

## HazMat Liquid Release Following a Tank Truck Accident: Cross-Check Modelling and Field Data Validation

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In this paper, after discussing QRA uncertainties connected to consequence modeling (release rates, evaporation, and dispersion), we consider an hazardous release of hydrochloric acid due to a loss of containment of a tank truck. Following the source term characterization, we applied widely used integral approaches, providing modeling for the combination of all physical phenomena involved after the release. The applicative phase of this work, representing its main appeal, is the validation of the simulation results against field data sets in the near field, directly collected during emergency response activities. More advanced modeling can be performed by a computational fluid dynamics method (CFD) to solve the Navier-Stokes equations, together with specific model equations. Quantitative conclusions are drawn about the cross-check validation performed. The comparison based on experimental data evidences the ability and limitations of the adopted models in estimating the actual post-release gas behavior, as well as the implications for hazard predictions that support decision makers in emergency planning and response.

### 1. Introduction

The science of process safety and risk analysis and related approaches require further progress, as illustrated by the sequence of major hazard accidents, e.g. in the downstream oil industry (Fabiano and Currò, 2012). Notwithstanding the use of risk assessment has become rather widespread and more decision making depends on it, as amply recognized the methodology produces still unsatisfactory results: choices, complexity, available computing time, limited knowledge and experience contribute all to unavoidable spread. Variance of outcomes of an analysis is high and can cover in some cases two orders of magnitude in risk, defined as the product of expected event frequency and likely damage. Many of the available consequence models are of the “integral” type, allowing many complex problems to be solved with limited input data. A specific cause of result spread is consequence modelling (release rates, evaporation, dispersion), while reliability of software forms a sector of science in itself (Pasman and Fabiano, 2008). Ditali et al. (2006) reported examples of how outcomes of pure physical models of release, vaporisation and dispersion can differ with at least a factor 2. Starting from it, in Table 1, some results are reproduced and updated with results modelled by EFFECTS 5.5 (TNO, The Netherlands) and PHAST, thus contributing to obtain an overall picture. Mean value and standard deviation are calculated as well, evidencing the significant output variability. The relative error of the near and far field estimation, by adopting suitable dispersion simulation, can be quantified in a first approximation as the sum of the relative error of the source term and of the dispersion model. In addition, damage probit parameters, based on dose-response rates obtained by experimental trials and actual accidents, are also object of much discussion. Furthermore, from one side the probit constants for a given toxic compound differ according to different authors, so that the extent of hazard range varies substantially (Fabiano and Pasman, 2010). From the other side, the knowledge of the fluctuations around the average concentration induced by turbulence is required for the accurate application of a toxicity model sensitive to the time dependence of the exposure.

Table 1: Hazardous substance loss of containment effect calculations with different integral models.

| Scenario   | Variable   | EFFECTS<br>4 | PHAST | GASP            | EFFECTS<br>5.5 | Mean<br>value | Standard<br>deviation |
|--|--|--------------|-------|-----------------|----------------|---------------|-----------------------|
| Toluene<br>confined pool                             | Max<br>evaporation<br>rate, [kg s <sup>-1</sup> ]                | 0.21         | 0.15  | 0.11            | 0.21           | 0.17          | 0.05                  |
| Toluene<br>unconfined pool                           | Max<br>evaporation<br>rate, [kg s <sup>-1</sup> ]                | 3.5          | 1.2   | 1.1             | 3.5            | 2.3           | 1.4                   |
|  | Max pool<br>area, [m <sup>2</sup> ]                              | 2005         | 995   | 1042            | 2000           | 1510          | 568                   |
| Scenario   | Variable   | DISPGAS      | PHAST | PHAST<br>6.53.1 | EFFECTS<br>5.5 | Mean<br>value | Standard<br>deviation |
| Dense gas<br>dispersion<br>(10%w/w H <sub>2</sub> S) | Vertical max.<br>distance to<br>100 ppm<br>H <sub>2</sub> S, [m] | 625          | 275   | 205-380         | 367            | 370           | 159                   |
|  | Horizontal<br>max. dist. to<br>100 ppm<br>H <sub>2</sub> S, [m]  | 150          | 205   | 215-400         | 372            | 268           | 111                   |

Even if minimizing hazards or fostering inherent safety based on the use of chemicals that reduce or eliminate hazards started already in the early 1980's and is nowadays applied also to non-conventional chemical processes (Fabiano et al., 2011), still large quantities of hazardous materials (HazMat) are continuously transported, stored and handled worldwide. Loss of confinement on storage tank, vessel or piping implies atmospheric dispersion of pollutants and, depending on the compound inherent hazard, requires considering the source term, local environment and meteorological parameters. As amply reported, the accidental release of a toxic compound into a residential area may pose acute and long term hazards in addition to tremendous public anxiety.

In this paper, we consider a real hazardous release of hydrochloric acid connected to an accidental loss of containment of an ADR tank truck. After a detailed characterization of the source term, we firstly applied a widely used integral approach, providing modelling for the combination of all physical phenomena involved after the release. The applicative phase of this work, representing its main appeal, is the validation of the simulation results against field data sets directly collected during emergency response activities, in the near field. More advanced modelling can be performed by means of a computational fluid dynamics method (CFD) to solve the Navier-Stokes equations, together with specific model equations. As expected, the CFD modelling allows obtaining more refined results, when compared with integral model outputs, clearly under the constraints of a larger amount of effort and computer time. Quantitative conclusions are drawn about the cross-check validation performed. The comparison based on experimental data evidence the ability and limitations of the adopted models in estimating the actual post-release gas behaviour, as well as the implications for hazard predictions that support decision makers in emergency planning and response. From the evidence of this study, in view of public health protection, the decision of evacuating or sheltering people potentially exposed to the chemical can be based, with enough reliability, on proper integral modelling, provided that the validation is limited to the near field and in the absence of local geometrical/orographic complications.

## 2. Case-study description

On January 19, 2007, in the first hours of the day, a tank truck carrying concentrated aqueous hydrogen chloride (30 % w/w) parked at a parking area just in the proximity of the exit toll of Rapallo (Highway A12 - Genoa District, Italy) started a low flow rate, continuous spilling, due to a loss of containment connected to a weld failure. The discharged liquid formed a pool, vaporizing and diffusing into the ambient atmosphere, transported by a light wind within an area of plain terrain. The emergency team of the Genoa Fire Brigade unit in connection with the Regional Protection Agency promptly responded and applied all technical measure to stop and contain the release. As a cautious approach, nearly 20 people in the lightly populated surrounding area were evacuated, mainly from caravans and trailers, while other residents were advised to shelter and stay inside their homes. The same sheltering measure was taken for a school in the neighbourhood. In the subsequent modelling inter-comparison, we used meteorological data from a nearby

station to run the models, so as to predict the average pollutant concentration, within the context of emergency planning.

## 2.1 Materials and Methods

Hydrogen chloride is a colourless gas with a pungent odour, and has a vapour pressure of 42,200 hPa at 20°C and a water solubility of 823 g/L at 0°C. Its aqueous solution (hydrochloric acid) possesses strong acidity, and reacts with most metals producing explosive hydrogen gas. Hydrogen chloride is readily dissociated in water into hydrated protons and chloride ion. The physico-chemical properties indicate that hydrogen chloride released into the environment is distributed into air and water. Hydrochloric acid can pose a moderate to severe risk to users due to its predisposition to emit significant amounts of HCl fumes even with moderately dilute solutions. Inhalation exposure to high concentrations of HCl fumes may result in coughing, choking sensation, burning of the respiratory tract, and pulmonary edema (Proctor et al., 1991). Short-term exposure to airborne concentration up to 1.8 ppm did not cause irritation to the respiratory tract of sensitive asthmatic volunteers (Stevens et al. 1992). The American Industrial Hygiene Association (AIHA) lists the Emergency Response Planning Guideline – 1 (ERPG-1) for HCl to be about 3 parts per million (ppm); the ERPG-1 is the highest concentration where a worker can be exposed to it for up to an hour and have no perceivable negative consequences acute or chronic. The AIHA lists the Emergency Response Planning Guideline – 2 (ERPG-2) for hydrochloric acid to be 19 ppm. The ERPG-2 is a measurement of the highest concentration at which 1 hour of exposure will not cause permanent or life threatening injury. Finally, the National Institute for Occupational Safety and Health (NIOSH) has set the Immediately Dangerous to Life or Health (IDLH) limit for hydrochloric acid at 48 ppm. The IDLH is the minimum level at which life threatening or permanently debilitating injuries would occur immediately on exposure (ACGIH, 2001). Gaseous samples were taken on a triplicate basis and analyzed by different techniques. We use chemical tubes (Dreager, Aqua Air Industries, Louisiana, USA) to carry out a preliminary air testing. In addition to personal sampling, fixed-point sampling was carried out at a number of positions to determine the concentration of hazardous substances in the air at these positions and to compare the performance of different methods for sampling HCl. It was hoped that the results would give an indication of the likely inter-comparability of results obtained by the different methods. Airborne hydrogen chloride samples were collected according to the method n° 7903 (inorganic acids) (NIOSH, 1994) using a treated silica gel tube at a flow rate of 0.5 L/minute and subsequent analysis by ion chromatography. Each analysis was made in triplicate with the median of HCl measurements performed by the two methods not dissimilar especially in the immediate proximity of the source term.

## 2.2 Integral model comparison

The well-known ALOHA program (Areal Location of Hazardous Atmospheres) developed in USA with first publication in 1989, is primarily intended for emergency planning and is developed on the basis of well established sub-models. In order to properly apply the model to the considered release it was adopted a sequential procedure making reference as starting point to the partial pressure of aqueous solutions of hydrogen chloride calculated starting from the experimental data reproduced in Figure 1.

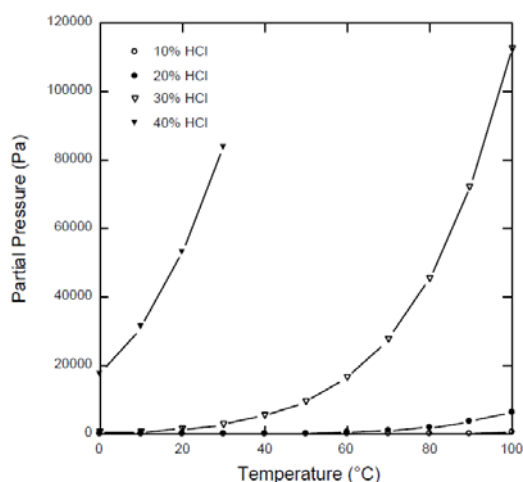


Figure 1: Partial pressure of different solutions of hydrochloric acid (w/w) as a function of the temperature.

Starting from the accidental event, we considered as the source term a circular pool resulting from field observation and proper definition of the pool spread according to Webber (1990). Following local and meteorological conditions were considered, according to BNL (Brookhaven National Laboratory):

wind speed: 5 m/s

ground temperature: 293 K

atmospheric stability: class D

relative humidity: 50%

surface roughness: rural type

cloudy conditions.

The evaporation rate was calculated adopting eq. (1) (Kawamura and Mackay, 1985):

$$E = AK_M \left( \frac{M_W P_V}{RT} \right) \quad (1)$$

where:

E = evaporation rate kg/s;

$P_V$  = vapour pressure, Pa

A = pool area,  $m^2$ ;

R = universal gas constant, 8314 J/kmol K;

$M_W$  = molar mass (HCl = 36.5 kg/kmol);

T = temperature, K.

The mass transport coefficient of hydrochloric acid  $K_M$  [m/s] was evaluated according to eq. (2) (Mackay and Matsugu 1973):

$$K_M = 0.0048 u^{7/9} Z^{1/9} Sc^{-2/3} \quad (2)$$

where:

u = wind velocity at 10 m, m/s;

$Sc = \nu/D_M$

Z = pool diameter, m;

$\nu$  = air kinematic viscosity,  $m^2/s$ ;

The diffusivity in air,  $D_M$  [ $m^2/s$ ] is evaluated by eq (3), (Thibodeaux 1996), starting from the water diffusivity

$D_{H_2O} = 2.4 \cdot 10^{-5} m^2/s$  at 281 K ,

$$D_M = D_{H_2O} \sqrt{\frac{M_{W H_2O}}{M_{WM}}} \quad (3)$$

The second integral model utilized was EFFECTS 5.5, mainly based on the well-known Yellow Book (TNO, The Netherlands). The employed sub-model allowed direct evaluation of the dispersion from the evaporating pool. In addition, we performed also a calculation of the spread of hydrochloric liquid on ground, utilizing the suggested Webber model, solving a self similar pool surface profile. Comparing experimental evidence with calculated pool spread it was evidenced an overestimation by a large factor (ca. 30 %) of the pool spreading, even in the rather simplified geometry here considered. As a general observation, when dealing with small spills, the momentum of the falling liquid can become the driving factor in determining the spreading.

### 3. Results and discussion

It must be observed that the theory of pool evaporation adopted by the utilized models do not take into account the reduced vapour pressure of hydrophilic compounds in water.

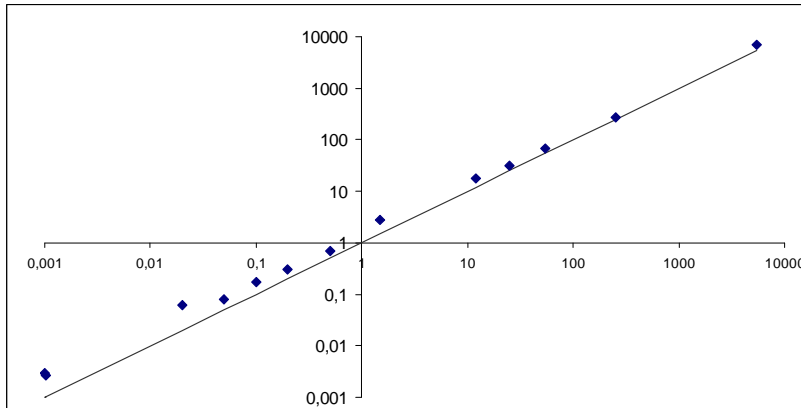


Figure 2: Correlation between atmospheric concentrations of hydrochloric acid experimentally obtained and calculated by ALOHA.

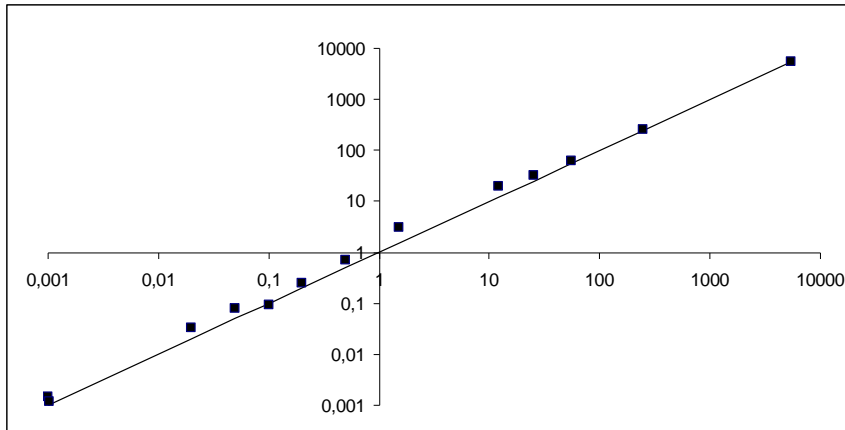


Figure 3: Correlation between atmospheric concentrations of hydrochloric acid experimentally obtained and calculated by EFFECTS 5.5.

So the utilization in case of strong acid aqueous solutions can introduce significant uncertainties when performing a QRA study. In case of small spill and to the purpose of emergency planning the results summarized in visual graphs of immediate readability evidence a fairly good agreement between calculated and experimental data. An overall high degree of correlation between experimental results obtained by on-site sampling and calculated values for both approaches is clearly evidenced in Figures 2 and 3. In Figure 4, an overall high degree of correlation ( $R > 0.99$ ) in the near-field evaluation between the two modelling approaches is evidenced, in connection with the explored small liquid release, during HazMat transportation. Figure 5 shows the relative error between predictions and experimental concentrations detected in the near field, up to a distance corresponding to a value lower at least by an order of magnitude than ERPG-1.

Experimental data are compared also with results obtained by the short range dispersion model ADMS 5 (Cambridge Environmental Research Consultant Ltd., UK), describing the boundary layer by the well-known boundary layer height and Monin-Obukhov length. One can notice that the maximum error corresponds to a distance of nearly 100 m, for all the tested simulation models. In any case, the integral models allow obtaining conservative estimates of airborne concentrations, globally within the range of experimental uncertainty, at least in the limited time and spatial scale here explored. In case of a detailed QRA study, including a range of risk reduction measures, a more advanced and accurate approach is possible, starting from an integral or analytical model and combining it, at a second level of refinement, with computational fluid dynamics modelling, appropriately tuned with experimental data.

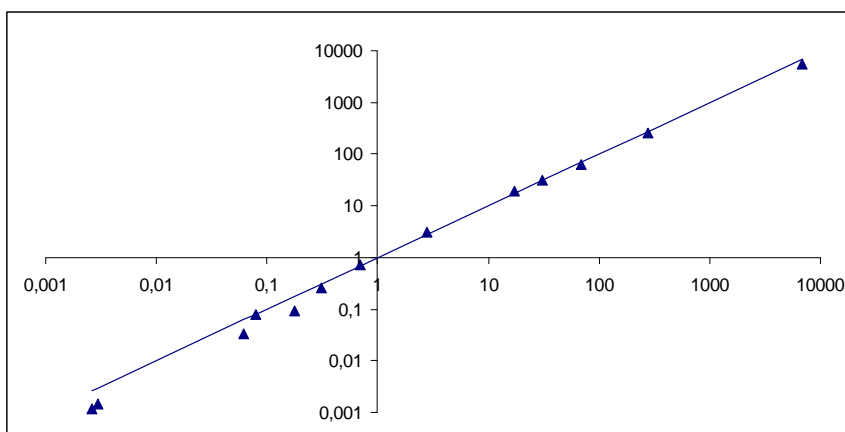


Figure 4: Correlation between hydrochloric acid atmospheric concentrations in the near field, calculated by the integral models ALOHA and EFFECTS 5.5.

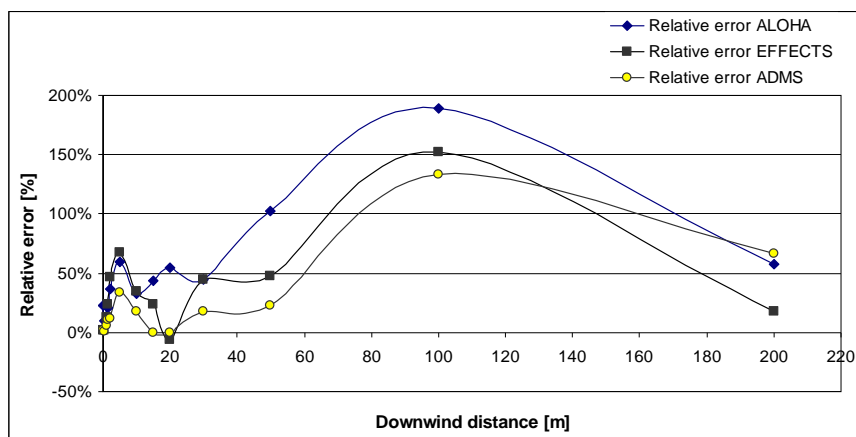


Figure 5: Relative percentage error between experimental and calculated data by the two selected integral models and by ADMS model.

#### 4. Conclusions

The investigated small HCl spill scenario would lead to limited impact on emergency units, or nearby population, since concentration levels stay below critical threshold at distances as low as two hundred meters. The tested approaches predict conservatively the consequences of the atmospheric toxic release in the short range. The approaches can help decision-makers to prepare recommendations for emergency response support and consequent evacuation or sheltering decisions, without resorting to more complex and time expensive modelling, e.g. CFD.

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