CY-1018: Environmental Chemistry Theory

Know our environment (chemistry of lithosphere, energy balance, sustainability and recycle), Know about global warming (infrared absorption, molecular vibration, atmospheric window, residence time of greenhouse gases, evidences and effects of global warming), Deeper analysis of atmospheric pollution (Chemistry of CO, NOx, VOCs, SO_2, Industrial smog, photochemical smog), Ozone depletion (production, catalytic destruction), **Organic Chemicals in the Environment, Insecticides, Pesticides, Herbicides and Insect Control, Soaps, Synthetic Surfactants, Polymers, and Haloorganics. Fate of organic/inorganic chemicals in natural and engineered systems (fate of polymers after use, detergents, synthetic surfactants insecticides, pesticides etc. after use),** Aspects of transformations in atmosphere (microbial degradation of organics-environmental degradation of polymers, atmospheric lifetime, toxicity). Green Chemistry and Industrial Ecology. Future challenges (CO_2 sequestering, Nuclear energy). A project on environment related topic.

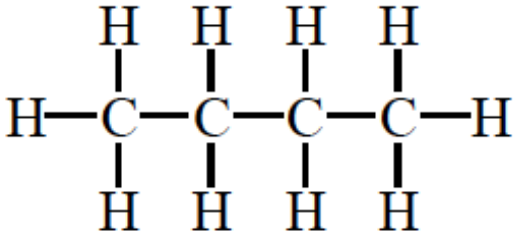
Reference: Principles of Environmental Chemistry By James E. Girard, Third Edition

Dr. Venkata Rao Kotagiri
Assistant Professor
Department of Chemistry

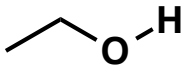
Organic Chemicals in the Environment

Organic compounds: Compounds that mainly contain Carbon and Hydrogen atoms

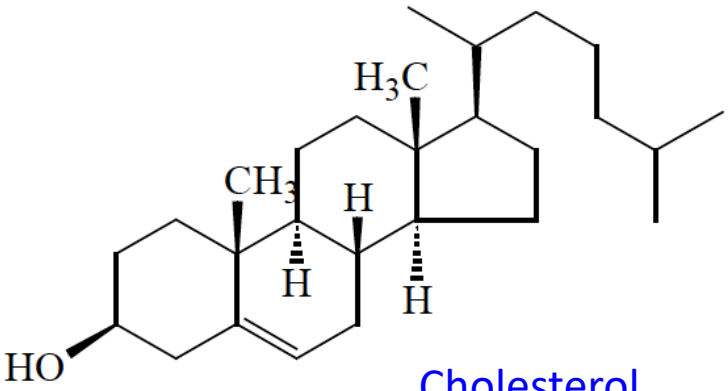
Ex.



n-butane



Ethanol



Cholesterol

Glucose: $C_6H_{12}O$

DNA

Amino acids

Proteins

Medicines

Plastics

Pesticides

Organic Chemicals in the Environment

- Thousands of different organic chemicals are synthesized each year for use as cosmetics, insecticides, detergents, and plastics
- Some of them are not adequately tested for toxicity before being put on the market
- Many of these chemicals persist in the environment for long periods of time

Persistent organic pollutants (POPs)

	Half-Life of Chemical		
Media	**Not Persistent**	**Persistent**	**Highly Persistent**
Water	< 2 months	≥ 2 months	> 6 months
Soil	< 2 months	≥ 2 months	> 6 months
Air	≤ 2 days		> 2 days
Sediment	< 2 months	≥ 2 months	> 6 months

Organic Chemicals in the Environment

Persistent organic pollutants (POPs)

- POPs can enter into water and food chains and can cause serious health and environmental problems
- POPs can go from one place to other via wind and water
- POPs generated in one country can affect the people and wildlife in other countries even though they are very far from each other
- Some POPs evaporate from water or land surfaces into the air, then return to Earth in snow, rain, or mist

Organic Chemicals in the Environment

Insecticides: Substances used to kill insects

Pesticides: Substances used to kill pests including weeds

Herbicides: Pesticide used to kill unwanted plants

Fungicides: Substances used to kill fungus

Approximately 80,000 synthetic chemicals are on the market today and most of them have never been tested for toxicity

Organic Chemicals in the Environment

- POPs contamination is also found in arctic regions, which are thousands of miles from anywhere the POPs are manufactured or used

Stockholm Convention

In 2001 **"dirty dozen" POPs**

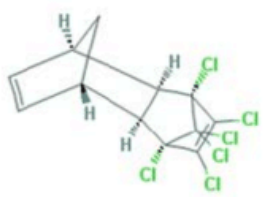
- Out of 12 chemicals, 10 were intentionally produced by industry
- 9 were produced as **insecticides or fungicides**
- Two are are unintentionally produced in combustion processes

Organic Chemicals in the Environment

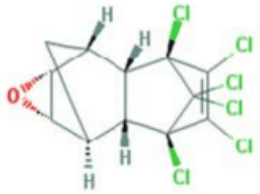
The 12 Key POPs—the Dirty Dozen

POP	Use
Aldrin	crop insecticide (corn, cotton)
Chlordane	crop insecticide (vegetables, citrus, cotton, potatoes)
DDT	crop insecticide (cotton)
Dieldrin	crop insecticide (cotton, corn)
Endrin	crop insecticide (cotton, grains)
Heptachlor	insecticide (termites and soil insects)
Hexachlorobenzene	fungicide for seed treatment
Mirex	insecticide (termites, fire ants)
Toxaphene	insecticide (livestock and crops)
PCBs	industrial chemical (heat exchange fluid for electrical transformers, paint and plastic additive)
Dioxins	unintentionally produced during combustion
Furans	unintentionally produced during combustion

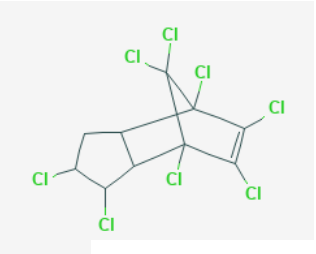
Organic Chemicals in the Environment



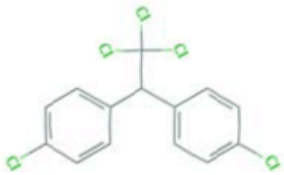
Aldrin



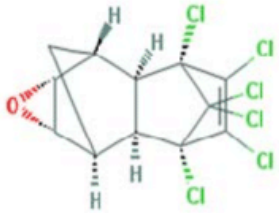
Dieldrin



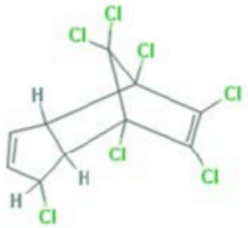
Chlordane



DDT (Dichlorodiphenyltrichloroethane)

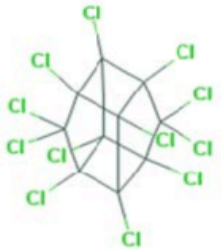


Endrin

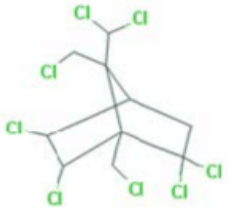


Heptachlor

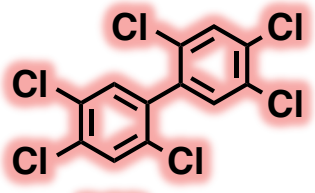
HCB



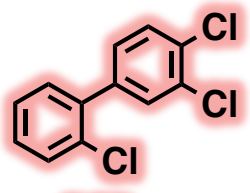
Mirex



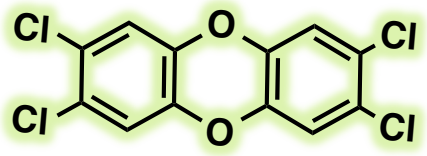
Toxaphene



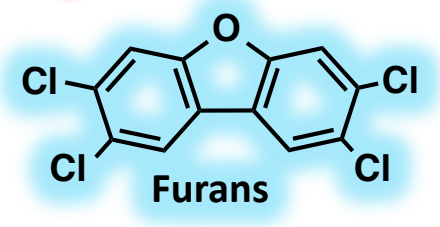
PCB_1



PCB_2



Dioxins



Furans

Polychlorinated compounds

2,3,7,8-tetrachlorodibenzo[*b*,*d*]furan

Organic Chemicals in the Environment

Stockholm Convention

Added 8 more substances to the agreement in 2009 and one more in 2011

New POPs Added to the Stockholm Convention in 2009 and 2011

POP	Use
Hexachlorocyclohexane	Unintentional by-product of lindane production
Chlordecone	Insecticide (ant and roach)
Hexabromobiphenyl	Fire-suppressing chemical
Hexabromodiphenyl and Heptabromodiphenyl ether	Flame retardant
Lindane	Broad-spectrum insecticide
Pentachlorobenzene	PCB
Perfluorooctane sulfonic acid	Key ingredient in Scotchgard fabric protector
Tetrabromodiphenyl ether	Flame retardant
Endosulfan	Crop insecticide

Organic Chemicals in the Environment

Stockholm Convention

Added 8 more substances to the agreement in 2009 and one more in 2011

- Five of the new POPs are also poly chlorinated compounds which are used as insecticides
- Polychlorinated hydrocarbons are insoluble in water but soluble in fats
- Polychlorinated hydrocarbons concentrated in the fatty tissues of fish and of birds, and of humans who eat them
- For the first time, polybrominated compounds that were used in the 1970s as flame-retardant agents were added to the list
- Perfluorooctane sulfonic acid, the key ingredient in Scotchgard fabric protector, was added to the list of new POPs

Organic Chemicals in the Environment

Persistent, Bioaccumulative, and Toxic (PBT) Pollutants Program

- Launched by **EPA** (Environmental Protection Agency) in 1998
- Wider scope than the Stockholm Convention and has the same goals of reducing the use and release of PBT pollutants while making sure that these chemicals are disposed of properly
- PBT program is also focusing a list of 12 priority pollutants and most of them are already listed in **dirty dozen**
- PBT list includes inorganic elements, such as mercury or organometallic compounds that contain an inorganic atom

Organic Chemicals in the Environment

Persistent, Bioaccumulative, and Toxic (PBT) Pollutants Program

The EPA's Priority Level-1 PBTs

PBT Compound	Use
Aldrin/Dieldrin	crop insecticide (corn, cotton)
Alkyl-lead	octane booster in leaded gasoline
Benzo(a)pyrene	unintentionally produced during combustion
Toxaphene	insecticide (livestock and crops)
Chlordane	crop insecticide (vegetables, citrus, cotton, potatoes)
DDT	crop insecticide (cotton)
Dioxins/Furans	unintentionally produced during combustion
Hexachlorobenzene	fungicide for seed treatment
Mercury and mercury compounds	incineration of medical and municipal waste
Mirex	insecticide (termites, fire ants)
Octachlorostyrene	produced from carbon electrodes used in electrolytic process for producing chlorine
PCBs	industrial chemical (heat exchange fluid for electrical transformers, paint and plastic additive)

Organic Chemicals in the Environment

Why we are producing these dangerous chemicals intentionally?

- Humans always have had to contend with pests
- The Black Death, which killed millions of people in the Middle Ages, was transmitted to humans by fleas (insects) on rats carrying bubonic plague
- The failure of the potato crop in Ireland in 1845, which caused widespread starvation and mass emigration to the United States, was caused by a potato blight (fungus)

Organic Chemicals in the Environment

Why we are producing these dangerous chemicals intentionally?

- Malaria, spread by the Anopheles mosquito, still kills millions of people annually in less developed countries
- Swarms of locusts continue to devastate crops in many areas of the world

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Home / Cities / New generation of locusts may attack crops in UP after monsoon

New generation of locusts may attack crops in UP after monsoon

A new generation of swarms may attack crops in Uttar Pradesh and Rajasthan after the monsoon even as the toxic chemicals sprayed to kill them may have adverse environmental and health consequences

Organic Chemicals in the Environment

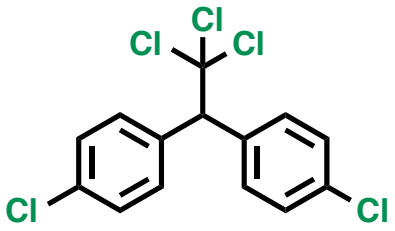
Why we are producing these dangerous chemicals intentionally?

- Humans depends on plants for food
- Plants that produce food grains are under constant attack from insects, fungi, bacteria, viruses, and other microorganisms
- Before 1940, only a few pesticides were available and most of the insect poisons are naturally extracted from plants

Ex. 1. Pyrethrins obtained from the pyrethrum flower
2. Nicotine sulfate obtained from tobacco
3. Garlic oil

United States uses approximately 500,000 metric tons of pesticides annually to control pests

Organic Chemicals in the Environment



DDT (Dichlorodiphenyltrichloroethane)

- The introduction of DDT at the end of WW-II (late 1940s) escalated the use of pesticides and the development of several other pesticides

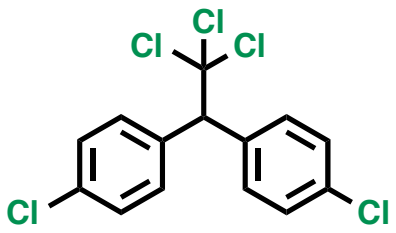
Advantages

- Inexpensive
- Nontoxic to humans and other mammals
- Stable
- Continued to kill insects for a long period after application

Disadvantages

- Harmful to fish-eating birds such as bald eagles, peregrine falcons, and brown pelicans

Organic Chemicals in the Environment

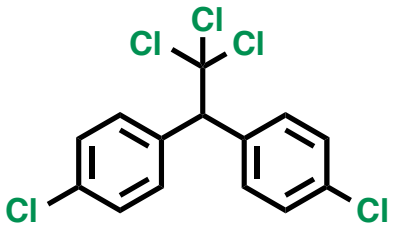


DDT (Dichlorodiphenyltrichloroethane)

Disadvantages

- Harmful to fish-eating birds such as bald eagles, peregrine falcons, and brown pelicans
- Water gets contaminated with DDT from aerial spraying and runoff from treated land
- With time, insects also became increasingly resistant to DDT and larger amounts had to be applied to achieve the desired results
- DDT interferes with calcium metabolism in birds and it causes eggshells to become thin and break when parent birds attempt to incubate the eggs

Organic Chemicals in the Environment

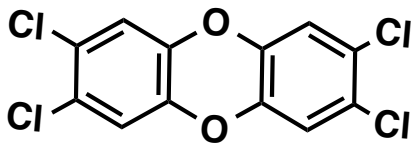


DDT (Dichlorodiphenyltrichloroethane)

- The first person to draw public attention to the dangers of pesticides was biologist **Rachel Carson** and she a played key role for the establishment of Environmental Protection Agency (EPA) in 1970
- In 1973, the use of DDT was banned in the United States and fish-eating birds population restored shortly
- Still DDT is partially banned in several countries such as India
- DDT is banned for agriculture but allowed for fumigation to kill mosquitoes to prevent malaria

Organic Chemicals in the Environment

Dioxins

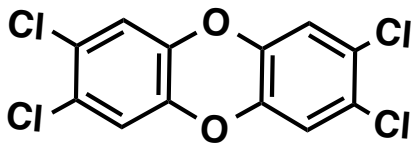


2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)

- TCDD persists in the environment for a very long time and bioaccumulates within the food chain
- TCDD is extraordinarily toxic to guinea pigs and is a known carcinogen for many animals
- During Vietnam war, USA used **Agent Orange** (defoliant) in which TCDD present as an impurity
- EPA concluded that exposure to dioxin, increase the risk of cancer, may disrupt some reproductive mechanisms and suppress the immune system

Organic Chemicals in the Environment

Dioxins



2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)

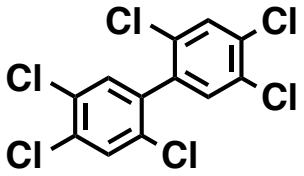
Major sources for TCDD

- Burning of chlorine-containing medical and municipal wastes
- Paper mills that use chlorine to bleach paper pulp
- During the manufacture of Trichlorophenol a precursor for herbicides

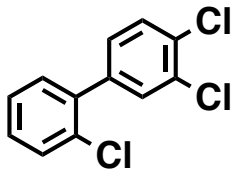
Currently, proper solutions were found for above three problems

Organic Chemicals in the Environment

PCBs (Polychlorobiphenyls)



PCB_1



PCB_2

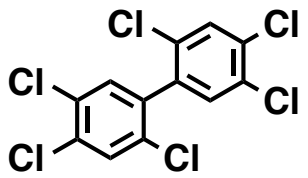
- PCBs are not water soluble but readily soluble in fat
- PCBs are chemically and thermally stable, fire and electricity resistant and persist in the environment for many years

Uses of PCBs

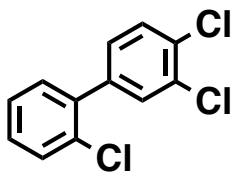
- Heat exchange fluid in transformers,
- Paints and plastic additive (platicizer)

Organic Chemicals in the Environment

PCBs (Polychlorobiphenyls)



PCB_1

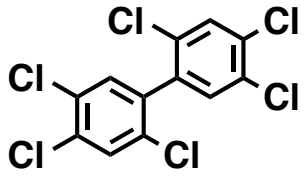


PCB_2

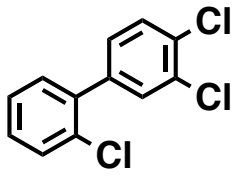
- When plastic wastes and other PCB-containing materials are burned, PCB vapors condense on airborne particles, which then fall directly onto water or reach water in runoff from the land
- PCBs present in water in a negligible concentration but can become more than 1 million times concentrated in fish
- PCBs cause eggshell thinning and neurologic damage in birds and impair reproduction of aquatic species
- In humans, they cause, chloracne, liver damage, reproductive disorders, birth defects, and cancer

Organic Chemicals in the Environment

PCBs (Polychlorobiphenyls)



PCB_1



PCB_2

- In 1977, production of PCBs in the United States was halted, and disposal of PCB-containing products is now strictly regulated
- Fish in many lakes still contain significant levels of contaminants
- Unfortunately, PCBs are still produced in Russia and many developed countries

CY-1018: Environmental Chemistry Theory

Know our environment (chemistry of lithosphere, energy balance, sustainability and recycle), Know about global warming (infrared absorption, molecular vibration, atmospheric window, residence time of greenhouse gases, evidences and effects of global warming), Deeper analysis of atmospheric pollution (Chemistry of CO, NOx, VOCs, SO_2, Industrial smog, photochemical smog), Ozone depletion (production, catalytic destruction), **Organic Chemicals in the Environment, Insecticides, Pesticides, Herbicides and Insect Control, Soaps, Synthetic Surfactants, Polymers, and Haloorganics. Fate of organic/inorganic chemicals in natural and engineered systems (fate of polymers after use, detergents, synthetic surfactants insecticides, pesticides etc. after use),** Aspects of transformations in atmosphere (microbial degradation of organics-environmental degradation of polymers, atmospheric lifetime, toxicity). Green Chemistry and Industrial Ecology. Future challenges (CO_2 sequestering, Nuclear energy). A project on environment related topic.

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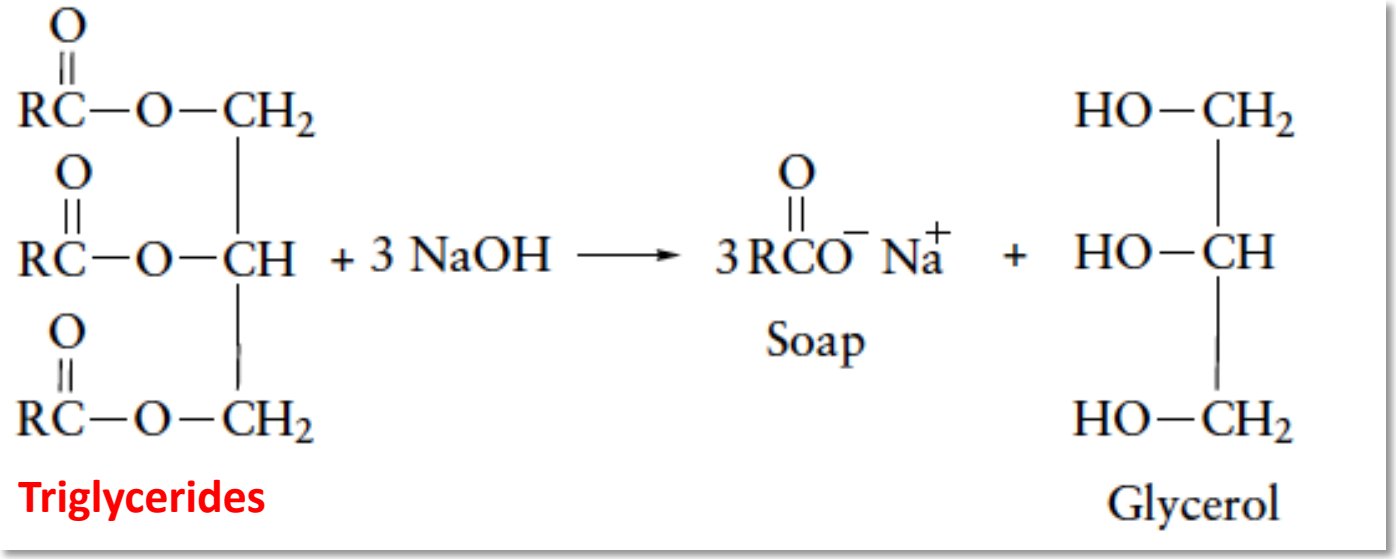
Dr. Venkata Rao Kotagiri
Assistant Professor
Department of Chemistry

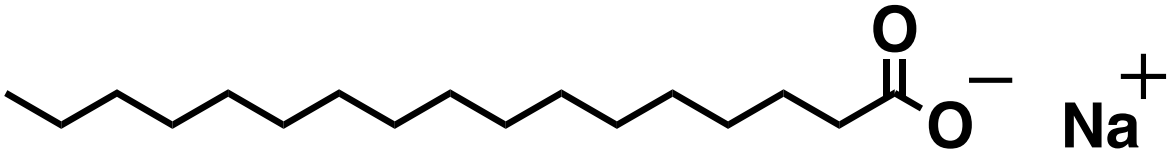
Organic Chemicals in the Environment

Soaps and Synthetic Surfactants

Soap: Sodium salts of fatty acids

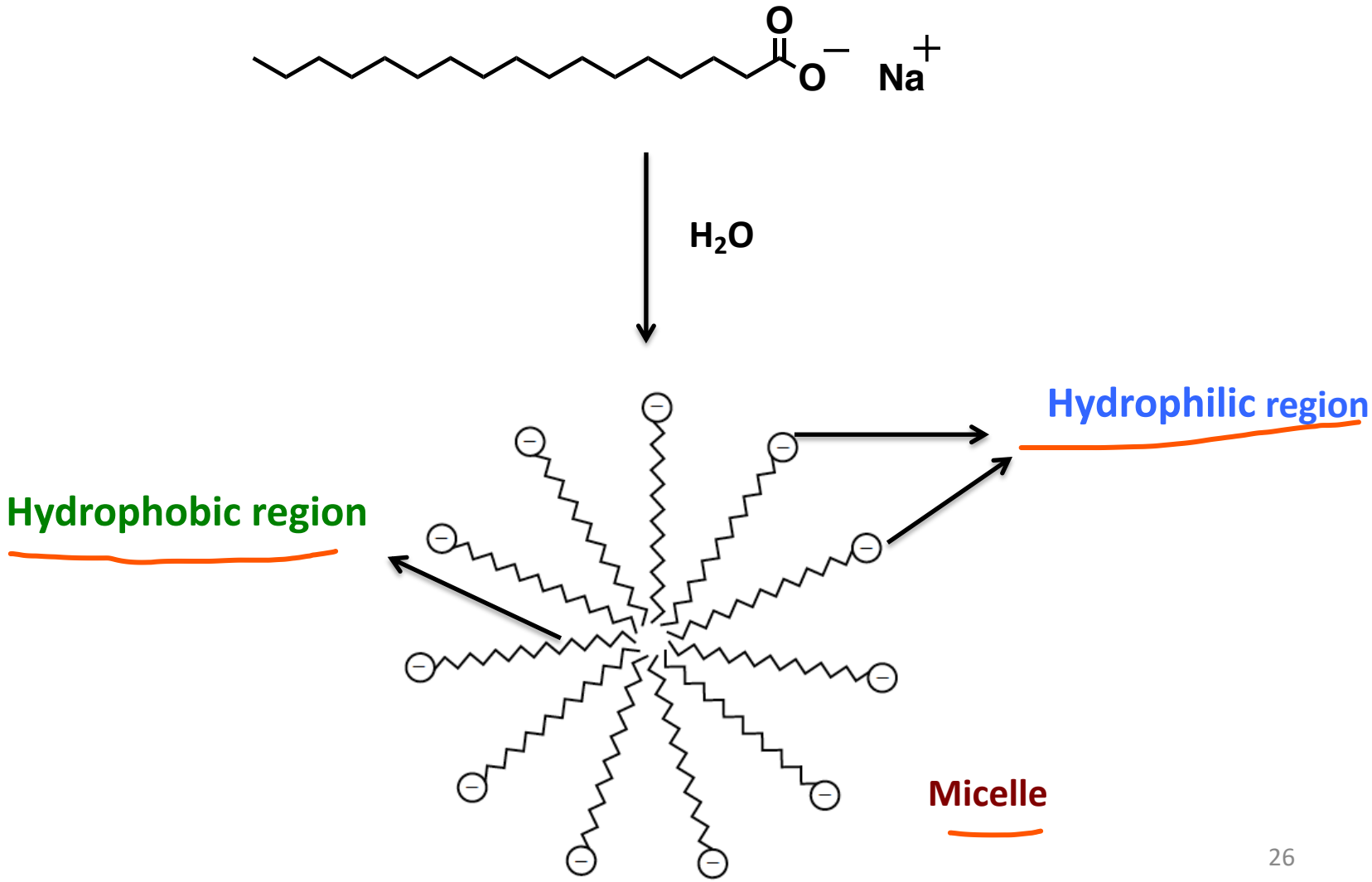
Prepared by the saponification (base hydrolysis) of animal or vegetable fats





Organic Chemicals in the Environment

Soaps and Synthetic Surfactants



Organic Chemicals in the Environment

Soaps and Synthetic Surfactants

IMP.

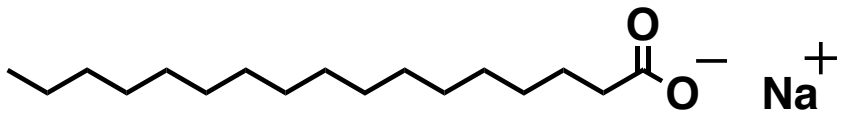
- The sodium salt of stearic acid, $CH_3(CH_2)_{16}CO_2H$, is the major product released upon hydrolysis of animal fat

- The sodium salt of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, is the major product released upon hydrolysis of olive oil

- Hydrolysis of palm oil yields approximately equal amounts of the salts of oleic acid and palmitic acid, $CH_3(CH_2)_{14}CO_2H$.

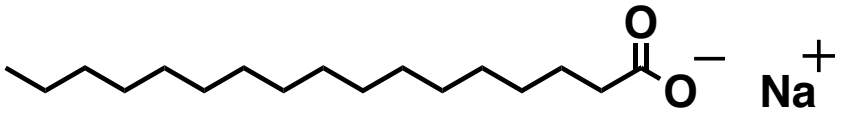
Organic Chemicals in the Environment

Soaps and Synthetic Surfactants



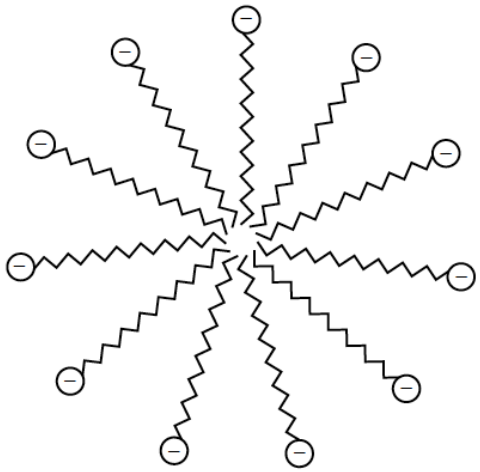
- All these are naturally occurring fatty acids and contain linear hydrocarbon chains.
- They are synthesized biochemically from the acetate ion ($CH_3CO_2^-$).
- They are also readily degraded back to acetate by microorganisms in the environment.

Soaps and Synthetic Surfactants



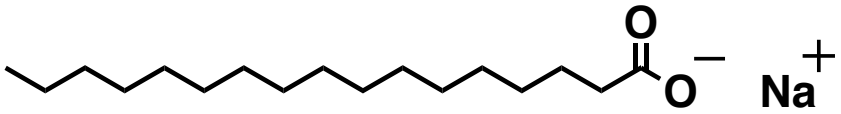
Disadvantages

- Carboxylic acid salts form insoluble precipitates with Ca^{2+} and Mg^{2+} in water (hard water)
- Weak acidic nature of carboxylic acids allows protonation even in mildly acidic solutions
- Polarity of the head group decreases when protonated and solubilizing ability of oils and greases is diminished



Organic Chemicals in the Environment

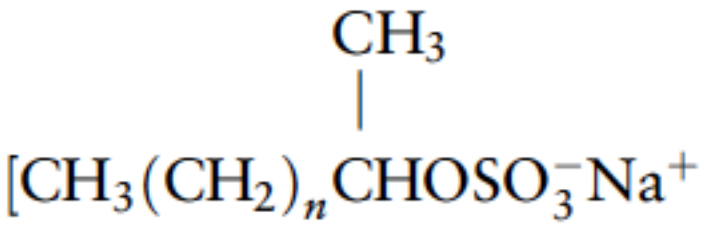
Soaps and Synthetic Surfactants



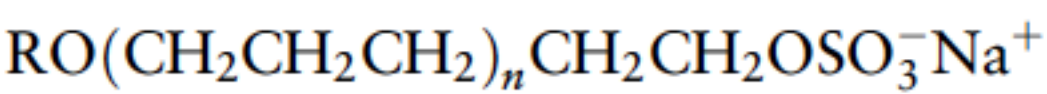
Detergents A mixture of synthetic surfactants, builders, bleaches, enzymes, and other materials designed to enhance the specific cleaning power

Synthetic surfactants

$R–SO_3^-\ Na^+$ **Alkyl sulfonates**



$[CH_3(CH_2)_nCHOSO_3^-Na^+$ **Alcohol sulfate**



$RO(CH_2CH_2CH_2)_nCH_2CH_2OSO_3^-Na^+$ **Alcohol ether sulfate**

Organic Chemicals in the Environment

Soaps and Synthetic Surfactants

Detergents A mixture of synthetic surfactants, builders, bleaches, enzymes, and other materials designed to enhance the specific cleaning power

- The main advantage of synthetic surfactants over soaps is that they do not precipitate in hard water
- Builders enhance the cleansing action of synthetics by inactivating the Ca^{2+} and Mg^{2+} in hard water

Ex. polycarboxylic acids, silicates, zeolites (inorganic aluminosilicates) and poly-phosphates

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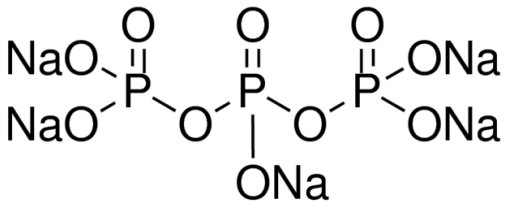
Soaps and Synthetic Surfactants



Sodium triphosphate

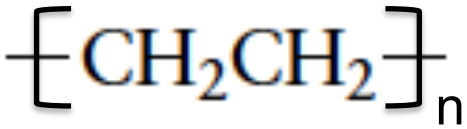
- Polyphosphates, which were used extensively as builders in the 1970s, were replaced in large part by zeolites because it was believed that phosphate from polyphosphates initiated algal blooms on lakes

Phosphates are nutritious food for alge

- Detergents account for only 20-25% of the phosphate in lakes and rivers, while the bulk of the remainder comes from fertilizer and animal waste runoff from farms

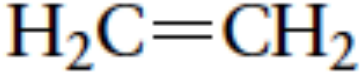
Polymers

- Polymers are also called macromolecules
- They have very large size and high molecular weight (10 kDa to 100 kDa)

Ex. 

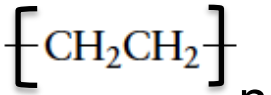
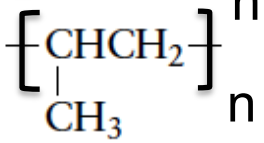
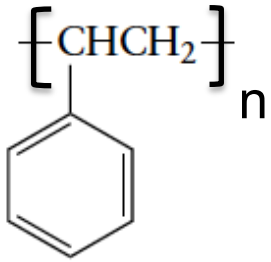
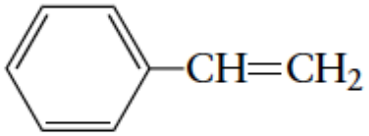
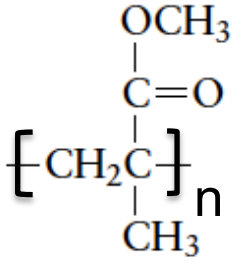
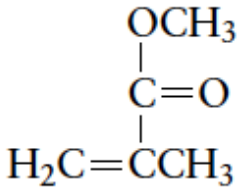
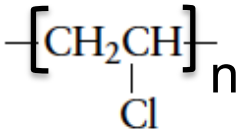
Polyethylene

n = degree of polymerization

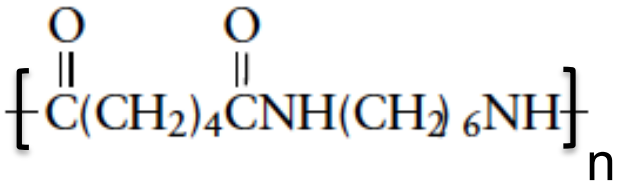
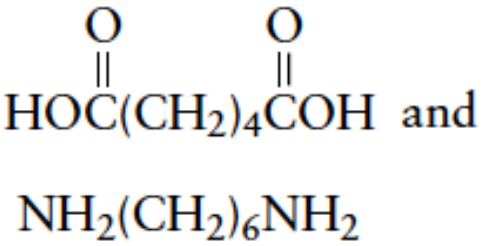
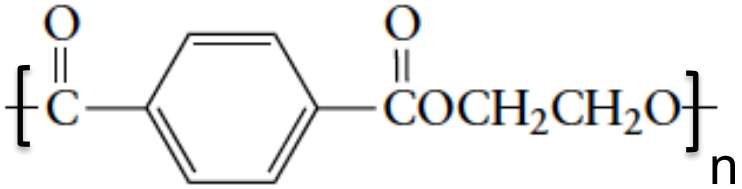
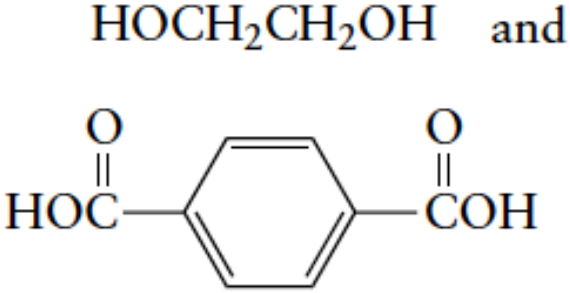
Synthesized from ethylene 

Organic Chemicals in the Environment

Polymers

Polymer	Repeat unit	Monomer(s)
Polyethylene		$H_2C{=}CH_2$
Polypropylene		$CH_3HC{=}CH_2$
Polystyrene		
Poly(methyl methacrylate)		
Poly(vinyl chloride)		$H_2C{=}CHCl$

Organic Chemicals in the Environment

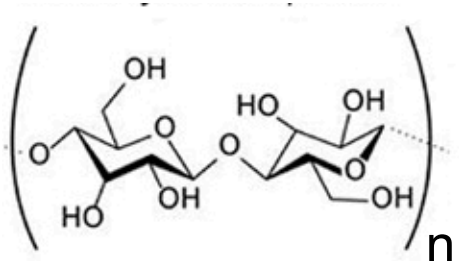
Polymer	Repeat unit	Monomer(s)
Nylon 66		
Poly(ethylene terephthalate) (PET)		

Polymers

- Many macromolecules are components of living systems

Proteins: polymers of amino acids

Starch and Cellulose: polymers of sugars



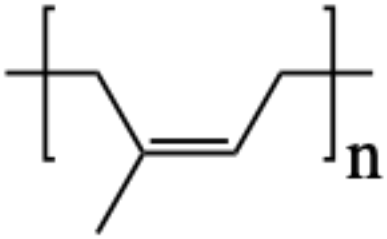
Cellulose

These naturally occurring polymers are biodegradable and will not cause long-term environmental problems

Polymers

- Natural rubber is not easily biodegradable

Major component



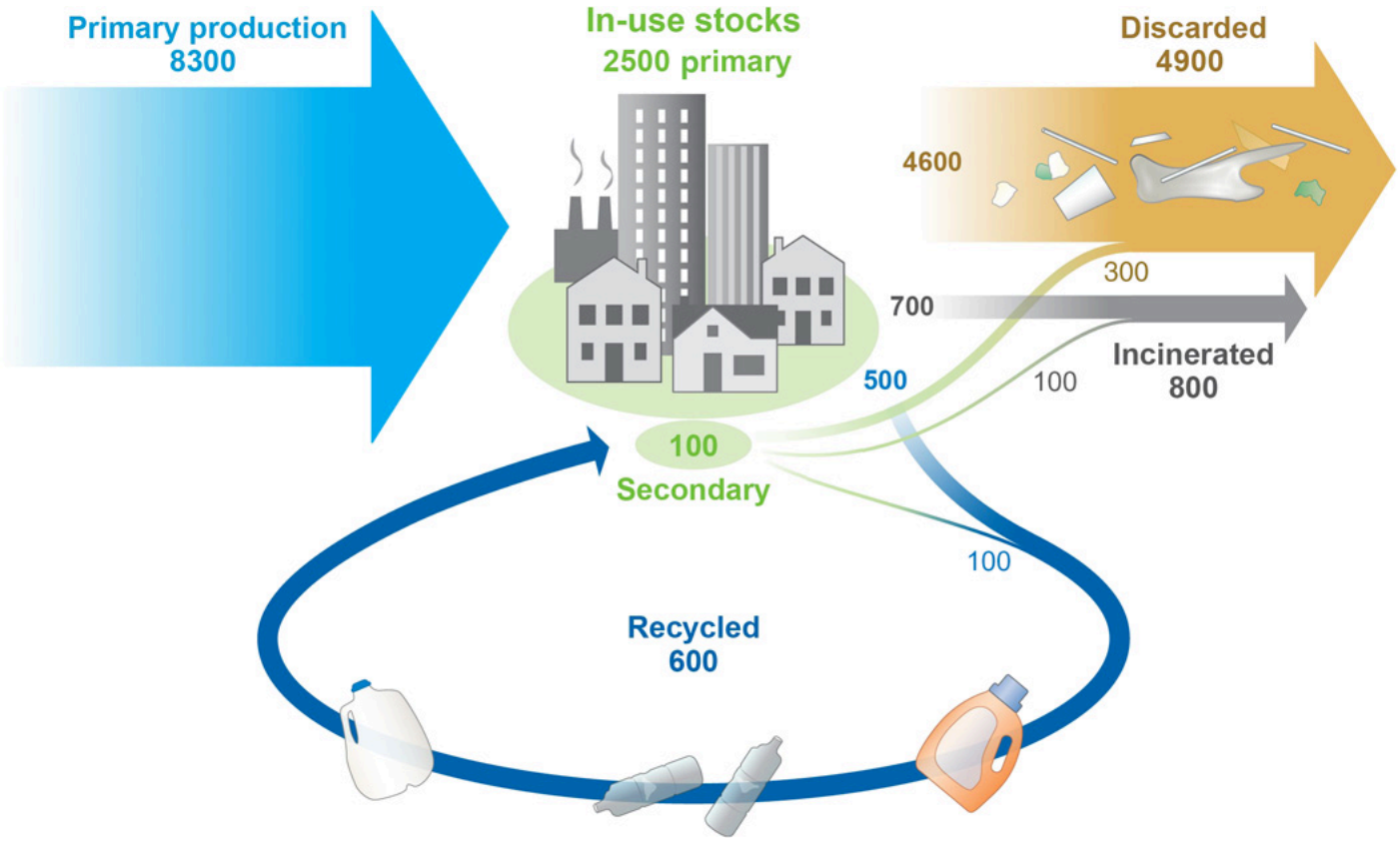
***cis*-1,4- polyisoprene**

Highly resistant to water

Organic Chemicals in the Environment

Fate of polymers after use

Global production, use, and fate of polymers (1950 to 2015 in million metric tons)

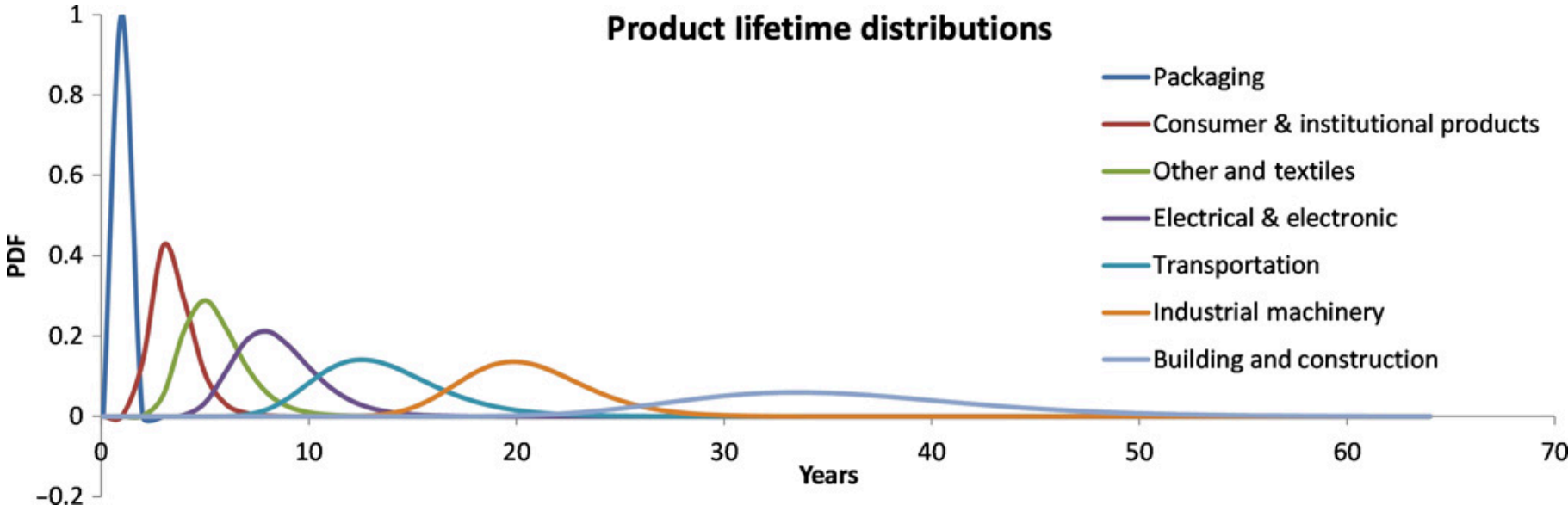


Reference: 10.1126/sciadv.1700782

Organic Chemicals in the Environment

Fate of polymers after use

How long plastics are in use before they reach the end of their useful lifetimes



- In 1990 25 million tons of plastics was manufactured in the United States, while during the same time period 16 million tons was placed in landfills (dumping yards)

Reference: 10.1126/sciadv.1700782

Fate of polymers after use

- Globally, only 18% of plastics waste are recycled, and 24% are incinerated
- 58% is placed in landfills (dumping yards)
- Relatively little decomposition takes place in landfills, so very little of this plastic material disappears with time (stable for more than 500 years)
- At current growth rates, the accumulation of plastics waste in landfills and/or in the natural environment is projected to reach nearly 12,000 Mt globally by 2050
- The total amount of plastics waste in the ocean is expected to grow from 50 Mt in 2015 to 150 Mt by 2025

Reference: https://dx.doi.org/10.1021/acssuschemeng.9b06635?ref=pdf

Organic Chemicals in the Environment

Fate of polymers after use

- It has been estimated that plastics kill or injure tens of thousands sea birds, seals, sea lions, and sea otters each year, and hundreds of whales, porpoises, bottlenose dolphins, and sea turtles

- A large portion of the reported fatalities are due to the entanglement of birds and mammals in the drift nets of commercial fishing boats

Possible solutions

- Development of biodegradable polymers
- Increase recyclability
- Reducing the usage of single use plastic