

CHEMICAL ACCIDENT PREVENTION & PREPAREDNESS

Major accidents having significant impact to the environment

The aim of the bulletin is to provide insights on lessons learned from accident reported in the European Major Accident Reporting System (eMARS) and other accident sources for both industry operators and government regulators. In future the CAPP Lessons Learned Bulletin will be produced on a semi-annual basis. Each issue of the Bulletin focuses on a particular theme.

Summary

This bulletin follows a slightly different approach in the analysis of accident reports to the previous two issues, due to the uniqueness of the topic. Prior bulletins have focused on accidents with common causal factors. In this particular bulletin, the aim is to study a set of accidents with a similar impact, that is, significant environmental damage. Identifying such accidents for study therefore sometimes involved additional research just on consequences to ascertain whether its environmental impact was sufficiently high to be included in this study. In addition, it was considered that the precise nature of the impact might also be of some interest.

Included in the bulletin is an accident caused by a malicious act that resulted in a significant release of liquid hydrocarbons from an oil depot. In principle intentional acts are not considered major accidents in the context of the Seveso Directive. Nonetheless, this accident was selected because it contained lessons learned also applicable to prevention of Seveso major accidents. In addition, this issue also includes one so-called Natech event, a natural hazard triggered industrial accident, that also had a major impact on the environment.

Please note:

The accident descriptions and lessons learned are reconstructed from accident reports submitted to the EU's Major Accident Reporting System

<https://emars.jrc.ec.europa.eu>
or <http://emars.jrc.it>

as well as other open sources. EMARS consists of over 800 reports of chemical accidents contributed by EU Member States and OECD Countries.

Accident 1

General chemicals manufacture

Sequence of events

A factory unit that packs and stores swimming pool and water treatment chemicals was completely destroyed by fire with resulting water body contamination and a large plume of smoke. The fire started in the production area at the back of the factory unit. A 1 t bulk bag of sodium dichloroisocyanurate dihydrate was being emptied by closed screw conveyor from ground level to holding hoppers at mezzanine floor level. The chemical was then used to fill small plastic containers, under gravity, for retail. The electric motor driving the screw conveyor was located above the holding hoppers.

The equipment had been running for about an hour, and was left running while the operators went on a break, as it had automatic level switches which would switch off the auger when the hoppers were full. Witnesses reported smoke seen rising from the auger tube of the screw conveyor. The smoke was followed by a 20 m high fireball. Due to the speed of the development of the fire, chemicals (with a pH of 1) entered into the nearby river following the rupture of IBC (intermediate bulk container) containers before emergency bunds were in place. The factory unit involved in the incident was completely destroyed but no human injury was reported.

Causes

The fire appears to have started inside the polypropylene tube of the conveyor, probably due to the unintentional mechanical heating (for reasons unknown) of the sodium dichloroisocyanurate dihydrate when it reached thermal decomposition temperature. Once at decomposition temperature, the chemical, which is an oxidiser, is self-reactive and generates heat. The polypropylene tube would have been heated until it started to deform and melt, mixing plastic with the oxidiser, leading to flaming combustion of the plastic. No forensic evidence has been available to identify with certainty the method of rapid fire spread or cause of fireball as yet.

Important findings

- Mitigation measures to prevent the run off into nearby water bodies appear to have been inadequate.
- Intermediate bulk containers of hydrochloric acid and other chemicals, which were stored in the yard area immediately adjacent to the factory building, were damaged by the fire and released their contents, which may have been one of the sources of water contamination.

Environmental impacts

- The pollution of the river was classed by the Environment Agency as Category 1 (incident having a major environmental impact) under their Common Incident Classification Scheme.
- More than 2500 fish were killed over a 6 km stretch of the river.
- It is estimated that the river would take 4 to 7 years to return to pre-incident condition.

Lessons learned

- The operator should be aware of the layout of the drainage system and how their inventory could get into the watercourse.
- Separation of chemicals in warehouses, reduction of the size of their fire compartments are advisable in order to mitigate the consequences of an accident.
- Prevention of fire is not always efficient also to prevent secondary (e.g. environmental) consequences.
- The UN classification of the sodium dichloroisocyanurate dihydrate does not appear to give an accurate description of the reactive nature of the chemical and possible hazardous conditions. Under the classification system it is not classified as a Division 4.1 self-reactive because it has oxidising properties. If it were classified as a self-reactive it would be limited to transport in packages of 50 kg or under, rather than be available as it is in 1000 kg FIBC (flexible intermediate bulk container) 'big bags'.

[EMARS Accident # 534.]

(Continued on page 3...)

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KEYWORDS

Environmental impact

Pollution

Watercourses

Fire water run-off

Contamination

Natech

Rivers

Upstream

Toxic plume

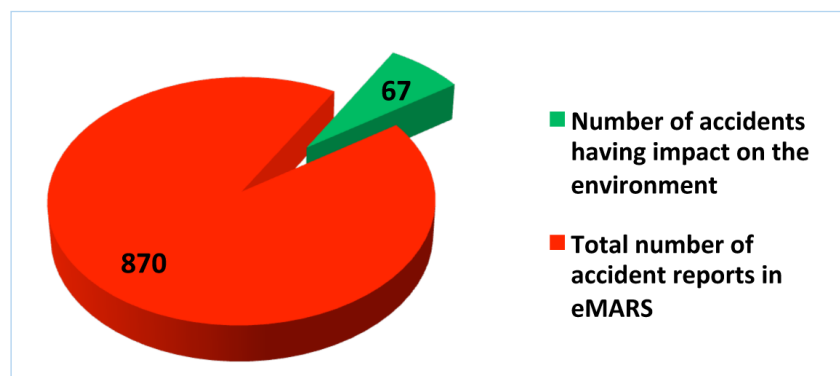
Contaminated fire water

Mitigate consequences

Common factors

Given the uniqueness of environmental consequences for each case, no summary describing the range and type of environmental damage is possible. However, it is possible to derive some common elements in regard to the environmental impacts of these accidents as follows:

- For example, 48 accidents (80%) occurred near water resources, which were heavily contaminated as a result of the accident. Moreover, this impact effects was both immediate and direct.
- Another notable commonality is that in such cases operators of the involved establishments were not or were hardly able to stop the contamination of the aquatic environment (rivers, sea) or mitigate the consequences, either because they did not recognize the loss of contaminant in time to stop the flow or they did not have adequate means to suppress the release once it had started.
- Accident reports often indicated an insufficient and/or failure to adopt appropriate procedures for identifying and mitigating risks connected with the environmental consequences in the risk assessment.
- In some cases the pollution was caused due to contaminated from fire water run-off (EMARS Accident # 803, # 157, # 167, # 529 and # 563). In some cases there was no knowledge from the management side that a drainage system was directly connected to a nearby water body, instead of being separated from it.



Major accidents with significant impact on the environment in eMARS

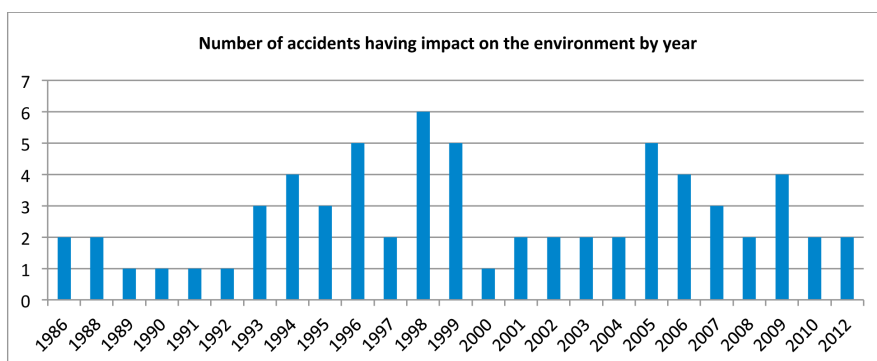
Major accidents with significant impact on the natural environment

In preparing this bulletin, over 60 eMARS accident reports relating to environmental issues were studied. Out of these reports, a definitive set of cases was identified composed of accidents demonstrated to have led to measurable pollution to different environmental receptors, such as water and soil, often contaminating them over large areas.

As it is illustrated in the pie chart below, around 7% of the total accident reports in the eMARS major accident database have been identified as causing minor or major impact on the environment. In the majority of these cases natural water bodies, e.g. rivers, dikes or the sea, were polluted via the direct connection of the drainage system to the environmental components or due to the release of the fire

extinguishing water used for rescue operations. Approximately 80% of these cases demonstrate that escaping dangerous substances may easily reach a nearby water resource. For instance, an environmental release might occur if storage tanks are not surrounded by bunds or even if they are, the bund is not designed to collect the fire water or be resistant to heavy rainfall.

The bar graph below shows that major accidents with environmental consequences continue to occur with a regular frequency over the last 25 years and there is no particular historical trend.



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Accident 2 Petrochemical

Sequence of events

While loading an oil tanker at the refinery wharf, a corroded pipe began to leak and 478 t of cargo fuel oil spilled, of which 180 t flowed into the nearby river. A presence of hydrocarbons on the water surface was observed by a person on a barge who triggered the alarm. The leak itself was only detected 5 hours later by a rounds man who identified and isolated the leak at 500 m upstream from the point that the hydrocarbons were detected. As a precautionary action, subsequent to the spill, public access restrictions to several beaches and fishing prohibition in the river estuary were issued. Over 750 people were involved for three and a half months in cleaning up the 90 km of polluted banks (6170 t of waste was recovered and stored on-site before disposal).

Causes

The defective pipeline, 12 inches (~300 mm) in diameter and lined with thermal insulation, forms part of a pipe-rack composed of some 20 pipes on two levels. An examination of the defective pipe section revealed the presence of a longitudinal crack approximately 16 cm long by 1 cm wide adjacent to the observed local corrosion underneath the thermal insulation lining. Water flowing from a perforated pipe, positioned vertically above the fuel oil pipeline, infiltrated under the leaky thermal insulation layer, first causing the steel to corrode and then perforating the pipe.

Important findings

- A pipe verification and maintenance programme was adopted for the refinery in accordance with a procedure developed and designed to establish the various inspection and maintenance frequencies depending on the type of pipe configuration and potential vulnerabilities. The importance of specific maintenance works on the pipe where the leak occurred was however poorly evaluated in this programme, despite a number of

warning signs during the preceding months on this particular group of pipes and despite the potentially serious consequences of an accident affecting one of these pipes given the proximity to the riverbank.

- The lack of an adequate feedback system from the tank to the control room to indicate the tank level during uploading was one of the most important causes of the accident. The control room remained unaware for several hours that the fuel was not reaching the tank.

Environmental impacts

- Due to the effect of tides and currents, the 180 t of fuel oil dispersed onto the northern and southern shores of the river estuary.
- A high number of bird deaths was caused by this contaminating spill throughout the entire area.
- Several tonnes of dead animals were recorded over the days following the accident.

Lessons learned

- The last inspection of the leaking pipeline dated back 4 years prior to the accident. Inspection and monitoring of the pipeline should have been carried out more frequently.
- No visual surveillance or regular sampling of the water and/or the surrounding area was executed which might have been effective to detect hydrocarbons release in due time before the accident occurred.
- There was no safety barrier installed that could have blocked or slowed down the intensity of the hydrocarbons flowing towards the river.
- Operators in the control room should be sure that what is being sent to the tank is actually going into the tank (e.g. a level control system).

[EMARS Accident # 701]

More information: <http://www.aria.developpement-durable.gouv.fr/IMPEL-2009--5438.html>
Effects of water pollution by hydrocarbons: <http://www.aria.developpement-durable.gouv.fr/CD-rom-250-fiches--7211.html> No. 56-2

TIPS

If a dangerous establishment is placed close to water resources, the operator must be sure that the drainage system does not let dangerous substances escape into those water bodies directly.

Risk assessment should take account of potential extreme weather phenomena and their consequences.

Operators need to consider potential environmental releases in the safety management system, e.g., in maintenance planning, inspections and feedback on findings of audits.

Safety barriers should be established to mitigate the consequences where there is potential for a major spill.

Seveso authorities should continue to monitor dangerous industrial activities during the entire life cycle of a process unit from design (when possible) to decommissioning. Progressive decommissioning of an installation may eventually incur a reduction in the level of attention from the site operator in particular if the Seveso Directive ceases to apply.

When a potential accident trigger is newly identified (e.g., inundation by flood waters, security threat, etc.), the operator should consider recalculating the risk to the establishment.

For some sites, there are preventive measures that should be automatically considered to avoid a major release to the environment. For example, separation of chemicals in warehouses and reduction of the size of their internal fire compartments is advisable in order to mitigate the consequences of an accident.



The unit involved in the accident (source: ARIA No. 34351 and Gendarmerie Nationale)

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Accident 3 Production and storage of pesticides, biocides, fungicides

Sequence of events

A fire started in a pesticide warehouse where approximately 1350 t of agricultural pesticides and chemicals were stored. Shortly after midnight, a worker on site detected a fire in the warehouse and alarmed the fire brigades. Around 400 firemen were deployed to fight the fire and protect the other warehouses nearby. The flames had consumed a third of the 4500 m² hangar in just a few minutes. The warehouse was completely destroyed by the fire.

A threatening plume spread over the agglomeration of Basel and a runoff of the major part of the 10000 – 15000 m³ water used for fire fighting, heavily contaminated, reached the river Rhine with around 30 t of very toxic pesticides. The main contamination of the Rhine was due to organophosphate pesticides such as Disulfoton, Thiometon, Etrimphos and Propetamphos. Also fungicides containing mercury were released.

Causes

The causes of the accident were reconstructed by the investigators as being most likely due to the plastic film shrink wrapping of palettes of Prussian Blue (Source: Humi, B. (Amt für Umweltschutz und Energie, Kantons Basel-Landschaft, Liestal, Schweiz - The Sandoz accident, in Organic Micro pollutants in the Aquatic Environment, Proceedings of the Fifth European Symposium, Rome, Italy, October 20-22, 1987, pp 128-131 DOI:10.1007/978-94-009-2989-0_19, Pub. Springer 1988). The fire probably smouldered undetected for several hours before breaking into flame. The speed with which the fire developed meant that the foam extinguishers were not effective and that large amounts of water were used (400 litres per second). In addition to trying to extinguish the fire in the warehouse the fire brigade was also trying to ensure that a neighbouring warehouse containing metallic sodium was cooled and at the same time the sodium did not come into contact with water.

Important findings

- The International Rhein Alarm was issued at 3 am. However there was some confusion in the communication and it took until 23:40 for the written communication to reach Strasbourg.

- Water intakes on the left bank between Basel and Strasbourg were not closed in time.
- There was weak legislation in place at that time for preventing catastrophic releases of dangerous substances (Ordinance on Protection against Major Accidents, MAO; http://www.admin.ch/ch/e/rs/c814_012.html).

Environmental impacts

- The river Rhine was seriously polluted and colored red on a stretch of 250 km. The marker dye "Rhodamin B" meant that the contamination was readily visible due to the red colouration.
- Within 10 days the pollution had travelled the length of the Rhine and into the North Sea.
- An estimated half a million fish were killed, and some species were wiped out entirely.
- All water suppliers along the Rhine up to the Netherlands stopped pumping water for drinking water generation for up to 18 days.
- The lack of adequate fire-water retention systems as well as surface water drainage from the site into the Rhine rapidly led to a major contamination of the river water.

Lessons Learned

- Chemicals in warehouses should be adequately separated, the size of fire compartment should be reduced.
- Warehouses close to natural water resources should consider the possibility of secondary (e.g. environmental) consequences.
- There is a need to manage fire water and define fire-water retention volumes, taking account of the likely nature of the contamination (pH, toxicity, flammability, etc).
- The need for timely and effective alarm systems, which ensure that the correct information is provided to downstream communities, thus allowing them to take appropriate action.

[EMARS Accident # 803. See also EMARS Accident # 48 and # 563.]

Similar events:

- ANAVERSA plant accident in Cordoba, Mexico 1991
- Spill in the Songhua River (http://en.wikipedia.org/wiki/2005_Jilin_chemical_plant_explosions <http://homepage.env.dtu.dk/stt/teaching/Example%20for%204%20page%20homework.pdf> http://www.unep.org/PDF/China_Songhua_River_Spill_draft_7_301205.pdf)

More information on managing fire water spillages:
<http://a0768b4a8a31e106d8b0-50dc802554eb38a24458b98ff72d550b.r19.cf3.rackcdn.com/pmho600bbud-e-e.pdf>
Fire water run-off containing PFOS lead to large scale ground water contamination as a result of the fire and explosions at Buncefield (<http://www.buncefieldinvestigation.gov.uk/reports/index.htm#final>)

Accident 4 Fuel storage

Sequence of events

In the early morning hours of 23 February, 2010 there was a huge spill of mineral oil at a fuel storage, caused by an intentional action. About 2600 t of a mixture of hydrocarbons, diesel fuel and heavy fuel oil were released from the pipes of the loading docks of the plant. From that point, after reaching the treatment plant of the neighbouring town through the main sewer, the product was discharged into the nearby river Lambro, causing major contamination of that river as well as the river Po downstream

Causes

The release of hydrocarbons occurred at a loading arm located on loading docks for diesel and heavy fuel oil, and directly connected with an additional tank in the fuel depot. The released substances, collected by the sewage system inside the plant, migrated towards the API oil separator overflowing it. Part of the products flowed in the oil separator directly from the yard of the depot bypassing mitigation barriers due to the high level of saturation. Subsequently, the substance drained from the pool separator through the main valve, which was kept permanently open to allow discharge of waste water from an hydraulic barrier as a remediation measure, to the sewer outside the plant. The sewer is connected to a main municipal sewage collection unit. By this route the flow of hydrocarbons eventually ended up at the treatment plant of the nearby city where it was finally discharged into the nearby river.

Important findings

- The product likely escaped from the loading arm by the opening of the fill valve at the base of each tank (normally closed) and by the activation of the electric pumps (normally switched off). Officials investigating the accident judged that the spill was the result of a malicious act. According to police, the saboteur must have

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had a working familiarity with the refinery to be able to open the oil tank's main valve to release its contents.

- Clean-up was particularly challenging because the Lambro River was running fast and full after a month of wet weather. The currents were too strong for barriers to stop the oil, which covered the 50 km between the fuel depot and the Po in well under a day. The Civil Protection Department announced a five-day alert on Italy's largest waterway and a ban on dredging water from the city of Piacenza onwards. It advised boatmen to be especially careful, as the oil slick is highly flammable and could be easily ignited.
- The plant had been declassified a year earlier after having received a declaration by the operator under Seveso Article 6 concerning the forthcoming permanent closure of the activity and reclamation of the site. A subsequent inspection under Article 18 verified that the quantity of substances did not meet coverage criteria. However, the accident indicated that a much greater quantity of substances may have been present on the site. In fact, diesel fuel was leaked from three tanks, two of 2500 cubic meters, one of which was full, and one smaller tank. A criminal investigation of the operator was launched following the incident for potential infringement of the Seveso Directive among other violations.

Environmental impacts

- Nearby water bodies were affected by the oil spill. The Po river is Italy's largest water body used by thousands of farmers to water their crops. The wetlands of the Po Delta are also a wildlife preserve and home to over a 1000 plant species and 300 different types of birds, some of them on the endangered list. The spill reportedly killed dozens of birds and animals and a state of alert was declared on some stretches of the river, one of the longest in Europe.
- The quantity of the mixture of hydrocarbons (oil/fuel oil) released into these water bodies. Their impact on water quality was varied. It was however particularly severe on the first river (Lambro) and to a lesser extent on the second river (Po). The level of contamination progressively decreased as the polluting substances were carried towards the sea.
- Approximately 1250 t of oil product was retrieved at the treatment plant of the town - 300 t recovered in the yards of the depot - for a total amount of about 1550 t of product recovered upstream the treatment plant itself. Part of the remain-

ing 1050 t of oil released into the nearby river downstream of the treatment plant of the town (about 550 t) was recovered by means barrier systems set up by emergency teams.

- Around 500 t of oil was scattered along the rivers between the treatment plant of the town and the sea with a total length of river courses involved more than 300 km.

Lessons learned

- Adequate technical systems such as automatic level control system on the tanks or automatic locking systems should be in place to serve the loading docks and/or its pumping equipment or systems for automatic sensory devices on the equipment (under a remote control) such as pumps for the transportation of hydrocarbons.
- In case of decommissioning of the establishment, anti-intrusion alarm systems should have been introduced in addition to the service of security personnel outside of regular working hours to prevent acts of tampering or theft within the store or to allow the immediate activation of the actions of an emergency out of the regular time of opening.
- Procedures for identifying and mitigating risks connected with the environmental consequences should be adopted such as

the closing of the valve located immediately downstream of the tank in the presence of hydrocarbons.

- Procedures for maintenance of manual shut-down system, especially considering the difficulties encountered in closing the valve downstream of the pool separator should be in place.
- This is also a reminder that Seveso authorities should continue oversight of dangerous industrial activities even in cases of progressive decommissioning, because of a reduction in the level of attention from the operators of companies when Seveso coverage ceases.

[EMARS Accident # 756 See also EMARS Accident # 48]



Motto of the semester

"Don't blow it
- good planets
are hard to find"

Quoted in Time

MAHBULLETIN

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European
Commission

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Accident 5

General chemicals manufacture

Sequence of events

Large flooding of Vltava River in August and the beginning of September in 2002 inundated the premises of the Spolana chemical plant. As the site became flooded, water entered into two different establishments and inundated the emergency retention sumps, in which were located liquid chlorine storage tanks. As a result, chlorine was released to the air and water.

Causes

The containers were lifted by the force of the flood, which led to a burst in the piping and detachment of the socket on a tank. The tanks in the chlorine storehouses contained different amounts of chlorine. Some contained only gaseous chlorine as a residue after discharging, some were filled up to 20% of the capacity and one tank was practically full. After being flooded with water exceeding the 'hundred year water level' by 1.3m, the empty and lighter tanks were lifted by buoyancy forces and displaced from their normal positions. The buoyancy forces were so strong that their action deformed and lifted the walkways situated above the tanks (see above). The closing valves in the full tank got caught by the walkway and were completely torn off as the walkway kept moving upwards. As a consequence of the valves being torn off from the full tank, a massive leakage of chlorine occurred.

Important findings

- The extent and timing of the natural disaster had not been forecasted correctly.
- The flood came from an unexpected direction because the company premises were flooded by the backwater from the junction of the rivers Elbe and Vltava due to the flood on the Vltava river.

- It is a paradox but due to the fact that gaseous chlorine entering very quickly into the river, it had fewer effects via inhalation exposure route because most of it was diluted in the water very quickly.

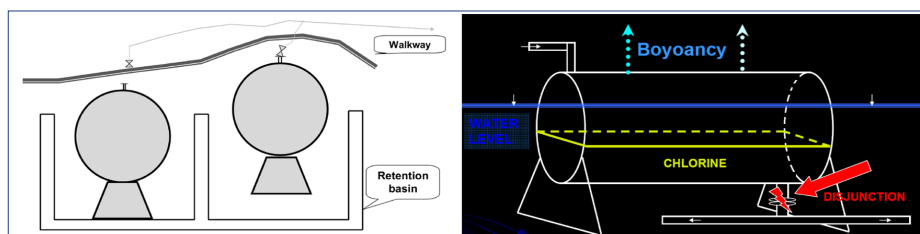
Environmental impacts

- In total, 80 t of chlorine was released into the river.
- Following the accident, analysis of river Elbe water, samples of sediments and also poultry from nearby farms proved elevated concentrations of dioxins and polychlorinated biphenyl (PCB).

Lessons Learned

- In case of severe flood, due to inundation Natech accidents are more likely where the establishment is near a water body. Therefore these establishments should be prepared for unexpectedly severe floods and maintain updated protocols to control the risks associated with these events. (See also: Lessons from the tsunami Japan, 2011 <http://www.livescience.com/27776-tohoku-two-years-later-geology.html>).
- The storage tanks/containers were not fixed to the ground, therefore they could be lifted by the flood water. Storage tanks/containers encompassing dangerous substances should be fixed to the ground.
- The walkways were attached to each other, therefore once one container was lifted, it also lifted the adjacent container too. To avoid this kind of chain reaction, the walkways should be segmented.
- It was found that emergency monitoring detectors were located at a very low height, easily reachable by the flood, rendering them virtually useless in this particular accident. Monitoring detectors should be positioned at a reasonable height based on estimated flood risk potential associated with the site's location.

[EMARS Accident # 45 and # 46.]



The release

(Source: *iChemE Loss Prevention Bulletin Issue 180 "Flood at Spolana a.s. in August 2002"* and http://www.umweltbundesamt.de/nachhaltige-produktion-anlagensicherheit/anlagen/dokumente/wrrl/vortraege_des_2_workshops_in_luebeck/danihelka_luebeck_2008.pdf)