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Review of leaching characteristics of triazines and their degradation products

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Summary. - Only few data have been published on the environmental impact of pesticide degradation products on soil and groundwater. It is known that some of the degradation products of triazines, particularly those formed from N-dealkylation reactions, can be phytotoxic and more mobile than their parent compounds. In some cases it has been shown that they are present at even higher concentrations than the latter. Yet, their impact on groundwater quality is unknown since information on both environmental levels and chemiodynamic parameters are generally lacking. The conclusions of this work are that many triazine degradation products may pose a significant hazard to the quality of groundwater and that there is a need to promote and extend the production of experimental data on this topic.

Key words: herbicides, triazines, groundwater pollution, mobility, degradation.

Riassunto *(Rassegna delle caratteristiche di lisciviazione delle triazine e dei loro prodotti di degradazione)*. - Sono relativamente pochi i dati disponibili sull'impatto ambientale dei prodotti di degradazione dei pesticidi sul suolo e sulle falde acquifere. Le triazine sono erbicidi dotati in genere di elevato potenziale di lisciviazione. Alcuni dei loro prodotti di degradazione, in particolare quelli dovuti a reazioni biotiche di N-dealchilazione, possono mantenere le proprietà fitotossiche, essere più mobili dei pesticidi dai quali derivano e rispetto a questi ritrovarsi nelle falde idriche a concentrazioni anche più elevate. Sfortunatamente l'analisi del significato ambientale di questi prodotti è molto limitata in quanto sono spesso carenti sia i dati sui loro livelli ambientali che quelli sui parametri chemiodinamici. Sulla base del presente lavoro si ritiene di considerevole utilità sviluppare questa problematica con adeguate attività sperimentali.

Parole chiave: erbicidi, triazine, inquinamento, acque sotterranee, mobilità, degradazione.

Introduction

A lot of data have been produced on the environmental and soil behaviour of pesticides [1, 2] as well as on their presence in drinking water supplies [3-5]. For pesticides for which these data are lacking, it is possible to roughly predict their leaching potential on the basis of their chemiodynamic parameters, which are available for a large number of products.

However, little is known about the degradation products of pesticides. Indeed, only few data appear to be available concerning their presence in groundwater, their formation and degradation in soils as well as their chemiodynamic parameters.

Yet, in various studies it has been reported that compared to their parent compounds, these degradation products being generally more polar are also more mobile [6, 7], can keep or enhance their phytotoxicity [8-10], and can be present in groundwaters at higher levels [6, 11, 12].

The aim of this paper is to describe the most relevant processes involved in the formation of the degradation products from most of the triazine herbicides, and their behaviour in soil.

Factors affecting degradation processes of herbicides in soil

The degradation of herbicides is generally a complex process which involves abiotic and/or biotic reactions. These latter can occur under aerobic or anaerobic conditions. Therefore, many factors can influence this process.

Abiotic reactions include essentially hydrolysis, oxidation and photodegradation. The main environmental factors that can influence the rate of abiotic hydrolysis of herbicides are temperature, pH, nature and moisture of soils.

Abiotic hydrolysis of triazines is enhanced by increased temperature [13].

pH of soils can influence the hydrolysis reactions of triazines indirectly, by modifying the adsorption process and so the availability of molecules, and directly through two different mechanisms of reaction. In basic or neutral conditions, the hydrolysis of some s-triazines appears to be due to a nucleophylic substitution of chlorine with the hydroxyl group. In acid condition, hydrolysis appears to be a consequence of protonization of the triazine nitrogen [14].

Hydrolysis reactions of chloro-triazines can be influenced by the clay composition of the soil, as it can exert a strong electrostatic attraction on the water giving rise to an increase of local acidity [15, 16].

Oxidation reactions are influenced by the oxygen content as well as the organic and mineral composition of soils. Humic acids can also contain free-radicals which can act as oxidative agents [16, 17] and some metals such as iron, manganese and cobalt, can promote oxidation reactions [16].

Photodegradation of pesticides is essentially due to reactions of hydrolysis, dehalogenation, oxidation, isomerization and polymerization which are activated by light energy [18]. Under normal environmental conditions photodegradation does not appear to be a significant degradation process for triazines which absorb at a wavelenght of about 220 nm [19]. Photodegradation can also be promoted by the presence of photosensitizers, which are mediators for the transport of photochemical energy or formation of free-radicals [16, 18].

The processes of biotic degradation of herbicides involve many enzymatic reactions catalyzed by microorganisms. These reactions are influenced by environmental conditions (i.e., temperature and moisture), nature of soils (i.e., pH, amounts of oxygen, organic matter, clay) and agronomic conditions (i.e., addition and nature of manure).

Temperature can influence the biotic reactions either directly, increasing the rate of the reactions within a limited range, or indirectly, influencing the amount of the pesticide adsorbed [20]. Indeed, it is known that the degradation of atrazine is faster in southern areas and summer months [19]. DT_{50} *(*)* for atrazine of 37-64 and 125 days have been reported in summer and winter seasons, respectively [21]. An increase of 10 °C of the soil temperature in the range from 10 to 30 °C doubles the rate of atrazine degradation [22]. An increase of the soil temperature from 8.5 to 25 °C causes a seven fold increase of the degradation rate of simazine [23]. A reduction of the soil temperature from 30 to 5 °C has been associated with an increase of the simazine DT_{50} from 29 to 209 days [24].

The available data on various triazines show that their persistence decreases with the increase of the soil moisture [25, 26]. For instance, an increase from 40 to 80% of the soil moisture has been associated with a sixteen fold increase of CO_2 production from the applied atrazine [27].

The role of soil pH on microbial activity is not well understood. Nevertheless, while in some studies a relative influence of pH variation on persistence of some triazines has been observed [28], this influence has not been confirmed in other studies [29].

Oxygen content influences the rate of microbial reactions and their typology, determining anaerobic or aerobic conditions. Biodegradation of some triazines can occur in an anaerobic environment [30, 31], but aerobic reactions appear to play a far more important role [7].

The organic matter content of a soil from one hand promotes microbial reactions [22] but on the other hand causes a major adsorption of herbicides so decreasing their availability as substrates for these reactions [32].

The degradation of an herbicide by soil bacteria is more rapid if the substance has been already applied to the soil. Indeed, when an herbicide is applied for the first time on a soil there is a period of time in which the herbicide is not degraded because of the absence of bacteria able to metabolize that compound (lag phase); in the following applications the lag phase can be consistently reduced as a consequence of the selection of appropriate bacterial strains or the induction of enzymes which catalyze these reactions [33].

Chloro-s-triazines: general characteristics

Chloro-s-triazines are herbicides characterized by the presence in an heterocyclic ring, in which the three nitrogens are in a symmetric disposition, of a chlorine and of two N-alkylated substituents.

As is shown in Table 1, on the basis of the sales of herbicides in Italy in 1988, chloro-s-triazines turned out to be the most important group among the triazines.

Chloro-s-triazines are generally characterized by relatively high values of water solubility and DT_{50} while they have low values of pKa and Koc *(**)* (Tables 2-4). These properties can be considered as indexes of their tendency to leach.

The main degradation reactions in soil for chloro-s-triazines are hydrolysis and N-dealkylation.

Hydrolysis of these herbicides is considered to be substantially an abiotic process [34]. Nevertheless, biotic hydrolysis of atrazine and of some chloro-s-triazine degradation products have been reported [35-37].

N-dealkylation is an important enzymatic reaction in the microbial degradation of chloro-s-triazines [31]. Some of the degradation products of this reaction have a phytotoxic action like that of or even higher than their parent compounds [8, 9].

The ring of s-triazines is particularly resistant to cleavage [22, 38].

Chloro-s-triazines have been detected in many cases in groundwater, while only a few data are available on the frequency or presence of their degradation products, as is reported below.

(*) DT_{50} is the time required for the applied concentration to decrease 50% from its initial value.

(**) Koc is the soil-water partition coefficient normalized to soil organic carbon.

Table 1. - Sale of triazine herbicides in Italy in 1988 *(a)*

Herbicide	**Class**	**kg or l**
Atrazine	chloro-s-triazine	633,852
Metamitron	a-triazinone	263,864
Simazine	chloro-s-triazine	239,471
Terbuthylazine	chloro-s-triazine	225,392
Cyanazine	chloro-s-triazine	24,769
Terbumeton	methoxy-s-triazine	18,697
Metribuzin	methylthio-a-triazine	15,677
Terbutryn	methylthio-s-triazine	15,531
Prometryn	methylthio-s-triazine	10,630
Hexazinone	s-triazinone	8,431
Ametryne	methylthio-s-triazine	6,135
Secbumeton	methoxy-s-triazine	5,332
Methoprotryne	methylthio-s-triazine	791
Propazine	chloro-s-triazine	0
Total triazines		1,468,572
Total herbicides sold		10,801,472

(a) Data from the Information System of the Italian Ministry of Health.

Table 2. - Some chemiodynamic parameters of triazine herbicides [39]

Herbicide (mg/l)	**Water solubility**	**Kow**	**pKa**
Ametryne	185,000 (20 °C)	676	4.1
Atrazine	30 (20 °C)	219	1.7
Cyanazine	171 (25 °C)		
Hexazinone	33,000 (25 °C)		
Metamitron	1700 (20 °C)	6.8	
Methoprotryne	320 (20 °C)		4.0
Metribuzin	1050 (20 °C)	40	
Prometryn	33 (20 °C)	2190	4.1
Propazine	5 (20 °C)		1.7
Secbumeton	600 (20 °C) [106]		4.4 [106]
Simazine	5 (20 °C)	91.2	1.7
Terbumeton	130 (20 °C)	1097	4.6
Terbuthylazine	8.5 (20 °C)	1096	2.0
Terbutryn	25 (20 °C)	3070	4.3

Table 3. - Koc values of some triazines

Herbicide	**Koc**	**Reference**
Ametryne	380; 250-392	[53, 115]
Atrazine	180; 149-640; 100; 150	[53, 115-117]
Cyanazine	180; 200; 168	[53, 115, 118]
Metamitron	71-189-380	[90]
Methoprotryne	180	[115]
Metribuzin	150; 88-95	[53, 115]
Propazine	152	[119]
Prometryn	680; 520-810; 610	[53, 115, 118]
Secbumeton	130	[115]
Simazine	135; 140; 284; 501	[115, 120-122]
Terbumeton	300	[115]
Terbuthylazine	1350	[115]
Terbutryn	700-740	[115]

Table 4. - DT_{50} values of some triazines

Herbicide	**DT_{50} (days)**	**Reference**
Ametryne	70-120	[39]
Atrazine	60-150; 130; 71; 74	[39, 117, 123, 124]
Cyanazine	108; 6; 10-29	[118, 124, 125]
Hexazinone	30-180; 90-360	[39, 107]
Metamitron	11-26-49	[90]
Metribuzin	37; 4-25; 17-301	[120, 126, 127]
Propazine	80-100	[39]
Prometryn	40-70; 94; 60	[39, 124, 128]
Simazine	56; 46-174	[124, 129]
Terbumeton	300	[39]
Terbuthylazine	30-90; 84-170; 5-50	[39, 82, 130]
Terbutryn	14-28	[39]

Atrazine

General characteristics

Atrazine, whose chemical name is 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, is a selective pre or post-emergency herbicide used to control annual weeds in maize, sorghum, asparagus, forestry, grasslands, grass crop, pineapple, roses, sugarcane and non selectively in non-crop areas [39].

The widespread use of atrazine in many countries, mainly for controlling the presence of weeds in corn cultivation areas, is due to some agronomical advantages, such as:

- its selectivity: it is an herbicide with physiological selectivity; it is quickly metabolized by maize through a conjugation reaction with glutathione;
- its effectiveness in different environmental and agronomic conditions;
- its agronomic versatility of use and the low cost of the commercial products.

Due to its high leaching potential, the use of atrazine has been banned or limited in some countries. In Italy, after a series of restrictions, atrazine was banned in 1990.

On the basis of its chemiodynamic parameters, atrazine is considered a leacher. Taking into account the range of Koc and DT_{50} values published in the literature (Tables 3 and 4), and by applying the GUS Index *(*)* at three combinations representing the maximum, medium and minimum scenarios of leaching [41], atrazine turns out a leacher in the two worst cases (Table 5).

Indeed, atrazine is one of the herbicides most frequently detected in groundwater.

Soil degradation

The main reactions involved in the soil degradation of atrazine are N-dealkylation and hydrolysis. In several field studies on atrazine degradation in different soil conditions, deethylatrazine (DEA), deisopropylatrazine (DIA), deethyldeisopropylatrazine (DEDIA) and hydroxyatrazine have turned out to be the main degradation products [42-47]. In some cases, it has been reported that chemical degradation is more important than biodegradation in soil or in water [48, 49]. In the first soil layers, both chemical and biological degradation can be relevant; in anaerobic conditions fewer metabolic pathways seem possible while at greater depth even hydrolysis does not appear to occur [50].

The most common mechanism of microbial degradation of atrazine is an N-dealkylation [51]; some microorganisms remove the ethyl- side chain preferentially, while others remove the isopropyl side chain [7].

In a metabolic study of the bacterial degradation of atrazine, it was observed that DEA and DIA were the first metabolites formed and that these metabolites were further dealkylated to 2-chloro-4,6-diamino-s-triazine (DEDIA) and then to 2-chloro-4-amino-s-triazine [52].

Hydrolysis of atrazine is mainly considered as an abiotic process the rate of which is affected by its concentration and pH [34]. An hydrolysis DT_{50} of atrazine of 160 days has been reported [53].

Some atrazine degradation products can undergo deamination reactions catalyzed by some bacterial strains under nitrogen-limited conditions [54, 55].

The triazine ring is very resistant to cleavage and its soil degradation is particularly slow [10, 56, 57]. In a metabolic study using 2,4,6-trihydroxy-s-triazine (cyanuric acid), biuret, which was further degraded to urea, was the first product of ring cleavage [58].

The main pathways of atrazine degradation in soil are summarized in Fig. 1.

Soil behaviour and characteristics of some atrazine degradation products

DEA

Some chemiodynamic parameters of DEA are reported in Table 6. DEA has a water solubility one order of magnitude higher than that of atrazine; it is more polar and mobile than its parent compound [6, 7].

Kd *(**)* values ranging from 0.3 to 0.8 were determined for DEA, which were lower than those measured in the same conditions for atrazine (0.669-1.288) [59].

A DT_{50} of 26 days has been reported for DEA in soil, without taking into account the soil-bound residues and so likely underestimating the real value [10].

As shown in Fig. 1, the soil degradation of DEA can give rise to the formation of DEDIA and 4-amino-2-hydroxy-6-isopropylamino-s-triazine. These degradation products as well as 4-amino-1,2-dihydro-s-triazin-2-one were identified in a metabolic study with a Nocardia strain, which was isolated from a soil treated with atrazine for 5 years [60].

DEA is phytotoxic almost like atrazine [10].

DIA

As shown in Table 6, DIA is more soluble in water than atrazine.

On the basis of the amounts of extractable residues, a DT_{50} in soil for DIA of 17 days has been determined [10].

DIA is degraded through different pathways. Both in aerobic and anaerobic conditions enzymatic hydrolysis by *Rhodococcus corallinus*, leading to the formation of 2-hydroxy-4-ethylamino-6-amino-s-triazine (N-ethylammeline), has been observed [36]; the deamination of this product gives rise to 2,4-dihydroxy-6-ethylamino-s-triazine (N-ethyl-ammelide) which have been detected in soil, plants and animals [7, 61]. From field studies it has been observed that it does not accumulate in soil.

DIA is five times less phytotoxic than atrazine [10].

(*) GUS = $\log_{10}(DT_{50}) \times (4 - \log_{10} Koc)$; GUS is the Goal Ubiquity Score used by Gustafson to estimate the leaching potential of pesticides [40].

(**) Kd is the soil-water partition coefficient.

Table 5. - GUS index calculated for some triazines for scenarios of maximum, mean and minimum contamination *(a)*

Substance	**Gus Index**		
	min	**mean**	**max**
Ametryne	2.59 T	2.89 L	3.33 L
Atrazine	2.12 T	3.20 L	4.34 L
Cyanazine	1.31 NL	2.78 T	3.61 L
Metamitron	1.48 NL	2.44 T	3.63 L
Metribuzin	1.09 NL	3.68 L	5.08 L
Propazine	3.45 L	3.54 L	3.64 L
Prometryne	1.76 NL	2.15 T	2.54 T
Simazine	1.53 NL	2.21 T	4.18 L
Terbumeton		3.77 L	
Terbuthylazine	0.6 NL	1.42 NL	1.9 T
Terbutryne	1.29 NL	1.51 NL	1.67 NL

(a) GUS indexes have been calculated for each herbicide using three different combinations of the Koc and DT_{50} values of Table 3. They represent the minimum (min: highest Koc and lowest DT_{50}) mean (mean value of Koc and DT_{50}) and maximum (max: lowest Koc and highest DT_{50}) leaching potential scenarios. NL = non leacher (GUS < 1.8); T = transient (1.8 < GUS > 2.8); L = leacher (GUS > 2.8)

Hydroxyatrazine

Hydroxyatrazine has a very limited mobility since it is strongly adsorbed on the soil, where it is only slowly degraded [62, 63]. Degradation of hydroxyatrazine is slower in submerged soils than in aerated ones [57].

The degradation pathways of hydroxyatrazine are not yet sufficently known. N-dealkylation of hydroxy-compounds is a reaction which has been observed in soil and higher plants [31, 43]. In the soil, it seems possible its microbial degradation by heterocyclic ring cleavage [64].

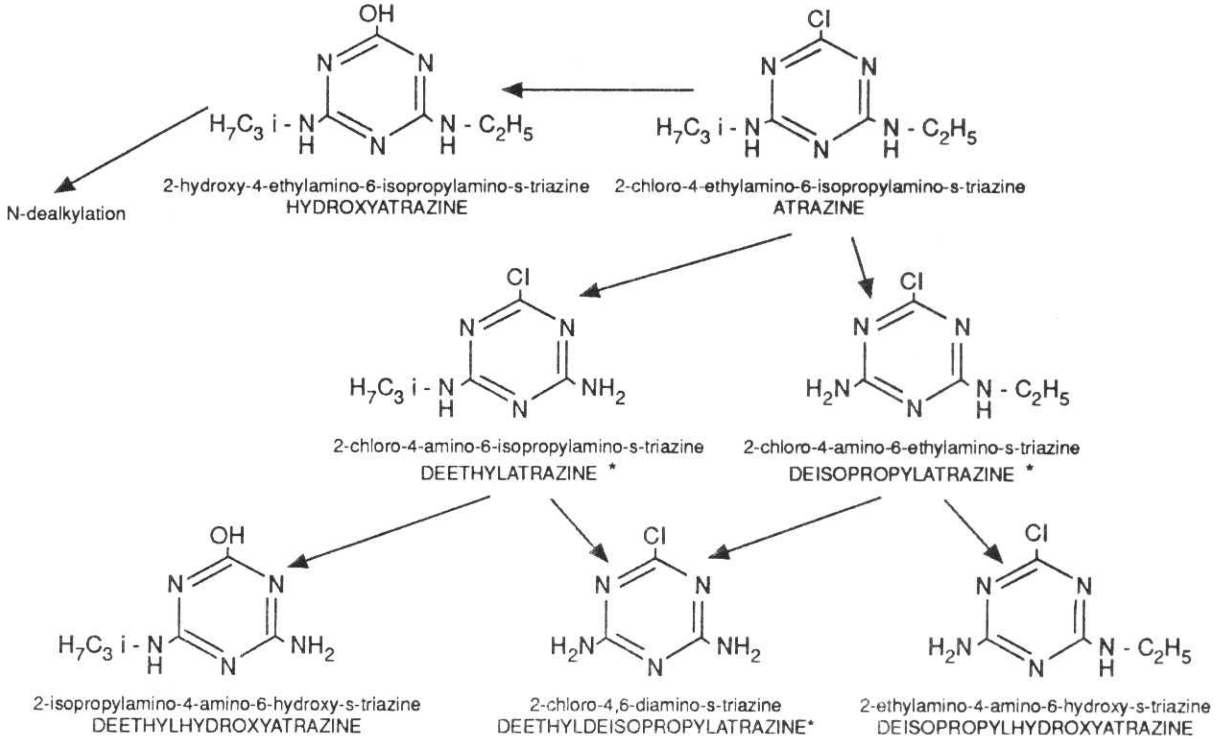
On the basis of the amounts of extractable residues a DT_{50} in soil of hydroxyatrazine of 121 days has been measured [10]; this value is much higher than those of atrazine and the dealkylated metabolites.

Hydroxyatrazine does not maintain the phytotoxic properties of atrazine [34].

Some chemiodynamic parameters of hydroxyatrazine are shown in Table 6.

DEDIA

DEDIA is a substance capable of forming high amounts of bound residues [62]. A DT_{50} in soil of 19 days has been reported. After 180 days from the application of ring-labelled DEDIA to a soil, 59% of the ^{14}C evolved as $^{14}CO_2$ [10]. DEDIA is not phytotoxic [65].



** Metabolites detected in groundwater*

Fig. 1. - Degradation of atrazine in soil.

Table 6. - Chemiodynamic parameters of atrazine and some of its main metabolites

Substance	Water solubility (mg/l)	Ref.	Kd	Ref.	pKa	Ref.	DT_{50} (days)	Ref.
Atrazine	33	[7]	0.669-1.288	[59]	1.71	[131]	60-150	[39]
DEA	375	[7]	0.355-0.858	[59]	1.65	[131]	26	[10]
DIA	208	[7]			1.58	[131]	17	[10]
Hydroxyatrazine	47	[7]			5.15	[131]	121	[10]

Levels in waterbodies

Atrazine has been found in groundwater in the United States in the range from 0.3 to 3 µg/l as a consequence of agricultural activities [66]. A maximum concentration of 1500 µg/l has also been detected.

In Germany, The Netherlands and France maximum levels of 17, 0.6 and 29 µg/l, respectively, have been reported [67-69].

DEA and DIA have been detected in groundwaters at the same or greater levels than atrazine [6, 11, 12, 70-73].

DEDIA levels up to 1 µg/l have been reported in a study in the Netherlands [11].

Simazine

General characteristics

Simazine is an herbicide whose chemical name is 2-chloro-4,6-bis(ethylamino)-s-triazine. It is used in pre-emergency to control broad-leaved and grass weeds in deep-rooted crops such as asparagus, berry crops, broad beans, citrus, cocoa, coffee, forestry, hevea, hops, oil palms, orchards (pome and stone fruits), ornamental, sisal, sugarcane, tea, tree nurseries, turf, artichoke, vines, olives and non-crop areas. A major use is on maize. In the United States it is also used to control vegetation and algae in farm ponds and fish hatcheries [39]. On the basis of the data on the sales of herbicides in Italy shown in Table 1, simazine was the third herbicide sold among triazines in 1988.

As reported in Tables 2 and 3, in spite of its low water solubility, simazine has a Koc of 135-501 which is an index of its significant tendency to move through the soil. Simazine is being considered a persistent herbicide [74]. In summer conditions, a persistence of about 3-6 months in moist soils have been reported [75]. Simazine volatilization and hydrolysis in water do not seem to be relevant dissipation processes of the herbicide [76]. In the soil, simazine undergoes hydrolysis, with a DT_{50} of 30-110 days [53, 75, 76].

In Tables 2-4, some main chemiodynamic parameters of simazine are shown. Taking into account the range of Koc and DT_{50} values of Tables 3 and 4, and applying the GUS Index [40] for the three combinations, representing the maximum, medium and minimum scenarios of leaching, as described above in Table 5, simazine turns out a leacher, transient and non leacher, respectively.

Soil degradation

Like other s-triazines, simazine can be degraded through chemical hydrolysis or microbial N-dealkylation [7, 13].

DIA, DEDIA and hydroxysimazine have been determined as main soil degradation products of simazine [13, 42, 77].

Simazine can be used by some soil microorganisms as a source of energy [31]. The products of microbial degradation of simazine in soil include DIA and 2,4-dihydroxy-6-amino-s-triazine (ammelide) (Fig. 2) [31]. Simazine can be only slowly mineralized: indeed around 10% of labelled simazine has been detected as CO_2 in more than 100 days in a clay-lime soil [78].

Levels in waterbodies

As a consequence of its agricultural use, simazine has been found in groundwaters of 3 States in the USA with typical concentrations from 0.2 to 3 µg/l [66].

In groundwaters of Germany, simazine and DIA levels of <0.01-0.15 µg/l (average: 0.03 µg/l) and <0.02-0.06 µg/l (average: 0.01 µg/l) have been reported, respectively [79].

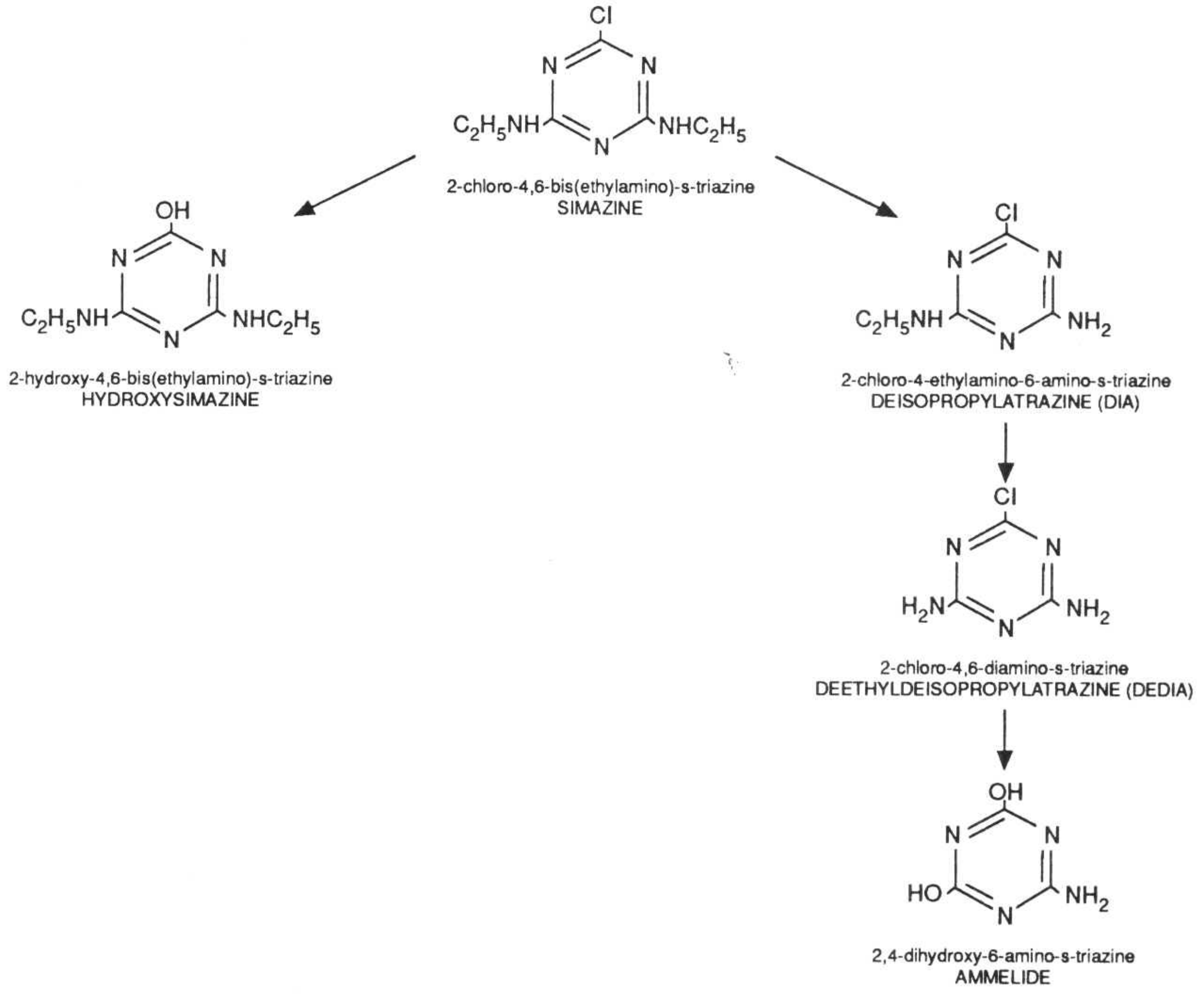


Fig. 2. - Degradation of simazine in soil.

Cyanazine

General characteristics

Cyanazine is the commercial name given to the chemical substance 2-(4-chloro-6-ethylamino-s-triazin-2-ilamino)-2-methyl-propyonitrile. It is an herbicide used for general control in pre-emergency in broad beans, maize and peas, in post-emergency in bearley and wheat during the early tillering stage in combination with a variety of other herbicides for the control of broad-leaved weeds. Other crops for which it is used include: cotton, oil-seed rape, forestry, potatoes, soyabeans, sugarcane [39]. As shown in Table 1, the sale of cyanazine in Italy in 1988 was by far below that of atrazine and simazine.

In Tables 2-4, some chemiodynamic parameters of cyanazine are reported. The GUS indexes calculated for the three scenarios previously described, as shown in Table 5, indicate that this herbicide can behave as a leacher, transient and non leacher compound, respectively.

Soil degradation

Cyanazine is less persistent than atrazine and simazine, presumably for the presence of the nitrile group which can be easily hydrolyzed [80].

On the basis of a study in soil [42], cyanazine seems to degrade as summarized in Fig. 3. Of the two possible way of degradation, that due to a first reaction of hydrolysis seems by far the most relevant. Indeed, DIA and DEDIA have been detected at very low concentrations. No hydroxycyanazine has been determined.

In another study, from the analysis of a drain water from a soil treated with cyanazine, the parent compound, cyanazine amide, and DIA were detected at concentrations of 0.5, 0.45 and 0.29 μg/l, respectively [6].

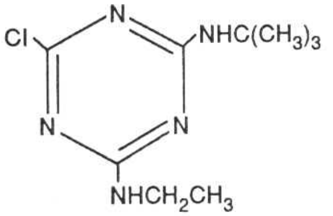
Levels in waterbodies

As a consequence of routine agricultural practices cyanazine was found in groundwater in 2 states in the United States in the range of 0.1 to 1 μg/l [66]. In another study cyanazine was also detected in groundwater at maximum and mean concentrations of 7 μg/l and 0.4 μg/l, respectively [81].

In The Netherlands concentrations of 0.6 μg/l were reported at depth of 2-5 m [71].

Terbuthylazine

Terbuthylazine is the technical name of the chemical 2-(terz-butylamino)-4-chloro-6-(ethylamino)-s-triazine.



Terbuthylazine is an herbicide used in pre-emergency in sorghum and for the selective weed control in citrus, maize, pod forestry and vineyards. Mixed with terbumeton it controls perennial weeds in established apples, citrus and grapes. Also it is used in combination with bromofenoxim as a wide-spectrum, broad-leaved herbicide in winter and spring cereals [39]. As reported in Table 1, a relevant amount of this herbicide was sold in Italy in 1988.

A very wide range of DT_{50} values have been reported for this herbicide, while only one value of Koc is available as is shown in Tables 3 and 4. The combinations of these values in the three scenarios mentioned above give rise to three GUS indexes corresponding to a non leacher in two cases and a transient in the worst case, respectively (Table 5).

Terbuthylazine has an hydrolysis DT_{50} of 63 days at pH 5 and >200 days at pH 7 and 9 [82]. Volatilization does not appear to be an important dissipation process of this herbicide from soils [83].

Terbuthylazine can be degraded through N-dealkylations of the side chain, hydrolysis of the chlorine and the amino group after its dealkylation, ring cleavage [84].

In lysimeter tests using a sandy soil with a little content of organic matter, some tendency of terbuthylazine to leach was observed, mainly depending upon the amount of infiltrating water [85].

In the United States after 1 year from the application of terbuthylazine, it was detected at a mean concentration of 0.6 μg/l in samples of drain water at 0.8-1 m depth, [86]. In another study terbuthylazine and its metabolite, deethyl-terbuthylazine, were determined in the tile-drain water in the first few months after the application of the parent compound, at mean concentrations of 0.49 and 0.05 μg/l, respectively [79].

Terbuthylazine was detected in groundwater in Germany at a maximum concentration of 1 μg/l [67].

Methylthiotriazines: general characteristics

Two of the three methylthiotriazines examined in this review, prometryne and terbutryn, beyond the thiomethylic group, have two N-alkylated groups, while the third, metribuzin, has a carbonilic group and an amino substituent.

As reported in Table 1, in Italy, 48,764 kg of these herbicides were sold in 1988, representing about 3% of the total triazines. Methylthiotriazines have a pKa around 4; prometryn and terbutryn have similar values of water solubility as shown in Table 2.

Methylthiotriazines are resistant to chemical hydrolysis, nevertheless they have low persistence in soil because undergo biodegradation reactions [31, 87]. Indeed, they are degraded more rapidly than chloro-s-triazines [88].

In the soil, oxidation of methylthio-s-triazines to the corrispondent sulfoxide and sulfone is a common pathway of biodegradation [89].

Metribuzin

Metribuzin is the chemical name given to 4-amino-6-terz-buthyl-3-methylthio-1,2,4-triazin-5(4H)-one.

Metribuzin is an asymmetric triazine with a carbonilic and a thiomethylic group.

It is used pre- or post-emergence to control weeds in asparagus, sugarcane, tomato, potato, soyabean, lucerne and other crops [39].

As reported in Tables 2 and 3, on the basis of its water solubility and Koc, this herbicide can be considered highly mobile. As to its DT_{50}, ranges from 4 to 25 and from 17 to 301 days have been reported. The combinations of the values of Tables 3 and 4 in the three scenarios mentioned above, give rise to three GUS indexes corresponding to a leacher in the worst and medium combinations and a non leacher in the most favourable combination (Table 5).

The rate of degradation of metribuzin is related to the microbial activity of soils [90, 91]. Nevertheless, there is evidence showing that metribuzin can also be degraded abiotically [92].

As reported in Fig. 4, two degradation pathways have been reported, in one the sulfur atom is oxidised up to sulfone and then replaced by an hydroxyl group in the chetonic form. In the other pathway the amino group is eliminated before or after hydrolysis of the thiomethyl group [93].

Metribuzin has been found in groundwaters of the United States at typical concentrations ranging from 1 to 4.3 μg/l as a consequence of agricultural practice [66]. A maximum concentration of 300 μg/l has been reported in private wells in agricultural areas [94].

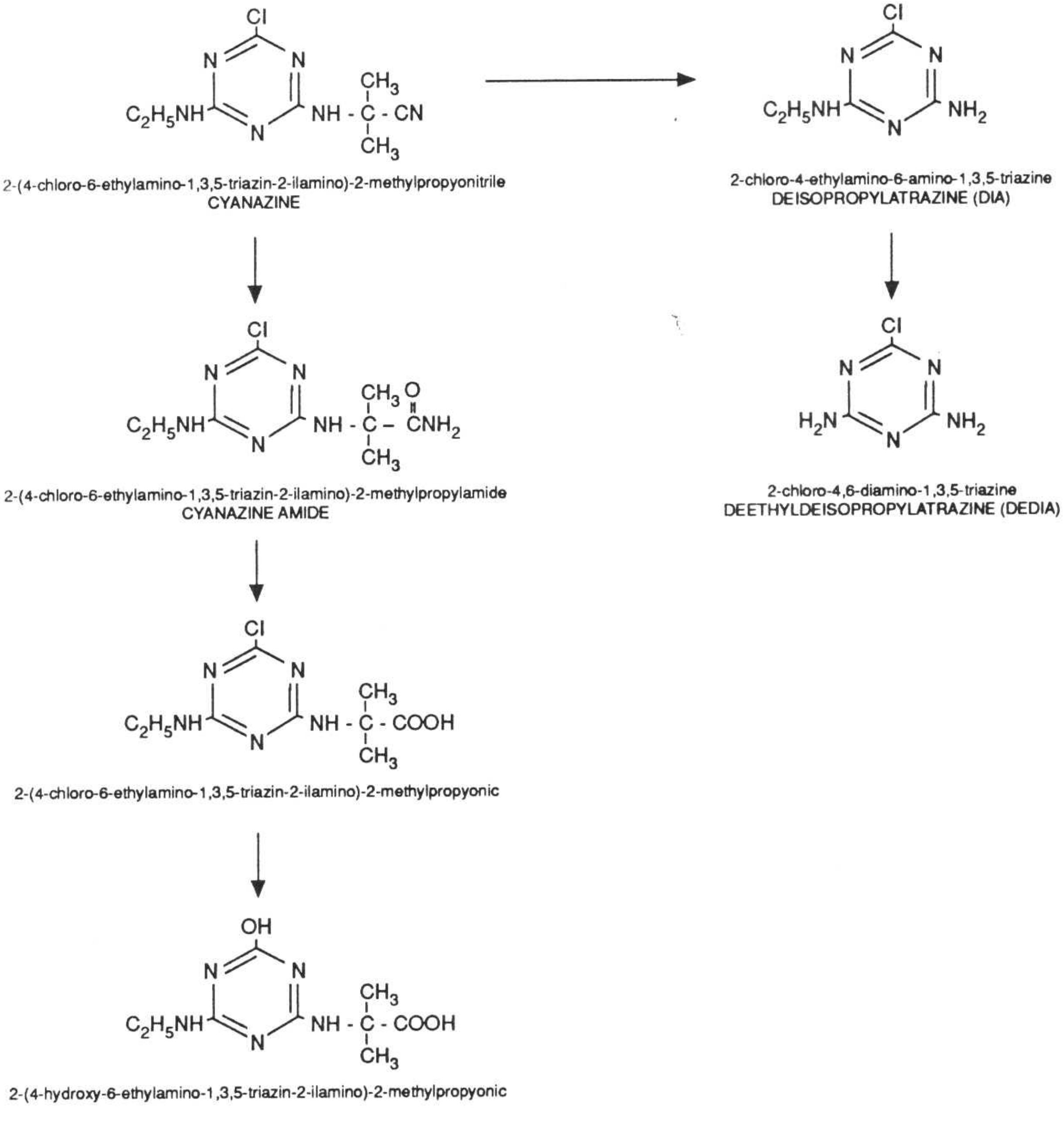


Fig. 3. - Degradation of cyanazine in soil.

Prometryn

General characteristics

Prometryn is the commercial name of 2,4-bis(isopropylamino)-6-methylthio-s-triazine. It is a selective herbicide used against annual mono and dicotyledons in pre- or post-emergency in broad beans, carrot, celery, cotton, leeks, lentils, parsley, peas, potato and sunflowers [39]. According to the methods above mentioned for calculating its leaching potential, prometryn turns out a non leacher in the best case and a transient in the other two cases, respectively (Table 5).

Soil degradation

Prometryn is stable in neutral, weakly acid or basic environments. It is hydrolyzed to 2-hydroxy-1,6-bis-isopropylamino-s-triazine (hydroxypropazine) in acid or basic environment but only at high temperature [95, 96]. Photodegradation in normal field conditions is negligible [97].

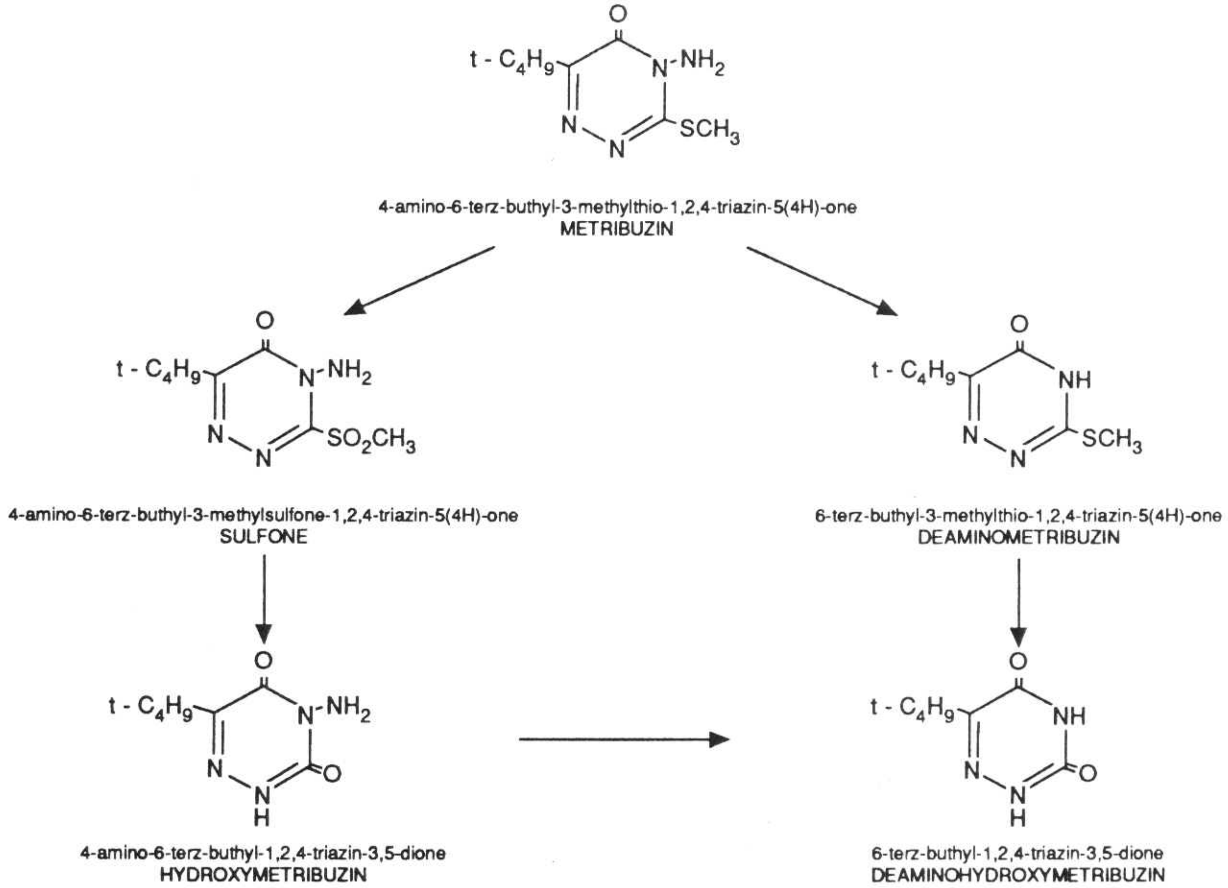


Fig. 4. - Degradation of metribuzin in soil.

A lot of microorganisms, which can use this molecule as a source of energy, nitrogen and sulfur, have an important role in the soil degradation of prometryn [98]. Nevertheless, the degradation of prometryn in the soil is likely to be due to a combination of microbiological and chemical reactions [97].

Hydrolysis seems to be precedeed by oxidation reactions which are responsible for the formation of the sulfoxide and the sulfone [31,99]. Yet, hydroxypropazine has also been detected in the absence of these products [97, 100, 101]. Hydroxypropazine has a pKa of 5.2, a water solubility of 41 mg/l [102] and is not phytotoxic [96].

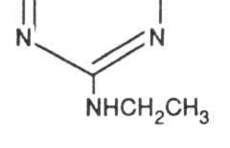
Prometryn and its N-dealkylated metabolite, deisopropylprometryn, have been identified in soils as the main components of bound residues [103]. Also, hydroxypropazine has been identified as bound residues associated to the fulvic acid fraction [103].

In a study aimed at identifying the nature of the bound residues derived from the applications of prometryn to soil after 1 year of incubation of a soil with the herbicide, it was observed that 54% of the total bound residues was in the form of the parent compound or its dealkylated metabolites, 8% in the form of hydroxypropazine and 18% as unidentified compounds; 20% of soil bound residues was thermally decomposed to CO_2 during the extraction procedures [104]. In this study it was also demonstrated that these bound residues had an inhibitory effect on the microbial activity of the soil and that bacteria can partially contribute to the release of these soil bound residues [104].

The soil degradation pattern of prometryn is summarized in Fig. 5.

Terbutryn

Terbutryn is the commercial name of the chemical 2-terz-buthylamino-4-ethylamino-6-methylthio-s-triazine.



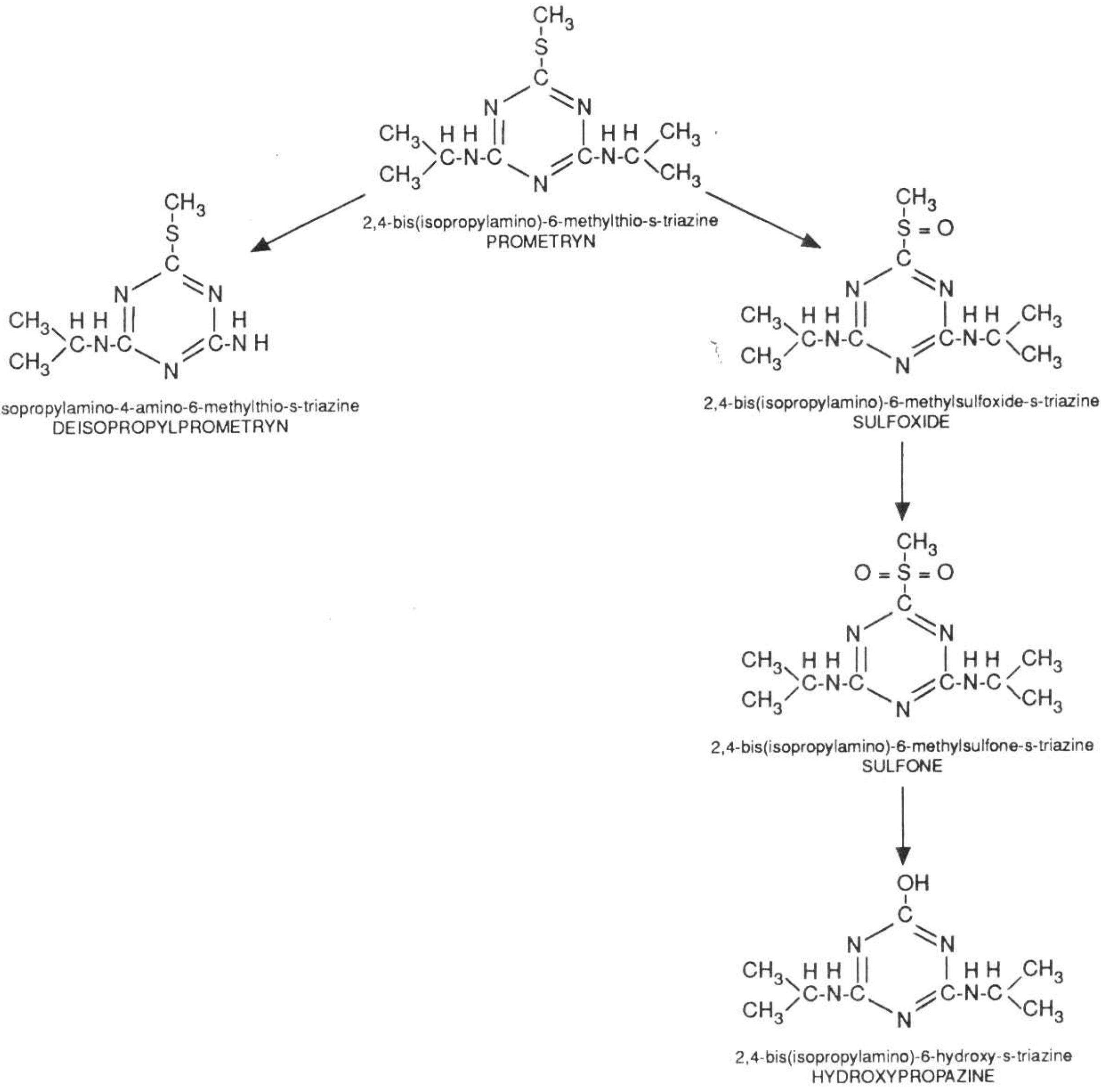


Fig. 5. - Degradation of prometryn in soil.

Terbutryn is a selective herbicide used in pre-emergency in winter cereals to control blackgrass and annual meadow grass. Other pre-emergency uses are on sugarcane and sunflowers and in mixture with terbuthylazine on peas and potatoes. It is also used post-emergence in maize and to control algae and submerged vascular plants in waterways, reservoirs and fish ponds [39].

The GUS indexes calculated as described above, indicate that this herbicide behaves as a non leacher in all the three combinations used.

Terbutryn can be hydrolyzed only at very high temperature to 2-hydroxy-4-ethylamino-6-terz-buthylamino-s-triazine [96].

In The Netherlands, a maximum concentration of 2.4 μg/l of terbutryn was detected in groundwater at a depth of 4 m [105].

Methoxy-s-triazines: general characteristics

Methoxytriazines are molecules characterized by the presence of a methoxyl group as substituent in the triazine ring.

Taking into account the sales of herbicides in Italy, methoxy-s-triazines are less important compared to the other triazine herbicides. As shown in Table 1, 24,029 kg of these herbicides were sold in Italy in 1988, representing about 2% of the total sales of triazines.

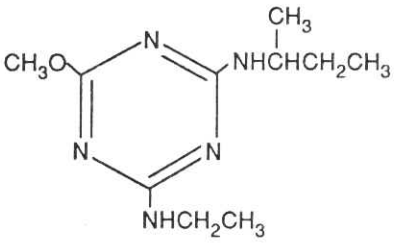
On the basis of the chemiodynamic properties reported in Table 3, these herbicides can move quite easily in the soil.

They are more resistant to acid hydrolysis than chloro- and methylthio-s-triazines [31].

Methoxy-s-triazines are also more resistant to degradation by fungae than chloro- and methylthio-s-triazines [31]. However on the whole they are degraded more rapidly than the corresponding chloro-s-triazines [88]. The contribution of demethoxylation, dealkylation, deamination and ring cleavage to the degradation process is not known [31].

Secbumeton

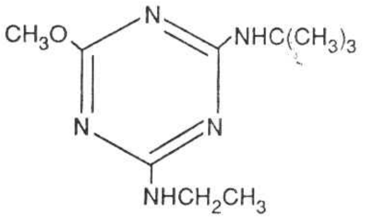
Secbumeton is the commercial name of the substance N^2-sec-buthyl-N^4-ethyl-6-methoxy-s-triazin-2,6-diamine.



Secbumeton is an herbicide used on the control of annual and perennial mono- and dicotyledonous weeds [106]. No data on the leaching potential of secbumeton seem available. From studies in mammals, it has been demonstrated that the main metabolic pathways responsible for the degradation of this herbicide are oxidation, hydrolysis and N-dealkylation reactions [93].

Terbumeton

Terbumeton, is the commercial name of 2-terz-buthylamino-4-ethylamino-6-methoxy-s-triazine.



Terbumeton is an herbicide effective against both annual and perennial grasses and broad-leaved weeds. It is used for post-emergence weed control in apple and citrus orchards, forestry and vineyards [39].

Only a few chemiodynamic parameters of terbumeton are available, as reported in Tables 3 and 4. By applying the GUS index to the single values available of Koc and DT_{50}, terbumeton turns out a leacher (Table 5).

Other triazines

Hexazinone and metamitron are herbicides characterized by the presence of at least a carbonilic group; differently from other triazines, they have a cyclic and an aromatic ring, respectively.

Hexazinone

Hexazinone is the commercial name given to the chemical 3-cyclohexyl-6-dimethylamino-1-methyl-s-triazin-2,4-(1H,3H)-dione. It is a post-emergency contact herbicide, effective against many annual, biennal and perennial weeds. Used for selective control in lucerne, pineapple, sugarcane and in plantations of certain coniferous species; also on non-crop areas, but not on sites adjacent to deciduous trees or other desirable plants [39].

As shown in Table 1, on the basis of its sale in 1988, this herbicide is not widely used in Italy.

No Koc values on hexazinone seem available. Nevertheless, this herbicide has a high water solubility, as reported in Table 2.

DT_{50} values ranging from 3 to 12 months and from 1 to 6 months have been reported [39, 107].

On the basis of data reported in Tables 2 and 4, this herbicide seems to have the properties of a good leacher.

Hexazinone can be photodegraded forming the products 2, 3 and 5 of Fig. 6 [108].

Yet, the main degradation reactions in soil are catalyzed by microorganisms, N-demethylation and oxidation (this latter on position 4 in cyclohexyl ring) being the main metabolic reactions [107].

No hexazinone degradation has been observed under anaerobic conditions [107].

In field studies, the metabolite 1 of Fig. 6 was the main product detected; other metabolites detected in significant amounts were metabolites 2, 3 and 4 of the same figure [107].

In the United States, hexazinone has been detected in groundwaters in 1 out of 2 states examined at maximum and mean levels of 9 and 8 ppb, respectively, as a consequence of agricultural activities [81].

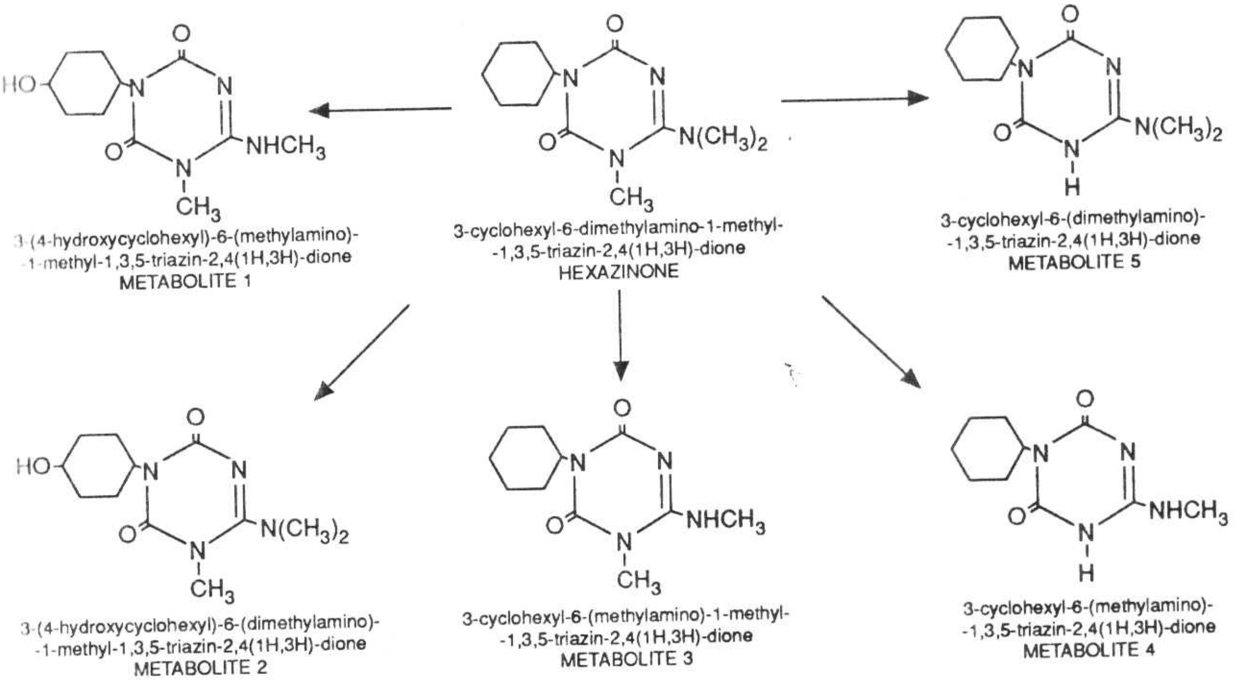
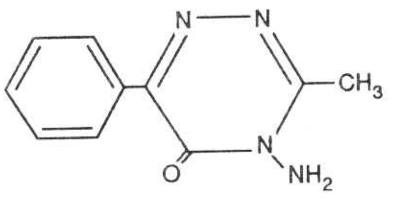


Fig. 6. - Degradation of hexazinone in soil.

Metamitron

Metamitron is the commercial name of the chemical substance 4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one.



Metamitron is mainly used against grass and broad-leaved weeds in sugar and fodder beets, and also in mangold, red beet and certain strawberry varieties [39]. As shown in Table 1, metamitron is largely used in Italy, being the second herbicide among the triazines sold in 1988.

Metamitron is an asymmetric triazine with polar groups which are responsible for the high water solubility and the low values of Kow *(*)* and Koc, as reported in Tables 2 and 3, respectively.

Degradation of metamitron in soils has been examined in different studies. This herbicide is degraded in a way which is represented at its best by a first order rate equation [90]. By applying this equation to the results obtained from degradation studies in different soils, minimum, mean and maximum rate costants of 0.014, 0.027, 0.065 day^{-1}, respectively, were calculated [90]. These values have been used in this study to calculate the DT_{50} of Table 3. Finally, by applying the Gustafson's equation to the combinations of the Koc and DT_{50} values of Tables 3 and 4, as reported above, metamitron can be classified as a leacher, transient and non leacher for the three scenarios examined, respectively.

Metamitron is rapidly degraded to its main metabolite deamino-metamitron and then to unstable products which are mineralized [109].

Metamitron is degraded also through abiotic reactions. Indeed, in a study in which the bacterial inhibitor sodium azide was used, it was observed that a percentage of 30-35% of the applied herbicide was degraded in 26 days [91].

In a lysimeter study, the radioactivity was around 1% of applied labelled metamitron, at a depth of 20-30 cm, 20 weeks from application [110]. In aqueous solution, under anaerobic conditions, a DT_{50} of 14 days has been reported [111].

After 13-20 weeks from the application of metamitron about 20% of the applied dose was unextractable [109].

Metamitron has been detected in groundwater in The Netherlands at levels of 0.73 µg/l at a depth of 1.6-2.1 m [112].

(*) Kow is the n-octanol-water-partition coefficient.

Conclusions

On the basis of the data and information examined in this review, it turns out that many triazine degradation products have been detected in groundwater and/or have chemiodynamic parameters indicating a high leaching potential. Little information is available on the toxicological properties of these compounds but in some cases they mantain the phytotoxic characteristics. For instance, on the basis of the few available data, it seems that some atrazine degradation products have toxicological properties equal to or higher than the parent compound [113]. Moreover, one or more atrazine metabolites may be to some extent responsible for mutagenic activity [114].

Triazine degradation products are in some cases of concern in relation to their environmental fate and toxicological properties. More monitoring and scientific data should be produced in order to better understand the relevance of this problem.

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