

## Bioremediation of terbuthylazi ne contaminated soil: a bibliometric and systematic review

### Biorremediação de solo contaminado com terbutilazina: uma revisão bibliométrica e sistemática

Carolina Zuanazzi Tonello<sup>1\*</sup>, Natalia Buttini Correa<sup>1</sup>, Luciane Maria Colla<sup>1</sup>

#### RESUMO

A contaminação por pesticidas representa um perigo para o meio ambiente em todo o mundo devido a seus processos de mobilidade e infiltração. Os herbicidas compreendem 47,5% dos pesticidas disponíveis no mundo sendo usados geralmente para proteger a cultura, porém existem várias maneiras pelas quais podem contaminar o solo. A atrazina tornou-se um dos herbicidas mais populares do mundo, porém seu uso causou contaminação de águas superficiais e subterrâneas pela molécula e seus produtos de degradação, sendo proibido em diversos países Europeus. A terbutilazina é utilizada nos países europeus como substituta no manejo químico em razão de suas características de menor solubilidade em água, maior hidrofobicidade e potencial de maior retenção no solo. Apesar de suas características favoráveis, a terbutilazina é atualmente um dos pesticidas mais frequentemente detectados em águas marinhas em países da União Europeia. A contaminação prolongada do solo está associada à liberação do metabólito DET e ao alto risco de contaminação também em águas subterrâneas. Um melhor conhecimento sobre as interações e agregação de materiais do solo facilitará o desenvolvimento de materiais biorremediadores para aumentar a sorção e diminuir a dissipação de pesticidas nos solos.

**Palavras-chave:** Atrazina, fitorremediação, desetilterbutilazina.

#### ABSTRACT

Contamination by pesticides represents a danger to the environment all over the world due to their mobility and infiltration processes. Herbicides comprise 47.5% of the world's available pesticides and are generally used to protect crops, but there are many ways in which they can contaminate the soil. Atrazine has become one of the most popular herbicides in the world, but its use has caused contamination of surface and ground water by the molecule and its degradation products, and it has been banned in several European countries. Terbuthylazine is used in European countries as a substitute in chemical management because of its characteristics of lower water solubility, greater hydrophobicity, and higher soil retention potential. Despite its favorable characteristics, terbuthylazine is currently one of the most frequently detected pesticides in marine waters in European Union countries. Prolonged soil contamination is associated with the release of the DET metabolite and a high risk of contamination also in groundwater. Better knowledge about the interactions and aggregation of soil materials will facilitate the development of bioremediation materials to increase sorption and decrease dissipation of pesticides in soils.

**Keywords:** Atrazine, phytoremediation, desethylterbutylazine.

<sup>1</sup> Universidade de Passo Fundo

\*E-mail: caroltonello@gmail.com

## INTRODUCTION

Although the use of pesticides in agriculture is a practice that has ensured agricultural production and food security and takes part in economic development, it has been shown that the use of agrochemicals can lead to environmental contaminations, generating controversies and concerns (CHOUDRI et al, 2019). Anthropogenic activities, not only linked to agricultural activities, have introduced xenobiotics into ecosystems and can pose risks to fauna, flora, and the environment (TASCA,2018).

Contamination by pesticides and their metabolites pose a danger to the environment worldwide due to their mobility and infiltration processes. The chemical composition of pesticides, their structure, and their partition coefficient (Kow) justify their ability to migrate throughout the soil from one location to another (RAO et al, 1982). The persistence of a pesticide means that its distribution allows it to be transported away from its target, as it happens for herbicides since their sorption and/or solubility allow them to move within the soil and to be directed to water sources (CARTER et al., 2000).

Of all the herbicides used worldwide, 47,5% are herbicides (GILL et al., 2014) and they are generally used to protect the crop. However, there are several ways in which they can contaminate the soil. In soil, they can be leached, sorbed, and/or degraded - leaching being the main form of transport, where the herbicide reaches seeds and plant roots. Yet, when in excess, they can be carried to deep soil layers contaminating groundwater (VELINI et al., 2000). This downward movement of herbicides is influenced by factors such as organic matter, soil composition, size and distribution of soil particles, as well as pH, density, and porosity (PRATA et al., 2003).

Atrazine (ATZ) (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) has become one of the most popular herbicides in the world due to its high efficiency and low cost. It is a systemic, selective herbicide used in crops such as corn and sugarcane to control grasses and broadleaf weeds (GIANNINI-KURINA et al., 2022). ATZ has been banned in Europe since 2004 (FINGLER et al., 2017), as after being widely used the ATZ molecule and its degradation products caused contamination of surface water and groundwater (BLAHOVÁ et al., 2013) due to several environmental behaviors that this pesticide can fulfill, such as hydrolysis, volatilization, sorption-desorption, transformation, degradation, leaching, runoff, and bioaccumulation (CYCÓN et al., 2016).

Since the ban of the use of atrazine, terbuthylazine (6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine) (TBA) has been used in European countries as a substitute in weed control due to its characteristics of lower water solubility, higher hydrophobicity, and higher soil retention potential (STIPICEVIC et al. 2015; ODENDAAL et al., 2015). Both ATZ and TBA belong to the triazine chemical group, which are widely used as pre- and post-emergent to control preferably broadleaf weeds in agriculture (CHENG et al., 2021).

Despite its favorable properties, TBA is currently one of the most frequently detected pesticides in water sources in EU countries (BRUMOVSKY et al., 2016). TBA's high persistence in the topsoil layer is associated with the release of the metabolic distillate desethylterbutylazine (DET) which is currently one of the most ubiquitous and abundant plant protection metabolites found in aquifers in Europe (LOOS et al., 2010). Both TBA and DET pose a risk to the environment and are toxic to living organisms at low doses (BRUMOVSKY et al., 2017). The greater the degradation of TBA in the soil, the less likely the processes of leaching and runoff will occur, avoiding the herbicide to reach surface water and groundwater (CARACCIOLO et al., 2022). TBA degradation depends on the history of the use of the molecule in that agricultural region which can increase the potential for self-correction by selecting populations of microorganisms capable of metabolizing this molecule (MORAN et al., 2006).

Indeed, natural communities of microorganisms have been shown to play a key role in triazine degradation. The remediation capacity of these communities can be explored and improved so they can be used for bioremediation purposes (CARACCIOLO et al., 2022). Remediation of the environment aims to eliminate, reduce, isolate, or stabilize one or more contaminants through technologies involving physical, chemical, and/or biological processes (GAVRILESCU et al., 2004). Bioremediation is the fastest-developing technique in ecosystem restoration that uses microorganisms to reduce the concentration and toxicity of various chemical pollutants, including pesticides (FOGHT et al., 2004; KUHARD et al., 2004). Thus, this has been considered a more environmentally safe and cost-effective method as an option for detoxification and decontamination of the environment (ZHANG et al., 2002).

The contamination of soil by terbuthylazine and its metabolites, how they behave in soil, and remediation strategies are issues debated over time and will be discussed in this review aiming to provide information on minimizing the negative impacts caused by

these herbicides that are, nonetheless, important tools for agricultural management practices.

## METHODOLOGY

The methodology of this review to address bioremediation techniques of terbuthylazine-contaminated soils was conducted through a bibliometric and systematic review by the analysis of articles produced in international databases found in the Scopus repository from keywords related to the subject of the study. The search was carried out in September 2022.

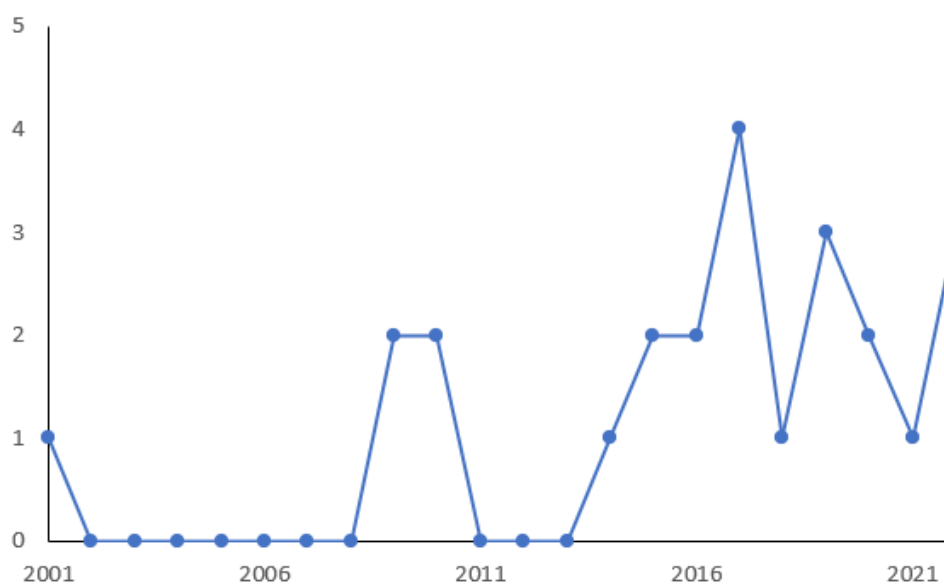
The terms defined for the database search were "terbuthylazine" AND "soil" AND "bioremediation". The search yielded 24 articles, including 22 research articles, 1 review article, and 1 book chapter; these articles were selected to build this literature review based on their focus: terbuthylazine bioremediation. Articles that did not present results related to terbuthylazine were eliminated. To better understand the soil behavior of this pesticide articles beyond the Scopus research was used to create the context presented throughout this review.

The VOSviewer software (version 1.6.18) was used to generate a word cloud to identify clusters and to create a connection between the keywords of this research, as shown in Figure 1. The keywords used for this purpose during the search were "terbuthylazine" AND "bioremediation" AND "atrazine" AND "bioremediation of soil", using the Scopus platform. The words were chosen to create a complete research on the topic. The word cloud provides an analysis of the most common terms and frequent associations or relationships shown by the lines connecting the words.

Figure 1: Wordcloud from Scopus database using the keywords “terbuthylazine” AND “bioremediation” AND “atrazine” AND “bioremediation of soil”.



Figure 2: Annual growth of scientific production with the terms “terbuthylazine” AND “soil” AND “bioremediation”.



Source: Authors

## SOIL BEHAVIOR

Pesticide accumulation in the environment has become a serious problem that has been harming ecosystems. Since only a small proportion of pesticides are actually absorbed by their target and large amounts are retained in the soil, they have become a threat to food production, food safety, and human health (LU et al., 2016; YU et al., 2021). In addition, some herbicides remain active in the soil for long periods reaching water resources and non-target crops on the field, or bioaccumulating toxins throughout the food chain (PIOTROWICZ-CIRESLAK et al., 2012).

After reaching the soil there are basically three pathways by which the herbicide can follow: it can move within the soil via water, it can adhere to soil particles, or it can be metabolized by soil organisms and/or enzymes (GAVRILESCU et al., 2005). Several factors can influence herbicide transport in the soil, such as application timing and chemical characteristics (CALDERON et al., 2016), as well as soil texture and structure which play a key role in this movement (GAVRILESCU et al., 2005). When compared to ATZ, TBA dissipates more slowly in soil, i.e., it is more persistent in the environment, considering its greater hydrophobicity and greater resistance to biodegradation (FARLIN et al., 2013; STIPICEVIC et al., 2017). The main mechanisms of dissipation of triazines in soil are chemical and biological degradation, adsorption, volatilization, and leaching (MUDHOO et al., 2011).

The interactions along the herbicide-soil interface essentially determine the bioavailability of an herbicide, which depends on sorption and volatilization rates, transformation by biotic and abiotic processes, and leaching and/or runoff processes that create the possibility of surface water or groundwater contamination (PATAKIOUTAS et al., 2002). Herbicide sorption is one of the most important processes in that regard and it is influenced by soil properties such as organic matter content, texture, mineralogy, cation exchange capacity (CEC), and pH (MENDES et al., 2016). TBA has a low sorption coefficient indicating that the herbicide gets little adsorbed to the soil (CABRERA et al., 2008). The high leaching risks associated with TBA may be explained by its characteristics of high solubility in water, slow degradation rate, and low sorption coefficient (CALDERON et al., 2016).

Soil processes that decrease pesticide water contamination are those that contribute to its disappearance, such as irreversible adsorption of residues on soil particles (FADAYOMI et al., 1977), degradation pathways (ARIAZ-ESTÉVEZ et al., 2008), photodegradation (SCRANO et al., 2004), biodegradation, and bioremediation (CARACCILOLO et al., 2013). TBA can persist in soil twice as long as ATZ, which may result in higher molecule transportation through runoff and slower leaching rates to groundwater (STIPIČEVIĆ et al., 2015).

Terbuthylazine half-life (DT<sub>50</sub>) varies from 20 to 180 days depending on each soil singularity based on their chemical characteristics and clay/organic matter content (CARACCILOLO et al., 2013). The half-life of the herbicide indicates the time required to degrade 50% of the herbicide and can be considered an important criterion of persistence (MUELLER et al., 2015). Excessive rainfall or heavy rainfall and practices such as soil tillage may decrease TBA's half-life to approximately 18 days. On the other hand, in aqueous soil suspension (pH=7-9) the hydrolysis of TBA is slow and its transformation depends on biodegradation, thus the half-life can reach up to 200 days or more (SING et al., 2003).

In soils of high organic matter contents, biodegradation is the main route of TBA dissipation, whereas, in low organic matter soils there is a higher risk of leaching and of runoff due to the low rate of microorganisms' degradation, which implies a higher risk of water contamination (STIPIČEVIĆ et al., 2015). In the case of a high biodegradation potential, sorption may be a limiting factor for terbuthylazine mineralization, whereas, in



the case of a low biodegradation potential, the limiting parameter would be the number of degrading microorganisms (JACOBSEN et al., 2001).

An herbicide's soil behavior can be a fundamental indicator of the water contamination risks by that molecule. TBA is highly persistent in soil and if not degraded it can be leached or it could runoff reaching groundwater and surface water or it may negatively affect subsequent crops in arable soils. Because spontaneous biodegradation of terbuthylazine is very slow, processes such as bioremediation are important tools to preserve ecosystems.

## **BIOREMEDIATION TECHNIQUES**

One way to mitigate the environmental risk of triazine contamination is by using bioremediation strategies. The technique was defined by Mueller et al. (1996) as a process by which organic wastes are biologically degraded under controlled conditions to a harmless state, or to levels below concentration limits set by regulatory authorities. This process offers several advantages such as wide applicability, low cost, minimal local disturbance, and versatility, along with the ability to reduce and nullify the concentration of the contaminant toxicity (VIDALI, 2001; JAIN et al., 2005) using biological activity (bacteria, fungi, or plants) (SHINDE, 2013). This process can be done in situ (contaminants are treated on-site, without soil excavation or water transport) or ex-situ (contaminated soil is excavated, treated, and brought back to the original site).

Microbial communities play key roles in the natural ecosystem, such as production, decomposition of organic matter, nutrient cycling, and contaminant removal, contributing to soil purification. Microorganisms can degrade and use triazines as a source of carbon and nitrogen for growth (catabolic degradation); in other cases, they degrade the pesticide by co-metabolic actions (CYCÓN et al., 2017).

Some studies address the issue of biostimulation by adding a nitrogen and a carbon source in terbuthylazine-contaminated soils in order to stimulate the mineralization of this herbicide through the local microbial population (intrinsic mineralization) (OSTROFSKY et al., 2002) based on the fact that soils with a history of herbicide application show more significant mineralization than soils without a history of herbicide addition (SILVA et al., 2015).

The soil mineralization rate of TBA is low and it takes time since it is not an attractive mean of bioremediation because the longer the time interval the greater the



possibility of the contaminated soil leaching and consequently the contamination of aquifers occurring (SILVA et al., 2015; LIMA et al., 2009). Therefore, many studies (SHAPIR et al., 2007) have focused on the isolation of bacteria with degradative capacity. Triazine biodegradation and mineralization can be performed either by single bacteria or by single strains (GRENNI et al., 2009). Bacteria and fungi capable of degrading terbuthylazine are present in Tables 1 and 2, respectively.

Some bioremediation techniques for terbuthylazine-contaminated soils such as bioaugmentation, biostimulation, and phytoremediation will be described next.

Table 1: List of prokaryotic organisms capable of degrading terbuthylazine.

Prokaryotic	Name	References
<b><math>\beta</math>-Proteobacteria</b>	<i>Advenella incenata</i>	Caracciolo et al., 2010
	<i>Janthinobacterium lividum</i>	
<b><math>\gamma</math>-Proteobacteria</b>	<i>Pseudomonas</i> sp. strain MHP41	Jacobsen et al., 2001
<b>Actinobacteria</b>	<i>Arthrobacter</i> sp.	Shapir et al., 2005
	<i>Rhodococcus wratislaviensis</i> FPA 1	Grenni et al., 2009

Table 2: List of fungi organisms capable of degrading terbuthylazine.

Prokaryotic	Name	References
<b>Eurotiomycetes</b>	<i>Aspergillus oryzae</i>	Pinto et al., 2012
	<i>Penicillium brevicompactum</i>	
<b>Agaricomycetes</b>	<i>Lentimula edode</i>	

Source: Authors.

## BIOAUGMENTATION

To decrease the environmental risk of soils with triazine, bioremediation strategies based on soil and water bioaugmentation have been proposed to convert these compounds into less toxic products.

Bioaugmentation is a biodegradation process involving the addition of endogenous or exogenous microorganisms to a contaminated site where they will promote the degradation of polluting compounds. This method is applied when natural degradation rates (intrinsic degradation) are slow due to a lack of microbial population, or when microorganisms lack the ability to metabolize and degrade the contaminants (SINGH, 2016).

There are few papers reporting that adding microbial strains to soil enhances the degradation of triazines in field studies. On the other hand, many papers show triazine degradation in laboratory bioaugmentation studies. Mandelbaum et al., (1995) tested *Pseudomonas* sp strain ADP for the degradation of  $> 1,000 \mu\text{g mL}^{-1}$  of

atrazine. Struthers et al., (1998) showed the ability of *Agrobacterium radiobacter* J14a to degrade 50-200 µg g<sup>-1</sup> of atrazine with mineralization rates higher than those obtained from uninoculated soil.

Another study with bioaugmentation for atrazine degradation by the bacterium *Arthrobacter aurescens* strain TC1, showed its effectiveness in soil and aquatic environments, also noting that 95% of terbuthylazine was removed from soil microcosms during the first three days of bioaugmentation (Silva et al., 2015).

*A. aurescens* TC1 has been reported to biodegrade atrazine more efficiently than most described triazine-degrading microorganisms (SHAPIR et al., 2007). The triazine catabolism of this bacterium is well established, occurring via hydrolytic displacement of the chlorine and amine substituents of the s-triazine ring mediated by the enzymes TrzN (catalyzes the initial dechlorination step to produce the hydroxy-s-triazine metabolite), AtzB and AtzC (both catalyze the sequential deamination of N-alkyl side chains) (SHAPIR et al., 2007). The performance of these reactions is environmentally relevant due to the fact that hydroxy-s-triazines and cyanuric acid pose lower risks to soil and aquatic organisms compared to the parent compounds (EFSA, 2011; WACKETT et al., 2002).

Regarding the time required to achieve effective soil decontamination, the work of Silva et al. (2015) showed that the inoculum density of the bioaugmentation bacteria is an important factor influencing the time required to achieve effective soil decontamination. The latter situation is relevant to represent real cases of associated soil contamination, such as accidental spills or poor storage/operation at utilities and inadequate loading or unloading sites (WACKETT et al., 2002).

Apparently, the lower efficacy of *A. aurescens* TC1 in removing terbuthylazine already aged in soil compared to the newly added herbicide may be related to the decreased availability of terbuthylazine during aging (BARRIUSO et al., 2004) due to its sorption to the soil organic carbon along with its hydrophobic nature

## BIOESTIMULATION

Biostimulation is a technique that requires the addition of nutrients to the soil that improves the degradative capacity of microorganisms capable of metabolizing the pollutant compound present in the site (WACKETT et al., 2002). This technique refers to

the addition of limiting nutrients such as phosphorus, nitrogen, oxygen, and electron donors to polluted sites (CARACCIOLO et al., 2009).

Sodium citrate is a compound widely used as a soil supplement to enhance the degradation of herbicides by stimulating the ability of the bacteria to degrade (biostimulation). Some studies show that this component has been an excellent source of carbon to aid the metabolism of atrazine in soil (SILVA et al., 2015; LIMA et al., 2009; CHELINHO et al., 2010).

Surfactants are organic molecules also used in biostimulation processes, that present a hydrophobic and a hydrophilic part. The hydrophilic part makes the surfactant water soluble while the hydrophobic part makes it bind to interfaces (VOLKERING et al., 1998). Surfactants can be natural (biosurfactants) or synthetic (produced by microorganisms from chemicals) (BUSTAMANTE et al., 2012).

Organic compounds can affect triazine degradation differently. For example, organic waste can adsorb herbicides, hindering their availability for biodegradation (CARACCIOLO et al., 2009), as in a study with pine waste where they hindered microbial degradation due to their high sorption capacity of terbutylazine, decreasing the bioavailability of the herbicide. On the other hand, oak residues did not increase herbicide sorption and terbutylazine degradation (GRENNI et al., 2009).

The organic correctives sheep dung, coffee grounds, composted pine bark, and coconut fiber were tested to reduce the leaching of atrazine, simazine, and terbutylazine in a soil with low organic matter content (0.9%), and a decrease in soil herbicide concentrations was also found when compared to unamended soils (FENOLL et al., 2014)

Recent data from Siedt et al., (2021) compared straw, compost, and biochar for suitability as an agricultural soil amendment to improve the microbial communities present and reduce pesticide mobility. These effects varied due to various aspects such as soil type, application rate, and production procedure of the organic material.

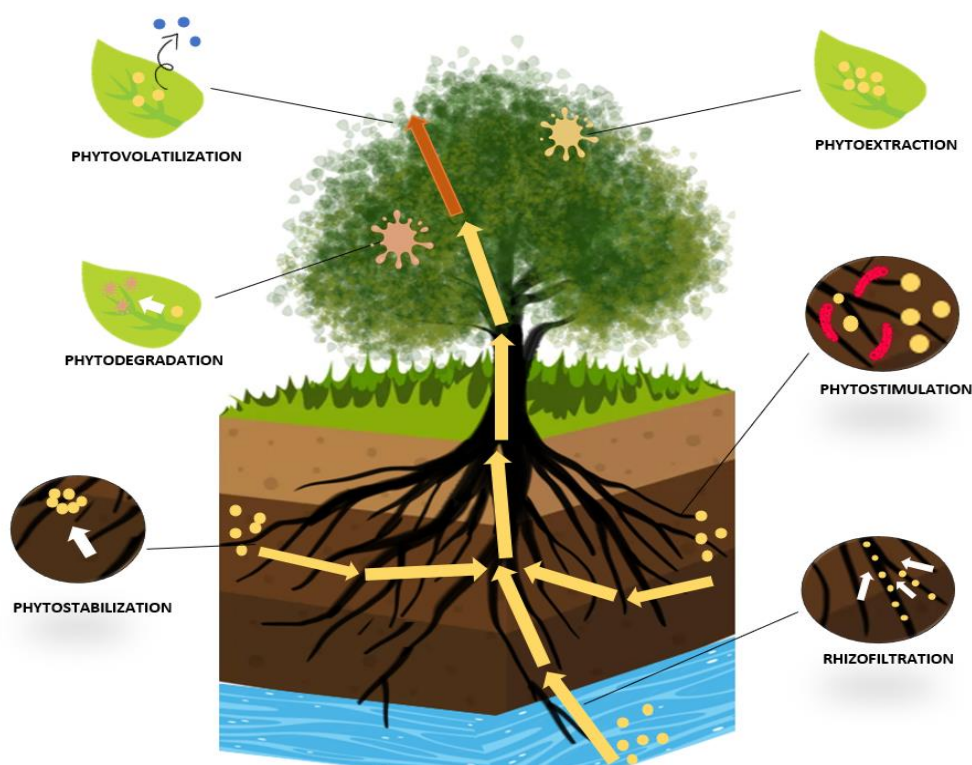
## **PHYTOREMEDIATION**

Phytoremediation consists on the use of herbaceous and woody plants in order to improve the microbial degradation of contaminated environments. It is based on the interactions between roots and rhizosphere microbial community (MERINI et al., 2009), having as an advantage the possibility to treat contaminated soil or water on-site

(ANCONA et al., 2017; ANCONA et al., 2020) including pesticides (SINGH et al., 2017).

According to Singh et al (2017), it is generally known that plants can remediate organic pollutants through phytoextraction, i.e., the direct uptake of contaminants by roots and subsequent accumulation of non-phytotoxic metabolites in the plant tissues (phytoaccumulation). By the process of phytodegradation, xenobiotic substances are removed from the soil and from water, and they are broken down into less toxic or non-toxic compounds within the plant by various metabolic processes through the action of plant-produced compounds. Through the rhizodegradation mechanism, plants release exudates and enzymes that enhance biochemical transformations and/or mineralization due to microbial activity in the rhizosphere. The stimulation of microbial activity in the rhizosphere of plants can also stimulate the biodegradation of various toxic organic substances by the dynamic synergy that exists between plant roots and soil microorganisms (ANDERSON et al., 1995; ANDERSON et al., 1993; WILSON et al., 2000; SING et al., 2003; DZANTOR et al., 2002).

Figure 3: Mechanisms used by plants in the phytoremediation process.



Source: Authors.

During and after herbicide application on agricultural land, triazines can be transported to ground and surface water and also to the atmosphere (PIONKLE et al., 1988). In water and soil, the terbuthylazine molecule undergoes various biotic and abiotic degradation processes, such as photolysis, oxidation, hydrolysis, and biodegradation, leading to dealkylation of the amine groups, dechlorination, and subsequent hydroxylation (BEHKI et al., 1986).

The effectiveness of phytoremediation in removing triazines is impaired by their intrinsic toxic effects (they act on photosynthesis and glycogenesis by inhibiting photosystem II) and depends on the plant's ability to resist their biocidal effect and to form synergistic interactions with microorganisms (CARACCIOLO et al., 2009).

Studies show that herbaceous plants such as *Lolium* sp species were able to degrade atrazine in soil. *L. multiflorum* was able to germinate and grow in the presence of 1 mg kg of atrazine, with pesticide removal exceeding natural attenuation (MERINI et al., 2009). Maize demonstrated atrazine removal capacity, but with high herbicide accumulation (SÁNCHEZ et al., 2019).

Arbuscular mycorrhizal fungi *Funneliformis mossae* in cooperation with the plant *Canna indica* were able to degrade atrazine in water, where 96% removal of atrazine was found in 21 days, compared to 68% with phytoremediation only (DONG et al., 2016). Some plants are able to translocate atrazine and partially degrade it; simazine was found to accumulate in aquatic plants such as *Myriophyllum aquaticum* and *Canna* hybrids (KNUTESON et al., 2002). Phytovolatilization of pesticides from leaves is not considered very important (NEDJIMI et al., 2021).

In recent years, electrokinetic phytoremediation technology has also been tested to improve the phytoremediation of atrazine. In these tests, phytoremediation of corn with electric current (with voltage gradients of 2 and 4 V cm<sup>-1</sup>) was used. The combined technology significantly (by 20-30%) improved the total accumulation of atrazine in plant tissues because atrazine was mobilized by the electric current (SÁNCHEZ et al., 2019).

Other electrokinetic phytoremediation tests were performed with ryegrass (*Lolium perenne* L.). The total removal of atrazine (2 mg kg<sup>-1</sup> soil) by the plant increased by 7% with the help of low voltage gradients (1 V cm<sup>-1</sup>, 6 and 24 h per day) (SÁNCHEZ et al., 2019).

## CONCLUSIONS

- Terbutylazine has become a commonly found pesticide in water resources in Europe, especially after its frequent use following the European-wide ban on atrazine.
- Terbutylazine has a high soil persistence due mainly to its high hydrophobicity and slow biodegradation rate. However, its low sorption coefficient indicates that this herbicide is poorly adsorbed in soil increasing its leaching capacity.
- Terbutylazine half-life is quite variable depending on the characteristics of each soil and it is also influenced by external factors. The non-dissipation of this molecule in the soil also increases the risks of leaching and runoff, and thus the contamination of groundwater and surface water.
- Although plants capable of resisting the toxic effects of triazine can promote degradation through their exudates, the removal of terbutylazine occurs by microorganisms (bacteria, archaea, and fungi). Furthermore, only prokaryotes can perform the complete degradation pathways up to their mineralization.
- Alternatively, bacteria capable of enhancing herbicide degradation can be bioaugmented.
- The DET metabolite promotes extended soil contamination and higher groundwater contamination risk.
- A better understanding of soil interactions and of soil aggregation will facilitate the development of bioremediating materials to enhance sorption and decrease the dissipation of pesticides in soils.

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