

Historical Perspectives on Apple Production: Fruit Tree Pest Management, Regulation and New Insecticidal Chemistries.

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I Historical Use of Pesticides in Apple Production

Overview of Apple Production and Pest Management Prior to 1940

The apple has a rather ominous origin. Its inception is framed in the biblical text regarding the genesis of mankind. The backdrop appears to be the turbulent setting of what many scholars believe to be present day Iraq. The original eating qualities of the fruit, although touted by a serpent of dubious character, were stated that ‘...when you eat of it your eyes will be opened, and you will be like God, knowing good and evil’¹. The account has it that the visual allure of the apple and the desire for wisdom prevailed. Defiance resulting from a clearly stated Divine consequence for eating the forbidden fruit was expulsion from a life of bliss. The occupants of Eden were subsequently thrust into a life of agricultural turmoil, "Cursed is the ground because of you; through painful toil you will eat of it all the days of your life. It will produce thorns and thistles for you, and you will eat the plants of the field. By the sweat of your brow you will eat your food..."² Any apple grower will attest to this state of agriculture as their present condition.

Historically the apple has evolved from simply a seasonal food gathered by the migratory nomadics, no more than 1 to 2 inches in diameter, acid and astringent in flavor³, to a place of prominence in agricultural civilizations, often greatly sought after by those designing and developing cultivated gardens of the wealthy elite and emperors. These ancient gardens were considered places of retreat, a personal paradise. In the year 401 B.C. the Greek historian and essayist, Xenophon became so inspired by walled fruit gardens throughout the Persian empire that he establishes one on his own estate in Greece. He then proceeds to coin a new Greek word from the Persian *pairidaeza*, or walled garden, later becoming the Latin *paradisus*, and finally the English *paradise*⁴. Boasting an abundance of cultivated fruit, these paradise gardens were portrayed as places of sexual and romantic connotations. The apple not only tasted heavenly and considered good for digestion, but often the apple was presented to a intimate guest as a cunning transitional aphrodisiac for the pleasures that followed, powerful reasons why apples came as dessert at the end of the meal.

The tree and its fruit is classified with the groupings of plants known to produce fleshy fruit that contain its seed in a ‘bony’ parchment-like carpel. It is classified in the

order, Rosales in the family, Rosaceae, the subfamilies Maloideae (five capsules) and its genus being *Malus*, retaining credit to Linnaeus⁵. The wild ancestor to *Malus domestica*, our present day apple, is probably *Malus sieversii*, still found wild in the mountains of central Asia in southern Kazakhstan, Kyrgyzstan, and Tajikistan⁶. The region extends from the Caspian to the Black Sea. Obtaining ancestral genotype specimens has been the work of pioneering pomologists seeking to both preserve the genetic lineage as well as in obtaining genetic traits for transfer into future commercial varieties.

In attempts to produce a better apple, both the tree and fruit have undergone numerous transformations. Through natural cross-pollination and artificial manipulation by selective breeding and genetic modification, the plethora of varieties now exceeds 7500 varieties presently available to apple producers⁷. As pomologists have sought for the re-creation of the perfect apple, none so far has brought mankind enlightenment or the return to Eden he so desires. It appears that the closer we come to the development of the “perfect apple”, the more difficult the production and management process seems to be. Yet the benefits of health and extending ones life from the eating of the apple are just now coming to the surface. The old adage of ‘an apple a day’ has just recently been confirmed, as they have been found to help in protecting apple lovers against brain-cell damage that triggers Alzheimer's, Parkinsonism disease⁸. The phenolic acids and flavanoids that protect the apple against disease have been discovered to provide anti-oxidant and anti-cancer benefits through reduction of cell-damaging free radicals and inhibition of the production of reactive chemicals that could damage normal cells.

In regards to apple production, not much has changed since the ousting from Eden for we continue, through painful toil and the sweat of our brow, to eat of our food all the days of our lives. Apple pest management is the epitome of intensive agricultural, observed in the chemical dependency of our management programs. Today's apple varieties are subject to perennial onslaught from a multitude of insect, disease, wildlife, weed and weather conditions, reducing a potentially profitable crop to a few worthless, worm riddled, scab encrusted fruit. Without intensive multidisciplinary management and rigorous chemical intervention, the apple as we know it, displayed on farm market and retailers shelf, would not exist.

If we consider the history of apple production beginning in the old world we find that it is limited primarily to cultivation practices and physical control methods. Budding and grafting practices, which allow for desirable fruiting traits to be propagated, have been known to exist for thousands of years. One example of early cultural practices comes from Chinese writings ("The Precious Book of Enrichment", part I, chapt. 4⁹). It appears that Feng Li, living around 5000 B.C., gave up a prominent position as a Chinese diplomat, when he becomes consumed by grafting peaches, almonds, persimmons, pears and apples as a commercial venture¹⁰. Theophrastos, considered the father of Botany, describes in 323 B.C. 6 varieties of apples and discusses why budding, grafting, and general tree care are required for optimum production¹¹, In his writings, Inquiry into plants (De historia plantarum), he confirms the importance of budding and grafting as he describes seed propagation to almost always produce trees of inferior quality fruit. The emphasis on fruit production up to the 17th century primarily followed cultural practices to obtain fruit quality with sparse emphasis on pest management.

There is however evidence that supports the use of chemical pest management practices up to this period. In a historical summary of 'Insect Pest Management' (CAB International, Wallingford, 1991), Dr. D. R. Dent summarizes an overview of historical insect pest management¹². He states that animal oils on rice are believed to be one of the early forms of insecticides used in China followed by the use of inorganic mineral insecticides by the Sumerians, first recorded in 2500 BC, in which sulfur compounds were employed to control insects and mites. Botanical insecticides were being used for seed treatments and as fungicides in China as early as 1200 BC. The Chinese were also considered to have been the first to use mercury and arsenical compounds to control body lice during that same period. A Chinese alchemist in the year 400 AD, Ko Hung, had written recommendations for root applications of white arsenic when transplanting rice to protect against insect pests. Also in China in the year 300 AD came the first recorded use of biological controls through the use of predatory ants (*Oecophylla smaragdina*) to control caterpillar and beetle pests in citrus orchards. Another example of early biological control comes from Arabia during 1000-1300 A.D. where date growers seasonally transported cultures of predatory ants from nearby mountains to oases to control phytophagous ants which attack date palm. It is the first

known example of movement by man of natural enemies for purposes of biological control.

The use of chemical derivatives as both poisons and medicinal drugs flourished during the Roman Empire, from 331 BC to the end of the 1st century. The history of poisons and poisoning goes back about 5,000 years to the earliest written records of the human race. Menes, first of the Pharaohs, approximately 3,000 years BC studied and cultivated poisonous and medicinal plants – an interest retained by the Egyptian court¹³. Under the Roman Empire during the 1st century AD Dioscorides wrote his famous *De Materia Medica*, which outdated existing literature in classifying remedies and drugs from the animal, vegetable, and mineral kingdoms. This work, which dealt about 1,000 drugs, became the standard text for centuries to come. Information on poisons was also available in the writings of Scribonius Largus (AD 1-50), Pliny the Elder (AD 23-79) and the poet Nicander (2nd century AD)¹⁴. Poisons, relative to insecticides developed in the 17th century, that were found in the literature dating back to the Roman Empire were arsenic, lead, mercury, copper silicate, from mineral sources, *Black hellebore* (*Veratrum nigrum*), and *White hellebore* (*Veratrum album*) from plant sources, Romans using hellebore to kill insects and rodents¹⁵.

Arsenic has been known since antiquity in the form of its sulphides. Aristotle (384-322 BC) makes reference to sandarach and his student Theophrastus of Eresos (370-286 BC) named it arhenicum¹⁶. The oxide known as White Arsenic is mentioned by the Greek alchemist Olympiodorus of Thebes (5th century AD), obtained it by roasting Arsenic Sulphide. Pliny, in his *Historia Naturalis* said: "Sandarach is found in Gold and Silver mines. The redder it is, the more powerful its odour, the better its quality... Arsenicum is composed of the same matter as sandarach; the best in quality has the same color as that of the best gold, and that which is pale in color resembling sandarach is of inferior quality." It was not until 1649 that Johann Schröder (1600-1664) clearly reported the preparation of metallic Arsenic by reducing White Arsenic with charcoal. Thirty-four years later, Nicolas Lemery (1645-1715) observed that metallic Arsenic was produced by heating White Arsenic with soap and potash. This and all other metals were considered compounds until Antoine Lavoisier (1743-1794) established a new definition for elements¹⁷.

It was during the early 1600s that it was discovered that many plants used for medicinal purposes had insecticidal properties. Some of these included: nicotine from tobacco plants, caffeine from tea and coffee, quinine from cinchona bark, morphine from the opium poppy, cocaine from cocoa leaves, ricinine from castor oil bean, strychnine from strychnos plants, coniine from hemlock¹⁸. By 1690 "Black Leaf 40" (containing 40% nicotine sulphate) was being marketed as a poison containing nicotine, which was used to control pear tree pests¹⁹. The use of arsenic also appeared as an insecticide in the form of ant bait formulations used in Europe by 1699²⁰.

The settling of the Americas and the challenges faced by farmers, many of which had small fruit plantings, were numerous. The pest complex in the new world was vastly different than that of Europe, and the diversity of pest infestations lead many to contrive a vast array of remedies, published as articles in papers throughout the colonies. Regarding a single pest, the plum curculio, *Conotrachelus nenuphar* (Herbst), most all of these remedial suggestions had no impact on the damage caused to plantings of apricot, nectarines, peach, cherry, apple, or sloe (the blackthorn or North American plum). These included treatments of fumigation using sulphur, wood ash during bloom, sulphur and powder fired from a gun into the trees in successive mornings, burning pans of leather on pans of charcoal, whale-oil soap, sulphur, lime and tobacco sprays²¹. One of the earliest accounts in the newly establishing American colonies of apple infestation and plausible treatment for plum curculio was found in a letter from Peter Collinson to John Bartram dated February 3, 1736 (considered the "father of American Botany")²². The remedy of using straw smoke and or subsequent water applications of tincture of tobacco leaves were recommended.

With the escalation of insect descriptions after Carolus Linnaeus (1707-1778) and biological discoveries during the Renaissance, more refined methods of pest management and agricultural production methods were practiced. In 1763 Linnaeus wrote an essay on how orchards could be freed from caterpillars, suggesting use of mechanical and biological control methods in orchard pest management²³. During the early 1800's crop protection became more extensive and international trade promoted the discovery of the botanical insecticides such as pyrethrum (Dalmatian powder) and derris, in particular derivatives from the roots of the Derris plant (found and imported from tropical regions) cultivated for the manufacturing of the insecticide Rotenone. The

production of pyrethrum beginning in 1870 by a Mr. Milco (a native of Dalmatia) near Stockton California trade named 'Buharh' from the *Pyrethrum cinerarioefolium*²⁴.

During the late 18th early 19th century came the appearance of the first books and papers devoted entirely to pest control, covering cultural control, biological control, varietal control, physical and chemical control of agricultural crops. With greater understanding of botany, plants with insecticidal uses were recommended as insecticides. The dried and powdered root of *Veratrum californicum* or hellebore was used as an insecticide and a parasiticide, effective against caterpillars and recommended against the imported cabbage worm in 1861²⁵. With the advent of monoculture came wide spread disease and insect outbreaks, causing devastation in crop losses and human famine as was observed in the Potato blight (*Phytophthora infestans*) outbreak in Ireland, England and Belgium in 1840 and the introduction of the Grape Phylloxera (*Viteus vitifoliae*) from the Americas from 1848 to 1878, that nearly put an end to the French wine industry²⁶. The release of the natural enemy *Tyroglyphus phylloxerae* to France from North America in 1873 began to provide adequate levels of control to grape production. The multi-disciplinary approach of biological and chemical control for insect and disease came in the form of the introduction of Paris Green, a copper acetoarsenite pigment in 1867, used for control of the Colorado potato beetle²⁷, and the Bordeaux mixture, used on French grapes for mildew control in 1883²⁸. Along with the use of resistant rootstalks and grafting that allowed the French wine industry to flourish. In 1880 the first barrel pump spraying machine was released for commercial applications of these newly developed products, followed by dusting machines in 1893, steam and gas powered sprayers in 1884 and 1885 respectively, followed by the Cyclone spray nozzle for insecticide spraying in 1887, all of them used in various forms for applications in fruit pest management²⁹.

By the late 1800's there was a growing arsenal of insecticides used for commercial fruit production, the principal insecticide being Paris Green, first recommended in 1869 for the control of the Colorado potato beetle³⁰. In the 1882 report by Lintner to the N.Y. State Legislature, he lists the discovery and uses of valuable insecticides. Recommended in this report were Paris Green (arsenic and copper) and London Purple (calcium arsenite), a byproduct of aniline dyes (consisting of rose

aniline, arsenic acid, lime, iron oxide, water), for control of codling moth (apple-worm *Carpocapsa pomonella* (L.)) and spring canker worm (*Anisopteryx vernata*), Pyrethrum (Persian or Dalmatian Insect Powder) for aphid and caterpillars by dusting, Hellebore for sawfly control, oils (kerosene, coal oil, and paraffine oil) for scale and wooly apple louse (aphid), Bisulfide of Carbon for peach tree borer (*aegeria exitiosa* Say), Carbolic Acid, Soluble Phenyle (0.79% carbolic acid, 80-90% tar oil, and potash soap) for apple aphid, Coal tar and sulphur burning to deposit soot on the trees for plum curculio control, and GasLime (waste product of gas light manufacturing) containing 'sulphuretted hydrogen'.

Most of these materials came as individual compounds, either mixed by the farmer or formulated by a 'druggist'. Paris Green for example contained 58% arsenic, in the form of arsenious acid, known as arseniate of copper. To this insecticide were added diluents such as flour, plaster of Paris, finely sifted wood ashes, air-slacked lime and road dust. The use of flour to Paris Green, in the ratio of one part Paris Green and twelve to thirty parts flour, depending on both the insect and the crop, would allow for a dry mixture applied as a insecticidal dust, to vegetable crops. The dilution of Paris Green and plaster of Paris was used with success when applied at 1 pound Paris Green to 150 to 200 pounds of plaster of Paris for control of early nymphs of the Colorado potato beetle, 'made in the early morning when dew on the foliage allowed for greater adherence of the mixture to the plants'. A 'wet mixture' was obtained by applying a half-pound of Paris Green with 40 gallons of water for spraying fruit trees, resulting in faster application, more equable distribution, 'obviating' the danger of inhalation³¹. These applications were recommended for fruit insect control using a hand pump called the "Hydronette" or "Aquet", capable of sending the liquid formulation forty to fifty feet to the tops of fruit trees. Combined with a flattened nozzle with many small holes for broad spray distribution, this technique for application of the early arsenicals was effective for fruit tree pest management.

The introduction of newly developed chemicals and their uses were not without opposition, prompting the scientific community to speak out concerning the safety of insecticides such as London purple and Paris green. Recommendations on proper chemical use of pesticides were put forth in Lintners report, containing brief precautions regarding labeling and storage of these poisons, application methods, days to harvest, exposure to farm animals, potential foliar and fruit phytotoxicity, concentrations of

mixtures, and crop rotation³². Regarding the toxicity of residues on crops, U.S.D.A. chemist Wm. McMurtrie conducted early studies on soil contamination, through the use of insecticidal Paris green, in 1875. At the time these studies showed no evidence of soil residue phytotoxicity or potato plant tissue absorption of arsenic from the soil when the material was applied at one to two pounds per acre, which at the time was a standard dosage³³.

Beginning in the 1890's, lead arsenate became the standard stomach insecticide used on apple for the control of plum curculio and apple maggot³⁴. And in general, lead arsenate was the most extensively used of all the arsenical insecticides. It was first prepared as an insecticide in 1892 for use against gypsy moth (*Lymantria dispar*) in Massachusetts, after its introduction from France into Medford, MA in 1869. Since Paris green was found to be very phytotoxic at the rates required for gypsy moth control, the use of lead arsenate gained popularity due to its lower solubility rates. Lead arsenate applied in foliar sprays also adhered well to the surfaces of plants, allowing for long insecticidal residual. Lead arsenate was initially prepared by farmers by reacting soluble lead salts with sodium arsenate, but pastes and powders which were sold commercially became widely used. Grasselli Chemical Company, later becoming a part of E.I. Dupont, started manufacturing lead arsenate insecticides beginning in 1907³⁵. Formulations became more refined over time and two principal forms evolved in the form of basic lead arsenate [Pb₅OH(AsO₄)₃] for use in certain areas in California, and acid lead arsenate [PbHAsO₄] for all other locations³⁶.

The search for substitutes for lead arsenate began in earnest when it was discovered in 1919 that contemporary practices for washing produce were failing to adequately remove residues. Numerous investigations were conducted to this end. One such study conducted in 1923 by the USDA tested 42 readily available organic compounds when applied as contact insecticides³⁷. The chemicals were applied to the black aphid, *Aphis rumicis* L., to determine baseline levels of toxicity. As they inhabit nasturtium, which are relatively sensitive to chemical applications, the study allowed for of both efficacy and phytotoxicity evaluations to be made. Of these materials tested, nicotine and nicotine sulfate were found to be most toxic to the aphid, confirming a report by Hodgkiss and Fulton in 1913 on the recommended effectiveness of nicotine (Black Leaf 40) on Rosy and Wolly apple aphid on apple³⁸.

By 1926 the USDA began conducting tests on methods for removing lead-arsenate spray residues from apples and pears to meet export tolerances. And in 1933 the Federal Food and Drug Administration fixed a limit to lead, whereby creating a 'desirable' zero tolerance to insecticides containing lead³⁹. Unfortunately, the majority of the tested alternative materials were found to provide less effective insect control, owing to greater solubility in the insect digestive tract, additional insecticidal action by lead, and greater adhesion by lead arsenate. Other materials tested, such as calcium arsenate, were gaining popularity by 1923, owing to both its effectiveness in managing the boll weevil and reduced residual on food⁴⁰. Yet the formulations of calcium arsenate were maintained to be more toxic to plants due to the formation of water soluble arsenate through the release of carbon dioxide and water⁴¹. No adequate substitutes were found until 1947, when the synthetic organic insecticide dichlorodiphenyltrichloroethane (DDT) was introduced⁴². Continuing use of lead arsenate was documented in New York through 1965 and Michigan, Pennsylvania, and Georgia during the mid-1960s. Insecticidal uses of lead arsenate on food in the USA were officially banned on 1 August 1988 with all registrations for insecticidal use having lapsed before that date⁴³.

By 1929, prior to the introduction of synthetic pesticides, the production of agricultural chemicals was a multi-million dollar a year business. The U.S. industry manufactured insecticides were valued at \$23,505,000. Of this amount, household insecticides were valued at \$13,350,000. Huge amounts of insecticides were produced including calcium arsenate at 31,314,000 pounds worth \$1,733,000; arsenate of lead 29,903,000 pounds worth \$3,304,000; carbon bisulfide \$2,860,000; carbon tetrachloride \$1,728,000; and various arsenical compounds valued at \$500,000⁴⁴.

Synthetic Pesticide Development and Use in Apple Production

The 1930's was an era that brought about the development and use of organic synthesized compounds for insect pest management. Although synthesis of compounds had occurred prior to this time, use of these materials as insecticides in fruit was minimal in the United States. An example of this progression began with the synthesis of the chlorinated hydrocarbon HCH, by Michael Faraday in 1825, not rediscovered until 1940⁴⁵. DDT had a similar history. The German chemistry student by the name of Othmer Zeidler, was credited for this work for his thesis in 1874. Yet, Paul Müller, in Switzerland, did not discover the insecticidal property of DDT until 1939⁴⁶. In 1892

Antinonnin (derived from the German name for gypsy moth), the first synthetic chemical crop protection product was produced in Barmen (now Wuppertal) Germany, by Friedrich Bayer and a master dyer named Johann Friedrich Weskott under the name "Friedr. Bayer et comp, eventually to become The Bayer Group."⁴⁷. Antinonnin, or Dinitrocresol, 4,6-dinitro-o-cresol (DNOC) was made available in the United States by July of 1893 for gypsy moth control and general pest management (rats, insects, wood preservatives)⁴⁸.

The synthesis of compounds as insecticides in mass production appears to have begun in 1929 with Alkyl phthalates patented as insect repellents, and n-Butyl carbitol thiocyanate being produced commercially as a synthetic contact insecticide⁴⁹. This was followed by work conducted in Leverkusen, Germany by Dr. Gerhard Schrader of the I. G. Farbenindustrie laboratory, in search for nicotine insecticide replacements. He first discovered the phosphoric acid ester Tabun (ethyl dimethylphosphoramidocyanidate) on 23 December 1936. He found Tabun was extremely potent against insects at 5 ppm killing all the leaf lice he used in his initial experiment⁵⁰. This information (chemical toxicant data), was decreed by the Nazi government to be exclusively government property, eventually leading the government to large-scale manufacture and use of Tabun (and Sarin) by Germany for genocidal purposes.

Chemical research was well under way in the U.S. by the early 1930's, giving rise to the development of the early synthetic organic compounds for insecticidal use⁵¹. A study conducted in 1937 at the University of Delaware Agricultural Experiment Station, under guidance and support of a E.I. du Pont de Nemours and Company fellowship, evaluated some 1000 compounds, making up 800 stomach poisons, in five different chemical groups⁵². Representatives of the groups, phosphoniums, coordinated chromium salts, thiazines, thiuram sulfides, and thiocarbamates were comprised of synthesized compounds found to approach the toxicity of lead arsenate, the more toxic selections were studied on codling moth larva on apple.

Many synthesized organic insecticides were introduced and employed in tree fruit pest management leading up to the widespread use of DDT. Phenothiazine (also known as dibenzothiazine, thiodiphenylamine) was introduced as one of the early members of the new synthetic age of pesticides in 1935⁵³. It was used for codling moth control on tree fruits and widely used as worming agents in veterinary medicine effective against a

wide range of parasitic insects in animals. Dinitro derivatives of phenol and cresol came into use prior to WWII as dormant fruit tree sprays as insecticides and miticides, especially for rosy apple aphid pre-bloom⁵⁴. They were first introduced in the form of 4,6-Dinitro-o-cresol (DNOC) or commonly called DN's, followed by their analogs such as dicyclohexylamine salts which were more water soluble thus easier to use⁵⁵. It is registered in a number of countries for use as an acaricide, larvicide and ovidicide to control the dormant forms of many insects in orchards. It is applied during the winter on pome and stone fruits and grapes ("winterwash"). These were extremely toxic compounds, very lipophilic and easily absorbed through the skin. Aliphatic, alicyclic, and aromatic esters of thiocyanic acid soon followed, primarily in the form of thiocyanates that came into use prior to the 1940's as insecticides. They tended to produce injury to plants and soon fell out of favor as a fruit tree management tool.

The use of chlorinated hydrocarbons in the form of carbon tetrachloride and p-dichlorobenzene had been well under way by 1940. The first introduction of DDT into the United States was made in August of 1942 when the dye firm of J.F. Geigy shipped from Switzerland to New York two formulations of wettable powder and dust to be used experimentally by research entomologists⁵⁶. Production of DDT in the United States the following year and made available to the Armed Forces for disease control efforts. Civilian use of DDT began immediately after the war. And by 1950 fruit tree management had incorporated more than 14 different chemicals into their pest management arsenal, applying 11 or more sprays throughout the course of the growing season. The number of chemical applications doubled from 1920 recommendations of 5-6 applications per season through the use of only recommended 6 materials⁵⁷.

By 1952 fruit tree spray programs had incorporated DDT as the replacement for lead arsenate for the control of codling moth (CM), red banded leaf roller (RBLR), and apple maggot (AM), the chlorinated hydrocarbon analogs of DDT known as DDD (dichloro-diphenyl-dichloro-ethane) and TDE (tetrachloro-diphenyl-ethane) for RBLR and AM, Chlordane (1,2,3,4,5,6,7,8,8-Octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane) for plum curculio (PC), Methoxychlor (80% of 1,1,1,-trichloro-2,2-bis(p-methoxyphenyl) ethane) for PC, Aldrin (95% 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a - hexahydro-1,4,5,8-dimethanonaphthalene) and Dieldrin (85% 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,8,8a-oc-tahydro-1,4,5,8-dimethanonaphthalene) for PC. Nicotine Sulfate, in

the 40% formulation, was still used for aphids and leafhoppers. Organophosphates in use primarily as miticides were Parathion (0,0-diethyl-0*p*-nitrophenyl thiophosphate), TEPP (Tetraethyl pyrophosphate), 'EPN 300' (Ethyl *p*-nitrophenylthionobenzine phosphonate), 'Dimite' (Di-*p*- (chlorophenyl) – methylcarbinol), 'DN-111' (Dinitro-*o*-chlorohexylphenol, dicyclohexylamine salt), and 'Aramite' (β -chloroethyl- β (*p*-*tert*butylphenox) - α - methyl ethyl sulphite), as was 60 and 80 sec oil and highly refined 'white summer oil' with low unsulfonatable residue, also used as stickers⁵⁸.

II. Influences Changing the Pest Management Profile in Apple Production

By 2004 there no less than 35 agrichemical companies that manufactured and or distributed 181 crop protectants in the form of 91 active ingredients comprising acaricides, bactericides, fungicides, herbicides and insecticides used on tree fruits in the New York State.(Table 1). Of that number 38% (36) are insecticides and or acaricides manufactured by 16 different companies. These insecticides and or acaricides exist as 52 different trade names, 28% of them having the same active ingredient. Of the 119 chemical companies producing chemicals worldwide, the 7 leading companies producing 63% of the insecticides and acaricides on tree fruits are DuPont, Gowan, Bayer, Dow AgroScience, Drexel, Syngenta, and Valent BioSciences (Table 2 and 2a). Both the number of crop protectant materials available for use in tree fruits and the number of companies producing these materials has diminished over the past 40 years. Chemicals have been lost through product registration cancellations (or banning), and company reductions primarily through consolidation.

The pioneers in the manufacture of chemicals for agricultural purposes were most often involved in the manufacture of products other than pesticides. The manufacture of colored dye, London Purple and Paris Green for instance, were later found to be useful in controlling insects. The fungicidal Bordeaux mixture originated from the manufactured purpose of repelling would be pilferers from the roadside borders of French vineyards, the green residue of the copper oxide believed to be poisonous by travelers passing the ripening grapes.

Many of the agrichemical industries of the latter 20th century were conceived during the dawn of chemistry of the 18th century. Merck is one of the few surviving names in the manufacture of agrichemicals that had its beginnings as an apothecary shop in

Darmstadt Germany in 1668. In 1758 Geigy was founded, the company eventually responsible for the introduction of DDT. The manufacturing of gunpowder by Eleuthère Irénée du Pont (E.I.) (1771-1834), an immigrant of revolutionary France in 1799, was the start of the E.I. DuPont Chemical Company in 1802⁵⁹. In 1863, dye makers Friedrich Bayer and Johann Friedrich Weskott established what has become the present day Bayer Group, discovered their synthetic dye aniline to have insecticidal properties. In 1876 Sandoz was founded and shortly there after, in 1884, Ciba was founded. The first record of consolidation of companies involved in the manufacture of agrichemicals was the purchase of Grasselli Chemical Company, by E.I. Dupont. Grasselli Chemical being the first company to manufacture lead arsenate insecticides⁶⁰.

Chemical Residues in Early Insect Management

During the early use of newly developed agrichemicals it soon became evident that their use in pest management were directly related to an assortment of secondary problems and risks. The early agricultural ills that arose from the use of various treatments such as oils used to control San Jose scale⁶¹ and metals, such as copper on foliage (Paris Green), became apparent and advisory literature regarding phytotoxicity to foliage and tree mortality was made available. Additional concerns regarding chemicals in foods surfaced from food adulteration in processing, beginning with the addition of copper and zinc salts to enhance color and preserve freshness⁶².

During the late 1800's the concerns of poisonous residue on fruit was only alluded to, and reports rejecting toxic residue concerns were published by credible sources⁶³. With the insecticidal residue tolerance used by the British government for food imports containing arsenicals becoming established in 1903, and the manufacturing and introduction of lead arsenate powder beginning in 1908, residue on export fruit became greater cause for concern. Compounding the residue issue was the adoption of findings in 1928 of fixing nicotine with tannic acid in combination with lead arsenate and oil to increase the efficacy of codling moth management, allowing the 'triple spray' to adhere to the fruit longer, making removal of the 'tile' residue from fruit more difficult⁶⁴.

The disruption of natural predation through the use of insecticides such as lead arsenate, nicotine sulfate and Bordeaux, derris, phenothiazine and sulfur had been studied by 1938⁶⁵ and the detrimental effect of arsenicals on honeybees during pollination and foraging in fruit trees had been confirmed as early as 1894⁶⁶.

Historical Chemical Regulation

With the advent of mechanized sprayers and reliable chemicals for fruit insect pest management, came the repetitive 'calendar sprays' and yearly cyclic applications of oils of kerosene, coal oil, paraffine, tar or whale oil, sulfur, pyrethrum, hellebore, bisulfide of carbon, carbolic acid, coal tar, various arsenicals, nicotine, and heavy metals, beginning in early spring and ending just prior to harvest. Predictable pest management allowed for fruit growers to produce larger crops of higher quality fruit year after year, generating surplus for wholesale in unprecedented volume.

But with greater ease in production came chemical quality, food quality, and chemical residue concerns. This prompted the government to pass the Federal Food and Drug Act of 1906 (Pure Food Law) that required fresh, canned, or frozen food that is shipped through interstate commerce be of 'pure and wholesome' quality. Under this law pesticide residues were not considered but were disputed over during the enactment process.

The regulation of pesticides by the federal government began in 1910 with the passage of the Federal Insecticide Act by Congress. This act was passed in response to concerns from the United States Department of Agriculture and farm groups regarding the sale of imitation or substandard pesticide products. Thus, the first federal pesticide legislation was to ensure the quality of pesticide chemicals purchased by consumers. Specifically, the act set standards for the manufacture of Paris green, lead arsenate, insecticides, and fungicides, and also provided for inspections, seizure of adulterated or misbranded products, and prosecution of violators⁶⁷.

With more and more fruit and vegetables harboring residues, Federal Food, Drug and Cosmetic Act of 1938 authorized the recently established Food and Drug Administration to set tolerances for chemicals in food, primarily for the arsenicals lead arsenate and Paris green. The tolerances for chemicals in food were deemed 'desirable', for which there was no retribution. The law also required the addition of coloring for certain pesticides to prevent their use as flour.

After WWII came a wave of synthetic pesticides in the form of insecticides, fungicides, herbicides, rodenticides, vying to replace the older more toxic arsenical and heavy metal chemical arsenal. To regulate this deluge of technology the Federal Insecticide, Fungicide and Rodenticide Act of 1947 was enacted to extended coverage

of previous laws to include herbicides and rodenticides. With the passage of this legislation, pesticide products previously grandfathered into the arsenal would be required to be registered with the U. S. Department of Agriculture, which established labeling standards for all pesticides. With greater concern for food safety came the Federal Food, Drug and Cosmetic Act of 1954, known as the Miller Amendment, which created specific tolerances required for all pesticides. Unlike the Act of 1938, raw agricultural commodities were now condemned if they contained pesticide residues above FDA tolerance levels.

On the heels of the Miller Amendment came the Federal Food, Drug and Cosmetic Act 1958 Food Additives Amendment, which covers food additives and pertains to chemicals remaining on food after processing. This amendment included the “Delaney Clause” which established a zero tolerance for food additives found to cause cancer. The concept of zero tolerance was acceptable given the ability to detect residues in 1958.

The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) Amendments of 1959 and 1964 added nematicides, plant regulators, defoliants and desiccants to the definition of “pesticide” or “economic poison”. It established federal registration numbers and signal words on labels and allowed the Secretary of Agriculture the power to suspend hazardous pesticide registrations. With the publication of *Rachel Carson's* ‘Silent Spring’ in 1962, that sowed the seeds of the environmental movement, the federal government established the Environmental Protection Agency (EPA) and passed the Federal Environmental Pesticide Control Act of 1972. This legislation enacted that pesticides must register with the newly created EPA as “general” or “restricted” use pesticides. This is the first legislation directed at both protecting public health and the environment. During that year DDT was banned from use in the U.S.

The FIFRA Amendments of 1975, 1978, 1980 and 1981 brought about improvements in the registration process and allowed for considerations of agricultural benefits of pesticides during the regulatory decision making process. Conditional registrations of pesticides were allowed to reduce the registration backlog. Pesticide Re-registration was initiated by the EPA in 1975 to bring the older pesticide chemicals up to current registration standards. A “Special Review” process was established to further review those pesticides that posed a risk or concern. FIFRA was amended in 1988 to

impose a 9-year schedule for the completion of re-registration along with the establishment of substantial registration fees. The Worker Protection Standard for Agricultural Pesticides was instituted and revised in 1992. Product labels were modified to restrict entry of workers into pesticide-treated fields, specification of protective clothing, and notification of workers of fields that are treated with pesticides was initiated. Employers must provide safety training, sites for decontamination, and emergency treatment for employees in pesticide handling and exposure risk positions.

The specific departments of the federal government act together to establish and enforce pesticide related laws. The EPA is responsible for establishing tolerances for pesticide residues on raw and processed food, the FDA enforces tolerances on most domestic and imported food, and the USDA enforces tolerances on meat, poultry and egg.

Recent Regulation Developments Changing Tree Fruit Pest Management

The Food Additives Amendment to the Federal Food, Drug and Cosmetic Act in 1958 containing the Delaney Clause required a zero tolerance for potential cancer-causing chemicals in processed food. Regarding raw foods, the EPA had a “negligible risk” approach to pesticide residues (cancer risk of one-in-one-million). Yet advances in technology now allows for detection of extremely small residue levels. The two different standards for both raw and processed food created a regulatory problem for EPA. To resolve the disparity between raw and processed foods new legislation was required.

Much of the incentive behind changing present federal laws was a view called “toxics populism”, the belief that current toxic laws are not tough enough. California's Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986, established a new incentive structure for toxics regulation in an attempt to end the regulatory paralysis affecting conventional approaches to hazard identification, risk assessment, and enforcement⁶⁸. Proposition 65 was the paving stone to shift the burden of proof in the regulatory process from government to industry. Use of chemicals known to cause cancer or reproductive toxicity is no longer considered "innocent" until proven "guilty" of harming public health by governmental agencies.

Food Quality Protection Act of 1996

The adoption of this new regulation philosophy by the federal government was made law on August 3, 1996, when the President signed the Food Quality Protection Act

(FQPA) of 1996 as part of the Farm Bill. This law amended the two major laws that governed the use of pesticides: Federal Food, Drug, and Cosmetic Act (FFDCA) as related to food safety, and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) regarding pesticide registration and use⁶⁹. The provisions of the law revolve around health based safety standards for all foods, eliminating prior multiple standards and taking into account non-foods and non-occupational sources of exposure centering on mechanisms of toxicity. Special considerations for infants and children requiring child safe tolerances, including children's 'special sensitivity' to pesticides, given their size, developmental requirements, etc. The law states that EPA should give priority consideration to reassessment of tolerances that appear to pose the greatest threat to human health. And that EPA must reevaluate pesticides in order of their perceived greatest risk, which is why the organophosphate pesticides were evaluated first.

As part of the FQPA implementation process, EPA and USDA formed the Tolerance Reassessment Advisory Committee (TRAC), an advisory panel of 52 key persons representing diverse agricultural interests. Regarding tolerances and exemptions for pesticide chemical residues, most of the law, pertaining to residues on tree fruit crops, originates in title 21, chapter 9, subchapter IV, § 346a⁷⁰. Under Section 408(b)(2)(A), the standard for establishing a tolerance is based on whether the tolerance is "safe". Safety is defined as "a reasonable certainty that no harm will result from aggregate exposure to the pesticide chemical residue, including all anticipated dietary exposures and all other exposure for which there is reliable information." A significant requirement of the new law is that EPA apply up to a ten fold safety factor for pesticides that have uncertain toxicity data . Under Section 408(b), Aggregate exposure includes dietary exposures under all tolerances for the pesticide, as well as exposure from all other non-occupational sources.

Therefore, in making a safety assessment, EPA considered dietary exposure data, including exposure through drinking water and also any existing reliable exposure data from non-food uses, such as inhalation and dermal exposure contributions from residential use, lawn and garden use, etc... to determine aggregate exposure. Safety regarding dietary risk is considered by the EPA to be the amount of chemical ingested divided by the reference dose (a safe dosage based on toxicological data & uncertainty factors) multiplied by 100. Since the chemical ingested or exposure is based on

estimated quantity of chemical in food and quantity of food eaten, the exposure is considered the residue multiplied by the consumption amount considered to be safe⁷¹.

Organophosphates were the first group of agricultural chemicals to be evaluated under the new FQPA guidelines. This class of insecticides is used on approximately 75% of fruit, vegetable and grain crops produced in the U.S.⁷². The measure of determining the specific amount of chemistry an individual will be exposed to over the course of their lives, through food and non-food sources, gave rise to the term cumulative 'risk cup'. In a letter addressed to all pesticide registrants in October of 2001, regarding organophosphate assessment, the EPA outlined the direction of mitigation measures, based on the 'risk cup' methodology. In this letter they state that the "FQPA directs the EPA to consider available information on the basis of cumulative risk from substances sharing a common mechanism of toxicity, such as the toxicity expressed by the organophosphates through a common biochemical interaction with the cholinesterase enzyme. The Agency (EPA) will evaluate the cumulative risk posed by the entire organophosphate class of chemicals after completing the risk assessments for the individual organophosphates. The Agency is working towards completion of a methodology to assess cumulative risk and the individual risk assessments for each organophosphate are likely to be necessary elements of any cumulative assessment. The Agency has decided to move forward with individual assessments and to identify mitigation measures necessary to address those human health and environmental risks associated with the current uses of azinphos-methyl. The Agency will issue the final tolerance reassessment decision for azinphosmethyl once the cumulative assessment for all of the organophosphates is complete⁷³."

The benefits that pesticides offer, taken into account in prior legislation, no longer will be given an open ended provision when new tolerances are set, but will be limited by risks (yearly and lifetime i.e. aggregate exposures) and thresholds such as carcinogenic factors, reproductive factors, and health based standards for children. The new legislation will require that all presently registered pesticides meet the requirements of the new health based safety standards. Included in re-evaluation are testing requirements for endocrine disruptors, requiring chemical manufacturers provide data on their products, including data on potential endocrine effects.

The law, seeing the need for replacement of crop protective materials, initiates expeditious review of safer pesticides to help them reach the market sooner and replace older and potentially more risky chemicals. It also establishes minor use programs within EPA and USDA to promote coordination on minor use regulations and policy, and provides for a revolving grant fund to support development of data necessary to register minor use pesticides. It encourages minor use registrations through extensions for submitting pesticide residue data, extensions for exclusive use of data, flexibility to waive certain data requirements, and requiring EPA to expedite review of minor use applications. These incentives are coupled with safeguards to protect the environment. The establishment of new requirements to expedite the review and registration of anti-microbial pesticides will also be under the FQPA umbrella, ending regulatory overlap in jurisdiction over liquid chemical sterilants. Under new FQPA guidelines a national uniformity of tolerances is established, whereby the states may not set tolerance levels that differ from national levels unless the state petitions EPA for an exception, based on state-specific situations.

In an effort to make the public aware of pesticide treated foods they are purchasing, a 'Right to Know' feature of the law is required through the distribution of brochures in grocery stores on the health effects of pesticides, how to avoid risks, and which foods have tolerances for pesticide residues based on benefits considerations. The law specifically recognizes a state's right to require warnings or labeling of food that has been treated with pesticides.

FQPA reauthorizes and increases (from \$14M to \$16M per year) user fees necessary to complete the review of older pesticides to guarantee they meet the new standards, requiring tolerances to be reassessed as part of the re-registration program. It will require the EPA to review periodically the pesticide registrations over a 15-year cycle, verifying that all pesticides meet updated safety standards. The law provides for enhanced enforcement of pesticide residue standards by allowing the FDA to impose civil penalties for tolerance violations.

The Science Behind The Methodology

In order to determine the complex exposure and risk assessments for pesticides to the general public, the EPA uses state-of-the-art software developed by the International Life Sciences Institute (ILSI). The software designed to conduct cumulative

and aggregate risk evaluations to make the assessments required under the 1996 Food Quality Protection Act⁷⁴. CARES was originally developed under the auspices of CropLife America (CLA) (formerly the American Crop Protection Association), which conceived the project, provided funding, and oversaw the program's evolution. Scientific and technical contributions to the program came from a broad team of experts, including: scientists from CLA's member companies and staff; consultants from infoscience.com, Novigen Sciences (now Exponent), Sielken & Associates, and Summit Research; and scientists from EPA and USDA.

Using the CARES software allows EPA risk assessors to estimate exposure to a single pesticide occurring via ingestion, dermal, and inhalation routes from food, drinking water, and residential sources (i.e., aggregate exposure). The software can also estimate concurrent exposure to multiple pesticides having the same mechanism of toxicity (i.e., cumulative exposure). Risk can be estimated for the U.S. population (a 100,000 sample size) or for a user-specified subset population, for a range of durations (acute, short-term, intermediate-term and chronic).

Pesticide Revisions – Requirements For New Registrations

Initially there was considerable concern regarding the vast changes in fruit tree pest management materials expected through the employment of FQPA. During the preliminary stages of evaluations regarding FQPA's impact on agriculture, the EPA has identified the top 20 foods consumed by non-nursing infants less than one year old that will have the 10X factor applied. They include apples, peaches, pears, carrots, corn, potatoes, fresh green beans, tomatoes and peas. Given the "cumulative risk" of aggregate exposure possibilities with specific classes of chemistry, most people in the fruit industry were especially concerned about the potential loss of organophosphates. Jim Cranney, USApple's director of industry services said regarding this issue "It is not a foregone conclusion that we would necessarily lose all these pesticides and uses. Certainly some will go, but not on the level of all OP's and all carbamates. But that will require a change in the current state of affairs with EPA on how they're viewing and implementing the law⁷⁵." These are critical insecticides, and especially for the apple and blueberry industries. Apple growers use them to control plum curculio, leafrollers, codling moths and late-season apple maggots while blueberry growers use them for fruit

flies late in the season. For both industries, alternative pest control measures are either non-existent, not economical or not thoroughly researched”.

The process for pesticide revisions applied by the EPA to fulfill the implementation of FQPA involved a special effort to maintain open public ‘dockets’ on the first of the classes of pesticides, the organophosphates, and to engage the public in the re-registration and tolerance reassessment processes. This open process included the guidance developed by the Tolerance Reassessment Advisory Committee (TRAC), a large multi-stakeholder advisory body that advised the Agency on implementing the new provisions of FQPA⁷⁶. During the evaluation of the first class of which was based on the EPA review of all relevant information and public comments through 5 phases of evaluation, the EPA identified interim risk mitigation measures, primarily focused on dietary risks, and recognized additional mitigation that the EPA deemed necessary to confront the human health and environmental risks associated with the use of azinphosmethyl.

The EPA Petition process for the registration of new materials requires the company to provide toxicology data to meet FQPA standards, pursuant to section 408(d) of the FFDCA (21 U.S.C. 346a(d), to amend 40 CFR part 180) by establishing a tolerance for residues⁷⁷. These include residue data from 6 diverse areas, which include residue chemistry, toxicological profiles, aggregate exposures, cumulative effects, safety determinations, and international tolerances.

Regarding residue chemistry, residues found on or in plants from plant metabolism in the form of the actual active ingredient or metabolites are determined and established using analytical method to detect metabolitic moieties. The methods include the utilization of oxidation, derivatization, and analysis by capillary gas chromatography with a mass-selective (MS) detection. Confirmatory methods specific for active ingredient and metabolites, utilizing high performance liquid chromatography (HPLC) with Electrospray MS/MS detection may also be conducted. The amount (magnitude) of residue data is collected from samples taken using residue harvesting protocols. Applications on tree fruit are made as foliar sprays at narrow intervals in field trials throughout different EPA regions. Typically fruit samples are collected at assumed label pre-harvest intervals (PHI) and residues evaluated for pomace, juice and juice concentrate.

Regarding toxicology profiles, acute toxicity data is taken from a variety of test organisms, primarily mammals, in feeding, dermal, inhalation, In vitro, and In-vivo studies, under chronic and sub-chronic conditions. Data generated is presented as NOELs (No Observed Effect Levels), NOAELs (No Observed Adverse Effect Levels), and LOAELs (Lowest Observed Adverse Effect Levels), on the populations, evaluated as a range of mg/kg. Organisms responding to a dose at the LOAELs level show slight changes, often as body weight reduction, delays in maturation, function etc. Reproduction, carcinogenicity, gene mutation assays, chromosomal aberration studies, animal metabolism, metabolite toxicology, endocrine disruption are all included in the residue analysis.

Dietary exposure regarding food and drinking water as well as non-dietary exposures, such as landscape, urban and industrial uses, are evaluated and exposure models are then assigned (such as the CARES software or Food Commodity Intake Database (DEEM-FCID_{TM}), which incorporates food consumption data reported by respondents in the USDA 1994–1996 and 1998 Nationwide Continuing Surveys of Food Intake by Individuals (CSFII), and accumulated exposure to the chemical for each commodity). Aspects of residue parameters include margin of exposures (MOE), toxicological level of concern (LOC) and uncertainty factors (UF) which models generate during the extrapolation of data, assigned to predictive human subjects. Models separate the use of a broad U.S. population base or a population base specific to the more susceptible infant and children grouping.

III. Resistance of Insects to Pest Management

The drive behind the development of newer compounds is both broad and comprehensive. As in the past the challenge to synthesize chemistries with lower mammalian toxicity was ever present. Yet concerns for the development of environmentally friendly materials and the replacement of older materials due to high degrees of mammalian toxicity (human acute and chronic toxicity) and escalating insecticide resistance, was changing the course of pesticide development and its use. With the ever-increasing loss of effective control measures from insecticide resistance new materials offer, at least in the short term, the possibility of continued pest management and minimal crop loss.

Resistance may be defined as a reduction in the sensitivity of a population, which is reflected in repeated failure of a product to achieve the expected level of control when used according to the label recommendations for that pest species⁷⁸. True resistance would not be influenced by problems of product storage, application and unusual climatic or environmental conditions. Insecticide resistance is also viewed as "*Accelerated Evolution*", in which a portion of a population that responds to intensive selection pressure possess genes that confer resistance. Resistance is in general considered pre-adaptive as it is the result of random mutations in which a small number of individuals have traits allowing their survival of what is typically a lethal dose of insecticide. The insecticide itself does not produce a genetic change, the individual posses the trait.

Numerous forms of resistance can develop to crop protection products and fall into four categories. Metabolic resistance in which resistant insects naturally detoxify or destroy toxins faster than susceptible insects and can quickly rid their bodies of the toxic molecules. Metabolic functions involved in detoxification include oxidation, reduction, hydrolysis, and conjugation. A second form is altered target-site resistance in which the site where the toxin typically binds in the insect is genetically modified to decrease the product's effects. Penetration resistance will occur when resistant insects absorb toxins more slowly than susceptible insects. Behavioural resistance occurs when resistant insects detect danger and avoid the toxin.

Other more dynamic forms of resistance have been observed once resistance populations began to develop. The cross resistance of an insect to one pesticide that generates resistance to other compounds typically involves an altered target site specific for a certain class of insecticides, or mode of action, as is observed in insects resistant to both DDT and pyrethroids. Resistance resulting from an increase in metabolic detoxification and confer resistance to other insecticide classes if each chemistry contains a functional group susceptible to the same detoxification mechanism. Multiple resistance, a higher level of pesticide resistance, is a population resistant to different compounds due to the coexistence of different resistance mechanisms, resulting from selection pressure of an insect by multiple classes of insecticides.

The first case of resistance developed by insects to insecticide was discovered in California red scale to hydrogen cyanide and of San Jose scale to lime sulphur in

1908⁷⁹. Resistance to insecticides was documented in 1914 by A.L. Melander in the *Journal of Economic Entomology*⁸⁰. He described scale insects, still alive, under a "crust of dried spray" of an inorganic insecticide. Between 1908 and 1945, only 13 cases of resistance to pesticides were recorded⁸¹. Of most importance observed in tree fruits was the resistance of scale to hydrogen cyanide, the resistance of codling moth, peach tree borer to arsenicals. Resistance was also observed of a variety of insects to tartar emetic, cryolite, selenium and rotenone during that period⁸². Shortly after the 1940 patent of DDT by Mueller of Geigy Corp., Switzerland, housefly resistance to DDT was documented in Denmark in 1946⁸³. By 1955, synthetic pesticides controlled 90% of the agricultural pest control market, and yet by 1960 it was observed that 137 species of insects had developed DDT-resistance (54 species), deldrin-resistance, ie resistance to the cyclodine group of chlorinated hydrocarbons (74 species), and OP-resistance (28 species). By 1984 resistance was reported in 447 insects and mites, 100 plant pathogens, 28 weed species, 2 nematodes and 5 mammals. With every new insecticide introduction cyclodienes, carbamates, formamidines, organophosphates, pyrethroids, *Bacillus thuringiensis*, cases of resistance surfaced 2 to 20 years later.

Long before the rumblings of FQPA, the research divisions of agricultural companies were continuing their search into new pesticide chemistries. The three major classes of chemistries dominating the 3 decades between 1940-1970 were the organochlorines (chlorinated hydrocarbons including DDT and its analogs, the cyclodienes and benzene hexachloride and its isomers), carbamates, and organophosphates. The broad development of pesticides was expanded within these classes during this era. Pyrethroids were first synthesized as esters as early as 1948 (Allethrin) but the synthesis and manufacturing of pyrethroids for fruit tree pest management began in earnest in the late 1970's continuing to the present day. Pyrethroids formed a fourth class of insecticides with similar modes of action as DDT, also acquiring the insect resistance inherent in its synonymous target site.

Due primarily to environmental concerns, a movement for reduction in the volume of pesticides was initiated through the development of land grant university pest management programs, beginning in the 1970s. This led to the development of methodologies using the integration of pest management techniques (IPM). These methods included the establishment of thresholds for tree fruit insect pests based on

scouting and sampling models, promoting pesticide application only after populations had reached economic damage levels.

The integration of in-depth pest biology, precise timing of highly susceptible life stages, and the use of the lowest pesticide rates based on the density of foliage (tree row volume in tree fruit management⁸⁴) led to considerable pesticide reductions by the early 1980's. This reduction, is at least in part, is also credited to the lower dose of active ingredient needed for control of pests using newer more potent pesticides.

With increasing insecticide resistance to both the older classes and newly developed pyrethroids, along with registration withdrawals by the EPA of pesticides deemed environmentally detrimental, growers were finding it more and more difficult to manage tree fruit pests during the mid-1980's. Although the pyrethroids were and continue to be very effective pest management tools, having very low mammalian toxicity levels (to dermal exposures), fruit tree growers found secondary effects of phytophagous mite 'flare ups' and high levels of toxicity to beneficial insects, especially the predatory mite *Galendromus* (= *Typhlodromus*) *pyri* (Acarina: Phytoseiidae) and *Neoseiulus* (= *Amblyseius*) *fallacis* Garman, led them to increase miticide use (as was experienced with DDT).

Resistance Pest Management Strategies

Although diverse classes of chemistries often differ in mode of action, attacking different target sites, it has been observed that insects having acquired resistance to a pesticide can acquire a propensity to develop resistance to new compounds within the modes of resistance development. One such example in tree fruit pest management is the resistance of the Obliquebanded Leafroller, *Choristoneura rosaceana* (Harris) to azinphosmethyl and chlorpyrifos and its cross-resistance to tebufenozide (Confirm 2F)⁸⁵.

This understanding of resistance patterns may help in the development of pest management strategies employing new chemistry introductions. Various strategies such as alternating insecticides may actually result in the development of resistance to several insecticide chemistries simultaneously⁸⁶. The key to managing resistance is to reduce selection pressure caused by the over-use or misuse of a pesticide, as this could result in the selection of resistant forms of the pest and the consequent evolution of populations that are resistant to that insecticide or acaricide⁸⁷.

Some principles for managing insecticide resistance on tree fruit have been developed by IRAC, a global Insecticide Resistance Action Committee. A specialized group formed by the fruit industry in 1984 to assess the threat of insecticide resistance and develop solutions. The U.S. member companies include Abbott Laboratories, AgrEvo, American Cyanamid, BASF Agricultural Products, Bayer Corp., Novartis Crop Protection, Cotton Incorporated, DowAgroSciences, DuPont, Elf Atochem, FMC Corp., Gowan Co., Monsanto, National Cotton Council, Rhone-Poulenc, Rohm & Haas, Uniroyal Chemical Co., Valent and Zeneca. They have listed both surveys of insects that have developed resistance to specific insecticides and comprehensive strategy for managing resistance. These strategies include Identifying the scope of resistance problems through surveys, the development of methods for detecting and monitoring resistance, to discover how insecticide resistance occurs, to formulate programs to counteract the loss of pest susceptibility, to develop and disseminate information on susceptibility management strategies, and interact with regulatory authorities responsible for insecticide registration.

IRAC recommends that growers try to minimize insecticide application by employing basic strategies. These include monitoring orchards through scouting to determine pest populations and trends, as well as presence of beneficial insects, the use of insecticides only if target pests are numerous enough to cause economic losses greater than the cost of the materials plus application and to use an integrated approach to pest management, combining as many different control mechanisms as possible, such as protection of beneficial organisms, rotation of insecticide classes, use of transgenic crop varieties, developing refuge habitat and the use of crop rotation.

A 'proactive' approach based on preventative strategies to resistance management can be developed based on a number of factors (genetic, ecological, behavioural, and operational). The primary objective in using preventative strategies only allows for the manipulation of operational factors, those directly determined by the pesticide application. The growers ability to manage resistance applies to the use of knowledge of earlier used materials and future use of materials in mode of action rotation. The use of materials with reduced residual activity or persistence will target pests in a narrow timeframe, aimed at the most susceptible life stage, reducing low dose residual that fosters resistant populations. Proper application technique, concentration,

and the degree of coverage are also within the grasp of the grower that will allow for greater efficacy and prolonged pesticide use.

Reduced Risk Chemistries:

New Modes of Action and the Insecticide Treadmill

There are 31 different species of insects and mite for which insecticides and miticides are labeled in NY State for tree fruit (Table 4). Presently there are no less than 444 different active ingredients used as insecticides⁸⁸, 28 classes of chemistries are used on U.S. tree fruit production. Of these, 25 classes are recommended for use in New York State, comprising 39 different active ingredients of insecticide and miticides (Table 5). There have been numerous reductions in the number of pesticides due to the evaluation process of re-registration beginning shortly after the establishment of the EPA. Yet we now have significantly more classes of chemistries with diverse modes of action to aid in managing both the insect and growing insecticide resistance of specific tree fruit pests. The use of these new classes in a rotation program will be an important part of future tree fruit insecticide resistance strategies.

Of the new classes of chemistries, the earliest of these third level or reduced risk materials developed were the fermentation microbial products and juvenile hormone analogs. The fermentation microbial products include newly developed products of Bt's, the abamectins and spinosads. The and juvenile hormone analogs include insect growth regulators: Formamidines and Thiadiazines, and the juvenile hormone mimics. These were followed by a wave of new chemistries in the following classes: neonicotinyls, carboxamides, carboxylic acid esters, granulosis viruses, diphenyloxazolines, insecticidal soaps, benzoyl urea growth regulators, tetrionic acids, organotins, oxadiazenes, particle films, phenoxy pyrazoles, pheromones for mating disruption, pyridazinones, tetrazines, and the quinolines.

Fermentation Microbial Products

Bt (*Bacillus thuringiensis*), a bacterium with insecticidal qualities, first became available as a commercial insecticide in France in 1938 and in the 1950s it became available for commercial use in the United States. Bt primarily came in the form of a spray to be applied to crops but the non-persistent nature of the insecticide necessitated repeat applications during the season. The Bt bacterium produces insecticidal proteins during sporulation undergoing the fermentation process. The bacterium is found as a

common soil organism, which was first discovered in Japan in 1901 by Ishawata, and then in 1911 by Berliner in Germany⁸⁹. Numerous strains of Bt exist, each strain producing its own unique insecticidal crystal protein, or delta-endotoxin. The insecticidal activity of the toxins from each strain differs, affecting a variety of species from the families of Coleoptera, Lepidoptera and Diptera. Bt exhibits a toxicity equal with that of organophosphates. The Bt toxins tend to be specific to insect pests and are relatively harmless to most beneficial insects, vertebrates including mammals. Bt toxins biodegrade in the environment and are not as persistent as are most other pesticides.

The mode of action of Bt requires that the insect ingest delta-endotoxin crystals and spores. Upon entering the digestive tract of the insect they are dissolved in the insect midgut, liberating the protein toxins of which they are made. These are processed into fragments that bind to cells of the midgut epithelium. The activated protein forms pores in the cell membrane causing the cells to rupture. The gut becomes paralyzed and the insect stops feeding. Gut contents flow into the body cavity causing septicemia.

In tree fruit the prime target for Bt are the lepidopterous complex pests. Due to resistance to the OP's, the Oblique banded leafroller has become a very difficult pest to control in NY State, and use of the Bt formulations for OBLR management has been very effective. Codling moth and some the pest lepidopteran complex are not as effectively managed using Bt's as the larvae tend to feed directly on fruit upon egg hatch.

Abamectins

Agri-Mek (**Abamectin**) avermectin B1a and B1b, is a natural fermentation product containing a macrocyclic glycoside. Avermectins belong to the glycoside class of insecticides. Abamectin is used on apples and pears as an acaricide/insecticide. The mode of action of Abamectins is most likely a chloride channel agonist in GABA mediated neurotransmission. It has been shown to have efficacy on European red mite and pear psylla, and suppresses populations of spotted tentiform leafminer. Abamectin is toxic to bees and predator mites on contact, but the foliar residue dissipates quickly, making it essentially non-toxic to these species after a few hours (low bee-poisoning hazard).

Proclaim (**Emamectin Benzoate**) (4*R*)-4"-deoxy-4" (methylamino) avermectin B1 is a similar chemistry as Agri-Mek and Mesa. The active ingredient in Proclaim is

avermectin B1, whereas Agri-Mek is a mixture of avermectin B1a and B1b. Laboratory bioassays indicated that Proclaim was highly toxic to codling moth neonate larvae⁹⁰. It does not appear to be fast acting and larvae are able to enter the fruit and feed for a short time before dying. Field-aged residue tests showed moderate to high level of activity through 21 days. Field trials (3 applications at 14 day intervals) also demonstrated the impact of delayed mortality. Proclaim offered only a moderate suppression of fruit injury yet a high degree of mortality is achieved of the larvae that entered the fruit, 95% reduction in live larvae. Laboratory bioassays conducted in Washington State indicated that Proclaim was extremely toxic to both obliquebanded and pandemis leafroller larvae (LC50= 0.0006 and 0.0008 ppm, respectively). Yet, field-aged bioassays revealed that Proclaim residues were short lived in the field with a decrease in activity observed at 14 days. Proclaim provided excellent control of pandemis leafroller in field trials. Two applications will probably be needed against high populations, especially during the summer generation.

Mesa (**Milbemectin**) (6*R*,25*R*)-5-*O*-demethyl-28-deoxy-6,28-epoxy-25-ethylmilbemycin B is similar to abamectin with a similar spectrum of activity to mites and leafminer. Residual activity appears shorter than abamectin and cross-resistance must be a consideration. Efficacy is greatest on the motile forms of mites. West coast studies have shown moderate mite activity against both spider mites and pear psylla. But pear psylla management requires rates above the labeled rates and is not presently recommended for this pest. Spider mite populations with developing resistance to abamectin may not be controlled by applications of Mesa. Fortunately, Agri-Mek resistance in pear orchards is limited in distribution to west coast / Washington state populations.

Spinosads

Success/Entrust (**spinosad**) are spinosyns produced through a fermentation process of the microorganism, *Actinomyces spinosa*. Spinosyns are active in the nerve synapse, binding at the nicotine receptor site, having little contact activity and requiring ingestion prior to expressing toxicity. Spinosad is active against many important lepidopteran pests and the potential exists to use this product many times during the growing season. Resistance management must be a concern for maintaining its use for as long as possible.

West coast laboratory bioassays with spinosad indicated it was only moderately toxic to codling moth (CM)⁹¹. Results from initial field trials showed that spinosad would provide suppression of codling moth, but not commercially acceptable control. Recent trials have shown that combining spinosad with 1% oil significantly increases the observed efficacy, utilizing two different modes of action. The oil suppresses egg hatch and spinosad kills hatching larvae. If re-treatment intervals are frequent enough (10-14 days), spinosad plus oil can provide effective codling moth control. This combination makes the Entrust formulation of spinosad a potentially valuable tool for organic growers. However, season long control is probably not an option as the frequency of application required may be both cost prohibitive and consume the total active ingredient for the season for only the first generation of CM. Therefore, an organic management program must still use all tools available to manage CM.

Spinosad is a very effective insecticide for the control of leafrollers, effective as a single spray in the spring at petal fall to control the overwintering larvae. Spinosad is effective as two to three summer treatments timed to coincide with the presence of early stage larvae. Presently there is no change in the susceptibility of the populations that had been exposed to spinosad for up to three years. Spinosad is also effective against *Lacanobia* larvae on the west coast but only against the young larvae (first through third instar). If the timing is late control will not be as effective. Spinosad has strong efficacy against leafminer populations by using spinosad at a slightly earlier timing than the standard 10% tissue feeding timing with improved efficacy by the use of an adjuvant (oil or organosilicone). Spinosad also has thrips activity.

Spinosad does not appear to have direct effect on predatory mites, but has acute toxicity to *Colpoclypeus florus* and *Pnigalio flavipes*. Field-aged residue trials indicated the negative effect on these parasitoids was seen for up to 14 days.

Juvenile Hormone Analogs

Identification of the juvenile hormones by Carrol Williams in 1967 gave rise to a new generation of insect specific insecticides, which he described as 'third generation insecticides'. The development of the synthesized aromatic terpenoid ethers of the juvenile hormones, were found to be several hundred-fold more active than the natural hormones.

Insect Growth Regulators: Formamidine

Mitac (**Amitraz**) *N*-(2,4-dimethylphenyl)-*N*-[[[(2,4-dimethylphenyl)imino]methyl]-*N*-methylmethanimidamide in the formamidine class, was one of the first endocrine-based insecticides, registered as a technical grade pesticide in 1975. EPA received an application for registration of an end-use product for apples and pears in 1976⁹².

The formamidines are characterized by a variety of behavioral effects, primarily mites and ticks. The endocrine-based insecticides involve activity at receptors of the biogenic amines, such as octopamine receptors. Biogenic amines act as neuromodulators. They are released by neurons, modulating the reaction of a transmitter with its receptor. Octopamine, as a neuromodulator in insects, functions similarly to adrenaline in vertebrates. The effects of formamidines are diverse, having a repellent action and feeding deterrent. Organisms may suffer increased excitability, leading to ineffectual probing of the food source or aimless walking, flight, or disrupted mating patterns.

The generally accepted target site for formamidine insecticides is the octopamine receptor via agonistic response by sustained and abnormal octopamine-like stimulation. Another possibility is formamidine interaction with octopamine-sensitive adenylate cyclase, the enzyme that catalyses the production of cyclic AMP and functions as an intracellular messenger.

In tree fruit Mitac is labeled on pears for the control of pear psylla primarily to control organophosphate-resistant pear psylla populations. It controls the European red mite and suppresses codling moth and other lepidopterous pests, but not very effective against the pear rust mite. It has a relatively low mammalian toxicity, also having a low bee-poisoning hazard. Slight injury to fruit has been observed where overcast, cool, moist conditions contribute to poor drying conditions.

The Juvenile Hormone Analogs And Mimics

Esteem (**Pyriproxyfen**) 2-[1-methyl-2-(4-phenoxyphenoxy)ethoxy]pyridine is an insect growth regulator functioning as a juvenile hormone mimic. In fruit, pyriproxyfen was registered in the late 1990's for use in apples and pears. It interferes with the insect's normal metamorphosis and kills by retarding its growth and causing sterility. It also has translaminar properties and displays ovicidal activity. Although leafrollers and codling moth appear on the label, results from preliminary field trials in NY suggest that it has greatest efficacy on San Jose scale, pear psylla, leafminers and aphids. Esteem

does have activity against the *codling moth* egg, acting as an ovicide if the moth deposits its eggs on top of pyriproxyfen residue. Pyriproxyfen for codling moth management is most accurately applied using DD models for oviposition predictions (100DD after 1st adult catch, followed by a second application in 14 to 21 days). It can be a highly selective insecticide providing control without disrupting activities of biological control agents. It has low toxicity or is non-toxic to most beneficial species, and has a low bee-poisoning hazard. Esteem has low toxicity to mammals and has a short worker reentry period (12 hours), but a long pre-harvest period (45 days).

Esteem works well against pear psylla, working similarly to the carbamate Comply (fenoxycarb). Esteem has been shown to act on eggs and first through third instar nymphs, and may have sublethal effects on later instars ('hardshells') and adults as well. The first generation of *pear psylla* is the best target for Esteem applications, as the life stage distribution is the most synchronized at this time. The use of delayed dormant oils, sulfurs, Thiodan, and Surround greatly enhance this synchrony, further increasing the effectiveness of Esteem. Applications against the first generation can be made from delayed dormant (targeting early eggs) through 2 weeks post-petal fall (targeting third instar nymphs). The optimal timing, however, is from clusterbud to petal fall, when there is peak egg hatch. Results with Esteem have been variable, in some cases being able to control high populations while in others not controlling low populations. This may be a result of a predisposition of some orchards to resistance. Orchards with some degree of developing resistance to fenoxycarb may have reduced control effectiveness with Esteem. Esteem does not appear to have significant effects against *grape mealybug*. Esteem has no known negative impacts on beneficial arthropods.

Confirm 2F (**tebufenozide**) manufactured by Dow AgroSciences, petitioned and received NY State registration in March of 2002. Tebufenozide mimics the action of the natural insect hormone 20-hydroxyecdysone, the physiological inducer of the molting and metamorphosis process in insects⁹³. Tebufenozide controls lepidopterous larvae through the induction of a premature lethal molt, which initiates within hours of ingestion of treated crop surfaces. Contact activity has also been observed in some insects. Actual death of the larvae will take several days to occur, although feeding by the insects generally ceases within 24 hours of ingestion. Tebufenozide is highly active

against most lepidopterous larvae while having practically no activity at typical use rates against other orders of insects. While use of tebufenozide in NY State orchards has allowed for management of OP resistant obliquebanded leafroller in western parts of the state, cross resistance became apparent shortly after its introduction. In regions where resistance is not a concern, the selectivity of tebufenozide allows for the maintenance of the populations of beneficial and predatory insects.

Intrepid (**methoxyfenozide**) is very specific to lepidopteran pests, acting to initiate a premature lethal molt in caterpillars. In some cases methoxyfenozide will not kill the larva but the subsequent adult will not be able to reproduce. Methoxyfenozide has little or no contact activity and must be ingested by larvae to have a toxic effect. Methoxyfenozide has strong ovicidal activity applied topically or if eggs are laid on residues.

Methoxyfenozide controls codling moth as an ovicide and as a larvicide, highly toxic to both eggs and larvae in laboratory studies, but not providing the same amount of crop protection as OP's under the same use pattern. The reduced efficacy in field applications relative to OP's is probably due to reduced residual control. We expect only about 14 days of activity against susceptible populations. Ovicidal timing of methoxyfenozide may also provide a new strategy for use. Washington State data suggests that an ovicide timing of 100 degree days is at least equivalent to the traditional larvicide timing of 250 degree days⁹⁴. Methoxyfenozide appears to be a poor "stand alone" tool for codling moth except where very low pressure is present. It's best fit appears as a component of a pheromone-based IPM program where it is integrated with the use of codling moth mating disruption. Codling moth populations resistant to organophosphates may also become tolerant or cross resistant to methoxyfenozide due to OP mediated cross-resistance, as observed with the IGR tebufenozide and OBLR populations in NY state.

Methoxyfenozide also has good activity against leafrollers. Its use in the petal fall period could simultaneously control codling moth and leafroller. Methoxyfenozide has primarily been evaluated at its full field rate against leafrollers, yet the data suggests reduced rates may also be effective. Methoxyfenozide has demonstrated effectiveness against leafrollers in the spring from bloom to about 14 days after petal fall. One application of methoxyfenozide can be effective against low leafroller densities but a

second application might prove necessary against high populations. In the spring when weather forecasts predict warm conditions, 65°F or better for at least 3 days, applications of methoxyfenozide can be made against active feeding larvae. Methoxyfenozide has a longer residual activity against leafrollers not as subject to the heavy weather on efficacy as are Bt products. Methoxyfenozide is also effective against leafroller larvae in the summer, with optimum timing is when larvae are young. When applied at 20% egg hatch of leafroller methoxyfenozide provided excellent control, comparable to spinosad in most tests. Methoxyfenozide has a long residual activity but has no contact activity, requiring good coverage. Leafroller populations have shown a highly variability degree of susceptibility to methoxyfenozide, the variability appears directly related to OP resistance in the same populations. The genetic basis for resistance to methoxyfenozide exists in some leafroller populations in WA, and rotation with different modes-of-action materials as part of a resistance management program is essential.

On the West Coast, methoxyfenozide is very effective against *Lacanobia* fruitworm. The best timing against this insect is 80% eggs hatch, prior to the presence of large larvae, approximately 700DD after first flight. A single application seems adequate to control this pest and it is very likely that reduced rates will be as effective as the full field rate. *Lacanobia* densities were suppressed in orchards that used Intrepid in multiple applications against codling moth. These timings overlapped with the optimal timing for *Lacanobia* providing control of both pests at the same time.

Methoxyfenozide has no known effects on campylomma, leafhoppers, aphids, or phytophagous or predatory mite. Suppression of leafminer depends on timing, with greater success being achieved where it has been used in codling moth programs than in single-application leafminer timings .

Methoxyfenozide has been tested against codling moth in pear, and appears to work effectively against low to moderate populations. At low densities, Methoxyfenozide was comparable with Guthion treatments against CM. However, when challenged with very high codling moth populations, methoxyfenozide treatments sustained significant damage. Methoxyfenozide is ineffective against pear psylla or grape mealybug. Methoxyfenozide has no known negative impacts on beneficial arthropods, having a short REI (4 hours) and PHI (14 days).

Insect Growth Regulators: Thiadiazine class

Applaud (**buprofezin**) - 2-[(1,1-dimethylethyl)imino]tetrahydro-3-(1-methylethyl)-5-phenyl-4H-1,3,5-thiadiazin-4-one, is a unique chemistry, belonging to the thiadiazine class of insecticides. Nichino America, Inc has submitted to the EPA a petition for registration of buprofezin on December, 2004. Its mode of action is unique in that it can be used as a contact insecticide, stomach poison, or insect growth regulator as a chitin synthesis inhibitor. Applaud is likely to only have registration on pear.

Applaud is very active against grape mealybug and pear psylla. Because of its activity against the same primary pests as the chloronicotinyls, Applaud could be an excellent rotation candidate in a resistance management program. Field tests of Applaud conducted in Washington State against pear psylla have been studied at numerous timings, all with good success⁹⁵. Applaud has activity comparable to the neonicotinyls against pear psylla, although the residual activity appears shorter (less than 2 weeks). It has been shown to be the most active compound available against grape mealybug, particularly in summer applications. It has no known adverse effects on beneficial arthropods.

Neem (**Azadirachtin**) Dimethyl (2aR,3S,4S,4aR,5S,7aS,8S,10R,10aS,10bR)-10-(acetyloxy)octahydro-3,5-dihydroxy-4-methyl-8-[[[(2E)-2-methyl-1-oxo-2-butenyl]oxy]-4-[(1aR,2S,3aS,6aS,7S,7aS)-3a,6a,7,7a-tetrahydro-6a-hydroxy-7a-methyl-2,7-methanofuro[2,3-b]oxireno[e]oxepin-1a(2H)-yl]-1H,7H-naphtho[1,8-bc:4,4a-c"]difuran-5,10a(8H)-dicarboxylate, trade names Aza-Direct (Gowan) 1.2L, Azatin XL Plus (Certis), Neemix 4.5 (Certis), is derived from the seeds of the neem tree, *Azadirachta indica*, which is widely distributed throughout Asia and Africa. Azadirachtin has been shown to have repellent, antifeedent, or growth regulating insecticidal activity against a large number of insect species and some mites. It has also been reported to act as a repellent to nematodes⁹⁶. Neem extracts have also been used in medicines, soap, toothpaste and cosmetics. It shows some activity against leafminers, leafhoppers, mealybugs, aphids, caterpillars, tarnished plant bug and pear psylla, but repeated applications at short intervals are probably necessary for acceptable control of most pests. Azadirachtin is relatively short-lived and mammalian toxicity is low (rat oral LD50 >10,000). It can be used up to and including the day of harvest and reentry is permitted without protective clothing after the spray has dried. It is relatively nontoxic to beneficial organisms, but

toxic to fish, aquatic invertebrates, and bees exposed to direct treatment, although relatively non-toxic when dried. It is therefore categorized as having a moderate bee poisoning hazard. Aza-Direct (Gowan) 1.2L, Azatin XL Plus (Certis), Neemix 4.5 (Certis)

Neonicotinyls

Beginning in 1979 a new class of chemistries was developed by Kagabu and coworkers of Nihon Tokushu Noyaku Seizo in Japan (presently Nihon Bayer Agrochem) based on the heterocyclic nitromethylenes, identified earlier by the Shell development Co. in California. These neonicotinyls have a 'novel' mode of action and have become the most successful of the new classes, with numerous analogs becoming registered in fruit tree management. The neonicotinyls are grouped into three chemical categories based on their chemical structure. The nitroguanidine insecticides contain clothianidin, dinotefuran, and thiamethoxam. The nitromethylene insecticides include nitenpyram and nithiazine and the pyridylmethylamine insecticides include acetamiprid, imidacloprid, nitenpyram and thiacloprid⁹⁷.

There are presently 3 of the 5 federally registered neonicotinyls available in NYS for tree fruit pest management. These include structural analogs of imidacloprid known as thiacloprid, acetamiprid, clothianidin and thiamethoxam, which act in the nerve synapse like nicotine acetylcholine. Their mode of action is not so completely new as their target site is nearly the same as nicotine, used for decades in tree fruit as "Black Leaf 40". They have been found to act as agonists at the insect nicotinic acetylcholine receptor (nAChR).

The selectivity of the neonicotinyls for insects and not mammals is a strong characteristic of its success. Neonicotinoids and nicotinoids are defined by their common structural features and action as agonists at the nicotinic acetylcholine receptor (nAChR) with further differentiation by their ionization at physiological pH and target site specificity between insects and mammals, i.e., the neonicotinoids are not ionized and selective for the insect nAChR, and the nicotinoids are ionized and selective for the mammalian nAChR. Whereas ionized nicotine binds at an anionic subsite in the mammalian nAChR, the negatively tipped nitro or cyano neonicotinoids interact with a proposed unique subsite consisting of cationic amino acid residue(s) in the insect nAChR making for both a safe yet highly effective insecticide⁹⁸.

Provado (**imidacloprid**) 1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine, in the nitroguanidine group, was introduced in 1991 as the first neonicotinyl in pest management, presently manufactured by Bayer Agricultural Products. In tree fruits it is generally used as a systemic insecticide and stomach poison. It does have contact insecticidal properties, however the residue is relatively short-lived in the environment. Instead, it is absorbed into leaves, where it can have a long effective residue. It has very high levels of toxicity at very low rates⁹⁹. The chemical works by interfering with the transmission of stimuli in the insect nervous system, causes a blockage in the neuronal nicotinic pathway. As this is more abundant in insects than in warm-blooded animals, the chemical selectively is more toxic to insects than mammals. The blockage leads to the accumulation of acetylcholine resulting in insect paralysis and mortality¹⁰⁰.

On Lepidopteran pests such as codling moth Provado has only low to moderate toxicity in laboratory studies and provided very little suppression of fruit injury in a field trials. Against pandemis leafroller and *Lacanobia* fruitworm it provided very little suppression of larval densities in west coast studies¹⁰¹. Provado is primarily used as an aphicide in Washington state. In New York it has provided adequate suppression of leafminers, white apple and rose leafhopper and has shown activity against apple maggot in recent studies¹⁰². Provado has shown apparent in-direct effect on mites in regards to mite build-up. Provado doesn't appear to have a negative impact on primary mite predators via contact but appears to have detrimental effects upon feeding on phytophagous mite that have fed on imidacloprid.

In NYS imidacloprid has also been shown to be effective against whiteflies, thrips, scale crawlers, pear psylla, mealybugs, some beetle and weevil species. It has also shown activity against pear midge when applied at petal fall. This material is detrimental to *Stethorus punctum*, an important predatory beetle on mite. Provado is relatively safe for mammals but has a high bee-poisoning hazard, exhibiting toxicity on contact plus repellency and hive disorientation.

Actara (**thiamethoxam**) 3-[(2-chloro-5-thiazolyl)methyl]tetrahydro-5-methyl-*N*-nitro-4*H*-1,3,5-oxadiazin-4-imine, in the nitroguanidine group, by Syngenta, has activity and use much the same as Provado, with the same target pests and 'transtemic' activity. It has demonstrated efficacy against the mired campylocoma, although it cannot be used

during bloom due to high bee toxicity. Actara is effective against the green apple and spirea aphid, with suppression of woolly apple and rosy apple aphid. It has little activity against leafminer but works well against the leafhopper complex.

On pears actara has much the same activity against pear psylla and grape mealybug as Provado. And like Provado, Actara is very effective against the early instars. Effectiveness against older instars of these pests is greatly reduced, and there is relatively little activity against adults. As with the other neonicotinoids in general the use of oil as an adjuvant has shown increases in mortality of pear psylla and grape mealybug.

Actara, unlike Provado, is registered for prebloom use in pear. It should not be applied later than whitebud when used prebloom, to avoid any potential for effects on bees. Actara can also be effective in petal fall applications, as with Provado, provided the pear psylla and grape mealybug are of the appropriate stage. Actara is at least equal in efficacy to Provado when used against summer generations of both pear psylla and grape mealybug. On the west coast summer applications of Actara have negative effects on the bio-control agent campylomma where populations of this important beneficial aid in late season pest management.

Actara does not appear to be directly toxic to predatory mites, thus the overall risk of mite disruption is currently rated low. Actara has a high degree of toxicity to bees and bee exposure should be avoided.

Assail (**acetamiprid**) (1*E*)-*N*-[(6-chloro-3-pyridinyl)methyl]-*N'*-cyano-*N*-methylethanimidamide, in the pyridylmethylamine group, is the first neonicotinyl registered on apples and pears that has a high degree of lepidopteran activity, primarily limited to codling moth. It was originally developed by Bayer Agricultural Products but was acquired by Nippon Soda Company and Aventis CropScience (U.S. distribution and marketing rights obtained by Cerexagri)¹⁰³. Assail was very active against codling moth, performing more like the standard OP's. Assail can be applied at the same timing as Azinphosmethyl and Phosmet for CM management with 2 applications per generation starting at egg hatch. This program has provided control of codling moth larvae similar to the industry standards. When Assail is applied topically it is also highly toxic to codling moth eggs. A good resistance management strategy would be to limit Assail applications

to one generation/year. Regarding the leafroller complex, laboratory bioassays indicate that Assail has only low toxicity to leafroller neonate larvae.

As with the other neonicotinyls, assail has good activity against leafhopper and the green aphid complex, with less activity on rosy apple and woolly apple aphid. Assail also is a good Hemiptera material having a bee toxicity rating of III it can be used at bloom when bees are not active, the ideal timing for the mired bug complex. Leafminers suppression, like other neonicotinyls, has been observed

Assail has much the same activity as Actara and Provado for pear psylla and grape mealybug. It is relatively safe for bees, and can be used before bloom at the optimal timing for controlling both pear psylla and grape mealybug. The relative efficacy of Assail against pear psylla is reduced with late summer applications.

Assail appears to have potential to become a viable alternative to OP's for codling moth control in pear. Due to resistance management concerns it should be viewed primarily for pear psylla and grape mealybug management. Neonicotinyls such as Assail should be used carefully against Leps as they would be selecting for resistance in pear psylla.

Given the efficacy against codling moth, the tendency may be to use multiple applications in a season. As with provado and the pyrethroids, two or four spray programs have caused substantial mite flare-ups on apple. At least some of this effect is attributable to efficacy on predatory mites. The risk can be mitigated if only a single application is made to an orchard with a stable mite situation using the addition of 1% oil to the Assail applications.

Brief worker Restricted Entry Interval (REI) of 12 hrs, a moderate Pre-harvest Interval (PHI) of 7 days and low toxicity rating (Category III) allow the use of Assail as a viable organophosphate replacement. Practical resistance management strategies would limit the number of neonicotinyl applications in any given season. The use of multiple neonicotinyl applications by the use of Assail, Provado and Actara should be limited or avoided when possible.

Calpyso (**thiacloprid**) (Z)-[3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene]cyanamide in the pyridylmethylamine group is next in the line of neonicotinyls with federal registration on apples and pears (it has not received NY registration as of the end of 2004). It is also presently manufactured by Bayer

Agricultural Products. It targets aphids, leafhoppers, leafminers, psylla, plum curculio, apple maggot, Oriental fruit moth and codling moth. This material is also translaminar but its residue has a stronger plant surface profile than the other neonicotinyl. Calypso has a broad spectrum of pest activity, and is effective on piercing/sucking insect pests, plum curculio, and the internal feeding insects of fruit, including codling moth and apple maggot. West coast emphasis is for its use on codling moth, and in NY as an OP replacement for plum curculio.

Calypso also has greater restrictions on its label than the earlier neonicotinyls. Restrictions for use of Calypso in pome fruit include a REI of 12 hours, a PHI of 30 days, and a maximum usage of 16 fluid ounces (0.5 lb AI) per acre during one growing season. It is not allowed use between pink and petal fall in both pears and apples, and a 100 ft buffer for aerial applications are imposed near rivers and streams. There are also several endangered species restrictions.

Clutch (**chlorothianidin**) [C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N"-methyl-N"-nitroguanidine, in the nitroguanidine group of neonicotinyls, from Arvesta Corp. (a group member of Tokyo-based Arysta LifeScience Corporation). It has shown activity against aphids, leafhoppers, thrips, whiteflies, Colorado potato beetles, leafminers, scale, mealy bugs and certain Lepidopteran species. Clutch is currently undergoing expedited registration review by the U.S. Environmental Protection Agency as an "organophosphate replacement" compound¹⁰⁴.

As the chlorothianidin chemistry is quite new in tree fruit, field trials on insect efficacy are limited. Laboratory bioassays of Clutch against codling moth neonate larvae indicate that although it has a fairly low LC50, it does not appear to have the same acute toxicity as Calypso or Assail¹⁰⁵. However, laboratory bioassays indicate that Clutch has only low toxicity to leafroller neonate larvae.

Clutch appears to have the same activity against pear psylla and grape mealybug as the other neonicotinyls. Use of this material against codling moth in pear indicates that it may be more important to direct this class of insecticides at pear psylla rather than codling moth, where there are other effective alternatives.

Carboxamides

Savey (**Hexythiazox**) *rel*-(4*R*,5*R*)-5-(4-chlorophenyl)-*N*-cyclohexyl-4-methyl-2-oxo-3-thiazolidinecarboxamide carboxamide, is a carboxamide used as a contact and

stomach-poison acaricide. It is effective against eggs and larvae of European red mite but it will not kill adults. It is registered for a single application in all pome and stone fruits in NY State, and may be used up to 28 days before harvest. It has demonstrated excellent residual control, and has a low bee-poisoning hazard, is safe to beneficial insects and predatory mites.

Carboxylic Acid Esters

Acramite (**Bifenazate**) 1-methylethyl 2-(4-methoxy[1,1'-biphenyl]-3-yl)hydrazinecarboxylate is a hydrazine compound from a relatively new class of chemistries, carboxylic acid ester. Its mode of action is a GABA (gamma-aminobutyric acid) agonist in insects, but has not been confirmed in mites. Bifenazate was recently registered for use on tree fruits, including apple, pear, peach, nectarine, plums, prunes. Bifenazate is a specific and selective miticide, with good activity against spider mites but with no rust mite activity. Bifenazate is primarily used against motile stages, but may have some ovicidal activity.

In pears bifenazate can control low to moderate populations of twospotted spider mites, and will suppress heavy infestations. Bifenazate is limited to one application per year in pear to help slow the first development of resistance and maintain efficacy.

Granulosis Viruses

Cyd-X, Carpovirusine, and Virosoft CM are active formulations of codling moth granulosis virus available in Washington State. Data suggests that they all are highly virulent, with similar efficacy between the products if used at equivalent rates of virus particles/acre. Bioassays of field-aged residues have shown residual control of these products broke down after 7 days in the field suggesting a re-treatment interval of 10-14 days.

The codling moth granulosis virus has been known for many years and different companies have attempted to formulate it as a biological reduced risk pesticide. Most formulations have not provided consistent control. The virus is subject to rapid degradation by UV light and high temperatures. The virus has the potential if effective to cause mortality of codling moth larva but this usually does not occur fast enough to prevent its entry into the fruit. Granulosis viruses are species specific, and have been identified for many lepidopteran pests. The advantages of the codling moth granulosis

virus is its specificity on codling moth and will not interfere with activities of natural enemies.

Field trials indicated that delayed mortality is common and after 14 days many larvae exposed to virus were still alive and actively feeding, allowing little suppression of fruit injury in high pressure orchards after one generation of use¹⁰⁶. The full effect of the virus treatments was not noted until the subsequent generation, when the population did not develop to expected levels. After the first generation there was no significant reduction in fruit damage relative to the untreated control in any virus treatment. However, a greater than 90% reduction of second generation adults was noted in all virus treatments. It was not clear whether the larvae were dying prior to exiting the fruit, as fully mature larvae or pupae. Codling moth granulosis virus has no activity against leafrollers, and although a pandemis granulosis virus for this leafroller has been identified, it has never been formulated into an insecticide. No activity against beneficial arthropods has been observed.

Granulosis virus have greatest value for organic growers. Granulosis virus treatments in a rotational program using diverse tools such as mating disruption, oil, and a fast acting larvicide provide a strong resistance management strategy.

Diphenyloxazolines

Zeal, Secure (**Extoxazole**) 2-(2,6-difluorophenyl)-4-[4-(1,1-dimethylethyl)-2-ethoxyphenyl]-4,5-dihydrooxazole, is an insect growth regulator (IGR) for mites and aphids, manufactured by Valent USA. Extoxazole was registered in 2004. The mode of action (MOA) is unclassified or unknown at this time. As a miticide, extoxazole is an adulticide, active as a adult mite sterilant having no toxicity on mite adults but does have ovicidal efficacy and shown to have motile mortality.

Insecticidal Soaps

M-Pede, produced by Mycogen, is a concentrate made from biodegradable fatty acids. As a contact insecticides it is effective against soft bodied arthropods such as aphids, mealybugs, and pear psylla. In providing suppression of pear psylla in a seasonal spray program, the residual period is short and uniform drying conditions are required to prevent droplet residues on the fruit surface. It has a low bee-poisoning hazard.

Benzoyl Urea Growth Regulators

Diamond (**novaluron**) is a chitin inhibitor developed by Crompton Corporation, registered in May 2004. Novaluron is active on the lepidopteran complex, plant bugs, stink bugs, and shows suppression of whiteflies and thrips. Makhteshim-Agan of North America, Inc. has a Section 24(c) supplemental label for use in West Virginia for the control of codling moth, oriental fruit moth, and various leafroller species on apple¹⁰⁷. Novaluron is an insect growth regulator (IGR) that interferes with the insect's ability to form chitin, thus disrupting the molting process, effective only against the immature stages of insects, and will not kill adults. Route of insect entry is primarily through ingestion, with some contact activity. Toxicity to eggs has also been demonstrated for some insect species. Presently it has a maximum of 4 applications (150 fl oz/acre) per season, a 12 hour REI and 14 day PHI.

Tetronic Acids

Envidor (**Spirodiclofen**) 3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl 2,2-dimethylbutanoate, is a tetronic acid acaricide, a new class of chemistry which disrupts the endocrine system, affecting energy production. Spirodiclofen is an IGR-type insecticide with slow activity not acutely toxic to adults. Spirodiclofen may affect some insect pests as well as mites, but has not been well studied in tree fruits¹⁰⁸. Unlike many of the other new chemistries, there is evidence that oil may be antagonistic to Spirodiclofen. Results to date have shown that spirodiclofen has promising activity against mites on apple. One example of a trial conducted on a rising population showed the typical slow activity expected of an IGR insecticide. After five days, a population of 10-15 mites/leaf was still present, but sufficient control for the rest of the season was noted. On pear spirodiclofen has been demonstrated in field tests to be an effective miticide. Its activity is much like that of Acramite and Secure, working well to control moderate populations and suppress high populations. These products will likely not be adequate 'rescue' treatments due to their relatively slow activity. Spirodiclofen will fit well with Acramite and Zeal in an acaricide resistance management program as all three miticides effectively employ different modes of action.

Organotins

Vendex (**Hexakis Or Fenbutatin Oxide**) hexakis(2-methyl-2-phenylpropyl)distannoxane is an organotin compound registered for the control of a wide range of plant-feeding mites on several fruit crops, including strains that are resistant to

some other miticides. Resistance to the organotin Plictran has been well documented in the Pacific Northwest, and it is highly likely that resistance to Fenbutatin oxide is also present¹⁰⁹. Fenbutatin oxide is nontoxic to honey bees, and is relatively nontoxic to predatory mites. Fenbutatin oxide is toxic to fish and has a low bee-poisoning hazard. It is not to be applied more than 4 times/season or more than 3 times between petal fall and harvest.

Oxadiazenes

Avaunt (**Indoxacarb**) is the first member of the oxadiazine class of chemicals registered for insect control on apple and pear. It is primarily effective against various lepidoptera, and has activity against selected tree fruit insects. Avaunt acts primarily through ingestion by inhibiting sodium ion entry into nerve cells, resulting in paralysis and death of the pest species. Indoxacarb results in rapid inhibition of insect feeding, pest knockdown within 1 to 2 days, and provides crop protection for 7 to 14 days. Indoxacarb has low mammalian toxicity and has efficacy relative to OP's and pyrethroids in toxicity to beneficial insects and mites. Indoxacarb is limited to a maximum of 4 applications per season and total of 24 oz per acre up to 14 days before harvest.

Particle Films

Surround (**Kaolin**) is a naturally occurring clay mineral that has many uses as a direct and indirect food additive, in food contact items, cosmetics and toiletries, and as an inert ingredient in many pesticide formulations. When applied, the 95WP crop protectant forms a white, mineral-based particle film which reduces the damage to plants caused by arthropod pests, as well as environmental stress caused by solar effects. In research trials in apples in NY State, it has been shown to be efficacious against the major tree fruit pests such as plum curculio, internal Lepidoptera such as codling moth and oriental fruit moth, leafrollers, phytophagous mites, leafhoppers, and apple maggot. In pears, it has also been shown to suppress pear psylla, and in stone fruits it reduces feeding damage from Japanese beetle. Frequent applications at 7 to 10-day intervals beginning pre-bloom and maximal coverage and high rates at 25 to 50 pounds per acre are advised in New York while there is active foliar growth. The preventative layering of material onto fruitlets prior to pest presence Surround has a low bee-poisoning hazard.

Phenoxy pyrazoles

Fujimite (**Fenproximate**), 1,1-dimethylethyl 4-[[[(E)-[(1,3-dimethyl-5-phenoxy-1H-pyrazol-4-yl)methylene]amino]oxy]methyl]benzoate is both a contact acaricide/insecticide developed by Nichino America, became federally registered in 2004. Fenproximate is registered on apple and pear for the control of various mite species, white apple leafhopper, and pear psylla. Like Nexter, its mode of action is to block cellular respiration by acting as a mitochondrial electron transport inhibitor (METI). It also acts to inhibit molting of immature stages. Mite feeding and oviposition stop soon after application, with death occurring in 4-7 days. FujiMite has a restricted entry interval of 12 hours and a preharvest interval of 14 days.

Pheromones For Mating Disruption

Synthetic pheromones for disrupting the chemical communication of certain insect pests have been formulated to prevent them from mating and producing larvae that injure the crop. Pest-specific pheromones are released from dispensers or microcapsules placed or sprayed in the orchard before the initiation of flight, and can reduce or in some cases eliminate the need for supplementary insecticidal sprays. This approach works best in large (5-10A or more), rectangular plantings, where the pheromone concentration in the air is more uniform and can be maintained at a high level. Border insecticide sprays may be needed in orchards adjacent to sources of adult immigration or in other high-pressure situations. Each lepidopteran pest requires pheromones specific for its species and commercial development at present is limited. The oriental fruit moth formulations are the 3M Sprayable Pheromone for OFM, manufactured by 3M, Checkmate OFM-F, manufactured by Sutterra, Isomate-M 100 manufactured by CBC. Peachtree borer formulation is the Isomate-LPTB also manufactured by CBC.

Recently 3M Canada has made a decision to exit the sprayable pheromone business for forestry and agriculture. Sprayable pheromones are also produced by Sutterra Inc. (Bend, OR), has submitted an application for registration of CheckMate OFM-F (for oriental fruit moth).

Pyridazinones

Nexter (formerly Pyramite) (**pyridaben**) 4-chloro-2-(1,1-dimethylethyl)-5-[[[4-(1,1-dimethylethyl)phenyl]methyl]thio]-3(2H)-pyridazinone belongs to the pyridazinone class

of miticides. Nexter's mode of action is as a mitochondrial electron transport inhibitor (METI), blocking cellular respiration. Resistance management would suggest that the use of METI miticides be limited to one application/year. Pyridaben has been shown to be an effective miticide in apple, showing greater activity against European red mite than twospotted spider mite. Pyridaben is also toxic to apple rust mites. Pyridaben has been shown to be an effective miticide in pear, having good efficacy against European red mites. Pyridaben provides good control of pear rust mites and variable, control of twospotted spider mites. Pyridaben displays control of pear psylla in low to moderate pressure situations when applied at clusterbud. Pear psylla control is rate dependent, so rates may need to be increased as pear psylla densities increase.

Tetrazines

Apollo (**Clofentezine**) 3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine is a tetrazine compound used as a contact acaricide. It acts primarily as an ovicide/larvicide and is particularly effective against the over wintering eggs of European red mite and is not an effective adulticide. Following early season applications, it gives excellent residual control. As it is not a systemic acaricide expanding foliage will not contain residue to control mite moving into untreated foliage.

In apples it is restricted to a 12 hour re-entry interval, a PHI of 45 days, but in pears, cherries, peaches and apricots it may be used up to 21 days before harvest. It has a low bee-poisoning hazard, and is safe on beneficial insects, and predatory mites. Development of resistance to clofentezine in mite populations has occurred.

Quinolines.

Kanemite (**Acequinocyl**) 2-(acetyloxy)-3-dodecyl-1,4-naphthalenedione Kanemite belongs to the quinoline class of insecticides from Arvesta Corporation registered for the control of European red mite and twospotted spider mite on apple and pear. Its mode of action is as a mitochondrial electron transport inhibitor (METI), blocking cellular respiration, similar to Nexter and Fujimite yet at a differing target site than the other compounds. In pear acequinocyl appears to be a good miticide alternative for the control of twospotted spider mites with activity against European red mite. Limited and inconclusive data requires further studies on this compound. It has been classified by EPA as a reduced risk compound, and has a 14-day PHI and 12-hour REI.

**Table 1 CHARACTERISTICS OF CROP PROTECTANTS USED ON TREE FRUITS
CROSS REFERENCE OF CHEMICAL VS. TRADE NAMES OF PESTICIDES. 2004**

Trade Name	Formulation	Active Ingredient	Type	Company
2,4-D Amine	3.8 EC	2,4-D	H	Agrialiance
2,4-D Amine 4	3.8 EC	2,4-D	H	Agrialiance
Accel	2% L	6-BA + gibberellic acid	GR	Valent BioSciences
Acramite 50WS	50WS	bifenazate	A	Crompton
Actara 25WDG	25WDG	thiamethoxam	I	Syngenta
Agree 3.8WG	3.8WG	Bacillus thuringiensis (aizawai)	I	Certis
Agri-Mek 0.15EC	0.15EC	abamectin	A, I	Syngenta
Agri-mycin 17WP	17WP	streptomycin	B	Syngenta
Aliette 80 WDG	80WDG	phosetyl-Al	F	Bayer
Ambush 25WP	25WP	permethrin	I	AMVAC
Ambush 2EC	2EC	permethrin	I	Syngenta
Amid-Thin W	8.4WP	naphthalene-acetamide	GR	AMVAC
Amine 4 2,4-D	3.8EC	2,4-D	H	UAP
Apogee 27.5DF	27.4DF	prohexadione calcium	B, GR	BASF
Apollo 4SC	4SC	clofentezine	A	Makhteshim-Agan
Asana XL 0.66EC	0.66EC	esfenvalerate	I	DuPont
Avaunt 30WDG	30WDG	indoxacarb	I	DuPont
Aza-Direct 1.2L	1.2L	azadirachtin	I	Gowan
Azatin XL Plus 3L	3L	azadirachtin	I	Olympic
Basicop	53WP	Copper sulfate	F	Griffin
Bayleton 50DF	50DF	triadimefon	F	Bayer
Biobit XL 2.1FC	2.1FC	Bacillus thuringiensis	I	Valent BioSciences
Captan 50WP	50WP	captan	F	Micro Flo
Captan 80WP	80WP	captan	F	Micro Flo
Captec 4L	4L	captan	F	Micro Flo
Carbaryl 4F (Drexel)	4F	carbaryl	I	Drexel
Carbaryl 4F (UAP)	4F	carbaryl	I	UAP
Carzol 92SP	92SP	formetanate hydrochloride	A, I	Gowan
Casoron 4G	4G	dichlobenil	H	Crompton
Checkmate OFM-F	24.60%	pheromone	I	Suterra
Confirm 2F	2F	tebufenozide	I	Dow AgroSciences
Cornerstone	4EC	glyphosate	H	Agrialiance
Cuprofix Disperss	20%	Copper sulfate	F	Cerexagri
Damoil	98%Oil	petroleum oil	I, M	Drexel Chemical Co.
Danitol 2.4EC	2.4EC	fenpropathrin	I	Valent BioSciences
Devrinol 50DF	50DF	napropamide	H	United Phosphorus
Diazinon 50WP	50WP	diazinon	I	Microflo
Diazinon 50WP	50WP	diazinon	I	UAP
Diazinon 50WP	50WP	diazinon	I	Makhteshim Agan
Diazinon AG600WBC	5L	diazinon	I	UAP
Diazinon AG600WBC	5L	diazinon	I	Syngenta
D.z.n. Diazinon 50WP	50WP	diazinon	I	Syngenta
Dicofol	4EC	dicofol	A	Makhteshim Agan
Dimate	4EC	dimethoate	I	Agrialiance
Dimethoate E267	2.67EC	dimethoate	I	Gowan
Dimethoate 4EC	4EC	dimethoate	I	Helena
Dimethoate 4EC	4EC	dimethoate	I	Drexel
Dimethoate 400	4EC	dimethoate	I	UAP
Dimethoate 267EC	2.67EC	dimethoate	I	UAP
Dimethoate 4EC	4EC	dimethoate	I	Micro Flo
Dipel DF	54 DF	Bacillus thuringiensis	I	Valent BioSciences
Dithane DF Rain Shield	75DF	mancozeb	F	Dow AgroSciences
Dithane M-45 80WP	80WP	mancozeb	F	Dow AgroSciences
Dithane DF	75DF	mancozeb	F	Dow AgroSciences
Dithane F-45 80WP	4F	mancozeb	F	Dow AgroSciences
Diuron 4L	4L	diuron	H	Agrialiance
Endosulfan 3EC	3EC	endosulfan	I	Gowan
Endosulfan 50 WSB	50WSP	endosulfan	I	Gowan
Endosulfan 3EC	3EC	endosulfan	I	Micro Flo

Endosulfan 50 WSB	50WSP	endosulfan	I	Micro Flo
Endosulfan 3EC	3EC	endosulfan	I	Drexel
Entrust	80WP	spinosad	I	Dow AgroSciences
Esteem 35WP	35WP	pyriproxyfen	I	Valent BioSciences
Ethephon 2	L	ethephon	GR	Micro Flo Co.
Ethrel	2 EC	ethephon	GR	Bayer
Exilis Plus	2%Sol	BA	GR	Fine Agrochemicals
Ferbam Granuflo	76 WDG	ferbam	F	UCB
Flint 50WG	50WG	trifloxystrobin	F	Bayer
Fruitone N	3.1% sol	NAA	GR	AMVAC
Galigan 2E	2EC	oxyfluorfen	H	Makhteshim Agan
Goal 2XL	2lb AI/gal	oxyfluorfen	H	Dow AgroSciences
Gramoxone Max	2AS	paraquat	H	Syngenta
Guthion 50WS	50WS	azinphos-methyl	I	Bayer
Hyvar X 80WP	80WP	bromacil	H	DuPont
Hyvar XL	2lb AI/gal	bromacil	H	DuPont
Imidan 70WP	70WP	phosmet	I	Gowan
Isomate LPTB	tie	pheromone	I	CBC Americas
Isomate-M 100	tie	pheromone	I	CBC Americas
Isomate-M Rosso	tie	pheromone	I	CBC Americas
Javelin 7.5WG	7.5WG	Bacillus thuringiensis	I	Certis
Karmex 80DF	80DF	diuron	H	Griffin
Kelthane 35WP	35WP	dicofol	A	Dow AgroSciences
Kelthane 50WP	50WP	dicofol	A	Dow AgroSciences
Kelthane 50WSP	50WSP	dicofol	A	Dow AgroSciences
Kerb 50WP	51WP	pronamide	H	Dow AgroSciences
Kocide 4.5LF	3 LF	copper hydroxide	F	Griffin L.L.C.
Kocide 101	77WP	copper hydroxide	F	Griffin L.L.C.
Kocide 2000	58.3WP	copper hydroxide	F	Griffin L.L.C.
Kocide DF	61.40%	copper hydroxide	F	Griffin L.L.C.
Fruit Fix Conc 200	0.44F	NAA	GR	AMVAC
Fruit Fix Conc 800	1.76F	NAA	GR	AMVAC
K-Salt Fruit Fix 200	0.44F	NAA	GR	AMVAC
K-Salt Fruit Fix 800	1.76F	NAA	GR	AMVAC
KOP-Hydroxide 50	50WP	copper hydroxide	F	Drexel
Kumulus 80DF	80DF	sulfur	F	Micro Flo
Lannate 90SP	90SP	methomyl	I	DuPont
Lannate LV 2.4L	2.4L	methomyl	I	DuPont
Lorsban 4EC	4EC	chlorpyrifos	I	Dow AgroSciences
Lorsban 50WS	50WS	chlorpyrifos	I	Gowan
Mankocide	DF	mancozeb + cu hydroxide	F	Griffin
Manzate 4F	4F	mancozeb	F	Griffin
Manzate 80W	80WP	mancozeb	F	Griffin
Manex	4F	maneb	F	Griffin
Manzate 75DF	75DF	mancozeb	F	Griffin
Mertect 340-F	4.1F	thiabendazole	F	Syngenta
Messenger 3WDG	3WDG	harpin protein	B	Eden Bioscience
Microthiol 80WP	80WP	sulfur	F	Cerexagri
Miller Lime Sulfur Solution	LC	calcium polysulfide	FIM	Miller Chemical & Fe
Mirage Plus	4EC	glyphosate	H	Monsanto
M-Pede 49L	49L	insecticidal soap	I	Dow AgroSciences
Neemix 4.5L	4.5L	azadirachtin	I	Certis
Nova 40WS	40WS	myclobutanil	F	Dow AgroSciences
NuCop 3L	3L	copper hydroxide	F	Micro Flo
NuCop 50DF	50DF	copper hydroxide	F	Micro Flo
Oryza AG	4EC	oryzalin	H	Ayvalue
OxiDate 27F	27F	hydrogen dioxide	F	Biosafe Systems
Penncozeb 75DF	75DF	mancozeb	F	Cerexagri
Penncozeb 80WP	80WP	mancozeb	F	Cerexagri
Perlan	3.6%Sol	GA4+7 + BA	GR	Fine Agrochemicals
Phaser 50WSB	50WSB	endosulfan	I	Bayer
Phaser 3EC	3EC	endosulfan	I	Bayer
Poast	1.5EC	sethoxydim	H	Micro Flo

Polyram 80DF	80DF	metiram	F	UAP
Pounce 25WP	25WP	permethrin	I	FMC
Pounce 3.2EC	3.2EC	permethrin	I	FMC
Princep 4L	4L	simazine	H	Syngenta
Princep Caliber 90	90	simazine	H	Syngenta
Procure 50WS	50WS	triflumizole	F	Crompton, Uniroyal
Pro-Gibb 4%	4% S	GA3	GR	Valent BioSciences
Pro-Gibb Plus 2X	20SP	GA3	GR	Valent BioSciences
Pro-Vide	2%S	GA4+7	GR	Valent BioSciences
Promalin	1.8+1.8L	GA(4+7) +BA	GR	Valent BioSciences
Provado 1.6F	1.6F	imidacloprid	I	Bayer
Prowl 3.3EC	3.3EC	pendimethalin	H	BASF
Pyramite 60WS	60WS	pyridaben	A, I	BASF
Pyrellin EC	1.6EC	pyrethrins/rotenone	I	Webb Wright
Rely 1L	1L	glufosinate-ammonium	H	Bayer
ReTain	15%S	AVG	GR	Valent BioSciences
RiteSize	2%S	GA(4+7) +BA	GR	Nufarm
Ridomil Gold 4EC	4EC	mefanoxam	F	Syngenta
Roundup Original	4 lb AI/gal	glyphosate	H	Monsanto
Roundup Ultra Max	4 lb AI/gal	glyphosate	H	Monsanto
Rubigan 1EC	1EC	fenarimol	F	Gowan
Savey 50WP	50WP	hexythiazox	A	Gowan
Serenade 10WP	10WP	Bacillus subtilis	B,F	AgraQuest
Sevin 80S	80S	carbaryl	I	Bayer
Sevin 80WS	80WS	carbaryl	I	Bayer
Sevin XLR	4F	carbaryl	I	Bayer
Sevin 4F	4F	carbaryl	I	Bayer
Simazine 90DF	90DF	simazine	H	Drexel
Sinbar 80WP	80WP	terbacil	H	DuPont
Solicam 80DF	80DF	norflurazon	H	Syngenta
Sovran 50WDG	50WDG	kresoxim-methyl	F	BASF
SpinTor 2SC	2SC	spinosad	I	Dow AgroSciences
Supracide 25WP	25WP	methidathion	I	Gowan
Supracide 2EC	2EC	methidathion	I	Gowan
Surflan AS	4AS	oryzalin	H	Dow AgroSciences
Surround 95WP	95WP	kaolin	A,E,I	Engelhard
Syllit 65WP	65WP	dodine	F	UAP
Tenn-Cop 5E	5E	copper salts	F	Griffin
Thiodan 3EC	3EC	endosulfan	I	Bayer
Thiodan 50 WP	50WP	endosulfan	I	Bayer
Thiodan 3EC	3EC	endosulfan	I	FMC
Thiodan 50 WP	50WP	endosulfan	I	FMC
Thionex 3EC	3EC	endosulfan	I	Makhteshim Agan
Thionex 50 WP	50WP	endosulfan	I	Makhteshim Agan
Thiram Granuflo	75WDG	thiram	F	UCB
T Methyl 70W	70WP	thiophanate methyl	F	MicroFlo
Topsin M 70WSB	70WSB	thiophanate-methyl	F	Cerexagri
Topsin M WSB	70WSB	thiophanate-methyl	F	Cerexagri
Tree-Hold A-112	15.1% Sol.	NAA	GR	AMVAC
Tree-Hold RTU	1.15% Sol.	NAA	GR	AMVAC
Typy	3.6% Sol.	GA(4+7) +BA	GR	Nufarm
Vanguard 50WG	50WG	cyprodinil	F	Syngenta
Vendex 50WP	50WP	hexakis, fenbutatin-oxide	A	DuPont
Vydate 2L	2L	oxamyl	I	DuPont
Warrior	1CS	lambda-cyhalothrin	I	Syngenta
Weedar 64 3.8	3.8 lb AI/gal	2,4-D (phenoxy)	H	Nufarm
Wilthin	79% L	AMADS	GR	Entek Corp
Ziram 76DF	76DF	ziram	F	Cerexagri
Ziram Granuflo	76DF	ziram	F	UCB

Retrieved from www.nysaes.cornell.edu/ent/treefruit/04pdf/04cocpuotf.pdf

Table 2 Chemical Manufacturers 2004 – CDMS (<http://www.cdms.net/manuf/manuf.asp>)

Aceto Agricultural Chemicals Corp.	LT BioSyn, Inc.
Ag Formulators, Inc.	Makhteshim-Agan of North America, Inc.
AgraQuest, Inc.	MGK Company
Agrilience Crop Nutrient	Micro Flo Company LLC
Agrilience, LLC	Miller Chemical & Fertilizer Corp.
Agrimar Corporation	Milliken Turf Products
Agrivert, Inc.	Mineral Research & Devel. Corp.
AgroSolutions LLC	Monsanto Canada, Inc.
AgValue, Inc.	Monsanto Company
Albaugh, Inc./Agri Star	Monterey AgResources
Amvac Chemical Corporation	Moore Agricultural Products Co., Inc.
Applied Biochemists	Nichino America, Inc.
Arvesta Canada	Nufarm Americas Inc.
Arvesta Corporation	Nufarm Turf & Specialty (formerly Riverdale)
BASF Ag Products	Olympic Horticultural Products Company
BASF Canada	ORO Agri, Inc.
BASF Specialty Products	Pace International LLC
Bayer CropScience	Pacific Biocontrol Corporation
Bayer ES Mosquito Control	PBI Gordon Corporation
Bayer ES Professional Pest Control	Phelps Dodge Corporation
Bayer ES Turf & Ornamental (Chipco)	PROKoZ, Inc.
Becker Underwood, Inc.	RICECO
BioWorks, Inc.	RNA
Brandt Consolidated, ClawEI Division	Roots Plant Care Group/Novozymes Biologicals, Inc.
Britz Fertilizers, Inc.	Royster-Clark, Inc.
Cerexagri, Inc.	Sanitek Products Inc./Sanag
Cerexagri, Inc. Decco Post-Harvest	Scentry Biologicals, Inc.
Certis USA, L.L.C.	Sipcam Agro USA, Inc.
Chem One Ltd.	Stoller Enterprises, Inc.
Cheminova, Inc.	Sunoco, Inc. (R&M)
Cleary Chemical Corporation	Suterra LLC
Continental Sulfur Company	Sylvan Bioproducts, Inc.
Crompton/Uniroyal Chemical	Syngenta Crop Protection Canada, Inc.
Custom Agricultural Formulators	Syngenta Crop Protection, Inc.
Diamond R Fertilizer Company, Inc.	Syngenta Professional Products
Dow AgroSciences LLC	Taminco, Inc.
Drexel Chemical Company	Target Specialty Products, Inc.
Dupont Canada Crop Protection	TENKOZ, Inc.
E.I. du Pont de Nemours and Company	Tessengerlo Kerley, Inc. (TKI)
EcoSMART Technologies, Inc.	Tri Corporation
EDEN Bioscience Corporation	TRICAL
EDM Industries, Inc.	UAP - Loveland Industries, Inc.
Emerald BioAgriculture Corporation	UAP - Loveland Products, Inc.
Engelhard Corporation	United Phosphorus Inc.
Entek Corporation	United Phosphorus Inc. Canada
FarmSaver.com / Quali-Pro	United Suppliers, Inc.
FarmSaver.com, LLC	Universal Crop Protection Alliance LLC
Fine Agrochemicals Ltd.	Valent Agricultural Products
FMC Corporation	Valent BioSciences Canada, Ltd.
Georgia Gulf Sulfur Corporation	Valent BioSciences Corporation
Gowan Company	Valent Professional Products
Griffin LLC	Valent U.S.A. Corporation Canada
Gro-Pro LLC	Van Diest Supply Company
Helena Chemical Company	Vegetation Management LLC
Helm Agro US, Inc.	Verdicon (formerly United Horticultural Supply)
Independent Agribusiness Professionals, Inc.	Webb Wright Corporation
J. R. Simplot Company/Plant Health Tech.	Western Farm Service
JH Biotech, Inc.	Wilbur-Ellis Company
JMS Flower Farms, Inc.	Wilco Distributors, Inc.
Knapp Manufacturing Company	

Table 2a Number And Percent Of Crop Protectant By Manufacturer Used On Tree Fruits in 2004

Company	# of total fruit protectants (fungi.,insect.,herb. etc.) (N=91)	% of total	# of fruit insecticides / acaricides
1. Syngenta	16	18	5
2. Bayer	12	13	5
3. Dow AgroSciences	11	12	5
4. DuPont	8	9	6
5. Gowan	8	9	6
6. Griffin	7	8	-
7. BASF	6	7	-
8. Cerexagri	4	4	-
9. Drexel	4	4	5
10. UAP	4	4	1
11. Certis	3	3	2
12. Crompton	3	3	-
13. Valent BioSciences	3	3	4
14. Agriliance	2	2	-
15. FMC	2	2	2
16. Helena	2	2	2
17. Makhteshim	2	2	2
18. Micro Flo	2	2	1
19. UCB	2	2	-
20. Arvesta	1	1	-
21. Biosafe Systems	1	1	-
22. Clean Crop	1	1	-
23. Eden Bioscience	1	1	-
24. Engelhard	1	1	1
25. Monsanto	1	1	-
26. Nufarm Americas	1	1	-
27. Prentiss	1	1	1
28. United Phosphorus	1	1	-
29. Webb Wright	1	1	1

Table 3 Pounds of Pesticide Active Ingredient Used in U.S. Fruit and Nut Crop Production, Two Year Periods, 1988-97

Crop Group	Years	Pounds of active ingredient in thousands						Total
		Acres Grown (000)	Herbicides/PGR	Ins./Miticide	Fungicides	Nem./Fumigants	Sulfur/oil	
Fruits & Nuts	1988/89	4,458	11,447	34,885	30,871	17,051	102,343	196,597
	1992/93	4,616	15,061	37,051	29,954	16,653	117,867	216,585
	1996/97	5,126	20,103	40,439	35,608	10,703	117,563	224,416

Table 4 Insect and Mite Pests on Apple requiring Control Measures Cornell Recommends for NY State - 2004

American Plum Borer	American Plum Borer	San Jose Scale
Apple & Spirea Aphid	European Apple Sawfly	Spotted Tentiform Leafminer
Apple Maggot	European Corn Borer	Apple Blotch Leafminer
Apple Rust Mite	European Red Mite	Tarnished Plant Bug
Codling Moth	Green Fruitworm	Variegated Leafroller
Lesser Appleworm	Mullein Plant Bug	Sparganothis Fruitworm
Oriental Fruit Moth	Obliquebanded Leafroller	White Apple Leafhopper
Comstock Mealybug	Oystershell Scale	Rose Leafhopper
Cutworms	Plum Curculio	Potato Leafhopper
Dogwood Borer	Redbanded Leafroller	Woolly Apple Aphid

Table 5 Various Classes of Insecticide and Miticide used on Tree Fruit. 2004

Chlorinated Hydrocarbon

Endosulfan (Thiodan)
Dicofol (Kelthane)

Organophosphates

Azinphos-Methyl (Guthion)
Chlorpyrifos (Lorsban)
Diazinon (D.Z.N.)
Dimethoate
Malathion
Methidathion (Supracide)
Phosmet (Imidan)

Carbamates

Carbaryl (Sevin)
Methomyl (Lannate)
Oxamyl (Vydate)
Formetanate Hydrochloride (Carzol)

Pyrethroids

Esfenvalerate (Asana XI)
Fenpropathrin (Danitol)
Lambda-Cyhalothrin (Warrior)
Permethrin (Ambush, Pounce)

Horticultural Mineral Oils

Petroleum Oil Emulsions
(Sunspray 6e, Ultra-Fine, Stylet-Oil
Damoil)
Insecticidal Soaps
Biodegradable Fatty Acids (M-Pede)

Abamectin

Abamectin (Agri-Mek)
*Emamectin Benzoate (Proclaim)
*Milbemectin (Mesa)

Amidene

Amitraz (Mitac)

Bacillus Thuringiensis

(Bt, Dipel, Biobit, Jav-Elin,
Agree, Mvp)

Carboxamide

Hexythiazox (Savey)

Carboxylic Acid Ester

Bifenazate (Acramite)

Chloronicotinyl

Imidacloprid (Provado)
Thiamethoxam (Actara)
Acetamiprid (Assail)
*Thiacloprid (Calypso)
Chlothianidin (Clutch)

CM Granulosis Virus

Cyd-X, Carpovirusine, Virosoft CM

Diphenyloxazoline

Extoxazole (Zeal, Secure)

Insecticidal Soaps

Biodegradable Fatty Acids (M-Pede)

Insect Growth Regulator

Azadirachtin

Aza-Direct, Azatin XI Plus,
Neemix 4.5)

Thiadiazine

*Buprofezin (Applaud)

Formamidine

Amitraz (Mitac) Pears only

Juvenile Hormone Analog / mimic

Pyriproxyfen (Esteem)
Tebufenozide (Confirm)
Methoxyfenozide (Intrepid)

Benzoyl Urea Growth Regulator

Diflubenzuron (Dimilin)
Novaluron/difluorobenzamide
(Diamond)

***Tetronic Acid**

*Spirodiclofen (Envidor)

Organotin

Hexakis Or Fenbutatin Oxide
(Vendex)

Oxadiazene

Indoxacarb (@ Avaunt)

Particle Film

Kaolin (Surround)

***Phenoxypropylazole**

*Fenpyroximate (Fujimite)

Pyridazinone

Pyridaben (Pyramite = Nexter)

Spinosad

Spinosyn A And Spinosyn D
(Spintor, Entrust)

Tetrazine

Clofentezine (Apollo)

***Quinoline**

*Acequinocyl (Kanemite)

* Not registered in NYS as of 2004. ** Not registered, @ not registered for use in Nassau or Suffolk Counties.
Taken from: Cornell Recommends for Tree Fruit Management 2004; New Insecticides and Miticides for Apple and Pear IPM, Washington State Tree Fruit Research and Extension Center, WA

Table 6 Compendium of Pesticide Common Names

Insecticides	aminocarb	novaluron	chlordecone
* antibiotic insecticides	bufen carb	noviflumuron	dieldrin
allosamidin	butacarb	penfluron	dilor
thuringiensin	carbanolate	teflubenzuron	endosulfan
* macrocyclic lactone	cloethocarb	triflumuron	endrin
insecticides	dicresyl	* juvenile hormone mimics	HEOD
spinosad	dioxacarb	epofenonane	heptachlor
* avermectin insecticides	EMPC	fenoxycarb	HHDN
abamectin	ethiofencarb	hydroprene	isobenzan
doramectin	fenethacarb	kinoprene	isodrin
emamectin	fenobucarb	methoprene	kelevan
eprinomectin	isoprocarb	pyriproxyfen	mirex
ivermectin	methiocarb	triprene	
selamectin	metolcarb	* juvenile hormones	* organophosphorus
* milbemycin insecticides	mexacarbate	juvenile hormone I	insecticides
lepimectin	promacyl	juvenile hormone II	* organophosphate
milbemectin	promecarb	juvenile hormone III	insecticides
milbemycin oxime	propoxur	* moulting hormone	bromfenvinphos
moxidectin	trimethacarb	agonists	chlorfenvinphos
	XMC	chromafenozide	crotoxyphos
	xylylcarb	halofenozide	dichlorvos
		methoxyfenozide	dicrotophos
* arsenical insecticides		tebufenozide	dimethylvinphos
calcium arsenate	* dinitrophenol insecticides	* moulting hormones	fospirate
copper acetoarsenite	dinex	É α -ecdysone	heptenophos
copper arsenate	dinoprop	ecdysterone	methocrotophos
lead arsenate	dinosam	* moulting inhibitors	mevinphos
potassium arsenite	DNOC	diofenolan	monocrotophos
sodium arsenite	* fluorine insecticides	* precocenes	naled
* botanical insecticides	barium hexafluorosilicate	precocene I	naftalofos
anabasine	cryolite	precocene II	phosphamidon
azadirachtin	sodium fluoride	precocene III	propaphos
α -limonene	sodium hexafluorosilicate	* unclassified insect growth	TEPP
nicotine	sulfuramid	regulators	tetrachlorvinphos
pyrethrins	* formamidine insecticides	dicyclanil	* organothiophosphate
cinerins	amitraz		insecticides
cinerin I	chlordimeform	* nereistoxin analogue	dioxabenzofos
cinerin II	formetanate	insecticides	fosmethilan
jasmolin I	formparanate	bensultap	phenthoate
jasmolin II	* fumigant insecticides	cartap	* aliphatic
pyrethrin I	acrylonitrile	thiocyclam	organothiophosphate
pyrethrin II	carbon disulfide	thiosultap	insecticides
quassia	carbon tetrachloride	* nicotinoid insecticides	acethion
rotenone	chloroform	fonicamid	amiton
ryania	chloropicrin	* nitroguanidine	cadusafos
sabadilla	para-dichlorobenzene	insecticides	chlorethoxyfos
* carbamate insecticides	1,2-dichloropropane	clothianidin	chlormephos
bendiocarb	ethyl formate	dinotefuran	demephion
carbaryl	ethylene dibromide	imidacloprid	demephion-O
* benzofuranyl	ethylene dichloride	thiamethoxam	demephion-S
methylcarbamate	ethylene oxide	* nitromethylene	demeton
insecticides	hydrogen cyanide	insecticides	demeton-O
benfuracarb	iodomethane	nitenpyram	demeton-S
carbofuran	methyl bromide	nithiazine	demeton-methyl
carbosulfan	methylchloroform	* pyridylmethylamine	demeton-O-methyl
decarbocufuran	methylene chloride	insecticides	demeton-S-methyl
furathiocarb	naphthalene	acetamiprid	demeton-S-methylsulphon
* dimethylcarbamate	phosphine	imidacloprid	disulfoton
insecticides	sulfuryl fluoride	nitenpyram	ethion
dimetan	tetrachloroethane	thiacloprid	ethoprophos
dimetilan	* inorganic insecticides		IPSP
hyquin carb	borax	* organochlorine	isothioate
pirimicarb	calcium polysulfide	insecticides	malathion
* oxime carbamate	copper oleate	bromo-DDT	methacrifos
insecticides	mercurous chloride	camphechlor	oxydemeton-methyl
alany carb	potassium thiocyanate	DDT	oxydeprofos
aldicarb	sodium thiocyanate	ppA α -DDT	oxydisulfoton
aldoxycarb	see also arsenical insecticides	ethyl-DDD	phorate
butocarboxim	see also fluorine insecticides	HCH	sulfotep
butoxycarboxim	* insect growth regulators	gamma-HCH	terbufos
methomyl	* chitin synthesis inhibitors	lindane	thiometon
nitrilacarb	bistrifluron	methoxychlor	* aliphatic amide
oxamyl	buprofezin	pentachlorophenol	organothiophosphate
tazimcarb	chlorfluazuron	TDE	insecticides
thiocarboxime	cyromazine	* cyclodiene insecticides	amidithion
thiodicarb	diflubenzuron	aldrin	cyanthoate
thiofanox	flucycloxuron	bromocyclen	dimethoate
* phenyl methylcarbamate	flufenoxuron	chlorbicyclen	ethoate-methyl
insecticides	hexaflumuron	chlordane	formothion
allylxy carb	lufenuron		

mecarbam
omethoate
prothoate
sophamide
vamidothion
* **oxime**
organothiophosphate
insecticides
chlorphoxim
phoxim
phoxim-methyl

* **heterocyclic**
organothiophosphate
insecticides
azamethipos
coumaphos
coumithoate
dioxathion
endothion
menazon
morphothion
phosalone
pyraclofos
pyridaphenthion
quinothion

* **benzothioapyran**
organothiophosphate
insecticides
dithicrofos
thicrofos

* **benzotriazine**
organothiophosphate
insecticides
azinphos-ethyl
azinphos-methyl

* **isindole**
organothiophosphate
insecticides
dialifos
phosmet

* **isoxazole**
organothiophosphate
insecticides
isoxathion
zolaprofos

* **pyrazolopyrimidine**
organothiophosphate
insecticides
chlorprazophos
pyrazophos

* **pyridine**
organothiophosphate
insecticides
chlorpyrifos
chlorpyrifos-methyl

* **pyrimidine**
organothiophosphate
insecticides
butathiofos
diazinon
etrimfos
lirimfos
pirimiphos-ethyl
pirimiphos-methyl
primidophos
pyrimitate
tebupirifos

* **quinoxaline**
organothiophosphate
insecticides
quinalphos
quinalphos-methyl

* **thiadiazole**
organothiophosphate
insecticides
athidathion
lythidathion
methidathion
prothidathion

* **triazole**
organothiophosphate
insecticides
isazofos
triazophos

* **phenyl**
organothiophosphate
insecticides
azothoate
bromophos
bromophos-ethyl
carbophenothion
chlorthiophos
cyanophos
cythioate
dicapthion
dichlofenthion
etaphos
famphur
fenchlorphos
fenitrothion
fensulfothion
fenthion
fenthion-ethyl
heterophos
jodfenphos
mesulfenfos
parathion
parathion-methyl
phenkapton
phosnichlor
profenofos
prothiofos
sulprofos
temephos
trichlormetaphos-3
trifenofos

* **phosphonate insecticides**
butonate
trichlorfon

* **phosphonothioate**
insecticides
mecarphon

* **phenyl**
ethylphosphonothioate
insecticides
fonofos
trichloronat

* **phenyl**
phenylphosphonothioate
insecticides
cyanofenphos
EPN
leptophos

* **phosphoramidate**
insecticides
crufomate
fenamiphos
fosthietan
mephosfolan
phosfolan
pirimetaphos

* **phosphoramidothioate**
insecticides
acephate
isocarbophos
isofenphos
methamidophos
propetamphos

* **phosphorodiamide**
insecticides
dimefox
mazidox
mipafox
schradan

* **oxadiazine insecticides**
indoxacarb

* **phthalimide insecticides**
dialifos
phosmet
tetramethrin

* **pyrazole insecticides**
acetoprole
ethiprole
fipronil
pyrafluprole
pyriprole
tebufenpyrad
tolfenpyrad
vaniliprole

* **pyrethroid insecticides**

* **pyrethroid ester**
insecticides
allethrin
bioallethrin
barthrin
bifenthrin
bioethanomethrin
cyfluthrin
beta-cyfluthrin
cyhalothrin
gamma-cyhalothrin
lambda-cyhalothrin
cypermethrin
alpha-cypermethrin
beta-cypermethrin
theta-cypermethrin
zeta-cypermethrin
cyphenothrin
deltamethrin
dimefluthrin
dimethrin
empenthrin
fenfluthrin
fenpirithrin
fenpropathrin
fenvalerate

esfenvalerate
flucythrinate
flualinate
tau-flualinate
furethrin
imiprothrin
metofluthrin
permethrin
biopermethrin
transpermethrin
phenothrin
prallethrin
profluthrin
pyresmethrin
resmethrin
bioresmethrin
cismethrin
tefluthrin
terallethrin
tetramethrin
tralomethrin
transfluthrin

* **pyrethroid ether**
insecticides
etofenprox
flufenprox
halfenprox
protrifenbutate
silafloufen

* **pyrimidinamine**
insecticides
flufenimer
pyrimidifen

* **pyrrole insecticides**
chlorfenapyr

* **tetronic acid insecticides**
spiroresifen

* **thiourea insecticides**
diafenthuron

* **urea insecticides**
flucufuron
sulcofuron
see also chitin synthesis
inhibitors

* **unclassified insecticides**
closantel
crotamiton
EXD
fenazaflor
fenoxacrim
flubendiamide
hydramethylnon
isoprothiolane
malonoben
metaflumizone
metoxadiazone
nifluridide
pyridaben
pyridaly
rafoxanide
triarathene
triazamate

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