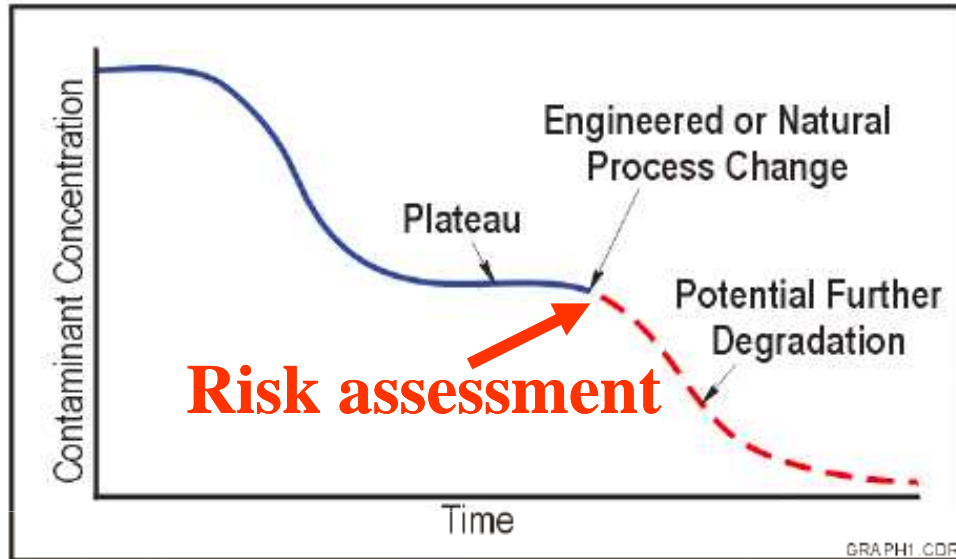


Fractionating Hydrocarbons For Hazard and Risk Assessment; Chemical and Biological Analysis



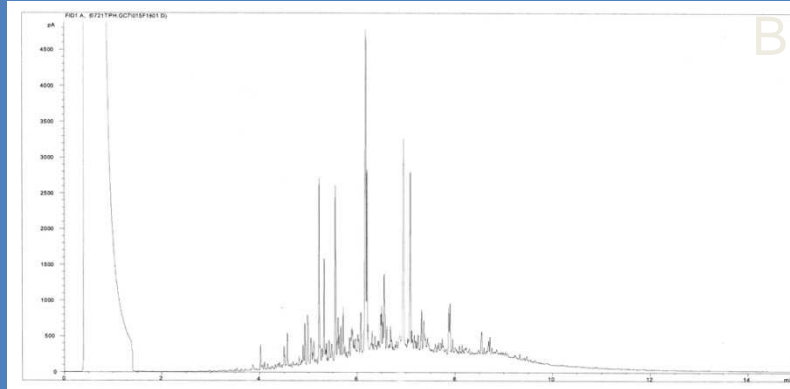
Why do this?



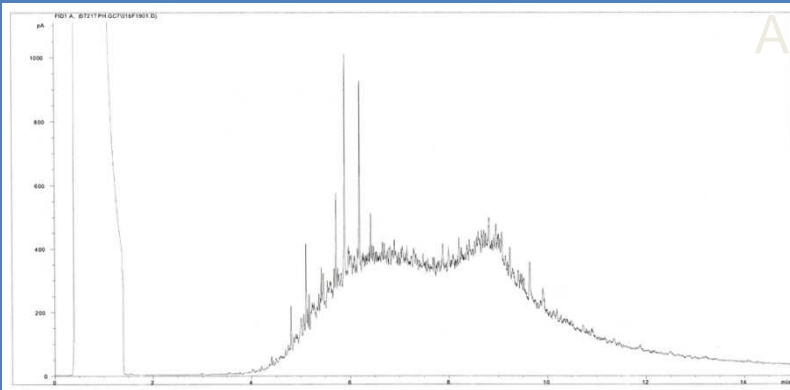
➤ **Risk management** is the language of business and regulation

➤ Showing we can manage risk instils **confidence**

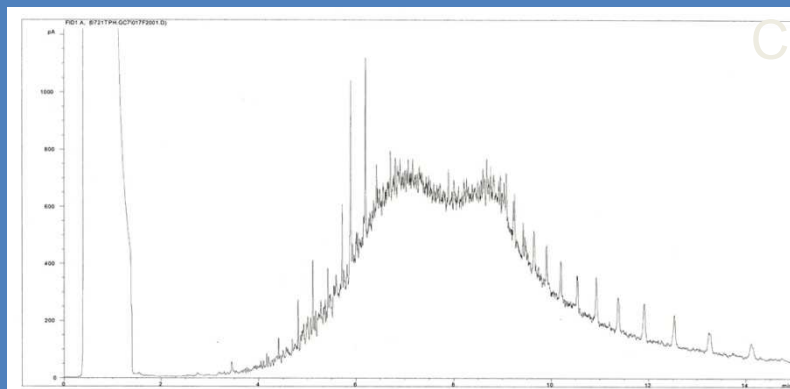
- Confidence builds trust in stakeholders
- Trust supports **legitimacy** and **community buy-in** into regeneration – a critical ‘quality of life’ endpoint for sustainable communities



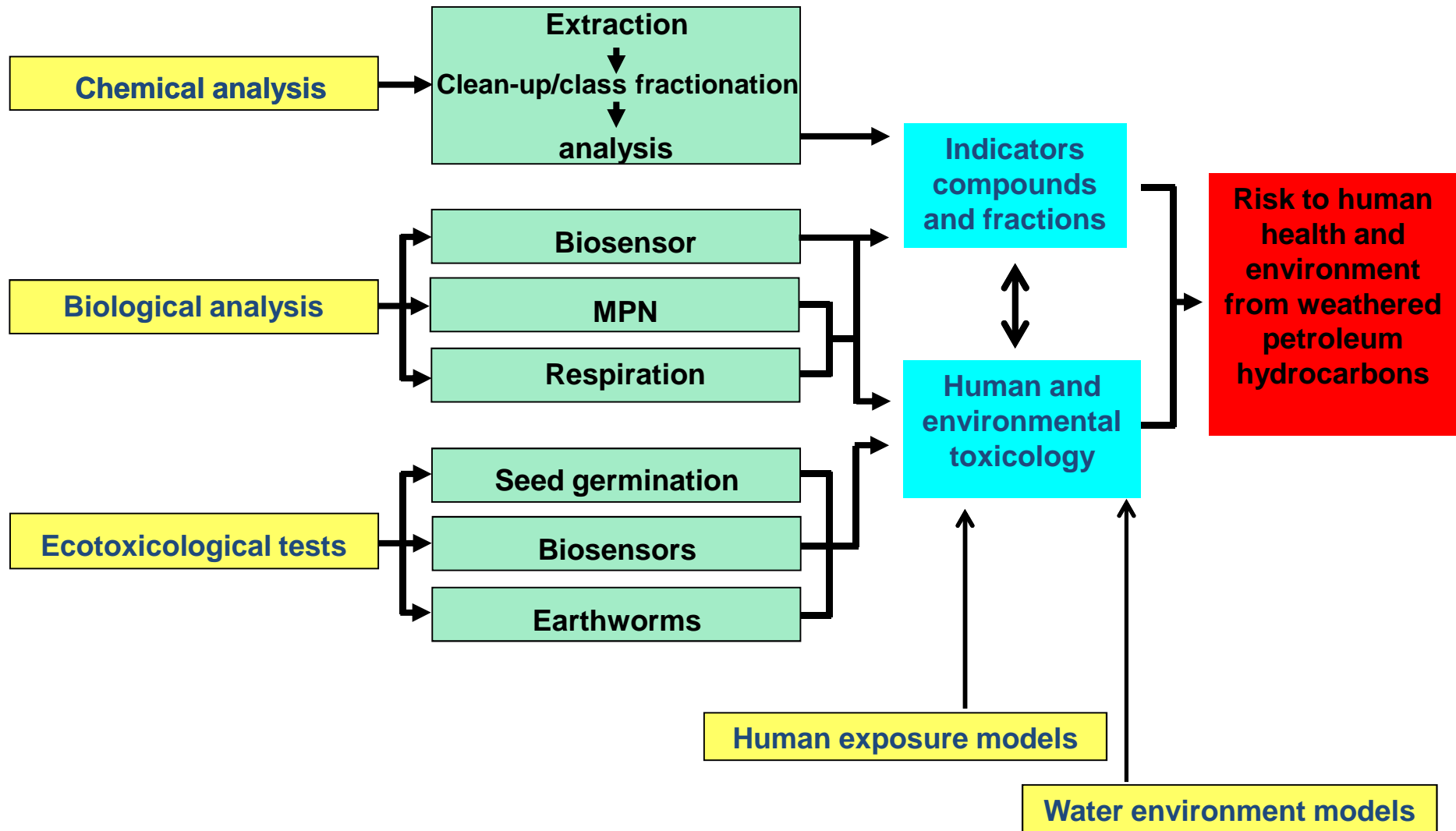
- B – oil extracted from a oil-contaminated clay soil prior to remediation.



- A – residual oil remaining after windrow treatment.



- C – oil extracted from heavily contaminated peaty soil from a decommissioned oil refinery.



SECOND LINK BIOREMEDIATION PROGRAMME

BIOREM 35

Optimising biopile processes for weathered hydrocarbons
within a risk management framework - PROMISE

S. Pollard, F. Coulon, G. Paton, J. Bellarby,
K. Semple, G. Risdon, B. Bone, K. Brassington and
S. Mitchell.



ENVIRONMENT
AGENCY



SCOTTISH EXECUTIVE



NATURAL
ENVIRONMENT
RESEARCH COUNCIL

Chemical analysis

Figure 6
Analytical schematic recommended for analysing soil contaminated with weathered hydrocarbons.

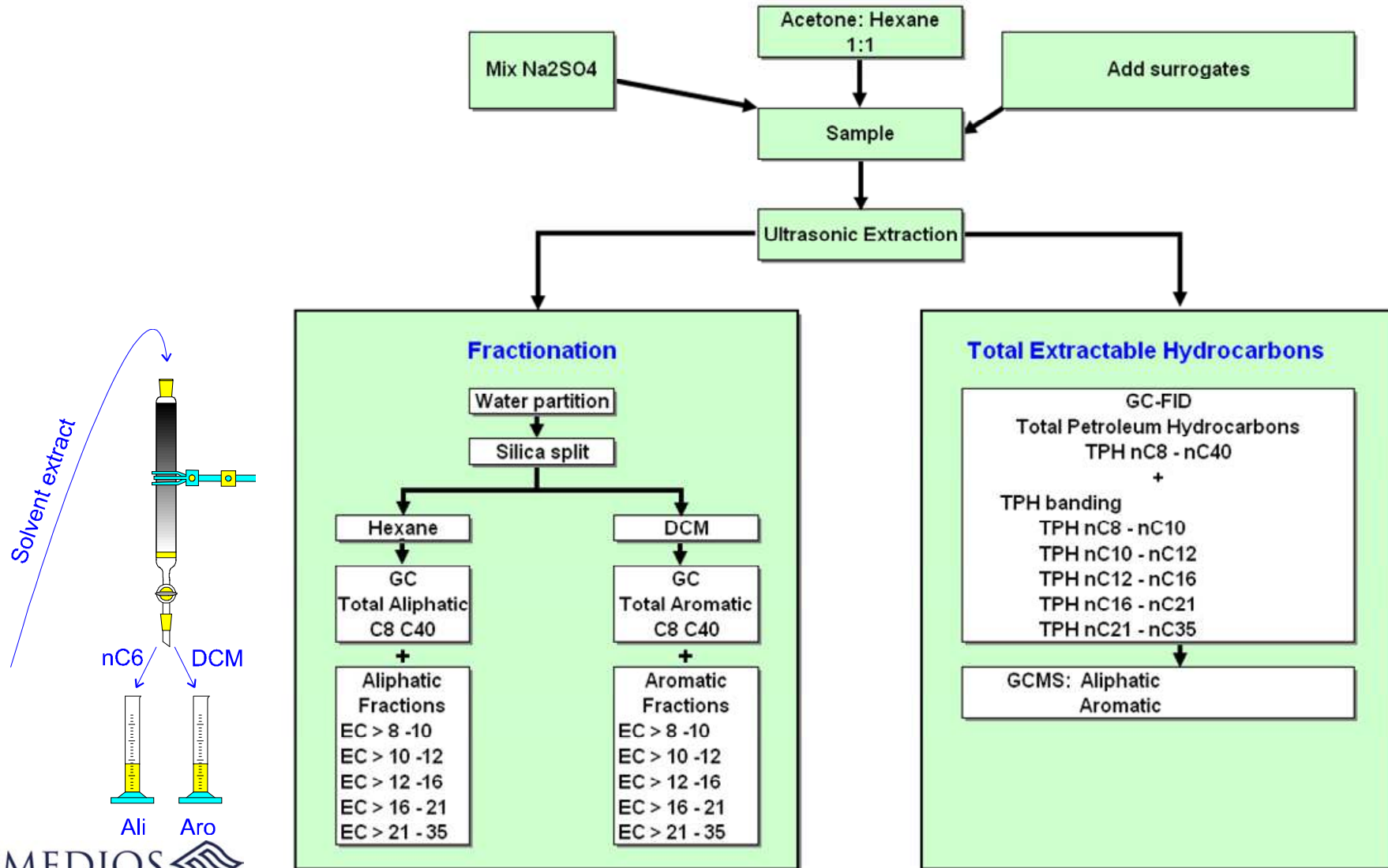
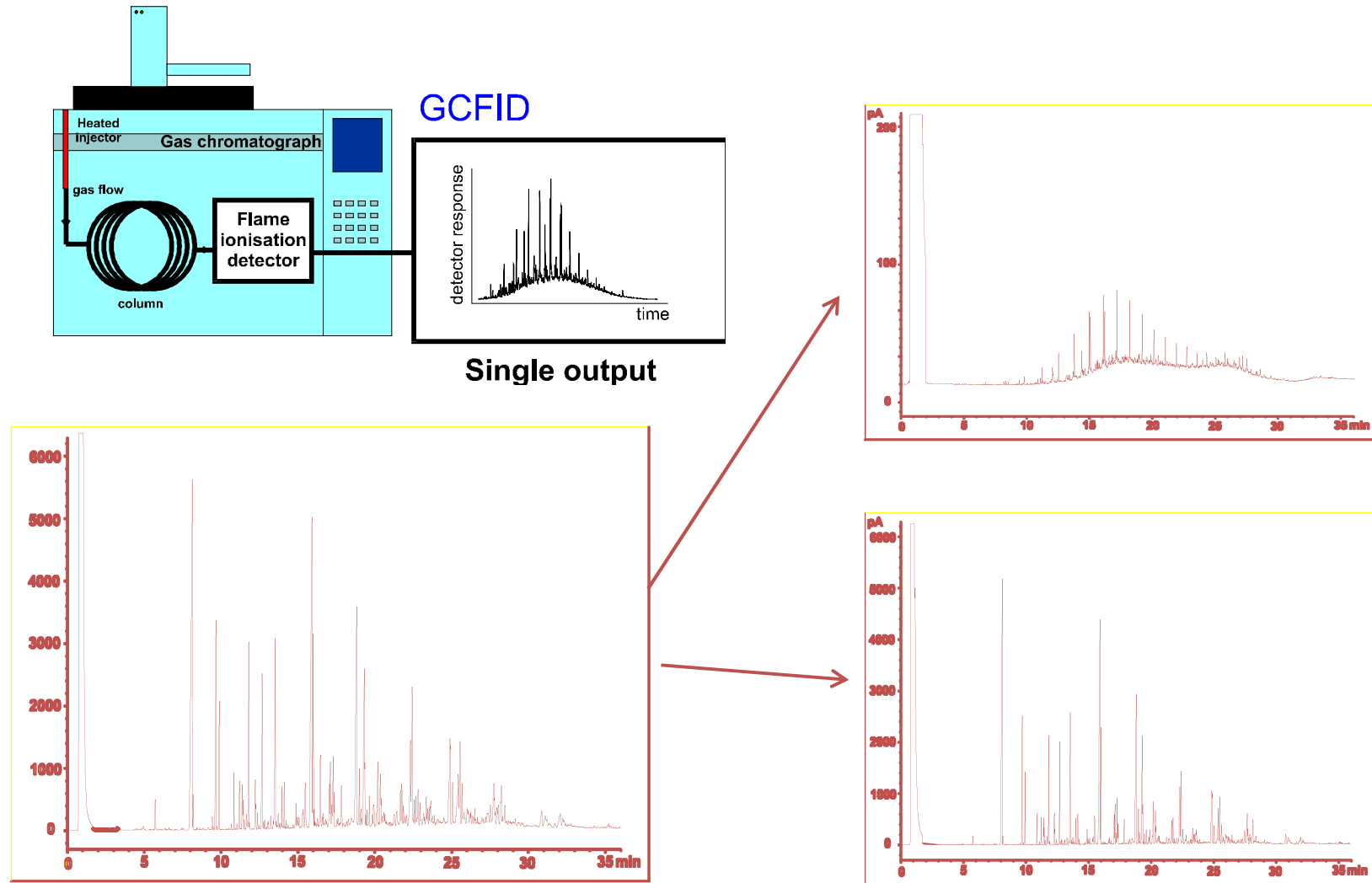


Table 4

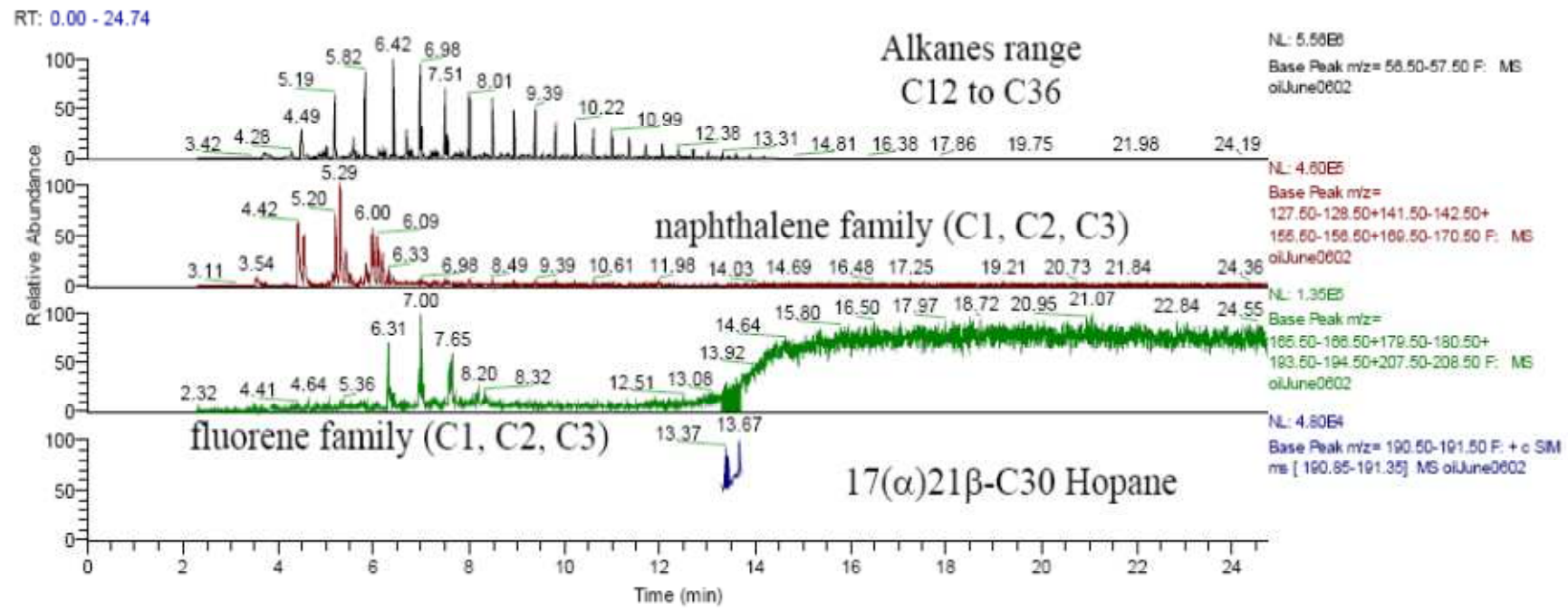
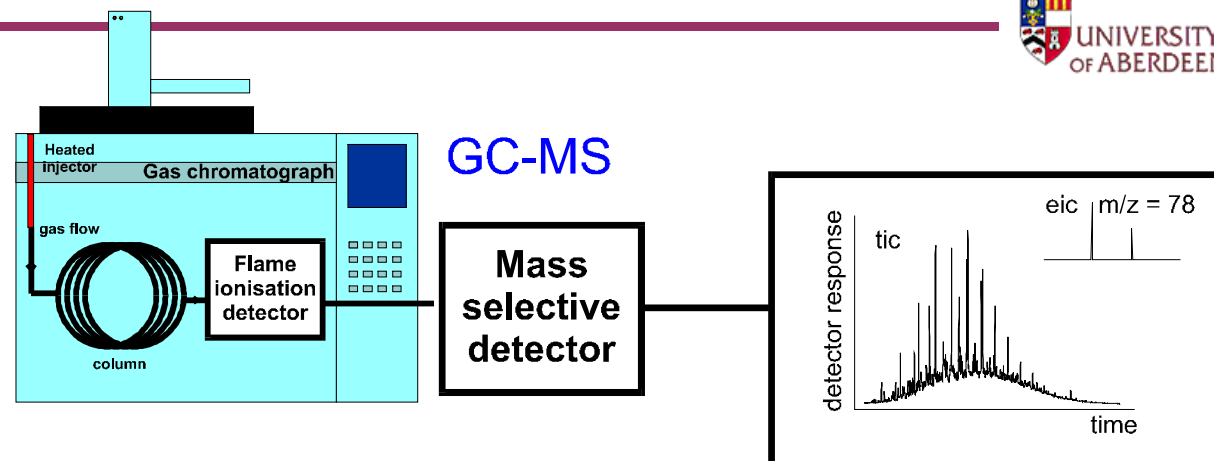
Mean concentration, precision & bias for duplicate samples extraction from each soil matrix

Matrix	Spike concentration mg kg ⁻¹	Mean concentration mg kg ⁻¹	Precision mg kg ⁻¹	Precision % RSD	Bias mg kg ⁻¹	Bias %	
Silty soil	0	65	6.8	10.5			
	10000	9988	301	3	-77	-0.8	
	30000	29280	800	2.7	-785	-2.6	
Clay soil	0	81	22.6	27.9			
	10000	10142	680	6.7	61	0.6	
	30000	30104	2171	7.2	23	0.1	
Sandy soil	0	9.4	5.8	61.7			
	10000	9727	377	3.9	-282.4	2.8	
	30000	28759	611	2.1	-1250.4	4.2	
Made ground	0	286	63.5	22.2			
	10000	10802	320	3	516	5	
	30000	31166	1497	4.8	880	2.9	
RTC CRMPR		Mean Certified value mg kg ⁻¹	Mean concentration mg kg ⁻¹	Precision mg kg ⁻¹	Precision % RSD	Bias mg kg ⁻¹	Bias %
		9510	11124	374	3.4	1614	17

Speciation of oil extract (class fractioning)



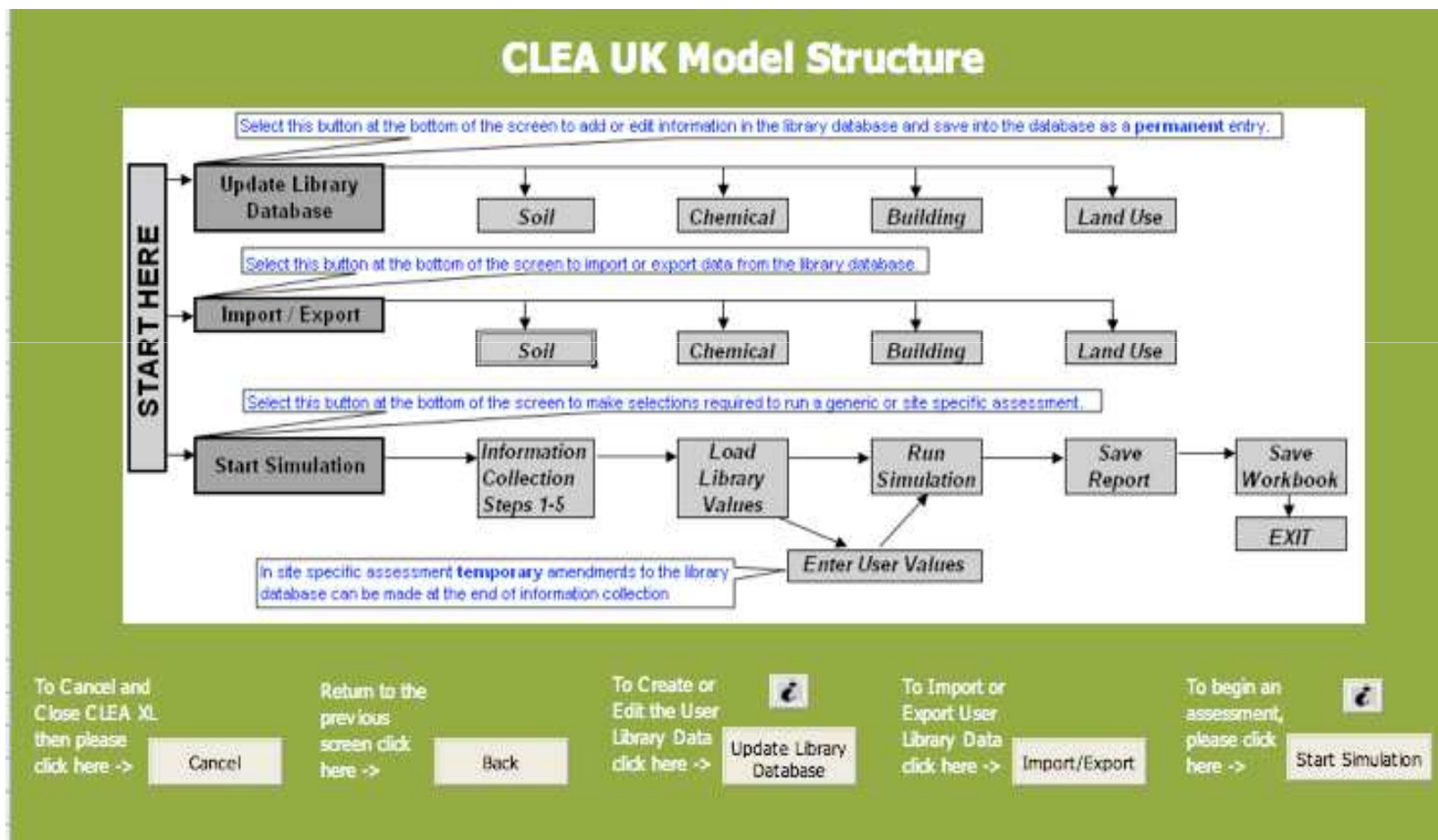
Identification of oil target compounds



Chemical analysis

- **Develop a robust analytical procedure for diagnostic tool kit**
 - » Complete recovery (low bias)
 - » Good precision (within and between batch)
 - » Conform to Environment Agency *mCERTs* performance targets (30% bias, 15% precision)
 - » Compatible with UK risk framework (Carbon banding convention(s) and Class fractionation)
- **Outputs:**
 - » Move to ultrasonic sequential solvent extraction with Acetone and hexane
 - » Generate high throughput and fast process.
 - » scalable
 - » Remove evaporative steps
 - » Solvent exchange via water partitioning prior to class fractionation

Exposure Assessment



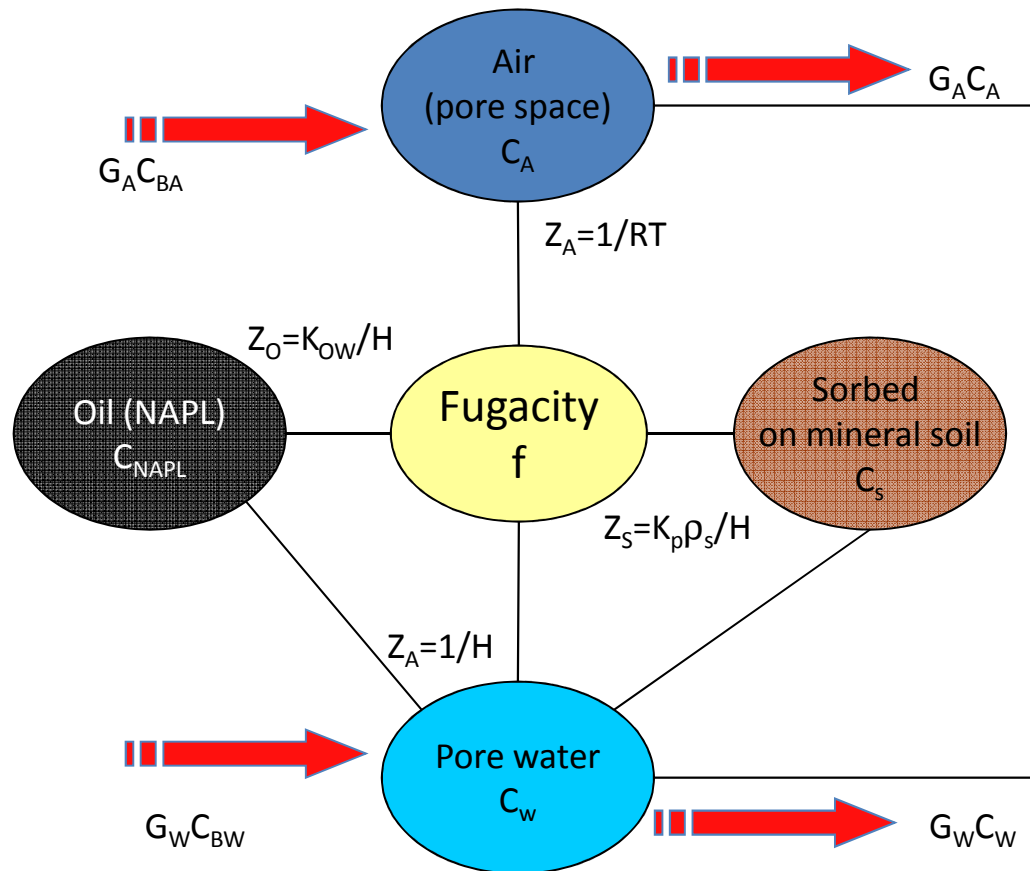
Tolerable daily intake

Hydrocarbon fractions	TDI _{oral} ($\mu\text{g kg}^{-1} \text{bw day}^{-1}$)			TDI _{Inhalation} ($\mu\text{g kg}^{-1} \text{bw day}^{-1}$)			Target organs/systems or effects
	EA (2006)	MADEP (2002)	TPHCWG (1997)	EA (2006)	MADEP (2002)	TPHCWG (1997)	
Aliphatic fractions							
>C5-C6	60	40	5000	200	60	5250	Neurological
>C6-C8	2000	40	5000	770	60	5250	
>C8-C10	100	100	100	60	60	285	Liver, blood
>C10-C12	100	100	100	60	60	285	
>C12-C16	100	100	100	60	60	285	
>C16-C35	2000	2000	2000	-	-	-	Liver
>C35-C44	6000	-	20000	-	-	-	
Aromatic fractions							
>C5-C7	-	-	2	-	-	9	Liver, neurological
>C7-C8	200	-	200	74	-	115	
>C8-C10	100	30	40	63	15	60	Body weight
>C10-C12	40	30	40	15	15	60	
>C12-C16	40	30	40	15	15	60	
>C16-C21	30	30	30	NA	15	-	Kidney
>C21-C35	12.5	30	30	NA	-	-	
>C35-C44	12.5	-	30	NA	-	-	
Combined Aliphatic and aromatic fractions							
>C44-C70	12.5		30	NA		-	

Typical targets values in petroleum hydrocarbon-contaminated soils

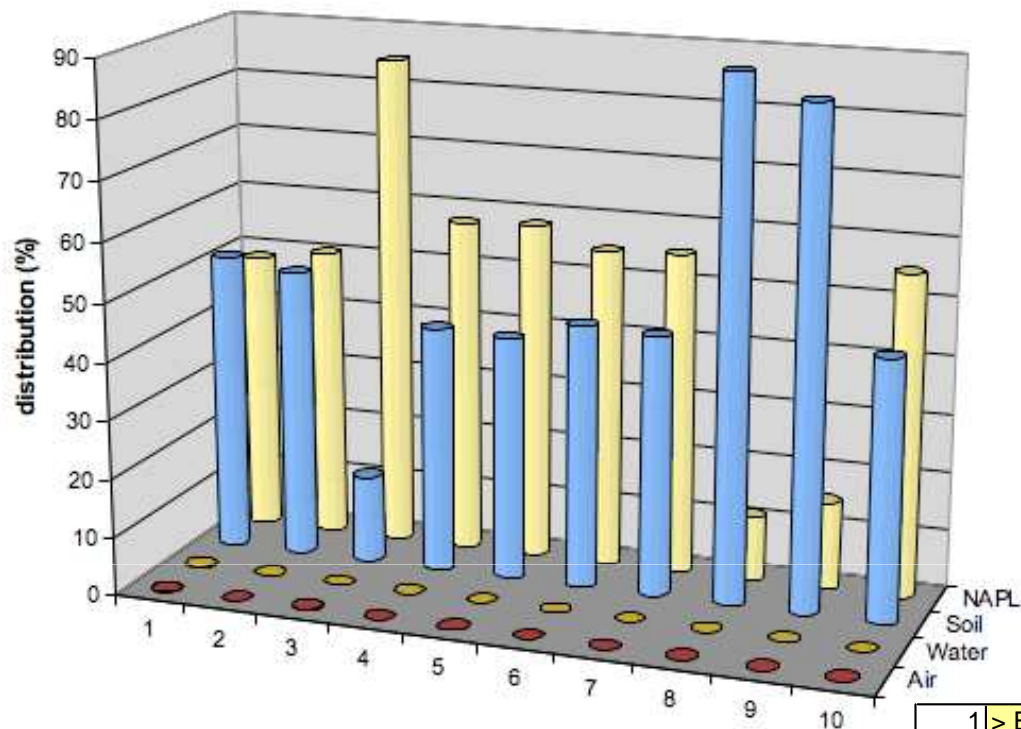
Petroleum Hydrocarbon fractions		GAC ^a (mg kg ⁻¹) UK		SSAC ^b (mg kg ⁻¹) UK		Targets organs/ systems or effects
		Residential without plant uptake	Industrial/commercial	Residential without plant uptake	Industrial	
Aliphatic fractions	>C5-C6	2.11	95.3	8.79	397	Neurological
	>C6-C8	5.37	242	17.20	69000	
	>C8-C10	1.46	65.9	3.53	11300	Liver, blood
	>C10-C12	8.6	29900	17.49	15700	
	>C12-C16	42.1	29900	4888	16800	
	>C16-C35	27600	617000	137957	n.d	Liver
	>C35-C44	27600	617000	414509	n.d	
Aromatic fractions	>C5-C7	0.613	26.9	1.85	84	Liver, neurological
	>C7-C8	0.694	30.4	4.12	186	
	>C8-C10	2.39	107	5.54	250	Body weight
	>C10-C12	14.2	625	29.5	45021	
	>C12-C16	72.7	12200	148	60650	
	>C16-C21	291	9190	1825	46430	Kidney
	>C21-C35	417	9250	2074	46553	
	>C35-C44	417	9250	2074	46553	
	>C44-C70	417	9250	2073	46553	

Fugacity approach: Level I and II



- fate drives analysis, exposure and performance
- $\log K_{oil-soil}$ coefficients
- weathering increases PAH $\log K_{oil-soil}$
- risk = f (availability and toxic response)
- Combination of advective processes and degrading reactions
- Determination of compounds persistence or residence time

Partitioning behaviour: Fugacity level I



General partitioning behaviour and preferential partitioning in a constructed biopile

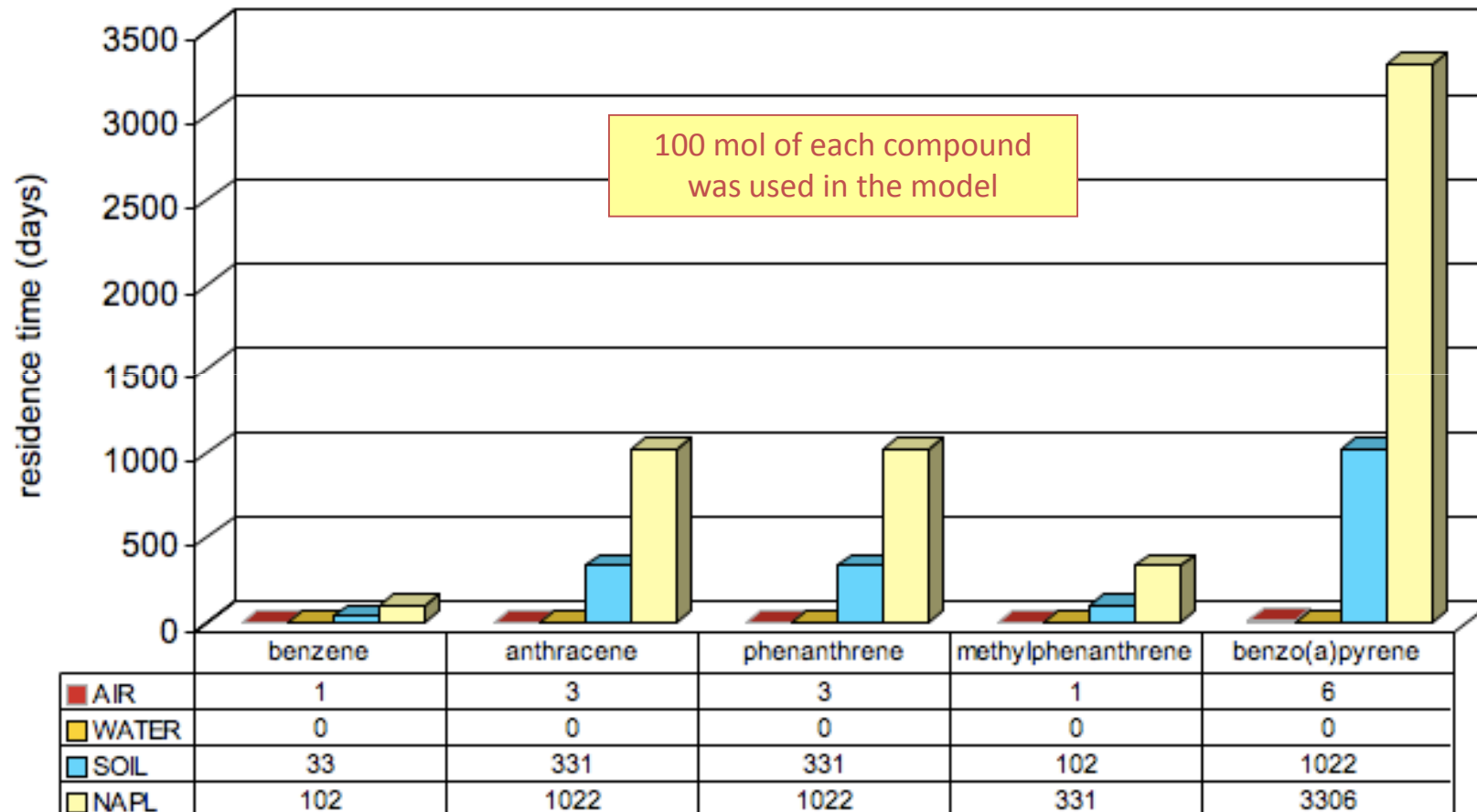
Fugacity calculator for subsurface environments. Available at

<http://www.infoclearinghouse.com/files/FugacityEXCEL.xls>

			Air	Water	Soil	NAPL
1	> EC10-EC12	Naphthalene	0.0	0.2	51.5	48.4
2	> EC12-EC16	Acenaphthene	0.0	0.0	49.8	50.2
3		1-methylphenanthrene	0.2	0.0	15.1	84.7
4	> EC16-EC21	Anthracene	0.0	0.0	42.4	57.6
5		Phenanthrene	0.0	0.0	41.8	58.2
6		Pyrene	0.0	0.0	45.2	54.8
7	> EC21-EC35	Chrysene	0.0	0.0	44.7	55.3
8		Benzo(a)pyrene	0.0	0.0	88.7	11.3
9		Benzo(a)anthracene	0.0	0.0	84.8	15.2
10		Benzo(ghi)perylene	0.0	0.0	44.7	55.3

Residence time: Fugacity level II

Distribution of 5 chemicals modelled in soil microcosms where advection and degradation reaction were combined





Hydrogeological risk assessment for land contamination

Remedial Targets Worksheet , Release 3.1

Date of Workbook Issue: October 2006

This worksheet has been produced in combination with the document 'Remedial Targets Methodology: Hydrogeological risk assessment for land contamination (Environment Agency 2006).

Users of this worksheet should always refer to the User Manual to the Remedial Targets Methodology and to relevant guidance on UK legislation and policy, in order to understand how this procedure should be applied in an appropriate context.

© Environment Agency, 2006. (Produced by the Environment Agency's Science Group)

The calculation of equations in this worksheet has been independently checked by Entec (UK) Ltd on behalf of the Environment Agency. All rights reserved. You will not modify, reverse compile or otherwise dis-assemble the worksheet.

Liability: The Environment Agency does not promise that the worksheet will provide any particular facilities or functions. You must ensure that the worksheet meets your needs and you remain solely responsible for the competent use of the worksheet. You are entirely responsible for the consequences of any use of the worksheet and the Agency provides no warranty about the fitness for purpose or performance of any part of the worksheet. We do not promise that the media will always be free from defects, computer viruses, software locks or other similar code or that the operation of the worksheet will be uninterrupted or error free. You should carry out all necessary virus checks prior to installing on your computing system.

IMPORTANT: To enable MS Excel worksheet, click Tools, Add -Ins, Analysis Tool Pak and Analysis Tool Pak-VBA

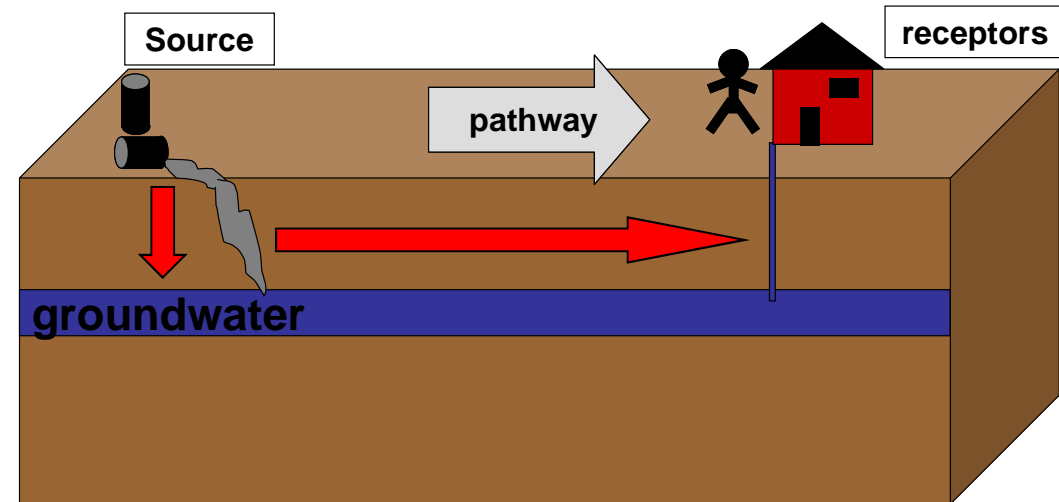
Details to be completed for each assessment

Site Name:	TCE site		
Site Address:	Aberdeen		
Completed by:	LM	Version:	x.xx
Date:	14.Feb-13		
Contaminant	TCE		
Target Concentration (C _T)	0.01	mg/l	Origin of C _T : Specify basis for target concentration



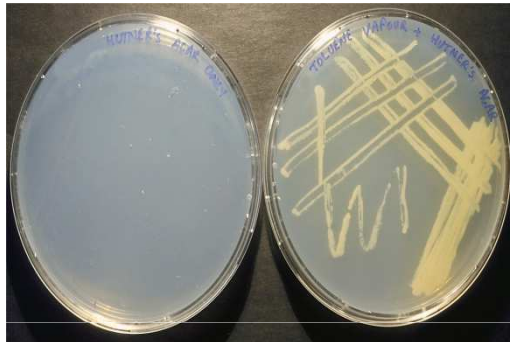
Environmental Standards and DWS values

COC	EQS/DWS ($\mu\text{g/l}$)
Phenols Monohydric	30
Benzene	10
Toluene	10
Ethyl benzene	10
m & p Xylene	10
o Xylene	10
Aliphatics C5-C6	10
Aliphatics >C6-C8	10
Aliphatics >C8-C10	10
Aliphatics >C10-C12	10
Aliphatics >C12-C16	10
Aliphatics >C16-C21	10
Aliphatics >C21-C35	10
Aromatics C6-C7	10
Aromatics >C7-C8	10
Aromatics >EC8-EC10	10
Aromatics >EC10-EC12	10
Aromatics >EC12-EC16	10
Aromatics >EC16-EC21	10
Aromatics >EC21-EC35	10
Naphthalene	10
Benzo(b)fluoranthene	0.10
Benzo(k)fluoranthene	0.10
Benzo(a)pyrene	0.01
Indeno(123cd)pyrene	0.10
Benzo(ghi)perylene	0.10



Bioassays

Microbial



↓

Biomass
Respiration
Nitrification
Enzyme assays
lux-based bacteria

Earthworms



↓

Lethal and Sub-lethal
Eisenia fetida
Lumbricus terrestris

Plants

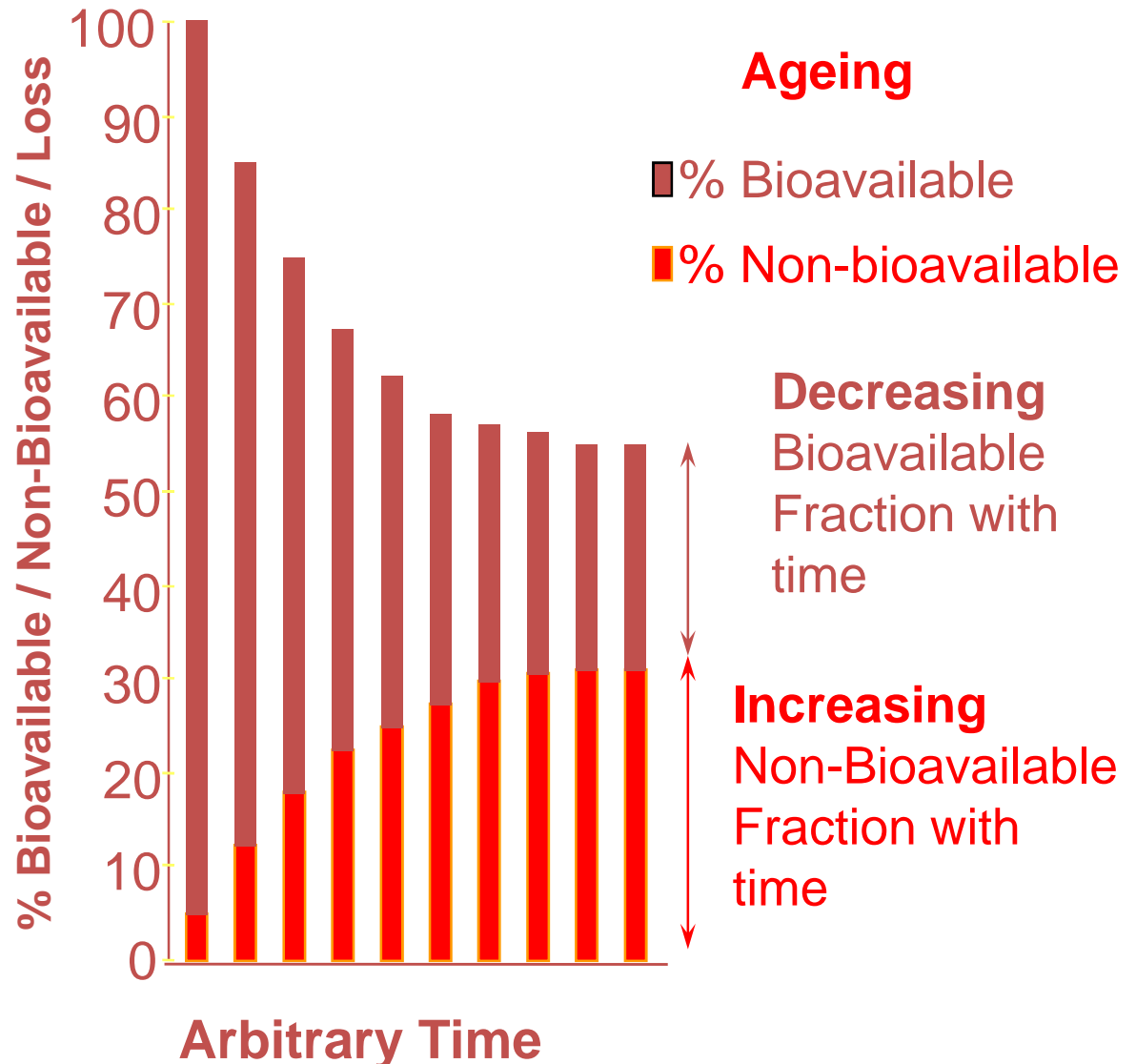


↓

Seed Germination
Mustard
Rye grass
Pea

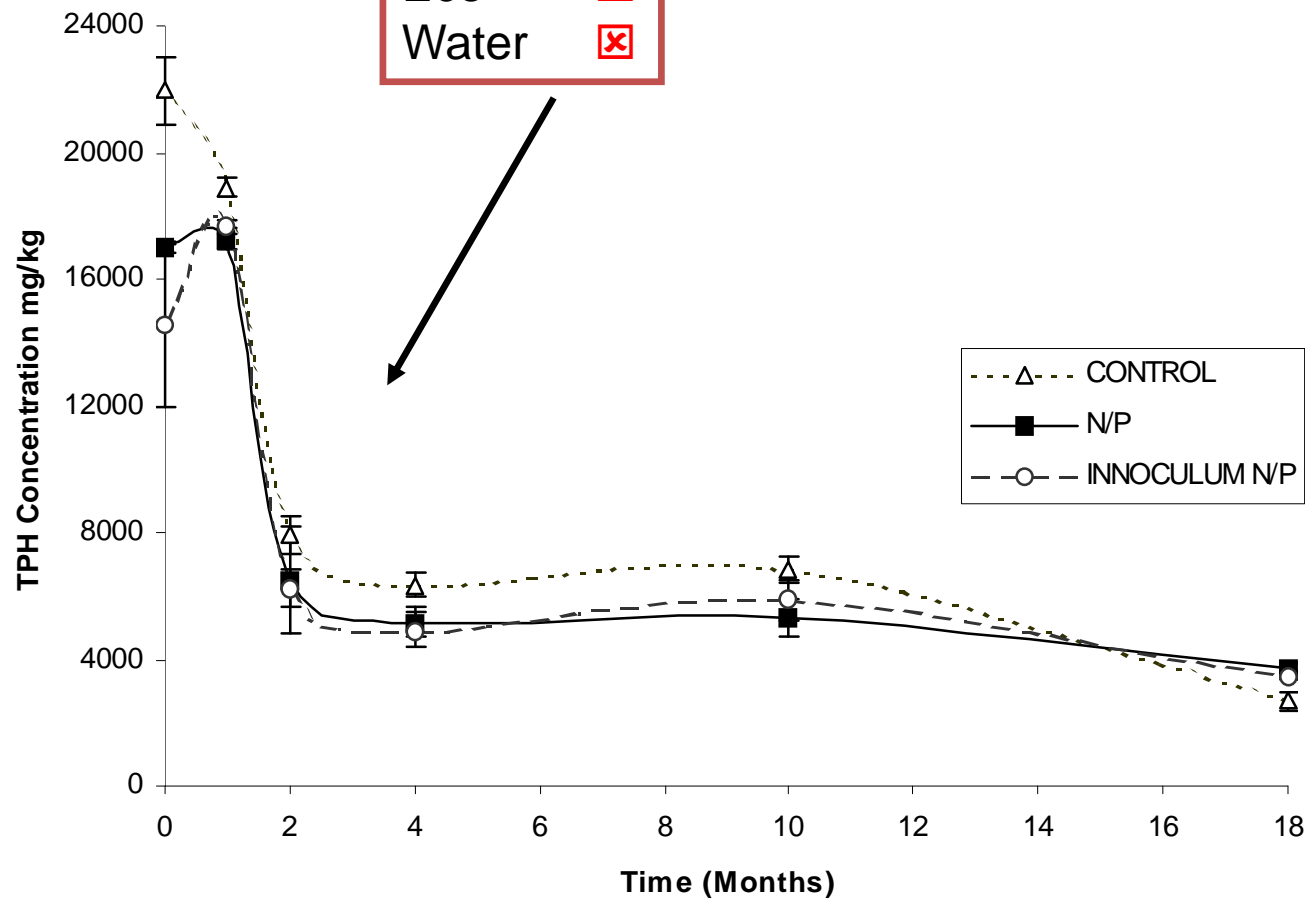
What do we expect to happen

- The hydrocarbons will age and the bioavailability (as a function of degradation and toxicity) will change
- Toxicity may increase and then decrease in association with biodegradation
- Field scale validation may respond in parallel



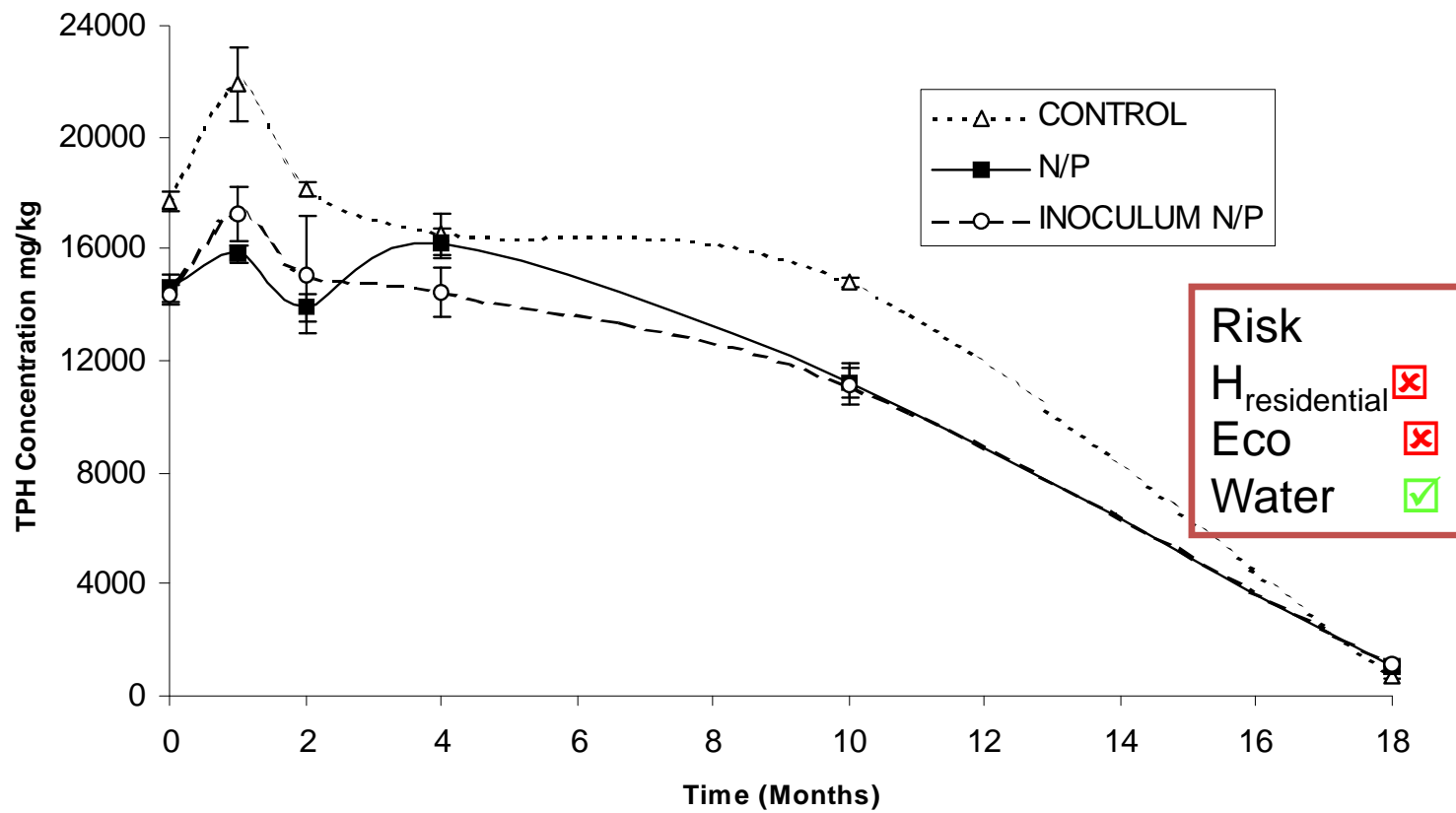
Soil B

Risk	
H _{residential}	✓
Eco	✗
Water	✗



Promise
Promise

Soil C



Promise
Promise

Risk	
H _{residential}	<input checked="" type="checkbox"/>
Eco	<input checked="" type="checkbox"/>
Water	<input checked="" type="checkbox"/>

Pre-mixing



Inoculum



Windrow Turning



Windrow Turning



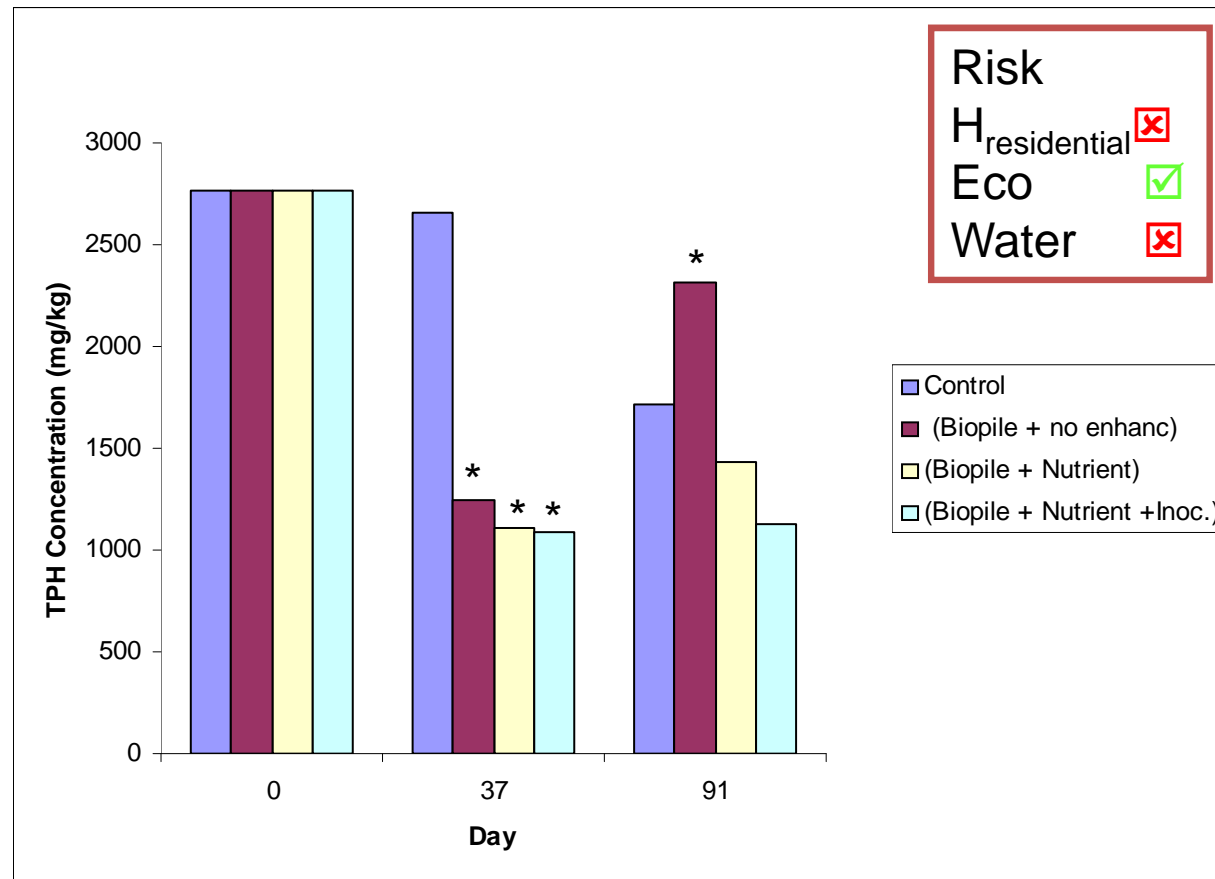
Importance of Irrigation



Routine Monitoring Continues

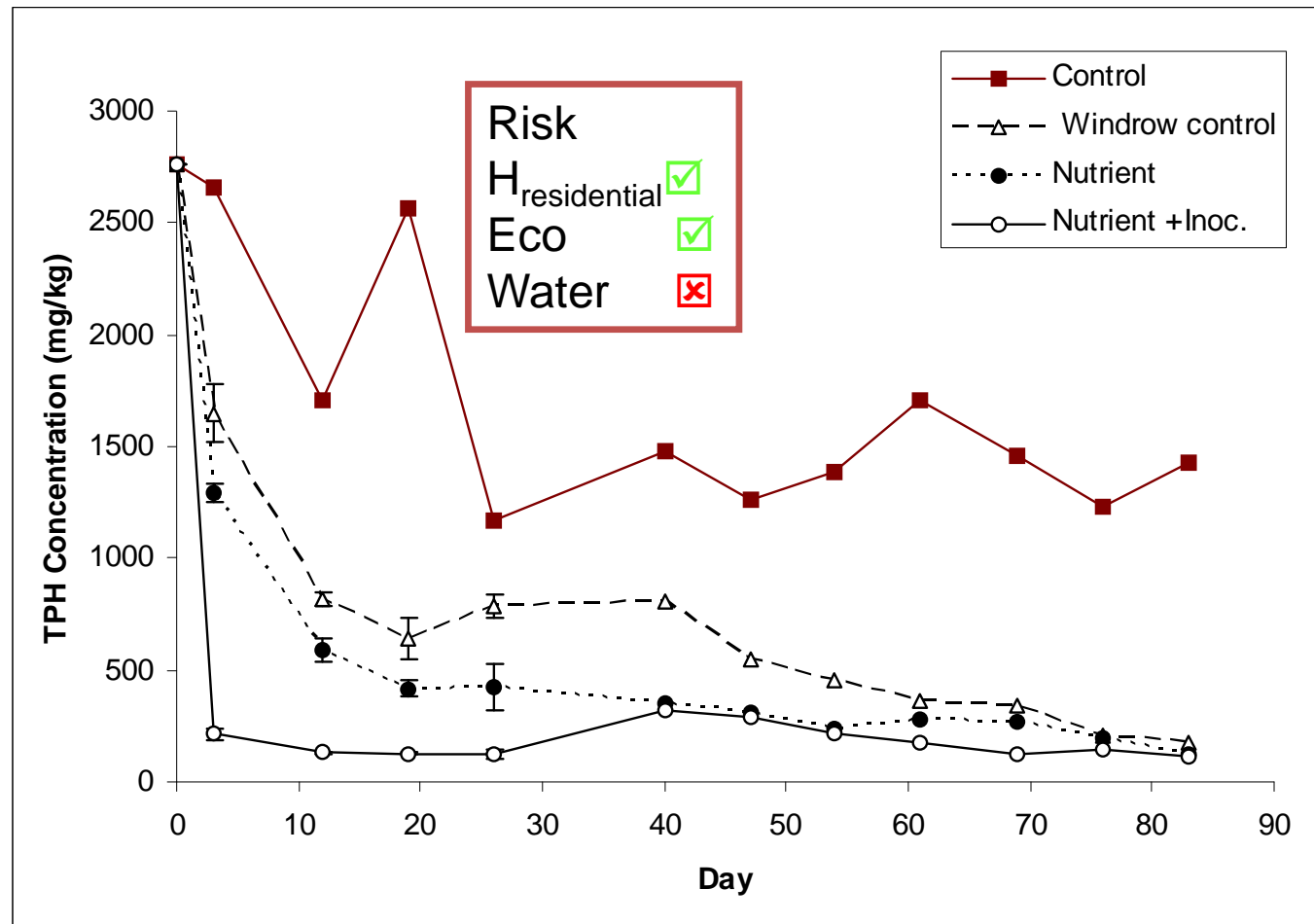


TPH Degradation- Biopiles



Promise
Promise

TPH Degradation- Windrows



Promise
Promise

Remediation Decision Support Tool



- Developed support tool based on 3 tiers, designed to reduce uncertainty in technology selection
- Road tested on genuine scenarios
- The tool assists in the decision making process of remediation technologies:
 - Enabling transparent justification of selection
 - Gives focussed and streamlined support for targeting best options.
 - Interfaces with web to enable continual updating as practices become established and lessons are learned

Predicting Hydrocarbon Remediation?

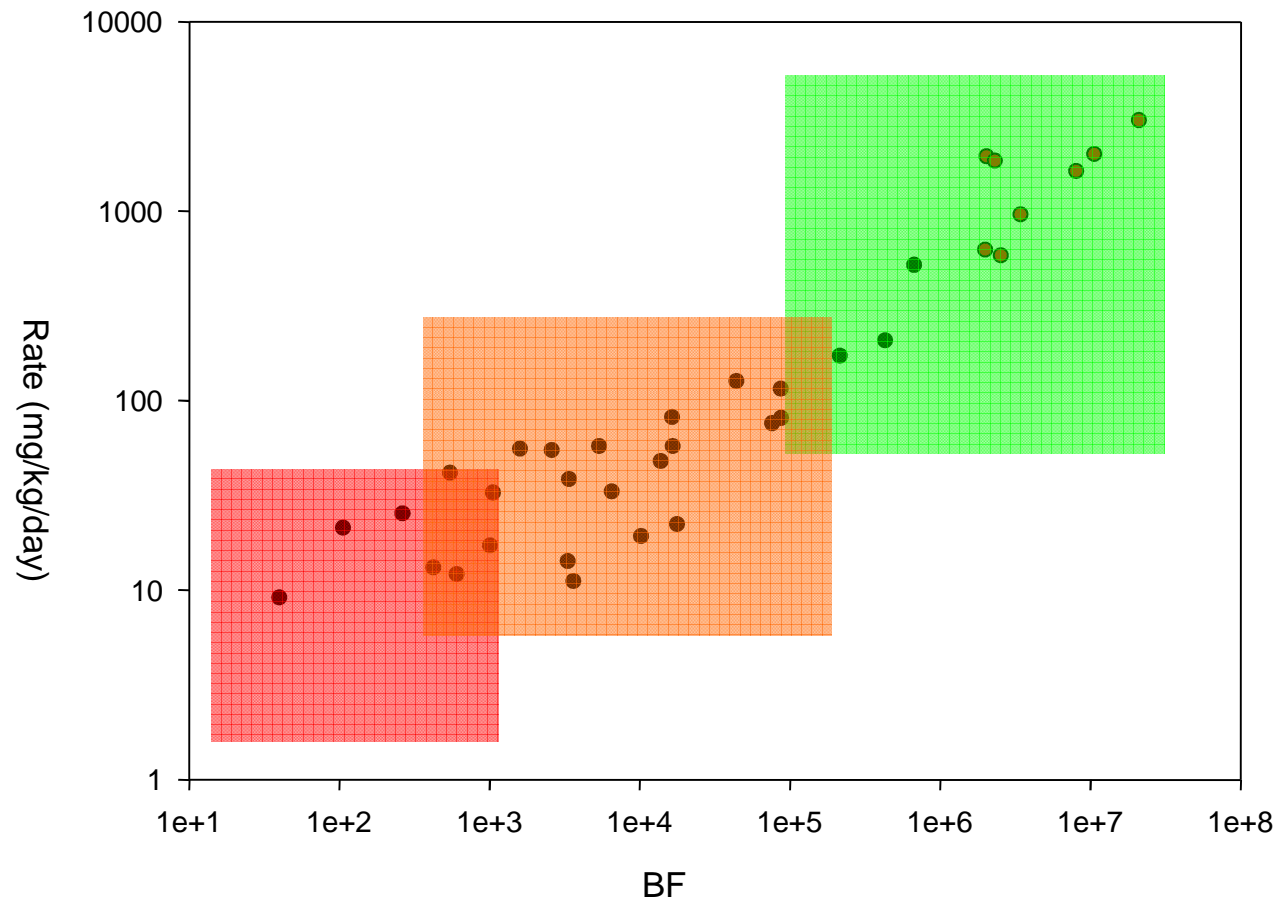
- Empirical data from thirty sites have been generated & applied to appraise and validate.

$$\text{BF} = \left(\frac{\text{Resp}}{I \times [\text{TPH}]} \right) \times \left(\frac{[\text{TPH}]}{\log(\text{MPN})} \right) \times \text{Inhibition}$$

BF = bioremediation function
 I = induction
 [TPH] = TPH concentration
 MPN = most probable number
 Resp = respiration



BF & Rate of Degradation



Hydrocarbon Validation

Environmental Pollution

Predicting bioremediation of hydrocarbons: Laboratory to field scale
 R.E. Dyrstad^{1,2}, D.R. Muzilin³, K.S. Nithum³, G.J. Pober⁴

ABSTRACT

INTRODUCTION

CONCLUSIONS

REFERENCES

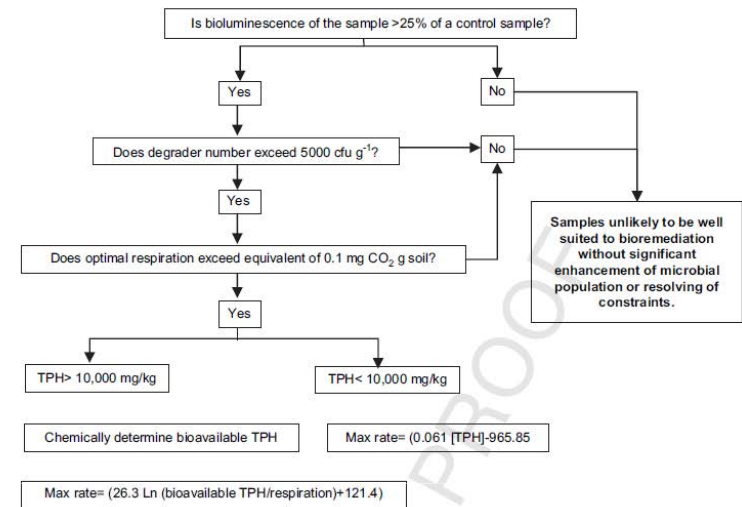


Fig. 3. Decision support tree to make use of derived equations in the assessment of suitability of materials for bioremediation.

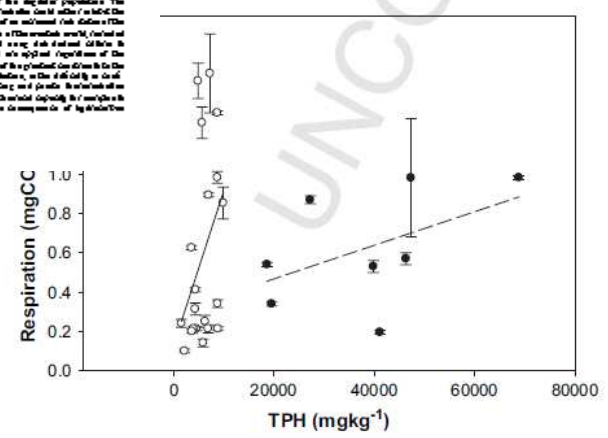


Fig. 2. Total measured petroleum hydrocarbon concentration plotted against the maximum measured rate of respiration ((○) >10,000 mg kg⁻¹ (●) <10,000 mg kg⁻¹).

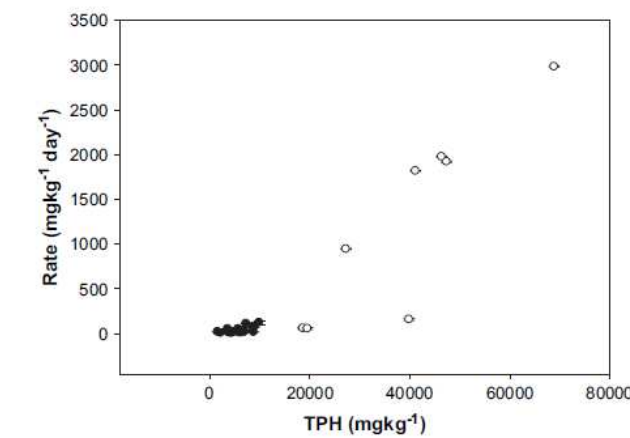
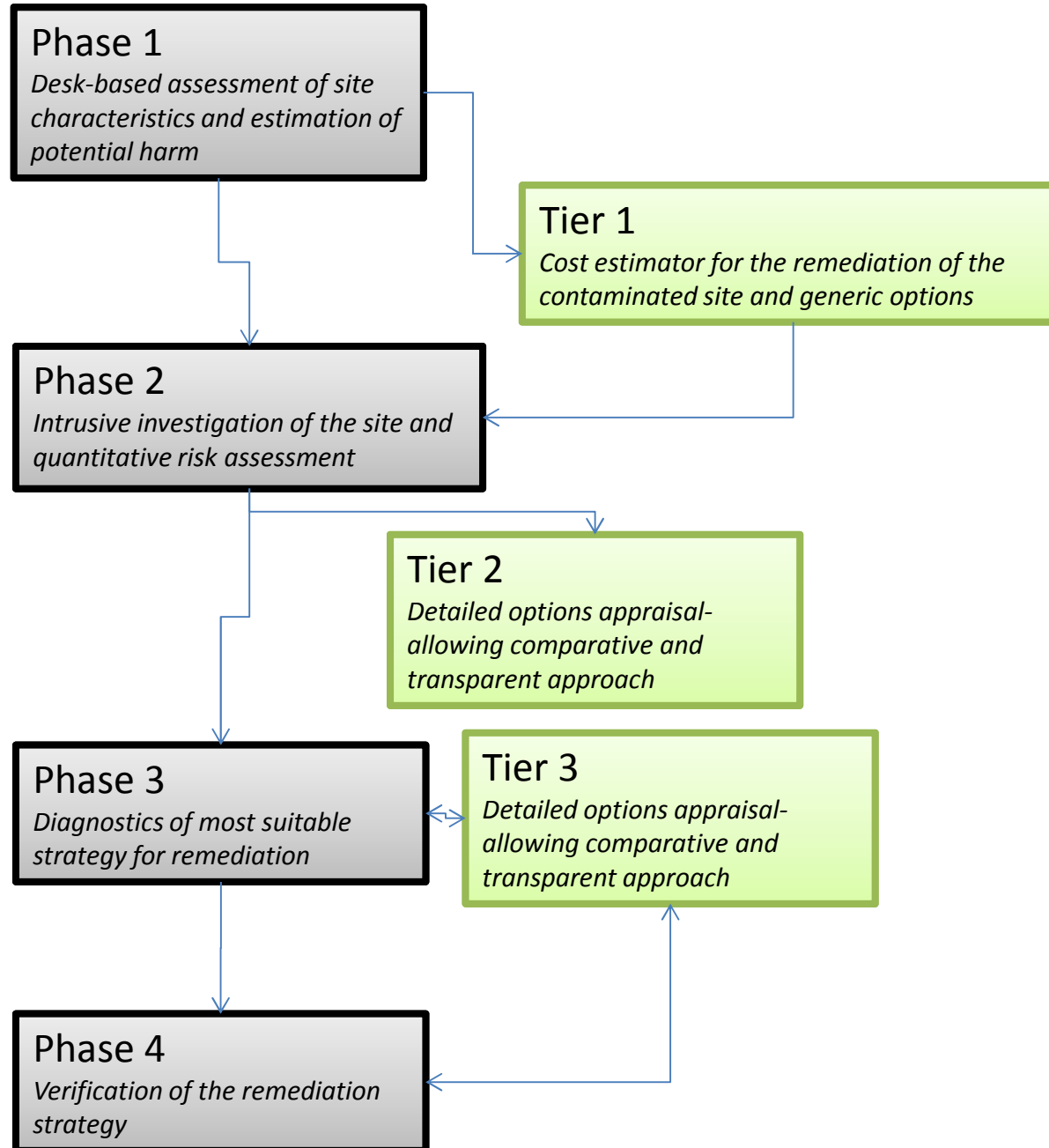


Fig. 1. Total measured petroleum hydrocarbon concentration plotted against the maximum rate of measured hydrocarbon degradation ((○) >10,000 mg kg⁻¹ (●) <10,000 mg kg⁻¹).

OVERVIEW- *ORGANISING A SUITABLE MATRIX*

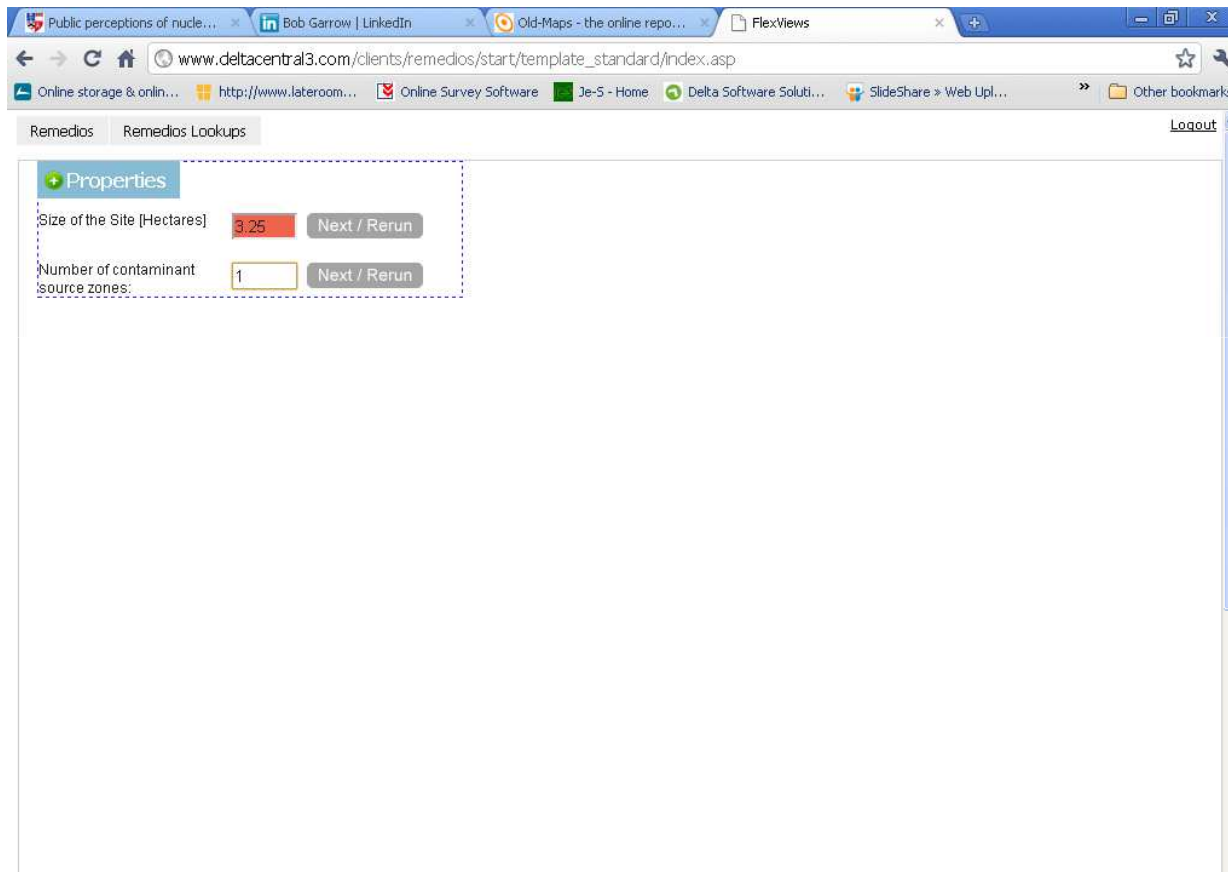


TIER 1- RAPID OVERVIEW WITH LIMITED DATA

Probability/ Consequence Matrix

		Consequence			
		Severe	Medium	Mild	Minor
Probability	V. Likely	V High Risk	High Risk	Moderate Risk	Moderate/ low risk
	Likely	High Risk	Moderate Risk	Moderate/ Low Risk	Low risk
	Low Likely	Moderate Risk	Moderate/ Low risk	Low Risk	Very low risk
	Unlikely	Moderate/ Low Risk	Low risk	Very low risk	Very low risk

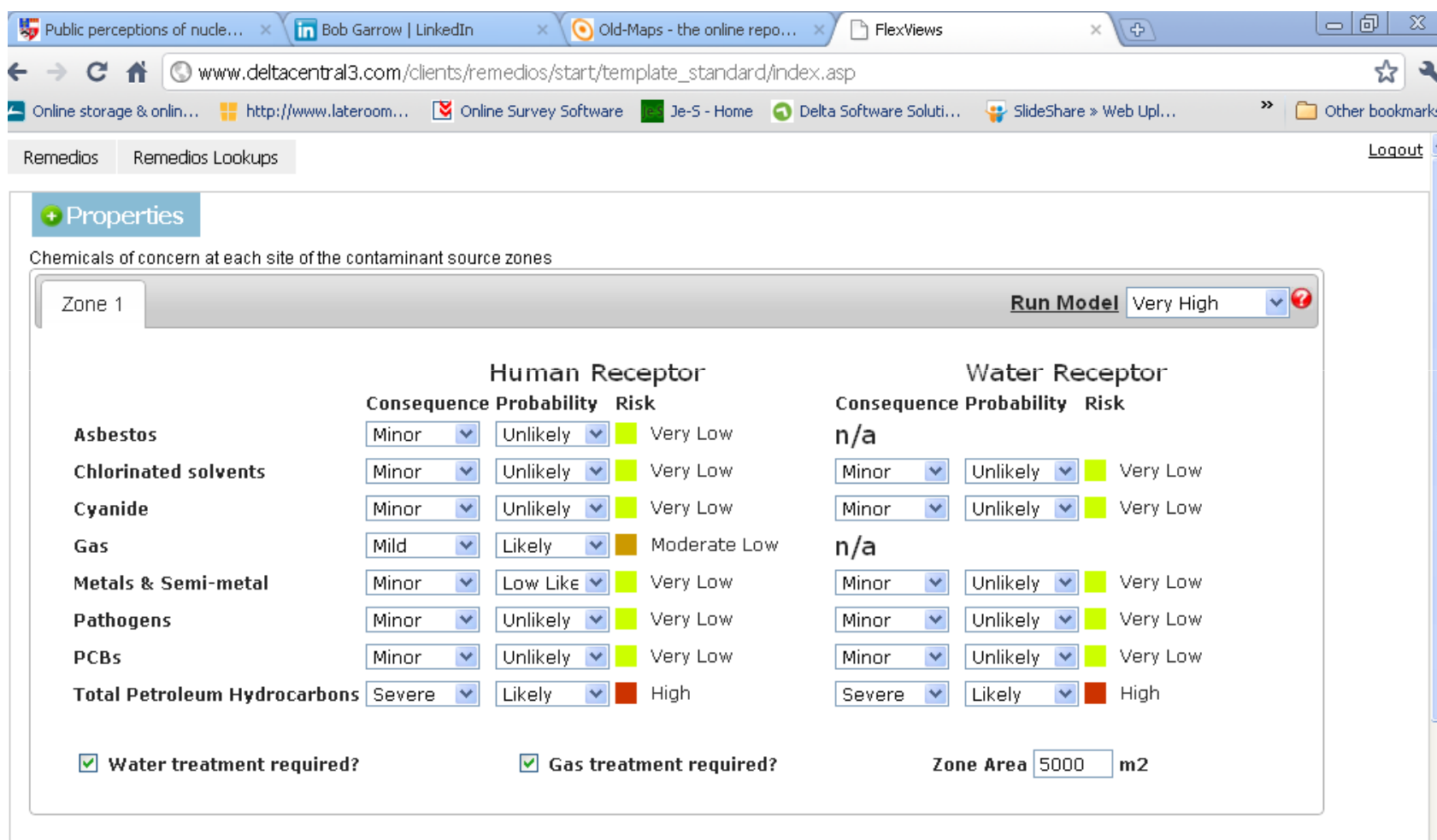
Data Input from Phase 1



The screenshot shows a web browser window with the URL www.deltacentral3.com/clients/remedios/start/template_standard/index.asp. The page has a navigation bar with "Remedios" and "Remedios Lookups" tabs, and a "Logout" link. A "Properties" section is highlighted with a dashed box, containing two input fields:

- "Size of the Site [Hectares]" with a text input containing "3.25" and a "Next / Rerun" button.
- "Number of contaminant source zones:" with a text input containing "1" and a "Next / Rerun" button.

Data Input from Tier 1



Remedios Remedios Lookups [Logout](#)

Properties

Chemicals of concern at each site of the contaminant source zones

Zone 1 **Run Model** Very High

	Human Receptor			Water Receptor		
	Consequence	Probability	Risk	Consequence	Probability	Risk
Asbestos	Minor	Unlikely	Very Low	n/a		
Chlorinated solvents	Minor	Unlikely	Very Low	Minor	Unlikely	Very Low
Cyanide	Minor	Unlikely	Very Low	Minor	Unlikely	Very Low
Gas	Mild	Likely	Moderate Low	n/a		
Metals & Semi-metal	Minor	Low Like	Very Low	Minor	Unlikely	Very Low
Pathogens	Minor	Unlikely	Very Low	Minor	Unlikely	Very Low
PCBs	Minor	Unlikely	Very Low	Minor	Unlikely	Very Low
Total Petroleum Hydrocarbons	Severe	Likely	High	Severe	Likely	High

Water treatment required? Gas treatment required? Zone Area 5000 m2

Output

Public perceptions of nucle... | Bob Garrow | LinkedIn | Old-Maps - the online repo... | FlexViews

www.deltacentral3.com/clients/remedios/start/template_standard/index.asp

Online storage & onlin... | http://www.lateroom... | Online Survey Software | Je-S - Home | Delta Software Soluti... | SlideShare » Web Upl... | Other bo

Total Petroleum Hydrocarbons Severe v. Likely Very high Severe v. Likely Very high

Water treatment required? Gas treatment required? Zone Area **5000** m2

Results 1

human receptor

Methods Using Excavation

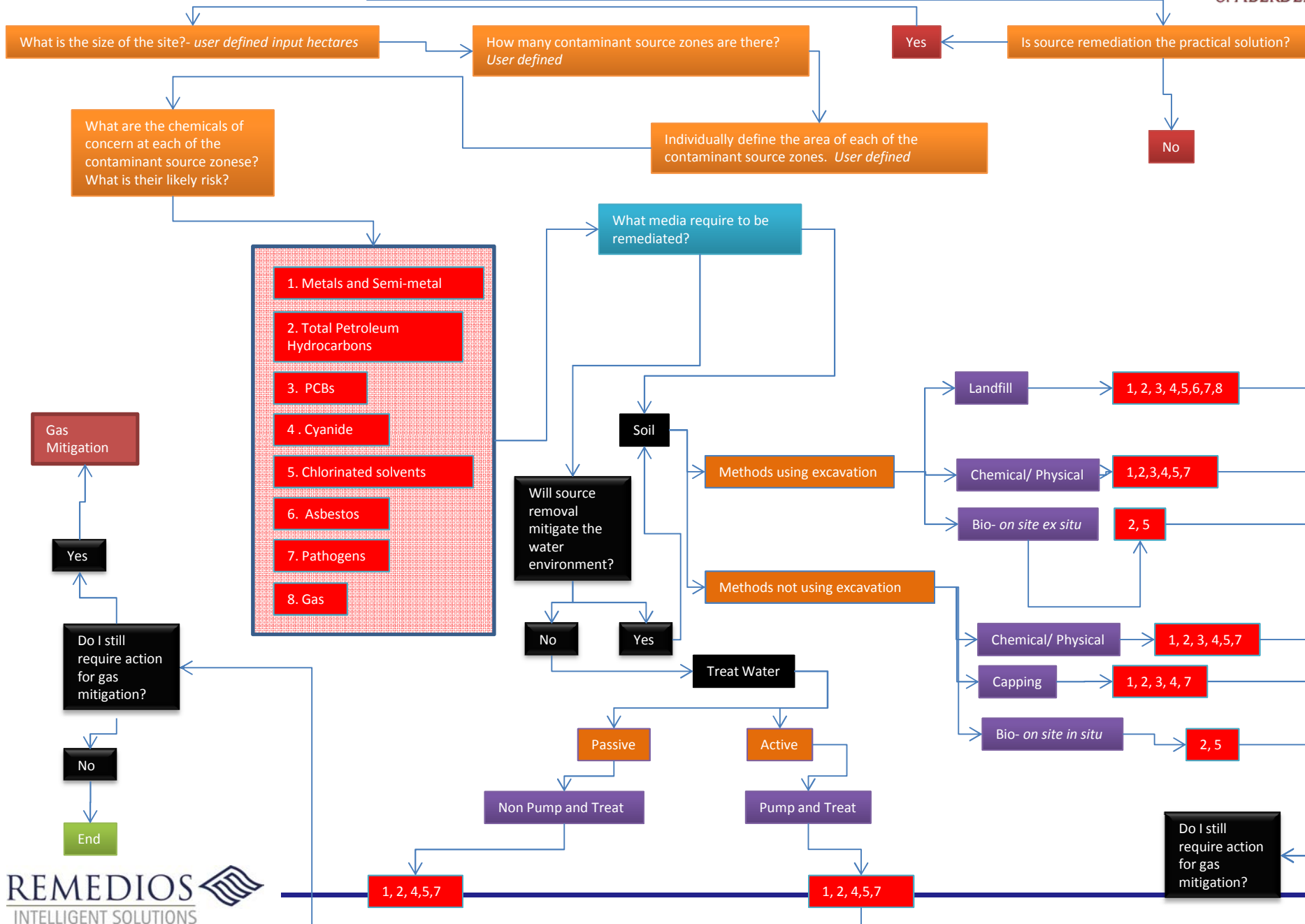
	Landfill	Chemical / Physical	Bio - on site
Asbestos	✓	✗	✗
Chlorinated solvents	✓	✓	✓
Cyanide	✓	✓	✗
Gas	✓	✗	✗
Metals & Semi-metal	✓	✓	✗
Pathogens	✓	✓	✗
PCBs	✓	✓	✗
Total Petroleum Hydrocarbons	✓	✓	✓
	£756000	£360000	£300000

Excavation Cost:

Methods NOT Using Excavation

	Chemical Physical	Capping	Bio - on site
Asbestos	✗	✗	✗
Chlorinated solvents	✓	✗	✓
Cyanide	✓	✓	✗
Gas	✗	✗	✗
Metals & Semi-metal	✓	✓	✗
Pathogens	✓	✓	✗
PCBs	✓	✓	✗
Total Petroleum Hydrocarbons	✓	✓	✓


TIER 2- SITE SPECIFIC MATCHING OF TECHNIQUES



Which does what?

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF
				in situ				soil				ex situ				groundwater																
				MHA	bioventing	enhanced bioremediation	phytoremediation	chemical oxidation and reduction	electrokinetic remediation	soil flushing	SVE	solidification/stabilization	thermal treatment	bioremediation	chemical oxidation, reduction & dehalogenation	soil washing/separation	solidification/stabilization	incineration	thermal desorption	effluents disposal	MHA	enhanced bioremediation	phytoremediation	soil flushing	air sparging	chemical oxidation	soil pore extraction	thermal treatment	in-situ air stripping	passive/reactive treatment walls	physical/chemical (e.g. sump & treat)	physical barrier
5																																
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Chemicals of Concern

1	
2	
3	
4	Remediation DST Tier 2
5	Site name
6	Contaminated material
7	Completed by
8	Date completed
9	
10	What COCs require remediation?
11	other TPH and LMWPAH
12	halogenated aromatics
13	
14	other TPH and LMwPAH
15	HMwPAH
16	MTBE
17	non-recalcitrant pesticides, halogenated phenols
	PCBs, recalcitrant pesticides, dioxins, furans
	chlorinated solvents
	carbon disulphide
	pathogens
	yes

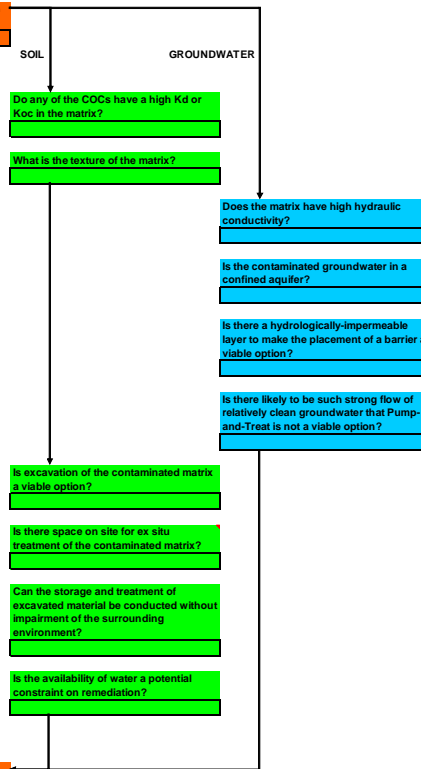


Remediation DST Tier 2
 Site name
 Contaminated material
 Completed by
 Date completed

What COCs require remediation?

Is the COC present as a NAPL in the matrix/ groundwater?

Is the matrix capable of supporting high bioactivity?



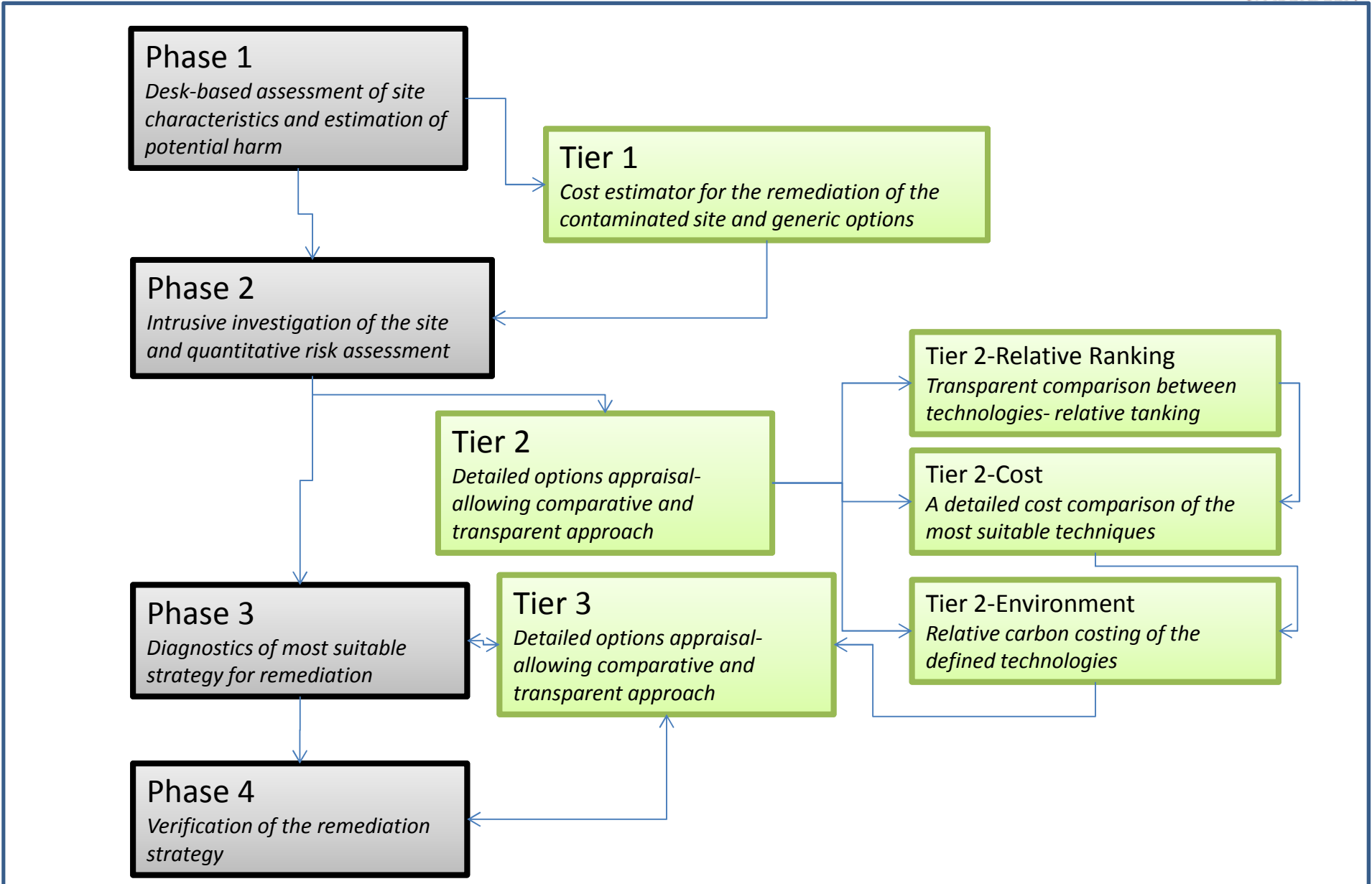
For how long can site use or redevelopment be constrained by remediation activities?

How long until remedial targets must be achieved?

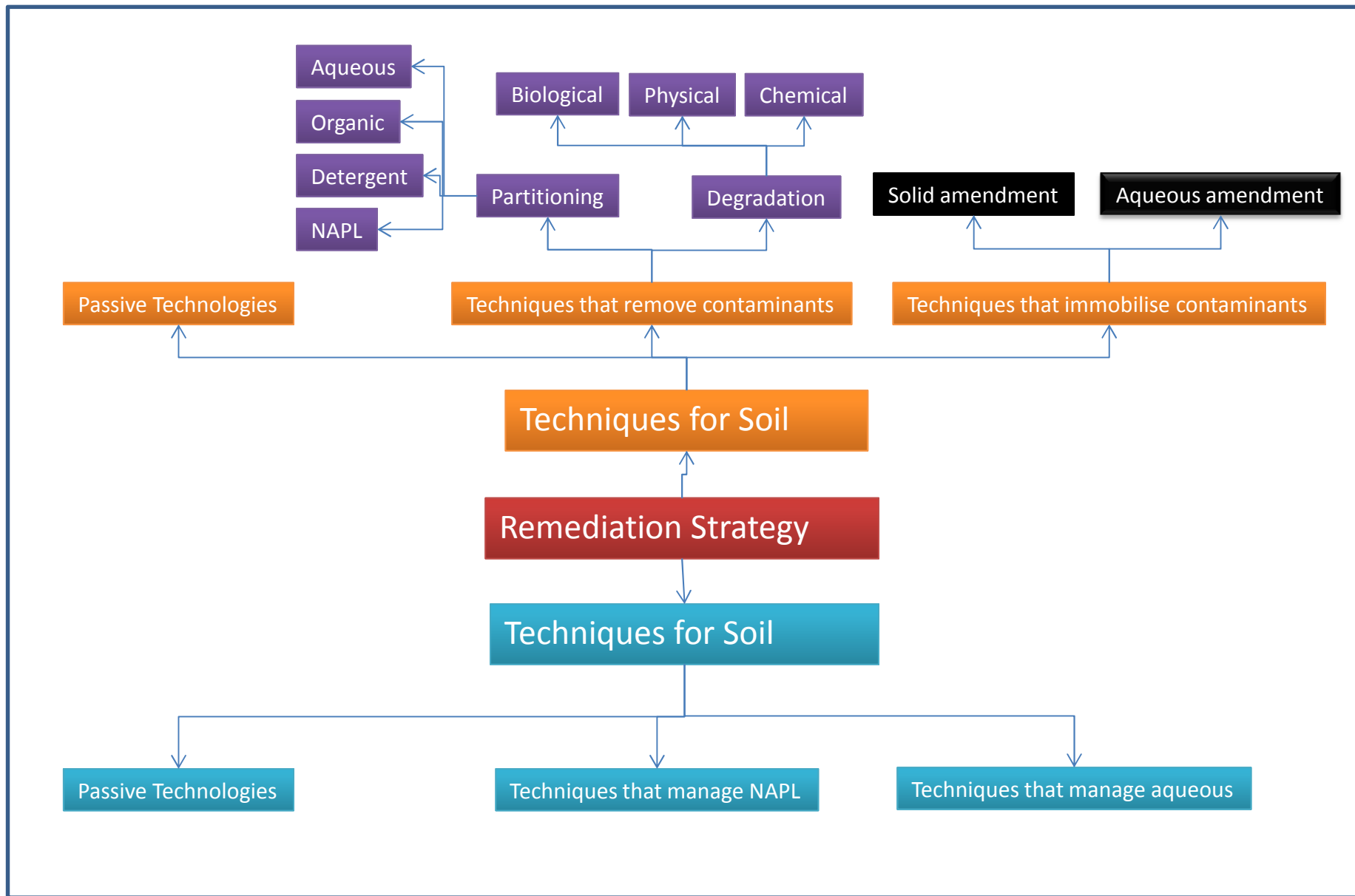
Does COC removal have to be achieved?

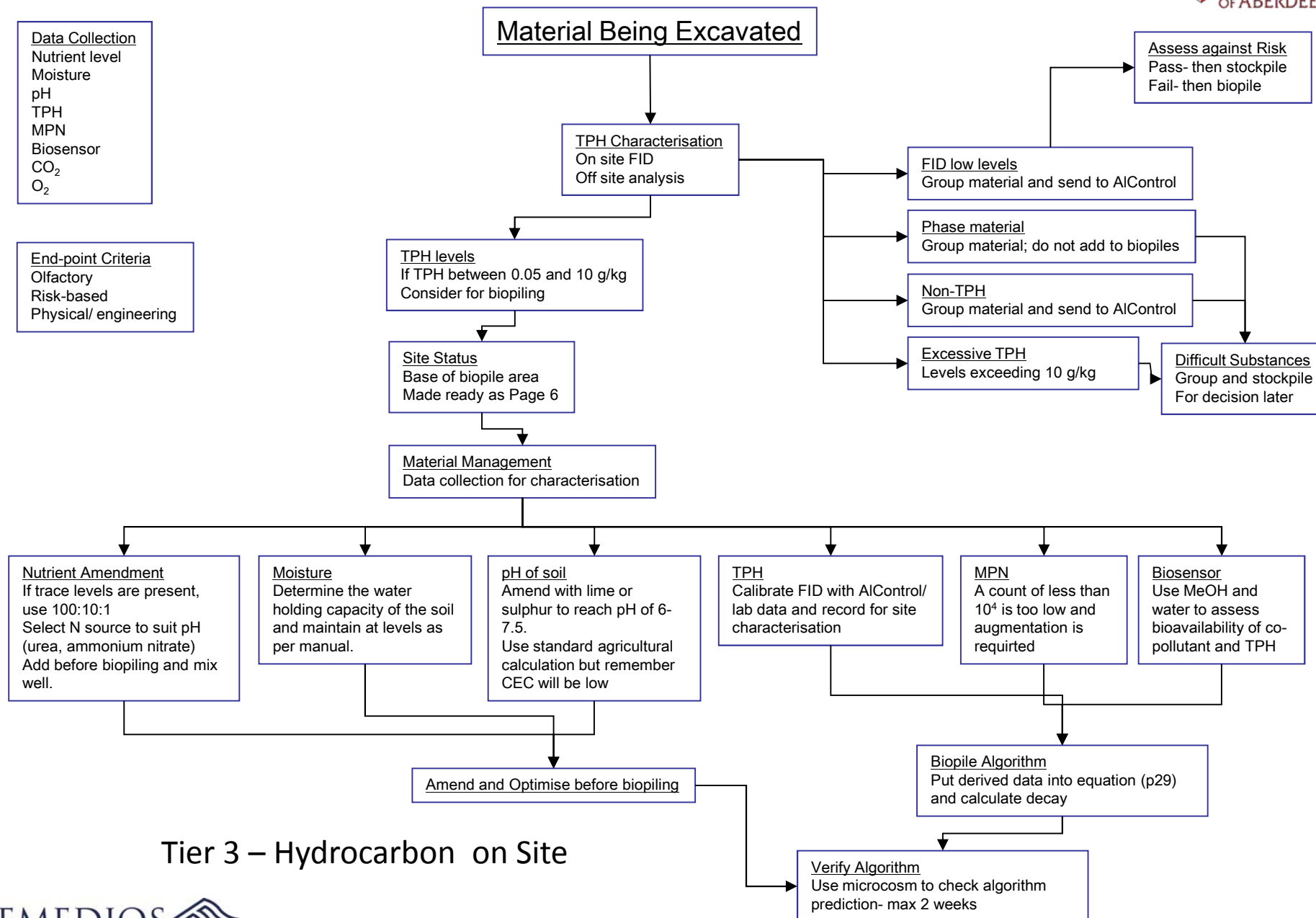
- Visual basic interface
- Multi-pollutant credible
- Considers major processes
- Links to a ranked output

		Technique	Site Specific Applicability	Permissibility	Certainty	Capital Costs	O and M Costs	Market Constraints	Remediation Duration	Environmental Credits	Weighted Score	Rank	
Soil, Sediment, Bedrock and Sludge Treatment Technologies	Priority Techniques from Stage 1	Do nothing	7	6	5	10	10	10	3	5	77.00	3	
		Monitor	9	8	5	8	8	10	5	10	96.00	1	
		Chemical oxidation	4	8	5	3	8	8	7	4	57.00	9	
		Solidification/ Stabilisation (in situ)	4	9	9	5	8	7	7	7	8	79.50	2
		Biopiles	0	8	6	6	6	9	5	8	60.50	7	
		Windrowing	0	8	6	6	6	9	5	8	60.50	7	
		Separation	4	8	9	4	7	9	6	7	74.50	5	
		Soil washing	3	7	10	3	8	8	7	4	63.00	6	
		Solidification/ Stabilisation (ex situ)	6	8	8	4	6	8	6	7	77.00	3	
		Landfill cap	0	8	10	2	4	10	8	3	48.00	11	
Excavation and off site	2	8	10	2	4	10	8	3	54.00	10			
		Technique	Site Specific Applicability	Permissibility	Certainty	Capital Costs	O and M Costs	Market Constraints	Remediation Duration	Environmental Credits	Weighted Score	Rank	
Groundwater, Surface Water and Leachate Treatment Technologies	Priority Techniques from Stage 1	Do nothing	6	6	5	10	10	10	3	5	74.00	8	
		Monitor	9	8	5	8	8	10	5	10	96.00	2	
		Monitored Natural Attenuation	9	8	5	8	8	10	5	10	96.00	2	
		Bioslurping	6	8	7	6	5	9	6	7	76.50	6	
		Chemical oxidation	6	6	8	6	6	9	8	6	74.50	7	
		Passive/ Reactive Walls	8	8	10	6	8	8	8	8	94.00	4	
		Groundwater Pump and Treat	9	9	7	5	6	8	7	7	86.00	5	
		Physical Barriers	9	8	10	5	9	9	9	8	97.50	1	
		Membrane Separation	4	7	6	4	5	5	7	6	60.50	10	
		Oxidation	4	7	6	4	6	6	7	6	62.00	9	



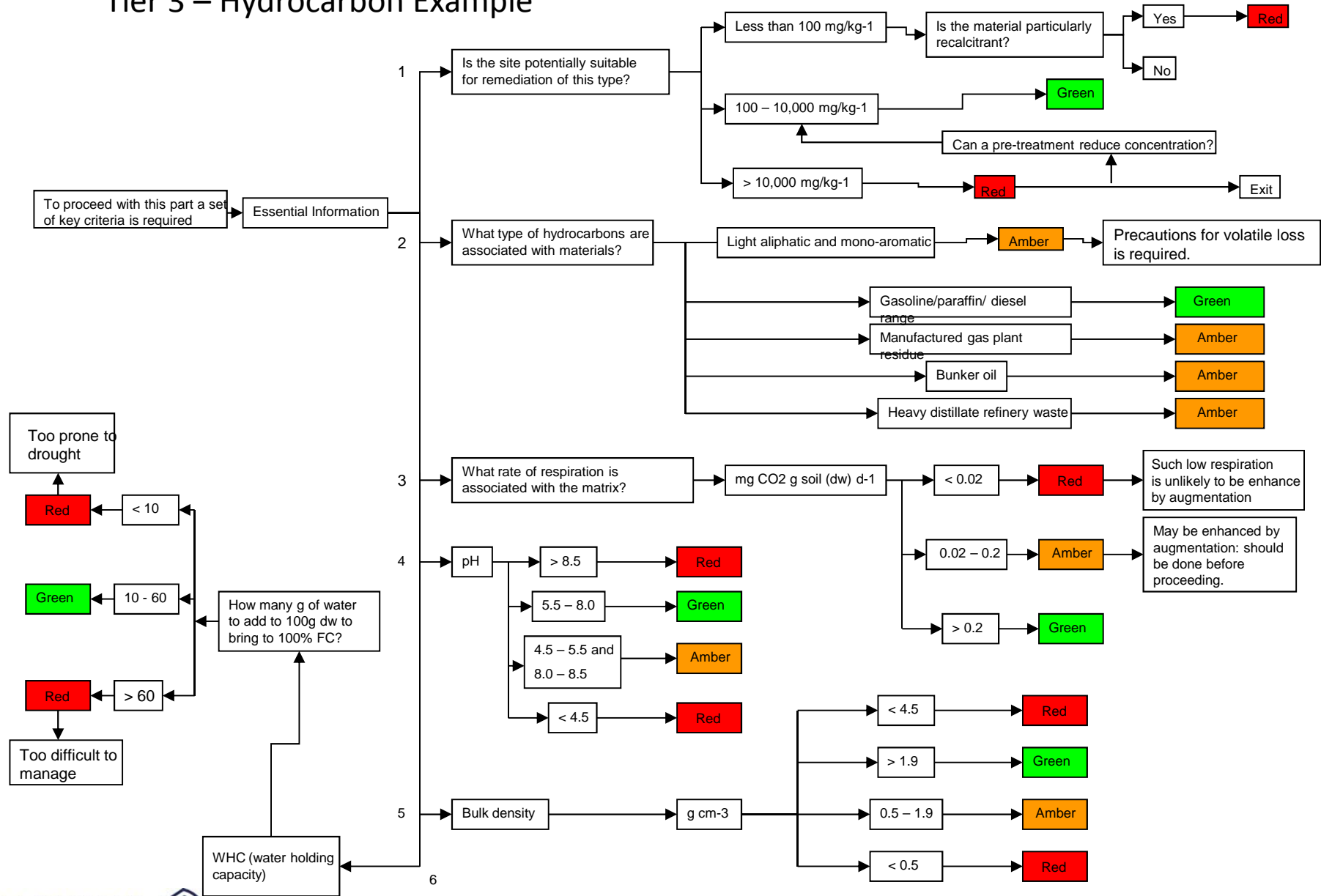
TIER 3- SITE SPECIFIC PROCEDURES WITH REGULATORY ENGAGEMENT





Tier 3 – Hydrocarbon on Site

Tier 3 – Hydrocarbon Example



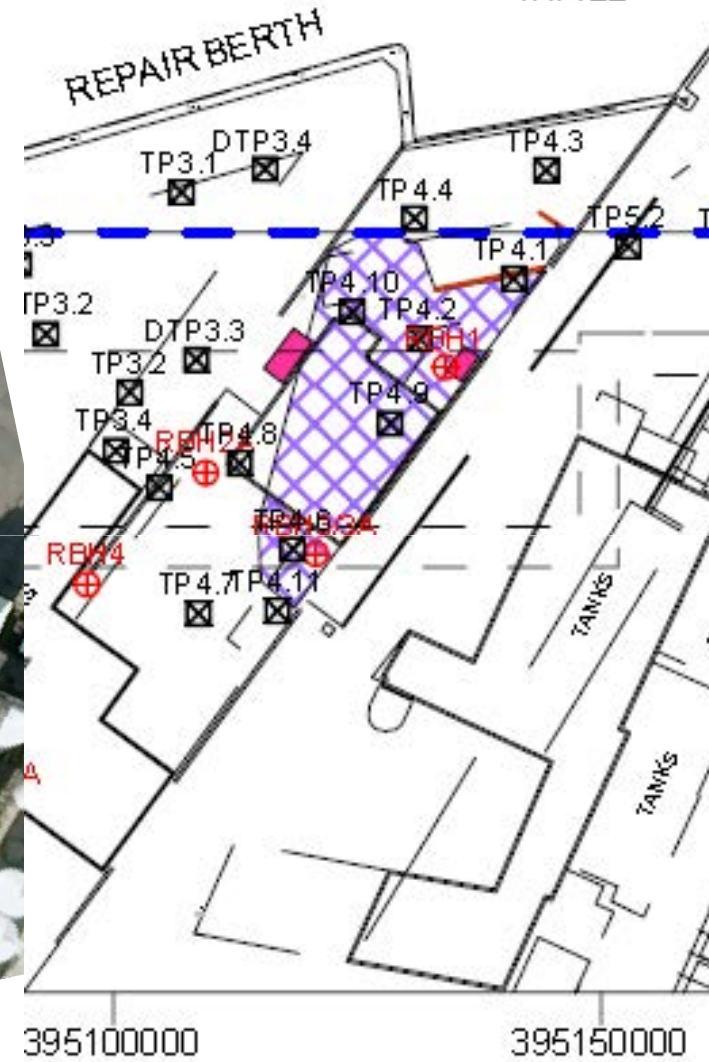
Integration of Tiers

- Information in tiers integrated together to form more manageable and aesthetically pleasing interface.....the Remediation DST support tool.



CASE STUDIES

SLIPWAY INFILL



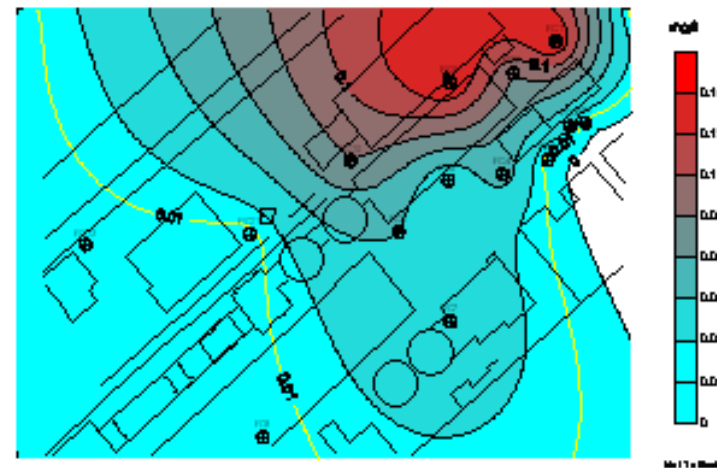
What we know and what we need to know

- ✓ The slipway area is impacted with hydrocarbons
 - ✓ Contamination starts from 2 m bgl
 - ✓ The area is tidal
 - ✓ The contamination is within a defined zone
 - ✓ Limited ability to excavate
 - ✓ Over 2000 tonnes of soil has been removed
 - ✓ Over 1700 tonnes of water has been treated
 - ✓ Phase has been effectively managed
- Biodegradation and partitioning work is well underway
 - Unlikely that neighbouring sites contribute to contamination source

		Technique	Site Specific Applicability	Permissibility	Certainty	Capital Costs	O and M Costs	Market Constraints	Remediation Duration	Environmental Credits	Weighted Score	Rank	
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		Biopiles	0	8	6	6	6	9	5	8	60.50	7	
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		Oxidation	4	7	6	4	6	6	7	6	62.00	9	

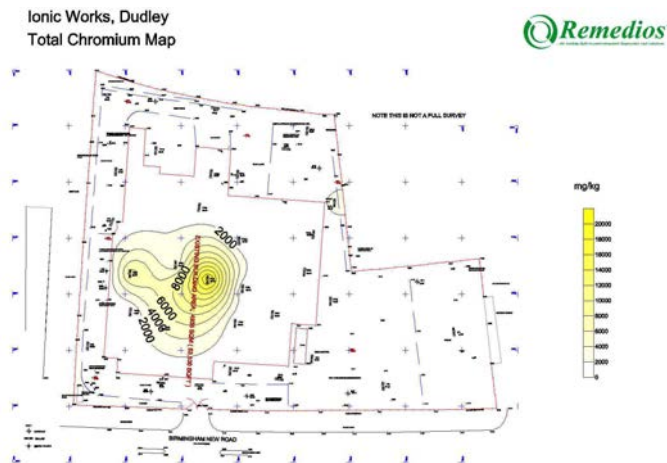
Case Studies DST – Application to Genuine Environment

- A former railway yard, contaminated with an excess of heavy and mid-range hydrocarbons
- DST proposed action: windrow/biopiling or landfarm
- Actual action: as DST suggested, biopiling was evaluated
- Cement and aggregate provider concerned about the environmental liability associated with a landfill site
- DST proposed action: MNA, windrow/biopile or landfill
- Actual action: as DST suggested, MNA was evaluated.



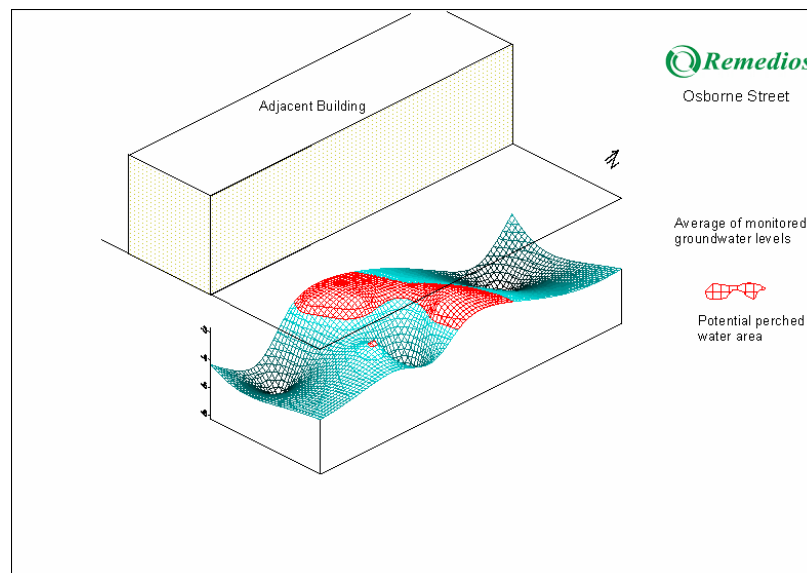
Case Studies DST – Application to Genuine Environment

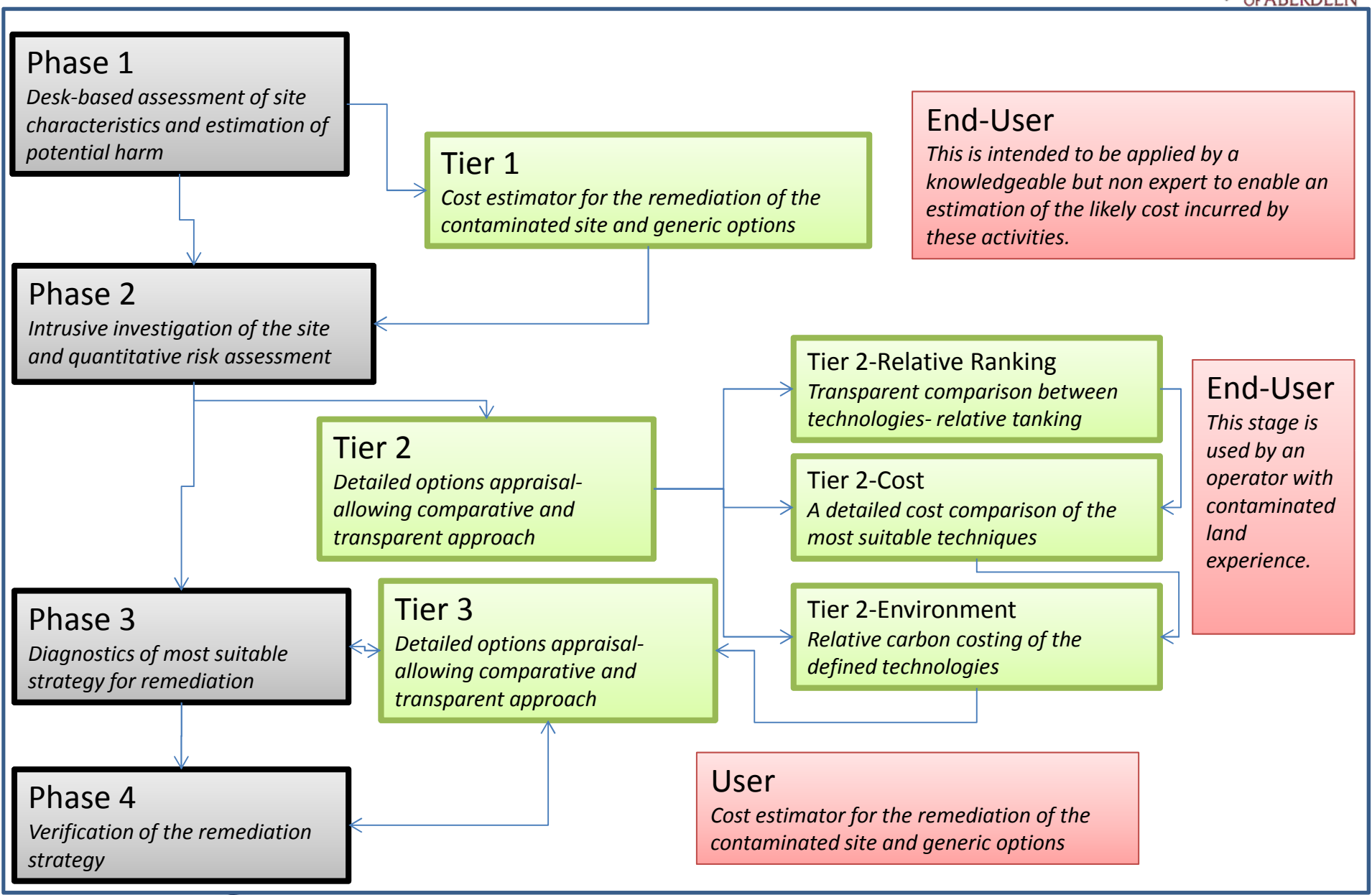
- A former metal works facility to be re-used for light industry
- DST proposed action: excavation and some complexation agents
- Actual action: as DST suggested
- Cement factory with significant contamination issues and need for “greening”
- DST proposed wide range of actions and these are being systematically developed and applied



Case Studies DST – Application to Genuine Environment

- A impacted plume in an urban setting
- DST proposed action: pump and treat through a range of processes
- Actual action as DST
- Former goods yard was grossly hydrocarbon impacted
- DST proposed action: barrier and bioremediation
- Actual action: as DST suggested, MNA was also evaluated.







Thank you for your attention