Journal of Hazardous Materials 260 (2013) 602–608

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Mobility of 2-amino-4,6-dinitrobenzoic acid, a photodegradation product of TNT in a tropical soil under saturated abiotic conditions

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HIGHLIGHTS

- 2-Amino-4,6-dinitrobenzoic acid (2ADBA) shows the potential to enter and travel through the environment.
- In the presence of RDX, TNT, and their degradation products, 2ADBA shows the ability to migrate faster than parent compounds.
- Little to no sorption to clay soils was witnessed.

ARTICLE INFO

Article history:
Received 23 November 2012
Received in revised form 11 April 2013
Accepted 25 May 2013
Available online 5 June 2013

Keywords:
TNT
RDX
2-Amino-4,6-dinitrobenzoic acid
Photodegradation
Tropical soil

ABSTRACT

We examined the mobility of 2-amino-4,6-dinitrobenzoic acid (2-A-4,6-DBA) a common photodegradation product of TNT, in soil taken from a former military training area on Oahu Island, Hawaii, USA. 2-A-4,6-DBA is stable and polar and has the potential to migrate to groundwater. Little experimentation has been conducted on explosives in tropical soils which differ chemically from soils in temperate climates. 2,4,6-Trinitrotoluene (TNT) and 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) are the most commonly used secondary military explosives. Composition B (Comp B) is a frequently used 59/40/1 combination of RDX, TNT, and wax binder. In order to examine the effect of the presence of Comp B and its degradation products on the mobility of 2-A-4,6-DBA in soil, we dissolved field-collected Comp B fragments in water, exposed the solution to light and pumped it through soil and sand-packed stainless steel columns under abiotic saturated conditions. We found that in the presence of a complex mixture of explosives and degradation products, 2-A-4,6-DBA migrated faster than the parent compound (TNT) and other degradation products through both tropical soil and Ottawa sand (used as a reference) under sterile saturated conditions. The relatively rapid movement of 2-A-4,6-DBA suggests that it has the potential to contaminate underlying groundwater. However, the amount of 2-A-4,6-DBA produced under field conditions and its rate of biotic degradation were not part of this research, therefore, it is unknown how these factors might affect the transport and fate of 2-A-4,6-DBA.

1. Introduction

The United States military conducts live-fire training and testing activities to ensure readiness. The Pacific region is the site of many current and past military activities. These activities, including training exercises, may introduce explosives into the environment [1]. It is possible for residues of these explosives to contaminate groundwater. 2,4,6-Trinitrotoluene (TNT) and 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) constitute the largest quantity of secondary explosives used in military applications [2]. These secondary explosives are less sensitive than other explosives and are therefore safer to handle and transport. Composition B (Comp B), a compound widely used in ordnance, is a 59/40/1 mixture of RDX/TNT/wax binder. Table 1 shows the structures of TNT (a nitroaromatic compound), RDX (a nitramine compound), and their common breakdown products.

Weathering of TNT and TNT-containing explosives, such as Comp B, generates extremely complex mixtures of compounds, including highly polar TNT derivatives, such as 2-amino-4,6-dinitrobenzoic acid (2-A-4,6-DBA) [3].

Various intermediates and their degradation products, along with their parent compounds, are typically found at

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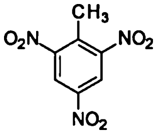
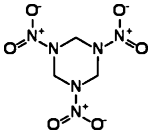
http://dx.doi.org/10.1016/j.jhazmat.2013.05.048

Table 1
Explosive compounds and their common degradation products used in the study.

Molecular group	Common name	Chemical name	Structure	Chemical formula	Common breakdown products
Nitroaromatic compound	TNT	2,4,6-Trinitrotoluene		$C_7H_5N_3O_6$	2-Amino-4,6-dinitrobenzoic acid (2-A-4,6-DBA)
					1,3,5-Trinitrobenzene (1,3,5-TNB) 1,3-Dinitrobenzene (DNB) 2,4-Dinitrotoluene (2,4-DNT) 2,6-Dinitrotoluene (2,6-DNT) 2-Amino-4,6-dinitrotoluene (2-ADNT) 4-Amino-2,6-dinitrotoluene (4-ADNT)
Nitramine compound	RDX	1,3,5-Hexahydro-1,3,5-trinitrotriazine		$C_3H_6N_6O_6$	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX)
					Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX) Hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)

Note: Composition B (Comp B) is a 59/40/1 mixture of RDX/TNT/wax binder.

TNT-contaminated sites [4]. While many degradation products of TNT are known to be toxic [5]; little is known about 2-A-4,6-DBA, and further inquiry into its mobility in tropical soils as part of a complex mix of degradation products is warranted.

Dissolution in water is the first step toward transport of explosive chemicals through soil [6,7]. 2-A-4,6-DBA is chemically stable and water soluble, and does not readily degrade in the environment (Ronald Spanggord SRI Intl., Menlo Park, CA, 2011; personal communication). In leaching experiments involving outdoor exposure and dissolution of Comp B, the resulting 2-A-4,6-DBA has been seen in higher concentrations than TNT in the leachate [6]. Light exposure has been found to result in significant degradation of solid explosives in the field [6]. Based on these facts it is believed that there is potential for 2-A-4,6-DBA to leach through soil and move to water sources.

A detailed literature search on 2-A-4,6-DBA and its transport in the environment revealed little existing information. Some basic characteristics of 2-A-4,6-DBA are included in Table 2. Sun and rain promote photodegradation and dissolution of solid explosives, and accelerate their entry into the sub-surface. The low soil pH, year-round warm weather, and frequent wetting/drying cycles typical of tropical regions promote corrosion of unexploded ordnance casings, thus expediting the entry of 2-A-4,6-DBA and other explosive chemicals into the environment [8].

RDX and TNT sorb reversibly to soil. Ainsworth et al. [9] found that RDX and TNT appear to occupy the same sorption sites, and sorption of either compound decreased in the presence of the other as a cosolute. Furthermore, explosives with higher distribution coefficients have been found to displace those with lower distribution coefficients [10]. As nitroaromatic compounds, such as TNT, all adsorb by the same mechanisms onto phyllosilicates (clays), competition for sorption sites is expected in mixtures of nitroaromatics at many contaminated sites, and the transport of nitroaromatic mixtures is generally enhanced relative to single nitroaromatic compounds [4].

Alavi et al. [8] ranked the adsorbability of explosives and their degradation products in volcanic Hawaiian soils in the order of: DNT > TNT > HMX > RDX (Appendix A contains a list of chemicals and abbreviations). Haderlein et al. [10] determined that distribution coefficients of explosive chemicals for K^+-saturated montmorillonite (expandable 3-layer clay) rank thus: 1,3,5-TNB > TNT > 2-A-4,6-DNT > 4-A-2,6-DNT > 2,4-D-6-NT. In addition, they found desorption of these chemicals from clays to be rapid and thorough with up to 90% recovery.

Under field conditions attenuation of these chemical's movement takes place via multiple mechanisms including sorption, biological degradation, and abiotic degradation (such as hydrolysis and photodegradation). The objective of this study was to elucidate the movement of 2-A-4,6-DBA through soil and sand columns under abiotic conditions.

2. Materials and methods

2.1. Soils

Waikane series soil (taken from the Waikane Valley, Oahu, Hawaii) and commercial-grade Ottawa sand were used in this study. Some basic characteristics of these media are compiled in

Table 2
Physicochemical properties of explosives and their major degradation products found in the experiments.

Common name	Molecular weight (g/mol)	Melting point (°C)	Water solubility at 25 °C (mg/L)	Octanol/water partition coefficient ($\log K_{ow}$)	Henry's law constant at 25 °C (atm m^3/mol)	Vapor pressure (mm Hg)
2-A-4,6-DBA	227.13[a]	264[b]	309[b]	1.97[c]	N/A	1.40E−10[c]
TNT	227.13	80.1	130	1.6	4.57E−07[c]	1.99E−04[c]
1,3,5 TNB	213.11	123.2	350	1.36	2.21E−09	3.20E−06
RDX	222.26	205	56.3	0.9	1.96E−11	4.00E−09

Note: N/A: not available; unless otherwise noted, data is from U.S. Department of Agriculture et al. [15].

[a] Pennington et al. [3].

[b] SciFinder-Chemical Abstract Service (CAS) registry number 140380-55-8. Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2012 ACD/Labs) [accessed July 10, 2012].

[c] At 20 °C.