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Review

Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment

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ABSTRACT

Pesticides are released intentionally into the environment and, through various processes, contaminate the environment. Three of the main classes of pesticides that pose a serious problem are organochlorines, organophosphates and carbamates. While pesticides are associated with many health effects, there is a lack of monitoring data on these contaminants. Traditional chromatographic methods are effective for the analysis of pesticides in the environment, but have limitations and prevent adequate monitoring. Enzymatic methods have been promoted for many years as an alternative method of detection of these pesticides. The main enzymes that have been utilised in this regard have been acetylcholinesterase, butyrylcholinesterase, alkaline phosphatase, organophosphorus hydrolase and tyrosinase. The enzymatic methods are based on the activation or inhibition of the enzyme by a pesticide which is proportional to the concentration of the pesticide. Research on enzymatic methods of detection, as well as some of the problems and challenges associated with these methods, is extensively discussed in this review. These methods can serve as a tool for screening large samples which can be followed up with the more traditional chromatographic methods of analysis.

Contents

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1. Introduction

Pesticides play an important role in the high productivity achieved in agriculture through the control of pests. However, pesticides are intentionally toxic, often towards non-target organisms and their intentional release into the environment has serious environmental consequences. They are often very persistent with half-lives of decades and are transported over long distances by global circulation, and through run-off, find their way into aquatic systems. For example, DDT has been found in remote areas such as the Arctic, and even the Antarctic, even though it has been banned in many countries (Ongley, 1996; Smith and Gangolli, 2002; Lintellman et al., 2003). Thus the pollution of the environment, and particularly water, by pesticides has become a global problem (Ongley, 1996).

Three classes of pesticides have been problematic, namely organochlorines, organophosphates and carbamates. Organochlorines include a variety of chemicals such as polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs) and a range of pesticides, of which DDT is the most well-known example (Smith and Gangolli, 2002). Other examples of organochlorine insecticides are dieldrin, chlordane, heptachlor, toxaphenes, mirex, lindane, endosulfan, dicofol, hexachlorobenzene and chlordecone. These chemicals are very persistent in the environment, for example DDT which has a half-life of 3–20 years (Lintellman et al., 2003). They are further able to bioaccumulate in the food chain which refers to the uptake of a chemical in fatty tissues, where it becomes concentrated as it is passed through different levels of the food chain. The ability of these chemicals to bioaccumulate has been reported for mussels, where uptake and concentration of DDT by a factor of 690 000 was measured (Risebrough et al., 1976). During the 1970s, many countries thus banned or limited the production and use of organochlorine chemicals. However, some of these chemicals, such as DDT, are still manufactured and used in some countries for vector disease control. The Stockholm Convention on persistent organic pollutants (POPs), which came into force in 2004, require parties to the convention to eliminate or reduce the release in the environment of several organochlorine pesticides, namely aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, chlordecone, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, lindane and pentachlorobenzene (http://www.chm.pops.int/Convention/tabid/54/language/en-US/Default.aspx#convtext). Some of these pesticides, such as DDT, are still permitted for certain applications such as vector control and are thus still able to contaminate the environment.

Organophosphate pesticides include parathion, malathion, methyl parathion, chlorpyrifos, diazinon, dichlorvos, phosmet, tetrachlorvinphos, triazophos, oxydemeton and azinphos methyl. Organophosphate pesticides obtain their toxicity from their ability to inhibit acetylcholinesterase, causing neurotoxicity (Fukuto, 1990). The presence of this enzyme in insects, birds, fish and all mammals give this class of pesticides enormous toxicity towards unintended targets. Carbamate pesticides are also cholinesterase inhibitors with a similar mechanism of action as organophosphate pesticides (Fukuto, 1990).

Apart from the toxic effects of many of these pesticides, long-term effects include their ability to disrupt the endocrine systems in mammals, birds and fish (Lintellman et al., 2003). The ability of pesticides to interact with estrogen receptors, androgen receptors, thyroid receptors and other types of endocrine disrupting effects have been researched to a limited extent and many long-term effects are still unknown (Katzenellenbogen, 1995; Klotz et al., 1996; Klotz et al., 1997; Jaeger et al., 1999; Crews et al., 2000; Degen and Bolt, 2000; Hodges et al., 2000; Andersen et al., 2002; Kojima et al., 2004; Tabb and Blumberg, 2006; Li et al., 2008).

It should also be noted that many pesticides are transformed in the environment through physical, chemical and biological processes which are intended to detoxify them, but often the transformation process forms products that are more toxic than the parent compound (Sinclair and Boxall, 2003).

An effective strategy for dealing with pesticide contamination in the environment has to commence with an assessment of the extent of the problem. However, monitoring data for pesticides is poor, particularly in developing countries (Ongley, 1996; Schwarzenbach et al., 2006). Traditionally, chromatographic methods have been used to analyse the presence of compounds in environmental samples. Such analysis, used with techniques such as mass spectrometry, can identify pesticides and their concentrations. However, these methods are complex, costly and time-consuming, while requiring highly skilled personnel. They are therefore unsuitable for screening of large volumes of samples, and due to their cost, developing countries do not readily have access to such methods.

Thus researchers have been investigating alternative methods of detection and screening that are cheaper and more user-friendly. As many pesticides are designed to inhibit various enzymes within insects and other pests, utilising these enzymes for detection purposes seemed a logical route. In this manner, enzymes such as acetylcholinesterase, butyrylcholinesterase, alkaline and acid phosphatase, tyrosinase, organophosphorus hydrolase and aldehyde dehydrogenase and others were investigated for their ability to detect pesticides in water and other matrices such as soil, food and beverages. Most of these enzymes have been incorporated into biosensors for this purpose. Due to the potential for miniaturisation, biosensors can be very suitable for onsite monitoring of pesticide concentrations in the environment.

This review summarises research in literature involving the use of the above enzymes for the detection of pesticides. It is not intended as a review on biosensors. The specific pesticides tested using these enzymes, as well as the detection limit achieved in each case, are examined. Various obstacles associated with enzymatic methods are addressed, such as the ability of enzymes to function in the presence of solvents, as well as the ability of enzymes to distinguish between different pesticides within the same sample. An important aspect, which is seldom addressed in research on enzymatic detection, is whether these methods are able to achieve sufficient sensitivity to detect pesticides at their maximum allowable limits as described in regulations. Therefore a background to legislation and regulations for different countries is discussed as a basis of comparison. Furthermore, the limits of detection achievable through traditional chromatographic methods are provided as a reference.

From the literature reviewed, it is clear that enzymatic methods are not able to achieve the sensitivity of traditional chromatographic methods. However, enzymatic methods should not be seen as a means of replacing existing, traditional methods of analysis. We would argue that enzymatic methods have a role to play as a screening tool which could allow the screening of hundreds of samples in a short period of time. Particularly, anticholinesterase activity can serve as a "toxicological index", a measure of the toxicity of a sample (Bernabei et al., 1993). Some obstacles still have to be overcome before enzymatic methods will be utilised on an extensive basis, but these methods could complement existing methods and allow for a more rapid assessment of problematic environments to allow appropriate steps to be taken to address contamination issues. Where pesticides are detected through enzymatic methods, follow-up analysis can be conducted using chromatographic methods as a validation. This argument is also put forward by Rodriguez-Mozaz et al. (2007), indicating that each method has unique advantages which can complement each other.