Properties and determination of pesticides in fruits and vegetables

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The intensive development of agriculture means that more and more toxic organic and inorganic compounds are entering the environment. Because of their widespread use, stability, selective toxicity and bioaccumulation, pesticides are among the most toxic substances contaminating the environment. They are particularly dangerous in fruit and vegetables, by which people are exposed to them. It is therefore crucial to monitor pesticide residues in fruit and vegetables using all available analytical methods.

We set out the problems in the determination of organonitrogen and organophosphorus pesticides in samples of fruit and vegetables, including the complexity and the diversity of matrices in biological materials, and the very low level of pesticides present, as a result of which target analytes have to be isolated and then enriched prior to final determination.

We discuss the various stages in the determination of pesticide residues in fruit and vegetables. We present results from the literature in the context of Maximum Residue Levels (MRLs) of target pesticides in fruit and vegetable samples. We discuss the merits of the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) technique and two-dimensional gas chromatography.

Keywords: Determination; Fruit; Maximum Residue Level (MRL); Pesticide; Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS); Organonitrogen pesticide; Organophosphorus pesticide; Residue; Two-dimensional gas chromatography; Vegetable

Abbreviations: See Appendix A

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1. Introduction

Pesticides are a numerous and diverse group of chemical compounds, which are used to eliminate pests in agriculture and households. They enable the quantities and the quality of crops and food to be controlled, and help to limit the many human diseases transmitted by insect or rodent vectors. However, despite their many merits, pesticides are some of the most toxic, environmentally stable and mobile substances in the environment. Their excessive use has a deleterious effect on humans and the environment; their presence in food is particularly dangerous. With their environmental stability, ability to bioaccumulate and toxicity, pesticides may place the human body at greater risk of disease and poisoning [1].

Pesticides enter the environment in various forms (e.g., powders, moistened powders, powders for preparing aqueous solutions, and concentrates for making up emulsions or sprays). Pesticides are of enormous importance in increasing the yields and quality of agricultural products. They are used to:

- control the numbers of pests destroying whole plants or their parts;
- increase the production of animal and plant biomass;
- combat microorganisms causing farm produce to rot and to decay;
- combat algae, bacteria, fungi and weeds;
- combat animal pests damaging crops (e.g., mites, aphids, insects, larvae, and nematodes);
- stimulate or inhibit plant-growth processes (e.g., remove excess flowers, destroy foliage or dry out plants);
- make possible the action of other substances;
- counteract growths on boats and ships; and,
- kill harmful organisms in farm buildings, the home, hospitals, stores and vehicles.

The widespread use of pesticides not only contaminates water, soil, and air, but also causes them to accumulate in crops (e.g., fruit and vegetables) (Fig. 1). Pesticides are transported mainly by rain and wind from their points of application to neighboring crops and land, where their presence may be undesirable or harmful

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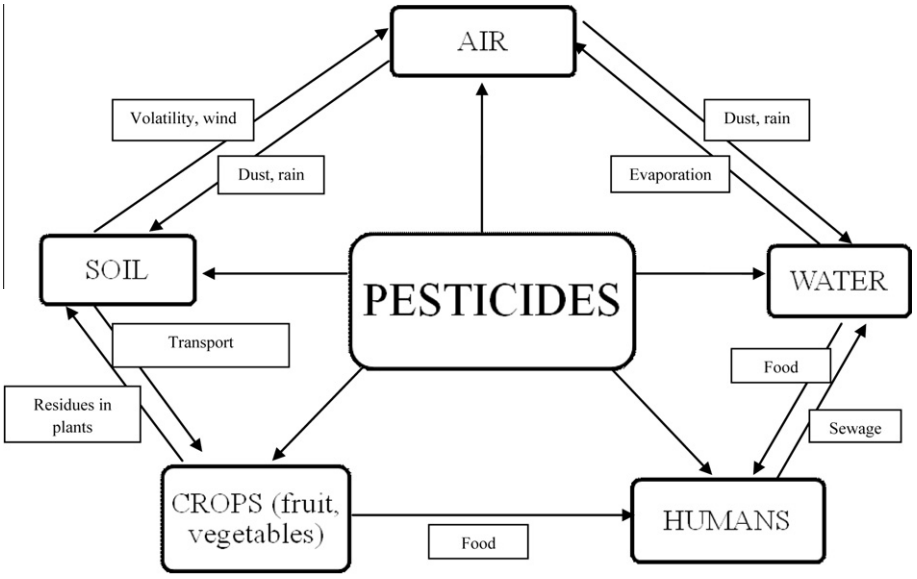

Figure 1. The circulation of pesticides in nature (including crops).

[2,3]. The quantities of pesticides in any particular region depend to a large extent on the intensity of pesticide application and the types of crops grown there.

Pesticides have many advantages, but they also do much harm to the environment [1–4]. Fig. 2 lists some of the effects of using pesticides.

In view of both positive and negative effects of pesticides, we should aim to achieve full selectivity of their action. Nonetheless, the latest studies show that pesticides still constitute a hazard to the environment and human health. Each year, 140,000 tons of pesticides are sprayed onto crops in the European Union (EU) alone. Fruit and vegetables are the crops most likely to be contaminated by pesticides, particularly grapes, citrus fruits and potatoes. According to data from the EU's Pesticide Action Network, as of 2008, some 350 different pesticides were detected in food produced in the EU. More than 5% of products contained pesticides at levels exceeding the EU's maximum permitted level (MPL).

The diversity of their chemical structures, actions and applications makes any classification of pesticides difficult [1]. There are a number of criteria according to which they can be categorized:

(1) toxicity;
(2) purpose of application;
(3) chemical structure;
(4) environmental stability; and,
(5) the pathways by which they penetrate target organisms.

Structurally, they can be divided into inorganic and organic compounds; the inorganic include arsenic insecticides, fluoride insecticides, inorganic herbicides and inorganic fungicides, while the organic comprise organochlorine, organophosphorus and organonitrogen pesticides.

Organophosphorus pesticides (OPPs) (e.g., dichlorvos, methyl parathion, chlorpyriphos, diazinon, demeton-S-methyl, phosalone, fonofos, metamidofos, monocrotophos, chlorfenvinphos, fenitrothion, malathion) are the principal group of compounds used to protect plants. They include all organic compounds containing phosphorus [5,6] and are used to combat pests in industrial plantations, orchards and vegetable cultivation. OPPs usually have an ester structure, decomposing fairly easily on the surfaces and interiors of plants, and in the soil. Their toxicity depends on inhibiting the activity of enzymes controlling the functions of the nervous system, mainly acetylcholinesterase. They permanently bind the group hydroxylating the enzyme, which prevents acetylcholinesterase from decomposing, and act through contact or systemically. Blockage of cholinesterase activity causes the amount of acetylcholine at the synapses to increase, leading to a state of hyperarousal, and paralysis of the muscles and the main respiratory center. Apart from OPPs, organonitrogen pesticides (ONPs) also play a major part in combating pests [7,8]. ONPs include phenylureas, carbamates, and triazines and their derivatives (e.g., aminocarb, propoxur, carbaryl, simazine, atrazine and propazine). Even though they are less stable in the environment than OCPs, they can get into the human digestive system, thus posing a health hazard. Some carbamate insecticides (e.g., carbaryl) can be teratogenic in large doses and nitrosated to form strongly carcinogenic nitroso-compounds.

OCPs, including aldrin, chlordane, lindane and DDT, have been withdrawn from use in many countries