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MANAGEMENT OF THE GROUNDWATER CONTAMINATED BY MILITARY EXPLOSIVES

Master of Science thesis

Examiner: University teacher Marja Palmroth
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ABSTRACT

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Residual concentrations of the most commonly used explosives 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-tetrazocine (HMX) have been identified in soil and groundwater at military training ranges in Finland. Military training areas are often located at groundwater areas classified as important drinking water resources. The aim of this thesis is to examine degradation, migration, toxicity and environmental fate of TNT, RDX and HMX and to evaluate remediation and treatment methods for explosives contaminated groundwater.

TNT, RDX and HMX are degraded by biological, chemical and abiotic processes. Dissolution and adsorption are important in determination of migration but are largely site-specific characteristics. Despite of different properties, TNT, RDX and HMX are all found in groundwater. Possible treatment methods for groundwater are pump-and-treat, permeable reactive barriers and in situ chemical oxidation, but soil remediation has to be coupled with water treatment.

The experimental part of this work contained two water treatment experiments and monitoring abiotic degradation of TNT and RDX. Efficiency of UV irradiation in degradation was tested with 407 J/m^2 and 550 J/m^2 UV doses. UV irradiation was chosen as it is used at some water work stations to ensure delivery of pathogen-free water. The aim was to evaluate feasibility of UV irradiation in degradation of explosives during standard water treatment practices. As a result, 29.6% of TNT and 36.9% of RDX was removed under 407 J/m^2 dose and 29.6% (TNT) and 46.7% (RDX) with 550 J/m^2. Hence, UV irradiation is not efficient enough for explosives degradation as sole method.

Removal of explosives from TNT/RDX containing water by reverse osmosis (RO) was tested using Kärcher water purification system. The equipment can be used for production of drinking water at crisis management sites for military forces and civil population. As a result, TNT, RDX and intermediates present were removed below detection limit and safe drinking water can be produced by RO from explosives contaminated water. Due to quantity of reject water (60% of intake), method is not suitable for treatment at water works.

Abiotic degradation was evaluated by monitoring removal of TNT and RDX from water exposed to natural light and in dark conditions. Under exposure to natural light, TNT and intermediates were removed within first week, while only 3.7% (7 d) and 33.3% (14 d) of TNT was degraded in dark. In contrast, only 16.0% and 28.6% of RDX was degraded during first and second week. RDX was not degraded under dark conditions.

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Yleisimpien räjähdeaineiden 2,4,6-trinitrotolueenin (TNT), perhydro-1,3,5-trinitro-1,3,5-triatsiinin (RDX) ja oktahydro-1,3,5,7-tetranitro-1,3,5,7-tetratsokiinin (HMX) jäännöspitoisuuksia on viime vuosien aikana todettu maaperästä ja pohjavedestä Puolustusvoimien harjoitusalueilla Suomessa. Alueet sijaitsevat usein tärkeiksi pohjavesialueiksi luokitelluilla alueilla. Työn tavoitteena on selvittää TNT:n, RDX:n ja HMX:n hajoamista, toksisuutta ja kulkeutumista sekä arvioida kunnostus- ja puhdistusmenetelmien soveltuvuutta räjähdeaineita sisältävän pohjaveden kunnostuksessa.

TNT, RDX ja HMX hajoavat biologisin, kemiallisin ja abioottisin mekanismein. Liukeneminen ja adsorptio ovat kulkeutumisen kannalta merkittävimmät prosessit, mutta ovat paikkakohtaisia. Huolimatta erilaisista ominaisuuksista sekä TNT, RDX että HMX voivat kulkeutua pohjaveteen. Mahdollisia pohjaveden kunnostusmenetelmiä ovat pump-and-treat, reaktiiviset seinämät ja kemiallinen kunnostus, mutta myös maaperä on kunnostettava pohjaveden kunnostuksen yhteydessä.

Työn kokeelliseen osuuteen sisältyy kaksi vedenpuhdistuskoetta sekä TNT:n ja RDX:n hajoamisen seuranta. UV-säteilyn tehokkuutta räjähteiden hajotuksessa selvitetään 407 J/m^2 ja 550 J/m^2 säteilyannoksilla. Koska UV-käsittelyä käytetään joillakin vedenpuhdistamoilla varmistamaan taudinaiheuttajista vapaan veden tuottaminen, työssä selvitetään UV-säteilyn tehokkuutta räjähteiden hajotuksessa vedenkäsittelyprosessin aikana. Kokeessa 29,6% TNT:stä ja 36,9% RDX:stä hajosi 407 J/m^2 UV-annoksella ja 29,6% (TNT) ja 46,7% (RDX) UV-annoksella 550 J/m^2. Siten UV-säteilytys ei ole riittävä ainoana menetelmänä räjähdeaineiden hajotukseen.

TNT:n ja RDX:n poistamista vedestä käänteisosmoosi –menetelmällä tutkittiin Kärcher vedenpuhdistuslaitteiston avulla. Laitteistoa voidaan käyttää kriisinhallintakohteissa turvaamaan Puolustusvoimien henkilöstön ja siviiliväestön puhtaan juomaveden saanti. Kokeessa TNT, RDX ja TNT:n hajoamistuotteet poistuivat vedestä alle toteamisrajan. Muodostuvan rejektiveden suuren määrän (60% otetusta vedestä) vuoksi menetelmä ei kuitenkaan ole soveltuva vedenottamoilla veden puhdistuksessa käytettäväksi.

TNT:n ja RDX:n luonnollista hajoamista selvitettiin seuraamalla aineiden poistumista sekä luonnonvalossa että pimeässä säilytetyistä näytteistä. Luonnonvalolle alttiina säilytetyistä näytteitä TNT ja hajoamistuotteet hajosivat ensimmäisen viikon aikana kokonaan, kun pimeässä TNT:stä hajosi vain 3,7% ensimmäisen viikon ja 33,3% toisen viikon loppuun mennessä. Sen sijaan RDX:stä valossa hajosi 16,0% ensimmäisen viikon ja 28,6% toisen viikon aikana. RDX ei hajonnut pimeässä.

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I would like to show my appreciation and present my gratitude to each and every person who has contributed to writing and finishing this work. This Master of Science thesis has been written at Environmental Management Department of Sito Oy in Tampere. The experiments included in this work have been conducted at Finnish Defence Forces Logistics School in Riihimäki Garrison with the equipment, materials and expertise provided by The Finnish Defence Forces and The Construction Establishment of Finnish Defence Administration.

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Joanna Aalto

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

2-A-4,6-DNBA	2-amino-4,6-dinitro-benzoic acid
ADNTs	Aminodinitrotoluenes
2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
2-ANT	2-amino-4-nitrotoluene
AOP	Advanced oxidation processes
ATSDR	Agency for Toxic Substances and Disease Registry
C4	Plastic explosive consisting of 91% RDX and 9% plasticizers
CMR	Carcinogenic, Mutagenic, or toxic for Reproduction
COD_{Mn}	Chemical oxygen demand
2,4-DANT	2,4-diaminonitrotoluene
2,6-DANT	2,6-diaminonitrotoluene
2,6-DHAT	2,6-dinitro-4-hydroxylaminotoluene
DNAPL	Dense nonaqueous-phase liquid
DNB	1,3-dinitrobenzene
2,4-DNBA	2,4-dinitrobenzoic acid
2,5-DNBA	2,5-dinitrobenzoic acid
3,5-DNP	3,5-dinitrophenol
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,4-Dinitrotoluene
DNX	Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DOC	Dissolved organic carbon
DWEL	Drinking Water Equivalent Level
ECHA	European Chemicals Agency
Eh	Reduction potential
ERs	Energetic residues
EU	European Union
FDRA	The Finnish Defence Research Agency
f_{OC}	Fraction of soil organic carbon
GAC	Granular activated carbon
HADNT	Hydroxylaminodinitrotoluenes
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, octogen
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
ISCO	In situ chemical oxidation
K_d	Soil distribution coefficient
K_f	Freundlich coefficient
K_H	Henry’s Law constant
K_{OC}	Organic carbon partitioning coefficient
K_{OW}	Octanol-water partitioning coefficient

LCMS	Liquid chromatography mass spectrophotometry
LHA	Lifetime Health Advisory level
LNAPL	Light nonaqueous-phase liquid
LOLC	Lowest observed lethal concentration
MEDINA	Methylenedinitramine
MNX	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
NB	Nitrobenzene
NC	Nitrocellulose
NDAB	4-nitro-2,4-diazabutanal
NG	Nitroglycerin
NOAEL	No-observed-adverse-effect level
NOM	Natural organic matter
NQ	Nitroguanidine
2-OHA	2-hydroxylamino-4,6-dinitrotoluene
4-OHA	4-hydroxylamino-2,6-dinitrotoluene
PBT	bioaccumulative and toxic (
PRB	Permeable reactive barrier
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RO	Reverse osmosis
TAT	Triaminotoluene
TNB	Trinitrobenzene
TNBA	Trinitrobenzaldehyde
TNBAlc	2,4,6-trinitrobenzyl alcohol
TNBAld	2,4,6-trinitrobenzaldehyde
TNT	2,4,6-trinitrotoluene
TNX	Hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	Total organic carbon
US	United States
US EPA	United States Environmental Protection Agency
UV	Ultra violet radiation
UXO	Unexploded ordnance
vPvB	very Persistent and very Bioaccumulative
WHO	World Health Organization
ZVI	Zero valent iron

1. INTRODUCTION

During the past over 100 years ammunitions and explosives have been produced and processed in large-scale. The vast production has led to disposal of explosives and nitrated organic by-products containing wastes into the environment all over the world. (Lewis *et al.* 2004.) Earlier practices in ordnance production were discharging of wastewaters untreated into settling lagoons, drainage ditches or directly to streams (Singh *et al.* 1999). In addition, outdated ordnance was commonly disposed by burying on the ground and sinking into lakes and seas (Koponen 2016).

At present, the most commonly used military explosives 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-tetrazocine (HMX) end up in the environment mainly as a consequence of military activities (e.g. Pichtel 2012). The intended result of detonated military explosives is a complete explosion of fired ammunition referred as high-order detonation. However, the fired ammunition can detonate only partially (low-order detonation) or not explode at all and remain on the ground as unexploded ordnance (UXO). (Jenkins and Vogel 2014.) In some parts of the world, UXOs exist as remains of the wars, while in other places such as Australia, United States (US) and Canada, UXOs are resulted from military training and weapon testing. (Pichtel 2012.)

During last couple of decades the public awareness of environmental issues has increased. At the same time, more knowledge has been obtained about toxicity and mutagenic effects of military explosives and their degradation products. Therefore, military agencies around the world have started to identify explosives contaminated sites and to evaluate the effects caused by military activities on soil and aquifer. With the increasing knowledge, the will and necessity has arisen towards remediation of explosives contaminated areas. Also, considerable effort has been put on development of efficient remediation technologies. (Lewis *et al.* 2004; Pichtel 2012.)

TNT, RDX and HMX are secondary explosives (also referred as high explosives) that are generally used as bulk chemical component in explosives. Secondary explosives are stable and resistant to shock-induced unintentional detonation. Hence, primary explosives are needed for detonation of secondary explosives. In addition, propellants are also used in small arms, rockets, missiles as well as in artillery and mortars. (Lewis et al. 2004; Folly and Mäder 2004.) Chemicals used as propellants include 2,4-DNT, nitrocellulose (NC), nitroglycerin (NG), nitroguanidine (NQ) and ammonium perchlorate depending on propellant type (Jenkins *et al.* 2006).

Ordnances used at military training ranges are mostly long-range weapons. Hence, the military training areas used for explosives firing are vast. Several hundred hectares sizes are typical for antitank rocket ranges whereas, the largest training ranges in military use are artillery ranges, which typically span hundreds of square kilometers (Jenkins *et al.* 2006). The firing points and target areas are separated by mostly uncontaminated land. Therefore, from live-fire ranges the contamination sources can be described as randomly distributed point sources. (Pichtel 2012.) The content of energetic residues (ERs) found in military training areas is dependent on the use of the site. At *firing points* the energetic residues are originated from propellant formulations and detectable contaminants are generally either 2,4-DNT or NG depending on the propellant used. At *impact areas*, ERs are from explosives used in ammunition warheads. (Jenkins *et al.* 2006.)

Recently residual explosive concentrations of TNT, RDX and HMX have been identified in soil and groundwater in some of the military shooting and training ranges and impact areas administered by the Finnish Defence Forces. The military training areas are usually located on sandy, permeable soils which are often also classified as important (class I or II) groundwater areas. Military training and shooting ranges are typically in use for long periods of time even several decades. The discovery of explosive residues in groundwater has initiated research by Finnish Defence Forces in order to investigate the existence of explosive concentrations in soil and groundwater and to define risk management objectives. (Koponen 2016.)

The aim of this work is to study characteristics, degradation and migration of the most commonly used explosives, TNT, RDX and HMX, and to study properties of these compounds and their known degradation products. The main objective of this work is to examine possible remediation technologies and to identify suitable approaches for removal of explosives from groundwater. In the experimental part of this work, the efficiency of treatment technologies readily available for The Finnish Defence Forces are tested for removal (filtration and reverse osmosis) and degradation (UV irradiation) of explosive compounds TNT and RDX from water. The abiotic degradation of TNT and RDX kept in dark conditions and exposed to natural light are also monitored.

This work consists of comprehensive literature review section and of experimental water treatment section (chapters 6 and 7). In chapter 2, biological, chemical and abiotic degradation of the most commonly used military explosives TNT, RDX and HMX are discussed. Chapter 3 summarizes chemical characteristics and migration properties of these explosives and designates the intermediates and products formed in degradation. Toxicity of explosives and degradation products are shortly discussed in chapter 4. Based on these preceding chapters, the possible remediation techniques for explosives containing sites and groundwater are presented and discussed in chapter 5. In the experimental part of this work, the performance (chapter 6) and obtained results (chapter 7) of the designed experiments, removal of TNT and RDX by UV irradiation, treatment of TNT/RDX-contaminated water by reverse osmosis and monitoring abiotic degradation, are described and discussed. The most important aspects of this work are discussed in chapter 8. Additional information has been included in appendixes, i.e. products formed in biodegradation of explosives, diagrams showing biodegradation of TNT and a chart of samples taken during water treatment experiments.

2. DEGRADATION OF EXPLOSIVES

The persistence of organic substances in soil and aquifer are dependent on degradation of the compounds. In degradation, breakdown of the explosives can be complete resulting to degradation end-products (mineralization) or partial resulting to formation of other substances. Degradation can be due to biological processes (biodegradation, biotransformation) or by chemical, biological or abiotic processes (transformation) (Juhasz and Naidu 2007; Lawrence 2006.) The degradation rate is affected by contaminant type, environmental and biological factors such as temperature, physical and chemical properties of the aquifer, soil properties and microbiota on site. (Kalderis *et al.* 2011.)

Explosive compounds in soil and aquifer can be degraded by biological, chemical and abiotic processes (Talmage *et al.* 1999). Degradation products of TNT, RDX and HMX identified in different processes based on literature are summarized in table 11 (appendix 1). The degradation processes are discussed more closely in following subchapters.

2.1 Chemical structure of the explosives and related compounds

Energetic chemicals (explosives and propellants) contain nitro -NO_2 -functional groups and belong to nitroaromatic, nitramine or nitrate ester chemical groups (Jenkins and Vogel 2014). Chemical structures of common explosives and propellants are presented in figure 1.

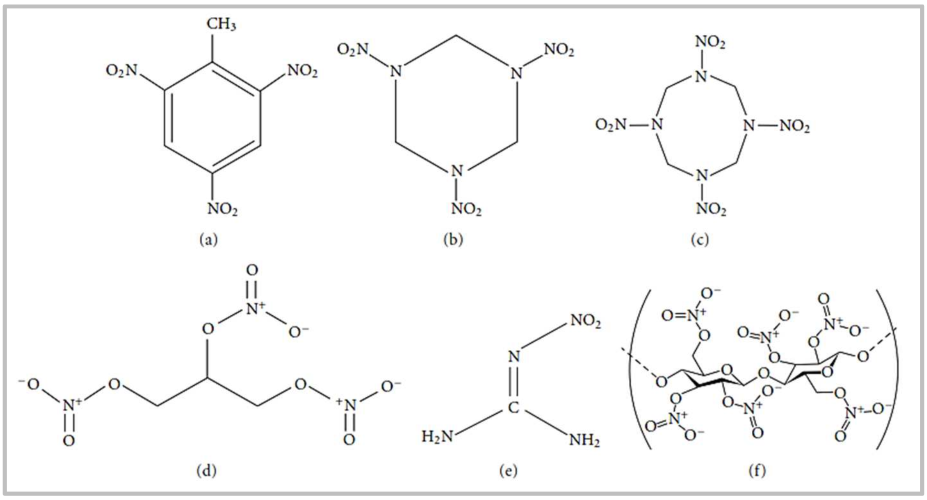

Figure 1. The chemical structure of explosive compounds (a) 2,4,6-trinitrotoluene (TNT); (b) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); (c) octahydro-1,3,5,7-tetranitro-1,3,5,7-terazocine (HMX) and propellants (d) nitroglycerin (NG); (e) nitroguanidine (NQ) and (f) nitrocellulose (NC) (Pichtel 2012).

TNT, RDX and HMX are chemically and thermally stable compounds, which are resistant to accidental detonation due to insensitivity to triggers such as shock and friction (Pichtel 2012). At room temperature, TNT, RDX and HMX have solid, crystalline structures. TNT is a nitroaromatic compound (Clausen *et al.* 2006), while RDX and HMX are heterocyclic nitramines (Crocker *et al.* 2006), which do not have double bonds in their structure. Instead, the NO_2 groups are bonded to nitrogen of an alicyclic ring. Propellants such as nitroglycerin (NG), nitroguanidine (NQ) and nitrocellulose (NC) are nitrate esters, with NO_2 groups bonded to oxygen attached to an aliphatic carbon (Jenkins and Vogel 2014).

2.2 Biological transformation and degradation

Biological degradation and transformation of pollutants is dependent on micro-organism population on site (Pichtel 2012). In addition, biodegradation pathways and subsequently transformation products and intermediates vary between aerobic and anaerobic conditions and other prevailing conditions on soil and aquifer. (Juhasz and Naidu 2007; Khan *et al.* 2013) TNT biodegradation under aerobic and anaerobic conditions is presented in figures 3-5 (appendix 2); RDX biodegradation by anaerobic sequential reduction of nitro groups and by direct ring cleavage pathway in figures 6-7 (appendix 3); and proposed pathways for HMX biodegradation in figures 8 and 9 (appendix 4).

Cyclic nitramine explosives (RDX and HMX) can be biotransformed to intermediates, which are subsequently degraded to end-products such as nitrite (NO_2^-), nitrous oxide (N_2O) formaldehyde (CH_2O) and formic acid (HCOOH) by spontaneous decomposing (Crocker *et al.* 2006; Michalsen *et al.* 2016). Instead, TNT is readily transformed to amino derivatives, but not mineralized (Khan *et al.* 2013). As non-aromatic compounds, stable amino derivatives are not formed in degradation of RDX and HMX (Monteil-Rivera *et al.* 2003).

The proposed pathways for degradation of cyclic nitramine explosives are mostly based on identified end-products, since the hypothesized metabolic intermediates are unstable in water and hence, not identified. The proposed pathways include 5 mechanisms which are: loss of nitro groups due to nitramine free radical formation; reduction of nitro functional groups; direct enzymatic cleavage; α-hydroxylation and hydride ion transfer. (Crocker *et al.* 2006)

2.2.1 TNT

TNT can be used as carbon source and degraded by variety of micro-organisms in aerobic and anaerobic conditions. (Hawari *et al.* 2000a; Anasonye *et al.* 2015) TNT is also degraded by cometabolic processes (Juhasz and Naidu 2007). As a result of TNT degradation, 21 products and intermediates produced in variable conditions have been identified (Thiboutot *et al.* 2002). The most common transformation products of TNT are aminodinitrotoluenes: 2-amino-4,6-dinitrotoluene (abbreviated as *2-ADNT*) and 4-amino-2,6-dinitrotoluene (*4-ADNT*). Also diaminonitrotoluenes 2,4-diamino-6-nitrotoluene (*2,4-DANT*), 2,6-diamino-4-nitrotoluene (*2,6-DANT*) are generally formed as a result of further reduction of nitro groups to amino groups (Kalderis *et al.* 2011).

Degradation by bacteria

The ability of multiple bacterial species to degrade TNT has been documented and several enzymes responsible for TNT degradation identified (Khan *et al.* 2013). TNT is biotransformed by stepwise reduction of nitro groups to amino groups resulting to amino derivatives (2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT) both in aerobic and anaerobic conditions. Aerobic bacteria are unable to reduce the third nitro group of TNT (McFarland 2014), but in anaerobic conditions also triaminotoluene (TAT) may be formed (Pichtel 2012) and subsequently transformed at least by microbial consortia (Crawford 1995). However, TNT is generally not mineralized as a result of bacterial degradation. (Clausen *et al.* 2006; Hawari *et al.* 1999; Kaplan and Kaplan 1982).

In few studies, also formation of less frequently identified products and intermediates of TNT degradation has been shown. Denitration (nitro group cleavage and release as nitrite) of TNT, trinitrobenzaldehyde (TNBA) and 2,4,6-trinitro-benzyl alcohol (TNBAlc) resulting to 2-amino-4-nitrotoluene (2-ANT) has been shown by bacterial extracellular catalysts in aerobic conditions (Stenuit et al 2009). Also formation of 2,4-dinitrotoluene (2,4-DNT) and nitrite as a degradation product of TNT by bacteria (*Pseudomonas savastanoi)* has been documented (Martin *et al.* 1997). Transformation of TNT to aminonitrotoluenes and 2,6-dinitro-4-hydroxylaminotoluene (2,6-DHAT), and further to tetranitroazoxytoluenes by *Pseudomonas sp.* Y strain has also been reported. Further, some bacteria also produce Meisenheimer complexes, which are hydride-TNT complexes resulting from addition of hydride to aromatic ring in TNT biotransformation (Khan *et al.* 2013).

The enzymes involved in biotransformation of TNT by bacteria include nitroreductases, ring hydroxylating dioxygenases, hydrogenases and some flavoproteins such as pentaerythritol tetranitrate reductase and xenobiotic reductase B (Anasonye *et al.* 2015; Khan *et al.* 2013). Nitroreductases catalyse reduction of TNT to aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs) and hydroxylaminodinitrotoluenes (HADNTs) (Rylott *et al.* 2010). The flavoproteins identified act as nitroreductases and catalyse the formation of Meisenheimer complexes (monohydride Meisenheimer H^--TNT, and dihydride Meisenheimer $2H^-$-TNT) by addition of hydride to aromatic ring (Khan *et al.* 2013).

According to current knowledge, the main end products of bacterial degradation of TNT in aerobic conditions are ADNTs, DANTs and tetranitroazoxytoluenes. Mineralization does not occur in significant amount. (Khan *et al.* 2013.) Pathways for TNT biodegradation in aerobic (pathways I and II) and in anaerobic conditions with the enzymes known to catalyze the reactions according to Khan *et al.* (2013) are presented in figures 3-5 in appendix 2.

Degradation by fungi and yeasts

Transformation of TNT can be also achieved by fungi in varying culture conditions (e.g. Hawari *et al.* 1999; Kalderis *et al.* 2011). Fungal degradation of TNT also starts with formation of ADNTs, but some fungal species have also been shown to mineralize TNT. Litter-decomposing and wood-rotting fungi excrete extracellular enzymes that are able to break the aromatic ring structure of the TNT degradation products hydroxylaminodinitrotoluene (HADNT) and ADNTs. (Scheibner *et al.* 1997; Anasonye *et al.* 2015). For instance, mineralization of 36% (*Stropharia rugosa-annulata*) and 42% (*Clitocybula dusenii*) of the TNT has been achieved. However, only few species are able to fully mineralize TNT in significant amounts over 10%. (Scheibner *et al.* 1997).

Some fungal and yeast species have been shown to transform TNT via formation of Meisenheimer complexes (Khan *et al.* 2013). Degradation of TNT by yeast (*Yarrowia lipolytica*) has been shown to occur preferentially by direct aromatic ring cleavage, but also via nitro group reduction pathway as minor pathway. The direct ring cleavage produces hydride complexes of TNT while ADNTs and HADNTs are produced in nitro group reduction. (Ziganshin *et al.* 2007.)

Degradation by microbial consortia

Bacterial and fungal species alone have limited resources for degradation of TNT but degradation is enhanced by degradation of microbial consortia (Crawford 1995). For instance, TNT has been shown to be degraded to intermediates such as 2,4,6-trihydroxytoluene, para-hydroxytoluene (p-cresol) and acetate (Crawford 1995; Funk et al. 1993), which can be subsequently transformed by biotic and abiotic processes (Pichtel 2012).

Degradation products resulting from TNT biotransformation by mesophilic consortium of micro-organisms in a composting system utilizing ^{14}C-labeled TNT were studied by Kaplan and Kaplan (1982). The compost contained 1.5% TNT by dry weight. After 91 days of degradation, the products identified from ether, ethanol and acetone extracts were 4-ADNT and small amount of 2-ADNT (both present in all extracts), polar metabolites (2,4-DANT, 2,6-DANT) (present in ethanol and acetone extracts) and more nonpolar metabolites 2,2',6,6'-tetranitro-4,4'-azoxytoluene and 2',4,6,6-tetranitro-2,4'-azoxytoluene (ether extract). 2,2’-Az isomer was not found. Azoxy products are formed by coupling of hydroxylamino compounds, which are intermediates of transformation of TNT to aminotoluenes. However, the 2-hydroxylamino-4,6-dinitrotoluene (2-OHA) and 4-hydroxylamino-2,6-dinitrotoluene (4-OHA) intermediates were not detected. In addition to products identified from the extract, a significant amount of ^{14}C-labeled material remained bound to organic material and was not recovered by solvent extraction. No indication of mineralization was detected, since significant amounts of ^{14}C-labeled CO_2 or volatile amines was not recovered. The results were reported to be similar with results obtained from mesophilic systems. (Kaplan and Kaplan 1982.)

2.2.2 RDX

Complete ***anaerobic*** mineralization of RDX in laboratory experiments has been reported. In anoxic conditions, RDX can be degraded by either direct ring cleavage or by sequential reduction of nitro groups resulting to formation of triazines. The triazines MNX (hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine), DNX (hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine) and TNX (hexahydro-1,3,5-trinitroso-1,3,5-triazine) are then further degraded. Via direct cleavage pathway, methylenedinitramine (MEDINA) and bis(hydroxymethyl) nitramine are formed as intermediates and are also subsequently degraded. (Hawari *et al.* 2000b; Sheremata *et al.* 2001.) Common end products of RDX by combination of biotic and abiotic degradation are NO_2^-, N_2O, formaldehyde (CH_2O) and NH_3. (Crocker *et al.* 2006.) In addition, also formic acid (HCOOH), CH_4 and CO_2 are produced as end products of direct cleavage pathway (Hawari *et al.* 2000b).

RDX degradation has been studied in varying conditions utilizing mesocosms formed from authentic RDX contaminated aquifer material. RDX was degraded under methanogenic and manganese-, iron- and sulfate-reducing conditions, but not in nitrate reducing conditions. Accordingly, sequential formation of triazines MNX, DNX and TNX (RDX degradation products) and subsequent reduction of these compounds was detected in mesocosms where RDX was degraded. However, RDX degradation pattern varied in regard to degradation rate, accumulation of triazines and subsequent degradation of triazines between different conditions. Especially under sulfate-reducing and methanogenic conditions, RDX was degraded at high rate and also the triazines formed were quickly degraded. (Cho *et al.* 2015.)

Sequential nitro group reduction is likely a predominant pathway of RDX degradation in manganese- and iron-reducing conditions while direct ring cleavage is probably the dominant path in methanogenic and sulfate-reducing conditions. Hence, the type of electron acceptor available has a notable effect on degradation of RDX. These results are important aspects to consider in remediation planning, since environmental conditions favoring ring cleavage -pathway are favorable in order to prevent the accumulation of toxic triazines. (Cho *et al.* 2015.)

Substantially less is known about RDX degradation under ***aerobic*** conditions, since RDX biodegradation has been studied mostly in anaerobic conditions (Kalderis *et al.* 2011). However, RDX can be fully mineralized due to utilization of RDX as a nitrogen source by bacteria in aerobic conditions (Fournier *et al.* 2002). According to the proposed pathway for aerobic degradation, destabilization of the ring structure and subsequent spontaneous cleavage is resulted from removal of one nitro group. As a result, NO_2^-, N_2O, CO_2, formaldehyde, ammonia and 4-nitro-2,4-diazabutanal (NDAB) are formed. However, although the formation of end products have been shown, only the NDAB intermediate on the pathway has been identified. (Fournier *et al.* 2002; Fournier *et al.* 2005.)

2.2.3 HMX

Degradation of HMX is less well known compared to TNT and RDX. Degradation pathways have been proposed but most intermediates on pathways have not been identified. (Kalderis *et al.* 2011.) Although RDX and HMX are both cyclic nitramines and have similar structure, HMX is more recalcitrant against degradation especially in aerobic conditions, compared to RDX (Fournier *et al.* 2004). Although limited information exists on HMX biodegradation by bacteria and fungi (Kalderis *et al.* 2011), degradation and also mineralization has been reported (Fournier *et al.* 2004; Monteil-Rivera *et al.* 2003).

Degradation of HMX has been shown in laboratory conditions. In a study observing sorption/desorption properties and long-term fate of HMX to evaluate effectiveness of HMX disappearance by natural attenuation, 60% degradation of HMX has been observed during 20 weeks in non-sterile agricultural top-soil under anaerobic conditions. And full mineralization of 19% HMX in 30 weeks was observed in experiments using uniformly radiolabeled HMX, UL-[^{14}C]-HMX. Four nitroso-derivatives of HMX were identified and mineralization was observed as liberated ^{14}C-labeled CO_2. The identified nitroso-derivatives were octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine, octahydro-1,5-dinitroso-3,7-dinitro-1,3,5,7-tetrazocine (or isomer octahydro-1,3-dinitroso-5,7-dinitro-1,3,5,7-tetrazocine), octahydro-1,3,5-trinitroso-7-nitro-1,3,5,7-tetrazocine and octahydro-1,3,5,7-tetranitroso-1,3,5,7-tetrazocine. (Monteil-Rivera *et al.* 2003.)

Complete fungal degradation by *P. chrysosporium* have been shown to occur also via nitroso intermediates, which are subsequently transformed by N-denitration or α-hydroxylation to NDAB, nitrite, formaldehyde, N_2O and further to CO_2 (Fournier *et al.* 2004). Further, biotransformation of HMX by anaerobic sludge has been shown to occur, apparently via two distinct routes; by formation of mono- and dinitroso derivatives and by via ring cleavage producing methylenedinitramine (MEDINA) and bis(hydroxymethyl)-nitramines. The intermediates were subsequently degraded to nitrous oxide and formaldehyde and finally, to CO_2. (Hawari *et al.* 2001.)

2.3 Chemical and abiotic degradation

Explosive compounds are degraded chemically and abiotically by hydrolysis, oxidation, reduction and photolytic processes. In hydrolysis reactions, functional groups of the compounds react with water resulting to formation of new carbon-oxygen bonds and transformation of the compound. Instead, in oxidation and reduction reactions (redox-reactions) transformation of the compounds are based on electron transfer between reactants. As a consequence, electrons are donated in oxidation and accepted in reduction of the compounds. By photolysis, compounds are chemically altered due to direct and indirect effects of light, as light energy adsorbs into a molecule (or another photosensitive compound transmitting the effect) causing irreversible reorganization of a molecule (McGrath 1995).

2.3.1 Hydrolysis

Nitroaromatic compounds, RDX and HMX are not readily degraded by hydrolysis except in highly elevated pH conditions ($pH > 10$) and temperatures, which are not relevant in environmental conditions. (Balakrishnan *et al.* 2003; Hwang *et al.* 2006; McGrath 1995) Hydrolysis of HMX is slow at elevated pH conditions and HMX is stable at neutral pH range. In pH 10 the half-life of HMX is much longer (288 days) compared to RDX (4 days). (Monteil-Rivera *et al.* 2003.) In a study of alkaline hydrolysis of explosives, RDX, MNX and HMX were hydrolysed at pH over 10. As a result of nitramines hydrolysis, NO_2^-, formaldehyde, N_2O, $HCOO^-$, NH_4^+ and 4-NDAB was formed. (Balakrishnan *et al.* 2003.)

TNT is not significantly degraded by hydrolysis except at highly elevated pH 12. In a study of TNT alkaline hydrolysis, over 95% degradation in 24 hours (85-90% within 5 hours) on TNT in solution was obtained at pH 12, while degradation efficiency was below 25% (within 24 h) at pH 11. (Bajpai *et al.* 2004.) As a degradation process, hydrolysis is relevant under environmentally feasible conditions for only few explosives, including TNT related explosive compound tetryl (2,4,6-trinitrophenyl-N-methylnitramine) (McGrath 1995). However, hydrolysis at high pH (alkaline hydrolysis) can be used as subsequent treatment method for explosives contaminated water after extraction of groundwater (Hwang *et al.* 2005).

2.3.2 Photolysis

Photolysis is an important mechanism for TNT, RDX and HMX transformation in the environment (Talmage *et al.* 1999). Especially in surface waters, phototransformation of explosives is a significant process. Due to phototransformation, methyl groups are oxidized, nitro groups reduced and dimer compounds are formed. (McGrath 1995) In the environment, 1,3,5-trinitrobenzene (TNB) is the main stable product of TNT photolysis (Jenkins and Vogel 2014), but in general, nitrobenzenes, benzaldehydes, azoxydicarboxylic acids and nitrophenols are formed as a result of TNT photolysis. (McGrath 1995.) The photolysis of RDX and HMX results for production of a variety of compounds such as azoxy compounds, NH_3, formaldehyde, NO_3^-, NO_2^-, nitrous oxide N_2O, n-nitrosomethylenediamine (Glover and Hoffsommer 1979 according to Juhasz and Naidu 2007). In addition, also 4-nitro-2,4-diaza-butanal, methylenedinitramine, nitramide H_2NNO_2 and several other photodegradation products which are identified by chemical formula has been observed (Hawari *et al.* 2002).

Some phototransformation products have been overlooked in many studies due to scarce commercial availability and special techniques needed for detection. For instance, 2,4-dinitro-benzoic acid (2,4-DNBA) and 2-amino-4,6-dinitro-benzoic acid (2-A-4,6-DNBA) are substances that have been found as abundant acidic compound resulted from TNT phototransformation. (Godejohann *et al.* 1998)

Photolysis has been reported to result 22 hours half-life for 1.1 ppm TNT in pure water due to direct photolysis in sunlight (at spring time). However, analysis of 1.1 ppm TNT photolysis in filter-sterilized natural waters indicates 10 to 100 times faster photolysis probably due to promotion of photolysis by natural substances and photosensitized reactions. Also presence of TNT degradation products enhances TNT photolysis possibly by indirect photosensitized reactions. Similarly, photolysis of 1.3 ppm RDX resulted half-life of 13 days as measured in distilled water at winter time. Due to bad weather, the measurements were renewed at spring time, when photolysis experiments resulted half-life of 1.8 days. With RDX, photolysis was not enhanced in natural waters compared to distilled water as was discovered for TNT. (Spanggord *et al.* 1980.) In experiments of photolysis by sunlight (at spring time) for 0.5 ppm HMX, the half-lives determined were 8.6 - 10 days for pure water and 8.3 - 9.3 days for river water. HMX photolysis was not affected by other compounds such as humic substances. (Spanggord *et al.* 1982.) All the half-life values given above are for 12 hour sunlight per day.

In addition to transformation of explosives due to UV light, UV irradiation effects also on dissolution and decomposition of explosives. At contaminated sites, residual explosive compounds are subjected to photodegradation. (Martel *et al.* 2009; Taylor *et al.* 2010). The effect of light and photodegradation has been studied with HMX by exposing HMX containing sediment surface to UV irradiation in column experiments. As a result, dissolution of HMX was higher on soil exposed to UV compared to soil without UV exposure. However, the results are also affected by higher evaporation (and hence more concentrated solution) of the UV exposed soil (Arel 2004 according to Martel *et al.* 2009).

2.3.3 Reduction

Nitro groups of aromatic explosives are reduced to amino groups by abiotic reactions. (McGrath 1995). TNT reduction and affecting environmental factors has been widely studied and the reduction rate in anaerobic conditions has been found far greater than in aerobic conditions. The production of 2-ADNT and 4-ADNT is energetically favorable, but all transformation products from reduction of one to three nitro groups are found. (Pichtel 2012.) However, understanding and modelling of explosives reduction under natural conditions is challenging because of uncertainty of electron sources in reduction reactions. Also, distinguishing between abiotic and microbial reduction is very difficult. (McGrath 1995).

Reduction of RDX in anaerobic condition leads to production of mono-, di-, and trinitroso compounds (triazines). As a result of abiotic reduction (for instance by iron) of explosives, triazines from RDX reduction and polyamines from TNT reduction can then be further degraded by biological degradation processes. Accordingly, the use of iron as zero valent iron (ZVI) has been applied for remediation in TNT and RDX reduction in soil and aquifer. (Pichtel 2012.)

In contrast to TNT and RDX, abiotic reduction of HMX does not appear as a significant process. (Park *et al.* 2004; Spanggord *et al.* 1982) Accordingly, HMX is not readily reduced by ZVI. However, reduction rate of HMX can be increased by presence of certain cationic surfactants (such as didecyl and hexadecyltrimethylammonium bromide). Also other surfactants and high temperature increase HMX solubility and hence, the amount of HMX available for reactions, but does not have the catalytic effect of facilitating HMD reduction. (Park *et al.* 2004.)

2.3.4 Oxidation

Degradation of TNT in water by physical processes has not been extensively studied (Ayoub *et al.* 2010). However, degradation of TNT has been documented during removal of TNT from water by activated carbon. During the treatment experiment, oxidation of TNT to 2,4,6-trinitrobenzyl alcohol (TNBAlc) was evidently catalyzed by activated carbon. The TNBAlc was then subsequently oxidized to 2,4,6-trinitrobenzaldehyde (TNBAld) and 2,4,6-trinitrobenzene (TNB). (Vasilyeva *et al.* 2002.)

More efficient oxidation of explosive compounds can be achieved by Fenton reactions, other Fenton related processes (such as photo-Fenton, where UV light is applied to Fenton process) and advanced oxidation processes (AOPs) (Ayoub *et al.* 2010; Liou *et al.* 2004). However, as oxidation of compounds in these methods are based mostly on unspecific reactions due to radical formation, the reactions are unspecific, and the byproducts formed during the reactions can be more harmful than the original parent molecules (Pignatello *et al.* 2006).

In a study of TNT oxidation by photo-Fenton process, formation of 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (2,4-DNT), 2,5-dinitrobenzoic acid (DNBA) and 1,3-dinitrobenzene (DNB) was described as a result of oxidation of methyl group, decarboxylation, breakage of the aromatic ring structure and hydrolysis mechanisms. (Liou *et al.* 2004.)

Degradation of several explosives and related compounds (namely TNT, RDX, HMX, 2,4-DNT, 2,4,6-trinitrophenol, ammonium picronitrate and tetryl) by Fenton and photo-Fenton (40W UV light source) processes have been examined and compared under same experimental conditions. The susceptibility of the compounds for degradation by Fenton process were found to be in the decreasing order of 2,4-DNT > trinitrophenol > ammonium picronitrate > TNT > Tetryl > RDX > HMX, with HMX as the least prone for degradation. The degradation of all compounds followed first-order reaction behavior. For TNT, photo-Fenton was slightly more efficient than Fenton process, with RDX both had about the same efficiency, and with HMX, neither Fenton nor photo-Fenton resulted to efficient degradation within the experimental time of over 120 minutes for HMX. In all cases, increasing concentration of FeII in process enhanced the degradation rate. (Liou *et al.* 2003)

3. CHEMICAL PROPERTIES, MIGRATION AND FATE OF EXPLOSIVES IN GROUNDWATER

Physical, chemical and toxicity characteristics are important in evaluation of migration routes, environmental fate of the explosives and risks formed by the substances (Ympäristöministeriö 2014, p. 48). The risks are dependent on properties such as water solubility, volatilization potential and factors affecting bioconcentration, partitioning and migration characteristics. (Juhasz and Naidu 2007; Pennington and Brannon 2002). The highest risks for migration are among soluble or volatile substances that are not easily retained in soil. These are also substances that are most likely found in groundwater (Jenkins and Vogel 2014; Ympäristöministeriö 2014, p. 48.)

Explosive characteristics are also affected by explosive compositions. Generally, the explosives are used as mixtures (Jenkins and Vogel 2014). *TNT* or *Composition B* (60:40 mixture of RDX and TNT) are generally used as explosives in artillery and mortar warheads (Jenkins *et al.* 2006; Morley *et al.* 2006). Plastic explosive *C4* consists of military-grade RDX (91%) and plasticizers (9%). *Octol* is composed mainly of HMX and TNT in different proportions (e.g. 75:25 or 70:30 ratios by wt % of HMX and TNT) including also <1 wt % RDX as impurity (Monteil-Rivera *et al.* 2003; Pichtel 2012). HMX is also a component of all explosive mixtures containing RDX, since military-grade RDX contain 8 to 10% HMX as an impurity (Morley *et al.* 2006).

Chemical characteristics also affect degradation rate, which in turn is a major factor determining persistence of organic contaminants in soil and aquifer (Juhasz and Naidu 2007; Lawrence 2006). Toxicity and bioconcentration properties are also determined by the chemical characteristics of the substances. Degradation has been discussed in previous chapter and toxicity of explosives is discussed in following chapter 4. Further, understanding contaminant properties is also essential for sampling and investigation of the contaminated site (Thiboutot *et al.* 2002.) and management of explosive contaminations (Brannon and Pennington 2002). In this chapter, chemical characteristics and migration properties of the TNT, RDX and HMX are discussed.

3.1 Solubility

With water solubility of 130 mg/L at 20ºC (Thiboutot *et al.* 2002), TNT is soluble in water according to classification used in evaluation of environmental effects (Työterveyslaitos 2016; Ympäristöministeriö 2014, appendix 5). RDX and HMX have lower solubilities (42 mg/l at 20ºC and 5 mg/l at 25ºC, respectively) and hence, dissolve in water less compared to TNT (Thiboutot *et al.* 2002). At the same 20ºC temperature, HMX solubility 3.34 (±0.12) mg/L was measured by Monteil-Rivera *et al.* (2004). However, the dissolution rate is highly temperature dependent as documented within the ambient temperature range of 3-33°C, but dissolution is not dependent on pH. (Lynch 2002; Monteil-Rivera *et al.* 2004). For instance, in lower temperatures at 10ºC corresponding to groundwater conditions, the solubility of HMX was only 2 mg/L whereas the solubility of TNT remained high at 110 mg/L as measured in dissolution test using octol (Martel *et al.* 2009).

Variable dissolution rates for explosives have been reported in literature. However, the results are not comparable, since varying materials such as pure compounds and explosive mixtures have been used in the experiments under different experimental conditions (Lynch 2002; Martel *et al.* 2009) However, based on dissolution studies of Morley *et al.* (2006), the dissolution of TNT, RDX and HMX from explosive mixtures (C4 and Compound B) is lower under both continuous and intermittent flow conditions in soil columns compared to aqueous solubility of the substances. Hence, the highest steady-state effluent concentrations remained low and reached only 60% (RDX), 58% (HMX) and 19% (TNT) of the aqueous solubilities of the compounds. (Morley *et al.* 2006.)

Numerous dissolution studies of explosives have been done concerning individual explosive substances and formulation in batch reactors. However, the results may have limited applicability for evaluation of the in situ dissolution of explosives in training areas under natural conditions. (Morley *et al.* 2006) The explosive residues originate mainly from unexploded ordnance (UXOs) and incomplete second-order detonations, and are mixtures of explosives and other compounds such as waxes, stabilizers and binders added in manufacturing processes. Therefore, the dissolution properties may be significantly different and dissolution rate slower than anticipated based on maximum solubility and batch studies in laboratory. (Morley *et al.* 2006; Pichtel 2012).

The relevance of the explosive compound formulation for solubility is illustrated in studies conducted at Arnhem Anti-Tank Range in Canada. Based on estimated HMX mass on site and observed HMX flux into the groundwater (in 2005), the estimated dissolution rate for HMX was 250 mg/kg HMX from detonation residues / day. In contrast, the dissolution rate previously determined by lysimeter experiments on the same site by Arel (2004) was only 1.2 mg/kg/d. The conditions in both cases were similar but dependent on environmental conditions such as temperature and rainfall. The large difference in solubility was suspected to arise from difference in initial explosive material which was octol in both but in a form of detonation residues in the *in situ* estimation and octol flakes used in lysimeter experiments. In octol flakes, HMX is encapsulated in TNT. (Martel *et al.* 2009.)

3.2 Volatilization properties

Volatilization capacity of the substance is indicated by vapor pressure and Henry's Law constant. Volatilization potential of explosives is negligible according to Henry's law constant (K_H), describing volatilization from aqueous phase with values ranging from

K_H 10^{-7} to 10^{-15} atm m^3/mol and vapor pressures in the order of 10^{-9} to 10^{-12} atm (at 20°C) for TNT, RDX and HMX. Volatilization properties are also very low for explosive degradation products and other explosive associated compounds (Juhasz and Naidu 2007; Thiboutot *et al.* 2002). Vapour pressures and Henry's law constants for explosives and related compounds have been shown in table 1.

Table 1. Vapour pressures and Henry's law constants for explosives (TNT, RDX and HMX) and explosives related compounds and degradation products (4-ADNT; 2-ADNT; 2,4-DNT; 2,6-DNT; 1,3,5-TNB and 1,3DNB).

	Volatilization	
Substance	**Vapour pressure 1)** (1 atm 20°C)	**Henry's law constant (K_H) 2) atm m^3 mol^{-1}**
TNT	1) $1.5*10^{-9}$	$1.1*10^{-8}$ (at 25°C, est.) **2)**
RDX	1) $5.5*10^{-12}$	$1.96*10^{-11}$ (at 25°C, est.) **2)**
HMX	1) $4.3*10^{-17}$	$2.6*10^{-15}$ (at 25°C, est.) **2)**
2-ADNT	1) $5.3*10^{-8}$	-
4-ADNT	1) $2.6*10^{-8}$	-
2,4-DNT	1) $2.9*10^{-7}$ (at 25°C)	$1.86*10^{-7}$ (at 25°C, est.) **2)**
2,6-DNT	1) $7.4*10^{-12}$	$4.86*10^{-7}$ (at 25°C, est.) **2)**
1,3,5-TNB	1) $2.9*10^{-17}$	$2.21*10^{-9}$ (at 25°C, est.) **2)**
1,3-DNB	1) $5.1*10^{-6}$	$8.01*10^{-7}$ (at 25°C, est.) **2)**

1) Thiboutot *et al.* 2002 (Vapour pressures converted to atm according to 1 atm = 1/760 torr); 2) Rosenblatt *et al.* 1989 according to Brannon and Pennington 2002

Generally, K_H values greater than 10^{-5} atm-m^3/mol are considered to indicate potential to volatilize from aqueous solutions. (Pichtel 2012.) The vapor pressures determined at 1 atm pressure and 20°C temperature are also very low for all explosive compounds. The vapour pressures are in a range of 10^{-9} to 10^{-17} for TNT, RDX and HMX (Thiboutot *et al.* 2002). Due to very low vapor pressures and Henry's Law constants evaporation of the explosives is negligible. Therefore, evaporation is not a significant process determining transport and environmental fate of explosives. (Jenkins and Vogel 2014; Clausen *et al.* 2006.)

3.3 Adsorption

TNT has both hydrophobic and hydrophilic characters as indicated by measured octanol–water partition coefficient (log K_{OW} = 1.6). Based on low K_{OW}, TNT is expected to be relatively mobile in the environment and not strongly sorbed on soil or sediment. (Ayoub *et al.* 2010.) However, adsorption properties of TNT remain controversial in regard to factors affecting affinity such as organic carbon content in soil. Yet, adsorption is important process due to major impact for estimation of TNT migration (Sharma *et al.* 2013).

Generally, RDX and HMX are sorbed to soil particles less than TNT as demonstrated by sorption coefficients up to 68 L/kg obtained for TNT and below 9 L/kg for RDX and 3 L/kg for HMX obtained in the same study. And especially for RDX, sorption properties seem weak based on column studies where breakthrough has been fastest for RDX. (Sharma *et al.* 2013; Sheremata *et al.* 2001.) Uncertainty exists also on HMX sorption properties, but according to most studies, sorption does not appear to be a significant process for HMX. Sorption of HMX is apparently reversible, although possibly slow (Clausen *et al.* 2006; Xue *et al.* 1995 according to Clausen *et al.* 2006). Also, the irreversibility of the sorption processes for TNT and RDX are controversial. While some authors state that TNT and RDX sorption is reversible, the results of others indicate almost full irreversibility of the process for TNT and RDX. (Clausen *et al.* 2006; Pichtel 2012; Sheremata *et al.* 2001). However, sorption of TNT degradation products are increased and sorption becomes irreversible as nitro groups become substituted by amino groups (Hawari *et al.* 2000a.)

3.3.1 Adsorption to organic carbon

Adsorption properties of substances are evaluated by affinity of the compounds to organic carbon in soil and are indicated by organic carbon partitioning coefficient (K_{OC}) (Reinikainen 2007, p. 20). K_{OC} –values can be obtained from literature (experimental and estimated values) or coefficients can be calculated from octanol-water partitioning coefficient (K_{OW}) using suitable equation. The equations formed to describe relation between K_{OW} and K_{OC} are based on experimental results obtained from similar group of substances. (Clausen *et al.* 2006; Hemond and Fechner 2015).

TNT

Reported K_{OC} coefficients for TNT vary between 300 to over 1500. In literature and databases K_{OC} values of 300 (US EPA TNT data sheet), 306.5 (ChemSpider database) and 1585 (as log K_{OC} 3.2 in Ek 2005 according to Ayoub *et al.* 2010) have been reported. These values differ notably and indicate properties from moderate to relatively strong adsorption in soil and mobility properties from slightly mobile to mobile compound. (Ympäristöministeriö 2014, appendix 5.)

Differences in K_{OC} coefficients are due to origins of the values and different methods for determination of affinity to organic carbon. Some of the values are computational estimates while others are based on experimental data and variable experimental setups. (Ayoub *et al.* 2010; ChemSpider 2016; Ek 2005; Spanggord *et al.* 1985; US EPA 2012a). However, original articles for cited literature values are inaccessible. Compounds (or groups of substances) used to generate the equations are not identified in subsequent references and hence, data used to generate the values are not available for evaluation. Therefore, it is difficult to assess and compare the accuracy of reported values.

RDX and HMX

Sorption parameters for RDX and HMX were determined by Monteil-Rivera *et al.* (2004). Water-octanol partition coefficients were measured using water-octanol and nitramines at different proportions. The coefficients determined were K_{OW} 8.0 ± 0.6 for RDX and K_{OW} 1.46 ± 0.02 for HMX. The results were reported to be in accordance with previously reported values. (Monteil-Rivera *et al.* 2004.)

The low K_{OW} values are in accordance with Log K_{OC} values in a range of 0.89 – 2.43 (K_{OC} 7.8 - 269) for RDX and 0.54 – 2.83 (K_{OC} 3.5 - 676) for HMX as reported in the 1980s based on estimations and measurements (McGrath 1995). The Log K_{OC} values reported denote very low to slight adsorption to organic carbon and hence, indicate mobility of the compounds (Ympäristöministeriö 2014, appendix 5).

3.3.2 Site specific adsorption

Although affinity to organic carbon and K_{OC} –values are characteristic to compounds, sorption and retention of the contaminants to soil particles on each particular ***site*** are largely dependent on soil type and chemical properties (such as cation content) of the soil. Therefore, it is more useful to evaluate adsorption characteristics of the explosives with soil/water partitioning coefficients (K_d) specific to each site (Ympäristöministeriö 2014, p. 48-49, 99). The K_d distribution coefficient is expressed in L kg^{-1} and denotes the ratio of the sorbed concentration (mg kg^{-1}) of the compound to dissolved concentration of the compound in pore water (mg L^{-1}) (Martel *et al.* 2009).

K_d –values for organic compounds in particular sites can be calculated by multiplication of measured organic carbon content on the site with the K_{OC} coefficient of the pollutant according to equation 1 (Clausen *et al.* 2006).

$$K_d = K_{OC} * f_{OC} \tag{1}$$

where K_d = soil/water partitioning coefficient
K_{OC} = compound specific organic carbon partitioning coefficient
f_{OC} = site specific organic carbon content

However, as noted in case of TNT, K_{OC} values obtained from the literature are divergent. Hence, better approach to obtain reliable K_d –values representing the site would be experimental determination of the value.

TNT

The K_d -values determined for TNT has varied from 2.3 to 11 L/kg in soil in most experiments (Pichtel 2012). For surface soils K_d coefficients between 2.7 to 3.7 L/kg (Xue *et al.* 1995 according to Pichtel 2012), 2.4 to 7.3 L/kg and 11.3 L/kg for clay (Pennington 1987) have been determined. Recently, considerably higher soil/water partitioning coefficients have been reported for TNT ranging between 42–68 L/kg in soils rich in organic carbon and between 19–21 L/kg in clay rich soils. The values are expressed in Freundlich coefficients (K_f), since adsorption of TNT was better described by Freundlich isotherm (r^2 0.91 - 0.99 for different soils) than linear equations. (Sharma *et al.* 2013.) For aquifer materials, K_d values between 0.04 to 0.27 L/kg for TNT has been reported (Pennington *et al.* 1999 according to Pichtel). Similarly, high K_d value 50 L/kg was recently determined for TNT in aquifer materials in sorption batch test consisting of 1:10 stream sediment and stream water. The sediment in the experiment was enriched with nutrients (filter-sterilized waste water) to increase dissolved organic carbon content to sediment naturally very low on organic matter. (Zheng *et al.* 2009.)

The K_d values reported for TNT show large variability and indicate marked differences in transport capacities from extremely migrating (K_d –values <0.75) in aquifer to weakly migrating (K_d 30 – 75) compounds. The migration properties in between can be classified as easily (K_d 0.75-2.25), moderately (K_d 2.25-7.5) and slightly migrating (K_d 7.5 – 30). Only the class of not migrating (K_d >75) is not included in K_d values reported for TNT. (Ympäristöministeriö 2014, appendix 5).

Adsorption properties of TNT are controversial according to results obtained by several authors. Some studies indicate that for TNT, K_d coefficient is dependent on organic carbon content in soil (e.g. Sheremata *et al.* 1999; Yamamoto *et al.* 2004) and based on other studies, organic carbon content is not a factor determining TNT adsorption. Instead, strong correlation with cationic exchange capacity, clay and iron content was reported (Brannon *et al.* 2002; Pennington and Patrick 1990). Further, characterization of interactions between soil and TNT is especially difficult, since TNT is often rapidly biotransformed and reduced to amino derivatives, which bind strongly to soil particles (Brannon and Pennington 2002; Thiboutot *et al.* 2002).

The sorption capacities are enhanced as the number of amino groups increase (Hawari *et al.* 2000a; Sheremata *et al.* 1999). Accordingly, the degradation products of TNT are sorbed on soil more strongly compared to TNT and the sorption of diaminonitrotoluenes is greater than of aminodinitrotoluene. In a study of Sheremata *et al.* (1999) sorption properties of TNT and its degradation products were assessed for three different types of materials; natural topsoil, illite shale (100% clay) and sandy aquifer. Sorption capacity and K_d values decreases in the order of 2,4-DANT > 4-ADNT > TNT in natural topsoil (8.4% organic matter, pH 5.6) with the corresponding K_d values of 11.96, 7.91 and 6.38, respectively. However, sorption properties were dependent on soil type, since the situation was reversed and the order of decreasing sorption was TNT (K_d 223.63) > 4-ADNT (K_d 58.52) > 2,4-DANT (K_d 19.73) for 100% clay material (pH 6.0). TNT and its degradation products were not sorbed on sandy aquifer materials (0.02 % organic matter, pH 8.4). The difference in sorption between top soil and sandy aquifer soil were considered to originate from difference in organic matter content, since mineralogy between the two soils was similar. (Sheremata *et al.* 1999).

RDX

Reported K_d -values for RDX in soil have been in the range of 0.06 to 8.7 L/kg (Pichtel 2012; Sharma *et al.* 2013). For instance, low sorption properties of RDX were indicated by K_d 0.83 obtained for agricultural top soil (Sheremata *et al.* 2001) and K_d 0.3 L/kg for sandy loam soil (Monteil-Rivera *et al.* 2004). More recently, slightly stronger sorption properties has been observed according to K_d coefficients 6.9–8.7 L/kg in organic carbon rich soil and 2.5–3.4 L/kg in clay rich soil determined for RDX (Sharma *et al.* 2013). K_d value 2.2 L/Kg was reported for RDX in river sediment enriched with nutrients and dissolver organic carbon (Zheng *et al.* 2009).

Dependence of sorption properties from soil organic carbon content (Yamamoto *et al.* 2004) and irreversibility of the sorption process (Brannon *et al.* 2002 according to Pichtel 2012; Sheremata *et al.* 2001) has also been reported for RDX. According to Price *et al.* (1998), RDX sorption is also affected by soil and aquifer oxidation/reduction potential (aerobic/anaerobic conditions) and pH. In their study, RDX sorption was lowest at highly reducing conditions (-150 mV) and highest at pH 8 under moderately reducing conditions (+250 mV). Compared to optimal conditions, sorption was also decreased in all pH conditions under aerobic conditions (+500 mV).

HMX

Uncertainty exists also on sorption properties of HMX and soil characteristics do not seem to predict HMX distribution coefficients well (Brannon *et al.* 1999). According to some studies, HMX sorption appears slightly higher compared to RDX (Monteil-Rivera *et al.* 2003 and 2004). K_d –values for HMX has varied between 0.12 – 17.7 L/kg depending on soil properties (Brannon *et al.* 1999), 0.087 - 0.125 L/kg at Arnhem military training site (Martel *et al.* 2009) and 0.7 L/kg for sandy loam soil (Monteil-Rivera *et al.* 2004). Sorption for aquifer material is weak, as indicated by low K_d –values between 0.09–0.37 L/kg (Pennington *et al.* 1999). However, notably higher sorption properties of HMX (with K_d 2.9 L Kg^{-1}) were reported to sediment containing high organic carbon content. In sorption batch test, sediment in 1:10 river sediment and river water set up was enriched with filter-sterilized waste water in order to increase dissolved carbon content in sediment. (Zheng *et al.* 2009).

Soil organic carbon content has some (although not significant according to authors) effect on HMX sorption, since K_d coefficient 2.5 L/kg was obtained for agricultural topsoil containing 8.4% total organic carbon content (TOC), pH 5.6 and only 0.7 L kg^{-1} for sandy soil with 0,33% TOC, pH 5.1. The results were obtained in otherwise same laboratory conditions at room temperature. (Monteil-Rivera *et al.* 2003). Similar results were recently reported for HMX with determined K_d values 2.6–3.1 L/kg for organic carbon rich soils and 0.9–1.2 L/kg for soil rich in clay (Sharma *et al.* 2013).

Both HMX sorption and desorption are rapid processes, and equilibrium has been achieved within 1 day in laboratory conditions. Supposedly HMX is adsorbed mainly by non-specific interaction, but also some form of specific interaction between HMX and soil containing high organic carbon content is indicated by sorption/desorption hysteresis (desorption coefficient K_d^D 4.5-5.0 L kg^{-1} > sorption coefficient K_d^S 2.5 L kg^{-1}). However, covalent bonds apparently are not formed, since full extraction of HMX has been obtained in extraction process. (Monteil-Rivera *et al.* 2003).

3.4 Migration

Migration properties of the explosive compounds are evaluated by water solubility and potential to bind organic carbon in soils and sediments. However, soil and aquifer properties, such as pH and redox potential, effect on migration and retention characteristics of the explosives. Biological degradation and transformation of compounds are also dependent on soil conditions. Therefore, the physical and chemical properties of soil and aquifer need to be taken into account in evaluation of transport and fate of explosive residues. (Pichtel 2012; Ympäristöministeriö 2014, p. 48, 54.)

Explosives in soil and unsaturated zone of the aquifer end up in groundwater by dissolution to infiltration water. The rate of water flow in soil pores effect on contact time between explosive compounds, water and soil particles. (Ympäristöministeriö 2014, p. 53-54.) The partition of the contaminants is generally assumed balanced and concentration of the contaminants approximately constant in soil, pore water and air in pores. Based on known K_d –value and the concentration of the explosive compounds on site, the concentration of the compound in pore water in balanced conditions can be calculated. (Ympäristöministeriö 2014, p. 99.)

Migration properties and fate of the explosives can be considered also by viewing the explosive concentrations reported from soil, water sources and sediments. Generally concentrations are very high on sites contaminated by operation of *ammunitions plant and ordnance disposal sites,* while significantly lower contamination levels are detected due to *military training and explosives testing* sites. Reported concentrations of TNT, RDX and HMX due to ammunitions plant and ordnance disposal are presented in table 2 and due to military training action in table 3.

Table 2. Explosive concentrations in soil and water reported at *Vicinity of ammunitions plant and ordnance disposal sites*

		Concentration	**Characterization of the site**	**References**
Soil	TNT	<0.1 – 10,056 mg/kg	Ammunition plant sites in US	Pennington *et al.* 1999
	RDX	0.587 – 75,000 mg/kg <0.1 – 0.50 mg/kg	Ammunition plant sites in US Ammunition plant sites in US	US Army 2011 in ATSDR 2012 Pennington *et al.* 1999
	HMX	<0.1 mg/kg	Ammunition plant sites in US	Pennington *et al.* 1999
Sediment	RDX	0.363 – 14,100 mg/kg	Iowa Army ammunition plant site	US Army 2011 in ATSDR 2012
Groundwater	TNT	3,400 ± 140 µg/L 34 ± 2 µg/L 910 – 1,370 µg/L 690 – 870 µg/L <0.02 – 15,100 µg/L 7.51 – 12,130 µg/L	Former ammunition production site; and well near former production site, Germany Former ammunition plant site from WW II in Germany Ammunition plant sites in US	Godejohann *et al.* 1998 Steuckart *et al.* 1994 Pennington *et al.* 1999
	RDX	< 50 - 18,000 µg/L 2,380 – 3,800 µg/L 310 – 400 µg/L 7.97 – 25,500 µg/L 2.18 – 22.7 µg/L	Ammunition plant sites, US Former ammunition plant site from WW II in Germany Ammunition plant sites in US	ATSDR 2012 Steuckart *et al.* 1994 Pennington *et al.* 1999
	HMX	<0.02 – 9,080 µg/L <0.02 – 2.04 µg/L	Ammunition plant sites in US	Pennington *et al.* 1999
Surface water	TNT	4.0 ± 0.3 µg/L	Former deposition site of neutralization sludge, Germany	Godejohann *et al.* 1998
	RDX	80 - 120 µg/L up to 36,900 µg/L	Ammunition plant sites Closed army munitions plant	ATSDR 2012
Porewater leachate	TNT	180 ± 7 µg/L	Leachate at former ammunition production site, Germany	Godejohann *et al.* 1998

Table 3. Explosive concentrations in soil and water reported at *Military training and explosives testing sites*

		Concentration	**Characterization of the site**	**References**
Soil	TNT	5.9 µg /kg	Anti-tank range impact area, Älvdalen, Sweden	Wingfors *et al.* 2006
		<0.01 – 36 mg/kg	Hand grenade ranges, US	Jenkins *et al.* 2006
		0.04 – 126 mg/kg	Antitank rocket range	
		<0.001 – 5.6 mg/kg	Artillery targets	
	RDX	16,000 mg/kg	US military training site operated for decades	Morley *et al.* 2006
		9.8 µg /kg	Anti-tank range impact area, Älvdalen, Sweden	Wingfors *et al.* 2006
		<0.01 – 51 mg/kg	Hand grenade ranges, US	Jenkins *et al.* 2006
		<0.01 – 5.3 mg/kg	Antitank rocket range	
		<0.001 – 6.5 mg/kg	Artillery targets	
	HMX	4,800 µg /kg	Anti-tank range impact area, Älvdalen, Sweden	Wingfors *et al.* 2006
		<0.01 – 9.1 mg/kg	Hand grenade ranges, US	Jenkins *et al.* 2006
		23 – 987 mg/kg	Antitank rocket range	
		0.003 – 5.6 mg/kg	Artillery targets	
Ground-water	TNT	128 ± 6 µg/L	Military training site, Germany	Godejohann *et al.* 1998
	RDX	0.0087–86.4 µg/L	Aberdeen Proving Ground in US	US Army 2011 in ATSDR 2012
		50 µg/L	shallow well (3-6 m) in silty sand aquifer at US explosives testing range (also contaminated by perchlorate)	Cho *et al.* 2015
		21 ± 1 µg/L	Military training site, Germany	Godejohann *et al.* 1998

Explosive contaminations have unusual nature of uneven distribution over large areas with various sizes of the contaminating material, and the information obtained from discrete soil samples may be misleading (Thiboutot *et al.* 2002). Accordingly, from 3 fold to even 315 fold variations in TNT concentrations have been reported on same site within 122 cm distances (Jenkins *et al.* 1996). Hence, screening of groundwater for explosive compounds and degradation products can be used as an indication of possible site contamination in case of scattered explosive contaminations (Thiboutot *et al.* 2002).

The solubility of TNT is higher compared to RDX and HMX. Especially HMX tend to retain in surface soils as a result of low aqueous solubility. However, due to their weaker sorption properties (lower soil/water partition coefficient), the soluble part of RDX and HMX are generally more mobile than TNT and are more frequently found in the groundwater. (Groom *et al.* 2002; Pennington *et al.* 2006.) The transport of TNT into the groundwater can be decreased by transformation properties of TNT and formation of products that bind irreversibly to soil (Kalderis *et al* 2011; Pennington *et al* 2006). TNT is biotransformed, but not mineralized (Martel *et al.* 2009). Total of 21 metabolites and degradation products of TNT with various characteristics and migration properties are known for TNT. For instance, aminodinitrotoluenes resulting from biodegradation and photolysis of TNT are considerably more soluble, but are retained in soil by binding covalently to humic acid. Therefore, aminodinitrotoluenes are stabilized on organic material of the soil and are not likely transported into groundwater. (Thiboutot *et al.* 2002).

Under aerobic conditions HMX is not biotransformed or mineralized in the aquifer and is only weakly retained on soil by sorption. (Martel *et al.* 2009). However, HMX sorption is increased at elevated pH 8 or under moderately reducing conditions. RDX is also relatively stable under oxidizing conditions and not significantly transformed, but the sorption of RDX is increased under aerobic conditions. In anaerobic conditions, however, RDX is unstable and efficiently transformed and mineralized under neutral pH conditions. (Price *et al.* 1998.)

The assumptions of prevailing balanced conditions in contaminated site and constant contaminant concentrations need to be made with precaution. Variable water levels and transitions between saturated and unsaturated conditions below military training areas may result on significant variation with the seasons. Higher mobility of explosive compounds may be resulted from increased infiltration rates, but also dilution of the compounds is possible. (Martel *et al.* 2009.)

In addition to migration as soluble substance, possibility of TNT colloidal transport has been shown by observation of approximately 36% of TNT in colloidal fraction of the samples in sorption experiments and 20% in the effluent of the transport experiment. Also RDX and HMX have been found in colloidal fraction, but similar association of migration within colloidal fraction has not been obtained in transport experiments (Sharma *et al.* 2013.) Instead, results indicating HMX tendency to retain in the uppermost soil layer has been reported. In some cases with simultaneous TNT, RDX and HMX contaminated sites, only HMX has resisted as a sole contaminant in topsoil. (Groom *et al.* 2002.)

3.5 Fate in the groundwater

In the vadose zone, contaminants are transported dominantly by vertical flow, while horizontal flow is more important in aquifer zone. Below the groundwater table, transport mechanisms are dispersion, diffusion and advection. Advection is movement of compounds along water in direction of groundwater flow, dispersion longitudinal or transverse spreading of compounds and by diffusion, compounds are migrated from higher concentration to lower according to concentration gradient. (Clausen *et al.* 2006.)

Based on results obtained by sorption and degradation experiments under variable conditions, RDX is expected to be mobile and persistent in groundwater under oxidizing or moderately reducing conditions. Instead, in highly anaerobic conditions and neutral pH, RDX is likely to be unstable and would not persist. Similarly, HMX is most likely persistent and mobile in groundwater, excluding highly reducing conditions with approximately pH 6. (Price *et al.* 1998.)

As compared to RDX, TNT is likely to be less stable in groundwater, since transformation of TNT has been reported to occur in any conditions, including groundwater and surface waters. For TNT half-lives of the order of days in soil and between 28 d to a year in groundwater have been proposed. However, as TNT degradation is generally not complete, TNT and its degradation products can be persistent in the environment. (Clausen *et al.* 2006.)

In accordance with predicted stability of explosives in groundwater, RDX has been shown to be stable in aerobic conditions close to neutral pH and to form groundwater plumes even thousands of meters long in 10-100 µg/L concentrations (US Army Corps of Engineers 2015 according to Michalsen *et al.* 2016). (See also table 2 for detected RDX concentrations at former ammunition plant site from WW II.) Explosives have also been shown remain in soil and aquifer for a long time, as demonstrated by over 1 mg/L levels of TNT and almost 4 mg/L RDX found in groundwater due to ammunitions production during World War II (table 2 presented in chapter 3.4) (Steuckart *et al.* 1994).

In addition to explosives in groundwater, also transformation products can be found in significant amounts. Groundwater, surface waters and leachate waters has been investigated at known nitroaromatic contaminated former ammunition sites in Germany. As a result, samples that were contaminated by TNT and related compounds, contained also significant amounts of acidic transformation products. Hence, samples contained also 2,4-DNBA (4.5 µg/L in leachate and 160 µg/L in groundwater), 45 µg/L 3,5-dinitrophenol (3,5-DNP) in groundwater and 2-A-4,6-DNBA (37 µg/L in leachate, 3.3 µg/L in surface water and 7.4 - 86 µg/L in groundwater). The discovery of acidic products was important, because the presence of these compounds have often been overlooked due to difficulties of detection in routine investigation under standard conditions. In addition, also dinitrotoluenes, aminodinitrotoluenes, dinitrobenzene and trinitrobenzenes were found at elevated concentrations. (Godejohann *et al.* 1998.)

4. TOXICITY OF EXPLOSIVES AND DEGRADATION PRODUCTS

The greatest ecological risks are caused by persistent, bioaccumulative and toxic (PBT) substances; very persistent and very bioaccumulative (vPvB) substances; and compounds interfering hormone functioning. (ECHA 2016; Ympäristöministeriö 2014, p. 48). Serious health risks and long-term effects for humans are also caused by CMR-substances which refer to substances that are Carcinogenic, Mutagenic, or toxic for Reproduction (ECHA 2012). None of the secondary explosives discussed in this study (TNT, RDX and HMX) have been classified into these groups of chemicals.

Many of the explosive compounds, their degradation products and related substances such as production impurities have toxical properties (Khan *et al.* 2013). Of the explosive compounds and related substances, assessment of PBT/vPvB –properties has been made for 2,4-DNT (CAS number 121-14-2) under previous EU chemicals legislation. As a result, 2,4-DNT did not meet the criteria set for PBT/vPvB –substances, since the B criterion for bioconcentration is not filled (ECHA 2016).

4.1 Bioaccumulation

Bioaccumulation potential of the organic pollutants may be evaluated by octanol-water partitioning coefficient (K_{OW}). K_{OW} is determined by the distribution of the compounds between water and octanol and is used to illustrate fat-solubility of the substance. (Reinikainen 2007, p. 40-41.) As discussed in chapter 3.3, the log Kow (and Kow) values are approximately 1.6 (Kow 39.8) for TNT (Ayoub *et al.* 2010), 0.90 (Kow 8.0) for RDX and 0.16 (Kow 1.46) for HMX (Monteil-Rivera *et al.* 2004).

Octanol-water partitioning coefficients are generally expressed as logarithmic values (log K_{OW}). The values are interpreted as log K_{OW} 0 meaning same proportions of a substance in water and octanol. Log K_{OW} -1 indicate preference for water and the concentration of the substance is 1/10 in octanol from the concentration in water. High log K_{OW} values (>3) indicate lipophilic properties and the substance has potential for bioconcentration. Log $K_{OW} > 4$ indicate moderate bioaccumulation and compounds with log $K_{OW} > 5$ are extremely bioaccumulating. (Työterveyslaitos 2016; Ympäristöministeriö 2014, appendix 5.)

Uptake of RDX by many plant species grown at RDX contaminated soil or irrigated with RDX contaminated water has been reported. Hence, RDX concentrations corresponding to soil or water levels have been shown with some agricultural crop species (lettuce, corn stover, alfalfa) and aquatic plants (e.g. Elodea, water star-grass, sweet flag). Also significant bioaccumulation has been shown with agricultural lettuce and aquatic parrotfeather. Exposure to RDX by eating agricultural crops containing RDX is possible, but estimates for oral exposure effects in humans are not available. Based on observations from humans and animal studies, RDX is supposedly degraded rapidly in the body. (ATSDR 2012.)

Accumulation of HMX to different indigenous and agricultural plant species has also been investigated in order to study phytoremediation in removal of HMX from contaminated soil. In the experiment, plants were grown in firing-range soil containing HMX. Indigenous plants were harvested on site and agricultural species were grown at greenhouse. As a result, all 5 studied agricultural species and several indigenous species accumulated significant amounts of HMX (up to 50 mg/kg fresh material) in plant foliar tissues. HMX was not degraded by plants. The only detected HMX transformation products in plant tissues was mononitroso-HMX, which was also present in soil. (Groom *et al.* 2002.)

TNT is also taken up by plant roots, but is either not transported to leaves or is transformed and immobilized as conjugates. However, TNT is toxic to plants and hence, TNT is not present in plants at high concentrations. (Jenkins and Vogel 2014.)

4.2 Toxicity of the explosive compounds

Possible exposure routes of explosives for humans are inhalation, dermal absorption and ingestion. Mostly health effect related data for explosives are based on observations of munition plant workers and animal studies. Toxicological data of TNT effects on microorganisms, invertebrates and plants are available, but data is scarce for other explosives. (Kalderis *et al.* 2011.)

TNT

Toxicity of TNT and its degradation products have been extensively studied. During recent years, the toxicity properties of TNT have been examined using aquatic and terrestrial organisms including earthworms, mammals and human cells. The results of toxicity analysis have been diverse indicating differences in sensitivity of the organisms to TNT. (Ayoub *et al.* 2010.) In animal studies with mammals, wide variety of adverse effects have been noted including effects on gastrointestinal track, liver, kidneys and cardiovascular, hematological, immunological, neurological, reproductive, developmental, genotoxic and carcinogenetic effects. (Kalderis *et al.* 2011.)

In humans, association of TNT with liver damage and anemia has been shown. TNT has been classified as possible human carcinogen to Group C according to classification of US EPA (US EPA 2012b) and to Group 3 by the categorization of the International

Agency for Research on Cancer. The classification of Group C (according to original 1986 guidelines) refer to compounds with limited evidence to cause cancer in animals and little or no human data (US EPA 2016b). Similarly, classification of Groups 3 (by IARC) refer to compounds, which are not classifiable as human carcinogen due to inadequate data (IARC 2016). US EPA has set a proposal for a Lifetime Health Advisory level (LHA) of 2 µg/L and Drinking Water Equivalent Level (DWEL) of 20 µg/L for TNT in drinking water. DWEL values describe exposure level at which no adverse effects (other than carcinogenicity) is expected to occur and are determined assuming 100% exposure for substances from drinking water (US EPA 2012b). Hence, for TNT and other explosive compounds, DWEL values can be considered suitable in regard to health risks caused by exposure from drinking water, since generally there is no other exposure sources in the environment for explosives and the adverse effects caused by explosives are other than carcinogenic.

RDX

RDX has no international (WHO) guidelines for air or drinking water quality and does not have IARC carcinogenicity classification. However, US EPA has classified RDX as possible human carcinogen (Group C substance) and set proposal for 2 µg/L LHA and 100 µg/L DWEL for RDX (US EPA 2012b). The US EPA carcinogenicity classification is based on historical data which was interpreted as indicating carcinogenicity at the time. However, no evidence of RDX carcinogenicity has been obtained from rats, and the possible evidence previously considered as indicative of carcinogenicity in mice, is equivocal and seems unlikely after re-evaluation of the study. Hence, RDX carcinogenicity classification is currently under re-evaluation. (ATSDR 2012; Michalsen *et al.* 2016)

The information about RDX toxicity for humans is limited and is based on individual cases of RDX exposure and data inferred from animal studies. The effects reported for humans are neurologic dysfunctions which occur primarily as convulsion and seizures. Similar effects have been reported for different animal species (rats, mice, dogs and monkeys) for acute and long term exposure. (ATSDR 2012.)

HMX

Limited data is available on effects of HMX to humans. Based on animal studies, high doses of HMX are hepatotoxic and have adverse effects on kidneys, gastrointestinal tract and also mild hematological effects are possible. (Kalderis *et al.* 2011.) The carcinogenicity classification according to US EPA is Group D (not classifiable as to human carcinogenicity) and the LHA and DWEL values have been set for 400 µg/L and 2,000 µg/L, respectively (US EPA 2012b).

4.3 Toxicity of the explosive degradation products and other explosive associated compounds

Traditionally, only the toxicity of explosives has been studied. However, during recent years, more focus has been put also on toxicity of the intermediates and degradation products of the explosive compounds. Available data of the toxicity of explosives degradation products has been recently reviewed by Khan *et al.* (2013). Toxicity to micro-organism, algae, plant, invertebrate and vertebrate reporter organisms was compared relative to the toxicity of the parent compound TNT. Available toxicity data from published studies is based on effects of the compounds to observed parameters such as mutation rate, growth, reproduction, survival and mortality. As a result, relative toxicity of the degradation products is dependent on compound, organism and parameters studied, but in many cases, the toxicity of the product is within the same range or even higher compared to TNT. (Khan *et al.* 2013.)

In addition to species sensitivity to substances, differences in relative toxicity for explosive compounds and degradation products obtained between studies, can also be due to variation in biotic and abiotic factors in soil, sediment or water used as exposure media affecting the result (Lachance *et al.* 2004). However, relative toxicity of several known TNT degradation products compared to TNT remain uncertain, since comprehensive studies with sufficient data has not yet been published (Khan *et al.* 2013).

4.3.1 Aminonitrotoluenes

The aminonitrotoluenes 2-ADNT and 4-ADNT are the most abundant degradation products of TNT and are generally found in TNT contaminated sites (Lachance *et al.* 2004). Traditionally, TNT degradation products have been considered more harmless compared to TNT. However, amino- and hydroxylaminonitrotoluenes has been found as less, even or more harmful depending on organisms and parameters studied. (Khan *et al.* 2013.)

Indication of relatively slightly more ecotoxic properties of TNT degradation products 4-ADNT and 2-ADNT compared to TNT for cricket (Acheta domesticus) reproduction (egg hatching, but not egg production), has been reported (Karnjanapiboonwong *et al.* 2009). Similar results for toxicity of 4-ADNT and 2-ADNT, were obtained in a toxicity test using earthworms (*Eisenia andrei*) grown in explosives amended sandy loam forest soil. Further reduced TNT degradation products 2,4-DANT and 2,6-DANT were not toxic for earthworms. However, all substances were found to bioaccumulate in worms with bioaccumulation factors 6.4 (4-ADNT), 5.1 (2-ADNT), 5.1 (2,4-DANT) and 3.2 (2,6-DANT). (Lachance *et al.* 2004.)

The data of toxicity properties of *Hydroxylaminodinitrotoluenes*, triaminotoluene (TAT) and azoxytoluenes is limited. 2-hydroxylamino-4,6-dinitrotoluene and 4-hydroxylamino-

2,6-dinitrotoluene seem to have similar toxicity properties than TNT while TAT and tetranitro-azoxytoluenes seem less toxic compared to TNT. (Khan *et al.* 2013.)

4.3.2 Dinitrotoluenes

Dinitrotoluene (DNT) exist 95% of the 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) isomers, while the remaining 5% consists of 2,3-DNT, 2,5-DNT, 3,4-DNT and 3,5-DNT isomers. DNT does not have a natural source in the environment and is generally found only at manufacturing or utilization source areas. DNT is produced commercially for TNT production and as an intermediate in toluene di-isocyanate manufacturing. (ATSDR 2013.) 2,4-DNT is used in propellants of the energetic compounds (Jenkins *et al.* 2006) and is also occasionally observed as degradation product of TNT (Liou *et al.* 2004; Martin *et al.* 1997).

In the environment, DNT is degraded at slow rate by micro-organisms and rapidly by sunlight induced photolysis in surface waters. In soil even over 110 mg/kg concentrations of DNT have been detected. (ATSDR 2013.) Dinitrotoluenes have also been found at *impact* areas of anti-tank range at Älvdalen in Sweden, probably due to incomplete combustion at detonation. 2,4-DNT was found with 200 µg/kg and 2,6-DNT with 69 µg/kg concentration. The concentrations were remarkably higher than of TNT and RDX found at site, but less than of HMX (table 3). (Wingfors *et al.* 2006). DNT is not strongly sorbed to soil and therefore, can be transported to groundwater. Concentrations as high as 10 000 µg/L have been found in groundwater at a location close to ammunition plant. (ATSDR 2013.)

Both isomers, 2,4-DNT and 2,6-DNT are classified in Group B2: Propable human carcinogen by US EPA (2012) and possible carcinogens by Agency for Research on Cancer (IARC). DNTs are also classified as priority pollutant by US EPA (2016a). The assessment of carcinogenicity is based on animal carcinogenicity data and data concerning human carcinogenicity is not available (US EPA 1990). The short- and long-term effects for DNT are similar based on animal studies. DNT ingestion has been reported to cause anemia and damages in liver, nervous system and male reproductive system. Exposure to DNT by breathing can cause lung damages. Also, exposure to high doses on DNT may cause death. (ATSDR 2013.)

In humans, data concerning exposure to DNT is not reliable and has been obtained from occupational exposure studies prior to 1950s. These studies lack knowledge of DNT concentrations, simultaneous exposure to other chemicals is possible and no control group has been used. However, consistent hematological findings of anemia and cyanosis with animal studies as well as some neurological effects (such as headache, dizziness, numbness and pain) have been noted. Also, heart disease and increased risk for urothelial cancer has been reported to be related to long-term exposure to DNT, but no indication of increased cancer risk for liver and kidney cancers has been found. (ATSDR 2013.)

4.3.3 Nitrobenzenes

Data concerning toxicity of 1,3-dinitrobenzene and 1,3,5-trinitrobenzene is scarce. According to toxicological profile of the substances (1995), nitrobenzenes cause similar effects and affect mainly blood oxygen carrying capacity. Nitrobenzenes can cause anemia and also headache, nausea, and dizziness. Long term effects in humans are unknown. In animals, long term exposure has caused male reproductive damages. (ATSDR 1995.)

US EPA has set proposal for 1 µg/L LHA and 5 µg/L DWEL for 1,3-dinitrobenzene. According to cancer classification, 1,3-DNB is a group D substance. No drinking water advisory levels or cancer classifications has been set for 1,3,5-TNB. (US EPA 2012b.)

4.3.4 Triazines

Triazines MNX, DNX and TNX are nitroso-metabolites formed as RDX degradation products in anaerobic conditions. Studies concerning toxicity properties of triazines are very limited, but possible indication of higher triazines toxicity compared to the parent compound RDX was reported by Zhang *et al.* (2006). However, as the current study is the only one found relating to explosives, the results should only be considered as indicative for need of further study.

In a study of Zhang *et al.* (2006), the effects of MNX and TNX in soil to earthworm growth and survival was examined. As a result, MNX and TNX were found to reduce growth of earthworms and were lethal at high concentrations. However, the toxicity of the substances were dependent on soil type and the effects of compounds were higher in sandy loam soil compared to silt loam soil. Accordingly, also faster degradation rate for triazines were observed in silty loam soil. (Zhang *et al.* 2006).

5. REMEDIATION OF GROUNDWATER

Explosives detected in groundwater are most commonly originated from military training activities at shooting and training ranges. As a result, low concentrations of energetig residues are transferred into the groundwater from scattered sources spread out at wide area. In contrast, contaminations due to previous ordnance disposal practices originate from more concentrated point sources. (Clausen *et al.* 2006.)

Due to exceptional main contamination pattern of explosives, *remediation of groundwater is inseparable from remediation of the explosives containing soil* at site. This is because a continuous source of explosive compounds into groundwater exists in compounds bound to soil particles, and in scattered particles containing explosives and additional substances. The possible strategies for management of explosives contaminated site are 1) remediation of soil and groundwater simultaneously with an appropriate *in situ* method; and 2) remediation of soil and groundwater separately. Utilization of separate methods enable selecting the best treatment option (*in situ* or *ex situ*) for soil and aquifer and also taking site specific factors into account more resiliently. When the concentrations detected are low as generally is the case Finland, 3) observing the situation (monitored natural attenuation, MNA) and preparing to act if necessary, is suitable option. Further, in small scale, 4) water can also be treated at the utilization site. This would permit the safe utilization of water as drinking water, although remediation is not achieved.

The remediation and treatment technologies can be divided into separation, destructive and immobilization processes. In methods utilizing separation processes, the contaminant is transferred from one media to another and further treatment of the contaminant is needed. In contrast, no additional disposal practices are needed after destructive processes. Immobilization are based on stabilization of the contaminant in place and are not considered as permanently effective solutions. (Van Deuren *et al.* 2002, section 3.)

The most frequently used approaches are pump-and-treat –technology for contaminated groundwater and excavation for contaminated soil. Both approaches are ex situ techniques coupled with suitable method for subsequent treatment of extracted material. (EEA 2014) As subsequent treatment method, incineration is the most frequently used for explosives contaminated soil. While incineration is effective and destructive method, the major disadvantages are air emissions such as CO_2 and NO_X, production of unusable ash by-product and high costs. (Snellinx *et al.* 2002.) The costliness of incineration process and the amount of adverse effects due to air emissions are clear considering the magnitude of actual remediation process where the contaminated area may be vast. For instance, in Nebraska at former military ordnance plant, the amount of soil requiring remediation was 10^7 kg soil. The estimated costs for incineration would have been several million dollars at the time. (Bier *et al.* 1999.)

In contrast to common and possible practices described above, full-scale remediation or treatment of explosive contaminated soil or groundwater has not been conducted in Finland. So far, detected explosive concentrations have been low and have not required remediation activities. In Finland, the management of explosive contaminations are based on prevention of contamination formation in the first place, and techniques for prevention of explosive transport are under survey. However, in case remediation is needed, incineration processes or any treatment requiring drastic actions do not seem likely methods of choice in Finland. Instead, MNA and limited treatment processes are likely actions. (Koponen 2016)

Military training ranges in Finland are generally sited at sandy soils and according to current knowledge, these locations often coincide with important groundwater formation areas and drinking water sources (Koponen 2016). The legislation concerning prevention of groundwater pollution is very strict. However, if groundwater contamination is nevertheless found, also the actions to correct the situation are regulated and require risk assessment. Hence, in addition to costs and technical feasibility, the choice of remediation method on site should include comparison between methods also on the basis of environmental effects due to remediation. For instance, utilization of *in situ* techniques can reduce the amount of material to be further treated and discarded, but also contain uncertainty factors relating to outcome and length of the remediation. However, possibility to utilize *in situ* or on site methods (even partially) is recommended to be assessed. Hence, the process to get authorization for remediation plans requires careful preliminary studies. (Ympäristöministeriö 2014, p. 26-27, 45, 134-139, 149)

Due to requirements set for remediation, possibility to utilize active in situ management strategies (i.e. chemical methods) is not self-evident in groundwater formation zone and spreading of chemicals inserted into aquifer has to be prevented and carefully monitored. Hence, utilization of separate approaches for environmentally friendly remediation of soil at site and temporary treatment of the groundwater (i.e. pump-and-treat technologies) until the source has been treated, appears to be justified approach.

In remediation of TNT and other nitroaromatics, the use of generally efficient air sparging and soil vapour extraction methods are not optional due to low volatilization properties (Khan *et al.* 2013). Here, the possible techniques for simultaneous treatment of soil and groundwater as well as the most important contaminated water treatment methods based on pump-and-treat –approach are discussed. In addition, bioremediation of explosives contaminated soil is discussed, as bioremediation is the most important approach coupled with pump-and-treat methods and is also a frequently utilized component in reactive barriers. As environmentally friendly method, bioremediation would also be acceptable in treatment of important groundwater at groundwater formation areas.

5.1 Pump-and-treat

Pump-and-treat technology has been used since 1980s and is one of the most utilized methods in groundwater remediation. (US EPA 1996.) Pump-and-treat approach has been used in several sites with explosives contaminated groundwater at former firing ranges, military ammunitions plants and depots (Jenkins and Vogel 2014). The basis of the method is extraction of the contaminated groundwater by pumping from groundwater wells and treatment of the water above ground by suitable method. The treated groundwater can be discarded or pumped back into aquifer by injection wells. (US EPA 1996.)

The greatest advantage of pump-and-treat method is possibility for effective containment of the contaminant plume (hydraulic control) and hence, restriction of contaminant migration. However, aquifer characteristics such as stratification, soil heterogeneity, water flow rate and hydraulic conductivity effect on pump-and-treat –efficiency and need to be taken into account in planning of the implementation. Treatment of the contaminated water above ground also enables safe utilization of effective contaminant removal or destruction technique (Jenkins and Vogel 2014.)

As a downside, the performance of the technology as sole remediation method is questionable, since the remediation goals set for contaminated sites and reduction of contaminants levels for adequate levels has failed in 5-10 year remediation times according to evaluation reports of the method. The outcome of treatment is not remediated groundwater, but instead, tailing, rebound and large remaining contaminant concentration in aquifer are typical for pump-and-treat. Tailing refers to decline of contaminant concentration at progressively slower rate with continuing pump-and-treat remediation, while rebound refers to rapid increase of contaminant concentration after pumping has been stopped. (US EPA 1996.)

Rebound and tailing are due to storage depot of the contaminants in soil, since pump-and-treat does not remove the contaminant from soil. As a consequence, the outcome of the remediation often is not sufficient and depository of the contaminant is left in soil. Hence, to overcome rebound problems caused by continuous source of new contaminant from soil, simultaneous source removal (e.g. by bioremediation of the soil) is recommended (US EPA 1996). Further, the remediation costs tend to be high due to high maintenance costs combined with long remediation time typical for pump-and-treat. (Jenkins and Vogel 2014).

Still, pump-and-treat approach remain as important technology in remediation of contaminated groundwater and especially in plume control. As restoration of the contaminated site to achieve decline of contaminant concentrations below remediation goal is the ultimate object, the primary goal of pump-and-treat is hydraulic containment and prevention of contaminant spreading. For effective containment, the hydrogeology and fracturing of the aquifer should be well characterized and extraction well placed accordingly to ensure effective contaminated water withdrawal to capture zone of the extraction wells. The pumping rate also needs to be sufficient to enable withdrawal all of the contaminant plume instead of flow by the well. (US EPA 1996.)

In remediation of groundwater contaminated by TNT and RDX, groundwater extraction and subsequent treatment with suitable method (most often treatment with granular activated carbon) has generally been the applied method (Jenkins and Vogel 2014).

5.1.1 Enhancement of pump-and-treat technology

In a broad sense of pump-and-treat technologies, enhancements such as utilization of physical treatment or chemical and biological agents can be included in pump-and-treat techniques. Injection wells can be used for delivery of reactive agents into aquifer and contamination plume. The main objective is to enhance mobility of the contaminants and hence, increase recovery of the contaminants from extracted groundwater for further treatment. Extraction wells are then used to withdraw both the contaminant and the reactive agent. (US EPA 1996)

Enhancement by physical processes include air sparging (in situ aeration), which is not discussed here, since as nonvolatile substances, air sparging is not an efficient method for explosives. Chemical enhancement processes include soil flushing and in situ chemical treatment (which is discussed in chapter 5.3 for reductive processes and chapter 5.4 for in situ oxidation). In biological enhancement processes oxygen and/or substrates, such as nutrients and other biodegradable compounds, are added in order to facilitate subsurface degradation of the contaminants by micro-organisms. (US EPA 1996)

Biological enhancement processes such as addition of micro-organisms and substrates has been successfully used for treatment of TNT, RDX and HMX contaminated groundwater. However, enhancements for pump-and-treat can have adverse effects on groundwater quality and require monitoring of groundwater. (Jenkins and Vogel 2014.)

Soil flushing

In soil, TNT is rapidly transformed to products that are adsorbed tightly on soil particles. Soil flushing can be used to enhance recovery of sorbed contaminants, residual contamination and substances with low solubility to water. Hence, cosolvents added to water injected to aquifer can be used to increase solubility of substances, or surfactants to increase desorption of compounds. (US EPA 1996)

Soil flushing has been tested in laboratory for capacity to increase TNT extraction compared to flushing with water, and to evaluate influence of flushing solution to treatment of extracted water by AOP. As a result, 2.1 times enhanced extraction of TNT was obtained using 5mM methylated-b-cyclodextrin as flushing solvent compared to water. Also, degradation of TNT by photo-Fenton process was enhanced due to flushing solution by factor of 1.3. However, only extractability of TNT was tested, since bioactivity and TNT biotransformation to aminonitrotoluenes was inhibited during the experiment. (Yardin and Chiron 2006.) In a study of Sheremata and Hawari (2000), also extractability of 4-ADNT and 2,4-DANT with cyclodextrind was tested in addition TNT. According to their results, extraction of 4-ADNT and 2,4-DANT was lower compared to TNT, but some enhancement of nitroaromatics solubilization was achieved by cyclodextrins. (Sheremata and Hawari 2000.)

5.1.2 Treatment technologies for extracted water

Possible treatment methods for extracted explosives contaminated groundwater include biological, chemical and physical methods of which some are destructive and others non-destructive. Contaminants can be treated biologically in bioreactors (Van Deuren *et al.* 2002 sections 2.10 and 4.47); chemically by alkaline hydrolysis (Hwang et al. 2005); oxidative processes such as AOPs (discussed below), Fenton processes (discussed as an in situ remediation method, chapter 5.4) and UV irradiation (US EPA 1996); and removed by physicochemical adsorption processes e.g. using granular activated carbon (GAC) (Van Deuren *et al.* 2002 section 4.47; US EPA 1996) and pine bark (Nefrenheim and Odlare 2008). Explosives can also be removed by physical separation processes using filtration or reverse osmosis (Van Deuren *et al.* 2002 section 4.50; US EPA 1996). Below, of the most utilized methods GAC and AOP technology and developmental method of adsorption to biomaterials have been discussed briefly.

GAC

Activated carbon has high capacity for adsorption of TNT and its degradation product TNB based on results obtained by Vasilyeva *et al.* (2002). The K_d values obtained for adsorption to activated carbon were 6800 ± 1500 L/kg for both TNT and TNB indicating strong adsorption. In addition, most of the attached TNT (62% for 0.5% solution and 95% for 1.0% solution) was not extractable by acetonitrile and hence, was irreversibly sorbed. Activated carbon also catalyzed oxidation of TNT to TNBAlc, TNBAld and TNB. (Vasilyeva *et al.* 2002.)

Adsorption to biomaterials

The major disadvantage in utilization of GAC as adsorbing material is the need for subsequent transport and destruction or regeneration of used GAC (Jenkins and Vogel 2014; Nefrenheim and Odlare 2008). Therefore, organic adsorbents such as pine bark have been studied, as the material can possibly be degraded biologically along with adsorbed explosives. Pine bark is also an abundant and low cost material obtained from forest industry and has been successfully tested for removal of other organic and inorganic contaminants as well. The efficiency of pine bark has been tested for TNT removal, and approximately

80% of the TNT (with initial 21.7 mg/L concentration) was adsorbed within 5 second contact time in a laboratory scale study. (Nefrenheim and Odlare 2008.)

AOP

AOP methods can be utilized as in situ treatment method for remediation of aquifers (Pignatello *et al.* 2006). However, as AOP has been extensively tested and proved as efficient method for destruction of explosives (Ayoub *et al.* 2010), it appears as AOP has not been utilized in large scale remediation processes, since such reports have not been found within literature survey of this work. Application of AOPs for soil remediation has been problematic because hydroxyl radicals are inefficient with contaminants sorbed on natural organic matter of the soil or clay (Lindsey and Tarr, 2000; Yardin and Chiron 2006).

In utilization of AOPs as in situ method, difficulties exist also due to short life-time of ozone. Hence, ozone needs to be produced on site and also efficient delivery of ozone spread over large areas is challenging (Clayton *et al.* 2011). The processes utilizing UV are not even feasible for in situ treatment (Pignatello *et al.* 2006). However, AOPs are suitable for on site treatment of extracted explosives. AOP-technologies include processes based on Hydrogen peroxide (combination of H_2O_2 and UV, Fenton reactions, Photo-Fenton and Fenton-like processes); Photocatalysis; Ozone (O_3 alone and in combination with UV); and Electrochemical processes (Ayoub *et al.* 2010).

5.1.3 Example of utilization of pump-and-treat technology

Pump-and-treat has been used for explosives contaminated groundwater remediation in US at Umatilla Chemical Depot, which is a former onsite explosives wash out plant. During 15 years of plant operation prior to 1965, the site was used for recovery and washing of the explosives. The process waters were discarded into unlined lagoons resulting to contamination of soil and groundwater. (Zheng and Wang 2003.) Based on preliminary investigations the contaminants of concern were identified as TNT, TNB, DNB, nitrobenzene (NB), 2,4-DNT, 2,6-DNT, tetryl, RDX, and HMX. The most abundant and mobile contaminant was RDX with concentrations up to 6,816 µg/L. The site was included on USEPA’s National Priorities List in 1987. (US Army Corps of Engineers 2010.)

Remediation of the site after preliminary studies started in 1993 for soil and in 1995 for groundwater. The full operation of the pump-and-treat system was reached in the beginning of 1997. Groundwater table on site is at 18-30 meters below ground surface. The original pump-and-treat system on site included three extraction wells (with total flow 4.92 m^3/min), treatment of the contaminated groundwater by granular activated carbon (GAC) (with 9,100 kg GAC filter) and infiltration of the treated water back into the aquifer from infiltration basins. In addition, in-situ flushing was applied for a year (completed in 2000) to enhance remediation of the subsurface soils beneath the lagoons used for disposal of process waters. The estimated treatment time for pump-and-treat system was 10 to 30 years. (US Army Corps of Engineers 2010).

The remediation of soil ended in 2001, but remedial action of groundwater was still ongoing at the time of third five-year report in 2010. During remediation, almost 6,000 kg of explosives was estimated to be extracted from the contaminated water (approximately 2.5×10^{10} L treated) by 2008. Expectedly, the removal efficiency and contaminant removal rate has decreased over time: During first year of the operation in 1997, the removal rate of the contaminants was 25 pounds/day, 16 pounds/day a year later and only 0.4 pounds/day in 2004. Due to observed rebound effect, pulse-pumping (cycling the extraction wells on and off) has been tried to increase contaminant mobility and concentration in groundwater, and hence, to improve recovery. As a result, pulse-pumping did not result increased efficiency in a long run, but a revision of pulse-pumping has been planned for time of higher groundwater level. During the last 5 year reported period, the contaminant concentrations have remained at the same level or even increased in some monitoring wells, and the concentrations at some monitoring wells have still exceed 100 µg/L for RDX and TNT. The yearly operation, maintenance and monitoring cost are estimated to be around $440,000. (US Army Corps of Engineers 2010.)

5.2 Bioremediation

Bioremediation can be utilized in groundwater treatment as enhancement in pump-and-treat and in permeable reactive barrier –technologies (Jenkins and Vogel 2014). Also, an efficient method for soil remediation is needed, since extraction and treatment of groundwater is insufficient for site remediation due to remaining depository of contaminants in soil. (US EPA 1996.)

During recent years, bioremediation has emerged as an alternative approach in treatment of explosives contaminated sites instead of traditional combustion processes for excavated soil with the advantage of bioremediation processes are environmentally friendly approach (Anasonye *et al.* 2015). However, challenges for bioremediation are caused by simultaneous contamination by several substances. Although RDX and HMX can be mineralized under suitable conditions, degradation of TNT is more challenging. TNT tend to be reduced and bind irreversibly on soil. (Jenkins and Vogel 2014.) Also, possible solid contaminant particles in soil cause difficulties for bioremediation, since solid particles act as constant supply of the contaminant. As a consequence, the concentration remains high and can be toxic to micro-organisms on site affecting biotransformation rates and suppress in situ bioremediation. (Bier *et al.* 1999).

Fungal bioremediation

Although promising results has been obtained for TNT degradation and mineralization by fungi, most of the experience so far has been from laboratory and small-scale experiments. Therefore, more experience is needed and some practical aspects solved before application of fungal degradation to large-scale bioremediation of TNT contaminated sites. In actual remediation sites, the chosen fungal species (strains grown in laboratory), should be able to degrade and mineralize TNT while also tolerating explosives (and possibly other simultaneous contaminants) in high concentrations and also compete and thrive with the indigenous micro-organisms on site. (Anasonye *et al.* 2015).

Fungal treatment of highly TNT contaminated soil mixed with composted green waste was recently examined in pilot-scale. The results showed that an elevated degradation of TNT within 50 days of incubation was obtained with the presence of one of the examined species (80±4 % degradation compared to initial concentration *P. velutina*) while the degradation rate was 50±14% for the soil containing only indigenous micro-organisms and no added fungus. No advantage was obtained using other species. Even negative effects were observed with presence of *K.* mutabilis (0% degradation), possibly due to inhibitory effects of the strain to indigenous organisms. However, successful scale-up from laboratory using *P. velutina* for degradation of high TNT concentration was shown. However, the results obtained do not correspond to conditions of natural environment, since the experiment was conducted in a greenhouse at constant temperature of 25˚C. Soil was also aerated and protected from drying during the experiment. As a further downside for fungal applications it has been noted, that to ensure degradation of the contaminants, nutrients should be added to obtain balance between carbon and nitrogen, phosphorous and minerals (Anasonye *et al.* 2015).

Biostimulation

In biostimulation, the growth of indigenous micro-organisms able to degrade contaminant compounds is enhanced by adding exogenous substrates into the aquifer on site. For instance, degradation of RDX can be enhanced in anaerobic condition by addition of organic substrates in order to generate reducing conditions (Michalsen *et al.* 2016). By addition of suitable substrates, prevailing conditions in soil and hence, prevalent degradation pathways, can be influenced. For instance, by inducing suitable sulfate-reducing or methanogenic conditions in soil, possibly accumulation of nitroso-intermediates as a result of RDX degradation can be avoided by favoring ring-cleavage pathway. For this purpose, good results have been obtained by utilization of emulsified vegetable oils as carbon substrates. (Cho *et al.* 2015.)

5.3 Permeable reactive barriers (PRBs)

Permeable reactive barrier (PRB) technology utilized for explosives is generally based on in situ chemical reduction of contaminants. Since development of PBRs in 1990s, the technology has been successfully and cost-effectively used for treatment of contaminated groundwater by more than 200 installed PRB systems (ITRC 2011; Kalderis *et al.* 2011). PRBs have also been applied to treatment of compounds containing multiple nitro groups including TNT, RDX and HMX. The reduction rate of TNT is fastest and as a result, TAT is formed via ADNT and DANT. Subsequent natural attenuation of TAT is presumed. (Jenkins and Vogel 2014: Tratnyek and Johnson 2011.) RDX is reduced to triazines (Pichtel 2012) while HMX is not readily degraded by abiotic reduction (Park et al. 2004).

PRBs are defined as "in situ permeable treatment zone designed to intercept and remediate a contaminant plume". PRBs are developed for passive action by allowing contaminated groundwater to flow through PRBs utilizing aquifer hydraulic conditions and without mechanical assistance. (ITRC 2011.) The main advantages of PBR technology is passive remediation after installation of the barriers. Also, pumping of groundwater and subsequent treatment and disposal of extracted material is not needed. (Jenkins and Vogel 2014.) Despite of utilization of PRBs as established technology, PRBs are still being evolved. Hence, new reactive materials are being deployed and new construction methods developed. (ITRC 2011.)

5.3.1 Elemental iron in PRBs

Iron is often used in chemical reduction, since metallic iron (zero-valent iron, Fe^0) is an avid electron donor in water. Hence Fe^0 act as strong reductive agent. Advantages of Fe^0 are also nontoxicity and low cost of the material. (ITRC 2011; Wilson 1995 according to Singh *et al.* 1999.)

The effectiveness of Fe0 in remediation is dependent on soil conditions. pH and reduction potential (Eh) effect of dissolution of iron which is coupled to reduction of suitable compounds. The purpose is reduction of contaminant compounds, but the presence of competing oxidants such as inorganic $NO^{3\,-}$ and SO_4^{2-} act as electron scavengers. (Snoeyink and Jenkins 1980 according to Singh *et al.* 1999.) Fe corrosion results to increasing pH which favors Fe hydrolysis reactions subsequently resulting to precipitation of iron(III) hydroxide ($Fe(OH)_3$) unavailable for reductive degradation (Snoeyink and Jenkins 1980 and Schwab and Lindsay 1983 according to Singh *et al.* 1999).

In general, degradation of RDX is enhanced as pH and Eh decreases and is highest at very low pH (at pH 2), but the method is applicable and efficient also at neutral pH range (Singh *et al.* 1999). Utilization of neutral pH in Fe^0 remediation has an additional advantage of promoting subsequent bioremediation and mineralization. In studies with ^{14}C-labeled RDX, enhanced production of ^{14}C-labeled CO_2 has been detected following Fe^0

treatment of RDX. The result indicates better biodegradability of Fe^0-treated RDX compared to untreated RDX. (Singh *et al.* 1999)

In laboratory, 95% reduction of RDX of 90 µM solution within 4 h and complete reduction in 8 h with pH 7 and -150 mV reduction potential has been reported. Similarly, 99% RDX degradation from soil slurry was achieved in 24 h in buffered pH 7 and Eh –150 mV conditions. The result was enhanced by 24% compared to unbuffered control. As a result, the authors concluded, that utilization of Fe^0 in RDX remediation can be enhanced by promoting conditions with neutral pH and lowering Eh. (Singh *et al.* 1999.)

In degradation of TNT using Fe^0-PRB, complete conversion of TNT to TAT in column studies has been reported. Not any of the TNT (or its partial reduction products) were found in effluent of 15 cm long column even at high flow rates and only TAT was found in the effluent. As TAT is transformed rapidly in aerobic conditions with low to moderate pH, TAT is expected to be passed into downgradient aquifer in full scale PRB systems and to become readily further degraded by natural attenuation. (Tratnyek and Johnson 2011.)

5.3.2 Coupling bioremediation with PRBs

A major advantage of PRB technology is a possibility to combine different methods with remediation. Hence, both chemical reduction by iron and bioremediation of explosives can be coupled and included in PRBs as simultaneous treatment. (Jenkins and Vogel 2014.) Zero-valent iron has been tested in remediation of explosives-contaminated groundwater using integrated bioremediation-Fe^0 –system for treatment of RDX. The combination of zero-valent iron and bioremediation system was found more efficient compared to either treatment (Fe^0 or bioremediation) alone. (Widman and Alvarez 2001)

As a downfall with iron containing PRBs is ageing of iron materials and decrease of the contaminant destruction rates over time. As a possible explanations for observed ageing is accumulation of precipitates blocking the barrier and corrosion of iron. (ITRC 2011; Tratnyek and Johnson 2011.) Also, utilization of PRBs is generally limited to shallow aquifers with maximum depth of approximately 12 meters. The PRB has to be set on path of groundwater flow and fitted to hydraulic conditions to prevent bypass of water around or beneath the barrier. Gates consisting of impermeable material can be set as funnel on sides of the barrier to aid in guiding of groundwater through the barrier. (Jenkins and Vogel 2014.)

5.4 In situ chemical oxidation (ISCO)

The basic idea of ISCO technologies is to transport and release oxidative agents directly into the contamination zone in groundwater and vadose zone. Due to high oxidation potentials, the most commonly utilized oxidants in ISCO are hydrogen peroxide (H_2O_2, which oxidation potential is 1.78 V), Fenton's reagent (combination of H_2O_2 and Fe^{2+}), ozone (O_3, 2.07 V), permanganate (MnO_4^-, 1.68 V) and persulfate ($S_2O_8^{2-}$) (Kalderis *et al.* 2011).

Challenges in ISCO technologies are on efficient delivery of an oxidizing agent and the effects of soil heterogeneities for uniform delivery. (US Department of Energy 1999).

Fenton reactions

Traditionally, Fenton reagent (combination of Fe^{2+} and H_2O_2) has been used for degradation of wide variety of persistent organic compounds including nitroaromatics, PCBs and compounds existing as LNAPL and DNAPL phases (Kalderis *et al.* 2011). The effect of Fenton reagent is based on production of highly reactive hydroxyl radicals (OH•) as a consequence of series of reactions involving alternation of iron between oxidative states (FeII and FeIII), formation of superoxide anion ($O2^{-}$•) and hydroxyl radicals. OH• is non-specific strong oxidant ($E^0 = 2.73$ V) capable of oxidation of wide variety of organic compounds (Bier *et al.* 1999; Pignatello *et al.* 2006).

The advantage of Fenton reactions is rapid degradation of pollutants but the reaction efficiency depends on pH and concentration of Fe^{2+} and H_2O_2 (Bier *et al.* 1999). Utilization of Fenton method is limited to conditions with pH range 3-7 (while the best results are obtained within pH 3-5). The effectiveness of the method is also decreased remarkably with presence of free radical scavengers such as carbonate (Kalderis *et al.* 2011; Siegrist *et al.* 2001 in Kalderis *et al.* 2011). However, applications of Fenton reactions have the advantage of suitability for simultaneous remediation of soil and water (Petri *et al.* 2011).

Bier *et al.* (1999) studied treatment of RDX-contaminated water and soil using Fenton reagent. Degradation of high concentration of RDX (20 mg/L) was observed utilizing ^{14}C- labeled RDX. Also the influence of pH and variable concentration of Fe^{2+} and H_2O_2 were assayed. As a result, complete RDX destruction was observed within 24 hours and the fastest rate for RDX destruction occurred at pH 3. According to mass balance experiments using ^{14}C-RDX, 76% of ^{14}C disappeared from the solution within 12 h. Most of the ^{14}C lost from the solution was identified as $^{14}CO_2$ (68%) indicating full mineralization.

Requirements groundwater characteristics for efficient utilization of Fenton reactions are maximum alkalinity 400 mg/L (expressed as $CaCO_3$), pH under 7.8 and sufficient hydraulic conductivity (over 10^{-6} cm/s). (Kalderis *et al.* 2011).

Ozone

Recently, O_3 has been utilized for in situ treatment of groundwater and the vadose zone. The advantage in exploiting ozone in ISCO is, that both soil in vadose zone and saturated groundwater zone can be treated simultaneously. Ozone vented in porous soil reacts with organic material and iron oxides in the soil producing OH radicals, which in turn are able to degrade explosives. In addition, O_3 is able to degrade organics directly in acidic conditions. (Kalderis *et al.* 2011). On the other hand, the downfall is that as highly reactive and short-lived gas, ozone has to be produced on site (Van Deuren *et al.* 2002).

Utilization of ozone for treatment of RDX in soil has been demonstrated by column studies. Degradability of RDX by ozone was observed using ^{14}C labeled RDX by treatment of authentic contaminated soil in columns with varying water contents. The results showed that 50% mineralization was obtained in one day and over 80% of the initial RDX was mineralized within 7 days. The water content of the soil had minimal effect on the results. During the study, also increased biodegradability of RDX was observed. (Adam *et al.* 2006.)

Fleming *et al.* (1997) used O_3 in combination with H_2O_2 (peroxone technology) in pilot system for treatment of TNT, RDX, HMX and other nitroaromatics in groundwater. With the best treatment technique used, removal rates of 96 – 98% for TNT, 90 - 98% for RDX, 69 – 88% for HMX for three treatment wells was reported. The initial concentrations varied between 11.5 – 1,378 μg/L for TNT, 13.6 – 97.6 μg/L for RDX and 2.8 – 16.5 μg/L for HMX. Although the removal rate was high for TNT, concentrations below required 2 μg/L was not reached at the most contaminated well.

Permanganate and persulfate

A pilot scale ISCO process utilizing permanganate for treatment of RDX contaminated groundwater was tested by Albano (2009). In the experiment, a current of permanganate was created on site by injecting the permanganate into the groundwater via injection well and extracting the plume from downstream extraction well. The process and degradation of RDX was observed by electrical resistivity imaging via field of monitoring wells covering the site. In the experiment, 70-80% of the RDX was degraded in the vicinity of the injection wells but even distribution of permanganate was challenging. Due to stratification of aquifer, the injected permanganate followed flow paths not concordant with groundwater flow leading to fingering of the plume. (Albano *et al.* 2010.)

Among most commonly used agents in ISCO, persulfate has the advantageous capability to produce highly reactive sulfate radicals in addition to direct oxidation. The production of radicals can be initiated with heat, alkaline pH, Fe^{2+} or H_2O_2. However, persulfate has been used very little for destruction of explosives. (Kalderis *et al.* 2011.)

6. TREATMENT EXPERIMENTS OF THE TNT/RDX -CONTAMINATED WATER

During recent years, along with improved sensitivity of available analysis methods, residual concentrations of the most commonly used explosives TNT, RDX and HMX have been identified in soil and groundwater in military training ranges in Finland. Permeable and sandy soil types are preferred as military shooting and training sites, but such soils are also ideal for groundwater formation. Hence, military training areas are often located at groundwater areas classified as important drinking water resource. Due to recent findings of trace concentrations, the Finnish Defence Forces have started investigation to examine and monitor explosive residues in groundwater at training ranges and to create strategy to manage possible findings. Detected concentrations have been at low (at 1 µg/l order of magnitude) level and assessed to cause no harm to health and environment. (Koponen 2016.)

Feasible strategies for the Finnish Defence Forces in management of removing explosives concentrations from groundwater could be limited water treatment strategies at individual groundwater wells or at water works stations, if explosive traces are found from ground water used as drinking water by a larger community. In addition, applicability of possible remediation methods is under evaluation, although efficient remediation of vast areas would be challenging. Further, current training areas are in operation and possibly different strategies need to be considered for situations of treatment due to past activities and for areas still in utilization. (Koponen 2016.)

In this study, the efficiency of pump-and-treat -based groundwater treatment methods by readily available equipment of The Finnish Defence Forces are tested for TNT/RDX containing water. As the experiments, 1) utilization of reverse osmosis (RO) with prefiltration is tested for removal of explosives from water; and 2) the efficiency of UV irradiation is evaluated for degradation of TNT and RDX in water. In addition, 3) rate of natural attenuation and abiotic degradation of TNT and RDX is evaluated by monitoring degradation of TNT and RDX from water in dark conditions and exposed to natural light for two weeks.

The experiments for treatment of the explosives contaminated water were conducted at Finnish Defence Forces Logistics School in Riihimäki during 8.-9.6.2016.

6.1 Sample preparation

In the water treatment experiments, TNT and RDX were used as explosive compounds. Authentic explosives containing groundwater was not available with sufficient concentrations of the explosive compounds for the experiments. Therefore, the experiments were conducted using synthetic samples containing TNT and RDX dissolved in test water from Riihimäki water supply network.

The water in Riihimäki Garrison is provided by Riihimäen Vesi and is pumped from groundwater wells from Piirivuori in Hausjärvi. Water is treated at Haapahuhta water works, where pumped groundwater is aerated, alkalized by NaOH and treated with UV irradiation prior to distribution into water supply network. The Haapahuhta station has capability for water chlorination if needed, but at the time of the experiments, no chlorination has been conducted. Hence, additional substances interfering the experiment have not been added to water supply. (Rämö 2016.)

The samples were manufactured on site by diluting aliquots of predissolved TNT/RDX – solution concentrate into tap water in temporary containers. The predissolved sample was prepared in The Finnish Defence Research Agency (FDRA) by dissolving 1,0011 g TNT into 10 ml acetonitrile and 1,0113 g RDX into 10 ml dimethylformamide. As a result, 100.11 mg/ml TNT and 101.13 mg/ml RDX concentrates was obtained. 1 ml of each concentrate was mixed to 50 ml acetone yielding solution containing 100.11 mg/ml TNT and 101.13 mg/ml RDX. In preparation of the samples for the experiments, the aim was to obtain final concentration 50 µg/L for TNT and RDX. Therefore, 1 ml of the solution was diluted with heavy mixing (caused by water flow into container) into 2 m^3 water for reverse osmosis experiment and 0.5 ml into 1 m^3 water for UV-degradation experiment to obtain desired concentration. The 2 m^3 container used was fully closed and protected from light, but the 1 m^3 water container was filled up from top, and hence, the sample was partially exposed for natural light for a short time during filling the container.

The solubility of the RDX is significantly lower compared to TNT especially in low groundwater temperatures (see chapter 3.1). The water used for the experiment was taken from fire hydrant and was cold (below 9 ˚C). Therefore, the possibility of RDX (and also TNT) to precipitate in sample preparation was suspected. To avoid precipitation, the concentrate was added slowly into large quantity of water with heavy mixing by water flow into container. However, from a closed container possible precipitates were undetectable. Hence, the final concentrations of RDX and TNT in initial samples were determined in laboratory and were not known at the time of performing the experiment.

6.2 UV-degradation experiment

Generally, groundwater delivered by water supply network in Finland is clean and free from pathogens and other contaminants (Vesilaitosyhdistys 2014a). However, according to Finnish legislation concerning water quality, capacity for water disinfection has to be arranged at water works (STM 1352/2015; Vesilaitosyhdistys 2014b). Therefore, UV irradiation is used as precautionary measure to ensure delivery of pathogen free water for consumers at many groundwater stations (Vesilaitosyhdistys 2014a). UV irradiation is rarely in constant use, but if needed, the capacity to fast deployment of the disinfection methods has to exist according to STM 1352/2015 at large groundwater station or at stations, where higher risk for water contamination exists. Since UV irradiation is also an effective method for degradation of wide variety of chemical contaminants and the method is already available at many groundwater stations, the efficiency of the method for degradation of explosives (TNT and RDX) was tested. The purpose of the experiment was to determine, whether UV irradiation alone is sufficient for degradation of TNT and RDX concentrations from the test water during simulated standard water treatment practices at water stations prior to delivery of the water to water supply network.

Degradation of explosives by UV-light irradiation was tested in two experiments, subjecting the sample for UV-irradiation with approximately 407 J/m^2 and 550 J/m^2 UV dose. The UV dosages used were chosen to correspond practices at water stations. At minimum, 400 J/m^2 dosage is used at water stations to ensure disinfection of (99.99% elimination of *B. subtilis* representing disease causing bacteria) (Vesilaitosyhdistys 2014a). The 550 J/m^2 dosage represent situation at lower water flow through UV equipment or deployment of new UV lamp resulting to higher UV dosage.

6.2.1 Calculation of UV intensity

In the experiment, Wedeco Aquada proxima 7 –UV equipment was used. The recommended maximum flow for the equipment is 5.5 m^3/h, when the 400 J/m^2 dosage for slightly turbid water source (with transmittance 87% or higher) is achieved according to manufacturer (Wedeco 2016). The water volume inside UV chamber is 6.3 liters (cylinder water volume), but the inside diameters (length of the light path) of the UV chamber were not known for calculation of UV intensity. Hence, UV dosage was calculated using a chart determining relations of UV dosage, water turbidity and water flow rate provided by equipment supplier. Since there were no knowledge of actual TNT/RDX -water sample turbidity and determination of turbidity was not possible at site, the UV dosages were calculated presuming UV transmittance 94%, which is typical for Finnish tap water (Viiala 2016).

According to manufacturer chart, 400 J/m^2 UV dosage is achieved at flow rate 6.2 m^3/h when UV transmittance (1 cm in %) is 94% and with same transmittance, 300 J/m^2 UV dosage results from 8.3 m^3/h flow rate. Dose calculations in the manufacturers chart are based on average intensities obtained by point source summation –method. (Wedeco 2016). Neither Aquada proxima 7 or the pump used in UV experiment set up are equipped with built-in flow rate meter, so adjusting flow rate for desired values were not feasible.

Therefore, the cylinder water volume 6.3 L and the information obtained from manufacturers chart were used for calculation of UV intensity (W/m^2) for 94% transmittance according to equations 2 - 3.

$$contact\ time\ [s] = \frac{cylinder\ volume}{flow\ rate} = \frac{6.3\ L}{6.2\ \frac{m^3}{h} * \frac{1000\ L}{m^3} * \frac{h}{60 * 60\ s}} \approx 3.66\ s \tag{2}$$

$$UV\ intensity\ \left[\frac{W}{m^2}\right] = \frac{UV\ dose}{contact\ time} = \frac{400\ \frac{J}{m^2}}{3.7\ s} \approx 109.2 \frac{W}{m^2} \tag{3}$$

The calculations of contact time and UV intensity were done similarly for 300 J/m^2 UV dosage. The values used for UV intensity calculations are shown in table 4.

Table 4. UV intensity calculation based on information obtained from manufacturers chart.

Flow rate	**m^3/ h**	**L / h**	**L / s**	**Cylinder water volume [L]**	**contact time [s]**	**UV dose [J/m^2]**	**UV intensity [W/m^2]**
6,2 m^3/h	6,2	6200	1,72	6,3	3,66	400	109.2
8,3 m^3/h	8,3	8300	2,31	6,3	2,73	300	109.9
							Avg. 109.6 ≈ 110

Based on information obtained from manufacturer’s chart, **average UV intensity 110 W/m^2** was obtained and used for calculation of UV dosage directed for samples during the experiments.

6.2.2 Experimental procedure

In the UV experiment, UV dosage directed to samples was regulated by adjusting the water flow through the UV equipment. The experimental set did not include flow meter, but the pump efficiency and output of the hose was grossly adjustable. Measurements of flow rate were achieved by taking time of triplicate filling up of 65 L tub. Prior the UV experiment, adjustment of flow through was tested with pure water and the adjustments were made, until flow was close enough to planned values of 6.2 m^3/h (resulting UV dose 407 J/m^2) and 4.5 m^3/h (UV dose 550 J/m^2).

RDX/TNT containing water sample for UV degradation experiment was prepared into 1 m^3 container, from where the sample was conducted to UV equipment using preadjusted flow rate. From the UV equipment, the irradiated sample water was conducted to tubs and the tub filling was timed. The tub filling time and tub volume 65 L were used to calculate the realized flow rate of the experiments. The tub filling times and realized flow rates are shown in table 5.

Table 5. Determination of flow rates in the experiments by measurement of 65 L tub filling time.

Experiment	Test	Tub filling time [s]	Tub volume [L]	flow L / s	flow m^3/s	flow m^3/h
407 J/m²	Tub1	37.1	65	1.8	0.0018	6.3
	Tub2	37.2	65	1.7	0.0017	6.3
	Tub3	39.4	65	1.6	0.0016	5.9
	avg.	**37.9**	**65**	**1.7**	**0.0017**	**avg. 6.2 m³/h**
550 J/m²	Tub1	49.2	65	1.3	0.0013	4.8
	Tub2	50.6	65	1.3	0.0013	4.6
	Tub3	52.9	65	1.2	0.0012	4.4
	avg.	**50.9**	**65**	**1.30**	**0.0013**	**avg. 4.6 m³/h**

Subsequently, realized sample contact time was calculated from flow rate (6.2 m^3/h and 4.6 m^3/h) and UV chamber volume 6.3 L (as described in equation 2). Finally, the UV dosage directed to the sample was calculated with calculated contact time and UV intensity (equation 4).

$$UV\ dose \left[\frac{J}{m^2}\right] = \ contact\ time\ [s] * UV\ intensity\ \left[\frac{W}{m^2}\right] \tag{4}$$

Determined UV dosages under experimental conditions were 550 J/m^2 for UV experiment 1 and 407 J/m^2 for UV experiment 2. Measurements of UV dosages for triplicate samples are presented in table 6.

Table 6. Determination of UV dosage directed to samples based on realized flow rates in the experiments.

	Flow rate m^3/h	Flow rate l / s	UV chamber water volume [L]	Contact time [s]	UV-intensity [W/m²] (UVT 94 %/ 1 cm)
407 J/m²	6.2	1.7	6.3	3.7	110
550 J/m²	4.6	1.3	6.3	5.0	110

Duplicate samples for explosives compound analysis were taken as collection samples from three tubs right after the experiment and sent for analysis.

6.3 Treatment of explosives contaminated water by reverse osmosis

Treatment of TNT/RDX contaminated water by prefiltration and reverse osmosis (RO) was tested using Kärcher WTC 1600 GT -modular water purification system. The Kärcher system has been developed for utilization as mobile water purification system transported on trailer and equipped with electrical power generator. The equipment is feasible for production of drinking water from natural raw water sources such as lakes, rivers and sea, and is efficient in removal of biological contamination (bacteria, viruses and toxins), chemical contamination (organic compounds and inorganic salts), minerals, particles and even salt from seawater. Water purification is based on RO, but the equipment also has prefiltration module with 0.5 µm filter and an additional UV treatment module (UV can be turned off) as back up precaution measure. Water flows through the system at maximum rate of 4 m^3/h in WTC 1600 models, of which up to 1.6 m^3/h purified drinking water can be produced depending on water source purity and temperature. The rest of the source water is discarded as reject from RO membranes. (Kärcher 2011).

The Finnish Defence Forces have Kärcher WTC 1600 GT water purification systems to ensure availability of drinking water for military forces where ever needed. Hence, the equipment can be used at sites where crisis management is needed. In such destinations, drinking water sources may be scarce and heavily polluted by biological or chemical agents including munitions and explosive compounds due to military action at site. (Koponen 2016) Here, utilization of reverse osmosis with preceding filtration step is tested for the equipment efficiency for removal of TNT and RDX from water. The purpose is to show the safety of the drinking water treated by reverse osmosis and the equipment utilized by The Finnish Defence Forces. Reverse osmosis is also a method, which can be utilized in water works for water treatment, especially in production of drinking water from sea water (ref?). Hence, the purpose of the experiment is also to evaluate suitability of the method for water treatment in case of possible explosives contamination at water stations.

The water sample containing TNT and RDX was prepared into 2 m^3 container. In the experiment, sample water was pumped directly from the container to prefiltration unit by pump and hose included in Kärcher water treatment system. The 0.5 µm prefilters are bag filters and hence, no reject is formed. All the filtered material is retained in the two sets of bag filters and water passing the filters is conducted to parallel sets of RO membranes (RO1 and RO2). All the water passing the first RO membranes are directed to third RO membrane (RO3). The purified water passing RO3 is subsequently conducted to drinking water output through UV unit of the system. During the experiment, the UV system was turned off. The reject from RO1-3 is discarded from reject water output. A diagram of water treatment in Kärcher system is shown in figure 2.

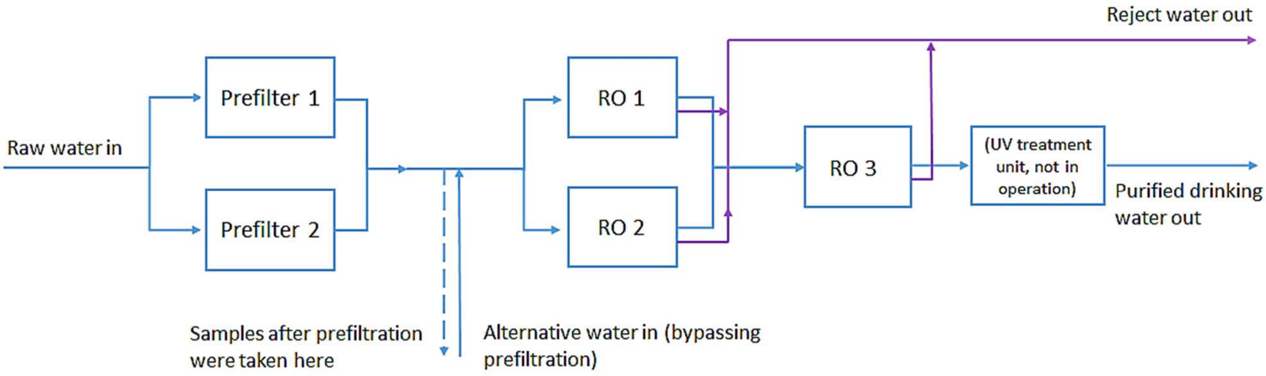

Figure 2. Diagram of water treatment in mobile Kärcher WTC 1600 GT water purification system. RO 1-3 are separate reverse osmosis treatment units (modified from Kärcher 2011).

Both the prefiltration and RO treatment start immediately after turning the equipment on. The water treatment system was prepared for utilization after storage and maintenance using tab water (which was used also in sample preparation) from separate 11 m^3 container. After initialization, equipment was ran with sample water for ten minutes before directing the output hoses for separate tubs where samples were then collected for analysis. Duplicate samples were taken after prefiltration from hose attached to additional water input valve, after reverse osmosis treatment from drinking water output and from reject water output.

6.4 Abiotic degradation of TNT and RDX

Abiotic degradation of TNT and RDX was monitored during two weeks. The TNT/RDX water sample used in the experiment was an aliquot of the sample, which was prepared for UV degradation experiment. The purpose of the follow-up experiment was to monitor abiotic degradation rate representing natural attenuation of TNT and RDX in water. Degradation of TNT and RDX was compared between dark conditions and exposed to natural light from samples kept outdoors for two weeks.

Samples were stored in 65 L tubs of which the other was tightly covered by black plastic protecting sample from natural sun light and rain and also preventing evaporation. The UV protection capacity of the plastic used to cover the sample was not tested and hence, it is possible that some of the UV radiation passed through the plastic. The other tub was kept under shed roof next to wall giving some protection from possible rain. Otherwise the sample container was open and directly affected by weather conditions similar to ponds and other surface waters. The follow-up samples were taken from both containers at 7th and 14th day and sent for analysis.

6.5 Analysis

All samples were kept in dark and packed in cool boxes with coolers right after the samples were taken. Samples were shipped instantly to laboratories to ensure the quality of the samples. Table summarizing all samples taken during experiments is presented in table 12 in appendix 5.

Water quality parameters were analyzed from Riihimäki water used for dilution of the samples before addition of TNT/RDX –solution concentrate. The analyses were made at accredited Finnish laboratory, SGS Inspection Services Oy in Kotka, where the samples were transported by bus. Water was analyzed for pH (according to ISO 10523:2008), oxygen content (based on inoperative SFS 3040:1990), electrical conductivity (SFS-EN 27888), chemical oxygen demand (COD_{Mn}) (SFS3036), hardness (modified SFS 3003), dissolved organic carbon content (DOC) (SFS-EN 1484), and additionally dissolved metals according to EN ISO 17294-2. Temperature was also measured from the solution containers prior the experiments.

Duplicate samples were taken from two initial sample solutions prepared for UV degradation and reverse osmosis experiments. The samples were sent to laboratory for analysis of the final concentrations of the explosives initial samples. From the 1 m^3 container used for sample preparation for the UV irradiation test, also sample from the bottom of the container was taken after UV-degradation tests in order to detect possible precipitation of RDX or TNT during the test in the container.

The analyses to determine concentrations of TNT, RDX and TNT degradation products from UV irradiation, reverse osmosis experiments and follow-up study of abiotic degradation were made at accredited laboratory SGS Institut Fresenius in Dresden, Germany. The samples were sent to laboratory by airmail and were received in destination the following morning each time after sampling. Sample preparation and analyses were initiated instantly. The samples were analyzed by high performance liquid chromatography (HPLC) with UV detection according to DIN EN ISO 22478. The method is intended for determination of explosives (nitrotoluenes, nitroamines and nitrate esters) and related compounds (frequently surveyed by-products and degradation products) in groundwater, surface water and drinking water (EN ISO 22478:2006). All samples were taken and analyzed as duplicates and a total of 23 explosive analysis were made.

In addition to samples analyzed in SGS laboratory (HPLC with UV detection), 3 samples from UV-degradation, 2 samples from reverse osmosis treatment experiments and 2 follow-up samples were analyzed at The Finnish Defence Research Agency (FDRA) to verify the results using another analysis method. In the method used by FDRA, the samples were preserved immediately after sampling using sodium bisulfate ($NaHSO_4$) and concentrated using solid phase extraction prior to analysis. The samples were analyzed by Liquid chromatography–mass spectrometry (LCMS) with atmospheric pressure chemical ionization (APCI). The analysis was also confirmed by HPLC after US EPA 8330b. The intent of using two different analysis techniques was to determine equivalence of the two methods and evaluate correspondence between results obtained by different methods for future use.

7. RESULTS OF WATER TREATMENT EXPERIMENTS

All 25 samples analyzed in SGS laboratories were analyzed as duplicates, water quality parameters from 2 samples in Finland and 23 samples of explosive compounds in Germany. In addition, analysis results were confirmed by analyzing 9 samples for explosive compounds in The Finnish Defence Research Agency (FDRA) (data not shown).

All duplicates analyzed with the same method had full correspondence indicating high reproducibility of the ISO 22478 analysis method. However, a difference in explosive compound concentrations was observed between results analyzed by different methods throughout all experiments. The concentrations obtained by LCMS analysis with APCI in FDRA, were consistently higher than results obtained from SGS laboratory using ISO 22478 analysis method. The issue will be examined in future studies, but possible explanations are differences in sensitivity between methods, or occurrence of some degradation within the samples during transportation to Germany. The samples were air mailed in cooler boxes without preservation of the samples (accordingly to standardized ISO 22478 method), but possibly the boxes were not sufficiently maintained at 4 °C temperature to prevent sample degradation.

Successful sample preparation and sample stability during experiment was shown by samples taken before and after the UV experiment from top and bottom of the sample container. The concentration of TNT and RDX were the same indicating that no explosive compounds precipitation on bottom of the container occurred during sample preparation. Also, no degradation products of TNT appeared in the container during the experiment.

Concentration of TNT and RDX were slightly higher in the sample prepared for RO treatment (32.0 µg/L and 37.0 µg/L, respectively) compared to sample in the UV experiment (27.0 µg/L and 35.7 µg/L, respectively). The sample concentrate used were the same in both cases but notable differences are resulted easily from taking aliquots of highly concentrated sample. Also, lower concentration in UV experiment samples can be resulted from short exposure of the sample for natural light while filling the container.

7.1 Water quality parameters

Water quality parameters (pH, oxygen content, electrical conductivity, chemical oxygen demand (COD_{Mn}), hardness (total Ca and Mg content), dissolved organic carbon content (DOC), iron and manganese content and dissolved metals) were analyzed from the water of Riihimäki water supply network used in sample preparation. The results of the analysis compared with water quality parameters set in Finnish legislation (STM 1352/2015) are presented in table 7.

Table 7. Water quality parameters determined from Riihimäki water and water quality parameters according to Finnish legislation (STM 1352/2015).

	Units	DL*	Sample A	Sample B	Avg. ± S.E.	STM 442/2014
pH	pH unit	2	7.80	7.90	7.85 ± 0.07	6.5 – 9.5
Oxygen	mg/l	0.5	12	11	11.5 ± 0.71	5.0
Electrical conductivity	mS/m	0.5	17.50	17.50	17.50 ± 0.0	2.5
COD_{Mn}	mg/l	1	<1.0	<1.0	<1.0	5.0
Iron	µg/l	20	<20	<20	<20	200.0
Manganese	µg/l	10	<10	<10	<10	50.0
Hardness	mmol/l	0.05	0.52	0.52	0.52 ± 0.00	-
Dissolved organic carbon (DOC)	mg/l	0.3	12	12	12 ± 0.00	-
Dissolved metals						
As	µg/l	0.4	<0.4	<0.4	n.a.	10.0
Cd	µg/l	0.1	<0.1	<0.1	n.a.	5.0
Co	µg/l	0.2	<0.2	<0.2	n.a.	-
Cr	µg/l	0.3	<0.3	<0.3	n.a.	50.0
Cu	µg/l	1.0	<1.0	<1.0	n.a.	2,000
Ni	µg/l	1.0	<1.0	<1.0	n.a.	20.0
Pb	µg/l	0.5	<0.5	<0.5	n.a.	10.0
V	µg/l	1.0	<1.0	1.1	n.a.	-
Zn	µg/l	5.0	<5.0	<5.0	n.a.	-
Sb	µg/l	1.0	<1.0	<1.0	n.a.	5.0
Fe	µg/l	10.0	<10	<10	n.a.	200.0
Mn	µg/l	3.0	<3.0	<3.0	n.a.	50.0

* DL, Detection limit; n.a., not available

Based on results obtained from water quality analysis, the Riihimäki water used for sample preparation is good except in regard to electrical conductivity and dissolved organic carbon, which are exceptionally high. The maximum value for electrical conductivity according to Finnish legislation (STM 1352/2015) is 2,500 µS/m (2.5 mS/m) is significantly lower than the value determined for Riihimäki water. The maximum value has not been set for DOC, but the value obtained is approximately an order higher compared to typical groundwater.

According to records of Riihimäki water quality in 2015, the value for electrical conductivity varied between 163 – 286 µS/m at different water works. DOC content has not been reported. (Riihimäen vesi 2016.) Despite of high DOC determined, COD_{Mn} was low indicating that humic material was not present at significant amount. Therefore, the source of contamination in water may be from rarely used fire hydrant line of in the container used for storing the water. However, the container was large, with 11.5 m^3 volume making the source from container walls resulting as high values unlikely. However, since laboratory results were obtained a month after the experiments, further clarification and analyses were not possible. Also the effects on results remain questionable.

7.2 Degradation of TNT and RDX by UV irradiation

TNT and RDX containing water was exposed to 550 J/m^2 and 407 J/m^2 UV radiation in two UV degradation experiments. The temperature of the sample was 8.8 ˚C as measured from the solution container prior the experiment. The results of the experiments for samples analyzed according to ISO 22478 as average values of the duplicate samples are presented in table 8.

Table 8. Concentrations of TNT, RDX and associated compounds after UV irradiation at 407 J/m^2 and 550 J/m^2 UV doses. The concentrations given are average values of duplicate samples (with standard deviations) except for initial TNT and RDX concentrations, which are averages of triplicate samples. (All units µg/l).

	DL*	Initial conc.	550 J/m^2	407 J/m^2
2,4,6-Trinitrotoluene (2,4,6-TNT)	**0.1**	**27.00** ± 1.00	**19** ± 1.41	**19** ± 0.00
Hexogen (RDX)	**0.2**	**35.67** ± 0.58	**19** ± 1.41	**22.5** ± 0.70
Octogen (HMX)	0.2	-	-	-
1,3-Dinitrobenzene (1,3-DNB)	0.1	-	-	-
1,3,5-Trinitrobenzene (1,3,5-TNB)	0.1	0.93 ± 0.04	3.25 ± 0.07	3.2 ± 0.14
2,4-Dinitrotoluene (2,4-DNT)	0.1	-	-	-
2,6-Dinitrotoluene (2,6-DNT)	0.1	-	-	-
2-Amino-4,6-dinitrotoluene (2-ADNT)	0.1	-	-	-
4-Amino-2,6-dinitrotoluene (4-ADNT)	0.1	0.14 ± 0.02	-	-

* DL, Detection limit

Initial concentrations were 27.0 µg/L for TNT and 35.67 µg/L for RDX in the sample prior the experiment. Also 1,3,5-TNB and 4-ADNT, which are degradation products TNT, were present at low concentrations 0.93 µg/L and 0.14 µg/L, respectively. Although RDX generally contain 10% HMX as impurity (Thiboutot *et al.* 2002), HMX was not present in the sample, since pure TNT and RDX were used for sample preparation.

The concentration of TNT decreased to 19 µg/L (29.6%) in both experiments with exposure to 407 J/m^2 UV dose and 550 J/m^2 UV dose. The degradation rate of RDX under UV exposure was even higher with final concentrations of 22.5 µg/L (36.9% decrease) when exposed to 407 J/m^2 UV dose and 19 µg/L (46.7% decrease) under exposure of 550 J/m^2 UV dose. Also the concentration of 4-ADNT decreased below detection limit in both experiments. Instead, concentration of 1,3,5-TNB increased during the experiment by the factor of ~3.5 indicating that 1,3,5-TNB is formed as UV induced degradation product of TNT.

7.3 Treatment of TNT and RDX contaminated water by reverse osmosis

Treatment of TNT and RDX contaminated water by prefiltration and reverse osmosis was tested using mobile Kärcher water purification system. The temperature of the TNT and RDX containing water prior to reverse osmosis experiment was 8.6 ˚C as measured from the sample container. The results of reverse osmosis treatment experiment are given in table 9.

Table 9. Results of reverse osmosis treatment of TNT and RDX contaminated water by Kärcher water purification equipment. Concentrations are averages of two duplicate samples with standard deviations. (All units µg/l).

	DL	Initial conc.	0,5 µm pre-filter	Reverse osmosis	Reject water
2,4,6-Trinitrotoluene (2,4,6-TNT)	**0.1**	**32** ± 2.83	**24.5** ± 0.71	**-**	**100** ± 0.00
Hexogen (RDX)	**0.2**	**37** ± 0.00	**31.5** ± 2.13	**-**	**110** ± 0.00
Octogen (HMX)	0.2	-	-	-	-
1,3-Dinitrobenzene (1,3-DNB)	0.1	-	-	-	-
1,3,5-Trinitrobenzene (1,3,5-TNB)	0.1	0.83 ± 0.14	0.75 ± 0.07	-	1.8 ± 0.14
2,4-Dinitrotoluene (2,4-DNT)	0.1	-	-	-	-
2,6-Dinitrotoluene (2,6-DNT)	0.1	-	-	-	-
2-Amino-4,6-dinitrotoluene (2-ADNT)	0.1	-	-	-	-
4-Amino-2,6-dinitrotoluene (4-ADNT)	0.1	0.15 ± 0.01	-	-	0.32 ± 0.04

* DL, Detection limit

The performance of reverse osmosis in removal of TNT and RDX from water was as expected, and all of the examined compounds were removed under detection limit in the experiment. Accordingly, the concentrations of TNT, RDX and TNT degradation products were increased in reject water, with TNT and RDX approximately by 3-4 fold. The degradation products of TNT were concentrated differently, but these compounds may also have been formed or degraded during the experiment. Especially 1,3,5-TNB is a abiotic degradation product of TNT and formed also by photolytic processes, as seen also here in the UV degradation experiment. Hence, it is possible that under experimental conditions of RO treatment, TNB has been formed after the experiment during the short exposure to natural light in sample collection tubs.

The concentrations of TNT, RDX and TNB (degradation product of TNT) are lower in samples taken after prefiltration compared to initial concentration. The concentrations are decreased by 10 – 15% indicating that some of the material is retained in the 0.5 µm filter. The most likely explanations are that 1) Despite of careful sample preparation, some precipitation has occurred and the precipitates have not passed filters; or 2) TNT and RDX compounds were adsorbed on organic particles contained in water that were capable to form aggregates large enough to be retained in filtration.

However, humic substances were absent in the water used for sample preparation according to water quality analysis (COD_{Mn} below detection limit). The possible source of particles in the water may be due to same unidentified origin as high COD and electrical conductivity noted in water quality analysis. No precipitation of TNT or RDX to previously filtered material contained in filter bags occurred here, since the Kärcher equipment was recently maintained after storage and the prefilters and RO membranes used in the experiment were new.

In addition to decreased TNT, RDX and TNB concentrations after prefiltration, also 4-ADNT seems absent in prefiltered material, although 4-ADNT is observed both in initial sample and in reject water. However, 4-ADNT is present in initial sample in low concentration close to detection limit. Hence, detection of 4-ADNT after prefiltration may have failed due to low concentration. Another possibility instead on retention of the compounds to prefilter, is adsorption of the compounds to the output hose used. In the experimental set up, the hose utilized in prefilter output was new and composed of different material than other hoses used. Also the water flow from this output was very low, since the vent used as output here, is intended for utilization as alternative *input* of the source water. The water flow was kept very low to ensure sufficient water pressure for RO membranes. Therefore, under the experimental conditions, adsorption to hose material was possible.

7.4 Abiotic degradation of TNT and RDX

Abiotic degradation of TNT and RDX were monitored from samples kept outdoors in conditions exposed to sun light and protected from light and rain for 2 weeks. The results of explosives and related compound analysis from samples taken during the experiment are presented in table 10.

Table 10. TNT and RDX degradation under natural light and dark conditions during 2 weeks period. Samples were taken at days 7 and 14. The concentrations are averages of two duplicate samples with standard deviations. (All units µg/L).

	DL*	Initial conc.	Light 7 d.	Light 14 d.	Dark 7 d.	Dark 14 d.
2,4,6-Trinitrotoluene (TNT)	**0.1**	**27.00** ± 1.00	**-**	**-**	**26** ± 0.00	**18** ± 2.83
Hexogen (RDX)	**0.2**	**35.67** ± 0.58	**30** ± 0.00	**25.5** ± 0.71	**37** ± 1.41	**37.5** ± 0.71
Octogen (HMX)	0.2	-	-	-	-	-
1,3-Dinitrobenzene (1,3-DNB)	0.1	-	-	-	-	-
1,3,5-Trinitrobenzene (1,3,5-TNB)	0.1	0.93 ± 0.04	-	-	0.87 ± 0.01	0.86 ± 0.01
2,4-Dinitrotoluene (2,4-DNT)	0.1	-	-	-	-	-
2,6-Dinitrotoluene (2,6-DNT)	0.1	-	-	-	-	-
2-Amino-4,6-dinitrotoluene (2-ADNT)	0.1	-	-	-	0.23 ± 0.04	0.52 ± 0.06
4-Amino-2,6-dinitrotoluene (4-ADNT)	0.1	0.14 ± 0.02	-	-	1.3 ± 0.14	2.5 ± 0.00

* DL, Detection limit

From the results, comparisons of degradation rates between RDX and TNT can be made within the samples from the same tub. However, absolute calculations of degradation rates cannot be made due to lack of information about original and final sample volume. The samples kept in dark conditions were weather proofed by plastic cover, but the sample tub exposed to natural light received only partial cover from shed corner and roof. Hence, the sample tub was exposed to weather conditions and evaporation during the experiment.

Based on the results, RDX is degraded at slower rate compared to TNT in follow-up samples exposed to natural light. 15.9 % of RDX was degraded after 1 week and 28.5 % in 2 weeks whereas TNT was completely disappeared within the first week. In addition to TNT, also 1,3,5-TNB and 4-ADNT present in initial sample were completely removed from the sample under light exposed conditions during the first week, and no degradation products appeared during the second week.

In contrast to light exposed sample, degradation of TNT was very slow in dark conditions and also accumulation of TNT degradation products was observed. TNT was reduced by 3.7 % during the first week and by 33.3 % within the two weeks experiment. At the same time, the concentration of 4-ADNT was increased from 0.14 µg/L to 1.3 µg/L (1 week) and 2.5 µg/L (in 2 weeks). Also another aminodinitrate isomer 2-ADNT appeared during the experiment and was present in the sample at 0.23 µg/L and 0.52 µg/L after weeks 1 and 2. The concentration of 1,3,5-TNB remained similar throughout the experiment in dark conditions.

In dark conditions, concentration of RDX increased very slightly by the factor of 1.05 (from 35.7 µg/L to 37.5 in two weeks). The possible explanations are sampling errors, analysis variation and also some evaporation of the sample despite of plastic cover is possible. The difference as a result of evaporation solely, would mean evaporation of 2 liters from approximately 40 liters initial sample volume, which does not seem plausible. However, evaporation from open container has been significantly higher compared to covered sample. The sample tub may also have obtained additional water due to occasional rains despite of moderate cover from shed corner and roof during the experiment. Also, records of weather and temperature at the site of the experiments are not available.

8. DISCUSSION

Large-scale production, utilization and disposal of explosives during last 100 years have led to contaminations of soil and groundwater (Lewis et al. 2004; Pichtel 2012). In recent years, trace amounts of TNT, RDX, and HMX have been found also in Finland at military training ranges, which are often located at groundwater formation areas classified as important drinking water resources. Hence, studies concerning energetic compounds, their environmental fate and best available treatment methods are currently under examination by Finnish Defence Forces. (Koponen 2016.)

8.1 Literature review

Degradation of explosives has been extensively studied. Information of resulting degradation products has been obtained by studies utilizing labeled C or N incorporated to explosives ring structure or nitroso groups. However, due to standardized analysis methods, mostly appearance of only previously identified and often detected products are monitored. Hence, more rarely detected or previously unidentified products may remain unnoticed in degradation studies and in environmental monitoring.

TNT, RDX and HMX are degraded by biological, chemical and abiotic processes (Talmage et al. 1999). Of these compounds, RDX and HMX are transformed to intermediates, which can subsequently be fully mineralized by biological processes (Crocker et al. 2006; Michalsen et al. 2016) Instead, TNT is highly recalcitrant for degradation and is mostly transformed to amino derivatives and not mineralized (Khan et al. 2013). Of the abiotic degradation processes, hydrolysis is not significant process for any of the explosives examined, except at high pH conditions (Balakrishnan et al. 2003; Hwang et al. 2006; McGrath 1995). Instead, photolytic degradation is important transformation mechanism for TNT, RDX and HMX in the environment (Talmage et al. 1999). By abiotic reduction, TNT is reduced to amino derivatives and RDX to triazines (Pichtel 2012), but HMX is not readily reduced by abiotic processes (Park et al. 2004). Further, TNT is transformed by abiotic oxidation, while RDX is more recalcitrant and HMX is not degraded in oxidation processes (Liou et al. 2003).

The most important properties affecting explosives migration are solubility and adsorption characteristics. Volatilization is not significant for any of the explosives (Thiboutot et al. 2002). Solubility properties of explosives are clear, TNT is the most soluble and HMX the least soluble of the compounds (Thiboutot et al. 2002). However, dissolution of explosives from solid particles, which contain also other substances such as binders, is more complex process under environmental conditions. Hence, variability exists between experimental results. Adsorption properties are the most controversial and uncertain characteristic of TNT, RDX and HMX, even though adsorption has been extensively studied due to its major impact on migration properties. Still, affinity of explosives to organic carbon and implications of soil properties, such as cationic and clay content, to adsorption remain uncertain.

TNT, RDX and HMX are often found in groundwater at explosives contaminated sites. RDX is possibly the most abundant due to low dissolution of HMX and high transformation rate of TNT to amino derivatives, which remain bound to soil particles. However, the explosives migrated to aquifer may remain stable for a long time as demonstrated by high concentrations detected from groundwater long after termination of pollution such as operation of ammunition plant (Steuckart et al. 1994).

Removal of explosives and their degradation products from contaminated soil and groundwater is important when the concentrations are high enough to cause harmful effects on environment or human health. Most of the toxicity data is based on animal studies and toxicity and carcinogenicity for humans is unclear. The available data con-cerning toxicity of explosives degradation products is even more limited. However, un-derstanding of relative toxicities and environmental effects of degradation products would be important in order to be able to choose remediation methods leading to less harmful substances.

In remediation, the reality of actual contaminated areas is simultaneous contamination of soil and aquifer by multiple compounds and their degradation products. The contaminating compounds involved have different chemical and physical characteristics and are degraded at different rates. Hence, portion of the contaminants are readily mobile and migrating to groundwater, while other substances may remain mostly as solid particles on top soil or tightly bound to soil organic material in varying depths. The compounds also differ in reactivity and respond variably for treatment methods. This causes multiple demands for the chosen remediation strategy to meet.

The emission pattern of explosives is generally different compared to single point contamination source. Explosive sources are typically spread over large areas and have implications to remediation method chosen. Due to depository of explosives in soil, remediation of soil at site has to be included in treatment of contaminated groundwater. In groundwater remediation, pump-and-treat approach with suitable treatment method for extracted groundwater has been traditionally used. Contaminated soil has been most often treated by excavation and subsequent incineration processes.

Pump-and-treat technology is efficient in prevention of contaminant spreading, but remediation time is long and remaining residual contamination often high due to tailing and rebound. However, the approach is suitable for any of the explosives, since above ground treatment method can be chosen freely. Extraction and removal of explosives can be further enhanced by physical, chemical and biological enhancements injected to aquifer to improve mobility and degradation of compounds. Bioremediation is important and emerging environmentally friendly technology, which can be coupled with pump-and-treat technology and permeable reactive barriers. Alternatively bioremediation can be used as sole treatment method on site. Many micro-organisms are capable for transformation and degradation of explosives, but typical remediation duration is long. Also, difficulties exist from simultaneous contamination by differential substances and competition of explosive degrading strains with indigenous organisms. PRB technology utilizing ZVI is efficient for remediation of TNT and RDX, but inefficient for HMX. However, the advantage of the method is possibility to couple different reactive media together, including combining of bioremediation with ZVI-PRB. In situ chemical oxidation (ISCO) utilizing Fenton reactions, ozone, permanganate or persulfate is efficient in treatment of explosives, but even and efficient delivery of reactive agent is challenging, especially in wide areas. Further, although promising result have been obtained in laboratory and pilot scale treatment experiments, published results from actual remediation projects for explosives using ISCO for soil and aquifer contaminated by explosives are scarce.

Due to typical pattern of scattered point sources over vast areas from several hundred hectares to even hundreds of square kilometers, soil and groundwater remediation appears challenging by any of the techniques introduced here. Hence, developing solutions and practices for prevention of contamination of groundwater should be a priority in future military training action. In regard to existing groundwater contaminations, pump-and-treat seems to still have importance in mitigation of the effects of the contamination and in restriction of contamination plume, although the method is inefficient in reaching the ultimate goal of fully remediated site. However, in coupled with simultaneous soil treatment, pump-and-treat seems efficient and suitable remediation approach. On sites with adequately shallow aquifer and well characterized groundwater conditions, groundwater flow rate and direction, PRB technology appears the most effective taken into account efficiency, cost and passive action in remediation after setting up the barriers. The efficiency of the barriers can be further increased by applying different layers, which also enables simultaneous biodegradation and sorption processes with chemical reduction.

In Finland, environmentally conscious military training strategies together with inclusive monitoring and investigations of the heavy weapon shooting and training sites have enabled the sufficient level of environmental protection on those sites. Thus to date, no remediation projects have been conducted due to high concentrations of energetic materials in soil or groundwater.

8.2 Water treatment experiments

The experimental part of this work contained UV degradation and reverse osmosis treatment experiments and monitoring of TNT and RDX abiotic degradation.

The efficiency of ***UV irradiation*** in degradation of TNT and RDX was tested with 407 J/m^2 and 550 J/m^2 UV doses. As a result, 29.6% of TNT and 36.9% of RDX was degraded under 407 J/m^2 dose and 29.6% (TNT) and 46.7% (RDX) with 550 J/m^2. The results showed that UV irradiation is not efficient enough to be used as sole method for explosives degradation.

UV irradiation is generally used for oxidation of explosive compounds in combination with strong oxidizers such as H_2O_2 or O_3 (AOP-techniques), or TiO_2 (photocatalysis) rather than alone as sole degradative agent (Ayoub *et al.* 2010; Vasilyeva *et al.* 2002). However, in studies concerning explosives degradation by AOP and Fenton processes, UV degradation has often been used as control and UV degradation rates can be referred from these studies. In a study of Liou *et al.* (2004) concerning TNT oxidation by photo-Fenton process, degradation rate constant for TNT was 0.002 min^{-1} under UV irradiation with 2.4 mW/cm^2 intensity. For comparison, degradation rate constants were higher in other experiments, 0.007 min^{-1} for UV/ H_2O_2 (2.4 mW/cm^2), 0.014 min^{-1} for Fenton process and 0.025 min^{-1} for photo-Fenton (2.4 mW/cm^2). TNT degradation rate followed pseudo-first-order kinetics in all experiments. Liou *et al.* (2004)

In previous work of Liou *et al.* (2003), UV irradiation as sole degrading agent was used for comparison in experiments of explosive degradation by Fenton and photo-Fenton processes. As a result, UV radiation alone was not efficient (during experimental time of 60 – 120 min.) for degradation of any the compounds studied, including TNT, RDX and HMX. (Liou *et al.* 2003)

However, photolysis of *solid* explosive residues may have been significantly underestimated according to recent findings on Taylor *et al.* (2010). According to their study of phototransformation by sunlight using chunks of TNT and RDX during three years, the loss of material was significantly higher than was recovered in dissolved mass taking into account possible error sources, such as handling, analysis and material sublimation. Only 20-40% of the material was recovered indicating formation of other compounds that are not detected by standard detection methods. Hence, significant amounts of products may be formed also in natural systems that are not currently known. (Taylor *et al.* 2010.)

The UV degradation experiment performed here provides information mainly about disappearance of the explosive compounds TNT and RDX. Limited information is obtained about products formed as a result of UV degradation, since only the products listed in table 8 (chapter 7.2) were detected with the analysis method used. Based on literature, 1,3,5-TNB which was also detected here, is the major product of TNT photolysis (Jenkins and Vogel 2014), However, also formation of other compounds such as nitrobenzenes, benzaldehydes, azoxydicarboxylic acids and nitrophenols (McGrath 1995) and acidic products such as 2,4-DNBA and 2-A-4,6-DNBA (Godejohann *et al.* 1998) can be formed due to TNT photolysis. Instead, photolysis of RDX leads to formation of variety of compounds such as azoxy compounds, NH_3, formaldehyde, NO_3^-, NO_2^-, nitrous oxide N_2O

and n-nitroso-methylenediamine (Glover and Hoffsommer 1979 according to Juhasz and Naidu 2007), which could have been formed here, but were unnoticed with the analysis methods used.

In ***reverse osmosis experiment***, removal of explosives from TNT/RDX contaminated water was tested using Kärcher water purification system. The result was as expected; TNT, RDX and intermediates present were completely removed by RO. Hence, safe drinking water can be produced by RO explosives containing water. The method is reliable in removal of contaminants from water, but the method (with utilized equipment) is not suitable for utilization in water works at constant use due to quantity of reject water produced that would need further treatment. With the normal 4,000 L/h water flow, the amount of purified water is 1,600 L at maximum. Hence, at least 2,400 L of reject water is produced for each 1,600 L purified water. Further, adjustment of pH and mineralization of water purified with RO is required after treatment. Common approach in utilization of RO at water works, is mixing of treated and untreated water in adequate proportions to obtain desired water quality parameters. (Liikanen 2007.)

With the results obtained from RO experiment, the variability of the two analysis methods was visible. As noted previously, the two methods used for analysis give variable results, and the concentrations obtained by LCMS/APCI being higher compared to HPLC analysis according to ISO 22478 (data not shown). However, the difference between two analysis methods is not straightforward as demonstrated by the pattern how compounds are concentrated on reject water. The flow rate passing Kärcher equipment is 4 m^3/h at maximum of which at least 2.6 m^3/h reject water is formed. Hence, the compounds present in source water were expected to concentrate at least by the factor of 1.54. According to analysis made in FDRA, the explosive compounds TNT and RDX concentrate by the factor of 2 from initial sample to reject water and by the factor of ~3 according to analysis made by ISO 22478. However, 4-ADNT and 1,3,5-TNB are concentrated differently and are found in reject water concentrated by x2.2. On the other hand, these compounds are not detected at all with FDRA analysis method, although the concentration of 1,3,5-TNB exceeds the detection level (0.4 μg/L). These results may be explained by differential sample processing and storing and will be examined in future studies.

Abiotic degradation of explosives was examined by monitoring degradation of TNT and RDX. Degradation was evaluated by monitoring disappearance of TNT and RDX from water exposed to natural light and in dark conditions. As a result, TNT and intermediates were completely degraded within first week under exposure to natural light, while little of TNT was degraded in dark conditions. In contrast to TNT, RDX was degraded only little during first and second week in light and was not degraded at all under dark conditions.

Similar results as was obtained here for TNT photodegradation in water was recently reported by Im *et al.* (2015) using low UV intensity (0.12 to 4.2 mW/cm^2) and 352 nm wavelength representing natural light intensity. TNT degradation was negligible in dark and only 10-20% TNT degradation was observed under low light intensity 0.12 mW/cm^2. However, degradation on TNT was almost complete within 6 to 12 hours under higher light intensities 1.2 and 4.2 mW/cm^2. The results indicate that degradation is highly dependent on light intensity and hence, time of the day and season. (Im *et al.* 2015.)

Although RDX was degraded less than TNT (15.9 % in 7 days and 28.5 % in 14 days) under natural light in our study, RDX has been reported to adsorb radiation at wavelengths as high as 330 nm. Hence, RDX could be susceptible for photodegradation by wavelengths (UVB 280 – 315 nm and UVA 315-400 nm) present in natural light. However, sunlight intensity varies with latitude and studies concerning photolysis by sunlight have been conducted mostly at southern locations. (Bordeleau *et al.* 2013). Information concerning weather conditions at experiment location and sample storing site during the two weeks of monitoring is not available. According to statistics, the amount of solar intensity is approximately 1000 W/m^2/hour at noon between May and July in Finland (Suntekno 2010). However, samples were stored under roof and next to shed wall during the experiment and hence, the amount on direct sun light has been greatly reduced.

In a study of Bordeleau *et al.* (2013), an average half-life of 1.1 day (in July) and 3.6 days (in October) was estimated for RDX dissolved in distilled water due to photodegradation. The experiments were conducted at 40 ° N latitude in natural sunlight with 20.8 MJ/m^2 (July) and 6.6 MJ/m^2 (October) average daily radiation. For comparison, our experiment site was located further north, at latitude 60 ° N. Hence, the low degradation rate observed for RDX in our study, was possibly due to weather conditions and partial coverage preventing direct sunlight.

Most likely light intensity is also the factor resulting for differences in RDX degradation by UV irradiation and under natural light observed here: RDX was found to be degraded at higher rate compared to TNT in the UV degradation experiment but only little under natural light. The wavelength used by UV lamp in Wedeco aquada 7 is low (240 nm) compared to wider range (up to 400 nm) in natural light. It seems likely, that degradation of RDX needs higher light intensity and lower wavelengths compared to TNT.

Based on results obtained here, both RO and photolysis by UV irradiation appears to have potential to be further improved as methods of choice for explosive removal depending on situation. RO is reliable for removal of explosives and would remove any other compound present as well. Further, RO is a ready technique and can be readily deployed with mobile system, but for large scale treatment, suitable practice for reject water treatment would improve the method. Also UV irradiation could be sufficient for degradation of low explosive concentrations. The results obtain here indicate, that further studies with more photolytic degradation products included in analysis would be worthwhile.

9. CONCLUSIONS

The aim of this thesis was to examine degradation, characteristics and migration of TNT, RDX and HMX, and to study toxicity of explosives and their known degradation products. The main objective was to examine suitable remediation technologies for sites contaminated by explosives and to identify suitable treatment technologies for explosives contaminated groundwater. In the experimental part of this work, the efficiency of two water treatment technologies, degradation of TNT and RDX by UV irradiation and removal of TNT and RDX from water by reverse osmosis, was tested. The purpose was to evaluate possibility for utilization of these methods at water works as part of standard water treatment practices. In addition, abiotic degradation of TNT and RDX was monitored from samples exposed to natural light and kept in dark.

TNT, RDX and HMX are degraded by biological, chemical and abiotic processes. TNT is highly recalcitrant for degradation by biological processes and is transformed to amino derivatives, but not mineralized. Instead, RDX and HMX are biotransformed to intermediates, which can be further degraded and mineralized. Chemical and abiotic degradation processes are hydrolysis, photolysis, chemical reduction and oxidation processes. Of these, photolytic degradation is important transformation mechanism for TNT, RDX and HMX in the environment, while hydrolysis is not significant process under environmentally relevant conditions for any of the examined compounds. Abiotic reduction processes are similar to biological reduction. TNT is reduced to amino derivatives and RDX to triazines, but abiotic reduction is not significant for HMX. Abiotic oxidation is relevant for TNT, RDX is more recalcitrant and HMX is not degraded in oxidation processes.

Solubility and adsorption are the most important physical and chemical characteristics affecting migration of the explosives. However, while solubility of pure compounds is simple, dissolution of explosives from solid particles under environmental conditions is more complex. Adsorption properties remain even more uncertain despite of extensive research on subject. Hence, implications of soil organic carbon content, clay content and other soil properties to adsorption of explosives remain uncertain. Therefore, migration appears to be strongly site-specific. However, TNT, RDX and HMX are all found from groundwater, with RDX most commonly. Explosives are also stable in groundwater and may remain as contaminants on site for a long period of time.

Traditionally only explosive compounds have been considered toxic for humans and the environment. However, although available data for toxicity is still scarce, many of the explosives degradation products and explosives related substances also have toxicological properties, even with the same magnitude as explosives. Hence, toxicity of degradation products and product formed by different degradation methods should be taken into account in planning of remediation.

In treatment of explosives contaminated groundwater, also remediation of contaminated soil is needed, which can be challenging due to spreading of contaminant source over vast areas. Generally utilized and efficient methods for remediation of explosives from soil are bioremediation and also traditional approach of excavation of contaminated soil with subsequent treatment of extracted material. In remediation of groundwater, pump-and-treat –approach and PRB systems are the most common treatment methods. Also ISCO has been used, but efficient and even delivery of the reacting agent is challenging over large area. None of the methods is suitable for all of the contaminants at every contaminated site. Hence, choice of the remediation method or combination of methods is affected by nature of simultaneous contaminants on site, extent of the contamination and site geography.

In the experiment of explosives degradation by UV irradiation in this work, both TNT and RDX were degraded under 407 J/m^2 and 550 J/m^2 UV doses. However, the degradation rate was not high enough (29.6% TNT and 36.9% RDX with 407 J/m^2) for utilization of UV irradiation as sole method for explosives degradation from groundwater for high concentrations during standard water treatment practices at water works. Instead, removal of explosives from water by reverse osmosis was complete and showed safety of the method in production of drinking water from explosives contaminated water for instance at crisis management sites. However, with the equipment used in this study, the quantity of reject water produced is high (60% of water flow into treatment) and hence, the method is not suitable for large scale water treatment at water works without further treatment practice for reject water.

Abiotic degradation was examined by monitoring TNT and RDX degradation from water. Two samples were kept outside, of which the other one was exposed to natural light and the other kept in dark. TNT and its degradation products were completely degraded within first week from the sample exposed to natural light, while only very little was degraded in dark during the first week and third of the initial amount by the end of the second week. In contrast, less than third of initial RDX was degraded in light during total two weeks and no degradation occurred in dark. The results obtained from UV degradation experiment and photolysis under natural light indicate, that light intensity and wavelength has major impacts on photolysis of TNT and RDX.

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APPENDIX 1: DEGRADATION PRODUCTS OF TNT, RDX AND HMX FORMED IN DIFFERENT PROCESSES

Table 11. TNT, RDX and HMX degradation products formed in biological, chemical and abiotic degradation processes.

Substance	**abbr.**	**Degradation process**	**Reference**
TNT degradation			
2-amino-4,6-dinitrotoluene	2-ADNT	Fungal degradation by *P. chrysosporium* Bacterial degradation by *P. Savastanoi* Degradation by yeast *Y. lipolytica* (nitro group reduction) Biodegradation Microbial transformation	Hawari *et al.* 1999 Martin *et al.* 1997 Ziganshin *et al.* 2007 Kaplan and Kaplan 1982 Vorbeck *et al.* 1998
4-amino-2,6-dinitrotoluene	4-ADNT	Fungal degradation by *P. chrysosporium* Bacterial degradation by *P. Savastanoi* Degradation by yeast *Y. lipolytica* (nitro group reduction) Biodegradation Microbial transformation	Hawari *et al.* 1999 Martin *et al.* 1997 Ziganshin *et al.* 2007 Kaplan and Kaplan 1982 Vorbeck *et al.* 1998
ADNT acyl derivatives (ortho, para)		Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,4-DANT acyl derivatives		Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,4-Diamino-6-nitrotoluene	2,4-DANT	Biodegradation Microbial transformation	Kaplan and Kaplan 1982 Vorbeck *et al.* 1998
2,6-Diamino-4-nitrotoluene	2,6-DANT	Biodegradation	Kaplan and Kaplan 1982
3,5-dinitroaniline		UV/O_3 process	Schmelling and Gray 1995
1,3-dinitrobenzene	DNB	Photo-Fenton process	Liou *et al.* 2004
2,5-dinitrobenzoic acid	2,5-DNBA	photo Fenton process	Liou *et al.* 2004
2,4-dinitrotoluene (1-methyl-2,4-dinitrobenzene)	2,4-DNT	Photo Fenton process Bacterial degradation by P. Savastanoi	Liou *et al.* 2004 Martin *et al.* 1997
2,6-dinitro-4-N-acetylamidohydroxytoluene	4-N-AcHDNT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,6-dinitro-4-N-acetoxytoluene	4-N-acoxyDNT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,4-dinitro-6-hydroxy-benzaldehyde or 2,6-dinitro-4-hydroxy-benzaldehyde		Fenton reaction	Ayoub *et al.* 2011

ortho-acetylamido-4,6-dinitrotoluene	2-N-AcDNT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
para-acetylamido-2,6-dinitrotoluene	4-N-AcDNT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
4-N-formamido-2-amino-6-nitrotoluene	4-N-FmANT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
4-N-acetylamino-2-amino-6-nitrotoluene	4-N-AcANT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2-formamido-4,6-dinitrotoluene	2-N-FmDNT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
4-formamido-2,6-dinitrotoluene	4-N-FmDNT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2-Hydroxylamino-4,6-dinitrotoluene	2-HADNT	Fungal degradation by P. chrysosporium Degradation by yeast *Y. lipolytica* (nitro group reduction) Microbial transformation	Hawari *et al.* 1999 Ziganshin *et al.* 2007 Vorbeck *et al.* 1998
4-hydroxylamino-2,6-dinitrotoluene	4-HADNT	Fungal degradation by P. chrysosporium Degradation by yeast *Y. lipolytica* (nitro group reduction) Microbial transformation	Hawari *et al.* 1999 Ziganshin *et al.* 2007 Vorbeck *et al.* 1998
3-hydroxy-2,4,6-trinitrophenol (assumed)		photo Fenton process with cyclodextrin flushing solution	Yardin and Chiron 2006
HADNT acyl derivatives (ortho, para)		Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2-hydroxylamino-4-amino-6-nitrotoluene acyl derivatives		Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
Nitrite NO_2^-		Bacterial degradation by P. Savastanoi	Martin *et al.* 1997
2,2',6,6'-tetranitro-4,4'-azoxytoluene		Biodegradation	Kaplan and Kaplan 1982
2',4,6,6-tetranitro-2,4'-azoxytoluene		Biodegradation	Kaplan and Kaplan 1982
2-nitroso-4,6-dinitrotoluene	2-NsT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
4-nitroso-2,6-dinitrotoluene	4-NsT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,4,6-trinitrobenzaldehyde	TNBAld	Sorption on activated carbon and subsequent oxidation Fenton reaction UV/O_3 process	Vasilyeva *et al.* 2002 Ayoub *et al.* 2011 Schmelling and Gray 1995
1,3,5-trinitrobenzene	TNB	Sorption on activated carbon and subsequent oxidation Photo-Fenton process UV/O_3 process	Vasilyeva *et al.* 2002 Liou *et al.* 2004 Schmelling and Gray 1995

2,4,6-trinitrobenzyl alcohol	TNBAlc	Sorption on activated carbon and subsequent oxidation Fenton reaction	Vasilyeva *et al.* 2002 Ayoub *et al.* 2011
2,4,6-trinitrobenzoic acid		UV/O_3 process	Schmelling and Gray 1995
2,4,6-trinitro-cyclohexa-2,4-dienol		Fenton reaction	Ayoub *et al.* 2011
2,4,6-trinitrophenol		photo Fenton process with cyclodextrin flushing solution	Yardin and Chiron 2006
Eight TNT hydride complexes (1- H^--TNT, two 3- H^--TNT isomers, 3,5-2 H^--TNT and three 3,5-2 H^--TNT·H^+ isomers)		Degradation by yeast *Y. lipolytica* (direct ring cleavage)	Ziganshin *et al.* 2007
hydride-Meisenheimer complex	H^--TNT	Microbial transformation	Vorbeck *et al.* 1998
dihydride-Meisenheimer complex	$2H^-$-TNT	Microbial transformation	Vorbeck *et al.* 1998
Oxalic acid		photo Fenton process with cyclodextrin flushing solution	Yardin and Chiron 2006
Formic acid		photo Fenton process with cyclodextrin flushing solution	Yardin and Chiron 2006
4,4’,6,6’-tetranitro-2,2’-azoxytoluene	TN-2,2'-AzoxyT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,2’,6,6’-tetranitro-4,4’-azoxytoluene	TN-4,4'-AzoxyT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
4,4’,6,6’-tetranitro-2,2’-azoxytoluene	TN-2,2'-AzoT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
2,2’,6,6’-tetranitro-4,4’-azotoluene	TN-4,4'-AzoT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
(4',6,6'-tetranitro-2,2'-hydrazotoluene) possibly	TN-2,2’-HydrazoT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
(2,2',6,6'-tetranitro-4,4'-hydrazotoluene) possibly	TN-4,4'-HydrazoT	Fungal degradation by P. chrysosporium	Hawari *et al.* 1999
RDX degradation			
hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine	MNX	Anaerobic biodegradation (reduction of nitro groups -pathway)	Hawari *et al.* 2000b
hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine	DNX	Anaerobic biodegradation (reduction of nitro groups -pathway)	Hawari *et al.* 2000b
hexahydro-1,3,5-trinitroso-1,3,5-triazine	TNX	Anaerobic biodegradation (reduction of nitro groups -pathway)	Hawari *et al.* 2000b
nitramide H_2NNO_2		Photolysis	Hawari *et al.* 2002
methylenedinitramine	MEDINA	Anaerobic biodegradation (direct ring cleavage -pathway) Strong evidence. Fenton oxidation Photolysis	Hawari *et al.* 2000b Bier *et al.* 1999 Hawari *et al.* 2002
bis(hydroxymethyl) nitramine		Anaerobic biodegradation (direct ring cleavage -pathway) Strong evidence.	Hawari *et al.* 2000b
4-nitro-2,4-diazabutanal	4-NDAB	Alkaline hydrolysis (pH 10)	Balakrishnan *et al.* 2003

		Photolysis	Hawari *et al.* 2002
Nitrous oxide N_2O		RDX degradation end products (anaerobic) Alkaline hydrolysis (pH 10) Photolysis	Hawari *et al.* 2000b Balakrishnan *et al.* 2003 Hawari *et al.* 2002
Formamide NH_2CHO		Photolysis	Hawari *et al.* 2002
Formic acid HCOOH $HCOO^-$		RDX degradation end products (anaerobic) Fenton oxidation Alkaline hydrolysis (pH 10) Photolysis	Hawari *et al.* 2000b Bier *et al.* 1999 Balakrishnan *et al.* 2003 Hawari *et al.* 2002
Formaldehyde CH_2O		RDX degradation end products (anaerobic) Alkaline hydrolysis (pH 10) Photolysis	Hawari *et al.* 2000b Balakrishnan *et al.* 2003 Hawari *et al.* 2002
CH_4		RDX degradation end products (anaerobic)	Hawari *et al.* 2000b
CO_2		RDX degradation end products (anaerobic) Fenton oxidation	Hawari *et al.* 2000b Bier *et al.* 1999
NO_2^-		Alkaline hydrolysis (pH 10) Photolysis	Balakrishnan *et al.* 2003 Hawari *et al.* 2002
NO_3^-		Fenton oxidation Photolysis	Bier *et al.* 1999 Hawari *et al.* 2002
NH_4^+		Fenton oxidation Alkaline hydrolysis (pH 10)	Bier *et al.* 1999 Balakrishnan *et al.* 2003
NO_2NHCH_2NHCHO		Photolysis	Hawari *et al.* 2002
$NO_2NHCH_2NHNO_2$		Photolysis	Hawari *et al.* 2002
HMX degradation			
octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine		Aerobic degradation Anaerobic biodegradation by sludge	Monteil-Rivera *et al.* 2003 Hawari *et al.* 2001
octahydro-1,5-dinitroso-3,7-dinitro-1,3,5,7-tetrazocine or octahydro-1,3-dinitroso-5,7-dinitro-1,3,5,7-tetrazocine"		Aerobic degradation Anaerobic biodegradation by sludge	Monteil-Rivera *et al.* 2003 Hawari *et al.* 2001
octahydro-1,3,5-trinitroso-7-nitro-1,3,5,7-tetrazocine		Aerobic degradation	Monteil-Rivera *et al.* 2003
octahydro-1,3,5,7-tetranitroso-1,3,5,7-tetrazocine		Aerobic degradation	Monteil-Rivera *et al.* 2003

methylenedinitramine	MEDINA	Anaerobic biodegradation by sludge (direct ring cleavage -pathway) Strong evidence.	Hawari *et al.* 2001
bis(hydroxymethyl) nitramine		Anaerobic biodegradation by sludge (direct ring cleavage -pathway) Strong evidence.	Hawari *et al.* 2001
4-nitro-2,4-diazabutanal	NDAB	fungal degradation Alkaline hydrolysis (pH 10)	Fournier *et al.* 2004 Balakrishnan *et al.* 2003
Nitrite NO_2^-		fungal degradation Alkaline hydrolysis (pH 10)	Fournier *et al.* 2004 Balakrishnan *et al.* 2003
Nitrous oxide N_2O		fungal degradation Anaerobic biodegradation by sludge Alkaline hydrolysis (pH 10)	Fournier *et al.* 2004 Hawari *et al.* 2001 Balakrishnan *et al.* 2003
Formaldehyde CH_2O		fungal degradation Anaerobic biodegradation by sludge Alkaline hydrolysis (pH 10)	Fournier *et al.* 2004 Hawari *et al.* 2001 Balakrishnan *et al.* 2003
Formic acid $HCOOH$		Anaerobic biodegradation by sludge	Hawari *et al.* 2001
CH_4		Anaerobic biodegradation by sludge	Hawari *et al.* 2001

APPENDIX 2: TNT BIODEGRADATION UNDER AEROBIC AND ANAEROBIC CONDITIONS

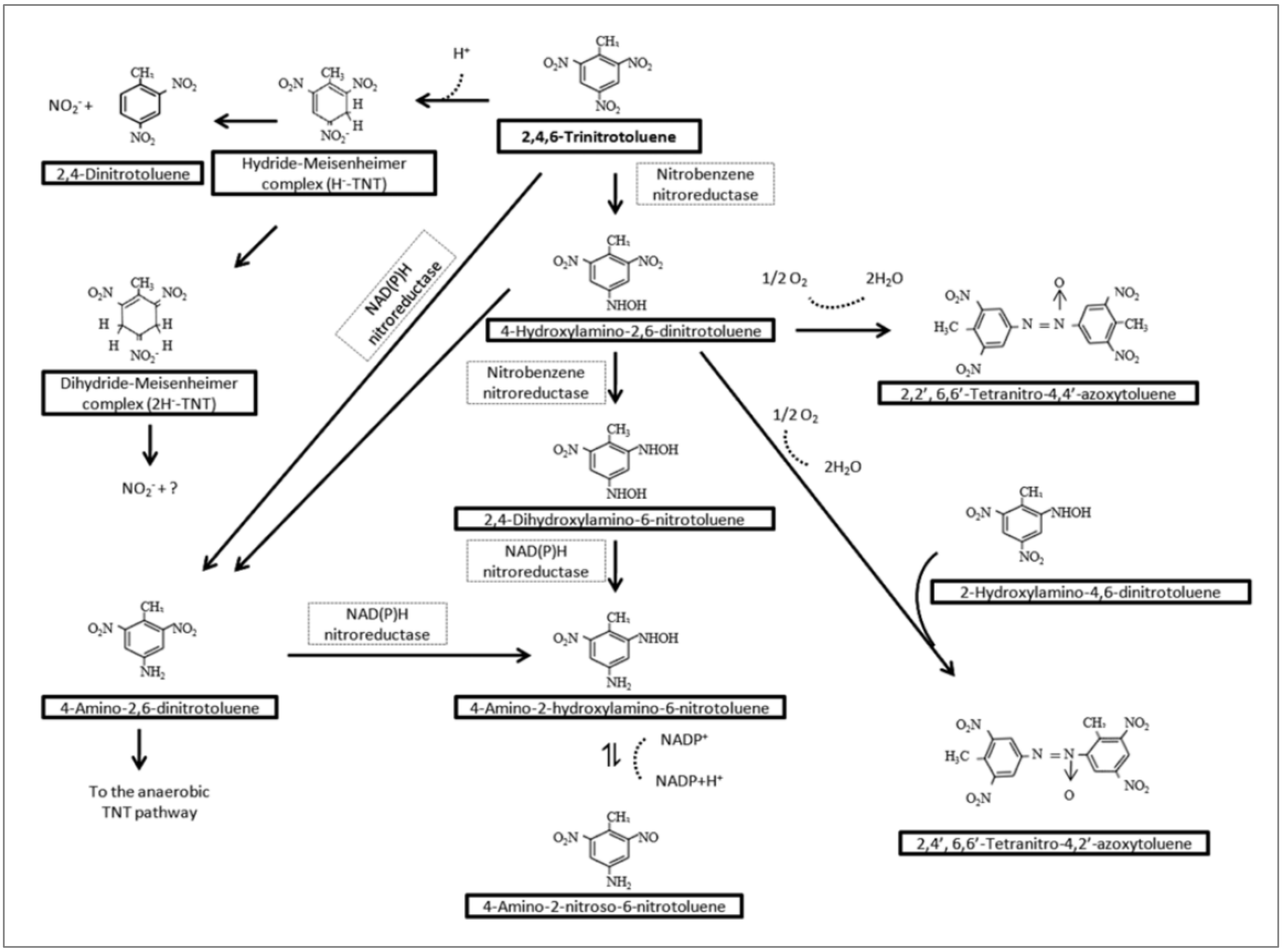

Figure 3. 2,4,6-Trinitrotoluene biodegradation pathway I under ***aerobic*** conditions (Khan *et al.* 2013).

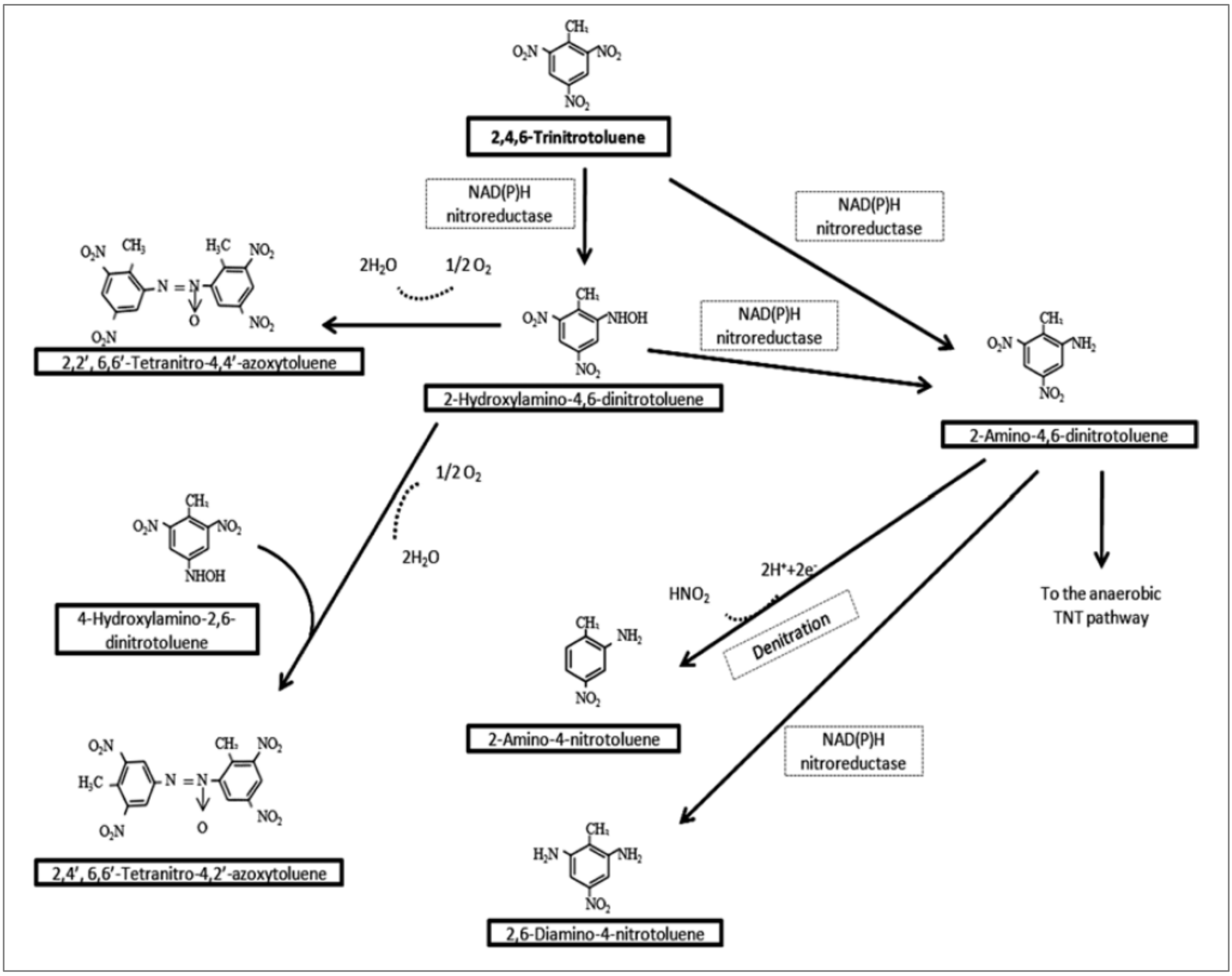

Figure 4. 2,4,6-Trinitrotoluene biodegradation pathway II under ***aerobic*** conditions (Khan *et al.* 2013).

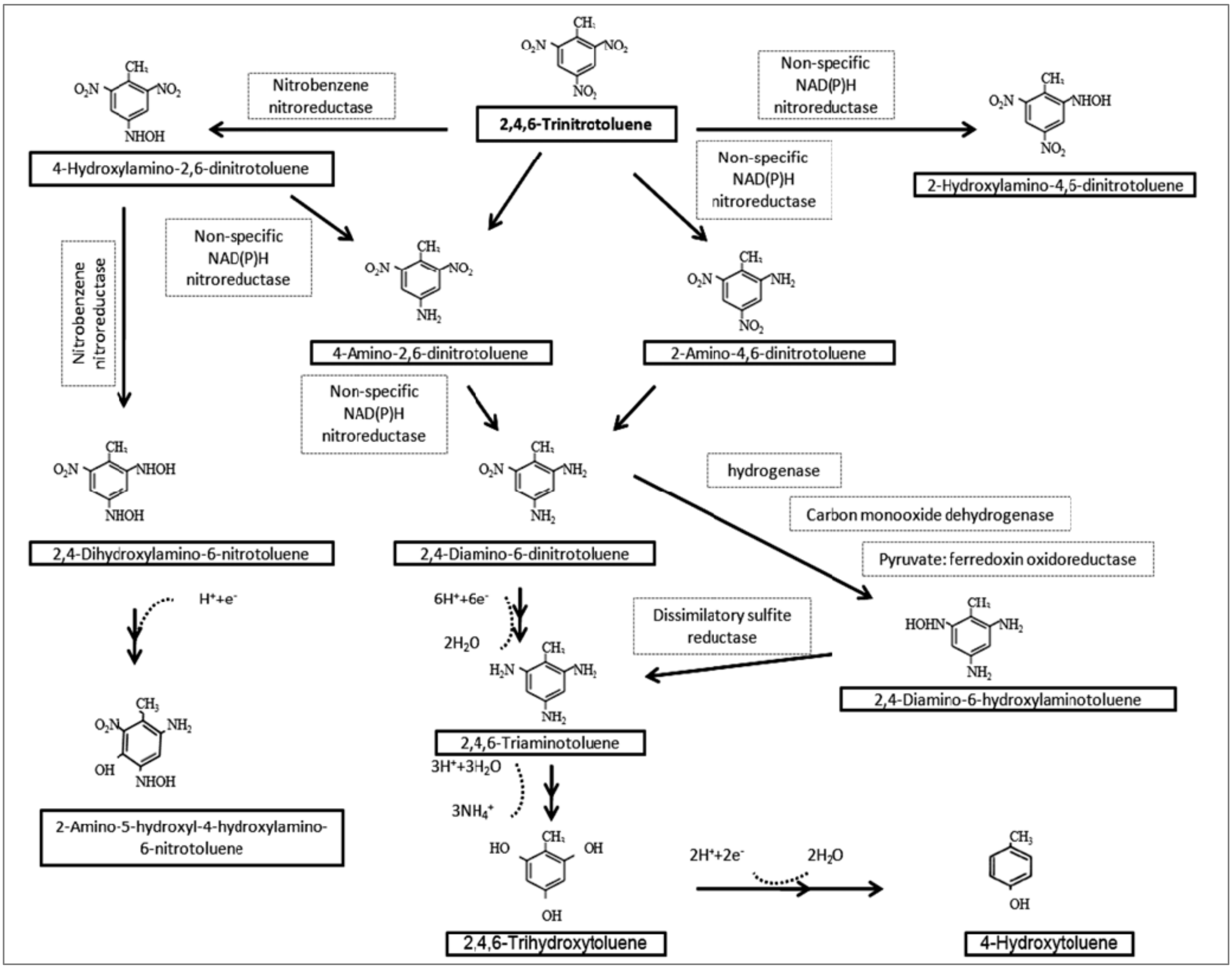

Figure 5. 2,4,6-Trinitrotoluene biodegradation pathway under ***anaerobic*** conditions (Khan *et al.* 2013).

APPENDIX 3: RDX BIODEGRADATION BY ANAEROBIC SEQUENTIAL REDUCTION OF NITRO GROUPS AND BY DIRECT RING CLEAVAGE PATHWAY

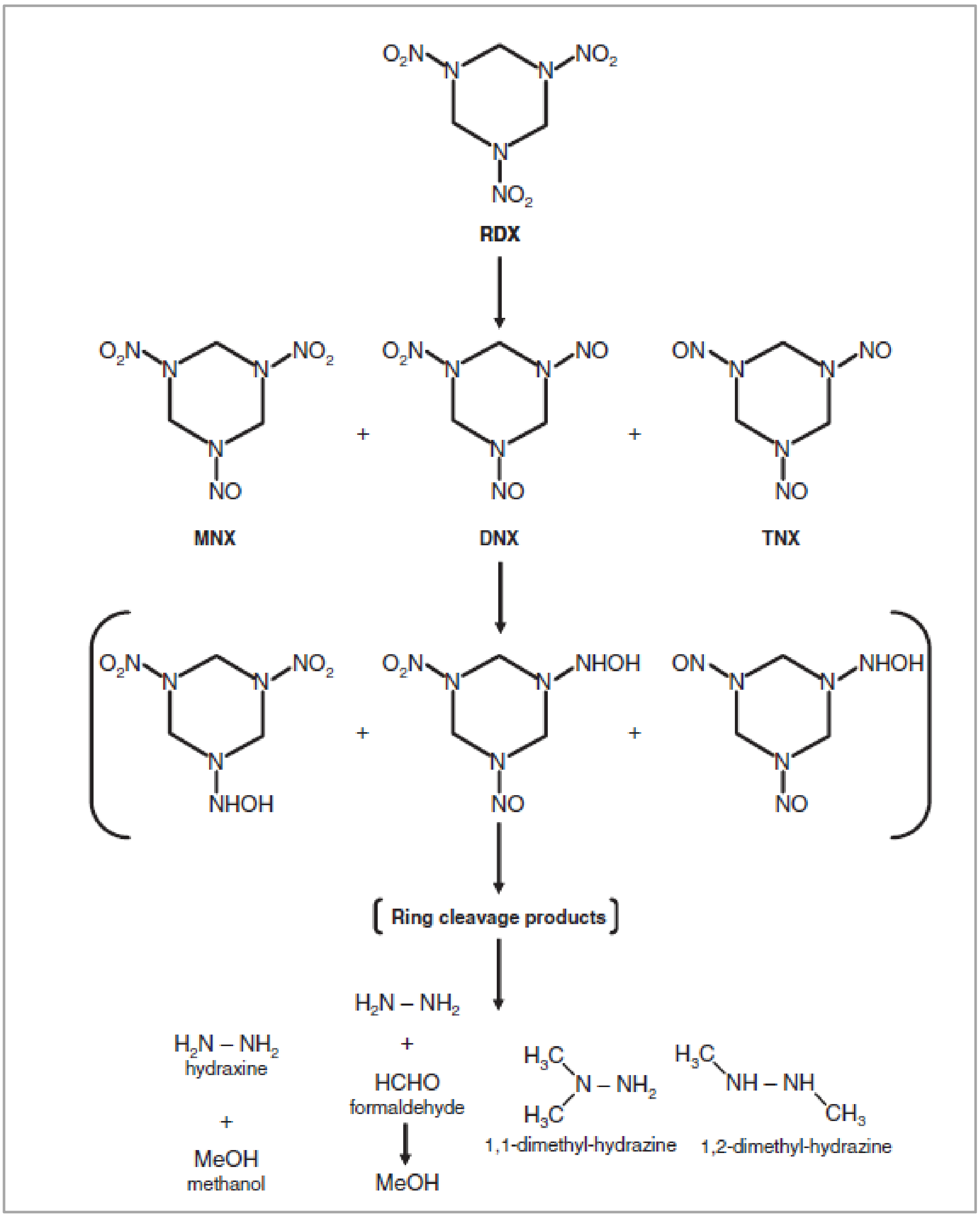

Figure 6. Anaerobic degradation of RDX: reduction of RDX to nitroso derivatives before ring cleavage and the formation of hydrazines (Juhasz and Naidu 2007).

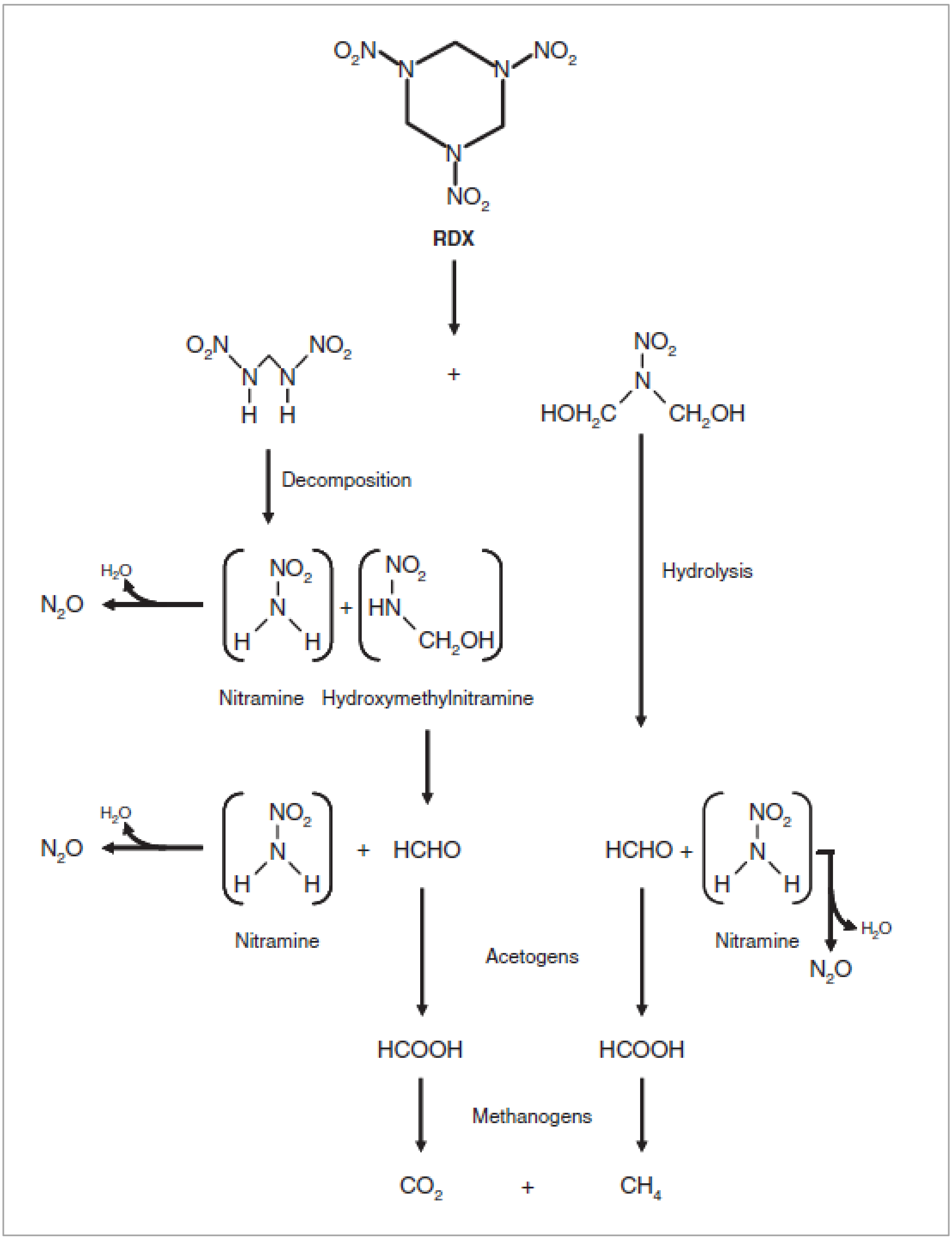

Figure 7. Biodegradation of RDX via direct ring cleavage pathway (Juhasz and Naidu 2007).

APPENDIX 4: PROPOSED PATHWAYS FOR HMX BIODEGRADATION

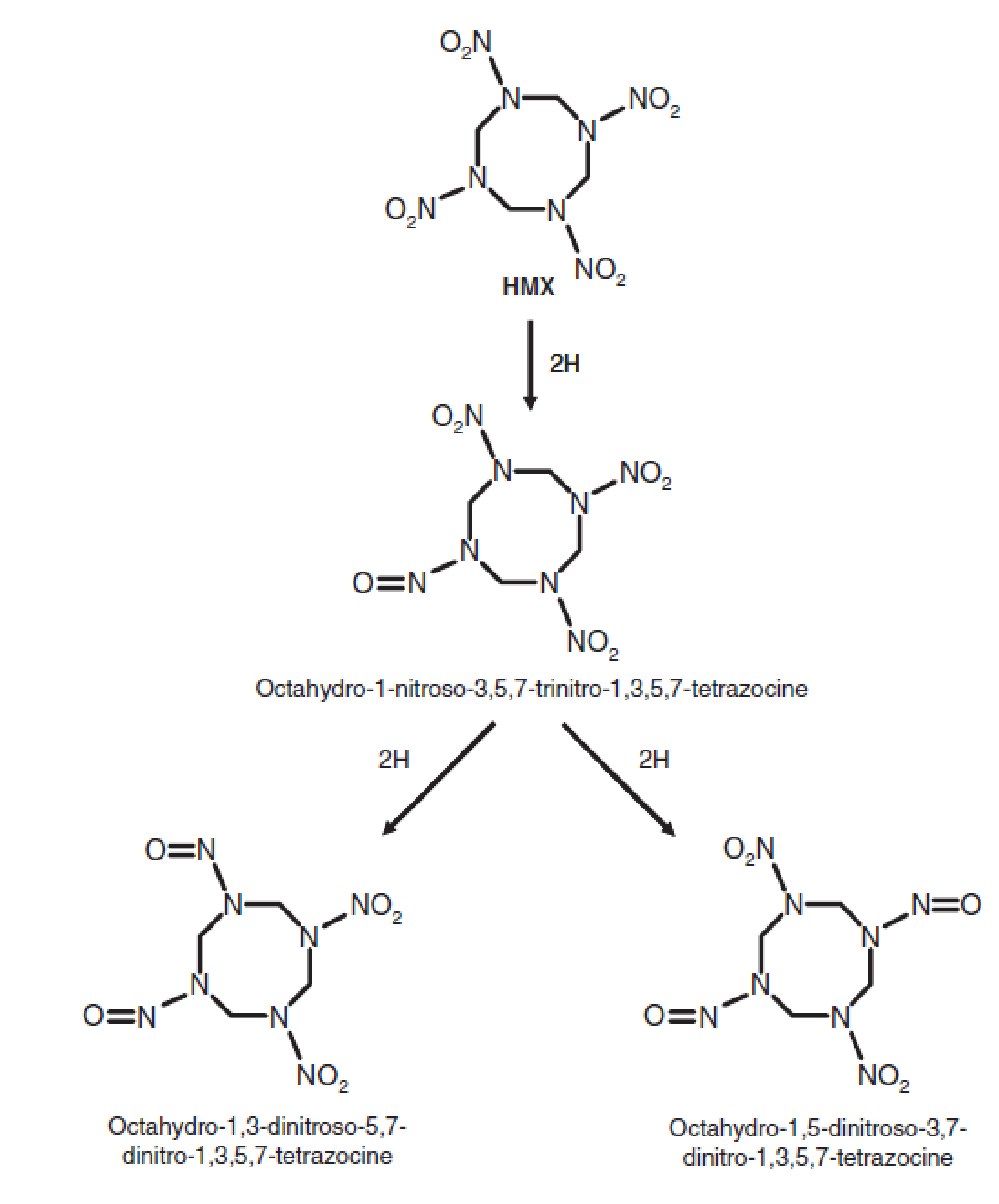

Figure 8. Proposed pathway for HMX degradation (Juhasz and Naidu 2007).

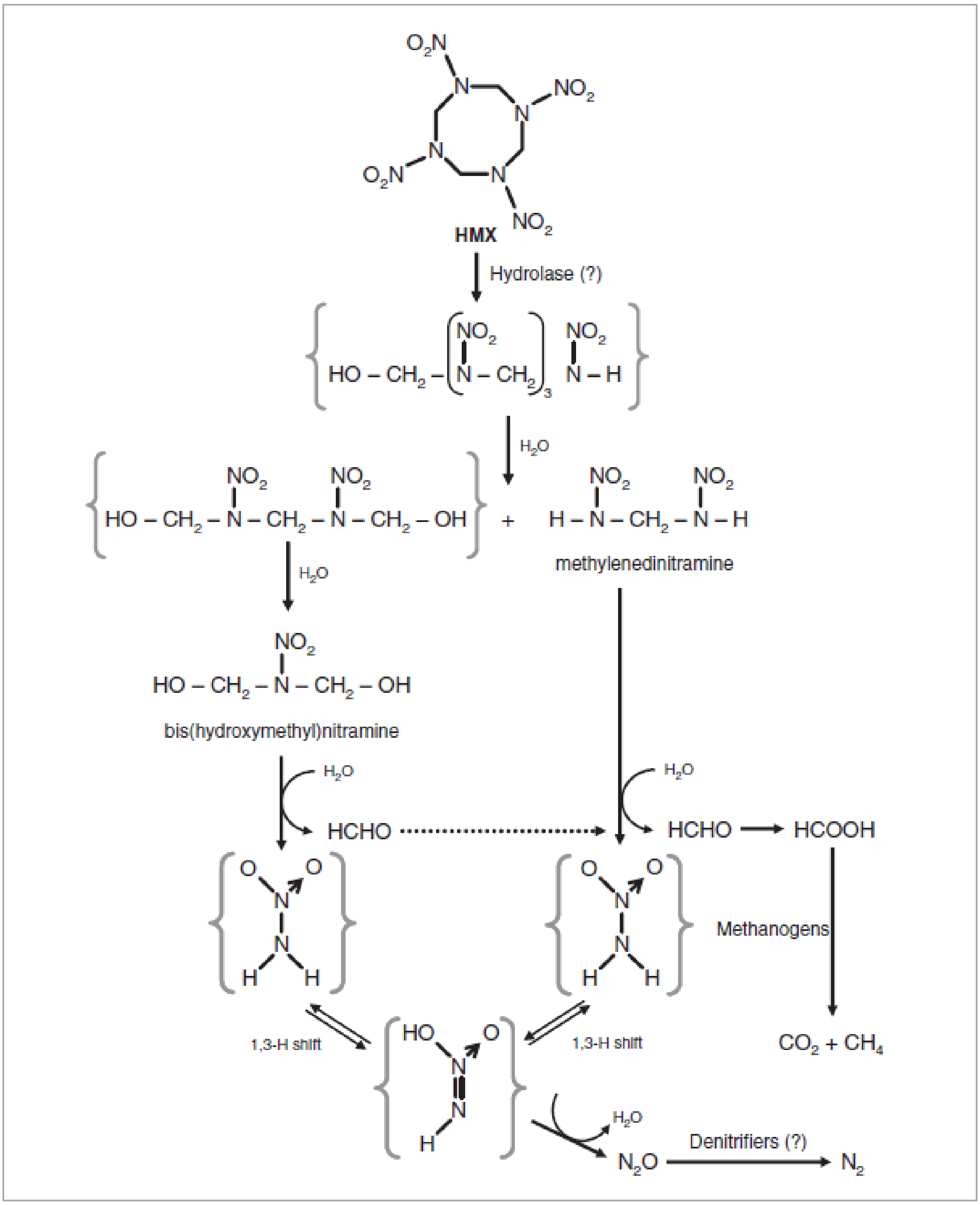

Figure 9. HMX ring cleavage pathway (proposed by Hawari et al. (2000a) according to Juhasz and Naidu 2007).

APPENDIX 5: ANALYZED SAMPLES DURING WATER TREATMENT EXPERIMETS

Table 12. Samples taken during water treatment experiments.

Water quality parameters	Samples analysed	
	SGS	**FDRA**
Analysis of the water quality parameters from the water used in sample preparation (alkalinized groundwater from water supply network)	x2	
Explosives and related compounds		
UV degradation experiment		
TNT and RDX initial concentration in prepared sample	x2	x1
UV test 1 (4,6 m^3/h flow rate, UV dose 550 J/m^2)	x2	x1
UV test 2 (6,2 m^3/h flow rate, UV dose 407 J/m^2)	x2	x1
Reverse osmosis treatment		
TNT and RDX initial concentration in prepared sample	x3	x1
Sample after prefiltration	x2	x1
Sample after prefiltration + reverse osmosis	x2	x1
Reject water	x2	x1
Follow-up, abiotic degradation		
1 week in dark	x2	x1
1 week in light	x2	x1
2 weeks in dark	x2	
2 weeks in light	x2	