Chapter 7: 2,4- and 2,6-Dinitrotoluene

A chapter from:

Regulatory Determinations Support Document for Selected Contaminants from the Second Drinking Water Contaminant Candidate List (CCL 2)

EPA Report 815-R-08-012

Executive Summary

2,4- Dinitrotoluene (2,4-DNT) and 2,6-Dinitrotoluene (2,6-DNT), semi-volatile organic compounds (SVOCs), are two of the most common of the six isomers of dinitrotoluene. Dinitrotoluenes are used in the production of polyurethane foams, automobile air bags, dyes, ammunition, and explosives, including trinitrotoluene (TNT). Neither 2,4- nor 2,6-DNT occurs naturally. They are generally produced as individual isomers or as a mixture called technical grade DNT (tg-DNT). Technical grade DNT contains approximately 76 percent 2,4-DNT and 19 percent 2,6-DNT, with the remainder consisting of the other isomers and minor contaminants.

In chronic exposures, oral dietary administration of 2,4-DNT to dogs primarily affected the nervous system, erythrocytes, and biliary tract. A study in dogs found a lowest-observed-adverse-effect level (LOAEL) of 1.5 mg/kg/day and a no-observed-adverse-effect level (NOAEL) of 0.2 mg/kg/day. Observed effects included neurotoxicity, hematologic changes, and effects on bile ducts. EPA established a reference dose (RfD) of 0.002 mg/kg/day for 2,4-DNT based on this study. An uncertainty factor of 100, to account for interspecies and intraspecies variability, was applied to derive the RfD.

The Environmental Protection Agency (EPA) established an RfD of 0.001 mg/kg/day for 2,6-DNT. This RfD was based on neurotoxicity, Heinz body formation, biliary tract hyperplasia, liver and kidney histopathology, and death in beagle dogs that were fed gelatin capsules containing 2,6-DNT daily for up to 13 weeks. The NOAEL for this study was 4 mg/kg/day, and an uncertainty factor of 3,000 (100 for inter- and intra-species variability, 10 for the use of a subchronic study, 3 to account for the limited database) was applied to derive the RfD.

DNT is considered likely to be carcinogenic to humans (it is classified as a B2 carcinogen). This determination is based on significant increases in hepatocellular carcinoma and mammary gland tumors in female rats fed a DNT mixture (98 percent 2,4-DNT with 2 percent 2,6-DNT) in the diet in a two-year study. Concentrations of 5 μ g/L, 0.5 μ g/L, and 0.05 μ g/L are associated with carcinogenic risks of 10^{-4} , 10^{-5} , and 10^{-6} respectively.

2,4-DNT has been shown to cause reproductive effects in rats, mice, and dogs. There are currently no studies on the reproductive or developmental toxicity of 2,6-DNT. A study of tg-DNT administered to rats in corn oil by gavage found significant increases in relative liver and spleen weight in the fetuses of dams administered DNT at levels of 35 mg/kg/day or greater. No teratogenic toxicity was seen in the study rats.

DNT toxicity might be different in children, compared to adults, since it undergoes bioactivation in the liver and by the intestinal microflora. Newborns might be more sensitive to DNT-related methemoglobinemia because an enzyme that protects against increased levels of methemoglobin is inactive for a short duration immediately after birth. However, there are no empirical data on differences in children's responses to 2,4-/2,6-DNT.

No recent quantitative estimates of DNT production or use are available. According to one older estimate, combined 2,4- and 2,6-DNT production amounted to 272,610,000 pounds in 1975. Estimates of industrial releases of 2,4-DNT and 2,6-DNT are available from 1988 to 2003 through the Toxic Release Inventory (TRI). Releases of both chemicals declined in the early

1990s, and then peaked again around 1999-2001. On-site air emissions and surface water releases were generally the most consistently reported types of releases, with surface water releases generally declining over the period on record. In addition, TRI lists mixed DNT isomer releases as a separate category over the same time period. Underground injections made up the bulk of on-site releases during the 1990s, but diminished thereafter. Total releases peaked in 1993 and 1997, and generally diminished in recent years.

The United States Geological Survey (USGS) has collected data on the ambient occurrence of these contaminants. A study of bed sediments from representative watersheds across the country found 2,6-DNT in between 1.6% and 6.9% of samples collected in various land-use settings. In all land-use settings, most detected concentrations of 2,6-DNT were below the reporting limit (RL). Detections of 2,4-DNT in bed sediment were much less frequent. In addition, a USGS review of highway and urban runoff studies shows no detects of either 2,4- or 2,6-DNT.

To determine the extent of 2,4- and 2,6-DNT contamination in drinking water, EPA included these contaminants as analytes in the First Unregulated Contaminant Monitoring Regulation (UCMR 1). Because the health reference level (HRL) for both 2,4- and 2,6-DNT (0.05 μ g/L) is lower than the minimum reporting level (MRL) of 2 μ g/L used for monitoring, EPA used the MRL to evaluate occurrence and exposure. The MRL is within the 10^{-4} to the 10^{-6} cancer risk range for 2,4- and 2,6-DNT. In evaluating the UCMR 1 data, EPA found that 1 of the 3,873 public water systems (PWSs) sampled (or 0.03 percent) detected 2,4-DNT at or above the MRL of 2 μ g/L, affecting 0.02 percent of the population served (or 38,000 people from 226 million). None of the 3,873 PWSs sampled (serving 226 million) detected 2,6-DNT at or above the MRL of 2 μ g/L.

The Agency has made a determination not to regulate 2,4- or 2,6-DNT with a national primary drinking water regulation (NPDWR). Because 2,4- and 2,6-DNT appear to occur infrequently at levels of concern in PWSs, the Agency believes that an NPDWR does not present a meaningful opportunity for health risk reduction.

The Agency's original Health Advisories for 2,4- and 2,6-DNT were developed for military installations. Since 1992 and because the Agency recognizes that 2,4 and 2,6-DNT may still be found at some military sites, the Agency has updated the Health Advisories to reflect recent health effects publications. EPA published a draft of the updated Health Advisory document for both 2,4 and 2,6-DNT as part of the regulatory determinations for these two isomers. The updated document is available on the Web at:

http://www.epa.gov/safewater/ccl/reg_determine2.html. The final Health Advisory document will be published in 2008 and will provide information to States with public water systems that may have either 2,4- or 2,6-DNT at concentrations above health levels of concern. If a State finds highly localized occurrence of 2,4- and/or 2,6-DNT at concentrations above the HRL, it should consider whether State-level guidance (or some other type of action) may be appropriate.

The Agency's regulatory determination for this contaminant is presented formally in the *Federal Register*.

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Abbreviations

AOAC Association of Analytical Communities
APHA American Public Health Association

ASTM American Society for Testing and Materials

CAS Chemical Abstracts Service
CCL Contaminant Candidate List
CWS Community Water System

DNT Dinitrotoluene
2,4-DNT 2,4-Dinitrotoluene
2,6-DNT 2,6-Dinitrotoluene

GAC Granular Activated Carbon

GC Gas Chromatography

GC/MS Gas Chromatography with Mass Spectrometry

GW Ground Water

HRL Health Reference Level

HSDB Hazardous Substances Data Bank

LOAEL Lowest-Observed-Adverse-Effect Level

LSE Liquid-Solid Extraction
MDL Method Detection Limit
MRL Minimum Reporting Level

MS Mass Spectrometry

NAWQA National Water Quality Assessment NOAEL No-Observed-Adverse-Effect-Level

NPDES National Pollutant Discharge Elimination System NPDWR National Primary Drinking Water Regulation

NPL National Priorities List

NTNCWS Non-Transient Non-Community Water System

PWS Public Water System

QC Quality Control

RCRA Resource Conservation and Recovery Act

RfD Reference Dose RL Reporting Limit

SVOC Semi-Volatile Organic Compound

SW Surface Water

tg-DNT Technical Grade DNT

TNT Trinitrotoluene

TRI Toxics Release Inventory

UCMR 1 First Unregulated Contaminant Monitoring Regulation

USGS United States Geological Survey

7 2,4- and 2,6-Dinitrotoluene

7.1 Definition

2,4- and 2,6-Dinitrotoluene are semivolatile organic compounds (SVOCs) with very similar physical characteristics. 2,4- and 2,6-Dinitrotoluene are just two of the six isomers of dinitrotoluene (DNT), but together they comprise approximately 95 percent of technical grade dinitrotoluene (ATSDR, 1998). The remaining 5 percent is composed primarily of the other four isomers (2,3-dinitrotoluene, 2,5-dinitrotoluene, 3,4-dinitrotoluene, and 3,5-dinitrotoluene). 2,4-Dinitrotoluene's Chemical Abstracts Service (CAS) registry number is 121-14-2, and 2,6-Dinitrotoluene's number is 606-20-2. There are multiple synonyms for 2,4-dinitrotoluene: 2,4-DNT, 1-methyl-2,4-dinitrobenzene, 2,4-dinitrotoluol, NCI-C01865, dinitrotoluene, and Resource Conservation and Recovery Act (RCRA) waste number U105. 2,6-Dinitrotoluene is also known as: 2,6-DNT, 1-methyl-2,6-dinitrobenzene, RCRA waste number U106, and 2-methyl-1,3-dinitro-benzene (NIST, 2001).

7.1.1 Properties and Sources

In pure form, both 2,4- and 2,6-dinitrotoluene are pale yellow solids with a slight odor. 2,4- and 2,6-Dinitrotoluene are not natural substances, but are made from reacting toluene (C₇H₈) with a mixture of nitric and sulfuric acids. 2,4- and 2,6-Dinitrotoluene are commonly used in the bedding and furniture industries to produce polyurethane foams; however, they are also used in the production of ammunition, explosives, dyes, and can be found in automobile air bags (ATSDR, 1998). The two contaminants are released to the environment predominantly through industrial wastewater discharges and improper waste disposal. Exhibit 7-1 summarizes the physical and chemical properties of 2,4- and 2,6-dinitrotoluene.

Exhibit 7-1: Physical and Chemical Properties of 2,4- and 2,6-Dinitrotoluene

Identification	2,4-Dinitrotoluene	2,6-Dinitrotoluene
CAS number	121-14-2	606-20-2
Molecular Formula	$C_7H_6N_2O_4$	$C_7H_6N_2O_4$
Physical and Chemical Properties		
Boiling Point	300 °C 1	285 °C ⁹
Melting Point	71 ° C ¹	66 °C ¹
Molecular Weight	182.14 g/mol ¹	182.14 g/mol ¹
Log K _{oc}	2.45 ²	2.31 ²
Log K _{ow}	1.98 ³	2.10 ¹⁰
Water Solubility	270 mg/L at 22 °C 4	180 mg/L at 20° C ¹¹
Vapor Pressure	1.4 x 10 ⁻⁴ mm Hg at 22 ° C ⁵	5.67 x 10 ⁻⁴ mm Hg at 25 ° C ⁵
Henry's Law Constant	8.67 x 10 ⁻⁷ atm-m ³ /mol ⁶ 4.6 x 10 ⁻⁵ (dimensionless), predicted ⁷	2.17 x 10 ⁻⁷ atm-m ³ /mol ¹² 0.22 (dimensionless), predicted ⁷ 7.4 (dimensionless), from literature ⁷
Freundlich Isotherm Constant (K)	17,200 (μg/g)(L/μg) ^{1/n 8}	15,900 (μg/g)(L/μg) ^{1/n 8}

¹ Lide, 1999 (as cited in Hazardous Substance Data Bank (HSDB), 2004)

7.1.2 Environmental Fate and Behavior

Both 2,4- and 2,6-dinitrotoluene are slightly mobile in soil (Howard, 1990). Degradation in soil is fairly rapid, as both compounds are broken down by sunlight and bacteria into

² Lyman, 1982 (as cited in Howard, 1990)

³ Hansch et al., 1995 (as cited in HSDB, 2004)

⁴ Spanggord et al., 1980 (as cited in HSDB, 2004)

⁵ Pella, 1977 (as cited in HSDB, 2004)

⁶ Smith et al., 1983 (as cited in Howard, 1990)

⁷ Speth et al., 2001

⁸ Dobbs and Cohen, 1980 (as cited in Speth et al., 2001)

⁹ USEPA, 1980 (as cited in HSDB, 2004)

¹⁰ Nakagawa et al., 1992 (as cited in HSDB, 2004)

¹¹ Mabey et al., 1982 (as cited in ATSDR, 1998)

¹² SGC, 1987 (as cited in Howard, 1990)

substances such as carbon dioxide, water, and nitric acid (ATSDR, 1998). At a munitions-contaminated site, microorganisms in the surface soil were reported to transform 2,4- and 2,6-dinitrotoluene to amino-nitro intermediates within 70 days (Bradley *et al.*, 1994 as cited in ATSDR, 1998). This process could take longer or shorter, however, as natural degradation of both compounds in soil has been found to be temperature-sensitive (Grant *et al.*, 1995 as cited in ATSDR, 1998). Aromatic nitro compounds such as 2,4- and 2,6-dinitrotoluene are not susceptible to hydrolysis (Lyman *et al.*, 1982 as cited in Howard, 1990).

In water, both 2,4- and 2,6-dinitrotoluene have a slight tendency to adsorb to sediments and suspended solids (Howard, 1990). Volatilization from water does not appear to be a significant transport process for either contaminant (Howard, 1990). Available data on 2,4- and 2,6-dinitrotoluene degradation in water are variable and inconsistent (Howard, 1990). Jenkins *et al.* (1995) note that rates of biodegradation of nitrotoluenes and similar compounds are sufficient to require that special steps be taken to preserve aqueous samples for laboratory analysis. However, 2,4- and 2,6-dinitrotoluene have relatively long half-lives in aquatic systems, facilitating aquatic transport (ATSDR, 1998). Degradation of dinitrotoluene in water can occur via several mechanisms, including photolysis, microbial biodegradation, ozonation and chlorination, and oxidation by strong oxidants such as hydrogen peroxide, ozone, or oxone (ATSDR, 1998). Analyses of both contaminants' log K_{ow} suggest that the bioaccumulation potentials of 2,4- and 2,6-dinitrotoluene in aquatic organisms are quite low (Hansch *et al.*, 1995 as cited in HSDB, 2004).

According to a model of gas/particle partitioning for SVOCs (Bidleman, 1988 as cited in HSDB, 2004), dinitrotoluenes are expected to exist solely as vapor in the ambient atmosphere. Vapor-phase 2,4- and 2,6-dinitrotoluene are degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals. The half-life for this reaction is estimated to be 75 days (HSDB, 2004).

7.2 Health Effects

In experimental animal studies, 2,4- and 2,6-DNT appear to be acutely toxic at moderate to high levels (LD₅₀s¹ ranging from 180 to 1,954 mg/kg) when administered orally. In subacute studies (4 weeks) conducted by Lee *et al.* (1978 as cited in ATSDR, 1998), dogs, rats, and mice were fed 2,4-DNT and studied for toxic effects. A no-observed-adverse-effect level (NOAEL) of 5 mg/kg/day was established; decreased body weight gain and food consumption, neurotoxic signs, and lesions in the brain, kidneys, and testes occurred at 25 mg/kg/day (the highest dose tested).

Subchronic studies in mice, rats, and dogs that administered 2,4- and 2,6-DNT in the diet produced similar effects in all species. All species exposed to 2,4-DNT exhibited methemoglobinemia, anemia, bile duct hyperplasia sometimes accompanied by hepatic degeneration, and depressed spermatogenesis. Neurotoxicity and renal degeneration occurred in dogs at a dose level of 20 mg/kg/day of 2,6-DNT (Lee *et al.*, 1976 as cited in USEPA, 1992). At a dose level of 25 mg/kg/day of 2,4-DNT, male and female dogs developed impaired muscle

 1 LD₅₀ = An estimate of a single dose that is expected to cause the death of 50 percent of the exposed animals. It is derived from experimental data.

movement and paralysis, methemoglobinemia, aspermatogenesis, hemosiderosis of the spleen and liver, cloudy swelling of the kidneys, and lesions of the brain (Ellis *et al.*, 1985 as cited in USEPA, 1992). These doses were determined to be lowest-observed-adverse-effect levels (LOAELs) for these studies.

2,4-DNT has been shown to cause reproductive effects in rats, mice, and dogs (Ellis *et al.*, 1979 as cited in USEPA, 1992; Lee *et al.*, 1985 as cited in ATSDR, 1998; Hong *et al.*, 1985 as cited in ATSDR, 1998; Ellis *et al.*, 1985 as cited in USEPA, 1992). Ellis *et al.* (1979 as cited in USEPA, 1992) observed effects in rats following dietary exposure after a dose of 35 mg/kg/day but not 5 mg/kg/day over three generations. Male mice fed 2,4-DNT for 13 weeks exhibited testicular degeneration and atrophy and decreased spermatogenesis at 95 mg/kg/day (Hong *et al.*, 1985 as cited in ATSDR). In another reproductive study, dogs exhibited mild to severe testicular degeneration and reduced spermatogenesis (Ellis *et al.*, 1985, as cited in USEPA, 1992) when administered 2,4-DNT in capsules at 25 mg/kg/day. There are currently no studies of the reproductive or developmental toxicity of 2,6-DNT, although a subchronic study in dogs identified atrophy of spermatogenic cells in males suggesting a one- or two-generation study as a data need for 2,6-DNT.

Some studies evaluated the effects of DNT in the form of a technical grade mixture (tg-DNT). In a study by Price *et al.* (1985 as cited in USEPA, 1992), the teratogenic potential of tg-DNT (containing approximately 76 percent 2,4-DNT and 19 percent 2,6-DNT) was investigated in rats. The study was conducted in two phases to evaluate the possible teratogenicity of DNT as well as DNT effects on postnatal development. For the first phase, rats were administered 0, 14, 35, 37.5, 75, 100, or 150 mg/kg/day of DNT in corn oil by gavage. In the postnatal phase, rats were administered 14, 35, 37.5, 75, or 100 mg/kg/day of DNT in corn oil by gavage. The NOAEL and LOAEL for developmental toxicity were 14 and 35 mg/kg/day, respectively, based on significant increases in relative liver and spleen weight in the fetuses of dams administered DNT at levels of 35 mg/kg/day or greater. No teratogenic toxicity was seen in the study rats.

In chronic exposures, oral dietary administration of 2,4-DNT to dogs primarily affected the nervous system, erythrocytes, and biliary tract (Ellis *et al.*, 1979; 1985 both as cited in USEPA, 1992). Based on neurotoxicity, hematologic changes, and effects on the bile ducts in dogs, the LOAEL was determined to be 1.5 mg/kg/day and the NOAEL was 0.2 mg/kg/day. EPA established a reference dose (RfD) of 0.002 mg/kg/day for 2,4-DNT (USEPA, 1992) based on this study. An uncertainty factor of 100, to account for interspecies and intraspecies variability, was applied to derive the RfD.

EPA established an RfD of 0.001 mg/kg/day for 2,6-DNT (USEPA, 1992). This RfD was also based on neurotoxicity, Heinz body formation, biliary tract hyperplasia, liver and kidney histopathology, and death in beagle dogs that were fed gelatin capsules containing 2,6-DNT daily for up to 13 weeks (Lee *et al.*, 1976 as cited in USEPA, 1992). The NOAEL for this study was 4 mg/kg/day, and an uncertainty factor of 3,000 (100 for inter- and intra-species variability, 10 for the use of a subchronic study, 3 to account for the limited database) was applied to derive the RfD.

DNT is likely to be carcinogenic to humans (classified as a B2 carcinogen; USEPA, 1990). This is based on significant increases in hepatocellular carcinoma and mammary gland

tumors in female rats fed DNT (98 percent 2,4-DNT with 2 percent 2,6-DNT) in the diet in a two-year study (Ellis *et al.*, 1979 as cited in USEPA, 1992). The tumor incidence in the female rats was used to establish a slope factor of 6.67 × 10⁻¹ according to the 1999 EPA guidelines. Concentrations of 5 μg/L, 0.5 μg/L, and 0.05 μg/L are associated with carcinogenic risks of 10⁻⁴, 10⁻⁵, and 10⁻⁶ respectively. There were no studies found in the literature that evaluated the effects of 2,4- or 2,6-DNT on children. There is evidence that the pups and fetuses from dams administered tg-DNT had significant increases in relative liver and spleen weights (Price *et al.*, 1985 as cited in USEPA, 1992). DNT toxicity may be different in children, compared to adults, since it undergoes bioactivation in the liver and by the intestinal microflora (ATSDR, 1998). Newborns may be more sensitive to DNT-related methemoglobinemia because an enzyme that protects against increased levels of methemoglobin is inactive for a short duration immediately after birth (Gruener, 1976 as cited in ATSDR, 1998; ATSDR, 1998). However, there are no experimental data on differences in children's responses to 2,4-/2,6-DNT.

7.3 Occurrence and Exposure

7.3.1 Use and Environmental Release

DNTs are not known to occur naturally in the environment. Generally, 2,4- and 2,6-DNT are produced as a mixture called technical grade DNT, or simply DNT, which contains approximately 76 percent 2,4-DNT and 19 percent 2,6-DNT. The remainder of technical grade DNT consists of other isomers and minor contaminants such as trinitrotoluene (TNT) and mononitrotoluenes (HSDB, 2004). DNT is commercially produced by reacting toluene with a mixture of nitric and sulfuric acids (Etnier, 1987 as cited in ATSDR, 1998). DNT is used in the production of toluene diisocyanate and urethane polymers, as well as automobile airbags, dyes, and explosives, including TNT (ATSDR, 1998).

No recent quantitative estimates of DNT production or use are available. The Hazardous Substances Data Bank (HSDB, 2004) cites a 1980 EPA Ambient Water Quality Criteria Document that places combined 2,4- and 2,6-DNT production at 272,610,000 pounds in 1975.

2,4-DNT, 2,6-DNT, and mixed DNT are all listed as Toxics Release Inventory (TRI) chemicals. For a discussion of the nature and limitations of TRI data, see Chapter 2.

TRI data for 2,4-DNT (see Exhibit 7-2) are reported for the years 1988-2003. TRI releases for 2,4-DNT were reported from facilities in 21 States (AK, CA, FL, IA, IL, IN, KY, LA, MI, MO, MS, NE, NJ, NV, OH, SC, TN, TX, VA, UT, WV). Releases of all kinds declined in the early 1990s, and then peaked again around 1999-2001. On-site air emissions and surface water releases were generally the most consistent types of releases (USEPA, 2006).

Exhibit 7-2: Environmental Releases (in pounds) of 2,4-Dinitrotoluene in the United States, 1988-2003

		On-Site I	Off-Site	Total On- &		
Year	Total Air Emissions	Surface Water Discharges	Underground Injection	Releases to Land	Releases	Off-site Releases
1988	93,257	12,055	106,400	14,961	124,281	350,954
1989	12,713	12,657	0	341	194,167	219,878
1990	57,593	3,735	74,000	2,153	99	137,580
1991	5,417	2,682	0	1,424	57	9,580
1992	1,764	105	0	0	0	1,869
1993	1,879	319	0	0	10	2,208
1994	1,899	399	0	0	255	2,553
1995	1,874	231	0	0	94	2,199
1996	1,891	349	0	0	0	2,240
1997	1,801	90	0	0	0	1,891
1998	1,995	187	0	10,000	1,408	13,590
1999	2,287	169	0	43,420	49,296	95,172
2000	1,931	177	250	27,609	19,601	49,568
2001	2,190	10	5	665,529	28,137	695,871
2002	205	6	0	0	2,381	2,592
2003	2,544	5	0	0	12,350	14,899

Source: USEPA, 2006

TRI data for 2,6-DNT (see Exhibit 7-3) are also reported for the years 1988-2003. TRI releases for 2,6-DNT were reported from facilities in 10 States (AR, CA, IN, KY, LA, MI, NV, OH, TX, WV) with no more than nine States having reporting facilities in any one year. These data show a similar trend of declining releases in the late 1980s and early 1990s, and a subsequent peak around 2001. Again, on-site air emissions and surface water discharges are the most consistent types of release (USEPA, 2006).

Exhibit 7-3: Environmental Releases (in pounds) of 2,6-Dinitrotoluene in the United States, 1988-2003

		On-Site I	Off-Site	Total On- &		
Year	Air Emissions	Surface Water Discharges	Underground Injection	Releases to Land	Releases	Off-site Releases
1988	87,597	957	27,000	0	30,882	146,436
1989	83,914	1,083	18,000	0	58,256	161,253
1990	17,737	416	19,000	0	0	37,153
1991	1,948	702	0	0	0	2,650
1992	425	126	0	0	0	551
1993	471	212	0	0	0	683
1994	516	374	0	0	0	890
1995	469	126	0	0	0	595
1996	472	94	0	0	0	566
1997	438	24	0	0	0	462
1998	472	62	0	0	0	534
1999	660	43	0	15,287	16,910	32,900
2000	513	32	250	0	2,030	2,825
2001	740	0	0	1,298,442	5,360	1,304,542
2002	117	1	0	0	855	973
2003	372	0	0	0	10,565	10,937

Source: USEPA, 2006

TRI data for mixed dinitrotoluene isomers (see Exhibit 7-4) are reported for the years 1990-2003. TRI releases for mixed isomers were reported from facilities in 9 States (CA, IA, LA, NV, NJ, OH, OK, TX, UT) with no more than seven States having reporting facilities in any one year. Two States, Louisiana and Texas, reported releases every year. Underground injections made up the bulk of on-site releases during the 1990s, but diminished thereafter. Air emissions remained relatively constant. Surface water discharges and releases to land were generally insignificant but peaked in 2003. Off-site releases varied widely. Total releases peaked in 1993 and 1997, and generally diminished in recent years (USEPA, 2006).

Exhibit 7-4: Environmental releases (in pounds) of Dinitrotoluene (Mixed Isomers) in the United States, 1990-2003

		On-Site F		Off-Site	Total On- &	
Year	Air Emissions	Surface Water Discharges	Underground Injection	Releases to Land	Releases	Off-site Releases
1990	4,159	7,112	0	363	15,832	27,466
1991	14,979	135	60,000	0	55	75,169
1992	16,744	291	50,000	0	61	67,096
1993	15,969	631	98,000	173	314	115,087
1994	15,930	10	28,000	0	6,515	50,455
1995	14811	284	17,000	0	6	32,101
1996	14,815	586	33,000	0	121	48,522
1997	11,551	63	56,000	0	46,491	114,105
1998	13,439	1	36,005	0	1,403	50,848
1999	9,657	1	1,100	0	322	11,080
2000	10,423	4	3,300	696	22,098	36,521
2001	9,839	8	3,000	15	696	13,558
2002	8,043	61	1,100	0	1,535	10,739
2003	6,767	1,318	190	4,110	1,405	13,790

Source: USEPA, 2006.

2,4-DNT and 2,6-DNT have been detected in soil, sediment, water, or air at 69 and 53, respectively, of the 1,467 current or former National Priorities List (NPL) hazardous waste sites (HazDat, 1998 as cited in ATSDR, 1998).

7.3.2 Ambient Water Occurrence

Ambient lakes, rivers, and aquifers are sources of drinking water. Data on the occurrence of 2,4- and 2,6-dinitrotoluene in stream bed sediment are available from the National Water Quality Assessment (NAWQA) program of the United States Geological Survey (USGS). For details on this program, see the discussion in Chapter 2. Limited data on the occurrence of 2,4- and 2,6-DNT in ambient water are also available from stormwater studies.

NAWQA National Pesticide Synthesis: SVOCs in Bed Sediment

Because SVOCs like 2,4- and 2,6-dinitrotoluene are hydrophobic and tend to sorb to sediment and particles, an analysis of bed sediment is often the best way to determine whether an SVOC is present in water. The NAWQA National Pesticide Synthesis includes an analysis of SVOC monitoring in bed sediment from representative watersheds across the country between 1992 and 2001. Sampling was conducted at 1,029 sites. The reporting level for all SVOCs was $50 \mu g/L$. Sampling techniques and analytical methods are described in detail by Nowell and Capel (2003).

NAWQA data indicate that 2,4-dinitrotoluene was not detected in bed sediment in agricultural, urban, or undeveloped settings (Exhibit 7-5). In mixed land use settings, 2,4-dinitrotoluene was detected in 1.3% of samples, with a maximum concentration of 173 μ g/kg dry weight (Nowell and Capel, 2003).

Exhibit 7-5: USGS National Synthesis Summary of NAWQA Monitoring of 2,4-Dinitrotoluene in Bed Sediment, 1992-2001

Land Use Type	No. of Sites	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	242	0.0%	<rl< td=""><td><rl< td=""><td><rl< td=""></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""></rl<></td></rl<>	<rl< td=""></rl<>
Urban	130	0.0%	<rl< td=""><td><rl< td=""><td><rl< td=""></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""></rl<></td></rl<>	<rl< td=""></rl<>
Mixed	306	1.3%	<rl< td=""><td><rl< td=""><td>173 μg/kg</td></rl<></td></rl<>	<rl< td=""><td>173 μg/kg</td></rl<>	173 μg/kg
Undeveloped	215	0.0%	<rl< td=""><td><rl< td=""><td><rl< td=""></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""></rl<></td></rl<>	<rl< td=""></rl<>

Abbreviations:

RL = Reporting limit. Reporting limits for 2,4-dinitrotoluene varied, but did not exceed 50 μg/kg.

For bed sediment, all weights are dry weights.

Most sites were sampled only once. In the case of sites sampled multiple times, USGS used a single sample (the earliest sample with complete data for all analytes) to represent each site in this analysis.

Percentile Concentrations were drawn from the range of detects and non-detects. The method for calculating Percentile Concentrations varied depending on how much of the data was censored at particular levels by the laboratory.

Source: Nowell and Capel, 2003

2,6-Dinitrotoluene was detected in bed sediment at frequencies ranging from 1.6% in urban settings to 4.4% in agricultural settings, 6.6% in mixed land use settings, and 6.9% in undeveloped settings (Exhibit 7-6). The 95th percentile concentrations were less than the reporting level in all settings. The highest concentration, 291 μ g/kg dry weight, was found in an undeveloped setting (Nowell and Capel, 2003).

Exhibit 7-6: USGS National Synthesis Summary of NAWQA Monitoring of 2,6-Dinitrotoluene in Bed Sediment, 1992-2001

Land Use Type	No. of Sites	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	137	4.4%	<rl< td=""><td><rl< td=""><td>196 µg/kg</td></rl<></td></rl<>	<rl< td=""><td>196 µg/kg</td></rl<>	196 µg/kg
Urban	63	1.6%	<rl< td=""><td><rl< td=""><td>34 µg/kg</td></rl<></td></rl<>	<rl< td=""><td>34 µg/kg</td></rl<>	34 µg/kg
Mixed	136	6.6%	<rl< td=""><td><rl< td=""><td>93 µg/kg</td></rl<></td></rl<>	<rl< td=""><td>93 µg/kg</td></rl<>	93 µg/kg
Undeveloped	130	6.9%	<rl< td=""><td><rl< td=""><td>291 µg/kg</td></rl<></td></rl<>	<rl< td=""><td>291 µg/kg</td></rl<>	291 µg/kg

Abbreviations:

RL = Reporting limit. Reporting limits for 2,6-dinitrotoluene varied, but did not exceed 50 µg/kg.

For bed sediment, all weights are dry weights.

Most sites were sampled only once. In the case of sites sampled multiple times, USGS used a single sample (the earliest sample with complete data for all analytes) to represent each site in this analysis.

Percentile Concentrations were drawn from the range of detects and non-detects. The method for calculating Percentile Concentrations varied depending on how much of the data was censored at particular levels by the laboratory.

Source: Nowell and Capel, 2003

USGS Stormwater Studies

For the National Highway Runoff Data and Methodology Synthesis, USGS conducted a review of 44 highway and urban runoff studies implemented since 1970 (Lopes and Dionne, 1998). 2,4-and 2,6-DNT were included as analytes in three of these studies. For more background on these studies, see Chapter 2.

All three studies were stormwater studies conducted in major metropolitan areas in connection with National Pollutant Discharge Elimination System (NPDES) permitting. In Maricopa County, Arizona, USGS collected 35 samples from five drainage basins and the City of Phoenix collected an additional 26 samples from seven sites (Lopes *et al.*, 1995). In Colorado Springs, Colorado, 35 samples were collected from five sites (von Guerard and Weiss, 1995). In the Dallas-Fort Worth area of Texas, 182 samples were collected from 26 stormwater drainage basins (Baldys *et al.*, 1998). For both 2,4- and 2,6-DNT, the reporting limit was 5 µg/L in all three studies. Not all samples were monitored for every contaminant. None of the three studies found any detections of 2,4- or 2,6-DNT.

7.3.3 Drinking Water Occurrence

Nationally representative data on 2,4- and 2,6-DNT occurrence in drinking water have been collected by large and small public water systems in accordance with EPA's First Unregulated Contaminant Monitoring Regulation (UCMR 1). For details on UCMR 1, see Chapter 2 and USEPA (2008).

UCMR 1

UCMR 1 monitoring was conducted primarily between 2001 and 2003, though some results were not collected and reported until as late as 2006. As List 1 contaminants, 2,4- and 2,6-DNT were scheduled to be monitored by all large community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) and a statistically representative sample of qualifying small CWSs and NTNCWSs. The data presented in this report reflect UCMR 1 analytical samples submitted and quality-checked under the regulation as of March 2006. 2,4- and 2,6-Dinitrotoluene data were collected and submitted by 797 (99.6 percent) of the 800 small systems selected for the small system sample and 3,076 (99.2 percent) of the 3,100 large systems defined as eligible for the UCMR 1 large system census. Data for each contaminant have been analyzed at the level of simple detections (at or above the minimum reporting level (MRL), \geq MRL, or \geq 2 μ g/L). Since the health reference level (HRL) of 0.05 μ g/L is less than the MRL, the data are not analyzed at the level of the HRL or half the HRL.

EPA set the MRL for UCMR 1 contaminants based on the capability of analytical methods, not anticipated health levels. For many UCMR 1 contaminants, including 2,4- and 2,6-Dinitrotoluene, the MRL was determined by multiplying by 10 the least sensitive method's minimum detection limit, or, when available, multiplying by 5 the least sensitive method's estimated detection limit (USEPA, 2000). MRLs were set approximately an order of magnitude higher than detection limits to ensure consistency, accuracy, and reproducibility of results. The MRL for 2,4- and 2,6-dinitrotoluene is within the risk range of 10⁻⁶ to 10⁻⁴ used by EPA to evaluate carcinogens (see Section 2.1.1).

Results of the analysis are presented in the following four exhibits (Exhibit 7-7, 7-8, 7-9, and 7-10). Among small systems, there were no detections of 2,4- or 2,6-dinitrotoluene. Among large systems, one had a detection of 2,4-dinitrotoluene; this surface water system represented 0.03% of large systems and 0.02% of the population served by them (approximately 38,000 people). The concentration of the single detection was 333 μ g/L. No 2,6-dinitrotoluene detections were reported from large systems.

Exhibit 7-7: Summary UCMR 1 Occurrence Statistics for 2,4-Dinitrotoluene in Small Systems (Based on Statistically Representative National Sample of Small Systems)

Frequency Factors	UCMR Data - Small Systems		National System & Population Numbers ¹
Total Number of Samples	3,2	251	
Percent of Samples with Detections	0.0	00%	
99 th Percentile Concentration (all samples)	< N	⁄IRL	
Health Reference Level (HRL)	0.05	$\mu g/L$	
Minimum Reporting Level (MRL)	2 μ	ıg/L	
Maximum Concentration of Detections	< MRL		
99 th Percentile Concentration of Detections	< N	⁄IRL	
Median Concentration of Detections	< N	MRL .	
Total Number of PWSs Number of GW PWSs Number of SW PWSs	797 590 207		60,414 56,072 4,342
Total Population Population of GW PWSs Population of SW PWSs	2,760,570 1,939,815 820,755		45,414,590 36,224,336 9,190,254
Occurrence by System	Number Percentage		National Extrapolation ²
PWSs (GW & SW) with Detections (≥ MRL)	0	0.00%	0
Occurrence by Population Served			
Population Served by PWSs with Detections	0	0.00%	0

^{1.} PWS and population numbers are from EPA September 2004 Drinking Water Baseline Handbook, 4th edition.

Abbreviations:

PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; N/A = Not Applicable; Total Number of Samples = the total number of samples on record for the contaminant; 99th Percentile Concentration = the concentration in the 99th percentile sample (out of either all samples or just samples with detections); Median Concentration of Detections = the concentration in the median sample (out of samples with detections); Total Number of PWSs = the total number of PWSs for which sampling results are available; Total Population Served = the total population served by PWSs for which sampling results are available; PWSs with detections, PWSs > ½ HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs > ½ HRL, or by PWSs > HRL = population served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, respectively.

Notes.

^{2.} National extrapolations are generated separately for each population-served size stratum and then added to yield the national estimate of GW PWSs with detections (and population served) and SW PWSs with detections (and population served). For intermediate calculations at the level of individual strata, see EPA's UCMR 1 Occurrence Report, entitled "The Analysis of Occurrence Data from the First Unregulated Contaminant Monitoring Regulation (UCMR 1) in Support of Regulatory Determinations for the Second Drinking Water Contaminant Candidate List."

⁻Small systems are those that serve 10,000 persons or fewer.

⁻Only results at or above the MRL were reported as detections. Concentrations below the MRL are considered non-detects.

Exhibit 7-8: Summary UCMR 1 Occurrence Statistics for 2,4-Dinitrotoluene in Large Systems (Based on the Census of Large Systems)

Frequency Factors	UCMR Data - Large Systems			
Total Number of Samples	30	,513		
Percent of Samples with Detections	0.0	003%		
99 th Percentile Concentration (all samples)	< 1	MRL		
Health Reference Level (HRL)	0.05	5 μg/L		
Minimum Reporting Level (MRL)	2	ug/L		
Maximum Concentration of Detections	333 μg/L			
99 th Percentile Concentration of Detections	333 μg/L			
Median Concentration of Detections	333 μg/L			
Total Number of PWSs Number of GW PWSs Number of SW PWSs	3,076 1,380 1,696			
Total Population Population of GW PWSs Population of SW PWSs	223,491,907 53,405,539 170,086,368			
Occurrence by System	Number	Percentage		
PWSs (GW & SW) with Detections (≥ MRL) GW PWSs with Detections SW PWSs with Detections	1 0.03% 0 0.00% 1 0.06%			
Occurrence by Population Served				
Population Served by PWSs with Detections Pop. Served by GW PWSs with Detections Pop. Served by SW PWSs with Detections	37,811 0.02% 0 0.00% 37,811 0.02%			

Abbreviations.

PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; N/A = Not Applicable; Total Number of Samples = the total number of samples on record for the contaminant; 99th Percentile Concentration = the concentration in the 99th percentile sample (out of either all samples or just samples with detections); Median Concentration of Detections = the concentration in the median sample (out of samples with detections); Total Number of PWSs = the total number of PWSs for which sampling results are available; Total Population Served = the total population served by PWSs for which sampling results are available; PWSs with detections, PWSs > ½ HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, respectively.

Notes

-Large systems are those that serve more than 10,000 persons.

⁻Only results at or above the MRL were reported as detections. Concentrations below the MRL are considered non-detects.

Exhibit 7-9: Summary UCMR 1 Occurrence Statistics for 2,6-Dinitrotoluene in Small Systems (Based on Statistically Representative National Sample of Small Systems)

Frequency Factors		R Data - Systems	National System & Population Numbers ¹
Total Number of Samples	3,2	251	
Percent of Samples with Detections	0.0	00%	
99 th Percentile Concentration (all samples)	< <i>V</i>	MRL .	
Health Reference Level (HRL)	0.05	$\mu g/L$	
Minimum Reporting Level (MRL)	2 μ	ıg/L	
Maximum Concentration of Detections	< N	MRL	
99 th Percentile Concentration of Detections	< N	MRL	
Median Concentration of Detections	< N	MRL	
Total Number of PWSs Number of GW PWSs Number of SW PWSs	5	97 90 07	60,414 56,072 4,342
Total Population Population of GW PWSs Population of SW PWSs	2,760,570 1,939,815 820,755		45,414,590 36,224,336 9,190,254
Occurrence by System	Number Percentage		National Extrapolation ²
PWSs (GW & SW) with Detections (≥ MRL)	0	0.00%	0
Occurrence by Population Served			
Population Served by PWSs with Detections	0	0.00%	0

^{1.} Total PWS and population numbers are from EPA September 2004 Drinking Water Baseline Handbook, 4th edition.

Abbreviations:

PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; N/A = Not Applicable; Total Number of Samples = the total number of samples on record for the contaminant; 99th Percentile Concentration = the concentration in the 99th percentile sample (out of either all samples or just samples with detections); Median Concentration of Detections = the concentration in the median sample (out of samples with detections); Total Number of PWSs = the total number of PWSs for which sampling results are available; Total Population Served = the total population served by PWSs for which sampling results are available; PWSs with detections, PWSs > ½ HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively.

Notes:

-Small systems are those that serve 10,000 persons or fewer.

^{2.} National extrapolations are generated separately for each population-served size stratum and then added to yield the national estimate of GW PWSs with detections (and population served) and SW PWSs with detections (and population served). For intermediate calculations at the level of individual strata, see EPA's UCMR 1 Occurrence Report, entitled "The Analysis of Occurrence Data from the First Unregulated Contaminant Monitoring Regulation (UCMR 1) in Support of Regulatory Determinations for the Second Drinking Water Contaminant Candidate List."

⁻Only results at or above the MRL were reported as detections. Concentrations below the MRL are considered non-detects.

Exhibit 7-10: Summary UCMR 1 Occurrence Statistics for 2,6-Dinitrotoluene in Large Systems (Based on the Census of Large Systems)

Frequency Factors	UCMR Data - Large Systems			
Total Number of Samples	30,	514		
Percent of Samples with Detections	0.0	00%		
99 th Percentile Concentration (all samples)	< 1/	MRL		
Health Reference Level (HRL)	0.05	$\mu g/L$		
Minimum Reporting Level (MRL)	2 μg/L			
Maximum Concentration of Detections	< MRL			
99 th Percentile Concentration of Detections	< MRL			
Median Concentration of Detections	< MRL			
Total Number of PWSs Number of GW PWSs Number of SW PWSs	3,076 1,380 1,696			
Total Population Population of GW PWSs Population of SW PWSs	223,491,907 53,405,539 170,086,368			
Occurrence by System	Number Percentage			
PWSs (GW & SW) with Detections (≥ MRL)	0 0.00%			
Occurrence by Population Served				
Population Served by PWSs with Detections	0 0.00%			

Abbreviations:

Abbreviations:

PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; N/A = Not Applicable; Total Number of Samples = the total number of samples on record for the contaminant; 99th Percentile Concentration = the concentration in the 99th percentile sample (out of either all samples or just samples with detections); Median Concentration of Detections = the concentration in the median sample (out of samples with detections); Total Number of PWSs = the total number of PWSs for which sampling results are available; Total Population Served = the total population served by PWSs for which sampling results are available; PWSs with detections, PWSs > ½ HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs > ½ HRL, or by PWSs > HRL = population served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, respectively.

-Large systems are those that serve more than 10,000 persons.

⁻Only results at or above the MRL were reported as detections. Concentrations below the MRL are considered non-detects.

2,4-Dinitrotoluene was only detected in one sample at or above the MRL of 2 μ g/L in all of the UCMR 1 sampling. This single detection was in a surface water sample taken in the State of Tennessee (see Exhibit 7-11). Since only one system detected the contaminant at or above the MRL, no further spatial analysis of this contaminant is presented.

Exhibit 7-11: Geographic Distribution of 2,4-Dinitrotoluene in UCMR 1 Monitoring
- States With At Least One Detection At or Above the MRL (≥ 2 µg/L)



Summary Analysis of Combined Large and Small System UCMR 1 Data

The UCMR 1 data indicate that 1 of the 3,873 public water systems (PWSs) sampled (or 0.03 percent) detected 2,4-DNT at the MRL of 2 μ g/L, affecting 0.02 percent of the population served (or 38,000 people from 226 million). None of the 3,873 PWSs sampled (serving 226 million) detected 2,6-DNT at the MRL of 2 μ g/L.

7.4 Technology Assessment

7.4.1 Analytical Methods

EPA evaluated the availability of analytical methods for all of the unregulated contaminants considered for UCMR 1 (64 FR 50556). Sources for these methods include publications by EPA and by voluntary consensus standard organizations such as the American Society for Testing and Materials (ASTM), the Association of Analytical Communities (AOAC), and the American Public Health Association (APHA).

2,4- and 2,6-Dinitrotoluene are UCMR 1 List 1 contaminants that can be detected in drinking water by EPA Method 525.2. This method was approved for monitoring 2,4- and 2,6-dinitrotoluene in 1999 (64 FR 50556). EPA Method 525.2 relies on capillary column gas

chromatography (GC) to separate the method analytes, and uses mass spectrometry (MS) for detection. A full description of this method can be found in EPA's *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III* (USEPA, 1995a).

EPA Method 525.2

In EPA Method 525.2 (Revision 2.0), "Determination of Organic Compounds in Drinking Water by Liquid-Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)," organic compound analytes are first extracted from a water sample by passing the water through a liquid-solid extraction (LSE) disk or cartridge containing a solid matrix with a chemically bonded C₁₈ organic phase. The organic compounds are eluted from the LSE cartridge or disk with small volumes of ethyl acetate and methylene chloride. These solvent extracts are concentrated further by evaporation of some of the solvent. An aliquot of the extract is injected into a gas chromatograph with a high resolution fused silica capillary column to separate the components. The analytes are transferred from the capillary column to the mass spectrometer and identified by comparing measured mass spectra and retention times to reference spectra and retention times. The concentration of each component is assessed by comparing the mass spectrometry response of the compound's quantitation ion to the response of the internal standard's quantitation ion (USEPA, 1995b). Mass spectrometry is advantageous as a detection method because it reports comparatively few false positive results.

The MDL for Method 525.2 is reported to range from 0.072 to 0.24 μ g/L for 2,4-dinitrotoluene and from 0.054 to 0.2 μ g/L for 2,6-dinitrotoluene, depending upon the extraction media used (USEPA, 1995b). The average recovery is reported to range from 59 to 119 percent for 2,4-dinitrotoluene and 56 to 121 percent for 2,6-dinitrotoluene, depending upon the method option used (USEPA, 1995b).²

Anecdotal reports from laboratories performing Method 525.2 for the analysis of dinitrotoluenes for UCMR 1 have indicated that they are having difficulty obtaining satisfactory recoveries for these compounds, and are therefore having difficulty meeting the quality control (QC) requirements of the method. A preliminary investigation indicates that this may be related to manufacturing changes to the LSE sorbent disks distributed by a major vendor. Satisfactory recoveries of these analytes are still obtained using LSE sorbent disks manufactured by other vendors or by using the method's cartidge option. In the event that regulatory action needs to be taken, a review of the suitability of Method 525.2 for compliance monitoring will be needed. It

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² The Method Detection Limit (MDL) is a statistical estimate of the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero, *i.e.*, greater than the background signal. The calculation of the MDL is based upon the precision of a series of replicate measurements of the analyte at low concentrations. The MDL incorporates estimates of the accuracy of the determination. The MDL is not a concentration that can typically be measured by the method on a routine basis. Detection limits may vary between analysts and laboratories under various laboratory conditions.

The average recovery is the fraction or percent concentration of a target analyte determined relative to the true or expected concentration from a sample containing a known amount of the target analyte. (This can result in apparent recovery values greater than 100 percent.)

is also possible that the dinitrotoluenes could be incorporated into other existing EPA drinking water methods available for compliance monitoring.

7.4.2 Treatment Technologies

Treatment technology status does not influence the determination of whether or not a contaminant should be regulated. However, treatment technologies must be readily available before a contaminant can be regulated with a national primary drinking water regulation (NPDWR). Potential treatment technologies for removing 2,4- and 2,6-dinitrotoluene include activated carbon and air stripping.

Granular activated carbon (GAC) treatment removes contaminants via the physical and chemical process of sorption: the contaminants attach to the carbon surface as water passes through the carbon bed. Activated carbon has a large sorption capacity for many water impurities, including synthetic organic chemicals, taste- and odor-causing compounds, and some species of mercury.

Adsorption capacity is typically represented by the Freundlich isotherm constant, with higher Freundlich (K) values indicating greater sorption potential. Activated carbon is considered to be cost-effective for removing a particular contaminant if the Freundlich (K) value of the contaminant is above 200 μ g/g (L/ μ g)^{1/n} (Speth *et al.*, 2001). Dobbs and Cohen (1980 as cited in Speth *et al.*, 2001) report that the Freundlich (K) values for 2,4- and 2,6-dinitrotoluene are 17,200 μ g/g (L/ μ g)^{1/n} and 15,900 μ g/g (L/ μ g)^{1/n}, respectively, which suggests that GAC is a promising treatment option for both.

Air stripping involves the continuous contact of air with the water being treated, allowing dissolved volatile contaminants to transfer from the source water to the air. Systems often consist of a large column (or tower) filled with molded plastic or ceramic packing material. As the water flows along the column, air is forced counter-current through the water. The packing material increases the area of air-liquid interface, enhancing mass transfer. After contact, the air is vented to an additional treatment device that safely contains or destroys the contaminant.

The Henry's Law constant is commonly used to indicate the tendency of a contaminant to partition from water to air. A larger Henry's constant indicates a greater equilibrium concentration of the contaminant in the air. Thus, contaminants with larger Henry's constants are more efficiently removed by air stripping. A compound is generally considered amenable to air stripping if it has a Henry's law constant above that of dibromochloropropane (0.003 mol/mol) or ethylene dibromide (0.013 mol/mol) (Speth *et al.*, 2001). Speth *et al.* (2001) compiled Henry's Law constants, both calculated by the authors and reported in the literature, for Contaminant Candidate List (CCL) compounds. These authors report Henry's Law constants of 0.22 mol/mol and 7.4 mol/mol for 2,6-dinitrotoluene, and 0.000046 mol/mol for 2,4-dinitrotoluene. These values suggest that air stripping is a promising treatment option for 2,6-dinitrotoluene, but that is not likely to be viable for 2,4-dinitrotoluene (Speth *et al.*, 2001).

7.5 Regulatory Determination

The Agency has made a determination not to regulate 2,4- or 2,6-DNT with a NPDWR. Because 2,4- and 2,6-DNT appear to occur infrequently at levels of concern in PWSs, the Agency believes that an NPDWR does not present a meaningful opportunity for health risk reduction. 2,4-DNT was detected only once at a minimum reporting level (MRL) of 2 μ g/L and 2,6-DNT was not detected at this same level in any of the PWSs monitored under the UCMR 1. While the MRL is slightly greater than the HRL of 0.05 μ g/L, this concentration is within the acceptable 10^{-4} to the 10^{-6} cancer risk range targeted by the Agency.

The Agency's original Health Advisories for 2,4- and 2,6-DNT were developed for military installations. Since 1992 and because the Agency recognizes that 2,4 and 2,6-DNT may still be found at some military sites, the Agency has updated the Health Advisories to reflect recent health effects publications. EPA published a draft of the updated Health Advisory document for both 2,4 and 2,6-DNT as part of the regulatory determinations for these two isomers. The updated document is available on the Web at: http://www.epa.gov/safewater/ccl/reg_determine2.html. The final Health Advisory document will be published in 2008 and will provide information to States with public water systems that

will be published in 2008 and will provide information to States with public water systems that may have either 2,4- or 2,6-DNT at concentrations above health levels of concern. If a State finds highly localized occurrence of 2,4- and/or 2,6-DNT at concentrations above the HRL, it should consider whether State-level guidance (or some other type of action) may be appropriate.

The Agency's regulatory determination for these contaminants is presented formally in the *Federal Register*.

7.6 References

- Agency for Toxic Substances and Disease Registry (ATSDR). 1998. *Profile for 2,4- and 2,6-dinitrotoluene*. Atlanta, GA: Agency for Toxic Substances and Disease Registry, Public Health Service, U.S. Department of Health and Human Services. Available on the Internet at: http://www.atsdr.cdc.gov/toxprofiles/tp109.html.
- Baldys, S, III, T.H. Raines, B.L. Mansfield, and J.T. Sandlin. 1998. *Urban Stormwater Quality, Event Mean Concentrations, and Estimates of Stormwater Pollutant Loads, Dallas-Fort Worth Area, Texas, 1992–93.* U.S. Geological Survey Water-Resources Investigation Report 98-4158. 51 pp.
- Bidleman, T.F. 1988. Atmospheric processes. Wet and dry deposition of organic compounds are controlled by their vapour-article partitioning. *Environmental Science and Technology*. 22:361-367. (As cited in HSDB, 2004.)
- Bradley, P.M., F.H. Chapelle, and J.E. Landmeyer. 1994. Microbial transformation of nitroaromatics in surface soils and aquifer materials. *Applied and Environment Microbiology*. 60:2170-2175. (As cited in ATSDR, 1998.)

- Dobbs, R.A. and J.M. Cohen. 1980. *Carbon Adsorption Isotherms for Toxic Organics*. EPA 600-8-80-023. Cincinnati, OH: Municipal Environmental Research Laboratory, USEPA. (As cited in Speth *et al.*, 2001.)
- Ellis, H.V., J.H. Hagensen, J.R. Hodgson, et al. 1979. *Mammalian Toxicity of Munitions Compounds. Phase BI: Effects of Lifetime Exposure. Part I: 2,4-Dinitrotoluene.* Final report no. 7. (As cited in USEPA, 1992.)
- Ellis, H.V., C.B. Hong, C.C. Lee, J.C. Dacre, and J.P. Glennon. 1985. Subchronic and chronic toxicity studies of 2,4-dinitrotoluene. Part I: Beagle dog. *Journal of the American College of Toxicology*. 4:233-242. (As cited in USEPA, 1992.)
- Etnier, E.L. 1987. Water Quality Criteria for 2,4-dinitrotoluene and 2,6-dinitrotoluene. Oak Ridge, TN: Oak Ridge National Laboratory. U.S. Army Medical Research and Development Command. Project order no.84PP4845. (As cited in ATSDR, 1998.)
- Grant. C.L., T.F. Jenkins, K.F. Meyers, and E.F. McCormick. 1995. Holding-time estimates for soils containing explosive residues: comparison of fortification vs. field contamination. *Journal of Environmental Toxicology and Chemistry*. 14:1865-1874. (As cited in ATSDR, 1998.)
- Gruener, N. 1976. Ontogenetic development of NADH-dependent methemoglobin reductase in erythrocytes of man and rat. *Journal of Toxicology and Environmental Health*. 1:787-791. (As cited in ATSDR, 1998.)
- Hansch, C., A.J. Leo, and D. Hoekman. 1995. *Exploring QSAR Hydrophobic, Electronic, and Steric Constants*. Washington, DC: American Chemical Society. (As cited in HSDB, 2004.)
- Hazardous Substance Release/Health Effects Database (HazDat). 1998. Atlanta, GA: Agency for Toxic Substances and Disease Registry (ATSDR). (As cited in ATSDR, 1998.)
- Hazardous Substances Data Bank (HSDB). 2004. Searches for 2,4-dinitrotoluene and 2,6-dinitrotoluene. Available on the Internet through TOXNET, sponsored by the National Institute of Health's National Library of Medicine. Available on the Internet at: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. Accessed November 1, 2004.
- Hong, C.B., H.V. Ellis, C.C. Lee, H. Sprinz, J.C. Dacre, and J.P. Glennon. 1985. Subchronic and chronic toxicity studies of 2,4-dinitrotoluene. Part III. CD-1 Mice. *Journal of the American College of Toxicology.* 4(4):257-269. (As cited in ATSDR, 1998.)
- Howard, P.H. 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Volume 1. Chelsea, MI: Lewis Publishers, Inc.
- Jenkins, T.F., P.G. Thorne, E.F. McCormick, and K.F. Myers. 1995. *Preservation of Water Samples Containing Nitroaromatics and Nitramines*. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory. Special Report 95-16. Available

- on the Internet at: http://www.crrel.usace.army.mil/techpub/CRREL Reports/reports/SR95 16.pdf.
- Lee, C.C., J.V. Dilley, J.R. Hodgson, D.O. Helton, W.J. Wiegand, D.N. Roberts, B.S. Andersen, B.N. Halfpap, L.D. Kurtz, and N. West. 1975. Mammalian Toxicity of Munition Compounds: Phase I. Acute Oral Toxicity, Primary Skin and Eye Irritation, Dermal Sensitization, and Disposition and Metabolism. Unpublished study. (As cited in ATSDR, 1998.)
- Lee C.C., H.V. Ellis III, J.J. Kowalski, J.R. Hodgsen, R.D. Short, J.C. Bhandari, T.W. Reddig, and J.L. Minor. 1976. Mammalian Toxicity of Munitions Compounds. Phase II: Effects of Multiple doses. Part III: 2,6-Dinitrotoluene. Unpublished study. (As cited in USEPA, 1992.)
- Lee, C.C., H.V. Ellis III, J.J. Kowalski, J.R. Hodgson, and S.W. Hwang. 1978. *Mammalian Toxicity of Munitions Compounds. Phase II: Effects of Multiple Doses. Part II: 2,4-Dinitrotoluene.* Unpublished study. (As cited in ATSDR, 1998.)
- Lee, C.C., C.B. Hong, H.V. Ellis III, J.C. Dacre, and J.P. Glennon. 1985. Subchronic and chronic toxicity studies of 2,4-dinitrotoluene. Part II. CD rats. *Journal of the American College of Toxicology*. 4:243-256. (As cited in ATSDR, 1998.)
- Lide, D.R. (ed.). 1999. *CRC Handbook of Chemistry and Physics*. 79th ed. Boca Raton, FL: CRC Press Inc. (As cited in HSDB, 2004.)
- Lopes, T.J., K.D. Fossum, J.V. Phillips, and J.E. Monical. 1995. *Statistical Summary of Selected Physical, Chemical, and Microbial Characteristics, and Estimates of Constituent Loads in Urban Stormwater, Maricopa County, Arizona*. U.S. Geological Survey Water-Resources Investigations Report 94-4240.
- Lopes, T.J. and S.G. Dionne. 1998. *A Review of Semivolatile and Volatile Organic Compounds in Highway Runoff and Urban Stormwater*. U.S. Geological Survey Open-File Report 98-409. 67 pp. Available on the Internet at: http://sd.water.usgs.gov/nawqa/pubs/ofr/ofr98-409.pdf.
- Lyman W.J., W.J. Reehl, and D.H. Rosenblatt. 1982. *Handbook of Chemical Property Estimation Methods*. New York, NY: McGraw-Hill Book Co. (As cited in Howard, 1990.)
- Mabey, W.R., J.H. Smith, R.T. Podoll, H.L. Johnson, T. Mill, T.W. Chou, J. Gates, I.W. Partridge, H. Jaber, and D. Vandenberg. 1982. *Aquatic Fate Process Data for Organic Priority Pollutants*. EPA 440-4-81-014, 239-243. (As cited in ATSDR, 1998.)
- Nakagawa, Y., K. Izumi, N. Oikawa, T. Sotomatsu, M. Shigemura, and T. Fujita. 1992. Analysis and prediction of hydrophobicity parameters of substituted acetanilides, benzamides and related aromatic compounds. *Environmental Toxicology and Chemistry*. 11:901-916. (As cited in HSDB, 2004.)

- National Institute of Standards and Technology (NIST). 2001. *NIST Chemistry WebBook*. Search for 2,4 dinitroluene and 2,6 dinitroluene. Available on the Internet at: http://webbook.nist.gov/. Accessed June 29, 2001.
- Nowell, L. and P. Capel. 2003. "Semivolatile Organic Compounds (SVOC) in Bed Sediment from United States Rivers and Streams: Summary Statistics; Preliminary Results of the National Water Quality Assessment Program (NAWQA), 1992-2001." Available on the Internet at: http://ca.water.usgs.gov/pnsp/svoc/SVOC-SED_2001_Text.html. Accessed August 25, 2004. Last updated May 12, 2003.
- Pella, P.A. 1977. Measurement of the vapor pressures of TNT, 2,4-DNT, 2,6-DNT, and EGDN. *Journal of Chemical Thermodynamics*. 9(4):301-305. (As cited in HSDB, 2004.)
- Price, C.J., R.W. Tyl, T.A. Marks., L.L. Paschke, T.A. Ledoux, and J.R. Reel. 1985. Teratologic evaluation of dinitrotoluene in the Fischer 344 rat. *Fundamental and Applied Toxicology*. 5:948-961. (As cited in USEPA, 1992.)
- Smith, J.H., D. Mackay and C. Ng. 1983. Volatilization of pesticides from water. *Residue Reviews*. 85:73-88. (As cited in Howard, 1990.)
- Society for German Chemists (SGC). 1987. *Dinitrotoluenes: BUA Substance Report 12*. The Advisory Board for Environmentally Significant Hazardous Wastes (BUA) of the Society of German Chemists, eds. Weinheim, Fed Rep of Germany: VCH Verlagsgesellschaft. (As cited in Howard, 1990.)
- Spanggord, R.J., W.R. Mabey, T. Mill, T.W. Chou, J.H. Smith, and S. Lee. 1980. Environmental Fate Studies on Certain Munition Wastewater Constituents. Final Report, Phase I - Literature Review. DAMD 17-78-C8081. (As cited in HSDB, 2004.)
- Speth, T.F., M.L. Magnuson, C.A. Kelty, and C.J. Parrett. 2001. Treatment Studies of CCL Contaminants. In: *Proceedings, AWWA Water Quality Technology Conference*, November 11-15, Nashville, TN.
- United States Environmental Protection Agency (USEPA). 1980. Ambient Water Quality Criteria Document: Dinitrotoluene. EPA 440/5-80-045. (As cited in HSDB, 2004.)
- USEPA. 1990. United States Environmental Protection Agency. Integrated Risk Information System (IRIS) for 2,4-/2,6-Dinitrotoluene Mixture. Available on the Internet at: http://www.epa.gov/iris/subst/0397.htm.
- USEPA. 1992. 2,4-& 2,6-Dinitrotoluene (DNT) Health Advisory. EPA 820-R-92-002. April.
- USEPA. 1995a. Methods for the Determination of Organic Compounds in Drinking Water, Supplement III. EPA 600-R-95-131. August.

- USEPA. 1995b. Method 525.2-Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS). Revision 2.0. In: *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III.* EPA 600-R-95-131. August.
- USEPA. 2000. Unregulated Contaminant Monitoring Regulation Analytical Methods and Quality Control Manual. EPA 815-R-00-006.
- USEPA. 2006. TRI Explorer: Trends. Searches for 2,4-dinitrotoluene, 2,6-dinitrotoluene, and dinitrotoluene (mixed isomers). Available on the Internet at: http://www.epa.gov/triexplorer/trends.htm. Accessed February 8, 2006. Last updated June 8, 2005.
- USEPA. 2008. The Analysis of Occurrence Data from the First Unregulated Contaminant Monitoring Regulation (UCMR 1) in Support of Regulatory Determinations for the Second Drinking Water Contaminant Candidate List. EPA 815- R-08-013. June.
- von Guerard, P. and W.B. Weiss. 1995. Water Quality of Storm Runoff and Comparison of Procedures for Estimating Storm-runoff Loads, Volume, Event-mean Concentrations, and the Mean Load for a Storm for Selected Properties and Constituents for Colorado Springs, Southeastern Colorado, 1992. U.S. Geological Survey Water-Resources Investigations Report 94-4194.