels of PCBs, PBDEs, and chlordanes. However, the highest concentrations of DDTs were found in whales feeding in southern California. While generally comparable to other mysticetes, contaminant levels in humpbacks were found to be lower compared to those measured in marine mammals of higher trophic positions, such as odontocetes and pinnipeds (De Swart et al., 1996; Barron et al., 2003; Metcalfe et al., 2004; Krahn et al., 2009; Elfes et al., 2010).

Another study by Remili et al. (2020) showed varying degrees of organic contaminant concentrations in humpback whales based off geographic zones, sex, and trophic levels. They collected biopsies from free-ranging humpback whales breeding off Mozambique and Ecuador. The study found that POP concentrations varied between populations of humpback whales feeding in different regions of the Southern Ocean. Although populations on both sides of the hemisphere had some of the lowest POP concentrations measured for humpback whales, there was no overlap in isotopic niches between the whales from Mozambique and Ecuador, demonstrating that the populations are feeding in different areas of the Southern Ocean. The





concentrations for those bars (in ng/g, lipid weight) (Elfes et al., 2010).

study also found that HCB (hexachlorobenzene) and DDTs comprised the greatest concentration of POPs present in humpback whale blubber in both populations. Males had higher levels of organic contaminants compared to females, likely due to maternal transfer of contaminants to offspring as described in several other marine mammal studies (Krahn et al., 2001, 2009; Kajiwara et al., 2008; Pinzone et al., 2015). The study also proposed that some whales may feed opportunistically at higher trophic levels within the Antarctic based on higher isotopic ratios and higher HCB and DDT concentrations (Remili et al., 2020).

### Common Bottlenose Dolphin

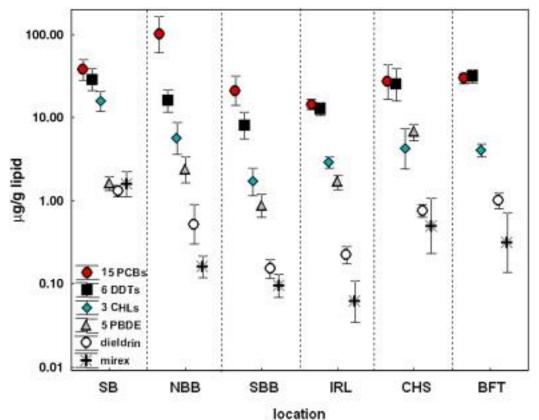
In comparison to other toothed whales, the common bottlenose dolphin (Figure 12) is relatively smaller, ranging from 2-4 meters in length and about 150-200 kg in weight (Wells and Scott et al., 1999, 2009; Wells et al., 2019). There are 6 families of dolphin and porpoise species, with the oceanic dolphins occupying the largest group. The common bottlenose dolphin (*Tursiops truncatus*) belongs to the family Delphinidae. Its population status is currently listed as least concern; however, it is still threatened by residential and commercial development, tourism, pollution, recreational activities, fishing and harvesting of aquatic resources, and shipping services (Fair et al., 2010; Wells et al., 2019). The common bottlenose dolphin generally occupies coastal waters in both tropical and temperate climates (Wells and Scott et al., 1999; Wells and Scott, 2009).

The common bottlenose dolphin is an apex predator that consumes a wide variety of species. Some of the most common prey items consumed based on stomach content analyses are squids and fishes (Barros and Odell, 1990; Barros and Wells, 1998); they will occasionally feed on shrimp and other crustaceans as well (Wells et al., 2019). Since they consume a large variety of species, they have developed extensive foraging strategies targeted for specific prey items, including passive listening of prey-generated sounds (Barros and Wells, 1998). Larger dolphins have also been observed to prey upon larger prey items, showing a positive correlation between total body length of dolphins and their prey items (Barros and Odell, 1990).

The common bottlenose dolphin has been the focus of many contaminant studies due to its habitat, size, population status, stock structure, and trophic dynamics (Balmer, 2010; Wells et al., 2004; Wells and Scott, 2009). Balmer et al. (2010) measured POPs in a localized population of bottlenose dolphins in Sarasota Bay, Florida (Figure 13), and found that sex and age can have



**Figure 12**. Two common bottlenose dolphins swimming in tropical waters. (https://www.marinemammalcenter.org/animal-care/learn-about-marine-mammals/cetaceans/common-bottlenose-dolphin).



**Figure 13.** Comparison of persistent organic pollutant (POP) concentrations (geometric mean, 95% CI) measured in Sarasota Bay (SB) male/juvenile bottlenose dolphins to published values for bottlenose dolphins at other geographic locations, including North Biscayne Bay, FL (NBB), South Biscayne Bay, FL (SBB), Indian River Lagoon, FL (IRL), Charleston, SC (CHS) and Beaufort, NC (BFT). POP analytes include PCBs, DDTs, CHLs (chlordanes), PBDEs, dieldrin, and mirex, several of which have been used as pesticides/insecticides. PBDE values shown for CHS and IRL are arithmetic mean  $\pm$  95% CI. (Balmer et al., 2010).

significant effect on variations in contaminant concentrations. PCBs and DDTs were the dominating contaminants in the blubber of these dolphins. POP concentrations varied among these dolphins due to differences in life history parameters, including age and sex; the mature females from the Sarasota Bay population exhibited significantly lower amounts of POPs compared to juveniles, which can be attributed to parturitional and lactational transfer of contaminants, primarily to their first-born offspring (Cockcroft et al., 1989; Aguilar et al., 1999; Wells et al., 2005; Balmer et al., 2010).

Wilson et al. (2012) identified the spatial distributions of bottlenose dolphins along the Florida Gulf Coast by comparing differences in persistent organic pollutants (POPs); they were able to divide 77 bottlenose dolphins into three distinct communities centered at three respective embayments (St. Andrews Bay, St. Joseph Bay, and St. George Sound) based on POP levels and isotopic values observed. Minimal spatial overlap was observed among these three embayments. Overall, bottlenose dolphins may serve as barometers of marine ecosystem health as they occupy a wide range of environments and feeding strategies; they can reflect the impacts of anthropogenic and natural stressors on themselves, but also on the lower trophic level communities that they consume (Wells et al., 2004).

# Killer Whale

The killer whale (*Orcinus orca*) is a toothed whale from the family Delphinidae. It is the largest of the delphinid species and occupies some of the highest trophic levels (Reeves et al., 2017). There is currently insufficient data on their population sizes, but they may be contributing to declines in other marine mammal populations, such as the Steller sea lions and sea otters due to predation (Reeves et al., 2017; Trites, 2019); They occupy a wide range of habitats, but mainly occur in colder waters with high productivity in higher latitudes (Ross et al., 2000). They have one of the most cosmopolitan distributions of both marine and terrestrial mammals (Rice, 1998). Killer whales are currently threatened by human exploitation, pollution, climate change, energy production and mining, and shipping and vessel traffic (Reeves et al., 2017).

Killer whales are carnivorous feeders, preying on a diverse group of marine species, with different populations occupying different trophic roles. They also have an advanced set of foraging tactics, including beaching to capture on shore pinnipeds, creating waves to push seals off ice floes (Figure 14), and herding of fish through cooperative feeding techniques (Baird et al.,

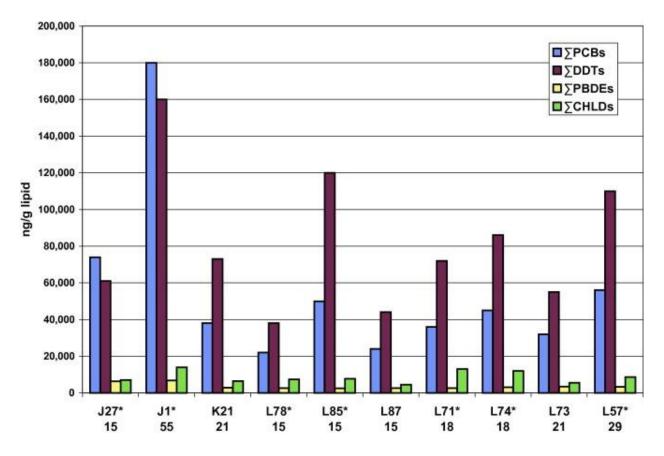


**Figure 14**. Two killer whales creating waves to push a crabeater seal off an icefloe. (https://www.nationalgeographic.com/science/article/orcas-hunt-seal-antarctica-ice-video-dolphin-intelligence-whale-culture-spd).

2001; Ford and Ellis, 2006; Berta et al., 2015; Reeves et al., 2017). Occupying one of the highest trophic levels of marine mammals, the killer whale may be considered at high risk for bioaccumulation and biomagnification of POPs (Reeves et al., 2017).

A study by Krahn et al. (2009) evaluated the effects of age, sex, and reproductive status on POP concentrations in southern resident killer whales. The study concluded that juvenile killer whales may be more vulnerable to high concentrations of POPs due to maternal transfer of pollutants; therefore, juveniles are at increased risk for immune and endocrine challenges during these rapid changes in development. Findings indicate that an increase in environmental pollutants as well as marine noise and decreased quantity/quality of food sources may contribute to declines in southern resident killer whale populations. Based on field observations and contaminant ratios of three different pods (K-, L-, and J-pods) of southern resident killer whales (Figure 15), the study found that the two pods (K- and J-pods) that traveled to California to forage had higher ratios of PCBs and DDTs, likely due to higher concentrations of contaminants in prey items, such as Chinook salmon (Calambokidis and Barlow, 1987; Myers et al., 1998; Baird et al., 2001; Ford and Ellis, 2006; O'Neill et al., 2006; Krahn et al., 2007, 2009).

Ross et al. (2000) looked at blubber biopsy samples from both the fish-eating 'resident' population and marine mammal-eating 'transient' population of killer whales in British Columbia, Canada; they found PCB concentrations were specifically correlated with age, sex, and diet. All the killer whale communities had PCB concentrations that surpassed those concentrations shown to be immune and endocrine disrupting in harbor seals; they also showed higher PCB concentrations in transient whales, as expected based on their higher trophic positions. The southern resident and transient killer whales in British Columbia may be some of the most highly contaminated cetaceans in the world (Ross et al., 2000). Another study (Ylitalo et al., 2001) also evaluated life-history parameters, including age, sex, and reproductive status on contaminant concentrations in Alaskan killer whales. Similar findings indicated higher levels of organic contaminants in mammal-consuming transient killer whales than the fish-eating resident killer whales had significantly less OCs than juvenile and mature adult animals, which has been seen in other studies (Wagemann and Muir, 1984; Aguilar and Borrell, 1994; Ylitalo et al., 2001; Krahn et al., 2007, 2009).



**Figure 15.** Concentrations of four types of persistent organic pollutants given in sum totals:  $\sum PCBs$ ,  $\sum DDTs \sum PBDEs$ ,  $\sum CHLDs$  in blubber samples from male Southern Resident killer whales (J-, K- and L-pods). Estimated ages of the whales are designated below their ID number. POP concentrations for whales identified with an asterisk (\*) were reported in Krahn et al., 2007. (Krahn et al., 2009).

### **Pinnipeds**

Pinnipeds are a widely distributed group of marine mammals that also offer ecological significance to the marine environment (Bowen, 1997). This group is made up of true seals (Phocidae), fur seals and sea lions (Otariidae), and the walrus (Odobenidae). Most pinnipeds are carnivorous feeders, but they have a diverse diet that can range from crustaceous amphipods, like krill, to penguins and other pinnipeds (Laake et al., 2002). Most pinnipeds demonstrate an amphibious lifestyle, which can increase their exposure to anthropogenic activities and their risk of contamination and transfer of POPs (Lehnert et al., 2014). Several pinnipeds, eg. the ringed seal (*Pusa hispida*), are also important keystone species that can represent trends in POP contamination and overall ecosystem health (Helle, 1980; Desforges et al., 2016).

#### California Sea Lion

The California sea lion (*Zalophus californianus*) (Figure 16) is a pinniped from the family Otariidae that occupies coastal waters, ranging from southeast Alaska to central Mexico (Berta et al., 2015; NOAA, 2021c). As their name implies, they are often found in the gulf of California on rocky coastlines and sandy beaches (Laake et al., 2018). The California sea lions are divided into three distinct stocks: United States, western Baja California, and Gulf of California (NOAA, 2021c). They are currently listed as least concern on the IUCN (2021f) as their numbers have been steadily increasing since approximately 1975, when protections were established under the Marine Mammal Protection Act (MMPA) (Laake et al., 2018). Although their populations are thriving in comparison to other marine mammals, they still encounter anthropogenic and environmental threats. Some of the primary threats to their populations include entanglement in fishing gear, accumulation of biotoxins, and invasive species and diseases (Holden, 1978; Gulland et al., 1996; Ylitalo et al., 2005; Randhawa, 2015; NOAA, 2021c).

California sea lions are considered opportunistic feeders. They forage primarily in coastal regions of upwelling, where they feed on a variety of prey items, including squid, anchovy, mackerel, rockfish, and sardines (Fiscus and Baines, 1966; Antonelis et al., 1990; NOAA, 2021c). Many of their primary prey items are susceptible to toxins from algal blooms and anthropogenic sources (NOAA, 2021c). These toxins can easily be transferred up to the sea lions



**Figure 16**. A California sea lion occupying a rocky shore. (https://www.montereybayaquarium.org/animals/animals-a-to-z/california-sea-lion). and pose threats to their health and reproductive success (Ross et al., 1996; Ylitalo, 2005; Randhawa, 2015).

The California sea lion has been shown to have one of the highest occurrences of cancer among both marine and terrestrial mammals (Gulland et al., 1996; Ylitalo, 2005; Randhawa et al., 2015; Gulland et al., 2020). Randhawa et al. (2015) evaluated the effects of PCBs and DDTs in 310 California sea lions sampled between 1992 and 2007. They found that cancer risk was almost eight times more likely in seals with higher summed concentrations of PCBs and almost six times more likely in seals with higher summed concentrations of DDTs.

Ylitalo et al. (2005) investigated the relationship between organochlorine tissue concentration and the likelihood of carcinoma-related mortality in wild California sea lions. Although age, sex, mass, and length can affect contaminant accumulation, they did not appear to influence the probability of these sea lions dying from carcinoma. The study found a positive correlation between carcinoma occurrence and summed PCBs and DDTs present in the blubber of California sea lions, which is likely causing immunosuppression and increased reproductive risks (Ross et al., 1996; Gulland et al., 1996; Ylitalo et al., 2005).

Gulland et al. (2020) also performed a study finding a positive correlation between organic contaminant concentrations and urogenital cancer. This study also concluded that contaminant exposure likely occurs early in the life of the California sea lion, with these animals accumulating PCBs and DDTs in utero, across the placenta, and in milk (Greig et al, 2007; Gulland et al., 2020).

Combined with the large foraging range of the California sea lions, the amount of POPs present in the blubber of these animals is likely in part due to the excessive dumping of industrial pollutants along the California coast during the 1960s, prior to the ban of production and use of these persistent compounds in the US (Young et al., 1976; Gulland et al., 2020). The California sea lion, like several other marine mammals, may act as a sentinel species for monitoring persistence of pollutants in the environment and how they affect predators, including humans and other animals exposed to tainted seafood (Ross, 2000b; Randhawa et al., 2015).

#### Hawaiian Monk Seal

The Hawaiian monk seal (*Neomonachus schauinslandi*) (Figure 17) is a pinniped from the family Phocidae that is endemic to the Hawaiian Archipelago. It occupies two primary

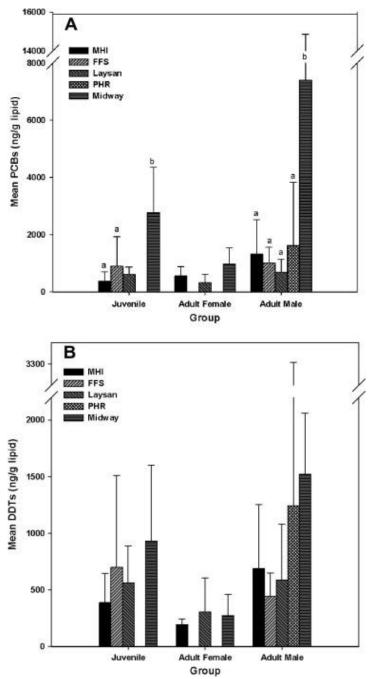


Figure 17. An adult Hawaiian monk seal (NOAA, 2021a).

regions, the Northwestern Hawaiian Islands (NWHI) and the Main Hawaiian Islands (MHI) (Willcox et al., 2004; Bohlander, 2012; Littnan et al., 2015). The single population is currently listed as highly endangered (Carretta et al., 2010; Littnan et al., 2015; IUCN, 2021a). Hawaiian monk seals are mostly solitary animals and are a non-migratory species, generally staying close to the atoll where they are born (Johnson and Kridler, 1983; Littnan et al., 2015; NOAA, 2021a). Some of the major threats to monk seal stocks are from pollution, lack of prey availability, invasive species, predation, legacy impacts of fisheries, climate change, military activities, resource use, and human disturbances (Lowry et al., 2011; Bohlander, 2012; Littnan et al., 2015; NOAA, 2021a).

Hawaiian monk seals are apex predators and are considered generalists, as they feed on a wide variety of prey items. They are often seen consuming several species of fishes, squid, octopuses, eels, and crustaceans (Goodman-Lowe, 1998). They typically forage near the seafloor and show a preference for cryptic prey items hiding under sand and rocks (Parrish et al., 2000; NOAA, 2021a). Their diets vary between geographic groups and may impact how they accumulate POPs (Bohlander, 2012).

The MHI sub-population has had greater exposure to human activities, including industrial and agricultural activities that are linked to increased POP exposure. POPs have been measured in both populations and have been linked with increased risk of reproductive and immune challenges (Brasher and Anthony, 2000; Ylitalo, 2008; Bohlander, 2012). Ylitalo et al. (2008) measured organochlorine concentrations in blubber and blood samples from the NWHI population and found OC concentrations were strongly influenced by age and sex. Mature females were found to have lower concentrations compared to juveniles and mature males, which may be related to transfer of lipophilic pollutants from pregnant and lactating females to their pups. A similar study by Bohlander et al. (2012) evaluated POP concentrations in blubber and serum of the MHI population and found similar findings to Ylitalo et al. (2008); mature males from the MHI population had greater concentration of POPs present in blubber compared to mature females. Overall, the average levels of POPs in the MHI population were not higher than those in the NWHI population; however, use of different habitats and foraging strategies may have led to increased contaminant concentrations in some individual seals from the MHI population (Figure 18) (Ylitalo et al., 2008; Bohlander et al., 2012).



**Figure 18**. Mean concentrations (ng/g lipid) of (A) 8 commonly analyzed PCB congeners (PCB 101, 118, 128, 138, 153, 156, 170, and 180) and (B) 5 commonly analyzed DDTs (o,p-DDD, p,p'-DDD, p,p'-DDE, o,p-DDT and p,p'-DDT) in blubber of Hawaiian monk seals, comparing 5 populations: main Hawaiian Islands (MHI; present study), French Frigate Shoals (FFS), Laysan Island, Pearl and Hermes Reef (PHR), and Midway Atoll (Ylitalo et al., 2008). Bars with unlike letters differ significantly (Bohlander et al., 2012).

### Walrus

The walrus (*Odobenus rosmarus*) (Figure 19) is a pinniped from the family Odobenidae that occupies Arctic waters and is currently considered vulnerable (IUCN, 2021b). Threats to its population include climate change, industrial pollution, human activity, transportation, and oil and gas drilling (Lowry, 2016). The walrus provides cultural significance to many arctic communities, such as Russian and Alaskan natives; it also provides subsistence for several of these groups (Dehn et al., 2006; Clark, 2021).

The walrus is a carnivore that feeds primarily on benthic bivalves, which possess some of the highest caloric densities of walrus prey items (Wilt et al., 2014; Young et al., 2017). Walruses depend upon these highly productive benthic communities, where the high-latitude, shallow water ecosystem supports the transport of organic matter from the sea surface to the benthos (Grebmeier et al., 1987). They are also generalist feeders by nature, and have been observed feeding on higher trophic levels, including other pinnipeds on occasion (Muir et al. 1995; Seymour et al., 2014).

A Study done by Muir et al. (1995) found that some walrus blubber samples obtained from the Canadian Arctic had higher than expected POP concentrations compared to previous studies done in Greenland and Alaska (Born et al., 1981). They concluded that this difference is based on the walrus feeding at a higher trophic level, likely consuming ringed seals as part of its diet in the Canadian Arctic. Muir et al. (2000) further elaborated on these studies by evaluating POP concentrations in blubber of the Atlantic walrus (*Odobenus rosmarus rosmarus*) in both the Avanersuaq region of north-west Greenland and the Ittoqqortoormiit region of east Greenland. Most organochlorine compounds were higher in the Ittoqqortoormiit (east Greenland) region, and these patterns of OCs were consistent with the seal-eating walrus populations from Hudson Bay in the Canadian Arctic based on principal component analysis (PCA) analysis and correlate with results for polar bears, seals, and gulls from the same region (Muir et al., 1995; Norstrom et al., 1998; Cleeman et al., 2000a, 2000b).

Tsygankov et al. (2015) measured organochlorine pesticides in the muscles and liver of the Pacific walrus (*Odobenus rosmarus divergens*) and compared concentrations to that of the gray whale in the western Bering Sea. Both the walrus and gray whale are benthic foragers, but their feeding habits and daily rations greatly affect how they bioaccumulate organic contaminants. Prey items in the walrus' diet bioaccumulate pesticides at a higher rate since the



**Figure 19**. An adult walrus (https://www.nationalgeographic.com/animals/mammals/facts/walrus)

coefficients of pollutant accumulation for mollusks and fish are higher than those for crustaceans, which comprise most of the gray whale's diet (Kingston and Li et al., 2007; Tsygankov et a., 2015).

# Sirenians

All marine mammals are not apex predators; the sirenians consist of herbivorous manatees and dugongs; these mammals occupy a trophic level of 2.0, which is low in comparison to other marine mammals. Sirenians are currently one of the least studied groups among marine mammals as they feed primarily on vascular aquatic plants and acquire organic toxins in a different way than other marine mammals (Reynolds III and Odell, 1991; O'Shea et al., 2018). Sirenians typically inhabit coastal marine waters; the dugong is strictly marine, but some manatees also inhabit freshwater rivers and estuaries (Marsh et al., 2012).

## Dugong

The dugong (*Dugong dugon*) is the only extant member of the family Dugongidae. It occupies nearshore environments of the Indian and western Pacific Oceans (Nishiwaki and Marsh, 1985; Marsh and Sobtzick, 2019). The Steller's sea cow (*Hydrodamalis gigas*) was also a member of the family Dugongidae. It was the closest relative to the dugong, but it went extinct due to over-hunting and harvesting in the 18<sup>th</sup> century and trophic cascades involving a loss of sea otters, a keystone species, and co-occurring loss of kelp, one of the Steller's sea cow's primary food sources (Estes et al., 2016). Dugongs are currently listed as vulnerable (IUCN, 2021c) and are susceptible to several threats, including climate change, severe weather, transportation and service corridors, residential and commercial development, and agricultural, industrial, military, and forestry effluents (Nishiwaki and Marsh, 1985; Marsh and Sobtzick, 2019).

Dugongs are herbivorous feeders, occupying a low trophic level; therefore, the level of contaminants present are generally expected to be much lower than those marine mammals that are piscivorous or carnivorous (Weijs, 2019). Dugongs feed mostly on seagrass (Figure 20), specifically photoautotrophic Phanerogams, and associated sediments (Heinsohn and Birch, 1972; Tol et al., 2016). Although they occupy a lower trophic position, they are still susceptible to organic contaminants through direct ingestion, often in areas with greater anthropogenic



**Figure 20**. A dugong feeding on seagrass along the ocean floor. (https://www.worldwildlife.org/species/dugong).

influences and industrial developments (Heinsohn and Birch, 1972; Duodo et al., 2017; Weijs et al., 2019).

One study (Haynes, 2001) evaluated both organochlorine pesticides and trace metals in intertidal and subtidal sediments and seagrasses along the Great Barrier Reef coasts and documented corresponding pesticide concentrations in stranded dugongs along the Queensland coast. Although they found that concentrations of insecticides and herbicides are generally low in this region, Queensland sediments may still pose a threat to seagrass communities and, consequently, an indirect risk to dugongs. Based on this study, accumulation of dioxins in dugong tissues is believed to be directly correlated with ingestion of sediments by dugongs feeding along the benthos (O'Shea, 1999; Haynes, 2001). Another study by McLachlan et al. (2001) found similar results and concluded that a large portion of organic contaminants, primarily dioxins, ingested by dugongs may be originating from the sediments.

Weijs et al. (2019) evaluated POP concentrations in dugongs located in Moreton Bay, a semi-enclosed embayment located near Australia's third largest city, Brisbane, and found that POP concentrations were below established toxicity levels established for other marine mammals (Weijs et al., 2016); however, concentrations were higher compared to global sirenian POP concentrations (Miyazaki et al., 1979; Vetter et al., 2001; Haynes et al., 2005; Hermanussen et al., 2008). Dugongs occupy a low trophic level and do not accumulate lipophilic compounds at the same rate as marine mammals that are apex predators; however, they do occupy relatively shallow, coastal, and estuarine waters, putting them near urban and agricultural contaminant sources (Haynes et al., 2000; O'Shea et al., 2018). This proximity to the highly populated and industrialized city of Brisbane is likely the reason for higher POP concentrations in dugongs compared to other locations (Hermanussen et al., 2008).

#### West Indian Manatee

Manatees belong to the family Trichechidae; there are currently three extant species, the West Indian manatee (*Trichechus manatus*) (Figure 21), West African manatee (*Trichechus senegalensis*), and the Amazonian manatee (*Trichechus inunguis*) (Hartman, 1979; Berta et al., 2015; O'Shea et al., 2018). The West Indian manatee (*Trichechus manatus*), also referred to as the North American manatee, is the largest extant member of the order Sirenia and has a vulnerable population status (Deutsch, 2008). It is currently threatened by both natural and



**Figure 21.** A West Indian manatee occupying the water column (https://www.nwf.org/Educational-Resources/Wildlife-Guide/Mammals/West-Indian-Manatee).

anthropogenic factors. Some of the most concerning threats are loss of warm-water habitats due to discharge from powerplants and human demand for groundwater and watercraft collisions due to increasing vessel density (Ackerman, 1995; Deutsch, 2008). Manatees occupy both fresh water and marine environments; many prefer areas where they have adequate access to fresh water in order to avoid unwanted osmotic stress (Ortiz et al, 1998).

Manatees are herbivorous, opportunistic feeders that feed on a wide range of floating, submerged, and emergent vegetation (Deutsch, 2008). They feed primarily on seagrasses with some of the most prominent species being manatee grass (*Syringodium filiforme*) and shoal grass (*Halodule wrightii*) (Deutsch, 2008). They exhibit two primary foraging methods in coastal seagrass beds, grazing, where they only consume exposed grass blades, and rooting, where the entire plant is uprooted and consumed (Packard, 1984).

Although they are at a lesser risk of contaminant bioaccumulation compared to other marine mammals due to their herbivorous feeding patterns, manatees still inhabit coastal regions and have long lifespans, which puts them at risk for POP and metal accumulations (Anzolin et al, 2012; Belanger and Wittnich, 2008; O'Shea et al., 2003). Anzolin et al. (2012) analyzed blood samples in West Indian manatees from Brazil for contaminants; they did not detect any PCBs or organochlorine pesticides. Ames and Van Vleet (1996) analyzed blubber, liver, and kidney samples from 12 Florida manatees (*Trichechus manatus latirostris*) and found that these manatees are not accumulating a large concentration of chlorinated pesticides and the concentrations detected coincide with findings in other marine mammals (Ames and Van Vleet, 1996; O'Shea et al., 2003).

# Discussion

Tables 1 and 2 show a comprehensive overview of common organic contaminants evaluated in the ten different marine mammal species outlined in this study. Although this study only looks at a small portion of contaminants and marine mammal species, the diversity in trophic positions, habitat, life-history parameters, physiology, and morphology among these species appears to have a substantial impact on how POPs bioaccumulate and biomagnify. Looking at the species collectively, there are some patterns that can be observed.

The least amount of data and the lowest overall value for organic contaminants belongs to the sirenians, which are herbivorous first order consumers. As expected, the sirenians have much lower contaminant loads compared to other marine mammals based on these studies (ranging from undetectable concentrations to 52,000 ng/g of summed DDTs and 3.4 ng/g to 32.98 ng/g of summed PCBs). Given that both the dugong (*Dugong dugon*) and the West Indian manatee (*Trichechus manatus*) are herbivorous feeders, allowing for minimal contaminant exposure through trophic linkages, they may experience the greatest contaminant exposure from direct consumption of contaminants, particularly in urbanized areas, and contaminated marine sediments. (O'Shea et al., 1984; Ames and Van Vleet, 1996; Haynes et al., 2005; Weijs et al., 2019).

The mysticetes, or second-order consumers, have greater average contaminant loads compared to the sirenians, but they do not exhibit as high contaminant values as top marine predators do. The bowhead whale (*Balaena mysticetus*), gray whale (*Eschrichtius robustus*), and the humpback whale (*Megaptera novaeangliae*) show comparable trends in contaminant loads (with blubber concentrations ranging from 8-330 ng/g of summed DDTs, 2.3-1400 ng/g of summed PCBs, and 0.3-329 ng/g of summed HCHs); however, there are some noticeable differences seen in contaminant uptake in different regions (i.e., southern vs. northern hemisphere and Pacific vs. Atlantic Ocean). (Tilbury et al., 2002; Hoekstra et al., 2005; Remili et al., 2020).

The greatest amount of data available and the highest total values of organic contaminants belong to odontocetes and pinnipeds, which we know to be higher order consumers at greater risk of biomagnification of persistent organic pollutants traveling up the food chain. The killer whale (*Orcinus orca*) and the California sea lion (*Zalophus californianus*) have the highest total concentrations of POPs out of the species studied, with DDTs and PCBs having some of the highest contaminant concentrations observed (ranging from 99,000 to 380,000 ng/g of summed DDTs in blubber and 77,000 to 180,000 ng/g of summed PCBs in blubber), which follows directly with their positions as apex predators and their overall distributions. The bottlenose dolphin (*Tursiops truncatus*) provides some of our most extensive knowledge on POPs in marine mammals, likely due to its cosmopolitan distribution and broad diet (Wells et al., 2004; Wilson et al., 2012).

There are also substantial differences between adult males and females in the studies that evaluated both groups. For example, blubber of the female common bottlenose dolphin contained 2990-4600 ng/g of summed DDTs while the male contained 18,600-29,000 ng/g of summed

60

Species	Tissue	Location	ΣDDTs	ΣHCHs	ΣPCBs	ΣPBDEs	ΣPAHs	References
Mysticetes								
Bowhead whale (Balaena mysticetus)	Blubber	Barrow, AK, USA	311 <sup>a</sup>	329 <sup>a</sup>	377 <sup>a</sup>	NA	NA	Hoekstra et al., 2005
	Liver		53.6 <sup>a</sup>	133 <sup>a</sup>	131 <sup>a</sup>	NA	NA	
	Muscle		110 <sup>a</sup>	94.9 <sup>a</sup>	66.3 <sup>a</sup>	NA	NA	
Gray whale (Eschrichtius robustus)	Blubber	Western Bering Sea	330	NA	1400	NA	NA	Tilbury et al., 2002
	Liver		120	NA	910	NA	NA	
			481	3081	NA	NA	NA	Tsygankov et al., 2015
	Muscle		340	NA	2400	NA	NA	Tilbury et al., 2002
			44	1144	NA	NA	NA	Tsygankov et al., 2015
Humpback whale ( <i>Megaptera</i>	Blubber	Mozambique	8.0	0.3	2.3	0.4	NA	Remili et al., 2020
novaeangliae)		Ecuador	24	0.7	1.8	0.4	NA	
Odontocetes		Antarctic Peninsula	11.0 (f) 28.7 (m)	5.2 (f) 6.1 (m)	56.5 (f) 40.0 (m)	1.49 (f) 0.89 (m)	NA	Dorneles et al., 2015
Common bottlenose dolphin	Blubber	Turkey, the Black Sea	5300	1000	370	NA	NA	Popa et al., 2008
(Tursiops truncatus)		Indian River Lagoon, FL	10,900 (j) 4600 (f) 18,600 (m)	0.200 (j) 0.100 (f) 0.300 (m)	48,400 (j) 25,500 (f) 79,800 (m)	1100.9 (j) 581 (f) 1490 (m)	1316	Fair et al., 2010
		Charleston, SC	14,700 (j) 2990 (f) 29,000 (m)	1.20(j) 1.40 (f) 1.70 (m)	47,800 (j) 14,300 (f) 94,000 (m)	4400 (j) 977 (f) 5917 (m)	3010	

**Table 1**. Mean concentration (ng/g lipid weight) of organic contaminants in tissues of marine mammals from different regions (calculated based on percent lipid levels).

Killer whale (Orcinus orca)	Blubber	West Coast of North America	160,000	1300	180,000	15,000	NA	Krahn et al., 2007
			99,000	1700	120,000	NA	NA	Krahn et al., 2009
		Northeastern Pacific Ocean (Southern residents)	NA	NA	NA	942 (m)	NA	Rayne et al., 2004
		Northeastern Pacific Ocean (Northern residents)	NA	NA	NA	415 (f) 203 (m)	NA	
D'auta la		Northeastern Pacific Ocean (transients)	NA	NA	NA	885 (f) 1015 (m)	NA	
Pinnipeds								
California sea lion (Zalophus californianus)	Blubber	Central California Coast	380,000 (m) 250,000 (f)	NA	83,000 (f) 77,000 (m)	NA	NA	Ylitalo et al., 2005
		Southern California Coast	NA	NA	NA	28,700	NA	Meng et al., 2009
Hawaiian monk seal ( <i>Neomonachus</i> schauinslandi)	Blubber	French Frigate Shoals, NWHI	NA	NA	980 (j) 1400 (m)	NA	NA	Ylitalo et al., 2008
		Laysan Island, NWHI	NA	NA	850 (j) 480 (f) 860 (m)	NA	NA	
		Midway Atoll, NWHI	NA	NA	3200 (j) 1100 (f) 8800 (m)	NA	NA	
		Pearl and Hermes Reef, NWHI	NA	NA	2200 (m)	NA	NA	
		MHI	390 (j) 190 (f) 690 (m)	0.82 (j) 6.1 (m)	800 (j) 770 (f) 1800 (m)	110 (j) 49 (f) 120 (m)	NA	Lopez et al., 2012
Walrus (Odobenus rosmarus)	Blubber	Svalbard, Norway	NA	NA	2160	15	NA	Wolkers et al., 2006
, 03mar us j	Liver	Western Bering Sea	4474	10,541	NA	NA	NA	Tsygankov et al., 2015
	Muscle		405	1623	NA	NA	NA	

#### Sirenians

Dugong (Dugong dugon)	Blubber	North-east coast of Australia (Queensland)	52,000	ND	NA	NA	NA	Haynes et al., 2005
		Moreton Bay, Australia	ND	ND	32.98	4.81	NA	Weijs et al., 2019
West Indian manatee ( <i>Trichechus</i>	Blubber	Florida, USA	ND	NA	3.4 <sup>b</sup>	NA	NA	O'Shea et al., 1984
(Inchechus manatus)			ND	NA	ND	NA	NA	Ames and Van Vleet, 1996

ND=not detected NA=not analyzed NWHI=Northwestern Hawaiian Islands MHI=Main Hawaiian Islands j=juvenile, m=adult male, f=adult female

а

Values recalculated from ww (wet weight) to lw (lipid weight) with a lipid percentage of 83% (blubber), 6.89% (liver), and 1.96% (muscle)

b

Values recalculated from ppm ww to ng/g lw with a lipid percentage of 75%.

Species	Tissue	Location	DDTs*	HCHs	PCBs	PBDEs	References
Mysticete							
Gray whale (Eschrichtius robustus)	Liver	Western Bering Sea		α-HCH: 1047			Tsygankov et al., 2015
robusius)		564		β-HCH: 1499			
				γ-HCH: 535			
	Muscle			α-HCH: 728			
				β-HCH: 131			
				γ-HCH: 285			
Odontocetes							
Common bottlenose	Blubber	Turkey, the Black		α-HCH: 70			Popa et al., 2008
dolphin ( <i>Tursiops</i>		Sea		β-HCH: 880			2008
truncatus)				γ-HCH: 40			
		Indian River Lagoon, FL	2,4'-DDD: 72.1 (j) 52.7 (f) 91.6 (m)	α-HCH: 0.200 (j) 0.100 (f) 0.300 (m)	Mono-PCBs: 3.2. (j) 3.6 (f) 4.5 (m)	PBDE 28: 20.1 (j) 18.5 (f) 19.8 (m)	Fair et al., 2010
			2,4'-DDE: 58.1 (j) 15.2 (f) 90.4 (m)	γ-HCH: ND	Di-PCBs: 4.4 (j) 5.4 (f) 6.2 (m)	PBDE 47: 686 (j) 288 (f) 905 (m)	
			2,4'-DDT: 53.4 (j) 22.0 (f) 38.9 (m)		Tri-PCBs: 149 (j) 111 (f) 135 (m)	PBDE 99: 75.9 (j) 56.3 (f) 81.1 (m)	
			4,4'-DDD: 543 (j) 274 (f) 566 (m)		Tetra-PCBs: 2480 (j) 959 (f) 3000 (m)	PBDE 100: 194 (j) 91.5 (f) 269 (m)	
			4,4'-DDE: 9850 (j)		Penta-PCBs: 7150 (j)	PBDE 153: 41.2 (j)	

**Table 2.** Individual concentrations (ng/g lipid weight) of POPs in tissues of marine mammals(calculated based on percent lipid levels).

			3750 (f) 17,400 (m)		3060 (f) 9700 (m)	36.6 (f) 55.8 (m)	
			4,4'-DDT: 203 (j) 132 (f) 217 (m)		Hexa-PCBs: 22,700 (j) 9520 (f) 37,400 (m)	PBDE 154: 71 (j) 52.8 (f) 114 (m)	
					Octa-PCBs: 4320 (j) 2790 (f) 8370 (m) Nona-PCBs: 1220 (j) 1080 (f) 2060 (m)		
					Deca-PCBs: 128 (j) 163 (f) 284 (m)		
					Mono/Ortho- PCBs: 1900 (j) 1000 (f) 2880 (m)		
Killer whale (Orcinus orca)	Blubber	Prince William Sound, AK	o,p'-DDD: 230 (r) 3800 (t)		2880 (11)		Ylitalo et al., 2001
			<i>p,p'</i> -DDD: 700 (r) 11,000 (t)				
			<i>p,p'</i> -DDE: 11,000 (r) 280,000 (t)				
			<i>o</i> , <i>p</i> '-DDT: 1400 (r) 26,000 (t)				
			<i>p</i> , <i>p</i> '-DDT: 320 (r) 5500 (t)				
Pinniped							
Walrus (Odobenus rosmarus)	Liver	Western Bering Sea		α-HCH: 8045			Tsygankov et al., 2015
				β-HCH: 440			
				γ-HCH: 2056			
	Muscle			α-HCH: 490			

β-HCH: 405

γ-HCH: 728

#### Sirenian

Dugong	Blubber
(Dugong	
dugon)	

Moreton Bay, Australia Penta-PCBs: 0.72 (f) 1.33 (m) 10.1 (j) Weijs et al., 2019

Hexa-PCBs: 3.11 (f) 3.80 (m) 36.4 (j)

Hepta-PCBs: 0.95 (f) 1.01 (m) 11.1 (j)

Octa-PCBs: 0.08 (f) 0.10 (m) 0.94 (j)

\*Including DDT metabolites j=juvenile, m=adult male, f=adult female r=resident killer whale, t=transient killer whale DDTs. Females also had a much lower concentration of summed PCBs (ranging from 14,300-25,500 ng/g compared to males ranging from 79,800-94,000 ng/g) (Fair et al., 2010).

# Conclusion

Although there is still much to learn and expand upon in relation to POPs and their impacts to marine life, the studies presented here give us a general framework of how POPs accumulate in the tissues of marine mammals and impact their health and survivability. The following are some general conclusions:

- Marine mammals are susceptible to persistent organic pollutant (POP) contamination and accumulation due to their long lifespans, high lipid content, and exposure of contaminants throughout the trophic food web in the marine ecosystem (O'Shea, 1999; Krahn et al., 2001; Macdonald et al., 2002; Fair et al., 2010).
- POPs are lipophilic, semi-volatile contaminants, which can be taken up both directly, through mechanisms such as filter feeding, and indirectly through prey consumption (Pauly et al., 1998; Tanabe, 2006; Krahn et al., 2009).
- In comparing sexes of species of marine mammals, mature females tend to have a noticeably lesser burden of POPs compared to both adult males and juveniles, which is supported by evidence of maternal offloading through lactational and gestational means. This is particularly evident in species like the Hawaiian monk seal and killer whale. (Addison et al., 1986; Ross et al., 2000; Krahn et al., 2007, 2009; Fair et al., 2010; Lopez et al., 2012).
- Odontocetes and pinnipeds are some of the top marine predators and may serve as some of the most beneficial bioindicators of marine ecosystem health as they can reflect the impacts of both human and natural stressors on themselves, but also on the lower trophic level communities that they prey upon (Wells et al., 2004; Ylitalo et al., 2005; Reeves et al., 2017).
- Sirenians, although less susceptible to higher contaminant concentrations, are still at risk of accumulating POPs from direct ingestion and contaminated sediments, particularly in industrialized or urban areas close to river runoff (Heinsohn and Birch, 1972; Duodo et al., 2017; Weijs et al., 2019).

• Several variables, including habitat, feeding strategy, age, sex, and physiology, contribute to bioaccumulation and biomagnification of POPs in marine mammals. Further studies will be important in determining the long-term immunological effects of POPs in marine mammals (Tanabe et al., 1994; Tilbury et al., 2002; Desforges et al., 2016).

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