



Effectiveness of urea in enhancing the extractability of 2,4,6-trinitrotoluene from chemically variant soils



Padmini Das^a, Dibyendu Sarkar^{a,*}, Konstantinos C. Makris^b, Pravin Punamiya^a, Rupali Datta^c

^a Department of Earth and Environmental Studies, Montclair State University, NJ, USA

^b Cyprus International Institute of the Environment, Harvard School of Public Health, Cyprus

^c Department of Biological Sciences, Michigan Technological University, MI, USA

HIGHLIGHTS

- We investigated the effectiveness of urea in increasing TNT extraction from soils.
- Adsorption and desorption of TNT are investigated in four chemically variant soils.
- Hysteretic desorption of TNT in soils suggested the need of using an extractant.
- Solubilizing effect of urea is influenced by the soil-properties.
- The effective urea concentrations are within the agronomic fertilizer-N rates.

ARTICLE INFO

Article history:

Received 5 January 2013
Received in revised form 24 May 2013
Accepted 4 June 2013
Available online 5 July 2013

Keywords:

TNT
Urea
Adsorption
Desorption
Solubilizing agent

ABSTRACT

One of the major challenges in developing an effective phytoremediation technology for 2,4,6-trinitrotoluene (TNT) contaminated soils is limited plant uptake resulting from low solubility of TNT. The effectiveness of urea as a solubilizing agent in increasing plant uptake of TNT in hydroponic systems has been documented. Our preliminary greenhouse experiments using urea were also very promising, but further characterization of the performance of urea in highly-complex soil-solution was necessary. The present study investigated the natural retention capacity of four chemically variant soils and optimized the factors influencing the effectiveness of urea in enhancing TNT solubility in the soil solutions. Results show that the extent of TNT sorption and desorption varies with the soil properties, and is mainly dependent on soil organic matter (SOM) content. Hysteretic desorption of TNT in all tested soils suggests irreversible sorption of TNT and indicates the need of using an extractant to increase the release of TNT in soil solutions. Urea significantly ($p < 0.0001$) enhanced TNT extraction from all soils, by increasing its solubility at the solid/liquid interface. Soil organic matter content and urea application rates showed significant effects, whereas pH did not exert any significant effect on urea catalysis of TNT extraction from soil. The optimum urea application rates (125 or 350 mg kg⁻¹) for maximizing TNT extraction were within the limits set by the agronomic fertilizer-N rates used for major agricultural crops. The data obtained from this batch study will facilitate the optimization of a chemically-catalyzed phytoremediation model for cleaning up TNT-contaminated soils.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

2,4,6-Trinitrotoluene (TNT) is a major component of composition B (Comp B), a commonly used military formulation composed of toxic explosive compounds (Douglas et al., 2012). Due to its long persistence in the environment and its toxic and mutagenic effects on organisms, including humans, substantial efforts have been put into developing effective remediation techniques for TNT contam-

inated soils. Most of the contaminated sites use traditional *ex situ* remediation methods like incineration – which destroys soil structure and disrupts ecology – and dumping which displaces untreated contamination to another site with potential leaching into groundwater (Peterson et al., 1998). However, over the past two decades, the search for a cost-effective, ecologically safe and environmentally sound remediation technique has led to the development of *in situ* remediation processes like immobilization of TNT using surface amendments (Hatzinger et al., 2004; Fuller et al., 2005; Douglas et al., 2012), bioremediation using TNT degrading bacteria and fungi (Nyanhongo et al., 2005), and phytoremediation using TNT accumulating plants (Hannink et al., 2002).

* Corresponding author. Address: Department of Earth and Environmental Studies, Environmental Management Program, Montclair State University, 1 Normal Avenue, Montclair, NJ 07043, USA. Tel.: +1 973 655 7273.

E-mail address: sarkard@mail.montclair.edu (D. Sarkar).

Bioremediation of TNT has met with mixed success due to the variability in binding of TNT to various soil types (Larson et al., 2008). Limited bioavailability resulting from the low aqueous solubility of TNT (100–200 mg L⁻¹ at room temperature; Ro et al., 1996) restricts plant uptake and reduces the effectiveness of phytoremediation. To overcome this problem, we propose using a solubilizing agent as an amendment to increase the solubility of TNT in soil solutions, thereby enhancing the uptake of TNT by plants. Our group has proposed a new innovative phytoremediation technique using urea – a common N-fertilizer – as the solubilizing agent to increase solubility and phytoavailability of TNT from aqueous solutions and soil. Urea has long been used as a chaotropic agent in increasing solubility of membrane proteins and dissociating antigen–antibody complexes (Hatefi and Hanstein, 1969). Chaotropic agents are specific anions (SCN⁻) or polar carbamide derivatives (urea) which modify the water structure around aggregated proteins or sugars, increasing the solubility of their hydrophobic regions in aqueous environments (Farrah et al., 1981). Ammonium thiocyanate (NH₄SCN), a commonly used chemical in gold mining operations to make gold soluble, was successfully used in phytomining studies, enhancing the uptake of gold by plants from aqueous media (Anderson et al., 1998). Although the effectiveness of urea versus thiocyanate in enhancing plant uptake of TNT from hydroponic systems was not compared, urea has much lower toxicity as compared to thiocyanate and its extensive use in agriculture over decades makes it a better choice for as a solubilizing agent in TNT contaminated sites (Makris et al., 2007a).

Our initial attempts of using urea to enhance the plant–TNT uptake were highly encouraging. Makris et al. (2007a,b) showed the effectiveness of urea as a solubilizing agent to enhance TNT uptake by vetiver grass and wheat from aqueous media. Presence of urea significantly increased the solubility of TNT at the root–hair/solution interface and hence increasing the TNT removal capacity and kinetics by different plants, irrespective of their varied affinity for TNT (Makris et al., 2007a). To investigate the applicability of this technique in soil, a preliminary soil–pot experiment was conducted using an acidic sandy soil which contains minimal TNT retaining capacity (Das et al., 2010). Significant ($p < 0.001$) urea enhancement of TNT removal by vetiver grass was achieved, allowing for complete removal of TNT from soil treated with 40 mg kg⁻¹ TNT and 1000 mg kg⁻¹ urea within 12 days (Das et al., 2010). However, the successful application of this technique in hydroponic systems and one soil which contains minimal TNT retention capacity does not promise its success in all soil environments.

Prior research has shown that retention and release of TNT at soil solutions highly varies with soil properties (Pennington and Patrick, 1990; Eriksson and Skyllberg, 2001). Hassett et al. (1983) suggested that nonpolar organic compounds such as TNT are distributed between water and SOM through hydrophobic partitioning. Eriksson and Skyllberg (2001) showed that the retention of TNT in soil is dependent on the ability of solid phase particulate organic matter (POM) to adsorb TNT. On the other hand, binding of TNT metabolites to dissolved organic matter (DOM) increases the mobility and possible transportation of TNT and its metabolites into soil solutions. The association between hydrophobic contaminants like TNT and SOM strongly limits its bioavailability and hence causes contaminant stability and prolonged persistence in the soils (Singh et al., 2010).

Another major challenge in developing the urea catalyzed phytoremediation technique for TNT is to optimize the solubilizing effect of urea within the environmentally safe and agro-recommended urea application rates. Urea application guideline for agricultural crops recommends use of more than 125 mg urea kg⁻¹ (250 kg ha⁻¹) (EFMA, 2000). A consistent yield depression of agricultural crop was found after 350 mg urea kg⁻¹ (320 kg N ha⁻¹) (Trierweiler and Omar, 1983). Makris et al., 2007b suggested that

solubilizing effectiveness of urea may or may not be achieved unless urea application rates greater than those used in agriculture are applied. However, beyond 1000 mg kg⁻¹ urea exhibited strong toxic effects on earthworms, which are considered as important indicators of soil health and environmental safety (Xiao et al., 2004). Hence, 1000 mg kg⁻¹ is the highest level of urea that can be used in soil without affecting the soil health. Another concern regarding the use of urea lies in the stability of urea in different soil environments (Makris et al., 2007a). Abundance of urease enzyme in soil and variation in soil pH may cause instability of urea and hence undermine its effectiveness in increasing the solubility of TNT in soil solutions.

Therefore, optimizing this remediation technique as a function of SOM and different urea application rates is of utmost importance to understanding its applicability in different soils environments. In the present study, batch adsorption, desorption, and extraction experiments were conducted to optimize the factors that may influence the effectiveness of urea in enhancing the TNT solubility in soil solutions. The specific objectives of the studies were (i) characterizing adsorption and desorption of TNT, in absence of urea, as functions of soil properties; (ii) characterizing the urea-catalyzed extraction of pre-adsorbed TNT in soil solutions as functions of soil properties and urea application rates; (iii) examining the stability of urea in different soils during the experiment; and (iv) investigating the effects of reaction time and pH on the urea-catalyzed extraction of TNT.

2. Materials and methods

2.1. Soils

Four soils were chosen based on their widely varied physico-chemical properties primarily focusing on their soil organic matter content: (1) Immokalee, an acid sand which contains minimal SOM (0.84%). (2) Millhopper, an acidic sandy loam with low pH and relatively low SOM content (4.38%), which is higher than that of Immokalee. (3) Orelia is an alkaline soil with moderate soil organic matter (23.9%). And (4) Belleglade is an acidic sandy soil but has very high organic matter content (85.4%). The Immokalee series soils were collected from surface horizons in the Southwest Florida Research and Education Center, Immokalee, Florida. Millhopper series soils were collected from the surface horizons in the University of Florida campus at Gainesville, FL. Orelia series soil was collected from Corpus Christi, Texas. Belleglade soil was collected from Everglades Research and Education Center at Belle Glade, Florida. Soil properties are summarized in Table 1.

2.2. TNT

2,4,6-Trinitrotoluene (TNT) was purchased from Chem Service (West Chester, PA, USA) in an aqueous slurry form. TNT was air-

Table 1
Physico-chemical properties of soils. (reproduced from Datta and Sarkar, 2005).

Properties	Immokalee	Millhopper	Orelia	Belleglade
pH	6.0	6.4	8.2	5.9
EC ^a (μs/cm)	59	145	203	558
CEC ^b (C mol/kg)	777	2356	3810	18908
SOM ^c (%)	0.84	4.38	23.9	85.4
Clay content (%)	0.57	1.62	21.91	4.67
Oxalate extractable Fe + Al (mg kg ⁻¹)	66	704	380	1957
Total Fe + Al (mg kg ⁻¹)	212	4745	6100	6010

^a Electrical conductivity.

^b Cation exchange capacity.

^c Soil organic matter.

Download English Version:

<https://daneshyari.com/en/article/6310087>

Download Persian Version:

<https://daneshyari.com/article/6310087>

[Daneshyari.com](https://daneshyari.com)