MDI and TDI: Safety, Health and the Environment.

A Source Book and Practical Guide

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environmental, medical and other aspects of the diisocyanate industry, it does not purport to
be, and is not, a comprehensive guide thereto.*

Contents

4   The environment

Exposure

Releases of MDI and TDI into the environment are very low, as a result of rigorous control of all aspects of their lifecycle and their low volatility and insolubility in water. MDI and TDI are not persistent in the environment, being degraded in air and water, and indeed are so inherently reactive in water as to be almost unavailable for biological uptake or bioaccumulation. In environmental contact with water the major products are inert, insoluble, solid polyureas. As a result, environmental exposure to MDI and TDI, arising either from normal use or from accidental release, is very low.

Hazard (ecotoxicity)

Both MDI and TDI generally show low toxicity to a wide range of water- and soil-based species: bacteria, algae, invertebrates, fish, earthworms, plants and birds. Water soluble products of the reaction with water are considered to be responsible for any observed ecotoxicity: they constitute a minor fraction of total reaction products under most realistic environmental conditions. A study simulating the spillage of polymeric MDI into the natural ecosystem of a pond showed no direct ecotoxic effects.

Risk

Consideration of the sources of release of MDI and TDI and the environmental behaviour of these materials, both physicochemical and biological, suggests that no significant risk is presented to the environment from releases arising from normal use or accidents.

A general approach to environmental risk assessment

There is growing concern about damage to the environment caused by the release of man-made chemicals. Assessment of the potential risks associated with a chemical provides a rational basis for deciding whether measures are needed to reduce exposure. Such assessment procedures have been developed for the environmental risks associated with the lifecycle of a substance; that

is, as arising from normal operation at any stage of production, transport, use, storage, processing or disposal. It is also possible to apply the same logic, if less quantitatively, to the risks connected with an abnormal, temporary release such as a spillage.

The structure of this Part is formed around the basic concept of risk assessment, that risk is a function of exposure and hazard. Significant risk arises when the concentration of a substance at a place exceeds the threshold concentrations for adverse effects. Hence, in assessing environmental risk for any substance, we seek to estimate exposure (concentration or dose) and hazard (toxic effect). For convenience this is done separately for each environmental compartment: water, soil and air. Biota, living organisms, are generally considered in the compartment in which they normally reside (see Figure 4.1). By contrast two other key areas of concern, toxicity to sewage plant micro-organisms and secondary toxicity in the food chain, are usually treated separately.
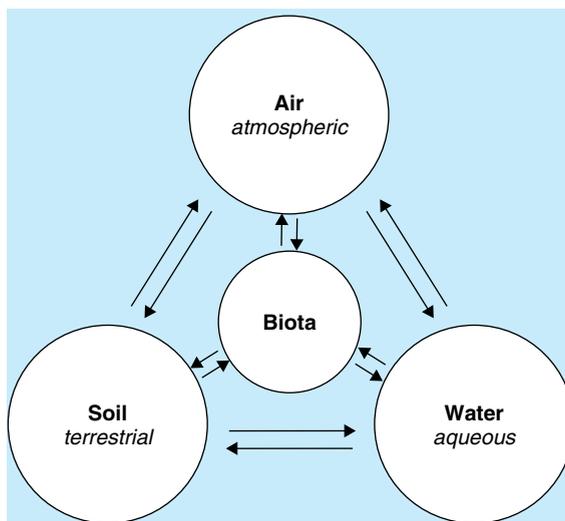
Figure 4.1   **Environmental compartments**

Estimation of exposure includes the type of release (source, scale and duration) and its fate (distribution and persistence). Each environmental compartment has its own general characteristics with regard to the fate of a release. In *water*, dilution is rapid but may be limited by the volume of the system and the solubility of the substance. Transfer to air or sediment occurs, and the rate of degradation is important. In *soil*, migration is often slow and transformation, namely degradation or irreversible binding, has a more important effect on concentration. Hence steep concentration gradients can occur close to sources. In *air*, substances can disperse rapidly and extensively, and degradation processes can be fast. The air compartment is often treated as a reservoir, affecting concentrations in water, soil and plants by volatilization, deposition and partition.

Estimation of hazard is the identification of adverse effects on the environment and can include the measurement of concentration- or dose-related

responses for these. Adverse physical effects of concern are predominantly those connected with atmospheric pollution, such as enhancement of the green-house effect, formation of ozone in the troposphere or its destruction in the stratosphere. In general, with the exception of certain specific chemical types, the quantification of dose–responses is not well developed. Consequently these effects are not discussed in the hazard section of this Part, but in the risk section where the estimation of exposure permits a qualitative assessment of the associated risk. Adverse biological effects are, for example, on the growth, survival and reproduction of organisms present. The aquatic ecosystem is usually seen as being at greatest risk, so most available toxicity data relate to this. For satisfactory insight, the data should cover a minimum of three of the four levels of the food chain (Figure 4.2), since interference with one can have significant effects on the others. The trophic (feeding) levels are usually represented by algae (primary producer), daphnia (primary consumer) and fish (secondary consumer/predator). Studies on model ecosystems, such as pond studies, can provide a valuable and more complete view of environmental behaviour under natural conditions, and in sectors such as sediment, which cannot be studied in isolation. Ecotoxicity data for the soil (terrestrial) compartment are taken to include not only organisms affected directly through contact with soil or water (e.g. plants, earthworms) but also, for convenience, vertebrates (including birds) affected mainly through the food chain. Ecotoxicity data for the air compartment are rarely available, most inhalation studies being mammalian and related to human health risk rather than ecotoxicology.
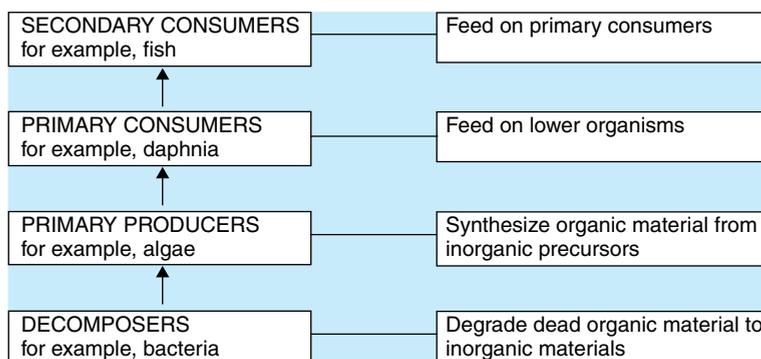
Figure 4.2 Trophic levels of the aquatic food chain

Secondary exposure is addressed via the potential of the substance to bioaccumulate along a food chain up to concentrations likely to have adverse effects on predators. Waste water treatment plants are an area of concern in that an adverse effect on their biodegradative organisms can seriously impair their overall performance and thereby increase the risk of significant environmental exposure to a variety of other materials. Exposure can be predicted from physicochemical properties of the materials and treatment plant process information. Hazard can be estimated from toxicity to bacteria, preferably species typical of waste water treatment plant biomass.

The structure of this Part mirrors the considerations of these risk assessment procedures by covering:

Exposure:

- Sources: both those arising throughout the normal lifecycle of a substance during manufacture, transport, storage, use and disposal, and also those arising from accidental releases, e.g. transport spillages.
- Distribution and persistence: physicochemical behaviour in water, soil and air, biodegradation and bioaccumulation.

Hazard:

- Ecotoxicity: to representative species in the aquatic and terrestrial compartments.

Exposure and hazard are integrated, with more detailed discussion as necessary, in the final section of this Part, where approaches to assessing environmental risk arising from accidental release and from normal lifecycle are considered.
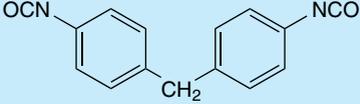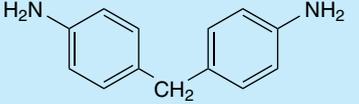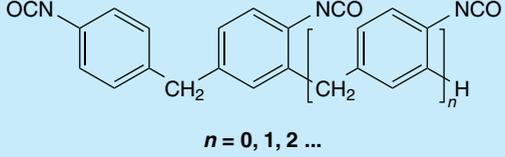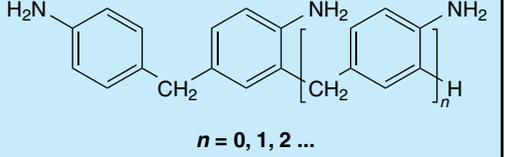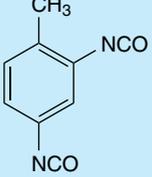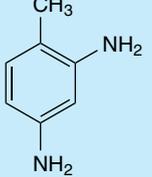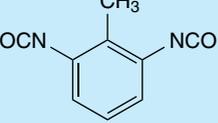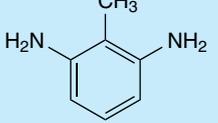
Figure 4.3   **Chemical structures MDI, TDI and the related diamines MDA, TDA**

The materials dealt with in this text are those which are commercially produced and have been used in ecological studies, i.e. polymeric MDI and 80/20 TDI, together with their individual monomeric components, 4,4′-MDI, 2,4-TDI and 2,6-TDI.

It is important when evaluating data to appreciate the complexities of the reaction of these materials with water. As discussed later, the only products of significant toxicity arising from this reaction are the diamines methylenediphenyl diamine (MDA) and toluene diamine (TDA). These are generally minor products, but it is important to be able to predict the extent of their formation (avoiding the common misconception that this is stoichiometric) and their environmental impact. For this reason the behaviour of MDA and TDA is discussed where appropriate. Much of the information in this text was generated in projects sponsored by the International Isocyanate Institute (III), and has been submitted to regulatory authorities in connection with risk assessment procedures.

Chemical structures for MDI, TDI, MDA and TDA are given in Figure 4.3. Further information on their chemical and physical characteristics is given in *Parts 5.3* and *5.4*.

Exposure

Sources of exposure

Releases of MDI and TDI from all stages of their lifecycles are very low. Of these, emissions to air from use are the most significant. Extent of accidental release, from spillages, is minimized by the properties of the materials. No significant adverse effects on the environment have been recorded from spillage incidents.

Product lifecycle

All stages of the lifecycle of MDI and TDI are rigorously controlled to minimize emissions, due to concerns over potential risks to human health.

Manufacture of MDI and TDI takes place in essentially closed systems under strictly anhydrous conditions as the presence of water would adversely affect the quality of the products. Releases to air are extremely low. They are even lower than is the case with polyurethane production, as a proportion of MDI or TDI processed. Neither MDI nor TDI is released to water under normal operating conditions. Plant residues are incinerated.

Transport and *Storage* are usually closed systems, with negligible opportunity for releases (see *Part 2*).

Use of MDI and TDI, such as in the manufacture of polyurethanes, including foams, elastomers, adhesives and coatings, is the main source of release, predominantly to air. However, any release is naturally constrained by the low volatility of MDI and TDI, and is further subject to rigorous regulatory control due to human health concerns. Abatement devices such as carbon adsorbers or

water scrubbers can be used to reduce releases to air (see *Part 2, Releases to the atmosphere from polyurethane manufacturing sites*).

Decontamination and waste disposal procedures are, in general, strictly controlled to minimize health risk, and hence environmental release of diisocyanate is insignificant. Part 2 deals with detailed aspects of the operational containment of MDI and TDI.

Accidental release

There are well-established procedures in most countries to minimize and contain accidental emissions during the manufacture and use of MDI and TDI. Transport and storage are also usually strictly controlled, but accidents can occur, particularly during transport, and a relatively small number of major incidents (involving spillage of >1 tonne of diisocyanate) have been recorded (Tables 4.1 and 4.2). MDI is transported as drumstock much more frequently than is TDI, which would account for the lower incidence of major spillages with MDI. Dispersion of these materials from spillages is constrained by their physical behaviour: low volatility and immiscibility with water. Well-established procedures for the treatment and disposal of spillages further constrain movement of the diisocyanate (see *Part 2*). For liquid spills onto ground

Table 4.1 **Polymeric MDI: major spillage incidents (>1 tonne).**
Information collected from a variety of sources by the Scientific Office of the III.

Year reported	Location	Incident	Amount released (tonne)	Action taken	Observations
1979	Germany	Storage tank leaked into tunnel and onto ground	30	Pumped out, neutralized.	No problems recorded.
1984	Italy	Tank leaked	4	Not recorded.	No problems recorded.
1986	USA (Ohio)	Road trailer spilled into river	6	Removed solid polymeric MDI in sheets	MDI sank, collected in calm deep depressions in river bed, froze (water 3 °C). Slowly reacted over 4 months (water to 20 °C). No problems recorded.
1991	USA (Kentucky)	Rail tank car spilled mainly into river. Fire broke out from contents of other cars.	50	Delayed for 2 days by fires. Solid material skimmed off river, soil removed to 15 cm (6 inches) depth at site of spill and incinerated.	Only 2 to 4 ppb MDI in air 6 m (20 ft) downwind. MDI failed to burn. Much MDI reacted to solid polyureas. USEPA testing of river completed after 3 days and material in river declared non-hazardous.

Table 4.2 **TDI: major spillage incidents (>1 tonne).**
Information collected from a variety of sources by the Scientific Office of the III.

Year	Location	Incident	Amount released (tonne)	Action taken	Observations	Reference
1975	Germany (Helmstedt)	Road tanker spill affecting 300 m^2 marshy woodland.	14	Covered with sand (about Im deep). Soil and water analysed periodically over 6 years.	TDI converted to polyureas within 6 weeks. No TDA detectable in soil (<3 mg/kg) or water (<50 μg/l) at any stage. No environmental damage observed.	Brochhagen and Keller (1983)
1976 to 1983	USA (various)	Nine spills/leaks from road, rail and storage tanks.	1 to 90	Not recorded.	No problems recorded.	
1979	Italy	Road tanker spill into creek and lake.	22	Site cleaned. Details not recorded.	No problems recorded.	
1980	Italy	Road tanker spill.	3	Covered with sand and sodium carbonate.	No problems recorded.	
1980	USA (Ohio)	Road tanker spill of TDI and polyol. Small fire soon extinguished.	100	Neutralized by aqueous ammonia/alcohol. Soil and foam removed.	TDI/polyol reacted to form foam. No environmental problems noted.	
1981	USA (NY State)	Road tanker spill into river.	5	Site cleaned. Details not recorded.	None recorded.	

Table 4.2   (continued)

Year	Location	Incident	Amount released (tonne)	Action taken	Observations	Reference
1982	Germany (Burgheim)	Storage tank leak to sewers.	15	Polyureas flushed from water treatment plant.	Up to 10 % entered water treatment plant and formed solid polyureas. Performance of plant was temporarily affected.	Steinhäuser (1985)
1985	France	Road tanker spill into fast-flowing river.	20	Stream cleaned out. Analysed river water for 2 weeks.	TDI reacted to white solid (polyureas) and distributed for 2 to 3 km downstream. Amine detected at 5 mg/litre in river downstream after 2 days (however, only 2 mg/litre dissolved organic carbon), but was below detection level (<0.3 mg/l) after 2 weeks.	Rhône-Poulenc (1985)
1989	Canada	Pipe spill onto dockside.	40	Frozen TDI with ice and soil removed and decontaminated with aqueous ammonia.	None recorded.	
1989	Australia	Rail tanker derailed with leak onto ground.	8	TDI neutralized by aqueous ammonia, then buried elsewhere.	Prior to decontamination air sampling showed >20 ppb TDI close to spill and up to 12 ppb within 50 m.	EPA Australia (1989)

these involve containment and, where possible, coverage with adsorbent, such as wet sand, in which the diisocyanate is totally reacted. Spills into water are often left to react. Solid spills can be removed for decontamination. In consequence, environmental exposure to diisocyanate from spillage incidents is minimal and, as can be seen in Tables 4.1 and 4.2, no adverse environmental effects of significance have been recorded from treated spills. In almost all cases careful monitoring of the effects of the spillage had been undertaken. The levels of exposure to be expected from spillages, and the associated environmental risks, are discussed further in Part 5.6.

Distribution and persistence
Physicochemical behaviour with water

MDI and TDI are insoluble in water, and do not disperse readily. They form globules which react at their surface forming a crust of solid, insoluble polyurea. The rate of this surface reaction depends on the efficiency of any mixing, and under static conditions, such as are found in a typical spillage, may take several weeks for completion. Diamine is usually only a minor product, particularly when agitation is poor. Typical diamine concentrations produced at diisocyanate loadings of up to 1 g/l in laboratory studies range from ≤3 mg/l for MDA and 0.5 to 16 mg/l for TDA. In pond studies and actual spillages, levels of diamine are even lower, often below the detection limit. Any MDI or TDI present in aqueous *solution* would react very rapidly, within minutes. Because of this, and their low inherent water solubility, MDI and TDI are almost unavailable in aqueous solution.

The interaction of MDI and TDI with water, with all its complexities, is a critical determinant of much of their environmental behaviour. A clear understanding of the overall reaction process is vital for a realistic prediction of the impact of releases of diisocyanate, and for a full appreciation of the design and relevance of physicochemical and ecotoxicity studies. The fate of MDI and TDI in the aquatic environment has been reviewed by Yakabe *et al.* (1999).

Two sequential steps are believed to be involved in the reaction of an isocyanate with water. Hydrolysis (*Step 1*) proceeds via formation of a carbamic acid which decarboxylates readily to the amine. This amine can itself react with more isocyanate to produce a urea (*Step 2*). See *Part 5.3, The chemistry of MDI and TDI* for more information.

$$RNCO + H_2O \longrightarrow RNHCOOH \longrightarrow RNH_2 \quad + CO_2 \qquad (1)$$

$$RNCO + RNH_2 \longrightarrow RNHCONHR \qquad (2)$$

Hydrolysis (*Step 1*) in aqueous solution is rapid, with a half-life of 20 s for phenyl isocyanate (Castro *et al.*, 1985; Ekberg and Nilsson, 1976). It is catalysed by bases but not by acids. The corresponding homogeneous hydrolysis of

MDI and TDI would be expected to be similarly rapid. However, the subsequent reaction of the amine with further isocyanate (*Step 2)* is even faster. For phenyl isocyanate in 90:10 water/dioxan, the ratio of the rate constants for the addition of amine and hydrolysis has been found to be about 4×10^4 (Ekberg and Nilsson, 1976). A similar ratio can be derived from a published study on the reactivity of phenyl isocyanate (Hegarty *et al.*, 1975). During reaction of the isocyanate the concentration of amine would be expected to build up to a low, equilibrium level at which formation by *Step 1* is balanced by removal by *Step 2*. Only at high dilution would amine be predicted to be the major final product.

In the light of this high reactivity it might be presumed that contact of MDI or TDI with water would result in a vigorous, exothermic reaction. However, this is not so. The behaviour of MDI and TDI in water is complicated further by two factors. Firstly, MDI and TDI have a functionality greater than one. *Step 1* of the process will lead ultimately to diamine (MDA or TDA), but *Step 2* is now a typical polymerization reaction and leads to oligo- and poly-ureas:
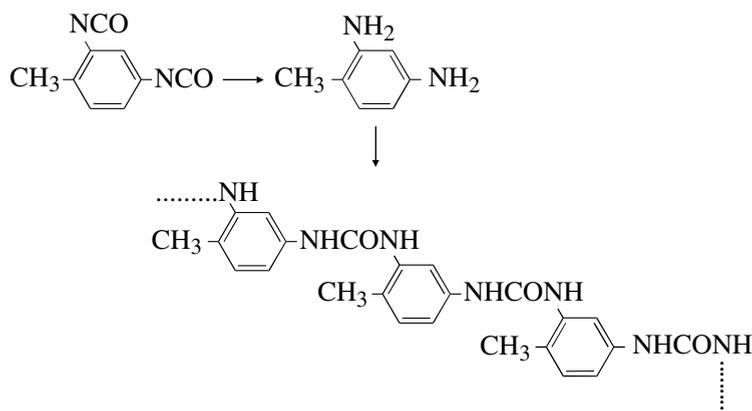
These are solids and, apart from the lowest oligomers, are insoluble in all common organic solvents and water.

Secondly, it is difficult to disperse MDI and TDI in water, because they are relatively dense, hydrophobic materials. This situation is exacerbated for polymeric MDI which is a semiviscous liquid. All evidence points to their having low inherent solubility, and slow rates of dissolution. Consequently, in contact with water, both MDI and TDI sink as globules or solid masses, which react at their interface with water. This heterogeneous interaction is relatively slow because of the low surface area involved and the slow diffusion of water into the reaction zone. The polyurea produced, being inert and insoluble, forms a crust at the surface. This hinders diffusion of any diamine or other soluble species from the reaction site and hence promotes production of more polyurea and markedly reduces the overall yield of diamine. A globule thus solidifies from the outside inwards. When the MDI or TDI is solid (as in a cold river) this behaviour is exacerbated in that the diffusion-controlled heterogeneous interaction is now slower, and diisocyanate within the globule can remain unreacted for a surprisingly long time; up to 5 weeks has been recorded. Entrapped carbon dioxide (released from hydrolysing diisocyanate) can cause the globule to float temporarily and hence move from its initial location.

Because of this behaviour it is not possible to produce a solution of a pre-determined concentration of MDI or TDI in water. As it is very difficult to mix these materials thoroughly into water, it is improbable that a high level of dispersion could ever occur in the environment, particularly for MDI. The proportions of soluble products (diamines and oligoureas) formed will depend on the reaction conditions, in particular the concentration and degree of dispersion of the material. This has profound consequences on all aquatic studies of MDI and TDI, as discussed later.

It is a common misconception that MDA and TDA are the major products arising from the reaction of MDI and TDI with water. This is a quite erroneous generalization and its application to exposure and hazard assessment will lead to unrealistic and misleading conclusions. Under conditions pertinent to those arising in the environment, polyureas are usually the major products. Only under conditions of high dilution and good agitation, or as a notional concept in modelling a homogeneous solution, would diamine be predicted to be the major product. Nevertheless, it is useful to be able to predict the approximate level of diamine likely to be produced under specific conditions, and hence the associated ecotoxicological behaviour. Studies sponsored by the III have helped to provide this insight and are discussed below.

Early studies were essentially spill simulations and, although valuable as qualitative indications of behaviour, analytical limitations which are now apparent render quantitative conclusions less secure, particularly in the differentiation of diisocyanate and diamine. In one such study, TDI (2.5 % in water) was added to water over the pH range 5 to 9. The TDI agglomerated and formed a hard crust, which thickened over 35 days until no liquid organic core was left and only traces of TDI and TDA were detectable. TDA was present at low levels, averaging 0.6 to 1 mg/l in solution in the water, corresponding to a yield of about 0.003 % (Abele and Brochhagen, 1976).

This relatively slow rate of reaction under unstirred conditions contrasts with a later study in which 80/20 TDI was stirred vigorously into water, at a loading of 28 mg/l, at ambient temperature. Approximately half the TDI was lost in 30 s. With less efficient stirring, the half-life was about 3 to 5 min (Yakabe *et al.*, 1999).

The most comprehensive studies have been performed by the Chemicals Inspection and Testing Institute (CITI), Japan. In these studies, diisocyanate was stirred vigorously into water over a range of nominal concentrations. The loss of MDI or TDI and the formation of soluble species, including diamine, were followed over the course of reaction. The major part of these studies was conducted at 25 to 27 °C. Some comparative experiments in sea water were also made. However, attempts to repeat the studies at 12 °C were only partially successful because of the greater difficulty of dispersion of the diisocyanates at this temperature due to their increased viscosity, or even solidification in the case of 2,4-TDI.

Experimental detail and significant results of the study with polymeric MDI at 25 °C are presented in Table 4.3 (Yakabe *et al.*, 1994a). It is important to note that real dispersion was not achieved at loadings above 100 mg/l, at which half-lives were approximately 20 h. The major product at these loadings, produced in a yield of 99 % or more, was a solid, insoluble polyurea. Soluble product, as measured by dissolved organic carbon (DOC), amounted to only

Table 4.3 **Reaction of polymeric MDI with water, with vigorous stirring, at 25 °C.**

Method

For loadings above 100 mg/l, the polymeric MDI was vigorously stirred in water. However, it did not disperse but quickly formed a lump around the stirrer. Better dispersions of the lower loadings were made by addition of polymeric MDI from a stock 1 % solution in dimethylsuphoxide. At appropriate intervals the organic phase was analysed for polymeric MDI (monomer and four lower oligomers) by HPLC and the aqueous phase for 4,4′-MDA, by HPLC, and for dissolved organic carbon. Rates of loss of polymeric MDI roughly fitted zero-order kinetics.

Results

Loading of PMDI mg/l	Half-life of 4,4′-MDI h	Final concentration of 4,4′-MDA mg/l
20[a]	(<2)[a]	(1.8)[a]
100[a]	(<2)[a]	(1.5)[a]
400	ca 20[b]	1.5
1000	ca 20[b]	1.8
10 000	ca 20[b]	2.6

[a]Not directly comparable with other results in that the mixing procedure gave better dispersion; also equivocal in that pre-reaction of some of the polymeric MDI with small amounts of water adventitiously present in the dimethylsulphoxide may have occurred.
[b]Approximately the same for oligomers also.

about 6 mg/l. The only identified component of this soluble product was 4,4′-MDA, present at only 1.5 to 2.6 mg/l over the entire range of polymeric MDI loadings. Mixing of polymeric MDI into water proved even more difficult at 12 °C and the reaction was, unsurprisingly, markedly slower. The reaction rate in sea water, at 25 °C, was similar to that in fresh water.

The vigorous stirring employed in these studies does not relate to the conditions typical of an environmental spillage of diisocyanate. Therefore studies of the reaction of polymeric MDI with water under unstirred conditions were also made (Table 4.4) (Yakabe *et al*., 1994a). The loading in these studies was 17 g/l. The course of reaction was similar to that in stirred systems but slower, and the rate was observed to increase in proportion to the interfacial area, as would be expected for a heterogeneous reaction. The material solidified from the interface downwards during reaction, which was substantially complete in 10 to 12 days. The concentrations of soluble products formed were even lower than those formed in the stirred experiments, and final MDA concentrations were only about 0.5 mg/l.

At 27 °C, the isomer 2,4-TDI proved to be more readily dispersible than polymeric MDI and a more rapid reaction was found (Table 4.5) (Kitano *et al*., 1989; CITI, 1991). However, the observed dependence of half-life on the initial nominal TDI concentration is an indication of a heterogenous, interfacial reaction. Low final concentrations of soluble species were formed, and these built up predominantly during the early stages of reaction. At 1000 mg/l TDI the total soluble product, amounting to a measured 40 mg of DOC per litre,

Table 4.4   **Reaction of polymeric MDI with water, unstirred, at 25 °C.**

Method

Polymeric MDI (5 g) was added to each of three beakers, of 10, 50 and 100 ml
capacity, and each of these was itself immersed in a larger beaker containing 300 ml
of water. The polymeric MDI formed a layer on the base of each small beaker. At
appropriate intervals the organic phase was analysed for polymeric MDI (monomer
and four lower oligomers) by HPLC, and the aqueous phase for 4,4'-MDA, by HPLC,
and dissolved organic carbon (DOC).

Results

Surface area of PMDI cm^2	Half-life of 4,4'-MDI days	Final MDA concentration mg/l	Final DOC mg/l
5.7	6.2[a]	ca 0.5	3
13.2	4.5[a]	ca 0.5	2
18.1	3.8[a]	ca 0.5	3

[a] Approximately the same for oligomers.

Table 4.5   **Reaction of 2,4-TDI with water, with vigorous stirring, at 27 °C.**

Method

The TDI was stirred vigorously into water. At appropriate intervals the organic phase
was analysed for 2,4-TDI (by GC), and the aqueous phase for 2,4-TDA (by HPLC)
and for dissolved organic carbon. The pH was observed to vary between 6.3
and 6.8.

Results

Loading of TDI mg/l	Half-life of TDI h[a]	TDA produced	
		Final concentration mg/l	**Yield from TDI** %
10	<0.5	4.3	61
100	<0.5	13.0	19
1000	ca 0.7	16.1	2
10 000	ca 1.6	27.5	0.4

[a] Loss rates fitted to first order kinetics.

was analyzed by HPLC as 28 % TDA with the remainder being mono- and di-
ureas. Separately prepared and characterized samples of these ureas were used
as HPLC standards. Final TDA concentrations were low, and only at the lowest
loading of TDI (10 mg/l) was TDA a major product. After 13 days of contact,
the water-insoluble product was predominantly soluble in a solution of lithium
chloride in dimethylformamide and was found to have a molecular weight of
about 5600. At 12 °C there was considerable scatter of the experimental data,
ascribed to poor and irreproducible dispersion of TDI. The rate of reaction in
sea water (at 27 °C) was similar to that in fresh water, but slightly slower.

Under unstirred conditions similar to those used for MDI, at a nominal TDI concentration of 15 g/l, the loss of TDI was considerably slower and followed zero-order kinetics over the initial stages. The rate increased proportionally to the interfacial area, as would be expected. The material gradually solidified and most of the TDI had reacted within 30 days. Final concentrations of TDA ranged from 17 to 30 mg/l. Soluble products other than TDA amounted to only about 2 mg/l, expressed as DOC, for all but the sample of lowest surface area (Yakabe *et al.*, 1994b).

In a restricted set of similar experiments, 2,6-TDI behaved similarly to 2,4-TDI but reacted with water more slowly, by a factor of about 3 when stirred and 15 when unstirred. Levels of diamine were roughly double those of 2,4-TDA when stirred, but only half when unstirred. The other major soluble product of this reaction was identified as the monourea N,N'-di-(2-methyl-3-aminophenyl) urea:

$$\text{H}_2\text{N} \overset{\text{CH}_3}{\diagup} \text{NH–CO–NH} \overset{\text{CH}_3}{\diagup} \text{NH}_2$$
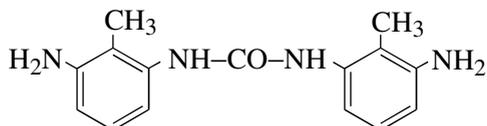
80/20 TDI behaved in a manner intermediate between that of its two components (Kitano *et al.*, 1991).

Considerable data on the production of TDA resulting from reaction of TDI with water are found in a series of studies by CITI on the ecotoxicity of TDI. In most of these, reported in the ecotoxicity section below, 80/20 TDI was stirred into water, at various loadings, for 24 h prior to the reaction medium being used for tests conducted over 2 to 4 days. In many of the studies the TDA concentration in the test medium was measured at the beginning and end of the test. A correlation of the concentration of TDA produced with the TDI loading under these stirred conditions is shown in Figure 4.4 (grey circles). In some of these ecotoxicity studies the TDI was not stirred after being added to the test medium. In these cases the TDA concentrations produced were significantly below the corresponding ones from stirred tests, at all concentrations. Some examples, at relatively low loadings of TDI where complete reaction should have occurred over the duration of the test, are plotted on the graph to exemplify this point (filled squares). Two other sets of data are also plotted on this graph. The first is from studies on the chronic toxicity of TDI to *Daphnia magna* (Table 4.15). In these, low loadings, 0.28 to 4.4 mg/l, of 80/20 TDI were stirred into water for 24 h. The data plotted (open circles) are the maximum TDA concentrations found in the media, after storage for 1 week. The TDA concentrations produced were about a half of the TDI loadings used, and corresponded to chemical yields of 58 to 71 %. The second set (filled lozenge) is of final TDA concentrations from the physicochemical studies on the interaction of 2,4-TDI with water, described earlier. In these studies particular care was taken to achieve good agitation, and it is noteworthy that the TDA concentrations produced lie at the top of the range. It is apparent that production of TDA is critically dependent on the efficiency of mixing. The spread of the data is probably indicative of the difficulty of
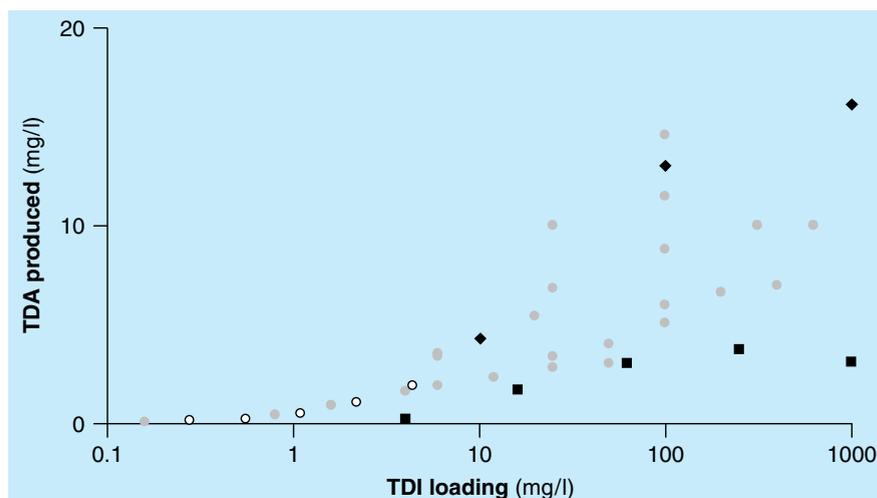
Figure 4.4 **Concentrations of TDA produced from reaction of TDI with water:** •**, ecotoxicity studies, stirred (Tadokoro, 1997); ■, ecotoxicity studies, unstirred (Tadokoro, 1997); ♦, physicochemical studies, well stirred (Table 4.5) (Kitano, 1989; CITI, 1991); ○, ecotoxicity studies, stirred (Cerbelaud, 1997).**
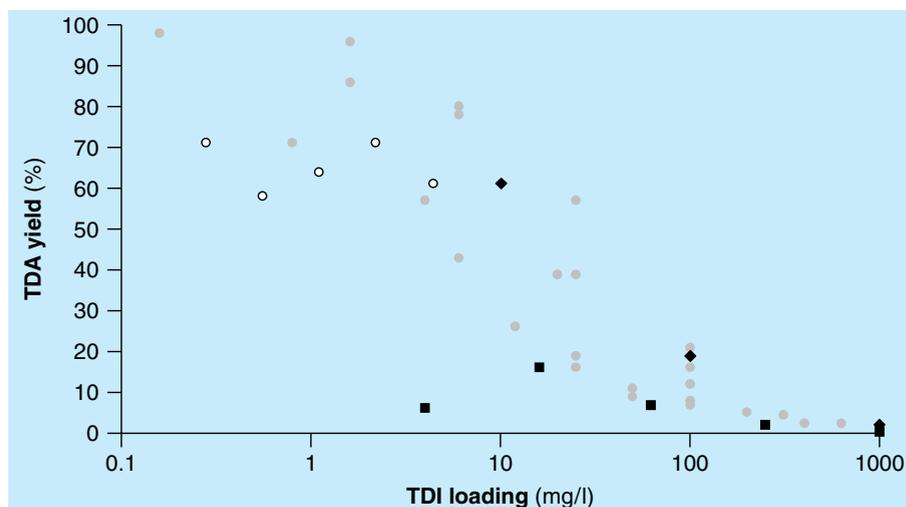
Figure 4.5 **Yield of TDA from reaction of TDI with water:** •**, ecotoxicity studies, stirred (Tadokoro, 1997); ■, ecotoxicity studies, unstirred (Tadokoro, 1997); ♦, physicochemical studies, well stirred (Table 4.5) (Kitano, 1989; CITI, 1991); ○, ecotoxicity studies, stirred (Cerbelaud, 1997)**

maintaining precise control and reproducibility of agitation over several sets of experiments.

A plot of the average chemical yield of TDA from TDI, against TDI loading, from these data (Figure 4.5) illustrates even more clearly that only with good dispersion, and at low nominal concentrations of TDI, is TDA a major reaction product.

There are no such data available from ecotoxicity studies on MDI. However, MDA concentrations of only 1.5 to 2.6 mg/l were found for a wide range of nominal concentrations of polymeric MDI (20 to 10 000 mg/l) in the physicochemical studies described above. Production of MDA by reaction of MDI with water thus appears to be even less, by a factor of about 3 to 5, than that of TDA from TDI.

The correlations shown in Figures 4.4 and 4.5 may serve to predict the concentrations of TDA likely to arise from TDI hydrolysis in laboratory studies. However, in more realistic conditions of environmental contact with water, although the same physical behaviour is seen, levels of diamine found are much lower. In spillage incidents, low levels only of TDA, and no MDA, have been detected. Similarly, in the pond study of polymeric MDI (see *Ecosystem study*) neither MDI nor MDA could be detected in pond water (<4 and $<10 \mu$g/l, respectively). In only one analysis, in the early stages of the study, was any MDA detected in the sediment. The major reason for these lower levels of diamine under more realistic spillage conditions is probably that there was little or no agitation of the spilled material. The polymeric MDI remained almost undisturbed, a condition shown to be conducive to the formation of polyurea at the expense of diamine. Strong binding of diamine to soil or sediment and photodegradation in water may also be contributing factors under certain conditions.

Physicochemical behaviour in soil

MDI and TDI are not mobile in wet soil or sand but are converted to solid polyureas. Little or no diamine has been detected in laboratory studies or spillage incidents.

An understanding of the behaviour of diisocyanates in soil is important in assessing not just the potential exposure of soil organisms but also their uptake of diisocyanate and the risk from secondary exposure this poses to predators, and the potential contamination of drinking water. The behaviour of MDI and TDI in soil is dominated by their ready reaction with the water which is always present. In this heterogeneous process, described earlier, diisocyanate is trapped within a crust of solid, insoluble polyureas. No free diisocyanate, and only low levels of diamine, can be detected in solution. A study in which 80/20 TDI was covered by wet sand showed only 3.5 % TDI remaining and no detectable TDA ($<10 \mu$g/kg) after 8 days (Abele and Brochhagen, 1976). Studies of the migration of polymeric MDI and TDI through soil, in which attempts were made to extract the materials from light sandy soils with water over 2 days, showed no detectable levels of diisocyanate or diamine (<0.2 mg/l) in the leachate (von Blumencron, 1978).

In a road accident (Table 4.2), 14 tonne of TDI were spilled onto marshy ground and treated by covering with wet sand. Soil concentrations of TDI and TDA were <3 mg/kg after 6 weeks and $<50 \mu$g/kg (not detectable) after 1 year, and neither substance was detectable ($<50 \mu$g/l) in groundwater.

Behaviour of hydrolytic reaction products in water and soil

The polyureas, which are usually the major products of reaction of MDI or TDI with water, are solid, insoluble and stable in the environment to both chemical and biological attack. The diamines, MDA and TDA, are water soluble but are not mobile in soil, to which they bind strongly. These diamines are photodegradable, and are biodegradable in industrial waste water treatment plants and in aerobic soil.

The polyureas, which are usually the major products of reaction of MDI and TDI with water, appear to be stable in the environment, as would be expected from their comprehensive insolubility and the stability of ureas generally.

In one study the solid insoluble polyureas resulting from reaction of polymeric MDI and 2,4-TDI with water were stirred at 40 °C in buffer solutions of pH 4, 7 and 9, for 2 weeks. No soluble products, dissolved organic carbon or diamines, were detected. In similar tests at pH 1.2, slight degradation was found for the TDI polyurea, but no diamine was detectable (Yakabe, 1994a).

In another study, simulating a decontamination procedure, solid insoluble polyureas from radiolabelled 4,4'-MDI and 80/20 TDI were mixed into wet soils, ranging from sandy to clay, sealed under CO_2 traps for 4 months, then extracted with acid. No radioactivity was detected in the traps or in the acid leachate, indicative of no biotic or abiotic degradation having occurred to form carbon dioxide, diamines or soluble oligoureas (Martens and Domsch, 1981). The insoluble diureas resulting from reaction of MDI and TDI with water have been shown to be not readily biodegraded.

The diamines, MDA and TDA, which occur in the soluble portion of the reaction product are resistant to hydrolysis but have been shown to be subject to photodegradation in aqueous solution (Hellpointner and Dehner, 1997; Hellpointner and Hoffend, 1997). They are easily biodegraded by microorganisms such as are found in industrial waste water treatment plants, adapted to the metabolism of related chemicals. They also appear to degrade easily in aerobic soil. More detail on the biodegradation of the diamines is given below.

MDA and TDA have low mobility in soil. In one study residues from TDI manufacture, containing TDA, were applied to soil which was leached over 85 weeks by water and acetate buffer at pH 4.6. No TDA ($<3 \mu g/l$) was detected in the leachate (Ode, 1993). In another study, landfill simulators containing MDA and TDA, operating in a fermentative anaerobic mode, were leached over 2 years. The very low levels of diamine found in the leachates corresponded to extraction of only about 0.1 % of the TDA added, and even less for MDA (Kennedy *et al*., 1996).

A chemical of close structural similarity to these polyureas, the bis(phenylurea) derived from MDI:

has been found to hydrolyze with a half-life of 45 days at 70 °C in a neutral mixture of dimethylsulphoxide and water (Chapman, 1989). Applying to this the known temperature dependence of the hydrolysis of diphenylurea, taken from another study (Audu and Heyn, 1988), gives a predicted half-life of about 25 years at 25 °C. Degradation of the insoluble polyurea in contact with water should be even slower, constrained by being restricted to the surface of the material and by the low concentration of water within the reaction zone.

The reason for the low mobilities of MDA and TDA lies in the strength of their binding to soil. A study of the adsorption of radiolabelled 4,4′-MDA, 2,4-TDA and 2,6-TDA to sterile soils under both aerobic and anaerobic conditions showed strong binding which, for TDA in particular, increased markedly over several days. A summary of the relevant results under aerobic conditions (Cowen *et al.*, 1998) is presented in Table 4.6. Similar results were obtained under anaerobic conditions. According to the classification of McCall *et al.*, 1980, both MDA and TDA would be categorized as *immobile* from their soil organic carbon sorption coefficients after 7 days of adsorption. In addition, comparison of the sorption and desorption coefficients shows a degree of irreversibility of binding for TDA, and very little of either sorbed diamine could be removed from the soil even with strong acid or base. This behaviour suggests irreversible chemical interaction in addition to the expected physical adsorption processes of hydrophobic binding and ion exchange. This conclusion is supported by evidence in the literature for the chemical reaction of aromatic amines with humic acids from soil (see Thorn *et al.*, 1996 and references discussed therein).

Table 4.6   **Adsorption of TDA and MDA to soil under aerobic conditions.**

Method

Solutions of ^{14}C-labelled TDA and MDA in 0.01 M $CaCl_2$ solution were equilibrated with autoclaved soil, and the concentration of diamine in the aqueous phase determined by ^{14}C activity at intervals over 7 days. Distribution coefficients for sorption and desorption (R_s, R_d) were calculated as the ratios of the concentrations in soil (μg/g) and in solution (μg/l), after 7 days of sorption and a subsequent 1 day of desorption respectively.

Results

Soil adsorption built up markedly over 7 days. Values of R_s and R_d (after 7 days) are given below. A ratio R_d/R_s significantly greater than unity indicates some irreversibility of binding. All values are averages for a sandy loam and a silt loam, which behaved similarly.

Substance	$R_s{}^a$	R_d	R_d/R_s
2,4-TDA	205	525	2.6
2,6-TDA	149	485	3.3
4,4′-MDA	78	138	1.8

[a]These figures correspond to values of the soil organic carbon sorption coefficient K_{OC} (see Table 4.11) of about 5000 to 14 000.

Physicochemical behaviour in air

Atmospheric concentrations of MDI and TDI arising from releases are related to the low volatility of these materials, particularly of MDI. MDI and TDI do not hydrolyze to any significant extent in the vapour phase in air, but they, and their respective diamines, degrade rapidly

by reaction with hydroxyl radicals. In consequence, no atmospheric
accumulation of any of these materials would be expected. This degra-
dation of MDI and TDI is unlikely to enhance ozone formation in a
polluted atmosphere.

Both MDI and TDI have low volatility, and potential concentrations in air
from spillages or lifecycle releases are, therefore, low. The vapour pressures at
20 °C, about 1.4 Pa (0.01 mmHg) for both TDI isomers and about 3×10^{-4} Pa
(5×10^{-6} mmHg) for 4,4′-MDI, correspond to saturated vapour concentra-
tions of 100 mg/m³ for TDI and 0.03 mg/m³ for polymeric MDI. However, if
aerosols are present, the concentration of airborne MDI is raised above these
low saturated vapour concentrations. This might occur in operations involving
hot processing or spraying of polymeric MDI. Such aerosols could comprise
droplets of MDI itself (for example condensation aerosols formed on cooling
of hot vapours) or of MDI in admixture with other components of a reacting
system, or MDI coated onto particulate matter. To assess the potential impact
if these were vented to air, a study was performed modelling the deposition
and dispersion of a hypothetical release of MDI aerosol. Three locations in
the USA, of varied meteorological conditions, were considered. A selection
of the results for one location is shown in Table 4.7 to illustrate the findings
(Roffman and Rivkin, 1995).

The important conclusions drawn from the study were:

(a) Predicted air concentrations were similar, regardless of whether MDI was
    present as a vapour or aerosol, and were little affected by aerosol size
    within the range modelled.
(b) Ground-level air concentrations and deposition rates were significantly
    reduced by the provision of a stack.
(c) The deposition rate of aerosol was higher than that of vapour, but was still
    low. Deposition had little depleting effect on the predicted ground-level
    air concentrations.

These predictions apply equally well to TDI, but aerosol emissions of TDI are
unlikely because of its higher vapour pressure.

A wider implication of the first conclusion is that this calculation can be
used to predict dispersion of normal gaseous releases of MDI and TDI to
air. The dominant effect noted was that of a stack in reducing building down
draught. Without a stack, maximum ground-level air concentrations ranging
from 0.001 to 0.008 % of release concentrations were predicted, all within
100 m of the building. Addition of a stack significantly reduced these ground-
level air concentrations close to the release; maxima, generally of 0.001 %
or less of release concentrations, now occurred at or beyond 100 m of the
release point. Simple increase of building height, without a stack, did not
have such a marked effect. Typical data to illustrate this point are shown in
Table 4.8. The dramatic effect of adding a 15 m stack to a 10 m building is
shown in Figure 4.6. This also illustrates how dispersion of the release leads
to very low concentrations at greater distances from the building. At 800 m
distance, typical ground-level average air concentrations were considerably

Table 4.7   **MDI aerosol release model.**

Method

The USEPA COMPDEP model was used to calculate the dispersion of MDI aerosol released to air at various heights in the vicinity of three cities in the USA. A series of aerosol particle sizes was assumed, from 0.1 to 50 μm. The emission was set at 1 mg/s, 0.27 mg/m^3, in air for 12 h/day over 365 days/year. It should be noted that the calculation presumes that MDI is present entirely as aerosol at all times, though this concentration represents the saturated vapour concentration of MDI at about 35 °C.

Results

Selection from predictions for Jackson, Mississippi using climatic data for 1989. Release is from a building 10 m high, with and without a 5 m stack.

Release	Aerosol size μm	Annual average, maximum ground-level air concentration μg/m^3
No stack: release height 10 m	0.1 50	0.015 at 40 m 0.018 at 40 m
5 m stack: release height 15 m	0.1 50	0.006 at 100 m 0.007 at 100 m
		Wet and dry annual average deposition rate mg/m^2 year
5 m stack: release height 15 m	0.1	2.1 at 10 m maximum $\leq$0.3 at $\geq$100 m 0.2 over 600 m radius

Table 4.8   **Dispersion of MDI releases to air.**

Method

Aerosol release model (Table 4.7), 0.1 μm particle size. Selected from predictions for Jackson, Mississippi and Boston, Massachusetts.

Release height m			Highest annual average ground-level air concentration as % of release concentration	
Building	**Stack**	**Total**	**At 40 to 50 m**	**At 200 m**
10	–	10	0.005	0.002
15	–	15	0.003	0.001
10	5	15	0.0015	0.001

less than 0.001 μg/m^3 (<0.0004 % of the release concentration) both with and without a stack. This model takes no account of atmospheric degradation, discussed below, which would reduce background atmospheric concentrations over longer timescales.
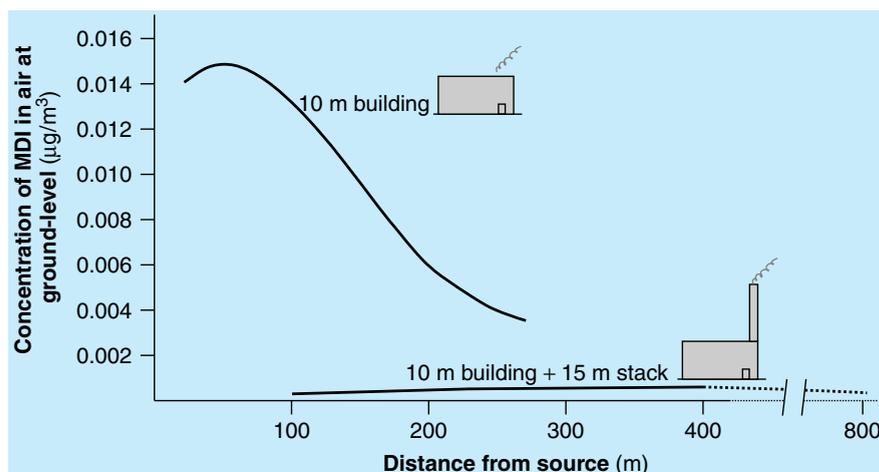
Figure 4.6 Dispersion modelling of MDI releases to air. Based on the aerosol release model given in Table 4.7 with aerosol of 0.1 μm diameter, and 1989 climate data from Jackson, Mississippi

Although intended to be site-specific, this model provides a reassuring view of the atmospheric concentrations of MDI and TDI likely to be encountered from typical releases. The emission rate of 1 mg/s, arbitrarily chosen for this calculation, corresponds to that from a foam manufacturing plant using 630 tonnes per year of TDI with a typical unabated release of 25 g/tonne processed. The predictions are for maximum average ground-level air concentrations of TDI of only $0.015\,\mu g/m^3$ very close to a plant with no stack and $0.006\,\mu g/m^3$ at 200 m distance. Use of a stack reduces these concentrations significantly, by a factor of 2 to 3 for a 5 m stack, and considerably more for a 15 m stack, as can be seen in Figure 4.6. For MDI the corresponding typical release, and hence the predicted air concentrations, are even lower.

A closely related study (Middleton, 1998) modelled the dispersion of measured MDI releases from two manufacturing sites in the USA, and concluded that annual average levels at the fenceline and beyond were within currently accepted limits. More detail is given in *Part 5.6, Occupational exposure limits, stack limits and community limits.*

The chemistry and fate of these materials when present in the atmosphere will now be considered. TDI has been shown to be readily degraded in air. Although the extremely low vapour pressure of MDI has precluded experimental studies, it is predicted to behave similarly. All reliable evidence indicates that MDI or TDI do not undergo atmospheric hydrolysis to the diamines. Several early studies reported fast atmospheric hydrolysis to TDA (for example Dyson and Hermann, 1971; Goellner, 1978), but were flawed due to failure to appreciate the high adsorptivity of TDI onto surfaces and the possible conversion of TDI to TDA during sampling and analysis. Since this was pointed out no further reports of this nature have been made. In more recent studies no TDA was detected in TDI atmospheres generated for biological monitoring (Brorson *et al*., 1989; Skarping *et al*., 1991).

Table 4.9   **Atmospheric degradation of 80/20 TDI: effect of irradiation.**

Method

Atmospheres containing 0.3 to 4 mg/m^3 of 80/20 TDI, and of relative humidity 7 to 70 %, were generated in a 17 m^3 PTFE-lined chamber. The atmospheres were monitored for TDI, TDA, TDA-urea, and for organic carbon and nitrogen, over several hours in darkness (Holdren *et al*., 1984). In the second phase of the project, in which the effects of irradiation (simulating sunlight and various pollutants) were studied, the atmospheres were of relative humidity 60 % at 28 °C. They were monitored for TDI, TDA, hydrocarbons, ozone, nitrogen oxides, aerosol concentration and size, humidity and temperature (Duff, 1985).

Results

No TDA was detected in any experiment, corresponding to less than 0.05 % conversion of TDI. An appreciable TDI loss rate was observed in darkness. However it did not vary with relative humidity, and the atmospheric concentrations of carbon and organic nitrogen fell in direct proportion to it. This indicates a physical loss of TDI itself, probably by adsorption onto the walls, rather than a degradation. This loss rate in darkness was subtracted from the other observations, to give the degradation rates summarized below.

Irradiation conditions	Average TDI loss %/h
Clean air	21
Clean air + 4 % nitric oxide	3
Urban air pollutant hydrocarbon mixture (UAPHM)	21
UAPHM + 0.5 ppm ammonia	18
UAPHM + 100 μg/m^3 (NH$_4$)$_2$SO$_4$[a]	25
UAPHM + 0.2 ppm triethylenediamine[b]	20
UAPHM + 2 ppm triethylenediamine	84

[a]Common urban aerosol.
[b]Catalyst in polyurethane manufacture.

A major study of the atmospheric stability of 80/20 TDI was carried out by the Battelle Institute (Holdren *et al*., 1984). Details of the method and significant results are summarized in Table 4.9. Irradiation caused a significant loss of TDI which was little affected by a variety of pollutants but was suppressed by nitric oxide, a free radical scavenger. This latter finding implicates free radical attack in the degradation. Loss of TDI was enhanced by the presence of triethylenediamine (TEDA), a common polyurethane foam catalyst, but only at concentrations well above those found in emissions from flexible foam plants. No TDA was detected in any experiment, corresponding to less than 0.05 % conversion of TDI. This clearly indicates the absence of hydrolysis in the vapour phase.

The major atmospheric degradation process for most chemicals is oxidation by hydroxyl radicals, themselves generated photochemically (Atkinson, 1995). This was confirmed as the significant mechanism for TDI, and for TDA and MDA also, by a subsequent study. Details of the method and the results are recorded in Table 4.10. This study measured the degradation of 80/20 TDI in air, when exposed to hydroxyl radicals generated photochemically. The observed degradation rate corresponds to a half-life of 52 h in air.

Table 4.10 **Atmospheric degradation of MDI, TDI, MDA and TDA by hydroxyl radicals.**

Method

The test substances at concentrations in air of 7 to 36 mg/m^3, in a 420 litre chamber at 25 °C, were exposed to hydroxyl radicals generated by photolysis of methyl nitrite in the presence of nitric oxide, to prevent formation of ozone and nitrate radicals. Concentration-time profiles of test substance were determined by *in situ* infrared absorption spectroscopy. Use of toluene as the reference substance removed the need for precise knowledge of the substrate and hydroxyl radical concentrations. The experiments were designed such that the results related only to gas-phase losses.

The results are given below.

Substance	Degradation rate		Reference
	k(cm^3/s)	$t_{1/2}$ (h)[a]	
Observed			
80/20 TDI	7.4×10^{-12}	52	Becker *et al.* (1988)
2,4-TDA	1.9×10^{-10}	2	Becker *et al.* (1988)
2,6-TDA	$\geq 1 \times 10^{-10}$	≤ 4	Becker *et al.* (1988)
4,4'-MDA	3×10^{-11}	13	Becker *et al.* (1988)
Predicted			
4,4'-MDI	1.2×10^{-11}	32	Carter *et al.* (1999)
Calculated			
4,4'-MDI	1.2×10^{-11}		Bailey (1993)
	3.0×10^{-12}		Klamt (1993)
2,4-TDI	6.6×10^{-12}		Bailey (1993)
	2.2×10^{-12}		Klamt (1993)
2,6-TDI	2.4×10^{-12}		Klamt (1993)
4,4'-MDA	3.1×10^{-10}		Klamt (1993)
2,4-TDA	2.3×10^{-10}		Klamt (1993)
2,6-TDA	2.3×10^{-10}		Klamt (1993)

[*]Calculated for an OH radical concentration of 5×10^5/ml. This represents a typical global seasonal average tropospheric concentration. Values predicted by QSAR calculations are also included for comparison.

The results also show that MDA and TDA, from any source, would degrade in the atmosphere even faster than TDI. It is generally accepted that the products of such photo-oxidation are themselves further degraded, ultimately to carbon dioxide and water (Atkinson, 1995).

Almost the same rate of degradation, 5.9×10^{-12} cm^3/s, was found for the structurally similar *p*-tolyl isocyanate, using a similar experimental system (Carter *et al*., 1999). This compound is also a close structural analogue of MDI which, however, having two aromatic rings available for reaction, would be expected to degrade at double the rate. This predicted degradation rate for MDI is included in Table 4.10. Also included in Table 4.10 are photo-oxidation degradation rates predicted by quantitative structure–activity relationship (QSAR) calculations, which correlate reasonably well with the experimental results.

Photochemical degradation can enhance the accumulation of ozone in the mixture of reactive organic gases (ROG) and nitrogen oxides (NO_x) present in a polluted atmosphere. This mixture is commonly referred to as photochemical smog. Simplified summaries of the complex reactions occurring in this system have been adopted for modelling of photochemical smog formation, for which the primary indicator is ozone concentration.

Carter *et al*. (1997) assessed the potential of TDI for formation of tropospheric ozone in a study which combined environmental chamber experiments with computer modelling of the observations. The effects of added 2,4- and 2,6-TDI on ozone formation, NO oxidation and OH radical concentrations were determined in three simulated photochemical smog systems, of varied ROG/NO_x ratio. Both isomers were found to inhibit ozone yields and OH radical levels in all experiments. The best-fit model to the data assumed 70 % radical inhibition, no conversion of NO to NO_x, and formation of significant yields of products (such as cresols) whose subsequent reactions led to removal of NO_x. The ozone inhibition effects extended for at least 2 days. The photooxidation model was then used in model scenarios representing a wide range of ozone pollution episodes, and in all cases TDI was predicted to reduce ozone formation. The overall conclusion was that TDI was unlikely to enhance ozone formation under any atmospheric conditions.

MDI could not be studied directly in such a system because of its low vapour pressure. However, in a similar study (Carter *et al*., 1999) *p*-tolyl isocyanate (PTI) was tested as a surrogate for MDI. The photochemical behaviour of PTI was expected to mimic that of MDI, because of their close structural similarity. PTI was found to inhibit ozone formation and to reduce OH radical concentrations in conditions of lower NO_x concentrations, but to have very small positive effects at higher NO_x levels. The results were fitted best by a model assuming 10 % radical inhibition, 70 % conversion of NO to NO_x, significant formation of a cresol-like product (an NO_x sink) and some formation of a photoreactive product which was represented in the model by methyl glyoxyl.

On the presumption that this model applied equally well to MDI, and fitting it to the environmental scenarios, it was concluded that MDI could be a less effective ozone inhibitor than TDI. It was predicted to have negative impact under conditions of lower NO_x, which constitute most of the scenarios used to represent high ozone episodes in urban areas of the United States, but positive impact under higher NO_x conditions. The authors pointed out that the reaction model for PTI might not be entirely appropriate for MDI, in particular with regard to the formation of photoreactive products. Any produced from MDI would be phenyl substituted rather than aliphatic, and should thereby be less photoreactive. They could also have a greater tendency to condense into aerosols and hence not contribute to ozone formation. For these reasons it was considered that the predicted positive impacts on ozone formation were probably over-estimated.

Multimedia distribution: partition

Because of the ease of their hydrolysis, MDI and TDI can have only transient existence in water and concepts of solubility and partition,

> **normally used to predict multimedia distribution, are notional. In modelling studies, where partition concepts have of necessity been used but where ready hydrolytic degradation has been incorporated, extremely low environmental concentrations have been predicted.**

The above discussion has concentrated on the behaviour of MDI and TDI in specific environmental compartments. As such it has been mainly concerned with the persistence of these materials. However, environmental concentrations are also influenced by the distribution of a substance between compartments.

This distribution can be predicted for stable substances from the relevant partition coefficients (see Table 4.11 for more detail). Where the coefficients for partition between water and soil or biota are not available they can often be estimated from the octanol–water partition coefficient K_{ow}. Indeed, water solubility and K_{ow} are usually regarded as essential parameters for assessment of environmental distribution. However, the application of such procedures to MDI and TDI is very difficult and can be misleading. In aquatic media, MDI and TDI can have only transient existence because of their ready hydrolysis, and thus they are virtually unavailable. This not only renders the measurement of aqueous solubility and partition coefficients extremely difficult, but also negates the relevance and applicability of the concepts of solubility, partition and translocation for these substances.

Values of log K_{ow} of 4.5 and 3.4 for MDI and TDI have been obtained using an HPLC method (Yakabe *et al.*, 2000).

Table 4.11 **Multimedia distribution: partition coefficients.**

Media	Partition coefficient	Comments
Air/water	Henry's Law constant	Ratio of vapour pressure and water solubility.
Soil/water	Soil sorption coefficient (K_d)	Ratio of concentrations sorbed to soil and to that in aqueous solution, at equilibrium.
	Soil organic carbon sorption coefficient (K_{oc})	K_d/fraction of organic carbon in soil for non-polar substances. Typical estimate from K_{ow}[a]: log K_{oc} = 0.63 log K_{ow} + 0.90.
Biota/water	Bioconcentration factor (BCF)	Ratio of internal concentration in an organism to the external concentration in water. Typical estimate from K_{ow}[a]: log BCF fish = 0.85 log K_{ow} − 0.70.

[a]The octanol–water partition coefficient, K_{ow}, has been found to correlate with the ability of a substance to distribute into organisms and with the strength of interaction of a substance with organic material. These correlations are quoted in the European Union Technical Guidance Document for Risk Assessment (CEC, 1996).

In a real environmental situation, therefore, MDI and TDI themselves are not partitioned. In the broader context of hazard assessment, potential exposure (other than atmospheric) is to the products of reaction with water and it

is the distribution of these which must be considered. The situation is further complicated by the fact that the composition of total reaction product varies with the conditions of hydrolysis. A satisfactory simplification is to note that the predominant product is a polyurea, chemically and biologically inert and insoluble, and therefore with limited potential for distribution. The minor, soluble products are mono- and di-ureas and the diamines, MDA and TDA. The latter are the main products of ecotoxicological interest, and it is useful here to consider briefly their potential for distribution. As water soluble compounds of relatively low volatility and strong adsorption onto soil (Table 4.6) they would be predicted to partition into soil and sediment. In these phases their bioavailability is reduced by their strong irreversible binding. Any bioavailable diamine is readily degradable under aerobic conditions.

Exposure modelling

The distribution and fate of a chemical in a real environment is extremely complicated, and is usually predicted by mathematical modelling. Multimedia models are generally based on the fugacity approach of Mackay (1991) and vary in sophistication from steady state, equilibrium with conservation of mass of the substance (Level I) through incorporation of mass transfer and degradation (Level II) to steady state, nonequilibrium (Level III) and nonsteady state, nonequilibrium (Level IV). The geographical and meteorological parameters used can be global (relating to an average for the world), generic (typical of a large region) or site specific (relating to a specific locality).

All such models are based on the concept of partition between phases which, as described above, is purely notional for materials as reactive as MDI and TDI. However, such models do provide some insight into the type and extent of distribution to be expected for materials with the physical properties of MDI and TDI, even if the quantitative predictions are not really meaningful. In the studies described below, degradation of the materials in water and air was incorporated in the model.

Neely (1991) used a global model to predict the distribution of MDI and TDI between air, water and soil arising from emissions to water. These releases were grossly over-estimated (10 % of production) but even so the predictions were that neither material would be persistent or would pose any exposure problem. Over 99 % of the environmental load was predicted to be in the air, at very low concentrations of the order of $10^{-6}\,\mu g/m^3$ (10^{-7} ppb), for both substances.

Yoshida (MITES, 1992a, 1992b) used two Level II generic models to predict the distribution arising from a point source release to water of MDI and TDI in Japan. The first was a multi-media model, the second an air/soil model. The predictions of both models were for low environmental concentration and persistence. Most of the diisocyanate was retained in the air phase, with concentrations close to the release point of $5 \times 10^{-7}\,\mu g/m^3$ from emission of 1 g/day for the first model and $8 \times 10^{-2}\,\mu g/m^3$ from an unrealistically high emission of 1.44 kg/day for the second model. These concentrations decreased significantly with distance from the source.

A generic exposure model was developed for European conditions by the European Union within the programme EUSES (National Institute of Public

Health and European Commission, 1997), to assist in regulatory risk assessment procedures. This has been used to predict the environmental concentrations arising from release of MDI and TDI, to air alone, from processing plants using these materials (Table 4.12: Pemberton, 1998, personal communication). As discussed earlier, this is the only significant source of atmospheric release of these materials. The release rate used in the calculation is in the range of reported data for a plant using 350 tonne per annum TDI and is probably rather high for most types of plant using 2000 tonnes/year MDI. The release is scaled to regional (10^5 tonnes/year) and continental (9×10^5 tonnes/year) usage.

As well as the general proviso made earlier about the notional nature of quantitative predictions, it should be noted that the calculation will not accept an aquatic half-life shorter than 1 day and so water and soil concentrations are considerably overstated. Also the air dispersion model used assumes release at only 10 m above ground level. Stack release would greatly reduce local air concentrations (Figure 4.6). Even so the predicted concentrations, close to the processing plant, are all very low and the background (regional) concentrations are even lower.

Table 4.12   EUSES multimedia model of MDI and TDI releases to air.

Method

Dedicated modelling of concentrations in air, water and soil local to a point source release. Nested Mackay-type Level III multimedia modelling of regional (ca 40 000 km^2) and continental (Western Europe) scales simultaneously. Default parameter values reflect a typical *W. European standard environment*.

Input

MDI or TDI released to air at 1 g/h continuously over the year from a processing plant using 2000 tonnes/year MDI or 350 tonnes/year TDI. This scaled up to a usage of 10^5 tonnes/year on the regional, and 9×10^5 tonnes/year on the continental scale. No other releases.

			MDI	TDI
Vapour pressure (25 °C)	Pa		1.3×10^{-3}	3
Water solubility (notional)	mg/l		1	10
Log K_{ow}			4.5	3.4
Degradation:				
air	$t_{1/2}$ (days)		2.17	2.17
water soil etc.	$t_{1/2}$ (days)		1	1
biota			No	No

Predictions				**MDI**	**TDI**
Local concentrations:					
air (100 m from source)	(annual average)		μg/m^3	6.7×10^{-3}	6.7×10^{-3}
deposition rate (1 km radius)			μg/m^2/d	2.6×10^{-2}	9.6×10^{-3}
soil (grassland)	(180 day average)		μg/kg	2.4×10^{-4}	8.1×10^{-5}
water (soil porewater)[a]			μg/l	2.4×10^{-6}	6.4×10^{-6}
Regional concentrations:					
air	(annual average)		μg/m^3	2.1×10^{-5}	1.2×10^{-4}
soil (agricultural)			μg/kg	4.8×10^{-6}	3.1×10^{-7}
water (surface)			μg/l	1.6×10^{-6}	1.6×10^{-6}

[a]Indicative of maximum concentration in surface water for this local calculation.

Biodegradation

Although standard tests show both MDI and TDI to be resistant to biodegradation, this is due to their rapid reaction with water giving inert, insoluble polyureas as the major product. The diamines MDA and TDA, minor soluble products of this reaction, are biodegraded in industrial waste water plants adapted to aromatic amines and by aerobic soil microorganisms.

Reaction of MDI and TDI with water is faster than any conceivable microbiological attack, and consequently consideration of their biodegradative fate relates, in reality, to that of the various reaction products. Not surprisingly, in a test for inherent biodegradability, following OECD Guideline 302C, MDI and TDI showed no perceptible biodegradation over 28 days as measured by respirometry (oxygen consumption) (Caspers *et al*., 1986).

As regards individual components of the total hydrolytic reaction product of MDI and TDI, the polyureas appeared to be stable to both hydrolysis and biodegradation, and the diureas showed no detectable biodegradation, and no formation of diamines, in a test for inherent biodegradability in the OECD Guideline 302 C test (Yakabe *et al*., 1994c). These diureas and polyureas are not soluble in water, however. No studies on the biodegradation of the total soluble fraction of reaction product have been performed. The position on biodegradation of the diamines, MDA and TDA, is rather complex. The situation is exemplified by the data shown in Table 4.13. Most standard laboratory tests show MDA to be inherently, but not readily, biodegradable and TDA to be resistant to biodegradation. However, the diamines are found to be easily biodegraded when the biomass is derived from industrial activated sludge, as indicated by test results of both real and simulated waste water treatment plants. A typical example of the effective removal of both MDA and TDA from actual industrial plant waste water in a bench scale simulation is given in Table 4.13.

In a study designed to elucidate these findings, it was found that activated sludge acclimatized to biodegradation of aniline can easily co-metabolize MDA and TDA. Such a sludge is typical of those found in industrial waste water treatment plants. This study also concluded that natural biota, in soil or sediment for example, will readily adapt to the metabolism of traces of diamine such as might be produced from release of the diisocyanates.

A study of the behaviour of ^{14}C-labelled MDA and TDA in soil provided evidence for biodegradation under aerobic, but not anaerobic, conditions (Cowen *et al*., 1998). In aerobic soil an initial daily biodegradation rate of 0.6 to 1.0 % was observed (Table 4.13). This later slowed markedly, and after 1 year 34 to 40 % of the diamines had been degraded as judged by loss of radioactivity from the soil. This slowing may have been due to reduced bioavailability of the diamines consequent on their strong binding to the soil, a factor also observed in this study (Table 4.6), or to depletion of oxygen during the test. Under anaerobic methanogenic conditions, no radiolabelled methane or carbon dioxide was recovered from studies on either diamine, during 71 days of incubation.

Table 4.13 **Biodegradation studies on MDA and TDA.**

Test Method	MDA	TDA	Reference
OECD 301C	Not readily biodegradable	2,4-TDA not readily biodegradable	CITI (1992)
OECD 301F	Not readily biodegradable	2,4-TDA not readily biodegradable	Yakabe (1994 b)
OECD 302C	Inherently biodegradable	80/20 TDA not inherently biodegradable	Caspers *et al.* (1986)
OECD 302B	Inherently biodegradable		BASF (1988)
OECD 302B		2,4- and 2,6-TDA inherently biodegradable[a]	BASF (1993)
Industrial waste water treatment plant simulation	>95 % removed from waste water[a]	>98 % degraded in 1 day[a]	Sandridge (1984)
Soil: respirometry (^{14}C-labelled diamine)	Mineralization rate: 2.9 % in 3 days 40 % in 1 year	Mineralization rate: 1.9 % (2,4-) and 2.7 % (2,6-) in 3 days 34 % (2,4-) and 36 % (2,6-) in 1 year	Cowen *et al.* (1998)

[a]Industrial activated sludge used in test.

Bioaccumulation

No significant bioaccumulation is expected from exposure to MDI or TDI, on account of the reactivity of these materials with water and the low bioaccumulation of the soluble, but generally minor, hydrolysis products MDA and TDA.

Uptake and retention of a substance into an organism is referred to as bioaccumulation. It is important in that, together with the associated process of biomagnification, it can lead to adverse effects in predators such as birds or mammals. A significant potential for bioaccumulation is associated with a bioconcentration factor (BCF: Table 4.11) of 100 or more.

In view of the rapid reaction of MDI and TDI with water no bioaccumulation of these chemicals is to be expected. In fact, as discussed earlier, since both have only transient existence in water, concepts such as partition and bioaccumulation have no relevance or application to their ecotoxicological behaviour. The diamines showed low bioaccumulation in fish (*Cyprinus carpio*) over 42 days in standard tests (OECD Guideline 305C). Values of the BCF were <5 for 2,4-TDA at 0.3 mg/l, and <14 for 4,4′-MDA at 0.2 mg/l (CITI, 1992).

The ecosystem study on polymeric MDI, which is described later, provided additional strong evidence for the lack of significant bioaccumulation. The fish (*Oncorhynchus mykiss*) in ponds treated with polymeric MDI at loadings of 1 and 10 g/l contained no detectable MDI or MDA (<0.5 and <1.4 mg/kg, respectively) after 112 days of exposure.

Hazard

Both MDI and TDI have shown generally low toxicity to a wide variety of aquatic species: bacteria, algae, invertebrates and fish. The diisocyanates and their respective amines have also shown low toxicity to terrestrial species, plants and earthworms: also there are indications of low toxicity of MDI and TDI to birds.

Because of the virtual unavailability of MDI and TDI in water, results of aquatic and terrestrial tests are not meaningful in terms of dissolved test substance but relate to the soluble fraction of reaction product. It is probable that the observed ecotoxicity of the diisocyanate is due primarily to the diamine produced at low concentrations in this reaction. The other soluble reaction products, monoureas, have been shown to have low ecotoxicity. An experimental pond study indicated low environmental risk arising from spillage of polymeric MDI into a natural aquatic ecosystem. No direct ecotoxic effects, and no bioaccumulation of MDI or MDA were observed. No MDI or MDA could be detected in the water.

Terms regularly used in this area are:

NOEC Highest concentration at which no effect was noted.

EC$_x$ Concentration at which the effect was noted on x % of the organisms.

LC$_x$ Concentration lethal to x % of the organisms.

These terms are generally preceded by an indication of the duration of the test.

The terms *overall loading rate* and *water soluble fraction* (WSF) are recommended for reporting ecotoxicity or exposure data for complex substances. The WSF is the aqueous medium containing only that fraction of a substance which remains in solution once mixing has ceased and phase separation has occurred.

Test procedures

Standard ecotoxicity test methods have been published by various authorities. The OECD Guidelines (OECD, 1993) are typical, and are referred to extensively within this section.

Most laboratory ecotoxicity tests are specific to a single species. The choice of a species is determined by its being representative of a specific trophic level of the food chain (Figure 4.2), and its relevance to a particular environment, and also by practical considerations such as ease of husbandry and economic importance. However, a model multispecies ecosystem test, as exemplified by the pond study on polymeric MDI, provides a more realistic view of the potential environmental hazard posed by a material.

It is necessary to repeat at the outset that, because of the reactivity and insolubility of MDI and TDI in water, neither is available in significant degree in water or soil. Any solution will be of very low and transient concentration, and it is not possible to produce an aqueous solution of constant and predetermined concentration. Results of aquatic ecotoxicological tests are therefore not meaningful in terms of dissolved test substance but relate to the soluble portion of the complex mixture of products resulting from the reaction with water of a nominal concentration of diisocyanate under specific test conditions. The nominal concentrations of diisocyanate in aquatic test media, referred to frequently in this section, are more precisely defined as *overall loading rates used in the preparation of the water soluble fraction (WSF)*.

Similar considerations apply to other tests where significant contact with water has occurred, for example in most of the terrestrial ecotoxicity tests recorded below. It follows that knowledge of the conditions under which test media were made up is crucial to a clear understanding of the significance of the results. It is also useful to consider such ecotoxicological data alongside similar

data for the diamines, and to quantify the generally very low concentrations of the latter in the water soluble fraction.

Aquatic ecotoxicity

Bacteria

Polymeric MDI, TDI and their related diamines MDA and TDA have been shown to have low toxicity to bacteria. All showed less than 50 % inhibition of respiration of activated sludge (water treatment plant biomass) over 3 h at 100 mg/l (Caspers *et al*., 1986). In this study the test substance was gently stirred into the medium prior to test. Both 2,4- and 2,6-TDA have been shown to inhibit biological nitrification by activated sludge, but at concentrations (50 mg/l) much higher than those found in the water soluble fraction from reaction of TDI with water (Snyder, 1987).

Algae

Both MDI and TDI have been shown to have very low toxicity to algae (Table 4.14). It should be noted that the exposure period in standard algae toxicity tests (OECD Guideline 201) is sufficient for several doublings of the cell population to occur. Consequently they are considered as multigeneration studies and a NOEC, or EC_{10}, over 72 h or longer, indicates a concentration without multigeneration, long-term effects on the existence of the species. In risk assessment procedures such a value is accepted as an indicator of the chronic toxicity to this species.

Table 4.14 **Toxicity of MDI and TDI to algae.**

Species	Test notes	PMDI mg/l	80/20 TDI mg/l	Reference
Scenedesmus subspicatus (fresh water)	1	72 h NOEC 1640	Not tested	Blom and Oldersma (1994)
Chlorella vulgaris (fresh water)	2a	Not tested	96 h EC_{50} 4300 96 h EC_{10} ≥2000	Tadokoro *et al*. (1997)
Skeletonema costatum (marine)	2b	Not tested	96 h EC_{50} 3230	Tadokoro *et al*. (1997)

(1) Following OECD Guideline 201. No effects observed at the test loading, which was prepared by reaction of polymeric MDI in test medium over 1 h. In range-finding tests, no effects were noted at a loading prepared by reaction of 1.12 g polymeric MDI in 1 litre test medium over 20 h.
(2) Similar to OECD Guideline 201. Test concentrations prepared by dilution of filtered liquor from reaction of 80/20 TDI at (a) 15 g/l and (b) 10 g/l over 24 h.

Studies on the ecotoxicity of MDI to algae.
Rufli and Müller, 1985; Neuhahn and Hamburger, 1988; Hanstveit and Oldersma, 1995.

In these studies it may be presumed that reaction had occurred to a major extent prior to test. The diamines, 4,4′-MDA, 2,4-TDA and 2,6-TDA, have themselves been shown to have only low to moderate toxicity to algae in standard tests. The 72 h EC_{50} values are 21, 126 and 23 mg/l, respectively for *Scenedesmus subspicatus*. The ecosystem study on polymeric MDI, described

below, serves to confirm the low ecotoxicity of this type of material to algae and other aquatic primary producers.

Invertebrates

The results of studies on the toxicity of MDI and TDI to a variety of invertebrates, freshwater and marine, are given in Table 4.15. MDI shows very low acute toxicity and low chronic toxicity, though tests were not extended beyond the guideline requirement of 24 h. TDI shows low to moderate acute toxicity and moderate chronic toxicity. In one study (Tadokoro *et al*., 1997) it was noted that 48 h was needed for full expression of the acute toxicity to *Daphnia magna*. In consequence this study must be accorded higher significance than tests over a shorter time.

Table 4.15 **Toxicity of MDI and TDI to invertebrates.**

Species	Test notes	Polymeric MDI mg/l	TDI[a] mg/l		Reference
Freshwater					
Daphnia magna	1, 10a		48 h EC$_{50}$	12.5	Tadokoro *et al*. (1997)
	2	(and 4,4′-) 24 h EC$_{50}$ ≥500	24 h EC$_{50}$	>500	Rhône-Poulenc (1977)
	3	24 h EC$_{50}$ >1000	24 h EC$_{50}$	750	Caspers *et al*. (1986)
	4	21 days NOEC ≥10	21 days NOEC	≥0.5	Caspers *et al*. (1986)
	5		21 days NOEC	1.1	Cerbelaud *et al*. (1997)
Limnea stagnalis	6, 10b	(and 4,4′-) 24 h EC$_{50}$ >500	24h EC$_{50}$	>500	Rhône-Poulenc (1977)
Estuarine					
Mysidopsis bahia	7, 10c	Not tested	48 h EC$_{50}$	18.3	Tadokoro *et al*. (1997)
Palaemonetes pugio	8	Not tested	48 h EC$_{50}$	>508	Curtis *et al*. (1979)
Marine					
Nitocra spinipes	9	Not tested	(TDI type not specified) 96 h EC$_{50}$12		Bengtsson and Tarkpea (1983)

[a]80/20 TDI, unless specified otherwise.
For each loading MDI or TDI was stirred into the test medium prior to test.

1. Static test following OECD Guideline 202/1. Reaction time 24 h.
2. Static test similar to OECD Guideline 202/1. Reaction time 18 h. 4,4′-MDI gave the same result.
3. Static test following OECD Guideline 202/1. Reaction time 0.5 h.
4. Semi-static test following OECD Guideline 202/2. Effect: reproduction rate. Reaction time 1 h.
5. Semi-static test following OECD Guideline 211 (formerly 202/2). Effect: reproduction rate. Reaction time 24 h. 2,4-TDI.
6. Static test similar to OECD Guideline 202/1. Reaction time 18 h.
7. Static test. Reaction time 24 hours.
8. Static test. No specified reaction time. 2,4-TDI.
9. Static test. No information on isomer used or method of loading.
10. TDA content of test medium at TDI EC$_{50}$ loadings: (a) 5 mg/l; (b) 10 mg/l; (c) 6 mg/l.

In some studies the concentration of diamine in solution was monitored, and that present at the EC$_{50}$ endpoint was estimated. These figures are included in

the notes to the tables. The diamines themselves show moderate acute toxicity to invertebrates, with EC_{50} values of >3.2 mg/l (24 h) for MDA and 4.3 mg/l (48 h) for TDA to *Daphnia magna*. The contribution of these diamines to the aquatic toxicity of MDI and TDI is discussed later.

Fish

Data for both MDI and TDI from studies covering a variety of fish are presented in Table 4.16. In one set of studies on TDI, the TDA content of the test medium was monitored and, for these, estimates of the TDA concentration present at the TDI endpoint are also recorded in the notes to the Table.

Table 4.16 **Toxicity of MDI and TDI to fish.**

Species	Test notes	Polymeric MDI mg/l	TDI[a] mg/l		Reference
Freshwater					
Brachydanio rerio (zebrafish)	1	96 h $LC_0 \geq 1000$	96 h LC_0	≥ 100	Caspers *et al*. (1986)
	2	24 h $LC_0 \geq 500$	24 h LC_0	>500	Rhône-Poulenc (1977)
Oryzias latipes (medaka)	3	96 h $LC_0 \geq 3000$			Nakata (1983)
	4, 6a		96 h LC_{50}	4170	Tadokoro *et al*. (1997)
Pimephales promelas (fathead minnow)	5	Not tested	96 h LC_{50}	164	Curtis *et al*. (1979)
Oncorhynchus mykiss (rainbow trout)	4, 6b	Not tested	96 h LC_{50}	133	Tadokoro *et al*. (1997)
Estuarine					
Mugil cephalus (striped mullet)	4, 6c	Not tested	96 h LC_{50}	4100	Tadokoro *et al*. (1997)
Marine					
Paralichthys olivaceus (olive flounder)	4, 6d, 7	Not tested	96 h LC_{50}	46	Tadokoro *et al*. (1997)
Pagrus major (Japanese red sea bream)	4, 6e, 7	Not tested	96 h LC_{50}	0.4	Tadokoro *et al*. (1997)

[a]80/20 TDI, unless other specified.
Acute tests. For each loading MDI or TDI was stirred into the medium prior to test.

1. Static test following OECD Guideline 203. No specified reaction time.
2. Static test similar to OECD Guideline 203. Reaction time 18 h. 4,4′-MDI gave the same result.
3. Semi-static, Japanese standard test. No specified reaction time.
4. Static test following or similar to OECD Guideline 203. Reaction time 24 h.
5. Static test. No specified reaction time. 2,4-TDI
6. TDA content of test medium at TDI LC_{50} loadings: (a) 16 mg/l; (b) 6 mg/l; (c) 11 mg/l; (d) 4 mg/l; (e) 0.2 mg/l.
7. Dissolved oxygen fell below 60 % of saturation level during test. This invalidates result according to OECD criteria.

The observed toxicity of MDI to fish is very low: no deaths occurred at the highest loading tested in all three studies. Extensive hydrolysis of the diisocyanate would have taken place in the first few hours of those studies where no pre-test hydrolysis period was given. The observed toxicity of MDA to fish is also low. The lowest acute LC_{50} recorded is 32 mg/l, to *Oryzias*

latipes (CITI, 1992). The ecosystem study, described below, further illustrates the very low toxicity of MDI to aquatic species including fish.

TDI similarly shows low toxicity to a wide range of fish, but with the one exception of *Pagrus major*. It is noteworthy that a similar situation pertains to the toxicity of TDA also. In studies of the toxicity of TDA to *P. major* it was found that high toxicity is confined to the 2,4-TDA isomer and the toxicity varies appreciably with size of fish, larger fish being considerably less sensitive (Tadokoro *et al*., 1997). The relevance to risk assessment of this singular higher sensitivity of *P. major* to 2,4-TDA and 2,4-TDI is unclear. This is a marine fish local to China and Japan and not commonly studied outside Japan, where its importance lies in farming for human consumption. Any real hazard lies in the specific situation of spillage into a fish farm rather than in any general environmental sense. This specific toxicity cannot be interpreted as a reliable indicator of general hazard to fish or indeed to other marine species which show no exceptional sensitivity to TDI or TDA. The results of ecotoxicity studies overall, using species represented in international test guidelines, confirm the generally low toxicity of TDI and TDA to fish.

Ecotoxicity of soluble hydrolytic reaction products

It can be confidently predicted from a consideration of the physical characteristics of MDI and TDI, and of their ready reactivities when dissolved in water, that in solution they are virtually unavailable to aquatic organisms. Any toxicity observed is due to soluble reaction products, which comprise the diamines MDA and TDA, and oligoureas. The latter are predominantly monoureas, and from their structure are expected to be less toxic than MDA and TDA.

It is indeed a reasonable assumption that the diamines MDA and TDA in the reaction products are primarily responsible for any observed aquatic ecotoxicity of MDI and TDI. In one study (Tadokoro *et al*., 1997) direct comparisons were made, for three species, of TDA ecotoxicity endpoints and the TDA concentrations in the test media at the relevant TDI endpoints (Table 4.17). There is seen to be a reasonably good correlation. In the test with *Daphnia magna* the toxicity of the soluble oligoureas was included in the comparison, and shown to be low ($EC_{50} > 50$ mg/l). Similar direct comparisons for MDI and MDA are not available, since the very low toxicity observed for MDI has prevented the measurement of ecotoxicity endpoints. A similar correlation with diamine content would also be predicted for ecotoxicity in soil, where water contact is also involved. An important extension of this to note is that under

Table 4.17 **Comparison of toxicity tests with TDI and TDA in water.**

Species	TDI test		TDA test end point mg/l
	End point mg/l	TDA concentration at end point mg/l	
Daphnia magna	48 h EC_{50} 12.5	5	4.3
Mysidopsis bahia	48 h EC_{50} 18.3	6	4.3
Pagrus major	96 h LC_{50} 0.4	0.2	0.2

conditions that are actually met with in a spillage of diisocyanate, where there is poor dispersion of material in the presence of sediment or soil, the aquatic concentration of amine produced is even lower than in laboratory studies and therefore the ecological risk is lower.

The production of carbon dioxide during reaction of a spillage of diisocyanate with water could have an indirect effect, albeit minor and temporary, on an aquatic ecosystem. Such was indeed noted, but only at a very high loading of polymeric MDI, in the following ecosystem study.

Ecosystem (pond) study

This study (Heimbach *et al*., 1996) investigated the effects on an aquatic freshwater ecosystem arising from a simulated accidental pollution of a pond with polymeric MDI. Three interconnected ponds (see Figure 4.7), each of volume $4.5\,m^3$, contained groundwater above natural lake sediment. Rainbow trout (*Oncorhynchus mykiss*), caged separately to reduce feeding pressure on plankton, were added to each pond and the ponds were allowed to equilibrate for 6 months, to establish nearly identical physicochemical and biological conditions in each. During this period, a biological community of natural variability was established, with a natural relationship between prey and predator organisms. The ponds were then isolated from one another, and polymeric MDI was added onto part of the sediment of two of the ponds, at loadings of 1 and 10 g/l. The third pond constituted an untreated control.

Water chemistry, MDI and MDA concentrations, and the population and diversity of different trophic levels were monitored over 112 days. Neither
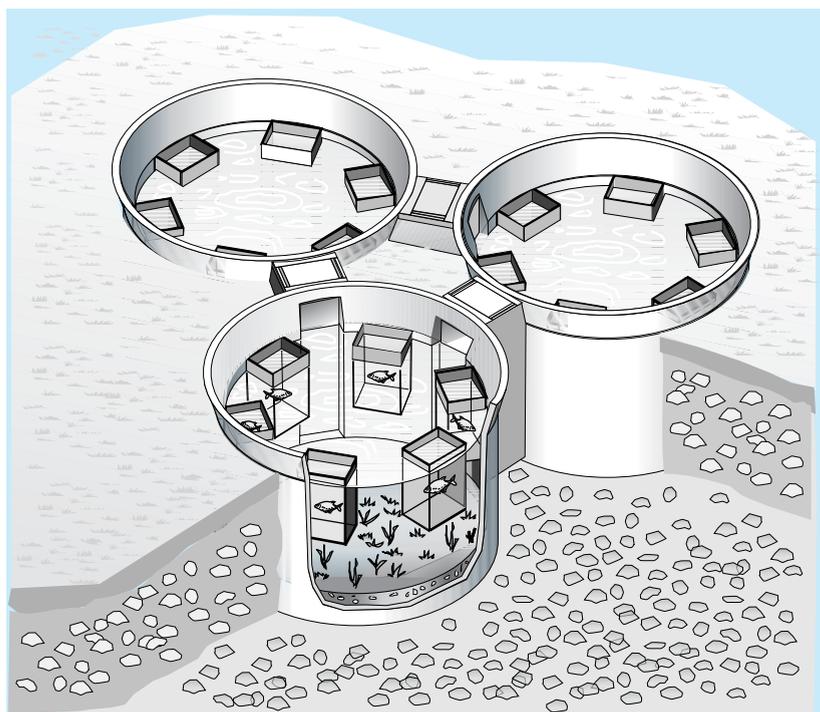
Figure 4.7 **Pond study**

MDI nor MDA was detected in water or fish at any stage. The detection limits were 4 and $10\,\mu g/l$ in water, and 0.5 and $1.4\,mg/kg$ in fish, respectively. The polymeric MDI reacted to inert solid polyurea on the sediment of the test ponds, and release of bubbles of carbon dioxide was observed. Solubilization of some of the carbon dioxide reduced the water pH, initially about 9, to 7.0 and 8.3 in the higher and lower dosed ponds, respectively.

Neither loading caused any direct effect on the free moving community comprising phytoplankton, zooplankton, fish and macrophytes (including algae). Some minor indirect effects caused by the production of carbon dioxide were observed in the phytoplankton and zooplankton structures of the higher-loaded pond, and an increase in macrophyte growth was noted. Organisms living in the untreated part of the sediment in the higher-dosed pond were temporarily affected by physical obstruction, caused by spillage and movement (flotation by trapped carbon dioxide) of test substance onto this habitat. These populations, however, regained densities equivalent to those of the control after some weeks, with the exception of Bivalvia which have too long a generation time for the test period of this study.

It will be appreciated that the results and observations of this study have significant relevance to most of the facets of the aquatic physicochemical and ecotoxicological behaviour of MDI already discussed, and indeed provide an experimental assessment of the risk associated with a spillage.

The most important observations can be summarized as:

- a relatively slow heterogeneous reaction of water with polymeric MDI lying on the sediment, gradually forming solid polyurea;
- no MDI or MDA detectable in the water at any stage;
- no direct ecotoxic effects even at the higher application rate $(10\,g/l)$;
- no evidence for bioaccumulation of MDI or MDA in fish.

The overall conclusion was that the risk to the aquatic environment arising from an accidental release of polymeric MDI is very low.

Terrestrial ecotoxicity

This section discusses the effects of MDI and TDI on organisms affected directly through contact with soil and also those affected by indirect exposure through the food chain. The conclusion that MDI and TDI are almost unavailable to aquatic systems and that any ecotoxicity observed is due to soluble hydrolytic reaction products also applies to this environmental compartment.

Plants
Both polymeric MDI and 80/20 TDI, have been shown to have low toxicity to *Avena sativa* (oat) and *Lactuca sativa* (lettuce) in the OECD Guideline 208 test (van der Hoeven *et al*., 1992a). No effects on emergence, survival or growth were noted during 17 days, even at the highest application rate, $1000\,mg/kg$. The diamines, MDA and TDA, were also shown to have low toxicity in this study; effects were noted at loadings considerably above the highest aquatic concentrations that have been found to be generated by reaction of the diisocyanates with water. As noted earlier, no diamines have been detected from reaction of MDI and TDI with soil.

Earthworms

In a similar study using OECD Guideline 207, both polymeric MDI and 80/20 TDI were shown to have low toxicity to *Eisenia foetida* (earthworm) (van der Hoeven *et al.*, 1992b). No effects on appearance, behaviour, weight or survival were noted even at the highest application rate of 1000 mg/kg. Effects noted for the diamines MDA and TDA in the same study were at loadings which far exceeded the highest concentrations that have been found after reaction of the diisocyanates with water or wet soil.

Birds

Birds and other animals in the terrestrial ecosphere are representatives of secondary consumers, at risk from exposure by feeding on other organisms. Only one study on birds has been reported, with very little detail given on the test procedure (Schafer *et al.*, 1983). This showed low toxicity of both 2,4- and 2,6-TDI to *Agelaius phoenicens* (Redwinged blackbird) and *Sturnus vulgaris* (European starling). For both birds the LD_{50} was quoted as 100 mg/kg for 2,4-TDI and $\geq$100 mg/kg for 2,6-TDI. Although MDI itself was not tested, MDA was found to have an LD_{50} of >148 mg/kg to *A. phoenicens* in this study, suggesting a low toxicity for MDI also.

Risk assessment

Consideration of the sources of release of MDI and TDI and the environmental behaviour of these materials, both physicochemical and biological, suggests that no significant risk is presented to the environment from releases arising in the normal lifecycle or from accidents. Major factors in this conclusion are the virtual unavailability of MDI and TDI in aqueous systems and their low ecotoxicity. Both are determined by the physicochemical behaviour of MDI and TDI in contact with water. Also, no significant risk is expected from the production of the diamines MDA and TDA arising from environmental releases of the diisocyanates. The observed absence of significant ecological effects arising from spillages of MDI and TDI, and the results of the pond study on MDI, strongly support the overall conclusion of low environmental risk.

As was pointed out in the introduction to this book, *risk* is a function of *exposure* and *hazard*. Previous discussions have covered the concentrations likely to be encountered in the various environmental compartments (exposure to MDI and TDI), and the adverse effects of these materials on organisms present in these compartments (hazard). In assessing risk it is necessary to quantify the possible exposures and the dose-related responses to the adverse effects, in order to estimate the probability of an adverse effect arising.

Two types of risk need to be considered. One is from accidental release of diisocyanate and the considerations here are usually about short-term risk to the immediate locality but can include concerns about the material spreading and persisting, leading to a more general, longer-term impact. The second

is that arising from normal, lifecycle releases of diisocyanates, that is, from production, transport, storage, use and disposal. Here the risk is longer term and can be local to a specific release or widespread, covering many releases, throughout a region or even global. It is for this lifecycle risk that quantitative risk assessment procedures have been developed. These two types of risk are considered separately below, together with examples from the regulatory approaches from the EU to risk classification or assessment.

Accidental release of MDI and TDI

As explained in the exposure section of this environmental text, and in *Part 2*, the manufacture and use of MDI and TDI are strictly controlled in order to minimize health risk to the workforce. Hence the predominant environmental concerns in this area are spillages occurring during transport or storage.

Release to air

Because of the low volatilities of MDI and TDI, accidental releases to air are unlikely to have any significant environmental impact. Relatively low air concentrations have been recorded in the immediate vicinity of a spill prior to decontamination: up to $40\,\mu g/m^3$ (4 ppb) for MDI and up to $140\,\mu g/m^3$ (20 ppb) for TDI (Tables 4.1 and 4.2). It is not possible to *identify* any environmental hazard at these short-lived low concentrations, and in any case very few procedures for environmental hazard evaluation have been developed for the atmosphere. Hazards arising from the transfer to water or soil will be insignificant for such transient, low level releases.

Releases to water

Water is generally seen as the compartment of greatest environmental risk from toxic substances, and for which test procedures and methodology for hazard and risk assessment have been most fully developed. The hazard considerations for a spillage are both immediate, as represented typically by acute toxicity to fish, invertebrates and algae, and longer term, where the possibilities of persistence and bioaccumulation of the substances need to be assessed.

The aquatic ecotoxicological data show MDI to have low toxicity to a wide range of species, with LC_{50} or EC_{50} values all greater than 100 mg/l. TDI has low to moderate toxicity to a wide range of standard laboratory species (LC_{50} or $EC_{50} > 12$ mg/l). Since both MDI and TDI are readily degraded in water they cannot be regarded as persistent or bioaccumulative. It is more reasonable to consider the potential hazard from the total product of the reaction with water. Indeed, most ecotoxicity data relate to such products. Water soluble material, which includes the diamines MDA and TDA, are very much a minor fraction of these products under conditions of poor dispersion typical of spillages. The major portion of the total reaction products comprises highly insoluble polyureas, resistant to both chemical and biological degradation. As such they can be regarded as persistent, but not biologically available. On these considerations, no significant environmental aquatic hazard, immediate or longer term, would be expected to arise from a spillage of MDI or TDI.

The European Union (EU) has applied an aquatic hazard assessment of this type to the classification and labelling of dangerous substances (Vosser, 1991). The procedure assigns risk phrases according to the acute ecotoxicity to fish, daphnia and algae and the potential for long-term effects such as persistence, bioaccumulation and chronic toxicity. Substances with $LC_{50} > 100$ mg/l are *not classified*. Those with $LC_{50} \leq 10$ mg/l not only carry risk phrases but are labelled *Dangerous for the environment*, with the exception of those with $LC_{50} \geq 1$ mg/l and evidence for no long-term effects, which are *not classified*.

A strict application of this procedure to MDI and TDI as such, on the grounds that they have an appreciable lifetime, 1 week or longer, under typical spillage conditions, leads to a *not classified* toxic rating, since both are easily degraded in water to insoluble, inert material and cannot bioaccumulate. Application of the procedure to the total product of reaction with water, however, is a little more complicated. It is the water soluble fraction of the reaction product that should be considered (see *Ecotoxicity* above). Although the ecotoxicity data do relate to such material, they overstate the toxicity since the reaction conditions used are unrealistic and maximize production of diamine. It is important to understand that diamine is not a major product under spillage conditions. Even so, for both MDI and TDI, strict application of this procedure would still lead to non-classification. For MDI this follows directly from the low acute toxicity, and for TDI it follows from a chronic toxicity >1 mg/l. This is indeed the 1997 provisional EU classification for MDI. However, for TDI, concerns over the potential formation of TDA led in 1998 to a classification R52 (*Harmful*)/R53 (*Possible long-term effects*).

So far it has been the environmental *hazard* of the diisocyanate that has been evaluated, and found to be low. The associated *risk* could still be significant if exposure were found to be high. However, as is described earlier, exposure to free diisocyanate in water will be insignificant and the diamines are minor, or even trace, components of total reaction product under spillage conditions. Their concentration is even further reduced by binding to soil or sediment. The environmental risk associated with spillage of MDI or TDI into water can, therefore, be predicted to be very low.

The only potentially significant hazard revealed by the ecotoxicity data is that of 2,4-TDI (but not of 2,6-TDI) to *Pagrus major*, a marine fish local to China and Japan and not usually used in laboratory testing. It is not accorded the significance of other data, being a nonvalidated, outlying result. Even when it is taken into consideration, however, the associated risk is predicted to be low. Spillage of TDI into the sea will inevitably lead to high dilution of reaction products. Even in the very specific and unlikely event of spillage into a fish farm, the slower reaction and low yield of TDA under such conditions, and the strong adsorption of TDA onto sediment, might be expected to lead to an aquatic concentration of TDA below ecotoxic levels.

The examples of incidents recorded earlier in Tables 4.1 and 4.2 confirm these predictions of low environmental risk. A spillage of TDI into fast flowing water resulted in low levels of TDA being detected downstream soon after the incident, but none was detectable (<0.3 mg/l) after 15 days. The only incident in which environmental damage has been recorded was a sudden leakage of TDI from a storage tank into the drains (Burgheim). In this incident TDI itself entered a water treatment plant via the sewers. Many of the effects here seem

to have been associated with the physical presence of reacted polyurea in the plant. Although efficiency fell, the plant recovered completely over 5 months. A well-recorded incident is the spillage of 14 tonnes of TDI onto marshy ground (Helmstedt). Although this was an example of spillage onto soil, it should be noted that no TDI or TDA was detected in groundwater ($<50\,\mu$g/l) at any stage.

The pond study on polymeric MDI provides additional strong support for the predicted low risk from a spill. The loadings of polymeric MDI were high (1 and 10 g/l) and yet no MDI or MDA were detected in water or fish at any stage and no direct ecotoxic effects were observed. The only effects noted were transient and due to physical obstruction by reacting material and to raised carbon dioxide concentration in the water.

Releases to soil

The behaviour of MDI and TDI in contact with soil is determined by their reaction with water, and indeed a recommended procedure for treatment of a spillage is to cover with wet soil or sand. Many of the considerations discussed above in connection with spillages into water apply in this case also. The potential for exposure to free diisocyanate in wet soil will be very low. The diamines, which will be minor reaction products under typical soil contact conditions, are not only easily biodegraded in soil but are also readily and tightly bound. The ecotoxicity of MDI, TDI, and the diamines MDA and TDA to the plants, earthworms and birds studied is low ($LC_{50} \geq 100$ mg/kg).

No significant hazards or risks are therefore predicted for a spillage onto soil, particularly if recommended decontamination procedures are followed. The Helmstedt incident (Table 4.2) supports this conclusion. Following spillage of 14 tonnes of TDI onto marshy ground, only low levels of TDI/TDA were detectable in the soil after 6 weeks (≤ 3 mg/kg as TDA; not analysed separately) and no TDA was detectable after 1 year (detection limit 0.1 mg/kg). There was no evidence of environmental damage from this spill; vegetation developed normally during the ensuing year. Six years after the incident further analyses of soil and groundwater samples showed no detectable TDA ($<50\,\mu$g/kg).

Normal usage

General principles of risk assessment

Assessment of the risks arising from normal releases at any stage of the lifecycle of a substance involves estimation of the incidence and severity of likely adverse effects due to the actual or predicted exposure. It is necessary to consider the total environment which, for convenience, can be subdivided into the air, water and soil compartments together with the food chain (potential toxicity to predators) and sewage plants (potential release of other toxicants). The lifecycle of a substance is taken to comprise all stages from production, through transport, storage and use, to disposal.

Environmental exposure concentrations are not usually available and Predicted Environmental Concentrations (PEC) are generally estimated from dispersion and multi-media models. Wherever possible, monitored concentrations for specific releases such as stack emissions or waste water effluents are used

in the modelling to improve the realism of the estimates. Exposure needs to be estimated local to a point source release of any significance, and averaged over a larger region such as a country. Environmental fate, involving degradation and distribution processes, is taken into consideration but is of more significance in the regional case because of the greater spatial and temporal scale.

It is then necessary to identify the potential adverse effects for each compartment and estimate the concentration at or below which it is probable that no unacceptable effects will occur. These *Predicted No Effect Concentrations* (PNEC) have usually to be estimated from typical ecotoxicity data from laboratory tests on single species. Safety factors, termed *assessment factors*, are applied in this estimation to reflect the degree of uncertainty in extrapolation to an ecosystem.

Risk characterization, in its simplest form, entails comparison of the PEC and PNEC for each compartment. A ratio PEC/PNEC of less than one indicates no discernable risk, since the exposure is below that necessary to produce an effect.

The overall process is shown schematically in Figure 4.8.
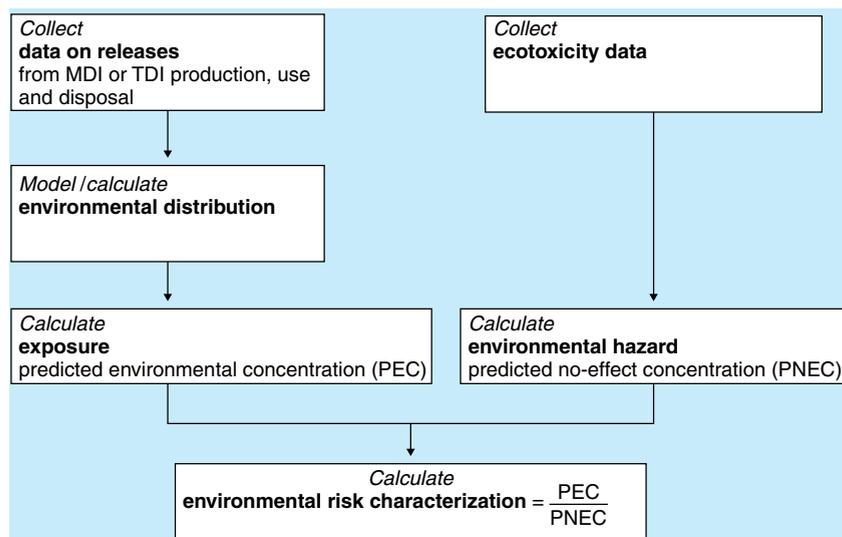
Figure 4.8 Sequence of data collection and environmental risk characterization for MDI or TDI

An example of this type of risk assessment is that used in the EU (see the EU Technical Guidance Document, CEC, 1996). The exposures and ecotoxicities to be considered are shown in Table 4.18, and assessment factors applicable to the aquatic compartment are shown in Table 4.19. At present it is considered that there is insufficient hazard information available to justify extension of the procedure to the air compartment, or to allow assessment factors to be reliably recommended for the terrestrial compartment. In this procedure, a PEC/PNEC ratio of <1 is taken to indicate no immediate need for further information or testing. A ratio >1 leads to an identified need for further information in the specific area of concern. If this additional information fails to reduce the ratio to below one, a risk limitation exercise must be considered.

Table 4.18   **EU environmental risk assessment: scenarios and species to be considered.**

Risk consideration	Exposure medium for PEC evaluation	Species for PNEC evaluation
Aquatic	Surface water	Aquatic species
Terrestrial	Agricultural soil	Soil species
Secondary toxicity	Earthworms/fish	Birds/mammals
Sewage plant	Sewage plant digester	Sewage plant bacteria

Table 4.19   **EU assessment factors: aquatic ecotoxicity.**

Available data	Assessment factor

Base set:
  1 or more acute LC_{50} or EC_{50} for each of the 3
  trophic levels (fish, daphnia, algae)
	1000

Base set + 1 long-term NOEC (fish or daphnia)	100
Base set + long-term NOEC for 2 of the 3 trophic levels (fish, daphnia, algae)	50
Base set + long-term NOEC for 3 trophic levels (fish, daphnia, algae)	10

PNEC = (lowest LC_{50} or EC_{50} or NOEC)/assessment factor.

EU risk assessment of MDI and TDI

No attempt is made here to carry out a fully comprehensive risk assessment, but it is of interest to follow through the procedure described above at a simple, general level, using the information on effects and exposure displayed in this part. As an example the assessment factors recommended by the EU (Table 4.19) will be used to allow calculation of PNEC values.

Application to air

No accredited procedures exist for the precise evaluation of environmental hazard in the atmosphere. Of possible adverse physicochemical effects, enhancement of the greenhouse effect by relatively high concentrations of infrared absorbers and destruction of stratospheric ozone (by long-lived chlorinated species) are unlikely to be of concern in this case. Formation of tropospheric ozone, leading to photochemical smog, has to be considered because of the ready reaction of MDI and TDI with hydroxyl radicals in air. However, the studies described earlier indicate that neither MDI nor, in particular, TDI are likely to have a significant positive effect on ozone formation. As regards ecotoxicity, the test methodology has not yet been significantly developed. Any inhalatory data are for mammals, and relate primarily to concerns over human health rather than the environment.

Qualitative conclusions with regard to environmental risk can be reached, however, by considering the potential for *exposure*. Atmospheric concentrations of MDI and TDI in the manufacturing or use environment are controlled to very low levels to protect the health of workers. In the wider environment, the concentration will be even less and photochemical degradation of MDI and TDI vapours will prevent any accumulation. This conclusion is supported by multimedia modelling (see Table 4.12). The very low concentrations predicted in the air from typical processing releases indicate that no significant adverse effects, physical or ecotoxicological, are to be expected. These were of the order of $10^{-4}\,\mu g/m^3$ regionally and only about $7 \times 10^{-3}\,\mu g/m^3$ very close to the source.

Application to water

With regard to aquatic *hazard*, data on toxicity to algae, invertebrates and fish are available for both MDI and TDI. The calculation of PNEC values from the data according to the EU methodology is shown in Table 4.20. Only freshwater species are considered. For MDI a *base set* of acute toxicity data (see Table 4.19) with three longer-term endpoints (including in these the ecosystem study for fish), leads to an assessment factor of 10. This is applied to the lowest endpoint, in this case a NOEC for invertebrates of $\geq 10\,mg/l$, to give a PNEC of 1 mg/l. For TDI, a *base set* of acute data with two longer-term end points allows an assessment factor of 50. This applied to the lowest end point, a NOEC for invertebrates of 1.1 mg/l, gives a PNEC of 22 μg/l.

Table 4.20 **Calculation by EU method of the aquatic PNEC for MDI and TDI.**

Base set: Acute LC_{50} or EC_{50} mg/l	MDI	TDI
Fish	>1000	133
Daphnia	>500	12.5
Algae	>1640	4300
Longer Term NOEC mg/l		
Fish	$\geq 10\,000$	–
Daphnia	≥ 10	1.1
Algae	≥ 1640	≥ 2000
Assessment factor (Table 4.19)	10	50
PNEC mg/l	**1**	**0.02**

As regards aquatic *exposure*, release of diisocyanate to water is negligible, whether from production, where closed anhydrous processes are used and any waste is incinerated, or from use, where any waste diisocyanate is treated with neutralizer. Release to air, from which diisocyanate could possibly migrate into the aquatic compartment, is also low. In this case the ready degradation of both diisocyanates in air reinforces the expectation that this will not be a significant source of aquatic MDI or TDI, and multimedia modelling supports this conclusion.

However, the major determinant of aquatic exposure to MDI and TDI is their physicochemical behaviour in contact with water. In consequence of this,

and in particular of the inherently very rapid hydrolysis, it can confidently be predicted that steady-state aquatic concentrations of MDI and TDI will always be extremely low, well below detection levels. In this situation where actual environmental concentrations are likely to be too low for successful monitoring, it is of interest to predict them by multimedia modelling. In particular, it is useful to model what is likely to be the worst-case situation: the environmental concentration of diisocyanate in close proximity to a plant emitting relatively high amounts of diisocyanate to air. Under such conditions atmospheric degradation is too slow to affect the calculation significantly. It has to be remembered, however, that such quantitative predictions are notional for substances as reactive as MDI and TDI.

Such a calculation is described earlier, using the exposure module within the EUSES risk evaluation programme (Table 4.12). Predicted environmental concentrations of MDI or TDI in soil porewater (indication of concentrations likely to be found in surface or groundwater) and in soil, close to a plant emitting 24 g/day, are well below detection levels, which themselves are below the predicted no-effect concentrations of these materials to aquatic organisms. This calculation indicates a very low level of risk in the aquatic compartment.

Application to soil

Both MDI and TDI show very low toxicity to plants and earthworms. Applying even the highest aquatic assessment factors of 1000 to the data gives values of PNEC (soil) ≥ 1 mg/kg for both materials.

With regard to exposure there are no direct releases to soil and the ready hydrolysis renders the concepts of distribution and partition meaningless and irrelevant. The EUSES model, referred to above, predicts very low soil concentrations for both MDI and TDI resulting from deposition close to releases of the diisocyanates to air. Evidence from laboratory studies and spillages supports the conclusion that significant exposure in this compartment is not to be expected and so no significant risk is predicted.

Secondary exposure

Bioaccumulation of MDI and TDI is not possible because of their rapid hydrolytic reaction. The diamines MDA and TDA have only low potential for bioaccumulation. There is therefore no appreciable risk to the food chain.

Application to waste water treatment plants

The available ecotoxicity data for MDI and TDI and for MDA and TDA show only low toxicity to bacteria. The arguments with regard to the low level of release to waste water, and the nonavailability of MDI and TDI in aquatic systems apply here also, and in consequence no risk would be predicted.

The EU has recently performed a draft risk assessment for MDI (Belgian Rapporteur, 1999). This was considerably more detailed and wider ranging than the simple exercise described above, and more conservative assumptions were made as to the degradation rates of the substance in water, soil and sediment. Even so, the overall conclusion was that MDI presented no environmental hazard.

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