Finding the Information of the Unknown DANPL Residual Source using Various Tracer Data, Wonju, Korea

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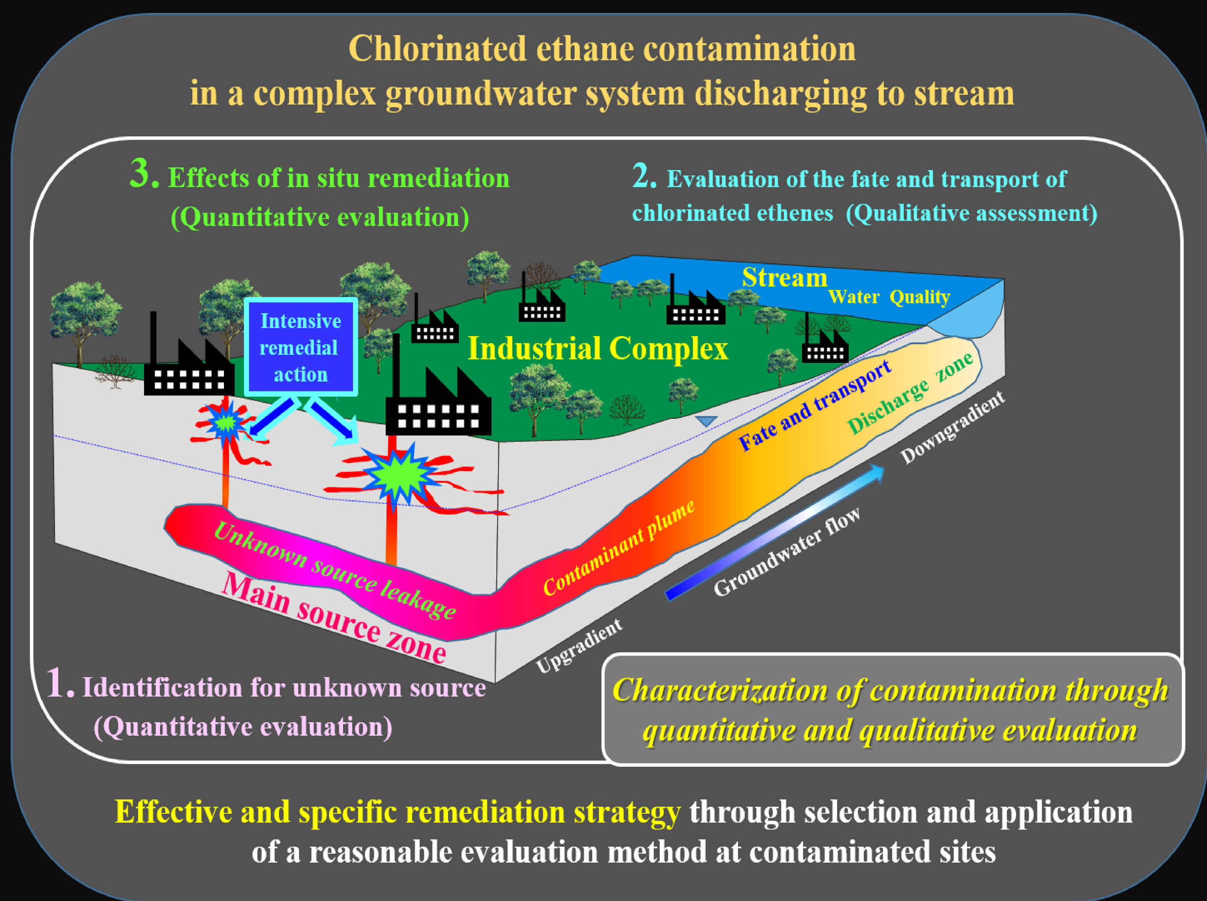
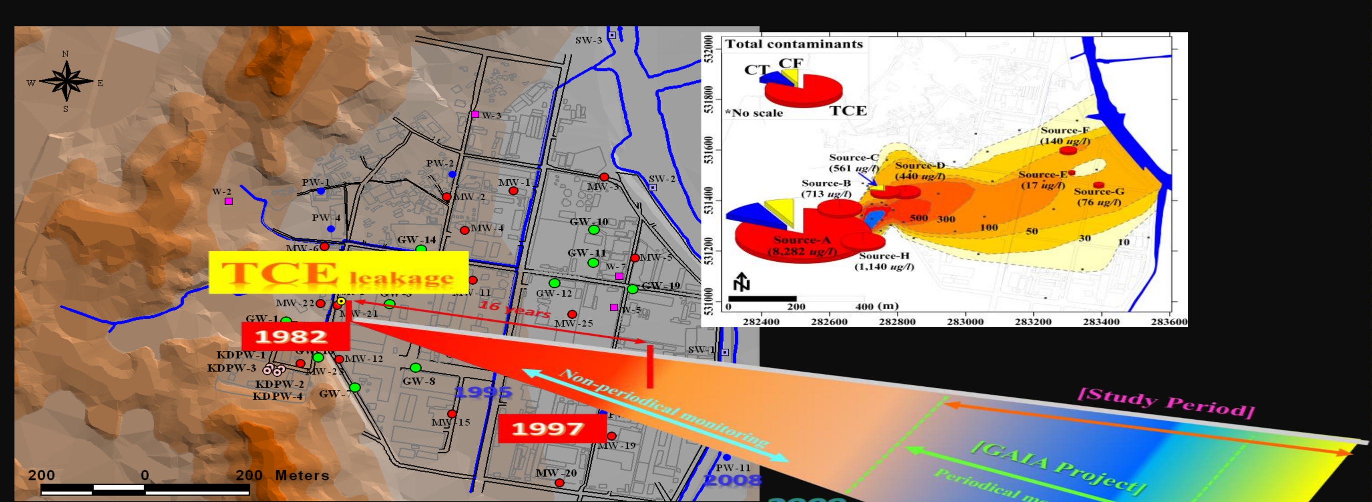


Abstract

In this study, analytical solution method which can evaluate and quantify the impacts of partial mass reduction by remedial action performed in study site is applied to estimate the unknown DNAPL source mass and dissolved concentration using long-term monitoring data collected from 2009 to 2019. Also, noble gas tracer method was applied to identify the partitioning processes which can be happened in TCE contaminated site. By using the source zone monitoring data during about 10 years and analytical solution, initial dissolved concentration and residual mass of TCE in spilled period at the main source zone were roughly estimated 150 mg/L and 1000 kg, respectively. These values decreased to 0.45 mg/L and 33.07 kg direct after an intensive remedial action performed in 2013 and then it expected to be continuously decreased to 0.29 mg/L and 25.41 kg from the end of remedial actions to 2020. From results of quantitative evaluation using analytical solution, it can be evaluated that the intensive remedial action had effectively performed with removal efficiency of 70% for the residual source mass during the remediation period. From the results of noble gas analysis, the distance from TCE source zone was divided into three groups from Zone 1 to 3. Zone 1 includes samples that are the closest from the TCE main source, and are highly partitioned to TCE compared to other zones. Zone 3 samples show least accordance with either of the fractionation lines, showing that sampling points are influenced highly by other mechanism rather than partitioning to TCE. Also, it is identified that seasonal variation of groundwater level can be affected to the distribution of noble gas at around TCE source zone. Samples from only "High TCE" zone are plotted along with ideal batch equilibrium and Rayleigh fractionation line again and divided into two groups according to their sampling date. From August 2018 to October, 2018, samples shift from right to left in the figure, getting closer to Rayleigh fractionation line. In August, noble gas was relatively in equilibrium between groundwater and TCE. However, as water table rises, noble gas became touch with residual TCE locating above the previous water-level, which is a receiving fluid in water-TCE system. Results of this study was support that it was able to estimate the unknown quantitative information for TCE contamination and noble gas as the indicator of DNAPL contamination could be applied in allocating the DNAPL source which is relatively hard to estimate.

Site description and Source history

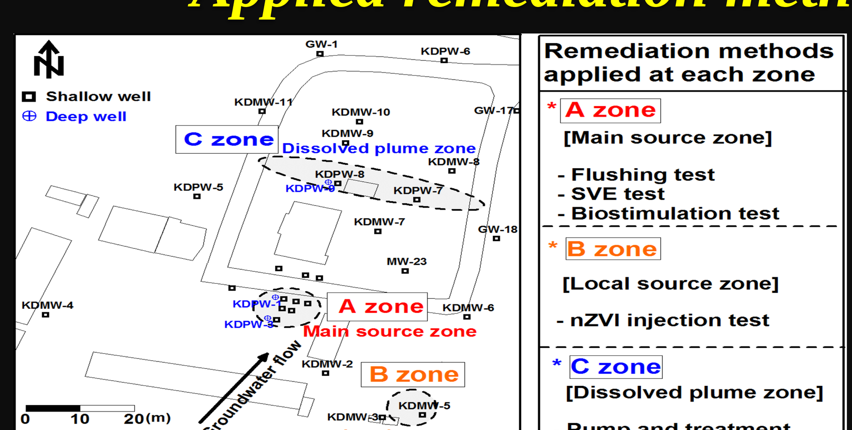
- Used for 16 year (1982 ~1997)
- Sources identified by Yang and Lee (2012)
- TCE: 8 spots / CT: 1 spot / Chloroform: 2 spots



- The existence of residual DNAPLs in the unsaturated zone (Yang et al., 2013)

: Groundwater recharge rate is low at study site ⇒ Due to a high surface pavement

Applied remediation method



- TCE at the initial study stage(2009)

: 15,748 (μg/L)

- Efficiency of remedial action

: reduced up to 2% (399 μg/L) of the concentration before the remedial action (15,748 μg/L)

Monitoring for mass discharge

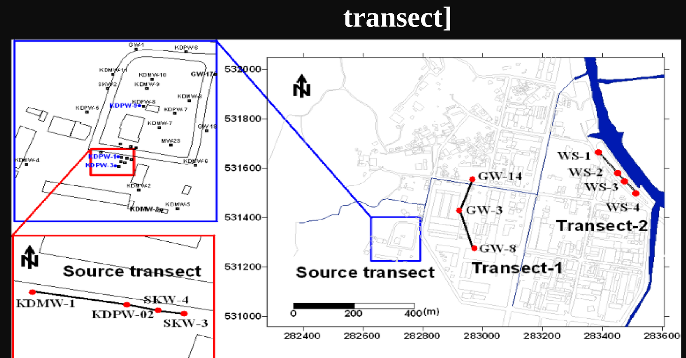
Transect line for the evaluation of mass discharge

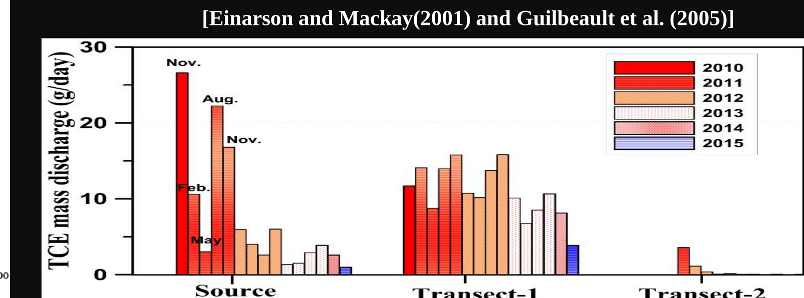
- Mass discharge calculation

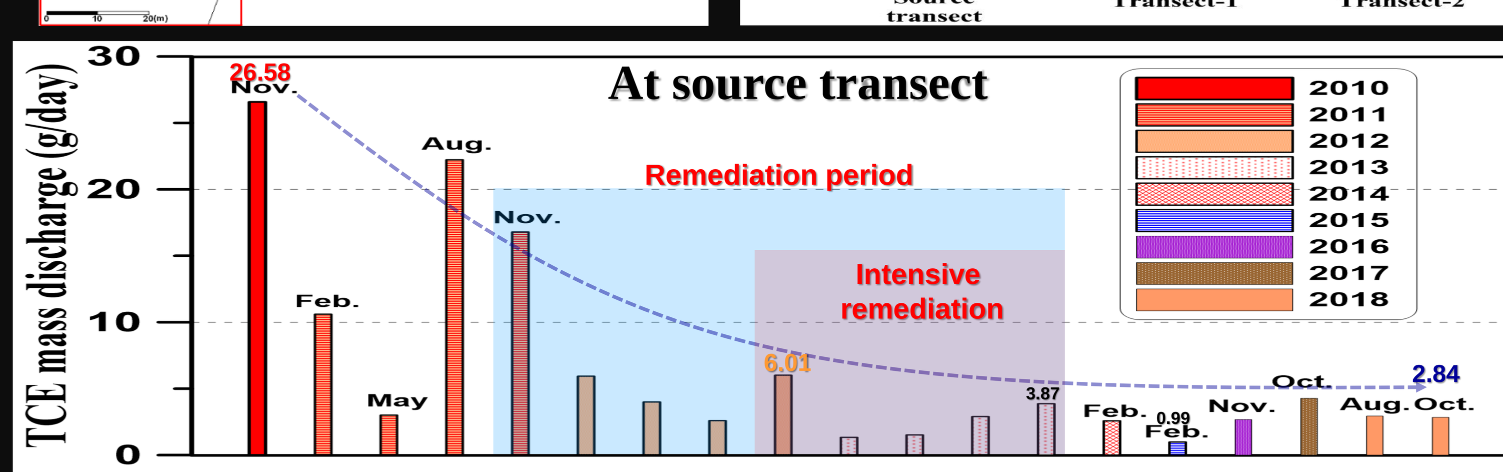
[Calculation of VOC mass discharge across each transect]

$$M_d = \sum_{i=1}^{n} C_i A_i q_i$$

[Einarson and Mackay(2001) and Guilbeault et al. (2005)]







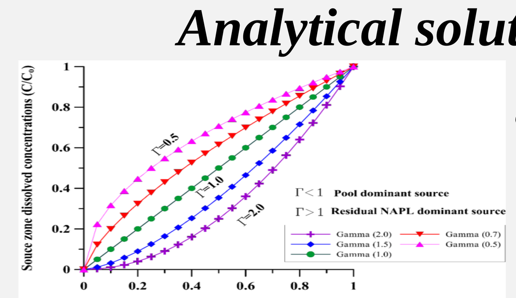
The TCE mass discharge was dramatically decreased at source zone during the intensive remediation period

- 26.58 g/day (9.7 kg/yr) at initial study stage → 2.84 g/day (about 90 % reduction compared to initial value)
- Intensive remediation period: Initial remediation stage (Nov. 2011 : 6.01 g/day) (2.2 kg/yr) ⟶ End of remediation (Nov. 2013: 3.87 g/day) (1.4 kg/yr)

Reduction rate of mass discharge by the intensive remedial action is about 64.4%

Tracing the historical TCE mass discharge and initial spilled TCE mass

Analytical solution



C_0 : Initial TCE concentration at the source zone
$C_s(t)$: Time dependent TCE concentration
M_0 : Initial source zone mass
$M(t)$: Time dependent source zone mass
Γ : Empirical parameter.

$$\frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma}$$

$$\frac{dM}{dT} = -\frac{V_d A C_0}{M_0^{\Gamma}} M^{\Gamma} - \lambda_s M \quad (\text{i.e } \lambda_s = 0)$$

No biological decay in the source zone

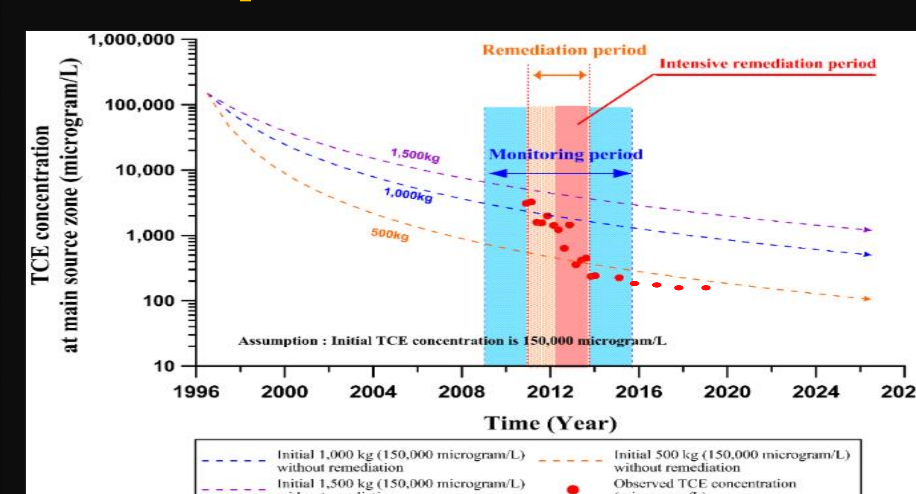
$\Gamma<1$: pool dominant source
$\Gamma>1$: residual NAPL dominant source

$$C_s(t) = \frac{C_0}{M_0^{\Gamma}} \left\{ \left(\frac{(\Gamma - 1) V_d A C_0}{M_0^{\Gamma}} \right) t + M_0^{1-\Gamma} \right\}^{\frac{\Gamma}{1-\Gamma}}$$

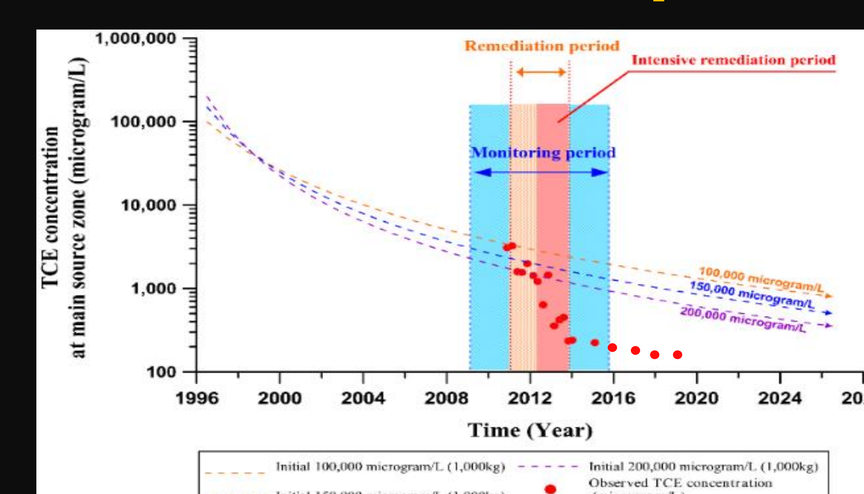
[Relationship between dissolved concentration and source mass]

<Initial spilled stage (1996)>

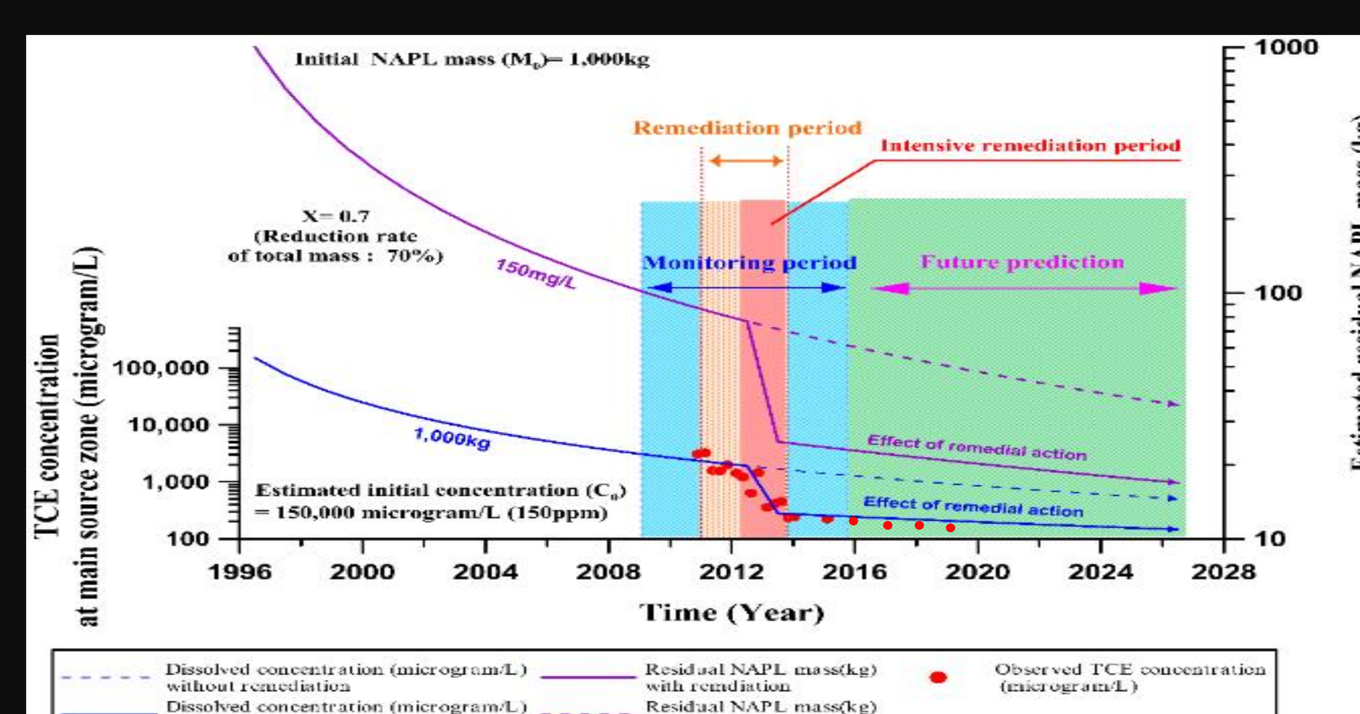
[Estimated historical TCE concentration in the main source area]



<Estimated initial NAPL mass 1,000kg>
(Max : 1,500kg, Min : 500kg)



<Estimated initial concentration 150,000μg/L>
(Max : 200,000 μg/L, Min: 100,000 μg/L)

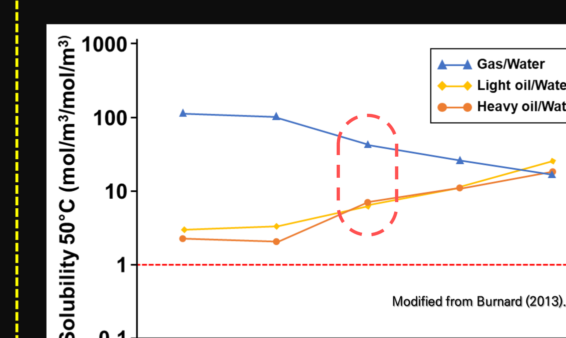


<Estimated concentration and mass of dissolved and residual TCE>

Estimation using analytical solution	Initial spilled stage (1996)	Before starting the research (2009)	Start remediation (2010)	Before the intensive remediation (2012)	After the intensive remediation (2013)	Prediction (2026)
Dissolved concentration (µg/L)	150,000 µg/L	2,875 µg/L	2,485 µg/L	1,902 µg/L	279 µg/L	146 µg/L
Dissolved concentration (µg/L)				No remediation	1,681 µg/L	502 µg/L
Residual NAPL mass (kg)	1,000 kg	97.67 kg	89.65kg	76.60 kg	22.98 kg (70%) (1)	15.25 kg (80%)(1)
Residual NAPL mass (kg)				No remediation	71.23 kg	35.00 kg (54%)(1)

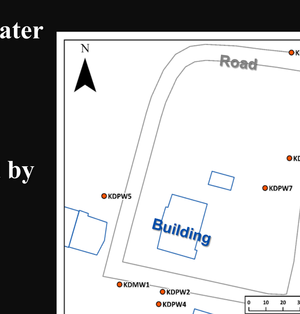
(1) Reduction rate compared to 2012

Partitioning of noble gases



- Prefer to dissolve in NAPL rather than water
- Mass dependent solubility of noble gas
- Shows effect of partitioning clearly
- Exclude Helium, which is mostly affected by radiogenic source
- Ne, Xe: Largest mass difference

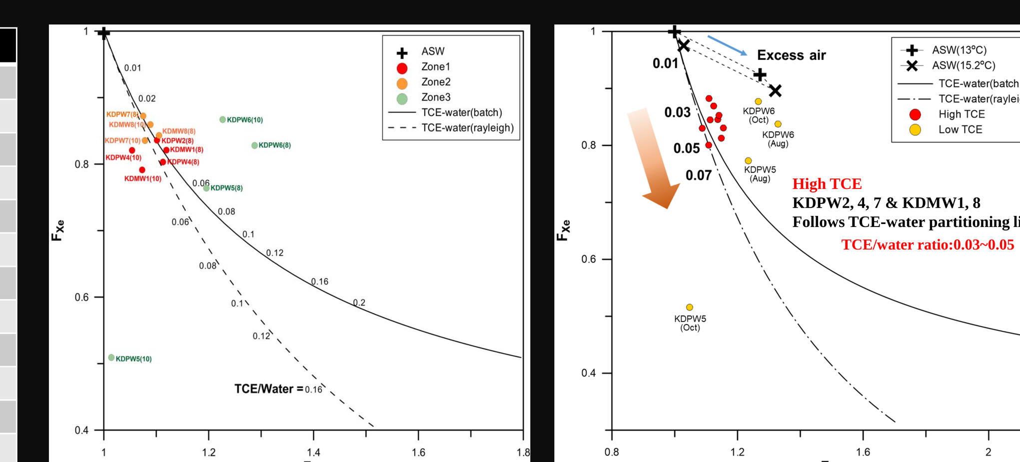
$F(i) = ([i]/[Ar])_{sample}/([i]/[Ar])_{ASW}$



Results of noble gases samples

F factors of noble gas samples

	Name	F_{Ne}	F_{Xe}
Zone 1	KDPW4(8)	1.113	0.805
	KDPW2(8)	1.101	0.838
	KDMW1(8)	1.119	0.823
	KDPW4(10)	1.054	0.822
	KDMW1(10)	1.073	0.793
Zone 2	KDPW7(8)	1.075	0.874
	KDMW8(8)	1.105	0.845
	KDPW7(10)	1.079	0.837
	KDPW8(10)	1.089	0.861
Zone 3	KDPW5(8)	1.196	0.766
	KDPW6(8)	1.288	0.830
	KDPW5(10)	1.014	0.511
	KDPW6(10)	1.227	0.869

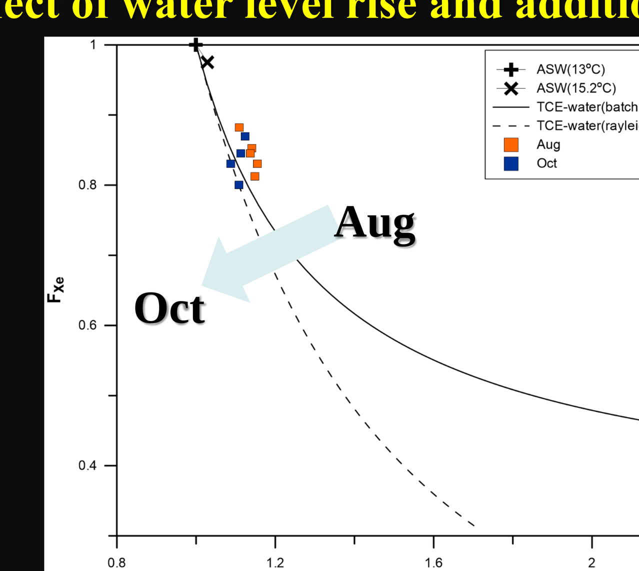


Fractionation of the F_{Ne} and F_{Xe} ratios in groundwater

From the distance from TCE source zone ▶ 3 groups from Zone 1 to 3

- Zone 1 : the closest samples from the TCE main source, and are highly partitioned to TCE.
- Zone 2 : relatively less TCE/water ratio than Zone 1 samples
- Zone 3 : least accordance with either of the fractionation lines showing they are influenced highly by other mechanism rather than partitioning to TCE.

[Effect of water level rise and addition of residual TCE]



- Aug (2018.08)
  - Low water level
  - Low TCE concentration
  - Follows batch equilibrium line
- Oct (2018.10)
  - High water level
  - High TCE concentration
  - Follows rayleigh fractionation line

⇒ Equilibrium is lost due to contact with residual TCE in lower unsaturated zone

- Mass discharge at main source zone was dramatically decreased to about 10 % of before the remedial action (avg : 26.58 g/day) by the intensive remedial action.
- Results considering the partial source mass depletion. (Assumption: fraction (X) is 0.7): initial dissolved TCE source concentration (150,000 µg/L) and source mass (1,000 kg)
- The TCE concentration and residual mass at the main source zone were decreased up to 1% and 3% of the initial spilled stage (150,000 µg/L and 1000 kg).
- The intensive remedial action had effectively performed with the removal efficiency of 70% for the residual source mass during the remediation period and, at 2026, residual NAPL mass decreased up to 80% compared to 2012.
- Noble gas tracer effectively reflect changes of TCE/water partitioning ratio in TCE contaminated groundwater system
- Noble gas tracers enable calculating the volume ratio of TCE relative to groundwater existing in the system (TCE/Water=0.03~0.05). ▶ effective method in allocating and quantifying TCE contamination
- As results of remedial actions performed at this study site, it is considered that the high level of TCE at the main source zone is effectively remediated.

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