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Voluntary Estuary Monitoring Manual

Chapter 12: Contaminants and Toxic Chemicals Heavy metals, Pesticides, PCBs, and PAHs

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Chapter 12
Toxins

Testing for toxins requires specialized equipment and expertise beyond the means of most volunteer monitoring programs. Nonetheless, it is important to understand the sources of toxins and the role they play in estuaries. Volunteers can provide valuable assistance with research projects by providing local knowledge of a watershed and potential sources of toxic compounds and by collecting fish and invertebrates for laboratory analysis.

Photos (l to r): G. Carver, R. Ohrel, R. Ohrel

Overview

Since industrialization in the late 1940s and 1950s, the amount of contaminants and toxic substances put into estuaries has greatly increased. These contaminants include heavy metals (such as mercury, lead, cadmium, zinc, chromium, and copper) and synthetic (manmade) organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides (e.g., dichlorodiphenyltrichloroethane—DDT), and human sewage. Many of these toxins such as PCBs and DDT do not degrade for hundreds of years and can concentrate in the sediment and in the tissues of local aquatic animals. Sources of toxins into estuaries include industrial discharges; runoff from lawns, streets, and farmlands; and discharges from sewage treatment plants. The estuary's own sediment can also serve as a source, as sediment contains years of toxic deposits. Other toxic substances are deposited into estuaries from the atmosphere. Mercury vapor and lead particles from industrial sources enter estuaries from the atmosphere as rain, snow, or dry particles. All toxins can affect an estuary's biological structure and populations. Humans, in turn, can be harmed by consuming bottom-dwelling organisms such as shellfish that are exposed to contaminated sediment as well as through exposure to contaminated water.

Testing for many of these toxins requires specialized equipment and expertise beyond the means of most volunteer monitoring programs. Nonetheless, it is important to understand the sources of toxins and the role they play in estuaries. Volunteers can provide valuable assistance with research projects by providing local knowledge of a watershed and potential sources of toxic compounds and by collecting fish and invertebrates for laboratory analysis.

This chapter reviews some of the toxic substances found in our nation's estuarine ecosystems, especially heavy metals, pesticides, PCBs, and PAHs, and introduces some testing techniques for toxins.

Toxins in Estuaries

There are two general classes of toxic pollutants found in estuaries—metals and organic compounds. Toxic metals include mercury, lead, cadmium, chromium, and copper. Some of these metals (e.g., copper) are required in small concentrations for metabolic processes but are toxic at higher levels. Organic compounds of interest include PAHs and several synthetic ones that are no longer produced, such as PCBs and DDT (USEPA, 1996). Other organic toxins of concern are biotoxins that are produced by harmful algal blooms (see Chapter 19). This chapter focuses on the more traditional organic compounds.

Sources of toxic substances include surface water from municipal and industrial discharges, runoff (e.g., from lawns, streets, and farmlands), and atmospheric deposition.

Lifespan of Toxins

How long pollutants remain in estuaries depends on the nature of the compound. Some pollutants bind to particles and settle, while others remain water soluble. Another factor is the flushing rate within the estuary. Many pollutants, including DDT and PCBs, have been banned in the United States since the 1970s, but are very chemically stable and persist in benthic sediment long after the pollution source has abated. ■

Toxicity

Toxins can affect the animals in an estuarine ecosystem through acute or chronic toxicity. Organisms suffer **acute toxicity** when exposure levels result in death within 96 hours. Lethal doses differ for each toxin and species, and are influenced by the potency and concentration of the toxin. **Chronic toxicity**—also referred to as sub-lethal toxicity—does not result in death (at exposures of at least 96 hours), but can cause impairment to aquatic animals, organ damage and failure, gastro-intestinal damage, and can affect growth and reproduction.

Why Monitor Toxins?

Monitoring for the presence of toxins provides information on possible effects to an estuary's community structure and populations. Human health is another important reason for monitoring. Bottom-dwelling organisms, like shellfish, can accumulate these metals and chemicals in their tissues, making them a potential risk to human health when consumed. When high concentrations of chemical contaminants are found in local fish and wildlife, state officials issue consumption advisories for the general population as well as for sensitive subpopulations such as pregnant women. Advisories include recommendations to limit or avoid consumption of certain fish and wildlife species from specific bodies of water. ■

Accumulation and Amplification of Toxins—Definitions

Biological accumulation (bioaccumulation)—The uptake and storage of chemicals (e.g., DDT, PCBs) from the environment by animals and plants. Uptake can occur through feeding or direct absorption from water or sediments.

Biological amplification (also called bioamplification, biomagnification or bioconcentration)—The concentration of a substance as it "moves up" the food chain from one consumer to another (Figure 12-1). The concentration of chemical contaminants (e.g., DDT, PCBs, methyl mercury) progressively increases from the bottom of the food chain (e.g., phytoplankton, zooplankton) to the top of the food chain (e.g., fish-eating birds such as cormorants).

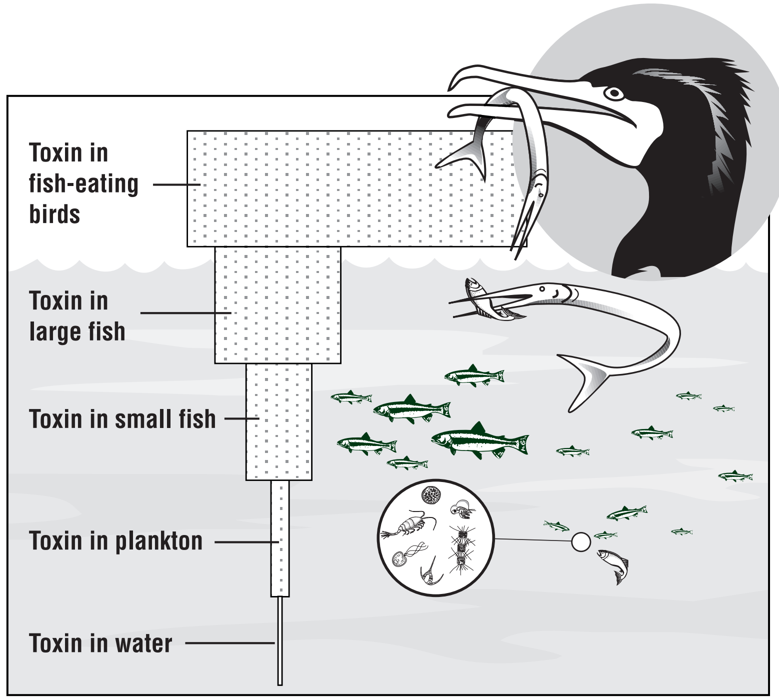

Figure 12-1. Biological amplification. Chemical concentrations progressively increase from lower to upper levels of the food chain.

The Role of Toxins in the Estuary Ecosystem

Though there are many toxic substances found in our nation's estuarine ecosystems, the categories of biggest concern are: heavy metals, pesticides, PCBs, and PAHs (USEPA, 1996).

Heavy Metals

Some toxic metals, such as copper and zinc, are needed in trace amounts for metabolism but are toxic in higher levels. Others, such as mercury, lead, chromium, and cadmium, have no known metabolic function. Their presence may prompt state officials to restrict water use, close shellfish waters, or issue fish consumption advisories. Generally, the three metals most closely monitored are mercury, copper, and lead because of their adverse effects on human health.

Mercury

Mercury is distributed throughout the environment from natural sources and from human activities. Sources of mercury from human activities (also called **anthropogenic sources**) include solid waste incineration and coal combustion facilities for electricity. Together, they contribute approximately 87 percent of the emissions of mercury in the United States. Other sources of mercury include municipal wastewater treatment plants and mining and industrial sources, such as smelting, pulp mills, paper mills, leather tanning, electroplating, chemical manufacturing, and cement production. In addition, mercury is deposited in surface waters through runoff from its natural occurrence in rocks and soils as well as from

Toxins in the water can make estuaries and other waterbodies unsafe for fishing or swimming (photo by R. Ohrel).

atmospheric deposition of volatile compounds from wetlands (USEPA, 1999c).

Methylmercury is the chemical form or "species" that bioaccumulates in the tissue of animals and bioamplifies in food chains. Mercury poisoning through consumption of methylmercury-contaminated food results in such adverse central nervous system effects as impairment to peripheral vision and mental capabilities, loss of feeling, and—at high doses—seizures, severe neurological impairment, and death. Methylmercury has also been shown to be a developmental toxicant, causing subtle to severe neurological effects in children.

Methylmercury makes up 90-100 percent of the mercury found in most adult fish. It binds to proteins and is found primarily in fish muscle (fillets). Concentrations of total mercury in fish are approximately 10,000 to 100,000 times higher than the concentrations of total mercury found in the surrounding waters.

Mercury contamination is one of the leading reasons that fish consumption advisories are issued in the United States. These advisories inform the public that concentrations of mercury have been found in local fish at levels of public health concern. State advisories recommend either limiting or avoiding consumption of certain fish from specific waterbodies (USEPA, 1999c).

Lead

Lead is used by the ton in products such as batteries, ammunition, solder, pipes, and in building construction. Lead poisoning is associated with kidney damage, anemia, and damage to the central nervous system. Of greatest concern are the dangers of lead poisoning to children, who can suffer permanent physical and mental impairments.

Cadmium

Cadmium is another heavy metal of concern because it can cause kidney and bone damage to people who suffer long-term chronic exposure to it. Sources of cadmium into the environment from human activities are mainly from the mining, extraction, and processing of copper, lead, and zinc. Other sources can include solid waste incineration, reprocessing of galvanized metal, and sewage sludge. Cadmium can also be found in some batteries, fertilizers, tires, and many industrial processes.

Copper

Copper is an essential nutrient, required by the body in very small amounts. However, the U.S. Environmental Protection Agency has found copper to potentially cause stomach and intestinal distress, liver and kidney damage, and anemia, depending on the level and term of exposure. Persons with certain diseases may be more sensitive than others to the effects of copper contamination.

Copper releases to land and water are primarily from smelting industries. Municipal incineration may also produce copper. Copper is also widely used in household plumbing materials.

Chromium

Depending on the level and term of exposure, chromium has the potential to cause skin irritation, ulcers, dermatitis, or damage to liver, kidney, circulatory, and nerve tissues.

Though widely distributed in soils and plants, chromium is rare in natural waters. The two largest sources of chromium emission in the atmosphere are chemical manufacturing industries and natural gas, oil, and coal combustion. Chromium may also reach waterways via:

- road dust;
- cement-producing plants;
- the wearing down of asbestos brake linings from automobiles or similar asbestos sources;

- municipal refuse and sewage sludge incineration;
- automotive catalytic converter exhaust;
- emissions from cooling towers that use chromium compounds as rust inhibitors;
- waste waters from electroplating, leather tanning, and textile industries; and
- solid wastes from chemical manufacture.

Pesticides

Another major category of toxins in estuaries is pesticides. Most of them will break down into nontoxic chemicals within a few days of application. Others are banned because they can persist for decades. Pesticides are developed to eliminate pests such as weeds (herbicides), insects (insecticides), rodents (rodenticides), fungi (fungicides), and other organisms that are considered undesirable.

Two of the more persistent pesticides are DDT and its breakdown product and closely related compound, DDD (dichlorodiphenyldichloroethane). They are both in a class of pesticides called organochlorines. These pesticides destroy living cells and affect the nervous system of organisms. DDT is a highly toxic, broad-spectrum poison that is capable of killing many different species. It was used extensively in the 1940s, 1950s, and 1960s because it was cheap to produce, effective, and not harmful to humans. For these reasons, it continues to be used in developing countries to eradicate the mosquito that transmits malaria. DDT was banned in the U.S. in 1972 because of its effects on wildlife, but it continues to be measured in sediment and in aquatic animals. In fact, buried sediments may be a large and continuing source of DDT compounds due to mixing processes such as flooding, dredging activities, and the disturbing of sediment by animals (called **bioturbation**), as well as other mechanisms.

Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs)

PCBs are another class of banned synthetic organic chemicals comprising 209 individual chlorinated biphenyl compounds. Similar to DDT, PCBs are resistant to biological and chemical degradation and can persist in the environment for decades. There are no known natural sources of PCBs. Millions of metric tons of PCBs were used as solvents and in the electronic industry as insulators for transformers. Most PCBs are soluble in fats; therefore, they accumulate in the tissues of animals. Once incorporated into an animal's fat, PCBs will stay there and cannot be excreted. They are rapidly accumulated by aquatic organisms, becoming amplified in the food chain when animals eat PCB-contaminated organisms. PCB concentrations in fish at the top of the food chain can be 2,000 to more than a million times higher than the concentrations found in the surrounding waters (USEPA, 1999d).

While the manufacture and use of PCBs have been banned in the U.S. since 1976, the sediment of many estuaries can have high levels of PCB contamination, and PCBs can continue to enter estuaries from leaking shoreside landfills or from improper disposal. PCBs in the sediment can reenter the water column though natural processes and dredging activities. Although PCBs are declining in the environment, health concerns are still warranted.

Recent findings indicate that susceptible populations (e.g., certain ethnic groups, sport anglers, the elderly, pregnant women, children, fetuses, and nursing infants) continue to be exposed to PCBs via fish and wildlife consumption (USEPA, 1999d).

Exposure to PCB compounds involves different levels of harmful risks. There is much interest in determining if PCBs are **endocrine disrupters**—chemicals that can mimic, block, or otherwise disrupt the body's hormones. Some have been shown to act as hormone disrupters in wildlife and possibly in laboratory animals. Human health studies indicate that eating fish containing PCBs can lead to significant health consequences including:

- reproductive dysfunction;
- deficiencies in neurobehavioral and developmental behavior, especially in newborns and school-aged children;
- other systemic effects (e.g., liver disease, diabetes, effects on the thyroid and immune systems); and
- increased cancer risks (e.g., non-Hodgkin's lymphoma) (USEPA, 1999d).

Polycyclic aromatic hydrocarbons, PAHs, are the byproducts of oil burning. They are carcinogenic (cancer causing) and mutagenic (change cell growth). They are also produced by burning coal and wood. They enter estuaries from leaking gas storage tanks, road runoff, sewage plants, industrial and municipal discharges, oil spills, and bilge water discharges. Creosote applied to wharf pilings also contains PAHs.

Other Notable Toxins

In addition to the toxins discussed above, there are many others that enter estuaries and affect their wildlife. Some of these include:

Dioxin

Dioxin, a byproduct of bleaching paper with chlorine, is associated with birth defects in humans. Chlorine combines with lignins (natural binders of wood fiber) to produce dioxin.

Tributyltin (TBT)

TBT, an antifouling paint additive used on boats and in marinas, is a fat-loving compound (lipophilic) that accumulates in the tissue of animals, and amplifies in the food chain. Contributions of TBT arise almost exclusively from anti-fouling bottom paints that are applied to boat hulls to retard the growth of barnacles and other fouling organisms. The greatest release of trace metals occurs when the paint is fresh or after hull cleaning when new layers of paint are exposed. Over the last few years, increasing regulation and controls have attempted to reduce emissions from this source to estuary waters. For example, TBT can no longer be used on small craft, but is used on ocean-bound tankers. Nonetheless, while the use of TBT is restricted, it is still in use and accumulates in harbor sediments.

Household chemicals, paints, cleaning chemicals, etc.

There are tens of thousands of chemicals used in industrial processes and in our homes. Little is known about their effects on aquatic life, how concentrated they are in estuaries, how long they persist in aquatic environments, or their interaction with each other. ■

Some Toxins Are from Biological Processes

Excessive algae growth can result in brown and red tides and other harmful blooms. Harmful algal blooms excrete biotoxins that can be hazardous to shellfish, fish, and humans. See Chapter 19 for more information.

Sampling Considerations

Toxic metal and organic pollutants are found in low concentrations in water—on the order of parts-per-billion and parts-per-trillion levels. But concentrations in the sediment are higher and range in the parts-per-million and parts-per-billion levels. Because of these low levels, collecting water and sediment samples for toxin analysis involves a high degree of rigor and training to limit inadvertent contamination of the sample. Sources of contamination include the polyethylene bottle, as well as the handling of the bottle. **Unless there is a clear justification and rigorous oversight, volunteer monitoring programs are discouraged from collecting samples for toxin analysis**. However, it is important that volunteer programs understand the general process of sampling for toxins and testing their impact.

Testing for the presence of toxic substances (metals and toxic chemical compounds) in estuary water and sediment usually requires a laboratory with expensive equipment, such as a mass spectrometer, high performance liquid chromatography, or atomic absorption spectrophotometer. Some toxins are in minute quantities and require a concentration step, such as organic extractions, to be analyzed.

One method scientists use to analyze the effects of a toxic substance on living organisms is called a **bioassay**, or biological assay. A bioassay is a controlled experiment using a change in biological activity as a qualitative or quantitative means of analyzing a material response to a pollutant. Depending on the test, microorganisms, planktonic animals, or live fish can be used as test organisms.

Scientists also look for biochemical indicators of contaminants by studying animals called biomarkers. They look for DNA damage in blood cells and the presence of stress proteins, which are produced in response to a wide variety of contaminants, including trace metals and organic pollutants. Volunteers may be able to assist with collecting fish and invertebrates to be used in the chemical analysis of tissue, or under a very high degree of training assist with the collection of sediment and water samples to be tested for toxicity. In some cases, volunteers collect shellfish and send them to a laboratory for tissue analysis. See Chapter 19 for more information.

Volunteer water quality monitoring programs interested in monitoring for toxins are recommended to work with a local college or laboratory which has the necessary equipment and knowledge. Any such study should carefully follow established protocols for analysis and testing (see, for example, APHA, 1998).

Volunteers can also assist with a field survey to identify potential sources of toxins in an estuary. See Chapter 7 for more information on field observations.

It should be noted that conventional toxicity tests and chemical analyses are rarely sufficient to identify the cause or sources of toxicity. Multiple contaminants are usually present in a toxic sample, and many of the contaminants may be at elevated concentrations. There are other important factors that influence toxicity, such as sediment organic carbon content or the size of sand grains.

Field test kits are available for some of the heavy metals and other pollutants that can be used in preliminary measurements. For example, one kit measures copper in estuaries that may exist as a soluble salt or as suspended solids. Test kits are also available for zinc, chlorine, chromate, iron, chloride, silica, and cyanide. Field test kits vary greatly in their detectable range and cost between $15 and $450. ■

Atmospheric Deposition of Toxins

Pollutants released into the air can be introduced to the estuary through atmospheric deposition (photo by R. Ohrel).

Over the past 30 years, scientists have collected a large amount of convincing information demonstrating that air pollutants can be deposited on land and water—sometimes at great distances from their original sources—and can contribute to declining estuarine water quality. This is called **atmospheric deposition**. Pollutants released into the air are carried by wind patterns away from their place of origin. These pollutants come from manmade or natural sources of emissions. For example, up to 25% of the mercury emitted worldwide is released naturally as part of the global mercury cycle.

Presently, atmospheric deposition monitoring by volunteers is in its early stages. In the future, there may be a role for volunteers to monitor the amount of toxins that are deposited from the atmosphere into estuaries. See Chapter 10 for more information on atmospheric deposition. ■

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Atmospheric Deposition

National Estuary Program (NEP): http://www.epa.gov/owow/estuaries/airdep.htm

Unit Two
Physical Measures

Temperature • Salinity • Turbidity and Total Solids • Marine Debris

Photos (l to r): U.S. Environmental Protection Agency, R. Ohrel, S. Schultz, P. Bergstrom