

## Methyl Isocyanate

The methyl isocyanate spill near Bhopal, India, during the night of December 2-3, 1984 was at the heart of what is often cited as the world's worst industrial disaster involving a chemical release. The exact number of people who died from this methyl isocyanate exposure is in dispute and depends upon the information source, but the government of Madhy Pradesh which includes Bhopal confirmed 3787 deaths initially related to inhalation exposure. Other estimates have been up to 10,000 deaths within 72 hours of the release, plus another 20,000 deaths due to long term effects. Another 100,000 to 200,000 people have been estimated to have permanent injuries. All this from a spill of 42 metric tonnes (42,000 kg; 92,400 lbs) of methyl isocyanate from a very large storage tank.

Methyl isocyanate is still used today in the United States mostly in the manufacture of pesticides. The quantities stored or used today at facilities are smaller than what was used at Bhopal in 1984, but a reactor tank explosion occurred recently (2008) at Bayer Crop Science in West Virginia has raised additional safety concerns by the U.S. Congress on the storage and use of this chemical. The explosion took place 80 feet from a 37,000 lb capacity storage tank of methyl isocyanate, which fortunately, was not released.

We will look at the safety and use of this controversial chemical in this newsletter. We will revisit the Bhopal accident and take a look at the 28 August 2008 chemical reactor explosion at Bayer which is being investigated by the U.S. Chemical Safety Board, who is reporting to Congress.

### **Methyl Isocyanate: The Chemical and Its Uses**

Some basic information displayed on the PEAC tool show that the chemical is deadly, flammable, and reacts with water:

#### **Methyl isocyanate**

CAS 624-83-9

UN 2480

[GUIDE 155 - SUBSTANCES - TOXIC and/or CORROSIVE \(Flammable / Water-Sensitive\)](#)

Colorless liquid; sharp pungent odor, causes tears

#### **NFPA Information**



Health (Blue): 4 Deadly  
Fire (Red): 3 Flash Point < 100°F  
Instability (Yellow): 3 Shock/Heat may Detonate  
Special (White): No Water

## Physical and Chemical Properties

Formula: CH<sub>3</sub>NCO

Molecular Weight: 57

Flash Point: 0°F

Lower Explosive Limit: 5.3%

Upper Explosive Limit: 26%

Auto Ignition Temp.: 995°F

Boiling Point: 102°F

Melting Point: -112°F

Rel Vapor Density @68°F: 2 (Heavier than air)

Vapor Pressure @68°F: 0.46 atm

Liquid Specific Gravity: 0.96 (Approximately the same density as water)

Ionization Energy: 10.67 eV

RAE Systems PID correction factor for 10.6 eV: [4.6](#)

RAE Systems PID correction factor for 11.7 eV: [1.5](#)

## Toxic Levels of Concern

IDLH: 3 ppm (6.99 mg/m<sup>3</sup>)

TWA: 0.02 ppm (0.047 mg/m<sup>3</sup>)

ERPG-1: 0.025 ppm (0.058 mg/m<sup>3</sup>)

ERPG-2: 0.25 ppm (0.58 mg/m<sup>3</sup>)

ERPG-3: 1.5 ppm (3.5 mg/m<sup>3</sup>)

## Acute Exposure Guideline Levels (Status: Final)

Ten Minute AEGL-2: 0.4 ppm

Thirty Minute AEGL-2: 0.13 ppm

One Hour AEGL-2: 0.067 ppm

Four Hour AEGL-2: 0.017 ppm

Eight Hour AEGL-2: 0.008 ppm

Ten Minute AEGL-3: 1.2 ppm

Thirty Minute AEGL-3: 0.4 ppm

One Hour AEGL-3: 0.2 ppm

Four Hour AEGL-3: 0.05 ppm

Eight Hour AEGL-3: 0.025 ppm

AEGL-2: The airborne concentration of a substance above which it is predicted that the general population, including "susceptible" individuals could experience irreversible or other serious, long-lasting health effects or impaired ability to escape.

AEGL-3: The airborne concentration of a substance at or above which it is predicted that the general population including "susceptible" individuals could experience life-threatening health effects or death.

Comment: The metric mode option can be selected in the PEAC tool to give temperatures in °C.

Methyl isocyanate reacts with water producing considerable heat plus varying amounts of the chemical products 1,3-dimethylurea, some 1,3,5-trimethylbiuret, and carbon dioxide. If the heat is not removed quickly enough from the water reaction, the methyl isocyanate will violently boil (102°F; 39°C, at sea level) producing significant deadly methyl isocyanate vapor. Even at temperatures below its boiling point, some methyl isocyanate will vaporize.

The American Conference of Government Industrial Hygienists has set a threshold limit value of 0.02 parts per million (ppm) concentration in air for an 8-hour TWA exposure. Prolonged exposure at concentrations as low as 0.4 ppm can cause damage by inhalation, ingestion, or physical contact. The EPA-recommended level-2 acute exposure guideline level limit (AEG-2) is 0.067 ppm for one-hour exposure, or 0.008 ppm for an 8-hour exposure, which is lower than some of the other numbers published by other governmental agencies. Exposure at concentrations as low as 0.4 ppm can produce coughing, asthma condition, and irritation of the eyes. Concentrations at 2 to 4 ppm quickly causes irritation of the eyes, even though most people would not detect an odor. Concentrations over 21 ppm even for a short period can result in pulmonary edema (fluid filling lungs), hemorrhages, and death. Animal studies (rat) indicate a 4-hour exposure LC50 value of 0.54 ppm (50% of rats die inhaling air containing 0.54 ppm for 4 hours).

Methyl isocyanate is used as an intermediate chemical in the manufacture of carbamate-based pesticides. Examples of carbamate-based pesticides include carbaryl [Sevin], carbofuran, methomyl, and aldicarb. Methyl isocyanate itself is manufactured from other chemicals, usually near or at the site where the chemical is to be used rather than transported by carrier. The usual method of methyl isocyanate manufacture involves reacting methylamine with phosgene in the gas phase, followed by additional steps to produce the chemical. Phosgene is also a very toxic chemical by inhalation.

## **Bhopal Disaster**

### **Background:**

The Union Carbide India, Limited pesticide manufacturing plant was established in 1969 near Bhopal, India; 51% was owned by Union Carbide Corporation and 49% by the Indian government. The facility produced the pesticide carbaryl under the trademark Sevin. The pesticide was produced by reacting methyl isocyanate with 1-naphthol in the presence of a catalyst to form the carbaryl. Initially, methyl isocyanate was imported, but in 1979 a plant was added at the site for producing methyl isocyanate from phosgene and methylamine.

Various articles on the Internet including a summary by Wikipedia citing many references and reports which give account of the tragedy were used in this Newsletter article.

The exact causes of circumstances leading up to the methyl isocyanate disaster are not clear, but apparently Union Carbide corporate had a “hands-off” approach to management of its overseas operations [from Trade Environmental Database Case Studies, see <http://ausolaris1.american.edu/ted/ted.htm>.] Local Indian engineers were under pressure by

the Indian government to reduce expenses and use locally produced materials rather than importing expensive instrumentation. This sometimes resulted in bypassing or ignoring or not repairing critical safety systems. The methyl isocyanate refrigeration system for the storage tank was shut down, resulting in a storage temperature of 20°C rather than the manual-recommended 4.5°C. A vent-gas scrubber designed to treat gases vented from the plant with a sodium hydroxide wash was out of service. Valves and piping were being replaced with carbon steel, which corroded; the corroded piping was flushed with wash water from time to time [recall methyl isocyanate reacts with water producing heat and various chemicals, which may be corrosive to steel]. One of the valves, of carbon steel construction, at the methyl isocyanate storage tank was leaking because of corrosion. At the night of the release, skip-blind plates that would have prevented water from pipe cleaning operation from entering the methyl isocyanate tank from the faulty valve were not installed.

These and other safety issues were brought out in civil action suits conducted in 1998.

### The Release:

Tank 610 containing 42 tonnes of methyl isocyanate was released during the night of December 2-3, 1984. The sequence of events is as follows:

- 2 December (21:00 hours): Workers begin water cleaning of the pipes. They did not add a skip-blind water isolation plate (at least they were not told by their supervisor to add the plate) which would have prevented water from entering tank 610.
- 2 December (22:00 hours): Water enters tank 610 and reacts with methyl isocyanate inside the tank releasing considerable heat. The tank refrigeration system is not working, and the temperature inside the tank increases to over 200°C boiling the methyl isocyanate.
- 2 December (22:30 hours): Gases vent from the tank through the vent gas scrubber, but the scrubber is not working, and even if it was working, it apparently was not designed to handle the volume of gases released during this event according to testimony heard in later court trials.
- 3 December (00:30 hours): A loud siren sounds warning of the leak and is turned off.
- 3 December (00:50 hours): Workers escape from the plant.
- 3 December (01:00 hours): Local police are alerted. The plant director denies any leak.
- 3 December (04:00 hours): The gases were brought under control.
- 3 December (06:00 hours): A police loudspeaker broadcasts, "Everything is normal".

But outside the facility, things were not normal. First sensations due to the gas (coughing, suffocation, burning eyes, vomiting) were felt starting at 2 December (22:30 hours). The dense gas hugged the ground spreading into the city of Bhopal. People were awakened by these symptoms and began to flee the area. People who ran inhaled more of the chemical than those who escaped in a vehicle. Children and others of short stature inhaled more of the dense gas. Some were trampled trying to escape. The first people reached the local hospital (3 December, 02:00 hours) with symptoms of visual impairment, blindness, respiratory difficulties, frothing at the mouth, and vomiting.

Eventually the toxic gas cloud spread out over an estimated 40 square kilometers affecting a population of 520,000 people. It was later estimated that approximately 27 tonnes of methyl isocyanate was released during a 1 to 2 hour period. Stable air conditions, low wind speed, and atmospheric inversion existed at the time of the release.

By the morning hours, several thousands of people succumbed to the gas. The local government (Madhya Pradesh) certified 3787 deaths due to inhalation exposure, which was later increased to 3928 deaths as brought out in court trials in 1991. The actual number of initial deaths was later estimated to be over 6000 deaths according to the Government of Madhya Pradesh in 1994. Causes of death included choking, pulmonary edema, and circulatory collapse. Unofficial counts by independent organizations estimated the number of deaths between 8000 and up to 30,000 within the first few days. A lot of people left the area at the time of the incident and died and were possibly not counted. There were mass funerals, and bodies were cremated and disposed in the nearby Narmada River. Approximately 170,000 people were treated at hospitals and temporary dispensaries. Approximately 100,000 to 200,000 people were estimated to have permanent injuries of varying degrees [reference: citations in Wikipedia under "Bhopal disaster"].

Approximately 2000 bloated animal carcasses were collected and disposed. Within a few days of the accident, the leaves on the trees turned yellow and fell off.

On 16 December 1984, methyl isocyanate was drained from tanks 611 and 619 at the facility. A precautionary second mass evacuation of Bhopal occurred.

#### The Aftermath:

A review of health effects resulting from the Bhopal disaster is presented by V.R. Dhara and R. Dhara, Archives of Environmental Health, Sept/Oct. 2002 (vol. 57 no. 5), pp 391-404. The paper can be obtained off the Internet at <https://webdrive.service.emory.edu/users/vdhara/www.BhopalPublications/Health%20Effects%20&%20Epidemiology/Health%20Effects%20Review%20articles/Health%20Effects%20Review%20AEH.pdf>.

An estimated 20,000 people later died from the accident from gas-exposure disease conditions. Another 100,000 to 200,000 people are estimated to suffer permanent injuries, which included eye problems, immune and neurological disorders, lung injury, female reproductive difficulties, and birth defects among children born to affected women.

On the day after the release, Union Carbide sent material aid and several international medical experts to assist medical facilities in Bhopal. The Chairman and CEO of Union Carbide (Warren Anderson) visited the site on the condition that he would not be arrested by Indian authorities, but he was arrested anyway and released on bail by the Madhya Pradesh Police on 7 December 1984. Union Carbide was also denied access to the facility to do an investigation as to the cause of the accident and was prohibited from talking to facility employees. Warren Anderson

was declared a fugitive from justice by the Chief Judicial Magistrate of Bhopal in February 1992 for failure to appear at court hearings; so far, he has avoided an international arrest warrant.

The Indian government claimed \$3 billion in damages from Union Carbide. An out-of-court settlement was reached with Union Carbide in 1989 for \$470 million in damages, which was upheld in 1991 by the Indian Supreme Court. According to the Bhopal Gas Tragedy Relief and Rehabilitation Department, compensation has been awarded to 554,895 people for injuries received and to 15,310 survivors of those killed, of which the actual amount awarded to victims was only a portion of the total.

Union Carbide, based on a 1988 investigative report by Arthur D. Little (the report is available at <http://www.bhopal.com/pdfs/casestdy.pdf> ) believes that the accident occurred as the result of sabotage. Their belief is that a single employee secretly and deliberately introduced a large amount of water into the methyl isocyanate tank by removing a meter and connecting a water hose directly to the tank through the metering port. Also a possible leaking carbon steel valve could not have accounted for the large water introduced to the tank. The report was presented (May 1988) at the Institution of Chemical Engineers Conference on Preventing Major Chemical Accidents in London, England, and included results of interviews with employees. The abstract opens with the statement that investigation of large-magnitude incidents requires an understanding of human nature in addition to technical and engineering details.

In 2001, the Dow Chemical Company purchased Union Carbide for \$10.3 billion in stock and debt. The purchase did not include the Indian Union Carbide Bhopal plant. The plant area is contaminated with organochlorines, heavy metals, and other chemicals, which have rendered local wells unusable. The contamination is unrelated to the December 1984 releases and includes a long history of dumping hundreds of tonnes of toxic wastes. The Madhya Pradesh Government is trying to legally force Dow to finance clean-up operations.

The writer (John Nordin) attended several lectures put on by the University of Wyoming Law Department a few years ago on the Bhopal disaster, which included a presentation by a lawyer representing the victims. The litigation which is still ongoing is much more complex than the abbreviated summary given in this newsletter.

### **August 2008 Bayer CropScience Explosion in West Virginia, 2 killed**

#### **Background:**

The explosion occurred on 28 August 2008 at 10:35 PM in a large industrial chemical complex of more than 400 acres located about 10 miles west of Charleston and owned by Bayer CropScience (referred to as "Bayer").

The chemical complex was constructed in the 1940's, and for four decades was used by Union Carbide which included manufacture of carbamate-based pesticides from methyl isocyanate and other chemicals. The methyl isocyanate was manufactured on site from phosgene and methyl amine and stored in a large tank for servicing nearby pesticide manufacturing

operations. In 1982, Union Carbide equipped the tank with a protective “blast blanket”, which is a steel mesh which hangs from a steel framework presumably to protect the tank from accidental process-related explosions. Union Carbide sold the complex in 1986 following the Bhopal disaster. Pesticide production continued, and in 1994 the owner Rhone-Poulenc installed a second section of the blast blanket on top of the methyl isocyanate (MIC) tank. Bayer acquired the complex in 2002 and continued pesticide production and has more than 500 employees at the site.

The MIC tank (8 feet in diameter, 19 feet tall) is pressurized and refrigerated and has a capacity of 37,000 lbs of methyl isocyanate. Normally, the tank is filled daily via pipeline from a MIC production facility located several thousand feet away. Methyl isocyanate is used in four pesticide production areas; the 28 August 2008 explosion took place in the nearby methomyl pesticide production area. Methomyl is combined with other ingredients and marketed under the trade name Larvin.

The MIC tank at Bayer is the largest methyl isocyanate storage tank in the United States. This is the only industrial facility in the U.S. which stores more than 10,000 lbs of methyl isocyanate, according to the U.S. Chemical Safety Board.

Although the MIC tank remained intact and no MIC was released from the tank as the result of the explosion, the U.S. Congress demanded an explanation of the accident. The accident already was being investigated by the U.S. Chemical Safety Board. On 21 April 2009, Chemical Safety Board Chairman John S. Bresland presented his testimony before the House of Representatives Committee on Energy and Commerce, which is available at <http://www.csb.gov/assets/document/BreslandBayerCombinedTestimony.pdf>. Three other House and Senate committees have requested explanations. The Chemical Safety Board also posts updates of their investigation at <http://www.chemsafety.gov/investigations/detail.aspx?SID=3>. Their final report is expected in 2010.

#### The Explosion at the Bayer Methomyl Production Facility:

The explosion claimed the lives of two Bayer employees. Eight people including six volunteer firefighters were treated for symptoms of chemical exposure, which included aches and respiratory and intestinal distress. Two sought treatment at a hospital emergency room and were released the next day.

Earlier, the plant had installed new and completely different computer control equipment for the methomyl production area. On the night of the explosion, the control room operator saw unexpected, rapidly rising pressure displayed on the control console for the residue treater vessel. He asked outside operators to investigate for a possible blockage of the residue treater vent line. As operators approached the equipment, at 10:30 PM, the vessel relief valves were already relieving excess pressure but could relieve the pressure fast enough. Without warning, the residue treater vessel suddenly ruptured, ejecting as much as 2500 gallons of highly flammable liquid. The 5500 pound residue treater vessel careened northeast into the

methomyl production area destroying steel columns, piping, and equipment along the way. By fortunate chance, the vessel did not slam into the MIC tank located 80 feet away from the explosion. The two operators were killed by the explosion.

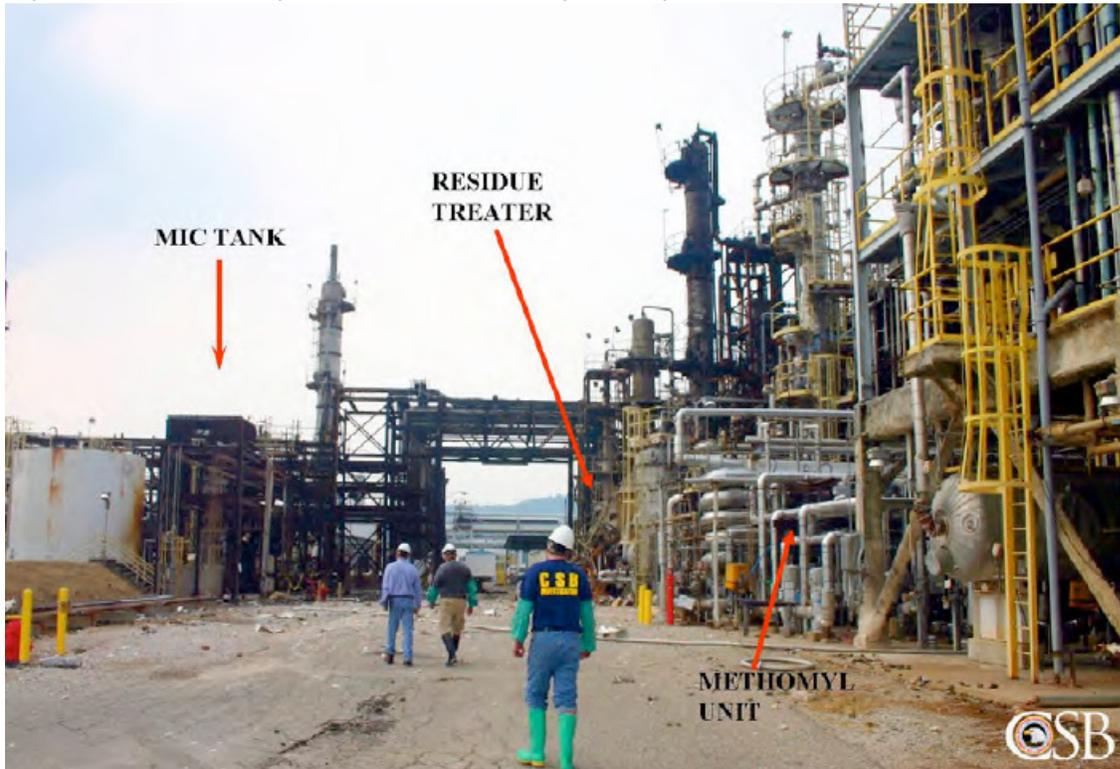


Figure 1: Relative locations of methyl isocyanate(MIC) tank, the residue treater which exploded, and methomyl production unit. A Chemical Safety Board investigator is in the foreground.



Figure 2: The blast blanket protecting the MIC tank. Note explosion debris in the foreground. Both illustrations from the CSB report on 21 April 2009 to the House Committee cited earlier.



Figure 3. Path of destruction caused by careening residual treater vessel, which came to rest as shown in the center of the picture (from CSB 21 April 2009 report). The residual treater is designed to decompose waste methomyl in a solvent carrier before final incineration.

The blast wave from the explosion damaged the control room several hundred feet away and broke windows and cracked ceilings in homes and businesses up to several miles away. A fire also occurred at the methomyl production unit. Projectiles were sent in all directions. Fortunately, none of the projectiles penetrated the MIC tank.

The MIC vessel contained between 13,000 and 14,000 lbs of methyl isocyanate at the time the residual treater vessel exploded.

#### CSB Investigation:

The CSB investigation uncovered several deficiencies of Bayer plant operations including insufficient employee training on the new computer control system and some bypassed safety systems. The cause of the explosion was a runaway thermal reaction at the residual treater vessel, when an excessively high concentration of waste methomyl was fed to the vessel. Details on these deficiencies are at the CSB website. We will look at CSB commentary on Bayer's response to the incident because it is of interest to emergency responders.

The CSB investigation noted that Bayer's incident commander called the county 9-1-1 center 15 minutes into the response and said that no dangerous chemicals had been released. This was

not true, as methomyl is toxic, and its uncontrolled decomposition (according to publically available Material Safety Data Sheets) may release toxic methyl isocyanate, hydrogen cyanide, acetonitrile, carbon monoxide, dimethyl disulfide, sulfur oxides, nitrogen oxides, and methyl thiocyanate. In addition, hazardous chemicals were likely released from severed chemical pipes resulting from the explosion.

Later, Bayer called the 9-1-1 center recommending that authorities issue a shelter-in-place advisory for surrounding communities, but local authorities had already decided on a shelter-in-place order after observing what they feared might be a hazardous chemical haze drifting from the plant.

The guard at the front gate at Bayer, evidently following instructions from Bayer, declined (for a period) to identify to 9-1-1 officials even where in the 400-acre facility the explosion and fire occurred.

The firefighters who reported symptoms of chemical exposure were not wearing full personal protective equipment, apparently relying upon the fact that Bayer personnel at the scene were not using such equipment.

#### Additional Follow Up:

On 4 May 2009, four House and Senate committee chairmen sent a letter to the U.S. Chemical Safety Board requesting an examination of whether Bayer CropScience continued use of methyl isocyanate can be justified in light of ongoing health and safety risks to company employees, emergency first responders, and the public. On 26 August 2009, the Chemical Safety Board posted a follow up statement on their website after discussions were carried out with Bayer.

The Chemical Safety Board noted that Bayer used 200,000 lbs of methyl isocyanate as the worst-case hypothetical release scenario for the Risk Management Program rule in their report to the EPA [see Title 40, Code of Federal Regulations, Part 68 for details on the EPA requirement].

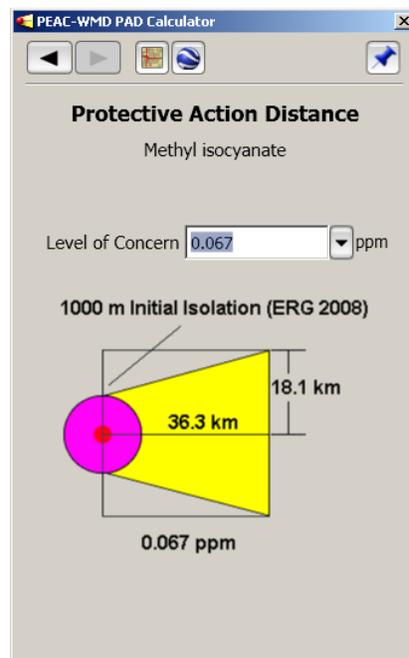
Bayer officials provided a plan to reduce the average methyl isocyanate inventory at their site by 80%. This would be done by eliminating the on-site production of two carbamate pesticides using methyl isocyanate as a raw ingredient, and restricting the inventory of methyl isocyanate for producing two remaining pesticides. Bayer would also eliminate aboveground storage of MIC tanks, including the 37,000-lb capacity storage tank located near the explosion site. All of the changes would be completed within 12 months, according to Bayer.

The Chemical Safety Board and Bayer will continue to examine the feasibility of switching to alternative chemicals or processes, as requested by Congress.

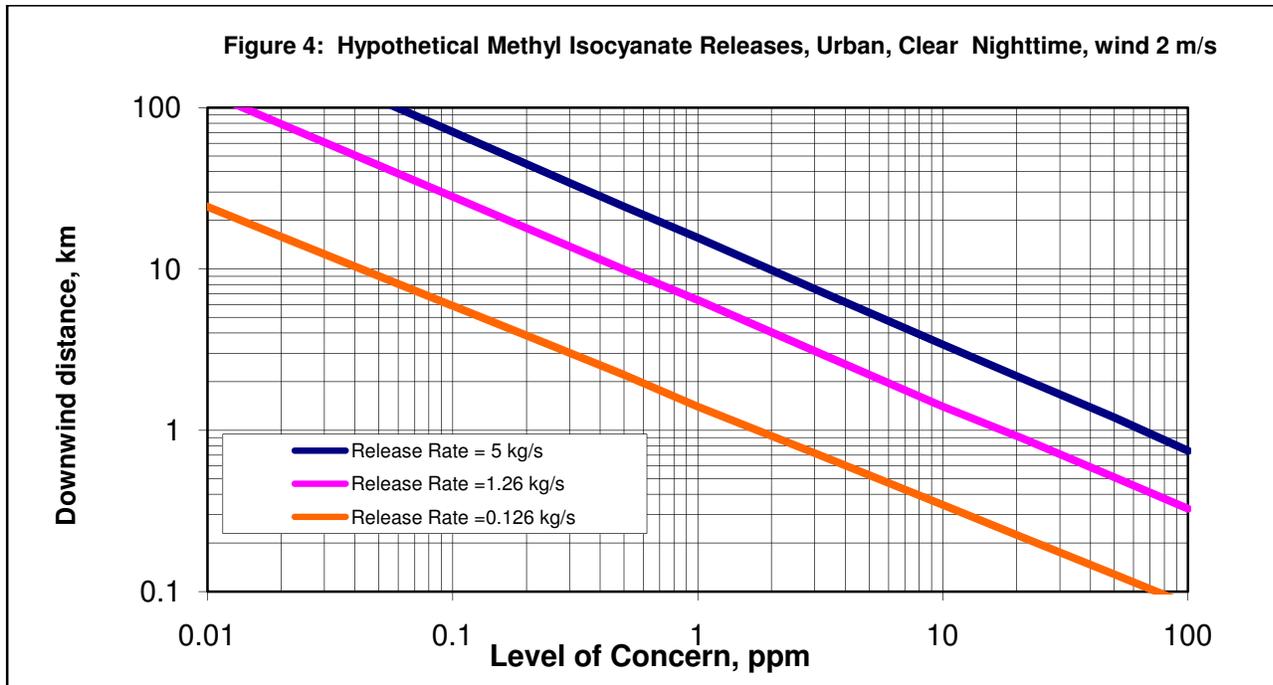
## Modeling a Hypothetical Release of Methyl Isocyanate Using The PEAC Tool

We will look at a hypothetical release of 10,000 lbs of methyl isocyanate to the atmosphere over a one-hour time period, which calculates to an average release rate of 2.78 lbs/sec (1.26 kg/s). We will assume a night time condition at a low speed, a stable air mass, clear skies, and the release occurs where there are nearby buildings and other structures instead of out in the open. Normally, methyl isocyanate would spill as a liquid, but the chemical evaporates quickly. Furthermore, as we have seen, if water enters the storage tank, the release could be a gas or a vapor aerosol. We will use the metric option, set the release rate at 1.26 kg/s, clear skies, nighttime, use a 2 m/s wind speed, and urban terrain.

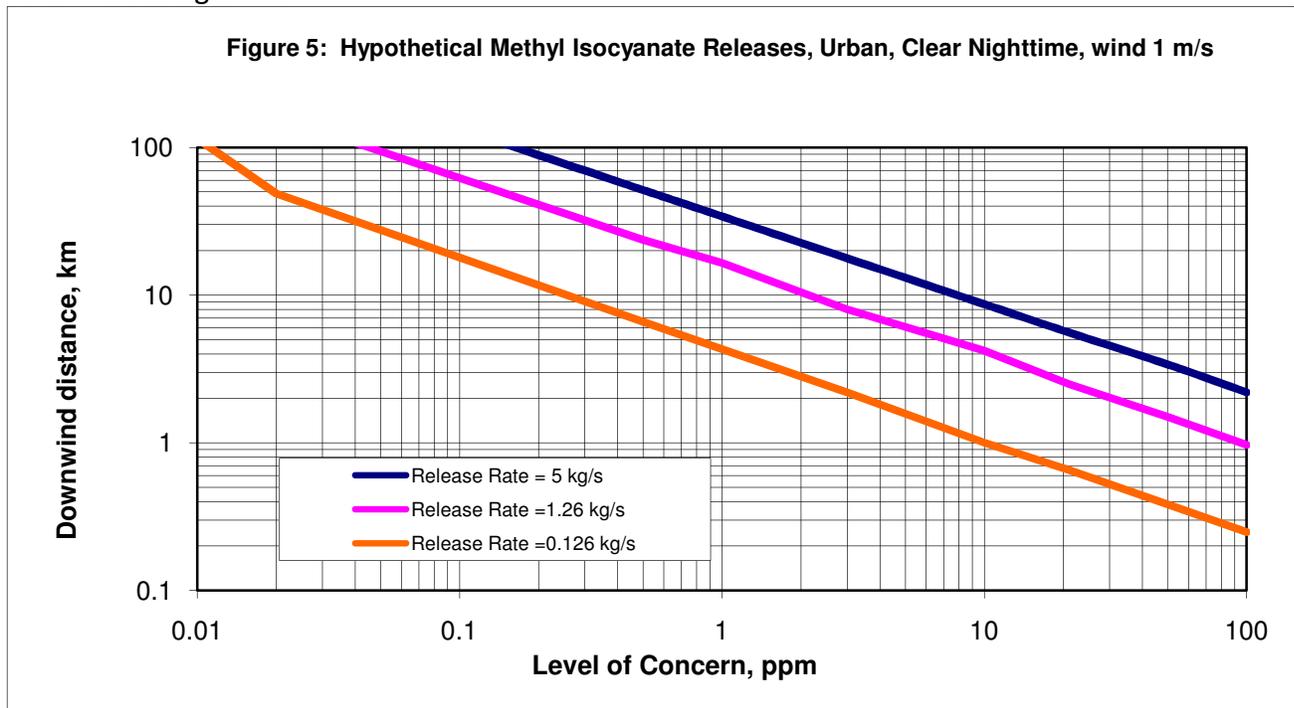
At a 21 ppm level of concern, the PEAC tool predicts this occurs at a downwind distance of 892 meters (0.892 km; about 0.6 miles). This concentration is lethal. The 21 ppm concentration is at the toxic cloud centerline near ground level. However, if we are looking at the AEGL-2 level of concern for one-hour exposure (0.067 ppm), a protective action distance of 36.3 km is predicted. We can rerun the PEAC tool at different levels of concern and plot the distances as a function of the levels of concern. We will repeat the exercise for a 5 kg/s methyl isocyanate release and for a 0.126 kg/s methyl isocyanate release. The results are shown in figure 4. Note that the scale is logarithmic.



The 5 kg/s release is equivalent to the average release rate if 27 metric tonnes of methyl isocyanate is released in 1.5 hours. The 1.26 kg/s release is the average release rate if 10,000 lbs is released in one hour. The 0.126 kg/s release is the average release rate if 1000 lbs is released in one hour.



The wind speed also makes a difference, especially under clear skies and during nighttime. The air becomes even more stable. We can repeat the same exercise for a 1 m/s wind speed. The results are in figure 5.



The modeling illustrated by figures 4 and 5 represent concentration levels near the ground and at the toxic cloud centerline. As one moves crosswind away from the centerline, modeling

predicts that concentrations should decrease. However, because of local topography and possible shifts in wind speed and direction, the location of the centerline is hard to predict and may even split into different directions. Additionally, the modeling does not include reaction of methyl isocyanate with air moisture to produce other chemicals which may be dangerous to inhale. The PEAC tool adopts the display used in the Emergency Response Guidebook for showing dimensions of a Protective Action Distance which is not a true shape of the toxic cloud dimensions.

Singh and Ghosh attempted to model the Bhopal toxic gas plume cloud. Their results are available in J. Hazard. Mat. Vol 17, pp1-22 (1987). An updated paper can be purchased from [http://www.sciencedirect.com/science?\\_ob=ArticleURL&\\_udi=B6VHC-3SWKV74-2&\\_user=10&\\_rdoc=1&\\_fmt=&\\_orig=search&\\_sort=d&\\_docanchor=&\\_view=c&\\_searchStrId=1032754613&\\_rerunOrigin=google&\\_acct=C000050221&\\_version=1&\\_urlVersion=0&\\_userid=10&md5=d2a3628b761056d21c9c6689674502ba](http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6VHC-3SWKV74-2&_user=10&_rdoc=1&_fmt=&_orig=search&_sort=d&_docanchor=&_view=c&_searchStrId=1032754613&_rerunOrigin=google&_acct=C000050221&_version=1&_urlVersion=0&_userid=10&md5=d2a3628b761056d21c9c6689674502ba). Based on 27 tonnes of methyl isocyanate released during 1 to 2 hours, they estimated a range of concentrations varying from 0.12 to 85.6 ppm over the 40 kilometer square area of the plume cloud where people were exposed. This release is approximated by the 5 kg/s release in figures 4 and 5.