

Assignment GEO4161



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GEO4161 – Contaminants in the geoenvironment

06.12.16

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Abstract

A case-study concerning the contamination of groundwater by jet-fuel has been performed. Compounds of concern, toluene and naphthalene, has been evaluated according to their distribution and availability for biodegradation. Toluene seems be the least disturbing agent of the two, as major concerns are made about the longevity of naphthalene with the site-specific data at hand. Both compounds however, is likely to remain in the aquifer for a very long time. It is still believed that monitored natural attenuation is a viable option for remediation, as evidence of biodegradation, reduction in compound concentration and limited movement of the plume is present.

Introduction

A fire-fighting training site is located due west of Gardermoen Airport, about 35 km northwest of Oslo, Norway (fig.1).

The site lies on top of glacial deposits consisting of poorly sorted, heterogenous material, with sediment particle size ranging from coarse sands to silt and clay (Zheng et al. 2001).

A scenario where the aquifer below the training-site has been exposed to a fresh spill of 500 liters of jetfuel is studied. Such scenarios are important to consider, as groundwater contamination by hydrocarbons is of great environmental concern (Cline et al. 1991).

Toluene, an aromatic hydrocarbon, is a constituent of the collectively called BTEX-group, consisting of benzene, toluene, ethylbenzene, and three xylene compounds. Naphthalene, a polycyclic aromatic hydrocarbon, is commonly found as a component alongside the BTEX compounds. As they are present in gasoline-products, and have impact on human health, fuel-contaminated aquifers can be of major concern (Lawrence 2006).

The main goal of the study is to evaluate distribution and concentrations of the compounds toluene and naphthalene present in the aquifer over time, to assess the potential risk involved, and consider methods of remediation.

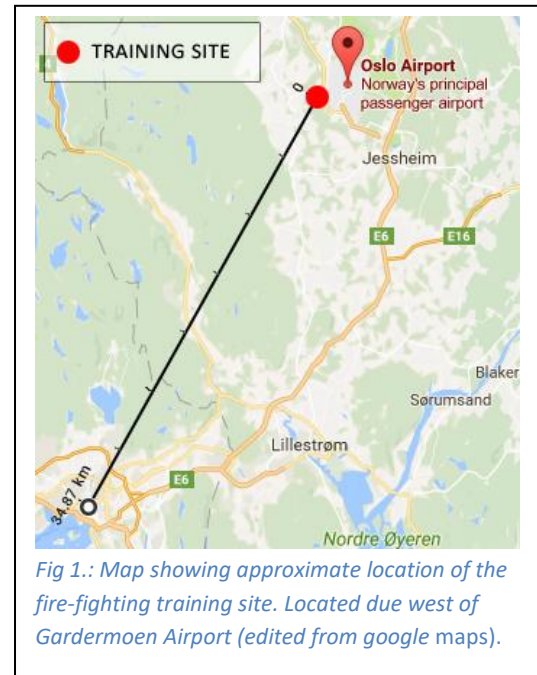


Fig 1.: Map showing approximate location of the fire-fighting training site. Located due west of Gardermoen Airport (edited from google maps).

Methods:

To approach the situation at hand, major simplifications have been made in relation to potential flow paths of diverse water-systems, heterogeneity of the glacier deposit material, infiltration-area of the spill, and the dimensions. A 1-dimensional box-model is therefore used, dividing the area of interest into sections containing 1) the unsaturated zone, 2) the saturated zone and 3) the groundwater-flow, considered via a row of slices of 1m^2 through the affected saturated area (fig.2). Movement and behaviour of this section is then considered through time.

Furthermore, a stepwise approach has been used in the time-related calculations, starting from the time the compounds have infiltrated the area, migrated through the unsaturated zone (solid phase), and been fully distributed in the unsaturated zone (free-phase). The calculations will consider transport in water- and gas-phase, water- and soil-concentrations, retardation and degradation-rates through biodegradation.

The infiltration-area is regarded as a square of 1m^2 , with a depth to the water-table of 4 meters, resulting in a cuboid with dimensions $1\times 1\times 4$ meters. This makes out the unsaturated zone, evaluated as a homogenous sand-deposit with a retention-capacity of 15 l/m^3 . The saturated zone is equally evaluated as a homogenous sand-deposit, but with a retention-capacity of 12 l/m^2 (data from table at page5, lecture7).

Jet-fuel is a complicated mixture of numerous compounds (Cline et al. 1991). For estimates the prominent middle-value from gas-chromatography is used (decane, $n\text{-C}_{10}$), giving a molecular weight of about 142 g/moles (lecture 3) and a bulk density for jet-fuel of about 0.8 g/cm^3 (course material). Calculations on determining concentrations of toluene and naphthalene are based on their weight-percentage in jet-fuel, given as 1.33% for toluene and 0.5% for naphthalene (Faroon et al. 1995, table 3-8, page 90).

The methods used are first described in detail. At the end of the section, key values used in calculations will be presented in a table to increase availability.

Compound solubility

Gradually mixing the compounds with groundwater will result in a lowering of the respective concentrations. A mixture of compounds will behave/develop differently than single compounds. The two will compete for space, resulting in deviations from single compound mixture concentrations, resulting in reduced solubility based on the mol-fraction of the compound in the mixture. If the concentrations are low, apolar organic compounds that do not form ionic bonds in water will follow Raoult's law in an aqueous solution (course material, chapter2, box 2.3). Concentrations by Raoult's law is determined by:

$S_i = X_i \cdot S_0$, where

S_i = solubility of compound i in equilibrium with mixture (mg/l)

X_i = Mol fraction of compound i in mixture (mol/mol)

S_0 = pure compound solubility (mg/l)

To find the molfractions, 1 litre jetfuel is used as a basis, where first the molar concentration is found by the relation: $\text{Molarity (mol/l)} = [(\text{g/l}) / (\text{g/mol})]$. The molfraction is then calculated by $\text{Molfraction} = [\text{compound molarity}] / [\text{bulk molarity}]$. Pure compound solubility for toluene is set to 515 mg/l , and for naphthalene set to 31 mg/l (course material chapter2, page4, table 2.4). The calculated solubility is then used in conjugation with a mixing-ratio of 10:1 with water, using the difference between initial concentration and S_i as a base. S_i is re-calculated each time the compounds have been mixed with a hypothetical stepwise water-volume increase of 10 litres.

Calculations for the gas-phase

Henry's law is used to estimate concentrations in the gas-phase, expressed by $C_g = K_H \cdot C_w$, where

C_g is the estimated concentration in the gas-phase (mg/l)

K_H is Henry's constant (---)

C_w is the estimated concentration in water (mg/l) [changing over time]

The dimensionless form of Henry's law is derived from a temperature-dependent relationship. For all calculations, values are based on 25°C conditions at 1 atm, given by $K_H=0.27$ for toluene and $K_H=0.02$ for naphthalene (course material, chapter2, table 2.3).

Groundwater

To evaluate the lateral distribution of the compounds over time, Darcy's law is first used to estimate the amount of water transported per time. Based on this, the porewater velocity is calculated by taking the porosity of the medium into account.

Darcy's Law: $Q = -K \cdot A \cdot (dh/dl)$, where

Q = water flow (m^3/s)

K = soil hydraulic conductivity (m/s)

A = outflow area (m^2)

dh/dl = hydraulic gradient:

dh = change in groundwater elevation (m)

dl = distance between observations (m)

Porewater velocity (m/s) $V_p = Q/(A \cdot n_e)$, where n_e = effective porosity.

Klonowski et al. 2008 (fig.3 page 8) shows distribution of hydraulic conductivity for sampling profile SP 16. Here a majority of measurements seems to fall averagely around a K-value of $3.0 \cdot 10^{-4}$.

Hydraulic conductivity (K) is therefore set to $3.0 \cdot 10^{-4}$.

Area (A) is set to $1m^2$, which is though to be a representative part of the entire area, assuming a homogenous distribution of the compounds.

The hydraulic gradient (dh/dl) used is an average of the values registered at the site (0.004598, 0.005208, 0.004705 and 0.004384 ($m \cdot m^{-1}$)(Klonowski et al. 2008)), and is set to $4.72 \cdot 10^{-3}$ (m/m)

n_e is set from aquifer data = 0.367 (Klonowski et al. 2008)

Watervolume and transport-velocity is then combined with concentration-reduction to provide a lateral distribution of the compounds.

Degradation

First-order biodegradation rates can be used to calculate biodegradation of hydrocarbons dissolved in groundwater (Zheng et al. 2001).

Considering factors of half-life, using 1st order decay-rate and $C_0 \cdot e^{-k_1 t} = C_t$ where

C_0 = the original concentration

k_1 = the decay-constant

t = time

C_t = Concentration after time t

Time t is incremented in steps according to the time it will take to mix the compounds in a 10:1 ratio.

Half-life times:

Value-set1 (course material, assignment D)

Toluene: 28 days, meaning $k_1 = 2.475 \cdot 10^{-2}$

Naphthalene: 258 days, meaning $k_1 = 2.686 \cdot 10^{-3}$

Value-set2 (Zheng et al. 2001, table 4, page 4):

Toluene, $k_1 = 0.009$.

Toluene mixed with other: $k_1 = 0.051/0.078$. Mean value used = 0.065

Naphthalene: no data (not seen to degrade).

Note that extreme variations in half-life-times are found according to both the setting in which the compound occurs, and the mixture in which the compound is found (Mackay et al. 2000).

The formula for estimating concentration after time t is dependent on initial concentration C_0 , so calculations from Raoult's law is used. The difference in concentration before and after degradation is also accounted for, and the loss is deducted from calculations when using Raoult's law.

Soil calculations

Variations between 0.08% and 0.41% for TOC were detected in samples from the aquifer (Klonowski et al. 2008). Using an average of this equals a TOC of 0.245, and an $f_{oc} = 0.00245$.

Concentrations in the soil are calculated in multiple steps:

The organic carbon-water partitioning coefficient, K_{oc} , is used for determining the amount of sorption, and is estimated by $K_{oc} = 10^{0.989 \cdot \log K_{ow} - 0.346}$. K_{ow} is the octanol-water partition coefficient and is an expression of the compound's hydrophobicity, that is, the tendency to be separated from water. Predefined values for $\log K_{ow}$ is used: 2.69 for toluene and 3.37 for naphthalene (data from table page 30, lecture 4). K_d , the soil-water distribution coefficient, is then evaluated by the fraction of organic carbon, f_{oc} , and the calculated value for K_{oc} by $K_d = f_{oc} \cdot K_{oc}$. Finally the concentration in soil is evaluated by $C_{soil} = K_d \cdot C_{water}$ where C_{water} is the corresponding calculated value for the concentration of the compound in water.

To summarize, concentrations in soil is found by

- 1) Estimating $K_{oc} = 10^{0.989 \cdot \log K_{ow} - 0.346}$ with $\log K_{ow} = 2.69$ for toluene and 3.37 for naphthalene
- 2) Calculating K_d from $K_d = f_{oc} \cdot K_{oc}$ with $f_{oc} = 0.00245$.
- 3) Finding the concentration in soil from $C_{soil} = K_d \cdot C_{water}$

Retardation

Here retardation describes the slowing of compounds relative to movement of the groundwater. As such, retardation affects the transport-velocity of the compounds. To evaluate consistency over time and space, retardation could e.g. be measured by synoptic sampling, by estimating the velocity of the groundwater (using a nonreactive tracer, e.g. chloride) divided by the velocity of the solute (Roberts et al. 1986). Here, the retardation factor (R) is calculated using

$R = 1 + [(pb)/n] \cdot K_d$, where

pb = bulk density of soil ($kg/l = tonnes/m^3$)

n = porosity (m^3/m^3) and

K_d = distribution coefficient soil-water (l/kg)

Estimates are using a bulk density of aquifer equal to $1.68 (g/cm^3) [= 1.68 (kg/l)]$ (Klonowski et al. 2008), and K_d from calculations above.

The transport-velocity of the compounds is then calculated by: $v_c = v_p/R$ where

v_c = transport velocity of contaminant (m/s)

v_p = groundwater velocity (m/s)

R = retardation factor (-/-)

Gas-phase transport

To evaluate the mass being transported through the gas-phase from the plume towards the surface, Fick's 1. law is used. The formula describes diffusive compound transport, expressed by

$F = -D_{eff} \cdot (\delta C / \delta z)$ where $D_{eff} = -D_a \cdot [(\theta_a^{10/3})/n^2]$ and

F = diffusive compound transport, flux (g/m²/s)

D_{eff} = effective diffusion coefficient (m²/s)

δC = concentration difference (g/m³)

δz = diffusion length (m)

$\delta C / \delta z$ = vertical concentration gradient

D_a = diffusion coefficient in air (m²/s)

θ_a = gas-filled porevolume (m³/m³)

n = porosity (m³/m³)

δC = [concentration top] – [concentration over plume]

δz = depth to saturated zone = 4 m

D_a toluene at 25 °C: 0.0820 cm²/s = $8.2 \cdot 10^{-6}$ m²/s (data from table page 12, lecture7)

D_a naphthalene at 25 °C: 0.0662 cm²/s = $6.62 \cdot 10^{-6}$ m²/s (data from table page 12, lecture7)

θ_a is set from "thumb-rule" stating that a valid value (for this sediment/medium) can be found from half the volume of the porespace, meaning $\theta_a = 0.367/2 = 0.1835$

n^2 is the porosity squared = 0.367^2

Biodegradation

To determine the amount of electron-acceptors required to maintain the degradation-processes, the following reactions are used as a base (course material, lecture7, page 15):

Oxygen: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Nitrate: $2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$

Manganese: $Mn^{4+} + 2e^- \rightarrow Mn^{2+}$

Iron: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Sulphate: $SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$

Methanogenesis: $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$

For evaluation of requirements, each of these reactions are balanced based on oxidation and reduction ratios compared to the properties of the electron donor (toluene or naphthalene), and used in conjugation with the development of compound-concentrations. All reactions assume reaction with H₂O and/or production of CO₂. Compound-concentrations are converted to millimoles, and the ratio from the balanced reaction is used to estimate required amount of reducing agent.

Table 1: Constants used in calculations

	Aquifer	Toluene	Naphthalene	Bulk jet-fuel
Spillsize (l)	500			
Dimensions, infiltration (m)	1x1x4			
Porosity, n	0.375			
Retention(sat)	15 l/m ³			
Retention(unsat)	12 l/m ²			
Fraction organic content, f_{oc}	0.00245			
Bulk density, ρ_b (kg/l)	1.68			
Hydraulic conductivity (K) (m/s)	$3.0 \cdot 10^{-4}$			
Hydraulic gradient (m/m)	$4.72 \cdot 10^{-3}$			
Gas-filled porevolume (m ³ /m ³)	0.1835			
TOC min/max	0.08/0.41			
TOC avg.	0.245			
Weightpercent in jet-fuel		1.33	0.5	
Density (g/l)				800
Molecular weight (g/mole)		92.1	128.2	142
Pure compound solubility (mg/l)		515	31	
Henry's law constant, K_H		0.27	0.02	
Degradation-rate (course material)		$2.475 \cdot 10^{-2}$	$2.686 \cdot 10^{-3}$	
Degradation-rate 1 st O. (Zheng et al.2001)		0.009/0.065*	----	
Octanol-Water coefficient, $\log K_{ow}$		2.69	3.37	
Diffusion coeifficient, D_a (m ² /s)		$8.2 \cdot 10^{-6}$	$6.62 \cdot 10^{-6}$	
* toluene alone/toluene in mixture				
Note: In general, large differences are found in discription of both compounds, concerning their solubility, vapor pressure, Henry's law constant, octanol water partition coefficient ($\log K_{ow}$), soprtion partition coefficient ($\log K_{oc}$), and more (Mackay et al. 2000). Listed above are the ones deemed most relevant for this assignment. Values are chosen based on Mackay et al. 2000 and course-material, which is beleived to represent a valid interpretaion of the compounds' properties.				

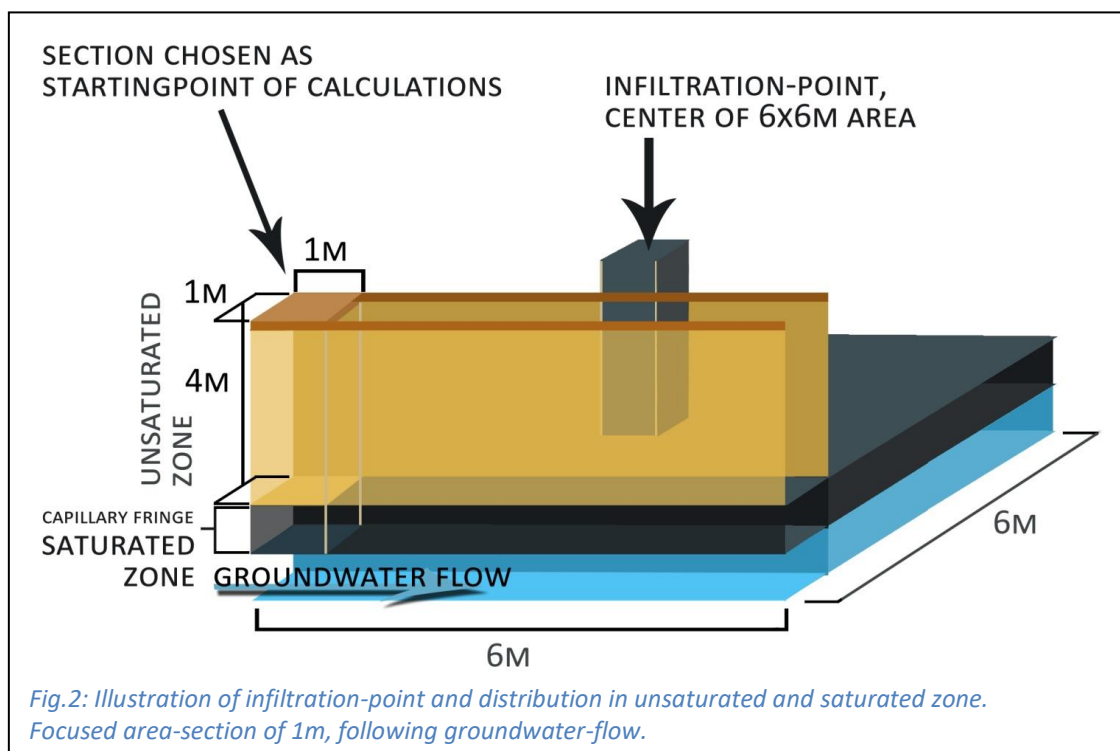
Matlab

All the calculations above are implemented as code in Matlab, which is used to produce graphical display of the development of the system.

Results

Idealized spill-scenario assumes bulk conditions in the aquifer approaching that of sand, and a concentration of the spill into two sections: 1) a cuboid with dimensions 1x1x4 meters (unsaturated zone), and 2) an underlying area with a calculated size in m² (saturated zone).

The retention in the unsaturated zone is estimated to 60l, giving 440l of potential spill to cover 36.67m² in the saturated zone. This would equal a square of approximately 6x6 meters (fig.2).



The bulk density of jet-fuel and weight-percent of toluene and naphthalene gives a content in g/l of toluene = 10.64 g/l and naphthalene = 4 g/l
 [Compound-content, using values from table 1: $800 \cdot 0.0133 = 10.64$ and $800 \cdot 0.005 = 4$.]

Using Raoult's law as described in the methods section gives the following results (table 2):

Table 2: Calculation of solubility by Raoult's law. S_1 represents no water-mixing and S_2 indicates first 10l mix

	Bulk jet-fuel	Toluene	Naphthalene
Density (g/l)	800		
Amount per liter jet-fuel (g/l)		10.64	4
Molecular weight (g/mole)	142	92.1	128.2
Molar concentration M (mole/l)	5.64	0.116	0.031
Molefraction		$2.05 \cdot 10^{-2}$	$5.54 \cdot 10^{-3}$
$S_1 = X_0 \cdot S_0$ (mg/l)		10.56	0.172
$S_2 = X_1 \cdot S_0$ (mg/l)		10.46	0.172

Further calculations by Raoult's law are presented graphically in figures 3 through 16.

Concentration in the gas-phase over the plume, determined by Henry's law and calculations from Raoult's law are given in figures 3 through 16.

Groundwater flow

Rate of water-flow calculated by Darcy's law looking at $A=1\text{m}^2$ yields $Q = -1.42 \cdot 10^{-6} \text{ m}^3/\text{s}$.

Porewater-velocity is subsequently evaluated to $V_p = -3.86 \cdot 10^{-6} \text{ m/s}$.

In relation to concentration-calculations, 10 litres of water per litre of jetfuel and 12 litres of jetfuel per m^2 would require a total of 120 liters of water.

Using calculated Q it will take: $(0.120 \text{ m}^3/\text{s}) / (1.42 \cdot 10^{-6} \text{ m}^3/\text{s}) = \text{ca } 84507 \text{ seconds } (0.978 \text{ days})$ to distribute water-proportion equalling 10:1 ratio with 12 liters of jetfuel per m^2 .

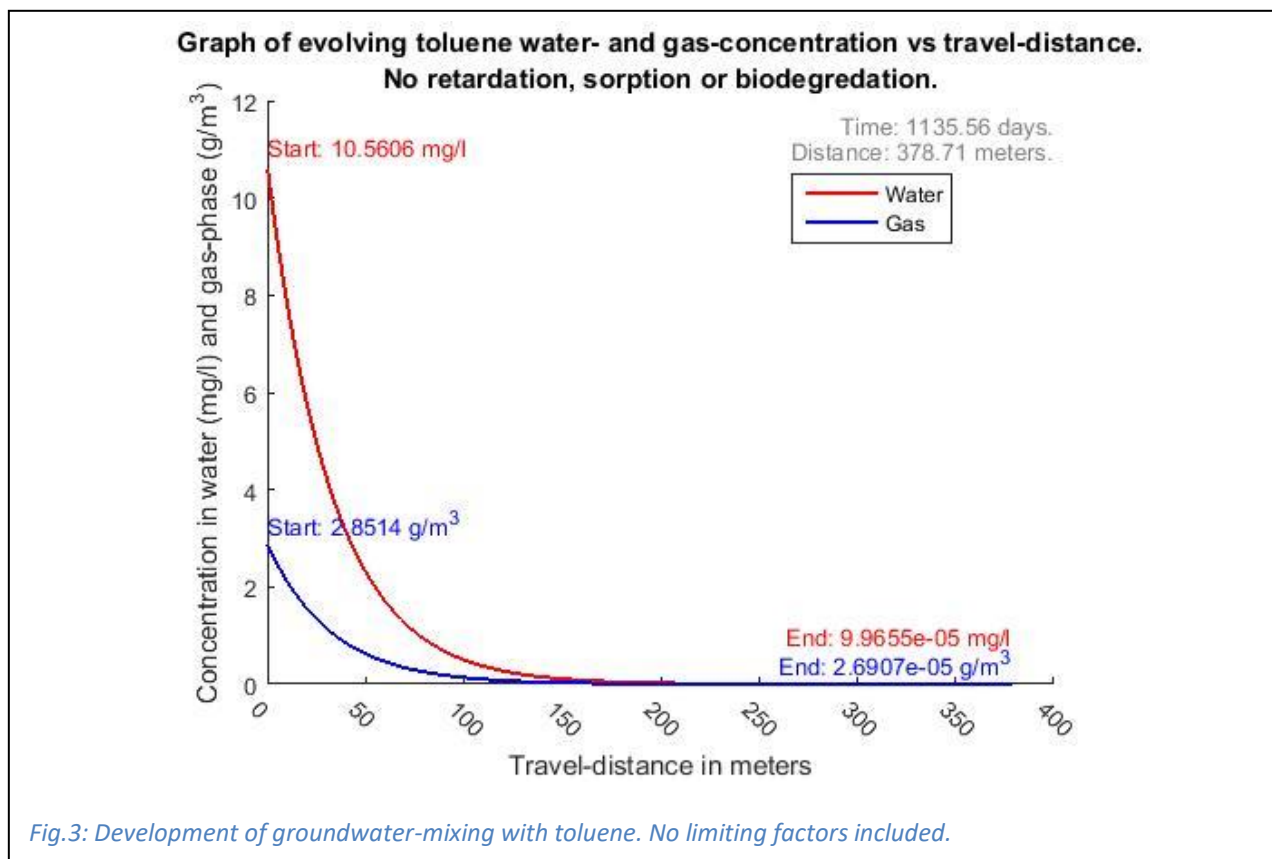
Using these estimations, each time the jetfuel in 1 m^2 has been mixed in a 10:1 ratio, the water (and compounds without any retardation) will have travelled $(-3.86 \cdot 10^{-6} \text{ m/s} \cdot 84507\text{s}) = \text{ca } -0.33\text{m}$.

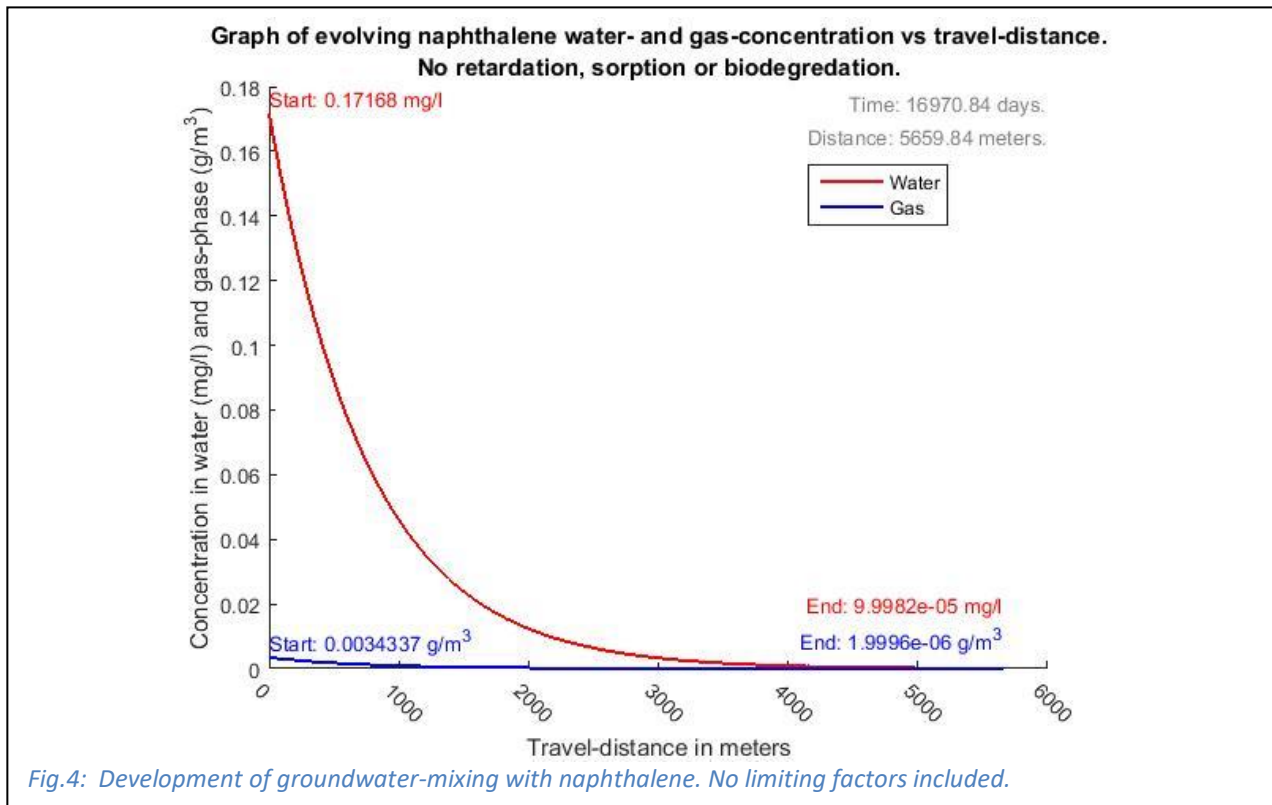
Considering general waterflow over a 1-year and 10-year period would give a travel-distance after 1 year of $(365\text{days} \cdot (-3.86 \cdot 10^{-6} \text{ m/s})) = \text{ca } -121.7 \text{ m}$, and a travel-distance after 10 years of -1217 m .

Table 3: Distribution and speed. Groundwater/Porewater/Jet-fuel. No retardation

	Groundwater	Jet-fuel
$Q = -K \cdot A \cdot (dh/dl)$	$-1.42 \cdot 10^{-6} \text{ m}^3/\text{s}$	
Porewater velocity, V_p	$-3.86 \cdot 10^{-6} \text{ m/s}$	
Mixingtime (10:1 per m^2)		0.978 days
Traveldistance per 10:1 mix	-0.33 m	-0.33m
Traveldistance after 1 year	-121.7 m	
Traveldistance after 10 years	-1217 m	

Using these results to provide a time-factor to the amount of mixing done to the compounds, a lateral movement can also be inferred. Combining this with both Raoult's law and Henry's law yields a distribution shown in figure 3 and figure 4. Note that all graphs are using drinkingwater-threshold of $0.1 \mu\text{g/l}$ as limit for calculations.





Degradation

Degradation combined with Raoult's law concentrations is calculated iteratively using procedure from method-section. This leads to the set of illustrations combining degradation with previous calculations in figures 5 through 16.

Sorption

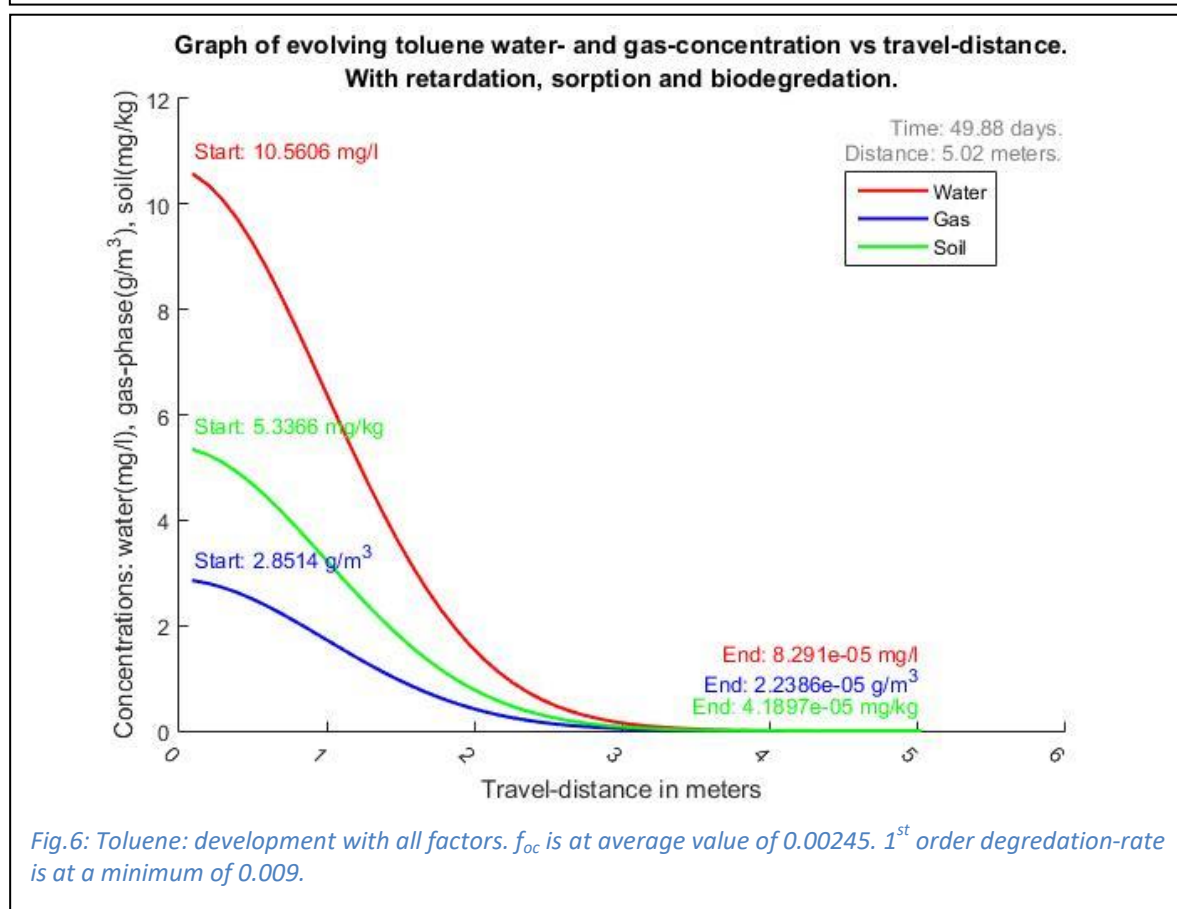
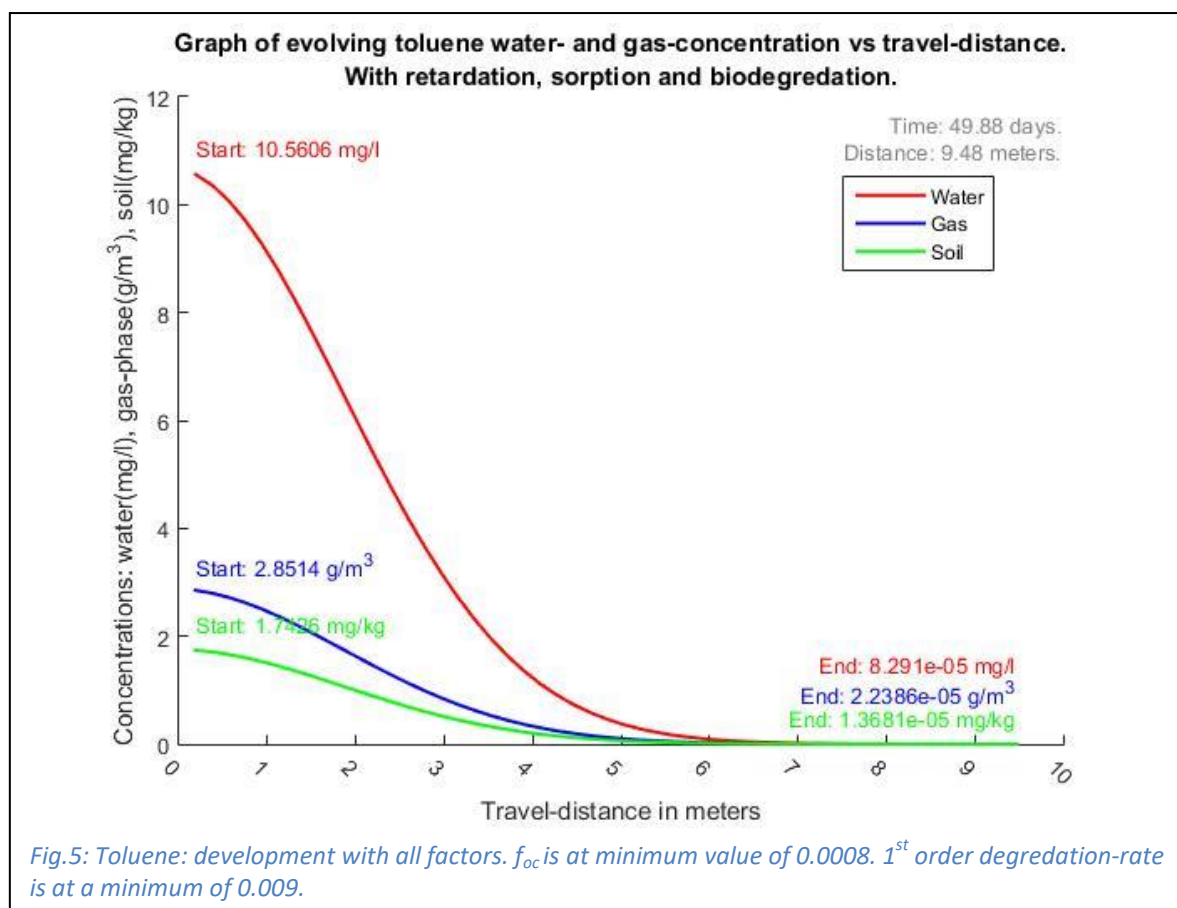
Estimating K_d , retardation-factor (R) and compound velocity (v_c), using values from table 1:

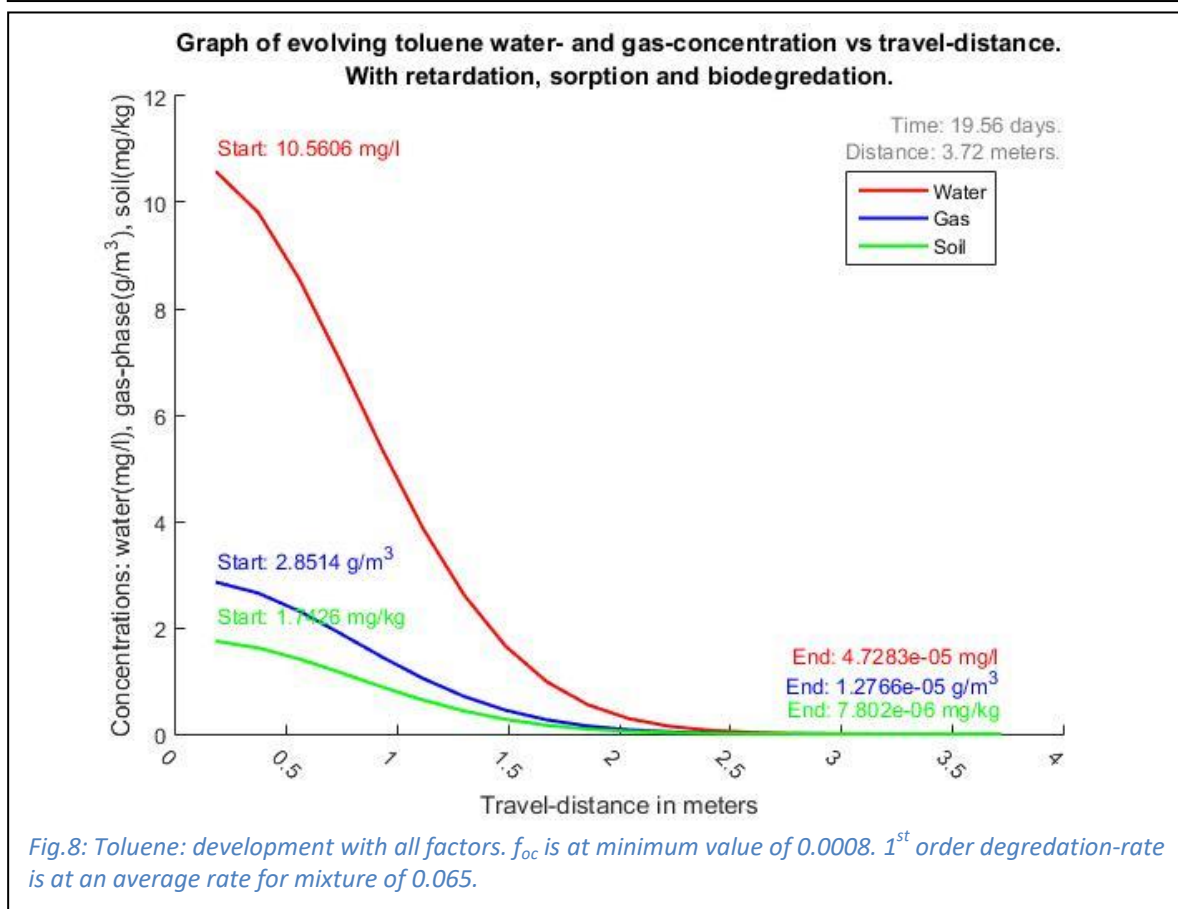
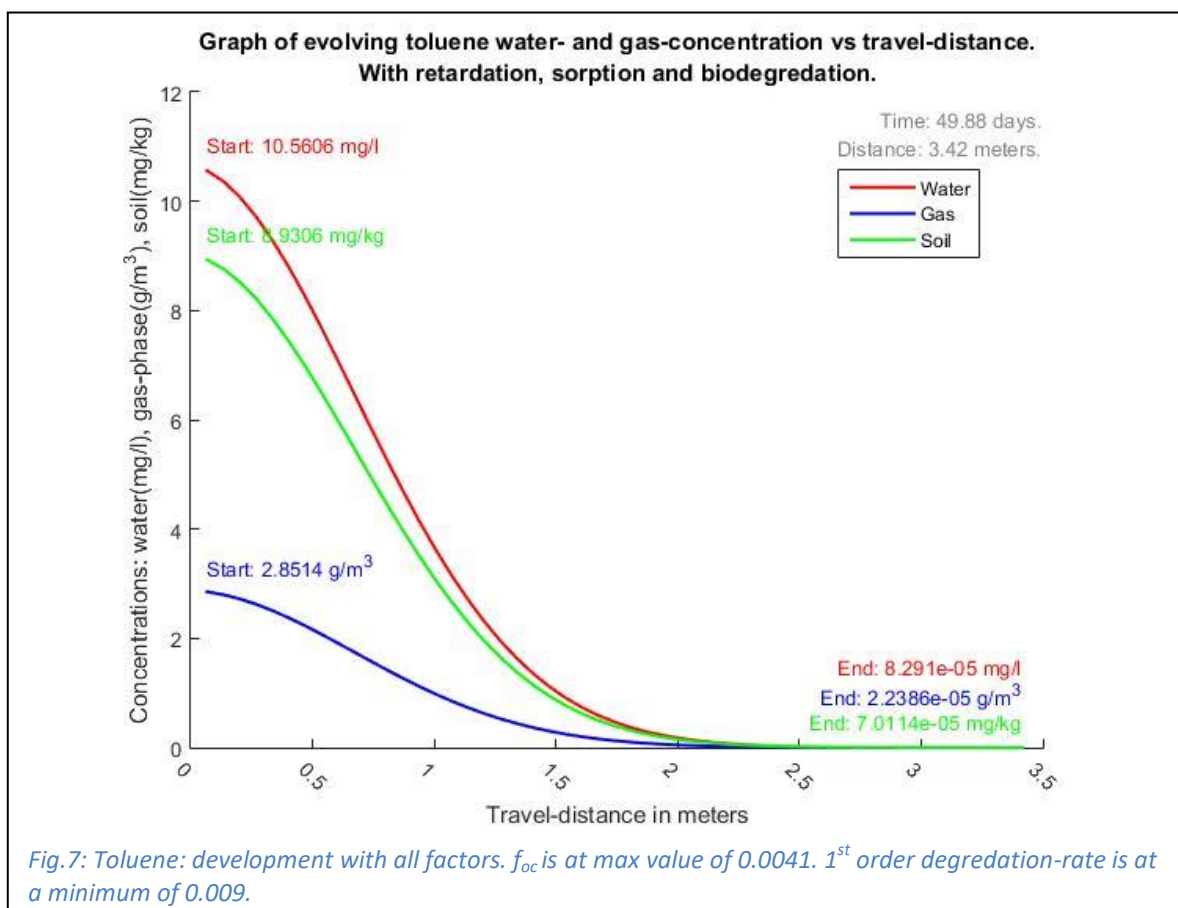
Table 4: Sorption related values for toluene and naphthalene

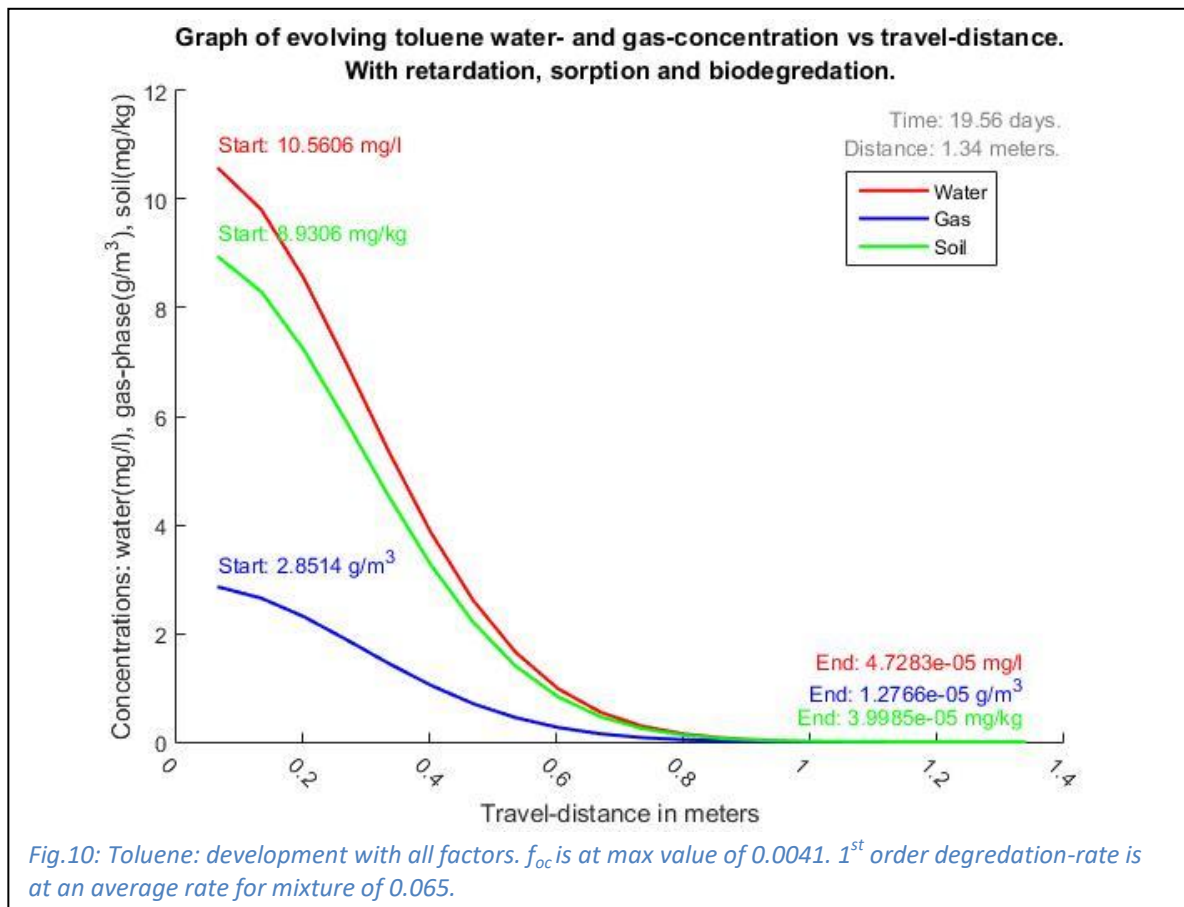
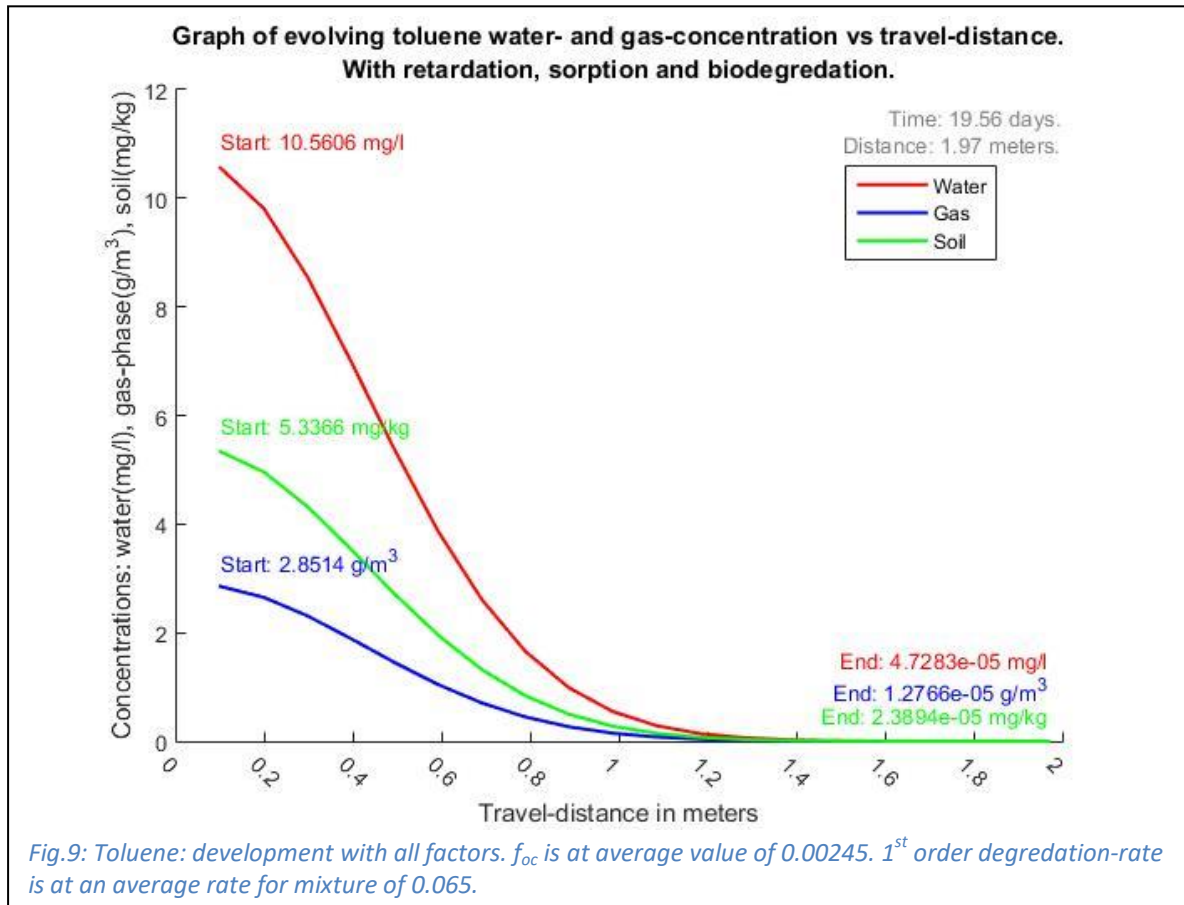
	Toluene	Naphthalene
K_d	0.51	2.38
$R = 1 + [(pb)/n] \cdot K_d$	3.31	11.88
$v_c = v_p/R$	$1.17 \cdot 10^{-6}$	$3.25 \cdot 10^{-7}$

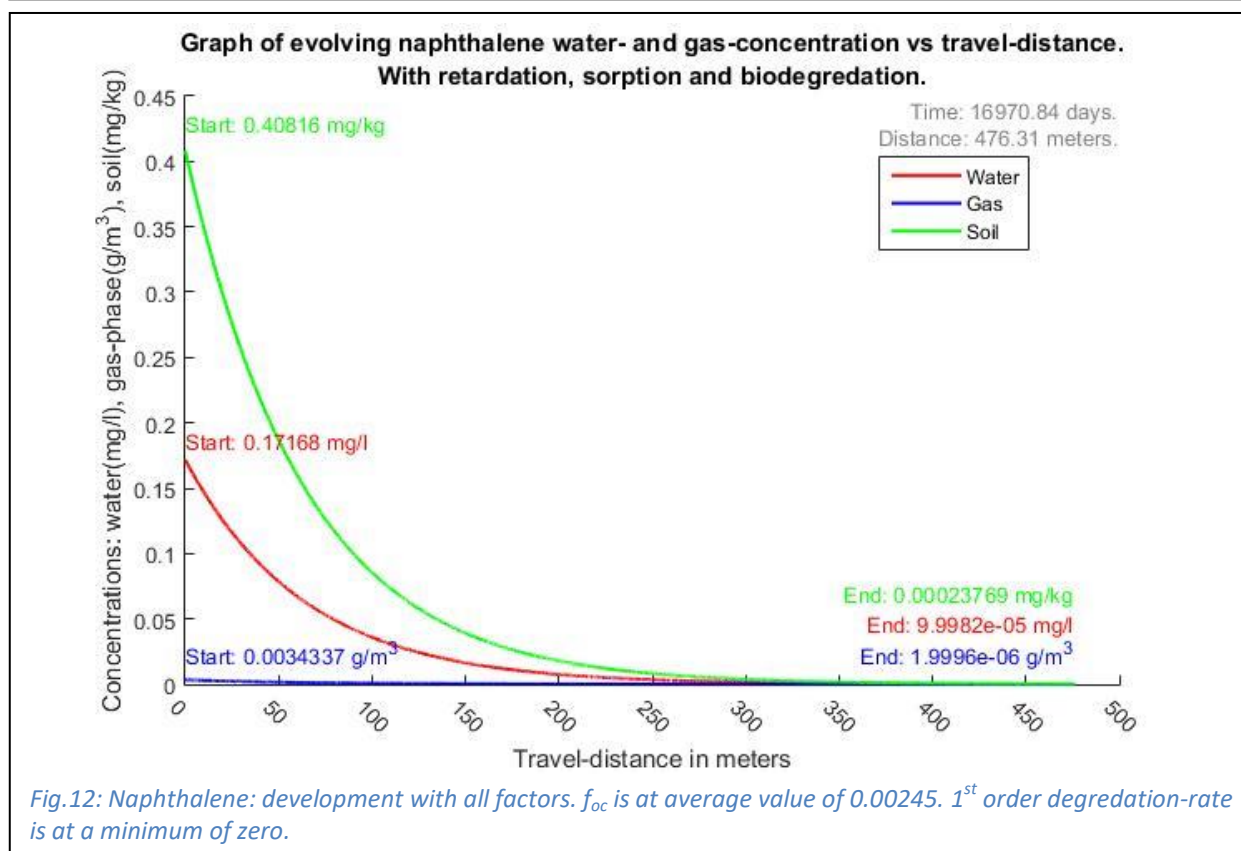
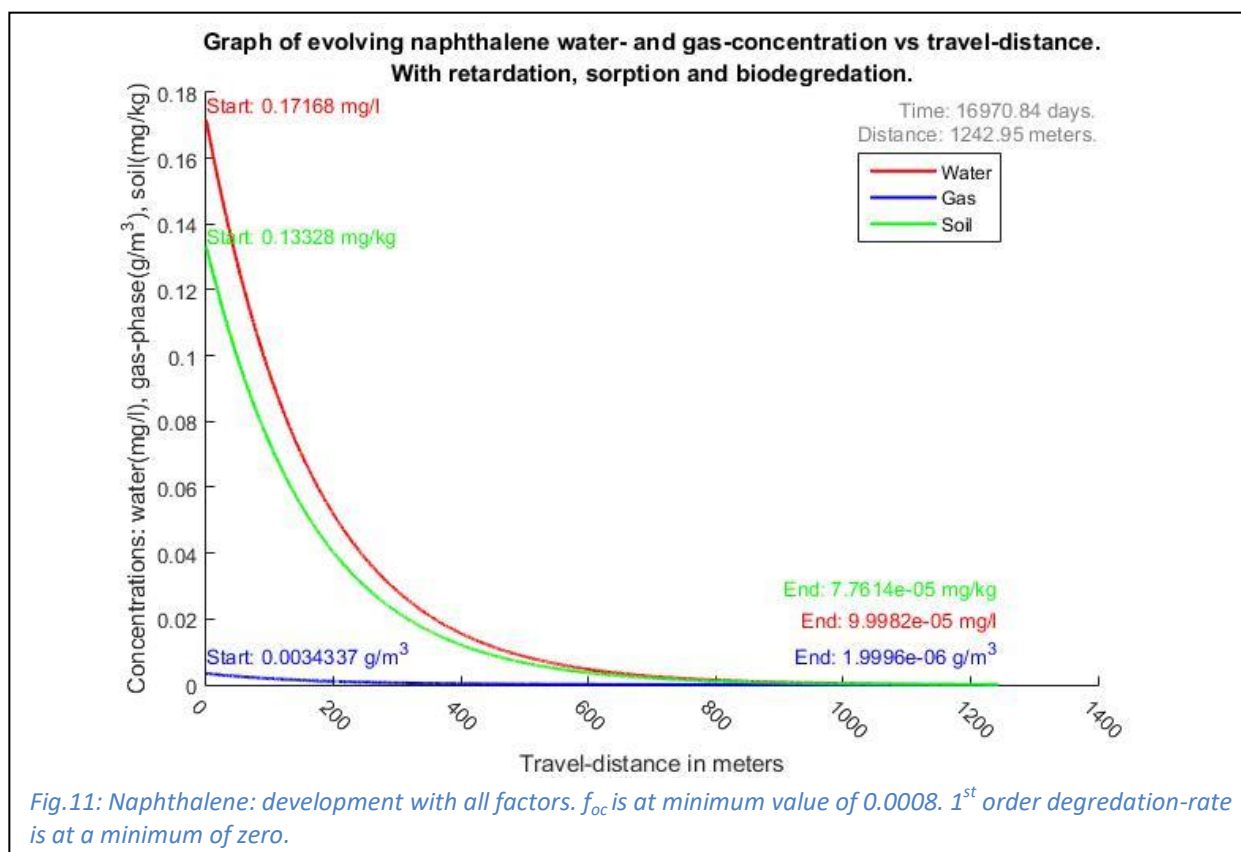
Concentration in soil by $C_{soil} = K_d \cdot C_{water}$ is dependent on concentrations in water estimated by Raoult's law and determined iteratively. Results and variations are shown in figures 5 through 18.

Following pages show various development-scenarios of toluene and naphthalene. Note again that all graphs are using drinking water-threshold of 0.1 $\mu\text{g/l}$ as limit for calculations. Figures are first showing toluene-graphs with minimum 1st order degradation-rate (0.009) and increasing f_{oc} -values, then toluene with average of mixture 1st order degradation-rate (0.065) and increasing f_{oc} -values. Naphthalene is then presented in the same manner, but with a minimum 1st order degradation-rate of zero, and a max of 0.002686. Note also that presented gas-concentrations are based on Henry's law, and does not represent diffusive compound transport.









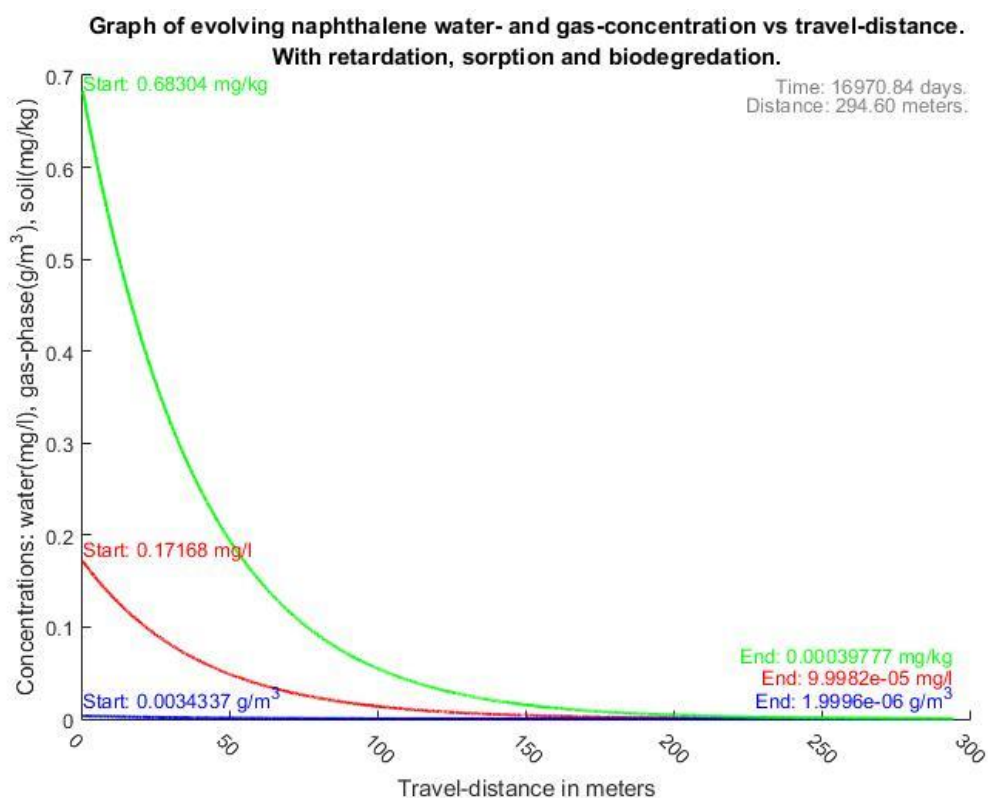


Fig.13: Naphthalene: development with all factors. f_{oc} is at max value of 0.0041. 1st order degradation-rate is at a minimum of zero.

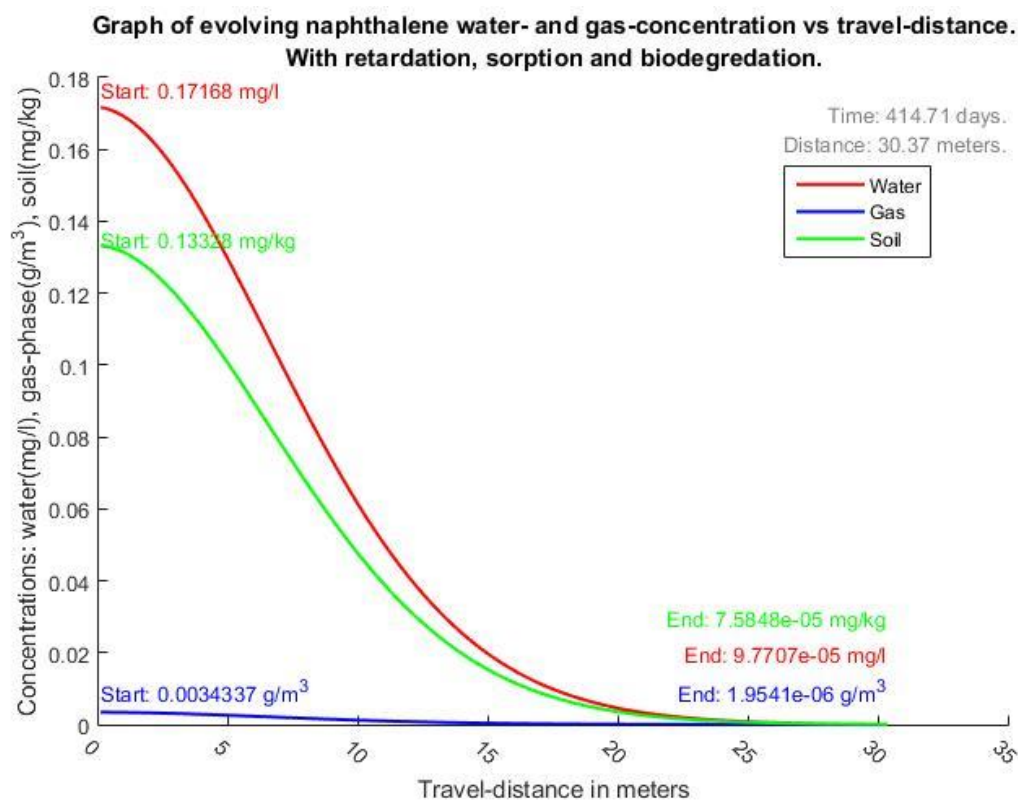


Fig.14: Naphthalene: development with all factors. f_{oc} is at minimum value of 0.0008. 1st order degradation-rate is at 0.002686.

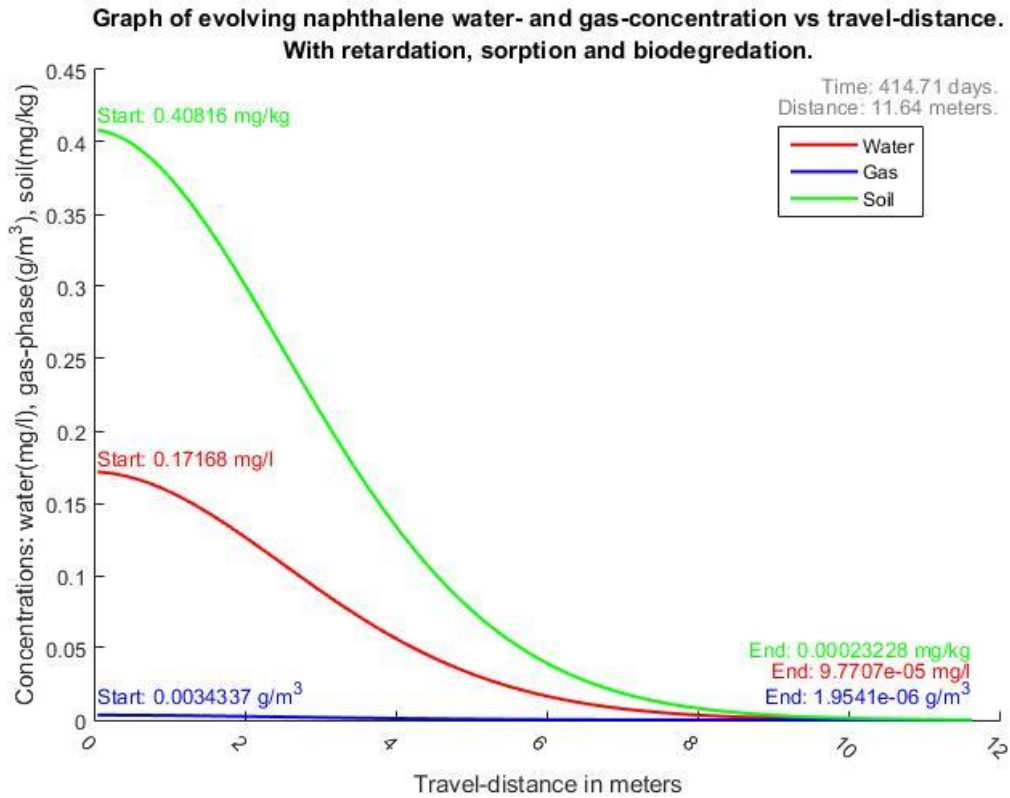


Fig.15: Naphthalene: development with all factors. f_{oc} is at average value of 0.00245. 1st order degradation-rate is at 0.002686.

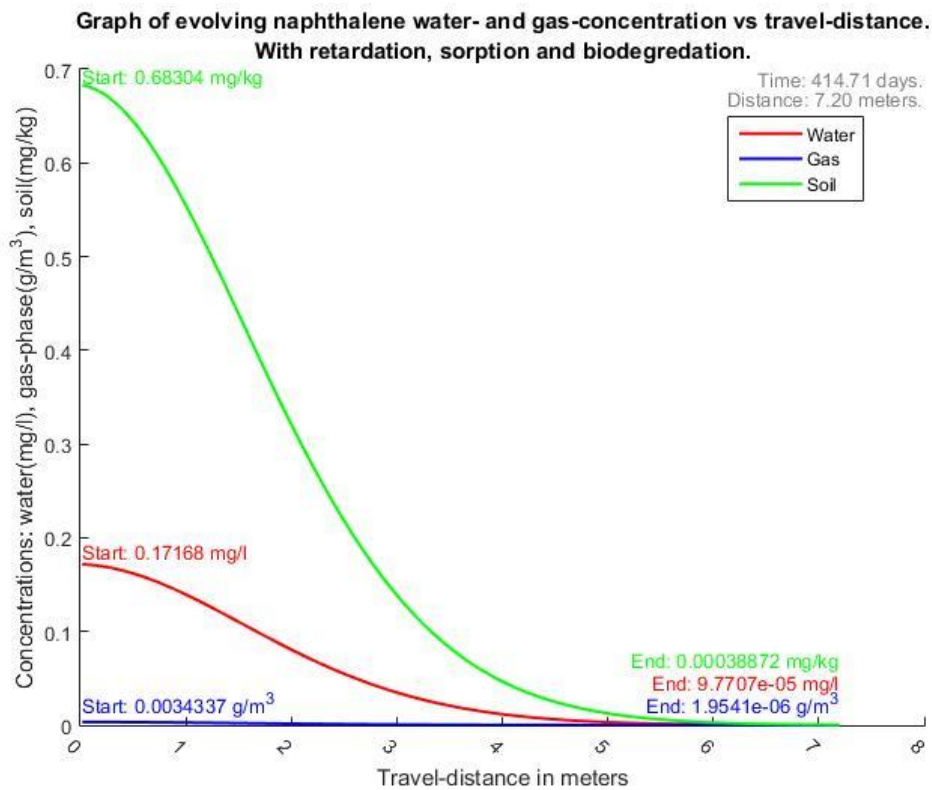


Fig.16: Naphthalene: development with all factors. f_{oc} is at max value of 0.0041. 1st order degradation-rate is at 0.002686.

To summarize scenarios, table 5 shows travel-distance and time for the compounds transported in groundwater. Distance and time equals the values for reducing dissolved amount of compounds in 1m² containing 12 liters of jet fuel to drinking water quality.

Table 5: Time/Distance relationship for compounds. Time in days and distance in meters.

	Toluene 1 st order d.-rate 0.009	Toluene 1 st order d.-rate 0.065	Naphthalene 1 st order d.-rate zero	Naphthalene 1 st order d.-rate 0.002686
<i>f_{oc}</i> 0.0008	49.88/9.48	19.56/3.72	16970.84/1242.95	414.71/30.37
<i>f_{oc}</i> 0.00245	49.88/5.02	19.56/1.97	16970.84/476.31	414.71/11.64
<i>f_{oc}</i> 0.0041	49.88/3.48	19.56/1.34	16970.84/294.60	414.71/7.20

Gas-phase transport

Estimating transport from free-phase compounds located in saturated zone in contact with unsaturated zone using Fick's 1. law. Compounds dissolved and transported by groundwater is not considered. δC in the formula for diffusive compound transport is dependent on the concentration over the plume, which is estimated by Henry's law where $C_g = K_H \cdot C_w$ and $C_g = -\delta C$. The formula initially estimates the flux per grams per m² per second. Using constants from table 1, results are shown in table 6.

$$C_g \text{ toluene: } 10.56 \text{ mg/l} \cdot 0.27 = 2.85 \text{ mg/l}$$

$$C_g \text{ naphthalene: } 0.172 \text{ mg/l} \cdot 0.02 = 0.00344 \text{ mg/l}$$

$$-D_{\text{eff}} \text{ toluene: } 8.2 \cdot 10^{-6} \text{ m}^2/\text{s} \cdot [(0.1835^{10/3})/0.367^2] = 2.138 \cdot 10^{-7}$$

$$-D_{\text{eff}} \text{ naphthalene: } 6.62 \cdot 10^{-6} \text{ m}^2/\text{s} \cdot [(0.1835^{10/3})/0.367^2] = 1.726 \cdot 10^{-7}$$

Table 6: Diffusive compound transport

	$C_g = -\delta C$	$-\delta C/\delta z$	$-D_{\text{eff}}$	$F \text{ (mg/m}^2/\text{s)}$	$F \text{ (mg/m}^2/\text{year)}$
Toluene	-2.85	0.7128	$-2.138 \cdot 10^{-7}$	$1.52 \cdot 10^{-7}$	4.8
Naphthalene	-0.00344	0.00086	$-1.726 \cdot 10^{-7}$	$1.48 \cdot 10^{-10}$	0.00468

Biodegradation

Completing the half-cell reactions described in the methods-section yields reactions and ratios presented in tables 7 and 9, with data from table 8.

Table 7: Redox-reactions for toluene and naphthalene according to reduction-type

Reduction-type	Toluene	Ratio	Naphthalene	Ratio
Oxygen	$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$	9:1	$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$	12:1
Nitrate	$5C_7H_8 + 36NO_3^- + 36H^+ \rightarrow 35CO_2 + 18N_2 + 38H_2O$	36:5	$5C_{10}H_8 + 48NO_3^- + 48H^+ \rightarrow 50CO_2 + 24N_2 + 44H_2O$	48:5
Manganese	$C_7H_8 + 18Mn^{4+} + 14H_2O \rightarrow 7CO_2 + 18Mn^{2+} + 36H^+$	18:1	$C_{10}H_8 + 24Mn^{4+} + 20H_2O \rightarrow 10CO_2 + 24Mn^{2+} + 48H^+$	24:1
Iron	$C_7H_8 + 36Fe^{3+} + 14H_2O \rightarrow 7CO_2 + 36Fe^{2+} + 36H^+$	36:1	$C_{10}H_8 + 48Fe^{3+} + 20H_2O \rightarrow 10CO_2 + 48Fe^{2+} + 48H^+$	48:1
Sulphate	$2C_7H_8 + 9SO_4^{2-} + 18H^+ \rightarrow 14CO_2 + 9H_2S + 8H_2O$	9:2	$C_{10}H_8 + 6SO_4^{2-} + 12H^+ \rightarrow 10CO_2 + 6H_2S + 4H_2O$	6:1
Methanogenesis	$2C_7H_8 + 10H_2O \rightarrow 5CO_2 + 9CH_4$	9:2	$C_{10}H_8 + 8H_2O \rightarrow 4CO_2 + 6CH_4$	6:1

Note: Further details on reactions are given in appendix

Table 8: Data of availability of electron acceptors. Here ordered after priority.

	Background (mg/l) [*]	Proximity to plume (mg/l) [*]
Oxygen (O₂)	8.3 ^{**}	Depleted
Nitrate	15	Depleted
Sulphate	15	Depleted
Manganese (II)	0.05 ^{***}	5
Iron (II)	0.7 ^{***}	70
Bicarbonate ^{****}	130	160

^{*}Values after Klonowski et al. 2008.

^{**}At saturation freshwater, 25°C, 1 atm (close to saturation reported in Klonowski et al. 2008).

^{***}Reported as two orders of magnitude less than concentrations in proximity to plume. However, values for proximity to plume should be used in calculations due to solid state of mineral (not regarded as dissolved and transported by water).

^{****}For methanogenesis. Not used directly in calculations.

Initial values of toluene = 10.56 mg/l and naphthalene 0.172 mg/l (table 2) gives a mole-content of compounds: Toluene: $[10.56 \text{ (mg/l)} / 92.1 \text{ (g/moles)}]$ mmoles = 0.1147 mmoles

Naphthalene: $[(0.172 \text{ mg/l}) / 128.2 \text{ (g/moles)}]$ mmoles = $1.34 \cdot 10^{-3}$ mmloes

Based on ratios (table 7), and availability (table 8), demand of acceptors are evaluated in table 9.

However, due to the site-specific nature of biodegradation, naphthalene is excluded from further calculations since no biodegradation of the compound has been observed at the site (Zheng et al. 2001).

Table 9: Electron acceptors; demand compared to ratio and compound-concentration (in mmols).

	Demand (mmol/l) · ratio	Weight (g/mole)	Required (mg/l)	Available (mg/l)	Removed (%)	Rest toluene (mg/l)
Oxygen (O₂)	1.032	32.00	33.02	8.3	25.14	$10.56 \cdot \% = 7.91$
Nitrate	0.618	62.00	38.34	15	39.12	$7.91 \cdot \% = 4.82$
Sulphate	0.236	96.06	22.67	15	66.17	$4.82 \cdot \% = 1.63$
Manganese(IV)	0.324	54.94	17.80	5	28	$1.63 \cdot \% = 1.17$
Iron (III)	0.458	55.85	25.59	70	100	$1.17 \cdot \% = 0$

Note: Bicarbonate (evaluated as CO₂) is disregarded.

Discussion, introduction:

Because of the simple methods applied in this study, it is not clear whether the assumptions made are viable. However, in a real-life scenario it is likely that a significant amount of the compounds would have to infiltrate the area in a matter approaching that of the scenario. Furthermore, simplification to systems is almost always the only option at hand because of the extreme variability and complexity of natural systems. This process has been referred to as 'justifiable simplification' (Karickhoff 1981). Because of inevitable simplification the acquired numbers are rather used as indicative of the general situation, and in general not used as hard facts (even though some numbers are given with many decimals).

Discussion

Without presence of organic matter or any form of degradation, naphthalene can have an extremely long residence-time, moving great distances. This scenario however is believed very unlikely to be satisfied under natural conditions. Observing e.g. fig.13 vs fig.4, the greater sorption of naphthalene limits its movements to a large extent, even without any biodegradation taking place. Including biodegradation the movement is even more limited (fig.16). With already low f_{oc} -values, even small increments show to limit the movement, and drastically increase sorption. Changing from minimum to average values of f_{oc} for naphthalene, increases sorption by over 200% (fig.14 vs fig.15). From minimum to maximum this increases by over 400% (fig.14 vs fig.16). However, the low to non-existing values for biodegradation seems to imply that even though the movement is being limited, the residence-time of the compound is still very long.

Toluene seems to be limited both in residence-time and spatial distribution. Biodegradation even at the lowest values are limiting. At the most likely value, toluene in mixture, the compound seems to have been reduced to drinkingwater quality during a period of under 3 weeks, moving within meters of the plume. Notably, this is not degradation of the plume, just the fraction of dissolved contaminant present in the water. The TOC content is a dominating factor concerning this compound as well, even though at a lower level than the more hydrophobic naphthalene. Spatial distribution is in the range of a few meters. This coincides with observations by Klonowski et al.2008.

The hydrophobicity of a compound is related to the sorption of the compound onto sediments/soils, where compounds that exhibit a large degree of hydrophobicity tend to show low water-solubility and high adsorption (Roberts et al. 1986). Hydrophobicity is expressed via the octanol-water coefficient K_{ow} . The more hydrophobic naphthalene, with its higher K_{ow} and lower solubility than toluene should in theory then be transported slower and have a longer residence-time than toluene. This tendency also seems to be the case for figures 5 through 10 versus figures 11 to 16.

Also being related to solubility, the difference in retardation of the two compounds could invite to a separation of the plume. This can be substantiated in observations that solutes with different sorption-characteristics tend to separate in time and space (Roberts et al. 1986). Here naphthalene would be the compound of greatest concern, if separation and/or plume-migration were to occur.

Biodegradation is site-specific, and can change over time according to availability of terminal electron acceptors, and the pollution history of the sediment (Zheng et al. 2001). In the aquifer Fe(III)-, nitrate- and sulphate-reduction as well as methanogenesis are the main controlling factors (Klonowski et al. 2008). The exact values for oxygen-concentration in the groundwater is not known, and may be lower than the value used. During degradation of the compounds, anaerobic conditions can quickly occur, as described as being the case near the center of the plume in Klonowski et al. 2008. Under anaerobic conditions, BTEX compounds are used metabolically as electron donors, and used by micro-organisms for cell growth (Lawrence 2006). Considering results in table 9, both oxygen, nitrate, sulphate and manganese (IV) will be depleted, resulting in iron(III) being the

terminal electron acceptor. This would coincide with results from Klonowski et al. 2008, where iron(III) is also described as being the terminal electron acceptor. From this point of view, the documented presence of methanogenesis (Klonowski et al. 2008) should not be initiated. A possible answer to this could be a general change in level of reducing conditions, where BTEX degradation rates have been shown to decline from mildly reducing conditions (nitrate), to strongly reducing conditions (methanogenesis) in shallow aquifers (Lawrence 2006). Also, heterogeneity of the site could lead to areas depleted of iron and/or manganese, but none of this can be further substantiated.

Depletion of electron acceptors is described in Klonowski et al. 2008 as being most prominent around the core of the plume. This could imply a somewhat restricted movement of the plume, coinciding with the lower transport-values for toluene as seen in graphs with the higher 1st order degradation-rates and/or higher f_{oc} -values, e.g. fig.12. The major constraining factor on this being the TOC-content. For neutral organic compounds of limited solubility, sorption is governed by organic carbon (Karickhoff 1981).

Another issue that could be addressed regarding sorption is the heterogeneity of the sediments, with an assumed large part down to 4 meters being that of sands. For high sands sediments (>95) a drastic reduction in K_{oc} (2 to 10 fold) has been observed, resulting in a suggested need for particle-size correction for attained values (Karickhoff 1981). The fine sands portion (0.063–0.25 mm) at the site is evaluated at 31% (Zheng et al. 2001). It is not known whether the sediment-distribution at the site would qualify for this need, but due to heterogeneity at the site, the fact is mentioned as a precaution.

The diverse yet quite low values for TOC in conjugation with heterogeneity of the sediments, could indicate great local variations and should be taken into account. Coarser material is documented already at a depth of 5 meters (Zheng et al. 2001). This would influence e.g. retention capacity, pore volume and transport-velocity, and contribute to a change in the all-over distribution, where vertical heterogeneity in the aquifer can influence the spatial distribution of solutes (Roberts et al. 1986).

High degradation rates for toluene compared to that of naphthalene suggests that toluene was preferred in favor of naphthalene in the biodegradation-process. Solubility-difference is believed to affect the bioavailability and, as such, the degradation rate. Since no biodegradation was observed for naphthalene, this could be explained by the low solubility and hence slow degradation rates, or that lack of degradation is due to site-specific conditions (Zheng et al. 2001). 'Site-specific' is as described above interpreted such that certain criteria's must be met (e.g. micro-biological factors) for degradation to take place. What mixture the compound is present in will also be of concern, as the least persistent compounds are believed to catalyze transformation of more resistant compounds (Zheng et al. 2001).

For total removal of the contaminants to drinking water quality, table 5 can be used to present best- and worst-case scenarios through minimum and maximum values. To only emphasize on the best-case scenario, the gravity of groundwater contamination cannot be exaggerated:

Using 0.065 as 1st order degradation-rate for toluene indicates that a section of 1 meter (fig.2) containing 10.56 mg/l of toluene will be reduced to drinking water quality in 19.56 days equalling about 197 mg/l/y. Using 0.002686 as 1st order degradation -rate for naphthalene indicates that a section of 1 meter containing 0.172 mg/l of naphthalene will be reduced to drinking water quality in approximately 1.14 years, equalling about 0.15 mg/l/y.

Given the amount of toluene at 10.6 g/liter and the rates described, toluene seems to reside in the aquifer for about $[10600/(197_{\text{water}} + 4.8_{\text{gas}})] = \text{ca } 52.5$ years. Naphthalene seems to reside almost indefinitely. For both compounds it seems that diffusive compound transport is negligible.

This would illustrate that low mobility of the compounds can influence the apparent severity of the contamination only meters from the contaminated site, giving the false impression of a much less severe scenario.

Remediation

For monitored natural attenuation to be a viable option for site remediation, evidence that natural remediation is taking place at the site should be provided. This is done via site-specific data and analysis. The most important part being observations of contaminant distribution, and decreasing concentration over time. This can further be supported by observing that micro-biological activity is taking place and supports natural attenuation (NJDEP 2012). If organic compounds are the source of contamination, monitored natural attenuation is most effective where natural processes permanently degrade or destroy the contaminants (NJDEP 2012). Data showing stabilization of the plume is also indicative of natural attenuation, along with changes in groundwater chemistry (Klonowski et al. 2008).

The different scenarios seems to a large extent to limit the spatial distribution of the contaminants, evidently reducing the mobility of the plume. The presented reduction in gas-concentration could be used in conjugation with other results (including soil-samples), to support changes in groundwater chemistry. Also, considering the availability and depletion of electron acceptors it seems extremely likely that natural attenuation is taking place at the site.

The observation that naphthalene does not seem to be subject to biodegradation could be due to before-mentioned site specific nature. Here, slow or non-existing degradation of naphthalene could be due to lack of previous exposure, resulting in a 'time-lag', where the necessary micro-biological population needs to increase in numbers before it is capable of substantial transformation (Roberts et al. 1986).

Conclusion

Factors showing limited spatial advancement of the plume, including presence of biodegradation of toluene, supports monitored natural attenuation as a choice of remediation. However, since biodegradation of naphthalene is not documented at the site, the faith and longevity of the compound is difficult to determine. This could be due to lack of previous exposure to the contaminant, resulting in a time-lag before effective microbial degradation, but this cannot be verified. Also, the time required for total degradation of the plume makes it more likely for other external factors to influence the development, e.g. in terms of other anthropogenic sources.

Continued observation of the site should therefore be maintained. The proximity of, and the draining of the aquifer by, the Sogna river (Klonowski et al. 2008) can be of further concern as the contaminants, especially naphthalene, could be introduced to the aquatic life.

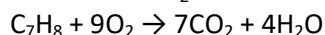
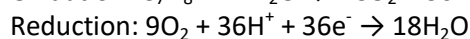
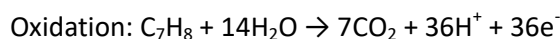
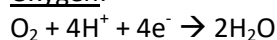
References

- Cline Patricia V., Delfino Joseph J., Rao P. Suresh C. 1991. *Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures*. Environ. Sci. Technol. 1991, 25, 914-920
- Faroon Obaid, Mandell Diane, Navarro Hernan. 1995. *Toxicological profile for jet fuels JP-4 and JP-7*. U.S. Department of health and human services, Public Health Service, Agency for Toxic Substances and Disease Registry. 1995. 150 pages.
- Karickhoff Samuel W. 1981. *Semi-Empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils*. Chemosphere, Vol.10 , No.8, 1981, pp 833 – 846.
- Klonowski Maciej R., Breedveld Gijs D., Aagaard Per. 2008. *Spatial and Temporal Changes of Jet Fuel Contamination in an Unconfined Sandy Aquifer*. Water Air Soil Pollut (2008) 188:9–30
- Lawrence S.J. 2006. *Description, properties, and degradation of selected volatile organic compounds detected in ground water — A Review of Selected Literature: Atlanta, Georgia, U. S.* Geological Survey, Open-File Report 2006-1338, 62 p., a Web-only publication at <http://pubs.usgs.gov/ofr/2006/1338/>.
- Mackay Donald, Shiu Wan Ying, Ma Kuo-Ching, Lee Sum Chi. 2000/2006 (ambiguity in material). *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition*. Taylor & Francis Group. 2000/2006. Excerpt for GEO4161, course material, 22 pages.
- NJDEP (New Jersey Department of Environmental Protection). 2012. *Site Remediation Program. Monitored Natural Attenuation Technical Guidance*. 175 pages. Available from: http://www.nj.gov/dep/srp/guidance/srra/mna_guidance_v_1_0.pdf
- Roberts Paul V., Goltz Mark N., Mackay Douglas M. 1986. *A Natural Gradient Experiment on Solute Transport in a Sand Aquifer 3. Retardation Estimates and Mass Balances for Organic Solutes*. Water Resources Research, Vol.22, No.13, December 1986, Pages 2047-2058.
- Zheng Z., Breedveld G., Aagaard P. 2001. *Biodegradation of soluble aromatic compounds of jet fuel under anaerobic conditions: laboratory batch experiments*. Appl Microbiol Biotechnol (2001) 57:572–578

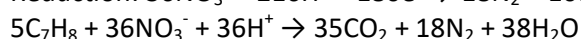
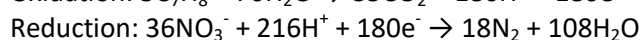
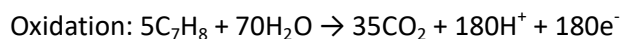
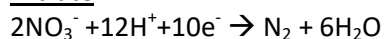
Redox-reactions

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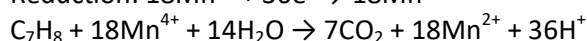
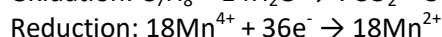
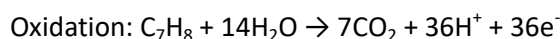
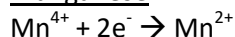
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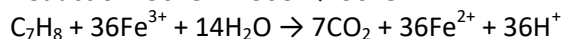
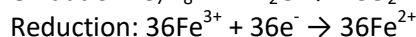
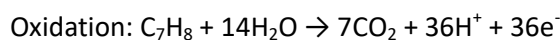
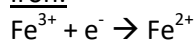
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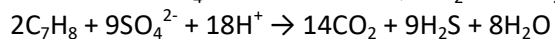
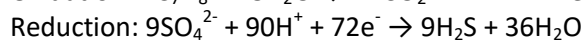
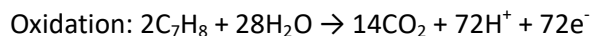
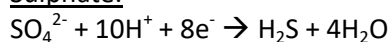
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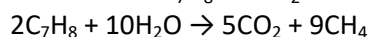
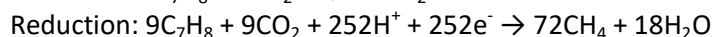
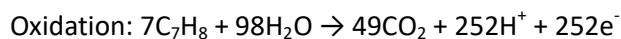
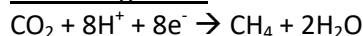
Iron:



Sulphate:

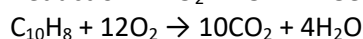
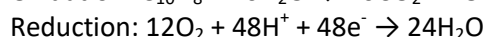
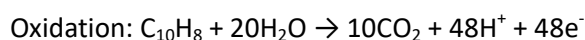
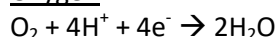


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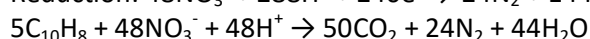
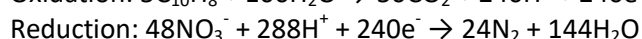
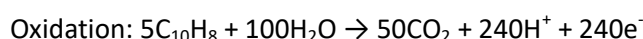
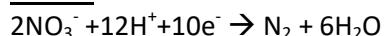


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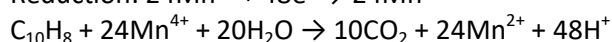
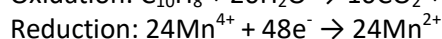
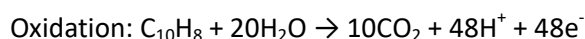
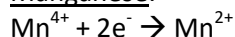
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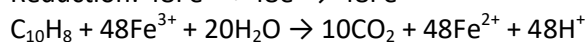
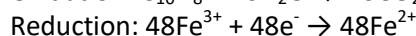
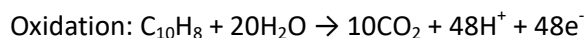
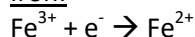
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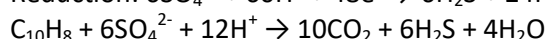
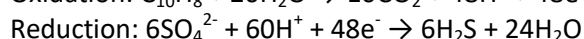
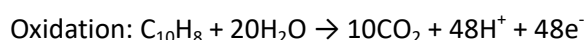
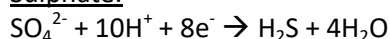
Manganese:



Iron:



Sulphate:



Methanogenesis:

