Chemosphere 185 (2017) 119–126

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Assessing the phytoremediation potential of crop and grass plants for atrazine-spiked soils

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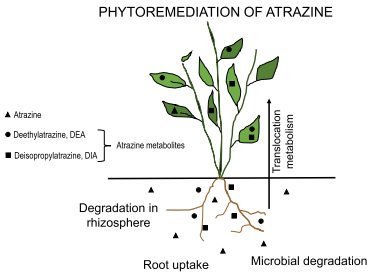
HIGHLIGHTS

- The presence of plants increased atrazine removal up to 36% with respect to unplanted pots.
- Plants were capable of accumulating atrazine and its N-dealkylated metabolites in their tissues.
- Maize was the plant species with the highest ability to accumulate atrazine derivatives.
- Atrazine was mainly removed by biochemical degradation in the rhizosphere.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 May 2017
Received in revised form
3 July 2017
Accepted 3 July 2017
Available online 4 July 2017

Handling Editor: T. Cutright

Keywords:
Atrazine
Crops
Grasses
Phytoremediation
Rhizodegradation
Polluted soil

ABSTRACT

Pollution of soil and groundwater by atrazine has become an increasing environmental concern in the last decade. A phytoremediation test using plastic pots was conducted in order to assess the ability of several crops and grasses to remove atrazine from a soil of low permeability spiked with this herbicide. Four plant species were assessed for their ability to degrade or accumulate atrazine from soils: two grasses, i.e., ryegrass (*Lolium perenne*) and tall fescue (*Festuca arundinacea*), and two crops, i.e., barley (*Hordeum vulgare*) and maize (*Zea mays*). Three different doses of atrazine were used for the contamination of the pots: 2, 5 and 10 mg kg^{-1}. 16 days after spiking, the initial amount of atrazine was reduced by 88.6–99.6% in planted pots, while a decrease of only 63.1–78.2% was found for the unplanted pots, thus showing the contribution of plants to soil decontamination. All the plant species were capable of accumulating atrazine and its N-dealkylated metabolites, i.e., deethylatrazine and deisopropylatrazine, in their tissues. Some toxic responses, such as biomass decreases and/or chlorosis, were observed in plants to a greater or lesser extent for initial soil doses of atrazine above 2 mg kg^{-1}. Maize was the plant species with the highest ability to accumulate atrazine derivatives, reaching up to 38.4% of the initial atrazine added to the soil. Rhizosphere degradation/mineralization by microorganisms or plant enzymes, together with degradation inside the plants, have been proposed as the mechanisms that contributed to a higher extent than plant accumulation to explain the removal of atrazine from soils.

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http://dx.doi.org/10.1016/j.chemosphere.2017.07.013
0045-6535/

1. Introduction

Atrazine (6-chloro-*N*-ethyl-*N*-isopropyl-1,3,5-triazine-2,4-diamine) is a selective systemic herbicide used for the pre- and-post-emergence control of annual grasses and broadleaf weeds being usually applied, among other crops, to corn, sorghum and sugar cane. Following its first introduction into the market approximately 50 years ago, it has become one of the most heavily used agricultural herbicides in the world, especially in the United States and developing countries such as China (Jablonowski et al., 2011; Mudhoo and Garg, 2011). Atrazine has also been widely used in Europe until 2006, when its commercial use was banned in the European Union.

Atrazine has a moderate aqueous solubility; nevertheless, it has the potential to act as both non-point and point source for the contamination of surface and groundwater, due to its low adsorption and moderate half-life in soils (Ribeiro et al., 2005; Fan and Song, 2014). In fact, high levels of atrazine have been detected in drinking waters in Europe and the USA (Mahía et al., 2007). Bioremediation technologies (including phytoremediation) have been shown to be effective in the removal of atrazine from soils; nevertheless, a recent review by Fan and Song (2014) has concluded that the existence of contradictory results suggests further research is needed in this field.

Phytoremediation is a well-known technology that uses plants to remediate inorganic and organic contaminants in the environment. The role of the plants includes the degradation, adsorption, volatilization and accumulation of pollutants and/or the promotion of the soil rhizosphere activity (Newman and Reynolds, 2004). Phytoremediation has several advantages, such as its low cost and relative simplicity and, moreover, it is environmental friendly and does not produce secondary pollution. So, there is a bright future for the phytoremediation of contaminated soils (Ibrahim et al., 2013).

The uptake and translocation of organic compounds by plants are dependent on the physical-chemical characteristics of the pollutants, i.e. hydrophobicity (lipophilicity), solubility, polarity and molecular weight, the plant species and environmental factors (Turgut, 2005). Atrazine is moderately hydrophilic (log K_{ow} 2.5) and is likely to partially be adsorbed into roots or to be taken up by roots and move across cell membranes to reach the above-ground portion of plants. The fate of pesticides in the soil is strongly related to vegetation; in fact, organic pollutants are usually removed more quickly in planted soils than in soils without plants (Singh et al., 2004). Rhizosphere, the narrow layer of soil together to plant roots, is a zone of high microbiological activity, which is caused by root exudates containing carbohydrates, amino acids and organics acids (Curl and Truelove, 1986). Therefore, the use of vegetation at the polluted sites can overcome some of the inherent limitations to the biological clean-up approach, such as low microbial population or inadequate microbial activity (Singh et al., 2004).

This work forms part of a wider research project focused on the combination of phytoremediation and electrokinetic remediation to decontaminate soils polluted by atrazine. As a prior step, it is advisable to carry out preliminary studies in order to select plant species capable of degrading and/or accumulating atrazine. The main goals of this work were to assess the tolerance of several crops and grass plants to increasing atrazine soil concentrations and to study the role of plants in the removal of atrazine by phytoremediation. This paper shows the results from a pot experiment conducted with a low-permeability soil spiked with atrazine using four different plant species: the grass species *Festuca arundinacea* (tall fescue) and *Lolium perenne* (ryegrass), and the crop species *Hordeum vulgare* (barley) and *Zea mays* (maize). These plant species were selected based on previous studies about biomass production and survival capability in soils contaminated by atrazine and/or other organic pollutants. Moreover, all of them have been reported to be effective in the removal of organics by phytoremediation (Singh et al., 2004; Huang et al., 2007; Li et al., 2012; Ibrahim et al., 2013).

2. Materials and methods

2.1. Soil

The soil used in the present study was a clay loam collected from a region of high agrarian activity in central Spain (Mora de Toledo, Toledo), which could be vulnerable to pollution by pesticides. The most important physical-chemical characteristics of the soil are shown in Table 1. Soil pH and electrical conductivity (EC) were measured in a 1:5 soil/water mixture; organic carbon was determined using a total organic carbon analyser (Shimadzu TOC-VCSH, Columbia, USA); particle size distribution (clay, silt and sand content) was determined using laser diffractometry (Beckman Coulter LS, Fullerton, USA); cation exchange capacity (CEC) was measured by the ammonium acetate saturation method (MAPA, 1994). Specific gravity and water holding capacity were determined according to the ASTM Standards D854 and D2980, respectively. The soil was air dried and passed through a 2-mm sieve to remove stones and any plant residues prior to the experiment.

2.2. Plants and experimental design

Four plant species were used in the phytoremediation experiment: tall fescue (*Festuca arundinacea*), ryegrass (*Lolium perenne*), barley (*Hordeum vulgare*) and maize (*Zea mays*). Barley (spring two rows cultivar) and maize (dent corn hybrid cultivar) commercial varieties were used. Ryegrass and tall fescue seeds were purchased as certified seed at the Oregon Seed Certification Service (Corvallis, USA). All seeds were pre-germinated using a 0.5 mM calcium sulphate solution; pre-germination was carried out in a germination chamber for 3 days at 28 °C. After the germination period, only healthy seedlings with uniform size were selected. Plants were then gently removed from the growing medium and then transplanted to the soil of the plastic pots used in the experiment.

The phytoremediation experiment was carried out in a growth chamber with a 16-h day length and mean day and night temperatures of about 27 °C and 16 °C, respectively. Relativity humidity was maintained between 60% and 70%. The light source consisted of Sylvania Gro-lux Cool White Fluorescent Light (36 w) and Philips Master HPI-T Plus Metal Halide Lamps (400 w) in a 14:1 ratio, supplying a light intensity of 64,000 lux and photosynthetically active radiation (PAR) of 1010 μmol m^{-2} s^{-1} at the top of the canopy. 350 g of air-dried soil were put in plastic pots of 10 cm diameter and 7 cm depth. Twenty seedlings of tall fescue and

Table 1
Selected properties of soil used in the experiment.

Property	Value
Soil organic carbon content (%)	0.60
Specific gravity (g cm^{-3})	1.54
Water holding capacity	33%
pH	9.42
CEC (cmol kg^{-1})	23.42
Electrical conductivity (mS cm^{-1})	0.15
Clay (<0,002 mm)	39.6%
Silt (0,002–0,05 mm)	22.6%
Sand (0,05–2 mm)	37.8%