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Modeling formation and distribution of toluene-2,4-diamine (TDA) after spillage of toluene-2,4-diisocyanate (TDI) into a river

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HIGHLIGHTS

- TDA is a minor hydrolysis by-product of TDI spilled into water.
- After spillage of TDI into water, maximum TDA concentration is about 30 mg/L.
- TDA formation and distribution after hypothetical TDI spillage is modeled.
- With appropriate experiments, the model can be adopted to other, water-reactive chemicals.

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ABSTRACT

Toluene diisocyanate (TDI) is a large volume chemical used for the production of polyurethanes. It is sparingly soluble in water, but hydrolyses instantaneously liberating toluene diamine (TDA), which is highly reactive to TDI. The ecotoxicity of TDI is dominated by TDA. The hydrolysis of TDI under static and dynamic conditions was investigated previously. Previously published data on TDI hydrolysis were revisited, and based on these data a model was developed that allows a conservative and quick estimation of TDA concentrations in rivers following a major incident with TDI. As earlier published model experiments indicate, the maximum achievable TDA concentration is about 30 mg/L. Model simulations based on these experiments indicate that the TDA concentrations in a river after TDI discharge may be up to three orders of magnitude lower.

1. Introduction

Toluene diisocyanate (TDI) is a large production volume chemical that is mainly used in Flexible Polyurethane Foam production. The commercial most important product is an 80:20 mixture (CAS-No.: 26471-62-5) of the two isomers, toluene-2,4-diisocyanate (2,4-TDI; CAS-No.: 584-84-9) and toluene-2,6-diisocyanate (2,6-TDI; CAS-No.: 91-08-7). TDI is a hazardous good (class 6.1, UN-No.: 2078) and it is a hazardous substance, classified as very toxic by inhalation, irritating, a skin and respiratory sensitizer, a suspected carcinogen and harmful to aquatic organisms. This latter aspect is of special interest in case of TDI spillage into rivers due to transport accidents. Actually, the reaction between TDI and water has been investigated intensively (e.g. Yakabe et al. [1,2] Kitano et al. [3]). Due to its higher relative density (about 1.27 g/cm^3), TDI poured into water sinks to the bottom of the water body [2]. TDI reacts with water instantaneously at the contact surface and forms mainly TDI-based, insoluble polyurea and small amounts of toluene-2,4-diamine (2,4-TDA; CAS-No.: 95-80-7) and toluene-2,6-diamine (2,6-TDA; CAS-No.: 823-40-5). The aquatic toxicity of TDI is attributable to the 2,4-TDA formed upon hydrolysis [4], which can easily be seen when – e.g. – the EC$_{50}$(48 h) against daphnia of TDI is compared to that of TDA; at the nominal ED$_{50}$ for TDI, the measured TDA concentration is in the range of the ED$_{50}$ for TDA. The polyurea formed is comparatively stable, and the half-life time hydrolysis to TDA is calculated as 18,000–300,000 years at 25 °C (Sendijarevic et al. [5]). Taken together, when TDI is spilled into a river, the risk is dominated by the formation of the hydrolysis product TDA. 2,4-TDA is the most active isomer in terms of ecotoxicity and human toxicity [6]. Therefore, the emphasis of this paper is on 2,4-TDA.

A modeling of a TDI spillage into a river with respect to release and spread of toluene diamine (TDA) is of high interest for appropriate preparation for emergency response measures. Such modeling, based on previously published data is presented in the following text.

Models for the spread of chemicals discharged in rivers have been published previously. Kilic and Aral [7] presented a combined hydrodynamic transport and fugacity model; that model addresses releases, transport, first order reactions and exchange between compartments for a target substance. The biogeochemical modeling published by Massoudieh et al. [8] addresses water quality

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in a similar manner; here, the focus is on the spatial and temporal change of water quality parameters like dissolved oxygen, ammonium ions et cetera. McCready and Williams [9] describe a simplified dispersion model for quick exposure assessment and risk evaluation in case of spillages. Although less sophisticated as the other models [7,8], it has its benefits. In spill situations, the forecast of peak concentrations with respect to time and position is of prime interest to frame emergency response measures. The following work has similarities to [9]; however, here TDI is addressed as a model for a sparingly soluble, water reactive, polymerizing substance.

2. Materials and methods

2.1. Kinetics of the TDI-water reaction and yields of TDA

Data of the hydrolysis reactions of TDI were taken from literature and are published elsewhere [1–3]. Briefly, in dynamic experiments different loadings of TDI (pure 2,4-TDI or 80:20 ratio of 2,4- to 2,6-isomer) were dispersed into purified water at 27 °C. After certain time periods, samples were taken and analyzed for DOC as well as for TDA and TDI.

In static experiments [2], a fixed amount of 5 g 2,4-TDI was carefully placed in 300 mL of purified water at 25 °C at different surface to volume ratios. After certain time periods the bottom layer was analyzed for TDI, and the supernatant water was analyzed for TDI, TDA and DOC.

For the treatment of the kinetics, the reaction of TDI with water leads to TDA which itself is reactive with TDI. This is illustrated in Fig. 1.

The simplified reaction scheme is given in Eqs. (1) and (2):

$$\text{TDI} \rightarrow \text{TDA} \tag{1}$$

$$\text{TDI} + \text{TDA} \rightarrow \text{Mono-Urea} \rightarrow \text{oligo- and poly-Urea.} \tag{2}$$

The urea itself is reactive to TDI, and finally an insoluble polurea is formed. Such a reaction implies that over a certain period of time, a steady state is achieved for TDA. The simplified rate expression, assuming a steady state for TDA, is

$$\frac{d[\text{TDA}]}{dt} = k_1 \times [\text{TDI}] - k_2 \times [\text{TDI}] \times [\text{TDA}] \tag{3}$$

Further it is assumed that the concentration of dissolved TDI also achieves a steady state. Therefore, with $k_1 \times [\text{TDI}] = K_1$ and $k_2 \times [\text{TDI}] = K_2$ Eq. (3) is transformed to:

$$\frac{d[\text{TDA}]}{dt} = K_1 - K_2 \times [\text{TDA}]. \tag{4}$$

The solution of this differential equation is

$$[\text{TDA}] = \frac{K_1}{K_2} \times (1 - \exp[-K_2 \times t]). \tag{5}$$

The concentration of TDA is zero at the very beginning of the process, then increases exponentially and finally achieves its steady state concentration, for which $K_1/K_2 = k_1/k_2$. If the amount of TDI is limited, the reaction may not run for a sufficient period of time to achieve the steady state for TDA. The result is theoretically equivalent to a snapshot of the TDA concentration taken early in a hydrolysis reaction with sufficient TDI. Therefore, the time t in Eq. (5) is replaced by the initial concentration of TDI (= $[\text{TDI}]_0$):

$$[\text{TDA}] = A \times (1 - \exp\{-B \times [\text{TDI}]0\}) \quad A = \frac{K_1}{K_2} \quad B = K_2 \tag{6}$$

For the non-linear fit of data, the program Origin 8.5.1 from OriginLab Corporation, One Roundhouse Plaza, Northhampton, MA 01060, USA, was used (www.OriginLab.com).

2.2. The river model

To model the formation of TDA in a river for a given scenario, the amount of TDA formed per unit of time is dependent on the contact surface between TDI and water.

$$\frac{d[\text{TDA}]}{dt} = \frac{R_S \times S}{V} \tag{7}$$

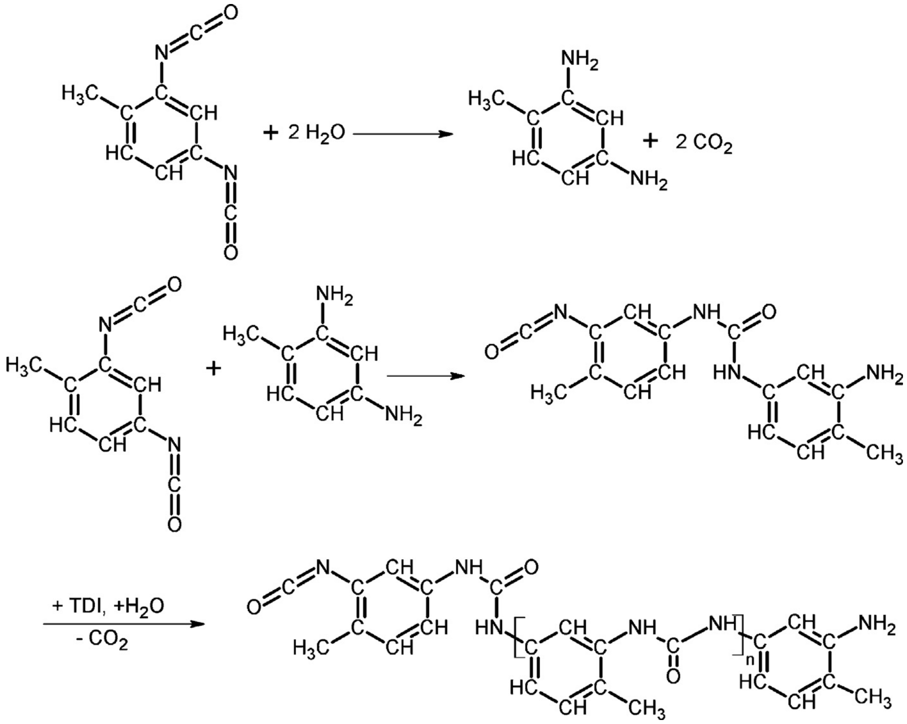

Fig. 1. Reaction scheme for hydrolysis and polymerization of 2,4-TDI in water.