Apply THMC software to simulate the porosity reduction in a permeable reactive barrier-aquifer system

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2 Methodology

3 Results and discussion

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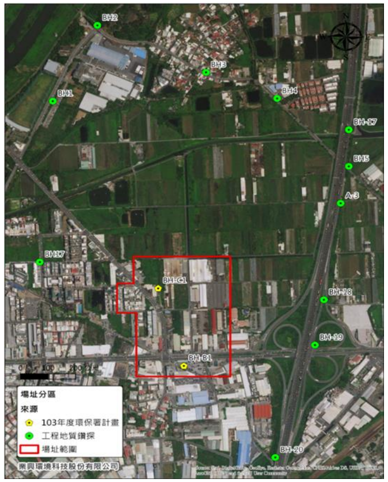
INTRODUCTION

Motivation

Evolution of contaminated sites

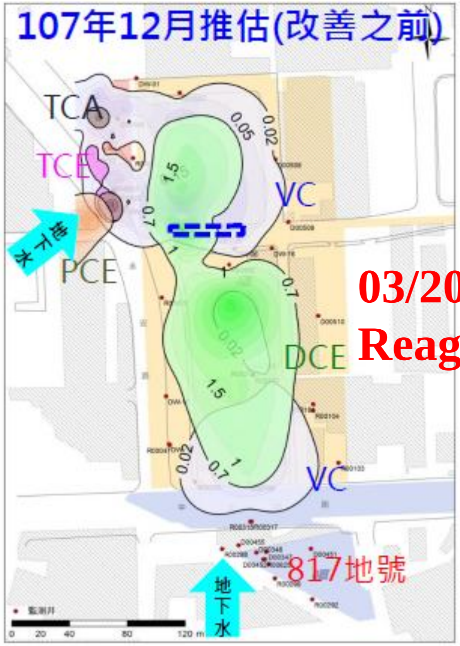
Yongkang site



The concentrations of DCE and VC at this site have decreased significantly.

DCE and VC concentrations increased.

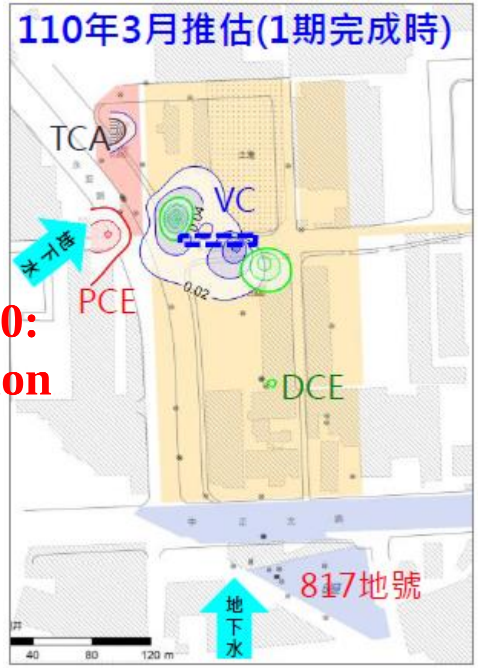
Before remediation



12/2018

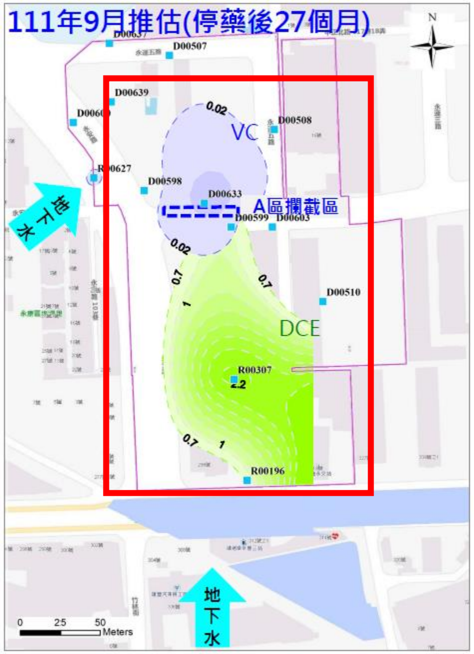
03/2019-06/2020: Reagent injection

After remediation



03/2021

After two years of remediation



09/2022

Permeable reactive barrier (PRB)

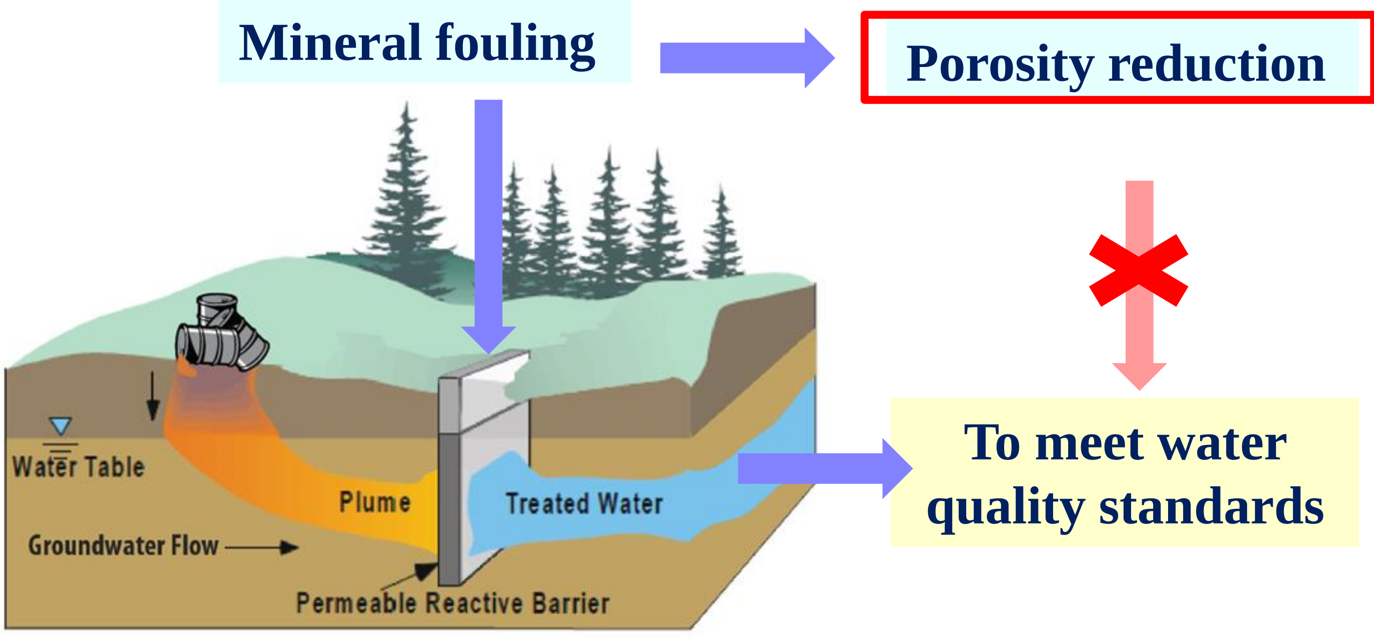
What is the long-term effectiveness of PRBs?

Reactive materials:

- **Zero-valent iron (ZVI)**
- Activated alumina
- Activated carbon
- Pea gravel
- Limestone

Advantages:

- No external power
- No ground space
- Low operation cost
- Longevity (30 years)



Mineral fouling

Porosity reduction

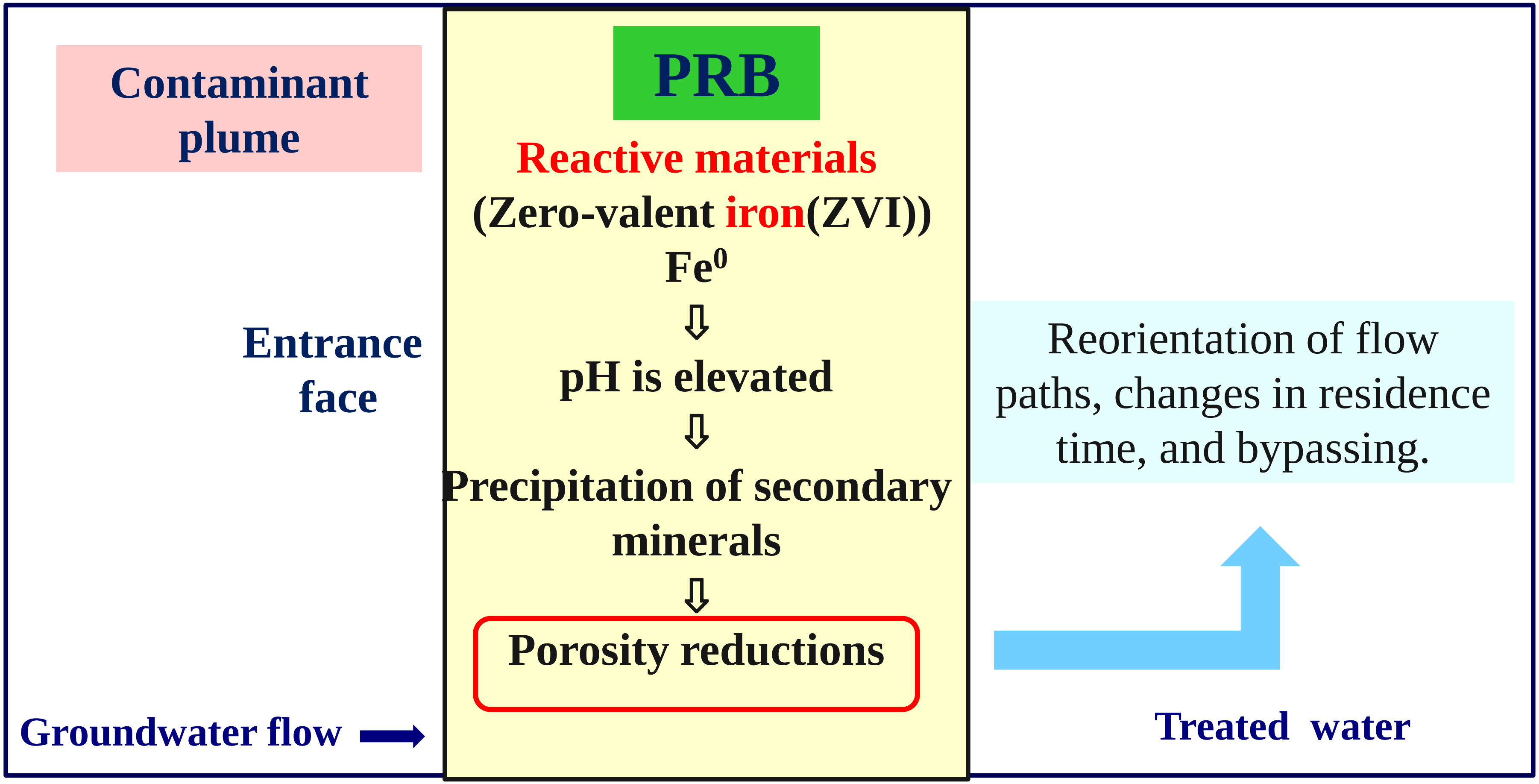
To meet water quality standards

Permeable reactive barrier (PRB)

Why does porosity reduce, and how does it affect PRB?

Literature Reviews

Porosity reduction ranges from 0.0007 to 0.03 per year and depends on in situ geochemistry and flow conditions (Li et al., 2006).



Contaminant plume

Entrance face

Groundwater flow →

PRB

Reactive materials

(Zero-valent iron(ZVI))

Fe^0

⇩

pH is elevated

⇩

Precipitation of secondary minerals

⇩

Porosity reductions

Reorientation of flow paths, changes in residence time, and bypassing.

Treated water

Objective

Apply **THMC** software to simulate the porosity reduction in a permeable reactive barrier aquifer system

- Evaluate the effectiveness of PRB after a long time.
- To identify the most significant variables to consider when evaluating porosity reductions and their impact on PRB performance.
- Analyzing porosity reduction in PRB.

METHODOLOGY

1. Ground water flow model

The steady-state flow through the aquifer and PRB

$$\nabla.\left[K.(\nabla h+\frac{p}{p_0}\nabla z)\right]=0$$

K: hydraulic conductivity (L/T)
h: pressure head (L), z: potential head (L)
p: fluid density with dissolved biogeochemical concentrations (M/L^3)
p_0 : referenced fluid density at zero biogeochemical concentration (M/L^3)

2. Reactive transport model

$$\frac{\partial\theta C_i}{\partial t}+\underbrace{\boxed{\nabla(\theta C_i V_f)}}_{\text{Advection}}+\underbrace{\boxed{\nabla J_i}}_{\text{Dispersion \& diffusion}}=\underbrace{\boxed{\theta r_i}}_{\text{Reactions}}$$

C_i: concentration of the ith species (M/L^3)
V_f : fluid velocity (L/T)
r_i: production rate (M/L^3)/T)
θ : effective porosity
J_i: surface flux due to dispersion and diffusion

The porosity effect by precipitation

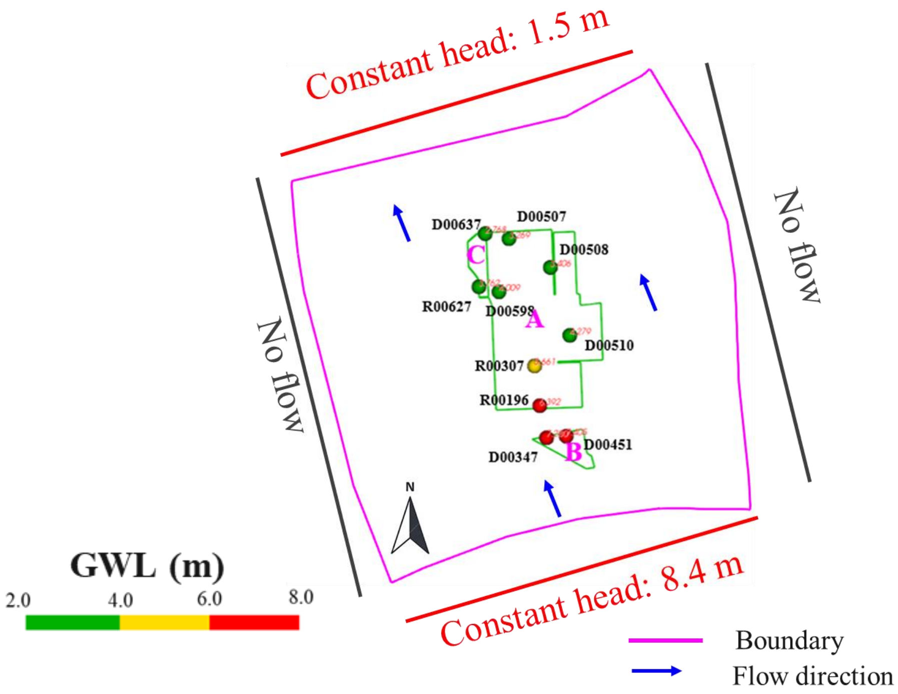
$$\theta=\frac{S_e\theta_o}{1+S_eP_iV_i}$$

The porosity reduction

$$\Delta\theta=\theta_o-\theta$$

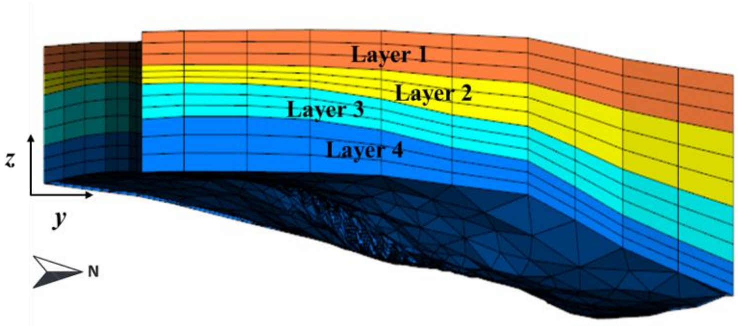
θ_o: initial porosity
S_e : effective degree of saturation of water
P_i: precipitated concentration of the ith mineral ($mole/dm^3$)
V_i : mole volume of the ith mineral (dm^3 of solid/mole)

Groundwater flow model boundary setting



Dirichlet BC

Number	Monitoring well	GWL (m)
1	D00451	7.405
2	D00347	7.280
3	R00196	6.392
4	R00307	5.661
5	D00510	4.279
6	D00598	4.009
7	R00627	3.762
8	D00508	3.406
9	D00507	3.269
10	D00637	2.768



Vertical layering of hydrogeology in this case

Hydrogeological parameters

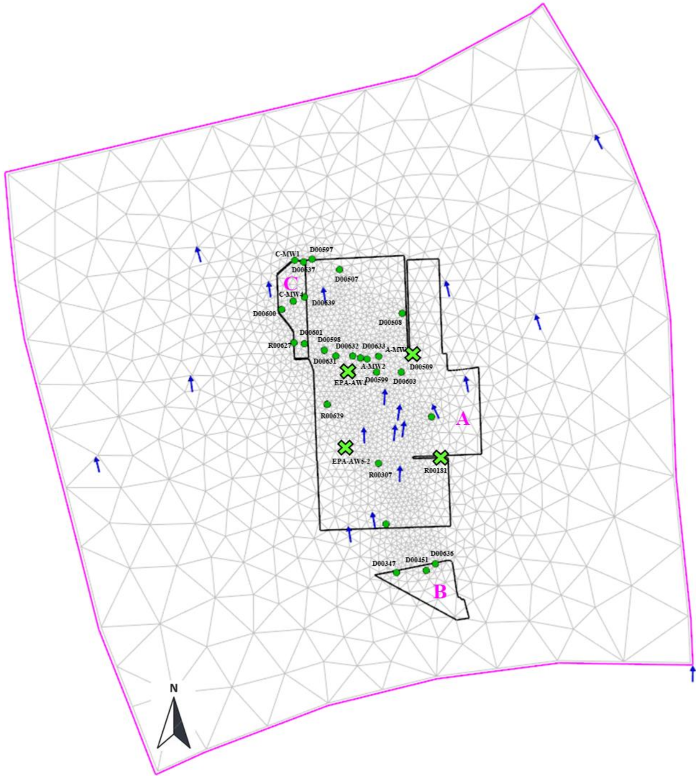
Layer	Porosity	Kxx (m/day)	Kyy (m/day)	Kzz (m/day)
1	0.25	8.64d-2	8.64d-2	8.64d-4
2	0.25	8.64d-2	8.64d-2	8.64d-4
3	0.28	8.64d-1	8.64d-1	8.64d-2
4	0.2	8.64d-6	8.64d-6	8.64d-8

Source: 107 污染場址地下環境分析模式整合發展與審查制度建置計畫

Contaminant source zone setting

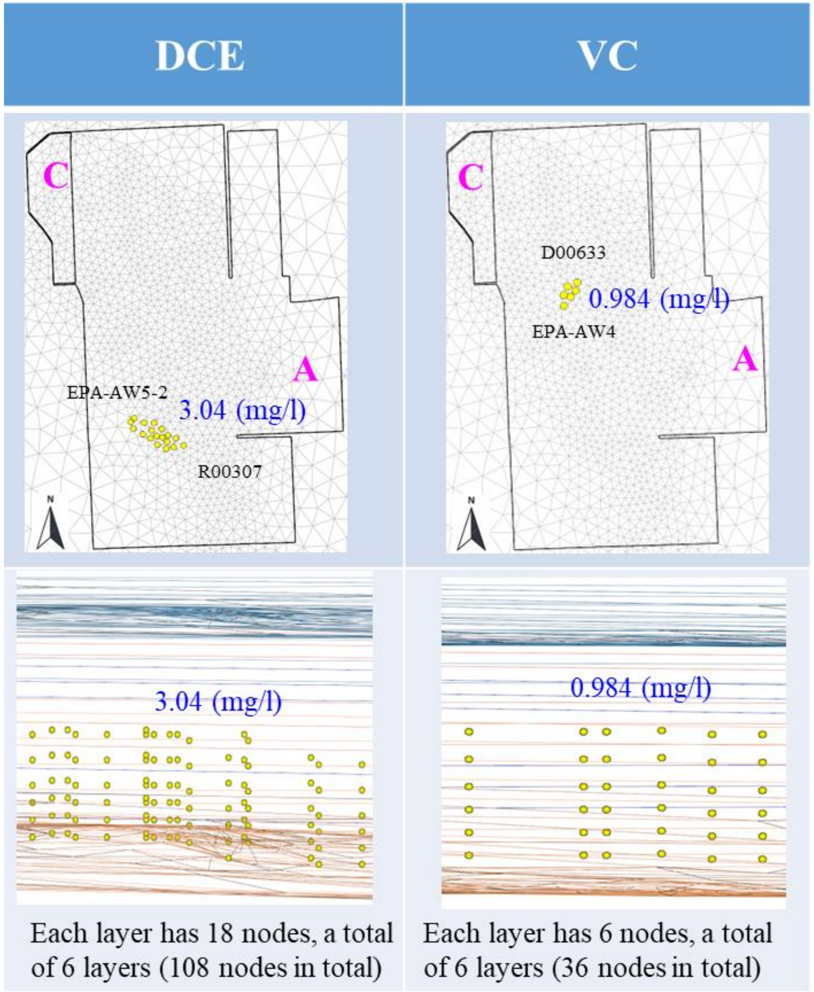
Concentrations are based on the latest data (2023/03)

Source zone depth and thickness are based on analysis of on-site monitoring data



Boundary

Flow direction



Each layer has 18 nodes, a total of 6 layers (108 nodes in total)

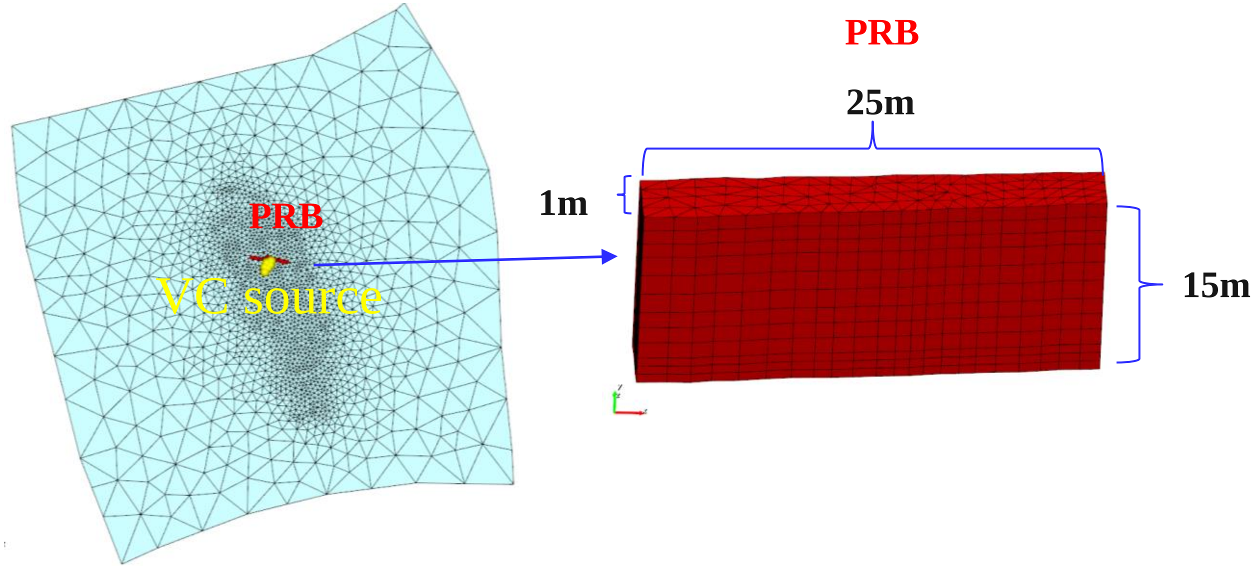
Each layer has 6 nodes, a total of 6 layers (36 nodes in total)

(Dirichlet BC)

PRB setting

PRBs containing zero-valent iron (ZVI) as the reactive medium

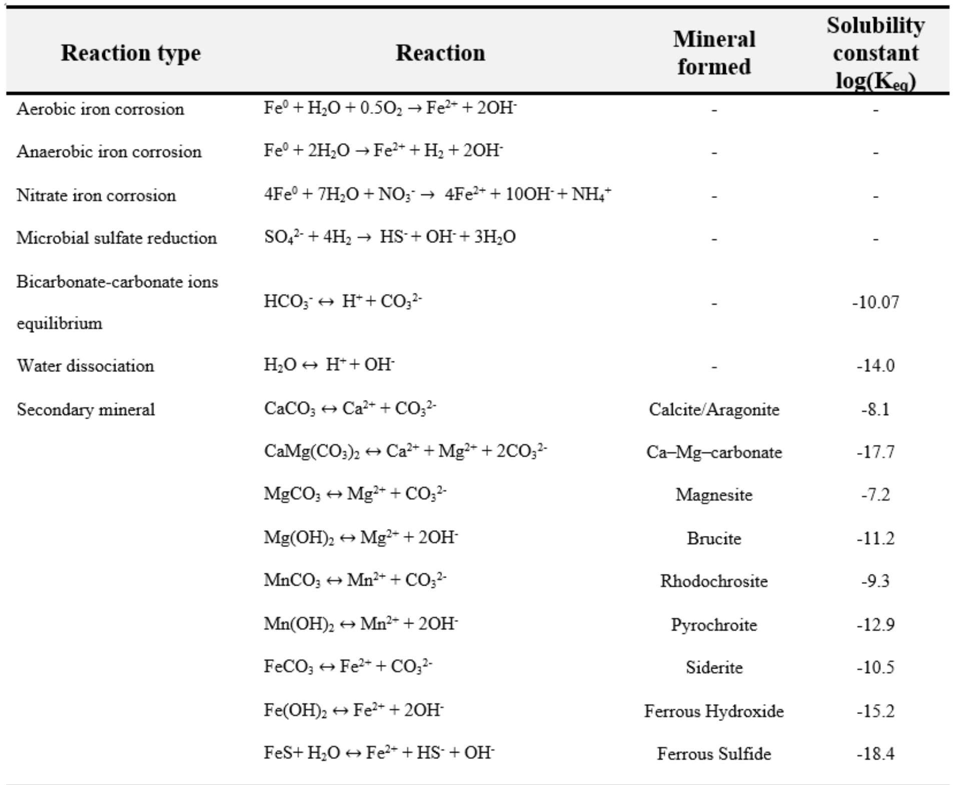
$$Fe^{0}(s)+\frac{1}{2}VC+\frac{3}{2}H^{+}\rightarrow Fe^{+2}\frac{1}{2}ETH+\frac{1}{2}Cl^{-}$$



Layer	Porosity	Kx (m/day)	Ky (m/day)	Kz (m/day)
PRB	0.6	86.4	86.4	86.4

Parameter

Geochemical reactions (Li et al., 2006)



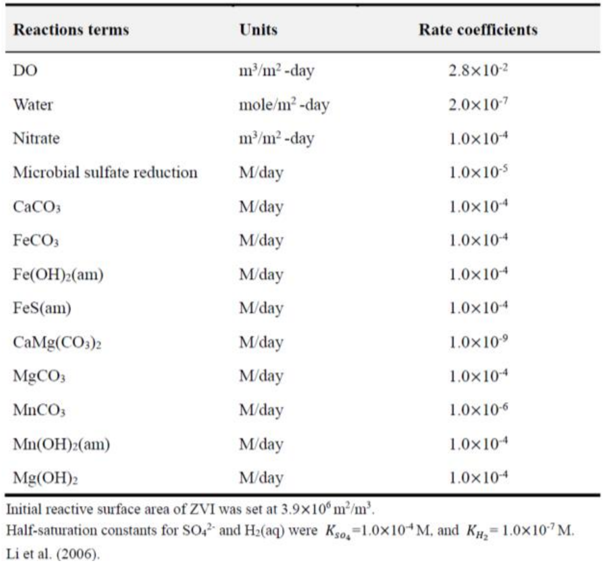
Reaction type	Reaction	Mineral formed	Solubility constant log(K_{eq})
Aerobic iron corrosion	$Fe^0 + H_2O + 0.5O_2 \rightarrow Fe^{2+} + 2OH^-$	-	-
Anaerobic iron corrosion	$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$	-	-
Nitrate iron corrosion	$4Fe^0 + 7H_2O + NO_3^- \rightarrow 4Fe^{2+} + 10OH^- + NH_4^+$	-	-
Microbial sulfate reduction	$SO_4^{2-} + 4H_2 \rightarrow HS^- + OH^- + 3H_2O$	-	-
Bicarbonate-carbonate ions equilibrium	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	-	-10.07
Water dissociation	$H_2O \leftrightarrow H^+ + OH^-$	-	-14.0
Secondary mineral	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	Calcite/Aragonite	-8.1
	$CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	Ca–Mg–carbonate	-17.7
	$MgCO_3 \leftrightarrow Mg^{2+} + CO_3^{2-}$	Magnesite	-7.2
	$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$	Brucite	-11.2
	$MnCO_3 \leftrightarrow Mn^{2+} + CO_3^{2-}$	Rhodochrosite	-9.3
	$Mn(OH)_2 \leftrightarrow Mn^{2+} + 2OH^-$	Pyrochroite	-12.9
	$FeCO_3 \leftrightarrow Fe^{2+} + CO_3^{2-}$	Siderite	-10.5
	$Fe(OH)_2 \leftrightarrow Fe^{2+} + 2OH^-$	Ferrous Hydroxide	-15.2
	$FeS + H_2O \leftrightarrow Fe^{2+} + HS^- + OH^-$	Ferrous Sulfide	-18.4

Initial concentrations of species in groundwater

Aqueous species in influent groundwater	Aqueous species concentrations (M)
Fe^{2+}	1.0×10^{-10}
Ca^{2+}	1.0×10^{-3}
Mg^{2+}	1.0×10^{-3}
Mn^{2+}	1.0×10^{-7}
Fe^{2+}	1.0×10^{-7}
Alkalinity (HCO_3^-)	1.0×10^{-3}
$O_2(aq)$	1.0×10^{-10}
NO_3^-	1.0×10^{-5}
SO_4^{2-}	1.0×10^{-3}

Li et al. (2006).

Rate coefficients used in simulations



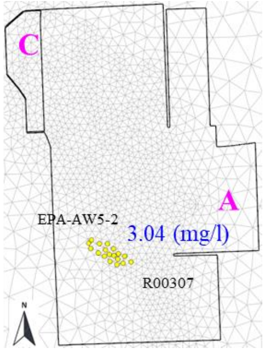
Reactions terms	Units	Rate coefficients
DO	m^3/m^2 -day	2.8×10^{-2}
Water	mole/m^2 -day	2.0×10^{-7}
Nitrate	m^3/m^2 -day	1.0×10^{-4}
Microbial sulfate reduction	M/day	1.0×10^{-5}
$CaCO_3$	M/day	1.0×10^{-4}
$FeCO_3$	M/day	1.0×10^{-4}
$Fe(OH)_2(am)$	M/day	1.0×10^{-4}
FeS(am)	M/day	1.0×10^{-4}
$CaMg(CO_3)_2$	M/day	1.0×10^{-9}
$MgCO_3$	M/day	1.0×10^{-4}
$MnCO_3$	M/day	1.0×10^{-6}
$Mn(OH)_2(am)$	M/day	1.0×10^{-4}
$Mg(OH)_2$	M/day	1.0×10^{-4}

Initial reactive surface area of ZVI was set at 3.9×10^6 m^2/m^3.
Half-saturation constants for SO_4^{2-} and $H_2(aq)$ were $K_{SO_4}=1.0\times10^{-4}$ M, and $K_{H_2}=1.0\times10^{-7}$ M.
Li et al. (2006).

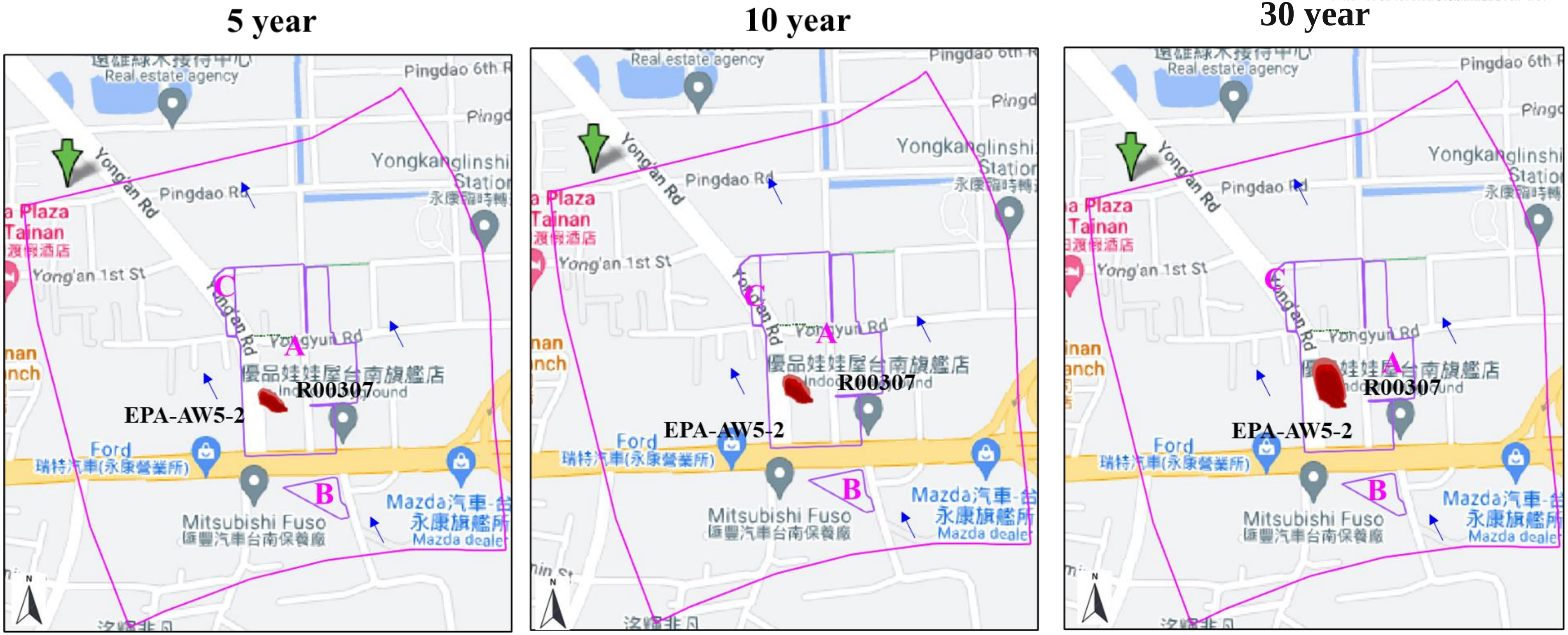
RESULTS AND DISCUSSION

1/ Contaminant source migration

DCE (plan view)

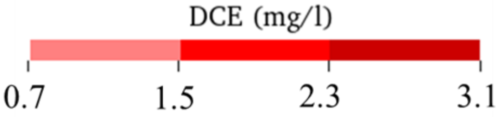


Plume source DCE will increase over time and will spread in the flow direction of the area


5 year

10 year

30 year

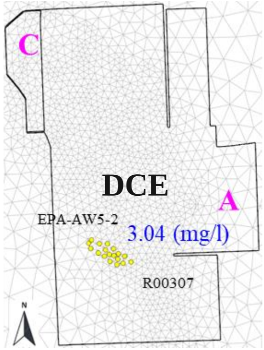


Groundwater drinking water quality standard : 0.7 mg/l

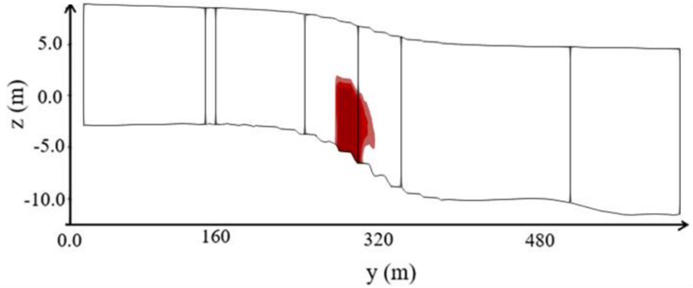
→ Flow direction

1/ Contaminant source migration

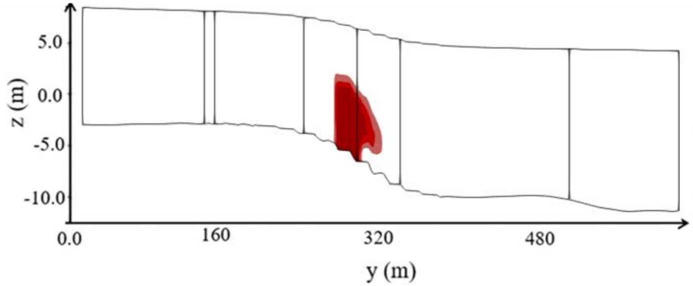
DCE (cross section view)



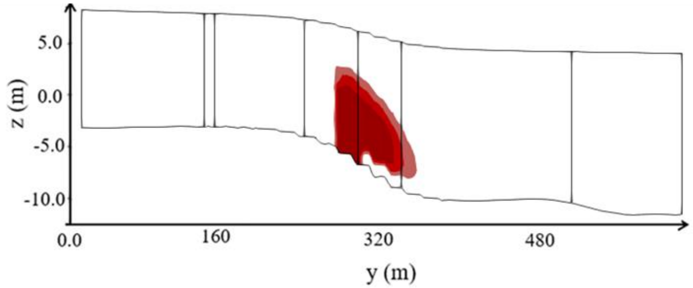
In layer 3 plume source will spread wider than the remaining layers



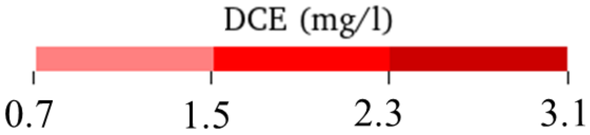
5 year



10 year



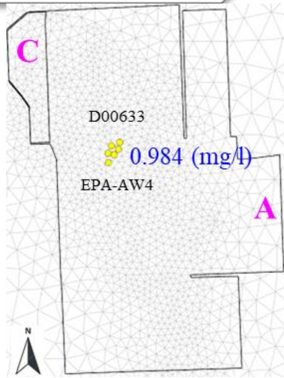
30 year



Groundwater drinking water quality standard : 0.7 mg/l

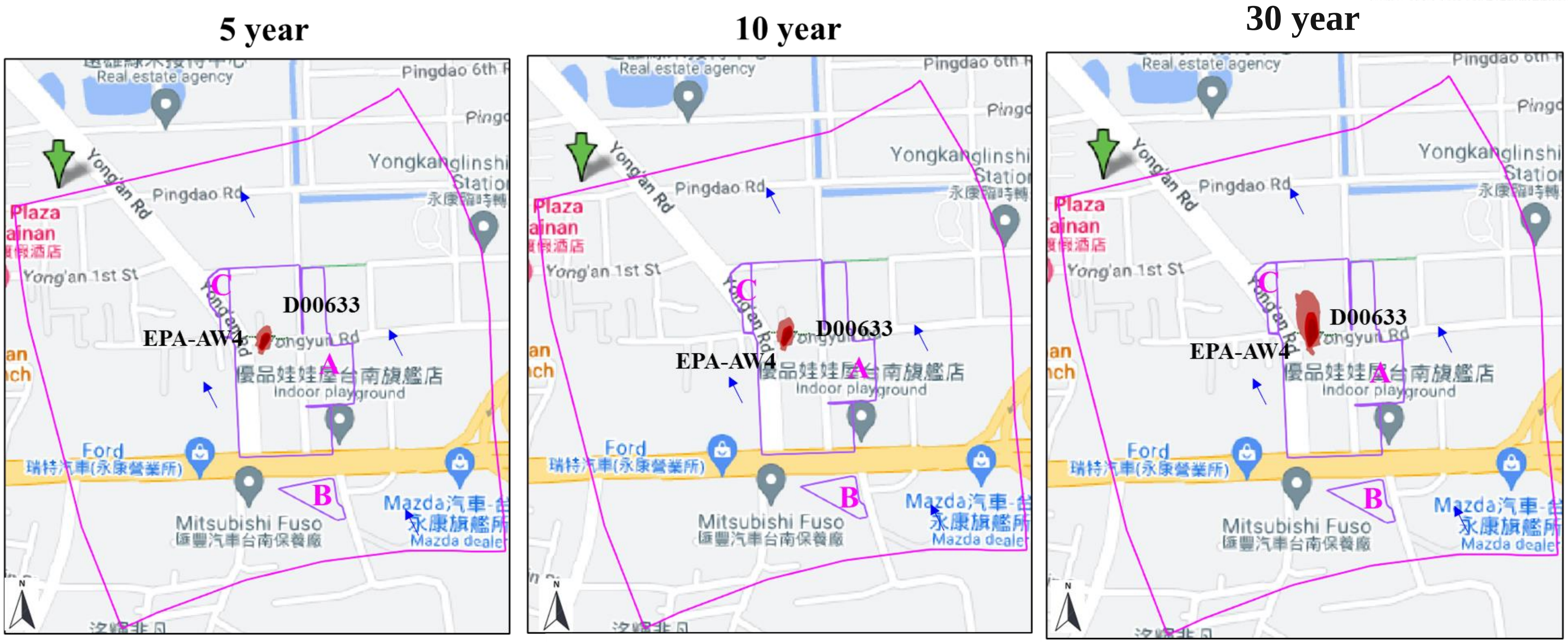
→ Flow direction

1/ Contaminant source migration

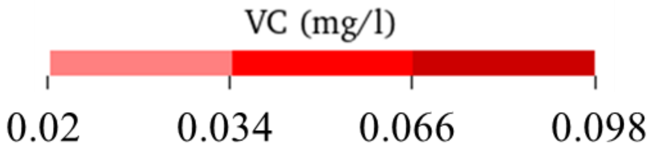


VC (plan view)

Plume source VC will increase over time and will spread in the flow direction of the area



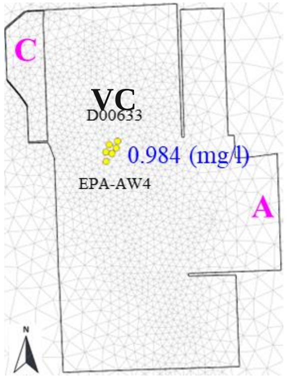
Groundwater drinking water quality standard : 0.02 mg/l



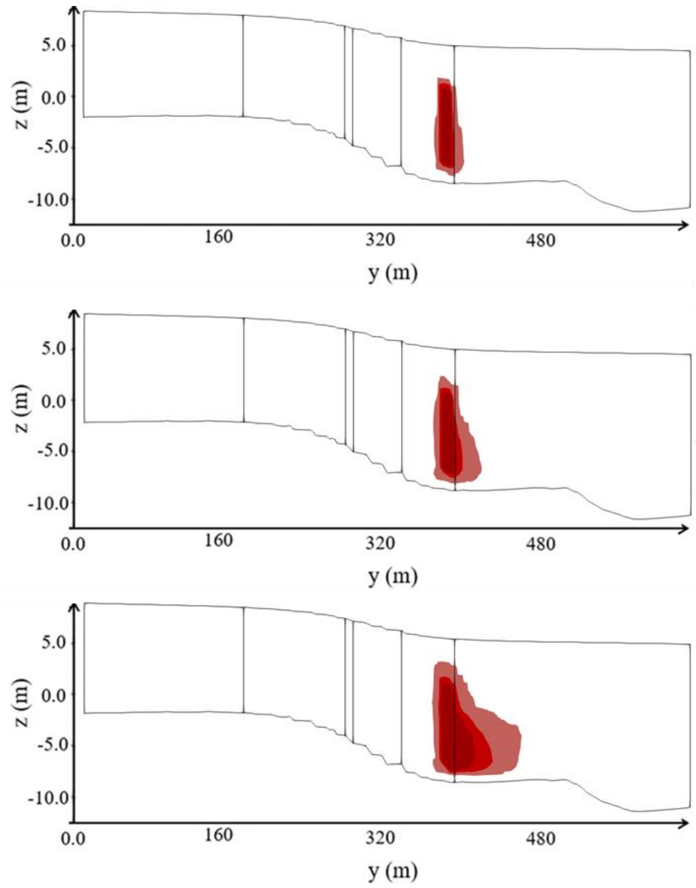
→ Flow direction

1/ Contaminant source migration

VC (cross section view)



In layer 3 plume source will spread wider than the remaining layers



5 year

10 year

30 year

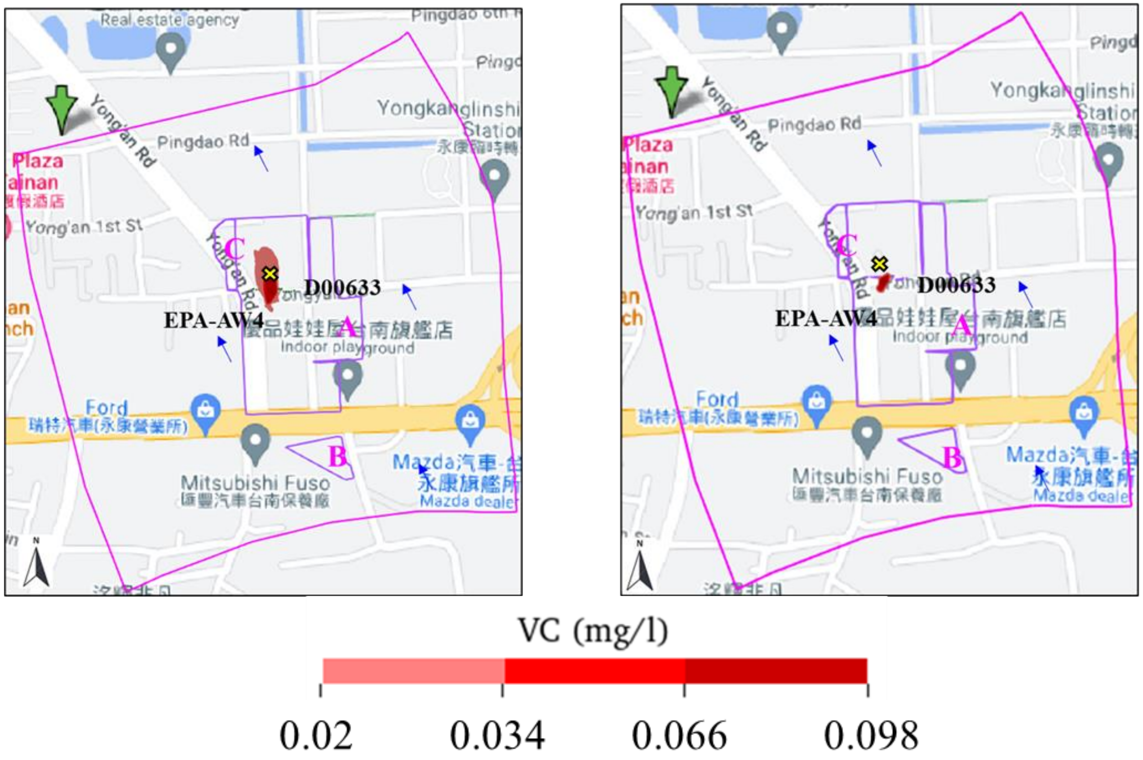
Groundwater drinking water quality standard : 0.02 mg/l

→ Flow direction

2/ Performance of PRB

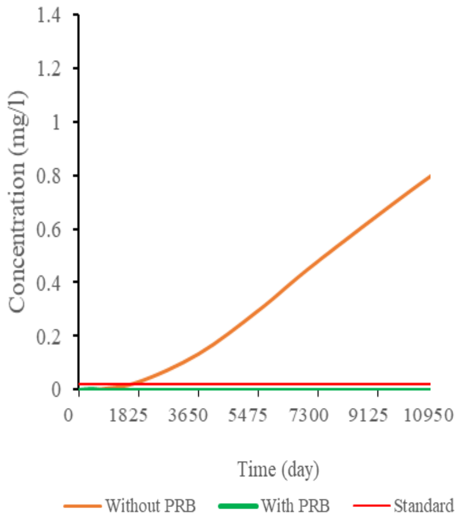
PRB has maintained great helpful efficiency throughout the last 30 years.

Without PRB **With PRB**



30 year

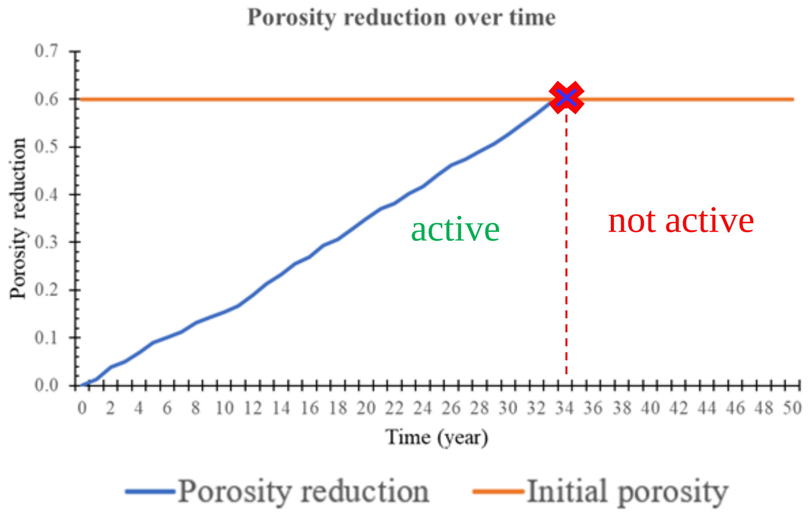
Observation well



Groundwater drinking water quality standard ：0.02 mg/l

→ Flow direction

3/ Porosity reduction over time



After 34 years, the maximum porosity reduction reaches 0.6, and significant blockage of the PRB has occurred.

34 year

35 year

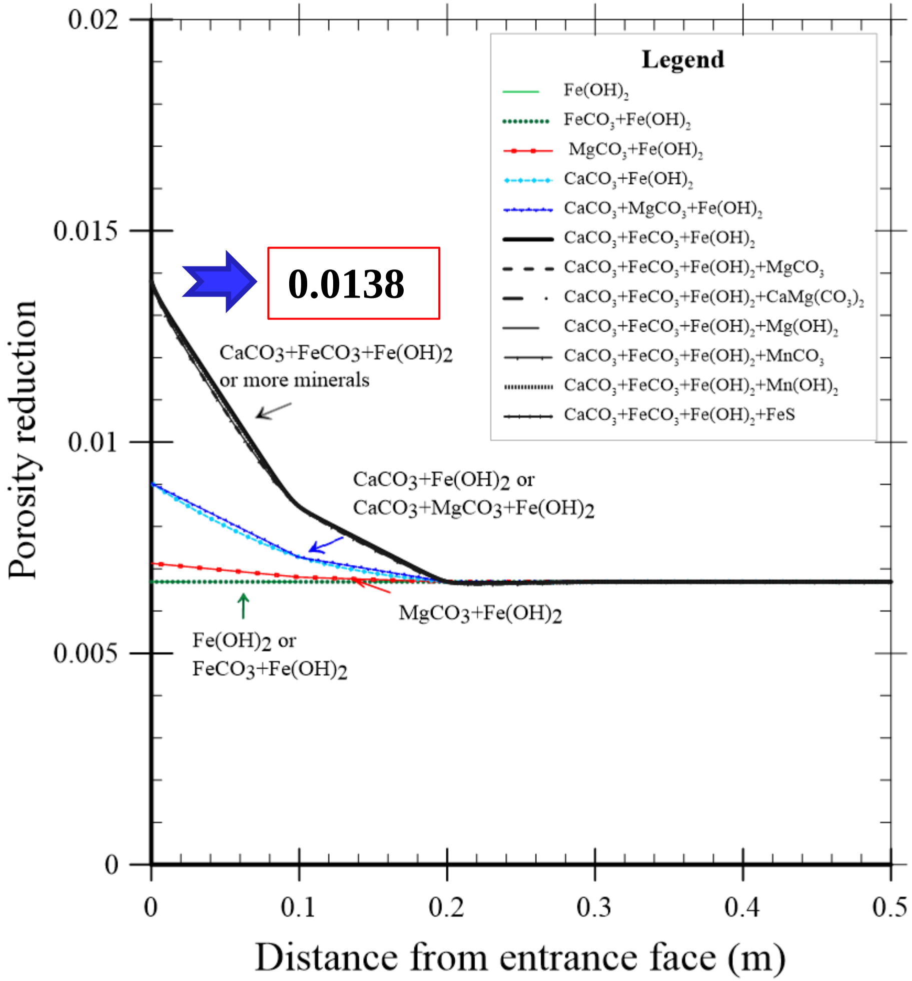
50 year

Groundwater drinking water quality standard : 0.02 mg/l

→ Flow direction

4/The effect of mineral type on porosity reduction

Porosity reduction for different combinations of minerals



$Fe(OH)_2$

⇩

$Fe(OH)_2$ + Carbonate minerals

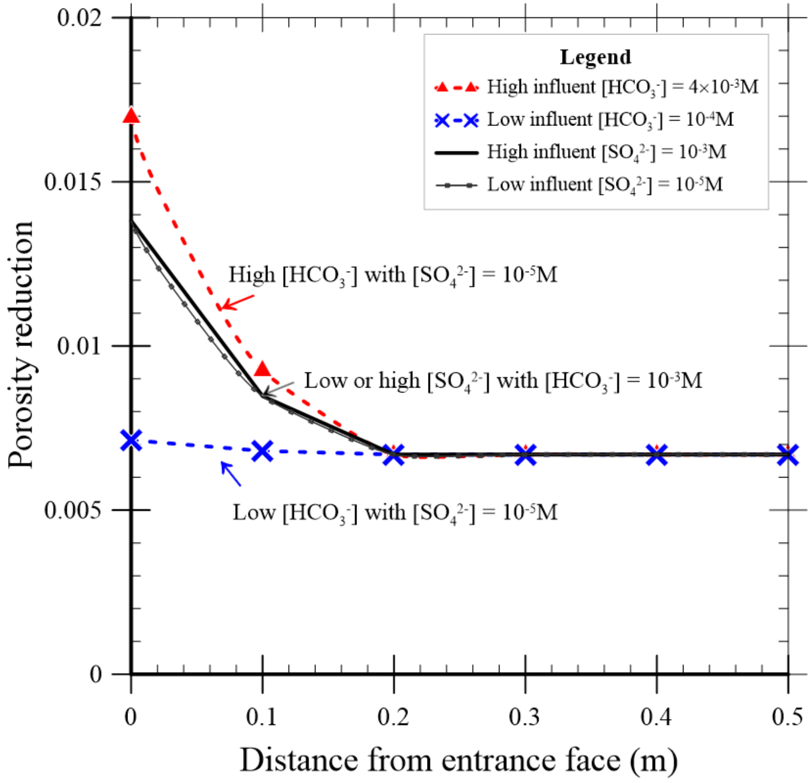
⇩

$Fe(OH)_2$ + carbonate minerals + remaining minerals (FeS, $Mg(OH)_2$, $Mn(OH)_2$)

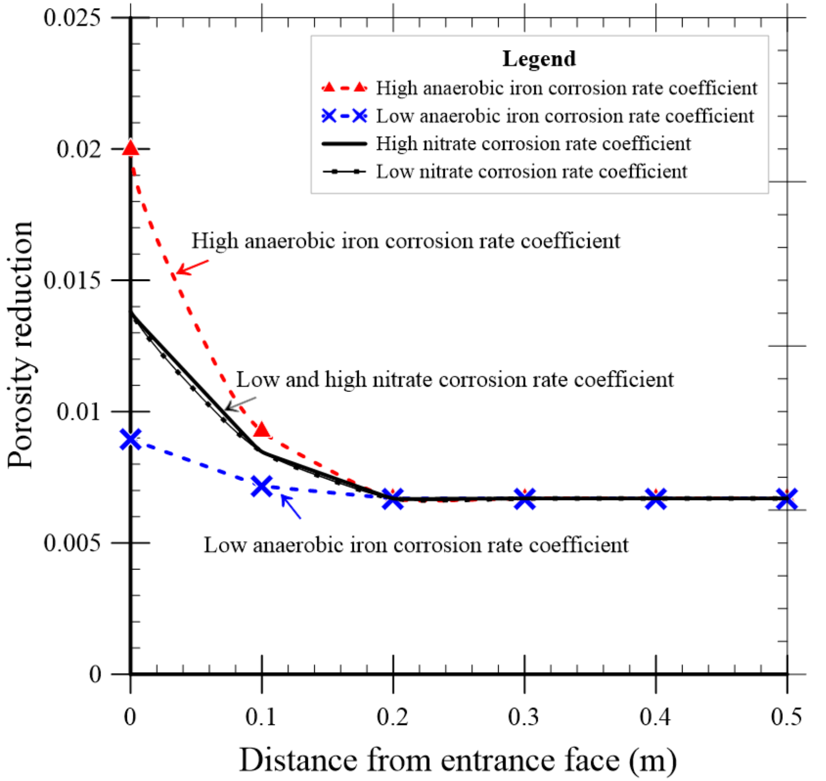
☑ **Porosity reduction** is mainly caused by three minerals: aragonite (**$CaCO_3$**), siderite (**$FeCO_3$**), **and** ferrous hydroxide **$Fe(OH)_2$.**

5/Effect of concentrations and rate coefficients

Porosity reduction for high and low concentrations of HCO_3 and SO_4^{2-}



Porosity reduction for high and low rate coefficients of anaerobic iron and nitrate iron corrosion



☑ The most significant impact on porosity reduction occurs from the concentration of bicarbonate (HCO_3^-).

☑ The anaerobic iron corrosion has the greatest impact on porosity reduction.

CONCLUSIONS

Conclusions

- The maximum porosity drop is 0.6 after 34 years, causing PRB blockage.

- The porosity reduction reaches the greatest **extent in the entrance face,** followed by a decline, and remains at the same level.

- Aragonite ($CaCO_3$), siderite ($FeCO_3$), and ferrous hydroxide $Fe(OH)_2$ are the most **important minerals** to include in the **geochemical model**.

- **Porosity reduction** is most affected by **HCO_3^-** concentrations and **the rate coefficient for anaerobic iron corrosion**.

Thank you
for your attention