

INORGANIC-BASED PESTICIDES: A Review Article

BY

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ABSTRACT: Pesticides involving the following elements are cited: aluminium, antimony, arsenic, boron, cadmium, chlorine, copper, fluorine, lead, mercury, phosphorus, selenium, silicon, sulphur are cited. The chemistry, biology and toxicology of these elements are also pointed out. Aluminium as a pesticide may have low uses at the present time. It may have been used as insecticides, fungicides or rodenticides. Antimony is toxic metal similar to arsenic poisoning. Antimonyl potassium tartrate is an insecticide of antimony. It was used as a poison for ants and for the control of thrips. Arsenic is highly poisonous at elevated levels. Arsenic was used as insecticide, fungicide and herbicide. Boron is a deadly poison for crawling insects. It could be used also as a disinfectant, herbicide and fungicide. Borates are toxic to arthropods. Boric acid and its salts have a strong herbicidal and fungicidal effect. It is mainly applied for structural pest control of termites, carpenter ants, powderpost beetles, wood-rot fungi and in management of crack and crevice pests and bait treatments for ants and cockroaches. Cadmium was used in the past as a fungicide in form of the quaternary salt of cadmium-calcium-copper-zinc chromate-sulfate obtained by mixing the appropriate ratios of these components. Chlorides have fungicidal and bactericidal effects at relatively high concentrations. Copper is used as fungicide and algacide. Copper is used as seed disinfectant for cotton, phytocide Copper sulfate is recommended to prevent the powdery mildew and black spot of roses. Fluorides of sodium, potassium, and ammonium have been used as disinfectants for wood and also as agents for the control of moths. Lead is a highly poisonous metal (whether inhaled or swallowed). Lead arsenate is commonly used as insecticide. It is used to control the potato leaf hopper and as a repellent for flea beetles on various vegetables and flowering plants. Mercuric and mercurous chlorides are used against fungus, gnats, earth worms, cabbage maggots, onion maggots and as rat poison. Organomercury compounds considerably beat the inorganic ones as bactericides and fungicides. Compounds of the aliphatic series can be more powerful as fungicides, and those of the aromatic series are stronger as bactericides. Phosphorus pastes, prepared by grinding yellow elemental phosphorus in the presence of water, flour and glycerin; can be used as an ingredient against the American cockroach. Selenium compounds have been tested as insecticides, but because of their toxicity to life, their use is not recommended on crops intended for human or animal consumption. Sodium selenate was applied to soil to kill aphids feeding on the plants. This salt may be toxic to some strains of the spider mites. Fluorosilicate of Sodium had been used in dust and spray forms to control some insects on field crops, as a poison for cutworm, mole cricket, and grasshopper baits. It was additionally effective as a mothproofing agent for woolen fabrics. Sulphur is used as insecticide and fungicide. Elemental sulphur is used for controlling pathogens in grapes, strawberry, many vegetables and several other crops. Sulphur is applied to plants in three formulations as wettable powders, as colloidal sulphur and as lime sulphur. It has a high efficacy against a wide range of powdery mildew diseases as well as black spot.

KEYWORDS: Inorganic pesticides, Aluminium, Antimony, Arsenic, Boron, Cadmium, Chlorides, Copper, Fluorides, Lead, Mercury, Phosphorus, Selenium, Silicon, Sulphur, Chemistry, Occurrence, Biology, Toxicology.

1.INTRODUCTION

A pesticide is simply a substance that kills pests (ATSDR, 2008). Pests involve insects, weeds, mites, ticks, nematodes, bacteria, viruses, spiders, rodents, herbs, etc. (Horsak *et al.*, 1964 and Jack DeAngelis, 2004b). Cida - which means to kill - is the Latin root

word for cide (Horsak *et al.*, 1964). Ancient civilizations cultivated venomous and nutritious vegetation in the same place to make a shield of the toxic plants for insect rejection. Later on came the Ebers papyrus and the traditional Chinese medicine that used primitive sulfides.

Also, Homer's epic work "Odysseus" described the use of substances to eliminate insects. In about the 1500's, the use of the "para-pesticides" such as mercury and arsenic was mentioned. In 1763 pesticides were first named when tobacco was used to fight louse (**Junfeng and Gang Yu, 2008**). These substances were used until the manufacture of synthetic pesticide was developed in about 1940's (**Horsak et al., 1964**). The first synthetic organic pesticide; 1,1,1-trichloro-2,2-bis[4-chlorophenyl] ethane (DDT) was initially prepared in 1874 for curiosity. The Swiss chemist Muller, who received the 1948 Nobel prize in Physiology or Medicine, and his co-workers discovered the insecticidal properties of DDT in 1939. In the following years, DDT was used in public health, mainly against the malaria vector anopheles' mosquito, and in 1946 for protection of cotton, deciduous fruits, cereals and potatoes. The ban of DDT was in the end of the 1960's. Toxaphene was a widely used pesticide on cotton, other crops, and in livestock and poultry (**EPA, 2016**). Toxaphene is a mixture of over 670 chemicals, including chlorinated camphene with the empirical formula: $C_{10}H_{10}Cl_8$. In 1982, most of its uses were cancelled and in 1990, all uses were cancelled in the United States. In 1970's the development and use of the organophosphorus ester compounds started. Earlier, the damage of food reserves during the World War II necessitated the production of foods consumed daily. Since 1960, when pesticides have been extensively explored and studied, several scientists have noted the side effects of pesticides on human health.

A pesticide is either natural, synthetic or biorational, inorganic or organic (**Jack DeAngelis, 2004e**). For a specialist organic pesticides are that contain at least one carbon atom, while consumers refer to organic pesticides as those which are made of natural origins. Diatomaceous earth insecticide is an example of biorational pesticides (**Jack DeAngelis, 2004c**). An insect powder, which is a dust form of natural pesticides, is made from the ground leaves of the chrysanthemum flower (**Jack DeAngelis, 2004d**). Spinosad is another example of natural insecticides that is synthesized by soil microbes (**Jack DeAngelis, 2004g**).

As late as the 1950's some inorganic chemicals such as calcium arsenate, copper sulfate, lead arsenate and sulphur were used as pesticides (**Plimmer, 2001**). About 18 elements are used as inorganic pesticides or are involved in pesticidal agents (**Clarkson, 2001**). Arsenates, aluminates, copper, halogens, mercurials, phosphorus, sulphur, and other salts are examples of inorganic pesticides (**Melnikov, 1971**). However, only sulphur and copper of these are still widely being used nowadays (**Karuppuchamy and Venugopal, 2016**). Inorganic pesticides are manufactured from ores originating from the earth crust (**Jack DeAngelis, 2004f and Speight, 2019**). These inorganic substances may

contain toxic heavy metals as impurities. Many inorganic water soluble salts of organic compounds with pesticidal activity are common today. During and after World War II, many organic insecticides were developed that have largely displaced these inorganic and organometallic substances (**Melnikov, 1971**). Only small amounts of the organic pesticides are needed and thus smaller amounts of chemicals contaminate the environment. The organic pesticides may be generally less toxic to humans than some inorganic ones, particularly, since the former are more degradable. Currently about 100 thousand tons of inorganic pesticides are used only in the United States annually (**Speight, 2019**).

2. Aluminium

2.1. Occurrence, Chemistry and Uses:

The first written record of alum, which comes from *alumen* - a Latin word meaning "bitter salt", was made by Greek historian Herodotus and dated back to the 5th century (**Drozdov, 2007**). Aluminium is a metallic element has the atomic number of 13 and atomic mass of 27 (**Dayah, 2017**). It is a silvery-white, soft, non-magnetic and ductile metal in the post-transition group. It has low melting temperature of 660 °C. By mass, aluminium makes up about 8% of the Earth's crust. It is the most abundant metal and also the third most abundant element. Aluminium has low density and resist corrosion by the passivation phenomenon. Its density is 2.70 g/cm³, about 1/3 that of steel and much lower than other most known metals. Aluminium combines characteristics of pre- and post-transition metals. Aluminium³⁺ is a small, highly charged cation, and has a strong polarization, however, aluminium compounds tend to be covalent rather than ionic. Aluminium has a high chemical affinity to oxygen, which renders it suitable for use as a reducing agent. Aluminium hydroxide forms both salts and aluminates and dissolves in acid and alkali, as well as on fusion with acidic and basic oxides. This behaviour of Al(OH)₃ is termed amphotericism, and it is water insoluble. Applications of aluminium compounds are as follows: Aluminium acetate in solution is used as an astringent, phosphate is used in the manufacture of glass, ceramic, pulp and paper products, cosmetics, paints, varnishes, and in dental cement and hydroxide is used as an antacid and it is used also in water purification and in the waterproofing of fabrics (**Hudson et al., 2005**). Aluminium hydroxychlorides are used as antiperspirants. Sodium aluminate is used as an accelerator of solidification of cement. Aqueous aluminium sulfate is used to treat against fish parasites. Certain aluminium salts serve as an immune adjuvant to allow the protein in the vaccine to achieve sufficient potency as an immune stimulant.

2.2. Biology and Toxicology:

Aluminium salts have no known essential role for life (Frank, 2009). However, the metal salts are not toxic for plants and animals, aluminium sulphate has an LD₅₀ of 500 grams per 80 kg person. Aluminium precipitates in water as the hydroxide; which most elements behaving this way have no biological role or are toxic (Environmental Applications, 2019). Aluminium is classified as a non-carcinogen by the United States Department of Health and Human Services (Dolara, 2014).

2.3. Pesticides of Aluminium:

Aluminium phosphate is used as a fumigant, which are pesticides that exist as a vapour at room temperature, and used as insecticides, fungicides or rodenticides (WHO, 2008). They are extremely toxic, due to their easily environmental dissipation and absorption by humans and animals. They almost kill every living organism. Aluminium phosphide was used in baits to control murine species and other rodents (Melnikov, 1971). It was used also to prevent pests from stored products through the evolution of hydrogen phosphide as a result of the reaction of aluminium phosphide with moisture. Aluminium phosphide was sold to the grain warehouse in special packets (Phostoxin) from which hydrogen phosphide is evolved under the influence of moisture. Cryolite (sodium hexafluoroaluminate, Na₃AlF₆) is a stomach insecticide for the control of chewing insects by spraying plants with 0.2% aqueous suspensions. This compound has the advantage of low acute toxicity to animals. In spite of the cheapness and availability of cryolite, it had not been very widely used. Khairy *et al.* (2018) described a chemical modification of commercial kaolin (kaolinite, Al₂Si₂O₅(OH)₄, hydrous aluminium silicates) for generation of inorganic pesticides. Where, kaolinite is the major mineral component of kaolin. Fungus *Geotrichum candidum* consumes the aluminium in compact discs (Bosch, 2001). The bacterium *Pseudomonas aeruginosa* and the fungus *Cladosporium resinae* are commonly detected in aircraft fuel tanks that use kerosene-based fuels and can degrade aluminium (Sheridan *et al.*, 2013).

3. Arsenic

3.1. Occurrence, Chemistry and Uses:

Arsenic has the atomic number 33 and atomic mass of 75 (Dayah, 2017). It is a metalloid and occurs in nature as crystalline structures and also in minerals, usually in combination with sulphur and metals. It has various allotropes.

3.2. Biology and Toxicology:

The essential role of arsenic was discovered 1977 (Meharg and Hartley-Whitaker, 2002). Arsenic coupled with iron were prescribed as a general tonic till

the beginning of the last century (Berman, 1980). However, the toxicity of arsenic is well known historically. Arsenic interacts with proteins in humans. This causes the gastrointestinal irritation and irreversible inhibition of important enzyme systems. Recently arsenic carcinogenesis has been reported. Inorganic arsenic causes cancer to skin, lung, urinary bladder, liver, kidney and all other human organs (Kitchin, 2001).

3.3. Pesticides of Arsenic:

Some arsenic compounds are known to show insecticidal, fungicidal, herbicidal, and zoocidal effects (Melnikov, 1971). Inorganic arsenic pesticides were known much older than modern era of organic compounds. The use of arsenic and its compounds as insecticides dated up to about the year 900, and became widespread till World War II (Junfeng and Gang Yu, 2008). Paris Green was a popular insecticide in the year 1867. Arsenate ion, AsO₄³⁻, has also been applied for killing insects through ingestion. Other common arsenic insecticide is lead arsenate, Pb₃(AsO₄)₂ and sodium arsenite which is a white crystalline substance, highly soluble in water (Melnikov, 1971). Calcium arsenite is a white solid substance, slightly soluble in water and practically insoluble in organic solvents and was used anciently as a seed disinfectant and to control codling moths, chewing plant pests, rodents and locusts. In the United States zinc arsenite and arsenate were used for wood impregnation to protect it from microorganisms and insects. Methylarsine bis lauryl sulfide is a thick, clear oil with unpleasant odor insoluble in water, miscible with benzene, acetone, methyl alcohol and ethyl alcohol, and in the soil under the influence of microorganisms, it is oxidized with the complete mineralization of arsenic. This compound was used in the form dust to control *Piricularia* of rice. Methylarsine bis (dimethyldithiocarbamate) was used in the form of aqueous suspensions to prevent diseases of the cacao trees. Insecticides of arsenic compounds continued to be used between the 1930's and early 1950's (Junfeng and Gang Yu, 2008). The use of arsenic compounds in agriculture was continually decreasing, and in some countries it was completely forbidden (Melnikov, 1971). Although arsenic pesticides usage has decreased, environmental pollutions by these compounds still exist in some areas of the world (Junfeng and Gang Yu, 2008). Unfortunately, inorganic and organometallic pesticides of arsenic are highly toxic (Melnikov, 1971). Even some organoarsenic compounds, which have relatively lower toxicity, may be converted to toxic inorganic compounds when they are metabolized in animals, plants or in the soil. When arsenic compounds are used regularly they can accumulate in the soil and then in plants, and finally poison domestic animals, especially where feeding crops have been treated with such pesticides. These compounds are not biodegradable like the organic ones. Once these

released into the environment, arsenic will remain indefinitely polluting the environment.

4. Boron, Boric acid and Borates

4.1. Chemistry, Occurrence and Uses:

Boron atomic number is 5 and atomic mass is 11 (**Dayah, 2017**). Elemental boron is a metalloid. It is produced entirely by cosmic ray spallation and supernovae. It is a low abundant element in the Earth's crust. Boron is concentrated on earth by the water solubility of borate minerals. About half of all boron consumed globally. It is used as an additive in fiberglass, for insulation, in structural materials, in polymers, in ceramics, in lightweight structural and in refractory materials. Borosilicate glass is desired for its greater strength and thermal shock resistance than ordinary soda lime glass. A small amount of boron is used as a dopant in semiconductors.

4.2. Biology and Toxicology:

Borates have very low toxicity in mammals (compared with that of table salt), but are more toxic to arthropods (**Irschik et al., 1995**). Boric acid is mildly antimicrobial, and several natural boron containing organic antibiotics are used. Boron is essential plant nutrition. Therefore, boron compounds such as borax and boric acid are used as fertilizers in agriculture. While boric acid is a necessary plant micro nutrient, high soil levels of elemental boron are toxic to plants (**Jack DeAngelis, 2004a**). Hence, care must be taken not to contaminate soil with boric acid insecticides. Boron compounds play a strengthening role in the cell walls of plants. There is no agreement on whether boron is essential for animals and humans, although there are some indications that it supports bone health (**Irschik et al., 1995**).

4.3. Pesticides of boron:

Boric acid and its salts have a strong herbicidal and fungicidal effect (**Melnikov, 1971**). Compounds of boron have been recommended as disinfectants for the preservation of nonmetallic materials but with limitations due to their relatively high cost and moderate efficacy. Boric acid is used as insecticides and wood preservative (**Jack DeAngelis, 2004a**). It is mainly applied to structural pest control for termites, carpenter ants, powderpost beetles, wood rot fungi and in treatments of crack and crevice for pest management and in bait usages for ants and cockroaches. Boric acid must be consumed orally by insect to be effective. While it is a relatively safe compound for humans and other animals. Nevertheless, boric acid is highly toxic to insects. Insects typically ingest boric acid when they clean themselves, or during feeding. If borate powder is used, insects pick up the fine particles when they pass through it. They

ingest the particles when they later groom their legs and antennae. They can also ingest it directly when it is applied to feed sources or in baits. Boric acid insecticides are very effective in cockroach baits in single family residences and as "crack and crevice" treatments in commercial buildings. It is very effective as ant bait incorporates. And, there were several sprays that use boric acid to protect wood against wood destroying insects. A commercial product named "Bora Care" "combined borate with a glycol was used as wood penetrant.

5. Copper

5.1. Occurrence, Chemistry and Uses:

Copper is a transition d-block metal with atomic number 29 and atomic mass of 63 (**Dayah, 2017**). Copper is one of the few metals that can occur in nature in a directly usable metallic form. Man has used copper since 8000 BC. Thousands of years later, it was the first metal to be smelted from sulfide ores. Copper was principally mined in Cyprus, the origin of the name of the metal. Later changed to *cuprum* in Latin, and then to *coper* in Old English and finally to copper in about 1530. Most common copper compounds are Cu (II) salts, which have blue or green colors in minerals such as azurite, malachite, and turquoise, and have been used prehistorically as pigments.

5.2. Biology and Toxicology:

The essentiality of copper has been known since 1928 when its importance in foods and compositions, together with iron, in blood formation was reported (**Berman, 1980**). Copper plays very important role in the vitality of the living cell (**Hefnawy and El-khaiat, 2015**). Copper deficiencies (hypocuprosis) were noticed when long term parenteral nutrition was applied. Deficiency of the element causes different clinical symptoms such as pale coat, anemia, spontaneous fractures, poor capillary integrity, myocardial degeneration, impaired reproductive performance, decreased resistance to infections, diarrhea and generalized illness. Lower copper concentrations occur in cases of cystic fibrosis and kwashiorkor diseases (a syndrome occurs due to a severe protein deficiency in the diet and characterized by retarded growth, changes in skin and hair pigments, gastrointestinal disorders, low serum albumin, and mental apathy) (**Berman, 1980**). However, similar to any chemical substance, higher doses of copper (hypercuprosis) may lead to toxic effects (**Dameron and Harrison, 1998**). It is generally agreed that copper metal is less toxic than its salts (**Browning, 1969**). Copper salts fumes and dust cause irritation of the upper respiratory tract. Copper toxicity may include intravascular haemolysis and antagonism with other vital factors such as iron absorption and zinc enzyme catalysis, etc. (**Dameron and Harrison, 1998**). Abnormally high

copper concentrations in human serum and/or urine may indicate diseases such as Wilson's disease (hepatolenticular degeneration), thalassemia (Mediterranean anemia), hemochromatosis, and cirrhosis, yellow atrophy of liver, epilepsy, leukemia, hyperthyroidism, Hodgkin's disease, atherosclerosis, nephrosis, tuberculosis, and carcinomas (Berman, 1980).

5.3. Pesticides of Copper:

Copper and sulfur compounds represent about 13.6% of diseased farmers due to pesticides (Das *et al.*, 2013). In the United States 13-17,000 tons of copper sulfate were consumed yearly (Melnikov, 1971). As late as 1800's copper sulphate was used specifically as an herbicide (Colditz, 2015). Copper is used as fungicide and algaecide (Junfeng and Gang Yu, 2008). Copper fungicide exists as sulphates, oxides, hydroxides and carbonates (Melnikov, 1971). Wettable powder of copper oxychloride or cuprous oxide fungicides can be prepared by precipitation of soluble solutions of the ingredients. The precipitants are spray dried without the need for grinding the solid products. Copper sulfate has been used for more than 100 years as a fungicide on growing plants in the form of so called Bordeaux mixture (basic copper sulfate with lime). In England and the United States cuprous oxide is used as protective fungicide and seed disinfectant. This product is known in Russia as Compound AB. Paris Green (copper aceto-arsenite) was first used against Colorado beetle in 1865 (Junfeng and Gang Yu, 2008). Paris Green was one the most familiar pesticides in the markets between 1900s-1910s (Strekopytov *et al.*, 2017). Paris green - a green powder poorly soluble in water - was used to control chewing plant pests but it is phytotoxic (Melnikov, 1971). Copper arsenates are used as disinfectants for wood. Copper 2,4,5-trichlorophenolate is used as seed disinfectant for cotton cultivation and for nonmetallic materials. Copper naphthenate is a powerful fungicide, phytocide and is used to cure plant diseases and disinfect nonmetallic materials. Copper salt of phenyl salicylic acid is used in seed boxes treatment and shelves in greenhouses. Double salt of copper sulfate and dihydrazine sulfate is recommended to prevent the powdery mildew and black spot of roses. Copper 8-quinolinolate-copper oxinate is used in plant pathology, seed disinfectants of crops, and also in the form of a wettable powder for spraying of green plants and for the treatment of nonmetallic materials - such as textiles - against microorganisms.

6. Halides

6.1. Biology and Toxicology:

The chloride anion is essentially required for metabolism (Dayah, 2017). Chloride is needed for the production of hydrochloric acid in the stomach and in

cellular pump functions. The main dietary source is sodium chloride (table salt). Very low or high concentrations of chloride in the blood are examples of electrolyte disturbances. Hypochloremia (very low levels of chloride) rarely occurs in the absence of other abnormalities (Lavie *et al.*, 1986). It can be associated with chronic respiratory acidosis (Levitin *et al.*, 1958). Hyperchloremia (very high levels of chloride) usually does not produce symptoms. When symptoms do occur, they tend to resemble those of hyponatremia (having too much sodium). Reduction in blood chloride leads to cerebral dehydration; symptoms are most often caused by rapid rehydration which results in cerebral edema. Hyperchloremia can affect oxygen transport (Cambier *et al.*, 1998). The fluorides have the highest biological activity among halides (Melnikov, 1971).

6.2. Halogen Pesticides:

Halids such as sodium chloride have fungicidal and bactericidal effects at relatively high concentrations (Melnikov, 1971). Concentrated solutions of potassium, magnesium, and other chlorides also show herbicidal properties. Powerful bactericidal and fungicidal effects are exerted by the hypochlorites of the alkali metals, chloride of lime, and calcium hypochlorite, which are used for disinfection in veterinary practice. The chlorates of various metals show herbicidal effects. Thus, magnesium and sodium chlorates and mixtures of them with some other compounds are used as nonselective herbicides and as defoliants for cotton and other crops. Potassium chlorate is used also as an herbicide. A large number of inorganic and organic fluoride compounds had been patented for use as mothproofing agents (Carter, 1952). About 30% of agrichemicals contain fluorides, most of them as herbicides and fungicides with a few crop regulators (ICIS, 2006). Sodium monofluoroacetate is a mammalian poison. First synthesized in the late 19th century, it was recognized as an insecticide in the early 20th, and was later used as a refrigerant. Sodium, potassium, and ammonium fluorides have been used as disinfectants for wood and also as agents for the control of moths by impregnation (Melnikov, 1971). The salts of hydrofluorosilicic acid, such as sodium, potassium, ammonium, and magnesium fluorosilicates, have similar properties. Magnesium fluorosilicate, which is highly soluble in water, is convenient for the impregnation of wood and other fibrous materials. Sodium and barium fluorosilicates were previously used as stomach insecticides.

7. Lead

7.1. Occurrence, Chemistry and Uses:

Lead is a post-transition metal with the symbol Pb (from the Latin plumbum) and atomic

number 82 and atomic mass of 208 (Dayah, 2017). Lead use dated back to 7000–6500 BC in Asia (Rich, 1994). The major reason for the spread of lead production in association with silver was the formation of bronze alloy (Winder, 1993). The Ancient Egyptians were the first to use lead minerals in cosmetics, and then spread to Ancient Greece and beyond the Egyptians. It may have used for sinkers in fishing nets, glazes, glasses, enamels, and for ornaments. Various civilizations of the Fertile Crescent used lead as a writing material, as currency, and as a construction material. Lead was used in the Ancient Chinese royal court as a stimulant, as currency, and as a contraceptive. The Indus Valley civilization and the Mesoamericans used it for making amulets; and the eastern and southern African peoples used lead in wire drawing. The Roman used to add it as bronze utensils as they believed that it lessened the bitter tastes of these food containers (Berman, 1980). This was believed that it led to the breakdown of the Roman Empire. Lead is a relatively unreactive metal (Dayah, 2017). Its weak metallic character is illustrated by its amphoteric nature; lead and lead oxides react with both acids and bases, and it tends to form covalent bonds.

7.2. Biology and Toxicology:

In the late 19th century, lead's toxicity was recognized, and since then its use has been phased out of many applications. Lead is a highly poisonous metal (whether inhaled or swallowed), affecting almost every organ and system in the human body (USFDA, 2015). At airborne levels of 100 mg/m³, lead becomes an immediate risk to health. Most ingested lead is absorbed into the bloodstream. The primary cause of its toxicity is its predilection for interfering with the proper functioning of enzymes. It does so by binding to the sulfhydryl groups found in many enzymes, or imitating and displacing other metals which act as cofactors in many enzymatic reactions. Among the essential metals that lead interacts with are calcium, iron, and zinc. High levels of calcium and iron tend to provide some protection from lead poisoning, however, low levels may cause increased liability. Lead is a neurotoxin and accumulates in soft tissues and bones; it damages the nervous system and interferes with the function of biological enzymes, causing neurological disorders, such as brain damage and behavioral problems. However, many countries still allow the sale of products that expose humans to lead, including some types of fuels, paints and bullets.

7.3. Pesticides of Lead:

Some lead arsenate compounds are commonly used as insecticides (Carter, 1952). Acidic lead arsenate (PbHAsO₄), which is a white powder insoluble in water and basic lead arsenate (lead hydroxyl arsenate, Pb₄OH(AsO₄)₃) which is also a white insoluble powder

are two insecticides of them. Acid lead arsenate was used extensively to control chewing insects on fruits, such as apple and pear, on flowers, trees, and shrubs, and on vegetables, such as potato and tomato. It had been also extensively used in treating soil to control Japanese beetle and Asiatic garden beetle larvae and related soil infesting forms. Bordeaux mixture (basic copper sulfate with lime), which is primarily a fungicide, was often used in connection with insecticides such as nicotine, lead arsenate, and calcium arsenate. It was sometimes used to control the potato leafhopper and as a repellent for flea beetles on various vegetables and flowering plants. It was sometimes used also as an emulsifier for lubricating oil sprays applied to fruit trees, such as apple, pear, quince, and peach. However, In Russia, the agricultural use of lead arsenate was forbidden because of the high chronic toxicity of lead (Melnikov, 1971).

8. Mercury

8.1. Occurrence, Chemistry and Uses:

Mercury is a liquid metal with the symbol Hg and atomic number 80 and atomic mass 202 (Dayah, 2017). It is commonly known as quicksilver and was formerly named hydrargyrum (Hydrargyrum, 2014). A heavy, silvery transition d-block element, mercury which is the only metallic element that is liquid at standard conditions of temperature and pressure. The metal tends to form complexes more readily with the highest stability Hg (+II) among all the transition d block elements (Cotton and Wilkinson, 1972 and Lee, 1979). The coordination chemistry of mercury (II) with 5B, 6B and 7B family elements has been intensively studied because these interactions are in the biological systems (Lee *et al.*, 1999). Organomercury compounds, which are volatile, have the formula HgR₂ and when are solids, have the formula HgRX, where R is aryl or alkyl and X is usually halide or acetate (Dayah, 2017). Mercury most known function is as an ingredient in dental amalgams (Merck's Manual, 2013). Gaseous mercury is used in mercury vapor lamps and in some advertisements "neon sign" and fluorescent lamps (Dayah, 2017). Mercuric oxide is used in skin ointments (Frei and Hutzinger, 1975). Mercuric sulphate is used as a catalyst in organic chemistry. Vermilion, a red pigment, is mercuric sulphide. The crystalline form of the sulphide, which is black, is also used as a pigment. Mercury fulminate, Hg(CNO)₂, is used as a detonator. Thiomersal is an organomercury compound containing ethyl mercury which is used as a preservative, a well-established antiseptic and antifungal agents, to prevent bacterial and fungal growth in some inactivated vaccines in multi-dose vials. Mercury, as thiomersal, is widely used in the manufacture of cosmetics (Mercury in your eye, 2008).

8.2. Biology, Toxicology and Environmental Fate:

Mercury is not naturally found in foodstuffs, but it may be spread within food chains by smaller organisms that are consumed by humans (**Frei and Hutzinger, 1975**). Mercury enters the environment as a result of normal breakdown of minerals in rocks and soil through exposure to wind and water. Release of mercury from natural resources has fairly remained over the years. Still mercury concentrations in the environment are increasing; this is ascribed to human activity. Some forms of human activity release mercury directly into soil or water, for instance the application of agricultural fertilizers and industrial wastewater disposal. All mercury that is released in the environment will eventually end up in soils or surface waters. In the soil mercuric oxide is converted to mercury sulfide (**Melnikov, 1971**). Mercury sulfide is one of the least toxic compounds for both animals and microorganisms. Methylmercury (MeHg), a generic term for compounds with the formula CH_3HgX , is a dangerous family of compounds that are often found in polluted water. It interferes with the ability of cells to make energy from the cellular metabolism of sugar and oxygen (**Juan et al., 2017**). The body burns carbohydrates and oxygen in an effort to generate energy in the form of adenosine triphosphate (ATP), but MeHg blocks ATP formation and the energy is released as heat. Consequently, the principal symptom and toxic effect of MeHg poisoning is a fever and may be easily confused with a severe case of flu. Since MeHg is eliminated from the body rather slowly, occupational exposures may result in accumulation of MeHg over time. Thus, chronic exposure may result in what appears to be an acute poisoning, although symptoms may also develop slowly. They arise by a process known as biomethylation. The problem of mercury pollution came into focus after the discovery of high levels of methylmercury in fish and shellfish in Minamata Bay of Japan, that resulted in thousands of poisonings and hundreds of deaths (**Roane et al., 2009**). The mercury contamination originated from a chemical factory which was disposed of into Minamata Bay and ultimately accumulated in fish. It is also likely that microbial activity in the sediment converted elemental mercury that was existed in the bay into methylmercury.

8.3. Pesticides of Mercury:

Some compounds of mercury were used as insecticides (**Carter, 1952**). The fungicidal properties of mercuric chloride with respect to phytopathological fungi were discovered at the end of the nineteenth century, and since then, it had been used to protect plants from diseases (**Melnikov, 1971**). However, its high toxicity to man, animals, and plants made it important to seek more active and safer compounds for use in agriculture.

Mercuric chloride, HgCl_2 (corrosive sublimate), and mercurous chloride, HgCl (calomel), were used against fungus, gnats, earth worms, cabbage maggots, onion maggots and as rat poison (**Carter, 1952**). Mercuric chloride was also used for the protection from dormant gladiolus worms and as a fungicide and germicide. Formulations containing mercury compounds were sometimes used against insects hurting man and animals. Disinfection of seeds with aqueous solutions of organomercury compounds was widely applied (**Melnikov, 1971**). Investigation of various mercury derivatives of the aliphatic, alicyclic, aromatic, and heterocyclic series has shown that organomercury compounds considerably exceed the inorganic ones in bactericidal and fungicidal effect. Compounds of the aliphatic series can be more powerful fungicides, and those of the aromatic series are stronger bactericides. Also, organomercury compounds have a favourable chemotherapeutic index, the concentration that kills plant disease organisms, is much less than the concentration dangerous to the plants. Moreover, many organomercury compounds at the concentrations used not only are harmless to plants, but even stimulate their growth. Sometimes the stimulation is so great that it leads to a substantial increase in yield. Nevertheless, studies have shown that strong microbiological activity of organomercurials occurs only with the formula: RHgX , where R is a hydrocarbon radical, and X is an organic or inorganic acid group. Methyl mercury is widely used fungicides (**Juan et al., 2017**). Ethyl mercury phosphate gives the same result as with methyl mercury but with about 20% of weight (**Melnikov, 1971**). Methoxyethylmercury derivatives, used as seed disinfectants, are close to the latter two in activity. Beforehand, in a number of countries use of organomercury compounds for apple trees was applied, due to prophylactic and curative effects. They were also used to control some weeds. However, their use as insecticides was negligible. Mercury, in general, is less used in modern agriculture (**Juan et al., 2017**).

9. Silicon, Silica dust and diatomaceous earth (DE) insecticides

9.1. Occurrence, Chemistry and Uses:

Silicon is a metalloid element with the symbol Si and atomic number 14 and atomic mass of 28 (**Dayah, 2017**). It is a hard, brittle crystalline solid with a blue grey metallic luster, tetravalent and relatively unreactive. Its melting point is 1414°C . Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure element in the Earth's crust. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. More than 90% of the Earth's crust is composed of silicate minerals, making

silicon the second most abundant element in the Earth's crust (about 28% by mass) after oxygen. Jöns Jakob Berzelius in 1823 was the first to able to prepare silicon and characterize it in pure form. The late 20th century to early 21st century has been described as the Silicon Age (also known as the Digital Age or Information Age) due to that elemental silicon having a large impact on the modern world economy. The relatively small portion of very highly purified elemental silicon used in semiconductor electronics (<10%) is essential to the metal oxide silicon (MOS) transistors and integrated circuit chips that is used in most modern technology (such as computers and cell phones, for example). The most widely used silicon device is the MOSFET (metal oxide silicon field effect transistor), which has been manufactured in larger numbers than any other device in history. Free silicon is also used in the steel refining, aluminium casting, and fine chemical industries (often to make fumed silica). Diatomaceous earth chemical name is amorphous silicon dioxide (SiO₂)_n (Villaverde *et al.*, 2017). Diatomaceous earth is composed of the fossilized shells of tiny marine organisms called diatoms (Jack DeAngelis, 2004c). The shells are made mainly of silica. Diatomaceous earth is a fine, light powder that is slightly abrasive but highly absorbent. Anciently diatomaceous earth was used in agriculture applications. Nowadays Diatomaceous earth has a variety of uses in filtration, adsorbents, a component of dynamite (another name for diatomaceous earth is diatomite), and as a natural insecticide.

9.2. Biology and Toxicology:

Silicon is an essential element in biology, although only traces are required by animals. However, various sea sponges, microorganisms, such as diatoms and radiolarian, and secrete skeletal structures made of silica. Silica is deposited in many plant tissues (Cutter, 1978). Silicon is currently under consideration for elevation to the status of a "plant beneficial substance" by the Association of American Plant Food Control Officials (Miranda and Barker, 2009). People may be exposed to elemental silicon in the workplace by breathing it in, swallowing it, or having contact with the skin or eye (Dayah, 2017). In the latter two cases, silicon poses a slight hazard as an irritant. It is hazardous if inhaled. The Occupational Safety and Health Administration (OSHA) has set the legal limit for silicon exposure in the workplace as 15 mg/m³ total exposure and 5 mg/m³ respiratory exposure over an 8-hour workday. The National Institute for Occupational Safety and Health (NIOSH) has set a Recommended exposure limit (REL) of 10 mg/m³ total exposure and 5 mg/m³ respiratory exposure over an 8-hour workday. Inhalation of crystalline silica dust may lead to silicosis, an occupational lung disease marked by inflammation and scarring in the form of nodular

lesions in the upper lobes of the lungs (Plant *et al.*, 2012).

9.3. Pesticides of Silicon and Diatomaceous Earth:

Sodium fluorosilicate, Na₂SiF₆, is a white crystalline powder insoluble in water (Carter, 1952). It was used as a dust and spray in the control of some insects on field crops, as a poison in cutworm, mole cricket, and grasshopper baits and is effective as a mothproofing agent for woolen fabrics. Diatomaceous earth insecticide is very effective against a number of crawling insect such as cockroaches, ants, earwigs, silverfish, sow bugs, pill bugs, and bedbugs (Jack DeAngelis, 2004c). It must be kept dry to be effective, whether used indoors and outdoors. It works as an insecticide because it absorbs and removes the protective waxy covering of insects that are exposed to it. Its action is based on dehydrating the waxy cover water of the insect and removing this protective layer. A dust mask should be worn when applying the powder. Diatomaceous earth is safer and more effective than conventional insecticides as it exhibits very low mammalian toxicity compared to many other insecticides. Another form of silica used as pesticides is amorphous silica which is made by heating ordinary sand to elevated temperatures. Amorphous silica is often used combined with the natural insecticide "pyrethrum" or alone.

10. Sulphur

10.1. Occurrence, Chemistry and Uses:

Sulphur is a nonmetallic element in the group VI of the Periodic System (Dayah, 2017). Sulphur atomic number is 16 and atomic mass is 32. Sulphur accounts for 15% of the inner core of the earth and 0.052% of its crust (Seiler *et al.*, 1988). Under normal conditions, sulphur atoms form cyclic octatomic molecules with a chemical formula S₈ (Dayah, 2017). Elemental sulphur is a bright yellow, crystalline solid at room temperature. Colours of sulphur are: shades of yellow, yellowish brown, yellowish green, reddish. Sulphur stone is a synonym for pyrite. Sulphur melting point is 115.21°C. Sulphur is the tenth most common element by mass in the universe, and the fifth most common on Earth. It is abundant in native form. Sulphur was known in the ancient civilizations of India, Greece and China. Though sometimes found in pure, native form, sulphur on earth usually occurs as sulphide and sulphate minerals. Today, almost all elemental sulphur is produced as a byproduct of removing sulphur-containing contaminants from natural gas and petroleum oil. Sulphur is an indirect food additive used in adhesives.

10.2. Biology and Toxicology:

Sulphur is an essential element for all life, but almost always in the form of organosulphur compounds

or metal sulphides (**Mohammed et al., 2018**). Many amino acids, proteins and cofactors contain sulphur. Disulphides, S-S bonds, confer mechanical strength and insolubility of the protein keratin, found in outer skin, hair, and feathers. Sulphur is one of the core chemical elements needed for biochemical functioning and is an elemental macro-nutrient for all living organisms. Prolonged use of sulphur may result in a characteristic dermatitis (**Osol, 1980**). The element plays an important role in growth and development of plants (**Radwan et al., 2017**). Sulphur constitutes three amino acids in plants (methionine, cysteine and cystine). Endophytic microorganisms oxidize elemental sulphur to sulphates which benefit the plants and produce phytochemicals which are antagonistic to plant pathogens as well as having secondary metabolites contributing to plant vitality. Chemotrophic (i.e., chemosynthetic) organisms gain energy from chemical substances (**Camacho, 2009**). When the source is an inorganic substance such as sulphur, it is called chemolithotrophic. Sulphur compounds are used by sulphur bacteria to obtain its needed energy. Reduced sulphur compounds are used either by colorless sulphur bacteria or the colored photosynthetic bacteria (**Maier and Pepper, 2009**). *Chlorobium*, a green sulfur bacterium, can utilize longer wavelengths of light than many other phototrophs and are also anaerobic organisms, requiring H_2S rather than H_2O for photosynthesis (**Sandrin et al., 2009**). The chemotrophic bacteria which undergo oxidation of sulphide to sulphur are aided by bacterial oxidation of sulfide ores (thiobacilli) (**Wetzel, 2001**).

10.3. Pesticides of Sulphur:

Sulphur is the oldest recorded fungicide and has been used for more than 2000 years (**CIPAC Handbook, 1992**). The element is used to manufacture fertilizers, insecticides and fungicides (**Junfeng and Gang Yu, 2008**). Elemental sulphur is one of the oldest pesticides. The earliest recorded pesticides were the burning of sulphur to fumigate Greek homes about 1000 B.C. Fumigants are used through the entrance of the insect as an inhaled gas. Dusting elemental sulphur, in powdered form, is a common fungicide for grapes, strawberry, many vegetables and several other crops (**Robert, 2001**). It has a good efficacy against a wide range of powdery mildew diseases as well as black spot (**Bostanian et al., 2009**). Early in agricultural history, the Greeks recognized its efficacy against rust diseases on wheat (**CIPAC Handbook, 1992**). Sulphur is applied to plants in three formulations as Wettable powders, as colloidal sulphur and as lime sulphur. In inorganic production, sulphur is the most important fungicide. It is the only fungicide used in organically farmed apple production against the main disease apple scab under colder conditions. Biosulphur (biologically produced elemental

sulphur with hydrophilic characteristics) can be used well for these treatments. Standard formulation dusting sulphur is applied to crops with a sulphur duster or from a dusting plane. It has similar applications, and is used as a fungicide against mildew and other mold related problems with plants and soil. A common method of use is to dust clothing or limbs with sulphur powder. Some livestock owners set out a sulphur salt block as a salt lick. In organic agriculture, sulphur is the most important fungicide (**Bostanian et al., 2009**). Wettable sulphur is the commercial name for dusting sulfur and is formulated with additional ingredients to make it water miscible. Elemental sulphur powder is used as an "organic" (or "green") insecticide, actually an acaricide, against ticks and mites. A diluted solution of lime sulphur (made by combining calcium hydroxide with elemental sulphur in water) is used as a dip for pets to destroy ringworm (fungus), mange, other dermatoses and parasites. Sulphur is also used as a bactericide in winemaking and food preservation.

11. Other Inorganic Compounds

Very few citations are available concerning elements exerting pesticide action such as antimony, cadmium, phosphorus and selenium:

11.1. Antimony:

Antimony is a chemical element with the symbol Sb (from Latin: *stibium*) (**Dayah, 2017**). Certain compounds of antimony appear to be toxic, particularly antimony trioxide and antimony potassium tartrate (**ATSDR, 2019**). Effects may be similar to arsenic poisoning (**Encyclopedia Britannica, 2018**). Occupational exposure may cause respiratory irritation, pneumoconiosis, antimony spots on the skin, gastrointestinal symptoms, and cardiac arrhythmias. In addition, antimony trioxide is potentially carcinogenic to humans (**Sundar and Chakravarty, 2010**).

Carter (1952) cited that antimony potassium tartrate, tar-tar emetic, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ as an insecticide of antimony. It is a white powder soluble in water. It was used at that time as a poison for ants and for the control of thrips.

11.2. Cadmium:

Cadmium is a highly toxic metal (**Berman, 1980**). Cadmium competes with the absorption of some essential elements such as iron, zinc, and copper. The element may also interfere with the release of iron by transferrin. Cadmium ingestion produces symptoms such as nausea, salivation, vomiting followed by diarrhea with abdominal discomfort and pains. Cadmium is accumulated in the human body. A characteristic disease of chronic cadmium poisoning is called Itai-itai manifested by renal dysfunction in combination with osteomalacia or severe osteoporosis.

Cadmium was mentioned once as a fungicide in form of the quaternary salt cadmium-calcium-copper-zinc chromate-sulfate obtained by mixing the appropriate components (**Melnikov, 1971**). The composition of this salt in % is: CdO 4.5, CuO 11.7, ZnO 4.8, CaO 32.9, CrO₃ 5.9, SO₃ 11.7, and H₂O 26.5. This preparation was marketed in the form of a 90% wettable powder for the control of a number of plant diseases.

11.3. Phosphorus:

Inorganic phosphorus in the form of the phosphate PO₄³⁻ is required for all known forms of life (**Ruttenberg, 2013**). Phosphorus plays a major role in the structural framework of DNA and RNA. Living cells use phosphate to transport cellular energy with adenosine triphosphate (ATP), necessary for every cellular process that uses energy. Adenosine triphosphate is also important for phosphorylation, a key regulatory event in cells. Phospholipids are the main structural components of all cellular membranes (**Lipmann, 1944**). Calcium phosphate salts assist in stiffening bones (**Greenwood and Earnshaw, 1997**).

While organophosphorus pesticides at present time dominate, elemental phosphorus pesticides are seldom cited. Pastes containing elemental phosphorus were made from yellow phosphorus in water and then mixed with flour and glycerin (**Carter, 1952**). Such pastes were effective against the American cockroach. Various phosphorus compounds were used as pesticides, including derivatives of phosphorous, thiophosphorous, phosphoric, thiophosphoric, dithiophosphoric, phosphonous, and thiophosphonous acids (**Melnikov, 1971**).

11.4. Selenium:

Although it is toxic in large doses, selenium is an essential micronutrient for animals (**Dayah, 2017**). The element essentiality was discovered in 1957 by Schwarz, Foltz, Patterson, Milstrey, and Stockstad (**Berman, 1980**). It is a component of glutathione peroxide and it reacts with harmful heavy metals. The lack of selenium results in the Keshan disease which is a congestive cardiomyopathy caused by a dietary deficiency of the metal. In plants, it occurs as a bystander mineral, sometimes in toxic proportions in forage, some plants may accumulate selenium as a defense against being eaten by animals. Other plants, such as locoweed, require selenium in their growth show the presence of selenium in soil (**Ruyle, 2009**). In high concentrations, selenium acts as an environmental contaminant.

Selenium compounds have been tested as insecticides, but because of their toxicity to man their use is not recommended on crops intended for human or animal consumption (**Melnikov, 1971**). Sodium selenate, Na₂SeO₄, is a water soluble salt. Plants can take selenium up from the soil in sufficient amounts to kill aphids

feeding on the plants and when applied to crops as carnations and chrysanthemums, it may be toxic to some strains of the spider mites. The metal is ineffective on roses or other plants with woody stems. It is also a systemic insecticide absorbed by the roots and translocated with the sap to the foliage and flowers of herbaceous plants. It poisons mite as they feed. However, it is not recommended in agriculture due to its toxicity. A product known as selocide containing selenium and sulphur of the formula (KNH₄S)₂Se had been used in the Pacific Northwest to fight mites on apples and grapes, but it was successful at first against spider mites, then became ineffective despite repeated applications.

Conclusion

Inorganic pesticides are mainly manufactured from ores originating from the earth crust. Most inorganic pesticides, except copper and sulphur, have lower applications at the present time. Inorganic pesticides may be cheaper and less toxic than some organic ones. However, pesticides containing metals as antimony, arsenic, lead, mercury and selenium can be hazardous. Only natural pesticides may be safer. Most inorganic pesticides are now abandoned except those of copper and sulphur. However, some inorganic compounds such as silicates (diatomaceous earth) and boric acid have reasonable applications against crawling insects. Also some organometals, such as organomercurials, may have limited usages due to their prophylactic and curative effects. Since only small amounts of the organic pesticides are needed, smaller amounts of these chemicals may contaminate the environment. Moreover, the organic pesticides may be generally less toxic to humans than some inorganic ones, as the former are more degradable

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المبيدات ذات الأساس الغير العضوى: مقال مراجعى

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المعمل المركزى للمبيدات ، مركز البحوث الزراعية ، الدقى ، الجيزة ، مصر

الملخص العربى:

المبيد هو ببساطة كل مادة تقتل الآفات و التى تشمل آفات الحشرات والأعشاب الضارة والعثة والقراد والديدان الخيطية والبكتيريا والفيروسات والعناكب والقوارض و يكون مبيد الآفات إما طبيعياً أو صناعياً أو بيولوجياً و يكون غير عضوي أو عضوي و بالنسبة للمبيدات العضوية المتخصصة فهي تحتوي على ذرة كربون واحدة على الأقل بينما يشير المستهلكون إلى مصطلح المبيدات العضوية على أنها المبيدات المصنوعة من أصول طبيعية و من المبيدات الطبيعية الدياتومي المستخرج من الأرض وهو مثال على مبيدات الآفات البيولوجية ، كما يتم تصنيع المبيدات الطبيعية من زهرة الأقحوان على شكل غبار و كذلك المبيدات الحشرية الطبيعية التي يتم تصنيعها بواسطة ميكروبات التربة (Spinosad) و قد قامت الحضارات القديمة بزراعة نباتات سامة ومغذية في نفس المكان لصنع وافي من النباتات السامة لإبعاد الحشرات عن النباتات المغذية ، وفي وقت لاحق ظهرت بردية إيبيرس والطب الصيني التقليدي الذان إستخدما كبريتيدات بدائية لمكافحة الآفات ، وذكر سابقاً عمل هوميروس الملحمي "أوديسيوس" والذي إستخدام مواد كيميائية للقضاء على الحشرات ، وفي القرن الخامس عشر الميلادي بدأ ذكر استخدام "المبيدات شبه الحشرية" مثل الزئبق والزرنيخ و في عام ١٧٦٣ تم تسمية مبيدات الآفات لأول مرة عند استخدام التنغ لمحاربة القمل و تم استخدام هذه المواد و في أواخر الخمسينيات من القرن الماضي تم استخدام بعض المواد الكيميائية غير العضوية مثل زرنيخات الكالسيوم وكبريتات النحاس وزرنيخات الرصاص والكبريت كمبيدات للآفات و يستخدم حوالي ١٨ عنصراً كمبيدات غير عضوية أو تدخل في مبيدات الآفات و منها الزرنيخات والألومينات والنحاس والهالوجينات والزئبق والفوسفور والكبريت وأملاح أخرى ولا يزال يتم استخدام الكبريت والنحاس على نطاق واسع في الوقت الحاضر و تُصنع مبيدات الآفات غير العضوية من خامات مصدرها القشرة الأرضية وقد تحتوي هذه المواد غير العضوية على معادن ثقيلة سامة على شكل شوائب والعديد من الأملاح غير العضوية للمركبات العضوية والقابلة للذوبان في الماء تستخدم كمبيدات للآفات بصورة شائعة حتى اليوم ، وقد تم تطوير تصنيع المبيدات الاصطناعية في حوالي عام ١٩٤٠ ، و كان أول مبيد عضوي اصطناعي يتم تحضيره باسم DDT (2,4,6-trichloro-2-bis-2-كلوروفينيل الإيثان) وذلك في عام ١٨٧٤ كمركب تجريبي ، واكتشف الكيميائي السويسري مولر - الحاصل بعد ذلك على جائزة نوبل عام ١٩٤٨ في علم وظائف الأعضاء والطب - وزملاؤه الخصائص الإبادية لمادة الـ دي.دي.تي على الحشرات في عام ، بعد ذلك تم استخدام الـ دي.دي.تي في عام ١٩٤٦ لحماية القطن والفاكهة المتساقطة والحبوب والبطاطس من الآفات ، ثم كان بعد ذلك حظر إستخدام الـ دي.تي في نهاية الستينيات ، ثم ظهر بعد ذلك التوكسافين كمبيد للآفات واسع الاستخدام على القطن والمحاصيل الأخرى والماشية والدواجن و التوكسافين هو خليط من أكثر من ٦٧٠ مادة كيميائية و منها الكامفين المكلور (بالصيغة التجريبية C₁₀H₁₀Cl₈) و في عام ١٩٨٢ تم إلغاء معظم استخدامات التوكسافين وفي عام و في عام ١٩٧٠ بدأ تطوير استخدام مركبات الإستر العضوية الفسفورية و ذلك بسبب الحاجة السابقة لحماية مخزون الغذاء من التلف خلال الحرب العالمية الثانية و الذى إستلزم إنتاج الأطعمة للإستهلاك و من ثم تم تطوير العديد من المبيدات الحشرية العضوية التي أدت إلى حد كبير إلى إزاحة هذه المواد غير العضوية والمعدنية العضوية ، ومنذ عام ١٩٦٠ عندما تمت دراسة مبيدات الآفات على نطاق واسع لاحظ العديد من العلماء الآثار الجانبية لمبيدات الآفات على صحة الإنسان ، حيث قد تكون بعض مبيدات الآفات العضوية أقل سمية للإنسان بشكل عام من بعض المبيدات غير العضوية ، على وجه الخصوص ، لأن الأولى أكثر قابلية للتحلل كما أنه لا يلزم سوى كميات صغيرة من المبيدات العضوية ، وبالتالي فإن كميات أقل من هذه المواد الكيميائية يمكن أن تلوث البيئة.

حالياً يتم استخدام حوالي ١٠٠ ألف طن من المبيدات غير العضوية سنوياً في الولايات المتحدة وحدها ، و بعض هذه المبيدات الغير عضوية قد تشتمل على العناصر التالية: الألمنيوم ، الأنتيمون ، الزرنيخ ، البورون ، الكلوريدات ، النحاس ، الفلوريد ، الرصاص ، الزئبق ، الفوسفور ، السيليونيوم ، السليكون ، الكبريت .

تم عرض بعض مبيدات الآفات التي تشتمل على العناصر التالية: الألمنيوم ، الأنتيمون ، الزرنيخ ، البورون ، الكلوريدات ، النحاس ، الفلوريد ، الرصاص ، الزئبق ، الفوسفور ، السيليونيوم ، السليكون ، الكبريت وتمت الإشارة إلى كيمياء وبيولوجيا وسمية هذه العناصر ، على الرغم من أن الألمنيوم ليس له دور في الدورات البيولوجية ، إلا أن سمية الألومنيوم للحيوانات والنباتات محدودة و قد يكون استخدام الألمنيوم كمبيد للآفات قليلاً حالياً ولكن يمكن استخدامه من ضمن المبيدات الحشرية أو المبيدات الفطرية أو مبيدات القوارض.

الأنتميون وهو معدن سام مشابه لسمية الزرنيخ يستخدم على هيئة طرطرات البوتاسيوم كمبيد حشري كسم للنمل والسيطرة على العثة. الزرنيخ له ضرورة حيوية لحياة الكائنات ، ومع ذلك فإن الزرنيخ سام للغاية عند مستويات تركيزات مرتفعة ، وتم استخدام الزرنيخ كمبيد حشري و فطري ومبيد للحشائش.

في حين أن البورون عنصر منخفض السمية للحيوانات البورون وهو عنصر غذائي نباتي أساسي ، وتستخدم مركبات البورون مثل البوراكس وحمض البوريك كسماد في الزراعة و البورات لها سمية منخفضة على الثدييات (مثلها مثل ملح الطعام) ، إلا أنه سم مميت للمفصليات و الحشرات الزاحفة و يمكن استخدامه أيضاً كمطهر ومبيد للحشائش والفطريات ، وحمض البوريك وأملاحه لها تأثير قوى كمبيدات للحشائش والفطريات و يتم تطبيقه بشكل أساسي في مكافحة الآفات المفصليّة كالنمل الأبيض ، والنمل أكل الخشب ، والخنافس الساحقة ، والفطريات المسببة للتتعفن في الأخشاب وفي التحكم في الآفات المزعجة و كعلاج للشقوق وكطعم للنمل والصرارصير.

الكاديوم معدن شديد السمية ، يتنافس الكاديوم مع امتصاص بعض العناصر الأساسية في الجسم مثل الحديد والزنك والنحاس وقد يتداخل العنصر أيضاً مع إطلاق الحديد ويتسبب ابتلاع الكاديوم في ظهور أعراض مثل الغثان وجفاف اللعاب والقيء يليه الإسهال مع تقلصات في البطن و

يتراكم الكادميوم في جسم الإنسان والذي يسبب الفشل الكلوي ولين أو هشاشة العظام الشديدة و تم ذكر الكادميوم كمبيد للفطريات على هيئة ملح كبريتات الكادميوم - الكالسيوم - النحاس - الزنك - وهى الكبريتات التي يتم الحصول عليها عن طريق خلط هذه المكونات بنسب معينة و تم تسويق هذا المستحضر على شكل مسحوق قابل للبلل بنسبة ٩٠٪ لمكافحة عدد من أمراض النبات.

أملاح الكلوريد تعتبر شق أساسي لعملية التمثيل الغذائي و كلوريد الصوديوم له تأثيرات على الفطريات وكمبيد للجراثيم عند التركيزات العالية نسبياً.

يلعب النحاس دوراً مهماً للغاية في حيوية الخلية الحية و مع ذلك يستخدم النحاس كمبيد للفطريات والطحالب و يستخدم كمطهر لبذور القطن و مبيد للحشائش و كبريتات النحاس تستخدم لمنع البياض الدقيقي و البقع السوداء في الورود و تحتوي الفلوريدات على أعلى نشاط بيولوجي بين الهاليدات و تم استخدام فلوريد الصوديوم و البوتاسيوم و الأمونيوم كمطهرات للخشب أيضاً كعناصر للسيطرة على العثة.

الرصاص معدن سام للغاية (سواء تم استنشاقه أو ابتلاعه) ، عادة ما يستخدم زرنيخ الرصاص كمبيد حشري و يتم استخدامه أحياناً للتحكم في هوبر أوراق نبات البطاطس و طارد لخنائس البزاع في مختلف الخضروات و النباتات المزهرة.

يدخل الزئبق البيئة نتيجة للانهيار الطبيعي للمعادن في الصخور و التربة من خلال التعرض للرياح و المياه ، يستخدم كلوريد الزئبق الأحادي و الثنائي ضد الفطريات ، البعوض ، وديدان الأرضية ، وديدان الكرنب ، وديدان البصل و كسم للفئران و تتفوق مركبات الزئبق العضوي إلى حد كبير على المركبات غير العضوية في التأثير كمبيدات للجراثيم و الفطريات و يمكن أن تكون مركبات السلسلة الأليفاتية كمبيدات فطرية أكثر قوة ، و مركبات السلسلة الأروماتية كمبيدات جراثومية أقوى.

الفوسفور الغير العضوي له ضرورة لجميع أشكال الحياة المعروفة و يتم صنع المعاجين المحتوية على عنصر الفسفور عن طريق طحن الفوسفور الأصفر في وجود الماء و الدقيق و الغليسرين كمكون ضد الصرصور الأمريكي.

يعتبر السيلينيوم من المغذيات الدقيقة الأساسية للحيوانات ، ولكنه سام في الجرعات الكبيرة و تم اختبار مركبات السيلينيوم كمبيدات حشرية ولكن بسبب سميتها للإنسان لا يوصى باستخدامها على المحاصيل المعدة للاستهلاك البشري أو الحيواني ويمكن لسيلينات الصوديوم في التربة قتل حشرات المن التي تتغذى على النباتات و عند وضعها على المحاصيل مثل القرنفل و الأقحوان فإنها تكون سامة لبعض سلالات سوس العنكبوت.

السليكون عنصر أساسي للحياة ، و تحتج الحيوانات فقط كميات ضئيلة منه و يستخدم فلوروسيليكات الصوديوم كغبار و رذاذ في السيطرة على بعض الحشرات في المحاصيل الحقلية و كمادة سامة في دودة القصب و الكركيت ، و الطعوم الجندب و هي فعالة كعامل ضد عثة الأقمشة الصوفية.

بعد الكبريت عنصرًا أساسيًا لجميع الكائنات الحية ولكنه دائماً ما يكون في شكل مركبات كبريتية عضوية أو كبريتيدات معدنية و يستخدم العنصر في صناعة الأسمدة و المبيدات الحشرية و مبيدات الفطريات و عند وجود غبار الكبريت على شكل مسحوق فإنه يكون مبيد فطري شائع يستخدم للسيطرة على مسببات الأمراض في العنب و الفراولة و العديد من الخضروات و العديد من المحاصيل الأخرى و يتم استخدام الكبريت على النباتات في ثلاث تركيبات منها المساحيق القابلة للبلل و الكبريت الغروي و كبريت الجير و هي لها فعالية جيدة ضد مجموعة واسعة من أمراض البياض الدقيقي وكذلك البقع السوداء. على الرغم من أن الألمنيوم ليس له دور في الدورات البيولوجية ، إلا أن سمية الألمنيوم للحيوانات و النباتات محدودة ، قد يكون استخدام الألمنيوم كمبيد للأفات منخفضاً حالياً ولكنه يمكن استخدامه من ضمن المبيدات الحشرية أو المبيدات الفطرية أو مبيدات القوارض ، الأنثيمون هو معدن سام مشابه للتسمم بالزرنيخ. أنتمونيل طرطرات البوتاسيوم هو مبيد حشري يحتوى الأنثيمون ، تم استخدامه كسم للنمل و السيطرة على العثة ، الزرنيخ له دور أساسي في دورات الحياة ، و مع ذلك فإن الزرنيخ سام للغاية عند مستويات تركيزات مرتفعة ، تم استخدام الزرنيخ كمبيدات حشرية و مبيدات فطريات و مبيدات أعشاب ، في حين أن البورون عنصر منخفض السمية للحيوانات ، إلا أنه سم مميت للحشرات الزاحفة ، يمكن استخدامه أيضاً كمطهر و مبيد للأعشاب و مبيد فطريات. البورون هو عنصر غذائي نباتي أساسي ، و تستخدم مركبات البورون مثل البوراكس و حمض البوريك كسماد في الزراعة ، البورات لها سمية منخفضة على الثدييات (مثل ملح الطعام) ، ولكنها أكثر سمية للمفصليات ، حمض البوريك و أملاحه لها تأثير قوي كمبيدات للأعشاب و الفطريات ، يتم تطبيقه بشكل أساسي في مكافحة الآفات المفصلية كالنمل الأبيض ، و النمل أكل الخشب ، و خنافس المسحوق ، و الفطريات المتعفنة في الأخشاب و في إدارة الآفات المزعجة و كعلاج للشقوق و كطعم للنمل و الصراصير ، الكادميوم معدن شديد السمية ، يتنافس الكادميوم مع امتصاص بعض العناصر الأساسية مثل الحديد و الزنك و النحاس ، قد يتداخل العنصر أيضاً مع إطلاق الحديد ، يتسبب ابتلاع الكادميوم في ظهور أعراض مثل الغثيان و اللعاب و القيء يليه الإسهال مع الانزعاج البطني و الآلام ، يتراكم الكادميوم في جسم الإنسان والذي يتجلى في الفشل الكلوي مع تلين العظام أو هشاشة العظام الشديدة ، تم ذكر الكادميوم كمبيد للفطريات في شكل كبريتات ملح الكادميوم - الكالسيوم - النحاس - الزنك - الكبريتات التي تم الحصول عليها عن طريق خلط المكونات المناسبة ، تم تسويق هذا المستحضر على شكل مسحوق قابل للبلل بنسبة ٩٠٪ لمكافحة عدد من أمراض النبات ، الشق الحامضي (الكلوريد) هو شق غذائي أساسي لعملية التمثيل الغذائي ، كلوريد الصوديوم له تأثيرات فطرية و كمبيدات للجراثيم عند التركيزات العالية نسبياً ، يلعب النحاس دوراً مهماً للغاية في حيوية الخلية الحية ، يستخدم النحاس كمبيد للفطريات و الطحالب و يستخدم كمطهر لبذور القطن و مبيد للحشائش ، كبريتات النحاس يستخدم لمنع البياض الدقيقي و البقع السوداء من الورود ، تحتوي الفلوريدات على أعلى نشاط بيولوجي بين الهاليدات ، تم استخدام فلوريد الصوديوم و البوتاسيوم و الأمونيوم كمطهرات للخشب و أيضاً كعناصر للسيطرة على العثة ، الرصاص معدن سام للغاية (سواء تم استنشاقه أو ابتلاعه) ، عادة ما يستخدم زرنيخ الرصاص كمبيد حشري ، يتم استخدامه أحياناً للتحكم في هوبر أوراق نبات البطاطس و طارد لخنائس البزاع في مختلف الخضروات و النباتات المزهرة ، يدخل الزئبق البيئة نتيجة للانهيار الطبيعي للمعادن في الصخور و التربة من خلال التعرض للرياح و المياه ، يستخدم كلوريد الزئبق الأحادي و الثنائي ضد الفطريات ، البعوض ، وديدان الأرضية ، وديدان الكرنب ، وديدان البصل و كسم للفئران ، تتفوق مركبات الزئبق العضوي إلى حد كبير على المركبات غير العضوية في التأثير كمبيدات للجراثيم و الفطريات و يمكن أن تكون مركبات السلسلة الأليفاتية مبيدات فطرية أكثر قوة ، و مركبات السلسلة العطرية هي مبيدات جراثومية أقوى ، الفوسفور الغير العضوي ضروري لجميع أشكال الحياة المعروفة ، تم صنع المعاجين المحتوية على عنصر الفسفور عن طريق طحن الفوسفور الأصفر في وجود الماء و الدقيق و الغليسرين كمكون ضد الصرصور الأمريكي ، يعتبر السيلينيوم من المغذيات الدقيقة الأساسية للحيوانات ، ولكنه سام في الجرعات الكبيرة ، تم اختبار مركبات السيلينيوم كمبيدات حشرية ، ولكن بسبب سميتها للإنسان ، لا يوصى باستخدامها على المحاصيل المعدة للاستهلاك البشري أو الحيواني. يمكن لسيلينات الصوديوم في التربة قتل حشرات المن التي تتغذى على النباتات و عند وضعها على المحاصيل مثل القرنفل و الأقحوان فإنها تكون سامة لبعض سلالات سوس العنكبوت ، السليكون عنصر أساسي للحياة ، و تحتج الحيوانات فقط كميات ضئيلة منه ، تم استخدام فلوروسيليكات الصوديوم كغبار و رذاذ في السيطرة على بعض الحشرات في المحاصيل الحقلية ، كمادة سامة في دودة القصب ، و الكركيت ، و الطعوم الجندب و هي فعالة كعامل ضد عثة الأقمشة الصوفية ، يعد الكبريت عنصرًا أساسيًا لجميع أشكال الحياة ، ولكنه دائماً ما يكون في شكل مركبات كبريتية عضوية أو كبريتيدات معدنية ، يستخدم العنصر في صناعة الأسمدة و مبيدات الحشرات و مبيدات الفطريات ، عند وجود غبار عنصر الكبريت على شكل مسحوق ، فإنه يكون مبيد فطري شائع يستخدم للسيطرة على مسببات الأمراض في العنب و الفراولة و العديد من الخضروات و العديد

من المحاصيل الأخرى ، يتم إستخدام الكبريت على النباتات في ثلاث تركيبات منها المساحيق القابلة للبلل ، مثل الكبريت الغروي وكبريت الجير و لها فعالية جيدة ضد مجموعة واسعة من أمراض البياض الدقيقي وكذلك البقع السوداء.