

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

TDI has been identified in 4 of the 1,854 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2017). Diisocyanates were not found at the sites most likely due to their rapid hydrolysis in the environment. The frequency of these sites can be seen in Figure 6-1.

TDI and MDI are extremely reactive compounds that are widely used in the production of polyurethane materials. There are no natural sources of diisocyanates. Almost all of the potential exposures to these compounds are associated with the production, handling, use, and disposal of diisocyanates and diisocyanate-containing products and material. Exposure of the general population to diisocyanates could potentially result from industrial exposures, as well as from the use of consumer products containing uncured TDI and MDI (EPA 2011a, 2011b).

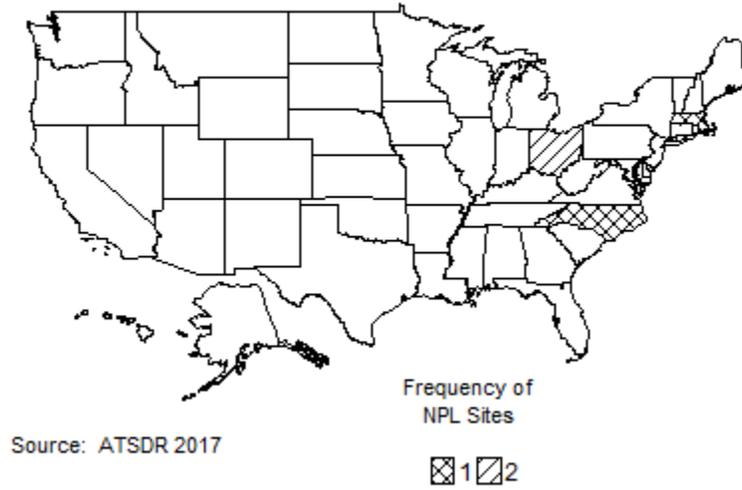
The dominant process affecting the overall environmental fate, transport, and bioaccumulation potential of diisocyanates is hydrolysis (EPA 2011a, 2011b). Diisocyanates react with water forming the respective amines, which in turn may react with more diisocyanates to produce inert, insoluble polyureas (WHO 2000). Hydrolysis half-lives of MDI and TDI have been measured to be on the order of a few minutes to a few hours (HSDB 2012).

### 6.2 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.),

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**Figure 6-1. Frequency of NPL Sites with 1,3-Toluene Diisocyanate Contamination**



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5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes  $\geq 25,000$  pounds of any TRI chemical or otherwise uses  $>10,000$  pounds of a TRI chemical in a calendar year (EPA 2005).

TDI can enter the environment through industrial releases, such as through vent stacks of facilities handling this compound or as an accidental spillage to land or surface waters during transit (Duff 1983).

EPA's National Emission Inventory (NEI) database contains comprehensive and detailed estimates regarding sources that emit criteria air pollutants and their precursors, and hazardous air pollutants (HAPs) for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands. The NEI database includes point and non-point source emissions, on-road sources, non-road sources, and event sources such as emissions from wildfires. According to data from the 2014 NEI, 26,0381 pounds of MDI were released and 764,987 pounds of TDI were released (EPA 2014f).

### 6.2.1 Air

Estimated releases of 19,050, 737, and 381 pounds ( $\sim 8.64$ ,  $0.33$ , and  $0.17$  metric tons) of TDI (mixed isomers), 2,4-TDI, and 2,6-TDI to the atmosphere from 134, 53, and 29 domestic manufacturing and processing facilities in 2016 (TRI16 2017) are summarized in Tables 6-1, 6-2, and 6-3. Table 6-4 summarizes releases of 207,137 pounds ( $\sim 93.96$  metric tons) of the diisocyanates category, which consists of MDI and 19 other substances, to the atmosphere from 1,304 domestic manufacturing and processing facilities in 2016 (TRI16 2017).

There is no information on releases of MDI to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1998a).

During processing in a polyurethane foam plant, TDI emissions are removed from the workplace air by ventilation systems. However, any residual TDI leaving the plant vent stack is then dispersed into the atmosphere (Duff 1983).

Researchers studying six flexible foam manufacturing plants in Germany found that discharge concentrations of TDI emitted in factory exhaust gases ranged from 3 to 8 mg/m<sup>3</sup>. Concentrations

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**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Toluene Diisocyanate (Mixed Isomers)<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							Total release	
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site	
AR	1	373	0	0	0	0	373	0	373	
AZ	1	No data	No data	No data	No data	No data	No data	No data	No data	
CA	11	1,993	0	0	70	32	1,993	102	2,095	
DE	2	4	0	0	0	0	4	0	4	
FL	3	1,230	0	0	0	9,563	1,230	9,563	10,793	
GA	6	623	0	0	0	209	623	209	832	
IA	2	382	0	0	0	0	382	0	382	
IL	3	234	0	0	3	0	234	3	237	
IN	6	960	0	0	0	0	960	0	960	
KS	2	295	0	0	0	0	295	0	295	
KY	2	2,555	0	0	7	0	2,561	0	2,561	
LA	3	37	0	0	77	0	37	77	114	
MA	4	167	0	0	0	0	167	0	167	
MD	2	294	0	0	0	0	294	0	294	
ME	2	5	0	0	0	574	5	574	579	
MI	5	48	0	0	11	0	59	0	59	
MN	1	325	0	0	0	0	325	0	325	
MO	5	121	0	0	0	0	121	0	121	
MS	6	2,070	0	0	0	0	2,070	0	2,070	
NC	11	894	0	0	0	0	894	0	894	
NH	1	1	0	0	0	352	1	352	353	
NJ	7	625	0	0	0	9,129	625	9,129	9,754	
NM	2	214	0	0	0	2,195	214	2,195	2,409	
OH	8	468	0	0	14,195	0	14,363	300	14,663	
OR	1	122	0	0	0	0	122	0	122	
PA	7	1,547	0	0	0	430	1,547	430	1,977	
PR	1	No data	No data	No data	No data	No data	No data	No data	No data	
SC	2	No data	No data	No data	No data	No data	No data	No data	No data	
TN	4	676	0	0	0	0	676	0	676	
TX	14	916	0	892	223	52	916	1,167	2,084	
VA	4	610	0	0	0	0	610	0	610	
WA	2	276	0	0	0	0	276	0	276	
WI	2	500	0	0	0	0	500	0	500	

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**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Toluene Diisocyanate (Mixed Isomers)<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Reported amounts released in pounds per year <sup>b</sup>		
							Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
WV	1	486	0	0	0	0	486	0	486
Total	134	19,050	0	892	14,586	22,536	32,963	24,101	57,064

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI16 2017 (Data are from 2016)

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**Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-Toluene Diisocyanate<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
AL	1	5	0	0	0	0	5	0	5
AR	2	1	0	0	2	0	1	2	3
CO	1	5	0	0	0	0	5	0	5
CT	1	1	0	0	0	0	1	0	1
GA	2	255	250	0	0	0	505	0	505
IA	1	No data	No data	No data	No data	No data	No data	No data	No data
IL	1	No data	No data	No data	No data	No data	No data	No data	No data
IN	2	47	0	0	0	0	47	0	47
KS	1	No data	No data	No data	No data	No data	No data	No data	No data
KY	1	10	0	0	0	0	10	0	10
MA	1	0	0	0	0	545	0	545	545
MD	1	10	0	0	0	0	10	0	10
MI	5	28	0	0	0	0	28	0	28
MN	1	0	0	0	1,020	0	0	1,020	1,020
MO	2	59	0	0	0	0	59	0	59
MS	4	173	0	0	0	0	173	0	173
NC	1	No data	No data	No data	No data	No data	No data	No data	No data
NE	1	22	0	0	0	0	22	0	22
NJ	3	10	0	0	0	0	10	0	10
NY	1	10	0	0	0	0	10	0	10
OH	5	28	0	0	4,745	0	4,773	0	4,773
PA	4	1	0	0	0	540	1	540	541
RI	1	No data	No data	No data	No data	No data	No data	No data	No data
TN	2	23	0	0	0	250	23	250	273
TX	3	22	0	0	0	0	22	0	22
UT	1	No data	No data	No data	No data	No data	No data	No data	No data
VA	1	21	0	0	0	0	21	0	21
WI	2	1	0	0	0	0	1	0	1

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**Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-Toluene Diisocyanate<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Reported amounts released in pounds per year <sup>b</sup>		
							Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
WV	1	2	0	0	0	0	2	0	2
Total	53	737	250	0	5,767	1,335	5,732	2,357	8,088

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI16 2017 (Data are from 2016)

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**Table 6-3. Releases to the Environment from Facilities that Produce, Process, or Use 2,6-Toluene Diisocyanate<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							Total release	
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site	
AR	1	No data	No data	No data	No data	No data	No data	No data	No data	No data
CO	1	1	0	0	0	0	1	0	1	1
GA	1	255	5	0	0	0	260	0	260	260
IL	1	No data	No data	No data	No data	No data	No data	No data	No data	No data
IN	1	11	0	0	0	0	11	0	11	11
KS	1	No data	No data	No data	No data	No data	No data	No data	No data	No data
MA	1	1	0	0	0	2,365	1	2,365	2,366	2,366
MD	1	10	0	0	0	0	10	0	10	10
MI	4	8	0	0	0	0	8	0	8	8
MO	2	2	0	0	0	0	2	0	2	2
MS	2	27	0	0	0	0	27	0	27	27
NE	1	11	0	0	0	0	11	0	11	11
OH	5	3	0	0	1,726	0	1,729	0	1,730	1,730
PA	1	No data	No data	No data	No data	No data	No data	No data	No data	No data
TN	2	47	0	0	0	250	47	250	297	297
TX	1	No data	No data	No data	No data	No data	No data	No data	No data	No data
WI	2	3	0	0	0	0	3	0	3	3
WV	1	2	0	0	0	0	2	0	2	2
<b>Total</b>	<b>29</b>	<b>381</b>	<b>5</b>	<b>0</b>	<b>1,726</b>	<b>2,615</b>	<b>2,112</b>	<b>2,615</b>	<b>4,727</b>	<b>4,727</b>

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI16 2017 (Data are from 2016)



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**Table 6-4. Releases to the Environment from Facilities that Produce, Process, or Use Diisocyanates<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>					Total release		
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
RI	7	0	0	0	0	5,512	0	5,512	5,512
SC	32	2,097	0	0	5,013	0	2,097	5,013	7,110
SD	2	No data	No data	No data	No data	No data	No data	No data	No data
TN	58	1,687	0	0	102,845	622	1,687	103,467	105,154
TX	85	6,936	38	0	130,388	5,839	87,152	56,049	143,201
UT	14	1,154	0	0	0	723	1,154	723	1,877
VA	20	564	0	0	2	5,609	564	5,611	6,175
VT	1	No data	No data	No data	No data	No data	No data	No data	No data
WA	11	272	0	0	0	250	272	250	522
WI	71	2,234	0	0	10,263	121,093	2,234	131,356	133,590
WV	13	6,634	0	0	44,014	1,500	6,634	45,514	52,147
Total	1,304	207,137	43	0	1,709,025	538,106	353,646	2,100,666	2,454,312

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI16 2017 (Data are from 2016)

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released were dependent on the foam density produced at a given time. The study reported that only 0.005% of all of the TDI processed within the facilities was lost to the atmosphere (Duff 1983).

It has been reported that 2,6-TDI dominates TDI emissions to air from newly manufactured polyurethane foams, despite the 80:20 ratio of 2,4-TDI to 2,6-TDI in the original TDI formulation used. This is due to the lower reactivity of 2,6-TDI (Kelly et al. 1999). This information mainly relates to releases to indoor air.

Due to the diversity of applications and wide variety of MDI formulations, typical emission levels of MDI are difficult to quantify. Emissions may be comprised of MDI vapor, MDI aerosol, or a reacting mix of aerosol and vapor, which is predominantly converted to polyurethane. Emission levels are generally much lower than those of TDI flexible foam processes. A survey conducted in the United Kingdom of polyurethane production facilities (comprising 50% of total U.K. rigid foam manufacture) producing insulation board by spray and liquid laydown techniques and rigid foam slabstock produced by both continuous and discontinuous processes found typical emission levels to be  $\leq 0.2 \text{ mg/m}^3$  (Gilbert 1988). The American Chemistry Council Center for the Polyurethane Industry has developed an emissions calculator to estimate emissions from typical process applications and activities, which may be downloaded at <https://polyurethane.americanchemistry.com>. Tury et al. (2003) estimated that typical environmental loadings are less than 1 gram per metric ton of MDI used and about 25 grams per metric ton of TDI used.

Developments in polyurethane processing to control emissions of TDI and MDI include increasing the use of reaction injection moulding closed-circuit technology and advancement in the carbon absorption of emissions (Gilbert 1988).

During the application of MDI in foam or film coating of surfaces by spray gun techniques, the measured environmental contamination during application showed levels of total MDI as high as  $5 \text{ mg/m}^3$ . More than 95% of air samples contained MDI particulates of respirable size, and counts were from 2 to 8 million parts/feet<sup>3</sup> (ACGIH 2001).

Available information on the releases of TDI and MDI to the air in occupational settings and indoor air, along with exposure levels, are discussed in Section 6.5.

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**6.2.2 Water**

Estimated releases of 0, 250, and 5 pounds (~0, 0.11, and 0.002 metric tons) of TDI (mixed isomers), 2,4-TDI, and 2,6-TDI to surface water from 134, 53, and 29 domestic manufacturing and processing facilities in 2016 (TRI16 2017) are summarized in Tables 6-1, 6-2, and 6-3. Table 6-4 summarizes releases of 43 pounds (~0.02 metric tons) of the diisocyanates category, which consists of MDI and 19 other substances, to surface water from 1,304 domestic manufacturing and processing facilities in 2016 (TRI16 2017).

Because of their reactivity with water, TDI and MDI are not likely to be found in waste water streams or in other aquatic environments, except possibly near point sources after immediate release.

**6.2.3 Soil**

Estimated releases of 14,586, 5,767, and 1,726 pounds (~6.62, 2.62, and 0.78 metric tons) of TDI (mixed isomers), 2,4-TDI, and 2,6-TDI to soils from 134, 53, and 29 domestic manufacturing and processing facilities in 2016 (TRI16 2017) are summarized in Tables 6-1, 6-2, and 6-3. Table 6-4 summarizes releases of 1,709,025 pounds (~775.2 metric tons) of the diisocyanates category, which consists of MDI and 19 other substances, to soils from 1,304 domestic manufacturing and processing facilities in 2016 (TRI16 2017). Estimated releases of 892, 0, and 0 pounds (~0.4, 0, and 0 metric tons) of TDI (mixed isomers), 2,4-TDI, and 2,6-TDI via underground injection from 134, 53, and 29 domestic manufacturing and processing facilities in 2016 (TRI16 2017) are summarized in Tables 6-1, 6-2, and 6-3. There were no releases of the diisocyanates category, which consists of MDI and 19 other substances, via underground injection (TRI16 2017). These releases are summarized in Tables 6-4.

**6.3 ENVIRONMENTAL FATE**

Diisocyanates are extremely reactive compounds (Geens et al. 2012), especially with water. The dominant process affecting the overall environmental fate, transport, and bioaccumulation potential of diisocyanates is hydrolysis (EPA 2011b).

**6.3.1 Transport and Partitioning**

Based on their vapor pressures (see Table 4-2), MDI is expected to exist in both the vapor and particulate phases in the ambient atmosphere, while TDI isomers are expected to exist solely as a vapor (Bidleman

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1988; Eisenreich et al. 1981). Based on a study of the atmospheric hydrolysis of TDI (Dyson and Hermann 1971), it is likely that wet deposition of particulate-phase MDI from the atmosphere is not an important removal process because of its reactivity with water. TDI and MDI may be stable enough to be transported some distances under conditions of low humidity (EPA 2011a, 2011b); however, no studies were found on long distance transport in the available literature.

If released to water or moist soil/sediment, TDI and MDI will rapidly undergo hydrolysis (EPA 2011a, 2011b), and therefore, the potential to volatilize to air and leaching or adsorption to soil and sediments will be negligible. The rapid hydrolysis of these compounds also suggests that they will not bioconcentrate in aquatic organisms or bioaccumulate in the food chain. This is supported by a study using three artificial ponds to determine the fate and biological effects from a simulated accidental pollution event with MDI on an aquatic ecosystem. MDI did not accumulate in fish after 119 days post-MDI addition due to its rapid reaction on the sediment surface with water to form polyurea and carbon dioxide (Heimbach et al. 1996). Also, during another study by the International Isocyanate Institute (1981), no accumulation of TDI or its respective amine hydrolysis product was found in the whole bodies of carp after 8 weeks of exposure in a model river system with an initial TDI concentration of 0.1 ppm. No bioconcentration factors (BCFs) for TDI or MDI were found in the available literature.

Volatilization from dry soil surfaces is not expected to be an important fate process for TDI, TDI isomers, or MDI based on their vapor pressures (see Table 4-2).

### 6.3.2 Transformation and Degradation

TDI and MDI are extremely reactive compounds and are well known to react with water (Yakabe et al. 1999). Hydrolysis is the dominant environmental process for TDI and MDI (EPA 2011a, 2011b), forming the respective amines, which in turn may react with more diisocyanates to produce inert, insoluble polyureas (WHO 2000).

#### 6.3.2.1 Air

Kelly et al. (1994) reported that TDI and MDI have half-lives of <1 day due to reaction with OH radicals in the atmosphere. The International Isocyanate Institute (1987) also measured the rate constant for the reaction of TDI with OH radicals in the atmosphere to be  $7.4 \times 10^{-12}$  cm<sup>3</sup>/molecule-second, which corresponds to a half-life of 26 hours. These experimental half-lives are in good agreement with estimated half-lives for the reaction with photochemically produced hydroxyl radicals of 20 and 11 hours

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based on vapor phase reaction rate constants of  $7.07 \times 10^{-12}$  and  $1.2 \times 10^{-11}$   $\text{cm}^3/\text{molecule-second}$  at  $25^\circ\text{C}$ , for TDI and MDI respectively, determined using a structure estimation method (HSDB 2012). Aromatic isocyanates, such as TDI and MDI, do not absorb light in the ultraviolet region (wavelengths  $>290$  nm) (Lyman et al. 1990), and therefore, direct photolysis by sunlight is not expected to be an important degradation process in the atmosphere.

In an experiment using an environmental chamber to assess the impact of photolysis, reaction with free radicals, and adsorption onto particulate matter as atmospheric removal processes of TDI, the loss rate of TDI in irradiated clean air was first order, with a half-life of 3.3 hours. It was shown that free radicals were responsible for removal, not photolysis. The removal rate was not altered by the addition of an urban surrogate hydrocarbon mixture to simulate urban air, demonstrating that adsorption onto particulate matter had minimal effect (Duff 1985).

Gas-phase TDI was originally thought to react with water vapor in the atmosphere to form TDA. One study measured a maximum reduction of 50% for TDI concentrations of 0.4 and 0.034 ppm after 8 seconds and showed that the disappearance of TDI in air depends almost solely on the water vapor concentration. The percent reduction of TDI increased 3.2% per unit increase in absolute humidity (g water/kg dry air) and a 50% reduction was obtained at 15 g water/kg dry air (Dyson and Hermann 1971). A study conducted by Holdren et al. (1984) contradicts early findings of TDI reaction with water vapor, indicating that TDI loss was likely due to gas-surface or heterogeneous reactions in reaction chambers with large surface to volume ratios. In this study, gas-phase reactions between TDI and water vapor were observed in a room-sized environmental chamber. It was found that the loss rate of TDI was independent of humidity, measured over a relative humidity range of 7–70%, and that no TDA or other hydrolysis product could be detected. Loss was stated to be caused by the adsorption of TDI to the chamber walls. These studies, however, did not investigate the condensed phase atmospheric hydrolysis of TDI, such as reactions with rain drops, fog, or clouds. The average hydrolysis half-lives of TDI and MDI are on the order of a few minutes to a few hours (HSDB 2012), which suggests that the heterogeneous condensed phase atmospheric hydrolysis of these compounds may be rapid.

### 6.3.2.2 Water

Diisocyanates that are released to water hydrolyze rapidly, forming amines that can react with residual diisocyanates, ultimately producing inert insoluble polyureas (WHO 2000). Polyureas have been reported to be the main degradation products resulting from environmental contact of TDI and MDI with water,

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with smaller amounts of soluble diamines being formed (Yakabe et al. 1999). Hydrolysis half-lives of MDI and TDI have been measured to be on the order of a few minutes to a few hours (HSDB 2012). The hydrolysis half-lives of polyureas are on the order of millennia (Sendjarevic et al. 2004).

TDI added to a model river system and a seawater system at initial concentrations of 50 ppm was monitored over the course of 30 days. In the freshwater system, the concentration of TDI declined rapidly ranging from not detected to 0.1 ppm after 1 day. Low levels of diamine degradation products were detectable only during early sampling periods. In the seawater system, the concentration of TDI also declined rapidly to 0.1 ppm after 1 day (Duff 1983). The concentration of MDI added to a model marine system and a model river to simulate spill situations fell to a maximum of 5% of the initial value within 1 day (Gilbert 1988).

Yakabe et al. (1999) examined the kinetics of the hydrolysis of TDI and MDI in well-stirred and unstirred environments, with unstirred reactions representing conditions of an environmental spill. The reported half-life was 30 seconds for 28 mg/L of TDI in a well-stirred water system, while with less efficient stirring, the half-life for TDI was in the region of 3–5 minutes. At a loading of 1,000 mg/L, the half-lives of 2,4- and 2,6-TDI were about 0.7 and 1.7 hours, respectively, demonstrating that reaction rate was a function of the concentration of TDI. After 30 minutes in well-stirred water, the extent of TDI reacted varied from 85% at 10 mg/L to 20% at 10,000 mg/L. The observed half-life of about 20 hours for polymeric MDI was much slower than TDI, due to its greater viscosity. Because of the viscosity and difficulty mixing with water, the reaction rate was affected by surface area contact with water and not on concentration. The well-stirred, homogeneous environments showed that TDI and MDI are expected to be rapidly degraded in water and never attain any significant concentrations. However, the complete reaction of both TDI and MDI may take several weeks under poorly mixed conditions, typical of an environmental spill, due to the formation of insoluble, solid polyurea crusts. These predictions are consistent with field observations. For example, when 14 tons of TDI were accidentally spilled onto marshy woodland in 1975, the material was covered with wet sand and monitored for 6 years. The TDI was converted to polyureas within 6 weeks, while no TDA was detected in soil (<3 mg/kg) or water (<50 µg/L) at any point and no adverse environmental effects were reported. In another accidental spill involving 20 tons of TDI into a fast-moving stream, the TDI reacted to form polyureas that were distributed for 2–3 km downstream, while TDA was detected at 5 mg/L downstream after 2 days, but fell below the detection limit after 2 weeks. In 1991, about 50 tons of prepolymeric MDI was spilled into a river and a majority was reported to have formed solid polyureas when it was scooped out after 2 days. The EPA testing of the river ceased after 3 days and the material in the river was declared nonhazardous.

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During a study using three artificial ponds to determine the fate and biological effects from a simulated accidental pollution event with MDI on an aquatic ecosystem, MDI was not detected in water after 119 days post-MDI addition due to its rapid reaction on the sediment surface with water to form polyurea and carbon dioxide (Heimbach et al. 1996).

TDI and MDI are expected to be hydrolyzed much more quickly than they would undergo biodegradation in water, although the resulting diamines should be subject to biodegradation (HSDB 2012). TDI, MDI, and prepolymeric MDI, at concentrations of 50 ppm each, were reported to be completely biodegraded within 15 days at 25 °C in a freshwater model river system with bottom sludge, and in a saltwater system, TDI could not be detected after 4 days, while MDI disappeared after 1 day (International Isocyanate Institute 1980, 1983, 1987). However, hydrolysis was not taken into account during these experiments, and it should be the predominant degradation process, not biodegradation.

### 6.3.2.3 Sediment and Soil

No studies of the transformation and degradation of TDI and MDI in dry soil could be located in the available literature. When monomeric MDI, and under many circumstances TDI, are handled as a liquid, they will solidify on contact with soil (Gilbert 1988). TDI and MDI will hydrolyze in moist soil and sediment due to their rapid reaction with water to form diamines and polyureas (HSDB 2012; WHO 2000) and hydrolysis is expected to occur much more rapidly than biodegradation (HSDB 2012). Therefore, reaction with water is expected to be the only significant fate process in moist soil and sediment.

In a laboratory experiment involving TDI in undisturbed moist sand, 5.5 and 3.5% of unreacted TDI remained after 24 hours and 8 days, respectively, indicating that TDI is converted to polyureas at a decreasing rate. The diamine hydrolysis product was not found above the detection limit (0.01 ppm). These results suggest the encapsulation of unreacted TDI within a rapidly forming water-insoluble polyurea crust (Gilbert 1988).

Ten days after a spill of 13 tons of TDI onto swampy, wet forest soil, the TDI solidified and the area was covered with sand. The concentration of TDI and degradation product, TDA, combined declined from the parts per thousand to the parts per million range in the soil between 10 days and 12 weeks after the spill.

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After 6 years, soil samples showed only TDI-derived polyureas (Brochhagen and Grieveson 1984; HSDB 2012).

#### 6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to TDI and MDI depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of TDI and MDI in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on TDI and MDI levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring TDI and MDI in a variety of environmental media are detailed in Chapter 7.

##### 6.4.1 Air

Most monitored TDI and MDI concentrations in air are found in occupational settings (see Section 6.5). Limited data were located in the available literature on measured concentration of TDI and MDI in the ambient atmosphere, likely due to their relatively short half-lives (<1 day) (Kelly et al. 1994) from reaction with hydroxyl radicals.

Detectable concentrations may be found near point sources of TDI and MDI, such as near waste streams from manufacturing and processing facilities and hazardous waste sites. In an exposure assessment to TDI from a polyurethane foam manufacturing plant in North Carolina conducted in 1997, concentrations of TDI in ambient air were as high as 29 ppbv at a monitoring station approximately 100 feet outside the facilities fence line (MMWR 1998). Stack exhaust streams from a polyurethane foam manufacturing plant had reported concentrations of 100–17,700  $\mu\text{g}/\text{m}^3$  of TDI (HSDB 2012). In a study conducted by the North Carolina Department of Health and Human services from 2007 to 2010, TDI was detected in only one air sample at a concentration of 0.001 ppbv near polyurethane foam plants in North Carolina (NCDHHS 2017). Levels of MDI and TDI were monitored at six schools in the United States in order to assess outdoor air quality in representative schools (EPA 2017). MDI and TDI were not detected in the outdoor air near these schools.

A monitoring study conducted from 1984 to 1999 analyzed 4,551 area and 3,583 personal air samples in which airborne MDI concentrations were measured in a wide variety of manufacturing processes that use either polymeric MDI (PMDI) or monomeric (pure) MDI (Booth et al. 2009). Nearly 50% of the area

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samples were below the level of quantification. Detectable levels ranged from  $8.5 \times 10^{-5}$  to  $9.5 \text{ mg/m}^3$ , with an arithmetic mean (standard deviation) of  $0.057 (0.32) \text{ mg/m}^3$  (Booth et al 2009).

Both MDI and TDI are included in EPA's National Air Toxics Assessment (NATA), which is an ongoing comprehensive evaluation of air toxics in the United States. Emissions inventory statistics are collected from data reported by large individual facilities (point sources) and estimated for area and mobile sources using various emissions inventory models. Ambient air levels are estimated using the air dispersion model, AERMOD. Nationwide estimated average concentrations of MDI and TDI from point sources were  $7.3 \times 10^{-5}$  and  $1.4 \times 10^{-5} \text{ mg/m}^3$ , respectively, for the 2011 assessment (EPA 2015).

#### 6.4.2 Water

No information on the concentration of TDI or MDI in natural water was located in the available literature. Significant concentrations are not likely to be found in the aquatic environment due to the rapid hydrolysis of these compounds; however, small amounts may be detected near point sources such as industrial waste streams and hazardous waste sites immediately after release.

#### 6.4.3 Sediment and Soil

No information on the concentration of TDI or MDI in soil or sediment was located in the available literature. Significant concentrations are not likely to be found in moist soil or sediment due to the rapid hydrolysis of these compounds; however, small amounts may be detected near point sources such as industrial waste streams and hazardous waste sites.

#### 6.4.4 Other Environmental Media

Commercial TDI has been detected in a urethane foam fabric coating in concentrations of  $<200 \text{ mg/kg}$  (HSDB 2012). Application of a water sealant to a concrete slab resulted in measured TDI emission rates of 319,000 or 257,000  $\mu\text{g/m}^2/\text{hour}$  in 30-minute tests at  $21^\circ\text{C}$  and 360,000  $\mu\text{g/m}^2/\text{hour}$  in a 1-hour test at  $27^\circ\text{C}$  (Kelly et al. 1999). These emission rates corresponded to 35, 38, and 179  $\mu\text{g}$  of total TDI emitted, respectively; 75.2, 97.8, and 79.2% of the TDI emitted was 2,6-TDI. MDI emissions were detected at 60 ppt for aluminum and wood substrates cured with polyurethane glue in the first 8 hours of sampling, but was below the detection limit (20 ppt) thereafter (Parekh and Karoly 2001). No data on the concentrations of TDI or MDI in other environmental media, including food, were found in the available

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literature. Due to the rapid hydrolysis of these compounds, TDI and MDI will not bioaccumulate in the food chain and are therefore not expected to be found in significant concentration in fish and foods.

**6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

Exposure of the general population to TDI from its use in polyurethane products in household materials was once thought to be negligible. An increase in the number of uncured diisocyanate-containing products used by consumers has been noted by researchers. These researchers also noted that exposure of the general population to TDI and MDI could potentially result from industrial exposures, as well as from the use of consumer products containing uncured TDI and MDI (EPA 2011a). In a study of the emission rates from polyurethane household product and materials, TDI emissions were not detectable from carpet padding, mattress and sheet foam, furniture cushion foam, spray varnishes, brush-on varnishes, general purpose water sealers, mastic construction adhesive, or high-performance caulk (Kelly et al. 1999). The only product with a large, detectable TDI emission rate was a concrete sealant. Total TDI emitted from these samples were 35 and 38  $\mu\text{g}$  over 30 minutes at 21°C and 179  $\mu\text{g}$  over 1 hour at 27°C, where 75–98% of the TDI released was the 2,6-isomer (Kelly et al. 1999). The predominant possible sources of exposure to MDI to the general population comes from its use in the construction and installation of foams, glue and putty, dyes, varnishes, and furniture (EPA 2011a).

Due to the concern about the presence of TDI and MDI in an uncured form in products used by or around consumers, the EPA created Action Plans to address the use of MDI, TDI, and related compounds that may result in consumer and general population exposures. The Action Plans are intended to describe courses of action to pursue to mitigate concerns over exposure (EPA 2011a, 2011b). It should be noted that these Action Plans are focused on concerns for unreacted uncured TDI and MDI products, as the completely cured products are considered inert and nontoxic.

Exposure to TDI and MDI is mainly an occupational problem due to their manufacturing and processing in many different industries. Diisocyanates are used in the production of polyurethane foam during foaming, casting, spraying, and other processes. Exposure may also occur after production when the polymer is processed. Thermal degradation of polyurethane foam during processes such as heat cutting of foam blocks, flame lamination with textiles, and welding, cutting, or grinding of polyurethane-coated metal, can also release diisocyanates into the air (Dahlin et al. 2008). MDI emission levels due to thermal degradation from the use of polyurethane core binder materials in foundry molds was reported to be <0.02–1.0 mg/kg (Renman et al. 1986).

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Workers may be predominantly exposed to TDI and MDI by inhalation of aerosol and vapor (TDI only). Another route is through dermal exposure (Tinnerberg et al. 1997). Most occupational diisocyanate exposure studies have focused on TDI because of its widespread industrial use in the manufacture of polyurethane foam (Tinnerberg et al. 1997). A common way of assessing workplace exposure is through air monitoring. The average air concentration of TDI measured in a TDI flexible foam plant was  $29.8 \mu\text{g}/\text{m}^3$ , while the highest exposure peak was approximately  $3 \text{ mg TDI}/\text{m}^3$  (Tinnerberg et al. 1997). Mean TDI levels ranged from 0.7 to  $180 \mu\text{g}/\text{m}^3$  for workplace air in U.S. factories manufacturing TDI between 1973 and 1978 (IARC 1985). Mean TDI levels ranged from not detected to  $540 \mu\text{g}/\text{m}^3$  for personal and workplace air in U.S. factories producing polyurethane foam between 1972 and 1981 (IARC 1985). A monitoring study conducted from 1984 to 1999 analyzed 3,583 personal air samples in which airborne MDI concentrations were measured in a wide variety of manufacturing processes that use either PMDI or monomeric (pure) MDI (Booth et al. 2009). Nearly 75% of the personal samples were below the level of quantification, and detectable levels ranged from  $2 \times 10^{-5}$  to  $3.9 \text{ mg}/\text{m}^3$  (Booth et al. 2009). The highest airborne levels tended to occur when MDI was heated or sprayed, and control measures such as appropriate ventilation and protective equipment were recommended to reduce occupational exposures.

Diem et al. (1982) performed a 5-year (April 1973 to October 1978) longitudinal study of 277 workers in a new TDI manufacturing plant in Louisiana in which over 2,000 personal air samples were measured for TDI concentrations. The 8-hour TWAs ranged from 0.1 to 25 ppb. Different jobs in the facility fell into low, moderate, and high TWA exposure categories. The average time periods spent above 20 ppb were 1.3, 8.6, and 28.2 minutes per 8-hour shift for workers in the low, moderate, and high exposure categories, respectively.

In a study conducted in 2000 involving a plastic production plant using TDI, the concentration of TDI detected in the air ranged from 0.007 to  $0.016 \text{ mg}/\text{m}^3$  (Bilban 2004). Ambient air concentrations that included 60 personal breathing zone samples collected from workers in a petrochemical industrial complex in Korea contained mean TDI and MDI concentrations of 0.0174 and  $0.0013 \text{ mg}/\text{m}^3$ , respectively (Jang et al. 2000). Tarlo et al. 1997 reported an air sampling study of 223 companies in Ontario, Canada that had potential diisocyanate exposure to workers during 1984–1988. The highest exposure levels of MDI in 123 companies were  $<0.005 \text{ ppm}$  in 95 companies and  $\geq 0.005 \text{ ppm}$  in 38 companies. The highest exposure levels of TDI in 78 companies were  $<0.005 \text{ ppm}$  in 58 companies and  $\geq 0.005 \text{ ppm}$  in 20 companies (Tarlo et al. 1997).

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At a facility that manufactures refrigerated tractor trailers in the United States, MDI was detected in the personal breathing zone of workers in the polyurethane foaming area at levels ranging from not detected to  $9.1 \mu\text{g}/\text{m}^3$ , with a mean concentration of  $1.5 \mu\text{g}/\text{m}^3$  (Lushniak et al. 1998). Workplace air sampled during spraying operations had MDI concentrations of 21.4, 5.9, and  $2.1 \text{ mg}/\text{m}^3$  at distances of 2, 6, and 10 m away from production machinery, respectively (D'Eril et al. 1995).

A study determining the workplace air exposure concentrations of MDI to sprayers, helpers, and personnel produced during the spray application of polyurethane foam during typical indoor and outdoor construction operations was conducted by Bilan et al. (1989). In outdoor locations (three rooftops), sprayers were exposed to MDI air concentrations ranging from 0.003 to 0.05 ppm, helpers were exposed to 0.013–0.038 ppm, area personnel 5–40 feet away were exposed to 0.003–0.006 ppm, and area personnel 45 feet away were in an area with no detectable MDI. In five indoor locations ranging from 750 to 3,375 square feet, sprayers were exposed to MDI air concentrations ranging from 0.008 to 0.129 ppm, helpers were exposed to 0.001–0.018 ppm, area personnel 6–<25 feet away were exposed to 0.007–0.093 ppm, and area personnel 25–100 feet away were in an area with no detectable MDI to 0.002 ppm. This study determined that the dominant factor in worker exposure to MDI was the distance from the spray operation and the time spent near the spray operation (Bilan et al. 1989). In another study measuring the exposure of sprayers and helpers to MDI during applications of polyurethane foam to dwellings and office buildings, MDI was measured in the personal air samples of sprayers at concentrations of 0.018–0.077 and  $0.017\text{--}0.400 \text{ mg}/\text{m}^3$  during outdoor and indoor applications, respectively (Crespo and Galan 1999). Helpers were exposed to MDI concentrations of 0.034–0.045 and  $0.025\text{--}0.308 \text{ mg}/\text{m}^3$  during outdoor and indoor applications, respectively. Maximum airborne MDI concentrations measured 15, 45, and >45 minutes after spray foam application inside five single-family homes were  $0.019 \text{ mg}/\text{m}^3$ ,  $0.003 \text{ mg}/\text{m}^3$ , and below the limit of quantification (LOQ) ( $0.036 \mu\text{g}/\text{sample}$ ), respectively (Lesage et al. 2007). Measured MDI concentrations sampled 1–3, 3–6, and 6–12 m away from application in this study were 0.147–1.55, 0.005–1.12, and <LOQ– $0.822 \text{ mg}/\text{m}^3$ , respectively (Lesage et al. 2007). During the application of MDI in foam or film coating of surfaces by spray gun techniques, >95% of air samples contained MDI particulates of respirable size, and counts were from 2 to 8 million parts/feet<sup>3</sup>.

In general, MDI levels decreased rapidly and were undetectable 1 hour postapplication. Many of the airborne MDI samples collected in the breathing zone of the applicators during spraying exceeded the OSHA permissible exposure limit (PEL) of  $0.2 \text{ mg}/\text{m}^3$ , and thus, there are recommendations that workers use an air-purifying respirator equipped with a combination organic vapor cartridge and prefilter during

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application. Additionally, in order to decrease dermal exposure, personal protective equipment such as gloves, coveralls, and goggles are recommended. Additional industry recommendations when spray polyurethane foam (SPF) insulation is being applied to buildings are to vacate the structure and ventilate the area following installation. Building occupants should not return until after the manufacturer's recommended re-occupancy time (typically 24 hours) has elapsed.

Air monitoring methods may not fully characterize exposure patterns to workers, as they do not take into account possible dermal absorption (Austin 2007). In a study of 19 workers at an iron foundry, the average personal air concentration of MDI was  $0.55 \mu\text{g}/\text{m}^3$  and dermal exposure to MDI ranged from 0.006 to  $0.34 \mu\text{g}$ , indicating that dermal exposure can be a significant exposure pathway (Liljelind et al. 2010). Therefore, biological markers of isocyanates in urine and plasma may be valuable indicators in the work environment (Austin 2007). TDI in biological samples are hydrolyzed to form TDA for analysis (Tinnerberg et al. 1997). Austin (2007) conducted a study that showed how urinary TDA was a useful indication of the contribution of skin exposure to total TDI exposure in a polyurethane foam plant using 80:20 mixture of 2,4- and 2,6-TDI. This was done by comparing urinary TDA levels in two groups: 13 workers who had physical contact with uncured polyurethane foam (handlers) and 13 workers in the same plant environment who had no physical contact with uncured foam (non-handlers) on the day of sampling. Both groups were exposed to the same TDI air concentrations, ranging from  $<3.5$  to  $8.4 \mu\text{g}/\text{m}^3$ . In hydrolyzed post-shift urine samples, 10 handlers were found to have urinary TDA above detection limits with a mean level of  $2.21 \mu\text{mol}/\text{mol}$  creatinine, compared to only 2 non-handlers (mean  $0.11 \mu\text{mol}/\text{mol}$  creatinine).

Hydrolyzed post-shift urine samples collected from 15 workers in a polyurethane foam plant had TDA concentrations of  $0.6$ – $4.0 \mu\text{g}/\text{L}$ , while all urine samples from 12 people with no known history of TDI exposure had urinary TDA concentrations of below the detection limit of  $0.1 \mu\text{g}/\text{L}$  (Carbonnelle et al. 1996).

In a study of four exposed workers and one volunteer working 8-hour shifts in a TDI flexible foam plant using an 80:20 mixture of 2,4- and 2,6-TDI, plasma concentrations were  $1$ – $38$  and  $7$ – $24 \mu\text{g}/\text{L}$  for 2,4- and 2,6-TDA, respectively. Over a 3-day period, the individual plasma levels among the workers varied between 7 and 73%. An increase in plasma TDA for each workday was observed for the volunteer, and reached a maximum concentration 24 hours after the last exposure. The half-life in plasma was estimated to be about 10 days (Tinnerberg et al. 1997). In the urine samples of the workers, TDA concentrations varied greatly with time and exposure, reaching a maximum shortly after exposure. Measured

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concentrations of TDA in urine ranged from not detected to about 2.0  $\mu\text{g}/\text{mmol}$  creatinine (Tinnerberg et al. 1997). Lind et al. (1996) performed a study monitoring 2,4- and 2,6-TDA in plasma from 11 workers at two separate flexible foam polyurethane production plants after their occupational exposure to 2,4- and 2,6-TDI. The TDI concentration and relative percent concentrations of 2,4- and 2,6-TDI were 0.4–4  $\mu\text{g}/\text{m}^3$  and 60/40–5/95% in plant 1, respectively, and 10–120  $\mu\text{g}/\text{m}^3$  and 65/35–30/70% in plant 2, respectively. The lower exposure levels in plant 1 compared to plant 2 was reflected in the plasma TDA concentrations. Plasma 2,4- and 2,6-TDA concentrations were 0.4–1.3 and 1.8–5.6  $\text{ng}/\text{mL}$ , respectively, in plant 1 and 2–23 and 7.0–23  $\text{ng}/\text{mL}$ , respectively, in plant 2 before a summer holiday.

In a study comparing the exposure to TDI in air and the concentration of TDA in urine of nine workers from two production lines in a polyurethane foam production plant using an 80:20 mixture of 2,4- and 2,6-TDI, it was reported that exposure to TDI in personal air during a shift resulted in an increase in TDA in the urine of the workers (Geens et al. 2012). Sampled over 4 days, personal air TDI concentrations ranged from 4.2 to 141.9  $\mu\text{g}/\text{m}^3$  and hydrolyzed pre- and post-shift urine TDA concentrations were 1.0–19.5 and 4.4–142.6  $\mu\text{g}/\text{L}$ , respectively (Geens et al. 2012). Kaaria et al. (2001a) performed another study on the determination of airborne TDI and urinary 2,4- and 2,6-TDA during the production of flexible foam in two separate plants in which samples were collected during one work shift on 2 consecutive days. Plant 1, which applied high-pressure molding, had TDI air concentrations ranging from not detected (LOD 0.2  $\mu\text{g}/\text{m}^3$ ) to 230  $\mu\text{g}/\text{m}^3$ , while Plant 2, which applied low-pressure molding, had concentrations ranging from not detected to 41  $\mu\text{g}/\text{m}^3$ . The proportions of 2,4- and 2,6-TDI in the total exposure varied during different stages of the production process, but 2,6-TDI constituted about 75% of all TDI detected. In urine samples collected from 17 workers, total TDA (2,4- and 2,6-TDA) was detected at concentrations of 0.11–39  $\text{nmol}/\text{mmol}$  creatinine in Plant 1 and <0.05–7.1  $\text{nmol}/\text{mmol}$  creatinine in Plant 2. The higher urinary TDA concentrations in Plant 1 compared to Plant 2 parallels the higher TDI concentrations in Plant 1. Kaaria et al. (2001b) observed similar results in the study of exposure to airborne MDI during the molding of rigid polyurethane foam in a refrigerator and freezer manufacturing plant. MDI was below the limit of detection (3  $\mu\text{g}/\text{m}^3$ ) in 64% of air samples collected from the workers' breathing zone, with detectable samples containing 0.03–3.3  $\mu\text{g}/\text{m}^3$  MDI. However, detectable amounts of urinary MDA were found in 97% of urine samples ranging from 0.12 to 0.20  $\text{nmol}/\text{mmol}$  creatinine, showing that monitoring of MDA in urine may be a useful method of assessing MDI exposure in workplaces that have low MDI concentrations in air.

During a study assessing MDI exposure by monitoring a specific MDI hemoglobin adduct, 5-isopropyl-3-[4-(4-aminobenzyl)phenyl]hydantoin (ABP-Val-Hyd), in human blood, blood samples from 25 workers

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from an MDI plant had ABP-Val-Hyd marker concentrations ranging from 0.15 to 16.2 pmol/g, while 40 people from the general population with no known exposure had no detectable amounts of ABP-Val-Hyd (limit of detection of 0.062 pmol/g) (Gries and Leng 2013).

The National Occupational Exposure Survey (NOES) conducted by NIOSH in 1983 estimated that 53,321 workers employed at 2,896 facilities were potentially exposed to MDI in the United States (RTECS 2009a). The 1983 NOES also estimated that 10,921 and 2,872 workers employed at 838 and 415 facilities were potentially exposed to 2,4- and 2,6-TDI in the United States, respectively (RTECS 2009b, 2009c). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace.

### 6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume than adults. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and may spend more time outdoors. Children also are generally closer to the ground and have not yet developed the adult capacity to judge and take actions to avoid hazards (NRC 1993).

Exposure to TDI and MDI is mainly an occupational problem due to their manufacturing and processing in many different industries. There is limited data pertaining to the use and exposure of consumer and commercial products containing uncured TDI and MDI. Because of this, exposure levels to children have not been well characterized (EPA 2011a, 2011b).

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**6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES**

Exposure to TDI and MDI is mainly an occupational problem. Workers involved in the production of MDI and TDI, as well as those involved in the production of polyurethane foams, have the potential for high exposure, mostly via inhalation (Dahlin et al. 2008). However, the general population could be exposed to higher than background levels through the use of uncured polyurethane consumer products such as adhesives, sealants, paints, craft materials, and insulating foams.

Diisocyanates, such as MDI and TDI, are generally supplied as raw materials to formulators who use their reactivity to combine them with other chemicals to create various polyurethanes with a wide diversity of applications. This diversity of applications leads to worker exposures in a broad range of production facilities, from small businesses to automated production lines. Diisocyanates are commonly available in unreacted, uncured forms as part of product mixtures that require an end-use reaction to form a final product. Since some of these applications can occur beyond the confines of a controlled production facility, workers and formulators need to be careful to prevent exposures (EPA 2011a).

**6.8 ADEQUACY OF THE DATABASE**

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of TDI and MDI is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of TDI and MDI.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

**6.8.1 Identification of Data Needs**

**Physical and Chemical Properties.** The physical-chemical properties of TDI and MDI are provided in Chapter 4. Important properties such as melting point, boiling point, and vapor pressure are available.

## 6. POTENTIAL FOR HUMAN EXPOSURE

Other properties such as water solubility and octanol/water partition coefficient are not applicable due to the rapid rate of hydrolysis. No data needs are identified.

**Production, Import/Export, Use, Release, and Disposal.** According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Production, use, and import/export data are available (EPA 2011a; NTP 2011). Continuous updated information regarding these quantities is necessary.

**Environmental Fate.** The environmental fate and transport of TDI and MDI is well understood. Hydrolysis is the dominant process affecting the overall environmental fate, transport, and bioaccumulation potential. Additional research on the heterogeneous condensed phase atmospheric hydrolysis of TDI and MDI would be helpful in determining the significance of atmospheric hydrolysis for these compounds.

**Bioavailability from Environmental Media.** The rapid hydrolysis of TDI and MDI suggests that these compounds will not be biologically available in the environment. No data needs are identified.

**Food Chain Bioaccumulation.** The rapid hydrolysis of TDI and MDI suggests that these compounds will not bioconcentrate in aquatic organisms or bioaccumulate in the food chain. No data needs are identified.

**Exposure Levels in Environmental Media.** Reliable monitoring data for the levels of TDI and MDI in contaminated media at hazardous waste sites are needed so that the information obtained on levels of TDI and MDI in the environment can be used in combination with the known body burden of TDI and MDI to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** In order to evaluate the possible correlation between the air levels of diisocyanates and the urine and plasma levels of the amine metabolites, more studies monitoring the concentration in workplace air and concentration in biological samples of workers exposed to diisocyanates are needed (Tinnerberg et al. 1997).

## 6. POTENTIAL FOR HUMAN EXPOSURE

There is limited exposure data pertaining to the use and exposure of consumer and commercial products containing uncured TDI and MDI (EPA 2011a, 2011b). Additional studies on the personal air and dermal exposure characterizing the concentration of TDI and MDI during application of these products is needed to assess the exposure to the general population.

This information is necessary for assessing the need to conduct health studies on these populations.

**Exposures of Children.** There are limited data pertaining to the use and exposure of consumer and commercial products containing uncured TDI and MDI. Because of this, exposure levels to children have not been well characterized (EPA 2011a, 2011b). Additional studies on the personal air and dermal exposure characterizing the concentration of TDI and MDI during application of these products is needed to assess the exposure to children.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children's Susceptibility.

**Exposure Registries.** The information amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to these substances; however, no exposure registries for TDI and MDI were located. TDI and MDI are not currently compounds for which a sub-registry has been established in the National Exposure Registry. TDI and MDI will be considered in the future when chemical selection is made for sub-registries to be established.

### 6.8.2 Ongoing Studies

No ongoing environmental fate studies for TDI or MDI were identified using the NIH RePORTER (2014) or the Defense Technical Information Center (DTIC) online database.