"ARA-CoS$_{SSLs}$" risk analysis approach (on a computer worksheet basis) for contaminated sites: implementation and case study application

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Abstract

Within the increasing attention to absolute risk analysis at Italian level, as a University research study, the definable "ARA-CoS$_{SSLs}$" approach for human health ("Absolute Risk Analysis for Contaminated Sites", on "Soil Screening Levels" basis) has been derived (as an initial, simplified version) and directly implemented on a series of interactive computer worksheets. The basic conditions of the "ARA-CoS$_{SSLs}$" approach derivation are: 1) the predominant reference to a fundamental international scientific protocol, also considering its temporal evolution (the US.EPA "SSLs"); 2) a modular, open, common for users, and easily extensible computer calculation. This paper reports on the basic aspects and the specific calculation structure of the "ARA-CoS$_{SSLs}$" approach; additionally, a simplified case-study application is summarised.
Keywords: absolute risk assessment, case-study, contaminated sites, exposure pathways and scenarios, model implementation.

1 Introduction

Within the integrated management for contaminated site identification, characterisation and final remediation [1], an indispensable step deals with the application of reliable and scientifically based absolute risk analysis criteria [2], in order to: 1) evaluate the contamination level of environmental media at a given suspected site, as quantification of the associated risks for human and/or ecological targets; 2) eventually, define risk-based residual chemical concentrations, if a remedial action is required at the given site. As far as the

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Italian situation is concerned, despite a restricted regulative application of absolute risk analysis up until the present time forced by the existing "D.M. No. 471/99" Ministerial Decree on contaminated soil management [2, 3], some international and/or national software tools for absolute risk analysis are currently adopted or at least recognized in Italy, *inter alia*: "RBCA Tool Kit for Chemical Releases", based on the specific ASTM Standard for "RBCA, Risk-Based Corrective Action" [4]; "ROME", developed by the Italian Environmental Protection Agency [5]; and "GIUDITTA", proposed by the Province of Milan [6]. Additionally, the Italian Environmental Protection Agency and Technical Services has recently produced a technical document on basic methodological criteria for absolute risk analysis applications at Italian contaminated sites [7]. With this increasing attention to the absolute risk analysis at Italian level, the definable "ARA-CoS$_{SSLs}$" modelling approach for human health ("Absolute Risk Analysis for Contaminated Sites", on "Soil Screening Levels" basis) is synthetically described in this paper, as derived (exclusively due to a University research study) in its initial, simplified version and implemented on a series of interactive computer worksheets. Basic conditions for the "ARA-CoS$_{SSls}$" approach derivation have been expressly: 1) the predominant reference to a fundamental and unique international scientific protocol, also considering its temporal evolution (the US.EPA "SSLs, Soil Screening Levels" procedure); 2) a modular, open, common for users, and easily extensible computer calculation structure. A simplified case-study application of the "ARA-CoS$_{SSls}$" modelling approach is also finally summarised.

2 The scientific reference procedure: US.EPA SSLs

The "SSLs" procedure has been defined and temporally updated by US.EPA as a tiered sanitary risk assessment framework for deriving risk-based (generic or site-specific) soil screening levels, according to three, possible site information approaches [10]: a first, generic approach (reasonable, conservative assumptions); a second, simple site-specific methodology; a third, more detailed site-specific modelling approach. The original "US.EPA 1996 SSLs" procedure [8, 9] was expressly focused on residential land use scenario (with on-site residents as receptors), including: 1) the detailed derivation of risk equations related to the assumed pathways of concern (direct soil ingestion, outdoor inhalation of fugitive dusts and volatiles, and ingestion of contaminated ground water); 2) the accurate summary of default values (according to the generic assessment approach) for human exposure factors, soil and ground water characterising parameters, and meteorological data; 3) the database of all relevant contaminant physical-chemical and toxicological parameters; and 4), the definition of sampling and representative concentration estimation procedures for surface (usually top 2 cm) and subsurface soils, with related statistical data quality tests (for surface soil). Then, the supplemental "US.EPA 2002 SSLs" guidance [10] has updated and extended the original procedure, synthetically according to the following, main aspects: 1) as related to the previous residential scenario, new risk equations for the concurrent exposure via ingestion and dermal absorption, a new site-specific modelling for the volatile migration into indoor air, and updated dispersion modelling data for the air exposure model; 2) additional, detailed consideration of a commercial/industrial scenario (outdoor and indoor workers as targets) and a construction scenario (construction workers and off-site residents as receptors); and finally 3), additional statistic option of the "$UCL_{95\%}$, Upper Confidence Limit" for the proper definition of representative chemical concentrations in surface and subsurface soils.

3 "ARA-CoS_{SSLs}" modelling approach

3.1 General calculation structure and contaminants of concern

The "ARA-CoS_{SSLs}" absolute sanitary risk analysis model, with a modular structure based on the US.EPA "SSLs" procedure (see Section 2), has been directly implemented in Microsoft Excel® format [11]. According to the usual international approaches for absolute risk analysis [7], "ARA-CoS_{SSLs}" model performs two risk assessment modes: 1) the "direct" (or "forward") evaluation of health risks associated with site contamination; and 2) the "inverse" (or "backward") calculation of risk-based soil quality limits or cleanup targets. Additionally, for both modes, two assessment tiers are considered: a first, "site-generic" assessment level, expressly based on the US.EPA generic, reasonable conservative exposure scenario assumptions (see Section 2); and a second, "site-specific" assessment level, based instead on simple site-specific characterisation data. According to Figure 1, the calculation structure of "ARA-CoS_{SSLs}" model has been specifically arranged with three correlated "Modules" ("I-O, Input-Output", "A_{B-DIR}, Bi-directional Analysis" and "DB, DataBase"), eventually conceptual "Sub-modules", and finally "iWSs, individual Worksheets". With specific reference to the selection of contaminants of concern (from all detected chemicals, at a given suspected site), two different procedures have been currently implemented in "ARA-CoS_{SSLs}" model [11]: the so identifiable "Toxicity Score" approach (as described in [12]), and alternately the "normalised Comparative Hazard Index" approach (as defined in [13]).

3.2 Module "I-O"

It conceptually consists of three Sub-modules ("Input", "Output", and "Statistical Tests"), which are articulated according to the specific iWSs named in Figure 1.

3.2.1 Sub-module "Input"

The interactive "iWS CSM, Conceptual Site Model" (Figure 2) allows to define: the type of risk analysis (generic or simple site-specific), the land use scenario, and the corresponding, significant exposure pathways. At present [11], the following exposure pathways have been included in "ARA-CoS_{SSLs}" model, under either a residential or a commercial/industrial scenario: direct ingestion and dermal absorption (related to surface soil), outdoor inhalation of fugitive dusts (surface soil) and volatiles (related to subsurface soil), and ingestion of contaminated ground water (also subsurface soil). As a flexible and realistic approach, in "ARA-CoS_{SSLs}" model direct ingestion and dermal absorption can be selected either as unique, combined pathway (according indeed to the original US.EPA “SSLs” procedure: see Section 2), or as two independent pathways.

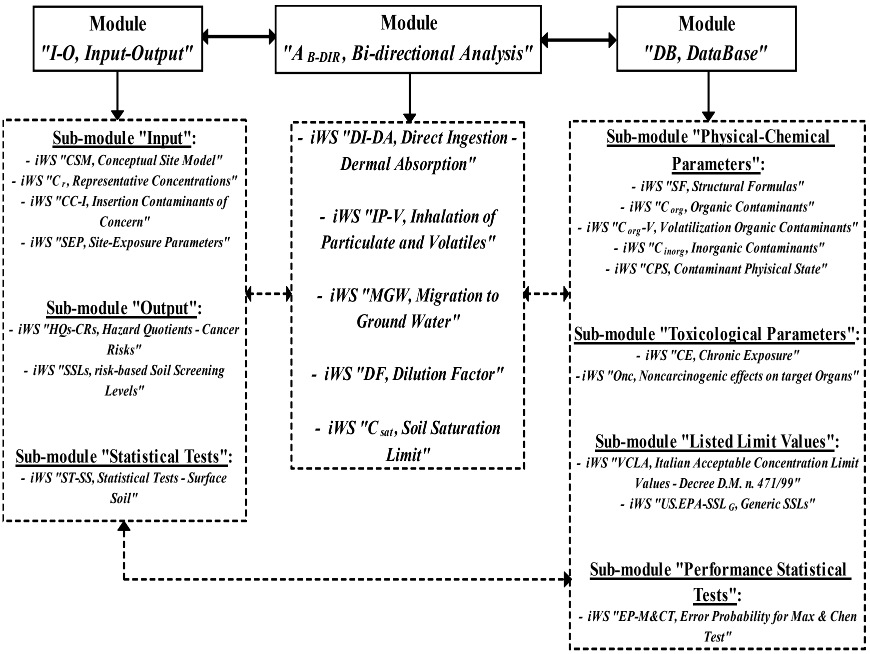

Figure 1: Flow-chart of “ARA-CoS$_{SSLs}$” model.

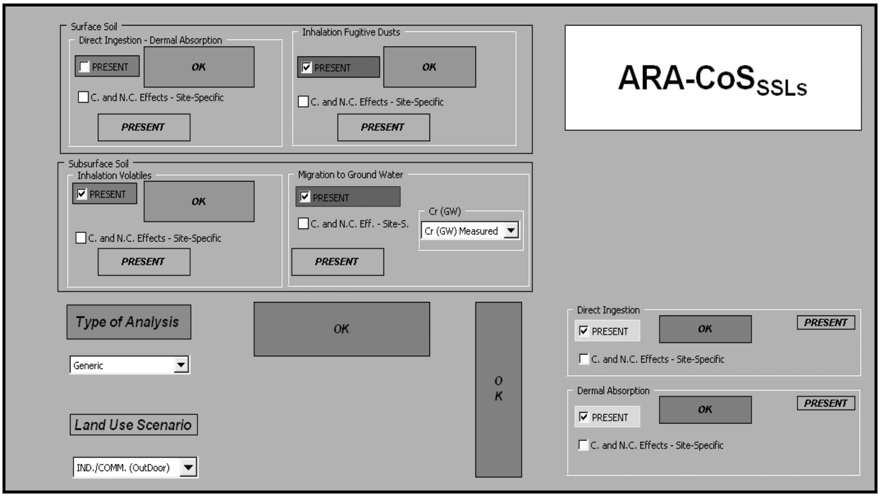

Figure 2: “ARA-CoS$_{SSLs}$” model: view of “iWS CSM, Conceptual Site Model”.

Within a “direct” assessment mode, “iWS Cr, Representative Concentrations” provides for the definition of representative chemical concentrations in surface soil (as arithmetic mean or max value, according to a composite or individual sampling procedure [9]), and subsurface soil [11] (as arithmetic mean or max value, according to a proper core length-weighted averaging procedure [9]); additionally, this iWS performs the contaminant indicator selection procedures summarised in Section 3.1. The “iWS CC-I, Insertion Contaminants of Concerns” permits the tabulation of representative concentrations for the selected chemicals of concern, as ppm values for surface and subsurface soil (weight-to-weight ratio, equivalent to mg kg^{-1}) and ground water (weight-to-volume ratio, equivalent to mg l^{-1}). As far as specifically ground water is concerned, “measured” concentrations can be directly inserted (“M” indicative symbol), or alternately “estimated” values (“E” symbol) are automatically generated based on the US.EPA theory of soil/water/air contaminant partition in unsaturated zone and subsequent aquifer dilution [8, 9]. Additionally, this iWS provides for some useful, visual indications [11]: 1) representative soil concentrations above the officially tabulated US.EPA generic “SSLs” [10], and representative ground water concentrations above the officially tabulated Italian generic quality limits [3] (see Section 3.4); and mainly 2), the potential presence of Non-Aqueous Phase Liquid (NAPL) for contaminants (liquid at typical soil temperature) with representative subsurface concentrations exceeding the corresponding “C_{sat}, Soil Saturation Limit” [mg kg^{-1}] [9, 10]. It should be pointed out that, according at least to the theoretical derivation of US.EPA risk approaches related to inhalation of volatiles and migration to ground water [9, 10], in “ARA-CoS_{SSLs}” calculation model chemical soil contents should be adequately inserted as dry weight (with a resulting, conservative risk assessment condition [13]); moreover, again expressly for volatile inhalation and ground water migration pathways [11], subsurface soil chemical concentrations should be theoretically assumed as total, three-phase (soil, water, air) contents [9].

Finally, “iWS SEP, Site-Exposure Parameters” summarises all relevant parameters (exposure, exposed population, soil and aquifer, meteorological conditions) for conducting risk analysis, with default values (under a generic mode analysis) expressly according to US.EPA “SSLs” indications [10].

3.2.2 Sub-module “Output”

It consists of two iWSs (Figure 1). According to the “direct” assessment mode, “iWS HQs-CRs” (Figure 3) calculates the sanitary risks associated with contaminant non-carcinogenic and carcinogenic effects, respectively as “HQ, Hazard Quotient” and “CR, Cancer Risk” [14]. Precisely, risk quantification is carried out either for individual effects (individual toxic effect and pathway of exposure) or for cumulative effects with risk aggregation as follows [8, 9]: 1) for carcinogenic effects, firstly contaminant CRs are simply added for each pathway of exposure, and consequently all pathway CRs are added together; 2) for non-carcinogenic effects, HQs are added only for those contaminants with the same toxic endpoint (human organ). Expressly for inhalation exposures, a visual indication is given in “iWS HQs-CRs” for those chemicals with route-to-route extrapolation of the corresponding toxic parameters ("URF, Unit Risk Factor" [μg^{-1} m^3] and "RfC, Reference Concentration" [mg m^{-3}]) from those related to ingestion (respectively, "SF, Slope Factor" [mg^{-1} kg d] and "RfD, Reference Dose" [mg kg^{-1} d^{-1}]), according to the simple US.EPA derivation approach [9].

According to the "inverse" assessment mode, "iWS SSLs" (Figure 4) defines risk-based Soil Screening Levels (generic or site-specific) for individual pathway and toxic effect (with acceptable individual risk levels assumed as $1 \cdot 10^{-6}$ for CR and 1 for HQ [8, 9, 14]). Expressly for ground water migration pathway, two alternating calculations are possible [11]: 1) the original US.EPA approach [8–10], based on the soil/water/air partition and subsequent dilution theory and the consideration of official acceptable water levels; and 2) a proper "risk-based" approach (see Section 3.3). Finally, also this iWS gives some useful, visual indications [11]: for instance, the eventual, non-reliable condition of resulting calculated SSLs for volatile inhalation and ground water exceeding C_{sat} [9, 10].

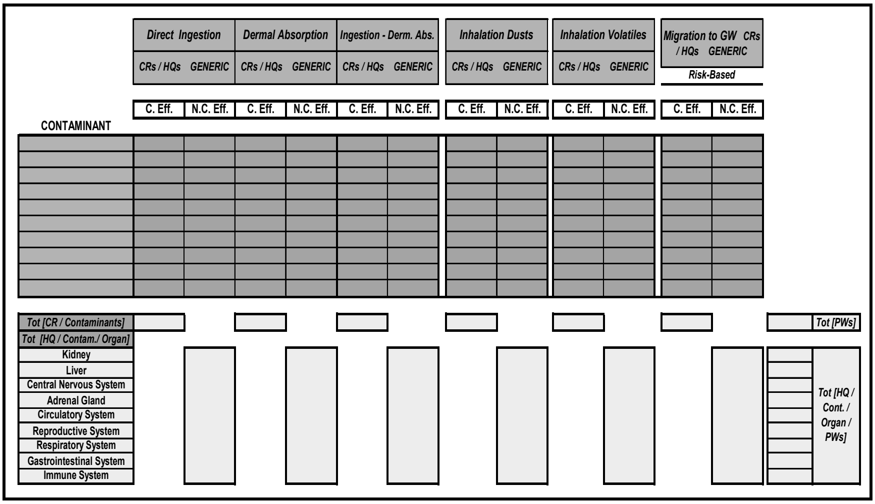

Figure 3: "ARA-CoS_{SSLs}" model: partial view of "iWS HQs-CRs". Legend: C., N.C. Eff. = carcinogenic, non-carcinogenic effects; PWs = pathways.

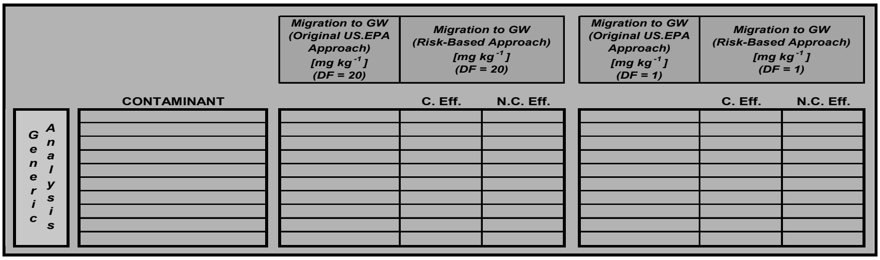

Figure 4: "ARA-CoS_{SSLs}" model: partial view of "iWS SSLs". Legend: DF = Dilution Factor.

3.2.3 Sub-module "Statistical tests"

Consisting of a unique iWS (Figure 1), this Sub-module implements the possible execution of "Max" and "Chen" statistical tests for surface soil sampling data validation, within an individual "EA, exposure area" of 0.5 acre (~ 2,000 m^2) [9].

3.3 Module "A_{B-DIR}"

This fundamental Module, properly executing the risk calculation, is composed of the iWSs schematised in Figure 5. Precisely, "iWS DI-DA" implements the US.EPA modelling approaches for direct ingestion and dermal absorption pathways, while "iWS IP-V" concerns with the US.EPA modelling approaches for outdoor inhalation of particulate and volatiles [10]. As far as instead the migration to ground water pathway is concerned, "iWS DF" and "iWS MGW" contain respectively [11]: 1) the US.EPA derivation of "DF, Dilution Factor" [8, 9, 10]; 2) the above mentioned US.EPA soil/water/air partition theory in unsaturated zone [8, 9, 10], in due combination with the US.EPA risk equations related to human intake from contaminated water ingestion [14]. Finally, "iWS C_{sat}" performs the derivation of the soil saturation limit (see Section 3.2.1), with some different parametric default values proper of inhalation of volatiles ("IV" in Figure 6) or migration to ground water ("MGW" in Figure 6) modelling (that is, "θ_w, water-filled soil porosity" and "f_{oc}, fraction organic carbon in soil") [10].

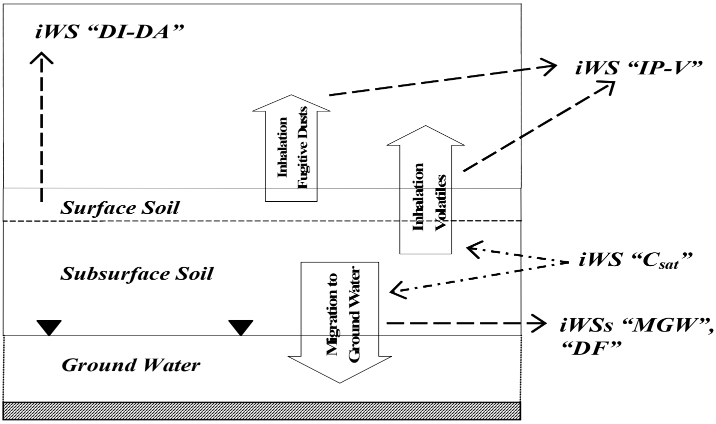

Figure 5: "ARA-CoS_{SSLs}" model: scheme of the environmental sectors of concern for the individual Worksheets within the "A_{B-DIR}" Module.

3.4 Module "DB"

Comprehensive of four conceptual Sub-modules (Figure 1), this Module contains all parametric data necessary for "ARA-CoS_{SSLs}" modelling [11]: contaminant physical-chemical factors (influencing environmental fate and transport) and toxicological parameters, official (Italian and U.S.) soil and ground water generic limits, and error probabilities for "Max" and "Chen" tests (see Section 3.2.3).

4 Summary of a simplified case-study application

A first, simplified application of "ARA-CoS$_{SSLs}$" modelling approach has regarded a service station site with leaching underground storage tanks, and consequential subsoil and ground water detection of BTEX (benzene, toluene, ethylbenzene and xylene), MTBE (methyl ter-butyl ether) and TPH (Total Petroleum Hydrocarbons, C<12 and C>12 fractions). Specific site history and characterisation, developed conceptual site model and consequential assumptions are reported in [15]; expressly, a non-residential scenario has been assumed, with outdoor workers as considered targets. Figures 6 and 7 show the resulting contaminant representative concentrations respectively in soil (surface, subsurface) and ground water. As far as specifically Figure 6 is concerned, it should be pointed out that two "hypothetical" conditions have been considered for subsurface soil [15]: 1) the sampling and analytical condition of desirable preservation, conservation and detection of the "real" three-phase chemical contents (in soil, water and air: "[S-W-A]r" symbol) [9, 16]; 2) the alternating (and probably more realistic) condition of real detection only of the chemical soil and water contents ("[S-W]r" symbol), with consequential, automatic (within "ARA-CoS$_{SSLs}$" model) derivation of the "estimated" total three-phase concentration ("[S-W-A]e" symbol) based on a proper and original mathematical adaptation and extension of the US.EPA contaminant partition theory [9].

	Cr-SS [ppm w/w]	Cr-SSS [ppm w/w - DM] [S-W-A] r *(o [S-W] r)*	*[S-W-A] e / [S-W] r*		***Cr-SSS [ppm w/w - DM] [S-W-A] e***	
			θ_w - f_{oc}			
			IV	*MGW*	***IV***	***MGW***
Chemical Name						
Benzene	1.00E-1	1.00E-1	*1.095E+00*	*1.064E+00*	***1.10E-01***	***1.06E-01***
Ethylbenzene	3.50E+0	3.50E+0	*1.027E+00*	*1.031E+00*	***3.59E+00***	***3.61E+00***
MTBE	8.00E+0	8.00E+0	*1.035E+00*	*1.010E+00*	***8.28E+00***	***8.08E+00***
Toluene	2.60E+0	1.50E+0	*1.043E+00*	*1.043E+00*	***1.56E+00***	***1.56E+00***
TPH (>C8-C10: Aliph.)	8.34E+2	3.73E+2	*1.078E+00*	*1.111E+00*	***4.03E+02***	***4.15E+02***
TPH (>C12-C16: Aliph.)	1.56E+3	7.16E+2	*1.003E+00*	*1.005E+00*	***7.18E+02***	***7.19E+02***
o-Xylene	3.43E+1	3.43E+1	*1.018E+00*	*1.021E+00*	***3.49E+01***	***3.50E+01***

Figure 6: Case-study application of "ARA-CoS$_{SSLs}$" model: partial view of "iWS CC-I" [15]. Legend: SS = surface soil; SSS = subsurface soil; DM = dry weight; [S-W-A]r, [S-W]r, [S-W-A]e= see Section 4; IV, MGW = see Section 3.3 (θ_w, f_{oc} different pathway default values).

	Cr-GW [ppm w/v] - M	Cr-GW [ppm w/v] - E		NAPL Csat [mg/kg]
		[S-W-A] r	*[S-W-A] e*	
Benzene	1.38E+01	1.48E-02	*1.57E-02*	---
Ethylbenzene	2.10E+00	1.83E-01	*1.89E-01*	---
MTBE		1.88E+00	*1.90E+00*	---
Toluene	1.35E+01	1.27E-01	*1.33E-01*	---
TPH (>C8-C10: Aliph.)	8.24E+02	2.65E-01	*2.94E-01*	*8.80E+01*
TPH (>C12-C16: Aliph.)		3.55E-03	*3.57E-03*	*2.29E+01*
o-Xylene	8.60E+00	1.81E+00	*1.85E+00*	---

Figure 7: Case-study application of "ARA-CoS$_{SSLs}$" model: additional, partial view of "iWS CC-I" [15]. Legend: M, E (DF = 20) = see Sect. 3.2.1.

The resulting individual risks, according to a "direct, generic" assessment mode (see Section 3.1), are reported in Table 1. Generic risks associated with direct ingestion and inhalation of fugitive dusts and volatiles appear as negligible, while the risk-based approach for ground water migration shows non-negligible carcinogenic (benzene) and non-carcinogenic (on liver – toluene, on kidney – toluene and ethylbenzene [9], under measured concentrations) generic risks [15]. Finally, risks related to the "estimated" three-phase approach are increased (but not significantly) compared with the hypothetic "real" two-phase approach [15].

Table 1: Simplified case-study application of "ARA-CoSS$_{SLs}$" model: calculated, generic risks (CRs and HQs) [15]. Legend: N/D = not derivable.

	Direct Ingestion		Dermal Absorption		Inhalation of Dusts	
	CR	HQ	CR	HQ	CR	HQ
Benzene	1.73E-09	N/D	N/D	N/D	1.26E-13	N/D
Toluene	N/D	1.14E-05	N/D	N/D	N/D	2.95E-09
Ethylbenzene	N/D	3.08E-05	N/D	N/D	N/D	1.59E-09
o-Xylene	N/D	1.51E-05	N/D	N/D	N/D	2.22E-09
MTBE	N/D	N/D	N/D	N/D	N/D	1.21E-09
TPH (>C8-C10)	N/D	7.34E-03	N/D	N/D	N/D	3.78E-07
TPH (>C12-C16)	N/D	1.37E-02	N/D	N/D	N/D	7.07E-07
	Inhalation of Volatiles ("IV")					
	[S-W-A]r *(or [S-W]r)*		*[S-W-A]e*			
			$\theta_w - f_{oc}$ *(IV modelling)*		$\theta_w - f_{oc}$ *(MGW model.)*	
	CR	HQ	*CR*	*HQ*	*CR*	*HQ*
Benzene	7.05E-08	N/D	*7.72E-08*	*N/D*	*7.50E-08*	*N/D*
Toluene	N/D	6.51E-04	*N/D*	*6.79E-04*	*N/D*	*6.79E-04*
Ethylbenzene	N/D	4.48E-04	*N/D*	*4.60E-04*	*N/D*	*4.62E-04*
o-Xylene	N/D	5.51E-04	*N/D*	*5.61E-04*	*N/D*	*5.63E-04*
MTBE	N/D	4.51E-04	*N/D*	*4.67E-04*	*N/D*	*4.56E-04*
TPH (>C8-C10)	N/D	NAPL	*N/D*	*NAPL*	*N/D*	*NAPL*
TPH (>C12-C16)	N/D	NAPL	*N/D*	*NAPL*	*N/D*	*NAPL*
	Migration to Ground Water ("MGW") (risk-based approach)					
	Measured Cr		Estimated Cr			
			[S-W-A]r *(or [S-W]r)*		*[S-W-A]e*	
	CR	HQ	CR	HQ	*CR*	*HQ*
Benzene	4.77E-03	N/D	5.12E-06	N/D	*5.44E-06*	*N/D*
Toluene	N/D	1.19E+00	N/D	1.12E-02	*N/D*	*1.17E-02*
Ethylbenzene	N/D	3.70E-01	N/D	3.23E-02	*N/D*	*3.33E-02*
o-Xylene	N/D	7.57E-02	N/D	1.60E-02	*N/D*	*1.63E-02*
MTBE	N/D	N/D	N/D	N/D	*N/D*	*N/D*
TPH (>C8-C10)	N/D	NAPL	N/D	NAPL	*N/D*	*NAPL*
TPH (>C12-C16)	N/D	NAPL	N/D	NAPL	*N/D*	*NAPL*

5 Conclusions

As a University research study, the "ARA-CoS$_{SSLs}$" modelling approach for sanitary risk analysis has been derived (as initial version) with predominant reference to the international US.EPA "SSLs" scientific procedure, and directly implemented on a computer worksheet basis. A first, simplified case-study application has been performed. A further "ARA-CoS_{SSLs}" model application at a relevant Italian national priority contaminated site is now being carried out.

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