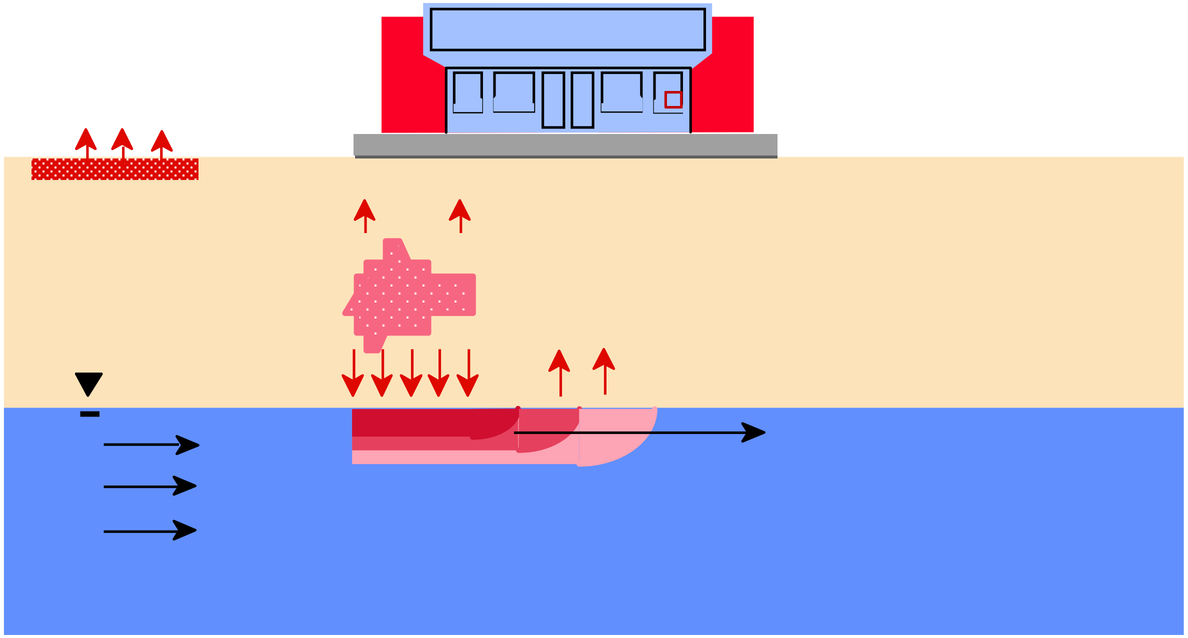
Contaminant Fate and Transport



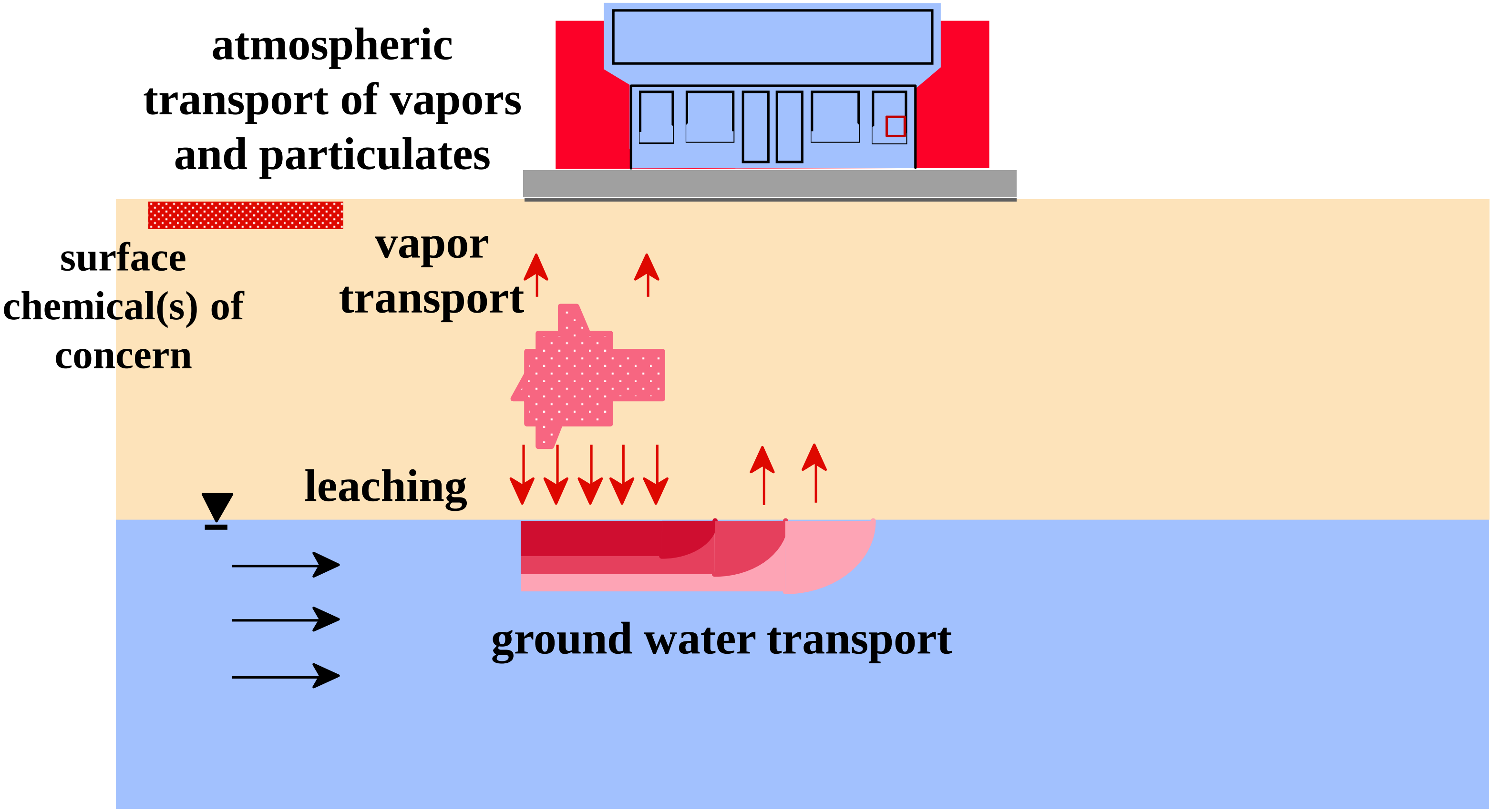
Jimmy Kao

National Sun Yat-Sen University

Common Questions to be Addressed When Contaminants Fate and Transport are Evaluated

- How far might contaminant travel?
- How fast might contaminant travel?
- What will concentrations be some distance away from the source area?
- How long will it take contaminants to reach a given distance?
- How often should I monitor?
- Where should I monitor?
- What chemical(s) of concern should be monitored?
- How much do I need to reduce source area concentrations to be sufficiently protective?

Common Transport Pathways



Contaminant Fate and Transport

- **Advection**

  $v = Q/A = -K/n\ (dh/dL)$

- **Hydrodynamic dispersion**

  D_x = mechanical mixing (mechanical dispersion)
  + molecular diffusion = $\alpha \times v_x + D_d$

- **Adsorption Effects**

  Retardation factor (R) = $1 + K_d\ (\rho/n)$
  Distribution coefficient = K_d (mL/g) = $f_{oc}\ K_{oc}$
  $K_{oc} = 0.63\ K_{ow}$
  K_{oc} = soil water partition coefficient (mL/g)
  K_{ow} = octanol water partition coefficient (mL/g)
  f_{oc} = fraction of organic carbon

- **Biodegradation**

soil particle density, ρs

– $\rho_s = W_s / V_s$

bulk density, ρb

– $\rho_b = W_s / V_t$

porosity, n

– $n = (V_a + V_w) / V_t = V_v / V_t$

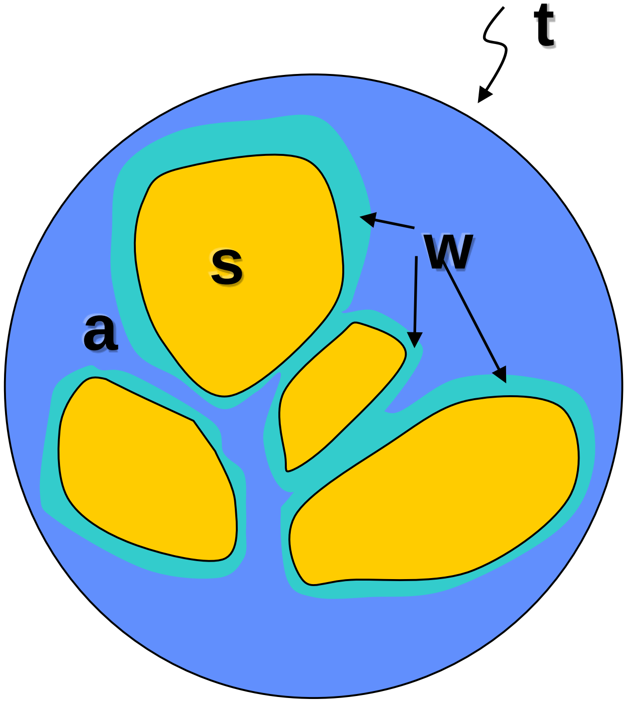
– $n = 1 - \rho_b / \rho_s$

void ratio, e

– $e = V_v / V_s = (V_w + V_a) / V_s$

– $e = n / (1 - n)$

– $n = e / (1 + e)$



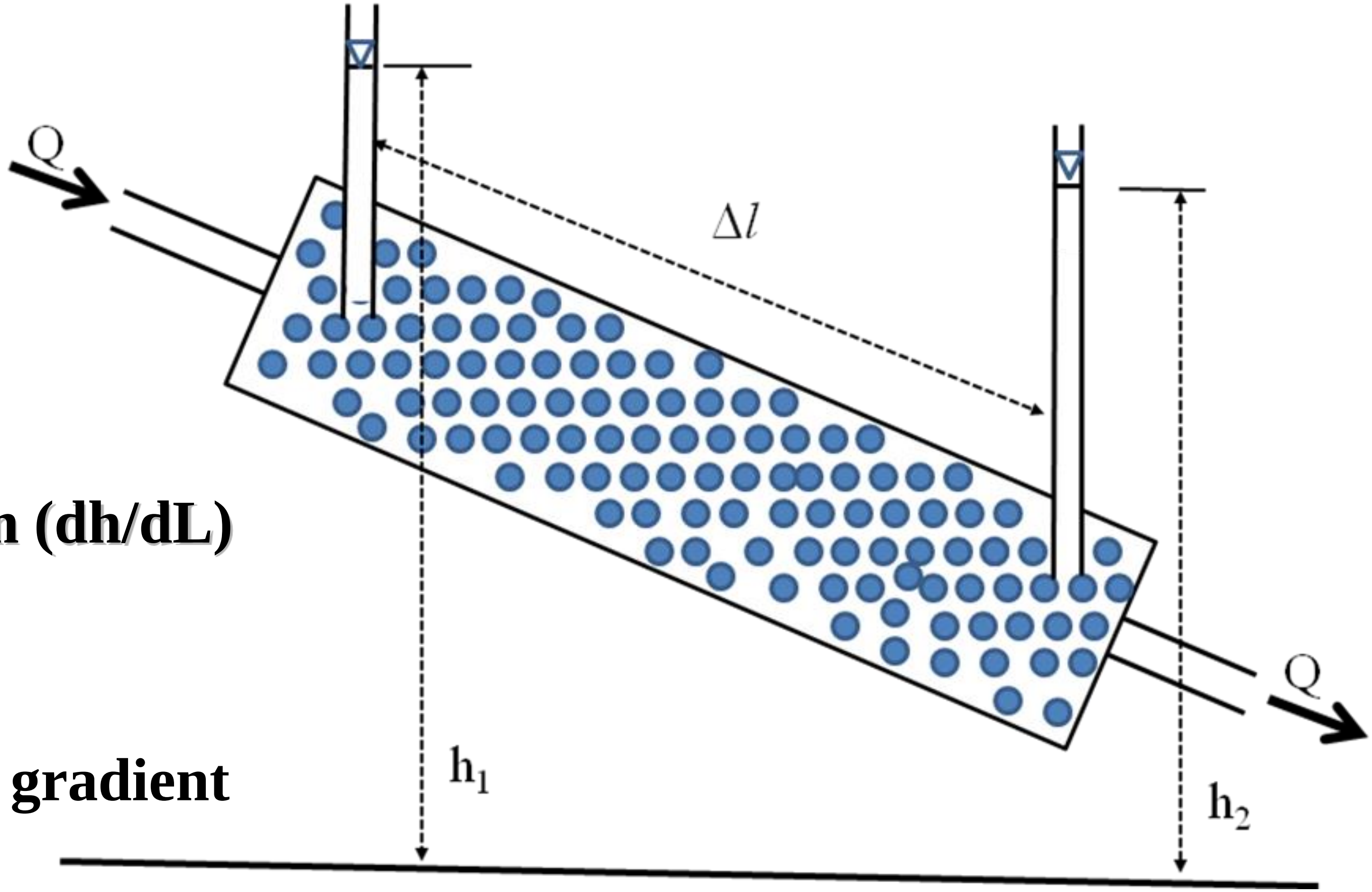
s: solid
a: soil air
w: soil water
t: total volume

W: weight
V: volume

$$v = Q/A = -K/n\,(dh/dL)$$

$$v = \frac{K\,i}{n}$$

i = hydraulic gradient



Darcy’s column experiment

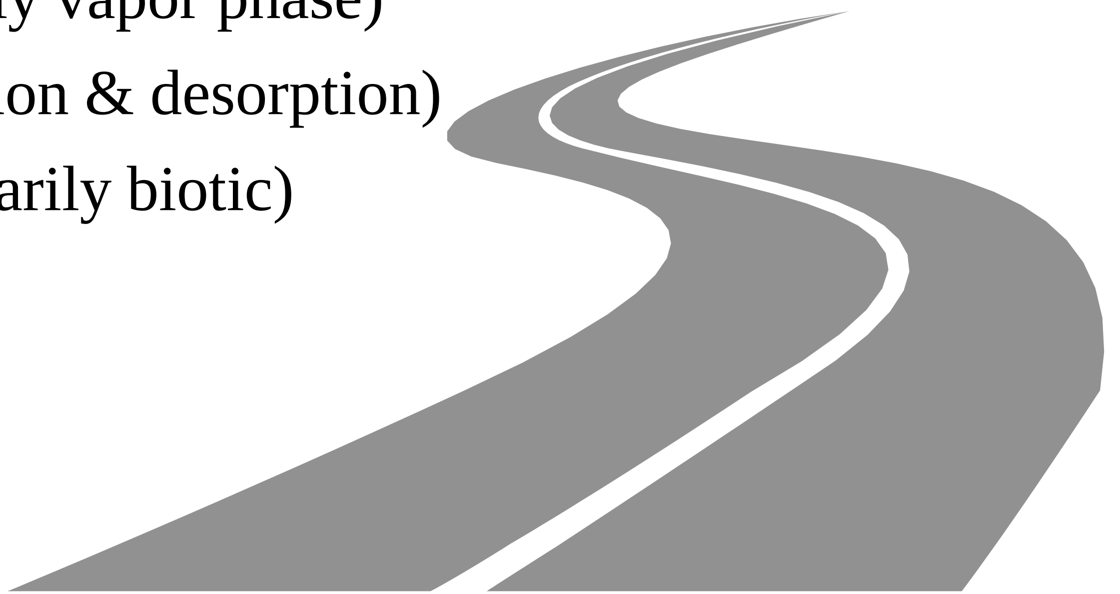
Contaminant Fate and Transport

- The physical processes that control the flux into and out of the elemental volume are advection and hydrodynamic dispersion. Loss or gain of solute mass in the elemental volume can occur as a result of chemical or biochemical reactions.

- Advection is the component of solute movement attributed to transport by the flowing groundwater. The rate of transport is equal to the average linear groundwater flow velocity.

Fate and Transport Mechanisms

- Advection (primarily dissolved phase)
- Dispersion (primarily dissolved phase)
- Diffusion (primarily vapor phase)
- Partitioning (sorption & desorption)
- Degradation (primarily biotic)



Fate & Transport

•Fate processes - persistence of a chemical

•Transport processes - mobility of a chemical

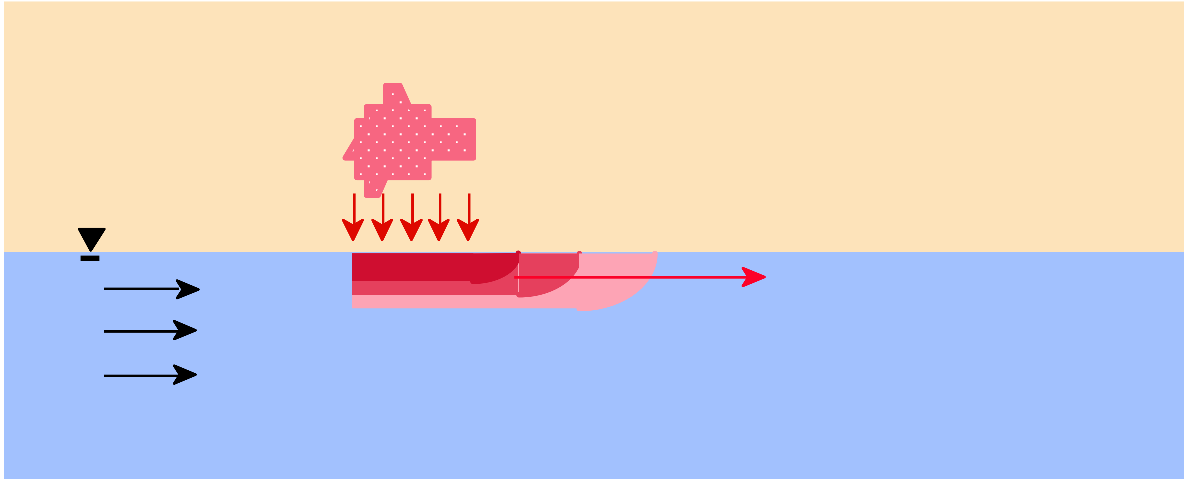
- advection (flow or movement in the media)
  - vapor
  - liquid
  - dissolved

- diffusion
- dispersion
- adsorption
- decay (chemical and biological)

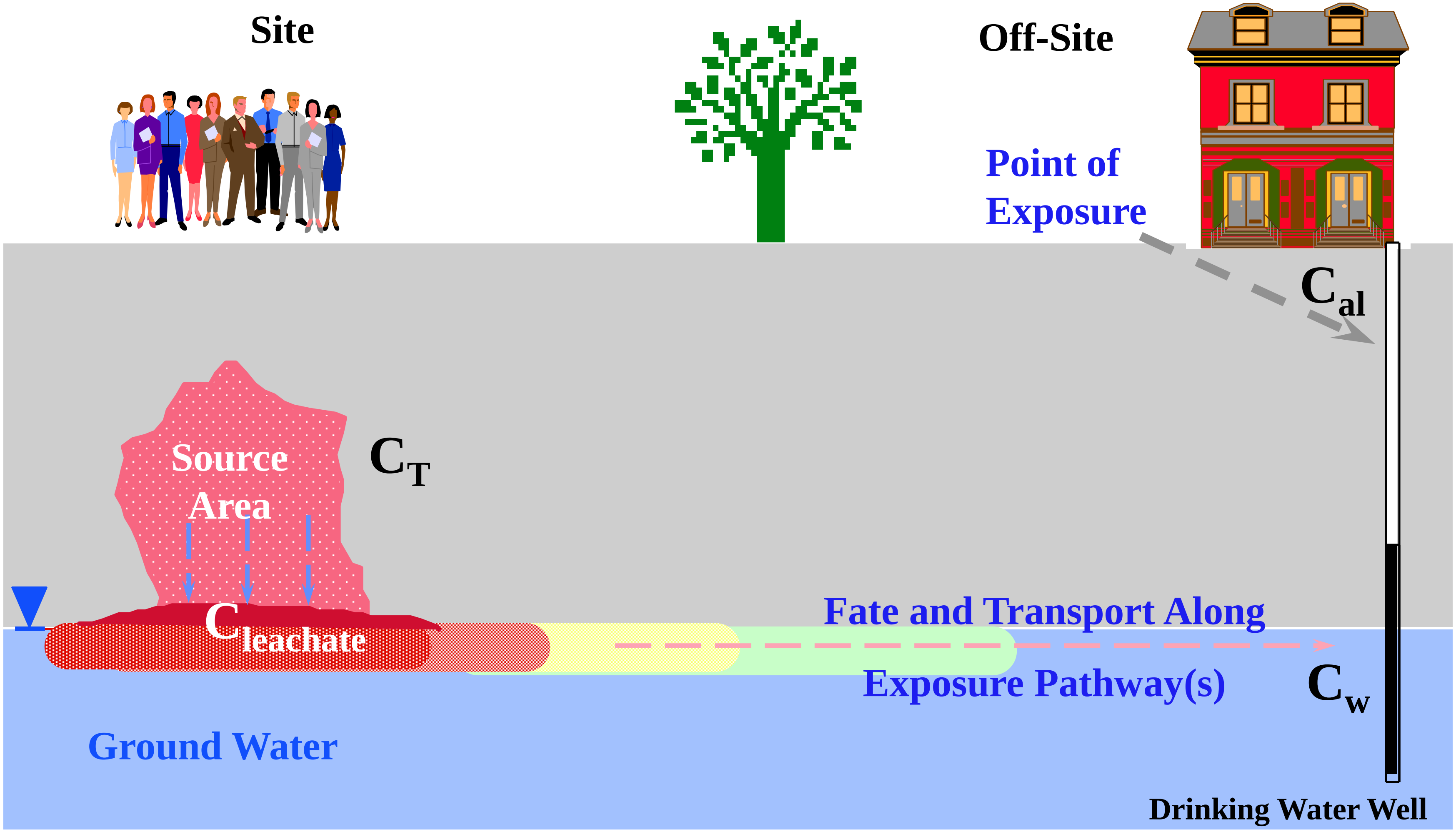
Fate & Transport

- There is natural variability and uncertainty.
- Uncertainty and variability can be addressed by making conservative assumptions.
- The effect of conservative assumptions is to:
  - overestimate mass
  - overestimate the concentration at the point(s) of exposure

Ground Water Fate and Transport Processes



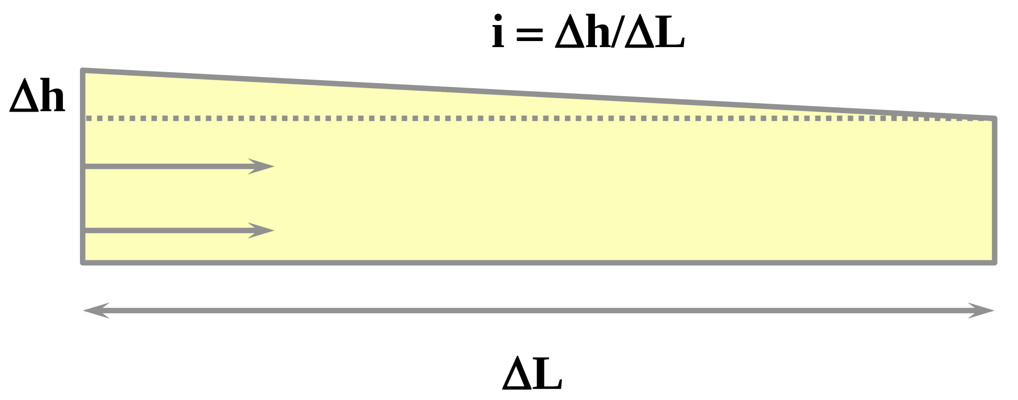
Ground Water Fate and Transport



Advection

"Advection" refers to the bulk motion of a fluid; it is also sometimes called "convection".

$$V_{GW} = \frac{K\,i}{\theta_E}$$



V_{GW} = average ground water linear velocity [cm/s, ft/d]

K = hydraulic conductivity [cm/s, ft/d]

i = hydraulic gradient [cm/cm, ft/ft]

θ_E or n = effective porosity [l-H_2O/l-soil]

Advective Transport - Dissolved Hydrocarbons

Due to partitioning effects (primarily sorption), hydrocarbons move at a speed less than that of the bulk ground water movement.

$$V_{HC} = \frac{V_{GW}}{R} \qquad R = 1 + \frac{k_d \rho_s}{\theta_E}$$

V_{HC}	= chemical of concern velocity [cm/s, ft/d]
V_{GW}	= ground water linear velocity [cm/s, ft/d]
R	= retardation factor
k_d	= distribution coefficient [(mg/kg-soil)/(mg/l-H_2O)]
ρ_s	= soil bulk density [kg-soil/l-soil]
θ_E	= effective porosity [l-H_2O/l-soil]

Advective Transport - Dissolved Hydrocarbons

- Estimation of distribution coefficient (k_d)
  - laboratory experiments or
  - calculated for organic chemicals

$$k_d = K_{oc} \times f_{oc}$$

k_d = distribution coefficient ([mg/kg-soil]/[mg/l-H_2O])

f_{oc} = fraction of organic carbon of soil (unitless)

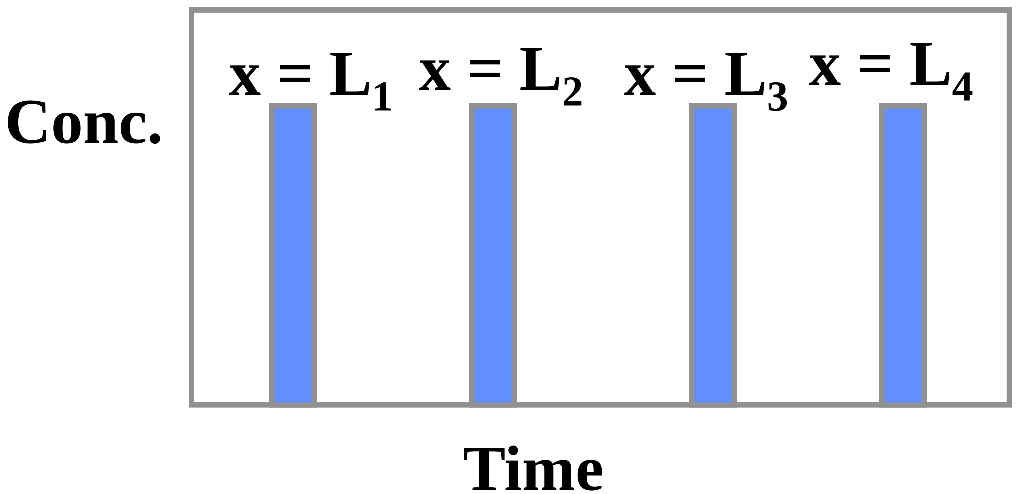
K_{oc} = organic carbon partition coefficient ([mg/kg-organic carbon]/[mg/l-H_2O])

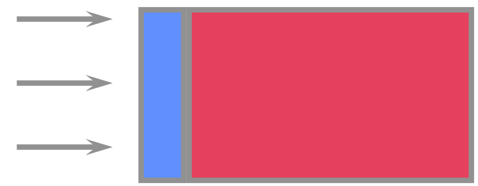
estimated using regression equations with solubility inputs

estimated from K_{ow} (octanol/water partition coefficient)

Advective Transport - Summary

Advection moves dissolved hydrocarbons with the bulk fluid flow, but the dissolved concentrations are not expected to change.





Advective rate estimates are affected most by uncertainties in the distribution coefficient and ground water velocity.

Hydrodynamic dispersion

D_x = mechanical mixing (mechanical dispersion) + molecular diffusion = $\alpha \times v_x + D_d$

where

α is a characteristic property of the porous medium known as the dynamic dispersivity, or dispersivity;

D_d is the coefficient of molecular diffusion for the solute in the porous medium.

Molecular diffusion

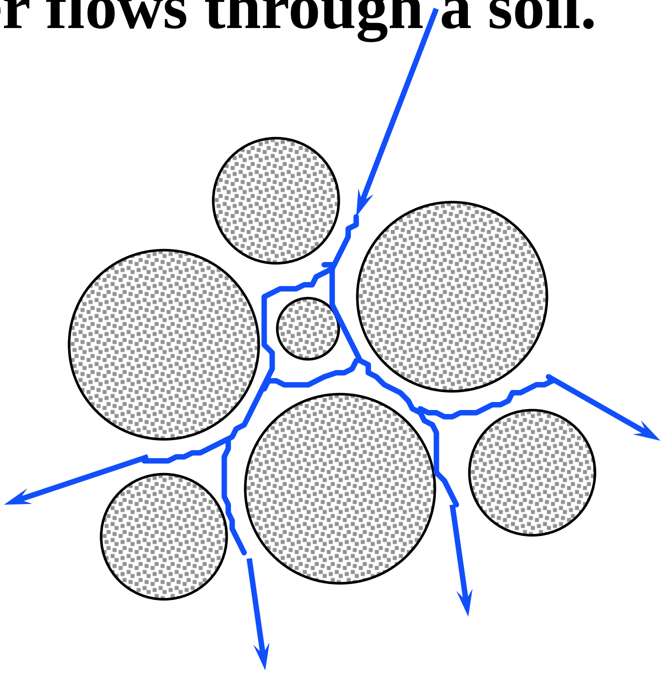
Fick's first law

$$f_x = -D_d \frac{\partial C}{\partial x}$$

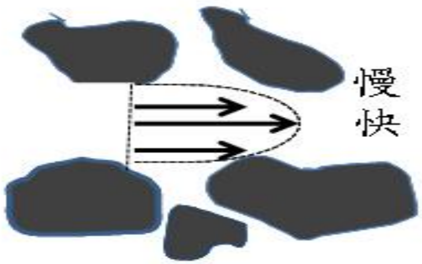
$\mathbf{D_d}$ is the coefficient of molecular diffusion for the solute in the porous medium.

Dispersion

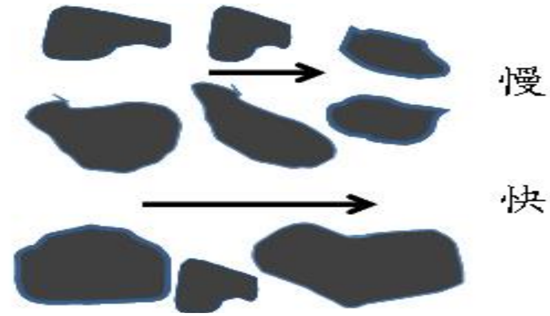
“Dispersion” refers to the in-situ mixing that results as a ground water flows through a soil.



Hydrodynamic dispersion occurs as a result of mechanical mixing (mechanical dispersion) and molecular diffusion. The coefficient of hydrodynamic dispersion can be expressed in terms of the two components.



(a) friction within a single pore channel



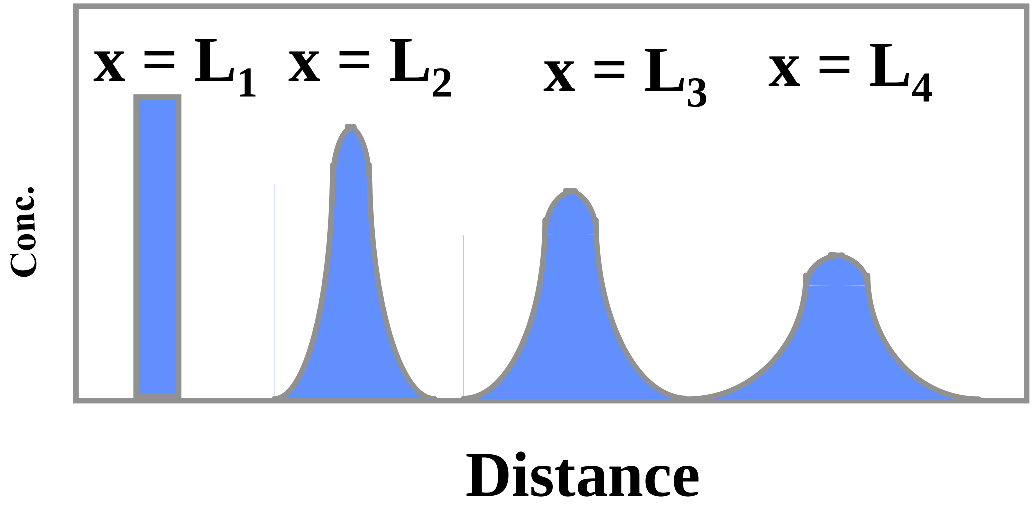
(b) velocity differences from one channel to another

(c) variable path lengths

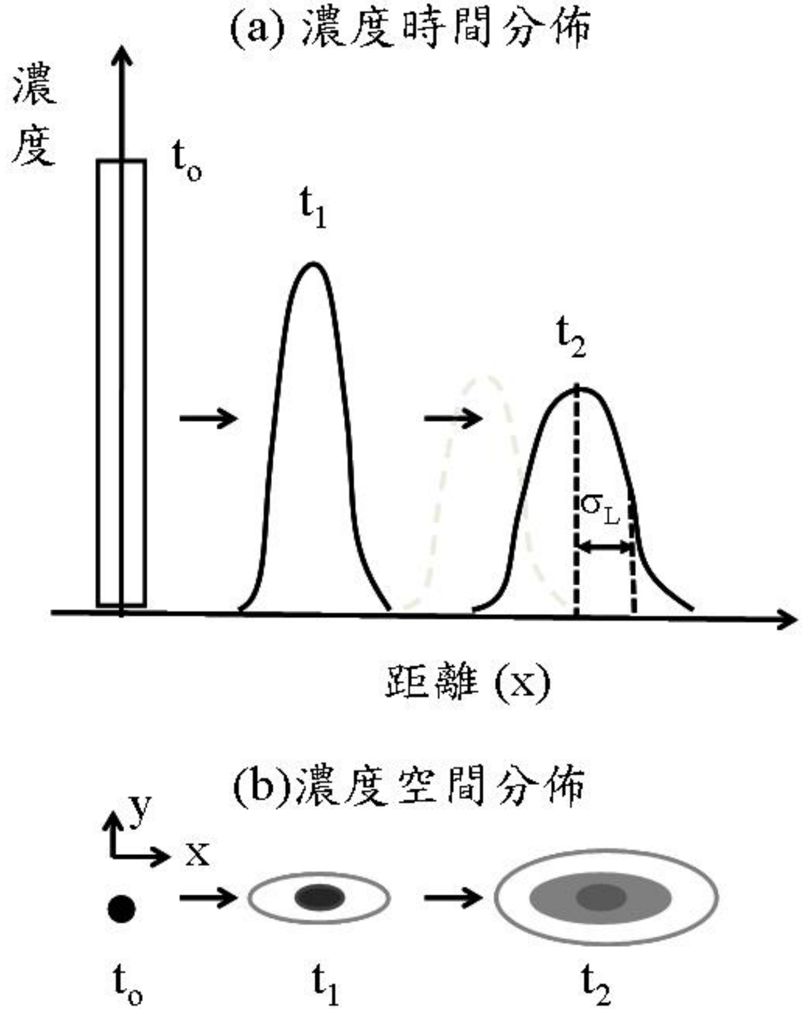
Hydrodynamic dispersion is caused by heterogeneities in the medium that create variations in flow velocities and flow paths. These variations can occur due to friction within a single pore channel, to velocity differences from one channel to another, or to variable path lengths.

Dispersion

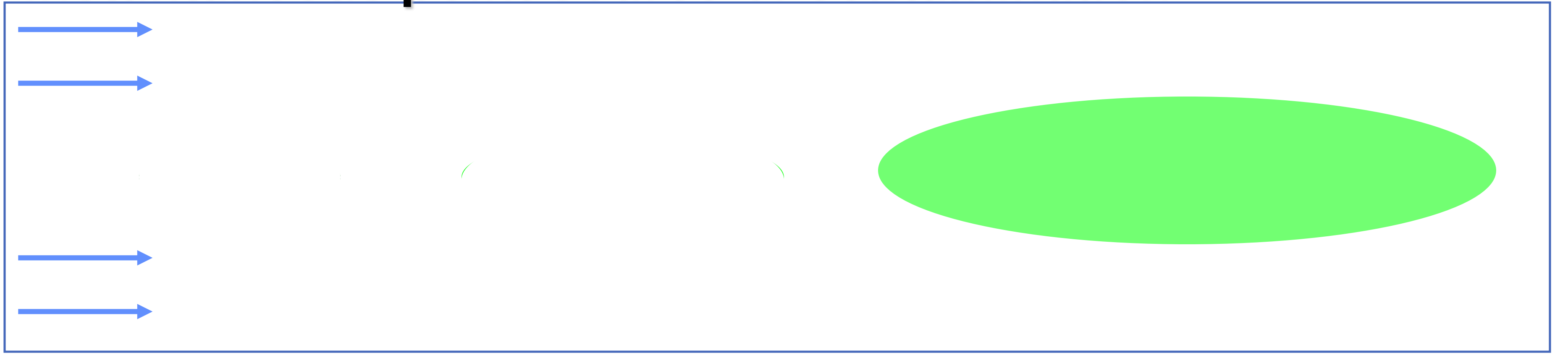
Dispersion results in the three dimensional spreading of the dissolved hydrocarbons, but does not affect the total dissolved mass of hydrocarbons present.



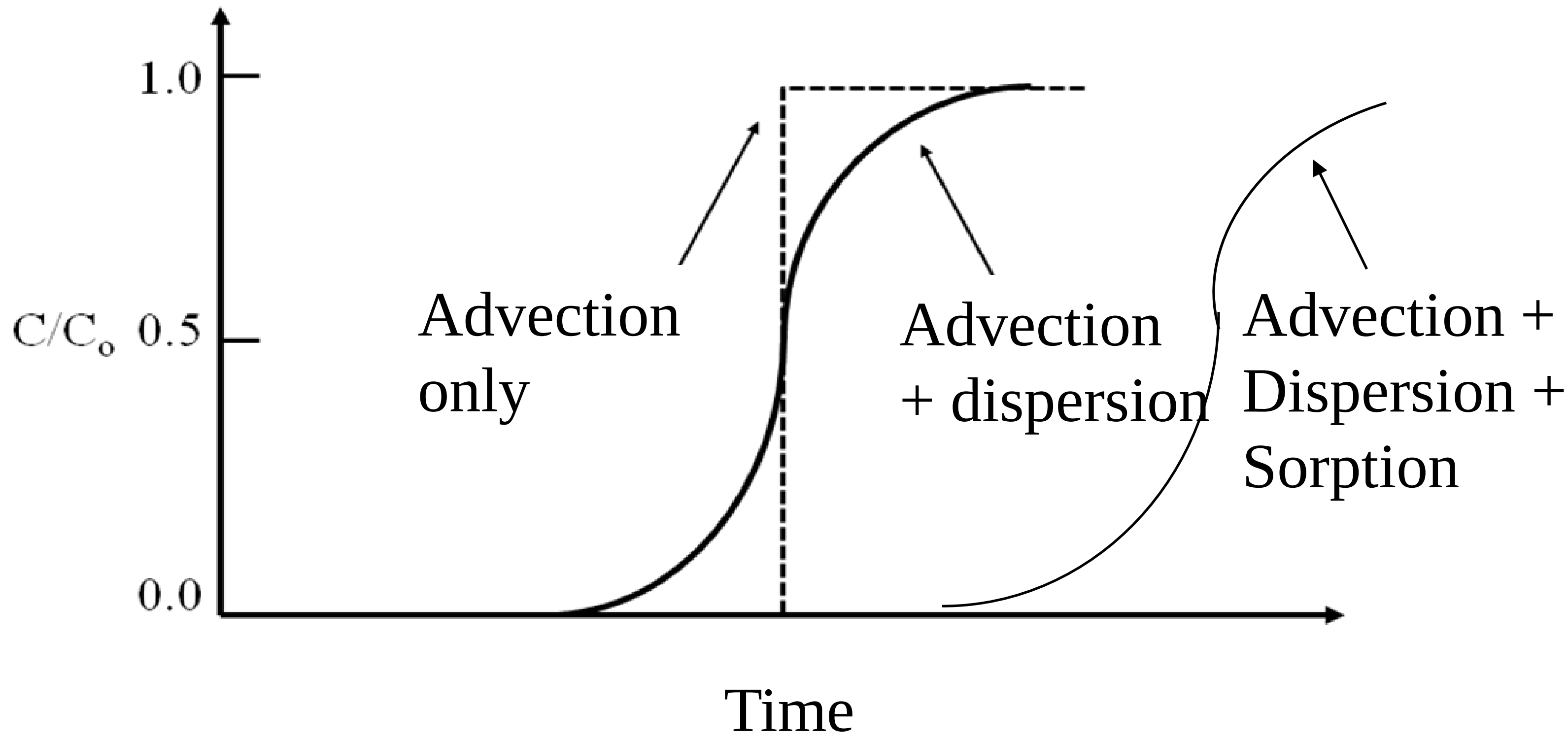
Dissolved concentrations generally decrease as the chemical moves away from a source.


(a) 濃度時間分佈
濃度
t_o
t_1
t_2
σ_L
距離 (x)
(b)濃度空間分佈
y
x
t_o
t_1
t_2

Instantaneous point source of contamination



Continuous point source of contamination

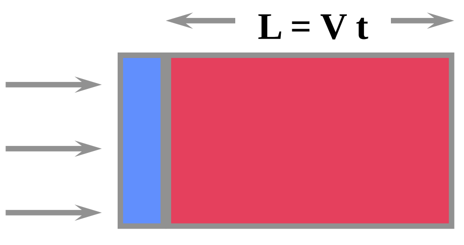


Breakthrough Curve of a 1-D column experiment

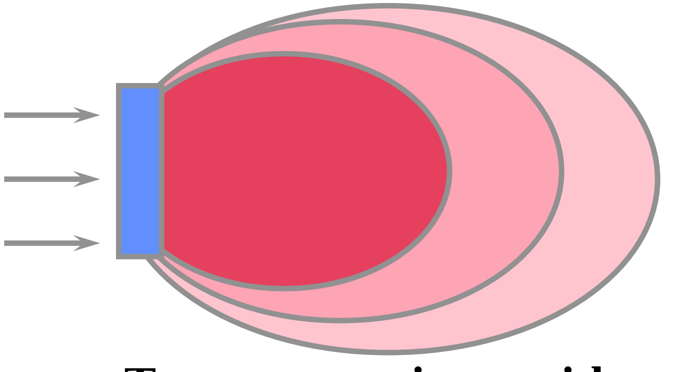
Hydrodynamic Dispersion

The extent of spreading, or mixing, caused by dispersion is characterized by a "dispersion coefficient", D [ft^2/d, cm^2/s], where:

$$\left\{\begin{array}{l}\textbf{width of}\\ \textbf{spreading in}\\ \textbf{direction i}\end{array}\right\} \approx \sqrt{D_i\ t}$$



Transport at time t without dispersion



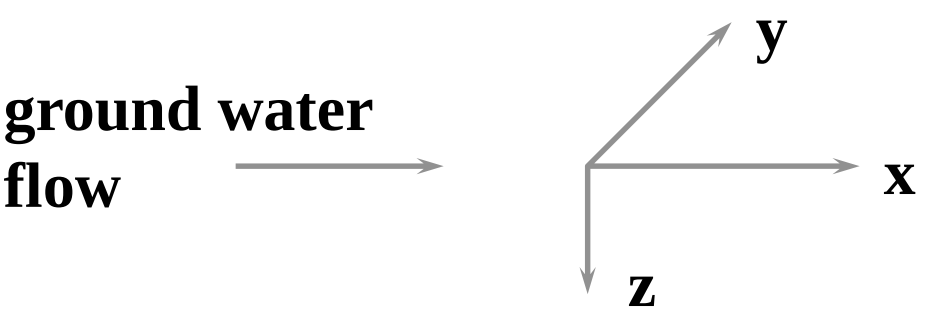
Transport at time t with dispersion

Hydrodynamic Dispersion

For one-dimensional ground water flow, with velocity V [ft/d, cm/s] in the x-direction, "dispersion coefficients" are typically expressed as the product of a "dispersivity" and the ground water velocity V:

$D_x = \alpha_x V$ = longitudinal (x-direction) dispersion coefficient [ft^2/d]
$D_y = \alpha_y V$ = lateral (y-direction) dispersion coefficient [ft^2/d]
$D_z = \alpha_z V$ = vertical (z-direction) dispersion coefficient [ft^2/d]

α_x, α_y, α_z = dispersivities in x, y, and z direction [ft, m, cm]

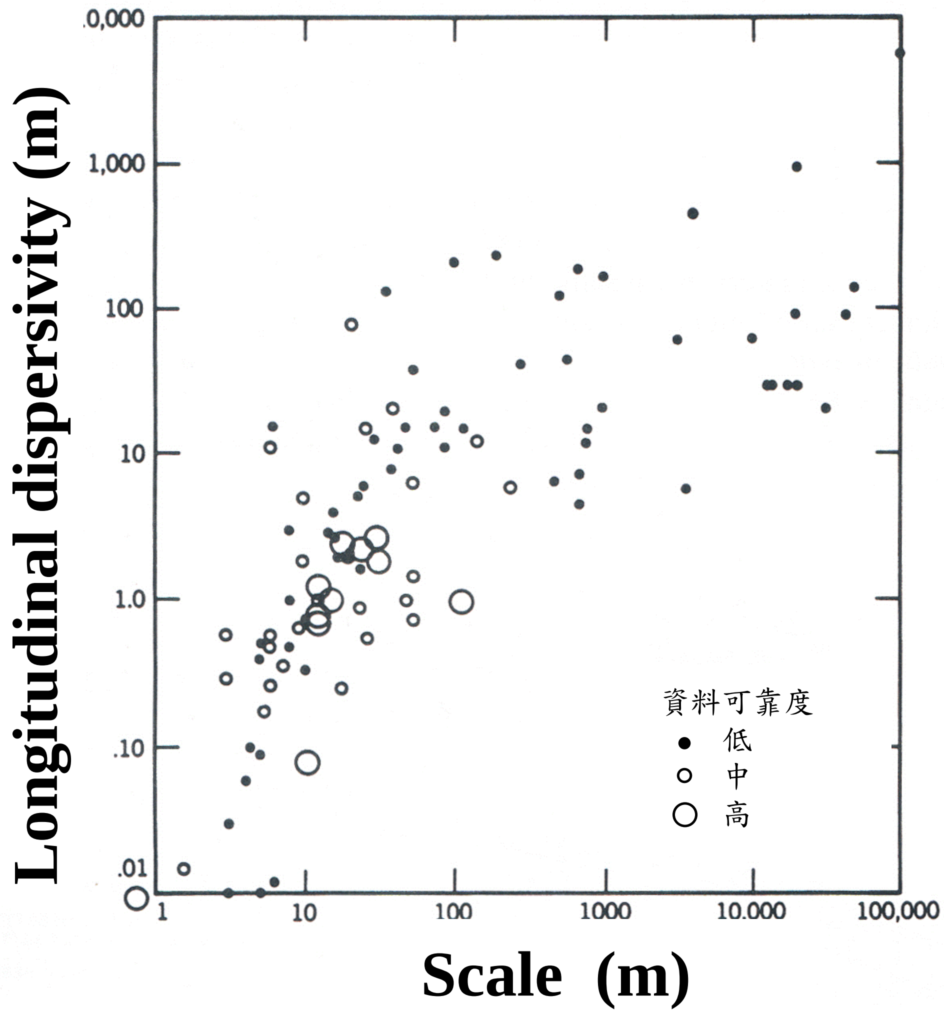


Hydrodynamic Dispersion

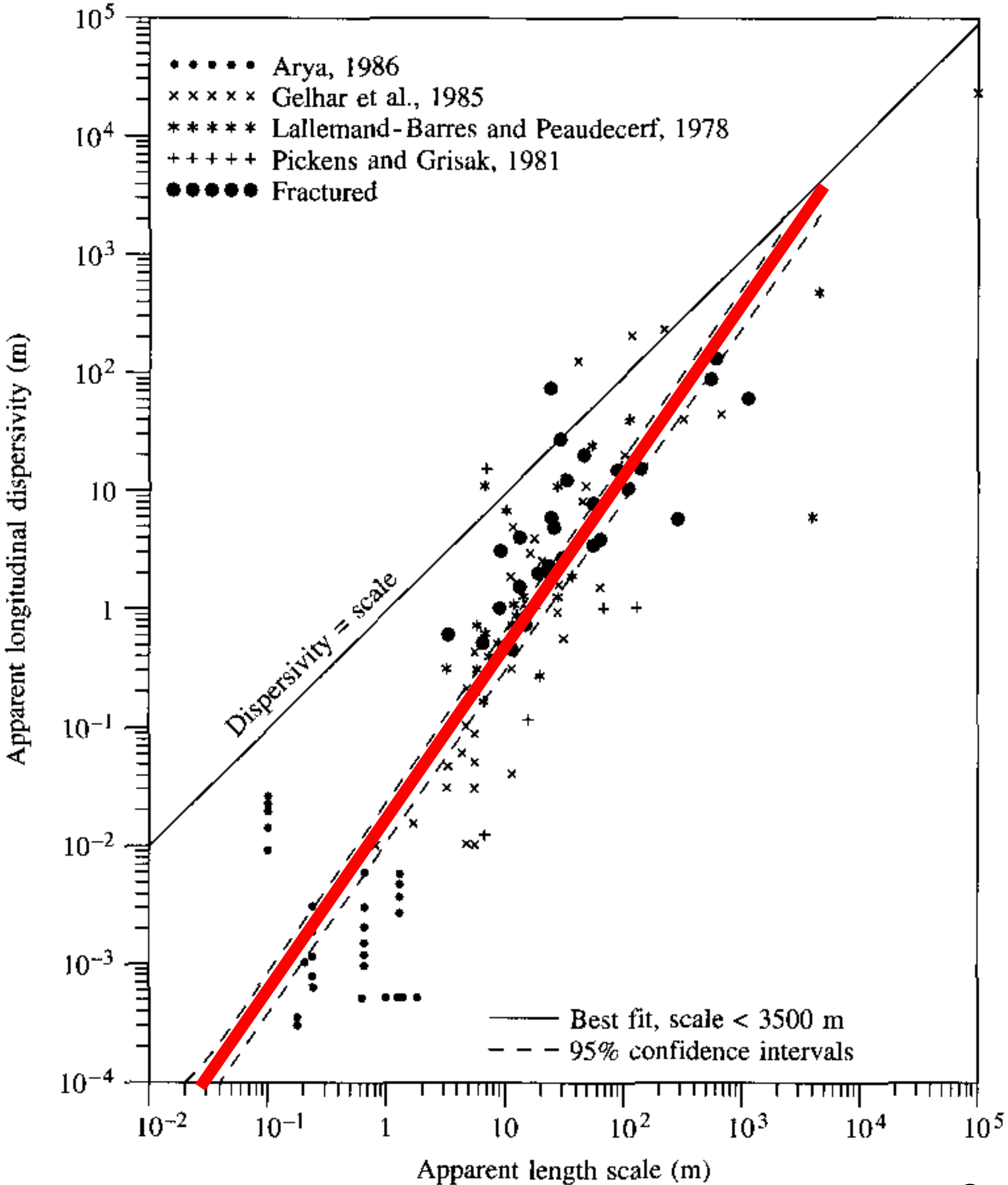
Two-well tracer tests have been used to estimate dispersivities, but are not routinely performed at most sites.

Often, generalized approximations are used to estimate the dispersivities. Examples are:

α_x = L/10
α_y = α_x/3
α_z = α_x/20
L = distance away from source



Longitudinal dispersivity (m)
10,000
1,000
100
10
1.0
.10
.01
1
10
100
1000
10,000
100,000
資料可靠度
低
中
高
Scale (m)



Source: S. Neuman, Water Resources Research 26, no. 8 (1990):1749-1758.

Biodegradation

Aerobic Biodegradation

- **Oxygen acts as an "electron acceptor." Indigenous micro-organisms exist that are capable of degrading most fuel-range petroleum hydrocarbons. The most significant rates of degradation occur aerobically**
- **Field studies conducted to date indicate that the factor that most significantly controls biodegradation in subsurface environments is the rate of oxygen transport.**

Anaerobic Biodegradation

- **Oxygen acts as an "electron acceptor." There are other potential electron acceptors commonly found in aquifer environments, including NO_3^{2-}, SO_4^{2-}, Fe^{3+}.**

Biodegradation

For mathematical simplicity, most hydrocarbon degradation reactions are treated as being "first-order" reactions. In other words:

$$\left\{ \text{decay rate} \right\} \text{ is proportional to } \left\{ \begin{array}{c} \text{concentration} \\ \text{of hydrocarbon} \end{array} \right\}$$

$$\frac{dC}{dt} = -\lambda C$$

Biodegradation

Decay

The concentration can be determined by:

$$C_{(t)} = C_o e^{(-\lambda t)}$$

$$[\ln(C_{(t)}/C_o) = -\lambda t]$$

λ = first order decay rate constant (t^{-1})

$C_{(t)}$ = concentration at time t (μg/l)

C_o = initial concentration (μg/l)

Typical values for the rate constant (λ) for benzene fall in the range 0.1% - 1% per day.

Biodegradation

Decay

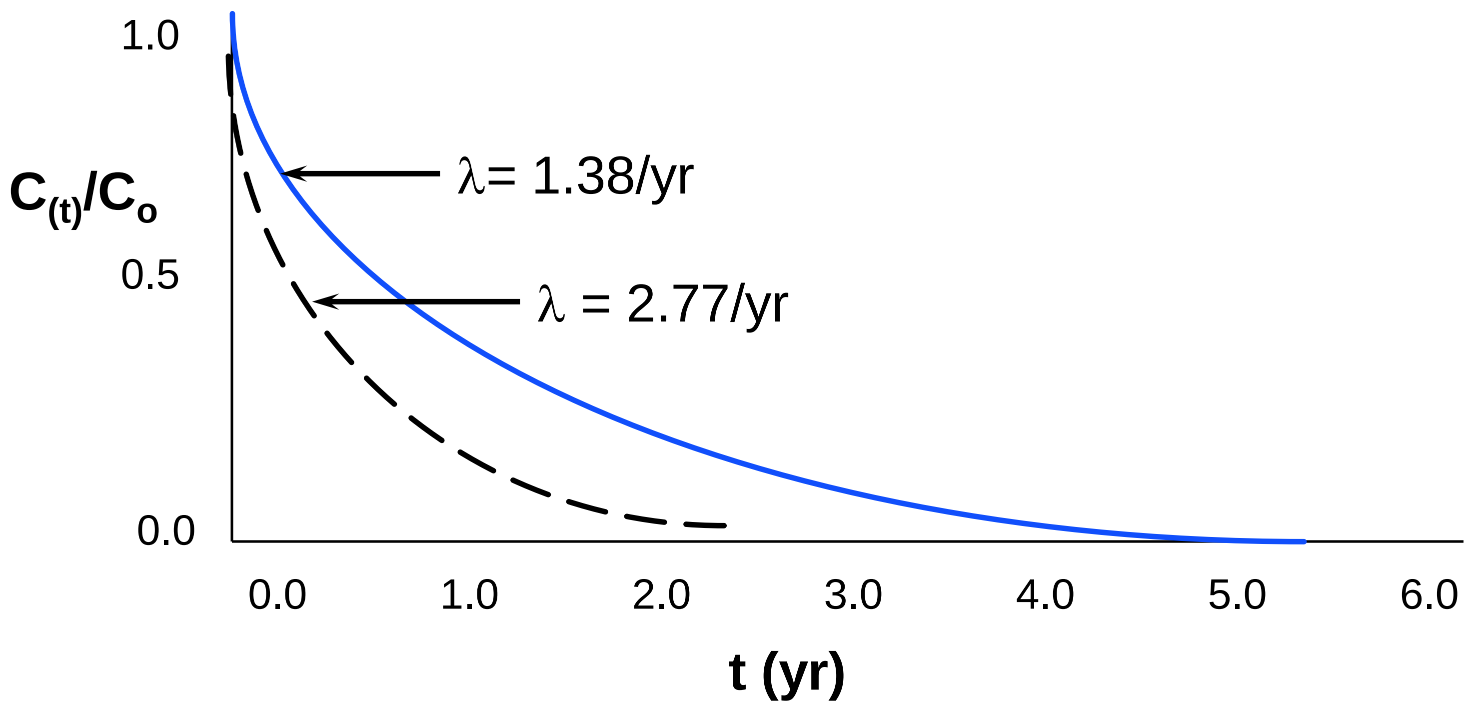
The half-life of a chemical is defined as the time it takes for the first-order reaction to transform half of the initial mass of the chemical. If $C_{(t)}/C_o$ is replaced with 0.5, then:

$$\mathbf{t_{0.5} = -(\ln 0.5)/\lambda \text{ or } t_{0.5} = 0.693/\lambda}$$

$t_{0.5}$ = half-life of the chemical (days)

Biodegradation

Illustration of first-order decay

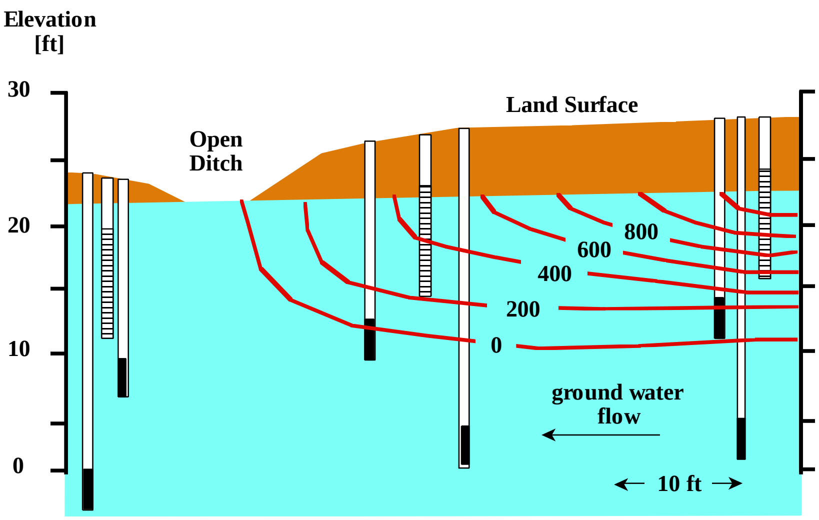


Natural Attenuation

- "Natural Attenuation" refers to the reduction in mass, mobility, or concentration of chemical(s) of concern by intrinsic processes (advection, dispersion, diffusion, dilution, sorption, degradation).
- Dilution Attenuation Factor (DAF)

Data collection needs include:

- flow direction & gradient
- hydraulic conductivity
- lithology
- depth to ground water
- ground water fluctuations
- extent of source
- historical monitoring data



Benzene Concentration in Ground Water [ppb]
April 1987

Modeling

Advection-dispersion equation

The 1-D form of the advection-dispersion equation for nonreactive dissolved constituents in saturated, homogeneous, isotropic, materials under steady-state, uniform flow is:

advection $= \bar{v}_x nCdA$

dispersion $= nD_x \dfrac{\partial C}{\partial x} dA$

$$D_x \frac{\partial^2 C}{\partial x^2} - \bar{v}_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

Adsorption and Biodegradation effects

Sink/Source

$$D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + \sum_{k=1}^{N} R_k = \frac{\partial C}{\partial t}$$

Adsorption

$$\frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

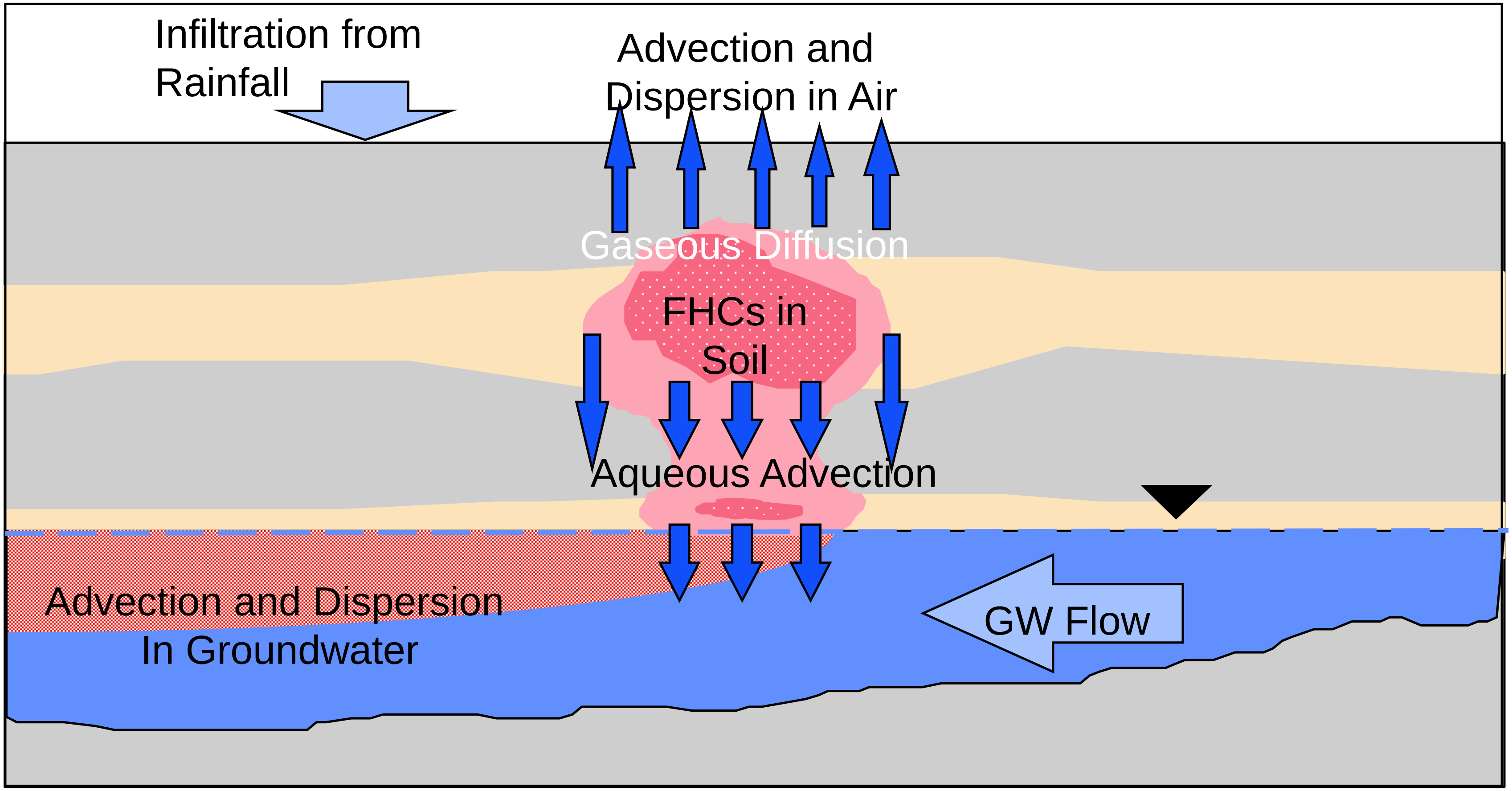
R = retardation factor

First order decay

$$D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t}$$

λ = first-order decay rate [1/t]

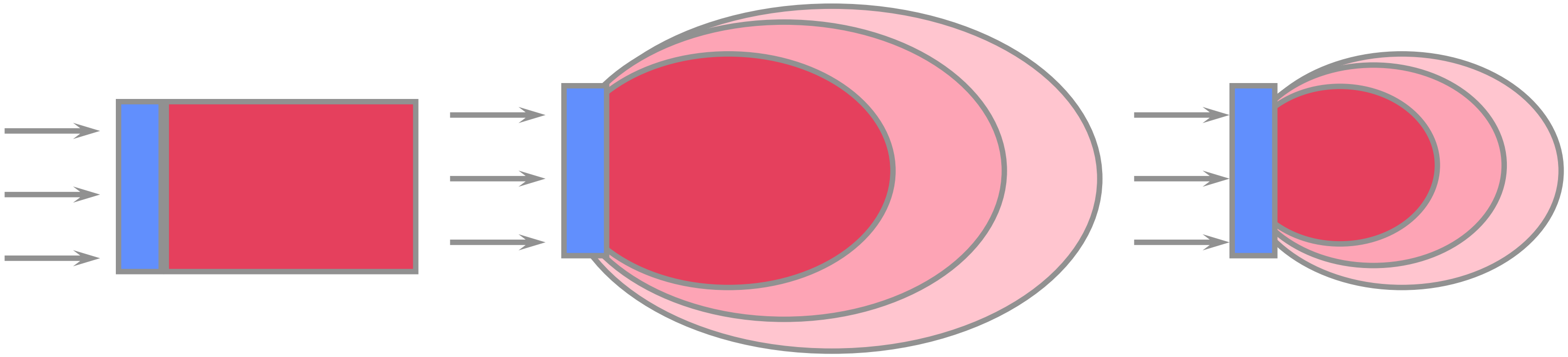
Example of a Conceptual Model, Showing Significant Transport Processes



Ground Water Transport Modeling

All ground water transport models are based on the advective-dispersive-reactive equations.

{ rate of change in HC conc. at any point } = { net rate of advective transport to that point } + { net rate of dispersive transport to that point } - { net rate of degradation at that point }



Transport at time t advection only

Transport at time t with dispersion

Transport at time t with dispersion & degradation

Ground Water Transport Modeling

- **At a low velocity, diffusion is the important contributor to the dispersion. At a high velocity, mechanical mixing is the dominant dispersive process.**

- **One of the characteristic features of the dispersive process is that it causes spreading of the solute.**

- **An elliptical shape of the contaminant plume usually occurs because the process of mechanical dispersion is anisotropic.**

- **Dispersion is stronger in the direction of flow (the longitudinal dispersion) than in direction normal to the flow line (transverse dispersion).**

Ground Water Transport Modeling

Given the typical level of information available for UST sites, ground water modelers likely have to resort to adopting the following assumptions:

- **homogeneous and isotropic conditions**
- **uniform, one-dimensional flow field**
- **constant source**
- **first-order degradation reaction**

P.A. Domenico (1987) developed an analytical solution for this case. All valid numerical codes should reduce to this solution, given the conditions listed above.

Ground Water in Source Zone → Ground Water at Receptor

Chemical transport involving dispersion in three directions, advection in one direction, and first-order degradation can be expressed as:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - V_x \frac{\partial C}{\partial x} - \frac{\lambda}{\theta}$$

The steady-state concentration along the centerline is expressed as:

$$\frac{C(x)}{C_0} = \exp\left\{ \frac{x}{2\alpha_x}\left[1 - \left(1 + \frac{4\lambda\alpha_x}{V}\right)^{\frac{1}{2}}\right]\right\} \operatorname{erf}\left[\frac{S_w}{4\sqrt{\alpha_y x}}\right] \operatorname{erf}\left[\frac{S_d}{4\sqrt{\alpha_z x}}\right]$$

$$V = \frac{k\,i}{\theta}$$

- $C(x)$: *Concentration at Downgradient Distance x Away from Source*
- C_0: *Concentration at Source*
- α_x: *Longitudinal Dispersivity*
- λ: *First-Order Decay Constant*
- S_w, S_d: *Ground Water Source Width and Depth*
- erf: *Error Function*
- α_y: *Transverse Dispersivity*
- α_z: *Vertical Dispersivity*
- V: *Ground Water Seepage Velocity*
- k: *Hydraulic Conductivity*
- i: *Hydraulic Gradient*
- θ: *Volumetric Water Content (Porosity)*

Typical Design Process

- **Detailed hydrological site assessment – delineate horizontal and vertical extent of contamination; determining site geologic and hydrogeologic conditions**
- **Cleanup goals/regulatory requirements**
- **Remedial action plan or corrective action plan**
- **Feasibility study or pilot test**
- **System design – engineering design of remedial system**

Approaches to implement hazardous waste management policies

- **Health-based approaches – zero risk, significant risk, acceptable risk**
- **Balancing approaches – cost-benefit, risk-benefit, decision analysis**
- **Technology-based approaches – best available technology, risks as low as reasonably practicable**

Selected technology needs to achieve the following results

- Overall protection of human health
- Compliance with applicable or relevant and appropriate requirements
- Long-term effectiveness and performance
- Reduction of toxicity, mobility, and volume of contaminants
- Short-term effectiveness
- No significant barriers in implementation
- Relatively cost effective
- Compliance with state/federal regulations
- Community acceptance

Technology Screening

Available technology → applicable to site → feasible to implementation → societal acceptability → need new data → long term remediation → prospective technology → (remedy screening → potentially feasible technology) → treatability study → meet performance goal → remedy selection → meet remediation goal → decision recorded → treatability study

Trend of Groundwater Remediation Technology Development

- **Late 1970s – Late 1980s**
  ex situ extraction: pump and treat

- **Mid 1980s – present**
  in situ extraction: soil vapor extraction/air sparging

- **Early 1990s – present**
  in situ non-extraction (passive treatment): funnel and gate), permeable reactive barrier

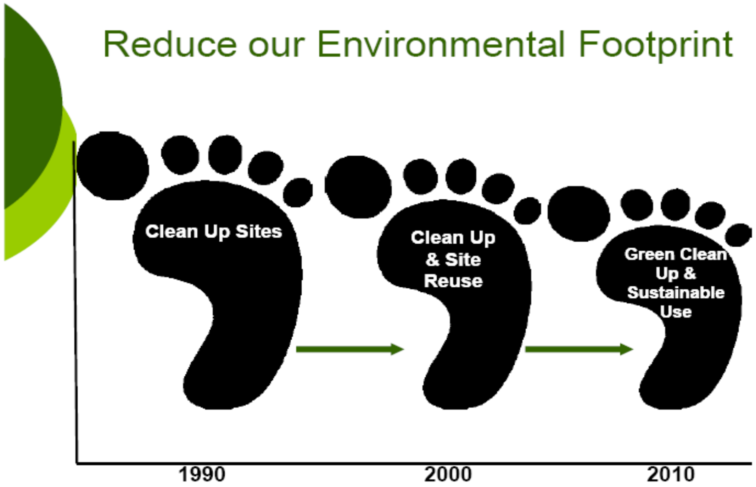
Trend of Groundwater Remediation Technology Development

- **Mid 1990s – present**
  - **in situ mass destruction**
  - **in situ reaction zone, IRZ**
  - **in situ chemical oxidation**
  - **in situ bioremediation**
  - **monitored natural attenuation, MNA**
  - **risk assessment**
  - **Brownfield**

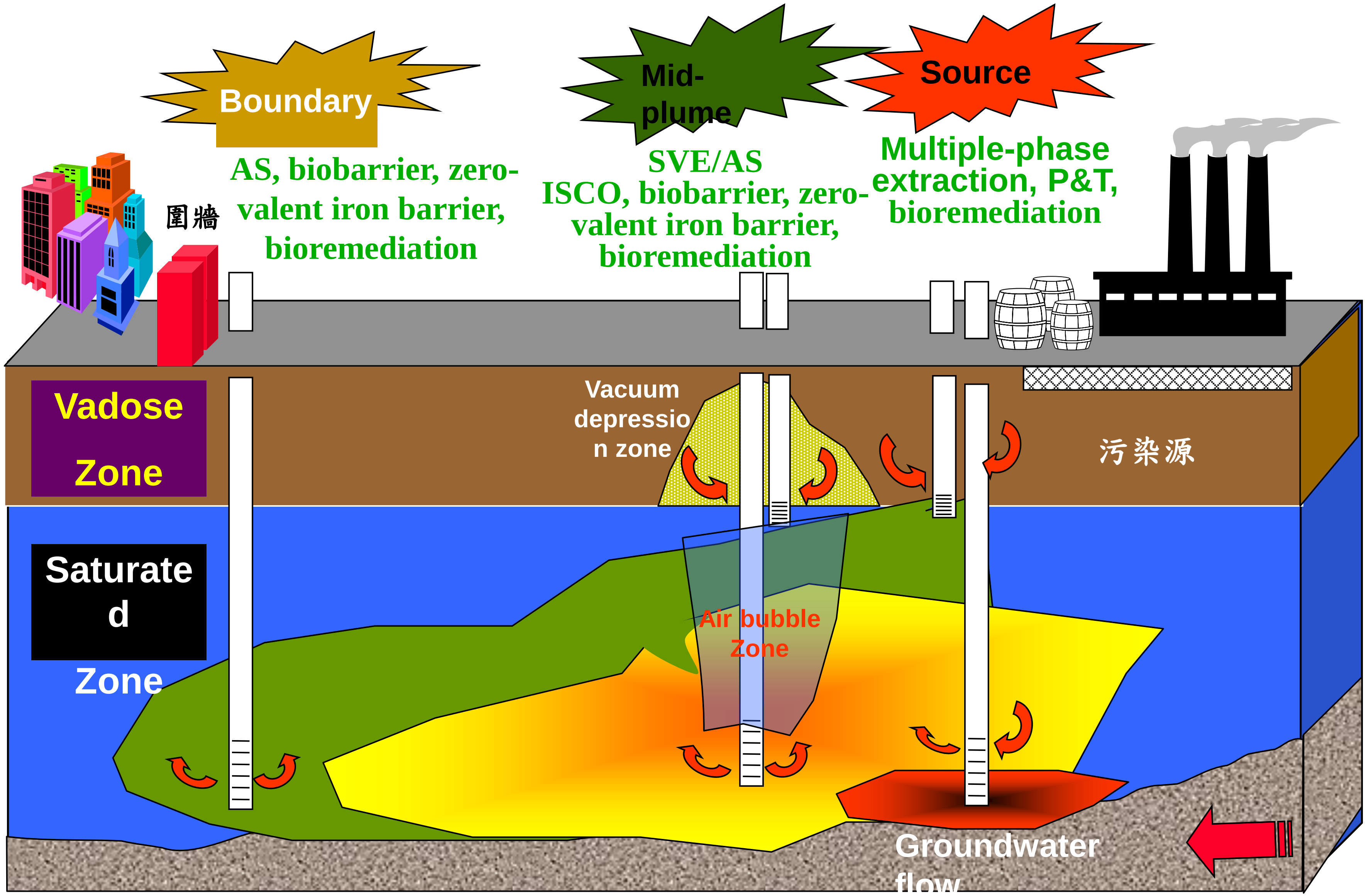
- **Current**
  - **treatment train**
  - **life cycle design**
  - **natural treatment system**
  - **green remediation**

Green Remediation

- US EPA encourages the application of green remediation technologies for site cleanup.
- Under the green remediation concept, in situ, passive, and biological technologies should be applied for contaminated groundwater remediation. Among the remediation technologies, the biobarrier system, which is a cost-effective remedial method, meets the requirements of the green remediation technology.



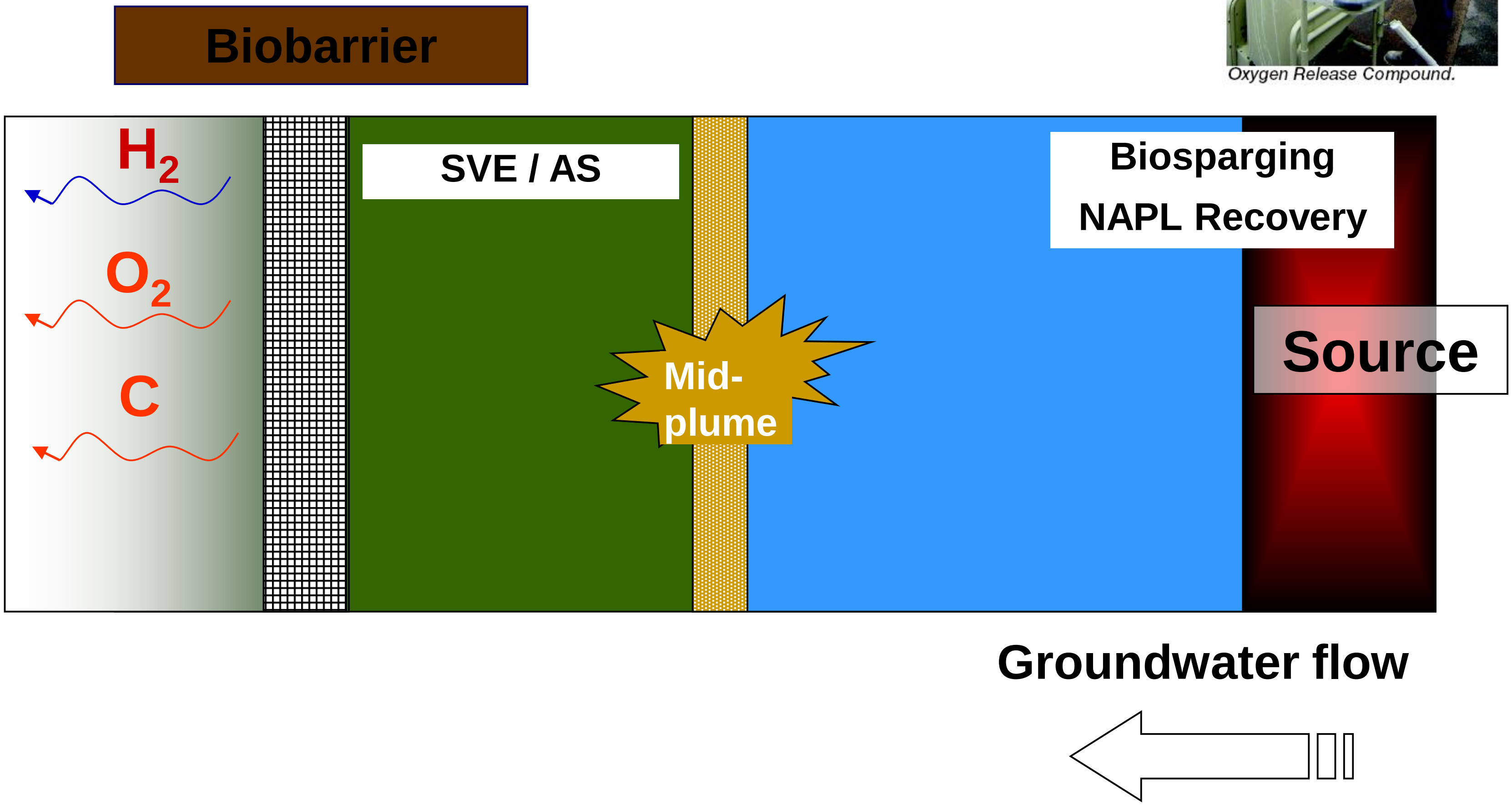
Whole-site Remedial Strategies



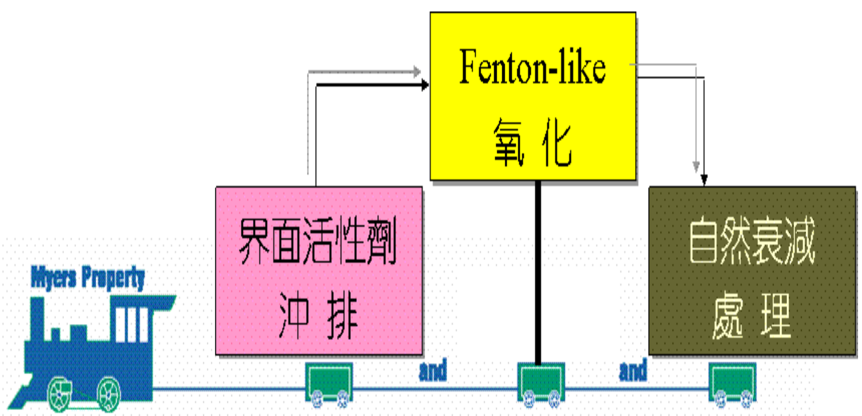
Biobarrier

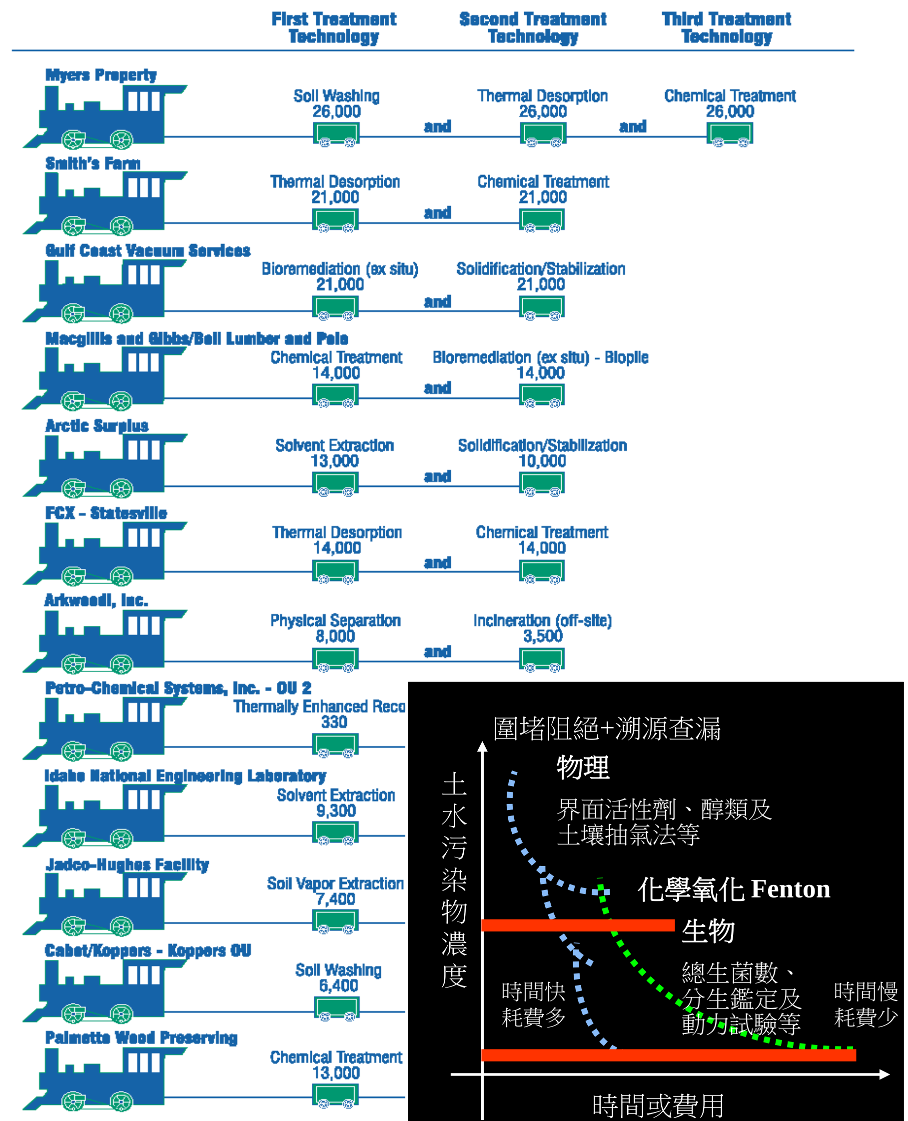
- Hydrogen Release Compound (HRC)
- Oxygen Release Compound (ORC)
- Carbon Release Compound

Oxygen Release Compound.



Treatment Train





Sources: 3, 4, 5, 6: Data sources are listed in the References and Data Sources section on page 38.

Challenges of Groundwater Remediation

- Source zone detection
- Low aquifer permeability or heterogeneity and preferential pathways
- Geochemical conditions outside optimal (e.g. low or high pH, low DO, high ORP)
- Biofouling
- May take several years
- Monitoring and system maintenance
- Adequate microbial populations
- Decreases in pH and redox conditions during bioremediation may solubilize metals
- Very large source zones require a combination of methods/technologies
- Inhibition/toxicity of contaminants & of co-contaminants to dechlorinating microbes
- Contact between injected chemicals and DNAL

2016 International Training Courses on
Survey and Remediation of Soil and Groundwater
Contaminated Sites

In-Situ Groundwater Remediation using ISCO (*In-Situ* Chemical Oxidation)

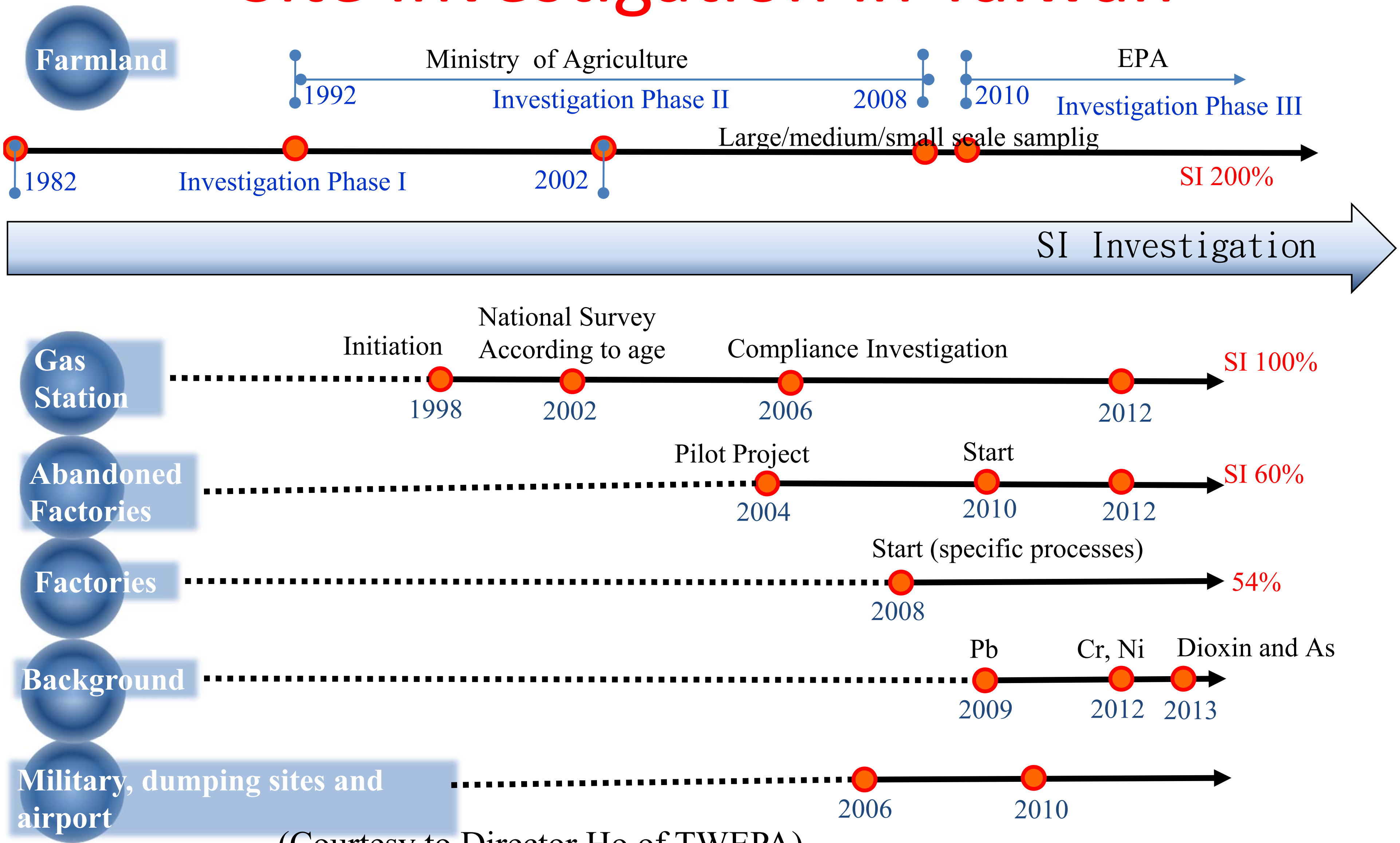
Tsair-Fuh Lin
Department of Environmental Engineering
Global Water Quality Research Center
National Cheng Kung University

March 23, 2016

成功大學
National Cheng Kung University

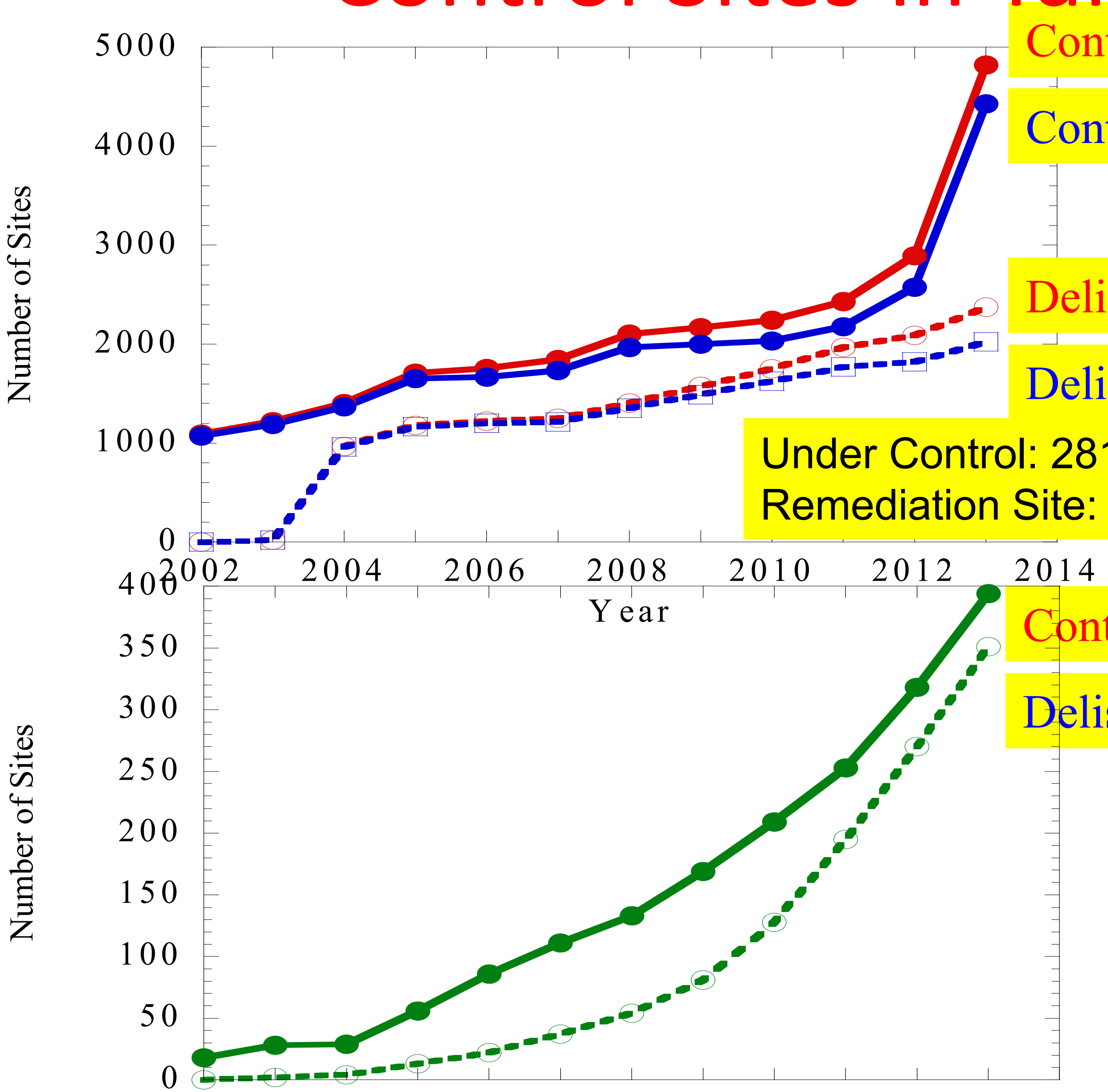
global wATer quality
research center

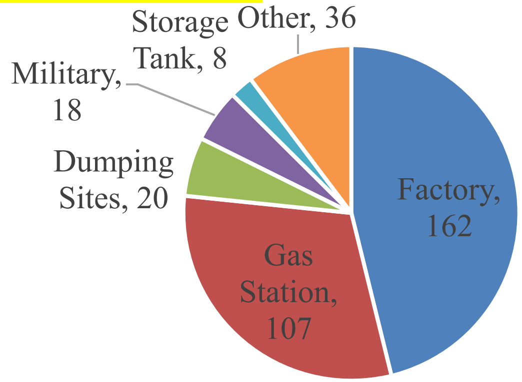
Site Investigation in Taiwan



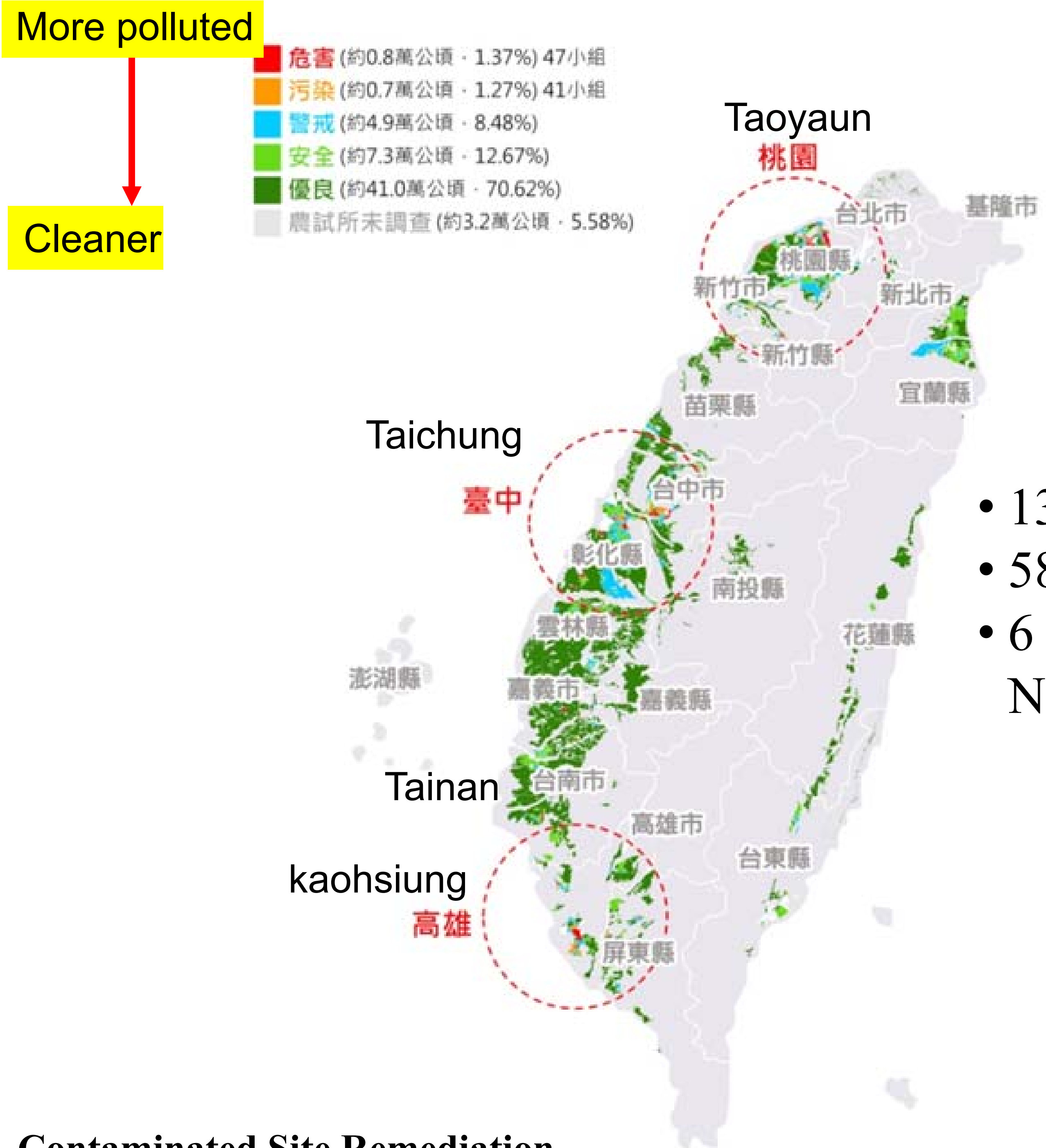
(Courtesy to Director Ho of TWEPA)

Control Sites in Taiwan

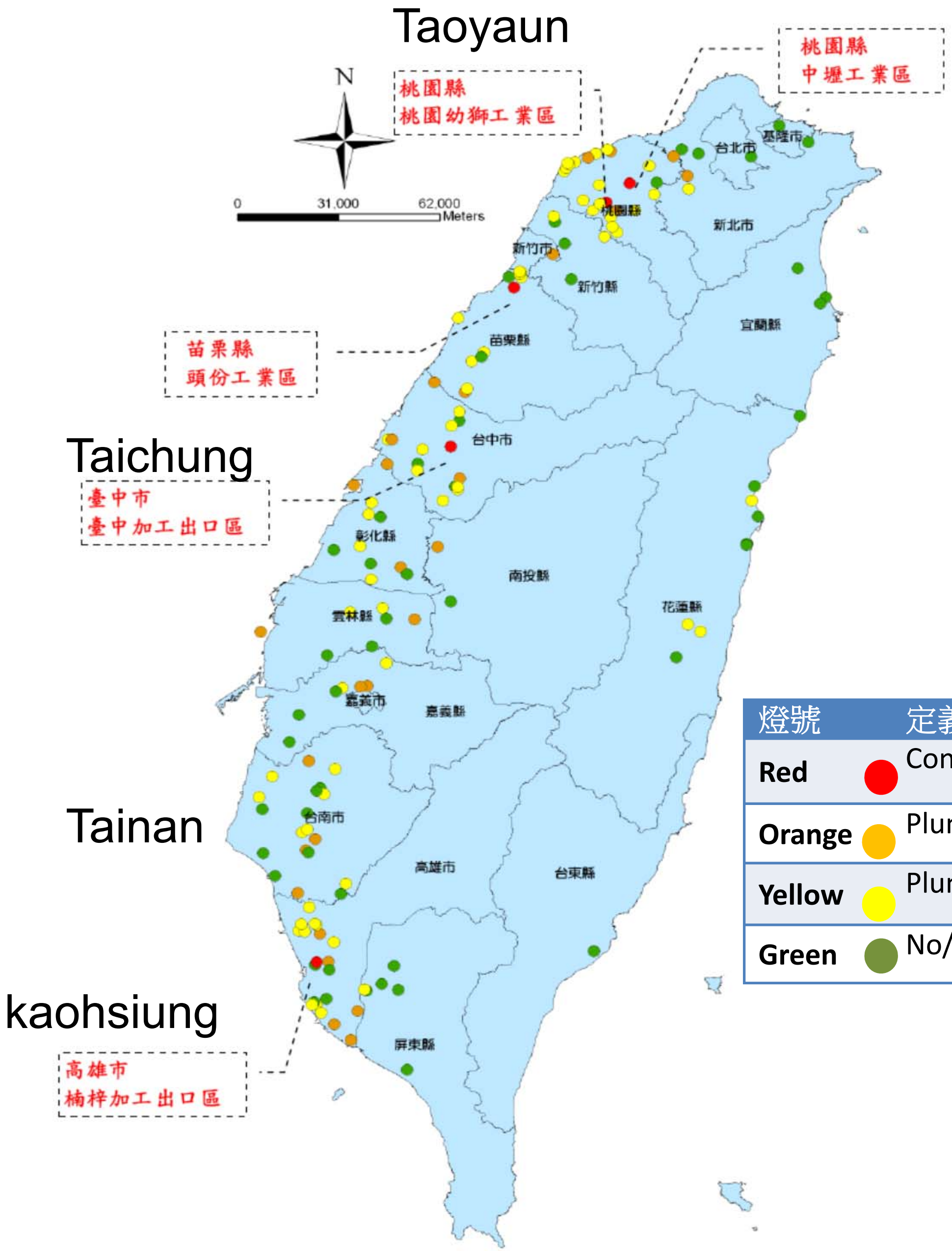




Farmland



- 130,000 samples
- 580,000 ha rice field
- 6 heavy metals (Cd, Ni, Cr, Zn, Cu, and Pb)



Industrial Park
(2014)

燈號	定義	處理情形
Red ●	Contaminant plume moved to outside park	5
Orange ●	Plume found (within the park)	27
Yellow ●	Plume found (remediated)	67
Green ●	No/low potential of contamination	52

151 Industrial parks

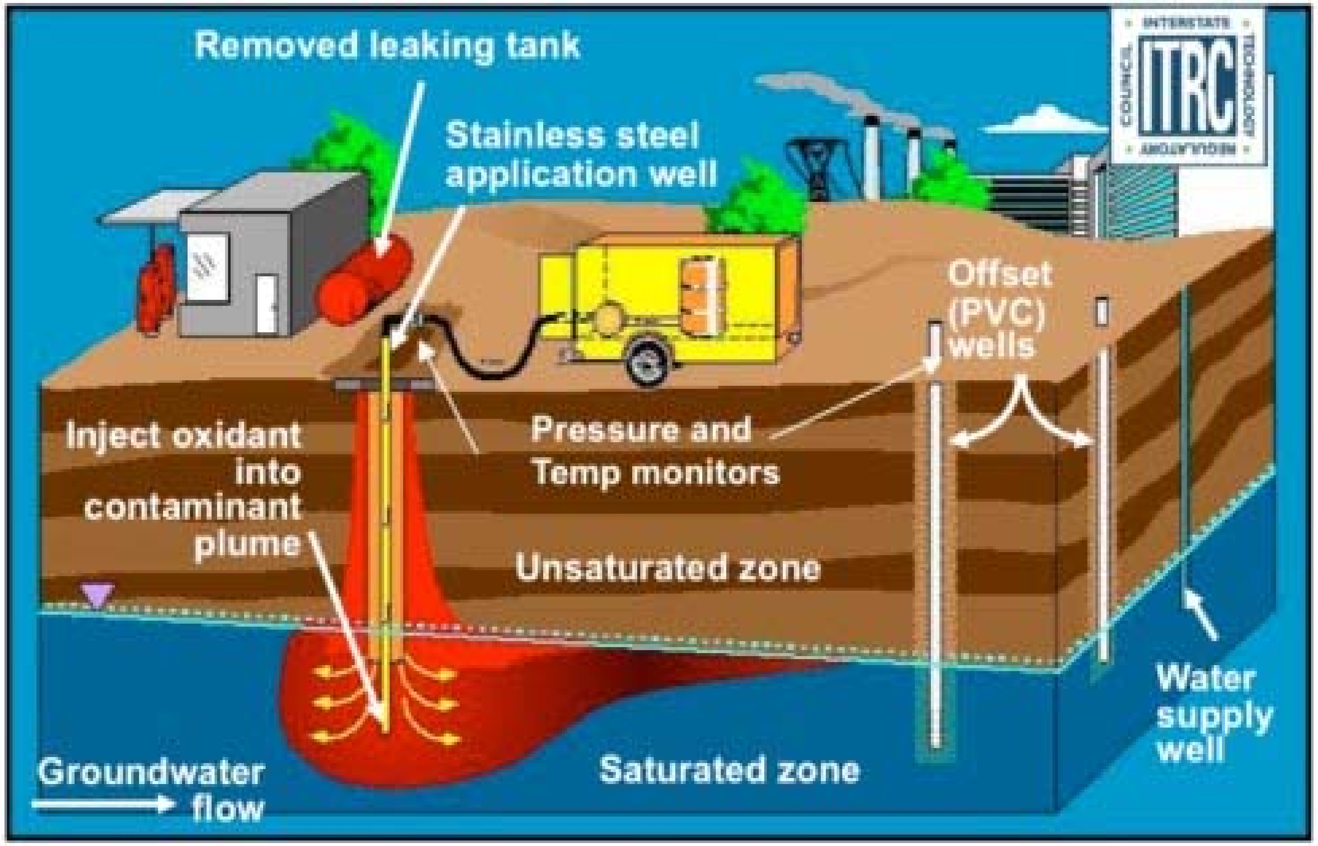
Soil and Groundwater Contamination in Taiwan

Type	Farm-land	Gas Station	UGS	Factories	Illegal Dumping	Others	Total
Control Sites	470	42	2	57	9	26	606
Remediation Sites	0	16	1	19	3	10	49
Delisted Sites	1737	19	1	22	3	3	1785

Contaminated Sites in Taiwan (2011)

- **Metals (Soil: 93.6%; GW: 6.3%)**
  - Cu (Soil: 1364 sites), Ni (1335), Cr (1094), Zn (1027)
- **Petroleum Hydrocarbons (Soil: 6.2%; GW: 42.2%)**
  - Benzene (GW: 104 Sites), Toluene (31), Ethyl Benzene, and Xylene (BTEX), Methyl *tert*-butyl ether (MTBE)
- **Chlorinated Hydrocarbons (GW: 43.2%)**
  - Trichloroethylene (TCE) (GW: 45 Sites), Dichloroethylene (DCE) (14), Tetrachloroethylene (PCE), and Vinyl Chloride (VC) (27)

Schematic of ISCO



In-Situ Chemical Oxidation (ISCO)

ISCO (*In-Situ* Chemical Oxidation)

- ISCO Involves the delivery of oxidants into subsurface to transfer contaminants of concern (COC), and to reduce the mass, mobility, and/or toxicity of contamination.
- May be used as a stand-alone remedial technique or used together with other means, such as bioremediation

Source Zone	Core zone of the plume	Distal zone of the plume
NAPL Recovery	Air Sparging and Soil Vapor Extraction	Monitored Bioremediation
Surfactant/Cosolvent Flushing	Engineered Bioremediation	Engineered Bioremediation
Steam Injection	*In-situ* Chemical Oxidation	*In-situ* Chemical Oxidation
Thermal Enhancement Recovery	Chemical Reduction	Chemical Reduction
In-situ Chemical Oxidation		Permeable Reactive Barrier

(ITRC, 2005)

- Best for high concentration plume zone (>10 mg/L)
- For low concentration zone (<1 mg/L) although applicable, it may be costly
- For residual NAPL or mobile NAPL zone, although it may succeed, it is very challenging

Important Criteria

- Four Criteria
  - Thermodynamics
    - Oxidation-reduction potential
    - Byproducts
  - Stoichiometry
    - SOD, Hydrolysis, Contaminants
  - Kinetics
    - Temp., pH, conc., catalyst, byproducts, background water quality, and organic matter
    - Free radicals and non radicals
  - Contact or not
    - Injection methods and homogeneity
    - Reductive matters

Advantages

- Advantages：
  - Ability to oxidize DNAPLs.
  - Reduction in overall treatment time.
  - Cheaper than capital-intensive pump-and-treat system.
  - No disturbing to above-ground structures.
  - No excavation of contaminated soil.

Oxidants Commonly Used

- Permanganate
- Catalyzed hydrogen peroxide (CHP)
- Ozone
- Persulfate
- Peroxone (ozone activated with hydrogen peroxide)
- Percarbonate

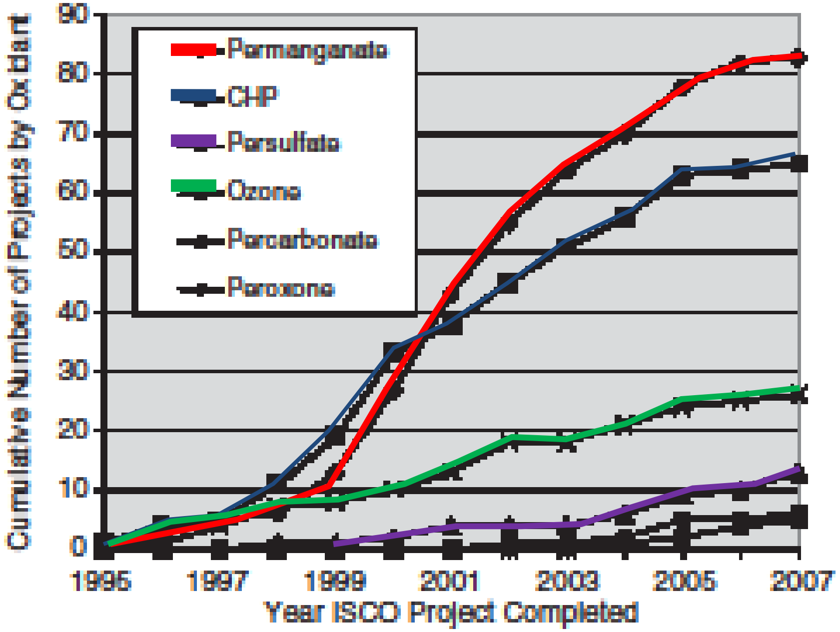
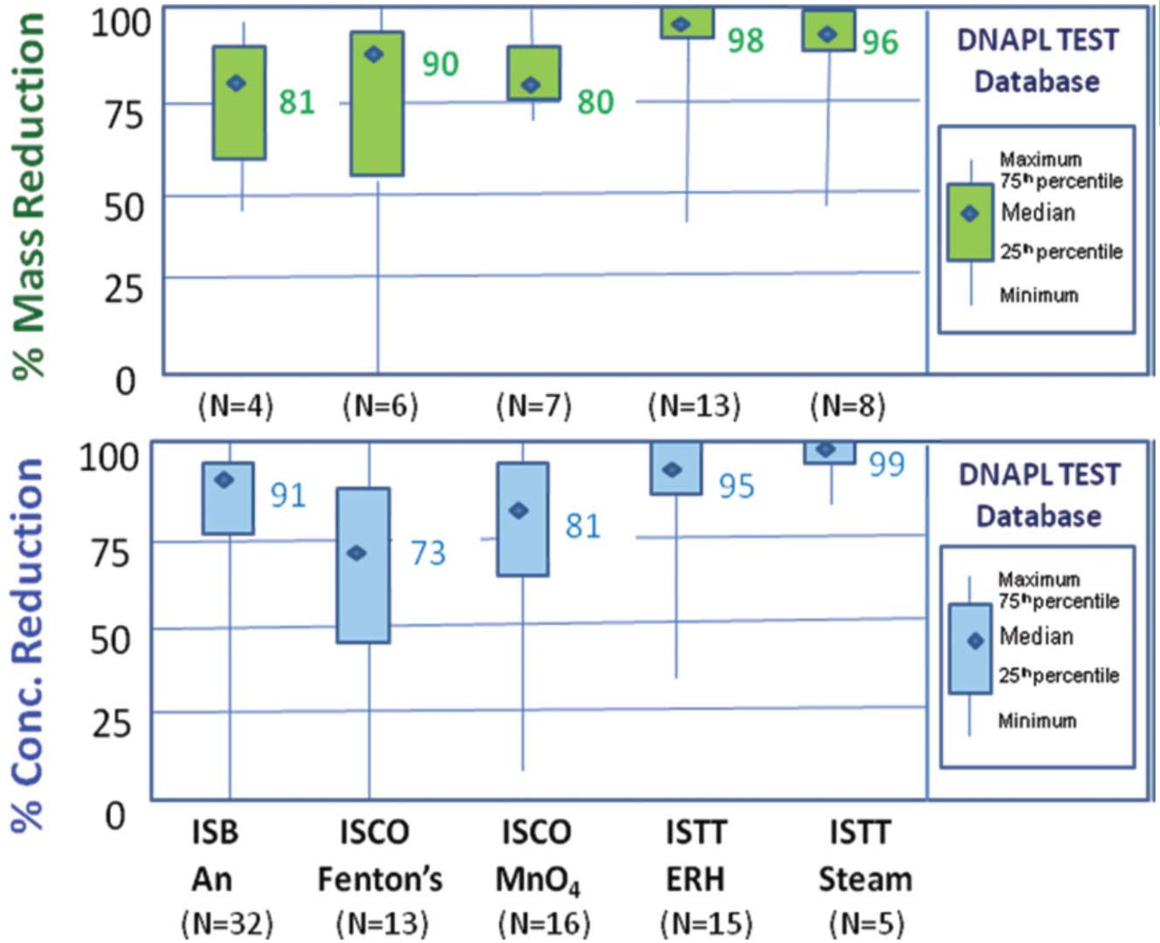


Figure 1. Cumulative frequency of oxidants used for ISCO projects over time. Notes: n = 182. The apparent decline in the frequency of the use of ISCO (the slope of the curves) is an artifact of the fact that there is a lag time between when a project is finished and when the results are made available to the public. Thus, the decrease in slope of the curves in this near the year 2007 should not be interpreted as a decline in the frequency of the use of ISCO as a remediation technology.

Krembs et al. (2010) GWMR: 30(4), 42–53

Performance



Stroo et al. (2012): ES&T, 46, 6438-47

Field-scale performance of the major source zone remediation technologies (Anaerobic ISB, ISCO with Fenton's Reagent or permanganate, and ISTT by electrical resistance heating or steam injection). Median values, percentiles, and ranges are shown for each technology. Results are taken from analyzing all chloroethene contaminated sites with relevant data in the DNAPL Technology Evaluation Screening Test database. Reductions in total chloroethene source mass and average concentrations (including daughter products) within or immediately downgradient of the source are plotted. N = number of case studies used for each technology and metric.

Key Limitations

- Delivery difficulties, Frequent concentration rebounds following treatment, and Relatively high costs.
- Rebound has been attributed to
- (1) reactants are short-lived and thus do not reach contaminants in low permeability matrices; (2) natural attenuation processes may be disrupted by reducing bacterial populations or oxidizing fermentable carbon; (3) sorbed contaminants may be released following oxidation of natural organic matter.

Stroo et al. (2012): ES&T, 46, 6438-47

ORP

Oxidant	Oxidation potential (volts)	Oxidation potential relative to chlorine
Hydroxyl radical	2.80	2.06
Sulfate radical	2.5-2.6	1.84-1.91
Ozone	2.07	1.52
Persulfate	2.01	1.48
Hydrogen peroxide	1.77	1.31
Permanganate	1.70	1.24
Chlorine	1.36	1.00
Oxygen	1.20	0.90

(Siegrist, 2001; Brown et al., 2003)

Treatability

(Derby 2009, http://www.tnenvironment.com/Pres09/Derby.pdf)

Contaminant	Percarbonate and Catalyst	Fenton's Reagent	Permanganate	Persulfate	Activated Persulfate	Ozone	Ozone + H2O2
Hydrocarbons	A	A	B	B	B	A	A
Benzene	A	A	D	B	B	A	A
MTBE	A	B	B	C	B	B	A
Phenols	A	A	B	C	B	A	A
Chlorinated ethenes	A	A	A	B	A	A	A
Chlorinated ethanes	A	B	C	D	C	B	B
PAHs	A	A	B	B	A	A	A
PCBs	B	C	D	D	D	B	
Explosives	A	A	A	A	A	A	A

Oxidant Effective Key	A	B	C	D
Half Life	Short	Intermediate	Intermediate	Long
Free Energy*	Low	Low	Intermediate	High
Degree of Completion	Most	Intermediate	Low	Very Low

* low is better

Oxidant Demand

- **Oxidant Demand**
  - Soil Oxidant Demand, SOD +
  - Oxidant decay (ex. H_2O_2) +
  - Dosage for oxidizing contaminant
- **Factors influencing SOD**
  - Inorganic (Iron, arsenic, sulfite)
  - Natural organic matter
  - Ranging from ＜1 to 20-30 g-oxidant/ kg-soil (> Dosage for oxidizing contaminant by several orders)

Site Characteristics

- Small Area: Four oxidants
- Large Area: Choose non-radical based, stable oxidants (permanganate and persulfate)
- High permeability area: Four oxidants
  - Advection is the major transport mechanism
- Low permeability area: As diffusion becomes important, choose non-radical based, stable oxidants

Advantages and Disadvantages for the Four Oxidants

Oxidant	Advantages	Disadvantages
Hydrogen peroxide	1) Potential to complete remediation in short time. 2) Nonspecific oxidant 3) More full-scale application experiences 4) Increase dissolved oxygen levels and may enhance aerobic bioremediation	1) Evolve substantial heat and gas 2) Short half-life time. 3) Narrow pH range. 4) Short transport distance under low permeability system
Ozone	1) Potential to complete remediation in short time 2) Nonspecific oxidant 3) Increase dissolved oxygen levels and may enhance aerobic bioremediation	1) Short half-life time 2) Increased risk of fugitive vapors entering building structures, utility conduits, particularly in absence of adequate vapor recovery technology 3) Short transport distance under low permeability system 4) On-site gas production and delivery equipment required
Permanganate	1) No heat, steam, and vapor production, less associated health and safety concerns 2) Oxidation over extended period, increasing possibility to contact with contaminants 3) Oxidize organics over a wider pH range	1) Solid precipitation and aquifer pore clogging 2) Short transport distance under low permeability system 3) Higher SOD 4) Few petroleum remediation projects completed using this technology due to limited effectiveness
Persulfate	1) High potential to complete remediation 2) Low SOD 3) Oxidations over extended period, increasing possibility to contact with contaminants 4) Oxidize organics over a wider pH range	1) Need catalysts 2) pH decrease sharply after reaction 3) Fewer application experiences

Design consideration

Engineering Application

Occupational Health

- Strong oxidants
- H_2O_2 may cause high temperature and oxygen.
  - Fire and explosion problems
- Solid permanganate powder is hazardous
- Ozone may increase flammability of other materials

Hydrogen Peroxide H_2O_2

- Direct oxidation

$$H_2O_2 + H^+ + e^- \rightarrow H_2O + OH^-$$

- Fenton reaction (+Fe2+) under acidic condition

radicals

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$

- May oxdize Cl-HCs, BTEX, PAH and phenols

Sodium Percarbonate

- Sodium carbonate + hydrogen peroxide
- $Na_2CO_3 \cdot 1.5H_2O_2$
- A colorless, crystalline, hygroscopic and water-soluble solid
- Used in some eco-friendly cleaning products

Ozone O_3

- The only gaseous oxidant in ISCO
- May oxidize PAHs, Petroleum HCs, Pesticides
- Direct Oxidation

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + 2H_2O$$

- Radical reaction (via OH^-, Fe^{2+} or humin)

  $OH\cdot$ and $HO_2\cdot$

Ozone O_3

- TCE degradation

$$C_2HCl_3 + O_3 + H_2O \rightarrow 2CO_2 + 3HCl$$

- MTBE degradation

  -intermediates, ex. TBF, TBA, formaldehyde , acetone and methyl acetate

- May provide O2 (for bioremediation)
- May form bromate, if Br- is present

Permanganate MnO_4^-

- $KMnO_4$ in solid salt form, $NaMnO_4$ in solution form
- Electron transfer

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

- Stable and may be monitored by color
- May oxidize Cl-HCs
- May change pH

  Cr(VI) and Hg may release ($Cr^{3+} \rightarrow Cr^{6+}$)

Persulfate $S_2O_8^{2-}$

- Catalyzed by light, heat, and catalysts (Fe for example)
- Pr … yl radicals

$$S_2O_8^{2-} + Heat/h\nu \rightarrow 2\cdot SO_4^{-}$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow \cdot SO_4^{-} + Me^{(n+1)+} + SO_4^{2-}$$

$$\cdot SO_4^{-} + H_2O \rightarrow \cdot OH + HSO_4^{-}$$

- Advantages
  - -$\cdot SO_4^-$ is more stable than ·OH
  - -may react with benzene
  - -Lower SOD with NOM (comp with MnO4)
  - -wider pH range (2.5-11)

More persulfate

Persulfate ($S_2O_8^{2-}$)

- A strong oxidant with ORP = 2.01 V
- End product is sulfate (relatively safe)
- May produce sulfate radical ($SO_4^- \cdot$, E^0=2.6 V) and hydroxyl radical ($OH\cdot$, E^0=2.8 V) under the conditions (addition) of
  - pH
  - UV light
  - Heat
  - Transition metals

General Persulfate Oxidation and Related Chemical Reactions

$$S_2O_8^{2-} \xrightarrow{\text{heat}} 2\cdot SO_4^- \quad (1)$$

$$S_2O_8^{2-} + Fe^{+2} \longrightarrow Fe^{+3} + \cdot SO_4^- + SO_4^{2-} \quad (2)$$

$$S_2O_8^{2-} \xrightarrow{h\nu} 2\cdot SO_4^- \quad (3)$$

$$\cdot SO_4^- + H_2O \longrightarrow \cdot OH + HSO_4^- \quad (4)$$

$$\cdot SO_4^- + Fe^{+2} \longrightarrow Fe^{+3} + \cdot SO_4^- + SO_4^{2-} \quad (5)$$

(US EPA)

More persulfate

Oxidant Demand

- Reductive compounds
- Soil Oxidant Demand
- Anions
  - Carbonate and bicarbonate
  - Chloride
    - Scavenger
    - Metal-complexing agent
    - Byproducts of chlorinated solvents
    - Chlorine radical formation

Activation methods	Related chemical reactions
Dissolved(or Chelate) Metals	$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-\cdot} + SO_4^{2-} + Fe^{3+}$
Activation with Alkaline	$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + OH^\cdot$
UV or Heat	$S_2O_8^{2-}$ + UV or Heat $\rightarrow 2SO_4^{-\cdot}$

Remediation Technologies Used in Gas Stations in Taiwan (Soil)

場址基本資料		離地(Ex-situ)處理		現地(In-situ)處理			
縣市別	場址名稱	Excavation 法	土耕 Land farming	土…SVE…法	現地化 ISCO …法	Bioventing 氣法	生物整治 Bioremediaiton
KH City 高雄市	自立加油站			✓	✓		
	台亞華盟加油站			✓	✓		
	山隆高雄加油站			✓	✓		
	展利加油站	✓		✓			
	全國仁武站			✓		✓	
CH 彰化縣	總來加油站	✓	✓				
	永益加油站			✓			
	竹塘加油站			✓		✓	
	寶群加油站			✓			
	福懋忠孝加油站			✓		✓	
YL 雲林縣	大學加油站			✓	✓		
	新南環路加油站			✓	✓		
TN 台南市	太子宮加油站			✓		✓	
	永信加油站	✓			✓		
	台亞新市加油站			✓	✓		
	一心加油站	✓					
	統一精工金華站			✓		✓	
YL 屏東縣	山隆東港加油站				✓		✓
Sum 合計	18 站	4	1	13	8	4	1

Remediation Technologies Used in Gas Stations in Taiwan (Groundwater)

場址基本資料		整治技術名稱				
		離地(Ex-situ)處理	現地(In-situ)處理			
縣市別	場址名稱	地 P&T 抽出處理法	空氣注 Air Sparging	Dual Phase/ Muitple Phase 相抽除法	現地化學 ISCO	Bioremediaiton 治法
彰化縣 CH	西門加油站	✓	✓	✓		
	統一精工和美加油站	✓	✓	✓		
	仁好加油站	✓	✓	✓		
	永益加油站		✓			
	竹塘加油站			✓		✓
	寶群加油站	✓	✓			
	和成加油站	✓	✓			
雲林縣 YL	五港加油站		✓			
	大學加油站	✓	✓		✓	
	新南環路加油站	✓	✓		✓	
台南市 TN	嘉南加油站		✓	✓		
	全國新營加油站	✓	✓		✓	
	太子宮加油站	✓	✓			
	永信加油站				✓	✓
	果毅加油站			✓	✓	
	一心加油站				✓	
	統一精工金華站		✓		✓	
高雄市 KH	大旗楠加油站				✓	✓
	展利加油站		✓	✓	✓	
	全國仁武站		✓			
屏東縣 PT	山隆東港加油站				✓	✓
澎湖縣 PH	天祥加油站				✓	✓
合計 Sum	22 站	9	15	7	11	5

Case Study

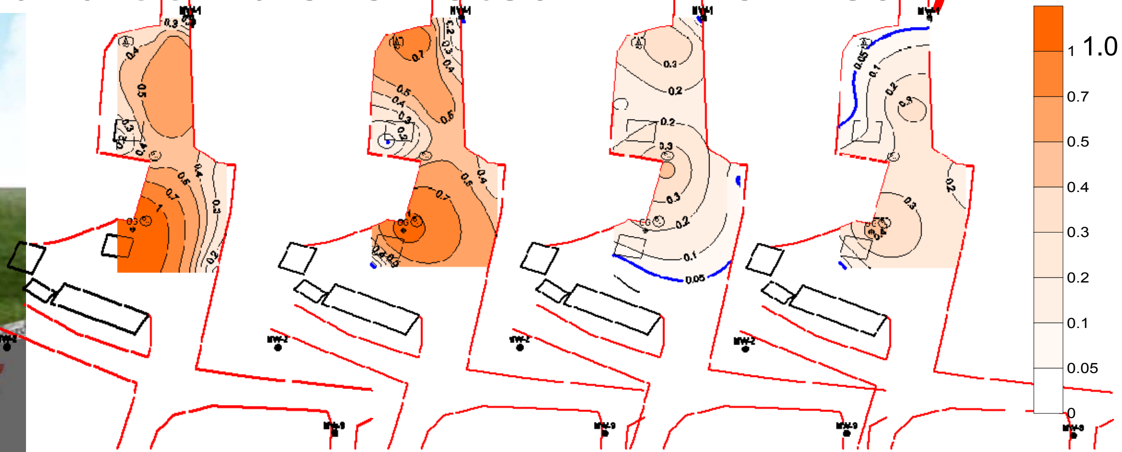
ISCO Case (Taiwan)

- Kaohsiung, Taiwan
- Time of project: Aug. 2003 – May 2005
- Major contaminant: TCE
- Maximum conc.: 4,340μg/L (Well OG)

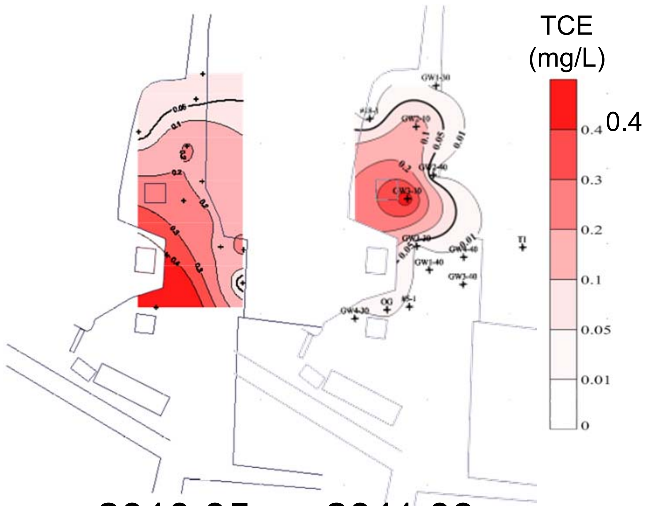
From Sinotech Corp.

A TCE Contaminated Site in Taiwan

(KH-TCE Site, Drs. SJ Pan and CC Liu of Sinotech Environ Tech)



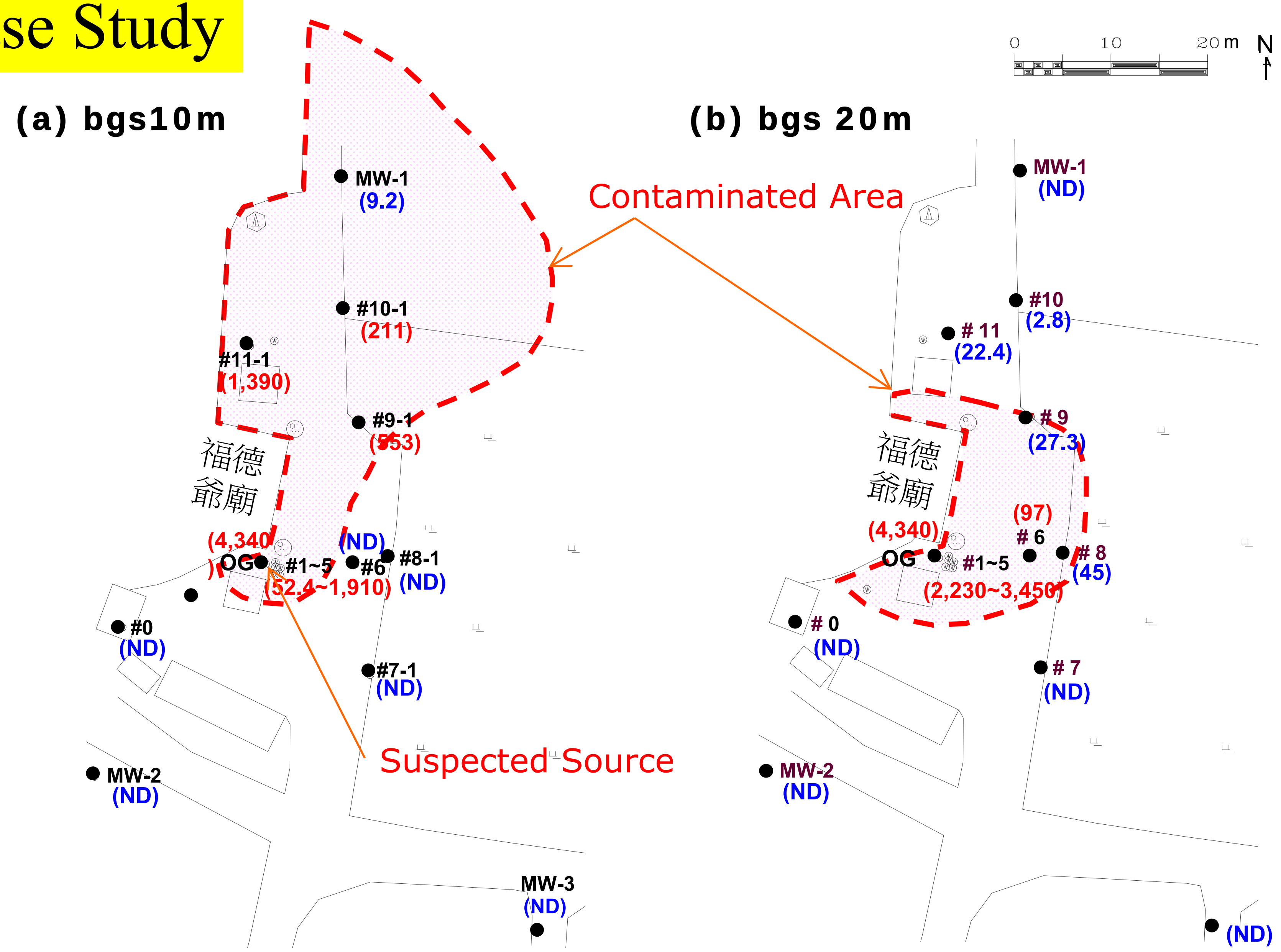
2006.02 2007.01 2008.01 2009.03



2010.05 2011.09

- Located in Kaohsiung, Taiwan
- DNAPL Contamination discovered in 2001
- TCE > 1 mg/L at hotspot

Case Study



TCE concentration (μg/L) before ISCO

Case Study

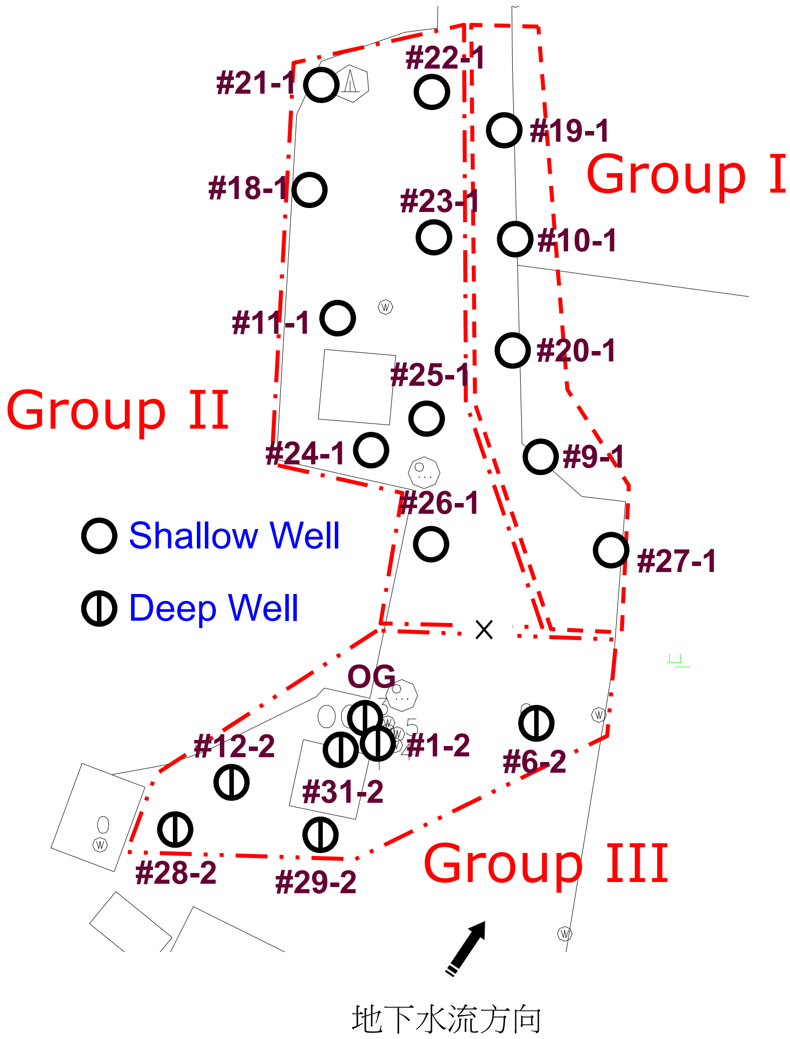
ISCO Case (2)

- Geology
  - NE and South side: higher permeability, $K = 1.5 \times 10^{-2}$ cm/sec
  - West side: less permeable
- Water table: 6-7 m bgs
- GW flow direction: SW to E or NE
- GW Velocity: 30 m/year (apparent)

Case Study

ISCO Design

- Oxidant: $KMnO_4$
- Wells
  - Group I, II, and III
  - Shallow (Screen at 8-11m)
  - Deep (Screen at 16-20m)



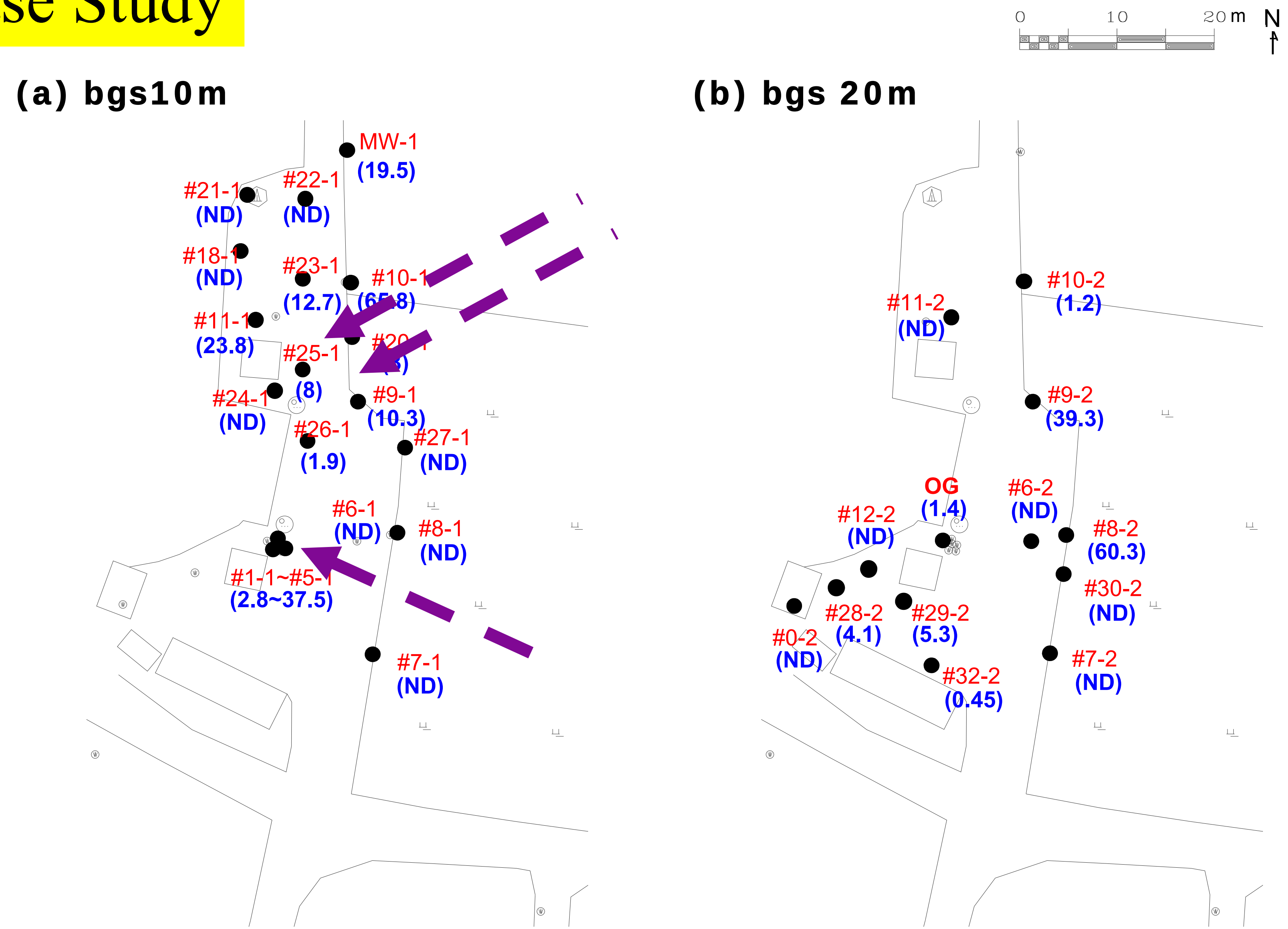
Case Study

ISCO Design

- Dosing Procedures
  - Phase I (Mar 2004-June): To treat known plume
  - Phase II (Oct. 2004-Nov. 2004): to treat the rebound in Well OG
  - Phase III (Apr. 2005): To polish

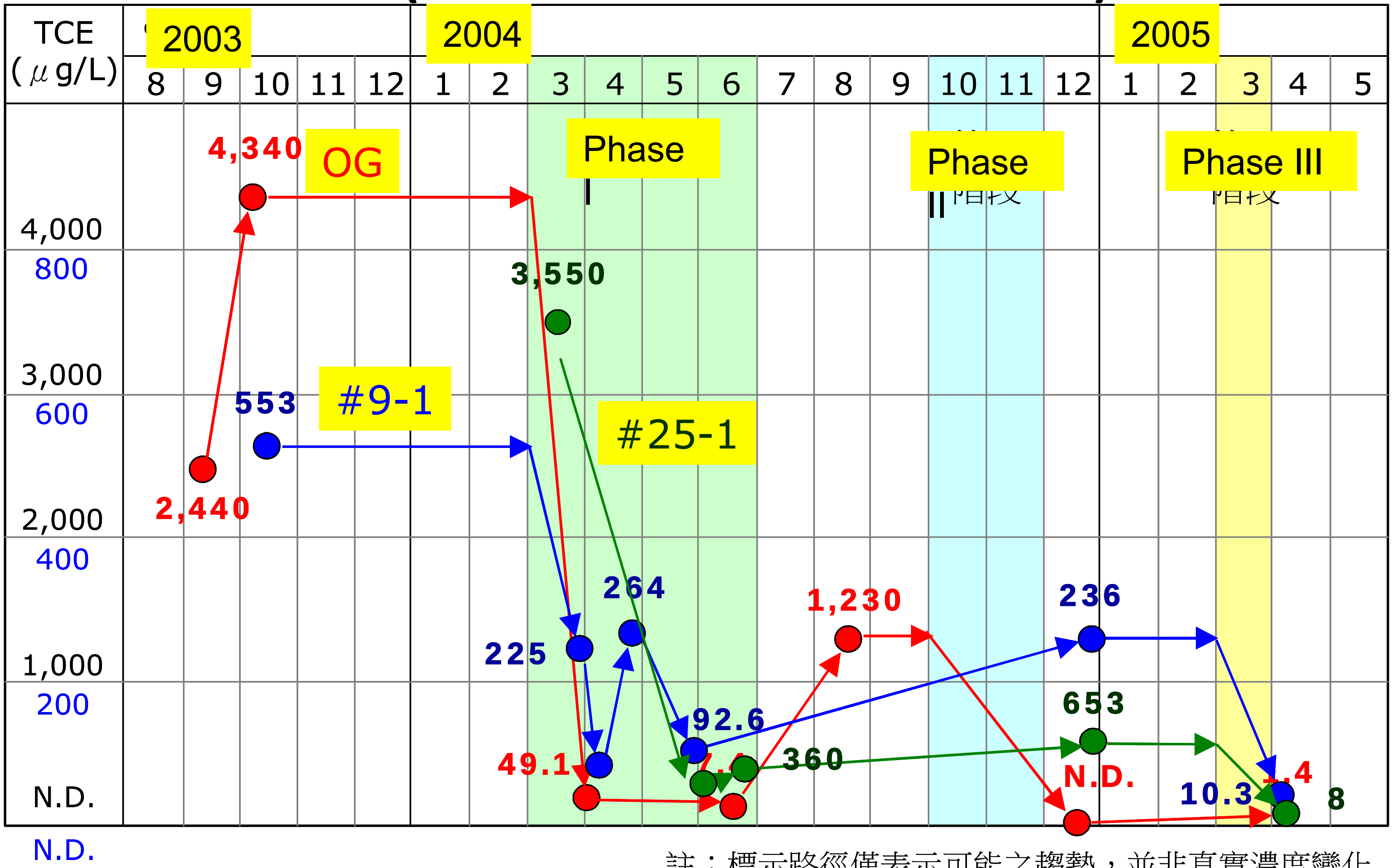
Zone		Group		
		I	II	III
I	Oxidant Con (mg/L)	**1,000**		
	Dose(m^3)	700	1,220	1,020
II	Oxidant Con (mg/L)	**5,000**		
	Dose (m^3)	35	30	35
III	Oxidant Con (mg/L)	**500**		
	Dose (m^3)	347	173	120

Case Study



TCE Concentration (μg/L) after ISCO

TCE Concentration Change (OG、#9-1、#25-1)



註：標示路徑僅表示可能之趨勢，並非真實濃度變化

Case Study

Water Quality after Treatment

- Organics
  - VOCs: among 60 chemicals
  - TCE is the major pollutants
  - Chloroform and trichloroethane were present in trace levels
- Inorganics
  - Carbonate, Chloride, conductivity and ORP level increased
  - Cr (VI) was found initially, and then reduced
  - Mn level increased

Case Study

Lesson Learned

- TCE plume shrank in short time
- In long term, the concentration bounced back
- Lesson learned
  - Consider SOD and Apply enough dose
  - TCE concentration rebounded, so add oxidant in different stages
  - Clogging by MnO_2. May use well purging
  - At low permeable zone, lower efficiency was obtained

Status Review

Status

Krembs et al. (2010) GWMR: 30(4), 42–53

Table 1
Summary of Previous Case Study Reviews that Included ISCO Projects

Name	Reference	Year	Sites[1]	Type[2]	Comments
In situ remediation technology: in situ chemical oxidation	USEPA	1998	14	D	Focused exclusively on ISCO case studies and showed examples of its use.
Technology status review: in situ oxidation	ESTCP	1999	42	BS	Focused exclusively on ISCO and included quantitative analysis, for example, the percentage of sites that were successful vs. those that were not and total project costs.
Technical and regulatory guidance for in situ chemical oxidation of contaminated soil and groundwater	ITRC	2001	8	D	Used case studies as supporting appendix to ISCO guidance document.
Assessing the feasibility of DNAPL source zone remediation: review of case studies	GeoSyntec for NAVFAC	2004	28	BS	Focused on DNAPL source zone remediation including ISCO and other technologies. Performed quantitative analyses of results.
DNAPL remediation: selected projects approaching regulatory closure	USEPA	2004	4	D	Examined selected case studies of DNAPL sites at or near regulatory closure, including what remediation technologies were used as well as regulatory framework.
Technical and regulatory guidance for in situ chemical oxidation of contaminated soil and groundwater, 2nd ed.	ITRC	2005	14	D	Used case studies as supporting appendix to ISCO guidance document.
Analysis of DNAPL source depletion costs at 36 sites	McDade et al.	2005	13	BS	Examined remediation cost data for 36 DNAPL sites, including ISCO as well as other technologies.
Performance of DNAPL source depletion technologies at 59 chlorinated solvent impacted sites	McGuire et al.	2006	23	BS	Examined remediation performance at 59 DNAPL sites, including ISCO and other technologies. Developed numerical metrics to assess success and rebound. Companion paper to McDade et al. (2005).
Critical evaluation of state-of-the-art in situ thermal treatment technologies for DNAPL source zone treatment	Johnson et al. for ESTCP	2007	0	BS	Performed case study review for the purpose of providing guidance on selection of thermal remediation technologies based on generic site scenarios.

[1]Sites refer to number of ISCO case studies in that source.
[2]Type: D = demonstration type case study review; BS = broad-scale type case study review; DNAPL = focus on sites with DNAPL.

Data:

- Total of 242 sites located in 42 U.S. states and 7 nations.
- Major site types: federal, manufacturing/industrial, and dry cleaning facilities.

Status

Applications with other methods

Krembs et al. (2010) GWMR: 30(4), 42–53

- 89% combined with other remediation technologies
  - 68% with a pre-ISCO couple
  - 30% coupling during ISCO
  - 38% used a post-ISCO couple, and
  - 26% used a pre-ISCO couple and a post-ISCO couple (n = 90).
- Coupling defined as
  - the use of multiple remediation technologies
    - in the same place (e.g., P&T + ISCO)
    - at two directly adjacent locations within the same site (e.g., SVE (vadose zone) + ISCO (gw))

Goal Attainment

Krembs et al. (2010) GWMR: 30(4), 42–53

(1) Meet MCLs;
(2) Meet alternative cleanup (ACLs);
(3) Reduce mass or concentration by a predetermined percent;
(4) Reduce mass/concentration/time to cleanup; or
(5) Evaluate effectiveness or optimize future work

Status

Table 2
Summary of ISCO Project Goals, Selection, and Frequency of Reported Goal Attainment

Goal of Remediation	Description	Percent of Sites Attempting Goal ($n = 151$)	Percent of Sites Attempting and Meeting Goal ($n = 121$)
Meet MCLs	The project team attempted to meet the most stringent regulatory groundwater criteria for COC concentrations.	37%	15%
Meet ACLs (risk-based)	The project team attempted to meet ACLs in groundwater. ACLs are numerical concentrations that are by definition higher than MCLs. Their use was often associated with a site-specific risk evaluation and/or a regulatory framework in which certain aquifers (e.g., low yield) are not required to meet MCLs.	25%	39%
Reduce mass by certain %	A given percent reduction in COC mass or concentration was targeted prior to remediation.	9%	46%
Reduce mass and/or time to cleanup	The goal of the project was to generally reduce contaminant mass and/or concentration, thereby reducing the time to cleanup. This goal differs from the above in that there was not a predetermined numerical percent reduction that was to be met.	31%	80%
Evaluate effectiveness and optimize future injections	This goal includes a field-scale evaluation of effectiveness as well as remedial design analysis, such as well spacing and oxidant persistence, and is most common in pilot studies.	27%	95%

Stringent → Less Stringent

Reduction =
(Max before ISCO – Max after ISCO)/ Max before ISCO

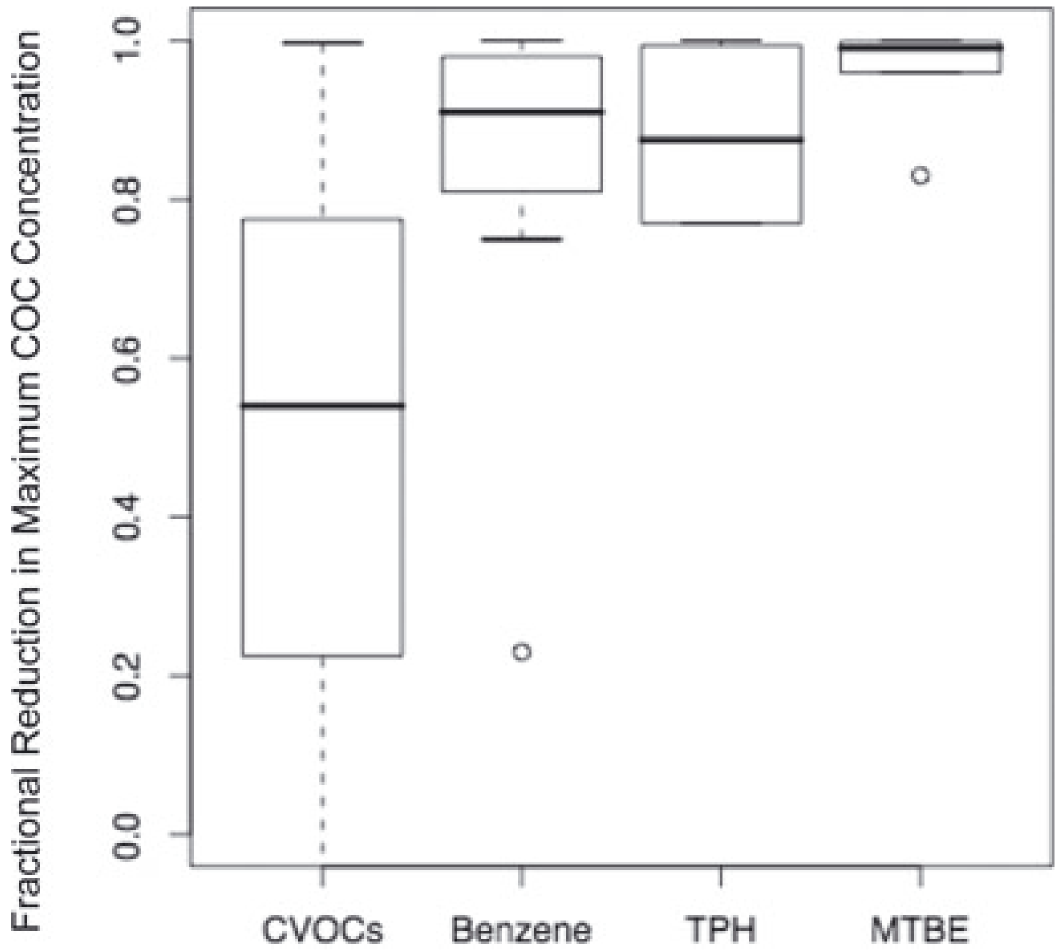
Rebound:
(One year post ISCO – lowest post ISCO)/pre-ISCO baseline ≥ 0.25

May have more than one goal

Status

Efficiency

Krembs et al. (2010)



Difficult → Easy to remediate

Figure 2. Boxplot of reductions in groundwater concentrations reported for chlorinated solvents and fuel-related COCs. Notes: The *n values are 55, 10, 6, and 6 from left to right.*

Chemical and Geology of Sites

Status

Table 3
Summary of COCs Treated and Subsurface Conditions at Sites Where ISCO Has Been Used

COCs Present[1]	Percent of Sites,[2] $n = 223$ (%)	Geologic Groups[3]	Percent of Sites, $n = 209$ (%)
Chloroethenes	70	Group A: permeable and homogeneous	21
Benzene, ethylbenzene, toluene, xylenes	18	Group B: impermeable and homogeneous	3
Total petroleum hydrocarbons/ GRO/DRO	11	Group C: permeable and heterogeneous	47
Chloroethanes	8	Group D: impermeable and heterogeneous	15
MTBE	7	Group E: fractured rock with low porosity	7
PAHs	7	Group F: fractured rock with high porosity	7
Chlorobenzenes	5		

[1]Other COCs with <5% of sites include methylene chloride, chloroform, carbon tetrachloride, pentachlorophenol, arsenic, cyanide, herbicides/pesticides, methyl isobutyl ketone, and TAME.
[2]Percentages sum to greater than 100% because multiple COC groups are present at some sites.
[3]Permeable = $K > 10^{-4}$ cm/s. Homogeneous = $K_{max}/K_{min} < 1000$

Krembs et al. (2010)

Data:

- > 99% involved treatment of VOCs, petroleum compounds, or semivolatile organic compounds,
- 70% focused on treatment of chlorinated ethenes
- 43% of sites contained DNAPL
- 11% contained LNAPL
- Among chlorinated solvent sites, 66% had GW > 1% of the solubility limit
- Groups A and C are the most common geological groups

Status

Table 4
Summary of Oxidant Delivery Methods Used at Sites Where ISCO Has Been Applied

Oxidant Delivery Method	Percent of Sites,[1] $n = 181$ (%)
Injection wells	40
Direct push	23
Sparge points	14
Infiltration	10
Injectors	7
Recirculation	7
Fracturing	6
Mechanical mixing	2
Horizontal wells	1

[1]Percentages sum to greater than 100% because multiple delivery techniques were used at some sites. "Injectors" refers to permanent well points that are designed to mix activators and oxidants at the well point so that they may be delivered simultaneously. "Infiltration" refers to trenches, galleries, or vertical well points installed in the vadose zone designed so that the oxidant will migrate vertically through the treatment zone.

Design Consideration

To help design

Krembs et al. (2010)

- 78 % projects (n = 121) with bench scale treatability studies

With different goals

- demonstrating COC degradation (53% of sites);
- measuring natural oxidant demand (48%);
- optimizing system chemistry (37%);
- evaluating secondary groundwater impacts (9%); and/or
- evaluating the buffering capacity or activating attributes of the natural soil (8%)

About 60% with a field pilot test (n = 87).

Status

Design Parameters *Krembs et al. (2010)*

Table 5
Summary of ISCO System Design Parameters for Projects Involving Four Common Oxidants[1]

Design Parameters and Median Values	Permanganate[2]	CHP	Persulfate	Ozone
Design radius of influence (feet)	14 (29)	15 (30)	13 (6)	25 (5)
Observed radius of influence (feet)	25 (11)	15 (6)	20 (3)	38 (2)
Oxidant dose (g/kg)	0.4 (36)	1.2 (19)	5.1 (6)	0.1 (4)
Number of pore volumes delivered	0.16 (32)	0.073 (26)	0.57 (6)	No data
Number of delivery events	2 (65)	2 (57)	1 (10)	1 (15)
Duration of delivery events (days)	4 (45)	6 (42)	4 (7)	210 (15)

[1]For additional data on these parameters refer to Krembs (2008).
[2]Values in parenthesis = number of sites included in computing the median value given.

DNAPL

- Less likely to meet MCLs (14% vs. 48%)
- Deliver a greater number of pore volumes (PVs) of reagents (median 0.13 vs. 0.056 PVs)
- *Higher oxidant dose (median 1.1 vs.* 0.27 g oxidant/kg contaminated media).

Status

DNAPLs

Krembs et al. (2010)

DNAPL (cont'd)

- Larger number of delivery events (median 2 vs. 1).
- Less likely to use ozone or peroxone at DNAPL sites (5% vs. 15% for ozone, 0% vs. 3%, for peroxone).
- Shorter mean duration of delivery events (9 d vs. 16 d)
- Performance results
  - Unable to meet MCLs (0% vs. 21%)
  - *More difficult to attain site closure (10% vs. 25%)*
  - no less likely to meet ACLs (39% vs. 50%)

  importance of setting realistic expectations for ISCO/DNAPL

Status

DNAPLs

Krembs et al. (2010)

DNAPL (cont'd)

- More likely to experience rebound in GW (82% vs. 50%) *and in* a greater percentage of monitoring locations (53% vs. 27%)
- A higher total treatment cost (median $390,000 vs. $187,000)
  - More difficult to remediate,
  - Greater duration of delivery events,
  - Greater number of PVs of reagents, and
  - Greater mass of oxidant
- Median unit costs ($161 vs. $48 per cubic yard treated) (not statistically significant)

Status

Table 6
Delivery Method by Geology Group

Delivery Method	Group A (*n* = 38)[2]	Group B (*n* = 4)	Group C (*n* = 80)	Group D (*n* = 19)	Group E (*n* = 13)	Group F (*n* = 10)
	Percent of Sites[1]					
Well injection	47%	0%	33%	37%	69%	30%
Direct push	24%	100%	24%	37%	8%	10%
Sparge points	21%	0%	16%	5%	0%	10%
Infiltration	3%	0%	9%	5%	15%	40%
Injectors	5%	0%	9%	5%	8%	10%
Recirculation	5%	0%	9%	0%	15%	10%
Fracturing	0%	25%	9%	5%	8%	0%
Mixing	0%	0%	0%	16%	0%	0%
Horizontal well injection	0%	0%	1%	0%	0%	0%

[1]Percentages sum to greater than 100% because multiple delivery techniques were used at some sites. "Injectors" refers to permanent well points that are designed to mix activators and oxidants at the well point so that they may be delivered simultaneously. "Infiltration" refers to trenches, galleries, or vertical well points installed in the vadose zone designed so that the oxidant will migrate vertically through the treatment zone.
[2]Value in parentheses = number of sites included in computing the percentage.

Table 3
face Conditions at Sites Where ISCO H

Geologic Groups[3]

Group A: permeable and homogeneous
Group B: impermeable and homogeneous
Group C: permeable and heterogeneous
Group D: impermeable and heterogeneous
Group E: fractured rock with low porosity
Group F: fractured rock with high porosity

Table 4
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Delivery Methods

Krembs et al. (2010)

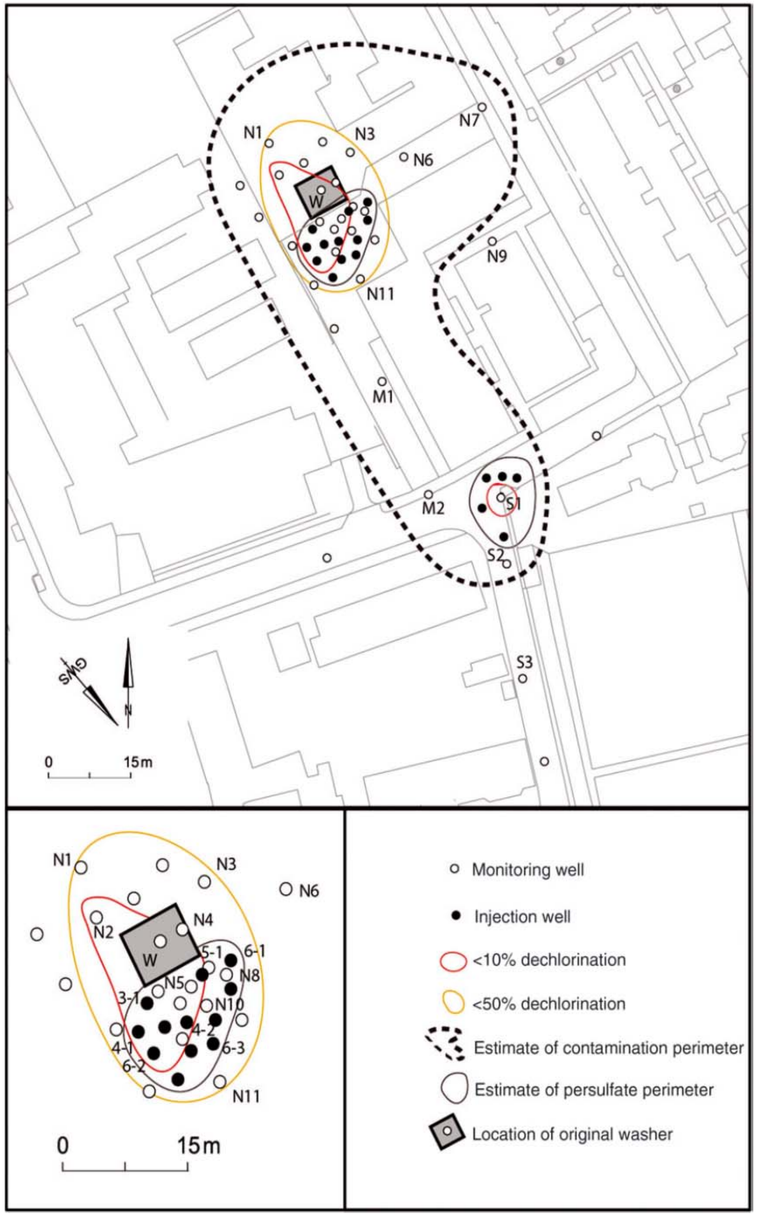
Cost

Status

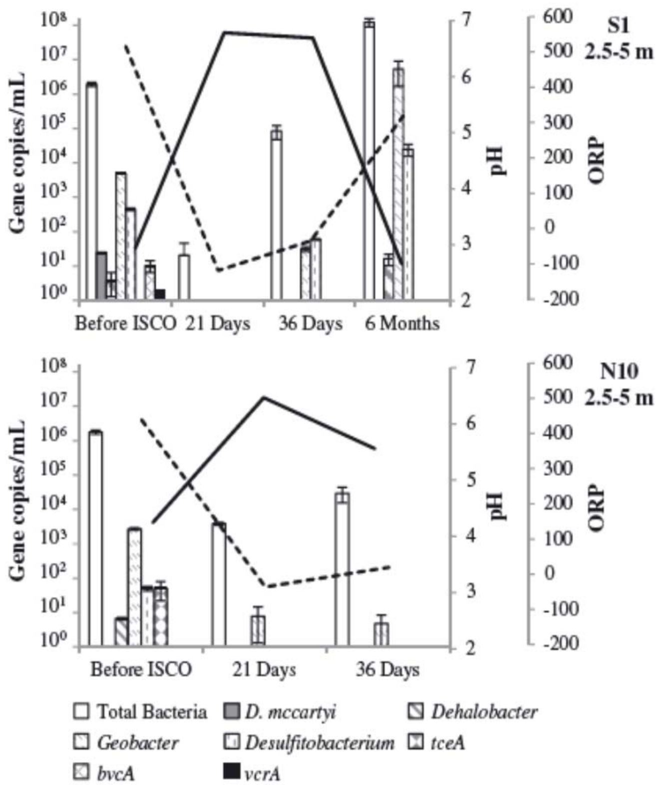
Krembs et al. (2010) GWMR: 30(4), 42–53

- Median cost = $220,000/project
- Median unit cost of $94/yd3 treated
- Total cost was greater for chlorinated compounds compared with fuel-related compounds
- Total cost was lower at homogeneous and permeable sites (geology group A)
- Costs were higher for the sites with DNAPL
- Total cost increases with a larger treatment volume
- Unit cost decreases with a larger treatment volume
- Costs are less when injection wells are used as the delivery method.

Biomolecular Methods



- Schematic of persulfate delivery and contaminant and dechlorination contours at a Netherland site.
- Sutton et al. (2015) *Groundwater*, 53, 2, 261-270



Technical Guidelines

Table 1
Screening of the optimal hydro-geological conditions for the ISCO application.

Site conditions		ISCO applicability
Geology	Homogenous soil	E
	Presence of "Lenses"	TBE
	Backfill soil	TBE
	Fractured soil	TBE
Matrix	Groundwater	E
	Unsaturated zone	TBE
Soil texture	Sandy soils	E
	Loamy soils	A
	Clayey soils	NA
Hydraulic conductivity (m/s)	$>10^{-4}$	E
	$10^{-4} \div 10^{-5}$	A
	$<10^{-5}$	TBE
Aquifer thickness (m)	<15	E
	>15	TBE
Depth of the water table (m)	<3	TBE
	3 ÷ 15	E
	>15	TBE
Groundwater velocity (m/day)	<1	A
	1 ÷ 4	E
	>4	TBE

E = excellent, A = applicable, TBE = to be evaluated, NA = not applicable.

Baciocchi et al., *J. Cleaner Production* 77 (2014) 47-55

Table 2
Screening of the optimal aquifer chemical properties for the ISCO application.

Site conditions		ISCO applicability
Salinity – Chlorides (mg/L)	<1000	A
	>1000	TBE
Alkalinity (mg/l $CaCO_3$)	<1000	A
	>1000	TBE
SOD/TOD (g/kg_{soil})	<30	A
foc (%)		

A = applicable, TBE = to be evaluated,

Technical Guidelines

Table 3
Typical effectiveness of different oxidizing systems for the different classes of contaminants typically found in contaminated sites.

Contaminants	H_2O_2	Activated $Na_2S_2O_8$	$KMnO_4$
Light hydrocarbons (gasoline, diesel, kerosene, jet fuel)	G	E	A
Heavy hydrocarbons (fuel oil, lubricating oils)	A	A	NVE
PAHs	G	A	G
PCBs	A	V, A	NR
BTEX	E	E	G, NR for benzene
MtBE	G	E	NVE
TBA	A	A	NR
Unsaturated chlorinated ethenes (PCE, TCE, DCE, VC)	E	E	O
Saturated chlorinated ethanes	A, G	V	NR
Chlorophenols	G	G	G
Chlorobenzenes	A	G	NVE

G = good, E = excellent, A = average, NVE = not very effective, NR = not recommended, V = variable depending on the type of activation.

Baciocchi et al., *J. Cleaner Production* 77 (2014) 47-55

Contact is always an Issue

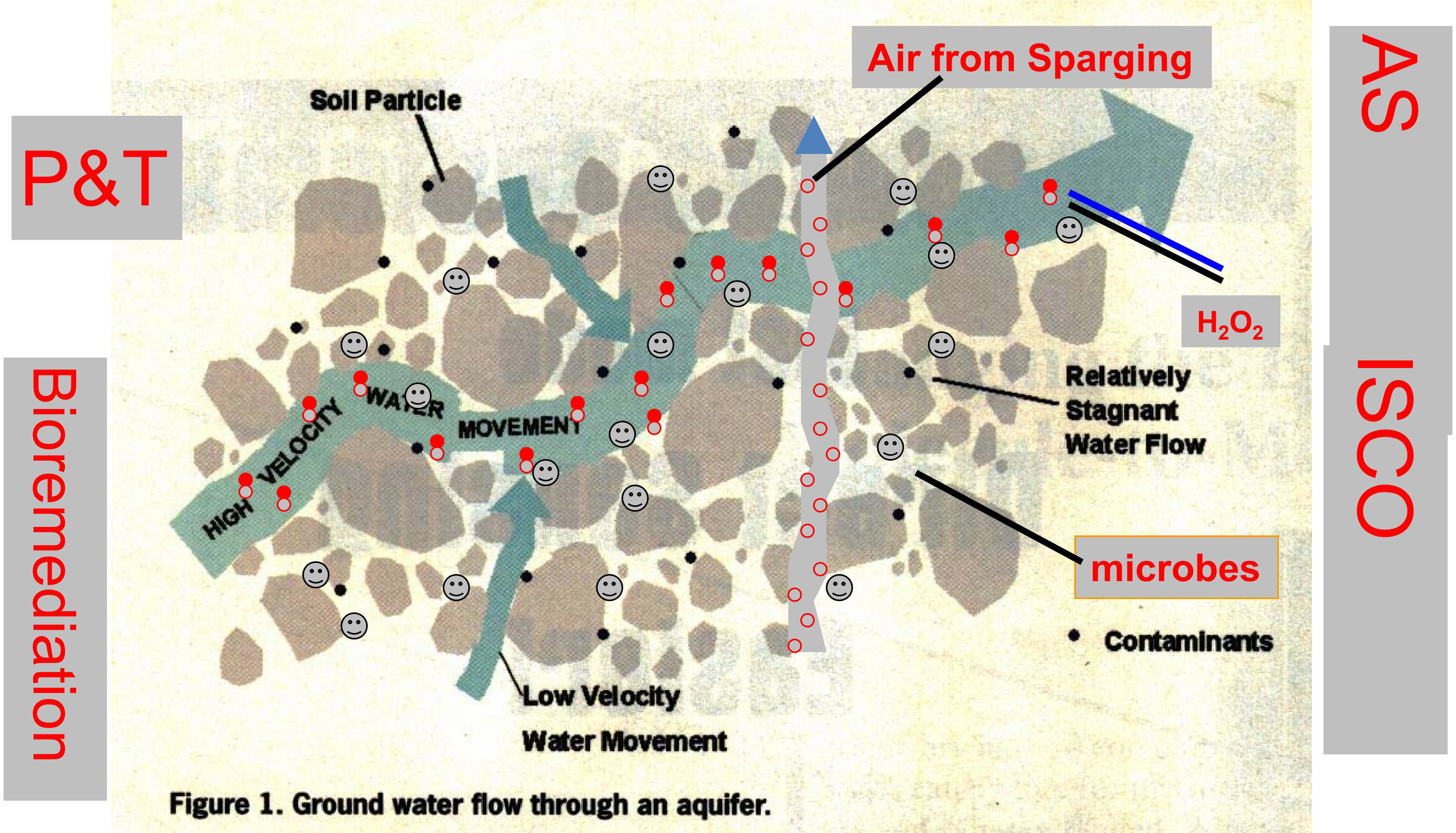


Figure 1. Ground water flow through an aquifer.

O2 and nutrient transport

Investigation and Remediation of a Chlorinated Solvent Contaminated Site: A Case Study

Yao-Tsung Chen

Apollo Technology Co., Ltd.

March 23rd, 2016

APOLLOTECH

Overview

- Brief Site History
- Investigation Tools Applied
- Contingency Measures
- Double Packer Injection Method
- Roadmap of Contamination Management

Brief Site History

Projects ：

2001 ：Gas station investigation

Chlorinated Solvents

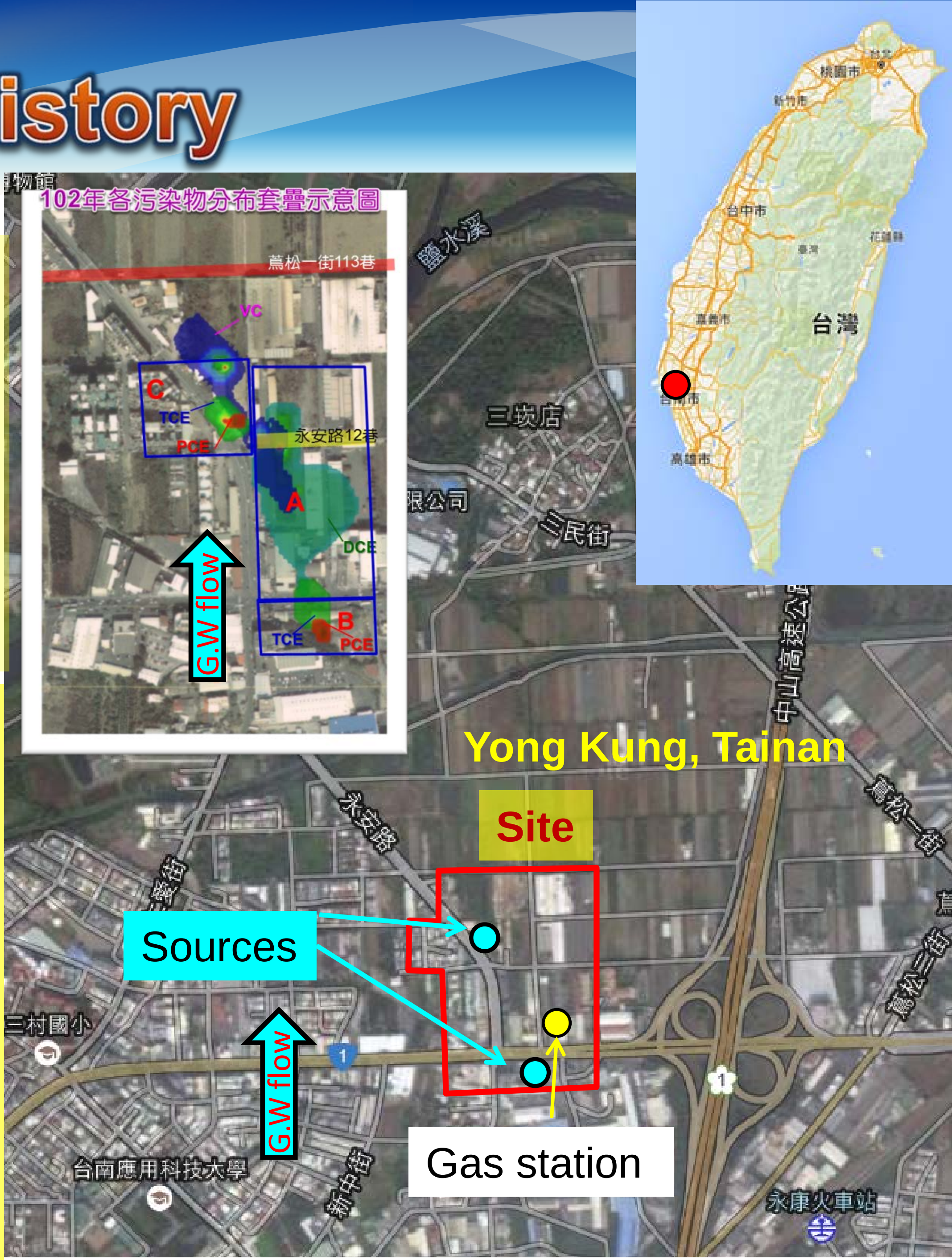
2003 ：Site Investigation

2005 、2008 、2010 、2012：Contingency Plan, SCM, Pilot Tests

2014 ：Pilot Test (Double Packing Injection ，DPI)

Contamination management strategies:

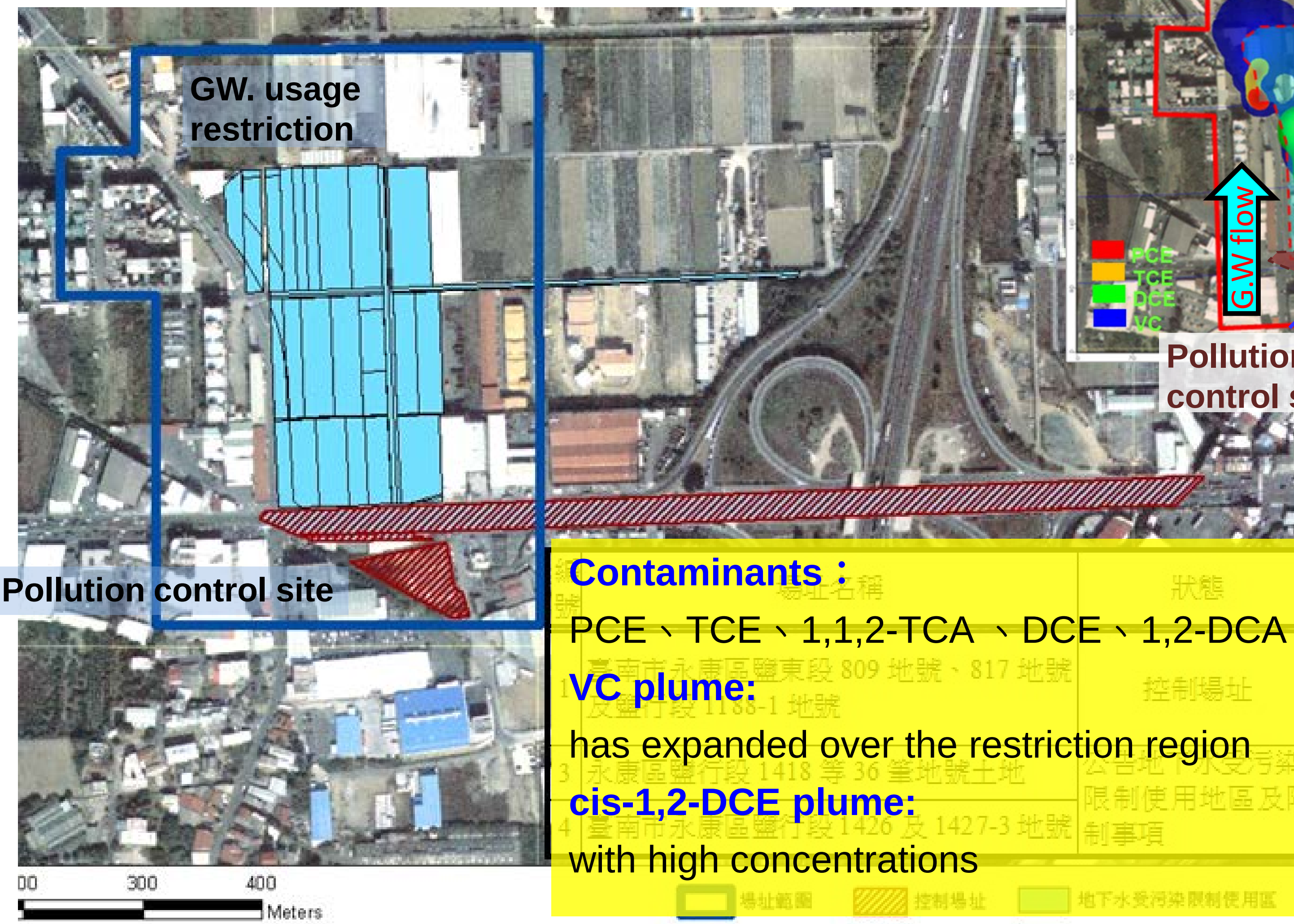
- Contamination source investigation
- Site characteristics investigation
- Remediation pilot tests
- Contingency measurements
- Long term contamination monitoring
- Health risk assessment
- Restriction on groundwater usage
  - Site patrol and acknowledge the locals
  - Communication with the locals (meetings)
  - Publish GW. pollution prevention Brochures

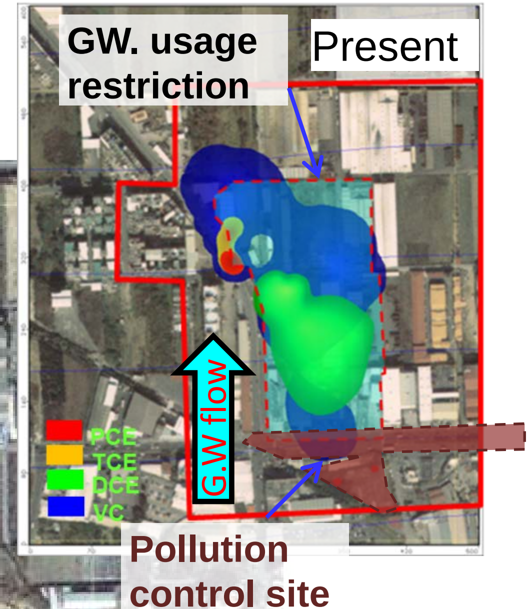


Groundwater Restriction regions

Pollution control site：3 pieces of land

Groundwater usage restriction region：37 pieces of land





Contaminants：

PCE、TCE、1,1,2-TCA 、DCE、1,2-DCA、VC

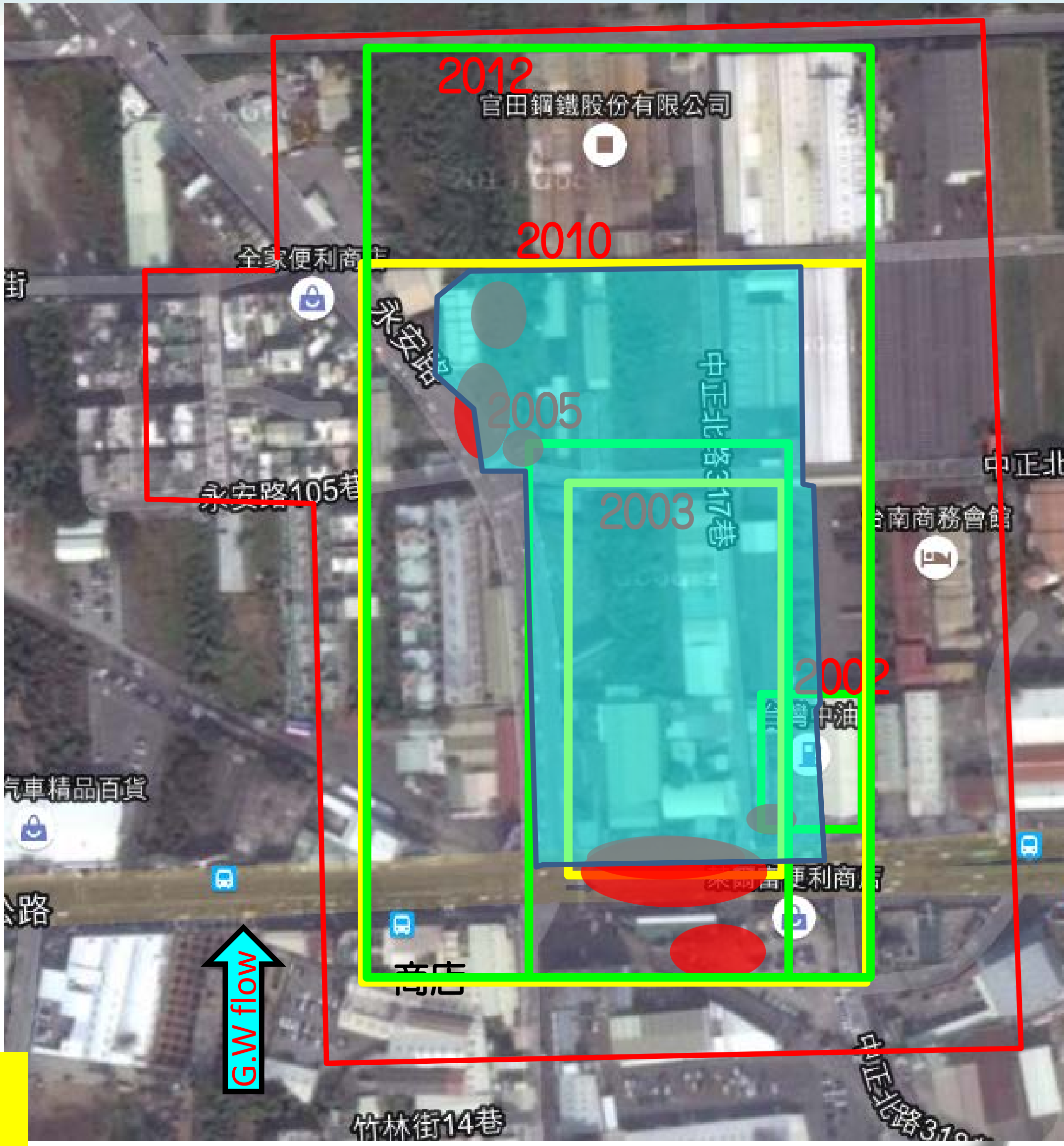
VC plume:

has expanded over the restriction region

cis-1,2-DCE plume:

with high concentrations

Investigation Tools Applied



Investigation Tools Applied ：

MIP-ECD 、 MIP-EC 、Slug Test 、 Core Sampling 、Soil/ Groundwater Sampling 、Multiple Levels Sampling 、 Electric Resistivity Tomography 、Stable Isotope Compounds 、Microorganism

Plume Boundaries did not be defined until 2012

- **High Chlorinated Solvents Location**

  2002：S.E of Gas Station

  2003：N. of Jung-Jeng R.

  2005：Intersection of Yan-an R. and 12 lane, Yan-an R.

  2010：Park Lot

  2012：Beneath Yan-an R.

Integrated Site Characterization Tools ?

Objectives-Based Data Collection

Objectives of Previous Projects

Year of Project	Objectives	Investigation Tools
2003	Identification of Contamination Source Geologic Investigation and Analysis	Soil/Groundwater sampling (simple and monitoring wells installtion) Cone penetration tests (CPT) Tracer test Core sampling
2005	Site conceptual model Pollution distribution Geological condition Contingency measurement installation (P&T)	Membrane interface probe (MIP-EC, -ECD) Soil/Groundwater sampling (simple and monitoring wells installtion) Pumping test/ slug test
2008	Potential responsible industries survey	Site visiting
2010	Tracing the source of pollution Potential source zone detail investigation Site conceptual model Potential responsible industries survey	Aerial photographs Membrane interface probe (MIP-EC, -ECD) Soil/Groundwater sampling (simple and monitoring wells installtion) Ground Penetrating Radar Flow Metering Slug test Core sampling

Objectives of Previous Projects

Year of Project	Objectives	Investigation Tools
2012	Identify the boundaries of contamiantion Verify pollution responsible parties Contengincy measurement installation (Bio-screen barriers)	Records review Electric resistivity tomography (ERT) MIP-ECD, MIP-EC Soil/Groundwater sampling (simple) Monitoring wells installtion/sampling Compound specific isptope analysis Microorganism analysis
2014	Detail investigation on the region of remediation pilot tests	Electric resistivity tomography Earth physical exploration (natural γ radiation) Core sampling Monitoring wells installtion/sampling Multi-depth slug test, flow metering Microorganism species and functional gene analysis

Site Investigation Procedure

Objectives of the year 2012 project

To identify the boundaries of contamiantion

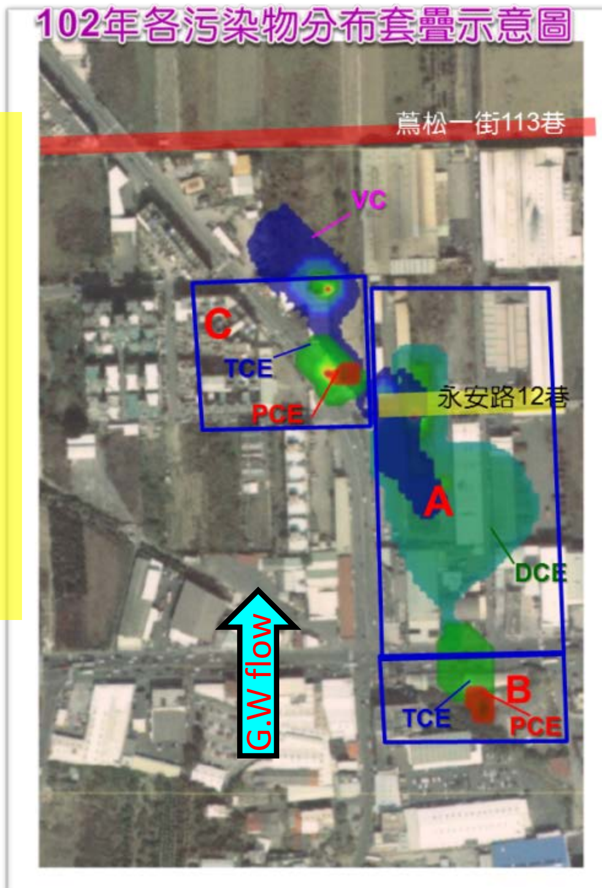
To verify responsible parties for contamination

Contaminants:

High chlorinated solvents:
PCE、TCE、1,1,2-TCA

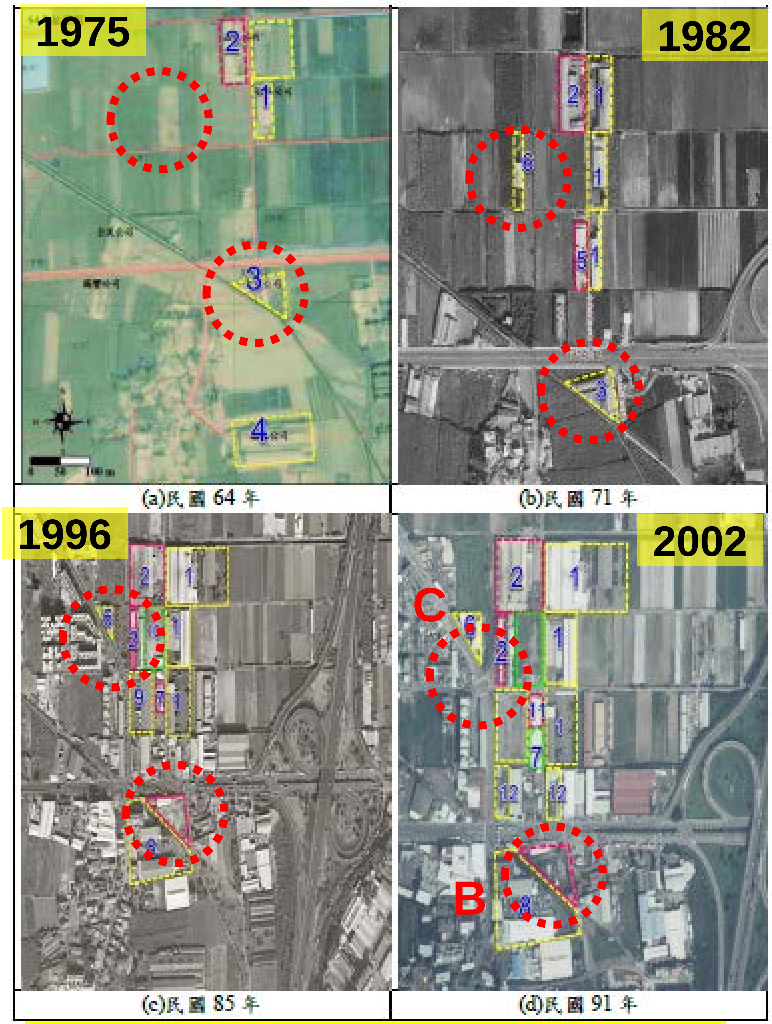
Low chlorinated solvents:
DCE、1,2-DCA、VC

2 Sources:
Region B, and C

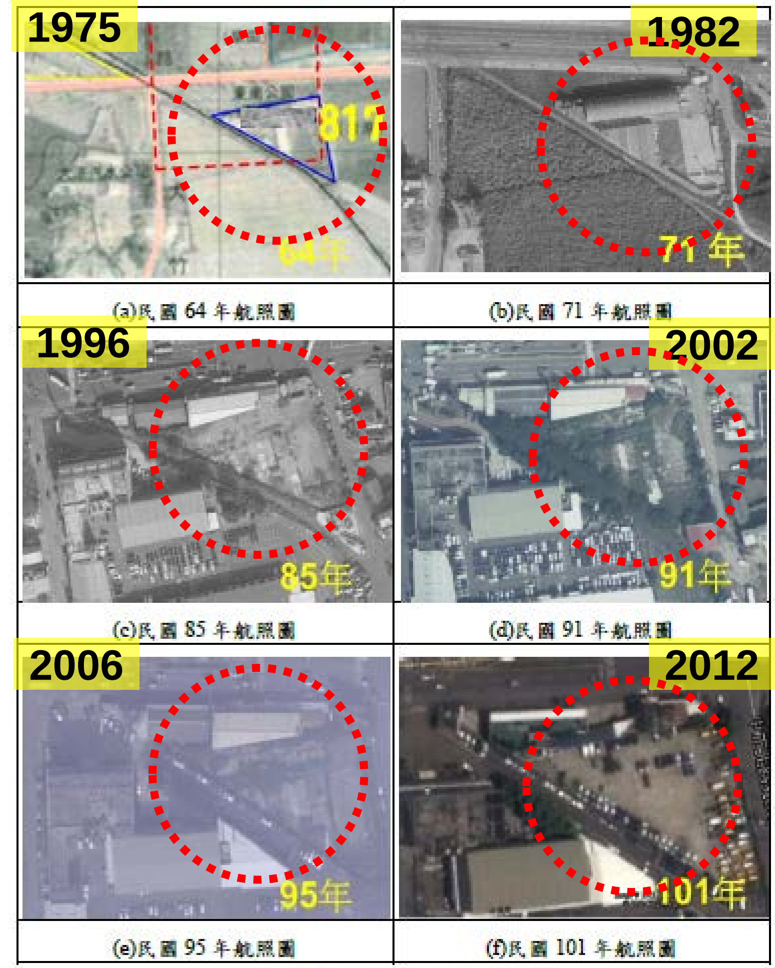


ERT
⇩
MIP
⇩
Soil Core Sampling | **Simple well Sampling**
⇩
Monitoring Well Installation
⇩
Monitoring Well Sampling
⇩
Data Processing

Aerial Photographs

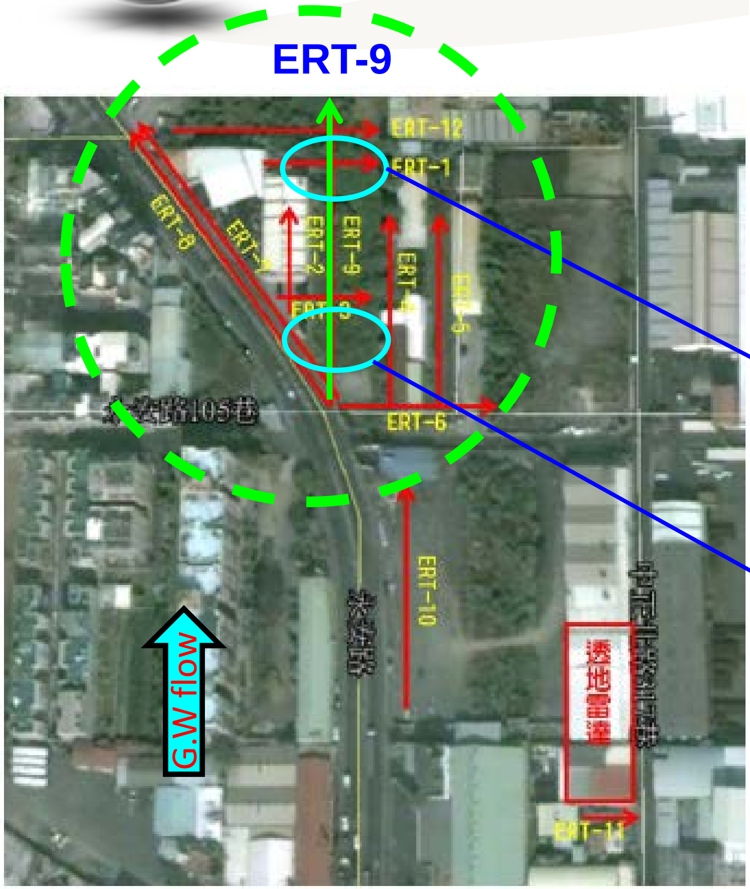


No obvious potential factory in region C



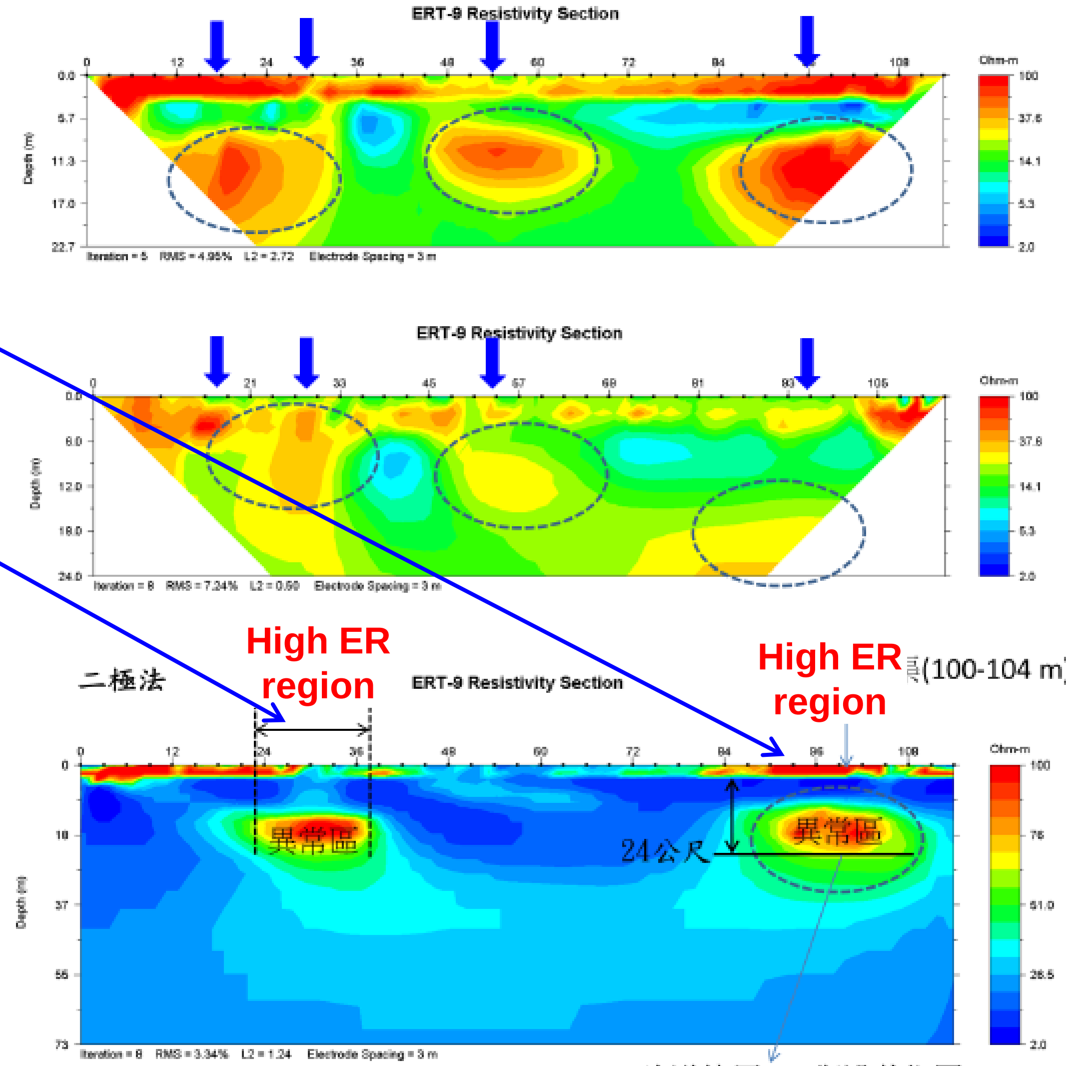
A potential factory had been in region B until 1996

Electric Resistivity Tomography



10 ERT Lines

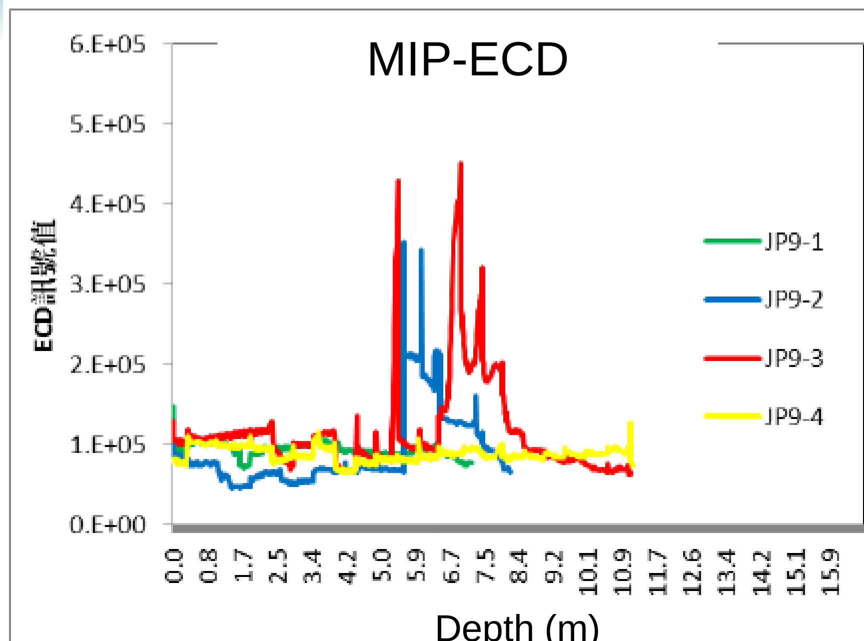
Potential source zones

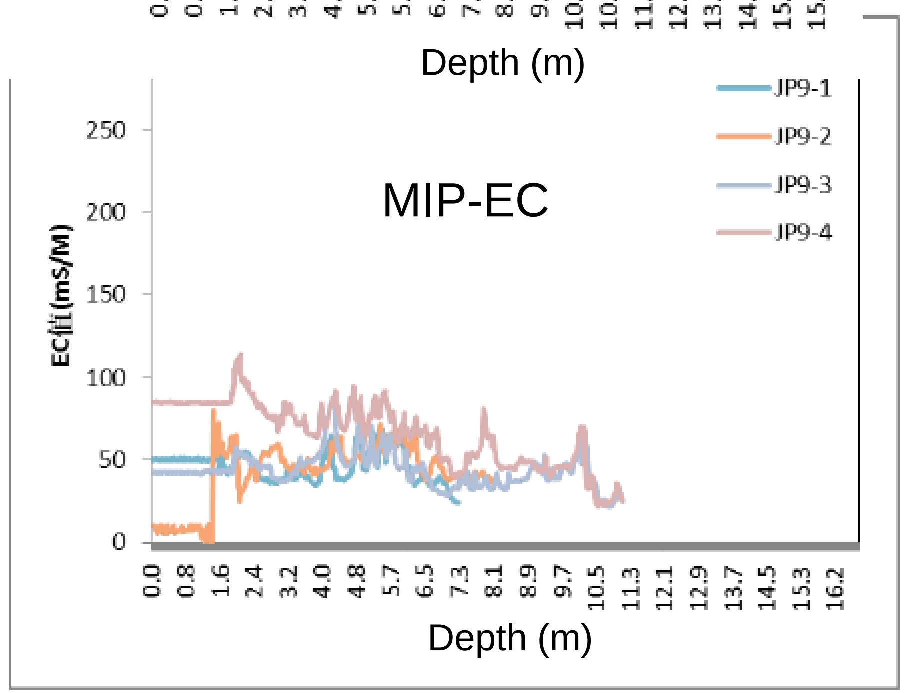


ERT-9 Resistivity Section

MIP-ECD, MIP-EC

18 MIP Points





MIP-ECD:

A VOC screening tool that provides real-time data

MIP-ECD:

Provide the geological material conditions

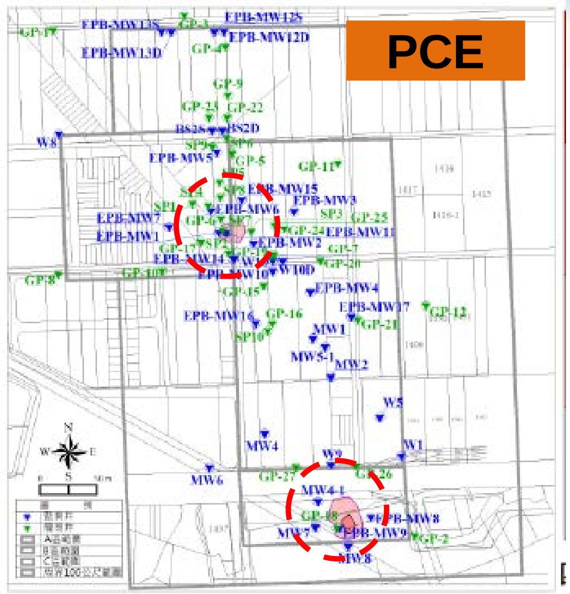
Well Installation

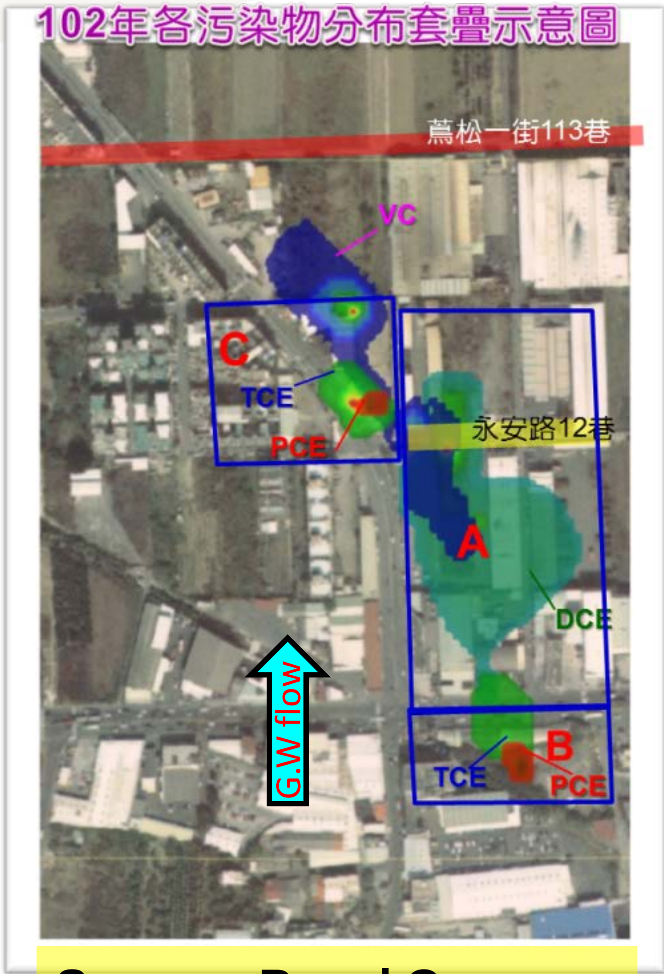
9 Simple wells

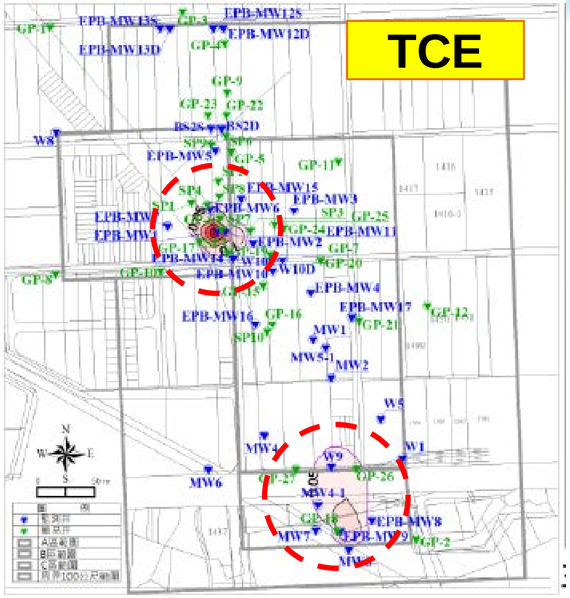
Instantly sampling

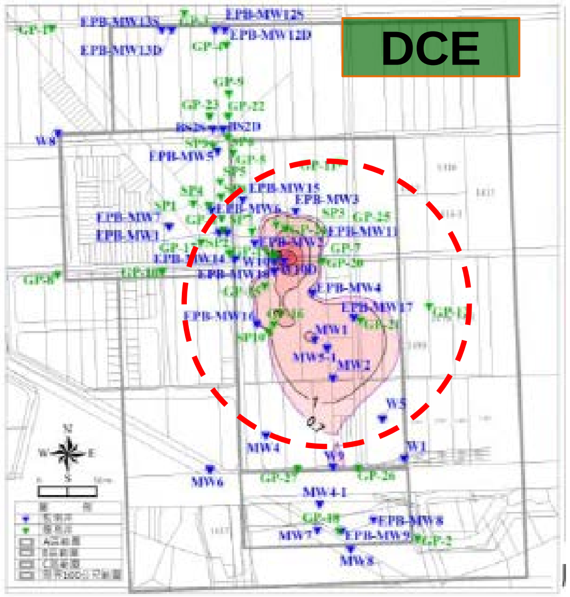
7 Monitoring Wells

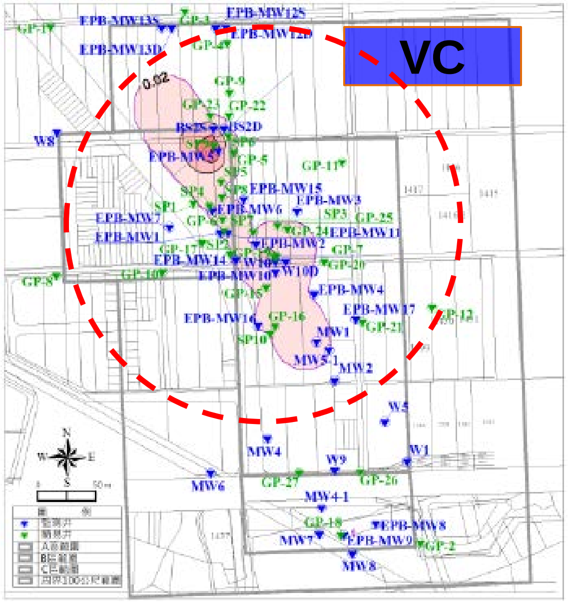
Concentration Contours









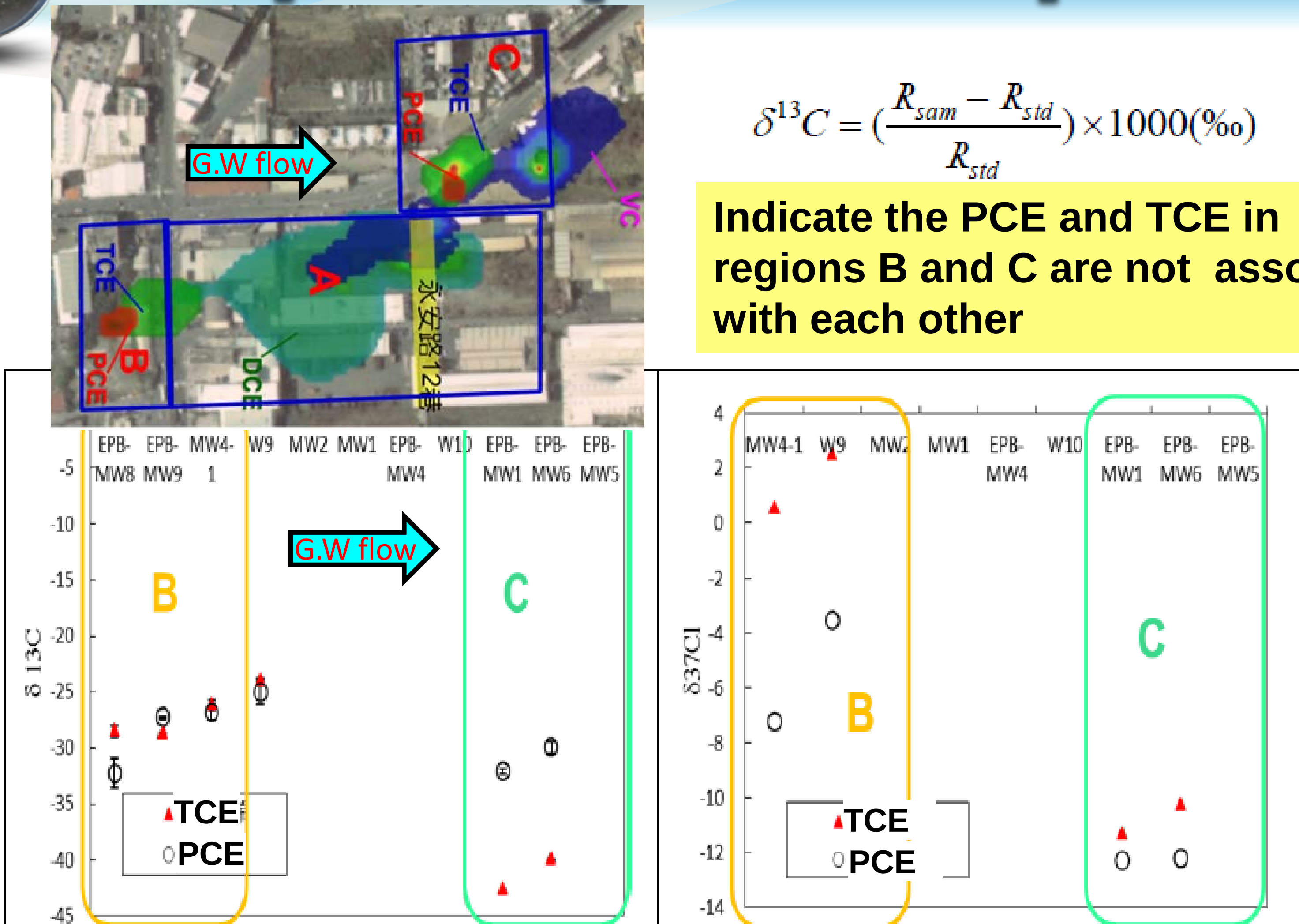


Sources B and C
Size of source zone
Size of various contaminant plumes

Compound Specific Isotope Analysis

$$\delta^{13}C = (\frac{R_{sam} - R_{std}}{R_{std}}) \times 1000(‰)$$

Indicate the PCE and TCE in regions B and C are not associated with each other

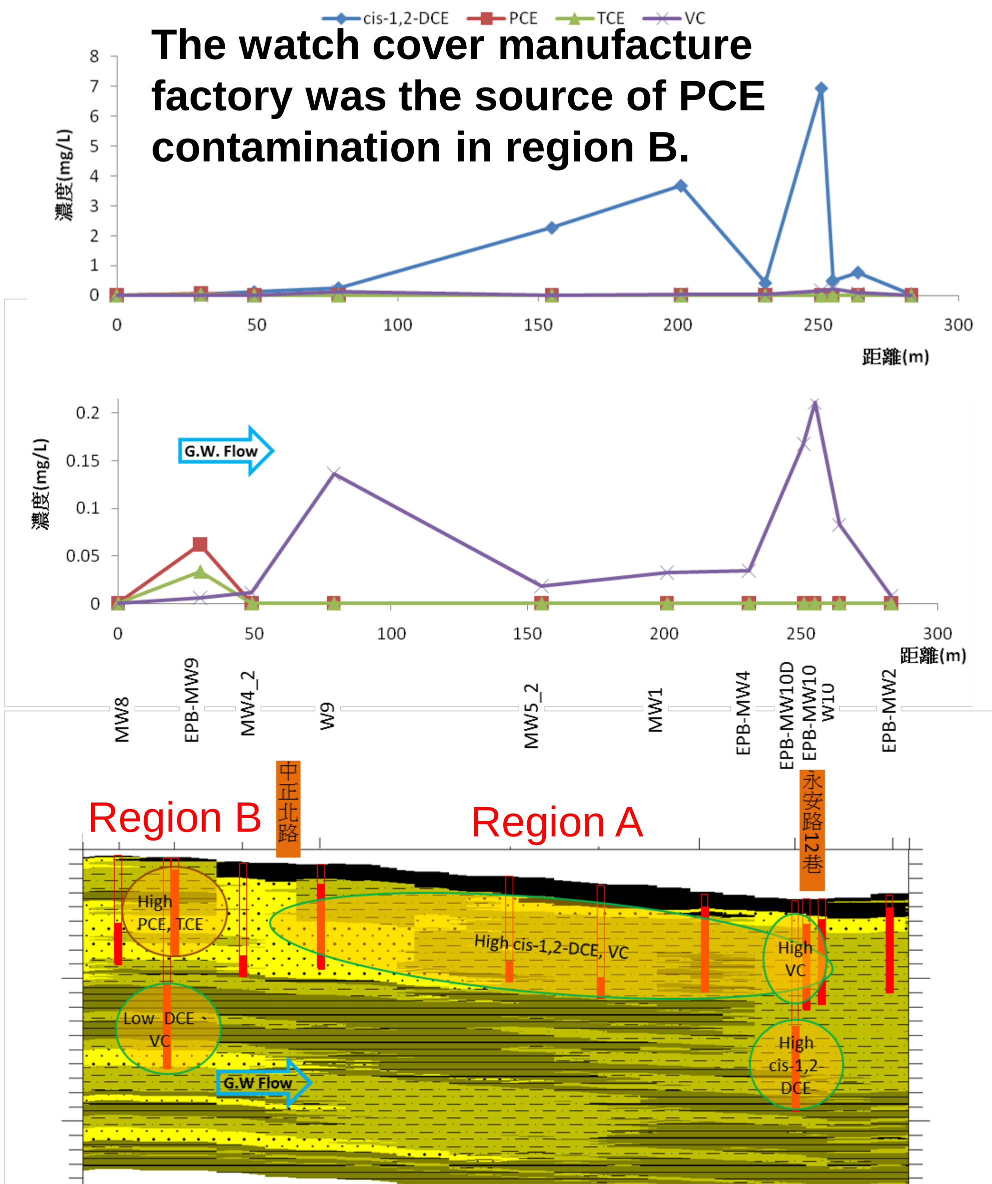


Carbon Isotopes | **Chloride Isotopes**

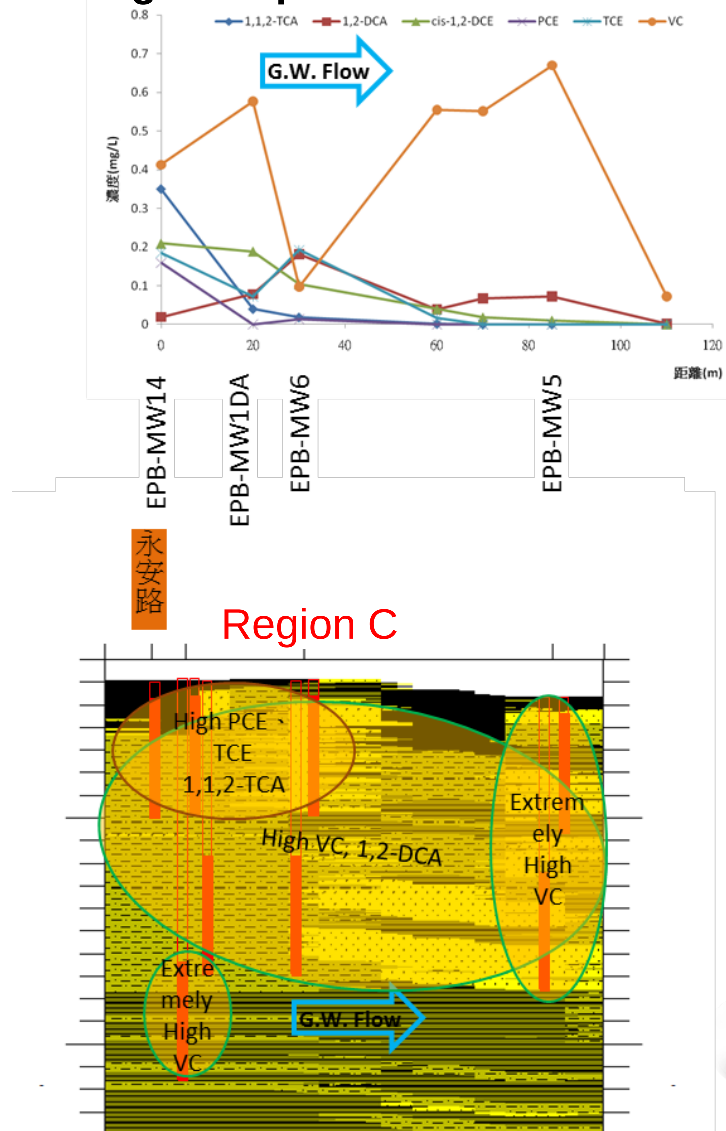
Comparison of the $\delta^{13}C$ and $\delta^{37}Cl$ of PCE and TCE from the up- gradient flow well EPB-MW8 to the down-gradient flow well EPB-MW5

Contaminants Species

The watch cover manufacture factory was the source of PCE contamination in region B.



The responsible parties for region C pollution are unknown.



Contingency Measures

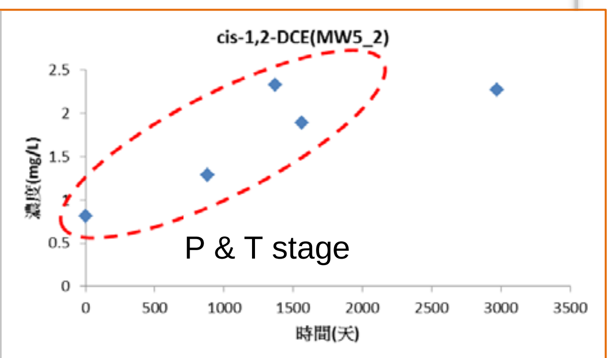
Pump & Treat

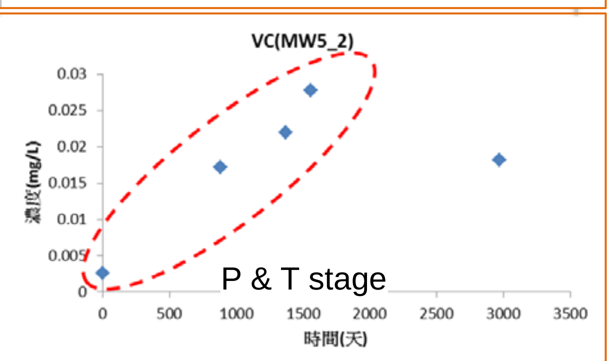
2005~2010

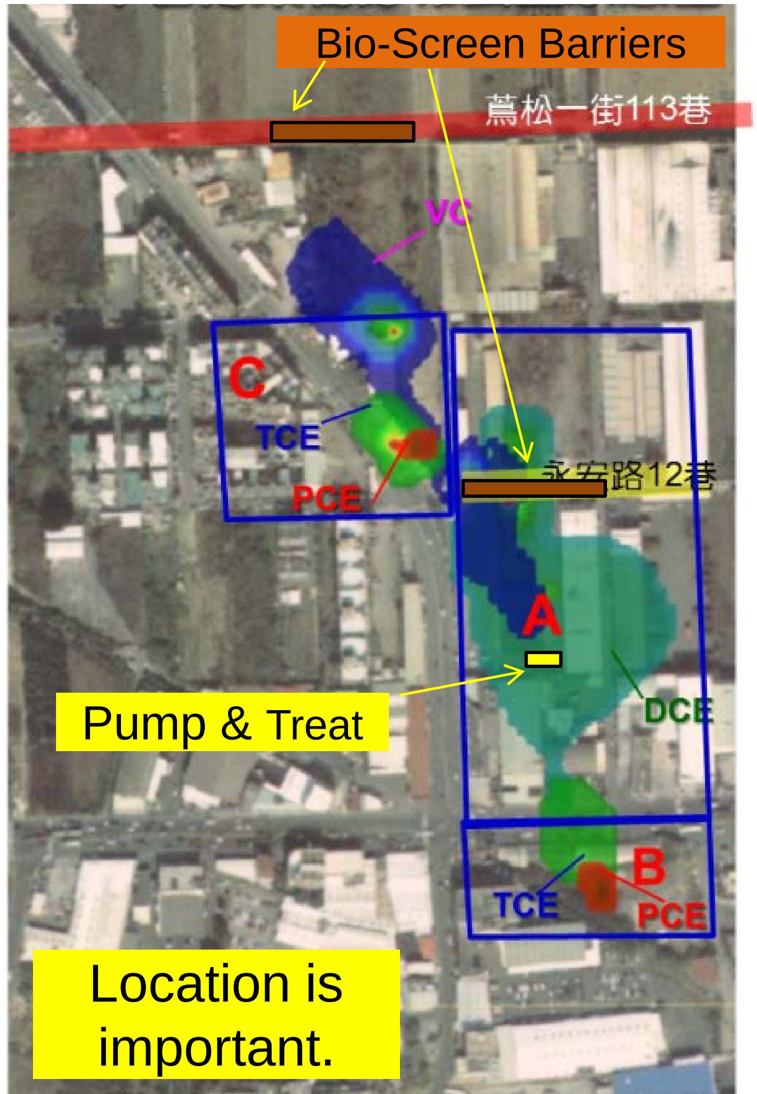
Pumping flow rate ：

Down to 0.3 L/min

Designed up to 1.7 L/min







2 Bio-Screen Barriers

2012/3~9

Well Type：

Injection and extraction

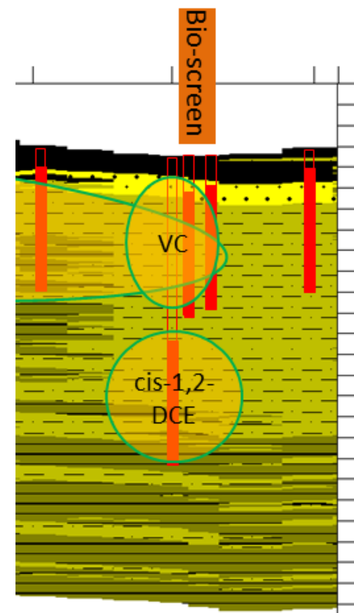
Depth：

Shallow wells：8 m

Deep wells：13 m

Injection flow rate ：

From 1.0 CMH in total of 10 injection wells down to 0.5 CMH

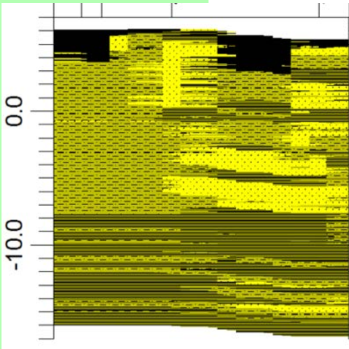


Contingency Measures

Previous contingency measures and performance:

1. Pump & Treat (2005~2010): stopped operating due to the concern of resulting in plume expansion
2. 2 bio-interception walls (2012): hard to inject due to the low permeability strata

Suggestions on the Experts Forum 2012



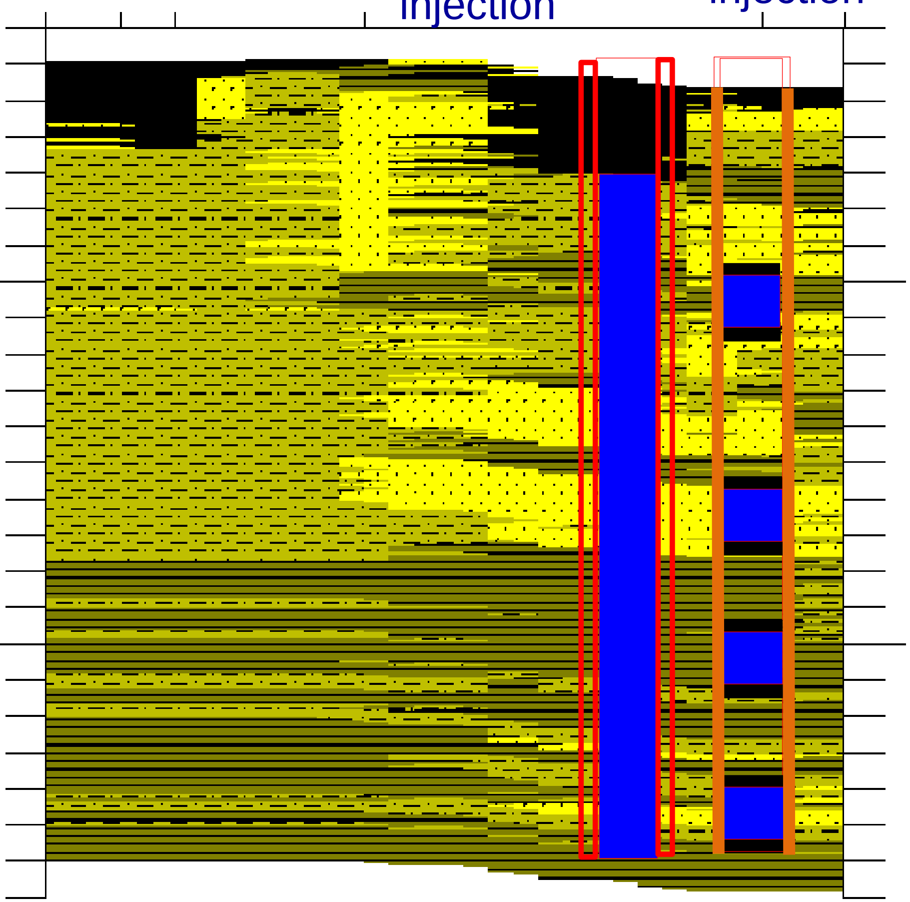
- In-situ bioremediation is the most cost efficiency and suitable for this site
- **Due to the geological heterogeneity, 2 highlighted issues**
  - ✓ **Depth of injection**: must to cover the depth of contaminated aquifer
  - ✓ **Method of injection**: be able to deliver chemicals effectively

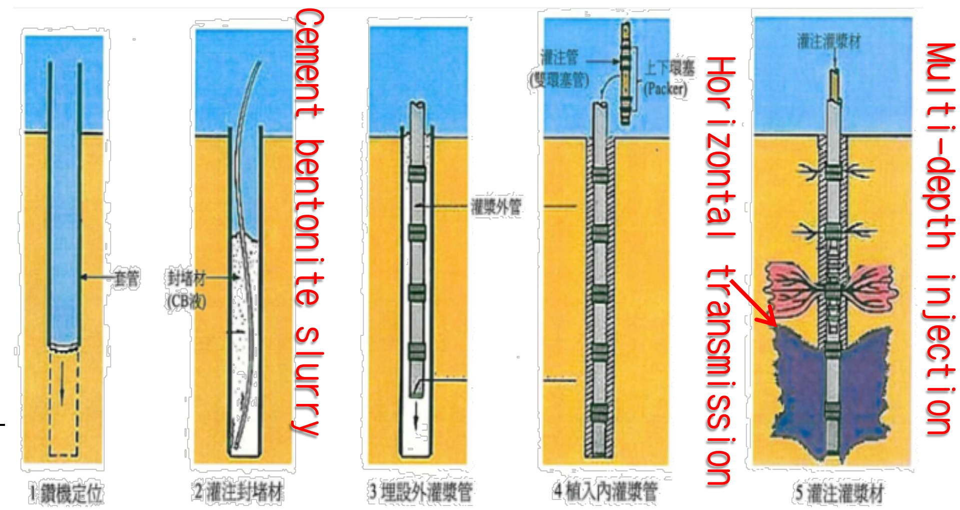
Main Goal of the Project 2014

- To verifying the proposed **double packer injection technology** is able to deliver reagents well into the geological heterogeneous strata with low permeability

Double Packer Injection (DPI)

A mature technology for structural reinforcement in geotechnical applications

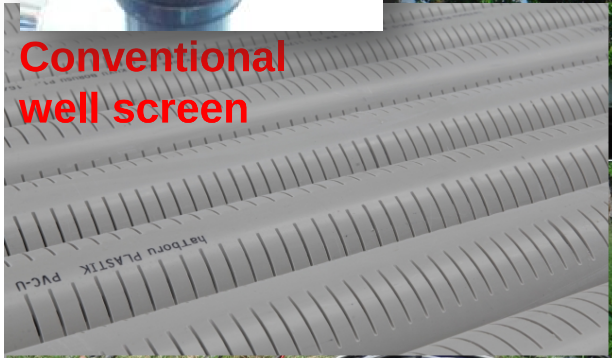




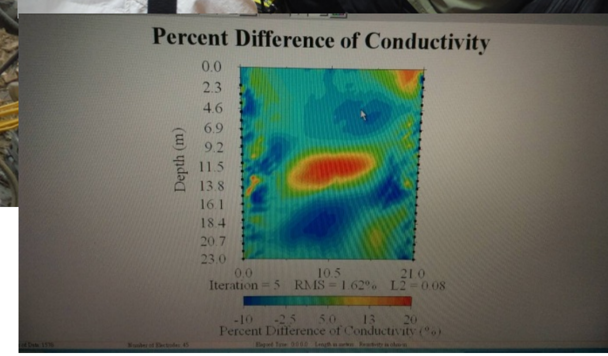
Injection Features

- The interval of each injection: 33~50 cm
- Injection pressures and flow rates are able to adjust according to the geological conditions and the depth of injection point
- Simultaneously multi-depth injecting
- Well horizontal transmission in low permeability strata

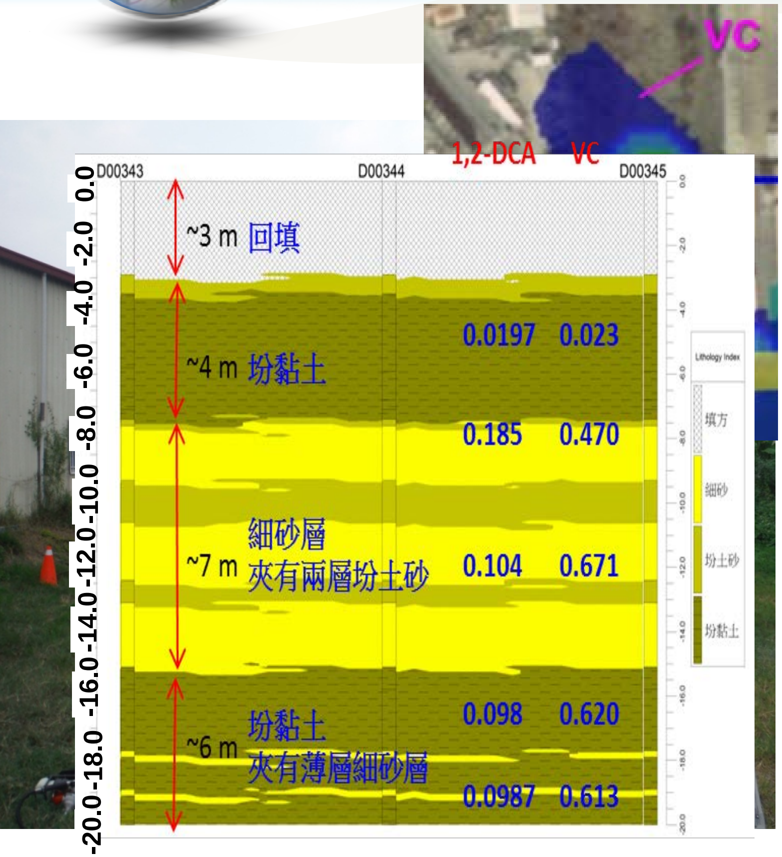
Double Packer Injection (DPI)

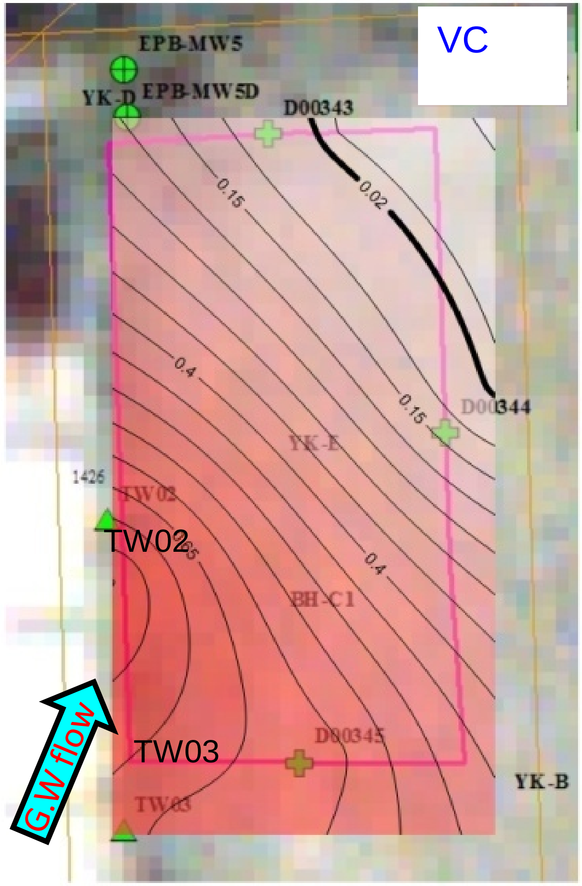


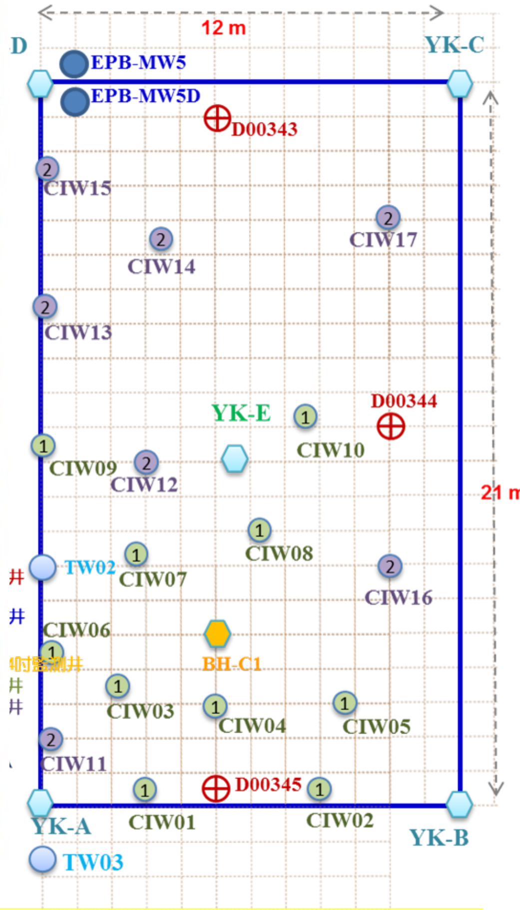
Cross Hole ERT (CHERT)



Site Properties of the Pilot







- Complicated high/low-permeability alternate layers
- VC concentrations at 23 m b.g.s of 5 CHERT wells were 0.218~0.967 mg/L
- High concentration at up-gradient and on the west side

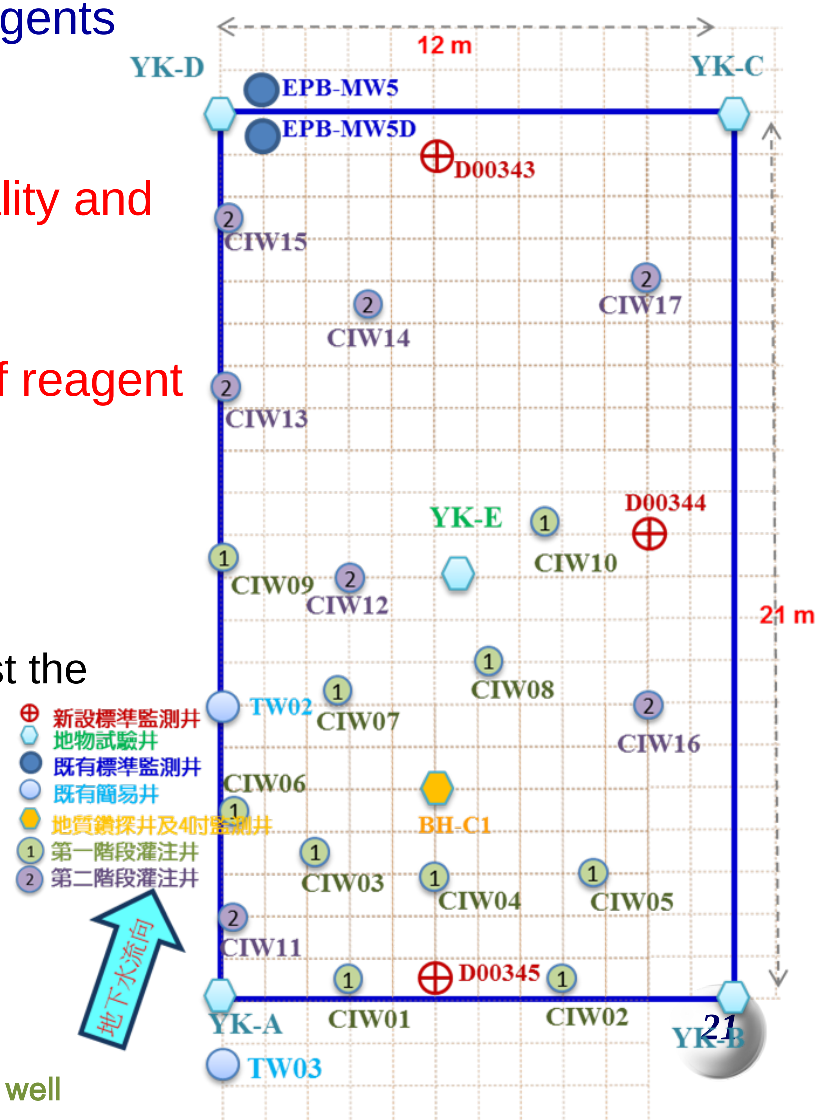
Injection in the pilot :

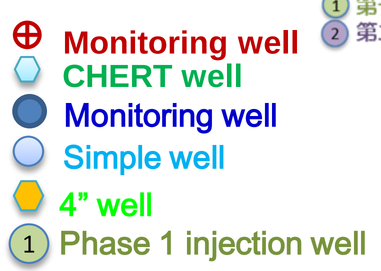
- Depth of Injection Wells: 24m b.g.s
- Range of Injection: 3 ~ 24 m b.g.s

Injection Plan

- 20 injection wells: to inject bio-stimulatiob reagents EcoClean/EcoClean-E
- 5 monitoring wells: to evaluate the water quality and the performance of bio-stimulation
- 5 CHERT wells: to assess the performance of reagent delivery in strata

- 2 phases of injection:
  - Phase 1: inject in the half up-gradient region to test the ROI and the injection pressure/flow rate
  - Phase 2: full site injection to verify the remediation performance



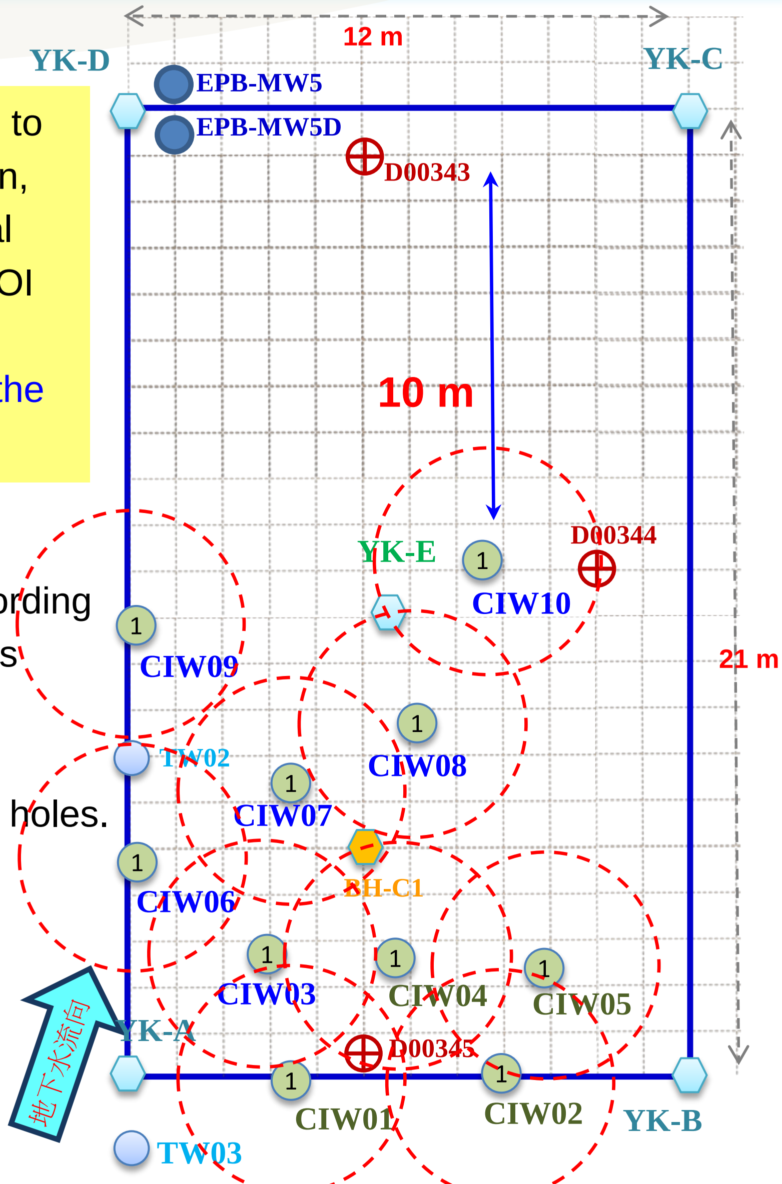


Phase-I Injection

- The purpose of this phase is to test the pressures of injection, flow direction, and geological permeability and evaluate ROI using monitoring wells.
- Traditional ERT to evaluate the transmission of reagents

Injection Method:

1. Injections are designed according to permeability and pollutants concentrations.
2. Multi-depth injections are conducted at different injection holes.
3. To control the flow pressure



- ⊕ Monitoring well
- CHERT well
- Monitoring well
- Simple well
- 4” well
- 1 Phase 1 injection well

Arrangement of Injection

[illegible]	CIW-03	CIW-06	CIW-07	CIW-08	CIW-09	CIW-10
500L, 3	1	13	11	12	10	9
500L, 4	14	12	10	11	9	8
500L, 5	13	11	9	10	8	7
500L, 6	12	10	8	9	7	6
500L, 7	11	9	7	8	6	5
500L, 9	10	8	6	7	5	4
500L, 11	9	7	5	6	4	3
500L, 13	8	6	4	5	3	2
500L, 15	7	5	3	4	2	1
380L	6	4	2	3	1	14
380L, 18	5	3	1	2	14	13
380L	4	2	14	1	13	12
380L	3	1	13	14	12	11
380L	2	14	12	13	11	10
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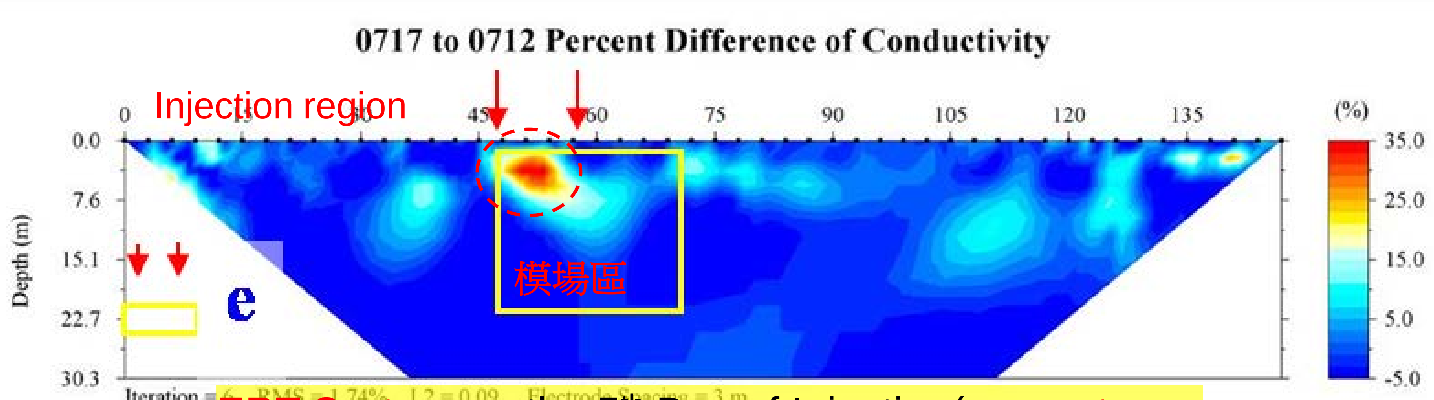
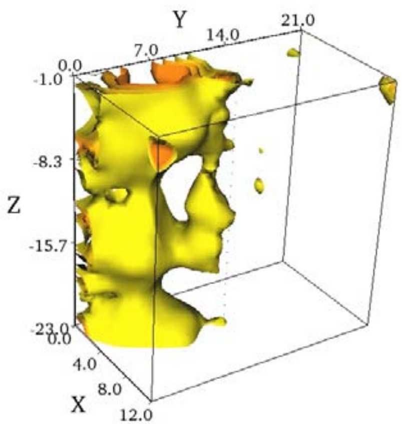
Simultaneous injection

Phase-I Injection and ERT Results

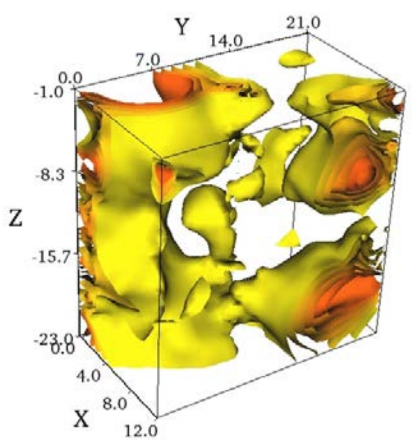


ERT System on the 5th Day of Injection(reagents have been transmitted to downgradient)

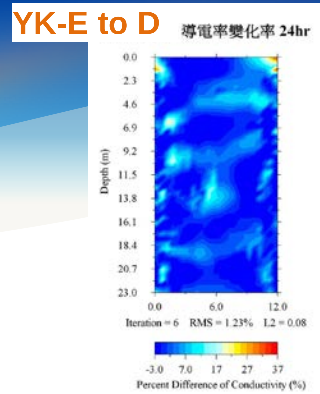
CHERT – phase 1

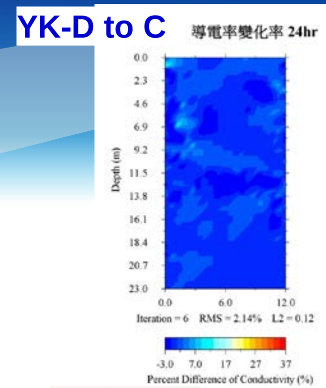


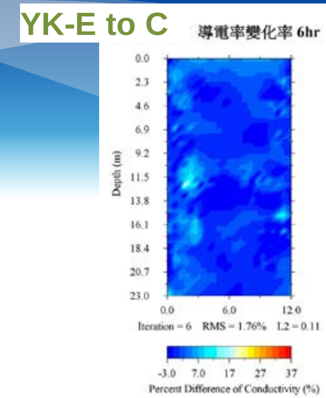
Early stage of injection

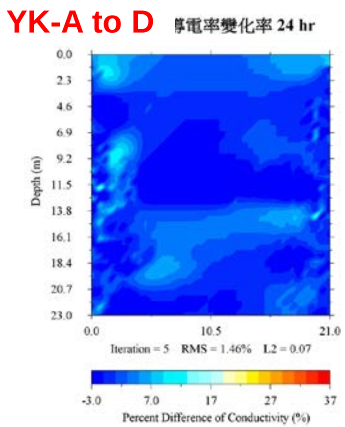


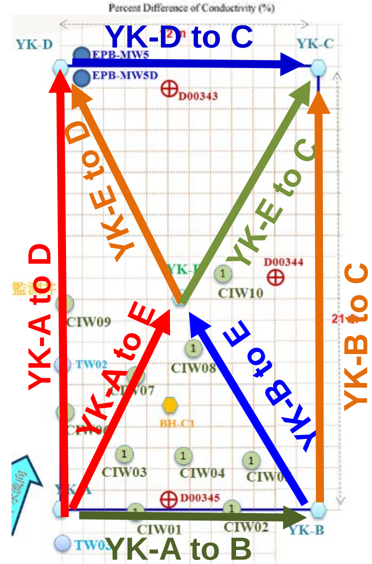
Later stage of injection

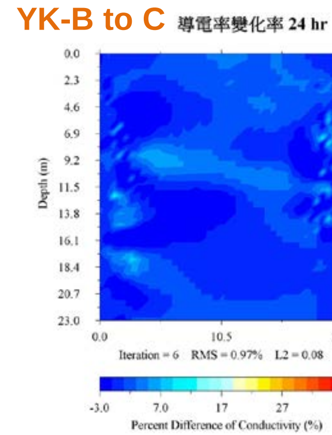


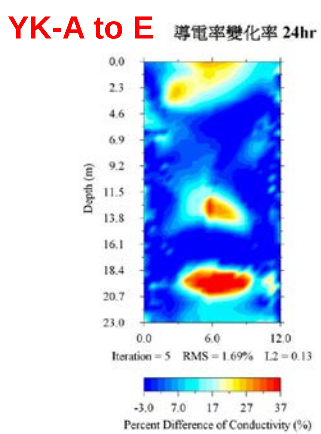


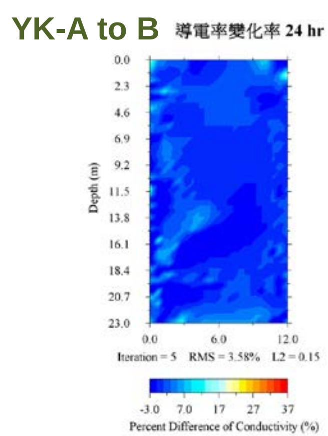


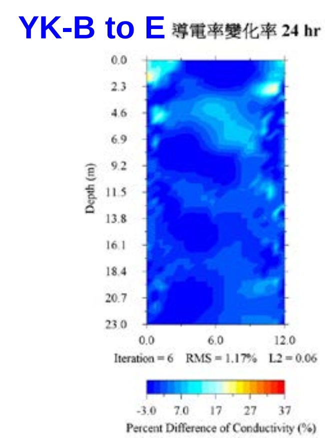






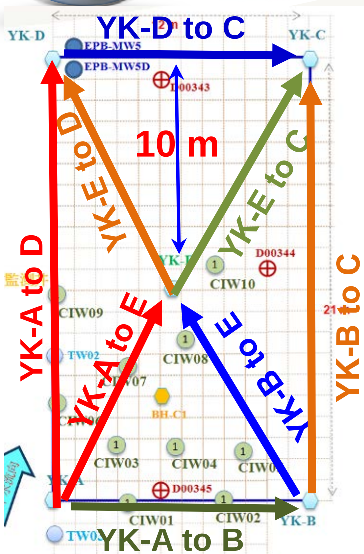


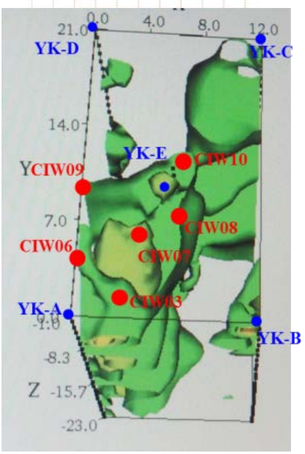


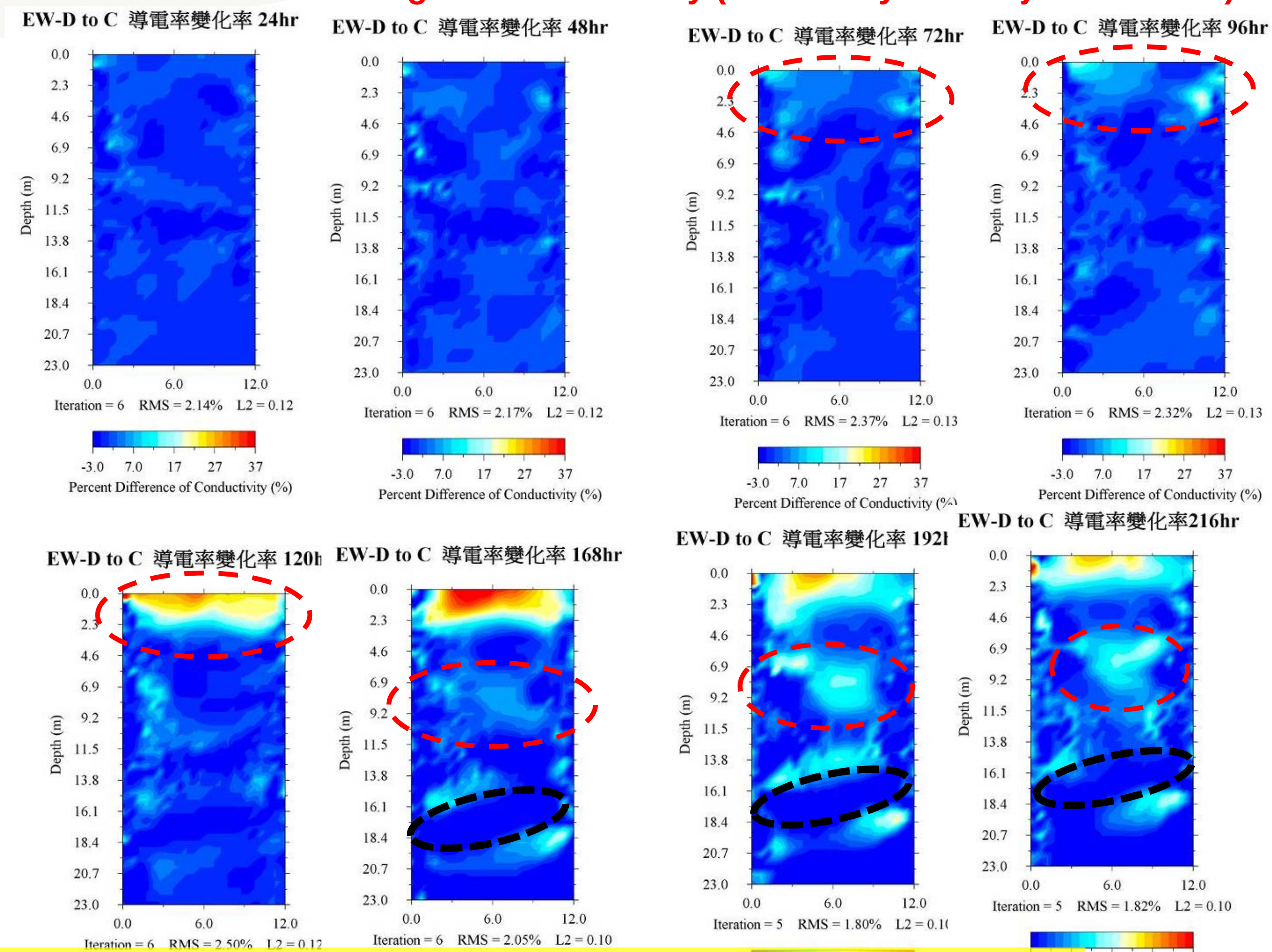


CHERT Results

120 hr after injection reagents reach the down-gradient boundary (10 m away from injection wells)



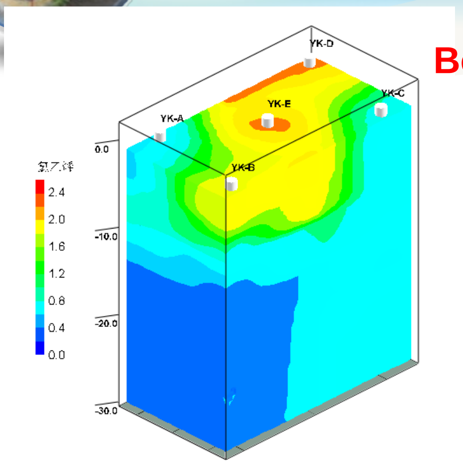




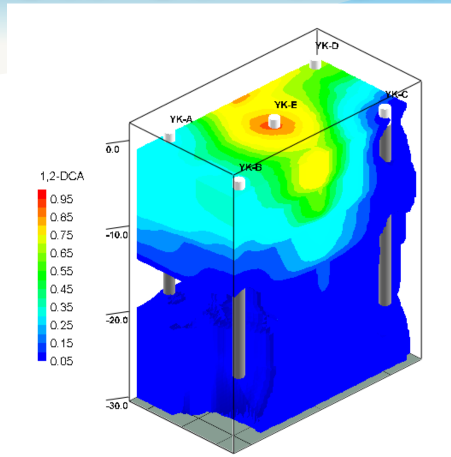
- **DPI can overcome the difficulties of transmission and influence down-gradient.**
- Reagents usually flow toward northeast side along with groundwater.

Comparison of VOCs Concentrations

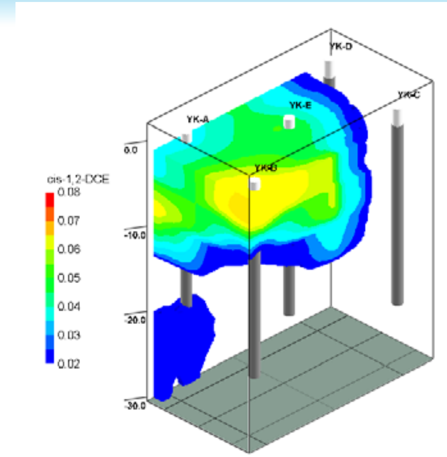
Before



VC distribution

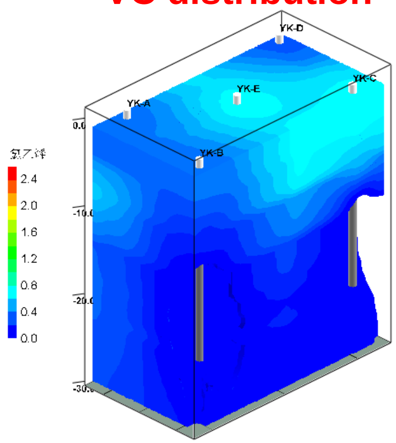


1,2-DCA distribution

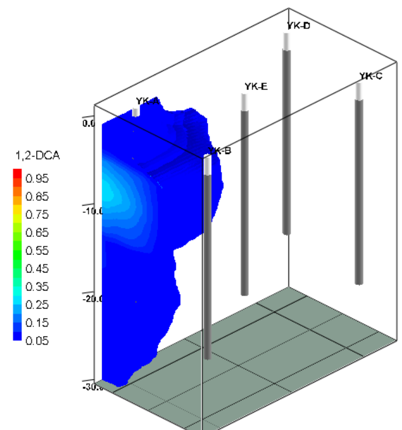


cis-1,2-DCE distribution

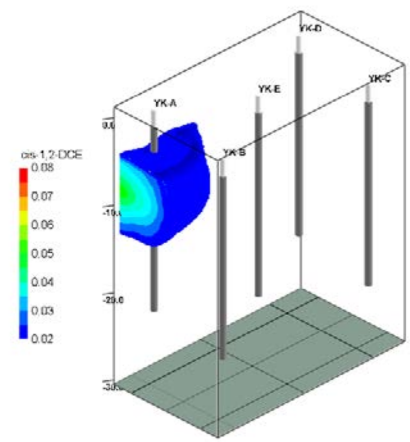
After



VC distribution



1,2-DCA distribution



cis-1,2-DCE distribution

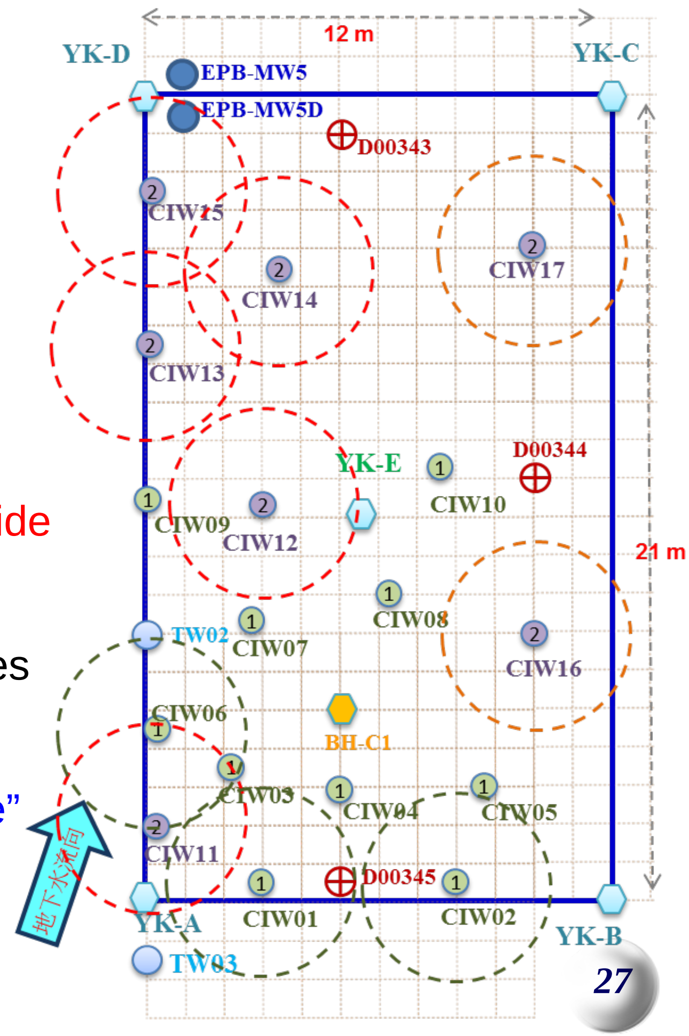
1. Pollutants concentration decreased significantly.
2. Up-gradient plumes continuously flew into the pilot test.
3. Samples collected from 8m underground indicated VC in excess of the control standard.
4. High-concentration pollution was detected at 13 m underground on the east side of the pilot site.

Phase-II Injection

- In Phase II, reagents were injected into 10 injection wells
- Injection wells were classified as 3 sections.
  - ✓ The first section is "enhancing injection zone" for new wells: located on the northwest side of the pilot.

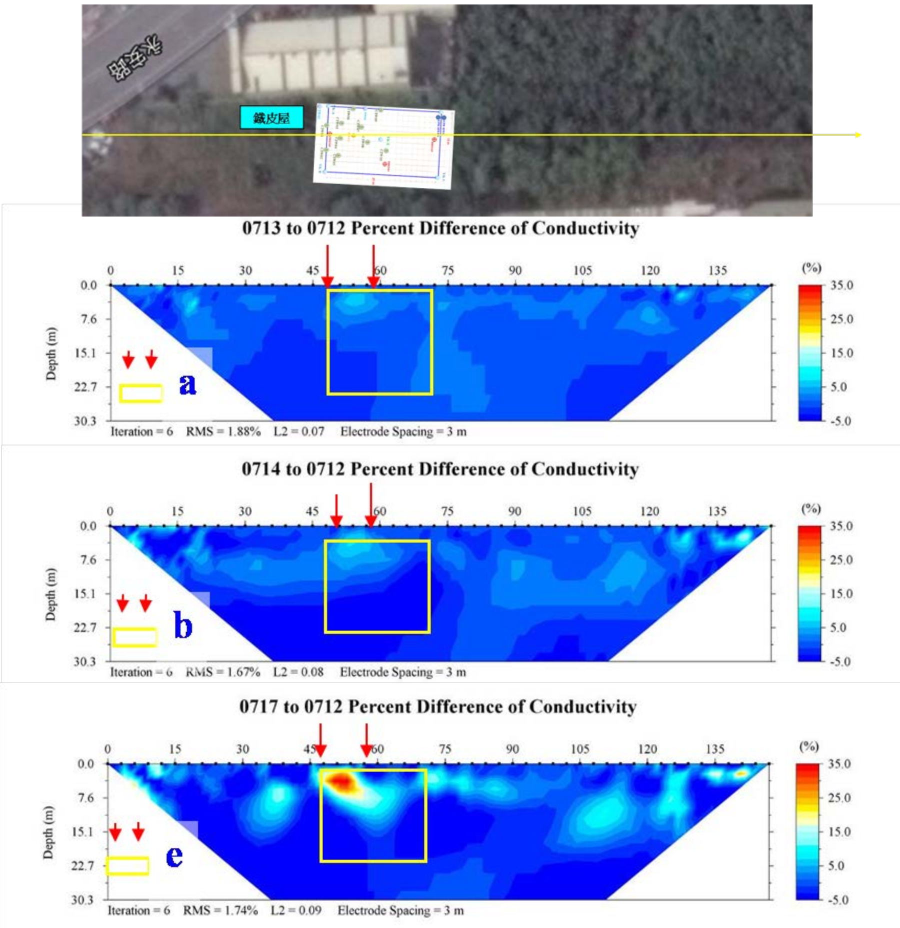
    West side was detected high-concentration pollutants.
  - ✓ The second section is "up-gradient plumes interception zone" for existing wells: located south and southwest side of the pilot.

    The purpose of the second injection is to prevent plumes from up-gradient region.
  - ✓ The third section is "east complementary injection zone" for new wells: located on the east of the pilot.

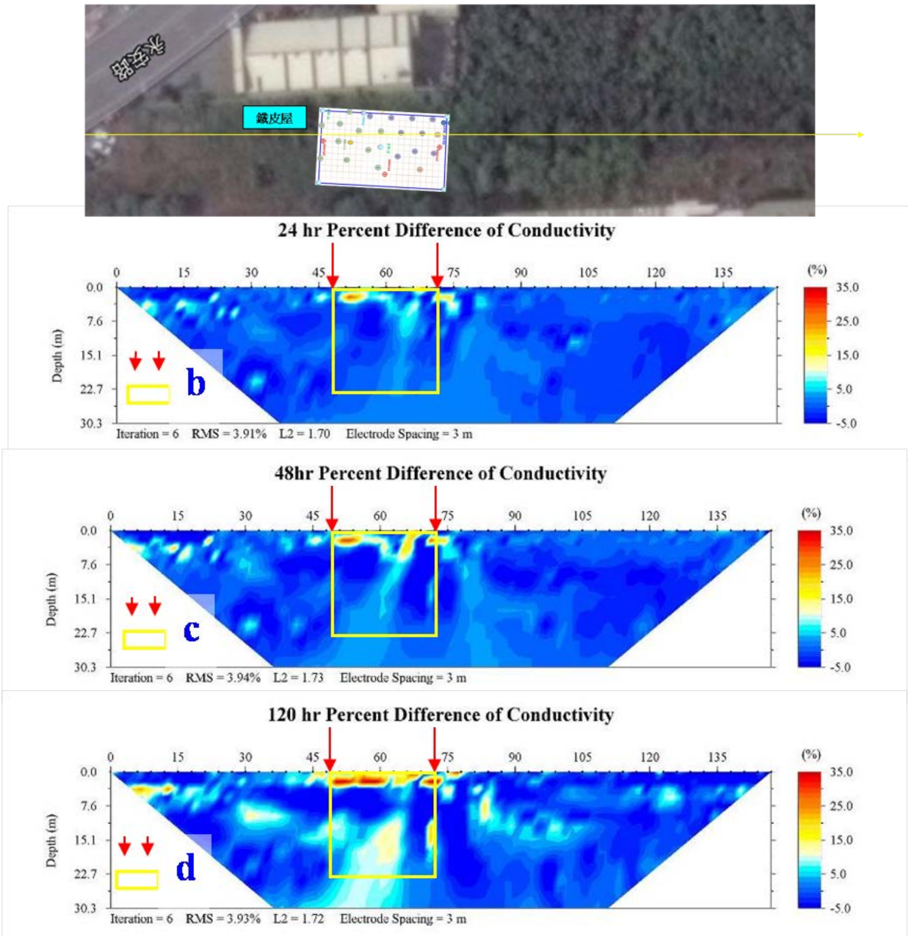


ERT Results for Phase I & II Injections

Phase-I Injection



Phase-II Injection



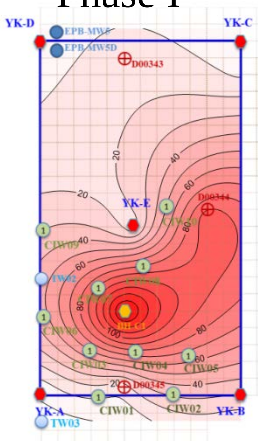
on 7/17 (5th day), reagents were close to downgradient of the pilot region.

Reagents reached 23 m in depth and flew to outside of the pilot region.

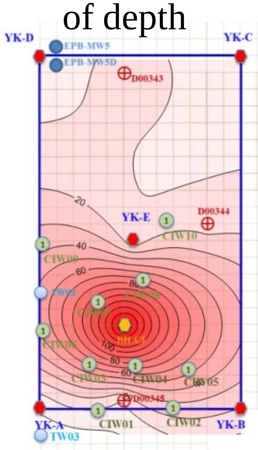
Distribution of TOC After Injection

Samples are collected on 7/20 which is 2 days after the injection (7/13~18).

Phase I



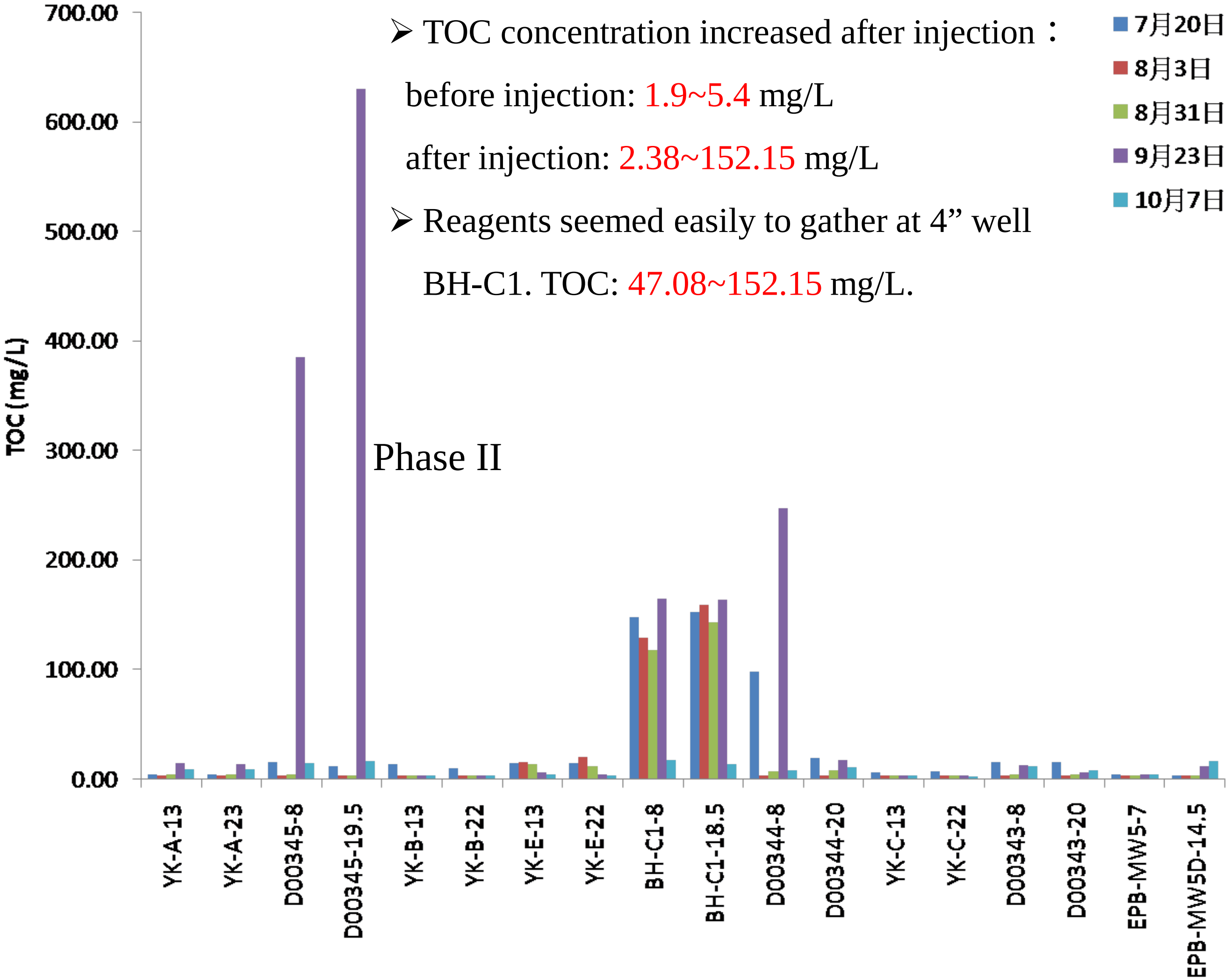
8～13 m of depth



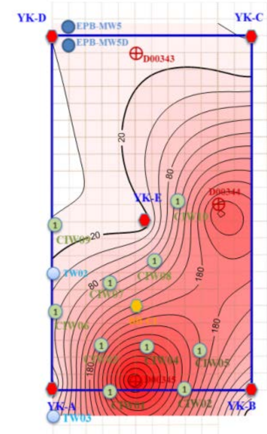
18～23 m of depth

- TOC concentration increased after injection：
  before injection: 1.9~5.4 mg/L
  after injection: 2.38~152.15 mg/L
- Reagents seemed easily to gather at 4” well BH-C1. TOC: 47.08~152.15 mg/L.

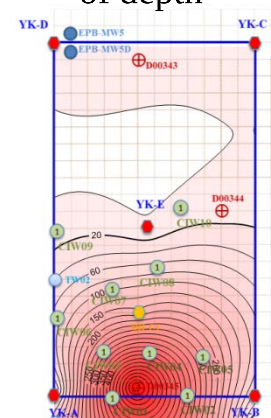
Phase II



Phase II

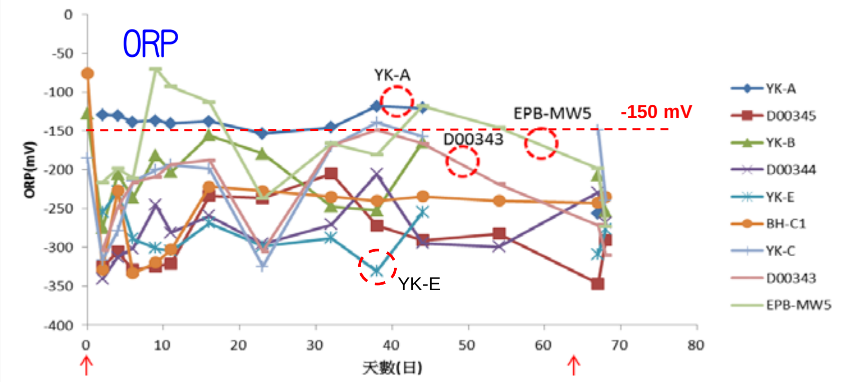


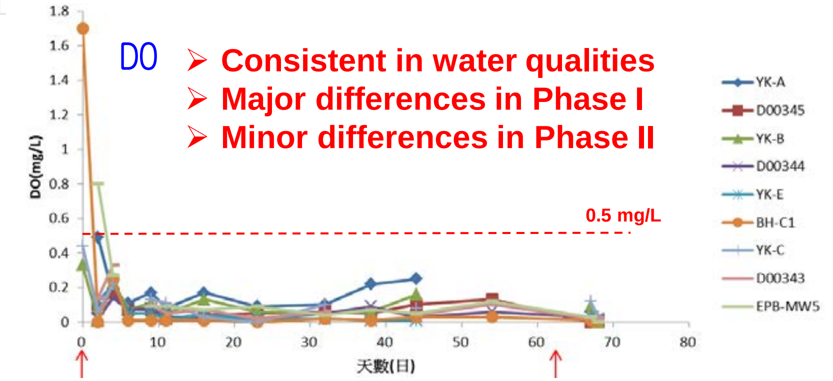
8～13 m of depth

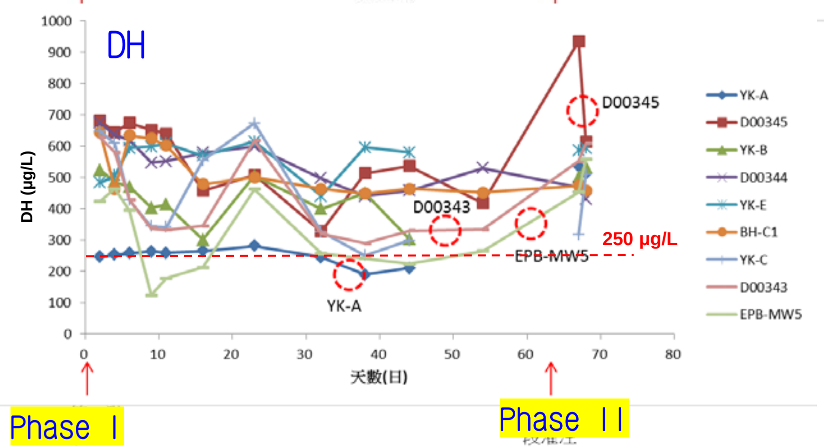


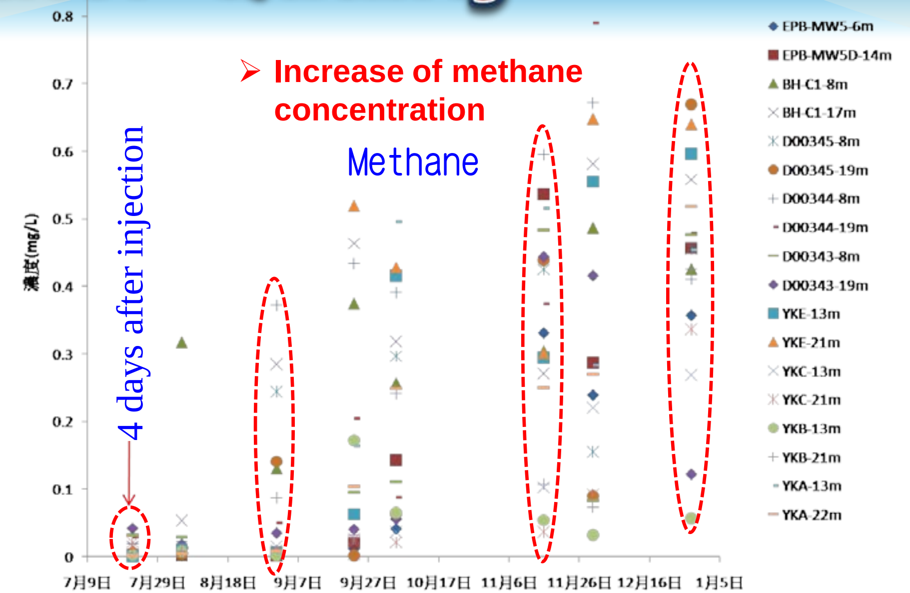
18～23 m of depth

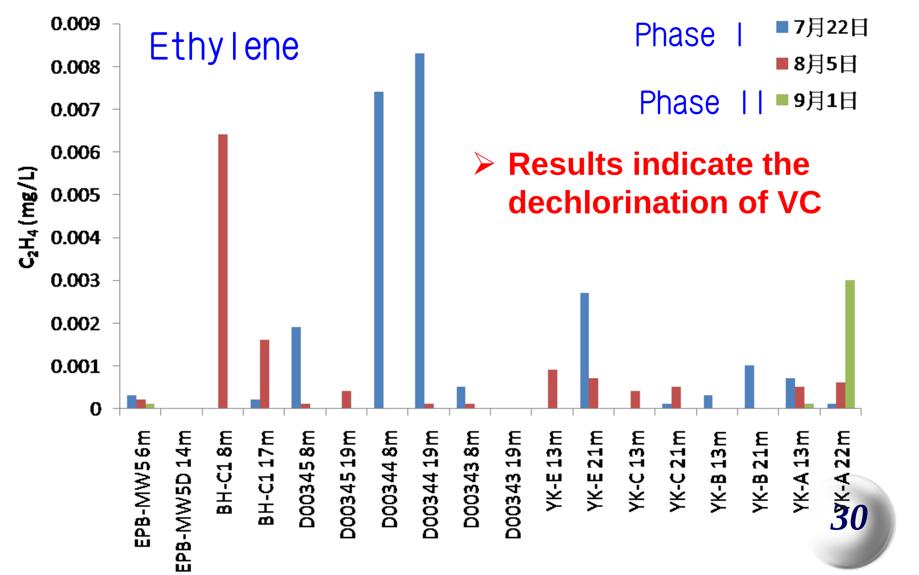
Analysis of Water Quality



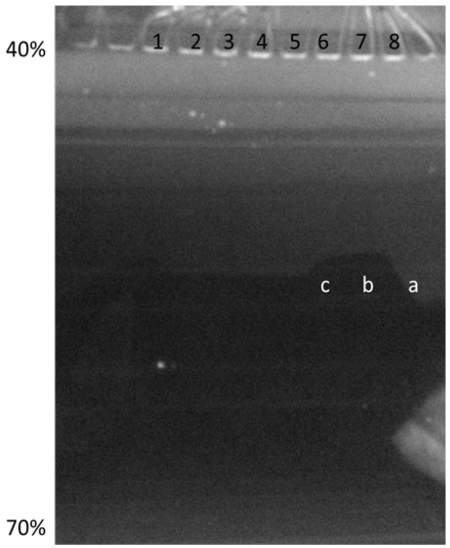








Analysis of Microorganism

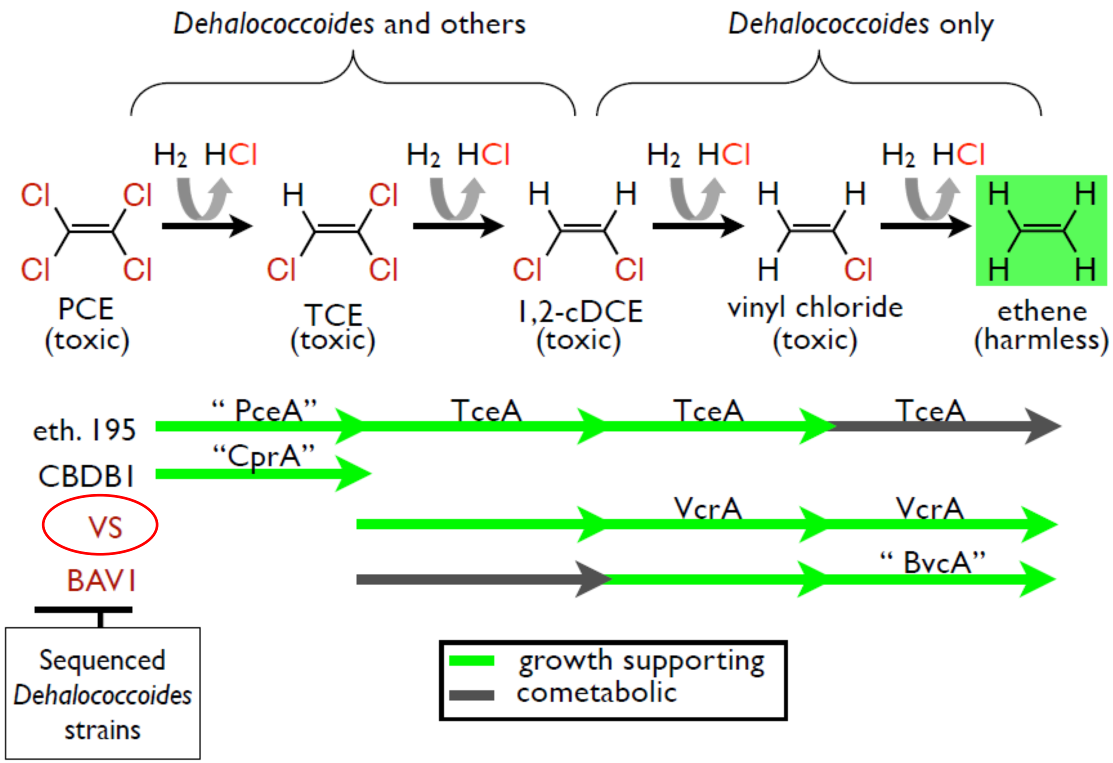


Three wells, D00343、D00344、D00345, had the band at the same level

Gene sequence:

- *Dehalococcoides* sp. strain VS
- Functional gene *vcr*A

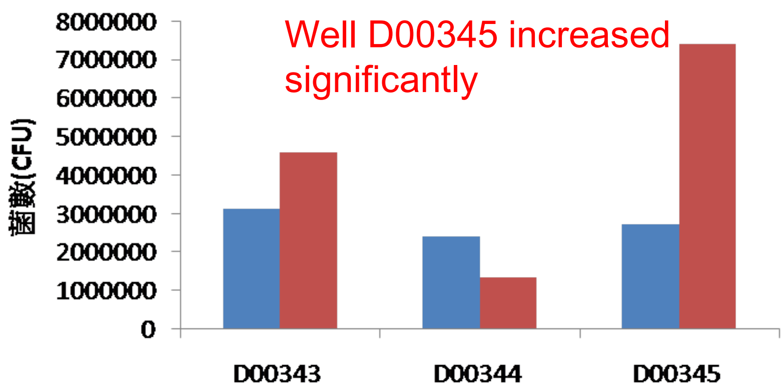
Reductive dechlorination of chloroethenes



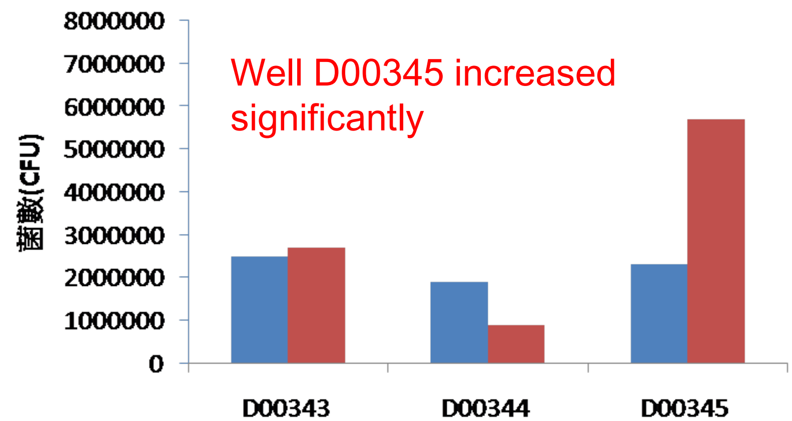
- *Dehalococcoides* sp. strain VS
  - ✓ TCE can be completely degraded to ethylene
  - ✓ It's right for in-situ remediation of CVOCs contaminated sites.

Analysis of Microorganism

Total amount of microorganism



Amount of viable microorganism



Functional gene

	gene	D00343	D00344	D00345
Before	*bvcA*	○	—	○
	vcrA	○	—	○
	tceA	—	—	—
After	*bvcA*	—	—	—
	vcrA	○	○	○
	tceA	—	—	—

sMMO (Methane monooxygenase)

wells	Specific activity of sMMO（μmol/h/mg）
YK-A	2.26×10^{-4}
YK-B	8.53×10^{-4}
YK-C	4.97×10^{-4}
YK-D	5.52×10^{-4}
YK-E	2.86×10^{-4}

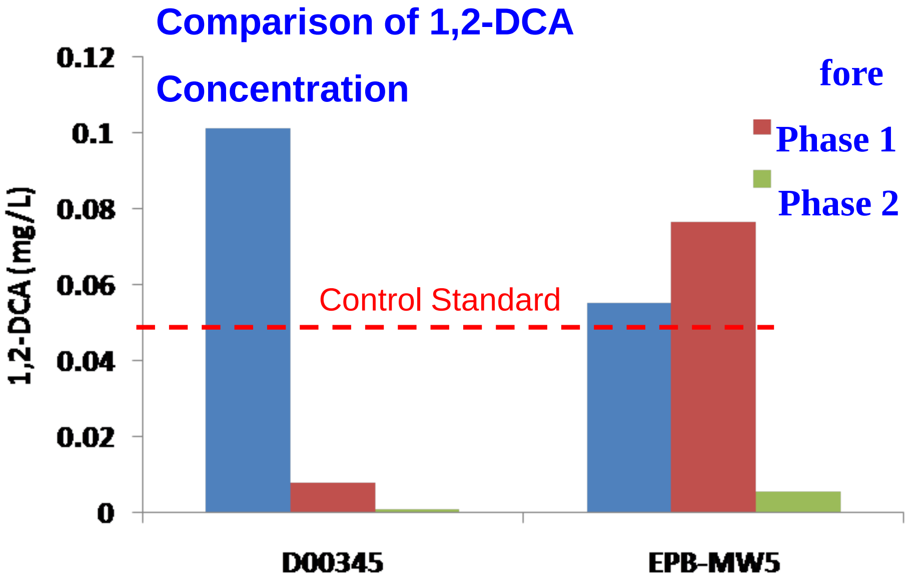
VOCs Reduce (Monitoring Well)

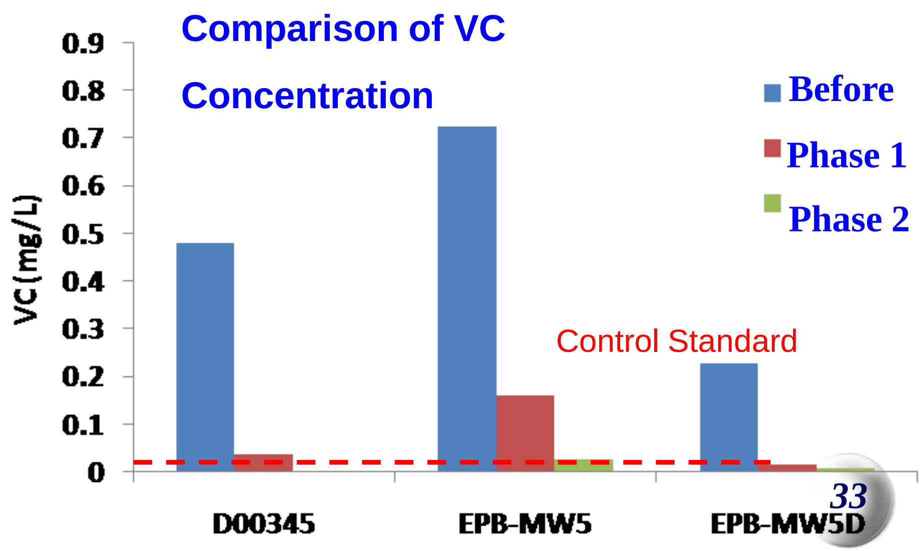
1,2-DCA	Before	Phase 1	Phase 2
D00345	0.1011	0.0077	0.0007
Reduce rate (%)		92.4	99.3
EPB-MW5	0.055	0.0762	0.0054
Reduce rate (%)		-38.5	90.2

- 1,2-DCA met the Control Standard.
- Reducing rates of concentration were between 90.2 ~ 99.3 %.

VC	Before	Phase 1	Phase 2
D00345	0.4794	0.0388	0.0018
Reduce rate (%)		91.9	99.6
EPB-MW5	0.766	0.1605	0.0249
Reduce rate (%)		79	96.7
EPB-MW5D	0.227	0.0167	0.0082
Reduce rate (%)		92.6	96.4

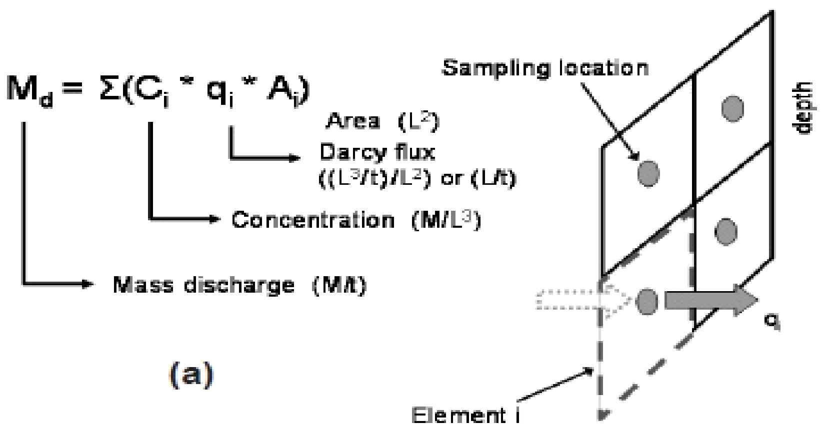
- Except EPB-MW5, no wells exhibited VC exceedance.
- Reducing rates of concentration were between 96.4 ~ 99.6 %.

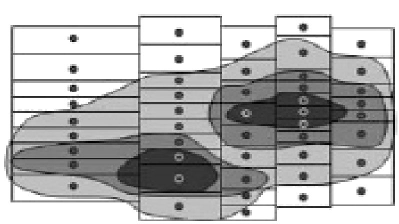




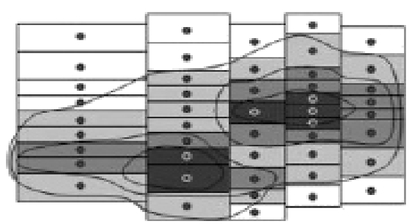
Evaluation of Mass Flux

- Samples are collected from different depths to evaluate the performance.
- Single well flow velocity and flow direction measurement.

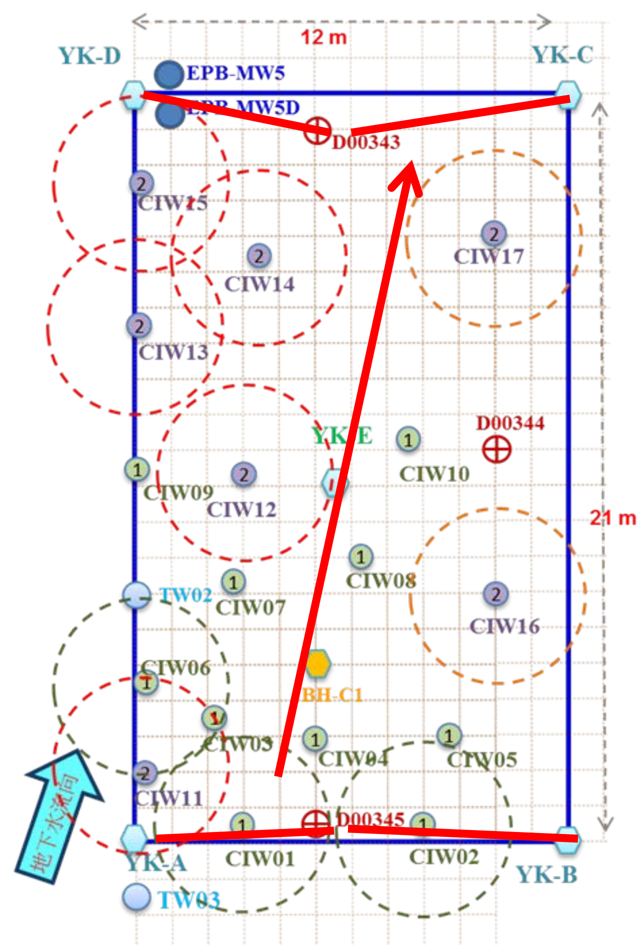




Concentration distribution



Setting concentration for each node



Evaluation of Mass Flux

Upgradient mass flux before injection (292 g/day)

TOTAL MASS FLUX 2.92E+02 (g/day) 1.07E+02 (kg/yr)

Next Step: Mass Flux Summary | Run/View Uncertainty Analysis (Optional) | View Final Concentration Grid | Back to Data Grid | Print | HELP

Downgradient mass flux before injection (255 g/day)

TOTAL MASS FLUX 2.55E+02 (g/day) 9.30E+01 (kg/yr)

Next Step: Mass Flux Summary | Run/View Uncertainty Analysis (Optional) | View Final Concentration Grid | Back to Data Grid | Print | HELP

Upgradient mass flux after Phase I injection (63.5 g/day)

TOTAL MASS FLUX 6.35E+01 (g/day) 2.32E+01 (kg/yr)

Next Step: Mass Flux Summary | Run/View Uncertainty Analysis (Optional) | View Final Concentration Grid | Back to Data Grid | Print | HELP

Downgradient mass flux after Phase I injection (46.9 g/day)

TOTAL MASS FLUX 4.69E+01 (g/day) 1.71E+01 (kg/yr)

Next Step: Mass Flux Summary | Run/View Uncertainty Analysis (Optional) | View Final Concentration Grid | Back to Data Grid | Print | HELP

Upgradient mass flux after Phase II injection (4.07 g/day)

TOTAL MASS FLUX 4.07E+00 (g/day) 1.49E+00 (kg/yr)

Next Step: Mass Flux Summary | Run/View Uncertainty Analysis (Optional) | View Final Concentration Grid | Back to Data Grid | Print | HELP

Downgradient mass flux after Phase II injection (0.831 g/day)

TOTAL MASS FLUX 8.31E-01 (g/day) 3.03E-01 (kg/yr)

Next Step: Mass Flux Summary | Run/View Uncertainty Analysis (Optional) | View Final Concentration Grid | Back to Data Grid | Print | HELP

Mass Flux of VC

	Up-gradient (g/day)	Down-grdient(g/day)	Degradation Rate (%)
Before Injections	292	255	12.7
After I-phase Injection	63.5	46.9	26.1
After II-phase Injection	4.07	0.831	79.6
I-phase Interception Rate	78.3 %	81.6 %	-
II-phase Interception Rate	98.6 %	99.7 %	-

- **98.6% of VC mass flux intercepted from up-gradient region**
- **Degradation rate increases from 12.7% to 79.6% in pilot**
- **99.7% of VC mass flux reduced through the down-gradient section**

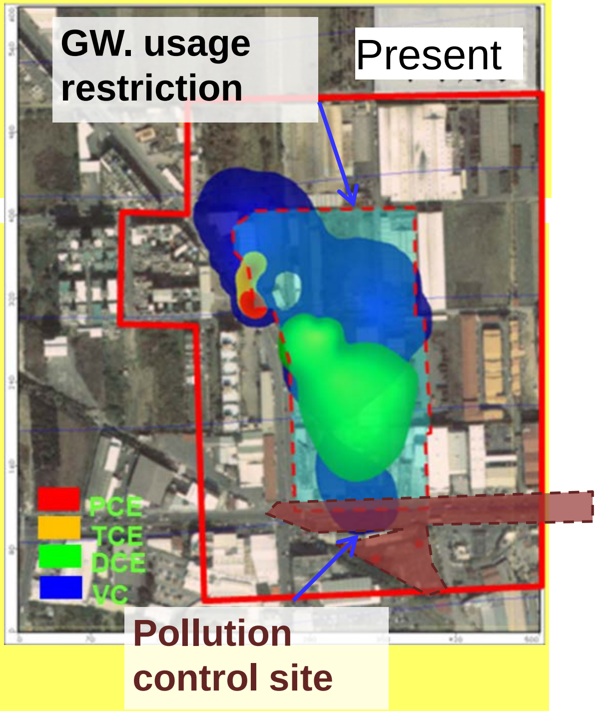
Roadmap of Contamination Management

Contaminant concentration tendency:

Stable conditions of high concentrations in the mainstream area of contamination plume.

Plume:

Still extending



Goals：

To control contamination

To reduce hazard

To prevent plume extension

To ensure public health

Strategies：

To Integrate the administration measures and contamination control

To Implement contaminant reduce contingency by stage and by area

Roadmap of Contamination Management

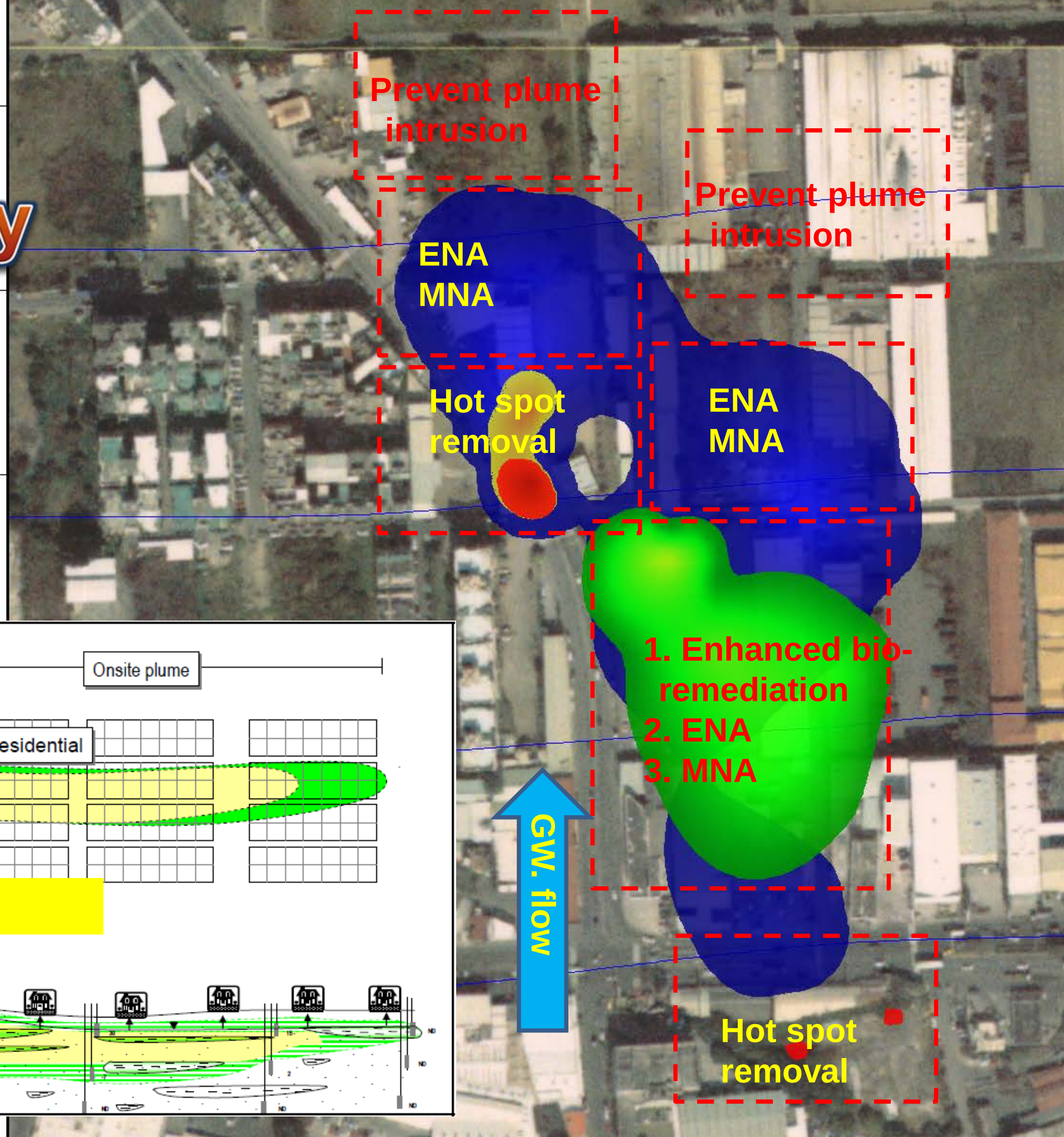
Term	Actions	Area			
		Down-gradient of plume	**High concentration region**	**Hot spots**	**Beyond GW. Usage restriction region**
		Plume fronts	Region A	Regions B and C	Beyond Plume fronts
Short-medium (2~8 years)	Tech.	In-situ bio-barriers	Enhanced in-situ bio-remediation	Removal	Monitoring
	Admin.	GW. Usage restriction	GW. Usage restriction	GW. Usage restriction	Communication with relevant parties Announced as restriction region
Long	Tech.	Monitoring natural attenuation (MNA)	Enhanced natural attenuation (ENA) Monitoring natural attenuation (MNA)	Monitoring natural attenuation (MNA)	Monitoring
	Admin.	GW. Usage restriction Lift restriction	GW. Usage restriction Lift restriction	GW. Usage restriction Lift restriction	Communicate with the locals

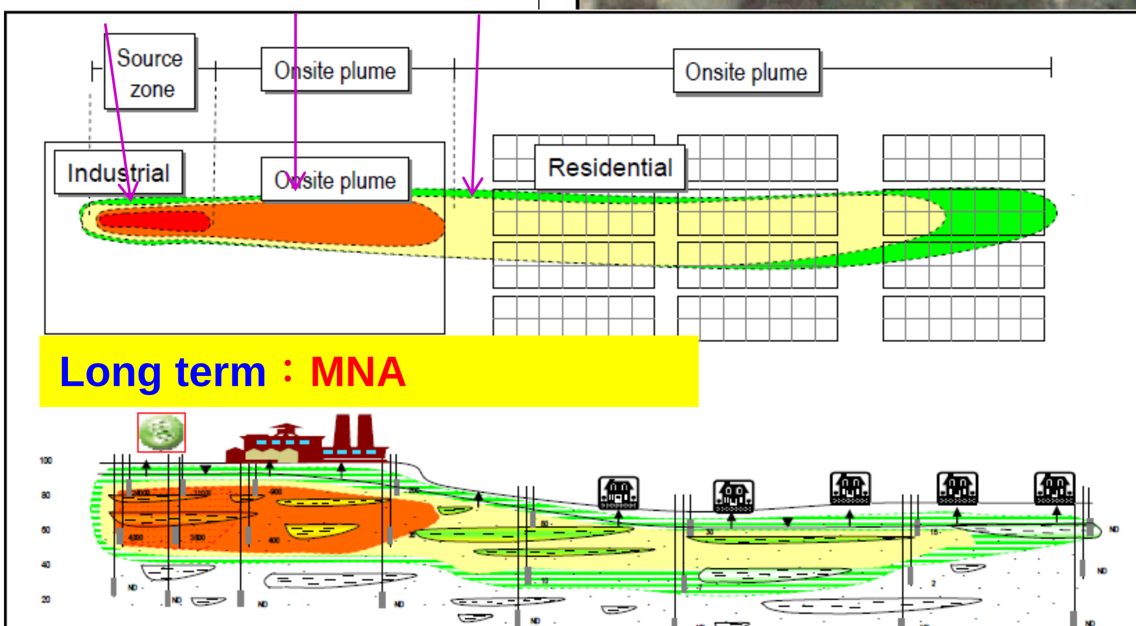
Contingency

Immediately：prevent plume extension

Medium term：Enhanced reducing

Short term：hot spots removal





Roadmap of Contamination Management

Contamination management strategies:

Restriction on groundwater usage

Contingency measurements

In-situ bio-barriers

In-situ bioremediation (bio-stimulation)

Enhanced natural attenuation

Long term contamination monitoring

Monitoring natural attenuation

Health risk assessment

The performance of double packer injection shows promise of overcoming the difficulty of reagents delivery resulted from the geological heterogeneity

Still a long way to go

Thank You

APOLLOTECH 瑞昶科技股份有限公司

聯絡地址：臺北市松山區南京東路三段248號6樓
聯絡電話：+886-2-7706-0566
E- m a i l：apollo@apollotech.com.tw
Website：www.apollotech.com.tw

Investigation and Remediation of Contamination at Gasoline Stations in Taiwan

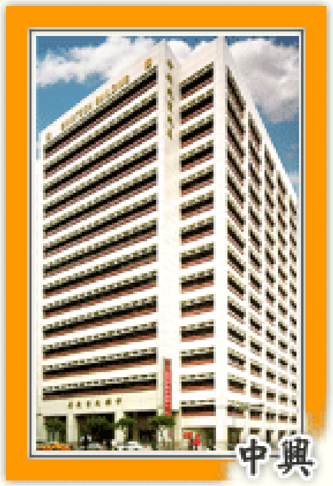
Dr. Chia-Hsin Li

2016.03.25

Company Profile

中興工程顧問股份有限公司
SINOTECH ENGINEERING CONSULTANTS, LTD.

Website: http://www.sinotech.com.tw
E-mail: sinotech@sinotech.com.tw



Head Office

- Contact: Kevin Chang
- Email: biz-dpt@sinotech.com.tw

- Address: 14th Fl. 171, Nanking East Road, Section 5, Taipei 105, Taiwan, ROC
- Tel: 886-2-2769-8388
- Fax: 886-2-2763-4555、886-2-2763-4558

Kaohsiung Office

- Address: 9th Fl., No. 260, Chungshan 2nd Road, Kaohsiung 806, Taiwan, ROC
- Tel: 886-7-537-2606
- Fax: 886-7-537-5127

Southeast Asia Regional Office

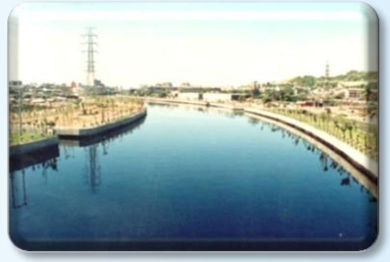
- Contact: Ivan Chen
- Email: sea@sinotech.com.tw

- Address: Graha Iskandarsyah, 11th Floor, Jl. Iskandarsyah Raya, No.66C, Kebayoran Baru, Jakarta 12160, Indonesia
- Tel: 62-21-720-1563
- Fax: 62-21-725-7335

Company Profile

- **As of Feb, 2016:**
  - 1,459 employees
  - 47% of staffs hold advanced degrees (M.S. or Ph.D.)
  - 282 licensed professional engineers
  - 89% of staffs have 5+ years of experience
- **Scope of services:**
  - Study, investigation, planning, design, inspection, construction supervision, project management and turnkey contract
- **Fields of expertise:**
  - Electric power, hydraulic, urban development, industrial and agricultural development, environmental, civil, transportation, architectural, mechanical and electrical engineering








Company Profile

- $106.5 million USD net revenue in 2014
- Up to date, completed ~4,500 domestic assignments, ~240 overseas assignments

Reputation from clients for efficient and high-quality service

Awarded an international certificate of the ISO 9001 Quality Management System

Company Profile

- Batutegi Dam, Lampung, Indonesia
- Cirata Hydroelectric Power Plant (Phase II), West Java, Indonesia
- Kuching Power Plant, Malaysia
- Various industrial parks development in Indonesia, Vietnam and Philippines
- Urban development for Semarang, Palembang, Bogor, Surakarta and Malang in Indonesia
- Java provincial highway improvement project (phase III), Indonesia

- Cirebon and Rengtang irrigation projects, Java, Indonesia
- Denpasar Sewerage Development Project (Phase I), Bali, Indonesia

http://www.sinotech.com.tw/econtent/download/download01.asp

Environmental Engineering Department:

EIA & EM	Water & Wastewater Treatment and Pipeline	Air pollution, Noise & Vibration Control	Waste Management	Soil & Groundwater Investigation and Remediation

Our Services:

- Environmental site assessment (ESA Phase I/II); health risk assessment; groundwater monitoring; design, construction, and operation of remediation work
- Extensive field experiences:

✓ petrochemical factories and oil refineries

✓ gas stations and oil depots

✓ abandoned factories

✓ illegal dumping sites

✓ chlorinated solvent contaminated sites

✓ heavy metal contaminated farmland

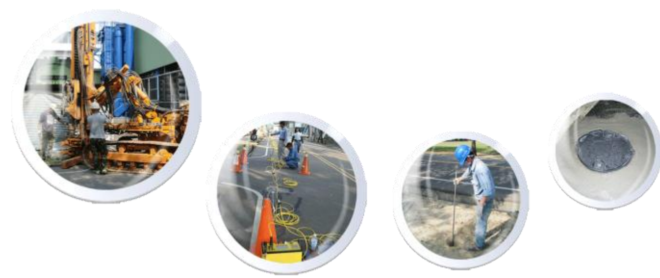
✓ military bases

✓ contaminated sites with accidental leakage

Contents

1

An overview of investigation and remediation of contamination at gasoline stations



Background

1987 Private enterprises were authorized to operate gas stations.

1995 EPA began to establish the database of gas stations .

1997 The diesel and gasoline kept in the underground storage tanks were announced by EPA and the retailers should install the equipments for preventing and monitoring groundwater pollution.

2000 " Soil and Groundwater Pollution Remediation Act" was promulgated by EPA.

2001 A severe oil spill incident occured in Shi-Xiang Gas Station in Taoyuan County.

Implementation of Gas Station Investigation

Overview

2002 **"Gas Station Regulations" was announced to regulate retailers to regularly submit the monitoring data online.**

2011 **"UST Regulations" was modified not only to broaden the announced enterprises but to regulate retailers to monitor soil and groundwater quality by the certified analytical laboratories.**

UST Regulations: Regulations for Installation and Management of Facilities for Preventing Pollution of Groundwater Bodies and Monitoring Equipment in Underground Storage Tank Systems

- Over 2,700 gas stations in Taiwan had been thoroughly inspected and investigated from 2001 to 2012, and more than 220 contaminated sites were found.
- Since 2013, Taiwan EPA have carried out spot-checks on 300 gas stations each year.

Pollution Potential Analyses

Business Subject

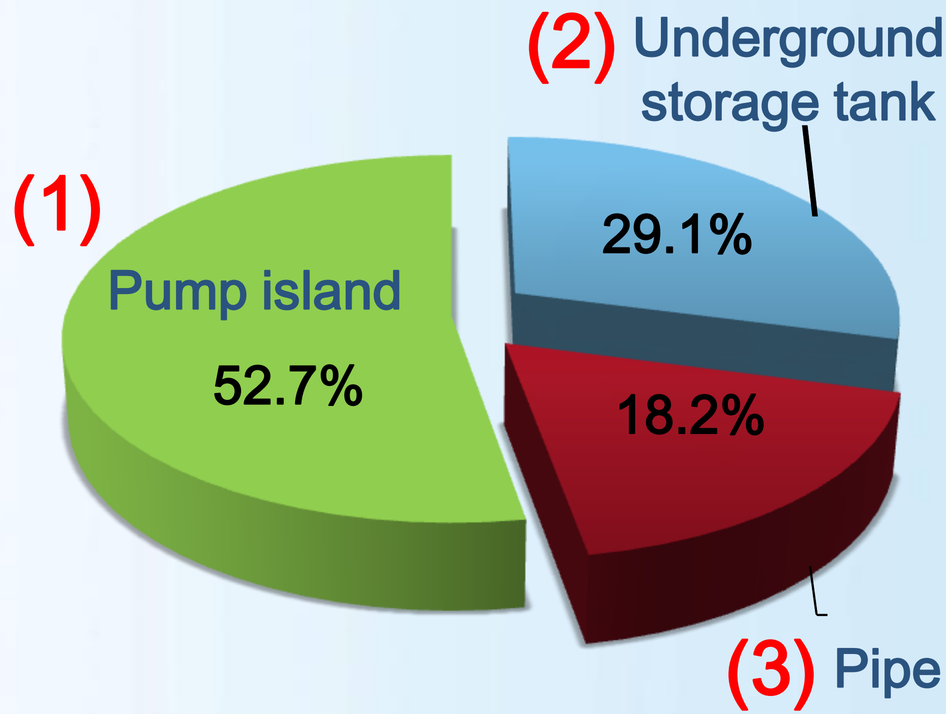
✓High pollution potential：

Site operators were tenants and had less control over the underground facilities.

✓Low pollution potential：

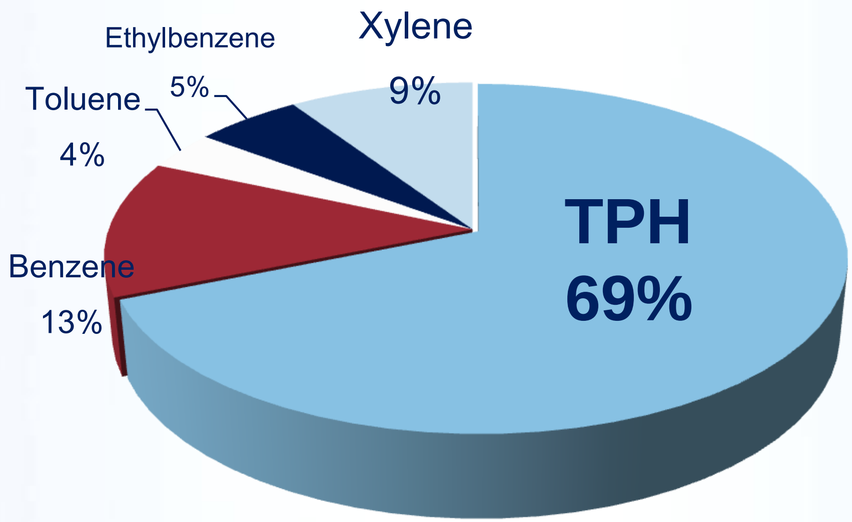
Sites were built and operated on the owners' own and managed by dedicated specialists.

Leakage Source

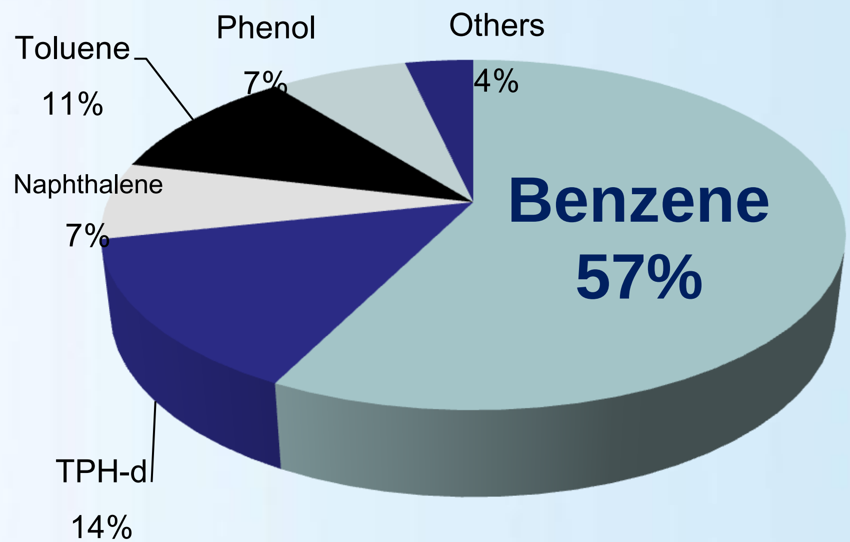


Pollution Potential Analyses

Soil pollutants



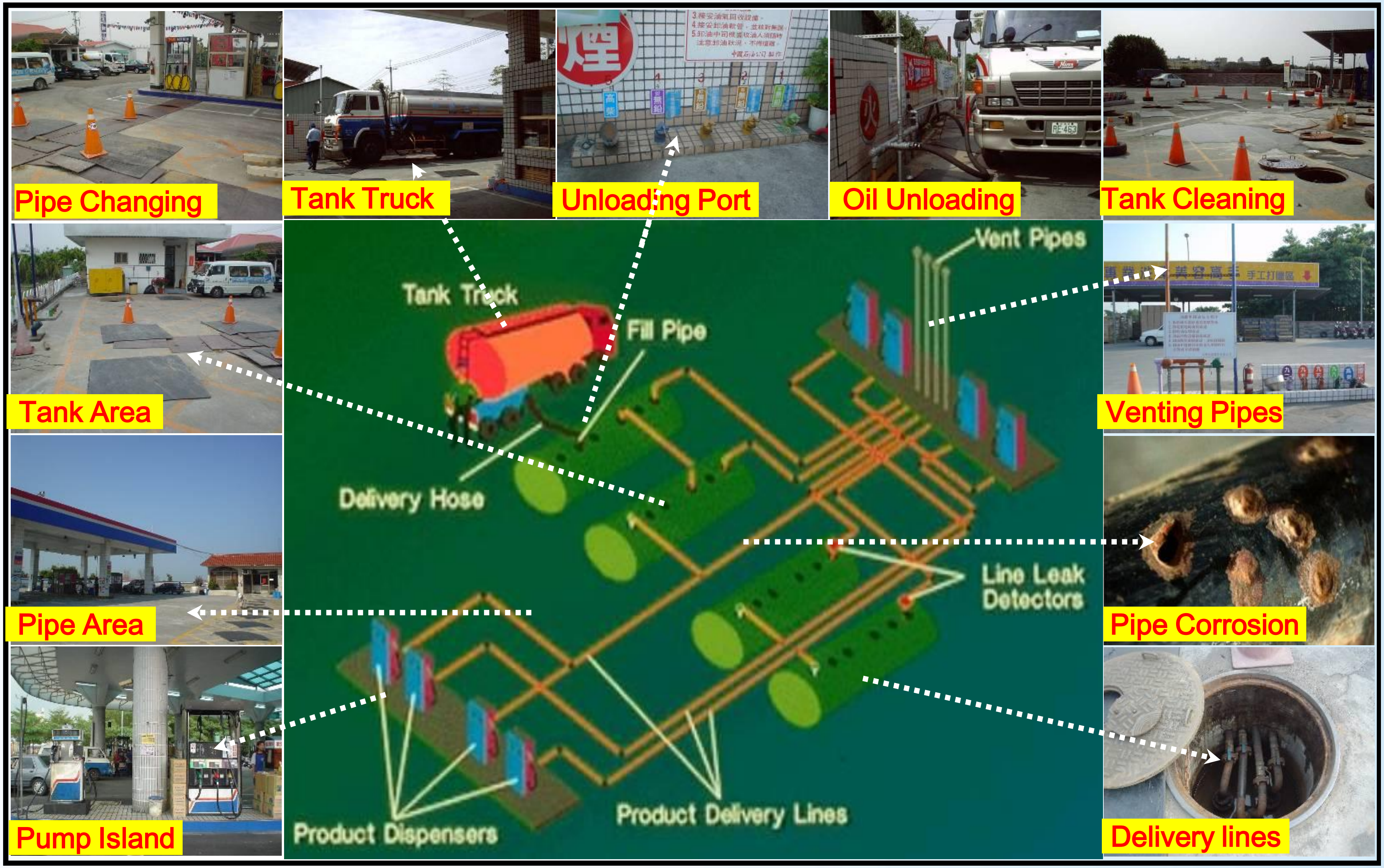
Groundwater pollutants



The most common pollutant found in soil is total petroleum hydrocarbons (TPH), and benzene is commonly found in groundwater.

Leakage Sources and Causes

Overview



1. Unloading Port

2. Gasoline Tank

Leakage Sources and Causes

Overview

3. Delivery Lines

4. Dispenser Bottom

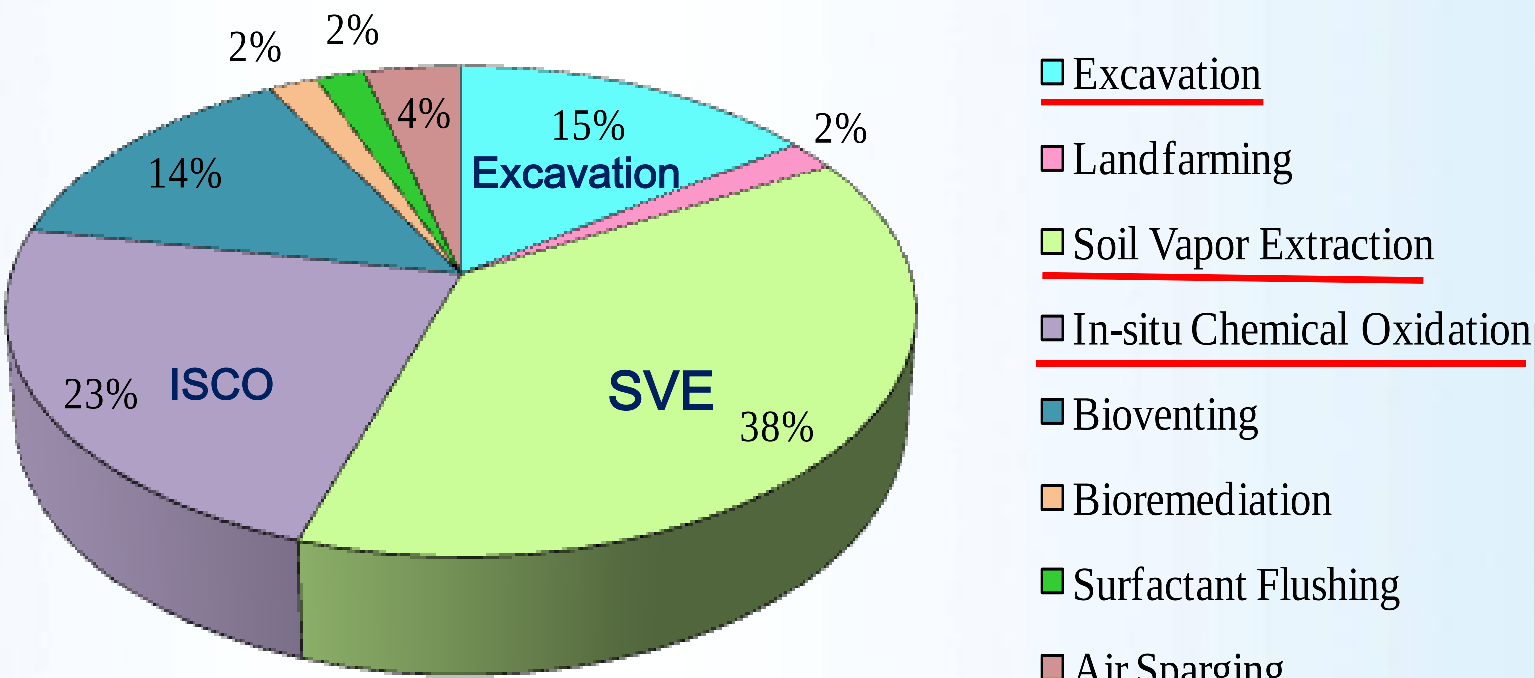
Pollution Prevention Measures

Overview

source	Unloading port and lines	Gasoline Tank	Delivery lines	Pump island (gas filling island)
Prevention measures	Spill dike	Secondary containment	Double-walled flexible pipe and pipe canal	Sump
	 	 	 	 

Remediation Methods

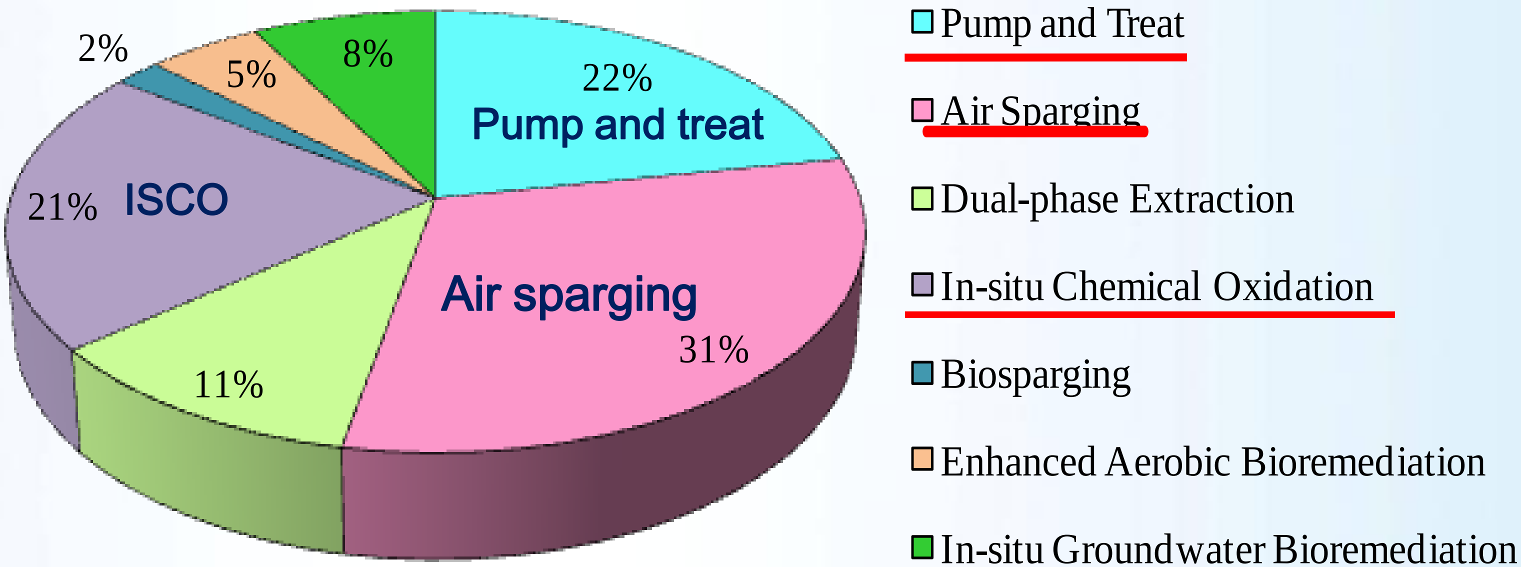
For soil remediation:



SVE & AS

In-situ treatment was mostly chosen for soil remediation; soil vapor extraction (SVE) was usually used in conjunction with other remediation method.

For groundwater remediation:



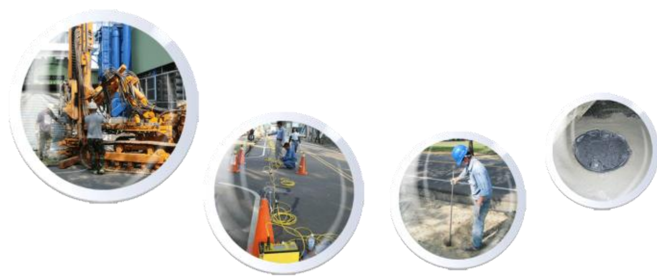
ISCO

In-situ treatment was mostly chosen for groundwater remediation; **air sparging (AS)** was usually used in conjunction with other remediation method.

ISCO remediation has been increasingly used in recent years.

2

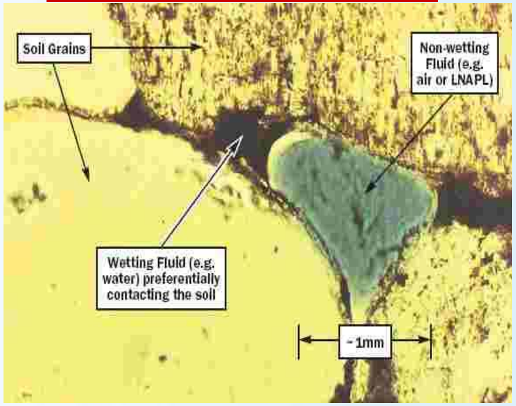
Planning and design considerations on ISCO remediation for gas station



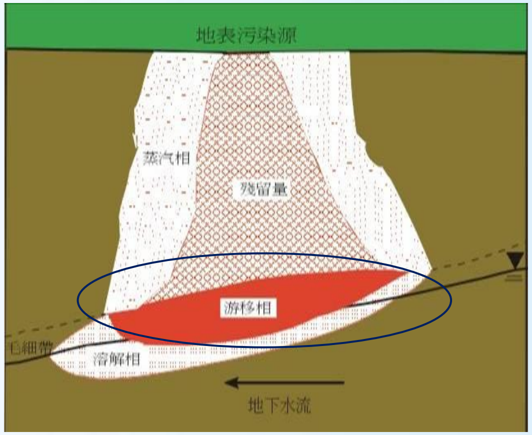
Before Remediation

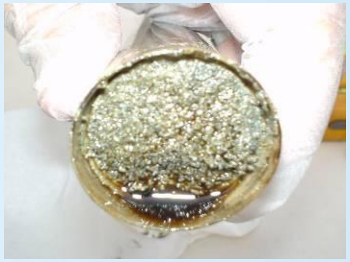
1. Pollution source removed?
2. Delineation survey done?
   (1) Soil/groundwater polluted?
   (2) Hydrogeological information?
   (3) With free product (oil slick) or residual phase?
3. Pilot test needed?

Residual phase

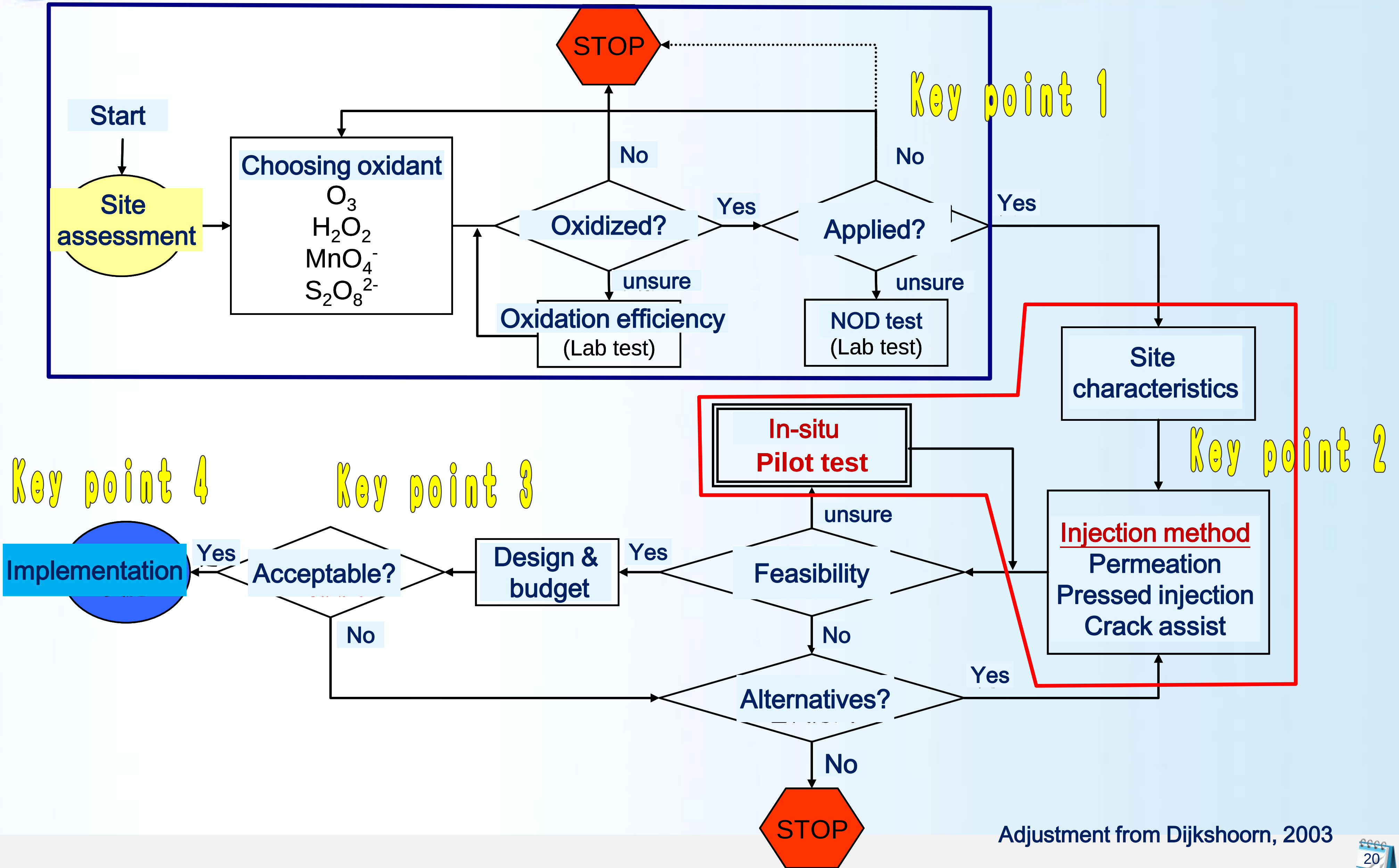


Free product





Feasibility Assessment



Adjustment from Dijkshoorn, 2003

Reagents

Target pollutants

Oxidants	Applied pollutants							
	TPH	benzene	phenol	MTBE	PAHs	Cl-ethylene	CCl_4	Cl-ethane
Hydrogen peroxide	++	++	++	+	++	++	×/+	+/++
Ozone	++	++	++	+	++	++	×/+	+
Permanganate	+	×	+	+	+	++	×	×
Persulfate	++	+/++	+/++	++	++	++	×/+	+/++

++ best ，+ good ， × bad

Cited from Lin, 2002；ITRC, 2002

➢ Dosage test：

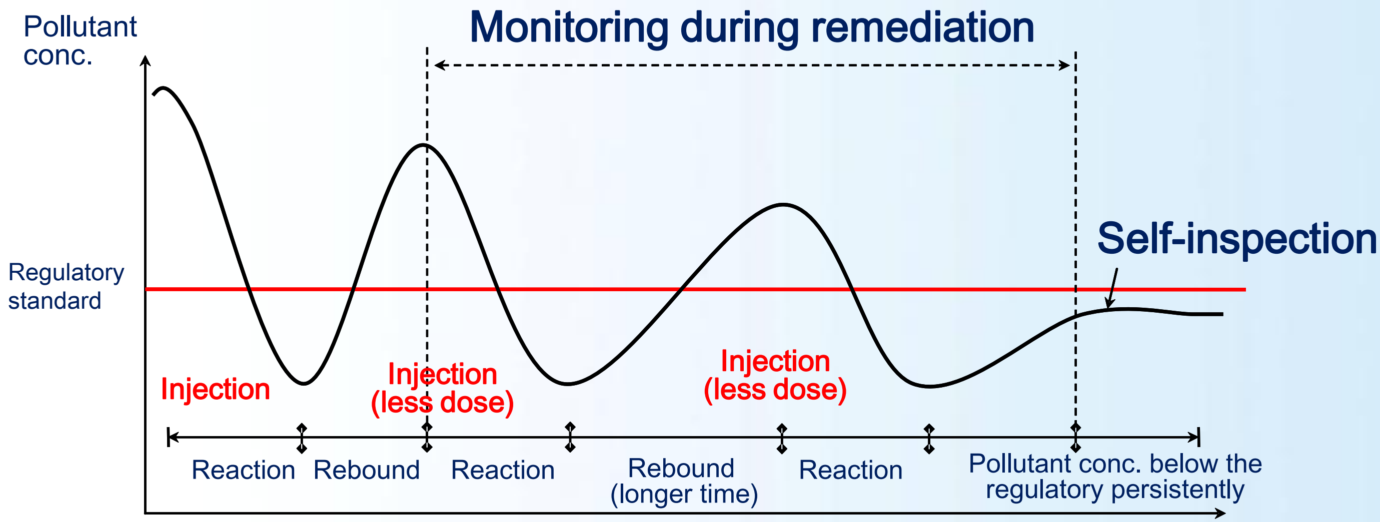
1. Taking soil samples at hot spot zone and uncontaminated zone
2. Testing items：pH, ORP, DO, CO_2, temperature, EC and ferric ion conc.
3. Formula selection：variables including dose proportionality of hydrogen peroxide / catalyst / chelating agents (solid to liquid ratio)
   ➡ radicals production and long residual action
4. Addition test ➡ removal efficiency
5. Column test ➡ to simulate the variation of removal efficiency with the increasing transporting distance

- **Injection diffusion distance (effective range) test：site specific**

1. **Well allocation** (Injection, monitoring and pumping)
2. **Factors**：reagents, water level, homogeneous or heterogeneous、sieving length of injection well, injection method and multi-well cluster allocation
3. **Injection method**:
   (1) gravity flow/pressure, (2) long/short sieving length, (3) single/multi depth sieving and (4) vertical/horizontal
4. **Injection volume: volume of Fenton reagent is several times more than pore volume.**

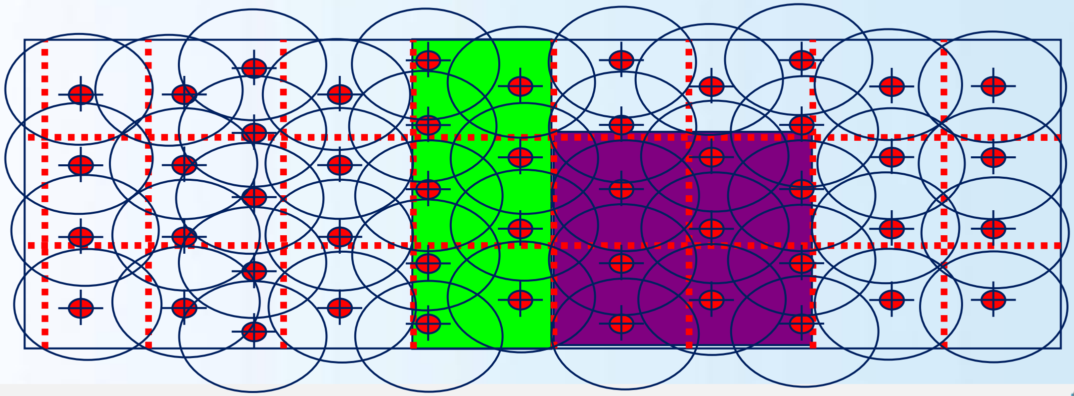
Monitoring Assessment

- **Monitoring indicator:** ORP, DO, CO_2, temperature and conductivity
- **Pollutant monitoring:** removal efficiency and reagent addition times
- **Rebound**

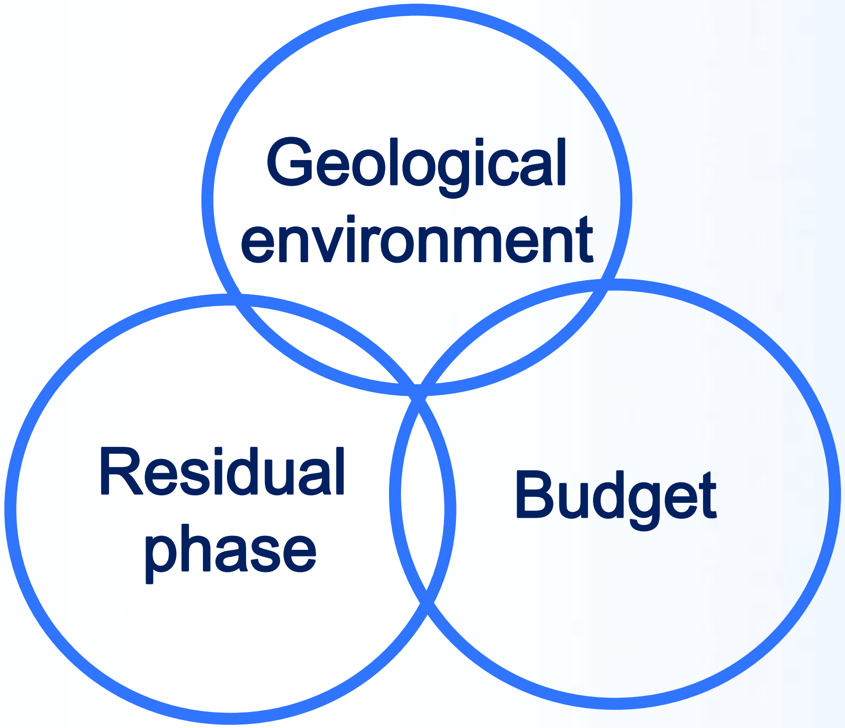


How to Monitor?

- 1st comprehensive monitoring should be conducted after completing injection and reaction.
- Regarding the budget, hot spot and its downstream area have the first priority in monitoring.
- 2nd overall sampling can be conducted when performing self-inspection
- Monitoring via newly-installed temporary wells is necessary.



Problem



- Shot-circuiting and corner pocket
- Rebound
- Limit of removal efficiency

- Budget vs. removal efficiency

Concerning: (1) unknown leakage source

(2) existed free product or residual phase

(3) conjunction with other remediation method

3

Case Study

The First Gas Station Removed from Taiwan EPA List of Contaminated Sites

Site Information

1 North side (parking lots)

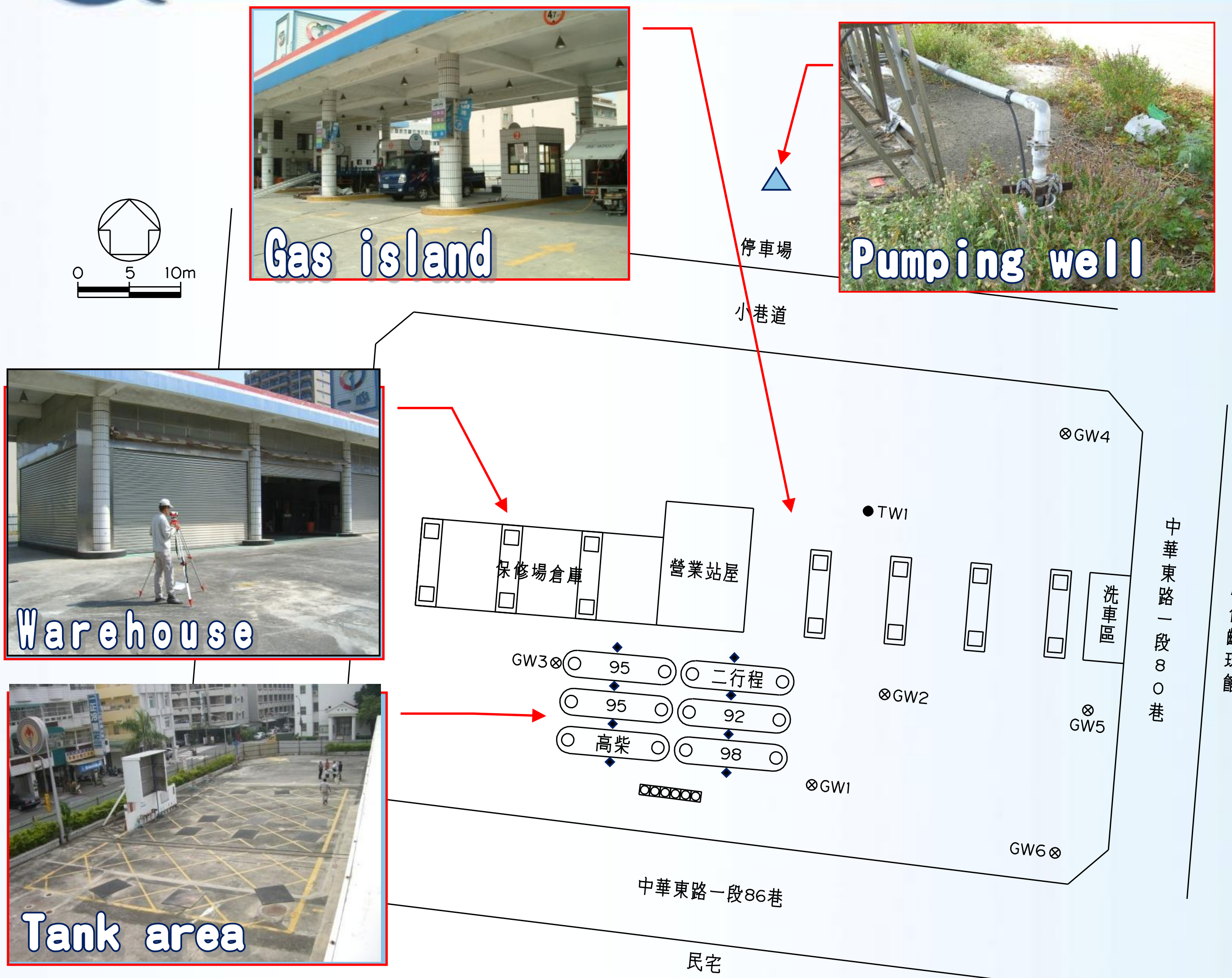
2 West side (residence)

3 South side (residence)

4 East side (bowling center)

1. Located in Tainan City and surrounded by parking lots, residence and KTV
2. Total Area = 3,525 m^2

Site Map before Remediation



- 6 tanks (50 KL per tank)
- 7 islands (3 of which on the western side have been terminated since 1994)
- 8 leakage detection pipes
- **Pipe type: pressure flow**
- **3 groundwater monitoring wells**
- One pumping well in the parking lot on the north side(terminated since 2006)

Established in October of 1989; suspended business on May 15th, 2006.

Remediation History

- In October 2006, a private gas station in Tainan City about 3.5 km^2 in area was declared a contaminated site by the Taiwan EPA.
- Soil pollutants: benzene, toluene, ethylbenzene, xylene and total petroleum hydrocarbon
  Groundwater pollutants: benzene, toluene, naphthalene and phenol
- Sinotech Engineering Consultants, Ltd. was contracted to carry out soil and groundwater pollution investigation and remediation.

The site before remediation work

Remediation History

- Stage 1 (September 2006 to December 2007):
  Supplementary survey of scope of pollution and control measures of groundwater pollution around the site were carried out ; a remediation plan was presented and approved by the EPB of Tainan City.

- Stage 2 (January 2008 to December 2008):
  Excavation and removal of highly contaminated soil, off-site transport and treatment, and in-situ chemical oxidation were performed; then after evaluation of remediation performance, backfilling the site with the clean soil and a continuous monitoring were conducted.

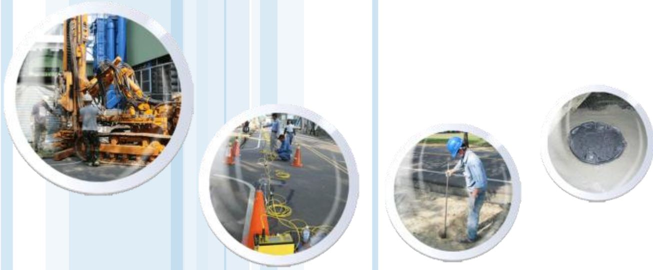
Remediation History

- **Stage 3 (January 2009 to March 2010):**
  For un-excavated contaminated soil, enhanced dual phase extraction and in-situ chemical oxidation were adopted. After receiving good results of self-inspection, all of the remediation procedures were complete.

- **Stage 4 (April 2010 to January 2011):**
  EPA removed the gas station from the list of contaminated sites upon verifying remediation results that showed pollutant concentration was within soil and groundwater control limits.

Remediation History

- After four years of remediation work, the site was removed from the EPA's list of contaminated sites in January 2011.
- It is the first among 55 contaminated gas stations in Taiwan to be successfully remediated since the promulgation of the Soil and Groundwater Pollution Remediation Act in February 2000.
- The service fee for this four-year project was NT$ 70 million (about US$2.12 million).



Delineation Survey

Pollutant Verification (2005.11)

Delineation Survey

1. Soil pollutants: benzene, toluene, ethylbenzene, xylene and TPH
2. Groundwater pollutants: benzene, toluene, naphthalene and phenol

S94-3

Soil pollutants(mg/kg)	
✓ Benzene	297
Toluene	699
Ethylbenzene	351
(meta-/para-) xylene	733
(ortho-) xylene	348
TPH-d	9,530
TPH-g	913

S94-4

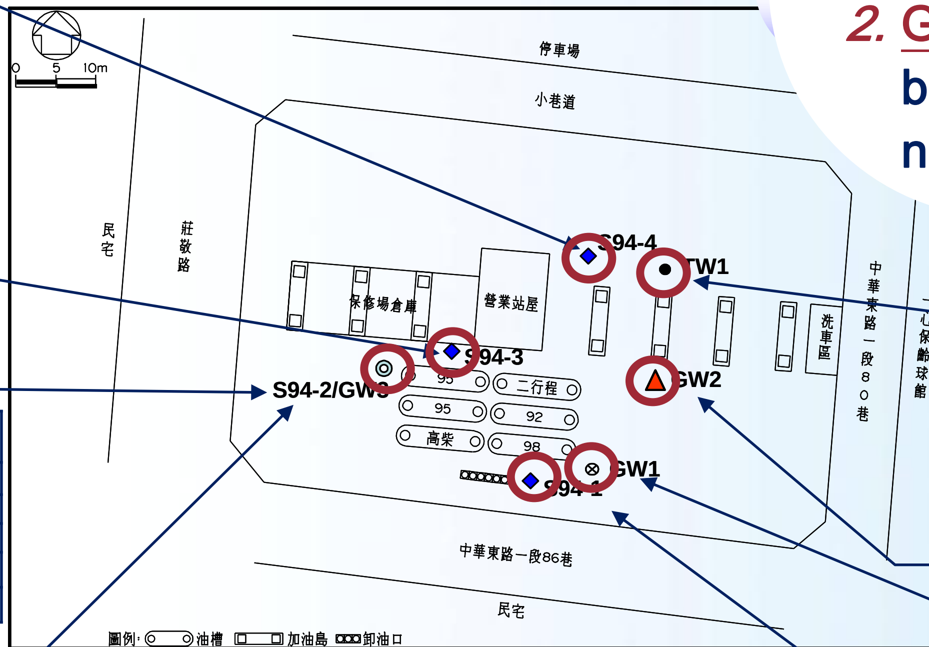
Soil pollutants(mg/kg)	
Benzene	3.34
Toluene	70.1
Ethylbenzene	49.4
(meta-/para-) xylene	147
(ortho-) xylene	79.7
TPH-d	8,790
TPH-g	110

S94-2

Soil pollutants(mg/kg)	
Benzene	<2
Toluene	<2
Ethylbenzene	3.47
(meta-/para-) xylene	117
(ortho-) xylene	73.4
TPH-d	2,220
TPH-g	561

GW3

Groundwater pollutants(mg/L)	
✓ Benzene	10.5
Toluene	8.27
Naphthalene	0.4
Phenol	0.152
1,2-DCE	0.188



Legend：◆ soil ▲ groundwater ◎ Soil/ groundwater

TW1

Groundwater pollutants(mg/L)	
✓ Benzene	58.9
Toluene	41.3
Naphthalene	0.866
Phenol	0.0323
1,2-DCE	0.296

GW2

Groundwater pollutants(mg/L)	
✓ Benzene	7.38
Toluene	7.98
Naphthalene	0.422
Phenol	0.16
1,2-DCE	0.0134

GW1

Groundwater pollutants(mg/L)	
✓ Benzene	24.8
Toluene	14.1
Naphthalene	0.409
Phenol	1.19
1,2-DCE	0.871

S94-1

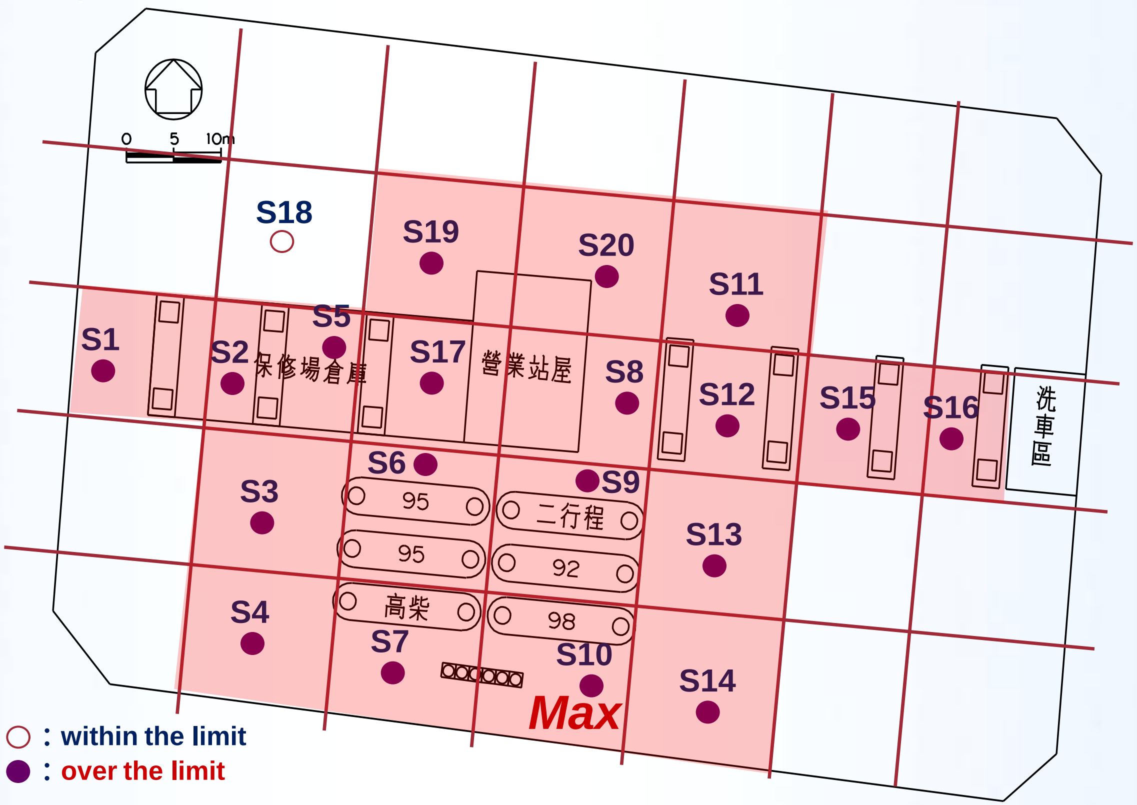
Soil pollutants(mg/kg)	
Benzene	26.0
Toluene	44.8
Ethylbenzene	<10
(meta-/para-) xylene	356
(ortho-) xylene	293
TPH-d	6,410
TPH-g	1,290

Soil control limits(mg/kg)	Benzene	Toluene	Ethylbenzene	Xylene	TPH
	5	500	250	500	1,000
Groundwater control limits(mg/L)	Benzene	Toluene	Naphthalene	Phenol	1,2-DCE
	0.05	10	0.4	0.14	0.05

✓：the value of benzene is over 20 times more than the regulatory standard

Delineation Survey (1/6)

Stage 1: soil



○ : within the limit
● : over the limit

Soil Pollutants

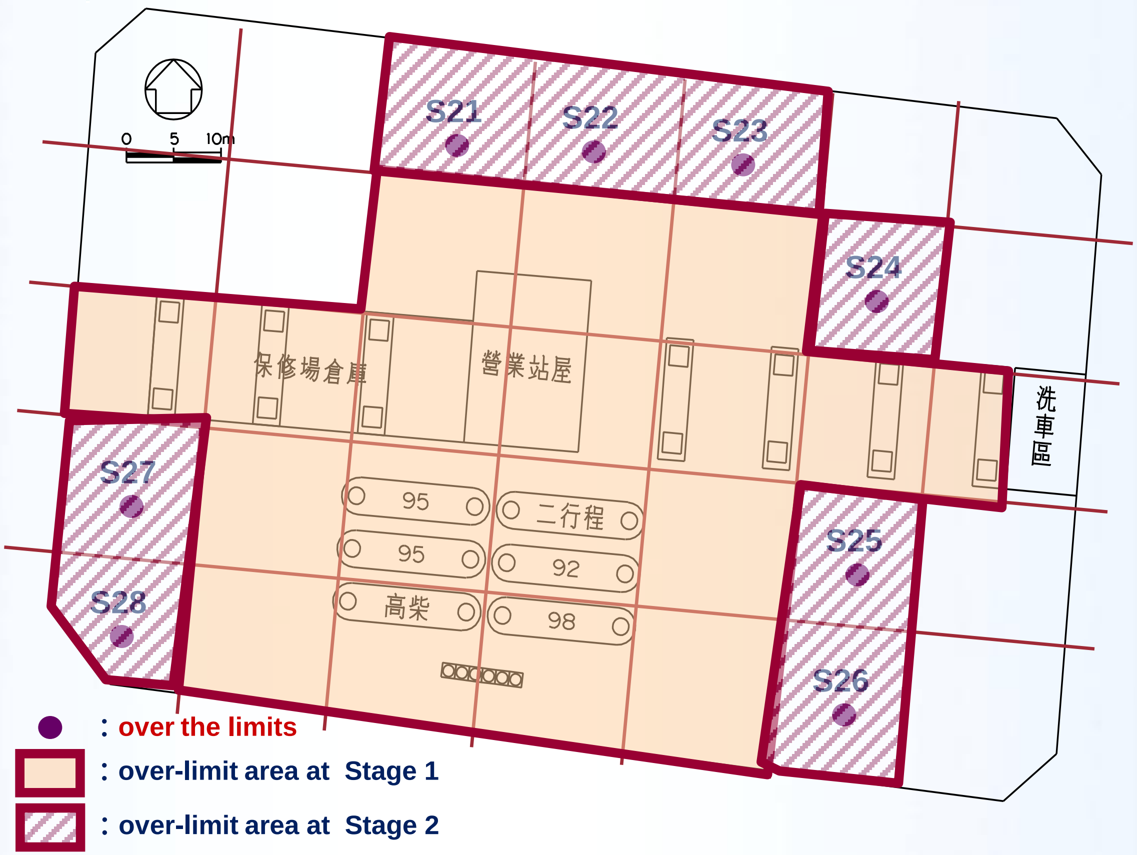
Item and limit (mg/kg) / Sampling depth	Benzene	Toluene	Ethyl-benzene	Xylene	TPH
	5	500	250	500	1,000
✓ S1 (2.5~3.0m)	107	198	118	459	7,641
✓ S2 (2.5~3.0m)	579	1,230	537	1,966	24,420
✓ S3 (1.5~2.0m)	434	1,110	470	1,869	24,060
✓ S3 (3.0~3.5m)	322	582	216	809	22,660
✓ S4 (2.5~3.0m)	379	576	214	829	9,726
✓ S5 (2.5~3.0m)	325	864	332	1,322	18,065
S6 (4.0~4.5m)	57.5	61.4	23.2	98	1,458.1
✓ S7 (3.0~3.5m)	276	458	173	696	10,365
✓ S8 (4.5~5.0m)	484	703	287	1,109	18,208
✓ S9 (2.0~2.5m)	148	491	205	879	13,806
✓ S10 (2.5~3.0m)	1,360	2,090	746	2,851	41,510
✓ S11 (3.5~4.0m)	468	714	281	1,105	10,607
S12 (2.5~3.0m)	16.4	142	66.5	321	3,247
✓ S13 (3.5~4.0m)	263	541	215	940	12,611
✓ S14 (4.0~4.5m)	1,180	1,580	554	2,246	14,070
✓ S15 (2.0~2.5m)	110	506	194	839	8,285
S16 (1.5~2.0m)	27.5	592	334	564	12,330
S17 (2.0~2.5m)	11.7	46.1	33.9	149.1	1,573.4
S18 (3.0~3.5m)	4.24	3.53	0.328	1.543	48.7
✓ S19 (3.5~4.0m)	308	441	173	724	8526
S20 (3.0~3.5m)	74.0	327	146	601	7487

✓ : the value of benzene is over 20 times more than the regulatory standard

1. 19 out of 20 polluted points over the soil pollution control limits
2. Soil pollutants: benzene, toluene, ethylbenzene, xylene and TPH
3. Pollution depth between 1.5~5.0 m

Delineation Survey (2/6)

Stage 2: soil



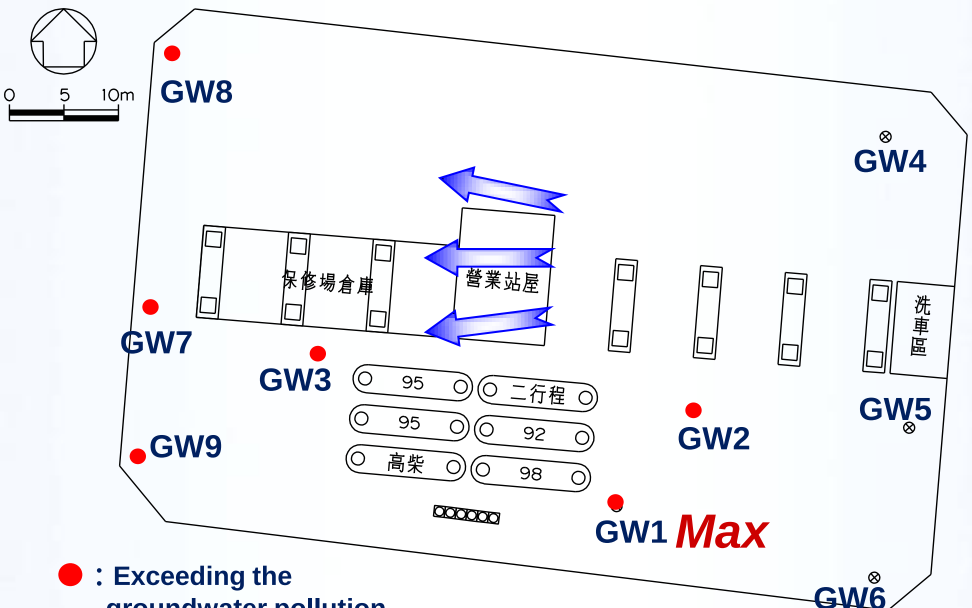
Soil Pollutants

Item and limit (mg/kg) / Sampling depth	Benzene	Toluene	Ethyl-benzene	Xylene	TPH
	5	500	250	500	1,000
S21 (4.0~4.5m)	10.4	6.57	0.794	3.57	9.43
S22 (3.5~4.0m)	＜5	＜5	71.9	99.2	1754.4
S23 (4.0~4.5m)	27.5	629	216	970	5766
S24 (3.5~4.0m)	＜5	＜5	175	701	5526
S25 (4.0~4.5m)	＜5	＜5	156	632	3668.6
S26 (3.5~4.0m)	＜5	231	109	484	3215.3
✓S27 (2.5~3.0m)	285	600	217	870	7853
S28 (3.0~3.5m)	32.0	98.4	37.2	145.1	1247.2

1. All of 8 polluted points over the soil pollution control limits
2. Soil pollutants: benzene, toluene, ethylbenzene, xylene and TPH
3. pollution depth between 2.5~4.5 m

Delineation Survey (3/6)

Groundwater: standard well



● : Exceeding the groundwater pollution control limit

1. Groundwater of 6 wells exceeded the control limit
2. Groundwater pollutants: benzene, toluene, naphthalene and phenol

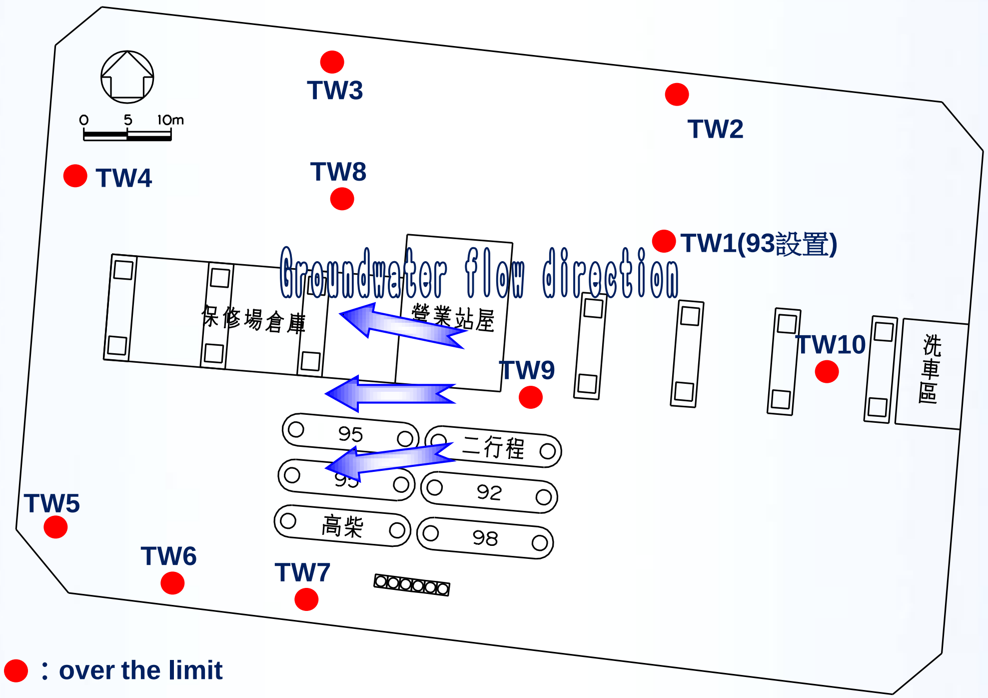
Groundwater Pollutants

Sampling Date		Item and standards (mg/L): benzene 0.05	toluene 10	naphthalene 0.4	phenol 0.14	1,2-DCE 0.05	lead 0.5	MTBE –
GW1	✓ 95.10.02	11.5	7.64	0.246	0.522	ND	–	0.0162
	✓ 95.12.15	33.2	23.0	0.684	0.676	<0.01	ND	<0.01
	✓ 96.02.03	32.9	22.2	0.515	0.496	<0.01	–	<0.01
		41.2*	34.0 *	0.777 *	0.226 *	ND *	–	ND *
GW2	✓ 95.10.02	6.87	5.84	0.24	0.177	ND	–	ND
	✓ 95.12.15	15.4	13.7	0.513	0.0806	<0.01	0.0081	<0.01
GW3	✓ 95.10.02	3.60	0.17	0.017	0.033	ND	–	0.39
	✓ 95.12.15	7.58	0.329	0.0729	0.0556	<0.01	ND	7.36
	✓ 96.02.03	7.74	0.204	0.059	0.026	<0.01	–	0.399
		10.3	0.361	0.0636	0.0176	ND	–	0.851
GW4	95.10.04	ND	ND	ND	ND	ND	–	0.003
	95.12.15	ND	ND	ND	ND	ND	–	ND
GW5	95.10.04	ND	ND	ND	0.0055	ND	–	ND
	95.12.15	<0.01	<0.01	<0.01	0.0081	<0.01	–	<0.01
GW6	95.10.04	ND	ND	ND	0.0046	ND	–	0.0035
	95.12.15	ND	ND	ND	0.0062	ND	–	ND
GW7	✓ 95.12.15	1.01	ND	ND	0.0082	ND	ND	0.0161
	✓ 96.02.03	3.30	0.0118	<0.01	0.0222	<0.01	–	0.0347
		5.80	0.014	ND	0.091	ND	–	0.0316
GW8	✓ 95.12.15	5.84	0.498	0.0515	0.0846	<0.01	–	0.0576
GW9	95.12.15	0.0728	0.0623	0.0084	0.0029	ND	ND	0.338
	✓ 96.02.03	1.50	0.614	0.0147	0.0268	<0.01	–	5.71
		3.05	1.28	0.0203	–	ND	–	7.75

✓ : the value of benzene is over 20 times more than the regulatory standard

Delineation Survey (4/6)

Groundwater: temporary well



● : over the limit

Groundwater Pollutants

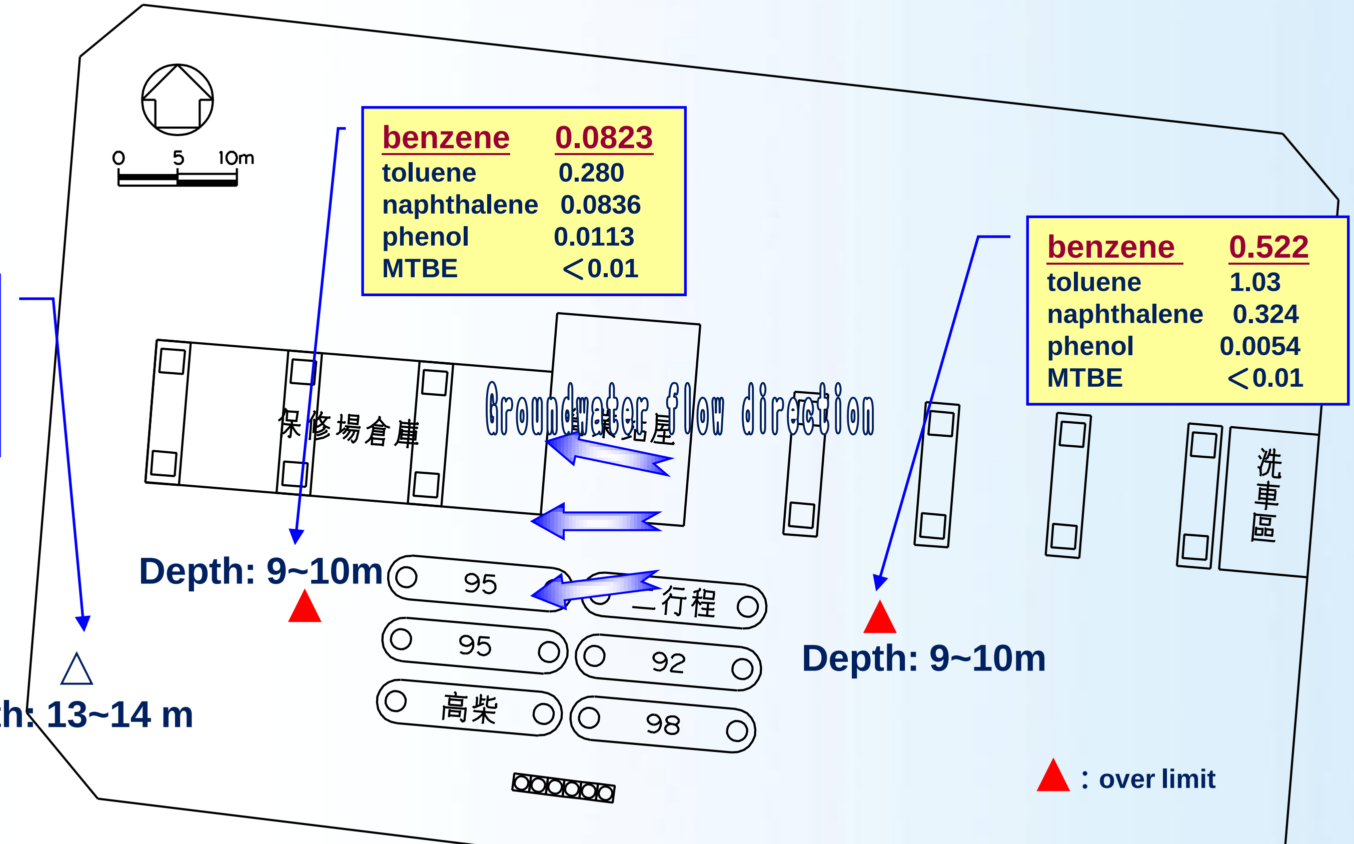
Sampling date \ Item and standards (mg/L)		banzene	toluene	Naphtha-lene	phenol	1,2-DCE	MTBE
		0.05	10	0.4	0.14	0.05	–
TW1	✓ 95.10.02	18.0	24.2	0.431	0.0813	＜0.01	＜0.01
	✓ 95.12.15	38.8	22.6	0.602	0.125	＜0.01	＜0.01
TW2	✓ 95.12.19	0.0985	6.22	0.307	0.027	ND	ND
TW3	✓ 95.12.19	1.19	1.93	0.140	0.021	ND	ND
TW4	✓ 95.12.19	3.74	ND	0.0135	0.057	ND	0.0733
TW5	✓ 95.12.19	3.49	0.382	0.0384	0.056	ND	11.0
TW6	✓ 95.12.19	20.3	4.12	0.207	0.303	ND	58.2
TW7	✓ 95.12.21	12.3	3.64	0.205	0.335	＜0.02	11.1
TW8	✓ 95.12.21	30.8	11.6	0.390	0.501	＜0.02	1.54
TW9	✓ 95.12.21	32.4	14.5	0.355	0.566	＜0.02	＜0.02
TW10	✓ 95.12.21	3.88	18.5	0.456	0.136	＜0.02	＜0.02

✓ : the value of benzene is over 20 times more than the regulatory standard

1. Groundwater of 10 wells exceeded the control limit.
2. Groundwater pollutants: benzene, toluene, naphthalene and phenol

Delineation Survey (5/6)

Groundwater: specified sieving depth



benzene	0.0448
toluene	0.0167
naphthalene	0.0012
phenol	0.0017
MTBE	0.688

benzene	0.0823
toluene	0.280
naphthalene	0.0836
phenol	0.0113
MTBE	＜0.01

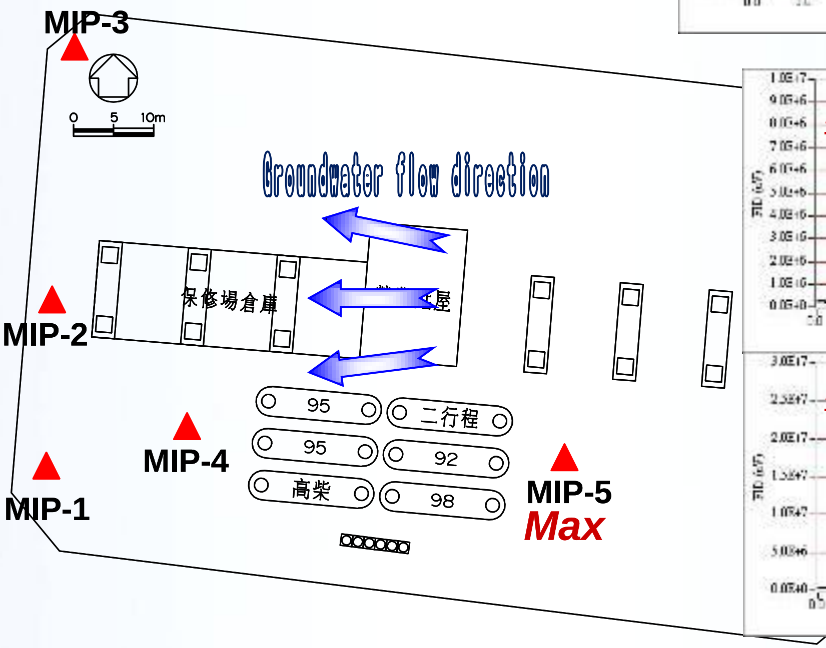
benzene	0.522
toluene	1.03
naphthalene	0.324
phenol	0.0054
MTBE	＜0.01

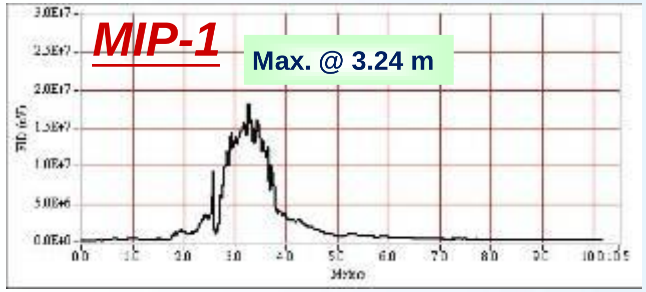
The depth of pollution was estimated to be over 10 m.

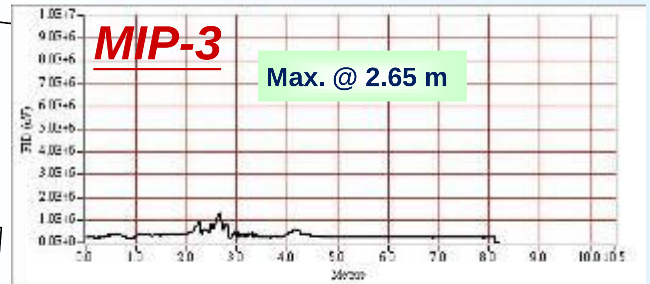
Delineation Survey (6/6)

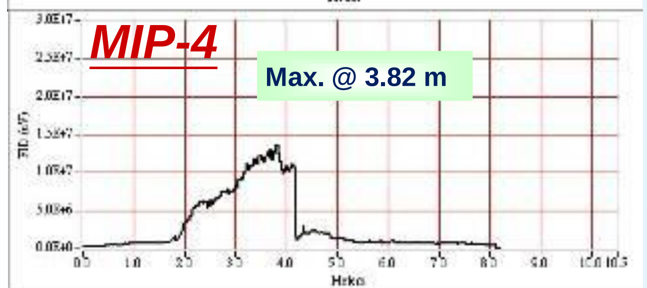
Delineation Survey

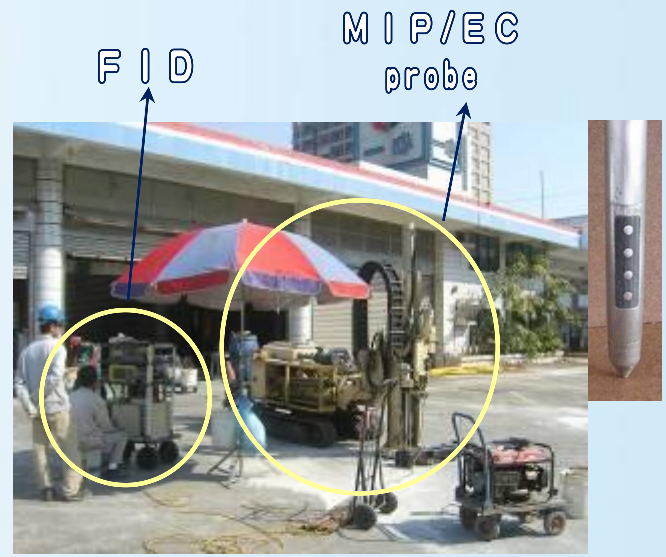
M I P results

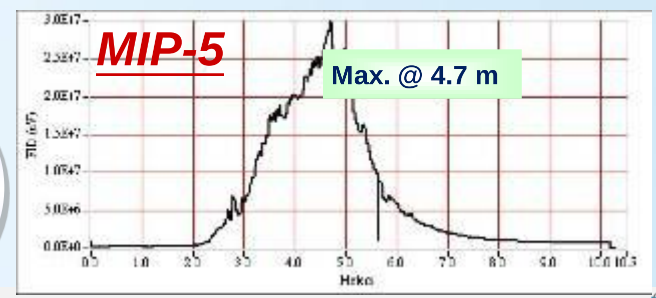










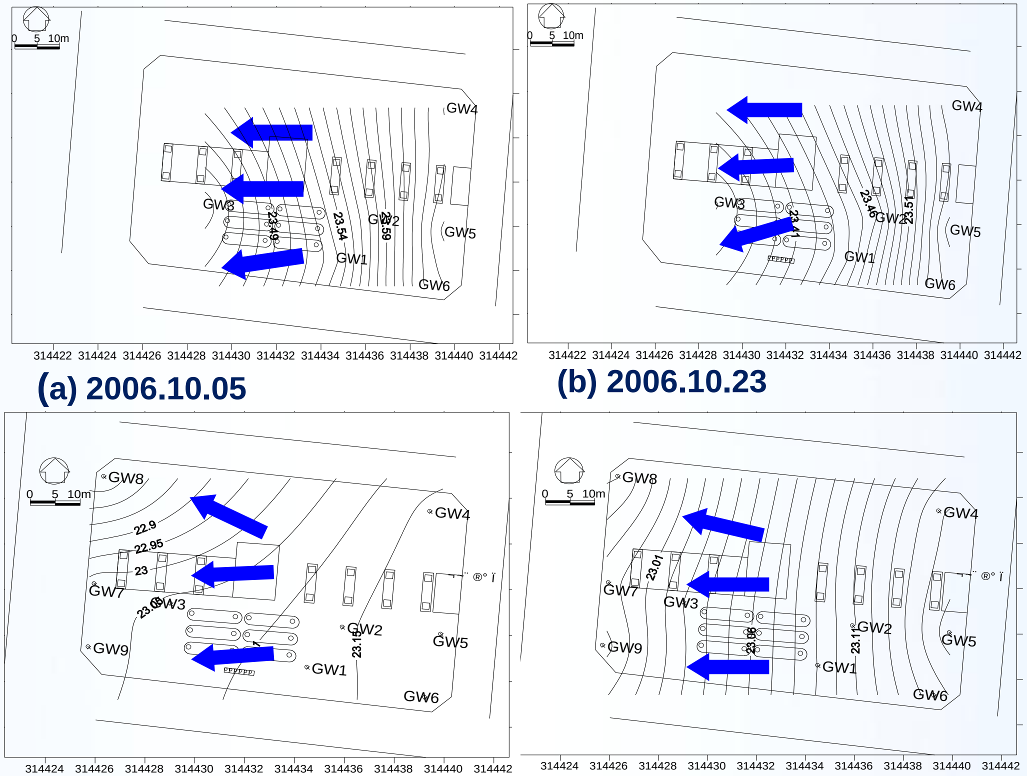


1. Max. pollution depth: 2.65~4.7m
2. Signals were not easy to read below 8 m deep.

Hydrogeological Survey (1/4)

Delineation Survey

Groundwater Flow Direction

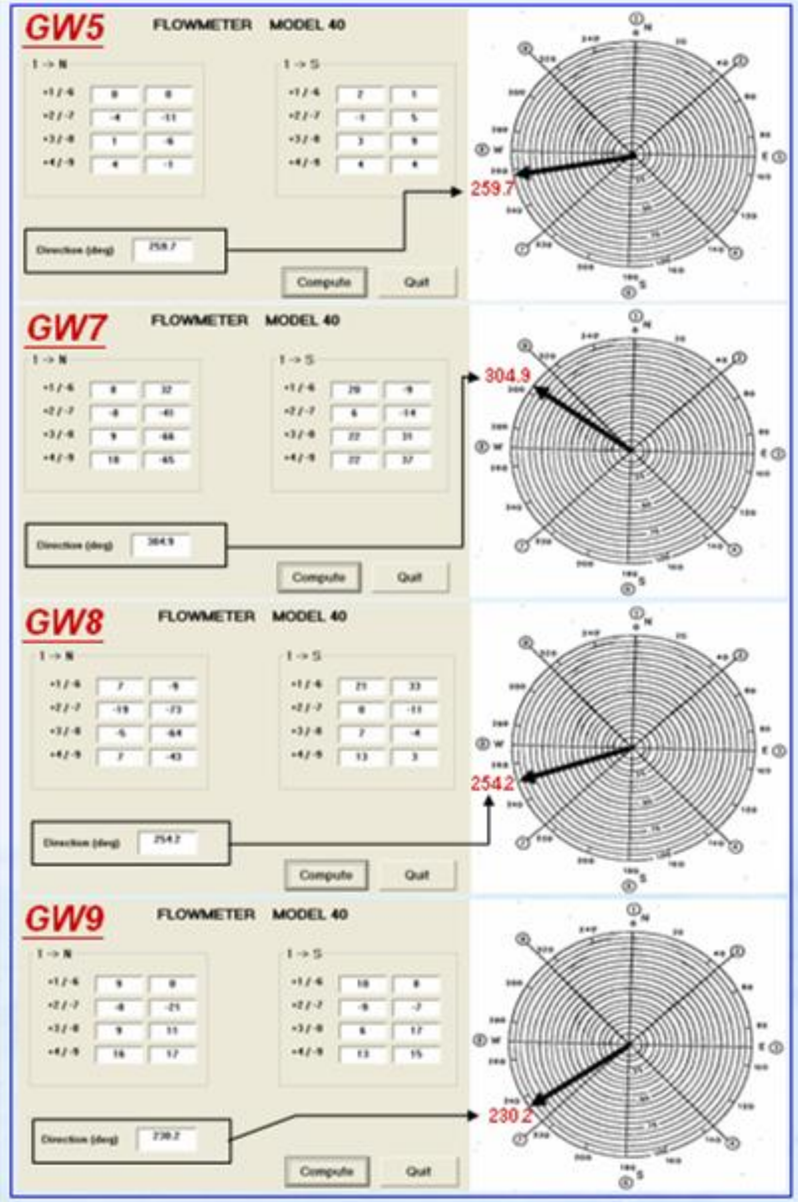


(a) 2006.10.05

(b) 2006.10.23

(C) 2006.12.30

(d) 2007.03.08



Flow from the east to the west

Hydrogeological Survey (2/4)

Geology Soil sampling

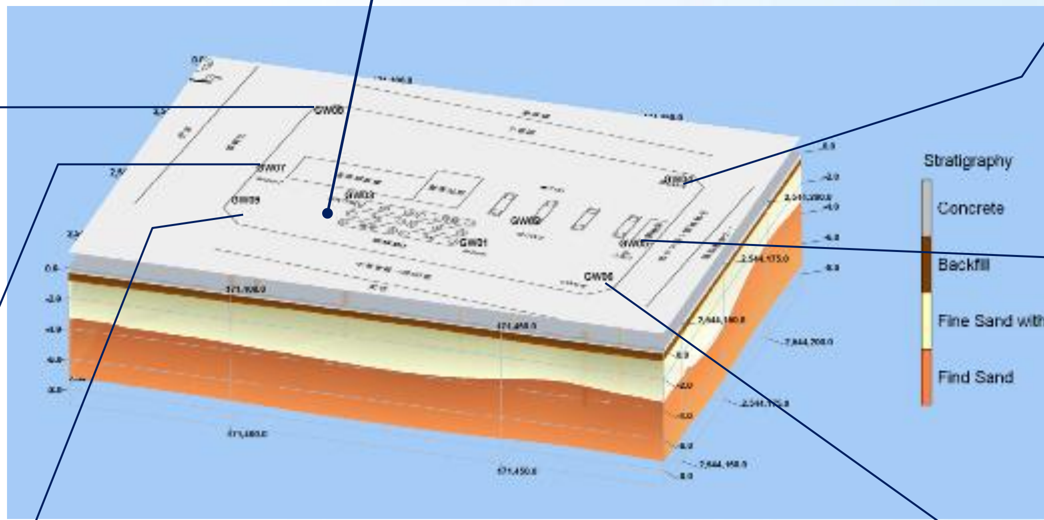
【Geological drilling】

1. 1~7.5m below the ground: fine sand with silt (silt<25%)
2. 10~15m below the ground: silt with fine sand (and 12~19%clay)

GW8

GW7

GW9



GW4

GW5

GW6

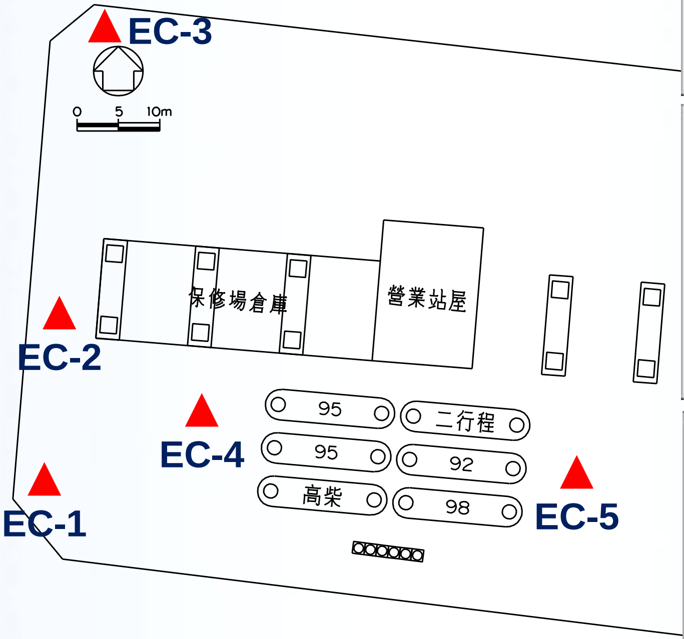
1. There were olive brown fine sand with silt between 1~8 m below the ground.
2. The soil properties of all sampling points were the same.

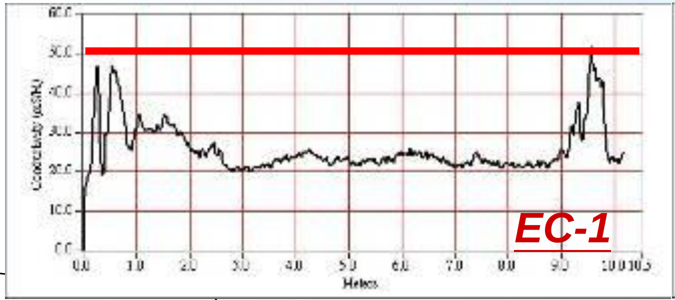
Hydrogeological Survey (3/4)

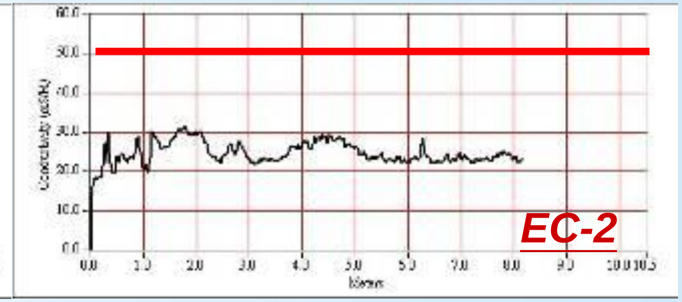
Delineation Survey

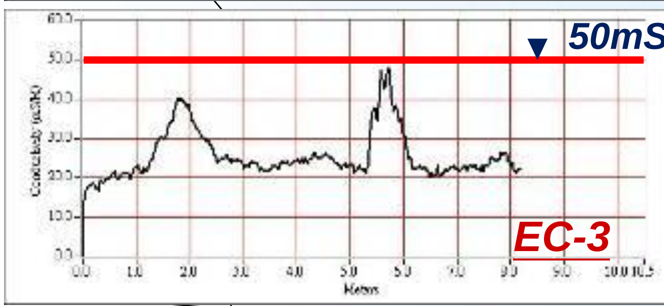
Geology

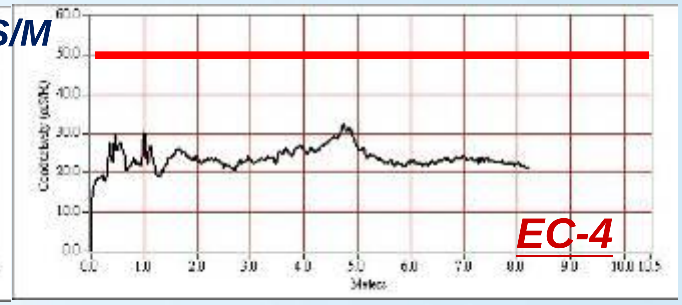
EC detection

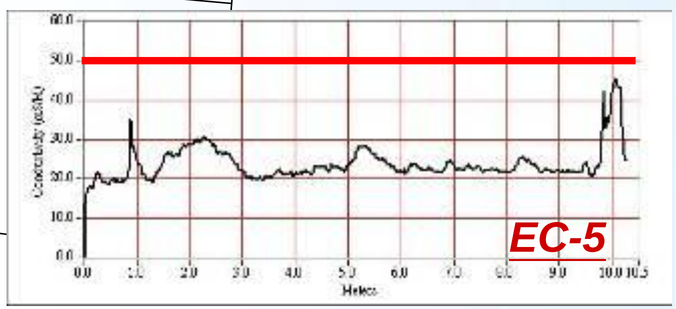


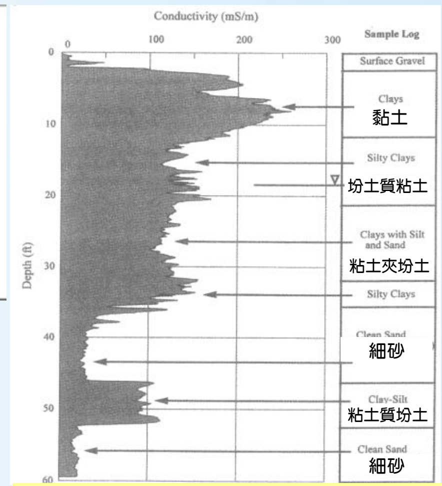












Soil property vs. EC

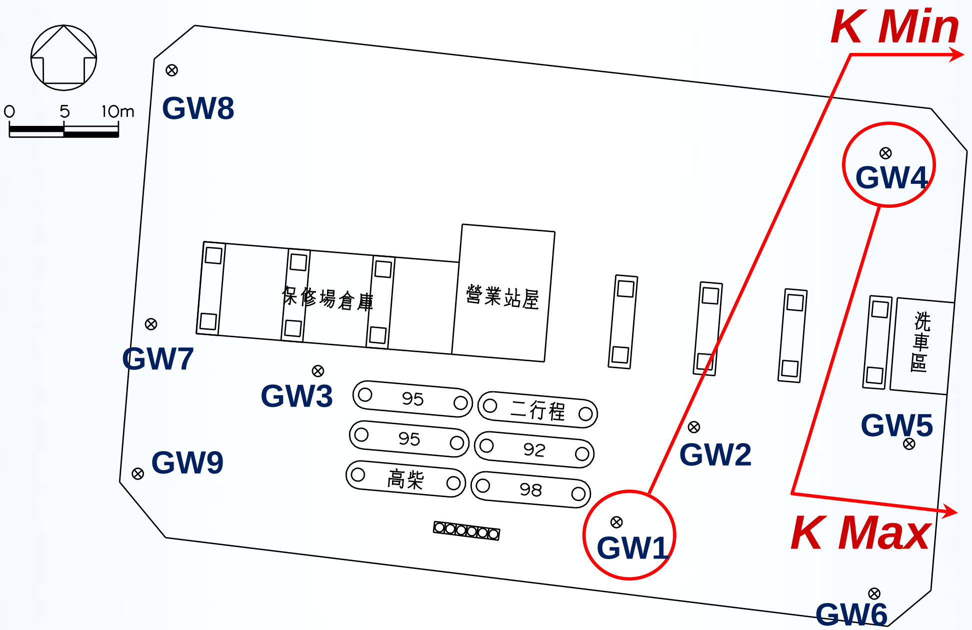
Generally, EC value of clay is beyond 100 mS/M and that of sand is below 50 mS/M.

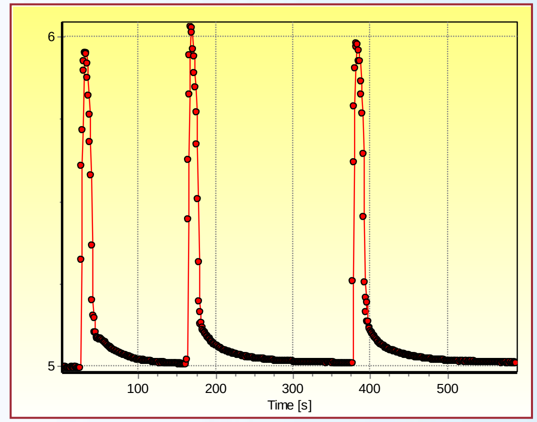
1. EC values of soil samples were below 50 ms/M.
2. Soil property was likely to be sand, which fitted the results of on-site consecutive sampling.

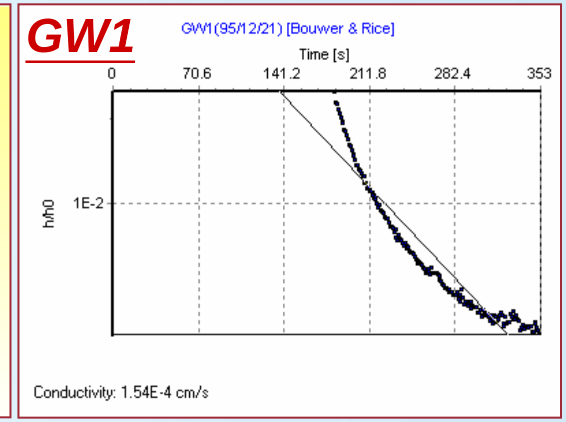
Hydrogeological Survey (4/4)

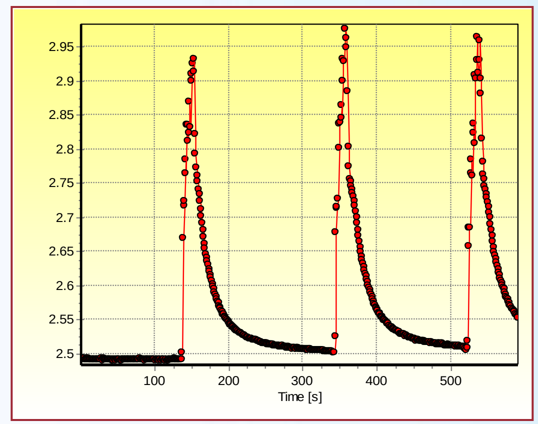
Delineation Survey

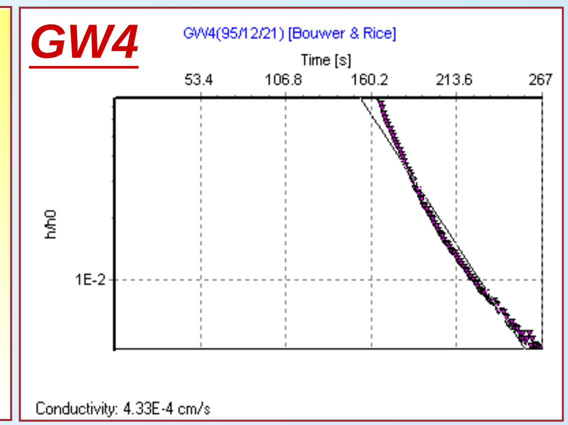
Slug test







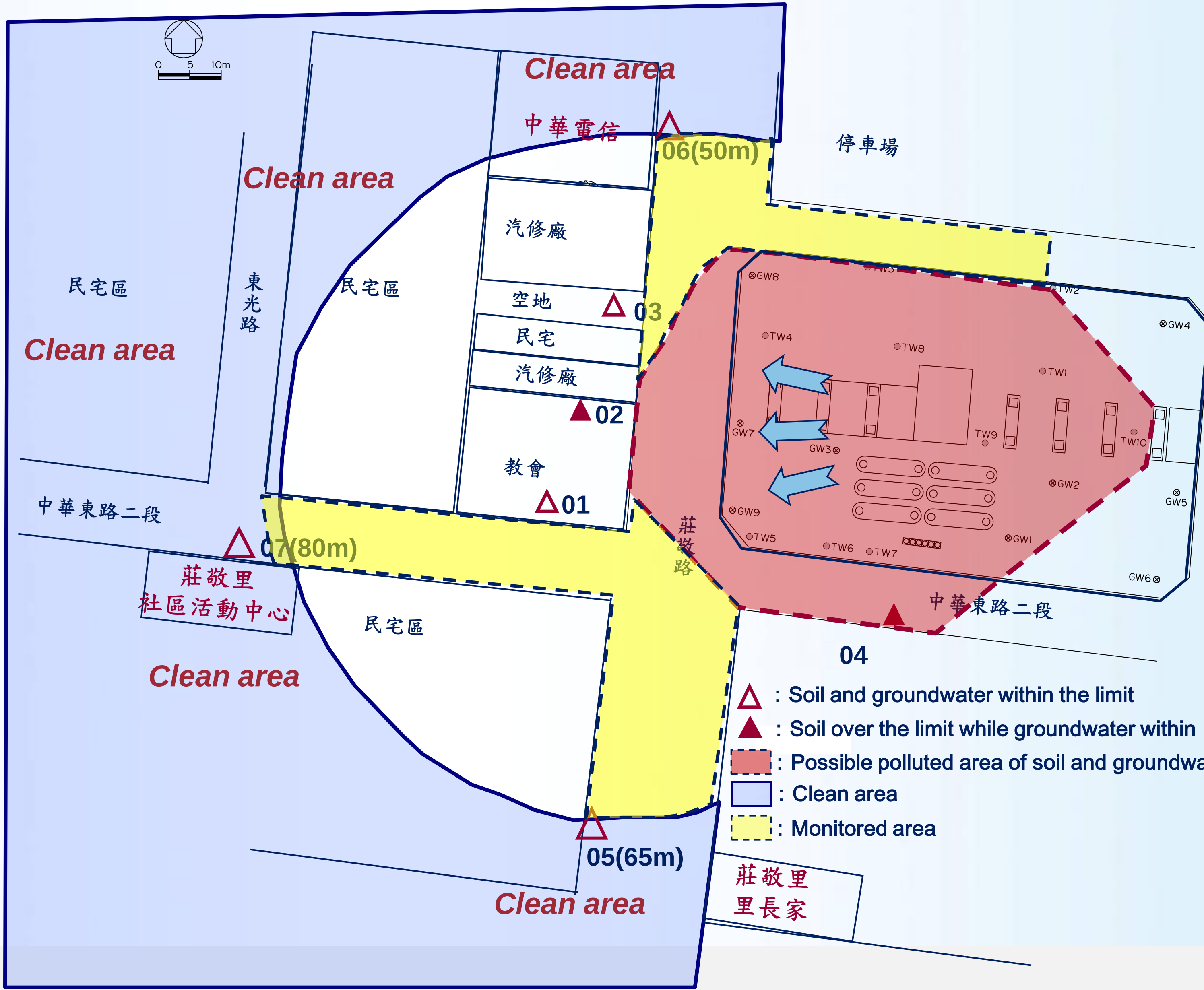




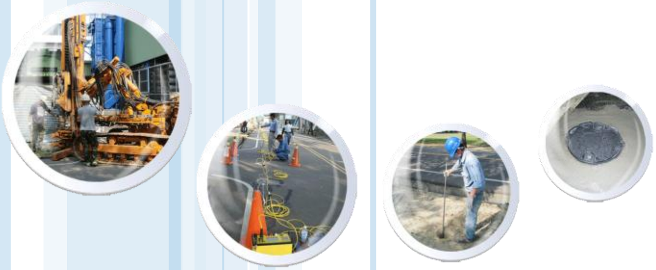
K values between 1.54~4.33×10^{-4} cm/sec fitted the property of sand.

Summary

Delineation Survey



1. The soil and groundwater of 75% area (2644 m^2) were polluted and the max. depth was 8 m.
2. The period of remediation was once every 3 months and the monitoring of sites was successively executed.
3. Soil pollutants: benzene, toluene, ethylbenzene, xylene and TPH
4. Groundwater pollutants: benzene, toluene, naphthalene and phenol



Remediation Method

Treatment Train

Remediation Method

- **Hot Spot (TPH > 10,000mg/kg) :**

  1. Excavation and removal of residual phase; injection well installation and ISCO remediation were performed directly in the open trench.
  2. In conjunction with necessary pumping/hydraulic control measures.

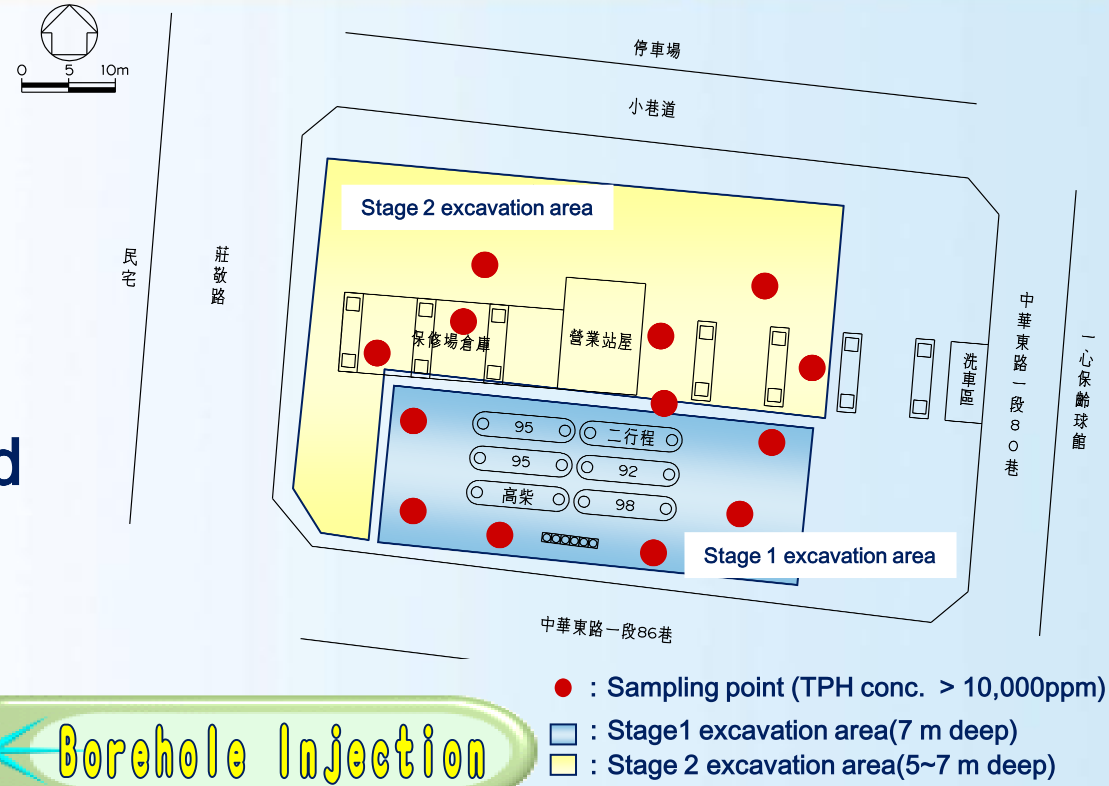
- **Less Contaminated Area:**

  Un-excavation and ISCO remediation with multi-phase extraction.

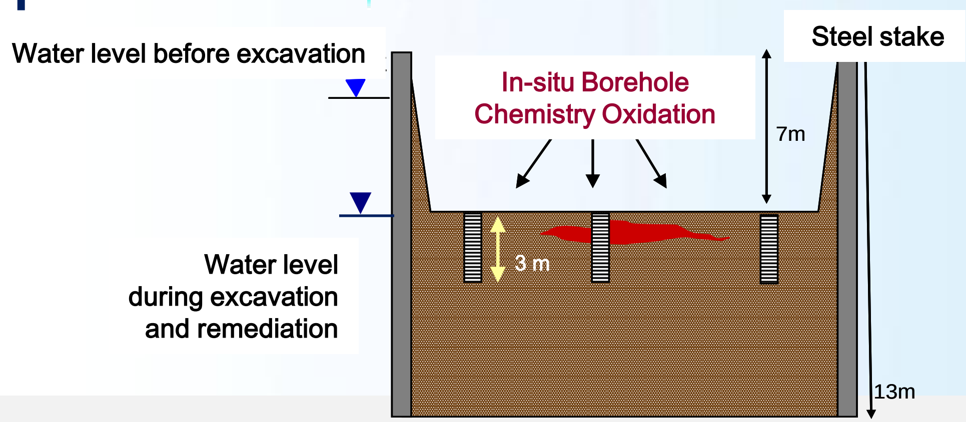
Hot Spot

Remediation Method

1. Excavate and remove the highly contaminated soil stage by stage.
2. In-situ borehole injection and backfill the site with the cleaned soil.
3. Off-site cleanup and treatment.



Borehole Injection



Excavation and removal of residual phase

Off-site restoration

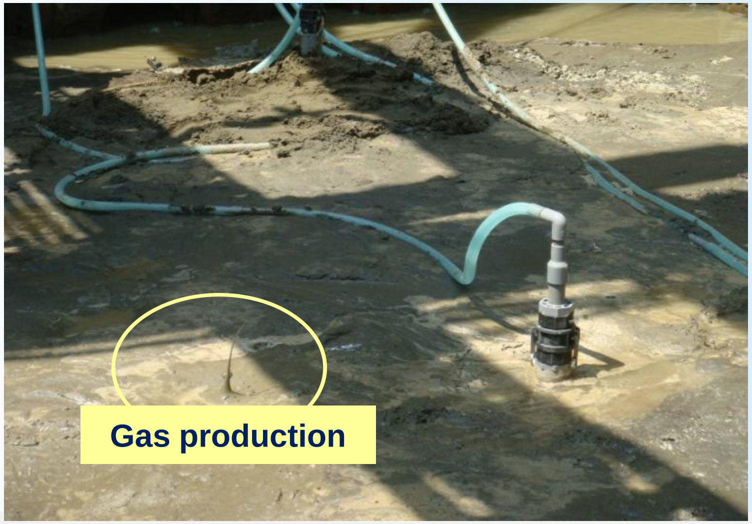
Excavation (Stage 1)

Excavation (Stage 2)

Summary

- Excavation: 7 m deep
- Contaminated soil: off-site treatment
- Backfill the site with the cleaned soil

➢ ISCO remediation performed at excavation zone



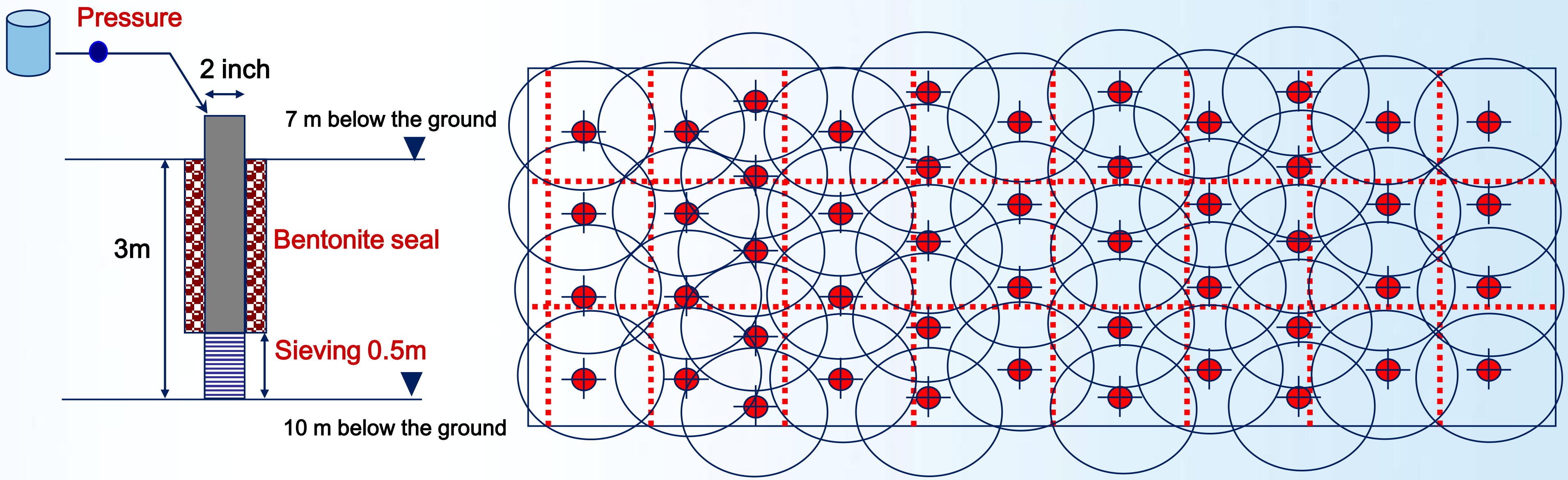
Hot Spot

Remediation Method

- Steel sheet piles and wastewater treatment facilities were supplied.




➢ Allocation design of injection wells



Hot Spot

Remediation Method

- Injection performance (video)

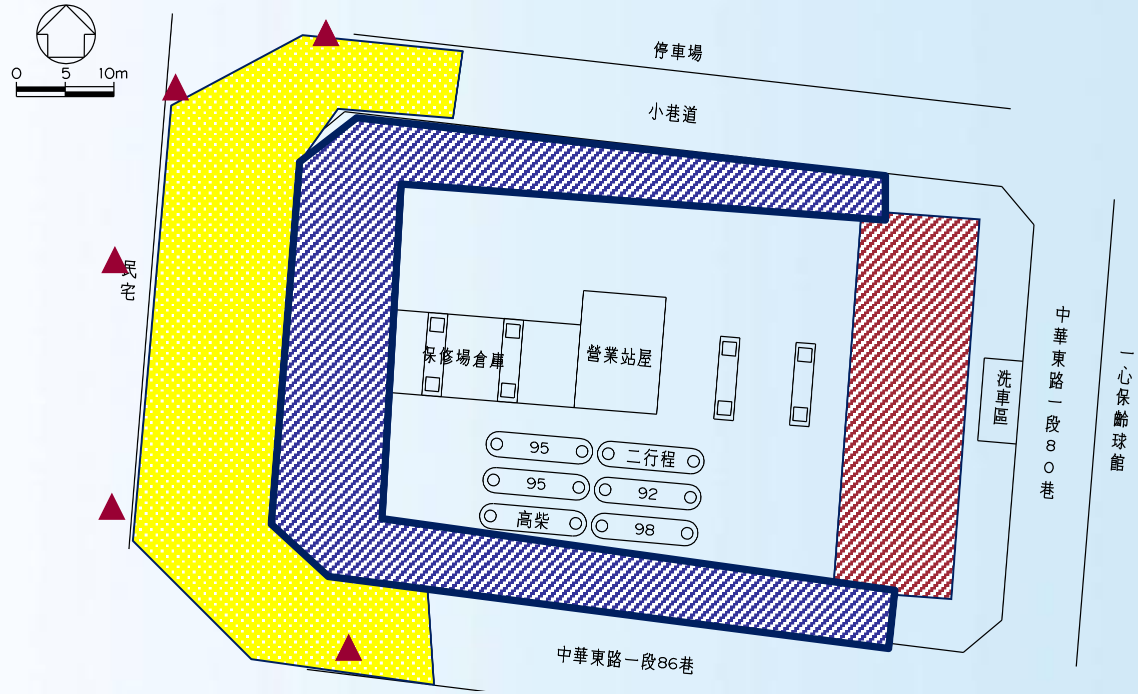
Short-circuiting and gas production in high temperature

➢ Monitoring assessment

Less Contaminated Area

Remediation Method

1. For un-excavated contaminated soil, **enhanced dual phase extraction** and **in-situ chemical oxidation** were adopted.
2. Outside the site, **monitored natural attenuation** was used.



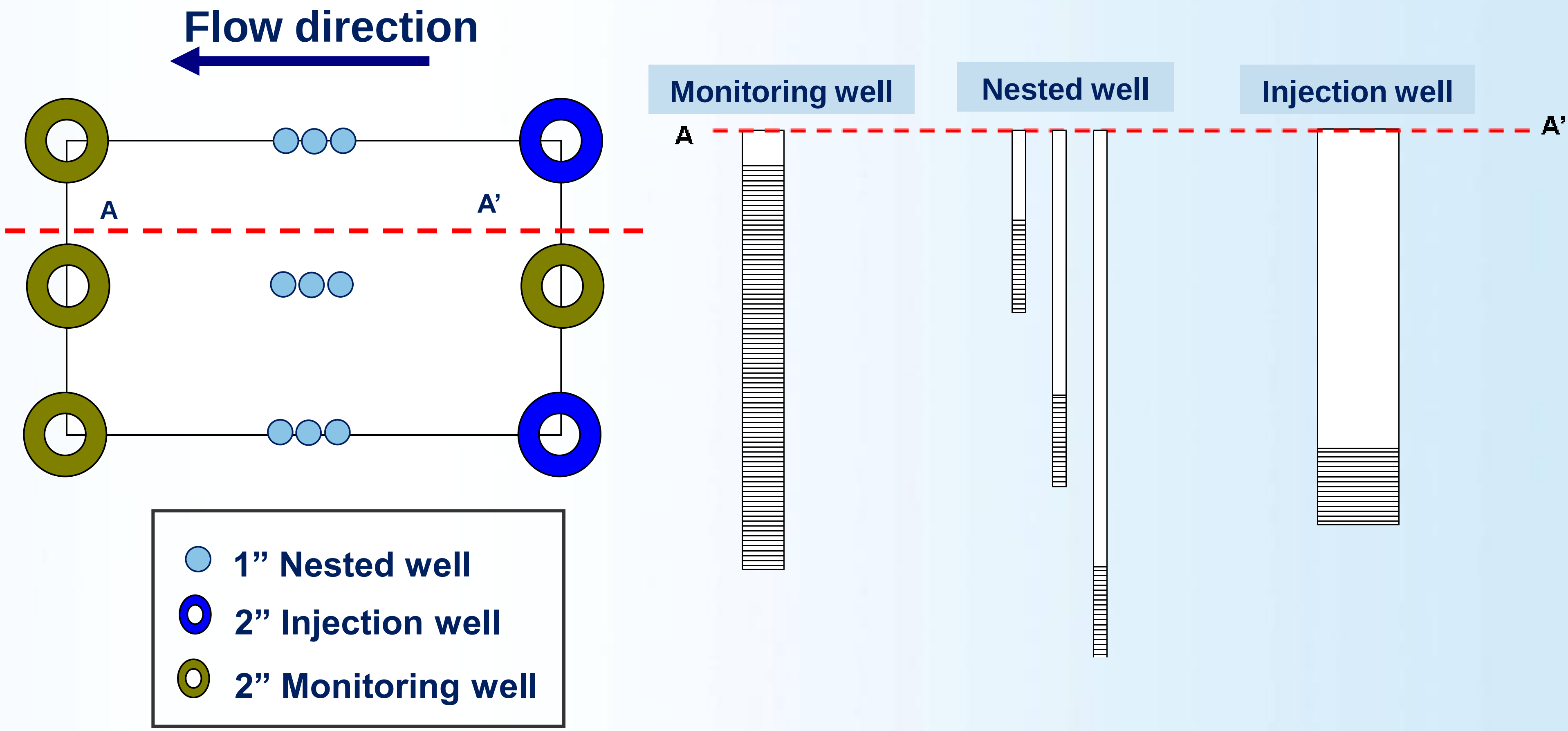
: Un-excavatied zone (ICO remediation)

: Monitored zone (outside the site)

▲ : Sampling point (outside the site)

Monitored zone (outside the site)

ISCO well allocation design



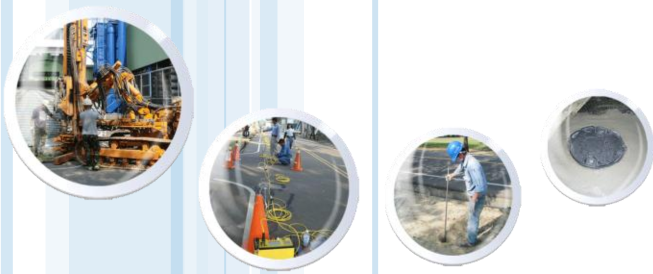
Less Contaminated Area

Remediation Method

Less Contaminated Area

Single depth injection

Multiple depth injection



Remediation Process

- Excavation
- In-situ borehole injection & assessment
- Backfill
- Off-site polluted soil clean-up
- Off-site polluted soil treatment
- Unexcavated zone remediation
- Summary

Excavation (Stage 1)

Remediation Process

Method

1. Excavation area: 40 m length × 14 m wide × 7 m deep
2. Working period: 2008.2.27~2008.4.12 (45 days)

1. Install steel sheet piles

2. Remove out oil tanks

3. Install intermediate piles

4. Install bracing structures

5. Excavate to 7 m bgs

6. Soil cleanup by trucks

7. Install ladders

8. Fences and alarm lights

Excavation (Stage 2)

Remediation Process

Method

1. Excavation area:1,400 m^2 (5~7 m deep)
2. Working period: 2008.9.11~2008.11.15 (66 days)

1. Tear down the building structures and gas filling islands

2. Install steel sheet piles

3. Excavation zone

4. Excavation

5. Off-site polluted soil cleanup by trucks

6. Relocate the wastewater treatment facilities

7. Ladders and fences

Excavation (Safety & Prevention)

Remediation Process

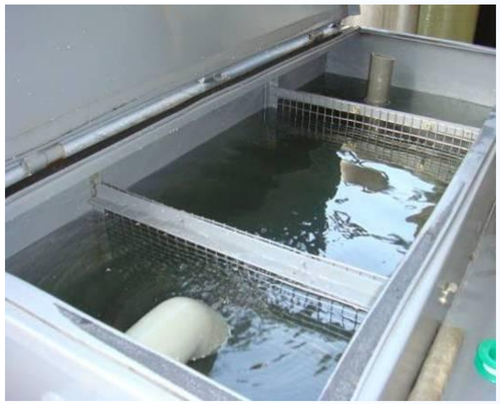
Method Necessary accident and pollution prevention measures

1. Fire prevention equipment

2. Monitor the displacement of bracings

3. Watering to reduce the dust raising

4. Workers with protection clothing if necessary



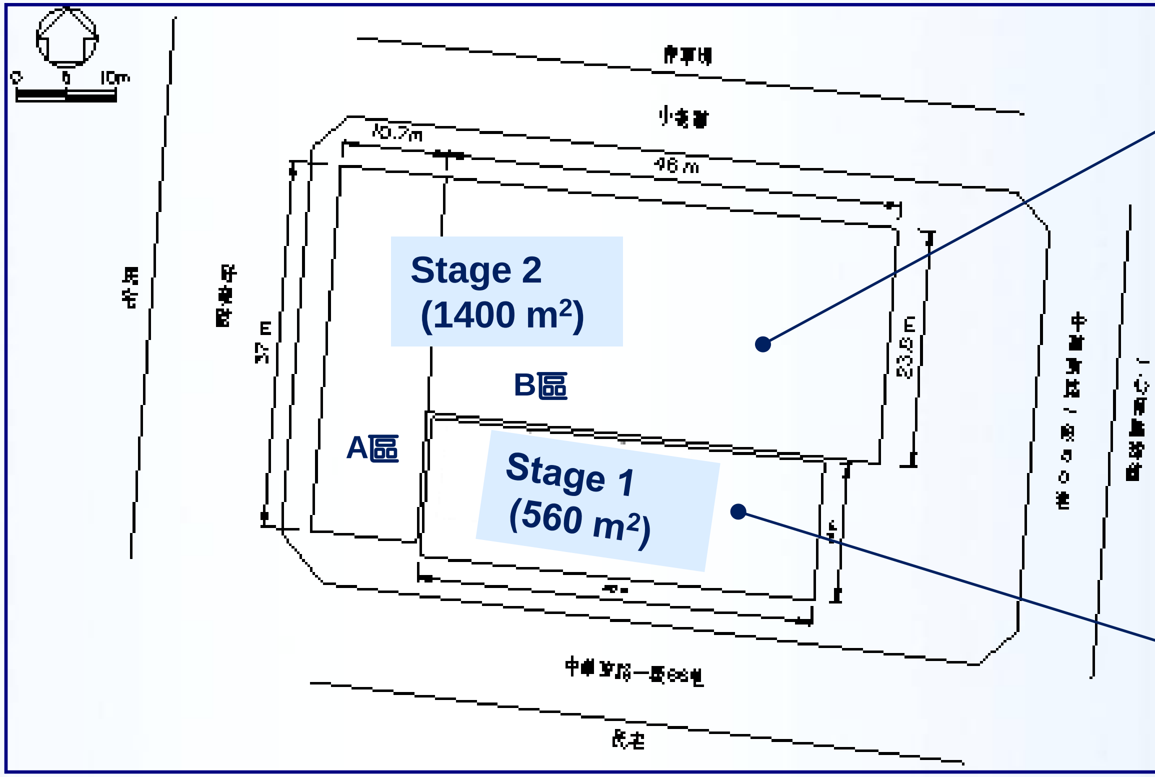
5. Wastewater treatment facilities

6. Monitor the noise and vibration

7. Air quality monitoring

Excavation (Summary)

Excavation Area



• Stage 2

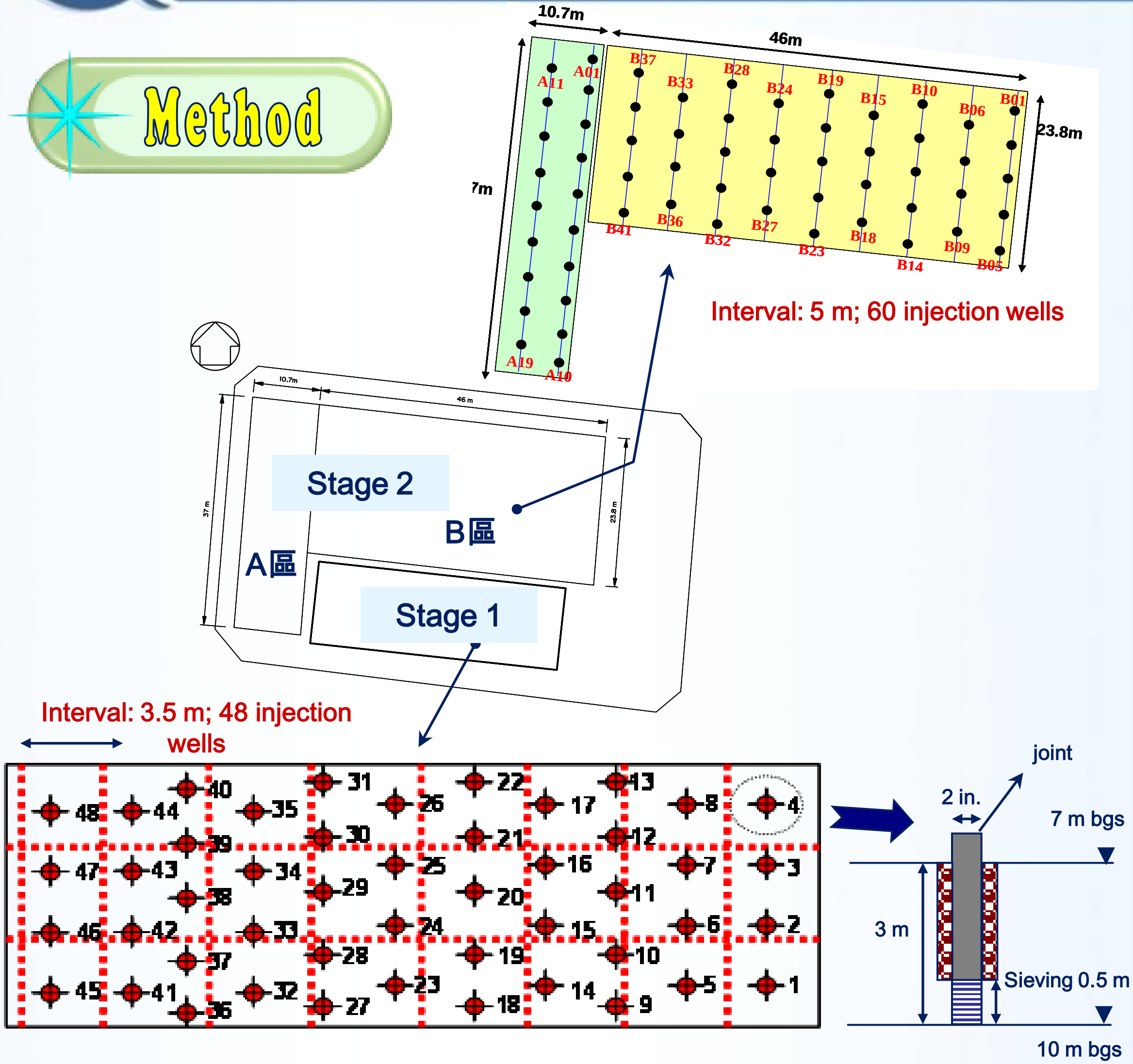
• Stage 1

1. Total excavation area was 1,960 m^2 (75% of the polluted area) and 5~7 m deep.
2. The polluted soil of high concentration was removed via the excavation.

In-situ Borehole Injection

Remediation Process

Method



1. Injection/monitoring well Installation

2. Injection tank and pipe

3. Flow meter and control valve

4. Catalyst injection

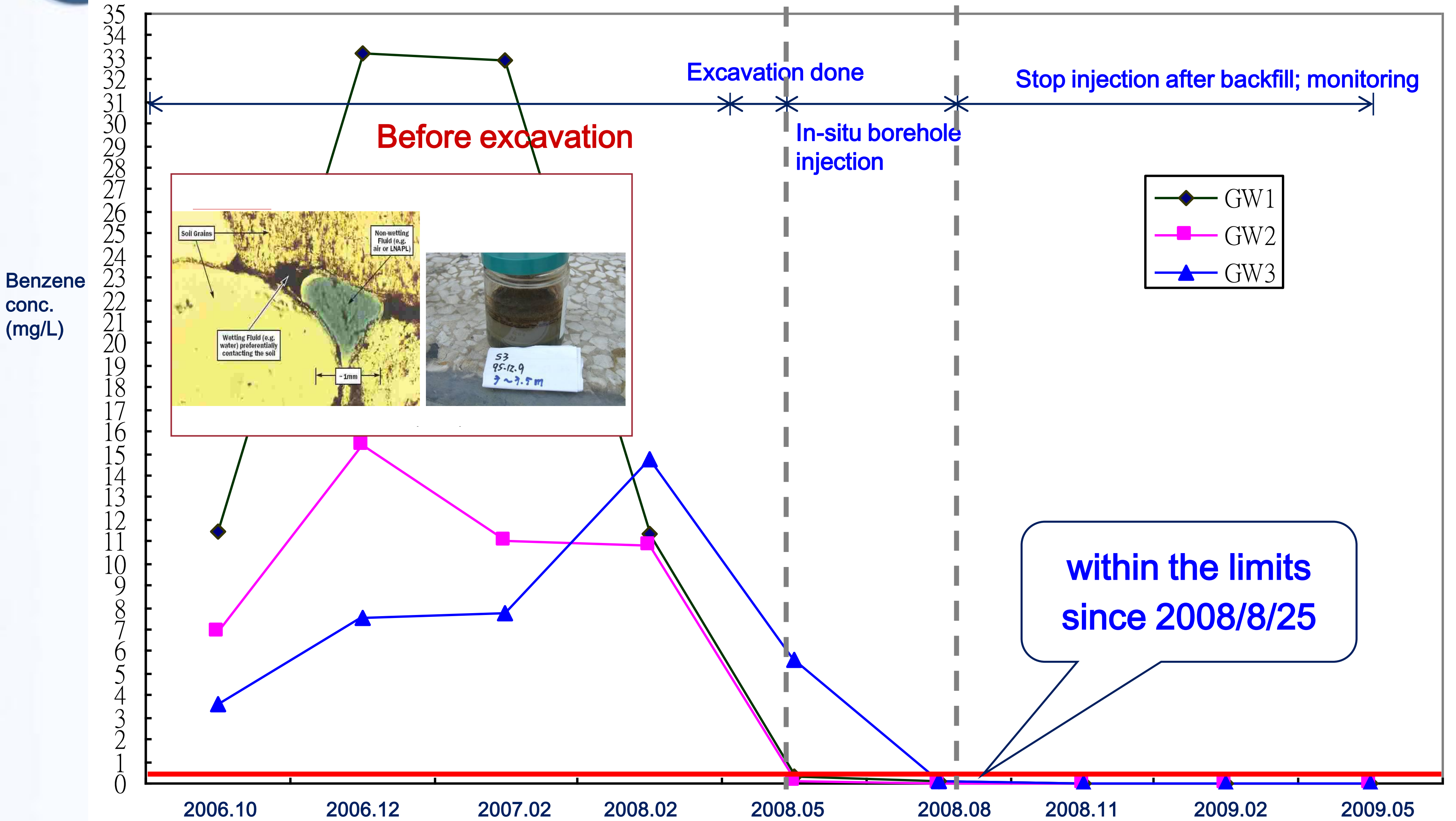
5. Oxidant injection

6. DO/ORP analysis

1. Stage 1 : 48 injection wells were installed(interval: 3.5 m).
2. Stage 2 : 60 injection wells were installed(interval: 5 m).

Remediation History & Assessment

Remediation Process



Removing the residual soil of Hot Spot was the key step to the remediation of borehole injection.

Backfilling clean soil at excavated zone

Remediation Process

Stage 1

1. 2008.8.27~2008.9.3 (8 days)
2. Groundwater monitoring seasonally


Clean soil refilling

Compact and flatten

3 newly-installed monitoring wells

Stage 2

1. 2009.4.11~2009.4.30 (20 days)
2. Groundwater monitoring seasonally


Clean soil soil refilling

Compact and flatten

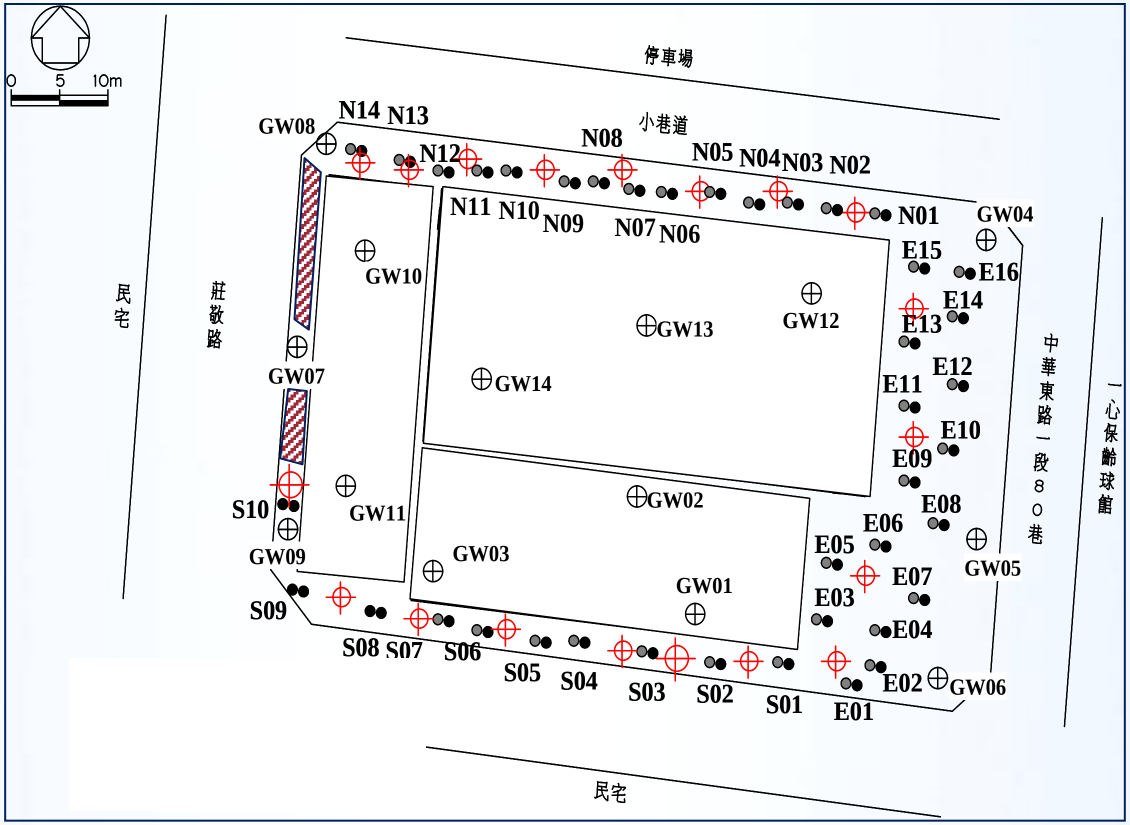
5 newly-installed monitoring wells

- After backfilling the clean soil, soil sample testing was conducted (testing items including target pollutants and heavy metals)
- Soil and groundwater qualities met the regulatory standards, and then groundwater quality monitoring was performed seasonally.

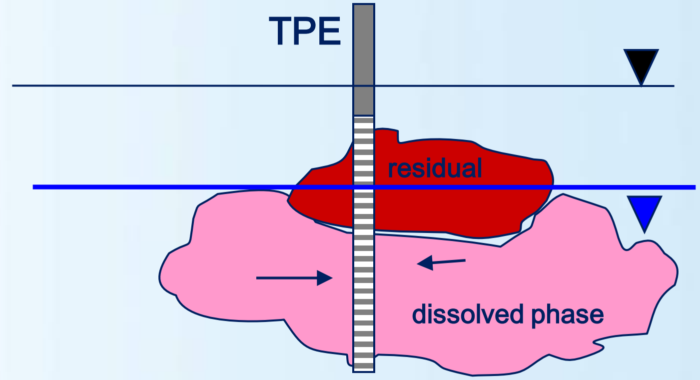
Remediation of Un-excavated Zone(1/3)

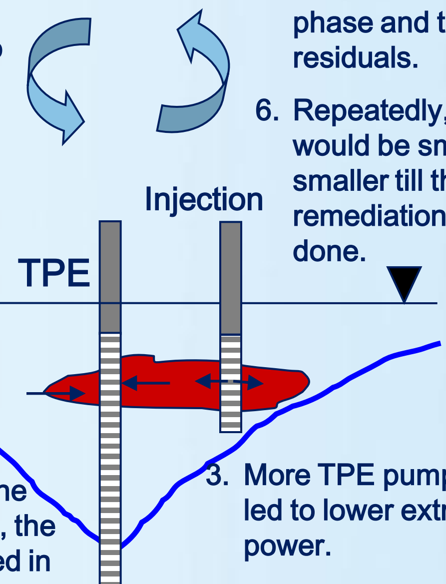
Remediation Process

Method In-situ Chemical Oxidation/ dual TPE



Totally, 80 injection wells and 19 high-vacuum pumping wells were installed.





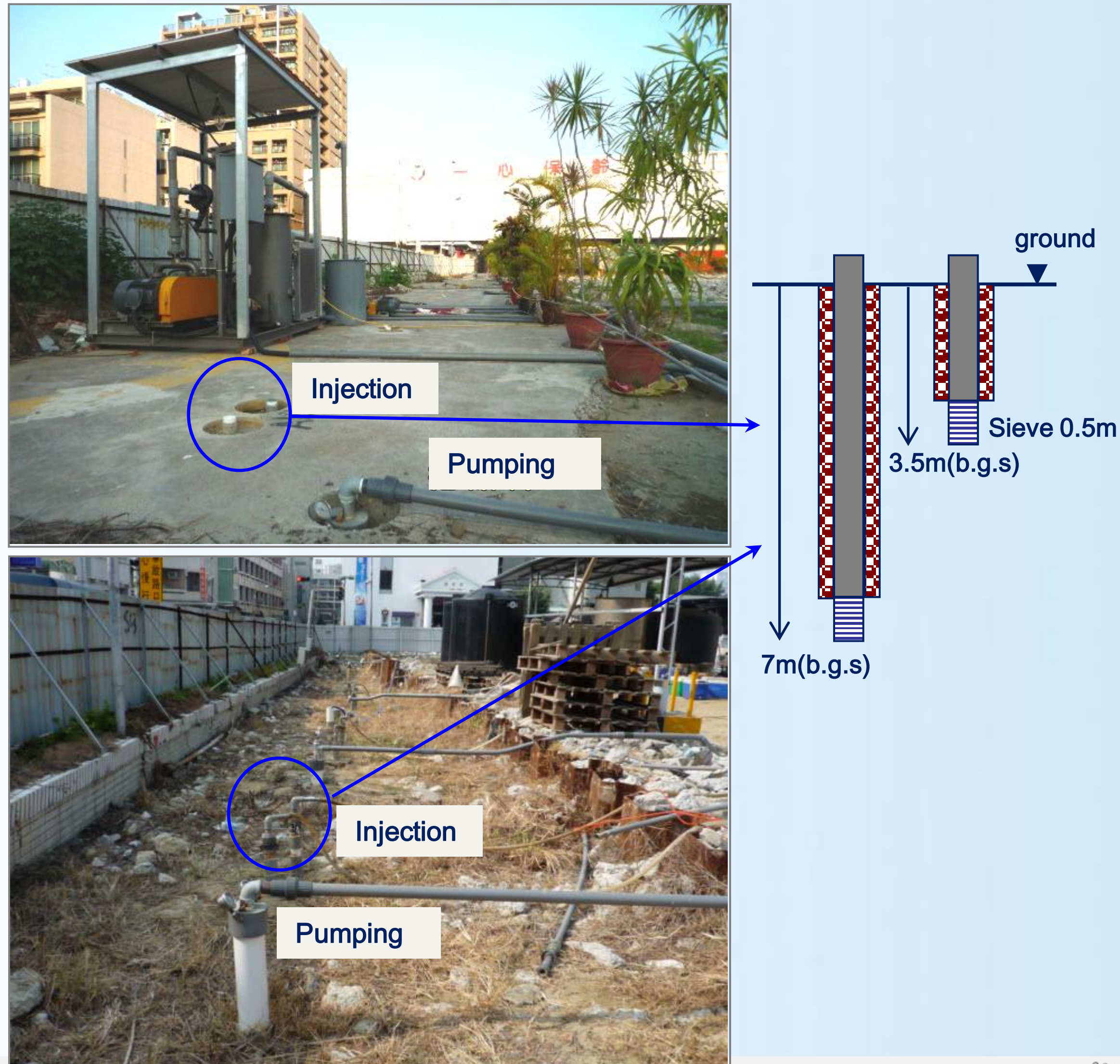
1. Keep pumping to lower the water level and to remove the dissolved phase.
2. After expanding the unsaturated zone, the residuals adsorbed in the pores were extracted via high vacuum.
3. More TPE pumping wells led to lower extraction power.
4. In-situ injection was used to transform the residuals to the dissolved phase.
5. TPE was used to extract the dissolved phase and the residuals.
6. Repeatedly, the plume would be smaller and smaller till the remediation work was done.

Remediation of Un-excavated Zone(2/3)

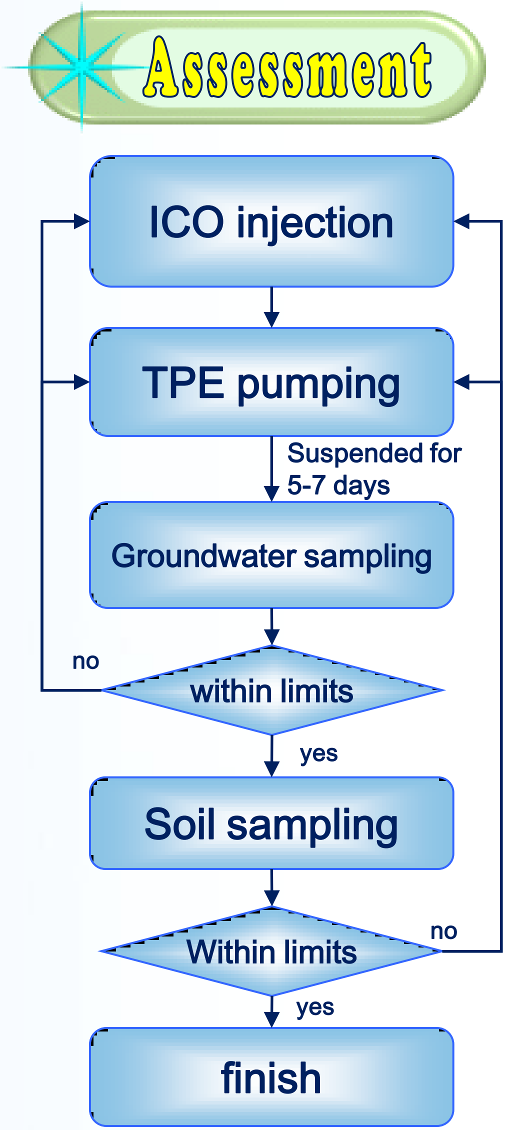
- *TPE system*

- *TPE probe*

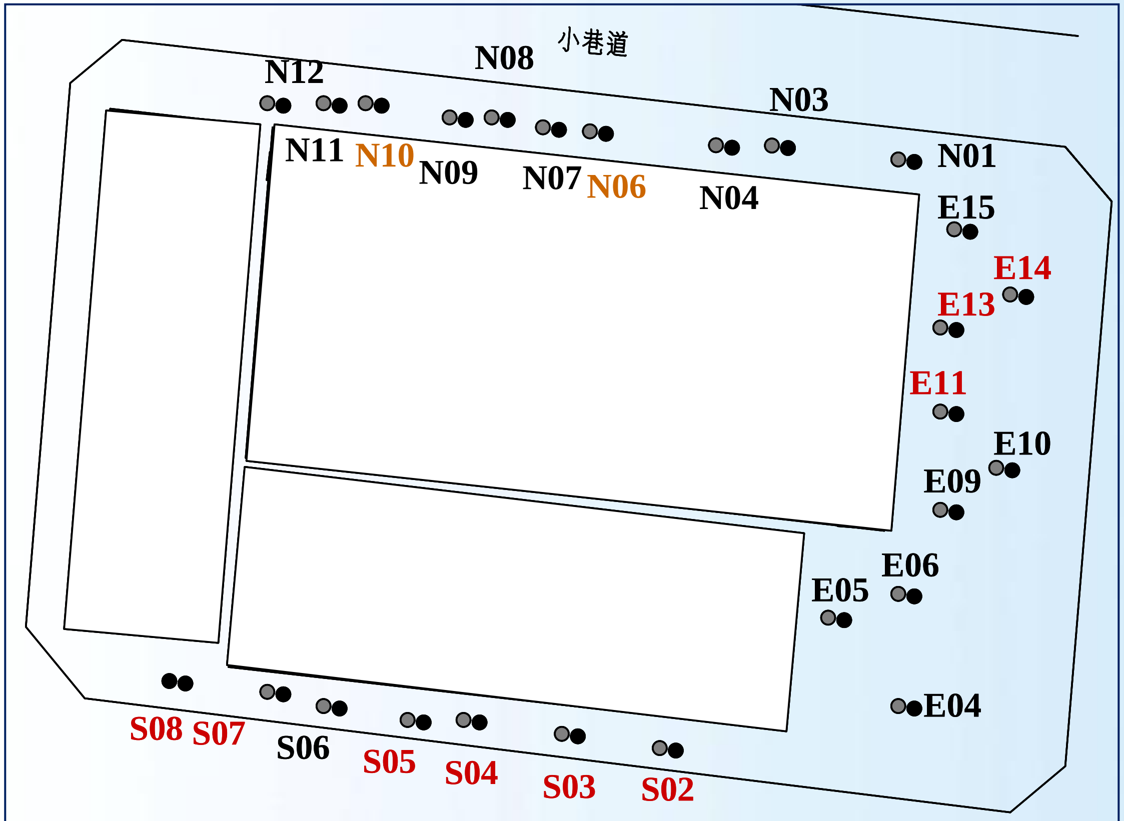
- *ICO injection system for un-excavated zone*



Remediation of Un-excavated Zone(3/3)



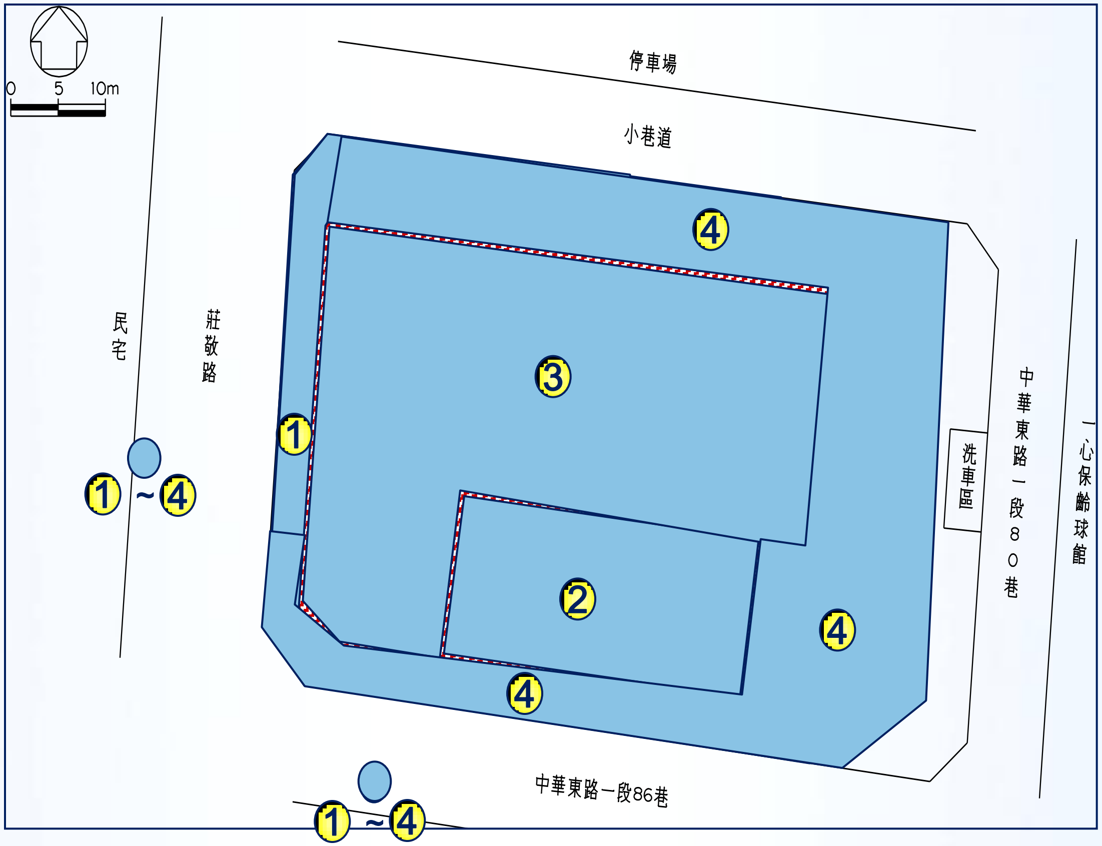
1. North side：2009.07.25~2009.09.08
2. East side：2009.08.15~2009.10.25
3. South side：2009.08.18~2009.12.05



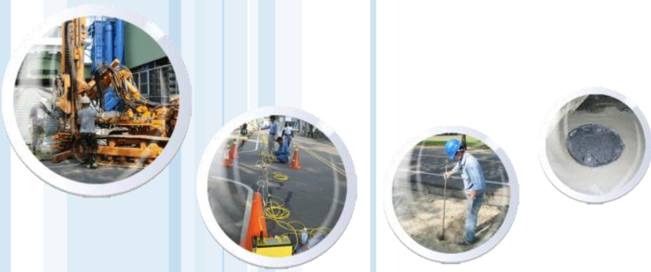
2,420 tons of catalysts and oxidants were used, respectively.

Summary

Remediation Process



No.	Process	Period
1	Before remediation, reagent injection and pumping control were conducted at the boundary to keep pollution from expanding.	May 2007~ April 2009
2	Excavated and removed highly contaminated soil (7 m deep); borehole chemical oxidation injection was used for groundwater remediation 7~10 m below the ground; backfilled the site with the cleaned soil after remediation.	Feb. 2008~ Sep. 2008
3	Excavated and removed highly contaminated soil (5~7 m deep); borehole chemical oxidation injection was used for groundwater remediation 7~10 m below the ground; backfilled the site with the cleaned soil after remediation.	Sep. 2008~ Apr. 2009
4	For un-excavated contaminated soil, enhanced dual phase extraction and in-situ chemical oxidation were adopted.	Apr. 2000~ Dec. 2009
1~ 4	Outside the site, injection and monitored natural attenuation was used for some slightly polluted area.	May 2007~ Oct.2009

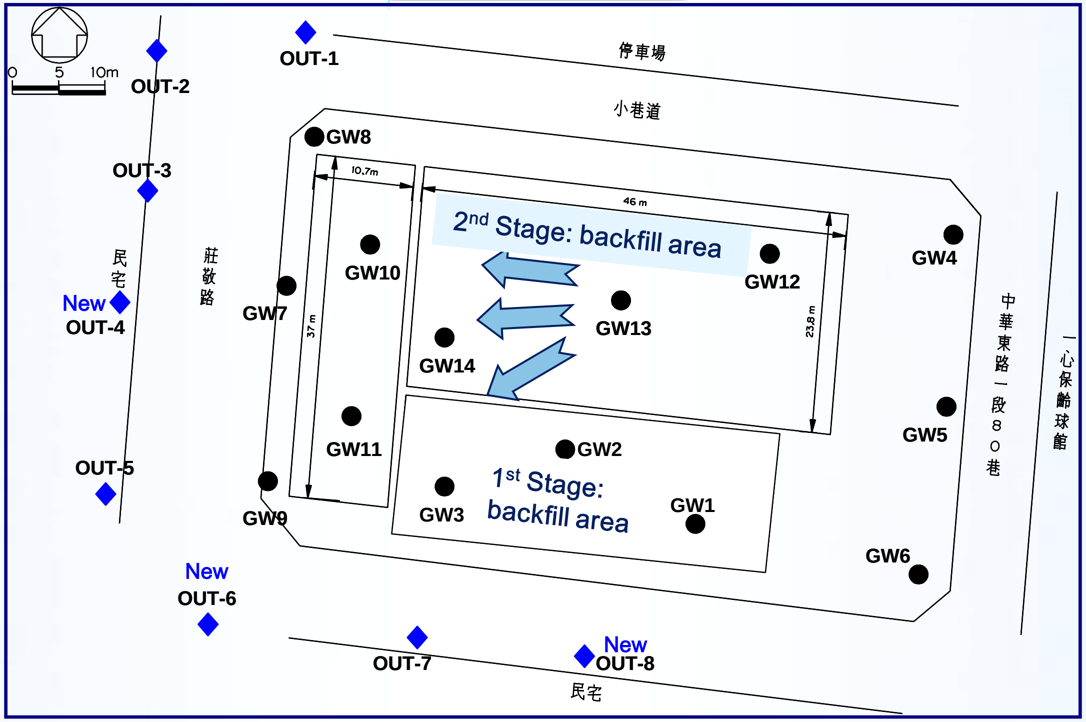


Monitoring & Verification

Pollutant Concentration Monitoring

Monitoring & Verification

Location



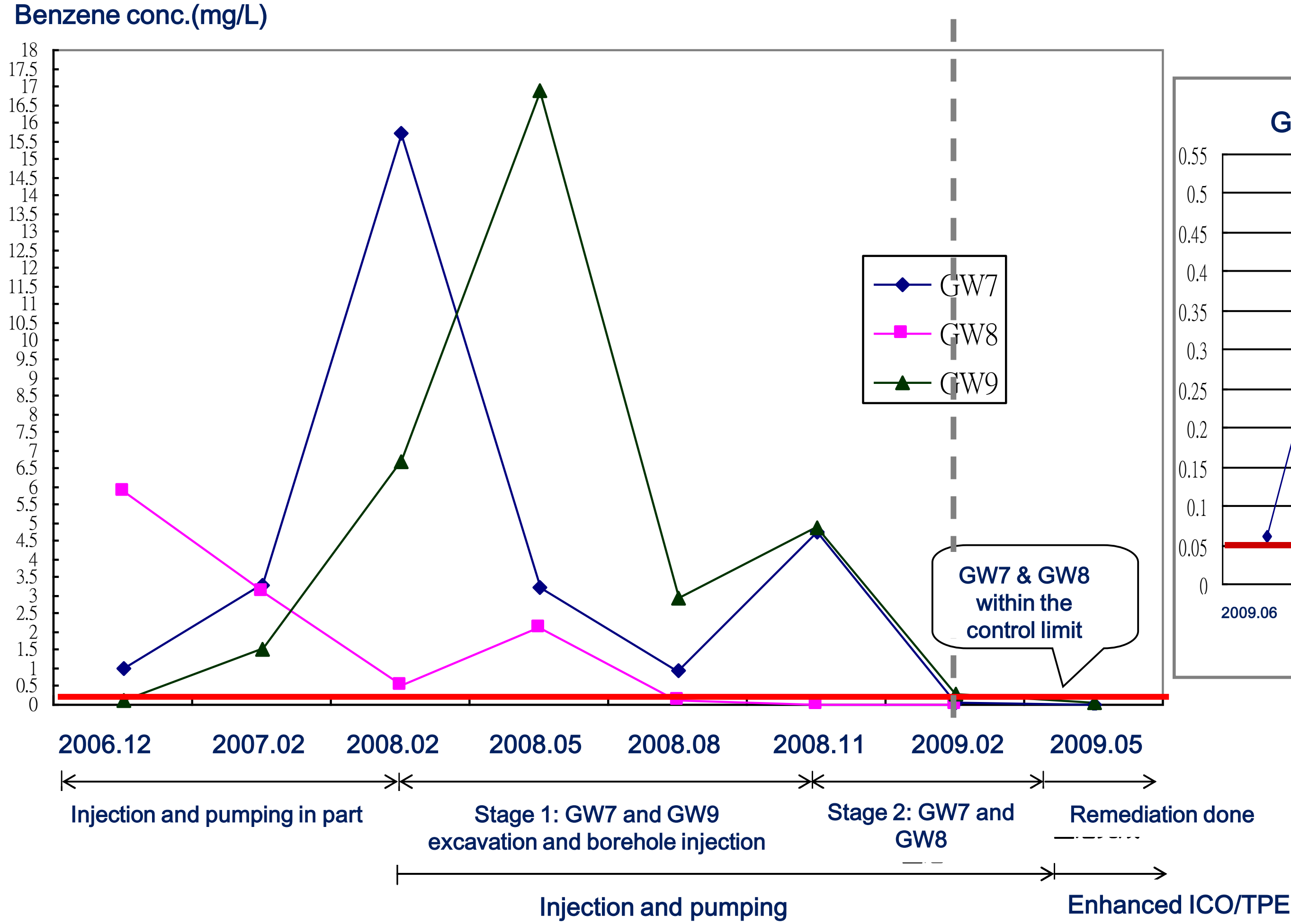
Results

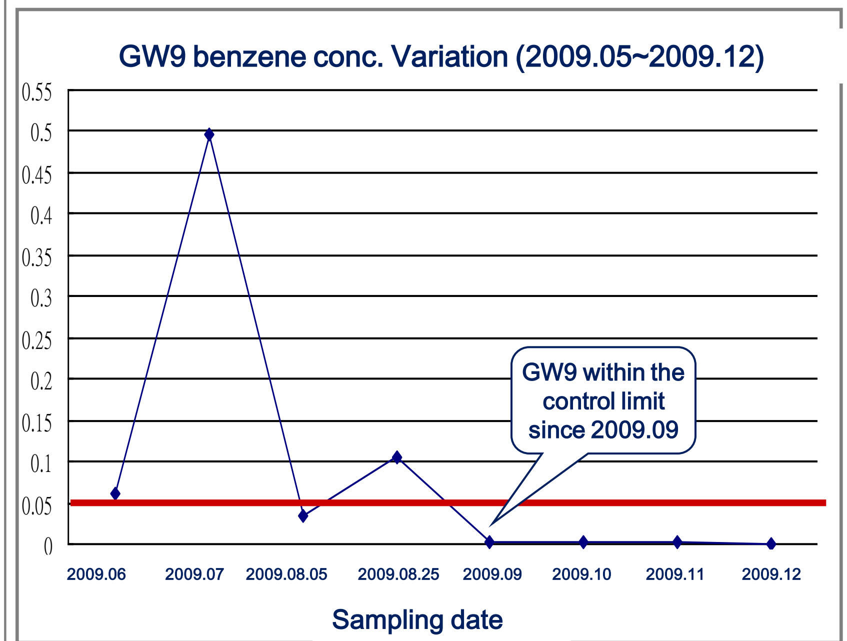
Item	Area	Results
Soil (benzene, toluene, ethylbenzene, xylene and TPH)	Inside (8 points)	1. No pollution in excavated zone after remediation.
	Outside (8 points)	1. In May 2008, benzene concentration of OUT-3 was over the limit; after injection, all were within the limit since August 2008. 2. Additional 3 points since May 2009.
Groundwater (benzene, toluene, ethylbenzene, xylene, naphthalene, phenol and TPH_d)	Inside (14 wells)	1. No pollution in excavated zone after remediation. 2. The pollutant conc. Went down in the un-excavated zone and its downstream.
	Outside (8 wells)	1. In May 2008, benzene conc. Of OUT-7 was over the limit; after injection, all were within the limit since August 2008. 2. Additional 3 points since May 2009.

1. Groundwater flow direction remained from the east to the west.
2. Additional monitoring item: ethylbenzene, xylene and TPH_d
3. Additional 3 monitored points since May of 2009.

Pollutant Concentration Variation

Monitoring & Verification





1. Because of the excavation and borehole injection, pollutant conc. had been within the control limit since February of 2009.
2. After enhanced ISCO/TPE adopted, there was no pollutant conc. detected since September of 2009.

Self-inspection

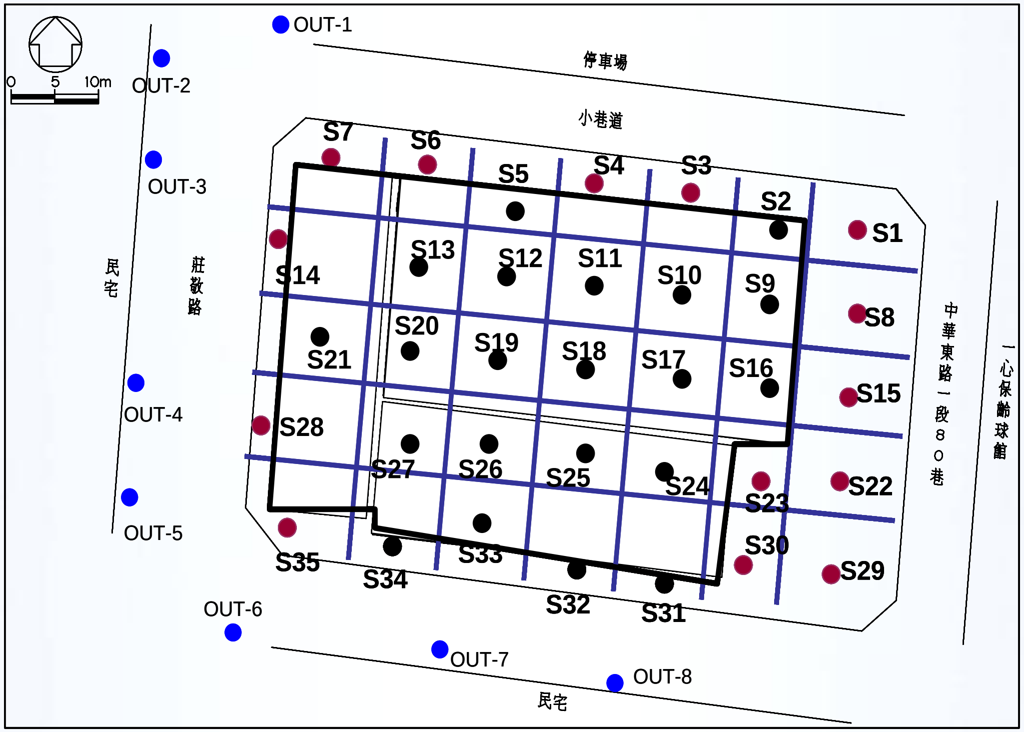
Monitoring & Verification

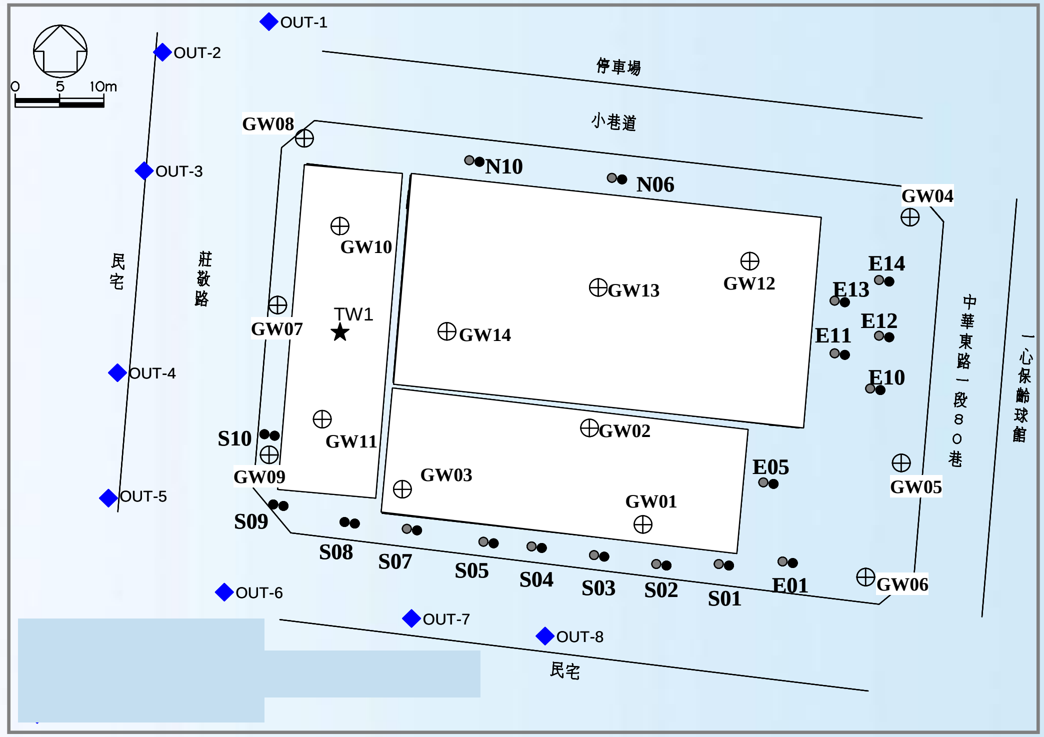
Soil

1. Inside: 35 points
2. Outside: 8 points
3. benzene, toluene, xylene、TPH

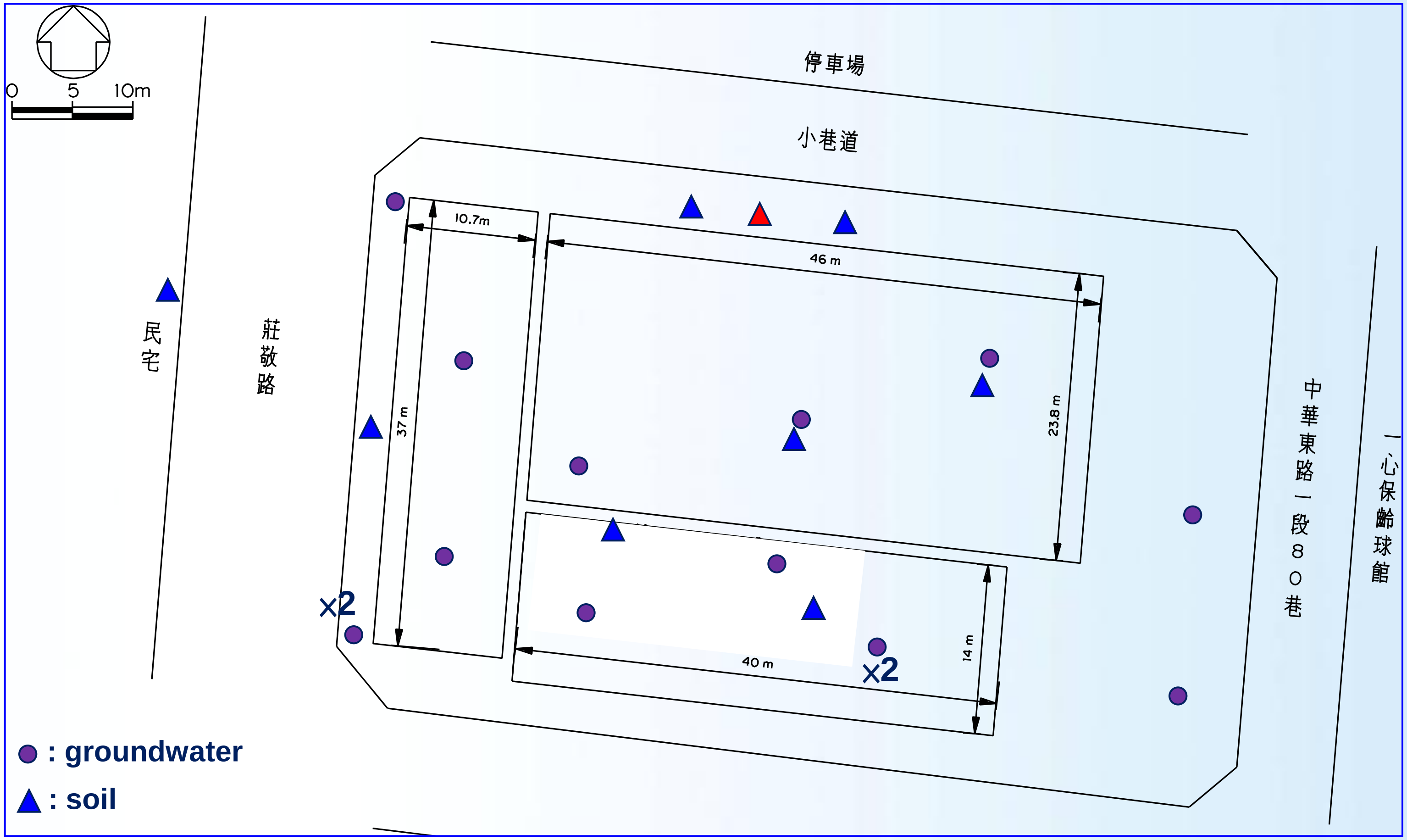
Groundwater

1. Inside: 32 points
2. Outside: 8 points
3. Pollutants: benzene, toluene, ethylbenzene, xylene, TPH_d, naphthalene, phenol, 1,2-DCE

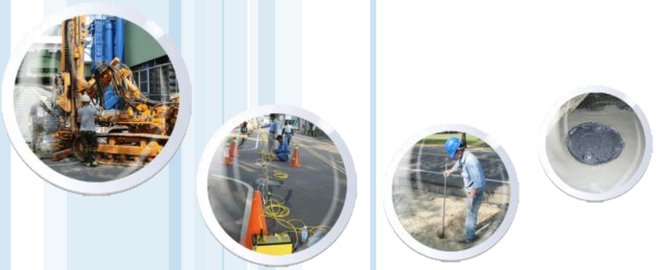




Verification by EPB



1. Verification dates: April of 2010 and August of 2010
2. Soil: 9 samples; groundwater: 14 samples



Summary

Special Features

- A site conceptual model was created by using multiple investigation technologies such as membrane interface probe/electrical conductivity detector, stratified slug test, single well flow velocity measurement, and geophysical survey.

  ➡ Uncertainty was significantly reduced by obtaining a comprehensive understanding of pollutants' spatial distribution and hydrological parameters of the contaminated site.

Special Features

- This project involved the first large-scale deep excavation in Taiwan with an excavation area of about 2,000 m^2. The depth of excavation ranged from five to seven meters, and 9,000 tons of contaminated soil was treated off-site after excavation.

Excavation and Wastewater Treatment

Special Features

- It was the first project that in-situ chemical oxidation was performed directly in the open trench.
The excavated zone was kept bare for eight months.
- This was also the first successful remediation case in Taiwan that integrated in-situ chemical oxidation with enhanced dual phase extraction.

ISCO installation

ISCO performance

Challenges

- Fully assessed the pollutant distribution and hydrological parameters of the contaminated site; planned excavation scope and depth in different stages; designed the optimal remediation method for follow-up works to shorten the period of remediation work.

- Carried out the feasibility study by using pilot-scale test to decide the most cost-effective chemical injection method and calculate the total amount of oxidant needed.

Challenges

- Completely removed the residual contaminants adsorbed to the saturated soil layer to prevent fluctuations in the concentration of pollutants in the water table, and to enhance the effectiveness of chemical oxidation remediation.
- Overcame the high groundwater level (2 m below the surface); maintained safety of the site around large areas of exposed surface and deep excavation (up to 7 m below the surface).

Benefits

- This is the first site to be removed from the Taiwan EPA's contamination list. It is a significant indicator that the Soil and Groundwater Pollution Remediation Act is progressing from survey and regulation to successful remediation.
- Located in an important urban area, the site is now available for development from which the owner and nearby residents stand to benefit.

What Factors Lead to Failure?

- ✗ Underestimation of state of soil or groundwater pollution
- ✗ Misunderstanding of hydrogeological characteristics
- ✗ Improper use of remediation techniques

Time!
Money!!
Achievement??

How to make a good remediation plan?

Summary

Consultant / executor

Site characteristics,
pollutant property,
remediation goal,
budget, techniques

Polluter / land owner

Time, budget,
future land use

EPA

Remediation goal,
human health risk,
public acceptance

All the factors are closely linked and inseparable.

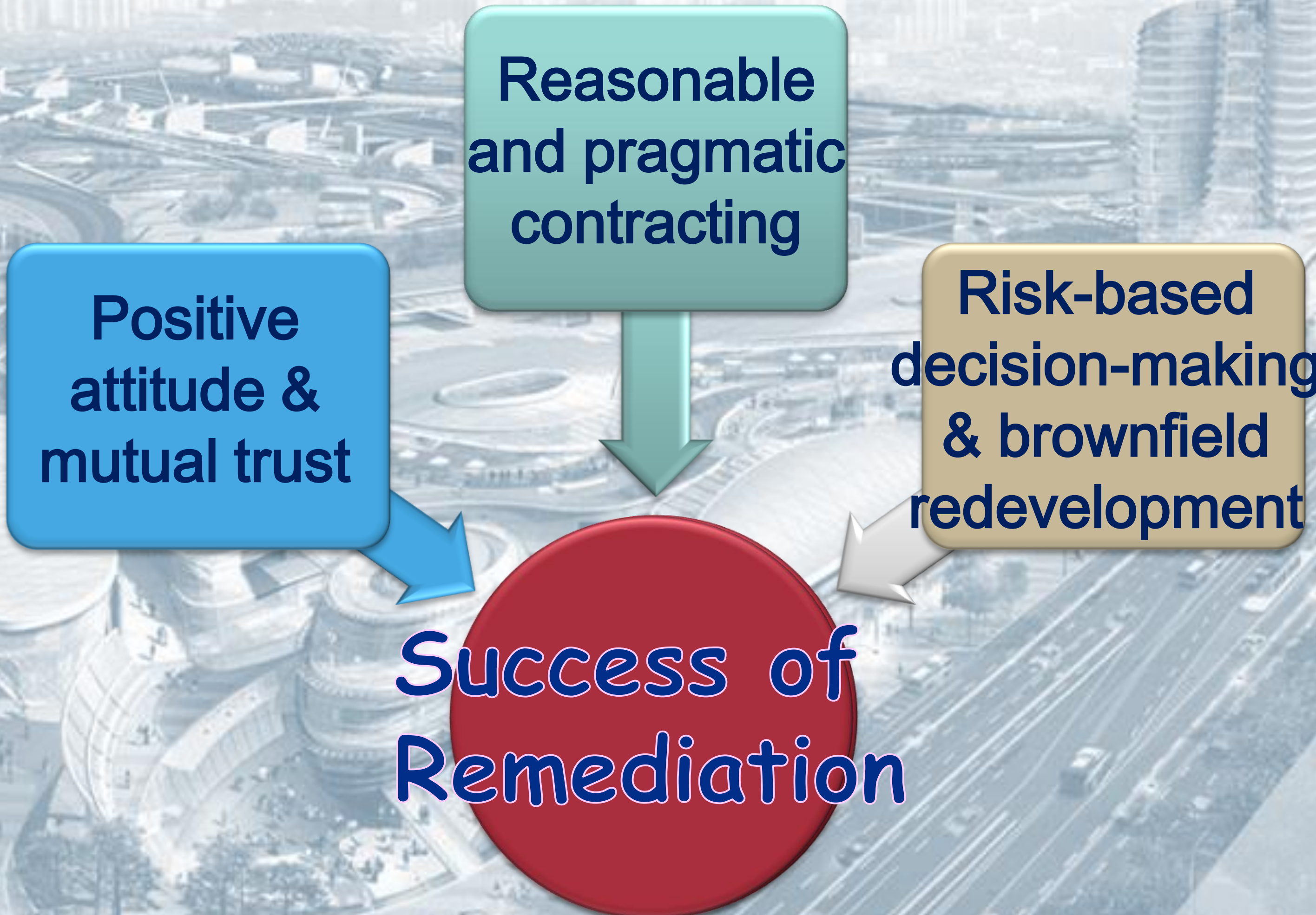
4

Conclusions

Conclusions

1. There is not the most effective and efficient remediation techniques; only exists the most suitable one.
2. A comprehensive understanding of pollutant distribution and hydrological parameters of the contaminated site lead to the success of remediation.
3. In this case, completing remediation work in a short period of time can be achieved by integrating TPE and ISCO techniques after the removal of residual contaminants.

Beyond the techniques,



"Soil and Groundwater Pollution Remediation Act"

amended in 2010

Human Health Risk

If factors such as the geological conditions, pollutant characteristics, or pollution remediation technologies preclude remediation until pollutant concentrations are less than soil and groundwater pollution control standards, soil and groundwater pollution remediation goals based on environmental impact and health risk assessment results may be submitted after requesting and obtaining the central competent authority's approval.

Brown-field Redevelopment

When remediation site land is to be used in conjunction with land development, the central competent authority may approve the soil and groundwater pollution remediation goals in consultation with relevant agencies.

Thanks for your attention!

Dr. Chia-Hsin Li

Environmental Engineering Dept. II,

Sinotech Engineering Consultants, Ltd.

- Tel: +886-2-27698388 ext. 20928
- E-mail address: chiahsin@mail.sinotech.com.tw

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Working Group on Remediation of Soil and Groundwater Pollution of Asian & Pacific Region Technical Training Workshop 2016

Remediation of a Chlorinated VOC contaminated Site A Case Study

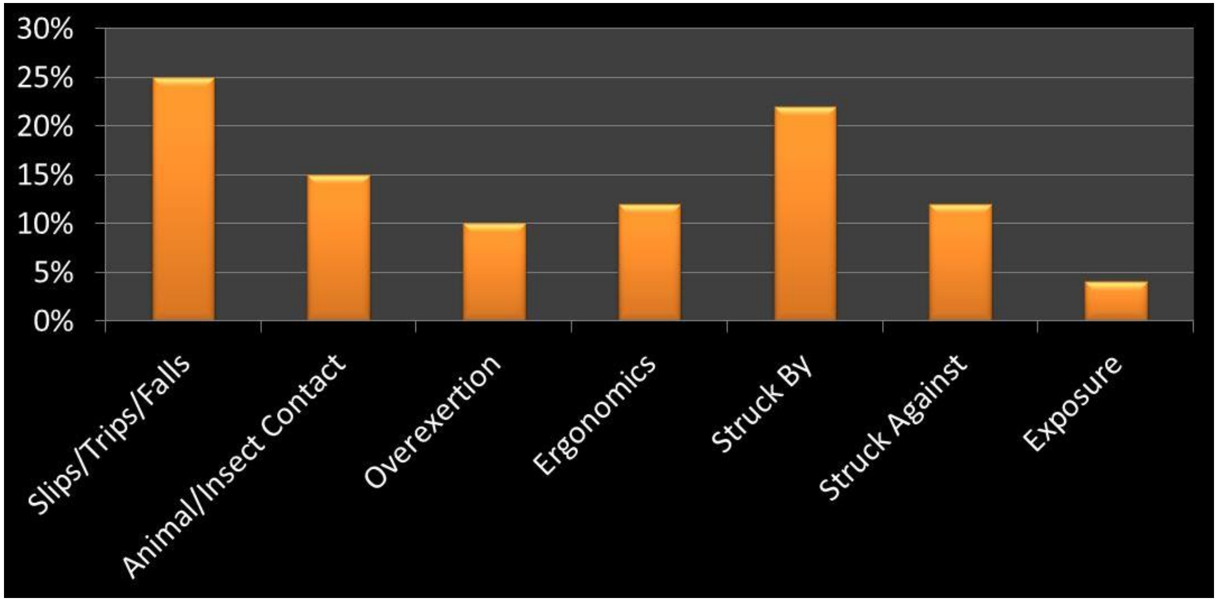
Dennis Tu
Executive Director, Environment of China
3, 25, 2016

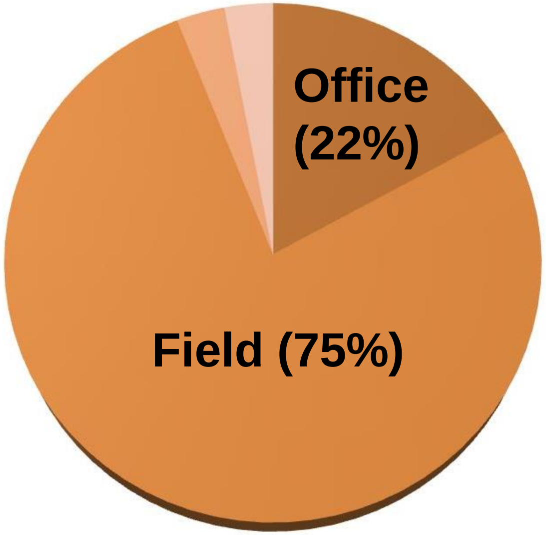
Outline

- Safety Moment
- CSI vs. CSI
- Management of Contaminated Site
- The Missing Link before Site Remediation
- Remediation of a cVOC contaminated Site- a Case Study
  - Site History and Background
  - Remedial Investigation and Conceptual Site Model
  - Development of Remediation Approaches
  - Implementation of Remediation Program
  - Performance
- Overview of AECOM in APAC Region

Safety Moment – Categories of Incident

Recordable Cases by Incident Type





Recordable Cases by Locations

CSI vs. CSI

- Contamination of soil and groundwater occurs beneath surface, and is difficult to identify its cause and impacted extents.
- Crime Scene Investigation (CSI) vs. Contaminated Site Investigation (CSI)
  - Suspected murderer and motive vs. Polluter and cause of contamination
  - Murder weapon and procedure vs. Contaminants and transportation model
  - Crime scene and time vs. Contaminated site and duration of contamination
  - Victim and condition of injury vs. Impact to environment and human
  - Both CSIs need solid QA/QC protocol to assure data accuracy and precision.

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Management of Contaminated Site

Two approaches for management of contaminated site

Soil and groundwater numerical criteria

- National Standards or Provincial Standards (Control Standards per TWEPA);
- International Standards: Dutch Intervention Value and USEPA Standards

Risk Assessment per liability consideration

- Site specific and more reasonable;
- Controversial due to lack of local factors;
- No action (in some cases) - public consensus?

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The Missing Link before Site Remediation

Phase I ESA
- Environmental settings
- Historical land usage
- Current operations
- Recognized environmental concerns (RECs)

Phase II ESA
- Sampling and Analysis Plan
- Boring and Installation of MWs
- Soil and GW sampling
- Lab testing of samples

Phase III RI/FS (missing link)
- Source and extents
- Conceptual site model
- Risk assessment
- Remediation goal
- Feasibility study, pilot test

Phase IV Remediation/Verification
- System installation and trial run
- Operator training and SOP
- System operation and checking
- Environmental monitoring
- Post-remediation verification

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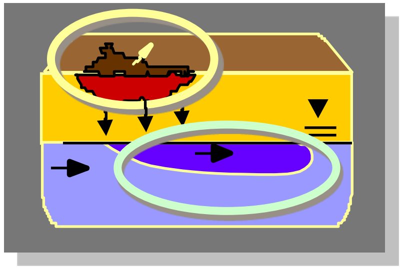
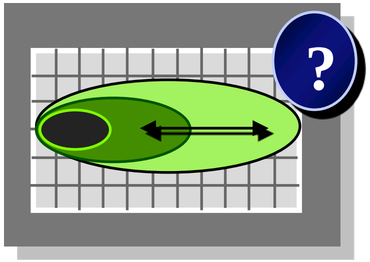
The Missing Link before Site Remediation (cont.)



- Remedial investigation (RI) and Feasibility Study (FS)
  - Identify Contamination Source: hopefully
  - Delineate Contamination Plume: horizontally and vertically extent
  - Establish Lithology and Hydrogeological Profile: type of soil intervals, groundwater aquifers, hydraulic conductivity
  - Verify Contaminants Transportation Paths: free phase products vs. residual products vs. dissolved phase contaminants
  - Determine appropriate remedial approach and cost.



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The Missing Link before Site Remediation (cont.)

- Conduct *remedial investigation (RI)* to verify the source(s) and type of contaminants, and impacted area (vertical and lateral extents)
  - Inorganic: metals, nitrate, sulfate;
  - Organic: VOC, SVOC, TPH, PCB, Dioxin, pesticides;
  - Dissolved phase vs. Residual phase vs. Non-aqueous phase liquid (NAPL)
    - Light Non-Aqueous Phase Liquid (LNAPL): distribution follows groundwater flow direction;
    - Dense Non-Aqueous Phase Liquid (DNAPL): distribution follows gravity through breaches of formation

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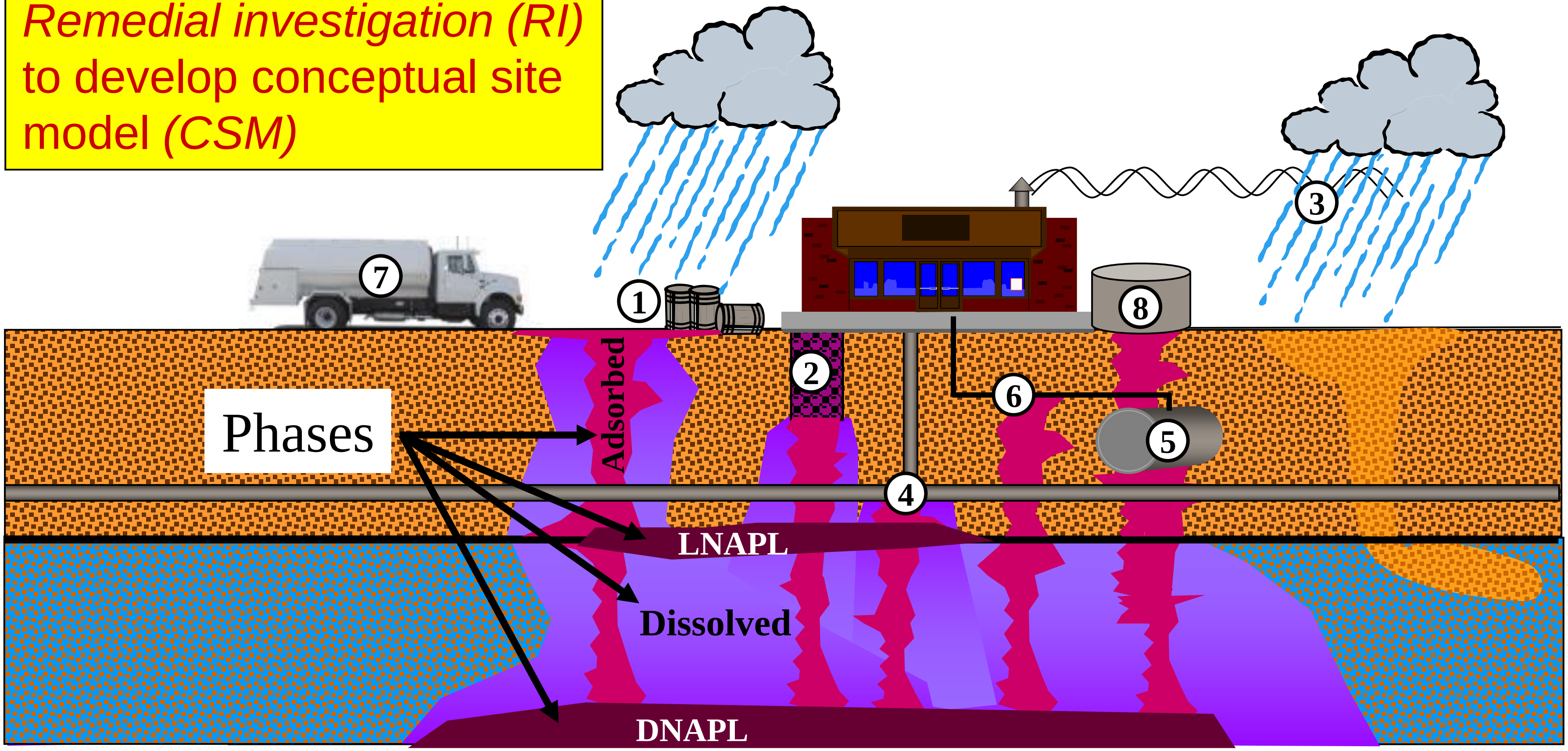
The Missing Link before Site Remediation (cont.)

Remedial investigation (RI) to develop conceptual site model *(CSM)*



1. Drums
2. Dry wells, floor drains
3. Vapors
4. Sewer lines
5. USTs
6. Leaking or ruptured buried pipelines
7. Truck loading/unloading
8. ASTs

The Missing Link before Site Remediation (cont.)

- *Feasibility study (FS)* of remediation technologies for treatment of contaminated soil and groundwater
  - *In situ* (treat soil and groundwater in place)
    - In-situ Chemical Oxidation and In-situ Bioremediation
  - *On site (Ex situ)*
    - Soil : excavation and treatment on site to put back in place or for elimination after treatment off site (Biopile, Land-farming, Soil Washing, or Bioventing)
    - Groundwater : pumping/treating/re-injecting into the aquifer or discharging to surface water bodies
  - *Off site*
    - Soil : excavation and treatment of contaminated soils off site (Land-farming, Incineration, Solidification and Disposal at landfill Site)

The Missing Link before Site Remediation (cont.)

- Screening parameters of Remediation Technologies
  - Physicochemical properties
    - Volatility (vapor pressure, Henry Constant, …)
    - Solubility
    - Biodegradability (half Time $t_{1/2}$)
    - Toxicity of compounds and *toxicity of by-products*
  - Microflora condition (aerobic vs. anaerobic)
  - Aquifer characteristics
    - Depth of the Groundwater
    - uses (drinking water, gardening, farming watering …)
    - Productivity of the aquifer (permeability / transmissivity, …)
    - Porosity of the geological materials
  - Cost, schedule, and site condition

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The Missing Link before Site Remediation (cont.)

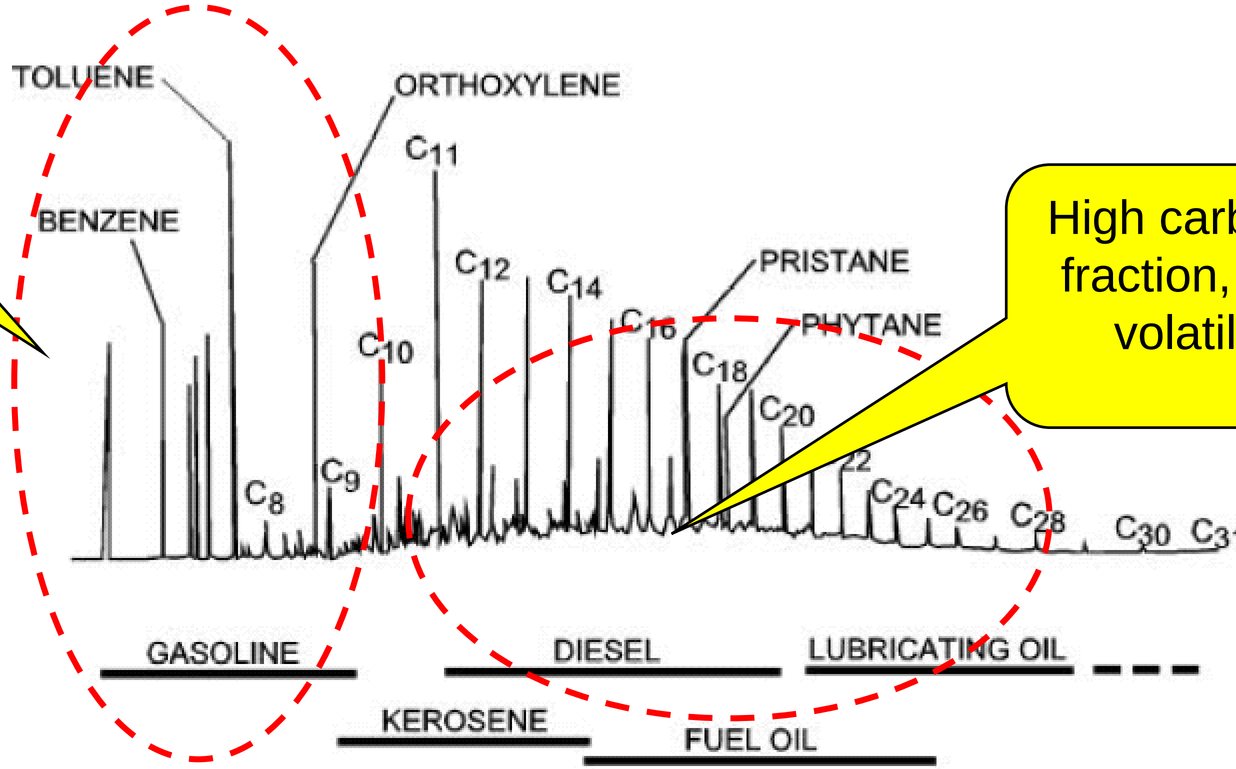
Properties of Total Petroleum Hydrocarbon (TPH) Contaminants

Compounds	carbon	MW	Density (g/cm^3) @20℃	Boiling point (℃)	Solubility (mg/L) @25℃	Vapor pressure (mm Hg) @20℃
benzene	C6	78.11	**0.885**	80.1	**1780**	**75.2**
toluene	C7	92.13	**0.867**	110.6	537	21.8
ethylbenzene	C8	106.17	**0.867**	136.0	167	7.1
ortho-xylene	C6	106.16	**0.864**	144.0	-	7.0
meta-xylene	C6	106.16	**0.864**	139.0	162	6.2
para-xylene	C6	106.16	**0.864**	138.0	-	9.0
MTBE	C5	88.15	**0.758**	55.2	**51000**	**249**

The Missing Link before Site Remediation (cont.)

Properties of Total Petroleum Hydrocarbon (TPH) Contaminants

Low carbons fraction, high volatile



High carbons fraction, low volatile

Light Non-Aqueous Phase Liquid (LNAPL)

The Missing Link before Site Remediation (cont.)

Properties of Select Chlorinated VOC (cVOC) Contaminants

Compounds	Structure	Density (g/cm³) @20℃	Boiling point (℃)	Solubility (mg/L) @20℃	Vapor pressure (mm Hg) @20℃
1,1,1-Tricholoethane	CH_3CCl_3	**1.32**	74	**4,400**	**127**
1,2-Dichloroethane	$C_2H_4Cl_2$	**1.25**	83.5	**8,700**	**61**
Tetrachloroethylene	C_2Cl_4	**1.623**	121	**150**	**15.8**
Trichloroethylene	C_2HCl_3	**1.46**	87	**1,100**	**60**
1,1-DCE/1,2-DCE	$C_2H_2Cl_2$	**1.21~1.28**	32~60	**2,500/ 3,500 ~6,300**	**591/ 273~395**
Vinyl chloride	C_2H_3Cl	**0.908**	-153.2	**2,700**	**2,500**

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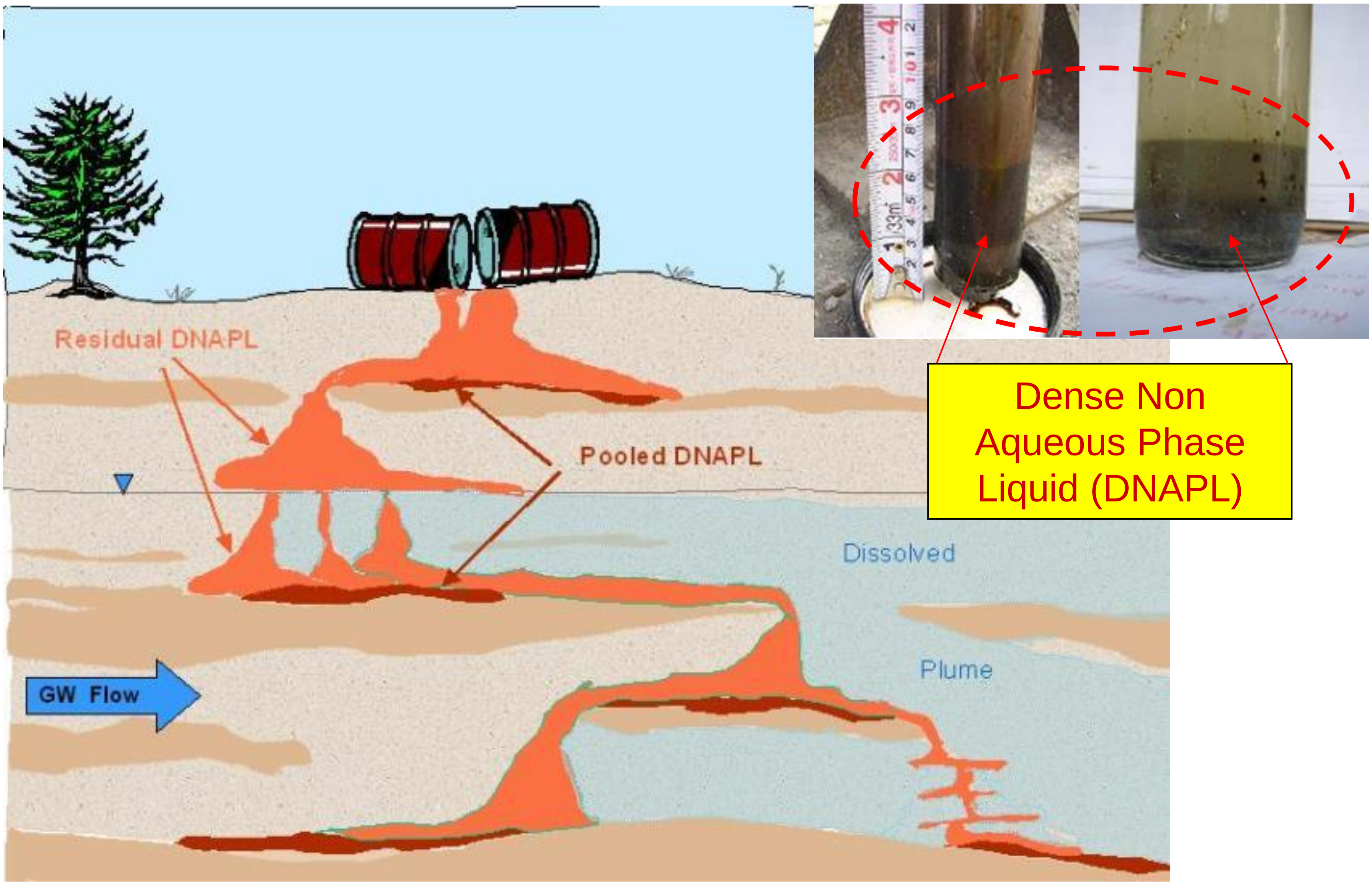
The Missing Link before Site Remediation (cont.)



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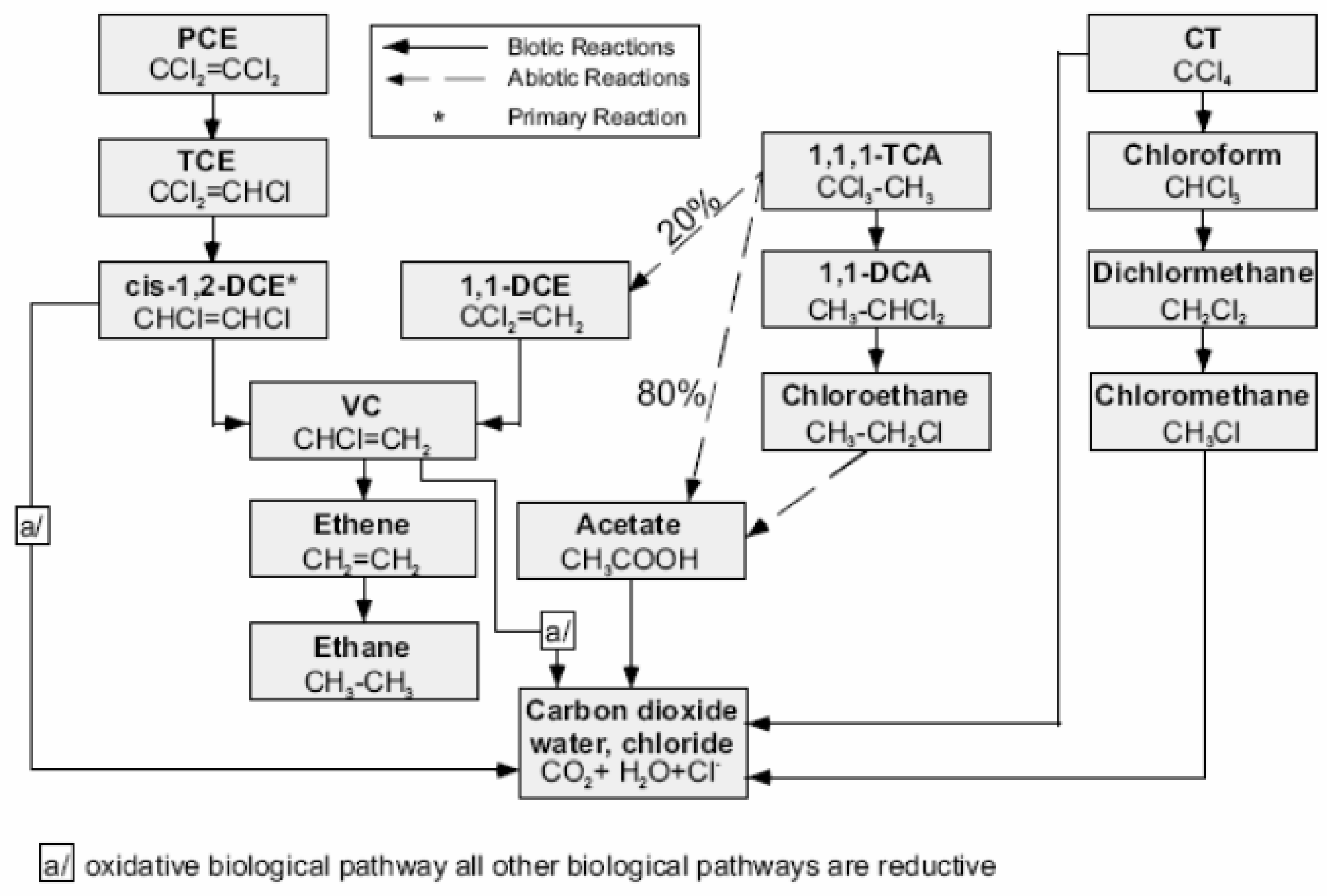
The Missing Link before Site Remediation (cont.)

Natural degradation pathways of cVOC



Curtsey of Solutions-IES prepared for ESTCP of DOD, USA

The Missing Link before Site Remediation (cont.)

- Selection parameters of Remedial Technologies
  - Development status
  - Availability in local
  - Utilization limitations by site condition
  - Installation cost vs. O&M cost
- Bench scale or pilot scale study (essential task)
  - Verify the feasibility of selected remediation technology
  - Collect site specific data for design of full scale system
  - Estimate the O&M factor, cost, and potential schedule

Remediation of a cVOC contaminated Site

Site History and Background

- Located in an industrial zone, but mixed with commercial and residential areas; occupied and area of 9,970 m^2.
- Major surface water body 30 m to the east, flowing north.
- One main complex workshop building (4 story) at the center. The site area is 100% covered by buildings and RC or asphalt pavement.

Remediation of a cVOC contaminated Site (cont.)

- Historical operation of the Site:
  - 1971 to 1982: Manufactured TV components with plating process in the northeastern area at the ground floor of the main building. A small solvent (1,1,1-TCA) wash tank at the south end of the building between the early 1970s and 1982.
  - 1983 to 1986: Ceased some manufacturing processes including pressing, plastic extrusion and plating. The production line was arranged for the assembly of parts provided by subcontractors.
  - From 1981 to date: The Site has been used to manufacture and assemble TV/cable converters.

Remediation of a cVOC contaminated Site (cont.)

Services Provided by AECOM:

- Phase I/II Environmental site assessment (ESA)
- Multiple site investigations (soil gas survey; MIP survey, soil sampling and GW investigation) for CSM.
- Human health risk assessment.
- Development of site control (remediation) plan.
- Pilot studies of remedial technologies.
- Implementation and operation of Two-Phase Extraction (TPE) systems.
- Implementation of full scale Enhanced In-situ Bioremediation (EIB) treatment.
- Performance sampling and groundwater monitoring program.

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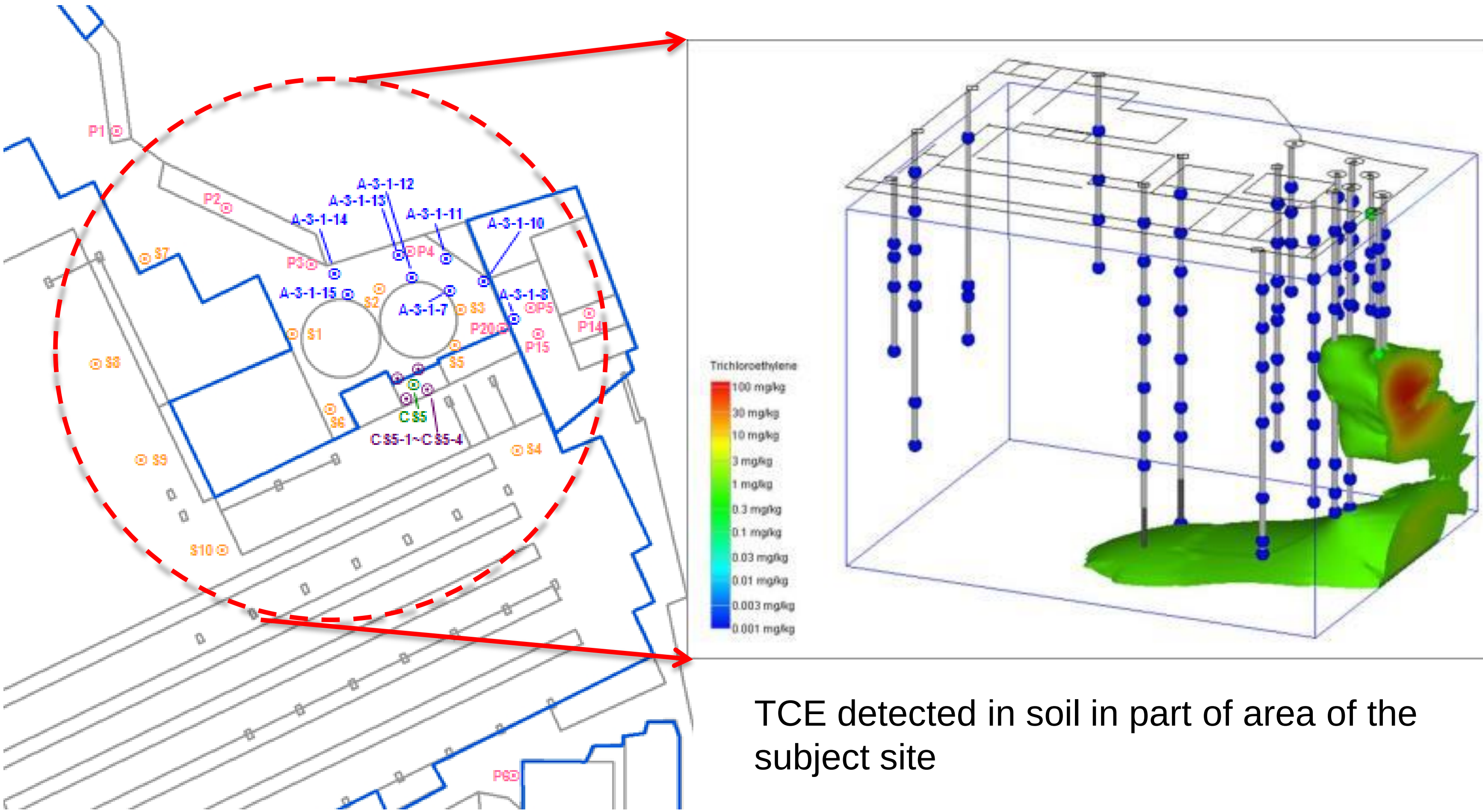
Remediation of a cVOC contaminated Site (cont.)

Investigation and Conceptual Site Model



TCE detected in soil in part of area of the subject site

Remediation of a cVOC contaminated Site (cont.)

Installation of clustered monitoring wells

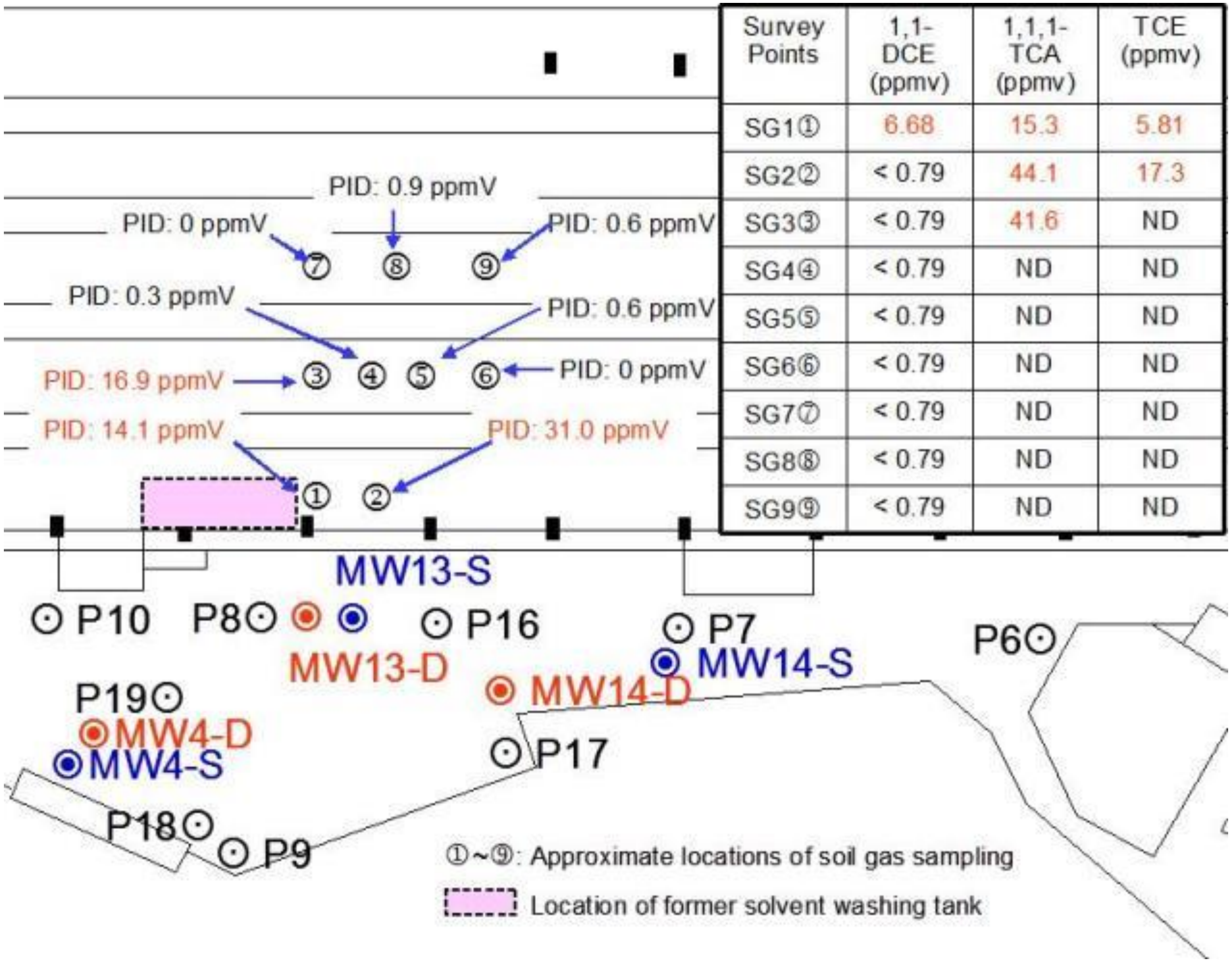



- 16 shallow monitoring wells (5-7 m deep);
- 23 deep monitoring wells (15-20 m deep)
- 2 m Screen section installed from well base for capturing potential DNAPL.

Remediation of a cVOC contaminated Site (cont.)

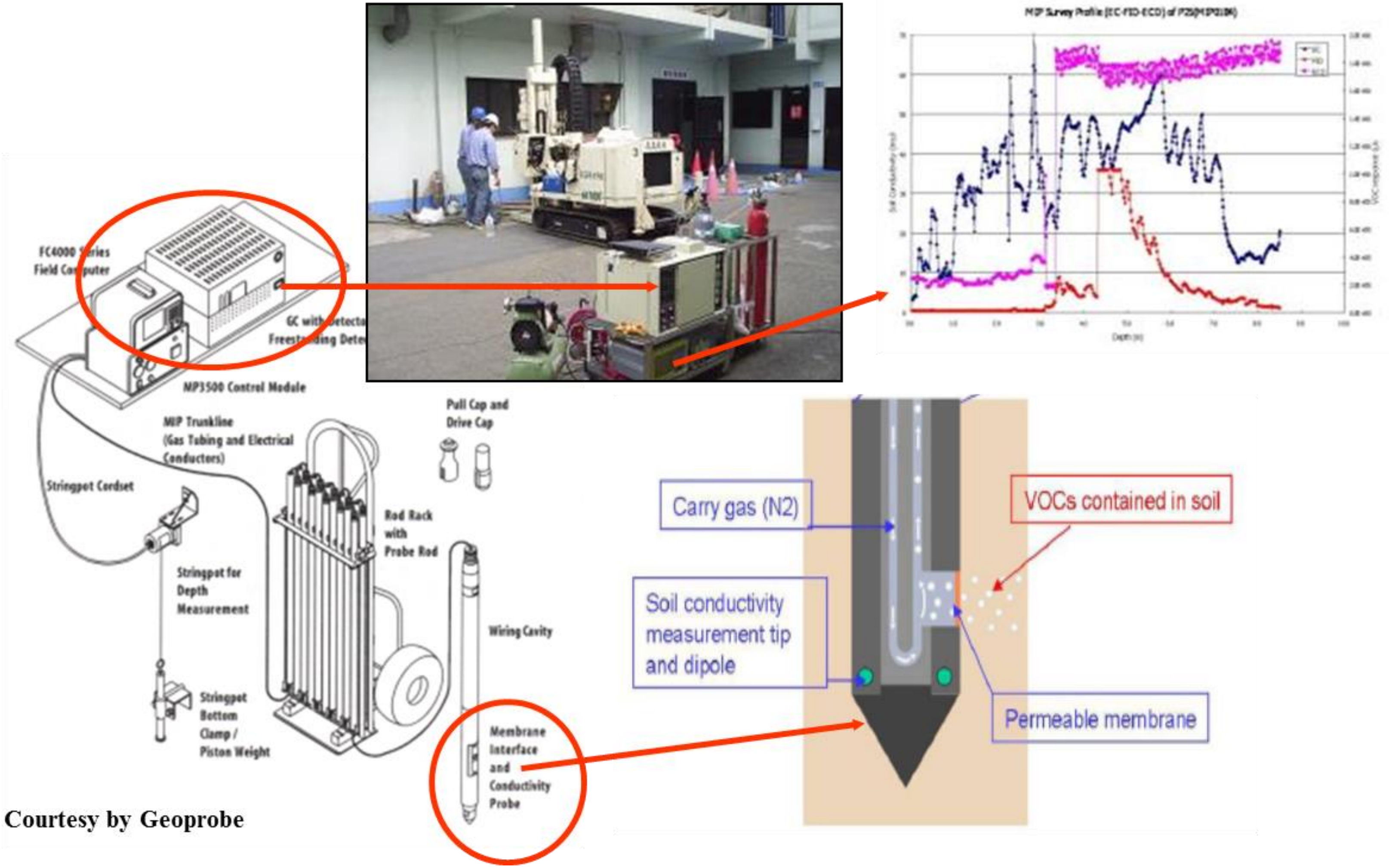
Soil gas survey inside of workshop building

Survey Points	1,1-DCE (ppmv)	1,1,1-TCA (ppmv)	TCE (ppmv)
SG1①	6.68	15.3	5.81
SG2②	< 0.79	44.1	17.3
SG3③	< 0.79	41.6	ND
SG4④	< 0.79	ND	ND
SG5⑤	< 0.79	ND	ND
SG6⑥	< 0.79	ND	ND
SG7⑦	< 0.79	ND	ND
SG8⑧	< 0.79	ND	ND
SG9⑨	< 0.79	ND	ND



Remediation of a cVOC contaminated Site (cont.)

- Membrane Interface Probe (MIP) – onsite direct sensing investigation



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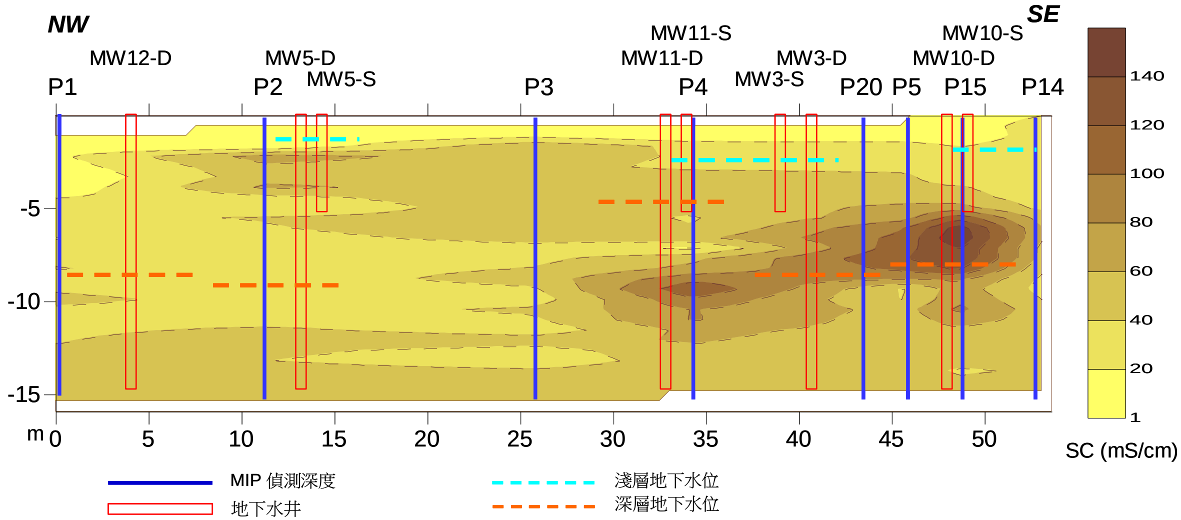
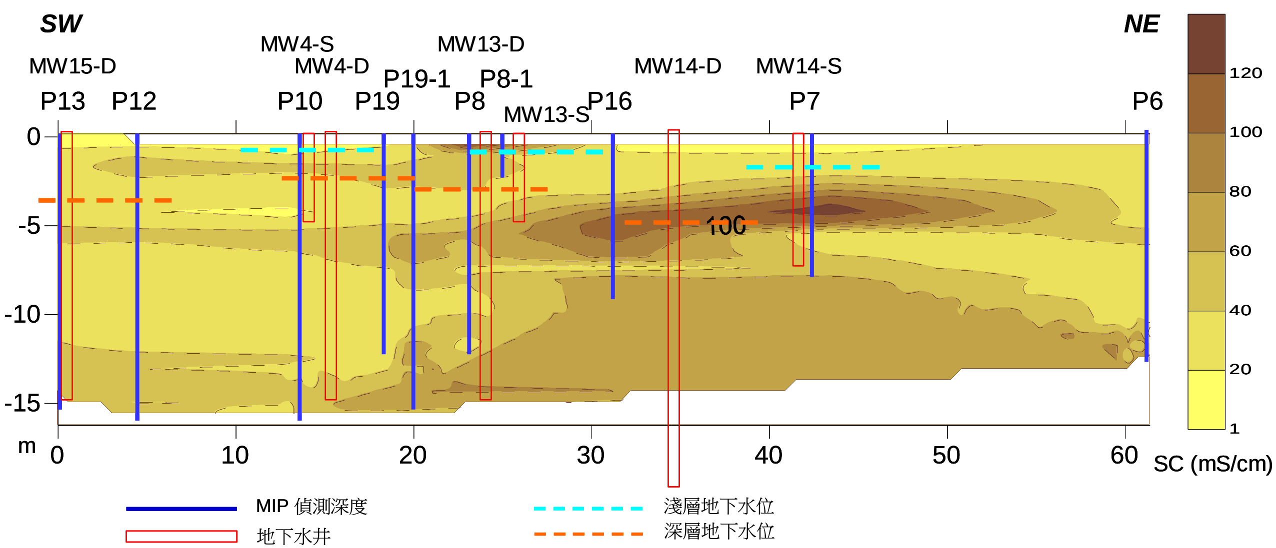
Remediation of a cVOC contaminated Site (cont.)





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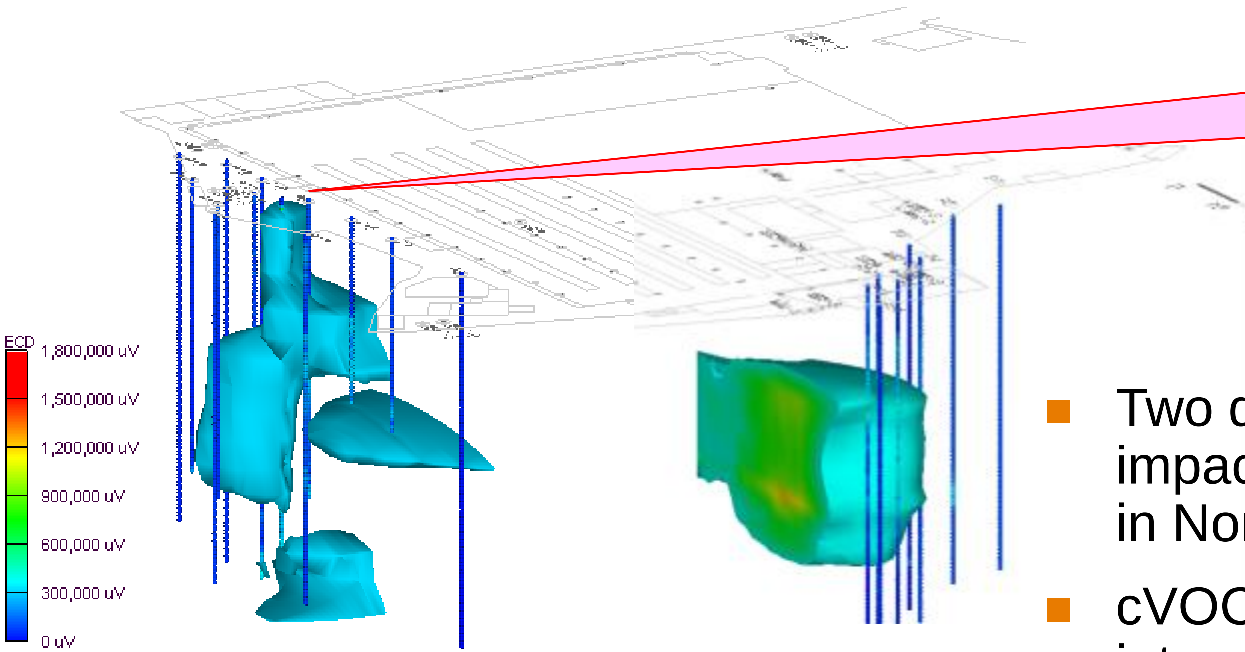
Remediation of a cVOC contaminated Site (cont.)

Location of Former TCA washing tank



conceptual site model

- Two distinguished cVOC impacted areas were identified in North Area and South Area.
- cVOC impacts soil in shallow interval, and both shallow and deep groundwater zones.
- Target cVOCs include TCA, TCE, DCA, DCE, VC.

Remediation of a cVOC contaminated Site (cont.)

Development of Remediation Approaches

- Contain cVOC plumes within site boundary.
- Remediate cVOC in both soil and groundwater to meet ***Control Standards*** promulgated by Taiwan EPA.
- Technologies reviewed for remediation of cVOC:
  - SVE & Air-sparging;
  - Groundwater pump and treat (P&T);
  - **Multiple-Phase Extraction (MPE);**
  - Thermal injection plus MPE;
  - Electrical resistance heating (ERH) plus SVE;
  - In-situ chemical oxidation (ISCO);
  - **Enhanced In-situ bioremediation (EIB)**

Remediation of a cVOC contaminated Site (cont.)

- Treatment Train concept applied:
  - Multiple-Phase Extraction (MPE) system can be implemented to remove cVOC mass from the subsurface of the source area(s) cost effectively and efficiently in the beginning of remediation stage.
  - Enhanced In-situ Bioremediation (EIB) will be used as a follow-up polishing technology to continue remediating dissolved cVOC in groundwater.

Remediation of a cVOC contaminated Site (cont.)

- Multi-Phase Extraction (MPE) - a modification to the conventional SVE and groundwater pump & treat
  - *SVE is generally applied to soil above groundwater level for vapor phase contaminants with low vacuum and high air flow rate. Efficiency is limited at low permeability formation.*
  - *Groundwater Pump & Treat is generally applied to remedial dissolved phase, residual phase, and NAPL contaminant in groundwater aquifer, under gravity drainage condition.*
- MPE - addresses VOC/TPH contaminations in both the saturated and vadose zones; able to remediate vapor, dissolved, residual, and NAPL contaminants.

Remediation of a cVOC contaminated Site (cont.)

- Highlights of MPE Capabilities
  - *Increase in groundwater recovery rate (compared to conventional pumping process; USEPA 1997)*
  - *Increase in radius of influence (ROI) of individual groundwater recovery well (Suthersan, 1997)*
  - *Recover NAPL and remediate capillary fringe and smear zone (USEPA 1996, 1997)*
  - *Most cost effective for cleaning up low to moderate permeability sites with halogenated VOCs in soil and groundwater (USEPA, 1997)*

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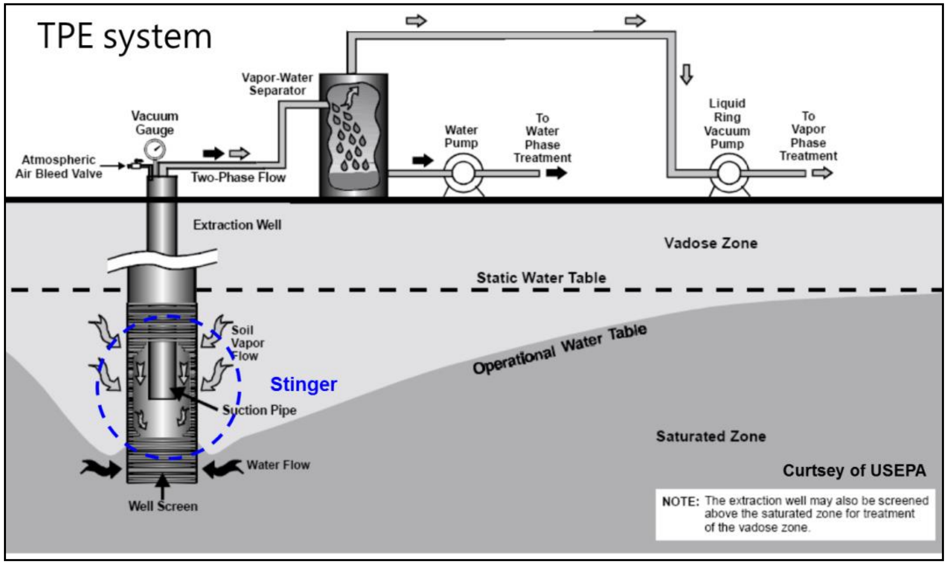
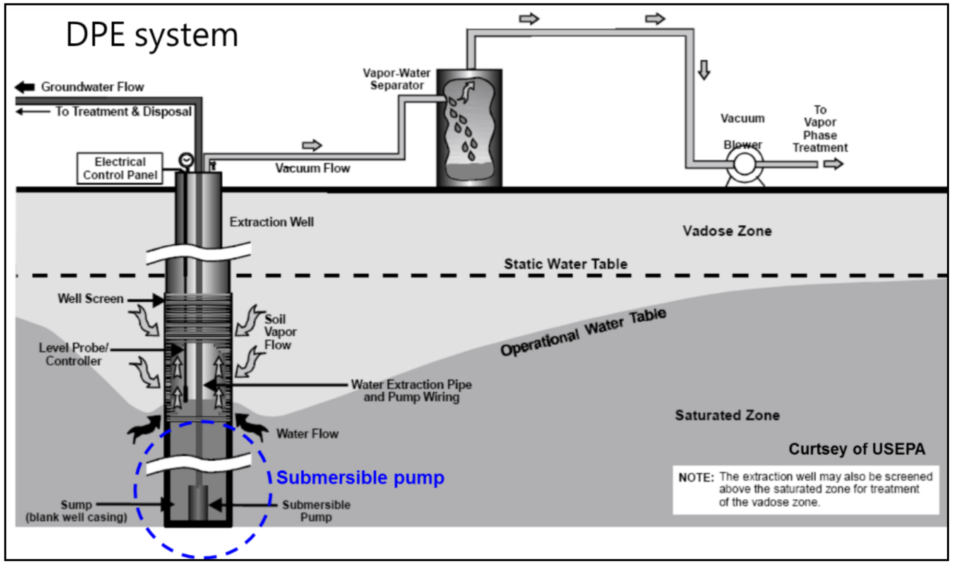
Remediation of a cVOC contaminated Site (cont.)

- Two Types of MPE
  - *Two Phase Extraction (TPE) - employs a high vacuum (18~26 in-Hg) pump to extract both soil vapor and groundwater from one extraction well with a suction pipe (drop tube)*
  - *Dual Phase Extraction (DPE) - employs a down-hole pump to extract groundwater and another vacuum extraction blower to extract soil vapor*





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Remediation of a cVOC contaminated Site (cont.)

MPE General Guidelines	
Site Condition	Guideline
Contaminants	▪ Halogenated VOC ▪ Non-Halogenated VOC, TPH
Contamination Location	▪ Below Groundwater Table ▪ Both Above/Below Water Table
Henry's Law constant	> 0.01 at 20 ^{o}C
Vapor Pressure	> 1.0 mm-Hg at 20 ^{o}C
Materials below Water Table	Sand to Clay
Air Permeability of Materials above Water Table	Moderate to Low Permeability

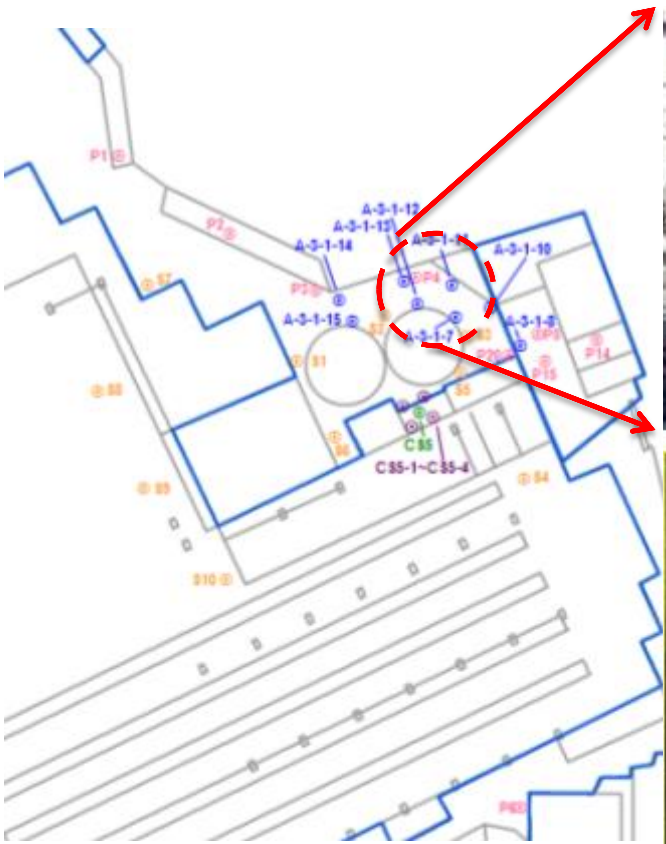
Remediation of a cVOC contaminated Site (cont.)

- Intrinsic factors of a successful MPE process
  - *Degree of Drawdown Achievable - smear zone dewatering is essential.*
  - *Subsurface Vacuum Distribution - assists volatilization of VOCs in the subsurface.*
  - *Air Flow Rate - provides enough air flow to remove VOCs*
- Pilot Study is required
  - *To measure Air flow, VOC mass removal rate, vacuums of wellhead and manifold, and groundwater production rate.*

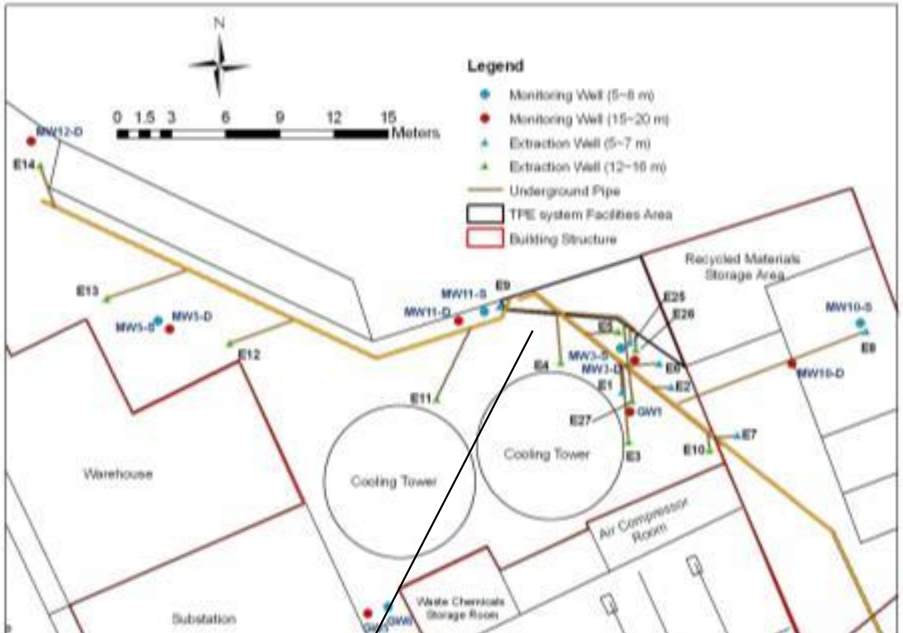
Remediation of a cVOC contaminated Site (cont.)

Remediation Progress :

TPE Pilot study between March 2007 and February 2008.



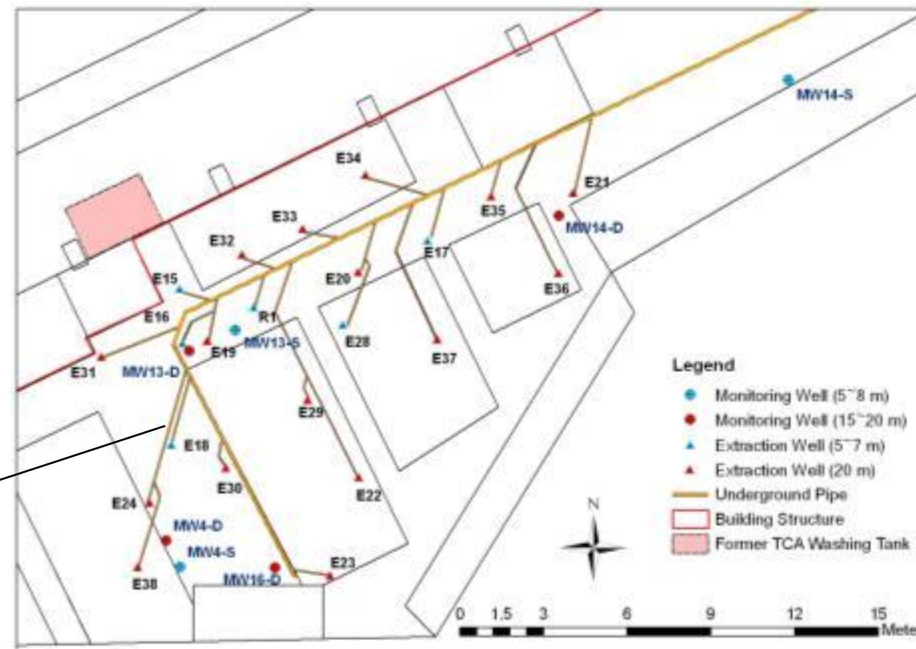
Remediation of a cVOC contaminated Site (cont.)



TPE system #1 for North Area

Remediation Progress:

Operated two TPE systems with 17 extraction wells (EWs) in North Area and 21 EWs in South Area since November 2008.



TPE system #2 for South Area

Remediation of a cVOC contaminated Site (cont.)






- *Extraction wells installation*
- *Underground piping*
- *Wellhead configuration*
- *Unit connection and assembly*

Remediation of a cVOC contaminated Site (cont.)

- *60-hp oil sealed liquid ring pumps*

- *Vapor-liquid separator*
- *Air stripping tank*

- *Configurations of No.1 and No.2 TPE systems*

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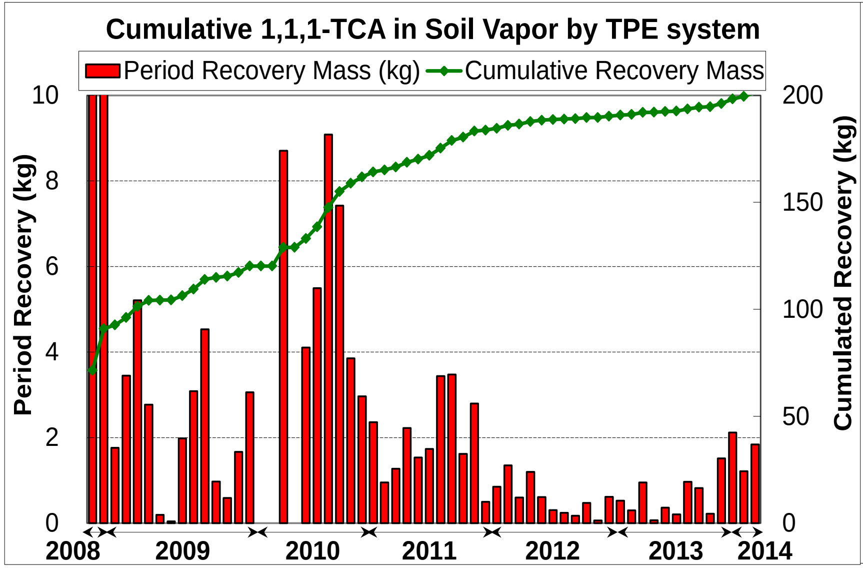
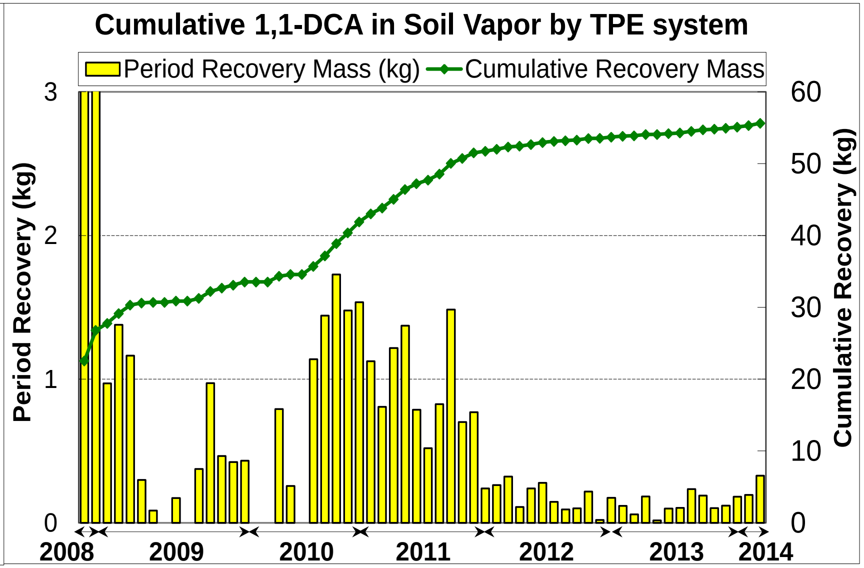
Remediation of a cVOC contaminated Site (cont.)

Performance of TPE operation

- Approximately 16,000,000 m^3 soil vapor have been extracted through TPE systems between 2008-2014.
- Estimated total of 290 kg cVOCs have been removed from subsurface of the Site.





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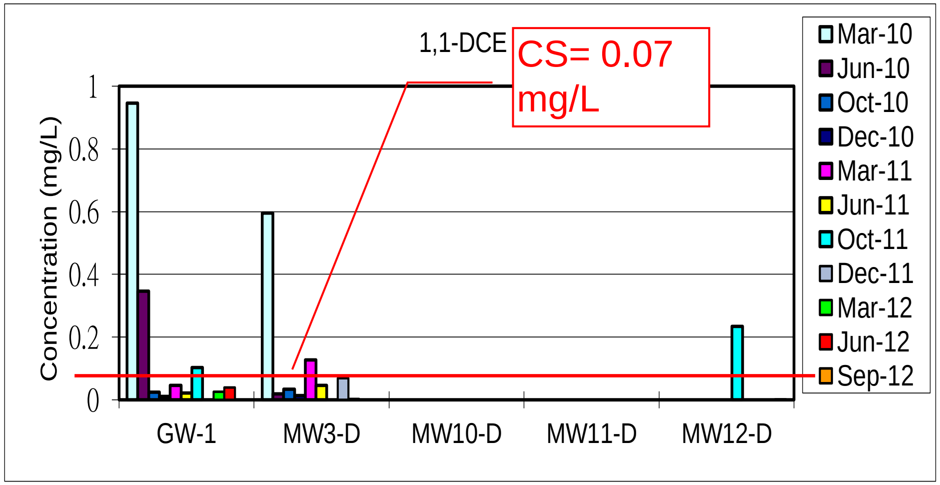
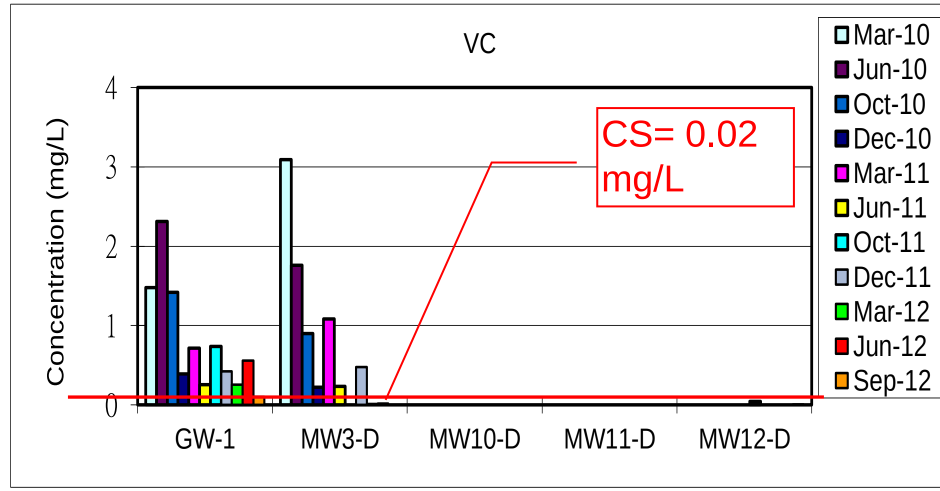
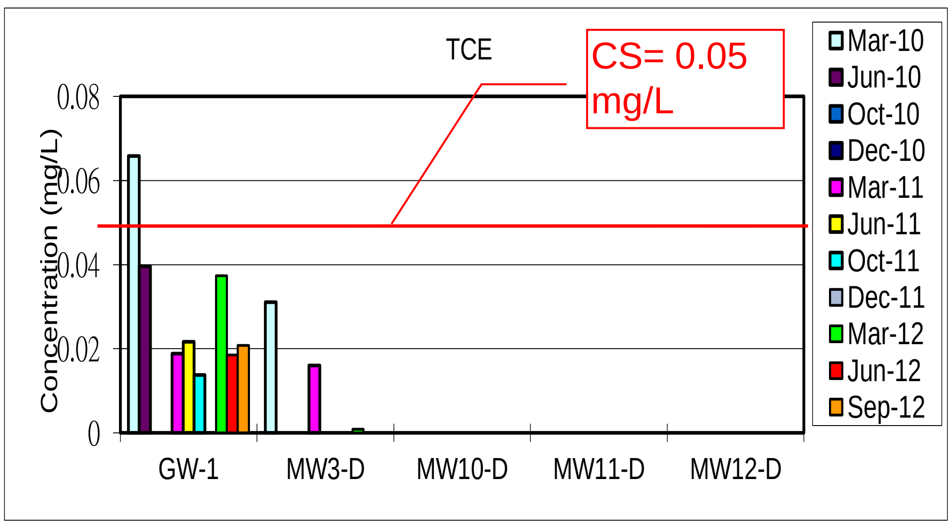
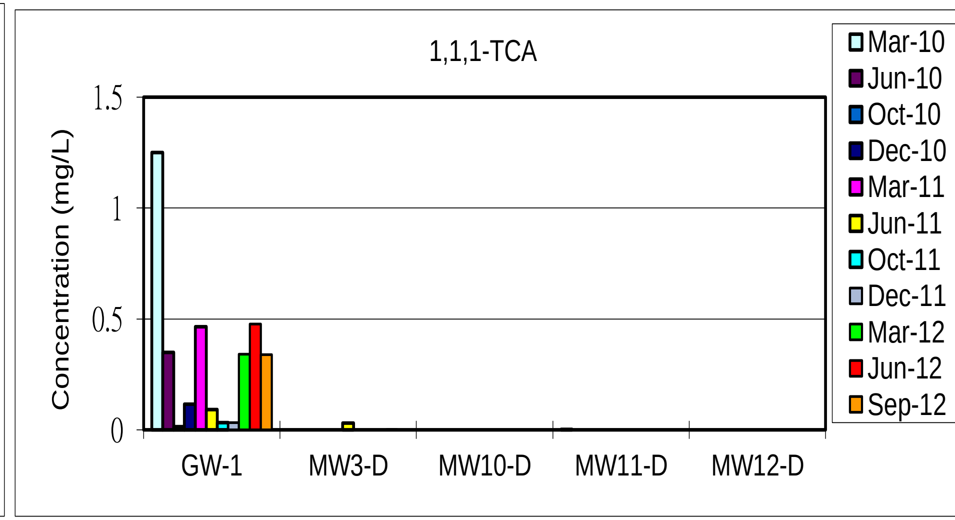
Remediation of a cVOC contaminated Site (cont.)

cVOC trends in deep groundwater at North Area after TPE operation









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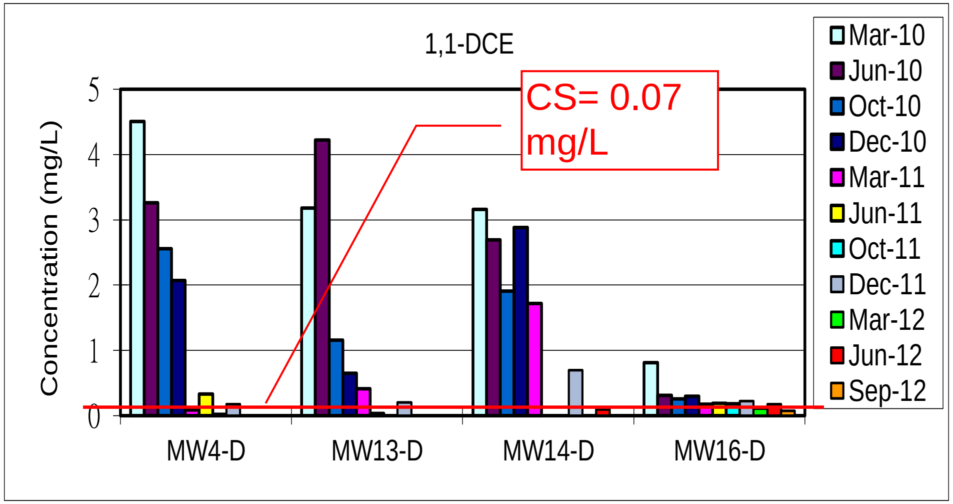
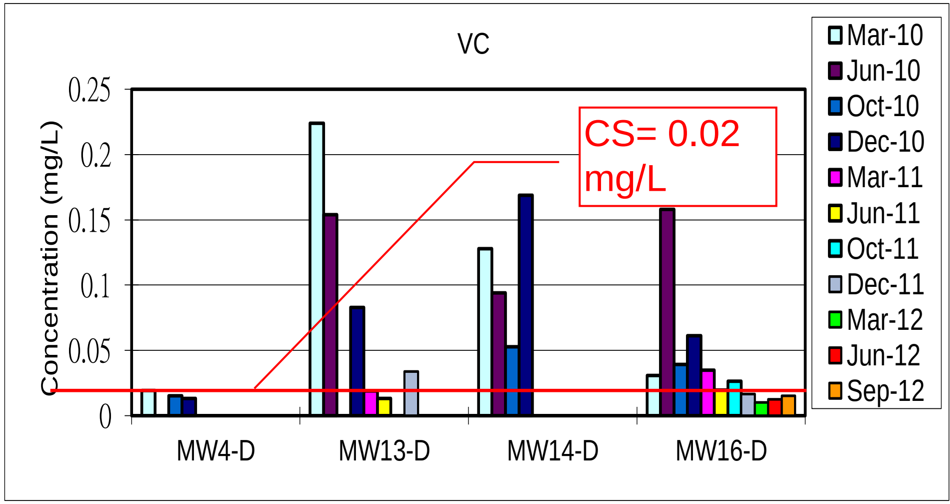
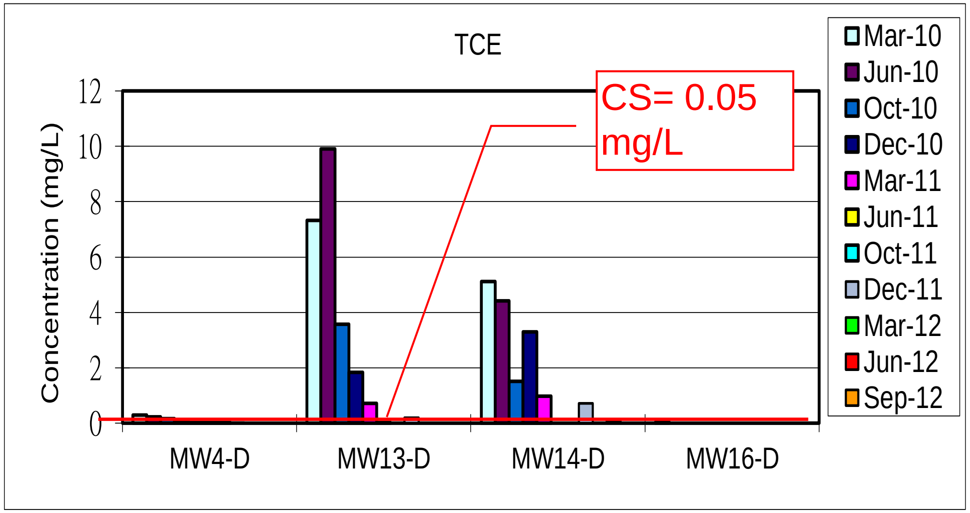
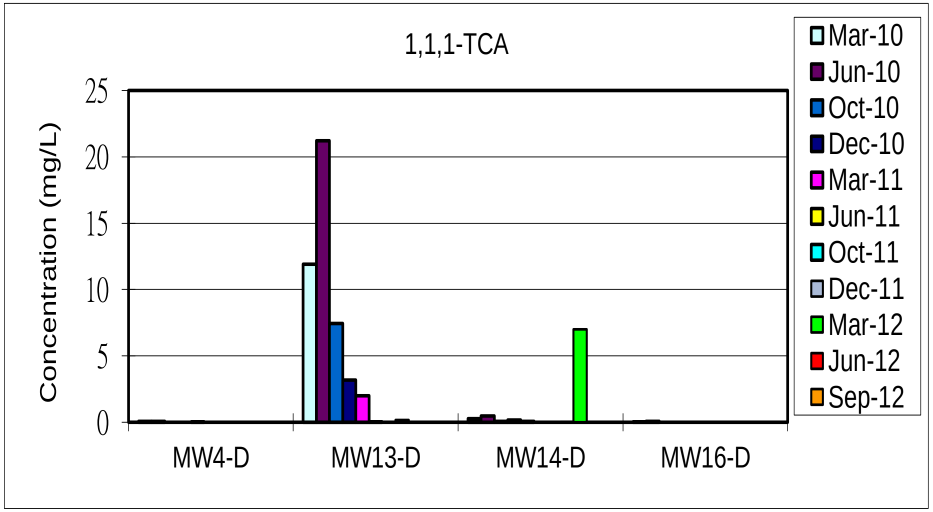
Remediation of a cVOC contaminated Site (cont.)

cVOC trends in deep groundwater at South Area after TPE operation





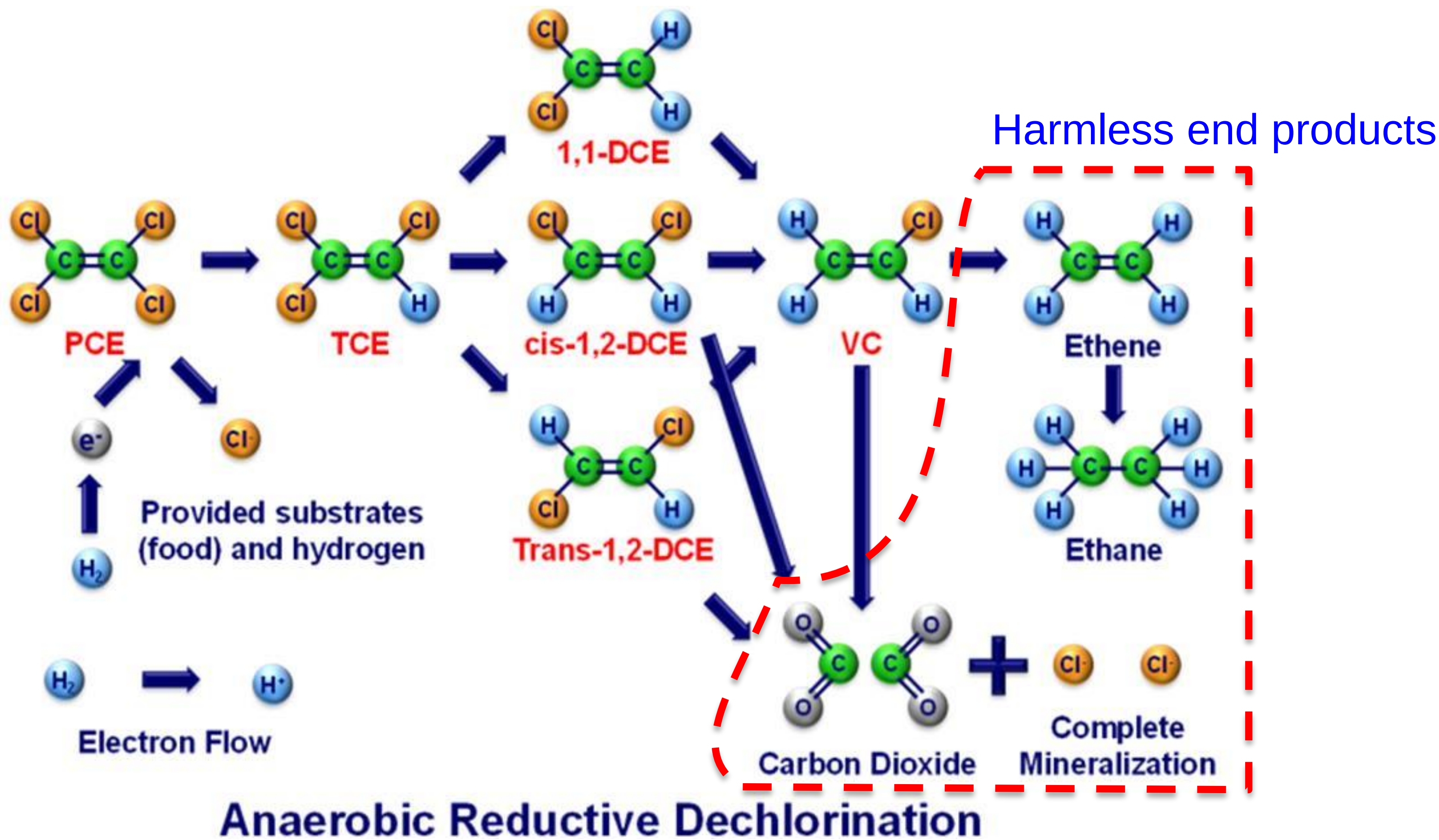




Remediation of a cVOC contaminated Site (cont.)

Second step remediation of cVOC impacted groundwater

- EIB pilot study at North Area between July 2010 and June 2012.
- Developed and Implemented a full scale EIB treatment system to replace TPE.



Reference: EOS Remediation Inc. 2007. Drawing Modified from AFCEE, Technology Transfer Division

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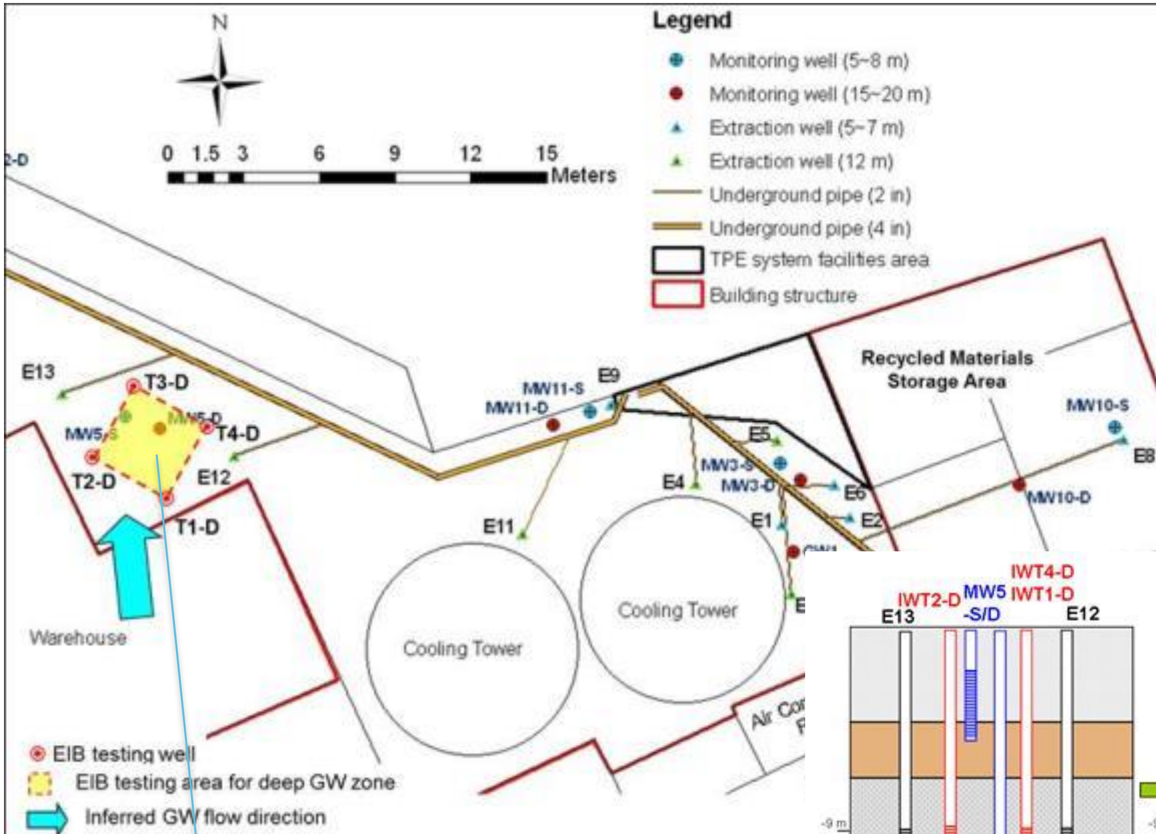
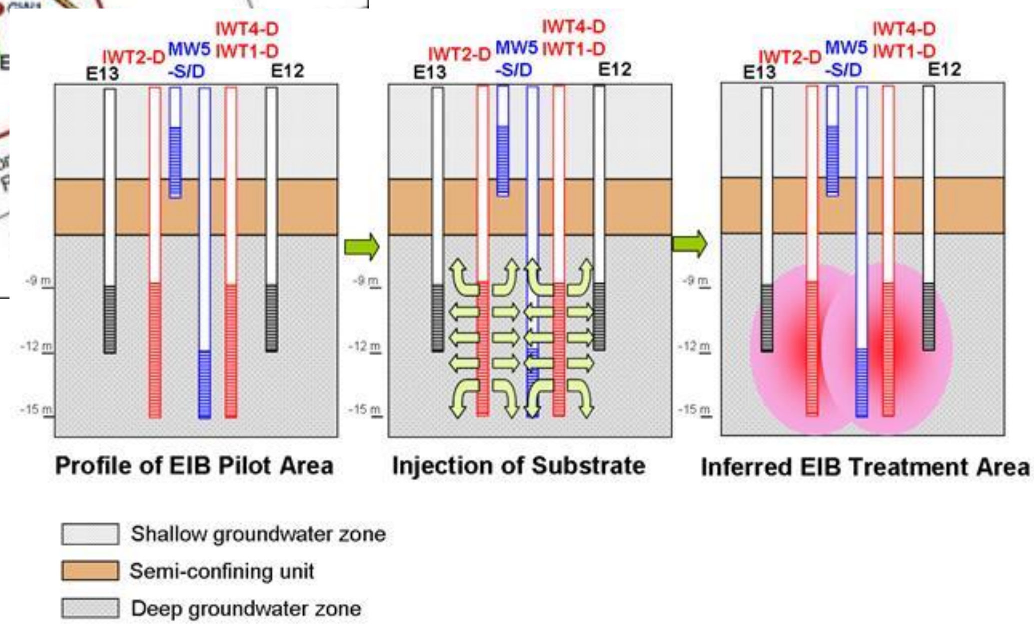
Remediation of a cVOC contaminated Site (cont.)



- 1,1-DCE 0.757~3.51 mg/L
- VC 0.153~1.11 mg/L

Remediation Progress

- EIB pilot study between July 2010 and June 2012.
- Only 1,1-DCE and VC were detected in groundwater.
- Installed 3 injection wells and 1 monitoring wells to encompass MW5-D.



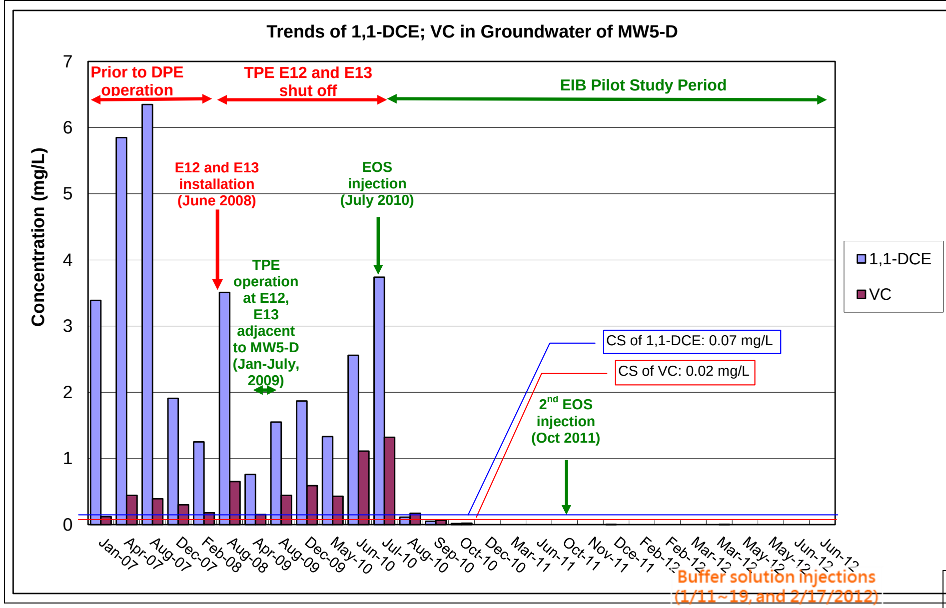
Remediation of a cVOC contaminated Site (cont.)

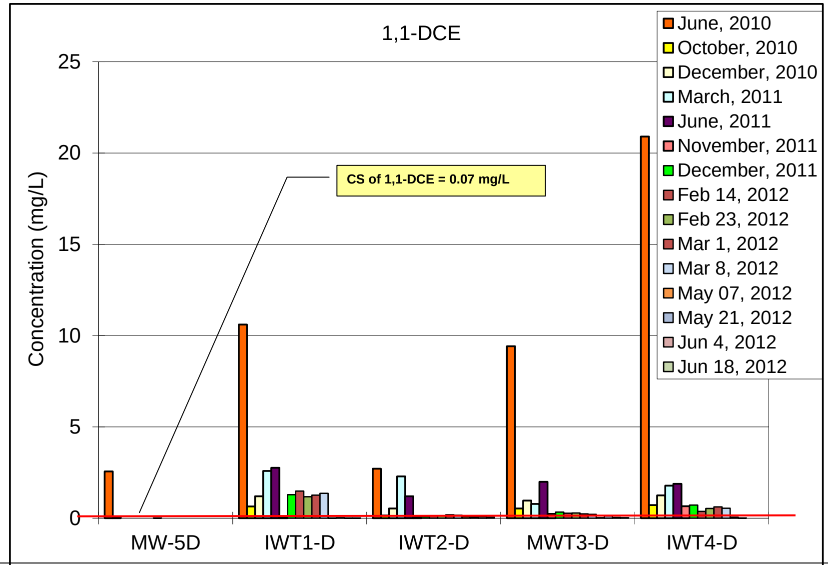
Remediation Progress: EIB pilot study

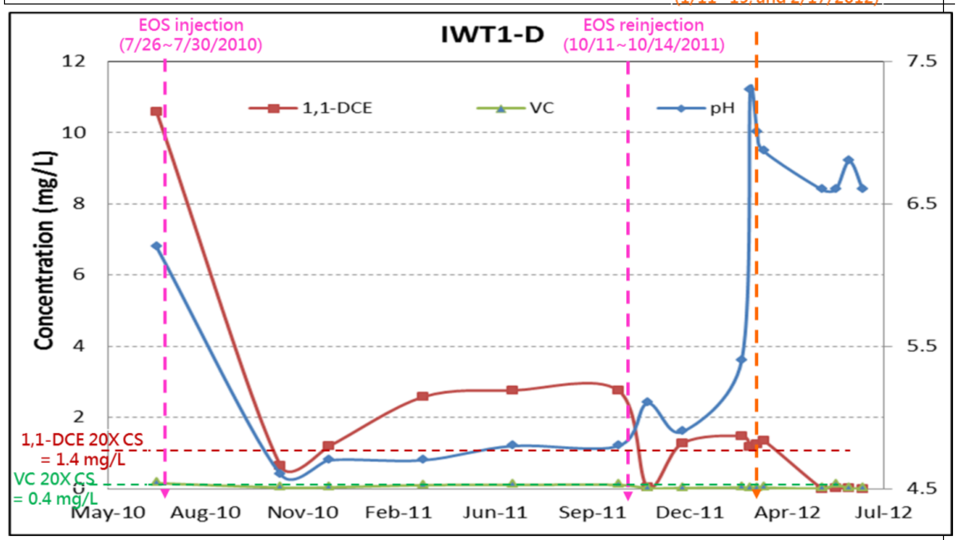
- Food grade patterned substrates (EOS) were injected into the aquifer of pilot area.
- Long term monitoring of cVOC and pH, DO, ORP in groundwater.
- Buffer solution was injected when needed.
- Confirmed feasibility and efficiency of EIB to treat dissolved cVOC in groundwater.

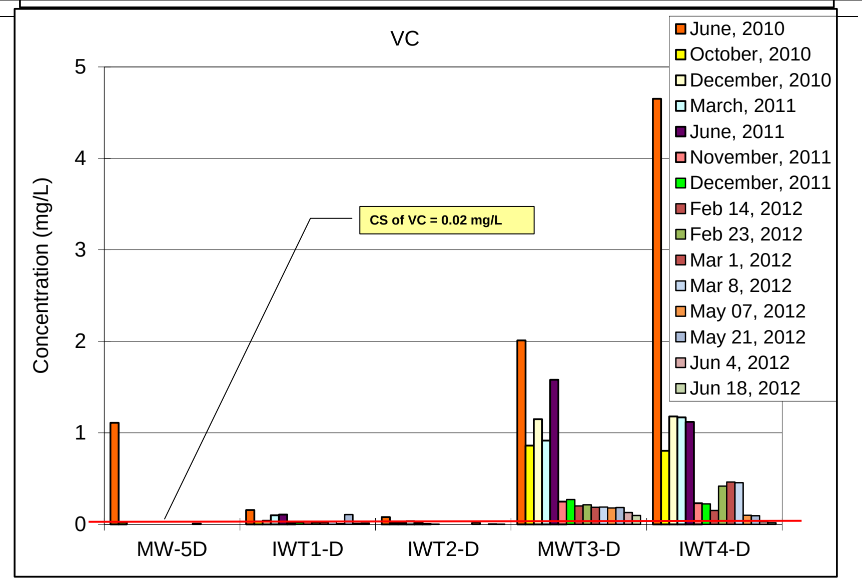
Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: EIB pilot study (cont.)



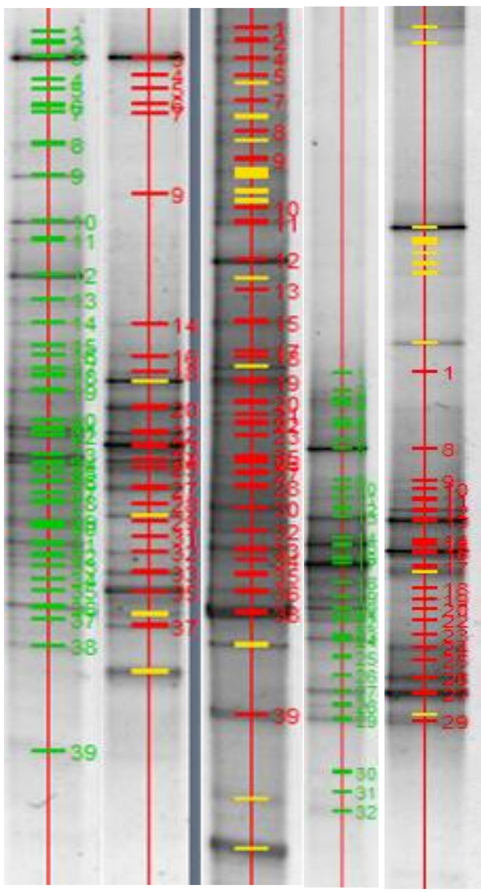






Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: EIB pilot study (cont.)

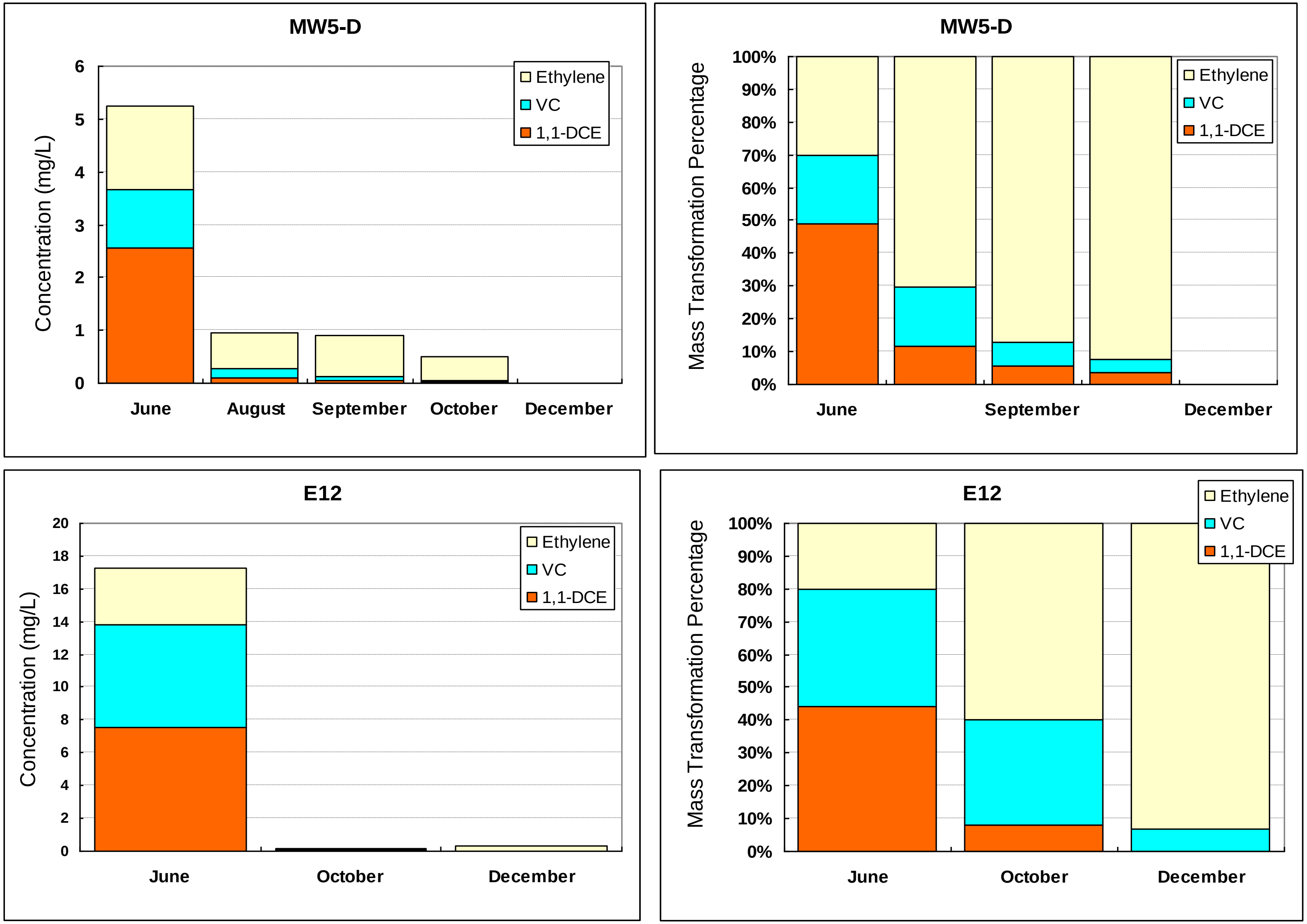


E12 MW5-D E13 T1-D T3-D

- Bacteria DNA analysis confirms that the injected substrate has developed an anaerobic condition supporting a microflora containing dechlorinating bacteria.
- Nine bacteria species (*Dehalococcoides ,Dhc.*) with dechlorinating capability were found naturally in groundwater -confirmed that the existing microflora were able to biodegrade chlorinated VOCs via reductive dechlorination processes.

Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: EIB pilot study (cont.)



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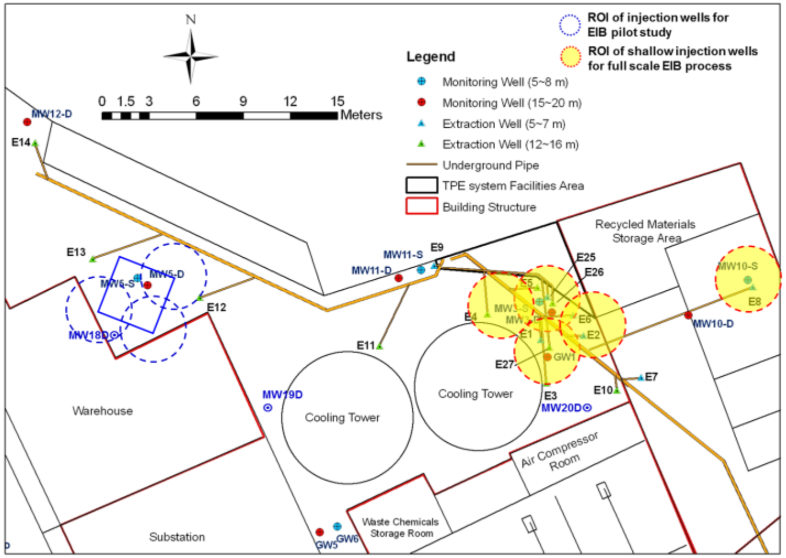
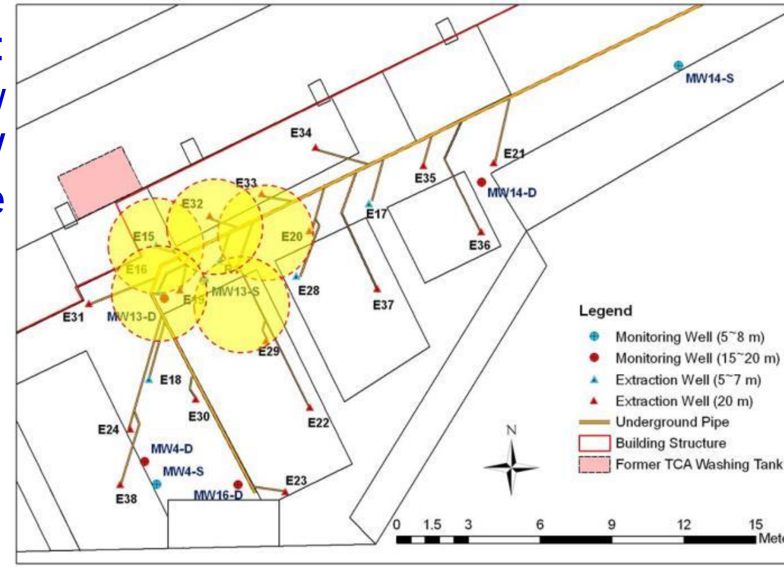
Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: Full Scale EIB implemented

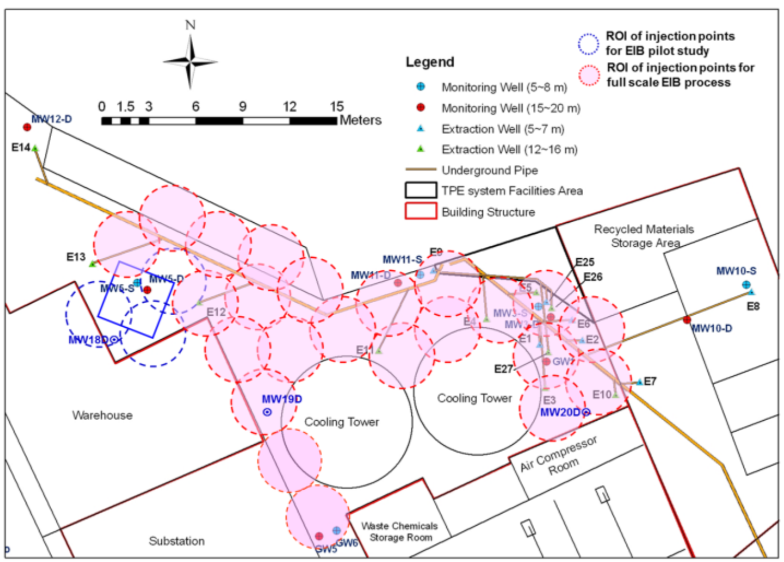
North: shallow GW zone



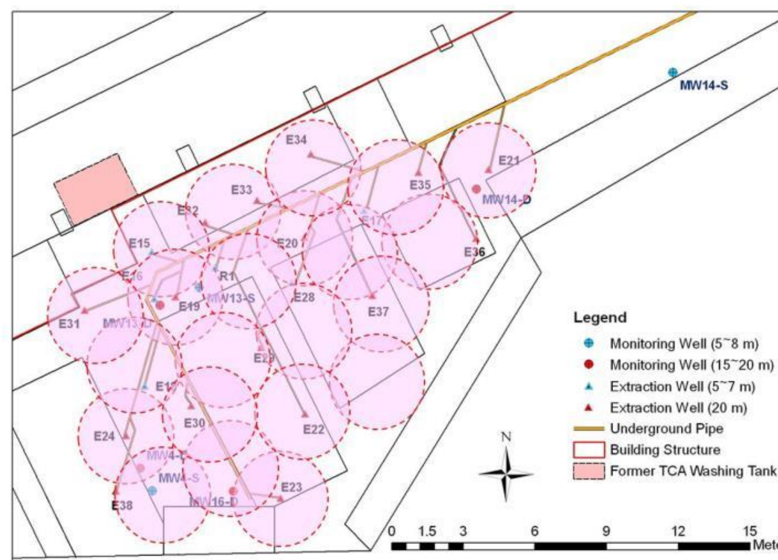
South: shallow GW zone



North: deep GW zone



South: deep GW zone



Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: Full Scale EIB implemented

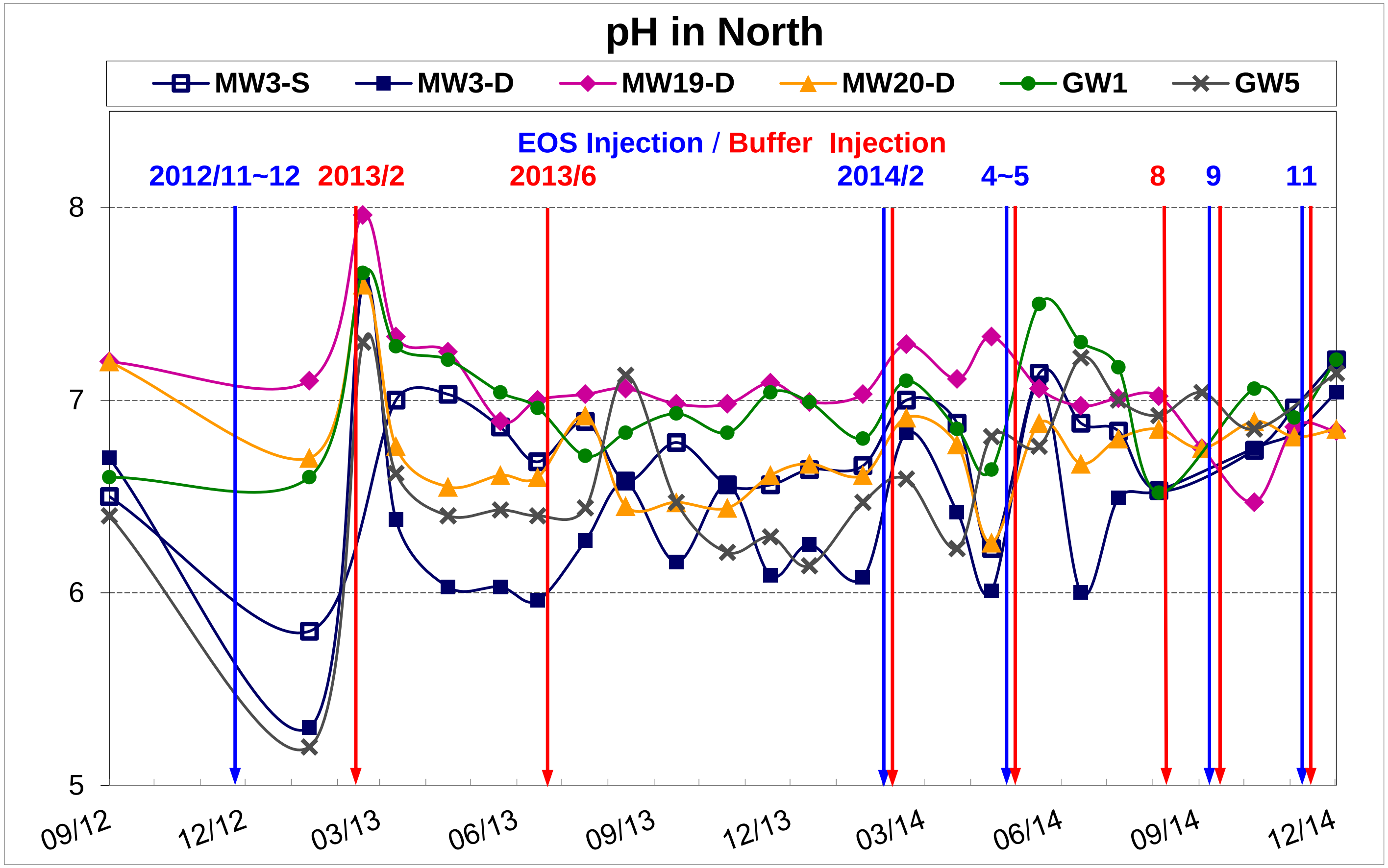
Installation of EIB injection wells

Preparation and injection of EOS solution

Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: Full Scale EIB implemented

- Optimizing EIB treatment via maintaining pH in the desired neutral range by buffer solution injection, as needed.
- Monthly monitoring to monitor substrate/buffer solutions needs.



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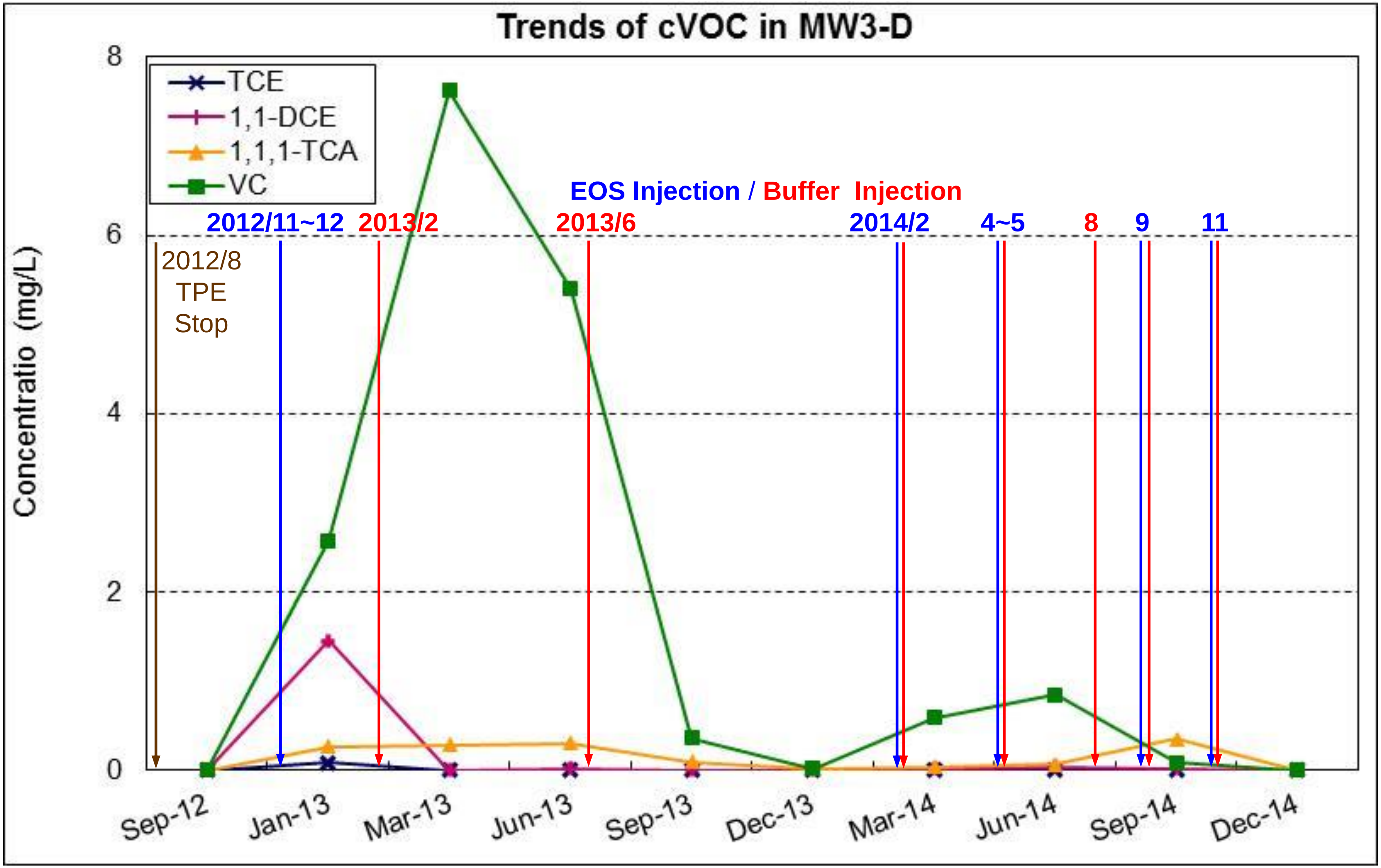
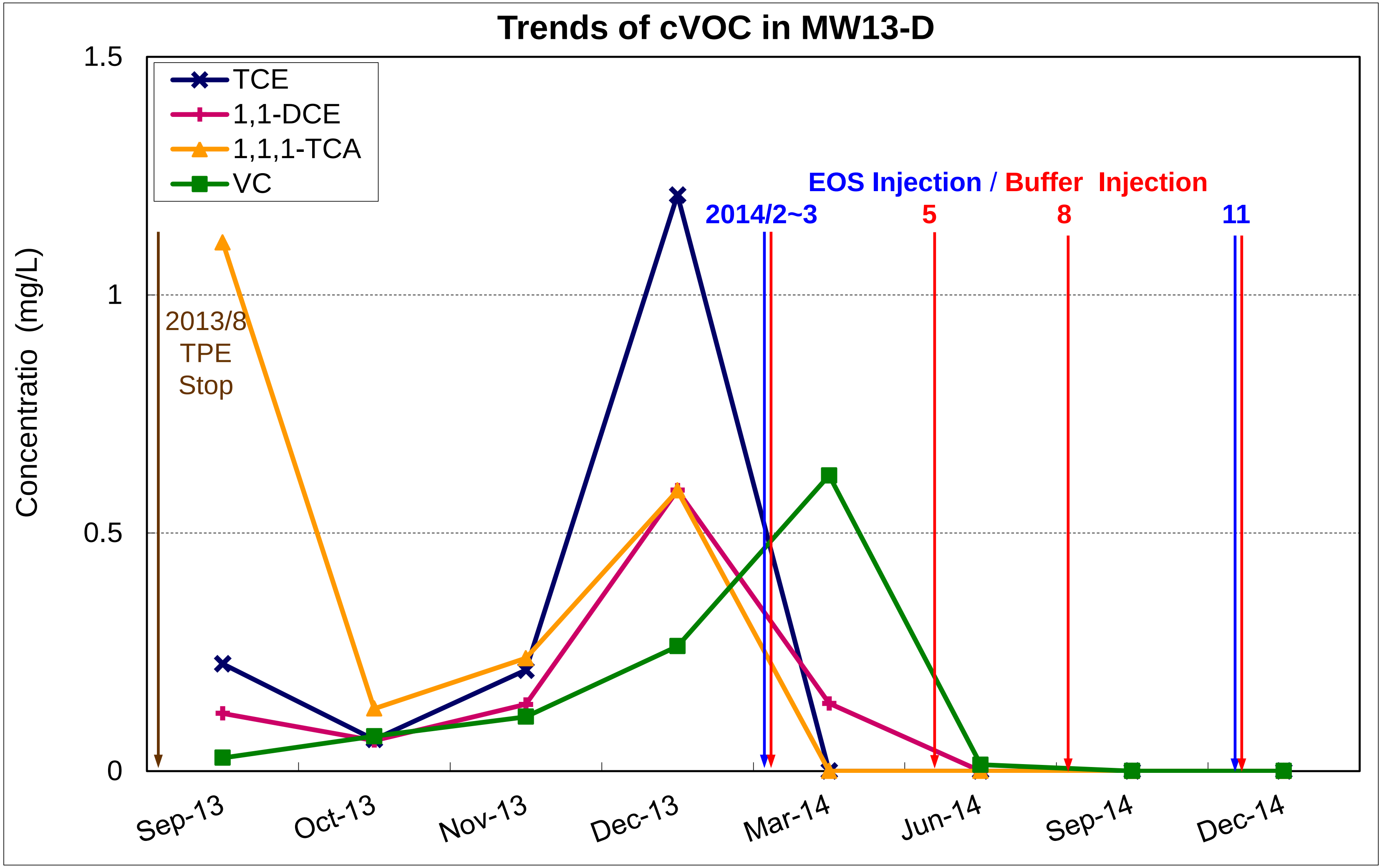
Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: typical cVOC reduction in North via EIB treatment



Remediation of a cVOC contaminated Site (cont.)

Remediation Progress: typical cVOC reduction in South via EIB treatment



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Remediation of a cVOC contaminated Site (cont.)

Final Performance via Verification Samplings

- VOCs in shallow and deep MWs all below *Control Standards (CS) for the first time at the end of 2014*.
- VOCs degradation process (dechlorination) is working as expected.
- The harmless end product “ethene” has been constantly detected in MW19-D, MW20-D, and GW1 installed within the hot zones.
- Post-remediation monitoring has been conducted on a quarterly basis since 2015.

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Built to Deliver a Better World

A Architecture

E Engineering

C Construction

O Operations

M Maintenance

Today, AECOM provides professional technical and management support services to a broad range of markets, including transportation, water and urban development, geotechnical, energy, environment, master planning, architecture, building engineering, landscape architecture, economic planning, cost consulting, project management and construction management.

提供全方位的專業工程諮詢與管理服務，包括交通、給水與廢水工程、市政開發、大地工程、能源、環境、規劃設計、建築、景觀、經濟分析、項目管理與施工管理等。

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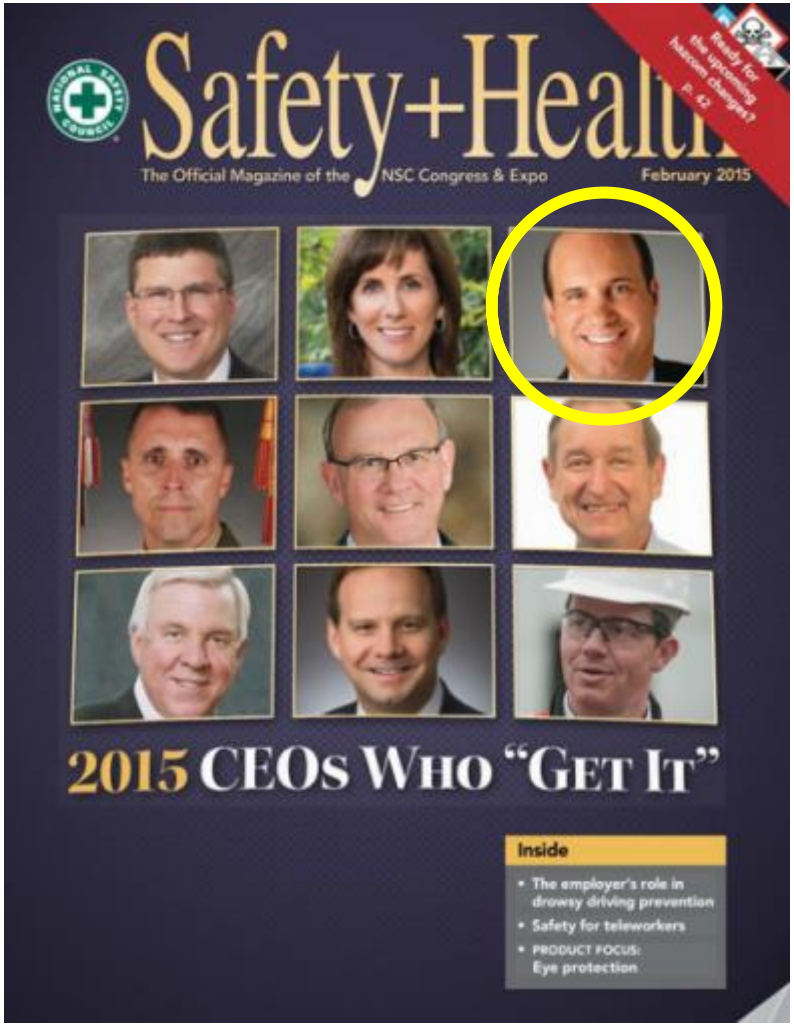
Safety is a Key Core Value



- AECOM is committed to safety excellence
  - Best in Class Performance
  - Safety for Life Process / Culture of Caring
  - Life-Preserving Principles / Safety Management Standards
  - Shared Learnings / Observation Database
  - Michael S. Burke, CEO of AECOM has been named by the National Safety Council as one of the 2015 CEOs Who "Get It"
- We achieve sustainable safety excellence by commitment through the entire organization, reaching every team member on every project

Safety Starts With Me

AECOM Overview

AECOM is built to deliver a better world. We design, build, finance and operate infrastructure assets for governments, businesses and organizations in more than 150 countries. As a fully integrated firm, we connect knowledge and experience across our global network of experts to help clients solve their most complex challenges. From high-performance buildings and infrastructure, to resilient communities and environments, to stable and secure nations, our work is transformative, differentiated and vital.

No.1

#1 Top 150 Design Firms
#1 Pure Design
#1 Transportation
#1 General Building
(2015 ENR Ranking)

343

Ranked No. 343 in *Fortune 500* *(2015)*

150+

Serving clients in more than 150 countries

85K+

More than 85,0000 dedicated professionals working globally

$19bn

$19 billion in revenue as of December 2014

Fortune "A World's Most Admired Company" 2015

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The New AECOM: effective October 20, 2014

1

OCT 20, 2014

AECOM acquisition of URS

2

JAN 5, 2015

Began operating as one company (AECOM)

3

A global, fully integrated infrastructure firm

4

Project life-cycle offering that spans design (including planning, architecture, and engineering), construction, finance, operations, and maintenance

5

Leading design firm in the U.S., UK, and globally: infrastructure, facilities, environmental

6

2015

#343 on *Fortune 500* ranking

AECOM in Asia Pacific

50+
Offices

11+
Countries

13k+
Employees

AECOM in Greater China

15 cities

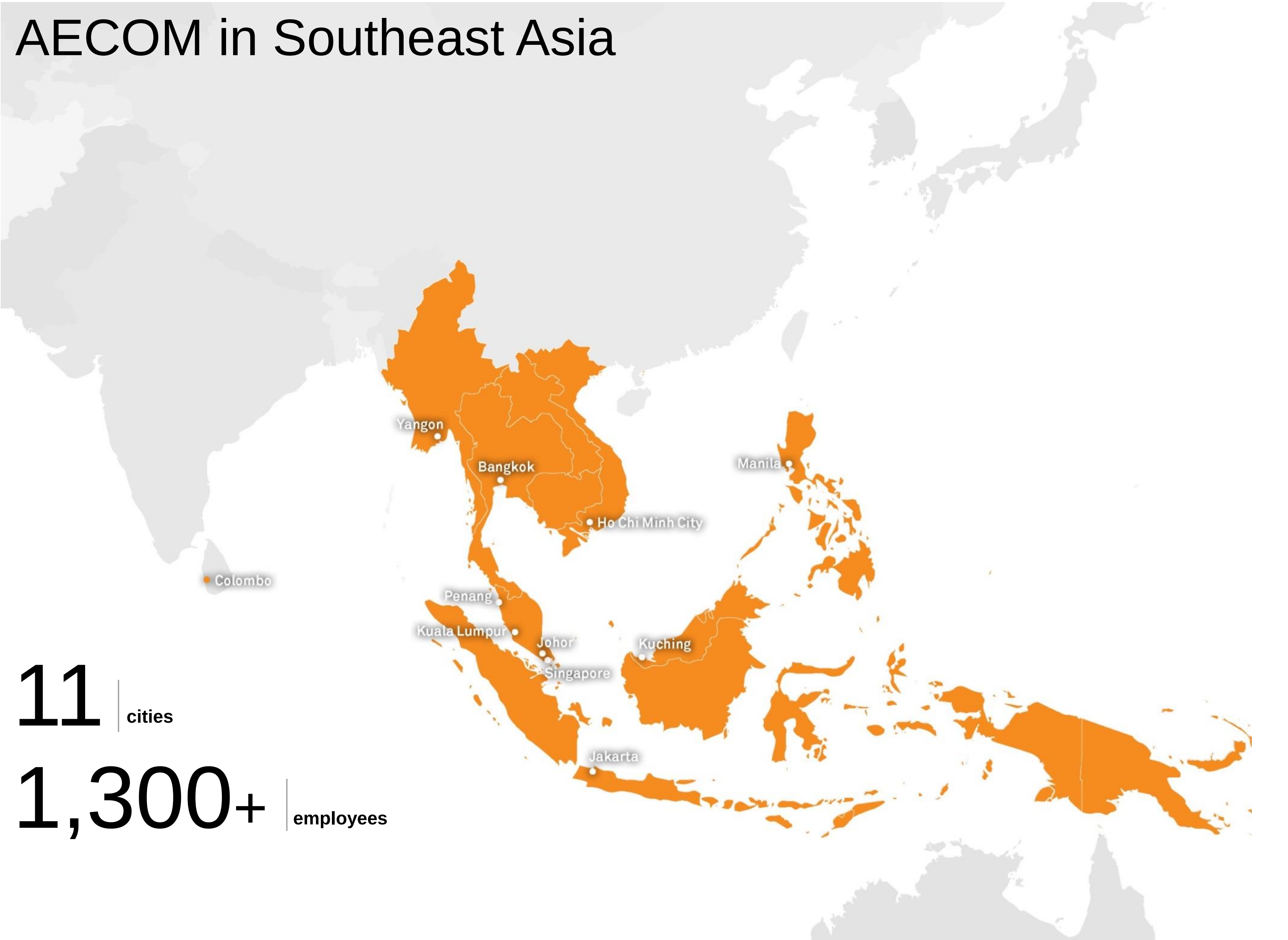
6,300+ employees

4 joint venture companies

1 design center

AECOM

AECOM in Southeast Asia



11 | cities

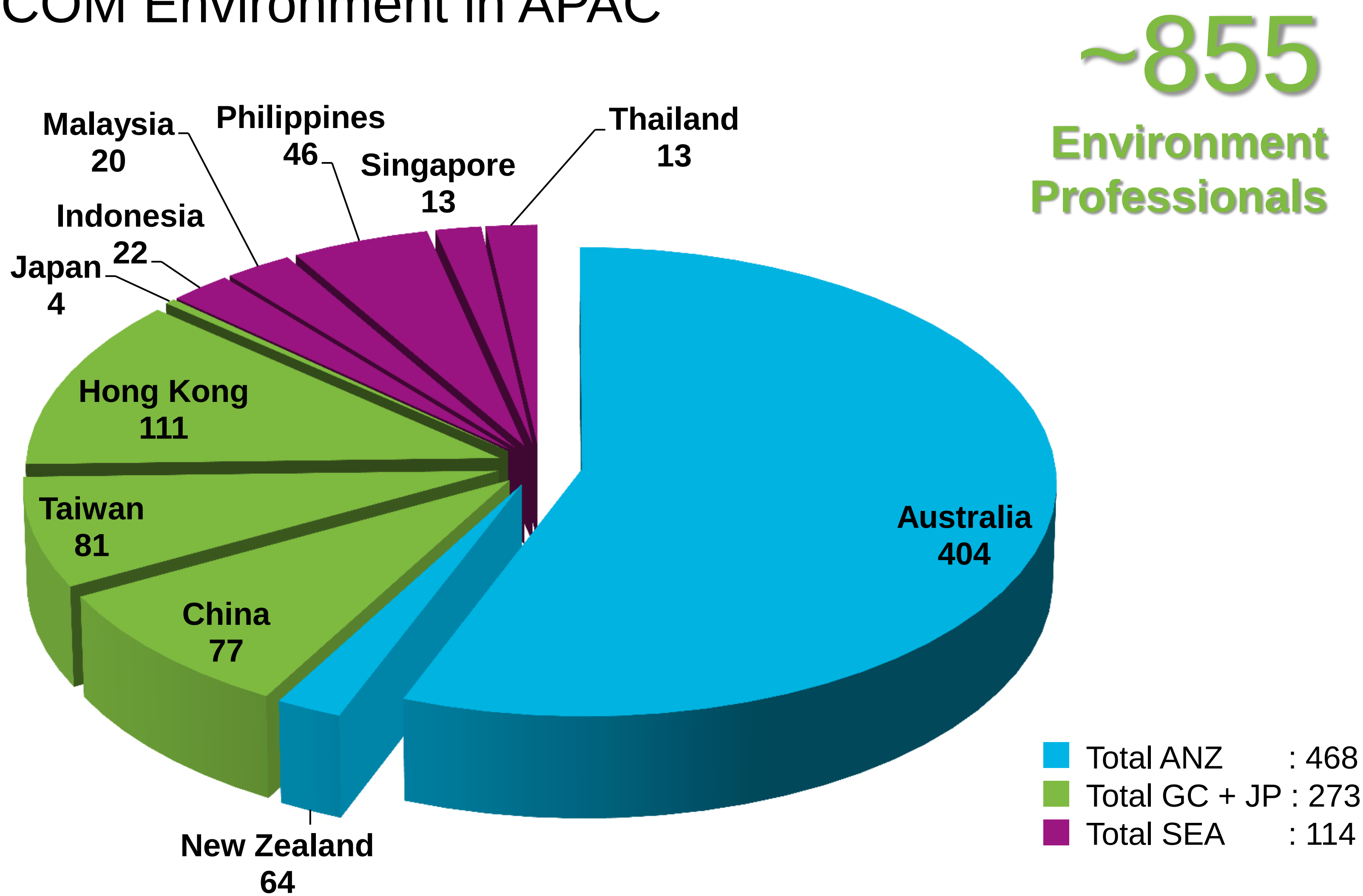
1,300+ | employees

AECOM in Australia and New Zealand

19 | cities

4,000+ | employees

AECOM Environment in APAC



Please note: India is part of the Europe, Middle East, Africa + India business in the AECOM structure. The AECOM team is approximately 2200, with 44 Environment team members and 15 Remediation/due diligence specialists. India experience is included within this presentation.

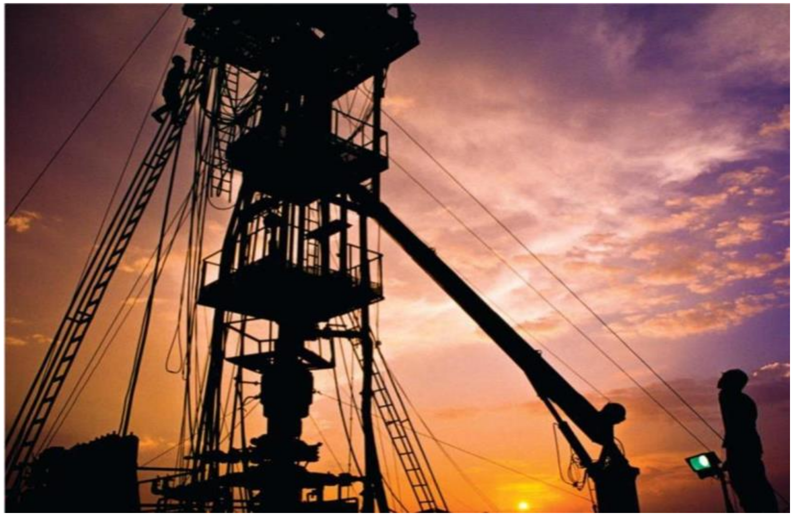
AECOM APAC Leadership of Environment

- Bengt von Schwerin – APAC Lead (Singapore, Bengt.vonSchwerin@aecom.com)
- Freeman Cheung – Greater China Lead (Hong Kong, Freeman.Cheung@aecom.com)
- Account Leaders in Region/Country:
  - China: Dennis Tu (Shanghai, dennis.tu@aecom.com);
  - Hong Kong: Josh Lam (Hong Kong, Josh.Lam@aecom.com);
  - Taiwan: Peter Yung (Taipei, peter.st.yung@aecom.com);
  - Japan: Risa Onishi (Tokyo, Risa.Onishi@aecom.com);
  - Australia/NZ: Brad Eismen (Sydney, Brad.Eismen@aecom.com);
  - South East Asia: Rajesh Jackson (Rajesh.Jackson@aecom.com);
    - Indonesia: Adrian Widjaya (Jakarta, Adrian.Widjaya@aecom.com);
    - Malaysia: Rajesh Jackson (Kuala Lumpur, Rajesh.Jackson@aecom.com);
    - Thailand : Ken Gilbert (Bangkok, ken.gilbert@aecom.com);
- The account team is supported by international remediation, EHS and impact assessment practice specialists who routinely work across APAC.

AECOM Greater China Environment

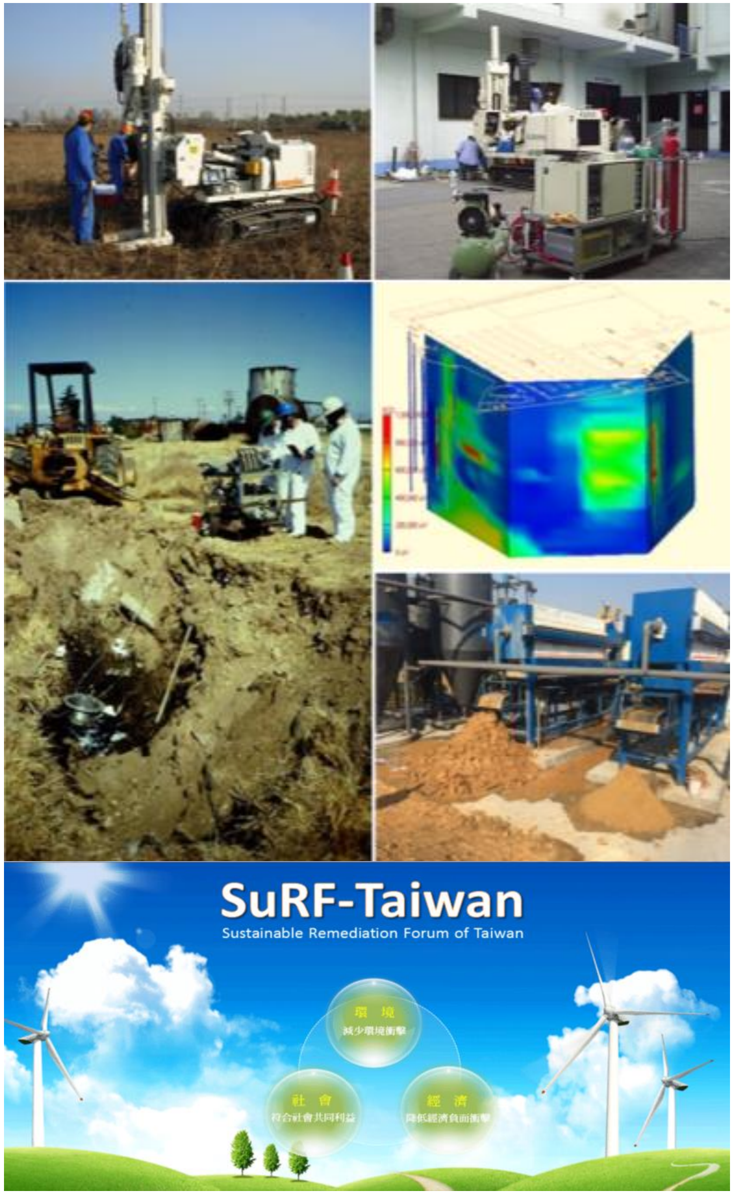
- Environmental, Health & Safety Assessment
- Site Investigation & Remediation
- Water, Industrial Wastewater & Engineering
- Regulation, Energy and Social Management

Environmental, Health & Safety (EHS) Assessment



- EHS Due Diligence
- EHS Regulatory Compliance Service
- Environmental Site Assessment
- Environmental Impact Assessment
- Industrial Hygiene Assessment
- Process Safety Study
- Waste Management and Hazard Operation Management
- Air Quality Sampling, Modeling and Assessment
- Air Emission Control Study
- EHS Management System & Training

Site Investigation & Remediation (SIR)



- Soil and groundwater investigations
- Sediment investigation & study
- Hydrogeological studies
- In-situ direct sensing involving soil gas survey and membrane interface probing (MIP) investigations
- Groundwater modeling and 3-D conceptual site model development.
- Remedial Investigation & Feasibility studies.
- Development of remediation programs.
- Design, implementation and monitoring.
- *Conducted investigation and remediation at 200+ gas stations in China.*
- *Assisted establishing SuRF-Taiwan as board member since 2013.*

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Water, Wastewater & Engineering (WWE)

- Conceptual, Preliminary, and Detailed Design of Water & Wastewater Treatment Facility (WWTF)
- Technical Evaluation of existing WWTFs, and Water & Wastewater Management
- Design Review and Support for Design Improvement
- Technical Support on WWTF Installation, Commissioning, Acceptance and Operations
- Water reuse and scarcity assessment
- Selected clients: McCormick, Carlsberg, SPX, Wrigley, Johnson Diversey, Eaton, Ashland, Goodyear, Lubrizol, John Deere, etc.

Regulation, Energy & Social (RES) Management

- EHS and CSR Regulatory News Letter
- Regulations Review and Consultancy and Regulatory Compliance Check List
- Energy-saving Performance Review and Audit
- ISO-50001 Audit
- LEED Consultation and Certification
- Social Baseline and Impact Assessment
- Social and Governance Compliance Audit
- Community Consultation and Engagement
- Social Due Diligence


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Bioremediation of Chlorinated Solvent Contaminated Groundwater

Shawntine Lai, Ph.D., P.E.

March 25, 2016

MWH

BUILDING A BETTER WORLD

Outline

- Groundwater Bioremediation Technologies
- Case Study I
- Case Study II

GROUNDWATER BIOREMEDIATION TECHNOLOGIES

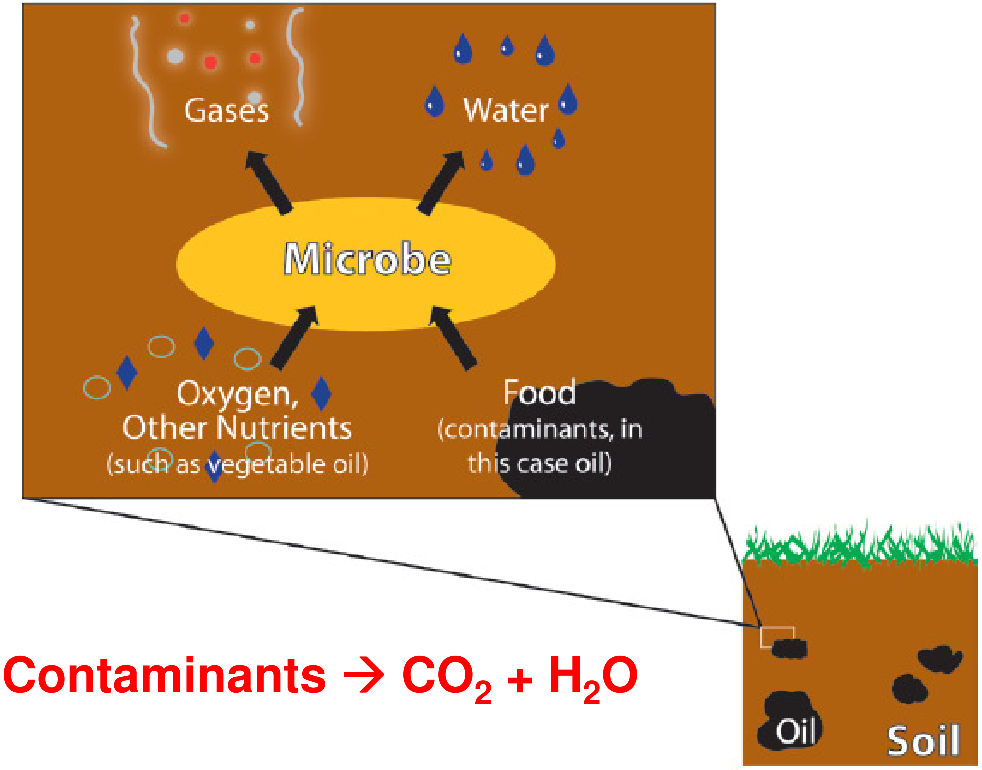
Bioremediation

- **What Is Bioremediation?**
- Bioremediation is the use of **microbes** to clean up contaminated soil and groundwater. Microbes are very small organisms, such as **bacteria**, that live naturally in the environment. Bioremediation stimulates the growth of certain microbes that **use contaminants as a source of food and energy**. Contaminants treated using bioremediation include **oil and other petroleum products, solvents, and pesticides**.

Source: USEPA a_citizens_guide_to_bioremediation

Bioremediation

- **How Does It Work?**
- Some types of microbes eat and digest contaminants, usually changing them into small amounts of **water** and harmless gases like **carbon dioxide** and ethene. If soil and groundwater do not have enough of the right microbes, they can be added in a process called "**bioaugmentation**".



Contaminants → CO_2 + H_2O

Microbe takes in oil, oxygen, and nutrients and releases gases and water.

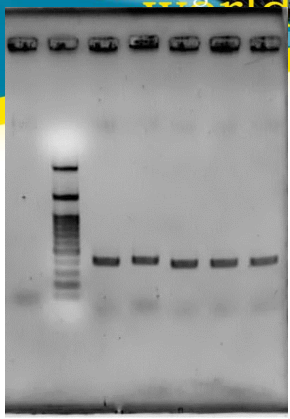
Source: USEPA a_citizens_guide_to_bioremediation

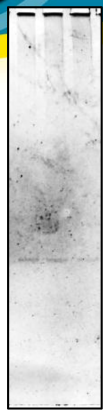
Bioremediation

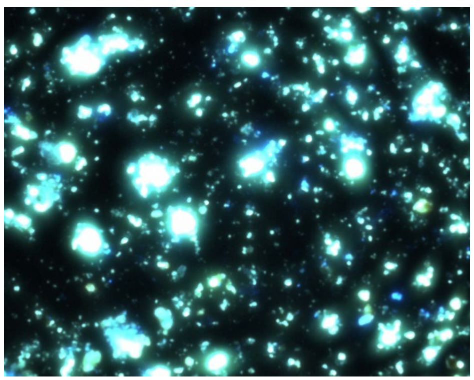
- For bioremediation to be effective, the right temperature, nutrients, and food also must be present. Proper conditions allow the right microbes to grow and multiply—and eat more contaminants. If conditions are not right, microbes grow too slowly or die, and contaminants are not cleaned up. Conditions may be improved by adding "amendments." Amendments range from household items like molasses and vegetable oil, to air and chemicals that produce oxygen. Amendments are often pumped underground through wells to treat soil and groundwater in situ (in place).
- It may take a few months or even several years for microbes to clean up a site, depending on several factors.

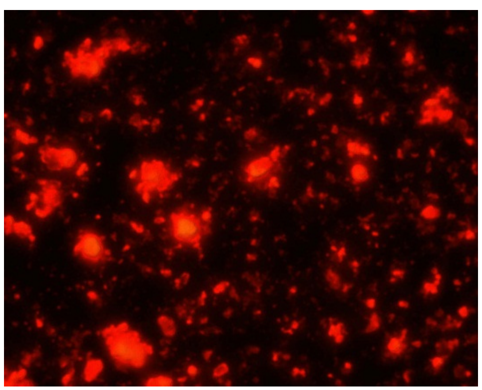
Source: USEPA a_citizens_guide_to_bioremediation

Bioremediation



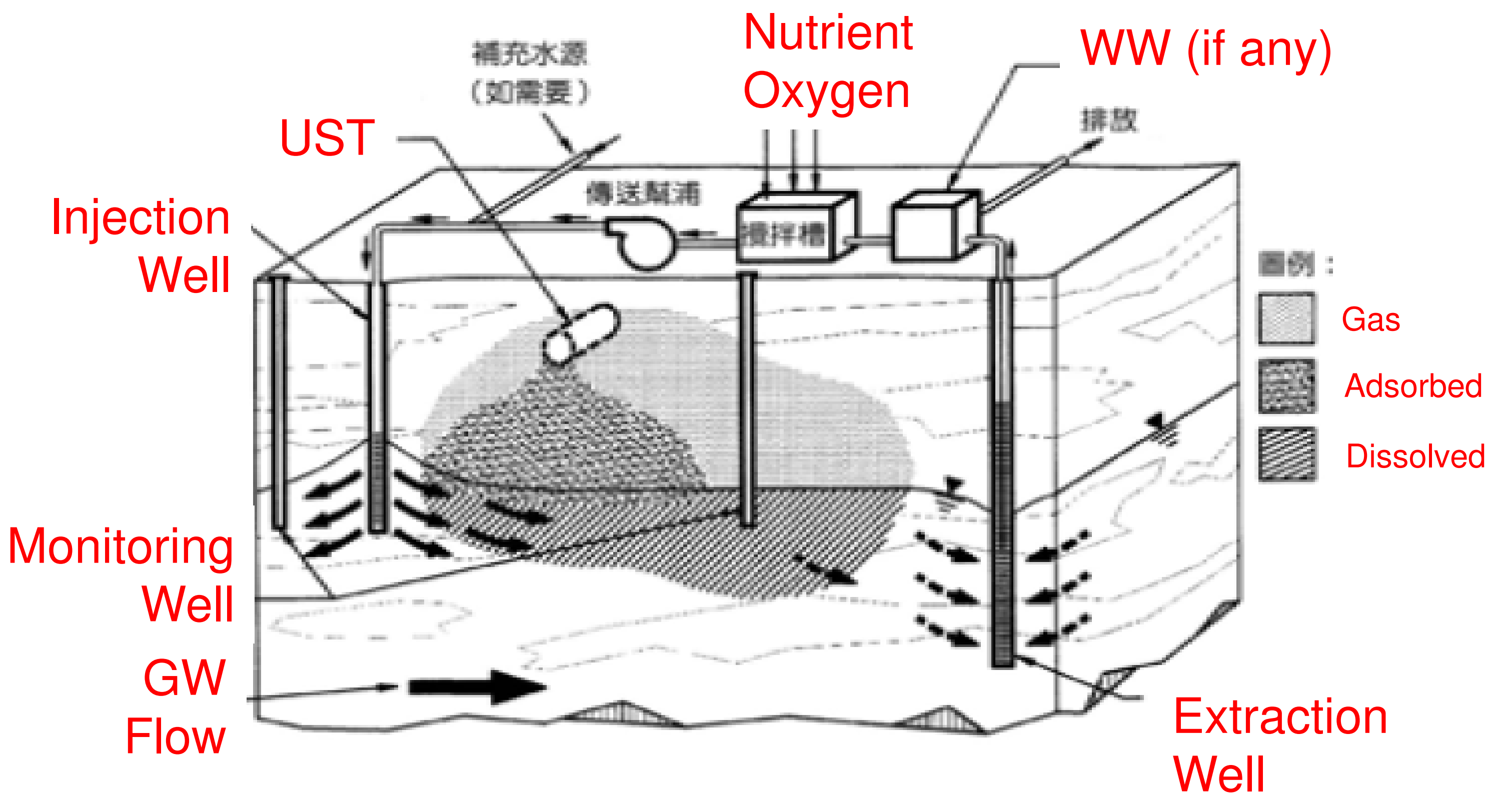






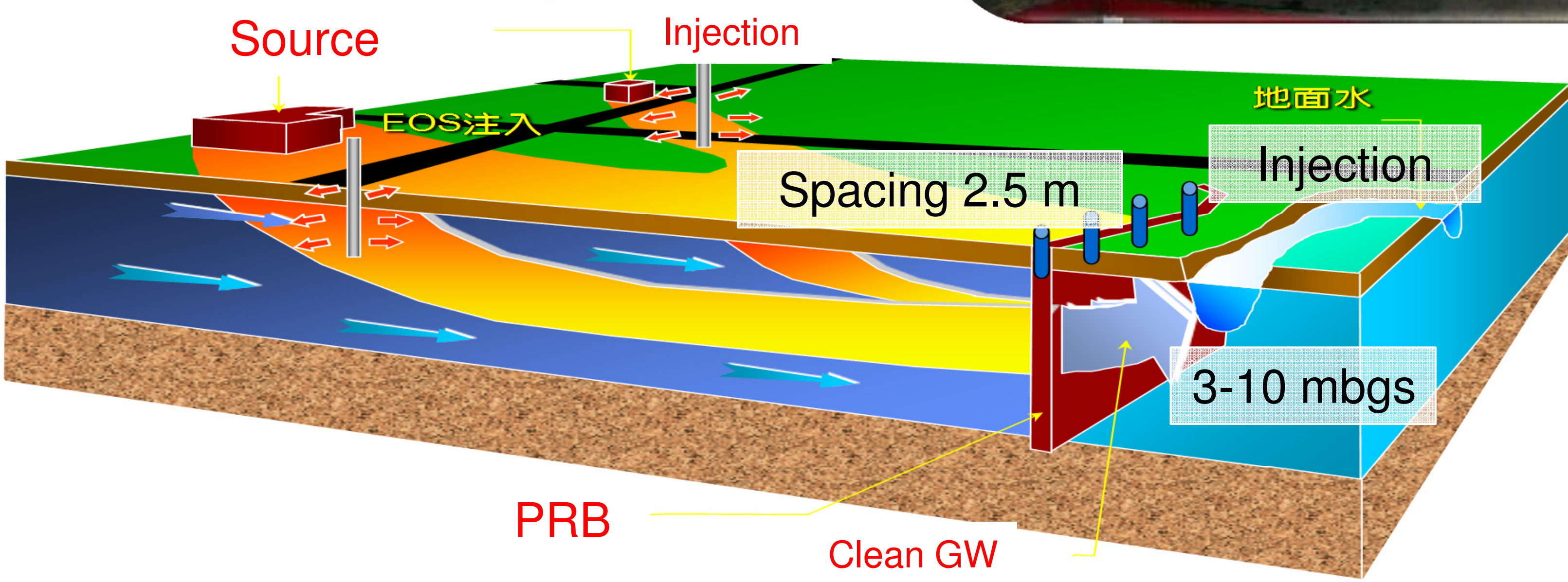
Cost

- Aerobic Bioremediation: $40-$80 per 1000-gallon of contaminated groundwater (USA FRTR)
- Nitrate (nutrient): $160-$230 per 1000-gallon of contaminated groundwater.



Bioremediation

- US Air Force, DE
  - EOS injection (PRB), PCE and TCE
  - Injection space 2.5 m, injection depths 3-10 m
  - Monitoring wells located at 5 m downgradient
  - 26% reduction after 181 days
  - 49% reduction after 345 days
  - Cost of EOS $3/kg
- Cost: $600-$1,200 per injection point



Bioremediation

EOS Dilution - Batch

EOS Dilution - Continuous

EOS Injection

Pressure Injection

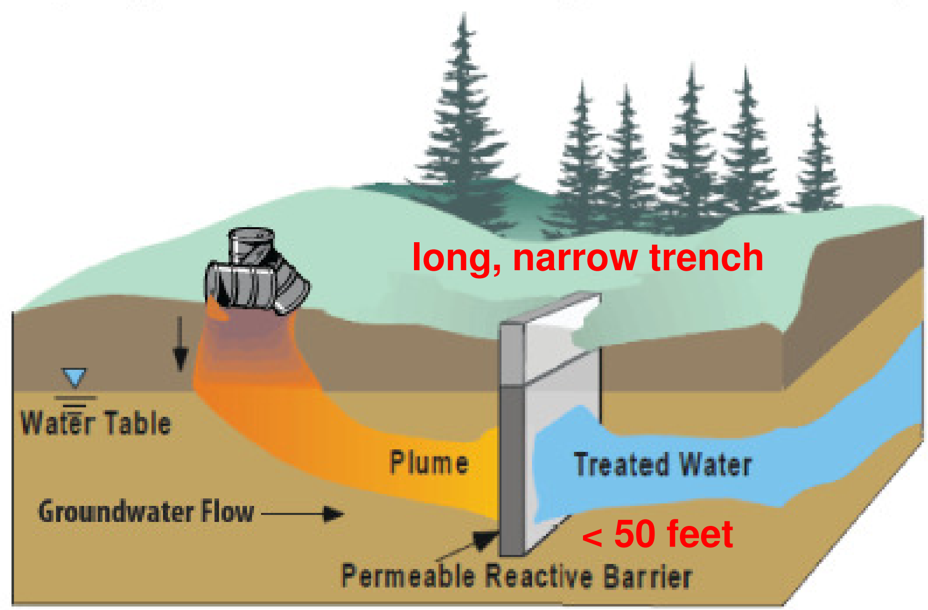
Permeable Reactive Barriers

- **What Are Permeable Reactive Barriers?**
- A permeable reactive barrier, or "PRB," is a **wall** created below ground to clean up contaminated groundwater. The wall is "**permeable**", which means that groundwater can flow through it. Water must flow through the PRB to be treated. The "reactive" materials that make up the wall either trap harmful contaminants or make them less harmful. **The treated groundwater flows out the other side of the wall**.

Source: USEPA a_citizens_guide_to_permeable_reactive_barriers

Permeable Reactive Barriers

- **How Do They Work?**
- A PRB is usually built by digging a **long, narrow trench** in the path of contaminated groundwater flow. The trench is filled with a **reactive material**, such as **iron**, **limestone**, **carbon**, or **mulch**, to clean up contamination. Due to limitations of excavation equipment, walls typically can be **no deeper than 50 feet**.



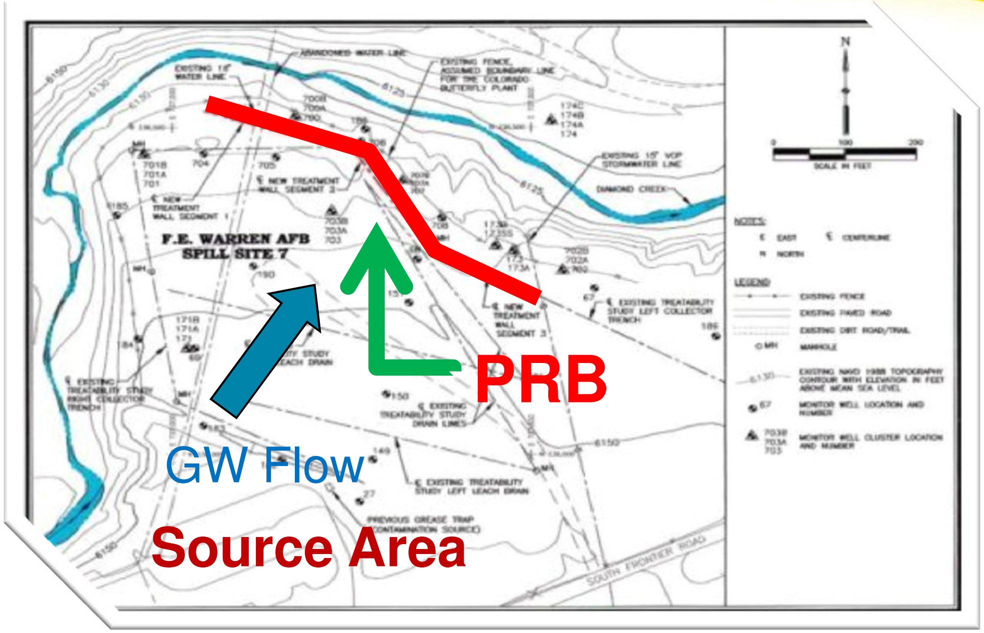
PRB treats a plume of groundwater contaminants.

Source: USEPA a_citizens_guide_to_permeable_reactive_barriers

Permeable Reactive Barriers

<u>Military Site</u>

- ◆Site: Spill Site 7 (SS7)
- ◆Remedial Technologies : PRB system to treat TCE, cDCE, VC
- ◆Completion: October, 1999



Reductive Dechlorination

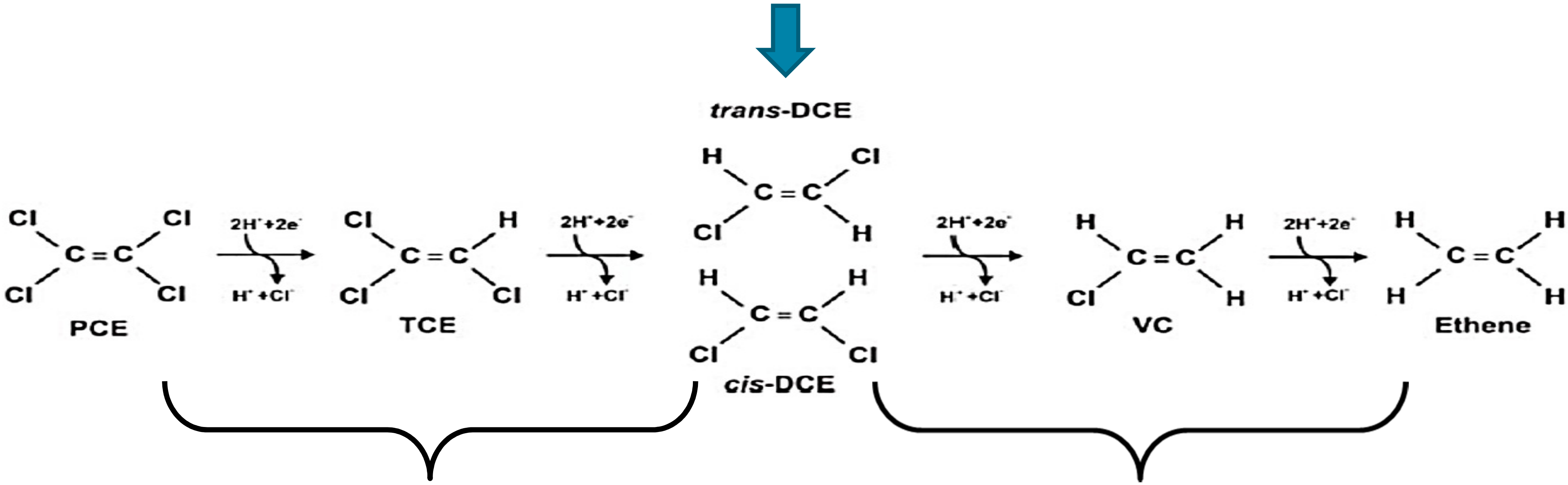
- Chloroethenes (example: TCE) can be remediated when microorganisms provide hydrogen as a byproduct of fermentation.
- Dechlorinating bacteria use hydrogen as their electron donor, replacing chlorine atoms in the chloroethenes with hydrogen atoms.
- Complete dechlorination to ethene can occur given enough organic electron donor and the appropriate strains of bacteria.

Conditions Conducive to Dechlorination

- Can occur naturally, but often is slow without enhancement.
- It can also be induced by creating anaerobic conditions and adding appropriate bacteria.
- Anaerobic – oxidation/reduction potential (ORP) < -100 mV.
- pH >6 or 6.5.
- Presence of halorespiring bacteria.
- Presence of a carbon food source for the halorespiring bacteria.

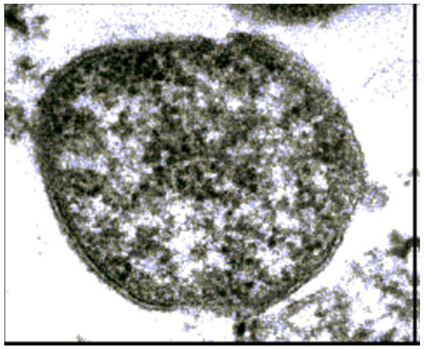
Biological Dechlorination

Can accumulate if DHC is absent



Dehalobacter
Dehalospirillum
Desulfitobacterium
Desulfuromonas
Dehalococcoides

Primarily Dehalococcoides (DHC)

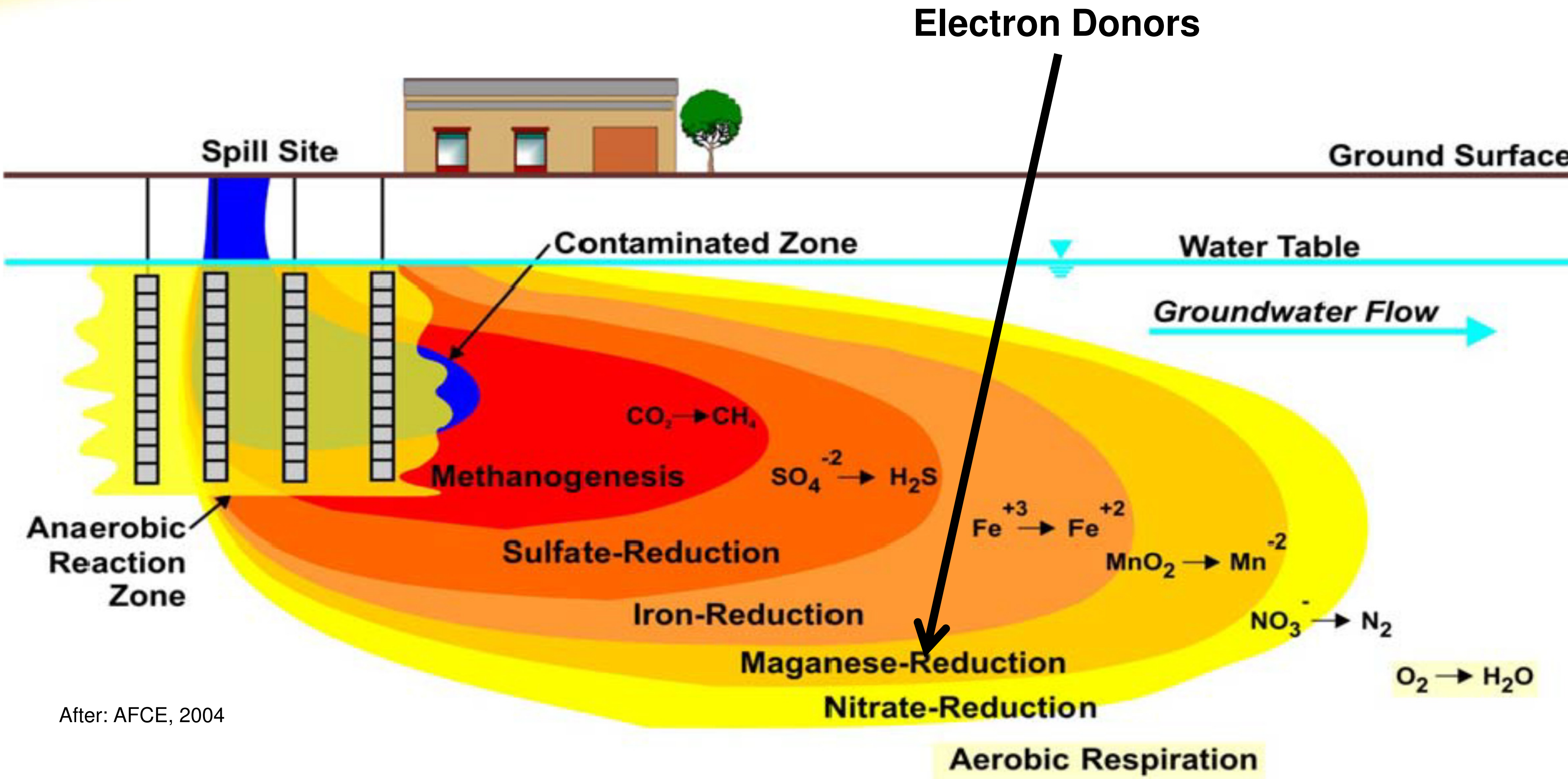


References: AFCEE, 2004,
http://www.genomenewsnetwork.org/articles/2004/04/02/toxic_microbe.php

Enhancing Reductive Dechlorination

- Can enhance natural biodegradation processes by adding carbon substrate (food), nutrients, and Dehalococcoide organisms.
- Many types of carbon substrates have been used:
  - Methanol and ethanol
  - Molasses, corn syrup, and lactate
  - Cheese whey
  - Emulsified soybean oil
- Dehalococcoides bacterial cultures can be purchased commercially.

Reducing Zones Downgradient of Substrate Injection

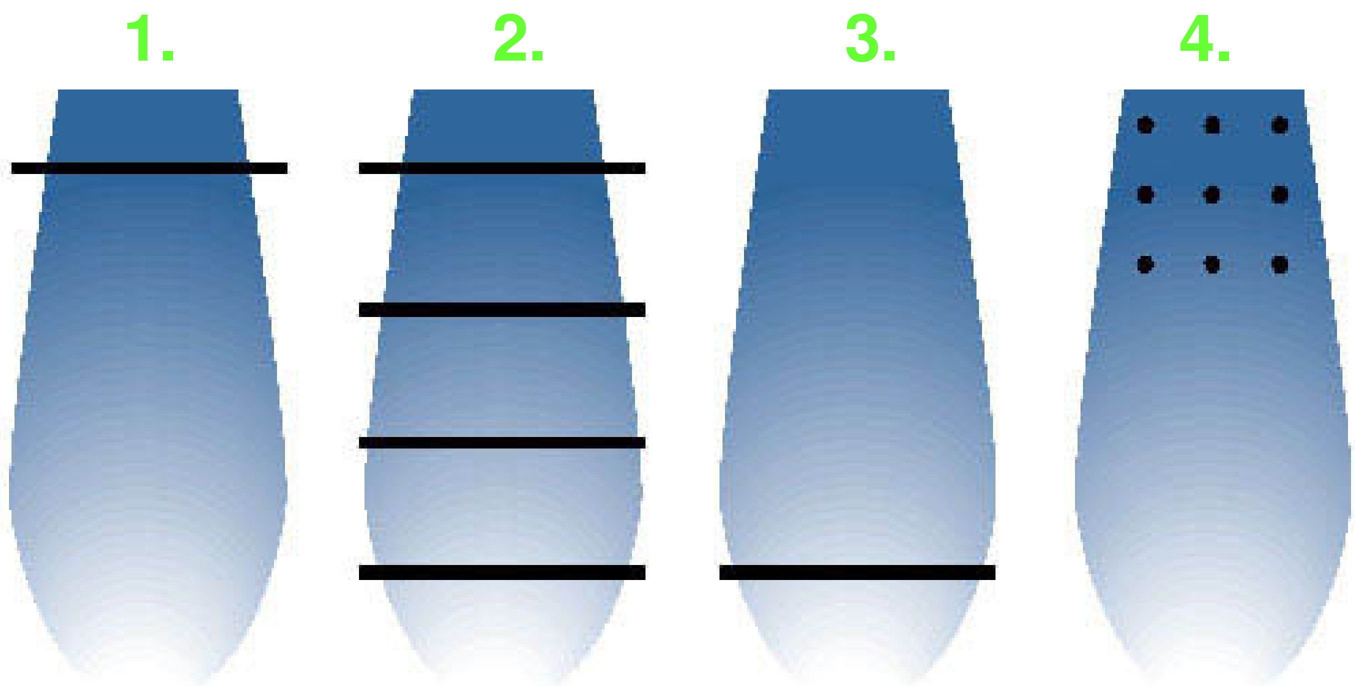


After: AFCE, 2004

TYPES OF IN-SITU TREATMENT

DESIGNS FOR BARRIERS

1. UPGRADIENT BARRIER
2. SERIES OF BARRIERS
3. DOWNGRADIENT BARRIER
4. “GRID” OF INJECTION POINTS (AQUIFER-WIDE)

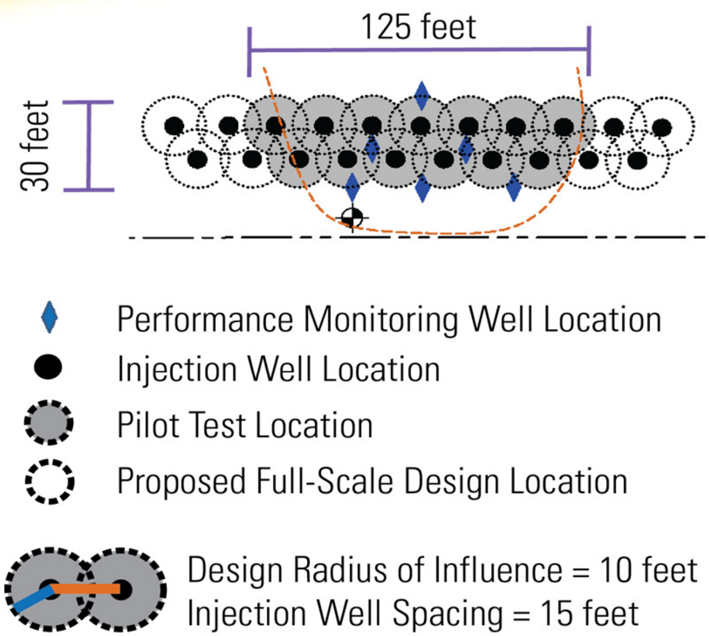


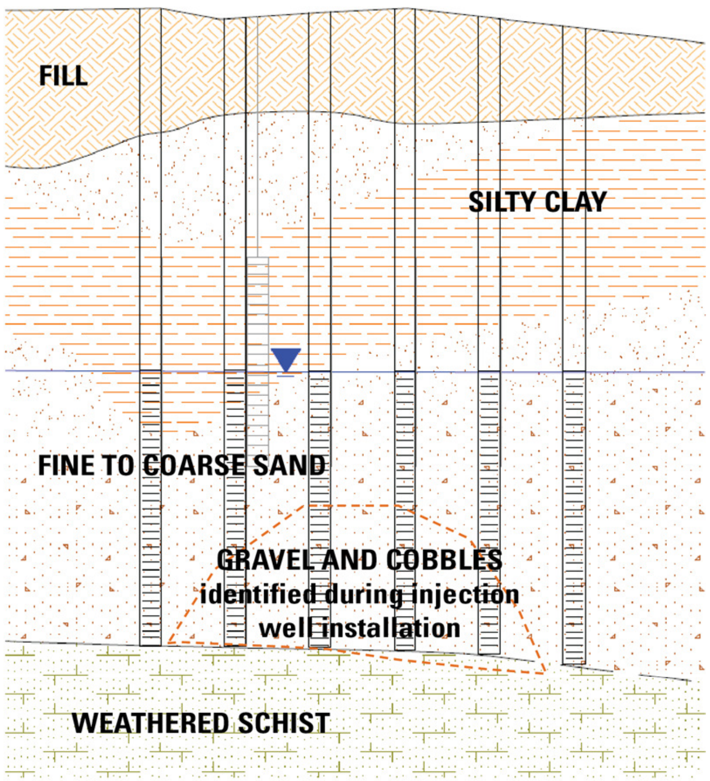
CONSIDERATIONS

- TIME
- COST
- REGULATORY

  ACCEPTANCE

Pilot Test Design





Injection Well Depth = 30-33 feet
Screened Interval = 15 feet

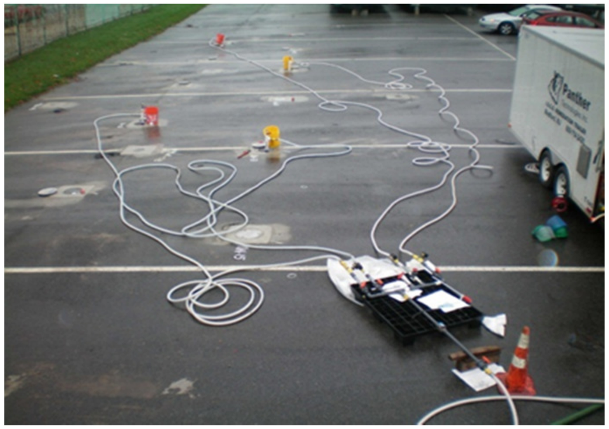
Products Chosen for Implementation

- **EOS® 598B42 –** Includes nutrients and lactate, provides longevity of carbon source in subsurface
- **Sodium Lactate –** Provides initial boost to degradation activity
- **EOS® Activator –** Added to raise pH in treatment area
- **SiREM KB-1® Plus –** Ability to degrade mix of VOCs

Target Donor Concentration
0.002 kg EVO / kg saturated soil

75% of Pore Volume Replaced with Donor Solution and Chase Water

Pilot Study Implementation

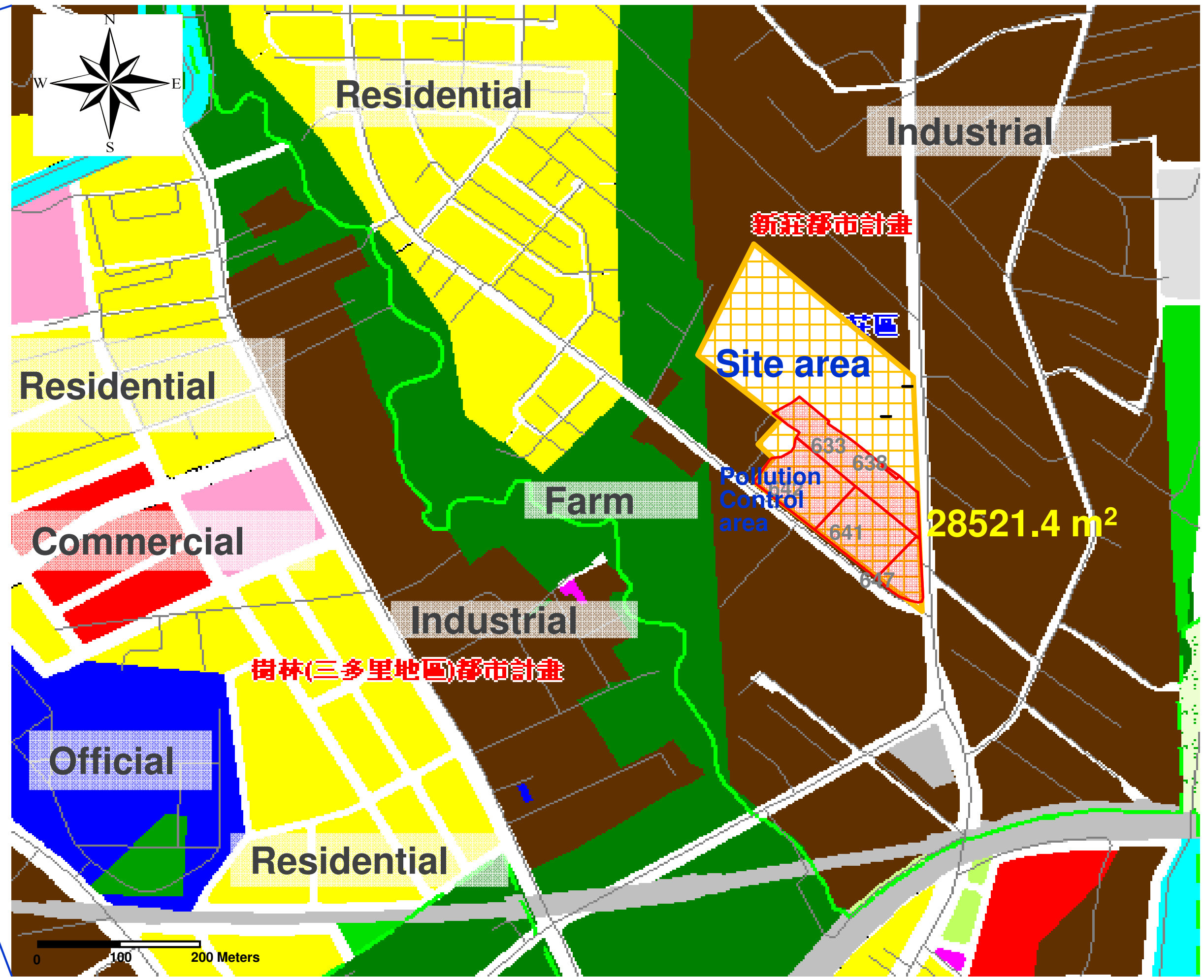


CASE STUDY I

Background Information

Location


No. 292
Hsin-Shu Rd.,
Hsin-Chuang,
New Taipei City


Residential
Industrial
新莊都市計畫
Site area
Residential
Pollution Control area
633
638
641
647
28521.4 m²
Farm
Commercial
Industrial
樹林(三多里地區)都市計畫
Official
Residential
0
100
200 Meters

Background Information

- Chemical Manufacturer
- Capital：270 million NTD (9 million USD)
- NO. of employees：300
- History：since 1952
- Business Category ：

  Plastic and Medical manufacturing

Site History

1962 Construction

1963 Started operation

- Plastic products：
  - Melamine Plywood、Plastic tubes

- Medical products

1992 Ceased production of plastic products

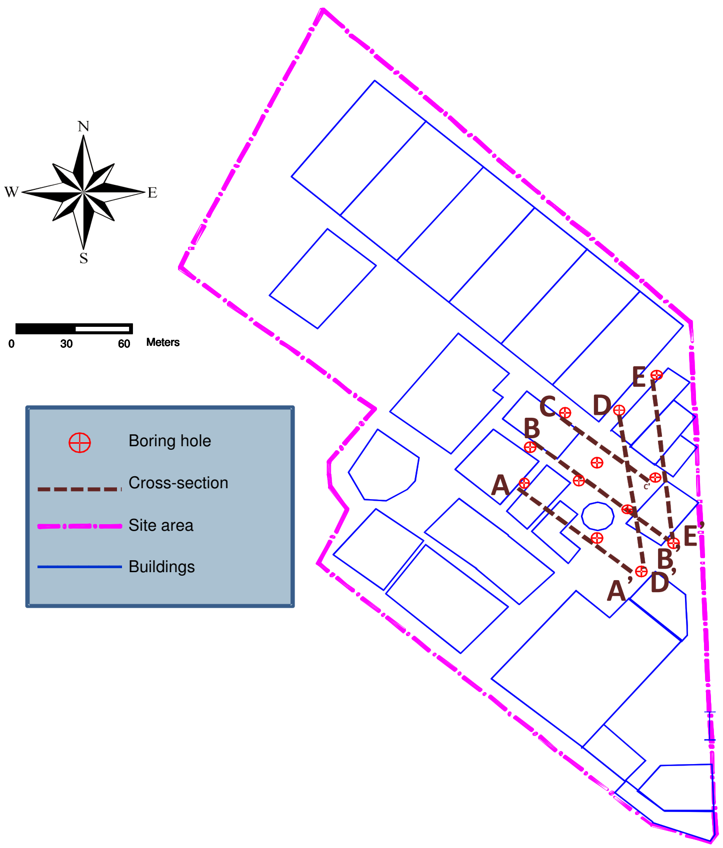
2008 VOC exceedances in Groundwater were identified by TW EPA project

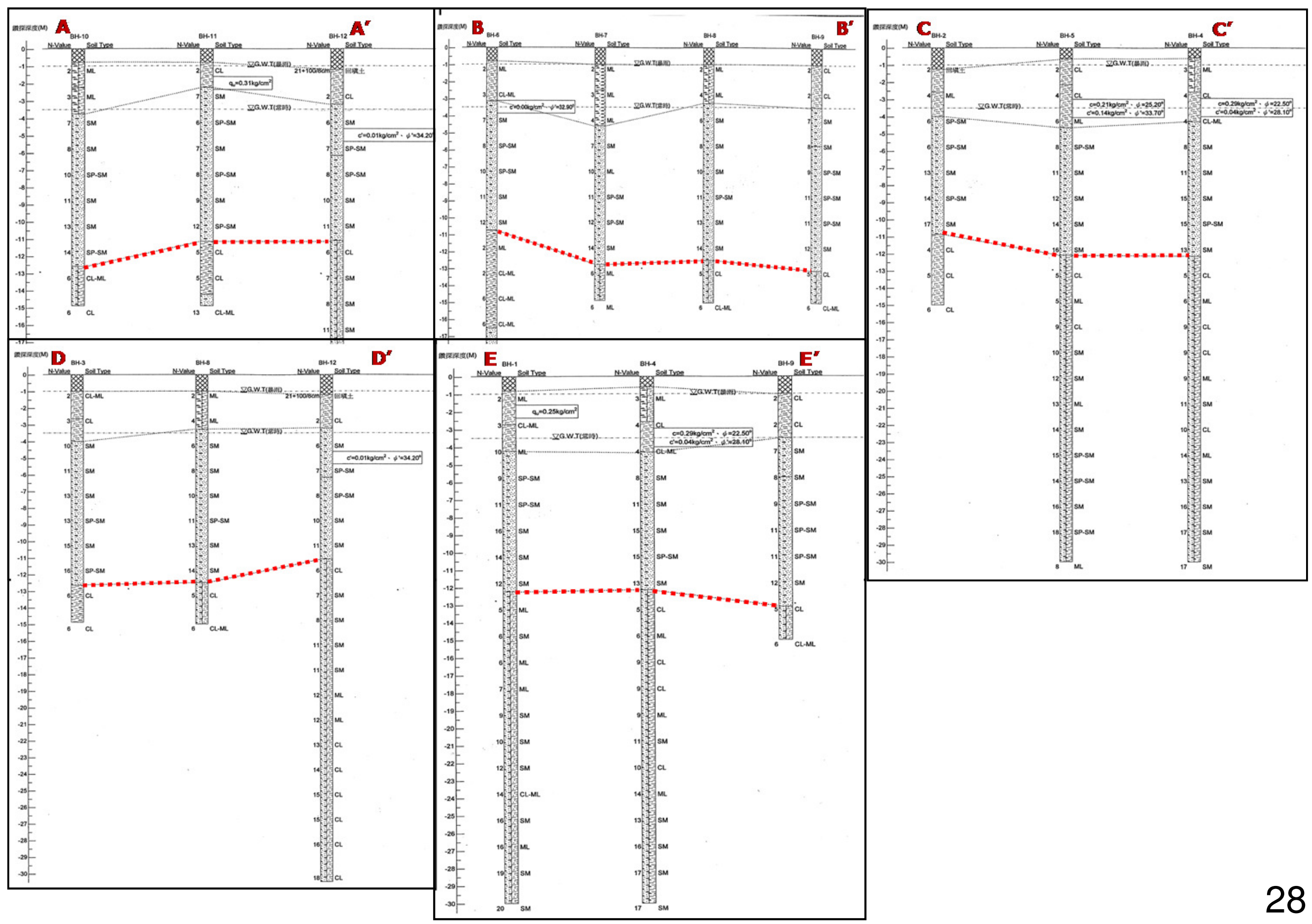
2 Investigation Results

Geological Information

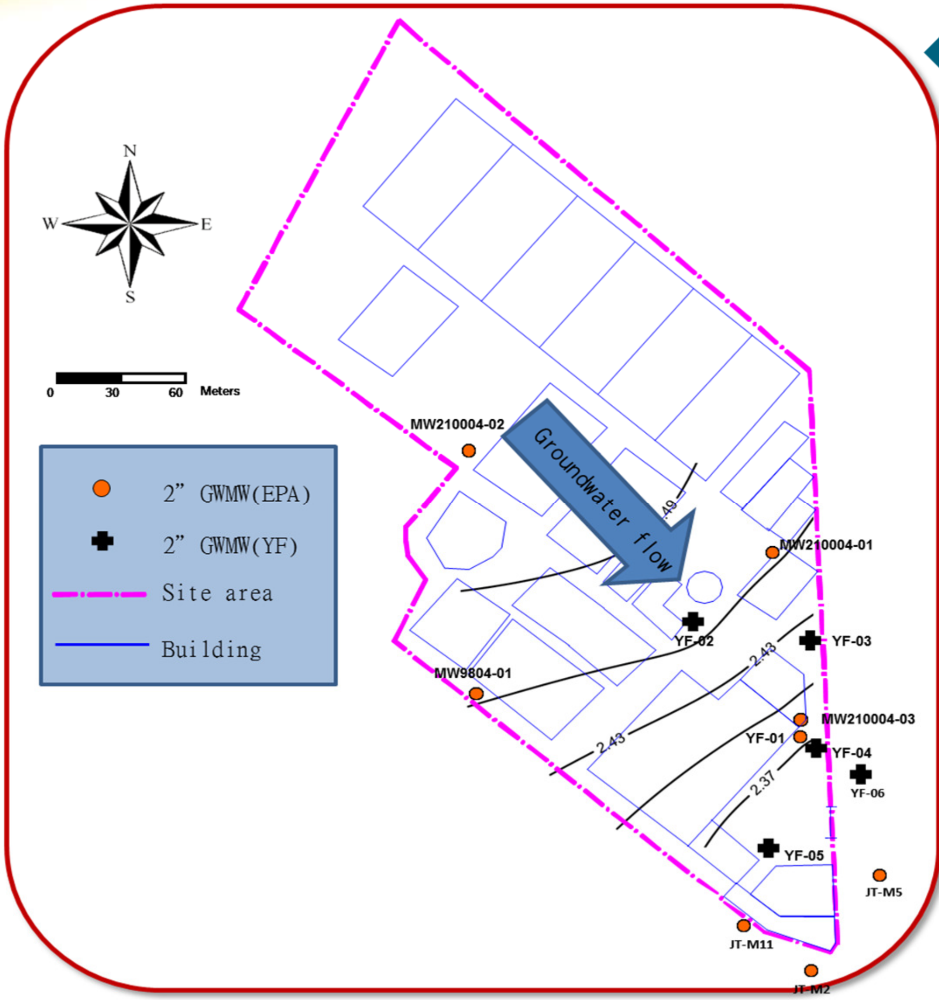
Geology

- Recent epoch alluvia, sandy silt, fine sand
- A 2~3 m silty clay layer at 11~15 mbgs





Hydrogeological Information



◆ Hydrogeology

- **Groundwater level**

  5.6~6.0 mbgs (August, 2011)

- **Direction of groundwater flow**

  Northwest to southeast

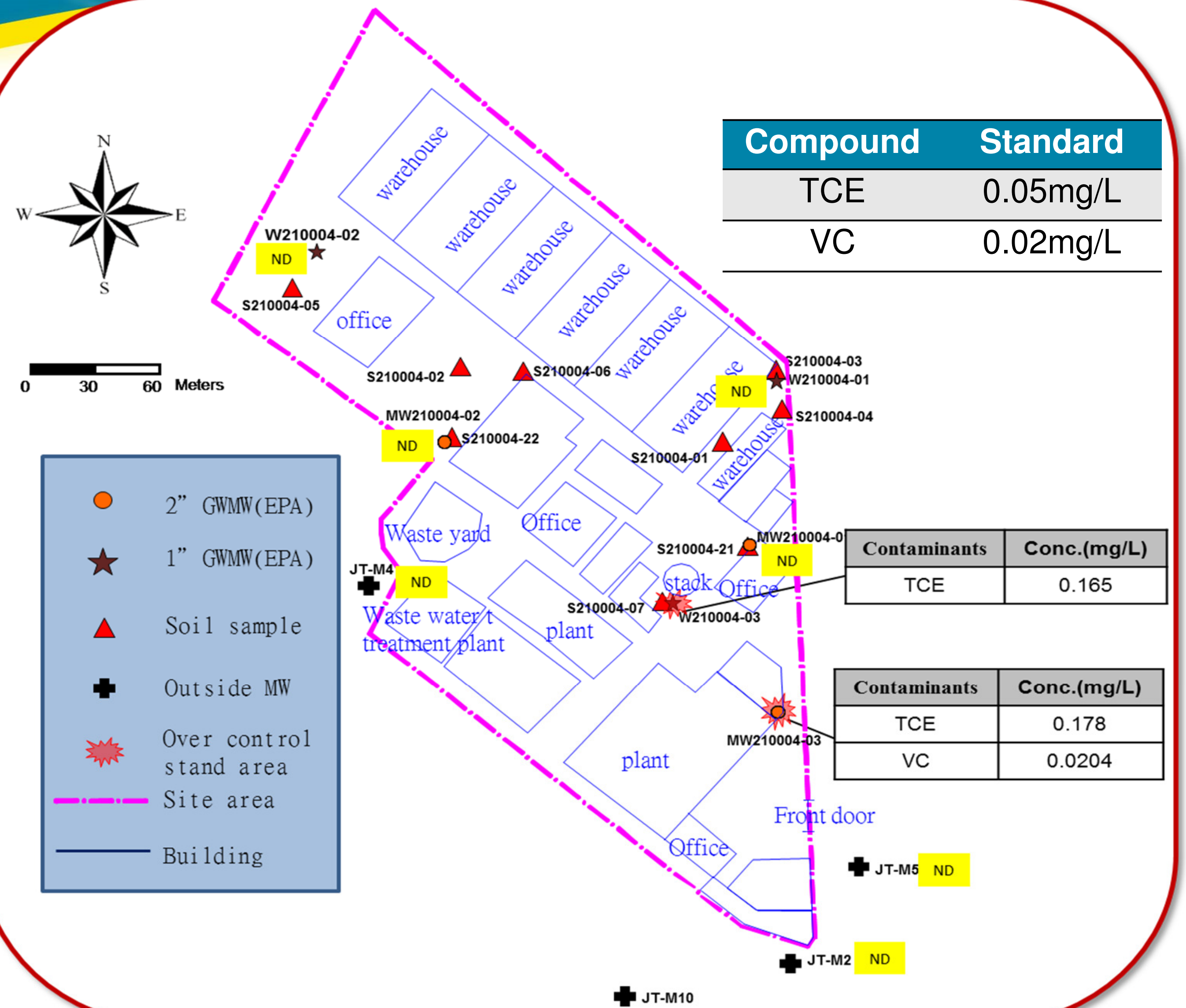
- **Hydraulic conductivity (K)**

  9.35×10-4~4.6×10-3 cm/sec

- **Groundwater flow rate**

  0.246 ~ 1.210 cm/day

2008 EPA Investigation Results



Compound	Standard
TCE	0.05mg/L
VC	0.02mg/L

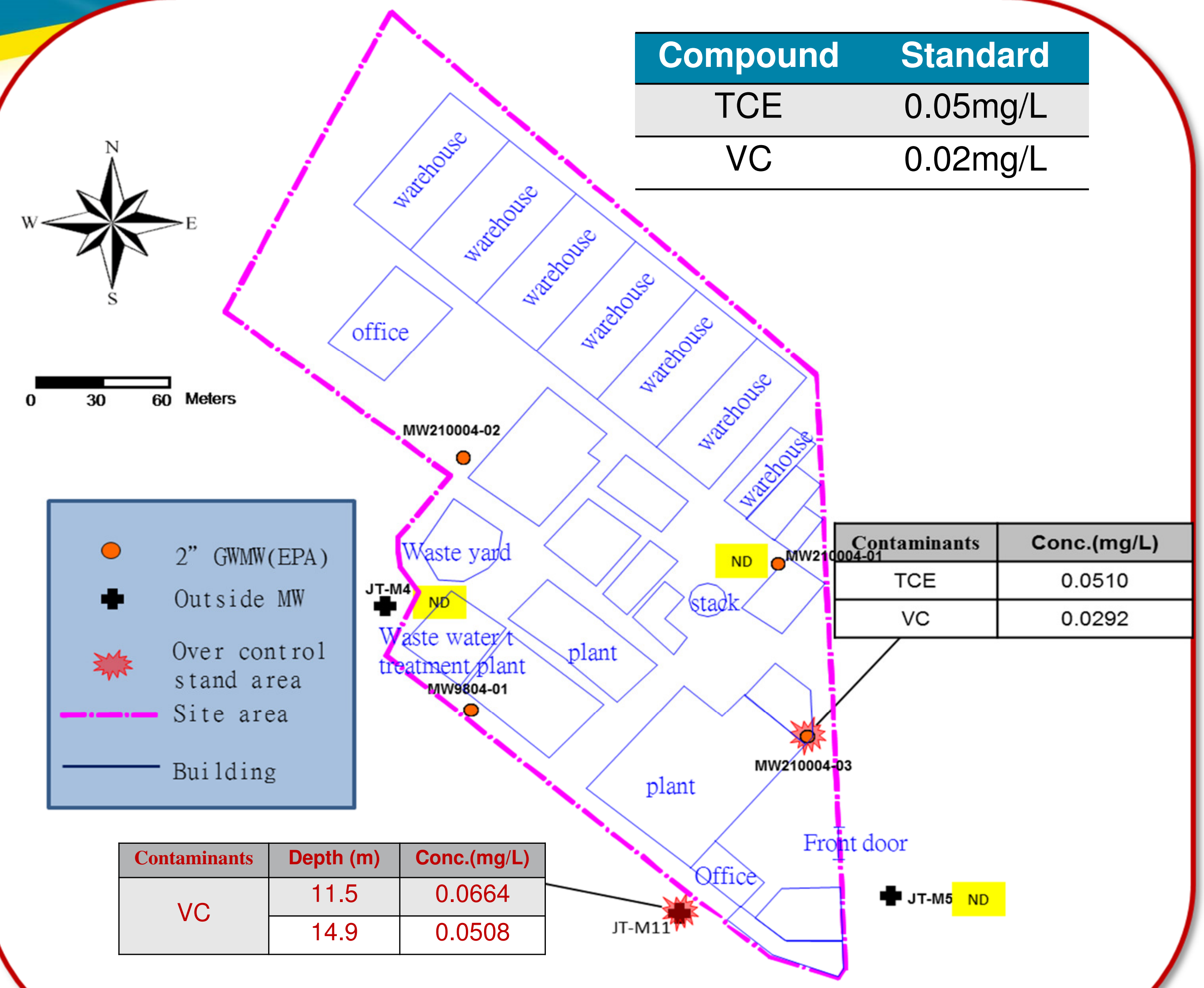
Contaminants	Conc.(mg/L)
TCE	0.165

Contaminants	Conc.(mg/L)
TCE	0.178
VC	0.0204

- **9 soil samples、6 GW samples**
- **VOCs were non-detected in soil samples.**
- **TCE exceedances were identified in 2 wells.**
- **VC exceedance was identified in 1 well.**

2009 EPA Investigation Results

Compound	Standard
TCE	0.05mg/L
VC	0.02mg/L

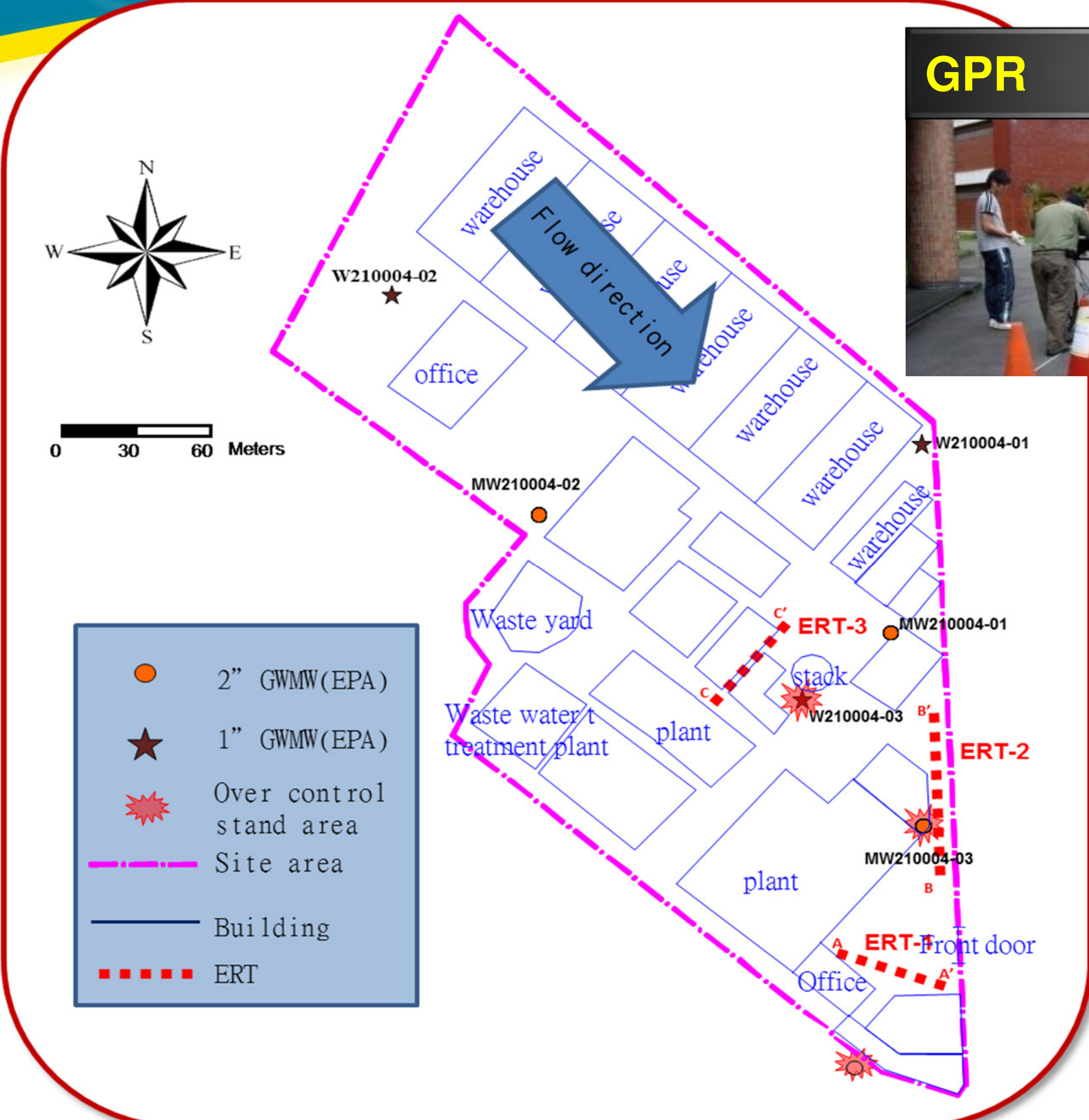


Contaminants	Conc.(mg/L)
TCE	0.0510
VC	0.0292

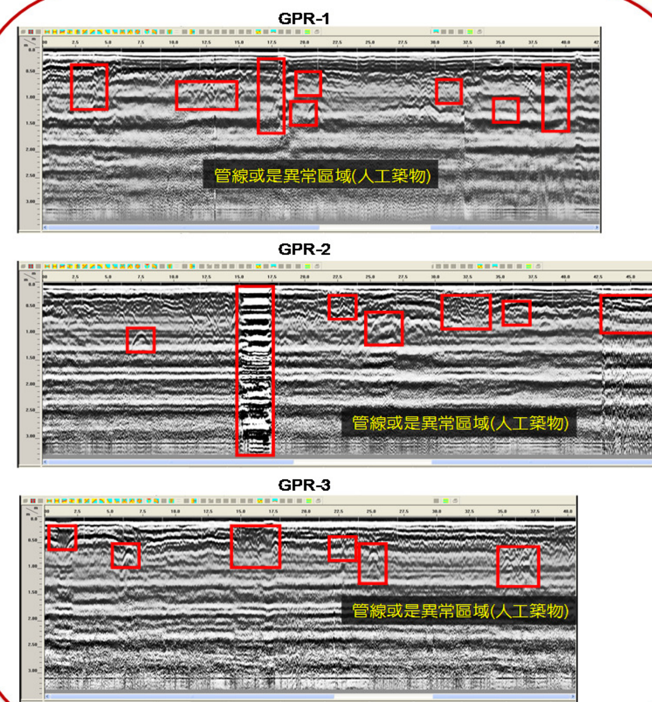
Contaminants	Depth (m)	Conc.(mg/L)
VC	11.5	0.0664
	14.9	0.0508

- **10 GW samples (4 wells sampled at 2 depths and 2 wells sampled at a single depth)**
- **TCE exceedance was identified in 1 well.**
- **VC exceedances were identified in 2 wells.**

2011 Investigation Results



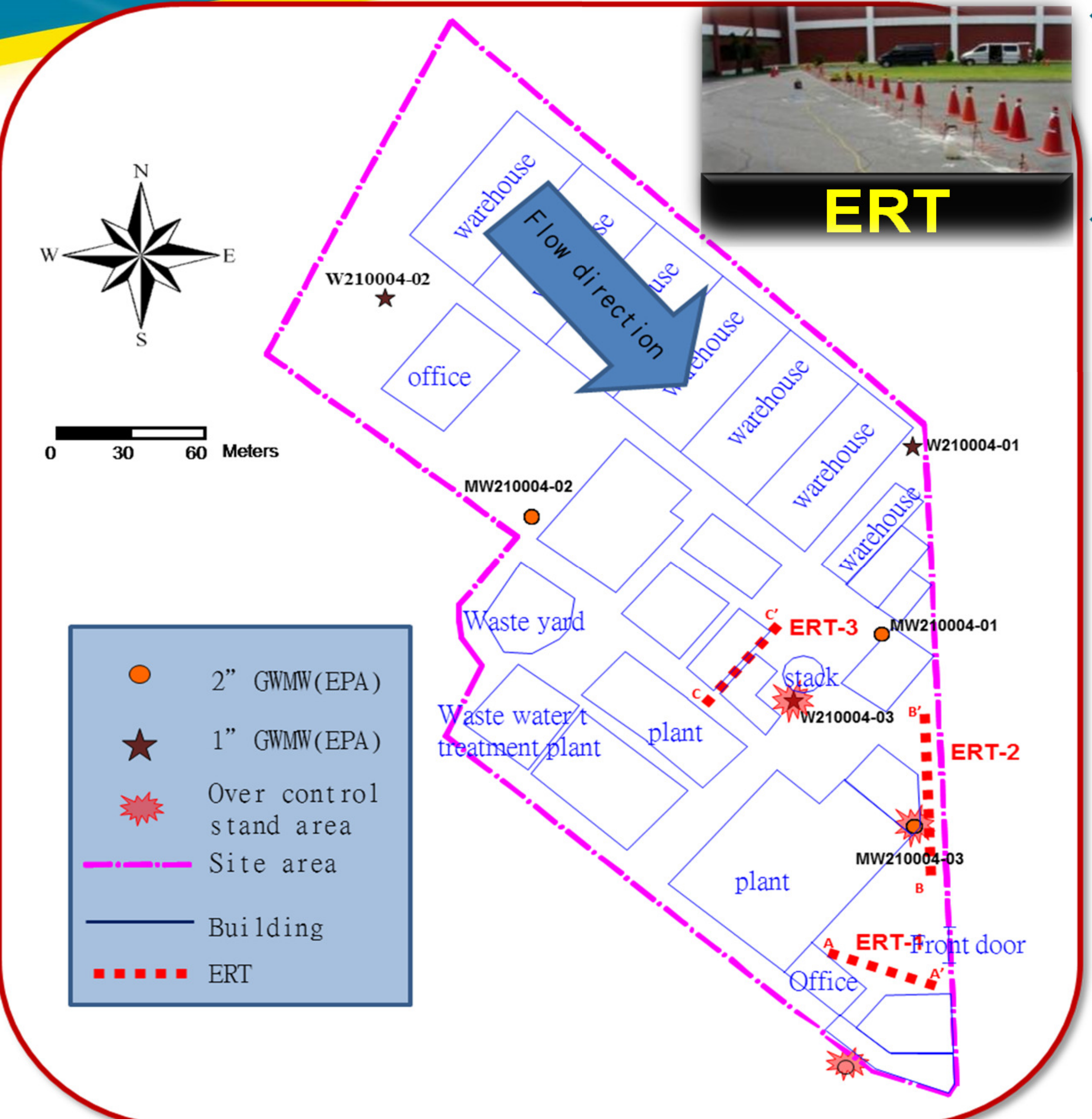
GPR

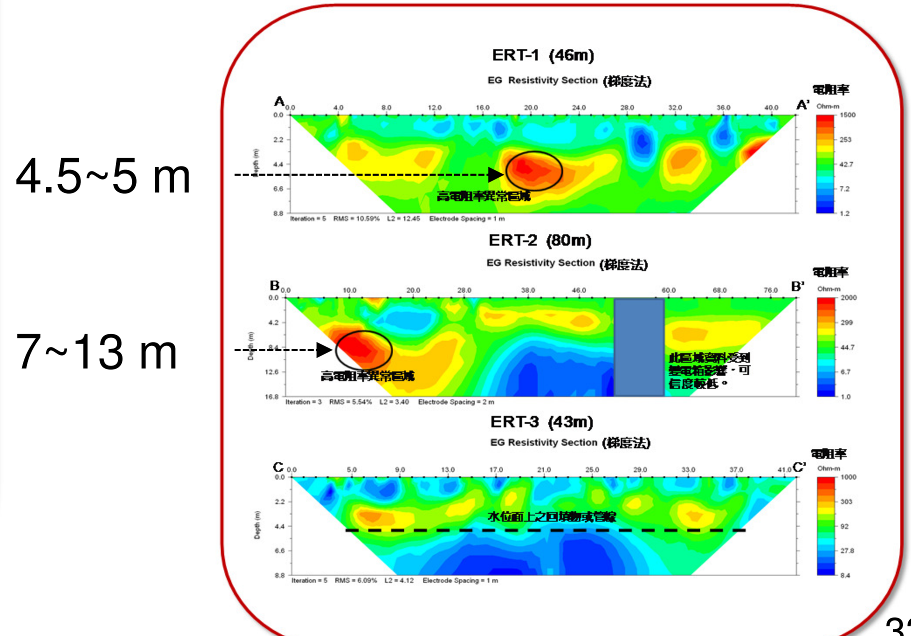


- **3 GPR (Ground Penetrating Radar) lines were performed before well installation to prevent hitting pipeline underground.**

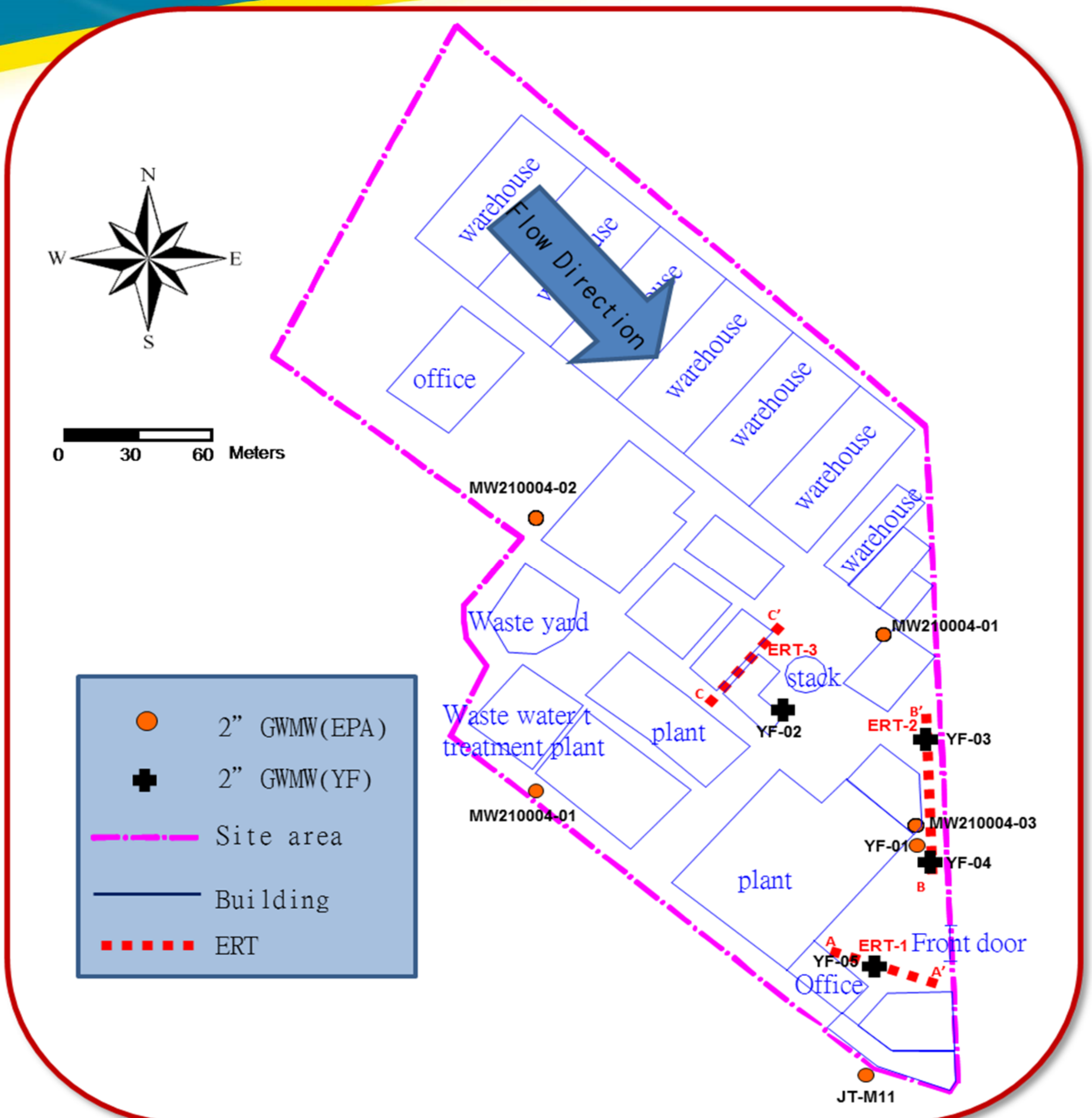
2011 Investigation Results

- **3 ERT (Electrical Resistivity Tomography) lines were also executed at the same time.**
- **The results of ERT showed unusual areas (high resistance) to present the potential locations of contaminates.**



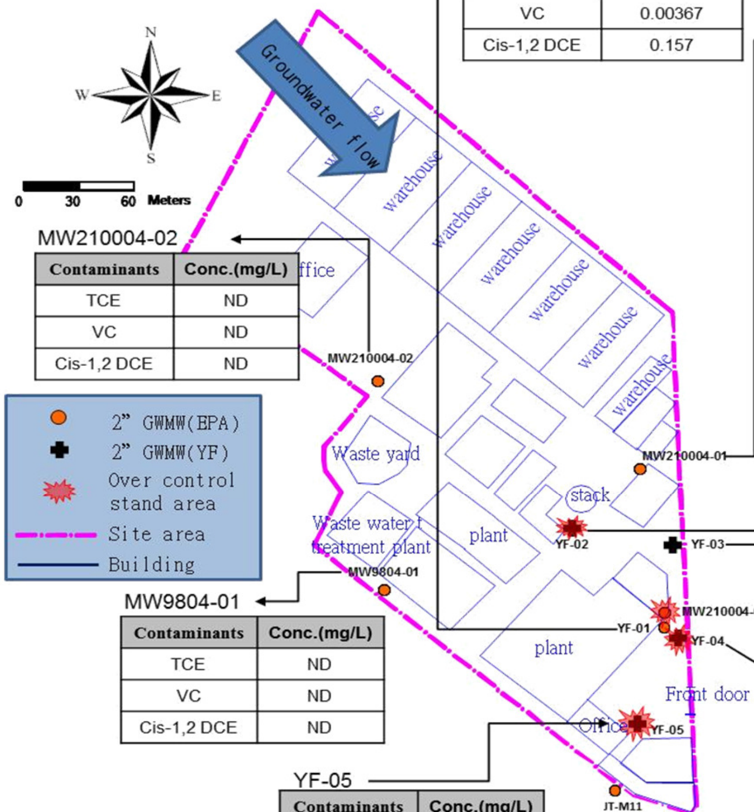


2011 Investigation Results



- **According to ERT and GPR results, monitoring wells were installed to confirm the boundary of groundwater plumes.**

2011 Investigation Results



YF-01

Contaminants	Conc.(mg/L)
TCE	0.00218
VC	0.00367
Cis-1,2 DCE	0.157

MW210004-01

Contaminants	Conc.(mg/L)
TCE	ND
VC	ND
Cis-1,2 DCE	ND

YF-02

Contaminants	Conc.(mg/L)
TCE	0.0687
VC	0.00523
Cis-1,2 DCE	0.162

MW210004-02

Contaminants	Conc.(mg/L)
TCE	ND
VC	ND
Cis-1,2 DCE	ND

YF-03

Contaminants	Conc.(mg/L)
TCE	ND
VC	0.00871
Cis-1,2 DCE	0.00201

MW210004-03

Contaminants	Conc.(mg/L)
TCE	0.0815
VC	0.0347
Cis-1,2 DCE	0.548

MW9804-01

Contaminants	Conc.(mg/L)
TCE	ND
VC	ND
Cis-1,2 DCE	ND

YF-04

Contaminants	Depth (m)	Conc. (mg/L)
TCE	9.5	0.0714
	12.5	0.0693
VC	9.5	0.00627
	12.5	0.00690
Cis-1,2 DCE	9.5	1.75
	12.5	1.6

YF-05

Contaminants	Conc.(mg/L)
TCE	ND
VC	0.0389
Cis-1,2 DCE	0.00763

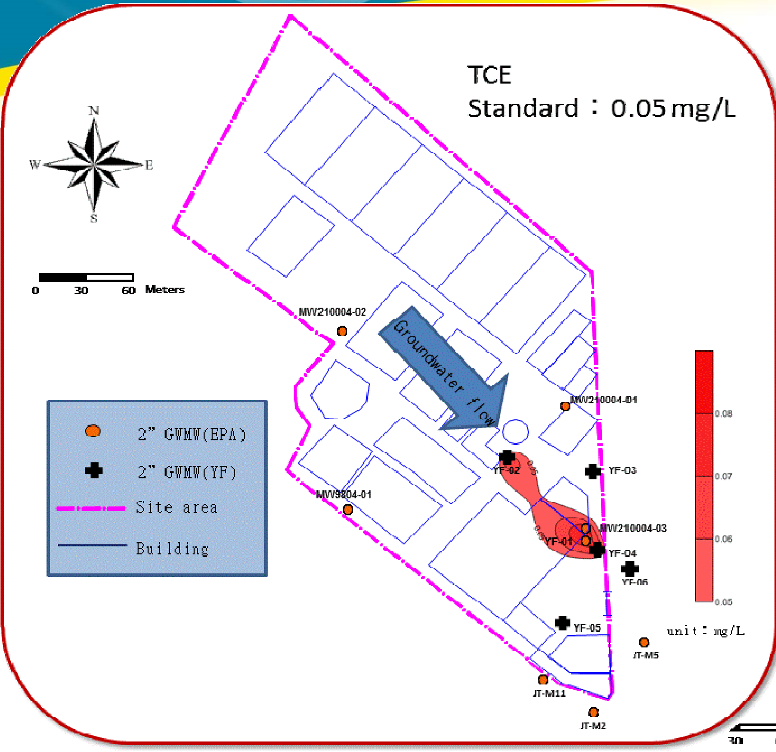
JT-M11

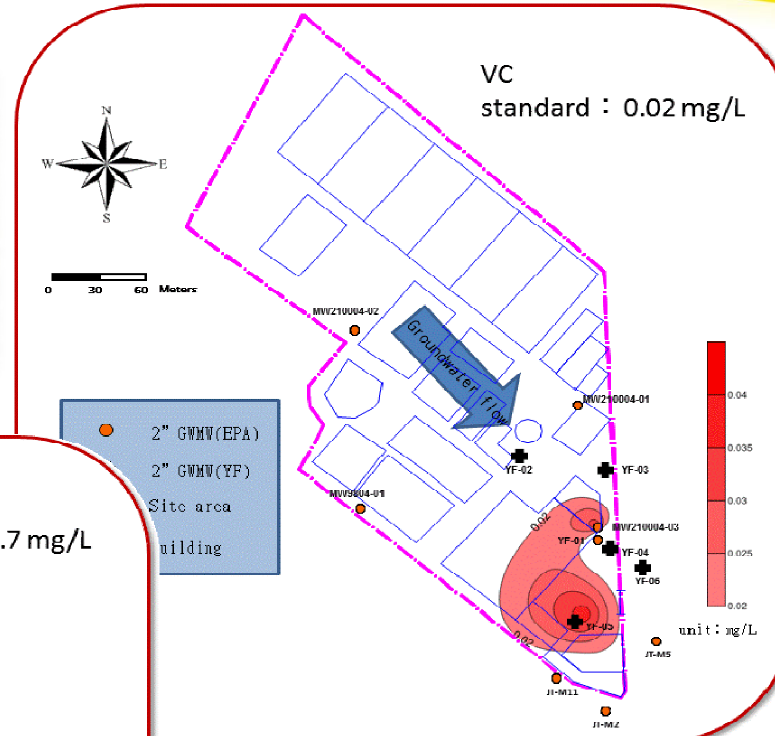
Contaminants	Conc.(mg/L)
TCE	ND
VC	0.00960
Cis-1,2 DCE	ND

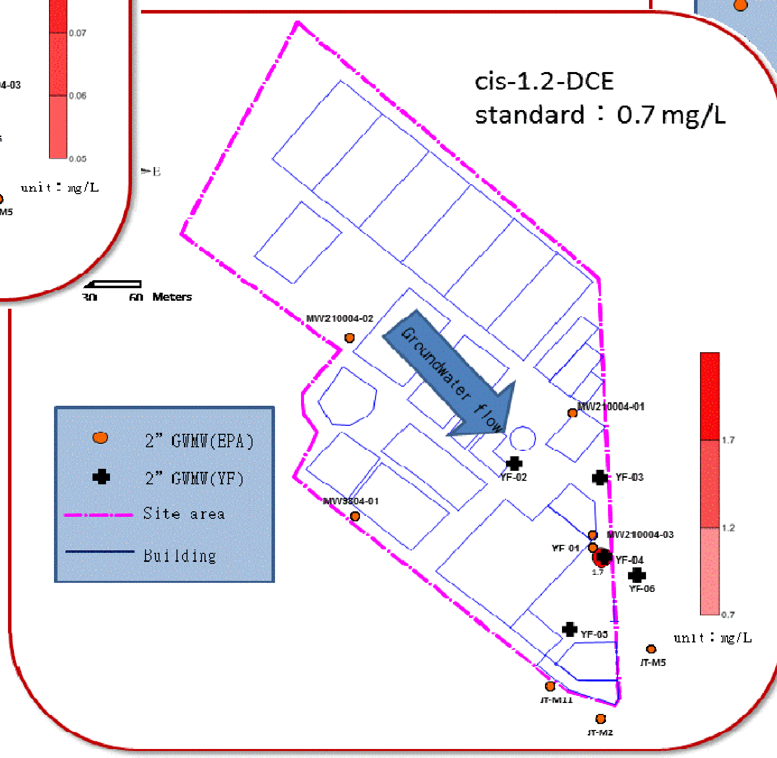
Compound	Standard
TCE	0.05 mg/L
VC	0.02 mg/L
Cis-1,2 DCE	0.7 mg/L

- **11 GW samples**
  YF-04 with 2 depths
- **TCE exceedances were identified in 3 wells.**
- **VC exceedances were identified in 2 wells.**
- **Cis-1,2 DCE exceedances were identified in 1 well at 2 depths.**

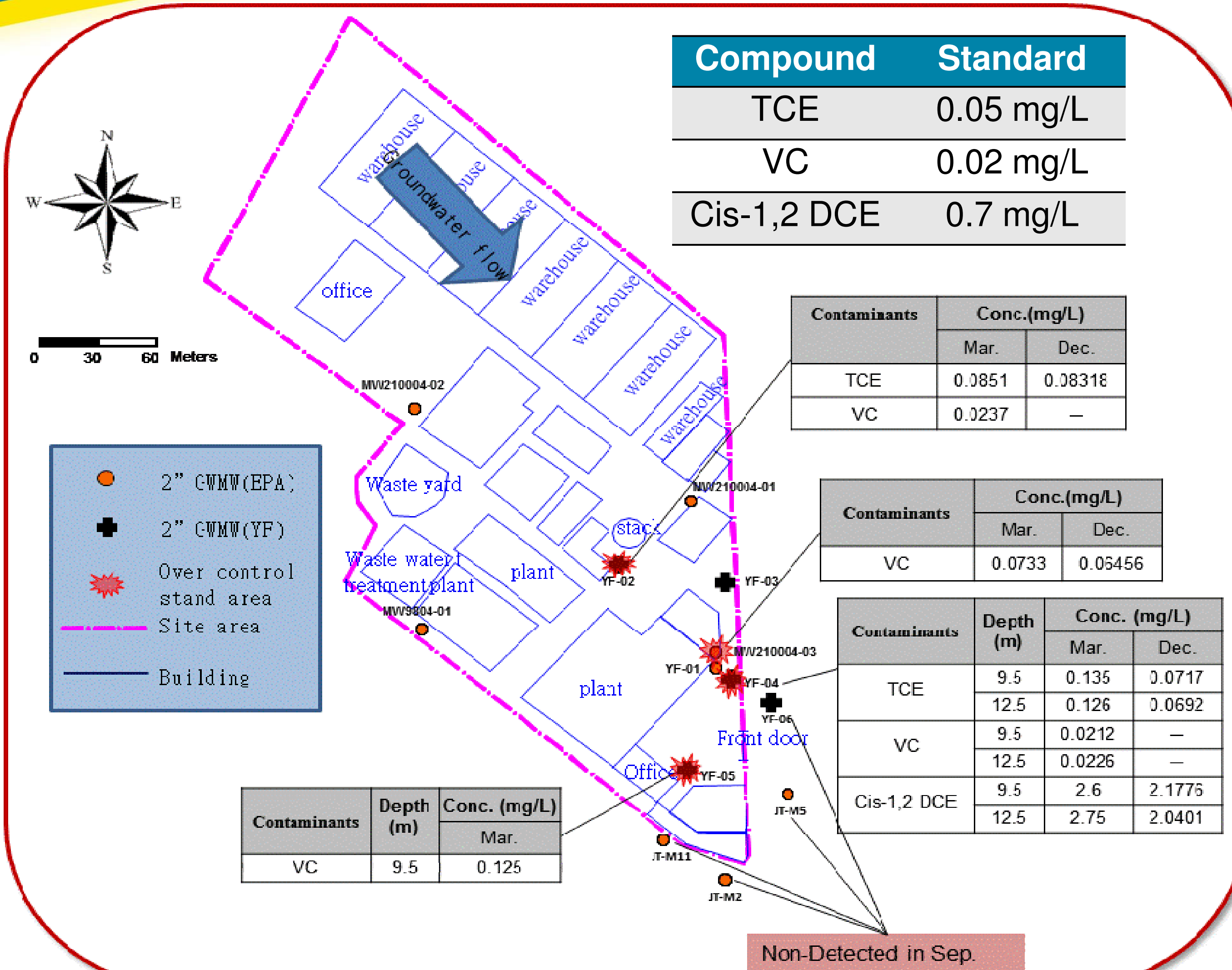
2011 Investigation Results







2012 Investigation Results



Compound	Standard
TCE	0.05 mg/L
VC	0.02 mg/L
Cis-1,2 DCE	0.7 mg/L

Contaminants	Conc.(mg/L)	
	Mar.	Dec.
TCE	0.0851	0.08318
VC	0.0237	–

Contaminants	Conc.(mg/L)	
	Mar.	Dec.
VC	0.0733	0.06456

Contaminants	Depth (m)	Conc. (mg/L)	
		Mar.	Dec.
TCE	9.5	0.135	0.0717
	12.5	0.126	0.0692
VC	9.5	0.0212	–
	12.5	0.0226	–
Cis-1,2 DCE	9.5	2.6	2.1776
	12.5	2.75	2.0401

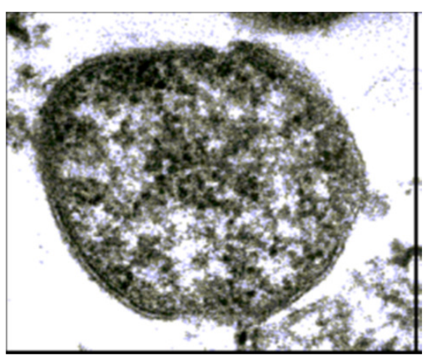
Contaminants	Depth (m)	Conc. (mg/L)
		Mar.
VC	9.5	0.125

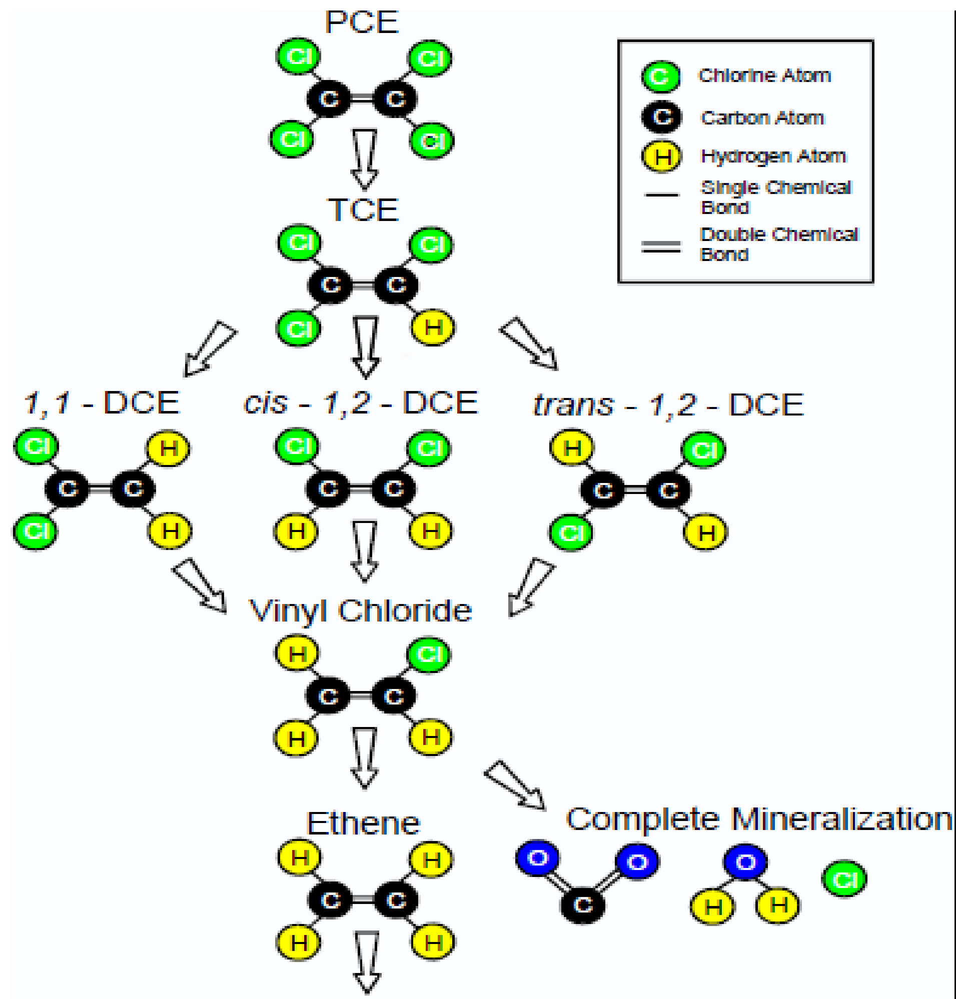
- **Sampled at 10 wells**
- **TCE exceedances were identified in 2 wells.**
- **VC exceedances were identified in 4 wells.**
- **Cis-1,2 DCE exceedances were identified in 1 well at 2 depths.**

3 Remedial Approach

Anaerobic Bioremediation (1/2)

- PCE & TCE will be degraded to DCE, then to VC at anaerobic conditions.
- **Anaerobic reductive dechlorination** is major mechanism of bioremediation.
- ***Dehalococcoides*** (DHC) must exit in soil or groundwater.



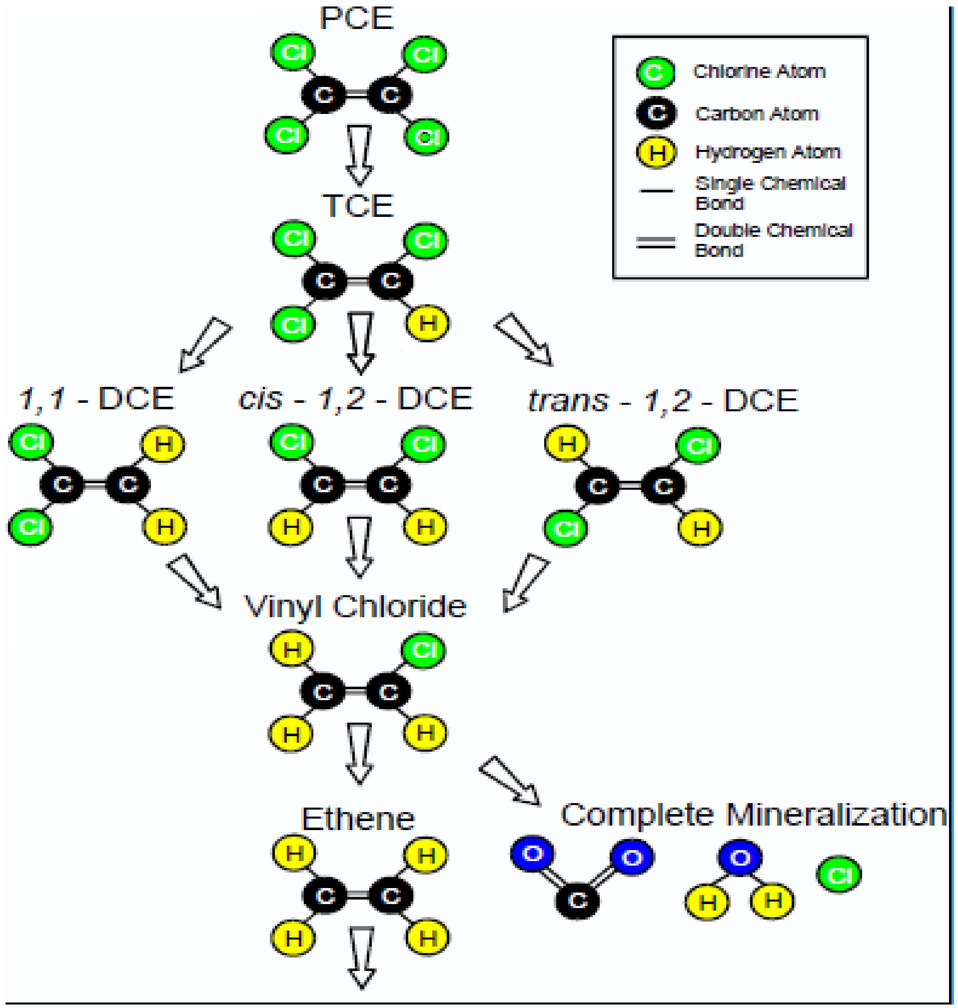


Anaerobic Bioremediation (2/2)

- Reductive Dechlorination
- Soybean Oil ($C_{18}H_{32}O_2$) ferments to H_2 and simple organics

$$C_{18}H_{32}O_2 + 34\ H_2O \rightarrow 18\ CO_2 + 50\ H_2$$

- H_2 and simple organics
  - Consume oxygen
  - Drive dechlorination



Anaerobic Condition Confirmation

MW NO.	Date	TCE	cis-1,2-DCE	VC	DO	ORP
unit		mg/L			mg/L	mV
MW210004-03	2008/10/15	0.178	0.548	0.0204	1.06	-43
	2009/12/25	0.051	0.513	0.0292	0.4	-28
	2011/8/30	0.0815	0.548	0.0347	1.87	-31
	2012/3/14	0.0249	0.425	0.0733	1.24	-40
Control standard		0.05	0.7	0.02	-	-

- TCE conc. decreased and VC conc. increased
- Low DO (dissolved oxygen) and ORP (Oxidation-Reduction Potential): Subsurface environment is suitable for anaerobic bioremediation.

Natural Attenuation Screening Protocol

BIOCHLOR22_2000 [相容模式] - Microsoft Excel

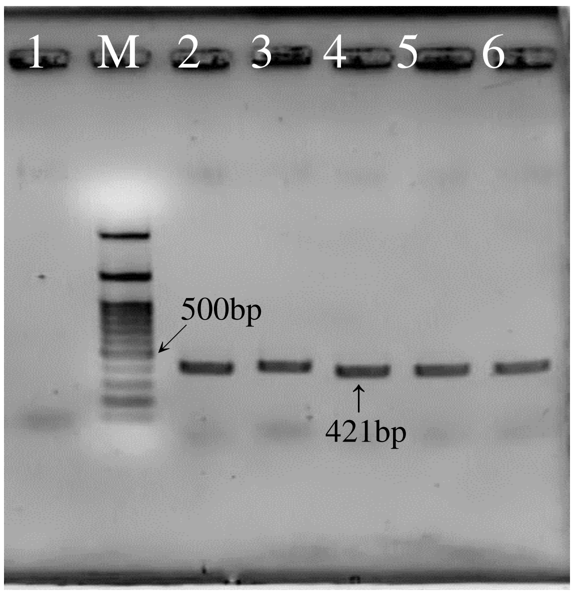
Natural Attenuation Screening Protocol	Interpretation	Score	TO INPUT
The following is taken from the USEPA protocol (USEPA, 1998). The results of this scoring process have no regulatory significance.	Inadequate evidence for anaerobic biodegradation* of chlorinated organics	0 to 5	Score: 16
	Limited evidence for anaerobic biodegradation* of chlorinated organics	6 to 14	
	Adequate evidence for anaerobic biodegradation* of chlorinated organics	15 to 20	
	Strong evidence for anaerobic biodegradation* of chlorinated organics	>20	Scroll to End of Table

* reductive dechlorination

Analysis	Concentration in Most Contam. Zone	Interpretation	Yes	No	Points Awarded
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	●	○	3
	> 5mg/L	Not tolerated; however, VC may be oxidized aerobically	○	●	0
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway	●	○	2
Iron II*	>1 mg/L	Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions	○	●	0
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	○	●	0
Sulfide*	>1 mg/L	Reductive pathway possible	○	●	0
Methane*	>0.5 mg/L	Ultimate reductive daughter product, VC Accumulates	●	○	3
Oxidation Reduction Potential* (ORP)	<50 millivolts (mV)	Reductive pathway possible	●	○	1
	<-100mV	Reductive pathway likely	●	○	2

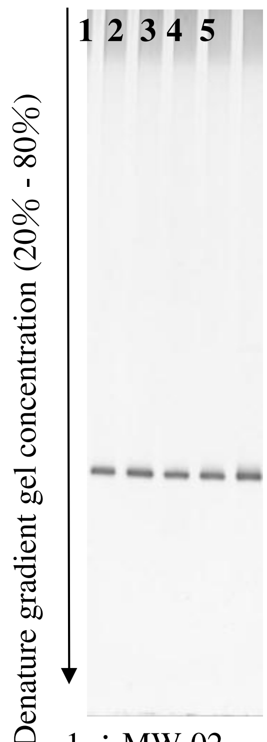
Microbial Identification (1/2)

◆ Results of PCR-DGGE



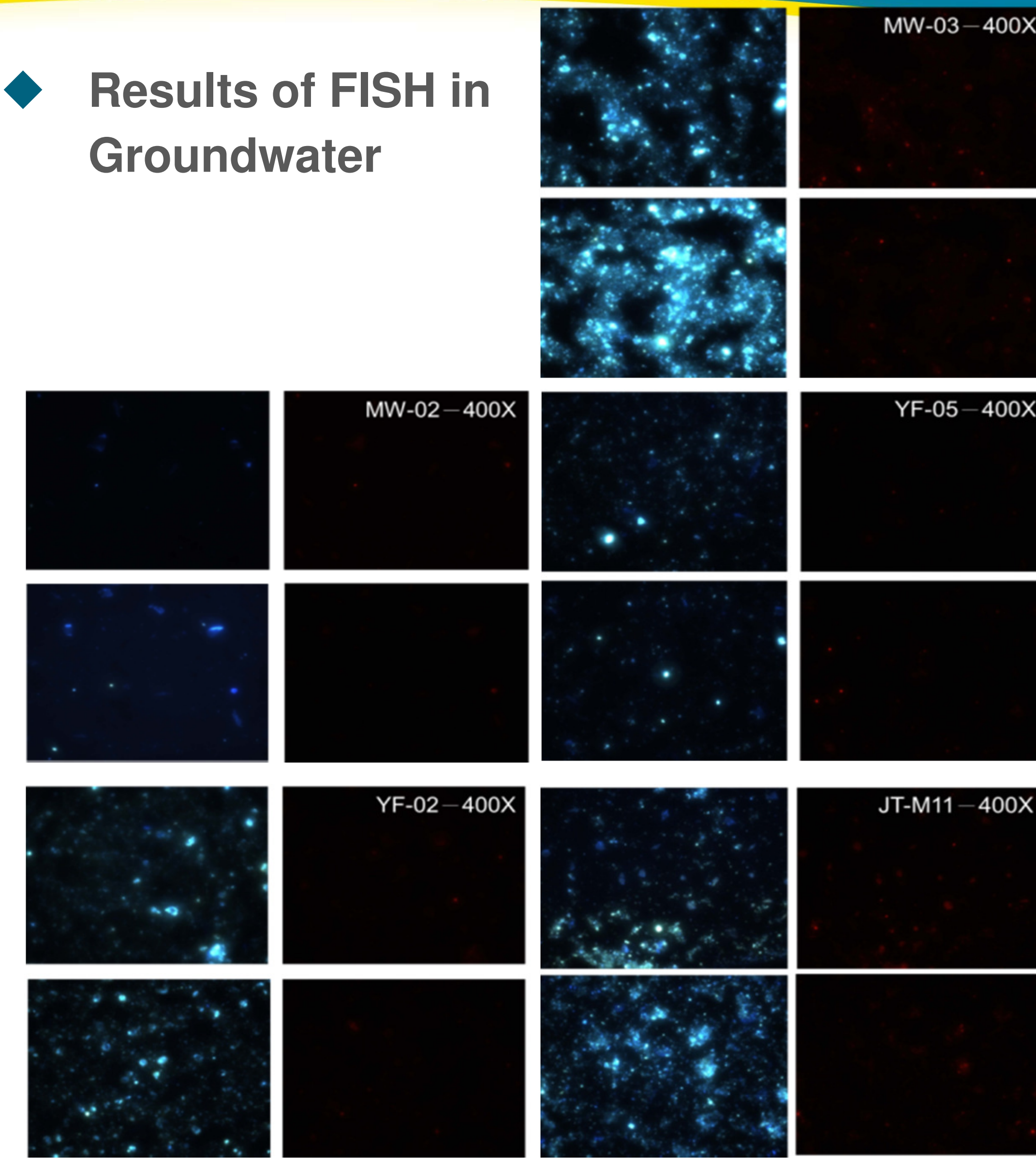
M ： marker
1 ：blank
2 ：MW-02
3 ：MW-03
4 ：YF-02
5 ：YF-05
6 ：JT-M11

notes：Markers are the DNA series of different length, which can identify if the target grows successfully.

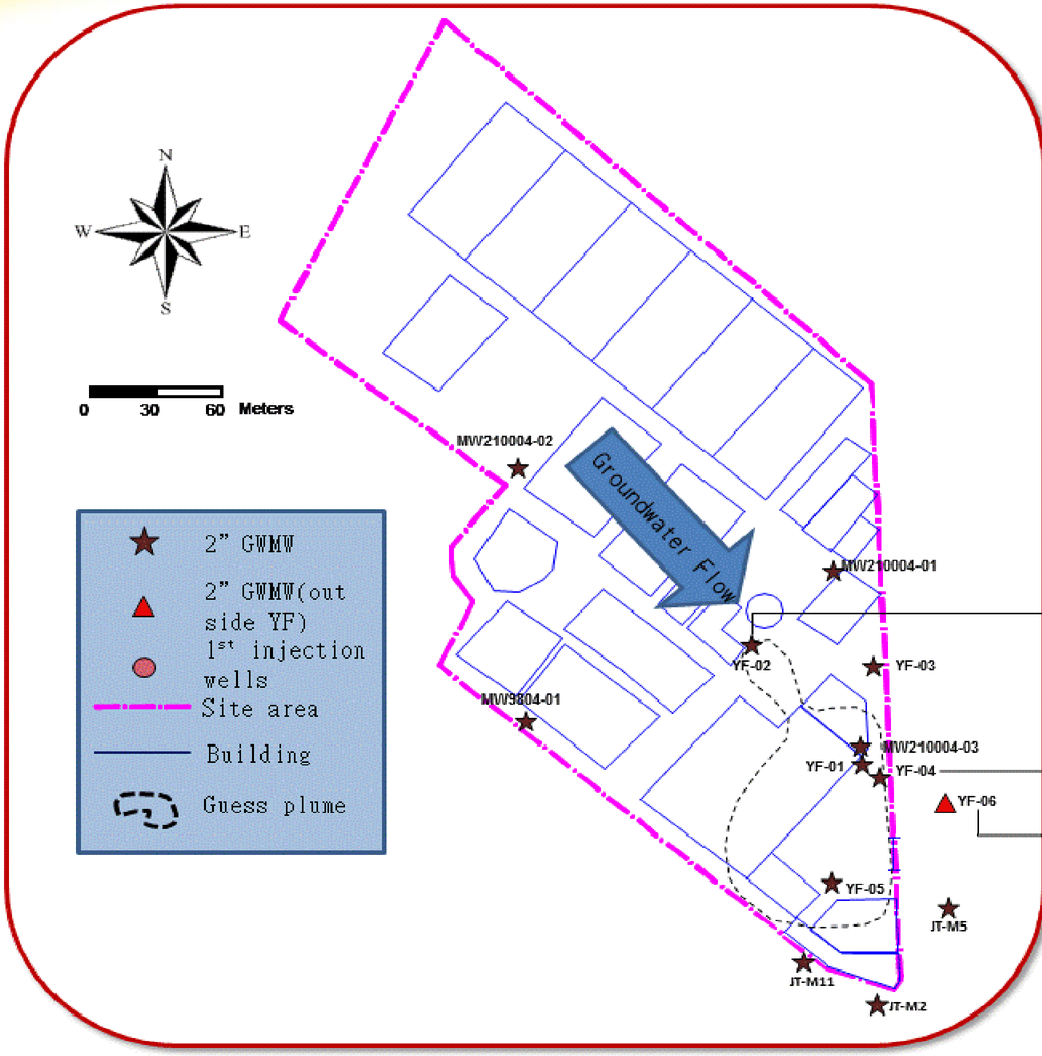


1 ：MW-02
2 ：MW-03
3 ：YF-02
4 ：YF-05
5 ：JT-M11

◆ Results of FISH in Groundwater



Microbial identification (2/2)



- **Real-time PCR**
  - **Qualitative**
    - *Dehalococcoides* sp.
  - **Quantitative**

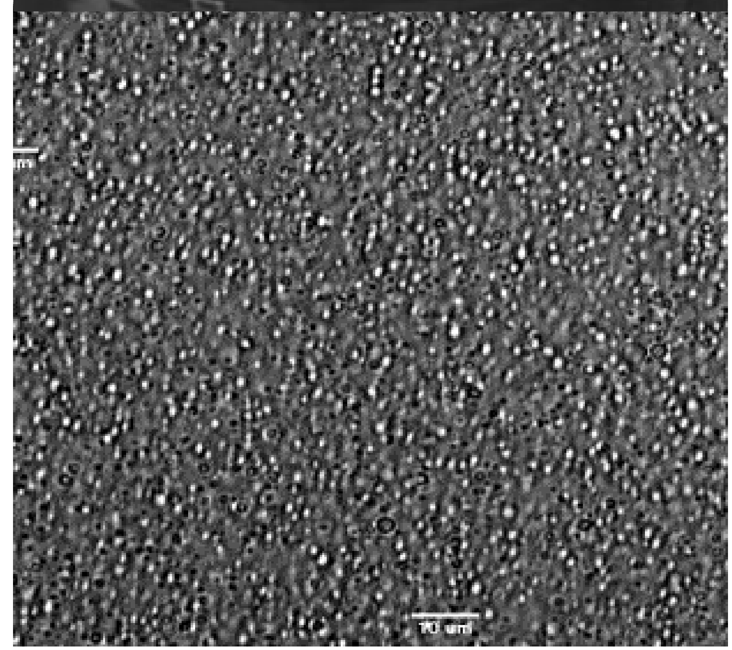
YF-02
3.64×10^3 gene copies/mL

YF-04
5.29×10^1 gene copies/mL

YF-06
2.28×10^2 gene copies/mL

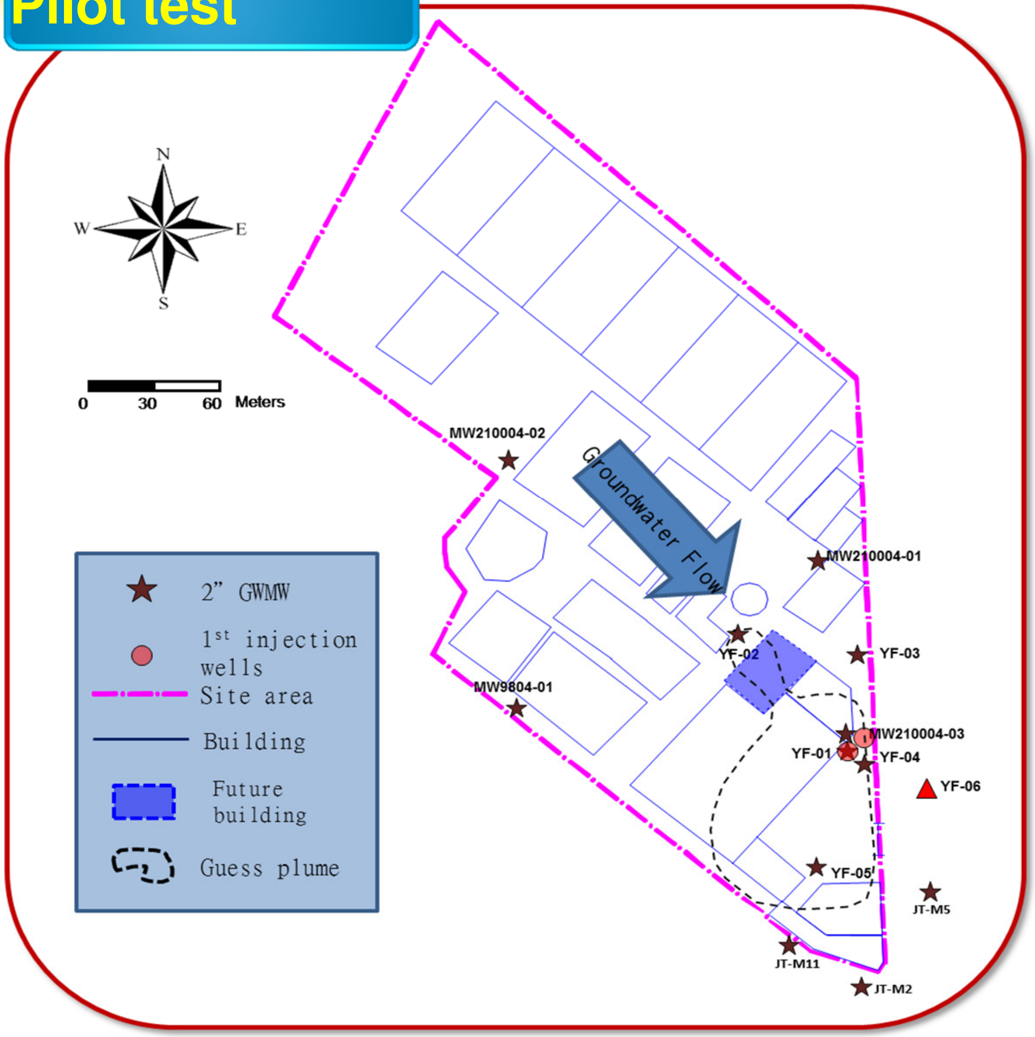
Emulsified Oil Substrate (EOS®)

- **Slow release substrate**
  - Emulsified soybean oil
  - Small, uniform droplets
  - Negative surface charge to reduce capture by sediments



Pilot Test

Pilot test



◆ **Purpose**

To obtain information, including **ROI**, **subsurface conditions**, **injection depth**, **injection volume**, **injection pressure**, **injection frequency**, **biodegradation rate**, etc., for subsequent full scale design

◆ **Injection using Geoprobe:**

Around MW210004-03

◆ **Injection method**

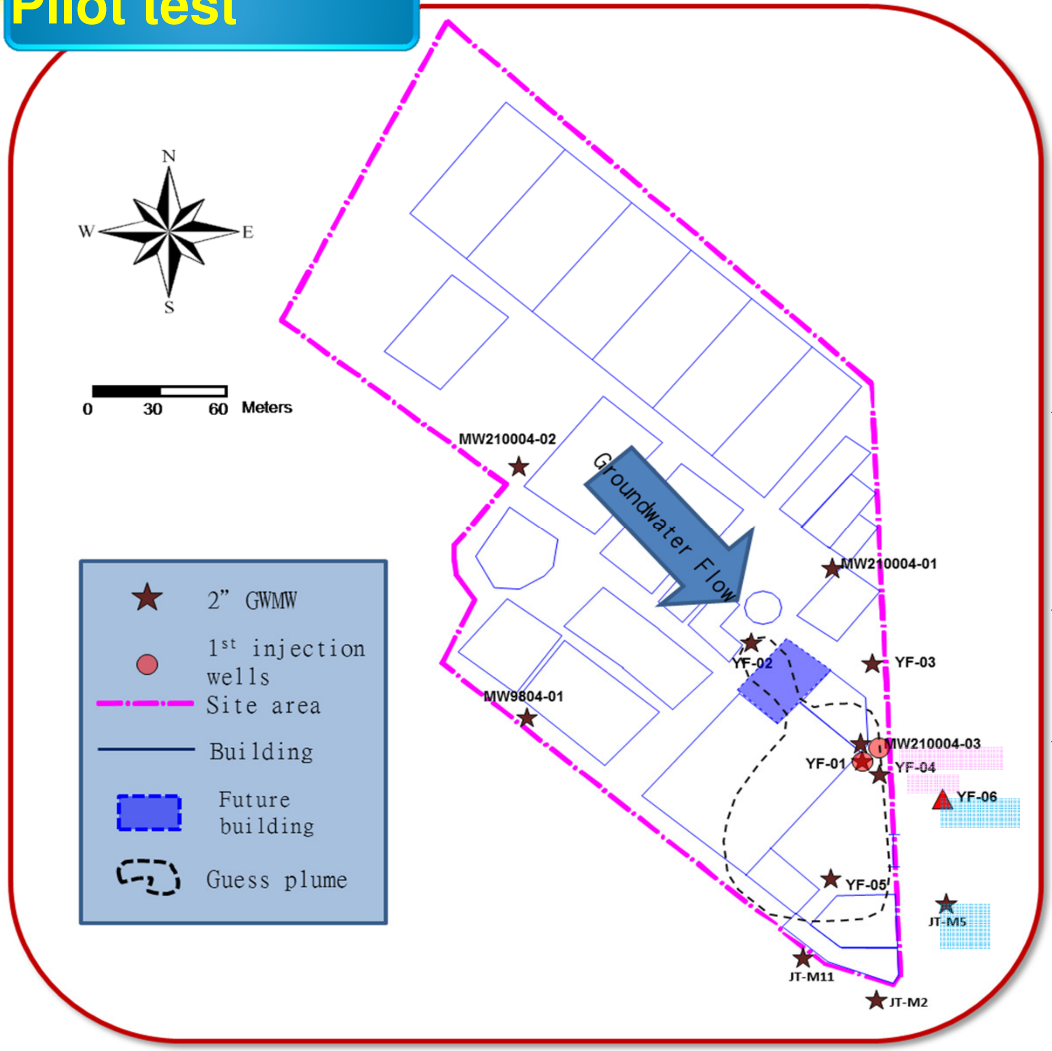
- 50 L of EOS
- 1:4 ~ 1:10 diluted (adjustment based on the effectiveness)
- Geo-probe injection
- Injection in the bottom of aquifer at 15 mbgs

◆ **Timeline**

Complete pilot test in 3 months

Pilot Test

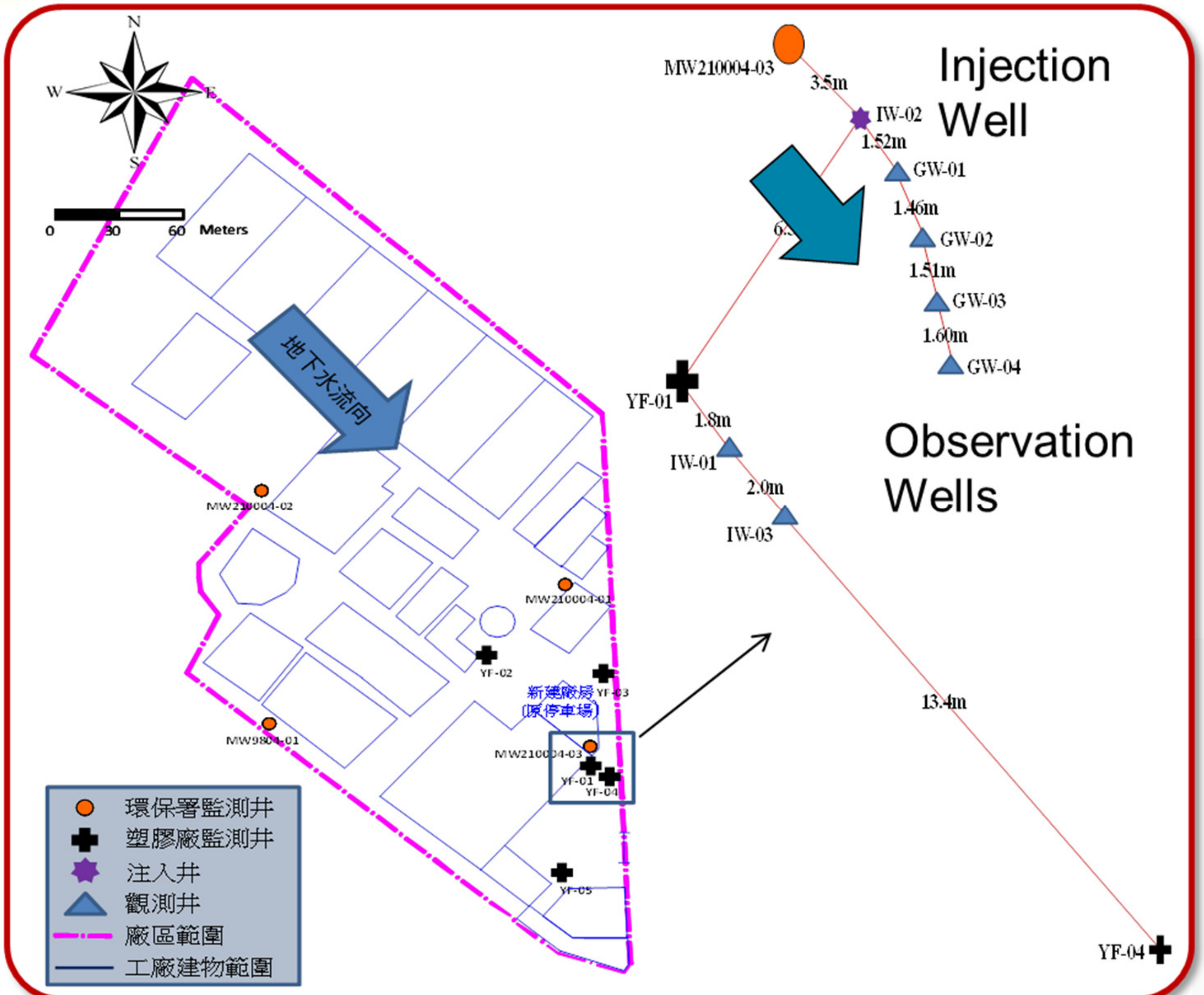
Pilot test



- **Onsite (effectiveness estimate)**
  - **Frequency**： baseline, weekly, monthly

  - **Numbers**：4 wells
    Downstream: YF-01, YF-04, MW210004-03
    Upstream: MW210004-01
- **Off-site (boundary confirmation)**
  - **Frequency**： monthly
  - **Numbers**： 2 wells (YF-06, JT-M5)
- **GW Parameters**
  - Temp., pH, DO, EC and ORP
- **Analysis**
  - VOCs, TOC, CO2, alkalinity, SO_4^{2-}, NO^{3-}, sulfide, Fe, and Mn

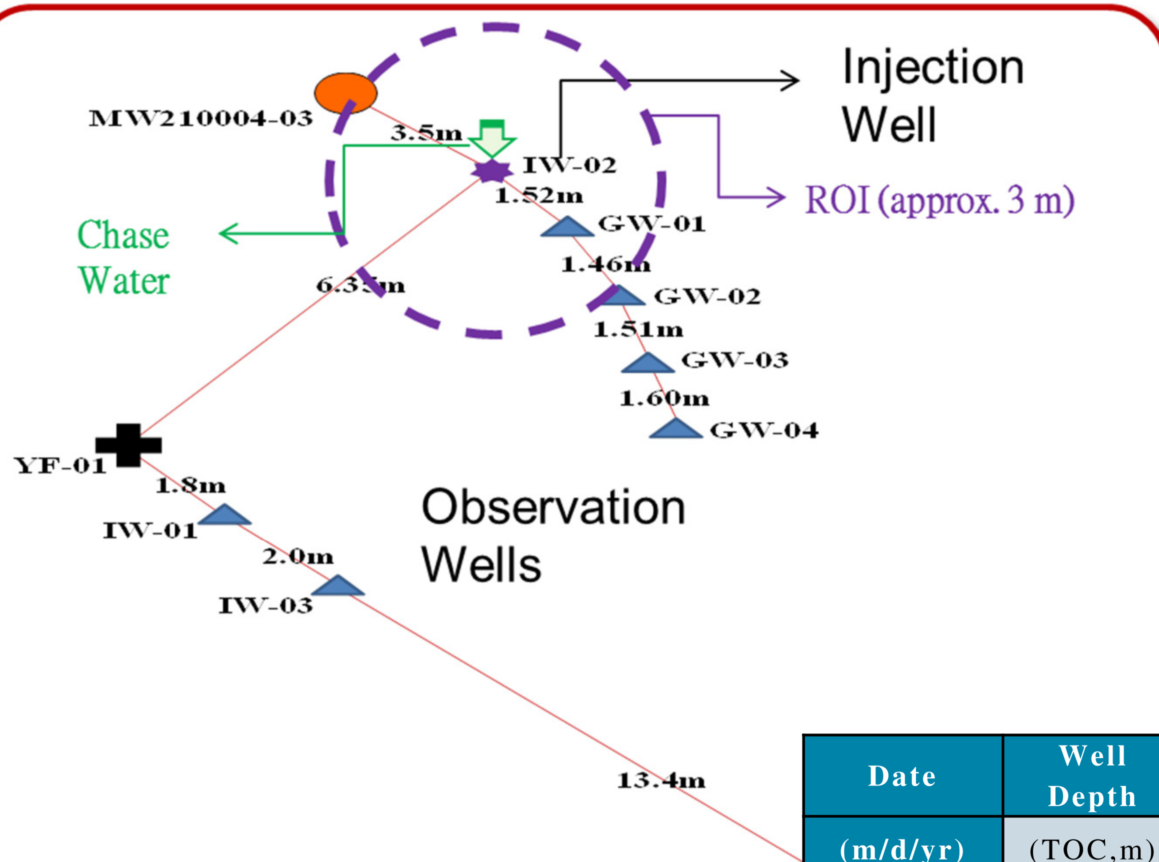
Pilot Test

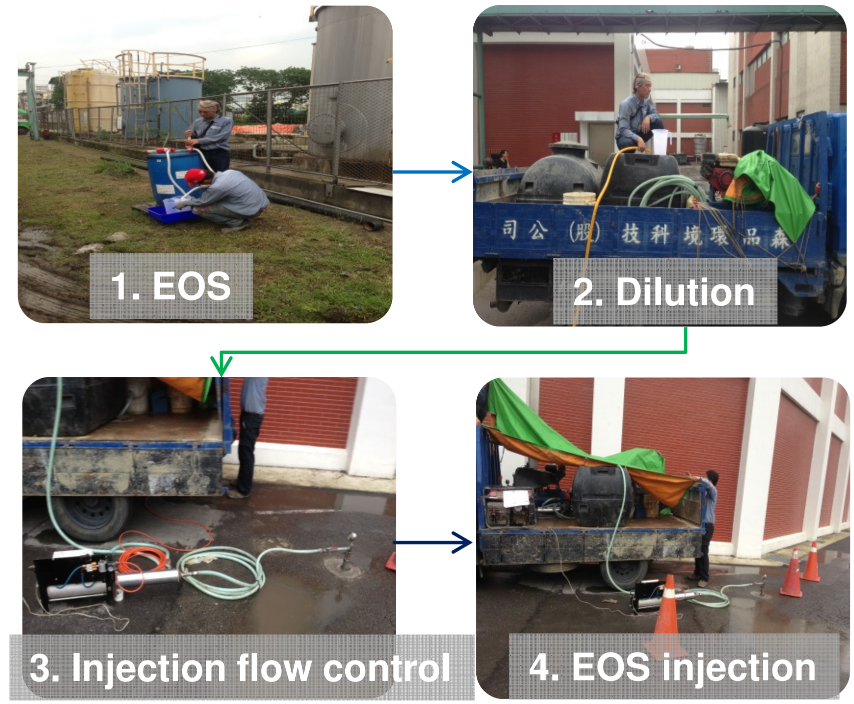


Near MW210004-03

- **1 injection well: IW-02**
- **6 observation wells: IW-01、IW-03、GW-01~GW-04**

Pilot Test





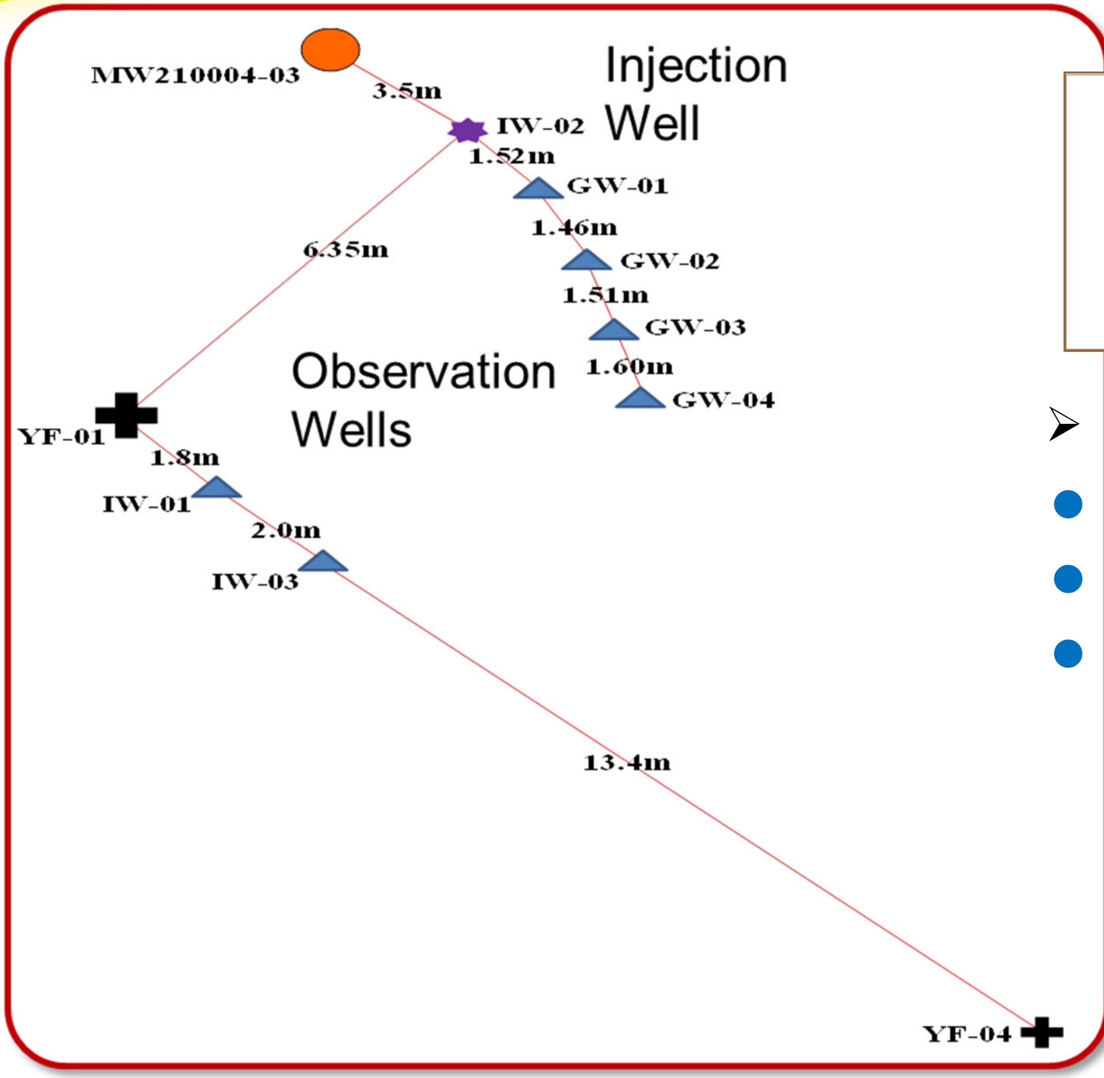
Date	Well Depth	Screen	Injection Depth	Flow Rate	EOS Quantity	Chase Water
(m/d/yr)	(TOC,m)	(m)	(TOC,m)	(L/min)	(L)	(L)
3/25/2013	11.85	3	11.85	5~7	10% 560	-
5/22/2013					5% 2000	3000

Assumptions:

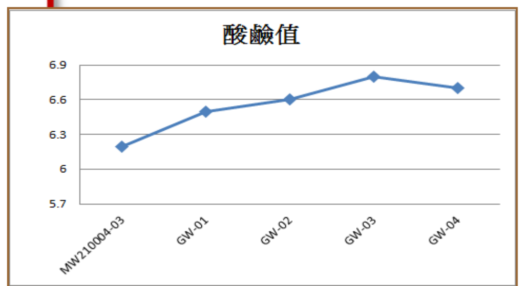
1. Effective Porosity: 0.23
2. Effective thickness: 25%

4 Remediation Results

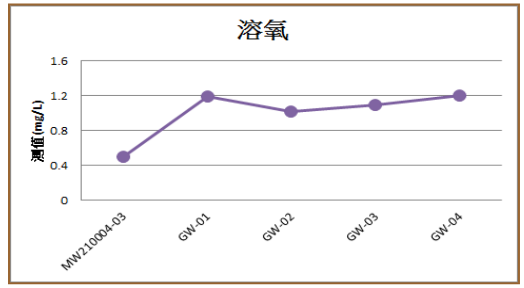
Pilot Test Results



pH

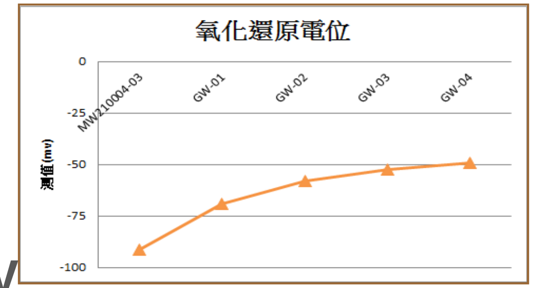


DO



➢ **GW Parameters**

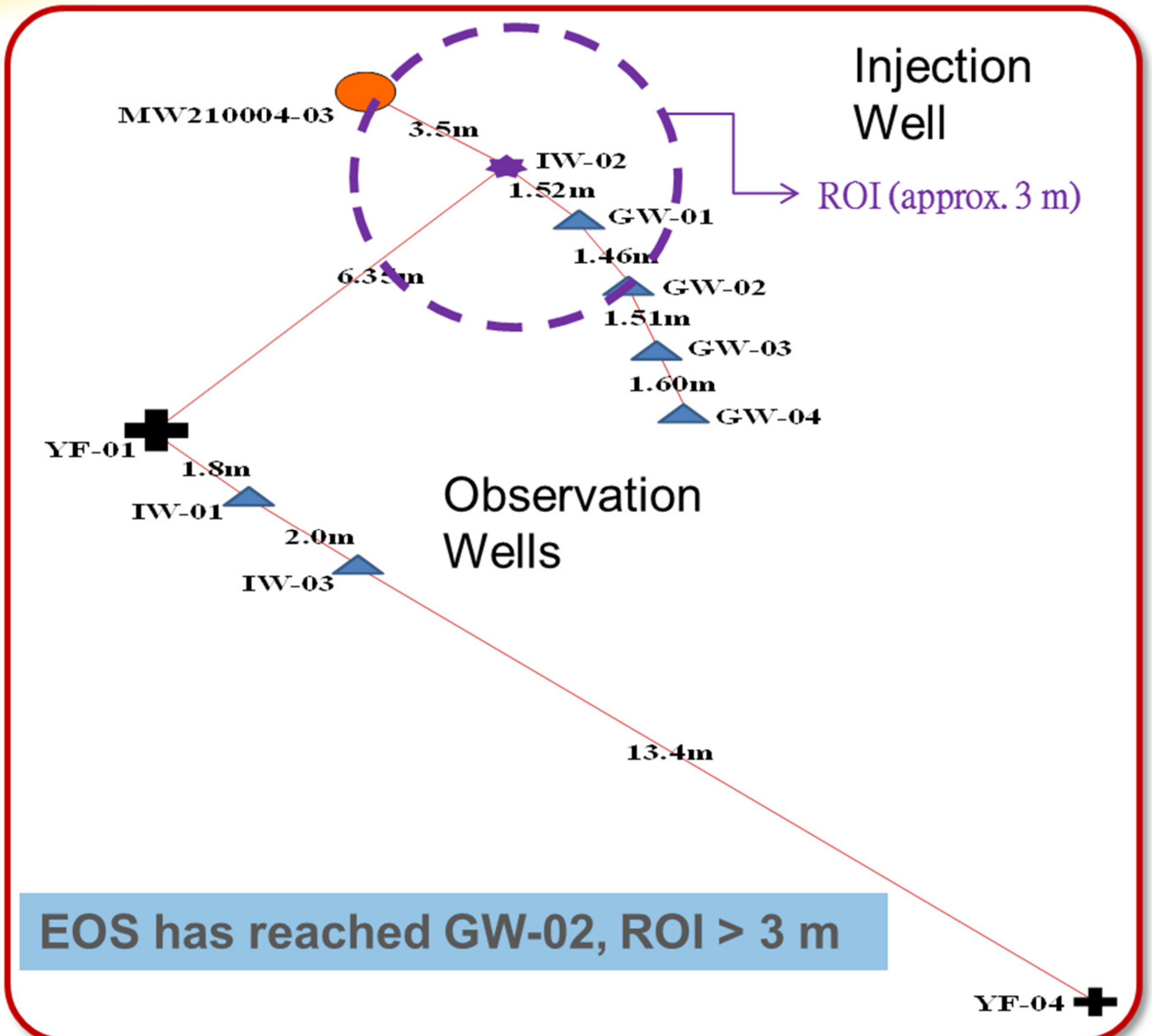
- **pH: 6.2~6.8**
- **DO: 0.5~1.2 mg/L**
- **ORP: -49.1~-91.2 mV**

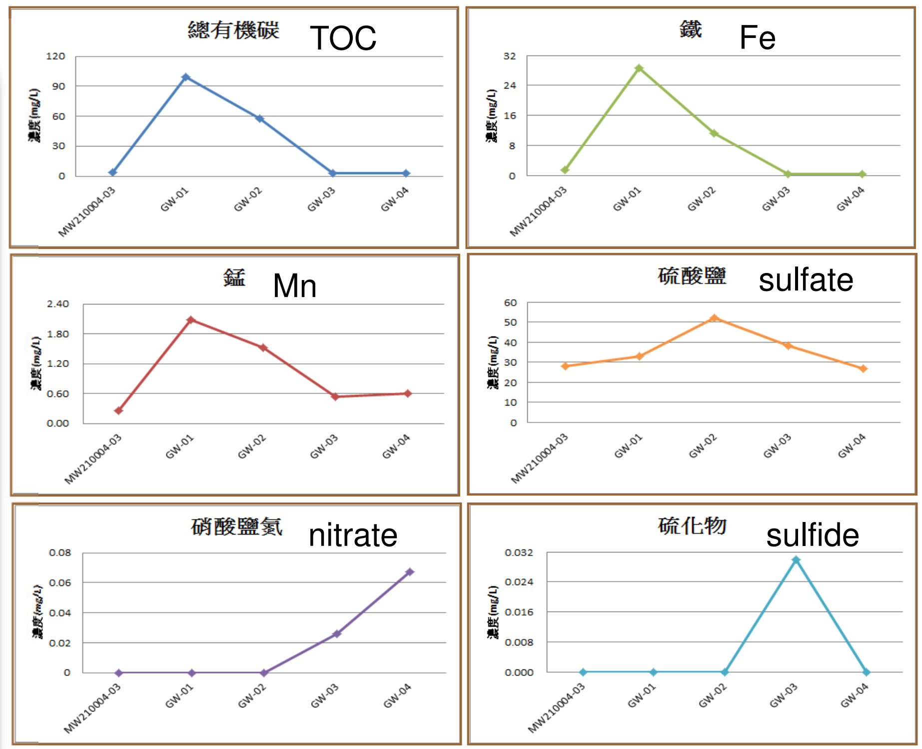


ORP

◆ Low DO and ORP: Subsurface environment is suitable for anaerobic bioremediation.

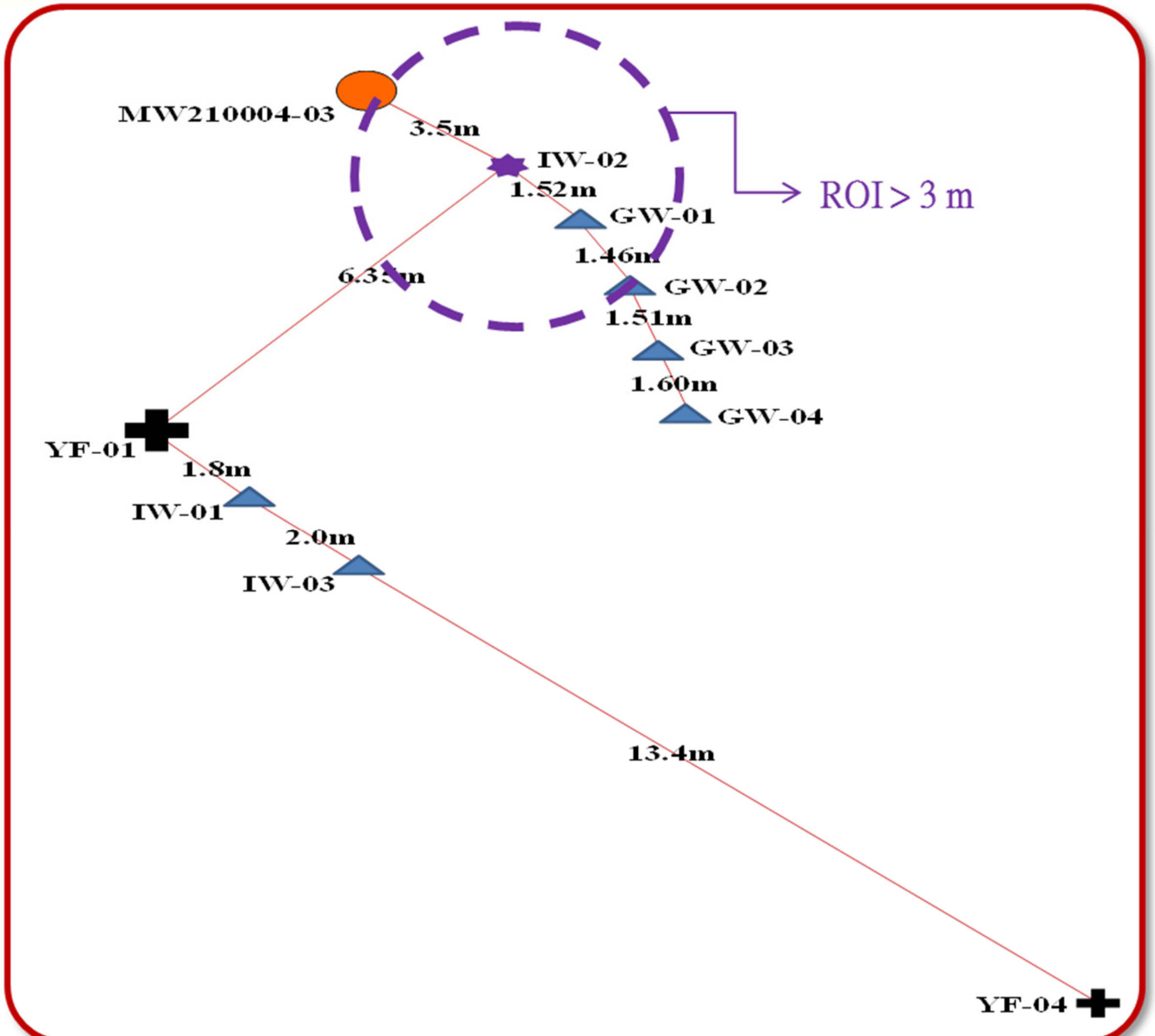
Pilot Test Results





- GW Analytical Data
- TOC > 15 mg/L in GW-01 and GW-02
- Nitrate = ND in GW-01 and GW-02

Pilot Test Results

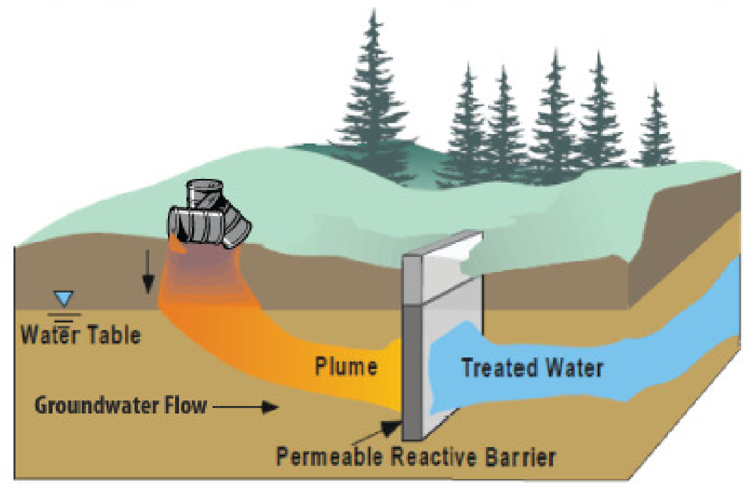


Analysis	MDL	IW-02 102.07.04 10.5m	IW-02 102.08.29 10.5m
DO	–	2	1.5
ORP	–	27.7	-60
Sulfate	2.19	9.0	5.2
Nitrate-N	0.0112	ND	ND
TOC	0.424	558.5	2270.0
Sulfide	0.019	ND	0.71
VC	0.0001	***0.0356***	ND
cis-1,2-DCE	0.00011	***0.743***	ND
TCE	0.00012	0.00580	ND

Injection System

◆ **Geoprobe® injection**

– Shorten the remediation time
– Easier to Infuse EOS ® into underground



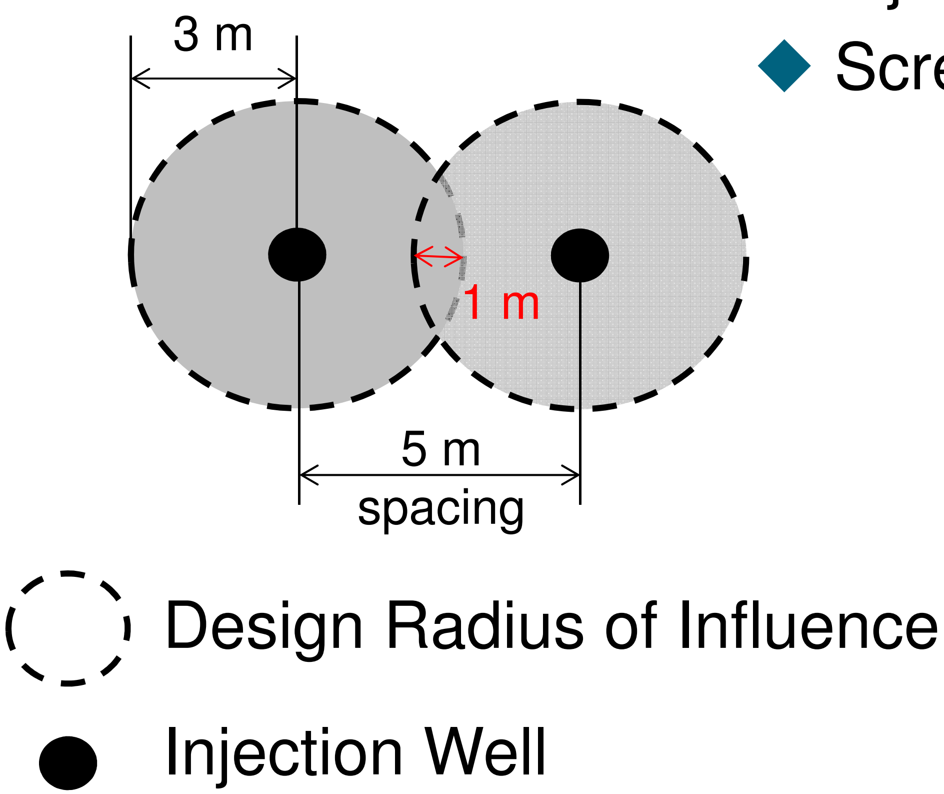
PRB treats a plume of groundwater contaminants.

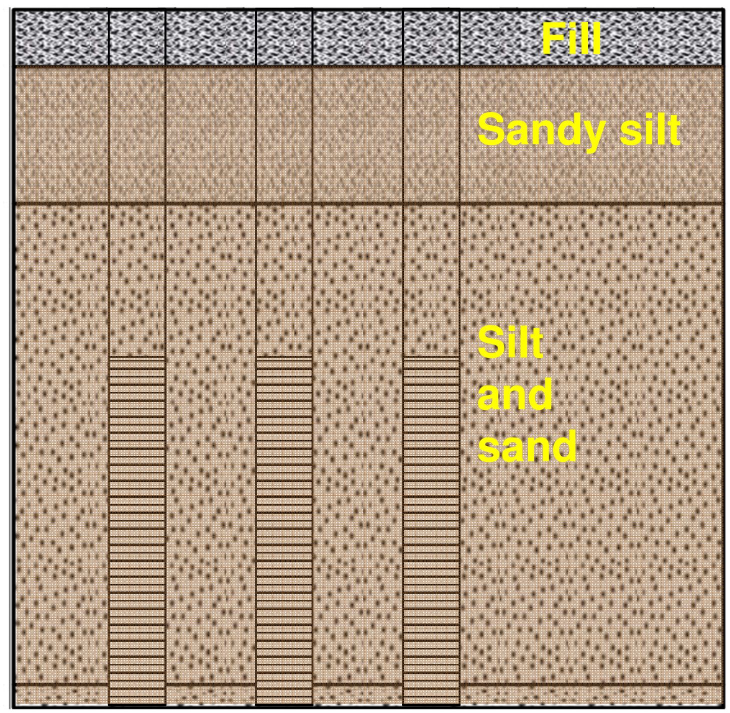
◆ **Permeable bio-reactive barrier**

– Injection wells are located at the down-gradient to prevent the migration of the contaminants.
– The required remediation time depends on the groundwater flow rate.

Specification of Injection Well

- Injection Well Depth = 11~15 m
- Screened interval = 6 m

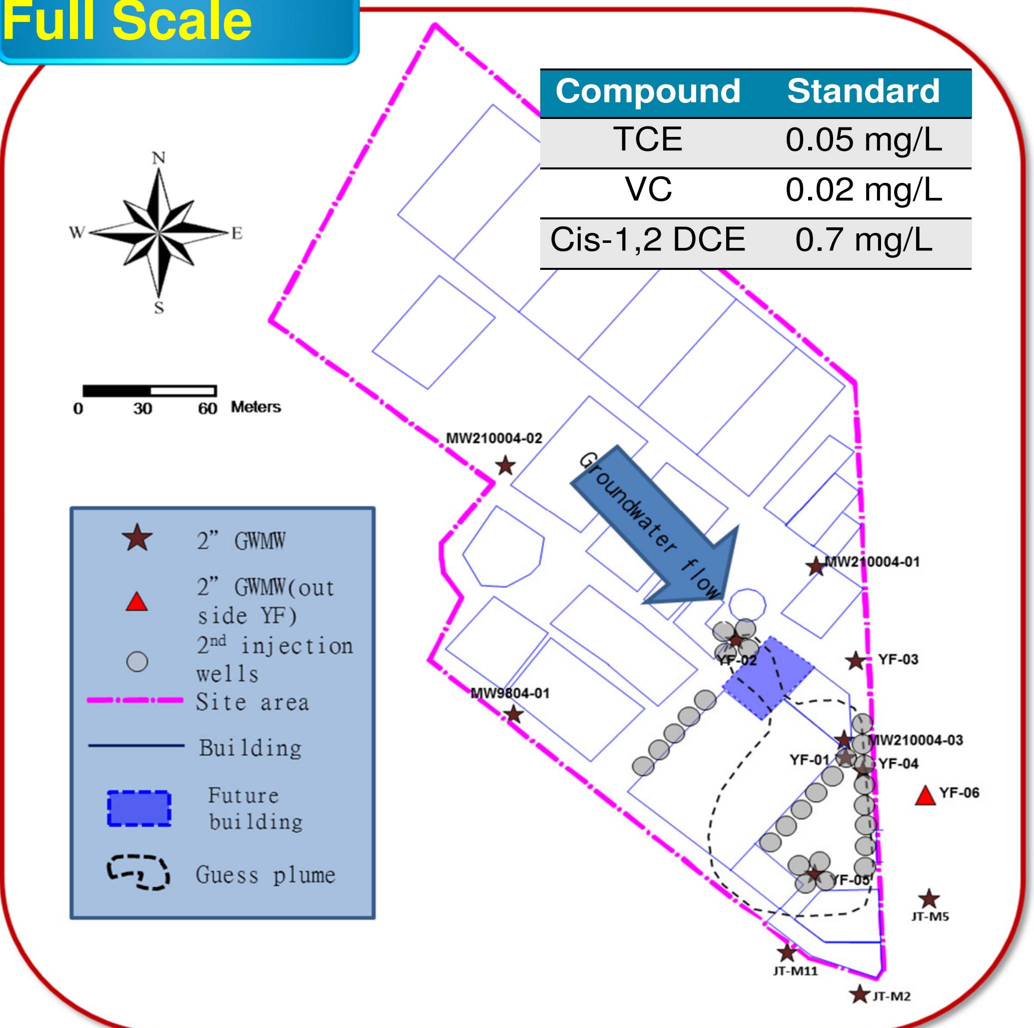




Identified during injection well installation

Full Scale Remediation

Full Scale



Compound	Standard
TCE	0.05 mg/L
VC	0.02 mg/L
Cis-1,2 DCE	0.7 mg/L

- **Remedial action objectives**

  All VOCs conc. below the TW EPA GW standards

- **Injection wells**

  YF-02、YF-04、YF-05

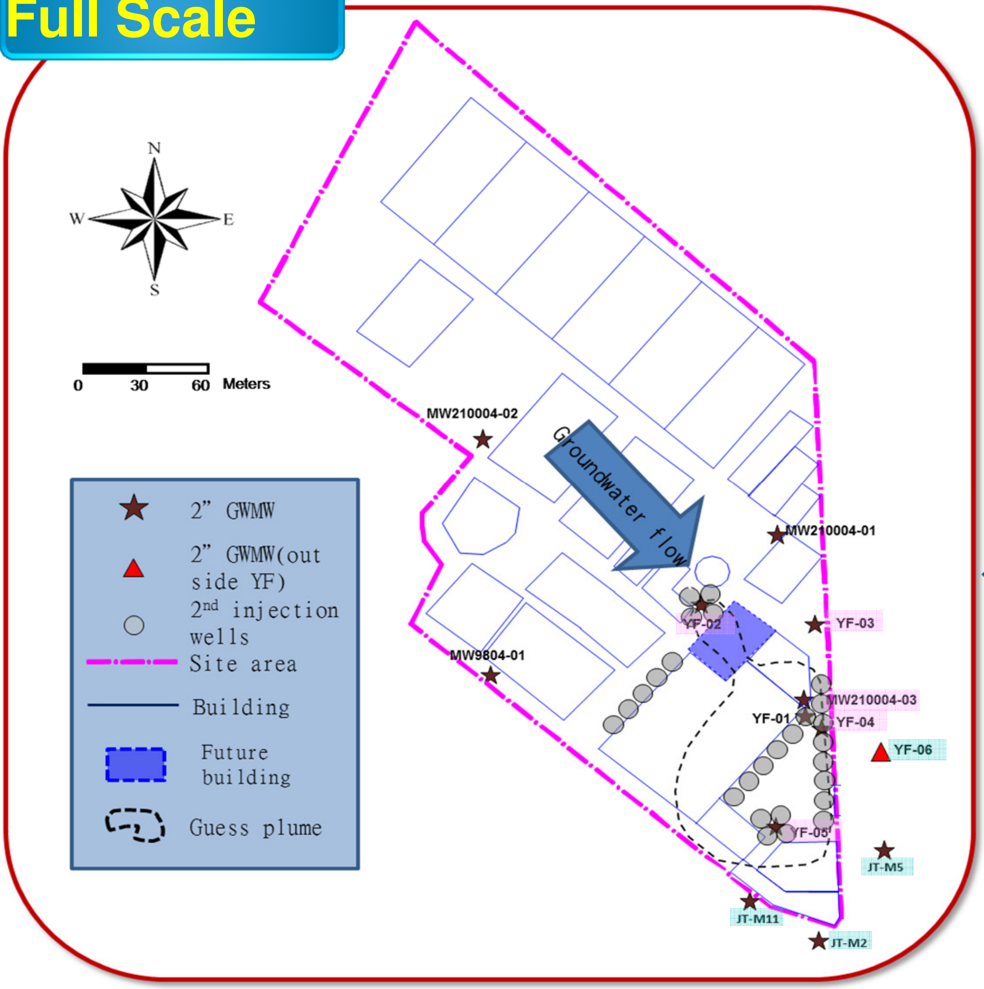
- **Permeable bio-reaction barriers**

  3 barriers will be installed. One of them will be located at the southeast boundary to prevent contaminates migrating offsite.

- **Hot spot injection**

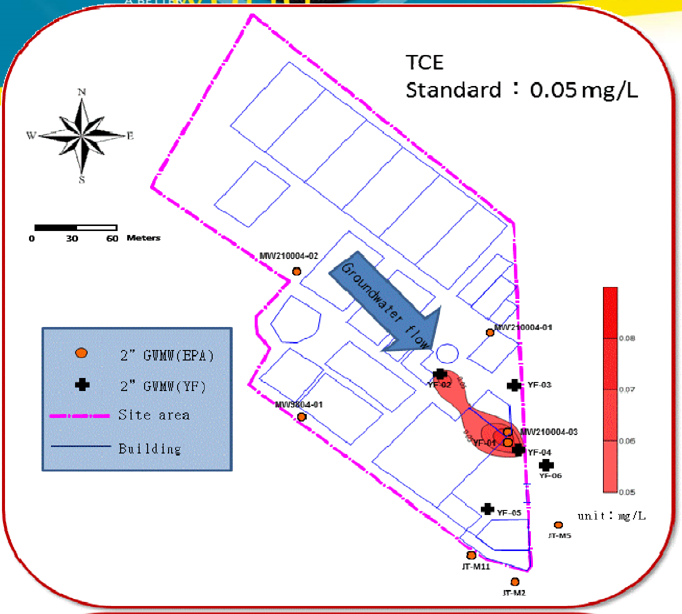
Full Scale Remediation

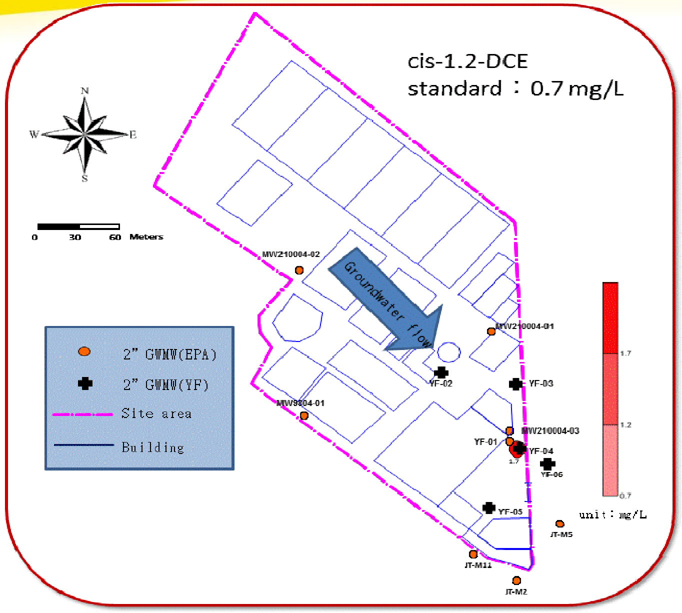
Full Scale

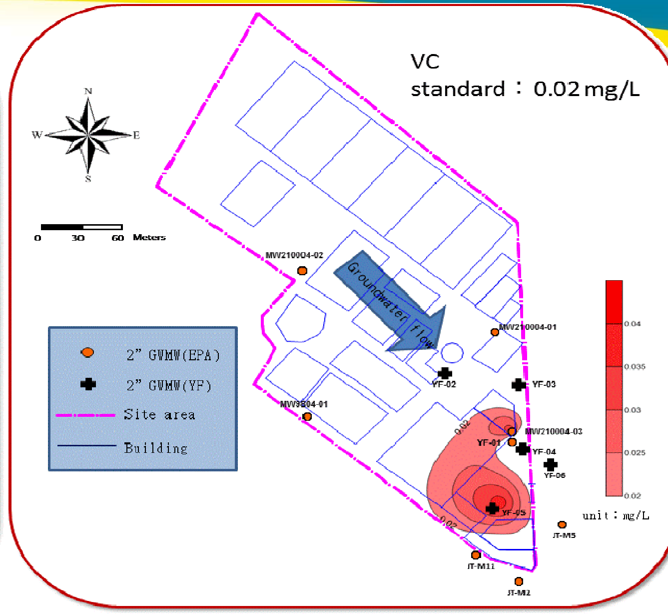


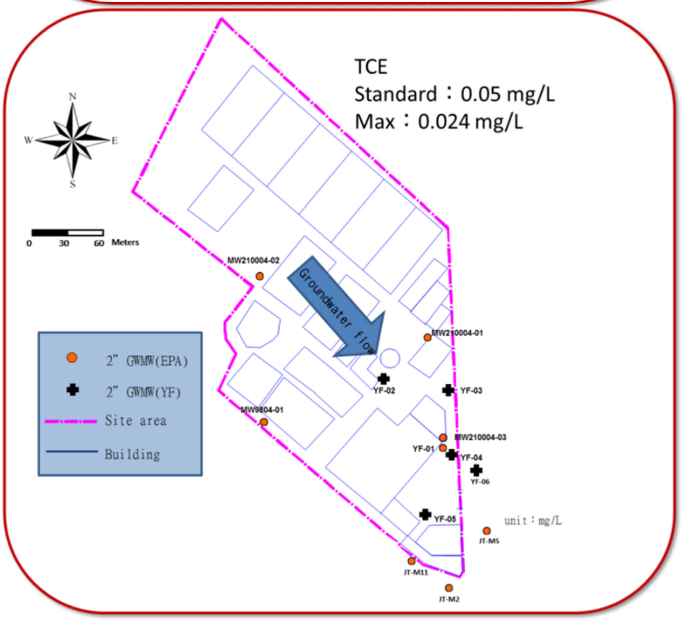
- **Onsite (effectiveness estimate)**
  - **Frequency**：quarterly
  - **Numbers**：5 wells
    (MW210004-03, YF-02, YF-03, YF-04, YF-05)
  - **GW Parameters**：
    Temp., pH, DO, EC and ORP
  - **Analysis**：
    VOCs, TOC, CO_2, alkalinity, SO4^{2-}, NO_3^-, sulfide, Fe, and Mn
- **Off-site (boundary confirmation)**
  - **Frequency**：twice a year
  - **Numbers**：4 wells
    (YF-06, JT-M2, JT-M5, JT-M11)
  - **GW Parameters**：
    Temp., pH, DO and ORP
  - **Analysis**：
    VOCsTOC, CO_2, alkalinity, SO_4^{2-}, NO_3^-, sulfide, Fe, and Mn

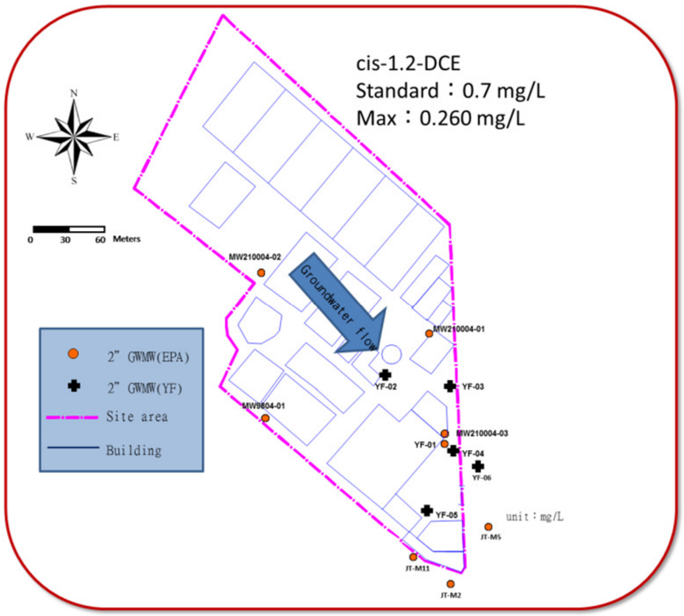
Remediation Results

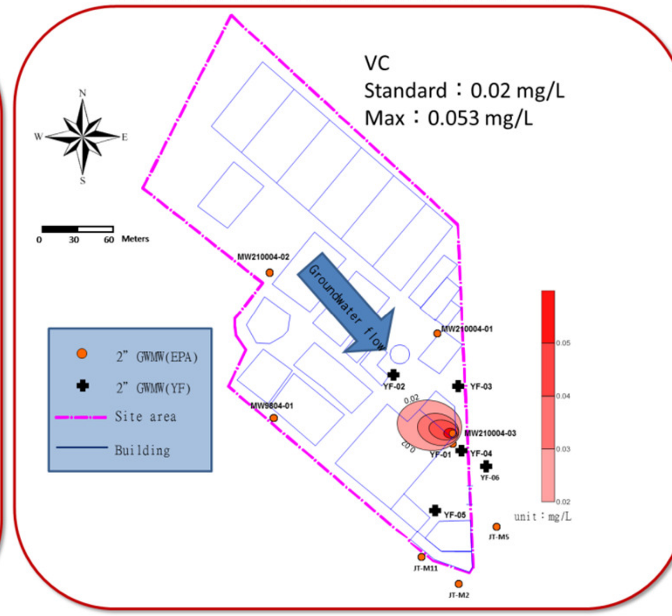




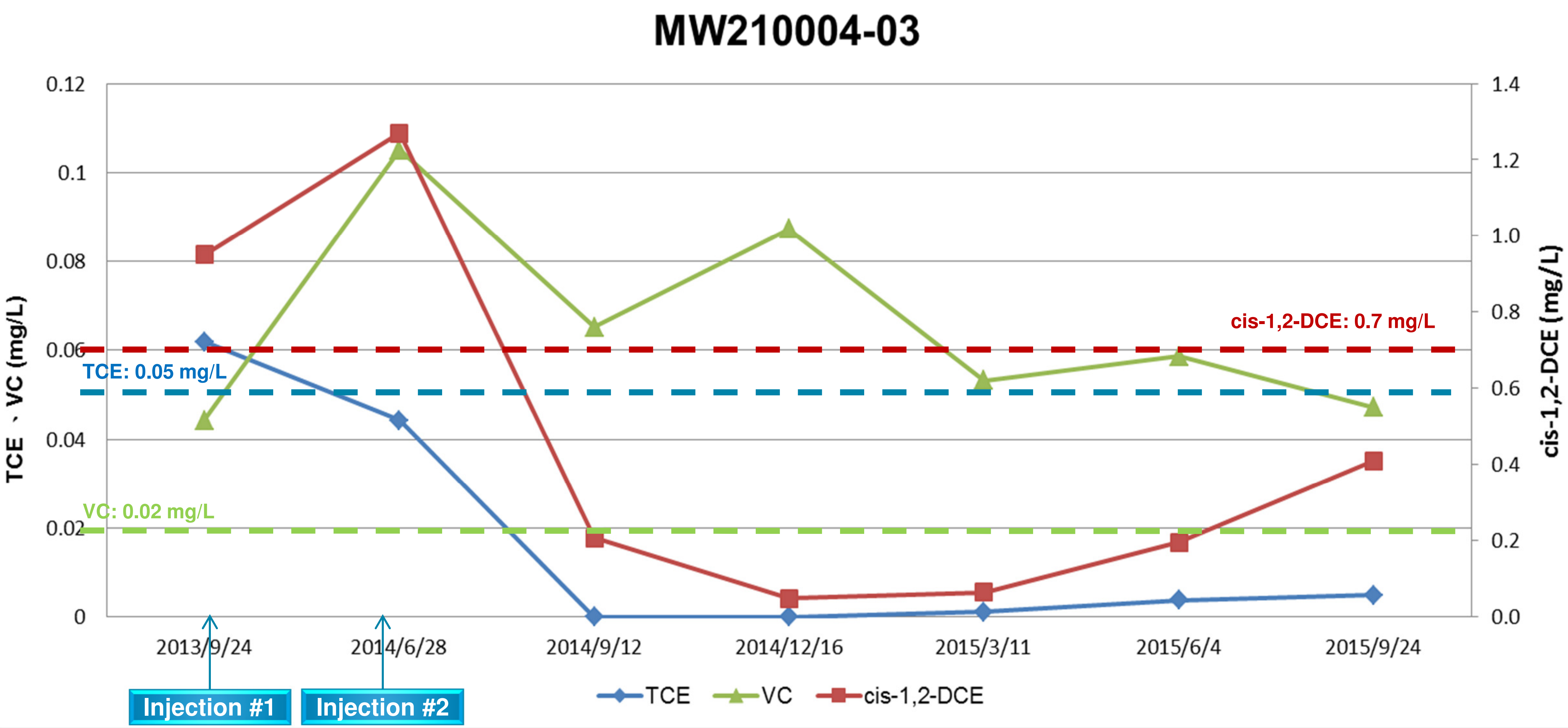








Cl-VOCs Concentrations



CASE STUDY II

1 Background Information

Client Information

- Name：Plant Kuolin, K.H.S. Corp. Ltd.
- History：since 1930
- Business Category: Musical instrument manufacturing
- Capital：1.5 billion NTD (50 million USD)
- Corporate revenue: 590 million USD
- NO. of employees：4,200

Location

NO.399
Fuling Rd.,
Zhongli City
Taoyuan County

Site History

KHS

1930 — Established

1987 — Started operation (Plant Kuolin)

JUPITER

Walden Guitars

MAPEX

majestic

HERCULES STANDS

Altus

2010 — **TCE** (49.3 mg/L) and ***cis*-1,2 DCE** (1.03 mg/L) conc. exceeded groundwater standards (0.05 mg/L for TCE and 0.7 mg/L for *cis*-1,2 DCE)

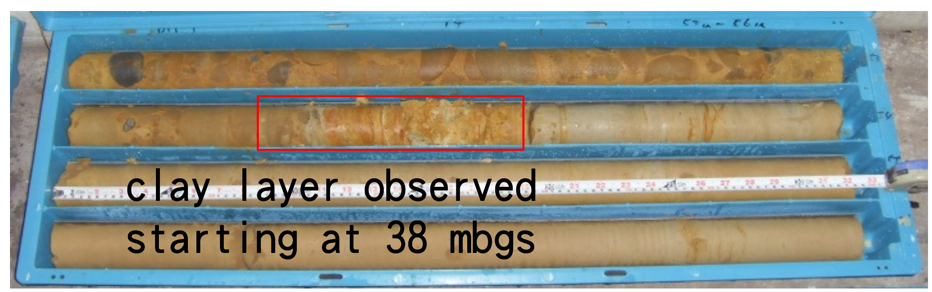
2 Investigation Results

Geological Information

◆ Geology: mostly gravel and sand

Soil texture measurements

Bore hole	Depth (m)	Composition (%)			
		Gravel	Sand	Silt	Clay
BH-01	**20.6~20.7**	**35**	**47**	**18**	**0**
	21.5~21.6	0	55	27	18
	40.0~40.1	0	76	22	2
	53.5~53.6	**0**	**6**	**64**	**30**
BH-02	20.9~21.0	0	33	42	25
	22.0~22.1	0	72	22	6
	37.9~38.0	**0**	**9**	**60**	**31**
	53.3~53.4	**0**	**3**	**79**	**18**



Hydrogeological Information

◆ **Hydrogeology**

- **Groundwater level**

  6.21~12.91 mbgs

- **Hydraulic conductivity**

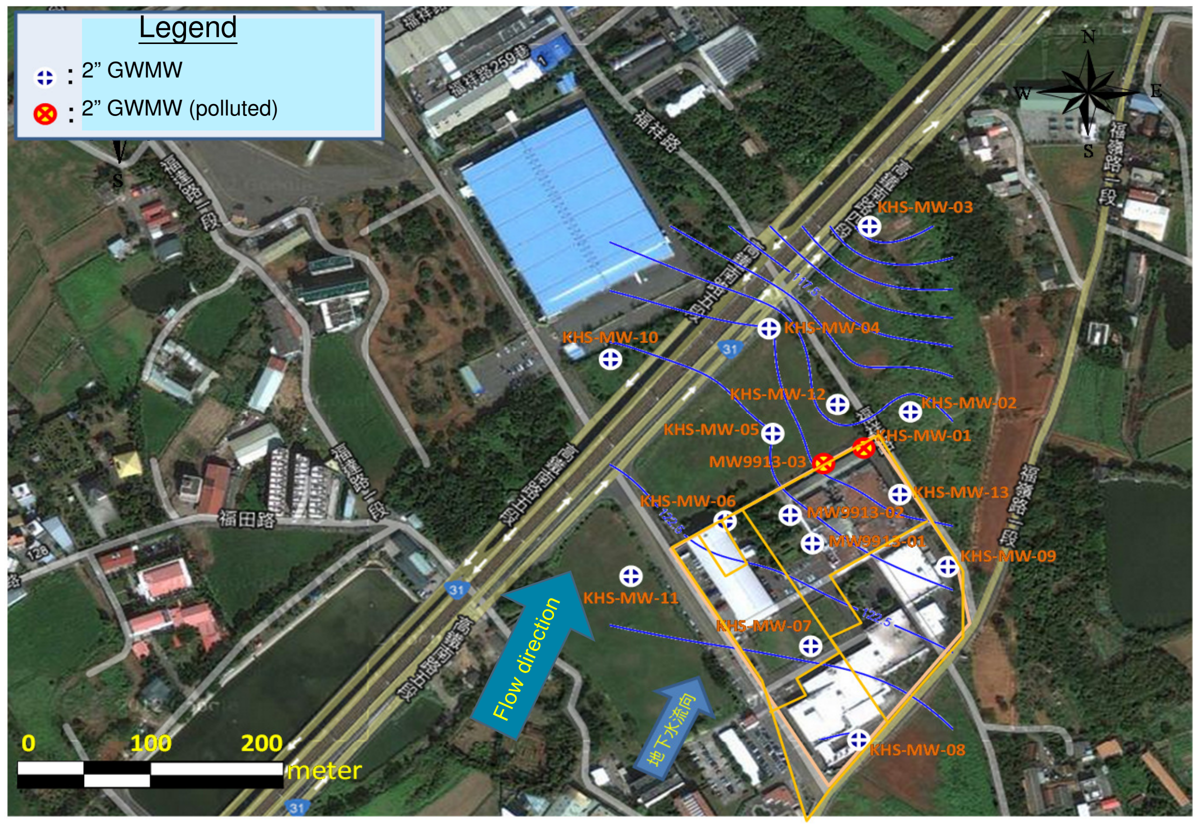
  4.26×10^{-5}~1.78×10^{-2} cm/sec

- **Groundwater flow rate**

  approx. 35 m/year

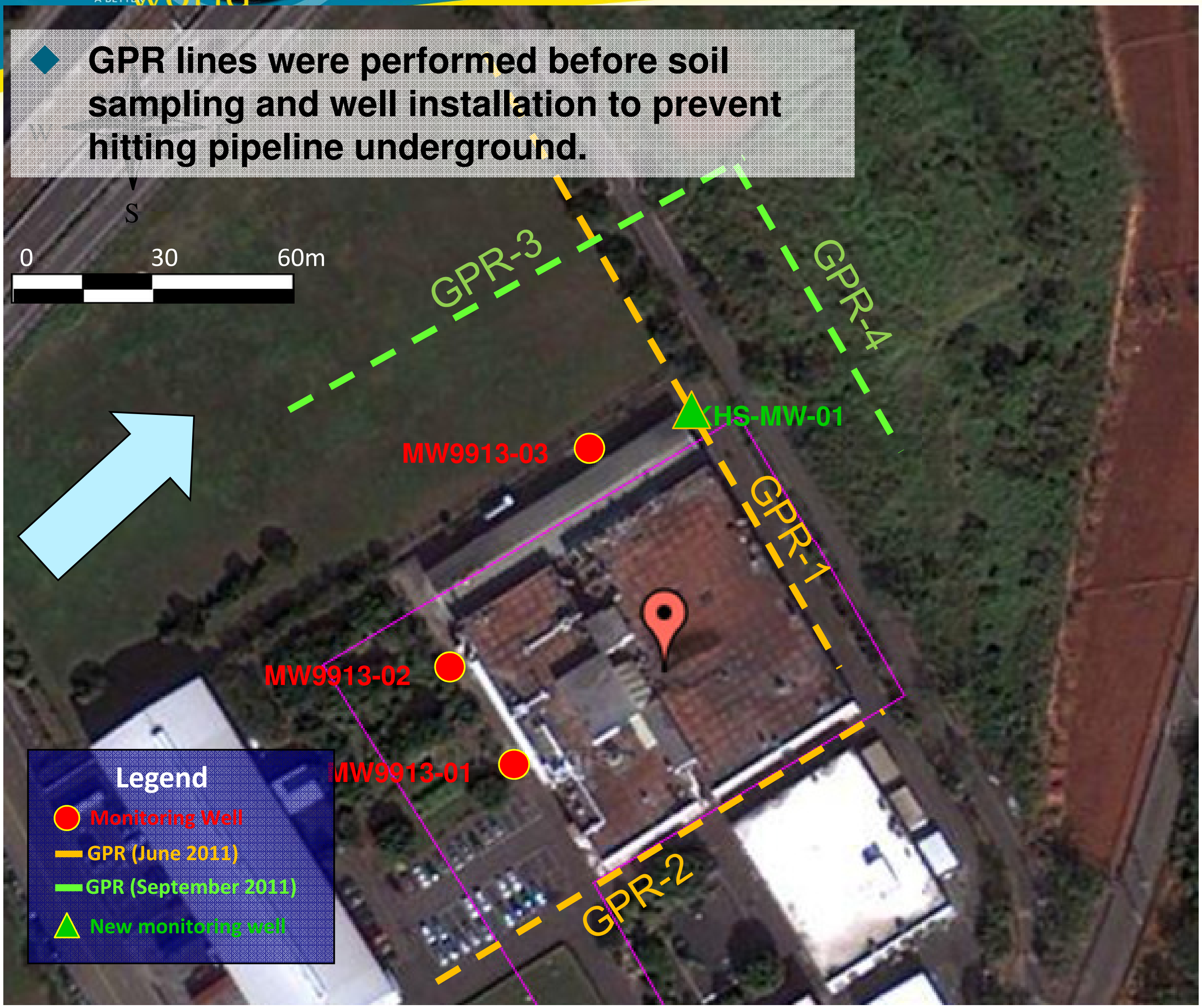
- **Groundwater flow direction**

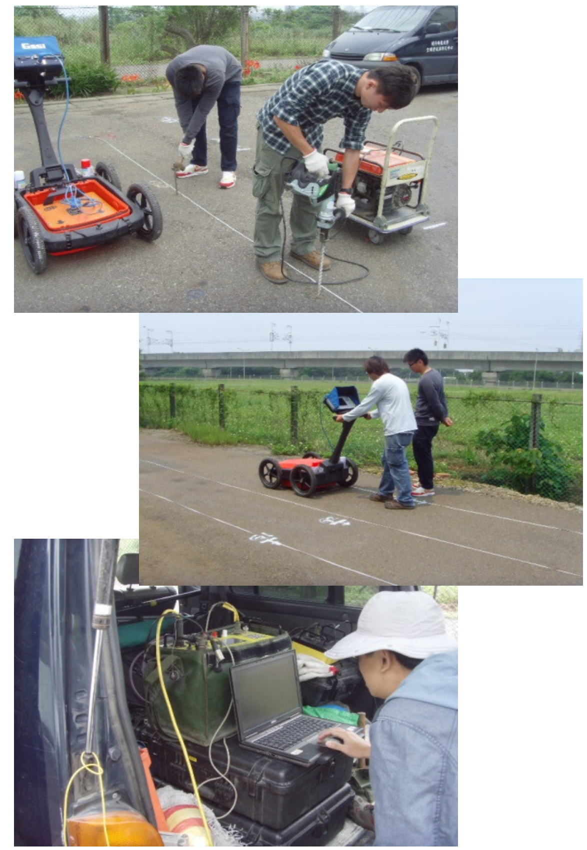
  southwest to northeast



Ground Penetrating Radar, GPR

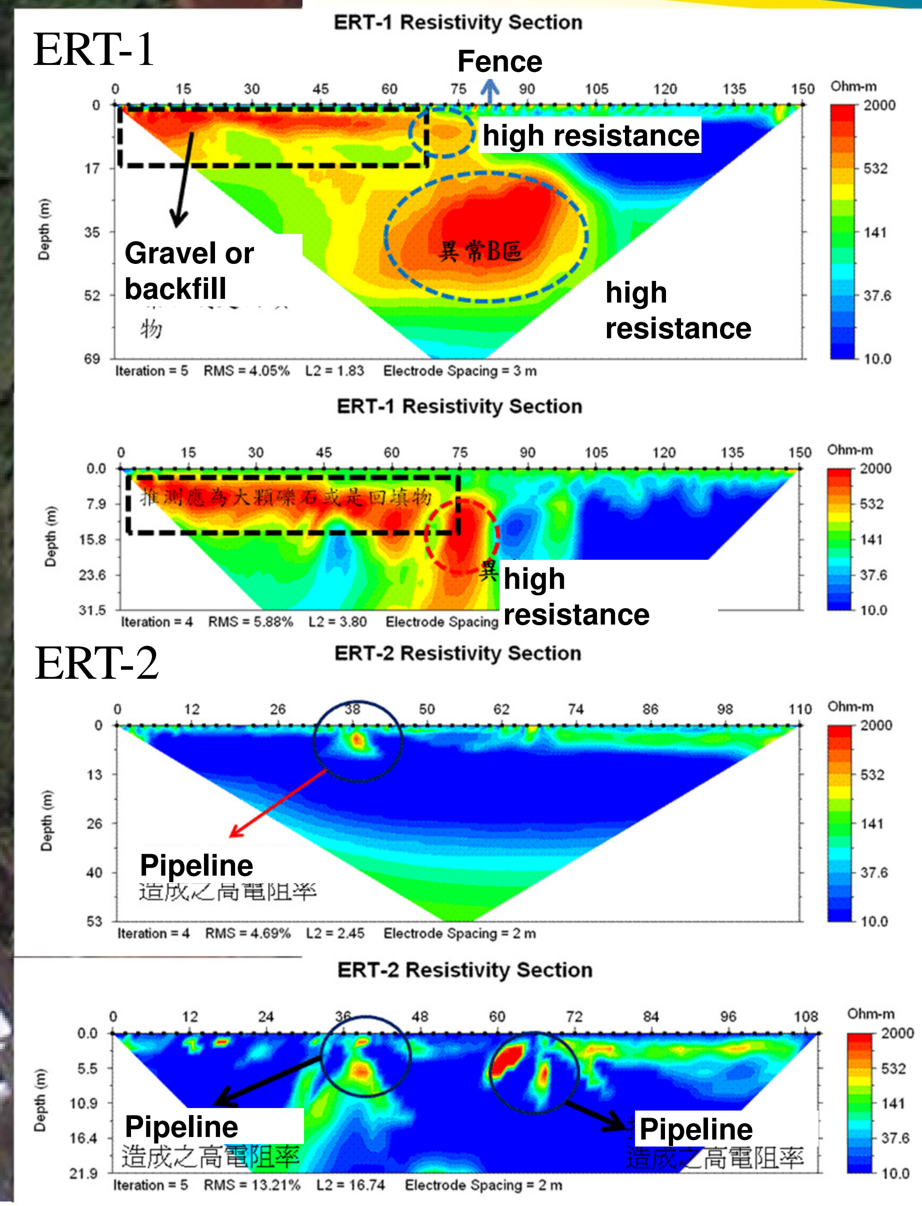
- GPR lines were performed before soil sampling and well installation to prevent hitting pipeline underground.





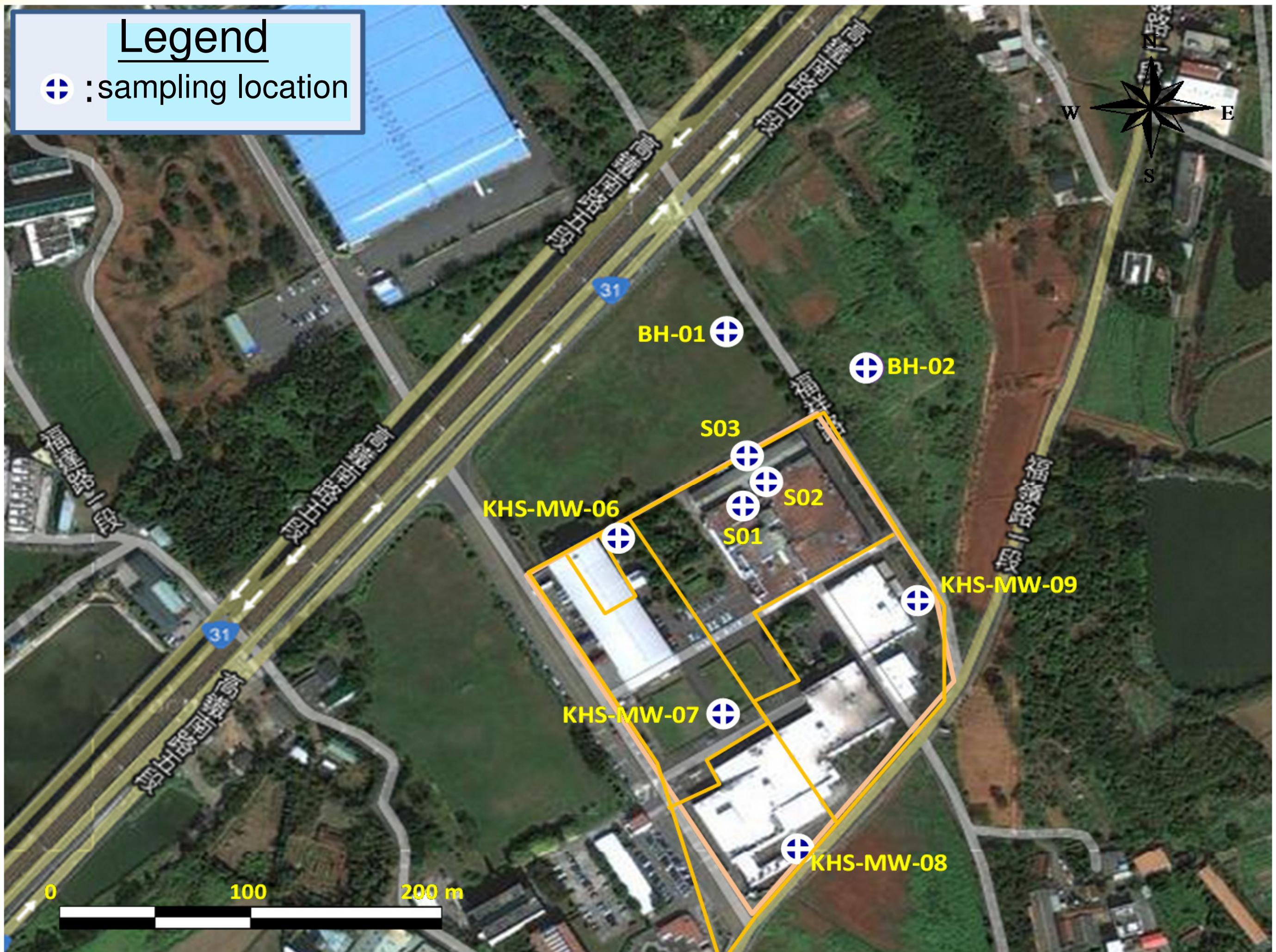
Electrical Resistivity Tomography, ERT

- **The areas showing high resistance represented possible migration of the contaminant plume.**



Investigation Results

9 soil samples collected, no exceedances



Sampling Date: 2012 .11.29~ 2013.1.4

Compound	Standard
TCE	60 mg/kg

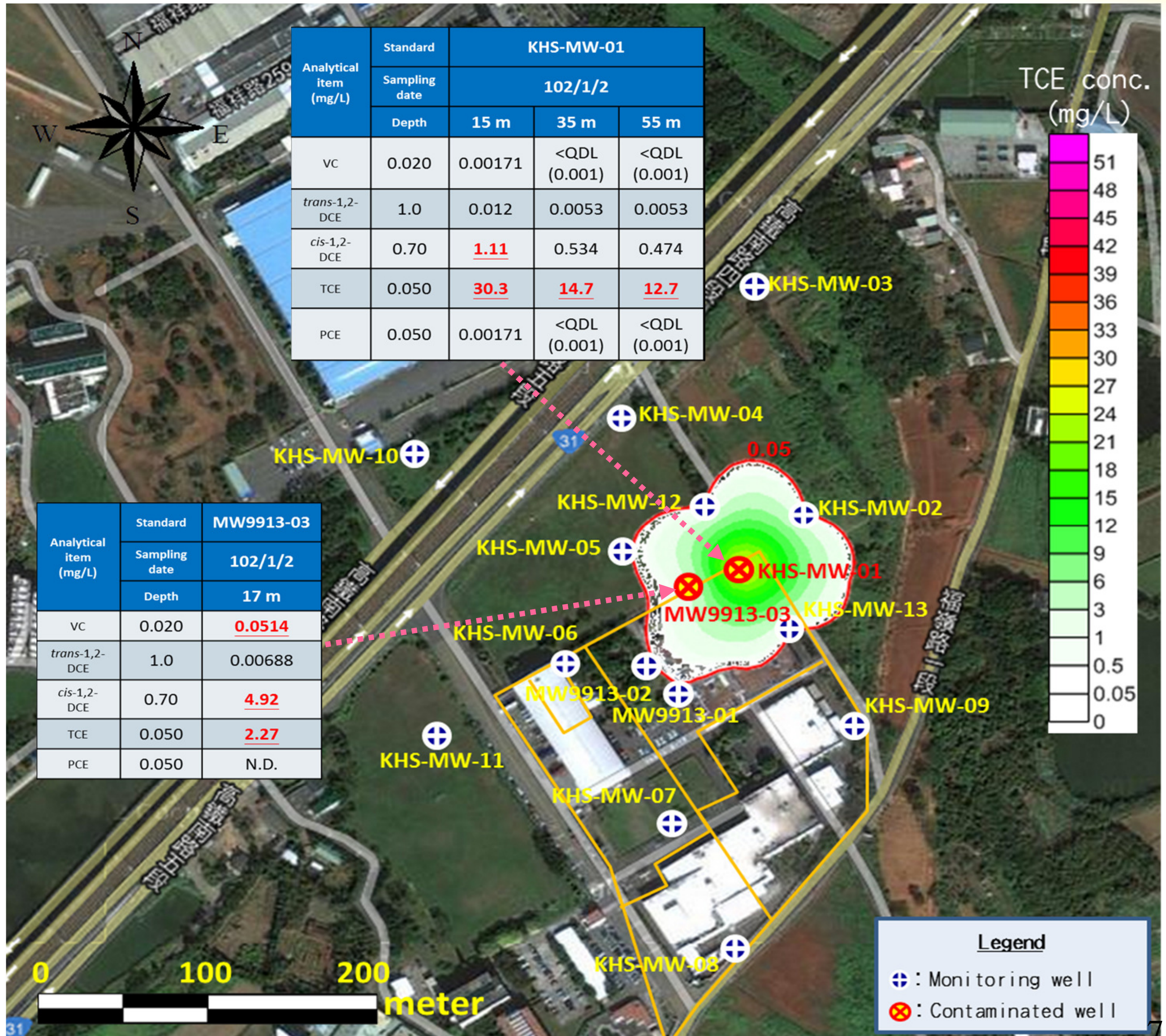
No.	Depth (m)	TCE (mg/kg)
S01	3-3.4	0.39
S02	2-3	0.39
S03	3-3.4	N.D.
BH-01	20.1-20.3 44.3-44.5 53.4-53.6	N.D.
BH-02	20.0-20.1 21.6-21.7 50.5-50.6	N.D.
KHS-MW-06	20-20.6	N.D.
KHS-MW-07	20-20.6	N.D.
KHS-MW-08	20-20.6	N.D.
KHS-MW-09	20-20.6	N.D.

N.D.: Not Detected.

Investigation Results

Analytical Results

- 16 monitoring wells
- Analyses：VOCs
- Chemical of concerns: TCE, *cis*-1,2 DCE, VC
- TCE exceedances: MW9913-03 and KHS-MW-01
- *cis*-1,2 DCE exceedances: MW9913-03 and KHS-MW-01
- VC exceedance: MW9913-03
- Approx. contaminated area: 10,000 m^2



Analytical item (mg/L)	Standard	KHS-MW-01		
	Sampling date	102/1/2		
	Depth	15 m	35 m	55 m
VC	0.020	0.00171	<QDL (0.001)	<QDL (0.001)
trans-1,2-DCE	1.0	0.012	0.0053	0.0053
cis-1,2-DCE	0.70	1.11	0.534	0.474
TCE	0.050	30.3	14.7	12.7
PCE	0.050	0.00171	<QDL (0.001)	<QDL (0.001)

Analytical item (mg/L)	Standard	MW9913-03
	Sampling date	102/1/2
	Depth	17 m
VC	0.020	0.0514
trans-1,2-DCE	1.0	0.00688
cis-1,2-DCE	0.70	4.92
TCE	0.050	2.27
PCE	0.050	N.D.

3 Remedial Approach

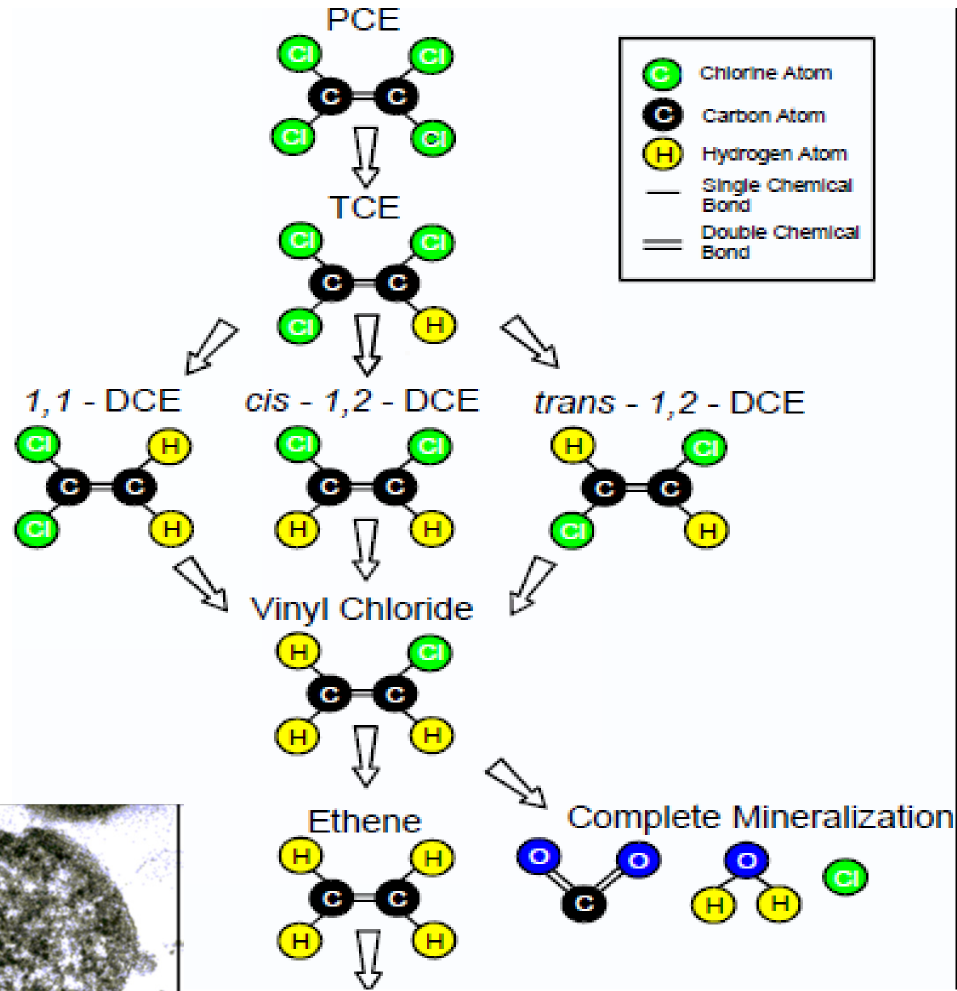
Scope of Work

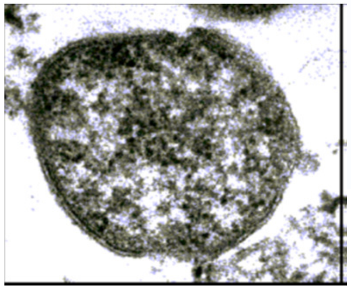
- **Pilot test**
  - Focus on the source area (KHS-MW-01)
  - 1 injection well and 3 observation wells down-gradient
- **Full scale remediation**
  - Remedial design from pilot test to full scale
  - Hot spot injection at KHS-MW-01 and MW9913-03
  - Permeable reactive barrier
- **Groundwater monitoring**
  - 18 wells (on-site and off-site) for 6 years
- **Self-verification sampling**
  - KHS-MW-01 and MW9913-03
- **Quarterly reports, semi-annual reports, and remediation completion report**

Overview of Anaerobic Bioremediation

- Reductive dechlorination: TCE will be degraded to DCE, then to VC under anaerobic conditions.
- *Dehalococcoides* (DHC) must exit in the soil or groundwater.
- Soybean oil ($C_{18}H_{32}O_2$) ferments to H_2 and simple organics

$$C_{18}H_{32}O_2 + 34\ H_2O \rightarrow 18\ CO_2 + 50\ H_2$$

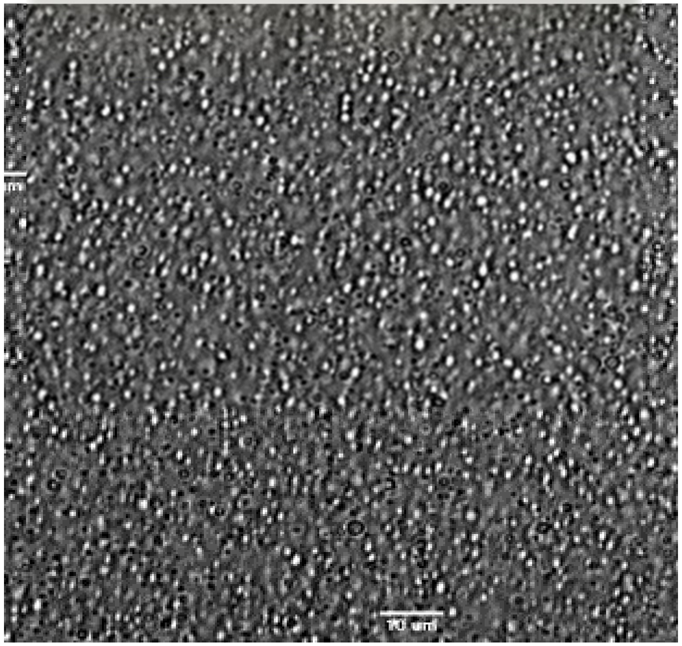




Emulsified Oil Substrate (EOS®)

- **Slow release substrate**
  - **Emulsified soybean oil (food grade)**
  - **Small, uniform droplets**
  - **Negative surface charge to reduce capture by sediments**

Ingredient	wt.%
Refined and Bleached US Soybean Oil	59.8±2%
Rapidly Biodegradable Soluble Substrate	4.0±0.2%
Other Organics (emulsifiers, food additives, etc.)	10.1±0.2%
Organic Carbon	74±2%

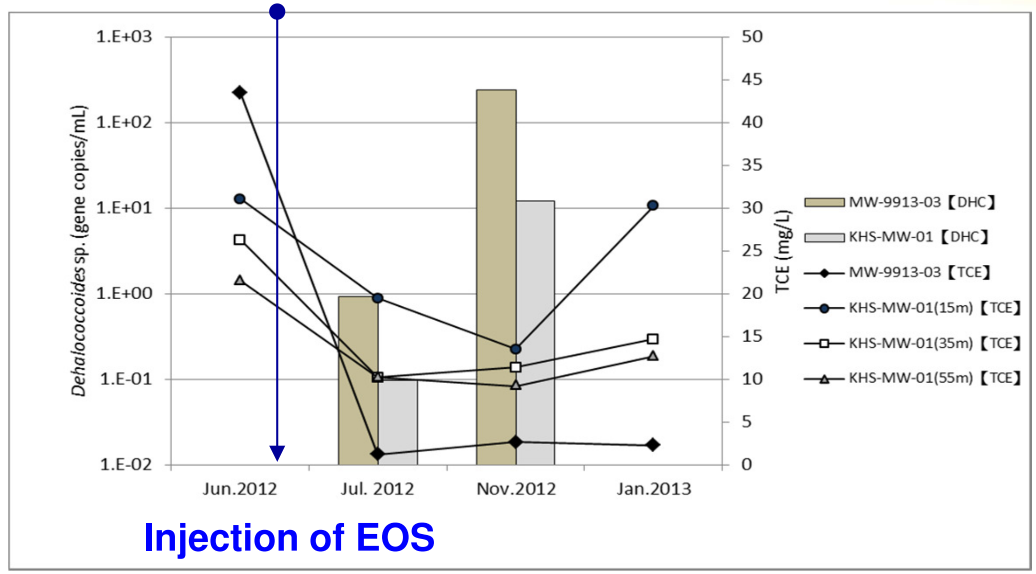


Anaerobic Condition Confirmation

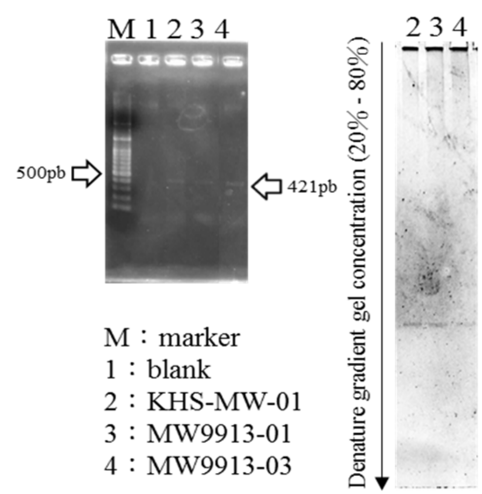
- EOS injected in June 2012.
- After 4 weeks of injection, the concentrations of nitrate and sulfate decreased and the DO value also declined.
- The population density of *Dehalococcoides* sp. increased after the injection.
- PCE concentration at MW-9913-03 decreased from 43.5 mg/L to 1.23 mg/L after 3 weeks.

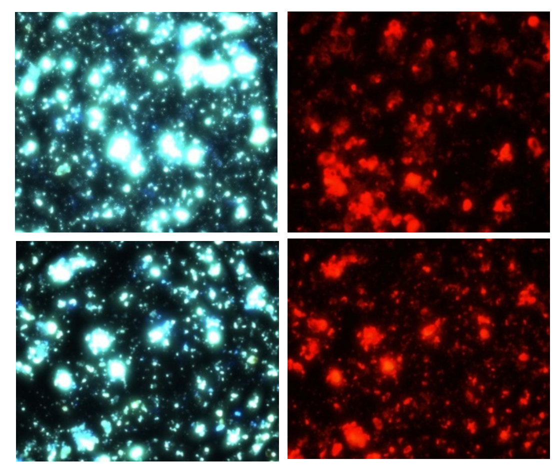
Date	2012/07	2012/11
MW9913-03 (Inj. well)	9.35×10^{2}	2.43×10^{5}
KHS-MW-01 (Obs. well)	9.65×10^{1}	1.21×10^{4}

Unit：gene copies/L



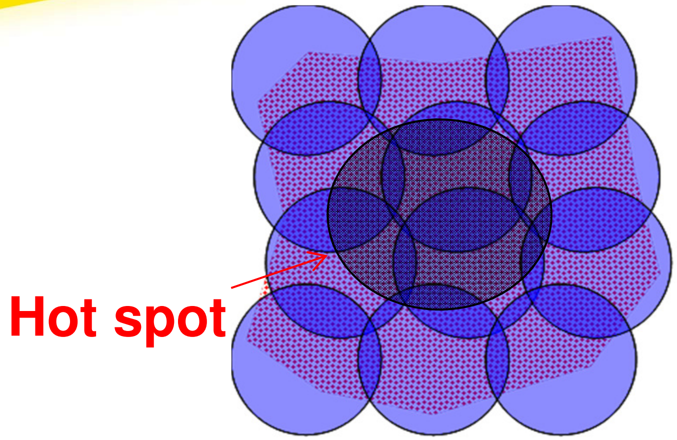
PCE conc. vs. *Dehalococcoides* sp. strains





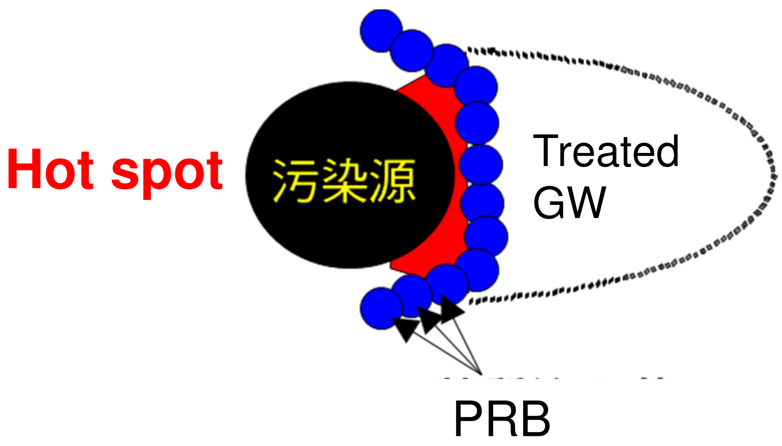
4 Remediation Results

Remediation Technologies



◆ **Hot spot injection**

- Increase the coverage of injection
- Enhance the contact with the contaminant
- Save remediation time



◆ **Permeable reactive barrier (PRB)**

- Injection wells are located at the down-gradient of the hot spot to prevent the migration of the contaminants.
- The required remediation time depends on the groundwater flow rate.

Scope of remediation

Stage I – Pilot test

Baseline sampling

- Obtain baseline concentrations in KHS-MW-01
- Analysis: VOCs, TOC, DHC, and other water quality parameters

Well installation

- Installation of Inj-MW01, ROI-MW-01, and ROI-MW-02
- Perform pressure test

Pilot test

- 2,000 L of 25% EOS, followed by 18,000 L of chase water at KHS-MW-01
- Adjust pressure, frequency, dosage, EOS concentration, etc.

Long-term monitoring

- Inj-MW01, ROI-MW-01, ROI-MW-02
- Analysis: VOCs, TOC, DHC, and other water quality parameters

Data evaluation

- Evaluate the remedial efficiency based on the results

No → **Alternatives**

- ZVI or ISCO
- Conduct pilot test

Yes → **Design parameters**

- Optimize injection parameters for full scale remediation

Stage II – Full scale remediation

Baseline sampling

- Collect groundwater samples from on-site and off-site
- Remedial design based on pilot test

Hot spot injection

- Near MW9913-03 and KHS-MW-01

PRB

- Down-gradient of MW9913-03 and KHS-MW-01

- According to the contamination levels, perform zonation injection

Long-term monitoring

- Long-term monitoring for on-site and off-site monitoring wells

Data evaluation

- Quarterly and semi-annual reports to EPB
- VOC concentrations below the standards for 2 consecutive quarters

Self-verification

- VOC concentrations below the standards

Remediation completion

- Summit remediation completion report to EPB

Pilot Test

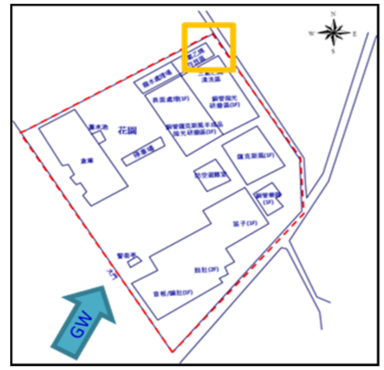
- Purpose

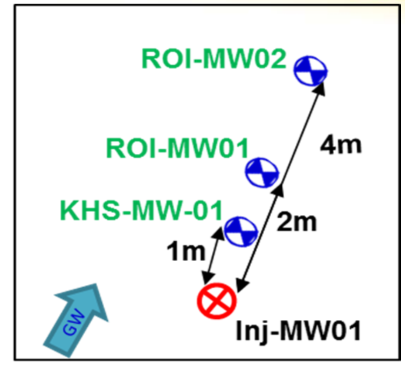
  To obtain information, including ROI, subsurface conditions, injection depth, injection volume, injection pressure, injection frequency, biodegradation rate, etc., for subsequent full scale design
- Injection

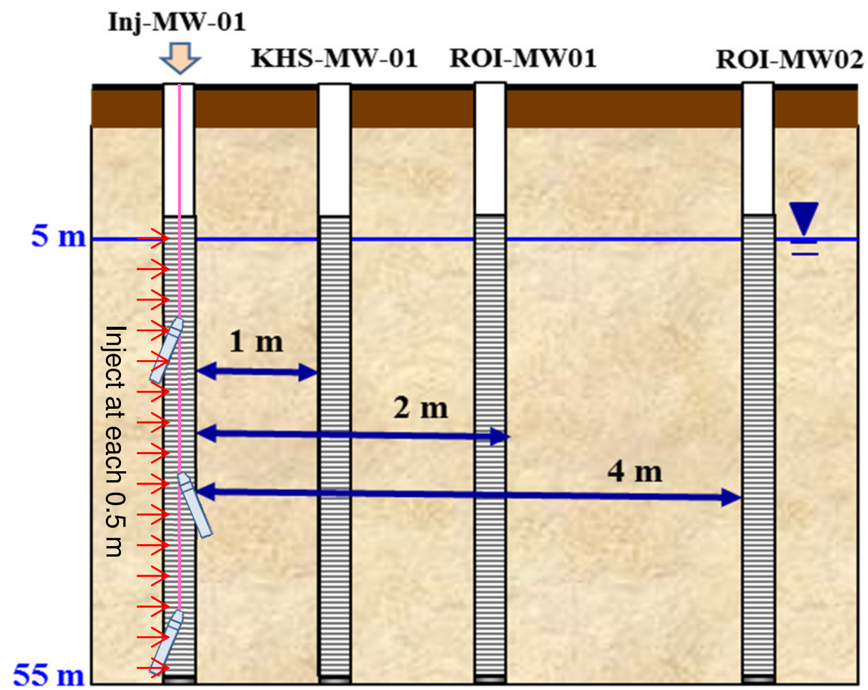
  2,000 L of 25% EOS, followed by 18,000 L of chase water at KHS-MW-01
- Observation wells
  - KHS-MW-01 (1 m down-gradient)
  - ROI-MW01 (2 m down-gradient)
  - ROI-MW02 (4 m down-gradient)
- Analysis

  VOCs, TOC, DHC, and other water quality parameters
- Timeline

  Complete in 12 months

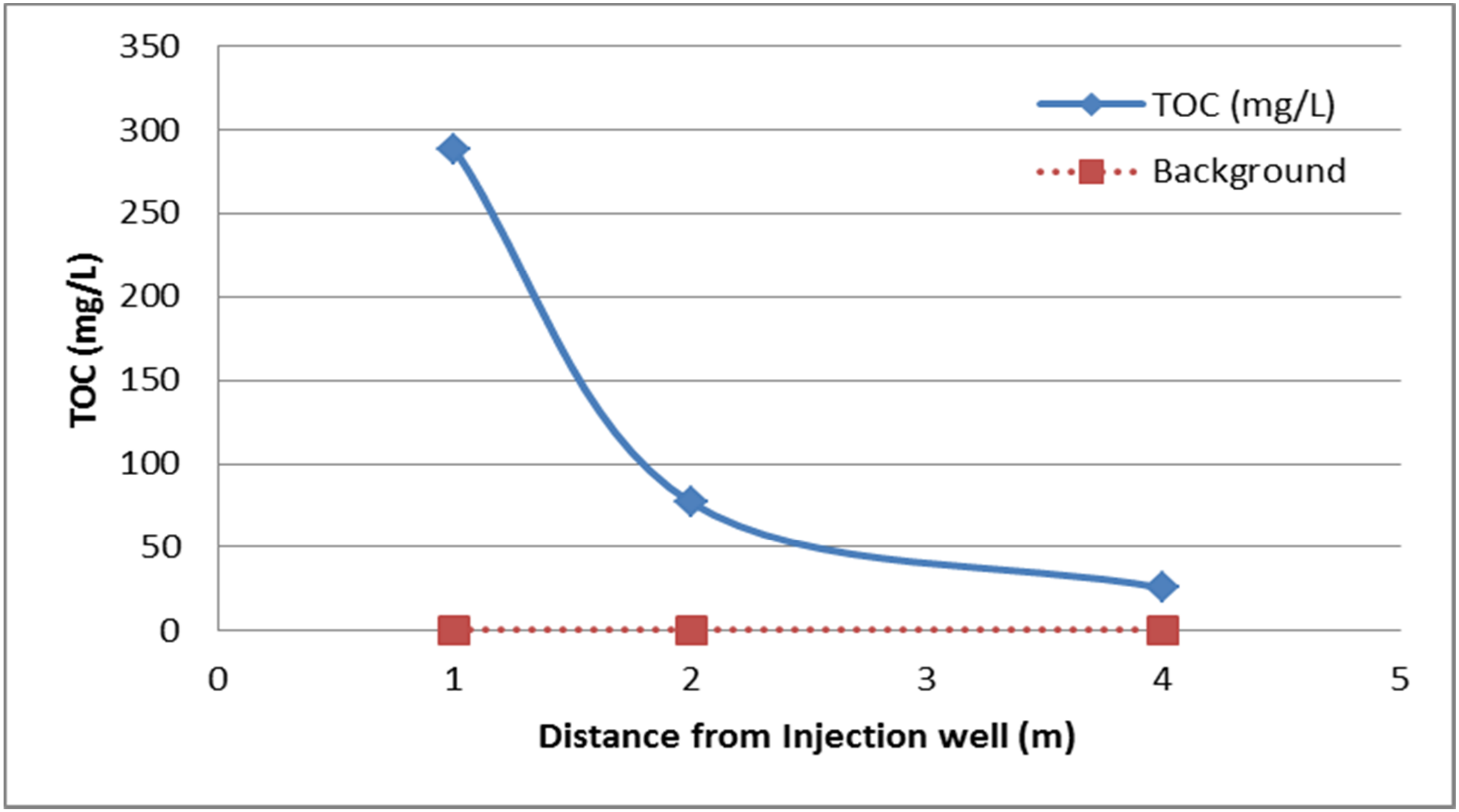






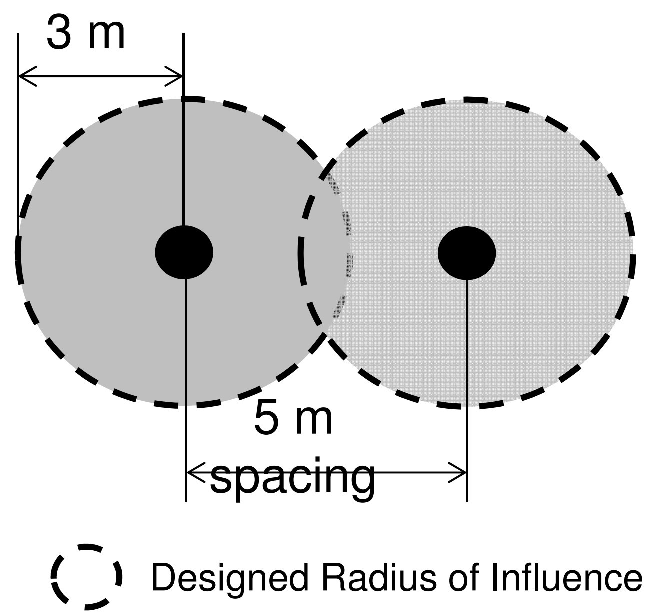
Conceptual diagram of pilot test

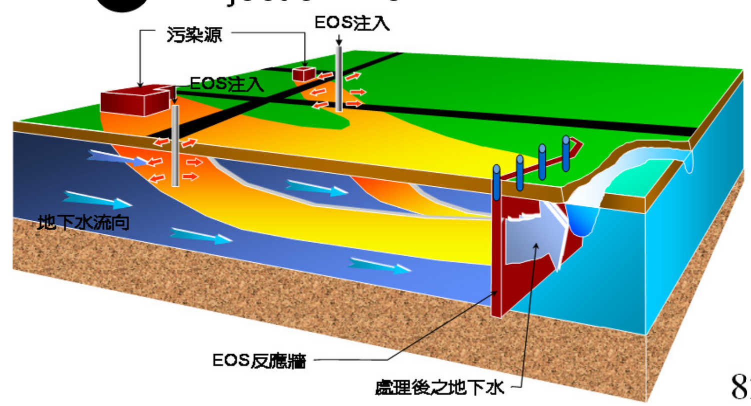
Radius of Influence



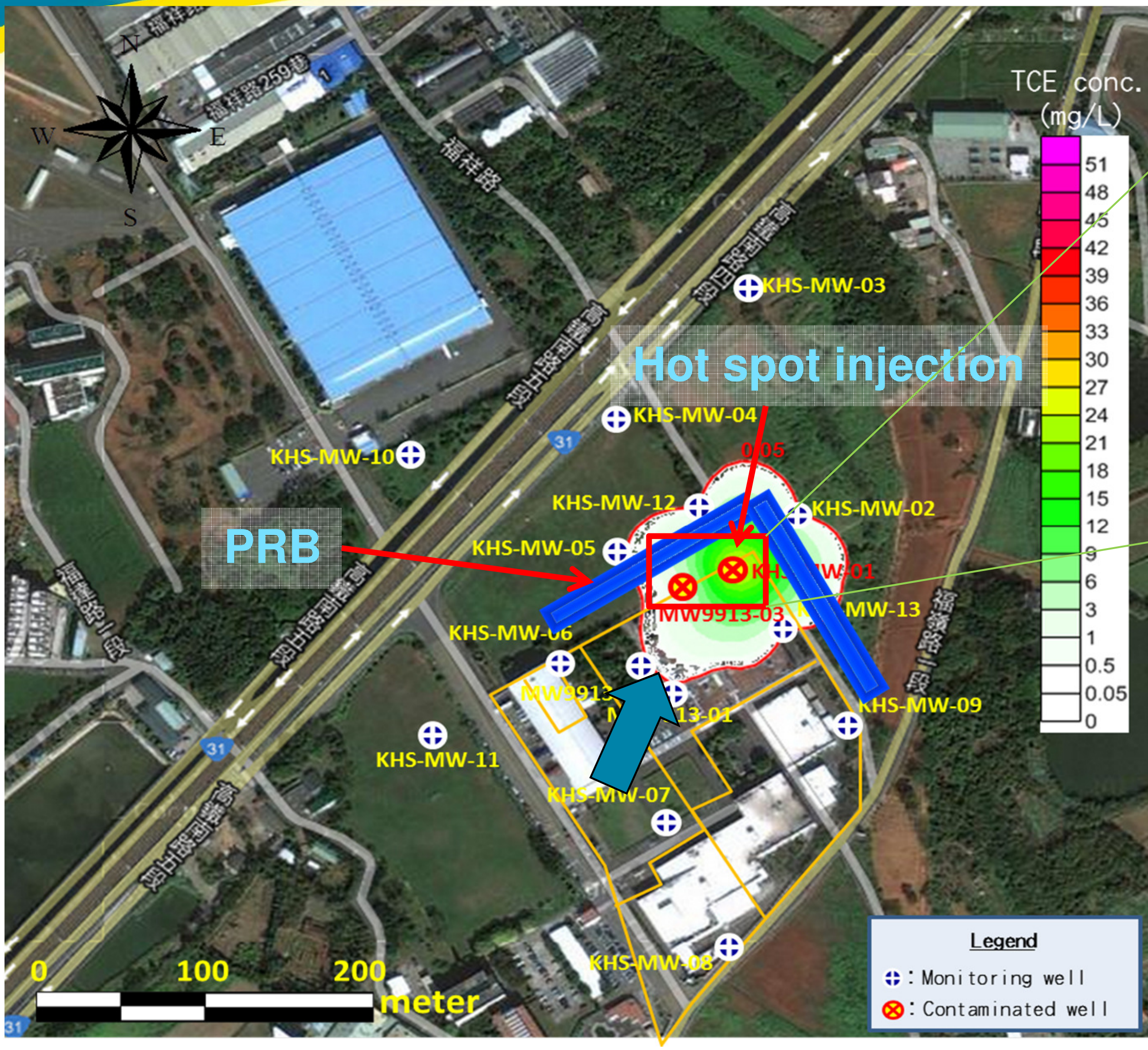
PRB Design

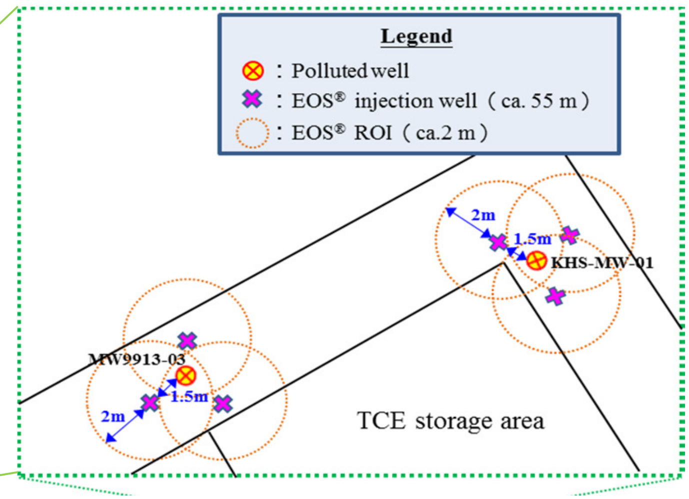
◆**PRB**





Hot Spot Injection





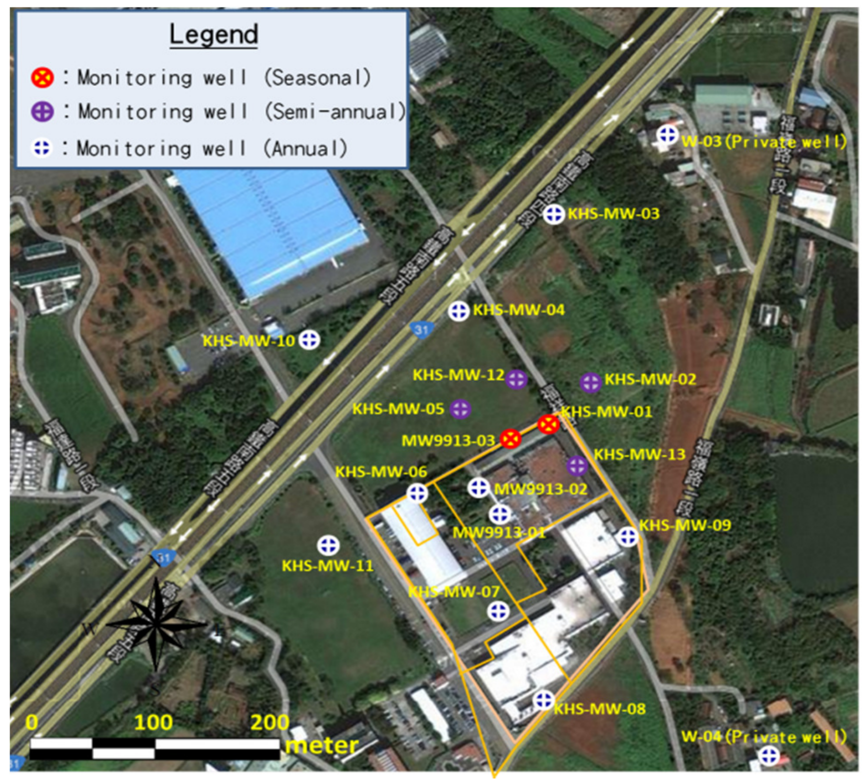
- **Hot spot injection**
  - Near MW9913-03 and KHS-MW-01
  - Designed ROI: 2 m
  - 3 injection wells for each hot spot

GW Monitoring

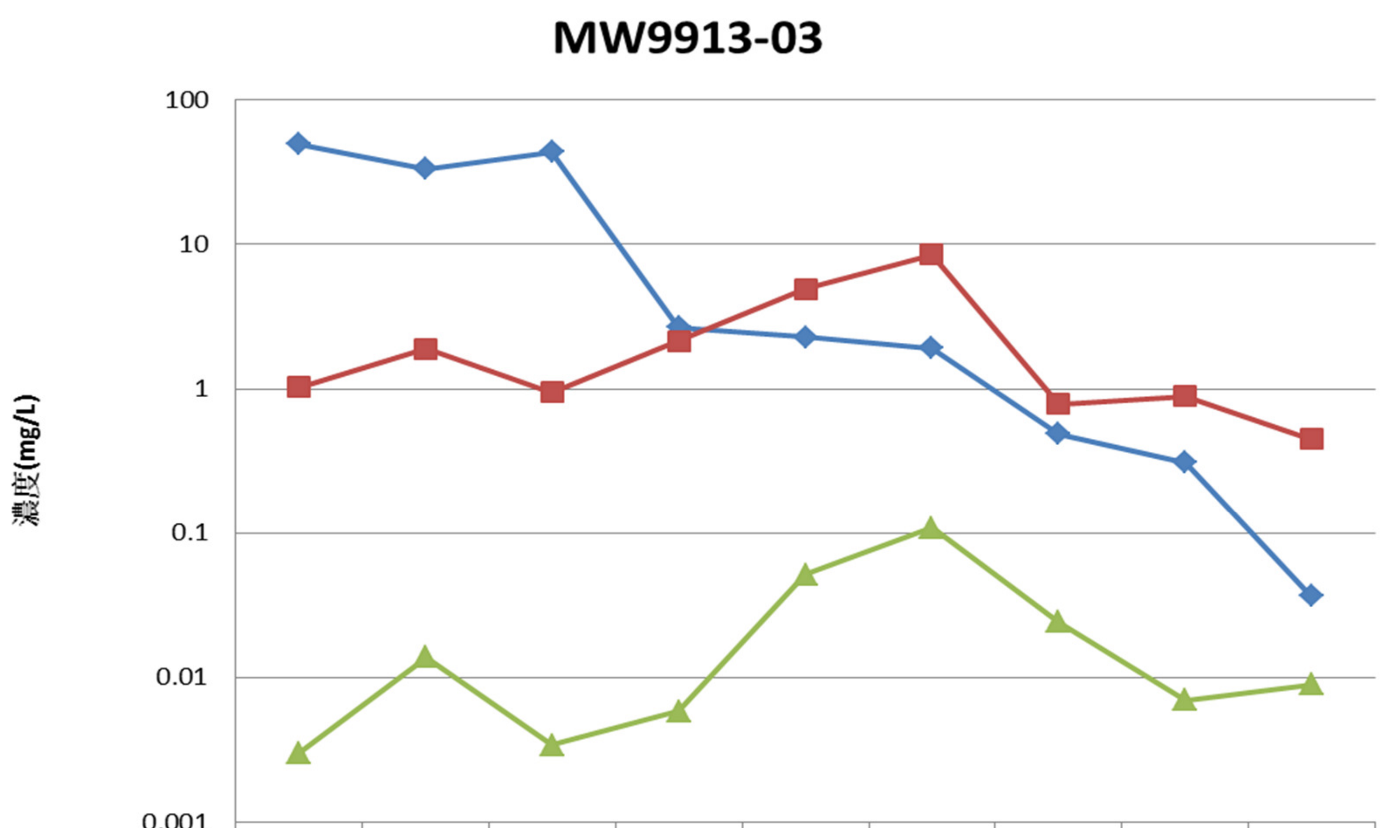
- **Long-term monitoring**
  - A total of 18 monitoring wells
  - Quarterly, semi-annually, and annually
  - Analysis including VOCs, TOC, DHC, water quality parameters, etc.
  - 6 years

Work content		Parameters	Frequency	Location
Hot spot area	GW sampling	VOCs, TOC, DHC strain counts, sample appearance, pH, DO, EC and ORP. If the concentration of EC decreases significantly, the sample will perform ethylene measurement.	Quarterly	MW9913-03 KHS-MW-01
Downstream area of hot spot area	GW sampling	VOCs, TOC, sample appearance, pH, DO, EC, and ORP	Semi-annually	KHS-MW-02 KHS-MW-05 KHS-MW-12 KHS-MW-13
Pre-monitoring of surrounding area	GW sampling	VOCs, sample appearance, pH, DO, EC, and ORP	Annually	MW9913-01 MW9913-02 KHS-MW-03 KHS-MW-04 KHS-MW-06 KHS-MW-07 KHS-MW-08 KHS-MW-09 KHS-MW-10 KHS-MW-11 W-03(private well) W-04(private well)

- **Self-verification sampling**
  - VOC concentrations below the standards for 2 consecutive quarters



MW9913-03



	99.11.16	100.07.11	101.06.25	101.11.29	102.01.02	102.07.15	102.10.30	104.05.14	104.08.06
TCE	49.3	33.4	43.5	2.65	2.27	1.91	0.488	0.308	0.0367
Cis-1,2-DCE	1.03	1.89	0.944	2.13	4.92	8.49	0.781	0.888	0.446
VC	0.003	0.0138	0.00342	0.00586	0.0514	0.108	0.0241	0.00698	0.0089

THANKS FOR YOUR ATTENTION

MWH