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Urea Pesticides

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1. Introduction

Urea herbicides form, together with phenoxy derivatives and triazines, the most important agricultural herbicide group. The urea-derivatives are typical pre-emergence herbicides applied usually as aqueous emulsions to the surface of soil. Almost all of the urea compounds with good herbicidal action are trisubstituted ureas, containing a free imino-hydrogen. According to the receptor theory, this hydrogen plays a role in the formation of the hydrogen bond being significant in the mode of action of ureas. Chemically, the urea type herbicides contain a urea bridge substituted by triazine, benzothiazole, sulfonyl, phenyl, alkyl or other moieties. Besides herbicidal activity, some analogous structures have other biological activity (Lányi&Dinya, 2005).

The general structure of a phenylurea herbicide (PU) is (substituted) phenyl-NH-C(O)-NR₂. The phenyl ring is often substituted with chlorine or bromine atoms, but methoxy, methyl, trifluoromethyl, or 2-propyl substitution is also possible. Most PU are N-dimethyl PU, but a combination of a methyl substituent and another group also occurs (Niessen, 2010). PU are used as selective and non-selective herbicides in substantial amounts, including the use as systemic herbicides to control broadleaf and grassy weeds in cereals and other crops, as total herbicides in urban areas, and as algicides in paints and coatings.

Sulphonylureas (SU) form a group of selective herbicides with R₁-NH-C(O)-NH-SO₂-R₂ as general structure. R₁ and R₂ generally are substituted heterocyclic rings such as 4,6-dimethylpyrimidin-2-yl and 2-(benzoic acid methyl ester) (Niessen, 2010). The mode of action of these herbicides consists of inhibiting acetolactate synthase (ALS) which is a key enzyme in the biosynthesis of branched amino acids (valine, leucine, and isoleucine). SU are low dose herbicides (10 – 40 g a.i. ha⁻¹) used to control broad leaved weeds in cereals exhibiting very low acute and chronic mammalian toxicities (Wang Y. S. et al., 2010).

Benzoylureas (BU), which were introduced in the early '70s, represent a class of insect growth regulators (IGRs) which act on the larval stages of most insects by inhibiting or blocking the synthesis of chitin, a vital and almost indestructible part of the insect exoskeleton during the molting stage; therefore, the failure to successfully cast off the old exoskeleton leads to the eventual death of the larvae. Diflubenzuron is the prototype of all benzoylurea chitin synthesis inhibitor insecticides (Shim et al., 2007).

The specificity of benzoylureas to species whose structural integrity depends upon chitin, their low acute toxicity to mammals along with their high biological activity, make them suitable for inclusion in integrated pest management programs for fruit and vegetables

(Shim et al., 2007). This kind of insecticide suffers a rapid degradation in both soil and water (Zhou et al., 2009). Nevertheless, residues can often reach populations through the food chain causing chronic exposure and long-term toxicity effects. Some studies show that several IGRs may affect nontarget arthropods, such as teflubenzuron and hexaflumuron at concentrations that are probably environmentally relevant (Campiche et al., 2006). Previous studies have shown that extremely low levels of metsulfuron-methyl, a SU herbicide, have phytotoxicity to sensitive crops in crop-rotation systems and have unintended side effects on non-target organisms (Wang H. Z. et al., 2010). Diuron, a PU herbicide, has been shown to cause a drop in photosynthesis in algal communities at concentration of 1.5 $\mu\text{g/L}$ (Ricart et al., 2010). The substituted urea herbicides are used for the control of many annual and perennial weeds, for bush control, and for weed control in irrigation and drainage ditches. Likewise, the benzoylurea insecticides are widely used on a large number of crops. In this chapter, the more relevant contributions of the last 5 years to the current knowledge on several aspects regarding urea pesticides, such as degradation in soil and natural waters, occurrence of residues in food, legislation and analytical determination will be discussed.

2. Degradation studies

Several studies have investigated the degradation pathways of urea pesticides in aqueous solutions and soil. In soil, their persistence is mostly influenced by the rate of chemical and microbial degradation. Degradation is particularly dependent on the soil pH, moisture content and microbiological activity. The ultraviolet (UV) radiation in the sunlight is one of the most powerful forces for pesticide degradation. Studies on the photodegradation of pesticides in both homogenous and heterogeneous systems contribute to elucidate the transformation, mineralization and elimination of these xenobiotics in the different environmental compartments. In a review by Burrows et al. (2002) the photodegradation of pesticides is reviewed, with particular reference to the studies that describe the mechanisms of the processes involved, the nature of reactive intermediates and final products.

The more recent herbicide formulations are designed to offer advantages of the highest selectivity together with the lowest persistence in the environment: SU meet these requirements. But, unfortunately, lower persistence in the environment does not necessarily correspond to lower toxicity, since many herbicides undergo natural degradation reactions in the environment that do not lead to mineralization but to the formation of new species potentially more toxic and stable than the precursors (Bottaro et al., 2008).

The most important pathways of degradation of SU in soil are chemical hydrolysis and microbial degradation, while other dissipation processes such as volatilization and photolysis are relatively insignificant (Saha & Kulshrestha, 2008; Si et al., 2005; Wang Y. S. et al., 2010). SU typical field dissipation half-lives ($t_{1/2}$) are about 1-8 weeks in some cases, but within a few days in the case of some newer compounds. Chemical hydrolysis is pH and temperature dependent: in most cases the degradation is faster in acidic rather than in neutral or in weakly basic conditions, and at high temperature (Wang Y. S. et al., 2010).

Degradation of ethametsulfuron-methyl, a SU, in soils was pH-dependent; calculated $t_{1/2}$ values ranged from 13 to 67 days. Ethametsulfuron-methyl was more persistent in neutral or weakly basic than in acidic soil. Five soil metabolites were isolated and identified by LC-MS/MS analysis. Different authors have shown that soil pH is the most important factor in affecting both sorption behaviour and chemical degradation of metsulfuron-methyl in soil because of its ability to influence the ionization state of the herbicide (Wang H. Z. et al.,

2010). The mineralization rate was negatively correlated with soil pH, organic carbon contents, and clay contents, while it was positively correlated with soil microbial biomass carbon and silt contents. Regression analyses suggested that soil properties did not act separately but in an interactive manner in influencing the overall metsulfuron-methyl mineralization in soils.

The dissipation mechanisms of two SU herbicides, chlorsulfuron and imazosulfuron, were both chemical and biological. Half-life calculation followed the first-order kinetics. The $t_{1/2}$ of chlorsulfuron was 6.8–28.4 days and that of imazosulfuron was 6.4–14.6 days. Persistence is strongly influenced by the temperature and soil pH. Both compounds dissipate faster in a more acidic soil. The two SU changed the soil bacterial composition, and the change was larger with imazosulfuron at 50 mg/kg. The selectivity of survival for bacteria was stronger in more alkaline soil (Wang Y. S. et al., 2010).

In soil, the hydroxylation of the aromatic ring of chlorsulfuron has been reported in the presence of the fungus *Aspergillus niger*. Photolysis of imazosulfuron was reported in aqueous solution under UV light. Chemical cleavage was the main degradation pathway in aerobic conditions, whereas in anaerobic conditions, microbial degradation was the main degradative pathway to demethylate imazosulfuron (Wang Y. S. et al., 2010).

The hydrolysis rate of rimsulfuron was as high as the photolysis rate, and decreased on diminishing the pH values of the solution. Sorption and photolysis reactions of rimsulfuron on silica and clay minerals were also investigated and compared with a natural soil sample. The photochemical degradation of the herbicide was strongly affected by retention phenomena, showing that silica and clay minerals can retain and protect rimsulfuron from photodegradation much more than soil (Bufo et al., 2006). Degradation products of rimsulfuron can leach through sandy soils in relatively high concentrations and could potentially contaminate vulnerable aquatic environments (Rosenbom et al., 2010). Rimsulfuron is moderately persistent to non-persistent in aqueous solutions/soil suspensions under anaerobic/aerobic conditions, with $t_{1/2}$ of 6–40 d in soil. Most of the rimsulfuron and its degradation products are available for either leaching or formation of non-extractable residues (sorption, exclusion/trapping) since mineralisation is negligible.

The kinetics of hydrolytic degradation of sulfosulfuron was investigated to predict the fate of the herbicide in an aqueous environment. The study revealed that the hydrolytic degradation followed first-order kinetics. The degradation was dependent on pH and temperature. Hydrolysis rate was faster in acidic condition ($t_{1/2}$ =9.24 d at pH 4.0) than alkaline environment ($t_{1/2}$ =14.14 d at pH 9.2). Under abiotic conditions, the major degradation mechanism of the compound was the breaking of the sulfonylurea bridge yielding corresponding sulfonamide and aminopyrimidine (Saha & Kulshrestha, 2008).

The UV induced photodegradation of metsulfuron in water has been studied. The mechanism involved hydrolytic cleavage of the sulfonylurea bridge to form the corresponding phenyl sulfonyl carbamic acid and s-triazine, with the carbamic acid subsequently decarboxylating to form a phenyl sulfonamide and a cyclic derivative (Burrows et al., 2002).

BU adsorb readily in soil with little subsequent desorption and, even though its mobility in soil is very low, some BU may be present in surface water after application (Martinez et al., 2007).

Diflubenuron is quickly degraded in the environment mainly by hydrolysis and photodegradation producing as major metabolites: 2,6-difluorobenzamide, 4-chlorophenylurea, 4-chloroacetanilide, 4-chloroaniline and N-methyl-4-chloroaniline, the last three of them classified as mutagens (Rodriguez et al., 1999).

In a review dealing with the degradation of phenylurea herbicides, Sorensen et al. (2003) reported that degradation proceeds mainly through a microbial way with the action of a wide variety of microbial strains.

Transport of pesticides from point of application via sub-surface drains can contribute significantly to contamination of surface waters. Many pesticides (particularly soil-acting herbicides) rely for their activity on a degree of mobility and persistence in soil, but these properties can confer vulnerability to leaching to sub-surface drains (Brown & van Beinum, 2009).

Due to the extensive use of urea pesticides for agricultural and non-agricultural purposes, their residues have been detected in wastewater effluents, surface water and raw drinking water sources, as well as food products, around the world, and have received particular attention because of their toxicity and possible carcinogenic properties. Among them, the highly persistent phenylurea herbicides can be found at concentrations reaching several $\mu\text{g}/\text{L}$ in natural waters. Since their possible activity as carcinogens, the control of the levels of the residues of these compounds in the environment and in crops has an outstanding importance.

3. Legislation

Increasing public concern about health risks from pesticide residues in the diet has led to strict regulation of maximum residue levels (MRLs). Food Safety legislation is not harmonized through the world. However, well-known international bodies, the most representative of which is the *Codex Alimentarius* Commission established by Food and Agriculture Organization (FAO) and World Health Organization (WHO), create risk based food safety standards that are a reference in international trade and a model for countries to use in their legislation. Actually, the *Codex Alimentarius* (2009) set MRLs only for the following ureas: diazinon (0.01 to 5 mg/kg); diflubenzuron (0.01 to 5 mg/kg); novaluron (0.01 to 40 mg/kg) and teflubenzuron (0.05 to 1 mg/kg).

The European Union, as one of the world's largest food importers, exerts a major influence on food safety testing globally and has also strict legislation in this area (Hetherington et al., 2004). Legislation on food at the European Community level dates back to 1976 when Council Directive 76/895/EEC specified MRLs for pesticides (43 active substances) in and on selected fruits and vegetables, 7 of them were urea herbicides (monolinuron, metsulfuron-methyl, thifensulfuron-methyl, triasulfuron, azimsulfuron, chloraxuron and flupyrsulfuron-methyl). Linuron and monolinuron were also included in the so-called "black list" of the 76/464/EEC Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Later, in order to prevent the contamination of groundwater and drinking water, a priority list which considered pesticides used over 50,000 kg per year and their capacity for probable or transient leaching was published; chlorotoluron, diuron, isoproturon and methabenthiazuron were included in this list. The 80/779/EEC Directive on the Quality of Water Intended for Human Consumption stated a maximum admissible concentration of 0.1 $\mu\text{g}/\text{L}$ for individual pesticide and 0.5 $\mu\text{g}/\text{L}$ for the total pesticides, regardless of their toxicity. The regulation (EC) No. 396/2005 made an important step forward in its efforts to ensure food safety in the European Union, as a regulation revising and simplifying the rules pertaining to pesticide residues entered into force. The new rules set harmonised MRLs for pesticides. They ensure food safety for all consumers and allow traders and importers to do

business smoothly as confusion over dealing with 27 lists of national MRLs was eliminated. If a pesticide is not included in any of the above mentioned lists, the default MRL of 0.01 mg/kg applies (Art 18(1b) of Reg. (EC) No 396/2005). Recently, regulation (EC) No 901/2009 has been produced concerning a coordinated multiannual Community control programme for 2010 to 2012 to ensure compliance with MRLs and to assess the consumer exposure to pesticide residues in and on food of plant and animal origin. The Member States shall, during 2010 - 2012 analyse samples for the product/pesticide residue combinations, including the ureas: flufenoxuron, linuron, lufenuron, pencycuron and triflumuron.

4. Analytical methods

Various approaches are described in the literature for detailed analysis of urea pesticides in environmental, biological and food samples. Tables 1-3 summarize the more relevant studies, published in the last five years, concerning the analytical methodologies applied for PU (Table 1), SU (Table 2) and BU (Table 3) determination. Research has been carried out in ureas extraction, separation and specific detection. It is a tremendous challenge to develop sensitive and selective analytical methods that can quantitatively characterize trace levels of residues in the several types of samples. This challenge is most evident in the detection of ureas due to the low dose used, their water solubility and chemical instability. At present, there is still a lack of officially approved methods that would solve the difficulties associated with quantitative isolation of urea pesticides from the various matrices, clean-up of the extract without significant loss of the analyte, separation of all individual pesticides contained in the purified extract, detection of the separated components, unequivocal identification and quantification of the identified compounds.

Sample pretreatment processes are crucial steps to achieve clean-up and effective enrichment of the target analytes before analysis. For solid samples, traditionally, Soxhlet and manual/mechanical shaking have been used for ureas extraction (Buszewski et al., 2006; Cydzik et al., 2007; El Imache et al., 2009; Ghanem et al., 2008; Mou et al., 2008; Scheyer et al., 2005; Tamayo et al., 2005a, b; Tamayo & Martin-Esteban, 2005). On the other hand, for aqueous samples the classical methodology is liquid-liquid extraction (Moros et al., 2005). However, these techniques have inherent disadvantages, for example the large volumes of organic solvents required. They are also time-consuming and involve multistep processes that have always the risk of loss of some analytes. Supercritical-fluid extraction, matrix solid-phase dispersion, pressurized liquid extraction (Bichon et al., 2006), microwave-assisted extraction (Paiga et al., 2008, 2009a; Paiga et al., 2009b) and batch extraction enhanced by sonication (Boti et al., 2007a; Buszewski et al., 2006; De Rossi & Desiderio, 2005) have been developed as alternative techniques to replace classical extraction methods mainly for solid samples. All these methods reduce extraction time and the volumes of solvent required, but some have the disadvantages of high investment and maintenance costs of the instruments (i.e., supercritical-fluid extraction, pressurized liquid extraction, and microwave-assisted extraction). Supercritical-fluid extraction is less frequently used, probably due to a strong dependence of optimal parameters setting on sample composition and analytes, which is the cause of a rather low robustness of supercritical fluid extraction-based procedures. Matrix solid-phase dispersion is relevant for tissue analysis, such as beef fat, catfish muscle or oysters (Bichon et al., 2006). Matrices are blended with C18 or Florisil phases before analyte elution with an adequate solvent. The major drawback of this procedure is the manual preparation which complicates the routine application (Bichon et

al., 2006). Nowadays, microwave-assisted extraction and pressurised liquid extraction are applied successfully for urea residues control in soils (Paiga et al., 2008), vegetables (Paiga et al., 2009a; Paiga et al., 2009b) and in oysters (Bichon et al., 2006a). Low temperatures must be selected due to urea's thermolability. Studies have shown that once optimized, these new extraction techniques are comparably efficient, with similar standard deviations. However, the main drawback is the wide range of co-extracted compounds leading usually to more purification steps.

Solid phase extraction (SPE) is a well-established preconcentration technique that allows both extraction (for liquid samples) and concentration of traces of contaminants using low amounts of solvents. It represents the most often-applied method in environmental and food analysis (Tables 1-3). The popularity of SPE has increased in recent years as it is easily automated and a wide range of phases is available. Octadecylsilica is the largely preferred sorbent over other supports for all the three groups of ureas (Crespo-Corral et al., 2008; Piccirilli et al., 2008; Sa et al., 2007). Moreover new multi-functionalized and selective sorbents are exploited to improve enrichment and clean-up performances (Breton et al., 2006; Carabias-Martinez et al., 2005; Mansilha et al., 2010; Tamayo et al., 2005b; Tamayo & Martin-Esteban, 2005; Zhang et al., 2006).

Molecularly imprinted polymers (MIPs) are synthetic polymers possessing specific cavities designed for a target molecule. By a mechanism of molecular recognition, the MIPs are used as selective tools for the development of various analytical techniques such as SPE. MIPs possess many advantages, for instance, easy preparation, chemical stability and pre-determined selectivity. The enhancement of the selectivity provided by the MIP has been largely described in the literature (Pichon & Chapuis-Hugon, 2008; Pichon & Haupt, 2006). MIPs were developed for SU (Liu et al., 2007) and PU (Breton et al., 2006; Carabias-Martinez et al., 2005; Tamayo et al., 2005b; Tamayo & Martin-Esteban, 2005). They were compared to classical sorbents in order to demonstrate the possibility to obtain cleaner baseline when using the MIP than when using C18 silicas or hydrophobic polymers (Breton et al., 2006; Carabias-Martinez et al., 2005; Tamayo et al., 2005b; Tamayo & Martin-Esteban, 2005). There are more and more applications of MIPs directly to real samples without a preliminary treatment (Bettazzi et al., 2007; Breton et al., 2006; Pichon & Chapuis-Hugon, 2008; Pichon & Haupt, 2006). The selectivity was also demonstrated by spiking the sample with compounds belonging to the same range of polarity as the target analytes; the lack of retention of these compounds on the MIP demonstrates the selectivity of the extraction procedure on MIPs (Pichon & Chapuis-Hugon, 2008; Pichon & Haupt, 2006).

Room temperature ionic liquids (RTILs) containing relatively large asymmetric organic cations and inorganic or organic anions have recently been used as "green solvents" to replace traditional organic solvents for chemical reactions. The application of immobilized ILs in separation and clean-up procedures has recently raised much interest. (Fang et al., 2010) showed that cartridges with ionic liquid-functionalized silica sorbent allow a better simultaneous quantification of 12 SU than the reached with C18 sorbent.

Recently, solid-phase extraction with polystyrene divinylbenzene and multiwalled carbon nanotubes (MWCNTS) as the packed materials were successfully used for enhancing the detection sensitivity of PU (chlortoluron (Zhou et al., 2007); diuron and linuron (Ozhan et al., 2005)) and SU (nicosulfuron, thifensulfuron and metsulfuron-methyl (Zhou et al., 2006)). On the basis of their peculiar electronic, metallic and structural characteristics, they have also been exploited in other fields such as biosensors, field-effect transistors and so on (Zhou et al., 2006).

The need to reduce the overall sample preparation time and the quantities of organic solvents has led to the emergence of several new extraction approaches, including solid-phase microextraction (SPME) (Mughari et al., 2007b; Sagratini et al., 2007), liquid phase microextraction (Zhou et al., 2009) and dispersive liquid-liquid microextraction (Chou et al., 2009; Saraji & Tansazan, 2009). The SPME technique is a solvent-free extraction technique that was successfully coupled to GC and LC (Mughari et al., 2007b; Sagratini et al., 2007) in order to analyze PU in fruit juices and groundwater. In dispersive liquid-liquid microextraction, a water-immiscible organic extractant and a water-miscible dispersive solvent are two key factors to form fine droplets of the extractant, which disperse entirely in the aqueous solution, for extracting analytes (Chou et al., 2009). The cloudy sample solution is then subjected to centrifuge to obtain sedimented organic extractant containing target analytes. Saraji & Tansazan (2009) and Chou et al. (2009) used this technique to isolate and concentrate several PU herbicides from river water samples.

Several polymers have been developed which change their structure in response to surrounding conditions, such as the pH, electric field, and temperature. Poly(*N*-isopropylacrylamide) (PNIPAAm) is one of these. There are considerable and reversible changes in the hydrophilic/hydrophobic properties of PNIPAAm-grafted surfaces in response to a change in temperature. Taking advantage of this characteristic, an LC column packed with PNIPAAm to selectively separate SU herbicides by controlling the external column temperature has been developed (Ayano et al., 2005).

Nowadays, the main analytical alternatives sufficiently sensitive for determining urea residues are gas chromatography (GC) and liquid chromatography (LC). GC is applied for the determination of many organic pollutants, but direct determination of ureas is difficult due to their low volatility and thermal instability (Crespo-Corral et al., 2008). Methods developed by GC usually involved a derivatization procedure with diazomethane or pentafluorobenzyl bromide (Scheyer et al., 2005). The derivative procedure made GC difficult to be a robust tool for monitoring ureas. However, (Crespo-Corral et al., 2008) showed the usefulness of the potassium tert-butoxide/dimethyl sulphoxide/ethyl iodide derivatization reaction to determine simultaneously PU, carbamate and phenoxy acid herbicide residues in natural water samples by GC-MS. They reached limits of detection for PU in the range of 0.12–0.52 ng/L which are ones of the lowest achieved (Table 1).

Methods based on LC coupled with different detectors are the most commonly preferred. Conventional UV, diode array or photodiode array detection have been extensively used in LC for the determination of PU, SU and BU in environmental samples (Zhou et al., 2006). MIPs were tested as stationary phases for PU separation (Tamayo et al., 2005b; Wang et al., 2005) before LC-UV detection.

Fluorescence detection (FLD) has been closely bound to the important development of LC instrumentation as it is generally more sensitive than classical UV absorption and less expensive than MS detection. It represents a very selective detector, overcoming matrix interferences (Mughari et al., 2007b). However, few compounds are fluorescent, although some of them possess the necessary degree of aromaticity and may be converted to fluorescent species by using derivatization methods. Several authors (Mou et al., 2008; Mughari et al., 2007a; Mughari et al., 2007b) studied the application of FLD combined with post-column photochemically induced fluorimetry derivatization to determine PU compounds in groundwater and rice and corn samples.

Amperometric detector has been also coupled with LC for the analysis of PU (Shapovalova et al., 2009).

Matrix	Phenylurea	Pretreatment	Extraction	Clean-up/ Elution	Detection	LOD	Ref.
Air samples	chlortoluron, diuron, isoproturon		Soxhlet with n-hexane/ CH ₂ Cl ₂ (1:1, v/v)		GC-MS/MS after derivatisation with pentafluoro- benzyl- bromide	100-500 µg/L	Scheyer et al., 2005
Corn	fenuron, metoxuron, chlortoluron, isoproturon, metobromuron, linuron	manual shacking with ACN; supernatant was filtered through a 0.45 µm filter	several MIPs conditioned with toluene	MeOH	LC-PAD	not provided	Tamayo et al., 2005b
Corn, potato, pea and carrot	fenuron, metoxuron, chlortoluron, isoproturon, metobromuron, linuron	dried	manual shacking with ACN	MIPs elution with MeOH	LC-UV	not provided	Tamayo et al., 2005a
Corn and rice	fenuron, tebuthiuron, metoxuron, monuron, chlortoluron, fluometuron, isoproturon, diuron, monolinuron, metobromuron, buturon, siduron, linuron, chlorbromuron, neburon	finely ground	mechanical shaker with ACN	Florisil SPE conditioned by sequential washing with acetone/n- hexane (40:60, v/v) and n- hexane.	LC-FLD after UV decomposition and post-column derivatization	0.003- 0.032 mg/kg	Mou et al., 2008
Courgette cucumber, lettuce and peppers	linuron, metobromuron, monolinuron	chopped	microwave- assisted extraction with ACN	filtration through a GF/C and 0.2 µm filters	LC-PAD	7.2-10.1 µg/kg	Paiga et al., 2009a
Drinking water	diuron, fluometuron, linuron, siduron, thidiazuron.		C18 disks, conditioned with MeOH water.	MeOH	LC-MS	0.010- 0.026 µg/L	Li et al., 2006
Fresh and processed Tomato	linuron, metobromuron, monolinuron	chopped	microwave- assisted extraction with ACN	filtration through a GF/C and 0.2 µm filters	LC-PAD and LC-MS	2.0-7.1 µg/kg	Paiga et al., 2009b
Fresh and estuarine waters	chlortoluron, diuron, linuron, metobromuron, metoxuron, monolinuron, monuron, neburon,	pH adjusted to 7; filtered using GF/F glass microfibre filters (0.7 µm pore size)	HLB cartridge conditioned with MeOH and water	MeOH	LC-MS/MS	5-59 ng/L	Mazzella et al., 2009

Fruit juices (orange, strawberry, cherry and apple)	diuron, monuron, monolinuron	Centrifugation and filtration through 0.45 µm nylon membrane	SPME with 50 µm Carbowax/templated resin, 60 µm (PDMS/DVB) and 85 µm polyacrylate		LC-MS and LC-MS/MS	0.005-0.01 mg/kg	Sagrati et al., 2007
Groundwater	monolinuron, diuron, linuron, neburon		SPME with a 60 µm (PDMS/DVB) fiber		LC-FLD after post-column photochemically induced fluorimetry derivatization with a Xenon lamp	0.019-0.031 µg/L	Mughari et al., 2007b
Groundwater	monuron, monolinuron, chlortoluron, diuron, neburon		C18 ethyl acetate followed by water	ethyl acetate	LC-FLD after post-column photochemically induced fluorimetry derivatization with a Xenon lamp	2.8-9.94 ng/L	Mughari et al., 2007a
Natural water samples	monolinuron, diuron, neburon	acidified to pH 2 with 0.1 mol/L HCl and filtered through 0.45 µm nylon membrane	C18 Sep-Pack cartridge conditioned with MeOH and water at pH 2.	of 5% ethanol in DMSO	GC-MS after potassium <i>tert</i> -butoxide/dimethyl sulphoxide/ethyl iodide derivatization	0.12-0.52 ng/L	Crespo-Corral et al., 2008
Natural Waters	diuron	filtered through a 0.45 µm syringe filter			one-shot screen-printed thylakoid membrane-based biosensor	1.3 µg/L	Bettazzi et al., 2007
Natural Waters	diuron		MIP based SPE conditioned with MeOH and water	Elution with MeOH/trifluoroacetic acid (98/2, v/v)	photo synthetic biosensor	0.35 µg/L	Breton et al., 2006
Natural waters and freshwater sediments	diuron, linuron	freeze-dried	Ultrasonic extraction with acetone, MeOH and DCM	Centrifugation and filtration through PTFE membranes (0.22 µm)	LC-DAD	0.6-0.7 µg/kg	Boti et al., 2007a
Natural waters	diuron, linuron		C18 conditioned with DCM: acetone (1:1, v/v)	DCM: acetone (1:1, v/v)	LC-DAD	1.4-5.7 ng/L	Boti et al., 2007b

Oysters	chlortoluron, diuron, isoproturon, linuron,		Pressurised liquid extraction	SPE CN/SiOH cartridge conditioned with cyclohexane SPE combined with LLE	LC-MS/MS	0.1-3.9 µg/kg	Bichon et al., 2006
Pesticide formulations	diuron		manual shaking with ACN		NIR spectrometry	0.08-0.18 mg/kg	Moros et al., 2005
Pure water	monuron, diuron, isoproturon, fenuron, chlortoluron, difenoxuron, metoxuron, neburon, buturon, fluometuron				LC-UV performed with a MIP column	not provided	Wang et al., 2005
River water	tebuthiuron, diuron, fluometuron, siduron, linuron, thidiazuron	filtered through a 0.45-µm nylon membrane filter	dispersive LLME with acetone, CS2 and toluene		LC-PAD	0.01-0.5 µg/L	Saraji & Tansazan, 2009
River water	fenuron, monuron, chlortoluron, isoproturon, diuron, metobromuron, linuron	Oasis HLB cartridges	several MIPs conditioned with ACN and toluene	ACN	LC-DAD	not provided	Carabias- Martinez et al., 2005
Sewage sludge	diuron		horizontal shaker; ethyl acetate- DCM 90:10 (v/v)	glass column with activated Florisil; elution with n- hexane- acetone (90:10 and 50:50 (v/v))	LC-MS/MS	0.4 µg/kg dw	Ghanem et al., 2008
Soil	chlortoluron, isoproturon, diuron, monolinuron, linuron, metobromuron, chlorbromuron, methabenzthiazu ron.		mechanical shaker, fast speeding mixer, and sonicator with MeOH, DCM, ethanol, and acetone	activated silica gel; elution with MeOH/DCM (1:5, v/v)	LC-DAD	0.07 - 0.13 mg/kg	Buszewski et al., 2006
Soil	diuron, linuron	air dried	MeOH in an automated Soxhlet		LC-DAD	1 µg/kg	El Imache et al., 2009

Soils	linuron, metobromuron, monolinuron	air-drying and sieving to a grain size of 2 mm	microwave-assisted extraction with ACN	filtration through a GF/C and 0.2 µm filters	LC-PAD	0.65-2.4 µg/kg	Paiga et al., 2008
Surface waters	chlortoluron, diuron, isoproturon, linuron, metoxuron	pH 2	HLB cartridge conditioned with ultrapure water acidified at pH 2	ACN and DCM (1:1, v/v)	ultra-pressure LC-MS/MS	4-12 ng/L	Gervais et al., 2008
Surface waters	isoproturon	filtered through 0.45-µm cellulose acetate filters; pH adjusted to 7.5, stored at 4 °C.	sol-gel immunosorbent	ACN	LC-MS/MS	5 ng/L	Zhang et al., 2006
Surface waters	chlortoluron, diuron, linuron, metobromuron, monolinuron	filtered through glass fiber filter (0.7 µm)	C18 cartridges activated with MeOH and water	ACN	LC-DAD	0.02-0.04 µg/L	Kotrikla et al., 2006
Surface waters	diuron, isoproturon	Filtration with 0.45 µm pore size cellulose nitrate membrane; pH adjusted to 4	on-line SPE		LC-MS/MS	0.5 ng/L	Stoob et al., 2005
Surface waters	diuron, linuron	filtered through 0.45 µm pore-size cellulosic membranes	C18 and styrene divinylbenzene cartridges (SDB)	DCM for C18 and ACN for SDB	dual-column LC-DAD	0.012-0.018 µg/L	Ozhan et al., 2005
Tap, underground and mineral waters	linuron	filtration	C18 silica gel disk conditioned with ACN and water	ACN	Flow-through photochemically induced fluorescence optosensor	0.13-0.22 mg/L	Piccirilli et al., 2008
Tap water and beetroot juice.	linuron, metoxuron, dicuron	filtration	LLE with ACN		LC-amperometric detection	0.003-0.17 mg/L	Shapovalova et al., 2009
Tap water, ground water, sewage water and snow water	chlortoluron	filtered through a 0.45 µm membrane	SPE multiwalled carbon nanotubes conditioned with MeOH and water	DCM	LC-UV	0.012 µg/L	Zhou et al., 2007

Urine, soil, water, pesticide formulation	fluometuron	soil was mixed with water and shaken	C18 conditioned with MEOH	ACN (10%)	photo-induced chemiluminescence in continuous-flow multi-commutation assembly	0.1 mg/L	Cydzik et al., 2007
Vegetables and vegetable processed food	diuron, isoproturon, linuron, metobromuron	chopped	MeOH or acetone in ultrasonic bath	carbograph cartridge eluted with DCM/MeOH (60:40, v/v)	Reversed phase capillary electrochromatography	not provided	De Rossi & Desiderio, 2005
Vegetable samples	isoproturon, metoxuron, fenuron, linuron, chlortoluron, metobromuron	dried	manual shacking during 10 min with ACN and centrifugation		LC-UV performed with imprinted-stationary phases	not provided	Tamayo & Martin-Esteban, 2005
Water	fluometuron		C18 conditioned with MEOH	ACN (10%)	photo-induced chemiluminescence in continuous-flow multi-commutation assembly	0.1 mg/L	Sa et al., 2007
Water	linuron	pH 6	octadecyl silanized magnetite	ethanol		1.0 µg/L	Katsumata et al., 2007

Table 1. Methods for phenylurea determination.

HLB- hydrophilic-lipophilic balance; ACN-acetonitrile, MeOH- methanol; THF- tetrahydrofuran; DCM- dichloromethane; LLE- liquid liquid extraction; LLME- liquid liquid microextraction; MIPs- molecularly imprinted polymers; PDMS - poly(dimethylsiloxane); DVB - divinylbenzene

Chemiluminescence (CL) is becoming an attractive technique to be used as detection system in LC due to its high sensitivity, wide linear range and simple instrumentation. Despite these advantages, CL has been used less than fluorescence and absorbance for pesticide residue analysis, but has been successfully applied to the determination of some BU insecticides (Galera et al., 2008; Garcia et al., 2007)

Actually, LC combined with mass spectrometry (LC-MS) is widely applied to determine ureas in environmental and food analysis (Table 1-3) mainly due to the high selectivity and sensitivity of the MS-detector, as well as, the possibility of performing reliable identification and confirmation. As regards LC-MS interfacing, atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) are the most widely applied LC-MS ionization techniques (Losito et al., 2006).

Time-of-flight-mass spectrometry (TOF-MS) analysis generates increased resolution of signals on the m/z axis in comparison to other quadrupole mass spectrometers.

Matrix	Sulfonylurea	Pretreatment	Extraction	Clean-up/ Elution	Detection	LOD	Ref
Soil	Thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron, sulfometuron-methyl, rimsulfuron, ethametsulfuron, tribenuronmethyl, bensulfuron-methyl, prosulfuron, pyrazosulfuron, chlorimuron-ethyl and primisulfuron	60 mL of soil-extraction solution, pH adjusted to 4.8	Cart. with ionic liquid-functionalized silica equilibrated with 10mL of DCM-MeOH 95:5 (v/v) and water.	Water / Elution with 15mL of DCM- MeOH 95:5 (v/v).	LC-MS	0.08 - 1.0 µg/g	Fang et al., 2010
		60 mL of soil-extraction solution, pH adjusted to 4.5	Cart. C18 preconditioned with MeOH and water.	MeOH -water (2:8). / Elution with ACN	LC-MS	0.05 - 1.78 µg/kg	
Soil and orange juice	Thifensulfuron-methyl	-	50% ethanol solution	-	Polarography	36.3 µg/L 159 µg/L	Inam et al., 2006
Soil	Cyclosulfamuron	-	-	-	Square wave stripping voltammetry	2.3 µg/L	Sarigul & Inam, 2009
Water						3.1 µg/L	
Soybean	Azimsulfuron and pyrazosulfuron-ethyl	-	ACN	AccuBOND C-18	LC-TOF-MS	1.3 - 9.7 µg/kg	Cui et al., 2007
Water	Thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron, sulfometuron-methyl, rimsulfuron, ethametsulfuron, tribenuronmethyl, bensulfuron-methyl, prosulfuron, pyrazosulfuron, chlorimuron-ethyl and primisulfuron	Filtered through a glass-fiber and pH adjusted to 4.8	Cart. with ionic liquid-functionalized silica equilibrated with DCM - MeOH 95:5 (v/v) and water.	Water/ Elution with DCM - MeOH 95:5 (v/v).	LC-MS	0.012 - 0.142 µg/L	Fang et al., 2010
		Filtered through a glass-fiber and pH adjusted to 4.5	Cart. C18 preconditioned with MeOH followed by water.	5 mL of MeOH -water (2:8). / Elution with 10mL of ACN.	LC-MS	0.013 - 0.175 µg/L	
Water	Amidosulfuron, bensulfuron-methyl, chlorsulfuron, iodosulfuron-methyl, metsulfuron-methyl, nicosulfuron, primisulfuron-methyl, prosulfuron, thifensulfuron-methyl, triasulfuron and triflusulfuron-methyl	-	-	-	LC-MS/MS	< 10 ng/L	Seitz et al., 2006
Water (drinking)	Metsulfuron-methyl	EDTA at 10 g/ L	MIP column washed with CH ₃ CN/H ₂ O (95:5, v/v) and then redistilled water.	ACN -water (10:90, v/v). /Elution with ACN -water (95:5, v/v).	LC-UV	6.0 ng/L	Liu et al., 2007

Water (drinking and paddy field)	Metsulfuron-methyl and bensulfuron methyl	-	Cart. C18 and HLB	-	LC-DAD	0.03 - 0.04 µg/L	Roehrs et al., 2009
Water (pure, tap and river)	Bensulfuron-methyl, flazasulfuron, pyrazosulfuron-ethyl, halosulfuron-methyl, Imazosulfuron	Ascorbic acid sodium salt 0.005% (w/v). River water was filtered through a glass-fiber	N-vinyl-pyrrolidone polymer resin (Oasis HLB Plus Extraction Cart.) equilibrated with MeOH and pure water.	Pure water / Elution with of MeOH.	UV using temperature-responsive chromatography	1 - 4 µg/L	Ayano et al., 2005
Water (surfaces)	Amidosulfuron, azimsulfuron, nicosulfuron, rimsulfuron, thifensulfuron methyl, tribenuron methyl	-	Strata RP-18 cart. conditioned with ACN and water acidified (1.5%, v/v) for acetic acid.	Elution with 1.0mL of an acidified (1.5%, v/v acetic acid) water/ ACN mixture.	LC-UV	< 48.3 ng/L*	Polati et al., 2006
			Strata-X cart. conditioned with ACN and water acidified (2.0%, v/v) for acetic acid.		LC-MS ⁿ	< 26.9 ng/L*	
Water (surface and drinking)	Chlorsulfuron	Filtration through a 0.45 µm membrane. pH adjust to 3.5	C18 disk conditioned with MeOH, ACN and Milli-Q water	Elution with 2 x 3 mL of DCM	LC-UV-DAD	0.035 µg/L	Ozhan et al., 2005
Water (river)	Thifensulfuron, metsulfuron and chlorsulfuron	Filtration through a 0.45 µm membrane	On-line pre-concentration with a Supelguard cart. packed with 5µm, C18 silica-bonded phase.	-	LC-MS	0.012 - 0.026 µg/L	Losito et al., 2006
Water (well, tap, reservoir and seawater)	Nicosulfuron, thifensulfuron and metsulfuron-methyl	pH adjust to 3	Cart. with MWCNTS. Washing with ACN and ultrapure water.	Pure water. / Elution with ACN containing 1% of acetic acid.	LC-UV	0.0059 - 0.0112 µg/L	Zhou et al., 2006

Table 2. Methods for sulfonylurea determination.

ACN-acetonitrile, Cart- Cartridges; MeOH- methanol; DCM-dichloromethane; *LOQ

Furthermore, this enhanced resolving power benefits analyses involving complex matrices. Although LC-TOF-MS has not become a widely used technique for the determination of pesticides, it will probably become as one of the main techniques for the unequivocal identification of contaminants (Cui et al., 2007).

Recently, a wide range of immunoassays and sensors for environmental analytes such as pesticides (including ureas) are being investigated, using various detection systems such as amperometric, capacitive, conductimetric, potentiometric and fluorimetric (Bettazzi et al., 2007; Breton et al., 2006; Cydzik et al., 2007; Piccirilli et al., 2008; Sa et al., 2007). Despite offering a number of advantages, such as low cost, easy to use, often portable, disposable and rapid analyte detection, they are normally restricted to aqueous solutions or solutions

Matrix	Benzoylurea	Pretreatment	Extraction	Clean-up/ Elution	Detection	LOD	Ref
Apple, grape and wine	flufenoxuron (+6 other pesticides)		cyclohexane-DCM (9:1, v/v)	Isolute SPE silica cartridges and elution with THF	HPLC-UV	5 - 20 $\mu\text{g}/\text{kg}$	Likas & Tsiropoulos, 2009
Cucumber	diflubenzuron, flufenoxuron, hexaflumuron, lufenuron and triflumuron	chopped and homogenized	DCM (50 mL + 2 \times 20 mL)	aminopropyl-bonded silica SPE cartridge elution with DCM	HPLC-CL	12 - 180 $\mu\text{g}/\text{kg}$	Garcia et al., 2007
Food (fruit, vegetable, cereals, and animal products)	chorfluazuron, diflubenzuron, flucycloxauron, flufenoxuron, fluometuron, hexaflumuron, lufenuron, teflubenzuron, triflumuron	chopped and homogenized	PLE (5 g of sample blended with diatomaceous earth in a 22 mL extraction cell; ethyl acetate as solvent at 80 °C and 1500 psi; evaporation and reconstitution in 0.5 mL of MeOH)		LC-MS/MS	0.7-3.4 $\mu\text{g}/\text{kg}$	Brutti et al., 2010
Peach juice	diflubenzuron, hexaflumuron, teflubenzuron (+ 2 carbamates)	filtered through 0.45 μm cellulose acetate membrane filter	Floated organic drop microextraction (FDME) with 1-dodecanol; 15 mL sample; 40 °C; NaCl, 30 g/L; pH 4; 420 rpm; 25 min		HPLC-UV	5 - 10 $\mu\text{g}/\text{L}$	Zhou et al., 2009
Tomato	diflubenzuron, triflumuron	chopped and homogenized	QuEChERS	PSA	HPLC-CL	2 - 17 $\mu\text{g}/\text{L}$	Galera et al., 2008
Vegetables and water (river)	diflubenzuron, flufenoxuron, hexaflumuron, lufenuron and triflumuron	400 mL H ₂ O + 100 mL MeOH filtered through a 0.45 μm membrane	DCM (25 mL + 2 \times 20 mL) for vegetable samples Plus C18 SPE cartridges (3 mL) containing 360 mg of the strongly hydrophobic silica-based phase for water samples	Elution with 5 mL of ACN and 5 mL of Cl ₂ CH ₂	LC-MS	0.68 - 1.75 $\mu\text{g}/\text{kg}$ (vegetables) 2.6 - 7.5 ng/L (water)	Martinez et al., 2007

Table 3. Methods for benzoylurea determination.

ACN - acetonitrile; CL - chemiluminescence; DCM - dichloromethane; PLE - pressurized liquid extraction; PSA - primary secondary 2/2 amine; THF - tetrahydrofuran.

containing only small amounts of organic solvents. Although their great potential more research is needed since, in most cases, the LODs obtained are rather high for environmental analysis (Bettazzi et al., 2007; Breton et al., 2006; Piccirilli et al., 2008; Sa et al., 2007). On the other hand, electroanalytical methods offer useful applications in kinetic and equilibria studies. A differential pulse polarographic method for the determination of trace amounts of thifensulfuron-methyl in soil and orange juice was validated and the obtained LODs were 36.3 $\mu\text{g}/\text{L}$ and 159 $\mu\text{g}/\text{L}$ (9.37×10^{-8} and 4.1×10^{-7} mol/L), respectively (Inam et al., 2006).

The square-wave electrochemical mode offered favourable signal-to noise characteristics and was used by Sarigul & Inam (2009) for determination of cyclosulfamuron in tap water and soil achieving LODs of 3.1 µg/L and 2.3 µg/L, respectively.

5. Conclusion

Urea pesticides form, together with phenoxy derivatives and triazines, the most important agricultural pesticide group. Ureas undergo natural degradation reactions in the environment that may lead to mineralization and/or to the formation of new species potentially more toxic and stable than the precursors. Several studies have shown that degradation is mainly dependent on the soil pH, moisture content and microbiological activity. Nevertheless, residues can reach populations through the food chain causing chronic exposure and long-term toxicity effects.

Actually, sensitive and accurate methods are available to meet the needs for compliance of urea MRLs in environmental and food matrices. Methods based on LC are the most commonly preferred, and in particular those using mass spectrometric detection. Limits of detection and recoveries for ureas are compound, matrix and method dependent. The detection limits typically range from ng/L to mg/L.

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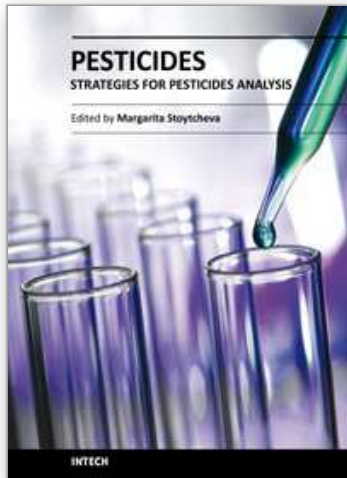
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This book provides recent information on various analytical procedures and techniques, representing strategies for reliability, specificity, selectivity and sensitivity improvements in pesticides analysis. The volume covers three main topics: current trends in sample preparation, selective and sensitive chromatographic detection and determination of pesticide residues in food and environmental samples, and the application of biological (immunoassays-and biosensors-based) methods in pesticides analysis as an alternative to the chromatographic methods for "in situ" and "on line" pesticides quantification. Intended as electronic edition, providing immediate "open access" to its content, the book is easy to follow and will be of interest to professionals involved in pesticides analysis.

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