

## PERSISTENT ORGANIC POLLUTANTS (POPS)

### KEY QUESTIONS

- What are POPs?
- What is the “Dirty Dozen Plus Nine?”
- What international agreements address the problems posed by POPs?
- What quantities of POPs are in the environment presently, and how will this change in the future?
- What are PCBs, how were they formed, and what threats do they pose to the global environment?

### THE CONVENTION ON PERSISTENT ORGANIC POLLUTANTS (POPS)

On May 23, 2001, U.S. officials signed the Convention on Persistent Organic Pollutants (POPs) in Stockholm, Sweden. Under the Convention, countries agree to reduce and eventually cease the production, use, and release of the twelve POPs of greatest hazard to the global environment. The agreement further sets up a scientific review process whereby additional chemicals may be added to the treaty as warranted.

The Stockholm Convention targets a group of POPs, informally called the “dirty dozen,” shown in Table 17-1.

The POPs agreement begins global action to reduce and eventually eliminate these chemicals. The Convention took effect in May 2004 after ratification by fifty nations. By 2012, virtually every nation on Earth had ratified the Convention except Iraq, Saudi Arabia, Afghanistan, Italy, Malaysia, Western Sahara, Turkmenistan, Uzbekistan, and the United States of America.

In 2009, the Convention added nine more POPs to its list. They are:

Chemical	Source
Alpha-and-beta Hexachlorocyclohexane	Pesticide
Chlordecone	Pesticide
Hexabromobiphenyl and hexabromobiphenyl ether	Pesticide
Lindane	Industrial chemical
Pentachlorobenzene	Pesticide and industrial chemical
Perfluorooctane sulfonic acid and its salts	Industrial chemical
Endosulfan and isomers of same	Pesticide
Tetrabromodiphenyl ether	Industrial chemical
Pentabromodiphenyl ether	

TABLE 17-1 ■ The Dirty Dozen and Their Origins (Sources: EPA and World Bank).

1 = Pesticide	2 = Industrial Chemical	3 = Combustion Byproduct
Chemical	Comments	
aldrin <sup>1</sup>	Fatal dose, 5g, adult male: fatal dose for women and children less.	
hexachlorobenzene <sup>1,2,3</sup>	Can be lethal: has been found in food of all types.	
chlordane <sup>1</sup>	Toxic to many animals. Human exposure is mainly by air.	
mirex <sup>1</sup>	Used against fire ants. Very stable and persistent. Possible human carcinogen.	
DDT <sup>1</sup>	Has been detected in breast milk. May harm infants.	
toxaphene <sup>1</sup>	Most widely used pesticide in the United States in 1975. Possible human carcinogen.	
dieldrin <sup>1</sup>	Mutagenic. Second most common pesticide detected in a U.S. survey of pasteurized milk.	
polychlorinated biphenyls (PCBs) <sup>2,3</sup>	Suppress human immune system; probable human carcinogen; readily transferred in breast milk.	
endrin <sup>1</sup>	Toxic, but can be metabolized, so little bioaccumulation.	
polychlorinated dibenzo-p-dioxins (dioxins) <sup>3</sup>	Seven types out of 75 are mutagenic, carcinogenic.	
heptachlor <sup>1</sup>	High doses fatal to birds, mammals; low doses mutagenic.	
polychlorinated dibenzo-p-furan (furans) <sup>3</sup>	135 different types; possible human carcinogen; can accumulate in breast milk.	

**Question 17-1:** Research one of these chemicals and report on its uses and toxicity.

## WHY ARE POPS OF GLOBAL CONCERN?

The World Bank reports that, of all the pollutants released into the environment by human activity, POPs are among the most dangerous. POPs are of global concern because there is firm evidence of *global* transport of these substances, by air and water, to regions where *they have never been used or produced* such as the North American Arctic. The ensuing threats posed to the entire global environment prompted the POPs agreement. The main threats POPs pose center on their tendency to (1) persist in the environment, (2) bioaccumulate in the food chain, and (3) adversely affect human and animal populations. People are mainly exposed to POPs by eating contaminated foods. In humans and other mammals, POPs can be transferred through the placenta and breast milk to developing offspring. We discuss this phenomenon with *orca*, killer whales, below.

POPs are extremely toxic. They cause a range of harmful effects among humans and animals, including cancer, birth defects, damage to the nervous system, reproductive disorders, disruption of the immune system, and even death. POPs can damage the reproductive and immune systems of exposed individuals as well as their offspring. Some POPs are *endocrine disrupters*. An endocrine disruptor is a chemical that interferes with the function of the endocrine system. It can mimic a hormone, block the effects of a hormone, or stimulate hormone production. Table 17-2 shows persistence in agricultural soils of a number of POPs.

**TABLE 17-2** ■ Persistence of POPs in Agricultural Soils (Courtesy of Ralph G. Nash and Edwin A. Woolson/AAAS.)

Chemical	Years since Treatment	% Remaining
Aldrin	14	40
Chlordane	14	40
Endrin	14	41
Heptachlor	14	16
Toxaphene	14	45
Dieldrin	15	31
DDT	17	39

## COSTS OF EXPOSURE TO POPS

In June 2000, the National Academy of Sciences, the federal government's premier science advisory organization, issued a report titled "Scientific Frontiers in Developmental Toxicology."<sup>1</sup> Here is a portion of the Executive Summary:

"Of approximately 4 million births per year in the U.S., *major* developmental defects [occur] in approximately 120,000 *live-born* (our emphasis) infants."

**Question 17-2:** According to the NAS, what percent of live births results in major developmental defects?

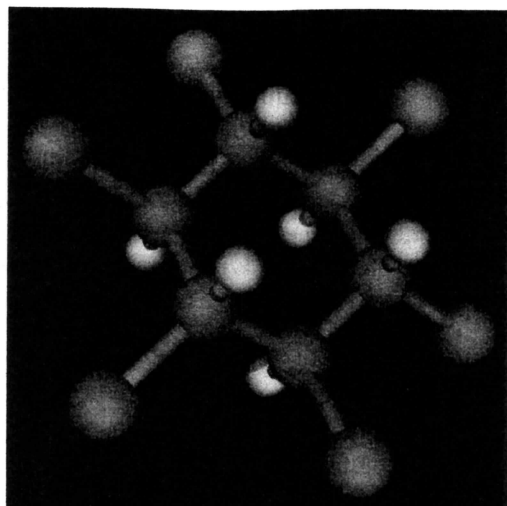
"At present, the causes of the majority of developmental defects are not understood; however, it is known that prenatal exposure to certain chemicals (such as POPs) and physical agents (such as radiation) found in the environment can cause developmental defects. Approximately 3% of all developmental defects are . . . caused by exposure to toxic chemicals and physical agents, including environmental agents, and almost 25% of all developmental defects might be due to a combination of genetic and environmental factors."

It is no longer controversial that environmental toxins impose a significant cost upon humans, especially fetuses and infants. If we were to assume a minimal cost of each human life at \$1 million (based on awards in liability lawsuits), then the *minimal costs* of such toxins in the environment could exceed \$3.6 billion annually in the United States alone, and is likely to be much more."

## POPS, ORGANOCHLORINES, AND THE PRECAUTIONARY PRINCIPLE

Recall the precautionary principle from the first section of this book. Restated, it reads, "Human society should avoid practices that have the potential to cause severe damage, even absent absolute scientific proof of harm." There is no better example of the need for application of the precautionary principle than that group of POPs produced when chlorine gas reacts with organic compounds. The compounds produced are called *organochlorines*.

<sup>1</sup> National Research Council: Committee on Developmental Toxicology, Board on Environmental Studies and Toxicology, Commission on Life Sciences. 2000. *Scientific Frontiers in Developmental Toxicology and Risk Assessment* (Washington, DC: National Academy Press).



**FIGURE 17-1** Molecular structure of an organochlorine. (Courtesy of Laguna Design/Science Photo Library/Corbis Images.)

Chlorine gas is greenish, heavy, extremely reactive, and does not occur in nature, not even in that cauldron of creation, active volcanoes. Chlorine gas readily reacts with any organic chemical it encounters, producing bleaches, disinfectants, insecticides and pesticides, and, incidentally, hundreds of additional by-products.

Organochlorines may be chemically organized in two fashions. One type, the *aromatics*, contains structures called benzene *rings* (see Figure 17-1). The other type, *aliphatics*, from the Greek for *fat* (fats have the chain structure as well), consists of *chains* of carbon atoms.

To give you an idea how these chemicals are named, consider PCBs. The chemical name for this family of compounds is *polychlorinated biphenyls*. A biphenyl is made of two linked benzene rings: If chlorines are added, it becomes a polychlorinated biphenyl. Some other extremely toxic chemicals are similar in structure to PCBs. DDT (*dichlorodiphenyltrichloroethane*), for example, has one chlorine attached to each of two benzene rings, in turn, attached to a trichloroethane.

The aliphatics, since they closely mimic the structure of fats, are highly bioaccumulative (that is, they build up in fatty tissue). For example, hexachlorobutadiene has a bioaccumulation factor of up to 17,000. Others have ratios approaching 70,000.

**Question 17-3:** How many chlorines are found in hexachlorobutadiene?

## HOW DOES CHLORINATION AFFECT ORGANIC CHEMICALS?

Chlorination radically changes the properties of organic compounds. It can increase the stability of the compound so that it may persist in the environment for decades or centuries. This property has been of great value to industry over the past hundred years and provided us with our first “safe” refrigerant, freon. The first generation of refrigerators used ammonia as a refrigerant, and ammonia is toxic when ingested. Freons were believed to be inert.

Since chlorinated hydrocarbons, by and large, are not naturally produced, there are few mechanisms that remove or degrade them once formed.



The addition of chlorine gas to organic compounds also increases their reactivity. And perhaps most important, adding chlorine to organic chemicals *increases their solubility in fats and oils*. This means they can bioaccumulate in fatty tissues of animals and can be passed on from generation to generation by mother's milk. They can also become concentrated in larger animals by the simple process of eating smaller ones, a process called *biomagnification*. Thus, humans can concentrate organochlorines in their bodies by eating contaminated fish, and seabirds and marine mammals can, and do, experience the same effect.

### How Safe Are Organochlorines?

Only a few hundred of the thousands of organochlorines produced by industry have been tested by scientists, and virtually all of them have been found to damage one or more of the following processes: fetal development, brain function, the immune system, the endocrine system, and/or sperm production and development. They may be *mutagenic* (causes genetic mutations) and *carcinogenic* as well.

Organochlorines cause changes in bone composition including reduced bone mineral density. Organochlorines have also been implicated in other bone diseases including periodontitis, a widespread disorder of the gums and bones around the teeth.<sup>2</sup>

**Question 17-4:** Should women with a tendency for bone-density loss or people with periodontitis be encouraged to be tested for organochlorines? Why or why not? Do you think this is routinely done?

Finally all of these harmful effects can occur at *parts-per-trillion concentrations*, which is described as "equivalent to one drop in a train of railroad tank cars 10 miles long."<sup>3</sup>

**Question 17-5:** Reread Jefferson's quotation on corporations, from "Basic Concepts and Tools," (p. 15). Do you believe that corporations should be held liable for any damage that their actions cause, in violation of the precautionary principle? How? Cite evidence to support your view, recalling that opinions uninformed by evidence are of little value in scientific inquiry.

### PCBs

Recall the "dirty dozen" from Table 17-1. One of these was polychlorinated biphenyls (PCBs). PCBs are a group comprising over 200 structures. Their formula is complex, and their atomic weight depends on the number of chlorine atoms in the structure. PCBs do not exist naturally on Earth. They were first synthesized during the late nineteenth century.

<sup>2</sup> National Institute of Health (NIH), [www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1331997](http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1331997).

<sup>3</sup> Thornton, J., in *Pandora's Poison: Chlorine, Health and a New Environmental Strategy*. 2000. (Columbia University, New York, New York).

Because of their stability when heated, they were widely used in electrical capacitors and transformers. In the 1960s, scientists began to report toxic effects on organisms exposed to PCBs, and by 1977, the manufacture of PCBs was banned in the United States, the United Kingdom, and elsewhere. By 1992, 1.2 million metric tonnes (2.6 billion lbs) of PCBs were believed to exist worldwide. As much as 370,000 metric tonnes (810 million lbs) could have been dispersed into the environment.

PCBs can be destroyed by incineration, but the process is expensive. Around 15 percent of PCBs in soils reside in developing countries, mostly from shipments of waste contaminated with PCBs from developed countries.

**Question 17-6:** What role, if any, should wealthy countries play in neutralizing PCBs in developing countries? Justify your answer by listing and defending your reasons.

PCBs are relatively heavy molecules (average atomic weight of around 360 g/mole) and are relatively insoluble in water. While concentrations in seawater can reach 1 part per million (ppm), PCBs typically concentrate in sediments. From there, they enter the food chain through the activities of organisms called sediment, or deposit, feeders. These creatures eat sediment, extract organic matter, and excrete the rest. Like other organochlorines, PCBs are *lipophilic* and thus tend to accumulate in the fatty tissues of animals. If other animals eat the deposit feeders, the PCBs are not metabolized and become more concentrated in the animal's fat (biomagnified). Concentrations exceeding 800 ppm have been measured in the tissues of marine mammals. According to the Environmental Research Foundation, this would qualify the creature for hazardous waste status!

PCBs are widespread pollutants and have contaminated most terrestrial and marine food chains. They are extremely resistant to breakdown and are known to be carcinogenic. PCBs have been linked to mass mortalities of striped dolphins in the Mediterranean, to declines in *orca* (killer whale) populations in Puget Sound, and to declines of seal populations in the Baltic.

While PCBs may threaten the entire ocean, the northwest Atlantic is believed to be the largest PCB reservoir in the world because of the amount of PCBs produced in countries that border the north Atlantic. PCBs have been shown to cause liver cancer and harmful genetic mutations in animals. PCBs may inhibit cell division, and they have been implicated in reduction of plant growth and even mortality of plants. According to a report edited by Paul Johnston and Isabel McCrea for Greenpeace UK,

Since the rate at which organochlorines break down to harmless substances [has been] far outstripped by their rate of production, the load on the environment is growing each year. Organochlorines (including PCBs) are arguably the most damaging group of chemicals to which natural systems can be exposed.<sup>4</sup>

### Bioaccumulation and Biomagnification of PCBs

POPs accumulate in the body fat of living organisms, as you have seen, and become more concentrated as they move from one creature to another. When contaminants found in small amounts at the bottom of the food chain biomagnify, they can pose a hazard to predators at the top of the food chain.

<sup>4</sup> Johnston P., & I. McCrea. 1992. *The Effects of Organochlorines on Aquatic Ecosystems*. London: Greenpeace International.

A 1997 study found that caribou in Canada's Northwest Territories had up to ten times the levels of PCBs as the plant matter on which they fed. PCB levels in the wolves that ate the caribou were nearly six times higher still.

J. Cummins, in a 1988 paper in *The Ecologist*, concluded that adding 15 percent of the remaining stock of PCBs to the ocean would result in the extinction of marine mammals.<sup>5</sup>

### Highly Exposed Populations<sup>6</sup>

The long-distance transport of POPs toward the poles has contaminated the Arctic food web. Indigenous peoples of the Arctic experience a high intake of organochlorines from consuming a traditional diet featuring marine mammals, which have accumulated high levels of organochlorines from their food. Populations who have a diet rich in fish from contaminated waters, such as residents of the Great Lakes region (in the United States and Canada) and of the shores of the Baltic Sea, have a high intake of organochlorines. Children can have a higher intake of organochlorines than adults because of their comparatively high food intake. In addition, exposure of the developing young is of great concern because these stages of life are most vulnerable to the toxic effects of POPs. Nursing infants have a particularly high intake of organochlorines because of bioaccumulation in breast milk.

**Question 17-7:** Should pregnant women, or those desiring to become pregnant, be encouraged to be tested for organochlorine contamination? Why or why not?

### Synergistic Effects: PCBs and Mercury

Combining exposure to toxic chemicals can multiply the harmful effects of each: This is called *synergism*. One particularly toxic mercury compound, methylmercury, biomagnifies powerfully as it goes up the food chain. Figure 17-2 shows this effect from the Florida Everglades. Water concentration of 0.1 part per trillion (ppt) was biomagnified to 2,000 ppt in plants, and so on. Mercury exhibits synergistic effects with PCBs and other POPs. A study of children born to mothers who consumed fish from Lake Ontario showed that prenatal PCB and mercury exposures interacted to reduce performance of three-year-old children on certain tests.

### PCBs and Orcas in Puget Sound

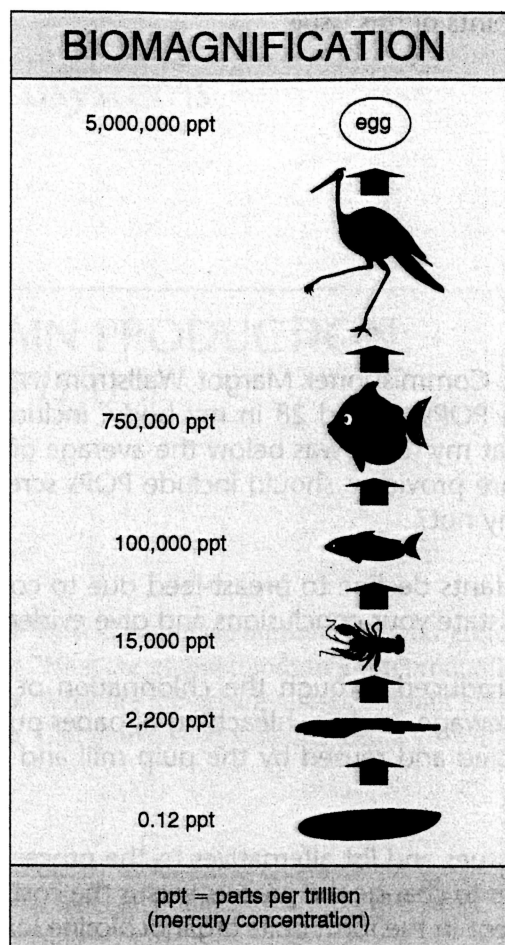
Even though soldiers during World War II used them for target practice, orca have become a symbol of the Pacific Northwest. In 1999, Dr. P. S. Ross, a research scientist with British Columbia's Institute of Ocean Sciences, took blubber samples from forty-seven live killer whales and found PCB concentrations of 46–250 ppm, up to 500 times greater than those found in humans. Ross concluded, "The levels are high enough to represent a tangible risk to these animals."<sup>7</sup>

Ross compared the orca population he studied with the endangered beluga whale population of the St. Lawrence estuary of eastern North America, in which a high incidence of

<sup>5</sup> J. E. Cummins, The PCB Threat to Marine Mammals. *The Ecologist*, Nov–Dec 1988.

<sup>6</sup> [www.greenpeace.org](http://www.greenpeace.org).

<sup>7</sup> "Toxin Threatens a Wonder of the Northwest," by M. L. Lyke Special to the Washington Post, Monday, November 8, 1999, Page A9.



**FIGURE 17-2** Biomagnification of methylmercury in the Florida Everglades. (www.usgs.gov)

diseases have been linked to contaminants and which have shown evidence of reproductive impairment.

For the orca, the PCBs are likely passed from generation to generation. PCBs are highly fat-soluble and are concentrated in mother's milk. Ross said, "Calves are bathed in PCB-laden milk at a time when their organ systems are developing and they are at their most sensitive."<sup>8</sup>

While PCBs have been banned in the United States for nearly three decades, they are still being used in some developing countries. Accordingly, Ross speculates that PCBs in the Pacific could be derived from East Asian sources and could end up concentrated in the tissues of migratory salmon, which are a prime food source for the Orca. Ross's study was done in collaboration with the University of British Columbia, the Vancouver, British Columbia, Aquarium, and the Pacific Biological Station of British Columbia.

**Question 17-8:** Discuss the topic of POPs from the perspective of sustainability and sustainable societies.

<sup>8</sup> "Killer Whales are Full of Toxic Chemicals, New Study Says PCBs Make Popular Orca Prey to Menacing Diseases." *Seattle Post-Intelligencer*, 10/25/99.



## **What exactly are PCBs?**

Polychlorinated biphenyls (PCBs) are a group of man-made chemicals that were once used in making electrical equipment. In 1977 the U.S. stopped making PCBs because there was evidence that they build up in the environment and can be harmful to people's health.

## **What happens to PCBs in the environment?**

PCBs entered the air, water and soil

- When they were made
- When they were used
- When they were disposed of
- From spills and leaks when they were transported, and
- From leaks or fires in products containing PCBs.

PCBs may stay in the environment for a long time because they do not break down easily. In water, a small amount of PCBs may stay dissolved, but most bind to the sediment at the bottom of lakes, rivers, and streams. Small organisms eat this sediment containing PCBs and then larger animals, such as fish and mammals, eat these organisms.

Bottom feeders, such as catfish, can have high levels of PCBs in their bodies. These levels can build up in the fish until they are thousands of times higher than levels found in the water or sediment. This can make the fish unsafe to eat.

**You are NOT permitted to take fish from Lake Crabtree or Crabtree Creek, just below the lake.**

**You may catch and release fish.**

## **How did PCBs get into Brier Creek Reservoir, Lake Crabtree and other local waters?**

The Ward Transformer Company is an electrical transformer factory built in 1964 that is located northwest of the Raleigh-Durham International Airport. A small stream is located near the Ward Transformer Company that leads to Little Brier Creek, Brier Creek Reservoir, Brier Creek, Lake Crabtree, and Crabtree Creek. Before 1972, storm water runoff from the Ward Transformer Company was not controlled, and the water bodies nearby began to get contaminated with PCBs.

In 1997 the State of North Carolina Superfund Section collected samples and PCBs were found in sediment collected from the stream near the Ward Transformer Company. PCBs were also found in Little Brier Creek, less than a mile downstream from the site.

In April 2003, the Environmental Protection Agency (EPA) put the Ward Transformer Company site on the National Priorities List of known releases or threatened releases of hazardous substances, pollutants, or contaminants throughout the United States and its territories. It is now part of the EPA's Superfund Investigation, and the Ward facility is scheduled to be cleaned up this summer. This will remove the known major source of contamination. At this time Ward Transformer Company reconditions only old transformers that are PCB-free.

[www.wakegov.com](http://www.wakegov.com)

## **Why did Wake County announce a policy of catch and release fishing at Lake Crabtree?**

The North Carolina Department of Health and Human Services (NCDHHS) has issued the following advisories:

- December 2003  
Little Brier Creek/Brier Cr. Reservoir:  
*Do not eat any fish.*
- May 2004  
Brier Creek:  
*Do not eat any fish.*  
Lake Crabtree:  
*Do not eat any carp or catfish. All other fish may be eaten at the rate of only one meal per month.*
- July 2005 & March 2006  
Crabtree Creek:  
*Eat only one meal per month of carp, catfish, and largemouth bass.*

**These advisories warned that eating more fish than advised could lead to health problems, including a higher risk of cancer, infections, skin problems, and learning problems in children born to women who eat fish from these waters.**

A local government Task Force was concerned that many people were still taking home and eating more fish than the State advised as being safe. In November 2005 Wake County Government adopted a policy of "catch and release only" fishing for Lake Crabtree and Crabtree Creek, just below the lake. There are plenty of fish to be caught safely; the County is simply asking people to return the fish to the water (release them).

**You may only catch and release fish.**

## **How are PCBs impacting wildlife and the ecosystem?**

The short and long-term effects of PCBs on Lake Crabtree's wildlife are still unknown.

*Here is what we do know:*

Lake Crabtree's wildlife has been exposed to PCBs from sediment and from eating contaminated prey. Lake Crabtree has one nesting pair of Bald Eagles, a nest rookery for Great Blue Herons, and many other fish and aquatic organisms dependent on food that could be contaminated by PCBs.

A North Carolina State University study found PCBs had an impact on Asiatic clams in Brier Creek, upstream of Lake Crabtree.

## **PCBs can cause the following problems in wildlife:**

- Low birth weight in offspring
- Harmful effects to unborn offspring
- Skin Effects
- Liver Damage

## **What are the risks associated with recreational activities at Lake Crabtree?**

Scientific research and current samples tell us that there is a very low cancer risk due to contact with PCBs from soil, water and sediment at Lake Crabtree. The PCB levels found in samples taken so far are within acceptable limits set by the EPA and NCDHHS.

Only a few samples have been taken from Lake Crabtree. The PCB Task Force asked the EPA to take more samples. At this time, the EPA is testing soil, sediment, and water samples to better understand any possible health risks to people who use the park. Based on the scientific information we have right now, there is no significant health risk for boating, wading, or catch and release fishing.

## **Swimming is not allowed in Lake Crabtree**

**You MAY NOT take fish from Lake Crabtree or Crabtree Creek, just below the lake.**

**You MAY catch and release fish.**

## **How can you find out more information and get involved?**

- For a list of State fish advisories  
[www.epi.state.nc.us/epifish/current.html](http://www.epi.state.nc.us/epifish/current.html)
- For a list of fish that are safe to eat go to  
[www.epi.state.nc.us/epi/fish/safefish.html](http://www.epi.state.nc.us/epi/fish/safefish.html)
- For EPA Superfund information:  
[www.epa.gov/superfund](http://www.epa.gov/superfund)
- Request to be placed on the EPA's Ward Transformer Superfund mailing list:  
Call Community Involvement Coordinator  
Angela Miller at 1-800-435-9234

Join a stream watch group, such as:

The Umstead Coalition: [www.umsteadcoalition.org](http://www.umsteadcoalition.org)  
The Neuse River Foundation: [www.neuseriver.org](http://www.neuseriver.org)

**Call Lake Crabtree County Park at:  
(919) 460-3390**

**[www.wakegov.com](http://www.wakegov.com)**

# **LAKE CRABTREE AND PCBs:**

## **What you should know.**

**SUMMER  
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For Question 5

Thomas Jefferson

"I hope we shall take warning from, and example of, England, and crush in its birth the aristocracy of our moneyed corporations, which dare already to challenge our Government to trial, and bid defiance to the laws of our country."

Persistent Organic Pollutants (POPS) Case Study Continued.....

"Lake Crabtree and PCBs: What You Should Know" article questions

9. What are PCBs?
10. What were PCBs used for?
11. Describe what happens to PCBs when they get in to the environment.
12. How did PCBs get into the Brier Creek Reservoir, Lake Crabtree, and other local waters?
13. What has the EPA done about the situation?
14. What are the hazards of eating fish from contaminated areas?
15. How are PCBs impacting wildlife and the ecosystem?
16. What are the risks associated with recreational activities (and community service!) at Lake Crabtree?