Modeling a phase partition problem to assess the appearance of NAPL in polluted soils

Álvaro Pérez Lada

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Orientadores:
Prof Maria João Correia Colunas Pereira
Prof Fernando Barrio Parra

Júri

Presidente/ Chairperson: Prof. Maria Matilde Mourão de Oliveira Carvalho Horta Costa e Silva

Orientador/ Supervisor: Prof Maria João Correia Colunas Pereira

Prof Fernando Barrio Parra

Vogal(is)/ Members of the Committe: Prof Leonardo Azevedo Guerra Raposo Pereira

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ABSTRACT

NAPL is a well-known term used to describe those non aqueous phase liquids. These non-aqueous liquids appear under certain edaphic conditions and the aim of this project is to truly understand how these conditions can affect the appearance of the NAPLs and in which measure.

NAPLs represent a major threat for the living organisms in the fields (so for the humans who consume contaminated vegetables for instance) and they appear in a situation where some hydrocarbons have been leaked to the ground. It becomes important to quantify the appearance of NAPL when the ground has reached the saturation point where no more liquids can be absorbed because that's when the NAPLs can move through the ground.

A mathematical model has been built, the series of equations describe the procedures needed to see whether there is NAPLs under the initial both edaphic and chemical conditions. A soil is described, characterizing the main parameters as the pollutant concentration in the soil, the total porosity, the water filled porosity, the air filled porosity, the organic carbon fraction etc. Afterwards the chemical inputs for a certain contaminant are also characterized. The programme build with Matlab code, allows to quantify the NAPL in the soil.

It is important to evaluate the already built programme, by variating some of the inputs to see whether the appearance of NAPL changes. The porosity inputs turned not to be a determinant for the appearance of the NAPLs under the initial conditions for the case of study. Evaluating the variation of the contaminant concentration in soil has led to the creation of a new programme that finds the limit for the pollutant concentration which verifies the appearance of NAPL.

Keywords: NAPL, saturated ground, porosity, groundwater contamination, DNAPL, LNAPL, FOC, Henry´s Law.

1. INTRODUCTION

NAPL s (Non-aqueous phase liquids) are hydrocarbons that exist as an immiscible and separate phase when in contact with water and / or air.

The problem arises when there is a leak of hydrocarbons to a terrain, these leak into it and it moves, due to the force of gravity, downwards. If the area is not saturated, the NAPL s (Non-aqueous phase liquids) are retained in the pores until their movement stops.

On the other hand, when the area is saturated, that is, there are no more free pores without liquid, the NAPL (Non-aqueous phase liquids) moves as a free phase, guided by the movement governed by the force of gravity and capillary forces.

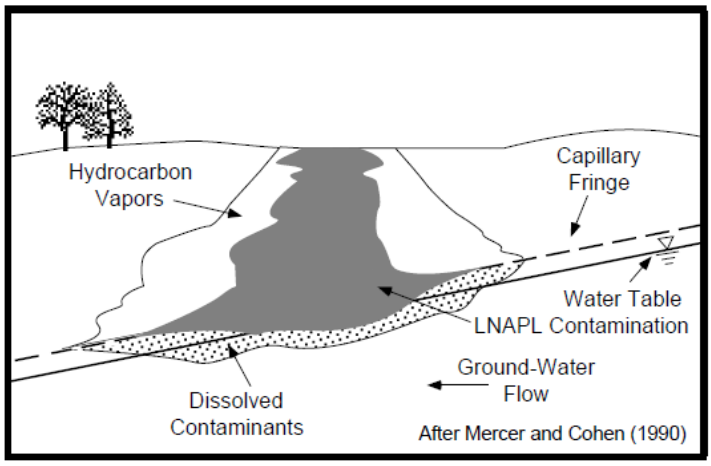

Figure 1- Outline of the NAPL s migration problem. Source (Charles J. Newell)

To characterize the problem, the following factors must basically be considered:

- Ground.
- NAPL s.
- Phase distribution.

Once these factors have been described, which form the Genesis of our problem, we will have to define the practical case at hand, that is, the construction of a mathematical model that describes and calculates the distribution in phases of the NAPL during their migration through saturated soil. For this, the MATLAB mathematical program will be used.

2. METHODS

In order to establish the methods for the calculation of NAPL free phase, it is extremely important to give the necessary condition for it to appear in the ground model.

The condition states that if the concentration of an organic chemical mixed in water exceeds its pure-phase aqueous solubility limit, then NAPL is present in the sample. By comparing the solubility limit of an organic compound to its concentration in water, the most fundamental qualitative and quantificative test for NAPL can be done.

NAPL is found when:

$$\sum Cwi > Si$$

$$Cwi > Sei$$

Cwi= Water concentration for pollutant i.

Si= Aqueous-phase solubility limit of the organic pollutant i.

Sei= Effective solubility limit of the organic compound i in a mixture.

Operating on this expression, the final condition is made for the appearance of NAPL free phase.

$$Csati > Cti$$

Csati= saturation limit for soil of pollutant i.

Cti= concentration limit of pollutant i.

The other important condition to understand the appearance of NAPL free phase is the establishment of an equilibrium partitioning theory, for mass balance.

Regarding Equilibrium Partitioning Theory, a compound distributes linearly between three separate phases in the ground. The four mass states are the following:

1. The aqueous state, e.g., dissolved in groundwater or soil-pore water.
2. the solid state, e.g., sorbed on soil particles.
3. Vapor state, e.g., vapor in the soil pore-air.
4. NAPL state, as free product, if any NAPL is present in the sample.

The partitioning equation can be expressed as the following:

$$Mti = Mai + Mwi + Msi + M_{NAPLi}$$

Mti= total mass for pollutant i in sample.

Mai = Mass of compound i in soil pore air.

Mwi = Mass of compound i in soil pore-water.

Msi = Mass of compound i sorbed on soil particles.

M_{NAPLi} = Mass of compound i as NAPL.

These are the main conditions for the construction of a mathematical model using the software Mathlab.

The construction will be based on object-oriented programming, that allows the user to obtain the maximum flexibility needed to variate equations and functions when needed.

2.1 EVALUATION OF POLLUTANTS IN THE GROUND

A function for evaluating the appearance of NAPL will be done, and the code attached to the main document.

The program reads an excel file with the pollutant data, and automatically outputs the results.

2.2 SENSITIVITY ANALYSIS

This is the second part regarding the construction of a solid and robust mathematical model. The following programs asses the sensitivity of the first one when some parameters of the model are changed.

This allows to see how can the program respond to a minimum change in:

- Total porosity.
- Water soil porosity.
- Air soil porosity.
- Pollutant soil concentration.

The second part of the sensitivity analysis basis on the construction of the code that outputs the minimum pollutant concentration that verifies the appearance of NAPL free phase for a specific soil.

3. RESULTS AND DISCUSSION

The assumption of the following soil, examined and analyzed experimentally in the lab, need to be made in order to begging with the evaluation of NAPL.

Table 1-Chemical parameters for soil 1

Chemical	Cti (mg/Kg)	nt (%)	sumW (%)	sumA (%)	Foc (%)
Trichloroethylene	100	40	30	10	0,0001
Arochlor 1260	60	40	30	10	0,0001

The data above establish the initial and most important conditions for the study of these two contaminants and the sensitivity analysis, all the study is going to relay on this data.

Cti= initial concentration for pollutant i in soil.

nt= total porosity.

sumW= water soil porosity.

sumA= air soil porosity

Foc= organic fraction.

3.1 EVALUATION OF POLLUTANTS

3.1.1 Trichloroenthylene

The next data is outputted by the program when executed.

Table 2-Obtained data

Xi	1,0000
d	1,4600
Sei	1100,0000
Sti	1100,0000
Vpei	74,3100
Kdi	0,0013
Icwi	430,7181
Csat	255,3875
Cconi	482,7590
Cwi	1100,0000
Cai	401,3900
Cavi	735440000,0000
Csi	1,3860
Mwii	232,7673
Mai	21,2342

Msi	1,3860
NAPL i	'N/A'
Mti	N/A'
NAPL t	N/A'
Sr	N/A'
Nv	'N/A'
Av	'N/A'
Vw	'N/A'
Sv	'N/A'

When calculating the total mass of NAPL , and the following parameters, N / A is obtained, which means NOT APPLICABLE, this occurs because for that soil and that contaminant it has been obtained:

Csati> Cti

255.3875> 100

This means that the condition that the concentration of that pollutant is bigger than the soil saturation limit for the same pollutant is not fulfilled, therefore there is no free phase.

3.1.1 Arochlor 1260

By introducing the data shown above and run the program, the next results are obtained:

Table 3-Obtained data

Xi	1,0000
d	1.5660
Sei	0.0144
Sti	0.0144
Vpei	1.1000e-05
Kdi	670
Icwi	0.0895
Csat	9.6511
Cconi	18.2434
Cwi	0.0144
Cai	1.4760e-04
Cavi	0.0095
Csi	9.6480
Mwii	0.0030
Mai	7.8083e-06
Msi	9.6480
NAPL i	50.3489
Mti	60
NAPL t	50.3489
Sr	1.5969
Nv	63.8756

Av	'N/A'
Vw	'N/A'
Sv	'N/A'

Arochlor 126 in this soil does produce NAPL free phase under these conditions, as it is shown in the results.

There is NAPL free phase because Csati<Cti, so that the saturation limit concentration for this pollutant under the soil condition exceeds the value of the total concentration of this pollutant in this soil, so free phase is formed, with the following concentration.

NAPL = 50.3489 mg / kg

3.2 SENSITIVITY ANALYSIS

The following results for Trichloroethylene and soil 1 were obtained by constructing the mentioned programs:

- No NAPL phase found when variating the total porosity from 0 to 0.6 (is a generous limit knowing that the average total porosity is 0.42 for sandy-clayey soils)
- No NAPL phase found when variating the soil water porosity from 0 to "TOTAL POROSITY- SOIL AIR POROSITY" (that would be the limit for soil water porosity)
- No NAPL phase found when variating the air water porosity from 0 to "TOTAL POROSITY- SOIL WATER POROSITY" (that would be the limit for soil air porosity)
- The program found that the value for Cti which is used to obtain a NAPL free phase concentration of 2.1385 mg/Kg is 270 mg/kg of Trichloroenthylene in soil 1.

3.3 DISCUSSION

The program allows to the calculation of the NAPL free phase, which in the first pollutant of study it isn't formatted for these soil conditions, however in the second case of study, there is NAPL free phase due to the condition of Csati<Cti .

The sensitivity analysis could help me to evaluate how good did the program respond towards any change in the variation of some parameters.

1. The porosity parameters are not that important regarding the variation of NAPL free phase under these conditions.
2. I could programme a code that finds the minimum value for Cti (contaminant concentration in soil) that verifies the appearance of NAPL free phase, so that is the limit for the concentration.

4. CONCLUSSION

The main factor in controlling the NAPL free phase formation is the solubility limit Csat because it is used to determine if NAPL is in the sample because it is used to perform the equilibrium mass balance. Any contaminant mass above the Csat value is NAPL by definition (Cti – Csati = NAPL i, if Cti>=Csati).

The program allows the user to asses the formation of NAPL contamination under certain conditions that he would have to input. The software construction also allows to save both money and time by not having to do a large number of calculations, in addition, the assessment of a contamination problem in a waste site for ex. May be better estimated using this software. Use of the software in conjunction with the characterization data can result in a detailed development of the subsurface mass of contamination. This will allow the establishment of a baseline against which a remedial system can be designed, and its performance assessed.

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