Degradation of Nitroaromatic Compounds and Explosives by Jim C. Spain, Joseph B. Hughes, Hans-Joachim Knackmuss, United States. Air Force. Office of Scientific Research, United States. Defense Threat Reduction Agency, 2000. Lewis Publications.
Pages 1, 30 and 31.

CHAPTER 1

Introduction

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Explosives and other nitrated compounds (Figure 1.1) are widely distributed environmental contaminants. Nitroaromatic pesticides such as dinoseb, dinitrocresol, parathion, and methylparathion are intentionally released in soil and water worldwide. They are also spilled accidentally at loading facilities and during agricultural use. Nitrophenols and nitrotoluenes are used extensively as feedstocks in industry and are often released to surface water in waste streams. The pesticides and simple nitroaromatic compounds are biodegradable by soil bacteria and do not accumulate in the environment unless concentrations exceed the assimilative capacity of the ecosystem. In contrast, explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) are less biodegradable and often persist for extended periods in soil or groundwater.

The major explosives manufacturing, handling, and storage sites in the U.S. (Figure 1.2) have been identified by the U.S. Army Environmental Center.[1] The most heavily contaminated sites are the army ammunition plants where explosives were manufactured for much of this century. Fortunately, most of the sites are owned by the U.S. government and are therefore not accessible to the public. A number of the sites have been cleaned up, and many are in the process of cleanup. Major exceptions include Volunteer and Ravenna Army Ammunition Plants where contamination is extensive and cleanup of contaminated soil and groundwater has not started. A substantial amount of dinitrotoluene-contaminated soil also remains at the Badger Army Ammunition Plant. The most recent public document on the scope of the problem[1] describes a timeline for the cleanup of contaminated soil at many of the sites, but does not provide information about contaminated groundwater. More detailed information about the scope of the problem and the current cleanup strategies is provided in Chapter 14.

In Germany, the situation is more problematic because many of the explosives manufacturing facilities (Figure 1.3) were demolished at the end of World War II

2.2.3.3 Natural Attenuation of DNT

Groundwater at Weldon Spring Ordnance Works in Missouri is contaminated with a DNT plume[23-25] as the result of surface spills of DNT. DNT concentrations in the plume decrease in the downgradient direction. In microcosms constructed with soil from the site and incubated for 70 days, almost equal fractions of added radiolabeled 2,4-DNT were mineralized, transformed to aminonitrotoluenes, transformed to unidentified products, or remained unchanged. Only 8% of the 2,6-DNT was mineralized, 67% was unchanged, and the rest was transformed to aminonitrotoluenes and unidentified products. Although it was proposed that MNA of DNT may be suitable for the Weldon Spring site because of the mineralization of DNT,[24] the high proportion of nonspecific transformations is a negative consideration. Clearly, a cometabolic population, possibly sustained by a

large reservoir of more readily degradable carbon sources (often associated with TNT production plants), was as active as the DNT-degrading population. When a population that reduces nitroaromatic compounds is active at a contaminated site, immobilization of reduced metabolites could be an alternative strategy to mineralization if absence of toxicity of the reduced products can be established. Reduced products of DNT are still toxic and do not bind as well to soil as the more thoroughly studied TNT reduction products.[117]

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The situation at BAAP is considerably different from that at Weldon Spring. Waste materials from the reprocessing of single-base propellants were deposited into large in-ground waste pits. Six waste pits, each roughly 40 ft in diameter and extending 100 ft down to the water table, contain soil heavily contaminated with 2,4-DNT.[195] One of the waste pits is the source of a DNT-contaminated groundwater plume. As at Weldon Spring, the first line of evidence for MNA is that DNT concentrations in the groundwater plume decrease in downgradient wells. 2,3-Dinitrotoluene (2,3-DNT) does not decrease at the same rate as 2,4- and 2,6-DNT. 2,3-DNT has not been demonstrated to be biodegradable and can thus be considered a conservative tracer that reflects the effects of abiotic processes. The much greater decrease in 2,4- and 2,6-DNT concentrations can therefore be attributed to biological activity. 2,4-DNT-degrading bacteria have been isolated from monitoring well water from the site, and 2,4-DNT disappears with stoichiometric release of nitrite from microcosms constructed with DNT-contaminated soil from the site.[148] The understanding of the 2,4-DNT catabolic pathway taken with laboratory studies with soil from the site, disappearance of DNT from the monitoring wells, and the isolation of bacteria able to degrade DNT from the same wells provides evidence that MNA might be applicable at the site. Stoichiometric release of nitrite demonstrates complete mineralization of DNT which precludes formation of significant amounts of amino compounds. MNA might not be suitable for bulk DNT in the soil at BAAP where 2,4-DNT occurs at concentrations up to 28% by weight.[195]

2.2.4 Sequential Anaerobic/Aerobic Strategies