MULTI-CONSTITUENT MODELLING OF A GASOLINE SPILL USING THE T2VOC NUMERICAL SIMULATOR

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ABSTRACT

Gasoline is a mixture of many constituents which have different physical and chemical properties. Because of differences in solubility, volatility as well as adsorption and biodegradation properties the different constituents partition differently between the phases. Taking multi-constituent behaviour of gasoline into account in numerical models is complicated by its large number of constituents.

To address this problem constituents with similar properties have been grouped together into eight fractions for which the fate and transport properties have been estimated. Using the T2VOC numerical simulator the migration of each fraction can be studied separately. Since the composition of the free-phase gasoline changes with time the simulations are conducted stepwise and chemical parameters are changed accordingly after each simulation step.

The approach has been used to simulate a gasoline spill in connection with a tanker accident in a geological setting typical of Sweden. The migration with time of the free-phase gasoline is presented together with the concentrations of one of the fractions in the aqueous and gaseous phases.

INTRODUCTION

Due to its widespread use throughout society, gasoline is one of the most commonly occurring hazardous chemicals of today. It is present as a soil and groundwater contaminant at an enormous number of contaminated sites and is together with diesel fuel the most commonly occurring chemical in spills in connection with accidents in Sweden (Björklund et al., 2001).

In order to assess risks and plan remedial actions at the sites of spills and leaks, it is necessary to understand the spreading behaviour of gasoline. Since it is immiscible with water but still partly soluble and highly volatile, gasoline may spread as a separate phase, as dissolved in soil- and groundwater and as fumes in the soil air. The migration of gasoline in the sub-surface is hence a matter of multi-phase flow.

Various numerical simulators have been developed to study multi-phase flow, e.g. Kaluarachchi and Parker (1989), Abriola and Pinder (1985), Falta et al. (1995). Modelling gasoline is, however, complicated by the fact that it is a mixture of more than a hundred different constituents which have different chemical and physical properties. Because of differences in solubility and volatility, the different constituents partition differently between the phases and consequently also the composition and properties of the free-phase gasoline change with time.

To correctly model migration behaviour in the subsurface and keep track of concentrations of especially interesting constituents (such as the BETX fraction) it is necessary to take into account the multi-constituent nature of gasoline. The work of Adenekan et al. (1993) and Pruess and Battistelli (2002) resulted in the TMVOC a numerical simulator which is capable of handling several chemical constituents at a time. Here a different approach is taken using a single-constituent multi-phase flow simulator, the T2VOC by Falta et al. (1995), simulating one constituent at a time.

Ideally, both using the TMVOC and when the approach described below is taken, every constituent should be treated separately. However, because of the large number of constituents, such approach would require a huge computational effort and is as of to date not feasible. It is therefore necessary to reduce the number of modelled constituents by assigning them to a smaller number of representative groups or fractions.

MODELLING APPROCH

Grouping of constituents

The approach taken here is to group constituents with similar physical and chemical properties into a smaller number of fractions, and is similar to that of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) (Gustafson et al., 1997).

Based on the equivalent carbon number (EC number), which describes the equivalent length of the carbon chain based on the boiling point, the hydrocarbon constituents are classified as belonging

to one of eight fractions, as shown in table 1. Data for gasoline constituents have been taken from LUFT (1988) and Gustafson et al. (1997). Difference is made between aliphatics and aromatics. For each fraction the physical and chemical properties can be estimated, for example by taking an average of the properties of the constituents building up the fraction or by using the fraction's average EC number. Some estimations of such fraction-specific fate and transport properties can be found in Gustafson et al. (1997). Properties of a number of organic compounds can also be found in Reid et al. (1987).

Table 1. Representation of gasoline as eight fractions

EC interval	Weight percentage			EC average	Fraction number
	Min	Max	Ave.		
Aliphatics					
4-6	25.7	44.2	35.9	5.04	1
>6-8	7.92	38.1	23.6	7.17	2
>8-10	1.73	9.6	5.8	8.12	3
>10-12	0.09	0.31	0.2	11.3	4
Aromatics					
Benzene (5-7)	0.12	3.5	1.9	6.5	5
Toluene (>7-8)	2.73	21.8	12.6	7.58	6
>8-10	5.42	22.3	14.2	9.13	7
>10-12	2.64	8.76	5.8	10.8	8

Numerical modelling

T2VOC (Falta et al. 1995), is a three-dimensional numerical simulation program for multi-phase, non-isothermal flow and transport of Non-Aqueous Phase Liquid- (NAPL) type contaminants. T2VOC very efficiently handles sub-surface migration of one chemical component at a time. The idea of this modelling approach is to characterise gasoline spreading by conducting a number of simulations, at least one for each of the eight fractions defined above (see table 1), to account for multi-constituent effects. After conducting simulations for all fractions the results are put together and analysed, giving a more complete picture of the spreading, since the spreading pattern of each fraction can be studied separately.

To do this the chemical input parameters to the model have to be carefully selected. For the simulation of each fraction the size of the spill and the free-phase gasoline transport properties are the same. Hence these properties are the average properties of gasoline. The volatilisation, solution and sorption parameters on the other hand are specific to the fractions, and depend on the estimated average properties of the fraction as well as the relative amount of the fraction present in the free-phase gasoline. The solubility and volatility are assumed to decline with relative concentration according to Raoult's law and are calculated as the product of the mole-fraction of the fraction in the free-phase gasoline and the average solubility/volatility of the fraction.

During the simulation the solubility and volatility remain constant, although in reality the mole-fraction of a fraction changes in the parent material (the free-phase gasoline) as the various fractions are dissolved and volatilised. The mole-fractions of the classes that are dissolved and volatilised the fastest tend to decline in the gasoline phase. By analysing them first and taking their disappearance into account in the following analysis of the other classes chemical concentration estimates remain conservative since underestimation of mole-fractions (resulting in underestimation of dissolution/ volatilisation) is avoided.

To make it possible to account for disappearance of a class from the free phase gasoline, the simulations are conducted stepwise. From the point of disappearance no further dissolution or volatilisation is possible and migration of the class can only take place in the aqueous and gaseous phases.

MODELLING EXAMPLE OF A TANKER ACCIDENT

Scenario and objectives

To test and develop the modelling approach, a tanker accident in a geological setting typical of many areas in central and northern Sweden has been simulated. Gasoline from the tanker is assumed to infiltrate the ground along a ditch parallel to the road. Also parallel to the road, at a distance of approximately 110 m is a small river.

The objective of the simulation is to study the multi-phase migration of the gasoline spill from the location of the tanker accident towards the river. A cross-section of the accident site is shown in Figure 1.
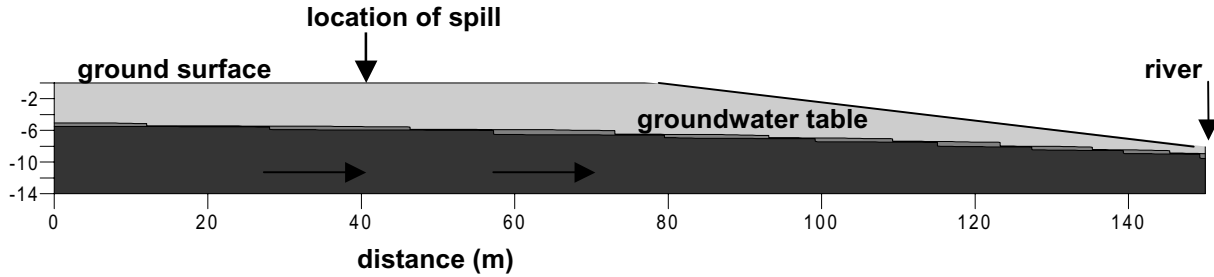
Figure 1. Cross-section of the gasoline spill site.

Model

The spill is approximated as line source of 1000 litres per metre at the most, and 2-D modelling has been used to simulate the gasoline migration in a cross-section (Figure 1) from the road down to the river. The horizontal distance from the spill site to the river is 110 m and the vertical distance is 10 m. The groundwater table at the location of the spill is at approximately 6 m depth, which results in a mean hydraulic gradient of 4/110 = 0.036 m/m towards the river. The soil is assumed to be homogeneous fine sand.

Due to the relatively large size of the spill site and the complexity of the modelled processes the grid used in this preliminary model is rather course. Grid blocks are 1 – 2 m in the x (horizontal) direction and 0.5 – 1 m in the z (vertical) directions, with the highest resolution (smallest blocks) near the spill and all along the groundwater table.

Results and discussion

The results presented here are the migration of the free-phase gasoline as well as the migration of fraction 2 (C6-C8 aliphatics) in the aqueous and gaseous phases. The concentrations of the other seven fractions in the soil-air and groundwater are obtained in the same manner as for fraction 2, and are omitted here.

Migration of the free-phase gasoline

As the first step of the modelling process the movement of the gasoline free-phase (NAPL-phase) is simulated. The spill is assumed to take place mainly during the first 30 minutes, after which the gasoline is redistributed with no external source. The distribution of the free phase gasoline after 4 months is shown in Figure 2. Smoothing interpolation between grid blocks has been avoided to show the "real" outcome from the modelling.
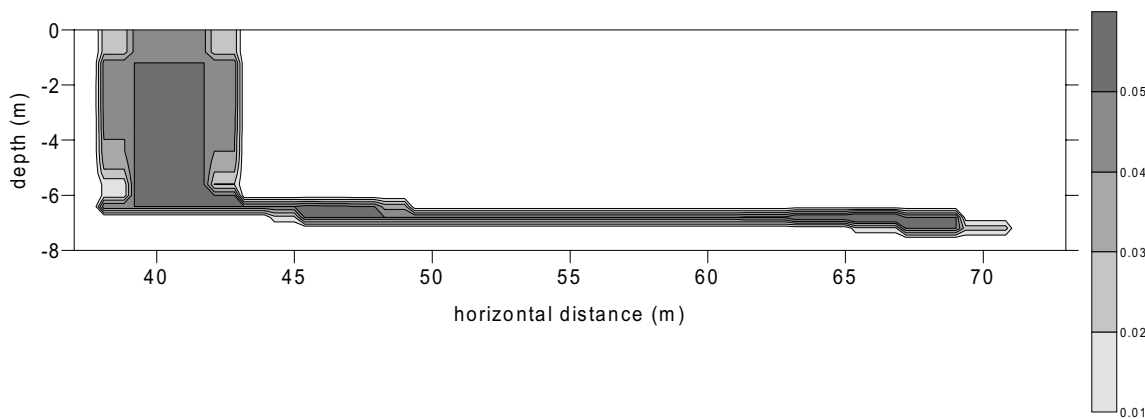

Figure 2. Simulated gasoline saturation 4 months after the spill.

As can be seen in Figure 2 the gasoline migrates downwards until it reaches the groundwater table. It then moves horizontally on top of the groundwater table, towards the river. At saturations at or below the residual saturation of 5% the free-phase gasoline cannot move and therefore the movement stops when the spill has spread out to such extent that it is at residual saturation everywhere. This happens approximately 4 months after the spill, when the gasoline has travelled approximately 30 m on top of the groundwater table, being at a distance of 80 m from the river. From this point on the gasoline constituents can only migrate as dissolved in the groundwater or volatilised in the soil-air, and the shape of the free-phase plume only changes as a result of dissolution and volatilisation.

Migration of C6 – C8 aliphatics in the soil gas

The second step of the analysis is to simulate the migration of the different fractions in the groundwater and soil-gas. The concentration of C6 – C8 aliphatics in the soil-gas one month, four months and two years after the gasoline spill respectively, are shown in Figure 3.

Short carbon-chain aliphatics are highly volatile which results in high concentrations in the soil gas. The concentration front spreads in both up and down along the groundwater table by diffusion in the gaseous phase. As the free gasoline phase spreads the source of gasoline vapours also spreads and extends towards the river. Volatilisation occurs more easily in a grid block that contains NAPL (free phase gasoline) as well as a relatively large proportion of soil air compared to a block that contains the same amount of NAPL but less air. Because along the groundwater table the air saturation in the (discrete) grid blocks vary, some effects of the discretisation into blocks can be seen as small concentration maxima at locations along the groundwater table where the NAPL containing grid blocks have more access to air. This effect, however, has very little impact on the overall result.
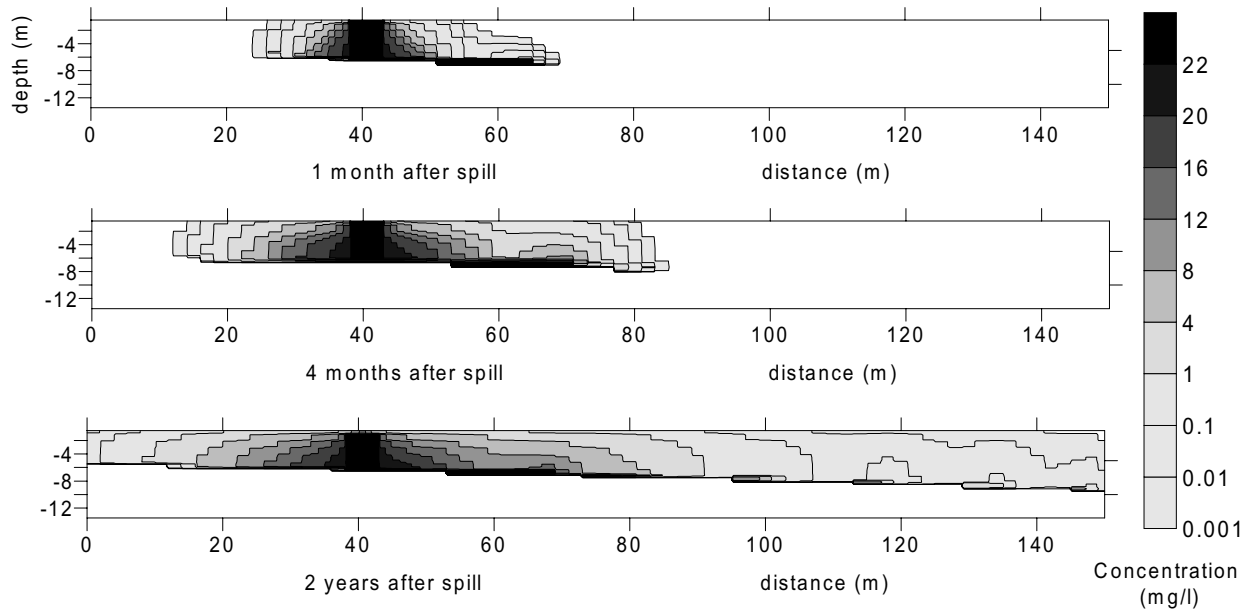

Figure 3. Simulated concentrations of C6 – C8 aliphatics (mg/l) in the soil-gas 1 month, 4 months and 2 years after the spill respectively.
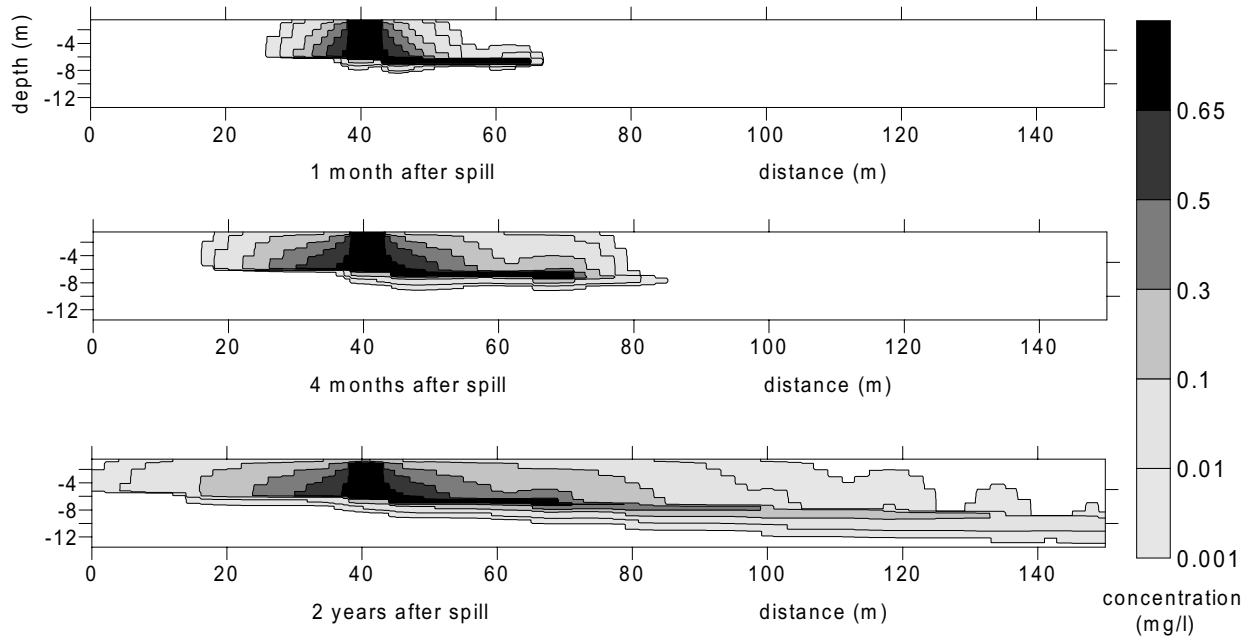
Figure 4. Simulated concentration of C6–C8 aliphatics (mg/l) in the soil- and groundwater 1 month, 4 months and 2 years after the gasoline spill respectively.

Migration of C6–C8 aliphatics in the aqueous phase

The migration of C6 – C8 aliphatics in the aqueous phase (soil-water and groundwater) is shown in Figure 4, which shows the concentration of this fraction one month, four months and two years after the spill respectively.

Because of the strong volatilisation of the C6 – C8 aliphatic fraction the dissolution into soil-water is mediated by vapour migration in the soil-gas. The irregularities in the gaseous phase concentrations described above can therefore also be seen in the soil-water concentrations (Figure 4). The dissolution of this fraction is relatively slow, but 2 years after the spill the plume of dissolved C6 – C8 aliphatics has clearly reached the river.

CONCLUDING REMARKS

A method of studying subsurface gasoline migration, treating it as eight different fractions consisting of similar constituents, has been proposed. Preliminary results show that the method may yield good results although further testing is needed.

The results presented here were obtained from coarse grid 2-D simulations and may be improved and validated using a more refined model. A finer grid may lead to greater migration of the free-phase gasoline since the migration stops at residual saturation and the use of large grid blocks may result in a "dilution" of the gasoline over the block volume.

The dissolution and volatilisation of the C6 – C8 aliphatic fraction should in reality decline as its relative concentration declines in the free-phase gasoline. Since this is not accounted for a slight overestimation of concentrations in the soil-gas and groundwater is obtained.

The methodology developed allows the studying of multi-constituent gasoline migration using a single component multi-phase flow simulator (T2VOC). Predictions of concentrations of toxic fractions (such as BTEX) are especially interesting for risk assessment and remediation planning purposes.

ACKNOWLEDGEMENTS

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