Chemosphere 209 (2018) 439–448

Contents lists available at ScienceDirect

Chemosphere

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

Phytoextraction and biodegradation of atrazine by *Myriophyllum spicatum* and evaluation of bacterial communities involved in atrazine degradation in lake sediment

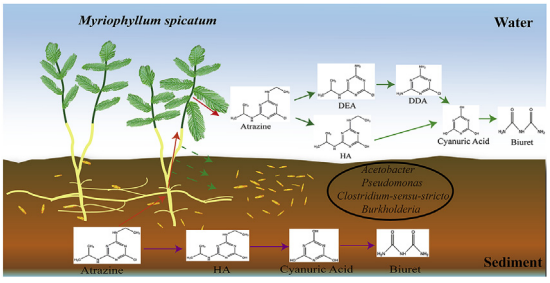
Mengjie Qu [a], Na Li [a], Huidong Li [a], Tewu Yang [b], Wei Liu [c], Yupeng Yan [a], Xionghan Feng [a], Duanwei Zhu [a, *]

[a] College of Resources and Environment, Huazhong Agricultural University, Wuhan, 430070, China
[b] College of Plant Sciences and Technology, Huazhong Agricultural University, Wuhan, 430070, China
[c] Shandong Analysis and Test Center, Shandong Academy of Sciences, Jinan, 250014, China

HIGHLIGHTS

- *M. spicatum* can absorb atrazine in sediment effectively.
- The formation of biuret suggested the ring opening of atrazine in *M. spicatum*.
- Degradation of atrazine followed via dechlorination rapidly in sediments.
- *M. spicatum* and atrazine can change the amounts of *Nitrospirae* and *Acidobacteria*.
- *Acetobacter* was most probably responsible for the degradation of atrazine.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 January 2018
Received in revised form
11 May 2018
Accepted 7 June 2018
Available online 14 June 2018

Handling Editor: T Cutright

Keywords:
Atrazine
Sediment
Myriophyllum spicatum
Phytoextraction
Degradation
Bacterial community

ABSTRACT

The accumulation of atrazine in lake sediments leads to persistent contamination, which may damage the succeeding submerged plants and create potential threats to the lake eco-environment. In this study, the degradation characteristics of atrazine and its detoxication by *Myriophyllum spicatum* and the associated bacterial community in lake sediments were evaluated. *M. spicatum* absorbed more than 18-fold the amount of atrazine in sediments and degraded atrazine to hydroxyatrazine (HA), deelthylatrazine (DEA), didealkylatrazine (DDA), cyanuric acid (CYA) and biuret. The formation of biuret suggested for the first time, the ring opening of atrazine in an aquatic plant. The residual rate of atrazine was $6.5 \pm 2.0\%$ in *M. spicatum*-grown sediment, which was significantly lower than the $18.0 \pm 2.5\%$ in unplanted sediments on day 60 ($P < 0.05$). Moreover, on day 15, the increase in contents of HA, CYA and biuret in *M. spicatum*-grown sediment indicated that *M. spicatum* promoted the degradation and removal of atrazine following rapid dechlorination. The colonization of *M. spicatum* and the addition of atrazine altered the structure of the dominant bacterial community in sediments, including effects on *Nitrospirae* and *Acidobacteria*. Based on the maximum amount among the genera of atrazine-degrading bacteria, *Acetobacter* was most likely responsible for the degradation of atrazine. Our findings reveal the natural attenuation of atrazine by aquatic organisms.

* Corresponding author.
E-mail address: zhudw@mail.hzau.edu.cn (D. Zhu).

https://doi.org/10.1016/j.chemosphere.2018.06.055
0045-6535/

1. Introduction

As a selective herbicide for annual grass and broadleaf weed control, atrazine is used worldwide (Brodeur et al., 2009; Udikovićkolić et al., 2012; Mahler et al., 2017). However, atrazine and its metabolites cause ecological damage in both groundwater and surface water sources (Grillo et al., 2014; Vonberg et al., 2014; Wirbisky et al., 2016). The half-life of atrazine biodegradation ranges from 10 to 105 day (d) in surface water (Cecilia and Maggi, 2016). Once released into aquatic ecosystems, atrazine tends to be adsorbed and immobilised by sediments because of the high lipophilicity and poor water solubility (Yang and He, 2015; Douglass et al., 2017; Qu et al., 2017). The contaminated sediments act as a source releasing atrazine to the overlying water (Guo et al., 2016). Moreover, the sediment feature is closely related with aquatic organisms, such as the aquatic plants and microbes, which play an important role in the processes of degrading herbicides (Paixão et al., 2011; Liu et al., 2016a; Singh and Singh, 2016).

Aquatic vegetation contributes to the natural attenuation of atrazine (Moeder et al., 2017). *Myriophyllum spicatum* is a cosmopolitan species that primarily colonises in eutrophic waters (Germ et al., 2006; Turull et al., 2017), and commonly grows in the shallow lakes at middle and lower reaches of the Yangtze River (Xing et al., 2013). *M. spicatum* was selected for investigation in this work. A report suggests that *M. spicatum* could accelerate the degradation of atrazine in sediments (Qu et al., 2017). However, under the influence of *M. spicatum*, the fate of atrazine remains poorly described.

Microbes can utilise herbicides as growth substrates. Various atrazine-degrading bacterial strains, such as *Rhodococcus*, *Microbacterium*, *Deinococcus*, *Delftia acidovorans* and *Pseudomonas* have been isolated from sediments and shown to degrade atrazine as the sole carbon resource (Vargha et al., 2005). Plant roots can promote the growth of specific bacterial groups and create well-defined bacterial communities around the rhizosphere (Liu et al., 2016b). Few attempts have assessed the influence of submerged plants on the bacterial community in sediments although some atrazine-degrading bacterial genera have been isolated from aquatic environments enriched with atrazine.

In this work, the degradation of atrazine, sediment bacterial diversity, and atrazine-degrading strains were studied in *M. spicatum*-planted and unplanted sediments. The objectives of this paper were to i) determine the uptake and degradation of atrazine by *M. spicatum*, ii) investigate the microbial degradation of atrazine in sediments and iii) explore the changes of bacterial functional diversity and potential atrazine degrading strains in sediment under the influence of *M. spicatum*. This study will be useful to assess the ecological risks in lakes after atrazine enters sediments and provides a potential bioremediation for atrazine polluted lakes.

2. Materials and methods

2.1. Sediment collection

The sediment used in the present study was collected from the centre of Nanhu Lake (30°28′ 55.17″, 114°22′ 37.65″), a typical eutrophic lake, which is located in a suburb of Wuhan City, China and receives agricultural nonpoint source pollution and urban wastewater. The sediment was passed through a 2-mm sieve to remove stones and plant residues. The initial background concentration of atrazine in this sediment was 0.10 ± 0.03 mg/kg. However, no atrazine or metabolites persisted in the sediment during storage with overlying water under a natural condition for three months from 15th May to 15th August, with the temperature at 31.70 ± 3.73 °C in the day and 23.93 ± 3.50 °C at night. At the beginning of the incubation, the physical and chemical properties of the tested sediment were as follow: pH 7.47, 64.64% of moisture content, 3.48 cmol/kg of cation exchange capacity, and 54.91 g/kg of organic matter content.

2.2. Chemicals and submerged macrophyte

Atrazine, hydroxyatrazine (HA), deethylatrazine (DEA), deisopropylatrazine (DIA), didealkylatrazine (DDA), cyanuric acid (CYA) and biuret standards were purchased from the German Dr. Ehrenstorfer Company, with purity ≥99.5%. The $^{13}C_3$-atrazine standard was purchased from Cambridge Isotope Laboratories Inc., with purity ≥98%. HPLC-grade methanol was purchased from Sigma-Aldrich Trading Co., Ltd in Shanghai City, China. All other chemicals in the experiment were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd in Shanghai City, China.

Plant material of *M. spicatum* was collected from Wuhan Botanical Garden, Chinese Academy of Sciences in Wuhan City, China. The *M. spicatum* was pre-cultivated in Nanhu Lake sediment for a period of 30 d.

2.3. Experimental design

2.3.1. Pre-treatment of the sediment

Intentionally high and low atrazine concentrations were selected to elicit a measureable response within the experimental duration. Hence, 10 mL of methanol (CH_3OH) containing 100 mg/L atrazine or 10 mL of CH_3OH without atrazine was added to 1.41 kg of wet sediment (0.5 kg of dry sediment) at concentrations of 2.0 or 0 mg/kg dry weight (DW) sediment, respectively. Moreover, to determine the transportation of atrazine by *M. spicatum*, 5 mL of *n*-nonane containing 100 mg/L $^{13}C_3$-atrazine was mixed with 5 mL of CH_3OH containing 100 mg/L unlabelled atrazine and then the mixture was added to 1.41 kg of wet sediment. Because of the high price of $^{13}C_3$-atrazine, the 2.0 mg/kg DW sediment of atrazine including 1.0 mg/kg DW sediment of $^{13}C_3$-atrazine was used for the plant cultivation in lake sediments. In brief, the sediments used in this incubation were divided into five groups: sediment with plants but without atrazine (CK-P); sediment without atrazine and plants (CK); sediment with 2.0 mg/kg DW sediment of atrazine and plants (AT-P); sediment with 2.0 mg/kg DW sediment of atrazine but without plants (AT); sediment with 1.0 mg/kg DW sediment of $^{13}C_3$-atrazine and 1.0 mg/kg DW sediment of unlabelled atrazine and plants ($^{13}C_3$-AT-P).

2.3.2. Plant culture

In the groups CK-P, AT-P and $^{13}C_3$-AT-P, six cuttings with 20 cm in length of the apical part of *M. spicatum* (approximately 12 g) were planted in a plastic pot (bottom diameter, depth and upper-stem diameter: 135 × 165 × 105 mm, respectively) with 1.41 kg of wet sediment, which contained 2 mg/kg DW sediment of atrazine or was without atrazine application. Then, three pots with plants were placed in a large tank (inner length, width and height: 680 × 520 × 390 mm, respectively), which was then flooded with 120 L of tap water after sunlight exposure for 30 min. Furthermore, the incubation steps of the groups CK and AT followed those of the groups CK-P, AT-P and $^{13}C_3$-AT-P, except no plants were added. Water was supplemented in tanks when necessary to maintain constant water content. Each group was replicated for 4 times and each sample was prepared in triplicate.

Exposure began on 15th August 2017 and was completed on 16th October 2017. During the experiment, the temperature was 27.51 ± 5.22 °C in the day and 20.53 ± 3.83 °C at night. Isotopic samples and plant samples were collected on days 15, 45 and 60.