

Chapter 5

Development of Source Emission Models in COWZ

5.1 Introduction

The past three decades have witnessed the development of increasingly sophisticated mathematical models for describing outdoor and indoor air quality. This was in response to the recognition that both outdoor and indoor air pollutant concentrations contribute to health risk for most people. For example, in 1980 the US EPA began developing the National Exposure Model (NEM) (Johnson and Paul, 1982), which addressed both indoor and outdoor exposures. More recently, concern for reducing environmental risks has focused on the need to consider the total exposure of a population – indoors and outdoors.

Indoor exposure estimates used in models such as NEM are limited to global estimates of indoor – outdoor relationships and the information content in the resulting exposure estimates may be low. As described in Chapter 2, many sophisticated models of indoor airflow patterns and temperature distributions were developed and used by the building design industry, but some of these models do not address concentration patterns caused by indoor emissions; thus, they are not relevant to the health risk context; while others involve concentration patterns in which the user needs to enter the emission rate for each averaging period as well as a ‘reactivity factor’ (a rate constant associated with heterogeneous surface decomposition used as a pollutant sink). Multizone airflow and contaminant dispersal models such as COMIS and CONTAM enable the analysis of building airflow patterns and airborne contaminants in a multizone building airflow system. These models have been used primarily to support ventilation research and air quality studies (when the pollutant emission rates are given), and, more recently, the CONTAMW model (developed from the CONTAM series at the US National Institute of Standards and Technology) addresses the pollutant emission process, and

includes a few different models of contaminant sources and sinks (Dols 2001; Persily and Ivy, 2001). All of these existing multizone models however, are applicable where room air is well mixed so that temperature and contaminant concentration are all uniform through the space. While this single node assumption may be adequate for assessing the effect of time average values for a day or for a longer period, these models fail to account for the localized peak concentrations of certain contaminants, which are sometimes considered more critical for health effects than the long term and overall average exposures (McNall et al., 1985).

In the COwZ approach, a well-mixed room is treated as a single zone and a room with widely varying thermal and/or concentration field is divided into a number of sub-zones. New sub-zonal source emission models, which are based on local conditions, have been developed and implemented in COwZ. The strength of COwZ is that it can be used to predict the spatial and temporal variation of pollutant concentrations within buildings with relatively modest computing facilities. For each zone (sub-zone) the prediction of air flow and thermal distribution has been described in Chapters 3 and 4 respectively. This chapter will address contaminant dispersion. The work of other researchers on source emission experiments and modelling is reviewed in section 5.2, while new zonal emission models for COwZ are described in section 5.3. Emphasis is placed on predicting source emission rates for sub-zones. The impacts of sinks are also considered in COwZ (section 5.4). Section 5.5 describes the solution procedure for pollutant emission and transport. The issues are summarized in section 5.6.

5.2 Review of previous studies on indoor source emissions

Emission rates are often determined by chamber testing and theoretical modelling. For prediction of contaminant concentration patterns and occupant exposure to indoor pollutants, a knowledge of the pollutant emission rates is a necessary input. The data from chamber tests are fitted to an empirical model. Although these models are useful, they do not provide the necessary information to scale the chamber data to real buildings. Without having to conduct

costly chamber testing, theoretical models provide a way to predict the emission rates in the indoor environment.

In the past two decades, indoor contaminant sources from materials, furnishings, equipment and activities have been studied extensively, though much work remains before comprehensive databases are available. Persily and Ivy (2001) reviewed some of them and the relevant details have been extracted and are summarized below.

Much of the source emission data have been obtained through measurement in test chambers and houses (ASTM 1997; Black et al. 1991; Matthews 1987; Sparks et al. 1991; Tucker 1991; Wolkoff et al. 1993a), and some of these data have been used to develop source models (Guo 1993). Some researchers have focused on the emissions of volatile organic compounds (VOCs) from building materials and furnishings (Brown 1999a; Chang and Guo 1998; Clausen et al. 1991; Fortmann et al. 1998; Haghighat and Zhang 1999; Hodgson 1999; Hodgson et al. 2000; Levin 1987; Howard et al. 1998; Jayjock et al. 1995; Tichenor and Guo 1991; Yang et al. 2001). Particular attention has also been given to surface coatings (Guo et al. 1996; Guo et al. 1999; Salthammer 1997; Tichenor et al. 1993), liquid spills (Reinke and Brosseau 1997), paint (Clausen 1994 and Sparks et al. 1996), adhesives (Girman et al. 1986 and Nagda et al. 1995), household cleaners and other products (Colombo et al. 1991), floor coverings (Clausen et al. 1993; Lundgren et al. 1999), contaminated water (Andelman et al. 1986; Howard and Corsi 1996 and 1998; Howard-Reed et al. 1999; Keating et al. 1997; Little 1992; Moya et al. 1999) and office equipment (Brown 1999b; Wolkoff et al. 1993b). Batterman and Burge (1995) have also investigated contaminant sources from building HVAC systems. In addition to VOCs, some data are available for indoor moisture (Christian 1993 and 1994), radon (Colle et al. 1981; ECA 1995; Gadgi 1992; Revzan and Fisk 1992, and combustion products from a range of appliances (Girman et al. 1982; Mueller 1989; Nabinger et al. 1995; Phillips 1995; Traynor 1989; Traynor et al. 1989) and from cigarettes (Daisey et al. 1991).

The United States Environmental Protection Agency (US-EPA) has been working on indoor air quality and occupational exposure models for many years. Their most recent model, known as IAQX, was released in December 2000 (Guo 2000a and 2000b). IAQX assumes that a building is divided into discrete zones (rooms) and that the air in each zone is well mixed. While this assumption may be considered valid for zones where air is thoroughly recirculated and strong localized sources and/or sinks of the contaminants do not exist, measurements often reveal significant stratification and localized concentration gradients, even in a well ventilated rooms (McNall et al. 1985). IAQX does not address air flow processes and flow rates between rooms are required as input data. The significant feature of IAQX is that it provides a detailed and advanced treatment of emission source modelling. Based on earlier study, over thirty types of emission source may be modelled using the program. These models address emission processes in significant detail, however, they seldom address more than the mean room concentration. To improve the accuracy of prediction of emission rates of indoor pollutants, Topp et al. (1999) applied CFD to model emissions from building materials. Much work remains before CFD is available for routine predictions of source emission rates of indoor contaminants.

The review of Persily and Ivy and Guo's program did not include source emission models for industrial accidental releases, which have been studied for many years. For example, for more than 40 years the American Institute of Chemical Engineers (AIChE) has been involved with process safety and loss control issues in the chemical, petrochemical, hydrocarbon process, and related industries and facilities. Accidental releases of hazardous materials inside buildings fall into various categories: gas or liquid, instantaneous or continuous, from storage tanks or pipelines, refrigerated or pressurized, confined or unconfined. In some cases, combinations of these scenarios may exist simultaneously. Storage tank or vessel accidental releases can result from corrosion, thermal fatigue, inlet or outlet pipe rupture, or valve failure.

In 1996 the Centre for Chemical Process Safety (CCPS), a directorate of the American Institute of Chemical Engineers, published *Guidelines for Use of Vapour Cloud Dispersion Models*

(CCPS, 1996). This book listed 7 different release mechanism scenarios that can occur with pressurized tanks and refrigerated liquids in outdoor conditions. Some of them also may happen indoors, including small holes in vapour space-pressurized tanks (pure vapour jet), intermediate holes in vapour space-pressurized tanks, high velocity fragmenting jets from refrigerated containment, catastrophic failure of pressurized tanks and escape of liquified gas from a pressurized tank.

Obviously, the method of calculation for a catastrophic tank failure (instantaneous release) and for a small puncture failure in a storage tank (continuous release) will be quite different. Also, different calculation techniques may apply depending on whether a tank failure occurs in the liquid region or in the vapour space above the liquid and whether the release contains one or two phases. Basic source emission models are described for gas and liquid jet releases, two-phase flow, evaporation from pools (cryogenic and nonboiling), and multi-component evaporation. In some cases the emission models may need to be applied sequentially. For example, a two-phase jet from a tank rupture will release gas emissions to the air from the rupture point, as well as forming a liquid pool on the floor that will then evaporate.

5.3 Source emission models

5.3.1 Introduction

In parallel with the development of the multizone air flow model, a multizone transport model defining the mass balance of each pollutant in each zone of a building was developed in COMIS. The main assumption here is that the concentration is well mixed in a zone and is transported from room to room by the flow of air. This would rarely be adequate for predicting the distribution of contaminants in large spaces, particularly where there is a large concentration stratification.

In COWZ rooms with thermal and/or concentration stratification are subdivided into a number of sub-zones. For each zone (or sub-zone), a general formula for conservation of air flow,

thermal energy and mass of each contaminant species is shown in equation (3.1). The conservation of mass of each contaminant species will be addressed in this section. Each term of equation (3.1) is expressed as:

$$\text{Rate of Accumulation} = \frac{d(\rho_i V_i C_{ip})}{dt} \quad (5.1)$$

$$\text{Rate In} = \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{jil}(t)(1-\eta_{jil})C_{jp}(t) \quad (5.2)$$

$$\text{Rate Out} = \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{ijl} C_{ip}(t) \quad (5.3)$$

$$\text{Rate of Source} = S_{ip}(t) \quad (5.4)$$

$$\text{Rate of Sink} = \text{Sink}_{ip}(t) \quad (5.5)$$

Substituting equations (5.1) to (5.5) into equation (3.1), the pollutant transport equation becomes:

$$\frac{d(\rho_i V_i C_{ip})}{dt} = \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{jil}(t)(1-\eta_{jil})C_{jp}(t) - \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} (m_{ijl}(t) + R_{ip})C_{ip}(t) + S_{ip}(t) - \text{Sink}_{ip}(t) \quad (5.6)$$

where

C_{ip} = pollutant p concentration in zone i

m = air flow rate through link l between zone i and j

N_z = total number of zones

N_l = number of links between zone i and j

t = time

V = control volume of zone i

ρ = air density

$S_{ip}(t)$ = a source of indoor pollutant p in zone i

$\text{Sink}_{ip}(t)$ = a sink of pollutant p in zone i

- η_{jil} = the filter effect of link between zone j and i on the incoming concentration
- R_{ip} = reactivity (a general term taking into account chemical reaction or nuclear reactivity of a radioactive pollutant in the zone)

In COwZ, the concentration is assumed to be uniform in each sub-zone. After the airflow variables are calculated by the sub-zonal model and the air density is modified due to any variation of concentration, if the pollutant emission rate $S(t)$ and the Sink(t) are known, the distribution of concentration in each sub-zone can be obtained by solving equation (5.6).

In COMIS, the emission rate from an indoor source can be described as one of two emission types: constant and time-varying. For the constant type, the emission rate remains constant during the entire simulation period. The time-varying type allows the user to define a source emission rate and a factor that presents the variation of source emission rate within a simulation period. This source type requires the user to provide the source emission rate at the start time and source factors at different simulation periods.

In addition to the constant and time-varying source types included in COMIS, three new types of zonal emission model have been developed and have been implemented in COwZ: non-boiling evaporation from pools; volatile organic compound (VOC) emissions from indoor coating materials; and, gas and liquid releases (they usually occur in large industrial buildings). Calculation of the source emission rates from these new zonal models is based on the local conditions rather than room-averaged values. The new zonal emission models do not assume that room conditions are uniform (as earlier well-mixed emission models do (for example, Guo's model (2000a and 2000b))). This will improve the accuracy of prediction of indoor pollutant dispersion and will be very useful to predict the occupational exposure of workers in industrial buildings.

5.3.2 Non-boiling evaporation from pools

Liquid spills can result from accidents ranging from a spillage to a small leak to a vessel failure, and may form a pool on the floor. Material emissions are the result of several mass transfer processes. There is normally interaction between these processes, but their effects on material emissions are somewhat complex. However, the emission can be considered as one of two main processes: diffusion within the material and surface emissions.

Diffusion of a compound through a material is described by Fick's Second Law (Bird et al. 1960):

$$\frac{\partial C_A}{\partial t} = D(\nabla^2 C_A) \quad (5.7)$$

where

$$\frac{\partial C_A}{\partial t} = \text{rate of change in concentration of compound } A \text{ (mg/m}^3 \text{ *h)}$$

$$D = \text{diffusion coefficient (m}^2\text{/h)}$$

$$\nabla^2 = \text{the Laplacian operator of } C_A \text{ (x, y and z directions)}$$

Each compound has its own diffusion coefficient, dependant upon its molecular weight, molecular volume, temperature, and the characteristics of the material within which the diffusion is occurring (Bird et al. 1960). For a given sample, such as paint, the overall diffusion factor is very difficult to determine.

Surface emissions occur between the material and the overlying air as a consequence of several mechanisms, including evaporation and convection. As long as a concentration gradient exists between the two phases, surface emissions will occur. This phenomenon is expressed as:

$$S_A = K_A A (C_s - C) \quad (5.8)$$

where

$$S_A = \text{source emission rate of compound } A \text{ (kg/s)}$$

$$K_A = \text{mass transfer coefficient (m/s)}$$

- A = surface area of pollutant (m²)
- C_s = concentration of compound A at the surface of the material (kg/m³)
- C = concentration of compound A in the overlying air (kg/m³)

The surface emission process involves evaporation, diffusion, convection, absorption and desorption, etc. For prediction of the pollutant emission rate, the parameters A, C_s, C and K_A in equation (5.8) must be determined.

In earlier indoor emission models, C is the room concentration under the assumption that the room is well mixed. In COwZ, C is the concentration of the appropriate local sub-zone, which can be predicted by solving simultaneous equations (5.6) and (5.8). The solution is described in section 5.5.

Estimating the parameters A, K_A and C_s is discussed in the following section for single and multi-component spills on hard flooring.

5.3.2.1 Single component liquid spills on hard flooring

Predicting area of an unrestrained spill - A

For spills on hard flooring (a surface with high wettability) an unrestrained small spill normally maintains a constant depth and the area decreases with time. According to this assumption Reinke and Brosseau (1997) devised a formula for A_{spill},

$$A_{spill} = A_{1spill} \exp\left[\left(\frac{-S_A A_{0spill}}{V_{0spill} \rho_{Aliq}}\right)(t - t_1)\right] \quad (5.9)$$

where A_{1spill} is the area of the spill pool at the beginning of the time period of integration (t₁), ρ_{Aliq} is density of liquid A, and A_{0spill} and V_{0spill} are maximum pool area and volume respectively, which is assumed to occur shortly after the spill.

Predicting mass transfer coefficient - K_A

A vapour phase mass transfer coefficient K_A is a function of the transfer conditions in the atmosphere immediately above the spill and is possibly a function of the molecular diffusion characteristic (i.e. Schmidt number) of the compound A in the vapour phase. Turbulent transfer is probably the dominant mechanism. K_A will also depend on the size of the pool.

The most detailed analysis has been published by Mackay and Matsugu (1973), who used Sutton's (1953) theory with experimental data and formed the correlation:

$$K_A = 0.00482 u^{0.78} d^{-0.11} Sc^{-0.67} \quad (5.10)$$

$$Sc = \mu_{air}/(\rho_{air} D_{Air})$$

where

K_A = mass transfer coefficient (m/s)

u = velocity of air flowing across pool (m/s)

$d = \sqrt{A_{spill}}$ = pool length in flow direction (m)

Sc = Schmidt Number

μ_{air} and ρ_{air} are air viscosity and density respectively. D_{Air} is diffusion coefficient of compound A in air, which was given by Perry and Green (1997) for prediction of binary air-hydrocarbon or nonhydrocarbon gas mixtures at low pressures,

$$D_{Air} = \frac{0.01013T^{1.75} \left(\frac{1}{MW_A} + \frac{1}{MW_{air}} \right)^{0.5}}{p \left[(\sum v_A)^{1/3} + (\sum v_{air})^{1/3} \right]^2} \quad (5.11)$$

where

MW_A = molecular weight of compound A (g/mol)

MW_{air} = molecular weight of air (g/mol)

P = air pressure (Pa)
 T = air temperature (K)

v_A and v_{air} are group contribution values of the compound A and air respectively for the subscript component summed over atoms, groups, and structural features, which are also given in Perry and Green (1997).

Air/source interface concentration of compound A - C_s

The air at the pollutant pool surface will always be saturated because of the direct contact with the pollutant pool liquid, and thus vapour pressure. Therefore, the vapour pressure at the pool surface will simply be the saturation pressure of liquid pollutant at the temperature of the liquid pool at the interface.

When contaminant concentrations in air are low and pressure is near atmospheric, Dalton's law of partial pressure (Çengel and Boles, 1998) is used to determine the saturation mole fraction of compound A (y_{As}):

$$y_{As} = p_{As}/p \tag{5.12}$$

y_{As} is mole fraction A at saturation, p is the sub-zone ambient pressure, and p_{As} is the vapour pressure of compound A , which is calculated using the Wagner equation (Reid et al., 1987) in the form:

$$\ln\left(\frac{p_{As}}{p_{Ac}}\right) = \frac{a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6}{(T_{spill} / T_{Ac})} \tag{5.13}$$

$$\tau = \left(1 - \frac{T_{spill}}{T_{Ac}}\right)$$

where

- p_{Ac} = critical pressure (Pa)
 T_{Ac} = critical temperature (K)
 T_{spill} = temperature of spill pool (K)
a,b,c,d = experimentally determined constants

According to the definition of concentration and gas state equation, the concentration of pollutant A can be expressed as

$$C = \frac{m}{V} = 10^3 \frac{P_A}{R_A T} = 10^3 \frac{P_A MW_A}{R_u T} \quad (5.14)$$

where

- C = concentration of pollutant A in a sub-zone (mg/m^3)
 m = mass of pollutant A in the sub-zone (mg)
 V = volume of the sub-zone (m^3)
 p_A = partial pressure of pollutant A in the sub-zone (Pa)
 R_A = R_u / MW_A , gas constant of pollutant A ($\text{J}/(\text{g},\text{K})$)
 R_u = universal gas constant ($8.314 \text{ J}/(\text{mol},\text{K})$)
 T = air temperature in the sub-zone where pollutant spills (K)

Substituting equation (5.12) into equation (5.14), the interface concentration of pollutant A can be expressed:

$$C_s = 10^3 \frac{P_{As} MW_A}{R_u T} = 10^3 y_{As} \frac{MW_A}{V_{air}} \quad (5.15)$$

$$V_{air} = R_u T/P$$

where

- C_s = the interface concentration of pollutant A (mg/m^3)
 P = the sub-zone ambient pressure (Pa) in which pollutant spills

V_{air} = gas molar volume at pool temperature (m^3/mol)

5.3.2.2 Petroleum-Based solvent spills on hard flooring

In a multicomponent liquid spill, the evaporative emission rate for each individual compound, as well as total evaporative rate, may have to be estimated.

Estimation of the spill area - A

The spill area decreases with time. Drivas (1982) and Reinke and Brosseau (1997) assumed that an unrestrained small spill maintains a constant depth and decreases only in area and not in depth, as it evaporates. Under this assumption the spill area at any time, $A(t)$, can be approximated by:

$$A(t) = A_0 \frac{W(t)}{W_0} \quad (5.16)$$

where

- A_0 = initial spill area (m^2)
- $W(t)$ = amount of solvent remaining on the floor (mol)
- W_0 = initial amount of solvent spilled (mol)

The remaining amount of solvent can be expressed by:

$$W(t) = W_0 - \sum_{k=1}^{k=Tstep} S(k\Delta t) \times A(k\Delta t) \times \Delta t / MW \quad (5.17)$$

where

- Tstep = number of time step from 0 to t
- Δt = time interval

Predicting mass transfer coefficient - K

In terms of the definition of mass transfer coefficient ($K = D/\delta$), mass transfer coefficient for an individual component (K_i) can be expressed as:

$$K_i = K D_i/D \quad (5.18)$$

where δ is apparent boundary layer thickness above the surface; D_i and D are diffusivity for the individual compound and the most dominant compound respectively. The diffusivity values for different compounds in a petroleum-based solvent are very close to each other (Tichenor et al. 1993). For example, the diffusivity values of consecutive alkanes, the major components of mineral spirits, are very close; the diffusivity decreases by only 20% with a molecular weight increase from C_8H_{18} (octane) to $C_{12}H_{24}$ (dodecane). The average diffusivity for the five alkanes from C_8H_{18} to $C_{12}H_{24}$ is $0.0209\text{m}^2/\text{h}$, which is very close to the decane diffusivity of $0.0207\text{m}^2/\text{h}$. In many cases a single mass transfer coefficient can be used for both of TVOC and the individual compounds. In this study, the method of Mackay and Matsugu (1973) described above in equation (5.10) is used to predict the value of K .

The interface VOC concentration - C_s

(i) The exact composition of the solvent is known

When we know the exact composition of the solvent, the partial pressure p_i of the component i on the gas side of the interface is given by Raoult's law (Çengel and Boles, 1998) as

$$p_i = y_{i,g} p_{\text{total}} = y_{i,l} p_{i,\text{sat}}(T) \quad (5.19)$$

So

$$y_{i,g} = y_{i,l} p_{i,\text{sat}} / p_{\text{total}}$$

$$P_{total} = \sum_{i=1}^{i=N} y_{i,l} P_{i,sat} \quad (5.20)$$

where $p_{i,sat}$ is the saturation pressure of component i at the interface temperature and p_{total} is the total pressure for TVOCs at the gas phase side; $y_{i,g}$ and $y_{i,l}$ is the mole fraction of component i on the gas and liquid sides of the interface respectively. $y_{i,l}$ is given as

$$y_{i,l} = \frac{m_i / MW_i}{\sum_{j=1}^{j=N} m_j / MW_j} \quad (5.21)$$

where

m_i = amount of component i remaining in the pool (g)

MW_i = molecular weight of component i (g/mol)

$\sum_{j=1}^{j=N} m_j / MW_j = m_T / MW_{m,l}$ sum of all N components remaining in the pool (mol)

m_T = amount of the TVOC remaining in the pool (g)

$MW_{m,l} = \sum_{i=1}^{i=N} y_{i,l} MW_i$, the average molecular weight of the TVOC on the liquid side of the interface (g/mol)

N = number of VOCs in the product

As described in the equation (5.14), the interface concentration $C_{i,s}$ of an individual component i is expressed as

$$C_{i,s} = 10^3 \frac{p_i MW_i}{R_u T} \quad (5.22)$$

Substituting equation (5.19) into equation (5.22):

$$C_{i,s} = y_{i,l} C_{i,0} \quad (5.23)$$

$$C_{i,0} = 10^3 y_{i,s} \frac{MW_i}{V_{air}}$$

where

$$C_{i,0} = \text{saturation concentration of component } i \text{ (mg/m}^3\text{)}$$

$$y_{i,s} = p_{i,sat}/p, \text{ the saturation mole fraction of component } i.$$

The total interface concentration of C_s for the TVOCs is given as

$$C_s = \frac{m_{total}}{V} = 10^3 \frac{P_{total} MW_{m,g}}{R_u T} \quad (5.24)$$

Substituting equation (5.20) into equation (5.24):

$$C_s = 10^3 y_s \frac{MW_{m,g}}{V_{air}} \quad (5.25)$$

where

$$y_s = \sum_{i=1}^{i=N} y_{i,l} P_{i,sat} / p, \text{ the gas side mole fraction of TVOC}$$

$$MW_{m,g} = \sum_{i=1}^{i=N} y_{i,g} MW_i, \text{ the average molecular weight of the TVOC on the gas side of}$$

the interface (g/mol)

(ii) The contents of major VOCs of the solvent are known

Petroleum-based solvents actually contain hundreds of compounds. It is difficult, if not impossible, to determine their exact composition. So it is impossible to predict the surface

concentrations for individual component i and the total TVOCs using equations (5.23) and (5.25), in which $y_{i,g}$ and $y_{i,l}$ are unknown and then the p_{total} and MW_m cannot be calculated exactly. Guo et al. (1999) recommended that total vapour pressure for TVOC (p_0) and average molecular weight for TVOC (MW_m) be represented by the vapour pressures and molecular weights of the major VOC in the product. Using this assumption the total vapour pressure (p_{total}) and the average molecular weight (MW_m) for TVOC can be estimated by equations (5.26) and (5.27) respectively.

The total vapour pressure can be calculated:

$$p_{total} = \frac{\sum_{i=1}^{i=n} y_i P_{i,sat}}{\sum_{i=1}^{i=n} y_i} \quad (5.26)$$

where

- n = number of major VOCs in the product
- y_i = mole fraction of major component i in the product

The average molecular weight for TVOC (MW_m) is estimated from the contents of major VOCs in the products:

$$MW_m = \frac{\sum_{i=1}^{i=n} y_i MW_i}{\sum_{i=1}^{i=n} y_i} \quad (5.27)$$

The parameters p_{total} and MW_m are readily obtained and the interface concentrations for individual and the TVOCs can be estimated by equations (5.23) and (5.25).

5.3.3 VOC emissions from indoor coating materials

The emission of VOCs from indoor coating materials is generally divided into two processes. The first process is diffusion from the interior of the material to the surface. The second is transfer from the interface to the air. So the emission rate can also be determined by equation (5.8). The parameters A , k and C_s are described below.

Area of coating materials - A

During the simulation of emissions from coating materials, the area of source is often assumed fixed and is given before the simulation begins.

Estimation of gas-phase mass transfer coefficients - K

Two theoretical models have been developed to estimate gas-phase mass transfer coefficients in indoor environments (Sparks et al., 1996; Zhang et al., 1996). The model proposed by Sparks et al. is the simpler one of the two, and is derived by finding the correlation between the Nusselt number (Nu) and the Reynolds number (Re) from experimental data:

$$Nu = 0.33 Re^{2/3} \quad (r^2 = 0.98, n = 24) \quad (5.28)$$

where

- Nu = $K L/D$
- Re = $Lu\rho/\mu$
- D = diffusivity of the VOC in air (m^2/s)
- L = characteristic length of the source (equal to the square root of the source area (m))
- u = air velocity over the source (m/s)
- ρ = air density (kg/m^3)
- μ = air viscosity ($kg/m s$)

So from equation (5.28) the mass transfer coefficient is

$$K = 0.33DL^{-(1/3)}\left(\frac{u\rho}{\mu}\right)^{2/3} \quad (5.29)$$

As described in the above section, the mass transfer coefficient for TVOC is represented by that for the most abundant component.

The interface VOC concentration - C_s

As the coated surface ages, the total vapour pressure at the surface (expressed as concentration C_s) decreases gradually and is assumed to be proportional to the amount of TVOC remaining in the source (Tichenor et al., 1993):

$$C_s = C_{v0} \frac{M_T}{M_{T0}} \quad (5.30)$$

$$C_{v0} = 10^3 \frac{p_0}{p} \frac{MW_m}{V_{air}}$$

where

- C_{v0} = initial airborne TVOC concentration at air/source interface (mg/m^3), based on the total vapour pressure of the TVOCs
- M_T = amount of TVOCs remaining in the source (mg/m^2)
- M_{T0} = amount of TVOCs applied (mg/m^2)
- P = the sub-zone ambient pressure (Pa) in which the wall surface is painted

The interface concentration for component i was estimated by a modified VBX model (Guo et al., 1999):

$$C_{i,s} = C_{vi} \frac{M_i}{M_T} \frac{MW_m}{MW_i} \quad (5.31)$$

$$C_{vi} = 10^3 \frac{P_{i,sat}}{p} \frac{MW_i}{V_{air}}$$

where

C_{vi} = airborne concentration of component i at air/source interface (mg/m^3),
based on the vapour pressure of component i

M_i = amount of component i remaining in the source (mg/m^2)

The estimation of the unknown parameters p_0 and MW_m for equations (5.30) and (5.31) is discussed below.

(i) The exact composition of the solvent is known

When the exact composition of the solvent is known, the total vapour pressure for TVOC (p_0) and the average molecular weight for TVOC (MW_m) can be calculated using equations (5.32) and (5.33) respectively:

$$p_0 = \sum_{i=1}^{i=N} y_i P_{i,sat} \quad (5.32)$$

$$MW_m = \sum_{i=1}^{i=N} y_i MW_i \quad (5.33)$$

where

N = number of VOCs in the product

y_i = mole fraction of component i in the product

(ii) The contents of major VOCs of the solvent are known

When the contents of major VOCs of the solvent are known, Guo et al. (1999) recommended that total vapour pressure for TVOC (p_0) and average molecular weight for TVOC (MW_m) be represented by the vapour pressures and molecular weights of the major VOCs in the product.

The total vapour pressure can be calculated:

$$P_0 = \frac{\sum_{i=1}^{i=n} y_i P_{i,sat}}{\sum_{i=1}^{i=n} y_i} \quad (5.34)$$

where

n = number of major VOCs in the product

y_i = mole fraction of component i in the product

The average molecular weight for TVOC (MW_m) is estimated from the contents of major VOCs in the products:

$$MW_m = \frac{\sum_{i=1}^{i=n} y_i MW_i}{\sum_{i=1}^{i=n} y_i} \quad (5.35)$$

5.3.4 Gas and liquid releases

In this subsection, two basic types of emission modelling of gas jet and liquid jet are modified and have been implemented in COwZ to predict the indoor concentration distributions after accidental releases.

Gas Jet Releases

As shown in Figure 5.1, one important type of accidental release is a gas jet from a small puncture in a pressurized gas pipeline or in the vapour space of a pressurized liquid storage tank. When gas releases from a small puncture, gas can exit the puncture only as fast as its

sonic velocity (namely the speed of sound in the gas), because of a 'choked' condition at the exit. An initial high release rate will decrease as the gas tank pressure decreases.

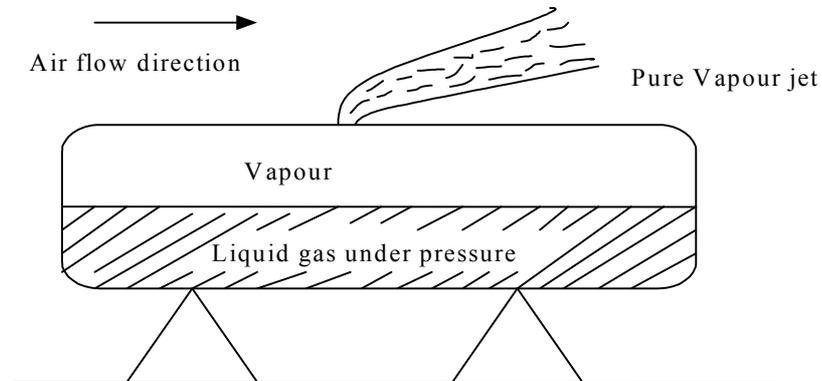


Figure 5.1 Small hole in vapour pressurized tank

Assuming an ideal gas exiting through a small hole, the pressure criterion for choked or critical flow to occur can be expressed (Perry et al., 1997):

$$p_{cr} = p_a \left(\frac{r+1}{2} \right)^{\frac{r}{r-1}} \quad (5.36)$$

where

- p_{cr} = critical pressure (Pa)
- p_a = absolute atmospheric pressure (Pa)
- r = gas specific heat ratio (the heat capacity at constant pressure, c_p , divided by the heat capacity at constant volume, c_v),

if the absolute tank pressure is not less than the critical pressure and the choked flow condition is met. For an ideal gas exiting through an orifice under isentropic conditions, the gas emission rate will be independent of downstream pressure and can be written as (Perry et al., 1997):

$$S = c_d A_h \left[p \rho_0 r \left(\frac{2}{r+1} \right)^{\frac{r+1}{r-1}} \right]^{1/2} \quad p \geq p_{cr} \quad (5.37)$$

where

- S = time-dependent gas mass emission rate (kg/s)
- c_d = discharge coefficient for orifice (-)
- A_h = puncture area (m²)
- p = absolute tank pressure (Pa)
- ρ_0 = gas density in tank (kg/m³)

The coefficient of discharge, c_d , depends upon nozzle shape and Reynolds number, and graphical relationships of c_d for various types of orifices can be found in handbooks and fluid mechanics textbooks (e.g., Perry et al., 1997).

For many gases, r ranges from about 1.1 to 1.4, and so choked gas flow usually occurs when the source gas pressure is about 1.71 atm to 1.90 atm or greater (see Table 5.1). Thus, the large majority of accidental gas releases will usually involve choked flow.

For using equation (5.37), the variations of the absolute storage gas pressure p with time must be known. For choked gas flows from a pressurized gas system, the source-term model of Rasouli and Williams (1995) is used:

$$p_2^c - p_1^c = c_d \left(\frac{A}{V} \right) \left(\frac{gR}{M} \right)^{1/2} \left(\frac{r-1}{2r} \right)^{r \cdot 3/2} \left(\frac{2}{r+1} \right)^{\frac{r+1}{2r-2}} \left(\frac{T_0}{p_0^a} \right)^{1/2} (t_2 - t_1) \quad (5.38)$$

where

- A = area of the source leak (ft²)
- V = source vessel volume (ft³)

g = gravitational constant of 32.17 ft/s²

R = universal gas constant of 1545 (ft lbs/lb-mol °R)

M = molecular weight of the gas

T_0 = initial gas temperature in the source vessel (°R)

p_0 = initial absolute gas pressure in the source vessel (lbs/ft²)

$a = (r-1)/r$

t_0 = the time of flow initiation through the leak (s)

t_1 = any time t_0 or later (s)

t_2 = any time later than t_1 (s)

p_1 = the absolute gas pressure in the source vessel at time t_1 (lbs/ft²)

p_2 = the absolute gas pressure in the source vessel at time t_2 (lbs/ft²)

$c = - (r-1)/2r$

Table 5.1 The values of r and P_{cr} for some commonly stored gases

| Stored gas | $r = c_p/c_v$ | Critical pressure (atm) |
|-----------------|---------------|-------------------------|
| Butane | 1.096 | 1.708 |
| Propane | 1.131 | 1.729 |
| Sulphur Dioxide | 1.290 | 1.826 |
| Methane | 1.307 | 1.837 |
| Ammonia | 1.31 | 1.839 |
| Chlorine | 1.355 | 1.866 |
| Carbon Monoxide | 1.404 | 1.895 |
| Hydrogen | 1.410 | 1.899 |

When the tank pressure decreases below the critical pressure, choked flow no longer applies and the flow rate becomes sub-critical (Perry et al., 1997):

$$S = c_d A_h \left\{ 2 \rho_0 p \left(\frac{r}{r-1} \right) \left[\left(\frac{p_a}{p} \right)^{\frac{2}{r}} - \left(\frac{p_a}{p} \right)^{\frac{r+1}{r}} \right] \right\}^{1/2} \quad p < p_{cr} \quad (5.39)$$

To use equation (5.39) the variations of pressure with time must be known. The gas release is assumed to be isothermal or adiabatic.

(i) *Pipeline releases*

A pipeline release can be approximately isothermal in cases with relatively small releases. Wilson (1979, 1981) modified an empirical correction developed by Bell (1978) to simplify the solution of isothermal, quasi-steady state flow from a gas pipeline:

$$S = \frac{S_0}{(1+\alpha)} \left(e^{-\frac{t}{\alpha^2 \beta}} + \alpha e^{-\frac{t}{\beta}} \right) \quad (5.40)$$

where

- S = time-dependent gas mass emission rate (kg/s)
- S₀ = initial gas mass emission rate at the time of rupture (kg/s)
- α = $\frac{m_T}{\beta S_0}$ (nondimensional mass conservation factor)
- m_T = the total mass in the pipeline (kg)
- β = time constant for release rates (s)
- t = time (s)

The time constant, β , is a function of three nondimensional parameters:

$$K_F = \frac{D_p}{rfL_p}; \quad K_A = \frac{A_h}{A_p}; \quad K_r = \left(\frac{r+1}{2}\right)^{\frac{r+1}{r-1}} \quad (5.41)$$

where

- D_p = pipe diameter (m)
- f = pipe friction factor (-)
- L_p = length of pipe (m)
- A_p = cross-sectional area of pipe (m²)

The friction factor, which is a function of pipe roughness and the Reynolds number of the flow, can be derived from standard charts (e.g., Perry et al., 1997).

By using these parameters, the time constant, β , can be expressed as (NOAA, 1992):

$$\beta = \frac{2L_p K_F K_r^{3/2}}{3cK_A^3} \left[\left(1 + \frac{K_A^2}{K_F K_r} \right)^{3/2} - 1 \right] \quad (5.42)$$

where

- c = speed of sound in the gas (m/s)

(ii) *Gas release from a pressurized liquid or cryogenic storage tank*

For a puncture in the vapour space of a pressurized liquid or cryogenic storage tank, the gas release is continually supplied by liquid evaporating (in the case of cryogenic liquids, boiling) in the tank. The rate of liquid evaporating can be expressed as:

$$m_l(t) = \{m_{tot}(t)c_p \Delta T_l + [q_0(t) + q_{st}(t) + q_{gl}(t)] \Delta t\} / (h_{vap} \Delta t) \quad (5.43)$$

where

- $m_l(t)$ = rate of liquid evaporating (kg/s)

- $m_{\text{tot}}(t)$ = total liquid mass remaining in the tank (kg)
 c_p = heat capacity of the liquid (average between $T_l(t)$ and $T_l(t+\Delta t)$) (J/kg.K)
 ΔT_l = $T_l(t)-T_l(t+\Delta t)$ = liquid temperature decreases (K)
 $q_o(t)$ = heat transfer through the tank surface into liquid (W), for an adiabatic system it is zero
 $q_{\text{st}}(t)$ = heat of storage tank into liquid (W)
 q_{gl} = convective heat transfer at the interface between liquid and gas (W)
 h_{vap} = heat of vaporization of the liquid (J/kg)
 Δt = time step (s)

At time t the volume of vapour space and vapour mass above the liquid in the storage tank can be described by equations (5.44) and (5.45):

$$V_g(t) = V_0 + \sum_{t=0}^t m_l(t)\Delta t / \rho_l \quad (5.44)$$

$$m_g(t) = m_0 + \sum_{t=0}^t m_l(t)\Delta t - \sum_{t=0}^t S(t)\Delta t \quad (5.45)$$

where

- $V_g(t)$ = the volume of vapour space above the liquid (m^3)
 V_0 = the initial volume of vapour space above the liquid (m^3)
 ρ_l = liquid density (kg/m^3)
 $m_g(t)$ = gas mass above the liquid remaining in the storage tank (kg)
 m_0 = the initial gas mass in the storage tank (kg)
 $S(t)$ = the gas release rate from the puncture, which can be calculated by equation (5.37) or (5.39) (kg/s)

From the ideal gas state equation, the vapour pressure above the liquid in the storage tank can be written as:

$$p(t) = \frac{m_g(t)RT}{V_g(t)} \quad (5.46)$$

where

- $p(t)$ = the vapour pressure above the liquid in the storage tank (Pa)
- R = gas constant = R^*/M (R^* is the universal gas constant and M is the molecular weight of the gas in the tank) (J/kg.K)
- T = the gas temperature in the tank (K)

The solution of the simultaneous equations (5.43) to (5.46) and (5.37) or (5.39), which are solved by an iterative method, predicts the gas emission rate of $S(t)$.

Liquid Jet Releases

A puncture or failure in the liquid space of a pressurized or cryogenic storage tank will be more complicated than the corresponding case of a vapour space failure. In the liquid release case, a liquid jet is typically propelled from the tank and some portion of the released liquid may instantaneously vaporize or ‘flash’, which is dependent on the normal boiling point of the compound or the flashing behaviour of a multi-component mixture. The simplified and well-known case of a pure liquid release is presented.

The equation typically used for calculating the liquid flow rate through a small puncture is based on the classic work of Bernoulli and Torricelli, and can be expressed as (Perry et al., 1997):

$$S_l = c_d A_h \rho_l \left[2 \left(\frac{p - p_a}{\rho_l} \right) + 2gH_l \right]^{1/2} \quad (5.47)$$

where

- S_l = liquid mass emission rate (kg/s)
- c_d = coefficient of discharge (dimensionless)
- A_h = puncture area (m²)
- ρ_l = liquid density (kg/m³)
- p = tank pressure (Pa)
- p_a = ambient pressure (Pa)
- g = acceleration due to gravity (9.81 m/s²)
- H_l = height of liquid above the puncture (m)

The height of the liquid in the tank, H_l , can be calculated for a specific geometry. For example, for vertical cylindrical tanks:

$$H_l = \frac{4V_l}{\pi d_t^2} \quad (5.48)$$

where

- V_l = liquid volume remaining in the tank (m³)
- d_t = tank diameter (m)

For horizontal cylindrical tanks, H_l and V_l are calculated by Wu and Schroy (1979) on a dynamic basis using the following equations:

$$H_l = \frac{d_t}{2} (1 - \cos \theta_l) \quad (5.49)$$

$$V_l = \frac{L_t d_t^2}{4} \left[\theta_l - \frac{\sin(2\theta_l)}{2} \right]$$

where

θ_l = the angle (in radians) relative to the upward vertical direction formed by the liquid surface remaining around the circumference of the tank

L_t = length of the horizontal tank (m)

The valve spacing and closing time are critical to the analysis of liquid pipeline failures. A considerably greater volume of material will be released if the distance between the valves is long or closing them is slow. Likewise, a storage tank failure will release liquid until the level falls below the puncture level. A gas phase release will then continue as described in last section.

5.4 Sink terms

The interface surfaces of a building act as a sink for contaminants. These sinks may be reversible or irreversible, depending on the pollutant and the nature of the sink. Tichenor et al. (1991) developed a dynamic sink model:

$$\text{Sink}(t) = k_a C A_{\text{sink}} - k_d M_s^n A_{\text{sink}} \quad (5.50)$$

where

$\text{Sink}(t)$ = the rate to the sink (mg/s)

k_a = the sink rate constant (m/s)

C = the room pollutant concentration (mg/m³)

A_{sink} = area of the sink (m²)

k_d = desorption rate constant (1/s)

M_s = mass collected in the sink (mg/m²)

n = an exponent

In the above equation, k_a can be estimated from properties of the pollutant, k_d and n must be determined from experiments. Sparks et al. (1991) summarized the sink constants for various materials (see Table 5.2).

The sink model used in COwZ is based on the model described by Tichenor et al. (1991). All the parameters for a room are substituted by the corresponding parameters of the sub-zones.

Table 5.2 Recommended values of sink constants (from Sparks et al 1991)

| Material | Pollutant | k_a (m/h) | k_d (1/h) | n |
|-------------------------------|--------------------------------------|-------------|-------------|---|
| Carpet | General VOC, Perchloroethylene | 0.1 | 0.008 | 1 |
| Carpet | p-dichlorobenzene | 0.2 | 0.008 | 1 |
| Painted walls and ceilings | General VOC and perchloroethylene | 0.1 | 0.1 | 1 |
| Painted walls and ceilings | p-dichlorobenzene | 0.2 | 0.008 | 1 |

5.5 Solution procedure for pollutant emission and transport

For the solution of the pollutant transport equations, COMIS assumes that pollutant concentration is low (less than 0.025 kg/kg), and that, at this level, any variation in concentration which changes the multizone mass flow distribution may be accounted for by modifying the density in different zones (Feustel and Raynor-Hoosen, 1990). COwZ inherits this assumption. After the solution of air mass flow and thermal energy balance, the prediction

of concentration distribution is obtained by solving the pollutant mass conservation equation (5.6).

The first term of equation (5.6) can be expanded to:

$$\frac{d(\rho_i V_i C_{ip})}{dt} = C_{ip} \frac{d(\rho_i V_i)}{dt} + \rho_i V_i \frac{dC_{ip}}{dt} \quad (5.51)$$

In equation (5.51), $d(\rho_i V_i)/dt$ defines the mass balance of dry air in zone i , which is expressed as (without mass source):

$$\frac{d(\rho_i V_i)}{dt} = \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{jil}(t) - \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{ijl}(t) \quad (5.52)$$

Substituting equation (5.52) into equation (5.6), a general definition of the concentration of pollutant p in zone i involving only the incoming flow can be obtained:

$$\rho_i V_i \frac{dC_{ip}}{dt} = \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{jil}(t) (1 - \eta_{jil}) C_{jp}(t) - \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} (m_{jil}(t) + R_{ip}) C_{ip}(t) + S_{ip}(t) - Sink(t) \quad (5.53)$$

By using a purely implicit finite difference scheme to integrate equation (5.53) over time, under matrix notation we obtain:

$$[A] \{C_{ip}^{t+\Delta t}\} = \{B\} \quad (5.54)$$

With:

$$A(i,j) = \sum_{l=0}^{l=N_l} -m_{jil}(t + \Delta t) (1 - \eta_{jil}) \quad i \neq j$$

$$A(i,i) = \frac{\rho_i(t) V_i}{\Delta t} + \sum_{j=0}^{j=N_z} \sum_{l=0}^{l=N_l} m_{jil}(t + \Delta t) + R_{ip}(t + \Delta t)$$

$$B(i) = \frac{\rho_i(t) V_i}{\Delta t} C_{ip}(t) + \sum_{l=0}^{l=N_l} m_{oik}(t + \Delta t) (1 - \eta_{oik}) C_{op}(t + \Delta t) + S_{ip}(t) - Sink_{ip}(t)$$

In the source term $B(i)$, the subscript o represents outside characteristics. At each time step, the boundary conditions are given by the user. The air density of moist air (relative humidity Xh) with Np pollutants is given by (Feustel and Raynor-Hoosen, 1990):

$$\rho = \frac{p \left[1 + Xh + \sum_{i=1}^{i=Np} C_i \right]}{287.055T \left[1 + Xh \frac{28.9645}{18.01534} + \sum_{i=1}^{i=Np} C_i \frac{28.9645}{MW_i} \right]} \quad (5.55)$$

As described in sections (5.3) and (5.4), the source emission rates and sink absorption rates may vary with time t , they can, however, be assumed to be nearly constant over a short time interval. To avoid the time-consuming solution of the simultaneous equations of pollutant transport and source emission by iterative methods, values from the previous time-step for source emission rates and sink rates are used in $B(i)$. An important problem when using this explicit scheme is the definition of a reasonable choice for the time step of the simulation.

For the transport of concentrations by the inter-zonal air flows, an approximation time constant is given by (Feustel and Raynor-Hoosen, 1990):

$$\tau_i = \frac{V_i \rho_i}{m_{ti}} \quad (5.56)$$

where m_{ti} is the total flow into zone i . As a first approximation the condition to fulfil for the time step can be taken as:

$$\Delta t \leq \min_{i=1}^{i=Nz} \tau_i \quad (5.57)$$

For the prediction of emission rate S for solvent liquid spills on hard flooring, Reinke and Brosseau (1997) recommended that the time interval was less than 20s. The emission from coating materials may be low, and the time interval can be more than 20s. However, if the gas and liquid releases are high, the time interval should be less than 20s. A time interval less than 5s is recommended. In COWZ, a time step is selected which is a minimum of 5s and the value calculated by equation (5.57).

After the equations of air mass flow and thermal balance are solved and the source term B (i) obtained by an explicit scheme, equations (5.54) become a system of linear equations. In COMIS, the Gaussian elimination with back substitution method is used to solve the pollutant transport equations for steady state and Gauss-Seidel iterative method for unsteady state. COWZ also uses these two methods for the solution of equations (5.6) for steady state

($\frac{d(\rho V_i C_{ip})}{dt} = 0$) and unsteady state (equation (5.54)) respectively. The solution procedures

for Gaussian elimination with back substitution for linear equations have been described in section 4.3. In the Gauss-Seidel method, previously computed results are used as soon as they are available:

$$C_{ip}^{(k)} = \left(b_i - \sum_{j<i} a_{i,j} C_{jp}^{(k)} - \sum_{j>i} a_{i,j} C_{jp}^{(k-1)} \right) / a_{i,i} \quad (5.58)$$

In matrix terms, the definition of the Gauss-Seidel method in equations (5.58) can be expressed as

$$C_p^{(k)} = (D - L)^{-1} (UC_p^{(k-1)} + B) \quad (5.59)$$

where D , $-L$ and $-U$ represent the diagonal, lower-triangular, and upper-triangular parts of A , respectively.

The solution procedures are:

- (1) Set $k = 1$.

(2) While ($k \leq N_z$) do steps 3-6.

(3) For $i = 1, \dots, N_z$

$$\text{set } C_{ip} = \frac{b_i - \sum_{j=1}^{i-1} a_{ij} C_{jp} - \sum_{j=i+1}^{N_z} a_{ij} C_{jp}^0}{a_{ii}}$$

(4) If $|C_{ip} - C_{ip}^0| / C_{ip} < \text{TOL}$ then OUTPUT (C_{1p}, \dots, C_{Nzp}); (The procedure was successful.)
STOP.

(5) Set $k = k + 1$.

(6) For $i = 1, \dots, N_z$ set $C_{ip}^0 = C_{ip}$.

(7) OUTPUT ('Maximum number of iterations reached'); (The procedure was successful)
STOP.

A sufficient condition for convergence is that

$$|a_{ii}| > \sum_{\substack{j=1 \\ j \neq i}}^{N_z} |a_{ij}|, \quad i = 1, 2, \dots, N_z.$$

For equation (5.54) this is true, $C_p^{N_z}$ will converge to the solution no matter what initial vector is used. In COwZ the break limit (tolerance) for convergence of concentration (TOL) is $1.0e-6$.

Two important facts about the Gauss-Seidel method should be noted. First, the computations in equation (5.58) appear to be serial. Since each component of the new iteration depends upon all previously computed components, the updates cannot be done simultaneously as in the Jacobi method. Second, the new iterate $C_p^{(k)}$ depends upon the order in which the equations (5.54) are examined. For details of Gauss-Seidel method, the reader is referred to Burden and Douglas Faires (2001).

5.6 Summary

COMIS does not include pollutant source emission modelling but this facility has been added to COwZ.

Source emission rates have, in the past, been estimated by scaling data collected in test chambers and models have assumed that rooms contain well-mixed air. For this project I have chosen to solve the simultaneous equations for conservation of mass of each contaminant species in each sub-zone and to implement a number of theoretically derived source emission models. The parameters are calculated using local conditions. In general, COwZ can be used to predict pollutant emission and dispersion within buildings and to resolve the spatial and temporal variation of contaminant concentrations within buildings. This is a distinct advance over the capabilities of one-zone models and would be useful, for example, in predicting the occupational exposure of workers in industrial buildings.

So far, three types of indoor source emission zonal modelling have been developed and implemented in COwZ: non-boiling liquid spills on hard floor (developed from methods for outdoor liquid spills on land); VOC emissions from indoor coating materials (derived from the modifications of the well-mixed source emission models of Tichenor et al. (1993) and Guo et al. (1999)); and gas and liquid releases (derived from CCPS (1996) models). Emphasis was placed on the prediction of related parameters such as pool area, mass transfer coefficient, air/source interface concentration, variation of tank pressure, etc.

When source emission modelling is incorporated into COwZ, the problem is constrained to the solution of the pollutant emission and transport equations. The choice for the time step of the simulation is a key factor which affects computing time and accuracy of the simulation. It is recommended that a time step less than 5s is used. Gaussian elimination with back substitution is used for the solution of the pollutant transport equations for steady state and the Gauss-Seidel method for unsteady state.

