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Inorganic Insecticides used in Landscape Settings and Insect Pests

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Abstract Tremendous benefits have been derived from the use of insecticides in agriculture, forestry, public health and the domestic spheres. Insecticides may be classified in a number of ways and these classifications can provide useful information about chemical's chemistry, how they work, and what they target. Insecticides fall into two types; inorganic and organic, organic molecules always contain carbon and inorganic do not have carbon-base. This article contains brief descriptions of some commonly used inorganic insecticides. Inorganic is a category of insecticides that lack carbon, being instead of mineral origin. Typically they are crystalline and applied as dusts or baits. The earliest chemical pesticides are inorganics, and included substance such as sulfur, lime, diatomaceous earth, borate, silica, and sodium fluoride employed against a broad range of insect pests. These materials vary from moderately toxic to quite toxic and tend to be quite persistent. Diatomaceous earth is powdered remains of fossilized diatoms and has extremely small but sharp protrusions that severely injure insects when they crawl over it. New insecticides require extensive laboratory and field testing and may take about few years to reach market. A pesticide company has to identify uses, test effectiveness and provide data on chemical structure, production, formulation, fate, persistence, and environmental impacts of a product. Extreme care should be taken to apply these pesticides or to clean application equipment near bodies of water.

Keywords Inorganic Insecticides, Agriculture, Public Health, Chemical Pesticides

1. Introduction

Because of a growing world population, there is pressure to increase and preserve the food supply by using insecticides and other agricultural chemicals. Insecticides are biocides designed to be toxic to particular groups of organisms like insects. Throughout history, various types of pests including insects and other biological organisms have bothered human's food or threatened human's health. The concept of insecticides is not new and the people have been using insecticides for thousands of years to try to control these pests. The humans used sulfur to control insects and mites, and used mercury and arsenic compounds to control body lice and other pests. Further, sulfur has been referred to use for fumigating of and by using of arsenic to control garden pests. The people used oil and other materials to protect themselves, their livestock and their crops from various pests. And people in various cultures have used smoke, salt, spices and insect-repelling plants to preserve food and keep pests away [1].

By chemical nature, one traditional classification of insecticides places them in one of two groups like organic and inorganic. Organic insecticides are based on chemicals having carbon as the basis of their molecular structure. The chemicals in organic pesticides are more complex than those of inorganic insecticides and usually do not dissolve easily in water. Inorganic pesticides are simpler compounds. They have a crystalline, salt-like appearance, are environmentally stable and usually dissolve readily in water. Inorganic insecticides are those that do not contain carbon. Usually they are white crystals in their natural state, resembling the salts. They are stable chemicals, do not evaporate and are usually water soluble. Inorganic insecticides are of mineral origin, mainly compounds of antimony, boron, copper, fluorine, mercury, selenium, sulfur, thallium and zinc, and elemental phosphorus and sulfur. Antimony potassium tartrate is a white powder soluble in water. It is sometimes used as the toxic agent in ant poisons and for the control of thrips. Arsenical compounds are the most widely used inorganic insecticides. Arsenic trioxide, also called arscnious oxide, is a white crystalline material sometimes referred to as white or gray arsenic. It is the starting material in the manufacture of arsenical compounds used as plant insecticides and it is sometimes used in weed killers. Arsenicals have included the copper arsenate, Paris green, lead arsenate and calcium arsenate. The arsenicals uncouple oxidative phosphorylation, inhibit certain enzymes that contain sulfhydryl (-SH) groups, and coagulate protein by causing the shape or configuration of proteins to change. The calcium arsenate that is commercially sold as an insecticide is not a single chemical compound, but a complex mixture of several calcium arsenates and an excess of calcium hydroxide. Others, like insecticidal soap products are allowed for use in certified state and federal organic food production programs, but are synthesized by a chemical reaction involving potassium salts and long-chained fatty acids, thus not of natural origin [2-6].

Several other inorganic compounds have been used as insecticides including mercury, boron, thallium, arsenic, antimony, selenium and fluoride. The inorganic fluorides were sodium fluoride, barium fluosilicate, sodium silicofluoride and cryolite. Cryolite has returned in recent years as a relatively safe fruit and vegetable insecticide, used in integrated pest management programs. The fluoride ion inhibits many enzymes that contain iron, calcium and magnesium. Several of these enzymes are involved in energy production in cells, as in the case of phosphatases and phosphorylases. Boric acid, used against cockroaches and other crawling household pests has also returned in uses. As a salt, it is non-volatile and can remain effective as long as it is kept dry and in adequate concentration. Consequently, it has the longest residual activity of any insecticide used for crawling household insects, and is quite useful in the control of all cockroach species when placed in wall voids and other protected or difficult to reach sites. Its function is to act as a stomach poison and insect cuticle wax absorber. Sodium borate resembles boric acid in its action. This water-soluble salt is used to treat lumber and other wood products to control decay fungi, termites and other wood infesting pests. The other group of inorganics is the silica gels or silica aerogels that is alight, white, fluffy, silicate dusts used for household insect control. The silica aerogels kill insects by absorbing waxes from the insect cuticle, permitting the continuous loss of water from the insect body, causing the insects to become desiccated and die from dehydration [7-12].

Insect pests management is always changing and anyone cannot predict its future. In fact, even in the same time period, people have different ideas about how pest management should be carried out. The following information is extracted from literature on inorganic insecticides in main use to enhance their effectiveness in pests control.

1.1. Sulfur

Sulfur, mentioned in the introduction, is very likely the oldest known, effective insecticide. Sulfur and sulfur candles were burned by our great-grandparents for every conceivable purpose, from bedbug fumigation to the cleansing of a house just removed from quarantine of smallpox. Today, sulfur is a highly useful material in integrated pest management programs where target pests specificity is important. The elemental sulfur has been used as an acaricide/ miticide and fungicide on orchard, ornamental, vegetable, grain and other crops. It is prepared as a dust in various particle sizes. Sulfur dusts are especially toxic to mites of every variety, such as chiggers and spider mites, and to thrips and newly-hatched scale insects. Sulfur dusts and sprays are also fungicidal, particularly against powdery mildews. However, elemental sulfur is irritating to the skin, and airborne dust is irritating to the eyes and the respiratory tract. In hot, sunny environments, there may be some oxidation of foliage-deposited sulfur to irritating gaseous sulfur oxides, which are very irritating to the eyes and respiratory tract. Ingested sulfur powder causes catharsis (dehydration and electrolyte depletion caused by diarrhea), and has been used medically (usually with molasses) for that purpose. Some hydrogen sulfide is formed in the large intestine and may present a degree of toxic hazard [13].

1.2. Silica (SiO_2)

This acts as a desiccant and strips off the waxy coating off the cuticle of the insect thus causing suffocation. This material also has a tremendous surface area which explains why it is a good absorbent. The silicified meaning is infiltration or replacement of organic tissues or of other minerals such as calcite by silica. Nano-silicaLD_{50} found to be 212.045 ppm with slope 4.553, is applied in six doses100, 150, 200, 250, 300, and 350 ppm of 50 ml/plant, to neonates of *Spodopteralittoralis* exposed daily to tomato leaves. Results of treatment of hydrophobic nano-silica in larval test indicated high toxic action at all concentrations used parallel with concentrations. High resistance in tomato plants is found against this insect-pest especially at 300, 350 ppm, respectively [14].

1.3. Aluminum Phosphide

Aluminum phosphide is a highly toxic inorganic compound with the chemical formula AlP and used as a wide band gap semiconductor and a fumigant. This colorless solid is generally sold as a grey-green-yellow powder due to the presence of impurities arising from hydrolysis and oxidation. Aluminum phosphide crystals are dark grey to dark yellow in color and have a zincblende. Aluminum phosphide is used as a rodenticide, insecticide and fumigant for stored cereal grains. It is mainly used to kill small verminous mammals such as moles and rodents. Its tablets or pellets, known as ‘wheat pills’, typically also contain other chemicals that evolve ammonia which helps to reduce the potential for spontaneous ignition or explosion of the phosphine gas [15-18].

Aluminum phosphide is used as both a fumigant and an oral pesticide. As a rodenticide, aluminum phosphide pellets are provided as a mixture with food for consumption by the rodents. The acid in the digestive system of the rodent reacts with the phosphide to generate the toxic phosphine gas. Other pesticides similar to aluminum phosphide are zinc phosphide and calcium phosphide. In this application, aluminum phosphide can be encountered under various brand names. It is used as a fumigant when other pesticide applications are impractical and when structures and installations are being treated, such as in ships, aircraft, and grain silos. All of these structures can be effectively sealed or enclosed in a gastight membrane, thereby containing and concentrating the phosphine fumes. Fumigants are also applied directly to rodent burrows for pest controlling [19-20].

1.4. Boric Acid

Boric acid(H_3BO_3)also called hydrogen borate, boracic acid, orthoboric acid and *acidum boricum*, is a weak, monobasic Lewis acid of boron often used as an antiseptic, insecticide, flame retardant, neutron absorber, or precursor to other chemical compounds. It exists in the form of colorless crystals or a white powder that dissolves in water. When occurring as a mineral, it is called sassolite. It is found natively in its free state in some volcanic, its salts are found in seawater and also found in plants, including almost all fruits. Boric acid is used for incorporating into baits for some ant control and for control of cockroaches. It has been used as an ant bait ingredient, but can cause phytotoxicity when applies to the landscape. Boric acid is registered as an insecticide for control of termites, fire ants, fleas, silverfish, and many other insects. The product is generally considered to be safe to use in household kitchens to control cockroaches and ants. It acts as a stomach poison affecting the insects' metabolism, and the dry powder is abrasive to the insect's exoskeletons [21-22].

In combination with its use as an insecticide, boric acid also prevents and destroys existing wet and dry rot in timbers. It can be used in combination with an ethylene glycol carrier to treat external wood against fungal and insect attack. It is possible to buy borate-impregnated rods for insertion into wood via drill holes where dampness and moisture is known to collect and sit. It is available in a gel form and injectable paste form for treating rot affected wood without the need to replace the timber. Concentrates of borate-based treatments can be used to prevent slime, mycelium, and algae growth, even in marine environments. Boric acid is added to salt in the curing of cattle hides, calfskins and sheepskins. This helps to control bacteria development, and helps to control insects. In agriculture boric acid is used to treat or prevent boron deficiencies in plants [23].

1.5. Scheele's Green

Scheele's green, also called schloss green, is chemically a cupric hydrogen arsenite (also called copper arsenite or acidic copper arsenite). It is chemically related to Paris green that is a yellowish-green pigment and in the past it is used in some paints, but has since fallen out of use because of its toxicity and the instability of its color in the presence of sulphides and various chemical pollutants. Scheele's green is used as an insecticide, together with Paris green. Despite evidence of its high toxicity, Scheele's green is also used as a food dye for sweets such as green blancmange. Fungi genera such as *Scopulariopsis* or *Paecilomyces* release arsine gas, when they are growing on a substance containing arsenic. Under wet conditions, the mold *Scopulariopsis brevicaulis* produced significant amounts of methyl arsines via methylation of arsenic-containing inorganic pigments, especially Paris green and Scheele's green. Scheele's green is a chemically simpler, less brilliant, and less permanent, synthetic copper-arsenic pigment used for a rather short time before Paris green is first prepared [24-25].

1.6. Paris green (Copper Acetate Triarsenite)

Paris greenis an inorganic compound more precisely known as copper acetoarsenite. It is a highly toxic emerald-green crystalline powder that has been used as a rodenticide and insecticide, and also as a pigment, despite of its toxicity. The color of Paris green is said to range from a pale, but vivid, blue green when very finely ground, to a deeper true green when coarsely ground. Paris green has been also used as an insecticide for produce such as apples, where it is blended with lead arsenate. This toxic mixture is said to have burned the trees and the grass around the trees. Paris green has been also heavily sprayed by airplane in to control malaria [26].

1.7. Lead hydrogen arsenate

Lead hydrogen arsenate also called lead arsenate, oracid lead arsenate has chemical formula $PbHAsO_4$, and is an inorganic insecticide used primarily against the potato beetle. As an insecticide, it is earliest used against the gypsy mot has a less soluble and less toxic alternative to the then used Paris green. It also adheres better to the surface of the plants, further enhancing and prolonging its insecticidal effect. Lead arsenate is widely used in many areas, principally against the codling moth. It was used mainly on apples, but also on other fruit trees, gardens, crops, turf grasses, and against mosquitoes. In combination with ammonium sulfate, it is used as a winter treatment on lawns to kill crab grass seed. Lead arsenate is also used in the early part of twentieth century for controlling pests of cranberry (fire worm, cranberry girdler).The search for a lead arsenate substitute is commenced, when it has been found that its residues remain in the products despite of washing their surfaces. Alternatives to use of lead arsenate are found to be less effective or more toxic to plants and animals. The morel mushrooms growing in old apple orchards that have been treated with lead arsenate may accumulate levels of toxic lead and arsenic that are unhealthy for human consumption [27-28].

1.8. Diatomaceous Earth

Diatomaceous earth, also known as D.E., or diatomite, is a naturally occurring, soft, siliceous sedimentary rock that is easily crumbled into a fine white to off-white powder. It has a particle size ranging from less than 3 micrometers to more than 1 millimeter, but typically 10 to 200 micrometers. Diatomaceous earth consists of fossilized remains of diatoms, which is a type of hard-shelled algae. Diatomite are formed by the accumulation of the amorphous silica (opal, $SiO_2 \cdot nH_2O$) remains of dead diatoms (microscopic single-celled algae) in lacustrine or marine sediments. The fossil remains consist of a pair of symmetrical shells or frustules. In order to be effective as an insecticide, diatomaceous earth must be uncalcinated (i.e., it must not be heat-treated prior to application) and have a mean particle size below about 12 µm [29-30]. Diatomaceous earth is available commercially in several formats:-

- Crushed silica-containing shells of microorganisms called diatoms, the sharply serrated crystals scarify an insect’s waxy outer coat destroying its moisture balance. Inhalation of diatomaceous earth dust can cause silicosis of the lungs.

- Silica gel- silica aerogel + ammonium fluosilicate to 3% fluorine content absorbs oils (oil absorption 40-70%) leading to moisture imbalance.
- Granulated diatomaceous earth is a raw material simply crushed for convenient packaging.
- Milled or micronized diatomaceous earth is especially fine (10µm to 50µm) and used for insecticides.
- Calcined diatomaceous earth is heat-treated and activated for filters.

Diatomite is used as an insecticide, due to its abrasive and physico-sorptive properties. The fine powder absorbs lipids from the waxy outer layer of insect's exoskeletons, causing them to dehydrate. Arthropods die as a result of the water pressure deficiency, based on Fick's law of diffusion. This also works against gastropods and is commonly employed in gardening to defeat slugs. However, since slugs inhabit humid environments, its efficacy is very low. It is sometimes mixed with an attractant or other additives to increase its effectiveness. Medical-grade diatomite has been studied for its efficacy as a deworming agent in cattle; in both studies cited the groups being treated with diatomaceous earth do not fare any better than control groups. It is commonly used in lieu of boric acid, and can be used to help control and possibly eliminate bed bug, house dust mite, cockroach, ant and flea infestations. This material has wide application for insect control in grain storage. Natural freshwater diatomaceous earth is used in agriculture for grain storage as an anticaking agent, as well as an insecticide. It is approved as a feed additive to prevent caking and may be used as a natural anthelmintic (dewormer), although studies have not shown it to be effective. Some farmers add it to their livestock and poultry feed to prevent the caking of feed. Food grade diatomaceous earth is widely available in agricultural feed supply stores [31].

1.9. Arsenic

Arsenic is a natural element having both metal and nonmetal physical/chemical properties. Sodium arsenite, calcium arsenite, sodium arsenate, calcium arsenate and zinc arsenatehave been registered and used as insecticides, particularly as ant baits. Copper arsenate ($Cu_3(AsO_4)_2.4H_2O$, or $Cu_5H_2(AsO_4)_4.2H_2O$), also called copper orthoarsenate, tricopper arsenate, cupric arsenate, or tricopperorthoarsenate, is a blue or bluish-green powder insoluble in water and alcohol and soluble in aqueous ammonium and dilute acids. Copper cyanide is an inorganic compound with the formula CuCN. This off-white solid occurs in two polymorphs; impure samples can be green due to the presence of Cu(II) impurities. Copper arsenate is an insecticide used in agriculture, and is also used as a herbicide, fungicide and a rodenticide. It is also used as a poison in slug baits. Copper arsenate can also be a misnomer for copper arsenite, especially when meant as a pigment [32].

1.10. Chromated copper arsenate

Chromated copper arsenate is a wood preservative that has been used for timber treatment and is a mix of chromium, copper and arsenic formulated as oxides or salts, and is recognizable for the greenish tint it imparts to timber. The chromium acts as a chemical fixing agent and has little or no preserving properties; it helps the other chemicals to fix in the timber, binding them through chemical complexes to the wood's cellulose and lignin. The copper acts primarily to protect the wood against decay fungi and bacteria, while the arsenic is the main insecticidal component of CCA, providing protection from wood attacking insects including termites and marine borers. It also improves the weather-resistance of treated timber and may assist paint adherence in the long term. The chromium acts as a chemical fixing agent and has little or no preserving properties; it helps the other chemicals to fix in the timber, binding them through chemical complexes to the wood's cellulose and lignin. The copper acts primarily to protect the wood against decay fungi and bacteria, while the arsenic is the main insecticidal component of chromated copper arsenate, providing protection from wood attacking insects including termites and marine borers. It also improves the weather-resistance of treated timber and may assist paint adherence in the long term [33-34].

2. Inorganic Insecticides and Food Safety

Inorganic Insecticides are biocides designed to be toxic to particular groups of organisms and they can have considerable adverse environmental effects, which may be extremely diverse. Some insecticides are highly specific and others broad spectrum; both types can affect terrestrial wildlife, soil, water systems, and humans. The most important aspect of insecticides is how they affect humans and animals. There is increasing anxiety about the importance of small residues of insecticides, often suspected of being carcinogens or disrupting to endocrine activities, in drinking water and food. Similar calculations are made for exposure to insecticides that may reach drinking water through percolation into groundwater or runoff into waterways. The movement of insecticides into surface and groundwater is well documented, wildlife is affected, and human drinking water is sometimes contaminated beyond acceptable safety levels. Insecticides have some of their most striking effects on birds, particularly those in the higher trophic levels of food chains, such as bald eagles, hawks, and owls. These adverse effects of pesticides on humans and wildlife have resulted in research into ways of reducing pesticide use. The most important of these is the concept of integrated pest management (IPM). This combines minimal use of the least harmful pesticides, integrated with biological and cultural methods of minimizing pest losses. It is linked with using pesticides only when threshold levels of pest attacks have been identified. There is also a move toward sustainable agriculture which aims to minimize use of insecticides based on a systems approach [35-40].

3. Conclusion

The earliest insecticides are inorganic substances such as sulfur, mercury, lead and arsenic, and some of these inorganic insecticides are still used today. Inorganic pesticides do not contain carbon and are often derived from mineral ores (copper, sulphur) or their salts (e.g., copper sulphate, sodium chlorate, ferrous sulphate). Most insecticides that have carbon in their chemical structure are made from petroleum-based compounds. Some insecticides (e.g., boric acid, silica dioxide or diatomaceous earth/ D.E.) contain no carbon molecules so they are technically inorganic molecules. Thus, when used in an organic pest control program, they are inorganic organics. The drawback for many of these products is their high rates of application, lack of selectivity and phytotoxicity. Today the pest management toolbox has expanded to include use of genetically engineered crops designed to produce their own insecticides or exhibit resistance to broad spectrum products or pests. In addition the use of Integrated Pest Management (IPM) systems which discourage the development of pest populations and reduce the use of agrochemicals have also become more widespread. These changes have altered the nature of pest control and have the potential to reduce and change the nature of agrochemicals used.

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