International Isocyanate Institute

CLICK ON THE IMAGES TO LEARN MORE

1. Production

2. Transportation

3. Polyurethane Manufacture

4. Polyurethane Use

5. End of Life Recycle/Reuse Energy Recovery Disposal

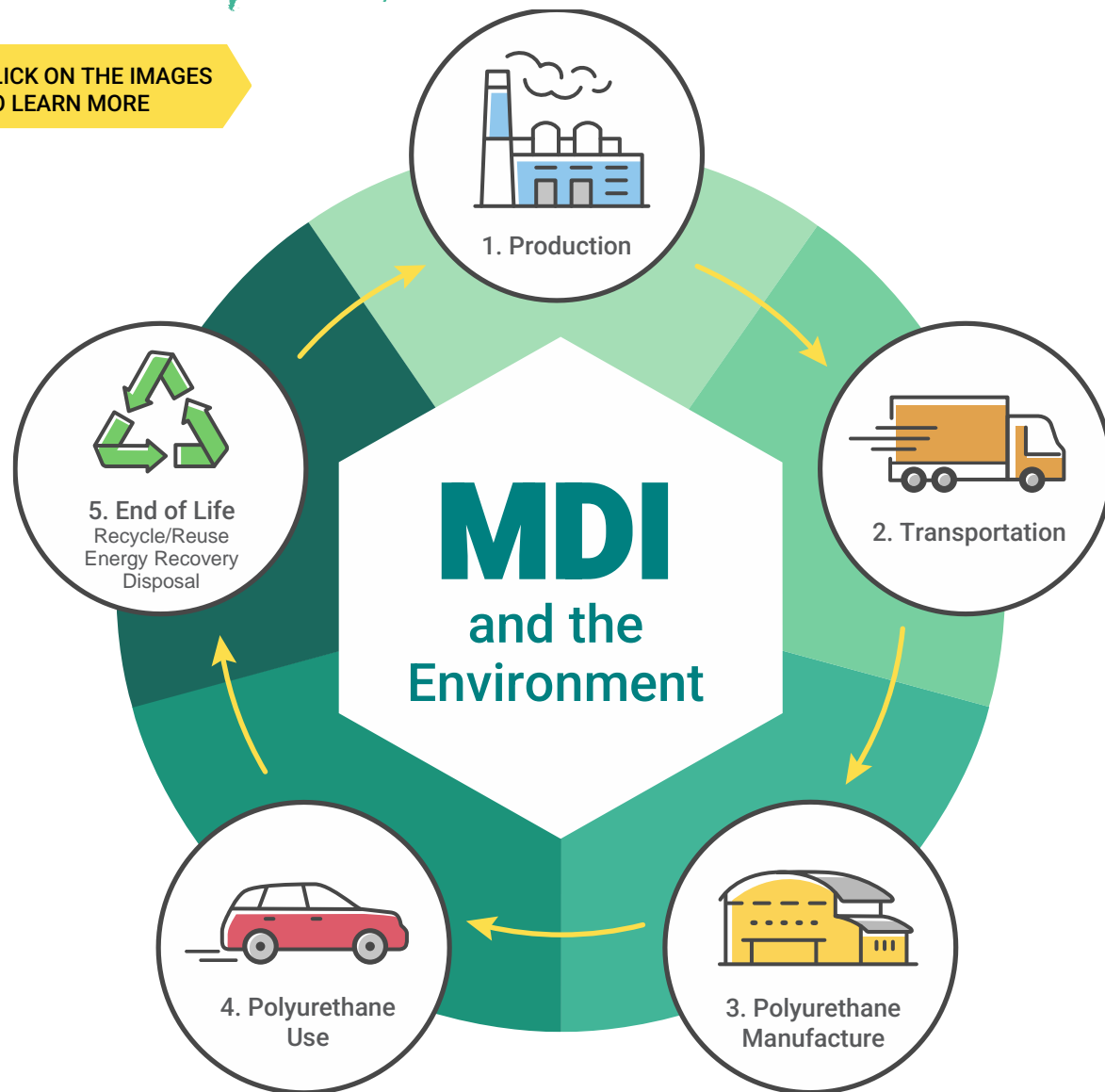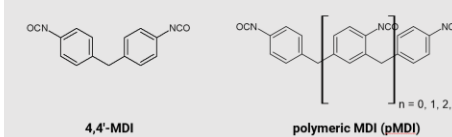# MDI and the Environment

Abstract

Methylene diphenyl diisocyanate (MDI) is a versatile chemical intermediate used in the manufacture of a variety of polyurethane materials, and has an estimated global production exceeding seven million tons/yr. This substance is highly reactive with water even with the water vapor in air which along with its potential health hazards compels very strict handling and containment during its manufacture, transportation, formulation, and application.

Click to read more

What is MDI?

4,4'-MDI

polymeric MDI (pMDI)

n = 0, 1, 2, 3...

Methylenediphenyl diisocyanate (MDI) is a reactive chemical intermediate used primarily in the manufacture of polyurethanes.

Click to read more

MDI in the Atmosphere → Photolysis → **Oxidation to CO2, H20, NOx**

MDI in the Aquatic Environment → **Hydrolysis** → **MDA in Water/Sediment** / **Polyurea in Sediment**

MDI in Soil → **Hydrolysis** → **Polyurea in Soil** / **MDA in Soil**

**References**

ABSTRACT

Methylene diphenyl diisocyanate (MDI) is a versatile chemical intermediate used in the manufacture of a variety of polyurethane materials and its estimated global production exceeds 5MM tons/yr (Carvajal-Diaz, 2015). This substance is highly reactive with water- even with the water vapor in air- which along with its potential health hazards compels very strict handling and containment during its manufacture, transportation, formulation, and application. These control measures ensure that only a negligible fraction of the large production volume could be emitted to the environment. This presentation summarizes existing information on the fate and potential effects of MDI which could be expected if its emission to air, water, or soil were to occur. The reaction of MDI with water (hydrolysis) present in the air, water, and soil converts the substance to solid inert polyureas. Much like the polyurethanes which are manufactured from MDI, the polyureas are stable in the environment and on disposal have no adverse impact on domestic waste handling processes, landfills, or incineration.

WHAT IS MDI?

Methylenediphenyl diisocyanate (MDI) is a reactive chemical intermediate used primarily in the manufacture of polyurethanes. The majority of MDI is produced and used in a dense viscous liquid form called "polymeric MDI (pMDI)" which contains about 50% wt. of the 4,4'-MDI substance and incrementally decreasing amounts of MDI homologues which have 3, 4, or more aromatic rings in their structure. Representative chemical structures of 4,4'-MDI and pMDI are shown below:

4,4'-MDI

$n = 0, 1, 2, 3...$
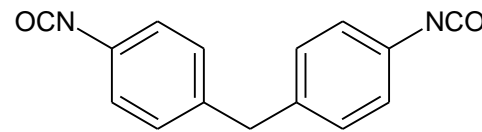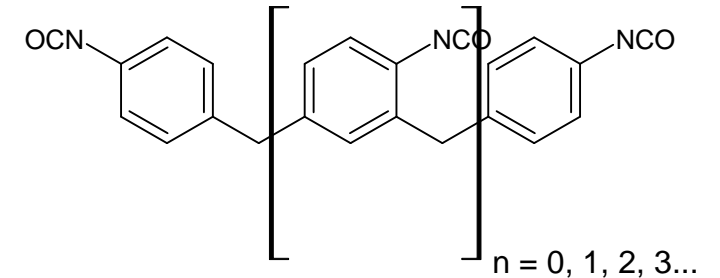
polymeric MDI (pMDI)

Next

MDI PHYSICAL-CHEMICAL PROPERTIES

Table 1. Summary of Key Physical-Chemical Properties of 4,4'-MDI and pMDI

PROPERTIES OF 4,4'-MDI	VALUE
Vapor Pressure (@ 20°C or 68 °F)*	0.7 mPa (5.3 x 10^{-6} mmHg)
Saturated Vapor Concentration (@ 20°C or 68 °F)*	0.07 mg/m³ 6.9 parts per billion (ppb)
Boiling Point (@ 101.3kPa, 760 mmHg)	Decomposes before boiling
Melting Point (range)	39 – 43 °C (102 – 109.4 °F)
Relative Density (@ 20°C or 68 °F)	1.32
Water Solubility (@ 20°C or 68 °F)	Insoluble; hydrolyzes in water

* Vapor pressures and saturated vapor concentrations at other temperatures are reported in Pemberton (2001)

PROPERTIES OF pMDI	VALUE
Vapor Pressure (@ 20°C or 68 °F)	0.4 mPa (3.0 x 10^{-6} mmHg)
Boiling Point (@ 101.3kPa, 760 mmHg)	> 300 °C (> 572 °F)
Freezing Point	< 5°C (< 41°F)
Relative Density (@ 20°C or 68 °F)	1.23
Water Solubility (@ 20°C or 68 °F)	Insoluble; hydrolyzes in water

Properties of pMDI may vary slightly with composition

MANUFACTURING AND USES

MDI PRODUCTION EMISSIONS

The production of MDI is carried out in closed equipment with emission controls on all vents. Emissions of MDI to the atmosphere are therefore very low. For example, for the year 1997 emissions to air and water associated with MDI production sites in Europe were < 0.000005% of annual production. Reported estimates of emissions to air and water associated with MDI production in the U.S. are also a negligible fraction of total production (US EPA, 2021).

POLYURETHANE MANUFACTURING EMISSIONS

Polyurethanes are produced by reacting diisocyanates such as MDI with polyols; other chemicals such as catalysts, surfactants, antioxidants, and flame retardants may be included in the formulation of polyurethanes. Atmospheric emissions of MDI during polyurethane production are very low. Emissions from rigid insulation board (Maddison and Vangronsveld, 2000) and flexible foam molding processes (Chapman, 2001) were measured at < 0.001 to 0.04 and 0.2 to 6 g per metric ton of MDI used, respectively. These values equate to emission rates of between 0.0000001 and 0.0006% of the amounts of MDI used in these production processes.

As part of a U.S. EPA community exposure assessment initiative, six schools which are located near large polyurethane production sites were monitored for MDI in the ambient air. In all samples collected, no MDI was detected at a typical detection limit of 1.19 µg/m3 or 0.12 ppb (US Environmental Protection Agency (US EPA), 2010).

POLYURETHANE USE   Next

MDI is used in the production of polyurethanes for many applications, including the manufacture of rigid polyurethane foams used for insulation in homes, commercial buildings, and appliances (e.g., refrigerators and spas).
Some additional uses of MDI in polyurethanes include coatings, adhesives, sealants, and elastomers (CASE) found in items such as paints, glues, and weather resistant caulks. MDI-based polyurethanes are also used to make many types of footwear, sports and leisure products and, to a much lesser extent, some specialty flexible foams. MDI can also be used as a binder for composite wood products (e.g., oriented strand board (OSB) and particleboard) and to produce mold cores for the metal casting industry.

MDI in the Atmospheric Environment

ATMOSPHERIC DISPERSION OF MDI

MDI has a very low vapor pressure and a saturated vapor concentration in air of only about 6 ppb at 25 °C (Allport et al., 2003). Therefore, atmospheric emissions of MDI are mostly concerned with the aerosol (fine particulate) forms which could be formed and emitted, especially from processing at elevated temperatures. Modeling studies of atmospheric MDI aerosol dispersion show that the maximum average air concentrations would occur very close to the emitting facility and are unlikely to result in adverse environmental impacts (Roffman and Rivkin, 1995).

ATMOSPHERIC FATE OF MDI

As is the case for most aromatic organic substances, the reaction with photochemically-generated hydroxyl radical is the most important atmospheric degradation process affecting the fate and lifetime of MDI in the atmosphere. The estimated atmospheric half-life of MDI is about one day when typical daylight hours (12 hr) and hydroxyl radical concentrations are assumed (Tury et al., 2003). Reaction pathways that could lead to the formation of aromatic diamines from the atmospheric reaction of aromatic diisocyanates with OH radicals are extremely unlikely (Pfeifle et al., 2021)

Because the atmospheric concentrations of both water vapor and MDI are very low, hydrolysis of MDI is not a major contributor to its fate and lifetime in the atmosphere. This lack of vapor-phase hydrolysis has been experimentally demonstrated for the structurally similar toluene diisocyanate (TDI) substance (Holdren et al., 1984). Smog chamber studies with another structural analog of MDI (p-toluene isocyanate) investigated the contribution of this substance to photochemical smog forming reactions under simulated urban ozone pollution episodes (Carter et al., 1999). The results of this work indicate that aromatic isocyanates such as MDI are unlikely to contribute to smog and ozone formation in the urban atmospheric environment.

TRANSPORTATION

TRANSPORTATION

Large quantities of MDI are routinely transported over road, rail, and sea in a variety of container types and sizes. Even the smallest spillages of MDI during its transport are rare; however, this is perhaps the most plausible mode of MDI emission to the environment since other modes are prevented through the strict emission controls implemented during manufacture, formulation, and end-use life cycle stages. In the unlikely event of a spillage to the aquatic or soil environments, MDI reacts (hydrolyzes) to form inert polyureas which can usually be collected and disposed as solid waste. The learnings derived from a limited number of past MDI spillage incidents have indicated no evidence for long-term impacts to the environment and biota; immediate physical impacts of the spill are most severe (e.g., due to potential physical contact of people, environment, and wildlife with unreacted TDI liquid and vapor) (Allport et al., 2003).

MDI NEUTRALIZATION

MDI residues remaining in emptied containers can often neutralized by application of water-based solutions. A simple formulation of water, nonionic surfactant (2% wt.) and monoethanolamine (MEA; 1% wt.) was optimized for neutralization of pMDI (and TDI) in emptied 200 L steel drum containers (Hugel and West, 2014). It was shown that relatively small volumes (~ 2 L) of neutralization solution are necessary, and that spent neutralization solution could be disposed via a domestic sewage treatment plant (STP) with no expected detrimental effects to the wastewater treatment microorganisms or to aquatic life in the STP effluent (Allmendinger et al., 2014). It was also shown that a household laundry detergent which contains nonionic surfactant and MEA could be diluted in water to approximate these optimum concentrations, and similarly safe and effective in MDI neutralization. Neutralization should never be applied in a sealed container, and all appropriate regulations should be followed when disposing of neutralized containers and spent neutralization solution.

MDI POLYUREAS

FORMATION

Various substituted polyureas are formed during reaction of MDI under heterogeneous mixing with water. The mono-ureas represent the first intermediate products in the stepwise formation of polyurea which is the ultimate end-product of such hydrolysis reactions. The isocyanato-terminated ureas are transient species. To the extent soluble, the terminal isocyanate (NCO) groups hydrolyze in water. Like isocyanates and their corresponding amines, the terminal NCO and amino (NH2) groups of the ureas will react to form oligo- and poly-ureas as the final hydrolysis product (see 'HYDROLYSIS' slide for structures). MDI polyureas are inert and insoluble in water and most organic solvents. The photo at the left shows MDI polyureas formed by stirring 50 g/L of pMDI in distilled water for 14 days.

FATE AND TOXICITY

The half-time for hydrolysis of pMDI-polyurea at 25 degrees C in deionized water has been estimated to range from about 110,000 to 12 million years, depending on the kinetic assumptions made (Sendijarevic *et al.*, 2004). The half-times for hydrolysis at buffered pH levels of 4, 7, and 9 were within a factor of 2 of those in deionized water. The additional data in Table 3 further supports the characterization of MDI polyureas as essentially non-toxic and inert.

Table 3. Summary of key environmental fate and acute hazard properties of amine- and isocyanate-terminated mono-ureas of MDI

Property	Method	Endpoint[1]	NCO-terminated mono-urea of 4,4'-MDI	NH$_2$-terminated mono-urea of 4,4'-MDI
CASRN			93805-48-2	172944-17-1
Acute toxicity information (from Neuhahn et al., 2020 and Steinhoff, 1973)				
Ready Biodegradability	OECD 301F		Not readily biodegradable	
72 h Algae Growth Inhibition [mg/L]	OECD 201	E_rL_{50} / E_rC_{50} NOEL$_r$ / NOEC$_r$	>100 / - >100 / -	>100 / - >100 / -
48 h Daphnia magna Immobilization [mg/L]	OECD 202	EL_{50} EC_{50}	>100 -	- >100
96 h Danio rerio Lethality [mg/L]	OECD 203	LL_{50} EC_{50}	>100 -	- >100
Acute oral toxicity in rat [mg/kg body weight]		LD_{50}	Not determined	>15,000

[1]**Endpoint Key**:
 $E_rC(L)_{50}$ – Median Effective Concentration (Loading Rate) [causing 50% reduction in growth rate of exposed population]
 NOEC(LR) – No Observed Effect Concentration (Loading Rate) [highest loading rate showing no effects of exposed population]
 EC(L)$_{50}$ - Median Effective Concentration (Loading level) [showing the measured effect in 50% of tested individuals]
 LL(D)$_{50}$ - Median Lethal Loading Rate Dose) [causing mortality in 50% of exposed population]

MDI Hydrolysis

Hydrolysis (reaction with water) is the most important process affecting the fate and potential hazards of MDI in the environment. A basic understanding of this reaction is necessary to understand and interpret the following sections on **MDI IN THE AQUATIC ENVIRONMENT, MDI IN SOIL, SPILLAGE SIMULATION STUDY and MDI ECOTOXICITY**. This reaction occurs between water and the two or more isocyanate (NCO) functional groups of MDI or pMDI as shown in the following (simplified) sequence of reaction steps**.**

Note: The rate of reaction between isocyanate and amine (Steps 2 and 4) has been determined to be ~ 10,000 times faster than that between isocyanate and water (Steps 1 and 3). Step 2 has a much higher probability to occur than Step 3. The practical implications of this complex hydrolysis reaction are further illustrated in **MDI IN THE AQUATIC ENVIRONMENT.**

A short, animated presentation of hydrolysis is available at the following <u>LINK</u>.

Step 1 (the amine-forming step) converts one of the isocyanate (NCO) functional groups to an amine group (via a carbamic acid intermediate, not shown) and releases carbon dioxide.

1. MDI (Diisocyanate) + Water → Amino-Isocyanate + Carbon Dioxide
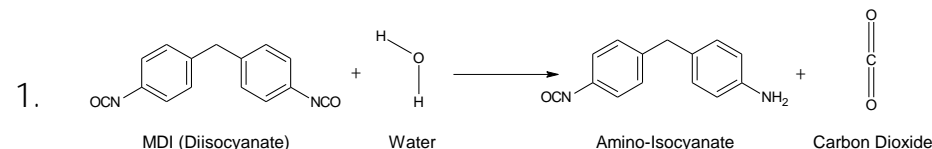
Step 2 (the urea-forming step) combines the amine group formed in Step 1 with an isocyanate group of another molecule of MDI or of the amino-isocyanate intermediate to form a mono-urea.

2. MDI (Diisocyanate) + Amino-Isocyanate → Mono-urea of MDI
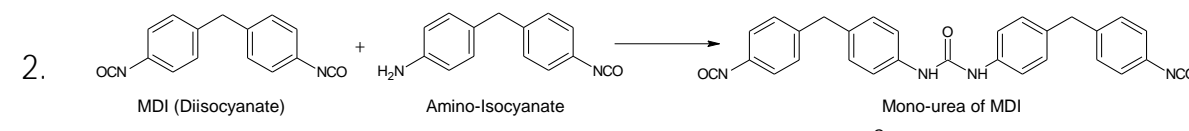
Step 3 (the diamine-forming step), the isocyanate group of the amino-isocyanate formed in Step 1 reacts with water to form a di-amine (i.e., MDA). Since formation of diamine requires simultaneous conversion of both isocyanate groups, this step has a low probability to occur under most realistic environmental conditions.

3. Amino-Isocyanate + Water → Di-amine (MDA) + Carbon Dioxide
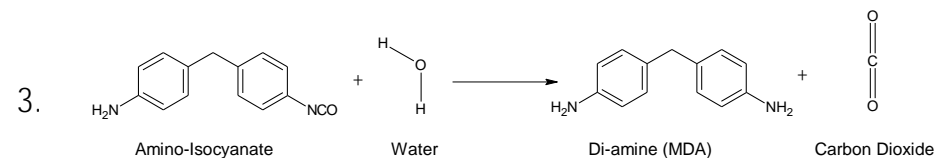
Step 4 (the polyurea-forming step), the isocyanate groups associated with urea formed in Step 2 continue to preferentially react with amine groups formed in Step 1, and polyureas are formed with continually increasing molecular weight while amine groups are consumed as quickly as they are formed.

4. Mono-urea of MDI + Amino-Isocyanate → Polyureas
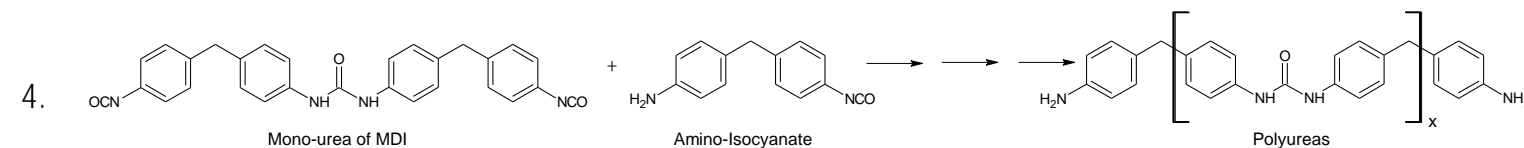
ENVIRONMENTAL DEGRADATION OF POLYURETHANE

DEGRADATION STUDY
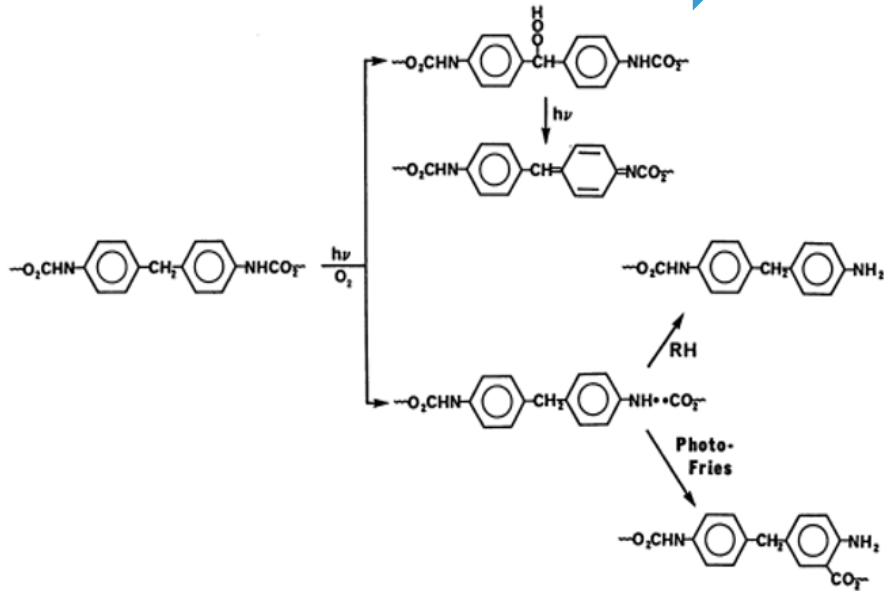
Photolytic Cleavage and Photooxidation of MDI Based Polyurethanes (Hoyle et al., 1989).

Many polyurethane products will be exposed to environmental conditions in the course of their use. The potential effects of such exposure on polyurethane has been investigated.

In a study of degradation of MDI-based polyester and polyether urethane coatings under environmentally-relevant conditions, it was found that exposure to sunlight produced the largest extent and rate of degradation compared to hydrolytic and biologically-mediated modes of degradation for both polyurethane coatings tested. This study showed near complete conversion of the polyurethane-based products to water-soluble degradation products under sunlight (Albright et al. 2018). However, under the photolysis and biodegradation conditions evaluated (i.e., at the soil surface with exposure to sunlight), the rate of MDA degradation was much faster than the rate at which it could be formed as a result of polyurethane degradation.

Photolysis (reaction with light) is a process affecting the fate and potential hazards of polyurethanes in the environment.

Direct photolysis is a potentially important mode of PU degradation in the environment

SPILLAGE SIMULATION STUDY

A constructed pond (mesocosm) study was designed and conducted to simulate the potential short- and long-term effects of a pMDI spillage in an aquatic ecosystem (Heimbach et al., 1996). Three interconnected and identical artificial ponds (4.2 m^3 volume, 1.3 m deep) were constructed which contained lake sediments and circulated well water. After populations of various algae, plankton, fish, and plant species were established and equally distributed among them, the ponds were isolated and liquid pMDI was added to two of the ponds in amounts equaling 1 or 10 g/L while the third pond served as a control. Aquatic chemistry and species population densities were monitored for 112 days following these simulated pMDI spills. There were no direct effects observed on the pelagic species (fish, plankton) and only temporary effects were noted with the sediment-dwelling organisms due to physical obstruction of the sediment surface by polyureas formed. Evolution of CO_2 from pMDI hydrolysis caused a temporary drop in water pH and an associated stimulation of aquatic plant and algae growth. After 112 days, water quality and biotic population parameters were essentially equal across all three ponds, and all the applied pMDI mass could be recovered as the converted polyurea solids. Analytical monitoring indicated that MDI and MDA were not detectable in the water (< 0.01 mg/L) and fish tissues (< 0.5 mg/kg MDI, < 1.4 mg/kg MDA) over the course of this study. These results are consistent with the observations of MDI behaviour and associated impacts associated with a limited number of actual spillages and demonstrate that such events will have no long-term impacts of the environment.
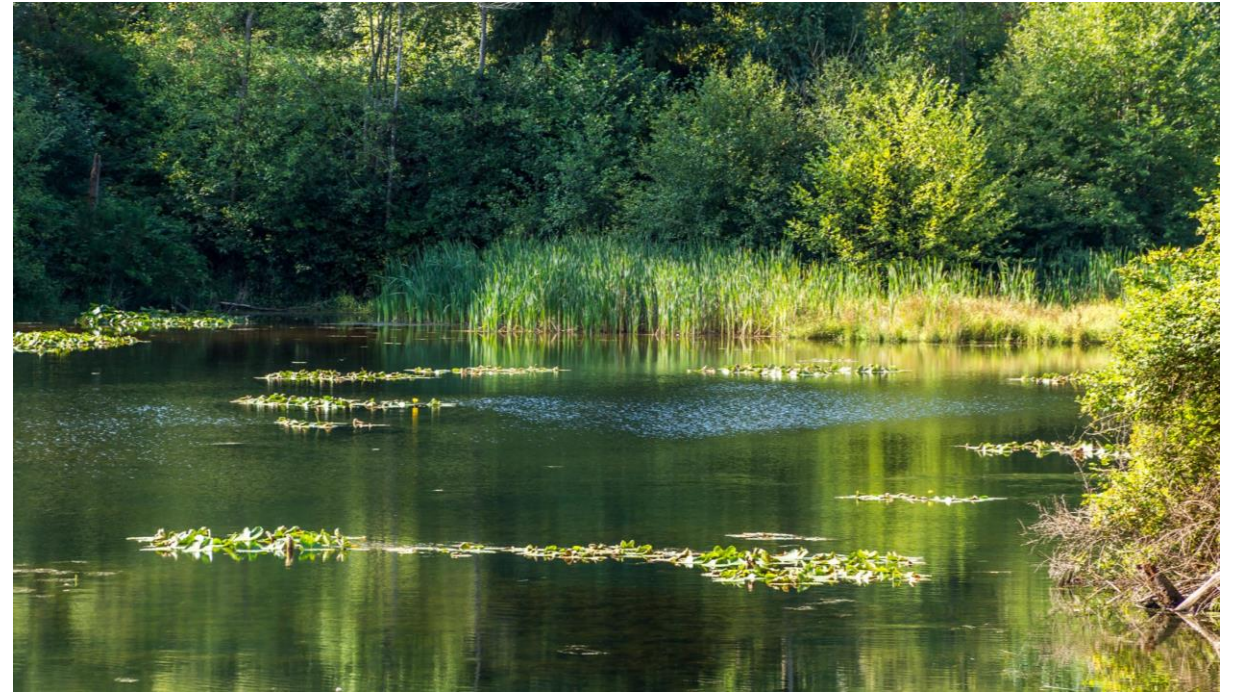
MDI in the Aquatic Environment

MDI IN THE AQUATIC ENVIRONMENT

MDI is a hydrophobic substance which will remain as solid crystals (4,4'-MDI) or as viscous oily droplets (pMDI) when introduced to water. Since the MDI substances have higher density than water (Table 1), they tend to sink through the water column and can coalesce into larger droplets or clusters as was observed in a pMDI spillage simulation study. As the MDI immediately begins to hydrolyze, carbon dioxide is released and a coating of polyurea will form over the surface of these particles or droplets. As the hydrolysis reaction continues, this coating continues to grow thicker until the original particle or droplet of MDI is fully converted to a polyurea particle.

This hydrolytic conversion of MDI to polyureas can take from a few hours to several weeks, depending on the size of the MDI particles, water temperature, and degree of mixing (see Figure 1). Under controlled laboratory conditions where small amounts of MDI can be combined with large volumes of water, small amounts of methylenedianiline (MDA) can be formed as a by-product of hydrolysis, with the yield of MDA increasing from ~ 0.005% (no mixing) to < 1% (vigorous stirring) conversion of the initial MDI mass (Yakabe et al., 1999). If a small amount of MDI is first dissolved in an organic solvent and then vigorously mixed into water, the conversion of MDI to MDA can theoretically approach 100%. However, there are no such conditions associated with known or plausible modes of MDI emission to the environment.

Bulk Water Phase

MDI or pMDI Droplet → Polyurea formation on Surface (hydrolysis) → Polyurea Particle

Reaction of MDI in water
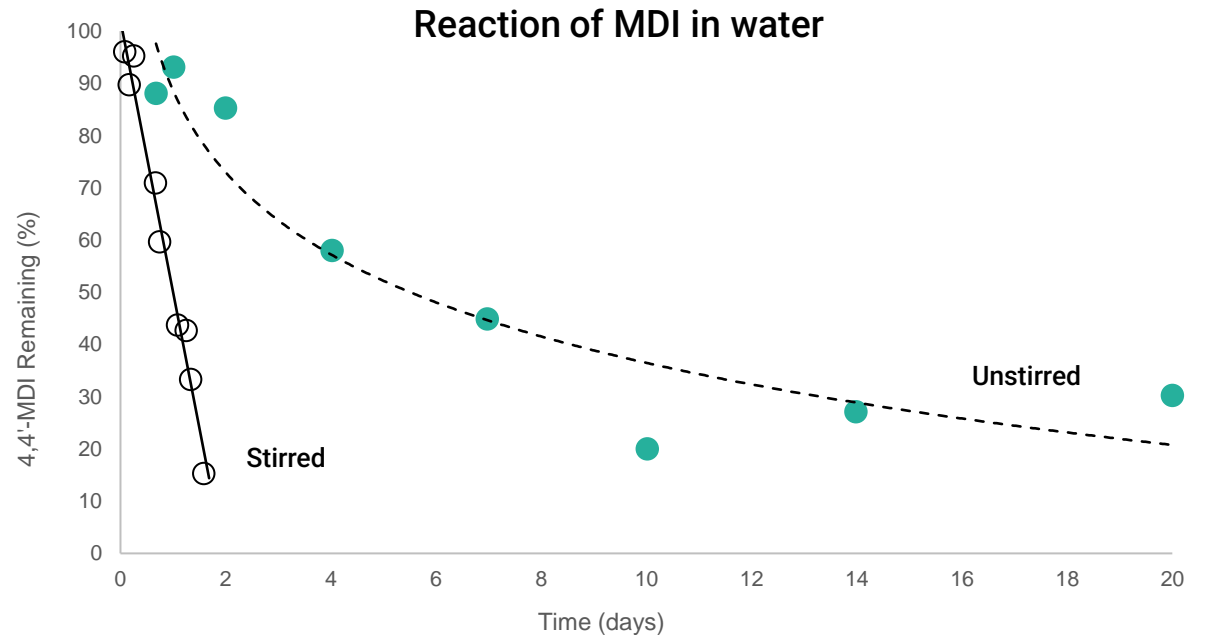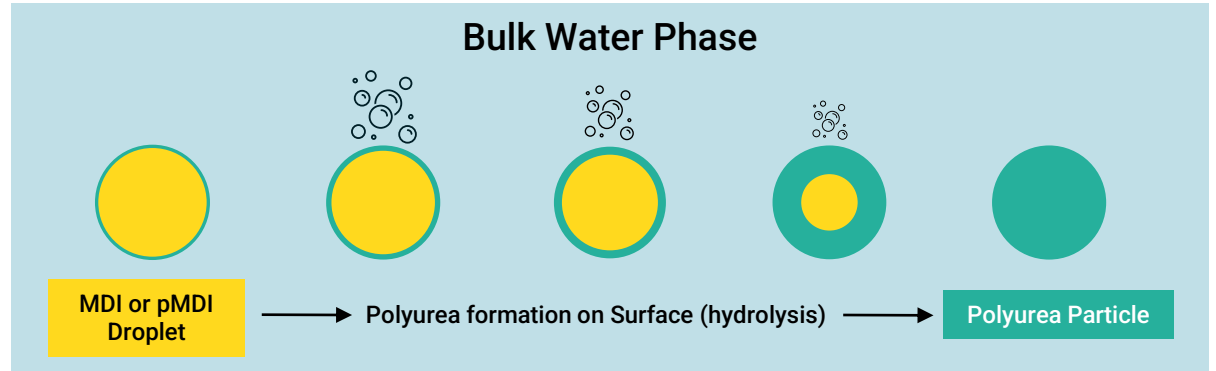
Stirred

Unstirred

Figure 1. Hydrolysis of the 4,4'-MDI component of pMDI (400 mg/L) under stirred and unstirred conditions in water.

Next

MDI ECOTOXICITY

The potential hazards of MDI to aquatic life have been investigated in numerous studies with fish, algae, and invertebrate species. Because MDI is primarily converted to the inert insoluble particles, if any impacts to aquatic life are observed they are not severe. The conditions associated with these standardized aquatic toxicity tests result in higher degrees of MDI conversion to MDA than would be expected under any plausible emission or spillage scenario. Adverse effects of MDI on aquatic life have been observed primarily with the aquatic invertebrates, and these effects have been directly attributed to the measured amounts of MDA formed under these uncharacteristic conditions of MDI exposure. A selection of aquatic hazard test results for MDI and pMDI are summarized in **Table 2**.

Note: Since MDI substances are not water soluble, aquatic effects are expressed based on nominal loading rates to water, and any observed effects are interpolated from the water-accommodated fractions associated with a series of individually prepared test substance loading rates.

EL_{50} = Median Effective Loading Rate (causing effects in 50% of exposed population)
LL_0 = Highest tested loading rate showing no mortality in the exposed population
LL_{50} = Median Lethal Loading Rate (causing mortality in 50% of exposed population)
E_rL_{50} = Median Effective Loading Rate (causing 50% reduction in growth rate of exposed population)
NOELR = No Observed Effect Loading Rate (highest loading rate showing no effects of exposed population)
EC_{50} = Median Effective Concentration in Soil (dry wt. basis)
NOEC = No Observed Effect Concentration in Soil (dry wt. basis)

Table 2. Summary of Ecotoxicological Studies Conducted with 4,4' – MDI and pMDI

| Substance	Tested Species	Toxicological Endpoint	Result (mg/L)
4,4'-MDI	Daphnia magna (invertebrate)	48 h EL_{50} (immobilization	9.0 mg/L
2,4'-MDI	Daphnia magna (invertebrate)	48 h EL_{50} (immobilization)	3.7 mg/L
4,4'-MDI	Desmodesmus subspicatus (algae)	72 h E_rL_{50} 72 h NOELR (growth rate inhibition)	> 100 mg/L ≥ 100 mg/L
4,4'-MDI	Danio rerio (Zebra fish)	96 h LL_{50} (mortality)	> 100 mg/L
4,4'-MDI	Activated Sludge (domestic sewage treatment)	3 h EC_{50} 3 h NOEC (respiration Inhibition)	> 1,000 mg/L 250 mg/L
pMDI	Daphnia magna (invertebrate)	48 h EL_{50} (Immobilization)	13.2 mg/L
pMDI	Daphnia magna (invertebrate)	21 d NOELR (Reproduction)	≥ 10 mg/L
pMDI	Desmodesmus subspicatus (algae)	72 h E_rL_{50} 72 h NOELR (growth rate inhibition)	> 1,640mg/L ≥ 1,640mg/L
pMDI	Danio rerio (Zebra fish)	96 h LL_0 (mortality)	> 1,000 mg/L
pMDI	Oryzias latipes (Rice fish)	96 h LL_0 (mortality)	> 3,000 mg/L
pMDI	Eisenia fetida (Earthworm)	14 d LC_{50} (mortality) 14 d NOEC (biomass) 14 d NOEC (behavior)	> 1,000 mg/kg ≥ 1,000 mg/kg ≥ 1,000 mg/kg
pMDI	Avena sativa (Oat)	14 d EC_{50} (growth rate) 14 d NOEC (emergence) 14 d NOEC (survival) 14 d NOEC growth rate)	> 1,000 mg/kg ≥ 1,000 mg/kg ≥ 1,000 mg/kg ≥ 1,000 mg/kg
pMDI	Lactuca sativa (Lettuce)	14 d EC_{50} (growth rate) 14 d NOEC (emergence) 14 d NOEC (survival) 14 d NOEC growth rate)	> 1,000 mg/kg ≥ 1,000 mg/kg ≥ 1,000 mg/kg ≥ 1,000 mg/kg
pMDI	Activated Sludge (domestic sewage treatment)	3 h EC_{50} (respiration Inhibition)	> 100 mg/L

MDI in the Soil Environment

MDI IN THE SOIL ENVIRONMENT

The introduction of MDI to soil, such as could occur during an accidental spillage event, will result in its reaction with water, organic matter, and solid mineral components of the soil. This reactivity makes the MDI immobile in soil, and coverts the spilled material to a solid mass of combined soil and polyurea. The time required for 50% conversion of 4,4'-MDI in soil has been determined to range from about 1 to 7 hours over a wide range of soil types (Holzaht-Grimme, 2018). Polyureas are the predominant reaction product of MDI in soil, and studies have shown these polyureas to be resistant to degradation for millennia (Sendijarevic et al., 2004). If a spill of liquid MDI or pMDI to soil occurs, it is often recommended to cover the material with wet soil to prevent spread of the material and promote the conversion to polyurea which can be later recovered and disposed as solid waste. As shown in Table 2, there are no observed or expected long-term effects of MDI to soil-associated invertebrates and plants.

MDI IN THE SOIL AND SEDIMENT

Any methylenedianiline (MDA) which might be formed from hydrolysis of MDI or from degradation of polyurethane materials in the soil environment is expected to be rapidly degraded. Primary aromatic amine substances such as MDA are known to be reacted with the organic matter component of soil and sediment (Schupp et al., 2018). This "chemisorption" of MDA is to a large extent irreversible and serves to reduce the mobility and bioavailability of MDA in soil and sediment compartments. Any MDA which is not consumed in this degradation pathway can be easily degraded to carbon dioxide and ammonia by microorganisms present in aerobic soils and sediments (Cowen et al., 1998; Schaefer and Ponizovsky, 2013).

DISPOSAL − END OF LIFE
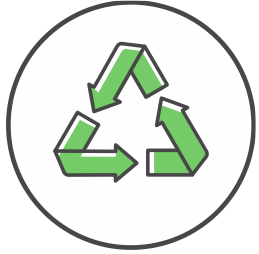
RECYCLE/REUSE

Technology continues to develop which enables re-use and recycling of polyurethane materials derived from MDI. Re-use can involve blending of recovered polyurethane foam with additional MDI to make re-bonded polyurethane foam. Thermal- and chemical-based recycling of polyurethane can sometimes result in recovery of the polyol and MDA components which can be repurified or blended with virgin materials to make new polyurethane products.

ENERGY RECOVERY

In some regions and for some types of polyurethane materials, re-use, recycle, and landfill are not available options for disposal or recovery of polyurethane waste material. The various MDI substances and the polyurethane materials derived from them are combustible and are expected to be completely consumed in a municipal solid waste incinerator. Incineration provides a means of energy recovery from polyurethane waste materials which might be difficult to recycle or are otherwise disposed in solid waste landfills. When properly incinerated the products of MDI and polyurethane combustion are indistinguishable from those of other solid waste materials composed on carbon, nitrogen, and oxygen.

DISPOSAL

Laboratory studies have been performed to examine the fate of MDI-based laminate board insulation and rigid spray foams under simulated landfill conditions over a two-year period (Brown et al., 1999). The results of this study showed no adverse impacts on landfill decomposition processes (methanogenesis), no visible changes to physical structure of the foams, and no MDA was detected in the simulated landfill leachate at a detection limit of 30 μg/L (equivalent to ~ 0.0001 % degradation of the MDI-based foam). When an amount of pure MDA equivalent to the amount reacted into the polyurethane foams added to the landfill simulator, only a small fraction of this could be detected in the leachate-indicating that MDA was being efficiently degraded or tightly bound within the simulated landfill components. These results indicate that if polyurethane degradation can occur within a solid waste landfill, any MDA released as a result has low potential to persist in the landfill leachate.

MDI REFERENCES

Allmendinger, H., Bossuyt, B., and West, R. J. (2014). Aromatic diisocyanate residues in emptied drums: full-scale evaluations of optimised monoethanolamine-based neutralization formulations. Finalised report. International Isocyanate Institute, Manchester, UK.

Allport, D. C., Gilbert, D. S., and Outterside, S. M. (2003). MDI and TDI: safety, health and the environment. A source book and practical guide. Wiley, Chichester. (ISBN 0-471-95812-3).

Brown, W. E., Bartlett, C., Aul, D. J., Blough, M. S., D'Andrea, M., Hauck, J. T., Kennedy, A. L., Minkley Jr., E. G., and Bailey, R. E. (1999). Monitoring potential degradation of polyurethanes in a landfill simulator. Paper, Innovation for the next millennium: API Polyurethanes Expo '99 Int. Tech. Conf.& Exposition, Orlando, 12-15 Sept., 1999.

Carter, W. P. L., Luo, D., and Malkina, I. L. (1999). Investigation of the atmospheric ozone formation potential of para toluene isocyanate and methylene diphenylene diisocyanate. Final report to the Chemical Manufacturers Association Diisocyanates Panel.

Carvajal-Diaz J (2015) IHS Chemical Economics Handbook: Aniline. IHS, Englewood

Chapman, J. F. (2001). Emissions from flexible polyurethane foam moulding operations in Europe. Finalised report. International Isocyanate Institute, Manchester, UK.

Cowen, W. F., Gastinger, A. M., Spanier, C. E., Buckel, J. R., and Bailey, R. E. (1998). Sorption and microbial degradation of toluenediamines and methylenedianiline in soil under aerobic and anaerobic conditions. Environ Sci Technol, 32, (5), 598-603.

US Environmental Protection Agency (US EPA). (2021) .Toxics Release Inventory (TRI) Program: TRI Data and Tools. Available at: https://www.epa.gov/toxics-release-inventory-tri-program/tri-data-and-tools (accessed 24 March 2022)

Heimbach, F., Jaeger, K., and Sporenberg, W. (1996). Fate and biological effects of polymeric MDI (4,4'-diphenylmethane diisocyanate and homologs) in small artificial ponds. Ecotoxicol Environ Saf, 33, (2), 143-53.

Holdren, M. W., Spicer, C. W., and Riggin, R. M. (1984). Gas phase reaction of toluene diisocyanate with water vapor. Am Ind Hyg Assoc J, 45, (9), 626-33.

Holzaht-Grimme, D. (2018). 4,4'-MDI: rate of degradation in soil. International Isocyanate Institute, Boonton, NJ, USA.

Hugel, E. and West, R. J. (2014). Investigation of monoethanolamine (MEA)-based formulations for neutralization of aromatic diisocyanate residues in emptied drums. Finalised report. International Isocyanate Institute, Manchester, UK.

Maddison, P. and Vangronsveld, E. (2000). III European Emission Project: stack emissions from rigid polyurethane foam production lines. Finalised report. International Isocyanate Institute, Manchester, UK.

Neuhahn, A., Neuland, M., and Sadler, T. (2020). Mono-ureas of MDA and MDI: determination of physico-chemical properties, biodegradability, and acute aquatic toxicity. Finalised report. International Isocyanate Institute, Manchester, UK.

Olf, G. (2018). Vapor pressure of various MDI-based substances. International Isocyanate Institute, Boonton, NJ, USA.

Pemberton, D. (2001). MDI and TDI: vapour pressures and saturated vapour concentrations. International Isocyanate Institute, Manchester, UK.

Pfeifle, M., Welz, O., Sure, R., and Deglmann, P. (2021). Atmospheric reactions of the OH radical with diisocyanates: in silico analysis using a quantum chemistry approach. International Isocyanate Institute, Mountain Lakes, NJ, USA.

Roffman, A. and Rivkin, C. H. (1995). Dispersion deposition study of MDI stack aerosols. 2 Vols. Finalized report. International Isocyanate Institute, Manchester, UK.

Schaefer, E. C. and Ponizovsky, A. (2013). 4,4'-MDA: aerobic and anaerobic transformation in aquatic sediment systems. Finalised report. International Isocyanate Institute, Manchester, UK.

Schupp, T., Allmendinger, H., Boegi, C., Bossuyt, B. T., Hidding, B., Shen, S., Tury, B., and West, R. J. (2018). The environmental behavior of methylene-4,4′-dianiline. In: Reviews of Environmental Contamination and Toxicology Volume 246. de Voogt P, ed., Springer International Publishing, 2018, 91-132. (978-3-319-97739-3).

Sendijarevic, V., Sendijarevic, A., Sendijarevic, I., Bailey, R. E., Pemberton, D., and Reimann, K. (2004). Hydrolytic stability of toluene diisocyanate and polymeric methylenediphenyl diisocyanate based polyureas under environmental conditions. Environ Sci Technol, 38, (4), 1066-72.

Steinhoff, D. (1973). Acute oral toxicities of (note: NCO-free) polyureas prepared from 80/20 TDI and 4,4'-MDI (peanut oil medium, rat). Finalised report. International Isocyanate Institute, Manchester, UK.

Tury, B., Pemberton, D., and Bailey, R. E. (2003). Fate and potential environmental effects of methylenediphenyl diisocyanate and toluene diisocyanate released into the atmosphere. J Air Waste Manage Assoc, 53, (1), 61-6.

US Environmental Protection Agency (US EPA). (2010). Assessing outdoor air near schools [for isocyanates]. Results and analysis.

Yakabe, Y., Henderson, K. M., Thompson, W. C., Pemberton, D., Tury, B., and Bailey, R. E. (1999). Fate of methylenediphenyl diisocyanate and toluene diisocyanate in the aquatic environment. Environ Sci Technol, 33, (15), 2579-83.