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DISPOSAL AND TREATMENT OPTIONS FOR THE WASTE PESTICIDES

The term *pesticide* describes a chemical compound capable of being used to control the effect of pests on humans, agricultural crops, commercial operations and households. These compounds are selectively sought or formulated for specific toxic properties. The hazards that various toxic compounds may present for us and environment vary greatly. The risks associated with the use of pesticide are: (1) acute poisoning resulting from the handling of toxic materials and (2) chronic risks from long-term exposure to small quantities of toxic materials or from ingestion of them.

This paper presents pesticide classification and some possibilities of the treatment methods for waste pesticides, e.g., incineration, stabilization, photolysis, ozone oxidation as well as toxicity reduction by chemical means. The applicability of these methods must be evaluated based on the specific type of pesticide compound to be treated or disposed.

1. INTRODUCTION

The term *pesticide* describes a chemical compound capable of being used to control the effect of pests on humans, agricultural crops, commercial operations and households.

The stored pesticides, not suitable for use, still pose human health hazards. The problem is also that certain pesticides are active for a long time (figure 1). The most efficient and inexpensive method for dealing with unused pesticides is recycling of the product either as it was intended or in an alternative way. By using the pesticide the economic value of the product is retained and obviates the need to purchase new product. Recycling also allows us to avoid the effort and expense associated with destruction. Reuse will depend on whether a use exists for a product, whether it is still approved by the appropriate regulatory authorities and on its quality. If recycling is not

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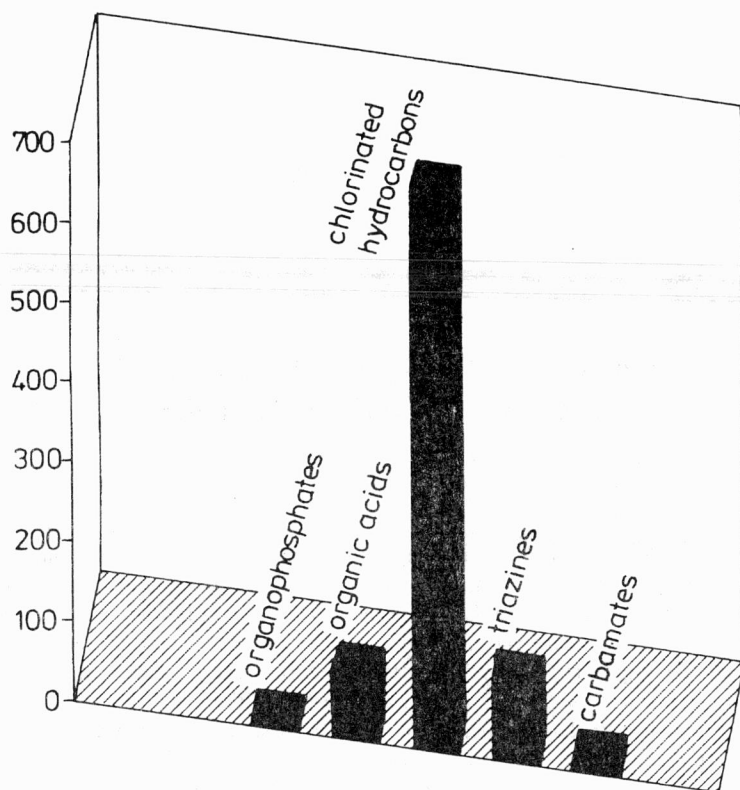


Fig. 1. Half-time (in weeks) for biological activity of some pesticides

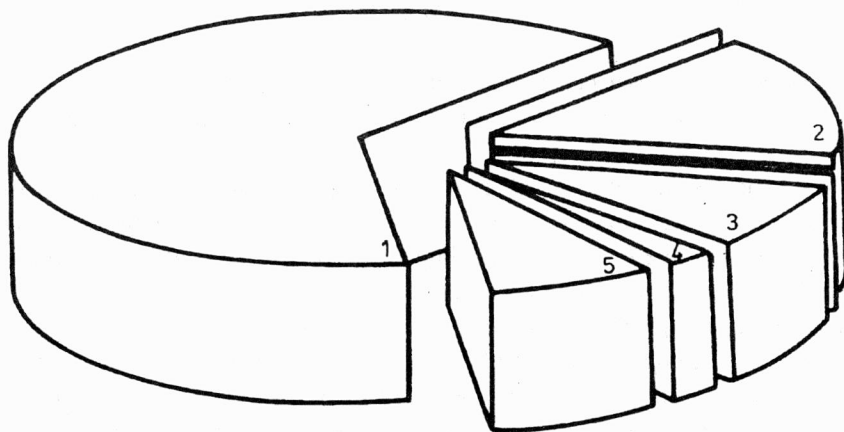


Fig. 2. Number of diseases caused by pesticides in industrial sector:
 1— organophosphates, 2— halogen derivatives, 3— sulfur compounds,
 4— compounds with As and Pb, 5— other pesticides

feasible then disposal by destruction or treatment that immobilizes the pesticides may be the only recourse. Also other treatment technologies can be useful in some cases to lessen the risk of hazards the pesticides pose to people and the environment.

The hazards that various toxic compounds may present for us vary greatly (figure 2). The risks associated with the use of pesticide are (1) acute poisoning resulting from the handling of toxic materials and (2) chronic risks from long-term exposure to small quantities of toxic materials or from ingestion of them.

2. CLASSIFICATION OF PESTICIDES

Most pesticides can be divided into one of following chemical classes:

1. Inorganic/metallo-organic compounds. These compounds contain heavy metal ions such as arsenic, copper, mercury, cadmium or antimony bound to carbon; inorganic fungicides are, e.g., copper oxychloride, barium polysulfide, sulfur, etc. The toxicity of these compounds can be reduced by relatively simple chemical means. Detoxifying procedures involve converting the metal ions to insoluble compounds, either to hydroxides, carbonates or to sulfides. Generally, the procedure involves dissolving the pesticides in water and rising pH to approximately 10 with sodium hydroxide and then recovering the precipitate. In the case of mercury, the pH adjustment is followed by addition of sodium thiosulfate which results in formation of mercuric sulfide [1].

2. Phosphorus-containing compounds. These compounds can be further divided into three common chemical classes: phosphates, phosphonates and phosphonodioxates. The group includes insecticides such as parathion, malathion, diazon, etc. Toxicity values of these pesticides range from high toxicity for parathion to low toxicity in the case of malathion. The organophosphorus pesticides can be absorbed dermally, orally or through inhalation of vapours. The pesticides of this group attack cholinesterase – an enzyme in the blood that is necessary for proper nerve functioning.

Most of these compounds can be detoxified similarly as the above group. Hydrolysis of any one of the bonds between the phosphorus atom and either an acidic group or a basic group in the structure will reduce or destroy biochemical effects of a compound. This is usually accomplished by treating with a strong base. However, some compounds react in neutral or acidic media. The rates at which hydrolysis occurs is dependent upon various conditions such as temperature and reactant concentrations [2].

3. Nitrogen-containing compounds. The nitrogen-containing class of pesticides is extremely diverse. Over 200 commercial pesticide formulations belong to this group. These compounds can generally be grouped into the following classes: carbamates, amides and anilides, ureas and uracils, triazines, quaternary ammonium compounds and nitrocompounds. For example, carbamates include aldicarb, carbaryl, carbofuran insecticides or cycloate and diallate herbicides. They differ in action from organophosphorous compounds in that the effect on cholinesterase is brief because the carbamates

are broken down in the body rather rapidly. Carbamate pesticides can be absorbed through the skin as well as by breathing or swallowing.

Because of the chemical diversity of these compounds, any generalizations about detoxification reactions cannot be made. Hydrolysis by acids or bases is an acceptable method for many of these, but cannot be recommended universally because exposure to extreme pH conditions for some of these compounds can produce compounds of similar or even high toxicity [1], [3].

4. Halogenated compounds. The chlorinated organic compounds have a wide variety of properties and uses and present some very difficult disposal problems. This group contains some of the most environmentally persistent pesticides (excluding the permanently persistent heavy metals) such as benzene hexachloride, dieldrin, DDT, DDD, HCH-Lindane. Various methods for detoxification and destruction of chlorinated compounds have been developed. We present the following two methods:

Reactions with bases. Dehalogenation as a result of reactions with a strong base can reduce the toxicity of some compounds. This method can be made more efficient through the use of metal catalysts such as iron, copper, manganese, chromium and aluminium [1], [4].

Reduction by active metals. The reduction ability of some compounds with active metals has been known for several years. For example, zinc, hydrochloric acid and aqueous solution of ethanol can successfully be applied in reducing DDT. Sodium has also been used to dechlorinate DDT in alcoholic solution as well as lithium in liquid ammonia [3], [4].

5. Sulfur-containing compounds. In addition to many sulfur-containing compounds discussed above, we describe a number of other compounds with sulfur-containing functional groups as their primary biological unit. The major sulfur-containing classes include: sulfides, sulfoxides and sulfates, sulfites and xanthalates, sulfonic acids and derivatives, thiocyanates.

Most of these compounds do not pose serious health threats. Incineration is generally most effective but must be done in incinerators equipped with the appropriate scrubbers to remove sulfur dioxide. Many of these compounds can be detoxified by hydrolysis or oxidation or a combination of these. A common oxidizing agent, when used in alkaline solution, is sodium hypochlorite, the principal ingredient of household bleach. Many of these compounds are resistant to oxidation, hence incineration may be the only disposal recourse [4], [5].

3. TREATMENT METHODS FOR PESTICIDES

3.1. INCINERATION

High-temperature incineration is the preferred and most common method allowing a safe disposal of the majority of waste pesticides. In the process, pesticides are thermally

oxidized into inorganic and harmless solid and gaseous products. Solid phase products are collected and disposed appropriately and gas phase components are emitted into the atmosphere following pretreatment. Efficient incineration requires an adequate supply of oxygen, high temperature, sufficient residence time in the combustion chamber and a measure of turbulence in the combustion process. The higher the temperature to which the pesticides are exposed, the greater the degree of destruction will occur. Chlorinated pesticides are among the most stable pesticide compounds and require temperatures in the range of 1200 °C for complete incineration. The longer the pesticides are kept at these temperatures, the more complete will be the degree of their destruction. At least two second residue time for the gas phase is generally necessary. Destruction efficiency is also increased by inducing turbulence in the combustion chamber for greater contact between the pesticides and oxygen and to reduce the potential of temperature gradients or cool spots from forming [6].

Pretreatment of gaseous emissions is performed by cooling the flue gases. Scrubbing of the gas stream in an alkaline unit removes acidic gases such as hydrogen chloride and is followed by electrostatic treatment or other methods to remove fine dust particulates.

Incineration can be accomplished in specially designed incinerators for hazardous waste or in preexisting high-temperature process facilities such as cement kilns. Specially built incinerators are designed to burn large amounts of hazardous waste and operate for long periods of time. These facilities are very expensive to build and operate. For this reason and because of unique siting criteria, relatively few such facilities are in existence. Disposal of wastes at these facilities requires high transportation and treatment costs and is of limited feasibility in smaller, less industrialized countries. Therefore, co-incineration at existing facilities may be the most practical approach.

Cement kilns provide ideal conditions for the destruction of pesticides because they operate at 1400–2000 °C and the residence time of the gas phase is between six and ten seconds. Cement-producing facilities utilize rotary kilns, a technology commonly used in hazardous waste incinerators. Co-firing liquid or semi-liquid combustible waste is relatively simple because pesticides can be used as a high-calorific fuel substitute and also allows the saving of fuel, reducing costs. Fortunately, cement product quality is relatively insensitive to the co-incineration of small quantities of organic wastes.

The co-firing process involves either mixing the pesticide in the primary fuel prior to its introduction to the burner or injecting the pesticide directly into the flame. Acidic gases generated during incineration are absorbed in the alkaline clinker produced by the cement process [7].

The principal advantages of using cement kilns are that these facilities are preexisting and are expensive to use. Depending on the specific types of pesticides to be disposed, emission scrubbers may not be required. However, the suitability of this method for disposal of solids may not be appropriate due to potential negative effects which solid materials may have on the final concrete product. Another disadvantage is that we are not able to incinerate many types of storage vessels in these facilities.

3.2. STABILIZATION AND SOLIDIFICATION

Many pesticides are not suitable for incineration, especially those containing heavy metals. In many cases, these materials will require pretreatment consisting in their chemical stabilization followed by placement into a landfill. Because the technology of pesticide disposal is relatively young, there is not a great deal of information about the applicability of stabilization technology to pesticides.

Stabilization and solidification processes are designed to improve the waste handling characteristics of the material and either to decrease the surface area across which pollutants can leach and limit their solubility or to detoxify the hazardous constituents of the pesticide.

Solidification is a process that mechanically binds the waste material into a block with high structural integrity and low permeability. Stabilization is a chemical process that limits the solubility of the contaminants or detoxifies them and may not produce a change in their physical characteristics [6].

Waste can be solidified by mixing with a variety of binders that are either inorganic or organic. Inorganic systems include hydraulic cements, lime, gypsum or pozzolans. Pozzolan systems consist in utilizing noncrystalline silica in fly ash and calcium in lime to produce a low-strength cementation. Physical entrapment of the contaminant is the primary mechanism of containment by formation of calcium silicate and aluminium hydrate compounds. Organic binders include epoxy, polyesters, asphalt and polyolefins such as polyethylene and polyethylene/polybutadiene. Solidification methods are often applied to wastes in their original drums. After mixing and settling, the final product is normally disposed of in the drum [8].

Stabilization processes are currently undergoing development and many are still in the experimental stage. Most research has been directed towards the treatment of soil or groundwater contaminated with pesticides.

3.3. PHOTOLYSIS

Photochemical processes utilize the energy contained in certain wavelengths of light to degrade certain types of chemicals. A light source and a reaction vessel are required for this process. Mercury vapour lamps are the most common light sources employed [9]. Photoreactor can be designed as a continuously stirred tank reactor. UV-lamps are installed in quartz wells inside the reactor or outside quartz windows in the sides of the reactor for aqueous waste treatment.

In soil treatment technique, UV lights with parabolic reflectors could be suspended over the soil to irradiate it. Water may have to be added to maintain the soil moisture content and to suppress dust generation. UV processes are commercially available and companies such as Photo-Catalysts, Veda, Inc. and Energy Environmental Engineering are active in the rapidly developing procedures of pesticide treatment based on photolytic degradation.

For direct UV photolysis in solution phase such factors as pH, dissolved oxygen level, light absorption characteristics and turbidity can strongly affect the photolysis performance. In a device for photolysis, photoreactor is the element of primary capital cost, and electric power used for artificial UV radiation [9] is expected to be the most significant operating cost.

3.4. OZONE OXIDATION

This method utilizes ozone gas as a powerful oxidizer to decompose wastes and has been used successfully for four pesticides: DDT, PCB, HCH and Malathion. In this case, ozone oxidation is combined with photolysis. One of the principal advantages in this method is low cost ozone production which can be obtained from air or oxygen.

The process is usually carried out in a specially constructed plant. The ozone generator is the principal piece of equipment required. Ozone is transferred to the waste in a tank using a ceramic or stainless steel diffuser. Turbulence is induced in the tank to promote mixing of the reactants [6].

Advantages of this method are as follows:

- ozone can be generated and used immediately with no storage or handling required,
- ozone is a very strong oxidizer (2.07 V), reacts with a large variety of organic compounds and does not form chlorinated compounds like traditional oxidizers.

Disadvantages include:

- capital costs are higher than in other oxidizing systems,
- low-molecular weight organics are resistant to ozone oxidation.

Total unit operating costs, which include capital related changes, will vary greatly for different aqueous streams depending on oxidant dosage, UV energy, system capacity and treatment efficiency.

Costs for treating excavated soils have been reported by Ensotech to range from 85 USD to 200 USD per tone [9].

4. CONCLUSIONS

In the last decades, there are adopted some approaches to stop manufacturing of such highly toxic compounds as arsenic and mercury or cyanide based pesticides and to develop only biopesticides – biologically degradable pesticides with low acute and chronic toxicity. Despite the fact that in most countries over the world the production of polychlorinated aromatic hydrocarbons has been restricted since 1970, certain amounts of pesticides still persist and can be found in nature even nowadays.

The most inexpensive and efficient method for dealing with unused, currently stored pesticides is their recycling.

If recycling is not feasible we can apply the other methods of pesticide destruction as e.g. high-temperature incineration, photolysis, ozone oxidation or chemical detoxification using hydrolysis, precipitation, reduction by active metals reactions, etc.

In some cases, solidification procedures consisting in mixing the waste pesticides with various organic or inorganic binders to entrap the environmental contaminants into stabilized matrix have to be employed. The selection of the mentioned methods is usually evaluated, depending on a specific type of pesticide.

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USUWANIE I OCZYSZCZANIE ODPADOWYCH PESTYCYDÓW

Termin „pestycyd” oznacza związek chemiczny, który jest używany do zwalczania szkodników żerujących na ludziach, roślinach użytkowych, a także w gospodarstwach domowych i zakładach przemysłowych. Związki te są syntetyzowane z powodu ich specyficznej toksyczności. Zagrożenia, jakie mogą stanowić różne związki toksyczne dla ludzi i środowiska, są bardzo zróżnicowane. Ryzyko związane z użytkowaniem pestycydów można zdefiniować jako: 1) ostre zatrucie podczas stosowania tych związków, 2) stałe zagrożenie wynikające z długiego wystawienia się na działanie małych ilości pestycydów lub połknięcia ich.

Przedstawiono klasyfikację pestycydów i pewne metody ich unieszkodliwiania, np. przez spalanie, stabilizację, fotolizę, utlenianie ozonem i redukcję chemiczną. Określając przydatność tych metod, musimy brać pod uwagę typ pestycydu, który ma być usunięty.