

INDUSTRIAL CHEMICALS

Junfeng Niu and Gang Yu

Department of Environmental Sciences and Engineering, Tsinghua University, Beijing, P. R. China

Keywords: Industrial chemicals, inorganic chemicals, organic chemicals, aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing compounds, nitrogen-containing compounds, organohalide compounds, organosulfur compounds, surfactants, metals, organometallic compounds, metalloids, radionuclides

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Summary

With the development of human society and industry, the usage and kinds of industrial chemicals have increased greatly over the past few decades. There is no doubt that these chemicals are indispensable to industrial production and greatly facilitate our daily life. Unfortunately, however, these chemicals are introduced into the environment in large quantities during manufacture, use and ultimate disposal. They are widely distributed in the air, soils, and water and cause great harm to our surroundings and human health.

Some industrial chemicals, particularly persistent organic pollutants, which occur in the environment are both highly toxic and difficult to remove. Moreover, industrial chemicals also include endocrine disrupting chemicals that cause adverse health effects in an intact organism, or its progeny, as a result of changes in endocrine function. All of these compounds can cause adverse effects on human health and damage ecosystems. As these chemicals in the environment cause great potential risk, great attention should be paid to recognizing them.

1. Introduction

Industrial chemicals are used widely in all kinds of industries. Although the use of these chemicals has played a major role in the development of industry and society in the past few decades, most current pollution problems are becoming more serious due to the ubiquitous industrial chemicals in the environment.

It is estimated that between 60 000 and 90 000 chemicals are in current commercial use. Industrial chemicals are released by volatilization, leakage or leaching, either during a product's lifetime or after ultimate disposal. Although not all of these constitute potential toxicity hazards, many will cause environmental pollution as a result of leakage during storage, from use in the environment or from their disposal—either directly, or of wastes containing them. Apart from industrial uses, a large number of chemicals are used in domestic products and so their use and disposal is less controlled than that of industrial chemicals. For example, industrial chemicals such as food additives, surfactants and medicines are used directly in human life.

Although industrial chemicals play an important role in improving our health and standard of living, they have caused significant problems to the no-linger pristine environment. These anthropogenic contaminants include inorganic compounds, organic substances, heavy metals and radionuclides. A health problem is posed whenever people become exposed to them, even at low concentrations. This chapter describes the origin and characteristics of industrial chemicals, their effect on the environment and on the health of humans or other living organisms.

2. Inorganic Chemicals

2.1. Ozone

Triatomic oxygen, O₃, called ozone, and monatomic oxygen, O, occur in small amounts in the upper atmosphere. Ozone shields the earth from excessive ultraviolet radiation, and there is accumulating evidence that it is being depleted by reaction with synthetic compounds produced on earth, particularly chlorine from the breakdown of chlorofluorocarbons (CFCs).

Ozone is a very powerful oxidizing gas and is used in water treatment for the destruction of organic compounds and for disinfection of harmful microorganisms prior to discharge of sewage to recreational waters or for ensuring potability of supply water. The use of ozone to disinfect water dates to 1893 in the Netherlands and 1901 in Germany. Ozonation is now used in about 1000 communities in Europe. Ozone is formed during naturally occurring electrical storms or from electrical discharges. Ozone has a distinctive odor, and is toxic even at low concentrations. It is formed at low levels of the atmosphere by the action of sunlight on oxygen and waste gases from vehicle exhausts, producing so-called photochemical smog. This can cause extreme discomfort to city dwellers, and people with asthma and other respiratory conditions are particularly vulnerable. Ozone can lead to visibility impairment; breathing and respiratory symptoms such as shortness of breath, coughing and wheezing; irritation of lungs and a lowering resistance to respiratory infection such as influenza; visual impairment; reduced work capacity, mental function and poor learning ability.

2.2. Carbon Monoxide

Carbon monoxide (CO), formed by incomplete combustion (e.g. forest fires and human activities) and as an intermediate compound in the tropospheric oxidation of substances such as methane, is a common cause of accidental poisonings. At CO levels in air of 10 parts per million (ppm) impairment of judgment and visual perception occur; exposure to 100 ppm causes dizziness, headache, and weariness; loss of consciousness occurs at 250 ppm; and inhalation of 1000 ppm results in rapid death. Chronic long-term exposures to low levels of carbon monoxide are suspected of causing disorders of the respiratory system and the heart.

After entering the bloodstream through the lungs, carbon monoxide reacts with hemoglobin (Hb) to convert oxyhemoglobin (O₂Hb) to carboxyhemoglobin (COHb). In this case, hemoglobin is the receptor acted on by the carbon monoxide toxicant. Carboxyhemoglobin is much more stable than oxyhemoglobin so that its formation prevents hemoglobin from carrying oxygen to body tissues.

2.3. Halogens and Halogen Compounds

Fluorine gas is the most reactive of the elements, and is a very strong oxidizing agent. Fluorides are used in the metal industry for plating, casting and welding, and in the manufacture of aluminum. They are also used in glass and ceramics manufacture, and for making phosphate fertilizers, insecticides and herbicides. Most fluorides associated with monovalent cations are water soluble, such as NaF and KF, whilst those formed with divalent cations are generally insoluble (CaF₂, PbF₂). The fluoride ion forms many stable complexes with aluminum and iron.

Sodium fluoride is used in the treatment of dental caries, and is added to water supplies in some countries to reduce tooth decay in children. Fluoride is discharged into the atmosphere from various manufacturing processes, mainly from aluminum production but also from steelworks, phosphate fertilizer manufacture (these contain 0.8 to 1.5% F) and from the burning of coal. Livestock are especially susceptible to poisoning from fluoride fallout on grazing land; severely afflicted animals become lame and even die. Industrial pollution has been a common source of toxic levels of fluoride.

Chlorine gas is used extensively in the chemical industry for making a variety of products. It is also used in the pulp and paper industry for bleaching fibers. Its ability to destroy pathogenic organisms is exploited in the water industry where chlorine is used to disinfect supply water and in some places to deactivate disease-producing organisms in sewage treatment plant effluents. Chlorine, present in water as hypochlorous acid and chloramines, is toxic to aquatic life. It is used to clear pipelines of adhering organisms such as freshwater mussels, reservoirs of excessive algae and cooling towers of bacterial slimes.

Bromine may be substituted for chlorine in many inorganic and organic compounds. It is always present as a contaminant when chlorine is produced by electrolysis. Thus when chlorine is used to disinfect water, if there are humic substance present in the water, then organobromine as well as organochlorine compounds are formed, e.g. trihalomethanes, which are undesirable in drinking water. Bromine compounds are generally readily soluble in water. Bromine gas has a pungent odor and is irritating to the skin, eyes and lungs. The bromides of sodium, potassium, calcium and strontium have been used in medicine because of their sedative properties.

The principal use of bromide compounds is in the manufacture of photographic materials. They also find use in dyes, medicines and insecticides. Organobromine compounds are used in the chemical industry. For example, bromine, as dibromoethane ($C_2H_4Br_2$), is added to high octane gasoline and, consequently, combustion gases from petrol engines are a source of bromine in the atmosphere in the form of lead bromide and lead bromochloride. Bromine is also contributed to the atmosphere in the form of lead bromide from sea spray because of its greater concentration in sea water. Thus, in coastal areas, the bromine content of the air is greater than in inland areas except in cities where there is a significant contribution from vehicles.

The industrial usage of iodine is small. It is used in medicine, veterinary products, dye manufacture, in photographic materials and as a catalyst. Occasionally it is used as a disinfectant for swimming pools. Iodine solution (also known as Lugol's solution, containing 5% iodine and 10% potassium iodide) contains free iodine as the triiodide ion I_3^- , and is an effective antiseptic for wounds. Iodine compounds at high concentrations are toxic to mammals, but they are rapidly excreted, and so intoxication is rare.

Hydrogen halides (general formula HX, where X is F, Cl, Br, or I) are relatively toxic gases. The most widely used of these gases are HF and HCl. Hydrogen fluoride, (HF, mp $-83.1\text{ }^\circ\text{C}$, bp $19.5\text{ }^\circ\text{C}$) is used as a clear, colorless liquid or gas or as a 30 - 60% aqueous solution of hydrofluoric acid, both referred to here as HF. Both are extreme irritants to any of the body that they contact, causing ulcers in affected areas of the upper respiratory

tract. Lesions caused by contact with HF heal poorly, and tend to develop gangrene. Gaseous hydrogen chloride and its aqueous solution, called hydrochloric acid, both denoted as HCl, are much less toxic than HF. Hydrochloric acid is a natural physiological fluid present as a dilute solution in the stomachs of humans and other animals. However, inhalation of HCl vapor can cause spasms of the larynx as well as pulmonary edema and even death at high levels. The high affinity of hydrogen chloride vapor for water tends to dehydrate eye and respiratory tract tissue.

Interhalogen compounds, including ClF, BrCl, and BrF₃, are extremely reactive and are potent oxidants. They react with water to produce hydrohalic acid solutions (HF, HCl) and nascent oxygen. Too reactive to enter biological systems in their original chemical state, interhalogen compounds tend to be powerful corrosive irritants that acidify, oxidize, and dehydrate tissue, much like those of the elemental forms of the elements from which they are composed. Because of these effects, skin, eyes, and mucous membranes of the mouth, throat, and pulmonary systems are especially susceptible to attack.

Major halogen oxides, including fluorine monoxide (OF₂), chlorine monoxide (Cl₂O), chlorine dioxide (ClO₂), chlorine heptoxide (Cl₂O₇), and bromine monoxide (Br₂O), tend to be unstable, highly reactive, and toxic compounds that pose hazards similar to those of the interhalogen compounds discussed above. Chlorine dioxide, the most commonly used halogen oxide, is employed for odor control and bleaching wood pulp. As a substitute for chlorine in water disinfection, it produces fewer undesirable chemical by-products, particularly trihalomethanes.

The most important of the oxyacids and their salts formed by halogens are hypochlorous acid, HClO, and hypochlorites, such as NaClO, used for bleaching and disinfection. The hypochlorites irritate eye, skin, and mucous membrane tissue because they react to produce active oxygen and acid.

2.4. Cyanides

Cyanides are a group of organic and inorganic compounds that contain the group CN⁻. The organic compounds are also known as nitriles. The inorganic cyanides are the salts of hydrocyanic acid (prussic acid) HCN, a weak acid ($K_a=6.17 \times 10^{-10}$) which dissolves readily in water.

Cyanide is widely used in gold mining and refining, in steel production, electroplating and in pharmaceutical formulations. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Chloride is sometimes used to treat cyanide solutions, as the ultimate products of the reaction are carbon dioxide, Cl⁻ ion, and ammonia. However, if the reaction is incomplete, cyanogen chloride (CNCl) is formed, which is a poisonous gas and gives rise to lachrymatory symptoms.

Both hydrogen cyanide (HCN) and cyanide salts (which contain the CN⁻ ion) are rapidly acting poisons; a dose of only 60 to 90 mg is sufficient to kill a human. Metabolically, cyanide bonds to iron(III) in iron-containing ferricytochrome oxidase enzyme, preventing its reduction to iron(II) in the oxidative phosphorylation process by which the body utilizes O₂. This prevents utilization of oxygen in cells, so that metabolic processes cease.

2.5. Asbestos

Asbestos is the common name given to a group of fibrous silicate minerals belonging to the serpentine and amphibole mineral groups. It is composed of silicon, oxygen, hydrogen and metal cations from the 'group' sodium, magnesium, calcium and iron; typically those of the serpentine group, for which the approximate chemical formula is $Mg_3P(Si_2O_5)(OH)_4$. Its general nature is of thin fibres of material up to a thickness of 0.1 μm . Asbestos has been widely used in structural materials, fireproofing materials, brake linings, insulation, and pipe manufacture. It is also used in the chemical industry because of its resistance to acid.

Inhalation of asbestos may cause asbestosis, mesothelioma, and bronchogenic carcinoma. In developed nations, the use of asbestos products is either banned or very restricted because of the harmful health effects. However, the use of asbestos in developing country is increasing.

2.6. Nitrogen Oxides

Nitrogen oxides are released into the atmosphere from combustion processes, particularly by power stations and vehicles. These compounds are formed as an incidental product of combustion, by the oxidation of atmospheric nitrogen gas. They are usually referred to collectively as NO_x . In the atmosphere, the nitrogen oxides combine with water vapor and fall as acid rain. It is estimated that one third of the acidity in precipitation is contributed by nitric acid, with the remainder as sulfuric acid. With the increase in vehicles on the world's highways, there is a steady rise in the amount of NO_x in the atmosphere and a consequent increase in the nitric acid in precipitation.

The two most common toxic oxides of nitrogen are NO and NO_2 , of which the latter is regarded as the more toxic. Nitrogen dioxide causes severe irritation of the innermost parts of the lungs resulting in pulmonary edema. In cases of severe exposures, fatal bronchiolitis fibrosa obliterans may develop approximately three weeks after exposure to NO_2 . Fatalities may result from even brief periods of inhalation of air containing 200-700 ppm of NO_2 . Biochemically, NO_2 disrupts lactic dehydrogenase and some other enzyme systems, possibly acting much like ozone. Free radicals, particularly HO, are formed in the body by the action of nitrogen dioxide and the compound probably causes lipid peroxidation in which the C=C double bonds in unsaturated body lipids are attacked by free radicals and undergo chain reactions in the presence of O_2 , resulting in their oxidative destruction.

Nitrous oxide, N_2O is used as an oxidant gas and in dental surgery as a general anesthetic. This gas was once known as "laughing gas," and was used in the late 1800s as a "recreational gas" at parties held by some of our not-so-staid Victorian ancestors. Nitrous oxide is a central nervous system depressant and can act as an asphyxiant.

2.7. Inorganic Silicon Compounds

Silica (SiO_2 , quartz) occurs in a variety of types of rocks such as sand, sandstone, and diatomaceous earth. Silicosis resulting from human exposure to silica dust from

construction materials, sandblasting, and other sources has been a common occupational disease. A type of pulmonary fibrosis that causes lung nodules and makes victims more susceptible to pneumonia and other lung diseases, silicosis is one of the most common disabling conditions resulting from industrial exposure to hazardous substances. It can cause death from insufficient oxygen, or from heart failure in severe cases.

Silicon tetrachloride, SiCl_4 , is the only industrially significant compound of the silicon tetrahalides, a group of compounds with the general formula SiX_4 , where X is a halogen. The two commercially produced silicon halohydrides are dichlorosilane (SiH_2Cl_2) and trichlorosilane, (SiHCl_3). These compounds are used as intermediates in the synthesis of organosilicon compounds and in the production of high-purity silicon for semiconductors. Silicon tetrachloride and trichlorosilane are fuming liquids which react with water to give off HCl vapor, have suffocating odors and are irritants to eye, nasal, and lung tissue.

2.8. Inorganic Phosphorus Compounds

The use of phosphorus includes inorganic and organic chemicals, manufacture of soaps and detergents, pesticides, alloys, animal feed supplements, catalysts, lubricants and corrosion inhibitors. Phosphates and metaphosphates are used in water treatment to prevent the formation of scale in boiler waters. For example, sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) is adsorbed on the surface of calcite and prevents it from being precipitated. Phosphates are used extensively in the production of washing powders, particularly sodium ortho-, pyro- and tripolyphosphates. They stabilize the particles of dirt and complex the hard water ions Ca^{2+} and Mg^{2+} whose presence otherwise reduces the efficiency of the surface active agents. Some washing powders contain 15 - 25% by weight of phosphates, but there is a trend to reduce the amount or to replace it with other sequestering chemicals such as nitrilotriacetic acid or zeolites.

Phosphine (PH_3), a colorless gas that undergoes autoignition at $100\text{ }^\circ\text{C}$, is a potential hazard in industrial processes and in the laboratory. Symptoms of poisoning from potentially fatal phosphine gas include pulmonary tract irritation, depression of the central nervous system, fatigue, vomiting, and difficult, painful breathing.

Tetraphosphorus decoxide, P_4O_{10} , is produced as a fluffy white powder from the combustion of elemental phosphorus and reacts with water from air to form syrupy orthophosphoric acid. Because of the formation of acid by this reaction and its dehydrating action, P_4O_{10} is a corrosive irritant to skin, eyes and mucous membranes.

The most important of the phosphorus halides is phosphorus pentachloride which is used as a catalyst in organic synthesis, as a chlorinating agent, and as a raw material to make phosphorus oxychloride (POCl_3). They react violently with water to produce the corresponding hydrogen halides and oxo-phosphorus acids. The phosphorus halides are strong irritants to eyes, skin, and mucous membranes.

2.9. Inorganic Sulfur Compounds

Sulfur is one of the most reactive of the elements. In its different forms it is used in many ways, such as for the vulcanization of rubber, the manufacture of gunpowder, for

bleaching fruit, making matches, in the pulp and paper industry, in the manufacture of fertilizer and, as gypsum, for making plasterboard. The largest source of sulfur in the atmosphere is from the combustion of fossil fuels. This represents about 85% of the total sulfur input, 95% of the emitted sulfur is in the form of SO₂, whilst the remainder consists of H₂S, SF₆, and mercaptans. The natural sources of atmospheric sulfur are from volcanoes and from low molecular weight volatile sulfur compounds emitted by marine plankton. Sulfides may be found in reduced wastewater or those with a high sulfur content such as from tanneries, paper mills, oil refineries, chemical plants and coal gas production. Of particular importance to workers in the municipal wastewater industry is the production of hydrogen sulfide in the sewerage system. The H₂S gas passes into the air space above the sewage in the pipes and can reach toxic levels for sewerage workers.

A colorless gas with a foul, rotten-egg odor, hydrogen sulfide is very toxic. In some cases inhalation of H₂S kills faster than even hydrogen cyanide; rapid death ensues from exposure to air containing more than about 1.0×10⁻³ kg/kg H₂S due to asphyxiation from respiratory system paralysis. Lower doses cause symptoms that include headache, dizziness, and excitement due to damage to the central nervous system. General debility is one of the numerous effects of chronic H₂S poisoning.

Sulfur dioxide, SO₂, dissolves in water, to produce sulfurous acid (H₂SO₃), hydrogen sulfite ion (HSO₃⁻) and sulfite ion (SO₃²⁻). Because of its water solubility, sulfur dioxide is largely removed in the upper respiratory tract. It is an irritant to the eyes, skin, mucous membranes, and respiratory tract. Some individuals are hypersensitive to sodium sulfite (Na₂SO₃), which has been used as a chemical food preservative. Because of threats to hypersensitive individuals, these uses were severely restricted in USA in the early 1990s. Sulfuric acid (H₂SO₄) is a severely corrosive poison and dehydrating agent in the concentrated liquid form. It readily penetrates skin to reach subcutaneous tissue necrosis with effects resembling those of severe thermal burns. Sulfuric acid fumes and mists irritate eye and respiratory tract tissue, and industrial exposure has even caused tooth erosion in workers.

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Biographical Sketches

Dr. Gang Yu is a professor and the Deputy Head, Department of Environmental Science and Engineering, Tsinghua University, Beijing, China. He received the M.S. (1989) degree in Environmental Chemistry from Nanjing University and the Ph.D. (1992) in Environmental Chemistry from the Research Center of Eco-environmental Science, Chinese Academy of Science. His current interests focus on persistent organic pollutants, including analytical methods, behavior in multiple media, disposal technology, remediation technology, and control strategy.

Dr. Junfeng Niu is a post doctoral in the Department of Environmental Science and Engineering, Tsinghua University, Beijing, China. He received a Ph.D. (2002) in environmental science from Dalian University of Technology. His current interests focus on behavior and quantitative structure-activity relationships (QSARs) of persistent organic pollutants.