Introduction

The biological efficacy of pesticides gradually decreases with time. The pesticide shelf-life is the period of time that a pesticide can be stored before it deteriorates. Nearly all pesticides have a limited shelf-life. As part of modern pesticide formulation technology, packing methods and storage practice aim to prolong shelf-life as much as possible.

Manufactures indicate the shelf-life of the pesticide on the container, but many pesticides may still be usable long after the indicated shelf-life has expired.

Shelf-life is a function of several variables such as: time, sensitivity (temperature, moisture, light), formulation stability (dry, liquid, concentrated, ready to use), and container integrity (metal, glass, plastic, paper).

Stock turnover organization needs to take into account the time that pesticides may have been in transit between manufacture and reaching the store. Pesticides in sealed containers may change over time in two main ways:

- The active ingredient may change chemically and break down into products that may no longer have pesticide properties, thus decreasing the concentration of the original active ingredient.
- The formulation of the pesticide may break down and a precipitate of flakes, crystals or sludges may form, making it possible to mix or use in sprayers.

An organochlorine such as endosulfan is chemically very stable, but some formulations may break down more rapidly.

Organophosphates are much less stable and therefore generally have a shorter shelf-life.

Dust and wettable powder formulations tend to break down and cake together, as a result of high temperature, high humidity, strong sunlight or compaction under pressure, more than liquids in sealed containers.

Shelf-life protection for pesticides includes:

1- Storage in the original container tightly sealed.
2- Storage in a cool, dry, and ventilated area.
3- Keeping liquids above their recommended minimum temperatures.
4- Keeping solids from becoming damp.

As a general rule of thumb, two years is considered the maximum storage life for most pesticides, although there are many exceptions to this, such as diazinon has a shelf-life from 5-7 years, captan has a shelf-life about 3 years and dinocap has a shelf-life about 5 years….etc.

There may be substantial differences in the chemical composition of technical-grade products of the same active ingredient manufactured under different conditions, from different raw materials, or by different routes of synthesis. Resulting differences in impurity content may significantly affect the toxicological properties of pesticides products. Humans can be exposed to pesticides and their impurities through direct handling, re-entry of treated areas, contact with environmental residues, and dietary intake. Occupational and accidental exposure to these compounds should be elevated primarily on the basis of acute toxicity and mutagenicity, whereas in the case of dietary intake, the chronic toxicity should also be taken into account.

Technical pesticides, although be definition being "pure active ingredient", also may contain complex mixtures of other minor chemical components due to process variables, side reactions, and impurities in starting materials. Relevant impurities are those that may exhibit pronounced toxic effects compared to the active ingredient affect phytotoxicity or physical properties of formulations, result in undesirable residues in food, or cause environmental contamination. For some impurities, this may lead to the allocation of maximum concentration limits in technical-grade products.

The toxicological tests carried out with technical products of typical composition for registration purposes include assessment of toxic potency of the impurities present in the test material.

However, the composition of the technical product may vary, particularly with respect to impurities and potentially also the toxicity of the product, depending on the manufacturing process and sources of starting materials. The use of various adjuvants and carrier materials in the preparation of the formulation may also result in marked differences in storage stability of formulations. This is especially of concern in the case of generic pesticides, which may be produced and formulated by many manufactures under widely varying conditions, with different materials, and under a range of quality control standards. Pesticides being no longer protected by patents may be produced by any manufacturer under varying quality-control programs. Once a pesticide is being manufactured by several or many producers, the resulting price competition places a premium on the minimization of manufacturing costs (e.g., quality assurance, safety testing). Thus, generic manufacturing processes may only focus on assay of the active ingredient content of the technical material and not consider levels of impurities to meet the full specification. In these instances, the amount of lower-quality technical material used in the formulation may merely be adjusted so as to produce a formulated product within the specified limits of active ingredient.

The results of analysis of commercial products indicate that, not only may impurity levels be different from those in the original technical product; even the active ingredient content and physical properties of these generic products may often not meet the specification. One example is provided by a survey of 348 samples obtained by GTZ (Deutsche

Gesellschaft fur Technische Zusammenarbeit GmbH) from 21 developing countries in Latin America, Africa, and Asia during 1989 to 1994. One average, the active ingredient content of more than one-third (34%) of the tested products did not meet the FAO specification.

Now in Egypt there are many requirements for the registration of pesticides are specified according to ministerial decision number 622/2008, as follow:

These requirements are briefly summarized below:

A) Information and materials required for characterization of the composition of technical products:

1- Detailed information on the manufacturing process, toxic impurities and potential precursors of toxic impurities in raw materials.
2- Typical composition of the technical product (certified by a qualified laboratory) including positive identification of major (and all toxicologically or environmentally relevant impurities and characterization of minor impurities (>0.1%).
3- Analytical methods suitable for monitoring of batch-to-batch uniformity of technical-grade product, including "finger print" chromatograms indicating the relevant impurities, UV-Vis, IR, NMR, and MS spectra with assignments.
4- Analytical procedures and standards to determine the relevant impurities.

B) Information for the toxicological assessment of generic pesticides.

1- Certificate(s) of the original manufacturer on the composition of technical product(s) used for toxicological evaluations.
2- All toxicological studies for pesticide from GLP Lab.

C) Actions by central agricultural pesticides laboratory in Egypt.

1- Evaluate impurities in imported batches of technical materials before formulation, and it compare "fingerprints" obtained with suitable chromatographic and or spectrometric methods.
2- Evaluate all physical and chemical properties of pesticides, before registration, and this the minimum requirements for registration of pesticides in Egypt.

These requirements are agreement with the minimum requirements by [3], and with the principles outlined in FAO manual on specification of plant protection products 2006.

The aim of this study was conducted to investigate the effect of storage at different intervals of temperature and time on the following:

1- Stability of three commercial chlorpyrifos emulsifiable concentrate (EC) formulations (48% w/v) (manufactured from various companies), shelf-life and the formation of its impurity sulfotep.
2- Stability of three commercial malathion 57% w/v EC (manufactured from various companies), shelf-life and the formation of its impurities isomalathion, malaoxon, MeOOOPS-triester and MeOOSPS-triester.
3- Physical properties such as emulsion stability, pH values and free acidity for pesticides under investigation.

1. Stability of pesticides

For each 15° rise in temperature between 60° and 90 °F, the rate of disappearance of phosphamidon was increased by approximately 2 days [4].

When dursban (O,O-diethyl O-3,5, 6-trichoro-2-pyridyl phosphorothioate) was exposed to ultraviolet light or to sunlight, it underwent hydrolysis in the presence of water with the liberation of (3,5,6-trichloro-2-pyridinol). The 3,5,6-trichloro-2-pyridinol would undergo photodehalogenation with the formation of a series of diols, triols and tetrols which were readily oxidized forming a series of colored derivatives. These compounds, polyhydroxyl compounds, could be further oxidized resulting in the cleavage of the pyridiniol ring with the liberation of CO2 [5].

The radiation energy of the sunlight is absorbed by a pesticide molecule principally at a given wavelength. The energy might increase the translational, rotational, vibrational or electronic energy of the molecule. If enough energy was absorbed to interact with the electrons of the molecules an electronically excited molecule resulted. Energy might be lost by the molecule in a number of ways, one of which is chemical reaction [6].

The decomposition of some organophosphate insecticides by UV-light was more effective than bromine or N-bromo-succinimide for decomposition of nuvacron, sumithion, dursban, cyolane and cytrolane, and also that during the first half hour, UV-light enhanced insecticide toxicity to the cotton leafworm S. littoralis, however, after three hours the toxicity decreased [7].

The rate of photodecomposition of sumithion {O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate} in various solvents, in air, or deposits on silica gel chromoplats exposed to UV-light and sunlight was greatly dependent on the solvents used and the presence or absence of air, and also sumithion suffered very rapid decomposition on silica gel chromoplates exposed to sunlight or UV-light. The half life of sumithion was approximately 15 min. with UV-light and around 6 days with sunlight. The photodecomposition of 14C-sumithion applied to bean leaves (*Phaseolus vulgaris*), it was lost rapidly from leaf surfaces. The same products formed during exposure to sunlight and UV-light on silica gel chromoplats, were identified after exposure of sumithion on leaf surfaces of bean plant [8].

The stability of three different diazinon formulations after storage at 54 ^{0}C for two weeks studied by [9]. They found that only one dust formulation had deteriorated significantly in diazinon contents

When phosvel was exposed to UV-light it decomposed to give seven photodegradation products in addition to the parent compound. The compound decreased by 5, 10, 30 and 53 percent after exposure to UV-light for 0.5, 2, 6 and 24 hrs, respectively. He also found that phosvel gave five degradation products when exposed to sunlight either as thin dry film or as solution in methanol. The rate of loss of the insecticide residues in the solid form was faster than in methanol solution [10].

The ultraviolet irradiation of fenitrothion in oxygenated solutions produced isomerization, oxidation and solvolysis. In hexane, both the P=S and the aryl methyl group were oxidized to give fenitrooxon and formyl fenitrothion. Small amounts of dinitrofenitrothion were also formed. Irradiation in methanol gave carbomethoxy fenitrothion formed from oxidation followed by solvolysis. Isomerization of fenitrothion to its S-methyl isomer took place on a small scale in the solvents, however an S-aryl isomer was detected [11].

14C-labeled organophosphorus insecticide O-ethyl O-(4-methylthio phenylo) S-propyl phosphorodithioate (BAY. NTN-9306) degraded rapidly when exposed to sunlight as deposits on cotton foliage, glass surfaces, or in water solution. The half life of the compound was in each case less than 2 days. Exposure of water solution of the insecticide to > 280 nm artificial light resulted in very rapid degradation (half life < 2 hr) to the same major photoproducts as were generated by exposure to sunlight. Degradation pathways included oxidation of the methylthio sulfur to sulfoxide and sulfone derivatives, hydrolysis of the phosphorus-O-phenyl ester, oxidative desulfuration of the P=S moiety and undefined transformations leading to high polar products that increased in quantity with time of exposure [12].

A highly significant effect of temperature and relative humidity on the persistence of dursban and nuvacron. Nuvacron tended to be more affected by temperature than dursban at longer periods of exposure [13].

The irradiation with UV-light and sunlight, salithion and phenthoate were rapidly decomposed in acetone solution and on both silica gel and soil surfaces whereas both compounds fairly stable in water solution exposed to sunlight. Under the tested conditions, both salithion and phenthoate were decomposed predominantly by ways of oxidation of P=S to P=O, oxidation of the methylene or methin groups of benzyl moiety, cleavage of P-O-aryl and P-O-alkyl linkages and decarboxylation. Salithion was isomerized to S-benzyl salithion. On soil surfaces, the carboxy ester linkage of phenthoate was also hydrolyzed [14].

When the EC formulations of gardona, cyolane and dursban were exposed to sunlight, the materials deteriorated especially at longer periods. Cyolane and dursban suffered much more degradation than gardona. The average rates of recovery after exposure for 45 days were 50, 52 and 66.67% for dursban, cyolane and gardona, respectively. Sunlight greatly affected the biological effectiveness of dursban, cyolane and gardona. Also they found that EC formulations of gardona and cyolane were the most persistent insecticides under high temperature, while dursban was the least. The rise of temperature from 25° to 35° and 45 °C tended to shorten the period of persistence of insecticides at rates differing according to their chemical nature. The longer the time of exposure to higher temperatures, the more rapid the loss of the tested insecticides was. The higher the temperature of exposure was the lower the toxicity to *S. littoralis* larvae and vice versa. The tested chemicals exhibited positive temperature coefficients between 25°and 35°C [15].

The effect of temperature on pesticides, it has been generally observed the rate of decomposition increased with the rise in temperature, and in case of methyl parathion may be degraded at elevated temperatures [16].

Dimethoate, malathion and chlorpyrifos are degraded when exposed to sunlight in opened beakers. The percentage loss of malathion was 30.9 after one day of exposure and increased to 80 after 6 days. In general, the percent loss of all studied insecticides was 100% after 9 days. The compounds are much more stable when exposed to lab. light comparing to the direct effect of sunlight [17].

The degradation of selected organophosphorus pesticides under two levels of temperature was studied by [18]. They found half-life at 20 °C ranged from 7.1 hr for phosmet to 130 days for parathion. Also they stated that the corresponding degradation rates at 37 °C were approximately five to seven times greater those at 20 °C.

The persistence of curacron, cyolane and reldan insecticides as affected by sunlight and UV-rays was studied by [19]. They found that curacron and reldan suffered much more degradation than cyolane when exposed to sunlight. The RL_{50} values of reldan, curacron and cyolane were less than 1, 5.2 and 30 hrs, respectively. On the other hand these insecticides could be arranged according to the loss within the period of exposure to UV-rays in the following descending order: cyolane, curacron and reldan.

The persistence and degradation of monitor and pirimiphos-methyl insecticides as affected by temperature, UV-light and direct sunlight. The results obtained were as follows: The tested insecticides suffered progressive loss as temperature increased, i.e., the percent loss of monitor was 95.19 and 97.00% 10 and 4 days after exposures at 35 and 45°C respectively. At that time the respective percent loss of pirimiphos-methyl was 45.82 and 76.93%. Monitor insecticide degraded faster than pirimiphos-methyl when they were exposed to UV-light. Also, both insecticides greatly deteriorated when they were exposed to direct sunlight [20].

The persistence of the active ingredient of thiometon, prothiofos and sulphrofos organophosphorus pesticides as affected by temperature was studied by [21]. The obtained results showed that sulphrofos suffer less degradation than the other tested chemicals. No loss occurred when sulphrofos was exposed to lower temperatures (25 and 30°C) for 10 successive days, but exposure to higher temperatures (40 to 50°C) increased the percent degradation progressively by the lapse of time. On the contrary, thiometon degraded rapidly within short intervals of exposure to the lower temperatures, while prothiofos was moderately influenced in this respect.

Incorporation of stability of several compounds including diazinon in peat blocks was studied by [22], and it was found that the compound was most affected by season's variation in temperatures.

The thermal decomposition of dimethaote at 100 ^{0}C increased with the time and with faster in closed system than in open one [23].

The effect of temperature, ultraviolet radiation and sunlight on the deposits of dimethoate in vitro was studied by [24]. The effect of climatic conditions on deposits of two types of formulation of dimethoate on cotton plants was also studied. Results showed that the half life of dimethoate in uncovered Petri dishes exposed to sunlight was 1.3 days. Dimethoate was not decomposed to any other compounds. The only metabolite detected inside the tissues of cotton leaves is believed to be the oxygen analog of dimethoate. Dimethoate exposed in closed ampoules to sunlight for 15 days was rather stable. It stayed intact without any decomposition for long in summer sunlight. Dimethoate was less affected by climatic conditions during the first 24 hrs. This could be attributed to the systemic properties of dimethoate where a considerable portion of the deposits penetrated into the leaves of cotton plants and consequently protected from dissipation by weathering destruction by light and oxidation.

The stability of the active ingredient deposited in Petri dishes of chlorpyrifos and fastac alone or mixed with chelating fertilizer or star oil under exposure to 20, 30, 40 or 50 °C for 10 days, UV-rays or direct sunlight for 10 hours. Chlorpyrifos alone or mixed with chelating fertilizer or star oil suffered progressive loss as temperature increased.

Only, at 20°C no less occurred in chlorpyrifos/ star oil mixture. The oil stopped the breakdown and volatility of chlorpyrifos. At 30 and 40°C it increased the half life periods of chlorpyrifos for 2.26 and 3.06 times, respectively. The chelating fertilizer slightly decreased the stability of chlorpyrifos. However, fastac alone or mixed with chelating fertilizer or star oil was stable at the tested temperature degrees. The addition of chelating fertilizer or star oil did not cause noticeable effect on both insecticides when exposed to UV-rays. The half life periods were 17.0 - 19.5 hours for chlorpyrifos and 19.6 - 21.7 hours for fastac. The two tested insecticides greatly deteriorated when exposed to direct sunlight as compared with exposure to UV-rays. Fastac was more photostable than chlorpyrifos. The chelating fertilizer had no effect on the stability of the two insecticides, while, star oil acted as a protectant in the first four hours when mixed with chlorpyrifos [25].

The Exposure of fenitrothion to 20°C for 10 days resulted in 35.34% loss. After 4 days exposure to 50°C, the loss of this insecticide reached 99.93%. The exposure of esfenvalerate to temperature up to 50°C caused no loss in the initial amount after 10 days [26].

The photodegradation of the insecticide phosalone under UV and simulated solar light conditions investigated by [27]. Irradiation of phosalone in hexane and methanol solvents yielded, dechlorophosalone formed as a result of photodechlorination of phosalone. Irradiation in methanol afforded, besides the usual hydrolytic products, three new compounds: phoslone-oxon: O,O-diethyl S-methyl phosphoro-dithioate: and 6-chloro-3-methoxymethyl-2-oxobenzoxazoline. Photolysis of phosalone in the solid state as thin film on a glass surface produced a number of photoproducts including two new compounds: 6-chloro-3-mercapto-methyl-2-oxobenzoxazoline and its dimeric disulfide. Under controlled laboratory conditions the half lives of disappearance of phosalone in UV and simulated solar light were found to be 2.5 and 4.75 days on the soil surface and 4.75 and 8.5 days on the glass surface.

The effect of exposure of five different phosphorothioate insecticides, methyl parathion, fenthion, methidathion, azinphos-methyl and malathion and a phosphoramidothioate, acephate, as thin films to irradiation by sunlight and ultraviolet light was studied by [28]. With the exception of acephate, measurable amounts of different trimethyl phosphorothioate and dithioate esters, some of them having delayed toxic activity, were formed from these insecticides as a result of irradiation. The extent of photo- alteration to these low molecular weight trialkyl phosphorothioates had a strong link with the UV extinction coefficient, as well as absorption maxima of the various insecticides. The photodegradation pathways of the organophosphorus insecticide fenitrothion (I) {O,O-dimethyl O-(3-methyl-4- nitrophenyl) phosphorothioate} in water are discussed from a theoretical point of view, using semi empirical molecular orbital (MO) calculations by [29]. Spectroscopic analysis and MO calculations showed that the Norrish type II intramolecular abstraction of the aryl methyl protons by the nitro group in the excited state is involved in the formation of O,O-dimethyl O-(3-carboxy-4-nitrophenyl) phosphorothioate. The photooxidation of P=S to P=O was considered to proceed via the reaction of I with a hydroxyl radical and not with singlet molecular oxygen.

To confirm the stability of emulsified chlorpyrifos (the active ingredient of Dursban), analytical tests were performed on dursban at various pH levels (4, 7 and 10) stored for extended periods at different temperatures (22.8 and 50 ^{0}C). Results showed that no differences were seen in chlorpyrifos degradation at different temperatures or different pHs for 60 days [30].

The cold temperature behavior of various pesticide solutions in solvents of different chemical composition, solutions of 7 pesticides (alachlor, alphacypermethrin, azinophos-methyl, chlorpyrifos, pendimethalin, propoxur and trifluralin) in solvents containing primarily C_9, C_{10} alkylbenzene and C_{11} - C_{12} alkylnaphthalene, were prepared and observed for precipitation between the ambient temperature and 10 °C. They found that the aromatic hydrocarbon fluids tests, those containing C_{11}-C_{12} alkylnaphthalene compounds were the best solvents for the a.i - s investigated. Removal of naphthalene from C_{10} alkylbenzene and C_{11} - C_{12} alkylnaphthalene fluid did not adversely after the solvency of the resultant pesticide solutions [31].

the stability of two pesticides mixture (kelthane-S and Amix as emulsifiable concentrates, Empire and Deenate, as flowable formulations) which were stored in local and imported packages under ambient conditions (shelf and roof) and heat conditions (54 and 72 °C) for three days. The effect of package types and storage conditions for 90 days on the physical properties and chemical stability of pesticide mixtures were studied when mixtures were diluted for motor and aircraft application. They found that the chemical properties. Percent of pesticide loss was very high under tropical storage (at 54 and 72 ° C) and less when stored under roof condition, however, shelf storage showed the highest stability for all studied pesticides. Degradation in local packages was slightly higher than imported one. Amix content was the most stable pesticide followed by Empire and Deenate while kelthane-S was the highest in decomposition among all studies pesticides [32].

The physical and chemical stability of dimethoate (40 % EC), dicofol (18 % EC) and methomyl (20 % SL) in laboratory under conventional (shelf and roof) and storage (at 54 and 72 °C) in local and imported packages was studied by [33]. They found that the best stability could be achieved if the formulations were stored in imported package under self conditions. Dimethoate oxidized into viscous separated layer of omethoate. The free activity and percentage loss of dimethoate increased during storage which does not comply with WHO specifications. Therefore, it should be reformulated or used for other purposes. On the other hand, dicofol showed good physical and chemical stability in imported packages under shelf storage. Methomyl gave a good chemical stability and its physical properties were complied with WHO specifications.

The effect of ultra violet rays and sunlight on the persistence of profenofos and pirimiphos-methyl insecticides was studied by [34]. The decomposition percentages of pirimiphos-methyl were 13.00, 30.50, 54.00, 81.94, 93.49, 95.52, 96.77 and 98.93% after 0.25, 0.5, 0.75, 1, 2, 3, 4 and 5 hours of exposure to UV-rays respectively. While these values were 13.50, 29.00, 43.00, 55.89, 69.05, 74.91, 79.88 and 83.88% where profenofos was exposed to UV-rays for the same periods of exposure, respectively. The half life values were 42 and 53 minutes for pirimiphos-methyl and profenofos, respectively. The decomposition percentages of pirimiphos-methyl were 66.65, 97.19, 98.25, 99.06 and 100% after 1, 2, 3, 4 and 5 days of exposure to direct sunlight. While these values were 45.39, 89.59, 90.76, 94.24 and 96.84% when profenofos was exposed to sunlight for the same periods exposure, respectively. From the above results it can be observed that the UV-rays is more effective than direct sunlight in accelerating the photodecomposition of pirimiphos-methyl and profenofos.

Fenitrothion was applied to irrigation ditches of the Ebre Delta at an estimated conc. of 200 and 20ml/L in order to eliminate the American crab. The evolution of the levels of fenitrothion and the formation of transformation products (TPs) were recorded during the 4-days after application. The TPs formed were 3-methyl-4-nitrophenol, fenitrooxon and 5-methyl isomer of fenitrothion. The half life of fenitrothion was 13 hours, with disappearance rate of 0.053 and photolysis being the main pathway. The degradation of fenitrothion and the formation of TPs were closely related to environmental conditions [35].

The degradation kinetics of organophosphorus and organonitrogen pesticides in different waters under various environmental conditions was studied by [36]. The evolution of a mixture containing 19 organophosphorus (OP) and organonitrogen (ON) pesticides at ppb level was studied over 6 months period in different water types (ultrapure water, natural seawater, river water, filtered river water) and under various conditions. The degradation kinetics was monitored in closed bottles in darkness at two temperatures (6 and 22°C) and in a system exposed to natural sunlight (variable temperature). The mixture was analyzed by GC coupled with a nitrogen phosphorus detector. Energy activation (Ea) and half-lives ($t_{1/2}$) were determined. The authors stated that there are very different degradation behavior with respect to physicochemical conditions and molecular structures of the pesticides studied. Many factors influence the behavior of OP and ON pesticides in water (pH, temperature, chemical composition, particulate, light, etc.). One of the major results in the great difference in degradation behavior between river water (RW) and filtered river water (FRW). The molecular structure of the pesticide itself (sulertituents) plays an important part in determining its behavior with respect to adsorption on particulate or absorption of light. The carbamate carbaryl degrades quickly as opposed to triazines, which may partly explain the fact that they are easily detected in the aquatic environment. For organophosphorus pesticides, the half-lives range from a few hours for phosmet up to 100 day for isofenphos (T=22°C, in darkness). It is consequently difficult to predict the persistence of OP insecticides in the environment. It has already been noted that there is greater stability in compounds containing an ethoxy group compared to those containing a methoxy group (ethyl parathion versus methyl parathion). The addition of the methyl group or the replacement of NO_2 by SMe does not change greatly the stability of the molecule but does modify the behavior of the molecule under photolysis. Fenthion and fenitrothion are much more sensitive to photodegradation ($t_{1/2}$=2-5 day with respect to $t_{1/2}$=8 to 34 day for methyl parathion and parathion). The presence of a sulfomethyl group also leads to a slight adsorption onto particulate as for fenthion. They also concluded that an increase in the pH generally led to a greater degradation rate.

Diazinon degraded quickly under acid conditions, whereas carbofuran degraded under base conditions. The metal oxides of aluminum hydroxide, hematite, goethite, and ferrihydrite were chosen to represent the soil phase in natural aquatic systems. The authors found that at room temperature, the hydrolysis of phorate at pH 5.7 and at pH 8.5 found to be comparable. The basic and neutral hydrolysis rate constants of phorate are similar in magnitude to those of other phosphoric and thiophosphoric triesters. While most of the organophosphorus triesters are relatively insensitive to acidic hydrolysis, hydrolysis rate constant of phorate was found to be quite significant. They also added that the acidic hydrolysis of disulfoton, which is only one-CH2- different from phorate, is negligible [37].

Increasing the degree of temperature and time of exposure increased the loss of malathion and prothiofos insecticides. Malathion was affected more than prothiofos. The results showed that malathion and prothiofos insecticides residues were more, when exposed to UV-rays and the half lives were 13.55 and 12.61 hours, respectively. The half lives values were 4.74 and 7.99 hours for malathion and prothiofos, respectively, when exposed to sunlight [38].

The stability of the widely used organophosphorus insecticides, Actellic (pirimiphos-methyl) and malathion was studied by [39]. For this study the two insecticides and some of their degradation products were investigated. The oxygen analogues of the two insecticides were obtained through oxidation of the parent compounds with various oxidizing agents, where yields depended on the nature of oxidizing agent. The effect of ultraviolet rays and direct sunlight on the two insecticides was studied. The data obtained showed that malathion is more persistent and more stable than pirimiphos-methyl under experimental conditions.

The thermal decomposition of dimethoate, an organphosphorus pesticide, with the aim at assessing the reaction kinetics, the energy released during the process and the decomposition products. Dimethoate showed a marked tendency to undergo thermal decomposition at temperature higher than 369 k. A moderate pressure increase has been recorded at the end of all runs. Many thiophosphoric compounds have been identified among the decomposition products [40].

The impact is described of the most important factors on the activity of soil insecticides of various types used to control whit grubs and other soil pests in forestry. The insecticide groups are organic phosphates (diazinon, terbufos, chlorpyrifos), and carbamates (carbosulfan, carbofuran, oxamyl) formulates as emulsifiable concentrates (Dursban 480 EC, pyrinex 480 EC), granules (Diazinion 10 GR, Basudin 10G, Diafuran 10 GR, Furadon 10 GR, counter 5G, vydate 10 G) or granules-slow release formulation (Marshal suscon 10 CG). The most important factors affecting the activity of the insecticides are the mechanism of action of the active ingredient; the defence mechanism of the treated insects; the type of formulation, systemic properties of active ingredients, and the mode of application; the type, moisture content and acidity of soils; and the soil temperature [41].

The degradation of chlorpyrifos to determine the effects of soil alkalinity on the longevity of termite protection when chlorpyrifos is applied as a termiticide in a range of Australian soils, particularly high pH substrates. The study also examines the effects of initial soil concentration on the degradation of chlorpyrifos in the range of soils. At an initial soil concentration of 1000 mg/kg for termite control, the degradation rate of chlorpyrifos is very strongly retarded in soils tested when compared with lower soil concentrations of 100 and 10 mg/kg in the same soils. The degradation data correlated with a logarithmic model of decay, and it was thus possible to produce half-lives and predict likely periods of termite control. Average half-lives for all soils for the three concentrations were 385, 155, and 41 days respectively. Soil pH had no effect on the rate of degradation at all concentrations tested [42].

The effect of selected UV absorbers on the photo degradation of fenitrothion insecticide under outdoor conditions was studied by [43].

Fenitrothion without the protection of UV absorbers was rapidly decomposed. The half life values of fenitrothion alone as thin film on glass surface and soil surface or fenitrothion dissolved in natural water were found to be 4.41, 4.82 hours, and 7.6 and 1.74days, respectively. The degree of protection of fenitrothion as thin film on glass surface increased with the increase in proportion of the three UV absorbers tested.

The degradation of two model insecticides, diazinon and malathion, and their degradation products 2-isopropyl-6-methyl-4-pyrimidinol (IMP) (diazinon hydrolysis product) and malaoxon (malathion oxidation product) was compared and studied in the environment (Slovenia). The pesticides and their metabolites were extracted from samples (water, soil, chicory cv. cesere) with ethyl acetate and subsequently the extracts were analysed by GC-FID. It was shown that hydrolysis is the major process in the degradation of these pesticides in water. In fact, 95% of diazinon was degraded, and only 10% of malation was oxidized. In soil 30% of diazinon exposed to the sunlight was decomposed by photolysis, whereas in soil left in the darkness no degradation products were observed. In soil left under environmental conditions, 90% of diazinon was degraded and 40% from its initial concentration was transformed into IMP. The concentrations of the pesticides after 21 days on chicory were under maximal allowable concentration, which is 0.5 ppm for malathion and for diazinon. The concentration of malaoxaon was more than twice as high as the allowable value, which is for the sum of malathion and malaoxon 3 ppm [44].

The determined average active content of malathion after storage at 54 ± 2 ^{0}C for 14 days shall not be lower than 90%, relative to the determined average content found before storage [2].

The estimation persistence of Malathion 57 % EC, Profenofos 72 % EC and Ethion 50% of pervious thiophosphate and dithiophosphate under certain environmental factors may include [storage at 54 ± 2 °C for a period (14, 21, 28 45 and 60 days) and 72 ± 2 °C for 3 days, different temperature degrees 25, 35 and 45 °C for (1 ,2 ,4, 8,12, 24, 96 and 192 h) the previous pesticides were evaluated chemically as detection by HPLC and GLC for each sample before and after storage. The results obtained could be summarized as follow: Malathion was more rapidly degraded than other tested pesticides and this confirms that Ethion more persistence under different applied conditions [45].

The effect of storage temperature and some environmental factors on stability of chemical and physical properties of some insect growth regulators (IGR,s) and benzylurea insecticide was investigated by [46]. The used IGR,s Atabron 5% EC (chlorfluazuron), Cascade 10% EC (flufenoxuron), and benzylurea insecticide Consult 10 % EC (Hexaflumuron) were stored at 45 °C for 14, 21, 28, 48 and 60 days, at 72 ° C for 3 days and at different temperature degrees 25, 35 and 45 °C for 1, 2, 4, 6, 8, 12, 24, 48, 96 and 192 hours to study the persistence of active ingredients of the previous pesticides. The chemical properties of chlofluazuron, flufenoxuron and hexaflumuron were determined by HPLC instrument. Results showed that the chemical analysis by HPLC of tested IGR,s were more stable when storage at 54 °C than storage at 72 °C. Also flufenoxuron was the more stable than other tested IGR.s, whereas the dissipation % in active ingredient was 9.80, 27.4 and 89.5 % at 72 °C for 3 days of storage for flufenoxuron, chlorfluazuron and hexaflumuron, respectively. And according to [47] all used insecticide formulations become non conformity when storage at 72 °C.

The effect of storage temperature on the stability of chemical and physical properties of certain local organophosphorus insecticide formulations was studied by [48]. Four insecticides formulation recommended for use on fruit, crop, and vegetable pests in Egypt were subject to storage conditions at the temperatures 25 °C (at room temp), 54 °C and sunny place for 14 days, and 72 °C for 3 days. The used insecticides were: Malathion 57 % EC, fenthion 50 % EC, Diazinon 60 % EC, and triazophos 40 % EC. The effect of storage on chemical stability of the tested insecticides was considered. They found that the chemical analysis by GLC of tested insecticides were more stability when storage at different temperatures than storage at 72 °C, whereas the dissipation % in active ingredient were 3.11, 100, 5.0 and 8.75 for malathion, fenthion, diazinon, and triazophos, respectively. And according to [47] all used insecticide formulations become non conformity when storage at 72 °C. The results showed the best stability could be achieved if the insecticide formulation stored at room temperature, 54 ° C, and in sunny place, while storage at 72 °C was the more effective on all used formulations.

The persistence of chlorpyrifos, fenthion and pirimiphos-methyl under different environmental conditions was studied by [49]. The present study was planned to study the following: stability of active ingredient of tested pesticides under accelerated storage by heating at 54 °C for 14, 21, 28, 45, and 60 days and 72 °C for 3 days, accelerated storage through different temperatures (25, 35 and 45°C) for 1-192 hours, under ultraviolet rays and sunlight, the physical properties for each unstored and stored pesticides was studied such as pH, acidity or alkalinity, density and emulsion stability. Also the chemical properties of the previous pesticides by GLC were evaluated. Data showed that the pervious pesticides when exposed to accelerated storage by heating 54

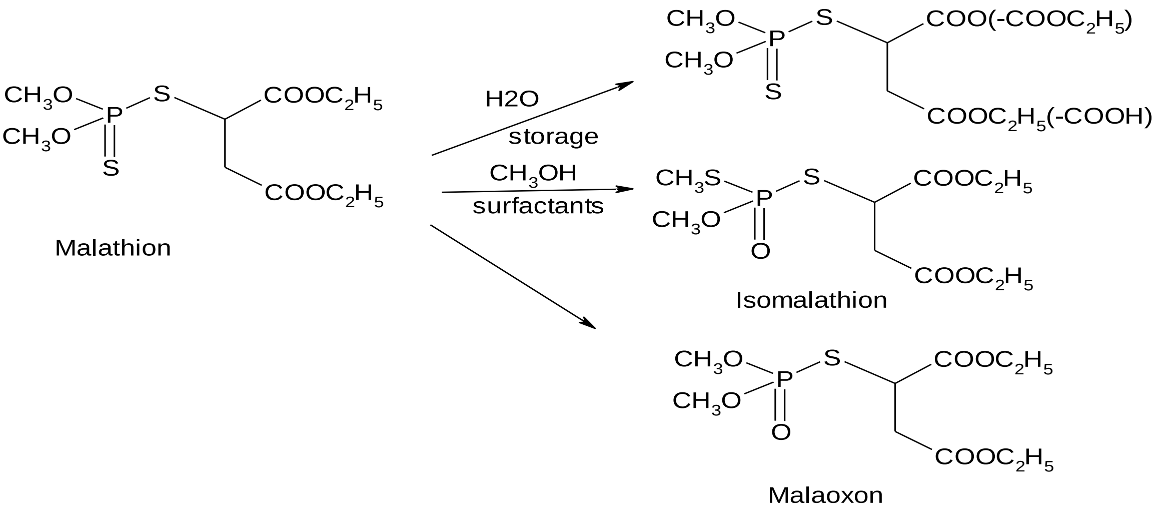
°C. Fenthion was more stable and Pirimiphos-methyl was more degraded than the other pesticides. Also, the previous pesticides when exposed to accelerated storage through different temperatures (25, 35 and 45 °C) for 192 hours, the residue present and calculated half life show that Fenthion was more stable than Chlorpyrifos. The latter more stable than Pirimiphos - methyl.

The determined average active content of chlorpyrifos after storage at 54 ± 2 ^{0}C for 14 days shall not be lower than 95%, relative to the determined average content found before storage [1].

2. Impurities of pesticides

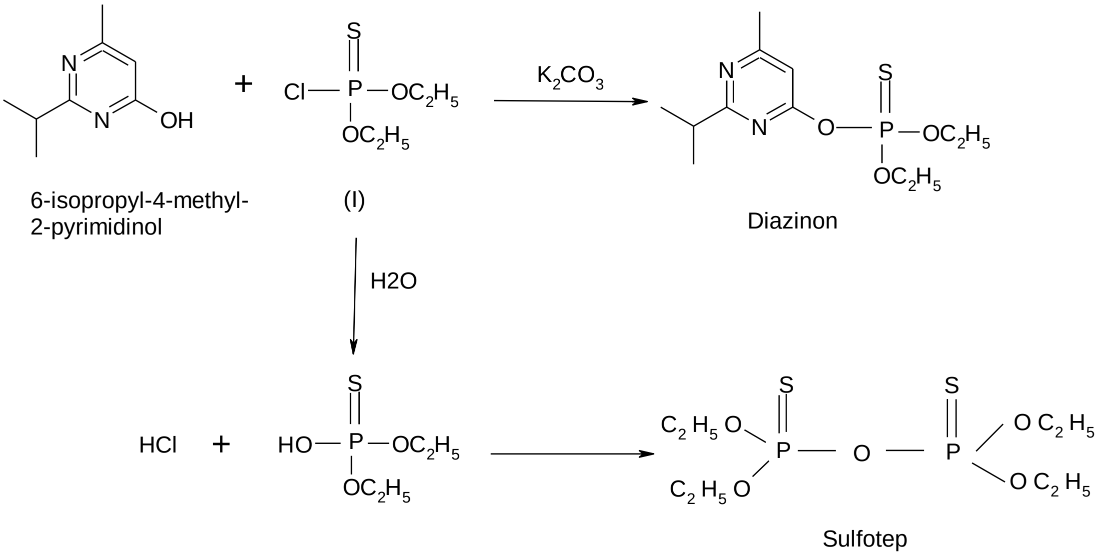
The relevance of impurities is assessed by taking into account their relative toxicity compared with the active ingredient, their effect on the physical and chemical properties affecting the storage stability of the product, their phytotoxicity to treated crops, their production of taint in food crops or their resulting in undesirable residues in food or the environment. In addition to the impurities in the technical active ingredient, the composition and impurities of the carrier materials used in the formulations may also affect these properties of the product. Hence, they should also be taken into consideration for the safety assessment of the pesticides.

A number of impurities present in technical malathion and acephate were isolated by column and thin-layer chromatography and the structures of 11 impurities in malathion and seven impurities in acephate were determined by nuclear magnetic resonance, infrared and mass spectroscopy, and by gas and thin-layer chromatography. Several of the impurities potentiated rat toxicity of purified malathion and highest potentiating activity was observed with O,S,S-trimethyl phosphorodithioate and S-methyl isomeride of malathion. Potentiating effects were significantly smaller in the mouse compared with the rat. Of the impurities isolated from acephate, O,O,S-trimethyl phosphorothioate showed slight potentiation of mouse toxicity when added to purified acephate, but an antagonizing effect was observed with O,O-dimethyl N-acetyl phosphoramidothioate. Storage of technical malation for 3 to 6 months at 40 ^{0}C resulted in materials which were noticeably more toxic to mice. In contrast, a significant reduction in mouse toxicity was observed after storage of technical acephate under the same conditions. Water and methanol content of formulations may result in hydrolysis of the active ingredient and formation of toxic impurities, as was shown in the case of malathion [50].



Possible pathways for the formation of impurities of malathion during storage.

Analysis of eight different diazinon formulations for sulfotep was studied by [51]. The results of these analyses showed that sulfotep is an impurity common to all formulations of diazinon. The concentration of sulfotep was not a function of the age of the formulation. As a matter of fact, the oldest sample had a sulfotep concentration lower than some of the other formulations analyzed. There are two potential sources of the sulfotep impurity in diazinon. It may occur as the result of hydrolysis of diazinon on storage in the presence of water. The monothio analog under these conditions was observed by [52]. However, our studies indicate that sulfotep is not produced by this mechanism in commercially available diazinon formulations. A second source is the production of diazinon. During the production process diethyl thiophosphoryl chloride (I) is added to the pyrimidinol and mixture is heated at reflux under anhydrous alkaline conditions. Small amount of water present during the synthesis of diazinon could react with the diethyl thiophosphoryl chloride in a mechanism similar to that used by [53] to produce sulfotep.



Also they reported that bioassay data showed that sulfotep is much more toxic than diazinon to the aquatic species tested.

The toxicological effects of impurities in technical malathion, three additional phosphorus containing compounds were identified by GC-MS and, together with four previously identified compounds, tested in mice. All potentiated to toxicity of purified malathion, though to varying degrees. O,S,S-trimethyl phosphorodithioate was the most powerful potentiator, while O,O,O-trimethyl phosphorothioate was the weakest. A direct relationship between inhibition of mouse serum and liver malathion carboxylesterase activities and malathion lethality in mice was observed. Irradiation of malathion on glass or silicic acid surfaces by ultraviolet light gave raped breakdown to three major products. Two of these were identified as O,O,O,O, tetramethyl pyrophosphorodithioate and bis (dimethoxyphosphinothioyl) sulfide. GC-MS analysis of technical fenthion (96%) allowed structural assignment to four phosphorus and four nonphosphorus containing impurities. However, toxicological studies suggest that potentiation phenomena are not involved for this material [54].

When they analyzed twenty samples of diazinon by gas chromatography using a flame ionization detector and 5% 0V-17 columns. The amount of the impurity sulfotep found in them ranged from 0.3% to 0.4% in accordance with the regulations of the world Health organization [55].

Isomalathion undergoes degradation on solid pesticide formulation carriers, container surfaces and vigna radiata (green gram) leaves was studied by [56]. Nearly 40-50% of the applied malathion was lost on the carriers bentonite, kaolinite, hydrated calcium silicate and silica gel H after a 12 days incubation at 55 ± 1 ^{0}C. The loss was 8-18% on different container surfaces under the same conditions on vigna radiata leaves, nearly 99% of the applied isomalathion was lost within 5 days of application, the loss being initiated within 30 min of application. Of the several degradation products formed on carriers, O,S,S-trimethyl phosphorodithioate, diethyl mercaptosuccinate and diethyl methyl mercaptosuccinate were identified.

Chlorpyrifos formulations of varying ages were analyzed for 3, 5, 6 trichloro- 2-pyridinol (TCP) and sulfotep. Levels of TCP ranged between

$<$ 0.05- 0.12 %, 0.1 – 0.2 %, 0.19 – 3.8 %, and 0.4 – 0.57 % in samples stored for 1, 3, 4, and 5 years, respectively. The sulfotep content of the commercial products did not show any correlation with storage time. One 2–year–old sample containing 13.8% TCP, 0.65% sulfotep and trace amounts of chlorpyrifos oxon was reported as the cause of the death of 50 bulls treated directly with the product for ecto-parasite control. Though the TCP was unlikely related to the toxicity of the product, the higher – than – normal levels detected were an indication of lengthy storage under adverse conditions [57].

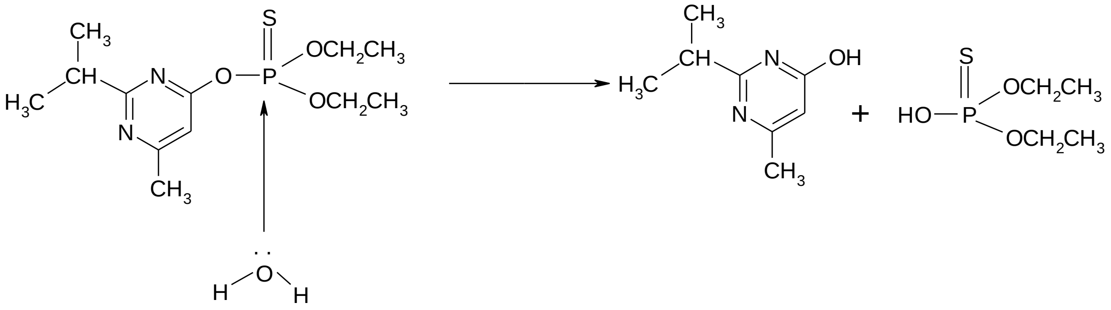
The malathion and its impurities (malaoxon, isomalathion, O,O,S-trimethyl phosphorodithioate, O,O,O-trimethyl phosphorothioate, O,O,S – trimethyl phosphorothioate, and diethyl fumarate (DEF) in air and on surfaces was studied by [58]. Concentrations in air and on surfaces of malathion and its impurities were determined at three sites during and for 9 days after a 1990 aerial spraying in California. Malathion spray was transformed vial oxidation to malaoxon, hydrolysis to DEF, and selective volatilization. Malathion half lives were 1.6 to $>$ 9days, and depositions at three sites ranged from 1100 to 2413 µg/ft^2, while malaoxon ranged from 2.9 to 6 µg/ft^2. Malaoxon increased fastest on filter paper surfaces, e.g., initial deposition of 7 µg/ft^2 increasing to 315 µg/ft^2 after 9 days. Malathion air concentrations increased to 80 ng/m^3 within 1 day, and malaoxon to 64 ng/m^3 at 24-48 h: both were detectable after 9 days. DEF surface levels increased over 9 days; air concentrations persisted for 72 h. the three phosphoro(di)thioate trimethyl esters were undetectable on surfaces within 24 h, producing an air burst apparently vial rapid volatilization. Accurate human exposure assessment during malathion spraying must consider environmental transformation.

Diazinon under certain conditions can deteriorate to harmful substances, particularly if the hydrocarbon solvent contains a small quantity of water (0.1-2%). Exposure to air, light and elevated temperature favor the formation of monothiotep (O,S-TEPP) and sulfotep (S,S-TEPP). These compounds are potent cholinesterase enzyme inhibitors and highly toxic. The cholinesterase inhibition activity of monothiotep was found to be about 14000 times higher than that of diazinon. Levels of 1600 and 6600 mg/L, respectively, of sulfotep and monothiotep were found in date-expired samples of dog wash, sheep dip, and insect killer formulations. The water content of the samples ranged from 0.5 to 6.4 mg/ml [59].

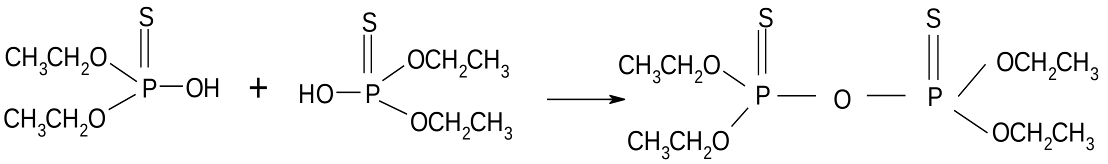
An unknown peak (peak A) was detected in a mass chromatogram of komatsuna (Brassica campestris) extract containing a high concentration of phenthoate (PAP), and it was considered to be O,O,S-trimethyl phosphorodithioate (OOS). Although it is generally known that OOS exists as an impurity in technical malathion and PAP, it has not been reported that (OOS) is present in crops. Since an OOS standard is not commercially available, OOS was separated and purified from commercial emulsifiable malathion. Peak A was confirmed to be OOS by GC/MS using the purified OOS. The concentration of OOS was estimated to be 0.02 micro g/g. It is supposed that OOS was detected in crops because they contained a high concentration of PAP residue [60].

The degradation of the active substance malathion and the formation of its impurities isomolathion and malaoxon during storage in ambient conditions of 15 commercial malathion dust formulations (1 and 5% w/w) from the Greek market (manufactured from various companies) was studied by [61]. Malathion dust formulations stability was found to depend on the pH of the inerts used. In alkaline samples, both malathion and isomalathion contents decreased rapidly during storage. On the contrary, malaoxon content was initially found at non detectable levels (> 0.0001 PPm) and remained at the same level during storage in all tested samples.

The formation of toxic impurities in diazinon. In excess of water the principal products of hydrolysis of diazinon are diethyl thiophosphoric acid and 2-isopropyl-4-methyl-6-hydroxypyrimidine. Under the reaction conditions, diethylthiophosphoric acid is further hydrolyzed to ethylthiophosphoric acid, thiophosphoric acid and ultimately phosphoric acid, which is non-toxic. This formation is supported by available stability data.

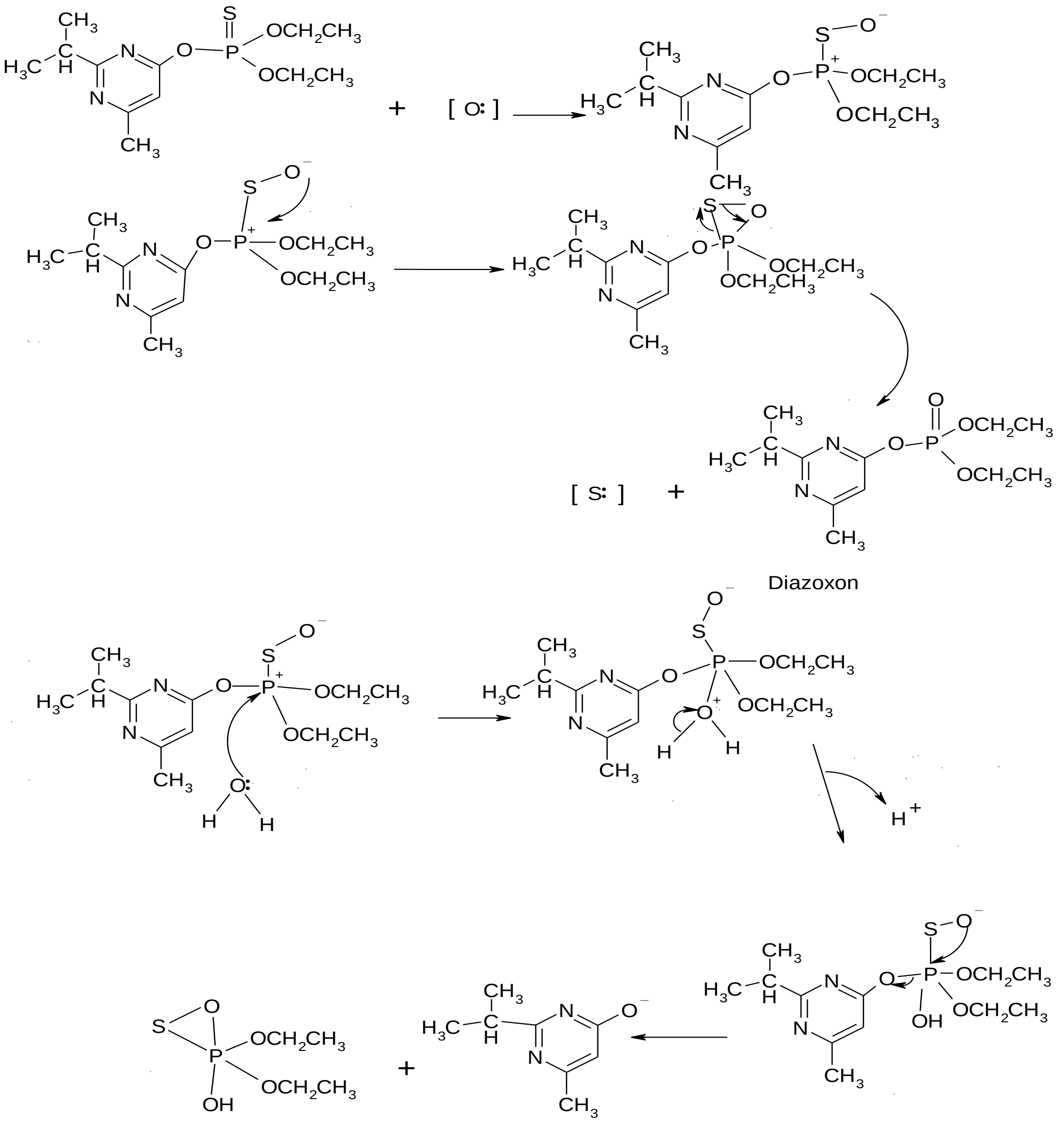


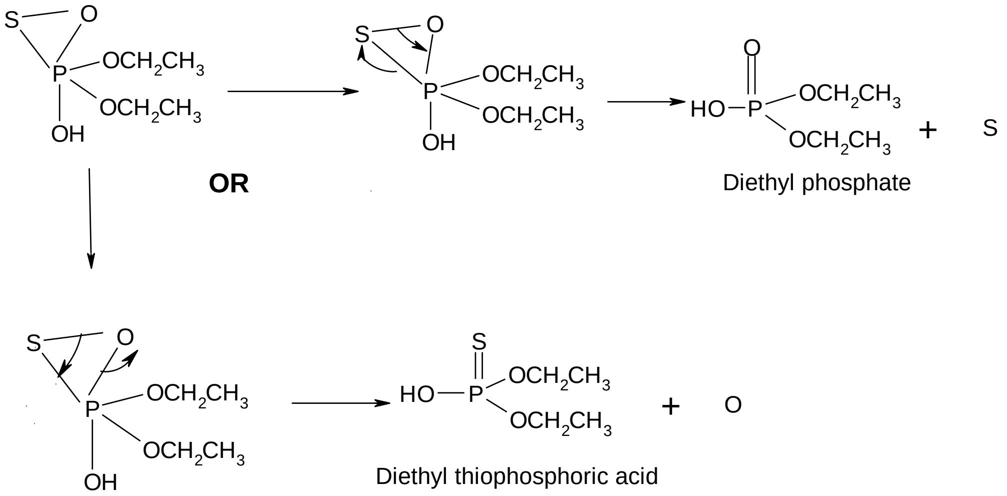
On the other hand, the presence of only trace amounts of water leads to the formation of the toxic impurities S,S-TEPP and O,S-TEPP. The initial hydrolysis of diazinon gives diethyl thiophosphoric acid and 2-isopropyl–4–methyl–6– hydroxypyrimidine (see above). Two molecules of diethyl thiophosphoric acid and combine in air acid catalyzed or radical initiated dimerization (radical ions are formed by UV radiation) to form S,S – TEPP.

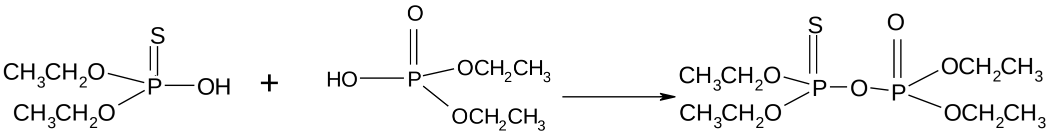


S,S-TEPP

The formation of O,S-TEPP occurs in a similar manner: The diazinon undergoes oxidation and hydrolysis to diethylphosphoric acid, which subsequently combines with diethylthiophosphoric acid to form the O,S-TEPP. The proposed mechanism of oxidation followed by hydrolysis is outlined below:

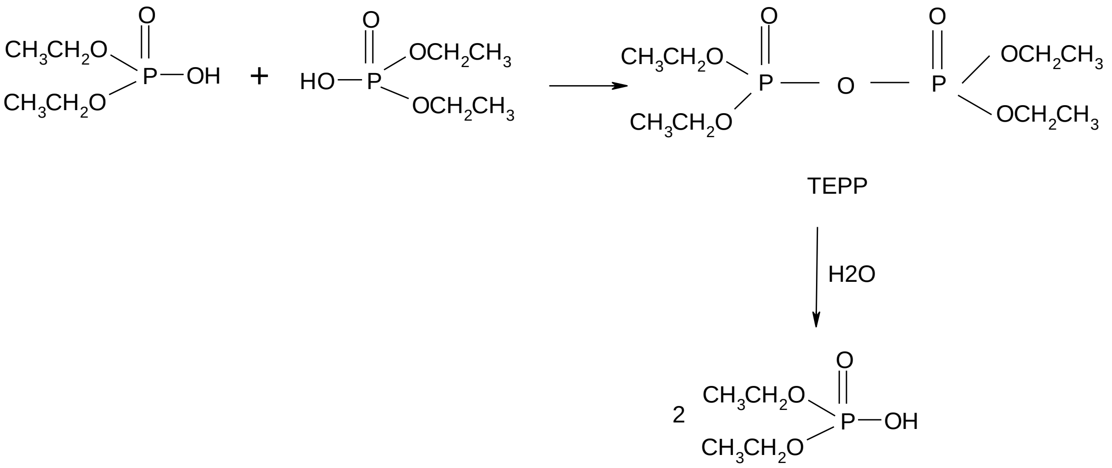






O,S- TEPP

Similarly, simultaneous oxidation and hydrolysis of diazinon in the presence of a small amount of water lead to the formation of TEPP, which is formed by the combination of two molecules of diethylphosphoric acid. However, TEPP is rapidly hydrolysed by water even at room temperature (DT_{50} "50% decomposition" of TEPP and S,S-TEPP is 6.8 hours and 8.2 days respectively, in neutral aqueous solution at 25 ^{0}C) forming diethylphosphoric acid, which is non-toxic to both insects and animals. TEPP is therefore not present in decomposed samples (O,S-TEPP and S,S-TEPP are more stable).



The TEPP compounds are stabilized with respect to hydrolysis by the increasing number of thiono groups, therefore, the order of hydrolysis is TEPP > O,S–TEPP > S,S–TEPP. The finding of S,S-TEPP, smaller quantities of O,S-TEPP and no TEPP in the decomposed samples are in accordance with their hydrolytic stabilities [62].

Malathion has four impurities in technical and all formulations 1-Malaoxon, maximum level in technical is 1 g/kg and in emulsifiable concentrate (EC) formulation 0.1% of the malathion content, 2-isomalathion, maximum level in technical is 4 g/kg and in EC formulations 0.8% of the malathion content 3-MeOOSPS-triester (O,O,S-trimethyl ester phosphorodithioic acid), maximum level in technical is 15 g/kg and in EC formulations 1.6% of the malathion content. 4-MeOOOPS-triester (O,O,O-trimethyl ester phosphorothioic acid), maximum level in technical is 5 g/kg and in EC formulations 0.5% of the malathion content. Also showed that isomalathion levels increased during storage. Average levels in the TC, EC, EW and DP after the storage test were 0.30%, 0.33%, 0.22% and 1.9%, respectively. Only a small proporation (3-4%) of the malathion was converted to isomolation in the EC and EW formulations, but 23% and 31% was converted to isomolathion in DP and TC, respectively. Storage didn't produce malaoxon, and produced very small reductions in the levels of MeOOSPS-triester and MeOOOPS-triester [2].

Sulfotep is the main impurity in chlorpyrifos (technical and all formulations), it shall not be higher than 3 g/kg for technical chlorpyrifos, and 0.3% of chlorpyrifos content in all formulations of chlorpyrifos [1].

3. Emulsion Stability

An emulsifying agent can be defined as a substance, which stabilizes a suspension of droplets of one liquid phase in another liquid phase. Without the emulsifying agent the two liquids would separate into immiscible liquid phases. Therefore, it is an essential ingredient in the formulation of liquid oily active ingredient and solvents, which need to be emulsified into water in the spray tank [63].

In general, the emulsifiers were used in agricultural formulations are blends of anionic and non ionic types. The emulsifiers, which blended, are used in the emulsifable concentrates and mixed with water, where a complex interfacial layer, which governs the emulsion stability, covers the resultant droplets. The emulsifier blend should be carefully selected and used in right quantity to provide better stability at higher dilution rate they improve spontaneity, increase stability and good performance even in hard water.

The degradation of 7 pesticides after storage for 9 months in 4 different agro-climatic regions in Ttanil Nudu, India was studied by [64]. They also, studied the effect of hard water on physical and chemical properties of pesticides endosulfan, dicofol, phosalone and fenvalerate. They found that temperature areas were generally most favorable for the stability of liquid formulations. Water with high pH and electrical conductivity (EC) affected the emulsion stability and wettability of tested pesticides suspensibility of mancozeb was adversely affected by high pH and EC and by starting in cool locations. The active ingredient content of the insecticide decreased marginally with an increase in acidity.

The term stability usually refers to the ability of an emulsion to resist changes in its properties overtime: the more stable the emulsion, the more slowly its properties change. An emulsion may become unstable due to a number of different types of physical and chemical properties. Physical instability results in an alteration in the spatial distribution or structural organization of the molecules. Whereas chemical instability results in an alteration in the chemical structure of the molecules. Creaming, flocculation, coalescence, partial coalescence and phase inversion are examples for physical instability [65].

The effects of water hardness (Ca^{+2} and Mg^{+2} content) on the emulsion stability of endosulfan fenitrothion, phosalone, azinphos methyl, ethion, diazinon, tetradifon, malathion, benzoxymate and brompropylate was studied by [66]. Stability of emulsion was reduced with increasing water hardness for all pesticides tested.

Changes in the physicochemical characteristics of oil / water emulsifiable concentrate formulations were investigated following the storage of components at 54 ^{0}C for 14 days before mixing. The formulations incorporated temephos or cypermethrin (100 or 200 g a.i /kg; resp.), a surfactant and a solvent preheating of any component resulted in increased deposition of oil, cream or sediment in emulsion stability studies. Preheating the insecticide component caused the greatest deterioration in emulsion quality while, of the surfactants, the greatest effect of preheating was with polyoxyethylene compounds [67].

The influence of storage temperature on the emulsion stability test for malathion 57% EC, fenthion 50% EC, diazinon 60% EC, and triazophos 40% EC insecticides formulations at 25, 54 ^{0}C and sunny place for 14 days and at 72 ^{0}C for 3 days was studied by [48]. The results showed that physical properties (Emulsification test) of all used insecticides formulations were not affected by storage temperature except in case of storage at 72 ^{0}C whereas a cream layers were found at the top of the containers was: 5, 4.5, 3 and 3.2 ml for malathion, fenthion, diazinon and triazophos, respectively. So the best emulsion stability for physical properties when the insecticide formulations stored at room temperature 25, 54 ^{0}C, and in sunny place while storage at 72 ^{0}C was the more effective on all used insecticides formulations in this study.

The persistence of malathion, profenofos and ethion of pervious thiophosphates and dithiophosphate under the environmental factors may be include (storage at different temperature degrees, photodecomposition by direct sunlight and UV lamp for different periods), where influenced by analytical techniques (physically such as pH, free acidity, density and emulsion stability test) was studied by [45]. The physical and chemical properties for the previous organophosphate pesticides were in allowed limits and agreement with the principles outlined in FAO and WHO specifications. The results indicated that all selecron and endo passed successfully through emulsion test while, malathion have 2.1 ml and 3 ml sediment after 60 days and 14, 21, 28 and 45 days during storage. But malathion (storage through 14, 21, 28, and 45 days) not passed successfully. Finally selecron, endo and malathion initial and storage at 72 ^{0}C for 3 days agree with [2] no sediment.