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# Fate and Determination of Triazine Herbicides in Soil

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## 1. Introduction

Triazine herbicides belong to the group of the most widely used herbicides worldwide. In this review paper, encompassing mostly the relevant research and publications done in the last decade, the fate of triazine herbicides after their introduction in the environment will be discussed. They are transformed in a variety of transformation products after their application, and some of these products are at least as important for the assessment of the overall fate of triazine herbicides and their impact on the environment. Both parent compounds and transformation products will be discussed with particular emphasis on their behaviour in the soil. Analytical methods for the determination of their residues and transformation products in the soil will be reviewed along with the consideration of the impact of the current analytical approaches on our knowledge about the fate of triazines.

## 2. Physico-chemical properties of triazines

Chemically, triazine herbicides are comprised of asymmetrical triazines (triazinones, triazidinones) and symmetrical or 1,3,5-triazines (*s*-triazines): chlorotriazines, methoxytriazines, methylthiotriazines. Structures of the more important triazines and their transformation products (TPs) are shown in Fig. 1.

Physico-chemical properties of compounds relevant for their behaviour in the environment are their polarity (expressed as *n*-octanol-water partitioning coefficient  $K_{ow}$ ), linked to water solubility, moreover their acido-basic properties (expressed as dissociation constant  $K_a$ ) and volatility (usually expressed as vapour pressure). These are listed in Table 1 for the more environmentally important triazines.

## 3. Toxicity and environmental effects of triazines

Triazine herbicides are generally of low acute toxicity for birds and mammals, although certain species show unexpected vulnerability for some of them, e.g. for sheep the fatal dose of simazine has been reported as 500-1400 mg/kg, while  $LD_{50}$  for rats is >5000 mg/kg (Stevens & Sumner, 1991). Acute toxicity data for some compounds are shown in Table 2.

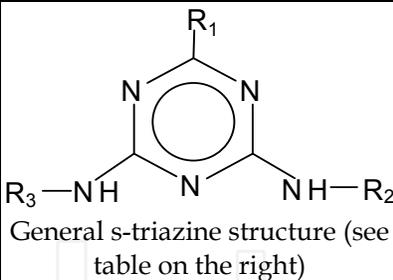
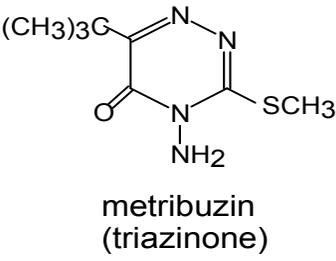
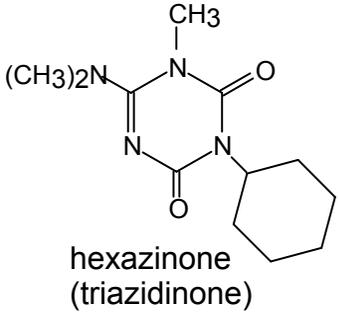
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	
 <p>General s-triazine structure (see table on the right)</p>	Chlorotriazines			
	atrazine	Cl	CH <sub>2</sub> CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
	simazine	Cl	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
	propazine	Cl	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
 <p>metribuzin (triazinone)</p>	Methoxytriazines			
	atratone	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
	prometon	OCH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
	terbumeton	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>
	Methylthiotriazines			
	ametryn	SCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
 <p>hexazinone (triazidinone)</p>	simetryn	SCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
	prometryn	SCH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
	terbutryn	SCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>
	Degradation products			
	desethylatrazine	Cl	H	CH(CH <sub>3</sub> ) <sub>2</sub>
	desisopropylatrazine	Cl	CH <sub>2</sub> CH <sub>3</sub>	H
	desethyl-desisopropylatrazine	Cl	H	H
	hydroxyatrazine	OH	CH <sub>2</sub> CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>

Fig. 1. Structures of some widely used triazines and more important transformation products.

Name	M / g/mol	Water sol. / mg/L	logK <sub>ow</sub>	pK <sub>a</sub>	p / Pa
Atrazine	215.7	33 (20 °C)	2.2-2.7	1.7	4.0·10 <sup>-5</sup> (20 °C)
Simazine	201.7	5 (20-22 °C)	2.2-2.3	1.65	8.1·10 <sup>-7</sup> (20 °C)
Cyanazine	240.7	171 (25 °C)	1.8-2.0	1.85	2.1·10 <sup>-7</sup> (25 °C)
Terbutylazine	229.8	8.5 (20 °C)	2.6-3.0	2.0	1.5·10 <sup>-4</sup> (25 °C)
Atraton	211.3	1800 (20-22 °C)	2.3-2.7	4.2	NA
Terbumeton	225.3	130 (20 °C)	2.7-3.1	4.7	2.5·10 <sup>-5</sup> (25 °C)
Ametryn	227.1	185 (20 °C)	2.7-3.1	4.0	1.1·10 <sup>-4</sup> (20 °C)
Prometryn	241.4	33-48 (20 °C)	3.3	4.1	1.3·10 <sup>-4</sup> (20 °C)
Terbutryn	241.4	25 (20 °C)	3.1-3.7	4.3	2.2·10 <sup>-4</sup> (25 °C)
Desethylatrazine	187.7	3200	1.5	1.65	1.2·10 <sup>-2</sup> (25 °C)
Desisopropylatrazine	173.6	670	1.1-1.2	1.58	NA
Hydroxyatrazine	197.3	5.9	1.4	5.2	1.1·10 <sup>-3</sup> (25 °C)

Table 1. Some relevant physico-chemical parameters for the environmentally important triazines and their transformation products (Kaune et al., 1998; Noble, 1993; Shiu et al., 1990; Tomlin, 1994). NA - not available.

Name	oral LD <sub>50</sub> /mg/kg (rats)	oral LD <sub>50</sub> /mg/kg (other species)
Atrazine	1900-3000	750 (rabbits)
Simazine	>5000	500-1400 (sheep)
Cyanazine	180-380	NA
Terbutylazine	1000-1590	NA
Atraton	1465-2400	NA
Terbumeton	>650	NA
Ametryn	110-1750	NA
Prometryn	3150-5235	NA
Terbutryn	2000-2980	3880 (mice)

Table 2. Acute toxicity data for some triazines (IUPAC Agrochemical Information, 2011; Stevens & Sumner, 1991). NA - not available.

However, the situation is less plausible when assessing the chronic toxicity of triazines. Significant scientific and public controversy has been increasing in the last decade especially regarding the effects of environmentally relevant concentrations of atrazine and its main transformation products desethylatrazine, desisopropylatrazine and hydroxyatrazine, resulting in the 2003 ban of atrazine products in European Union (Sass & Colangelo, 2006). Initial studies reported some carcinogenic, mutagenic and teratogenic effects of triazines only at the dose exceeding the maximal tolerable dose (Stevens & Sumner, 1991). However, environmentally relevant low concentrations of atrazine were later shown to adversely affect the normal male development in amphibians (Tavera-Mendoza et al., 2002), although the evidence is still not conclusive (Solomon et al., 2008). Adverse effects of atrazine were shown also for rats, both on male reproductive tract (Kniewald et al., 2000) and on oestrus in females (Eldridge et al., 1999). The latter is presumably due to the effect on hypothalamic-pituitary-gonadal axis and not on intrinsic estrogenic effect of atrazine (Eldridge et al., 1999; Taketa et al., 2011). Similar effects have been observed for the main atrazine transformation products (Stanko et al., 2010). Besides these endocrine-disrupting properties, atrazine has been shown to affect immune function in mice and the effects persist some time after the exposure (Filipov et al., 2005). Other triazine herbicides are not that extensively covered regarding their chronic toxicity, presumably because they are less widely applied. However, USA Environmental Protection Agency (EPA) concludes that triazines and TPs with chlorine attached to the ring (see Fig. 1) have the same common mechanism of toxicity regarding their endocrine-related developmental, reproductive and carcinogenic effects (Environmental Protection Agency [EPA], 2011).

#### 4. Distribution of triazines in the environmental compartments

After the introduction in the environment, triazines are distributed between the three main environmental compartments, namely gaseous (air), aqueous (ground and surface waters) and solid (soil, sediments). The fourth important compartment interacting with the environment is biota: uptake of triazines into microorganisms and plants, which will be considered separately. Distribution is governed by the physicochemical properties of the compounds (Table 1) and is an ongoing process. There is a dynamic interchange of temporary equilibrium states and re-distribution, influenced by weather conditions, input of materials and various pollutants into the environment etc.

Volatilization of triazines and their long-range atmospheric transport is a poorly researched process. It is supposed that, similar to other semivolatiles, triazines are transported by air masses absorbed on the particulate matter and deposit in cold atmospheric conditions (high mountains, higher geographical latitudes) mainly by wet deposition. Snow is an effective scavenger of particulate matter and associated pollutants from the atmosphere. Triazines have been detected both in snow and rainwater (Polkowska et al., 2000; Usenko et al., 2005).

Triazines are distributed mainly between aqueous and solids compartments. The main processes are partitioning and sorption on solid components, as well as solubilisation in the aqueous compartment followed by leaching into lower solid layers and eventually into groundwater. Living organisms present in both compartments contribute to the transport by uptaking the compounds and returning them mainly as transformation products. The majority of research has been done on atrazine in the last decade of 20th century and is encompassed in a recent review paper (Mudhoo & Garg, 2011). However, atrazine residues in soil have proven to be more persistent than previously expected (Jablonowski et al., 2011) and thus there is an ongoing need for further research on the soil behaviour of this compound (Barton & Karathanasis, 2003; Jablonowski et al., 2011; Kovaivos et al., 2006; Ling et al., 2006). Atrazine is expected to be in its non-ionized form at the environmentally relevant pH values (see Table 1) and for uncharged compounds, it is generally accepted that they are sorbed on organic carbon fraction of the soils/sediments (Mudhoo & Garg, 2011). The main mechanism in operation is partitioning between aqueous and organic carbon phase, predominantly humic substances. Both overall partition coefficient  $K_d$  and partition coefficient for organic carbon  $K_{oc}$  are used to quantitatively express the extent of interaction. The reported values for the latter differ considerably from 25 to 600 L/kg OC (Mudhoo & Garg, 2011), which may reflect the differences in organic matter structure. Humic substances (HS) are heterogeneous and still poorly characterized macromolecules or supramolecular associations (Schaumann, 2006). A number of mechanisms have been proposed for the interaction of atrazine and HS: partitioning resulting from hydrophobic interactions (Lima et al., 2010; Prosen & Zupančič-Kralj, 2000), hydrogen bonding (Prosen & Zupančič-Kralj, 2000), electron transfer, charge transfer (Mudhoo & Garg, 2011). While atrazine is sorbed primarily onto soil organic matter (SOM), presence or addition of dissolved organic matter (DOM) may enhance the sorption at lower DOM concentration, but decrease it at higher DOM concentration (Ling et al., 2006; Mudhoo & Garg, 2011), which is a consequence of increased solubilisation of atrazine in the aqueous fraction with DOM.

Atrazine is sorbed on some mineral components of soils/sediments as well: aluminium-saturated smectite (Mudhoo & Garg, 2011), silicagel (Kovaivos et al., 2006) and Florisil ( $\text{SiO}_2 + \text{MgO}$ ) (Prosen et al., 2007), but not calcite or alumina (Kovaivos et al., 2006; Prosen et al., 2007). The proposed mechanism is electrostatic or electron-transfer interaction of atrazine with silanol groups (Kovaivos et al., 2006; Prosen et al., 2007). Besides soil organic matter (SOM) content and presence of adsorbing minerals, other parameters govern the extent of atrazine sorption to environmental solids: pH, ionic strength, surface area, particle and pore size, presence of other compounds, especially surfactants (J.F. Lee et al., 2004), temperature (Mudhoo & Garg, 2011). Contact time is another important factor. Desorption hysteresis has been observed for longer contact times (Drori et al., 2005; Prosen & Zupančič-Kralj, 2000). The currently accepted model explaining the effect of contact time, nonlinear sorption kinetics, desorption hysteresis and conditioning effect of sorbate on sorbent affinity is the dual-mode sorption process of sorbate in the interchangeable rubbery and glassy state of polymeric SOM material (Schaumann, 2006).

Leaching of atrazine into lower layers of the soil and eventually groundwater is generally affected by the same parameters as sorption. The mobility of compound in soil/sediment is expressed by retardation factor  $R_f$  as determined by column lysimeters (Weber et al., 2007). For atrazine,  $R_f$  has been shown to be inversely proportional to SOM content and related to pH and soil leaching potential (Weber et al., 2007). Presence of more polar SOM with higher ratio of polar functional groups, e.g. from the manure, has been postulated to result in stronger hydrogen bonding of atrazine and reduced desorption and mobility (Lima et al., 2010), although completely opposite results, i.e. stronger bonding to more hydrophobic humic matter, were reported elsewhere (Celano et al., 2008). Desorption and leaching is enhanced by the presence of surfactants, especially anionic (J.F. Lee et al., 2004; Ying et al., 2005), as well as dissolved organic matter (DOM) (Ling et al., 2006). However, great caution is needed when extrapolating results from these studies to predict the dissipation behaviour of atrazine, as gross underestimations have been observed (Jablonowski et al., 2011).

Considerably less information about sorption and mobility in soil and sediments is available for other triazines or transformation products. Chlorotriazines are generally assumed to behave similarly to atrazine and this has been confirmed in some experiments for simazine (Mudhoo & Garg, 2011; Ying et al., 2005) or terbutylazine for humic organic matter (Celano et al., 2008). The latter is a less polar compared to atrazine and has been shown to exhibit greater extent of sorption on HS (Erny et al., 2011; Prosen & Zupančič-Kralj, 2000). In comparison of methylthio-, methoxy- and chlorotriazine sorption on sediments and mineral soil components, sorption intensity was related to the basicity ( $pK_a$ ) and water solubility of compounds, but not their  $\log K_{ow}$  (Prosen et al., 2007; Stipičević et al., 2009) - Fig. 2. Dealkylated triazine transformation products are weakly sorbed on humic substances compared to parent compounds (Erny et al., 2011), while hydroxyatrazine, a dechlorinated atrazine TP, is extensively sorbed on mineral components of the soil/sediment (Stipičević et al., 2009).

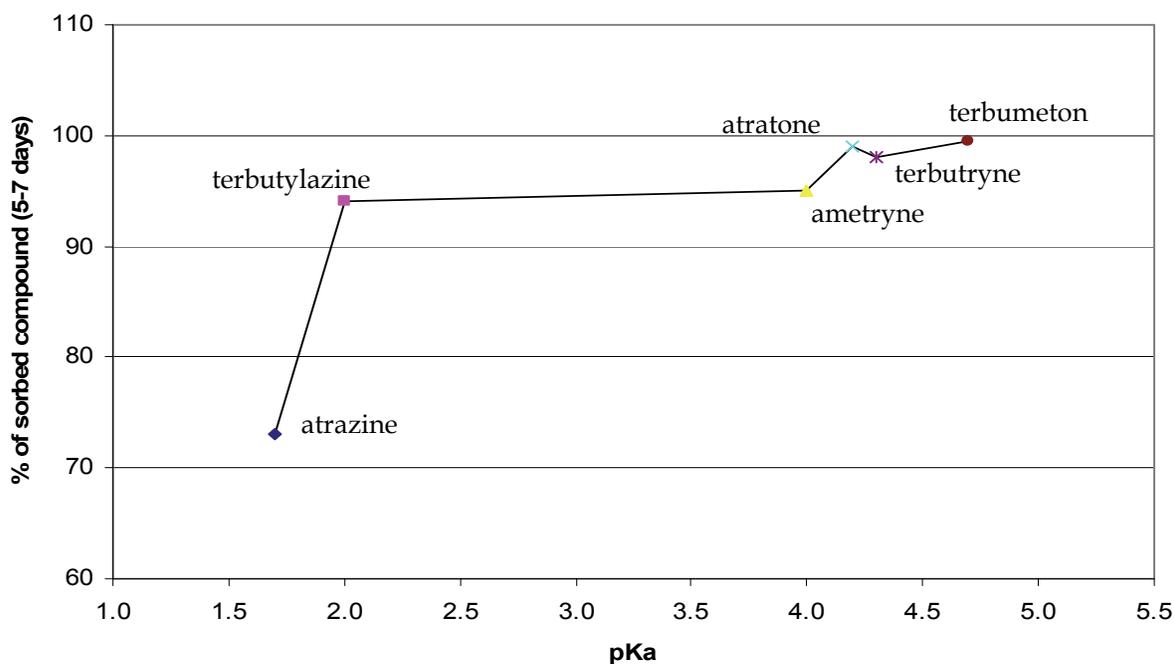


Fig. 2. Relation between  $pK_a$  and % of sorbed compounds after 5-7 days of batch equilibrium experiment on Florisil ( $SiO_2$ ,  $MgO$ ). Adapted after Prosen et al. (2007).

Knowledge of sorption/desorption behaviour of triazines is frequently applied in bioremediation either to enhance their leaching or to stabilise the residues in the contaminated sites (Delgado-Moreno et al., 2010; Jones et al., 2011; J.F. Lee et al., 2004; Lima et al., 2010; Mudhoo & Garg, 2011; Ying et al., 2005).

## 5. Triazine degradation and uptake in the soil

The sorption behaviour of triazines in soil directly influences their bioavailability to soil microorganisms and plants (Mudhoo & Garg, 2011), leading to their uptake and biodegradation. Numerous studies are available for atrazine as the most widely applied and apparently also persistent triazine in the soil (Jablonowski et al., 2011). Plant uptake of triazines from the contaminated soils is extensively studied as a means for bioremediation. The C4-metabolism plants show the greatest resistance to triazines and detoxify them by hydrolysis. Examples of plants shown to be useful in degrading atrazine in their rhizosphere are *Polygonum lapathifolium*, *Panicum dichotomiflorum* (Mudhoo & Garg, 2011), *Pennisetum clandestinum* (Popov & Cornish, 2006; Singh et al., 2004).

Ongoing research in the soil microorganisms capable of utilizing triazines as their energy source has resulted in an extensive array of isolated strains: *Acinetobacter* sp., *Cytophaga* sp., *Pseudomonas* sp., *Ralstonia* sp., *Agrobacterium* sp. (Mudhoo & Garg, 2011), *Klebsiella* sp. and *Comamonas* sp. (Yang et al., 2010), *Nocardioides* sp. and *Arthrobacter* sp. (Vibber et al., 2007). Most of them are capable of extensive mineralization of triazines (Mudhoo & Garg, 2011; Yang et al., 2010) and have a limited access even to aged herbicide residues in the soil (Jablonowski et al., 2008; Mudhoo & Garg, 2011). The species most often used for triazine degradation is *Pseudomonas* sp., its efficacy has been shown to be influenced by citrate addition (Jablonowski et al., 2008), soil humidity (Ngigi et al., 2011) and microorganism adsorption on simulated soil particle aggregates (Alekseeva et al., 2011). Green algae and diatoms (Mudhoo & Garg, 2011), as well as cyanobacteria (Gonzalez-Barreiro et al., 2006) are also capable of atrazine uptake and are thus a valuable option for the bioremediation of the contaminated waters. Certain fungal species able to grow on atrazine-contaminated soils and capable of its uptake have been identified as well (Mudhoo & Garg, 2011).

Compared to biotic degradation by microorganisms and higher plants, abiotic degradation of triazines in soils is a minor dissipation route. Humic substances at low pH catalyse the hydrolysis of atrazine and its chlorinated transformation products to their hydroxy analogues (Prosen & Zupančič-Kralj, 2005). Photolysis of atrazine under solar irradiation and in the presence of humic substances was found to be negligible (Prosen & Zupančič-Kralj, 2005); however, simazine and terbutylazine were found to dissipate faster under solar irradiation of the soil (Navarro et al., 2009). Photolytic transformation and eventual mineralization is enhanced by using a suitable photocatalytic agent, e.g. TiO<sub>2</sub>, which holds a potential for clean-up of contaminated sites (Konstantinou & Albanis, 2003).

## 6. Analytical approaches and cautions for triazine determination in soil

Triazine determination data for soil and other solid environmental samples are used to estimate the extent of the site pollution and potential toxicity (Jablonowski et al., 2011). However, determination of triazines and their TPs in solid samples is prone to many problems, as schematically depicted in Fig. 3.

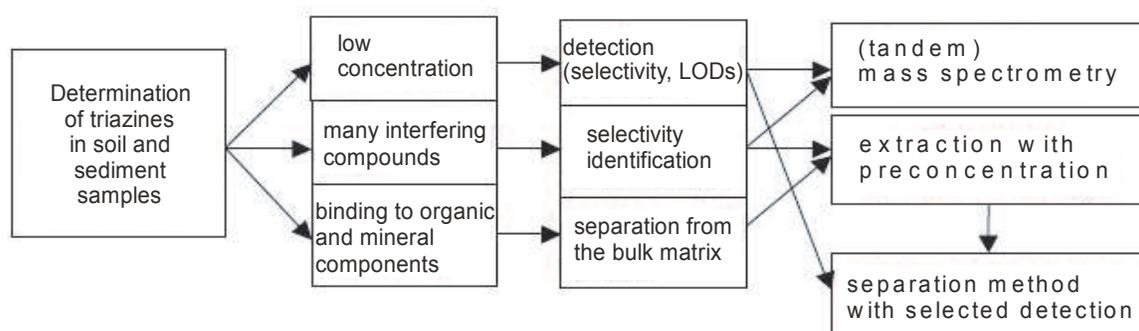


Fig. 3. Schematic representation of the problems and solutions for triazine determination in solid environmental samples.

Technique	Principle	Advantages	Disadvantages
Soxhlet Extraction (SE)	continuous percolation of organic solvent	- recoveries not dependent on sample type - cheap	- time-consuming - high consumption of organic solvents - extracts have to be concentrated
Ultrasonication Extraction (USE)	mixing, desorption of analytes from sample components	- recoveries not dependent on sample type - cheap	- moderately time-consuming - high consumption of organic solvents - work-intensive
Supercritical Fluid Extraction (SFE)	supercritical fluid of low viscosity better penetrates the sample	- fast method - solvent CO <sub>2</sub> non-toxic, environmentally acceptable	- limited sample amount - recoveries depend on sample type - high initial cost
Microwave-Assisted Solvent Extr. (MASE)	microwave- assisted desorption of analytes and sample components	- fast method - low consumption of organic solvents - additional regulation parameters	- polar solvents only - non-selective - extensive extract clean-up needed - high initial cost
Pressurised Liquid Extraction (PLE) / Accelerated Solvent Extr. (ASE)	enhanced extraction efficiency of analytes due to solvents at high temperature and pressure (liquids above boiling point)	- fast method - low consumption of organic solvents	- non-selective - extensive extract clean-up needed - high initial cost

Table 3. Common extraction techniques for triazines from the solid environmental samples (Andreu & Pico, 2004; Camel, 2000; Lesueur et al., 2008; Lopez-Avila, 1999).

The analytical procedure usually comprises of a suitable extraction technique (Table 3), preferably enabling preconcentration as well, possibly a clean-up step, and an appropriate determination technique (Andreu & Pico, 2004; Camel, 2000; Lesueur et al., 2008; Lopez-Avila, 1999). The first dilemma encountered is whether to use an exhaustive extraction technique or a more mild one. Extraction techniques regarded as exhaustive under most conditions are Soxhlet's, MASE and PLE (Camel, 2000). There is a high probability that even triazines bound to soil components would be extracted, although this may depend on the type of compound (Kovačić et al., 2004). However, most of the unwanted organic compounds from the sample would be transferred to extract as well, and these interferences have to be selectively removed prior to analysis by an appropriate clean-up technique. The key word in this case is selectivity, as the clean-up may otherwise lead to significant loss of analytes as well. A selection of frequently applied clean-up techniques is listed in Table 4. In the second case, i.e. by applying a mild extraction technique (0.01 M CaCl<sub>2</sub> solution or aqueous methanol), the obtained extract would better reflect the actual fraction of the triazines and TPs available to plants and microorganisms (Regitano et al., 2006) and could thus be more useful for the actual assessment of the residual toxicity of triazines (Jablonowski et al., 2008; Jablonowski et al., 2011).

Technique	Principle	Advantages	Disadvantages	Variants and improvements
Liquid-Liquid Extraction (LLE)	partitioning between two immiscible solvents	- high recoveries - broad choice of solvents	- time-consuming - automatization difficult - environmentally problematic	supported liquid membrane extr. (SLME) liquid-phase microextr. (LPME) / single-drop microextraction
Solid Phase Extraction (SPE)	adsorption / partitioning between aqueous and solid phase, followed by desorption with organic solvents	- high recoveries - low solvent consumption - automatization possible (on-line)	- lower selectivity - narrower choice of sorbents	restricted access material (RAM) molecularly imprinted polymer (MIP) immunosorbents multi-walled nanotubes
Solid Phase Micro-extraction (SPME)	partitioning between aqueous and non-polar phase on fibre, follow by thermal or solvent desorption	- fast - solventless - automatization possible	- mainly for volatile compounds - poor repeatability - non-exhaustive (low recoveries)	in-tube SPME

Table 4. Common clean-up techniques for triazines in soil/sediment extracts (Andreu & Pico, 2004; Hylton & Mitra, 2007; Jonsson & Mathiasson, 2000; Masque et al., 2001; Min et al., 2008; Psillakis & Kalogerakis, 2002; Stalikas et al., 2002).

Determination of triazines in the extracts after extraction and clean-up is usually accomplished using either gas (GC) or liquid chromatography (HPLC) (Andreu & Pico, 2004). Both techniques can be coupled with mass spectrometry, enabling simultaneous confirmation of compound identity (Andreu & Pico, 2004; Lesueur et al., 2008; Min et al., 2008; Tsang et al., 2009; Usenko et al., 2005). Other detectors frequently used in triazine analysis are spectrophotometric, preferably diode-array detector for HPLC (Andreu & Pico, 2004; Kovačić et al., 2004; Prosen et al., 2004), and nitrogen-phosphorous detector for GC (Andreu & Pico, 2004; Stalikas et al., 2002).

Besides chromatography, other analytical techniques are seldom applied to triazine determination, although they may offer some significant advantages: electromigration techniques, e.g. micellar electrokinetic chromatography (Lima et al., 2009; Prosen et al., 2004); voltammetry (De Souza et al., 2007). Biosensors and bioassays are used for preliminary screening of samples or sample extracts, but because of their cross-reactivity the samples with analyte content above the cut-off value should be re-analysed by a more specific analytical technique. The most widely applied is antibody-based ELISA, but some innovative approaches have been developed, e.g. sensors based on photosystem-II inhibition from plant photosynthetic membranes (Bengtson Nash et al., 2005; Varsamis et al., 2008).

Analytical determination of triazines in solid samples, although often seen as a routine procedure, is prone to many errors. Starting with sampling, the sample taken for analysis should be representative of that part of environment for which the information about pollutant concentration should be obtained. To achieve this goal, an appropriate number of samples, as well as time and site of sampling should be considered. Preservation of samples during the transport and storage is important as well and should be carefully selected (Kebbekus & Mitra, 1998). An example is the need to completely dechlorinate drinking water to prevent rapid degradation of triazines (Smith et al., 2008). Next step, namely extraction with clean-up, is again critical due to the possibility of significant analyte losses because of improper sample preparation conditions. These should be optimised and tested for every analyte. The choice between exhaustive and milder extraction techniques has already been mentioned, but mild conditions are also needed to avoid thermal degradation. Most triazines and their TPs are thermally stable, but not all (Tsang et al., 2009). Another caveat with extraction is the significant difference in analyte binding and thus extraction recoveries between freshly-spiked blank samples and real-life samples containing the so-called »aged residues«. Various authors have proposed to reproduce aging under environmental conditions by leaving spiked blank samples at room temperature for anything between 3 days and 2 years (Andreu & Pico, 2004). However, simulation may not necessarily yield equivalent results to field conditions (Louchart & Voltz, 2007). Finally, determination technique is important in terms of selectivity, limits of detection and reliable quantification. To achieve the latter, standard solutions for the calibration should always match the actual matrix as close as possible to avoid the significant matrix effects seen with some types of detectors (Kovačić et al., 2004), especially with electropray interface for LC-MS.

## **7. Elucidation of triazine fate in the soil as influenced by analytical determination**

As already explored in subchapter 4 of this review, we are mainly concerned with triazine sorption, desorption, leaching and plant/microorganism uptake when dealing with triazine

fate in the soil. Sorption in its broadest sense (i.e. partitioning, non-covalent and covalent binding) is usually evaluated by sorption isotherms conforming to various theoretical models: Freundlich, Langmuir, Polanyi-Dubinin-Manes, etc. (Aboul-Kasim & Simoneit, 2001; Kleineidam et al., 2002). The most frequently used method to obtain the experimental data for isotherm construction remains the batch equilibrium method (Celano et al., 2008; Kleineidam et al., 2002; Konda et al., 2002; Kovaivos et al., 2006; Lima et al., 2009; Ling et al., 2006; Stipičević et al., 2009). Other approaches are by chromatographic estimation (Bermudez-Saldana et al., 2006) or indirectly by structural descriptors (Schüürmann et al., 2006). In batch equilibrium method, several variables may influence the process of sorption and have to be carefully optimised: organic solvent content, ionic strength and pH, solid/solution ratio, sorption time (Celano et al., 2008; Kleineidam et al., 2002; Kovaivos et al., 2006; Prosen & Zupančič-Kralj, 2000; Prosen et al., 2007). After the equilibrium is reached, the solution has to be separated from the sorbent either by centrifugation or filtration (Kleineidam et al., 2002). By using the latter, another potential source of error is introduced as more hydrophobic compounds may bind to certain types of filters.

The equilibrium concentration of the pollutant in the solution after the separation is determined by any of the analytical methods mentioned in subchapter 6. Preferably, it should be performed without previous extraction as this introduces another equilibrium and another possible source of error. Thus, direct HPLC (Celano et al., 2008; Prosen & Zupančič-Kralj, 2000) or electromigration techniques (Erny et al., 2011; Lima et al., 2009) are the methods of choice. If radiolabelled compounds are used, their equilibrium concentration can be measured by radioactivity measurement (Jablonowski et al., 2008). A different approach is to determine the free concentration directly in a multi-phase system by a non-exhaustive solid-phase microextraction and subsequent GC analysis (Heringa & Hermens, 2003; S. Lee et al., 2003; Prosen et al., 2007). The depletion of the compounds from the solution is considered to be negligible, thus giving the opportunity to measure the true equilibrium concentration in the solution (Heringa & Hermens, 2003). Distribution coefficients  $K_d$  obtained by SPME-GC determination of equilibrium concentrations after the sorption experiment have been reported to be significantly different compared to those obtained by other determination methods (S. Lee et al., 2003).

As well as for sorption/desorption, the understanding of the leaching behaviour of triazines is significantly influenced by the determination method. The usual approach is to evaluate the mobility of the compound in soil columns by lysimeters (Jablonowski et al., 2011; Weber et al., 2007), but experiments should be conducted under the appropriate time-scale to avoid gross underestimations (Jablonowski et al., 2011). A different approach is the use of ceramic suction cups, but these are also prone to errors due to ageing effects (Domange et al., 2004).

## 8. Conclusions

This review attempts to cover a vast subject of triazine behaviour in the environment, especially soil, as well as their analytical determination in the same. Special attention was given to the various problems encountered in both. However, the broadness of the subject prevents its detailed evaluation; the interested reader can find more information in other excellent reviews that focus more on triazine behaviour in solid environmental compartment (Jablonowski et al., 2011; Mudhoo & Garg, 2011), their degradation and elimination (Konstantinou & Albanis, 2003) or the applied analytical methods (Andreu &

Pico, 2004; Camel, 2000; Hylton & Mitra, 2007; Jonsson & Mathiasson, 2000; Lopez-Avila, 1999; Masque et al., 2001; Psillakis & Kalogerakis, 2002).

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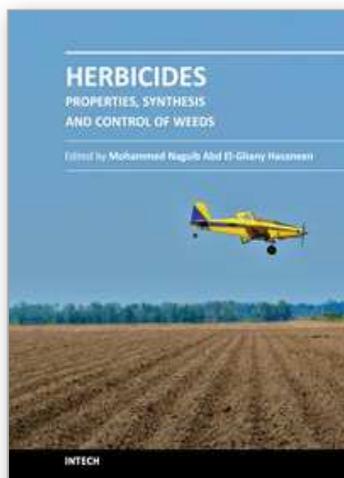
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## **Herbicides - Properties, Synthesis and Control of Weeds**

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This book is divided into two sections namely: synthesis and properties of herbicides and herbicidal control of weeds. Chapters 1 to 11 deal with the study of different synthetic pathways of certain herbicides and the physical and chemical properties of other synthesized herbicides. The other 14 chapters (12-25) discussed the different methods by which each herbicide controls specific weed population. The overall purpose of the book, is to show properties and characterization of herbicides, the physical and chemical properties of selected types of herbicides, and the influence of certain herbicides on soil physical and chemical properties on microflora. In addition, an evaluation of the degree of contamination of either soils and/or crops by herbicides is discussed alongside an investigation into the performance and photochemistry of herbicides and the fate of excess herbicides in soils and field crops.

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