

BHOPAL GAS TRAGEDY: MODEL SIMULATION OF THE DISPERSION SCENARIO

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Summary

In this paper, we present and analyse various aspects of the leak of toxic gas from the Union Carbide Plant at Bhopal, India in December 1984. The physicochemical properties of the deadly methyl isocyanate (MIC) and its biological activity, as well as the probable causes of the accident, are discussed. The role of meteorology and topography with regard to the dispersion process is also documented. To obtain an estimate of the possible concentration levels of MIC in the atmosphere, an analytic dispersion model has been formulated. The model output gives an estimate of the ground level concentration and the approximate time of arrival of the plume front in the various affected localities. Dry deposition and the aqueous phase conversion of MIC with the humid atmosphere were also featured in the model. The model results seem to be fairly well correlated with the scantily available mortality distribution records. Finally, the paper ends with descriptions of the disastrous effect of the gas on animals, plants and humans.

Introduction

The Bhopal gas tragedy is one of the world's worst ever industrial disasters. In this paper, we have tried to present and analyse several related aspects of this tragedy. We extensively document the physicochemical properties of the deadly gas methyl isocyanate and discuss the biological action of isocyanates.

One of the aims of this presentation is to illustrate the usefulness of mathematical dispersion models to study this catastrophic leak. The various physical and chemical processes which are strategically relevant to model formulation are extensively studied and on the basis of this study an analytic dispersion model is developed.

The role of meteorology in all air pollution episodes is of pivotal importance. Meteorological and topographical features of the Bhopal tragedy are also elucidated.

Model outputs have been correlated with the records of fatalities in various localities and also with the catastrophic imprint of the leak on animals, plants and vegetation.

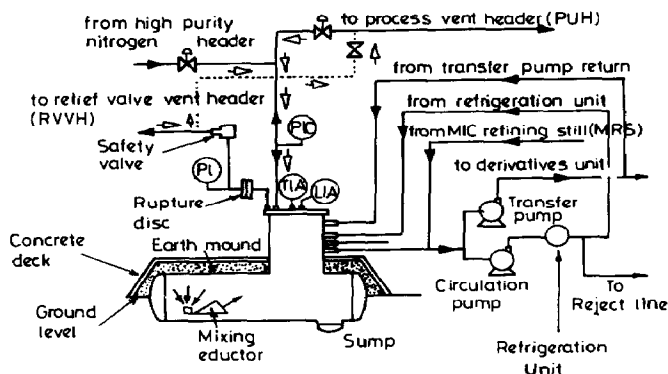


Fig. 1. MIC storage tank. PI=pressure indicator, PIC=pressure indicator/controller, TIA=temperature indicator/alarm, and LIA=level indicator/alarm.

History of the plant

The Union Carbide Plant (U.C.) was licensed by the Madhya Pradesh Government (M.P. Govt.) to manufacture phosgene, monomethyl amine (MMA), methyl isocyanate (MIC) and carbaryl (Sevin) with an output of 22 tons per day. MIC was produced by the reaction of MMA with phosgene, which gives MIC and HCl. The reaction products were then quenched with chloroform in a phosgene stripping still (PSS) to reduce the phosgene content according to specifications. The stripped product was then fed to a pyrolyser to separate MIC and HCl. The MIC was next fed to the MIC distillation still (MDS) to obtain commercial grade MIC (CG-MIC). The CG-MIC was stored in special stainless steel tanks — to be more precise, tanks 610 and 611 with a capacity of 45 tons each. The phosgene content of CG-MIC was about 0.07% and the chloroform content 0.3–0.5% as per the operations manual [1].

The basic layout of the various connections leading to and from the MIC tank are shown in Fig. 1 [1]. It was learnt that in May 1984 Union Carbide decided to change the pipelines. The process vent header (PVH) was interconnected to the relief valve vent header (RVVH) of the MIC tank leading to the vent gas scrubber. This was done to provide a route for the toxic gases to the scrubber, in order to neutralise them in the case of the repair of a defective vent header [1].

Physicochemical properties of MIC in relation to model formulation

Methyl isocyanate (MIC) is a reactive, toxic, volatile and flammable compound. Isocyanates ($R-N=C=O$) are, in general, reactive. They resemble aldehydes and ketones in their propensity to undergo addition reactions with a variety of compounds containing active hydrogen atoms. The cumulative effect

of the adjacent double bonds adds to the instability of the molecule, so that isocyanate addition reactions tend to be considerably more vigorous than similar reactions involving aldehydes or ketones.

MIC is an ester of isocyanic acid. It is produced industrially by the reaction of phosgene — the infamous deadly wartime gas — with a base called methylamine. As noted earlier, MIC reacts with many compounds. The reactions tend to be exothermic and vigorous. But from a practical standpoint, only a limited number of those reactions could conceivably have taken place at Bhopal, depending upon the presence of specific reactants during the episode. Some of these aspects are discussed by Singh and Ghosh [2].

Biological effects of isocyanates

One of the disturbing aspects of the chemical disaster at Bhopal is that scientists know relatively little about the toxic effects — especially the long term ones — of methyl isocyanate. Really good toxicological data of MIC are non-existent in the open literature.

The biological action of isocyanates can be well understood by two means: the general fumigant action of their vapours at the biophysical level and the more specific carbamylation action as isocyanates at the biochemical level. The low boiling and reactive MIC is an unbearable lachrymator, i.e. it causes irritation and burning of the eyes; when the gas is inhaled, it reacts vigorously with fluids in the lungs, with the formation of two gases, namely, methylamine and carbon dioxide. The latter two, being heavier than air, expel oxygen, choking the victim to death. However, it is very important to realise that MIC is rapidly hydrolysed by water to give methylamine and CO_2 . This, in a sense, is the compound's saving grace. Were it not for this reaction, the compound's reaction with biological material would have led to considerably more damage.

The few controlled experiments with human volunteers have been useful in setting occupational exposure limits. The American Conference of Governmental Industrial Hygienists (ACGIH) recommended that exposure to MIC in the work place be limited to 0.02 ppm averaged over an 8 h work shift. The so-called threshold limit value, or TLV, presently is the U.S. standard. By comparison, the TLV for phosgene is 0.1 ppm. The other two isocyanates of major commercial importance are TDI and MDI, and these have been studied far more extensively than MIC and so the toxicology and health effects of these compounds are also better known. Studies have shown that workers become sensitised to TDI and develop respiratory problems even when their average work place exposures do not exceed the federal standard of 0.02 ppm for an 8 h workday. Because of these findings, the U.S. exposure standard for TDI was lowered a few years ago to 0.005 ppm. The standard for MDI and MIC have not been reviewed and they remain at 0.02 ppm.

An important parameter to readily assess toxicity data is LD_{50} . LD_{50} is the

median lethal dose required to kill 50% of test population. In this context it is also necessary to specify the nature of the test population, the duration of the exposure and the exposure pathway (lung, skin, etc.), as well as the concentration. For MIC, the inhalation LD_{50} (for rats) = 5 ppm for 4 h. LD_{50} levels for phosgene are much more elaborately known. Toxicity data for various isocyanates and related compounds can be obtained from a number of sources [3-5].

For a long time isocyanates have been known to attack the respiratory system, eyes and skin. They can injure the lungs and bronchial airways and cause permanent eye damage. But until the Bhopal episode, the effects of MIC had never been observed on such a large and diverse population.

Most of the deaths have been attributed to various forms of respiratory distress. In some people, the gas caused such massive internal secretions that their lungs became clogged with fluid. In others, spasmodic constrictions of the bronchial tubes led to suffocation.

In the opinion of some scientists, however, it is debatable whether all these symptoms can be blamed on exposure to MIC alone. To add to the clinical confusion, it is worth noting that many of the victims are indigent and malnourished, and have suffered from tuberculosis and other ailments for a long time. If they had been healthier, the gas might not have affected them so severely.

The above paragraph serves to illustrate the fact that it is indeed very difficult to correlate concentration levels to casualties.

The value of the several clinical and laboratory studies will largely depend on building a database of high-quality epidemiological information. In pursuing this goal, researchers will need to answer at least three important and interconnected questions. These are:

- (i) Where were the victims when they were exposed to the gas?
- (ii) What dose did they encounter?
- (iii) What were the health effects?

The most difficult part of this investigation will be to estimate the concentration of MIC that individuals encountered.

There are two indirect ways to achieve the above goal. One way is by charting the degree of damage to sensitive trees and plants in different parts of the city. This will enable one to estimate the concentration of MIC. Several scientists from various organisations (mainly the Indian Agricultural Research Institute and Central Board for the Prevention and Control of Water Pollution) are, therefore, examining the trees and the foliage. The second way is far more straightforward and inexpensive. This is mainly concentration estimation through the use of atmospheric dispersion models.

On the fate of MIC in the environments

It is of vital importance to discuss the fate of MIC in the light of its chemical activity, in different environmental systems. In the environment, it is expected

to undergo degradation due to sunlight and to react chemically with atmospheric moisture. The major products of reaction will be methylamine (MA), di- and tri-methylurea and gases such as CO₂, CO, N₂, etc.

In soil and water, methylamine is the major product. It is held tenaciously by soil particles until decomposition is accomplished by weathering and biological reactions.

In plants, MIC could have competed with CO₂ in the process of photosynthesis. It could have been transformed into methylamine and other carbamylated derivatives of the plant constituents. The accidental release was so sudden that one really did not have a chance of measuring the concentration of the chemical in the air. MIC, and its thermally cracked products such as hydrogen cyanide are so highly reactive that there was practically no chance to prove its actual presence and amounts because it took almost 48 h before the investigation teams reached the scene on December 5 and 6. Most of the estimates are based on assessment of local factors. Even techniques and instruments to measure MIC were not available. The only available techniques were the determination of the presence of possible degradation products in air, water and soil. The presence of MIC can be indirectly detected by estimating methylamine (MA), di- and tri-methylurea (DMU and TMU) in air, water and soil.

It is clear that the presence of methylamine has a profound effect on the environmental system. It is, therefore, worth understanding the biological effects of methylamine. Michael L. Simenhoff (Jefferson Medical College, Thomas Jefferson University, Philadelphia) has suggested [6] that aliphatic amines are likely to participate in the complex metabolic derangements occurring in renal failure. In yet another study, he observed that in patients with kidney disease, clinical toxicity was demonstrated with methylamines by a correlation of abnormal neuro-behavioural parameters with serum amine levels and improvements were observed after administration of nonabsorbable antibiotics [6].

A brief description of the episode and the choice of meteorological variables

According to the factory authorities, the "Sevin" plant had been shut down since October 22, 1984, as sufficient "Sevin" was in stock. The 30 ton capacity refrigeration units serving MIC storage tanks 610 and 611 were shut down to save power. The tank 610 and 611 contained 41 tons and 43 tons of MIC, respectively. When the "Sevin" production was re-started, tank 610 could not be used, as sufficient pressure could not be obtained with nitrogen to effect the transfer [1].

The sequential steps leading to the accident are summarised below [1]:

December 2, 1984, 8.30 p.m.

Night-shift workers started washing the filter pressure safety valves of the lines located at ground level far from the storage tank. The washing with pressurised water was stopped at 9.30 p.m. and resumed, connecting the pipeline to a water hose, at 10.30 p.m. by persons on the second shift. At 10.55 p.m., the pressure rose to 10 psig.

December 2-3, 1984, 12.15 a.m.

Pressure rose to 12 psig; immediately, the plant supervisor was summoned by the shift in-charge, but before he could reach the location, the pressure gauge reached 55 psig, the top of the scale.

December 3, 1984, 1.00 a.m.

Employees noticed MIC vapours and activated the alarm; messages were sent to police, fire brigade and Works Manager.

1.45 a.m.

The Works Manager arrived and gave instructions for taking safety and precautionary measures. By this time the MIC discharge had stopped and the air in the plant area was clear. Later on, tank 610 was found to contain about 1 ton of polymerised MIC as a solid trimerised residue.

There were about 100 workers in and around the factory at that time and, except for one, they were not affected. The condition of the one affected was not fatal.

Investigation by others not associated with U.C. have [1] revealed the following additional information:

- (i) The PVH pipeline was not blinded to isolate it from the storage tank before washing was started.
- (ii) The operator tried to start the scrubber, the moment he saw the high pressure on the gauge, but the NaOH solution pump motor did not work. When it eventually started, the NaOH solution was not capable of neutralising the large amount of the gas.
- (iii) The scrubber was not designed to handle massive discharges of MIC.
- (iv) The vent pipe connecting the scrubber outlet to the flare was removed for the replacement of a corroded section by a new one. Thus, the flare was disconnected and the pilot flame was shut off. Consequently, one can assume that the entire discharge was released at almost 33 m from the ground level, through the scrubber outlet.
- (v) The alarm was activated at least 20 to 30 min after the gas had started leaking, and the people could have had little chance to run for safety, since a gas cloud had already enveloped them.

- (vi) The tank 610 contained polymerised MIC (trimerisation) residue of about 4.5 tons with some di-methyl urea and tri-methyl biurates. It is also likely that MIC was partially cracked at high temperature to form HCN, CO and N₂, or CO₂, but by how much exactly is uncertain.

There are basically two lines of thought attributed to the probable cause of the accident [1].

The first is the U.C. report (from Union Carbide Company Institute, West Virginia, U.S.A. by a seven member team led by Mr. Ronald Van Mynen) which is based on about 500 computer simulations to replicate the analysis of the residue samples. The report concluded that "the chemistry (described by simulation studies) indicates that the large amount of water and higher than normal levels of chloroform (1.5–3%) was necessary to obtain the particular mix of residue components found in the sample. The large amount of water was necessary to generate the heat needed to initiate and accelerate subsequent reactions.

As the temperature in tank 610 increased due to the exothermic reaction of MIC with water, the corrosion of the tank increased markedly because of the abnormally high level of chloroform. The iron thus produced, catalysed the concurrent exothermic trimerisation of MIC So the pressure and temperature increased rapidly, the rupture disc in the line to the safety valve burst, and the safety valve opened at 40 psi..."

In contrast, the second version, propounded by some Indian investigators [1], states that the water which entered tank 610 came from both the process vent headers (PVH). The two headers were heavily corroded and gave off rust particles in water, with a sufficient amount of iron to initiate trimerisation of the MIC which produced enormous heat and pressure. For this to occur only 1 or 2 l water from a leaking valve would be enough. It is well known that MIC can trimerise rapidly in the presence of anions, such as chlorides, or when it is catalysed by metallic ions of iron, nickel, zinc, etc. The main point is that phosgene reacts violently with water, forming HCl. This HCl will then be hydrolysed by water, releasing chloride ions. Also, the HCl can react with metals of the tank releasing sufficient ions of iron, nickel etc., which can catalyse and trigger exothermic polymerisation reactions.

The main differences between the U.C. and Indian interpretations [1] concern the start of the reaction; U.C. claims the reaction was initiated entirely by an internal reaction between MIC and a large quantity of water, while the Indian opinion is based on the assumption that a small quantity of water reacted with phosgene and/or dissolved iron and rust to initiate the reaction [1].

With the above discussions in our perspective, we are in a better position to visualise the actual scenario.

The count down to the Bhopal disaster started around 12.30 a.m. in the early hours of December 3, 1984, when untreated MIC vapour was seen escaping

through the nozzle of the 33 m high atmospheric vent-line out into Bhopal's cool atmosphere.

In this paper we do not intend to elaborate upon the conditions which conspired together to cause the tragedy rather, we will emphasise how best we can model the dispersion of the gas.

Reports indicate that about 40 tons of MIC escaped into the atmosphere in about 90 min. The meteorological variables such as the wind speed and direction and the vertical temperature structure at the site on the day of the episode were, of course, not available. Therefore, we had to depend on mean climatological data for Bhopal. We have adopted a wind speed value of 2.92 m s^{-1} at 10 m height. By charting the extent of the affected regions and also from climatological data it was confirmed that the wind direction changed quite swiftly, while MIC was leaking out from the U.C. plant. In this context it must be borne in mind that the affected regions in Bhopal are surrounded by smooth surfaces such as lakes and gently rolling terrain as well as undulations due to the presence of hillocks, and therefore, the fact that the wind that night could change its course quite swiftly is not unusual.

We quote below some of the observed records on the wind speed and direction [1]:

Wind speed: (Site: Bhopal Airport):

	Wind speed (km h^{-1})
December 2, 22.00 h } to	10.5
December 3, 06.30 h } December 3, 09.00 h	10
10.00 h	11
11.00 h	10.5
12.00 h	10

Based on the above observations on the wind speed, it is reasonable to adopt a value of 10.5 km h^{-1} for our model.

Wind direction

December 2, 22.00 h	90°N
24.00 h	50°N
December 3, 01.30 h	110°N
02.00 h	50°N
03.00 h	50°N
04.00 h	50°N
05.00 h	50°N

The above wind direction records, which may not be tenable at the site due to the typical topographic feature of the city, were made at Bhopal airport located at about 7 km due west of the plant beyond a hillock. We observe that these records do not indicate any north westerly wind. According to media reports, including that of Eklavya [7], a private non-profit organisation based in Bhopal, the wind that night was initially north westerly. Some wind observations were also made subsequently at the Agricultural Research Institute, located much closer due north to the actual site on relatively flat terrain. As an illustration, we quote below, the wind direction record for December 15, 1984, which indicates: N-W wind at 1.00 a.m.

Wind direction

December 15, 01.00 h	320°N
02.00 h	150°N
03.00 h	0°N
04.00 h	0°N
05.00 h	140°N

In the absence of on-site wind records, the best we could do was to study and chart the course of the wind by personal interviews and on observations on the scorched plants.

In view of the above facts, we adopted the following wind directions apportioned appropriately for the entire duration of the episode:

- (i) a wind from 285° for 45 min
- (ii) a wind from 340° for 30 min
- (iii) a wind from 45° for 15 min

This scheme gave a fairly realistic simulation of the GLC in relation to actual observations on the affected population and on the distribution of the affected vegetation.

Finally, we limited our upper boundary to 200 m, a fairly reasonable estimate for the mixing height for a December night in the Indo-Gangetic plain [8].

Model formulation

Prior to model formulation we must take into account the following facts, which are of immediate significance:

- (i) The density of MIC is about twice that of air.
- (ii) The velocity of ejection of the gas is of the order of 88 m s^{-1} , which is very large compared with the ambient wind speed at the stack height. Thus there is enough scope for a lot of entrainment and mixing. Based on the calculations outlined by Ooms and Duijm [9] (eqns. 52 and 53), the downwind distance to touch-down point is beyond a kilometer.

- (iii) Exothermicity of the MIC–moisture reactions suggests that a lot of heat that is generated in the process reduces the density of the plume further — though by how much we are still uncertain.
- (iv) The episode occurred under stable night-time conditions, which suggests a stability class F or G, and if we consider the plume to be neutral or passive, the vertical spread σ_z at 1 km is about 15 m, which implies that the maximum ground level concentration should occur between 1 and 2 km downwind.
- (v) By assuming the cloud depth h to be of the order of 10 m and the ambient wind speed u of the order of 4 m s^{-1} (estimated by power law profile at stack height), we can calculate the settling speed by estimating $[(\Delta\rho/\rho)/gh]^{1/2}$. This is also comparable to u_* , the friction velocity, both being of the order of 0.1 m s^{-1} , which implies that the plume in question is a borderline case between one having density effects and one which is a passive plume. This would mean that the maximum ground level concentration should occur at a place closer than 1–2 km downwind.
- (vi) Observations on the scorched plants indicate that ground effects of MIC were observed at about 400–500 m downwind.

On the basis of the above mentioned considerations, we deduce the following:

- (i) A purely passive plume in typical night conditions does not describe all the phenomena in question correctly.
- (ii) We assume that the vertical spreading is dominated by two factors; the first factor is the usual spreading due to passive diffusion, and the second factor corresponds to the spreading due to gravitation settling effects. This would mean a much larger σ_z . A typical value should be about 20 m at about 400 m downwind. This value of σ_z gives GLC estimates consistent with observations and we found that Briggs Urban Curves [10] for stable conditions (E–F) are suitable.
- (iii) The properties of miscibility and volatility, together with the adiabatic entrainment possibly led to a rapid initial dilution.

With the above considerations in our perspective we shall formulate our model. Our model necessarily cannot be steady state because we must consider time-dependent emissions; however, as with the Gaussian model, we will require the assumption of spatial homogeneity and flat terrain. It is also very important to consider material removal by chemical reaction with atmospheric moisture and also dry deposition. We will incorporate both these effects appropriately.

We consider the unsteady form of the usual atmospheric advection–diffusion equation:

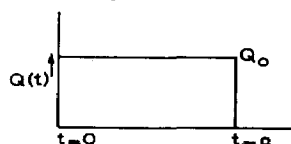
$$D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial x} - \frac{\partial c}{\partial t} = 0 \quad (1)$$

where c is the pollutant concentration at (x, y, z, t) and u is the constant average

wind speed along the downwind x direction and D_y and D_z are the eddy diffusivities in the crosswind and vertical directions, respectively. This equation strictly applies to level terrain. Since the major impact of the gas leak was felt over, more or less, smooth and even terrain, this assumption seems to be tenable. At this stage we wish to point out that we have taken u , D_y and D_z to be constant so that we are able to obtain an analytic solution. One of our aims in this presentation is to illustrate the use of simple analytic results to study the dispersion in lieu of complicated and expensive numerical models. However, we have tried to incorporate many important physical processes so that our model gives realistic simulations. The source condition is described as:

$$c(0, y, z, t) = \frac{Q(t)}{u} \delta(z-h) \delta(y) \quad (2a)$$

where $Q(t)$ is the step function shown below:



Q_0 = Source strength (40 tons in 90 min)
 a = Duration of emission (90 min)
 h = Effective stack height (39.6 m)

In eqn. (2a), which represents the limiting form of the mass continuity equation, δ is the dirac delta function. The step function is appropriate for steady emissions. However, if the emission first increases and then decreases, then $Q(t)$ can be described by a triangular function. Likewise if the emission first increases, then remains steady and eventually decreases, then $Q(t)$ can be appropriately described by a trapezoidal function. The solution corresponding to these situations can be obtained in a straightforward manner on the basis of the following analysis. The initial condition is given by

$$c(x, y, z, 0) = 0 \quad (\text{no emission at } t=0) \quad (2b)$$

and the boundary conditions are

$$D_z \frac{\partial c}{\partial z} = 0 \text{ at } z=0, H \quad (2c)$$

where H is the mixing height (200 m). (No flux of pollutants at the lower and upper boundaries.)

$$c(x, \pm \infty, z, t) = 0 \quad (2d)$$

(Negligible concentrations far away in the lateral direction.)

Before we attempt to formally solve the above equation by use of the initial and boundary conditions, we wish to consider material depletion by chemical and dry deposition effects. This is given below:

(a) *Parameterisation of chemical removal term*

It is important to consider material depletion by chemical removal and, owing to the presence of a large amount of moisture, it is appropriate to parameterise this term as a first order irreversible process. Hence this term can be described by including a removal term $-K_L C$ in the governing differential eqn. (1). Climatological records indicate a relative humidity of 50% for a December night.

For a more accurate prescription of the chemical removal term, detailed chemical kinetic data for the complete reaction pathway for aqueous phase reaction of MIC should be used. This approach would lead to nonlinear terms in the advection-diffusion equation, and would require numerical methods for the solution. We intend to model this aspect in a subsequent paper when we have more information on the chemical kinetic data for MIC reactions. For the present study we adopt an approximate method for estimating the reaction term which is consistent with the level of sophistication involved in this simple model.

A convenient means of examining the mass-transport aspects in a given situation of interest is evaluation and comparison of the characteristic times of the various processes. Such a procedure allows it to be ascertained readily, whether the aqueous phase reaction is sufficiently slow or fast. Following Schwartz [11], the characteristic time describing diffusive mass transport for reactions occurring in spherical droplets is given by: $\tau = D^2 / (4\pi^2 \cdot D_{aq})$, where D_{aq} is the aqueous phase diffusion coefficient and D the drop diameter. This characteristic time describes the rate of depletion of the dissolved substances by aqueous phase reaction. For a species undergoing irreversible first order reaction, the reaction rate k_L is easily obtained from the relation $k_L = \tau^{-1}$.

It is known from spectroscopic studies that atmospheric moisture particles typically have diameters of the order of 1–10 μm [12].

We have computed D_{aq} from the relation [13]

$$D_{aq} = \frac{7.4 \times 10^{-8} (\chi M)^{1/2} T}{\mu V_1^{0.6}} \text{ cm}^2 \text{ s}^{-1}$$

where M = molecular weight of water (18), μ = viscosity of water in centipoises (1.326 at 12°C), χ = association parameter of water (2.6), T = temperature in K, V_1 = molal volume of solute in $\text{cm}^3 \text{ g}^{-1}$ CMIC at normal boiling point).

To calculate V_1 for MIC, we adopted the standard procedure outlined in chemical engineering texts [14], where each element and certain bond linkages are assigned numerical values so that the molal volume at the normal b.p. may be calculated by the addition of these values. In this way, we obtained V_1 as 63.73 $\text{cm}^3/\text{g mole}$.

$$D_{aq} \sim 0.98 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$\tau \sim \frac{D^2}{4\pi^2 D_{\text{aq}}} \sim \frac{n^2 \times 10^{-8}}{4\pi^2 \times 0.98 \times 10^{-5}} \sim 2.6 \times 10^{-5} n^2 \text{ s}$$

where n is a value between 1 and 10 corresponding to D values ranging from 1 (i.e. to $10 \mu\text{m}$ (i.e. $D = 10^{-4} n \text{ cm s}$). The characteristic time estimated above pertains to mass transport and reaction in and about a single drop. Thus the reaction rate also pertains to a single drop. This is of course very different from the macroscopic reaction rate per unit physical volume, which corresponds to the term ' K_L ' in our governing differential equation. As a first approximation (and an upper limit) the reaction rate per unit physical volume is evaluated as the aqueous-phase rate times the liquid water volume fraction.

In our calculation we have taken the liquid water volume fraction, to be as $0.17 \text{ cm}^3/\text{m}^{-3}$ [11]. Thus

$$K_L \sim \frac{0.17 \times 10^{-6}}{2.6 \times 10^{-5} n^2} \sim \frac{0.0065}{n^2} \text{ s}^{-1}$$

Computations shown in Table 1 correspond to $K_L = 7.265 \times 10^{-4} \text{ s}^{-1}$ for $n = 3$.

(b) Parameterisation of dry deposition removal term

The chemical reaction term and dry deposition are interlinked and both can be conveniently parameterised as rates applied to the local concentration. We have also discussed the relative importance of this affect. We can assess the importance of the dry deposition term by comparing the ratio of V_d/d (where d is the depth of the layer of the gas) to the chemical removal rate K_L . Nocturnal values of the deposition velocity V_d might be expected to lie in the range $2\text{--}4 \text{ cm s}^{-1}$ and the depth of the layer of gas could be of the order of 30 m [15]. Taking $V_d \sim 2 \text{ cm s}^{-1}$ and $d \sim 30 \text{ m}$, we get the rate of removal of material due to dry deposition effects as 0.00067 s^{-1} , which is comparable to the chemical removal rate K_L . Accordingly, both these effects have been incorporated in our formulation.

(c) Solution

Having discussed the removal terms (chemical removal and dry deposition), we can reformulate our governing equation in the following form:

$$D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial x} - RC - \frac{\partial c}{\partial t} = 0 \quad (3)$$

where $R = K_L + V_d/d$ represents the total removal rate.

Equation (3) is solved by the method of integral transforms (Finite Fourier Cosine Transform w.r.t. ' z ', Laplace transform w.r.t. " t " and " x ", Fourier transform w.r.t. ' y ') subject to the initial condition (2a) and the boundary conditions (2b–2d).

TABLE 1

Model simulation results

Sites	GLC (ppm)	Vertically integrated concentrations (loading effects) (g m ⁻² s ⁻¹)	Time of affliction (min)
1	85.6	36.6	1.16
2	69.1	19.27	1.55
3	57.4	14.7	1.55
4	25.9	5.3	3.88
5	18.5	3.2	5.44
6	15.5	3.5	5.83
7	8.0	2.06	8.55
8	3.4	1.2	10.87
9	2.5	0.8	13.69
10	8.2	1.0	49.66
11	8.6	0.94	50.44
12	0.124	0.4	51.6
13	0.2	0.17	57.4
14	1.71	1.0	57.4
15	0.87	0.19	58.6
16	0.97	0.45	60.15
17	0.4	0.196	61.3
18	1.0	0.38	61.7
19	0.268	0.15	61.7
20	0.59	0.27	63.6
21	0.25	0.1	63.6
22	1.82	0.09	78.9
23	1.75	0.58	80.8
24	0.65	0.17	82.8
25	0.65	0.17	82.8
26	7.0	1.36	85.2
27	2.75	0.6	88.3

The solution obtained is given by:

$$c(x,y,z,t) = \frac{Q_0 e^{-\frac{y^2 u}{4D_y x}} e^{-Rx/u}}{H \sqrt{4\pi D_y x u}} F(t) \left[1 + 2 \sum_{n=1}^{\infty} \cos \frac{n\pi z}{H} \cos \frac{n\pi h}{H} e^{-D_z \frac{n^2 \pi^2 x}{H^2 u}} \right] \quad (4a)$$

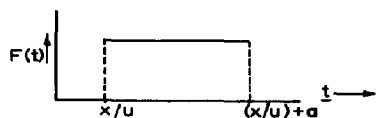
In order to facilitate practical application of eqn. (4a), we rewrite it in terms of the spreads σ_y and σ_z in the lateral and vertical directions:

$$\sigma_y^2 = 2 D_y x/u; \quad \sigma_z^2 = 2 D_z x/u$$

Thus we obtain:

$$c(x,y,z,t) = \frac{Q_0 e^{-y^2/2\sigma_y^2} e^{-Rz/u}}{\sqrt{2\pi} \sigma_y u H} F(t) \left[1 + 2 \sum_{n=1}^{\infty} \cos \frac{n\pi z}{H} \cos \frac{n\pi h}{H} e^{-\frac{\sigma_z^2 n^2 \pi^2}{2H^2}} \right] \quad (4b)$$

$F(t)$ is the 'pulse function' shown below:



α = duration of the episode

(d) Model evaluation

A computer programme was developed and run on the ICL 2960 system available at I.I.T. Delhi. The wind speed at the effective stack height was calculated from the power law profile

$$u = u_{10} \left(\frac{z}{10} \right)^P \quad (5)$$

where z is the vertical distance above the ground in metres and u_{10} is the wind speed at 10 m height. For the stable night time conditions we take P as 0.35 [16].

The spread σ_y , σ_z for urban conditions under the stability class E-F have been taken as [10]:

$$\sigma_y(x) = 0.11x(1 + 0.0004x)^{-1/2}$$

$$\sigma_z(x) = 0.08x(1 + 0.00015x)^{-1/2}$$

It was estimated that the exit velocity of the gas was of the order of 88 m s^{-1} and that the stack's inside diameter was 8" (0.2 m). It was reported that the stack gas temperature was of the order of 50°C and the ambient temperature about 17.5°C [1]. Simple plume rise calculations using Holland's equation [17] indicated a rise of about 6.6 m under stable conditions. Thus the effective stack height h was estimated to be about 39.6 m.

Correlation of model results with actual observations

It is clear that the wind during the period of the episode changed its course quite swiftly. It is observed that the superimposed GLC distribution shown in Table 1 seems to correlate very well with the extent of affliction at the specific sites. The section devoted to the biological effects of isocyanates extensively describes dose-effect relations and the recommended TLV for MIC exposure. In the discussions that will follow, we will keep the contents of that section in our perspective to state our observations.

In column 2 of Table 1 we have shown the GLCs at various locations. We

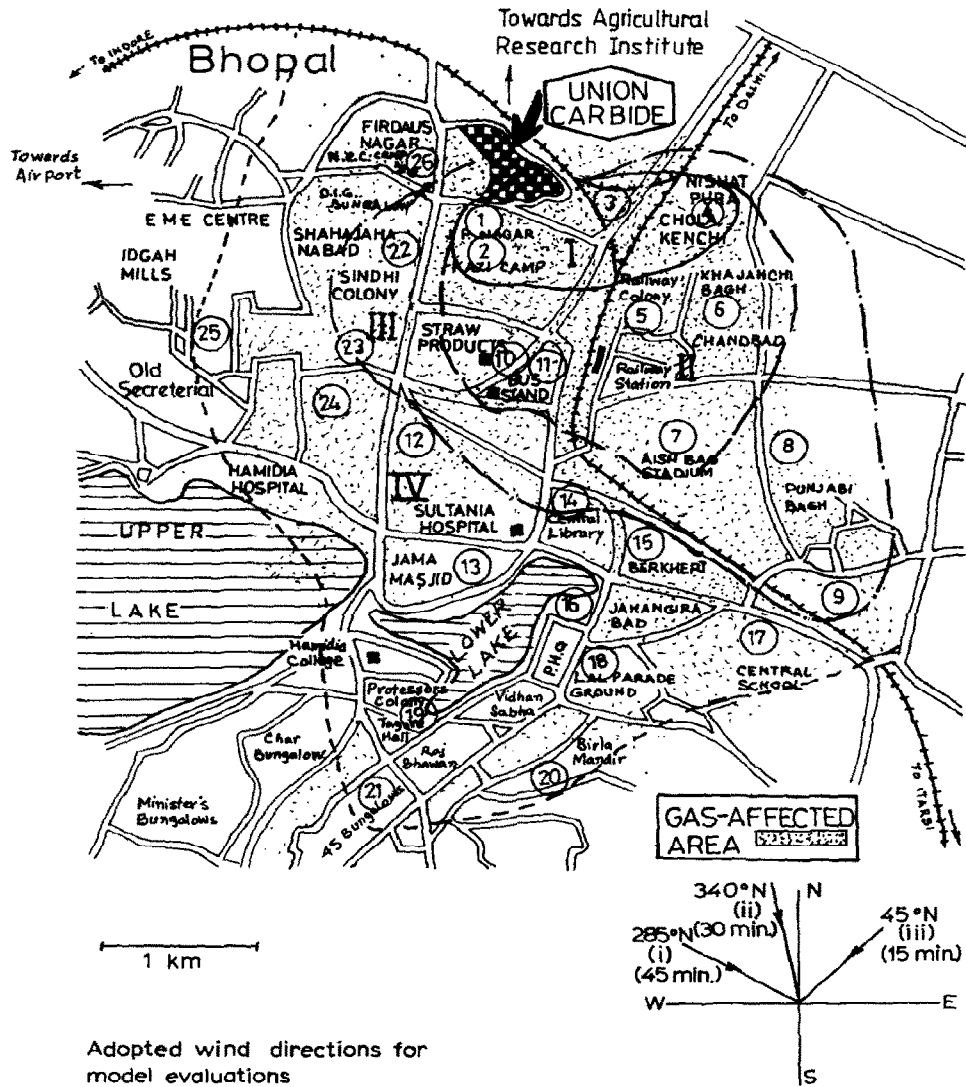


Fig. 2. Concentration contours based on model simulation.

find that areas such as J.P. Nagar, Kazi Camp, Chola Kenchi, Nisat Pura, Railway Colony and Khajanchi Bagh (Marked, 1,2,3,4,5 and 6 in Fig. 2) are the worst affected localities. At these places, lethal or dangerously high levels of MIC prevailed. In Fig. 2, we have drawn concentration contours demarcat-

TABLE 2

Correlation of model results with mortality statistics

Zones	Main areas included	GLC (ppm)	Area (km ²)	Mortality ^a statistics [1]	Mortality per km ²
I—Severely affected	J.P. Nagar, Chola, Kazicamp, Nisat Pura.	Exceeds 25 ppm	1.33	1265	951.1
II—Very badly affected	Khajanchi Bagh Chandbad, Railway colony, Straw products, Bus stand, Aish Bagh stadium.	Between 8–19 ppm	1.95	767	393.3
III—Moderately affected	Punjabi Bagh, Shah Jahanabad, Sindhi Colony.	Between 1.5–4 ppm	4.6	270	58.7
IV—Mildly affected	Firdous Nagar, Jama Masjid, Professor's Colony, Central Library, Central School, Lal Parade ground, Berkhari, Birla Mandir etc.	Lower than 1 ppm	7.5	108 2,410 + 166 deaths outside the area Total = 2,576.	14.4

^aThese figures were collected by personal contacts and many include deaths due to other causes as well.

ing various zones of the affected areas, and in Table 2 we have appended the zone-wise mortality statistics.

It is clear that, within zone I, extremely high concentrations of the gas prevailed. Model results indicate that here the GLCs were greater than 25 ppm, as against 0.02 ppm, which is the THV for MIC. The worst affected areas are J.P. Nagar and the Chola Area.

Zone II is also a very badly affected zone. Here the GLCs are above 8 ppm, which is about 400 times the TLV. Widespread casualties were reported in localities within this zone too. We feel that concentration levels several hundred times the TLV must be the dose required to kill human beings. From Table 2 we find that about 79% of the recorded casualties were within zone I and II; the percentage is likely to increase further if we include deaths reported from slums like Garib Nagar, Kalimbai Bagh, Silawat Pura, Dwarka Nagar, etc., which are not depicted in the map but are located within zones I and II. On the basis of these observations, we feel that zones I and II stand apart as the worst affected zones.

We have tried to estimate the quantity of MIC passing over a point and deposited over many points downwind by a process of vertical integration. These vertically integrated results are shown in column 3 of Table 1. MIC molecules are heavier than air, and the chemical nature of this gas indicates that the gas is sufficiently reactive to be characterised by a short atmospheric residence time; possibly MIC vapours are very much akin to NO_x , with the residence time of the order of few hours. This is, in a way, the compound's saving grace; otherwise the devastating effects would have been worse.

As such it is very likely that MIC had settled down on the ground within a couple of hours. These vertically integrated results can be used subsequently for corroborating the findings of the agricultural scientists, who are concerned with the study of the effect of MIC loading on soil and vegetation.

In the worst affected areas (sites 1–6) the vertically integrated concentrations range from $39.8 \text{ g m}^{-2} \text{ s}^{-1}$ at J.P. Nagar to $3.2 \text{ g m}^{-2} \text{ s}^{-1}$ at Railway Colony, which apparently are very high to account for such a large number of casualties. J.P. Nagar, where the maximum casualties occurred, is located just opposite the U.C. premises, barely 200–300 m from the stack. This colony consists mainly of hutments and shanties. According to local residents, the colony was engulfed with copious dense white fumes and visibility was very poor. The major medical symptoms were severe eye irritation, coughing, vomiting and excruciating chest pain. In this area and generally in zone I, the degree of severity of affliction increased with the passage of time, resulting in a large number of casualties by the time the smoky pall lifted at about 5.30 a.m.

At places like Firdous Nagar, Shahajahanabad, Sindhi Colony, Straw Products, Bus Stand, Aish Bagh Stadium and Punjabi Bagh (marked 26, 22, 23, 10, 11, 7, 8), the GLCs are comparatively much lower. All these localities also fall within zone III, which we demarcate as the "zone of moderate effects". Here perceptible deleterious effects were observed. People experienced severe eye irritation. However, as is evident from Table 2, the casualty figures were less than those in zones I and II. The vertically integrated concentrations in zone III are also comparatively lower.

At places like Jama Masjid, Professors Colony, Birla Mandir, Jahangirabad, Central School and Lal Parade Ground (sites 13, 19, 20, 16, 17, 18), the GLC levels are substantially lower. In fact, the GLC at all these sites, which are located in zone IV, are less than 1 ppm. We designate zone IV as the "zone of marginal effects". Personal interviews with the residents also indicated that indeed the effect was marginal at these places. For instance, people in Professor's Colony reported that at that location no traces of the fumes were visible. Some residents merely complained of slight eye and throat irritation; the GLC level at Professor's Colony is of the order of 0.3 ppm. Likewise, Jama Masjid was the place where many people took shelter and the corresponding GLC level is of the order of 0.2 ppm. It is interesting to note that the DIG Bungalow and the adjoining NCC Camp, though situated quite close to the plant, were affected very marginally. This fact clearly indicates that these buildings were in

a comparatively safer zone even when the plume changed its path. The NCC cadets and officials were therefore able to undertake relief work during the episode.

The last column of Table 1 represents the time at which the plume front arrived at the various sites. It is clear that J.P. Nagar, Kazi Camp, Chola Kenchi, Nishat Pura, Railway Colony, Khajanchi Bagh, and Chandbad were affected within 6 min of the episode. In general, the approximate time of affliction at the various sites seems to correlate very well with the reports obtained from interviews. For instance, within zones I and II the effects of the disastrous leak were perceived by the residents of these areas within a few minutes of the leak. Model computation indicates that these areas were affected within 6 min of the leak. Likewise, our model computation also suggests that Firdous Nagar was affected in about 85 min after the leak began, which is corroborated by the residents of this region, who experienced the tell-tale symptoms of MIC exposure at about 2 a.m.

While continuing our discussions of the fatality statistics we would like to point out that there were reports of population movement while the gas was sweeping over the city. Hence, there is an inherent subjectivity involved in this correlation study. However, the majority of the people who died were slum dwellers and socially deprived people, who could not afford to own a vehicle. These people died at locations close to their normal place of residence. However, a very important and startlingly clear fact is that the effect of the gas faded with increasing downwind distance. Among other reasons, one important physical basis from which to explain this trend is that MIC gas is characterised by a low residence time of the order of a few hours. Had the residence time been longer, the gas would have hung over the affected regions for a much longer time and would have dispersed over a much larger distance from the plant.

So far, we have been trying to correlate our model computation results with observation on records of fatalities and the observed effects of the gas on human beings only. Our study on model correlation would not be complete with-

TABLE 3

Extent of affliction	Deaths [1]	Area km ²	Deaths/km ²
Severe	1265	1.33	951.1
Bad	767 ^a	1.95	393.3
Moderate	270 ^a	4.6	58.7
Mild	108 ^a	7.5	14.4
	<u>2410</u>		
Deaths outside the area	166 ^a		
	<u>2576</u>		

^aThese figures were collected from the area by personal contacts, and may include deaths due to other causes as well.

out some discussion of the observed effects of the gas on vegetation and trees, situated in various parts of the city. By charting the degree of damage to sensitive trees and plants in different parts of the city, we can get an idea of the chemical's concentration. Several scientists from various organisations (mainly the Indian Agricultural Research Institute and the Central Board for the Prevention and Control of Water Pollution, New Delhi) have examined these trees and foliage. We discuss these aspects in the last section. Vegetation was mostly affected in the eastern, south-eastern and southern directions with regard to the factory. The concentration contours depicted in Fig. 2 indicate that plants and vegetation located within zone I, II and III could indeed have been affected by the spreading gas, with concentrations ranging from very high to moderate values. The concentration contours for zones I, II and III are also tilted towards the SE direction.

Bhopal disaster and its aftermath

(a) Effects on humans

The catastrophic release of the toxic cloud of MIC caught all the residents unawares, since most of them were sleeping. The death toll after 10 h was reported to be about 460; in the next 24 h it rose to 700, and in 5 days to 2500. Some deaths were reported after about another four weeks.

Most of the victims were slum dwellers living in J.P. Nagar, Chola Kenchi, etc. They were caught in their sleep in dwellings without any proper doors and windows. Children, adults and old people seemed to have been equally affected. Those caught in the open air, on night duty out doors, were worst affected. Most of the rail road staff, porters, etc. on duty at Bhopal station (total number about 126) were found dead at 2.45 a.m. The survivors were in a critical condition and another 16 died within the next 8 h. The number of cases with severe eye damage is estimated to be about 1200. The number of persons exposed to MIC is estimated to be about 150,000 to 200,000, out of a population of 800,000 [1].

The zone of affected areas, classified on the basis of occurrence of death, are summarised in Table 3.

Deaths registered by hospitals came to 516 only; the rest were based on counts of bodies collected and cremated by voluntary organisations. The total number of deaths reported by local bodies, as well as other voluntary organisations in Bhopal, was 883. Initially, the patients were treated without any guidance or knowledge of an antidote for MIC or its products. Thus, crucial immediate medical help was not available to many until it was too late, resulting in high mortality. However, only symptomatic treatment was given to prevent secondary infection and to ease pain (antibiotics, barbiturates, antihistamines, etc.), with limited use of oxygen, which was a scarce commodity [1].

Most of the toxicological and pathological investigations on MIC victims

were initially a blind search. Nearly 36 h later, when the first autopsy reports were available, understanding of the toxicological factors became clearer. Three hundred post mortem examinations were performed. The most striking changes were seen in the lungs and respiratory tracts. The lung weights were two to three times higher than normal and the lungs had a striking reddish colour. The respiratory tracts showed tracheitis, bronchitis, pulmonary edema and bronchopneumatic conditions. Most fatalities were probably due to pulmonary edema. Few cases showed damage to kidney, liver and brain (mostly cerebral edema). Some cases also showed evidence of sub-arachnoid, intraventricular and/or cortical haemorrhage. Cases of fatty degenerative changes in the liver and renal tubular damage were also noticed, possibly as secondary changes. Tissue anoxia was found in almost all cases, and in a large number of cases of tissue damage cyanide poisoning was found [1].

Amongst the 150,000 other affected people the main damage was to the lungs. The other most common complaints were [1]:

— eye irritation, watering and inflammation	: 99%
— dyspnea (breathlessness)	: 95%
— persistent dry cough	: 97%
— throat irritation	: 66%
— chest pain	: 68%
— vomiting	: 42%
— muscular weakness	: 22%

Eye damage of a serious nature was recorded in 1025 persons, but it is expected that most of them will recover fully except for a few with severe damage to the cornea, which may affect vision later [1].

(b) Effects on animals

The animal death toll due to MIC was equally large, numbering 1087: 240 cows, 280 buffaloes, 18 bullocks, 84 calves, 288 goats, 60 pigs, 12 horses, 99 dogs, 2 cats and 3 chickens were counted dead. Another 7334 animals were reported to be affected to various degrees. They were treated with the same drugs as humans. Autopsies of animals showed swollen livers and lymph glands, bloated digestive tracts, enlarged blood vessels or edema. Necrosis was also observed in lungs, with clots of blood; heart and kidney were found to be congested. An ICAR report also mentions the presence of a high nitrogen content in the blood of dead animals [1].

(c) Effects on vegetation

All broad-leaved trees suffered maximum damage. The worst affected were the 'Neem' (*Azadirachta indica*) and Peepal (*Ficus religiosa*), which showed total defoliation within 1 km of the plant. Other trees less affected were 'Karanj' (*Pongamia pinnata*), 'Chora Neem' (*Alianthus excelsa*) and to a lesser degree plants with thicker leaves. The damage to shrubs followed the same pattern. It was observed that small stems suffered least when they were located close to the water surface of lakes or ponds, even in high levels of exposure

zones. This clearly demonstrates the affinity of MIC to water. The damage to the trees was entirely by reaction with the leaf surface; stems or other hardy parts were not affected. The plant damage appeared to be entirely due to MIC and not due to cyanide, as was proved by laboratory tests. The damage seemed to be due to reaction of cellular water with MIC, which killed the cells of the leaves [1].

(d) Effects on soil

A survey of soil damage was done by evaluating chemical properties, bacterial and fungal counts and nematode populations. The pH of the soil was found to be in the range 7.9–8.6; the organic carbon content was 0.5–3.3; the total nitrogen content 0.3–0.6% with a C/N ratio of 1–5.27. There was no distinct trait whatsoever and it was not possible to arrive at any conclusion with respect to soil damage [1].

References

- 1 J.M. Dave, Proc. International Symposium on Highly Toxic Chemicals: Detection and Protection Methods, September 25–27, 1985, University of Saskatoon.
- 2 M.P. Singh and S. Ghosh, Perspectives in air pollution modelling with special reference to the Bhopal gas tragedy, CAS. Tech. Report IIT, New Delhi, 1985.
- 3 H.E. Bristenson, Toxic Substances List, U.S. Dept. of Health, Education and Family Welfare, Public Health Services, Centre for Disease Control, National Inst. for Occupational Safety and Health, U.S.A., 1974.
- 4 W.F. ten Berge, The toxicity of methyl isocyanates for rats, *J. Hazardous Materials*, 12 (1985) 309–311.
- 5 N.I. Sax, *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold, New York, 1979.
- 6 C. Deva Kumar and S.K. Mukherjee, Methylisocyanate: profile of a killer gas, *Sci. Today*, January (1985).
- 7 Eklavya, Bhopal — A reconstruction of the gas tragedy, its background and aftermath, from press reports and local information, Eklavya, EI/208, Arera Colony, Bhopal, 1985.
- 8 Manju Kumari, Diurnal variation of mean mixing depths in different months at Delhi, *Mausam*, 36 (1985) 71–74.
- 9 G. Ooms and N.J. Duijm, Dispersion of a stack plume heavier than air, IUTAM Symposium, Delft, Springer-Verlag, Berlin, 1983.
- 10 G.A. Briggs, Diffusion estimation for small emissions, ATDL Contribution File No. 79, ATDL, NOAA, U.S.A., 1973.
- 11 S.E. Schwartz, In: J.I. Teasley (Ed.), *Acid Precipitation Series*, Vol. 3, Butterworths, Stoneham, MA, 1984.
- 12 J.L. Durham, In: J.I. Teasley (Ed.), *Acid Precipitation Series*, Vol. 2, Butterworths, Stoneham, MA, 1984.
- 13 R.G. Reid and T.K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1958.
- 14 J.H. Perry, *Chemical Engineer's Handbook*, McGraw-Hill, New York, 1950.
- 15 B. Hicks, Personal communication, 1985.
- 16 J.S. Irwin, A theoretical variation of the wind profile power law exponent as a function of surface roughness and stability. Technical note, *Atmos. Env.* 13 (1979) 191–194.
- 17 J.Z. Holland, AEC Rep. CRC-99, Washington, DC, 1953, pp. 584.