DETECTION OF PESTICIDES IN STRAWBERRIES

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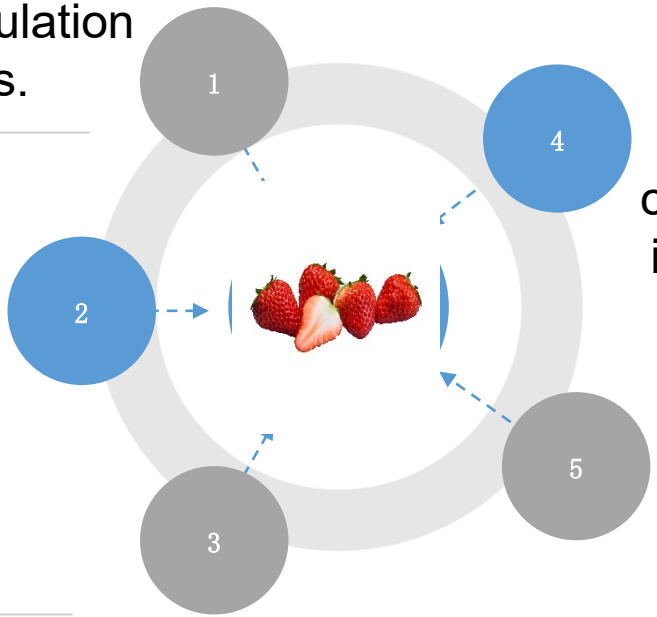
01 Introduction

Today, the world population is increasing at a very rapid rate and the increasing world population brings with it many problems.

One of the most important of these problems is that there will not be enough food to meet the needs in the future.

Therefore, it is of great importance to increase both yield and production, especially in agricultural products. (Yeşil and Ögür, 2011).



The use of biological control and biotechnical methods as alternatives to chemical control, especially cultural measures in agricultural control, is of great importance in terms of human health and the environment today.

However, chemical control is the most preferred method in Turkey as well as in the world due to its short duration and ease of use (Özercan and Özdem 2015).

Control of diseases, pests and weeds is very important in increasing the yield per unit area and obtaining quality products (Kaymak, Özdem, Karahan, Özercan, Aksu, Aydar, Kodan, Yılmaz, Başaran, Asav, Erdoğan and Güler 2015)

Definition of Pesticide

- Pesticides are a large group of organic and inorganic compounds with different properties that are widely used in the control or prevention of diseases, pests and weeds in plants (Cengiz et al. 2007, Pizzutti et al. 2007).

CLASSIFICATION OF PESTICIDES

- Pesticides are classified in different ways according to their formulation, mode of action and the pests they are used against:

1. According to their formulation:

- Pesticides can be classified as powder pesticides, wettable powder pesticides, dry seed pesticides, water-soluble powders, solutions or aqueous solutions, emulsion concentrates, summer and winter oils, granules, aerosols, pellets, poisonous baits, capsule-shaped formulations, fertilizer mixtures, flowable concentrates, oil concentrates, formulations suitable for Ultra Low Volume (ULV) spraying.

2. According to their mode of action:

In plants; systemic, semi-systemic and non-systemic, in pests; stomach poison, contact poison, respiratory poison can be counted in this class.

3. According to the pests for which they are used:

- Insecticides (insecticides),
- fungicides (fungicides = fungicides),
- bactericides (bactericides),
- herbicides (weed killers),
- aphicides (aphid killers),
- acaricides (red spider killers),
- molluxides (snail killers),
- rodenticides (rodenticides),
- nematocytes (nematocides),
- repellents can be counted in this class (Tiryaki et al. 2010).

- The use of pesticides is more preferred for reasons such as quick results and the ability to control large areas with less labor and expense.
- However, in addition to the positive aspects of these pesticides, there are also negative aspects such as leaving residues, developing resistance in target organisms or causing undesirable effects in the environment (Yeşil and Ögür, 2011).

Environmental Problems Caused by Using of Pesticide

Three environmental problems arise with the continued use of pesticides:.

Some disease-causing organisms (especially insects) develop resistance to the chemicals that affect them over time (Tatlı, 2006).

Some pesticides are very difficult to biodegrade. When applied, their residues are stored in the environment and cause negative effects on non-target living organisms. In other words, all natural life, including soil, fauna and flora, can be exposed to this danger. The concentration of pesticide residues accumulates at the end of the agricultural food web, causing a wider hazard to predator species

With the passage into the environment, these chemical residues can enter the food chain and accumulate in birds, fish, secondary and tertiary consumers, causing toxicity and irreversible damage (Tatlı, 2006).

The direct effect of the pesticide is through inhalation or ingestion of pesticide-contaminated foodstuffs. The indirect effect occurs during the utilization of plant and animal tissues containing pesticide residues as food (Durmuşoğlu, 2007). In addition, various non-targeted microorganisms in the soil are also affected. As a result, the balance of the soil ecosystem is disturbed.

Pesticides and Health Risks

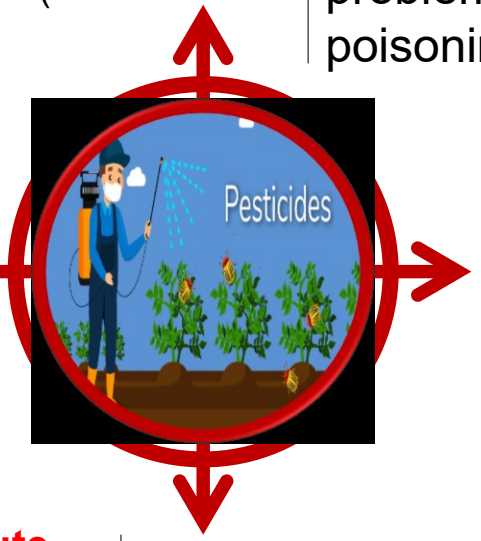
In humans, chronic poisoning can occur when food products containing pesticide residues are consumed. In addition, diseases such as **nephrosis of the lungs and kidneys can occur.**

Some pesticides can also act as teratogens (deformation of the baby in the womb) and mutagens (genetic disorders).

01

In order for pesticides to have a better effect, they need to be applied several times on food. However, in this way, more pesticide residues accumulate on the surface of the product.

This situation causes various problems for human health, up to poisoning.



02

Pesticides, when taken into the body, cause the structure of some enzymes to be disrupted and some of them to be excreted from the body.

03

04

Pesticide poisoning occurs through the skin, respiratory or digestive tract.

Poisoning can take two forms: acute toxicity (i.e. from a single, one-time dose) or chronic toxicity (long-term accumulation).

- Pesticide-related poisoning usually occurs in pesticide production facilities, during pesticide preparation and spraying, and also as a result of ingestion of contaminated food.
- Long-term exposure to pesticides causes damage to the nervous, respiratory, heart, stomach, intestinal and circulatory systems; internal organs such as the liver and kidneys; skin and eyes. According to World Health Organization data, about three million cases of pesticide poisoning occur every year and 220 thousand of these cases result in death (Tatlı, 2006).

Definition of Residue

1

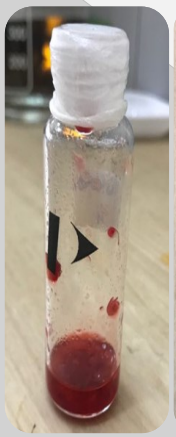
Residue (mg/kg), is the substances that we encounter in the plant, on the product, in the product, in the soil, in the air and in the water in the future due to errors during the use of chemicals used against pests such as diseases, pests and weeds that may have a negative effect on the plant (exceeding the specified application dose, not waiting for the time required between the last spraying and harvest, etc.) (Dülger, 2022).

2

When pesticides are not used in accordance with the recommendations, their residues cause adverse effects on human health and the environment. These residues also negatively affect the foreign market for agricultural products and domestic consumption.

3

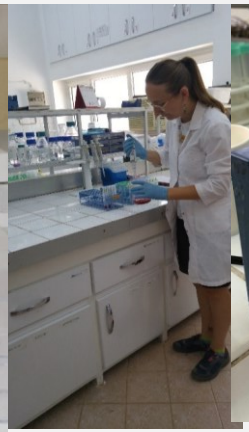
In addition, dermal and inhalation exposure during production, formulation preparation, transportation, loading and application (acute cause occupational poisoning in the form of they can be (Tiryaki et al. 2010).









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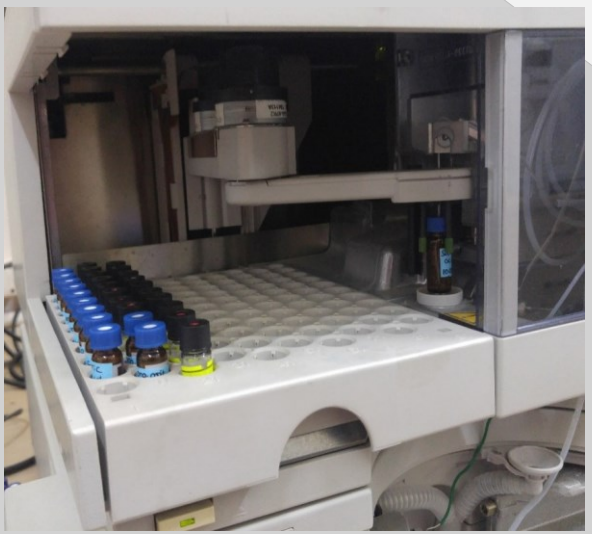









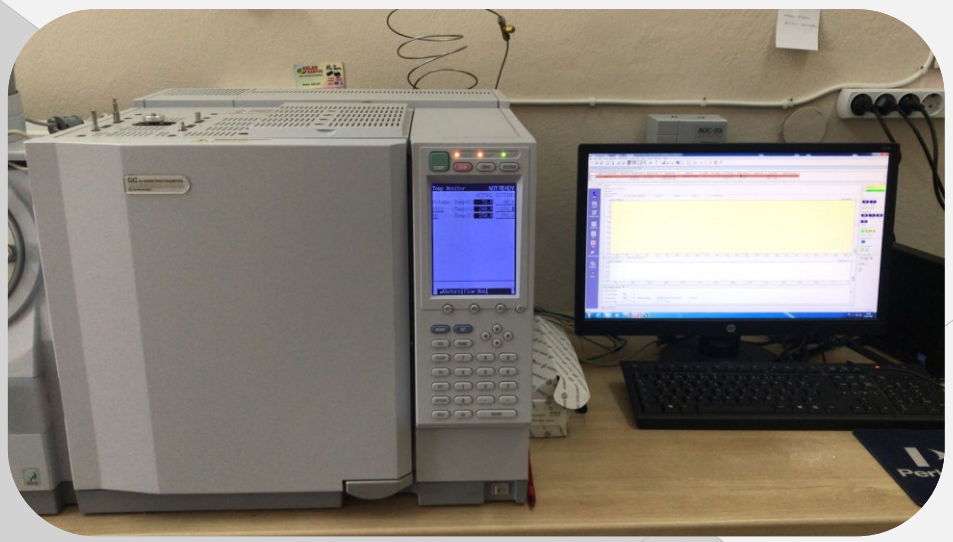

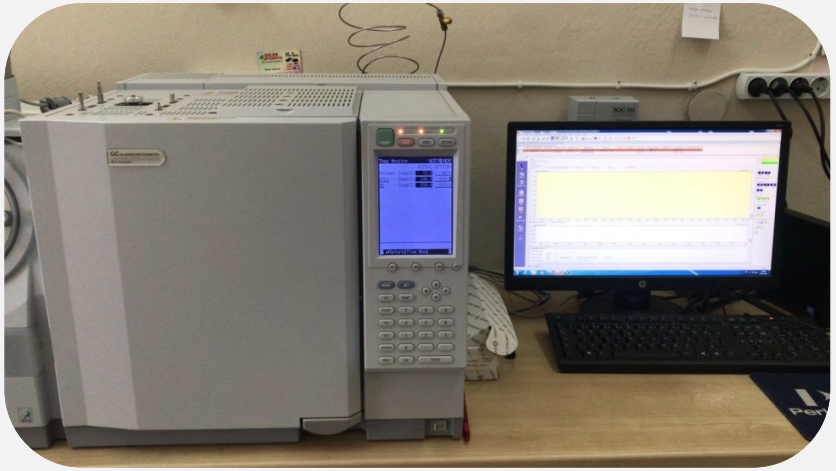


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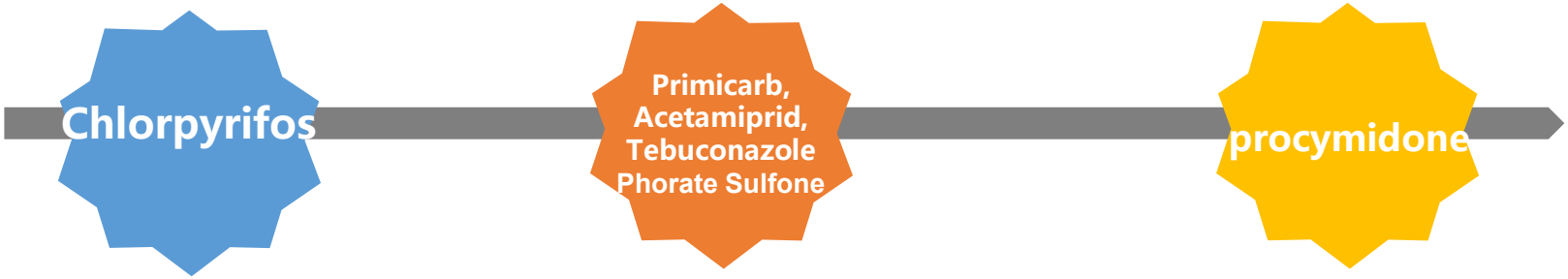
Studies on Pesticide Residues of Strawberry Fruits in Türkiye



In this research, 203 different pesticides' residue levels were investigated in 101 pieces of fresh grape and 10 pieces of strawberry which taken from local markets and wholesale markets in Konya City. According to results, Chlorpyrifos pesticide residue was determined at 5 µg/kg, 11 µg/kg and 10 µg/kg in three strawberry samples. (Ersoy et al. 2011)

In another study, Sancar et al. (2022) performed analysis and 393 pesticide active ingredients analyzed by LC-MS/MS were searched in 100 fruit and vegetable samples. The use of banned pesticides Phorate Sulfone in Türkiye was detected in a strawberry. Primicarb, Acetamiprid, Tebuconazole were also detected in strawberries.

In this study, conducted with 15 strawberry samples, no pesticide residues were found in 4 of the samples, while varying levels of pesticide residues were detected in the remaining 11 samples. They detected procymidone in their samples (Tatlı et al. 2006)

Studies on Pesticide Residues in Fruits and Vegetables

Studies in Türkiye

Researcher	Working	Year
Güncan and Durmuşoğlu	In a study conducted in Mustafakemalpaşa in 2002, tomatoes grown in this region were analyzed for organic phosphorus insecticides. A total of 15 samples were analyzed. Dichlorvos residues below the limits were detected in 10 of the samples. In 10 samples, methamidophos, which is prohibited for use, was detected. In one sample, parathion methyl residue was detected approximately 3 times higher than the MRL.	2003
Tağa and Bilgin	The samples obtained from the Aegean and Mediterranean regions of Turkey. They conducted a study on tangerine, orange and lemon samples. In total, 210 samples were analyzed for residues of organic chlorinated and organic phosphorus pesticides. for the presence of at least one pesticide residue. 105 out of 210 samples had at least one pesticide residue was detected. 5 quinalfos levels detected in the samples were found to be in compliance with TGK and EU MRLs. above their limits.	2008
Şensoy et al.	In a study conducted in Van, pesticide residues were investigated in fresh grapes, raisins and pickled grape leaves. 30 different pesticide residues were detected in all 16 fresh grapes. Among these, banned pesticides were found. In raisin samples, the number of active ingredients detected was 10 and no limit value was found for residues, so no evaluation could be made. In the pickled grapevine leaves analyzed, only one sample was found to contain pesticide residues.	2017
Gölge	Pesticide residue analysis was carried out in a total of 220 avocado samples collected from Gazipaşa and Alanya districts, which are two important centers of avocado cultivation in our country. Avocado samples were analyzed for a total of 490 pesticide residues using LC- MS/MS and GC-MS/MS devices. As a result of the analyzes, it was observed that avocado samples did not contain residues above the LOQ level.	2020

Studies on Pesticide Residues in Fruits and Vegetables

Studies in Other Countries

Researcher	Working	Year
Parveen et al.	Examined residues in 206 samples of 27 different types of vegetables such as carrot, garlic, ginger, onion, potato, radish, sugar beet, cucumber, mint, pepper, bean, tomato, zucchini, cabbage and cauliflower in Karachi, Pakistan. The samples were analyzed for pesticide residues belonging to different classes of pesticides such as organic phosphorus, organic chlorine, carbamates and pyrethroids using HPLC and GC-FID. They found that 63% of the samples contained one or more pesticide residues. In 46% of the contaminated samples, residues exceeded the MRL values given by FAO/WHO.	2005
Yuan et al.	Investigated chlorpyrifos and cypermethrin residues in 2082 vegetable samples between 2007 and 2010. They detected chlorpyrifos residues ranging from 0-22.8% and cypermethrin residues ranging from 4.2% to 29.3% in 17 different vegetable species. Chlorpyrifos and cypermethrin residues exceeded the MRL in 1.4% and 0.3% of the samples, respectively.	2014
Mac Loughlin et al.	In a study conducted in Argentina, a total of 135 vegetable and fruit samples obtained from marketplaces were analyzed for 35 pesticide active ingredients using GC-MS technique. They found that 65% of the samples contained residues. They found that 56% of the residue detected samples contained residues above the MRL. Chlorpyrifos, which was detected in 25.9% of the samples, was the most detected pesticide residues.	2018
Hadian et al.	Analyzed 85 vegetable and fruit samples for 47 pesticide active ingredients in terms of the quality of the fruit. In their study using GC-MS, they analyzed the fruits Residues were detected in 26.7% and 65.5% of vegetables. Analyzed 48.2% of the samples contained 11 different residues at detectable level in cabbage, melon and lettuce samples. No residues were found in cabbage, melon and lettuce samples.	2019

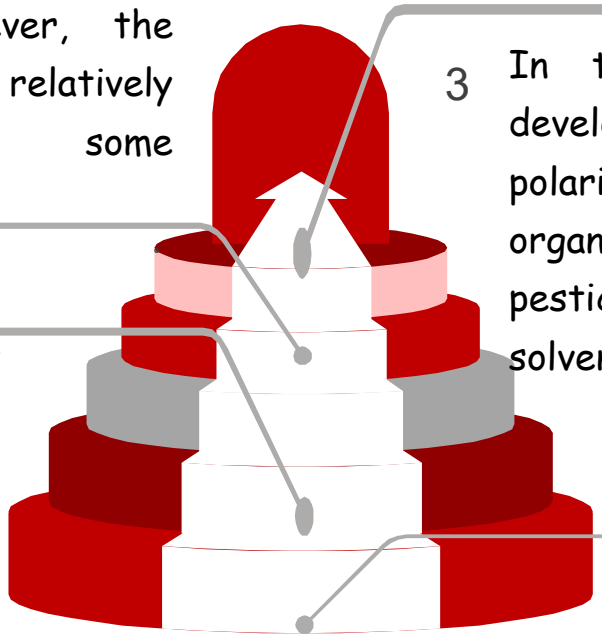
Residual Methods Used to Date

1

Pesticide residue analysis started in developed countries in the 1950s. In Türkiye, In 1959, the Ankara Agricultural Pesticides and Chemicals Institute Residue Analysis Laboratory was established. pesticide residue studies were initiated thanks to its establishment (Tiryaki, 2016).

2

This situation reveals the importance given to pesticide residue studies in Türkiye. The Mills method, developed in the 1960s, was the first residue analysis method. However, the method has some difficulties for relatively polar pesticides such as some organophosphorus insecticides.



3

In the 1970s, new methods were developed to extend the analytical polarity range to cover organochlorines, organophosphorus and organonitrogen pesticides by changing the extraction solvent from acetonitrile to acetone.

4

Luke et al. (1975) and Specht and Tilkes (1980) added sodium chloride to saturate the water phase, thus increasing polarity and achieving higher recoveries. The Luke method became the Official Method of the Association of Official Analytical Chemists (AOAC) a few years later.

5

Since the 1980s, environmental and health concerns about the use of chlorinated solvents have led to the development of many new methods in which dichloromethane is replaced by ethyl acetate/cyclohexane.

Methods

In 2003, Anastassiades et al. developed a new cost-effective method called QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) for use in pesticide residue analysis. The method was found to be suitable for the analysis of a large number of pesticides in a wide range of vegetable and fruit samples due to its simplicity, the use of small amounts of acetonitrile, and the possibility to analyze a large number of pesticides in several steps and with high efficiency.

Since 2003, the method has been used by various pesticide residue analysis laboratories and researchers adapted and validated the QuEChERS method. The QuEChERS method has been used in many Although it is widely used in national and international laboratories, it has its own local need to be verified in our laboratory conditions (Çetinkaya-Açar, 2015).

Researcher	Studies	Year
Hışıl and Tufan	He reported that some pesticides in fruits and vegetables can be determined by GC.	1984
Fillion and Thorp	Many pesticides in fruits and vegetables are identified and monitored by GC/MSD. In this study, it was aimed to detect and identify pesticide residues in samples. For this purpose, a simple sample preparation method was developed, C18 and Envirocarb solid phase extraction cartridges were used in the extraction process and GC/MSD conditions were also determined and many pesticides could be monitored in a single analysis.	1995
Sherma	Separation, identification and quantification of extracted pesticide residues are carried out using highly selective detectors in devices such as HPLC and GC. The most preferred method is the identification and quantitative analysis of pesticide residues by GC/ECD and then confirmation by GC/MS.	1999
Pire	In this study, some pesticide residues in raisins were analyzed using GC/ECD and GC/MS techniques. First of all, the optimum ions of the pesticides to be investigated in GC/MS Scan mode were selected and the pesticides were verified by switching to SIM mode, which is 200 times more sensitive than Scan mode, and the amounts of the pesticides detected by GC/ECD were calculated.	2001
Falqui et al. Montury et al.	In recent years, emphasis has been placed on method studies and residue monitoring programs to monitor residues in foods. In France, studies on SPME methods have been particularly emphasized.	2001 2001
Cochran et al.	Some fruit and vegetable samples were extracted with acetonitrile, filtered and passed through a C18 cartridge for cleaning. The solvent of the resulting extract was evaporated under nitrogen gas and dissolved in acetone. With the highly reproducible Multiple Residue Analysis Method developed in GC/MS, 77 pesticides were analyzed in as little as 13 minutes.	2002
Navarro et al.	A method for the detection of 8 fungicides (captan, carboxin, fludioxonil, flutolanil, flutolanil, folpet, pyrimethanil, quintozene and tebuconazole) in fruits and vegetables based on matrix solid phase dispersion and gas chromatography analysis was described. In this method, which is said to be a faster method (MSPD) than other methods used in the extraction of fungicides (solvent partitioning, SFE, SPE, SPME), fungicide residues were identified and calculated using NPD and ECD detectors and confirmed by MSD. 0.5 g of sample was cleaned with C18 bonded silica sorbent and ethyl acetate was used as solvent.	2002

Researcher	Studies	Year
Urruty and Montury,	In a method developed for the analysis of 20 pesticides used in strawberries, samples were extracted by solid-phase microextraction with the aid of microwave radiation and analyzed by GC and HPLC. The calculation limits for all pesticides were well below the MRLs and the relative standard deviation was less than 20% at 50µg/kg concentration.	2002
Taylor et al.	LC-MS-MS method has been developed for the quantification of many pesticide residues in fruits and vegetables. Isocratic LC conditions were combined with electrospray ionization mass spectrometry to detect and identify 38 pesticides in different matrices. The advantage of the method is that grape, kiwi, strawberry, spinach, lemon, peach and nectarine samples can be analyzed without cleaning. After taking 8 g of the homogenized sample and adding 70 g of anhydrous sodium sulfate, 2 g of sodium hydrogen carbonate and 50 ml of ethyl acetate, mixing, filtering and concentrating were performed. After addition of methanol to the extract, it was vialed and submitted to HPLC-MS.	2002
Anastassiades et al.	The most effective approach to pesticide analysis is to use multi-residue analysis methods. Various methods using different solvents and salts have been developed for this purpose. These methods also involve various extraction steps. Extraction methods such as supercritical fluid extraction (SFE), matrix solid phase separation (MSPD), microwave-assisted extraction (MAE), solid phase microextraction (SPME) and pressurized liquid extraction (PLE), also known commercially as accelerated solvent extraction (ASE), have been developed to be more convenient and less solvent-intensive for laboratories.	2003
Anastassiades et al. Wilkowska and Biziuk	After several studies, Anastassiades et al. (2003) developed the QuEChERS method for multi-residue and multi-class analysis of fruits and vegetables, which stands for "quick, easy, cheap, cheap, effective, rugged and safe". In this technique, a single-phase extraction with acetonitrile is performed first, followed by liquid-liquid separation with the addition of anhydrous magnesium sulfate (MgSO4) and sodium chloride (NaCl). After these processes, the sample is cleaned using dispersive solid phase extraction (dispersive-SPE).	2003 2011
De Pinho et al.	Pesticide residue analysis in fruits and vegetables consists of three steps: solvent extraction, sample cleaning step and instrumental analysis. Although solvent extraction is very useful in routine analysis, it has disadvantages such as the use of large amounts of solvent. The excessive use of solvents results in a high amount of organic waste and also prolongs the duration of the analyses.	2010

Pesticides Used in Strawberries

- Pesticides used against diseases and pests in strawberry cultivation consist of insecticides, acaricides and fungicides.

Çalış et al., (2003)

A study was conducted to determine which cultivar is more resistant to lead mold disease, which causes significant crop losses in strawberries. In this study, pathogenic development was tested on 10 cultivars (Aliso, Annepolis, Maralina, Elvira, Delmarwel, Muir, Tufts, Honeoye, Tudla, Tiago). Delmarwel variety was observed to be resistant to the disease due to its later flowering and later fruit setting compared to other cultivars.

Gonzales et al., (2009)

Botrytis cinerea is a netrotrophic and polyphagous pathogen that causes economic problems on soft fruits and crops. Four different strawberry cultivars (Cuntulmo, F. × ananassa cv Chandler, Vilches, Chillian) were studied for their resistance to lead mildew. The most resistant variety was Cuntulmo, followed by F. × ananassa cv Chandler and then Vilches. The most susceptible variety was Chillian.

Chen et al 1987

As a result of the application of mulch, procymidone and thiophanate methyl for the control of *B. cinerea* in strawberries, it was determined that 100% of the fruits were infected in control plots without mulch and 50% of the fruits were infected in mulched plots. Procymidone (Sumisclex) and thiophanate methyl (Topsin M) treated plots provided 84% and 52% control against B. cinerea, respectively, compared to the untreated control plot.

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Hjeljord et al 2000

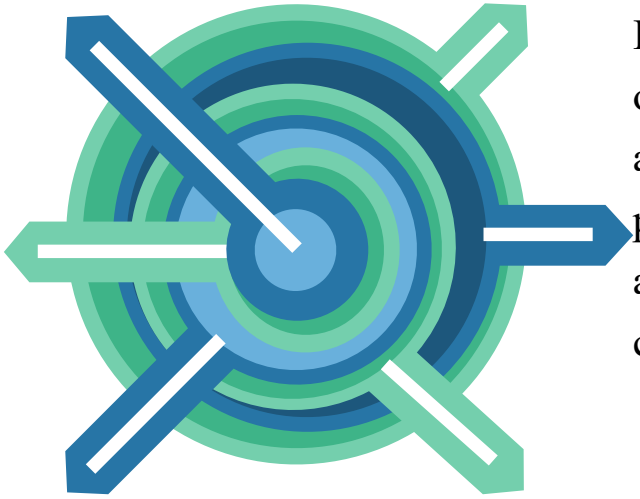
Three commercial Trichoderma products (Trichodex, Binap TFWP and Rootshield) were sprayed weekly during the flowering period of strawberry plants to suppress lead mold disease. As a result, none of the Trichoderma treatments significantly prevented the disease, but Binap TFWP was slightly more effective than the others.

Mertely et al. 2002

During the 1999-2000 and 2000-2001 growing seasons, fungicide (Fenhexamid) applications were made to understand the losses caused by B. cinerea during strawberry flower and fruit development. In order to minimize the damage caused by B. cinerea, fungicide applications should be concentrated on the strawberry period. Researchers have reported that strawberry flowers are more susceptible than immature fruit.

Conclusion

- As a result of this study, it has been stated by many researchers that the In Turkey, pesticides can be found above the MRL in fruit and vegetable samples.



- Also suggest that it may pose a risk to public health

It is important to use safe agricultural products in order to protect and sustain human, animal and environmental health.

It is thought that tightening official controls, educating agricultural workers about pesticide applications and harms, and monitoring pesticide residues can reduce pesticide use

- We believe that the information obtained as a result of this study will shed light on more detailed studies to be done in the future.

Med Berry

Breeding Value

cost

iPlanta

FruitCREWS

Thank you for listening

Presenter → Questions →

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