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

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In this paper, after a critical review on QRA uncertainties connected to consequence modeling, we consider an hazardous release of hydrochloric acid following an accidental loss of containment of a tank truck. After the source term characterization, we made a comparison of consequence results among different 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. Quantitative conclusions are drawn about the cross-check validation performed. At last, we provide some numerical examples on the proper model choice for atmospheric dispersion studies, depending on their main purpose.

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. In a first approximation, the relative error of the near and far field estimation, by adopting suitable dispersion simulation, can be quantified 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. 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.

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

Scenario	Variable	EFFECTS 4	PHAST	GASP	EFFECTS 5.5	Mean value	Standard deviation
Toluene confined pool	Max evaporation rate, [kg s^{-1}]	0.21	0.15	0.11	0.21	0.17	0.05
Toluene unconfined pool	Max evaporation rate, [kg s^{-1}]	3.5	1.2	1.1	3.5	2.3	1.4
	Max pool area, [m^2]	2005	995	1042	2000	1510	568
Scenario	**Variable**	**DISPGAS**	**PHAST**	**PHAST 6.53.1**	**EFFECTS 5.5**	**Mean value**	**Standard deviation**
Dense gas dispersion (10%w/w H_2S)	Vertical max. distance to 100 ppm H_2S, [m]	625	275	205-380	367	370	159
	Horizontal max. dist. to 100 ppm H_2S, [m]	150	205	215-400	372	268	111

Loss of confinement of storage tank, vessel or piping implies atmospheric dispersion of pollutants and, depending on the substance 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, starting from previous work of the authors (Vairo et al., 2013), 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 consists in the validation of the simulation results against field data sets directly collected during emergency response activities, in the near field. 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. Some numerical examples on the appropriate choice of the atmospheric dispersion model, in dependence of the issue to be tackled, are provided.

2. Case-study description

On January 19, 2007, in the first hours of the day, a tank truck transporting 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 in the lower section of the tank. 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 measures 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, characterized by a vapour pressure of 42,200 hPa at 20°C and a water solubility of 823 gL^{-1} 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 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).
The partial pressure of aqueous solutions of hydrogen chloride can be easily calculated starting from the experimental data reproduced in Figure 1.
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.

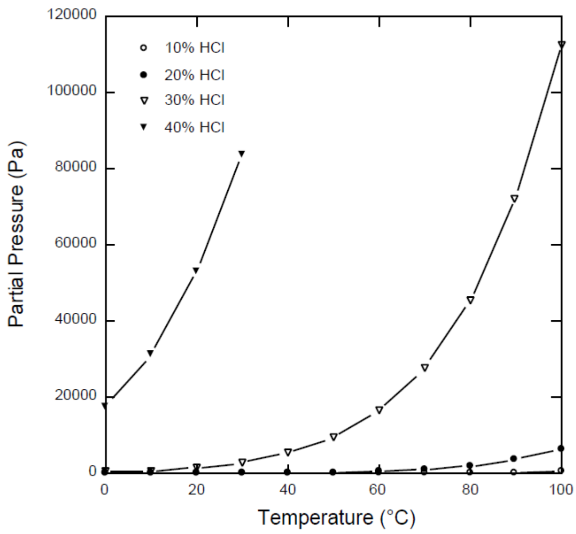

Figure 1: Partial pressure of different solutions of hydrochloric acid (w/w) as a function of the temperature.

2.2. Theoretical basis of model comparison

Computer models for atmospheric gas dispersion have been available for long time and are intended over space scales up to about 50 km from the release location.
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 experimental data depicted in the above mentioned Figure 1.
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 ms^{-1}
atmospheric stability: class D
surface roughness: rural type
ground temperature: 293 K
relative humidity: 50%
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^{-1};
A = pool area, m^2;
M_W= molar mass (HCl =36.5 kg $kmol^{-1}$);
P_V = vapour pressure, Pa
R = universal gas constant, 8314 J $kmol^{-1}K^{-1}$;
T = temperature, K.

The mass transport coefficient of hydrochloric acid K_M [ms^{-1}] 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, ms^{-1};
Z = pool diameter, m;
$S_C = vD_M^{-1}$
v = air kinematic viscosivity, m^2s^{-1};

The diffusivity in air, D_M [m^2s^{-1}] is evaluated by eq (3), (Thibodeaux 1996), starting from the water diffusivity D_{H2O} = 2.4 · 10^{-5} m^2s^{-1} at 281 K ,

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

The second dispersion model utilized in the comparative study was the Atmospheric Dispersion Modelling System (ADMS 5) utilizing current understanding of the structure of the atmospheric boundary layer. For calculations over flat terrain, like the investigated one in this case-study, the ADMS boundary layer properties are defined in terms of the Monin-Obukhov length, the boundary layer height and surface roughness (Carruthers et al., 1994), rather than in terms of the single parameter Pasquill-Gifford class (as adopted by ALOHA and EFFECTS). Dispersion under convective meteorological conditions uses a skewed Gaussian concentration distribution (shown by validation studies to be a better representation than a symmetrical Gaussian expression). Just as an example of the capabilities of ADMS 5, Figures 2 and 3 respectively show the 3D wind fields numerical simulation and the average ground level concentrations of a neutrally buoyant gas from stationary point source (elevated single stack).

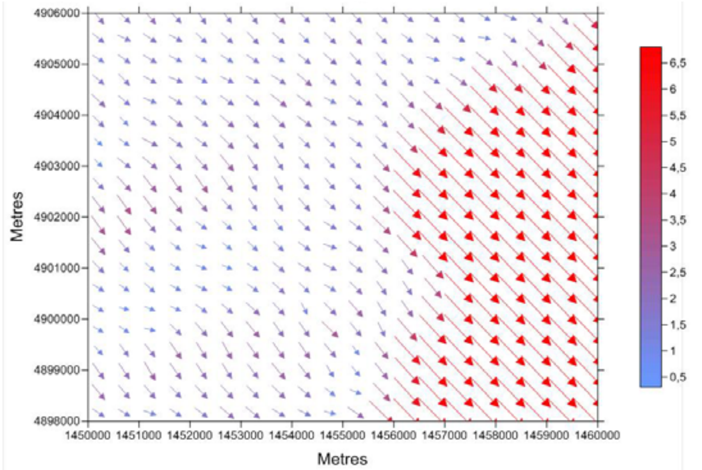

Figure 2: Example of 3D Wind Field in ADMS 5.

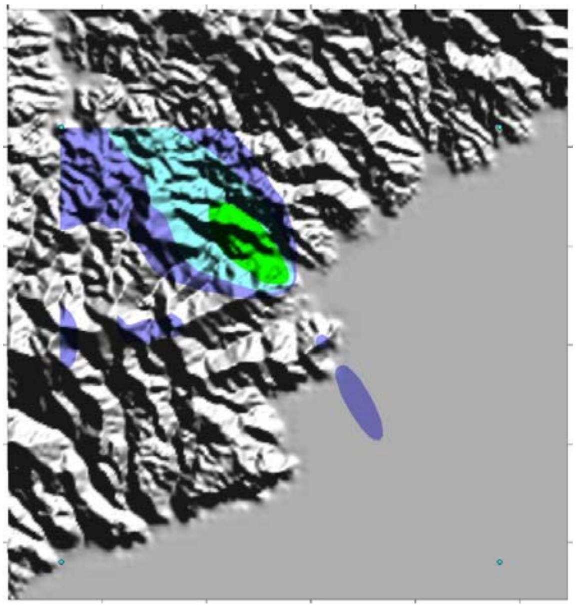

Figure 3: Example of Output in ADMS 5.

The last modelling package utilized in the comparison was EFFECTS 5.5 that is mainly based on the well-known Yellow Book (TNO, The Netherlands). This integral model allows calculating the physical effects of any accident scenario involving toxic and/or flammable chemicals. Contours of effects like overpressure and heat radiation and consequences like lethality and structural damage, provide information for hazard identification, safety analysis, quantitative risk analysis (QRA) and emergency planning. The whole chain of the considered real loss of containment scenario was modeled from the initial release, through the direct evaluation of the dispersion from the evaporating pool, to the end effects in terms of toxic dose results. 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

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. So the utilization in case of strong acid aqueous solutions can introduce significant uncertainties when performing a QRA study. In the explored case of a small spill and to the purpose of emergency planning, the results summarized in visual graphs of immediate readability demonstrate a fairly good agreement between calculated and experimental data.

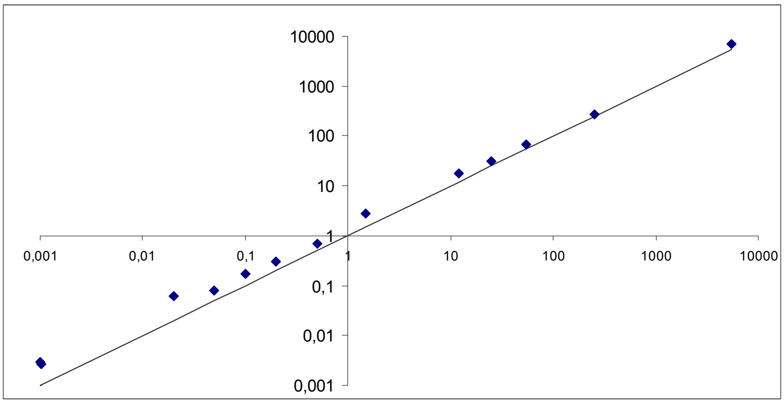

Figure 4: Correlation between atmospheric concentrations of hydrochloric acid experimentally obtained and calculated by ALOHA.

An overall high degree of correlation between experimental results obtained by on-site sampling and calculated values for the two first modelling approaches is clearly evidenced in Figures 4 and 5. In Figure 6, an overall high degree of correlation (R>0.99) in the near-field evaluation between ALOHA and EFFECTS 5.5 is evidenced, in connection with the explored small liquid release, during HazMat transportation. Experimental data are compared also with results obtained by the last version of the short range dispersion model ADMS 5 (Cambridge Environmental Research Consultant Ltd., UK) in Figure 7. This comparison evidences for the three models 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. 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. As a conclusive remark on results, 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.

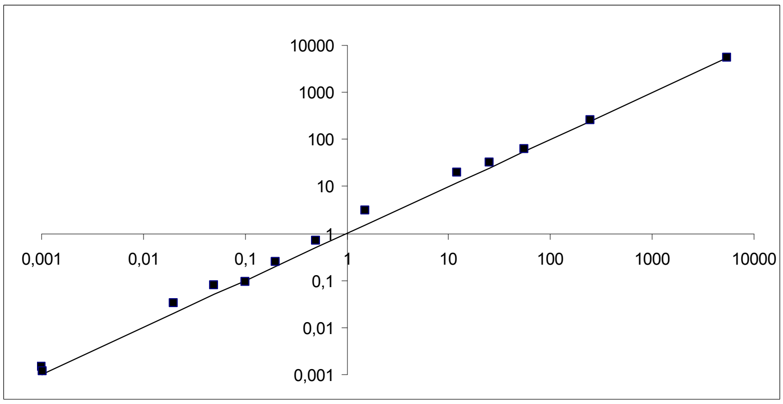

Figure 5: Correlation between atmospheric concentrations of hydrochloric acid experimentally obtained and calculated by EFFECTS 5.5.

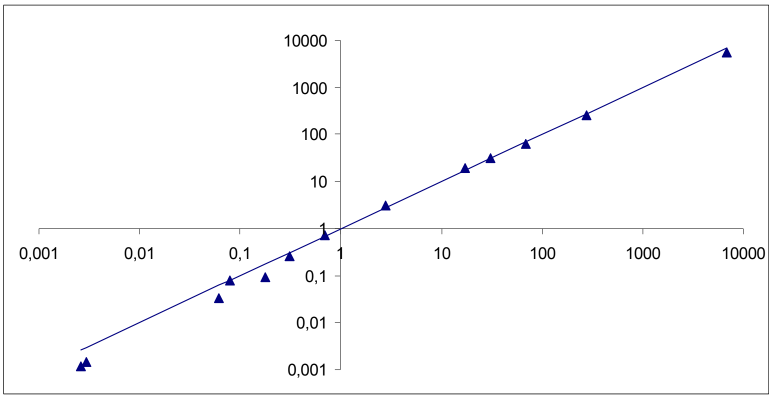

Figure 6: Correlation between hydrochloric acid atmospheric concentrations in the near field, calculated by the integral models ALOHA and EFFECTS 5.5.

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. 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.

4. Discussion

Starting from the comparison of the potentialities of the integral models in the representative case study, in the following we present some examples of the appropriate model selection for normal atmospheric dispersion studies, depending on the main scope of the study. Generally speaking, the modelling approach is able to provide answers to describe the dispersion of one species into another and the models can be used in forecasting (meteorology, for example, but also the dispersion of pollutants as a result of accidental releases), or for purposes of planning (mapping the fallout from industrial sources), or emergency response. As previously illustrated, the most common approach used for neutrally buoyant gases is the Gaussian dispersion equation for continuous releases, (ALOHA and EFFECTS 5.5 adopt a modified form of this equation) that can be effectively used in near-field evaluation, or short term, due to the standard Gaussian representation.

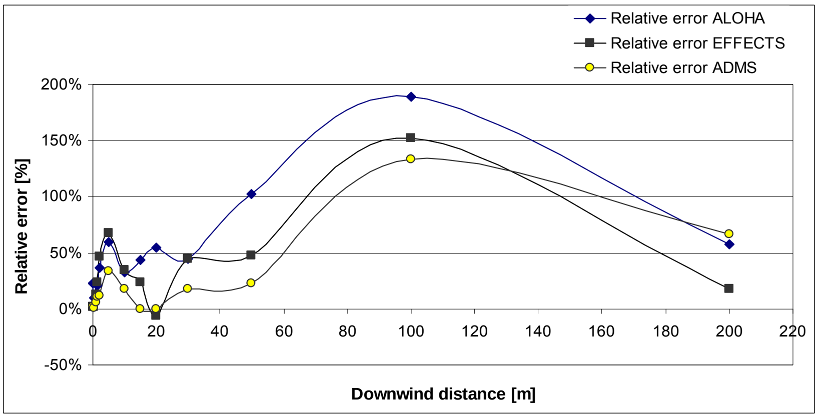

Figure 7: Relative percentage error between experimental and calculated data by ALOHA, EFFECTS 5.5 and by ADMS 5 model.

A first applicative example, Figure 8 shows the evaluation of the emission from the chimneys of merchant ships, where the previously mentioned skewed Gaussian model ADMS 5 model was used. The focus of the dispersion calculations is to verify ambient concentrations arising from ship emissions during port transit, for potential long-term human health and ecological reasons. It must be evidenced that for such an application the skewed Gaussian representation offers a high degree of application flexibility, as it can be effectively used in both short and long term calculations, as well as in performing near and far field evaluations, up to distances some ten kilometres from the source. However, we must remark that the tested atmospheric dispersion packages are not able to assess precisely the local effects of complex geometries, such as buildings on the flow fields and turbulence.
A second application is provided by an estimate of the consequences of a possible accident event in the railway station Doria Park (Savona, Italy), where railcars carrying chlorine to a nearby industrial plant are temporarily parked in horizontal cylindrical tanks characterized by a diameter of 2 m and a length of 12 m, with an average utilized storage volume of 45% and a total inventory of 24,000 kg. Calculations were performed by means of the already mentioned ALOHA model (EPA), which utilizes the Cox-Roe methodology for dense gases.
Two highly conservative loss of containment scenarios, as a consequence of an accidental impact and consequent medium size leak were simulated:

- Failure of the top of the tank (release from the top - gas phase).
- Failure of the lower part of the tank (release of aerosol - two phases).

Given the purpose of these simplified scenarios, addressed to the evaluation of emergency unplanned releases, and owing to the absence of possible impinging on walls or equipment, any rainout effect is not considered.
Each scenario was evaluated in terms of stability class D and F with wind velocity of 10, 5, 0.6 ms^{-1}. Results were evaluated considering following chlorine threshold values of the American Industrial Hygiene Association (AIHA): IDLH: 10 ppm; ERPG-2: 3 ppm and ERPG-1: 1 ppm. The calculation is primarily intended for emergency planning, without any range of risk reducing measures, so that the modelling tends to be deliberately over conservative, as it can be argued from Figure 9. In any case, this simulation shows the real effectiveness of ALOHA package also in short term evaluation, in addition to its ability for a proper representation of the near-field effects demonstrated in the previous field verification, connected to a real truck accident.
The last example, shown in Figure 10 is a long term evaluation of the emissions from a fossil fuel power station, where a more refined Lagrangian model (Safe-Air II) was used.

Figure 8: NO_x dispersion contours obtained by ADMS 5 model.

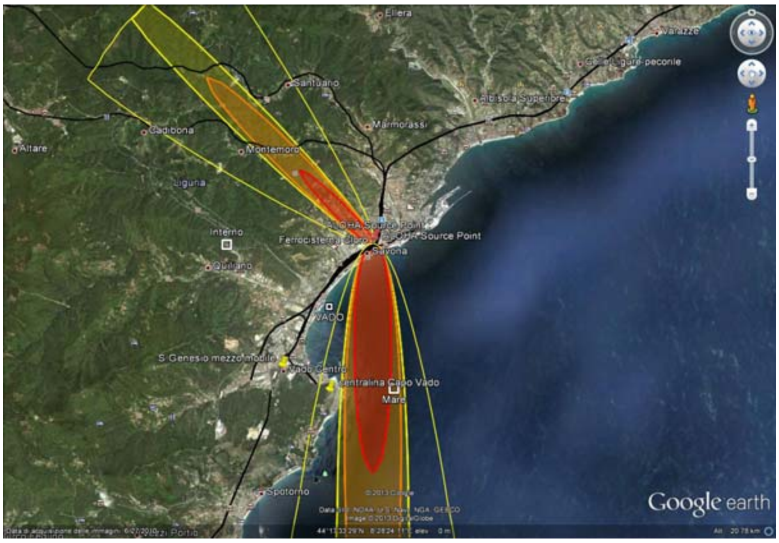

Figure 9: Chlorine dispersion scenarios following an accidental tank failure.

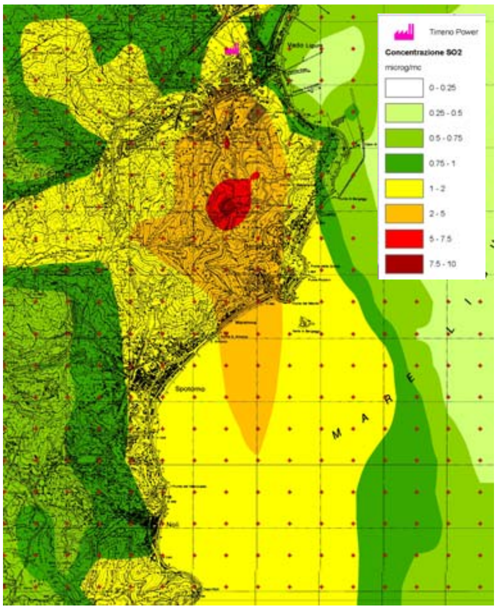

Figure 10: SO_2 dispersion contours obtained by Safe-AirII package.

The Lagrangian model can be effectively used for long-term evaluation and far-field dispersion; validation against field monitoring observations has confirmed that, in particular in the absence of geometrical complications, the predictions of the model are in reasonably agreement with experimental data resulting from the monitoring network.

5. Conclusions

The validation has confirmed that in particular under conditions of “quasi flat terrain” and in the near field, the tested atmospheric packages are in fairly good agreement with experimental observations. The maximum error corresponds to a distance of nearly 100 m, for all the considered 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. Also, in this near-field study, a more complex and refined model such as ADMS 5, describes the case in a more accurate way, even without including a complex terrain geometry, due to the near-field effects. ADMS 5 shows a high level of accuracy, even in comparison with the CFD most widely used, so it can be suitable for more detailed QRA studies. The tested approaches predict conservatively the consequences of the atmospheric toxic release in the short range and 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. 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. Clearly, CFD modelling allows obtaining more refined results, when compared with integral model outputs, under the constraints of a larger amount of effort and computer time. A further 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.

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