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Risk Assessment of Total Petroleum Hydrocarbons (TPHs) Fractions

Javier Pinedo*[a], Raquel Ibáñez[a], Ángel Irabien[a]

[a]Universidad de Cantabria, Departamento de Ingeniería Química y Química Inorgánica, Avda de los Castros s/n 39005, Santander, Spain.
pinedoj@unican.es

Leakages of oil products derived from petroleum can affect the environment, even causing risks to human. In order to study all the substances that usually are found in a petroleum leakage, it becomes interesting to apply the study to the Total Petroleum Hydrocarbons (TPH) fractions which have similar physico-chemical properties. The purpose of this paper is to perform a suitable risk specific site analysis for TPH fractions distribution and concentration, applying the RBCA (Risk Based Corrective Action) framework. As a case of study, this work is applied to a high populated area of a Spanish medium size city (Santander, approximately 182000 inhabitants). This simulation provides useful information about the pathways with higher risks, enabling to focus the analysis onto the parameters that mainly affect the risk assessment. This approach will simplify future site specific risk assessment and the corresponding decision making.

1. Introduction

Policies for contaminated soils management in Europe are evolving from total concentration-based approaches to current risk-assessmentapproaches (COM, 2006). Total Petroleum Hydrocarbon concentration is a global parameter which includes many derived petroleum products from C10 to C40, commonly applied to establish target soil cleanup levels approach implemented by different regulatory agencies (TPHCWG, 1998).
Nevertheless, TPH measurement does not give a useful basis for the evaluation of the potential risks, since it includes compounds with very different physical-chemical and toxicological properties (i.e. Table 3). A speciation process must be performed in order to quantify TPH risks. Several fractionation methods have been proposed to sort out this problem (TPHCWG, 1998). The TPH Criteria Working Group (TPHCWG) set a commonly used TPH fractionation, based not only on aliphatic and aromatic compounds, but also by their equivalent carbon number (EC). Different parameters such as solubility, vapor pressure, molecular weight, Henry's law constant or the organic carbon partition coefficient (K_{oc}) were defined for each fraction using correlations with the EC number. However, this method considers the evaluation of 13 different fraction categories, hindering the implementation of the risk site assessment. Improvement and reduction of these fractions can be achieved.
The purpose of this work is to identify the risks that may arise from a specific TPH fractions distribution and concentration, taking into account appropriate physico-chemical properties for each TPH fraction group. As a case of study, the risk assessment is focused in the surroundings of a petrol station located on a high populated area of a Spanish medium size city (Santander, 182000 inhabitants).
Therefore, the methodology to assess the simulation of the new TPH fractionation approach has been developed.

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2. Methodology

2.1 TPH fraction approach

A risk-based tiered approach was carried out based on the software RBCA Tool Kit for Chemical Releases Version 2,5e (Connor et al., 2009) that enables quantitative evaluation of site-specific risk by applying a site specific Tier-2 assessment. For this study, the adopted TPH concentrations were obtained from the averaging percent composition fractions proposed by the New Jersey Department of Environmental Protection Site Remediation Program (NJDEP, 2008), assuming a TPH concentration of 5000 mg/kg. Table 1 summarized soil concentrations for each TPH fraction. TPH correlations (TPHCWG, 1997) have been used to obtain physico-chemical properties of TPH fractions.

Table 1: TPH concentration in soil considered for each aliphatic and aromatic fraction (NJDEP, 2008)

TPH fraction	TPH percentage (%)	Soil concentration (mg/kg)
TPH aliphatic EC9-C12	4.6	230
TPH aliphatic EC12-C16	25.6	1280
TPH aliphatic EC16-C21	31.8	1590
TPH aliphatic EC21-C40	4.8	240
TPH aromatic EC10-C12	0.8	40
TPH aromatic EC12-C16	7.5	375
TPH aromatic EC16-C21	21.6	1080
TPH aromatic EC21-C34	3.3	165
Total TPH	**100**	**5000**

2.2 Evaluated scenario

The case study is focused in the surroundings of a petrol station located on a high populated area of a Spanish medium size city (Santander). Next to the petrol station there is a playground for children, the most sensitive receptor of contamination. Table 2 summarizes site specific data used to compute risks, with relation to the source of information. Two routes of contaminationwere assessed in this case, considering for each one different pathways:

- Volatilization & Particulates to Outdoor Air Inhalation (OA) through to the soil to ambient air volatilization of contaminants from affected soils and small particles of superficial affected soil.
- Surface Soil (SS) through direct ingestion, dermal contact and inhalation.

Table 2: Values of site specific parameters considered and their routes of information.

Input parameter	Specific value considered	Source
Thickness of the surface soil column (m)	1	Connor et al., 2009
Depth to top of affected soils (m)	0	Experimental data(1)
Depth to base of affected soils (m)	3.5	Experimental data(1)
Affected soil area (m^2)	2500	Experimental data(1)
Length of source zone area parallel to wind (m)	125	Experimental data(1)
Type of soil	ASTM defined	Connor et al., 2009
Fractional Organic Carbon Content	0.012	Hontoria et al., 2004
Soil pH	7.08	Experimental data(1)
Air mixing zone height (m)	2	Connor et al., 2009
Ambient air velocity in mixing zone (m/s)	3.506	PGOU, 2009
Particulate emission rate ($g/(cm^2 {*} s)$)	6.9E-14	Connor et al., 2009

(1): Data obtained in this study

3. Results and discussion

3.1 Calculation of physico-chemical properties for Aliphatic EC9-12 and EC21-40 fractions

A new eight TPH fractionation strategy was proposed, instead of the 13 TPHCWG fractions, according to table 1. Aliphatic EC12-16 and EC16-21 and all the aromatic fraction properties are included in the software, while aliphatic EC9-12 and EC21-40 must be approached to obtain new physico-chemical properties and toxicity values. Aliphatic EC22-40 was included to analyze heavier hydrocarbons in petroleum which can be found in contaminated soils (Park and Park, 2011). Table 3 summarizes results obtained from the application of TPHCWG correlations (TPHCWG, 1997). Lighter aromatic and aliphatic fractions were excluded since they are barely detected in soils due to their high volatility and also are usually measured in Gas Chromatography Mass Spectrometry (GC-MS) based in purge and trap technique.

Table 3: Specific physico-chemical and toxicity parameters adopted for new TPH fractions included

Estimated properties	Aliphatic EC9-12	Aliphatic EC21-40
Solubility (mg/L)	6.4 E-02	6.4 E-13
Vapor Pressure (mmHg)	8.5 E-01	4.2 E-08
Molecular Weight (g/mole)	150	430
Henry's Constant (cm^3/cm^3)	1.1 E+02	1.5 E+06
Log K_{oc}	5.2 E+00	1.4 E+01
Air diffusion coefficient (cm^2/s)	1.0 E-01	1.0 E-01
Water diffusion coefficient (cm^2/s)	1.0 E-05	1.0 E-05
Relative bioavailability factor	1.0 E-00	1.0 E-00
Bioconcentration factor	3.1 E+03	8.9 E+05
Dermal absorption factor	6.7 E-02	1.0 E-01
Gastrointestinal absorption factor	6.0 E-01	5.0 E-01
Oral Reference Dose (mg/kg*day)	1.0 E-01	1.6 E-00
Dermal Reference Dose (mg/kg*day)	1.0 E-01	1.6 E-00
Reference Concentration (mg/m^3)	2.0 E-01	-

3.2 Site specific analysis

Two indicators for risk assessment were evaluated for on-site and off-site exposure (Vianello and Maschio, 2011). Baseline risk level was calculated to assess potential adverse impacts associated with user-specified constituent concentrations. The toxicity parameter obtained is the Hazard Quotient (HQ) with an acceptable risk value of 1E+0. Risk-based clean-up standard level indicates remedial action target levels for the chemical(s) of concern developed for a particular site. For Tier-2 assessment the clean-up level is the Site-Specific Target Levels (SSTL)

a) <u>Baseline risk level</u>

Results from site-specific analyses for baseline risk levels are shown in Table 4. Outdoor air is the pathway with lower risk, with all the HQ below the upper limit of 1.0. TPH fractions with an equivalent carbon number above EC16, for both aliphatic and aromatic, do not present HQ for outdoor air as vapour pressures are low enough to migrate through air. Soil risks for each fraction are also below HQ limit; nevertheless cumulative risk is almost 1.6 higher than this limit. This cumulative risk is mainly due to aromatic EC16-21 fraction, with almost 50% of the total risk.

Taking into account risks for on-site and off-site studies, is noticeable that HQ becomes lower when the receptor is farther from the source of contamination, as it was expect.

Table 4: Hazard Quotient for each pathway and distance to source for the different TPH fractions

TPH fraction	Outdoor Air			Soil
	HQ 0 m	HQ 50 m	HQ 100m	HQ
TPH aliphatic EC9-12	0.12363	0.06087	0.01985	0.04593
TPH aliphatic EC12-16	0.68804	0.33874	0.11050	0.32919
TPH aliphatic EC16-21	-	-	-	0.02045
TPH aliphatic EC21-40	-	-	-	0.00386
TPH aromatic EC10-12	0.01192	0.00587	0.00191	0.02572
TPH aromatic EC12-16	0.03949	0.01944	0.00634	0.24110
TPH aromatic EC16-21	-	-	-	0.80029
TPH aromatic EC21-34	-	-	-	0.12227
Total TPH (sum)	**0.86308**	**0.42492**	**0.13861**	**1.58881**

b) Risk-based Clean-up standard level

Results from site-specific analyses for risk-based clean-up standard levels are shown in Table 5. SSTL concentrations for superficial soil and subsoil are exposed, as well as the soil concentration considered. SSTL values for the sum of TPH is not the sum of the different SSTL, but rather a specific value. Comparing these values, the only concentration which is above the SSTL obtained for this scenario is the total TPH in superficial soil, with a value 1.6 times higher than the SSTL. Furthermore, SSTL values obtained for each fraction are quite different, involving increasing risks fractions with lower EC number and highlighting the need of TPH fractionation.SSTL values for subsoil cannot be estimated. This fact could happen when the soil saturation limit is exceeded because values obtained do not represent a real framework to study.

Table 5: Site-Specific Target Levels (SSTL) for superficial soil and subsoil exposure pathways for the different TPH fractions and soil concentration considered for the comparison

TPH fraction	SSTL Sup. Soil (mg/kg)	SSTL Subsoil (mg/kg)	Soil concentration (mg/kg)
TPH aliphatic EC9-12	5007.5	>111E+0	230
TPH aliphatic EC12-16	3888.4	>46E+0	1280
TPH aliphatic EC16-21	NQ	NQ	1590
TPH aliphatic EC21-40	NQ	NQ	240
TPH aromatic EC10-12	1555.3	>756E+0	40
TPH aromatic EC12-16	1555.3	>349E+0	375
TPH aromatic EC16-21	NQ	NQ	1080
TPH aromatic EC21-34	NQ	NQ	165
Total TPH	**3147.0**	**>1.415E+0**	**5000**

NQ: Not Quantifiable

3.3 Sensitivity Analysis

In the ASTM-RBCA methodology of risk analysis, analytical multimedia models are used to assess contaminants fate and transport in the environment. However, the models results are highly dependent from the values of some input parameters, and therefore, potentially subject to manipulation. To increase reliability in models response is critical the identification of the input parameters that are mainly responsible of results variability. At this aim, a Sensitivity Analysis has been performed.

The Sensitivity Analysis was applied to soil and outdoor air parameters, shown in Table 2 and the results allow identify the input key parameters that need a deeper characterization during the data collection process. For those input key parameters that have shown a response on the results, a standardization process has been carried out, in order to assess their variability range. The process was first obtained multiplying and dividing the parameter values by a factor of 10 and 100 and then, in order to dimensionless them, each values was divided by the default value considered (X-axis). Risk values were normalized with respect to the acceptable limit value of 1 for HQ (Y-axis). Soil pH and particulate emission rate are the two input parameter with no effect to HQ for this case study. The thickness of the surface soil column has a low impact in HQ so it will not be considered as a sensitive parameter.

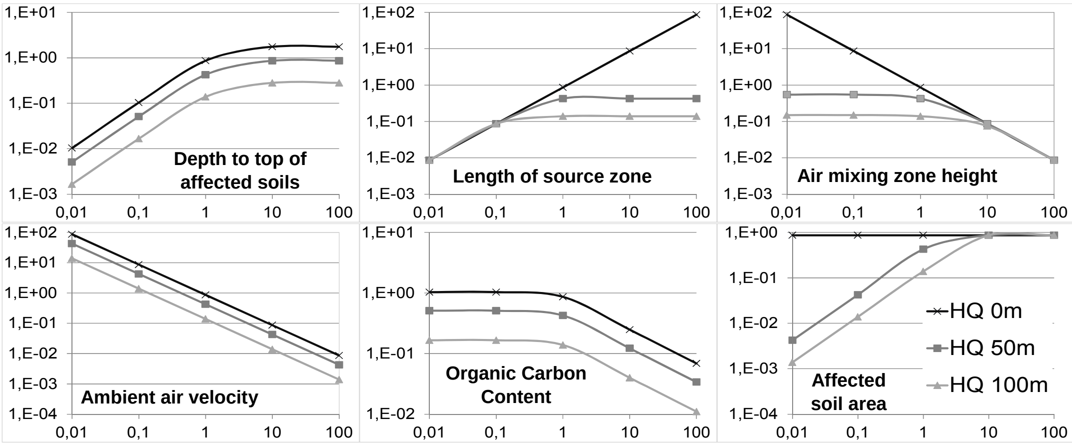

Figure 1: Sensitivity analysis for input parameters with higher influence in HQ [-] value.

In Figure 1 is exposed the parametric sensitivity of the input parameters that affect the model results, as well as their tendency. According to the representations exposed, the thickness of the surface soil column, depth to base of affected soils, length of source zone area parallel to wind, fractional organic carbon content, air mixing zone height and ambient air velocity in mixing zone are parameters that can induce the HQ to have higher values than the maximum limit adopted. Furthermore, the parameters that are able to modify hardly HQ results are length of source zone area parallel to wind, air mixing zone height and ambient air velocity in mixing zone.

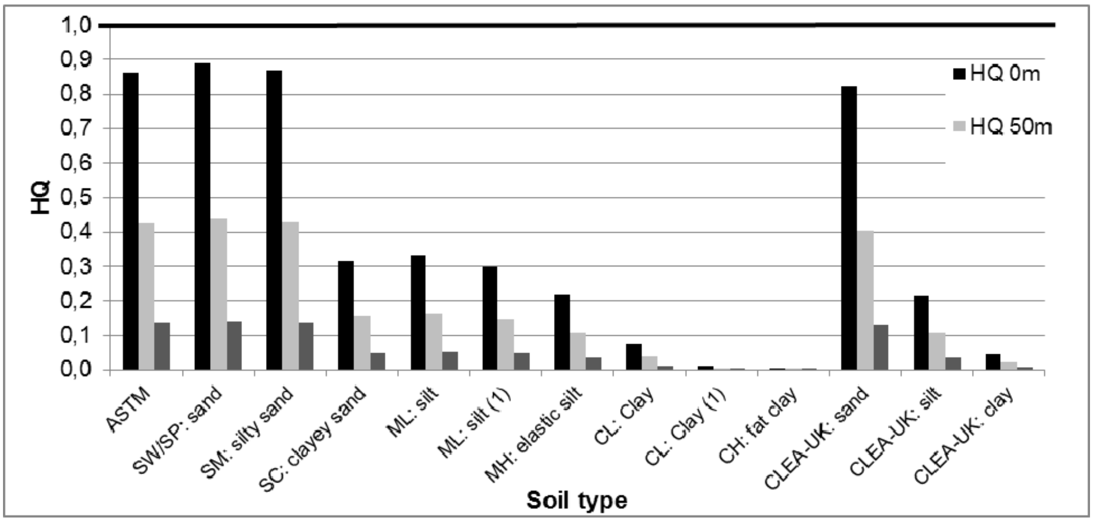

Figure 2: Hazard Quotient obtained for each soil type, at different distances from the source.

Soil type sensitivity is presented in Figure 2, representing the HQ for the sum of TPH fractions versus the different types of soil considered and also the distance to the source. Notable differences between

HQ results are observed. Sandy soils exhibit the higher HQ while clayey soils present values close to zero. This may be due to the fact that sandy soils have great porosity encouraging soil vapour migration.

4. Conclusions

In this study, a methodology to identify the risks that may arise from a specific TPH fractions distribution and concentration has been proposed. Regarding a tiered approach, reliable results require proper characterization of site-specific input parameters. It has been shown that the application of this methodology gives a comprehensive and suitable risk analysis.

TPH determination does not allow a risk assessment of polluted soils, because risks are highly dependent on the hydrocarbon composition. A first separation between aliphatic and aromatic hydrocarbons is necessary in order to get the quantitative risk assessment. Taking as a reference TPH concentration of 5000 mg/kg and the diesel composition, a case of study has been developed allowing the risk assessment using RBCA software.

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