REMTECH Europe

RSK

REDUCING COSTS BY QUANTIFYING NATURAL SOURCE ZONE DEPLETION PROCESSES IN RISK-BASED REMEDIATION

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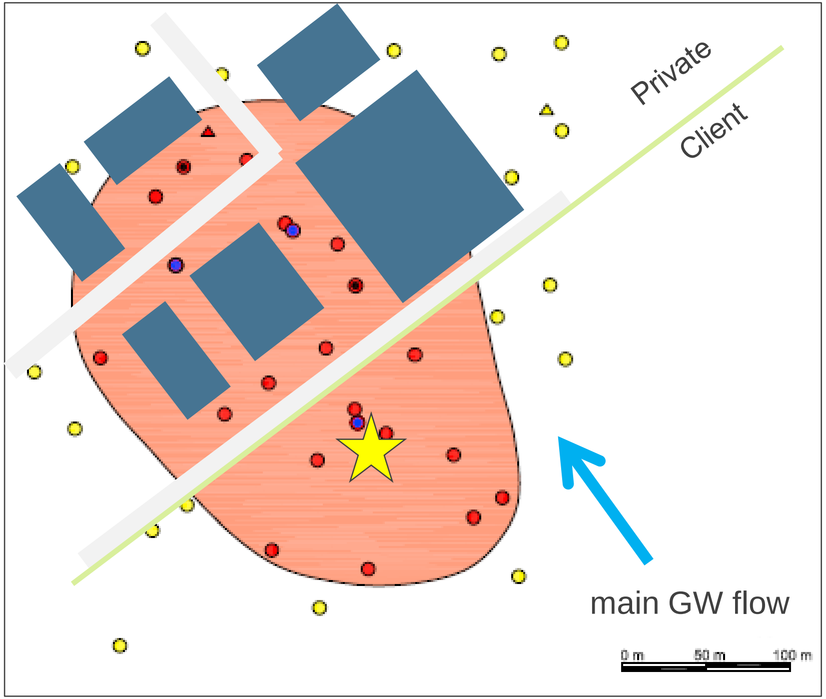
Project/site description

- Industrial site in Eastern Germany
- More than 50a of industrial history
- Leakage of approximately 500m³ of a mineral oil product (medium C-fraction) in 2013 through an underground pipeline
- Soil contamination in the vadose zone of ~ 500m³
- LNAPL in an area of ~ 40,000m², ~ 2/3 on private land
- Groundwater contamination with BTEX/TMB and TPH
- No use of groundwater, no water protection zone, no emissions into buildings, no risk to human health

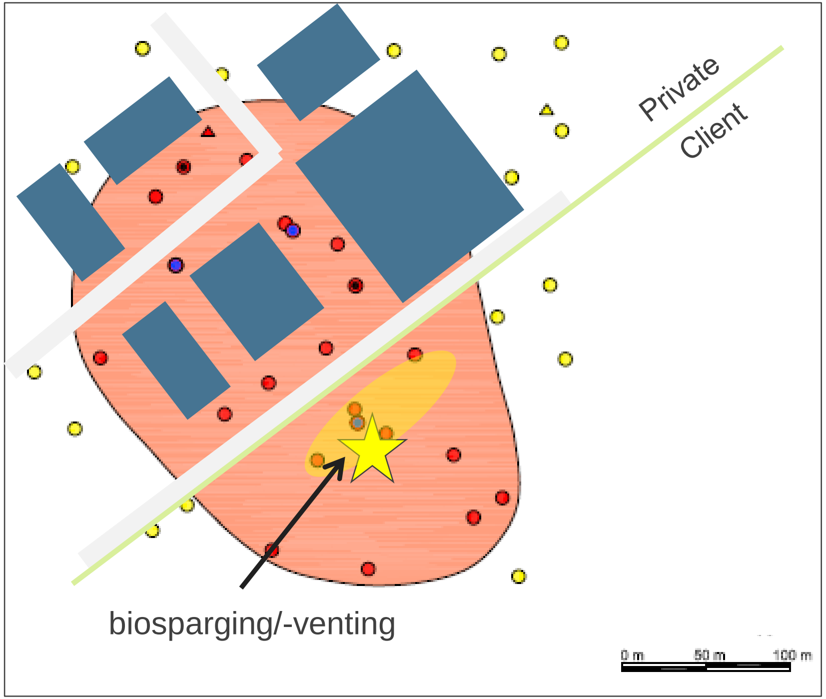
Hydrogeological setting

- Fluviatile sediments, sands and gravel, medium to high permeability
- Depth to groundwater 4 to 7m
- High fluctuation of groundwater levels caused by adjacent river (~ 500m NW) created a smear zone of ~ 2m
- Change of flow directions depending on river levels



Previous measures – authority requirements

- Intense investigation of the contaminated area
- Recovery of free product as long a technically feasible and proportional
  - Recovered product volume ~ 150 m³
  - Stopped in 2018
- Containment of dissolved plume (ongoing)
- Active measures in source zone (leakage point) impossible due to existing infrastructure
- Further remediation required
  - [Remediation of residual contamination]



Regulatory background

Authority expectations

- Remediation under German law comprises decontamination and containment (BBodSchG)

- Contaminations younger than 1st March 1999 shall be eliminated, only in case decontamination is unproportional, containment can be accepted

- Natural source zone depletion (NSZD) / monitored natural attenuation (MNA)
  - Is not accepted as a remedial measure!
  - MNA can only be applied in combination with or after active measures
  - Rates and prognosis required!

- Regulator required active measures to actively treat the residual contamination by, e. g.
  - Excavation and ex-situ treatment or deposition
  - Thermal measures incl. hot water flushing and steam injection
  - ISCO

- Expected costs for active measures do exceed 10 Million Euros

Strategy

Identification and quantification of NSZD processes and comparison with active measures

- **Hydrochemistry**
  - ➢ Providing initial information on potential biodegradation processes, consumption of electronic acceptors, methanogenesis
- **BACTRAPs**
  - ➢ Providing evidence that the environment is able to degrade contaminants of concern
- **CO_2 Traps**
  - ➢ Quantification of biodegradation processes, prognosis of ongoing processes and their duration
- **Synthesis**: Cost-benefit analysis of active measures vs. natural biodegradation including sustainability criteria

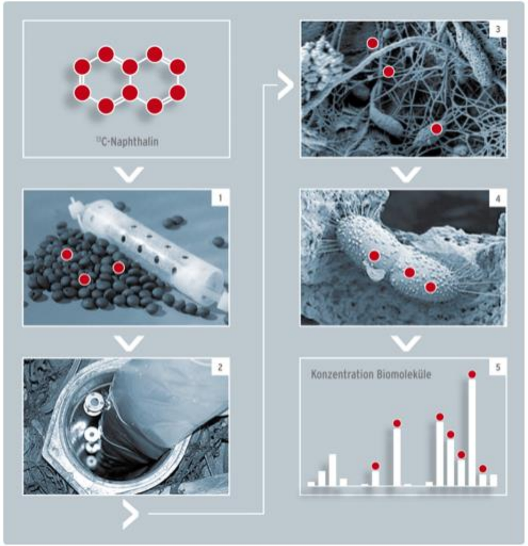
BACTRAPs – Technical Background

Sensitive and direct proof of biodegradation capability within a contaminant plume with *in situ* microcosms

- Direct monitoring of *in situ* biodegradation in a groundwater system by using microcosms (BACTRAPs) that are loaded with a isotopically (^{13}C)-labelled contaminant

- After recovery, incorporation of ^{13}C into the biomolecules of microorganisms will demonstrate that contaminant degradation can take place within the contaminant plume

- Application over a period of 2-4 months

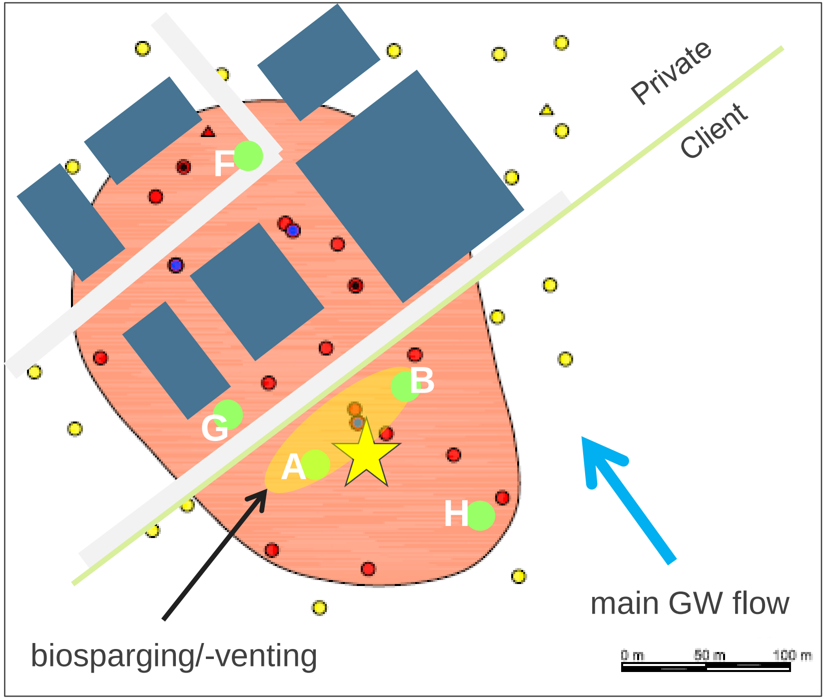


Processing steps of a BACTRAP examination. 1) The isotopically labeled contaminant (e.g., naphthalene) is adsorbed onto a carrier material, 2) exposed to groundwater well in the contaminant plume for 2-4 months (with packers if necessary), 3) colonized by microorganisms which 4) degrade and assimilate the isotope-labeled contaminant. After removal, certain biomolecules (fatty acids, amino acids) are extracted and 5) their concentrations and isotopic signatures are determined.

Source: Isodetect GmbH

BACTRAPs - Application

- m-Xylene (one of the main constituents of concern) as labelled substance
- Two campaigns in 2015 and 2016, 5 months each
- Application in total 5 new and existing wells
  - Area under treatment (biosparging/-venting)
  - Untreated area

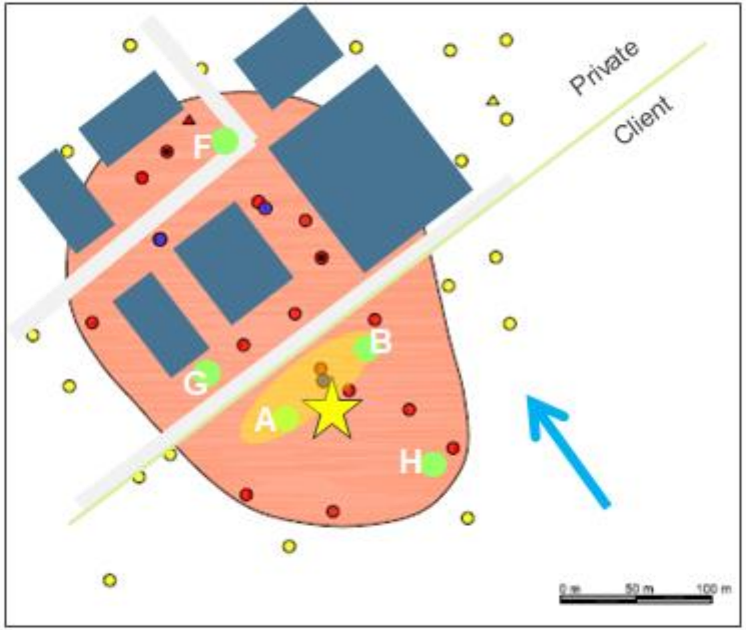


BACTRAPs - Results

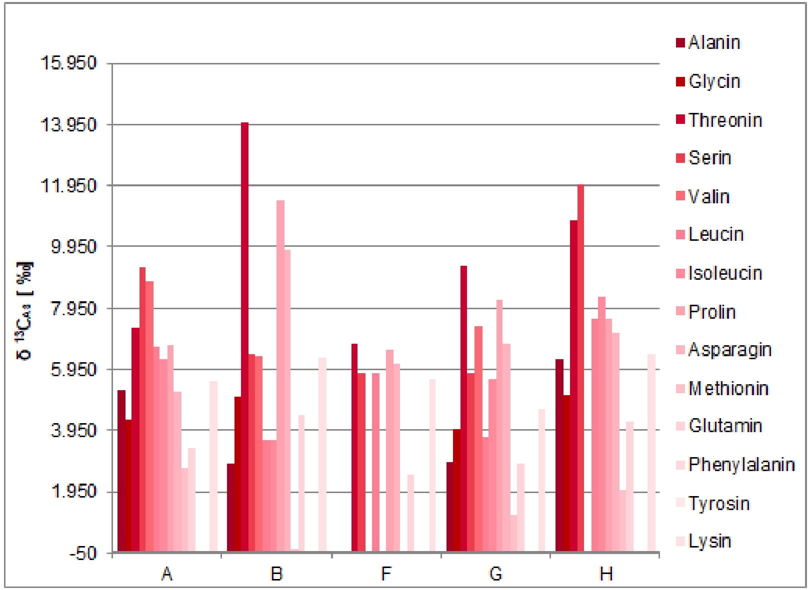
	A	B	F	G	H
Year	2016	2016	2016	2016	2016
Alanin	817	185	7	93	131
Glycin	703	212	16	83	124
Threonin	649	264	27	112	163
Serin	501	197	30	82	107
Valin	339	143	13	66	87
Leucin	250	107	28	69	76
Isoleucin	88	45	8	33	36
Prolin	381	150	36	73	93
Asparagin	1.263	631	116	307	355
Methionin	43	16	n.d.	6	13
Glutamin	962	532	105	221	313
Phenylalanin	n.d.	n.d.	n.d.	n.d.	n.d.
Tyrosin	n.d.	n.d.	n.d.	2	n.d.
Lysin	565	332	76	103	199
Total Biomass	**6.560**	**2.813**	**462**	**1.249**	**1.699**

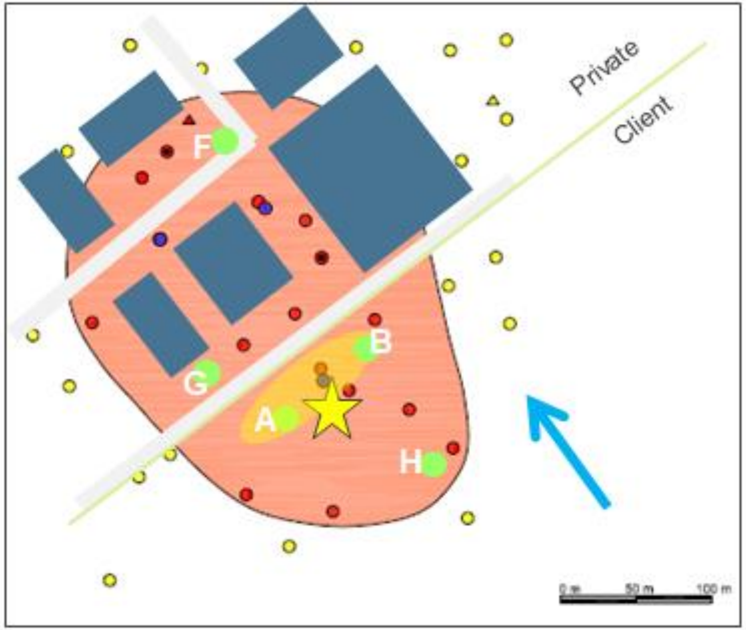
µg AS/bactrap

n.d. = not detected



BACTRAPs - Results





The environment is able to degrade m-Xylene in all areas of the site, regardless if NA is enhanced or not. However, microbiological activity seems higher in the stimulated area.

CO_2 Traps – Technical Background

CO_2 is end product of all biodegradation

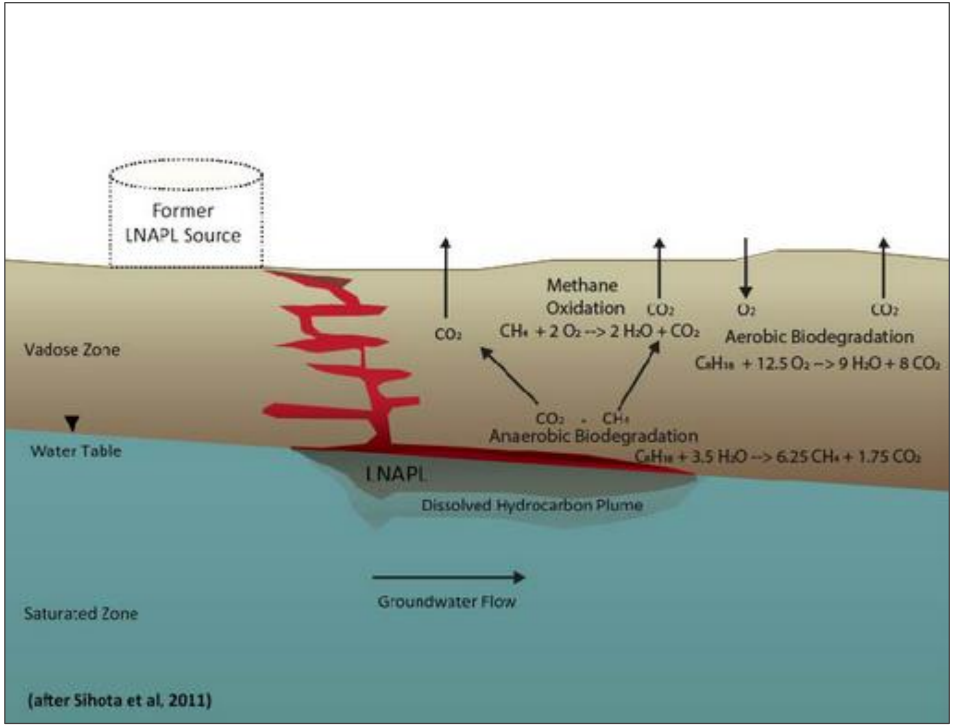
Anaerobic Degradation (Methanogenesis):

C_8H_{18} + 3.5 H_2O -> 6.25 CH_4 + 1.75 CO_2

Aerobic degradation:

C_8H_{18} + 12.5 O_2 -> 9 H2O + 8 CO_2

CH_4 + 2 O_2 -> 2 H_2O + CO_2



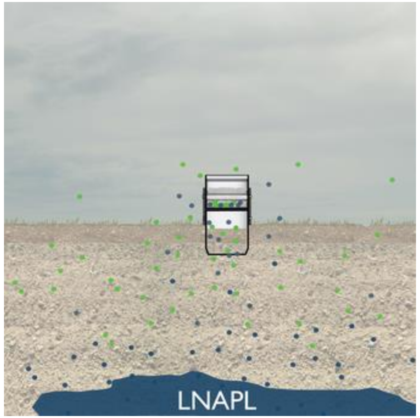
(after Sihota et al, 2011)

CO_2 Traps – Technical Background

Installation method:

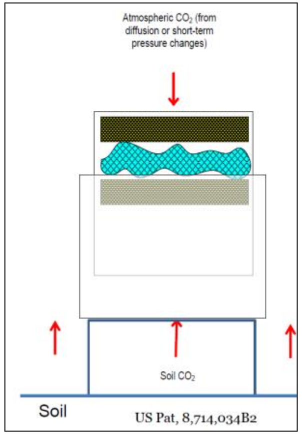
a) Installation of CO_2 traps by simple direct push (example)

b) Absorption of atmospheric and soil CO_2 in two different absorbent elements (Sodasorb®) over a period of approximately 2-4 weeks

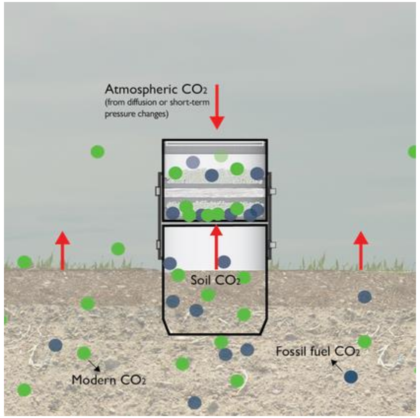


Absorption is the reaction of CO_2 with soda lime:

$$CO_{2(g)} + Ca(OH)_{2(s)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$



Source: E-Flux, LLC



CO_2 Traps – Technical Background

Lab procedure:

a) Calculation of CO_2 production in LNAPL area
- Weighing of absorbed CO_2
- Calculation of total CO_2 mass produced during application period

b) Calculation of CO_2 production outside LNAPL area
- Weighing of absorbed CO_2
- Calculation of total (natural) CO_2 mass produced during application period

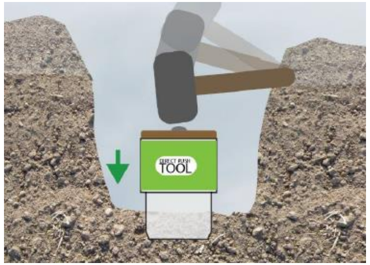
c) Analyses of carbon isotope ^{14}C
- Differentiation between fossil und recent carbon C*
- Calculation of natural and LNAPL induced CO_2 production

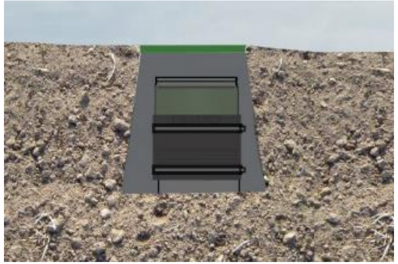
d) Synthesis
- Calculation of CO_2 as produced by LNAPL biodegradation
- Calculation of degradation rates

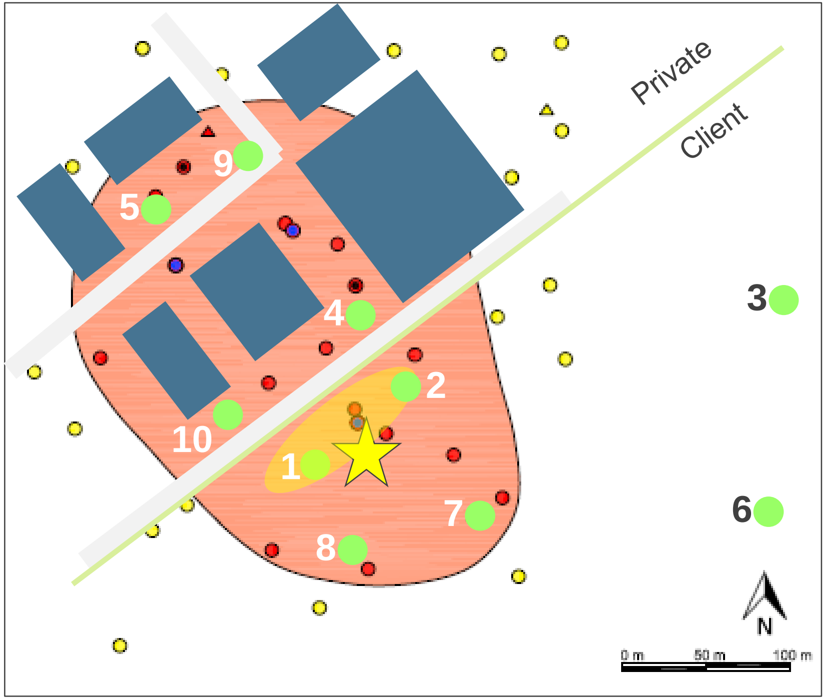
* Fossil Carbon: Mineral Oil
Recent Carbon: Younger organic material

CO_2 Traps - Application

- Two campaigns in winter 2015 and summer 2016, 2 weeks each
- Application at 10 locations, 2 thereof background
- Subsurface installations to prevent manipulation by third parties



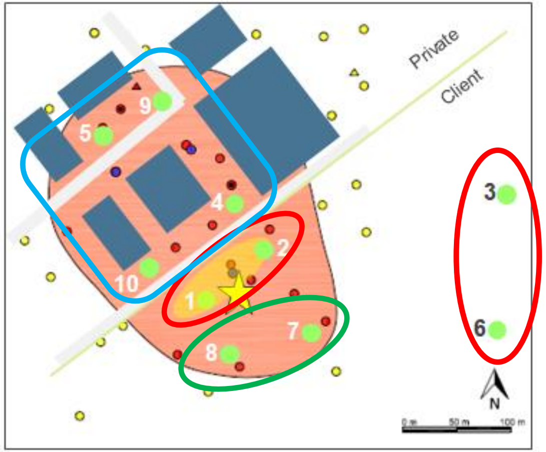




CO_2 Traps - Results

Sample ID	Deployment Dates					Raw Results (not blank corrected)				
	Deployment Period 1		Deployment Period 2		Total Days	Moisture	Dry Sorbent Mass (g)	Number of Replicates	Avg CO_2[b]	CV CO_2[c]
	Deployed	Retrieved	Deployed	Retrieved						
SHGER-R2-CO2-TB	NA	NA	NA	NA	0.00	13.9%	44.402	2	1.00%	1.95%
SHGER-R2-CO2-01	8/24/16 9:55	8/28/16 13:21	8/30/16 9:10	9/2/16 8:20	7.11	11.7%	46.227	2	4.14%	0.87%
SHGER-R2-CO2-02	8/24/16 10:13	8/28/16 12:39	8/30/16 8:05	9/2/16 8:10	7.10	17.9%	46.163	2	3.33%	2.35%
SHGER-R2-CO2-03	8/24/16 9:27	8/28/16 12:50	8/30/16 8:35	9/2/16 8:02	7.12	17.2%	45.012	2	5.44%	0.86%
SHGER-R2-CO2-04	8/24/16 10:31	8/28/16 13:13	8/30/16 8:43	9/2/16 8:31	7.10	17.6%	46.173	2	7.91%	2.04%
SHGER-R2-CO2-05	8/24/16 10:53	8/28/16 13:06	8/30/16 8:49	9/2/16 8:40	7.09	18.0%	45.114	2	4.12%	0.14%
SHGER-R2-CO2-06	8/24/16 11:42	8/28/16 12:57	8/30/16 8:57	9/2/16 8:52	7.05	17.9%	45.561	2	5.17%	0.88%
SHGER-R2-CO2-07	8/24/16 11:20	8/28/16 13:00	8/30/16 9:00	9/2/16 8:59	7.07	18.7%	45.023	2	4.70%	0.01%
SHGER-R2-CO2-08	8/24/16 13:15	8/28/16 12:43	8/30/16 7:56	9/2/16 7:55	6.98	16.6%	46.366	2	8.14%	1.00%
SHGER-R2-CO2-09	8/24/16 12:45	8/28/16 12:26	8/30/16 8:12	9/2/16 9:05	7.02	16.2%	46.263	2	4.51%	4.85%
SHGER-R2-CO2-10	8/24/16 13:05	8/28/16 12:35	8/30/16 8:00	9/2/16 7:50	6.97	16.5%	44.542	2	8.45%	1.60%

Sample ID	Blank Corrected Results[a] and ^{14}C Analysis (Fossil Fuel)									
	Carbon Content[d]		CO_2 Flux[e] (microM/m^2sec)	Modern Carbon, As Reported[g]	Std. Dev. Modern	Modern CO_2 Flux (microM/m^2sec)	Contemporary Fossil Fuel Carbon	Grams Of Fossil Fuel CO_2 (g)	Fossil Fuel CO_2 Flux (microM/m^2sec)	Equivalent Fossil Fuel NAPL Loss Rate (gallons/acre.yr)
	%	(g)								
SHGER-R2-CO2-TB	0.0%	-	-	66.6%	0.21%	-	36.6%	-	-	-
SHGER-R2-CO2-01	3.1%	1.45	6.61	89.8%	0.25%	6.12	14.5%	0.11	0.49	309
SHGER-R2-CO2-02	2.3%	1.07	4.91	87.5%	0.24%	4.51	16.7%	0.09	0.40	251
SHGER-R2-CO2-03	4.4%	2.00	9.11	93.4%	0.31%	8.62	11.1%	0.11	0.49	303
SHGER-R2-CO2-04	6.9%	3.19	14.57	90.7%	0.25%	13.06	13.7%	0.33	1.51	941
SHGER-R2-CO2-05	3.1%	1.41	6.44	70.1%	0.21%	4.36	33.3%	0.45	2.07	1,296
SHGER-R2-CO2-06	4.2%	1.90	8.73	92.0%	0.30%	8.15	12.4%	0.13	0.58	361
SHGER-R2-CO2-07	3.7%	1.66	7.64	61.1%	0.20%	4.33	41.8%	0.72	3.30	2,066
SHGER-R2-CO2-08	7.1%	3.31	15.40	74.8%	0.30%	11.14	28.7%	0.91	4.25	2,658
SHGER-R2-CO2-09	3.5%	1.62	7.50	73.7%	0.25%	5.41	29.8%	0.45	2.09	1,306
SHGER-R2-CO2-10	7.4%	3.32	15.43	87.6%	0.33%	13.29	16.6%	0.46	2.14	1,340



Green: High loss rate
Blue: Medium loss rate
Red: Low loss rate

Average loss rate:

~ 1 l per m² and year

Conclusions

Remedial alternative analysis (RAA) including MNA accepted by the regulator

- Residual contamination on the client’s property
  - Authority agrees, that further cost intensive unsustainable measures like excavation, hot water flushing and steam injection are not appropriate and proportional

- Monitored Natural Attenuation (MNA)
  - Is the appropriate method to further manage the contaminated area
  - Natural degradation rates are currently at 1l per m^2 and year
  - MNA to be continued to verify present results and prognosis

- Active measures to be continued as long as required, technically feasible and proportional:
  - Containment of the dissolved plume
  - Biosparging/-venting in source zone

Thank you!