

1. PUBLIC HEALTH STATEMENT

This public health statement tells you about fluorides, hydrogen fluoride, and fluorine and the effects of exposure presented in the toxicological profile. These profiles were specifically prepared by ATSDR for hazardous substances which are most commonly found at facilities on the CERCLA National Priorities List (Superfund sites) and are intended to describe the effects of exposure from chemicals at these sites.

The Environmental Protection Agency (EPA) identifies the most serious hazardous waste sites in the nation. These sites make up the National Priorities List (NPL) and are the sites targeted for long-term federal cleanup activities. Fluorides, hydrogen fluoride, and fluorine have been found in at least 188 of the 1,636 current or former NPL sites. However, the total number of NPL sites evaluated for these substances is not known. As more sites are evaluated, the sites at which fluorides, hydrogen fluoride, and fluorine is found may increase. This information is important because exposure to these substances may harm you and because these sites may be sources of exposure.

When a substance is released from a large area, such as an industrial plant, or from a container, such as a drum or bottle, it enters the environment. This release does not always lead to exposure. You are exposed to a substance only when you come in contact with it. You may be exposed by breathing, eating, or drinking the substance, or by skin contact.

If you are exposed to fluorides, hydrogen fluoride, and fluorine, many factors determine whether you'll be harmed. These factors include the dose (how much), the duration (how long), and how you come in contact with it/them. You must also consider the other chemicals you're exposed to and your age, sex, diet, family traits, lifestyle, and state of health.

1.1 WHAT ARE FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE?

Fluorides are properly defined as binary compounds or salts of fluorine and another element. Examples of fluorides include sodium fluoride and calcium fluoride. Both are white solids.

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Sodium fluoride readily dissolves in water, but calcium fluoride does not. Sodium fluoride is often added to drinking water supplies and to a variety of dental products, including toothpastes and mouth rinses to prevent dental cavities. Other fluoride compounds that are commonly used for water fluoridation are fluorosilicic acid and sodium fluorosilicate. Calcium fluoride is the compound in the common minerals fluorite and fluorspar. Fluorspar is the mineral from which hydrogen fluoride is produced. It is also used in the production of glass and enamel and in the steel industry. In this profile, we will often use the term “fluoride” to include substances that contain the element fluorine. The reason for this is that we generally measure the amount of fluorine in a substance rather than the amount of a particular fluorine compound.

Fluorine is a naturally occurring, widely distributed element and a member of the halogen family, which includes chlorine, bromine, and iodine. However, the elemental form of fluorine, a pale yellow-green, irritating gas with a sharp odor, is so chemically reactive that it rarely occurs naturally in the elemental state. Fluorine occurs in ionic forms, or combined with other chemicals in minerals like fluorspar, fluorapatite, and cryolite, and other compounds. (Ions are atoms, collections of atoms, or molecules containing a positive or negative electric charge.) Fluorine gas reacts with most organic and inorganic substances; with metals, it forms fluorides and with water, it forms hydrofluoric acid. Fluorine gas is primarily used to make certain chemical compounds, the most important of which is uranium hexafluoride, used in separating isotopes of uranium for use in nuclear reactors and nuclear weapons.

Hydrogen fluoride is a colorless, corrosive gas or liquid (it boils at 19.5 °C) that is made up of a hydrogen atom and a fluorine atom. It fumes strongly, readily dissolves in water, and both the liquid and vapor will cause severe burns upon contact. The dissolved form is called hydrofluoric acid. It is known for its ability to etch glass. Commercially, hydrogen fluoride is the most important fluorine compound. Its largest use is in the manufacture of fluorocarbons, which are used as refrigerants, solvents, and aerosols.

For more information on the chemical properties of fluorides, hydrogen fluoride, and fluorine, and their production and use, see Chapters 4 and 5.

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1.2 WHAT HAPPENS TO FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE WHEN THEY ENTER THE ENVIRONMENT?

Fluorides occur naturally in the earth's crust where they are found in rocks, coal, clay, and soil. They are released into the air in wind-blown soil. Hydrogen fluoride is released to the air from fluoride-containing substances, including coal, minerals, and clays, when they are heated to high temperatures. This may occur in coal-fired power plants; aluminum smelters; phosphate fertilizer plants; glass, brick, and tile works; and plastics factories. These facilities may also release fluorides attached to particles. The biggest natural source of hydrogen fluoride and other fluorides released to the air is volcanic eruptions.

Fluorine cannot be destroyed in the environment; it can only change its form. Fluorides released into the atmosphere from volcanoes, power plants, and other high temperature processes are usually hydrogen fluoride gas or attached to very small particles. Fluorides contained in wind-blown soil are generally found in larger particles. These particles settle to the ground or are washed out of the air by rain. Fluorides that are attached to very small particles may stay in the air for many days. Hydrogen fluoride gas will be absorbed by rain and into clouds and fog to form aqueous hydrofluoric acid, which will fall to the ground mainly in precipitation. The fluorides released into air will eventually fall on land or water.

In water, fluorides associate with various elements present in the water, mainly with aluminum in freshwater and calcium and magnesium in seawater, and settle into the sediment where they are strongly attached to sediment particles. When deposited on land, fluorides are strongly retained by soil, forming strong associations with soil components. Leaching removes only a small amount of fluorides from soils. Fluorides may be taken up from soil and accumulate in plants, or they may be deposited on the upper parts of the plants in dust. The amount of fluoride taken up by plants depends on the type of plant, the nature of the soil, and the amount and form of fluoride in the soil. Tea plants are known to accumulate fluoride in their leaves. Animals that eat fluoride-containing plants may accumulate fluoride. However, the fluoride accumulates primarily in the bones or shell rather than in edible meat.

For more information about what happens to fluorides in the environment, see Chapter 6.

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1.3 HOW MIGHT I BE EXPOSED TO FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE?

Fluoride is a natural component of the earth's crust and soil. Small amounts of fluorides are present in water, air, plants, and animals. You may be exposed to small amounts of fluoride by breathing air, drinking water, and eating food. In particular, fluorides are frequently added to drinking water supplies at approximately 1 part of fluoride per million parts of water (ppm) and to toothpaste and mouth rinses to prevent dental decay. Analytical methods used by scientists to determine the levels of fluoride in the environment generally do not determine the specific form of fluoride present. Therefore, we do not always know the form of fluoride that a person may be exposed to. Similarly, we do not know what forms of fluoride are present at hazardous waste sites. Some forms of fluoride may be insoluble or so tightly attached to particles or embedded in minerals that they are not taken up by plants or animals.

Fluorides are normally found in very small amounts in the air. Levels measured in areas around cities are usually less than 1 microgram (one millionth of a gram) of fluoride per cubic meter ($\mu\text{g}/\text{m}^3$) of air. Rural areas have even lower levels. The amount of fluoride that you breathe in a day is much less than what you consume in food and water. You may breathe in higher levels of fluoride in areas near coal-fired power plants or fluoride-related industries (e.g., aluminum smelters, phosphorus fertilizer plants) or near hazardous waste sites.

Levels of fluorides in surface water average about 0.2 parts of fluoride per million parts of water (ppm). Levels of fluorides in well water generally range from 0.02 to 1.5 ppm, but often exceed 1.5 ppm in parts of the southwest United States. Many communities fluoridate their water supplies; the recommended level of fluoride is around 1 ppm. In the United States, approximately 15,000 water systems serving about 162 million people are fluoridated in the optimal range of 0.7–1.2 ppm, either occurring naturally or through adjustment. Persons living in non-fluoridated areas may receive water exposure through beverages and foods processed in fluoridated areas. You will be exposed to fluorides in the water that you drink or in beverages prepared with fluoridated water.

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The concentration of fluorides in soils is usually between 200 and 300 ppm. However, levels may be higher in areas containing fluoride-containing mineral deposits. Higher levels may also occur where phosphate fertilizers are used, where coal-fired power plants or fluoride-releasing industries are located, or in the vicinity of hazardous waste sites. You may be exposed to fluorides through dermal contact with these soils.

You may also be exposed to fluorides in your diet. While food generally contains low levels of fluoride, food grown in areas where soils have high amounts of fluorides or where phosphate fertilizers are used may have higher levels of fluorides. Tea and some seafoods have been found to have high levels of fluorides. The average daily fluoride intake by adults from food and water is estimated to be 1 milligram (mg) if you live in a community with <0.7 ppm in your water, and about 2.7 mg if you have fluoridated water. You can contact your local water system to determine the level of fluoride in your drinking water or refer to the annual Consumer Confidence Report furnished by your water system operators. You may also be exposed to fluoride in dental products, such as toothpastes, fluoride gels, and fluoride rinses. Dental products used in the home such as toothpastes, rinses, and topically applied gels contain high concentrations of fluoride (range 230–12,300 ppm) and are not intended to be ingested. The most commonly used dental products, toothpastes, contain 900–1,100 ppm fluoride (ca. 0.10%), most often as sodium fluoride. If you swallow these products, you will be exposed to higher levels of fluoride. Swallowing toothpaste can account for a large percentage of the fluoride to which a child <8 years of age might be exposed. The Food and Drug Administration requires that toothpaste tubes be labeled with instructions to minimize ingestion of fluoride by children including the use of a “pea-sized” amount of paste and parental supervision of brushing.

You may also be exposed to higher levels of fluoride if you work in industries where fluoride-containing substances are used, most notably in the electronics industry where hydrogen fluoride may be used to etch glass in TV picture tubes or to clean silicon chips and in aluminum and phosphate fertilizer plants. Exposure will primarily result from breathing in hydrogen fluoride or fluoride-containing dust. Exposure will be reduced if exhaust systems or protective masks are used in the workplace.

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For more information on how you can be exposed to fluorides, hydrogen fluoride, or fluorine, see Chapter 6.

1.4 HOW CAN FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE ENTER AND LEAVE MY BODY?

Generally, most of the fluoride in food or water that you swallow enters your bloodstream quickly through the digestive tract. However, the amount that enters your bloodstream also depends on factors such as how much of the fluoride you swallowed, how well the fluoride dissolves in water, whether you ate or drank recently, and what you ate or drank. Factors such as age and health status affect what happens to the fluoride ion once it is in your body. After entering your body, about half of the fluoride leaves the body quickly in urine, usually within 24 hours unless large amounts (20 mg or more, which is the amount in 20 or more liters of optimally fluoridated water) are ingested. Most of the fluoride ion that stays in your body is stored in your bones and teeth.

When you breathe in air containing hydrogen fluoride or fluoride dusts, it enters your bloodstream quickly through your lungs. When hydrofluoric acid touches skin, most of it can quickly pass through the skin into the blood. How much of it enters your bloodstream depends on how concentrated the hydrofluoric acid is and how long it stays on your skin. Almost all of the fluoride that enters the body in these ways is quickly removed from the body in the urine, but some is stored in your bones and teeth.

When you breathe in air containing fluorine, fluoride can enter your bloodstream through your lungs, but it is not known how quickly this happens. Much of the fluoride leaves your body in urine, but some is stored in your bones and teeth. Exposure to fluorine gas is uncommon, except in industrial settings.

For more information on how fluorides, hydrogen fluoride, and fluorine enter and leave your body, see Chapter 3.

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1.5 HOW CAN FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE AFFECT MY HEALTH?

To protect the public from the harmful effects of toxic chemicals and to find ways to treat people who have been harmed, scientists use many tests.

One way to see if a chemical will hurt people is to learn how the chemical is absorbed, used, and released by the body; for some chemicals, animal testing may be necessary. Animal testing may also be used to identify health effects such as cancer or birth defects. Without laboratory animals, scientists would lose a basic method to get information needed to make wise decisions to protect public health. Scientists have the responsibility to treat research animals with care and compassion. Laws today protect the welfare of research animals, and scientists must comply with strict animal care guidelines and must be recertified regularly with training in updated and new guidelines.

Fluorides. Several medicines that contain fluoride are used for treating skin diseases (e.g., flucytosine, an antifungal) and some cancers (e.g., fluorouracil, an antimetabolite).

Small amounts of fluoride are added to toothpaste or drinking water to help prevent dental decay. However, exposure to higher levels of fluoride may harm your health. Skeletal fluorosis can be caused by eating, drinking, or breathing very large amounts of fluorides. This disease only occurs after long-term exposures and can cause denser bones, joint pain, and a limited range of joint movement. In the most severe cases, the spine is completely rigid. Skeletal fluorosis is extremely rare in the United States; it has occurred in some people consuming greater than 30 times the amount of fluoride typically found in fluoridated water. It is more common in places where people do not get proper nutrition. At fluoride levels 5 times greater than levels typically found in fluoridated water, fluoride can result in denser bones. However, these bones are often more brittle or fragile than normal bone and there is an increased risk of older men and women breaking a bone. Some studies have also found a higher risk of bone fractures in older men and women at fluoride levels typically found in fluoridated water. However, other studies have not found an effect at this fluoride dose. If you eat large amounts of sodium fluoride at one

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time, it can cause stomachaches, vomiting, and diarrhea. Extremely large amounts can cause death by affecting your heart.

We do not know if eating, drinking, or breathing fluoride can cause reproductive effects in humans. Reproductive effects, such as decreased fertility and sperm and testes damage, have been seen in laboratory animals at extremely high doses (more than 100 times higher than levels found in fluoridated water). However, other studies have not found any reproductive effects in laboratory animals.

A number of studies have been done to assess whether there is an association between fluoride and cancer in people who live in areas with fluoridated water or naturally high levels of fluoride in drinking water, or people who work in jobs where they may be exposed to fluorides. Most studies have not found any association between fluoride and cancer in people. A study in rats and mice found that a small number of male rats developed bone cancer after drinking water with high levels of fluoride in it throughout their lives. This was considered equivocal evidence that fluoride causes cancer in male rats. Fluoride did not cause cancer in mice or female rats. Another study found no evidence that even higher doses of fluoride caused cancer in rats. Both animal studies had problems that limited their usefulness in showing whether fluoride can cause cancer in humans. The International Agency for Research on Cancer (IARC) has determined that the carcinogenicity of fluoride to humans is not classifiable.

Hydrogen Fluoride. Hydrogen fluoride is also a very irritating gas. Hydrogen fluoride is not as dangerous as fluorine, but large amounts of it can also cause death. People breathing hydrogen fluoride have complained of eye, nose, and skin irritation. Breathing in a large amount of hydrogen fluoride with air can also harm the lungs and heart. Kidney and testes damage have been observed in animals breathing hydrogen fluoride.

Hydrofluoric acid is dangerous to humans because it can burn the eyes and skin. The initial exposure to hydrofluoric acid may not look like a typical acid burn. Skin may only appear red and may not be painful at first. Damage to skin may happen over several hours or days, and deep, painful wounds may develop. When not treated properly, serious skin damage and tissue

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loss can occur. In the worst cases, getting a large amount of hydrofluoric acid on your skin can lead to death caused by the fluoride affecting your lungs or heart.

Fluorine. Fluorine gas is very irritating and very dangerous to the eyes, skin, and lungs. Fluorine gas at low concentrations makes your eyes and nose hurt. At higher concentrations, it becomes hard to breathe. Exposure to high concentrations of fluorine can cause death due to lung damage.

For more information on the health effects of fluorides, hydrogen fluoride, and fluorine, see Chapter 3. For more information on fluoride and dental caries, see Appendix D.

1.6 HOW CAN FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE AFFECT CHILDREN?

This section discusses potential health effects from exposures during the period from conception to maturity at 18 years of age in humans.

When used appropriately, fluoride is effective in preventing and controlling dental caries. Drinking or eating excessive fluoride during the time teeth are being formed can cause visible changes in teeth. The condition is called dental fluorosis. The changes increase in severity with increasing levels of fluoride. Dental fluorosis develops only while the teeth are forming in the jaw and before they erupt into the mouth (age <8 years). After the teeth have developed and erupted, they cannot become fluorosed. Most enamel fluorosis seen today is of the mildest form, in which there are a few almost invisible white spots on the teeth. In moderate cases, there are large white spots on the teeth (mottled teeth), and some brown spots. In severe cases, the teeth are pitted and are fragile, and sometimes the teeth can break. The appearance of affected teeth is not identical for all children exposed to the same level of fluoride in the drinking water. Exposure to fluoride from other sources, such as fluoride tablets or rinses, may account for these differences. In general, some children who drink water with 1 ppm fluoride may get a few small spots or slight discolorations on their teeth. Some children who drink water with 4 ppm fluoride in it for long periods before their permanent teeth are in place may develop a more severe form of dental fluorosis.

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Fluoride can cross the placenta from the mother's blood to the developing fetus. Only a very small portion of fluoride ingested by women is transferred to a child through breast milk.

Several human studies found an increase in birth defects or lower IQ scores in children living in areas with very high levels of fluoride in the drinking water. Those studies did not adequately access other factors that could have contributed to the effects. Another study did not find birth defects in children living in areas with low levels of fluoride. Birth defects have not been found in most studies of laboratory animals.

1.7 HOW CAN FAMILIES REDUCE THE RISK OF EXPOSURE TO FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE?

If your doctor finds that you have been exposed to significant amounts of fluorides, hydrogen fluoride, and fluorine, ask whether your children might also be exposed. Your doctor might need to ask your state health department to investigate.

It is unlikely that the general population would be exposed to fluorine gas or hydrogen fluoride. Because fluorides are found naturally in the environment, we cannot avoid being exposed to them. Some areas of the United States, such as the Southwest, naturally have high levels of fluorides in well water. There has been an increase in the cosmetic condition of tooth enamel fluorosis in children in both fluoridated and non-fluoridated communities. Ask your health department whether your area has naturally high levels of fluorides in the drinking water. If you live in such an area, you should use bottled drinking water and consult your dentist for guidance on the need for appropriate alternative fluoride supplements.

These areas may also contain high levels of fluorides in soil. A few hazardous waste sites may contain high levels of fluorides in soil. By limiting your contact with such soil (for example, reducing recreational activities that raise dust), you would reduce your family's exposure to fluoride. Some children eat a lot of dirt. You should prevent your children from eating dirt. You should discourage your children from putting their hands or objects in their mouths or engaging in other hand-to-mouth activity. Make sure they wash their hands frequently and always before eating.

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If you work in a phosphate fertilizer plant or other industry that uses minerals high in fluorides, it is sometimes possible to carry fluorides home from work on your clothing, skin, hair, tools, or other objects removed from the workplace. You may contaminate your car, home, or other locations outside work where children might be exposed to fluoride-containing dust. Your occupational health and safety officer at work can and should tell you whether the chemicals that you work with are likely to be carried home on your clothes, body, or tools as well as whether you should be showering and changing clothes before you leave work, storing your street clothes in a separate area of the workplace, or laundering your work clothes at home separately from other clothes.

Children may be exposed to high levels of fluorides if they swallow dental products containing fluoridated toothpaste, gels, or rinses. Swallowing toothpaste can account for a large percentage of the fluoride to which a small child might be exposed. You should teach your children not to swallow these products. For children under age 8, parents should supervise brushing and place, at most, a small pea size dab of toothpaste on the brush.

1.8 IS THERE A MEDICAL TEST TO DETERMINE WHETHER I HAVE BEEN EXPOSED TO FLUORIDES, HYDROGEN FLUORIDE, AND FLUORINE?

Urine and blood samples can be analyzed to find out if you have been exposed to fluorides. The fluoride level in the sample is compared with the level of fluoride usually found in urine or blood. This will show if a person has been exposed recently to higher-than-normal levels of fluorides. However, this test cannot be used to predict any specific health effects that may occur after fluoride exposure. The test must be performed soon after exposure because fluoride that is not stored in the bones leaves the body within a few days. This test can be done at most laboratories that test for chemical exposure. Bone sampling can be done in special cases to measure long-term exposure to fluorides. Because fluorides, hydrogen fluoride, and fluorine all enter the body as fluoride, these tests cannot distinguish among exposure to these different chemicals.

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For more information on medical tests to determine exposure to fluorides, hydrogen fluoride, and fluorine, see Chapters 3 and 6.

1.9 WHAT RECOMMENDATIONS HAS THE FEDERAL GOVERNMENT MADE TO PROTECT HUMAN HEALTH?

The federal government develops regulations and recommendations to protect public health.

Regulations can be enforced by law. Federal agencies that develop regulations for toxic substances include the Environmental Protection Agency (EPA), the Occupational Safety and Health Administration (OSHA), and the Food and Drug Administration (FDA).

Recommendations provide valuable guidelines to protect public health but cannot be enforced by law. Federal organizations that develop recommendations for toxic substances include the Agency for Toxic Substances and Disease Registry (ATSDR) and the National Institute for Occupational Safety and Health (NIOSH).

Regulations and recommendations can be expressed in not-to-exceed levels in air, water, soil, or food that are usually based on levels that affect animals; then they are adjusted to help protect people. Sometimes these not-to-exceed levels differ among federal organizations because of different exposure times (an 8-hour workday or a 24-hour day), the use of different animal studies, or other factors.

Recommendations and regulations are also periodically updated as more information becomes available. For the most current information, check with the federal agency or organization that provides it. Some regulations and recommendations for fluorides, hydrogen fluoride, and fluorine include the following:

Sodium fluoride, hydrogen fluoride, and fluorine have been named hazardous substances by the EPA. The federal government has set regulatory standards and guidelines to protect workers from the possible health effects of fluorides, hydrogen fluoride, and fluorine in air. OSHA has set a legally enforceable limit of 0.2 milligrams per cubic meter (mg/m^3) for fluorine, $2.0 \text{ mg}/\text{m}^3$ for hydrogen fluoride, and $2.5 \text{ mg}/\text{m}^3$ for fluoride in workroom air to protect workers during an 8-hour shift over a 40-hour work week. NIOSH recommends air levels of $0.2 \text{ mg}/\text{m}^3$ for

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fluorine, 2.5 mg/m³ for hydrogen fluoride, and 2.5 mg/m³ for sodium fluoride in workroom air to protect workers during an 8-hour shift over a 40-hour work week.

The federal government has also set regulatory standards and guidelines to protect the public from the possible health effects of fluoride in drinking water. EPA determined that the maximum amount of fluoride allowed in drinking water is 4.0 milligrams per liter (mg/L).

For the prevention of dental decay, the Public Health Service (PHS) has, since 1962, recommended that public water supplies contain fluoride at concentrations between 0.7 and 1.2 mg/L. PHS scientists representing the National Institutes of Health, the Centers for Disease Control and Prevention, the FDA, ATSDR, and other government agencies conducted an extensive examination of the worldwide biomedical literature on the public health risks and benefits of fluoride in 1991. The PHS report stated that fluoride in the drinking water substantially reduces tooth decay.

For more information on recommendations regarding exposure to fluorides, hydrogen fluoride, and fluorine, see Chapter 8.

1.10 WHERE CAN I GET MORE INFORMATION?

If you have any more questions or concerns, please contact your community or state health or environmental quality department or

Agency for Toxic Substances and Disease Registry
Division of Toxicology
1600 Clifton Road NE
Mailstop E-29
Atlanta, GA 30333

* Information line and technical assistance

Phone: 1-888-42-ATSDR (1-888-422-8737)
Fax: 1-404-498-0057

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ATSDR can also tell you the location of occupational and environmental health clinics. These clinics specialize in recognizing, evaluating, and treating illnesses resulting from exposure to hazardous substances.

* To order toxicological profiles, contact

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Phone: (800) 553-6847 or (703) 605-6000
Web site: <http://www.ntis.gov/>