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REVIEW ARTICLE

# Simple Review of Environmental Analytic Methods for the Determination of Pesticide Metabolites

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## ABSTRACT

The findings of research proceedings on pesticide metabolites detection are both an environmental inventory and prevention of potential foodstuffs contaminants. Since, the requirement of a quality environment is a condition for ensuring food security, the newly designed methods with validated sensitivities and efficiencies should be highlighted as solutions for reducing pesticide metabolites. In this respect, this review provides information about pesticides metabolism subject to various analytical conditions applied to standard methods, in addition to the pesticide/related metabolites ratio (R) developed for the intended purpose.

## INTRODUCTION

With reference to the European Directives [1], rationalization of the pesticide's usefulness can contribute to environmental protection. Although the development of the pesticides use requires both constant management and control of their impact on the environment-taking over these measures will unavoidably allow agricultural resources use in a sustainable way. Indeed, it comes to setting a balance between food needs, the environment quality requirements and the disturbances that pesticide metabolites could bring about in some agricultural and food [2]. These risks are all the more concerning that most pesticide residues develop multiple-origin instability, usually by degradation pathway, and their metabolites with high lifetime in matrices. Pesticide residues for agricultural use subjected to an array of biotic and/or abiotic transformations generate potentially hazardous compounds. Therefore, the proposed diagram refers to the main known degradation types that pesticide residues are subjected, as illustrated in the figure 1. In fact, it is difficult to assess the consequences of the pesticides use, including their toxicological profile inherent in their nature, their chemical, biological, bacteriological degradations, as well as the various complex and interdependent internal and external factors of the environment components. To that end, research devoted to the determination of pesticide metabolites in the environment has well proven their presence in several biosphere points. For instance, the United States Environmental Protection Agency (USEPA) reports that as a result of agricultural pesticide use, 46 other compounds had been detected in surface water and 76 other in surface water bodies [3]. Also, these pesticide residues metabolites lead to serious environmental problems, in particular through contamination of the human food supply chain since according to a World Health Organization (WHO) report, one to five million pesticide poisoning cases, including several thousand fatal cases, occur annually worldwide

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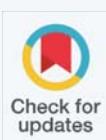
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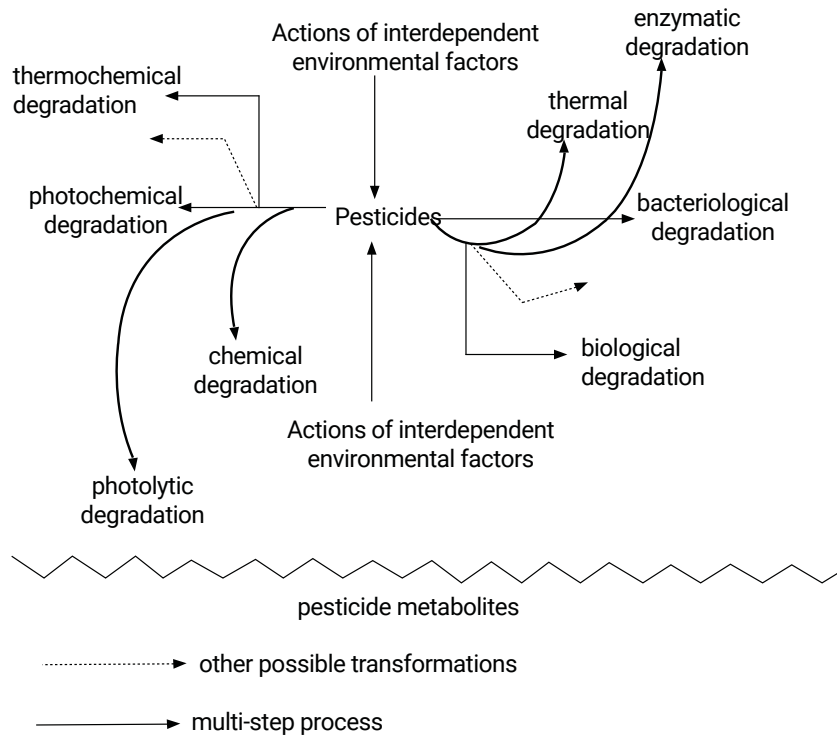
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**Figure 1** Simple illustrative scheme of probable metabolism pathways of pesticide residues used in agriculture.

[4]. For these reasons, Maximum Residue Limits (MRLs) for pesticides have been established by the Food and Agriculture Organization (FAO) of the United Nations and the World Health Organization (WHO) [5], as well as their metabolites. In fact, the MRL reflects the maximum amount of pesticide residues and its toxic metabolites that would be expected on a product if good agricultural practices were followed while using the pesticide. Therefore, pesticide concentrations and their metabolites levels in the environment should be monitored on an ongoing basis. In contrast, with the multi-sectoral development of analytical research, correlations between biological and chemical effects of pesticide metabolites measured in the environment have nevertheless been established. However, those correlations remain insufficient since the high systematic dissemination of metabolites tributary to environmental contours and unresolved properties remain problematic. In this context, the search for effective dosing methods is inevitable. It represents a huge health and economic stake. Also, the improvement of the environmental analytical chemistry continues with the innovative use of generally combined standard techniques including chromatography and mass spectrometry. These multi-residue methods have detected important pesticide metabolites for a wide range of samples, including water, soil, plants and animals [6-11]. However, due to the inherent properties of sensitivity, selectivity and versatility, the applicability of the newfound methods to environmental analysis should be an alternative suitable to the climatic conditions for better participation in the fields

of environmental control and management. This literature research is to collect data from environmental analytical applications relating to that pollution and toxicity problems posed by pesticide metabolites. Through this channel, this document describes the current state of the significant contribution of pesticide metabolites pollution from various environmental samples without forgetting the food chain.

### ANALYTICAL METHODS ESTABLISHED

Several techniques implemented have made tremendous progress—including Gas Chromatography (GC), liquid chromatography (GC), Thin-Layer Chromatography (TLC), High-Performance Liquid Chromatography (HPLC), Mass Spectrometry (MS) and Nuclear Magnetic Resonance (NMR). In addition to their possible combinations, these standard methods can be combined with Liquid Scintillation Counter (LSC), Radiolabel (RAD), Solid-Supported Liquid-Liquid Extraction (SS-LLE), Ion Trap (IT), Electrospray Ionization (ESI) and/or Diode Array Detection (DAD) for the analysis of pesticide metabolites, as the findings set out (Table 1) highlighting their problematic in the environment. These approaches, with their high resolution power and selectivity in full scan detection mode, have the ability to characterize pesticide metabolites as well as their degree of toxicity for a significant contribution to environmental control.

Hereby, two metabolites of the chloroacetanilide Herbicides-Ethane Sulfonic Acid (ESA) and Oxanilic Acid

**Table 1:** Overview of multi-residue methods for the analysis of pesticide metabolites in various environmental matrices.

Analytes	Pathway/condition/matrix	R	Methods	References
Atrazine (A) metabolites deethyl-atrazine (DEA); deisopropylatrazine (DIA); diaminochlorotriazine (DACT)	Atrazine can be degraded in surface water by photolysis and microorganisms via N-dealkylation and hydrolysis of the chloro substituent / soil	1/3	SPE-GC/MS	[12]
Metolachlor (MET) metabolites metolachlor-oxanilic acid (MET-OA); metolachlor-ethanesulfonic acid (MET-ESA)	Dealkylated metabolites/ hydrological environments.	1/ 2	HPLC/DAD LC/MS	[12]
Diuron metabolites (3-(3,4-dichlorophenyl)-1-methylurea; 3-(3,4-dichlorophenyl)-urea; 3,4-dichloroaniline; 4-chloroaniline; 4-chloroacetanilide; 3,4-dichloroacetanilide, aniline	Successive N-demethylation and amide bond cleavage involving demethylase and amidase reactions / bacteria from soil / soil of sugar cane.	1/7	HPLC LC-MS GC-MS	[13-15]
Amitraz metabolites N-(2,4-dimethylphenyl)-Nmethylformamidine; 2,4-dimethylformamidine; 2,4-dimethyl aniline; N,N'-bisdimethylphenylformamidine	Degradation / human blood Decomposition/ pears	1/4	UHPLC-QTOF SLE-MS/ MS QqTOF-MS MS/MS	[16] [17]
Fenthion metabolites Sulfoxide; sulfone	Degradation by sunlight photolysis / oranges	1/2	IT-MS QqTOF-MS	[18]
Simazine (SIM) metabolites 2-hydroxy-simazine (OH-SIM); desethyl-simazine (DE-SIM)	Formation, degradation, transformation, biotransformation and biotic and abiotic processes its main metabolites / presence - absence of urea, microbiologically active / sterilized soil	1/ 2	LC-ESI/MS	[19]
Fluometuron metabolites desmethyl fluometuron; trifluoromethyl phenylurea; trifluoro-methylaniline	Series of oxidative and hydrolytic transformations during / microbial metabolism / soil or aquatic environments/ Tillage soils	1/3	HPLC, LSC RAD-TLC, NMR	[20]
Carbaryl metabolites 4-hydroxycarbaryl; 5-hydroxycarbaryl; 7-hydroxycarbaryl; Hydroxymethylcarbaryl; 1-naphthol. 2-hydroxy-1,4-naphthoquinone; 1-naphthol and three other photoproducts	Rapid. Proceeds via hydrolysis, alkyl oxidation, arene oxide formation, epoxide hydrolysis and glutathione conjugation/ Pathways similar in humans, rodents and other species investigated / chicken urine.  Photo-oxidation process together with products from photo-Fries, photo ejection and methyl carbamate hydrolysis /excitation with a Suntest/silica-kaolin-sand.	1/5 1/5	TLC LC-DAD LC-MS HPLC/ESI/MS	[21] [22]
Penconazole (PEN) metabolites 4-(2,4-dichloro-phenyl)-5-[1,2,4] triazol-1-yl-pentane-2,3-diol ; 4-(2,4-dichloro-phenyl)-5-[1,2,4] triazol-1-yl-pentanol ; glucuronide conjugate of PEN-OH; 4-(2,4-dichloro-phenyl)-3-hydroxy-5-[1,2,4] triazol-1-yl- pentan-2-one, 4-(2,4-dichloro-phenyl)-5-[1,2,4] triazol-1-yl-pentanoic acid; glucuronide conjugate of iso-PEN-OH, 3-(2,4-dichloro-phenyl)-4-[1,2,4] triazol-1-methyl-butanol	multiple reaction following the protonated molecular ions different oxidized metabolites were found, both in the free and glucuronide conjugate forms / Farmers exposed to penconazole / human urine samples	1/7	LC/Q-TOF-MS, ESI	[23]
Carbosulfan metabolites carbosulfan sulfonamide ; carbofuran ; dibutylamine ; 3-hydroxycarbofuran ; 7-phenolcarbofuran; 3-ketocarbofuran; 3-hydroxy-7-phenolcarbofuran; 3-keto-7-phenolcarbofuran	oxidation of sulfur to carbosulfan sulfonamide and the cleavage of the nitrogen sulfur bond (N-S) to give carbofuran and dibutylamine / in vitro biotransformation by mammalian hepatic microsomes / hepatic microsomes from human, rat, mouse, dog, rabbit, minipig, and monkey.	1/8	LC-MS	[24]
Dimethoate metabolites desmethyl dimethoate ; dimethoate carboxylic acid ; dimethyl dithiophosphoric acid ; dimethyl thiophosphoric acid ; dimethyl phosphoric acid ; phosphoric acid	Degradation affected by hydrolysis followed by oxidation or oxidation followed by hydrolysis/ soil-alkaline solution	1/6	TLC	[25]
Bifenthrin metabolites cyclopropanecarboxylic acid; 2-methyl-3-biphenyl methanol; 4-trifluoromethoxy phenol; 2-chloro-6-fluoro benzylalcohol; 3,5-dimethoxy phenol.	Hydrolysis of ester linkage and cleavage of biphenyl/ microorganism/potential contaminated soils treatment.	1/5	GC-MS	[26]
Chlorpyrifos metabolites diethyl thiophosphate; diethyl phosphate; 3,5,6-trichloro-2-pyridinol	biotransformation products / urine samples / human urine	1/3	LC-ESI-MS/MS	[27]

LC: Liquid Chromatography; GC: Gas Chromatography; MS: Mass Spectrometry; TLC: Thin-Layer Chromatography; NMR: Nuclear Magnetic Resonance; HPLC: High-Performance Liquid Chromatography; DAD: Diode-Array Detection, LSC: Liquid Scintillation Counter, RAD: Radiolabel; ESI: Electrospray Ionization; Qqtof or QTOF: Quadrupole Time-of-Flight; SLE: Solid-Support Liquid-Liquid Extracts; UHPLC: Ultra-High Performance Liquid Chromatography; SPE: Solid Phase Extraction; MS/MS: Mass Spectrometry Tandem; IT: Ion Trap; R: Pesticide/Related Metabolites Ratio.

(OXA)–are detected by HPLC/DAD and LC/MS for metolachlor [12]. Seven and three phenylurea herbicides metabolites of diuron [13-15] and fluometuron [20] are, respectively, analyzed by HPLC, LC/MS and GC/MS on the one hand and HPLC/LSC, RAD/TLC and NMR on the other. Phenylurea herbicide analysis also includes the metabolites of simazine (SIM)-2-hydroxy-simazine (OH-SIM) and Desethyl-Simazine (DE-SIM) detected by LC/ESI/MS [19]. Phenylurea herbicides are widely used to selectively control weeds in a variety of crops. However, these compounds exhibit chronic toxicity, and their residues and degradation products are potential risks to human health through their accumulation in the environment and the food chain [28]. Elsewhere, metabolites, although tributaries of conditions and methods used, five carbamates insecticides metabolites of carbaryl are detected as well by TLC and combining HPLC/DAD, LC/MS and HPLC/ESI/MS techniques [21,22]. Carbosulfan toxicological evaluation was compiled by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) [29]. As such, eight carbamates insecticides metabolites of carbosulfan are only analyzed by LC/MS [24]. Other insecticide metabolites such as dimethoate [25], bifenthrin [26] and chlorpyrifos [27] are analyzed and detected under various conditions by TLC, GC/MS and LC/ESI/MS/MS, respectively, as well as amitraz and fenthion [16-18]. For both pesticides, their applications in conjunction with Time-of-Flight (TOF) or Quadrupole Time-of-Flight (QTOF) analyzers (TOF-MS or QTOF-MS) in detecting amitraz and fenthion metabolites in human blood and food samples such as UHPLC/QTOF, SLE/MS/MS, QTOF/MS, MS/MS and IT/MS, QqTOF/MS have been applied, respectively.

### Critical analysis of the findings

**Pesticide metabolites in samples:** The environment is a complex setting where the pesticide residues transition processes through metabolites accumulation in various environmental matrices follow degradation and/or transformation steps. That can be carried out in soil by hydrolysis and N-dealkylation. Indeed, fungi and soil bacteria can transform atrazine into hydroxy-atrazine, sometimes quickly [30]. The main product of acid or basic hydrolysis [31,32] is 3, 4-dichloroaniline, a highly toxic aromatic amine. Likewise, studies [33-35] have shown that measured concentrations in hydrological media environments from normal agricultural use reveal the presence of metolachlor metabolites. In diuron-contaminated environments, the main degradation products detected are methyl (3,4-dichlorophenyl methylurea) and dimethyl (3,4-dichlorophenyl-methylurea) [13]. Amitraz intermediate and its final products are more toxic, especially 2,4-dimethylaniline, characterized by mutagenicity, carcinogenicity and genotoxicity [36-38]. Elsewhere, photoproducts are derived from N-demethylation, hydroxylation and rearrangement reactions [39]. Photoproducts metabolites [12,40] of diflubenzuron, including p-chlorophenylurea, 2,6-difluorobenzamide

and 2,6-difluorobenzoic acid, have been detected in groundwater, surface water, soil and sediment [40] on the one hand, and sulfoxide and sulfone, metabolites of fenthion have been detected in oranges [12] on the other hand. Typically, the main degradation products obtained and less sensitive to photodegradation are more persistent and more toxic than the parent compounds. Consequently, contamination of waters, soils, crops [14-20,23-27], and biological matrices by simazine metabolites (Table 1), among other things, resulting from biotic and / or abiotic reactions of pesticides residues is a public health issue. Also, other processes such as oxidation followed by hydrolytic transformation of fluometuron, alkyl-oxidation and/or photo-oxidation of carbaryl penconazole, carbosulfan and dimethoate [20-25] have also been recorded. Through this, these compounds produced metabolites under the conditions of the applied method (Table 1). And, given the quality of the analytical methods applied, the validity and relevance of the experimental data collected in this document (Table 1) are as much among others illustrations. For a pesticide used, at least two related metabolites are detected (Table 1). In other words, the metabolites growth rate, although dependent on matrices conditions and analytical methods, doubles at least in each medium. Moreover, the lower the pesticide / related metabolites ratio, the more contaminated the matrix identified, since new contaminants are constantly being added to crop varieties. In this regard, a taxonomic study of contaminated matrix based on the identification, quantification and study of the pesticide metabolites toxicity would be an important information source. It would measure the level of danger of contamination. However, recommendations based on this classification will make it possible to operate on pesticides with lesser ecotoxicological consequences. From a holistic view point, it is necessary to move from a static analysis of the research achievements developed in the samples to a dynamic analysis which, in relation to real matrices, will unavoidably raise awareness, given the rates of accumulation and/or bioaccumulation of metabolites related to the pesticides used. Moreover, ecotoxicological studies [41-45] show that pesticides contribute to the development of various pathologies including carcinogenic, neurological, respiratory and reproductive diseases since thousands of deaths occur every year worldwide according to the World Health Organization (WHO) with one to five million cases of pesticide poisoning [46]. At this point, in addition to the complexity of the environmental conditions favorable to the transition from chemically and / or biologically unstable pesticides, the foodstuffs genuine contaminants relate to the toxic metabolites bioaccumulation.

On the other hand, we must affirm the absolute need to combat the pesticide metabolites which accumulate continuously in highly complex matrix such as surface and groundwater, soil, food and food products. With the development of suitable methods to assess the toxicity of pesticide metabolites in order to establish the Maximum

Residue Limits (MRLs) allowed, improving crop yields remains a feasible measure. It requires monitoring the rational and reasoned use of pesticides to ensure the regulation of authorized levels. In this context, newly designed, fast and reliable methods for improvements adapted to environmental conditions for the reduction of pesticide metabolites are needed. Thus, the transfer phenomena affecting highly complex plant protection products and the possible ecosystem reactions in their largely unknown presence will be reduced. For this purpose, chromatography (LC-HPLC-UPLC) and / or Mass Spectrometry (MS) are effective tools for a large-scale use analysis. Their assessment depends on the quality of the performance, and reasons our investigation. Their applications in conjunction with powerful tools in extraction to investigate the presence of pesticide metabolites in varied samples are the most appropriate, given the high sensitivity, the mass analysis precision, the spectra high resolution, the improvement selectivity and characterization of metabolites, including their degree of toxicity for both environmental quality control and management.

### Pesticide metabolites in foodstuffs

Despite the varied and rich agricultural potential, the critical nature and problematic of the pesticide metabolites in the environment have motivated the increasing use of several newfound, rapid and accurate techniques. Therefore, numerous analytical methods of multi-residue types developed have validated the determination of 83 pesticide residues in wine samples, 51 in grapes, 126 and 144 in cereals and dry foods for animals respectively, 129 in leafy vegetables and 260 in agricultural products [45-50]. Furthermore, with the network of biotic and/or abiotic reactions, one of the main food chain contamination remains related to the toxic effects of pesticide residue metabolites to which involving are subjected the food matrices. In fact, with food conservation and storage conditions, the pesticide residues detected are highly subjected to metabolic decompositions due to the biological, bacteriological and enzymatic factors, including several known mechanisms of actions. Besides, biomonitoring studies have often detected pesticide metabolites in consumer urine samples [23,27]. Such investigations achievements require an objective and thorough introspection in order to site the potential and hazardous contaminant. Indeed, it has been shown that between the pesticide residue and their metabolites, the latter are typically more toxic. At this level, the stable presence of the metabolites can be threatening. The irreversibility of such chemical and / or biological processes should guide the choice on pesticides with minor toxicological and ecotoxicological consequences. So the pesticide residues metabolites, often overshadowed, are those truly responsible. Therefore, is not it fair to mention the Maximum Residue Limits (MRLs) before any transformation and after, so that the problematic of food-borne poisoning pesticides-related could really be apprehended? Also, with the impressive number of pesticide metabolites more toxic [51-57] and more persistent than

their parent, detected along the food chain, the use of these foodstuffs can generate toxicological consequences often unknown and/or overlooked.

### Pesticide usefulness guidelines

It is difficult to assess the consequences of pesticide use, including the various complex and interdependent environmental factors. Originally, it should be stated at the outset that pesticides undergo the same storage mode followed by a lack of control and evaluation before use for possible denaturing. Thus, the pesticides risks losing their intrinsic values are tremendous. In addition, several pesticides are often used for selective weeding crops such as metolachlor (corn, sunflower, sorghum, peanut, bean, soybean), fluometuron (wheat, barley, corn, rye, oats, rice, sugar cane, cotton), diuron (pear, apple, quince, vegetables) and so on. However, we must be realistic and assert that each harvest type has its specific insect pest targets. And, the pesticide ineffectiveness on some of these crops may deplete their agricultural yield and contribute to the product release into the environment. Moreover, taking into account detection limits, and for a more targeted application, analytical research of pesticide metabolites on a variety of crops has proven the efficacy of the compound's convenience on a one-dimensional monoculture. In sum, we must develop a policy of rational measures relating to the usefulness of pesticides «a pesticide a one-dimensional monoculture» motivated by multidisciplinary lessons drawn from environmental research carried out on pesticide metabolites in the context of the globalization of strategies. Thus, there are still recommendations necessary to be adopted as benchmarks for sustainable agriculture:

- Integration of European directives [1];
- Analytical methods findings accessibility;
- Certification of the effectiveness of the pesticide's usefulness in monocultures;
- Improvement of storage conditions for pesticides;
- Optimization treatment techniques into minimizing the content of pesticide metabolites;
- Utilization of pesticides in adquation with the local cultures according to the climatic conditions.

With the strong integration of pesticides into modern agriculture, European pesticide legislation places more emphasis on risk assessment, source control measures and substitution. However, the substitution principle also obeys the above measures.

## CONCLUSION

This paper has examined some publications related to the analysis of pesticide metabolites in various environmental samples. Somewhat, this review quantifies the metabolites of

each pesticide in its investigative matrix, without forgetting their complexity. It is therefore sustainable that pesticide metabolites are potential environmental contaminants, particularly in the agri-food sector. This document also proposes a policy on the usefulness of pesticides with particular emphasis on some requests made in terms of comments and/or guidelines for improving food safety.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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