

**CHAPTER: 1**  
**General Introduction**

## 1.1 Introduction

Most explosive materials are toxic and due to this toxicity to biological systems, present health hazards to those who handle or are exposed to them. In the environmental field, disposal of explosives and their degradation products poses serious and potentially dangerous contamination issues. Large portion of land and groundwater have been polluted through the manufacture, detonation and disposal of explosives. Explosives are xenobiotic compounds and their recalcitrance leads to persistence in the environment. Environmental contamination by explosives occurs through several sources including wetlands and washout lagoons that had received red water, which comes strictly from the 2,4,6-Trinitrotoluene (TNT) manufacturing plants and pink water, stemming from munitions load, assemble and pack (LAP) operations, explosives research and development activities [1] and as well as from explosives use areas such as training ranges [2-6]. Explosives fall into several categories; however, the foci of this work are nitramine explosives including Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and nitroaromatic explosives including 2,4,6-Trinitrotoluene (TNT), Tetryl and metabolites of TNT. The three main explosives discussed *i.e.*, RDX, HMX and TNT have all been shown to possess significant and deleterious effects on human and environment. These compounds are typical recalcitrant constituents in soil at explosives contaminated sites and are the major contamination constituents found in aqueous streams emerging from explosives manufacturing plants. TNT and RDX are the persistent contaminants that are regulated in discharges from army ammunition plants. Under ambient environmental conditions, most explosives exhibit resistance to natural attenuation processes including volatilization, biodegradation and hydrolysis resulting in persistence in soil and

groundwater. An increased public awareness about the toxicity and risks associated with these compounds has stimulated research activities on the development of remediation technologies for cleaning up explosives contaminated water and soil. A sizeable amount of research has been conducted to determine how best to characterize the level of explosive contamination present in exposed environment and the most desirable method of remediation. The development of explosive molecules has been sought to provide both greater power and greater control and mass production of some of these compounds over the last century has led to extensive contamination of environment, which now requires remediation.

## **1.2 Explosives**

Explosives are the chemical compounds or mixtures, which will on application of an external stimulus such as heat, shock, friction or ignition, undergo rapid chemical decomposition. The chemical reaction results in sudden release of large amount of energy due to liberation of gases and temperature. The pressure thus released is thrust out equally in all directions. Explosives are of immense importance in many peaceful pursuits *e.g.*, in mining, quarrying and pyrotechnics, *etc.* Beside these applications, explosives are also used to project lifelines to ships in distress off storm beaten shores or to break roof of burning buildings to save many precious lives [Table 1.1]. However, the major use of explosives is in warfare. Explosives generally have high nitrogen and oxygen contents which aid the formation of the gaseous products, typically including carbon dioxide, carbon monoxide, oxygen, nitrogen and water vapor. All explosive mixtures can be considered to be composed of three components namely fuel, oxidizer and sensitizer. Carbon, hydrogen and sulphur, *etc.* provide the essential fuel for the oxygen in the oxidizer. Incorporation of a chemical or physical sensitizer enhances the

**Table 1.1: Applications of explosives**

Sr. No.	Area of Application	Uses
1	Aerospace	(a) Ejector seat (b) Separation devices for rocket stages
2	Agriculture	(a) Removing trees and stumps (b) Eradicating rabbit warrens (c) Desilting and defoliating dams and drains
3	Art	(a) Metal clad art (b) Mountain carving
4	Avalanche control	(a) Snow blast
5	Coal blasting	(a) Blasting in coal mines
6	Construction and demolition work	(a) Breaking concrete and rock (b) Roadwork and construction (c) Demolition of building, towers, bridges and chimneys.
7	Excavation	(a) Foundations (b) Underwater channels /dredging
8	Fire fighting	(a) Along fire path to cut off oxygen to a large fire
9	Forestry	(a) Trail blazing
10	Law enforcement and security	(a) Exploding dye capsule (b) Security systems
11	Logging	(a) For cutting and removing timber (b) For cutting drums and buckets
12	Manufacturing	(a) Man made diamonds
13	Medical uses	(a) Medicines (b) Fracturing kidney and gall stone
14	Metal working	(a) Hardening and shaping of steels (b) Metal cladding (c) Welding pipelines
15	Mining and quarrying	(a) Explosives are used to break up rocks and displace large quantity of earth. (b) Hardening and removing rail track parts (c) Oil well perforation (d) Blowing ditches and trenches
16	Pyrotechnics	(a) Fireworks and signal lights (b) Theatrical special effects
17	Seismic exploration	-----
18	Sports	(a) Rifle shooting

ease with which the explosives can be made to react by means of an initiator. The term detonation is used to describe an explosive phenomenon whereby the decomposition is

propagated by the explosive shockwave traversing the explosive material. The shockwave front is capable of passing through the explosive material at great speeds, typically thousands of meters per second. Explosives usually have less potential energy than petroleum fuels, but their high rate of energy release produces great blast pressure. TNT has detonation velocity of 6940 m/s compared to 1680 m/s for the detonation of a pentane-air mixture and 0.34 m/s stoichiometric flame speed of gasoline combustion in air. Explosive force is released in a direction perpendicular to the surface of the explosive. If the surface is cut or shaped, the explosive forces can be focused to produce a greater local effect; this is known as a sharpen charge.

### **1.3 History and Development of Explosives**

Black powder, the first chemical explosive, was invented in China some 1,000 years ago. It is a mixture of saltpeter (potassium nitrate), sulfur and charcoal, and originally was used exclusively for military purposes. Black powder was not used industrially until the 17<sup>th</sup> century, when it was adapted to blast out mines in Europe. To be detonated, black powder must be ignited by flame or intense heat. The original fuse systems were thin trailing lines of the powder itself or crude wicks made of straw or other combustible materials combined with sprinklings of the powder. Nitroglycerin and dynamite succeeded black powder as the chief explosives. An Italian chemist Ascanio Sobrero discovered nitroglycerin in 1846. The Swedish scientist Alfred Nobel invented dynamite in 1867, the original explosive being a mixture of 75 percent nitroglycerin and 25 percent ghour (a porous absorbent material that made the product easier to control and safer to use). Nobel developed gelatinous dynamite in 1875 by creating a jelly from the dissolution of a colloidion-type nitrocotton in nitroglycerin, producing a more powerful explosive than the straight dynamites and one that proved to be safer. It was not until

1867; however, when Ohlsson and Norrbin discovered that the addition of ammonium nitrate (AN) to dynamite increased its explosive potential. Ammonium nitrate was discovered centuries ago by Glauber but was not reported to have explosive properties until 1849 by Reise and Millon. Later, ammonium nitrate was used in dynamite, which made it even safer to use and less expensive to produce.

Two important developments in the history of explosives were the inventions of the safety fuse and the blasting cap (1831). In 1865, Nobel invented the blasting cap, providing the first safe and dependable means for detonating nitroglycerin and thereby considerably expanding its use for industrial purposes. Electrical firing, first used successfully in the late 19<sup>th</sup> century, allows greater control over timing. The development of shells for warfare required a less sensitive explosive than nitroglycerine which had a tendency to detonate on firing. 2,4,6-Trinitrophenol (Picric acid), a nitroaromatic compound characterized by NO<sub>2</sub> groups attached to an aromatic ring, had been discovered by Glauber in 1742. It was used as a dye until 1871 and Turpin in 1885 stated that picric acid was a good replacement for black powder and in 1894; Panpushko discovered its true explosive potential. Although being more stable than nitroglycerin, the drawback of picric acid was that it got reacted with the metals used in the shell casings. The resulting picrates made the shells susceptible to undesired detonation by shock or friction. 2,4,6-Trinitrotoluene (TNT) is another example of nitroaromatic explosive, first synthesized by Joseph Wilbrand in 1863, although its explosive properties were not discovered until 1891. By 1902, the Germans were using TNT instead of picric acid in shells and it had become commonly used in Britain by 1916. The advantages of TNT over the structurally similar picric acid included its lower shock sensitivity and lower acidity, although it can require the use of stronger detonators.

TNT has the dubious honor of being the most used military explosive of the twentieth century. Relative powers of explosives can be calculated using a power index in which explosives are compared to picric acid, which has a power index of 100. Power indices of nitroglycerin (GTN) and TNT are 159 and 117, respectively [7]. Tetryl was developed in 1877 by Mertens and was briefly used in blasting caps during the early 1900's. A second nitrate ester explosive, pentaerythritol tetranitrate (PETN) was developed in Germany in 1894 and came into use during World War II. This very powerful explosive (power index of 161 [7]) proved to be too sensitive and too easily detonated to be used alone. The first nitramine explosive (characterized by N-NO<sub>2</sub> groups) to be developed was hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), synthesized by Hans Hemming in 1899. In 1920, it was patented as an explosive and its further development at the War Department in Woolwich, U.K. led to its naming as *Royal Demolition Explosive* or RDX. It is as powerful as PETN and GTN (power index of 159 [7]), but much less sensitive. It is commonly used in explosive mixtures including cyclotol and composition C-4, etc. RDX is currently the most widely used military explosive. Synthesis of a second and even more stable nitramine explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (*High Melting Explosive* or HMX) followed in 1930. HMX has been in military use since the 1950's and has a power index of 160 [7]. A new generation of nitramine explosive, 2,4,6,8,10,12-hexanitrohexazaisowurtzitane (CL20 or HNIW) has since been developed and has recently undergone initial testing, where it was found to be even more powerful than HMX (power index unavailable). Other chemical explosives have been developed over the past 200 years although their commercial uses have been on a considerably smaller scale. Among them are chlorates and perchlorates, Sprengel explosives, liquid oxygen explosives (known as LOX) and those made from nitro starch. Later explosives

have included ammonium nitrate-fuel oil mixtures (ANFO) and water gels. A vast number of explosives consisting of mixtures of various explosive compounds and were developed by combatants in World War II. Many of these combinations include materials such as HMX, RDX, TNT, Aluminum powder, wax, and plasticizers with or without other ingredients [8] for special properties. A few worth mentioning are

- (i) Composition B: (60% RDX, 40% TNT plus wax)
- (ii) Cyclotol: (60-75 % RDX, 25-40% TNT)
- (iii) Torpex: (42% RDX, 40% TNT, 18% Al)
- (iv) Composition C4: (91% RDX, 9% plasticizers)
- (v) Picratol: (TNT + ammonium picrate)
- (vi) Tritonal: (TNT + aluminium powder)
- (vii) Amatol: (TNT + AN)
- (viii) MOX: (RDX + TNT + Al +  $\text{Ba}(\text{NO}_3)_2$  + Calcium stearate + graphite + wax)
- (ix) Pentolite: (PETN + TNT)
- (x) Semtex H: (RDX + PETN + Poly butadiene styrene + oil)
- (xi) PTX 1: (RDX + TNT + Tetryl)
- (xii) PTX 2: (RDX + TNT + PETN)

The desire for more powerful yet stable explosives has driven extensive research over the last century. The majority of explosives currently in use are nitramines and out of these RDX is the most important explosive used worldwide.

#### **1.4 Classification of Explosives**

Explosives can be classified in many ways according to different criteria. Chemical explosives are the most commonly used. A chemical explosive can be gaseous, liquid or solid although the later two are generally capable of producing more powerful explosions. There are also mechanical and nuclear explosives. A mechanical explosive is one in which a physical reaction is produced like that caused by overloading a container



with compressed air. Nuclear explosives, which produce a sustained nuclear reaction, are by far the most powerful but their use has been restricted to limited military weapons.

#### **1.4.1 Based upon velocity**

Based upon type and velocity of explosion involved, explosives have been divided into low and high explosives. No sharp distinction exists between low and high explosives because of the difficulties inherent in precisely observing and measuring rapid decomposition. The difference between two types is also related to their use *viz.*, high explosives as detonating charges versus low explosives as propellants.

##### ***1.4.1.1 Low explosives***

A low explosive is a combustible substance that decomposes rapidly (deflagration) and does not explode under normal condition but get detonate through combine use with high explosives. Low explosives are normally employed as propellants. They undergo deflagration at rates that vary from few cm/s to approximately 400 m/s. Included in this group are pyrotechnics and smokeless powder. The low explosives or propellants are combustible materials, containing within themselves all oxygen needed for their combustion, which burn but do not explode and function by producing gases which produce an explosion. In a low explosive, the decomposition is propagated by a flame front which travels much slower through the explosive material. In sufficiently massive quantities, almost all low explosives can undergo true detonation as high explosives.

##### ***1.4.1.2 High explosives***

High explosives are detonating explosives. The chemical reaction propagates with such rapidity that the rate of reaction zone into the material exceeds velocity of sound. High explosives are normally employed in mining, demolition and military warheads. They undergo detonation at rates of 1,000 to 9,000 m/s. High explosives are conventionally

subdivided into two classes namely primary explosives and secondary explosives, differentiated by sensitivity. Both explosives can be categorized based on following parameters [Table 1.2].

#### **1.4.2 Based upon sensitivity**

Based upon sensitivity of the chemical explosives to the external environment like heat, shock and friction, these can be categorized as follows

##### ***1.4.2.1 Primary explosives***

They are extremely sensitive to shock, friction and heat. They will burn rapidly or detonated, if ignited. Primary (or initiating) explosives are used to start the explosion. Primary explosives explode or detonate when they are heated or subjected to shock. Examples include mercury fulminate, lead azide, lead salts of picric acid and trinitroresorcinol. Primary explosives are often used to detonate a secondary explosive because their detonation is rapid and powerful enough to produce a shock wave that can detonate another explosive. Their explosive power is generally less than that of secondary explosives; however, due to their sensitivity and ability to be ignited by a simple flame or spark, they are used in small quantities. Primary explosives are often found in detonators and blasting caps and can be initiated with a firing pin or from the shock produced by an exploding bridge wire.

##### ***1.4.2.2 Secondary explosives***

These are also called base explosives and are relatively insensitive to shock, friction and heat. Secondary explosives are the main charge. They burn when ignited in small unconfined quantities but detonation can occur. Detonation is the process by which the energetic material decomposes due to a shockwave rather than via a thermal reaction. Secondary explosives detonate under influence of the shock of explosion of a suitable

primary explosive. They do not function by burning. They differ from primary explosives in not being exploded readily by heat or by shock, and generally in being more brisant and powerful. Dynamite, RDX, HMX, PETN, TNT are few examples of secondary explosives. PETN is often considered as benchmark explosive with materials that are more sensitive than PETN are being classified as primary explosives.

Thus in brief, secondary explosives require a separate detonator. The main function of Primary explosives is to initiate a secondary explosive by shock wave. Initiators are mainly used in military detonators, industrial blasting caps and stab, and shock primers. Secondary explosives are generally used as the main charge. Explosives also have been classified according to their chemical structure. The most important class includes organic compounds, which contain the nitro ( $\text{NO}_2$ ) group. They are sub divided according to the atom to which the  $\text{NO}_2$  group is attached. Nitro compounds contain a C- $\text{NO}_2$  group, nitrate esters a C-O- $\text{NO}_2$  group and nitramines C-N- $\text{NO}_2$  group.

Another definition add a third category *i.e.*, tertiary explosives or blasting agents which are so insensitive to shock that they can not be reliably detonated by practical quantities of primary explosives and instead require an intermediate explosive booster of secondary explosives. Examples included ammonium nitrate/fuel oil mixture (AFNO) and slurry of “wet bag” explosives. These are primarily used in large scale mining and construction operations.

### **1.4.3 Based upon priming composition**

Priming compositions are primary explosives mixed with other compositions to control (lessen) the sensitivity of the mixture to the desired value. For example, primary explosives are so sensitive that they need to be stored and shipped in a wet state to prevent accidental initiation.

#### **1.4.4 Based upon physical form**

Explosives are often characterized by the physical form that the explosives are produced or used in. These use forms are commonly categorized as

- Pressings
- Castings
- Plastic or polymer bonded
- Putties (AKA plastic explosives)
- Rubberized
- Extrudable
- Binary
- Blasting agents
- Slurries and gels
- Dynamites

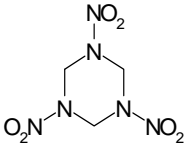
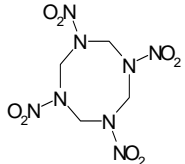
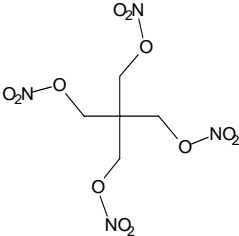
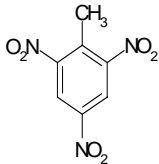
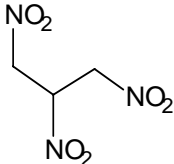
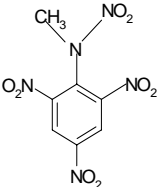
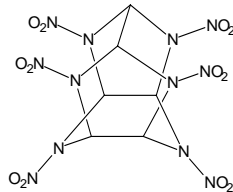
#### **1.4.5 Based upon applications**

Another classification *viz.*, military versus industrial explosives is based on the application for which an explosive is designed. These two classes are distinguished by the law enforcement agencies from a third one, which includes home made (improvised) explosives. Improvised explosive devices (IEDs) which have become popular among terrorists and amateur chemists can employ numerous combinations of high and low explosives.

**Table 1.2: Explosion characteristics of high and low explosives**

<b>Sr. No.</b>	<b>Parameter</b>	<b>High Explosives</b>	<b>Low Explosives</b>
1.	Method of initiation	Primary explosives by ignition and secondary explosives by detonation	By ignition
2.	Time of complete conversion of explosive to gaseous products	Micro seconds	Milli seconds
3.	Velocity of consumption of explosives grains	1.5 to 10 km/s	Few cm to m/s
4.	Velocity of flame front	1.5 to 10 km/s	0.5 to 1.5 km/s
5.	Pressure of explosion	350 to 27,600 kpa	Upto 350 kpa
6.	Exploded in gun	Shatters gun	Good propellant
7.	Demolition	Excellent to poor	Nil
8.	Uses	Demolition, blasting	Propellant, blasting
9.	Velocity of detonation (VOD)	More than 1,000 m/s	Less than 1,000 m/s

Table 1.3: Important characteristics of Nitroexplosives

Explosive	RDX	HMX	PETN	TNT	Nitro-glycerin	TETRYL	CL-20
<b>Common Name</b>	Cyclonite, hexogen	Octogen	Penthrite, nitropenta	Trotyl	Glyceryl trinitrate	Tetralite	Hexanitroisowurtzitane
<b>IUPAC Name</b>	1,3,5-Trinitroperhydro-1,3,5-triazine	1,3,5,7-Tetra nitroperhydro-1,3,5,7-tetraazocine	2,2-Bis(nitroxy methyl)-1,3-propane diol-1,3-dinitrate	2,4,6-Tri nitrotoluene	1,3-Dinitrooxypropan-2-yl nitrate	2,4,6-Trinitrophenyl-N-methyl-nitramine	Octahydro-1,3,4,7,8,10-hexanitro-5,2,6-(iminomethenimin o)-1H-imidazo [4,5-b]pyrazine
<b>Chemical structure</b>							
<b>Chemical formula</b>	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_5H_8N_4O_{12}$	$C_7H_5N_3O_6$	$C_3H_5N_3O_9$	$C_7H_5N_5O_8$	$C_6H_6N_{12}O_{12}$
<b>CAS No.</b>	121-82-4	2691-41-0	78-11-5	118-96-7	55-63-0	479-45-8	14913-74-7
<b>Molecular mass (g/mol)</b>	222.117	296.20	317.15	227.131	227.08	287.15	438.19
<b>Shock sensitivity</b>	Low	Low	Very high	Insensitive	Very high	Insensitive	---
<b>Friction sensitivity</b>	Low	Low	Very high	Insensitive	Very high	Insensitive	---

<b>Density (g/cm<sup>3</sup>)</b>	1.82	1.91	1.773	1.654	1.13	1.73	2.04
<b>Explosive velocity (m/s)</b>	8,750	9100	8400	6900	7700	7570	10300
<b>RE Factor</b>	1.60	1.70	1.66	1.00	1.50	1.25	---
<b>Melting point (°C)</b>	205.5	276 to 286	141.3	81	13.2	129.5	273
<b>Ignition temp. (°C)</b>	229	335	145	300	---	---	---
<b>Decomposition temp. (°C)</b>	170	280	190	295	50 to 60	---	---
<b>Appearance</b>	Colorless solid crystals	Colorless solid crystals	Odorless white crystalline solid	Pale yellow crystals	Clear yellow/colorless oily liquid	Odorless yellow crystalline solid	Odorless monoclinic crystals
<b>Oxygen balance</b>	21.6%	26.1%	10.1%	73.9%	13.5%	47.4%	---
<b>Nitrogen content</b>	37.84%	37.83%	17.72%	18.5%	18.5%	24.39%	---
<b>Volume of detonating gas (l/Kg)</b>	900	927	823	730	780	800	---
<b>Heat of combustion (Kcal/Kg)</b>	2285	2255	---	3590	---	---	---

<b>Heat of explosion/detonation (Kcal/Kg)</b>	---	1355	1421	1011	---	---	---
<b>Vapor pressure</b>	$4.6 \times 10^{-9}$ Torr at 25°C	---	$8.38 \times 10^{-4}$ Torr at 97°C	$5.8 \times 10^{-6}$ Torr at 25°C	$2.3 \times 10^{-4}$ Torr at 20°C	---	---
<b>Solubility</b>	Soluble in acetone and insoluble in water and sparingly soluble in alcohol, ether and benzene	Insoluble in water	Soluble in acetone and methyl acetate, sparingly soluble in alcohol, ether & benzene insoluble in water	Soluble in benzene and acetone sparingly soluble in alcohol, insoluble in water	Insoluble in water but soluble in other organic solvent	Slightly soluble in water and other solvents	---



## 1.5 Explosives as Environmental Pollutants

Indiscriminant use of explosives during warfare, land mining of sensitive zones, discharge from explosive manufacturing plants, storage depots, dumping sites and mock military exercises on sea and land surfaces has resulted into contamination of environment on large scale which can ultimately bring adverse changes in eco-biological balance. Explosives are the important contaminants which are carcinogenic and their accumulation in food chain has caused great problem for human survival. Explosives are highly recalcitrant compounds, resistant to degradation *in situ*, meaning that the contamination persists. Explosives of concern as environmental pollutants have been listed as TNT, RDX and HMX. Of these, RDX and TNT are found at higher concentrations in contaminated soil and groundwater than HMX [9, 10]. Several soil studies have therefore concentrated on RDX and TNT as the major pollutants [11-13]. TNT manufacturing involves stepwise nitration of toluene producing mono-, di-, and finally trinitrotoluene, respectively. The undesired isomers plus residual dinitrated species are removed from the reaction mixture by treatment with aqueous sodium sulfite solution, which reacts with everything except the desired 2,4,6-isomer. These impurities are made water soluble in the selling operation producing a waste stream commonly referred to as "**red water**". The "red water" is a complex mixture of nitroaromatics and various inorganic salts. The remaining TNT is washed and considerable amount of water is used to purify TNT, to clean equipment and interior of the finishing plant buildings. Wastewater from the TNT finishing process is called "**pink water**". "Pink water" is a saturated TNT solution (up to 150 ppm TNT), which turns pink in sunlight due to photolysis of dissolved TNT to form complex dye-like molecules [14,15]. It is estimated that a single manufacturing plant can generate as much as 2000 m<sup>3</sup> of wastewater per day

containing TNT as well as other nitro compounds [16]. Therefore, major route of entry of munition compounds into surface water and environment is through discharge of waste streams generated during their manufacturing and processing. The levels of their compounds in such wastewaters vary widely depending on the intensity of the manufacturing operations and efficacy of the treatment technologies employed. Similarly, explosives in huge amount are buried in soil as landmines over large areas. The vapors of signature compounds escaping from the mines are quickly adsorbed onto nearby soil particles or get dissolved in soil water.

Chemical compounds such as TNT and RDX are resistant to aerobic attack because the nitro compounds act as electron-withdrawing substituents. Under ambient environmental conditions, explosives are highly persistent in soils and groundwater, exhibiting a resistance to naturally occurring volatilization, bio-degradation and hydrolysis. The contamination problem worsens with the effect of leaching, as the water beneath the soil (groundwater) becomes polluted, which can lead to the spreading of the explosives. The degree to which the explosive remains in the soil or is mobilized and taken through to groundwater depends on its solubility and the degree to which it sorbs to the soil. TNT and RDX have low aqueous solubility (maximum 100 mg/L and 38 mg/L, respectively at 20° C [17]), meaning that groundwater is often saturated with the explosives. TNT sorbs to soil quite strongly but RDX binds less tightly [12, 13, 18] {TNT  $K_d$  (dissociation constant) = 6.4 – 12.0 l/kg, RDX  $K_d$  = 0.8 l/kg} [19]. RDX contamination is therefore less easily contained than TNT and RDX has been observed to move further than TNT in groundwater [18, 20]. RDX is now of primary concern due to its ability to migrate quickly through the soil matrix. Site investigations indicate that TNT is the least mobile and RDX and HMX are the most mobile explosives and present the large environment

contamination problem. Trinitrobenzene, dinitrotoluenes and Tetryl are of intermediate mobility and frequently occur as co-contaminants in soil and groundwater. Metals are co-contaminants at facilities where munitions compounds were handled, particularly at OB/OD sites. Where biodegradation of TNT occurs, 2-Amino-4,6-dinitotoluene and 4-Amino-2,6-dinitrotoluene are the most commonly identified transformation products. Photochemical decomposition of TNT to TNB occurs in the presence of sunlight and water with TNB being generally resistant to further photodegradation. TNB is subject to biotransformation to 3,5-dinitroaniline, which has been recommended as an additional target analyte in EPA Method 8330.

The degree of pollution of soil and groundwater demonstrated here is a serious environmental problem which needs to be addressed. The two major targets for remediation are RDX and TNT and both of which have been manufactured in enormous quantities over the last century. They are commonly found co-contaminating at munitions sites and are both toxic to mammals and aquatic organisms. The toxicity of these compounds means not only that these sites cannot be used for alternate purposes until they have been cleaned up, but also that remediation is necessary to control the movement of these compounds in soil and groundwater with RDX being the more urgent problem in this respect. Remediation is urgently required for these contaminated sites.

## **1.6 Environmental Fate and Toxicity of Explosives**

Modern explosives have been used extensively over the last century and becoming known as serious environmental pollutants in the past few decades. Most explosive compounds contain chemical groups such as the nitramine group, which were not previously found in nature. Environmental micro floras do not possess enzymes which could degrade or transform them. Therefore, in addition to their destructive capacity,

explosives commonly have toxic effects on biological systems. Micro organisms are able to degrade a wide range of compounds including xenobiotics which have been introduced into the environment relatively recently [21]. Microbial degradation has been found to be a major source of formation of degradation products from explosives.

Degradation of explosive residues in soil is a very complex phenomenon, occurring through combined natural biological and abiotic processes [22]. Transportation and contamination is due to the fact that explosives such as TNT, DNT and RDX are labile and in the environment can be transformed by sunlight, type of soil, temperature and soil moisture content, *etc.* Therefore, environmental fate of explosives can be attributed to three chemical properties:

- (a) Molecular structure
- (b) Water solubility
- (c) Adsorption to soil particles

For instance, nitroaromatics like TNT tends to degrade by photolysis while nitramines like RDX and HMX do not. TNT can be degraded into 21 metabolites with various solubilities and toxicities. For example, aminodinitrotoluenes that result from the photolysis or biodegradation of TNT are much more soluble than the parent compound but can be covalently bind to humic acid. Therefore, these metabolites are stabilized by the formation of an amide with the organic contents of the soil. Moreover, in soils that contain clays, sorption mechanisms are stronger with TNT and its metabolites than for RDX and HMX which adsorb very poorly to clay minerals. Therefore, the relative rates of soil leaching of these three explosives can be explained in terms of the relative water solubility and adsorption strengths. RDX leaches out faster than TNT, which in turn leaches out faster than HMX. TNT and its metabolites are more water soluble than RDX

but their migration is inhibited by strong bonding interactions with soil constituents. On the other hand, HMX has a tendency to remain at the surface of the soils because it is almost insoluble in water. Interactions with the soil are an important factor when characterizing explosives in terms of bioavailability and extractability. The characterization of RDX, HMX and TNT derivatives is important in establishing their overall toxicity, remediation, transport and extractability.

**Table 1.4: Some important physical parameters of nitroexplosives**

Component	$\lambda_{\max}$ (nm)	Henry's Law Constant (atm-m <sup>3</sup> /mol)	Log K <sub>ow</sub>	K <sub>oc</sub>	Vapor Pressure (mm Hg) @ 25°C	Aqueous Solubility
TNT	250	$2.1 \times 10^{-8}$	1.6	1100-1900	$8.02 \times 10^{-6}$	130 mg/L @ 20°C
Tetryl	--	$2.7 \times 10^{-9}$	2.0	406	$1.2 \times 10^{-7}$	75 mg/L @ 20°C
RDX	230	$2.0 \times 10^{-11}$	0.87	42 - 167	$4.10 \times 10^{-9}$	59.8 mg/L @ 25°C
HMX	230	$8.7 \times 10^{-10}$	0.59	30 - 290	$2.41 \times 10^{-8}$	2.6 – 5.0 mg/L
TNB	--	$6.5 \times 10^{-9}$	1.18	104	$6.44 \times 10^{-6}$	330 mg/L
DNB	238	$4.9 \times 10^{-8}$	1.49	150	$2 \times 10^{-4}$	180 mg/L
NB	265	$2.4 \times 10^{-5}$	1.84	130.6- 370	$2.45 \times 10^{-1}$	---
2,4-DNT	245	$1.3 \times 10^{-7}$	1.98	260 - 360	$1.47 \times 10^{-4}$	270 – 273 mg/L
2,6-DNT	238	$9.26 \times 10^{-8}$	1.9- 2.10	19-72	$5.67 \times 10^{-4}$	910 mg/L
2-NT	267	$1.25 \times 10^{-5}$	2.30	420	$1.88 \times 10^{-1}$	650 mg/L @ 30° C
3-NT	275	$9.30 \times 10^{-6}$	2.45	510	$2.05 \times 10^{-1}$	500 mg/L @ 30° C
4-NT	283	$5.63 \times 10^{-6}$	2.37	460	$1.64 \times 10^{-1}$	442 mg/L @ 30° C

### 1.6.1 Environmental fate and toxicity of RDX (Cyclotrimethylenetrinitramine)

Cyclotrimethylenetrinitramine (commonly known as RDX) is a non aromatic cyclic nitramine and is white crystalline powder. It is obtained by reacting concentrated nitric acid with hexamine. It has high chemical stability and explosive power than TNT [23,

24]. RDX was widely used during World War II, often in explosive mixtures with TNT such as Torpex. RDX is believed to be used in IEDs by the terrorists.

#### ***1.6.1.1 Fate and transport***

In soil, RDX is expected to have high to moderate mobility based upon  $K_{oc}$  range of 42-167 [25]. RDX will biodegrade under anaerobic conditions in soil with complete degradation [26] but show resistance to biodegradation under aerobic conditions [27]. Anaerobic degradation under proper conditions in aquatic sources may occur [25, 26, 28, 29]. RDX bioaccumulation from soils by plants causes food-chain contamination [30, 31]. Anaerobic biodegradation of RDX yields hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX) and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) as major degradation products [26, 32, 33].

#### ***1.6.1.2 Toxicity***

RDX poisoning manifests itself in hyperirritability, seizures, mental confusion and amnesia [34]. RDX is also a possible Class C carcinogen [35, 36]. Workers in RDX factories suffer from convulsions, unconsciousness, vertigo and vomiting after inhalation of RDX powder [37, 38]. Death in the rats was associated with congestion in the gastrointestinal tract and lungs [39, 40]. RDX has been used as a rat poison [41-43]. According to federal drinking water guidelines, maximum permissible limit is 2  $\mu\text{g/L}$ .

#### **1.6.2 Environmental fate and toxicity of HMX (Cyclotetramethylenetetranitramine)**

HMX is used in military application as booster charges for artillery shells and component of solid fuel rocket propellants. HMX has a higher ignition temperature and is more chemically stable than RDX [24]. HMX exists as  $\alpha$  (orthorhombic),  $\beta$  (monoclinic),  $\gamma$  (monoclinic) and  $\delta$  (hexagonal) forms, of which ' $\beta$ ' form is the least sensitive to impact and the most stable. It is therefore the form required for military use.

### ***1.6.2.1 Fate and transport***

In soil, HMX is expected to have very high to moderate mobility based upon  $K_{oc}$  values ranging from 30-290 [44]. Volatilization from moist soil surfaces is not an important fate process [45] based upon Henry's Law constant value [Table 1.4]. HMX is not expected to degrade aerobically in soil [46]; however, anaerobic biodegradation of HMX is expected with very low tendency to accumulate in aquatic life [47-50]. Anaerobic degradation pathway for HMX yield mono-, di-, tri-, and tetranitroso intermediates [51].

### ***1.6.2.2 Toxicity***

Toxic effects of HMX have been seen using rats, aquatic organisms, bacteria and the earthworm reproduction test [52-54]. Skin contact or inhalation appears to be harmful to workers [55]. HMX is considered Class D (not classifiable as to human carcinogenic). According to Federal drinking water guideline, maximum permissible limit is 400  $\mu\text{g/L}$ .

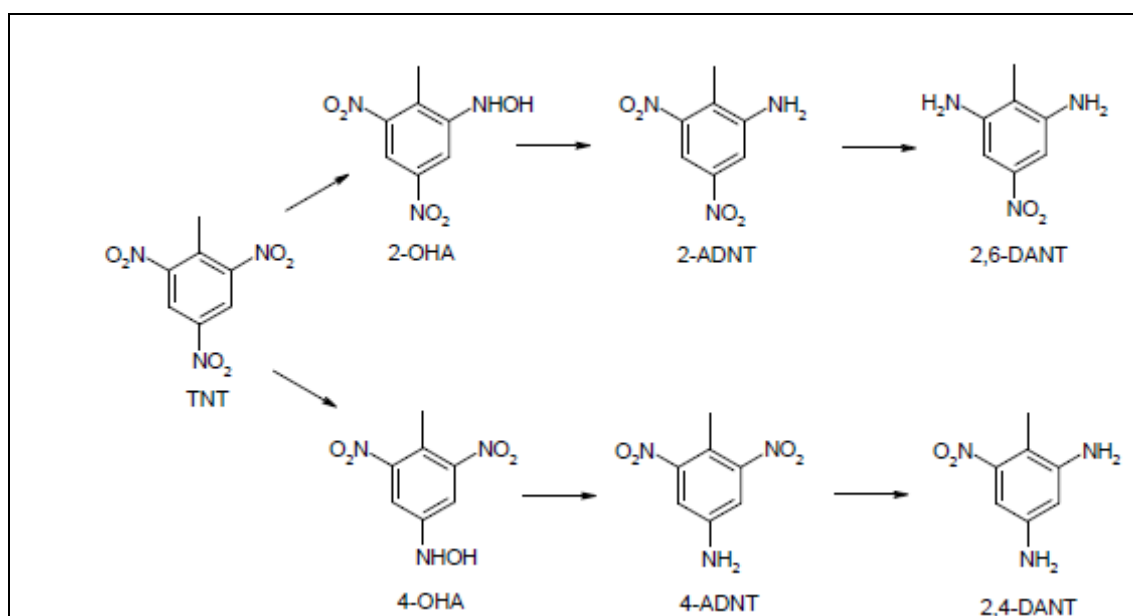
## **1.6.3 Environmental fate and toxicity of TNT (2,4,6-Trinitrotoluene)**

2,4,6-TNT is a non hygroscopic pale yellow solid and is relatively insensitive to impact, shock, friction and electrostatic energy. The synthesis process favors the production of 2,4,6-TNT but other unsymmetrical isomers can be formed in smaller quantities. Because 2,4,6-TNT melts at 82°C and does not explode below 240°C, it can be melted in steam heated vessels and poured into casings. For these reasons, it is the most favored chemical explosive extensively used in munitions and demolitions.

### ***1.6.3.1 Fate and transport***

In soil, 2,4,6-Trinitrotoluene is expected to have low mobility based upon an average  $K_{oc}$  value of 1,600 [25]. TNT is readily degraded in soils only under anaerobic conditions [56]. Due to the stability of the aromatic ring and the electron-withdrawing properties of the nitro groups in nitroaromatics, microbial action on TNT generally proceeds via

reduction of the nitro groups, reducing them successively to nitroso, hydroxylamino and amino groups [57]. The amino derivatives in particular are very stable and adsorb very strongly to soil [58], which strongly hinder further breakdown in the environment. In addition, the hydroxylamino and amino derivatives can dimerize to form azo and azoxy dimers, which are resistant to further metabolism [59, 60]. The main degradation products of TNT found in contaminated soils are; 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), 2,4-diamino-6-nitrotoluene (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,6-DANT) [25, 33, 61]. It has been suggested that the reduction of nitro groups to amino groups proceeds through the nitrous and hydroxylamino compounds. Photolysis in surface soils results in transformation to trinitrobenzene and trinitrobenzaldehyde. The extent of soil sorption is significant and positively correlated with both pH and temperature [62]. Soil mobility is thus limited because of strong adsorption to soil particles. Studies suggest that 2,4,6-TNT becomes incorporated into plants as polar metabolites [63, 64].



**Figure 1.1:** Some common degradation of TNT in soil and groundwater [24]



### ***1.6.3.2 Toxicity***

High oral doses of TNT to mammals are associated with tremors, convulsions, lassitude and red-stained urine. Other predominant effects include anemia, testicular degeneration, nephropathy, cataracts and decreased body weight gain [65-67]. Ninety-six workers in the U.K. died from exposure to TNT [68]. TNT is a Group C carcinogen (possible human carcinogen) [69]. The maximum limit by Federal drinking water guideline is 2 µg/L.

### **1.6.4 Environmental fate and toxicity of Tetryl (2,4,6-trinitrophenylmethylnitramine)**

#### ***1.6.4.1 Fate and transport***

Tetryl's low organic carbon partition coefficient ( $K_{oc}$ ) indicates that adsorption to soils is not a significant fate process [70]. Biodegradation and photolysis are the only significant degradation processes of Tetryl [71-73]. Slow hydrolysis has been occurred to Tetryl [74].

#### ***1.6.4.2 Toxicity***

Tetryl exposure results in dermatitis, conjunctivitis, keratitis and iridocyclitis of the eyes and acute irritation of nasal mucus membranes [75]. Chronic exposure results in abdominal pain, vomiting, chronic hepatitis, central nervous system effects and anemia [76].

### **1.6.5 Environmental fate and toxicity of nitrobenzene, 1,3-DNB and 1,3,5-TNB**

#### ***1.6.5.1 Fate and transport***

In soil, nitrobenzene is expected to have very high to moderate mobility [77, 78] while DNB and TNB have high mobility based upon an estimated  $K_{oc}$  values, respectively [79]. The movement of nitrobenzene in soil and water is dominated by its water solubility (1,900 ppm), moderate volatility [80], low octanol-water partition coefficient and soil/sediment sorption coefficient. Nitrobenzene is expected to biodegrade under both

aerobic and anaerobic conditions in both soil and water [81, 82] and harmful for aquatic life [83]. Microbes have been observed to degrade DNB under both aerobic and anaerobic conditions [84].

#### ***1.6.5.2 Toxicity***

Nitrobenzene and DNB exposure causes methemoglobin formation, cyanosis, anemia, ataxia and tachycardia [85, 86]. Exposure to TNB resulted in central nervous system and respiratory disorders. Nitrobenzene and DNB are considered as Group 2B compound (possible carcinogen to humans) by the World Health Organization. The Federal drinking water guideline limit for DNB is 1 µg/L.

### **1.6.6 Environmental fate and toxicity of dinitrotoluene isomers (2,4-DNT, 2,6-DNT)**

#### ***1.6.6.1 Fate and transport***

In soil, 2,4-DNT and 2,6-DNT are expected to have moderate mobility to very high mobility based upon estimated  $K_{oc}$  values [Table 1.4]. Their log octanol-water partition coefficient ( $K_{ow}$ ) of 2.01 and 2.05 respectively is sufficiently large to indicate significant adsorption of DNT isomers by humus. Leaching may occur and therefore, adsorption to soil and sediment may be very minor [87]. In general, nitrotoluenes are resistant to biodegradation by soil microorganisms and low bioaccumulation in aquatic organisms for both isomers [88].

#### ***1.6.6.2 Toxicity***

Due to greater covalent hepatic binding of 2,6-DNT and more carcinogenic potential compared to the 2,4-isomer, suggest that it is the more toxic of the two isomers [89]. DNT isomers are considered possible human carcinogen (Group 2B) and carcinogenic to experimental animals.

### **1.6.7 Environmental fate and toxicity of nitrotoluene isomers (2-NT, 3-NT, 4-NT)**

#### ***1.6.7.1 Fate and transport***

Nitrotoluenes have moderate mobility based upon estimated  $K_{oc}$  values of 420, 510, 460, respectively in soil [79]. Hydrolysis is not expected to be an important environmental fate process since this compound lacks functional groups that hydrolyze under environmental conditions.

#### ***1.6.7.2 Toxicity***

Nitrotoluenes are not classifiable as to their carcinogenicity to humans (Group 3). They are suspected of causing anemia in chronic exposures. Nitrotoluenes target blood cells, central nervous system, gastrointestinal, cardiovascular system and skin [90]. Other effects include irritation, kidney and liver damage.

Thus, all explosives are toxic to varying degrees. Most are classed as potential carcinogens and other toxic effects have been seen in munitions workers and animal studies. The dangers associated with exposure to explosives should not be underestimated.

### **1.7 Terrorism**

The terrorism is a worldwide menace and increasing its grip on the whole world day by day and no country on the globe is unaffected by this giant evil. Hardly a day goes by without any terrorist attack or bomb blasts somewhere in the world. Now a day, deadly explosives are being used in various terrorist activities all around the world. Detection and quantification of explosives in post blast residues and environmental matrices (soil, water) after terrorist attacks is major challenge before civilized human society. So, analysis of explosives in environmental matrices possesses great importance.

**Table 1.5: Recent major terrorist incidents in India**

<b>Date of Incident</b>	<b>Terrorist Incident</b>	<b>Casualties</b>
<b>Oct. 29, 2005</b>	Three bomb blasts in New Delhi	66 Persons killed
<b>March 7, 2006</b>	Three blasts in Varanasi	15 Persons killed
<b>July 11, 2006</b>	Seven local trains in Mumbai	Over 180 killed
<b>Sept. 8, 2006</b>	Malegaon town in Maharashtra	32 Persons killed
<b>Feb. 19, 2007</b>	Samjhauta Express train between India and Pakistan.	66 Persons killed
<b>May 18, 2007</b>	Friday prayers at Makkah Masjid in Hyderabad	11 Persons killed
<b>Aug. 25, 2007</b>	An amusement park and an eatery in Hyderabad	40 Persons killed
<b>May 13, 2008</b>	Seven bombs blasts in Jaipur	Over 60 killed
<b>July 25, 2008</b>	Coordinated small bomb blasts in Bangalore	1 Person killed and 24 injured
<b>July 26, 2008</b>	Sixteen small intensity bomb explosions in Ahmedabad in Gujarat	45 Persons killed and over 150 injured
<b>Sept. 13, 2008</b>	Crowded markets and streets in Delhi	25 Persons died
<b>Oct. 30, 2008</b>	Eleven bomb blasts triggered in quick succession at Guwahati, the capital city of Assam	70 Persons killed and wounding over 300
<b>Nov. 26, 2008</b>	Mumbai Taj hotel and other places	166 Persons killed including foreigners and 244 injured
<b>Feb. 13, 2010</b>	German Bakery (a popular eatery) in Pune	9 Persons killed and 57 injured

*(Reference: The Tribune, Chandigarh, India 15.2.2010, www.tribuneindia.com)*

## **1.8 Methods for Soil Decontamination**

Limited information regarding the remediation of explosive contaminated sites is available to the public. Some data regarding the clean up of contaminated installations can be obtained and following methods currently being used are presented.

### **1.8.1 Incineration**

Incineration is the commonly used method for clean up of explosive contaminated soil. Several sites have already been remediate using this technology [91]. The process

involves removing soil from the site to incinerate it and the contaminating explosives [92]. In practice; however, complete combustion rarely occur, with the result that explosive residues require disposal or further treatment [93]. Even if explosives fully combust, some harmful compounds forms *viz.*, nitrous oxides (NO<sub>x</sub>), carbon monoxide (CO), hydrogen chloride (HCl) and possibly dioxins [92]. In addition to the effects that these compounds may have on health, leading to poor public acceptance, the costs of incineration are very high. Each tonne of soil to be remediated has been estimated to cost \$ 800 (\$ 725 per tonne soil) [94].

### **1.8.2 Composting**

Composting of contaminated soil uses resident soil microbes to degrade the contaminants. Composted soil may be supplemented with organic matter (which reduces the concentration of the contaminant and provides carbon sources for the microbes), have its moisture content controlled and be aerated at intervals [95]. RDX and TNT levels have been found to decrease during composting [96-100]. Very few studies address the identities of metabolites and identified using <sup>14</sup>C-RDX [98] and the reduction of the nitro groups to give nitroso derivatives of RDX *i.e.*, MNX and DNX along with methanol, carbon dioxide and formaldehyde has been observed [93]. TNT tends to undergo transformations rather than mineralization [101]. These products bind to the soil and become unextractable [93] meaning that not all the compounds will be removed, which may be unacceptable for complete remediation. Composting is also an expensive process as it requires the movement of soil to form piles, amendment of the soil and possibly regular aeration; however, at an estimated cost of \$ 300 per tonne of soil [91].

The above two methods currently used for remediation of explosive contaminated sites appear to remove the parent compound but many of the products are uncharacterized and

may be toxic. Both methods require moving the material, either for mixing or for *ex situ* treatment. These greatly increase the costs of the remediation and are expensive methods. Given the large amount of land still requiring remediation and the costs of the existing technologies, new technologies are required for the low cost remediation of explosives.

### **1.8.3 Soil washing**

Soil washing is an important process for the remediation of explosives in soil. Soil washing is the process in which contaminants sorbed onto fine soil particles are separated from bulk soil in an aqueous based system on the basis of particle size. Wash water may be augmented with a basic leaching agents, surfactant, pH adjustment or chelating agent to remove organics and heavy metals. Washing separates the small particles (silt, clay or organic particles) from the large particles (sand, gravel) by breaking adhesive bonds. The separated material could be easily analyzed to check the level of contamination present and efficacy of the system used. The greatest advantage of soil washing is that it reduces the amount of soil needing further cleanup. This reduction lowers the cost of clean up and the cost of disposing of polluted material. Soil washing can remove many types of pollutants. It also works when the soil is much polluted. At the present time, soil washing is used extensively in Europe and has been progressively increasing use everywhere. Hence the technique provides a cost effective and environmentally proactive alternative to stabilization and land filling. Much work has been published on the soil washing with surfactant based aqueous solutions [102-108] and has been proved to be a much effective technique. Surfactants are particularly attractive for such applications as they potentially have low toxicity and favorable biodegradability in the environment than many organic-solvent based systems. Since washing fluid can be regenerated back, this increases the importance of soil washing with surfactants.

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