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Different dissolved organic matter (DOM) characteristics lead to diverse atrazine adsorption traits on the non-rhizosphere and rhizosphere soil of *Pennisetum americanum* (L.) K. Schum

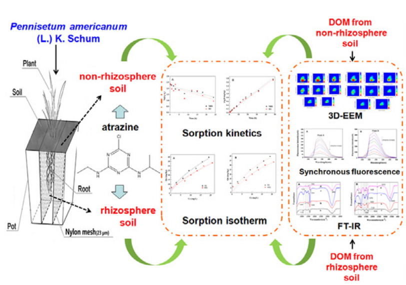
Bo Cao, Zhao Jiang, Jinmei Li, Xiuyuan Zhang, Yang Hu, Jianing Chen, Ying Zhang*

School of Resources & Environment, Northeast Agricultural University, Harbin, 150030, PR China

HIGHLIGHTS

- Rhizosphere soil (RS) exhibit different property from non-rhizosphere soil (NRS).
- RS exhibit higher atrazine adsorption capacity than that of NRS.
- DOM from RS exhibit stronger atrazine-binding ability than that of DOM from NRS.
- DOM from RS and NRS show different fluorescence traits when binding atrazine.
- *P. americanum* regulates the fate of atrazine in RS by changing the soil DOM traits.

GRAPHICAL ABSTRACT



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ABSTRACT

Plant activities might alter the environmental behavior of organic pollutants in rhizosphere soil during phytoremediation. To further illustrate the mechanisms underlying the varying adsorption about the different adsorbing abilities of rhizosphere soil (RS) and non-rhizosphere soil (NRS) for the same pollutant, atrazine was selected to investigate the adsorption traits in the NRS and RS of *Pennisetum americanum* (L.) K. Schum (*P. americanum*), a potential phytoremediator of atrazine pollution. Furthermore, the different fluorescence spectral properties of the dissolved organic matter (DOM) extracted from RS and NRS when binding with atrazine were also investigated. RS exhibited a higher atrazine adsorption capacity than NRS, although the kinetic and isothermal properties of atrazine adsorption onto the two kinds soil were described by a pseudo second-order model and the Freundlich model. The DOM extracted from RS showed a stronger atrazine-binding ability than that extracted from NRS, as proven by the much more obvious decrease in fluorescence intensity when binding with atrazine. Although synchronous fluorescence spectra analysis suggested that both DOM types bind atrazine using a static fluorescence quenching mechanism, Fourier transform infrared spectroscopy showed that some distinct functional groups, which might liable to combine with atrazine, were found in only the DOM extracted from RS. Considering the findings mentioned above and the fact that the typical chemical characteristics of RS were different from those of NRS, we concluded that the *P. americanum* enhances the atrazine adsorption ability of RS by regulating the chemical characteristics and atrazine-binding ability of DOM in RS.

* Corresponding author.
E-mail address: zhangying_neau@163.com (Y. Zhang).

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine), one of the most widely used triazine herbicides, is used worldwide for the inhibition of broad leaf and grassy weeds in crop farmland, such as corn, sorghum and sugar cane crops (Barr et al., 2007). Though atrazine controls weeds effectively at low cost, it may also pose risks to the environment and organism health after application. These adverse impacts triggered by atrazine can be mainly attributed to its long-term environmental residue properties, and atrazine is also considered an environmental endocrine disruptor that causes obvious bio-toxicity to various kinds of living things, including microorganism, plant, animal and human (Lasserre et al., 2009). Therefore, it is essential to avoid the harms caused by atrazine and eliminate it from the environment, especially from the soil, using proper technique.

Phytoremediation has long been considered as an eco-friendly pollution remediation technique for the soil polluted by organic contaminants or heavy metals (Hseu et al., 2010). Phytostabilization is one of the phytoremediation techniques for the contaminated soil. The key mechanism for this technique is illustrated as the stabilization of the soil contaminants by the combined effect of root exudates and associated microorganism (Mahar et al., 2016). It could reduce the harms to environment and organisms caused by pollutants according to decrease the migration of pollutants into deeper soil, groundwater, plant and food chain (Lebrun et al., 2018). In addition, the plant also could regulate the environmental behavior or bioavailability of the contaminants, as well as boost the metabolic abilities of the microorganism in rhizosphere soil by release root exudates which containing bioactive compounds, such as organic acids, amino acids, proteins, sterols and other compounds with various chemical groups (Lefevre et al., 2013; Vassilev et al., 2004). The interaction between the plant roots and the rhizosphere microorganisms described above also could accelerate the removal of the target pollutants from soil (Kong et al., 2018).

Soil sorption has an important impact on the fate and bioavailability of the contaminants including atrazine in the soil. Some previous literature reported that the soil organic matter (SOM) existing in the soil solid phase plays an irreplaceable role in adsorbing contaminants in soil particles (Palma et al., 2007). In particular, dissolved organic matter (DOM), the most active and mobile form of SOM, consists of both hydrophilic and hydrophobic components, which are rich in functional groups (Provenzano et al., 2010). These functional groups give DOM various natural binding sites and enable its preferential pollutants adsorption. Furthermore, it has been widely recognized that the quantity and quality of DOM, characterized by the contents of the hydrophilic and hydrophilic fractions as well as the kinds or number of functional groups, also could affect the interaction between the contaminants and DOM (Yuan et al., 2016). As a result, the contaminants might exhibit different fates in soil containing DOM with various characteristics.

Despite the plant that belong to *Pennisetum* genus have been found to have the potential to remediate soil contaminated by atrazine (Singh and Mukerji, 2006; Zhang et al., 2014), whether atrazine exhibit different environmental behaviours in the rhizosphere and non-rhizosphere soil of *Pennisetum* genus plant were unclear. In addition, the role of the DOM, extracted from the rhizosphere and non-rhizosphere soil of *Pennisetum* genus plant, in regulating sorption characteristics of atrazine onto the two kinds of soil mentioned above is also poorly reported. In the present work, we investigated whether the DOM extracted from the rhizosphere (RS) and non-rhizosphere soil (NRS) of *Pennisetum americanum* (L.) K. Schum (*P. americanum*) could exhibit different atrazine binding characteristics, thus changing environmental behaviors of atrazine in RS and NRS of *P. americanum*. In specific, the sorption property of atrazine onto RS and NRS of *P. americanum* was investigated by assessing the adsorption kinetics and isotherm data or models respectively. In addition, the different atrazine binding ability of the DOM extracted from RS and NRS was researched by detecting and comparing the different fluorescence quenching characteristics of the tested DOM during the period of binding with atrazine. In particular, the fluorescence quenching characteristics of the tested DOM were detected by three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy, synchronous fluorescence and Fourier transform infrared (FT-IR) spectroscopy technology. Together, these results of this study provide insightful information about the different environmental behaviors of atrazine in non-rhizosphere and rhizosphere soils of *P. americanum*. Furthermore, this study also contributes to better understanding that changing the properties of DOM in soil might be one of the mechanisms for *P. americanum* to regulate the fate of pollutants in rhizosphere soil during the phytoremediation process.

2. Materials and methods

2.1. Soil preparation

The soils used in this research were the rhizosphere and non-rhizosphere soils of *Pennisetum americanum* (L.) K. Schum (*P. americanum*). The two different kinds of soil were prepared as follows: the fresh black soil was collected from the surface layer (0–20 cm) of farmland located in the Shuang cheng City of Heilongjiang Province, China. The collected soil described above was air-dried and sieved through a 1-mm mesh. A rhizobox was used in this research to obtain the RNS and the RS of *P. americanum*. The rhizobox was divided into three sections by a 23-μm nylon mesh in a pot. The three sections, including the rhizosphere zone in the center of the rhizobox and the two non-rhizosphere zones were located on the left and right side of the rhizobox respectively (Fig. S1). The *P. americanum* seeds, which were germinated beforehand according to the method reported by Jiang et al. (2016a), were only sown in the rhizosphere zone of the rhizobox after the meshed soil was added to the rhizobox. All the pots described above were placed into a greenhouse kept at $27 \pm 1\ ^{\circ}C$ during the day and $20 \pm 1\ ^{\circ}C$ during the night, and they were watered every two days. After a 30-day culture, *P. americanum* was harvested, and the remaining soil in the rhizosphere zone mentioned above was considered as the RS, while the soil in the other two non-rhizosphere zones of the rhizobox that without sowing *P. americanum* was designated as the NRS. The two kinds of soil were kept at $-20\ ^{\circ}C$ before the subsequent adsorption experiments.

In addition, some of the typical soil physicochemical properties of RS and NRS were determined by the methods described below:(1) the contents of nitrate nitrogen (NO_3^--N), ammonia nitrogen(NH_4^+-N), available phosphorus and total phosphorus were determined with an Analytical continuous-flow AutoAnalyzer (Seal-AA3, Germany) by flow injection analysis technology; (2) soil pH was determined in water (1:2.5, soil/water) by a pH meter (Rex PHS-3C, China); (3) total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu TOC-VCPN, Japan) according to the method reported by Nan et al. (2016); and (4) the cation exchange capacity (CEC) was determined according to the method reported by Bielská et al. (2018). Each kind of soil sample was tested in triplicate.

2.2. Adsorption experiments

The adsorption characteristics of atrazine onto the two different soils described above were studied by batch experiment. Five