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Risk Assessment of Hydrocarbon Releases by Pipelines

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Pipelines can move large volume of hazardous substances quickly, relatively inexpensively and reliably, with relatively few associated impacts on the environment, at least as compared with other transport modes. However, releases of hazardous substances could happen also by pipelines, due to accidents or deliberate acts. In case of liquid hydrocarbons carried by pipelines, the risk for the surroundings is due to the possibility of rupture and the consequent release of the content, with resulting land contamination, other than risk of fire and explosions. In this case, the assessment of the environmental consequences in terms of contaminated volume soil and concentrations of the pollutants in the groundwater represents a fundamental step for any effective preventive or mitigating action as well as for the remediation management.
Based on this consideration the present work describes a methodological approach for the assessment of the environmental consequences associated with gasoline releases from transmission pipelines, in terms of contaminated volume soil and concentrations in groundwater of the hydrocarbon pollutants; the potential damage caused by the exposure of the receptor of concern is also taken into account. The different steps carried out for this purpose, combining qualitative information and quantitative techniques of risk analysis, are illustrates. The data obtained could provide useful information for managing the site contamination problems in case of accidental pipelines releases, as well as for planning remediation actions and timing.

1. Introduction

Although transmission pipelines are generally considered the safest and most economical way of carrying large quantities of dangerous substances (flammables, explosives and/or toxics), they can constitute a potential threat of major accidents, as defined in the European Directive 96/82/CE "Seveso II" (Directive 96/82/EC, 1996) extended by the Directive 2003/105/EC. The impact on man and the environment of a potential major accident associated with pipelines (Bersani et al, 2010) should therefore be fully assessed for the characterization and adoption of appropriate preventive and/or mitigation measures, aimed at protecting people and the environment in their proximity. In case of liquid hydrocarbons carried by pipelines, the risk for the surroundings is due to the possibility of the content release with resulting land contamination, other than risk of fire and explosions; as an example, can be mentioned the release of about 300 - 350 m^3 of crude oil due to a rupture of the pipeline around a welding occurred in Caslav (Czech Republic) in 2005, causing serious soil and groundwater contamination. In such circumstances, the assessment of the environmental consequences in terms of contaminated volume soil and concentrations of the pollutants in the groundwater represents a fundamental step for any effective preventive or mitigating action as well as for the remediation management. On these assumptions, therefore, this study proposes a methodological approach for evaluating environmental consequences associated with hydrocarbon releases. Once released, in fact, the hydrocarbon comes into contact with the soil and groundwater and it alters their physical and

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chemical properties. The degree of alteration depends on the specific composition and quantity of the hydrocarbon spilled, as well as the soil characteristics. In this study the analysis is focused on gasoline-related contaminants such as benzene, toluene, ethyl benzene, xylenes (BTEXs) and on Methyl-*ter*-butyl ether (MTBE), which is a oxygenated compounds and a substitute for lead in gasoline; these substances are known to have adverse impacts on the human health and environment due to their toxicity and relative high water solubility (Nadim et al., 2000; Kříž et al, 2008). On the basis of the know-how acquired in several decades of major accident risk analysis, a methodological approach for the assessment of the environmental consequences associated with gasoline releases from transmission pipelines has been developed. The different steps carried out for the risk assessment of hydrocarbon releases by pipelines, combining qualitative information and quantitative techniques of risk analysis, are presented in this paper. In the first step the identification of the accidental scenario is carried out by using gasoline-89 octane, with high content of MTBE, and site-specific parameters. Subsequently, the release and dispersion of the hazardous substance in the soil and groundwater is modelled. The maximum contaminated soil volume and groundwater concentrations of several gasoline components, as, for example, MTBE and BTEXs, are calculated at different temporal and spatial units through several mathematical models, supported by software packages commercially available. Finally, the analysis of the environmental consequences is completed by evaluating the exceeding toxicity thresholds in the aquatic compartment. The results of this analysis could support the decision-makers in the improvement of adequate safety strategies such as the development of emergency plans as well as remediation actions.

2. Methodological approach

2.1 Assumptions in the consequences assessment

As a preliminary stage the characterization of the accidental scenario and the most reliable input parameters to be used in the computational analysis has been performed.

According to the well consolidated approach used in the risk analysis for consequences assessment in case of major accident, the release of the hydrocarbons by pipeline is affected by many factors, among which: operating and release conditions (pipe temperature and pressure, hole size and duration of release), the properties and quantities of released substances, external factors such as site characteristics. Due to the fact that the values assigned to these factors strongly affect computational results, great care must be devoted to their selection.

Table 1: Input parameters for computational analysis

Release characteristics	Parameters involved	Values
Vessel	Length	10 m
	Diameter	3.6 m
	Volume	100 m^3
	Temperature	15°C
	Pressure	1 bar
	Degree of filling	80 %
Pipe	Length section	1000 m
	Diameter	200 mm
	Hole	20 mm (10 % diameter)
External conditions	External temperature	15 °C
	Air relative humidity	50 %
	Wind speed	5 m/s
	Thermal radiation	300 W/m^2 (day)
	Pasquill stability class	D (neutral)

As a case study, we have considered the release of unleaded gasoline by an interconnecting pipe between two industrial plants located in a coastal area 1 km long; the pipe connected to a vessel and it is not underground. The accidental rupture of the pipe corresponds to a 10 % of the pipe diameter break. To characterize the accidental scenario and to adopt the most appropriate input parameters for computational steps we have analyzed several sources of information which can be considered representative for the present study; these sources are, for example, existing databases storing information on pipeline accidents, technical documentations and guidelines and legislative provisions (Davis et al, 2007; EGIG, 2005; Arunakumar, 2007). The outcomes of this analysis, the most common values found, are summarized in Table 1. The degree of alteration of the soil and groundwater depends on the specific composition of the hydrocarbon spilled. The petroleum products are multi-component organic mixture composed of chemicals with varying degrees of water solubility. The most water soluble constituents in common refined petroleum (gasoline, diesel, etc..) are aromatic compounds and oxygenation additives. In particular, the composition of the selected gasoline for this study is illustrated in Table 2; Table 3, shows the chemical-physical parameters of gasoline components, required to evaluate the contamination of soil and groundwater. Finally, Table 4 summarizes the main characteristics of the soil.

Table 2: Components (% wt) in gasoline-89 octane

% wt	Components
0.726	Benzene
5.77	Toluene
1.15	Ethyl benzene
1.46	o-Xylene
2.64	m-Xylene
1.10	p-Xylene
12.9	MTBE

Table 3: Properties of gasoline-89 octane

Parameters	Value
density	0.75 g/cm^3
Dynamic viscosity	0.45 cp
Hydrocarbon solubility	125 mg/L
Soil/water partition coefficient	0.011 l/kg
Surface tension	$35 \cdot 10^{-5}$ N/cm

Table 4: "Sand soil" parameters

Parameters	Value
Hydraulic conductivity	7.1 m/d
Porosity, η	0.43
Bulk density	1.51 g/cm^3
Aquifer saturated thickness	15 m
Depth to water table	4.5 m
Capillary thickness	0.2 m
Groundwater gradient	0.01 (m/m)

2.2 Release and dispersion modelling

In the second step the modelling of release and dispersion of hazardous substances in soil and groundwater has been carried out: to this aim two software programs commercially available (Effects 7.6 elaborated by TNO; Hydrocarbon Spill Screening Model, HSSM elaborated by EPA), which are based on several simulation models, have been applied. The former, allows carrying out simulations of unleaded gasoline release; once released, the gasoline forms a liquid pool on the ground and due to its high boiling point it remains in the liquid state (Prins Maurits Research Laboratory, 1991). The output data obtained from this computation phase are described in Table 5 and they also represent the input parameters required by the latter software to model releases and dispersions of hazardous substances in soil and groundwater.

Table 5: Release parameters

Parameters	Value
Release rate	3 kg/s
Volume released	79 m^3
Radius pool	6.2 m
Area pool	121 m^2

The HSSM model is intended for simulation of releases of light non-aqueous phase liquids (LNAPLs), such as gasoline (Chen et al, 1998) and consists of three separate modules (KOPT, OILENS and TSGPLUME) for the evaluation of respectively: flow through the unsaturated zone (vadose zone), formation of the lens oil in the capillary fringe (spreading in capillary fringe), transport and dissolution of the chemical components of the LNAPL in aquifer and their concentrations to potential receptors (Weaver et al, 1995). As a result, the quantitative assessment of volume contaminated soil (VCS) and the concentrations of the pollutants in groundwater, at different temporal and spatial units, have been obtained.

3. Results and discussion

3.1 Contaminated soil volume

The remediation techniques are affected by the extension of the contaminated site: for a low volume of contaminated soil, operations such as superficial excavation and removal of contaminated soil could result adequate; if the contaminant reaches the saturated zone, instead, an intervention to contain the lateral spread of the contaminants dissolved in water may be required. The time of the emergency operations strongly affect the spreading of the contamination. In the present study has been evaluated the volume contaminated soil as function as time as summarized in Table 6.

Table 6: VCS vs time

Time (min)	Vcs (m^3)
30	8.5
60	18
120	33
240	73
360	104
480	145
600	175
720	206
1440	411
14,400	508

3.2 Concentrations of the contaminants in the groundwater
In the absence of emergency operations, NAPL reaches the water table; **the dispersion of the organic compounds in aquifer has been evaluated in terms of the** concentrations of pollutants in the receptors of concern placed at several distances from the release, i.e. 50, 100 and 150 m (Figure 1). In this analysis the environmental receptors considered are stream fed with the aquifer.

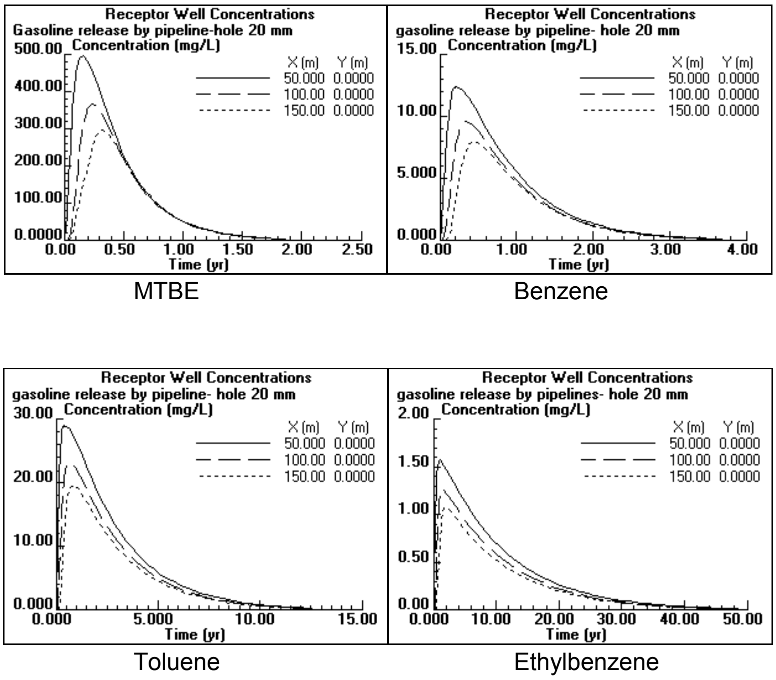

Figure 1. Concentrations of the hydrocarbon compounds in the aquifer

The Figure 1 shows that MTBE concentrations are higher than those of the other pollutants due to three main chemical-physical properties: the MTBE is about three times more soluble in water compared to benzene; it has a low partition coefficient which indicates a low tendency of the substance to be absorbed on the soil and a consequent high mobility through it; the diffusion coefficient in groundwater is higher than other aromatic compounds analyzed and therefore a greater extension of the plume of contamination is achieved. It is also worth noting that, due to the low diffusion coefficients indicating a low mobility of the substances in aquifer, it is possible to find traces of the ethyl benzene near the source of release even after years.

3.3 Toxicity threshold overtaking
Finally, the analysis of the environmental consequences is also carried out in terms of the exceeding toxicity thresholds in the aquatic compartment. It is assumed that the ecosystem sensitivity depends on the most sensitive species, i.e. invertebrates. More specifically, we have considered the acute toxicity values in aquatic compartment enclosed in the EPA's ECOTOX database (US EPA, 2009); they are normally determined on the basis of the following endpoints: for fish LC50 (96 h), invertebrates EC50 (48 h) and for algae EC50 (72 or 96 h). These species are considered representative of all aquatic organisms.
Due to higher concentration than other contaminants, the analysis is focused on MTBE. The substance concentration below which adverse effects in the environmental compartment of concern are not expected to occur is known as the Predicted No-Effect Concentration (PNEC). The computational results indicate that at about two years by the release the concentrations of MTBE can exceed the PNEC-aquatic. This implies that although the MTBE has lower toxicity for aquatic organisms than

BTEXs (a group of chemicals for which toxic effects have been extensively analyzed), its high concentrations in groundwater can cause severe damage to aquatic organisms.
Suggestions arising from this study could support the ecotoxicological tests which are necessary for an exhaustive site characterization.

4. Conclusions

The present paper focuses on the assessment of the environmental consequences in case of pollutants release by transmission pipelines; the analysis is carried out using software programs commercially available, on the basis of the experiences gained in the risk of major accident prevention and management. Results obtained are expected to provide useful information on the environmental damages produced by an hydrocarbon release in terms of contaminated volume soil, pollutant concentration in the groundwater and exposure of the most sensitive receptor.
Results obtained can also help stakeholders in adopting appropriate decisions regarding preventing or mitigation measures in case of chemical releases as well as better planning emergency or remediation management.

References

Directive 96/82/EC on the control of major accident hazards involving dangerous substances, 1997, Official Journal of the European Union, No L0/13.

Directive 2003/105/EC amending Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances, 2003, Official Journal of the European Union, No L345/973.

Bersani C., Citro L., Gagliardi R.V., Sacile R., Tomasoni A.M., 2010, Accident occurance evaluation in the pipeline tran sport of dangerous goods, Chemical Engineering Transactions 10, 249-254.

Nadim F., Hoag G.E., Liu S., Carley R.J., Zack P., 2000, Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview, Journal of Petroleum Science and Engineering 26, 169–178.

Kříž L., Wittlingerová Z., Chaloupka D., 2008, Gasoline pipeline accident-migration of MTBE, TPH and BTEX in a fractured rock environment, Scientia Agriculturae Bohemica, 39, 284-288.

Davis T.M., Dubois J., Olcese A., Uhlig F., Larivè J-F., Martin D.E., 2007, Performance of European cross-country oil pipelines, CONCAWE, No. 4/07, Brussels.

EGIG, 2005, 6th Report of the European Gas pipeline incident Data Group, Report 05.R.0002.

Arunakumar G., 2007, 5th Report of the UKOPA Fault Database Management Group, UKOPA, Report 6957.

Prins Maurits Research Laboratory, 1991, EFFECTS: A software for Hazard Assessment, TNO, Netherlands.

Chen Z., Huang G. H., Chakma A., 1998 , Integrated environmental risk assessment for petroleum-contaminated sites - a North American case study, Wat. Sci. Tech., 38, 131-138.

Weaver J.W., Charbeneau R.J., Tauxe J.D., Lien B. K., Provost J. B., 1995, The Hydrocarbon Spill Screening Model-HSSM, EPA, EPA/600/R-94/039a.US EPA, 2009

<cfpub.epa.gov/ecotox/>, Accessed 23.02.2009.