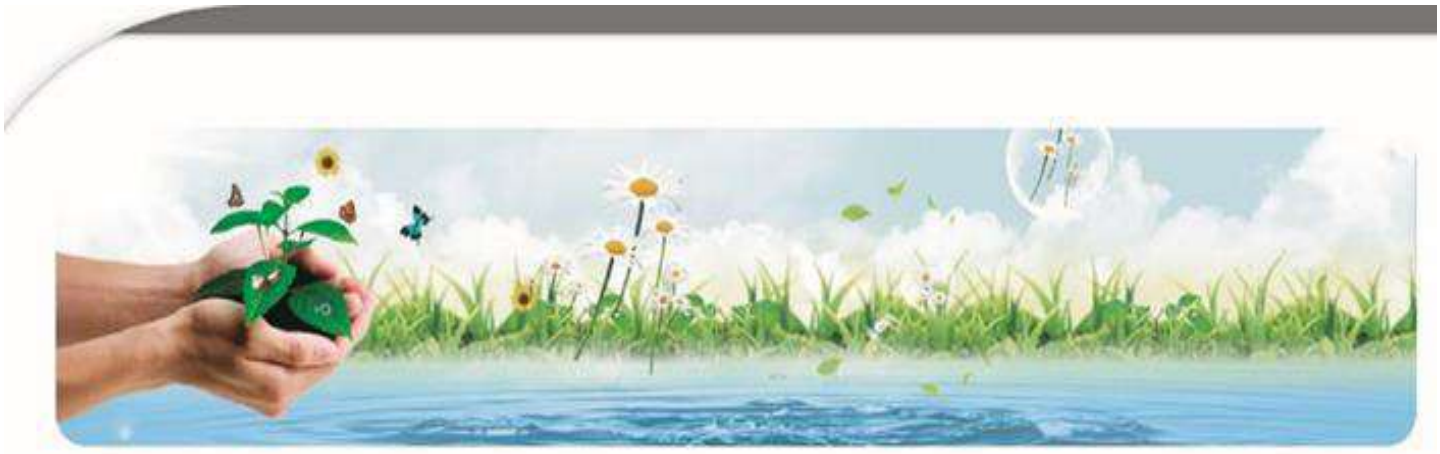

March 18-23, 2019

2019 International Joint-Research and Training Program

Training course of Working Group on ReSAGPAPR

International Workshop on promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

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Room 47118, Room 47222,

Department of Environmental Engineering,

National Cheng Kung University

Tainan, Taiwan

Proceedings

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2019 International Joint-Research and Training Program

Training course of Working Group on ReSAGPAPR

International Workshop on promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Date: March 17 to 24, 2019

Venue: Room 47118, Room 47222 Department of Environmental Engineering, National Cheng Kung University

上課日期：2019 年 3 月 17 日- 3 月 24 日

上課地點：國立成功大學（臺南市）文化參訪/臺南市 場址參訪/高雄市

DAY 1: March 17 (Sunday)

Transportation, Checking-in, and Reception Dinner 交通時間、入住飯店、報到與接待宴(雨荷舞水)

DAY 2: March 18 (Monday)

- Venue: Room 47118、Room 47222

Time 時間	Activity/Presentation Title 活動/標題	Presenter/Host 講師/主持人
08:30- 09:00	Registration 報到	成功大學環工系林財富教授 成功大學環工系黃良銘教授 Prof. Tsair-Fuh Lin Prof. Liang-Ming Whang National Cheng Kung University
09:15- 10:00	**Opening Ceremony** Minister Tzi-Chin Chang, Taiwan Environmental Protection Administration The Secretary General Professor Ching-Chang Lee, NCKU Director Tsair-Fuh Lin, Tainan Hydraulics Laboratory, NCKU Chair Yee-Lin Wu, Aerosol Laboratory, NCKU **開幕式** **張子敬 署長 行政院環保署** **李俊璋 主任祕書 國立成功大學** **林財富 主席 國立成功大學** **吳義林 系主任 國立成功大學**	
10:00- 10:10	Group Photo 大合照	

Topic 1: Soil and Groundwater Protection- Current Status and Future Directions 主題一、土壤及地下水保護之現況與未來方向		
10:10- 10:20	Overview of the Workshop 研習會綜述	Prof. Tsair-Fuh Lin National Cheng Kung University 成功大學環工系林財富教授
10:20- 11:10	Soil and Groundwater Protection in Asia: Status and Future Research and Practices 亞洲土壤及地下水環境保護：現況與未來之研究及實務發展方向	Prof. Tsair-Fuh Lin National Cheng Kung University 成功大學環工系林財富教授
11:10- 12:00	Soil and Groundwater Protection in Taiwan: Status and Future Directions 臺灣土壤及地下水環境保護：現況與未來方向	Dr. Shyh-Wei Chen Soil and Groundwater Pollution Remediation Funds, Taiwan EPA 環保署土污基管會陳世偉執行祕書
12:00- 13:30	Lunch 午餐	
13:30- 15:00	Bioremediation: Theories and Case Studies in US (for MOST) 生物整治：理論與美國案例(科技部邀請)	Prof. Kung-Hui Chu Texas A&M University, USA 德州農工朱宮慧教授
13:30- 15:00	Soil and Groundwater Pollution Remediation Fund(Room 47222) 土壤及地下水污染整治基金	Dr. Hao-Chun Hung Soil and Groundwater Pollution Remediation Funds, Taiwan EPA 環保署土污基管會洪豪駿博士
15:00- 15:20	Tea Break 茶敘	
15:20- 16:50	Current Research Directions on Groundwater Contamination and Remediation in US(for MOST) 美國地下水污染整治研究方向(科技部邀請)	Prof. Thomas B. Boving University of Rhode Island, USA
15:20- 16:50	Soil and Groundwater Protection in Taiwan - Policy and Regulation (Room 47222) 臺灣土壤及地下水保護-政策與法規	Dr. Ching-Jen Ho Soil and Groundwater Pollution Remediation Funds, Taiwan EPA 環保署土污基管會何建仁博士
18:00- 20:00	Welcome Dinner 歡迎晚宴(香格里拉)	

DAY 3: March 19 (Tuesday)

- Venue: Room 47118

Time 時間	Activity/Presentation Title 活動/標題	Presenter/Host 講師/主持人
Topic 2: Soil and Groundwater Protection- Investigation, Forensics and Risk Assessment 主題二、土壤及地下水環境保護 – 調查、法醫與風險評估		
08:30-10:00	Application of Molecular Biology Tools for Bioremediation – An Introduction 分子生物技術對生物整治之應用-導論	Prof. Liang-Ming Whang National Cheng Kung University 成功大學環工系黃良銘教授
10:00-10:20	Tea Break 茶敘	
10:20-11:50	Contaminated Site Investigation: Case Studies in Taiwan 污染場址調查：臺灣案例研究	Prof. Chih-Jen Lu National Chung Hsing University 中興大學環工系盧至人教授
11:50-13:20	Lunch 午餐	
13:20-14:50	Contamination Site Investigation: Common Methods Employed in Taiwan 污染場址調查：臺灣常見應用技術	Dr. Ming-Daw Che Apollo Technology Co., Ltd. 瑞昶公司副董事長車明道博士
14:50-15:20	Tea Break 茶敘	
15:20-16:50	Risk Assessment for Soil and Groundwater Contamination 土壤及地下水污染之風險評估	Dr. Chih Huang InnoFusion Environmental Management Co., Ltd 創聚環境管理顧問股份有限公司 總經理黃智博士
18:00-19:30	Dinner/ Social Activities (Tainan City Sense) 晚餐	

DAY 4: March 20 (Wednesday)

Tainan Culture Tour 台南古蹟文化及生態之旅

DAY 5: March 21 (Thursday)

- Venue: Room 47118

Time **時間**	**Activity/Presentation Title** **活動/標題**	**Presenter/Host** **講師/主持人**
Topic 3: Soil and Groundwater Protection- Monitoring and Sustainable Remediation		
08:30-10:00	Environmental Forensic Practices of Petroleum Hydrocarbon Contaminated Sites 環境法醫技術對於地表層下石油碳氫化合物污染鑑定	Prof. Colin S. Chen National Kaohsiung Normal University 高師大生科系陳士賢教授
10:00-10:20	Tea Break 茶敘	
10:20-11:50	Remediation of Organic Contaminated Sites: Theories and Case Studies 有機物污染場址整治：理論與案例研究	Prof. Jimmy C.M. Kao National Sun Yat-sen University 中山大學環工系高志明教授
11:50-13:20	Lunch 午餐	
13:20-14:50	Protection of Farmland Contamination: Investigation and Risk-based Approached Remediation Technology 農地污染保護：調查與以風險為本的整治技術	Prof. Zueng-Sang Chen National Taiwan University 臺灣大學農化系陳尊賢教授
14:50-15:20	Tea Break 茶敘	
15:20-16:50	Sediment Contamination: Protection and Remediation 底泥污染：保護與整治	Prof. Shu-Chi Chang National Chung Hsing University 中興大學環工系張書奇教授
18:00-19:00	Dinner/Team Project Discussion 晚餐/各組簡報討論(異人館)	

DAY 6: March 22 (Friday)

- Venue: Linyuan Petrochemical Plant, CPC, Kaohsiung 高雄中油林園廠
- Venue: Cenpro Technology Co. Ltd., Kaohsiung 高雄中環科技公司

Time **時間**	**Activity/Presentation Title** **活動/標題**	**Presenter/Host** **講師/主持人**
Topic 4: Soil and Groundwater Protection- Field Visits and Demonstration **主題四、場址參訪與技術展示**		
09:30-11:00	Introduction to the Remediation Works at Lin-Yuan Petrochemical Plant 中油林園廠整治工作介紹	Mr. Bing-Nan Wang Sinotech Environmental Technology, Ltd. 業興公司王炳南經理
11:00-12:00	Remediation Site Visits (Lin-Yuan Petrochemical Plant, CPC, Kaohsiung) 場址參訪(高雄中油林園廠)	
12:00-13:30	Lunch 參訪餐會	
13:30-15:00	Application of Geophysical and Direct Push Methods: Demonstration 地球物理及直接貫入法之應用：技術展示	Mr. Chun-Ming Tsai Cenpro Technology Co. Ltd. 中環科技公司蔡俊銘總經理
15:00-16:50	Laboratory Visits 實驗室參觀	
18:00-20:00	Dinner/ Team Project Preparation and Discussion 晚餐/各組簡報討論	

DAY 7: March 23 (Saturday)

- Venue: Room 47118

Topic 5: Soil and Groundwater Protection- Current Status and Needs for South East and South Asia **主題五、東南亞與南亞之土壤及地下水保護現況與需求**		
Time **時間**	**Activity/Presentation Title** **活動/標題**	**Presenter/Host** **講師/主持人**
08:30-09:00	Team Project Presentations and Discussion: Problems and Status of Soil and Groundwater Protection Conclusions from Previous Presentations 計畫推動小組簡報與討論：土壤及地下水保護所面臨的問題與情勢 先前簡報結論	Prof. Tsair-Fuh Lin National Cheng Kung University 成功大學環工系林財富教授
09:00-10:15	Representatives from 3 Countries: Australia, S.Korea, New Zealand 簡報：澳洲、韓國、紐西蘭 Topics Include: Country Report and Research Needs (one Presentation per country is expected, with 20 mins presentation & 5 mins of discussion) 國家現況報告與研究資源供需評估(各國簡報 20 分鐘/討論 5 分鐘)	InnoFusion Environmental Management Co., Ltd / Prof. Tsair-Fuh Lin National Cheng Kung University 創聚公司/成功大學環工系林財富教授
10:15-10:30	Tea Break 茶敘	
10:30-11:20	Representatives from 2 Countries: Cambodia, Philippines 簡報：菲律賓、柬埔寨 Topics Include: Country Report and Research Needs (one Presentation per country is expected, with 20 mins presentation & 5 mins of discussion) 國家現況報告與研究資源供需評估(各國簡報 20 分鐘/討論 5 分鐘)	Tainan Hydraulics Laboratory, National Cheng Kung University/ Prof. Tsair-Fuh Lin National Cheng Kung University 成功大學水工所/成功大學環工系林財富教授

11:20-12:30	Representatives from 2 Countries: India, Indonesia 簡報：印度、印尼 Topics Include: Country Report and Research Needs(two Presentations per country is expected, with 30 mins presentation & 5 mins of discussion) 國家現況報告與研究資源供需評估(各國簡報 30 分鐘/討論 5 分鐘)	SGS Taiwan Limited// Prof. Tsair-Fuh Lin National Cheng Kung University 台灣檢驗科技公司/成功大學環工系林財富教授
12:30-13:50	Lunch 午餐	
13:50-15:00	Representatives from 2 Countries: Malaysia, Sri Lanka 簡報：馬來西亞、斯里蘭卡 Topics Include: Country Report and Research Needs(two Presentations per country is expected, with 30 mins presentation & 5 mins of discussion) 國家現況報告與研究資源供需評估(各國簡報 30 分鐘/討論 5 分鐘)	Sinotech Environmental Technology, Ltd./ Prof. Tsair-Fuh Lin National Cheng Kung University 業興公司/成功大學環工系林財富教授
15:00-15:20	Tea Break 茶敘	
15:20-16:30	Representatives from 2 Countries: Thailand, Vietnam 簡報：泰國、越南 Topics Include: Country Report and Research Needs(Three Presentations per country is expected, with 30 mins presentation & 5 mins of discussion) 國家現況報告與研究資源供需評估(各國簡報 30 分鐘/討論 5 分鐘)	InnoFusion Environmental Management Co., Ltd / Prof. Tsair-Fuh Lin National Cheng Kung University 創聚公司/成功大學環工系林財富教授
16:30-16:50	More Discussion (including Questionnaire) 討論(含問卷)	Prof. Tsair-Fuh Lin National Cheng Kung University 成功大學環工系林財富教授
18:00-20:00	Farewell Dinner 歡送晚宴(香格里拉)	

DAY 8: March 24 (Sunday)

Departure 賦歸

Raising your Questions anytime anywhere

Give your comments for improving our activity

2019 International Joint-Research and Training Program

Training course of Working Group on ReSAGPAPR

International Workshop on promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Speakers

Photo	Presenter/Presentation Title
	Prof. Tsair-Fuh Lin **National Cheng Kung University** **Soil and Groundwater Protection in Asia: Status and Future Research and Practices**
	Dr. Shyh-Wei Chen **Soil and Groundwater Pollution Remediation Funds, Taiwan EPA** **Soil and Groundwater Protection in Taiwan: Status and Future Directions**
	Prof. Kung-Hui Chu **Texas A&M University, USA** **Bioremediation: Theories and Case Studies in US**

	Prof. Thomas B. Boving **University of Rhode Island, USA** **Current Research Directions on Groundwater Contamination and Remediation in US**
	Dr. Ching-Jen Ho **Soil and Groundwater Pollution Remediation Funds, Taiwan EPA** **Soil and Groundwater Protection in Taiwan - Policy and Regulation**
	Dr. Hao-Chun Hung **Soil and Groundwater Pollution Remediation Funds, Taiwan EPA** **Soil and Groundwater Pollution Remediation Fund**

	Prof. Liang-Ming Whang **National Cheng Kung University** **Application of Bio-molecular Monitoring Methods for Contaminated Sites**
	Prof. Chih-Jen Lu **National Chung Hsing University** **Contaminated Site Investigation: Case Studies in Taiwan**
	Dr. Ming-Daw Che **Apollo Technology Co., Ltd** **Contamination Site Investigation: Common Methods Employed in Taiwan**

	Dr. Chih Huang **InnoFusion Environmental Management Co., Ltd** **Risk Assessment for Soil and Groundwater Contamination**
	Prof. Colin S. Chen **National Kaohsiung Normal University** **Environmental Forensic Practices of Petroleum Hydrocarbon Contaminated Sites**
	Prof. Jimmy C.M. Kao **National Sun Yat-sen University** **Remediation of Organic Contaminated Sites: Theories and Case Studies**

	Prof. Zueng-Sang Chen **National Taiwan University** **Protection of Farmland Contamination: Investigation and Remediation**
	Prof. Shu-Chi Chang **National Chung Hsing University** **Sediment Contamination: Protection and Remediation**
	Mr. Chun-Ming Tsai **Cenpro Technology Co. Ltd.** **Application of Geophysical and Direct Push Methods: Demonstration**
	Mr. Bing-Nan Wang **Sinotech Environmental Technology, Ltd** **Introduction to the Remediation Works at Lin-Yuan Petrochemical Plant and Remediation Site Visits**

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

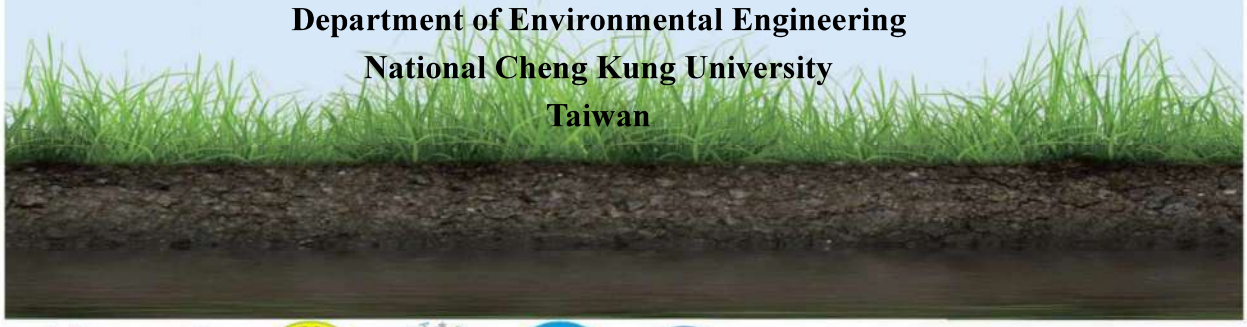
Soil and Groundwater Protection in Taiwan: Current and Future Research and Practices

Tsair-Fuh Lin (林財富)

Department of Environmental Engineering

National Cheng Kung University

Taiwan



Outline

- Soil and Groundwater Pollution in Taiwan
- International Trends
  - Web of Sci and ScienceDirect
- S&GW Research in Taiwan
- Field Applications
- Markets
- Field Experiences in Taiwan
- Idea from previous workshops
- Conclusions

2

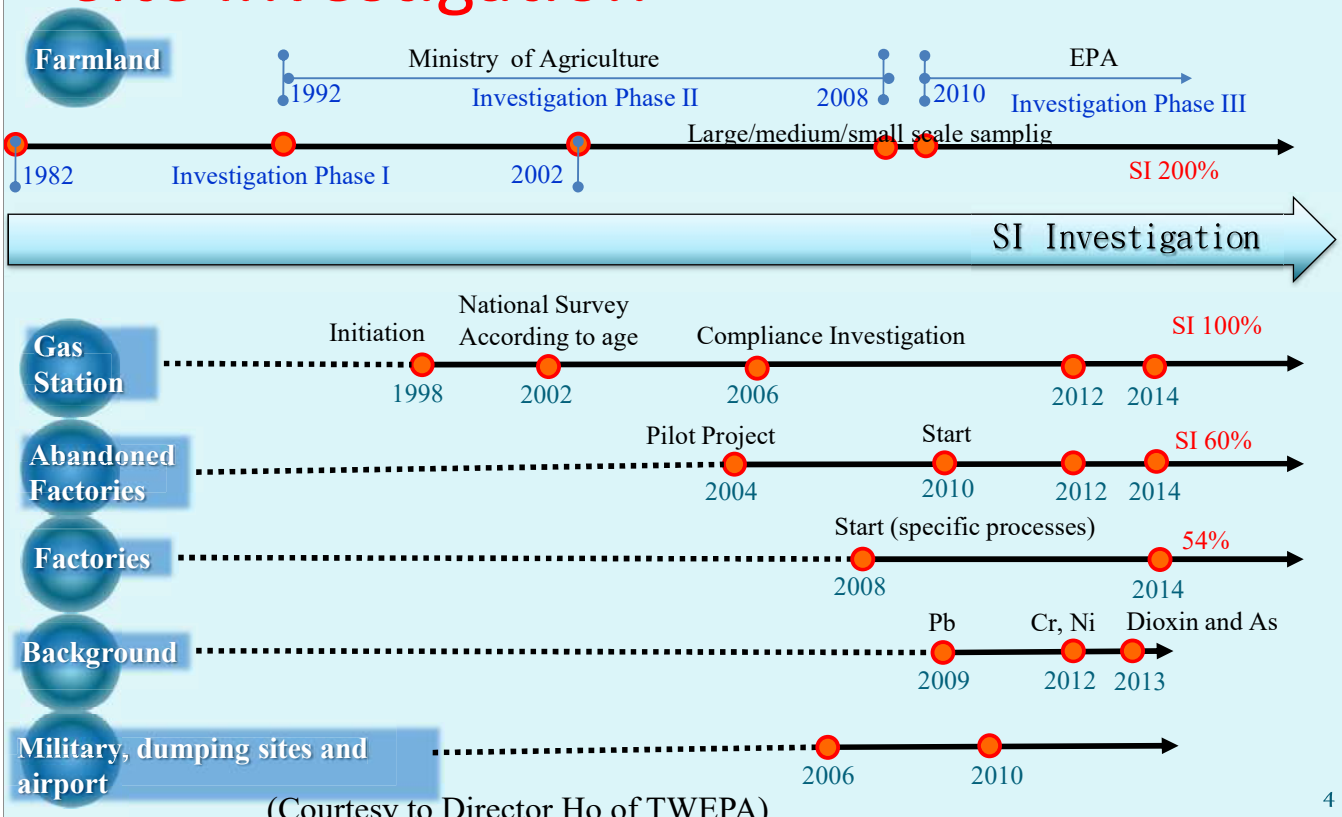
Soil and Groundwater Remediation Regulation in Taiwan

1980	Soil contamination cases
1991	EPA drafted Soil Pollution Prevention Act
1996	EPA withdrew the Act
1998	Renamed as Soil Pollution Remediation Act (draft)
1999	Renamed as Soil and Groundwater Remediation Act
2000	the Act was officially promulgated
2001	Enforcement Rules Announced
2006 ~ 2007	*May 2006, Public hearing of Amendment (draft)*
2010	Soil and Groundwater Remediation Act Amendment passed (Jan 2010) the Act Amendment was officially promulgated (Feb 2010)

(Courtesy to Director Ho of TWEPA)

3

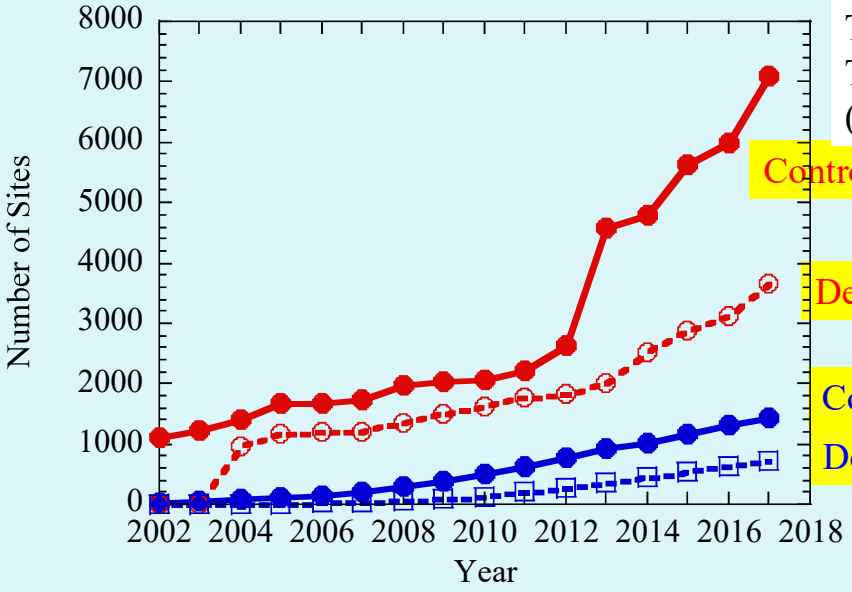
Site Investigation



(Courtesy to Director Ho of TWEPA)

4

Control and Delisted Sites



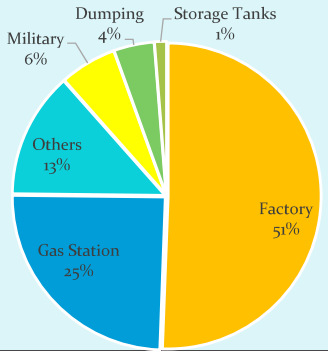
Total Control Sites: 8526
Total delisted Sites: 4374
(as Dec. 2017)

Control (farmland) (7097)

Delisted (farmland) (3643)

Control (others) (1429)

Delisted (other) (731)



5

More polluted

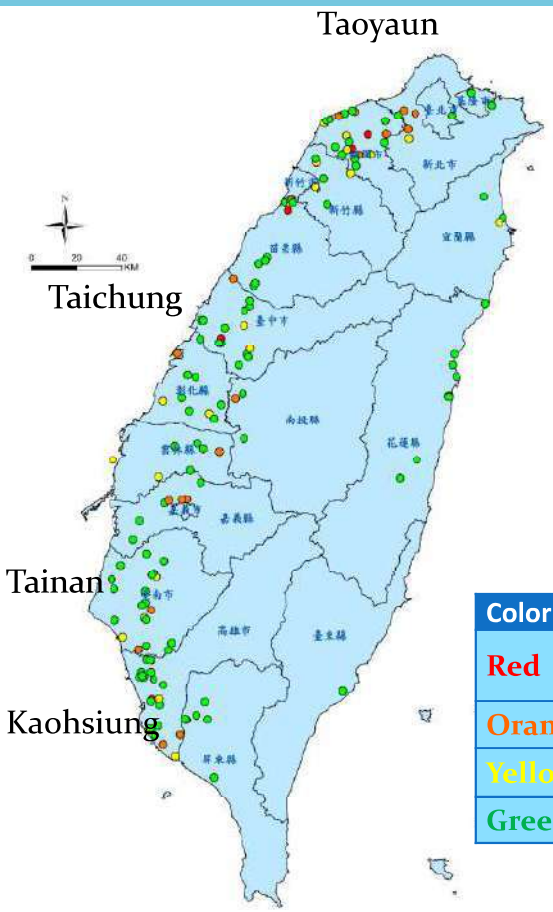
Cleaner

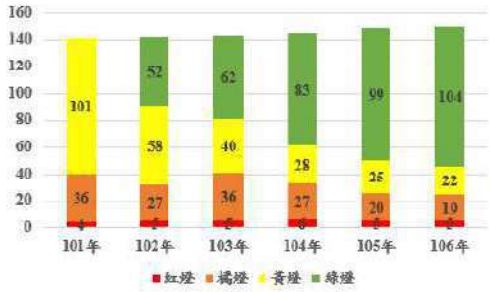
Farmland

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

6

Industrial Parks (2017)

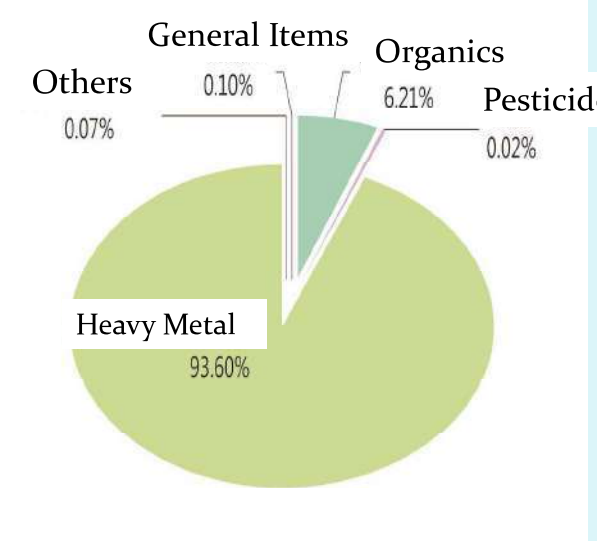




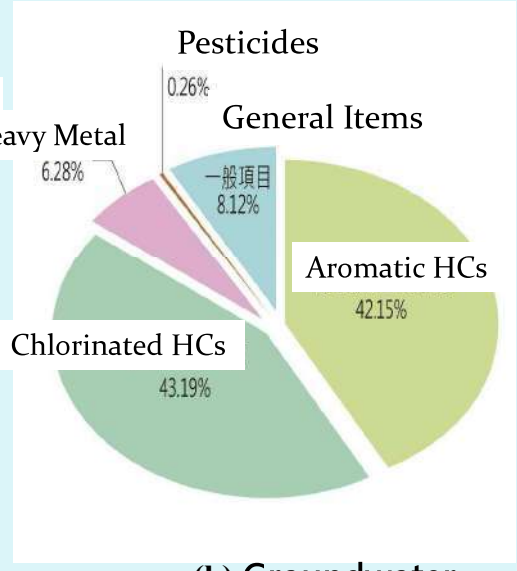
150 Industrial parks

Color	Definition	Number
Red	Contaminant plume moved to outside park	5
Orange	Plume found (within the park)	19
Yellow	Plume found (remediated)	22
Green	No/low potential of contamination	104

Contaminants Detected



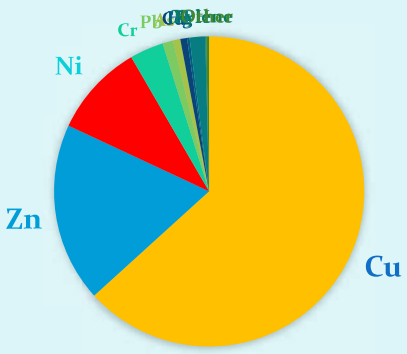
(a) Soil



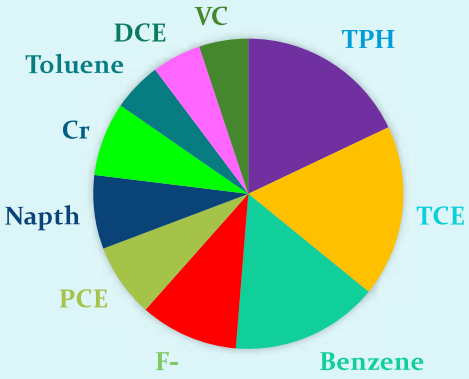
(b) Groundwater

TWEPA (2014)

Contaminants Detected



(a) Soil



(b) Groundwater

TWEPA (2017)

9

Types of Pollutants in Taiwan

- **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: 45Sites), Dichloroethylene (DCE) (14), Tetrachloroethylene (PCE), and Vinyl Chloride (VC) (27)

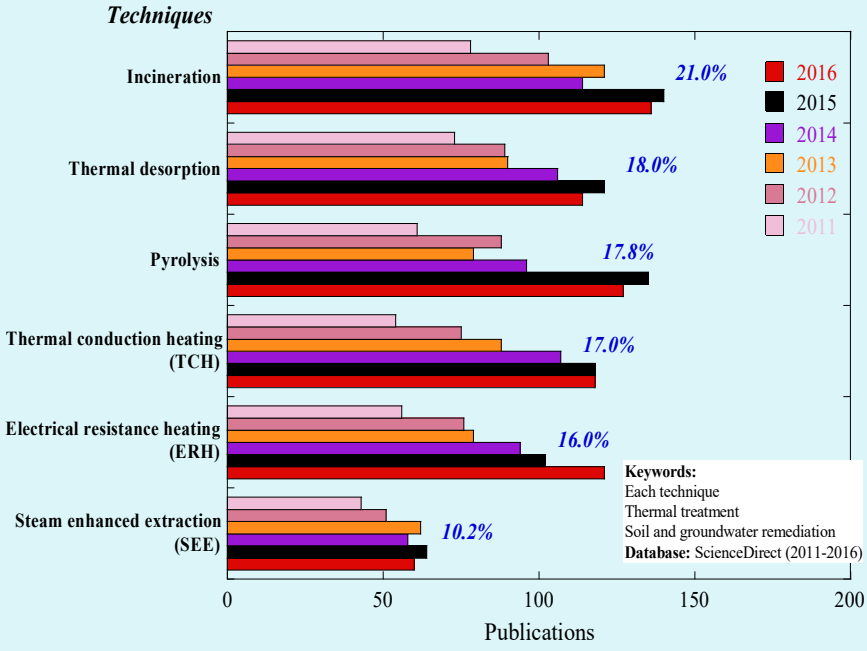
Contaminated Sites in Taiwan (2011)

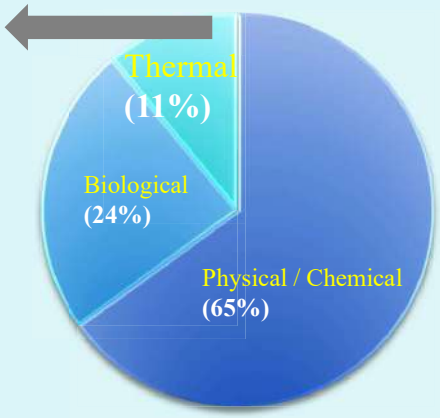
10

Science Direct

11

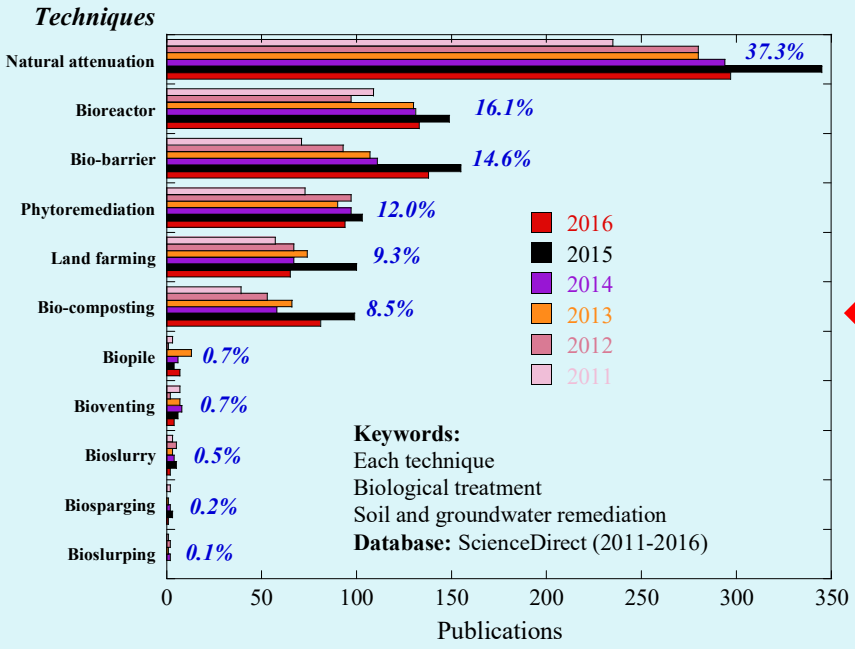
International Trend:
Thermal Treatment Technologies

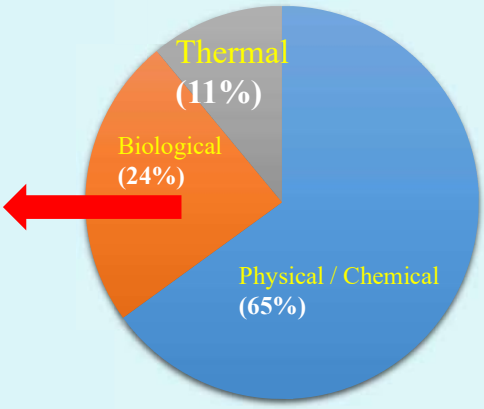




12

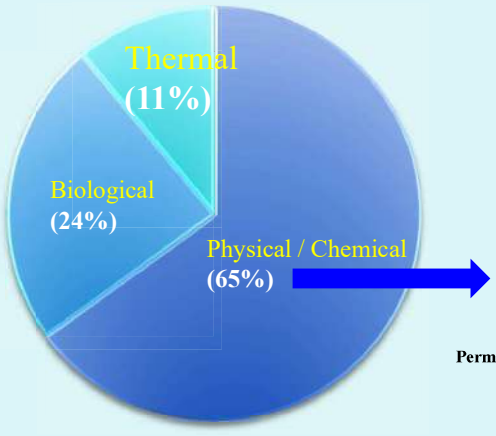
International Trend:
Biological Treatment Technologies

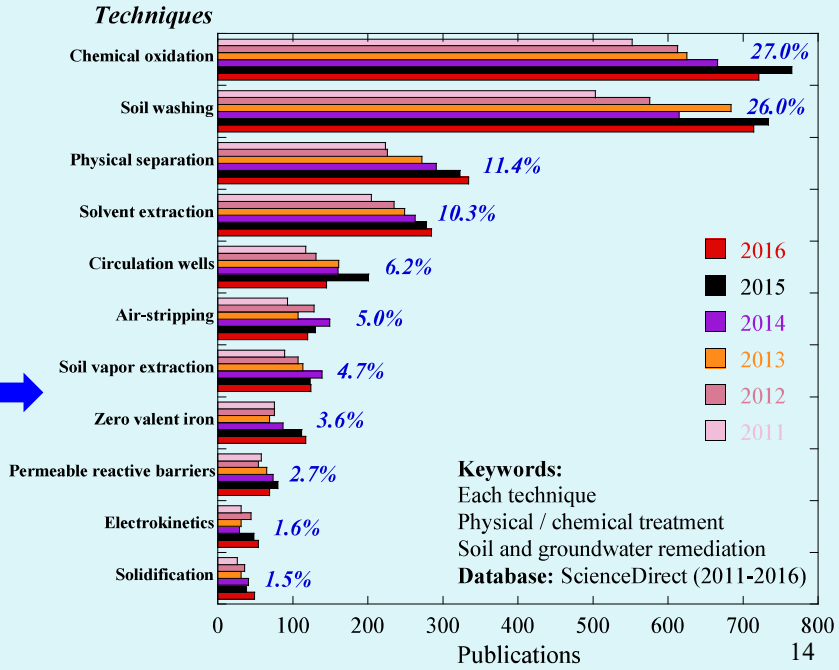




13

International Trend:
Physcio-chemical Treatment Technologies





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Summary (Sci. Direct)

- **Tech Categories:**
  - **Physico-Chemical: Biological: Thermo =** = 6: 2 :1

- **Thermal**: Incineration (21%), Thermal desorption (18%), Pyrolysis (17%), Thermal conduction (17%), Electrical resistance heating (16%), Steam enhanced extraction (10.2%)- all similar
- **Biological:** Natural attenuation (37%), Bioreactor (16%), Biobarriers (14.6%), Phytoremediation (12%), Land farming (9.3%), Bio-composting (8.5%)
- **Physico-Chemical:** Chemical Oxidation (27%), Soil washing (26%), Physical separation (11.4%), Solvent extraction (10.3%)

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Web of Science

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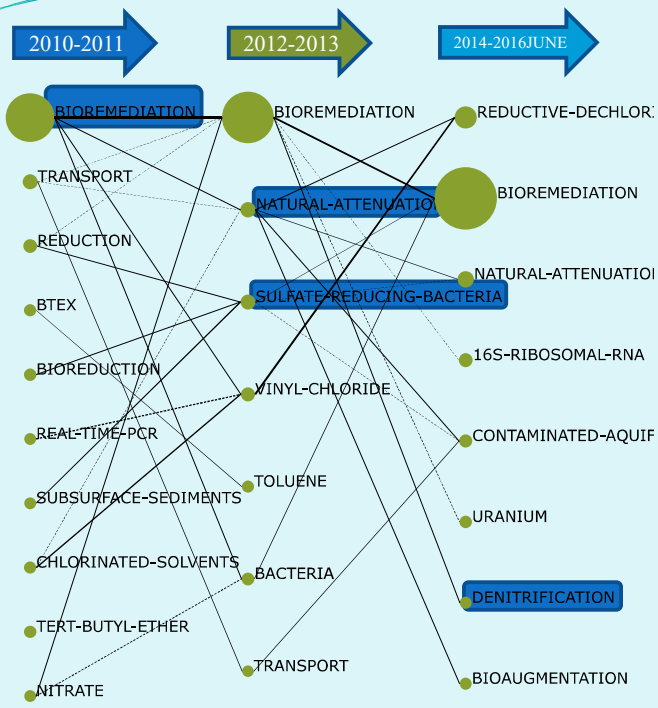
Topics

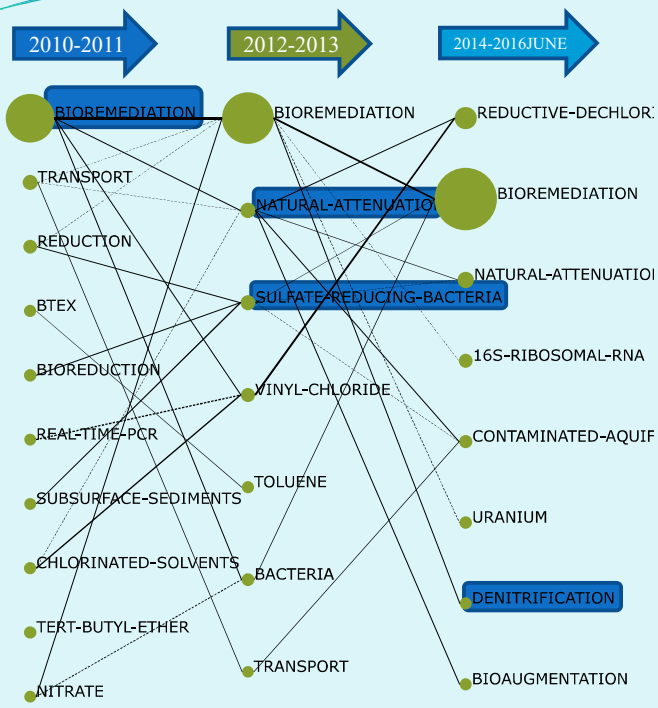
- Soil remediation: 5652
- Soil bioremediation: 3750
- Groundwater remediation: 2126
- Groundwater bioremediation: 791



*圓的大小代表相關文獻量；線的粗細代表關聯強度

Summary (WOS)

- **Soil Remediation:** Bioremediation, Phytoremediation, Heavy metals, Biochar, Zero valent iron, phenanthrene, Sequential extraction, TCE, Adsorption, Chemical oxidation
- **Bio (Soil):** Biosorption, Biodiversity, Biosurfactant, Accumulation, Bioavailability, Petroleum HCs, Bacteria, Bio-stimulation, Laccase



*圓的大小代表相關文獻量；線的粗細代表關聯強度

Summary (WOS)

- **Groundwater:** Zero valent iron, Adsorption, Hydrogen peroxide, Aggregation, Management, Biodegradation, Wastewater, Porous media, iron, contaminated soil
- **Bio (Groundwater):** Reductive dehalogenation, Natural attenuation, 16S RNA, Contaminated aquifer, Uranium, Denitrification, Bioaugmentation

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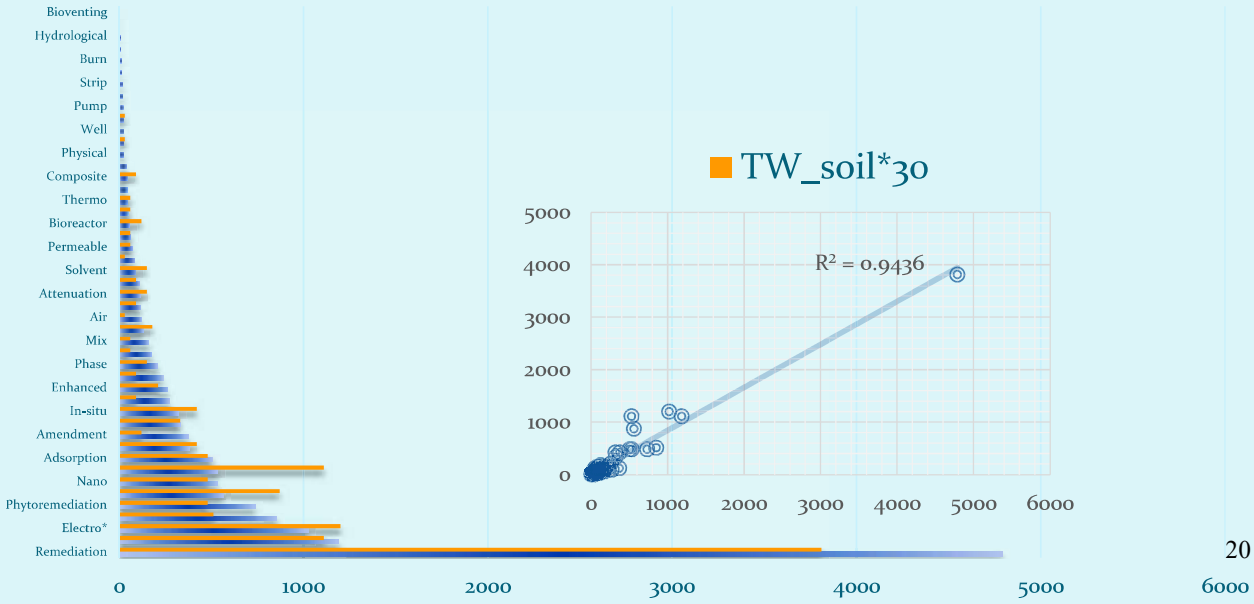
Comparison between Taiwan and the World

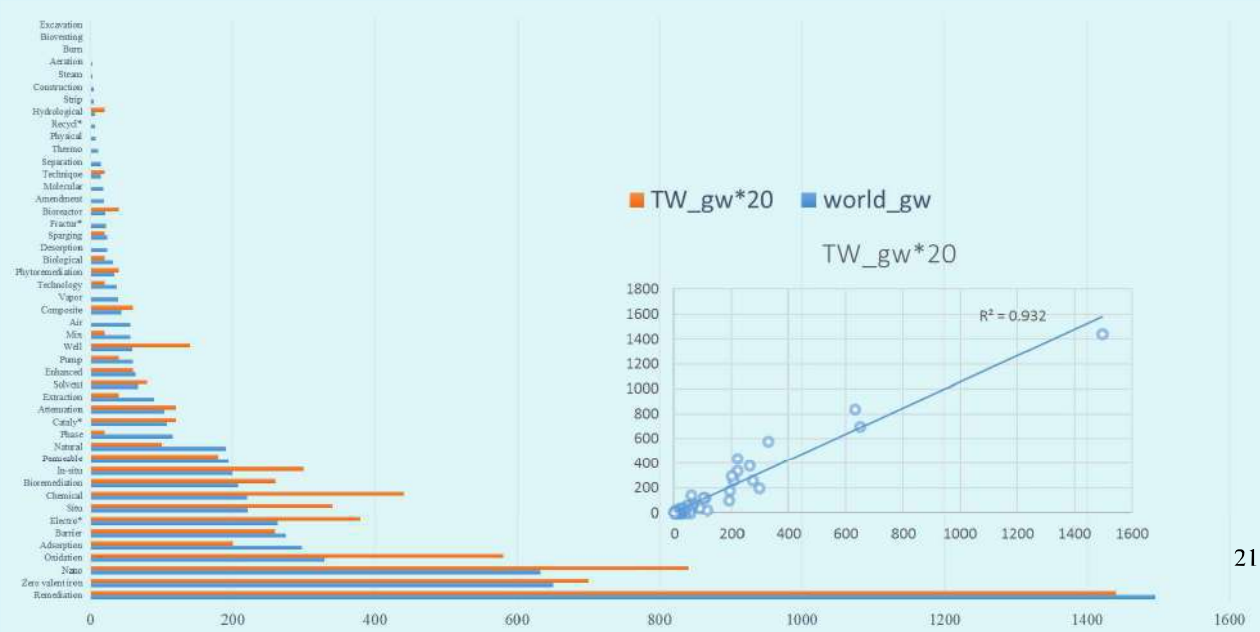
Key words: Soil Remediation



20

Comparison between Taiwan and the World

Key words: Groundwater Remediation



21

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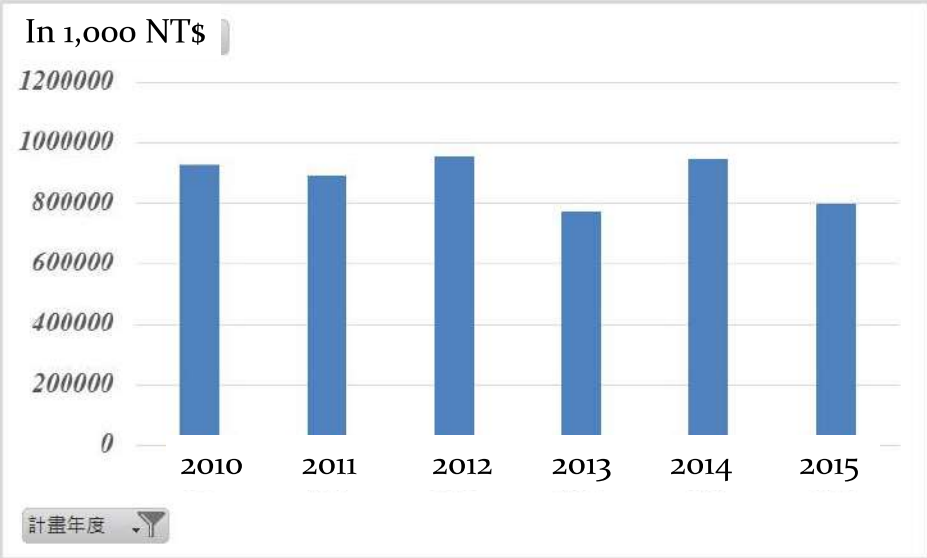
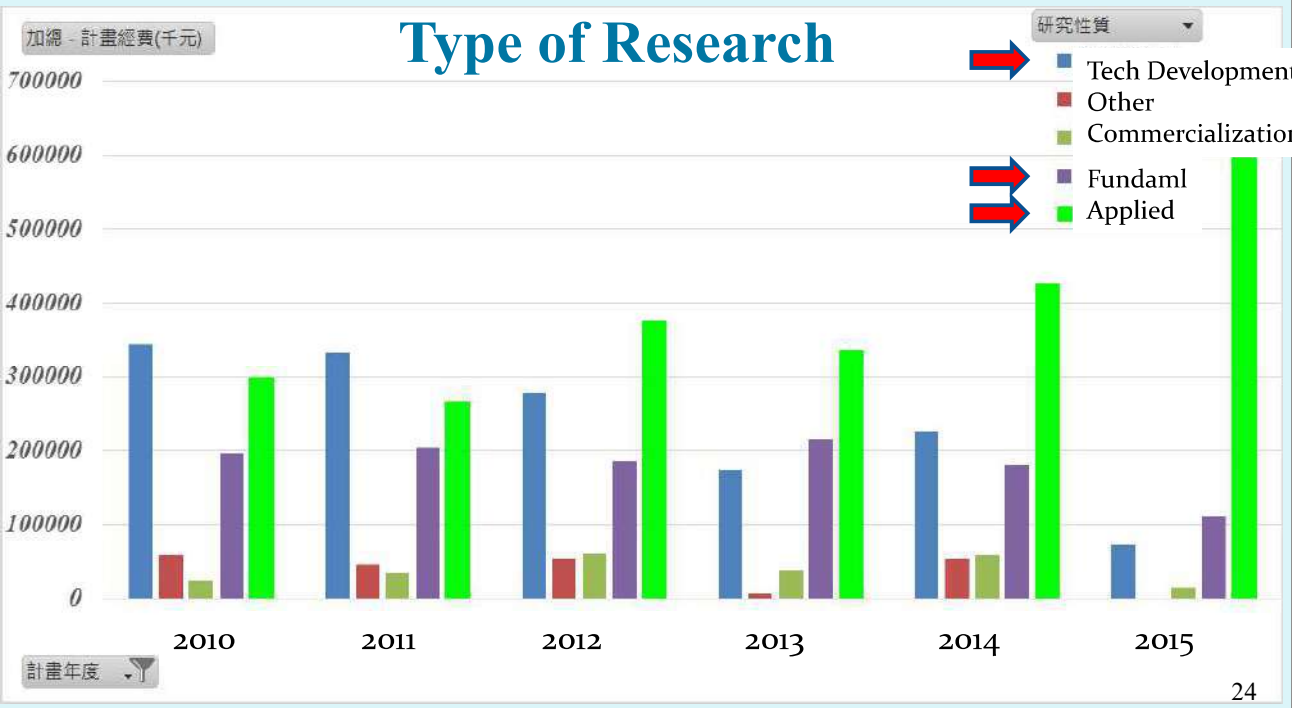
Research Budget (2010-2015) in S&GW Area



23

Type of Research



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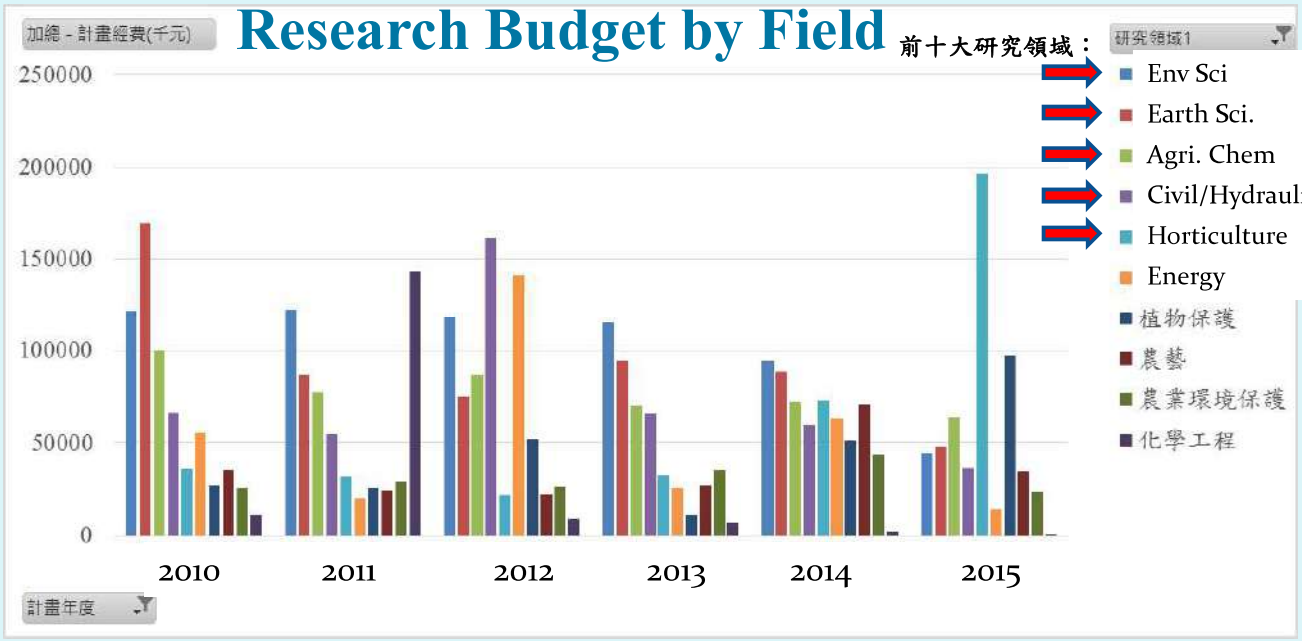
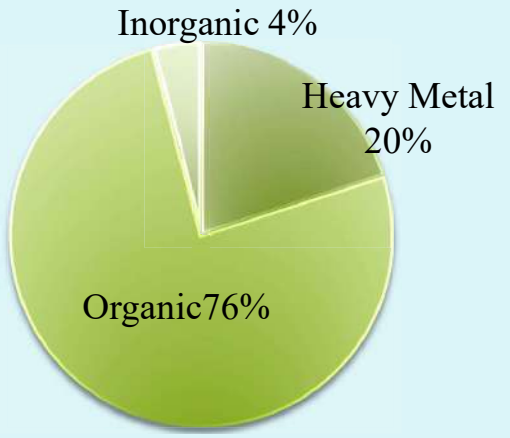
Research Budget by Field



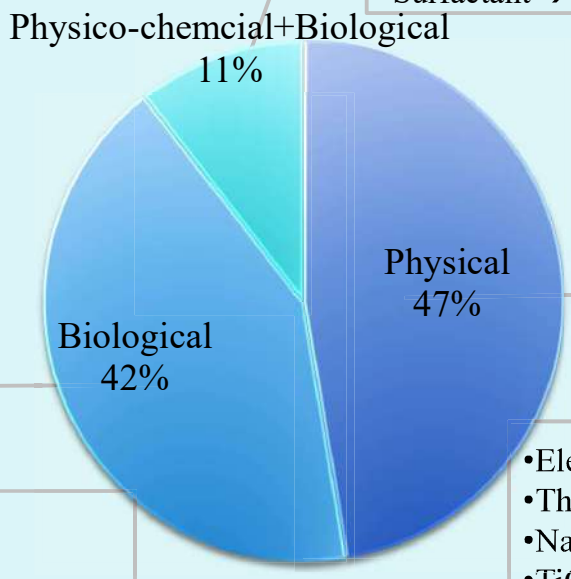
前十大研究領域：

SGW Remediation Fund (1)

- Soil and Groundwater Remediation Fund Management Board
  - 2010-16 (Research Projects)
  - 2014: 1 million US, 21 projects, lab (up to 66K)/field (up to 170K)



SGW Remediation Fund (2)



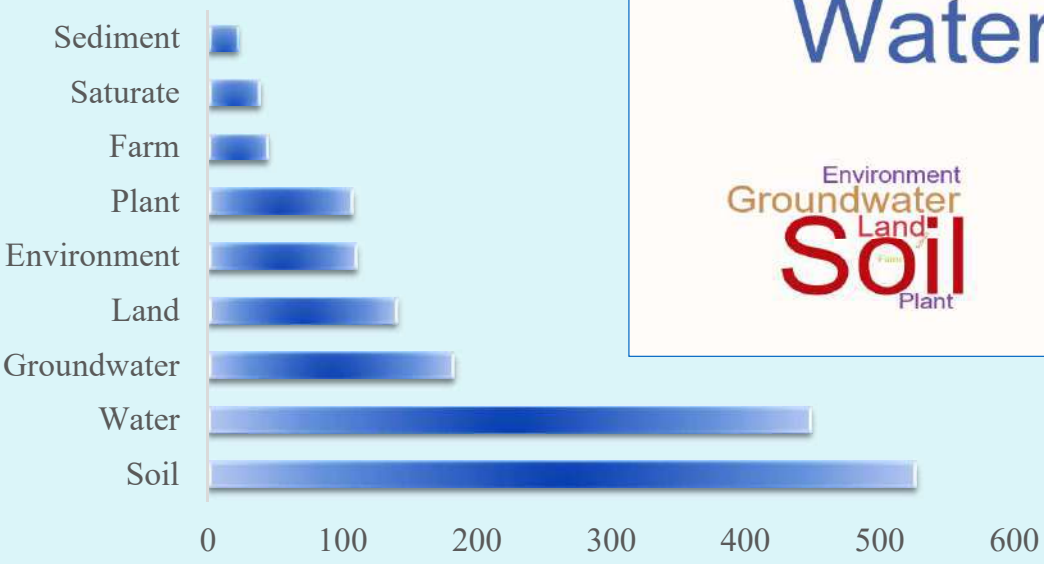
•Adsorption→ oxygen released immobilized bacteria grains
•Surfactant → oxidation → biobarrier

•Bioremediation
•Compost leachate
•Biobarrier
•Anaerobic dehalogenation

•Electro-kinetics
•Thermo-desorption
•Nano particle (iron)
•TiO2 nanotube
•Reactive barrier (oxidation)
•Dual phase extraction/Ozonation
•Super critical CO2 extraction

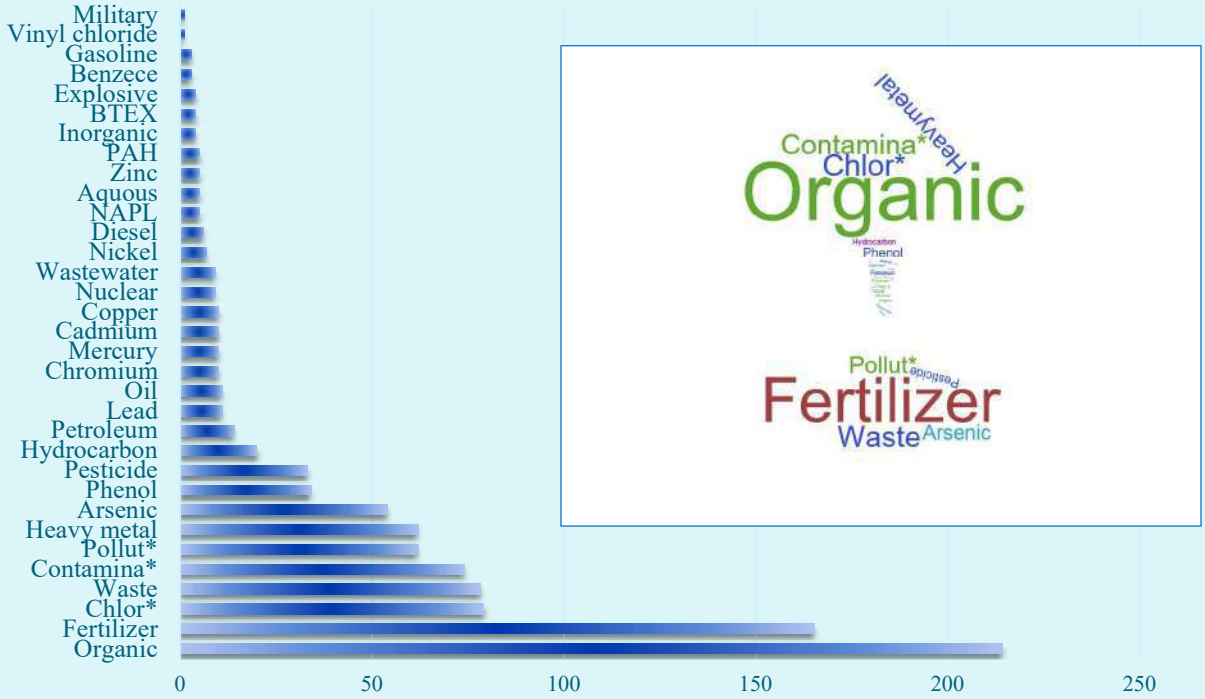
27

Keywords: media



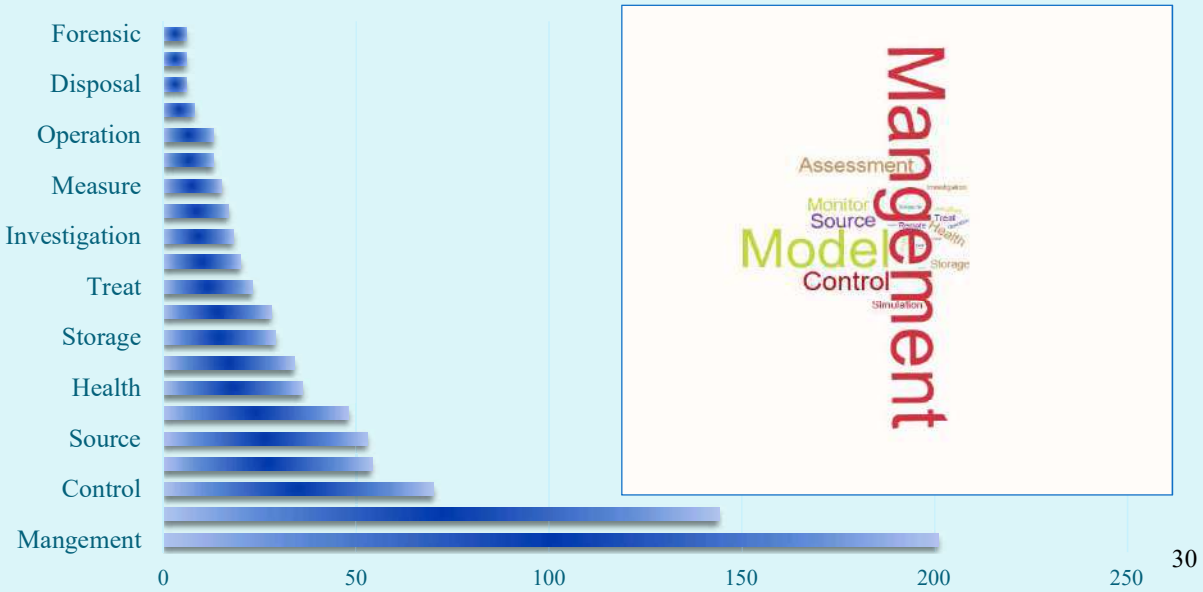
28

Keywords: Pollutants



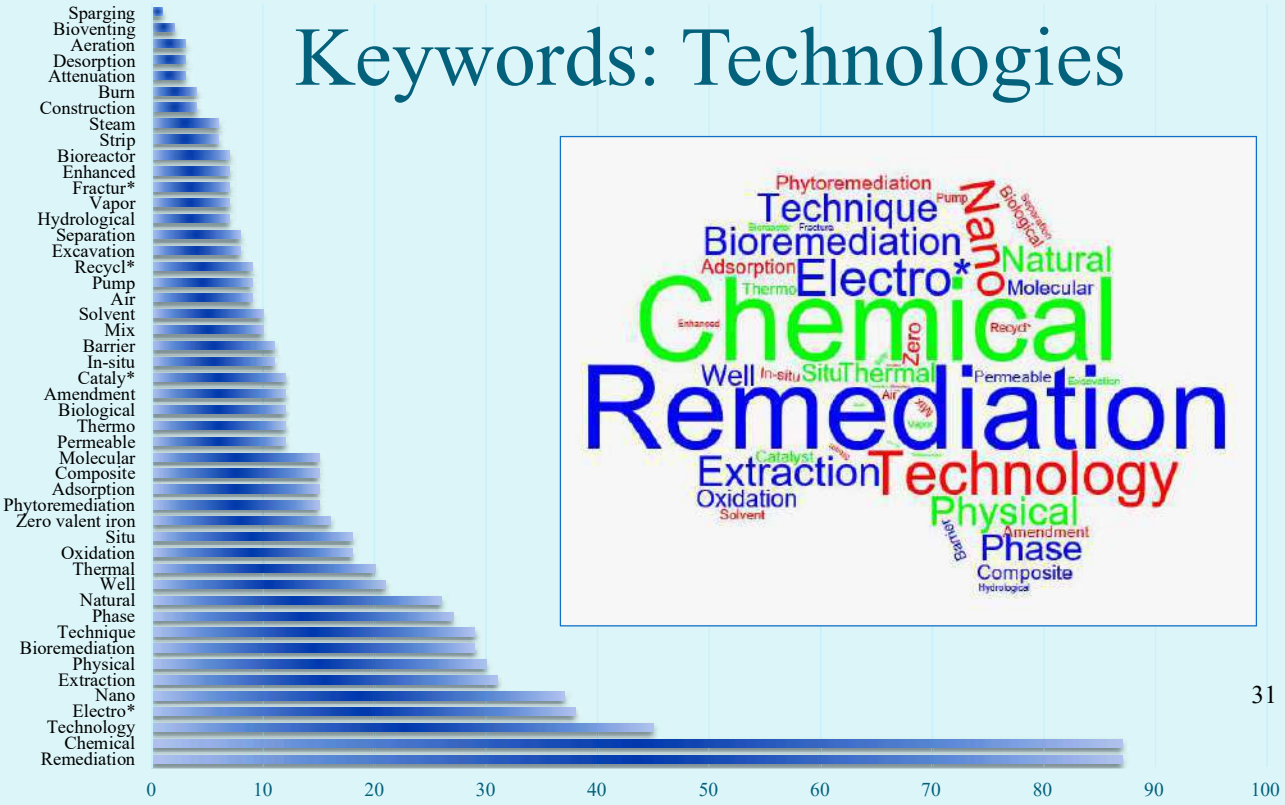
29

Keywords: Strategy



30

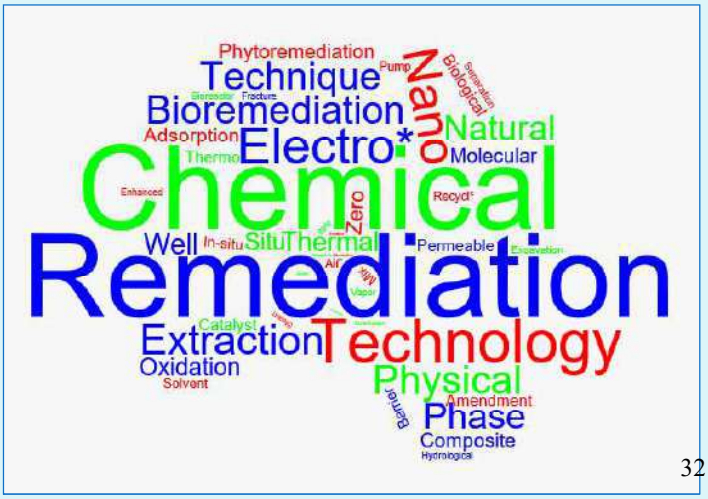
Keywords: Technologies



31

Keywords: Technologies

- Compared with (Sci Dir)
- **P/C: Bio: Ther =** = 6: 2 :1
- **Thermal**: Incineration, Thermal desorption, Pyrolysis, Thermal conduction, Electrical resistance heating, Steam enhanced extraction
- **Biological:** Natural attenuation, Bioreactor (16%), Biobarriers, Phytoremediation, Land farming, Bio-composting
- **Physico-Chemical:** Chemical Oxidation, Soil washing, Physical separation, Solvent extraction
- **Taiwan:** Bio (112/831) and Thermal (20/831) are not as popular



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Field Applications

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Summary

- **Soil (*in-situ*):** Soil vapor extraction (2009-2011, 21%), Chemical treatment (14%), Stabilization (9%), Thermal treatment (6%)
- **Soil (*in-situ*):** Physical separation (28%), Solidification and stabilization (13%), Extraction (13%), Off-site (9%), recycle (9%)
- **Groundwater:** Pump and treat (21%), Bioremediation (24%), Chemical treatment (14%), Air sparging (6%), natural attenuation (27%), Institutional control (IC) (84%)

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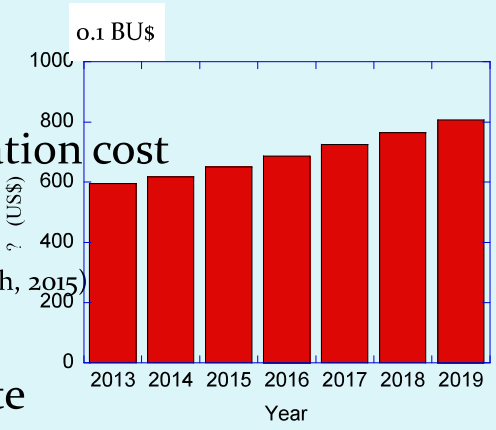
Global Market

- Site Remediation World Markets (McIlvaine Co., 2015)
  - $14 Billion in 2015
  - US is the largest market
  - Fukushima Site: 5% global remediation cost
- Global Markets for Environmental Remediation Technologies (BCC Research, 2015)
  - 59.5 Billion in 2013
  - 5.5 % compound annual growth rate (CAGR) (2014 – 2019)
  - China (Market share 4.7%, 2014; 10.8%, 2019)



Site Remediation Annual Revenues

Site Remediation Annual Revenues by 2015	
Expenditure Type	$ Billions
Engineering and consulting services	20.3
Excavation, construction and operational labor	9.5
Thermal treatment (depreciation)	0.7
Water treatment equipment (depreciation)	1.4
Monitoring and instrumentation (depreciation)	1.2
Chemicals and microbial preparations	1.2
Pumps and valves (depreciation)	1.4
Other	4.3
Total	40.0

McIlvaine Co. (2015)

Site Remediation Annual Revenues

McIlvaine Co. (2012)

- Taiwan's Environmental Protection Agency (EPA) has identified more than 2,000 contaminated sites nationwide to date. More sites continue to be flagged.
- Japan has a large established market.
- China is the fastest growing remediation market.
- Most of the developing Asian countries have large potential.

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Site Remediation Market (Asia)

2015 Asian Remediation Market ($ Millions)				
Region	Groundwater		Soil	Total
	Metals and VOCs	Other Contaminants		
East Asia	1,500	500	2,500	4,500
West Asia	300	100	500	900
Total	1,800	600	3,000	5,400

McIlvaine Co. (2014)

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US 2016 Top Markets Report Environmental Technologies (June 2016)

Figure 1: Environmental Technologies Top Markets Results

	Water		Air		Waste		Composite Environmental Technologies Score	
1	China	44.9	China	47.4	China	7.7	China	100.0
2	India	16.3	Mexico	26.2	Indonesia	4.2	Mexico	37.1
3	United Arab Emirates	15.8	Korea	18.3	Pakistan	3.7	India	31.7
4	Oman	15.3	Turkey	17.4	Brazil	3.6	Brazil	29.4
5	Saudi Arabia	12.0	Brazil	15.3	Thailand	3.3	Korea	27.3
6	Brazil	10.5	India	12.8	Saudi Arabia	3.0	Saudi Arabia	25.9
7	Mexico	9.5	Saudi Arabia	10.9	India	2.7	Indonesia	23.4
8	Indonesia	9.3	Indonesia	9.9	Vietnam	2.1	Turkey	22.1
9	Poland	8.4	Poland	8.6	Korea	2.1	Poland	17.7
10	Korea	6.9	Czech Republic	8.0	Egypt	1.9	United Arab Emirates	15.8

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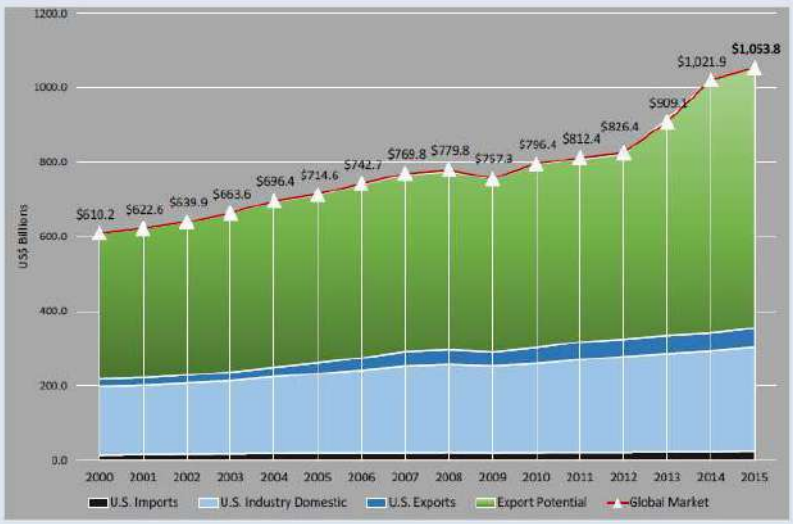
Global Market

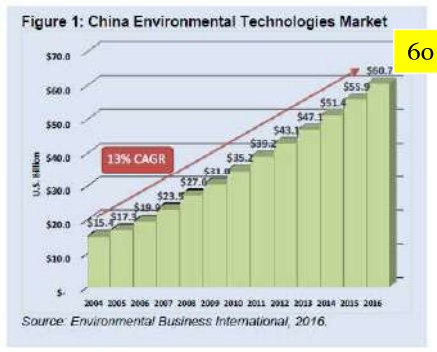
(US 2016 Top Markets Report Environmental Technologies, June 2016)

Figure 2: Global Environmental Technologies Market Overview



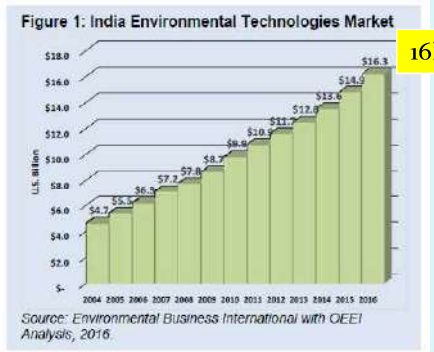
40

China



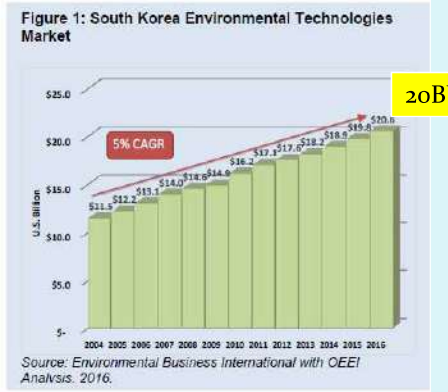
60 BU$

India



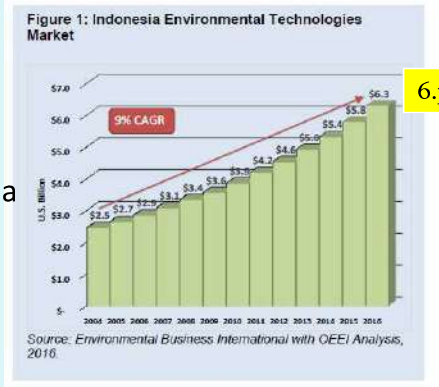
16BU$

South Korea



20BU$

Indonesia



6.3BU$

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Key Technologies in Demand (China)

Groundwater

- Monitoring equipment
- Source pollution control technologies
- Sparging
- Bioremediation
- Chemical treatment
- Flushing
- In-situ air stripping
- Multiphase extraction
- Permeable reactive barrier
- Phytoremediation
- Pump and treat

Soil

- Engineering and design
- Monitoring equipment

Environmental Consulting and Engineering

- Environmental impact assessment

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(US 2016 Top Markets Report Environmental Technologies, June 2016)

Key Technologies in Demand (Asia)

India
- Landfill design and engineering
- Hydrological mapping services (GW)
- Monitoring equipment (GW)
- Groundwater recharge technology (GW)

South Korea

Key issues are air pollution, waste management, and water and waste treatment

Philippines
- Sanitary landfill systems

Malaysia
- Waste treatment technologies
- Landfill gas recovery systems

Vietnam
- Sanitary landfill design, maintenance and associated technologies
- Brownfield site remediation design and equipment
- Soil contamination testing and monitoring equipment

Thailand
- Sanitary landfill design, maintenance and associated technologies

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(US 2016 Top Markets Report Environmental Technologies, June 2016)

Physical & Chemical technologies

Scope	Field application			Research				
Area	USA			Global			Taiwan	
Keywords/sources	Soil (In Situ)	Soil (Ex Situ)	GW	Sci. Direct	WOS*		Academic	
					Soil	GW	Soil	GW
SVE	▲**							
P&T		▲	▲**					
Physical Separation		▲**		▲				
Adsorption					▲	▲	▲	▲
Soil Washing				▲				
Air Sparging			▲					
Chemical Treatment	▲		▲	▲**	▲		▲	▲**
Thermal Treatment	▲#			▲***				
Extraction				▲	▲		▲**	
Solidification/Stabilization	▲	▲						
Recycling		▲						
Electrokinetics							▲	▲
Permeable Reactive Barrier								▲
Institutional control			▲**					

*: motor; **：the highest ratio within its column；***: Incineration (21%), Thermal desorption (18%), pyrolysis(17%), Thermal conduction heating (17%), Electrical resistance heating (16%), Steam enhanced extraction (10.2%); # Thermal desorption

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Biological Technologies

Scope	Field App.	Research						
Area	USA	Global					Taiwan	
Keywords/sources	GW	Sci. Direct	WOS*				Academic	
			Soil	Bio&Soil	Bio&GW	GW	Soil	GW
16S RNA(Identification)					▲			
Bioavailability				▲				
Biosorption				▲				
Bio-stimulation				▲				
Bioaugmentation					▲			
Accumulation				▲				
Biodegration						▲		
Bio-composting		▲						
Bioremediation	▲						▲	▲
Bio-barrier		▲						
Biodiversity				▲				
Denitrification					▲			
Monitoring/NA	▲	▲**			▲		▲	▲
Phytoremediation		▲	▲				▲	
Land farming		▲						
Reductive-Dechlorination					▲			
Bioreactor		▲						
*: motor; ** : the highest ratio within its column								

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Additives

Scope		Research				
Area		Global			Taiwan	
Keywords/Sources		WOS			Academic	
		Soil	Bio&Soil	GW	Soil	GW
Biological	Biochar	▲				
	Biosurfactant		▲			
	Bacteria		▲			
	Laccase		▲			
Physical&Chemical	Hydrogen peroxide			▲		
	Zero valent iron			▲	▲	▲
	Amendment				▲	
	Porous media			▲		▲

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Taiwan experiences

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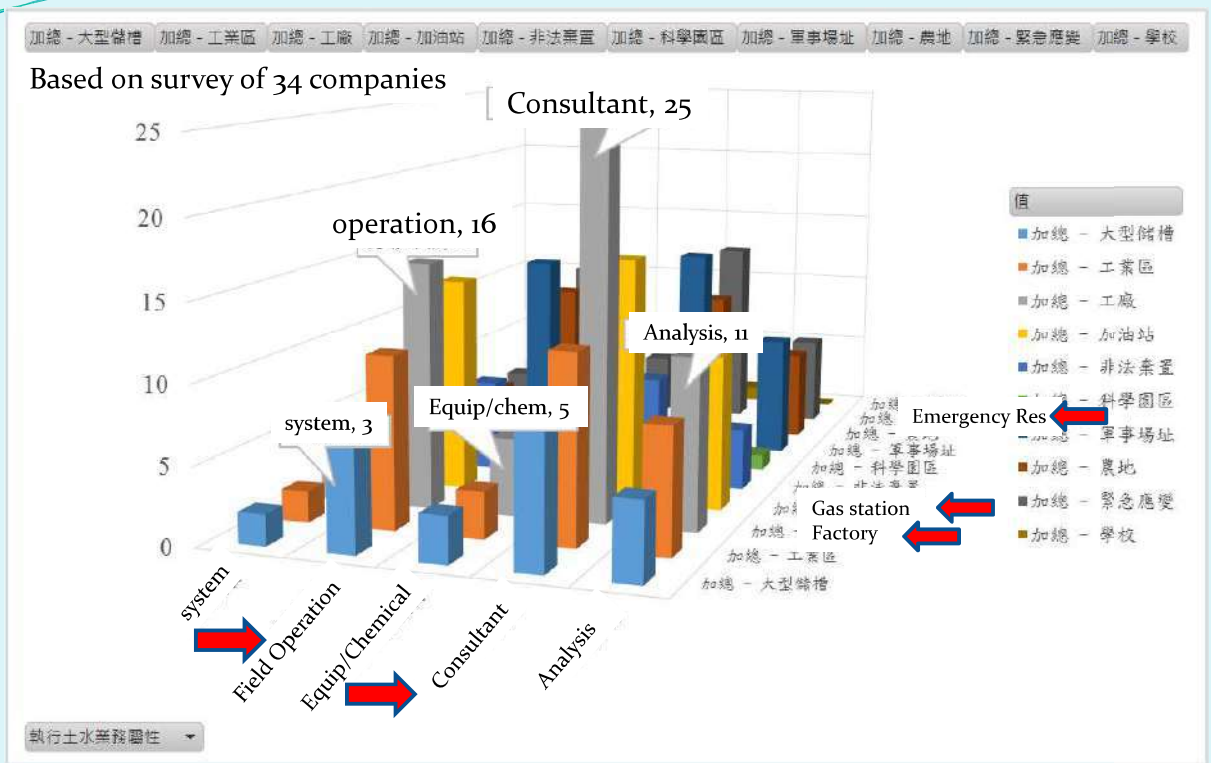
Based on survey of 34 companies



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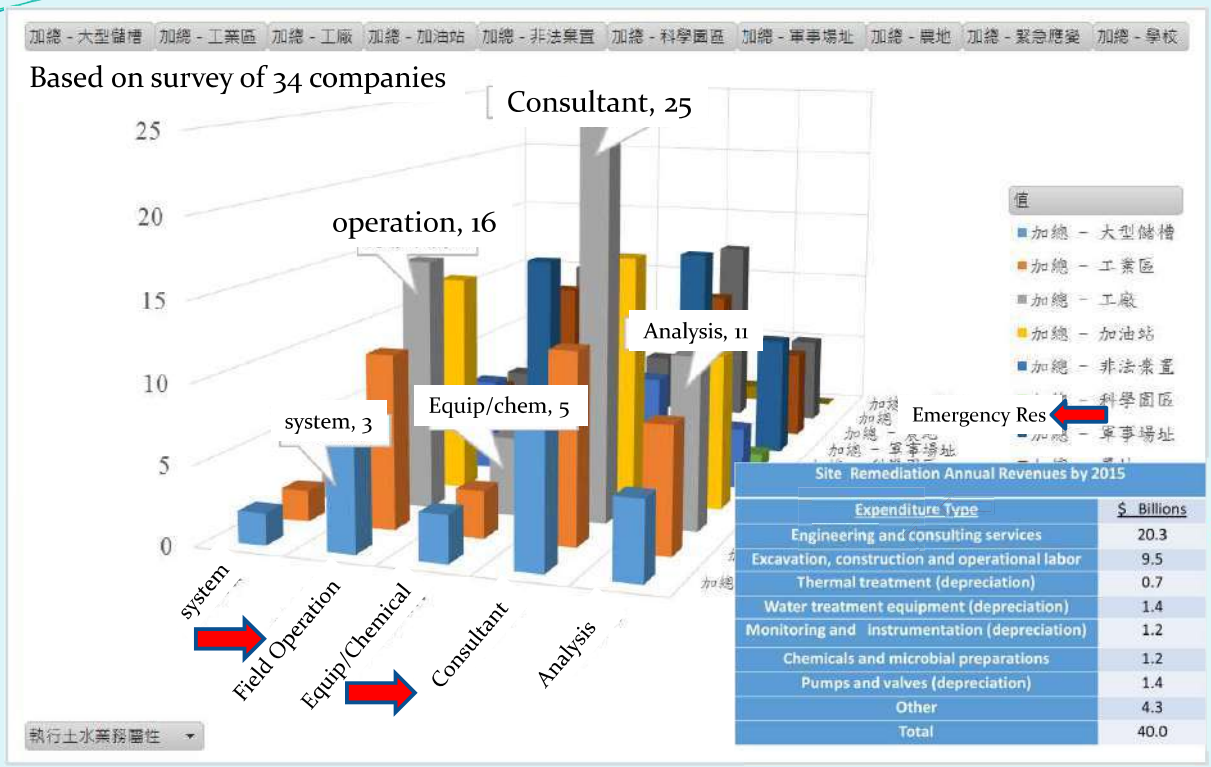

Site Remediation Annual Revenues by 2015

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Excavation, construction and operational labor	9.5
Thermal treatment (depreciation)	0.7
Water treatment equipment (depreciation)	1.4
Monitoring and instrumentation (depreciation)	1.2
Chemicals and microbial preparations	1.2
Pumps and valves (depreciation)	1.4
Other	4.3
Total	40.0

49

Taiwan (Common Technologies)

- 25 sites: Petroleum (15), Chlorinated HCs (5), Heavy metals (4), Dioxins (2)
- Soil vapor extraction (8/25), Dual phase extraction (9), chemical washing (5), water washing (4), bioremediation (8), bioventing(9), hydraulic control (7), soil exchange (6)、mixing and dilution (1), in-situ chemical oxidation (7), steam injection (2), pump and treat (7), off-site solidification (1)

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Taiwan (Common Technologies)

- 25 sites: Petroleum (15), Chlorinated HCs (5), Heavy metals (4), Dioxins (2)
- Soil vapor extraction (8/25), Dual phase extraction (9), chemical washing (5), water washing (4), bioremediation (8), bioventing(9), hydraulic control (7), soil exchange (6)、mixing and dilution (1), in-situ chemical oxidation (7), steam injection (2), pump and treat (7), off-site solidification (1)

North America

- **Soil (*in-situ*):** Soil vapor extraction, Chemical treatment, Stabilization, Thermal treatment
- **Soil (*in-situ*):** Physical separation, Solidification and stabilization, Extraction, Off-site, Recycle
- **Groundwater:** Pump and treat, Bioremediation, chemical treatment, Air sparging, Natural attenuation, Institutional control (IC)

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Taiwan (Common Technologies)

Groundwater (Asia, from US Trade Report)

- Monitoring equipment
- **Source pollution control technologies**
- **Sparging**
- **Bioremediation**
- **Chemical treatment**
- Flushing
- **In-situ air stripping**
- **Multiphase extraction**
- Permeable reactive barrier
- Phytoremediation
- **Pump and treat**

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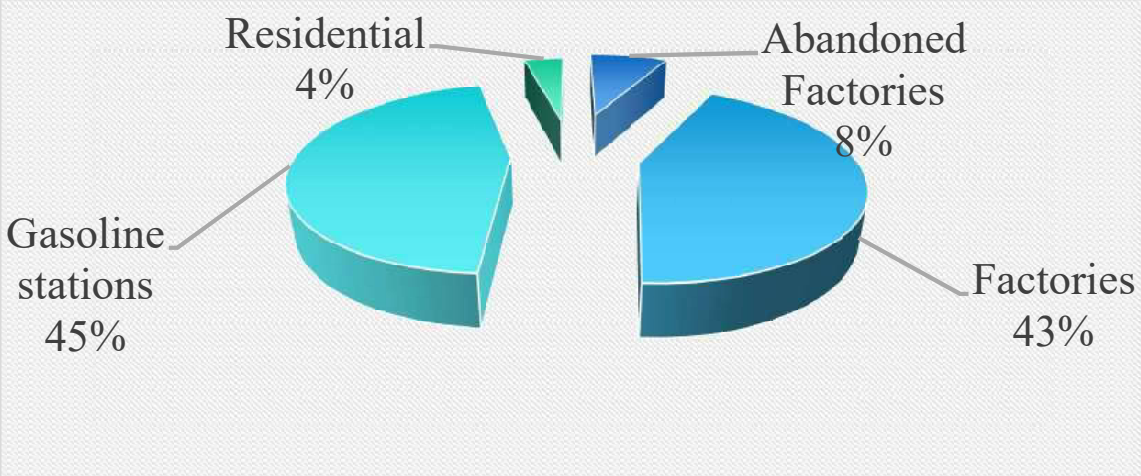
53 Taiwan remediation cases



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Visualization (Van Eck and Waltman (2010))

- Software: VOSviewer
- Association strength $s_{ij} = c_{ij}/(w_i w_j)$
  - S_{ij}: Similarity between item I and j,
  - c_{ij}: Times between item i and j,
  - w_i and w_j are times for item i and j,
  - Distance: cluster intensity, closer meaning stronger link
  - Font: frequency
  - Color: weighing factor, from blue (low), green, yellow, to red (high)

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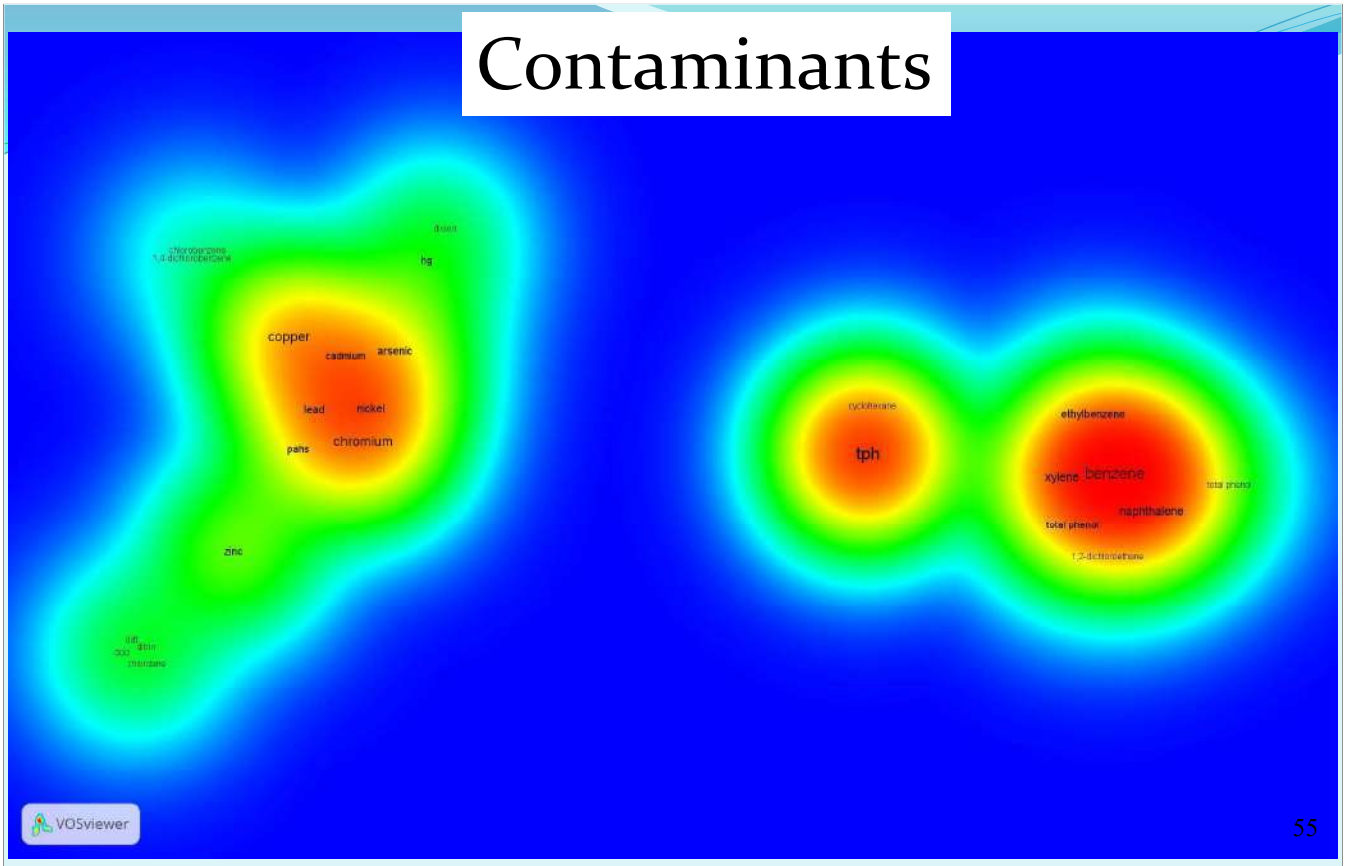
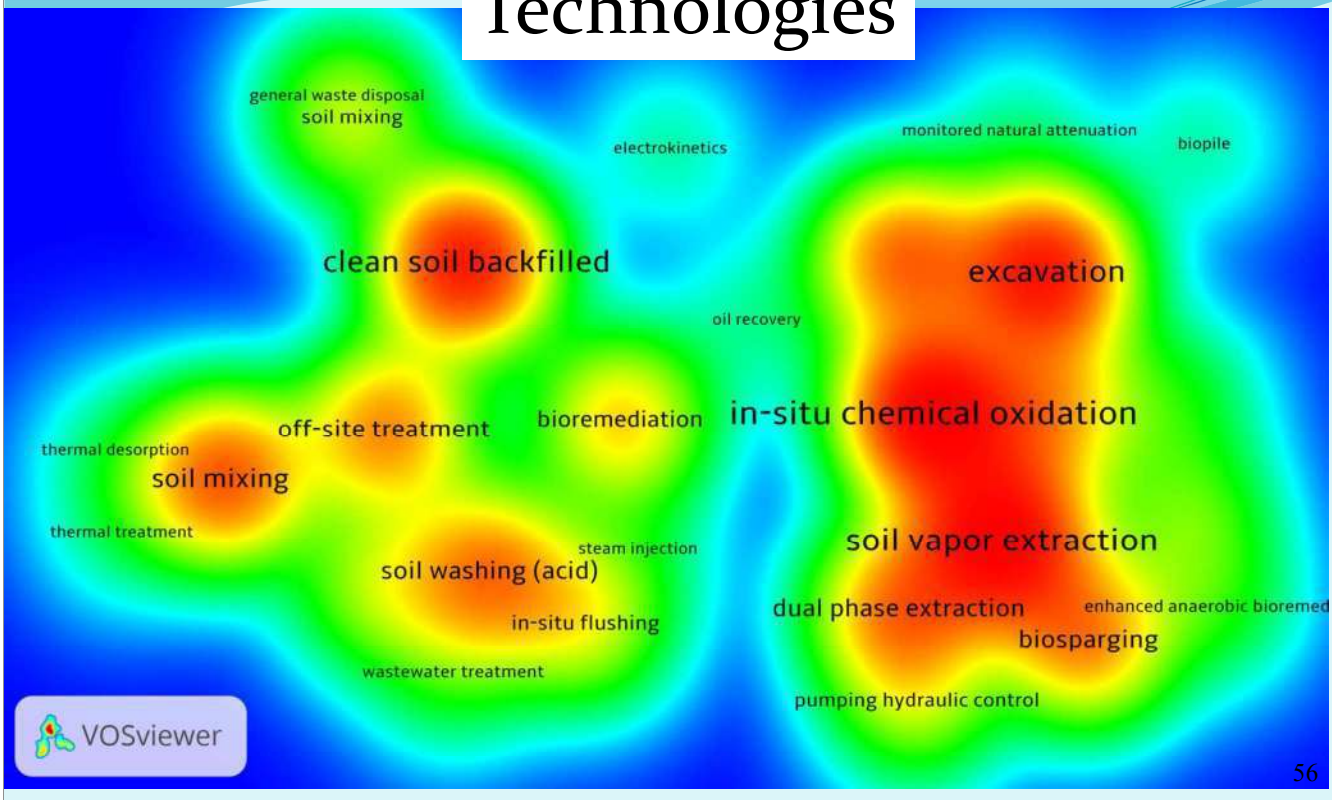
Contaminants



- Color: weighing factor, from blue (low), green, yellow, to red (high)
- Distance: cluster intensity, closer meaning stronger link
- Font: frequency

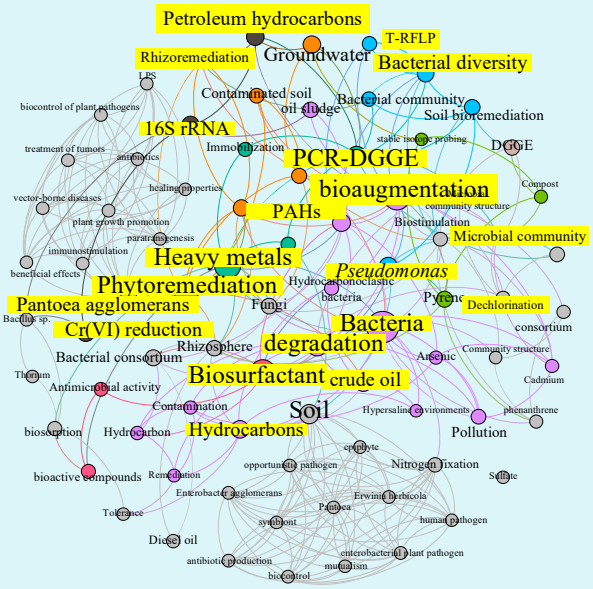
Technologies



- Color: weighing factor, from blue (low), green, yellow, to red (high)
- Distance: cluster intensity, closer meaning stronger link
- Font: frequency

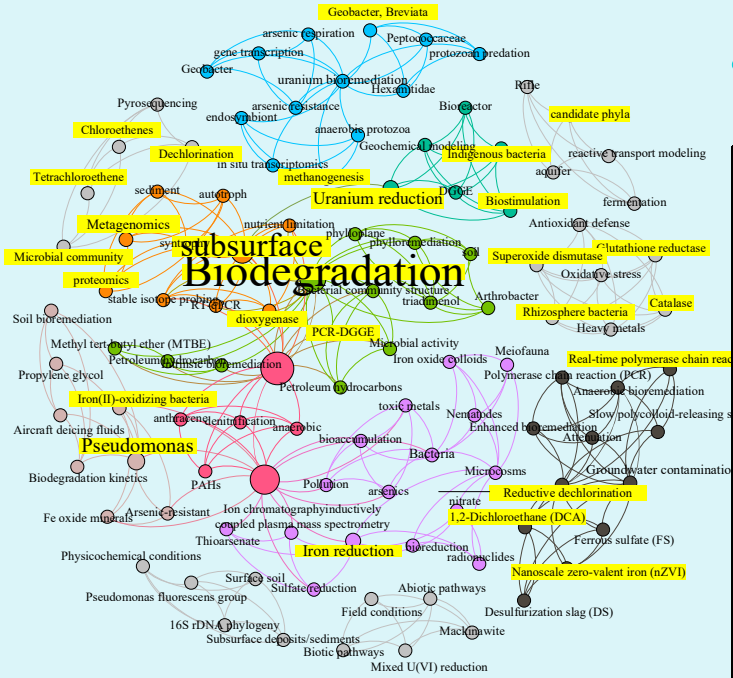
Biomolecular Monitoring

Bioremediation related to microorganisms_Soil (2015-2017)(564 papers)

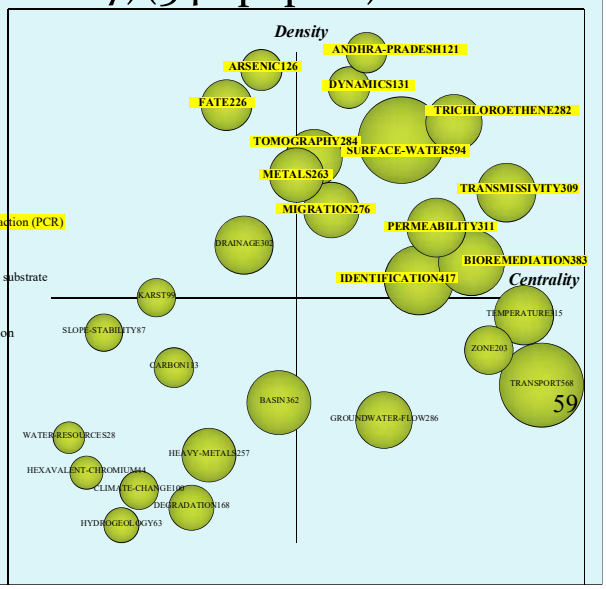


- **Contaminants**: Heavy metals, PAHs, TPH
- **Microbial community**: Bacteria, bacterial diversity, Pseudomonas, pantoea agglomerans, biosurfactant
- **Function/technology**: phytomediation, bioaugmentation, degradation, rhizoremediation, dechlorination, Cr(VI) reduction
- **Monitor tool**: PCR-DGGE, 16S rRNA

Bioremediation related to microorganisms_GW (2015-2017)(21 papers)



- Chlorinated Organic Compounds
- GW site investigation(2012-2017)(548 papers)



International Workshop on Sustainable Soil and Groundwater Protection and Remediation (IWSSGPR)

Country / Year	Thailand	Malaysia	Vietnam	Indonesia	Philippines	Cambodia	Total
2015	2	2	4	8	5	0	21
2016	3	2	6	4	7	1	23
2017	3	3	5	5	10	2	28
Total	8	7	15	17	22	3	72
Percentage	11%	10%	21%	24%	31%	4%	

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Key Issues suggested by the IWSSGPR participants

- Baseline investigation of soil and groundwater contamination
  - All countries (Monitoring)
- Bioremediation and application in different countries
  - Low cost treatment methods
- Seawater intrusion and land subsidence
  - Vietnam, Philippines, Thailand, Taiwan, India
- Landfill contamination
  - Vietnam, Philippines, Thailand, Indonesia, Malaysia
- Groundwater as drinking water source
  - Thailand (As), Vietnam (As, NH_3, Private Wells), Philippines (Coliform), Malaysia (Fe), India (Nitrate, As, F, Cr. CN, Hg, Dye, Fe, Pesticide, Nitrate, Coliform), Cambodia (As)

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Key Issues suggested by the IWSSGPR participants

- Policy and Laws
  - Bureaucratic issues: Indonesia (Central and Local), Philippines (Multiple agencies at national levels), Malaysia (Peninsula Malaysia, Sarawak, and Sabah; Central and Local government; Multiple Agencies)
  - Needs of laws, regulations, and standards (All)
  - Enforcement
- More Research Funding on Soil and Ground Water (All)
- Environmental Awareness (All)

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Key Issues suggested by the IWSSGPR participants

- Potential Contamination
  - Gas Stations (Vietnam, Philippines)
  - **Mining** (Philippines, Indonesia, Thailand, Malaysia, India)
  - Landfill (All)
  - Seawater intrusion (All)
  - Fluoride (India); **Arsenic** (Vietnam, India, Taiwan, Thailand); Nitrate (India); Coliform (Philippines and India); Ammonia (India, Vietnam, Malaysia, and Philippines)

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Investigation and Remediation Technologies on Soil Contamination

Site Classification/Contaminants / Investigation Technologies on Soil	Country: Indonesia	Philippines	Thailand	Total
Agricultural	1	4		5
Halogenated SVOCs		3		3
Gas Chromatography/ Mass Spectrometry		2		2
Infrared Spectroscopy		1		1
Halogenated VOCs	1			1
Gas Chromatography/ Mass Spectrometry	1			1
Metals and metalloids		1		1
Unknown		1		1
Battery recycling and disposal	1			1
Metals and metalloids	1			1
Direct Sensing Field-Portable X-Ray Fluorescence	1			1
Gasoline stations	2			2
Fuels	2			2
Gas Chromatography/ Mass Spectrometry	2			2
Landfills, municipal and industrial	1	3	1	5
Halogenated SVOCs		1		1
Gas Chromatography/ Mass Spectrometry		1		1
Halogenated VOCs			1	1
Gas Chromatography/ Mass Spectrometry			1	1
Metals and metalloids	1	2		3
Atomic Absorption Spectroscopy	1	2		3
Metal recycling and automobile salvage		2		2
Metals and metalloids		2		2
Direct Sensing Field-Portable X-Ray Fluorescence		1		1
Inductively Coupled Plasma-Atomic Emission Spectroscopy		1		1
Mining	1	6	4	11
Metals and metalloids	1	6	4	11
Atomic Absorption Spectroscopy	1	2		3
Direct Sensing Field-Portable X-Ray Fluorescence		1		1
Inductively Coupled Plasma-Atomic Emission Spectroscopy		1		1
Unknown		2	4	6
Unknown		2		2
Metals and metalloids		2		2
Atomic Absorption Spectroscopy		1		1
Inductively Coupled Plasma-Atomic Emission Spectroscopy		1		1
Total	6	17	5	28

Site Classification/Contaminants / Remediation technologies on soil	Country: Indonesia	Philippines	Thailand	Total
Agricultural		1		1
Battery recycling and disposal	1			1
Metals and metalloids	1			1
Solidification/Stabilization	1			1
Landfills, municipal and industrial	1	1	1	3
Mining	1	4	4	9
Metals and metalloids	1	4	4	9
Bioremediation		3	1	4
Incineration			1	1
Phytoremediation		1	2	3
Solidification/Stabilization	1			1
Total	5	6	5	16

- Mining is the major site category
- Metals and metalloids are the dominant contaminants

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Remediation Technologies on GW Contaminants

Remediation Technologies (Grwoundwater) Site Classification/Contaminants	Malaysia	Philippines	Total	
⊟(laboratory scale)			1	1
⊟BTEX (Benzene, Toulene, Ethylbenzene, p-xylene)			1	1
Ostrich bone wastes as biomaterials for adsorption; uptake experiment using volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer); specific surface area by BET procedure; pore-size analysis using Barrett-Joyner-Halenda method; Spectra by FTIR plus spectrophotometer; XRD analysis by Philips X'PERT MPD diffractometer. SEM-EDX using Seron microscope;			1	1
⊟Barangay Bangkal, Makati City, Philippines			1	1
⊟LNAPLs			1	1
Plume extraction by multi-phase extraction (MPE) system			1	1
⊟Davao and Mindoro, Philippines			1	1
⊟Arsenic			1	1
Bituminous fly ash as adsorbent			1	1
⊟Financial district in the Philippines (Metro Manila)			1	1
⊟Petroleum Products such as benzene, PAH,			1	1
Multiphase extraction system used in remediation			1	1
⊟Kampung teluk, Kelantan	1			1
⊟Iron (Fe)	1			1
Subterrenean Iron Removal	1			1
⊟Landfills, municipal and industrial			3	3
⊟Metals and metalloids			3	3
Physical Separation			2	2
Phytoremediation			1	1
⊟Petroleum refining and reuse			3	3
⊟Fuels			3	3
Multi-Phase Extraction			1	1
Multi-Phase Extraction			1	1
Quantachrome NOVA automated gas sorption analyzer			1	1
⊟Unknown			2	2
⊟Arsenic			1	1
Nanozeolites from rice hull ash and chitosan nanoparticles or nanofibers for possible in-situ remediation.			1	1
⊟Heavy metals			1	1
Phytoremediation-Tolerant plants for the removal of the contaminants such as metals, radionuclides, organic compounds (aromatic HC, pesticides, explosives and surfactants)			1	1
Total	1		12	13

Regions in Thailand	Problem Found
Northern Region	Iron, Fluoride
Central Region	TDS at deep level, Iron, Manganese, Arsenic
Northeastern Region	Iron, Manganese, Sulfate, Chloride, Hardness, TDS
Eastern Region	Chloride, TDS, Iron
Southern Region	Chloride, Hardness due to limestone

- Less information on GW than Soil.

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Possible Collaborations proposed by the IWSSGPR Participants

- Joint Publications
- Joint Workshops
- Student/Researcher Exchanges
- Joint Research Proposals/Projects
- Websites
- Inviting People from Governmental Agencies of SE/S Asian Countries

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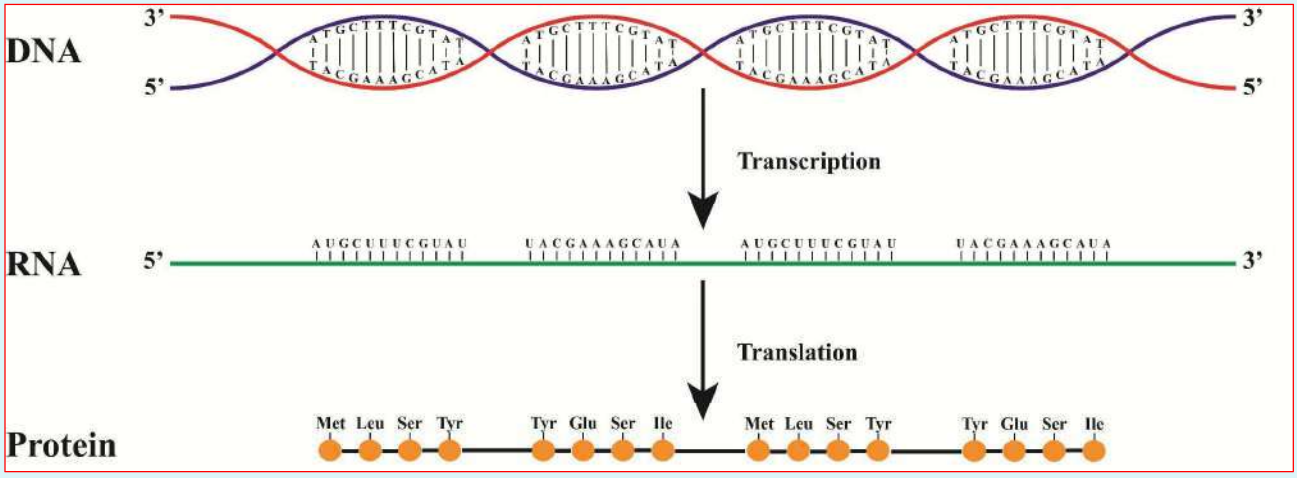
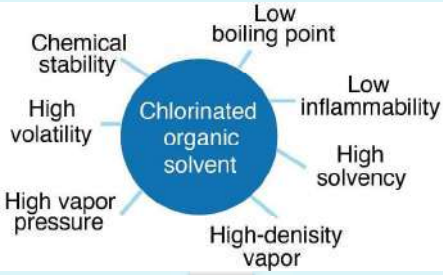
Biomolecular Monitoring

Central Dogma of Molecular Biology

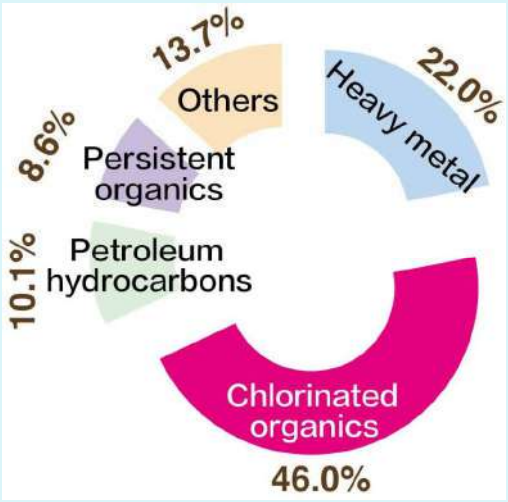


http://www.science-explained.com/wp-content/uploads/2013/08/DNA.jpg

Chlorinated Hydrocarbons/Ethenes



(1) Degreasing
(2) Dry Cleaning
(3) Electronic
(4) Paint Remover



Contaminants in Taiwan's Groundwater

Rapid Monitoring Molecular Methods for Functional Microorganisms in CHC contaminated Groundwater

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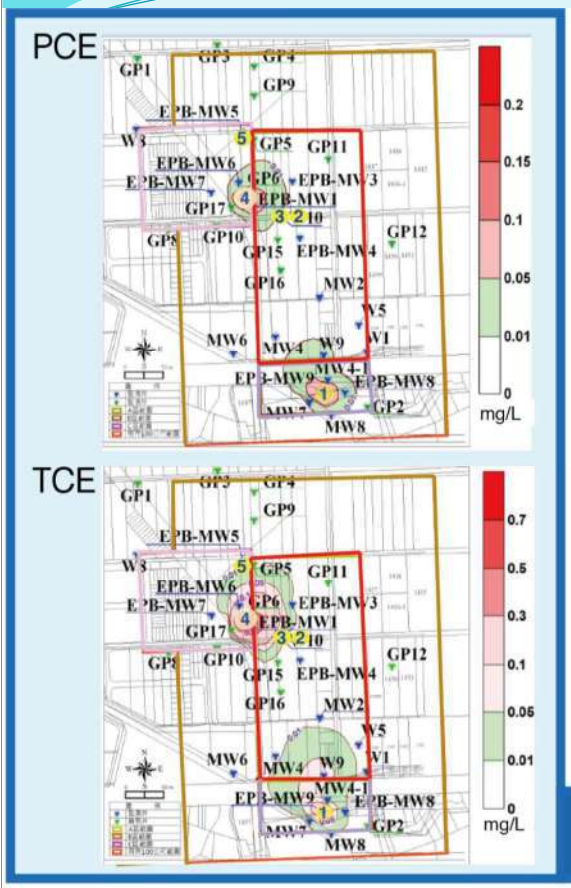
Case – YK Site, Tainan, Taiwan

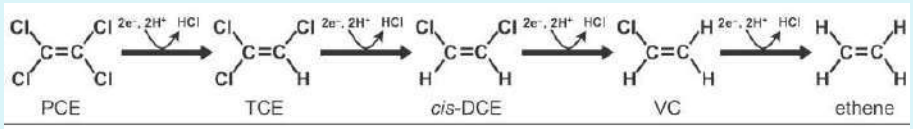


The sampling wells are numbered from upstream to downstream.

PCE and TCE hotspots: Location 1 and 4.

70

Dehalogenation Bacteria and Genes



(Futagami *et al.*, 2008)

Desulfitobacterium sp. strains PCE1 and KBC1

Desulfitobacterium hafniense strains PCE-S, TCE1, and Y51
Dehalobacter restrictus strains PER-K23 and TEA
Sulfurospirillum multivorans
Sulfurospirillum halorespirans strain PCE-M2
Desulfuromonas michiganensis strains BB1 and BRS1
Geobacter lovleyi strain SZ

Dehalococcoides ethenogenes strain 195

Dehalococcoides sp. strain FL2

Dehalococcoides sp. strain BAV1

Dehalococcoides sp. strain VS

Dehalococcoides sp. strains GT and KB1/VC

Dehalococcoides sp. strain MB

Dehalogenation Genes (RDase genes)

pceA, tceA

tceA

bvcA

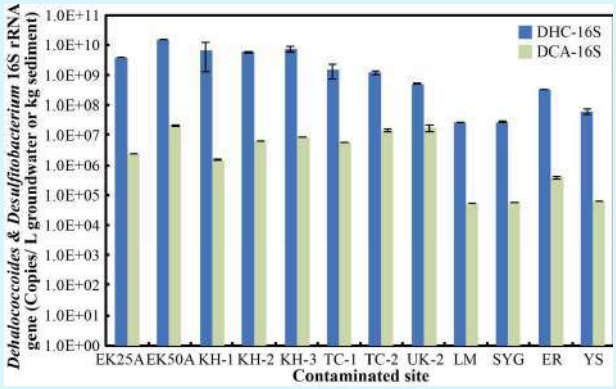
vcrA

vcrA

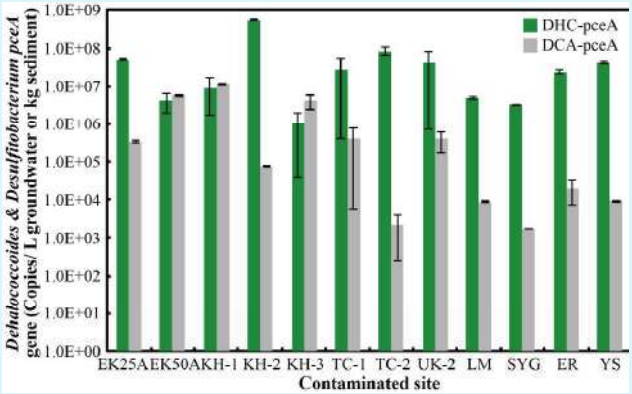
mbrA

Dehalococcoides genus is the key bacteria to degrade PCE/TCE to ethene

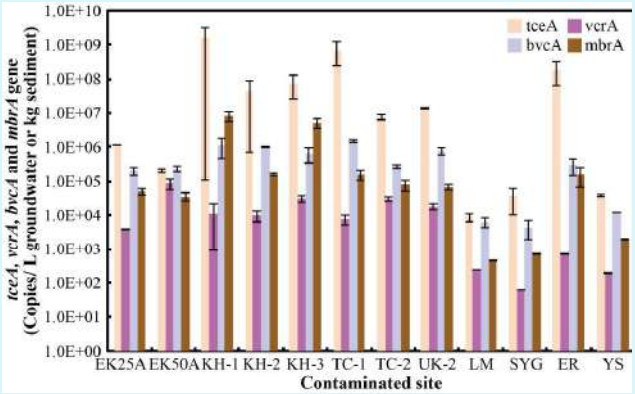
Abundance of *Dehalococcoides* and genes



Dehalococcoides genus and *Desulfitobacterium* genus 16S rRNA



pceA



tceA, vcrA, bvcA and *mbrA*

Nanoparticles in Groundwater: Transport and Remediation

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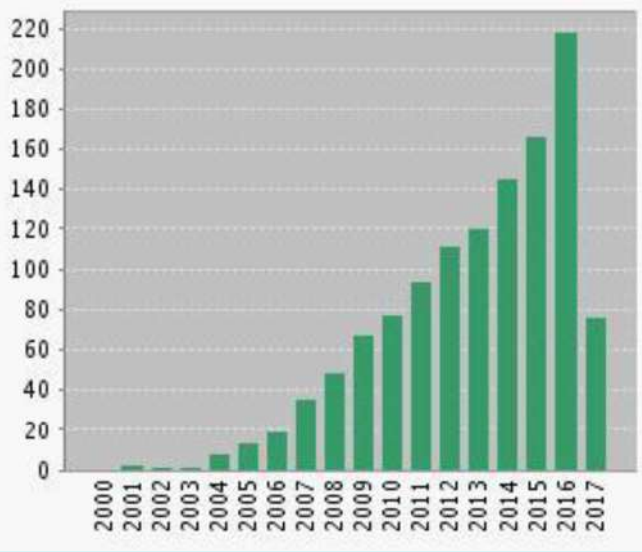
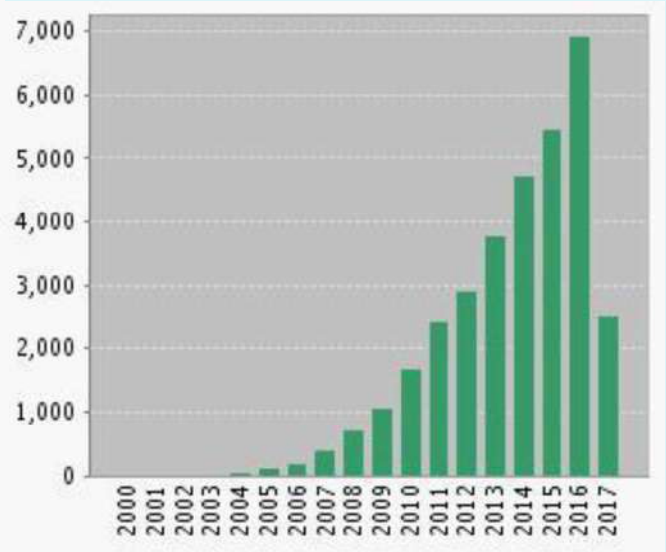
Nanoparticles and Groundwater (WOS)



Publications (1214)
First One in 2000



Citation (33051, 27.2/paper)
US 49.2 ; China: 24.0;
S Korea: 25.5; TW: 33.2

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Countries (1214)

• USA	391	32.2%
• PEOPLES R CHINA	346	28.5%
• INDIA	84	6.9%
• GERMANY	70	5.8%
• SOUTH KOREA	54	4.5%
• **TAIWAN**	**51**	**4.2%**
• IRAN	45	3.7%
• CANADA	44	3.6%
• ENGLAND	39	3.2%
• SPAIN	37	3.1%

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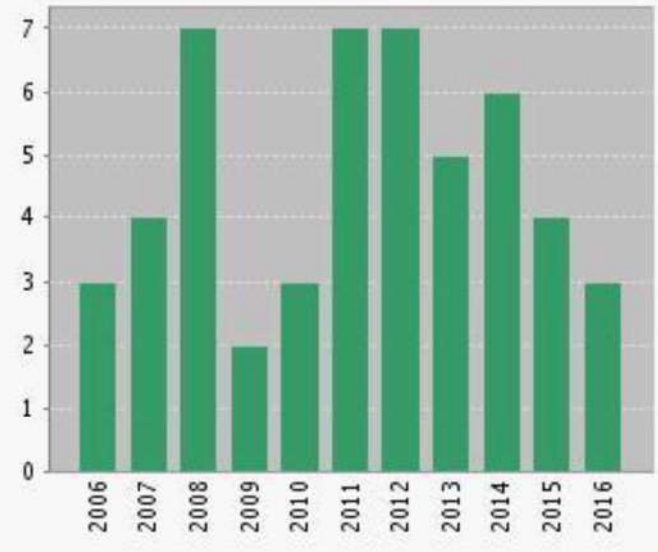
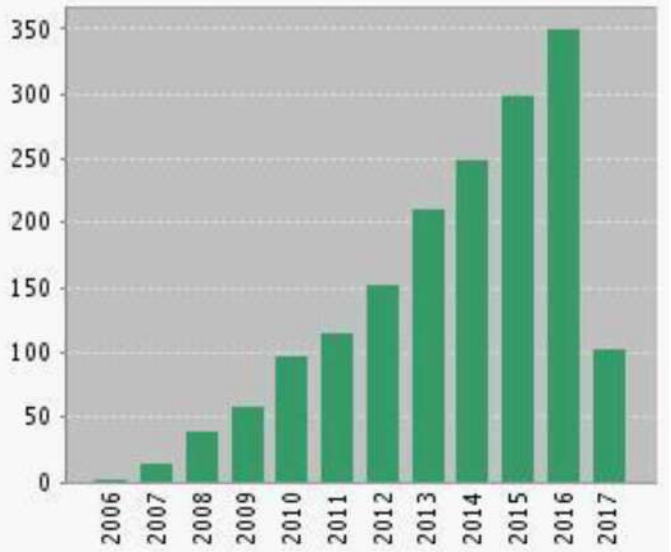
Nanoparticles and Groundwater (WOS)- Taiwan



Publications (51)
First One in 2006



Citation (1695, 33.2/paper)

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Materials for Remediation

- Mostly metals or metal oxides, most frequently nanoscale zerovalent iron (nZVI).
- May be modified to improve their performance: catalyst (often palladium), coatings or modifiers, or activated carbon or zeolites (for iron oxides).

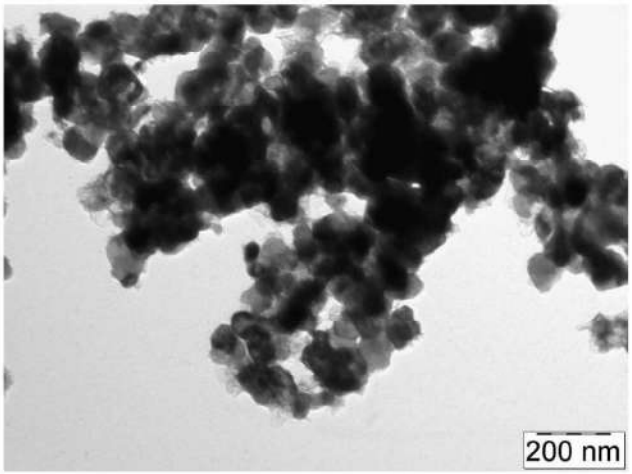

Figure 1. TEM image of nZVI particles injected at the Spolchemie I Site © J. Filip, UPOL, Palacký University in Olomouc, Czech Republic.

Nanotechnology for Contaminated Land Remediation – Possibilities and Future Trends Resulting from the NanoRem Project (2016)

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Field Applications and Limitations

- Appropriate Materials with Long-term Reactivity (?)
- Formation Byproducts
- Injection Methods
- Low Cost Production Techniques
- Transport and Models
- *In-situ* Monitoring and Analysis
- Toxicity and Risk Assessment
- Stakeholder Engagement/Communication

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Contact is always an Issue

P&T

Bioremediation

AS

ISCO NPs

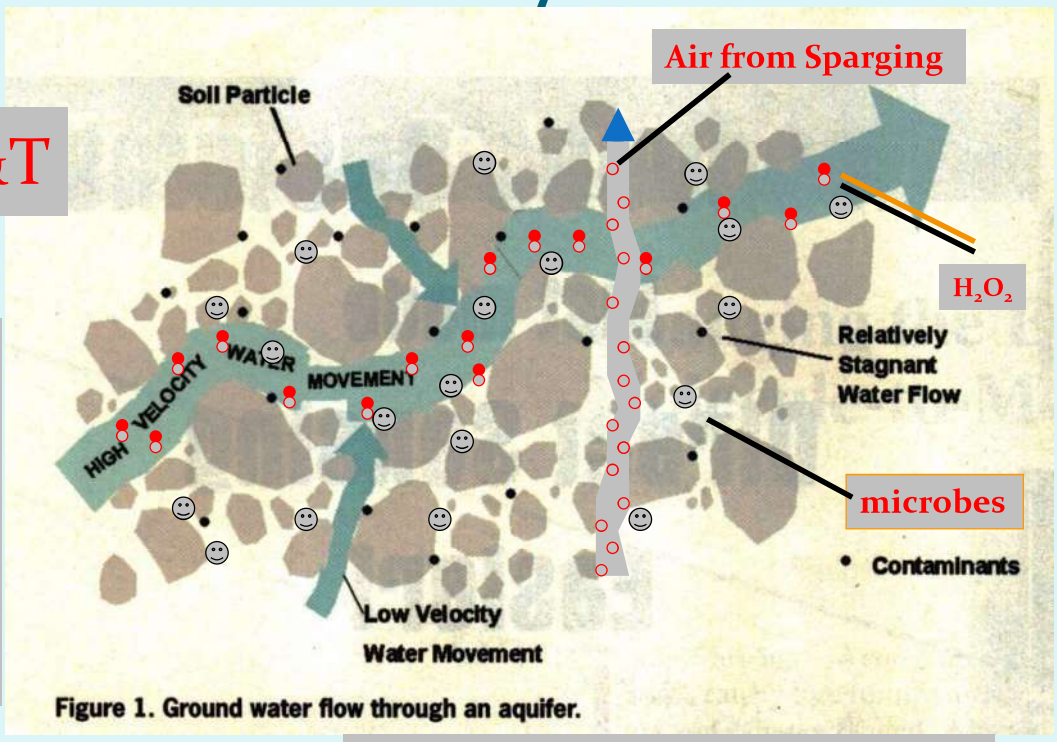

Figure 1. Ground water flow through an aquifer.

O2 and nutrient transport

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Conclusions

- Research in Taiwan
  - Similar between TW and other countries
  - More P/C, less Bio and Thermal
- Field Applications
  - Much experiences in soil remediation and Petroleum remediation
  - Less in mining industries and large, complexed sites
- SE Asia
  - S&GW is still new
  - Landfill and S&GW prevention
  - Drinking Water Sources

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Thank You for Your Attention

Co-authors: Drs Hsin-Ta Hsueh and Yi-Fong Pan

成功大學 National Cheng Kung University

global wATer quality research center

MOST 科技部 Ministry of Science and Technology

行政院環境保護署 Environmental Protection Administration Executive Yuan,R.O.C(Taiwan)

TASGEP

Web site of TASGEP：www.tasgep.org.tw

Acknowledgement:
TW MoST and TW EPA
for funding and data

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Soil and Groundwater Protection in Taiwan: Status and Future Directions

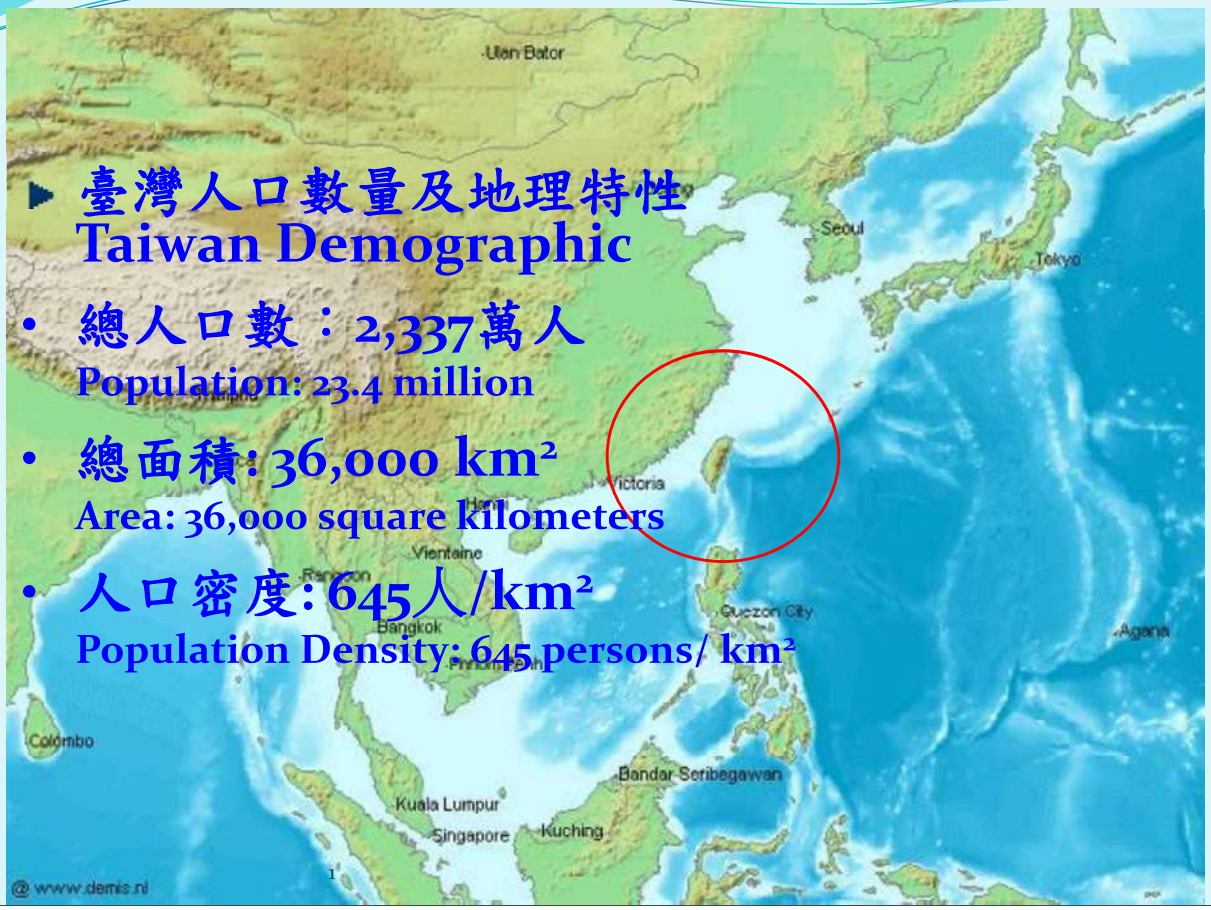
Speaker: Dr. Weber Chen

Taiwan EPA

Outline

- Background
- Contamination Investigation Policy, Remediation Standards, Remediation Order
- Taiwan Soil and Groundwater Pollution Map
- Pollution control and remediation
- The Fund
- Contaminated soil off-site treatment and reuse
- Site risk assessment and Brownfield
- International Exchange and Collaboration
- Prospect

Introduction



- 臺灣人口數量及地理特性
  Taiwan Demographic
- 總人口數：2,337萬人
  Population: 23.4 million
- 總面積：36,000 km²
  Area: 36,000 square kilometers
- 人口密度：645人/km²
  Population Density: 645 persons/ km²

Background

1980's~1990's

農地污染-鎘米事件

Farmland Pollution- Cd rice

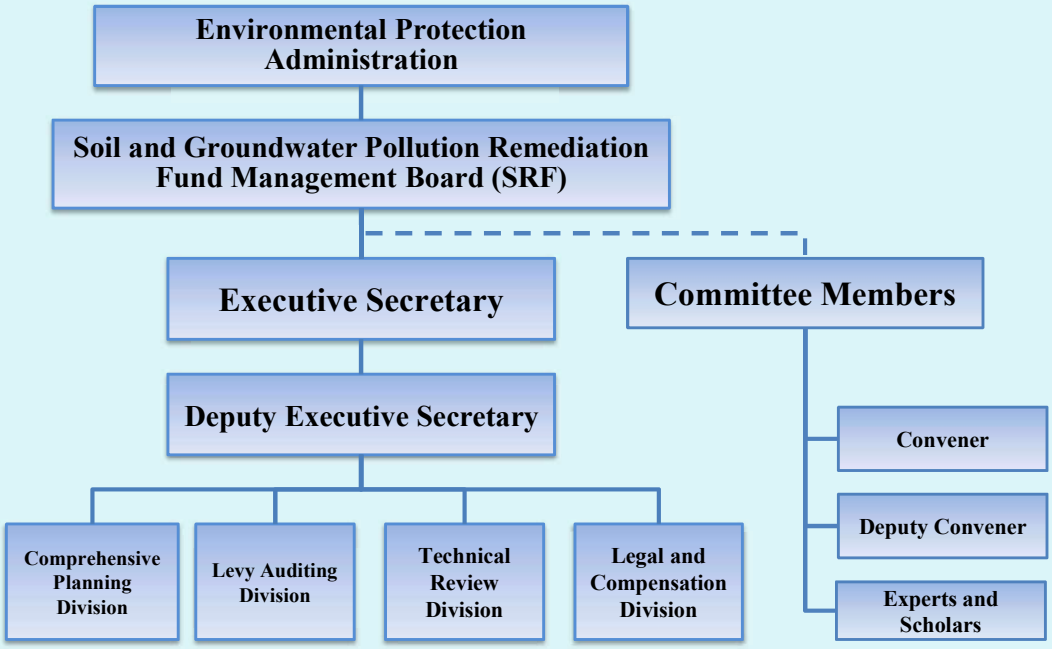
工廠污染-RCA，中石化

Factory Pollution- RCA, CPDC

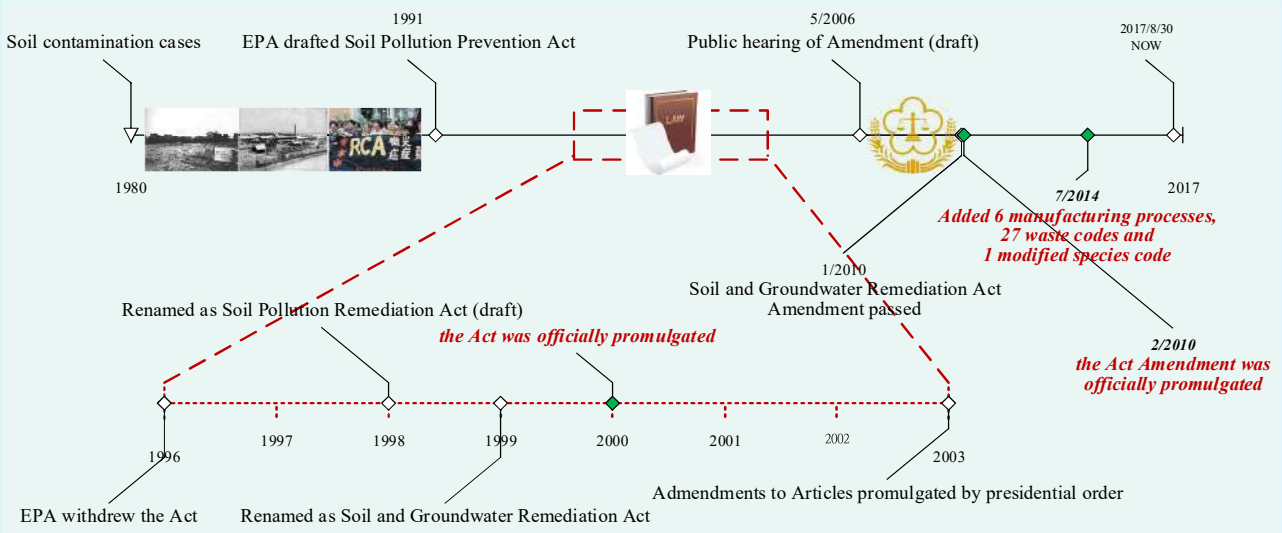
民眾健康

Public Health

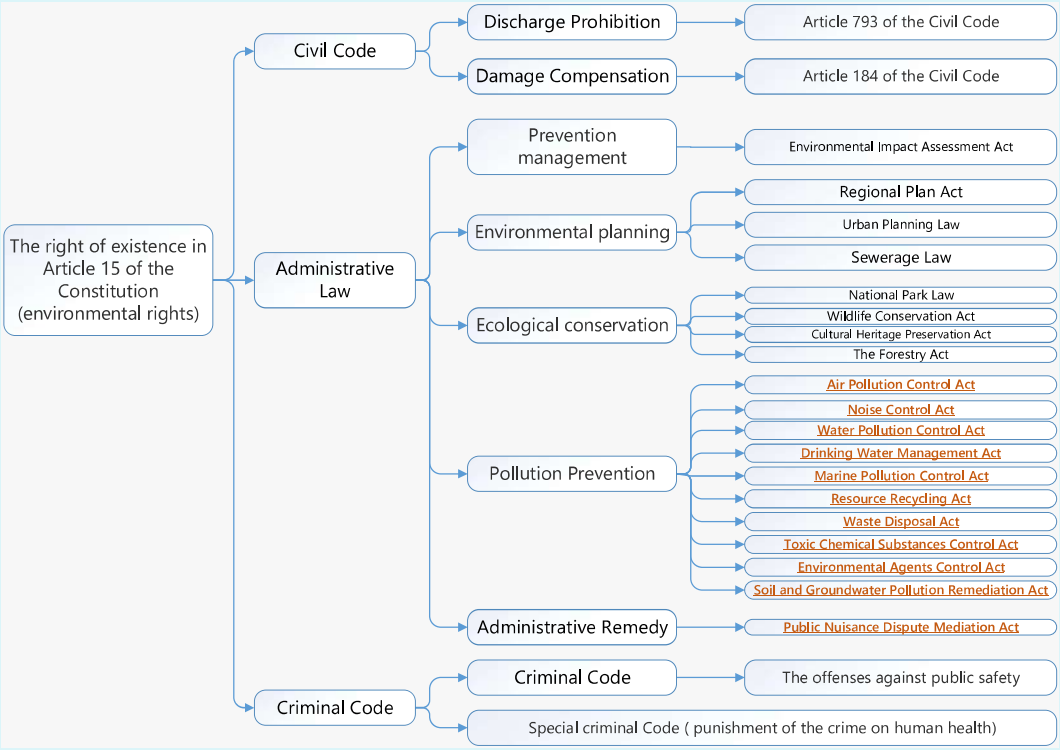
Organization Chart



Soil and Groundwater Remediation Regulation



Regulations related to environmental protection



S&GPR_Act

- (Composition) Soil and Groundwater Pollution Remediation Act (S&GPR_Act) consists of:
  - Ch. 1 General Principles (5 articles)
  - Ch. 2 Prevention Measure (6 articles)
  - Ch. 3 Investigation and Assessment Measures (3 articles)
  - Ch. 4 Regulatory Measures (6 articles)
  - Ch. 5 Remediation and Restoration Measures (6 articles)
  - Ch. 6 Financing and Responsibility (4 articles)
  - Ch. 7 Penal Provisions (16 articles)
  - Ch. 8 Supplementary Provisions (10 articles)

Article 1

This Act is formulated to prevent and remediate soil and groundwater pollution, ensure the sustainable use of soil and groundwater, enhance the living environment, and protect public health.

S&GPR_Act

Composition	Content
General Principles	*Purpose, terminology, and competent authorities jurisdiction;*
Prevention Measure	*Sediments quality evaluation, Soil and groundwater quality evaluation for designated areas(i.e. industrial parks), Investigation, necessary response measures, Assessment of enterprise officially announced by central competent authority, Analysis facilities and methods, Registered engineer certification;*
Investigation and Assessment Measures	*Declaration of control/remediation sites, Necessity for sediment investigation, Background contamination, Pollution control plan submission*
Regulatory Measures	*Emergency response measures, Publicly announced and management of control/remediation site, Entrust registration site for prohibition of land transaction*
Remediation and Restoration Measures	*Remediation plan submission and display, Remediation goal determination based on health risk assessment, Implementation of control/remediation site, Cancellation of control/remediation site, Delineation of groundwater pollution restriction zone if pollution source is unclear*
Financing and Responsibility	*Levy Soil and Groundwater Pollution Remediation Fund, Derivation of fund source, Establishment of fund management committee, Interested party obligation and responsibility*
Penal Provisions	*Penalties under various conditions*
Supplementary Provisions	*Joint liabilities for compensation, Retroactivity*

Execution

Environmental Background Monitoring

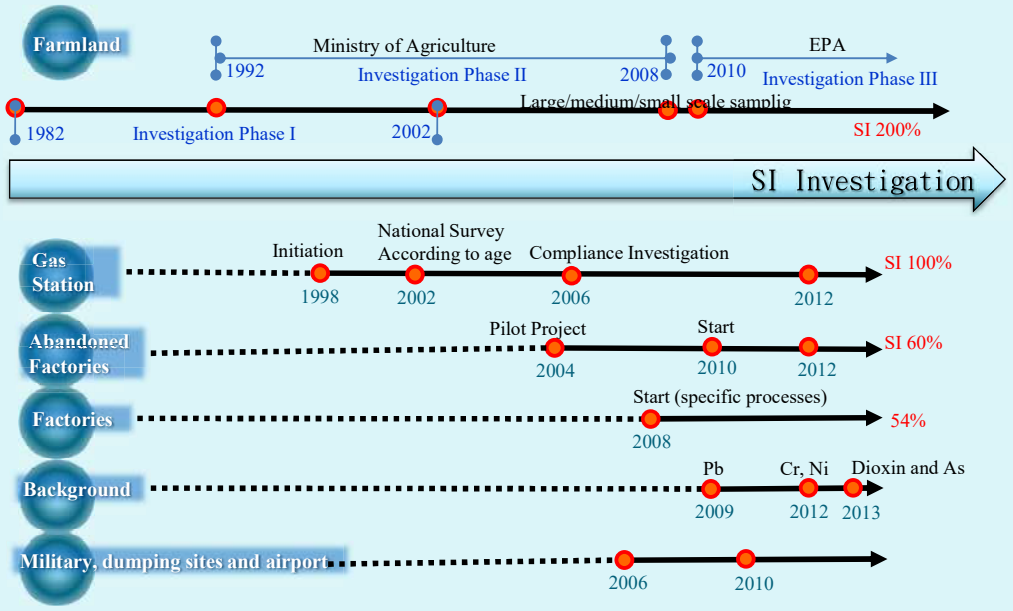
Polluted Site Investigation

Polluted Site Declaration

Pollution Remediation

Site Monitoring

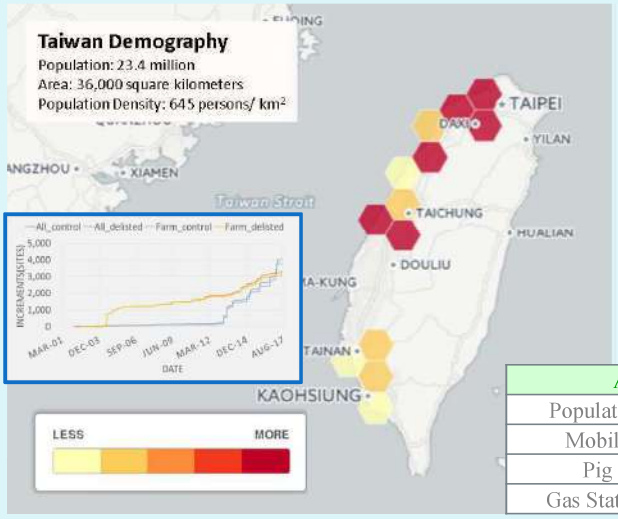
Site Investigation



(Refer to the information of Director Ho of TWEPA)

Taiwan Soil and Groundwater Pollution Map

Data updated: 2017



Control sites

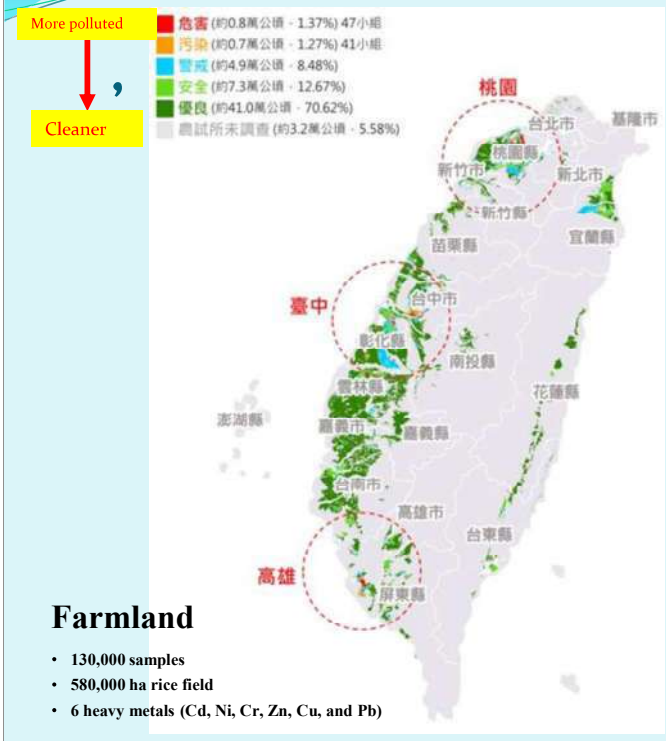
Number：4,032
(3767 for farm)

Control sites relieved from announced control list

(3142 for farm)
Number：3,220

1980's~1990's
Farmland Pollution-
Cadmium-Polluted Rice

Area	TW	CN	US	JP	KR	DE	UK	NL	FR
Population Density	645	143	32	337	503	226	263	404	116
Mobile Density	596	20	26	231	203	147	142	-	75
Pig Density	160	48	7	26	99	79	18	295	25
Gas Station Density	0.07	0.01	0.01	0.09	0.13	-	-	-	-



Farmland

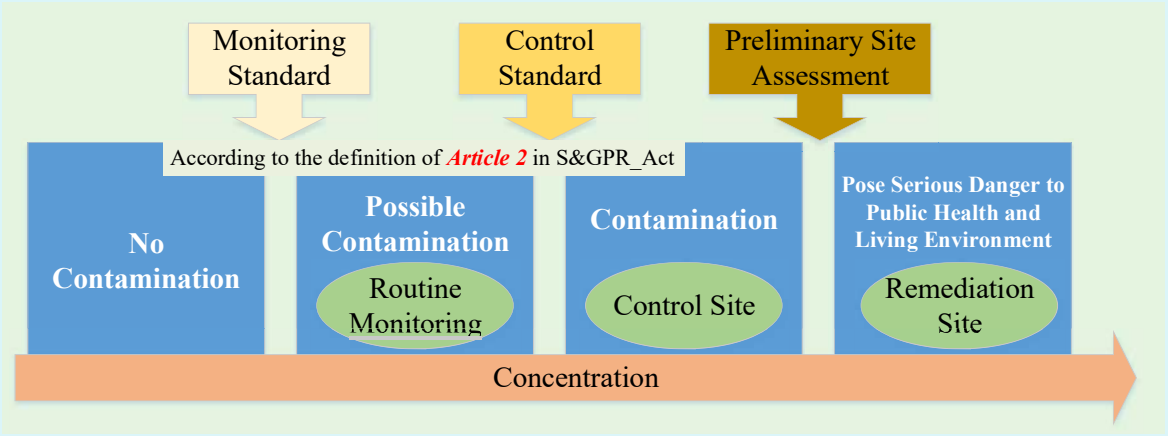
- 130,000 samples
- 580,000 ha rice field
- 6 heavy metals (Cd, Ni, Cr, Zn, Cu, and Pb)

151 Industrial Parks (2014)

Light	Definition	Number
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

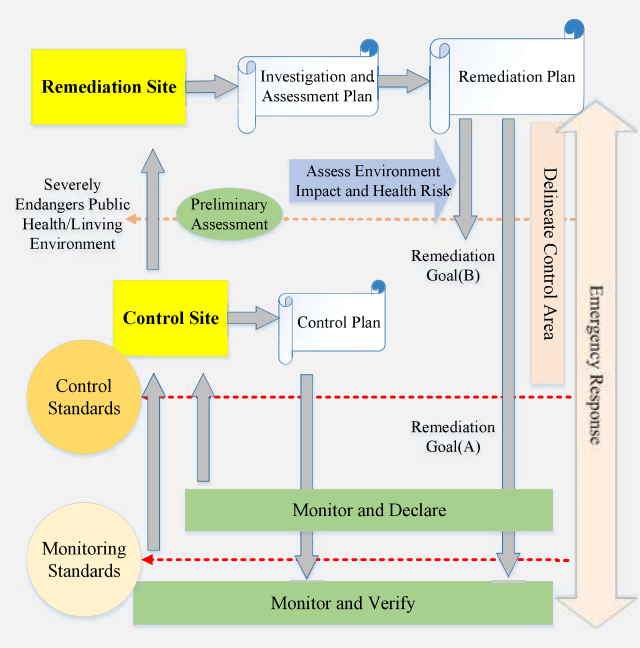
Determination of Soil & Groundwater Contamination

- Four steps between "No Contamination" to "Remediation Site" should be followed by comparison between concentration of Soil(GW) contamination and standards



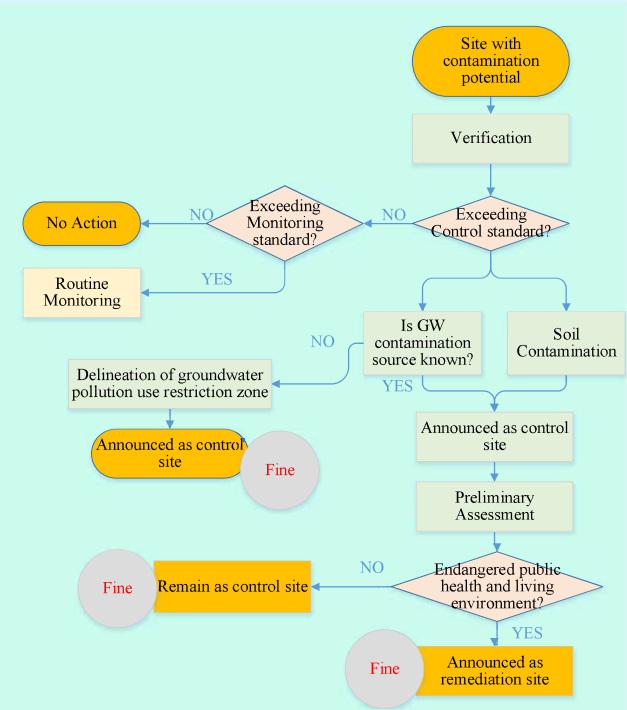
Responsibility

- (Control Site) Investigation, preparing and executing pollution control plan
- (Remediation Site)
  - Preparing and executing contamination investigation and assessment plan
  - Preparing and executing pollution remediation plan
- Conducting emergency response measures
- Execution Framework was shown in right side



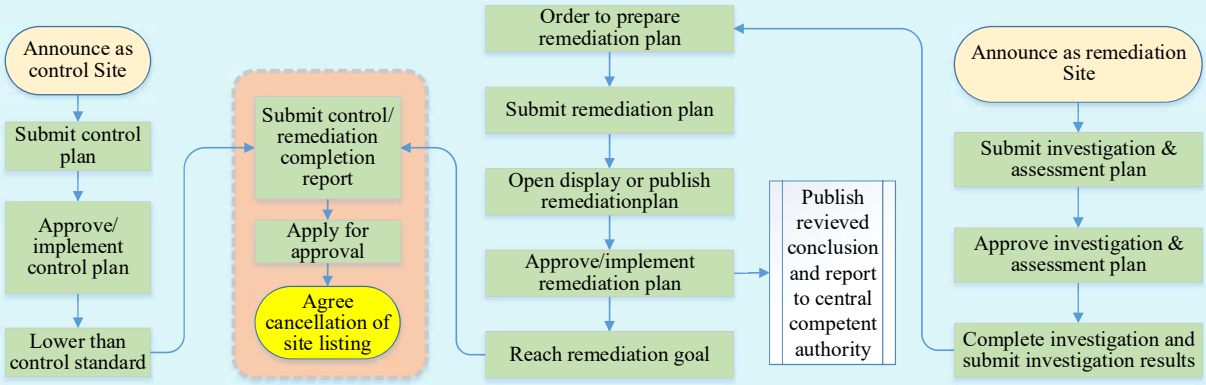
Publicly Declare Procedures and Related Fines

- (Potential) Polluter
  - Fine $100k-$500k if announced as control site; $150k-$750k as remediation site;
  - Announce personal or polluter name and shall order to receive 4hr lesson concerning relevant laws and regulation;
  - If fail to attend, fine $50k-$250k per violation until attending.
- Interested Party of the Polluted Land
  - Failure to demonstrate due diligence as a good manager;
  - Fine $50k-$250k if announced as control site; $100k-$500k as remediation site



Execution of Control & Remediation Plan

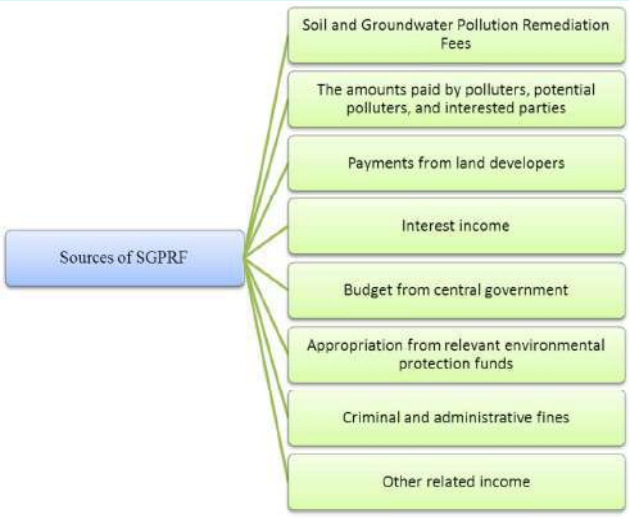
- Execution procedure of Control & Remediation Plan was shown below

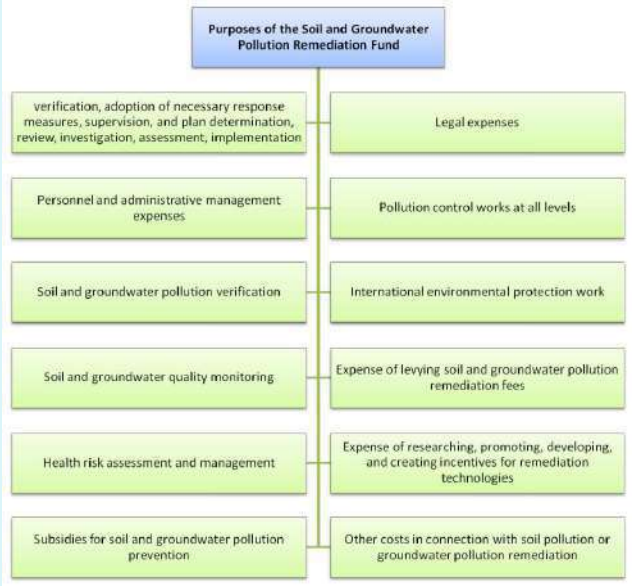


The Fund

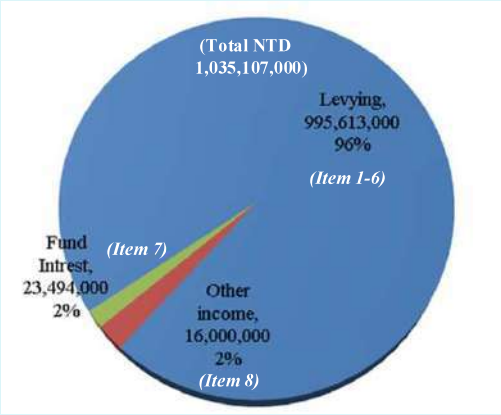
- ✓ **Like US Superfund**
- ✓ **Manufacturers and Importers Pay**
- ✓ **Amounts of Officially Announced Chemical Substances**
- ✓ **Just for Soil and Groundwater Pollution Prevention and Remediation Use**
- ✓ **Establish Soil and Groundwater Pollution Remediation Fund**

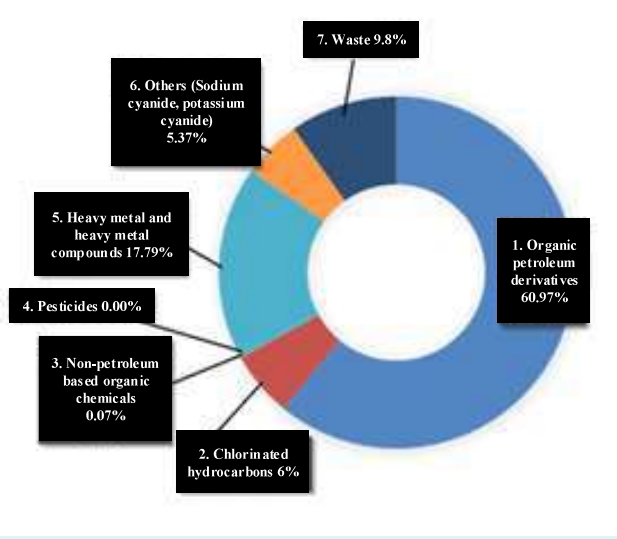
The sources and the purposes of the use of the Fund





Current SGPRF Income in 2016 and its Levy Ratio





- **Contaminated soil off-site treatememt, disposal and reuse**

21

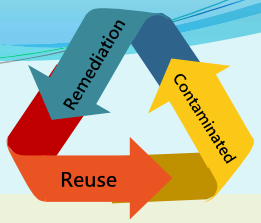
Future Directions

- Complete Farmland Remediation by 2021
- Promote Site Risk Assessment
- Risked Based Redevelopment and Reuse of Brownfields
- Strength International Cooperation

- **Site risk assessment**

23

Brownfield Development

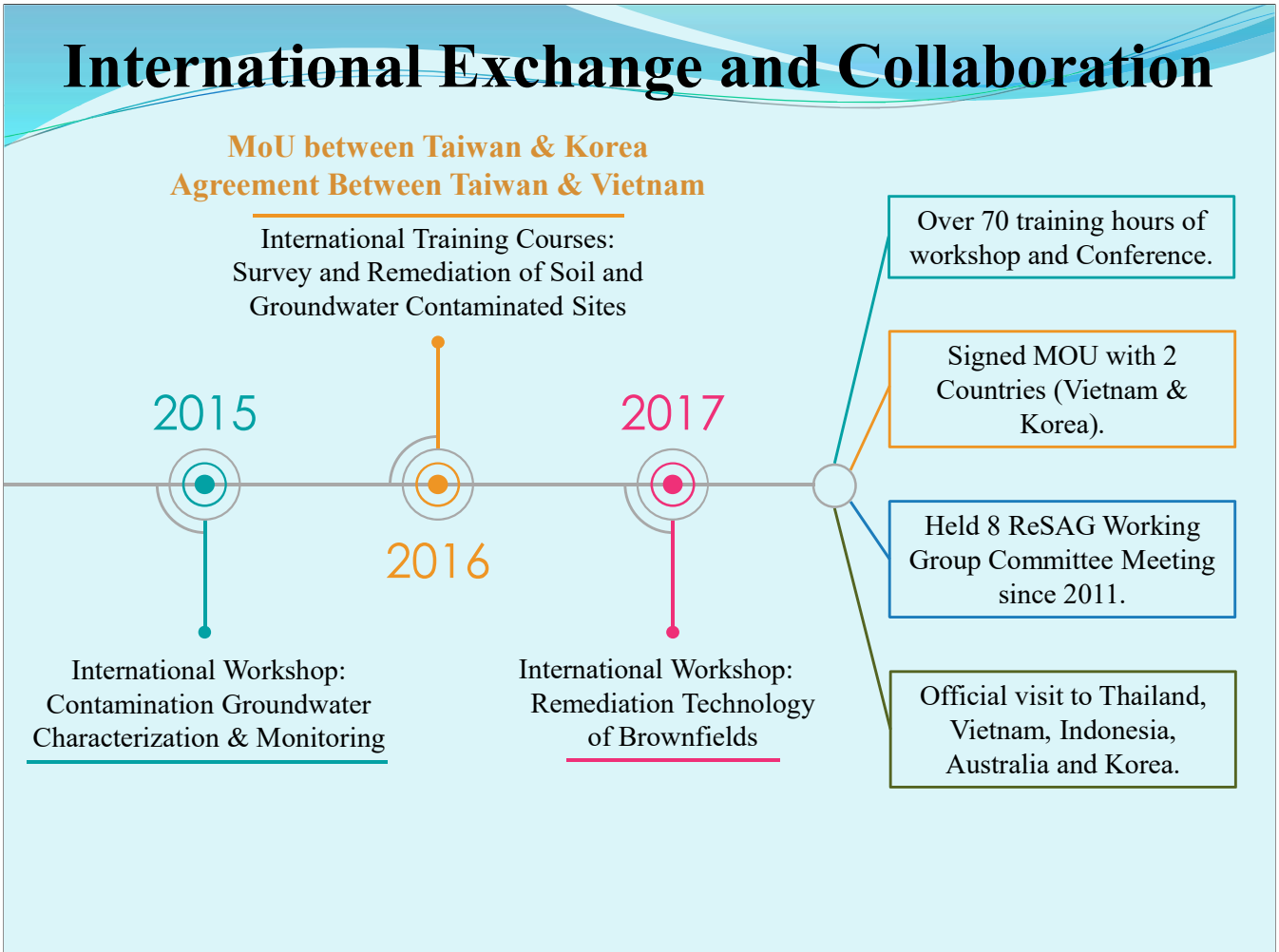


- Remediation Goal
  - Central competent authority may approve remediation goals in consultation with relevant agencies. Land development of the remediation site may not be changed after approval of the remediation goals;
  - Any changes in development may be implemented only after obtaining approval from central competent authority in consultation with relevant agencies.
- Land Development Plan
  - When land development plan involves with polluted land, it may be submitted concurrently with remediation plan, and shall reviewed in accordance with relevant laws and regulations;
  - Implementation of the land development plan only can proceed after the cancellation of regulatory listing of the remediation site.

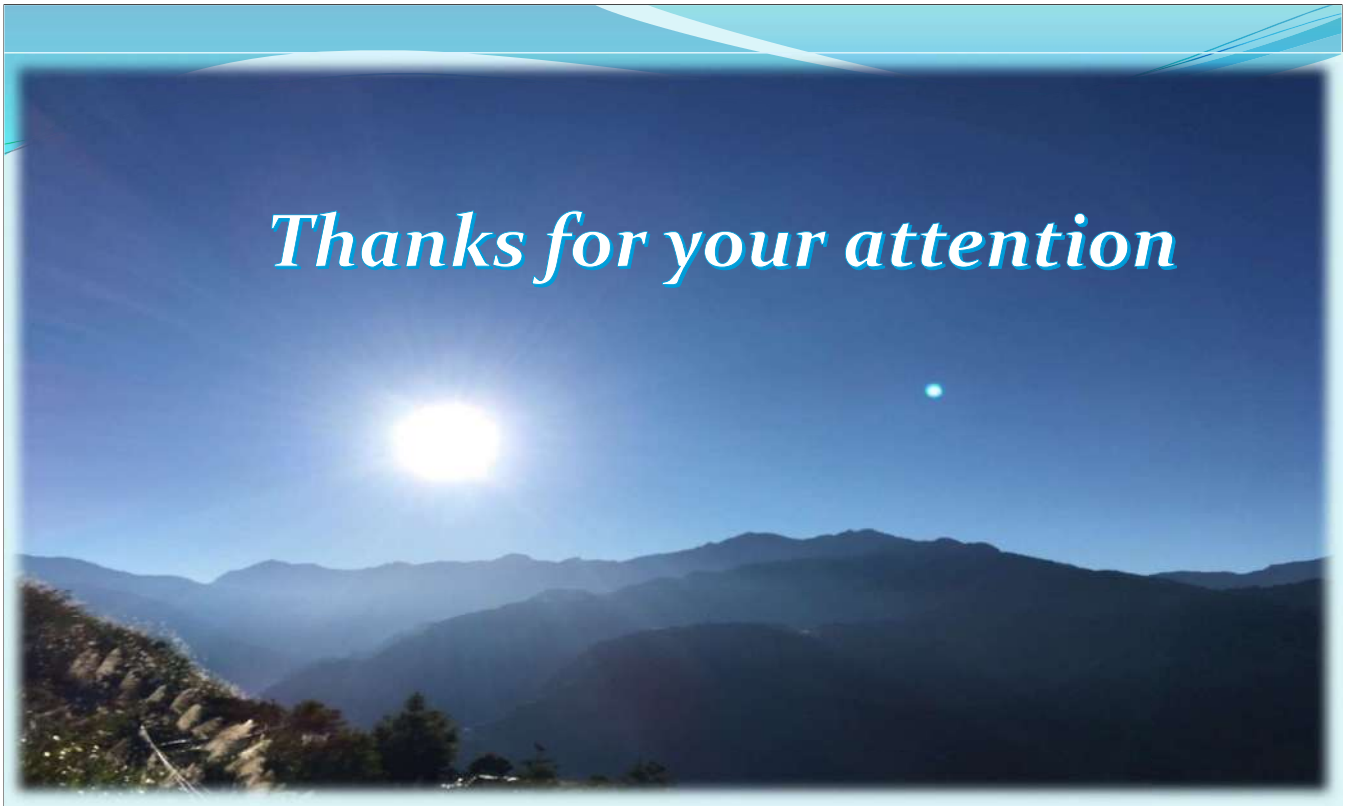
- Fee
  - Before cancellation of regulatory listing and implementation of land development plan, land developer shall pay 30% of the present value of the polluted area into the Soil and Groundwater Pollution Remediation Fund;
  - However, if the land developer had already submitted and completed a remediation plan prior to the day the special municipality, county, or city competent authority submitted a remediation plan, the case shall not be subject to this restriction.

International Exchange and Collaboration

International Exchange and Collaboration



Technology Sharing and Training



2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Bioremediation: Theories and Case Studies in US

Kung-Hui Chu, P.E

Associate Professor, Environmental, Water Resources and Coastal Engineering,
Zachry Department of Civil Engineering, Texas A&M University, College Station, TX.

kchu@civil.tamu.edu; http://ceprofs.tamu.edu/kchu

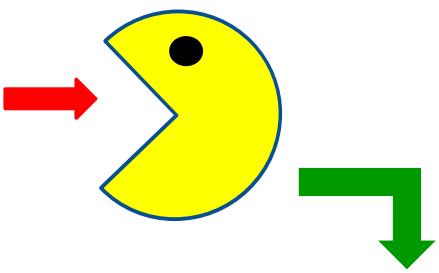
What is Bioremediation ?

⇒ Application of biological degradation reactions to destroy or detoxify environmental contaminants.

Contaminated soils and groundwater

- PCE, TCE,
- BTEX, MTBE, TBA
- PAHs, PCBs
- Pesticides
- Perchlorate
- ....

Microorganisms



Clean soil and groundwater

Bioremediation

Advantage

- Low cost
- Low tech
- Known technology
- Possible destruction of contaminants, particularly for organics
- Possible removal of metals

Disadvantage

- Not effective for recalcitrant compounds
- Interferences with co-contaminants or toxics

In-situ vs *Ex-situ*

In-situ: contaminated solids or groundwater remained in place during bioremediation

Ex-situ: contaminated solids (or groundwater) are excavated and transferred to an aboveground treatment system.

- Intrinsic *in-situ:* *e.x., Monitored Natural Attenuation (MNA)*
- Engineered *in-situ:* *e.x., Biostimulation, Bioaugmentation.*
- Engineered *ex-situ*: e.x., Pump-and-Treat

Factors Causing Compounds Recalcitrance

- Molecular Structure
  - Biodegradability: halogenated < non-halogenated compounds
- Environmental Conditions
  - Is compound accessible/available to microorganisms?
    - example 1: Non-aqueous phase liquid (NAPL)
      - Dense non-aqueous phase liquid (DNAPL)
      - Light non-aqueous phase liquid (LNAPL)
    - example 2: strongly sorbed to particles, or matrix
  - Are factors essential for growth present?
    - Electron acceptors, Electron donors, Nutrients (N or P), pH, Temp, Redox
  - Are inhibitory or toxic compounds to microbial growth present?
  - Are desired degradative enzymes active? Or expressed?
- Microorganisms
  - Are degradative microorganism present and active?
  - Can these degraders degrade target contaminants effectively?

Organics

Inorganics

Table 14.1 Categories of environmental contaminants, their frequency, and sources

Chemical Classes	Example Compounds[a]	Occurrence Frequency[b]	Examples of Industrial Sources or Applications
Organic			
Hydrocarbons			
low FW	Benzene, xylenes, toluene (BTEX); alkanes	F	Crude oil, refined fuels, dyestuffs, solvents
high FW	Polycyclic aromatic hydrocarbons (PAHs), creosotes	C	Creosote, coal tar, crude oil, dyestuffs
Oxygenated Hydrocarbons			
low FW	Alcohols, ketones, esters, ethers, phenols methyltertiarybutylether (MTBE)	F	Fuel oxygenates, solvents, paints, pesticides, adhesives, pharmaceuticals, fermentation products, detergents
Halogenated Aliphatics			
Highly chlorinated	Tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), carbon tetrachloride (CT)	F	Dry cleaning, degreasing solvents
Less chlorinated	Dichloroethane (DCAs), dichloroethene (DCE), vinyl chloride (VC), dichloromethane (DCM)	F	Solvents, pesticides, landfills, biodegradation by-products
Halogenated Aromatics			
Highly chlorinated	Pentachlorophenol, polychlorinated biphenyls (PCBs), polychlorinated dioxins (e.g., TCDD), polychlorinated dibenzofurans (e.g., TCDF)	C	Wood treatment, insulators, heat exchangers, by-products of chemical synthesis and combustion
Less chlorinated	Dichlorobenzene, PCBs	C	Solvents, pesticides
Nitroaromatics	Trinitrotoluene (TNT), RDX, HMX	C	Explosives
Inorganic			
Metals	Cr, Cu, Ni, Pb, Hg, Cd, Zn, etc.	F	Mining, gasoline additive, batteries, paints, fungicides
Nonmetals	As, Se	F	Mining, pesticides; irrigation drainage
Oxyanions	Nitrate, (per)chlorate, phosphate	F	Fertilizers, paper manufacturing, disinfection, aerospace
Radionuclides	Tritium (^{3}H), Pu, U, Ra, Ce, Tc	I	Nuclear reactors, weaponry, medicine, food irradiation

[a]Compound abbreviations: FW = formula weight; TCDD = 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, TCDF = 2,3,7,8-tetrachlorodibenzofuran; RDX = 1,3,5-trinitrohexahydro-*s*-triazine; HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

[b]Based on survey of groundwater contaminants, F = Very Frequent; C = Common; I = Infrequent. National Research Council. (2000). *Natural Attenuation for Ground Water Remediation*, Washington, D.C.: National Academy of Sciences Press.

Aerobic or Anaerobic

Aerobic

- electron donor
  - Pollutants
- electron acceptor
  - O_2

Anaerobic

- electron donor
  - Pollutants or H_2
- electron acceptor
  - nitrate
  - iron (III)
  - Mn (IV)
  - sulfate
  - CO_2
  - halogenated compounds (halorespiration), like perchlorate, chlorate, PCE/TCE

Contaminant	Microbial Degradability			Preferred Conditions
	High	*Low*	*No*	
Mineral oil hydrocarbons				
Short-chain mineral oil hydrocarbons	•			Aerobic
Long-chain/branched mineral oil hydrocarbons		•		Aerobic
Cycloalkanes		•		Aerobic
Monoaromatic hydrocarbons				
(Mono)aromatic hydrocarbons	•			Aerobic
Phenols	•			Aerobic
Cresols		•		Aerobic
Catechols	•			Aerobic
Polycyclic Aromatic Hydrocarbons				
2- to 3-ring-PAHs (e.g., naphthalene)	•			Aerobic
4- to 6-membered ring PAHs (e.g.,benzo(a)pyrene)		•		Aerobic
Chlorinated Aliphatic Hydrocarbons				
Tetrachloroethene, trichloroethane	•			Anaerobic
Trichloroethene	•			Anaerobic
Dichloroethane, dichloroethene, vinyl chloride	•			Anaerobic/aerobic
Chlorinated Aromatic Hydrocarbons				
Chlorophenols (superchlorinated)		•		Anaerobic
Chlorophenols (low-chlorinated)	•			Anaerobic/aerobic
Chlorobenzenes (superchlorinated)		•		Anaerobic
Chlorbenzenes (low-chlorinated)	•			Anaerobic/aerobic
Chloronaphthalene	•			Anaerobic/aerobic
* Polychlorinated biphenyls (PCBs) (superchlorinated)		•		Anaerobic
Polychlorinated biphenyls (low-chlorinated)	•			Anaerobic/aerobic

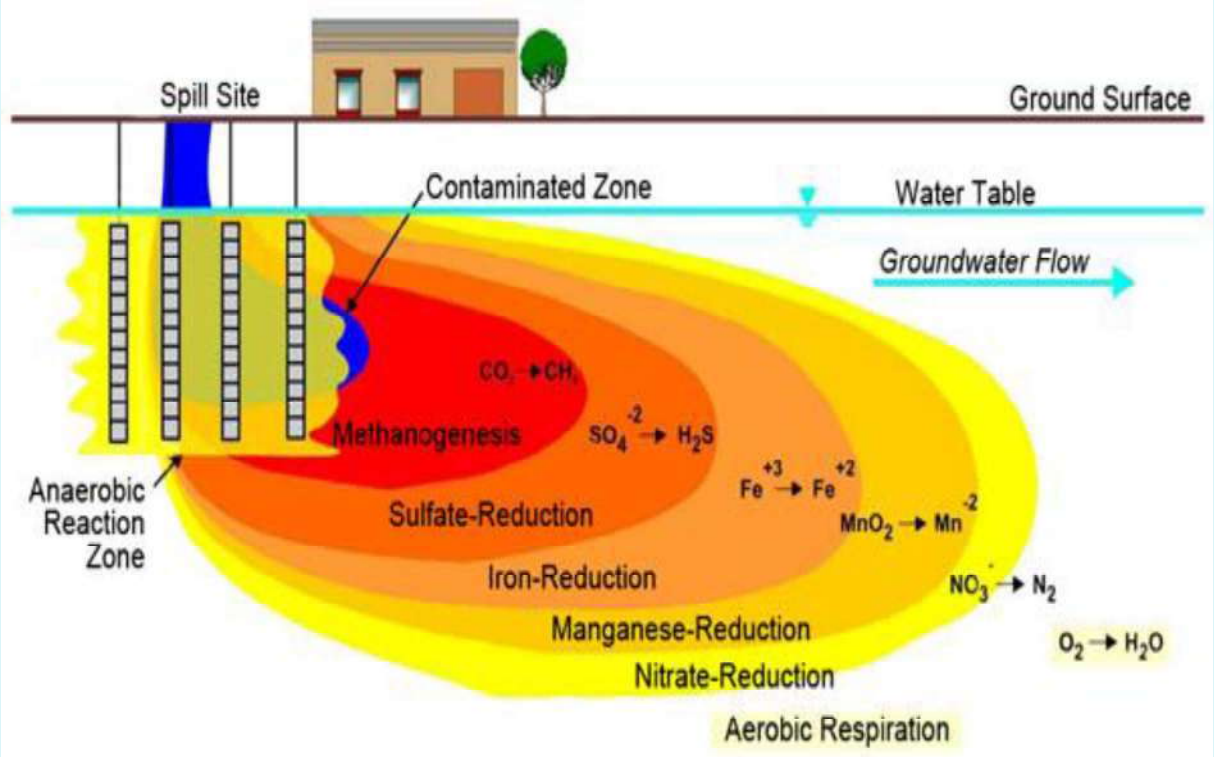
Chloronaphthalene	•			Anaerobic/aerobic
* Polychlorinated biphenyls (PCBs) (superchlorinated)		•		Anaerobic
Polychlorinated biphenyls (low-chlorinated)	•			Anaerobic/aerobic
Nitroaromatic Compounds				
Mono- and dinitroaromatics	•			Anaerobic/aerobic
Trinitrotoluene (TNT)	•			Anaerobic/aerobic
Trinitrophenol (picric acid)		•		Anaerobic/aerobic
Nitroaliphatic Compounds				
Glycerol trinitrate	•			Aerobic
Pesticides				
g-hexachlorocyclohexane (lindane)	•			Anaerobic/aerobic
b-hexachlorocyclohexane (lindane)		** •	•	Anaerobic/aerobic
Atrazines	•			Aerobic
Dioxins				
PCDD/F (several)		•		Anaerobic
2,3,7,8-PCDD/PCDF			•	
Inorganic Compounds				
Free cyanides		•		Aerobic
Complex cyanides		•		
Ammonium	•			Anaerobic/aerobic
Nitrate	•			Anaerobic
***Sulfate	•			Anaerobic

* The degradation process and susceptibility to degradation are different for planar and non-planar highly chlorinated PCB congeners

** Microbially transformable but not degradable

***Activity of sulfate-reducing bacteria results in precipitation of metal sulfides or production of hydrogen sulfide gas

Redox zones of a typical contaminant plume



(Source: Parsons 2004)

Methods to Introduce Oxygen Into Subsurface

- Injection of air or oxygen
- Introduction of oxygen-release compounds
  - Hydrogen peroxide
  - Ozone
  - Commercial oxygen-releasing compounds

Growth-linked vs Non-growth-linked

Growth-linked

- Microorganisms obtain nutrients (such as carbon or nitrogen) or energy when degrading the target compound.

Non-growth-linked (or so called "cometabolic" reactions)

- Some compounds are transformed by enzymes or cofactors that are originally designed for other compounds. Microorganisms gain no benefits (sometimes even harmful to themselves) when transforming these compounds.

  ex. Methane-oxidizing cultures and trichloroethylene (TCE)

=> Potential to degrade compounds to undetectable (part per trillion) concentrations (2010 Hazen)

Exhibit 4-5: Primary Reactants and Additives Typically Employed for Engineered *In Situ* Bioremediation of CAHs

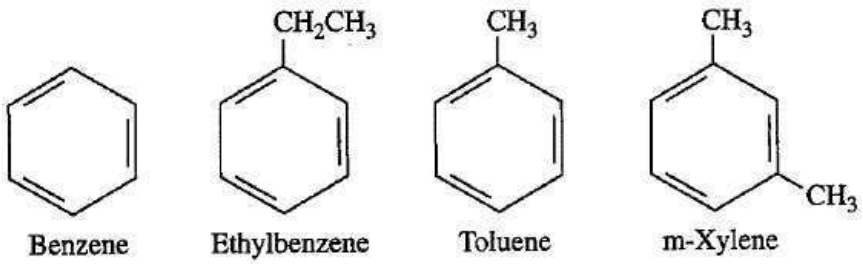
Engineered Bioremediation Mechanism	Targeted CAHs	Typical Primary Reactants and Additives in Engineered Systems	
		Primary Reactants	Typical Additives (primary reactant supplemented)
Aerobic oxidation (direct)	DCE, VC, DCA, CA, MC, CM	Oxygen, CAH	Air, oxygen, hydrogen peroxide, magnesium peroxide (oxygen)
Aerobic oxidation (cometabolic)	TCE, DCE, VC, TCA, CF, MC	Oxygen	Air, oxygen, hydrogen peroxide, magnesium peroxide (oxygen)
		Organic carbon or carbon from a contaminant source (anthropogenic)	Methane, propane, butane, ammonia (organic carbon)
Anaerobic reductive dechlorination	PCE, TCE, DCE, VC, TCA, DCA, CT, CF, MC	Hydrogen, organic carbon, or carbon from a contaminant source (anthropogenic)	Lactate, methanol, hydrogen, molasses (electron donor)

Sources: Anderson and Lovley 1997; McCarty 1994; McCarty and others 1998; USAF 1998; EPA 1998; Yager and others 1997

Growth-linked Bioremediation

Example 1: Aerobic and anaerobic bioremediation of aromatic compounds

Structure of BTEX



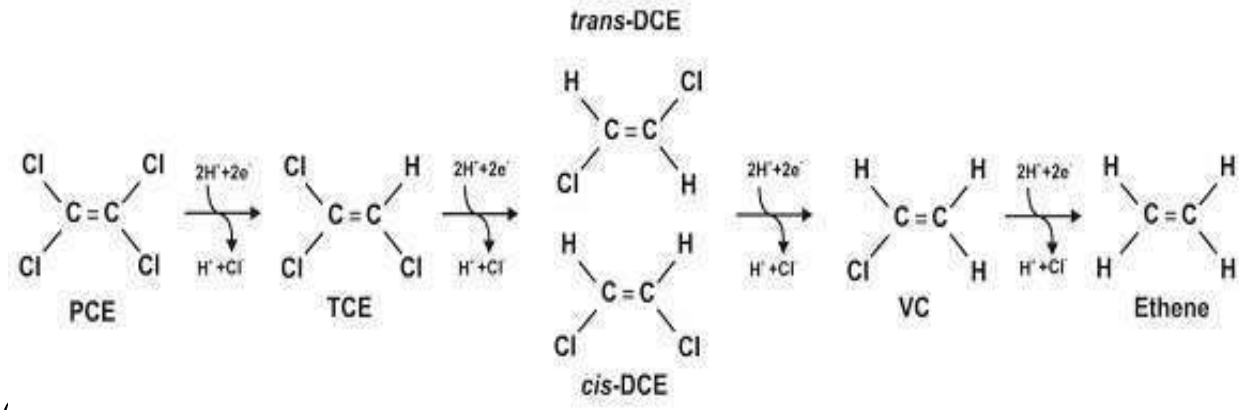
Benzene Ethylbenzene Toluene m-Xylene

Benzene (B) is a known carcinogen (cause leukemia). Ethylbenezene (E), Toluene (T), Xylenes (X) (three isomers, o-, m- and p-): suspected cacinogens.

Growth-linked Bioremediation

Example 2: Reductive Dechlorination of Tetrachloroethene (PCE)

- Tetrachloroethene or perchloroethylene (PCE)



(Source: Parsons 2004)

Redox Potential (Eh) and H_2

From Lovley et al., 1994. Environ. Sci. Technol. 28: 1205-1210)

- Many anaerobic microorganisms compete for H_2.
- Interspecies hydrogen transfer
  - H_2 is constantly produced by fermentative microorganisms and constantly consumed by respiratory microorganisms using nitrate, Fe (III), sulfate, and CO_2 as terminal electron acceptors.
- TEAPs = terminal electron-accepting processes

TEAPs and H_2 concentrations

Terminal Electron Accepting Process	Hydrogen (H_2) Concentration (nanomoles per liter)
Denitrification	< 0.1
Iron (III) Reduction	0.2 to 0.8
Sulfate Reduction	1 to 4
Reductive Dechlorination	>1
Methanogenesis	5-20

- Dechlorinators competed best against methanogens and homoacetogens when H_2 concentrations was maintained between 2-11nM

(From: Yang and McCarty. 1998. Environ. Sci. Technol. 32: 3591-3597)

Table 2-1. Examples of fermentation reactions using organic substrates to yield hydrogen

Electron donor	Electron-donor (oxidation) reaction
Ethanol	$C_2H_6O + H_2O \Rightarrow C_2H_3O_2^- + H^+ + 2H_2$ ethanol fermentation to acetate
Methanol	$CH_4O + 2H_2O \Rightarrow CO_2^- + H_2O + 3H_2$ methanol fermentation
Acetate	$C_2H_3O_2^- + 4H_2O \Rightarrow 2CO_2^- + 2H_2O + 4H_2$ acetate fermentation
Butyrate	$C_4H_7O_2^- + 2H_2O \Rightarrow 2C_2H_3O_2^- + H^+ + 2H_2$ butyrate fermentation to acetate
Propionate	$C_3H_5O_2^- + 3H_2O \Rightarrow C_2H_3O_2^- + CO_2^- + H_2O + 3H_2$ propionate fermentation to acetate
Lactate	$C_3H_5O_3^- + 2H_2O + \Rightarrow C_2H_3O_2^- + CO_2^- + H_2O + 2H_2$ lactate fermentation to acetate

(*Source:* AFCEE 2004b)

Table 2-2. Examples of reactions using hydrogen as the substrate

Electron acceptor	Electron-acceptor (reduction) half reaction
Oxygen	$2H_2 + O_2 \Rightarrow 2H_2O$ aerobic respiration
Ferric iron	$H_2 + H^+ + FeOOH \Rightarrow Fe^{2+} + 2H_2O$ "ferric oxyhydroxide" dissolution/reduction
Sulfate	$4H_2 + H^+ + SO^{2-}_4 \Rightarrow HS^- + 4H_2O$ sulfate reduction
Carbon dioxide	$4H_2 + CO_{2,g} \Rightarrow CH_{4,g} + 2H_2O$ methanogenesis
PCE	$H_2 + C_2Cl_4 \Rightarrow C_2HCl_3 + HCl$ PCE reductive dechlorination
TCE	$H_2 + C_2HCl_3 \Rightarrow C_2H_2Cl_2 + HCl$ TCE reductive dechlorination
DCE	$H_2 + C_2H_2Cl_2 \Rightarrow C_2H_3Cl + HCl$ cis-1,2-DCE reductive dechlorination
VC	$H_2 + C_2H_3Cl \Rightarrow C_2H_4 + HCl$ VC reductive dechlorination

(*Source:* AFCEE 2004b)

Most Commonly Used Substrates and Methods of Delivery (Anaerobic Bioremediation)

Common Soluble Substrates
Sodium lactate, lactic acid
Propionate and butyrate
Methanol and ethanol
Sodium benzoate
Molasses, high fructose corn syrup
Slow-Release Substrates
Hydrogen Releasing Compound® (HRC®) Products
Vegetable oils
Vegetable oil emulsions
Chitin
Whey

Solid Substrates
Mulch and compost
Chitin (solid)
Other
Zero valent iron (ZVI) and organic substrate
Emulsified ZVI
Hydrogen
Humic acids

Nongrowth-linked Bioremediation

Cometabolic degradation of contaminants by various oxygenase-expressing bacteria

- TCE
- MTBE
- NDMA
- 1,4-dioxane
- FTOHs (fluorotelomer alcohols)

Methane-, propane-, butane-, alkane-oxidizing bacteria -> monooxygenases

Table 2. Susceptibility of chlorinated aliphatic hydrocarbons to aerobic metabolism or cometabolism

Compound	Structure	Abbreviation	Metabolism	Cometabolism	Growth substrates
Chloromethane	CH_3Cl	CM	Y	Y	A, M
Methylene chloride	CH_2Cl_2	DCM	Y	Y	A, M
Chloroform	$CHCl_3$	CF	N	Y	A, B, M
Carbon tetrachloride	CCl_4	CT	N	N	–
Chloroethane	CH_3CH_2Cl	CA	Y	Y	A, M
1,1-Dichloroethane	CH_3CHCl_2	1,1-DCA	Y	Y	A, M
1,2-Dichloroethane	CH_2ClCH_2Cl	1,2-DCA	Y	Y	A, C, M, T
1,1,1-Trichloroethane	CCl_3CH_3	1,1,1-TCA	N	Y	A, M
1,1,2-Trichloroethane	$CHCl_2CH_2Cl$	1,1,2-TCA	N	Y	A, C
1,1,1,2-Tetrachloroethane	CCl_3CH_2Cl	1,1,2-TCA	N	Y	A
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	1,1,2,2-TCA	N	N	–
Pentachloroethane	CCl_3CHCl_2	PCA	N	N	–
Hexachloroethane	CCl_3CCl_3	HCA	N	N	–
Vinyl chloride	CH_2=CHCl	VC	Y	Y	A, B, C, M, Pr, Py
1,1-Dichloroethylene	CCl_2=CH_2	1,1-DCE	N	Y	A, C, M, Pr, T, V
1,2-Dichloroethylene (*cis*)	CHCl=CHCl	*cis* 1,2-DCE	N	Y	A, B, C, M, Pr, Py, T, V
1,2-Dichloroethylene (*trans*)	CHCl=CHCl	*trans* 1,2-DCE	N	Y	A, C, M, Py, T, V
Trichloroethylene	CHCl=CCl_2	TCE	N	Y	A, B, C, D, I, M, Ph, Pr, Py, T
Tetrachloroethylene	CCl_2=CCl_2	PCE	N	Y	T

Metabolism: Y, compound will serve as growth substrate; N, compound will not serve as growth substrate.
Cometabolism: Y, compound transformed through cometabolic processes; N, compound not transformed through cometabolic processes.
Growth substrates which support cometabolic transformations: A, ammonia; M, methane; B, butane; C, chloroethane; T, toluene; Pr, propane; Py, propylene; V, vinyl chloride; D, 2,4-dichlorophenoxyacetic acid; I, isoprene; Ph, phenol.

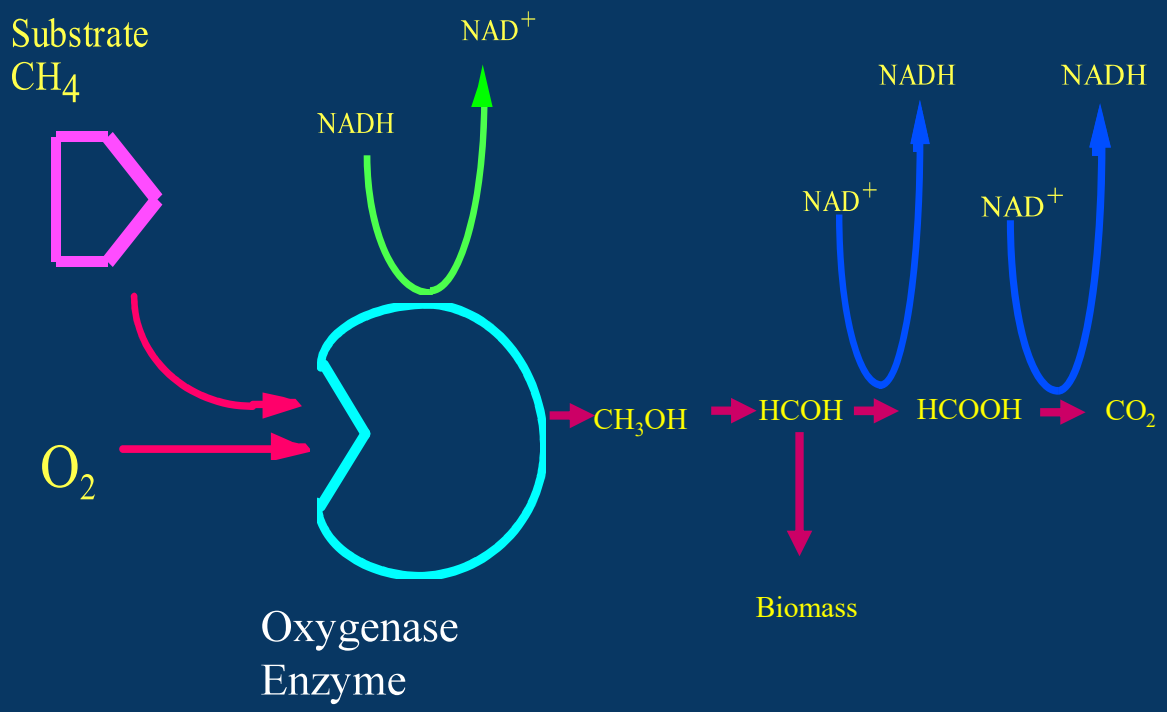
Aerobic Degradation of Chlorinated Compounds via Cometabolism

- Oxygenase-expressing bacteria
  - Monooxygenase vs dioxygenase
- Competitive inhibition
  - Growth vs cometabolic substrate
- Reducing energy consumption
  - NADH
- Product toxicity

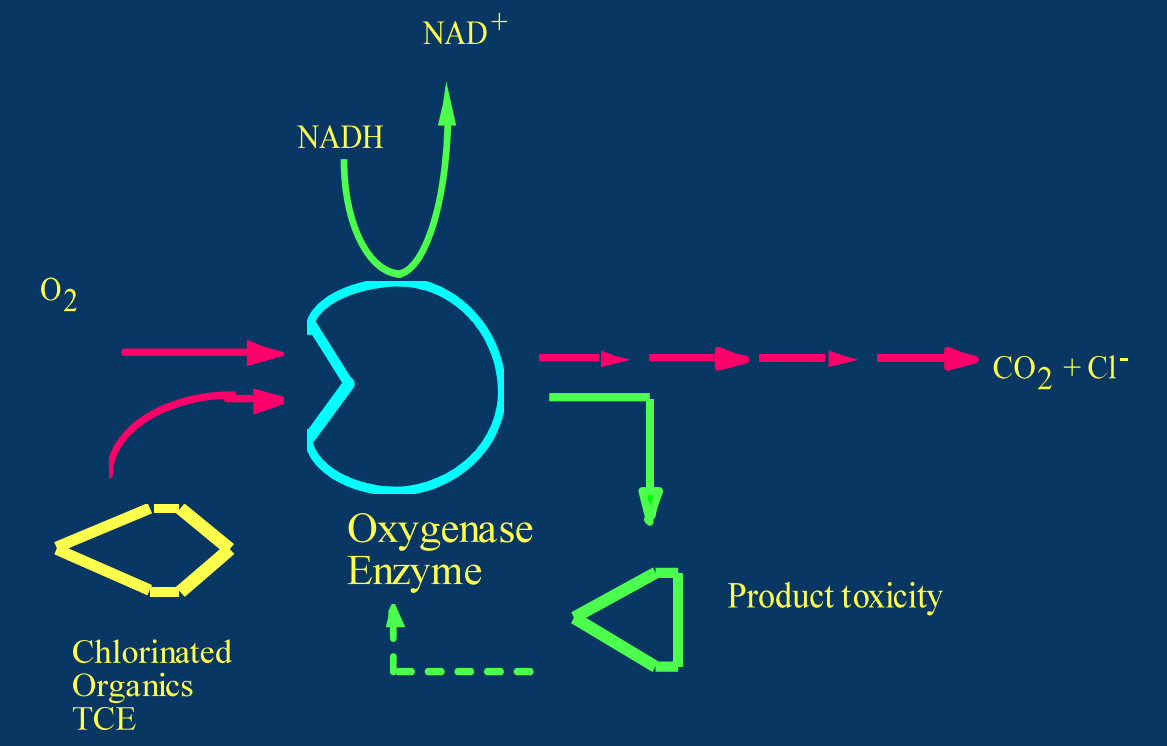
CH_4-Oxidizing Bacteria

- Indigenous to soil and water bodies
- Use gaseous substrates => CH_4 & O_2
- Produce non-specific enzyme (sMMO) that degrades a wide range of halogenated organics (ex. $t_{1/2, TCE}$ ~ 1 day).

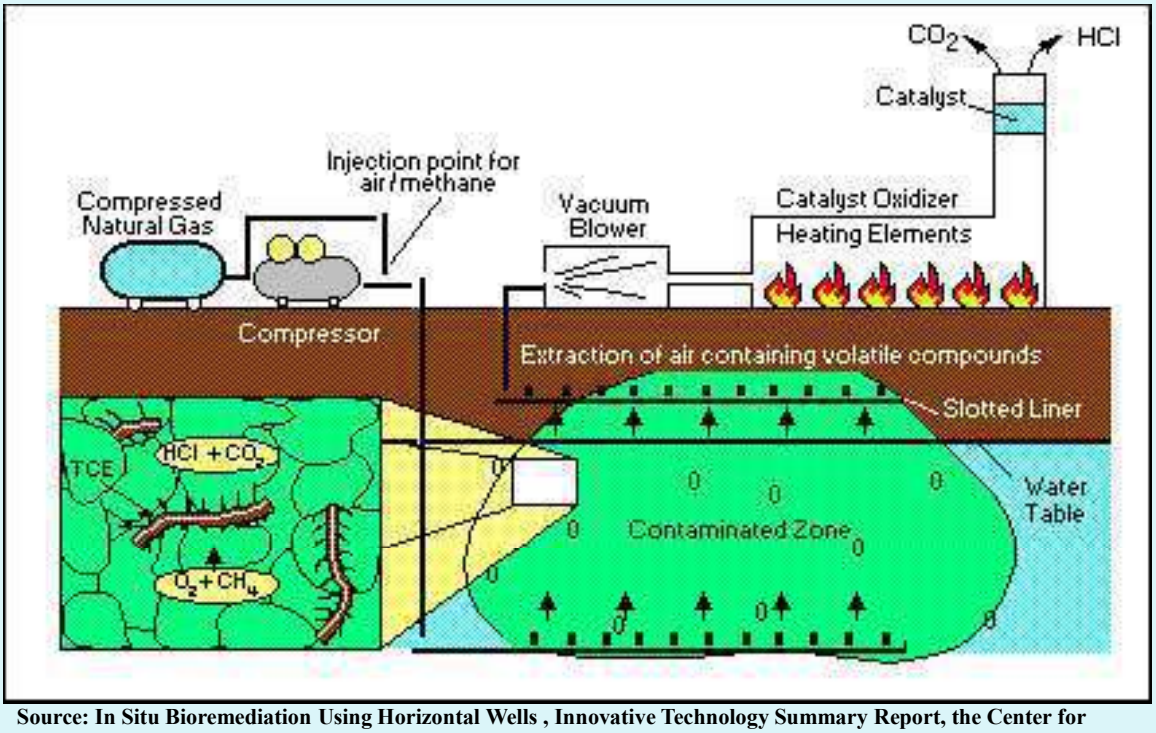
Oxidation of Methane



Oxidation of Chlorinated Organics



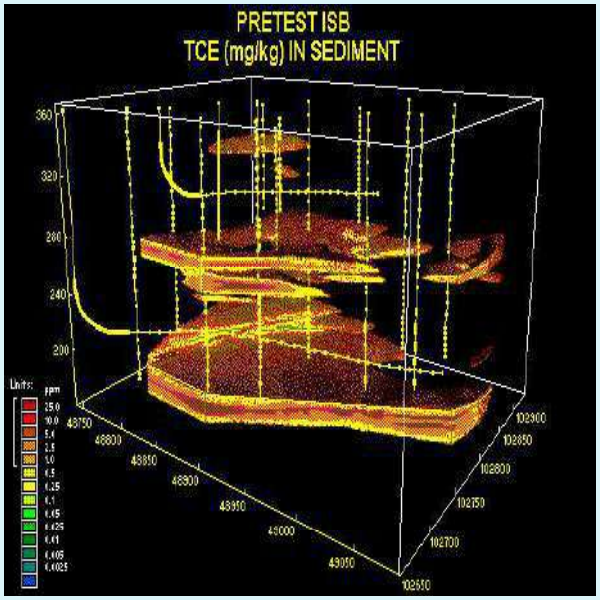
In-Situ Bioremediation Using Horizontal Wells



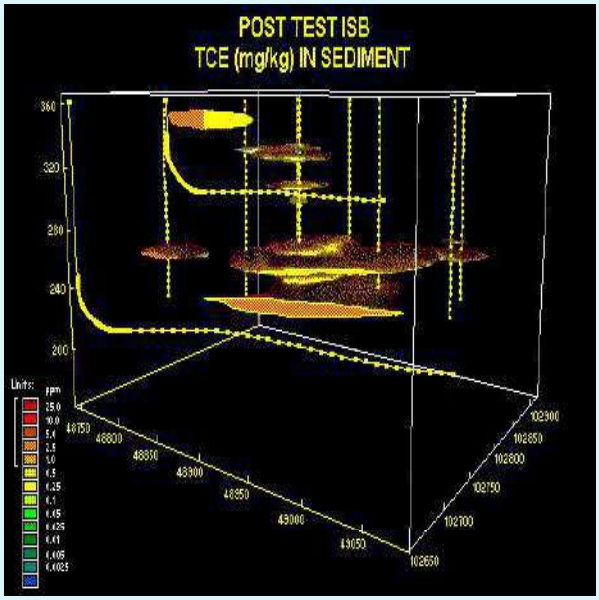
Source: In Situ Bioremediation Using Horizontal Wells , Innovative Technology Summary Report, the Center for Environmental Management, DOE, 1995 . http://www.em.doe.gov/plumesfa/intech/isbuhw/about.html

Concentration of TCE in Sediments

Before



After



Substrate Delivery Strategy

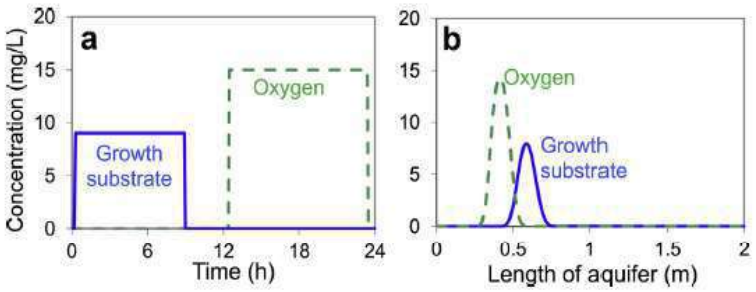


Fig. 1. Pulsed supply of O_2 and GS: (a) at the injection well, the supply of a GS pulse is followed by the introduction of an O_2 pulse (concentration vs. time plot); (b) as a result of dispersion and adsorption, a partial overlapping of the two pulses occurs, as they travel through the bioreactive zone (concentration vs. aquifer length plot).

Frascari et al 2015

Halogenated Aliphatic Compounds

- Bond strength C-F > C-Cl > C-Br > C-I.

=> Bond dissociation energies for C-F range from 106 to 115 Kcal/mol and for C-I are about 70 kcal/mol.

General Mechanisms of carbon-halogen bond cleavage catalyzed by bacteria

=>All the halogens must be removed and carbon skeleton must be transformed into common intermediate for a halogenated organic compound to enter intermediary metabolism.

=>Microorganisms can use halogenated organics by converting the compounds into intermediate of central pathway, or as terminal electron acceptors, or via cometabolic reactions.

Monitored Natural Attenuation

Source: *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water.*

EPA/600/R-98/128

Monitored Natural Attenuation (MNA)

• Also called " Intrinsic Remediation", " Bioattenuation", or " Intrinsic Bioremediation"

•Natural subsurface processes—such as dilution, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials—are allowed to reduce contaminant concentrations to acceptable levels.

•Natural attenuation is not a "technology" per se, and there is significant debate among technical experts about its use at hazardous waste sites

•Natural attenuation is not the same as "no action," although it often is perceived as such.

Mechanical Dispersion

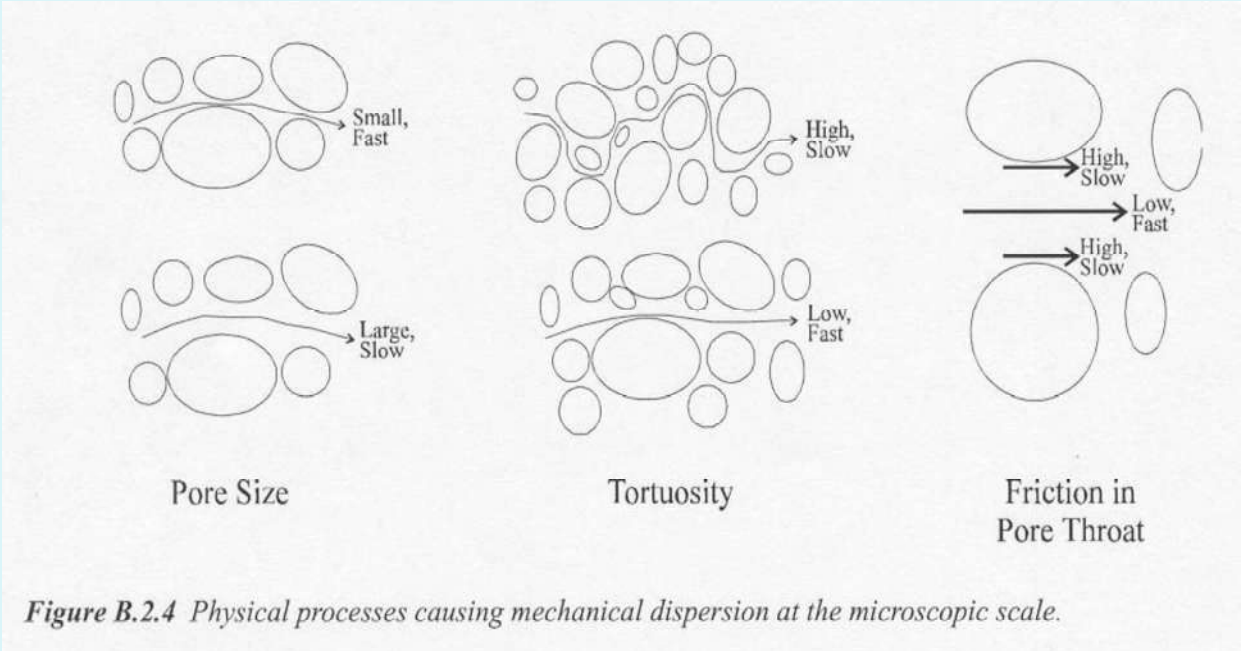


Figure B.2.4 Physical processes causing mechanical dispersion at the microscopic scale.

Advantages

- Less generation or transfer of remediation wastes;
- Less intrusive as few surface structures are required;
- May be applied to all or part of a given site, depending on site conditions and cleanup objectives;
- Natural attenuation may be used in conjunction with, or as a follow-up to, other (active) remedial measures; and
- Overall cost will likely be lower than active remediation.

Applicability

- Target contaminants for natural attenuation are VOCs and SVOCs and fuel hydrocarbons.
- Pesticides also can be allowed to naturally attenuate, but the process may be less effective and may be applicable to only some compounds within the group.
- Additionally, natural attenuation may be appropriate for some metals when natural attenuation processes result in a change in the valence state of the metal that results in immobilization (e.g., chromium).

Contaminant	Microorganisms	Comments/ Biodegradability
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa, Acinetobacter sp., Methylosinus trichosporium* OB3b, *Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichosporium* OB3b, *Bacillus sp., Pseudomonas sp., P. putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, P. aeruginosa, Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylenes	*Pseudomonas putida, methanogens, anaerobes*	High
Jet Fuels	*Cladosporium, Hormodendrum*	High
Kerosene	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Candidaparapsilosis, C. guilliermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae*	High
Chlorinated Ethenes	*Dehalobacter restrictus, Dehalospirillum multivorans, Enterobacter agglomerans, Dehalococcus entheogenes* strain 195,*Desulfitobacterium sp.* strain PCE1, *Pseudomonas putida* (multiple strains), *P. cepacia* G4, *P. mendocina, Desulfobacterium sp., Methanobacterium sp., Methanosarcina sp.* strain DCM, *Alcaligenes eutrophus* JMP 134, *Methylosinus trichosporium OB3b, Escherichia coli, Nitorsomonas europaea, Methylocystis parvus* OBBP, *Mycobacterium sp., Rhodococcus erythopolis*	Moderate
Chlorinated Ethanes	*Desulfobacterium sp., Methanobacterium sp., Pseudomonas putida, Clostridium sp., C. sp.* strain TCAIIB,	Moderate
Chlorinated Methanes	*Acetobacterium woodii, Desulfobacterium sp., Methanobacterium sp., Pseudomonas sp.* strain KC, *Escherichia coli* K-12, *Clostridium sp., Methanosarcina sp., Hyphomicrobium sp.* strain DM2,	Moderate
Chlorobenzenes	*Alcaligenes sp.* (multiple strains), *Pseudomonas sp.*(multiple strains), *P. putida, Staphylococcus epidermis*	Moderate to High

Lines of Evidence

- Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points

=> Loss of contaminant in area

(contaminants are being destroyed)

Lines of Evidence

- Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels

- Ex. Characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site
- => Field confirmation of microbial activity

- Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurance of a particular natural attenuation process at the site and its ability to degrade the occurrence of particular natural attenuation process at the sit and its ability to degrade the contamiants of concern.

=> Laboratory confirmation of microbial activity

Table 2.3 Analytical Parameters and Weighting for Preliminary Screening for Anaerobic Biodegradation Processes[a/]

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3
Oxygen*	>5 mg/L	Not tolerated; however, VC may be oxidized aerobically	-3
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	3
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide*	>1 mg/L	Reductive pathway possible	3
Methane*	<0.5 mg/L >0.5 mg/L	VC oxidizes Ultimate reductive daughter product, VC Accumulates	0 3
Oxidation Reduction Potential* (ORP) against Ag/AgCl electrode	<50 millivolts (mV) <-100mV	Reductive pathway possible Reductive pathway likely	1 2
pH*	5 < pH < 9 5 > pH >9	Optimal range for reductive pathway Outside optimal range for reductive pathway	0 -2
TOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	> 20°C	At T >20°C biochemical process is accelerated	1
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	1
Alkalinity	>2x background	Results from interaction between CO_2 and aquifer minerals	1
Chloride*	>2x background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of more complex compounds; carbon and energy source	2
BTEX*	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Tetrachloroethene		Material released	0
Trichloroethene*		Material released Daughter product of PCE	0 2[a/]
DCE*		Material released Daughter product of TCE If cis is > 80% of total DCE it is likely a daughter product 1,1-DCE can be chemical reaction product of TCA	0 2[a/]
VC*		Material released Daughter product of DCE	0 2[a/]
1,1,1-Trichloroethane*		Material released	0
DCA		Daughter product of TCA under reducing conditions	2
Carbon Tetrachloride		Material released	0
Chloroethane*		Daughter product of DCA or VC under reducing conditions	2
Ethene/Ethane	>0.01mg/L >0.1 mg/L	Daughter product of VC/ethene	2 3
Chloroform		Material released Daughter product of Carbon Tetrachloride	0 2
Dichloromethane		Material released Daughter product of Chloroform	0 2

* Required analysis. a/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

Table 2.4 Interpretation of Points Awarded During Screening Step 1

Score	Interpretation
0 to 5	Inadequate evidence for anaerobic biodegradation* of chlorinated organics
6 to 14	Limited evidence for anaerobic biodegradation* of chlorinated organics
15 to 20	Adequate evidence for anaerobic biodegradation* of chlorinated organics
> 20	Strong evidence for anaerobic biodegradation* of chlorinated organics

**reductive dechlorination*

Example 1

Example 1: Strong Evidence for Anaerobic Biodegradation (Reductive Dechlorination) of Chlorinated Organics

Analyte	Concentration in Most Contaminated Zone	Points Awarded
Dissolved Oxygen	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Iron (II)	10 mg/L	3
Sulfate	2 mg/L	2
Methane	5 mg/L	3
ORP	-190 mV	2
Chloride	3 times background	2
PCE (released)	1,000 µg/L	0
TCE (none released)	1,200 µg/L	2
cis-DCE (none released)	500 µg/L	2
VC (none released)	50 µg/L	2
	Total Points Awarded	23 Points

Example 2

Example 2: Anaerobic Biodegradation (Reductive Dechlorination) Unlikely

Analyte	Concentration in Most Contaminated Zone	Points Awarded
Dissolved Oxygen	3 mg/L	-3
Nitrate	0.3 mg/L	2
Iron (II)	Not Detected (ND)	0
Sulfate	10 mg/L	2
Methane	ND	0
ORP	+ 100 mV	0
Chloride	background	0
TCE (released)	1,200 µg/L	0
cis-DCE (none released)	ND	0
VC (none released)	ND	0
	Total Points Awarded	1 Point

Questions commonly asked during Bioremdiation

- Are contaminants at your site being degraded through biodegradation or being decreased through dilution?
- What rates are these contaminants being degraded?
- Can the size of monitoring network be reduced and thereby reduce the cost of monitoring?
- How to secure that final piece of evidence needed to close a site?

Questions commonly asked during Bioremdiation

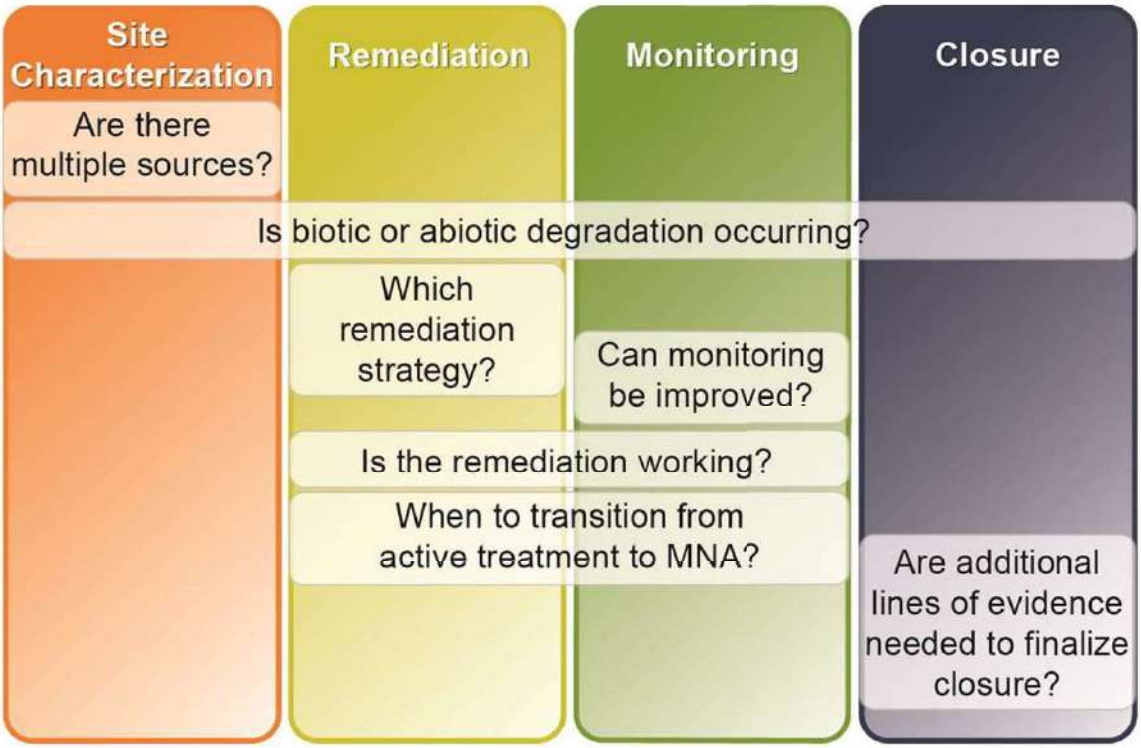
- Are contaminants at your site being degraded through biodegradation or being decreased through dilution?
- What rates are these contaminants being degraded?
- Can the size of monitoring network be reduced and thereby reduce the cost of monitoring?
- How to secure that final piece of evidence needed to close a site?

Environmental Molecular Diagnostics (EMDs)

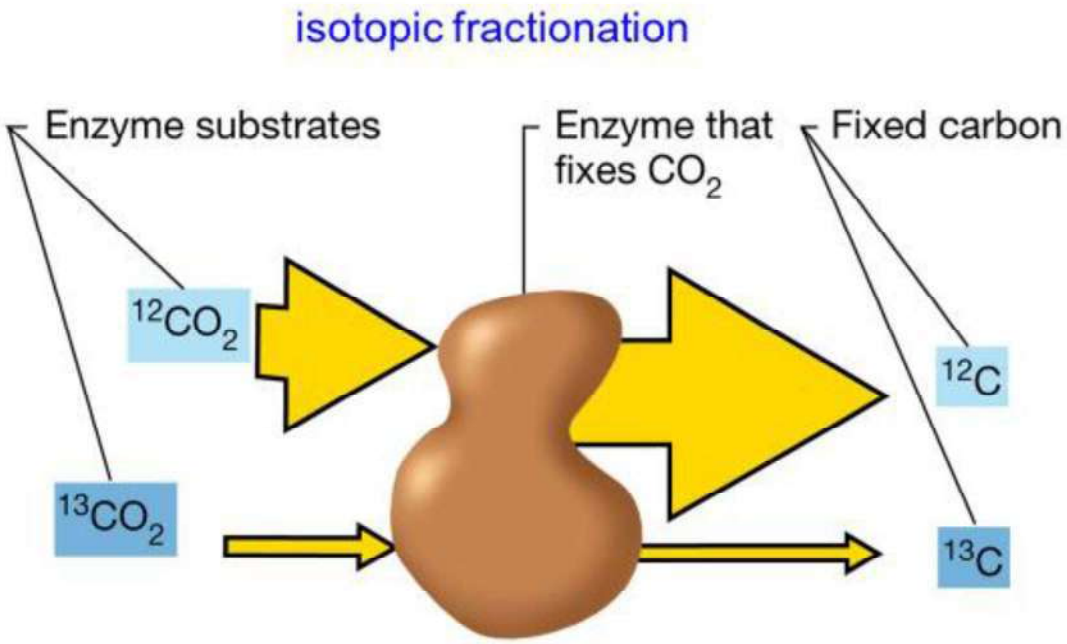
- Tools to analyze biological and chemical characteristics of soil, sediment, and water samples
- Originally developed for medicine
  - Adapted for environmental site management
- Two major categories
  - Chemical techniques
  - Molecular biological techniques (MBTs)

ITRC, EMD, Section 2, Figure 2-1

Using EMDs Throughout Site Management

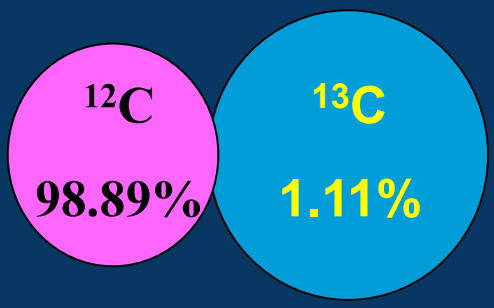


Compound Specific Isotope Analysis (CSIA)

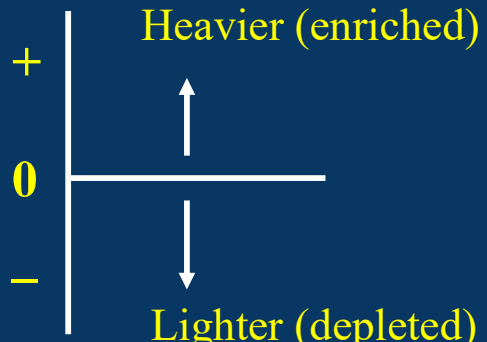


Stable Isotopes

- Do not decay radioactively
- Isotopes of the same element that differ by # neutrons in the atom's nucleus

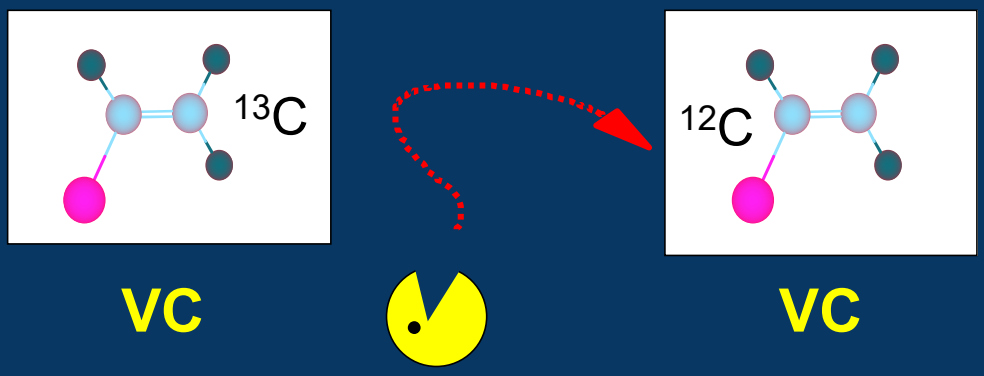


Stable Carbon Isotopes



Kinetic Isotope Fractionation

- Principle: lighter isotopes form weaker bonds, thus are more reactive

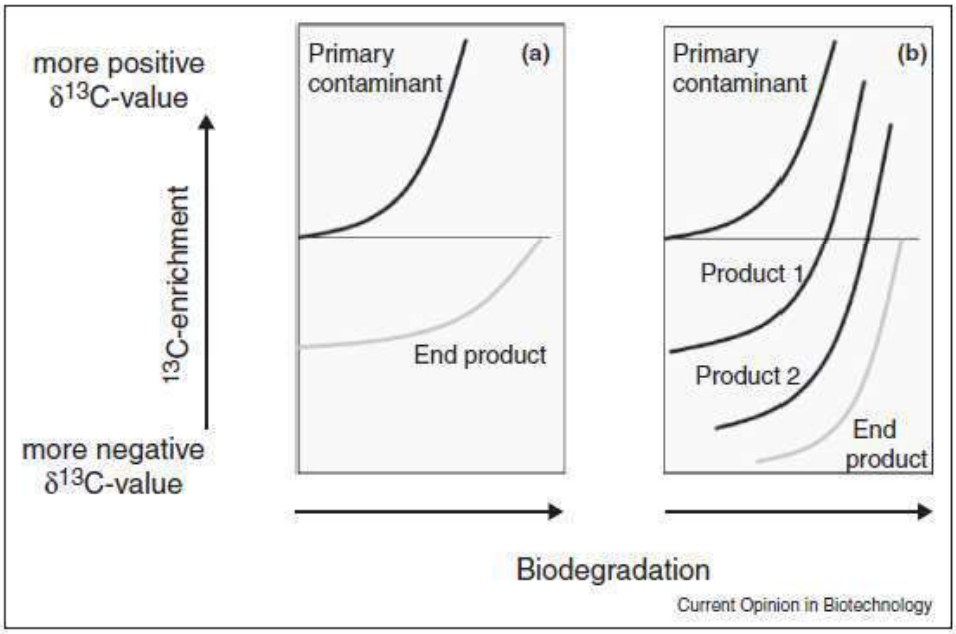


- Results in kinetic isotopic enrichment of reactant toward larger isotope and depletion of product

Stable Carbon Isotope Ratio (delta notation)

$$\partial^{13}C = \frac{\left(^{13}C/_{12}C\right)_{sample} - \left(^{13}C/_{12}C\right)_{VPDB}}{\left(^{13}C/_{12}C\right)_{VPDB}}$$

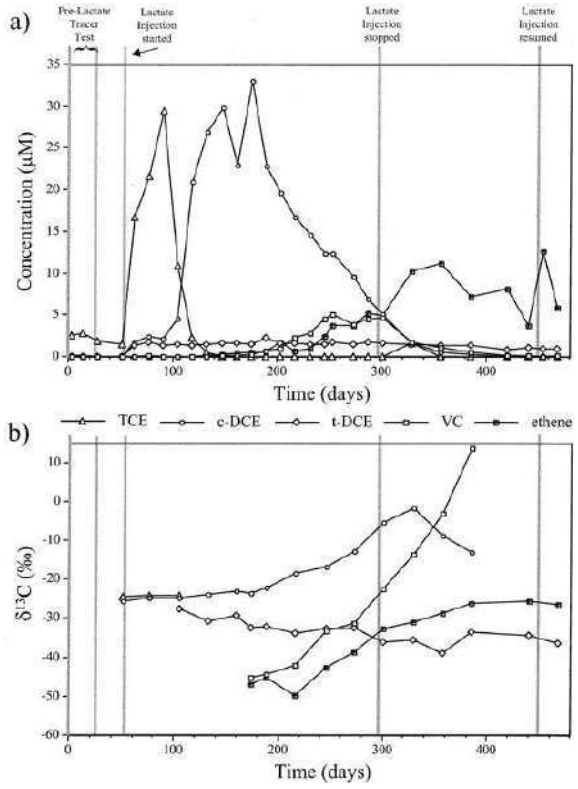
CSIA: What happen during biodegradation ?

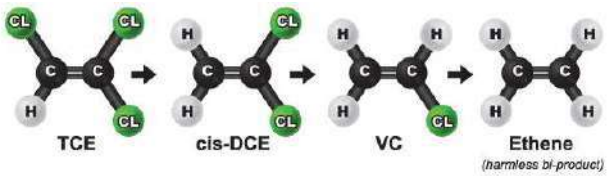


Evolution of stable carbon isotope ratios given as δ^{13}C-values during A) biodegradation with negligible accumulation of transformation products (*e.g.* mineralisation of toluene to CO_2) and B) transformation chain: biodegradation with significant accumulation of transformation products (*e.g.* reductive dechlorination of TCE to ethene).

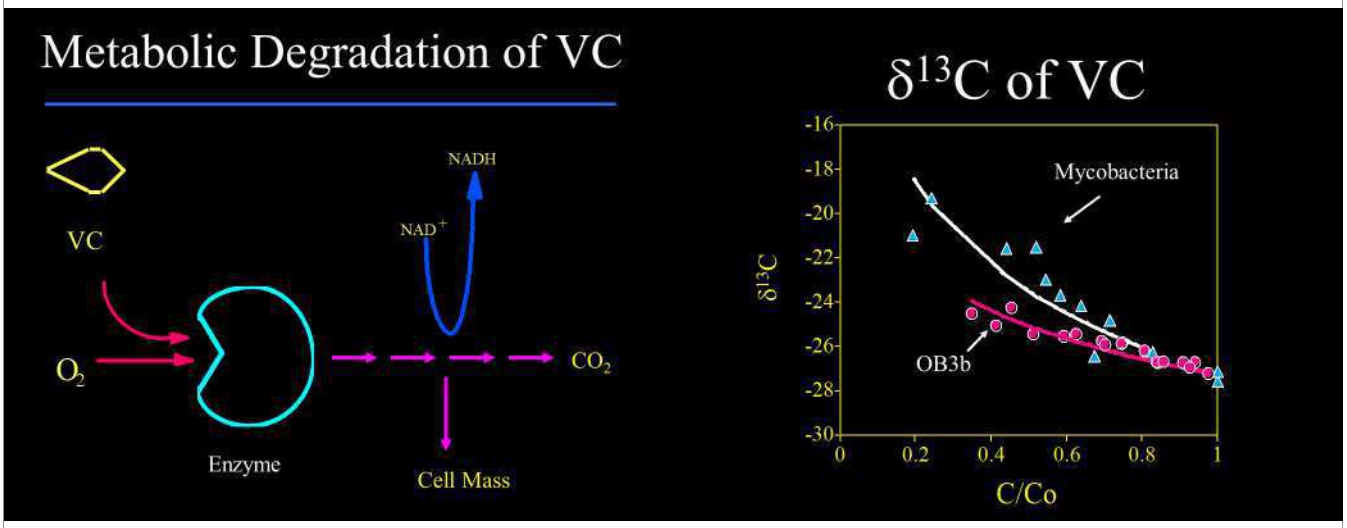
Current Opinion in Biotechnology 2016, 41:99–107

CSIA: Reductive dechlorination of TCE





CSIA: Aerobic degradation of VC



Metabolic and Cometabolic degradation VC by *Mycobacterium* JOB5 and *Methylosinus trichosporium* OB3b

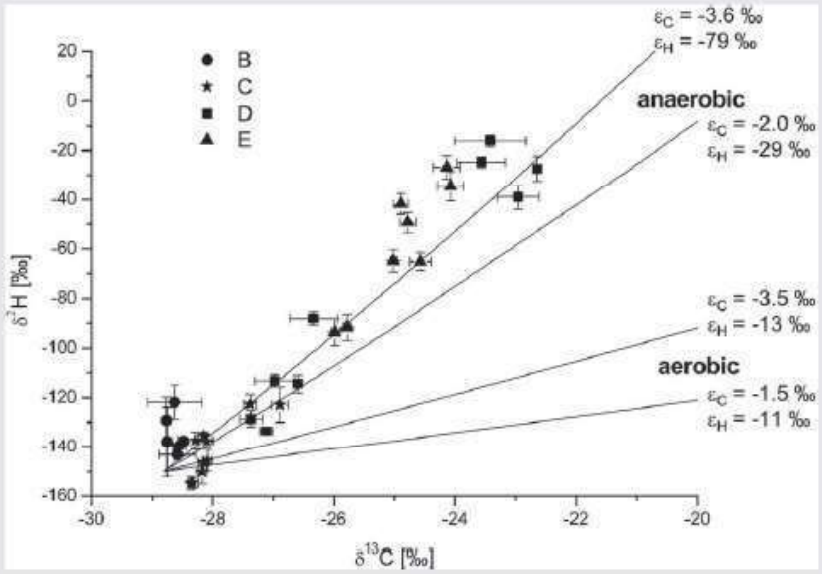


FIGURE 6-2 Concurrent carbon and hydrogen isotope ratios of benzene measure at various sampling depths (B through E) together with isotope patterns for aerobic and anaerobic benzene degradation calculated from published enrichment factors for carbon and hydrogen as well as the isotope signature of the contaminant source using the Rayleigh equation. SOURCE: Reprinted, with permission, from Fisher et al. (2007). © 2007 by American Chemical Society.

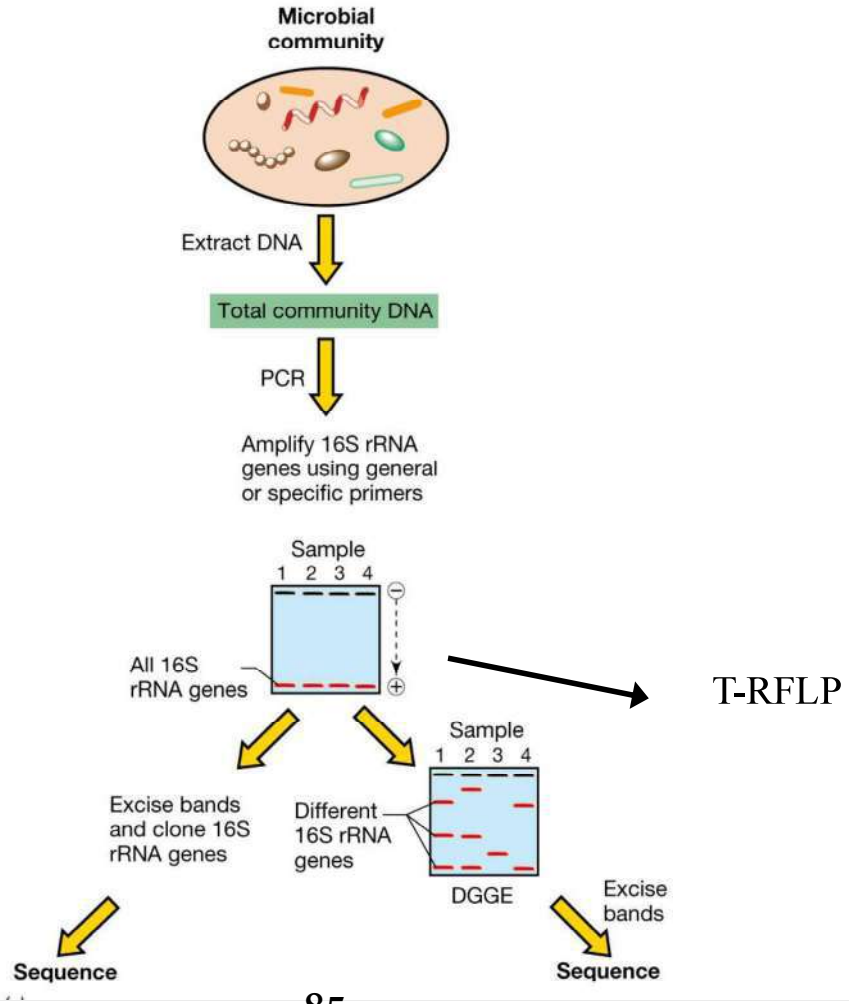
Molecular Biological Techniques (MBTs)

Culture-independent Techniques

- Quantitative PCR (qPCR)
- Fluorescence in-situ hybridization (FISH)
- Stable-isotope probing (SIP)
- Enzyme activity assays
- Microbial community fingerprinting methods
- Microarray

Nucleic Acid-based Techniques

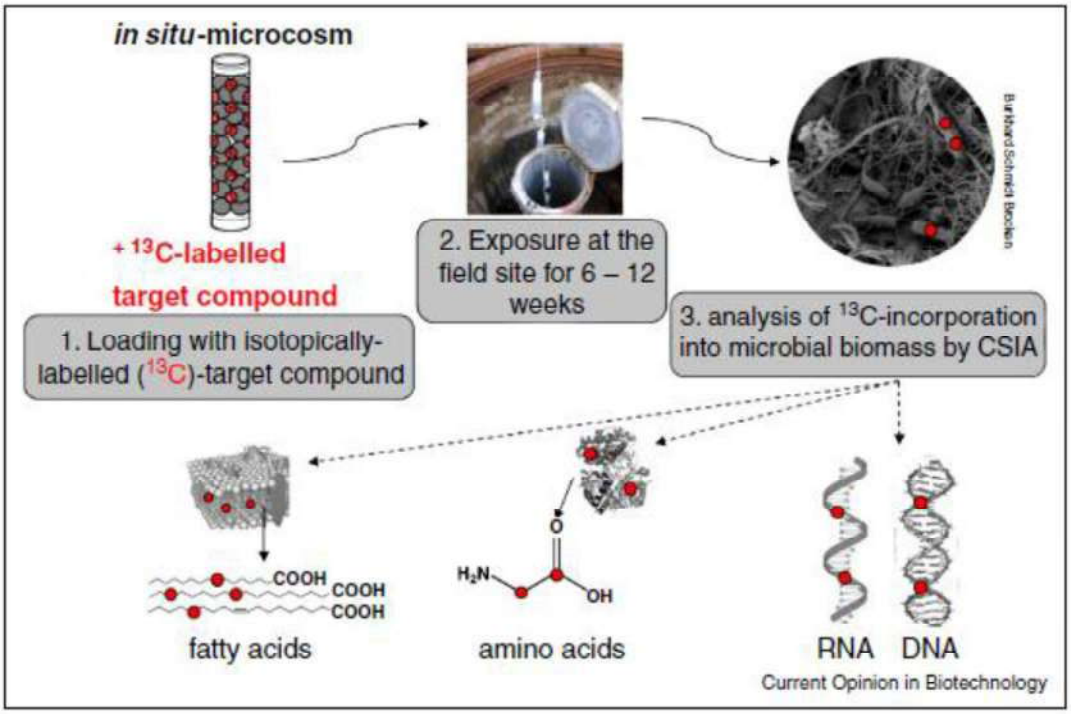
- Polymerase Chain Reaction (PCR)-based techniques
  - Using total community DNA
  - Using signature sequences, or catabolic genes
  - Restriction enzymes
  - Sequencing



Some Common qPCR Gene Targets

Contaminants		Target Gene	Organism or Encoded Enzyme
Chlorinated Solvents	PCE,TCE, DCE, VC	16s rRNA	*Dehalococcoides mccartyi* (*Dhc*)
	TCE & DCE	*tceA*	TCE Reductase
	VC	*vcrA, bvcA*	Vinyl chloride Reductase
Petroleum	BTEX	*tmo*	Ring-hydroxylating Toluene Monooxygenases
	B,T, & Chlorobenzene	*tod & tol*	Toluene Dioxygenase
	Naphthalene	*nah*	Naphthalene Dioxygenase
	Alkanes	*alk*	Alkane Monooxygenase
	MTBE	16s rRNA	MTBE-utilizing *Methylibium* spp
	Toluene & Xylene	*bss*	Benzylsuccinate Synthase (anaerobic)
Perchlorate		*per*	Perchlorate reductase
PCBs		*bph*	Biphenyl Dioxygenase

ITRC EMD Tech Reg, Appendix D, Tables D2 & D3



Concept of *in situ*-microcosms with ^{13}C-labelled target compound for assessment of pollutant biodegradation at a contaminated field site.

Q-FAST

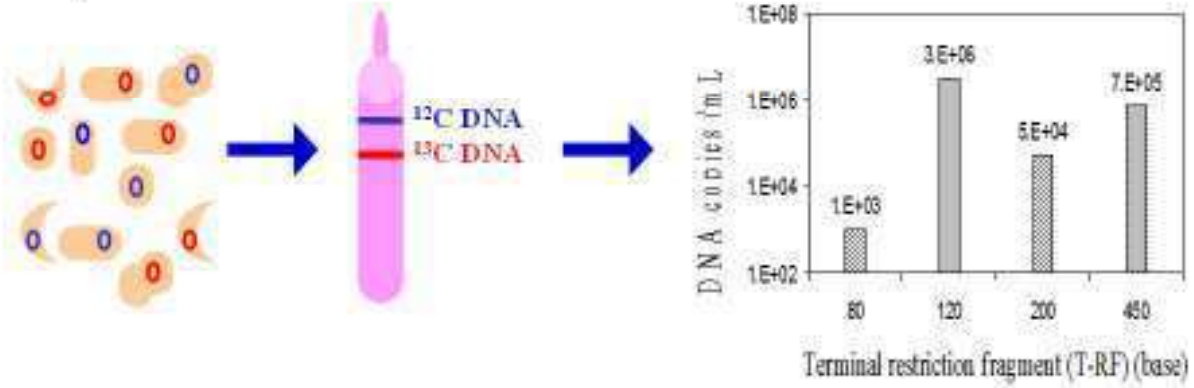
(Yu and Chu ES&T)

^{13}C-probing (SIP) | **Real-time-t-RFLP**

Enriched with ^{13}C-labeled compound

Ultracentrifuge community DNA

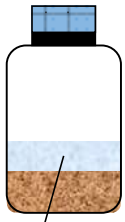
Real-time-t-RFLP analysis of 16S rDNA from ^{13}C DNA



A Quantitative Assay for Linking Microbial Community Function And STructure (Q-FAST)

Stable-Isotope Probing for RDX degraders under different electron-accepting conditions

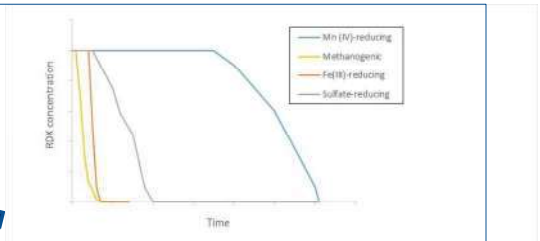
^{13}C-labeled RDX
or
^{15}N-labeled RDX
+



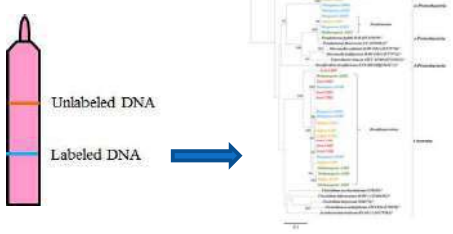
RDX-contaminated groundwater and soils

Different electron-accepting conditions:

- Mn(IV)- reducing condition
- Fe (III)- reducing condition
- SO_4^{2-}-reducing condition
- Methanogenic conditions



- RDX degradation rates and patterns were different under different electron-accepting conditions.



- Phylogenetic diverse RDX degraders were observed under different electron-accepting conditions

Source:Cho, K. C., D. Lee, M. Fuller, P. Hatzinger, and K. H. Chu. "Application of ^{15}N- and ^{13}C-stable isotope probing to identify RDX-utilizing microorganisms under reducing conditions. Journal of Hazardous Materials. 2015. 297:42-51.

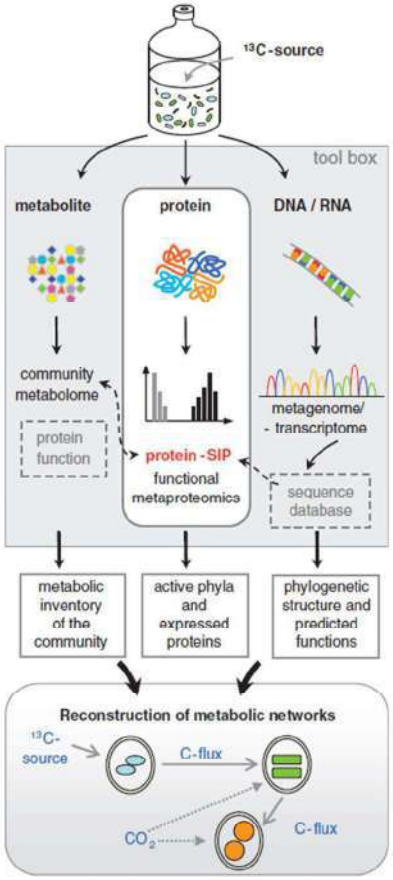


Figure 3 Integration of protein-SIP in the toolbox of microbial ecology and the combination of *OMICS* to reconstruct metabolic networks.

DNA–SIP
+
-omics
+
Metabolites

Bergent et al.
2013. ISME. 1-9

Questions?

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Collection Policy of Soil and Groundwater Pollution Remediation Fund in Taiwan

Hao-Chun Hung
Taiwan EPA
March 18, 2019

Outline

I. Origin
II. Foreign Policies
III. Collection Policy
IV. QA/QC
V. Conclusion

Origin of the Soil and Groundwater Pollution Remediation Fund

Need for Designated Fund

- The lack of environmental awareness has resulted the deterioration of our environment.
- The cost of remediation is heavy and time consuming; a sound financial support is necessary.

1981 Cadmium Rice Incident	Farmland
1994 RCA Incident and CPC Anshen Factory Incident	Factory
2000 Taoyuan Shixiang Gas Station Spill	Gas Station

The Establishment of Remediation Agency

- "Soil and Groundwater Pollution Remediation Act" was passed in 2000

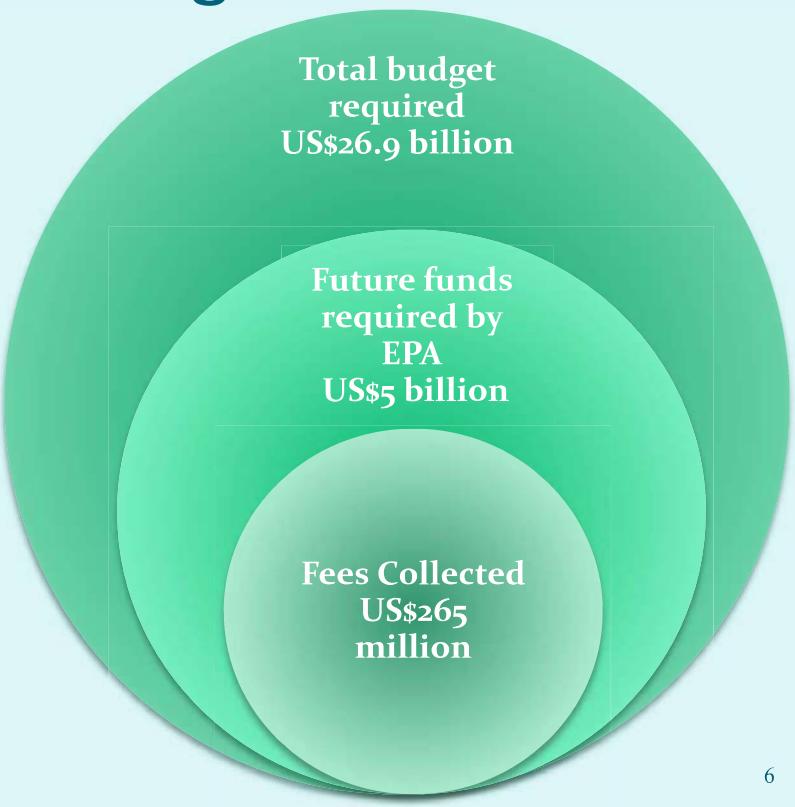
- In November, 2001, the "Soil and Groundwater Pollution Remediation Fund Management Board" was officially established.

Illegal Dumping Sites

- Primary uses of remediation fees⇨investigation of polluted sites, emergency response, and pollution remediation of orphan sites.
- Most polluted sites in Taiwan are related to illegal waste disposal.

Demand of Funding

- Total budget required for soil and groundwater remediation in the future is US$26.9 billion.
  - With existing data and treatment technology, it is estimated that Taiwan government requires about US$5 billion in the next 25 years.
  - Fund demand is determined based on site investigations, treatment methods, and regulation of pollutant limits. Review of fund demand must be held regularly.



How other countries fund their remediation projects?

Introduction

- Global Top 12 Leading Countries in Regulatory Framework
- North America
  - USA
  - Canada
- Western Europe
  - Netherland
  - UK
  - Germany
  - France
  - Switzerland
- Asia
  - Japan
  - **Taiwan**
- Australia and New Zealand

- Global Top 12 Leading Firms in International Market
  - URS Corporation
  - CH2M Hill
  - Arcadis
  - Golder Associates
  - ERM
  - MWH Global
  - RPS Group
  - AECOM
  - Parsons Brinkerhoff
  - ENVIRON
  - WSP Environment & Energy
  - WorleyParsons

Comparison of Funding Policies

- The sources of Taiwan Remediation Fund are more diversified than other nations. Currently Taiwan is the only nation conducting collection on chemical substances (Superfund has stopped the collection on 1995).
- In most countries, remediation funds are largely budgeted by the government

Type of Fund Source	Taiwan	U.S.	Japan	England	Netherland	Korea
1.Government Budget	V	V	V	V	V	V
2.Special Fees and Taxes for Chemical Substances	V	(V)				
3.Corporate Environmental Tax		(V)				
4.Commission Cost for Implementation Plan & Survey Agency			V			
5.Earthwork Delivery Management Fee			V			
6. Fines and Cost Recovery	V	V				
7. Local Government Bid				V		
8.Developer Investment in Remediation	V	V		V	V	
9. Corporate Voluntary Funding			V			
10.Fund Interest Income	V	V	V		V	

(V): Stopped collection currently.

United States

US Superfund Main reference of Taiwan Remediation Fund

- 17.0 Billion was collected between 1980 and 1995

Collection Target	Collection Rate	Percentage(%)
Petroleum Tax	$0.097/Barrel (1980~1986) $9.7Barrel (1986~1995)	40% - 46%
Chemical Taxes	$0.22 - $4.88/ton	20% – 24%
Environmental Income Tax	If revenue an enterprise is more than US$2 million, 0.12% of overall revenue of the enterprise shall be taxed.	31% - 38%

Stopped in 1995

Congress **Fund was enough for future operation**

Business **Not Compatible with Polluters-Pay Principle**

By 2003 the superfund was empty, now relying on federal Funding

Netherland

Netherlands Concept of Risk Management

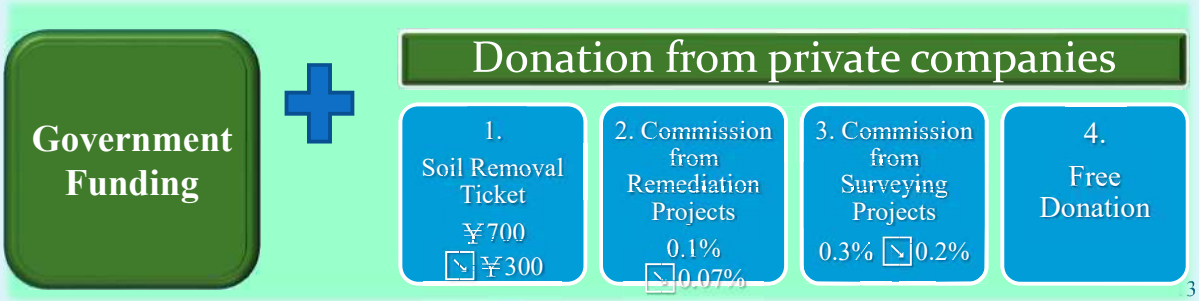
- Soil Protection Act in 1987
  - Set up a designated fund but funding rely on government appropriation.
- Control the expenditure by applying the concept of risk management in soil quality standards
  - Before 1987: soil quality restore to unpolluted level
  - After 1987: soil quality fit for future land use
- Encourage development of brownfield through urban planning

United Kingdom

- No designated fund, rely on government funding
- Strict polluter-pays principle
- Brownfields with unknown polluter manage through urban planning and neighborhood redevelopment
  - Central: Department for Communities and Local Government; Homes and Communities Agency
  - Local: London Land Commission
- Developers are given tax incentives

Japan

- 「 Soil Contamination Countermeasures Act 」 of 2002
  - Remediation Responsibility lie on land owner if polluter is unknown
  - Designated fund for soil remediation
  - **Land owner can apply for funding**
  - Both government and enterprises contribute
  - Percentage of corporate funding decreases in 2008
  - JPY 1.718 billion as been saved ➢ **Solely Used for Remediation**



Korea

Korea Lacks Designated Fund; Rely on Government Budget

- 1995 Soil Environment Conservation Act
  - 「 Worrisome Level 」and「 Countermeasure Standards 」, similar to Taiwan 「Monitoring Standards 」and 「 Control Standard 」
  - Goal to establish Remediation Fund in 2010~2019
  - Government budget decreases, expecting Remediation Fund to kick in.

年份	2014	2015	2016	2017	2018	2019
Total Soil and Groundwater Remediation Budget	128,392	116,957	113,030	61,203	38,336	44,754
1.Public Health Protection and Prevention Measure	86,325	67,512	67,215	13,123	13,636	13,654
2.Constructing Reasonable soil Management Policy	12,900	12,100	13,000	11,000	10,800	11,300
3.Developing Soil and Groundwater Technology and Personnel Training	22,267	24,445	25,215	23,780	5,600	5,700
4.Traning Soil Remediation Environmental Industry	4,800	10,800	5,000	10,500	5,500	11,000
5.Promoting International Cooperation	2,100	2,100	2,600	2,800	2,800	31,000

Unit: Million KRW，1 USD = 120 KRW

Collection Policy of Soil and Groundwater Pollution Remediation Fund

Financing and Responsibility

- Diverse source of Remediation Fund
- US$290 million was collected to help with the remediation

Remediation Fund

1. Remediation Fee
2. Fines from polluters, potential polluters, and interest party
3. Payment for land development
4. Interest
5. Central government budget
6. Allocation from other environmental funds
7. Penalties and administrative fines
8. Other income

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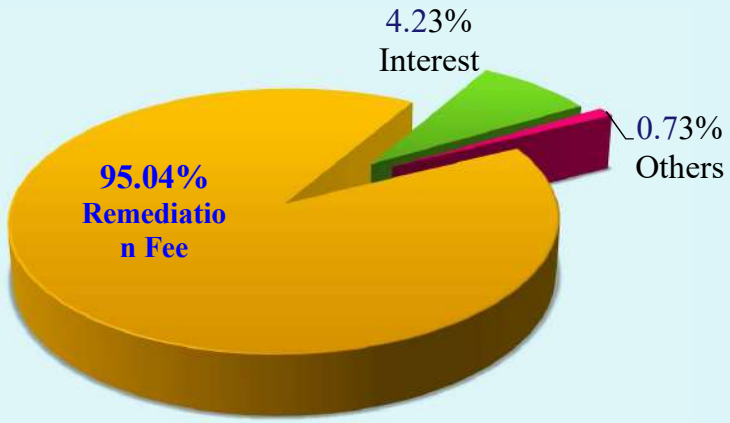
Remediation Fund Provisions

- The Soil and Groundwater Remediation Fee is the most important source of the Remediation Fund.
- Therefore, the Soil and Groundwater Remediation Fee becomes the key to a sound pollution remediation program.



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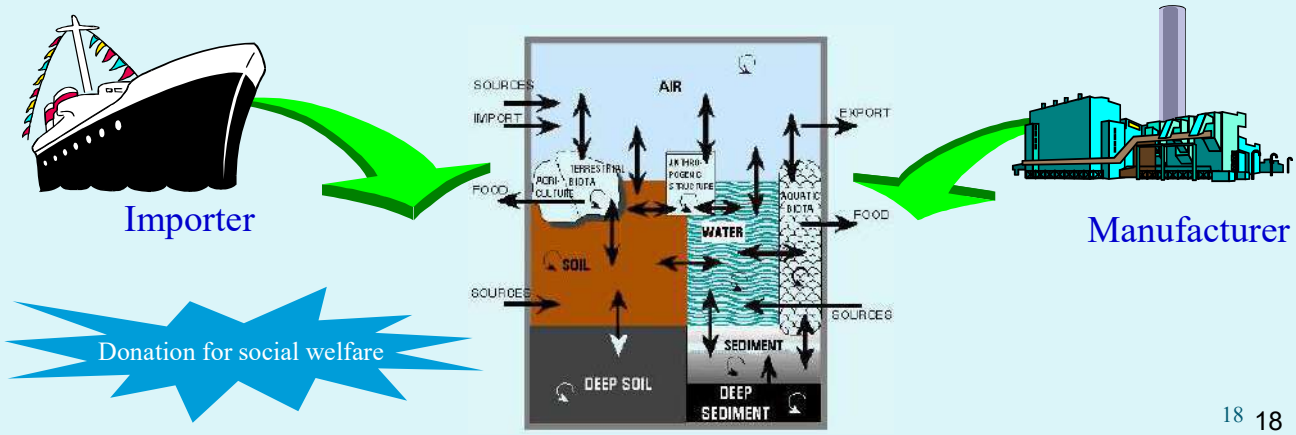
Remediation Fund Provisions

- Collection of remediation fee is authorized in accordance with Article 28 of Soil and Groundwater Pollution Remediation Act:
  - Soil and groundwater pollution remediation fees are levied from manufacturers and importers of certain chemical substances in accordance to the amount manufactured and imported by such enterprises"
  - Complete Act can be viewed from the following website. http://law.moj.gov.tw/Eng/LawClass/LawContent.aspx?PCODE=O0110001



Remediation Fund Provisions

- Original Six categories including 125 chemical substances.

Category		Original Collection Rate (US$/Metric ton)
Original Chemical Substance	1. Organic petroleum derivatives	0 ~ 1.22
	2. Chlorinated hydrocarbons	0.44 ~ 3.08
	3. Non-petroleum based organic chemicals	0.47 ~ 1.42
	4. Heavy metal and heavy metal compounds	1.05 ~ 3.56
	5. Pesticides	1.42 ~ 2.64
	6.Others (Sodium cyanide, potassium cyanide)	3.19

Remediation Fund Provisions

- Comprehensive evaluation of the fee collection policy was made in 2011.

Collection Scheme

Conduct reasonable review on existing remediation fee collection rates

- Comprehensive review on existing collection rates & items
- Reasonability review on existing export recoup policy & ratio

Include production of waste in the collection

- Improper waste disposal, resulting in soil and groundwater pollution
- Develop individual rate based on different waste characteristics

Raw material used by electric power industry & steel industry

- Slag & flue dust often appear in illegal dumping sites
- Collection is based on amount of raw materials used

Other sources of income

- Other fund allocation
- Penalties and fines income
- Expenditure recovered from polluters
- Fund interests
- Government budget

Collection Rate and Scale

- Price of original chemical substance is cut by 20%
- Added copper, nickel, steel billet, coal, and industrial waste from 13 industries

Category		Revised Rate (US$/Metric ton)	Original Rate (US$/Metric ton)
Original Chemical Substances	1. Organic petroleum derivatives	0 ~ 0.98	0 ~ 1.22
	2. Chlorinated hydrocarbons	0.34 ~ 73	0.44 ~ 3.08
	3. Non-petroleum based organic chemicals	0.47 ~ 1.15	0.58~ 1.42
	4. Heavy metal and heavy metal compounds	0.85 ~ 2.85	1.05 ~ 3.56
	5. Pesticides	1.15 ~ 2.10	1.42 ~ 2.64
	6.Others (Sodium cyanide, potassium cyanide)	2.54	3.19
Newly Added substance	1. Steel billet	0.20	Not included in the collection
	2. Coal	0.034	
	3. Industrial waste from 13 industries	0.27 ~ 5.59	
	4. Heavy metal – nickel	2.10	
	5. Heavy metal – copper	2.17	

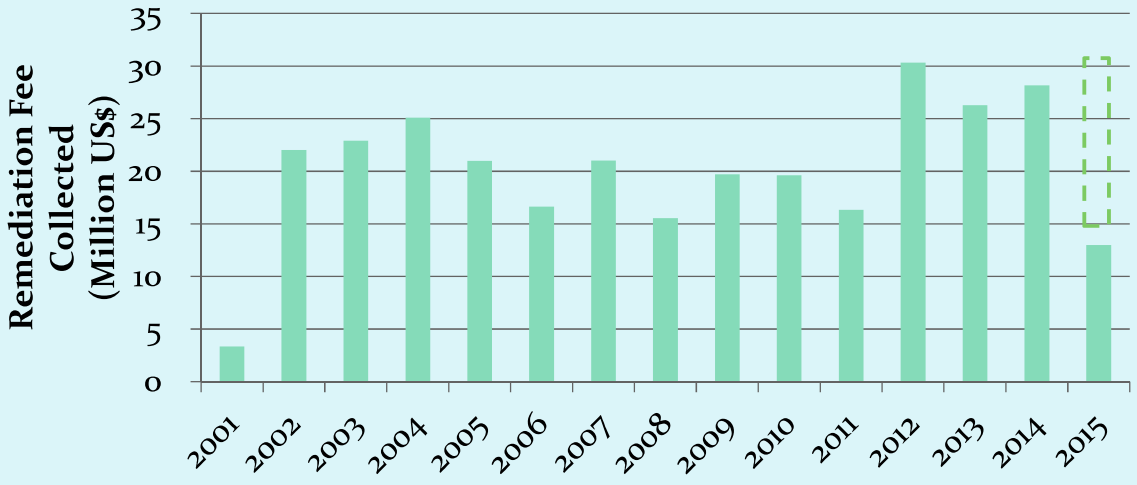
Collection Rate and Scale

❖ The rate of industrial wastes depends on its property.

Fee Category	Substance Subjected to Fees	Fee rate ($US)
Waste	Renewable resource	0.27
	General industrial waste (intermediate treatment or final disposal)	0.58
	General industrial waste(reuse)	0.27
	Hazardous industrial waste (intermediate treatment or final disposal)	5.59
	Hazardous industrial waste(reuse)	2.81
	Solidification	0.58

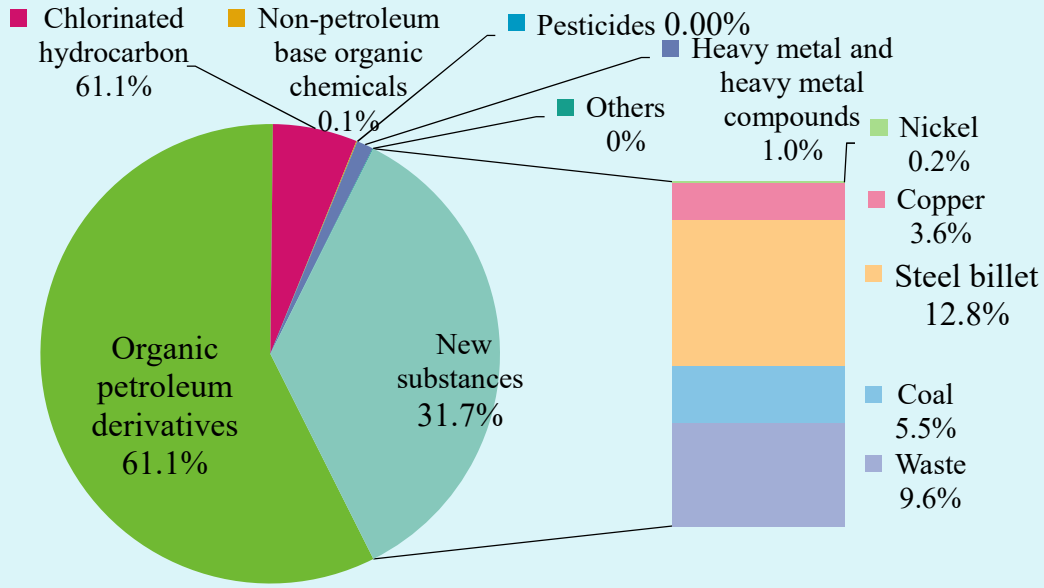
Current Collection Status

- Remediation fee collection has been implemented for nearly 10 years. Total amount is about US$265 million.
- Average annual amount is between US$17 million and US$25 million before revision.
- About US$27 million collected each year after the revision.



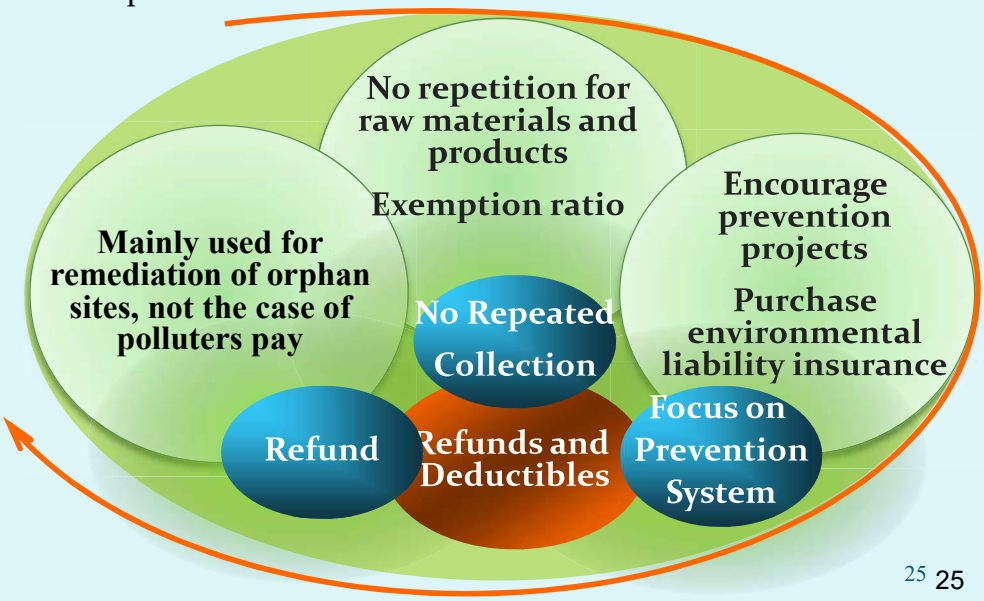
Current Collection Status

❖ US$27 million collected each year after the revision.



Collection Policy Characteristics

- The fee collection system strives to be fair and equitable
  - Non-Repetitive Collection
  - Export Refund
  - Encourage pollution prevention



Encourage Pollution Prevention

- Conducting pollution prevention projects or purchasing an environmental liability insurance can be combined to get reimbursement of maximum 25%.
  - It is explicitly stipulated that the pollution prevention project within a control or remediation site can not apply for reimbursements.
- All fee payers may apply.

Encourage Pollution Prevention

- New investment in facility for preventing soil and groundwater pollution

Pollutant interception facilities

Corrosion prevention coating

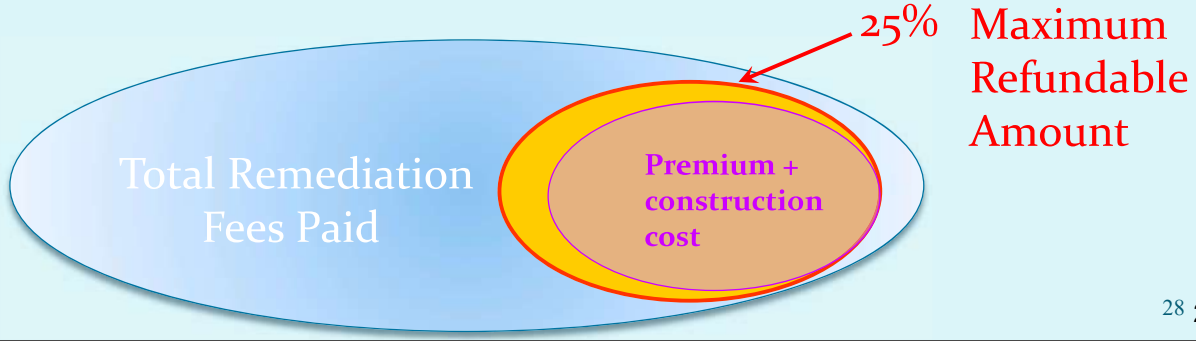
Stainless steel storage tanks

Cathodic corrosion protection

Encourage Pollution Prevention

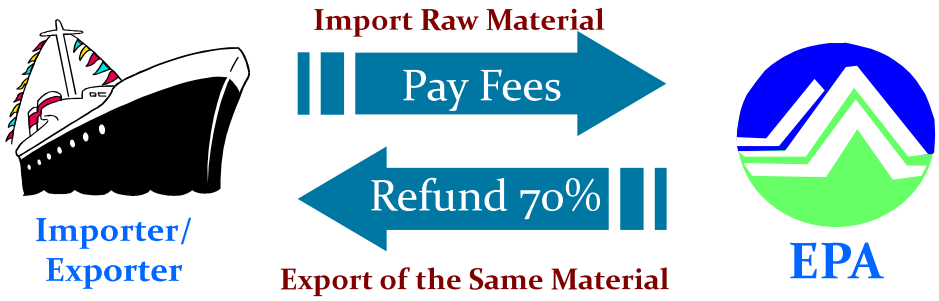
- Reimbursements are also given to companies that purchasing environmental damage liability insurance.
  - If incident of pollution occurs, insurance claim shall cover remediation fee which reduces the remediation burden of businesses.

- The reimbursable amount is 25% of remediation fee paid
  - If the payer has paid US$1 million remediation fee, the maximum amount of reimbursement is US$250,000. If the combination of construction cost and insurance premium is less than US$250,000, then the total money spent is reimbursed.



Export Refund

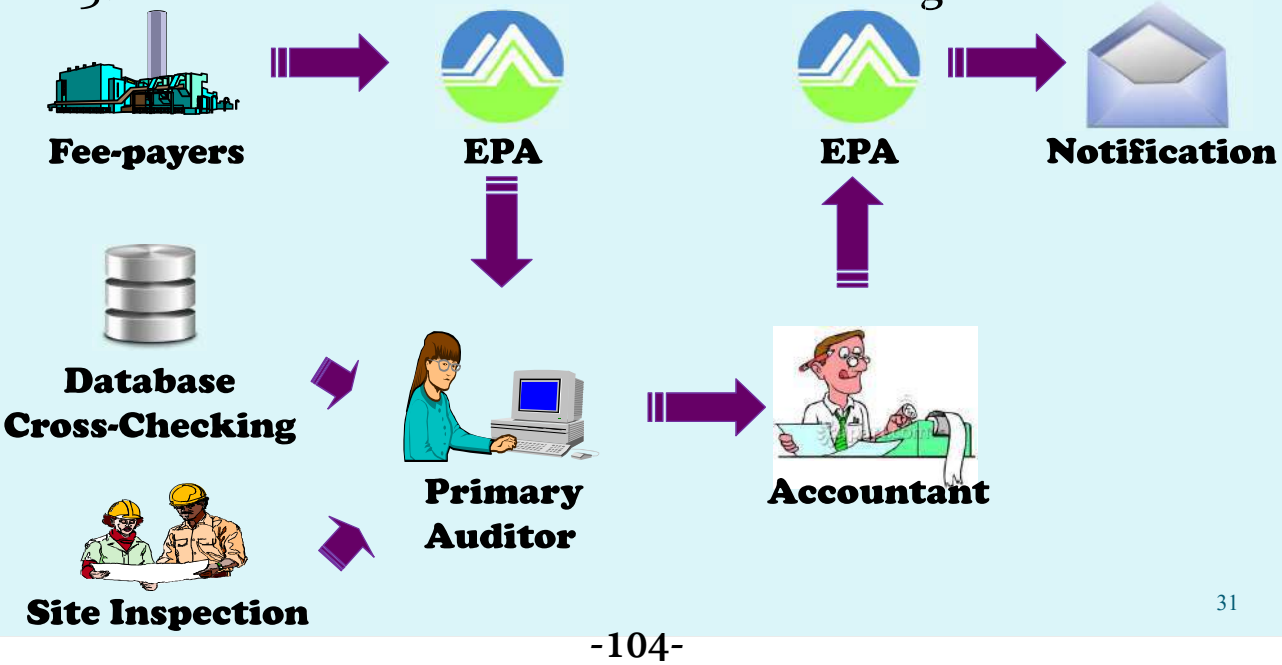
- Businesses express that no pollution is caused if imported substances that are not used up and then exported again. Since the remediation fee has already paid, reimbursements is granted to compensate the cost.
  - 70% of the fee is refunded



Quality Control and Quality Assurance

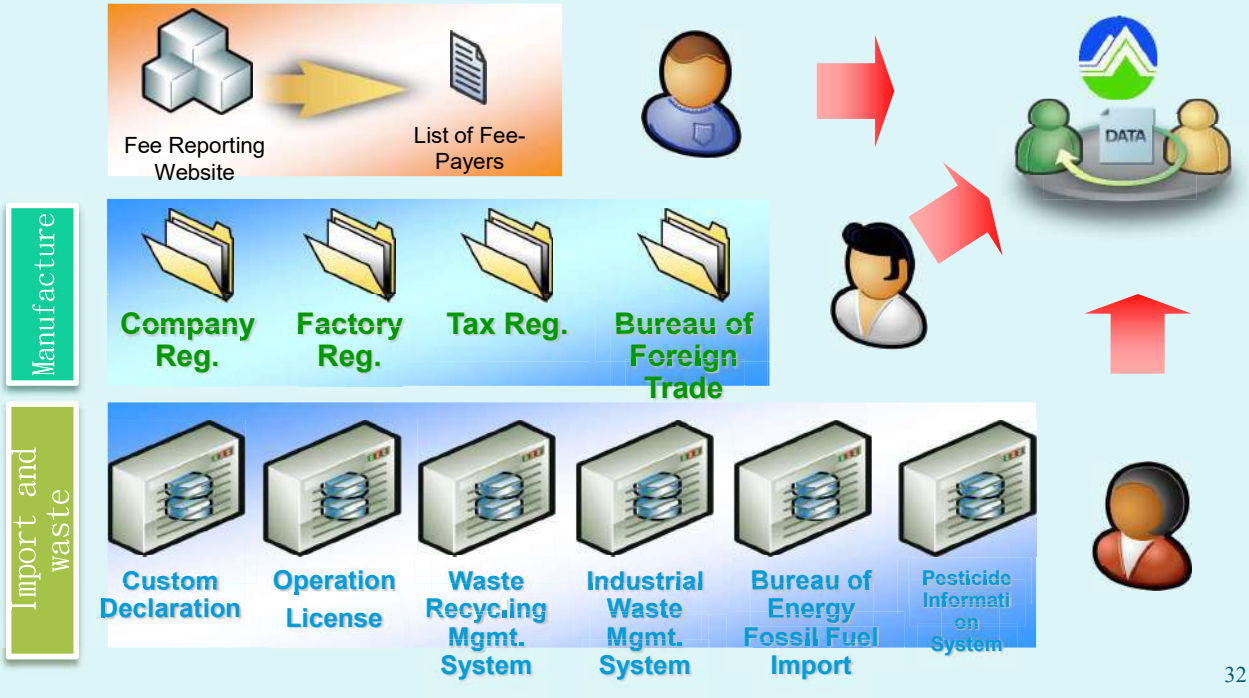
Auditing Process

- Payments of the Remediation Fee are audited through the following process.
- 3% of the fee collected is used in the auditing.



Database Cross-Checking

- Cross-checking with other government database



Third Party Inspection

- A registered accounting firm will further inspect the correctness of the payment.
- Audit through other channels such as financial records and tax records.
- Report any anomalies

Site Inspection

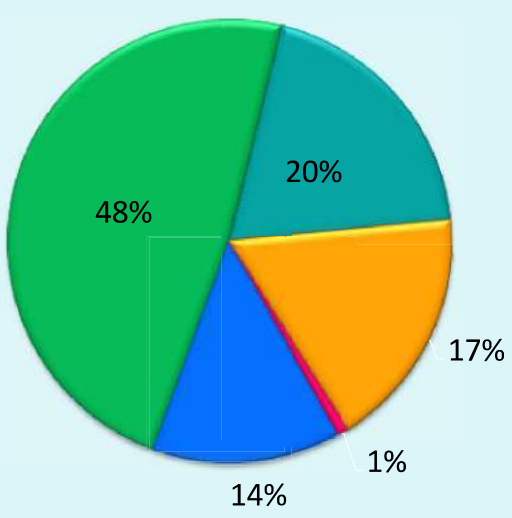
Selection Principals

- Normal Reporting
  - No sufficient supporting document
  - Did not report regularly
  - Major fee-payer
- Reporting Error
  - Reported Wrong Amount
  - Adjustment of wavering percentage
  - Export refund

Conclusion

Expenditure of Remediation Fund

- The expenditure of the remediation fund is US$33 million/year between 2010 and 2014.



Accomplishments

- A total of 3,090 polluted sites has been remediated and removed from the list.

Control Sites	Currently listed			Delisted			Total
	Groundwater pollution	Control sites	Remediation sites	Groundwater pollution	Control sites	Remediation sites	
Factory	9	121	54	0	53	0	237
Gas Station	0	63	18	0	60	3	144
Illegal Dumping Site	0	10	6	0	15	0	31
Farmland	0	2635	0	0	2940	0	5575
Storage Tank	1	3	1	0	1	1	7
Others	15	39	10	1	21	0	86
Total	**25**	**2871**	**89**	**1**	**3090**	**4**	**6080**

As of March 3rd, 2016

Conclusion

- The Soil and Groundwater Pollution Remediation Fund is established not only as resource **for authority to enhance pollution control and remediation of orphan sites** but as incentive **for industrial to modify highly potential polluted process**.
- The Fund is composed of 8 sources. **The main source is Pollution Remediation Fee**.
- The Fund is utilized for 7 objectives. **The main emphasis is pollution investigation & remediation**.

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Conclusion

- The fund is mainly used for **systematic pollution investigation, health risk assessment and control of pollution** in order to manage all contaminated sites and potential ones.
- **Soil and Groundwater Pollution Remediation Fund Management Board (EPA)** and **Soil and Groundwater Pollution Remediation Department (EPB)** are the main institution for the Fund execution.
- Employing **USD$1 from the fund does induce USD$1.43 real production transactions** in the macro economy and the total fund employing **averagely increases 271 employment**.

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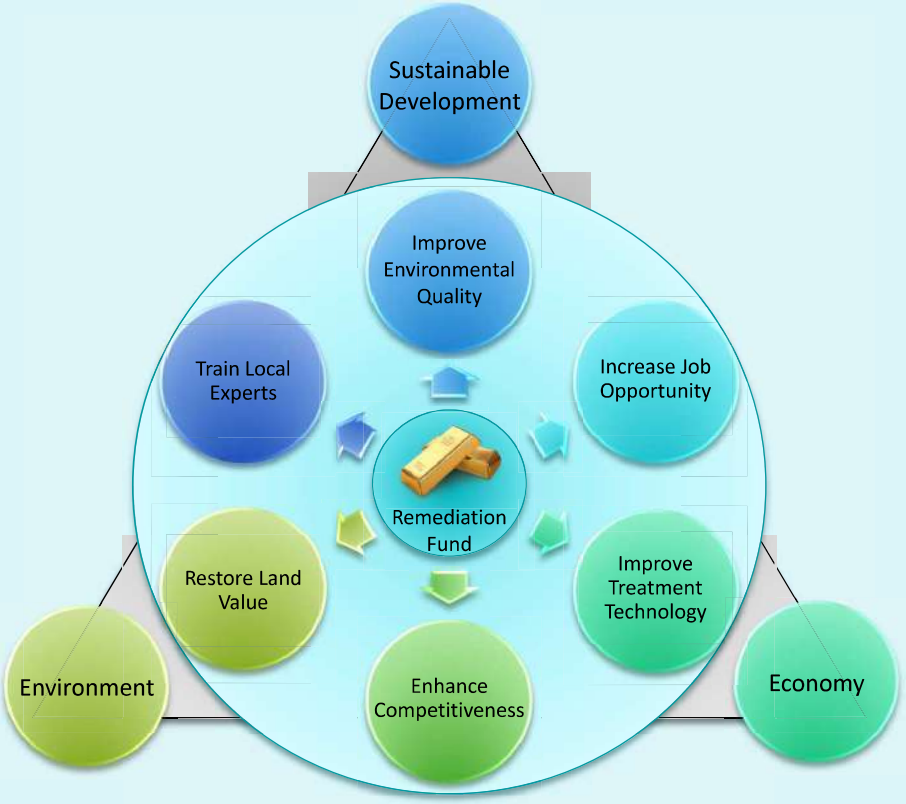
Thinking Further



Thank You for Attention

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

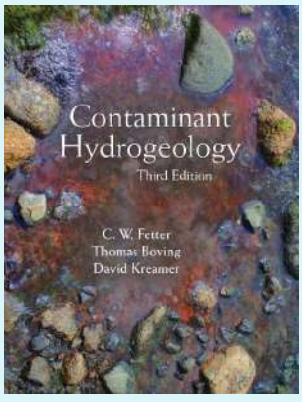
Current Research Directions on Groundwater Contamination and Remediation in the US

Tom Boving, Ph.D.
University of Rhode Island

Introduction

Dr. Boving

- Professor - Environmental Hydrogeology at the University of Rhode Island
  - Dept. Civil and Environmental Engineering
  - Dept. Geosciences



- Ph.D. in Hydrogeology from University of Arizona
- *Before*: Environmental Consultant in Germany: Responsible for site investigation and remediation

Areas of Research

- Innovative Remediation Technologies for Contaminated Soil and Groundwater
- Stormwater Runoff and Urban Flooding
- Sustainable Water Treatment Technologies for Developing Countries

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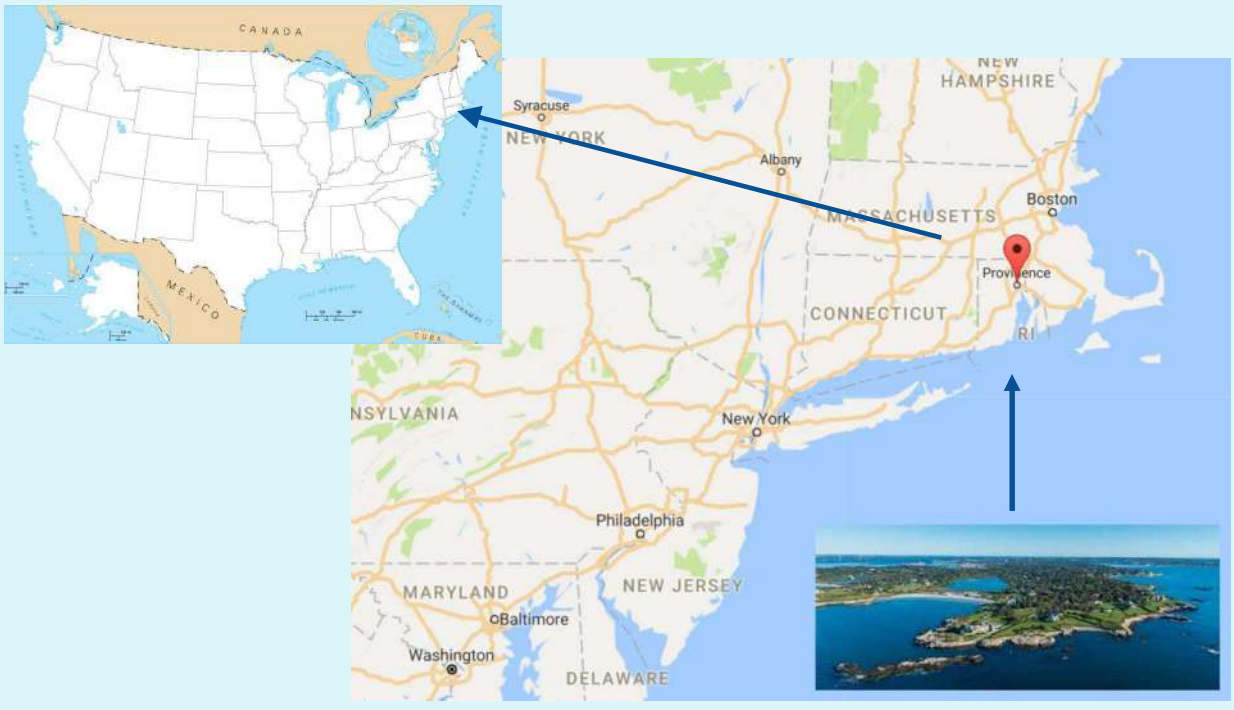
Where is Rhode Island?



New Engineering Building (2019)

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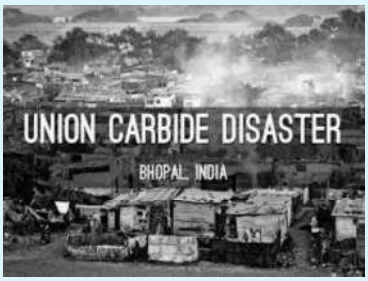
Overview

- Definition of Problem – A look back in time
- Current Research Priorities
- Future Directions
- Conclusions

Past Infamous Environmental Disasters

Thames River 1855



Union Carbide – Bhopal, India 1984

Fish kill after Sandoz spill - Rhine River 1986

Today

Where the Yangtze met the Jialin River

Citarum River, Java

Major Polluted Sites in U.S.

(commons.wikimedia.org)

Red indicates currently on final National Priority List, yellow is proposed, green is deleted (usually meaning having been cleaned up). This map is as of October 2013.

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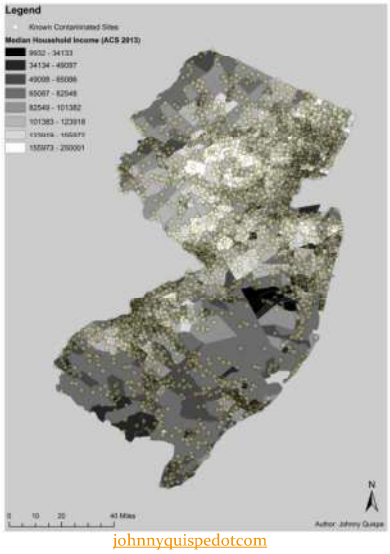
New Jersey



johnnyquispedotcom

- Most contaminated sites of all U.S. states
  - >14,000 known contaminated sites ranging from gas station spills, small historic industrial contamination, to Superfund Sites.

(NJDEP)

Remediation: Before and After

1952

1967

Cuyahoga River, Ohio (USA)

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Cuyahoga River - Today

It took decade How did we do it? to get there!

Key Regulatory Milestones

1970 20 million people celebrate the first earth day.

1970 U.S.EPA established

1976 Resource Conservation and Recovery Act (RCRA)

Regulates hazardous waste from its production to disposal.

1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERLA)

National Priorities List (Superfund).

1984 Health and Safety at Work Act

Introduces land ban of specific contaminants

Remediation – Then and Now

Emergence of U.S. Remediation Industry

1980's

- Primary focus: Petroleum contamination in Groundwater
- Dominant Remediation Technologies
  - Dig-and-haul and pump-and-treat technologies
- Emerging *in situ* technologies
  - Soil vapor extraction (SVE)
  - Air sparging
  - Aerobic bioremediation

Modified after Suthersan et al., 2016

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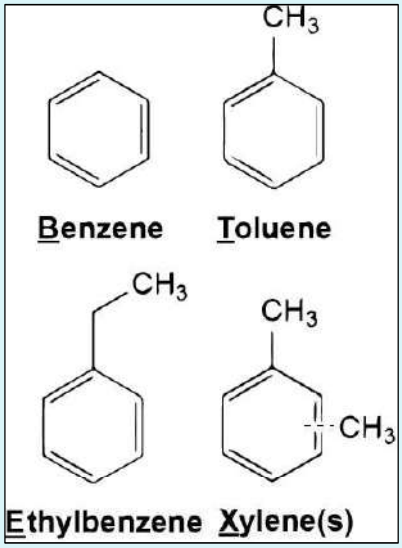
BTEX Contamination at Gas Stations



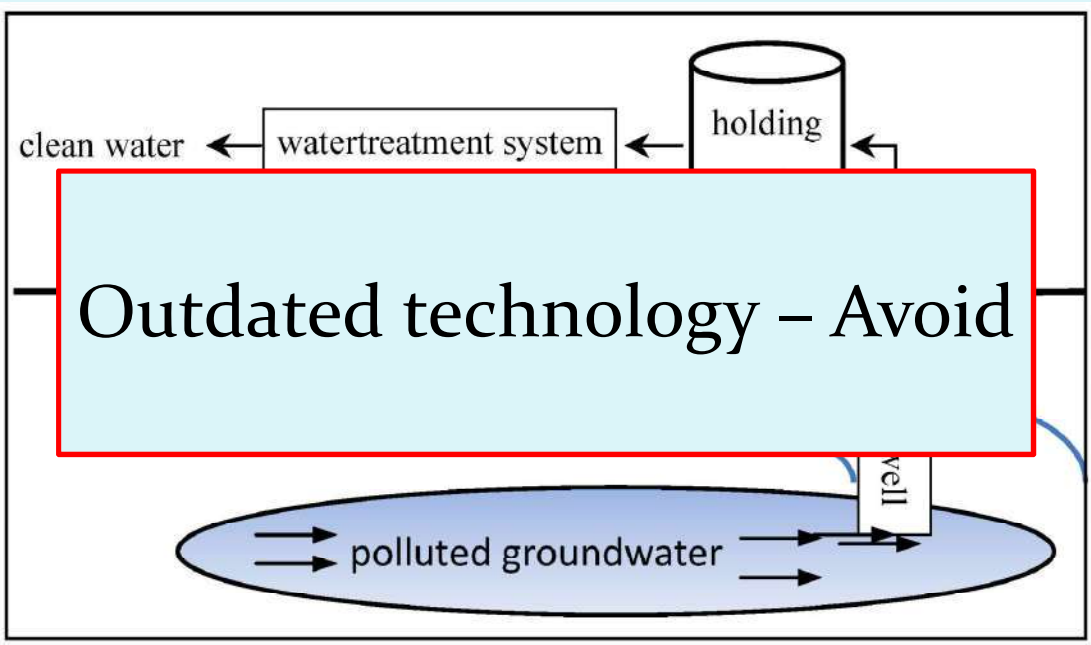
LUST: Leaking Underground Storage Tanks

Leaking Underground Storage Tanks

Anecdotal Evidence

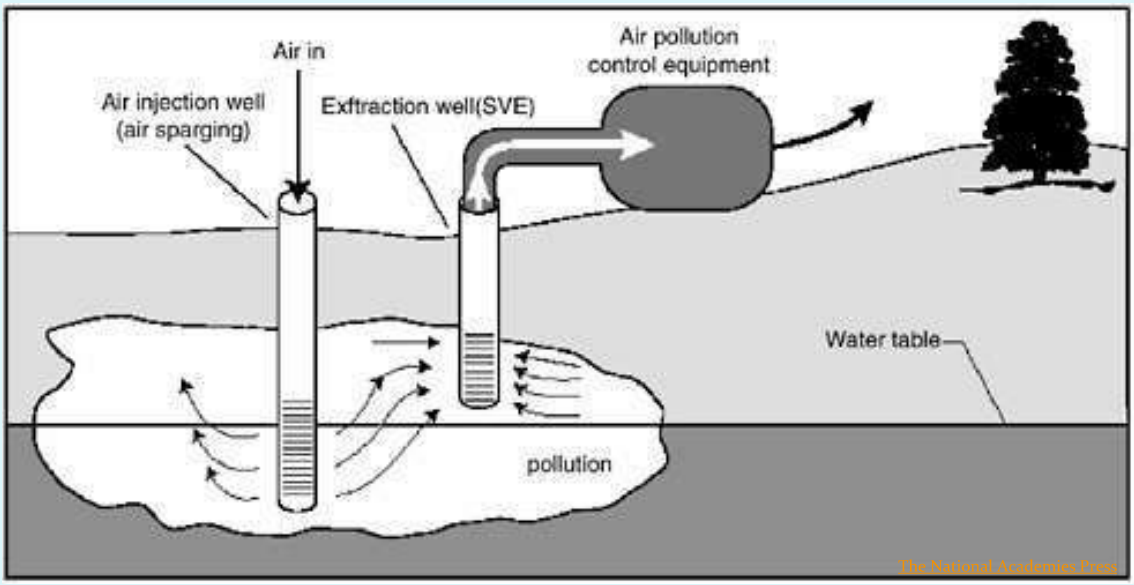
- My personal experience investigating petrol stations in Germany suggests that almost 40% of older stations are likely contaminated.
- ~10% of petrol stations have free product (gasoline, diesel etc.) present in the subsurface.
- Left unattended, these leaking fluids will contaminate massive volumes of groundwater.

Pump-and-Treat



www.intechopen.com

Air Sparging and Soil Vapor Extraction



1990's

- Chlorinated solvents become primary focus of concern.
  - Also: Dissolved metals
  - Sediments contamination gets attention
- Pump-and-Treat remains dominant treatment technology.
- Emerging *in situ* technologies
  - Anaerobic bioremediation
  - Engineered reductive dechlorination
  - Thermal technologies

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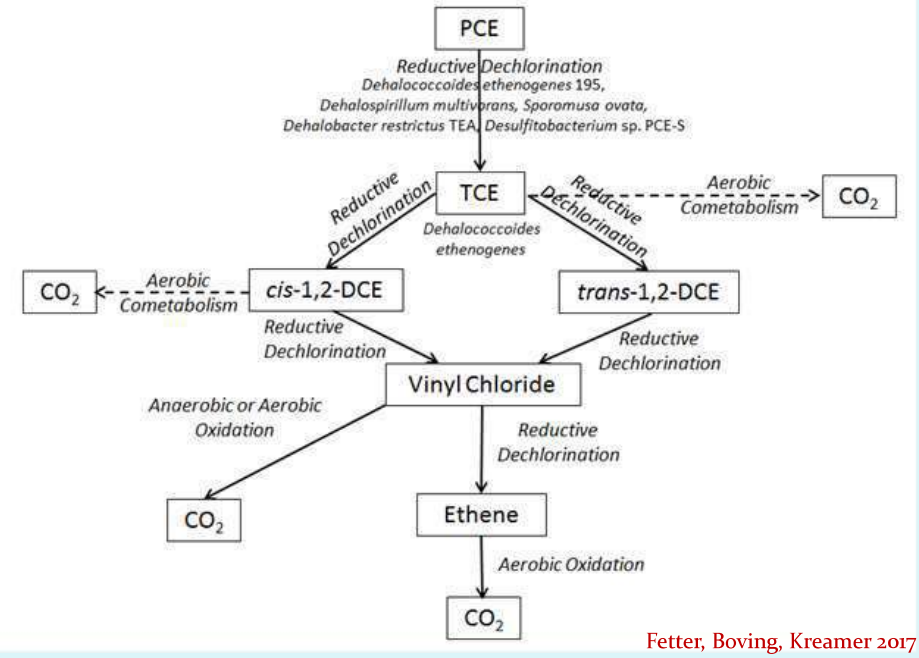
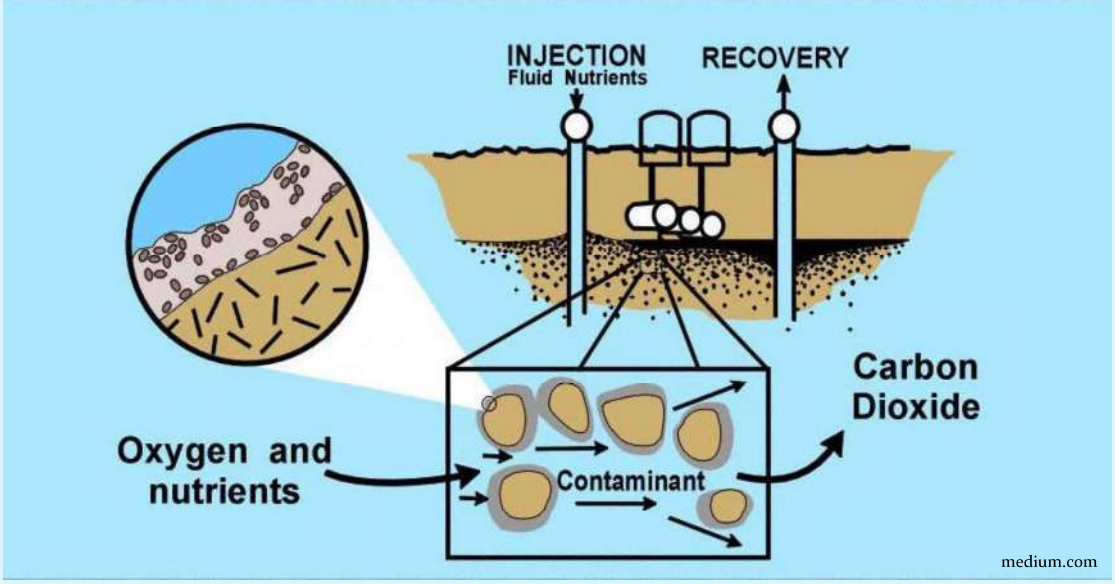
Chlorinated solvents and Reductive chlorination



Fetter, Boving, Kreamer 2017

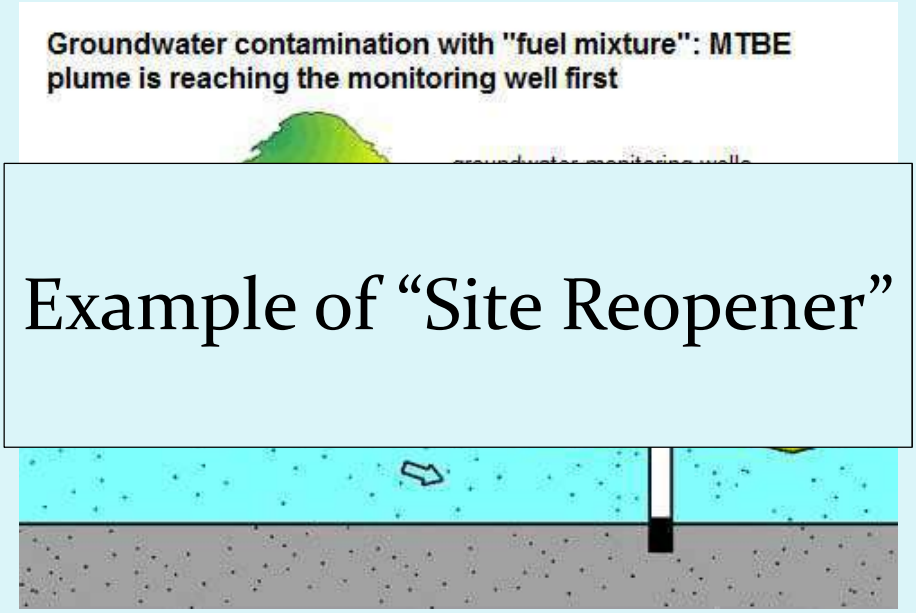
Bioremediation



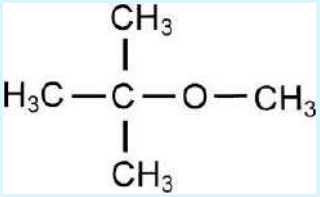
2000's

- MTBE groundwater pollution emerges as a focus of concern.
  - "Emerging contaminants" enter discussion
- Advances in remediation hydraulics and hydrogeology.
  - *Remediation Engineering* emerges as new field of study
- Emerging *in situ* technologies
  - In situ chemical oxidation (ISCO)

MTBE was mixed into gasoline



Example of "Site Reopener"



MTBE

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The Emergence of Remediation Engineering

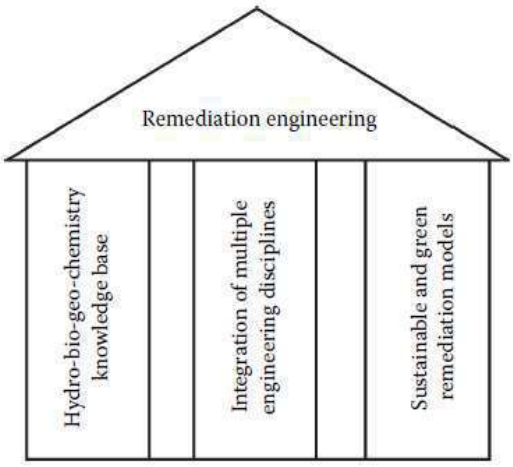


FIGURE 1.3 The three foundational columns that support the advancement of *remediation engineering* as a practice.

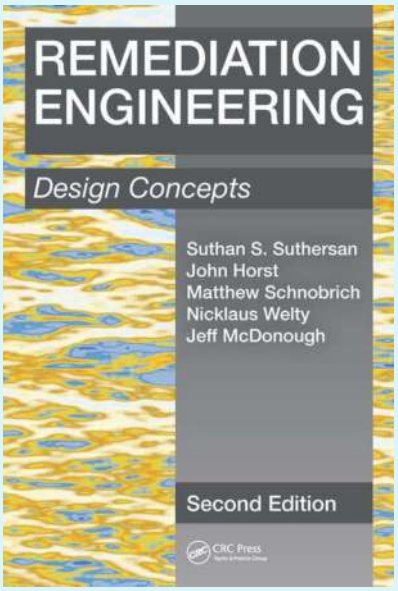


TABLE 9.1 Common and innovative contaminant remediation technologies.

Technology	Application	Development Status
Pump-and-Treat (P&T)	(Source Zone) / Plume / Containment	Established
Physical Containment	Source Zone / Plume	Established
Solidification/Stabilization	Source Zone	Established
Soil Vapor Extraction / Air Sparging	Unsaturated Zone; Source Zone / Plume	Established
Bioremediation and Monitored Natural Attenuation (MNA)	Source Zone / Plume	Innovative / Established
Permeable Reactive Barrier	Source Zone / Plume	Innovative / Established
Chemically Enhanced Flushing	Source Zone	Established
Thermal Treatment	Source Zone / Unsaturated Zone	Innovative / Established
In Situ Oxidation	Source Zone / Plume	Innovative / Established
Phytoremediation	Plume / Unsaturated Zone / Containment	Innovative / Established

Note: The boundary between what is a conventional and innovative technology is fluent.

Fetter, Boving, Kreamer 2017

T.Boving - URI

2010's

- Regulatory standards for some emerging contaminants are in place.
- Remediation of large plumes becomes a discipline on its own.
- Convergence of the remediation industry and water supply industry is beginning to take shape.

Modified after Suthersan et al., 2016

Emerging Contaminants

- A chemical or material characterized by a perceived, potential, or real threat to human health or the environment or by a lack of published health standards.

U.S.EPA

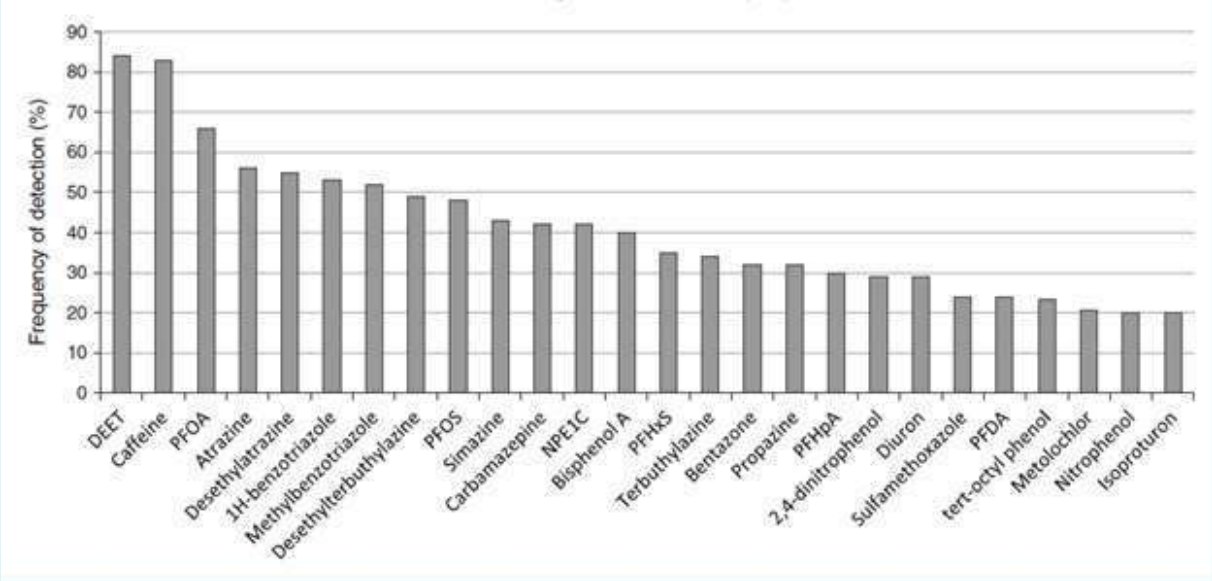
Emerging contaminants do not necessarily mean newly introduced chemicals but can also include naturally occurring compounds with previously unrecognized adverse effects on ecosystems (Suthersan et al., 2016).

T.Boving - URI

Emerging Contaminants

- Brominated flame retardants
- Pharmaceutical and personal care products (PPCPs)
- Nano-materials
- Endocrine disrupting compounds (EDCs)
- POPs: persistent organic pollutants
- Per/poly fluorinated compounds
- …

Emerging Contaminants



Frequency of detection and maximum detected concentrations of emerging contaminants in European groundwater (Loos et al., 2010).

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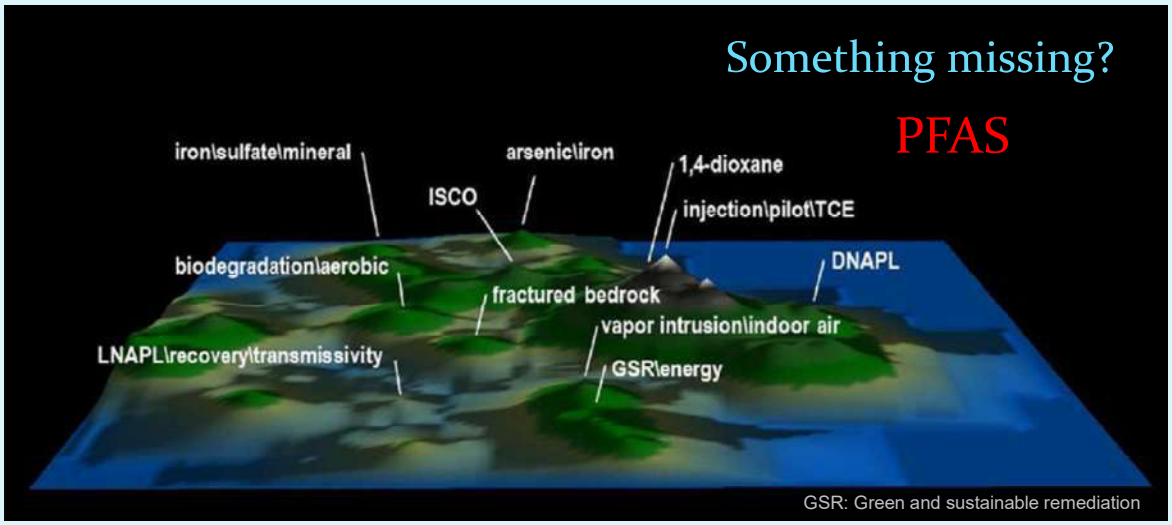
Current Research Priorities

W. Condit et al. / Journal of Environmental Management 204 (2017) 705–708

Environmental Key Topics



Key topics data mining results from over 4000 abstracts submitted 2006-2016 (Condit et al 2017)

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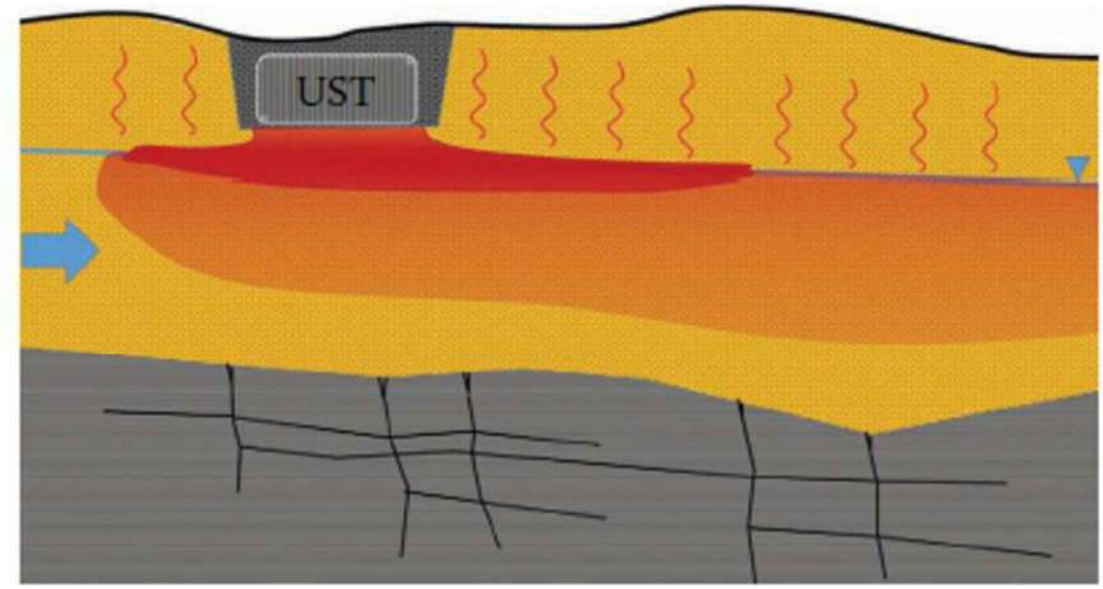
Current Environmental Key Topics

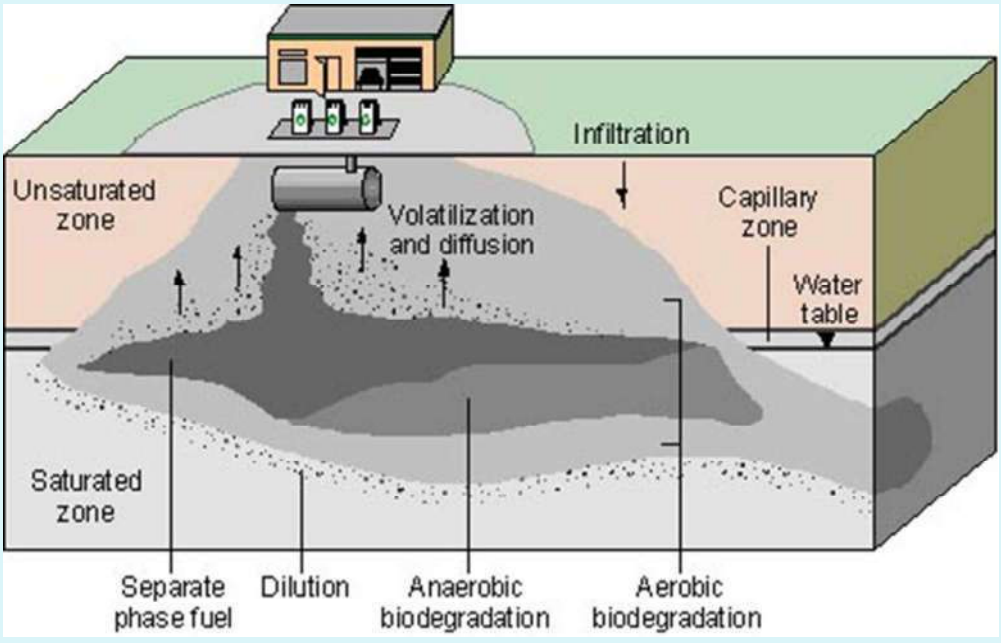
- Conceptual site models (CSM)
  - High-resolution site characterization / diagnostic tools
  - Long-term management of complex sites
  - Vapor intrusion
  - Fractured bedrock remediation
- Improving in situ technologies
  - Emerging contaminants
  - Advanced oxidation processes (AOP)
- Green and sustainable remediation

Example of Basic CSM

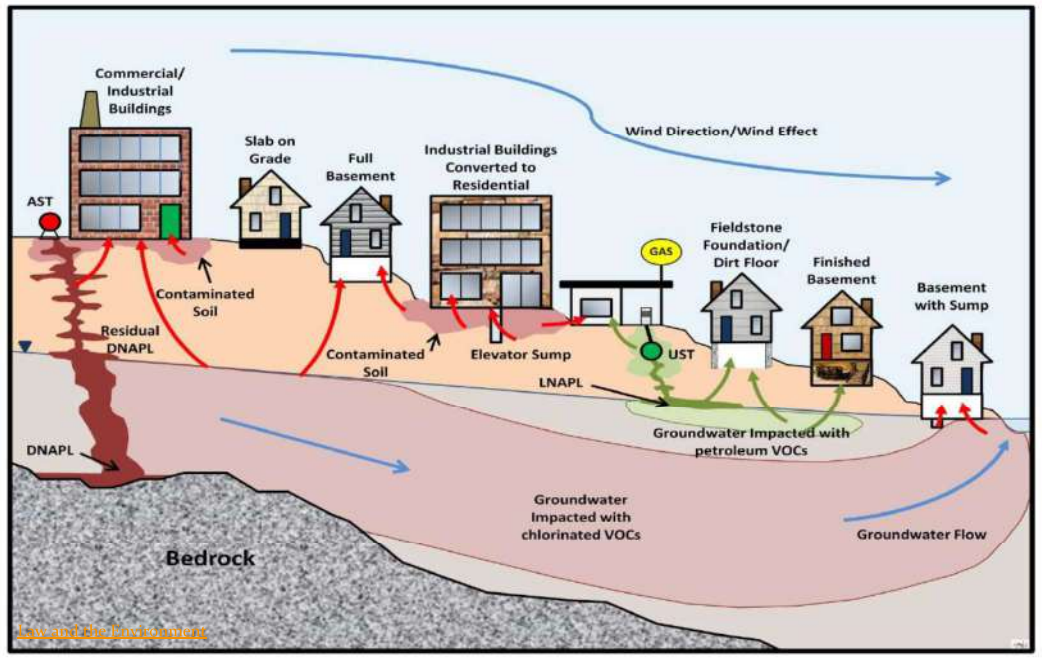


"Living" Conceptual Site Model

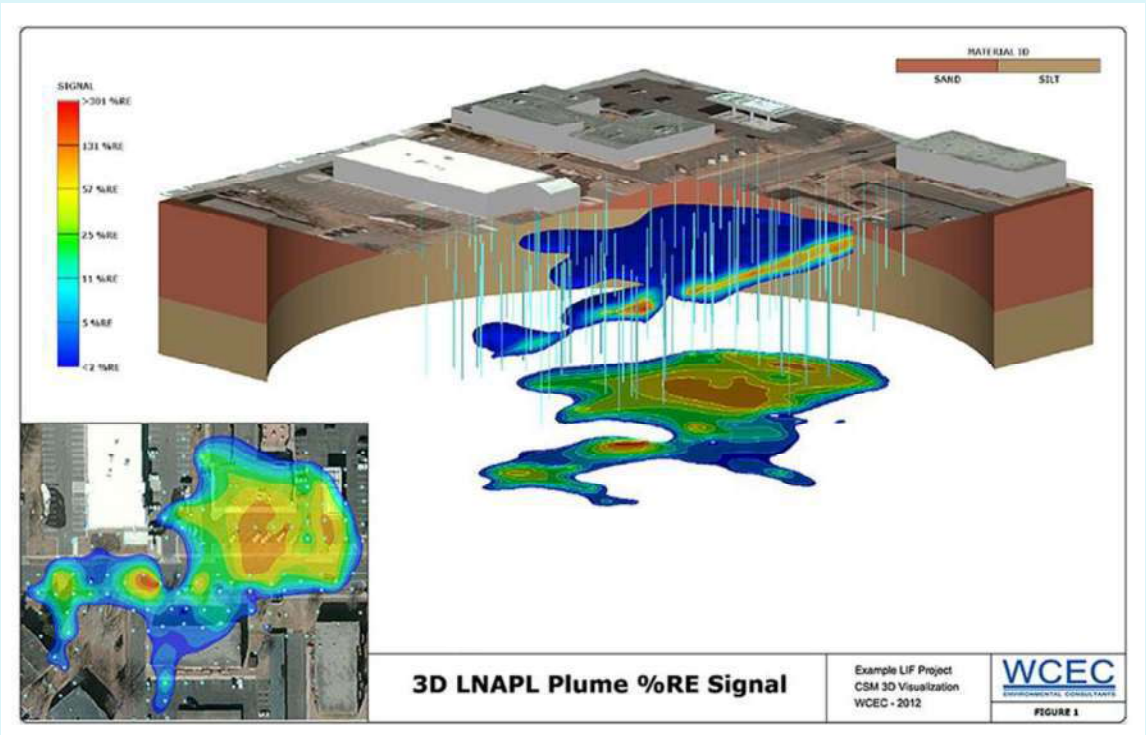
CSM evolves as more and more site information becomes available.



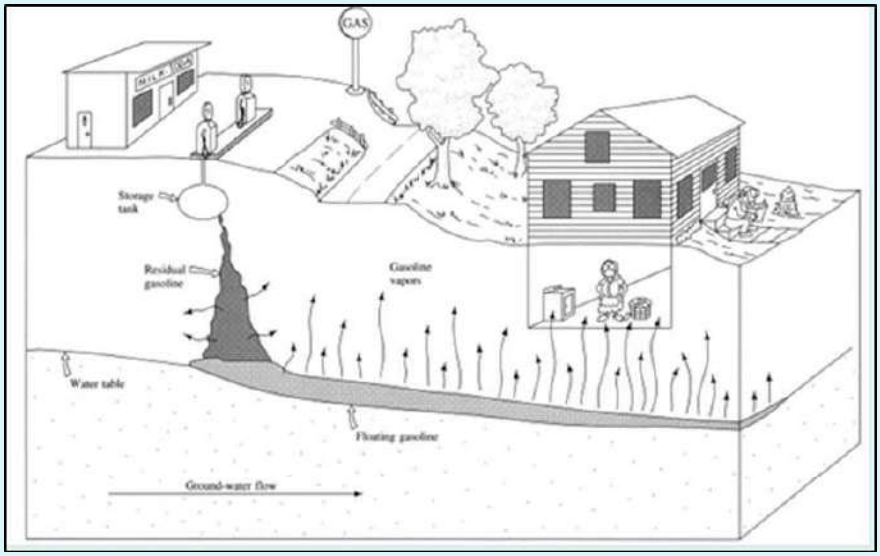
2D - CSM


Commercial/
Industrial
Buildings
Slab on
Grade
Full
Basement
Industrial Buildings
Converted to
Residential
Wind Direction/Wind Effect
AST
GAS
Fieldstone
Foundation/
Dirt Floor
Finished
Basement
Basement
with Sump
Contaminated
Soil
Residual
DNAPL
Contaminated
Soil
Elevator Sump
UST
LNAPL
DNAPL
Groundwater Impacted with
petroleum VOCs
Groundwater
Impacted with
chlorinated VOCs
Groundwater Flow
Bedrock

3D - CSM


SIGNAL
MATERIAL ID
SAND
SILT
3D LNAPL Plume %RE Signal
Example LIF Project
CSM 3D Visualization
WCEC - 2012
WCEC
FIGURE 1

Challenge: Vapor phase intrusion



Fetter, Boving, Kreamer 2017

Journal of Environmental Management 204 (2017) 783–792

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

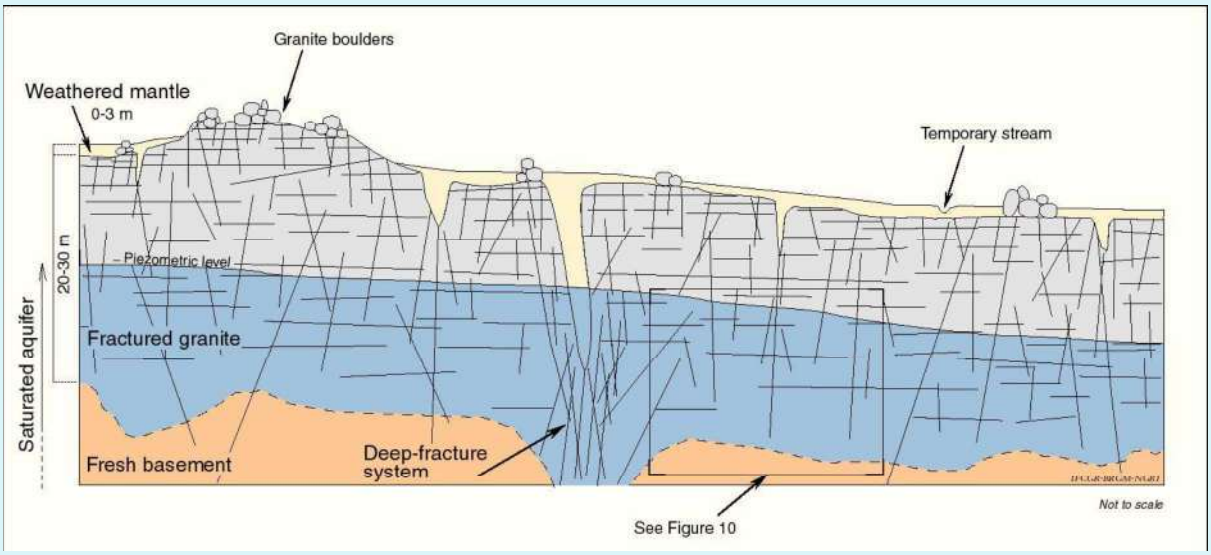
Research article

Recent advances in vapor intrusion site investigations

Thomas McHugh [a, *], Per Loll [b], Bart Eklund [c]

[a] GSI Environmental Inc., Houston, TX, United States
[b] DMR A/S, Jerslev, Denmark
[c] AECOM, Austin, TX, United States

Challenge: Fractured Bedrock Aquifers



jcmarechal.unblog.fr

T.Boving - URI

Journal of Environmental Management 204 (2017) 709–720

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

An overview of geophysical technologies appropriate for characterization and monitoring at fractured-rock sites

Frederick D. Day-Lewis [a, *], Lee D. Slater [b], Judy Robinson [b], Carole D. Johnson [a], Neil Terry [a, 1], Dale Werkema [c]

[a] formerly Rutgers University Newark, now at U.S. Geological Survey, Office of Groundwater, Branch of Geophysics, Storrs, CT, USA
[b] Rutgers University Newark, Department of Earth and Environmental Sciences, Rutgers University, Newark, NJ, USA
[c] U.S. Environmental Protection Agency, Office of Research and Development, 944 E. Harmon Ave., Las Vegas, NV, USA

Improving in situ Technologies

Need for more robust, cost-effective in situ technologies:

- Shorter operational timeframes
- Lower life-cycle costs
- Decrease overall carbon footprints

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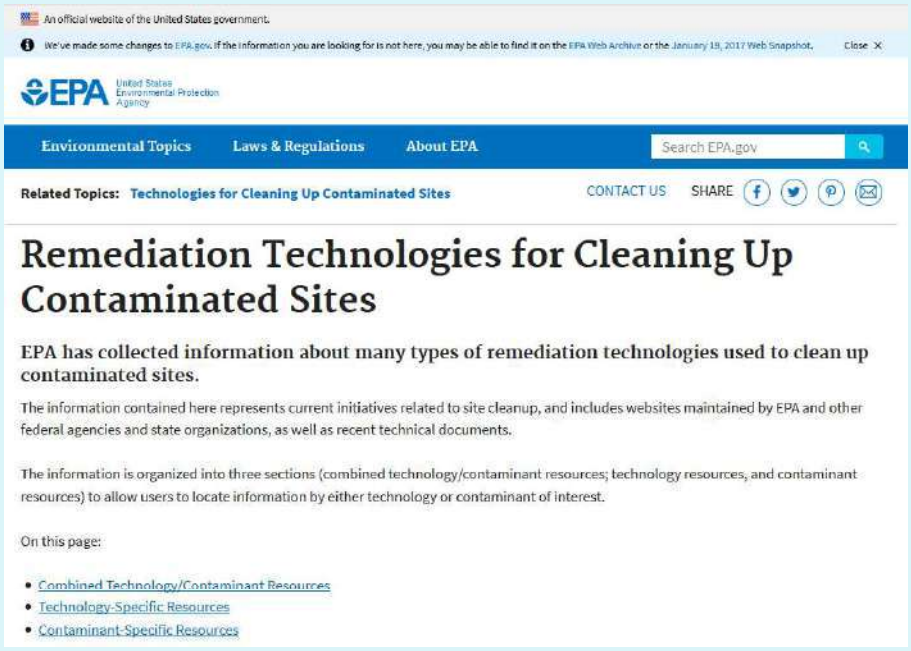
Useful Resources



https://www.epa.gov/remedytech/remediation-technologies-cleaning-contaminated-sites

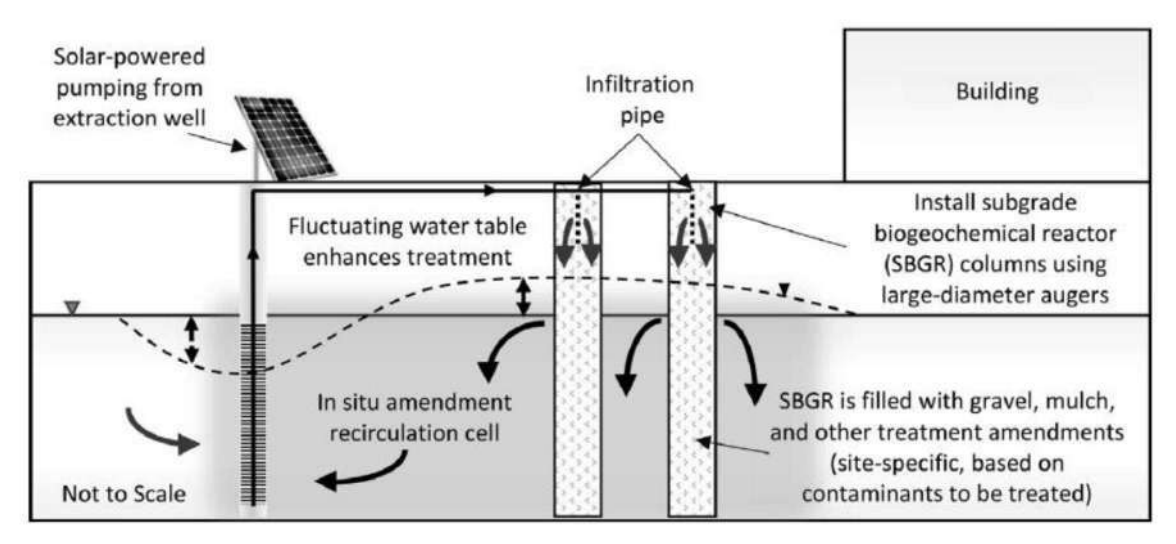
Useful Resources

https://www.enviro.wiki/index.php?title=Main_Page

Innovative Approaches

- Passive in situ remedial technologies
  - Trenches and Barriers
  - Injectable activated carbon substrates
  - Monitored natural attenuation (MNA)
- Enhanced amendment delivery methods
  - Electrokinetic-enhanced delivery, jet injection, viscosity modification, flux reduction techniques, large diameter, auger mixing, slow-release compounds.
- Biological diagnostic tools

Remediation by Biogeochemical Subsurface Reactors



Typical subgrade biogeochemical reactor "Column Reactor" configuration (Gamlin et al. 2017).

T.Boving - URI

Journal of Environmental Management 204 (2017) 804–812

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

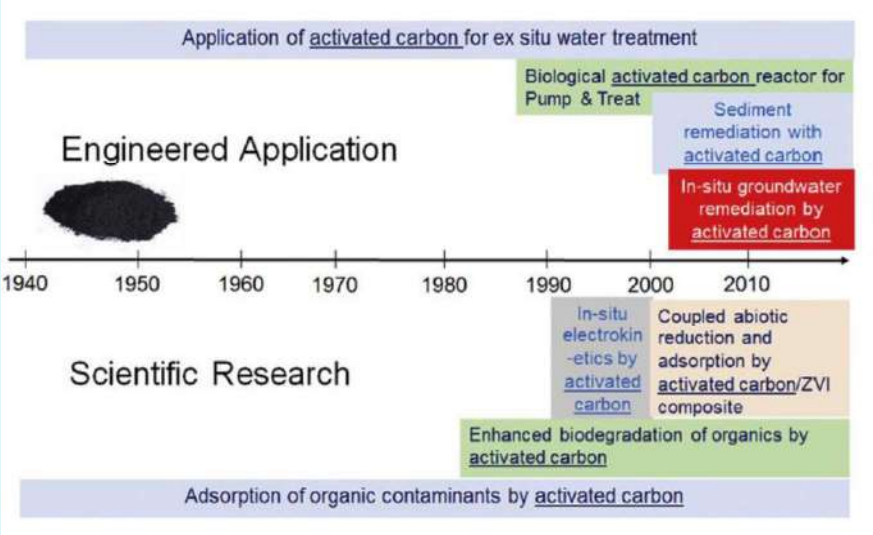
Research article

Design and performance of subgrade biogeochemical reactors

Jeff Gamlin [a, *], Doug Downey [a], Brad Shearer [b], Paul Favara [c]

[a] CH2M, 9189 S. Jamaica St., Englewood, CO 80112, USA
[b] CH2M, 2525 Airpark Dr., Redding, CA 96001, USA
[c] CH2M, 3011 SW Williston Rd., Gainesville, FL 32608, USA

Remediation by Activated Carbon-based Amendments



Timeline of the engineered application and scientific research of AC for ex situ and in situ water treatment (Fan et al. 2017).

T.Boving - URI

Journal of Environmental Management 204 (2017) 793–803

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Review

Current state of in situ subsurface remediation by activated carbon-based amendments

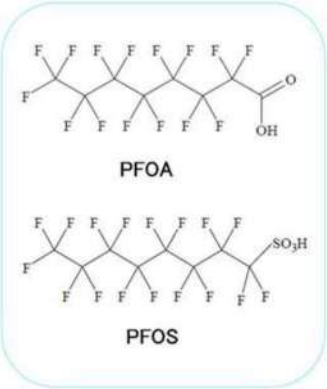
Dimin Fan [a, *], Edward J. Gilbert [b], Tom Fox [c]

[a] Oak Ridge Institute for Science and Education (ORISE) Fellow at the U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, Arlington, VA, 22201, USA
[b] Office of Superfund Remediation and Technology Innovation, U.S Environmental Protection Agency, Arlington, VA 22202, USA
[c] Colorado Department of Labor and Employment, Division of Oil and Public Safety (OPS), Denver, CO 80202, USA

Remediation of PFAS

Per- and polyfluoroalkyl substances (PFAS)

- A group of man-made chemicals, including PFOA, PFOS (= most commonly produced and studied).
  - Likely > 3,000 PFAS compounds
- Manufactured and use in United States since the 1940s, and around the globe
- Very persistent in the environment and in the human body



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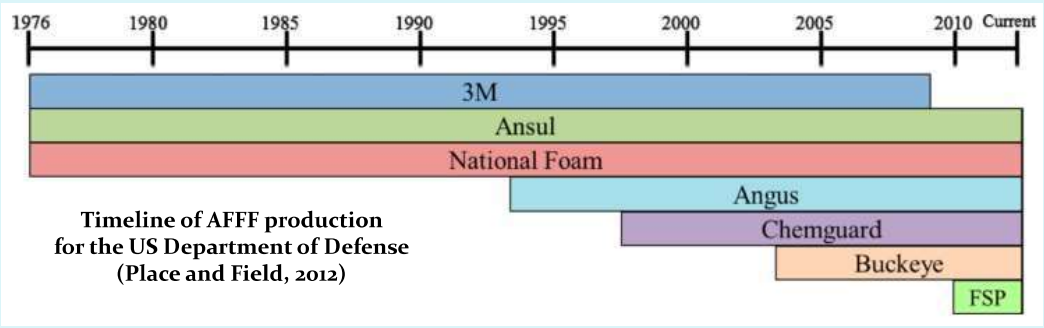
Physical and chemical properties of PFOS and PFOA.

Property	PFOS (Potassium Salt)	PFOA (Free Acid)
Chemical Abstracts Service Number	2795-39-3	335-67-1
Physical description (physical state at room temperature and atmospheric pressure)	White powder	White powder/waxy white solid
Molecular weight ($g\ mol^{-1}$)	538	414
Water solubility at 25 °C ($mg\ L^{-1}$)	550 to 570 (purified), 370 (fresh water), 25 (filtered sea water)	9.5×10^3 (purified)
Melting point (°C)	>400	45 to 54
Boiling point (°C)	Not measurable	188 to 192
Vapor pressure at 20 °C (mm Hg)	2.48×10^{-6}	0.017[a]
Octanol-water partition coefficient (log Kow)	Not measurable	Not measurable
Organic-carbon partition coefficient (log Koc)	2.57 (estimated based on anion)	2.06
Henry's law constant ($atm\text{-}m^3\ mol^{-1}$)	3.05×10^{-9}	Not measurable
Half-life	Atmospheric: 114 days Water: > 41 years (at 25° C)	Atmospheric: 90 days[b] Water: > 92 years (at 25° C)

[a] Extrapolation from measurement.
[b] The atmospheric half-life value identified for PFOA estimated based on available data determined from short study periods.

Kucharzyk et al. 2017

Aqueous Film Forming Foams (AFFFs)



Timeline of AFFF production for the US Department of Defense (Place and Field, 2012)

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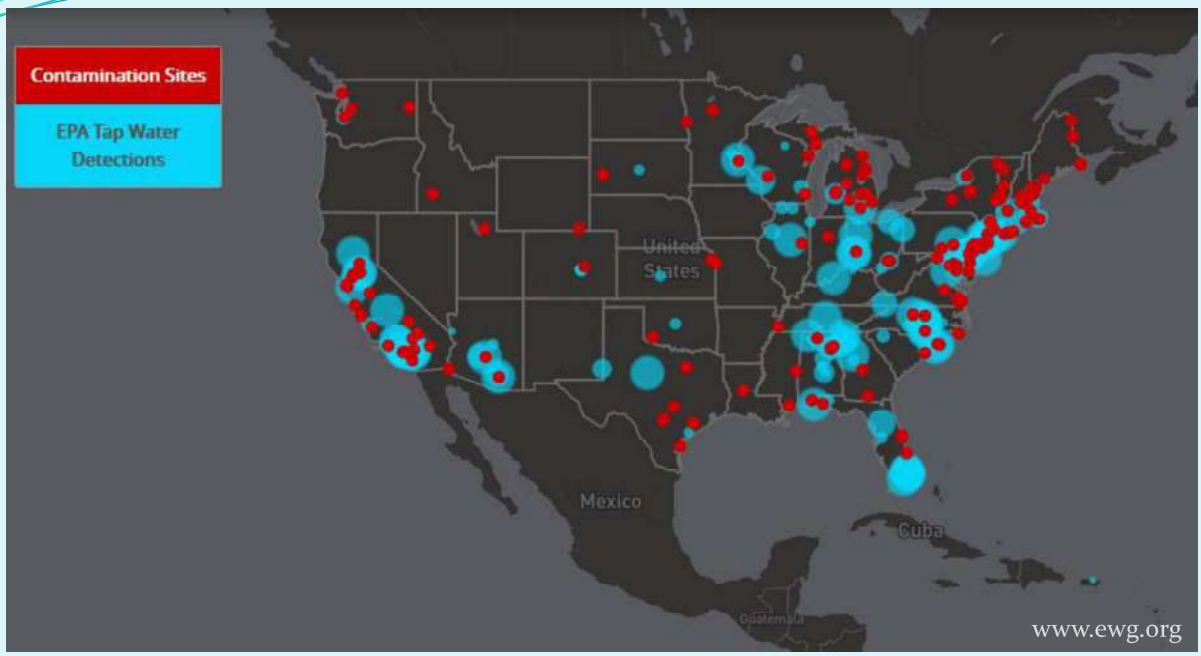

It is estimated that more than 1,500 drinking water systems, serving up to **110 million** Americans, may be contaminated with PFOA, PFOS and similar fluorinated chemicals.

Ex situ PFAS Treatment

- Sorption by activated carbon or resins/polymers
- Reverse osmosis and nanofiltration
- Sonochemical destruction

- Pros: fairly well established technologies

- Cons: relatively high cost of operation, effectiveness may be impaired by other groundwater contaminants.

In situ PFAS Treatment

- Microbial and Fungal PFAS degradation
- Chemical oxidation (Advanced oxidation processes; AOPs)
- Reduction processes
- Treatment trains

- Pros: In situ technologies often have shorter operational time frames, lower life-cycle costs and smaller carbon footprints.

- Cons:
- Largely unknown destruction mechanism(s), byproducts, effect of treatment conditions, and the impact of co-contaminants and other PFASs including precursors.
- Very limited field scale data.
- Mostly lab scale testing

Journal of Environmental Management 204 (2017) 757–764

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Novel treatment technologies for PFAS compounds: A critical review

Katarzyna H. Kucharzyk [a, *], Ramona Darlington [a], Mark Benotti [b], Rula Deeb [c], Elisabeth Hawley [c]

[a] Battelle Memorial Institute, Columbus, OH, 43201, USA
[b] Newfields Environmental, Rockland, MA, 02371, USA
[c] Geosyntec Consultants, Atlanta, GA, 30319, USA

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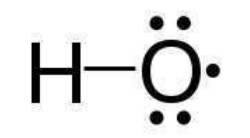
PFAS Treatment by Advance Oxidation Process (AOP)

- AOP = Chemical treatment procedures designed to remove organic materials in water and wastewater by oxidation through reactions with radicals.

Radical = molecule that contains at least one unpaired electron.



Hydroxyl radical

Following data and results are from (in review):

Feb. 22, 2019

Elsevier Editorial System(tm) for Journal of Hazardous Materials

Manuscript Draft

Manuscript Number:

Title: Identification of hydroxyl and sulfate free radicals involved the reaction of 1,4-dioxane with peroxone activated persulfate oxidant

Article Type: Research Paper

Keywords: 1,4-dioxane, Electron paramagnetic resonance (EPR), Radicals, Advanced oxidation process (AOP), Peroxone activated persulfate (PAP).

Corresponding Author: Dr. Thomas Boving, PhD

Study funded by : SERDP

T.Boving - URI

Peroxone Activated Persulfate

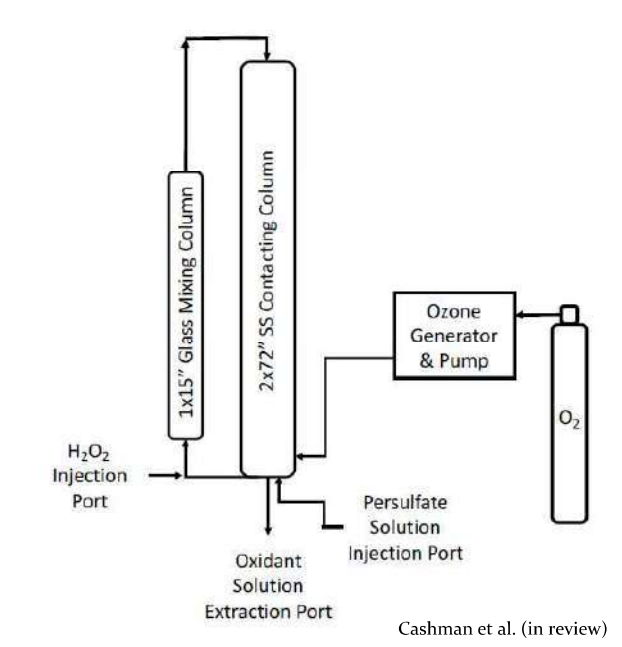
- Mix of persulfate ($S_2O_8^{-2}$), ozone (O_3), hydrogen peroxide (H_2O_2)

Oxidant	Reactive Products	Reaction
Peroxone Activated Persulfate ($S_2O_8^{2-}$)	Sulfate radical ($\bullet SO_4$) Hydroxyl radical ($\bullet OH$)	$S_2O_8^{2-} + H_2O_2 \rightarrow 2\ \bullet SO_4^-$ $2\bullet SO_4^- + 2H_2O \rightarrow 2HSO_4^- + 2\ \bullet OH$ $2\ \bullet OH + 2H^+ + 2e^- \rightarrow 2\ H_2O$

Cashman et al. (in review)

Oxidation potential
Sulfate radical = 2.5-3.1 V,
Hydroxyl radical = 2.7 V

PAP Generator

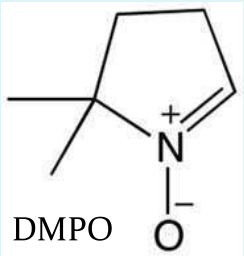


Cashman et al. (in review)

T.Boving - URI

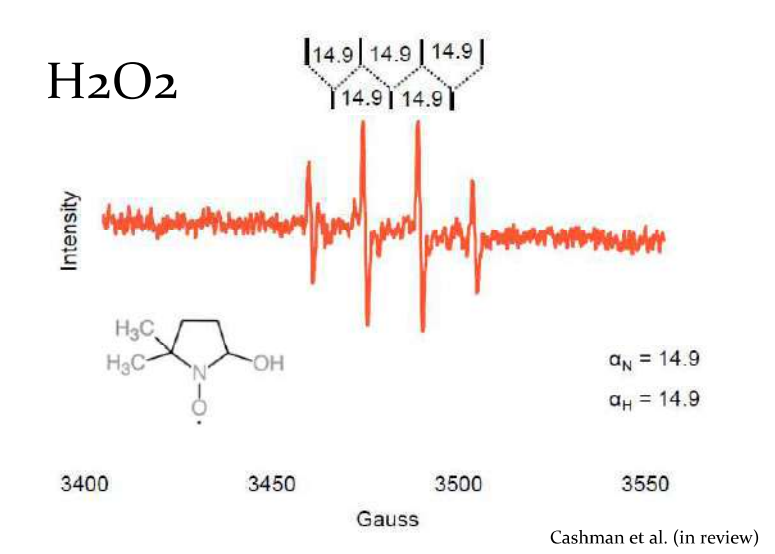
Electron Paramagnetic Resonance (EPR) Spin Trapping

Approach: addition of an organic compound (DMPO in this study) to rapidly trap free radicals and to form more persistent spin adducts that can be detected by EPR.



EPR spectra

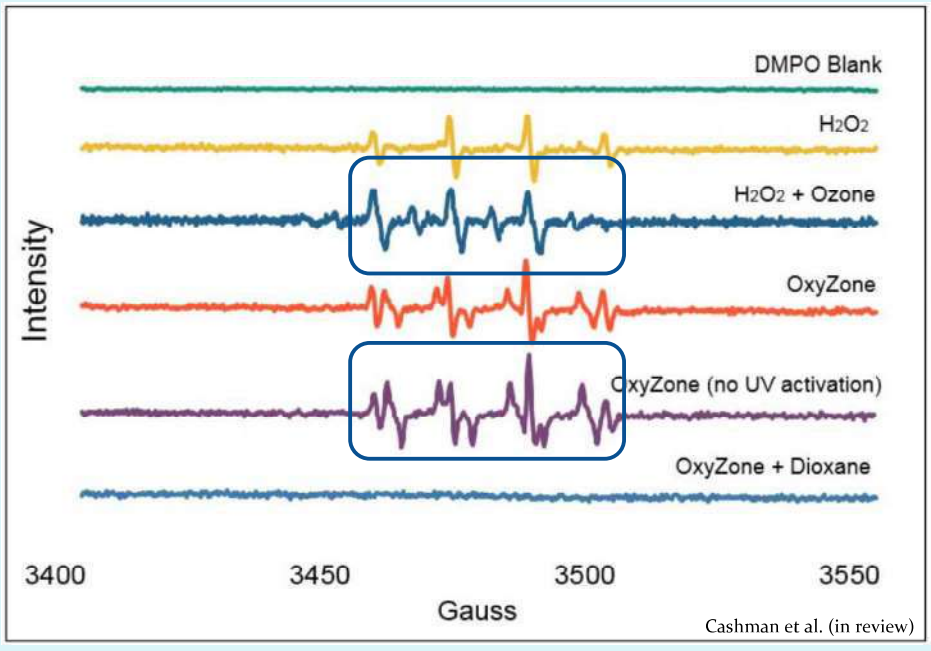
Hydroxyl Radical Spectrum



The distance between each of the peaks, or the hyperfine coupling constant (αN= 14.9, αH= 14.9) verified hydroxyl radical formation.

T.Boving - URI

PAP Radical Spectrum



Results

	No Radicals	Hydroxyl Radical (•OH)	Hydroxyl (•OH) *and* Sulfate ($•SO_4^-$) Radicals
Ozone		○	
Persulfate	○		
Hydrogen peroxide		○	
Ozone + hydrogen peroxide		○	
Persulfate + hydrogen peroxide		○	
Persulfate + ozone			○
OxyZone® (Ozone + hydrogen peroxide + persulfate)			○
OxyZone® (Ozone + hydrogen peroxide + persulfate) + 1,4-dioxane	○		

Cashman et al. (in review)

Following data and results are from (in review):

Chemosphere 144 (2016) 728–735

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

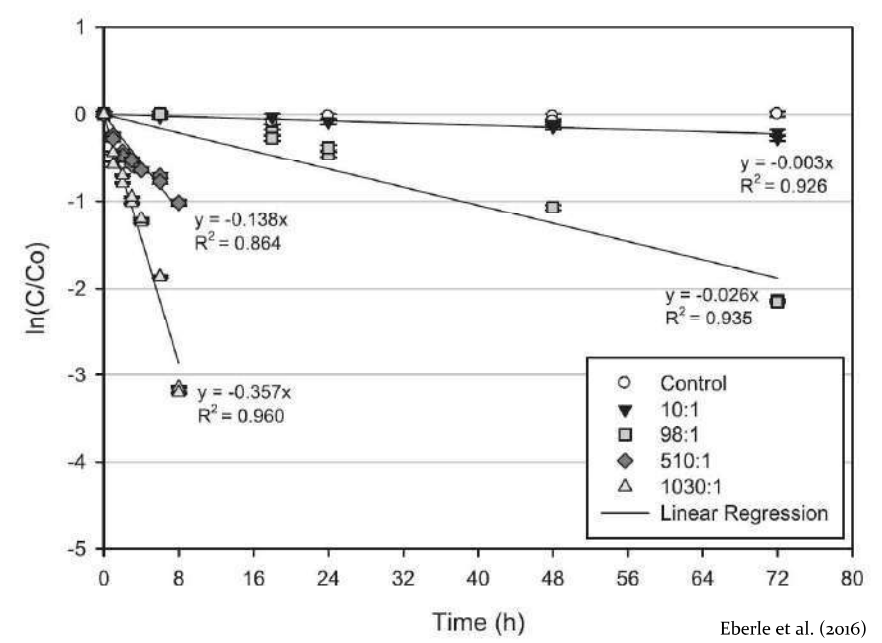
Peroxone activated persulfate treatment of 1,4-dioxane in the presence of chlorinated solvent co-contaminants

Dylan Eberle[a], Raymond Ball[b], Thomas B. Boving[a,c,*]

[a] Department of Geosciences, University of Rhode Island, Kingston, RI 02881, USA
[b] EnChem Engineering Inc., Newton, MA 02458, USA
[c] Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, RI 02881, USA

Study funded by Air Force Civil Engineer Center

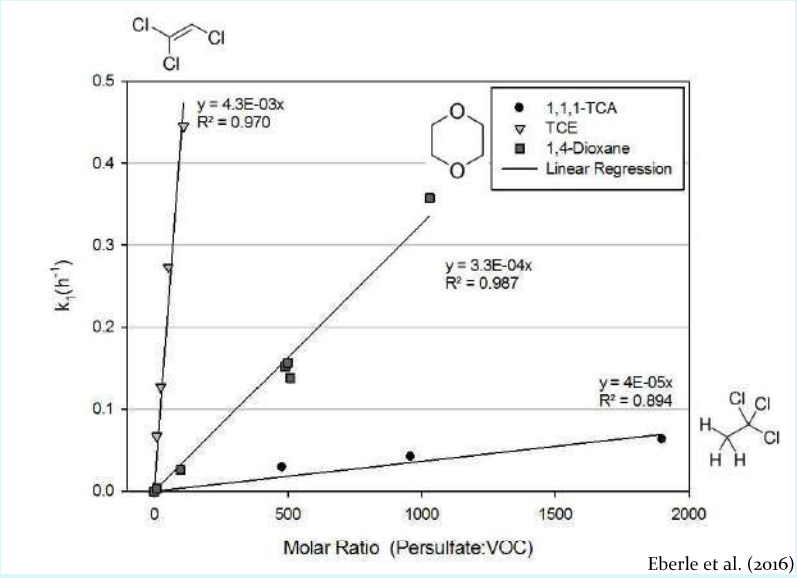
Oxidation of 1,4-Dioxane by PAP



Eberle et al. (2016)

Note: Oxidation by full-strength PAP is too rapid to measure with method used.

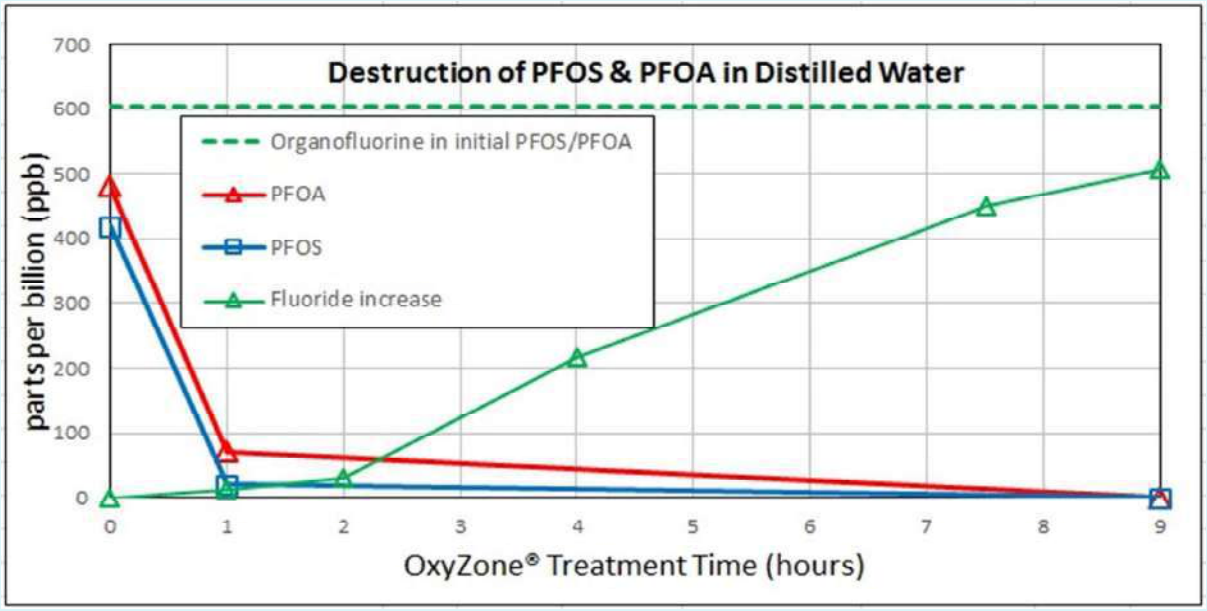
PAP Treatment of cVOC and 1,4-Dioxane



Eberle et al. (2016)

Rapid degradation: 1,1,1-TCA < 1,4-Dioxane < TCE

PAP Treatment of PFAS



Boving and Ball, 2018

Study funded by : SERDP

(Only?) Field Study

ENVIRONMENTAL Science & Technology

Article

pubs.acs.org/est

Impact of ISCO Treatment on PFAA* Co-Contaminants at a Former Fire Training Area

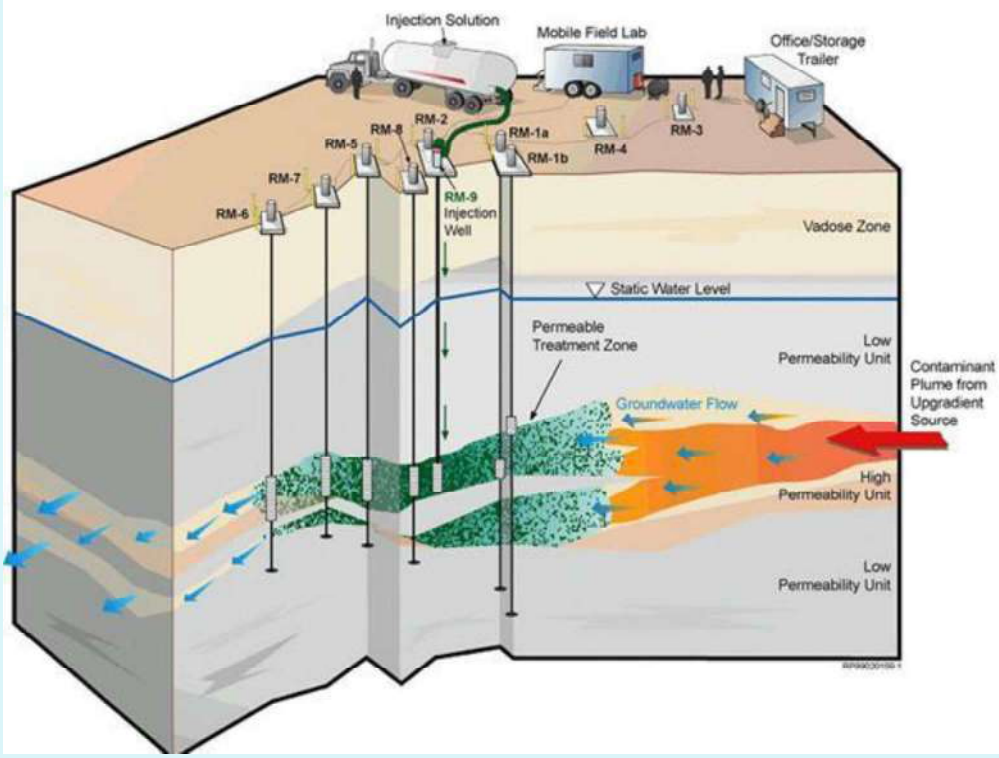
Dylan Eberle,[†] Raymond Ball,[‡] and Thomas B. Boving*[,†,§]

[†]Department of Geosciences, University of Rhode Island, Kingston, Rhode Island 02881 United States
[‡]EnChem Engineering Inc., Newton, Massachusetts 02458 United States
[§]Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, Rhode Island 02881 United States

Study funded by Air Force Civil Engineer Center

*Perfluoroalkyl acids

PAP In-Situ Chemical Oxidation



Site Set-up

Eberle et al. (2016)

OxyZone®

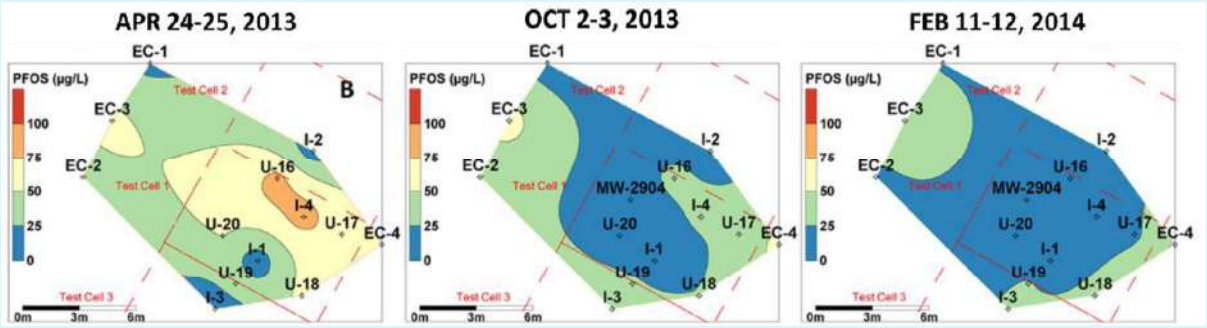
U.S. Patents: 7,667,087 & 8,049,056

EnChem Engineering, Inc.

Mobile
Treatment Unit

Eberle et al. (2017)

PFOS Results

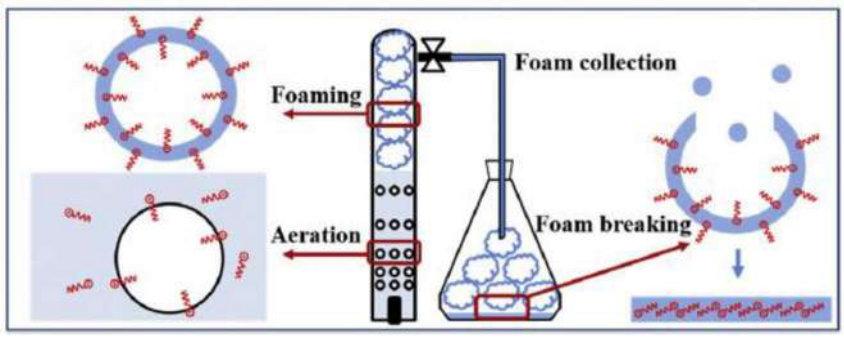


Eberle et al. (2016)

Concentrations decreased with little evidence of rebound

Dilution and displacement do not appear to account for the long term changes observed

Enhanced PAP



Chemosphere 203 (2018) 263–270

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Efficient removal of perfluorooctane sulfonate from aqueous film-forming foam solution by aeration-foam collection

Pingping Meng [a], Shubo Deng [a, *], Ayiguli Maimaiti [a], Bin Wang [a], Jun Huang [a], Yujue Wang [a], Ian T. Cousins [b], Gang Yu [a]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, POPs Research Center, Tsinghua University, Beijing, 100084, China

[b] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, SE-106 91, Stockholm, Sweden

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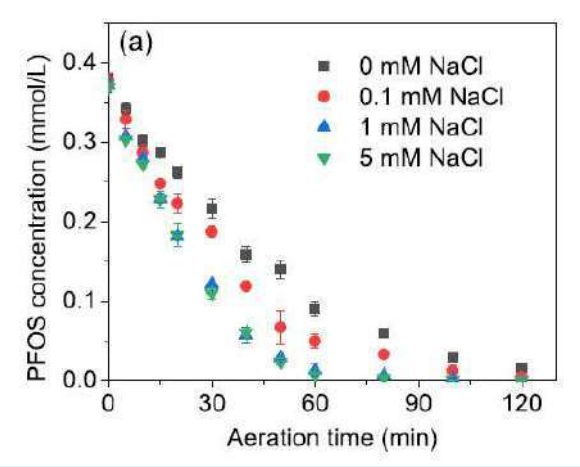
PFAS elimination by aeration-foam collection



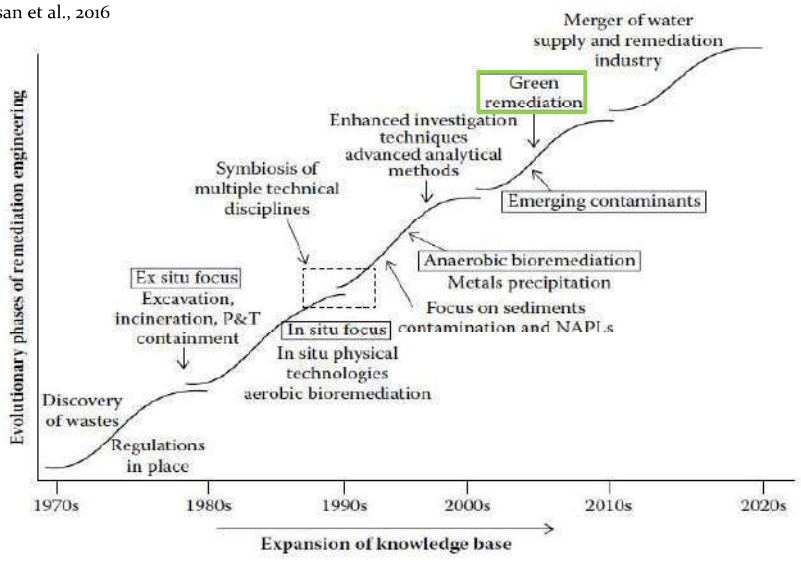
Meng et al. 2018

Our research group confirmed results.

Important:
We improved aeration process by almost 2 orders of magnitude.
(data not shown)

The Future of Remediation

Suthersan et al., 2016



Evolutionary developments in the expansion of remediation engineering knowledge base.

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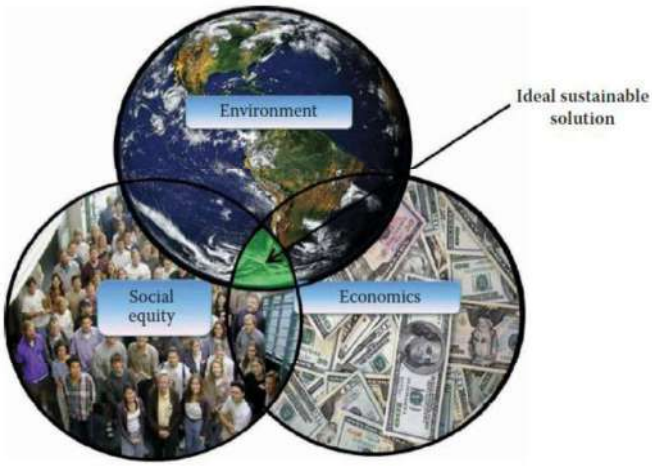
Sustainable (Green) Remediation

"Site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts, and environmental effects."

Suthersan et al. 2016

Concept of Sustainable Remediation



Sustainable Remediation Indicator Categories

Environment	Social	Economic
Emissions to air	Human health and safety	Direct economic costs and benefits
Soil and ground conditions	Ethics and equity	Indirect economic costs and benefits
Groundwater and surface water	Neighborhoods and locality	Employment and employment capital
Ecology	Communities and community involvement	Induced economic costs and benefits
Natural resources and waste	Uncertainty and evidence	Project lifespan and flexibility

Source: Bardos, P., *Remed. J.*, Winter, 23, 2014.

Suthersan et al., 2016

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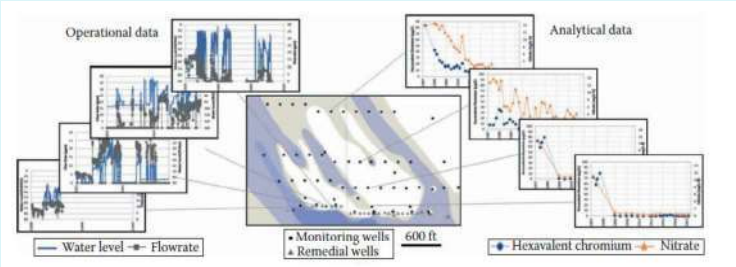
Smart Investigation

- Evaluation of contaminant transport must have a mass flux–based perspective at all sites.
  - Need improved sensor technology: benefits of real-time decision-making



Rethinking Large Plumes

- Many of the large plumes under treatment today were discovered more than 25 years ago.

Old Thinking
Large plumes cleanup is impracticable and thus the only solution is to contain and manage them.
Focus is always on containment.
Back diffusion is difficult to overcome and results in cleanup time frames of 30 to more than 100 years.
Modeling is used for decision-making.
New Thinking
Large plumes can be cleaned up within reasonable time frames and cost-effectively.
Focus on the mass flux and remove the mass that moves.
Back diffusion can be overcome. The term "back diffusion" may be an over simplification of very, very slow advection.
Data drive decisions.

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Complex Sites

"It has become increasingly clear that remediation of *complex sites* to drinking water standards is not only impractical, but also cost prohibitive to be completed within reasonable time frames."

Suthersan et al. 2016

Journal of Environmental Management 204 (2017) 738–747

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

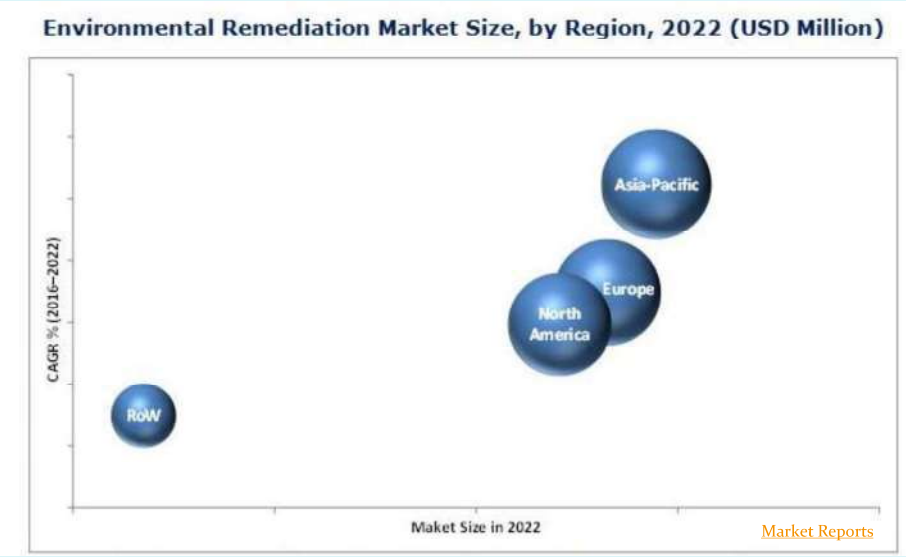
Research article

Remediation management of complex sites using an adaptive site management approach

John Price [a], Carl Spreng [b], Elisabeth L. Hawley [c], Rula Deeb [c, *]

[a] Washington State Department of Ecology, Richland, WA, 99354, United States
[b] Colorado Department of Public Health and Environment, Denver, CO, 80246, United States
[c] Geosyntec Consultants, Oakland, CA, 94607, United States

Environmental Remediation Market



Asia-Pacific region is expected to hold the largest share of the environmental remediation market in 2022.

Market Restring Factors

- One of the key restraining factors in the environmental remediation market is the **slow implementation** of environmental protection regulations due to the **lack of awareness** of various environmental technologies and **lack of training** for resolving environmental concerns in developing countries.

Market Reports

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Final thoughts

- Remediation industry is emerging in many Asian countries
- How will soil and groundwater remediation approaches fare under increasing urbanization and population pressures in Asian countries?

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Thank you!

多謝

Prof. Thomas Boving
University of Rhode Island
Kingston, USA

boving@uri.edu

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Soil and Groundwater Protection in Taiwan - Policy and Regulations

Environmental Protection Administration, Taiwan
Soil and Groundwater Remediation Fund Management Board

Dr. Ching-Jen, Ho
Chief of Comprehensive Planning Section

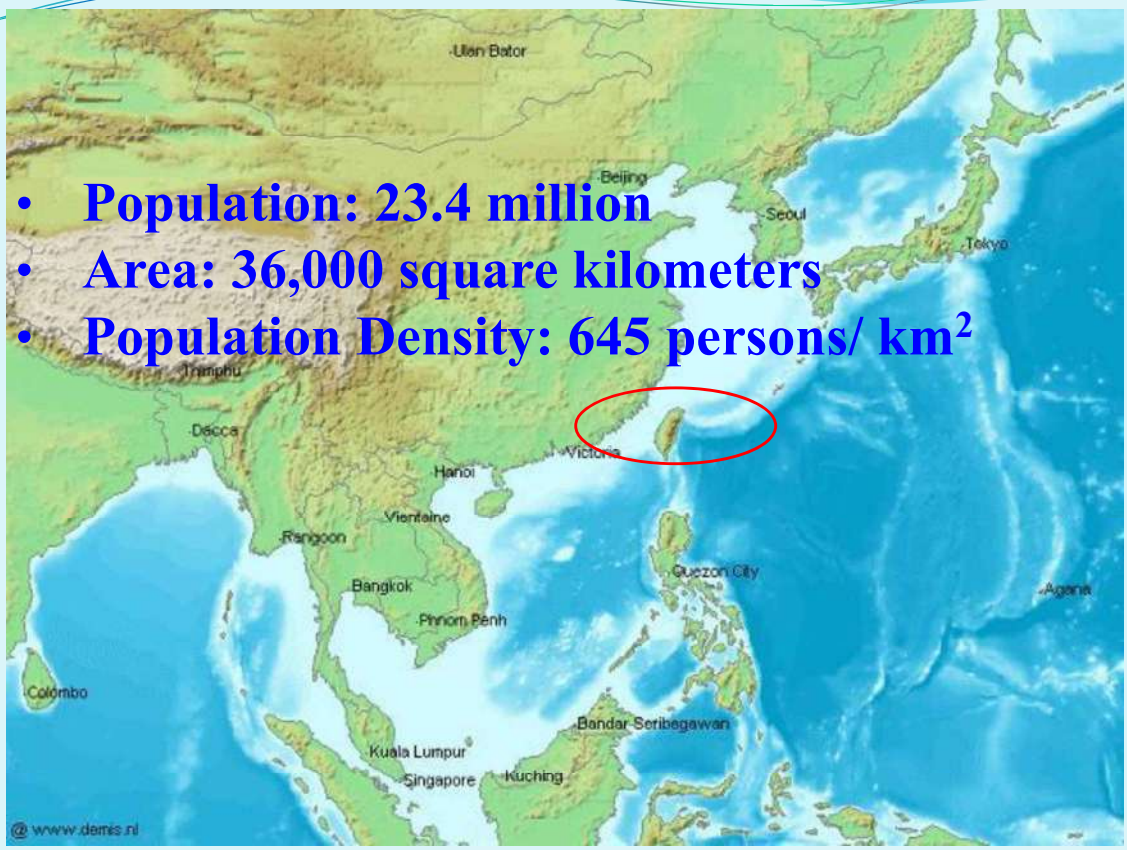
2019.03

Outline

- Introduction
- Remediation Fund
- Law
- Measures of SRF
- Accomplishments
- Conclusion
- Appendix

- **Introduction**

Taiwan Demography



- **Population: 23.4 million**
- **Area: 36,000 square kilometers**
- **Population Density: 645 persons/ km^2**

Environmental Load Comparison

Year 2014

Area	TW	CN	US	JP	KR	DE	UK	NL	FR
Population Density	645	143	32	337	503	226	263	404	116
Mobile Density	596	20	26	231	203	147	142	-	75
Pig Density	160	48	7	26	99	79	18	295	25
Gas Station Density	0.07	0.01	0.01	0.09	0.13	-	-	-	-

5

Background

- 1980's~1990's
- Farmland Pollution- Cd rice
- Factory Pollution- RCA, CPDC
- Public Health

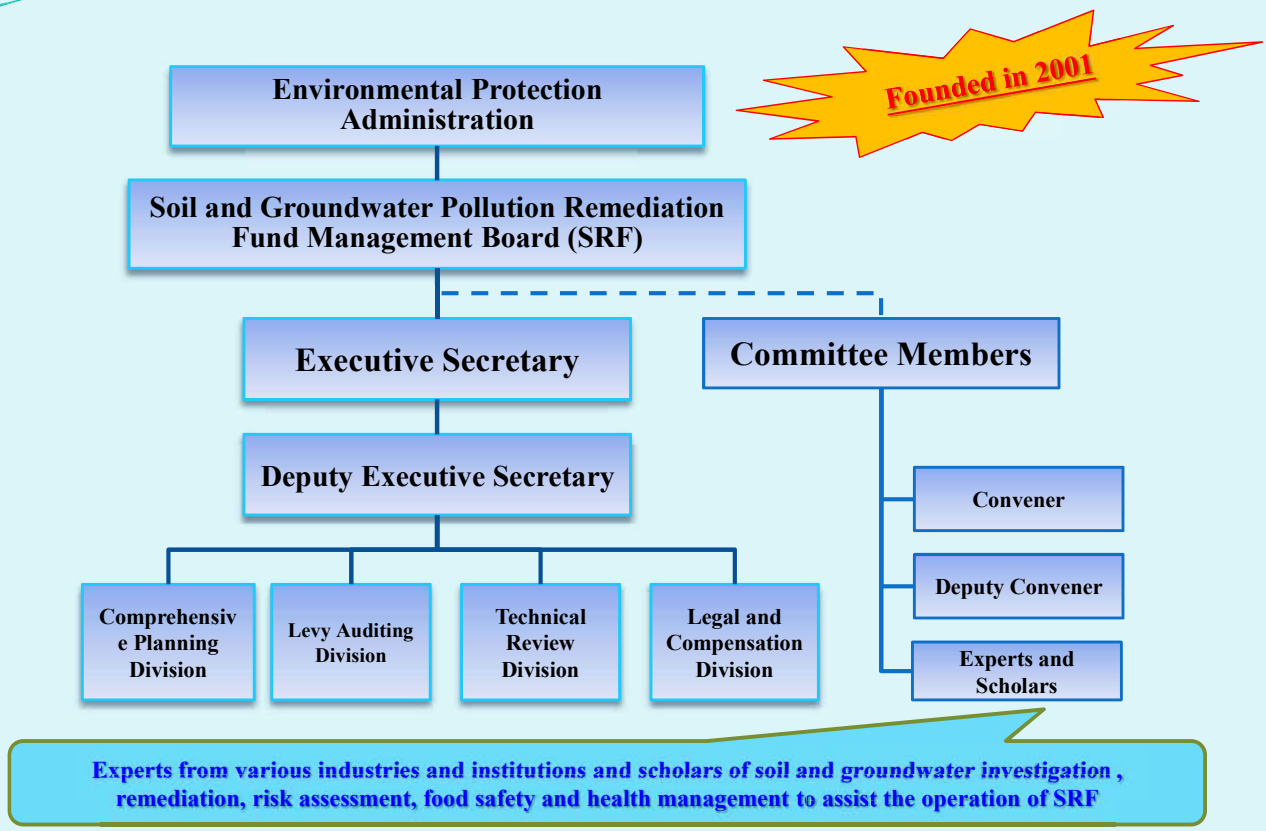
Before 2000

- **Water Pollution Control Act**
- **Groundwater Quality Monitoring**
- **Prohibit Discharge into Groundwater**
- **Soil Treatment Permit**
- **Store Designated Substances Shall Establish Groundwater Pollution Prevention Facilities and Leakage Monitoring Equipments**

SRF History

- Soil and Groundwater Pollution Remediation Fund Management Board (SRF) Established Nov.13, 2001.
- Main tasks are to manage the use of fund & to promote the prevention & remediation of soil & groundwater pollution.

SRF Organiztion Chart



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- **Soil & Groundwater Pollution Remediation Fund**

The Levy of SRF(2/2)

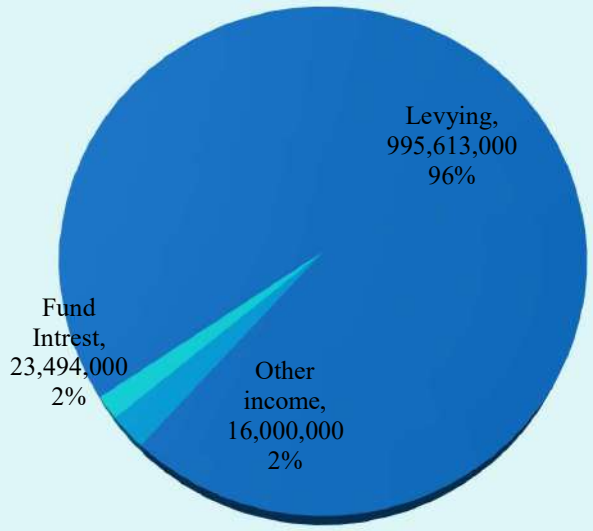
8 Major Sources of SRF

1. Remediation Fee Income
2. Polluter(Related) Compensation
3. Land Developer Compensation
4. Central Government Budget
5. Environmental Protection Related Funds
6. Environmental Pollution Fine

7. Fund Interest

8. Other Related Income

- Income of 2016：**NTD1,035,107,000**

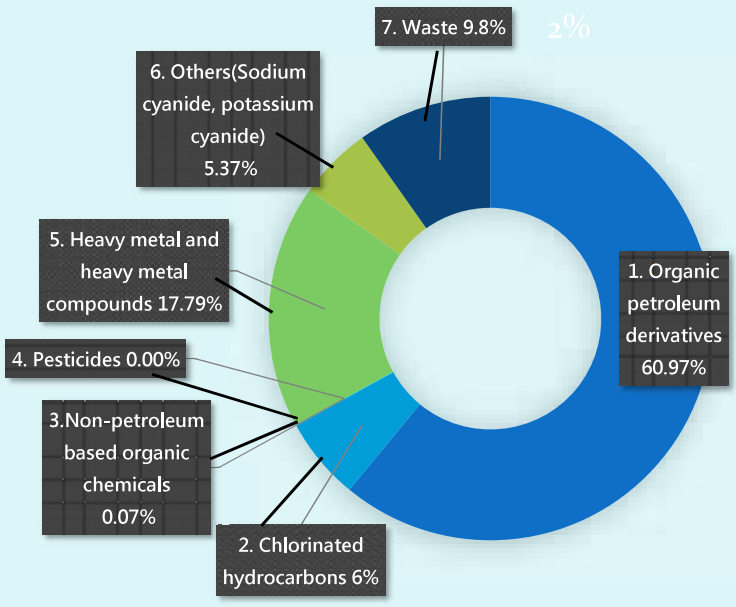


The Levy of SRF(1/2)

Purpose of SRF

1. Prevent and remediate soil and groundwater pollution and remediation fee associated with **unknown polluted sites.**
2. Continuation of promoting the implementation of soil and groundwater **pollution investigation and remediation** and other related issues

Current SRF Levy Ratio



Annual Income and Expense

	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
income	778,115	785,175	642,578	779,510	640,785	656,157	611,546	700,469	1,001,668	909,460	988,632	959,105	1,035,107	1,062,894
expense	276,157	316,488	197,301	206,462	283,074	415,821	529,811	909,227	1,036,667	1,309,257	1,261,845	1,316,581	1,497,597	1,391,213
Cumulative surplus	1,886,260	2,354,947	2,800,224	3,373,272	3,730,983	3,971,319	4,053,055	3,844,296	3,809,298	3,409,500	3,136,287	2,778,812	2,316,322	1,988,003

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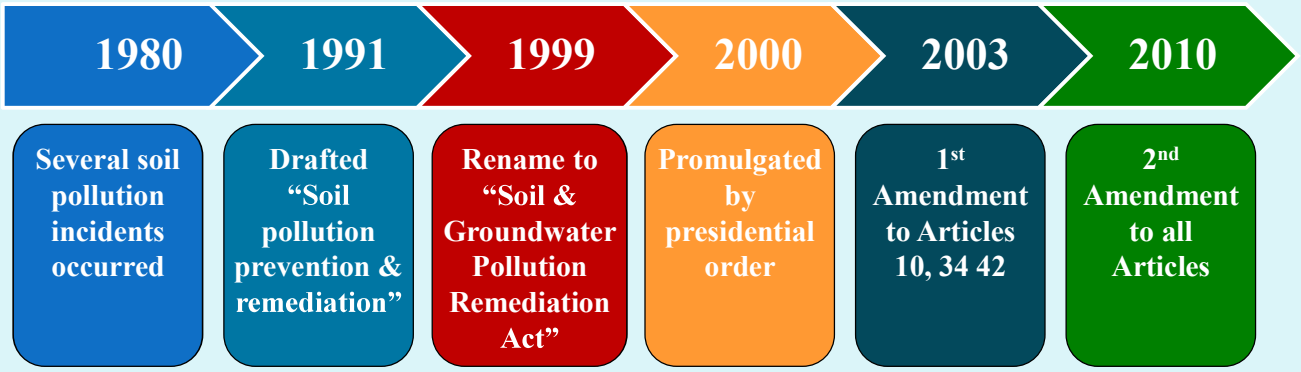
- **Law-Soil & Groundwater Pollution Remediation Act**

Legislative History of SGPRA(1/2)

- Soil and groundwater pollution prevention and remediation
- Enhance polluter and manager responsibility
- Monitoring and control standards
- Land management and monitoring responsibility
- Open information, public participation
- Remediation fund



Legislative History of SGPRA(2/2)

Amendments Summary

- Including sediment into SGPRA management scope
- Adding "Potential Polluter" to the liable entity
- Increasing "Interested Party of the Polluted Land" responsibility
- Appending routine soil and groundwater quality evaluation for high pollution potential area
- Revising contaminated site listing and de-listing methods
- Revising soil pollution investigation regulation regarding announced enterprise
- Making information more transparent and open
- Appending professional engineer certification
- Revising regulation regarding pollution due to natural background
- Improving health risk assessment framework
- Revising pollution remediation fee levy and reimbursement method
- Increasing penalty and responsibility for polluter
- Requiring polluter to pay compensation

Framework of SGPRA(1/2)

Soil and Groundwater Pollution Remediation Act (SGPRA) consists of 8 chapters, 57 articles in total

SGPRA

- General Principles (Ch. 1) → §1~§5: Purpose, terminology, and competent authorities' jurisdiction
- Prevention Measures (Ch. 2) → §6~§11:
  - Sediments quality evaluation
  - Soil and groundwater quality evaluation for designated areas (i.e. industrial parks)
  - Investigation, necessary response measures
  - Assessment of enterprise officially announced by central competent authority
  - Analysis facilities and methods
  - Registered engineer certification
- Investigation and Assessment Measures (Ch. 3) → §12~§14:
  - Declaration of control/remediation sites
  - Necessity for sediment investigation
  - Background contamination
  - Pollution control plan submission
- Regulatory Measures (Ch. 4) → §15~§21:
  - Emergency response measures
  - Publicly announced and management of control/remediation site
  - Entrust registration for prohibition of land transaction

(http://law.moj.gov.tw/Eng/LawClass/LawAll.aspx?PCode=O0110001)

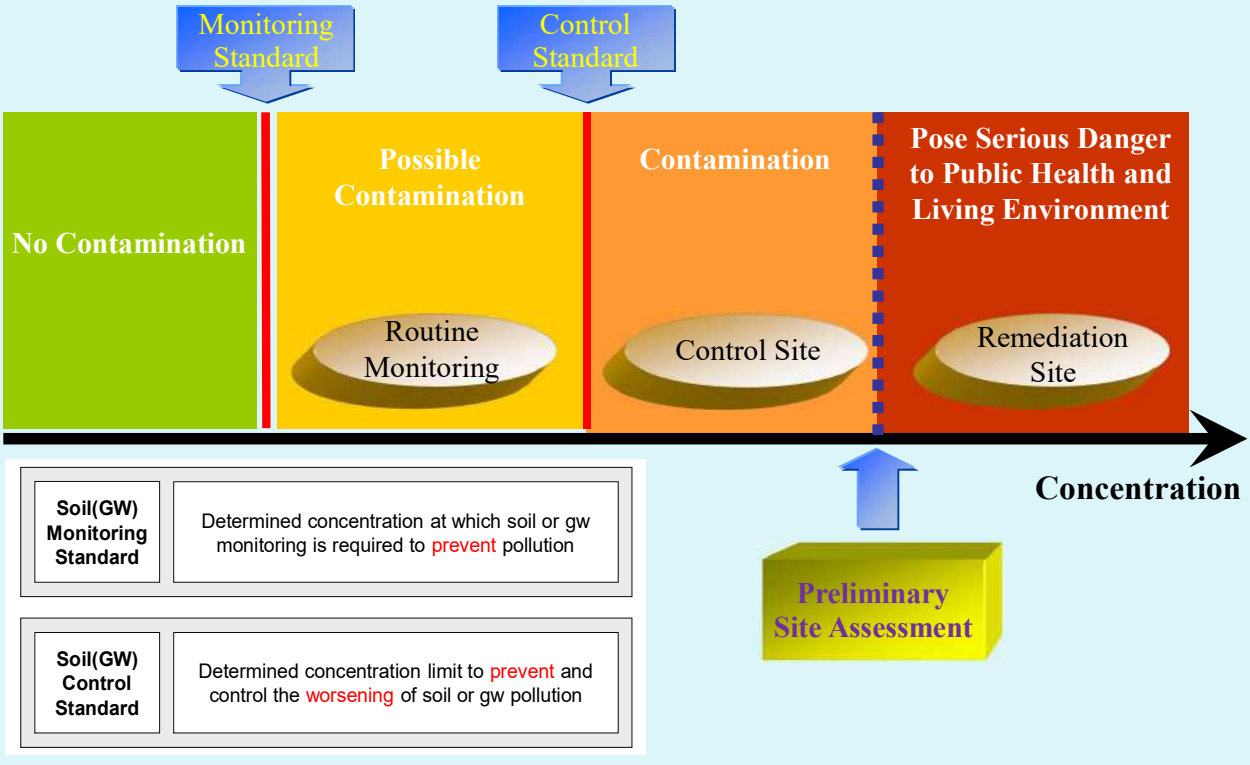
Framework of SGPRA(2/2)

SGPRA

- Remediation and Restoration Measures (Ch. 5) → §22~§27:
  - Remediation plan submission and display
  - Remediation goal determination based on health risk assessment
  - Implementation of control/remediation plan
  - Cancellation of control/remediation site
  - Delineation of groundwater pollution restriction zone if pollution source is unclear
- Financing and Responsibility (Ch. 6) → §28~§31:
  - Levy Soil and Groundwater Pollution Remediation Fund
  - Derivation of fund source
  - Establishment of fund management committee
  - Interested party obligation and responsibility
- Penal Provisions (Ch. 7) → §32~47:
  - Penalties
- Supplementary Provisions (Ch. 8) → §48~57:
  - Joint liabilities for compensation
  - Retroactivity

(http://law.moj.gov.tw/Eng/LawClass/LawAll.aspx?PCode=O0110001)

Determination of Soil & Groundwater Contamination



Definition of Contaminated Site

Pollution Control Site

- Source of pollution has been clearly identified
- Pollutants do not naturally exist in environment but have occurred through:
  - Scouring by rainwater
  - Dispersal
  - Deposition, or
  - Irrigation

  resulting in pollution that exceeds control standards

Pollution Remediation Site

- Pollution control site
- Declared by central competent authority after preliminary assessment indicates the site is likely to seriously endanger public health and the living environment

Definition of Polluter(1/2)

Polluter

A person causing pollution through:

- leaking or discarding of pollutants;
- illegally discharging or injecting pollutants;
- brokering or allowing the leaking, discarding, illegal discharge or injection of pollutants;
- failing to dispose of pollutants pursuant to applicable laws or regulations

Potential Polluter

A person causing pollutants to accumulate in soil or groundwater resulting in pollution due to following:

- discharging, injecting, spreading of pollutants;
- permitting or agreeing to the discharge of wastewater into irrigation and drainage systems or irrigation and water catchment areas

Responsibility -

- Control Site -
  - Investigation, preparing and executing ***pollution control plan***
- Remediation Site -
  - Preparing and executing ***contamination investigation & assessment plan***
  - Preparing and executing ***pollution remediation plan***
- Conducting emergency response measures

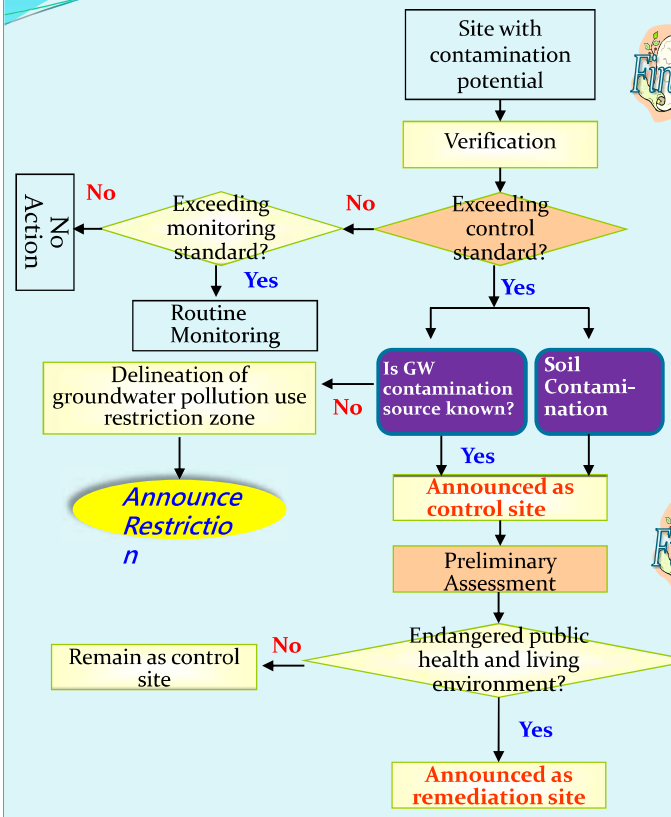
Definition of Polluter(2/2)

Interested Party of the Polluted Land

A person who is not a polluter of the land but is a user, administrator, or owner of the land when the land is declared a pollution remediation site

- Failure to demonstrate due diligence as a good manager:
  - Shall bear joint payment responsibility with polluter and potential polluter
  - Shall be fined when cause land to be publicly declared as control or remediation site

Publicly Declare Procedures and Related Fines



Polluter

- Pay fine if announced as control site or remediation site
- Publicly announce polluter's name and order to receive 4-hr lesson on relevant environmental laws and regulation
- If fail to attend, receive fine per violation until attending

Interested Party of the Polluted Land

Failure to demonstrate due diligence as a good manager:

- Pay fine if announced as control site or remediation site

Land Registration & Prohibition of Land Disposal

- Control Site
  - Enter in land register
- Remediation Site
  - Enter in land register
  - Prohibit land disposal

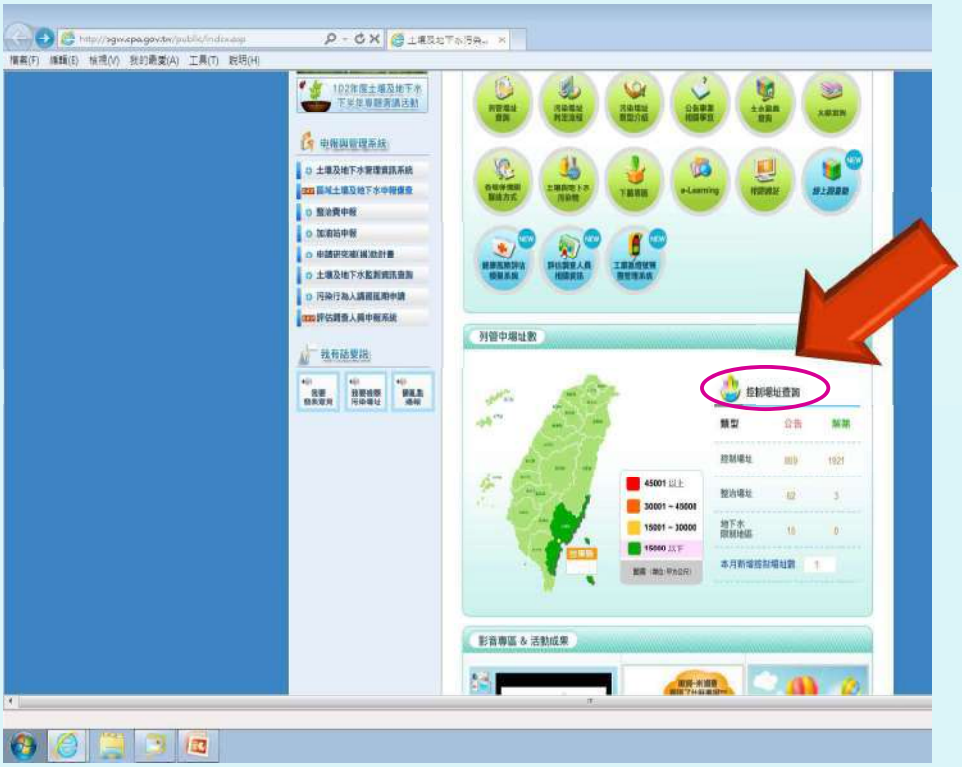
When compulsory auction procedures have been implemented for the land, such procedures may be cancelled

Register Information

- Land Register:
  - Name, personal identification document number, address of the landowner
  - Land markings
  - Date of announcement as a control or remediation site and document number
- Prohibit land disposal:
  - Scope of right
  - Legal basis for prohibition of disposal and background
  - Prohibition of land disposal via transfer, subdivision, or establishment of encumbrance

Searching Contaminated Site List

- **http://sgw.epa.gov.tw/public/Default.aspx**



Delineation of Pollution Control Zone and Other Restrictions

Control or Remediation Site

Competent authority shall delineate and publicly announce soil and groundwater pollution control zones

With the exception of control, remediation or other pollution improvement plans

Prohibited Actions

- Leaving pollutants in soil
- Injecting wastewater and sewage into groundwater
- Discharging wastewater and sewage into soil
- Other control activities officially announced by the competent authority

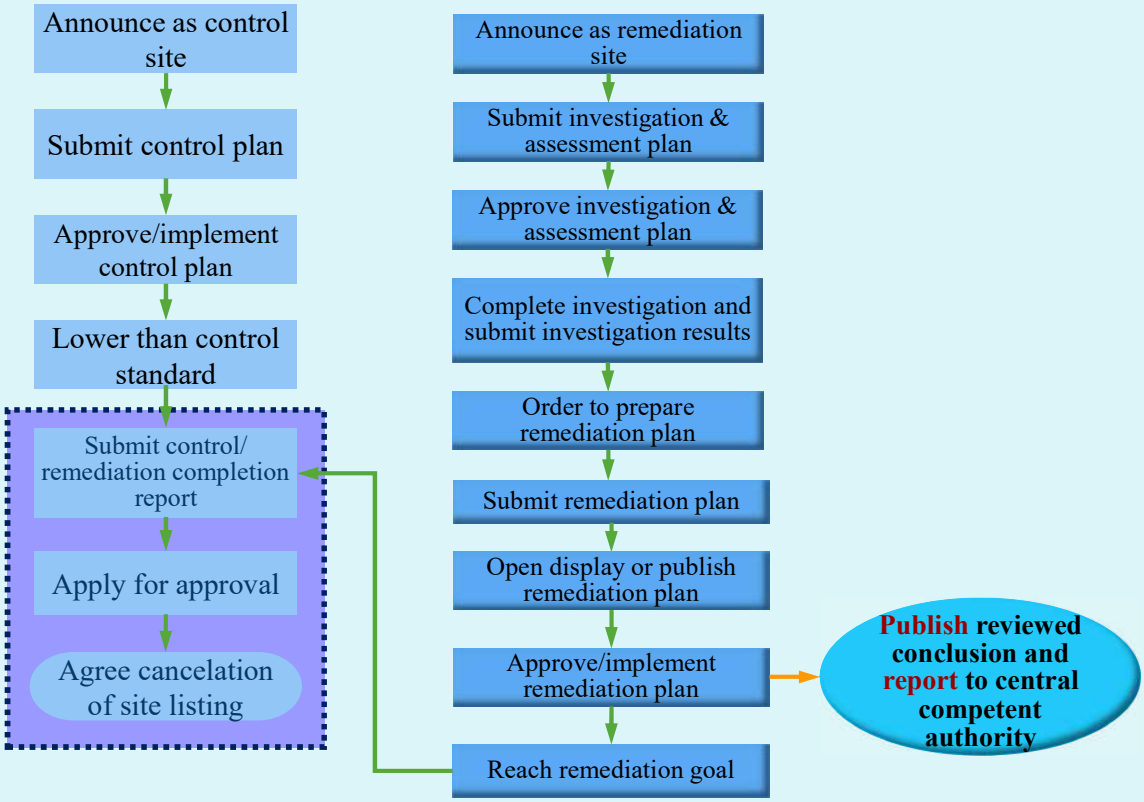
Soil pollution control area

Unless receive approval from central competent authority

Prohibited Land Use Activities

- Development prescribed in the Environmental Impact Assessment Act
- New construction, extension, alteration, renovation, or demolition not required for remediation actions
- Other land use activities that might affect the health and living environment of residents

Execution of Control and Remediation Plan



Registered Professional Engineer Certification

Certified Documents:

- **Pollution Control Plan**
- **Pollution Remediation Plan**
- **Assessment Investigation Data**
- **Pollution Investigation and Assessment Plan**

Certified Engineer:

- **Environmental engineer, applied geological engineer** or other relevant professional engineer

Announced Enterprises

Article 8

Land Transfer

- If land used by announced enterprise is transferred, the assignor shall provide and report soil pollution assessment data to competent authority for future reference

Announced Enterprise –

- Officially announced by central competent authority
- 30 industrial categories

Article 9

Business establishment, change or termination

- When following situations applies, announced enterprise shall submit soil pollution assessment data for review:
  - Enterprise establishment, registration, or application for a business license
  - Change of business operator
  - Change of industry category.
  - Change of scope of operating site.
  - Termination of business, cancellation of operating permit or business license, termination of operation, facility closure, or discontinuation of production, manufacturing, or processing

Pollution Remediation Fee Disbursement

- Expenditures made by competent authorities at all levels for contaminated site management related task
- Compensation and legal expenses
- Personnel and administrative management expenses
- Expense of pollution control work
- Expense of auditing pollution verification, quality monitoring and associated implementation effectiveness
- Expense of international environmental protection work
- Expense of levying soil and groundwater pollution remediation fees
- Expense of health risk assessment and management
- Expense of researching, promoting, developing, and creating incentives for remediation technology
- Subsidiaries for pollution prevention work
- Other costs related to remediation approved by central competent authority

Sediment – Regular Monitoring

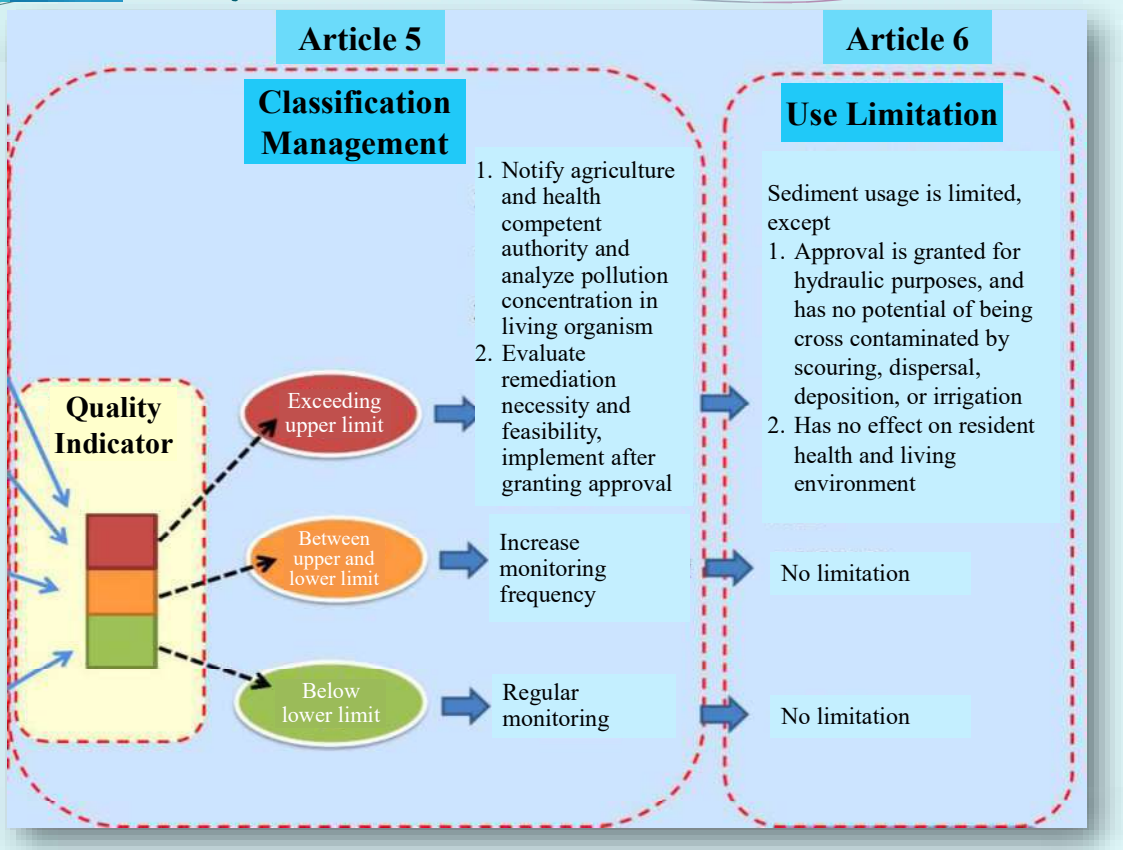
- **The industry competent authorities** in charge of the following water bodies shall regularly test sediment quality, and **submit** the data for future reference

Regular Monitoring

- **Rivers**
- **Irrigation canals**
- **Lakes**
- **Reservoirs**
- **Other surface water bodies specially designated by central competent authority**

The central competent authority shall determine classified management and use restrictions based on sediment quality indicators

Sediment–Classification Management and Use Limitation Regulation of Sediment Quality Indicator



Sediment - Control

If pollutants in living organisms in surface water body is discovered to be high

Sediment within the area of control/remediation site is suspected of being polluted

Notify special municipality, county, or city competent authority

Applicable

- Shall test sediment, and perform assessment on the basis of environmental impact, health risk, technology, and economic benefits
- If central competent authority feels remediation is necessary and feasible, a remediation plan must be drafted and submitted for approval

Note

Sediment remediation should be included in control or remediation plan

Brownfield Development

Remediation Goal

- Central competent authority may approve **remediation goals**
- **Land development may not be changed** after approval of the remediation goals
- Any development changes may be implemented only after obtaining approval from central competent authority

Land Development Plan

- Land development plan may be submitted concurrently with remediation plan, and shall reviewed in accordance with relevant laws and regulations
- Implementation of the land development plan only can proceed after the **cancellation of regulatory listing**

Fee

- Before brownfield development, land developer shall pay 30% of present land value into Soil and Groundwater Pollution Remediation Fund
- If land developer submitted and completed remediation plan prior to competent authority submitted a remediation plan, this case shall not be subjected to this restriction

- **Measures of SRF**

The Goals of SRF

1. **Security of Soil & Groundwater Quality**
2. **Promotion of remediation & restoration**
3. **Sustainable operation of Fund**

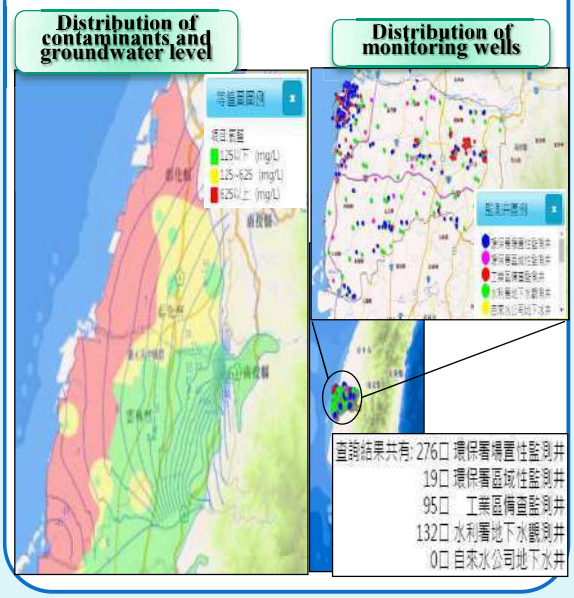
Performance Indicators

- **restoration of soil & groundwater contaminated sites**
- **450 accumulated contaminated sites** removed from control

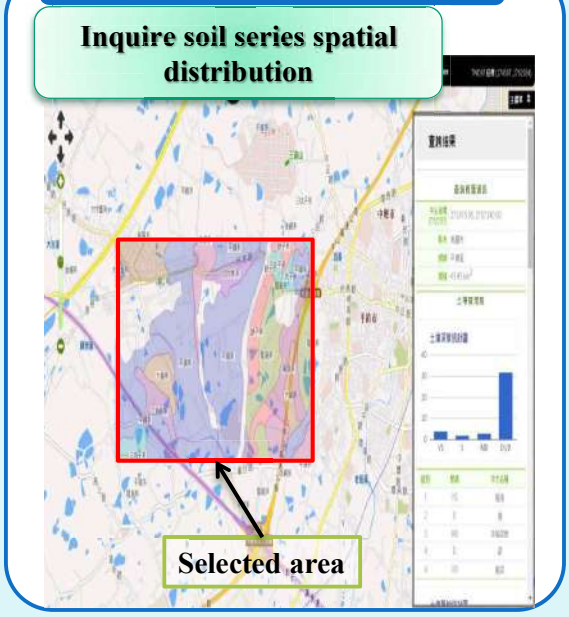
Establishing Quality Database

- **Establish the groundwater monitoring & soil quality database**

Groundwater

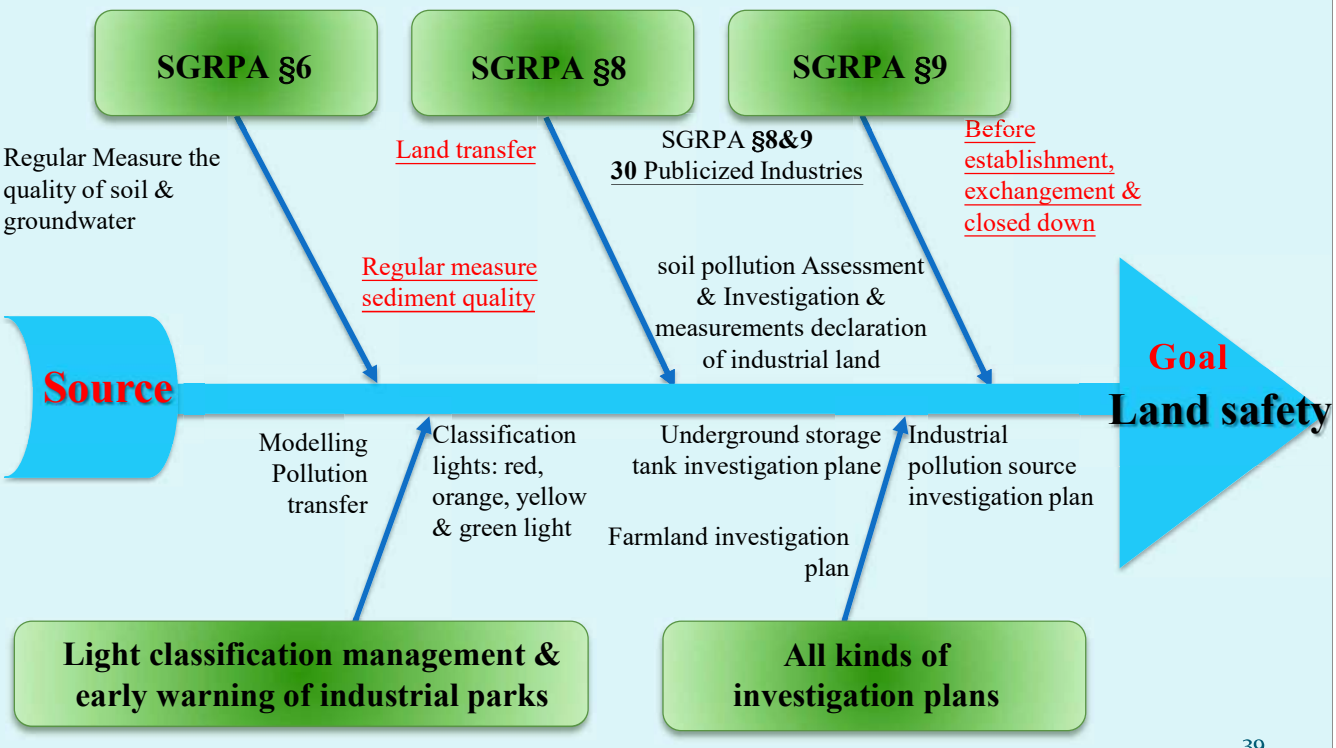


Soil



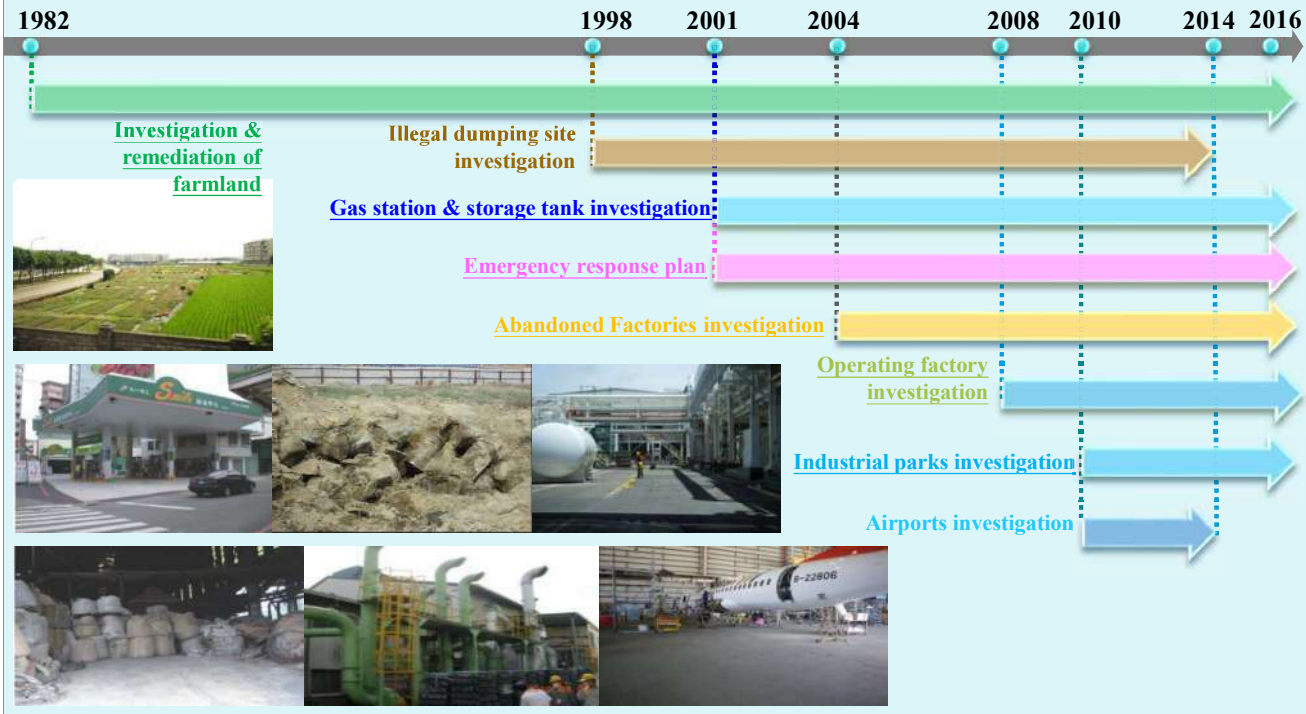
Prevention(1/2)

- mechanism to prevent pollution-protect the safety of land & resources



Prevention(2/2)

- High potential pollution site investigation



Site Management

- Specifically investigate severely polluted site.
- Develop local pollution prevention, investigation and remediation guides (11 types)
- Create Local Soil and Groundwater Database
- Create Pollution Risk Map of Taiwan

Site Management Procedure

Prevention Mechanism
↓
Pollution Investigation
↓
Risk Assessment
↓
Remediation
↓
Brownfield Reuse

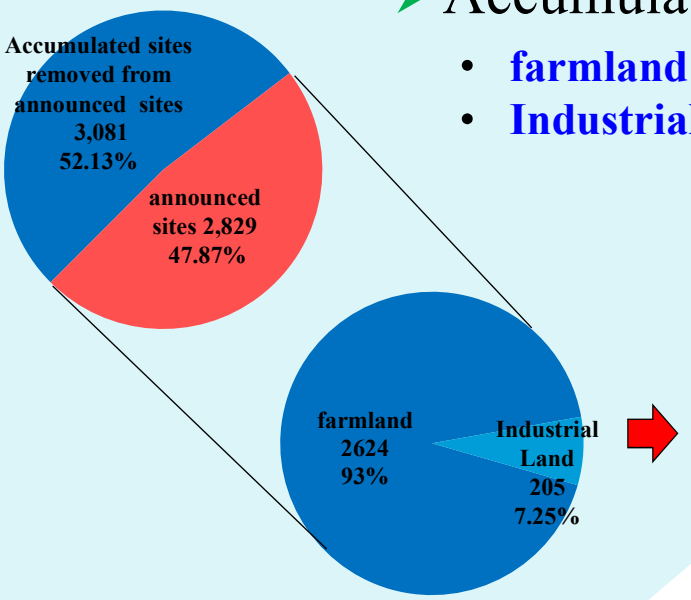
Responsibility Identification

SRF Management Strategy Objectives

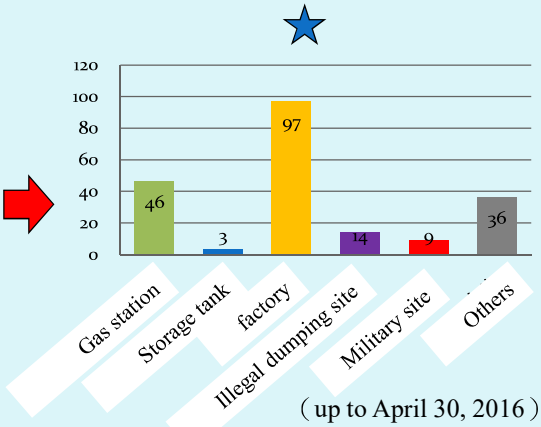
1. Research and Establish the Claims Responsibility Identification System
2. Establish The best mode of operation of the Fund in order to expand the income of the Fund

Remediation (1/2)

- Remediation of contaminated sites-types of announced sites



- Accumulated site:5,910
  - farmland：5,558
  - Industrial Land：352

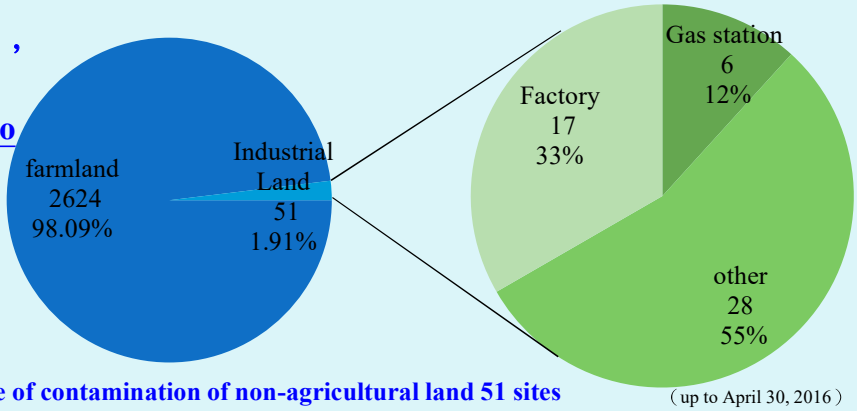


(up to April 30, 2016)

Remediation(2/2)

- Remediation of contaminated sites-promote orphant site to remediate

- **farmland site 2,624，budgeted NTD688 million from 2016 to 2019 to accelerate remediation**



- **Sequenced by the degree of contamination of non-agricultural land 51 sites**

（up to April 30, 2016）

County	Site name	Degree of contamination	Area
臺南市	永康區鹽行段1418等36筆地號土地	7539	41, 145
臺南市	臺南市安定區安定段等7筆地號	3779	12, 810
苗栗縣	苗栗縣頭份鎮永貞段887地號	3620	20, 181
台中市	大里區光正路地下水污染案	2066	50, 647
高雄市	高雄市大寮區福德爺廟場址	1455	77, 277
⋮	⋮	⋮	⋮
⋮	⋮	⋮	⋮

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Technology Development

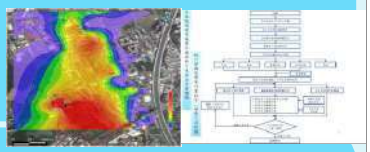
Investigative techniques

- Biological rapid detection in persistent & emerging contaminants
- Geophysical exploration & green technologies to assist the promotion of investigation quality

Tree core sampling　Geophysical exploration

Forensics techniques

- Develop environmental forensics techniques of chlorinated pollution, compile investigation & Forensic Evidence the guideline
- Develop & set up the forensics techniques of oil spill polluter to clarify pollution liability through science evidences



Technological development

- Import green sustainable remediation technology
- Develop multivariate farmland remediation techniques
- Compile oil & chlorinated pollutions of the guidelines

in-situ farmland washing techniques

- Develop risk management combined with human healthy & ecological risk assessment
- Complete nationwide parameter database

Remediation techniques

Risk assement techniques

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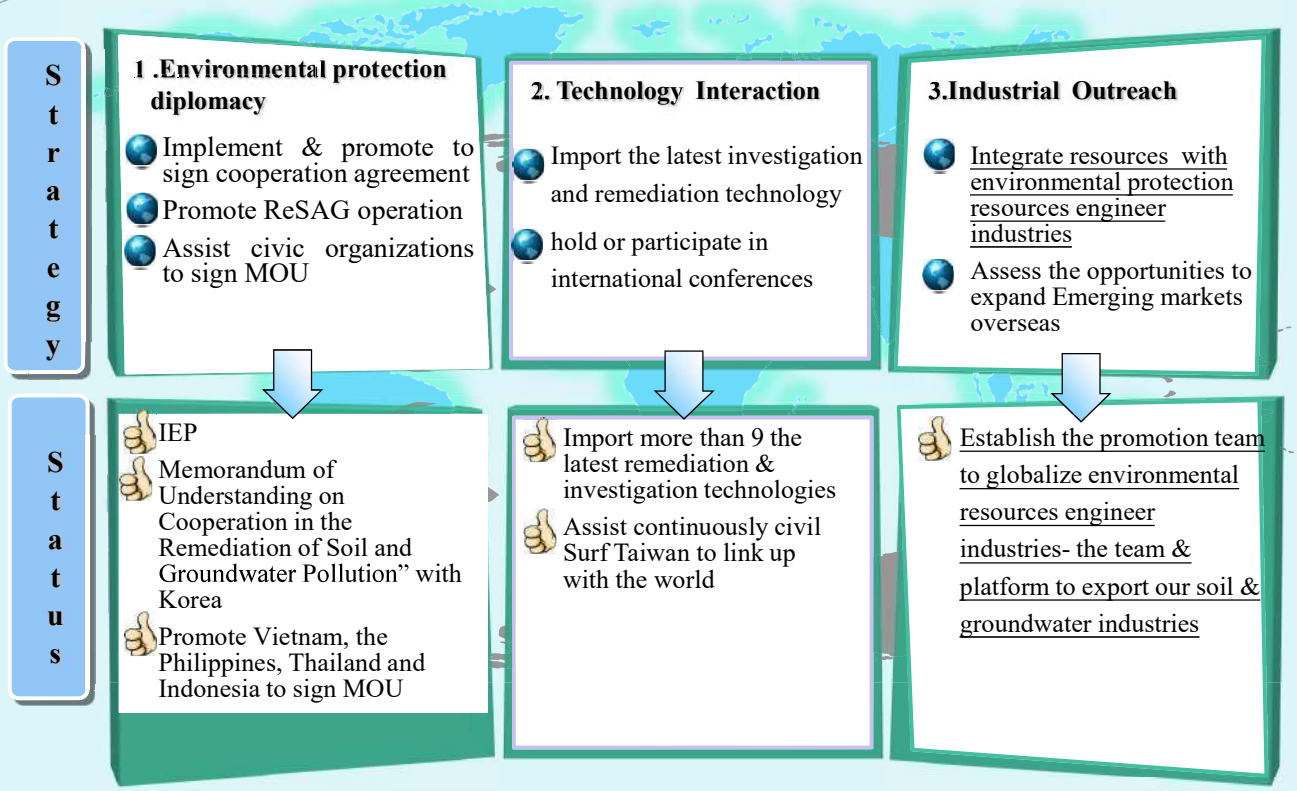
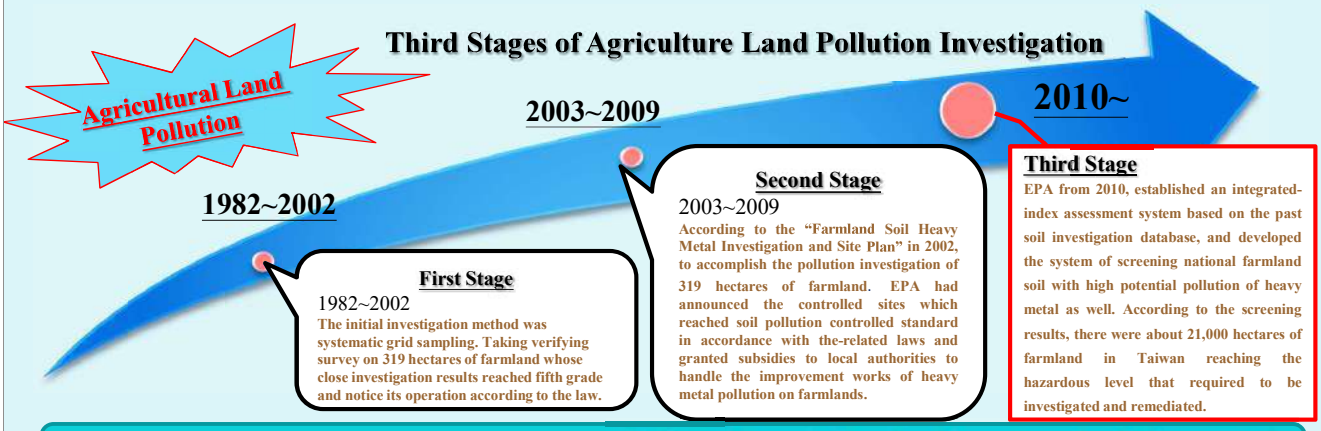
International Cooperation



- **Accomplishments**

Farmland Pollution



Agriculture Land Investigation Project in 2010：Nation-wide agriculture land heavy metal pollution control and investigation project.

- Create **agriculture land potential heavy metal pollution screening mechanism**, evaluate the connection between **polluted irrigation route** and **polluted agriculture land** and effective administrative management strategy
- Up to August 31 2016, there were **565 hectares of polluted farmlands which had been improved**, and therefore had been removed from the controlled list according to the law, so now farmland with soil control is 385 hectares.

Gas Station Pollution

◆ **Starting from 2001, approximately 2,600 gas stations and 10,400 large storage tanks have been investigated for potential soil and groundwater pollution. The extent of gas station pollution in Taiwan has been fully understood with 266 gas stations listed as control polluted sites and 168 gas stations have been de-listed.**

Phases	Year	Names of Gas Station Pollution Investigation Projects
Phase I	2001	Groundwater Potential Pollution Source Investigation Project
Phase II	2002~2003	Nation-Wide Gas Stations and Large Storage Tanks (Operated for more than 10 years) Pollution Source Investigation Project
	2003~2004	Gas Stations in Central-North Region(Operated for less than 10 years) Potential Pollution Source Investigation Project
Phase III	2006~2007	Gas Stations Operated for Less Than 10 Years Soil and Groundwater Pollution Investigation Project
Phase IV	2007~2009	Gas Station Soil and Groundwater Pollution Investigation Project (Phase IV)
Phase V	2009~2010	Gas Station Soil and Groundwater Pollution Investigation Project (Phase V)
Phase VI	2010~2011	Gas Station Soil and Groundwater Pollution Investigation Project (Phase VI)
Phase VII	2012~2013	Gas Station Soil and Groundwater Pollution Investigation Project (Phase VII)
Phase VIII	2014~2015	The inspection, consultation and auditing of declaration reports for underground storage tanks project
Phase IX	2015~2016	The inspection, consultation and auditing of declaration reports for underground storage tanks project (Phase II)

Abandoned Factories Pollution

- "Nationwide Abandoned Factory Pollution Investigation Project" started in 2004
- Approximately 120 thousand abandoned factories in Taiwan. Investigated 42 thousand abandoned factories with emphasis on 30 major industries that have the highest pollution potential.
- By the end of 2015, 102 sites were identified as controlled sites and 71 sites have been de-listed

- Completed the creation of Nationwide Abandoned Factory Geographic Information System Database.
- Completed data check and correction for 42,000 representative sites.
- Completed soil and groundwater pollution investigation work for 175 sites.

- Completed environmental site assessment for more than 2,200 sites.
- Soil Remediation Fund (SRF) projected to to exceed 4 billion NTD.
- Research and establish technical specification for the investigation of 30 major industries that have the highest pollution potential.

- Research and establish factory closure self-check operation guideline.
- Establish the risk system platform and risk map of abandoned factories in Taiwan
- Gain 3 patents from Intellectual Property Office Ministry of Economic Affairs, R. O. C.

Quality Management for Industrial Parks

The 4-year action program of soil and groundwater quality management for the industrial parks had been promoted since 2011; at the present, the scope is broadened to industrial land and the work is still going on.

Establishing a light classification system of early warning and management

- The monitoring information of 144 designated industrial parks was integrated.
- The status and the measures of administrative control of each industrial park is announced on a regular time schedule.

Conducting background survey, early warning monitoring, pollution investigation and verification

- The monitoring resources was coordinated and allocated through consultation and the soil & groundwater qualities of high potential polluted industrial parks were investigated.

Inter-agency collaboration of & pollution reporting and response mechanism

- 74 meetings were held among environmental protection and industrial competent authorities and the standard operating procedure when dealing with abnormal monitoring incidents was also formulated.

Management

Groundwater monitoring well management of 2015

- Conduct periodic groundwater quality monitoring to understand nationwide background water quality distribution.
- Installed 7 and 12 wells in Keelung city and Nantou county to ensure full coverage of the monitoring system (currently 453 regional monitoring wells).
- Modify monitoring frequencies by analyzing water quality trend and propose management plans for specific groundwater quality issues

Potential Groundwater quality distribution of Taiwan

Vision and objectives of groundwater management

- Control groundwater quality, protect the health of citizens, ensure sustainable usage of resources.

Display monitoring information

Management of contaminated sites

Groundwater - Management & Regulations Amendment

Regulations amendment

- 10 groundwater contamination control standards were regulated in 2013
- Pb, TPH_d, total phenol were amended in 2013
- Applicable scope of In and Mo were amended in 2013
- Amendment of the flowchart on "Discrimination of groundwater Arsenic concentration distribution and sources"

Potential contamination investigation

- Investigation of six POPs related industries
- Investigation of groundwater POPs distribution

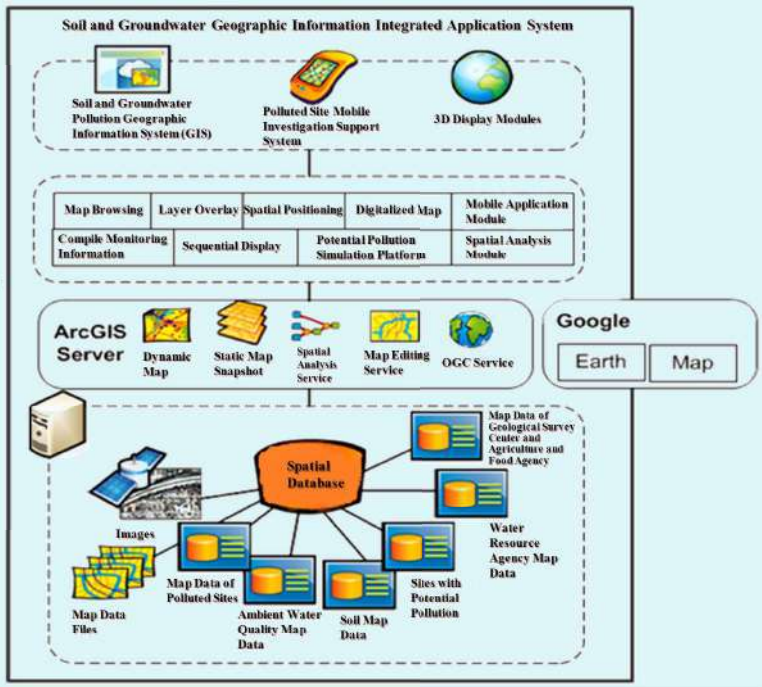
Contaminate Candidate list (CCLs)

- Establishment of CCLs and screening rules
- Proposal of PCCLs and CCLs in Taiwan

Examine and renew the groundwater PCCLs, select the priority groundwater contaminants and the related regulations amendment

Development of Information System

✓ **Polluted Land Management and Policy Support System**



Risk Assessment & Management(1/2)

Risk Assessment and Management

The concept of health risk was incorporated during the process of drafting SGPRA, which can use science to evaluate risk level, citizens' health and environmental impact, moreover to conduct contaminated site management.

2005	2008	2011
Establish health risk assessment framework, protocols and other related tools	Strengthen risk assessment protocol, reviewing process and establishing parameters database	

- Complete **health risk assessment protocol** and **report drafting guidelines**
- Building **online health risk assessment program**
- Establish **local parameter database** in order to localize health risk assessment system
- Establish risk communication and public involvement mechanism

Risk Assessment & Management(2/2)

2011 — Establish risk assessment system and complete comprehensive regulations and guidelines

2014 2015 — Establish ecological risk assessment protocol and promoting risk analysis application

- Complete preliminary assessment and priority ranking regulations for contaminated sites
- Declare/revise comprehensive regulations and guidelines with regards to risk assessment system
- Complete online "Risk Assessment System V2.0" and "Preliminary Assessment System"
- Complete ecological risk assessment framework and protocol (draft)

Risk Assessment System V2.0

Preliminary Assessment System

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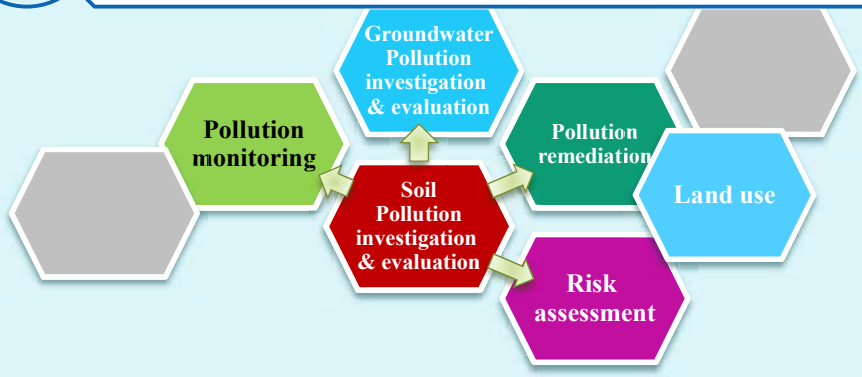
• Conclusion

Conclusion

- Continuously promote policy of soil and groundwater pollution prevention, investigation & remediation
- Apply risk assessment tools & develop multiple management mechanisms with social consensus to speed up contaminated land activation
- Properly plan and manage the fund incomes and expenses to ensure sustainable operation



- **Appendix**

Phases of A Polluted Site

- Environmental Background Monitoring
- Polluted Site Investigation
- Polluted Site Declaration
- Pollution Remediation
- Site Monitoring

Site Investigation

Authority	Investigation Items	Compared Standards
◆ Environmental Agency ◆ Agriculture Agency ◆ Health Agency ◆ Industrial Agency	◆ Soil ◆ Groundwater ◆ Sediment ◆ Crops ◆ Aquatic Products	◆ Soil/ Groundwater Monitory Standards ◆ Soil/ Groundwater control Standards ◆ Sedimentation Quality Indicators ◆ Edible Crop Heavy Metal Limitation Standards

Declare Polluted Site

	Control Site	Remediation Site	Land Register	Remove Corps
Authority	Local Authority	Central Authority	Land Agency	Agriculture Agency
Condition	Exceed Control Standards	Severely Endangers Public Health/ Living Environment	Control Site Remediation Site	
Action	Declare Control Site	Declare Remediation Site	Land Register	Remove Crops
Prohibition	Construct Buildings Use Groundwater Growing Edible Crops, Raising Livestock Harvesting Marine Animals and Plants	Land Buying and Selling		

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Pollution Remediation

	Control Site	Remediation Site
● **Polluter** ● **Person Potentially Responsible for Pollution** ● **Interested Party of the Polluted Land**	● Complete Investigation ● Submit Pollution Control Plan ● Implement Pollution Improvement	● Implement Investigation and Assessment Plan ● Submit Remediation Plan ● Implement Pollution Improvement
Authority	Adopt Suitable Improvement Measures	● Investigate Pollution Range ● Determined Cleanup Priority Ranking Grade ● Submit Remediation Plan

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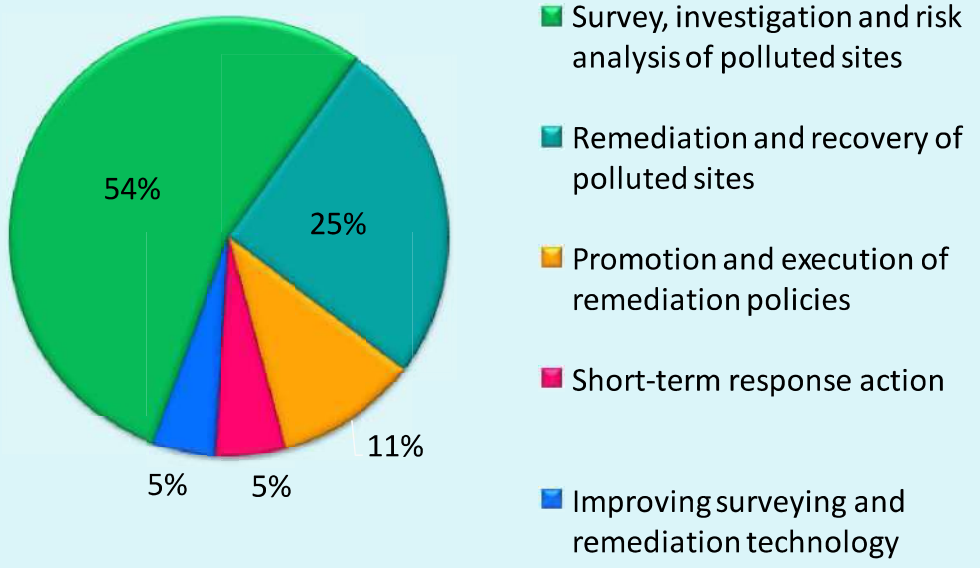
Site Monitoring

- **Exceed Monitoring Standards Lower Than Control Standards**
- **Ensure Remediation Complete**
- **Polluter, Person Potentially Responsible for Pollution, Interested Party of the Polluted Land Shall Have the Responsibility**
- **Monitor Twice a Year**

Expenditure of Remediation Fund

- The expenditure of the remediation fund is US$30.3 million/year as of 2011.



Thank You for Your Attention

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Application of Molecular Biology Tools for Bioremediation – An Introduction

- Liang-Ming Whang
- Department of Environmental Engineering
- National Cheng Kung University

Outline

- Introduction of Bioremediation
  - What is Bioremediation?
  - Why Bioremediation works?
  - Contaminants amenable to Bioremediation
  - Limiting factors (why bioremediation doesn't work?)
  - Engineering strategies for Bioremediation
- Molecular Biology Tools for Bioremediation
  - Fundamentals
  - Techniques
  - Applications
- Case Study

What is Bioremediation?

- "use of living organisms (e.g., bacteria, archaea, fungi) to clean up oil spills or remove other pollutants from soil, water, and wastewater." (*United States EPA)*
- "clean-up of pollution from soil, groundwater, surface water and air, using biological, usually microbiological processes" (*Philp et al., 2001)*
- It is a managed or spontaneous process in which biological, especially microbiological, catalysis acts on pollutants, thereby remedying or eliminating environmental contamination present in water, wastewater, sludge, soil, aquifer material, or gas streams. (a.k.a. biorestoration). Bioremediation relies largely on the enzymatic activities of living organisms, usually microbes, to catalyze the destruction of pollutants or their transformation to less harmful forms.

Why Use Bioremediation?

- Can be cheaper (at least 10x less expensive than removal & incineration, or pump and treat, cost of treating contaminated soil in place $80-$100 per ton, cost of excavating and trucking contaminated soil off for incineration is $400 per ton)
- Done on site, eliminates transportation cost & liability, minimum land and environmental disturbance (e.g., generation of lesser volume of remediation wastes)
- Environmentally sound (natural pathways), can attack hard-to-withdraw hydrophobic pollutants (Over 90% of the chemical substances classified as hazardous today can be biodegraded)
- Does not dewater the aquifer

Common Soil and Subsurface Contaminants

- **Gasoline**: Benzene and related fuel components (BTEX)
- **Total Petroleum Hydrocarbon (TPH)**: Diesel, fuel oil, Pyrene and other aliphatic and polycyclic aromatic hydrocarbons (PAHs)
- aliphatic and aromatic chlorinated solvents
- Herbicides and pesticides
- Nitroaromatic explosives and plasticizers

Contaminants amenable to Bioremediation I

- Hydrocarbons:
  - BTEX (aerobic and anaerobic biodegradation)
  - PAH (less amenable)
    - aerobic degradation via cometabolism
    - anaerobic biodegradation (naphtalene-denitrification)
- Chlorinated Aliphatic Hydrocarbons
  - aerobic electron donor (DCM, CM, DCA)
  - anaerobic electron donor (TCE, DCE)
  - anaerobic acceptor (PCE, TCE)- dehalorespiration
  - cometabolism (aerobic, anaerobic-reductive dechlorination)
- Chlorinated aromatic hydrocarbons
  - PCB (in general bioremediation recalcitrant)
    - -aerobic, less chlorinated
    - -anaerobic (dehalorespiration)
  - PCP; aerobic, anaerobic (groundwater-reductive dechlorination)
  - Dioxins; highly resistant to Bioremediation

Contaminants amenable to Bioremediation II

- **Pesticides**
  - -chlorinated; highly resistant to aerobic transformation
  - -phosphorus based and carbamate; quickly hydrolyzed
  - -triazine; biodegradable
- **Explosives**
  - -biotransformation is partial (TNT) or slow (RDX)
- **Inorganics**
  - -bacterial reduction of Hg^{2+} to Hg^{0}
  - -bacterial reduction of Cr^{6+} to Cr^{3+}

Contaminants Potentially Amenable to Bioremediation

Readily degradable	Somewhat degradable	Difficult to degrade	Generally recalcitrant
fuel oils, gasoline	creosote, coal tars	chlorinated solvents (TCE)	dioxins
ketones and alcohols	pentachloro-phenol (PCP)	some pesticides and herbicides	polychlorinated biphenyls (PCB)
monocyclic aromatics			
bicyclic aromatics (naphthalene)			

Why Bioremediation works?

- **direct metabolism** - microorganisms **obtain energy for growth by degrading organic contaminants** in an enzyme-mediated process

-aerobic biodegradation of BTEX in the presence of an oxygenase *(Pseudomonas)*

- **cometabolism**- some **enzymes are not very specific** and in addition to the growth substrate **transform other compounds**

-oxygenases are not very substrate-specific and can also degrade TCE (however TCE cannot be used as a growth substrate)

Factors that limit the potential for Bioremediation (why Bioremediation doesn't work)

1) Contaminant-related limitations:

- **Synthetic vs. natural contaminants**
  -bioremediation potential greater for natural compounds

- **Physical characteristics**
  -density, Henry's constant, solubility, octanol/water partition coefficient

- **Molecular structure of the contaminant**
  -extent of **chlorination**, **linear** vs. **branched** structure, **saturated** vs. **unsaturated** compounds

Factors that limit the potential for Bioremediation (why Bioremediation doesn't work)

2) Environmental conditions:

- **Hydrogeology**: permeability/hydraulic conductivity, heterogeneity, fracture bed rocks, soil properties, pH
- **Nutrients**: C:N:P-100:10:1
- **Electron acceptor**: oxygen (3 parts of oxygen to converts 1 part of hydrocarbon to CO_2), nitrate, sulfate, ferric iron

3) Microorganisms presence:

- Assessment of microbial activity, introduced microorganisms

Requirements for Biodegradation

1. Existence of organism(s) with required catabolic potential.

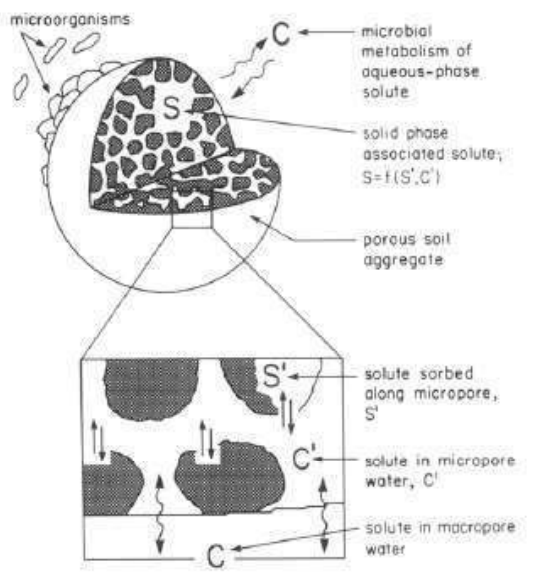
Xenobiotic will be degraded to an appreciable extent only if the organism has enzymes that catalyze its conversion to a product that is an intermediate or a substrate for common metabolic pathways. The greater the differences in structure between the xenobiotic and the constituents of living organisms (or the less common the xenobiotic building blocks are in living matter), the less likelihood of extensive transformation or the slower the transformation.

2. Presence of organism(s) in the environment.

Requirements for Biodegradation (cont)

3. Compound must be accessible to organism (bioavailability):

- The **bioavailability** is controlled by solubilization from a **non-aqueous-phase liquid** into the **aqueous soil water phase**.
- Bioavailability of oil components in contaminated soils is **important** in **regulating biodegradation rates**.



(Wu and Gschwend, 1986)

Requirements for Biodegradation (cont)

4. If catabolic enzymes involved are not constitutive, they must be induced

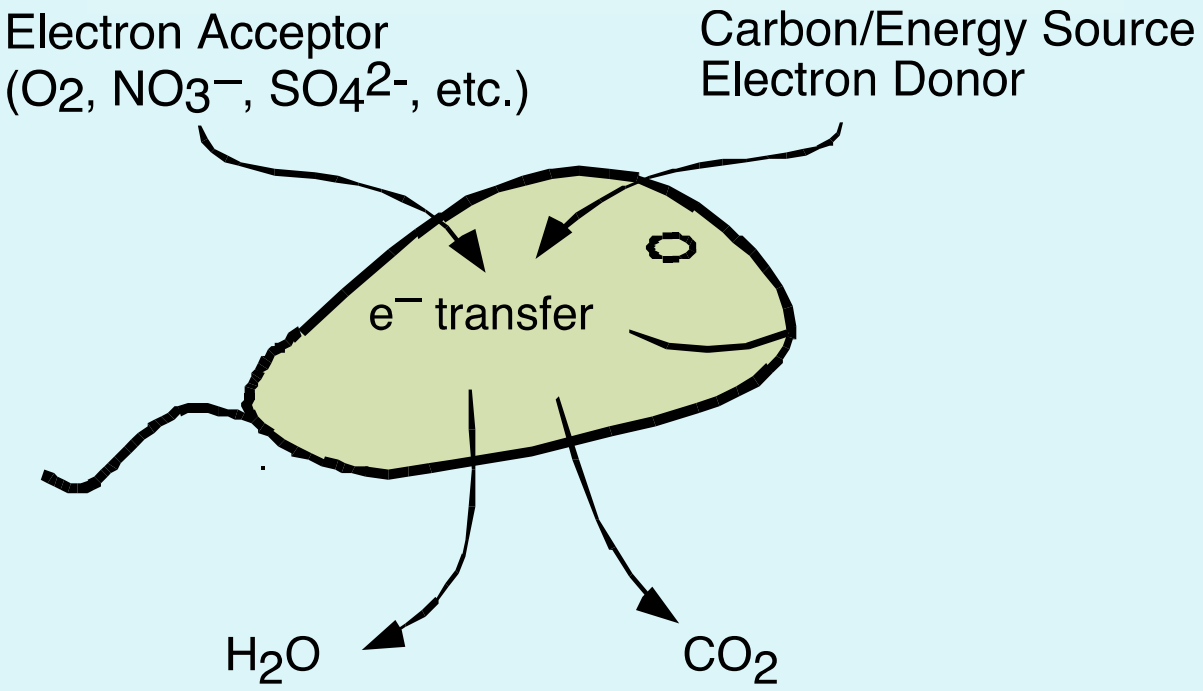
5. Environment favorable to growth of desirable phenotypes and functioning of their enzymes:

a) *Presence of "recognizable" substrate(s) that can serve as energy and carbon source(s) (e.g., the BTEX) and limiting nutrients (N and P, trace metals, etc.).*

b) *Moisture (80% of soil field capacity, or 15% H_2O on a weight basis, is optimum for vadose zone remediation. Need at least 40% of field capacity).*

c) *Availability of e^- acceptors (e.g., O_2 for oxidative reactions) or e^- donors (e.g., H_2 for reductive transformations). The e^- acceptor establishes metabolism mode and specific reactions.*

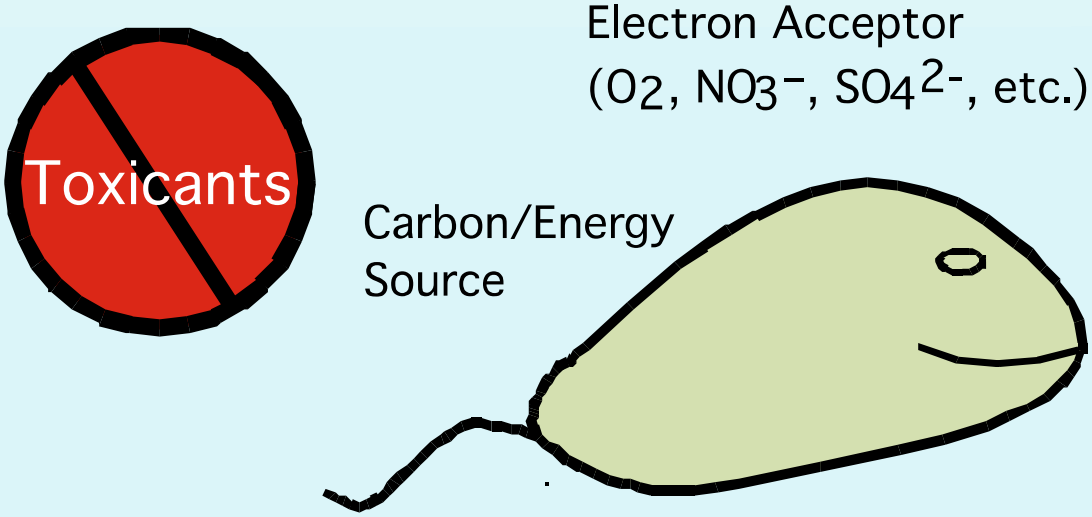
Biological Oxidation/Reduction Reaction Electron Transfer



How Microbes Use the Contaminants

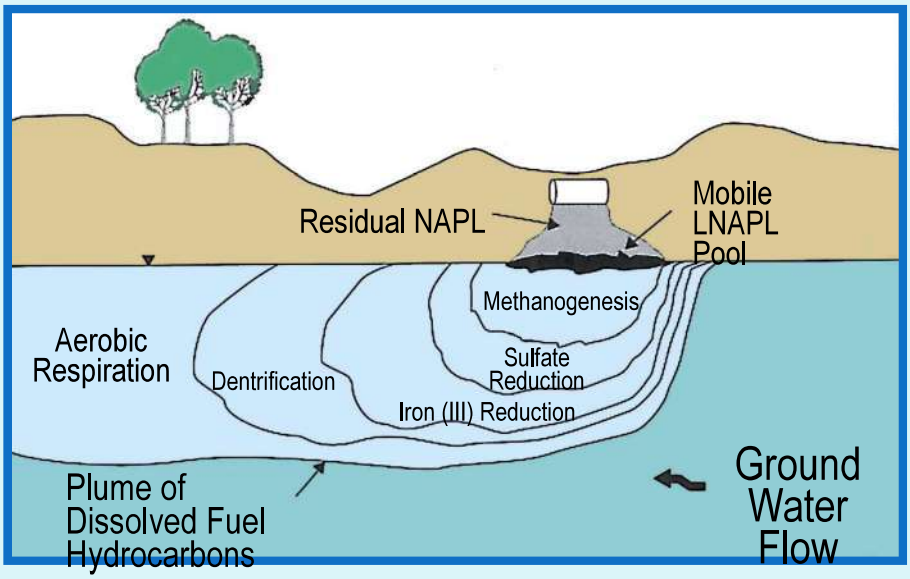
- **Contaminants may serve as:**
  - **Primary substrate**
    - enough available to be the sole energy source
  - **Secondary substrate**
    - provides energy, not available in high enough concentration
  - **Cometabolic substrate**
    - fortuitous transformation of a compound by a microbe relying on some other primary substrate

Requirements for Microbial Growth



Electron Acceptor Zones

In aquifers, electron acceptors are used in sequence. Those of higher oxidation potential are used preferentially: $O_2 > NO_3^- > Mn^{+4} > Fe^{+3} > SO_4^{-2} > CO_2$



Electron Acceptor Condition

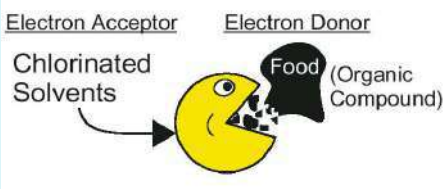
Compound(s)	Aerobic	Anaerobic
Acetone	1	1
BTEX	1	2 to 4
PAH's	1	3 to 4
PCB's		
highly substituted	4	2
minimally substituted	2	4
Chlorinated ethenes		
PCE	4	1 to 2
TCE	3	1 to 2
DCEs	3	2 to 3
Vinyl chloride	1 to 2	3 to 4

1 Highly biodegradable
2 Moderately biodegradable
3 Slow biodegradation
4 Not biodegraded

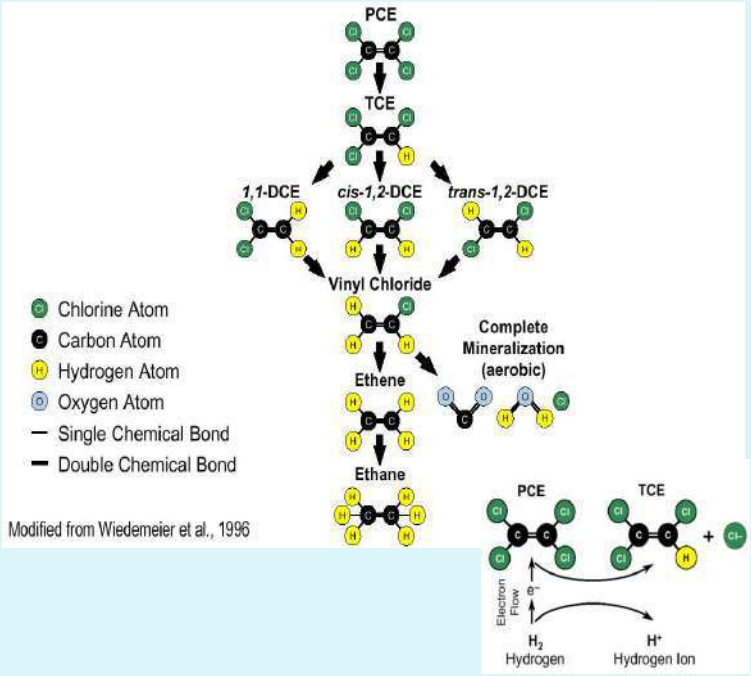
Dehalorespiration

- Certain chlorinated organics can serve as a terminal electron acceptor, rather than as a donor
- Confirmed only for chlorinated ethenes
- Rapid, compared to cometabolism
- High percentage of electron donor goes toward dechlorination
- Dehalorespiring bacteria depend on hydrogen-producing bacteria to produce H_2, which is the preferred primary substrate

Reductive Dechlorination



An **electron donor**, such as **hydrogen**, and an **electron acceptor** is needed to transfer from one product to the next



Cometabolism (Prof Wawa)

- Fortuitous **transformation of a compound by a microbe relying on some other primary substrate**
- Generally **a slow process - Chlorinated solvents don't provide much energy to the microbe**
- Most oxidation is of primary substrate, with only a few percent of the electron donor consumption going toward dechlorination of the contaminant
- Not all chlorinated solvents susceptible to cometabolism (e.g., **PCE and carbon tetrachloride**)

Methane-Oxidizing Bacteria and TCE

Requirements for Biodegradation (cont)

5. Favorable environment (continued):

d) *Adequate temperature (rates double for ΔT = +10 ℃).*

e) *Adequate pH (6-9).*

f) *Absence/control of toxic substances (e.g., precipitation of heavy metals, dilution of toxic conc.).*

g) *Absence of easily degradable, non-target substrates that could be preferentially metabolized (ethanol?).*

6. Time.

Without engineered enhancement, benzene half-lives on the order of 100 days are common in aquifers.

Want degradation rate > migration rate

Bioremediation Practice

- Many factors control biodegradability of a contaminant in the environment
- Before attempting to employ bioremediation technology, one needs to conduct a thorough characterization of the environment where the contaminant exists, including the microbiology, geochemistry, mineralogy, geophysics, and hydrology of the system

Bioremediation Practice

- Understand physical and chemical characteristics of the contaminants of interest
- Understand the possible catabolic pathways of metabolism and the organisms that possess that capability
- Understand the environmental conditions required to:
  - Promote growth of desirable organisms
  - Provide for the expression of needed organisms
- Engineer the environmental conditions needed to establish favorable conditions and contact organisms and contaminants

Engineering Strategies for Bioremediation

- *Ex Situ* (Above ground)
- *In Situ* (In its original place, below ground)
  - → Engineered Systems (biostimulation vs. bioaugmentation)
  - → Natural Attenuation (intrinsic/passive)

Microbial removal of contaminants from the environment often takes place without human intervention. This has been termed intrinsic bioremediation.
If the rate of intrinsic bioremediation is too slow, then environmental conditions can be manipulated to stimulate the activity of microorganisms that can degrade or immobilize the contaminants of concern.
Engineered bioremediation strategies include: the addition of electron donors or acceptors that will stimulate the growth or metabolism of microorganisms that are involved in the bioremediation processes; the addition of nutrients that limit the growth or activity of the microorganisms; and amendments to microorganisms with desired bioremediation capabilities.

EX-SITU Bioremediation technologies

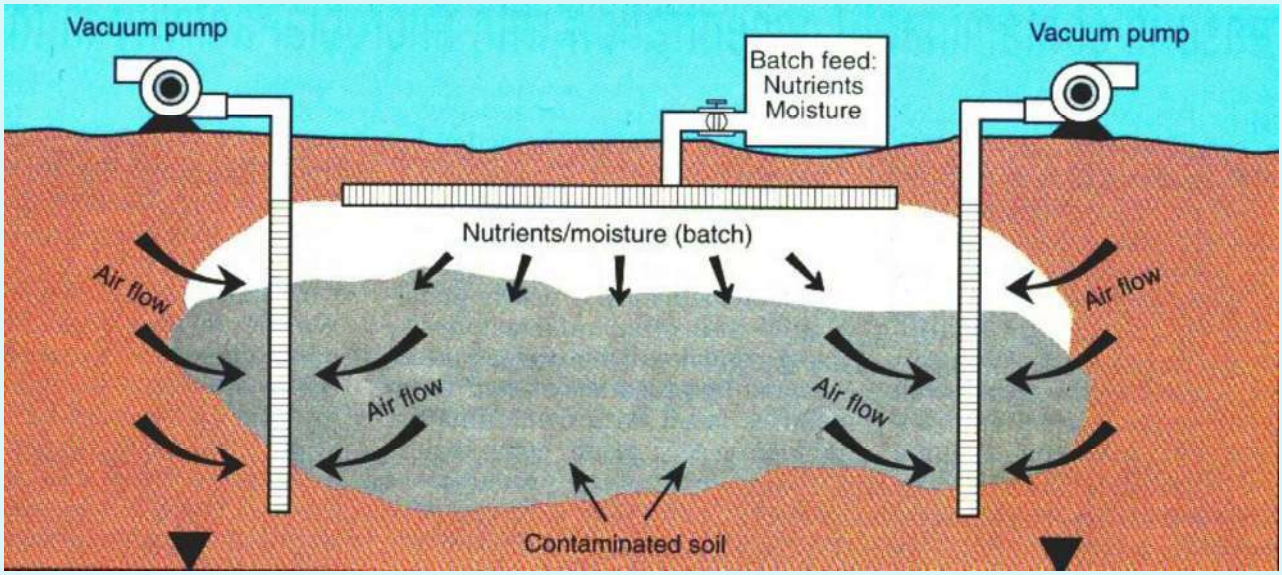
Composting suitable for **oil hydrocarbons**

ex-situ Biopiling – suitable for oil hydrocarbons up to 50000 ppm

IN-SITU Bioremediation technologies

Bioventing

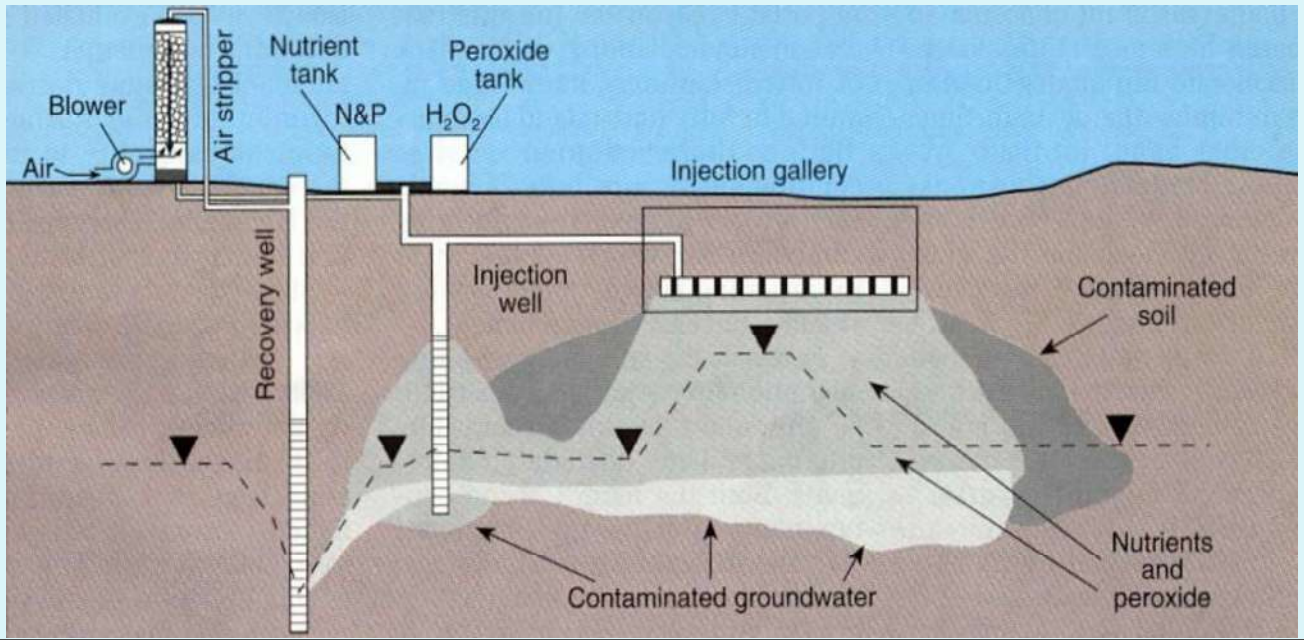
- Used to bioremediate BTEX trapped above water table
- **Vacuum pumps pull air through unsaturated soil**
- Need to infiltrate water (with nutrients) to prevent desiccation



Source: MacDonald and Rittmanm (1993) ES&T, 27(10) 1974-1979

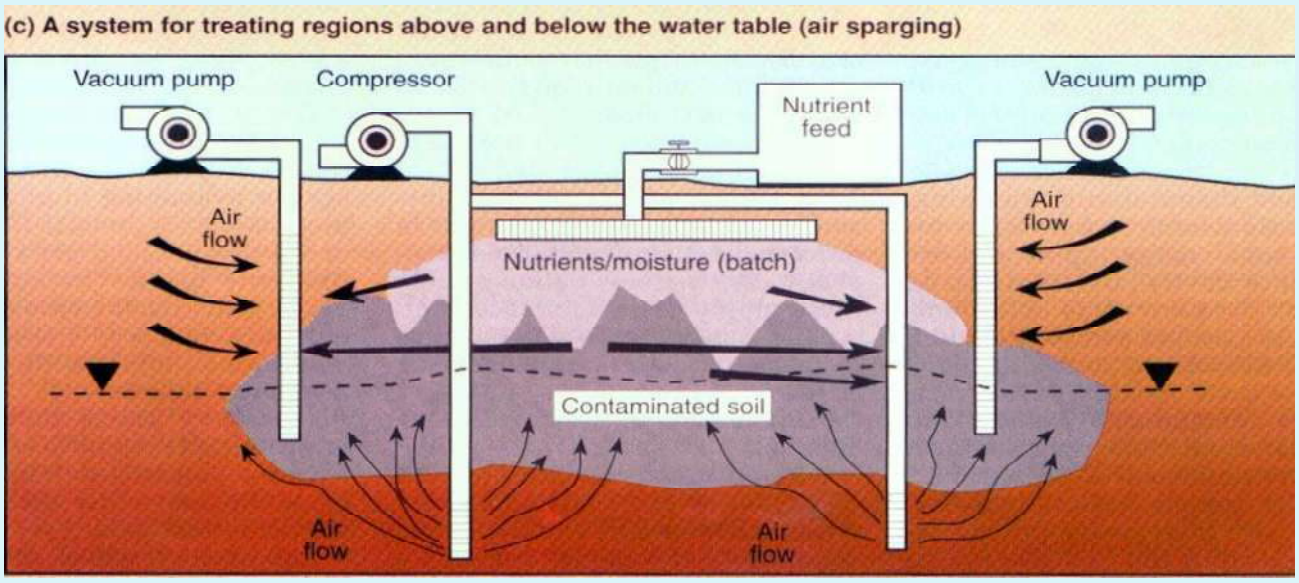
Water Circulation Systems

- Used to bioremediate BTEX in saturated zone
- **Contaminated water is extracted, treated (air-stripping, activated carbon, or biodegradation), and recycled. (pump and treat)**
- Some is amended with nutrients and reinjected (pulsing is better).

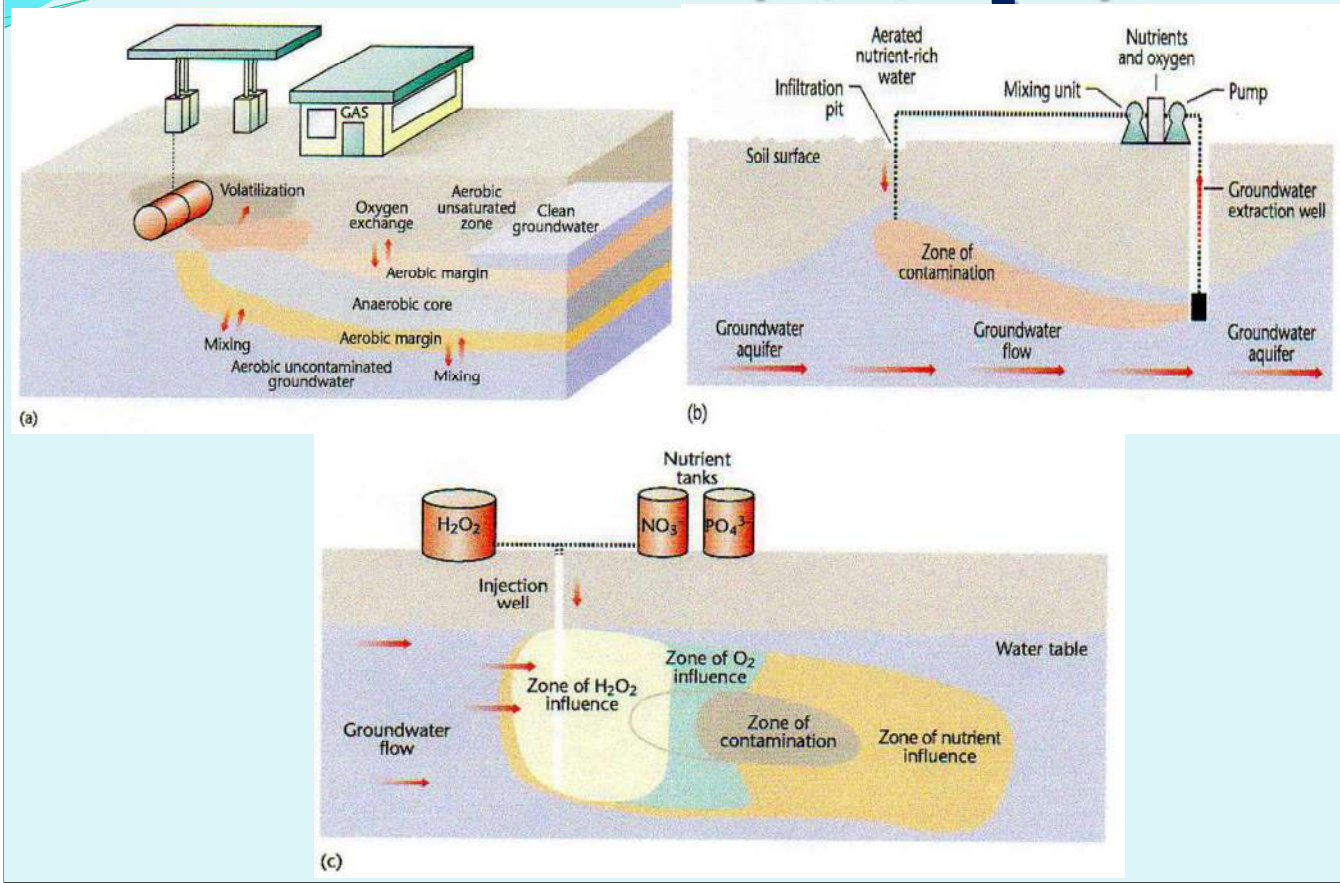


Air Sparging

- Injection of **compressed air** directly into contaminated zone **stimulates aerobic degradation**, strips BTEX into unsaturated zone to be removed by vapor-capture system
- Not effective when low-permeability soil traps or diverts airflow

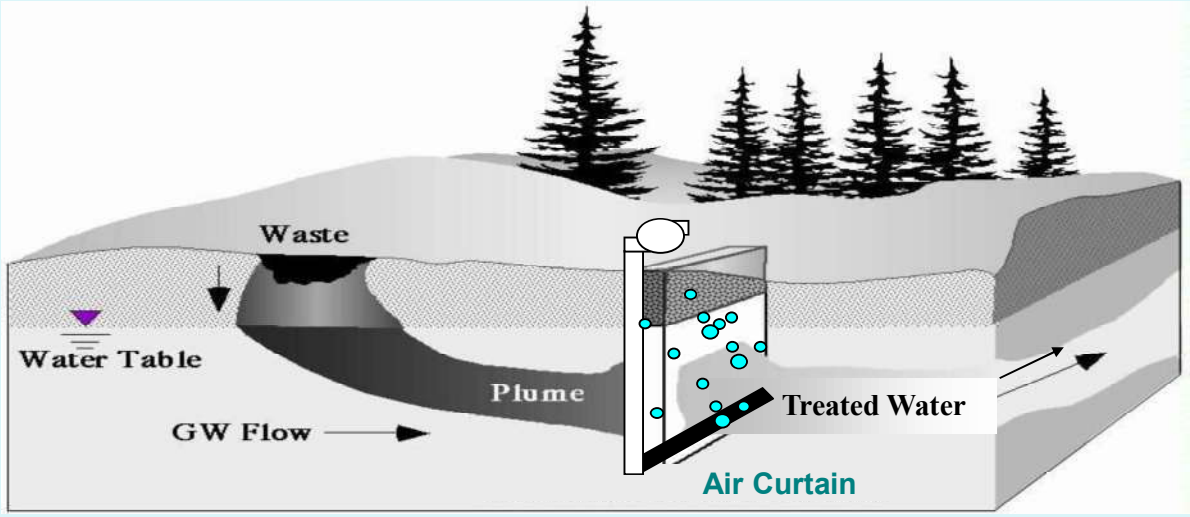


Biostimulation (N, P, O_2 …)



Biobarriers

- **Containment method** that **prevents further transport** (hydraulic or physical controls on groundwater movement may be required to ensure that BTEX pass through barrier
- **Biologically active zone** is created in the path of the plume **by injecting nutrients and electron acceptors** (could use oxygen-releasing compounds, or inject compressed air and form an air curtain)

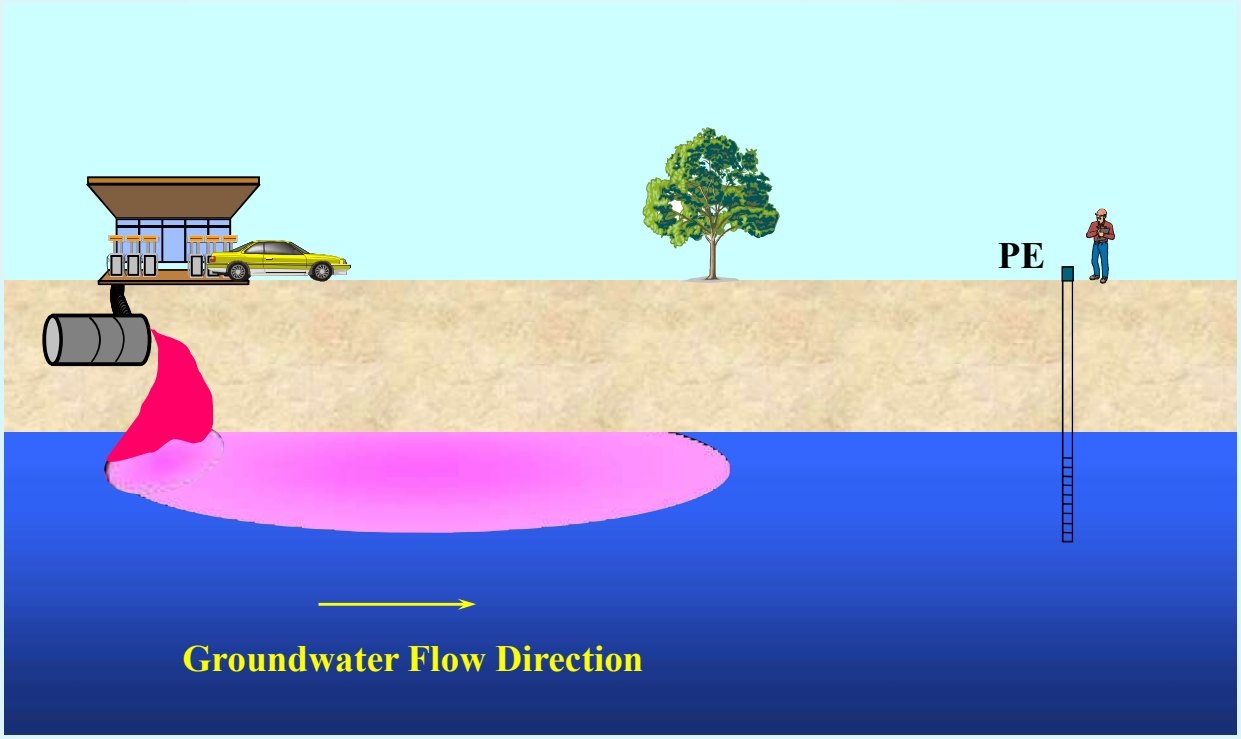


Monitored Natural Attenuation

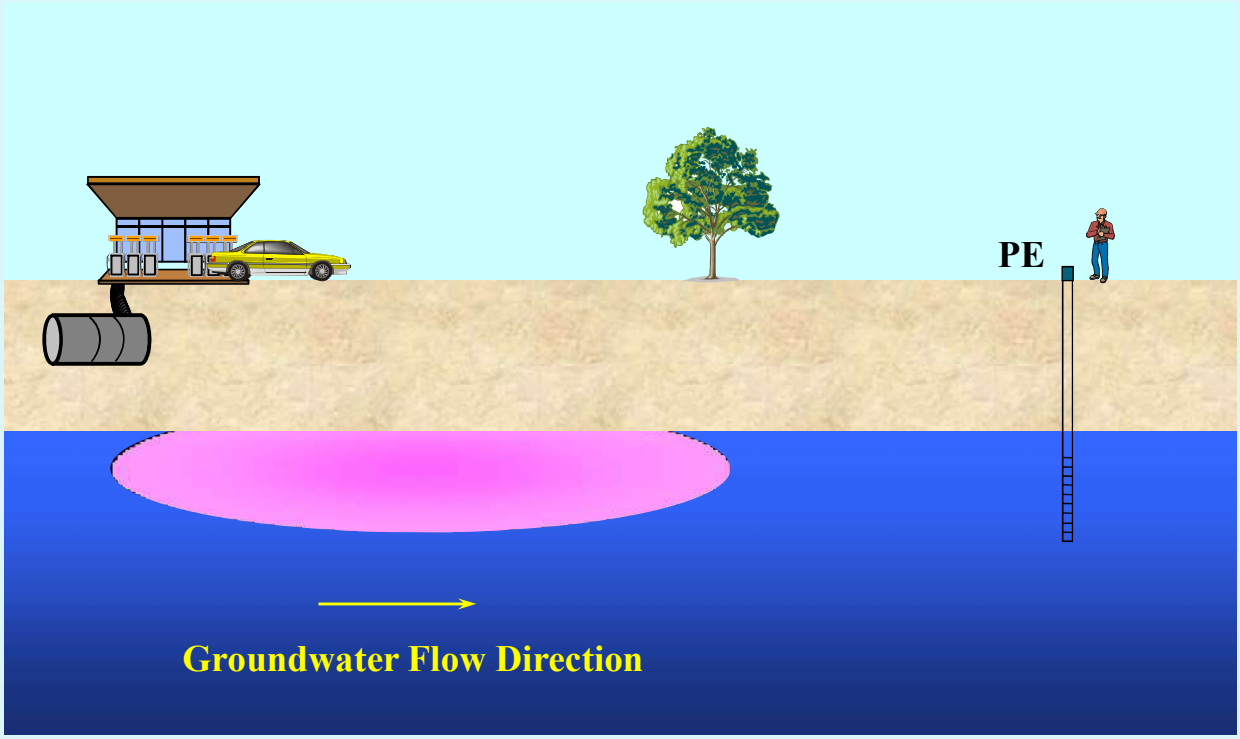
MNA is the combination of natural biological, chemical and physical processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of the contaminants.

Relying on intrinsic bioremediation (MNA) is increasingly the bioremediation option of choice if it can be shown that the contamination does not pose an immediate health threat and it remains localized.

Natural Attenuation



Natural Attenuation



Engineered Bioremediation

Bioaugmentation vs. Biostimulation:

Biostimulation involves the modification of the environment to stimulate existing microorganisms capable of bioremediation.

Indigenous populations may not be capable of degrading the xenobiotics or the wide range of potential substrates present in complex pollutant mixtures.

Bioaugmentation is the introduction of a group of natural microbial strains or a genetically engineered variant to treat contaminated soil or water.

Current Status of Bioremediation

- We have made **significant advances towards understanding the biochemical and genetic basis for *biodegradation*.** However**, *bioremediation* is still an *underutilized technology***.
- **Bioremediation is not universally understood, or trusted by those who must approve it.** To take full advantage of its potential, **we need to communicate better the capabilities and limitations of bioremediation**, and **answer**:
  - ***What is being done in the subsurface, Why, How, and Who is doing what?***
  - ***How fast is it being done, and can we control it and make it go faster?***
  - ***When can we meet cleanup standards in a cost-effective manner?***
  - ***Can we reasonably predict that what we want to happen, will happen?***

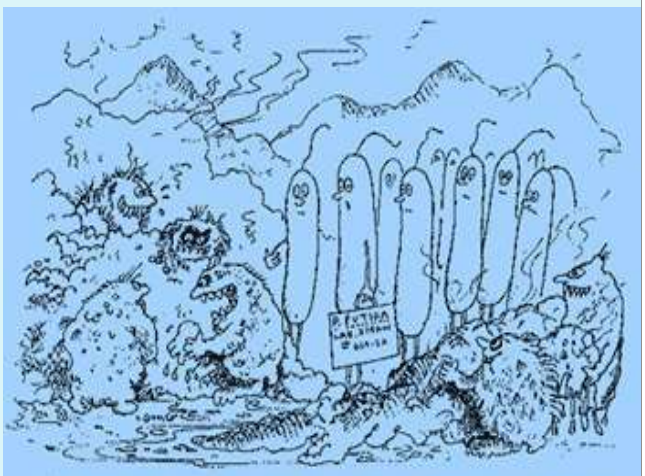
Uncertainty of Bioremediation

Bioremediation strategies that are successful in one location might not work in another, and microbial processes that remediate contaminants in laboratory incubations might not function well in the field.
The reasons for such failures are often not obvious and many practitioners are therefore unwilling to risk the bioremediation option.

Bioremediation strategies would be designed based on knowledge of:

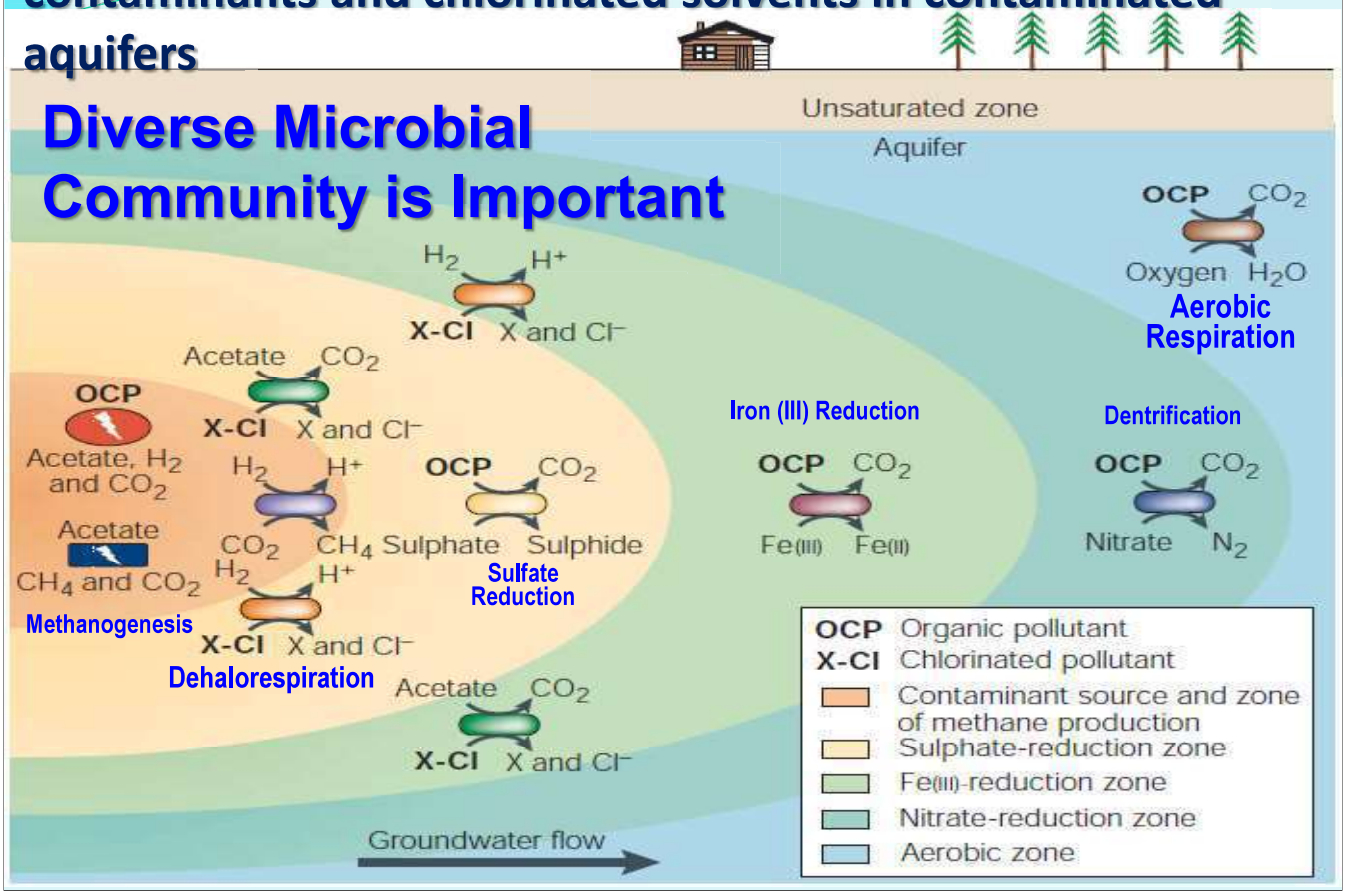
the microorganisms that are present in the contaminated environments;

their metabolic capabilities; and how they respond to changes in environmental conditions.
Unfortunately, much of the required information is not readily available and the use of microorganisms in bioremediation is highly empirical rather than knowledge-based.



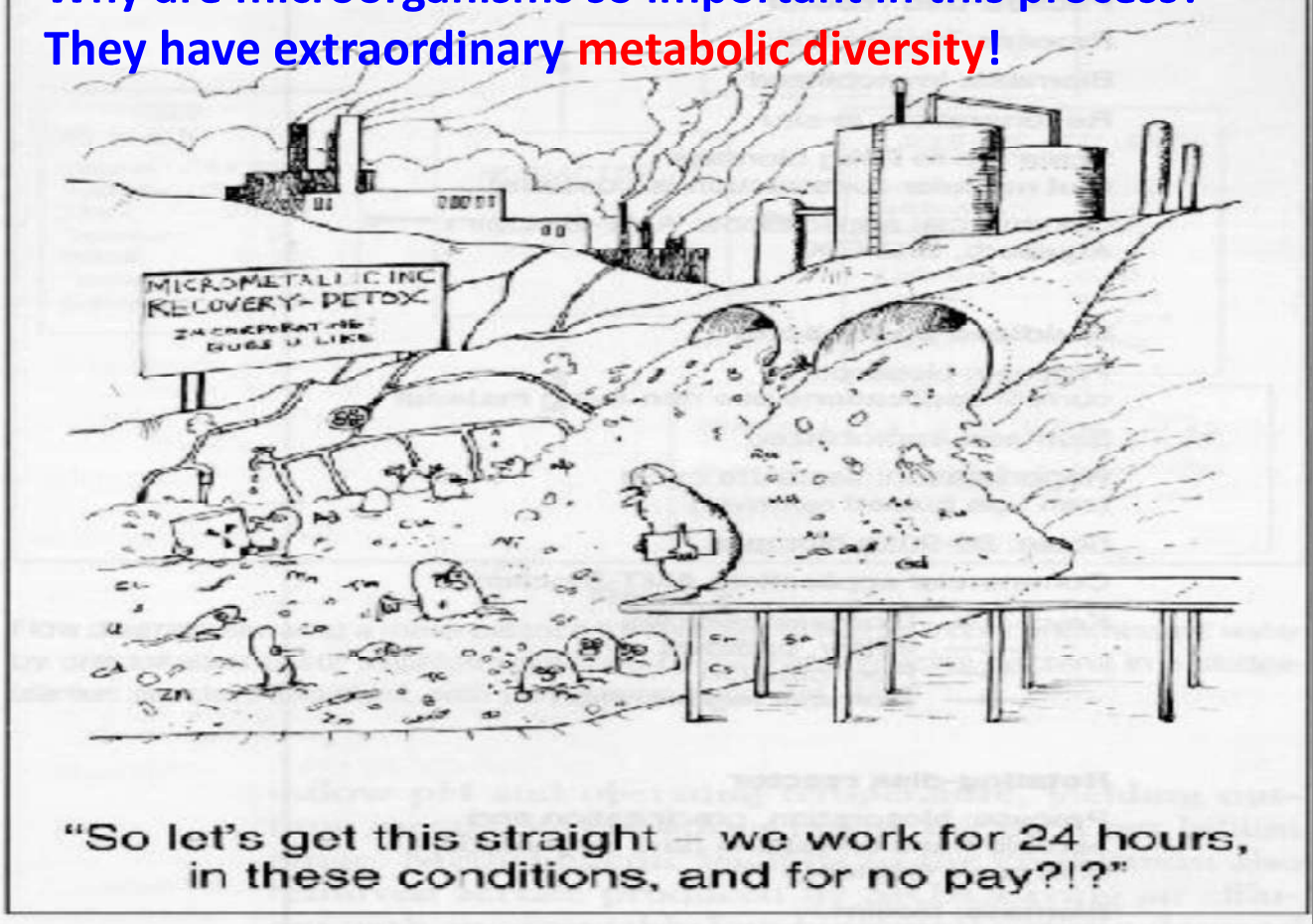
"Oh dear! I didn't realize 'in the field' would be like this! We should have stayed in the laboratory."

Typical bioremediation reactions for oxidizable, organic contaminants and chlorinated solvents in contaminated aquifers



Why are microorganisms so important in this process?

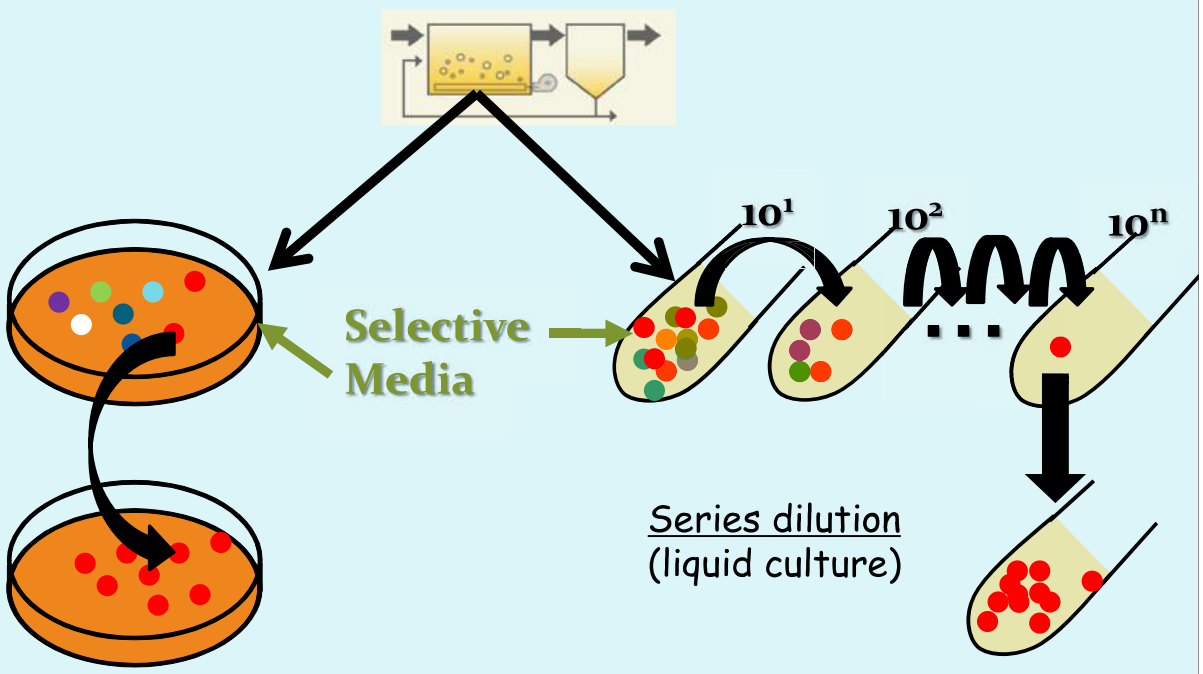
They have extraordinary metabolic diversity!



Non-Molecular Biological Techniques

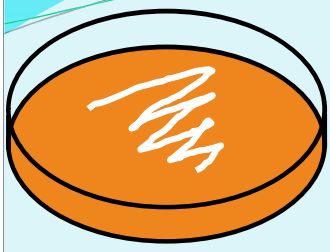
- Most applied bioremediation processes make use of the '**treatability study**', in which samples of the contaminated environment are incubated in the laboratory and the rates of contaminant degradation or immobilization are documented.
- Such studies provide an estimate of the **potential metabolic activity of the microbial community**, but **give little insight into the microorganisms that are responsible for the bioremediation**, or why particular amendments that can be evaluated for engineered bioremediation applications do, or do not, stimulate activity.
- When bioremediation processes are researched in more detail, attempts are generally made to **isolate the organisms responsible**. The isolation and characterization of pure cultures has been, and will continue to be, crucial for the development and interpretation of molecular analyses in microbial ecology.
- However, before the application of **molecular techniques** to bioremediation, it was **uncertain whether the isolated organisms were important in bioremediation *in situ***, or whether they were 'weeds' **that grew rapidly in the laboratory but were not the primary organisms responsible for the reaction of interest in the environment**.

limitation of Culture dependant approach

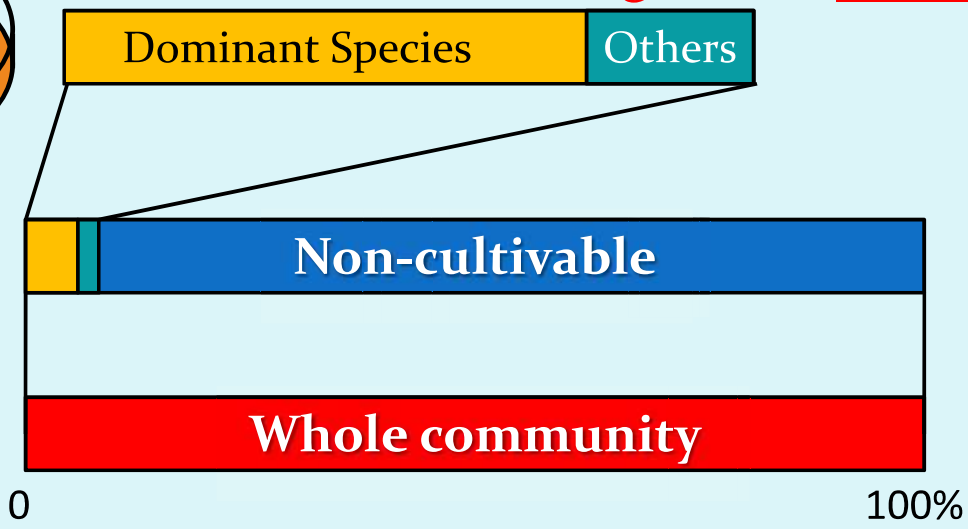


Example: TMAH-degrading methanogens

limitation of Culture dependant approach



Cultivable microorganisms <1%



 # Difficult to understand whole microbial community

Microbial Ecology

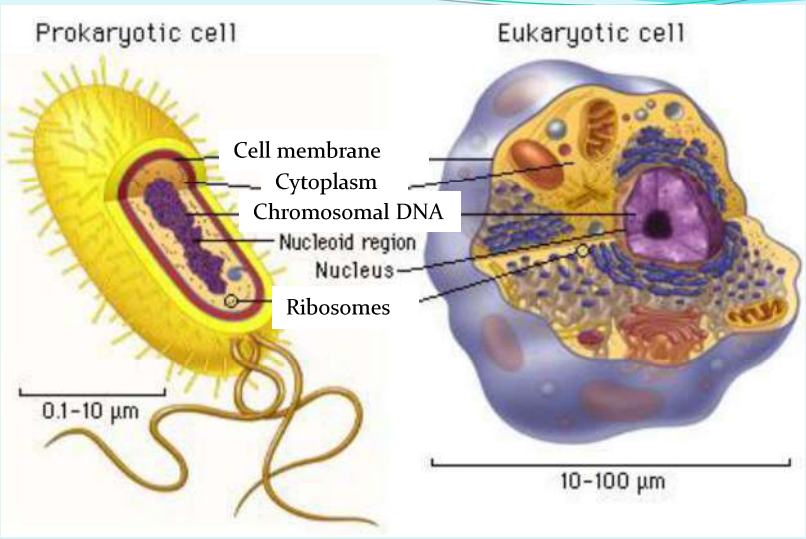
- The science of microbial ecology tries to answer four fundamental questions.
- First, what microorganisms are present in the community? The phylogenetic makeup (identity and number) of the microorganisms present in a community is called a *community structure*.
- Next, what are the capabilities of the microorganisms for carrying out reactions that transform the community's environment? The catalog of catalytic capabilities is called the community's *phenotypic potential*.
- Third, what reactions and transformations are the community members actually performing? The realization of phenotypic potential is called the community's *unction*.
- Finally, what are the interrelationships among the community's members and between them and their environment? Interrelationships involve spatial organization (i.e., who is near whom) and materials that the microorganisms exchange. Understanding these interrelationships is the ultimate goal of microbial ecology.
- Answers to these four questions usually change over time and especially in response to perturbations to the environment. The ability of microbial communities to respond to environmental changes is called community *resilience* and *stability*, and it influences each of the four questions.

Molecular Biology Techniques

The use of molecular biology tools, beginning around 1985, started to change the prospects for microbial ecologists.

Selective and reliable amplification of defined DNA with the polymerase chain reaction (PCR) and hybridization with DNA oligonucleotides made it possible to interrogate directly the genetic information of individual microorganisms and entire communities. The **small-subunit ribosomal RNA** (SSU rRNA, also known as **16S rRNA for prokaryotes**) was the first target for hybridization and is still the most widely used. This rRNA gives information on the **phylogenetic identity of the microorganisms**, and this addresses the **first fundamental question of microbial ecology**.

The cell

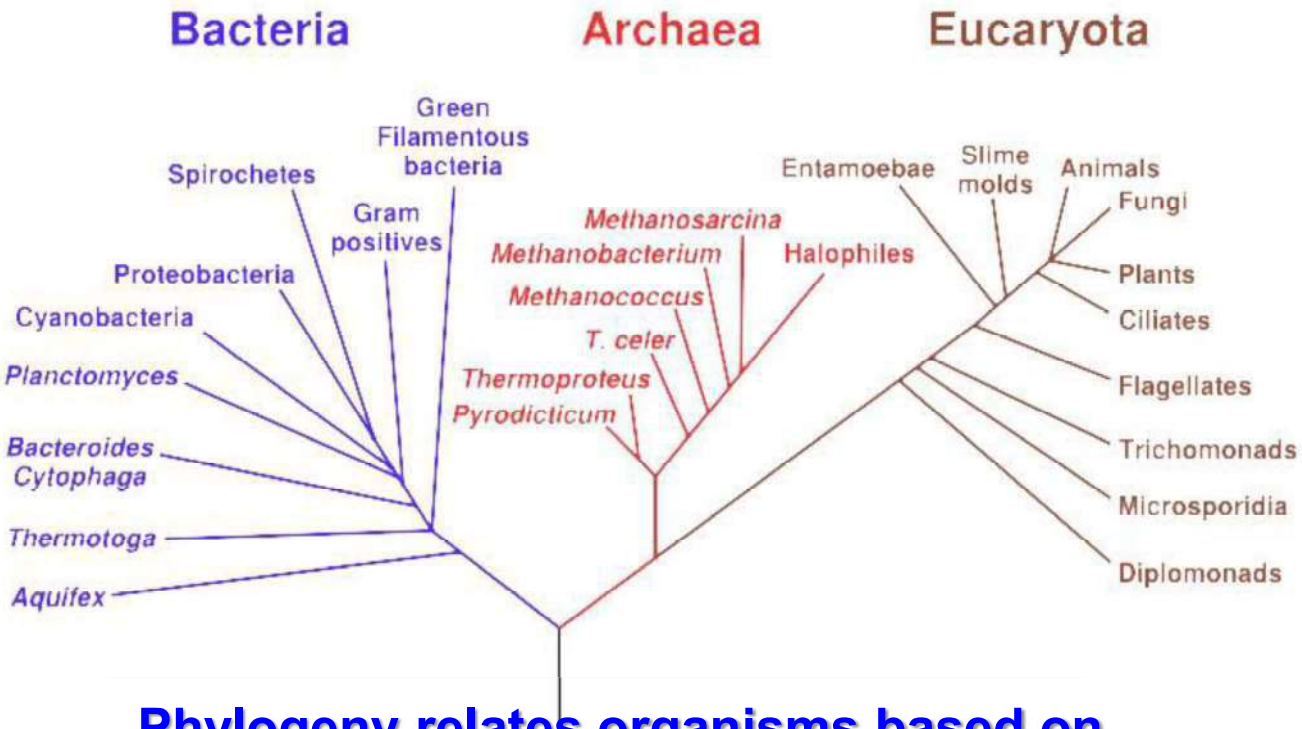


Common components

- ✓ **Cell membrane**: barrier between cell and its environment.
- ✓ **Cytoplasm** : water and macromolecules that the cells need to function
- ✓ **Ribosome**: protein synthesis
- ✓ **Chromosome (or Chromosomal DNA)**: storage of genetic information (e.g. for growth) in Nucleoid region or Nucleus

Phylogenetic Tree of Life

Based on small subunit (SSU) ribosomal RNA gene



Phylogeny relates organisms based on their evolutionary history.

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The 16S rRNA approach: what microorganisms are there?

In aquifers in which the indigenous microbial community was degrading the solvent **trichloroethene (TCE)**, 16S rRNA sequences that are ~99% identical to the 16S rRNA sequence of a pure culture of the **TCE-degrader *Dehalococcoides ethanogenes***, were detected.

Marine sediments with high rates of anaerobic **naphthalene degradation** were found to be specifically enriched in microorganisms with 16S rRNA sequences closely related to **NaphS2**, **an anaerobic naphthalene degrader that is available in pure culture**.

There was a close correspondence between the potential for aerobic degradation of the fuel oxygenate **methyl *tert*-butyl ether (MTBE)** in groundwater and the number of organisms with 16S rRNA sequences that had more than 99% similarity to the **MTBE-degrading organism, strain PM-1,**which is available in pure culture.

The **primary limitation of the 16S rRNA** technique is that knowledge of the **phylogeny of the organisms associated with bioremediation does not necessarily predict important aspects of their physiology.**

Predicting physiology from phylogeny is even more difficult if there are no closely related organisms available in pure culture.

Molecular Biology Techniques

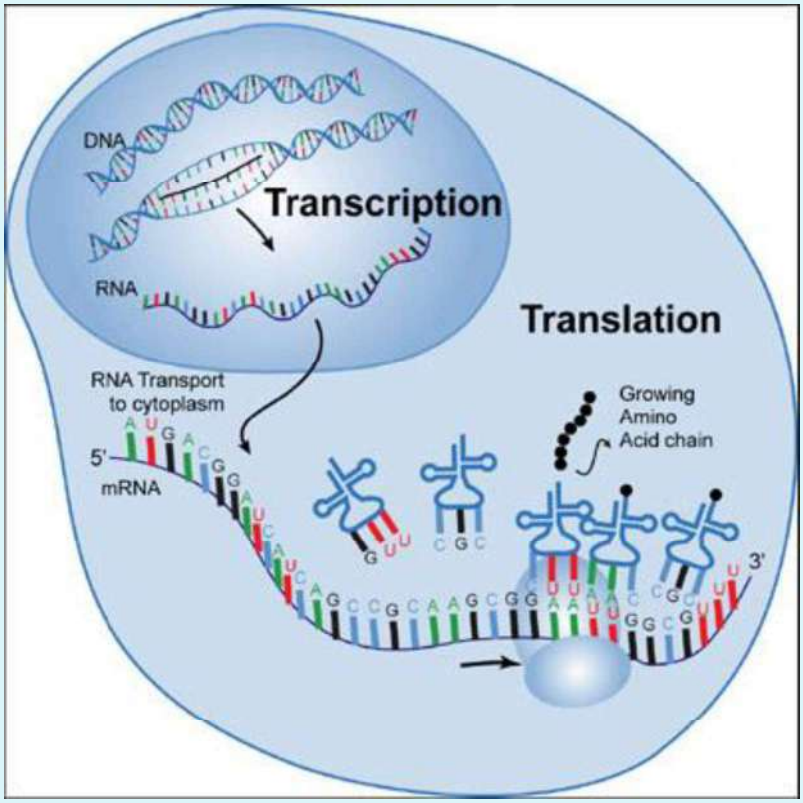
Other targets within the genetic system of microorganisms answer different questions. For example, amplifying and detecting **specific genes** in the genome of microorganisms in the community defines the **phenotypic potential**, and this addresses **the second question** about the **capability of microorganisms**.

Messenger RNA (mRNA) reveals which genes are being expressed and, therefore, which functional proteins likely are formed. This gives information on the **expressed phenotypic potential**, or the **third question** about the **community's function**.

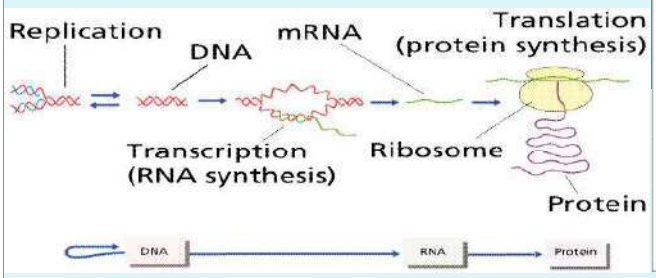
Assessing RNA targets by using microscopic visualization, such as with **fluorescence in situ hybridization (FISH)**, adds information on **spatial organization**. Recently, microbial ecologists have begun to **clone and sequence large genome fragments (metagenomic)** from various microbial communities; therefore, it is now possible, at least for low-diversity communities, to reconstruct entire genomes of uncultured community members.

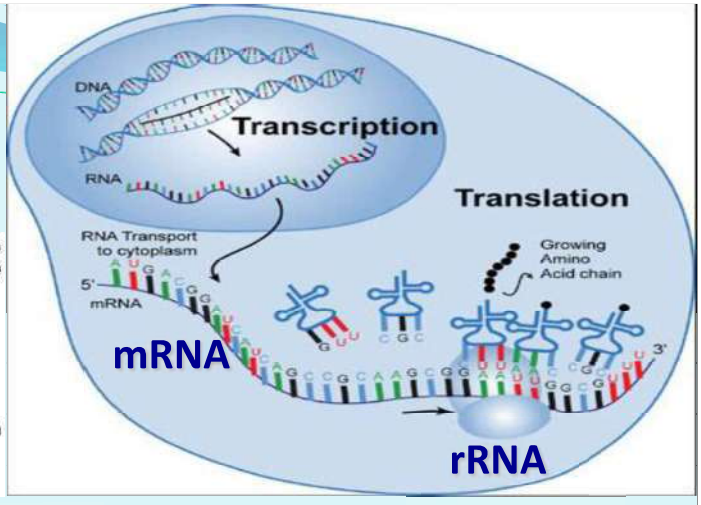
Genetic information flow

-The central dogma-



Genetic information flow

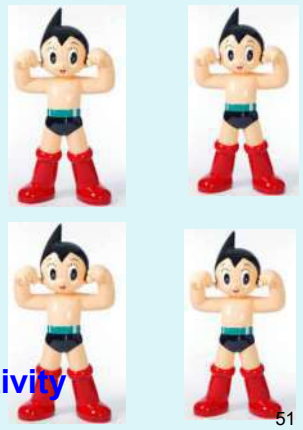




Original Blueprint (DNA)

Copied Blueprints (RNA)

Products (Proteins)



Ribosomal RNA (rRNA): growth activity

Messenger RNA (mRNA): functional activity

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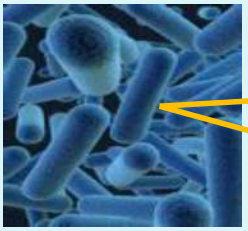
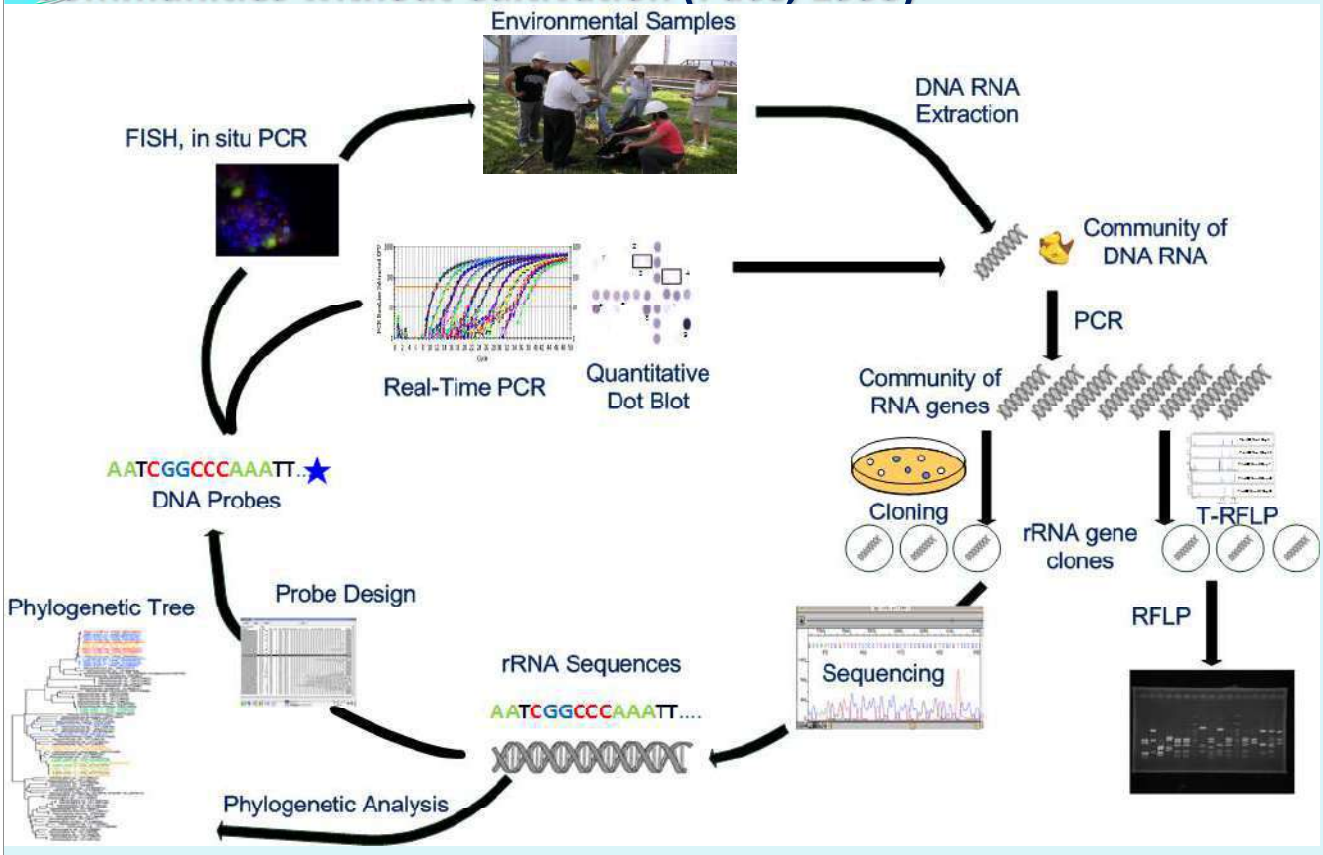
Biomarkers for biotransformation forensics and natural attenuation performance assessment

Target	Information Gained	Question Answered
Ribosomal (r)RNA	Phylogenetic Identity	Who is there?
Genes for rRNA on DNA	Phylogenetic Identity	Who is there?
Catabolic genes on DNA	Phenotypic Potential	What can they degrade?
Messenger (m)RNA	Phenotypic Activity	What genes are being expressed?
Protein	Phenotypic Activity or phylogenetic identity	Who is active and what are they doing?

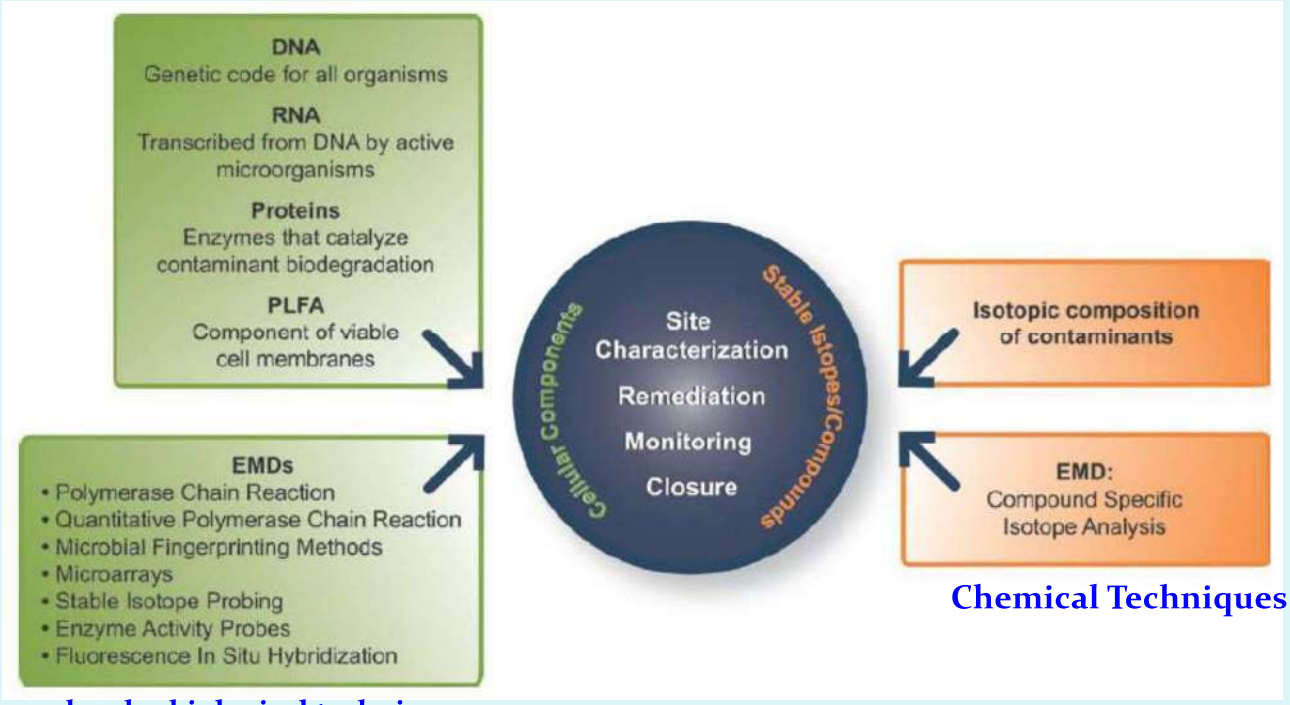


Alvarez and Illman 2006

Strategies based on rRNA Sequences for Characterizing Microbial Communities without Cultivation (Pace, 1995)



Environmental Molecular diagnostics (EMDs)

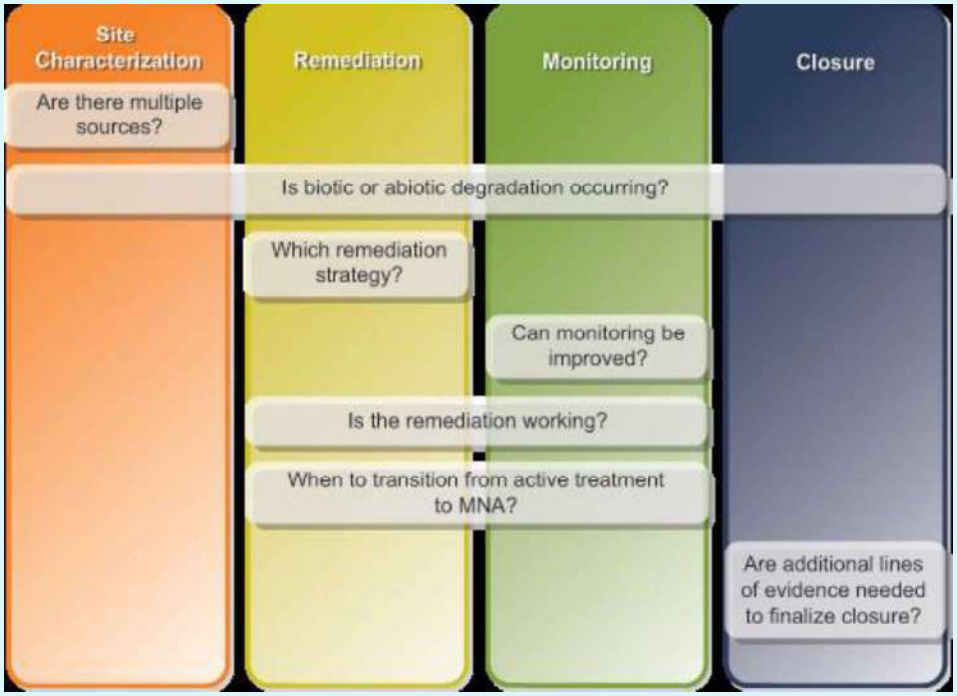


molecular biological techniques (MBTs)

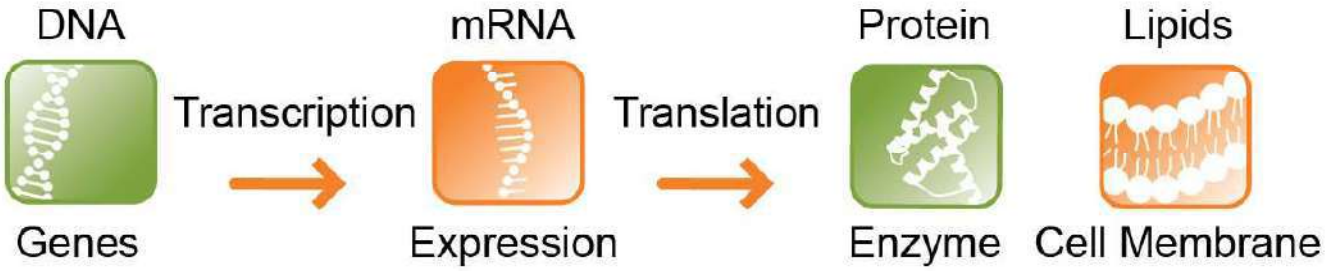
Chemical Techniques

by US Interstate Technology & Regulatory Coun

EMDs provide supplemental data for answering site management questions

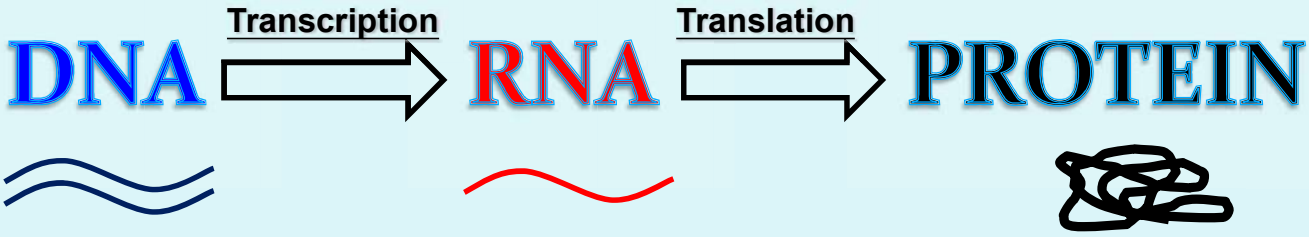


Flow of information within cells



Genes — The ability of microorganisms to degrade contaminants requires that they have the appropriate **genetic information** (genes) that confers a particular biochemical activity to the microbial cell.
A **gene** is a segment of DNA within a bacterial cell that contains specialized instructions that direct the cell to make a **specific protein**. Most proteins (enzymes) act as catalysts that the cell needs in order to metabolize (break down) a contaminant.
A typical environmental sample can contain **many thousands of different microorganisms**. However, **only a small fraction** may possess the genes necessary to break down a specific contaminant.

Genetic information flow



Original Blueprint

Copied Blueprints

Products

Abundance → Activity → Function

Ribosomal RNA (rRNA): growth activity

Messenger RNA (mRNA): functional activity

Polymerase chain reaction (PCR)

Polymerase chain reaction (PCR) is a technique that can test for **the presence of the specific microorganism**, family of microorganisms, or expressed genes in environmental samples such as soil, water, or sediment. When combined with traditional monitoring of contaminant concentrations over time, **using PCR to identify microorganisms capable of degrading contaminants** can provide project managers valuable information for site management and remedy selection.

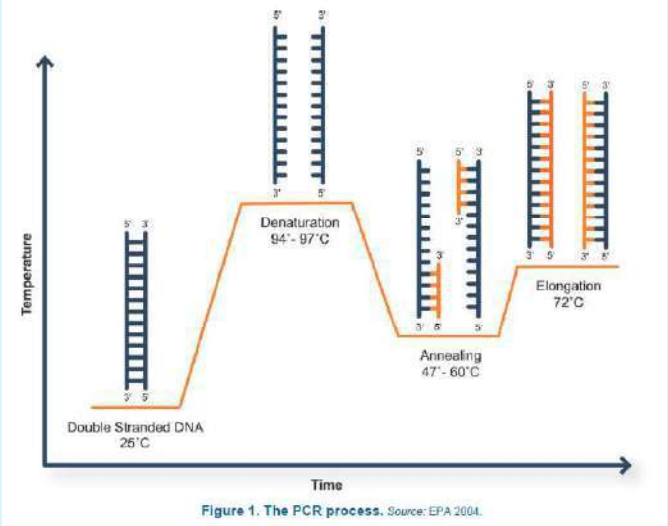
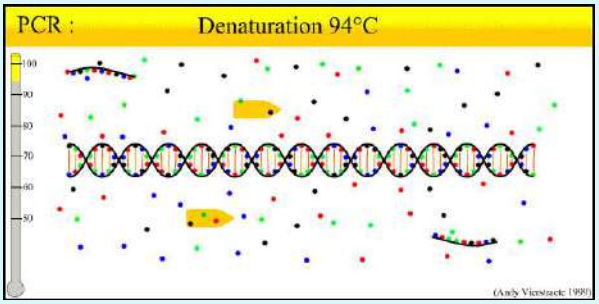
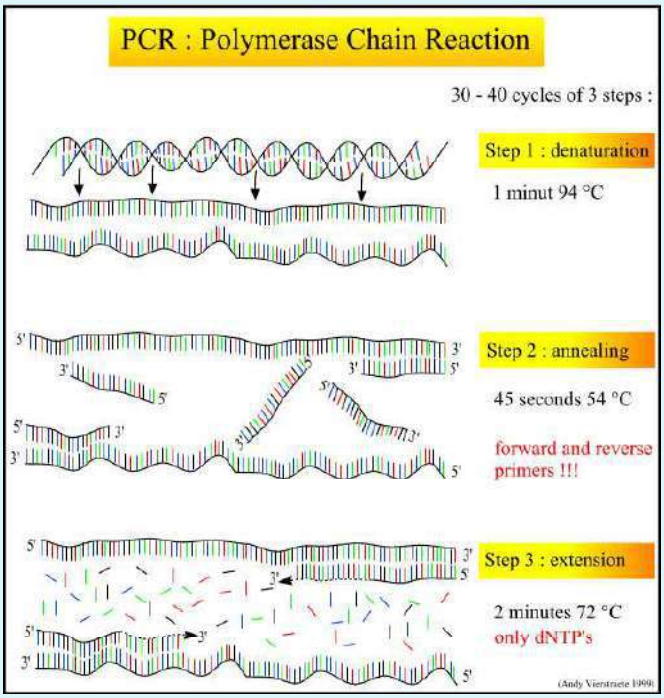
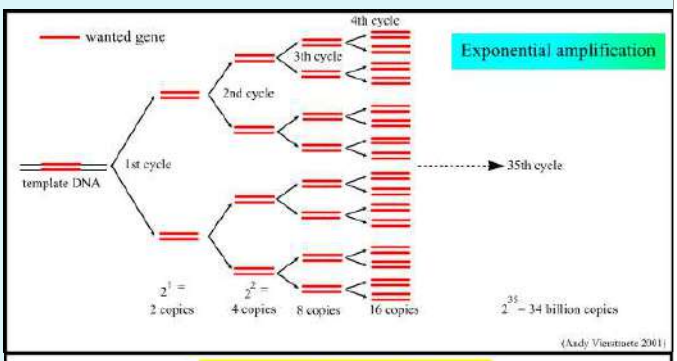


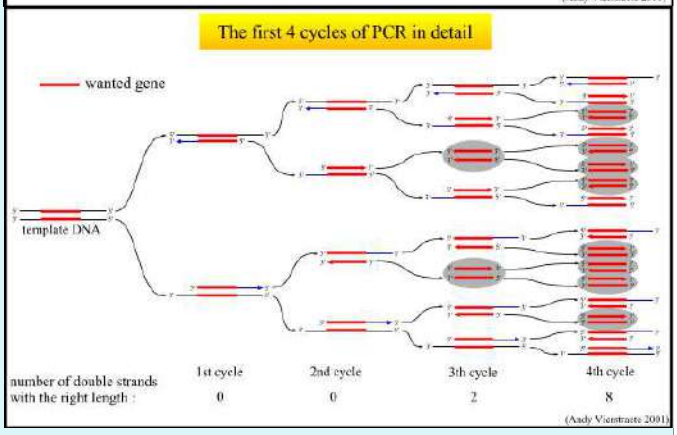
Figure 1. The PCR process. Source: EPA 2004.



PCR Amplification







PCR Summary

PCR can be used to amplify DNA sequences for use in further analysis of the sequence by other EMD techniques such as quantitative polymerase chain reaction (qPCR), microarray analysis, and microbial fingerprinting techniques.

PCR has been used to detect microorganisms capable of degrading contaminants such as petroleum hydrocarbons, pentachlorophenol, perchlorate, polychlorinated biphenyls (PCBs), metals, radionuclides, and chlorinated solvents.

PCR can be used to detect the presence of either (a) a specific microorganism or group of microorganisms that are known to be able to biodegrade a specific contaminant or group of contaminants or (b) DNA sequences (genes) that regulate the production of enzymes (proteins) that biodegrade or partially biodegrade these contaminants.

Quantitative Polymerase Chain Reaction

Quantitative polymerase chain reaction (qPCR) and reverse transcriptase quantitative polymerase chain reaction (RT-qPCR) are used to quantify the abundance and activity of specific microorganisms or expressed genes in pathways capable of biodegradation of contaminants present at a contaminated site.

qPCR results can reveal when contaminant-using microorganisms are present but not thriving, thus providing evidence that enhanced bioremediation options may need to be explored to stimulate the microbial community (Enhanced bioremediation or biostimulation)

Project managers can use qPCR in the characterization phase, remedy selection, monitoring, and site closure to assess microbial growth and activity. Within the environmental restoration industry, qPCR analyses have been offered on a commercial basis since 2002.

qPCR Applications

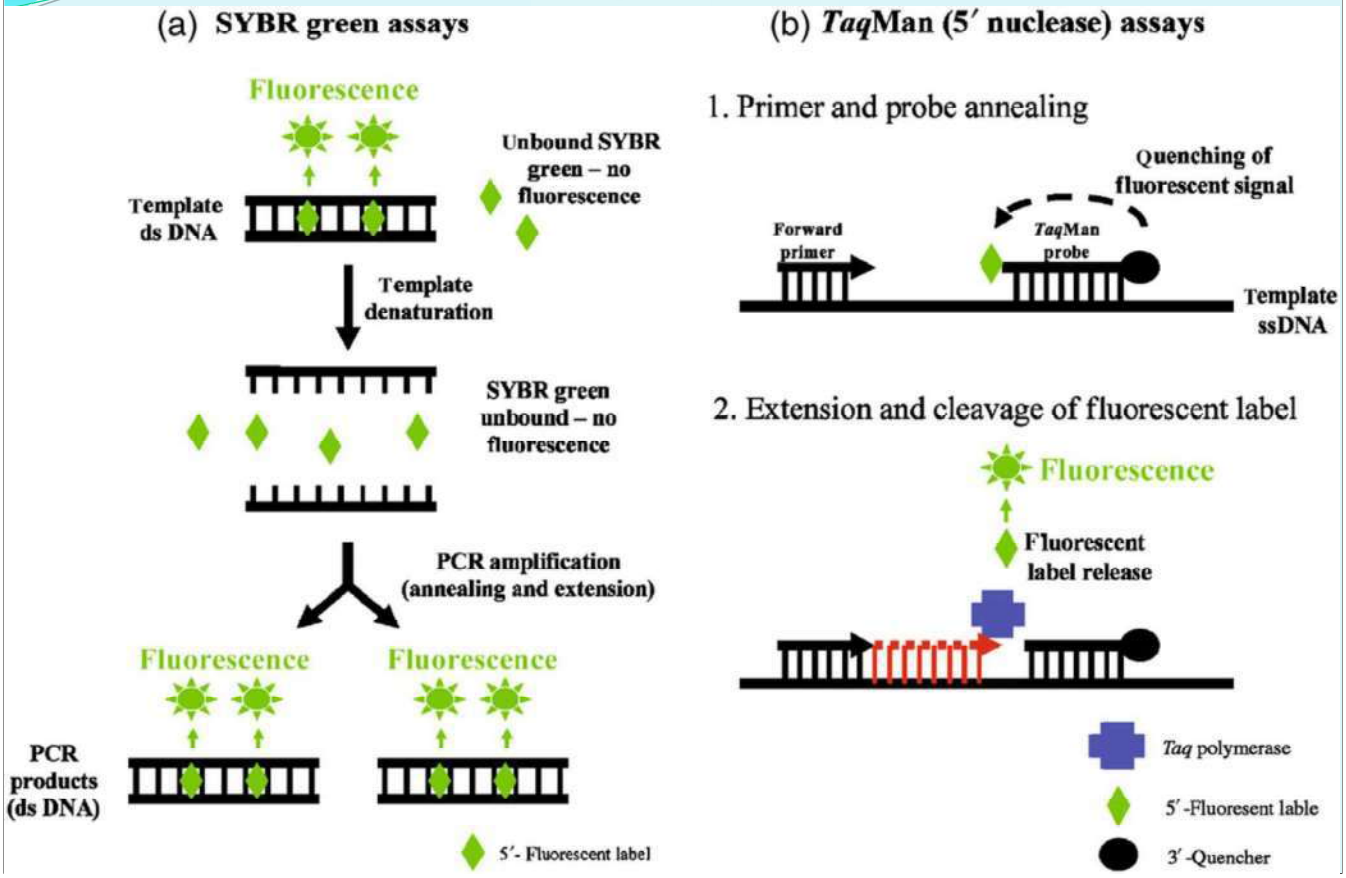
qPCR is an analytical method used to determine the number of copies of specific genes or DNA targets present in a sample.

qPCR analysis can quantify functional genes (e.g., trichloroethene [TCE] reductase [*tceA*]), specific microorganisms (e.g., *Dehalococcoides*), or groups of related microorganisms (e.g., sulfate-reducing bacteria) in soil, sediment, or groundwater samples.

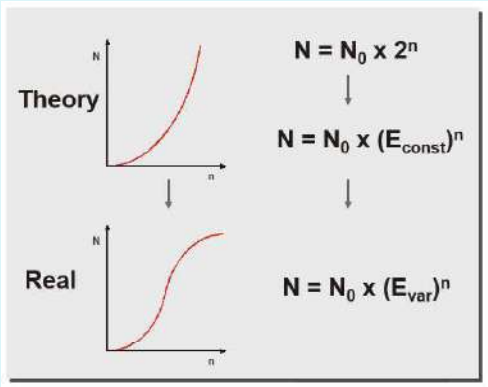
qPCR has been used to study: biodegradation of chlorinated solvents such as perchloroethene (PCE), TCE, etc. ; petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes; polycyclic aromatic hydrocarbons; fuel oxygenates such as methyl *tert*-butyl ether; and radionuclides

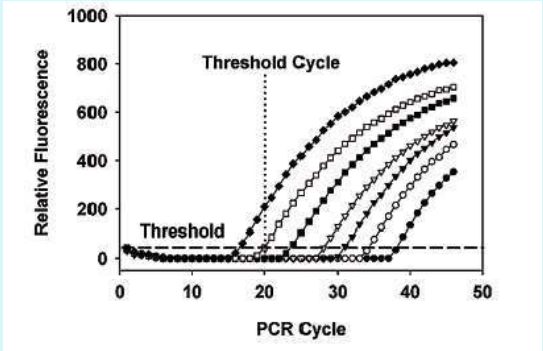
Quantification of specific genes or microorganisms capable of biodegradation of a contaminant provides a direct evidence that helps answer questions about site remediation.

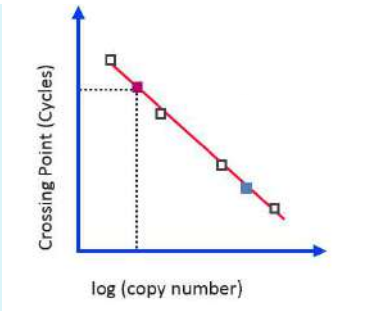
qPCR



Quantitative Polymerase Chain Reaction







N: copies after PCR
n: PCR cycle
N_0: Initial copies
E: PCR efficiency

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Current qPCR gene targets for assessing biodegradation pathways

Contaminant Group	Contaminants	Target	Redox Conditions	Environmental Relevance / Data Interpretation
Chlorinated Solvents	PCE, TCE, DCE, VC	*Dehalococcoides*	Anaerobic	• Only known group of bacteria capable of complete dechlorination of tetrachloroethene (PCE) and/or trichloroethene (TCE) to ethene.
Chlorinated Solvents	TCE and DCE	TCE Reductase	Anaerobic	• *Dehalococcoides* functional genes encoding reductive dehalogenases for trichloroethene (TCE) and *cis*-dichloroethene (*cis*-DCE).
Chlorinated Solvents	VC	Vinyl Chloride Reductase	Anaerobic	• *Dehalococcoides* functional genes encoding reductive dehalogenases for vinyl chloride (VC).
Chlorinated Solvents	TCA, PCE, TCE	*Dehalobacter*	Anaerobic	• Capable of dechlorination of PCE and TCE to *cis*-DCE • Some strains capble of converting TCA, a common co-contaminant at PCE/TCE-impacted sites, to chloroethane.
Chlorinated Solvents	PCE, TCE	*Desulfuromonas*	Anaerobic	• Capable of dechlorination of PCE and TCE to *cis*-DCE using acetate as an electron donor.
Chlorinated Solvents	PCE, TCE, DCA, DCP	*Desulfitobacterium*	Anaerobic	• Capable of dechlorination of PCE and TCE to *cis*-DCE • Some strains capable of dechlorination of chlorophenols, 1,2-dichloroethane and 1,2-dichloropropane.
Chlorinated Solvents	Chlorobenzene	Toluene Dioxygenase	Aerobic	• Catalyzes biodegradation of chlorobenzene by incorporation of oxygen into the aromatic ring.
Petroleum Hydrocarbons	BTEX	Ring-hydroxylating Toluene Monooxygenases	Aerobic	• Catalyzes the initial (and sometimes second) hydroxylation of BTEX compounds.
Petroleum Hydrocarbons	BTEX	Phenol Hydroxylase	Aerobic	• Catalyzes further oxidation of BTEX compounds.
Petroleum Hydrocarbons	T, X	Toluene/Xylene Monoxygenase	Aerobic	• Attacks toluene and xylenes at the methyl group.
Petroleum Hydrocarbons	B, T, chlorobenzene	Toluene Dioxygenase	Aerobic	• Catalyzes biodegradation of benzene and toluene by incorporation of oxygen into the aromatic ring.
Petroleum Hydrocarbons	Naphthalene	Naphthalene Dioxygenase	Aerobic	• Catalyzes aerobic biodegradation of naphthalene and other PAHs by incorporation of oxygen into the aromatic ring.
Petroleum Hydrocarbons	Naphthalene and PAHs	Naphthalene-Inducible Dioxygenase	Aerobic	• Catalyzes aerobic biodegradation of naphthalene and other PAHs by incorporation of oxygen into the aromatic ring.
Petroleum Hydrocarbons	Alkanes	Alkane Monooxygenase	Aerobic	• Catalyzes biodegradation of straight chain petroleum hydrocarbons.
Petroleum Hydrocarbons	MTBE	MTBE utilizing PM1	Aerobic	• Targets *Methylibium petroleiphilum* PM1, one of the few bacteria isolated that is capable of growth on MTBE
Petroleum Hydrocarbons	T, X	Benzylsuccinate Synthase	Anaerobic	• Targets gene encoding enzyme in anaerobic biodegradation of toluene.
Cometabolism Chlorinated Solvents	TCE	Methanotrophs	Aerobic	• Targets two types of methane oxidizing bacteria (methanotrophs) • Indicates the potential for cometabolic oxidation of TCE
Cometabolism Chlorinated Solvents	TCE	Soluble Methane Monooxygenase	Aerobic	• Targets the soluble methane monooxygenase gene • Soluble methane monooxygenases are generally believed to support faster cometabolism of TCE
Perchlorate	Perchlorate, chlorate	Perchlorate Reductase	Anoxic	• Catalyzes reduction of perchlorate and in most isolates reduction of chlorate to chlorite • Presence indicates the potential for aerobic BTEX biodegradation.
Polychlorinated biphenyls	PCBs (lightly chlorinated)	Biphenyl Dioxygenase	Aerobic	• Catalyzes catalyzes intial oxidation of lightly chlorinated PCB congeners.

Microbial Fingerprinting Techniques (MFTs)

Microbial fingerprinting methods can provide a **comprehensive assessment of the microbial community.**

Fingerprinting methods allow identification of **dominant members of the microbial community** to the family or even genus level.

Microbial fingerprinting methods **differentiate microorganisms or groups of microorganisms** based on **unique characteristics of a universal component or section of a biomolecule** (such as DNA or RNA).

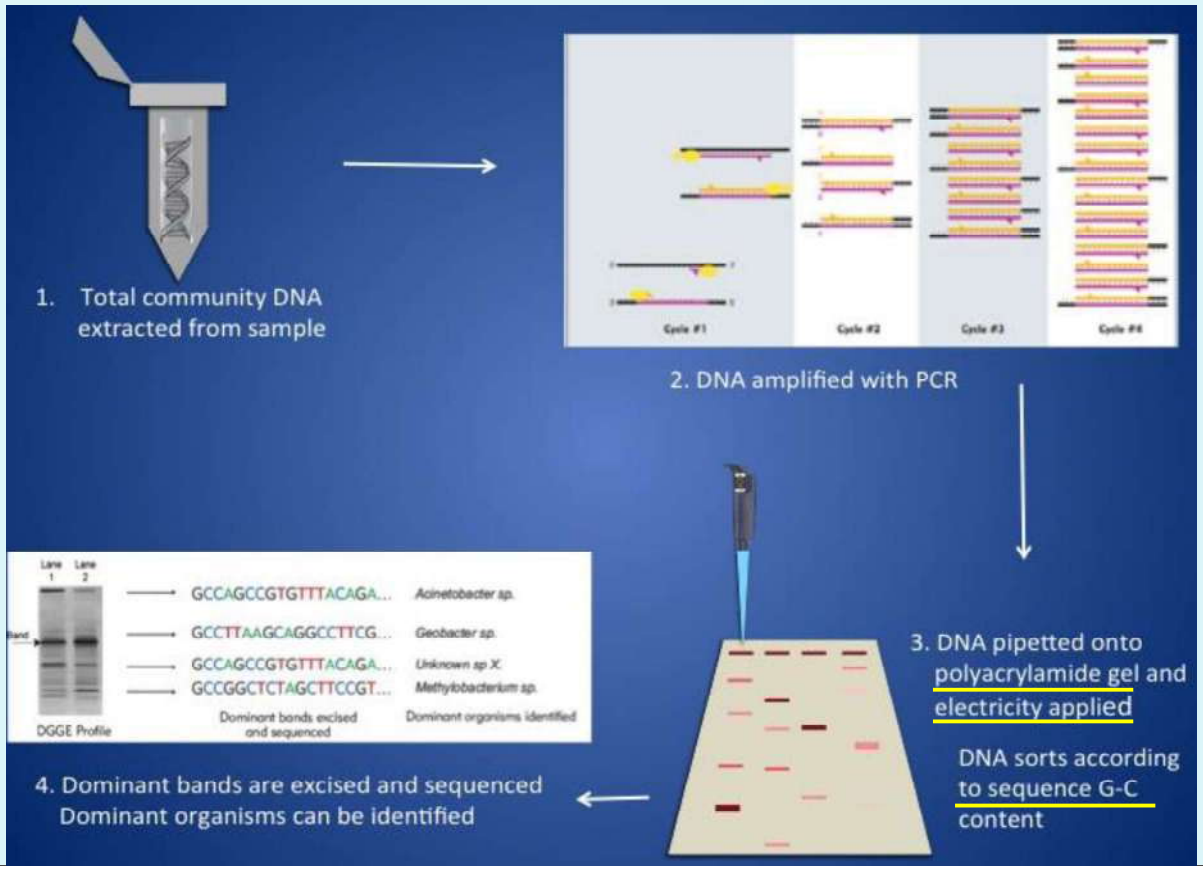
DNA Fingerprinting

- Genes have conserved regions of DNA sequence as well as different regions
- In a microbial community the different sequences of a gene will generate polymorphism → an expression of the community structure
- DNA fingerprinting is addressing the polymorphism of a target relevant gene, that is expected to respond to contamination

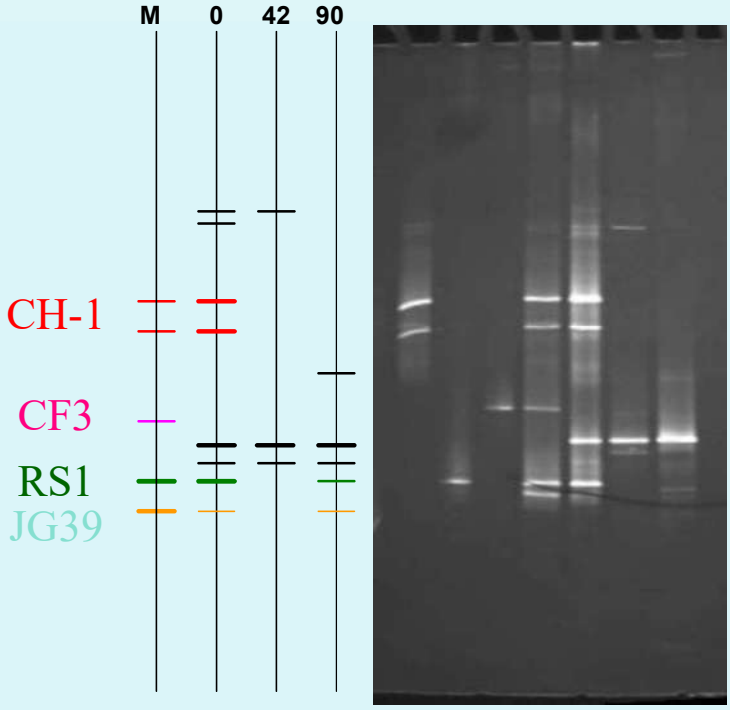
Denaturating Gradient Gel Electrophoresis (DGGE)

DGGE and sequence analysis provides a DNA- based profile of the microbial community and allows identification of the predominant organisms generally to the family or genus level.
DGGE cannot quantify specific organisms or microbial functions present within a sample.
DGGE profiles are used to visually display differences or shifts in microbial community composition over time or in response to treatment.
DGGE analysis followed by sequencing is performed when identification of the predominant organisms is required but little is known about the microbial community of the sample prior to the analysis.

DGGE Procedures



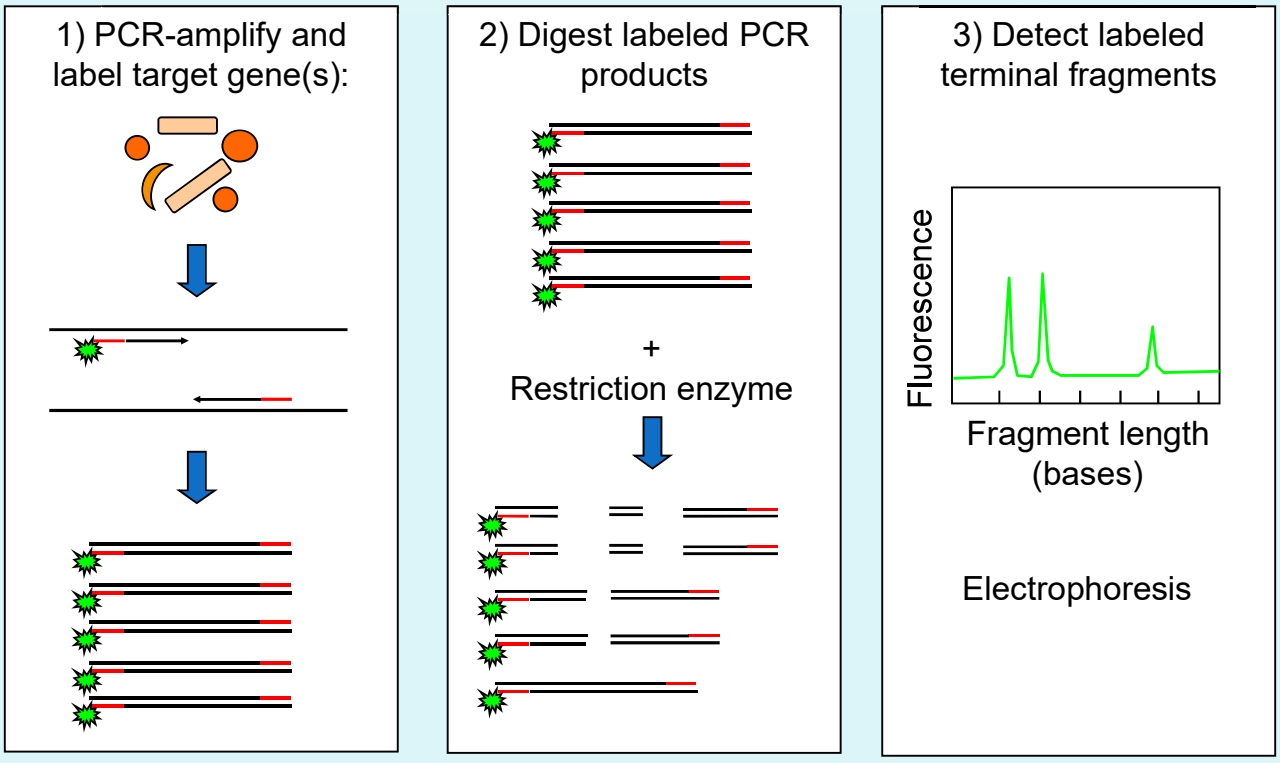
Microbial community structures analyzed using the DGGE fingerprinting (6%)of 16S rDNA fragments .The gradient concentration of the denaturant was 40-60%.



Terminal Restriction Fragment Length Polymorphism (TRFLP)

T-RFLP involves digestion of genetic material (DNA) with restriction enzymes that cleave DNA at specific sites. These sites differ between microorganisms, **resulting in different DNA fragment lengths** (and sequences), which can be used to identify some members of a microbial community and provide a fingerprint of its composition. **T-RFLP information is non-quantitative or at best semi-quantitative.**

General Procedure of T-RFLP



PCR = polymerase chain reaction

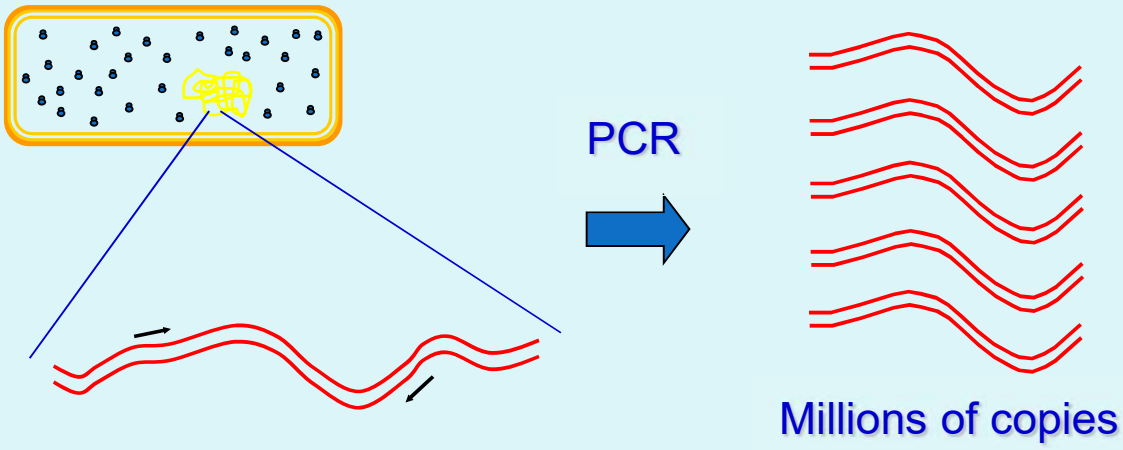
Key Components of T-RFLP

- PCR/Primers
- Restriction Enzyme
- Nucleic acid electrophoresis
- Comparative genomics/RFLP (Data Bases for Expected Terminal Fragment Length)

Key Components of T-RFLP (1)

1) Replicate DNA fragments using the polymerase chain reaction (PCR)

- uses DNA polymerase
- requires forward and reverse primers specific for gene of interest



Key Components of T-RFLP (2)

2) Digest DNA into smaller fragments using restriction enzymes

Example: *MspI* cleaves at C▼CGG

5' – CGTAGACTGTCCGGTGATCGT – 3'
3' – GCATCTGACAGGCCACTAGCA – 5'

5' – CGTAGACTGTC – 3'
3' – GCATCTGACAGGC – 5'

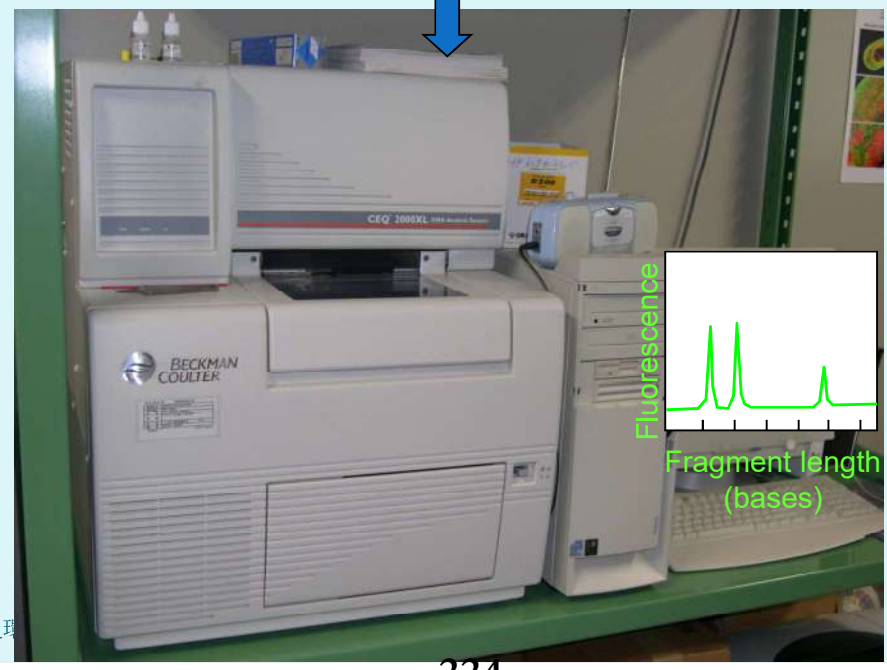
5' - CGGTGATCGT – 3'
3' - CACTAGCA – 5'

Key Components of T-RFLP (3)

3) Electrophoresis of digested nucleic acid fragments

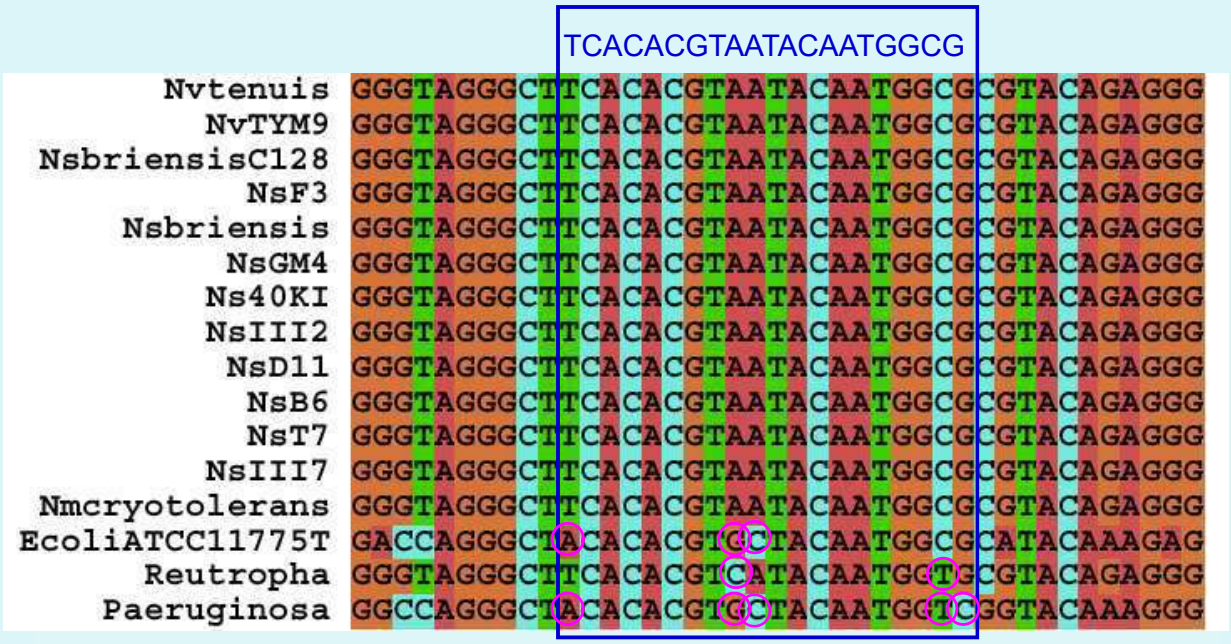
5' – CGTAGACTGTC – 3'
3' – GCATCTGACAGGC – 5'

5' - CGGTGATCGT – 3'
3' - CACTAGCA – 5'



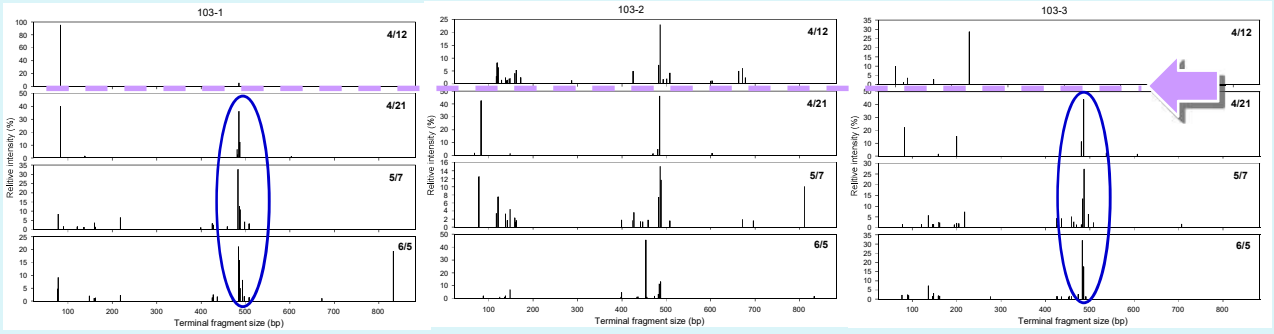
Key Components of T-RFLP (4)

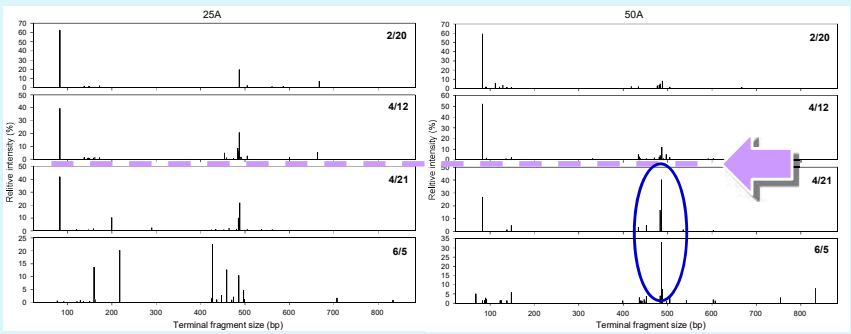
4) Data Bases for Expected Terminal Fragment Length



Alignment of gene fragment sequences from AOB and other bacteria

TRFLP Analyses for an in-situ TCE Bioremediation Site





- 注入EOS後，五口監測井總微生物多樣性(peak數目)均增加，微生物族群結構亦產生改變
- 監測井50A、103-1、103-3再注入EOS後，均出現長度約500的片段

LOGO

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Principal components analysis of TRF patterns revealed a series of sample clusters describing bacterial succession during the study.

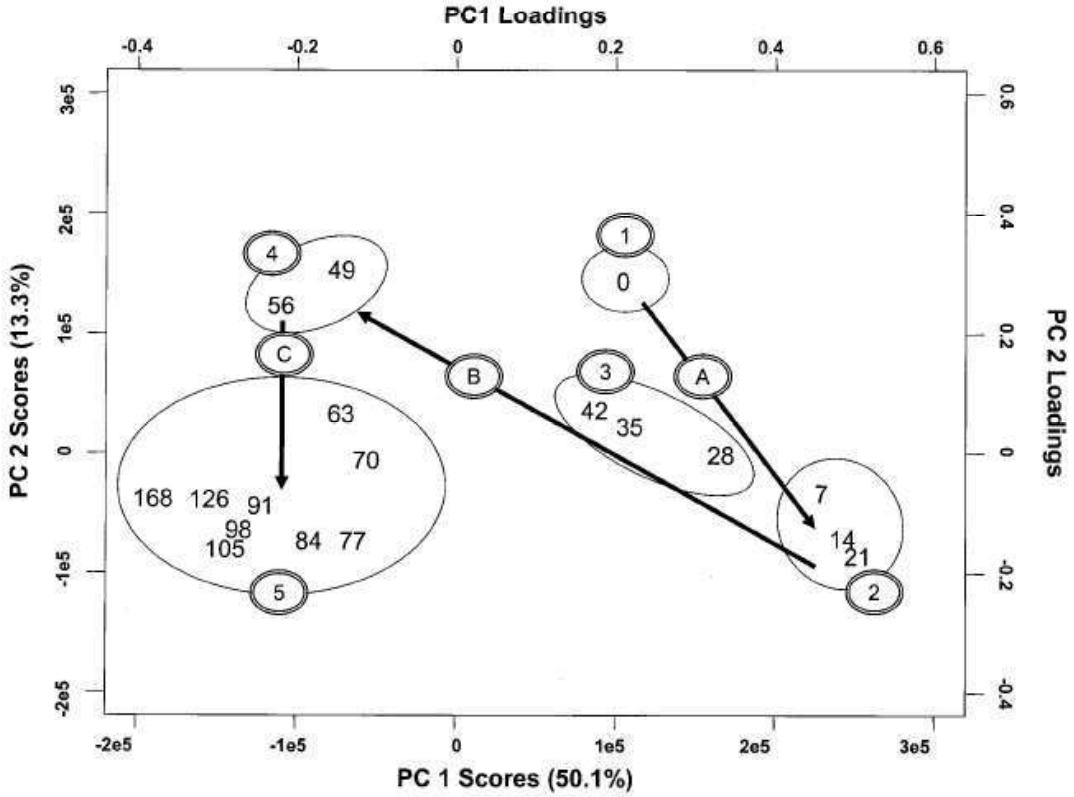
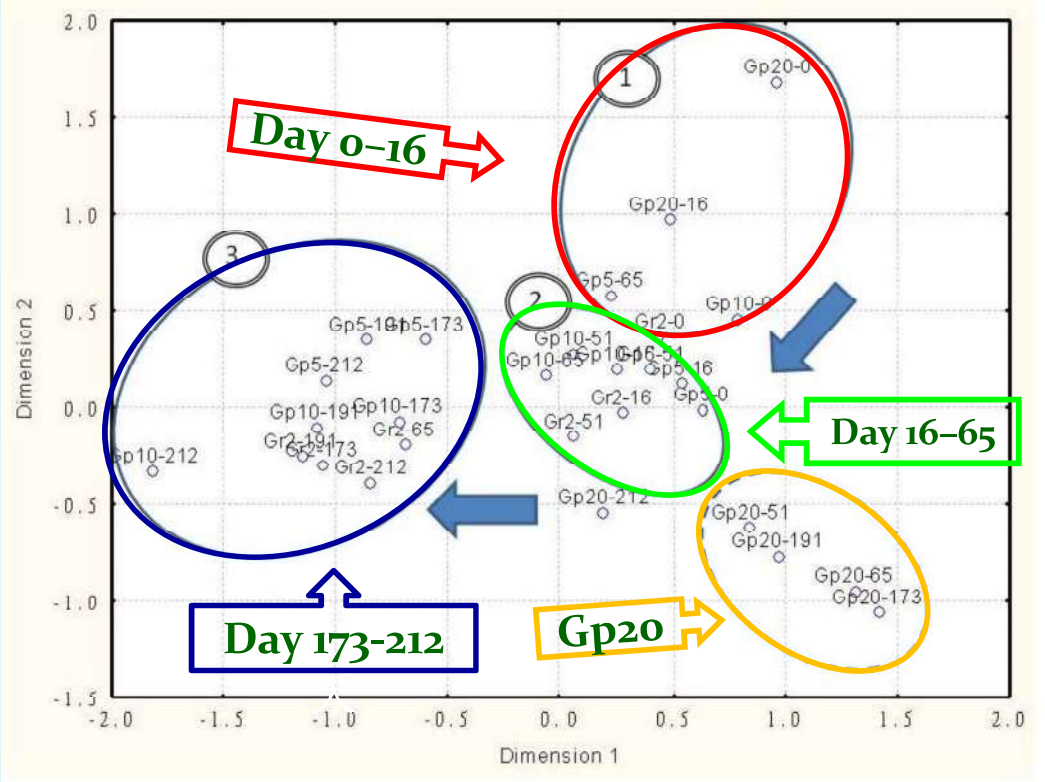
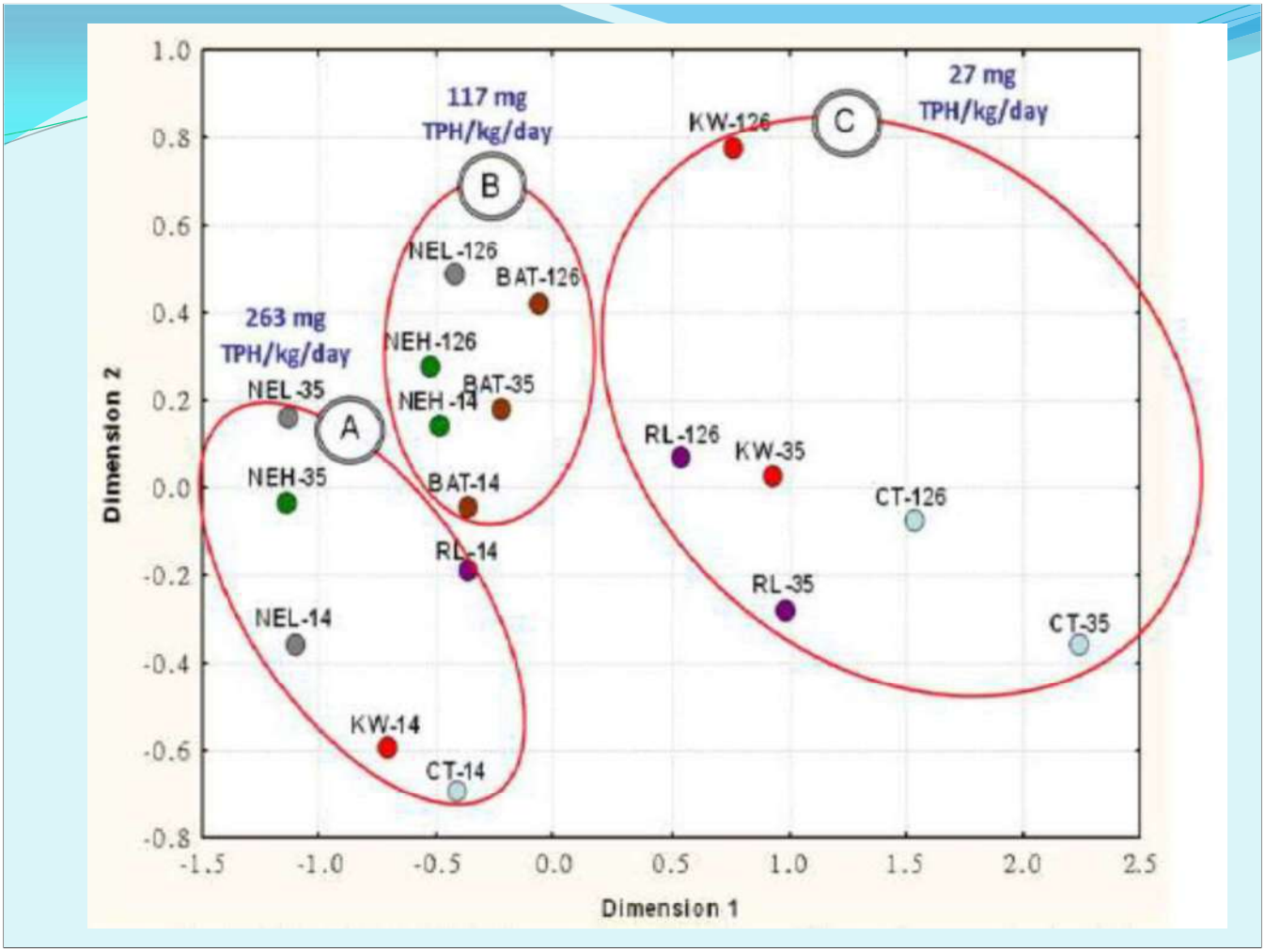


FIG. 4. PCA of combined enzyme TRF data from LTU samples. Each sample is labeled with the number of the day on which the sample was collected. Clusters determined by AHCA are labeled with numbers, and transitions between clusters are labeled with letters and arrows.

Microbial Community Shift (MDS)





Microarrays

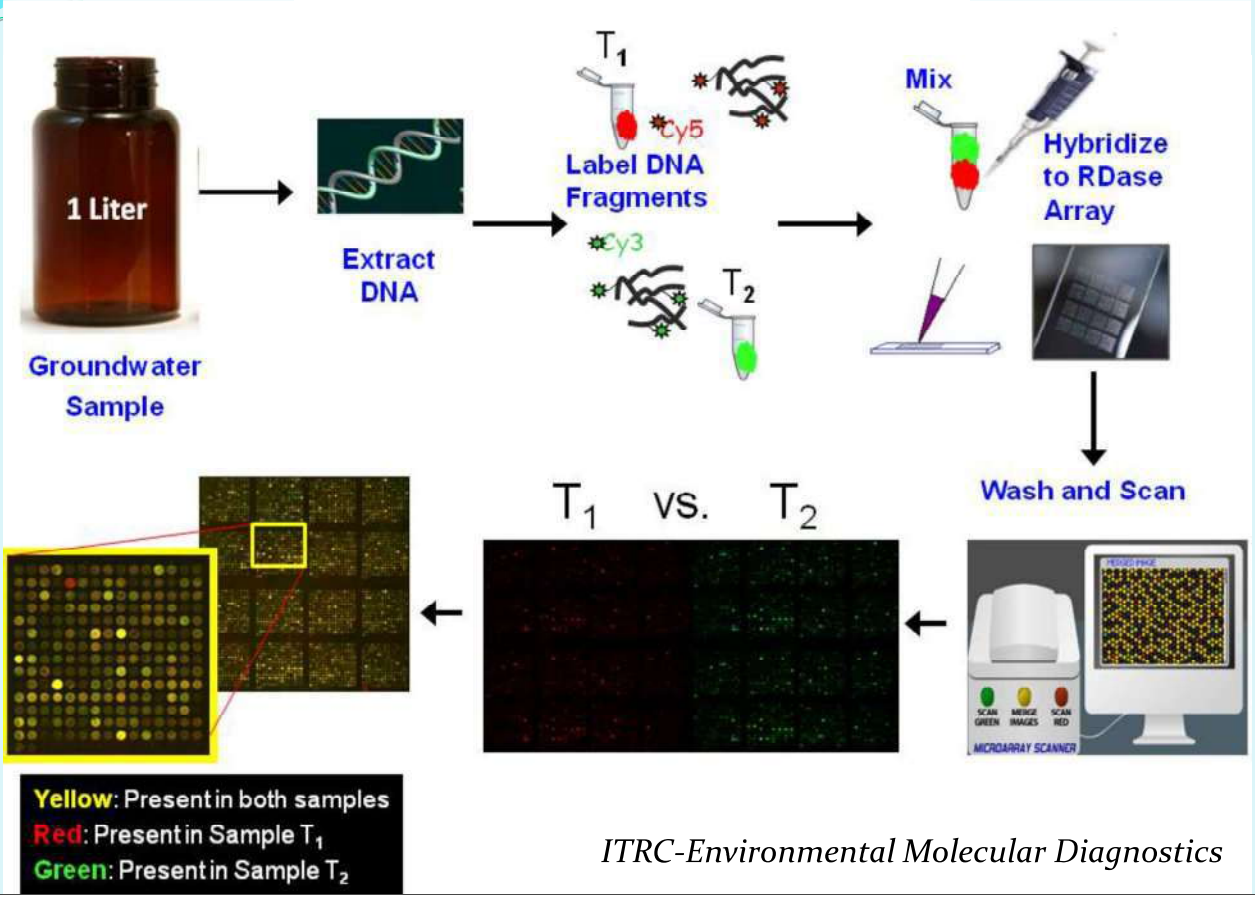
Microarrays exploit the hybridization effect between DNA strands to detect the presence of DNA sequences for specific genes using short single-stranded DNA molecules, called "probes", with known nucleotide sequences.

Microarrays can be fabricated in many forms and can contain up to hundreds of thousands of probes that target tens to thousands of genes.

Microarrays have been used for environmental research for at least 15 years but have only recently become widely commercially available.

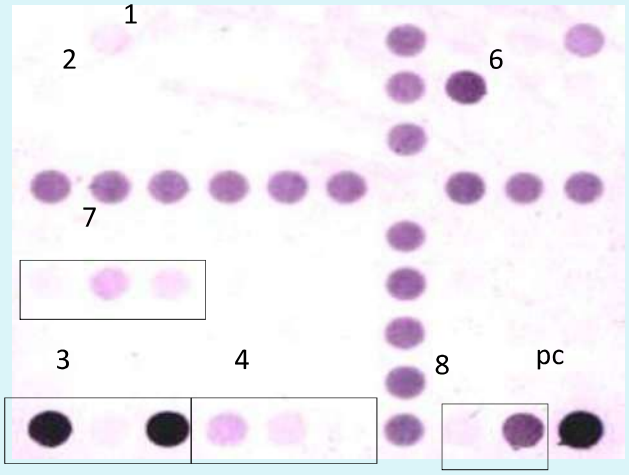
Microarrays can monitor changes in community structure and functional gene content in response to treatment such as biostimulation.

Generic microarray analysis



ITRC-Environmental Molecular Diagnostics

Microarray-Biochip for oil-degrading bacteria



1. ***Acinetobacter* sp.**
2. ***A. junii***
3. ***G. alkanivorans***
4. ***G. desulfuricans***
5. ***Pseudomonas* sp.**
6. ***P. aeruginosa***
7. ***R. picketti***
8. ***R. erythropolis***

Detection of oil-degrading bacteria in soil samples

Common phylogenetic primers used to detect and quantify specific degraders

Target group	Primer name	Sequence	Reference
Bacteria. Universal primers to determine total *Bacteria* concentration.	Unibac 8F Unibac 1541R	5′-AGAGTTTGATCCTGGCTCAG-3′ 5′-AAGGAGGTGATCCAGCCGCA-3′	Löffler et al. (2000)
Archaea. Universal primers to determine total *Archaea* concentration (including methanogens).	ARCH1-1369F ARCH2-1369F PROK1541R Probe	5′-CGGTGAATACGTCCCTGC-3′ 5′-CGGTGAATATGCCCCTGC-3′ 5′-AAGGAGGTGATCCTGCCGCA-3′ FAM-5′CTTGTACACACCGCCCGTC3′-BHQ-1	Suzuki et al. (2000)
Pseudomonas (16S rDNA), which is a catabolically versatile genus	Forward Reverse	5′-ACTGCATCCAAAACTGGCAA-3′ 5′-TCTCTGCATGTCAAGGCCT-3′	Duteau et al. (1998)
Dehalococcoides (16S rDNA), which dechlorinate PCE or TCE to ethane	FpDHC1 RpDHC1212	5′-GATGAACGCTAGCGGCG-3′ 5′-GGATTAGCTGTTCACACT-3′	Hendrickson et al. (2002)
Desulfitobacterium dehalogens (16S rDNA), which exhibits dechlorinating activity	Dd1 Dd2	5′-AATACCGNATAAGCTTATCCC-3′ 5′-TAGCGATTCCGACTTCATGTTC-3′	El Fantroussi et al. (1997)
Desulfomonile (16S rDNA), which exhibits dechlorinating activity	Dt1 Dt2	5′-CAAGTCGTACGAGAAACATATC-3′ 5′-GAAGAGGATCGTCTTTCCACGA-3′	El Fantroussi et al. (1997)
Geobacter sp. SZ (16S rDNA), an iron-reducing bacterium with dechlorinating activity.	*Geo*-F *Geo*-R	5′-GAATATGCTCCTGATTC-3′ 5′-ACCCTCTACTTTCATAG-3′	Sung (2004)
Bacteriophage (λ) primers are used as internal standard to calculate DNA recovery (%) from environmental samples	Forward reverse probe	5′-ACGCCACGCGGGATG-3′ 5′-AGAGACACGAAACGCCGTTC-3′ FAM 5′ CTTCTGGTTCTTCTGCACCTTGGACACC 3′-TAMRA	Beller et al. (2002)

(after Alvarez and Illman, 2006)

Catabolic gene primers used to detect and quantify biodegradation potential

Target group	Primer name	Sequence	Reference
Aerobic processes			
Catechol 2,3-dioxygenase, catalyzes aerobic degradation of BTEX, phenol, naphthalene, and biphenyl.	23CAT-F 23CAT-R DEG-F DEG-R QUANT-F	5′-CGACCTGATCTCCATGACCGA-3′ 5′-TCAGGTCAGCACGGTCA-3′ 5′-CGACCTGATC(AT)(CG)CATGACCGA-3′ 5′-T(CT)AGGTCA(GT)(AC)ACGGTCA-3′ 5′-CGACCTGATCTCCATGACCGATAACCGCA ACGAAGTGTTCTG-3′	Mesarch et al. (2000)
Naphtalene dioxygenase, which initiates the oxidation of napthalene and co-oxidizes other PAHs.	NAH-F NAH-R	5′-CAAAA(A/G)CACCTGATT(C/T)ATGG-3′ 5′-A(C/T)(A/G)CG(A/G)G(C/G)GACTTCTTTCAA-3′	Baldwin et al. (2003)
Toluene dioxygenase, which initiates aerobic degradation of BTEX, and chlorobenzene.	TOD-F TOD-R	5′-ACGGATGA(A/G)GA(C/T)CTGTACC-3′ 5′-CTTCGGTC(A/C)AGTAGCTGGTG-3′	Baldwin et al. (2003)
Xylene dioxygenase, which initiates aerobic xylene degradation.	TOL-F TOL-R	5′-TGAGGCTGAAACTTTACGTAGA-3′ 5′-CTCACCTGGAGTTGCGTAC-3′	Baldwin et al. (2003)
Biphenyl dioxygenase, which initiates the aerobic degradation of lightly chlorinated PCBs.	BPH1-F BPH1-R BPH2-F BPH2-RBPH3-F BPH4-F BPH3-R	5′-GGACGTGATGCTCGA(C/T)CGC-3′ 5′-TGTT(C/G)GG(C/T)ACGTT(A/C)AGGCCCAT-3′ 5′-GACGCCCGCCCCTATATGGA-3′ 5′-AGCCGACGTTGCCAGGAAAAT-3′ 5′-CCGGGAGAACGGCAGGATC-3′ 5′-AAGGCCGGCGACTTCATGAC-3′ 5′-TGCTCCGCTGCGAACTTCC-3′	Baldwin et al. (2003)

multicolumn4r@(Continued on next page)

(after Alvarez and Illman, 2006)

Catabolic gene primers used to detect and quantify biodegradation potential

Target group	Primer name	Sequence	Reference
Hydroxyl monooxygenases in the large subunits of the toluene monooxygenase gene.	RMO-F	5′-TCTC(A/C/G)AGCAT(C/T)CAGAC(A/C/G)GACG-3′	Baldwin et al. (2003)
	RMO-R RDEG-F	5′-TT(G/T)TCGATGAT(C/G/T)AC(A/G)TCCCA-3′	
	RDEG-R	5′-T(C/T)TC(A/C/G)AGCAT(A/C/T)CA(A/G)AC(A/C/G)GA(C/T)GA-3′	
		5′-TT(A/G/T)TCG(A/G)T(A/G)AT(C/G/T)AC(A/G)TCCCA-3′	
Phenol hydroxylases, hydroxylate (halo)phenols, and other phenolics	PHE-F	5′-GTGCTGAC(C/G)AA(C/T)CTG(C/T) TGTTC-3′	Baldwin et al. (2003)
	PHE-R	5′-CGCCAGAACCA(C/T)TT(A/G) TC-3′	
Anaerobic processes			
Benzylsuccinate synthase, which initiates anaerobic degradation of toluene and xylenes.	*bssA*-F	5′-ACGACGGYGGCATTTCTC-3′	Beller et al. (2002)
	bssA- R	5′-GCATGATSGGYACCGACA-3′	
	Probe	FAM-5′-CTTCTGGTTCTTCTGCACCTTGGACACC-3′-TAMRA	
TCE reductive dehalogenase system, which mediates the dechlorination of TCE to ethane.	*tceA*-797F	5′-ACGCCAAAGTGCGAAAAGC-3′	Magnuson et al. (2000)
	tceA-2490R	5′-GAGAAAGGATGGAATAGATTA-3′	

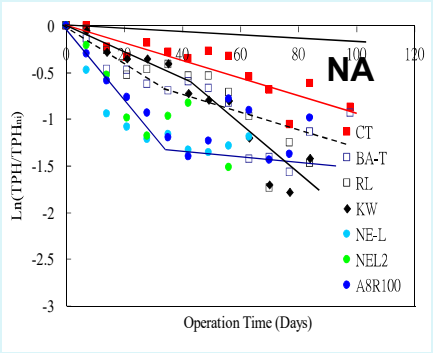
(after Alvarez and Illman, 2006)

Catabolic gene primers used to detect and quantify biodegradation potential

Vinyl chloride reductive dehalogenase, dechlorinates cis-DCE, and VC to ethane.	*vcr*A-F	5′ – CTATGAAGGCCCTCCAGATGC – 3′	Spormann et al. (2004)
	*vcr*A-R	5′ – GTAACAGCCCCAATATGCAAGTA - 3′	
Oxygen insensitive, nitro- and chromate-reductase subfamily NsfA, which reduces oxidized nitrogen and metal groups.	NfsA-F	5′-GTAGGATCCACGCCAACCATTGAAC-3′	Kwak et al. (2003)
	NfsA-R	5′-ACTGAATTCTTAGCGCGTCGCCCAAC-3′	
	NfsB-F	5′-GTAGGATCCGATATCATTTCTGTCGC-3′	
	NfsB-R	5′-ACTGAATTCTTACACTTCGGTTAAGGTG-3′	
NiFe hydrogenase gene, present in dissimilatory metal reducing bacteria.	Hyd1F	5′-CGCCCGCCGCGCCCCGCGCCCGTCCGCCGCCGCCCCCGCCG-3′	Wawer et al. (1995)
	Hyd5R	5′-GCAGGGCTTCCAGGTAGTGGGCGGTGGCGATGAGGT-3′	
Dissimilatory sulfite reductase (DSR) gene, present in all sulfate-reducing bacteria.	dsr1F	5′-ACSCACTGGAAGCACG-3′	Wagner et al. (1998)
	dsr4R	5′-GTGTAGCAGTTACCGCA-3′	
Nitrite reductases, present in denitrifying bacteria.	nirK1F	GG(A/C)ATGGT(G/T)CC(C/G)TGGCA	Braker et al. (1998)
	nirK2F	GC(C/G)(C/A)T(C/G)ATGGT(C/G)CTGCC	
	nirK3R	GAACTTGCCGGT(A/C/G)G(C/T)CCAGAC	
	nirK4R	GG(A/G)AT(A/G)A(A/G)CCAGGTTTCC	
	nirK5R	GCCTCGATCAG(A/G)TT(A/G)TGG	
	nirS1F	CCTA(C/T)TGGCCGCC(A/G)CA(A/G)T	
	nirS2F	TACCACCC(C/G)GA(A/G)CGGCGCGT	
	nirS3F	TTCCT(C/G/T)CA(C/T)GACGGCGGC	
	nirS4F	TTC(A/G)TCAAGAC(C/G)CA(C/T)CCGAA	
	nirS3R	GCCGCCGTC(A/G)TG(A/C/G)AGGAA	
	nirS5R	CTTGTTG(A/T)ACTCG(C/G)(C/G)CTGCAC	
	nirS6R	CGTTGAACTT(A/G)CCGGT	

(after Alvarez and Illman, 2006)

Case Study I
Demonstration of Bioaugmentation Application for TPH_d Bioremediation



Two Case Studies

- Case I – nine batch experiments
- Case II – five batch experiments

(Liu et al., 2009, JCTB)

Experimental Design

Bioaugmentation in Case I	Biostimulation in Case I
Consortia 1 ***Comamonas testosteroni* CC-CF3** ***Gordonia alkanivorans* CC-JG39** ***Pseudomonas aeruginosa* CC-RS1** **Consortia 2** ***Alcaligenes sp.* CC-ESB2** ***Gordonia desulfuricans* CC-DSM44462** ***Gordonia terrae* CC-NAPH129-6** ***Rhodococcus erythoropolis* CC-BC11**	**Rhamnolipid biosurfactant** **Glycolipid biosurfactant produced by *Pseudomonas spp.* J4.** **Reduce surface tension to less than 30 dyne/cm with a critical micelle concentration (CMC) value of 50 mg/L (Wei et al., 2005; Whang et al., 2007).**

Bioaugmentation in Case II	Biostimulation in Case II
Acinetobacter junii CC-FH2 ***Exiguobacterium aurantiacum CC-LSH-4*** **CC-JG39** **CC-BC11**	**Rhamnolipid biosurfactant** **Produced by *Pseudomonas spp.* S2 (Chen, et al., 2006).** **Belongs to anionic surfactant glycolipid, with mixed structure of mono- and di-rhamnolipid. E_{24} = 70%**

Experimental design - Case I

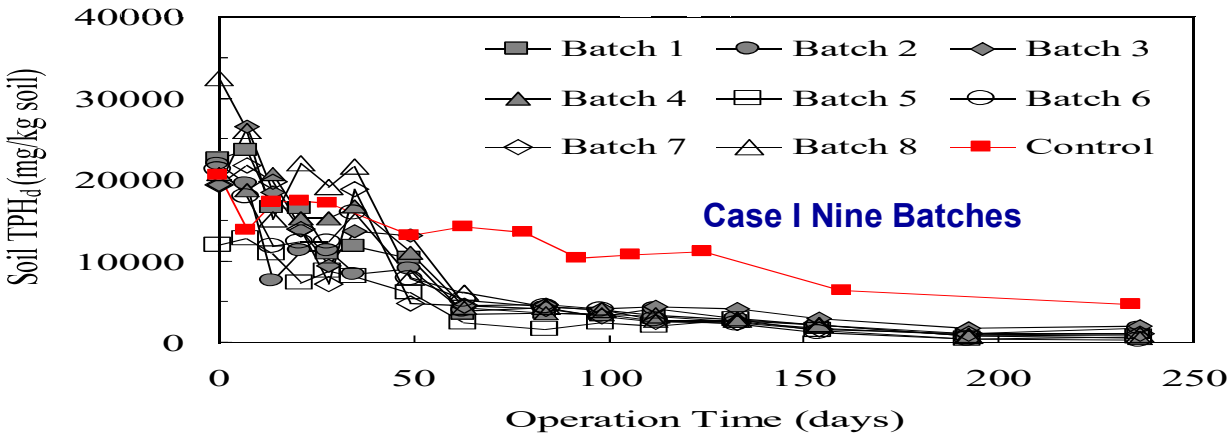
	Addition of diesel-degrading consortia	Bioaugmentation dosage (Log (CFU/g soil))	Biosurfactant dosage (mg RL/kg soil)
Batch 1	1	8	20
Batch 2	2	8	20
Batch 3	1	6	20
Batch 4	2	6	20
Batch 5	1	8	0
Batch 6	2	8	0
Batch 7	1	6	0
Batch 8	2	6	0
Control	0	0	0

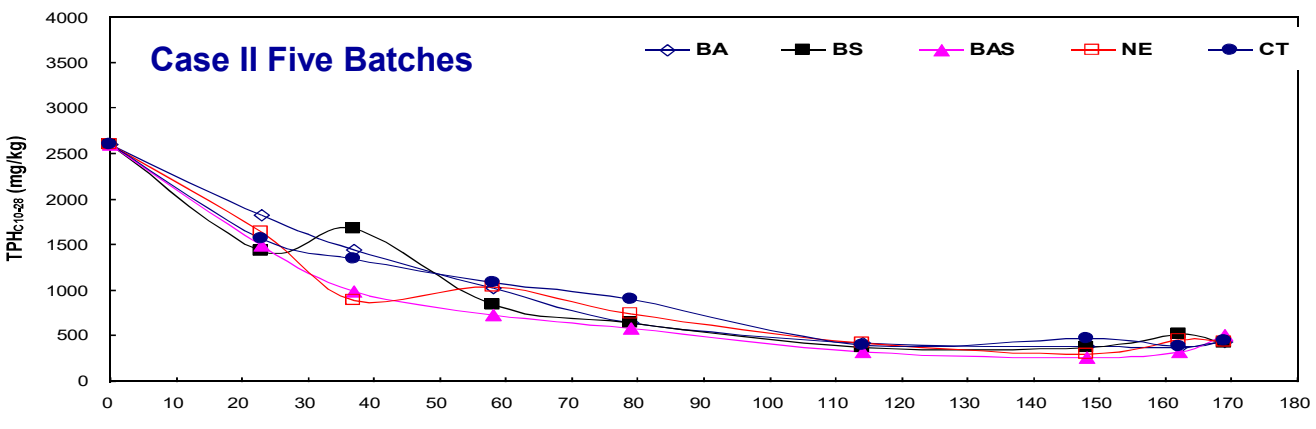
Consortia 1 (*Comamonas testosteroni* CC-CF3, *Gordonia alkanivorans* CC-JG39, *Pseudomonas aeruginosa* CC-RS1) and
Consortia 2 (*Alcaligenes sp.* CC-ESB2, *Gordonia desulfuricans* CC-DSM44462, *Gordonia terrae* CC-NAPH129-6, *Rhodococcus erythoropolis* CC-BC11)
RL: Rhamnolipids produced by *Pseudomonas aeruginosa*

Experimental design - Case II

Batch	BA	BS	BAS	NE	CT
Treatment	CC-FH2 CC-LSH-4 CC-JG39 CC-BC11	Rhamnolipid biosurfactant	CC-FH2 CC-LSH-4 CC-JG39 CC-BC11 + Rhamnolipid biosurfactant	Bushnell Hass medium	Treat the soil with nothing but turning over and watering

Variation of TPH_d for soil samples





Summary of rate constant estimations from one-stage and two-stage first-order kinetic approximation

Case I Nine Batches

Day	0-236	0-63	63-236
Treat-ment	k (d^{-1})	k_1 (d^{-1})	k_2 (d^{-1})
Bat 1	0.0144	0.0269	0.0087
Bat 2	0.0113	0.0220	0.0070
Bat 3	0.0113	0.0214	0.0063
Bat 4	0.0165	0.0215	0.0127
Bat 5	0.0140	0.0230	0.0093
Bat 6	0.0187	0.0192	0.0192
Bat 7	0.0142	0.0267	0.0049
Bat 8	0.0162	0.0243	0.0096
CT	0.0059	0.0045	0.0068

Case II Five Batches

Day	0-169	0-114	114-169
Treat-ment	k (d^{-1})	k_1 (d^{-1})	k_2 (d^{-1})
BA	0.0129	0.0164	0.0010
BS	0.0127	0.0175	0
BAS	0.0142	0.0196	0
NE	0.0130	0.0169	0
CT	0.0123	0.0158	0

Case I

k : 2 times faster than Control

k_1: 5 times faster than Control

Case II

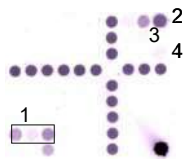
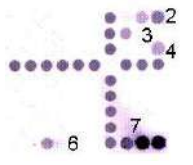
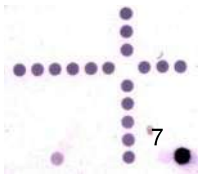
Similar Rates

Bioaugmentation: WHY It Works for Case I, but NOT Case II?

Identification of Diesel-Degrading Bacteria Using MicrroArray

Case I

Day 0

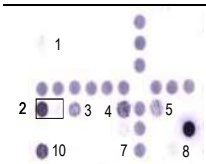
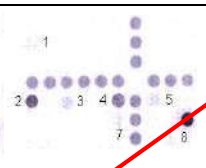
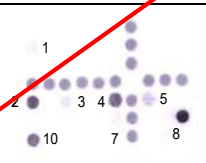
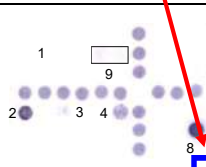
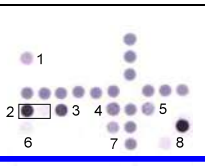
Batch 1	Batch 2	Control	Hybridization Mark v.s. Species
			1.*C. testosteroni* CF3 2. *Pseudomonas* sp. 3. *P. aeruginosa* RS1 4. *P. fluorescens* 5. *G. alkanivorans* JG39 6. *G. desulfuricans* DSM44462 7. *R. erythropolis* BC11
C. testosteroni *Pseudomonas* sp. ***P. aeruginosa*** *P. fluorescens*	***G. desulfuricans*** *Pseudomonas* sp. *P. aeruginosa* *P. fluorescens* ***R. erythropolis***	*R. erythropolis*	

Poor diversity on diesel-degarding consortia in Control

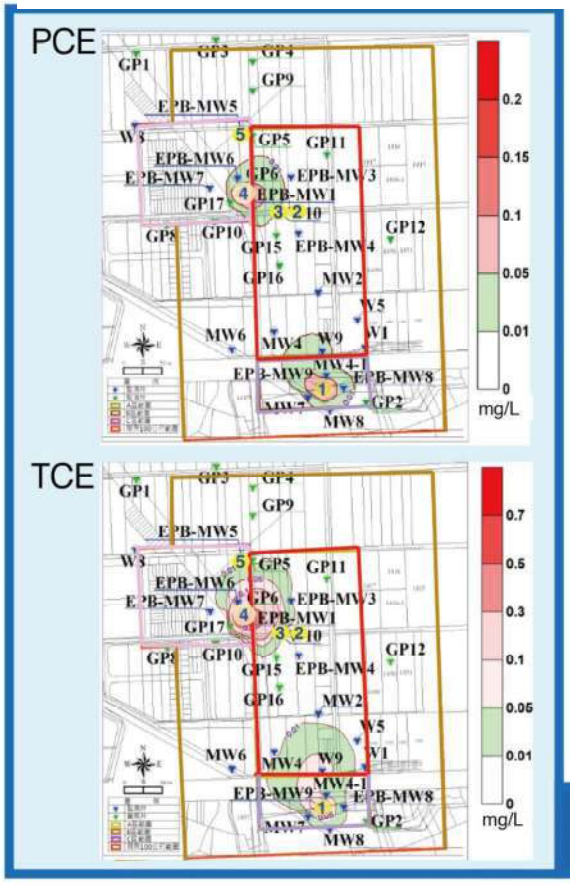
Rich diversity on diesel-degarding consortia in Augmenetd Batches

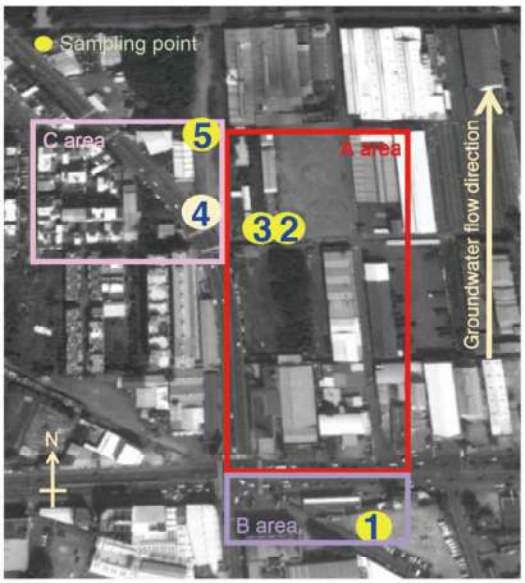
Case II

Day 0

BA	BS	BAS	NE	CT
				
1. Acinetobacter* sp.** ***2. G. alkanivorans *3. G. desulfuricans* *4. Pseudomonas* spp. *5. P. aeruginosa* *7. R. pickettii* *8. S. yanoikuyae* ***10. Rhodococcus erythropolis***	***1. Acinetobacter* sp.** ***2. G. alkanivorans*** *3. G. desulfuricans* *4. Pseudomonas* spp. *5. P. aeruginosa* *7. R. pickettii* *8. S. yanoikuyae*	***1. Acinetobacter* sp.** ***2. G. alkanivorans*** *3. G. desulfuricans* *4. Pseudomonas* spp. *5. P. aeruginosa* *7. R. pickettii* *8. S. yanoikuyae* ***10. Rhodococcus erythropolis***	***1. Acinetobacter* sp.** ***2. G. alkanivorans*** *3. G. desulfuricans* *4. Pseudomonas* spp. *8. S. yanoikuyae* *9. Bacillus cereus*	***1. Acinetobacter* sp.** ***2. Gordonia alkanivorans*** *3. Gordonia desulfuricans* *4. Pseudomonas* spp. *5. P. aeruginosa* *6. P. putida* *7. Ralstonia pickettii* *8. Sphingomonas yanoikuyae*

Case Study II Abundance of *Dehalococcoides* at in-situ PCE/TCE Bioremediation Sites

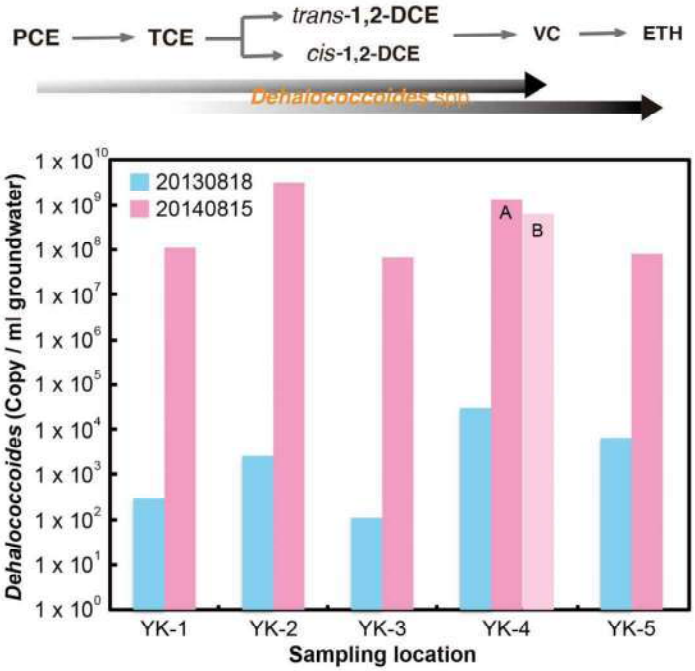




The sampling wells are numbered from upstream to downstream.

PCE and TCE hotspots: Location 1 and 4.

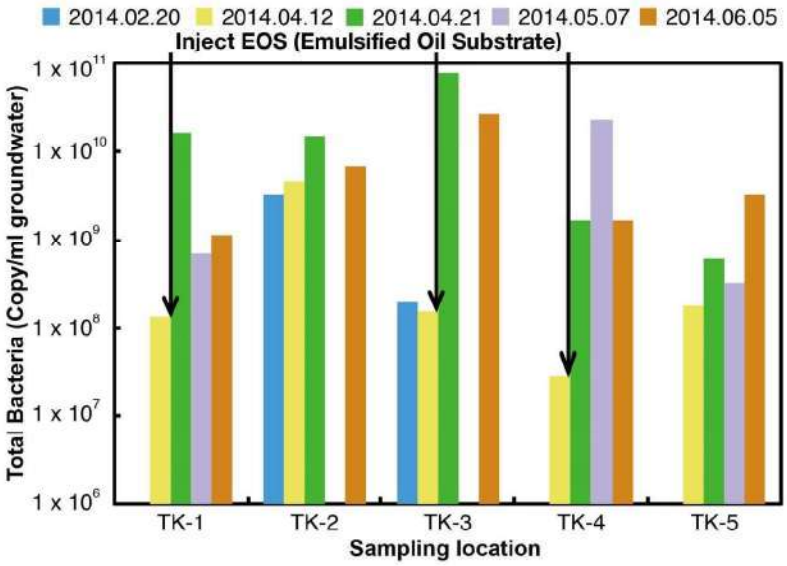
Case I - *Dehalococcoides* spp. in YK site

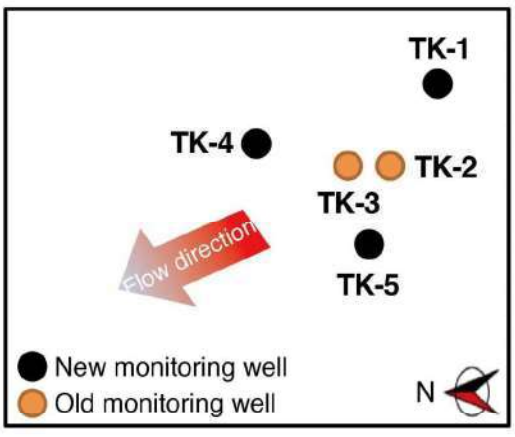


Dehalococcoides increased from 10^2 - 10^4 to 10^7 - 10^9 copies/ml groundwater after one-year remediation, suggesting that the addition of nutrients and biologics benefited to enrich targeted microbes in the chlorinated polluted site.

99

Case II - Total Bacteria in TK site



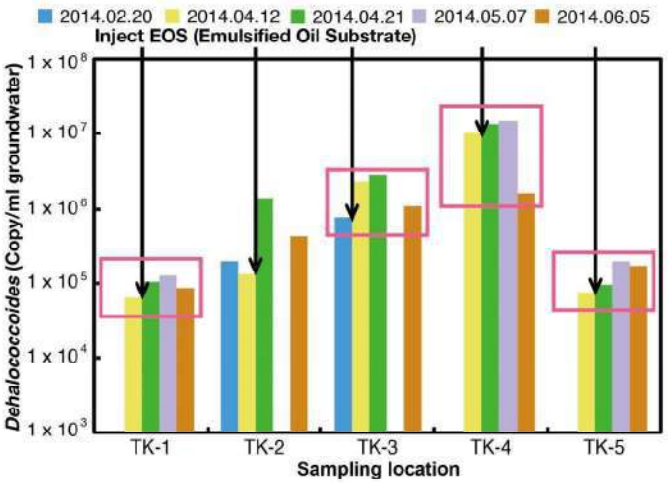


After injecting EOS, the concentratons of total bacteria increased and reached steady state after 1.5 months.

The sampling wells are numbered from upstream to downstream.

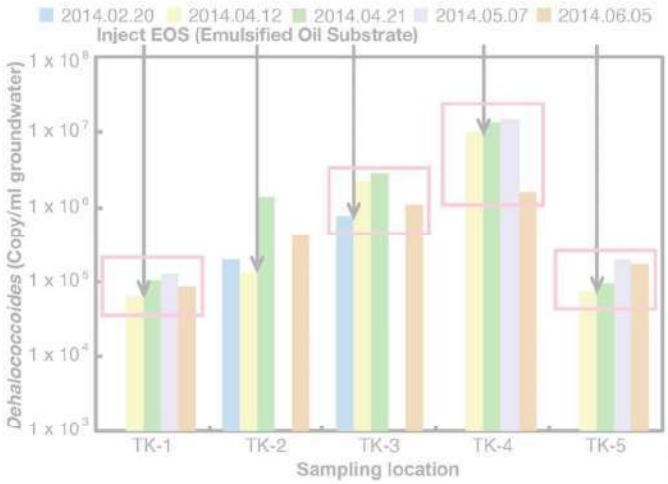
100

Case II - *Dehalococcoides* spp. in TK site



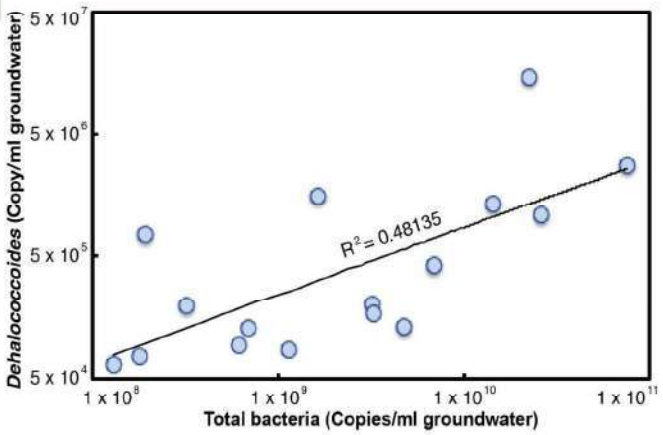
After EOS injection, slight increase of *Dehalococoides*

Case II - *Dehalococcoides* spp. in TK site

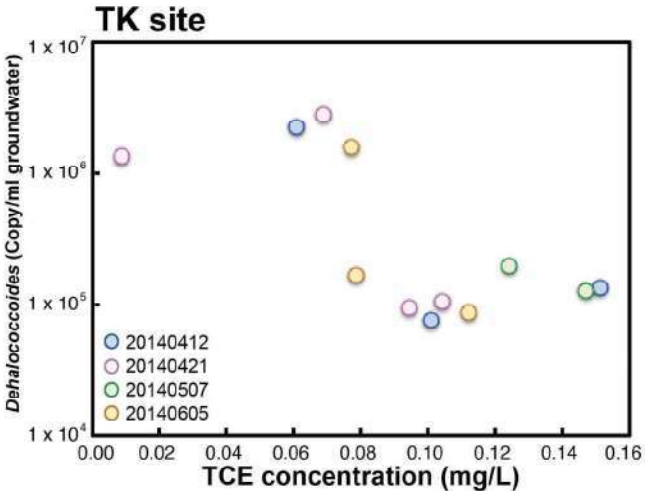


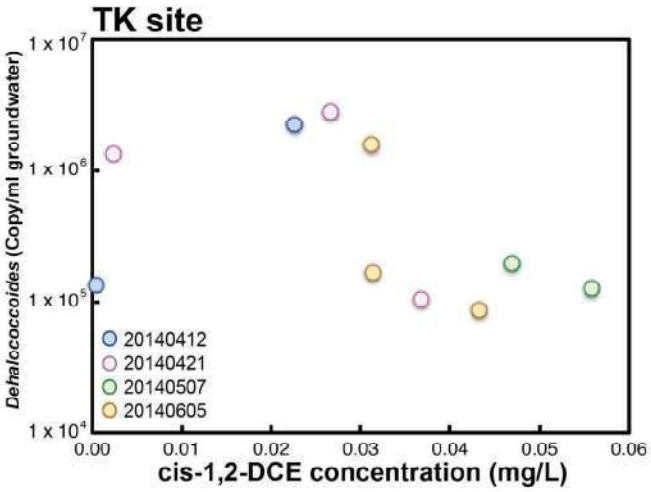
After EOS injection, slight increase of *Dehalococoides*

A postive correlation was observed for *Dehalococcoides* (*Dhc*) and total bacteria (TB), with *Dhc* to TB ratio of 0.005%.

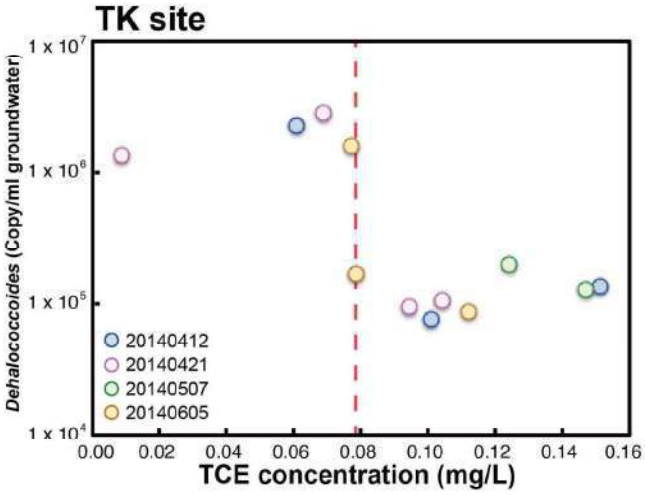


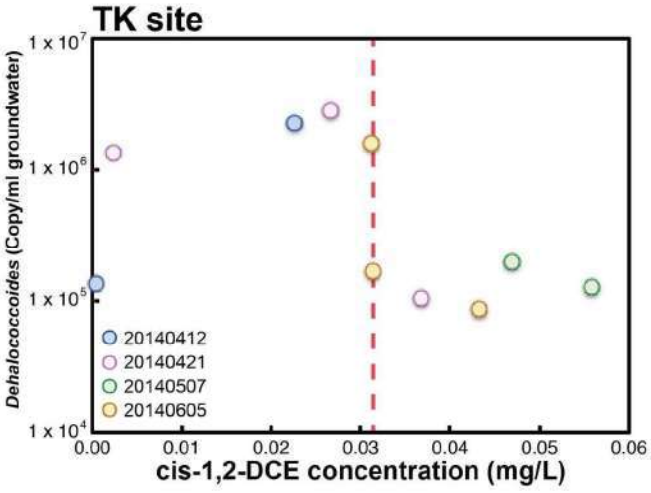
Dehalococcoides and TCE & DCE concentrations





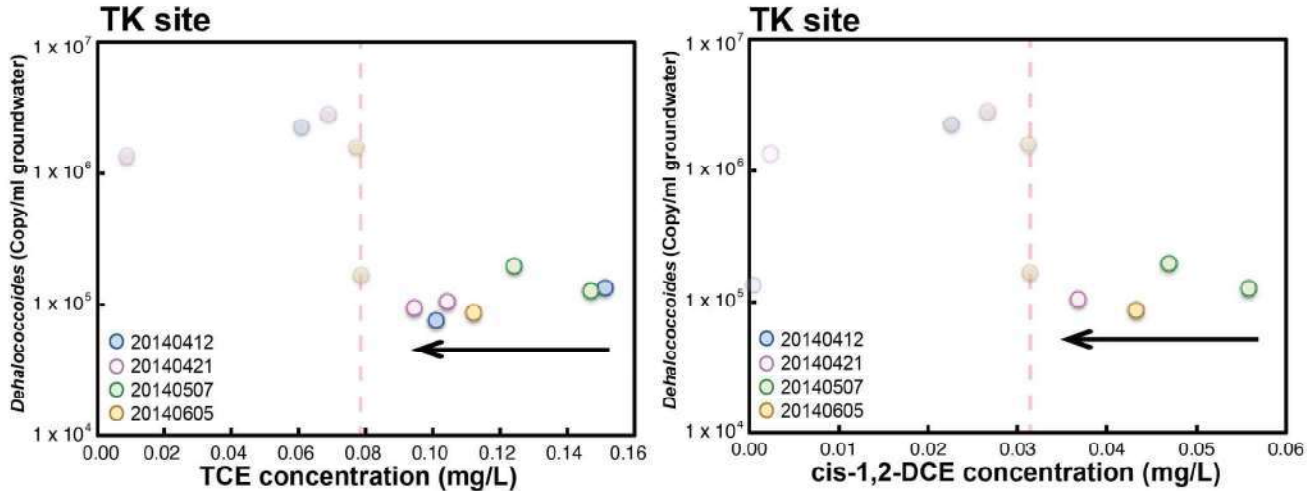
Dehalococcoides and TCE & DCE concentrations





High residual TCE and cis-1,2-DCE conc. were observed in the groundwater samples with lower *Dehalococcoides* concentrations (10^5 copies/ml), showing that microbial abundance may affect the degrading efficiency.

Dehalococcoides and TCE & DCE concentrations



High residual TCE and cis-1,2-DCE conc. were observed in the groundwater samples with lower *Dehalococcoides* concentrations (10^5 copies/ml), showing that microbial abundance may affect the degrading efficiency.

Under similar bacterial concentrations, TCE/DCE reduced with time, probably due to biodegradation.

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2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

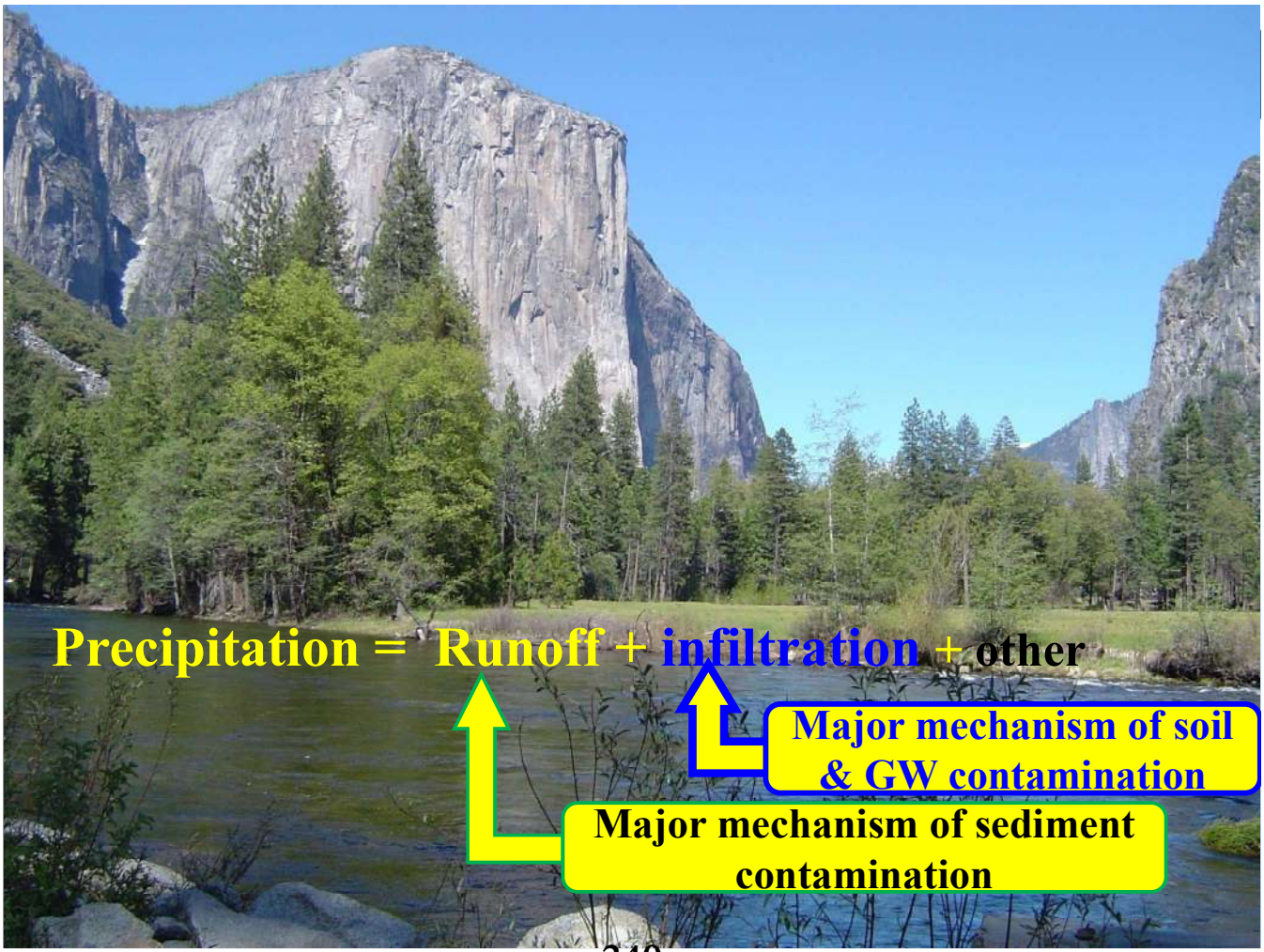
Contamination Site Investigation Case Studies in Taiwan

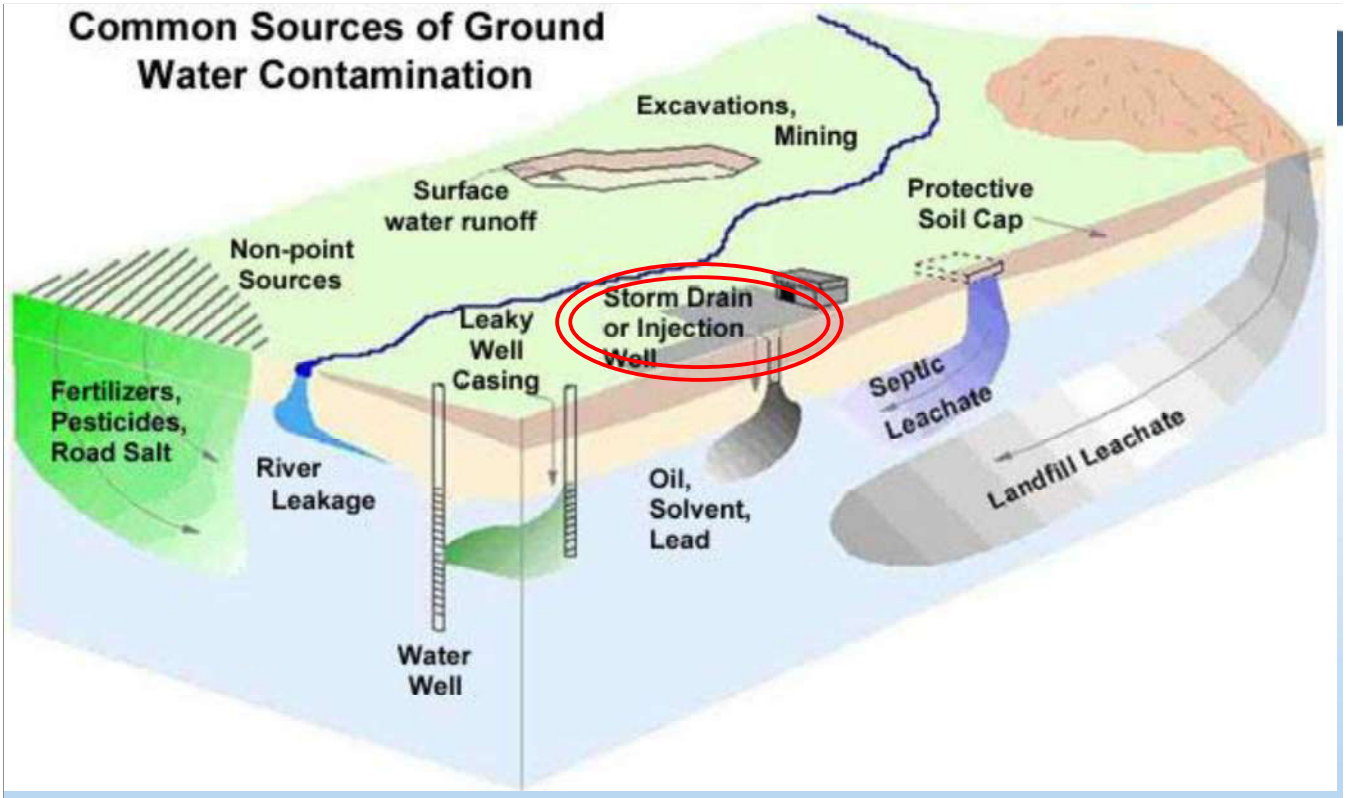
Chih-Jen Lu

Dept of Environmental Engineering

National Chung Hsing University

Taichung, TAIWAN



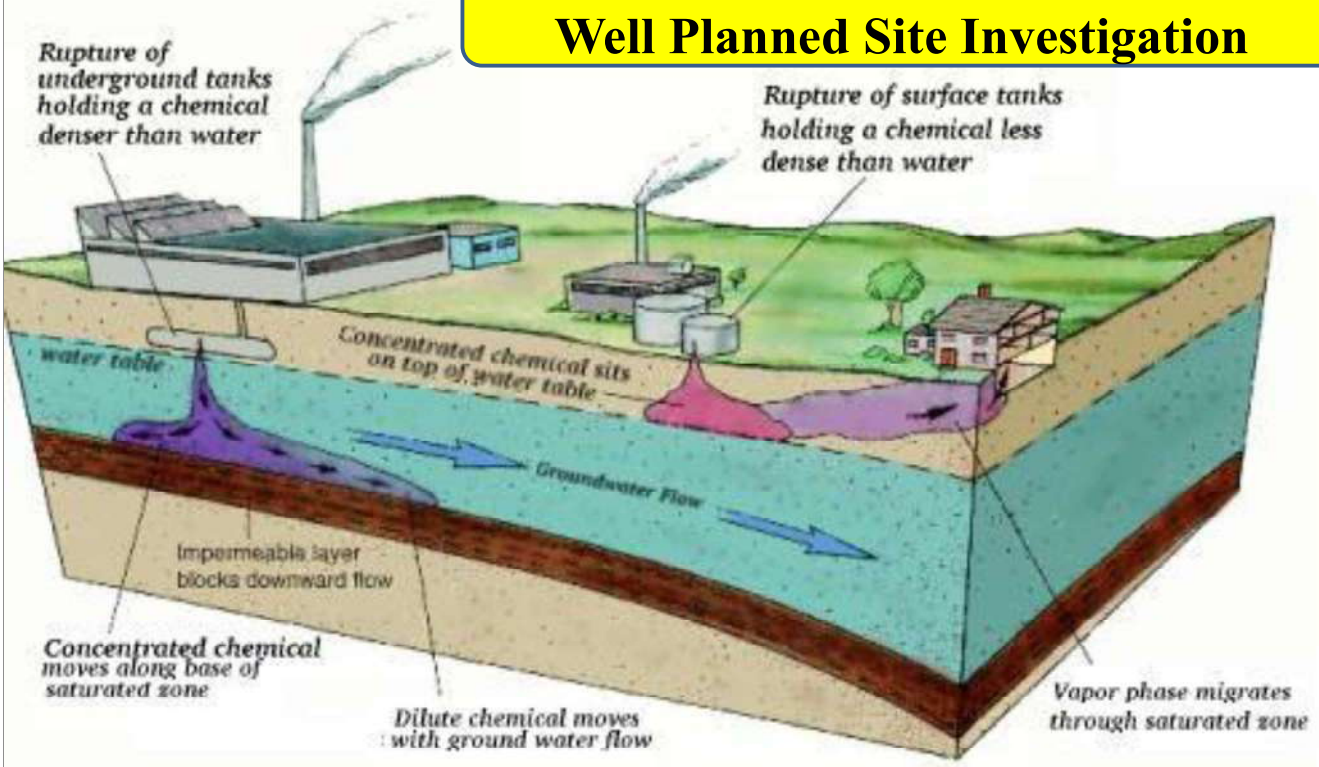


www.google.com.tw/search?q=groundwater+filtration

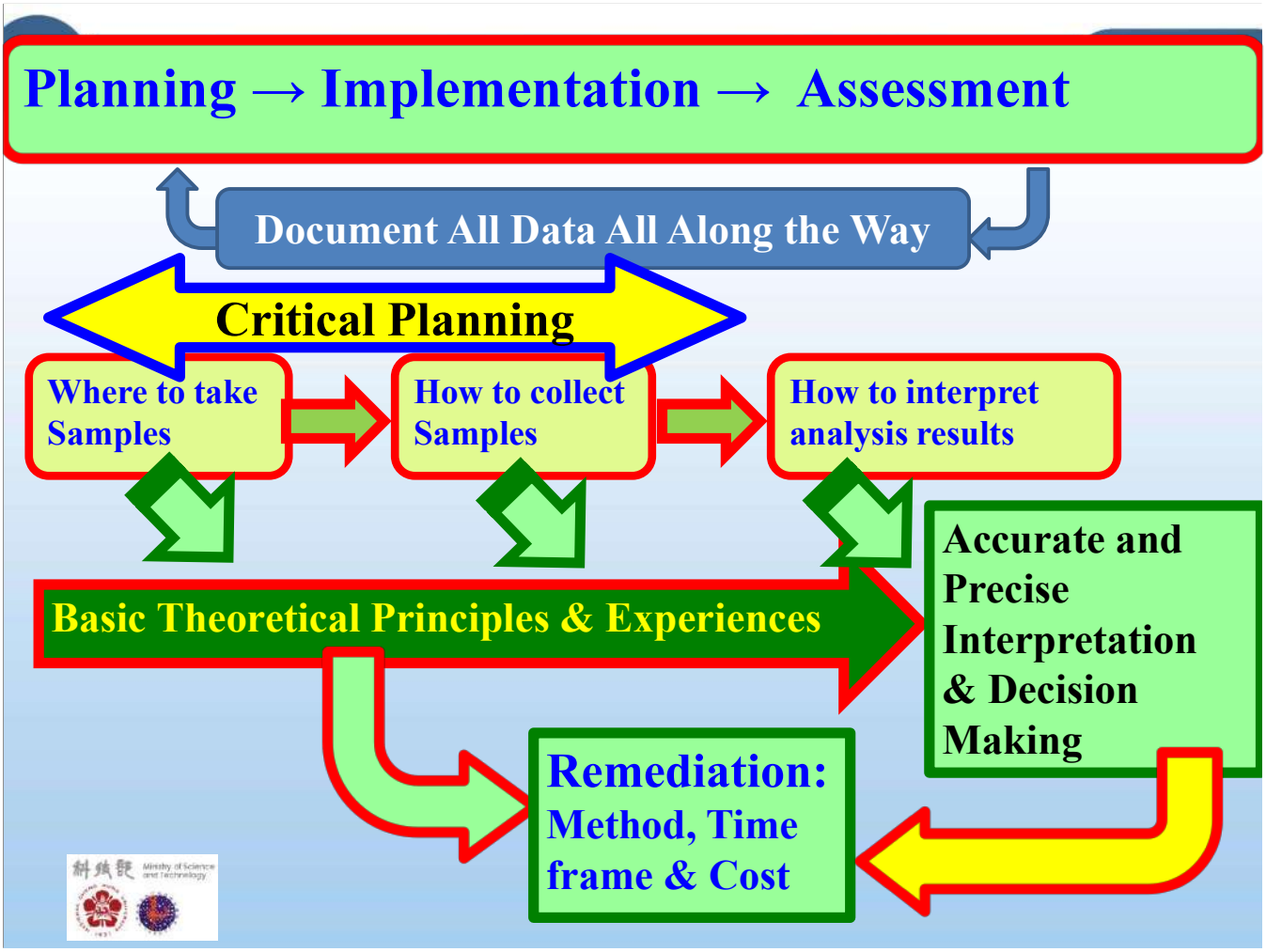
Soil & GW Contamination: Sources??

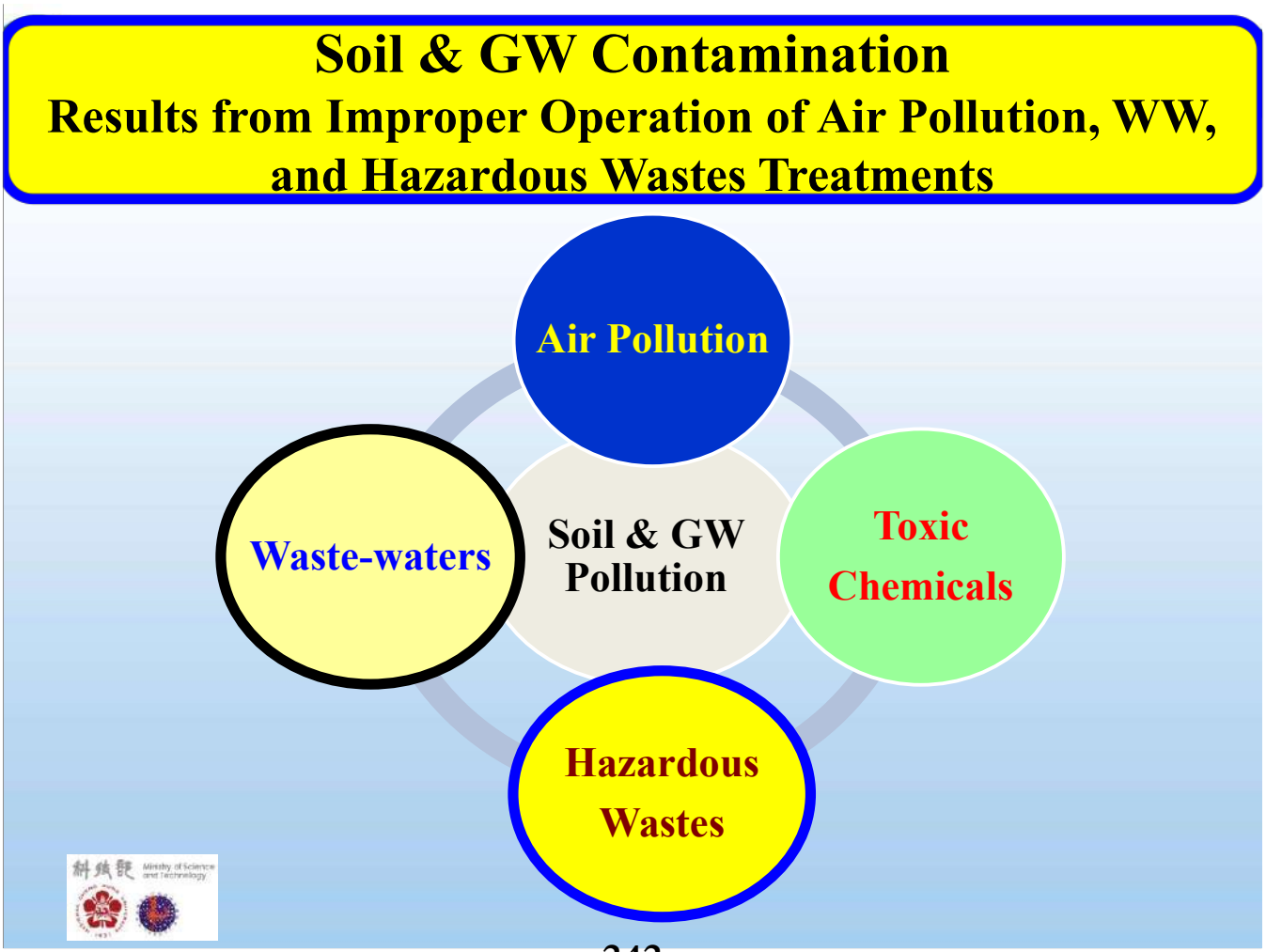
How to locate the contamination sources??

Well Planned Site Investigation

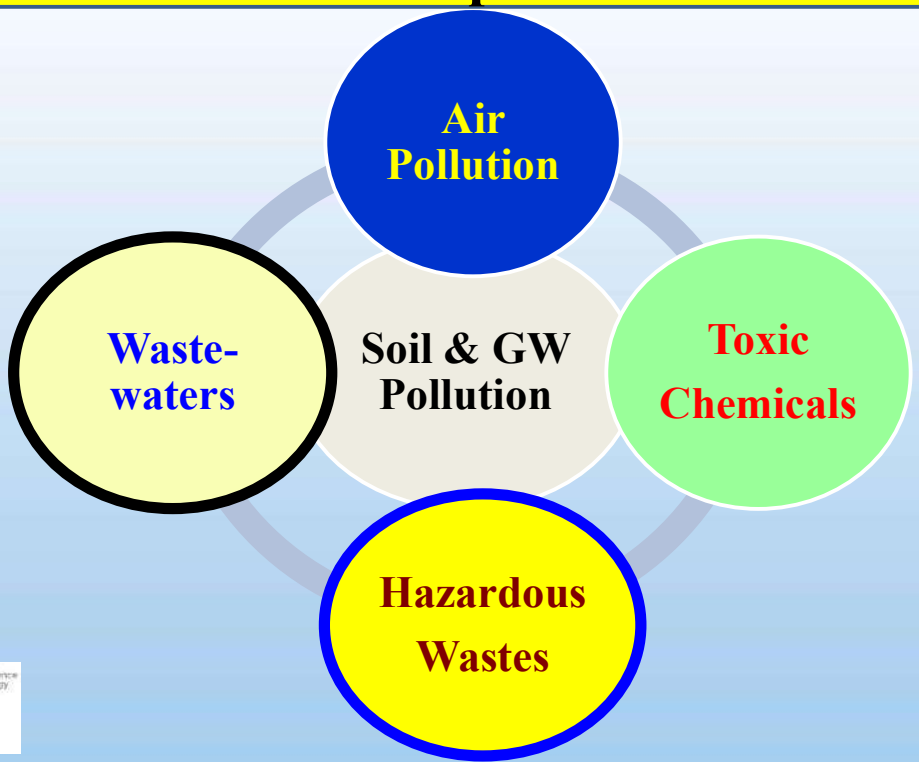


www.google.com.tw/search?q=groundwater+filtration


Planning → Implementation → Assessment
Document All Data All Along the Way
Critical Planning
Where to take Samples
How to collect Samples
How to interpret analysis results
Basic Theoretical Principles & Experiences
Accurate and Precise Interpretation & Decision Making
Remediation: Method, Time frame & Cost


Soil & GW Contamination
Results from Improper Operation of Air Pollution, WW, and Hazardous Wastes Treatments
Air Pollution
Waste-waters
Soil & GW Pollution
Toxic Chemicals
Hazardous Wastes

Soil & GW Contamination
Where were these Chemicals Stored, Operated, & Disposed



Site Investigation: Experiences in Taiwan

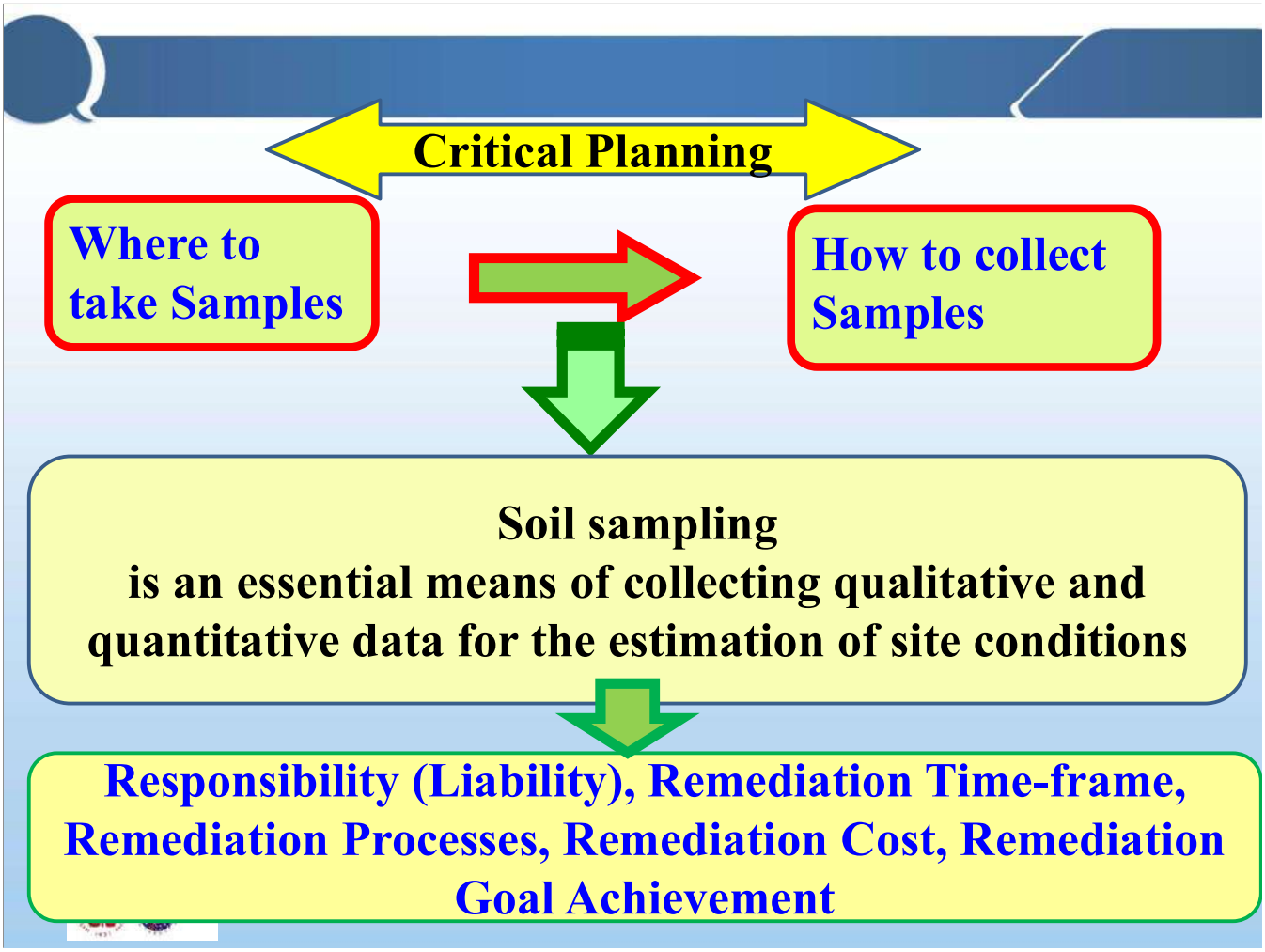
- **Site Investigation**
  - Gas Station (UST) (≒ 2600)
  - Abandoned Manufacturing Factories (> 2000)
  - Military Site
  - Operating Manufacturing Factories
  - Illegal Dumping Site (> 180)
  - Farmland (rice-paddy land)
  - Sanitary Landfill Site
  - Parks
  - Others (such as: residence area after the industrials being relocated, …)

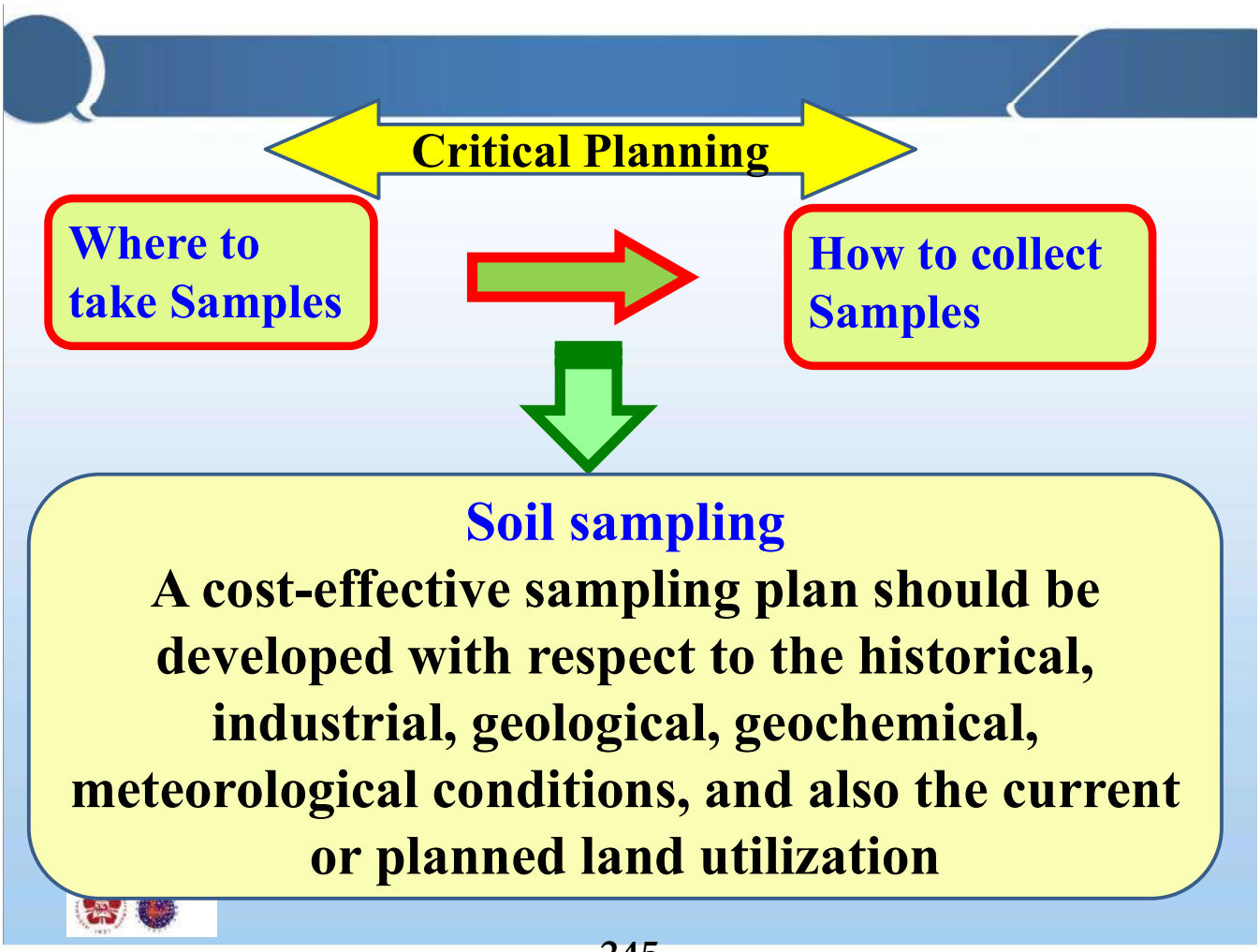
Sampling Design

- **Before the site investigation, we need to ask:**
  - **How much data do I need to make an acceptable decision**
  - **How much data do I need to make an adequate estimation about the extent of contamination (to define the contamination area)**
  - **How much data do I need to have a thorough search for a potential hot spot**

Sampling Design

- **Before the site investigation, we need to ask:**
  - **How should I design the sampling plan to provide the optimum information for the problem given when the sampling budge is limited**
  - **Where should I take samples**
  - **Does more data mean better data quality?**


Critical Planning
Where to take Samples
How to collect Samples
Soil sampling
is an essential means of collecting qualitative and quantitative data for the estimation of site conditions
Responsibility (Liability), Remediation Time-frame, Remediation Processes, Remediation Cost, Remediation Goal Achievement


Critical Planning
Where to take Samples
How to collect Samples
Soil sampling
A cost-effective sampling plan should be developed with respect to the historical, industrial, geological, geochemical, meteorological conditions, and also the current or planned land utilization

Site Investigation

- **Data from Site Investigation**
- To assure the environmental data being properly used to support decisions
  - Adequate quality and usability for their intended and original purpose
  - Managed to reduce potential errors
  - Defensible
  - Convincible

} **Liability**

Planning → Implementation → Assessment

Critical Planning

Where to take Samples → **How to collect Samples** → **How to interpret analysis results**

Basic Theoretical Principles & Experiences

Precise Interpretation & Decision Making

Make right decisions

Remediation: Method, Time frame & Cost

Site Investigation

- **Data from Site Investigation**
- Quality System for Data Collection
  - Make correct decisions
  - Conserve and/or optimize limited resource utilization
  - Make sure that environmental implementation programs and decisions are supported by data that are well-quality controlled and reliable

Sampling Design

- **Data Quantitative**
  - **Precision**
  - **Bias**
  - **Sensitivity**
- **Data Qualitative**
  - **Representativeness**
  - **Comparability**
  - **Completeness**

The collected data can represent the "realistic conditions"

Sampling Design: Representativeness

- **Representativeness expresses the degree to which data accurately used precisely represents a characteristics of a population, a parameter variation at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary**

Sampling Design: Representativeness

- **Representativeness**
- **Qualitative and quantitative statements regarding the degree to which data reflect the "true" characteristics of a well defined population**

Heterogeneity

No any single soil sample can be expressed as the "representative sample"

Error of Sample Heterogeneity

- **Representativeness**
- **Sample heterogeneity is a potential source of error**
  - **Soil is a heterogeneous medium**
  - **Soil exhibits variable properties with lateral distance and with depth**

Error of Sample Heterogeneity

- **Representativeness**
- **Sample heterogeneity is a potential source of error**

  - **The heterogeneity may also be present in the soil sample container**
  - **In the lab, the analysis uses only a small amount of the sample for analysis; if this soil sample container is not properly mixed and homogenized, the analysis may not be truly representative of the sample and of the corresponding site, even if the analysis is perfect**

Sampling Design: Representativeness

- **Representativeness**
- **Sample Representativeness**
  - **Includes procedures related to specimen selection, collection, and preservation**

Standard methods (procedures)

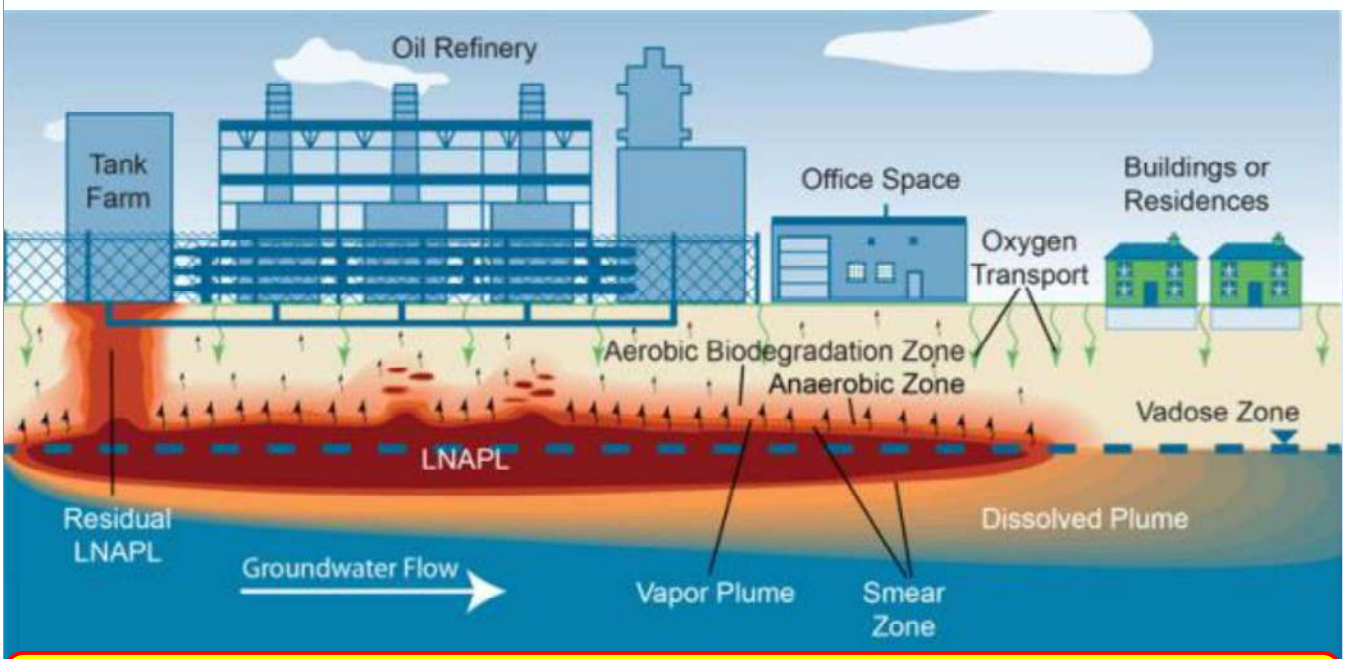
Sampling Design: Comparability

- **Comparability**
- **is a qualitative expression of the measure of confidence that two or more data sets may contribute to a common analysis**

Sampling Design: Completeness

- **Completeness**
- **is a measure of the amount of valid data obtained from a measurement system compared to the amount of data that was expected under normal conditions**
  - **In-completeness can be a source of bias**

Sampling Design: Conceptual Site Model



We need to define all the potential migration pathways
Unless, we do know the "exact" migration pathway

http://www.itrcweb.org/PetroleumVI-Guidance/

Sampling Design: Conceptual Site Model

- Develop the Conceptual Site Model (CSM)
  - What are the concerned contaminants
  - How did these contaminants arrive at this site
  - What are the fate and transportation of contaminants at this site
  - What is distribution of contaminants at this site

One of the most important components in the CSM

Sampling Design: Conceptual Site Model

- Conceptual Site Model
  - is a functional description of the contamination problems
    - Locations of contaminants/waste sources
    - Locations where contamination exists
    - Types and expected contaminants concentrations
    - Potentially contaminated media
    - Migration pathways
    - Potential receptors

A sampling plan should be developed based on the selected receptors of concern, the suspected contaminant sources, and pathways…

Sampling Design: Conceptual Site Model

- **Conceptual Site Model**
  - **is a functional description of the contamination problems**
    - **Locations of contaminants/waste sources**
    - **Locations where contamination exists**
    - **Types and expected contaminants concentrations**
    - **Potentially contaminated media**
    - **Migration pathways**
    - **Potential receptors**

Before the implement of any remediation process, all the contamination sources should be defined and contained

Sampling Design: Conceptual Site Model

- **Conceptual Site Model**
  - **is created as a site map or a flow diagram which is employed to describe the potential migration of contaminants to receptors.**
  - **Therefore, it is necessary to focus the sampling design to reduce the sampling errors**

Sampling Design: Conceptual Site Model

- **Conceptual Site Model**
  - Contamination sources
  - Contaminant releasing pathways
  - Contaminant dispersion
  - Contaminant migration (extent)
  - Contaminant fate (& potential mechanisms)
  - Contaminant concentration (spatial & temporal)
  - Contaminant & its intermediates (bio & chem)
  - Contaminated media & become as the contamination source
  - Exposure scenarios (receptors & media)

Sampling Design: Source of Contaminants

- **Source of contaminants**
  - Type of contaminations from every potential source
  - Where did the chemicals go if they were released into the environment

Site Investigation

- Migration Pathways
  - Migration pathways are routes by which contaminants have moved or may be moved away from a contamination source through the environmental media

Site Investigation

- Migration Pathways
  - Man-made pathways (such as: drainage channels, swage system …) (aerial photographs)
  - Surface drainage (such as: runoff, sediments…)
  - Vadose zone transport (vertical and horizontal movement) (readily adsorbed or highly soluble)
  - Wind dispersion (airborne particles, air pollution control system…)
  - Illegal WW re-charge
  - Others (such as: human or animal activity…)

Site Investigation: Sampling Media

- **Sampling Media**
- All potentially affected environmental media should be evaluated
  - Air Monitoring
  - Dust Sampling
  - Surface Water Sampling
  - Groundwater Sampling
  - Soil Sampling
  - Wastes (& Sludge) Sampling
  - WW Treatment Effluent Sampling
  - Sediment Sampling

Site Investigation: Contamination Boundary & Area

- **Contamination Boundary & Area**
  - The sampling data are representative
  - The data collected and sampling design incorporate with the areas or volumes that should be sampled
  - Spatial boundaries: define the physical area and volume from where the samples should be taken
  - Temporal boundaries: describe the time frame that the data will represent and when the samples should be taken

Site Investigation and Sampling

- **Analysis Results**
  - **Spatial and/or temporal variations**
  - **Species variations (disappeared species or "created" species)**
  - **The ratio of different species**
  - **The environmental factors to support these variations**

The assessment of the regular analysis results (such as: pH, ORP, DO, EC, TOC…) *vs.* environmental conditions

Aromatics, Aliphatics
Chlorinated Aromatics
Chlorinated Aliphatics
High MW Chemicals
VOC, PAH, PCB, BTEX
Pesticides, … & …

Species Variations & Environmental Factors

Samples Preservation & Analysis Instrument

Analysis: originally present contaminants and their intermediates in the natural environment

Sampling & Analysis

Contaminants and the potential intermediates

Site Investigation: Historical Site Data

- **Historical Site Data**
  - **All efforts should be made to first thoroughly review relevant site information (local and federal officers and relevant files…)**
  - **The historical information generally focuses on events and activities that affected current environment conditions at the site, such as manufacturing process, raw materials, accidents, leakage…**

Site Investigation: Historical Site Data

- **Historical Site Data**
  - **Therefore, the historical data review examines past and present site operations and disposal practices, providing an overview of known and potential site contaminations**

Site Investigation: Historical Site Data

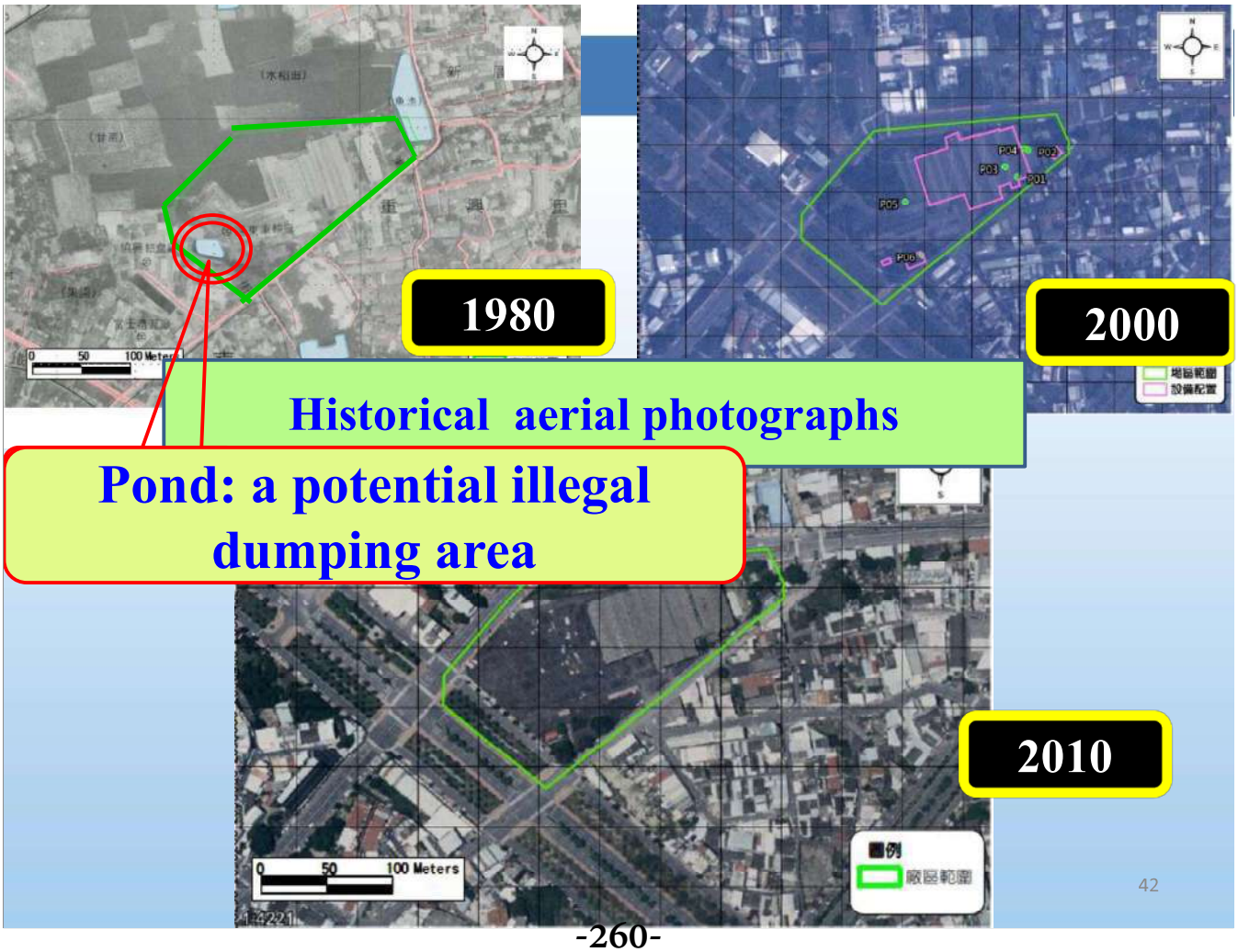
- **Historical Records**
  - **What industrial activities occurred at this site (manufacturing processes, waste storage, wastewater collection & treatment…)**
  - **What chemicals were used at this site (TPH, Cl-VOC, HM, Pesticides…)**
  - **Where and how were these chemicals used**

Site Investigation: Historical Site Data

- **Historical Records** (continued)
  - **Where and how were these chemicals stored & transported**
  - **Are these chemicals still in process, or have been wasted, or have been well stored**
  - **Were these chemicals spilled & spread**
  - **Were any remediation process employed in this site**

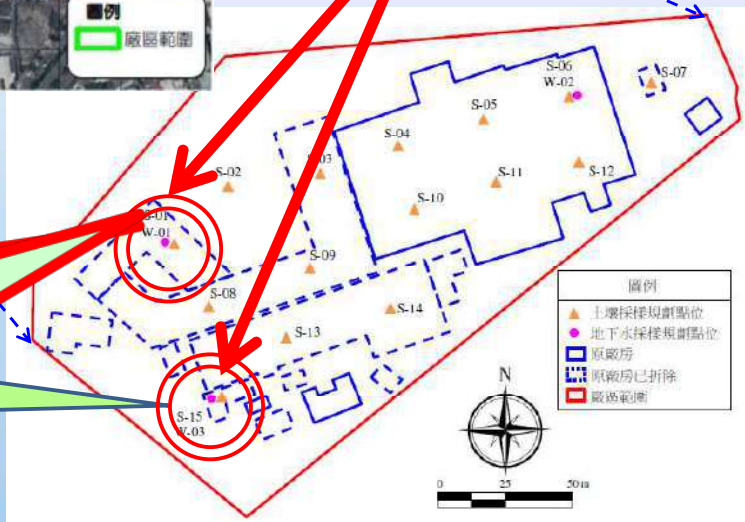
Site Investigation: Historical Site Data

- **Historical Records** (continued)
  - Collect site maps, facility blueprints, **historical aerial photographs**, storage tanks location, manufacturing processes, waste disposal location, utility pipelines, chemical transportation route (or pipeline), different manufacturing processes…

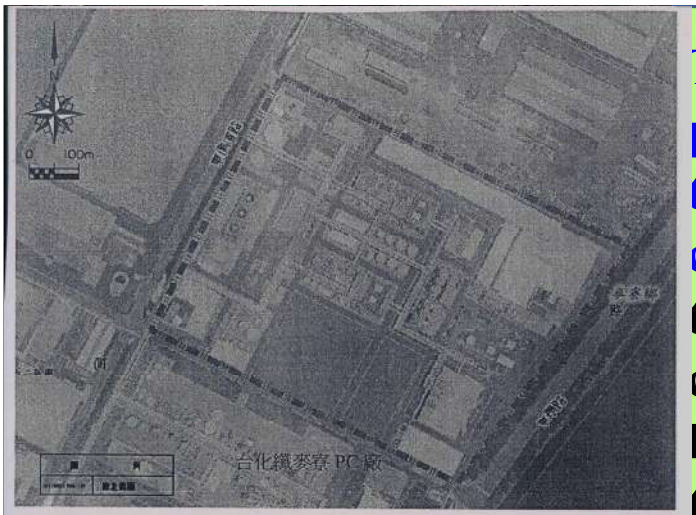


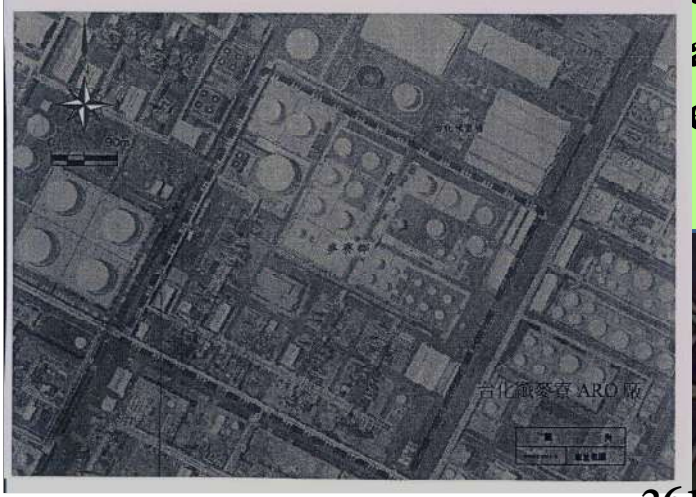
Historical aerial photographs

We found the pond area is one of the most terrible contaminated area in this site due to **the illegal dumping of hazardous wastes**

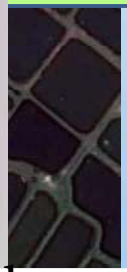


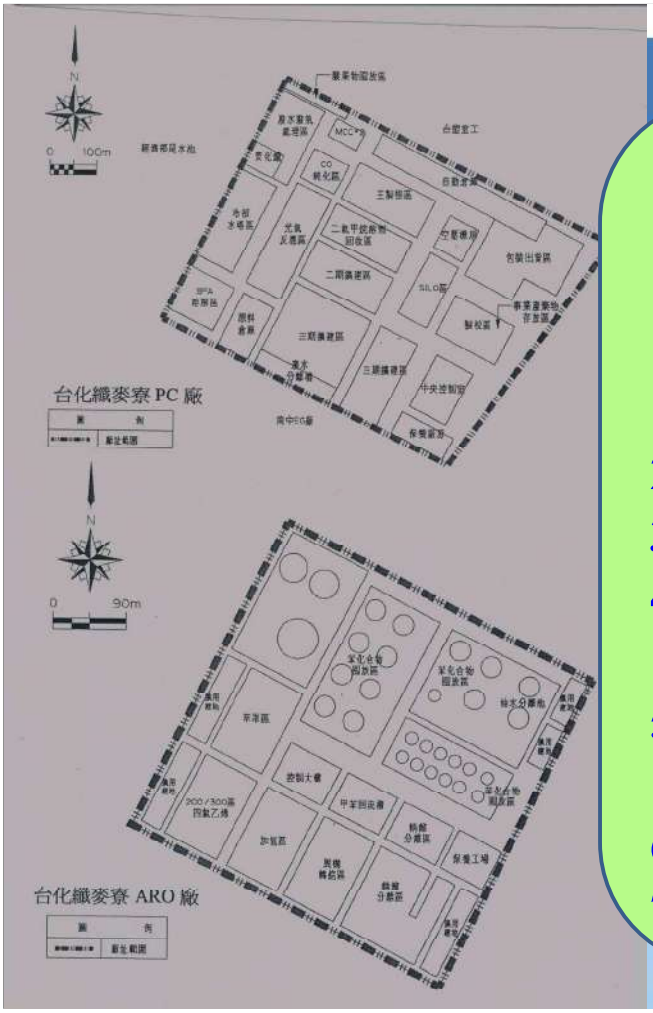
Soil Contamination: The source of GW contamination





The historical aerial photographs were employed to define the potential contaminated area (such as the fuel tanks, piping, WW collection channel, pits, hazardous wastes storage tanks, WW treatment plant, air pollution control equipments, …)

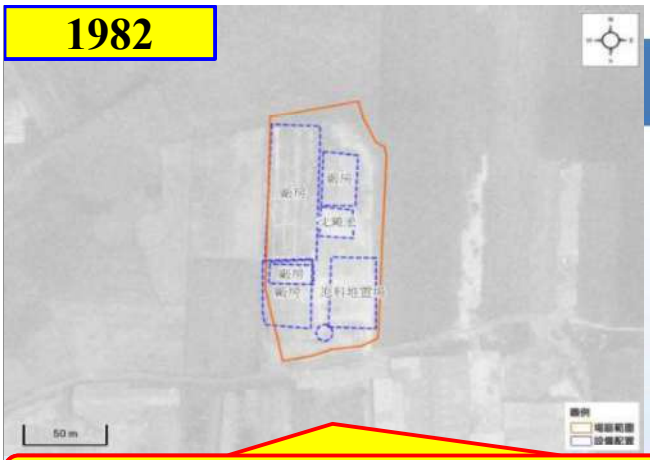




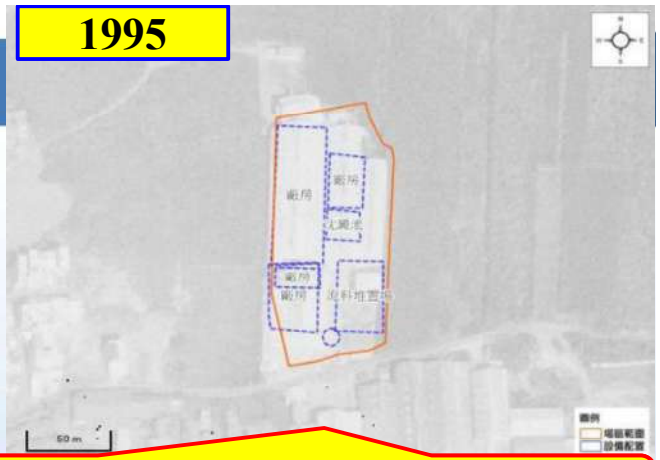
Sampling Area

1. Organic solvent (Cl-VOC) processing area (storage, recycling processes, wasted solvent tanks…)
2. Piping (pits…)
3. WW treatment
4. Hazardous wastes storage area
5. Air pollution control equipments
6. Tanks
7. …

1982



1995



The original processing area (blue dashes line)

2002

2014

Site Investigation: Abandoned Factories

- In Taiwan, a considerable number of up to 120,000 manufacturing factories have closed down before 2005

- In 2004, the EPA initiated a series of soil and groundwater investigations on abandoned factories in Taiwan.

Site Investigation: Abandoned Factories

- **Site Investigation**
  - **A comprehensive management of factories nationwide**
  - Establishment of a 2-stage screening mechanism
  - Establishment of the investigation standard operating procedure

It is impossible and impractical to have site reconnaissance on all the abandoned factories. Therefore, Taiwan EPA established a two-stage screen system to evaluate all the potential contamination sites.

Site Investigation: Abandoned Factories

- **Site Investigation** (continued)
  - Development of investigatory technical guidelines
  - Investigatory demonstration of abandoned plants
  - **Training of professional investigators**
  - Promotion of pollution prevention policies

Site Investigation: Abandoned Factories

- **Site Investigation**
- A comprehensive management of factories nationwide
  - The majority of soil and groundwater pollution originated from industrial activities. Therefore, Taiwan EPA comprehensively investigated potentially highly contaminated factories that closed down before January 1, 2005.

Site Investigation: Abandoned Factories

- **Site Investigation**
- A comprehensive management of factories nationwide
  - As well as, the factory manager must provide soil pollution investigation and assessment report to local Environmental Protection Bureau after 2005, when the enterprise or the manufacturing factories implement the transfer of land, establishment a new company, termination the operating processes, or closure the factories, according to Articles 8 and 9 of the Soil and Groundwater Pollution Remediation Act (Taiwan).

Site Investigation: Abandoned Factories

- **Site Investigation**
- A comprehensive management of factories nationwide
  - Based on these procedures, it is effective to manage the nationwide factories avoiding soil and groundwater contamination being purposely covered.

- Taiwan EPA established a quantitative screening assessment mechanism, providing a reference for priority investigation of factories. **The primary indicators included the following**:

- **(1)** the factory size indicators, such as area, capital and years of operation;
- **(2)** factory pollution indicators, such as raw material and its quantity, product and its quantity, and the categories and amount of wastes and wastewater;

- The primary indicators included the following:

- **(3)** factory management indicators, such as past records of environmental pollution, industrial safety incidents, and accidental hazards; and
- **(4)** environment indicators, such as type of land used, usage of neighboring lands, and crucial environmentally sensitive areas.

Abandoned Factories in Taiwan

Top 10 types of Potentially Highly Contaminated Abandoned Factories in Taiwan

Leather, Fur & Related Products Manufacturing
Wood and Bamboo Products Manufacturing
Basic Chemical Material Manufacturing
Petrochemicals Manufacturing
Fertilizers Manufacturing
Man-made Fibers Manufacturing
Synthetic Resin and Plastic Materials Manufacturing
Synthetic Rubber Manufacturing
Varnishes, Lacquers, Dyes, Pigments Manufacturing
Pesticides and Herbicides Manufacturing

Top 10 types of Potentially Highly Contaminated Abandoned Factories in Taiwan

Leather, Fur & Related Products Manufacturing
Wood and Bamboo Products Manufacturing

Leather: VOC, SVOC, preserves, Cr, HM-contained dye…

Wood Products: Cl-Aromatics (PCP), TPH, Cr…

Top 10 types of Potentially Highly Contaminated Abandoned Factories in Taiwan

Basic Chemical Material Manufacturing

Chemical Industries: Cl-VOC, Cl-Aromatics, HM-contained Catalysts…

Petrochemicals Manufacturing

Petrochemicals: TPH, Aliphatics, Aromatics, Cl-Aliphatics, Cl-Aromatics, …

Top 10 types of Potentially Highly Contaminated Abandoned Factories in Taiwan

Pesticides and Herbicides Manufacturing

Pesticides Industries: Cl-Aromatics (Cl-phenols, Cl-Benzenes), Dioxin, HM (Arsenic), …

ESA

- **The ESA process used by Taiwan EPA:**

- (1) Collection information: most data on abandoned factories in Taiwan were either lost or destroyed; thus, the evaluator has to obtain relevant data from the local government of Construction Bureau and Environmental Protection Bureau. Subsequently, the obtained information and **aerial photographs** were used to deduce the factory configuration and the possible contaminated regions.

aerial photographs: an important tool to locate the potential contamination area if the manufacturing factories are not in process during the investigation period

- The ESA process used by EPA is described as follows:

- (2) Reconnaissance: part of factories were destroyed and reconstructed or were transferred to other factory, the evaluator has to visit the actual realistic site to confirm the location of potential pollution sources and other crucial characteristics while recording any abnormalities in soil appearances, waste disposal areas, or any severe leakages

61

62

- The ESA process used by EPA is described as follows:
- (3) Interview: the evaluator conducts interviews with relevant responsible persons, employees, land owner and users to acquire additional data on factory operations.

- The ESA process used by EPA is described as follows:
- (4) Investigation plan: the evaluator has to determine potentially highly contaminated regions; subjective assessments were used to distribute sampling points and analyzed items.

The result of Site Investigation in 2013 (200 Sites)

Item	Soil Contamination	GW Contamination	
Type of Pollutant			
• Heavy metal	80	5	HM: Soil Contamination
• Total petroleum Hydrocarbons	22	0	
• Polychlorinated biphenyls	6	0	
• Volatile organic compounds	2	9	Cl-VOC: GW Contamination
• Dioxin	1	0	
• Pesticide	1	0	
• Total phenolic Compounds	-	1	

Priority List of 21 types of Potentially Highly Contaminated Abandoned Factories in Taiwan

No.	Industry	No.	Industry
1	Leather, Fur & Related Products Manufacturing	12	Plastic Products Manufacturing
2	Wood and Bamboo Products Manufacturing	13	Basic Metal Manufacturing
3	Basic Chemical Material Manufacturing	14	Metal Surface Treating
4	Petrochemicals Manufacturing	15	Metal Heat Treating
5	Fertilizers Manufacturing	16	Computers, Electronic & Optic Prod. Manufacturing
6	Man-made Fibers Manufacturing	17	Electronic Parts & Components Manufacturing
7	Synthetic Resin and Plastic Materials Manufacturing	18	Electrical Equipment Manufacturing
8	Synthetic Rubber Manufacturing	19	Electricity Supply
9	Varnishes, Lacquers, Dyes, Pigments Manufacturing	20	Waste Collection
10	Pesticides and Herbicides Manufacturing	21	Waste Treatment and Disposal
11	Petroleum and Coal Products Manufacturing		

The Major Contaminated Regions in the Abandoned Factory Investigations

- Manufacturing area
- Wastewater treatment facilities
- Open space
- Storage tank and pipeline area
- Waste disposal region
- Material storage area
- Boiler room, drying room, chimney area, and dust collection area
- Storage pond
- Other (cracked pavements or electrical room)

Cultivation of professional investigators

- Training of professional investigators

- The investigation of abandoned factories is different from operation factories. Investigators who are unfamiliar with the investigations and characteristics of the abandoned factories will frequently overlook the potential contaminated regions by factories and facilities disappearing or removing.

Cultivation of professional investigators

- **Training of professional investigators**
- **Therefore, Taiwan EPA has hosted seminars and training programs in which investigation experiences, feedback, and reviews are shared to relevant experts (e.g., those associated with environmental protection bureaus, local county and city governments, construction bureaus, industrial competent authorities, industrial associations, and technical consulting companies).**

A Comprehensive Survey of Abandoned Factories

- **A comprehensive survey of abandoned factories**
- Factories and lands in Taiwan are often converted for varying uses, which may cause the area of contamination to expand further. Moreover, the address at which early factories were registered may have changed when administration regions were readjusted or lands were reconstructed. The current status, usage, and location of the 42,000 abandoned factories are unknown, further elevating the uncertainty of pollution. Consequently, promoting a comprehensive survey of abandoned factories is critical.
-

A Comprehensive Survey of Abandoned Factories

- **A comprehensive survey of abandoned factories**

- By using the baseline data on abandoned factories, the developed support system, and portable data processors, Taiwan EPA has completely surveyed all the abandoned factories in Taiwan within 2 years, compared whether the address and location of the surveyed targets coincided with those registered, and subsequently established a database containing information on the current statuses of factory lands, existing facilities and operations, and the sensitivity of surrounding environments.

The Major Contaminants in the Abandoned Factory Investigations

- **Heavy metal**
- **Total petroleum hydrocarbons**
- **Polychlorinated biphenyls**
- **Volatile organic compounds**
- **Dioxin**
- **Pesticide**
- **Total phenolic compounds (phenols)**

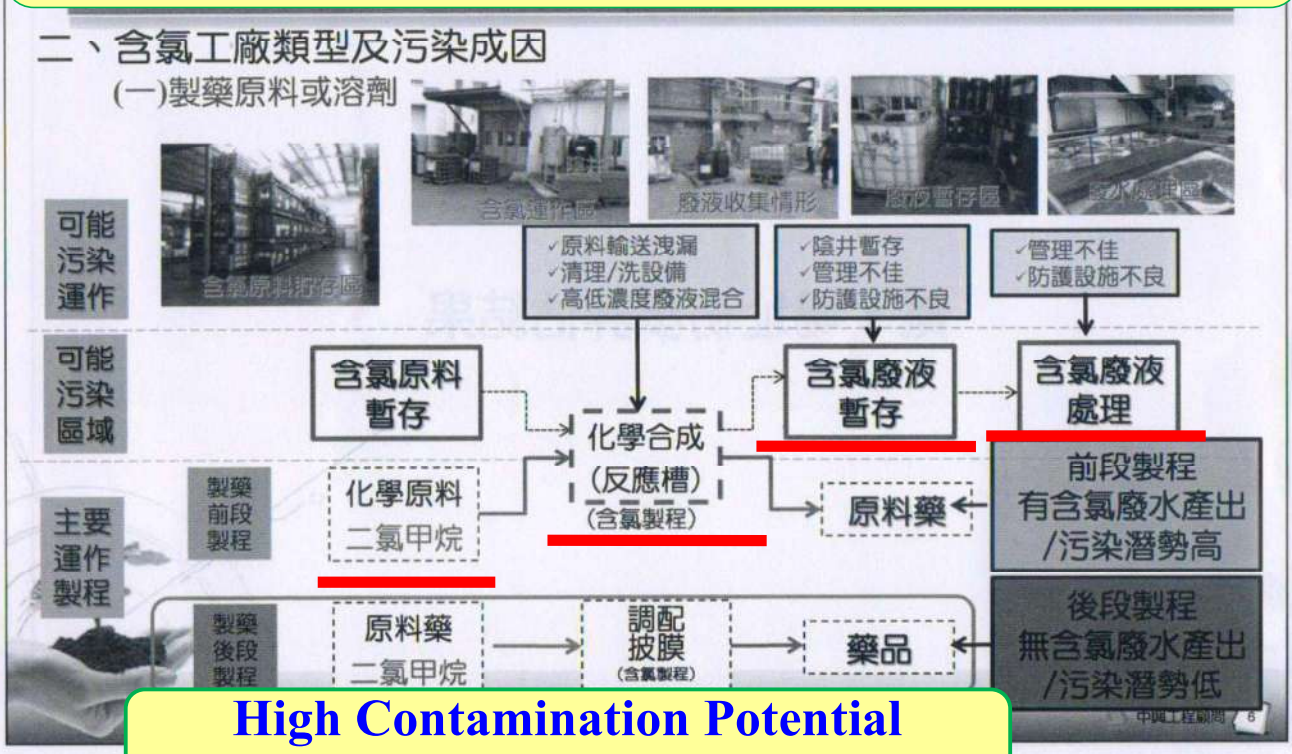
The contaminated regions in the abandoned factory investigations

Item	Soil Contamination	GW Contamination
Manufacturing area	**60**	**9**
Waste water treatment facilities	24	4
Open space	**23**	**3**
Storage tank and pipeline area	13	1
Waste disposal region	12	0
Material storage area	8	2
Boiler room, drying room, chimney area, and dust collection area	8	0
Storage pond	6	0
Other (cracked pavements or electrical room	9	0

Environmental risk map for abandoned factories in Taiwan

Abandoned Manufacturing Factories (Pesticide)

Raw Materials, Products, Processes

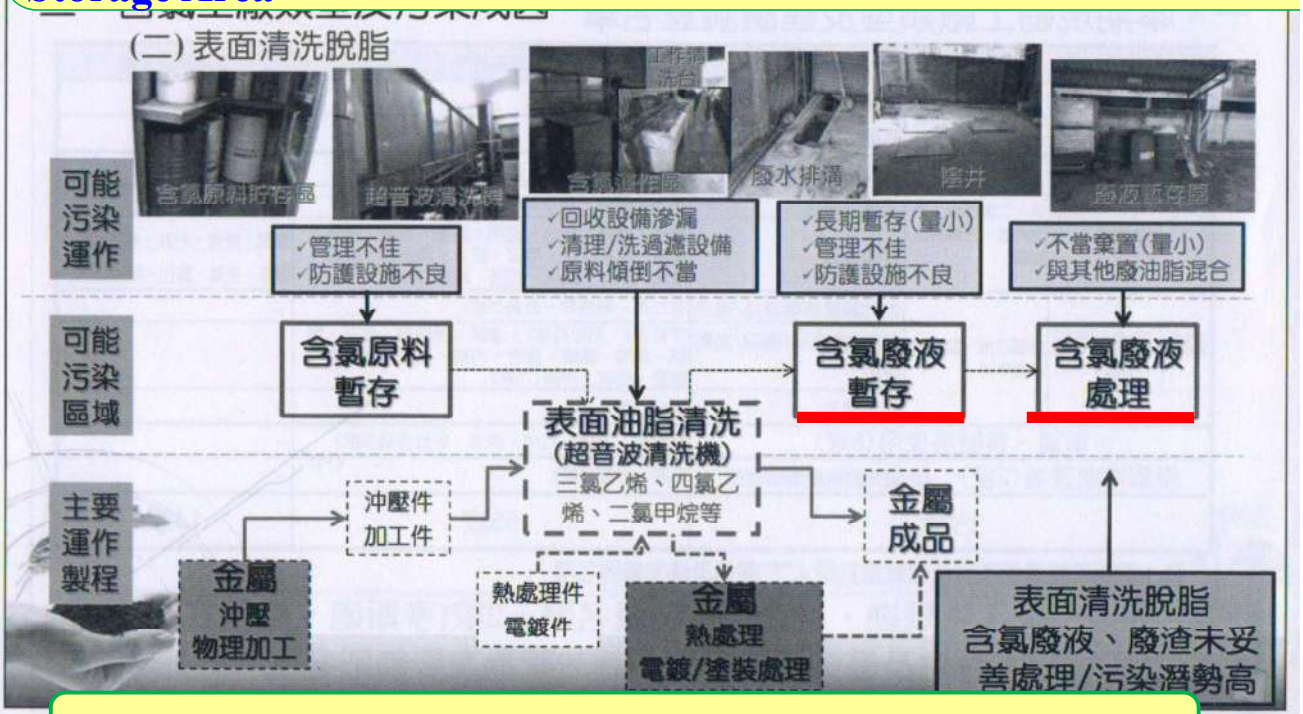


High Contamination Potential

Chemical: Dichloromethane

Operating Manufacturing Factories (Metal Plating)

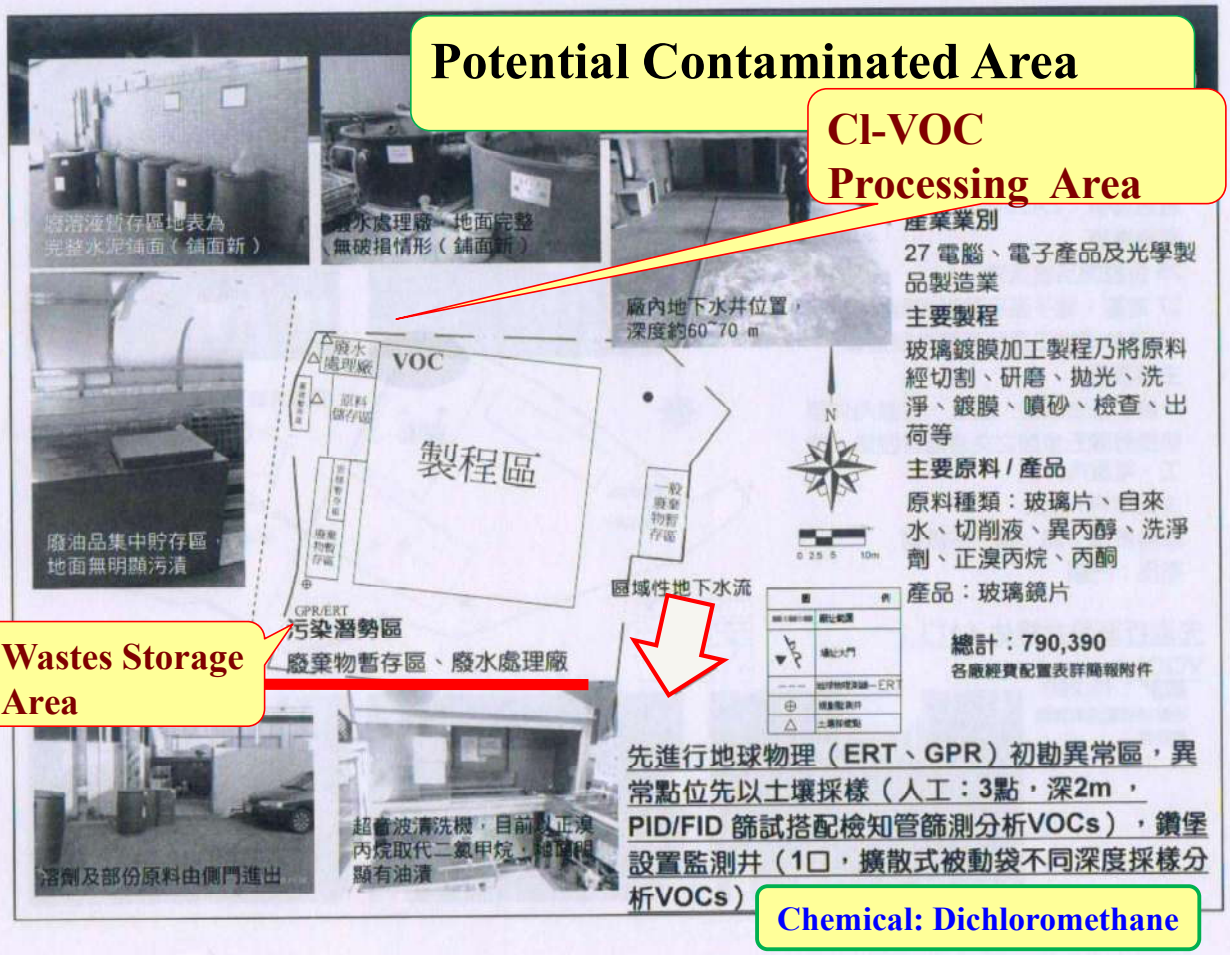
Wastewater, Wastes, Air pollution Control System & Sludge Storage Area



Chemicals: TCE, PCE, Dichloromethane…

Potential Contaminated Area

Cl-VOC Processing Area

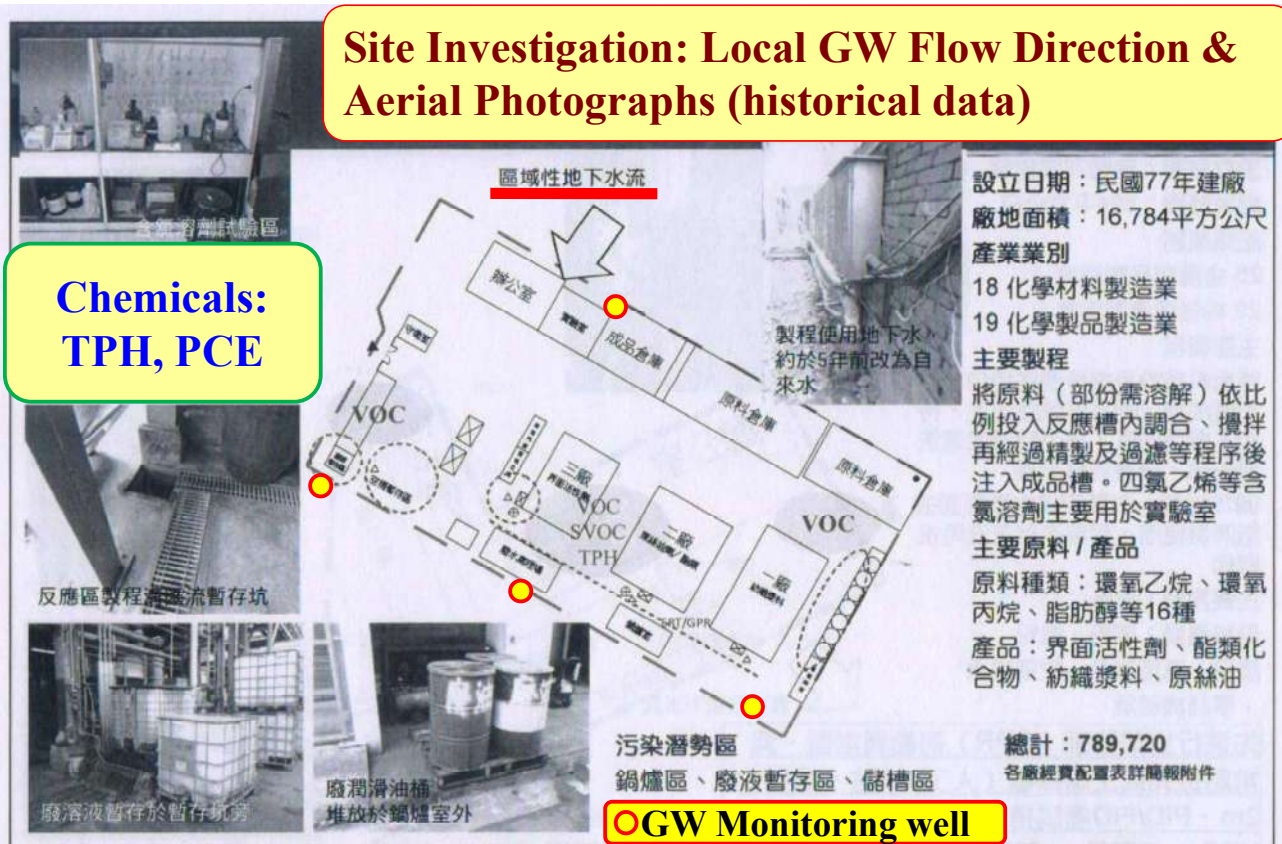


Wastes Storage Area

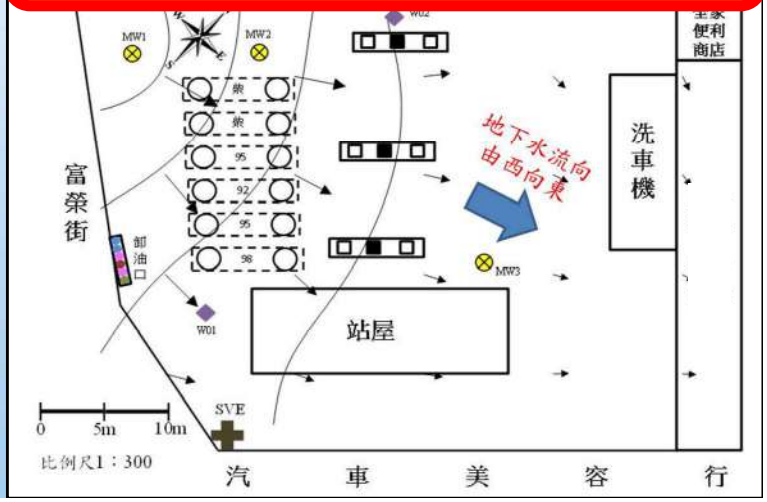
Chemical: Dichloromethane

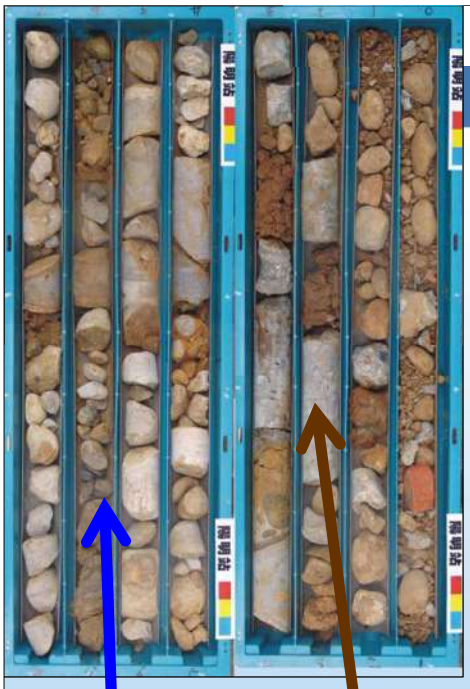
Site Investigation: Local GW Flow Direction & Aerial Photographs (historical data)

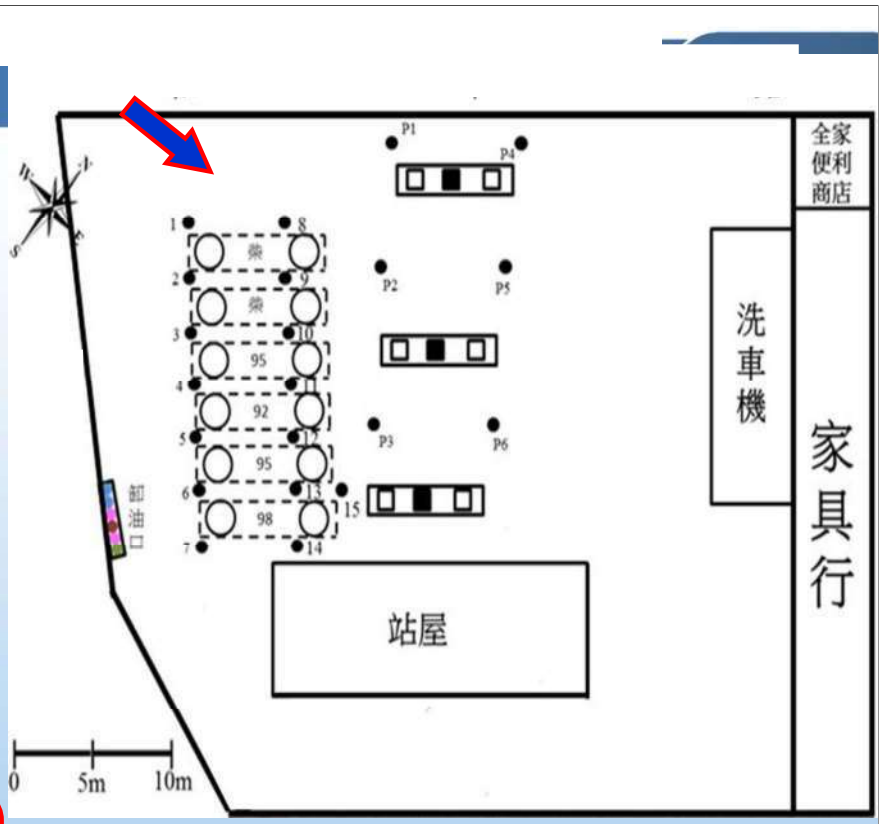
Chemicals: TPH, PCE



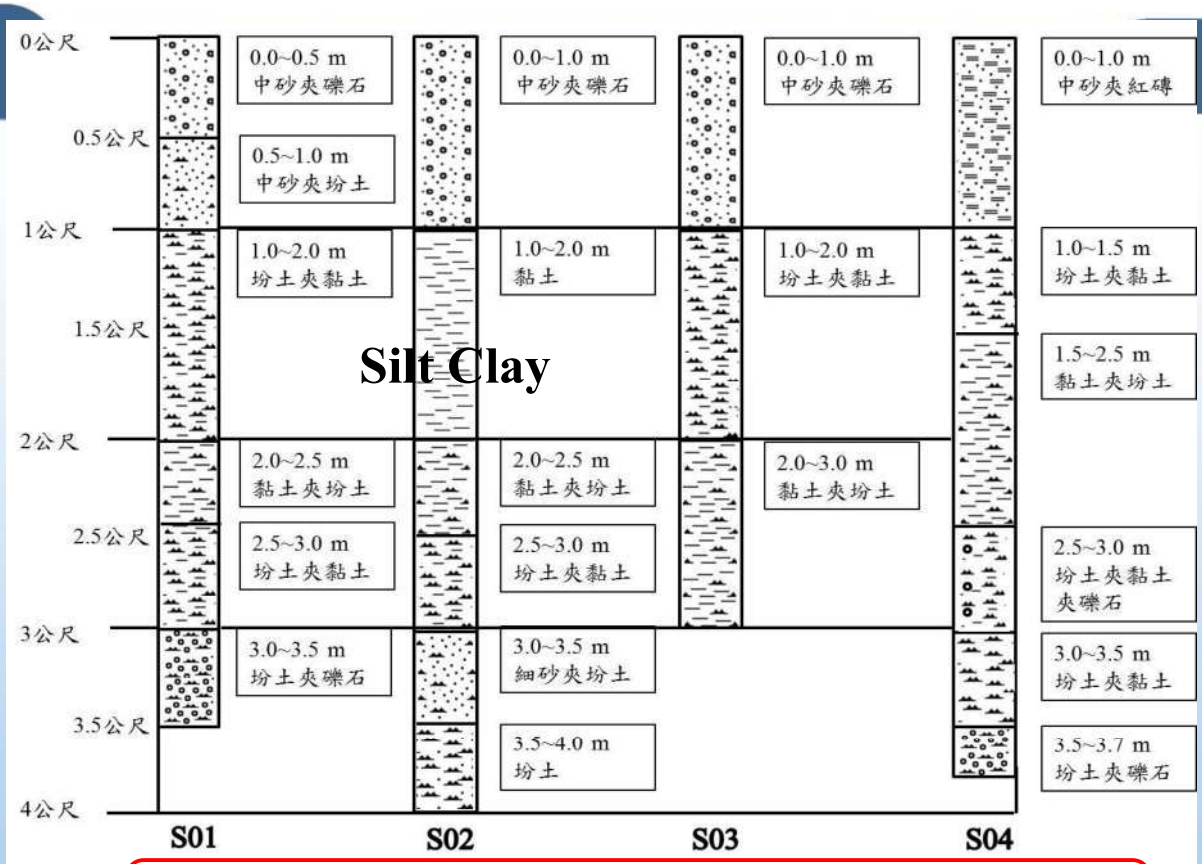
Gas Station







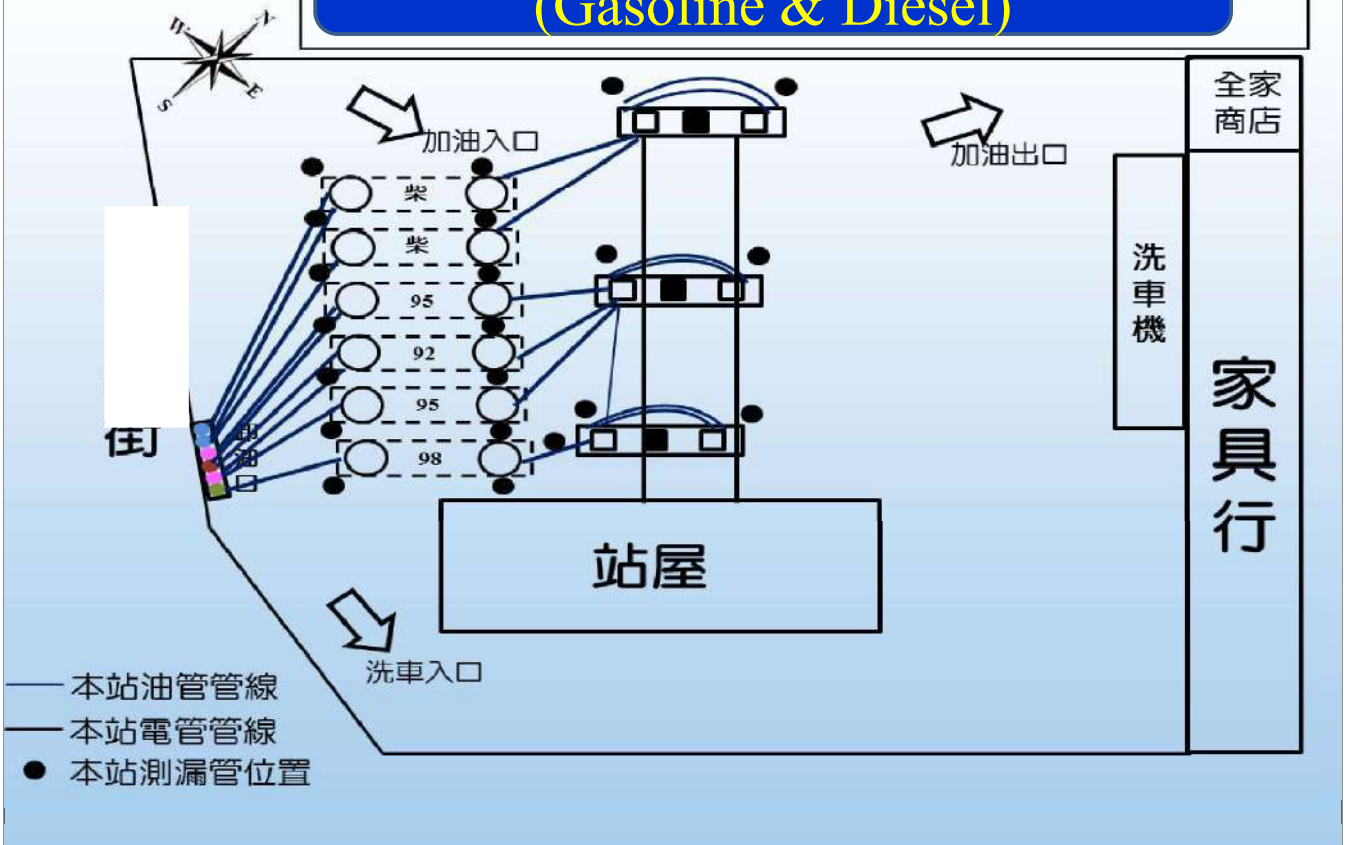
High & Low Permeability

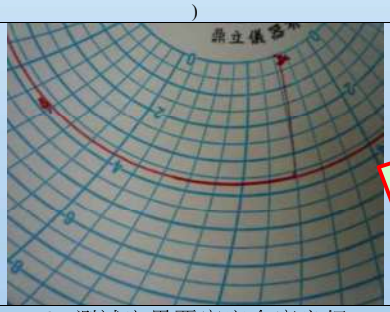


Silt Clay

The TPH contaminated area is limited

Underground Piping System (Gasoline & Diesel)

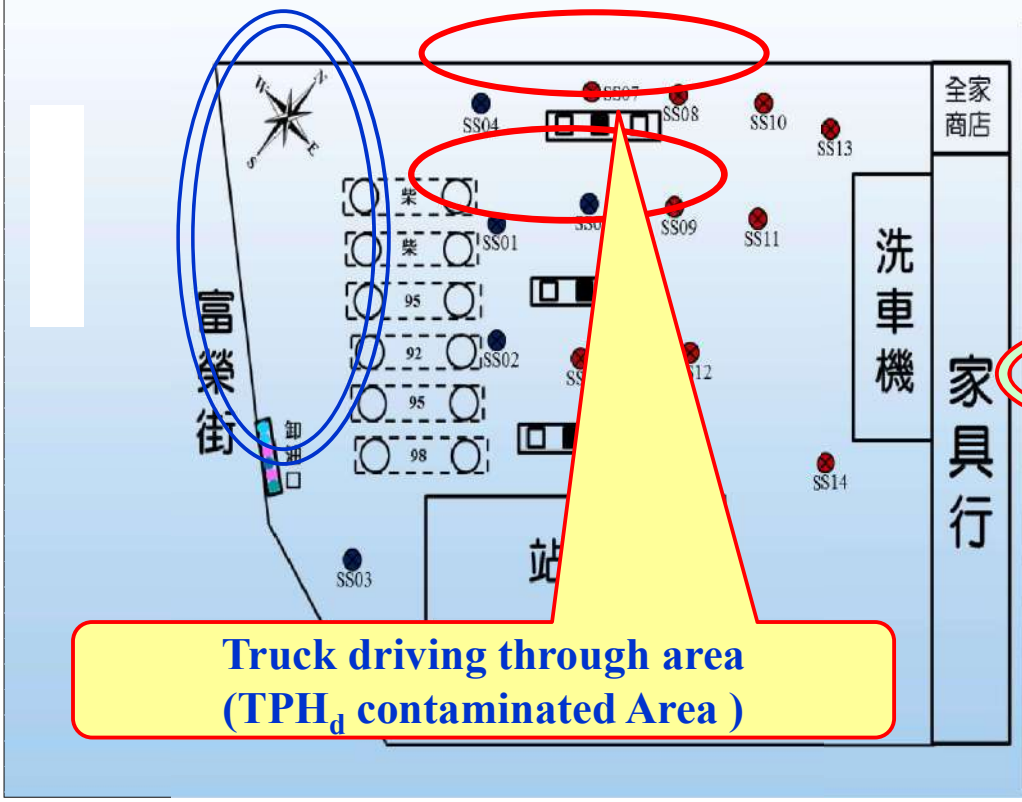


1. 將輸油管線油品卸回油槽	2. 盲封管線至加油機接頭
3. 灌入氮氣進行圓盤圖測試(油槽端)	4. 灌入氮氣進行圓盤圖測試(加油機端)
	
5. 確認圓盤圖是否出現壓降情形	6. 測試完畢覆寫密合度良好

No piping or tank leakage was detected

UST: a RC secondary containment was equipped

In UST area, no soil sample was collected (RC dual deck)

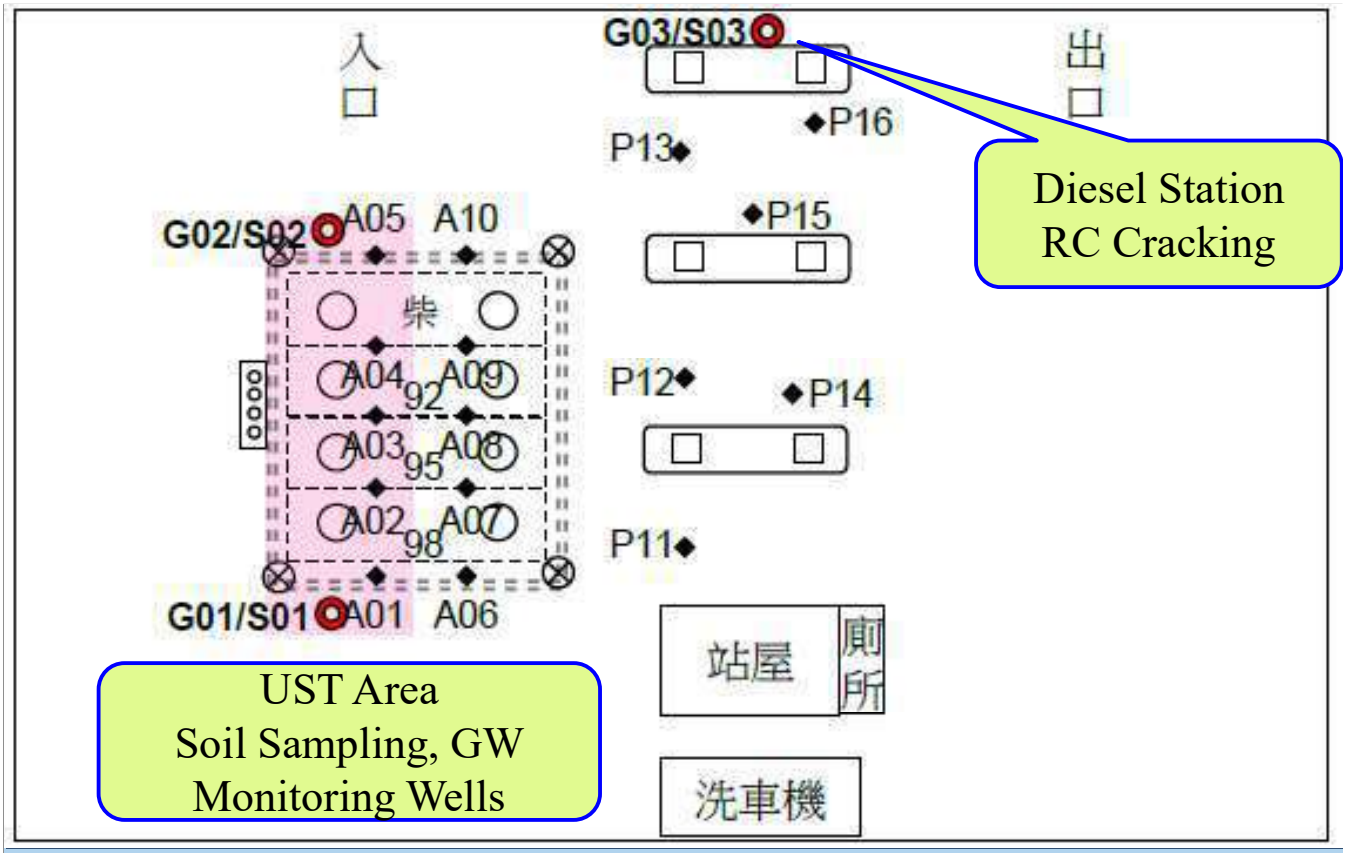


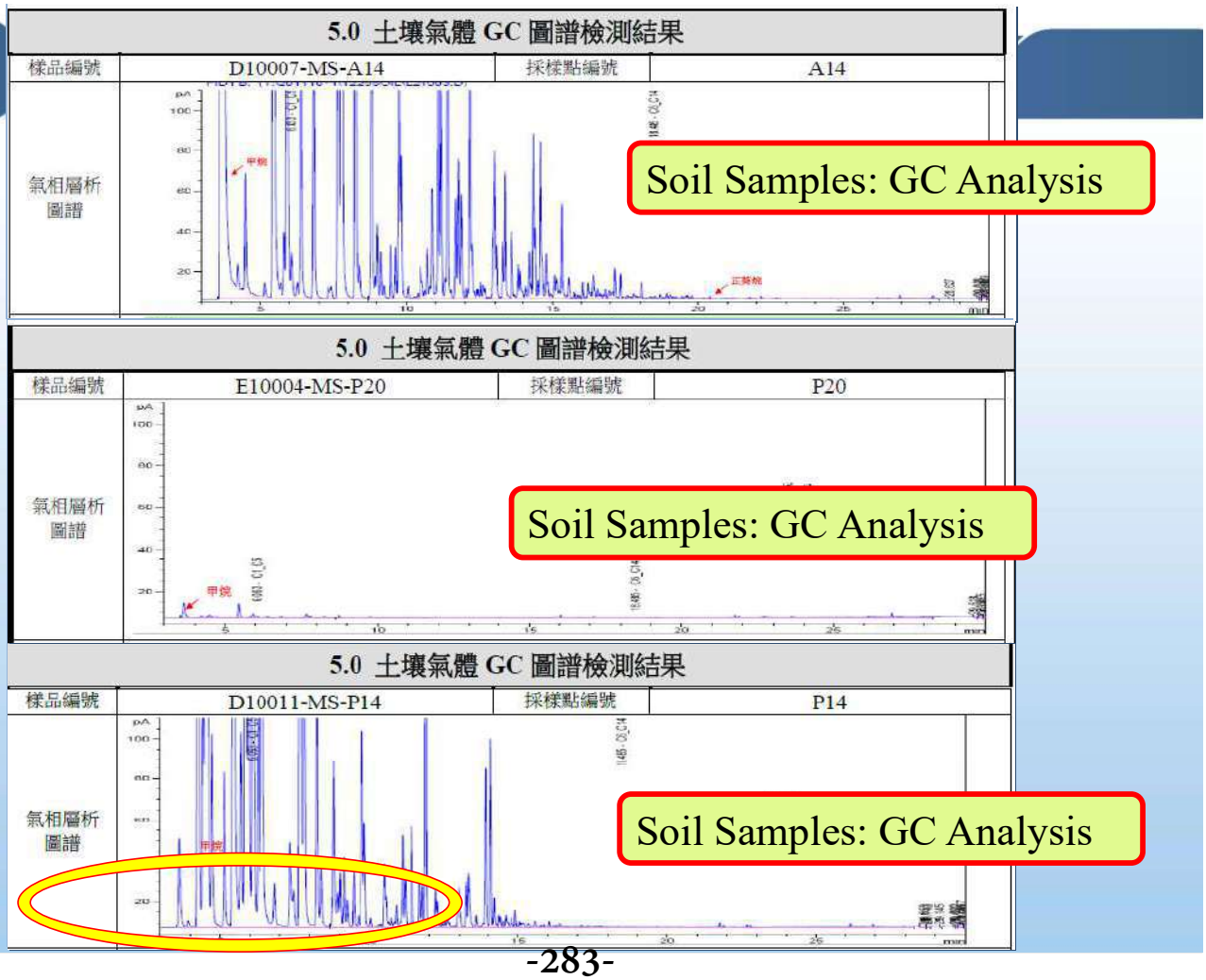
點位	深度 (m)	TPH 分析結果
SS01	2~3	190
SS02	1~2	378
SS03	2~3	224
SS04	1~2	64.3
SS05	1~2	66.3
SS06	2~3	3,930
SS07	2~3	8,710
SS08	1~2	1,310
SS09	2~3	3,420
SS10	2~3	2,100
SS11	2~3	1,350
SS12	2~3	4,060
SS13	1~2	1,270
SS14	1~2	1,460
TPH管制標準1,000mg/kg		

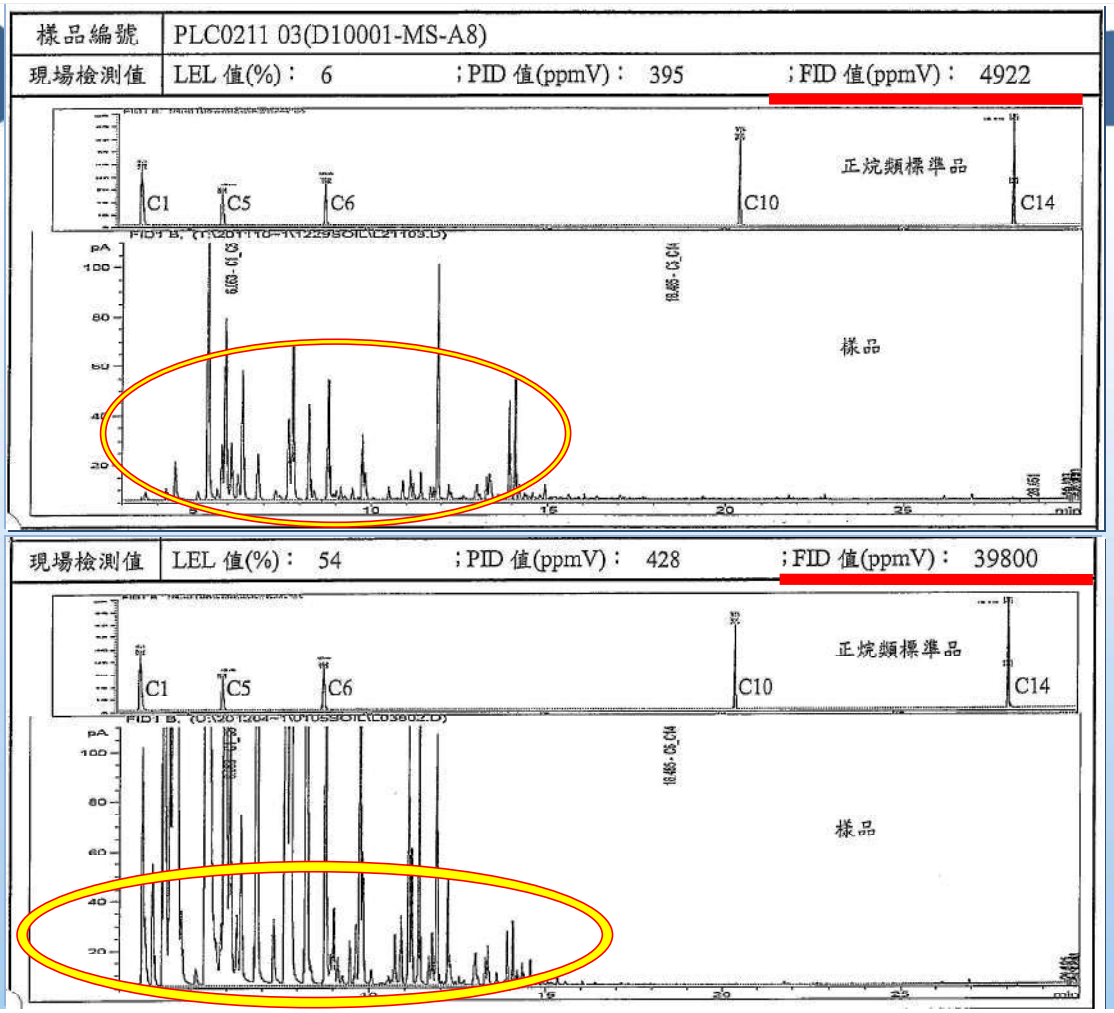
Truck driving through area
(TPH_d contaminated Area)

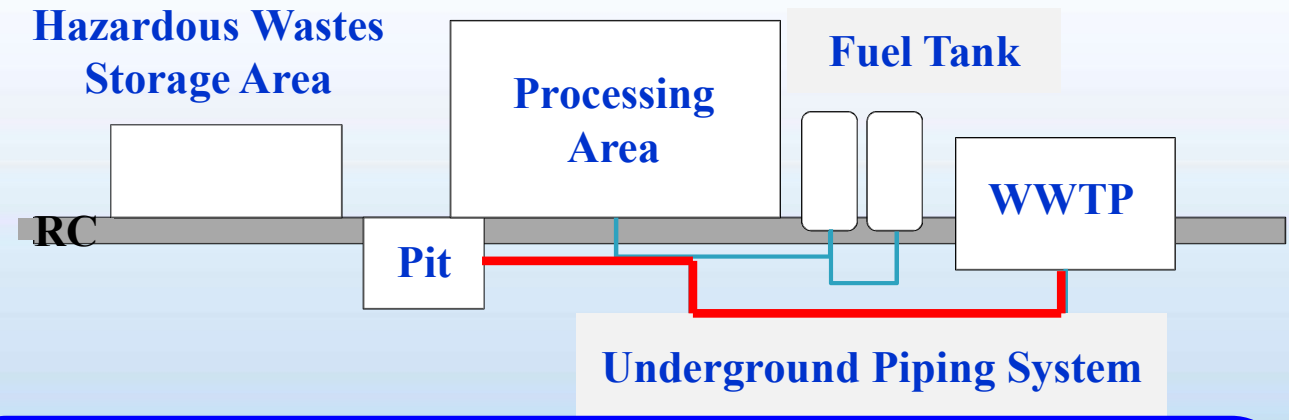
Gas Station: Site Investigation

Potential Contamination Area


入口
出口
G03/S03
P16
P13
P15
Diesel Station
RC Cracking
G02/S02
A05
A10
柴
A04
92
A09
P12
P14
A03
95
A08
A02
98
A07
P11
G01/S01
A01
A06
站屋
廁所
洗車機
UST Area
Soil Sampling, GW
Monitoring Wells


5.0 土壤氣體 GC 圖譜檢測結果
樣品編號
D10007-MS-A14
採樣點編號
A14
氣相層析圖譜
Soil Samples: GC Analysis
5.0 土壤氣體 GC 圖譜檢測結果
樣品編號
E10004-MS-P20
採樣點編號
P20
氣相層析圖譜
Soil Samples: GC Analysis
5.0 土壤氣體 GC 圖譜檢測結果
樣品編號
D10011-MS-P14
採樣點編號
P14
氣相層析圖譜
Soil Samples: GC Analysis

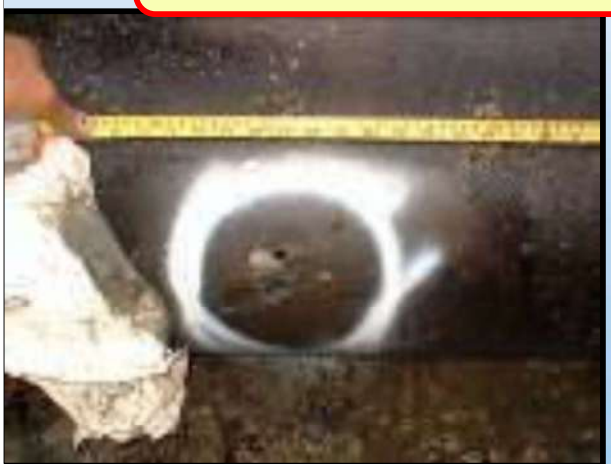




Soil Sampling (hot spot):

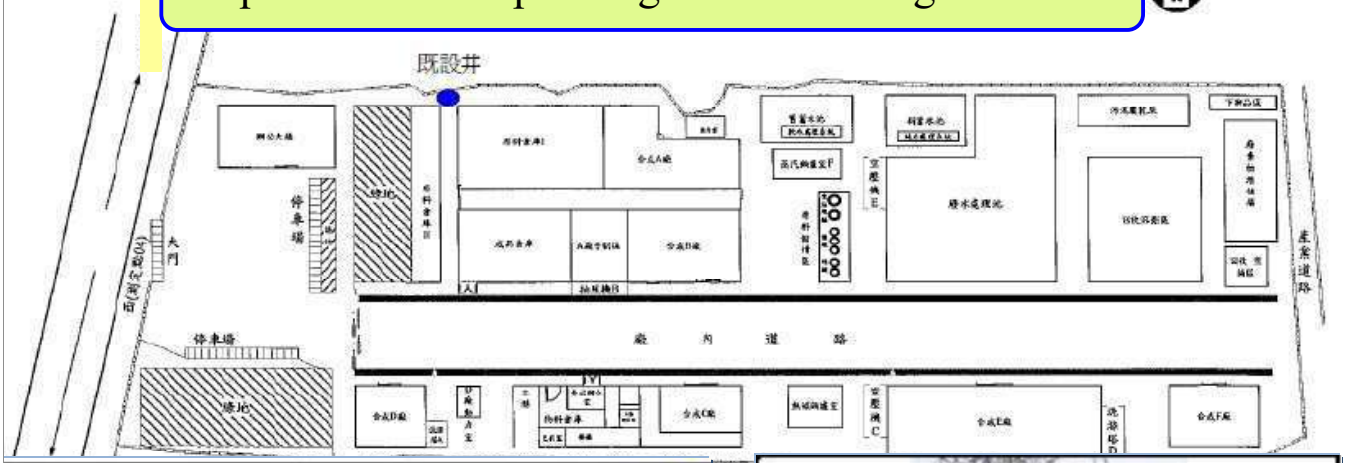
Processing Area, Wastewater Piping, Fuel Piping, WW Collection pit, Hazardous Wastes Storage Area, Fuel Tank, Chemical Storage Tank, WW treatment Plant, Air Pollution Control Area, et al.

Leakage of underground piping



Leakage of chemicals or fuel storage tank

Top View of the operating Manufacturing Facilities



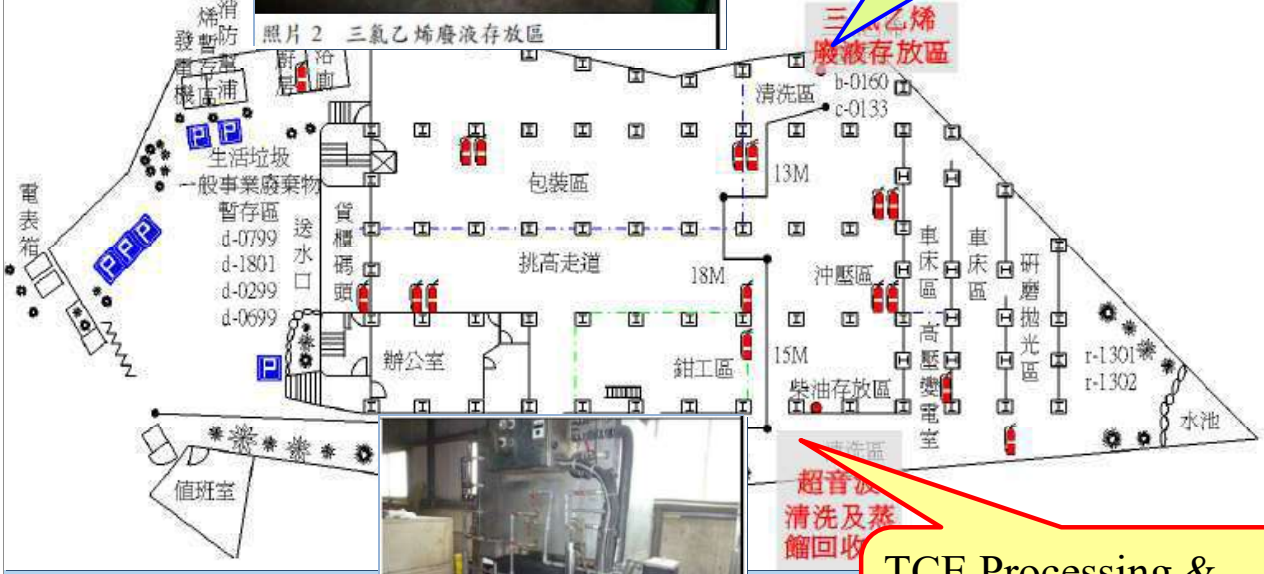
照片 4 廢棄物暫存

廠內設有 2 座重油槽，均有約 1.5 公尺高之防溢堤

Site Investigation: Potential Contamination Area

照片 2 三氯乙烯廢液存放區

Wasted TCE Storage Area



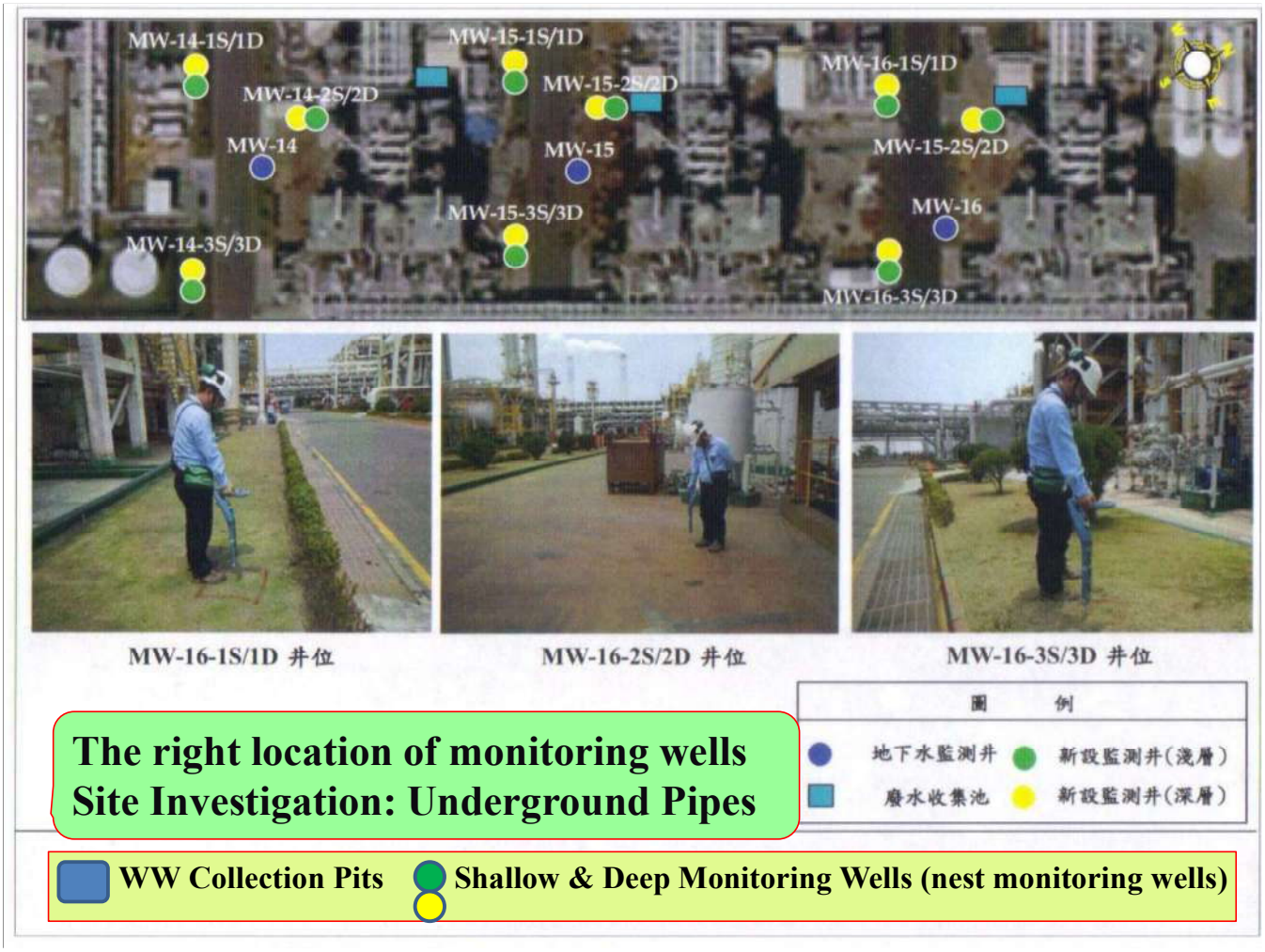
照片 6 三氯乙烯蒸餾回收設備

TCE Processing & Wasted TCE Recycle Processing Area

Potential Contaminated Area

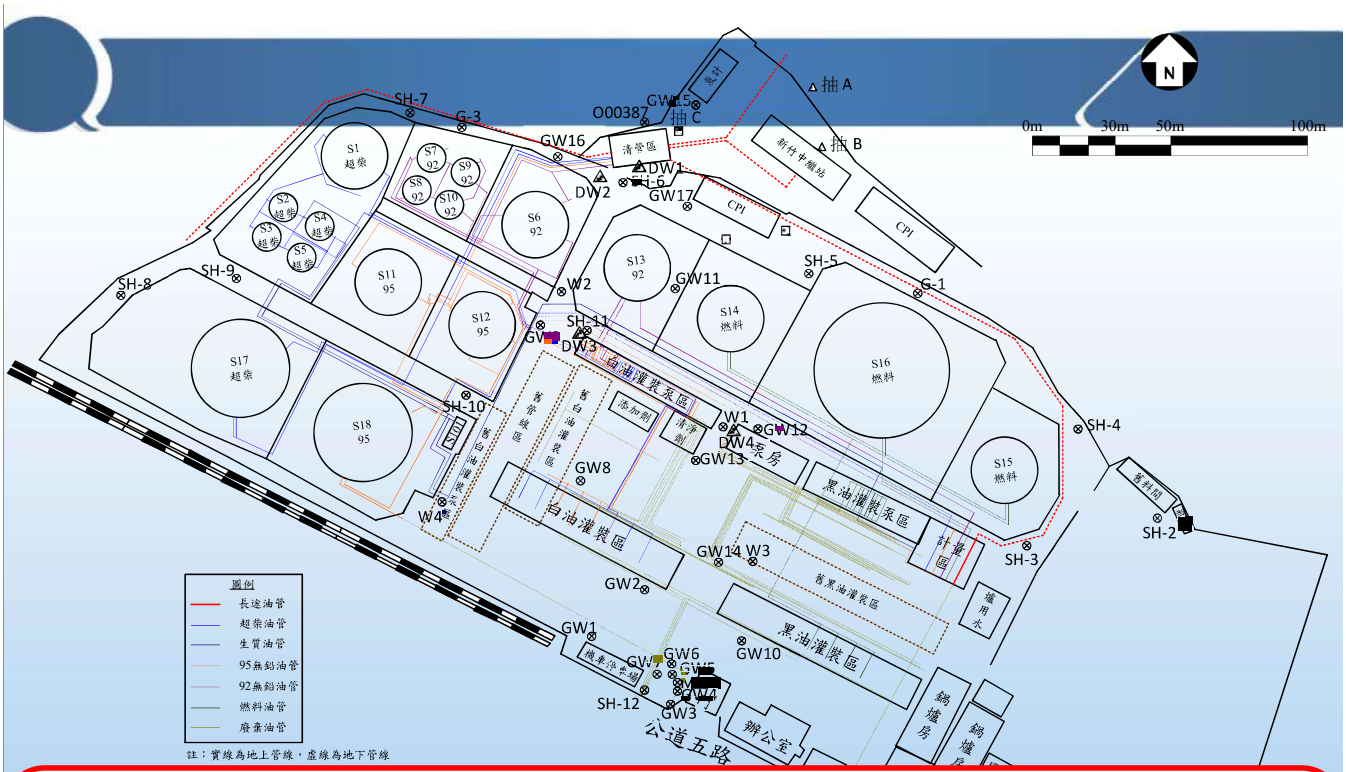
Sometimes it is very difficult to find enough space to install the monitoring well

Gas Station
Monitoring Well & GW Sampling



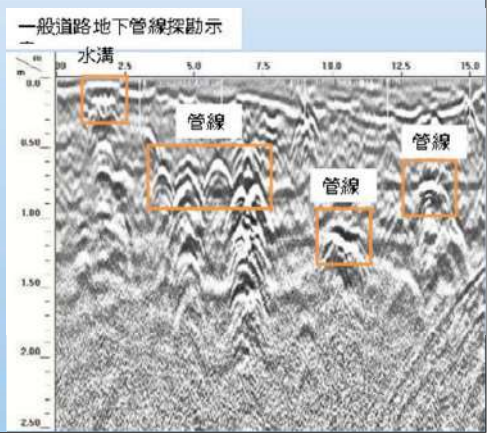
The site investigation of an abandoned Fuel Tank Site

Generally, we did not set monitoring wells inside the deck area with RC pavement.



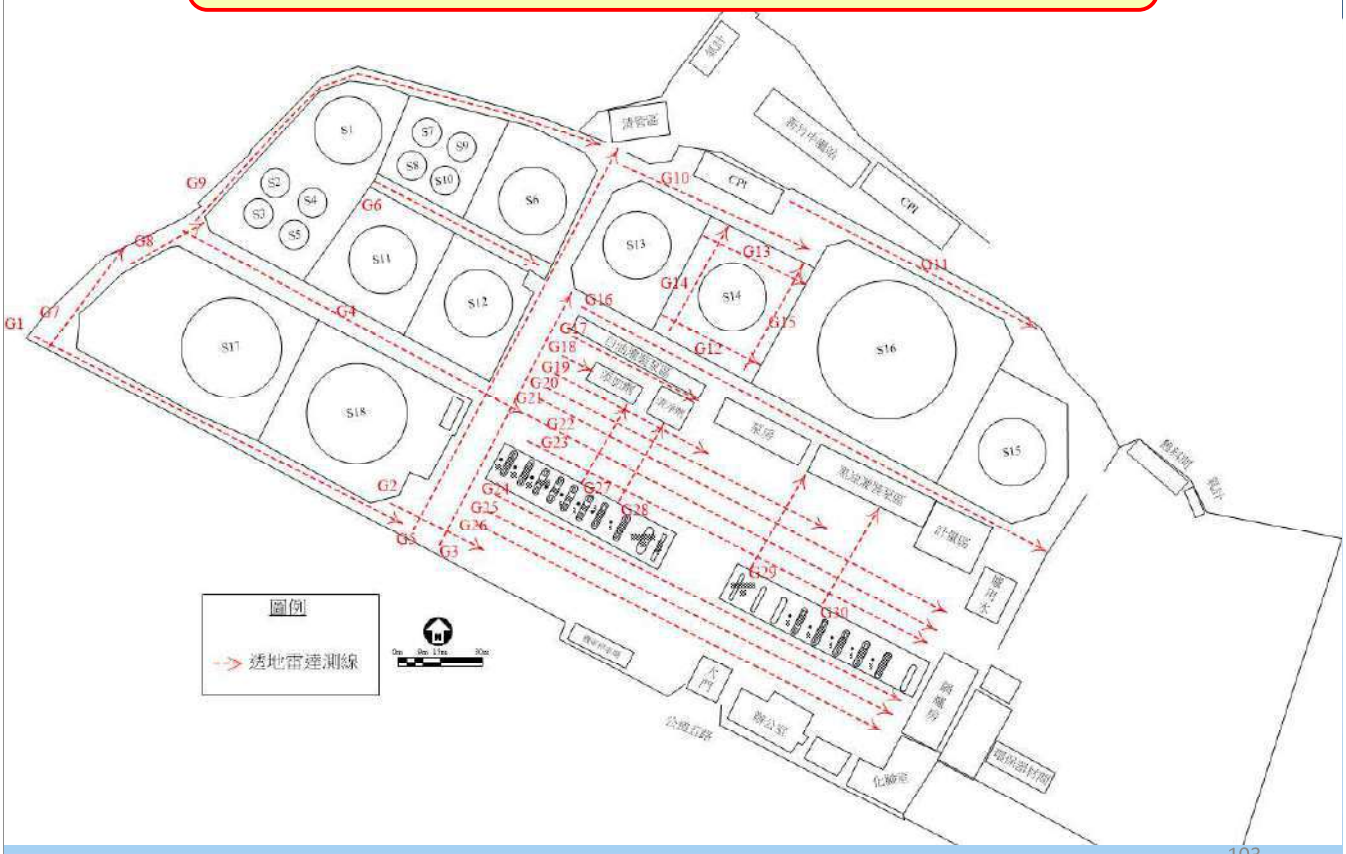
There are many petroleum piping in the subsurface within the fuel tank site. However, the piping diagram is not so reliable. It is a serious concern when we want to take soil samples in the petroleum tank site.

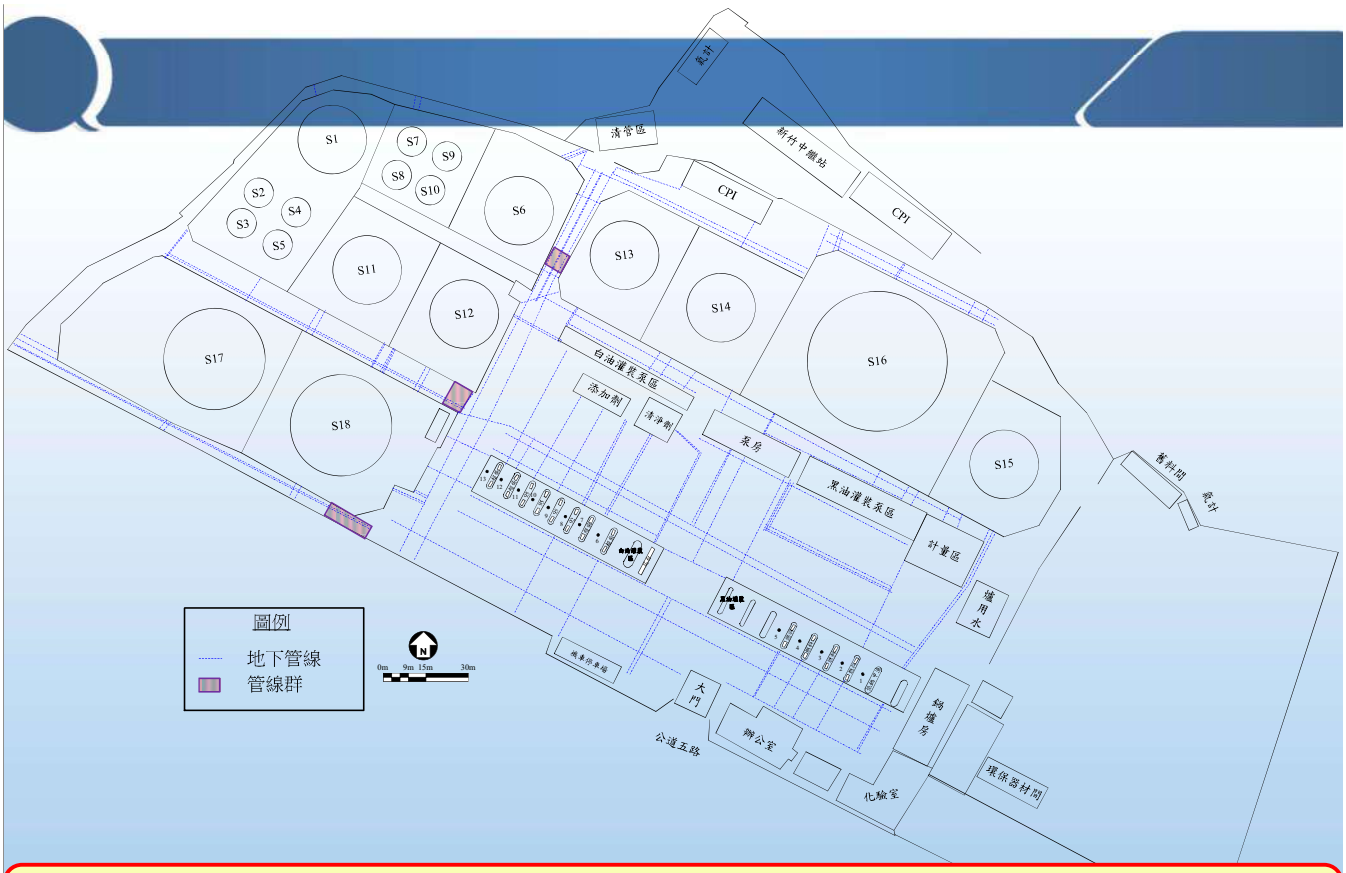
A GPR (ground penetration radar) was employed to "see" the distribution of different piping system before soil sampling



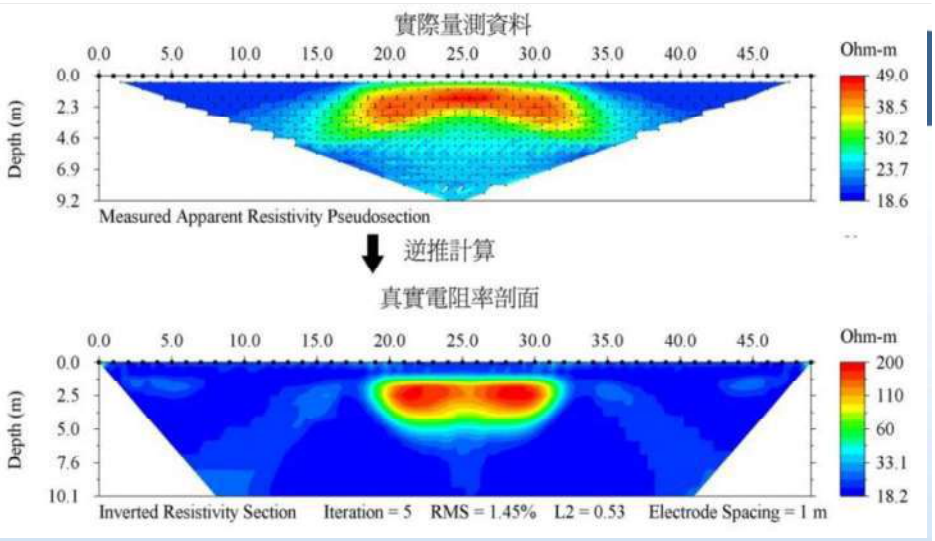
Located the distribution of underground piping

GPR Arrangement (red line)

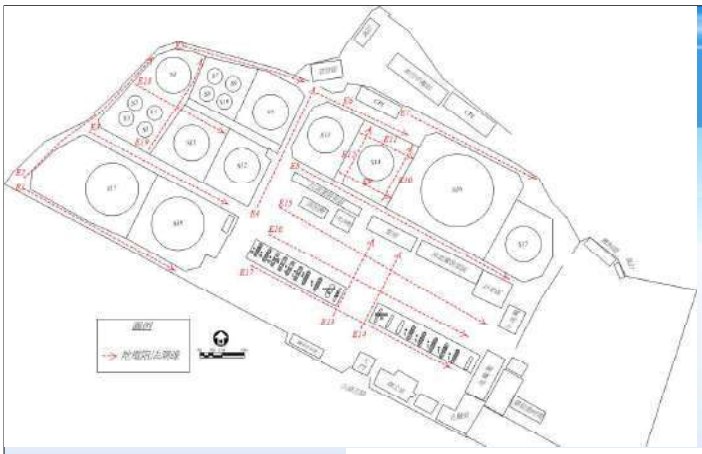


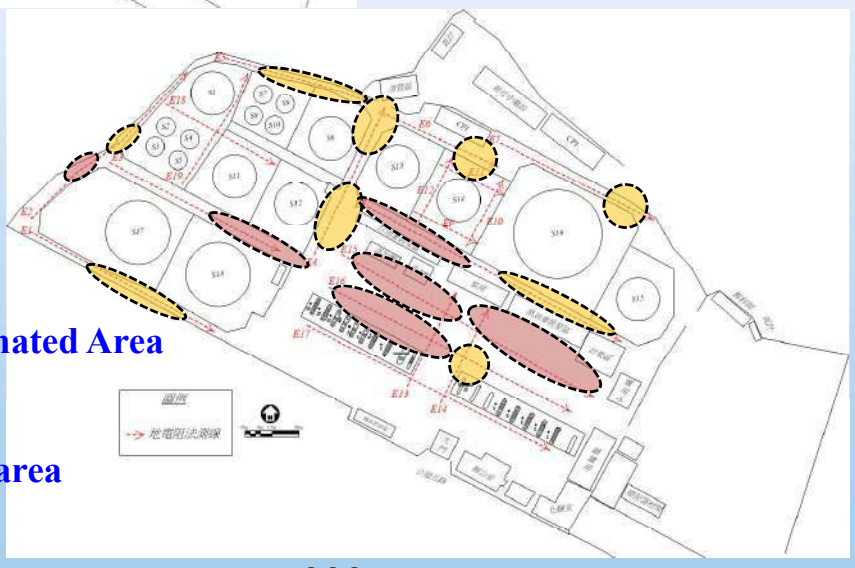


The distribution of underground piping (blue line)



An ERT (Electrical Resistivity Tomography) system was employed to pre-screen the hot spot



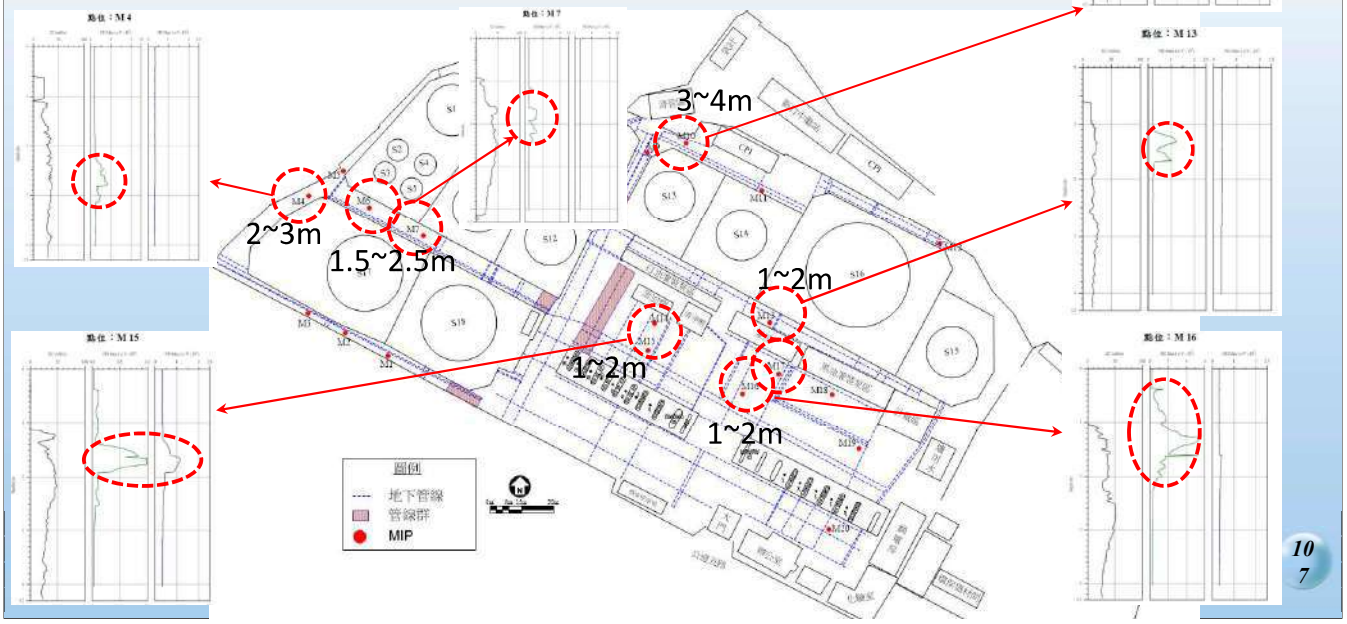


TPH Contaminated Area

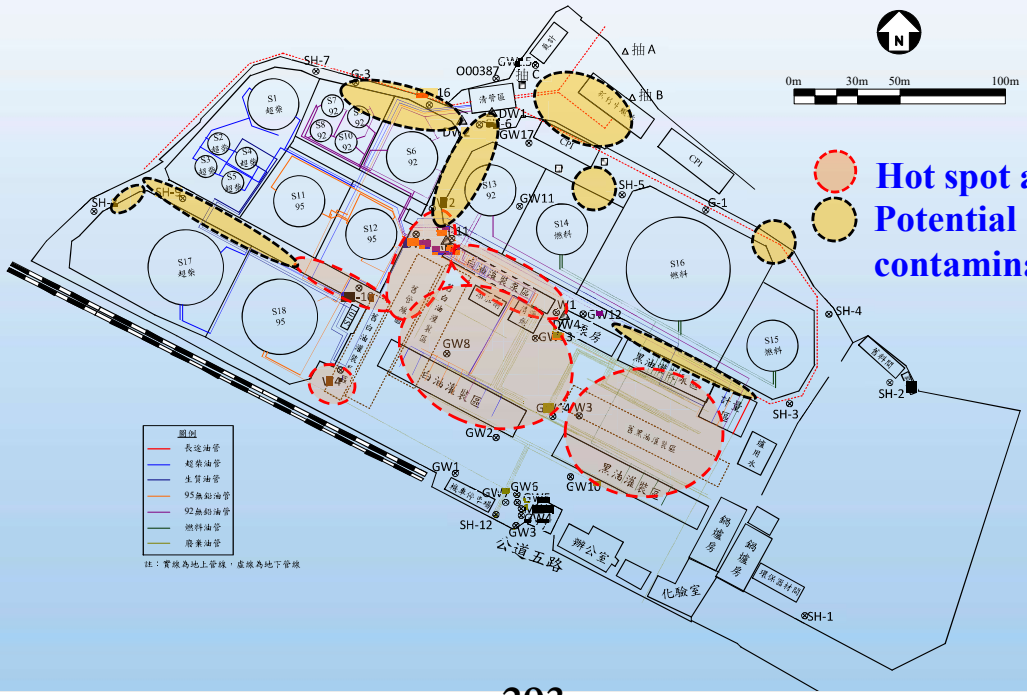
Potentially contaminated area

10
6

MIP Results

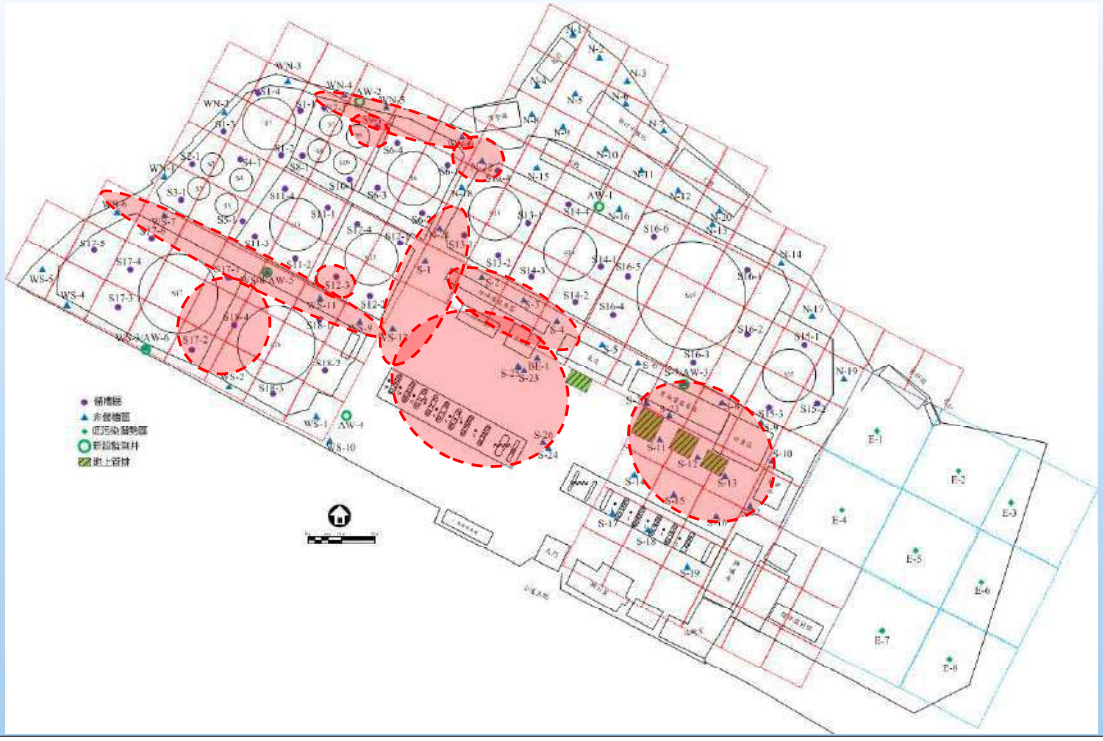


10
7



10
8

Totally, 126 soil samples were collected and analyzed



TPH Analysis (TPH$_g$ & TPH$_d$)

WN-5
TPH$_g$: 30.9 mg/kg
TPH$_d$: 2,690 mg/kg

N-22
TPH$_g$: 9.18 mg/kg
TPH$_d$: 33,000 mg/kg

S-8
TPH$_g$: 9.16 mg/kg
TPH$_d$: 7,950 mg/kg

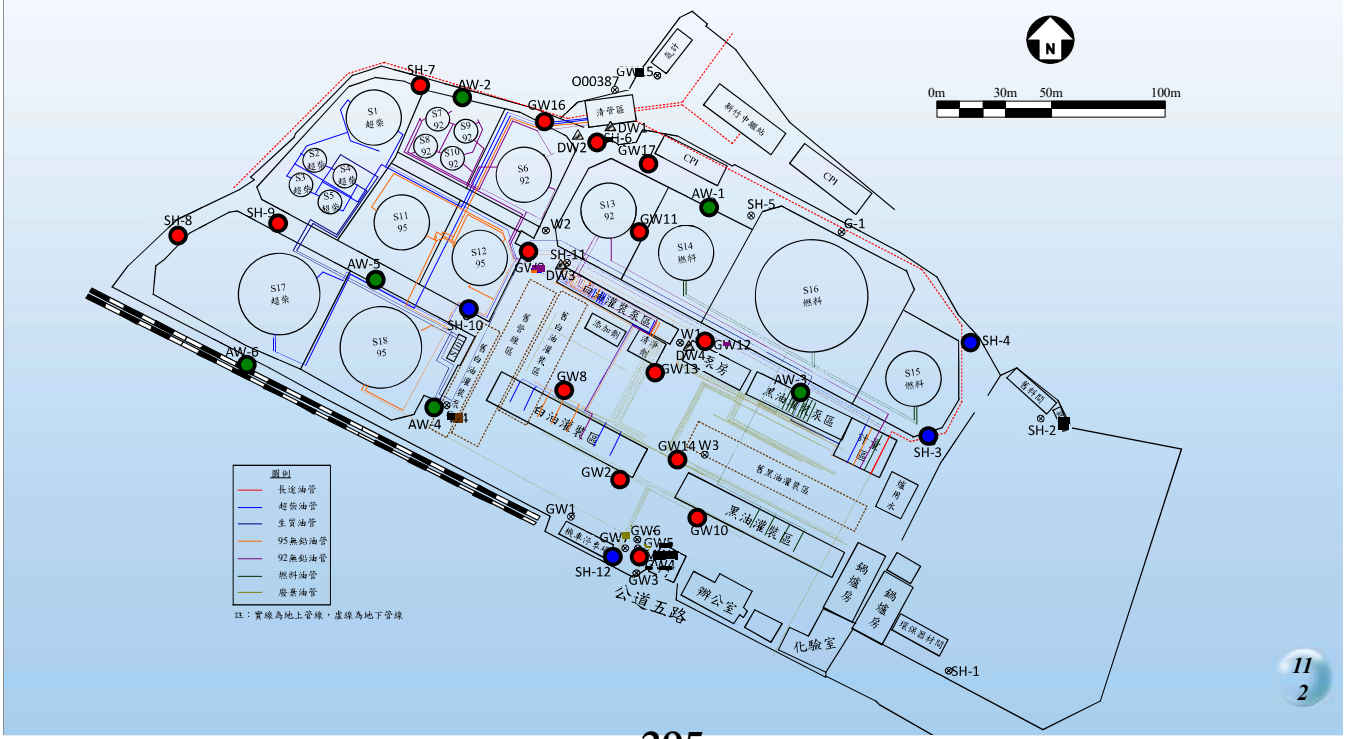
S18-4
TPH$_g$: 68.4 mg/kg
TPH$_d$: 5,430 mg/kg

S-25
TPH$_g$: 447 mg/kg
TPH$_d$: 8,790 mg/kg

Soil: Contamination Area

11
1

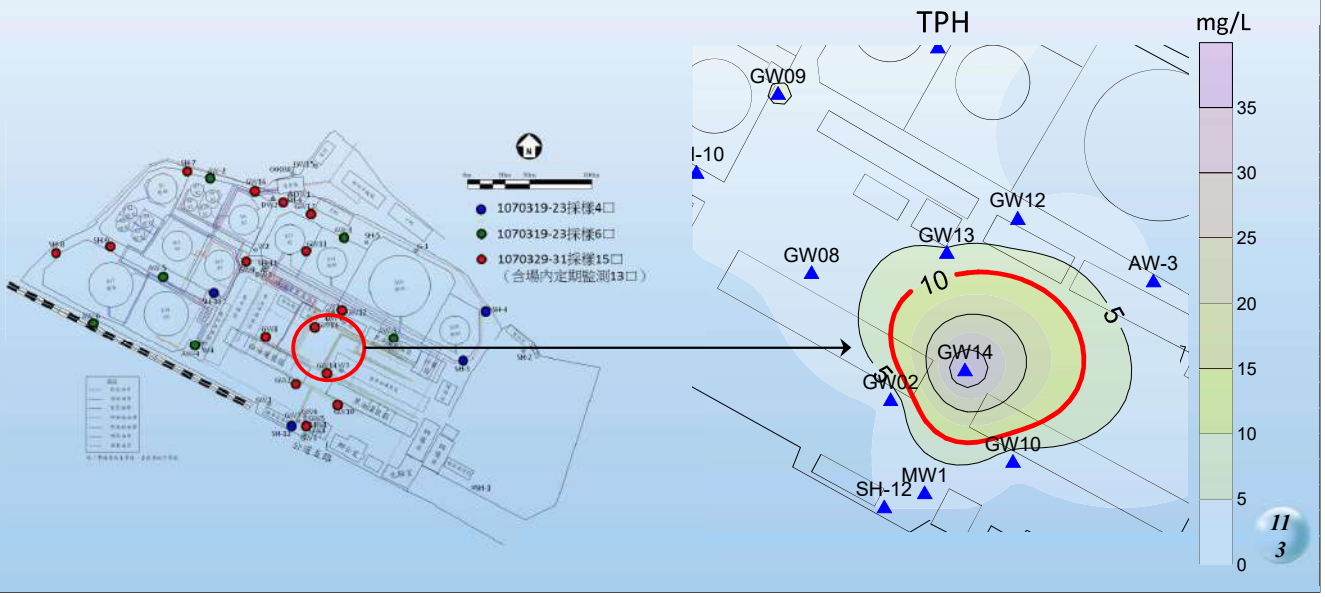
GW Monitoring Well

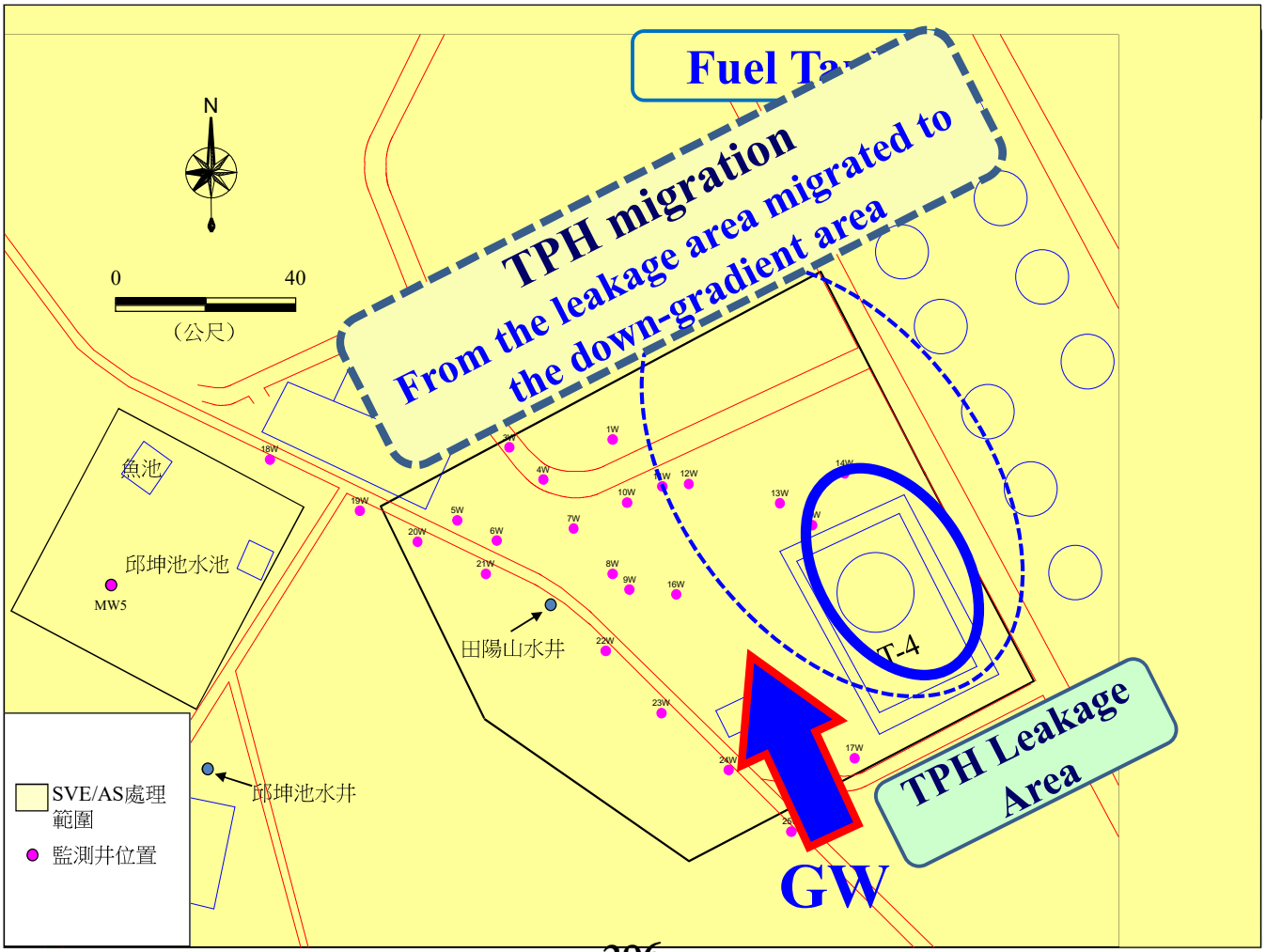


11
2

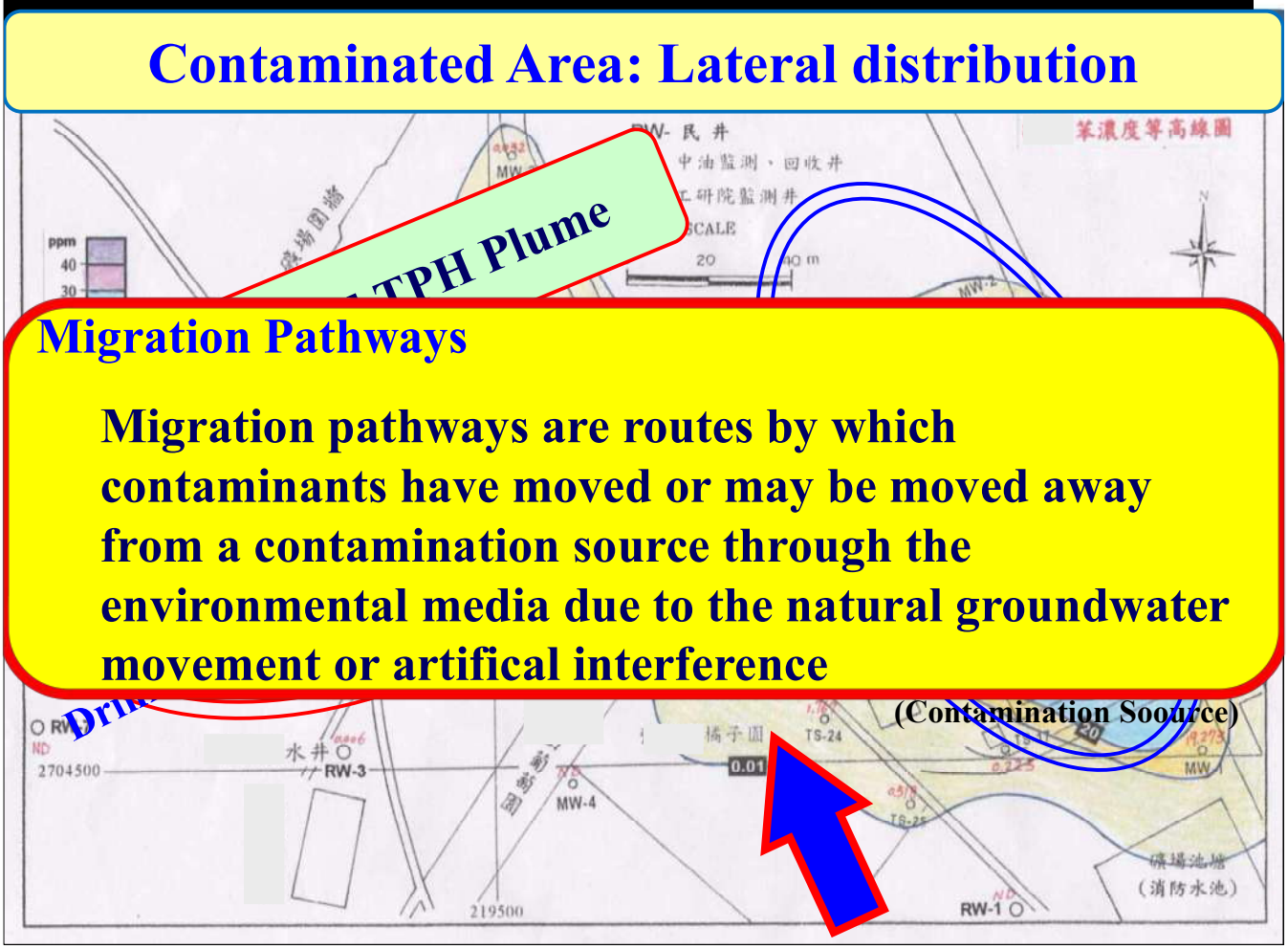
The confirmed GW Contamination area

(one of the hot spot of soil contamination)



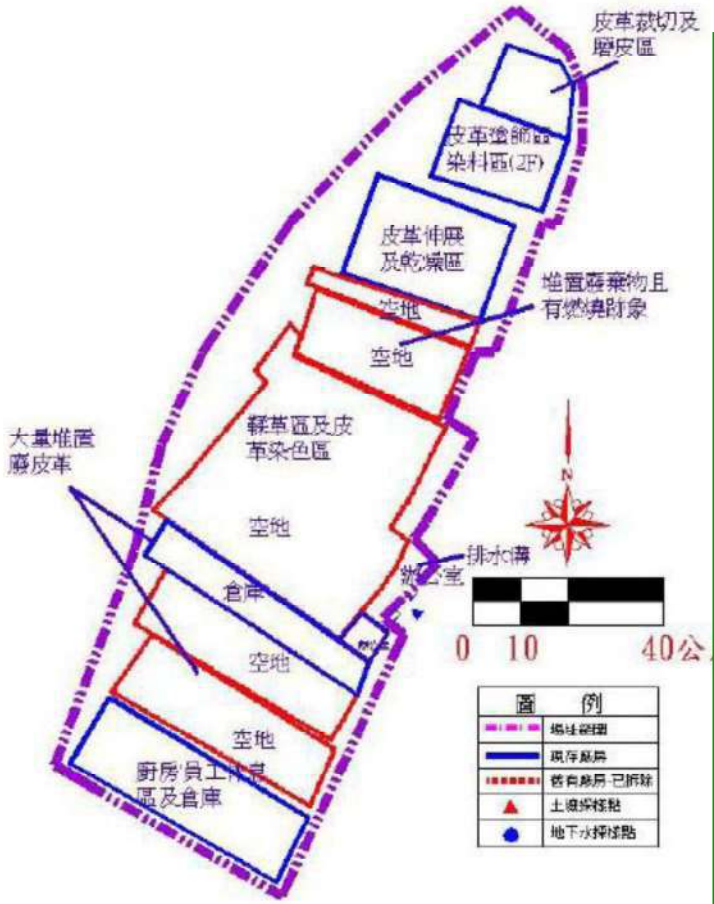


Contaminated Area: Lateral distribution



Migration Pathways

Migration pathways are routes by which contaminants have moved or may be moved away from a contamination source through the environmental media due to the natural groundwater movement or artifical interference

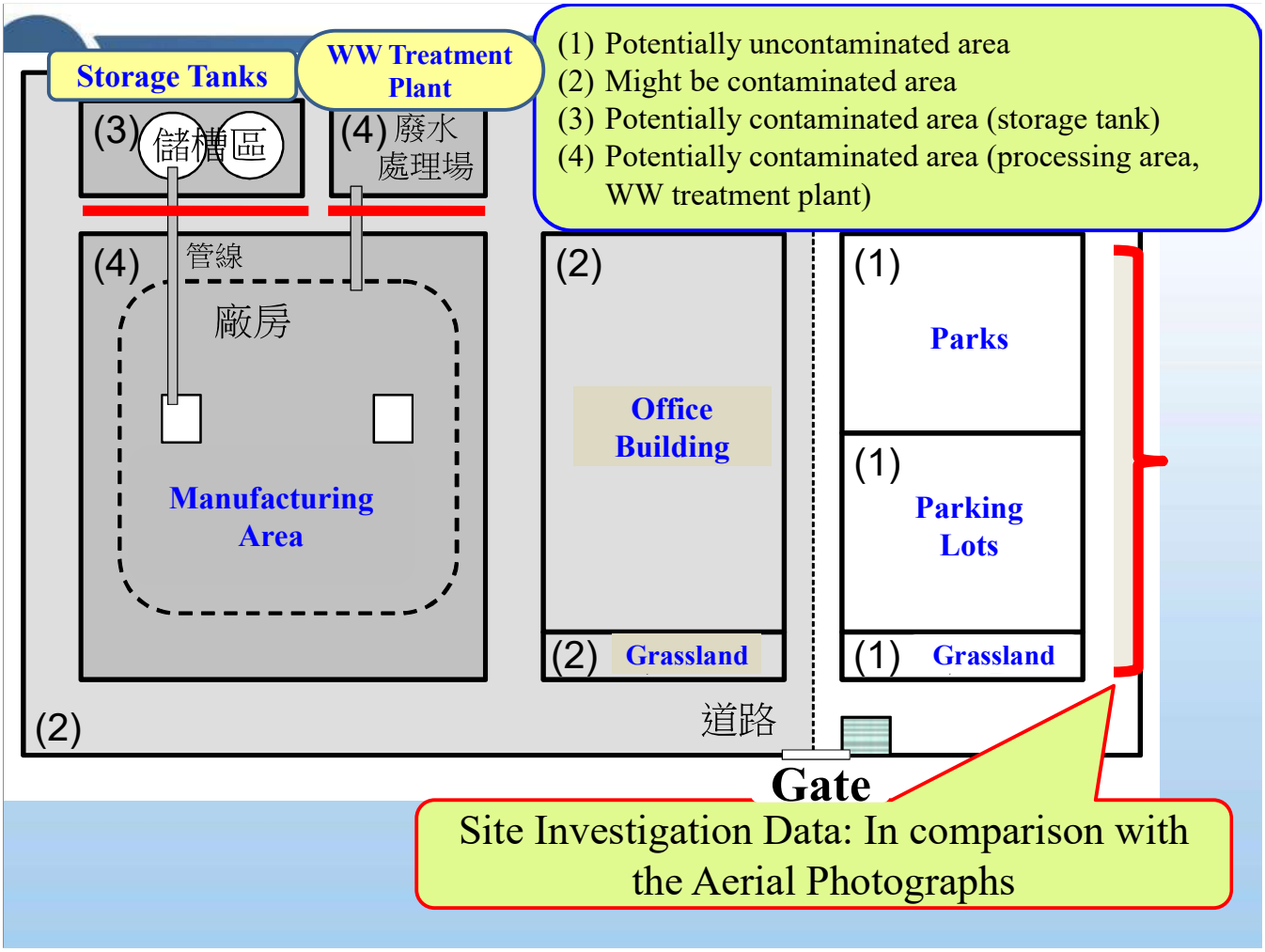


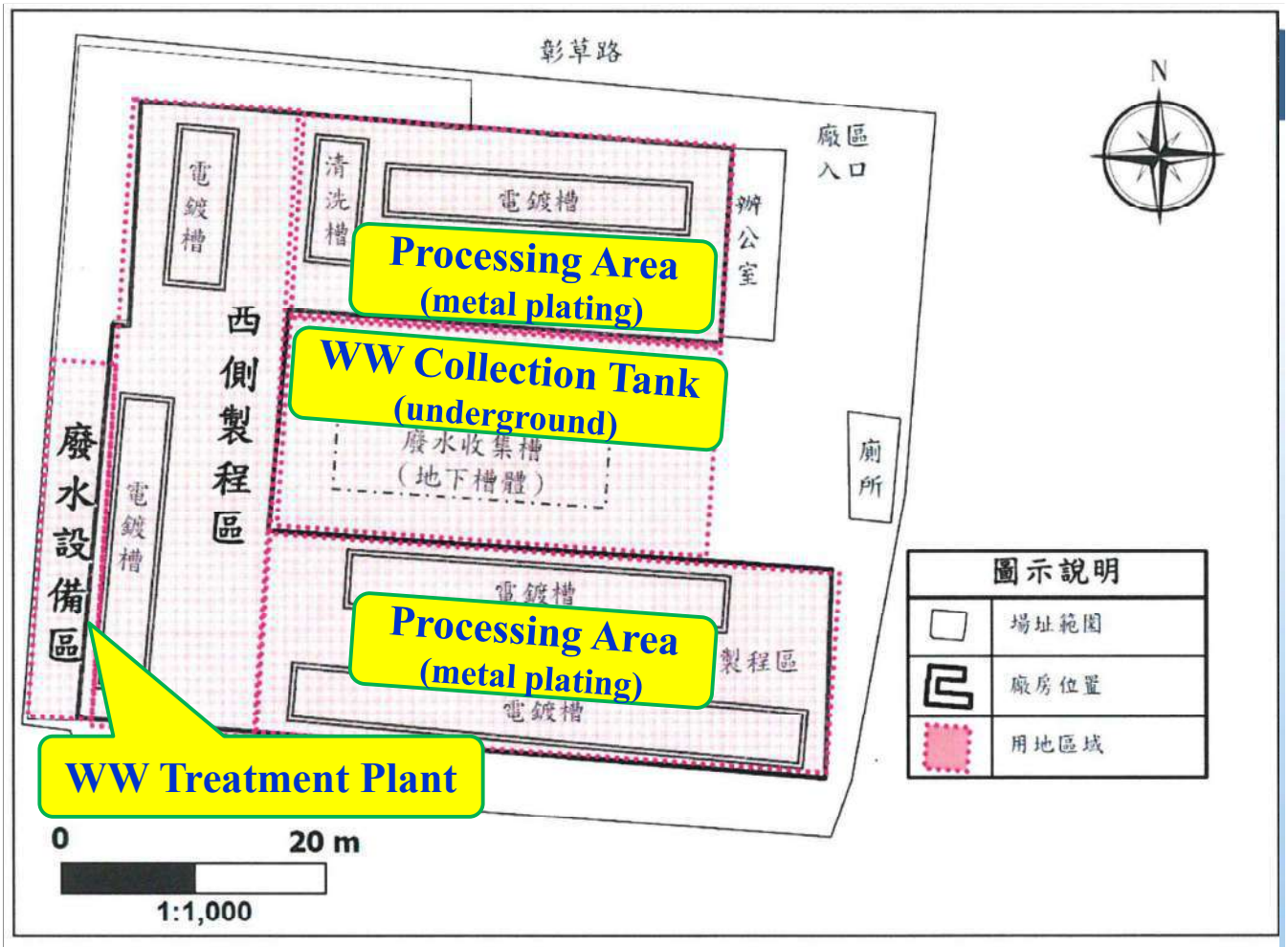
Sampling Plan

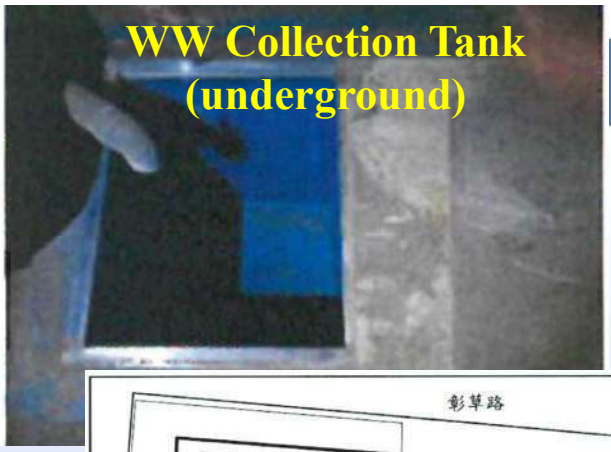
1. Understand the industrial
2. Manufacturing Process
3. Raw Materials
4. Location of each Process
5. Storage Tanks Area
6. Waste Storage Area
7. Piping
8. GW Flow Direction
9. Historical Data (Spilling…)
10. Aerial Photographs
11. Data from other Administration Offices

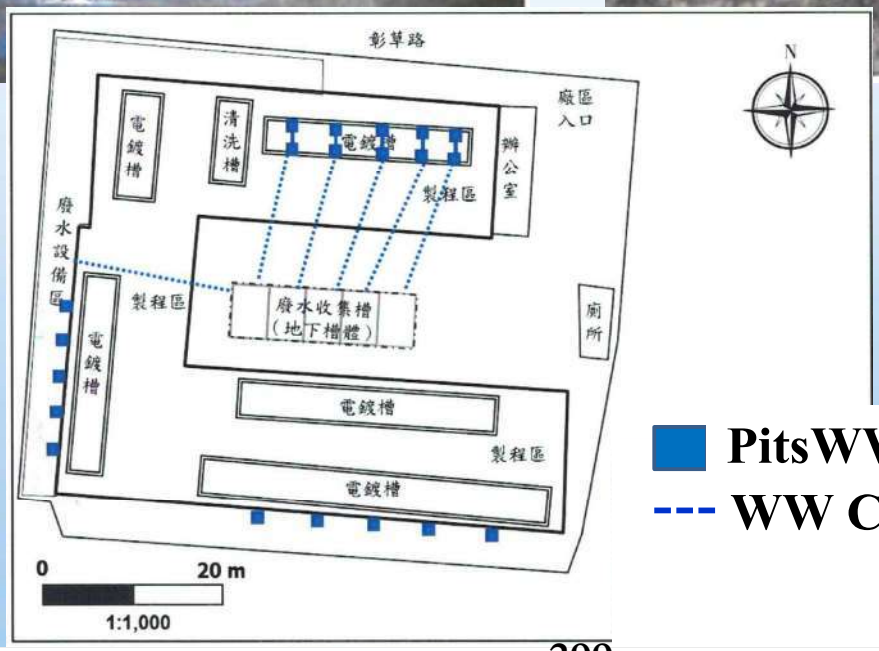
…

…


Storage Tanks
WW Treatment Plant
(1) Potentially uncontaminated area
(2) Might be contaminated area
(3) Potentially contaminated area (storage tank)
(4) Potentially contaminated area (processing area, WW treatment plant)
(3) 儲槽區
(4) 廢水處理場
(4) 管線
廠房
Manufacturing Area
(2)
Office Building
(2) Grassland
(1)
Parks
(1)
Parking Lots
(1) Grassland
(2)
道路
Gate
Site Investigation Data: In comparison with the Aerial Photographs





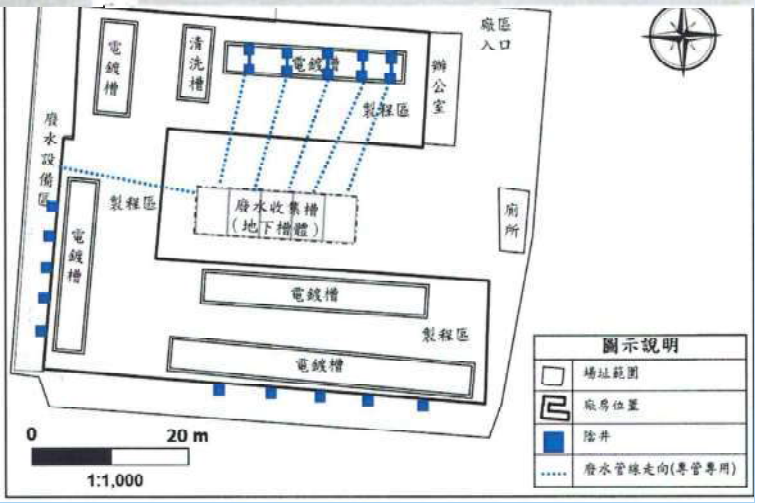


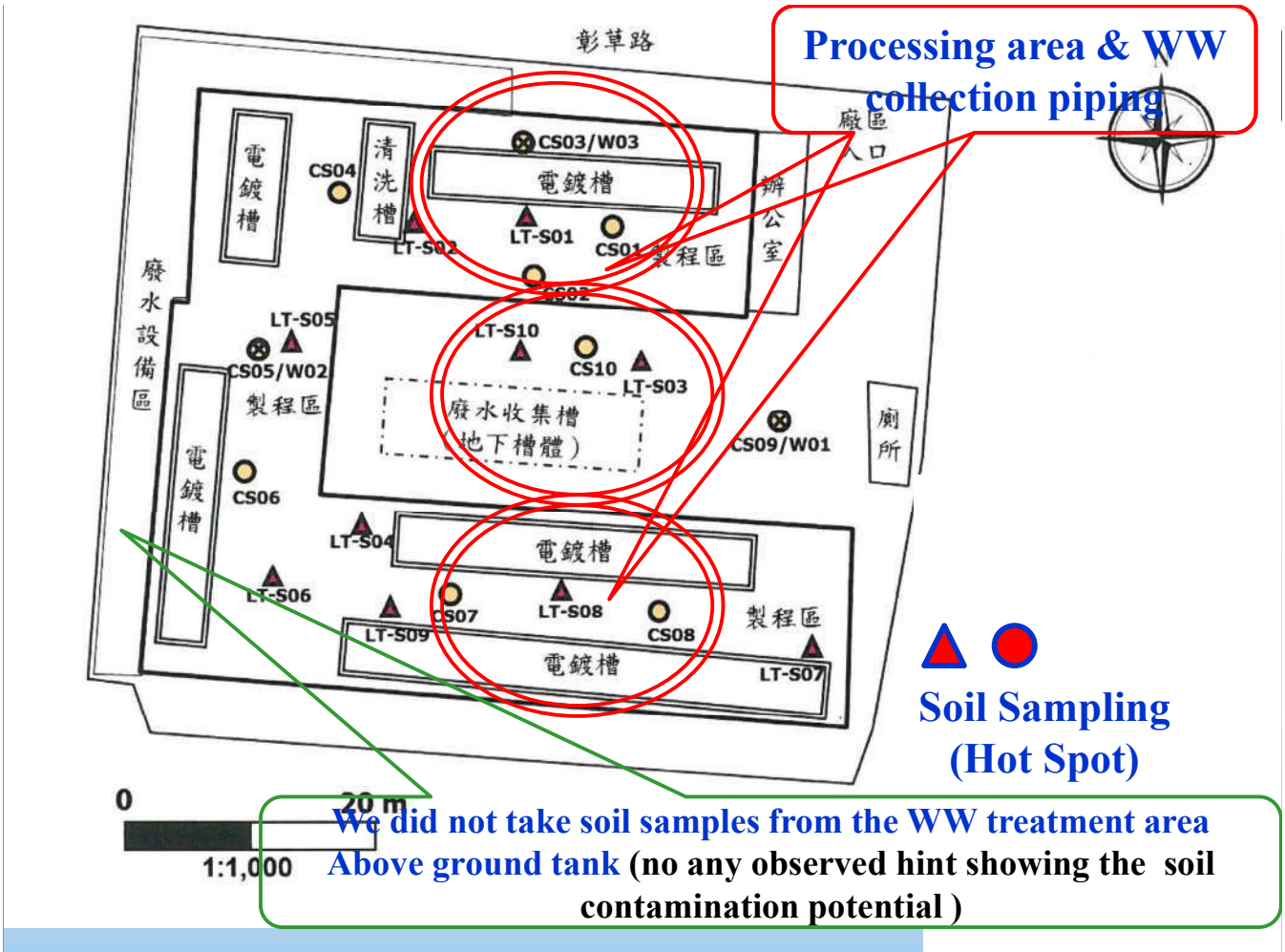
PitsWW Collection

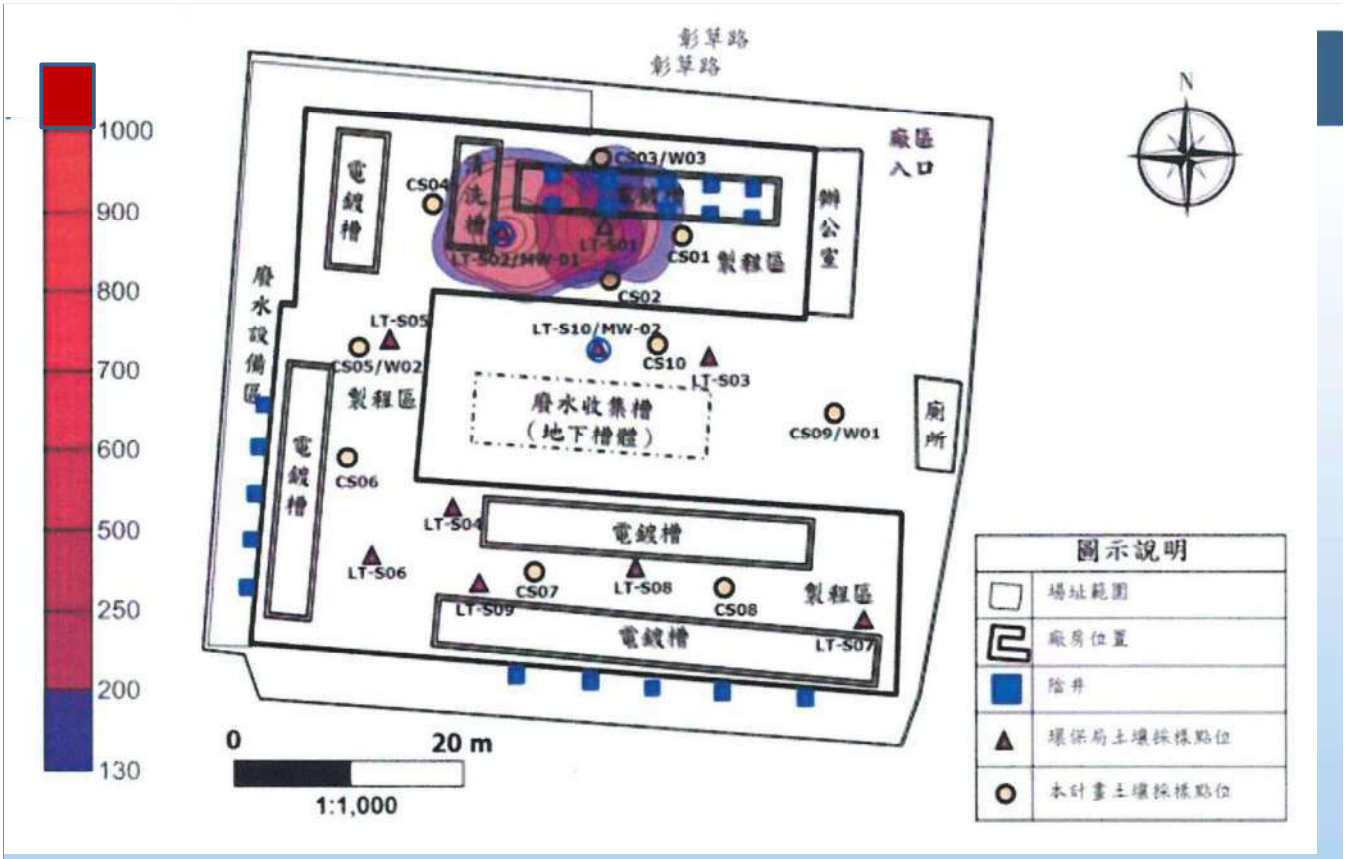
--- WW Collection Piping

Processing Area (metal plating)

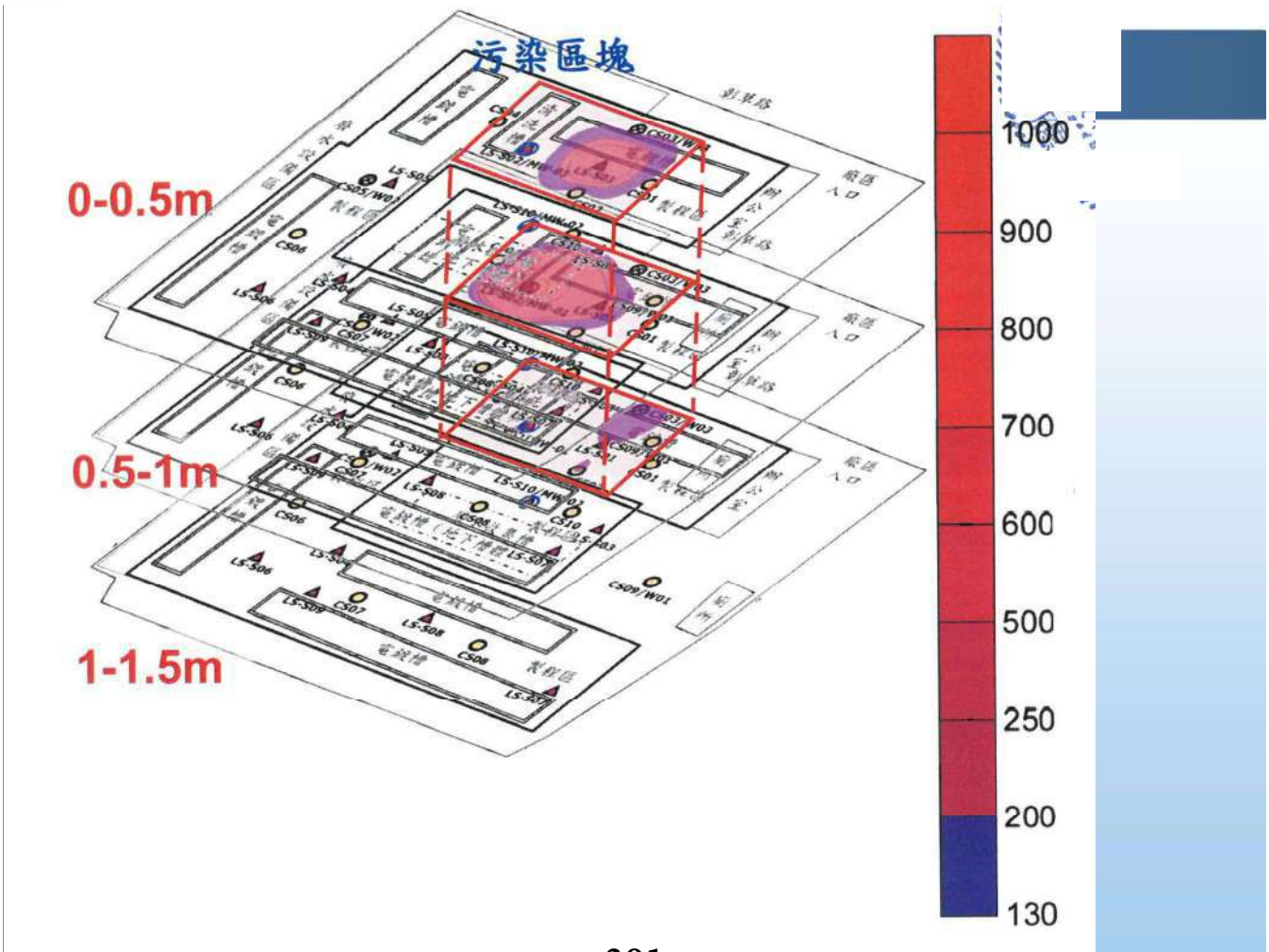
WW Treatment Plant (above ground)

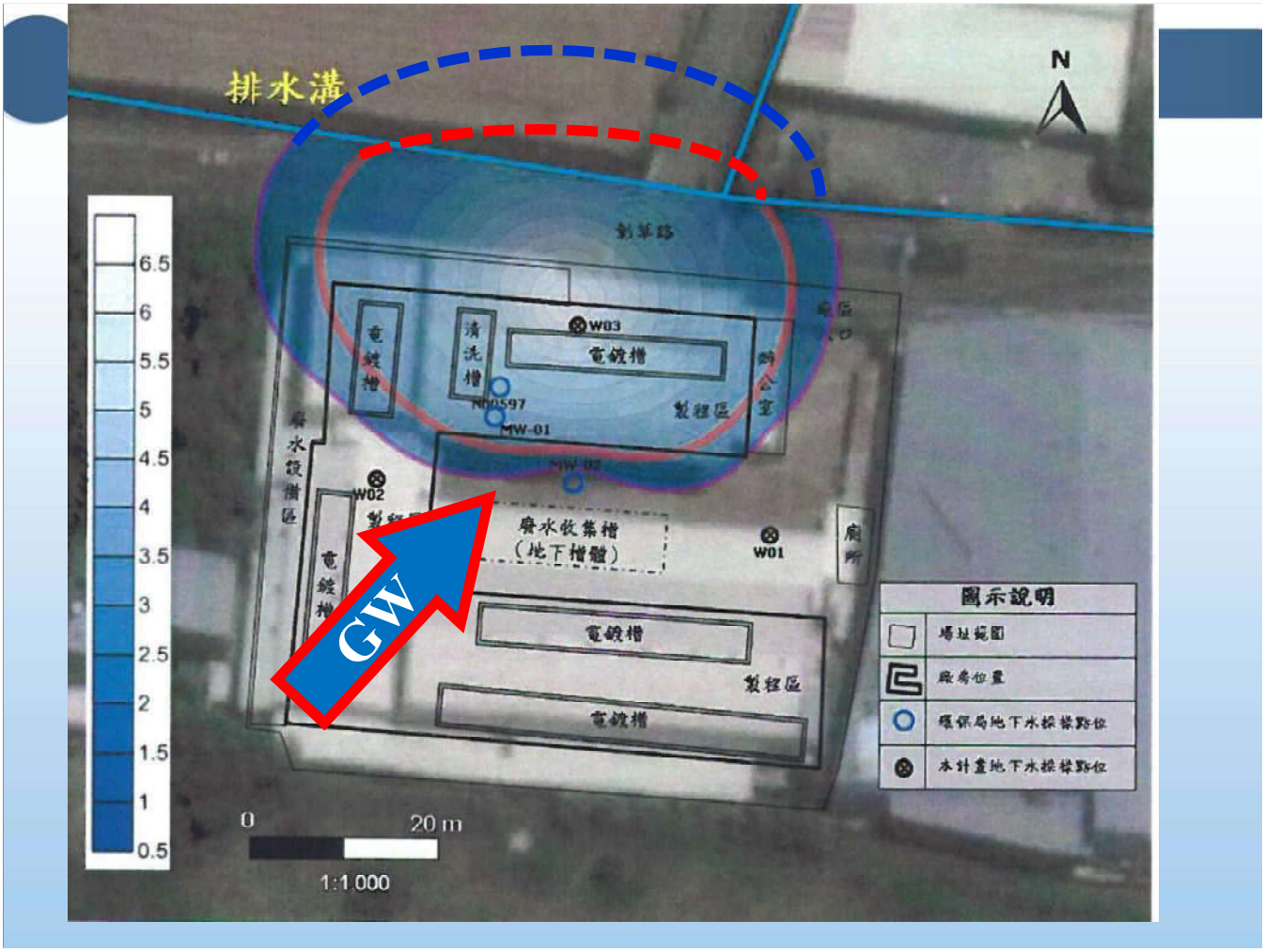


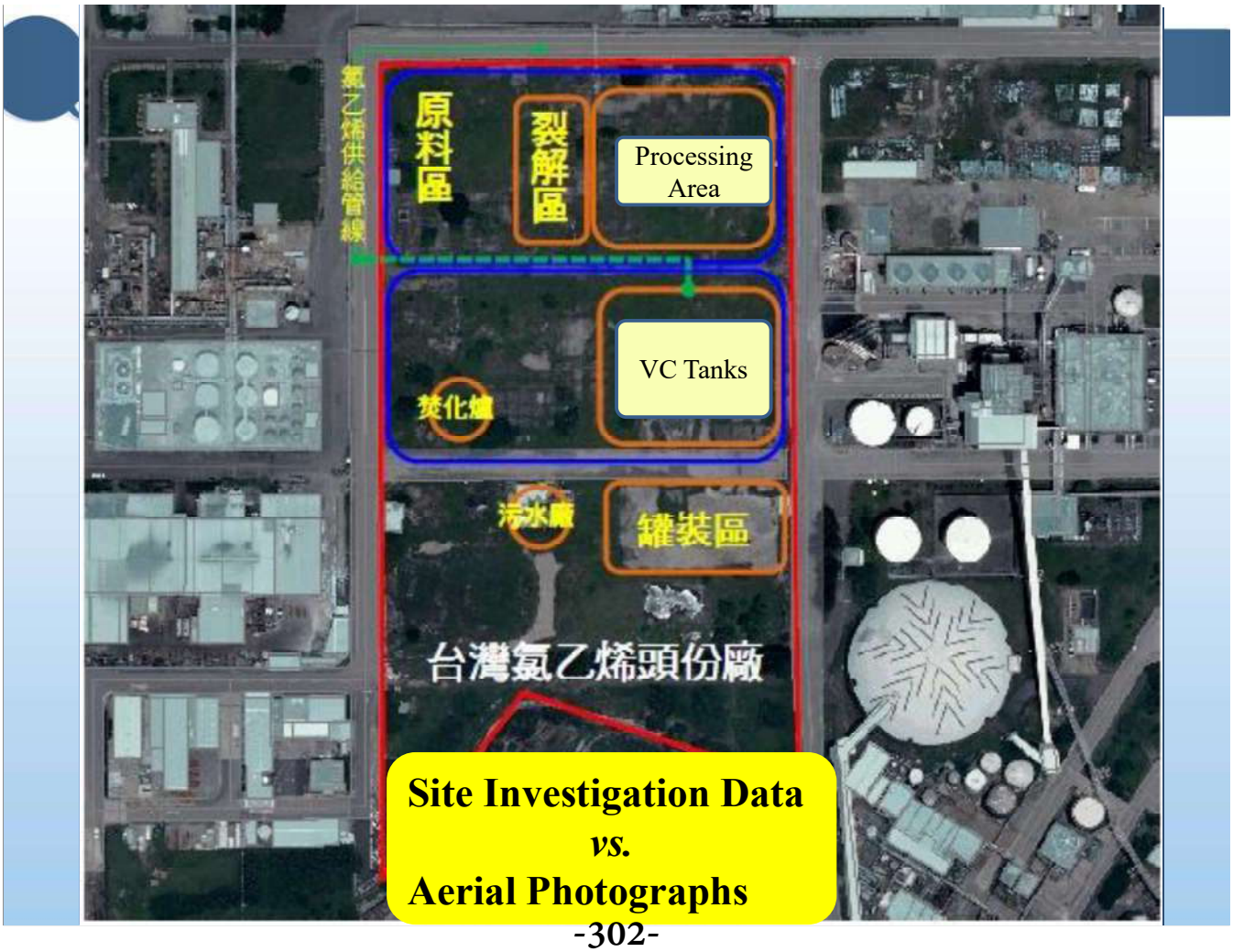




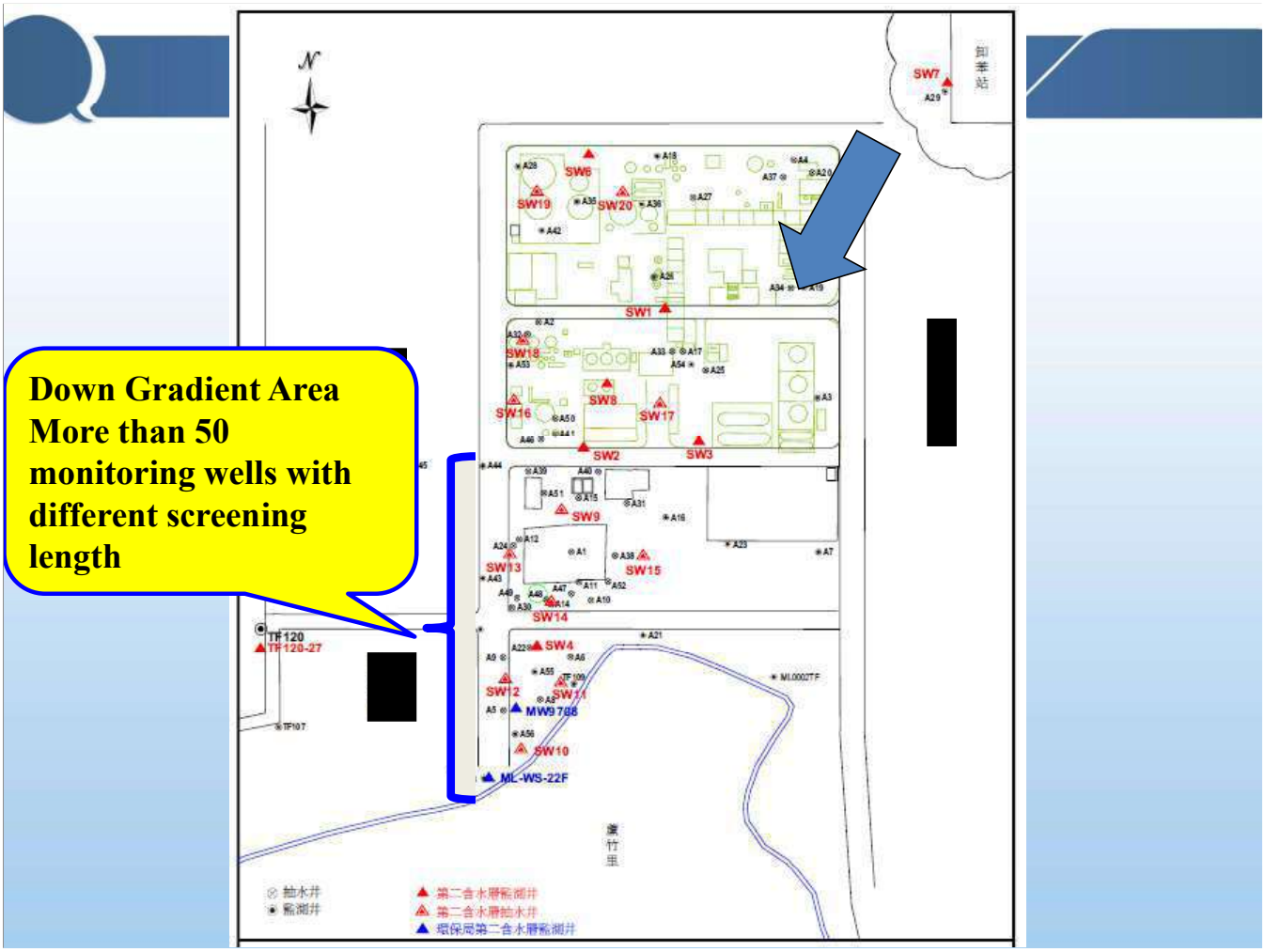
Contaminant: Ni (Soil & GW)

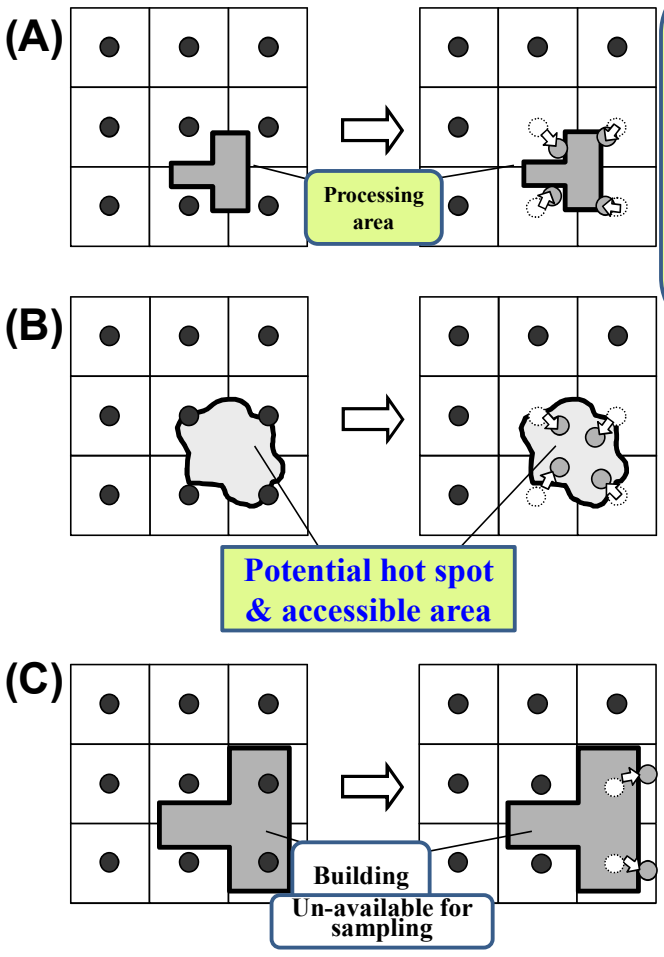






Site Investigation Data *vs.* Aerial Photographs



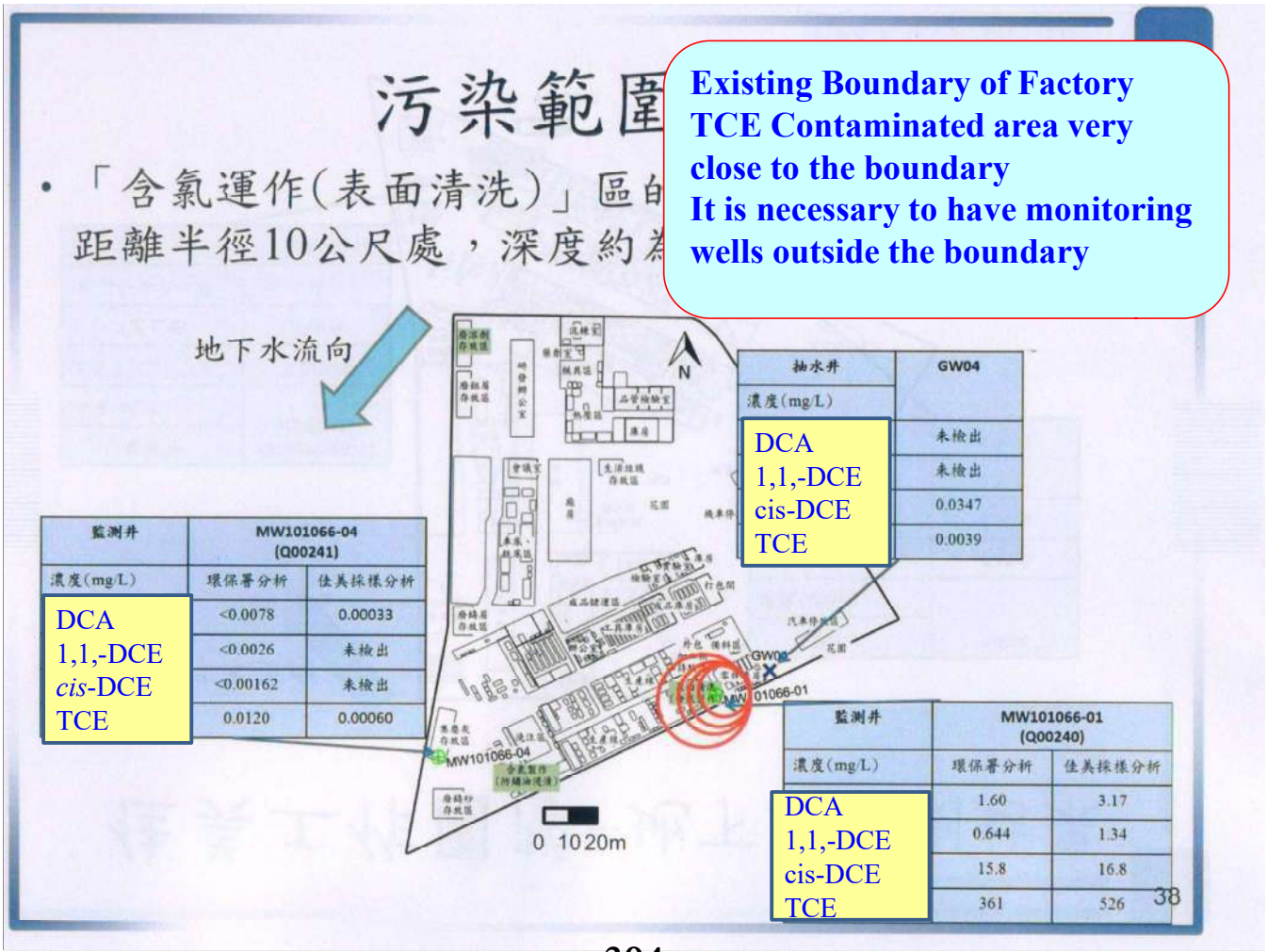


Potentially Contaminated Area
Soil Sampling Plan : inside or around the hot spot
A: difficult to sample in the operating manufacture area
B: Accessible area

Sampling Plan
1. Sampling at the center of each sub-unit
2. Planed sampling area ( )
3. Modified sampling area ( )

Sampling Plan
1. Sampling at the center of each sub-unit
2. Planed sampling area ( )
3. Modified sampling area ( ) due to in-accessible

基本資料-平面配
Operating pumping wells (manufacture purpose)
These wells may interrupt the GW flow direction
Wastes Storage Area
1. Organic solvents
2. Al dust
3. Iron dust
4. Other wastes
④ 集塵灰
⑤ 廢鑄砂
GW04
舊有抽水井,井深11m
Surface-clean processing area (solvent: Cl-VOC)
0 10 20m


污染範圍
• 「含氯運作(表面清洗)」區
距離半徑10公尺處，深度約
Existing Boundary of Factory
TCE Contaminated area very close to the boundary
It is necessary to have monitoring wells outside the boundary
地下水流向
抽水井 GW04
濃度(mg/L)
DCA 未檢出
1,1,-DCE 未檢出
cis-DCE 0.0347
TCE 0.0039
監測井 MW101066-04 (Q00241)
濃度(mg/L) 環保署分析 佳美採樣分析
DCA <0.0078 0.00033
1,1,-DCE <0.0026 未檢出
cis-DCE <0.00162 未檢出
TCE 0.0120 0.00060
監測井 MW101066-01 (Q00240)
濃度(mg/L) 環保署分析 佳美採樣分析
DCA 1.60 3.17
1,1,-DCE 0.644 1.34
cis-DCE 15.8 16.8
TCE 361 526
0 10 20m
38

2013/40/14

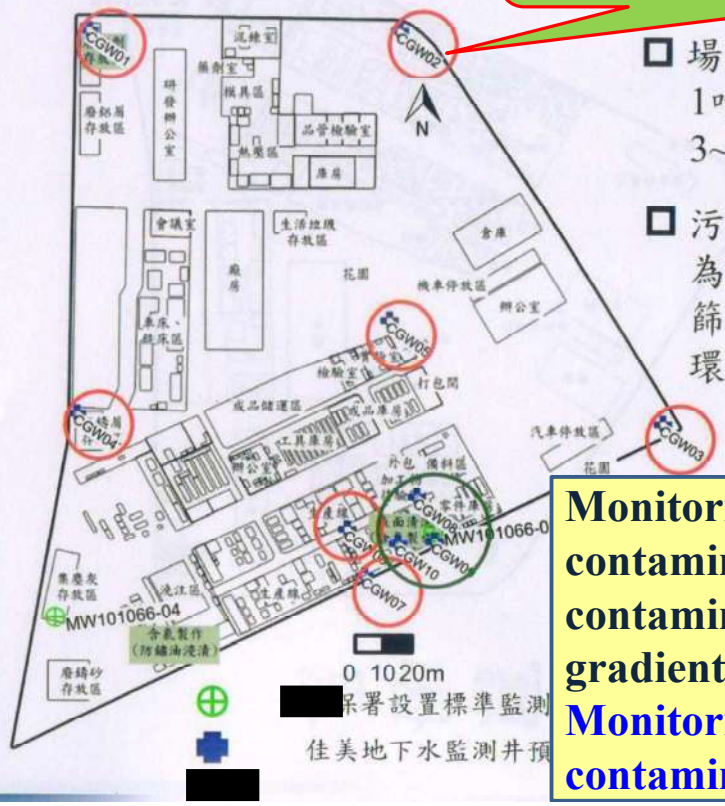
限制出貨暫存區
Block Area

嚴禁煙火

2013/10/15

細密調查-地

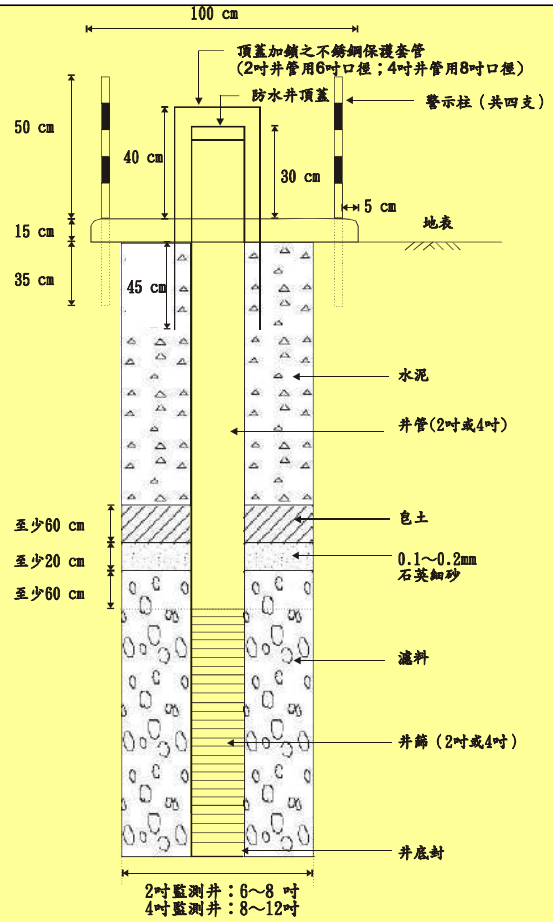
Monitoring well around the boundary (up-gradient)



- 場址周界設置CGW01~CGW07 1吋監測井，井深15公尺，開篩3~10公尺。
- 污染熱區設置CGW08~CGW10為2吋監測井，井深15公尺，開篩12~14公尺。(CGW09設置與環保署標準井Q00240設為群井)

Monitoring wells beside the contaminated area (soil contamination) and its down-gradient area

Monitoring well inside the soil-contaminated area??? (be careful)



圖一　監測井設計示意圖（未按比例）。圖中尺寸長度註明者為標準尺寸；井篩和井管長度未註明者依地質狀況及含水層型態而定。

井　號	N00281
站　名	彰化縣芳苑鄉漢寶村草漢路漢寶段（N004EPA0008）-MW1
性　質	□區域性 ■場置性
類　別 (選場置性續填本欄)	□加油站監測井 □掩埋場監測井 ■非法棄置場監測井 □工廠監測井 □科學園區監測井 □工業區監測井 □其他(　)
設置日期	100年10月12日
地　址	彰化縣芳苑鄉漢寶村草漢路漢寶段
管理單位	彰化縣環境保護局
聯絡電話	（04）7115655

監測井照片

監測井基本資料

監測井目的	監測場址第一含水層之水質
監測井形式	平台式
設井工法	□頓鑽 □中空螺旋鑽 ■鑽堡 □其他(　　)
井篩區間	2.1公尺至8.1公尺(距井頂深度)
井管型式	直徑2吋、螺牙式接頭、PVC材質、型號40
井篩型式	直徑2吋、螺牙式接頭、PVC材質、型號40
井　深	8.1公尺 (距井頂深度)，量測日期100年10月19日
井頂高程	6.507公尺 (海拔高程，設井時)，量測日期100年11月3日
高程測量方式	■引用水準點測量(編號：G021) □DGPS測量 □其他
地下水位	3.920公尺 (距井頂深度)，量測日期100年10月19日
水力傳導係數	2.2×10^{-3}公尺/秒，量測日期100年10月19日 (量測時)
二度分帶座標	TWD97 E(X) 187940.234，N(Y) 2656283.202
經緯度座標	東經：120.389992／北緯：24.010159

土壤取樣記錄表

工程名稱：地下水監測井設置
井　　號：P00164
開鑽日期：99.7.27　　完井日期：99.7.27
記錄人員：[redacted]　　氣候狀況：雨

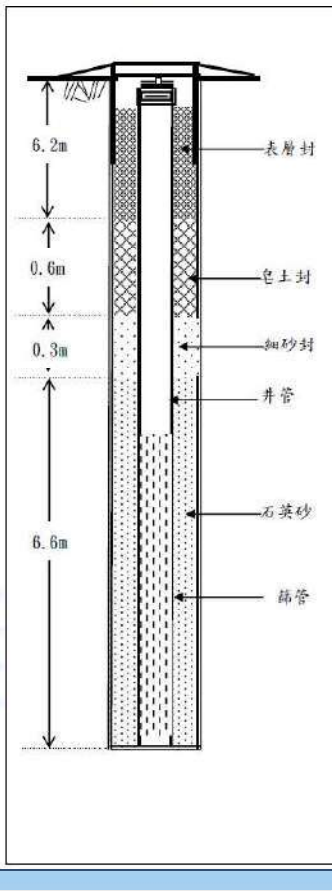
至地表下深度（呎）	土壤特徵描述		土壤柱狀圖
0-1	棕黃色砂質粉土	0.18M	ML
1-2	灰色黏土質粉土	1.9M	ML
2-3			
3-4			
4 5			
5-6			
6-7	灰色粉質細砂	6.8M	
7-8			
8-9	灰色粉質細砂偶夾薄層黏土	9.0M	CL
9-10			
10-11	灰色砂質沉泥	10.5M	
11-12			
12-13			
13-14	灰色粉質細砂	13.7M	

監測井構造紀錄表

工程名稱：地下水監測井工程

設置日期：	99.07.27		
井　　號：	P00164		
鑽井方法：	KH-2		
井孔直徑：	6"	至	13.7M
井頂高程：	9.138M		
座　　標：	N 2612334.023		
座　　標：	E 177946.177		
井管型式：	2" PVC SCH40		
井管接頭：	螺紋式		
井篩型式：	2" PVC SCH40		
篩孔尺寸：	0.01"	井篩長度	6M
井頂蓋型式：	平滑式		
井底封型式：	平滑式		
濾料型式：	石英砂		
濾料粒徑：	0.6~0.8mm		
濾料封：	7.1	至	13.7 m
細砂封：	6.8	至	7.1 m
皂土封：	6.2	至	6.8 m
表層封：	0.0	至	6.2 m
保護井管：	9" 隱藏式人孔蓋		
洗井方法：	氣提式	日期	99.07.28

監測井示意圖



工程名稱：地下水監測井設置

設置日期：101.6.29

井　　號：SY01

井頂高程：357.343M

座　　標：N 2696480.203

座　　標：E 223672.005

鑽井方法：頂擊式鑽堡

井孔直徑：6"　至 84.6M

井管型式：6" PVC SCH40

井管接頭：螺紋式

井篩型式：6" PVC SCH40

篩孔尺寸：0.01"　井篩長度 9M

井頂蓋型式：平滑式

井底封型式：螺紋式

濾料型式：石英砂

濾料粒徑：0.6-0.8mm

濾料封：75.0 至 84.6 m

細砂封：74.7 至 75.0 m

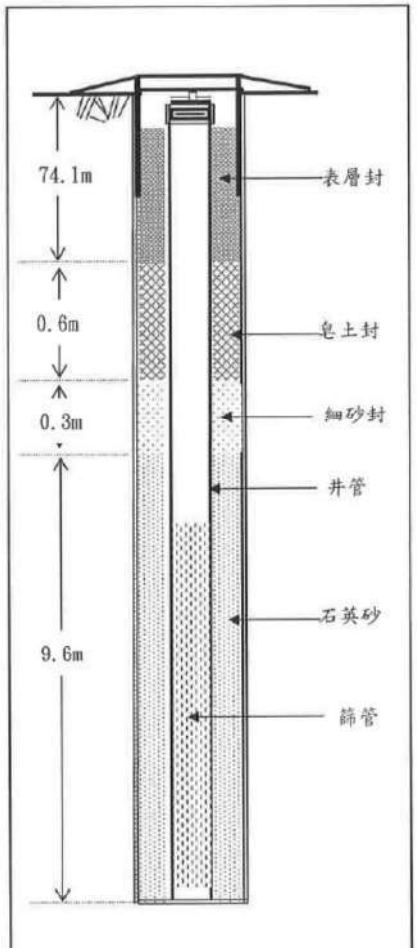
皂土封：744.1 至 74.7 m

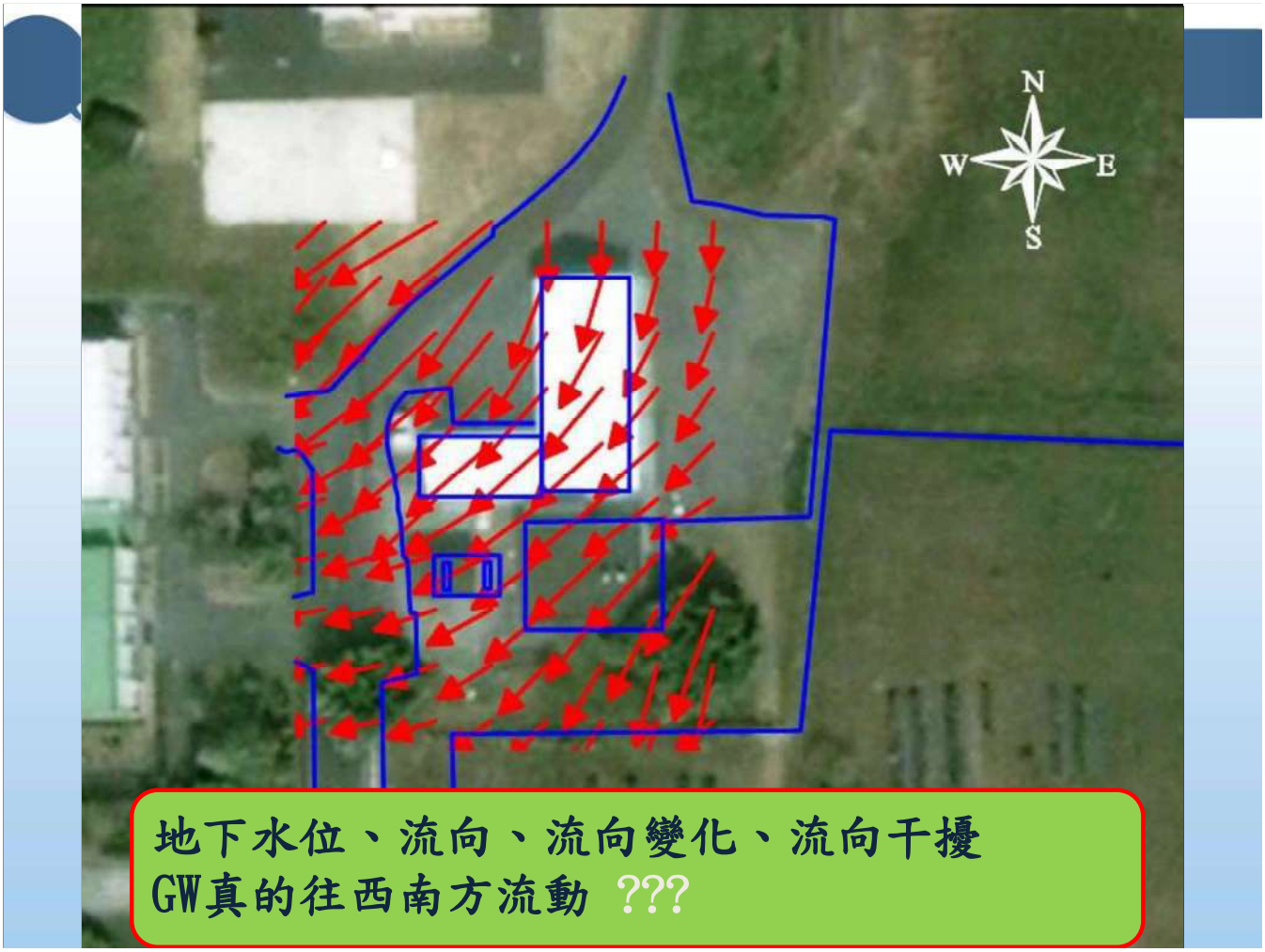
表層封：0.0 至 74.1 m

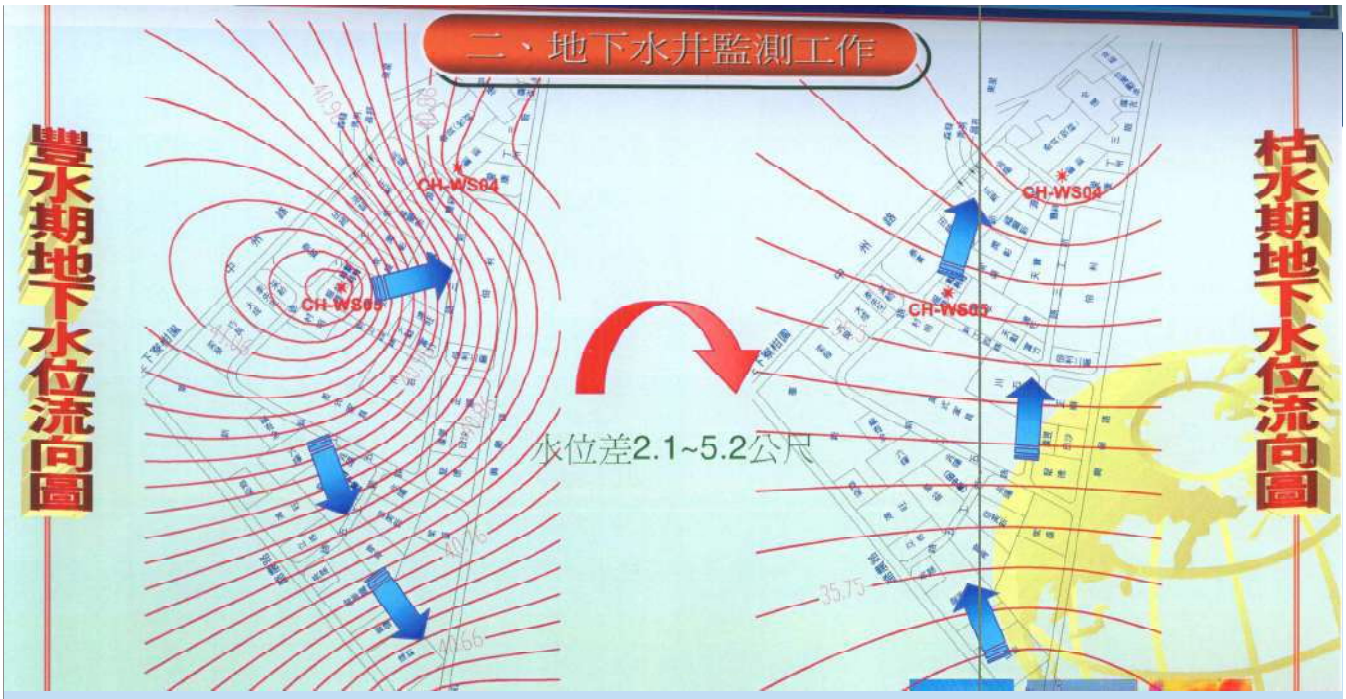
保護井管：不銹鋼管 直徑 9"

洗井方法：氣提式 日期 101.7.19

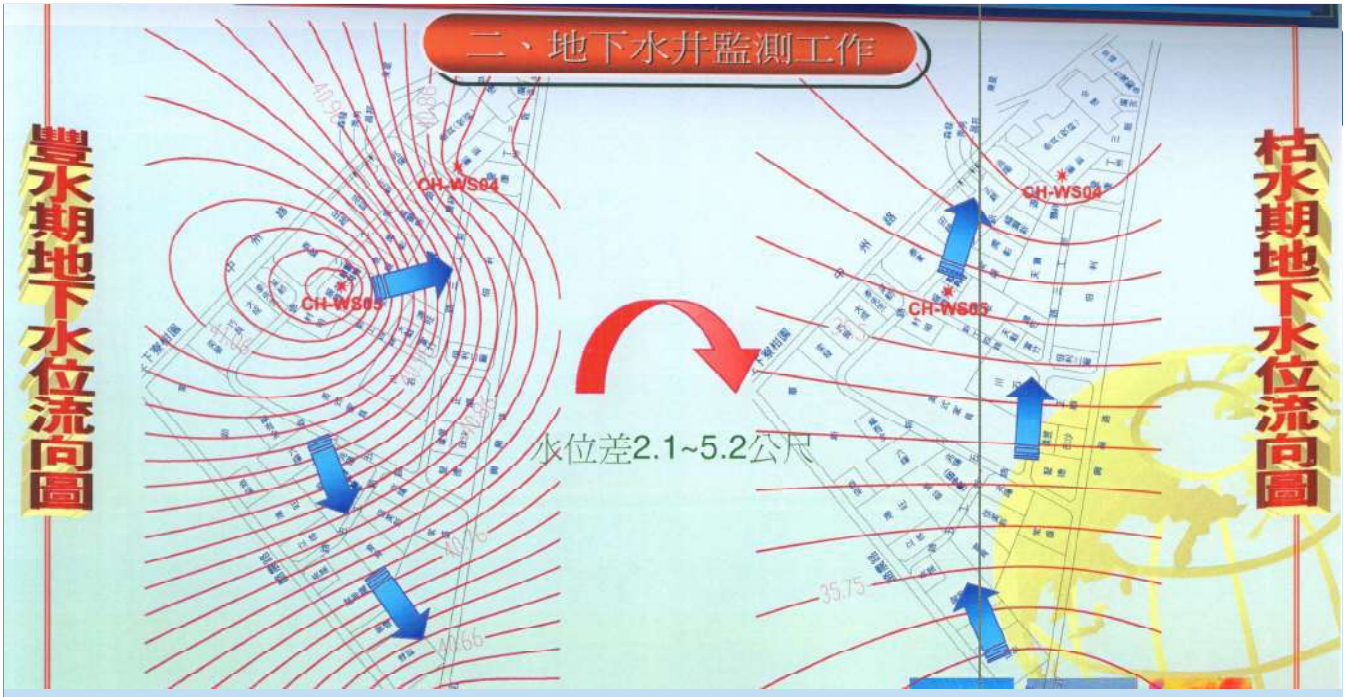
監測井示意圖







Raining and Dry Season
Down- & up-gradient: completely different



GW Flow Direction: re-check each season
The migration of contaminants & data explanation (& rationalization) should be very careful & precious

Monitoring wells: regular maintenance

Monitoring well: maintenance

曝氣系統操作調整與記錄

通氣井 PID/FID 監測

通氣井地下水水位量測

通氣井地下水水質量測

圖 4.2-5　現地曝氣法操作情形

氧化劑配製作業

催化劑配製作業

採重力流注藥劑

地下水質檢測

Monitoring well: not be used as injection wells

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154

- The ESA process used by EPA is described as follows:
- (3) Interview: the evaluator conducts interviews with relevant responsible persons, employees, land owner and users to acquire additional data on factory operations.

- The ESA process used by EPA is described as follows:
- (4) Investigation plan: the evaluator has to determine potentially highly contaminated regions; subjective assessments were used to distribute sampling points and analyzed items.

The result of Site Investigation in 2013 (200 Sites)

Item	Soil Contamination	GW Contamination	
Type of Pollutant			
• Heavy metal	80	5	HM: Soil Contamination
• Total petroleum Hydrocarbons	22	0	
• Polychlorinated biphenyls	6	0	
• Volatile organic compounds	2	9	Cl-VOC: GW Contamination
• Dioxin	1	0	
• Pesticide	1	0	
• Total phenolic Compounds	-	1	

Priority List of 21 types of Potentially Highly Contaminated Abandoned Factories in Taiwan

No.	Industry	No.	Industry
1	Leather, Fur & Related Products Manufacturing	12	Plastic Products Manufacturing
2	Wood and Bamboo Products Manufacturing	13	Basic Metal Manufacturing
3	Basic Chemical Material Manufacturing	14	Metal Surface Treating
4	Petrochemicals Manufacturing	15	Metal Heat Treating
5	Fertilizers Manufacturing	16	Computers, Electronic & Optic Prod. Manufacturing
6	Man-made Fibers Manufacturing	17	Electronic Parts & Components Manufacturing
7	Synthetic Resin and Plastic Materials Manufacturing	18	Electrical Equipment Manufacturing
8	Synthetic Rubber Manufacturing	19	Electricity Supply
9	Varnishes, Lacquers, Dyes, Pigments Manufacturing	20	Waste Collection
10	Pesticides and Herbicides Manufacturing	21	Waste Treatment and Disposal
11	Petroleum and Coal Products Manufacturing		

The Major Contaminated Regions in the Abandoned Factory Investigations

- Manufacturing area
- Wastewater treatment facilities
- Open space
- Storage tank and pipeline area
- Waste disposal region
- Material storage area
- Boiler room, drying room, chimney area, and dust collection area
- Storage pond
- Other (cracked pavements or electrical room)

Cultivation of professional investigators

- Training of professional investigators
- The investigation of abandoned factories is different from operation factories. Investigators who are unfamiliar with the investigations and characteristics of the abandoned factories will frequently overlook the potential contaminated regions by factories and facilities disappearing or removing.

Cultivation of professional investigators

- **Training of professional investigators**
- **Therefore, Taiwan EPA has hosted seminars and training programs in which investigation experiences, feedback, and reviews are shared to relevant experts (e.g., those associated with environmental protection bureaus, local county and city governments, construction bureaus, industrial competent authorities, industrial associations, and technical consulting companies).**

A Comprehensive Survey of Abandoned Factories

- **A comprehensive survey of abandoned factories**
- Factories and lands in Taiwan are often converted for varying uses, which may cause the area of contamination to expand further. Moreover, the address at which early factories were registered may have changed when administration regions were readjusted or lands were reconstructed. The current status, usage, and location of the 42,000 abandoned factories are unknown, further elevating the uncertainty of pollution. Consequently, promoting a comprehensive survey of abandoned factories is critical.
-

A Comprehensive Survey of Abandoned Factories

- **A comprehensive survey of abandoned factories**
- By using the baseline data on abandoned factories, the developed support system, and portable data processors, Taiwan EPA has completely surveyed all the abandoned factories in Taiwan within 2 years, compared whether the address and location of the surveyed targets coincided with those registered, and subsequently established a database containing information on the current statuses of factory lands, existing facilities and operations, and the sensitivity of surrounding environments.

The Major Contaminants in the Abandoned Factory Investigations

- **Heavy metal**
- **Total petroleum hydrocarbons**
- **Polychlorinated biphenyls**
- **Volatile organic compounds**
- **Dioxin**
- **Pesticide**
- **Total phenolic compounds (phenols)**

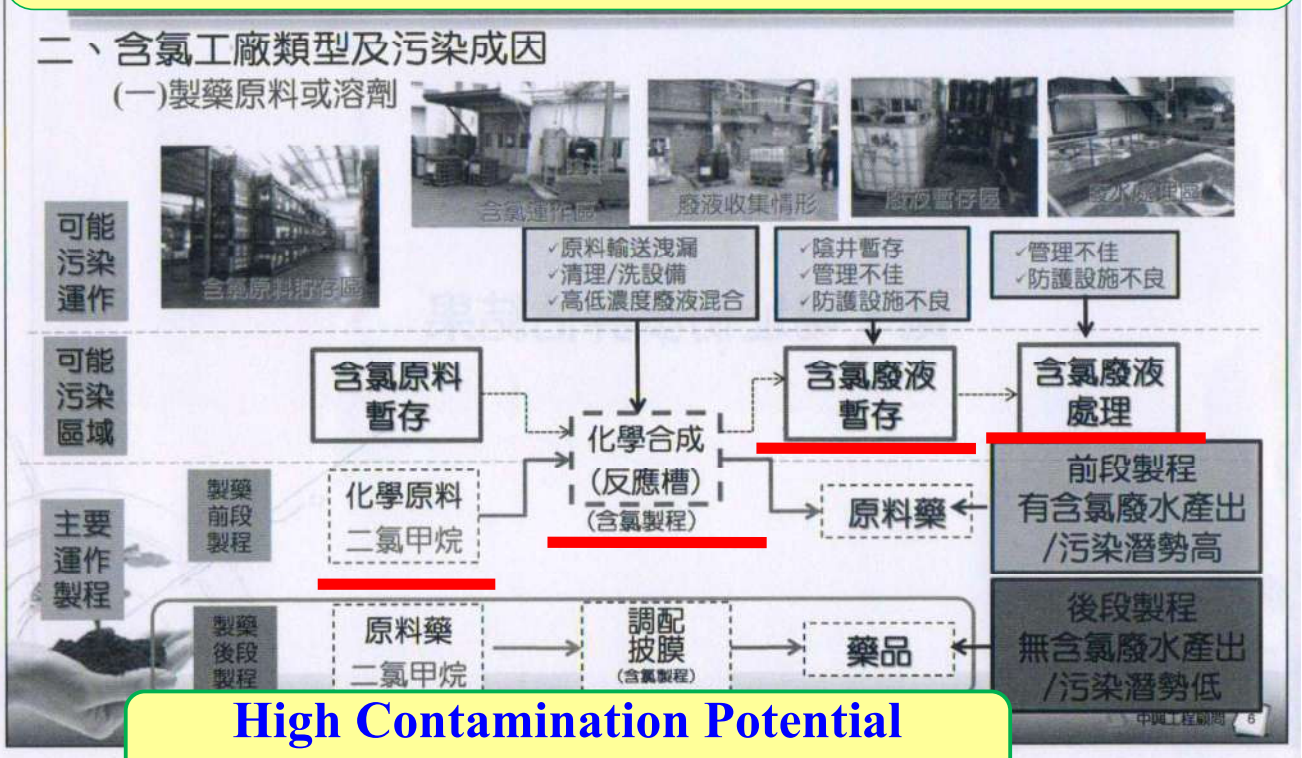
The contaminated regions in the abandoned factory investigations

Item	Soil Contamination	GW Contamination
Manufacturing area	**60**	**9**
Waste water treatment facilities	24	4
Open space	**23**	**3**
Storage tank and pipeline area	13	1
Waste disposal region	12	0
Material storage area	8	2
Boiler room, drying room, chimney area, and dust collection area	8	0
Storage pond	6	0
Other (cracked pavements or electrical room	9	0

Environmental risk map for abandoned factories in Taiwan

Abandoned Manufacturing Factories (Pesticide)

Raw Materials, Products, Processes

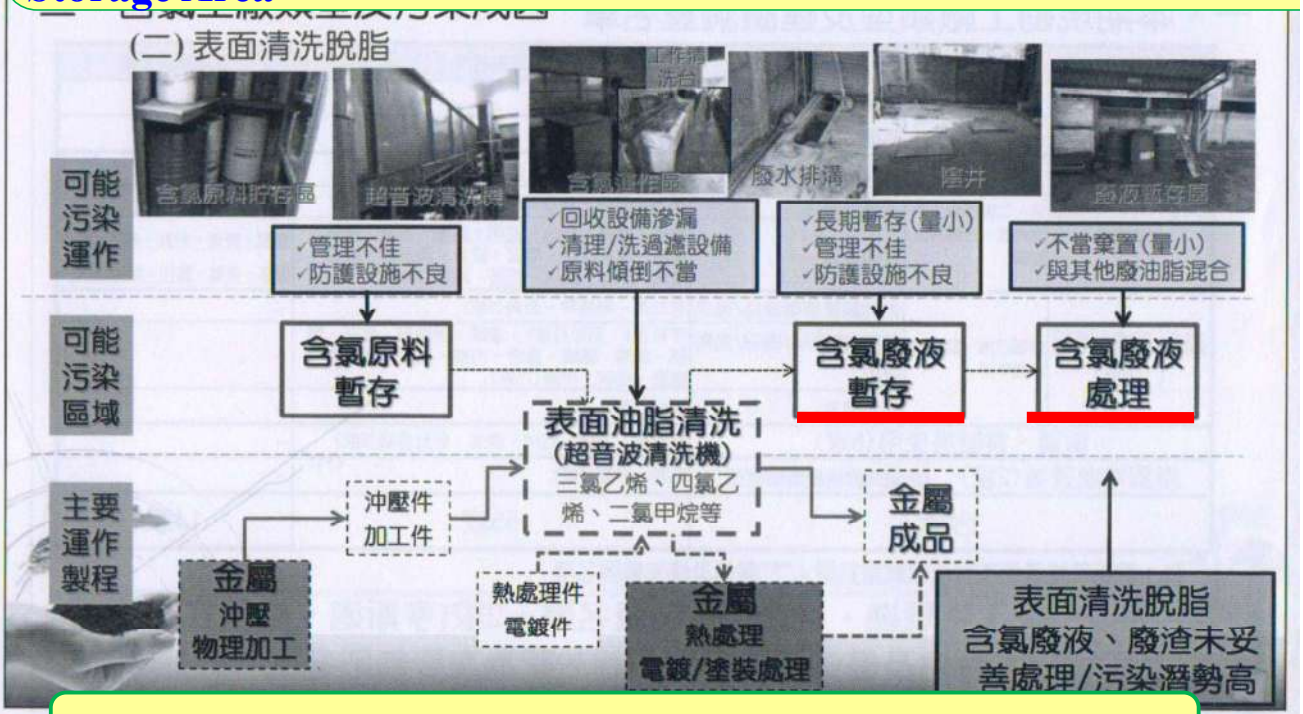


High Contamination Potential

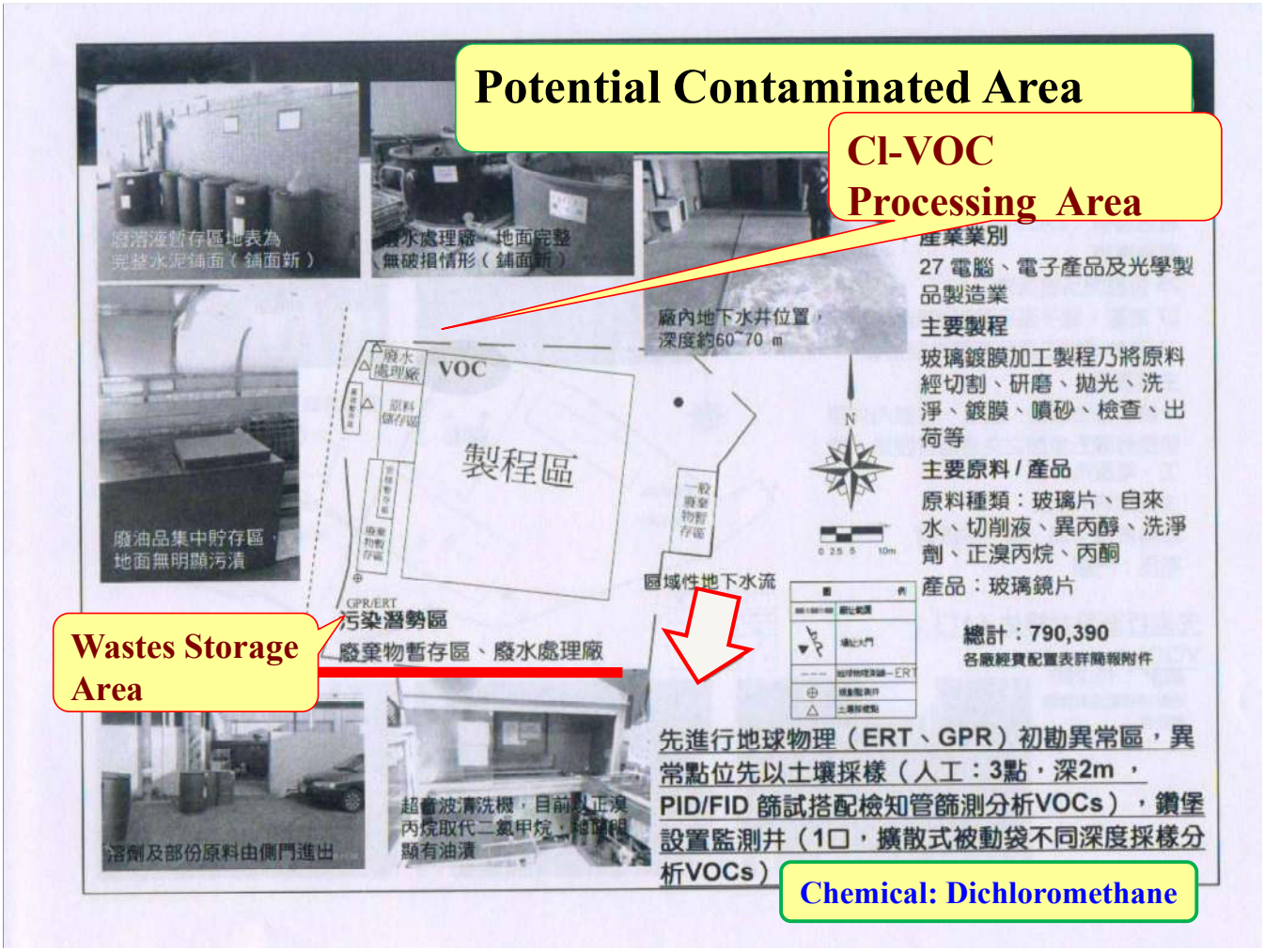
Chemical: Dichloromethane

Operating Manufacturing Factories (Metal Plating)

Wastewater, Wastes, Air pollution Control System & Sludge Storage Area

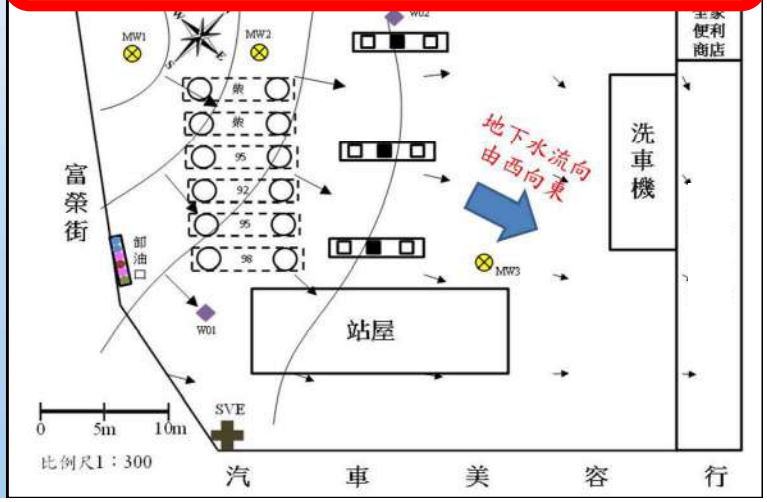


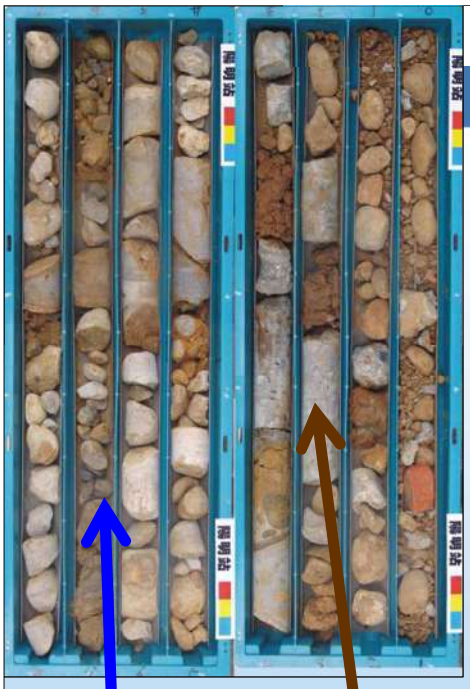
Chemicals: TCE, PCE, Dichloromethane…

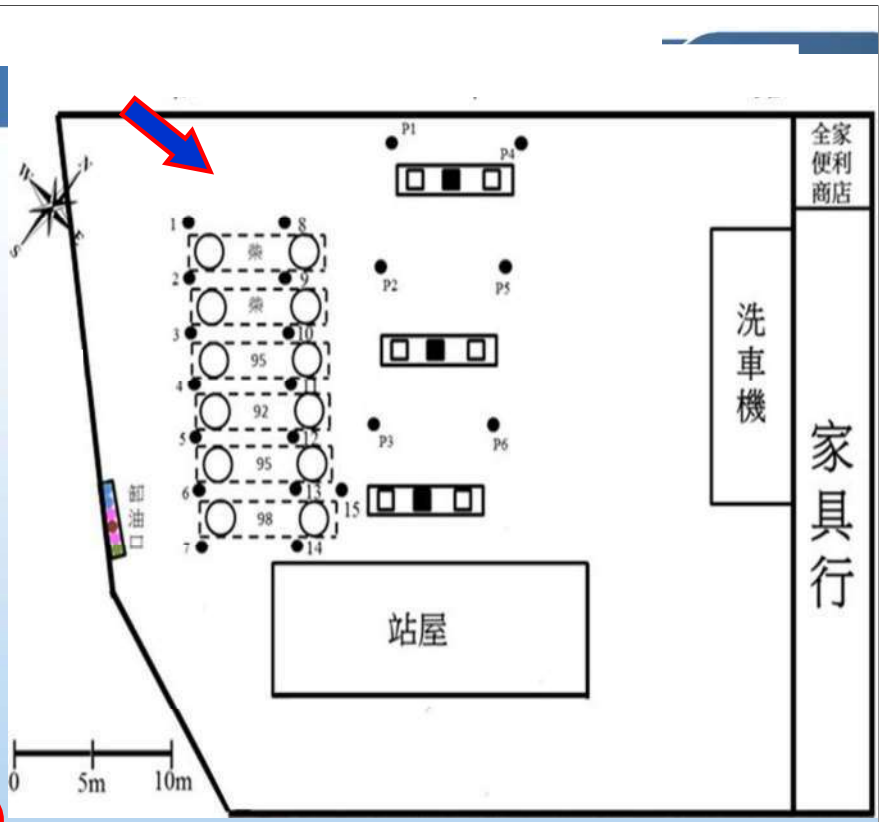

Potential Contaminated Area
Cl-VOC Processing Area
廢溶液暫存區地表為完整水泥鋪面（鋪面新）
廢水處理廠，地面完整（無破損情形（鋪面新）
廠內地下水井位置，深度約60~70 m
廢油品集中貯存區，地面無明顯污漬
VOC
製程區
廢水處理廠
原料儲存區
一般廢棄物暫存區
N
0 2.5 5 10m
區域性地下水流
GPR/ERT
污染潛勢區
廢棄物暫存區、廢水處理廠
Wastes Storage Area
溶劑及部份原料由側門進出
超音波清洗機，目前以正溴丙烷取代二氯甲烷，地面明顯有油漬
產業業別
27 電腦、電子產品及光學製品製造業
主要製程
玻璃鍍膜加工製程乃將原料經切割、研磨、拋光、洗淨、鍍膜、噴砂、檢查、出荷等
主要原料 / 產品
原料種類：玻璃片、自來水、切削液、異丙醇、洗淨劑、正溴丙烷、丙酮
產品：玻璃鏡片
總計：790,390
各廠經費配置表詳簡報附件
先進行地球物理（ERT、GPR）初勘異常區，異常點位先以土壤採樣（人工：3點，深2m，PID/FID 篩試搭配檢知管篩測分析VOCs），鑽堡設置監測井（1口，擴散式被動袋不同深度採樣分析VOCs）
Chemical: Dichloromethane

Site Investigation: Local GW Flow Direction & Aerial Photographs (historical data)
含氯溶劑試驗區
Chemicals: TPH, PCE
區域性地下水流
辦公室
成品倉庫
原料倉庫
製程使用地下水，約於5年前改為自來水
VOC
三級
二級
一級
VOC
SVOC
TPH
反應區製程廢液暫存坑
廢溶液暫存於暫存坑旁
廢潤滑油桶堆放於鍋爐室外
污染潛勢區
鍋爐區、廢液暫存區、儲槽區
GW Monitoring well
設立日期：民國77年建廠
廠地面積：16,784平方公尺
產業業別
18 化學材料製造業
19 化學製品製造業
主要製程
將原料（部份需溶解）依比例投入反應槽內調合、攪拌再經過精製及過濾等程序後注入成品槽。四氯乙烯等含氯溶劑主要用於實驗室
主要原料 / 產品
原料種類：環氧乙烷、環氧丙烷、脂肪醇等16種
產品：界面活性劑、酯類化合物、紡織漿料、原絲油
總計：789,720
各廠經費配置表詳簡報附件
先進行地球物理（ERT、GPR）初勘異常區，異常點位先以土壤採樣（人工：1點，深度：2m、機具：3點，深度：3~5m，PID/FID、TPH Test Kit篩試搭配檢知管篩測分析VOCs、S VOCs、TPH），鑽堡設置監測井（2口，貝勒管採樣分析VOCs、SVOCs、TPH）
10

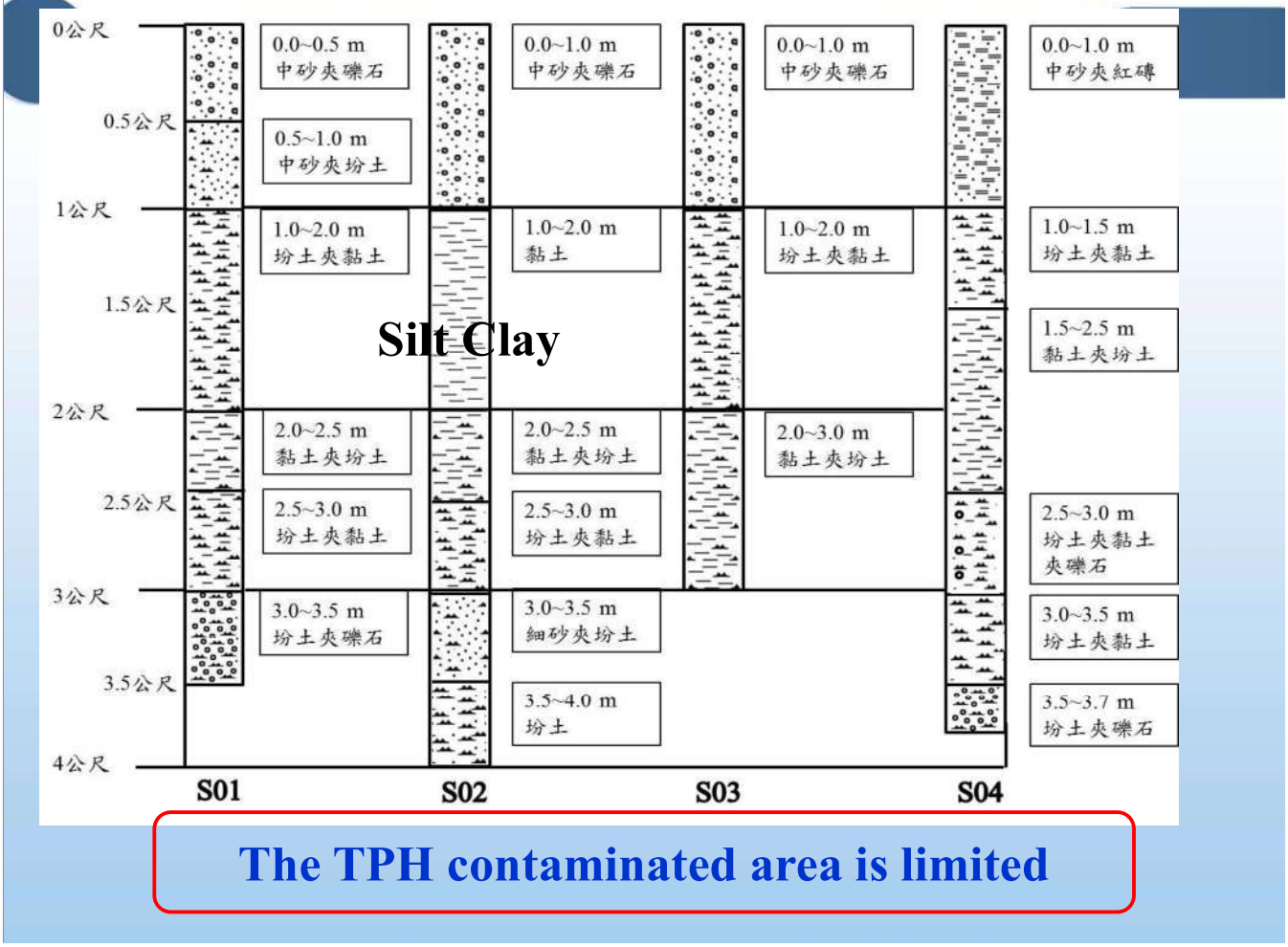
Gas Station







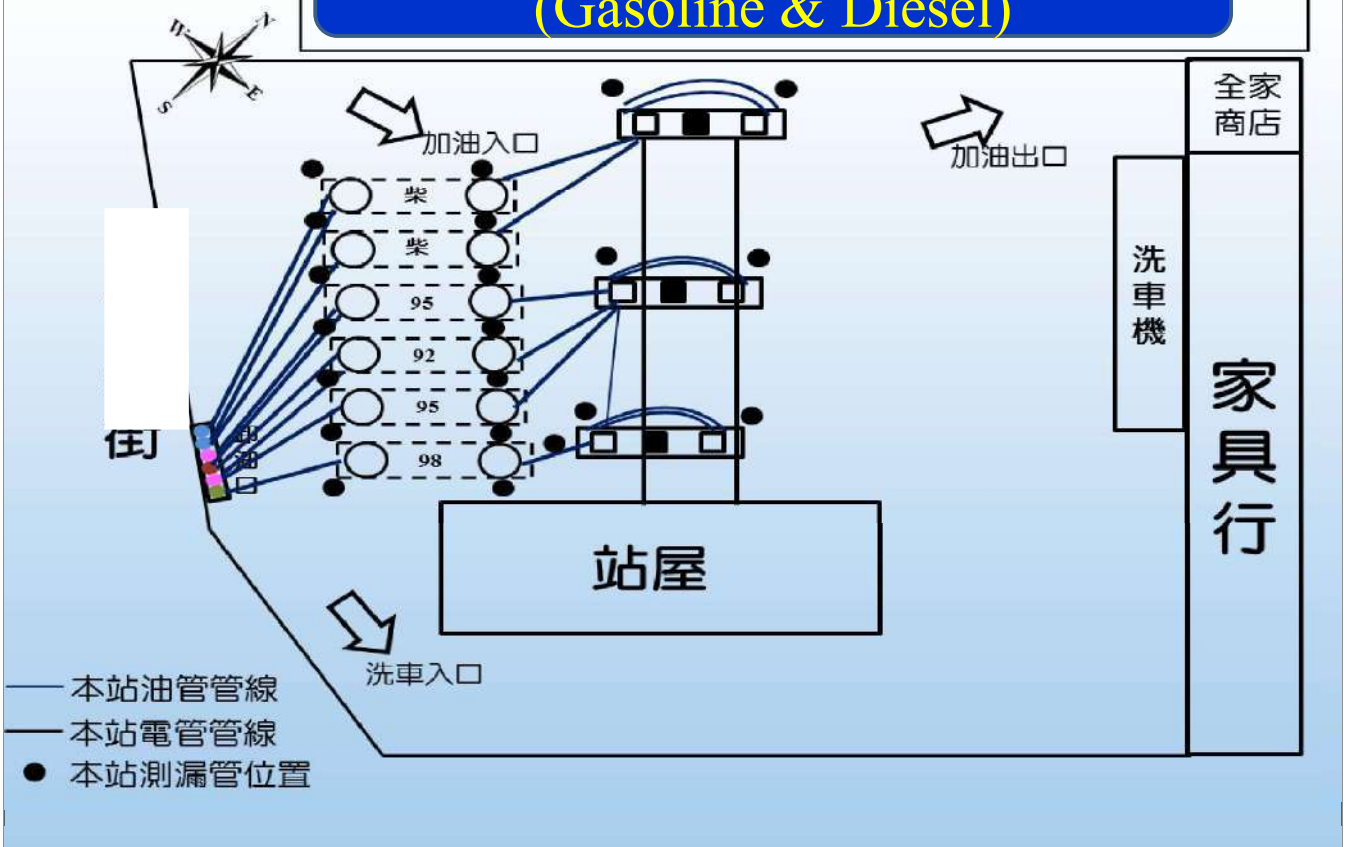
High & Low Permeability



Silt Clay

The TPH contaminated area is limited

Underground Piping System (Gasoline & Diesel)



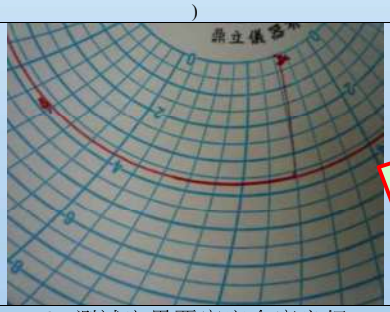
1. 將輸油管線油品卸回油槽

2. 盲封管線至加油機接頭

3. 灌入氮氣進行圓盤圖測試(油槽端)

4. 灌入氮氣進行圓盤圖測試(加油機端)

5. 確認圓盤圖是否出現壓降情形

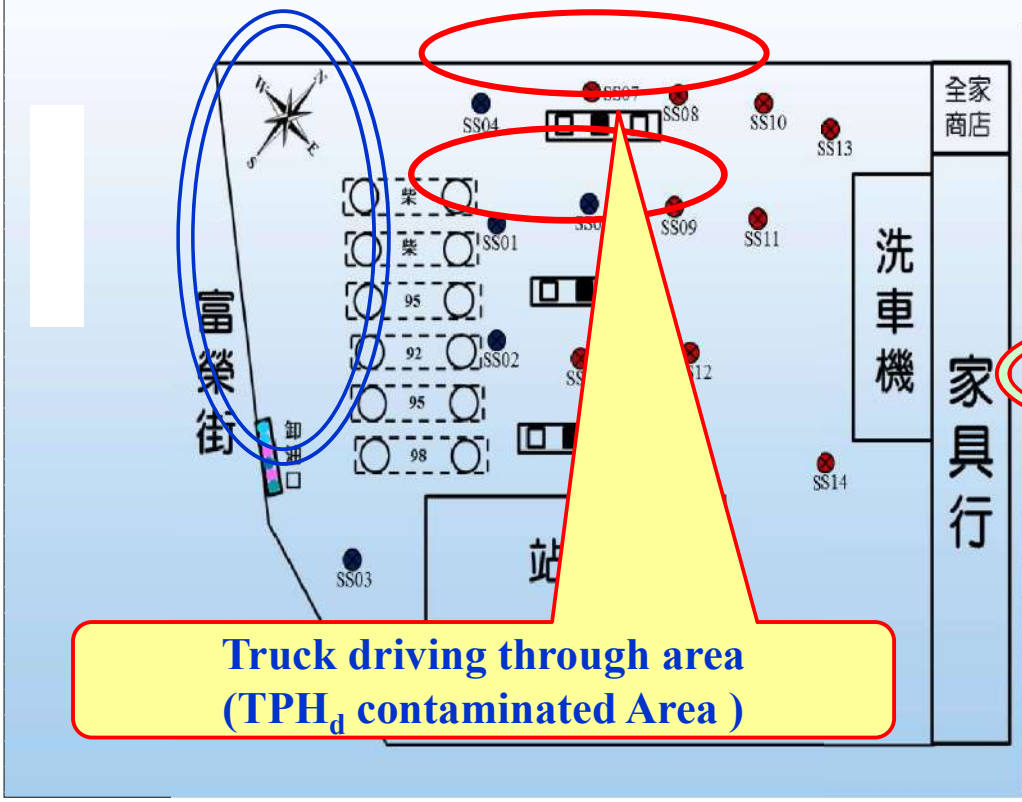


6. 測試完畢覆寫密合度良好

No piping or tank leakage was detected

UST: a RC secondary containment was equipped

In UST area, no soil sample was collected (RC dual deck)

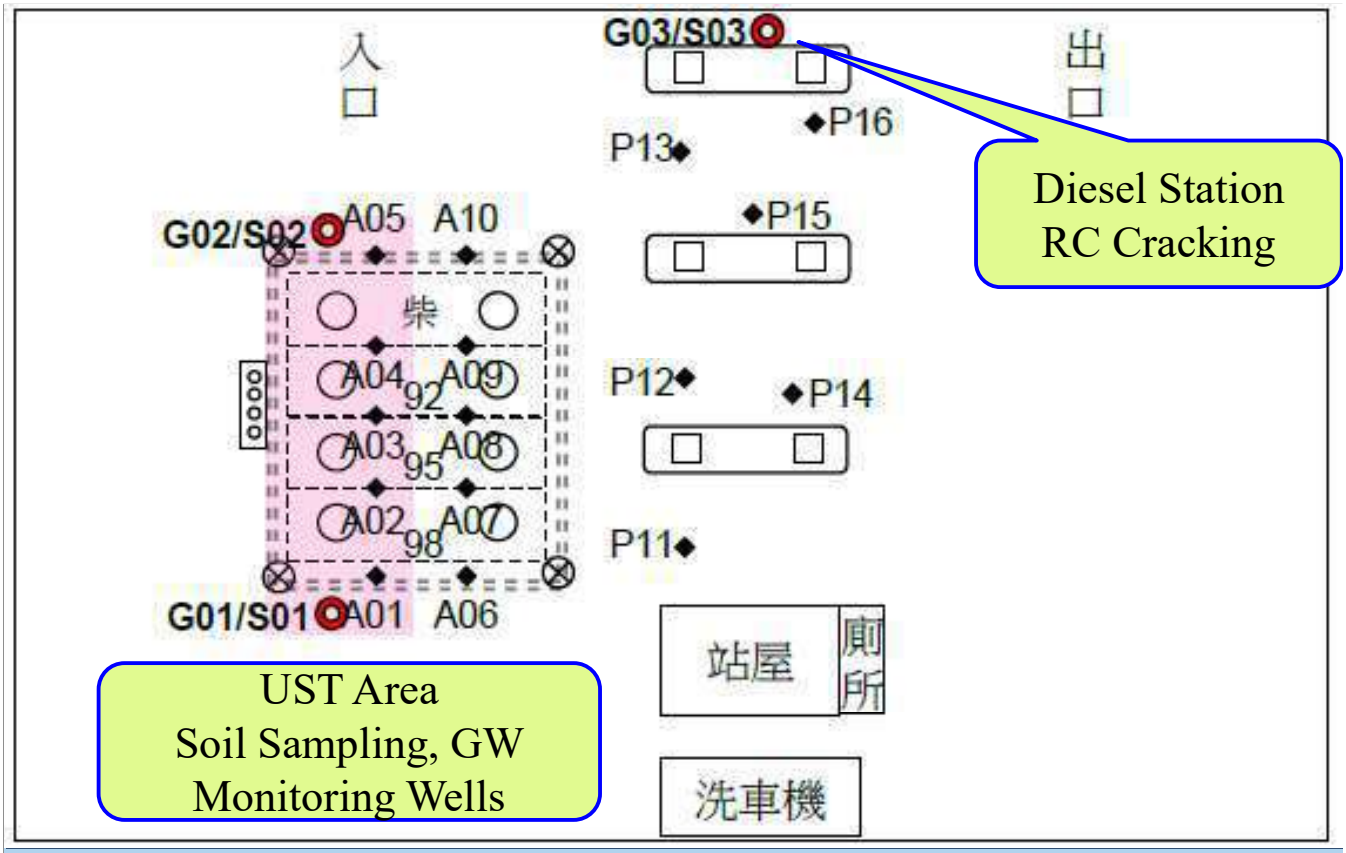


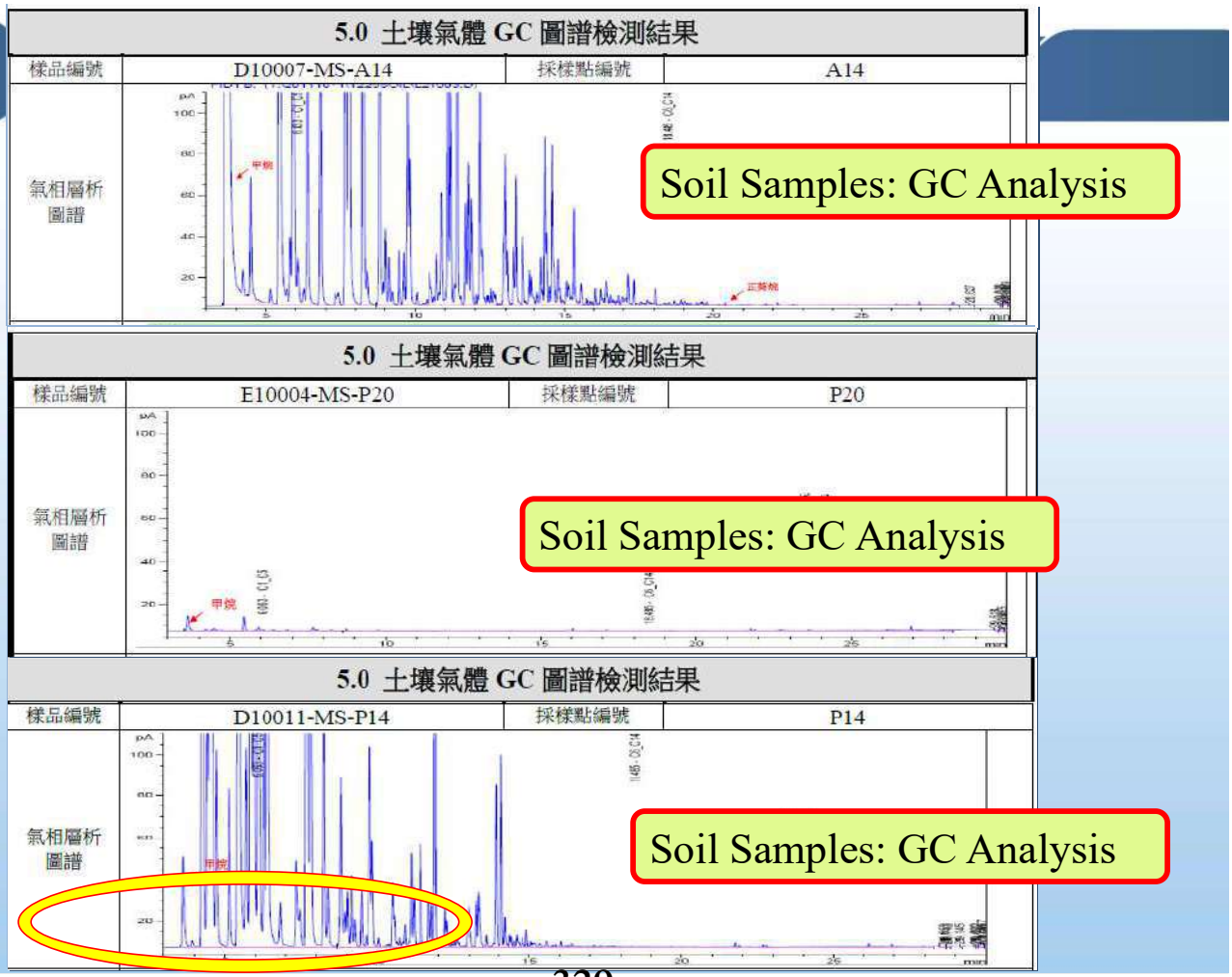
點位	深度 (m)	TPH 分析結果
SS01	2~3	190
SS02	1~2	378
SS03	2~3	224
SS04	1~2	64.3
SS05	1~2	66.3
SS06	2~3	3,930
SS07	2~3	8,710
SS08	1~2	1,310
SS09	2~3	3,420
SS10	2~3	2,100
SS11	2~3	1,350
SS12	2~3	4,060
SS13	1~2	1,270
SS14	1~2	1,460
TPH管制標準1,000mg/kg		

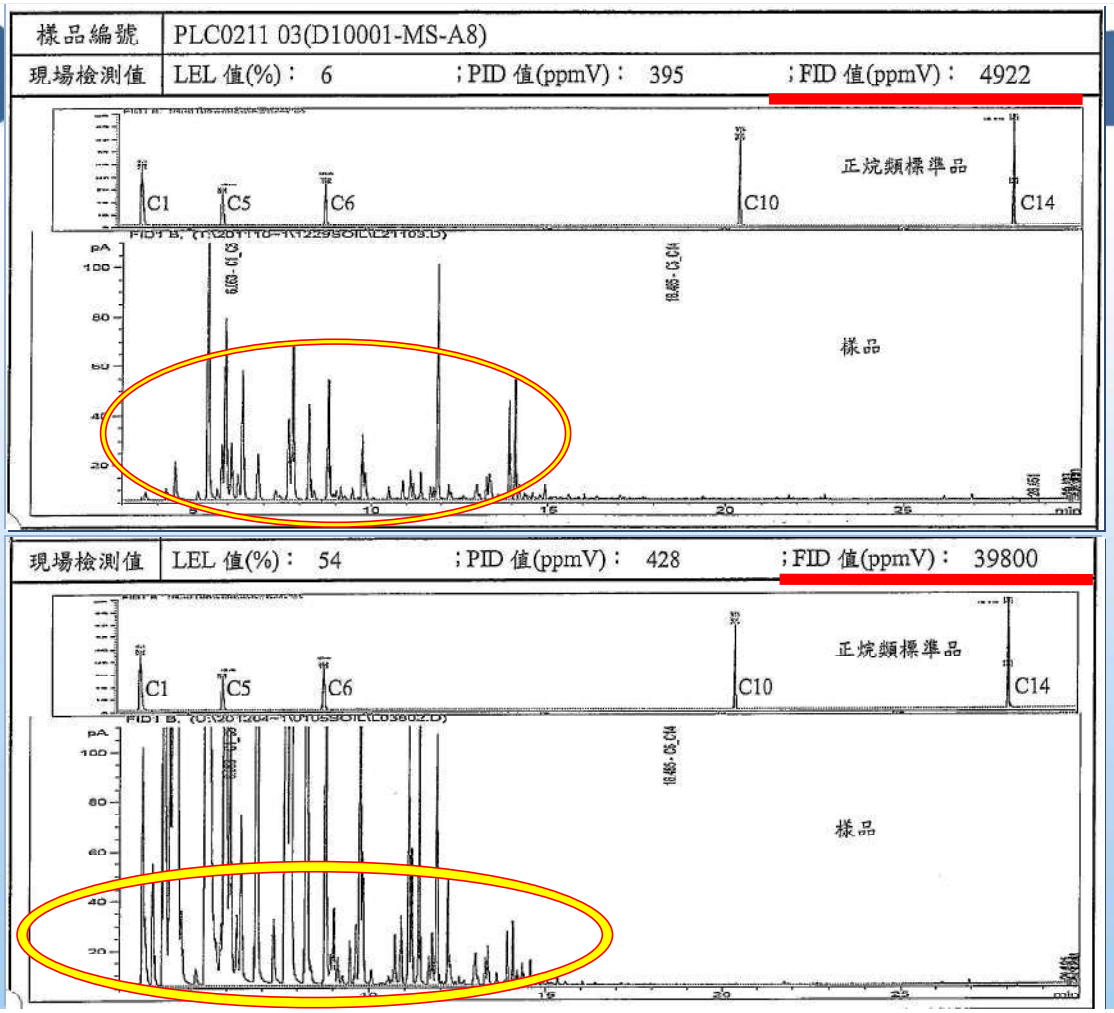
Truck driving through area
(TPH_d contaminated Area)

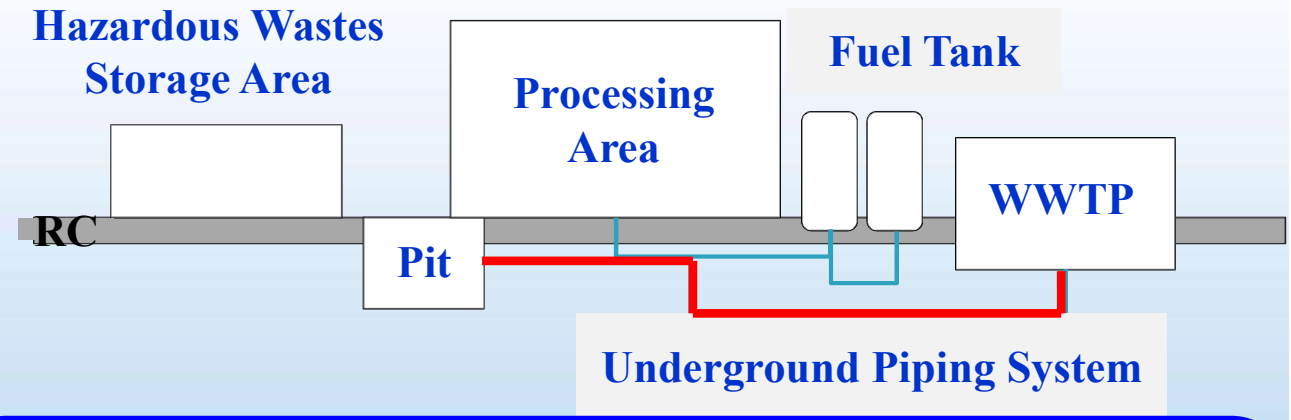
Gas Station: Site Investigation

Potential Contamination Area


入口
出口
G03/S03
P16
P13
P15
Diesel Station
RC Cracking
G02/S02
A05
A10
柴
A04
92
A09
P12
P14
A03
95
A08
A02
98
A07
P11
G01/S01
A01
A06
站屋
廁所
洗車機
UST Area
Soil Sampling, GW
Monitoring Wells


5.0 土壤氣體 GC 圖譜檢測結果
樣品編號
D10007-MS-A14
採樣點編號
A14
氣相層析圖譜
甲烷
正戊烷
Soil Samples: GC Analysis
5.0 土壤氣體 GC 圖譜檢測結果
樣品編號
E10004-MS-P20
採樣點編號
P20
氣相層析圖譜
甲烷
Soil Samples: GC Analysis
5.0 土壤氣體 GC 圖譜檢測結果
樣品編號
D10011-MS-P14
採樣點編號
P14
氣相層析圖譜
甲烷
Soil Samples: GC Analysis

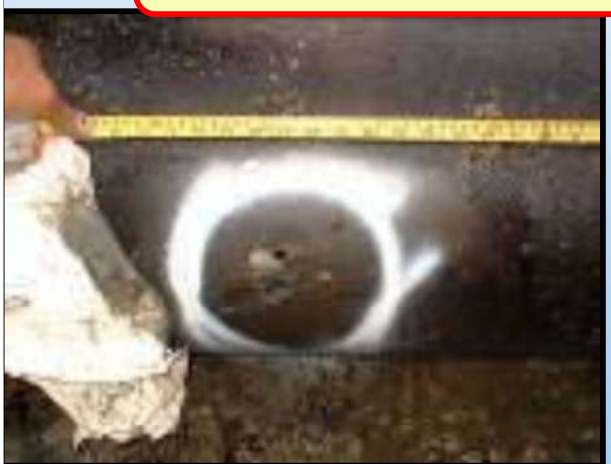




Soil Sampling (hot spot):

Processing Area, Wastewater Piping, Fuel Piping, WW Collection pit, Hazardous Wastes Storage Area, Fuel Tank, Chemical Storage Tank, WW treatment Plant, Air Pollution Control Area, et al.

Leakage of underground piping



Leakage of chemicals or fuel storage tank

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Contamination Site Investigation - Common Methods Employed in Taiwan

Ming-Daw Che, Ph. D.

APOLLO TECH **Apollo Technology Co., Ltd.**

2019/03/19

VITA

- Dr. Ming-Daw Che
  Vice President
  Apollo Technology Co., Ltd.
- Vice Chairman, Taiwan Association of Soil and Groundwater Environmental Protection
- Environmental Science, PH.D. The Ohio State University, U.S.A.
  Soil Science, M.S., The Ohio State University, U.S.A.
  Soil Science, B.S., National Chung-Hsing University, Taiwan
- Laboratory director , senior manager ,and soil/groundwater remediation group leader：Energy and Resource Laboratory, Industrial Technology Research Institute (1991-2009)
- Chief Technical Officer (CTO) of Environment and Development Foundation (2009-2013)
- Adviser： BOE, EPA, Local Governments, and Taiwan Development Institute

Outlines

- Introduction
- Investigation Methods
- Case Study - A Gas Stations
- Conclusions
- Discussions

Introduction

APOLLO TECH

Probability to find contamination?

- Probability of winning Taiwan Super Lottery
  1/(38*37*36*35*34*33/6*5*4*3*2*1)*8
  =1/22,085,448

- Probability of finding contaminated soil
  (10*10*20)/10,000*10,000*2,000
  =1/100,000,000

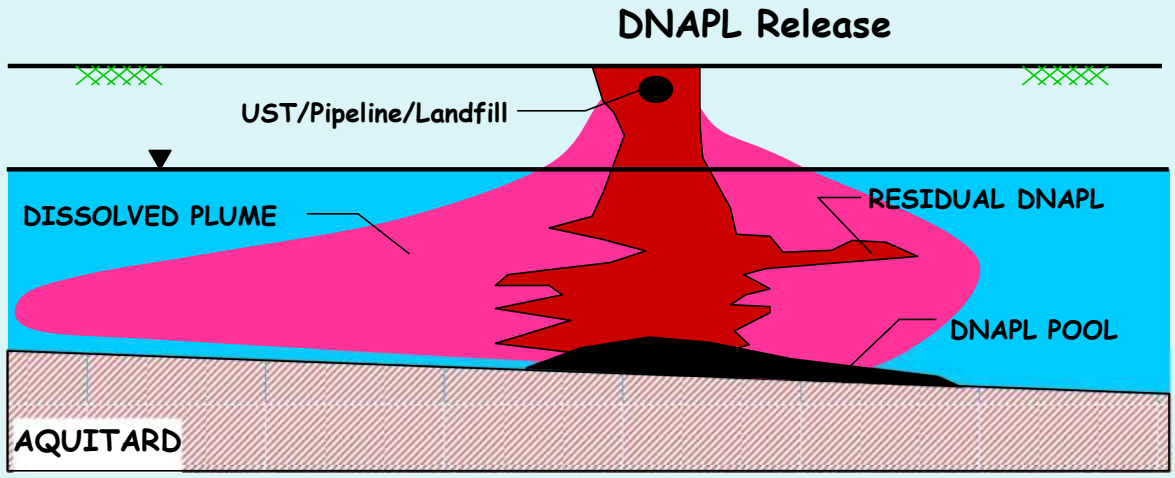
  (unit: cm, area: 1 ha., depth: 20m)

Fate of Contaminants

- **Soil pH:** Solubility, Transformation, Movement
- **Soil Texture:** Movement, Adsorption
- **Soil Structure:** Movement
- **Soil Water:** Movement
- **Soil Organic Matter:** Absorption
- **Clay Mineral:** Movement, Adsorption
- **Groundwater Flow Direction and Velocity:** Movement(horizontal)
- **Geology Layers:** Movement(vertical)
- **Pollution Behaviors:** Distribution, Movement,
- **Types of Pollutants:** Distribution, Movement, Transformation

Types of pollutants vs Distribution

- LNAPL
  - Ex.: Gasoline
- DNAPL
  - Ex.: PCE, TCE



7

Sources of Contamination

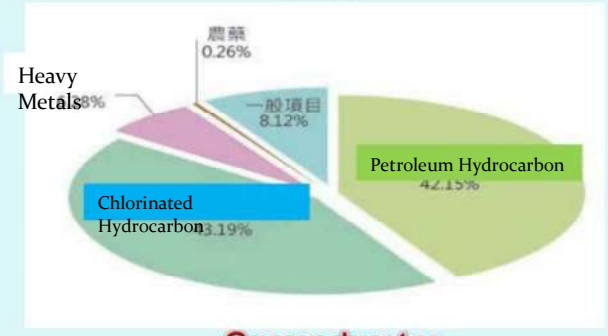
- Industrial Wastewater
- Leaking of UST and Pipeline
- Waste Dumping or Landfill
- Apply Pesticide or Herbicide
- Apply Fertilizer
- Livestock
- Home
- Air Pollution
- Acid Rain
- Seawater
-

8

Types of Pollutants

- Petroleum Products
- Solvents
- Heavy Metals
- Pesticide/Herbicide
- ……

Soil



Groundwater

9

Investigation Methods

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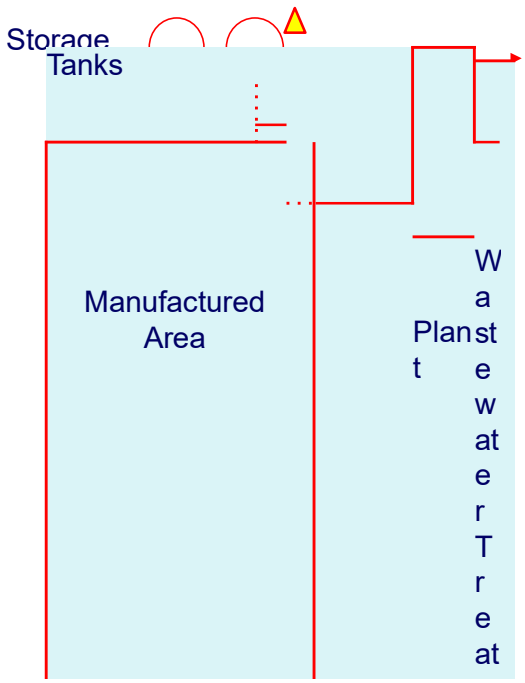
Purposes of Site Investigation

- Baseline survey
- Environmental Site Assessment, ESA
- Monitoring survey
- Remedial investigation and feasibility study, RI/FS
- Delineation survey
- Remedial action
- Validation after remediation
- Early warming system assessment

Investigation of Different Purposes (1/3)

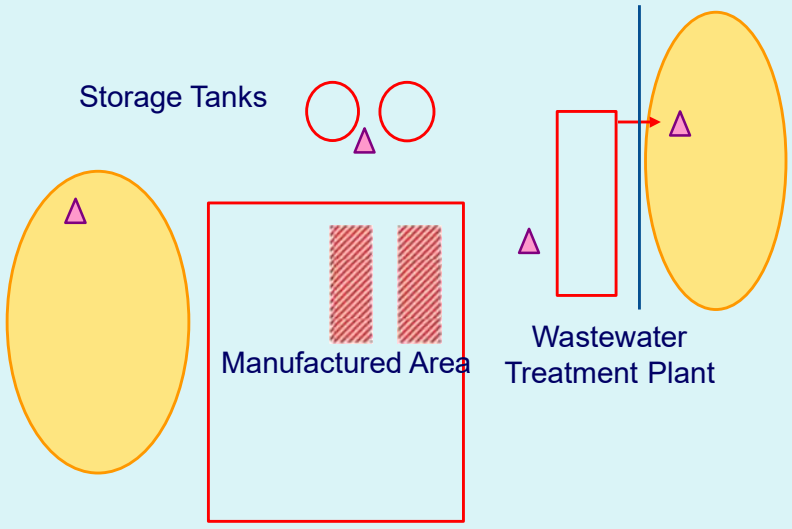
- Self-Investigation
- Find Pollution / Prevention
- Target: Most Probable Contaminated Area



12

Investigation of Different Purposes (2/3)

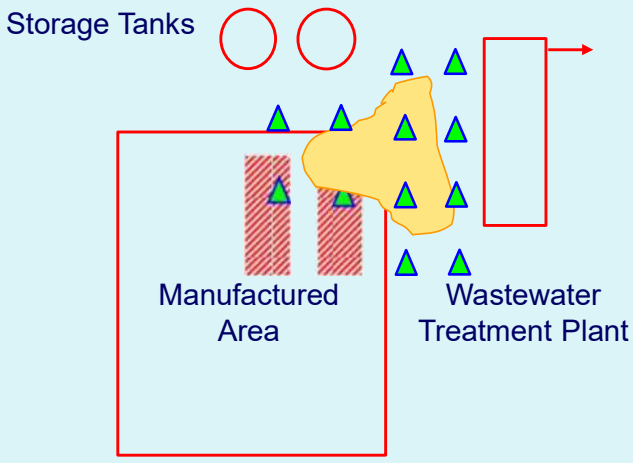
- Environmental Site Assessment
- Whole Area
- Potential problem area(Waste Disposal Fields?)



13

Investigation of Different Purposes (3/3)

- Remedial Investigation(RI)- Investigation of Contaminated Area
- Areas and Amounts
- Multiple Phases Investigation



14

Types of Site Investigation

- Industrial Plant
- Agricultural Land
- Gas Station
- Waste Dumping Site/Landfill
- Large Oil/Chemical Storage site
- Military facilities
- Others

15

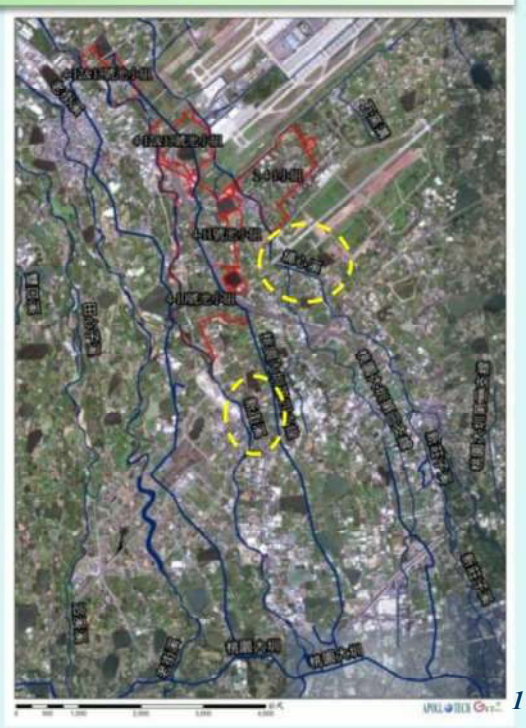
Site Investigation Process

1) Background Information collection
2) Site Visit/Observation/Record
3) Investigation Arrangement/Plan
4) Conduct Investigation
5) Results Assessment/Evaluation/Simulation
6) Investigation Report

16

Background Information Collection (1/5)

Map and Aerial Photos

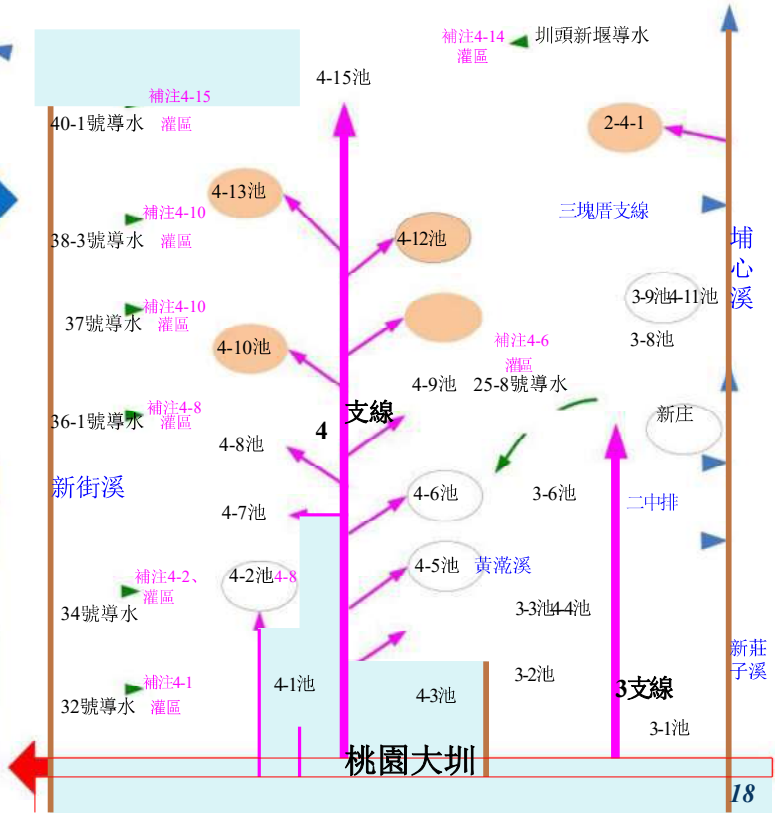


小組別	灌溉水
大竹工作站 2-4-1 灌溉小組	**埔心溪**（經 24 號河水堰、2-1-2 號池補助河水堰、25-7號河水堰）
大園工作站 4-10 號池灌溉小組	**新街溪**（經 37 號導水路）
大園工作站 4-11 號池灌溉小組	**4-11 號池、新街溪**（經 36-1 號導水路）
大園工作站 4-12 & 4-13 灌溉小組	**4-12 & 4-13 號池、埔心溪**（迴歸水）

17

Background Information Collection (2/5)

Irrigation Systems



小組別	灌溉水
大竹工作站 2-4-1 灌溉小組	**埔心溪**（經 24 號河水堰、2-1-2 號池補助河水堰、25-7號河水堰）
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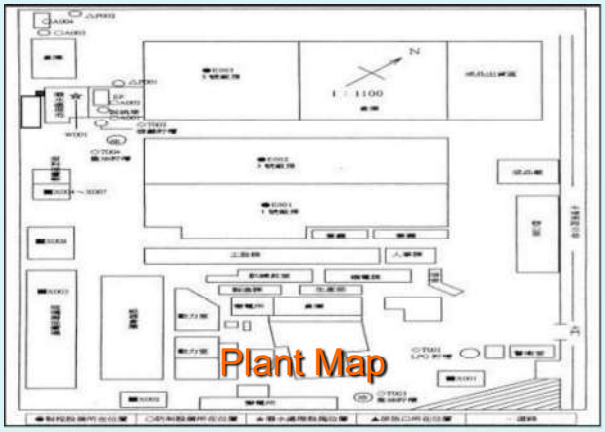
大園工作站 4-12 & 4-13 灌溉小組	**4-12 & 4-13 號池、埔心溪**（迴歸水）

18

Background Information Collection (3/5)

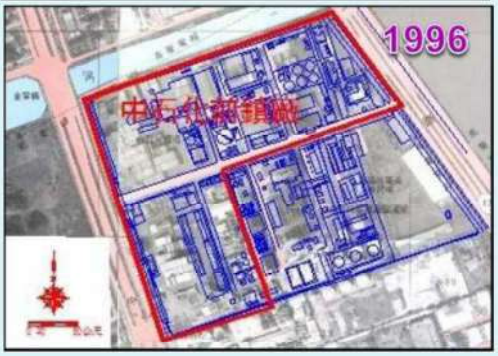


19

Background Information Collection (4/5)

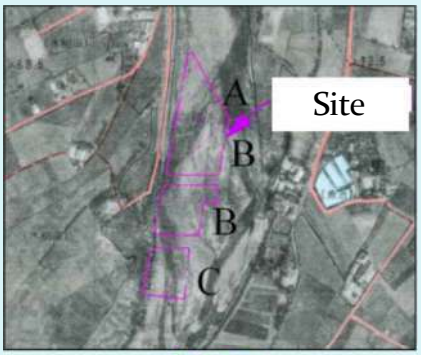
Industrial Plant History

- Site History
- Air Photos, Manufacturted Records, Chemicals Used, Registrations, Maps

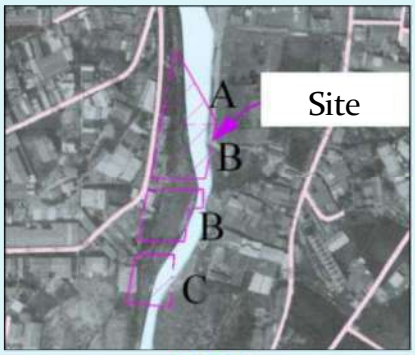


20

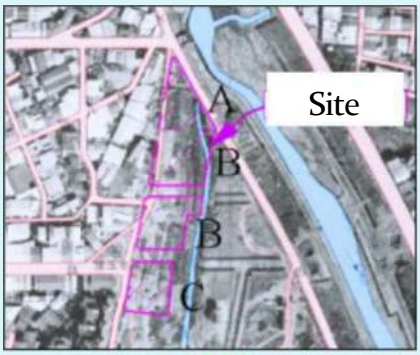
Background Information Collection (5/5)



1978
Site Altitude 65m



1991
Site Altitude 68m



2000
Site Altitude 70m

History Photos Analysis

- Waste Increase
- Population Increase

Site Visit/Observation/Record (1/2)

On-Site Investigation

- Surface Drainage
- Surface Waste Disposal / Broken Pipelines

- Underground Storage Tanks/Pipelines/Reaction Cells
- Transformers(PCB)
- Chemical Tanks

- Toxic Waste
- Soil
- Groundwater

Site Visit/Observation/Record (2/2)

Site Observation Record

Site Observation

Onsite Test

Common Investigation Methods in Taiwan

- Soil Sampling and Analysis
- Groundwater Sampling and Analysis
- Hydrogeology investigation
- Screening/ In-situ Detection Technologies
- Geophysical Technologies
- Other Investigation Methods

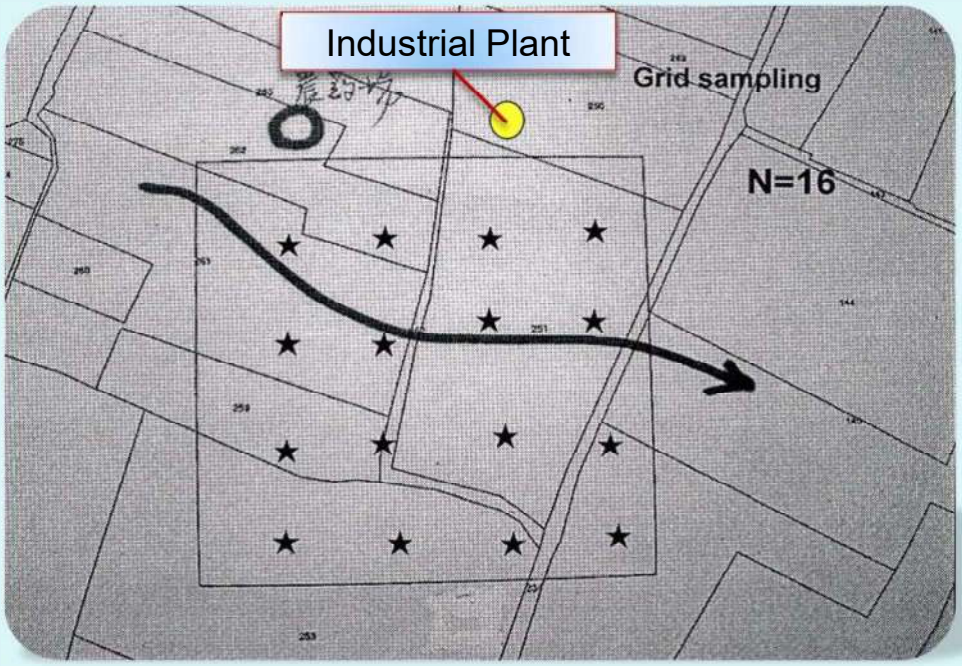
Types of Soil Sampling (1/6)

- Judgmental sampling
- Simple random sampling
- Stratified sampling
- Systematic and grid sampling
- Adaptive cluster sampling
- Composite sampling

25

Types of Soil Sampling (2/6)

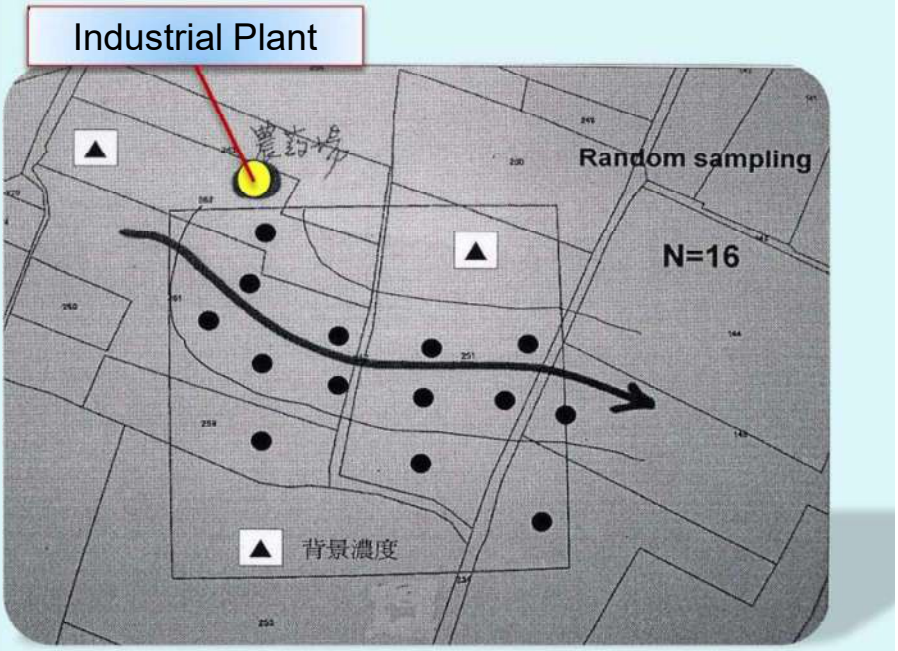
- **Systematic and Grid Sampling**



26

Types of Soil Sampling (3/6)

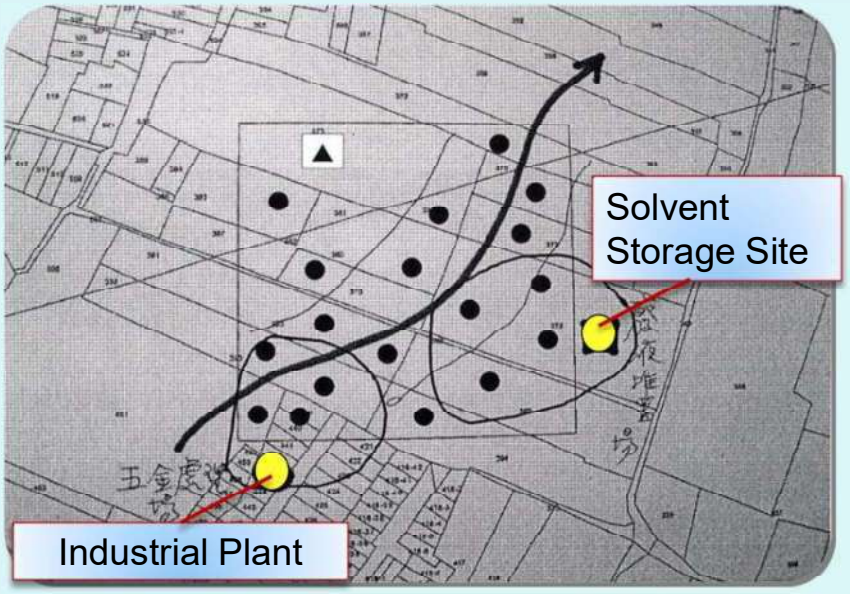
- Judgmental sampling
- Adaptive cluster sampling



27

Types of Soil Sampling (4/6)

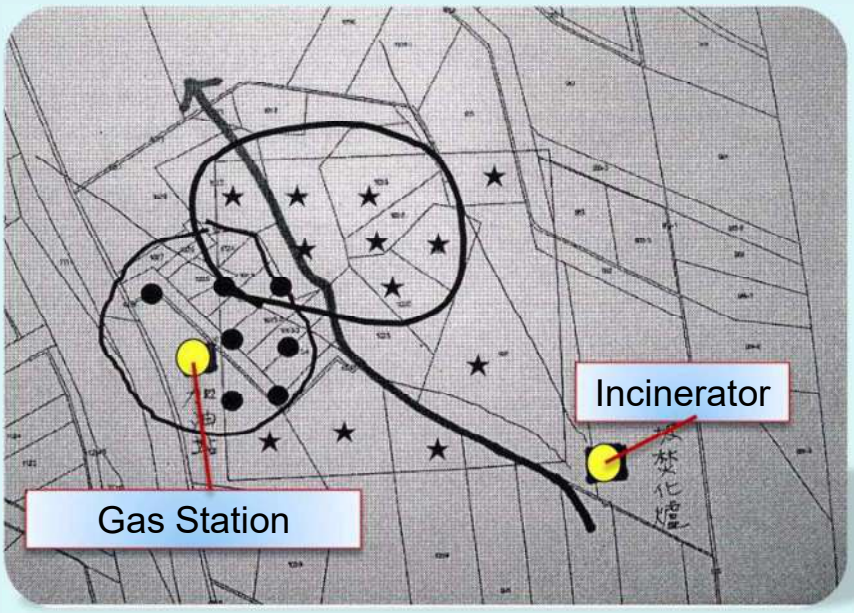
- Judgmental sampling
- Stratified sampling
- Adaptive cluster sampling



28

Types of Soil Sampling (5/6)

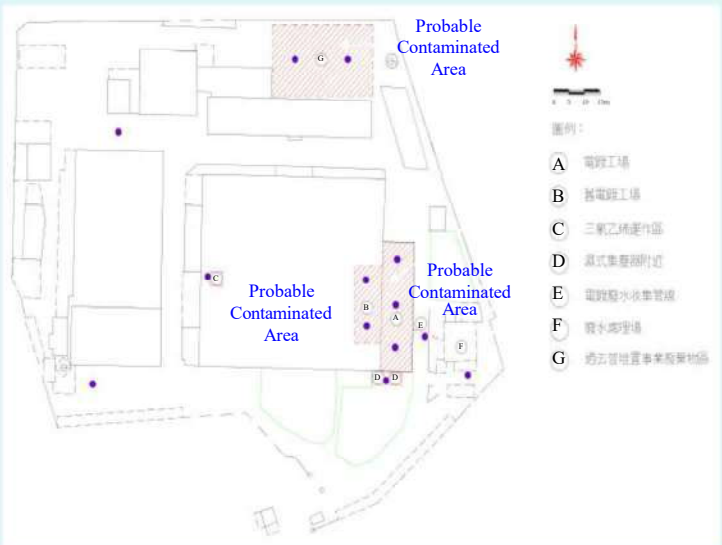
- Judgmental sampling
- Stratified sampling
- Adaptive cluster sampling

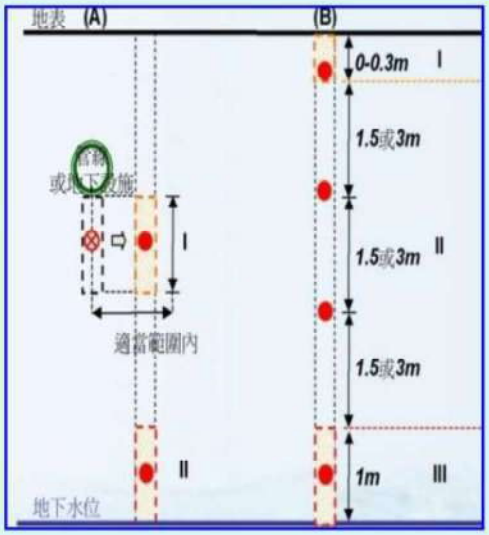


29

Types of Soil Sampling (6/6)

- Probable Contaminated Area: Judgmental sampling
- Contaminated Area Unknown: Grid Sampling





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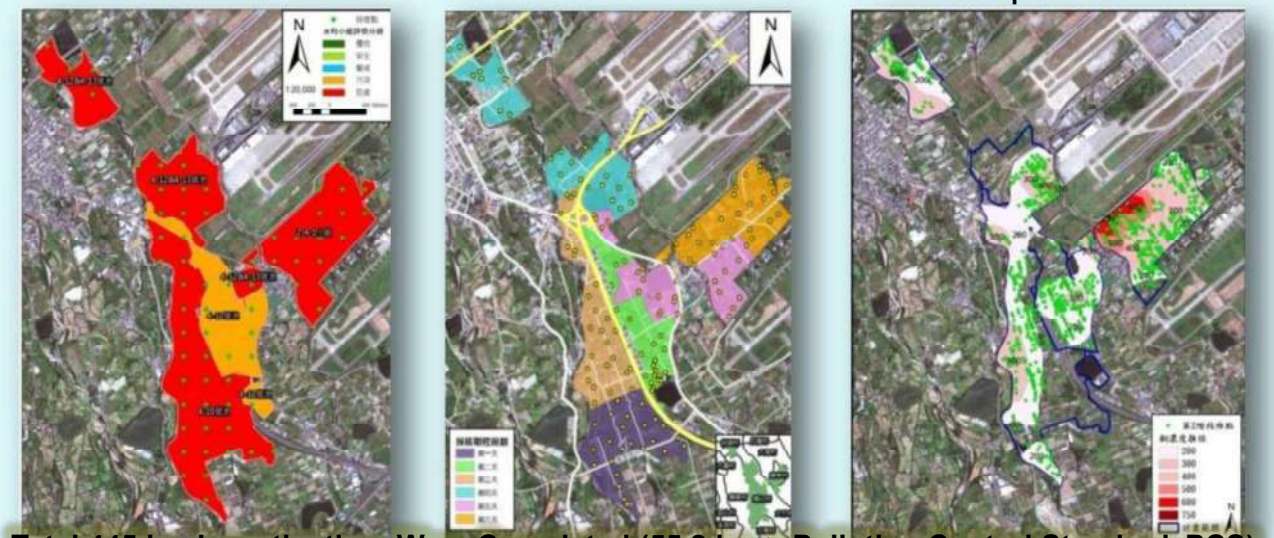
Agricultural Land Investigation (1/3)

1. Preliminary
- Irrigation system as Unit
- 3.125 ha grid sampling
- Total 66 Samples

2. Phase 1
- Grid sampling
- Total 150 Sample Sets
- 34 Samples > PCS

3. Phase 2
- Potential Contaminated Site Investigation
- Total 980 Sample Sets
- 320 Samples > PCS



Total 445 ha. investigation Were Completed (55.8 ha. > Pollution Control Standard, PCS)

Agricultural Land Investigation (2/3)

❖Remote Backup and Processing

(1) Preparation

(2) On-Site

(3) Data Transporting / Processing

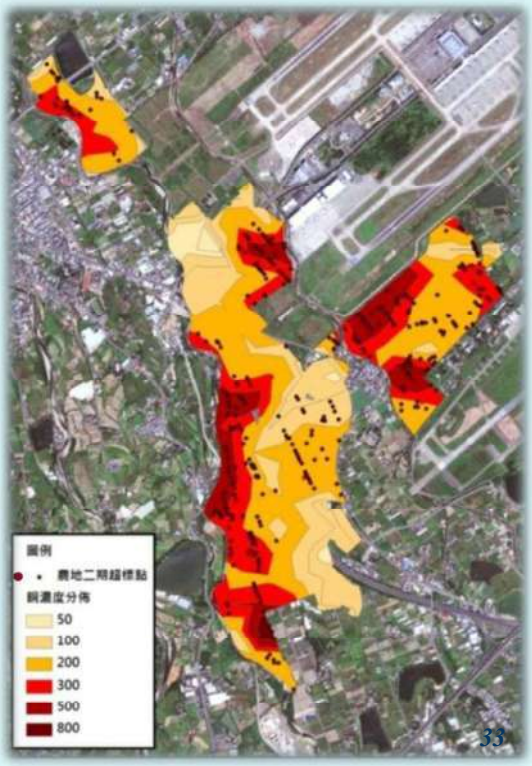
Main Systems (Cloud Computing)

Agricultural Land Investigation (3/3)

❖Soil Investigation Results

- Investigation area 446 ha., Soil sampling area 173 ha.
- Total soil samples:1,130, 354 samples>PCL, (31.3 %)
- Major contaminants: Cu (333 samples);
  Cu+Zn (17 samples), Zn (2 samples);
  Cu+Zn+Cr (1 sample),
  Cu+Cr (1 sample)

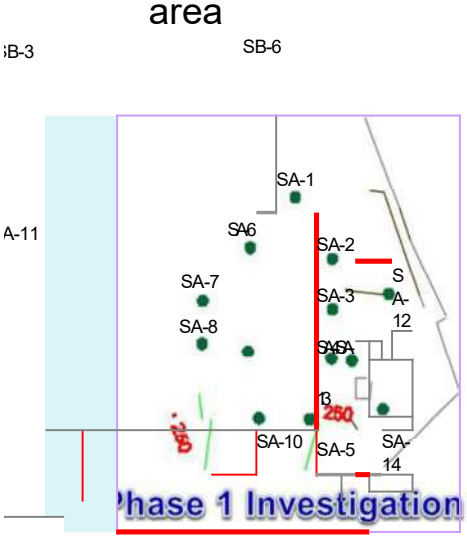
Stage	Investigate		Control		Monitor	
	sample	square measure (ha.)	sample	square measure (ha.)	sample	square measure (ha.)
First	150	31.1	34	6.1	22	4.1
Second	980	142.3	320	49.7	150	21.5
Amount	1,130	173.4	354	55.8	172	25.6

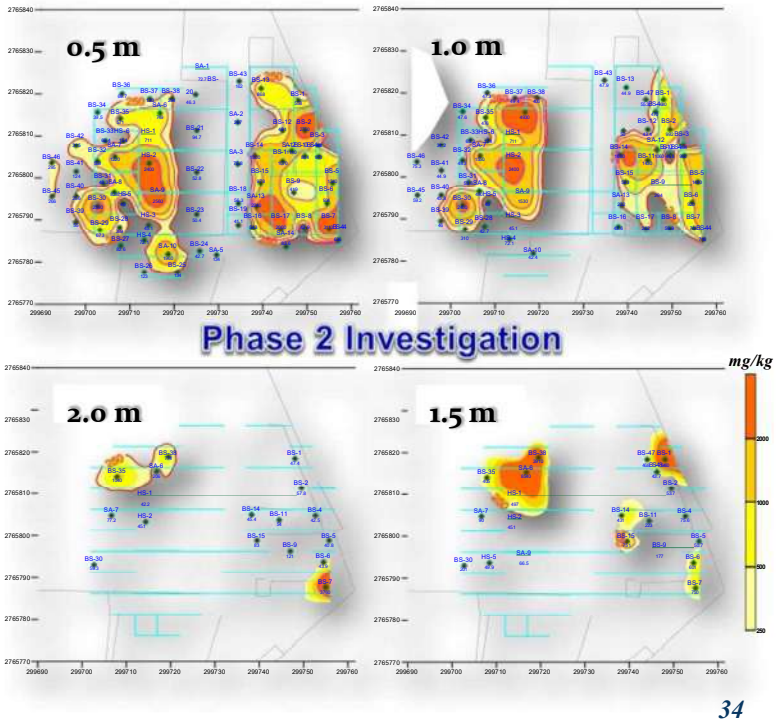


Multiple Phases Soil Investigation

Contaminated Area "Reduce"

❖SB-4Phase SB-5 2 investigation "reduce" contaminated area





Soil Sampling Tools (1/13)

- Hand - held shovel
- Hand - held auger
- Split - barrel sampler
- Thin - walled tubes sampler
- Piston rod soil sampler
- Dual tube soil sampler

Soil Sampling Tools (2/13)

- Sampling for heavy metals
- Maximun depth: 2m

Hand - held Soil Auger Set

Soil Sampling Tools (3/13)

- 7 types of auger head
- Maximun depth: 5 m
- 1 set of Piston Soil Sampler

Hand - held Soil Auger Set

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Soil Sampling Tools (4/13)

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Soil Sampling Tools (5/13)

- Split core1 3/8” x 6”
- 5 plastic inner tube with cap
- Slide Hammer
- For undisturbed soil sample

Split Core Sampler

39

Soil Sampling Tools (6/13)

- Stainless Thin-walled tube(4.0cm x 20cm)
- Handy Soil Sample Extruder
- For undisturbed soil sample

Thin - walled tubes sampler

40

Soil Sampling Tools (7/13)

- Stainless rod (3.8ψcm x 15.2cm)
- Hammer
- 5 plastic liner tube with cap
- For undisturbed soil sample

Dual Tube Soil Sampler

Soil Sampling Tools (8/13)

Electrical Mechanical Soil Sampler

Soil Sampling Tools (9/13)

Geoprobe

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Soil Sampling Tools (10/13)

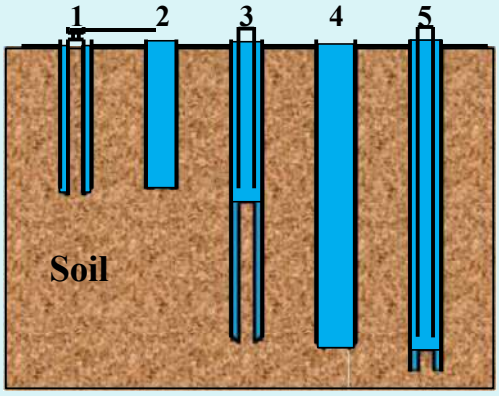
Power Probe

44

Soil Sampling Tools (11/13)

Soil Sampling-Direct Push

- Direct Push
- Connect with MIP or CPT



45

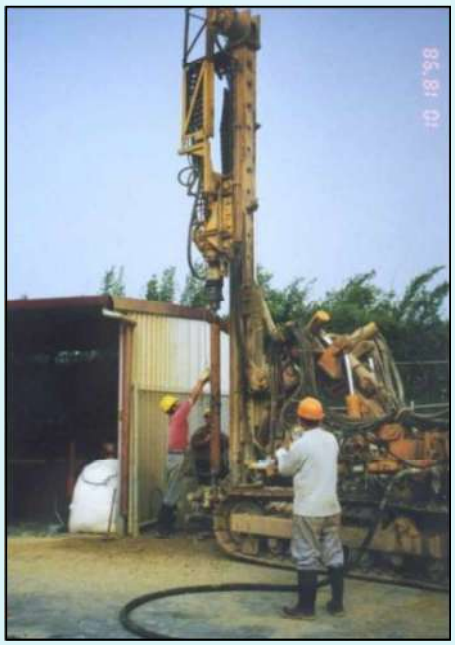
Soil Sampling Tools (12/13)

Hollow Stem Drill

46

Soil Sampling Tools (13/13)

Drill Jumbo



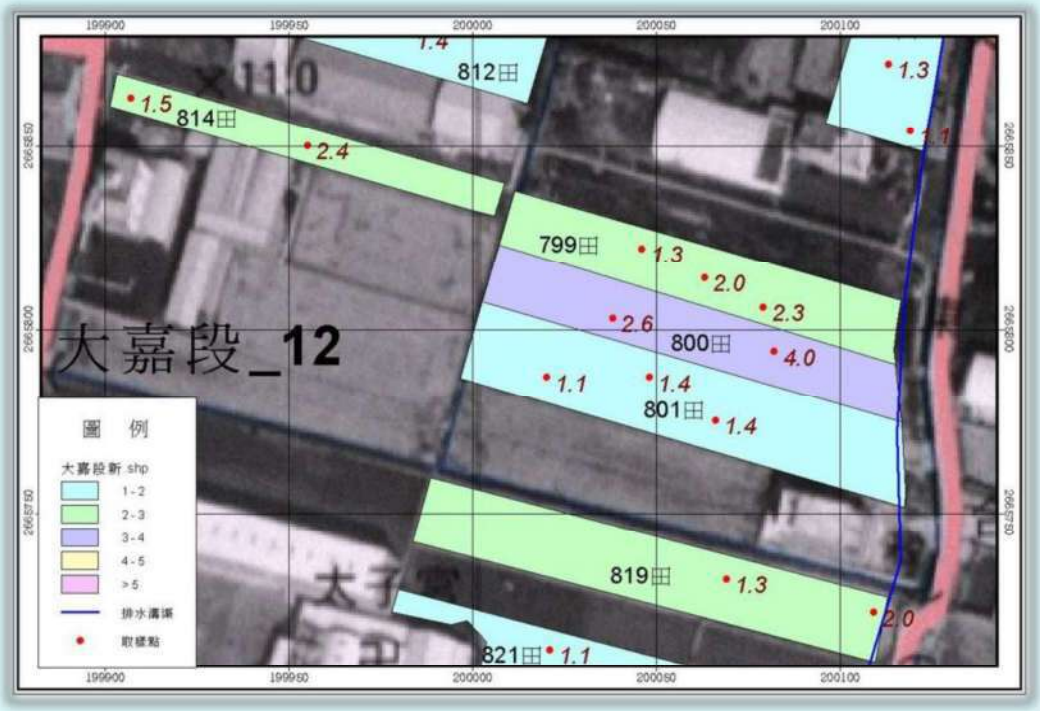
Cable Tool

47

Soil Sampling Results (1/4)

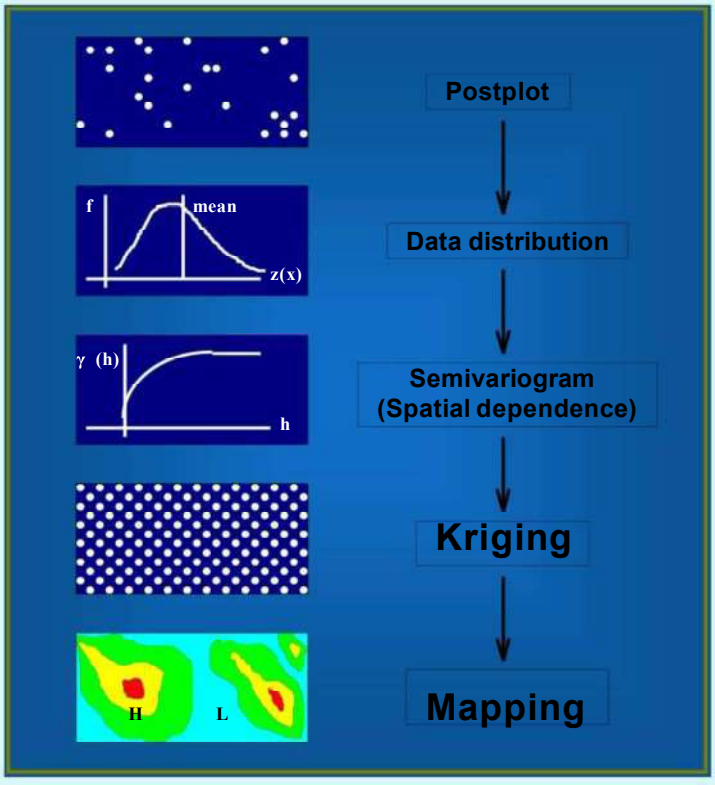
48

Soil Sampling Results (2/4)



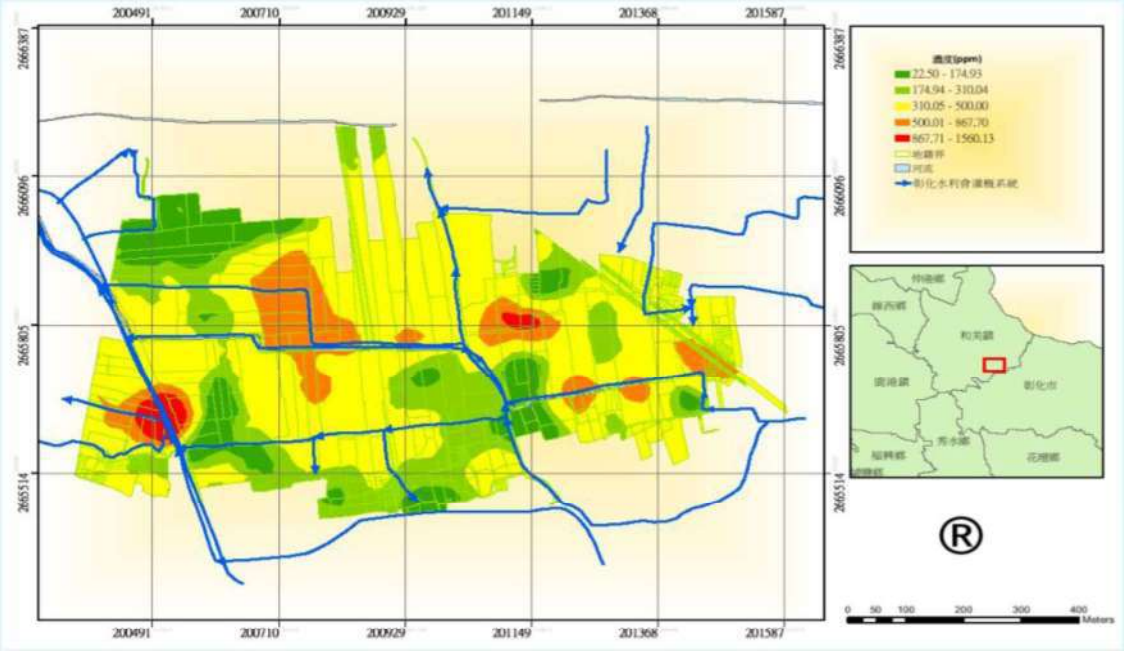
Soil Sampling Results (3/4)

Kriging



Soil Sampling Results (4/4)

- Map of Ni Concentration at agricultural site in Central Taiwan



Health and Safety

- Underground Pipeline
- Hand digging
- Don't trust paper

- Airtight / closed room
- Wear protection clothes / equipments

Common Investigation Methods in Taiwan

- Soil Sampling and Analysis
- Groundwater Sampling and Analysis
- Hydrogeology investigation
- Screening/ In-situ Detection Technologies
- Geophysical Technologies
- Other Investigation Methods

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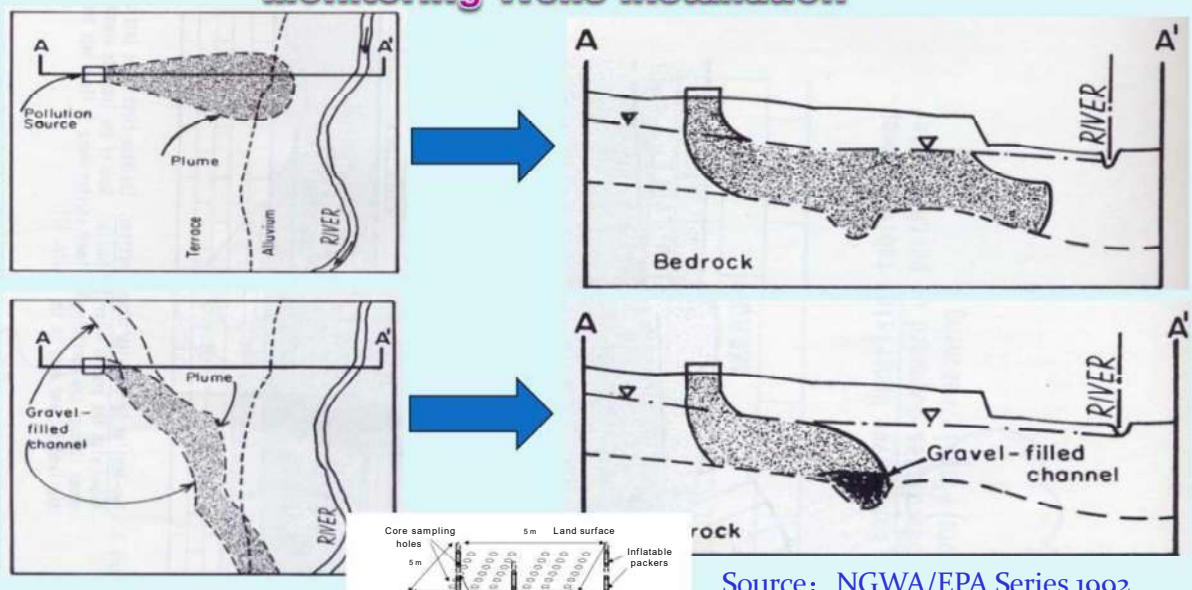
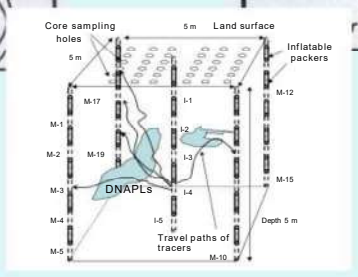
Groundwater Sampling and Analysis (1/7)

Monitoring Wells Installation





Source：NGWA/EPA Series 1992

Site Conceptial Model

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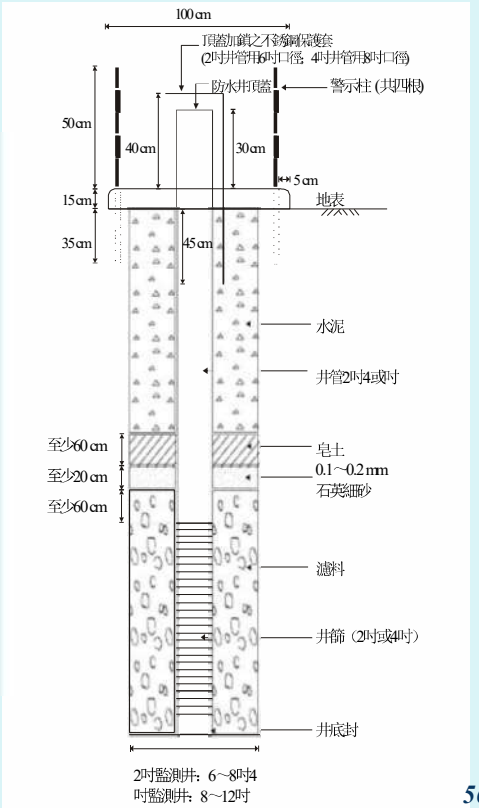
Groundwater Sampling and Analysis (2/7)

Monitoring Wells Installation

55

Groundwater Sampling and Analysis (3/7)

Monitoring Wells Installation



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Groundwater Sampling and Analysis (4/7)

Groundwater Sampling

Bailer Tube

MP1

Bladder Pump

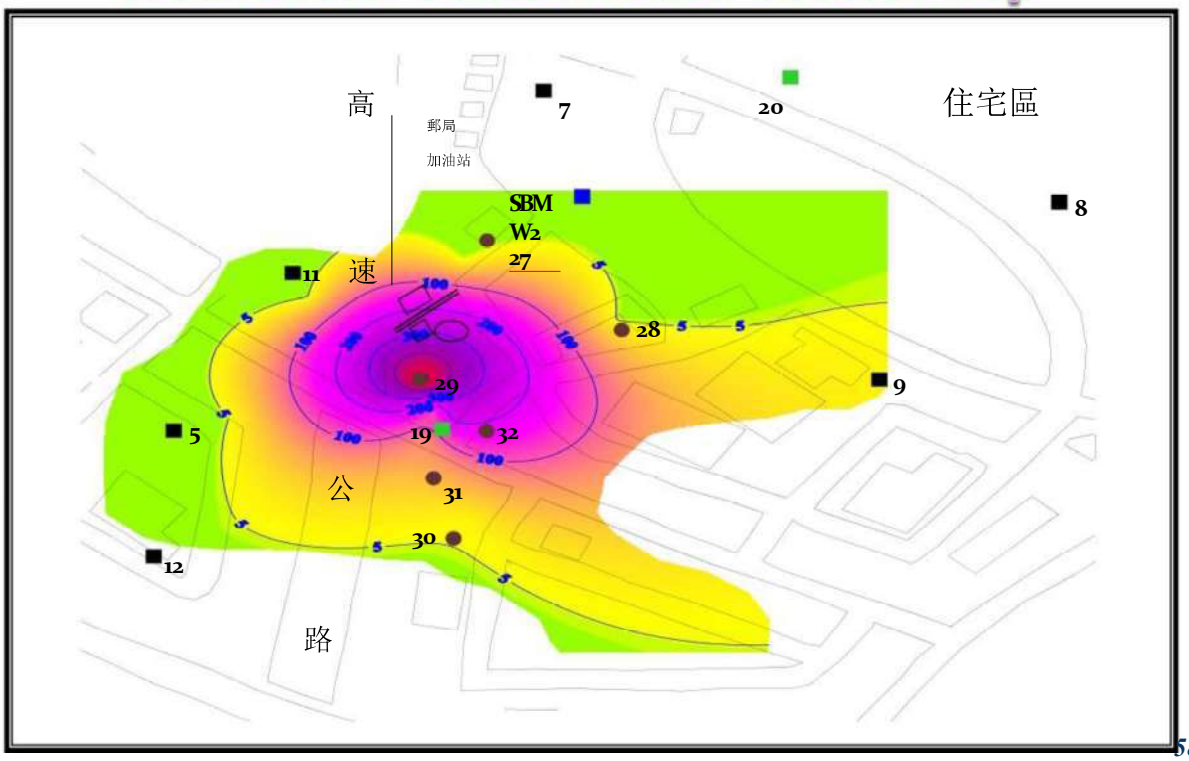
Bailer Tube(for VOC)

flow cell

57

Groundwater Sampling and Analysis (5/7)

Groundwater Contamination Contour Map



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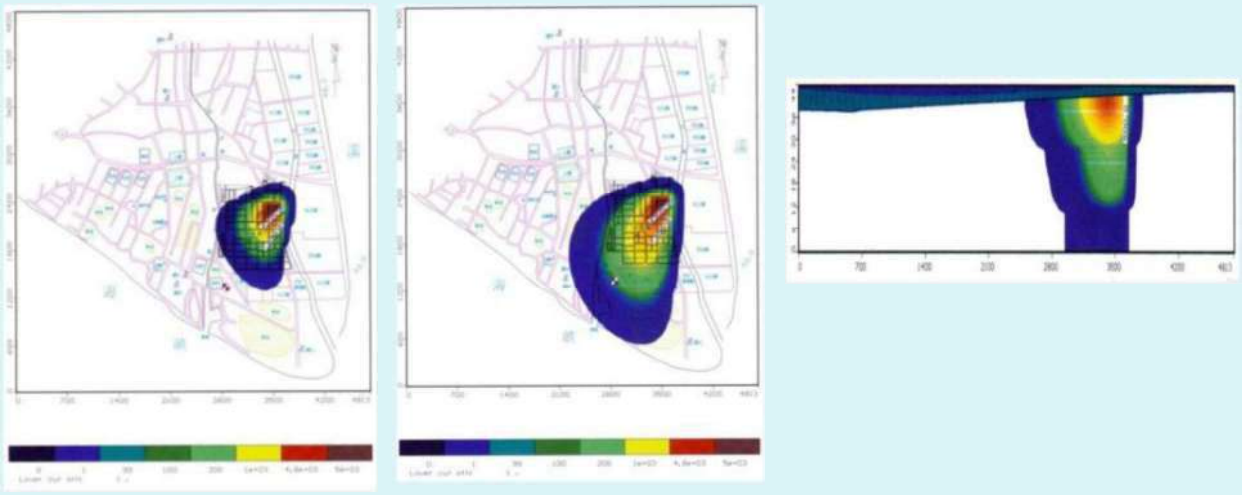
Groundwater Sampling and Analysis (6/7)

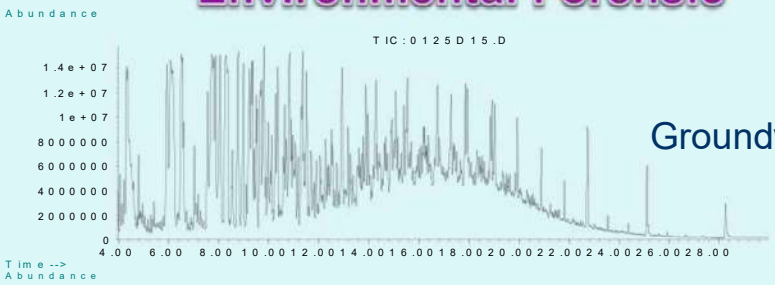
Groundwater Contamination Simulation

The Simulation of 500 days Release

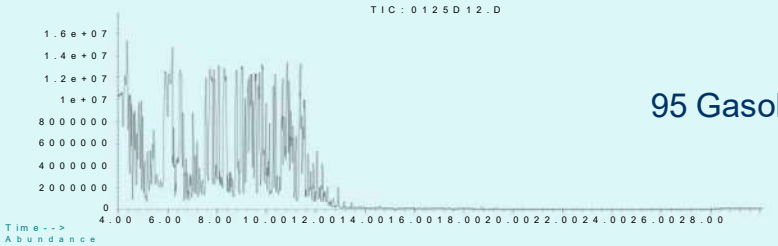


Groundwater Sampling and Analysis (7/7)

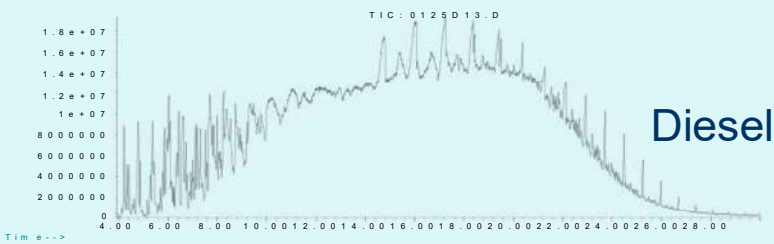
Environmental Forensic



Groundwater Sample



95 Gasoline



Diesel

Common Investigation Methods in Taiwan

- Soil Sampling and Analysis
- Groundwater Sampling and Analysis
- Hydrogeology investigation
- Screening/ In-situ Detection Technologies
- Geophysical Technologies
- Other Investigation Methods

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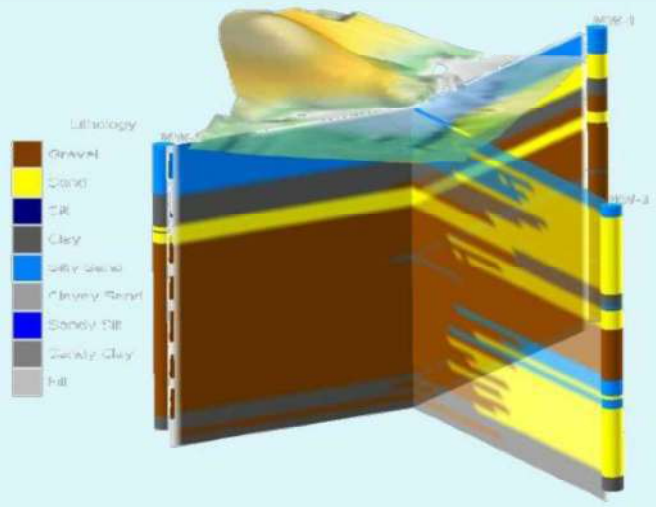
Hydrogeology investigation (1/5)

- Slug Test : Average K Values
- Particle Distribution : 3-D K Values



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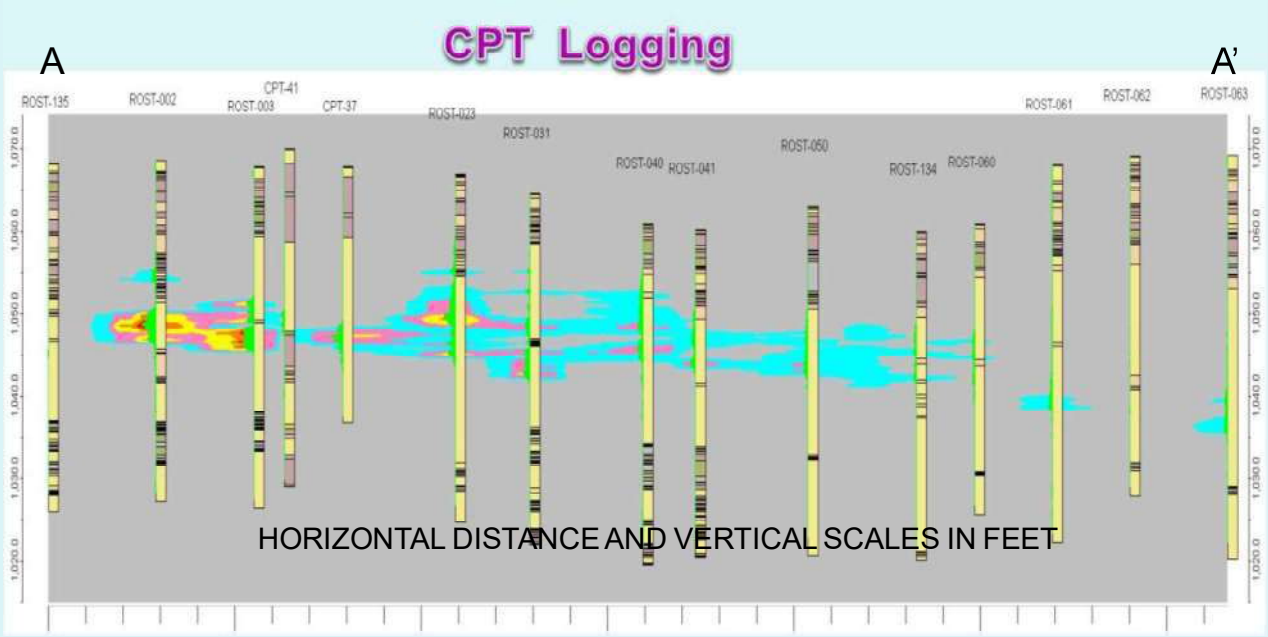
Hydrogeology investigation (2/5)



Laser Induced Fluorescence (LIF) technology or plume mapping of PAH and BTEX, phenols and fuels

CROSS SECTION % LIF

0 60 100 150 200 250 400

LITHOLOGY
(Lithology interpreted from CPT)

- SANDS
- SILTY SANDS
- CLAYEY SANDY SILTS AND SILTS
- CLAYEY SILTS AND SILTY CLAYS
- CLAY

63

Hydrogeology investigation (3/5)

Water Level Measurement

Groundwater Velocity and Flow Direction Test (Single Well)

Slug Test

Pumping Test

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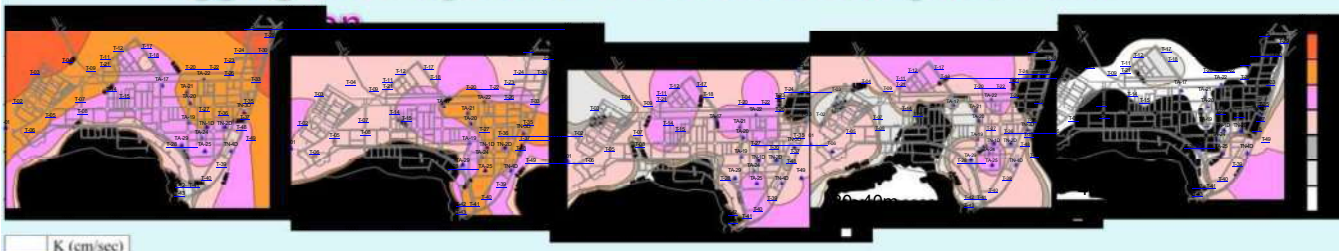
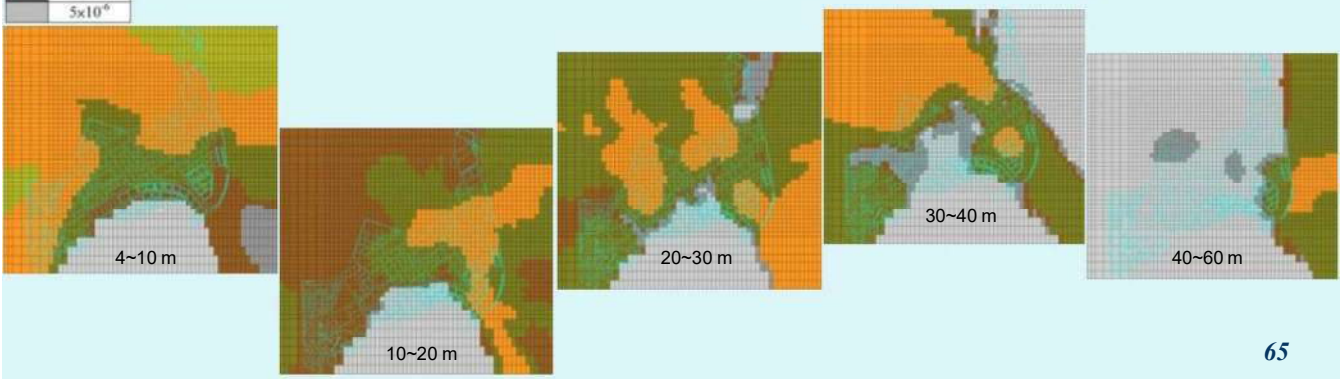
Hydrogeology investigation (4/5)

Logging Data+Hydraulic Test+Model Analysis: 3-D K



K (cm/sec)
0.1
0.008
0.001
0.0001
$5x10^{-5}$
$5x10^{-6}$

Use 3-D K Distribution to build Site Geology Model



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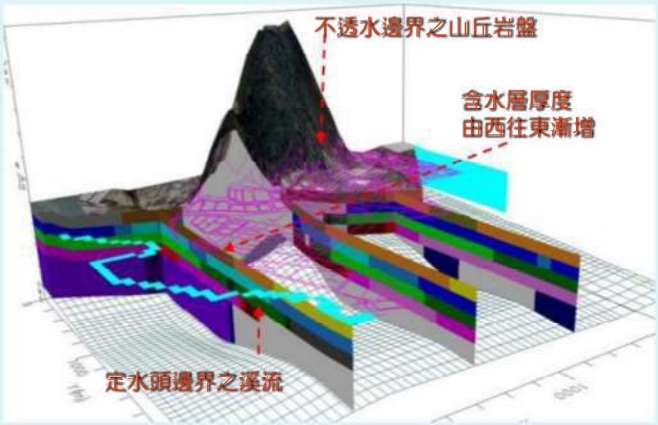
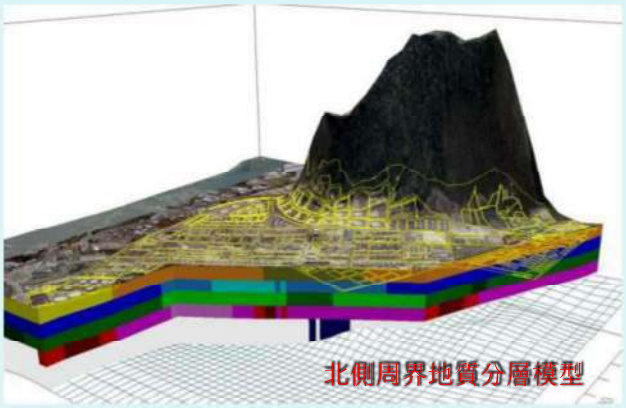
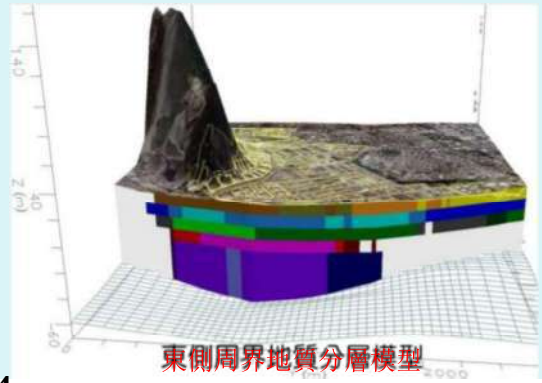
Hydrogeology investigation (5/5)





Build Site 3-D Geology Model



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Common Investigation Methods in Taiwan

- Soil Sampling and Analysis
- Groundwater Sampling and Analysis
- Hydrogeology investigation
- Screening/ In-situ Detection Technologies
- Geophysical Technologies
- Other Investigation Methods

Screening/Detection Technologies (1/11)

XRF Screening

Screening/Detection Technologies (2/11)

XRF Screening

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Screening/Detection Technologies (3/11)

Site Organic Pollution Screening

Soil Gas Survey

PID /FID

MIP (Membrane Interphase Probe)

TPH Test Kit

Screening/Detection Technologies (4/11)

Soil Gas Survey

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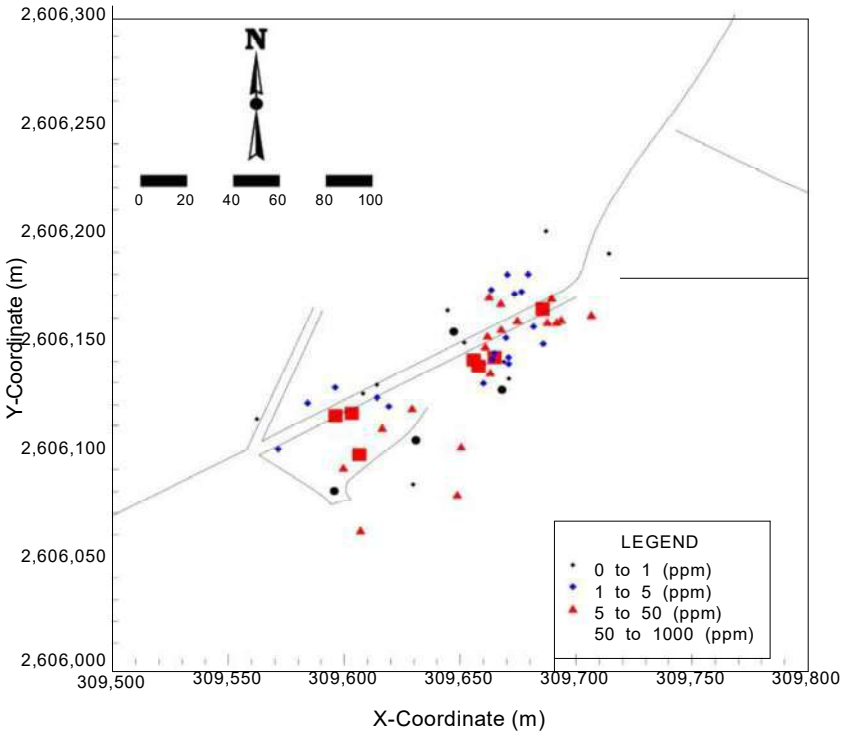
Screening/Detection Technologies (5/11)

Soil Gas Survey

72

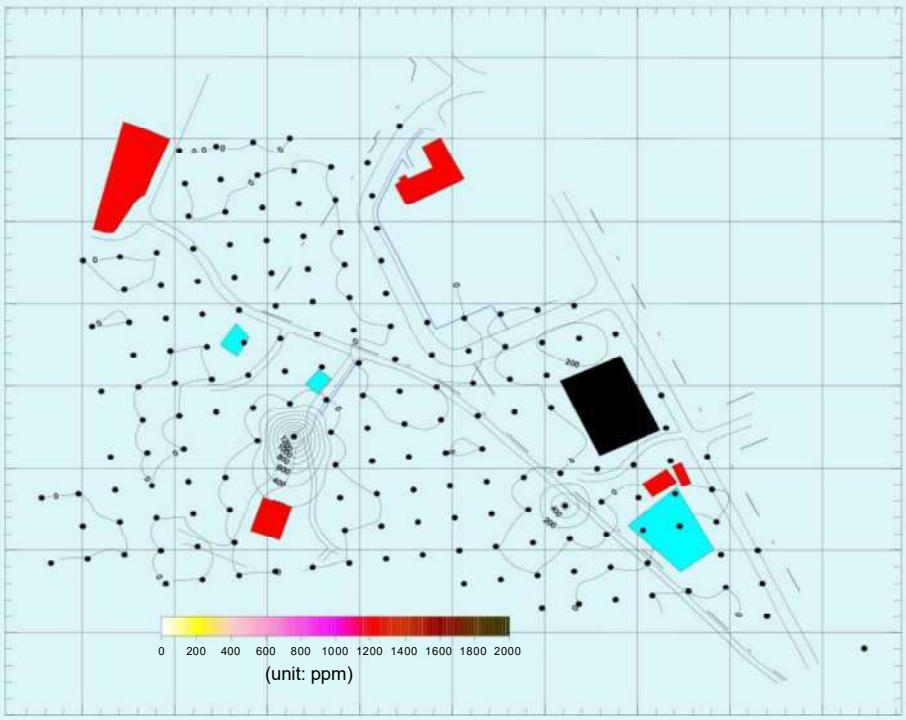
Screening/Detection Technologies (6/11)

Soil Gas Survey- A Case Study I



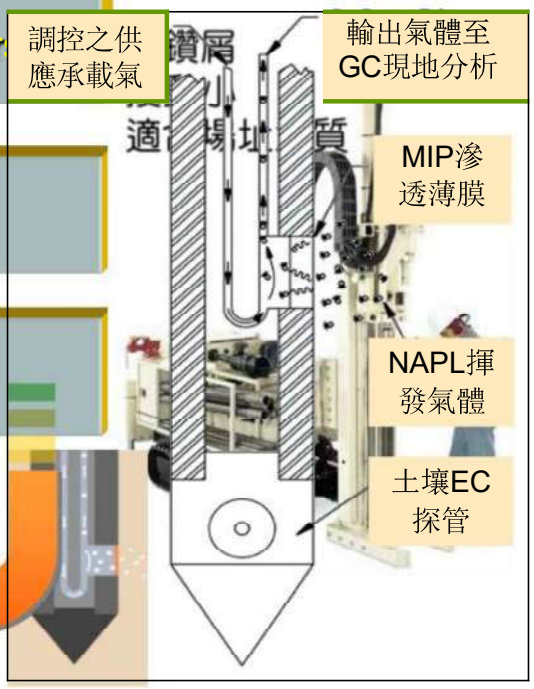
Screening/Detection Technologies (7/11)

Soil Gas Survey- A Case Study II



Screening/Detection Technologies (8/11)

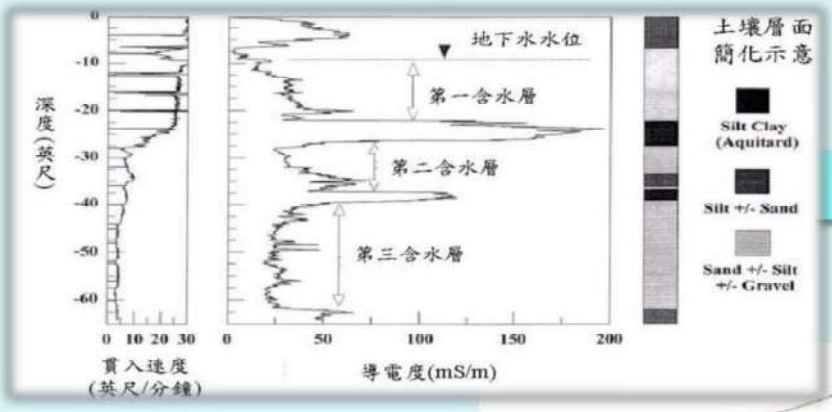
Geoprobe	Direct Push to Layer
MIP	Real-time VOC
EC	Real-time Geo-data



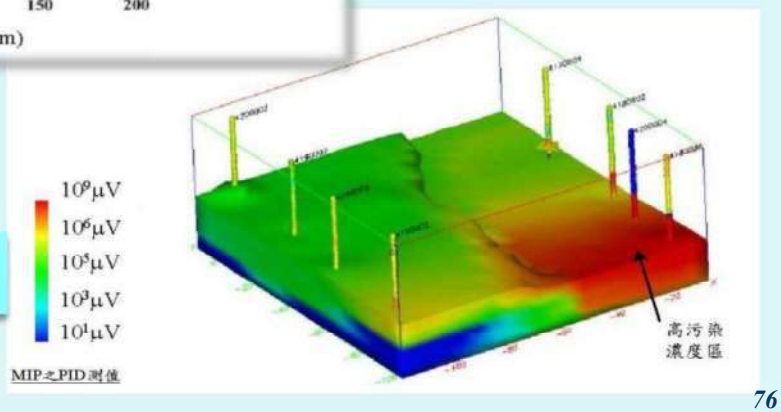
- Save Sampling Time,Point, and Cost
- Collect Geo-data at each Point Quickly
- Screening Soil Sampling Point/ MW Location

Screening/Detection Technologies (9/11)

Membrane Interface Probe, MIP

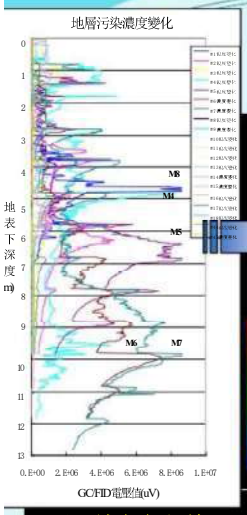


MIP vs Logging

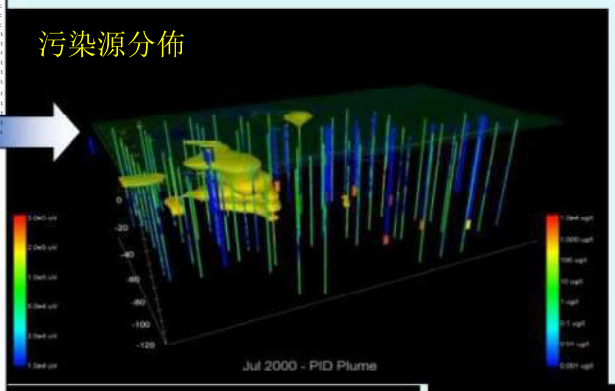


MIP Results (PID)

Screening/Detection Technologies (10/11)

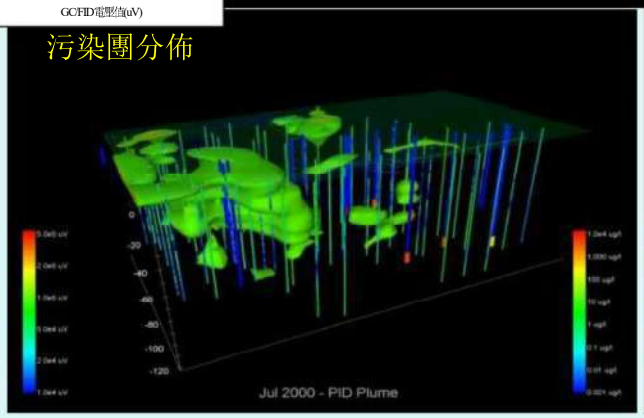


污染源分佈

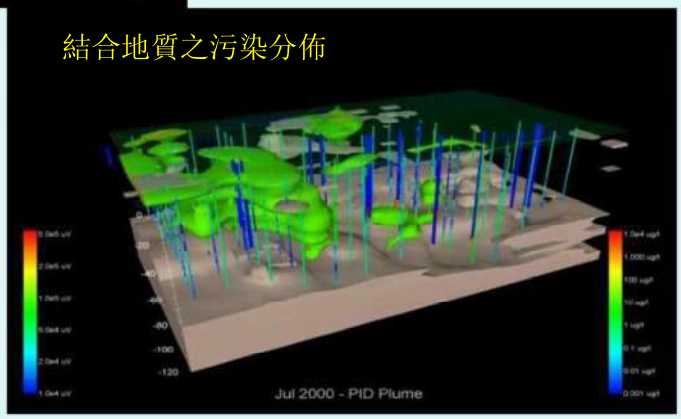


MIP Screening - Gasoline

污染團分佈



結合地質之污染分佈



Screening/Detection Technologies (11/11)

Cone Penetrometer Topography CPT

The Sampling Point EC - Depth

三維地質概念模式

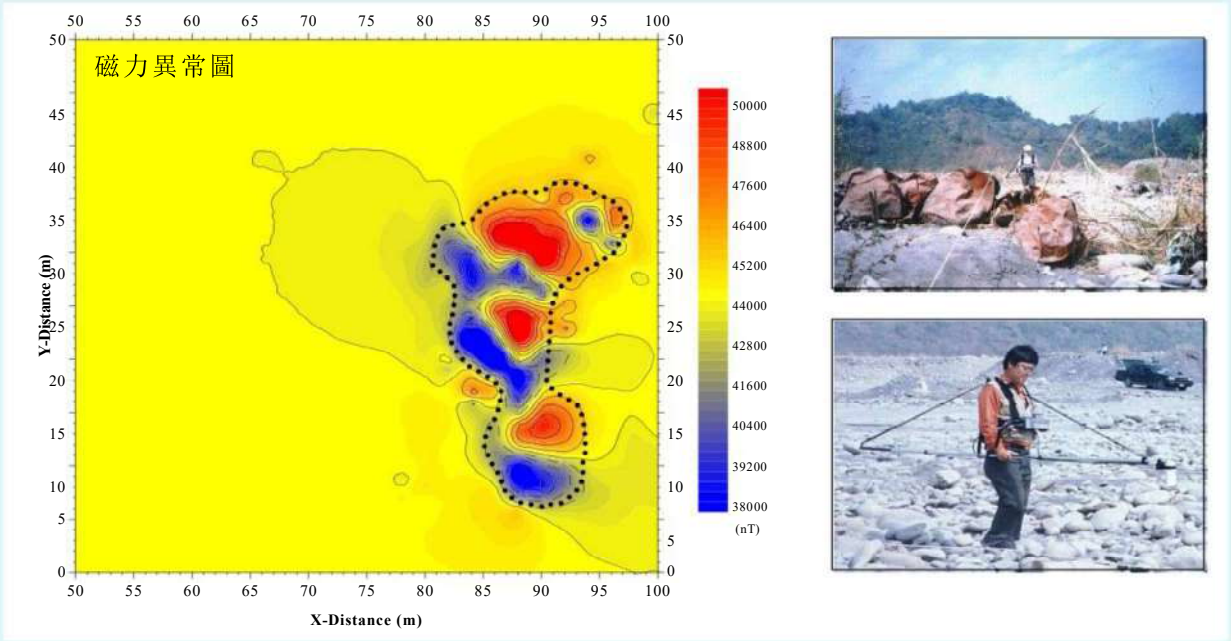
EC分佈與地質材料逆推

Common Investigation Methods in Taiwan

- Soil Sampling and Analysis
- Groundwater Sampling and Analysis
- Hydrogeology investigation
- Screening/ In-situ Detection Technologies
- Geophysical Technologies
- Other Investigation Methods

Geophysical Technologies (1/8)

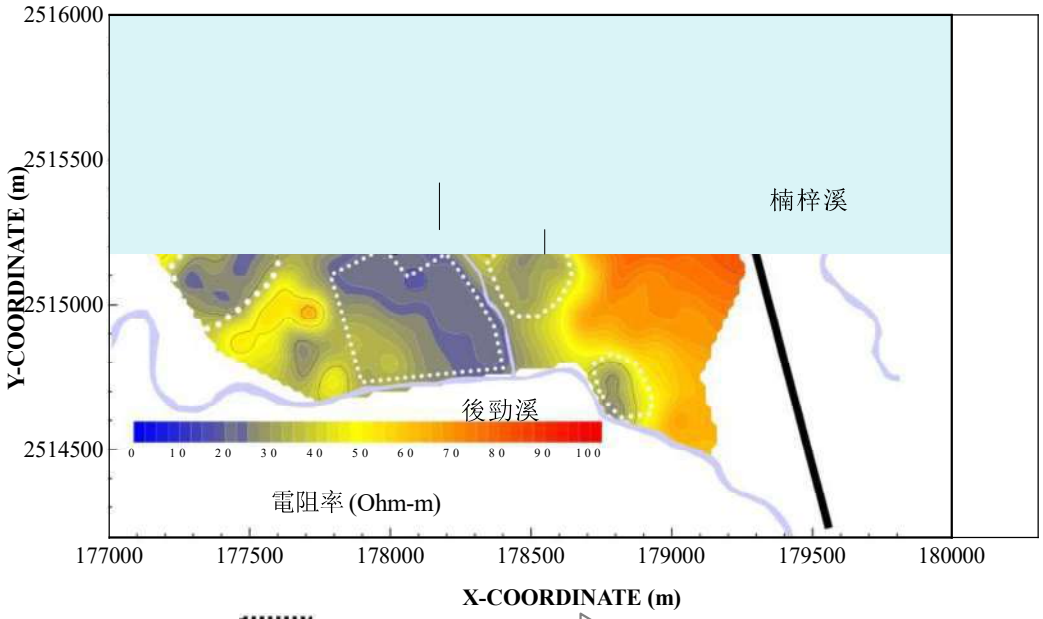
Magnetic Survey – A Waste Damping Site



Geophysical Technologies (2/8)

EM Survey – A Landfill Site

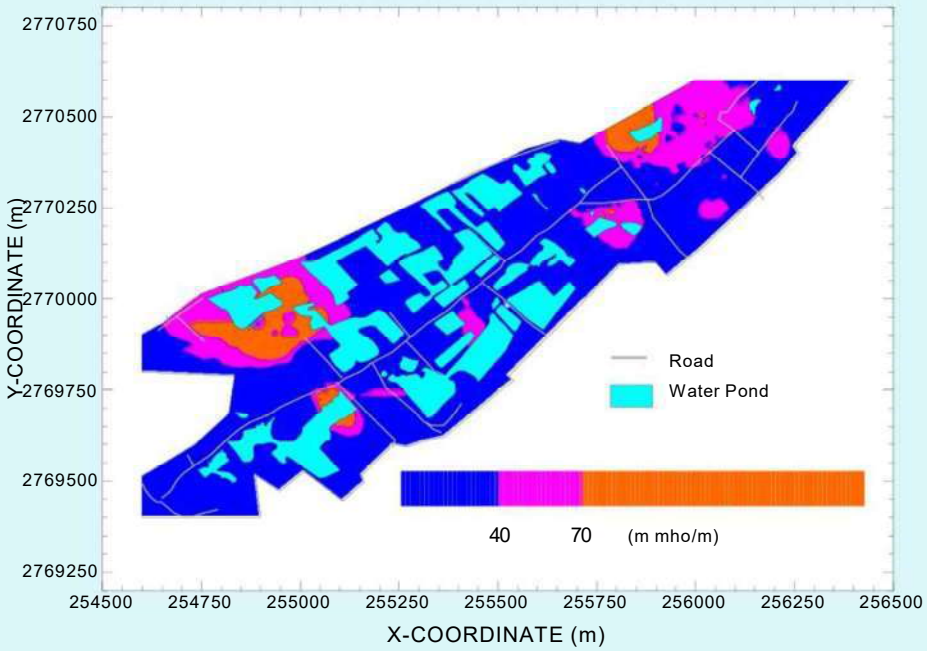
等視電阻率影像圖



地下掩埋場　　污染團移動方向

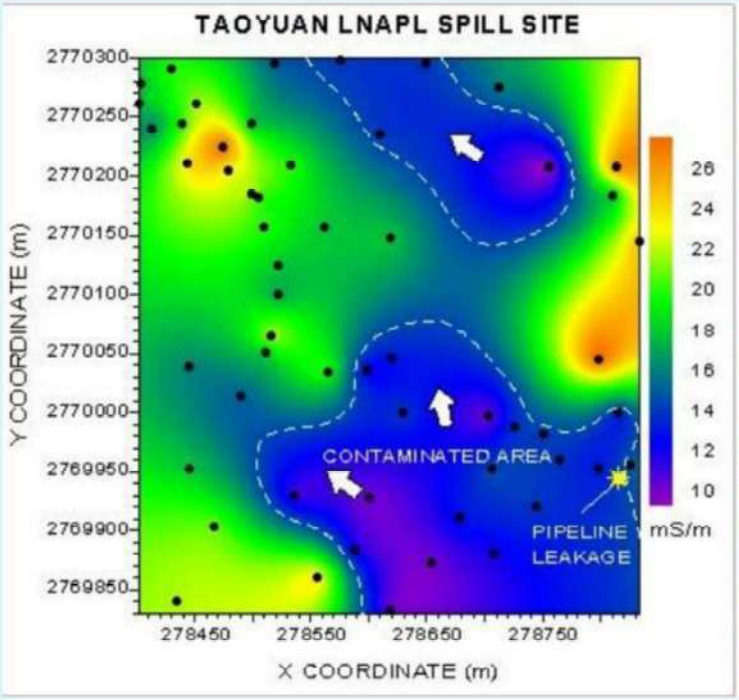
Geophysical Technologies (3/8)

EM Survey – A Waste Dumping Site



Geophysical Technologies (4/8)

EM Survey – A Leaking Oil Pipeline Site



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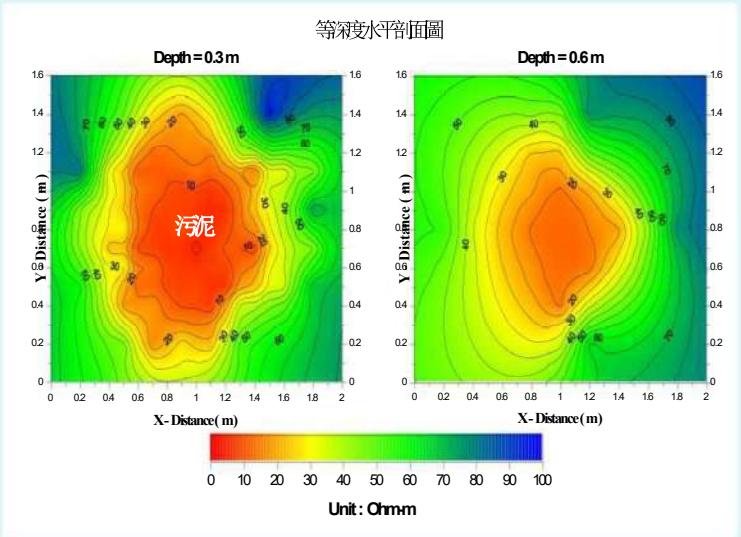
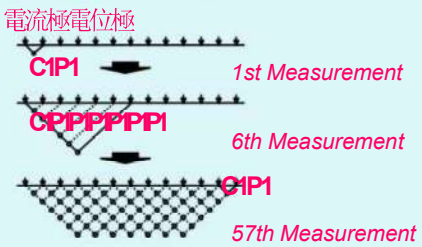
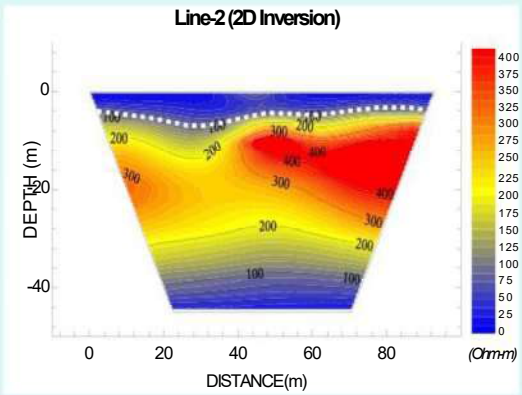
Geophysical Technologies (5/8)

ERT Survey – A Waste Dumping Site







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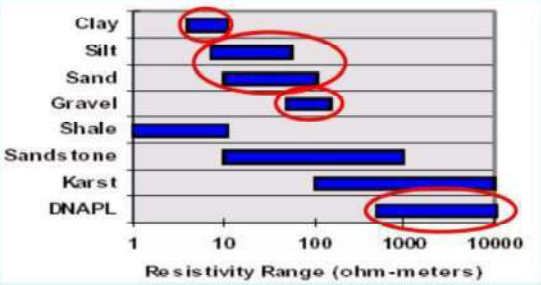
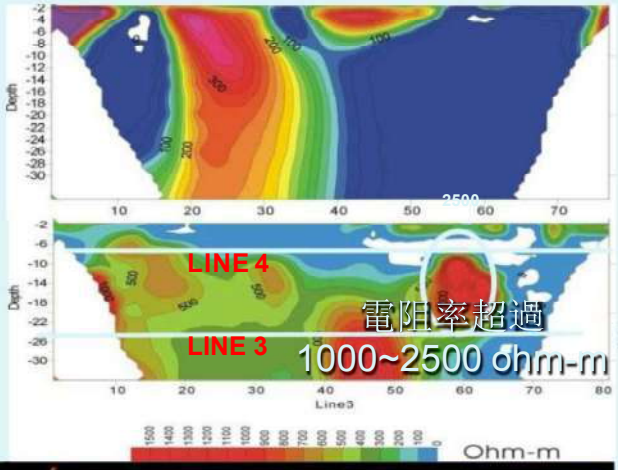
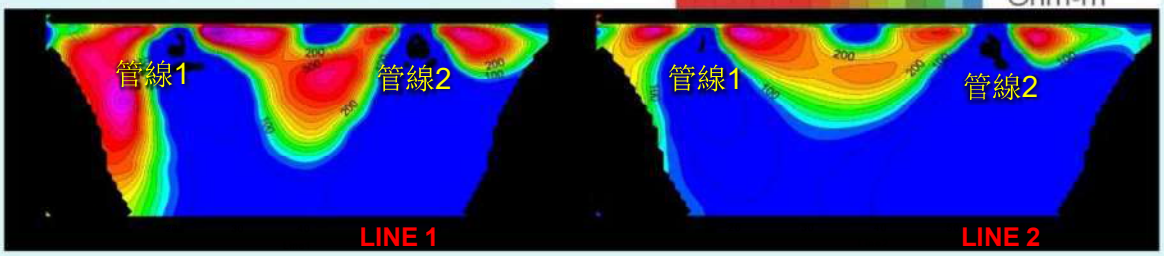
Geophysical Technologies (6/8)

ERT Survey – A DNAPL Site



- DNAPL Resistivity > 800 ohm-m
- ER Line~320m





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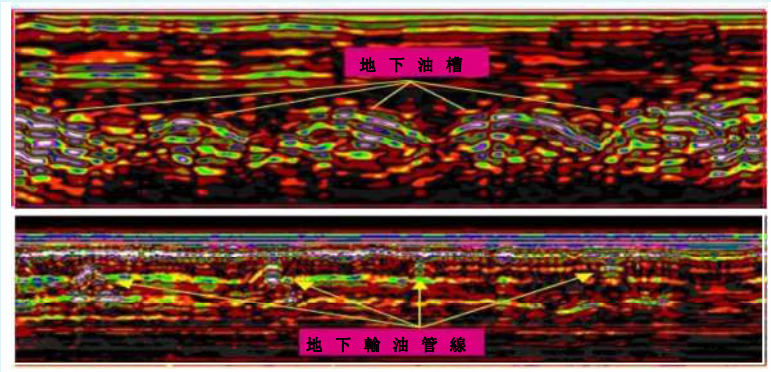
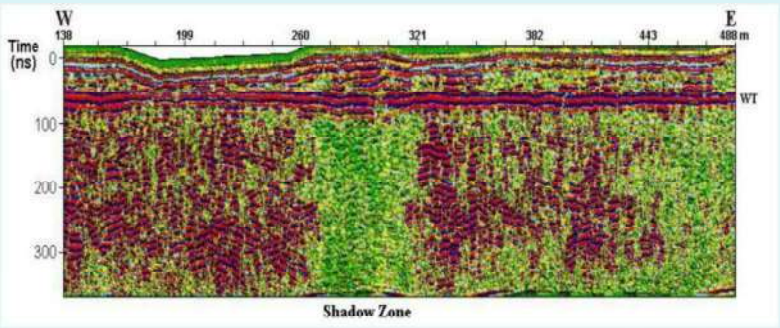
Geophysical Technologies (7/8)

GPR Survey – A Gas Station





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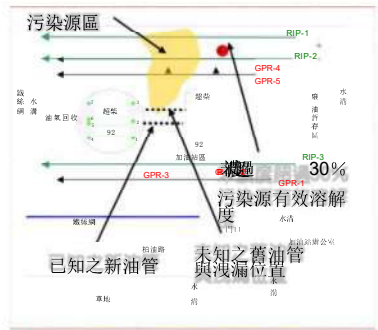
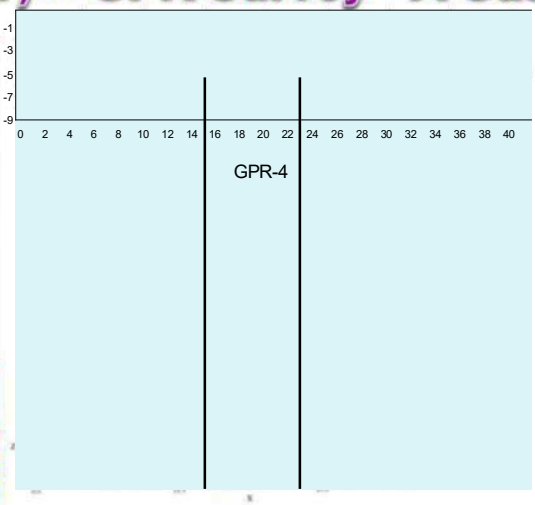
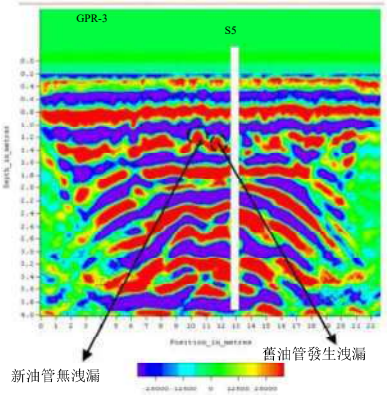
Geophysical Technologies (8/8)

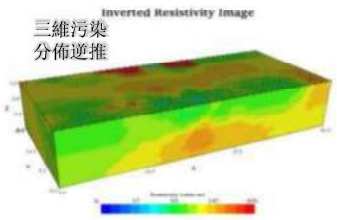
RIP(ERT) + GPR Survey - A Gas Station

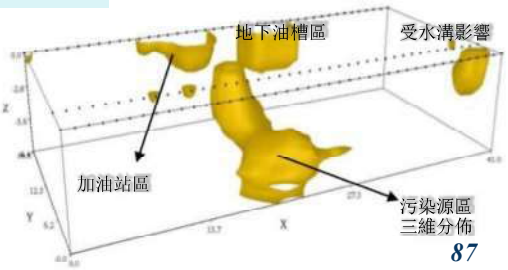




- Conduct both RIP & GPR
- 3-D Oil Distribution
- Both Soil and groundwater samples found LNAPLs







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Common Investigation Methods in Taiwan

- Soil Sampling and Analysis
- Groundwater Sampling and Analysis
- Hydrogeology investigation
- Screening/ In-situ Detection Technologies
- Geophysical Technologies
- Other Investigation Methods

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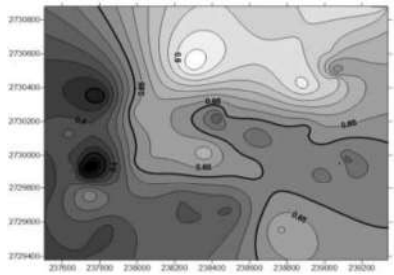
Other Investigation Methods

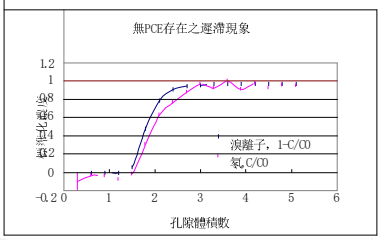
Radon Test /Analysis For DNAPLS

Radon and bromide analysis

Radon Distribution

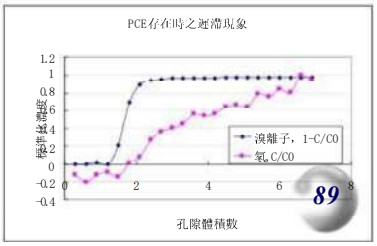


Radon free water with bromide



AlphaGUARD Radon Analysis

Bromide Deetor



Case Study – A Gas Stations

APOLLO TECH 90

Site History

- It was found by nearby residents that groundwater was contaminated in 2001
- Responsible Parties conduct：1)Tank and pipeline leaking test, 2) Soil gas survey, 3) GPR survey, 4) EM survey, 5)Soil and groundwater sampling and analysis in 2002.
- The contaminants flow out (down gradient) at least 2,000 meter from gas station
- 2002 listed as pollution controlled site

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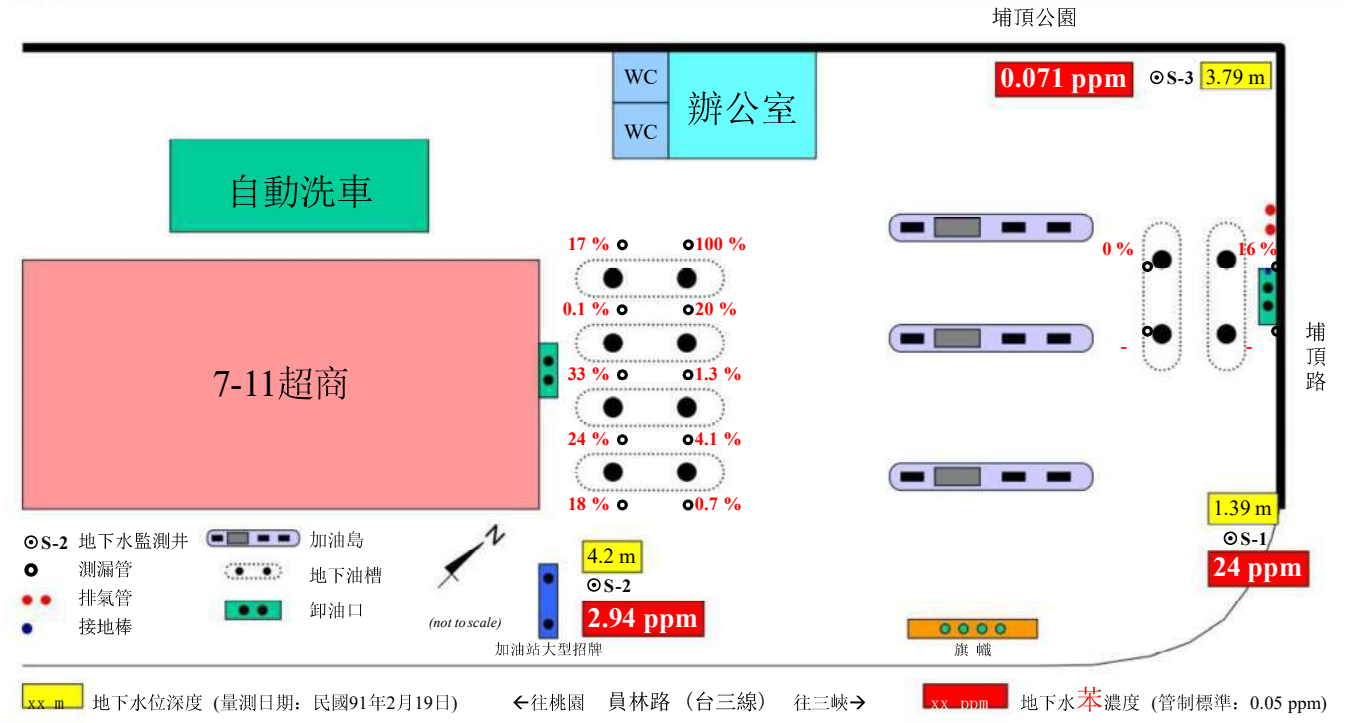
埔頂公園
WC
WC
辦公室
0.071 ppm
S-3
3.79 m
自動洗車
7-11超商
17 %
100 %
0.1 %
20 %
33 %
1.3 %
24 %
4.1 %
18 %
0.7 %
0 %
16 %
埔頂路
1.39 m
S-1
24 ppm
S-2 地下水監測井
測漏管
排氣管
接地棒
加油島
地下油槽
卸油口
(not to scale)
4.2 m
S-2
2.94 ppm
加油站大型招牌
旗 幟
xx m 地下水位深度 (量測日期：民國91年2月19日)
←往桃園 員林路（台三線） 往三峽→
xx ppm 地下水苯濃度 (管制標準：0.05 ppm)

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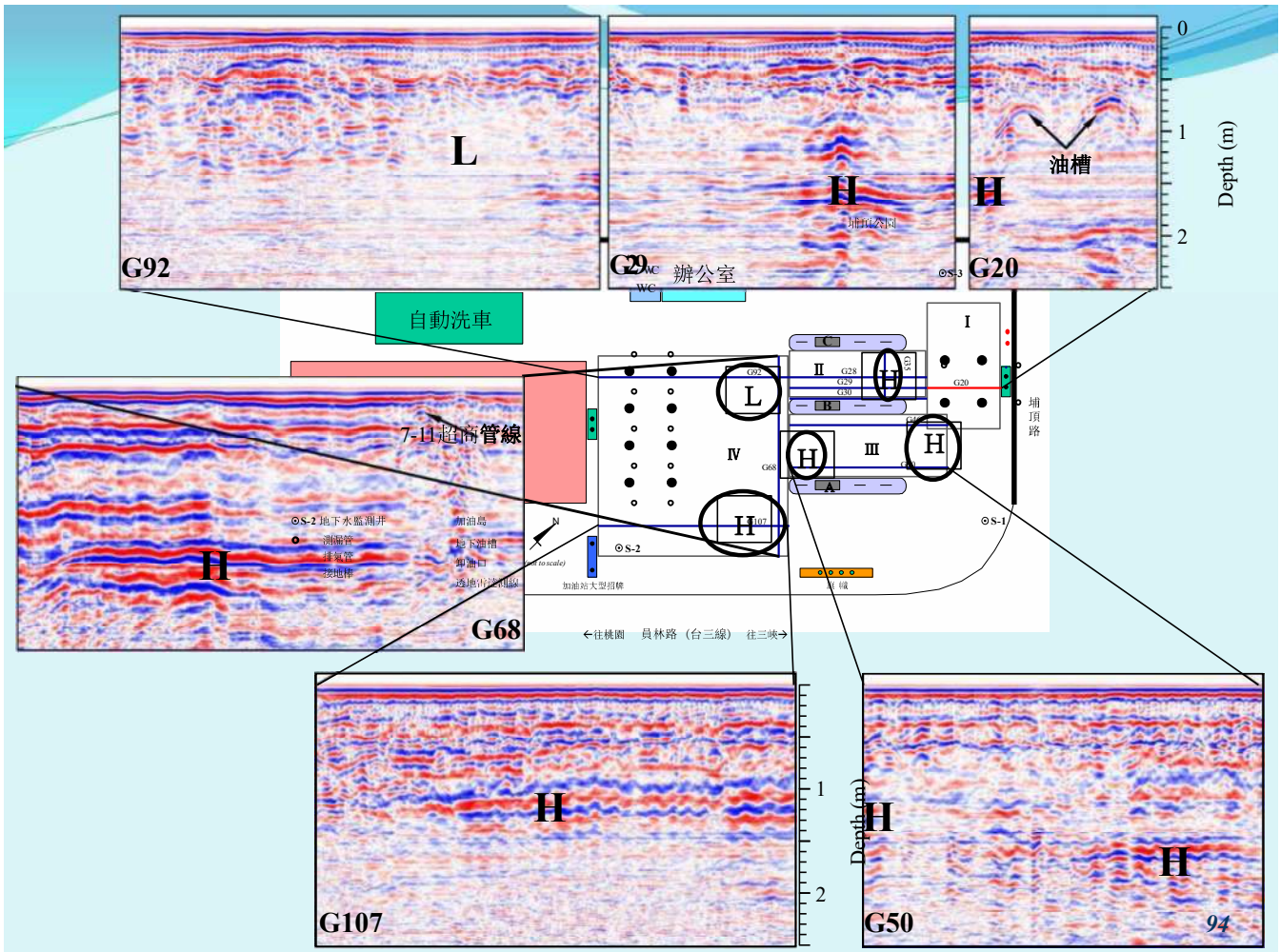
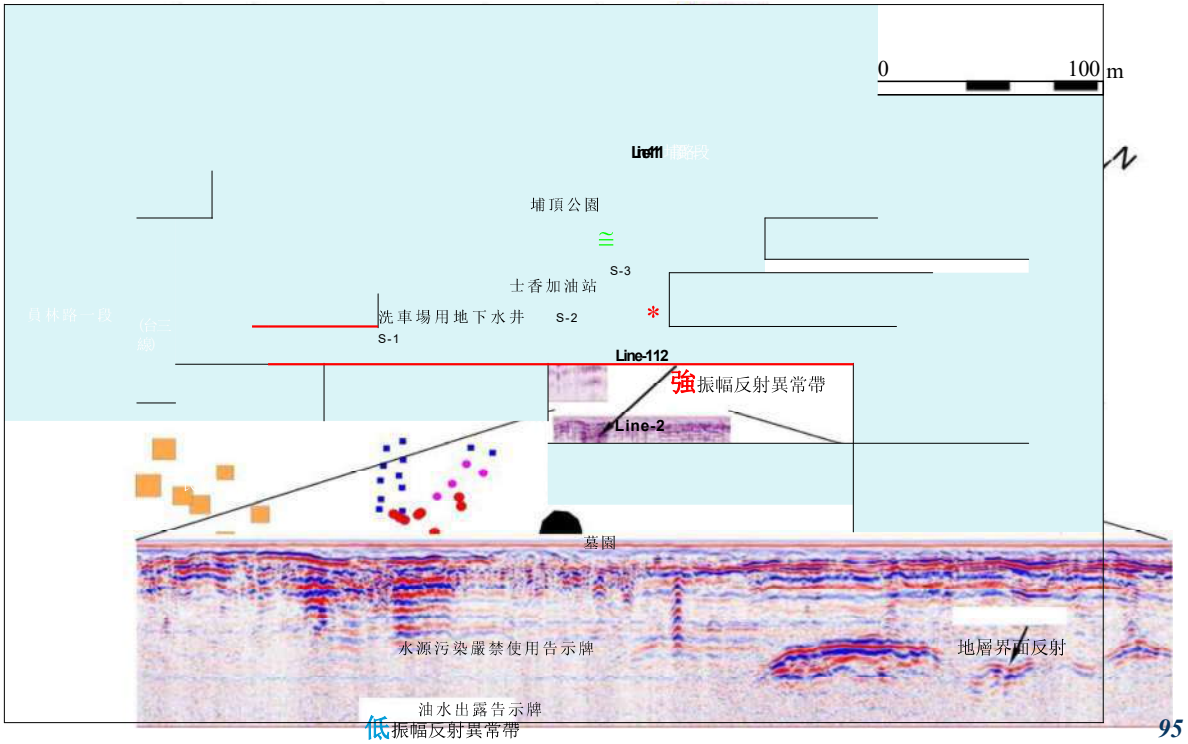

G92
L
G29
H
G20
H
油槽
Depth (m)
0
1
2
辦公室
自動洗車
7-11超商管線
G68
H
G107
H
G50
H
H
94

GPR Survey



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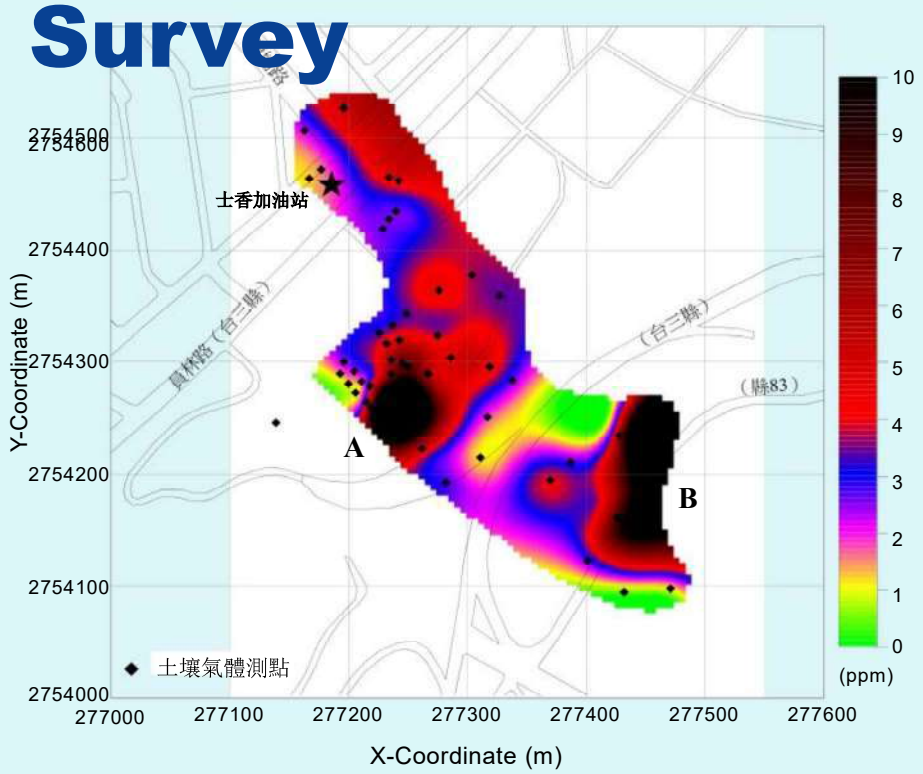
Soil Gas Survey



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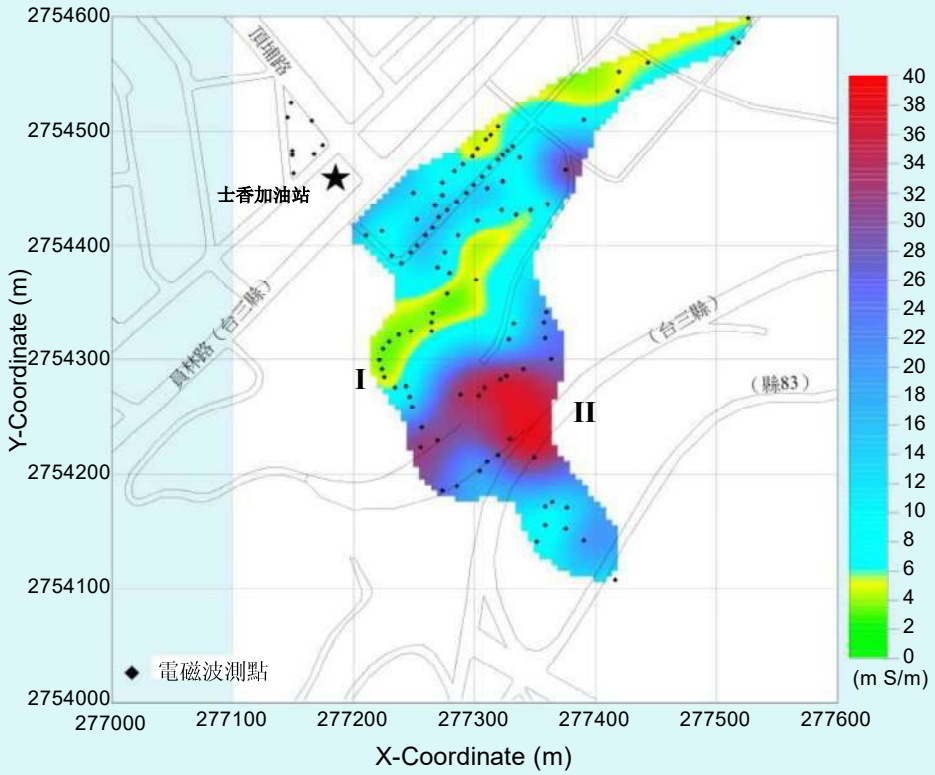
EM Survey



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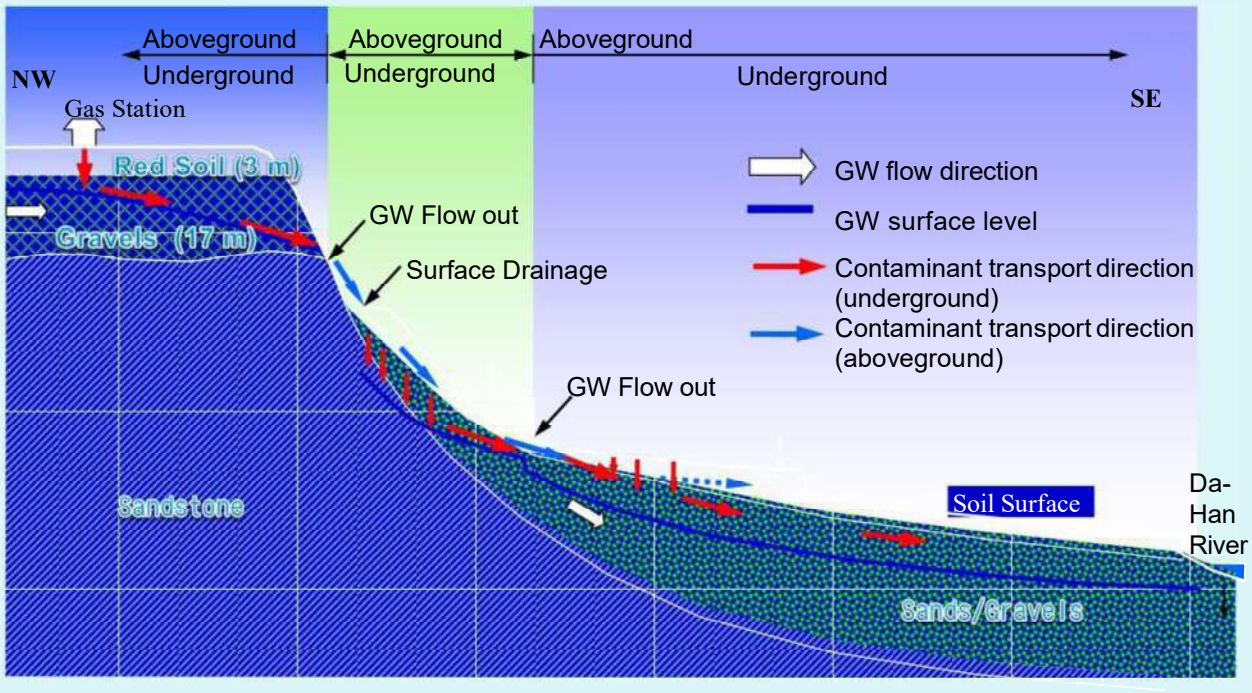
Site Conceptual Model



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Conclusions

Investigation for Success?

- Define Investigation Purpose
- Know Where and How to Collect Site Information
- Mapping
- Use Screening Tools (Methods)
- Potential Sources Survey
- Soil and Hydrogeology Data Collection
- Choose Appropriate Sampling and Analytical Methods
- Enough Cost and Time with Control

Conclusions

- Collect Data and Information
- Use Right Sampling Methods
- Use Screening Tools (Methods)
- Real Time in-Situ Supports
- Health and Safety
- Road to the Successful Remediation

Thank you for your attention

APOLLO TECH Apollo Technology Co., Ltd.

6A New Design Building, 22, Sec.3, Zhongshan N.Road, Zhongshan District,
Taipei City 10593, Taiwan, R.O.C.

Tel: +886-2-7730-6566 ext. 102 Fax:+886-2-7730-8225

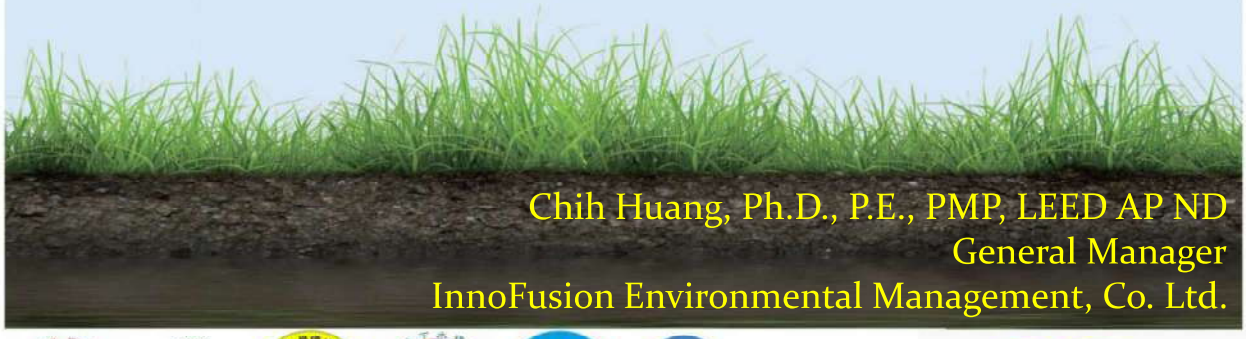
E-mail: mdchc@apollotech.com.tw

Website: www.apollotech.com.tw

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Risk Assessment for Soil and Groundwater Contamination



Chih Huang, Ph.D., P.E., PMP, LEED AP ND
General Manager
InnoFusion Environmental Management, Co. Ltd.

Outline

- Why risk-based
- About risk assessment
- Concept and methodology
- Uncertainty analysis
- Case Study on Regulatory Standard

Challenges in Regulation/Policy Making

- Criticisms against regulations
  - Not effective in delivering their goals
  - Efficient in doing so but not at least cost
  - Equity, administrative, political acceptability
- Regulatory measures transformation

Risk-based Regulation Reform

- International recognition and evolution
  - OECD-Guiding Principles for Regulatory Quality and Performance (2005)
  - EU-three strategic reviews of better regulation (2006)
    - an integrated approach to impact assessment
    - extended the requirement to do impact assessments beyond initiatives in the annual Legislative and Work Program
    - ensure that impact assessments conform to procedures and quality standards
    - a system which is transparent and accountable
  - UK-Better Regulation Task Force
    - Environment Agency adopted risk-based approach
    - Focus scarce regulatory resources on the highest risk and the worst performance

Risk-base Contaminated Site Management (UK)

MCL	Risk-Based
● Unlimited land use ● Consider all possible receptors	● Specific land use ● Consider specific receptors
● Cost-Benefit is not an issue ● Probably high cost (2 million pounds per ha) ● Permanent solution ● How sustainable?	● Sustainability is considered ● Cost- benefit is important ● With protecting public health and environment as priority, optimizing the resources commitment

5

Risk-base Contaminated Site Management (US)

1980's — CERCLA or Superfund enforced. Initial estimation for Superfund remediation was 1.6 billion USD (3.6 million per site x 400 sites)

1990's — Superfund sites could exceed 2000 sites as the remediation cost could be in a range of 100~500 billion USD)

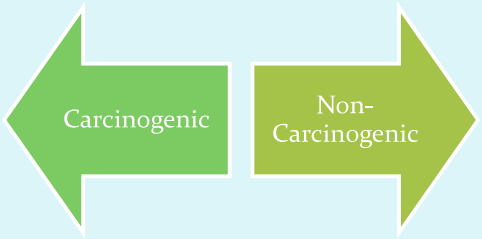
2000's — If based on MCL. The remediation cost was estimated to be over 1 trillion USD

How clean is clean?

6

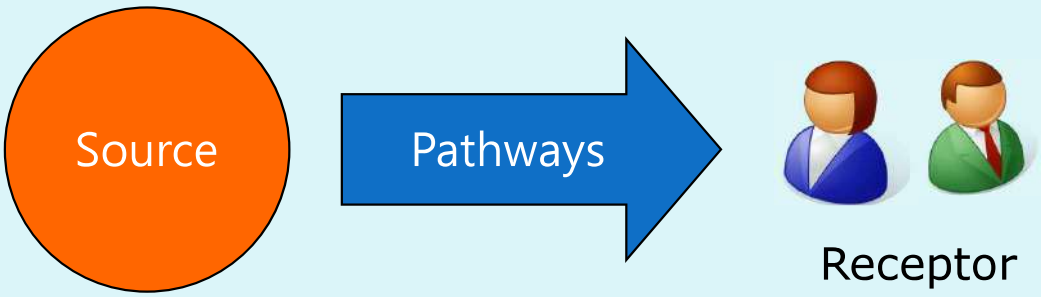
What is risk

- Risk
  - Probability of the occurrence of adverse consequence (injury, illness, or even death)
  - Quantitative concept
- Health risk
  - Probability of illness and death caused by the hazardous materials (e.g., contaminants)



What is risk

- Consist of three elements



S-P-R Model

Role of Risk Assessment

- Scientific tool within risk analysis system

Myth of Acceptable Risk

- General accepted rules
  - carcinogenic risk: 1×10^{-6}
  - non-carcinogenic (hazard index, HI): 1
- Two dimensional drivers
  - Objective definition
    - quantitative risk
    - scientific based
  - Subjective perception
    - Public awareness and knowledge
    - social based

Myth of Acceptable Risk

- A research in 1991 tried to reveal the myth or original of acceptable risk (1×10^{-6})

Agencies

- The White House
- The U.S. Environmental Protection Agency (EPA)
- The EPA's Science Advisory Board
- The EPA's Risk Assessment Forum
- The U.S. Food and Drug Administration (FDA)
- The U.S. Department of Agriculture
- The U.S. Conference of Mayors
- Oak Ridge National Laboratories
- The Congressional Office of Technology Assessment
- The Natural Resources Defense Council
- Citizen's Clearinghouse for Hazardous Waste
- Greenpeace
- Two former EPA Administrators
- A former state environmental commissioner
- Rockefeller University
- Environmental divisions of major law firms
- Staff members of several Congressmen
- And many other contacts in government and industry

Responses

- "My mind is a complete blank."
- "My, what an interesting question!"
- "I think it came from pesticides legislation or the Delaney Clause."
- "It came from the FDA in the 1950s."
- "It was derived from the Virtually Safe Dose used in the Safe Drinking Water Act."
- "It's an economic criterion."
- "It's based on the chance of being hit by lightning, which is one in a million."
- "I just assumed it was because one-in-a-million sounded like such a nice phrase."
- "It was selected because it was 'doable.' Or at least that's what we thought at the time."
- "It was a purely political decision made by several of the major agencies behind closed doors in the 1970s. I doubt very much you'll get anyone to talk to you about it."
- "You really shouldn't be asking these questions"

Basic Concept and Framework

Hazard Identification
Examines whether a stressor has the potential to cause harm to humans and/or ecological systems, and if so, under what circumstances.

Dose Response Assessment
Examines the numerical relationship between exposure and effects

Exposure Assessment
Examines what is known about the frequency, timing, and levels of contact with a stressor.

Risk Characterization
Examines how well the data support conclusions about the nature and extent of the risk from exposure to environmental stressors

General Procedure

- hazard identification
  - Define CoC
  - Site (assessment) boundary
- dose-response assessment
  - Toxicity information
  - Define toxicity factors to be uses (carcinogenic slope factor and non-carcinogenic reference dose)
- exposure assessment
  - Site conceptual model (SCM)
  - Fate and transport of CoCs
  - Intake
- risk characterization
  - Carcinogenic risk and non-carcinogenic hazard index
  - Uncertainty analysis

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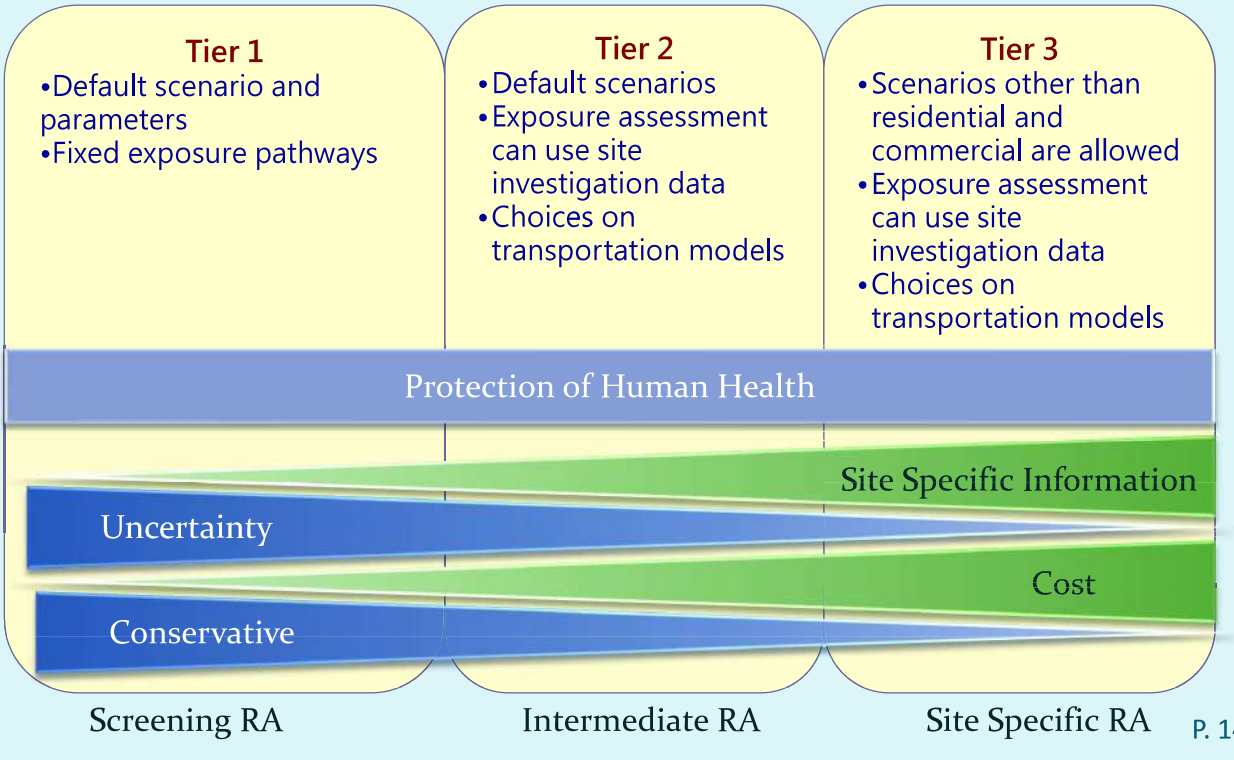
Tiered Approach and Decision



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Hazard Identification

- Data collection (boundary)
  - 1 km as a rule of thumb
  - should be defined according to the site contamination and characteristics

Regulatory Requirement	Search Distance (km)
NPL	1.6
Delist from NPL	0.8
CERCLIS Listed	0.8
RCRA Listed	0.8

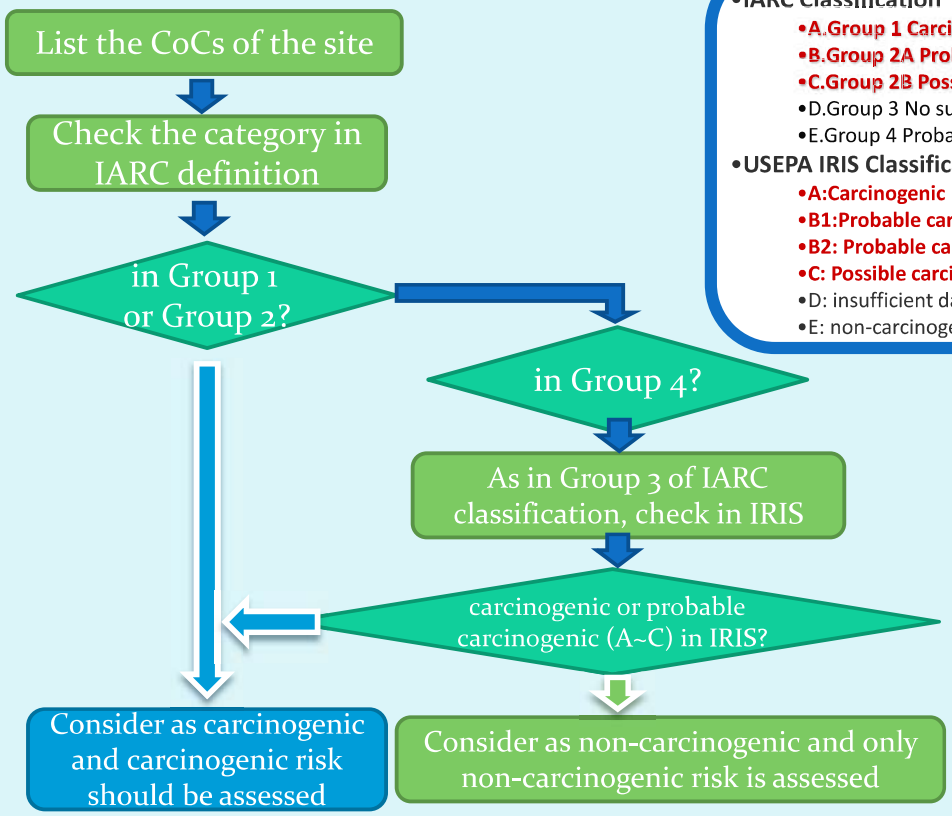
References : ASTM E1527-05

  - Minimum site information (at least in 10 years)
    - site environmental data
    - land (site) use data
    - contamination or site investigation data

Hazard Identification

- CoCs identification
  - At least include contaminants in Control Standard
  - include potential CoC
  - CoC relationship with the site conditions or environment
  - May exclude
    - Mixtures (total phenol)
    - contaminant without chronical toxicity information needed

Hazard Identification



- IARC Classification
  - A.Group 1 Carcinogenic
  - B.Group 2A Probable
  - C.Group 2B Possible
  - D.Group 3 No sufficient evidence
  - E.Group 4 Probable non-carcinogenic
- USEPA IRIS Classification
  - A:Carcinogenic
  - B1:Probable carcinogenic (human toxicity data)
  - B2: Probable carcinogenic (animal toxicity data)
  - C: Possible carcinogenic
  - D: insufficient data
  - E: non-carcinogenic

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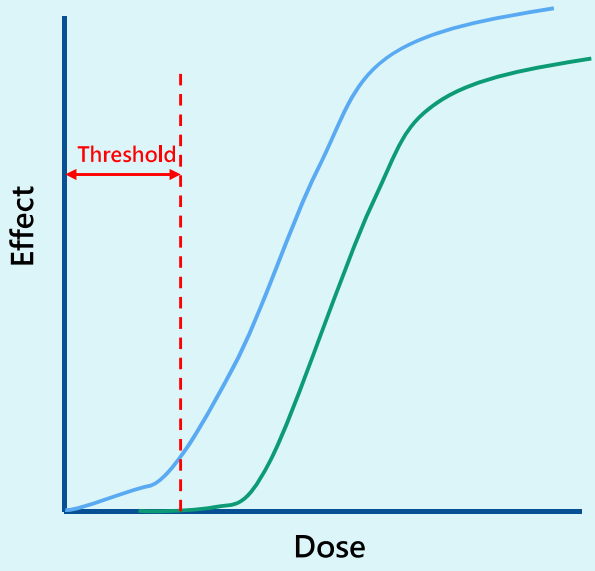
Dose-Response Assessment

- How toxicity factors defined
  - From animal tests or epidemiologic investigation
  - Find out the linkage between exposure and possible impact or harm to human health
- Dose vs. Health
  - How high the dose will be harmful to human health
  - How many people are harmed due to exposure



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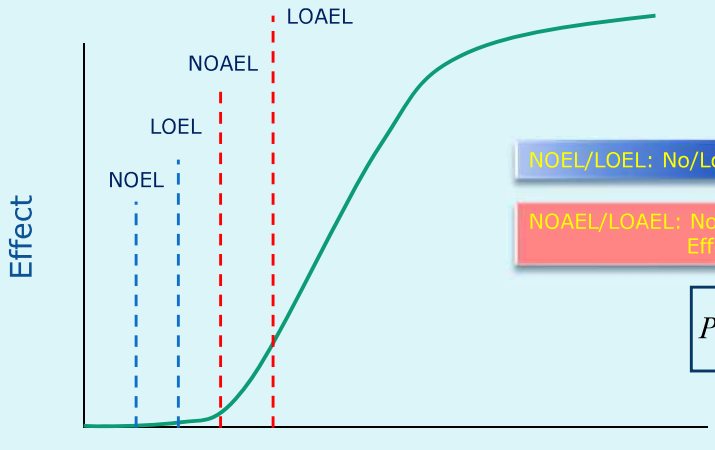
Dose-Response Assessment

- Dose-Response Curve
  - Non-carcinogenic
    - reversible
    - based on the possible occurrence of observable adverse effect



NOEL/LOEL: No/Lowest Observable Effect Level

NOAEL/LOAEL: No/Lowest Observable Adverse Effect Level

$$Potential = \frac{Intake}{NOAEL}$$

Dose-Response Assessment

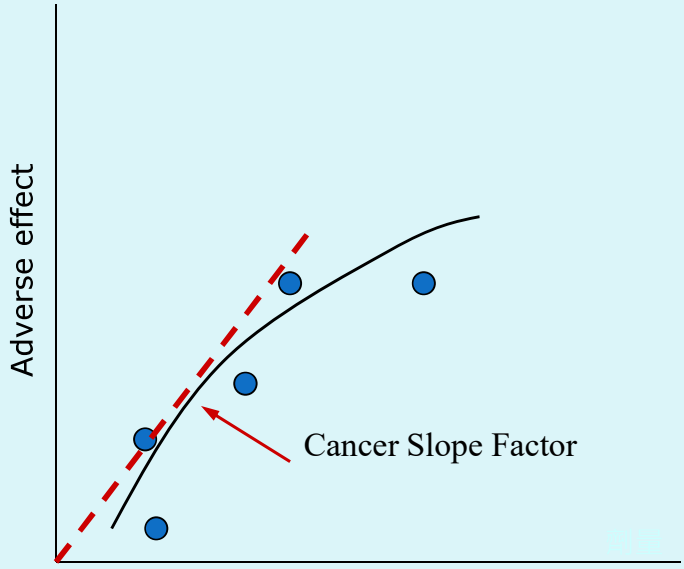
- How toxicity factors defined
  - Non-carcinogenic
    - reversible
    - based on the possible occurrence of observable adverse effect

$$RfD = \frac{NOAEL}{UF \times MF}$$

UF: Uncertainty Factor
MF: Modifying Factor
Due to lack of data or uncertainty, the toxicity factor needs to be adjusted to a lower level (more conservative)

Dose-Response Assessment

- How toxicity factors defined
  - carcinogenic
    - adverse effect is cumulative and non-reversible
    - Slope Factor (SF)



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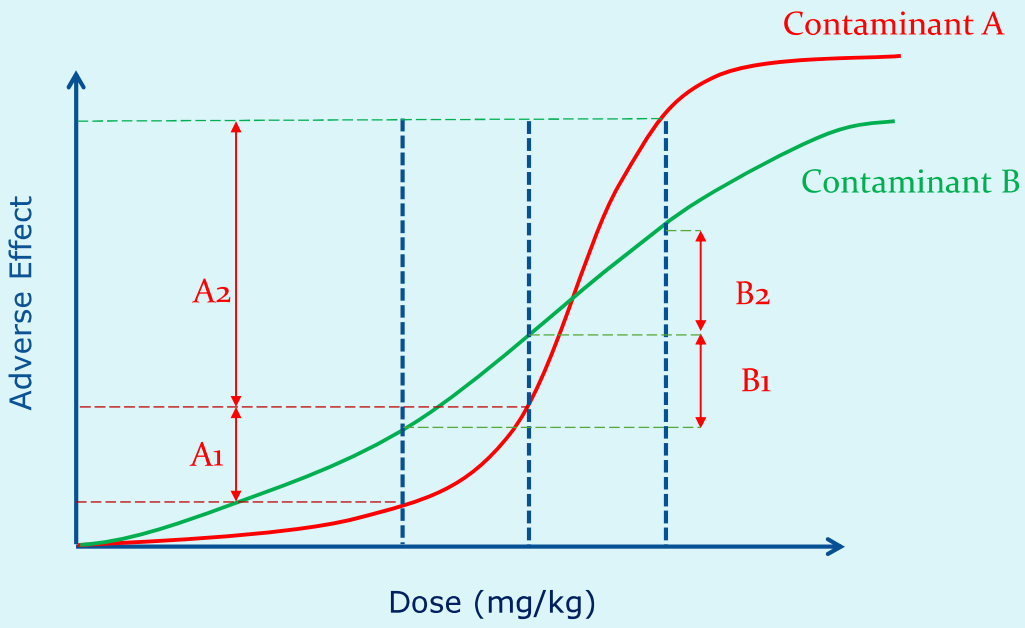
Dose-Response Assessment

- Multi-Component Effect
  - Additive
    - $E_{Total} = E_A + E_B$
  - Synergistic
    - $E_{Total} > E_A + E_B$
  - Antagonistic
    - $E_{Total} < E_A + E_B$

Dose-Response Assessment

- High and Low Dose Effect



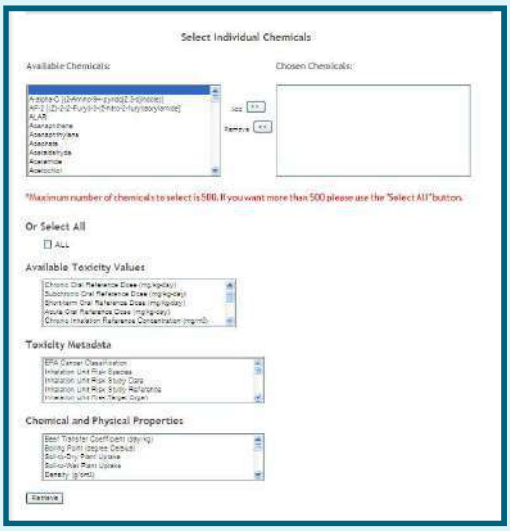
Dose-Response Assessment

- Recommended toxicity database
  - USEPA IRIS
  - WHO CICAD
  - USEPA PPRTVs
  - ATSDR Minimal Risk Level (MRL)
  - Health Effect Advisory Summary Table (HEAST)
  - Cal EPA

Dose-Response Assessment

- Risk Assessment Information System

http://rais.ornl.gov/



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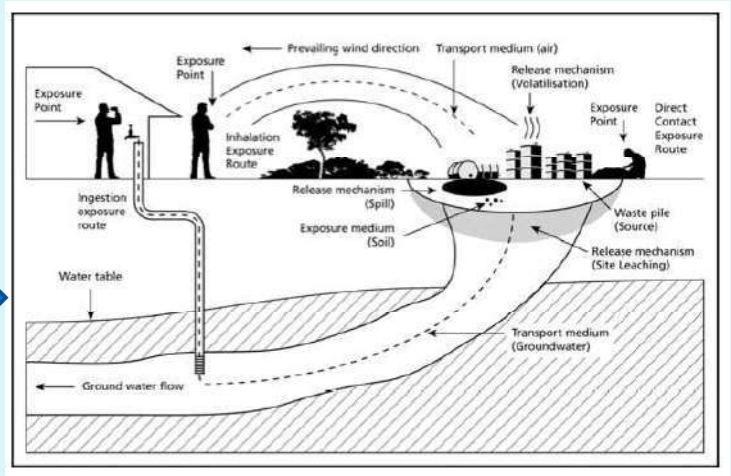
Exposure Assessment

- Scenario setting and Site Conceptual Model (CSM)
  - Land use (current and future)
  - Environmental matrix
  - Pathways
  - Receptor

- CSM includes source confirmation, contamination transport, potential receptor, exposure pathway
- Required continuously to be updated and revised



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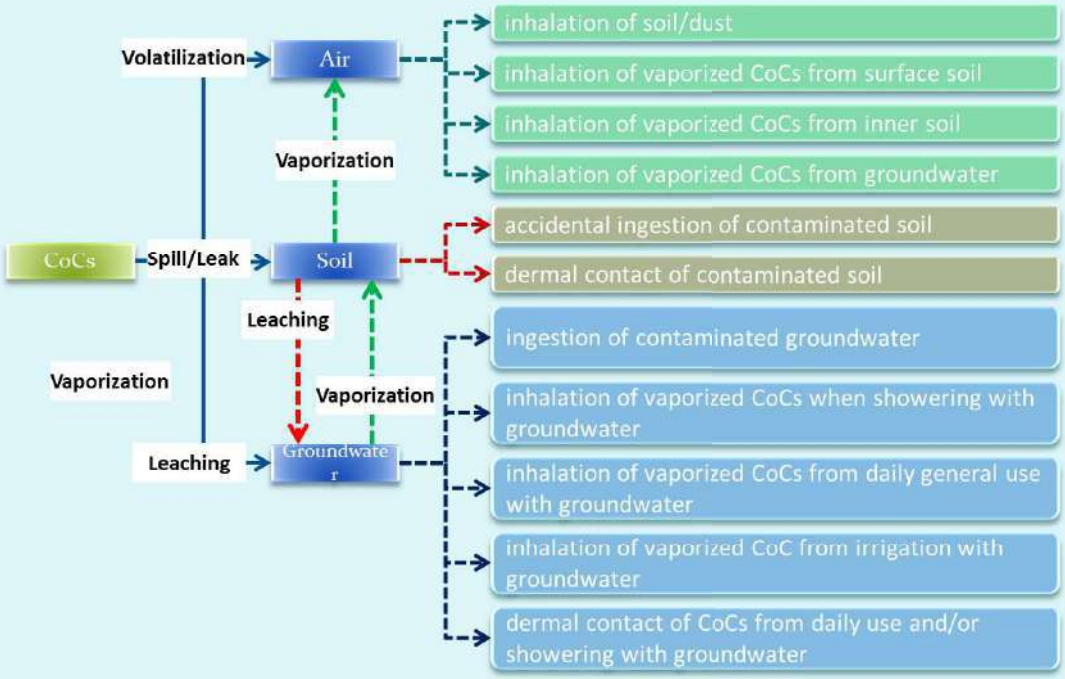
Exposure Assessment

- Pathways considered



Exposure Assessment

- Additional pathways may be considered
  - Food chain
  - irrigation
  - other pathways identified in CSM

Exposure Assessment

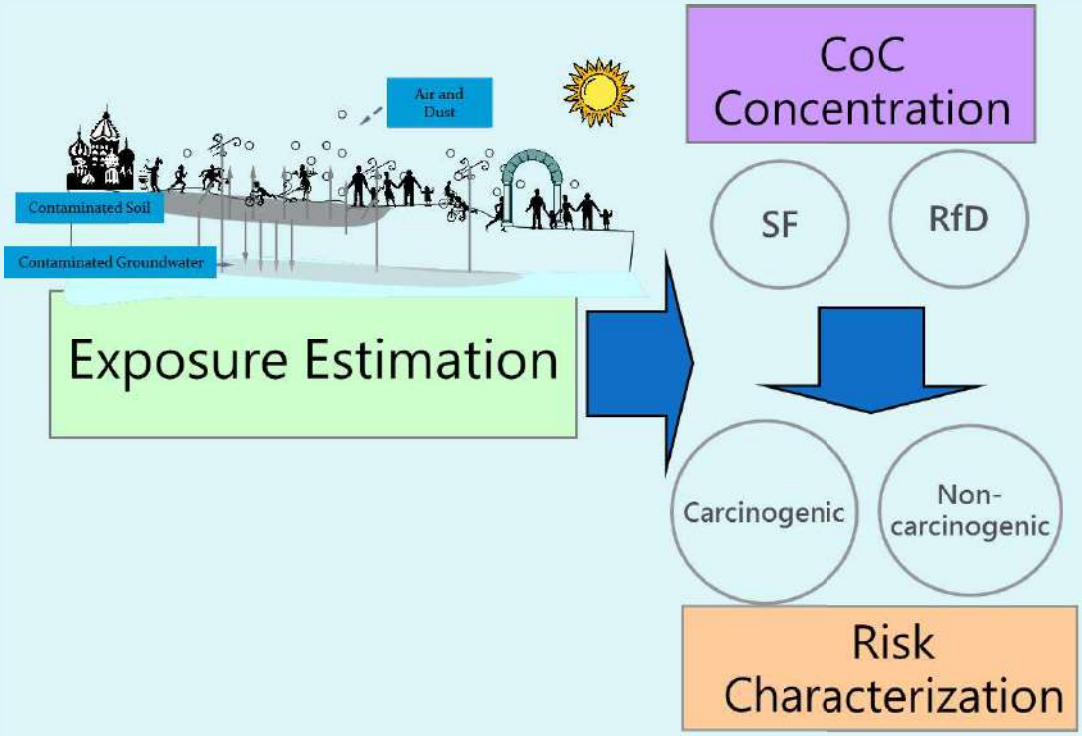
- CoC concentrations to be used
  - actual concentration measured at points of exposure (POE)
  - Model prediction/simulation
  - 95 percentile

Use of 95 percentile depends on
- Measured data points ($n \geq 7$)
- Distribution of measured data

Risk Characterization

- Risk characterization consists of
  - Risk calculation
    - Exposure and toxicity integrated
    - carcinogenic and non-carcinogenic
    - either one of the risks (above) exceeds acceptable level then remediation and risk management are required
  - Uncertainty analysis
    - Examination on the reliability and certainty of the risk calculated
    - the influence on the result by the calculation process (parameters, scenario, model)

Risk Characterization



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Risk Characterization

- Non-carcinogenic
  - Assumptions
    - Chronical
    - Additive
    - Adverse effect only happens when exceeding certain value (threshold)
    - acceptable risk is 1

- Calculation
  - Each pathways' Hazard Quotients (HQ)

$$HQ_{inh} = \frac{Intake_{inh}}{RfD_{inh}}$$

$$HQ_{oral} = \frac{Intake_{oral}}{RfD_{oral}}$$

$$HQ_{dermal} = \frac{Intake_{dermal}}{RfD_{dermal}}$$

  - Add up to Hazard Index (HI)

$$HI = \sum HQ_{oral} + \sum HQ_{inh} + \Sigma HQ_{dermal}$$

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Risk Characterization

- Carcinogenic risk
  - Assumptions
    - Chronical
    - Additive
    - Adverse effect is cumulative
    - acceptable risk is 1×10^{-6}
    - can be varied depends on land use
  - Calculation
    - Cancer Risk for different pathways

$$R_{oral} = Intake_{oral} \times SF_{oral}$$

$$R_{inh} = Intake_{inh} \times SF_{inh}$$

$$R_{dermal} = Intake_{dermal} \times SF_{dermal}$$

    - Added up to a total risk value

$$R_{total} = \sum R_{oral} + \sum R_{inh} + \sum R_{dermal}$$

Sources of uncertainty

- Deterministic risk assessment
  - One value representing the risk (non probabilistic)
  - conservative assumption (often over-conservative)

- Hazard identification
  - completeness of site information
- Exposure assessment
  - transport of contaminants
  - model selection
  - exposure parameters
- Dos-response assessment
  - toxicity factors
  - interaction of contaminants
- Risk characterization
  - interaction of toxicity
  - rationale of acceptable risk

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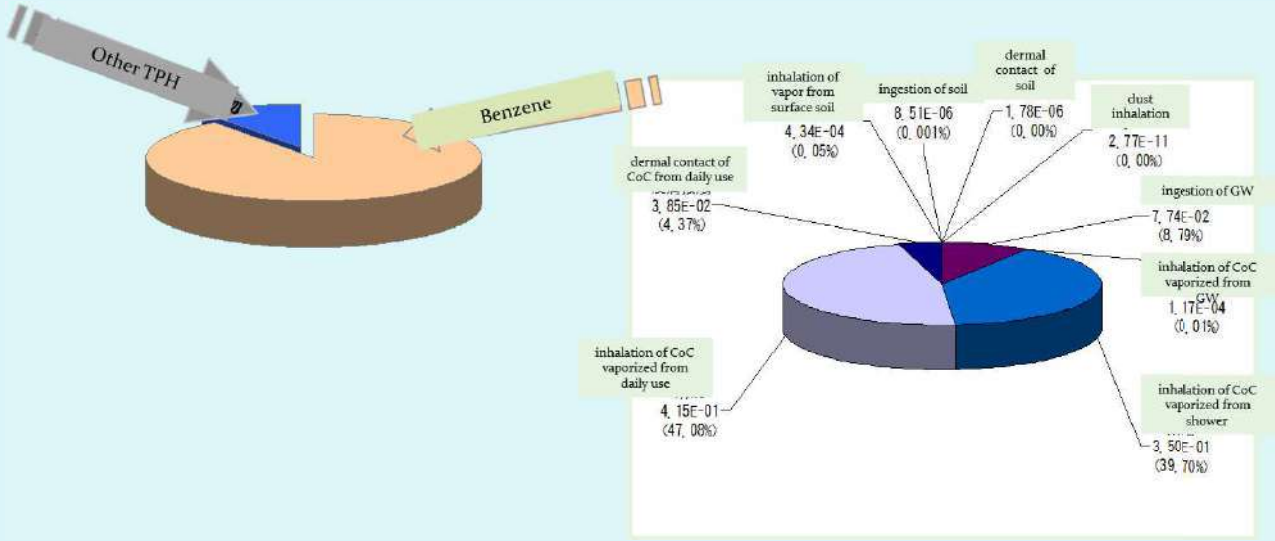
Sensitivity Analysis

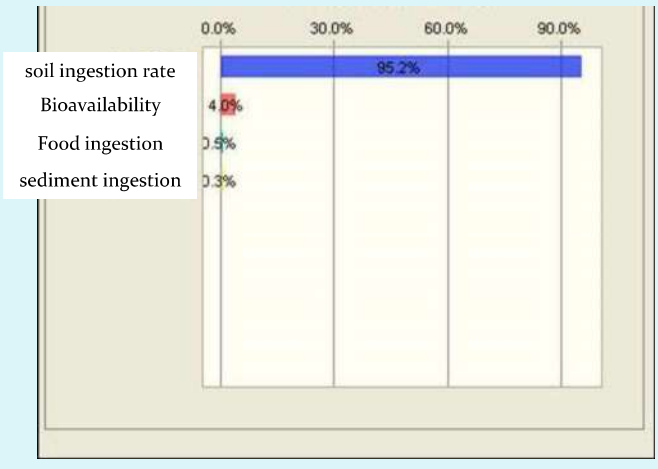
- Fractions of exposure pathways
- Fractions of contaminants



Sensitivity Analysis

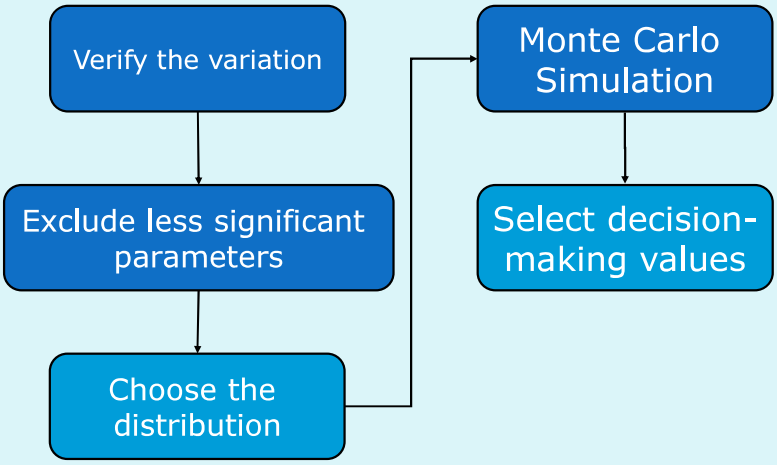
- Sensitivity ratio (SR)
  - higher the SR, the calculated risk is affected more significantly by the parameters

$$SR = \frac{\frac{R_2 - R_1}{R_1} 100\%}{\frac{P_2 - P_1}{P_1} 100\%}$$



Monte Carlo Analysis

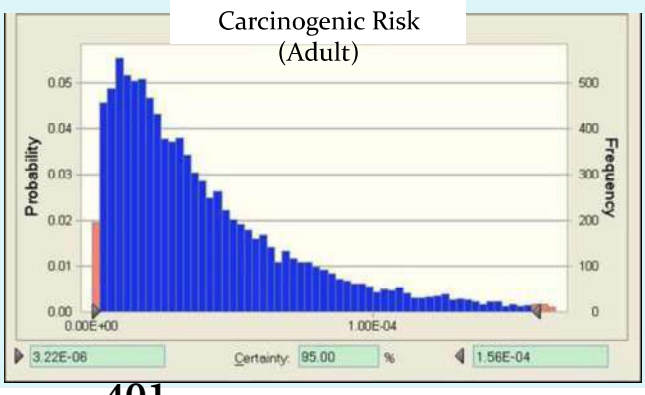
- the variations of parameters are defined differently to reflect actual variation/distribution
- Distribution of probability in risk
- Enhance decision making



Monte Carlo Analysis

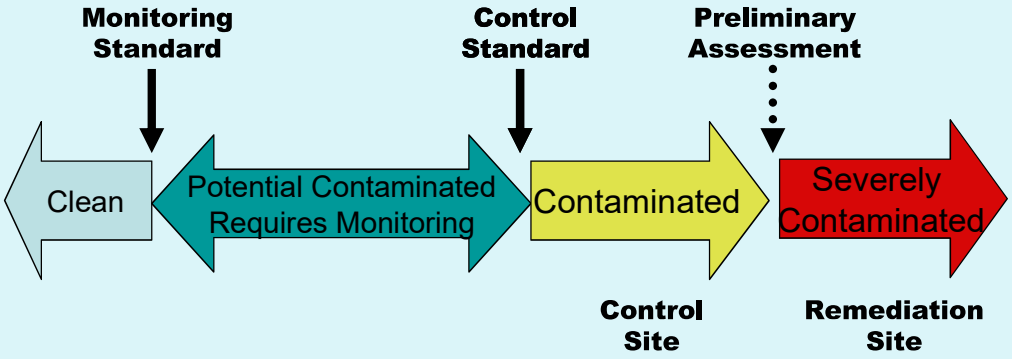
Parameters	Distribution	Range
A	Normal	18±1.8
B	Normal	137±45
C	Normal	180±18
D	Triangular	Max: 1, Min: 0, Most likely=0.67

Combination of parameters



Case Study- Regulatory Standard

- Introduction
  - Regulatory standards need to be revisited after 10 years since the promulgation of Soil and Groundwater Pollution Remediation Act (SGPRA)
  - Standards requires attention and revision for better contaminated site management practices

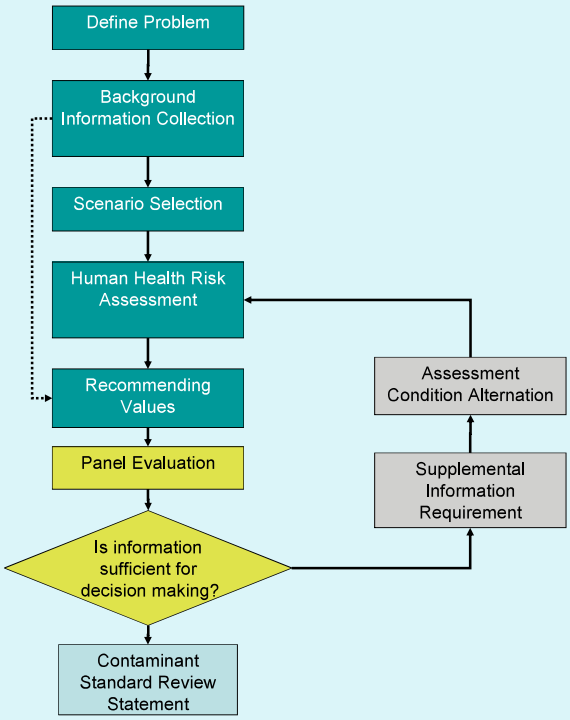


Case Study- Regulatory Standard

- Risk Based Control Standard Has been in practice for decades
  - Soil Screen Level (USEPA)
  - Soil Guideline Value (UKEA)
  - Target and Intervention Values (Netherlands)
- Localization for actual needs
- Availability of risk assessment protocol

Case Study- Regulatory Standard

- Conceptual Approach



Case Study- Regulatory Standard

- Approach
  - Defining problem
    - management objective clarified
    - prioritizing the targets of concerned
  - Background information collection
    - regarding the management target
  - Risk assessment
    - the Human Health Risk Assessment Guideline for Soil and Groundwater Contaminated Sites published by TWEPA
    - Acceptable risks for carcinogenic and non-carcinogenic are defined as $1x10^{-6}$ and 1, respectively
    - Represents residential use assessment

Case Study- Regulatory Standard

- Panel Evaluation
  - recommendation values are then submitted to a panel for evaluation
  - the economic and policy resource are taken into account along with the multiple decision choices for a feasible standard setting
- Standard Review Statement
  - provided as the basis for public comment and discussions
  - offer a scientific sound information
  - a vehicle for better communications

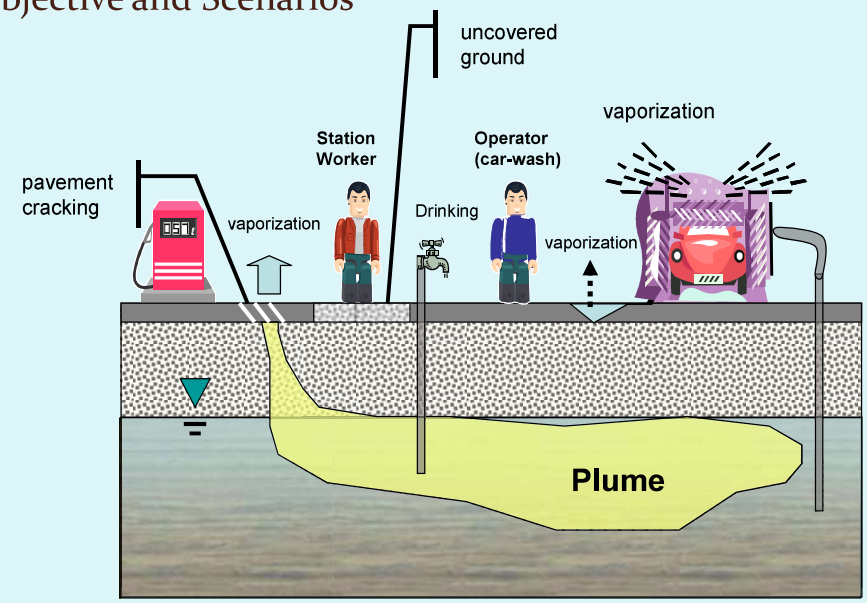
Case Study on Regulatory Standards

Case Study- Regulatory Standard

- Control Standards for MTBE
  - Current Status
    - the Soil Control Standard and Groundwater Control Standard do not include Methyl *tert*-butyl ether (MTBE) which is a common gasoline additive used as an oxygenate
    - recent comprehensive gas station investigation, MTBE contamination has been found in soil and groundwater
  - Defining Objective and Scenarios
    - historical investigation results suggested that the gas station is the main source of contamination
    - mitigate the MTBE contamination to the most probable receptors and reducing the risk by limiting the migration
    - based on the characteristics of MTBE, the Control Standard for groundwater is more important than the Control Standard for soil

Case Study- Regulatory Standard

- Control Standards for MTBE
  - Defining Objective and Scenarios



Case Study- Regulatory Standard

- Basis for Decision Making
  - operator of car washing machine exhibits the higher exposure risk than the general station worker

Exposure Pathways	Recommending Soil Concentration (mg/kg)	
	cacinogenic based	non-carcinogenic based
Inhalation (Dust)	2.29E+07	4.08E+09
Inhalation (vaporization from soil)	9.51E+03	1.69E+06
inhalation (car washing machine)	3.22E+01	1.74E+02
Ingestion of soil	1.50E+03	6.17E+03
ingestion of groundwater*	6.00E-01	N/A

*: based on the groundwater MCL of 0.03 mg/L recommended by USEPA.

Case Study- Regulatory Standard

- Lesson Learned
  - groundwater MTBE concentration dominates the decision for soil regulatory standard
  - recent investigation data

Percentile (%)	MTBE Concentration (mg/L)
20	<0.01
30	0.01
40	0.01
50	0.03
60	0.05
70	0.12
80	0.28
90	0.98

MTBE Control Standards promulgated in 2013 are 0.1 mg/L and 1 mg/L for protected areas and general areas, respectively.

Case Study on Regulatory Standards

Case Study- Regulatory Standard

- Focus of panel evaluation
  - the MCL might create a demanding resource input for site management
  - might face a challenge of listing over 50% of gas stations as contaminated sites
  - the policy and economic factors come into play at panel evaluation

Case Study- Regulatory Standard

- Lessons Learned
  - The risk-based Control Standard setting can provide a scientific sound basis and a defensible regulatory statement
  - The panel evaluation plays an important role in final decision making due to the characteristics of economic and policy making, the qualitative indicators should be defined and evaluated along with the quantitative risk assessment results
- Challenges
  - process of defining assessment target
  - parameters used for the risk assessment
  - comprehensive investigation and background information

Thank you for your attention

Chih Huang
InnoFusion Environmental Management Co., Ltd. (iFEM)
TEL: +886-2-27666808 Ext 13
E-mail: chih.huang@ifem.com.tw

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Environmental Forensic Practices of Petroleum Hydrocarbon Contaminated Sites

Colin S. Chen, Ph.D.
Department of Biotechnology
National Kaohsiung Normal University
Kaohsiung, Taiwan
March 21, 2019

Outlines

- Investigation and management of gas stations and underground storage tanks (UST) in Taiwan
- Introduction of environmental forensics
- Forensic tools for petroleum hydrocarbon releases
- Case study

Background

1987 Private enterprises were authorized to operate gas stations

1997 "Gas Station Regulations" was enacted by EPA. The objective was to regulate retailers to install the equipment for preventing and monitoring groundwater contamination

2000 " Soil and Groundwater Pollution Remediation Act" was enacted by EPA

2001 A severe gasoline leakage was found in Shi-Shang Gas Station in Taoyuan City

2002 "Gas Station Regulations" was amended to regulate retailers to update the monitoring data by cyberfiling

2011 "UST Regulations" was amended to require retailers to monitor soil and groundwater quality regularly by certified laboratories."

Around 2,600 gas stations were investigated for soil and groundwater contamination potential during 2002 to 2012

Processes of gas station investigation

Investigation Projects

2001	2002-2003	2006-2007	2007-2009	2009-2010	2010-2011	2011-2012
To determine potential contamination sources	To investigate gas stations operated for more than 10 years	To investigate gas stations established less than 10 years	Phase 4 investigation	Phase 5 investigation	Phase 6 investigation	Phase 7 investigation

Auditing Projects

2006-2007	2008	2009	2010-2012	2012-2013
Phase I	Phase II	Phase III	Phase IV	Phase V

Time

12.18.2002 Management regulations proclaimed

7.4.2006 First management regulations amended

1.14.2011 Second management regulation amended

Pollution prevention systems and monitoring device management regulations for UST system

Underground storage tanks which store gasoline and diesel should set up pollution prevention system and monitoring devices

To incorporate management regulations and on-site checking → Underground storage tank system online data filing, checking and consulting project (2013~2015)

History of Contamination Investigation of Gas Stations

Investigation Projects

✓ Investigations of 2584 gas stations were accomplished

2002
- SOP for 3 tiers investigation

2006
- To establish processes of necessary counter measures for fuel spill

2007
- Adopting GC chromatograms and TPH turbidity screening method

2009
- To employee Soil Screening test by Immunoassay
- To apply geophysical prospecting tools

2010
- Site Investigation completed

Auditing Projects

✓ To finish1842 gas stations data filing and verification
✓ Filing rate 95.37% in 2006 → 99.76% in 2013

2006
- To Establish cyber-filing system

2008
- Extended cyber- filing system

2009
- Incorporates military UST in the system

2010
- Management regulations revised
- Monitoring parameters amended

2011
- Addition of restricted enterprise types

Investigation Procedures

I

Regulation fitness checking

Soil vapor analysis

- Check pollution prevention systems, monitoring devices, monitoring record, corrosion-prevention potential, groundwater usage, oil slick measurement
- Soil vapor sampling, GC analysis, groundwater level and contaminated potential

II

Soil and groundwater verification

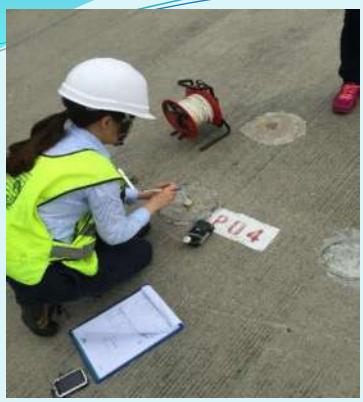
- Soil sampling and screening of highly potential contaminated samples by screening tools, such as PID/FID, TPHs Test kit, etc
- Temporary monitoring wells installation, groundwater sampling, groundwater analysis

III

Groundwater contamination verification

- Standard groundwater monitoring well installation
- Groundwater analysis including VOCs , TPH, etc.

Monitoring of Soil Vapor



Measurement of lower explosive limit (LEL)

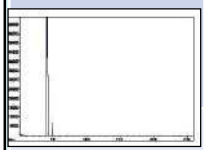
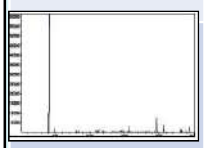
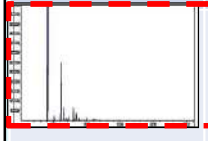
Soil gas measurement by GC/PID and GC/FID

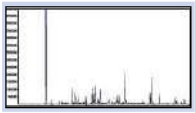
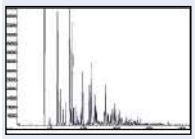
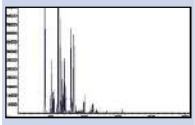
Analysis of Gas Chromatograms

Check Points

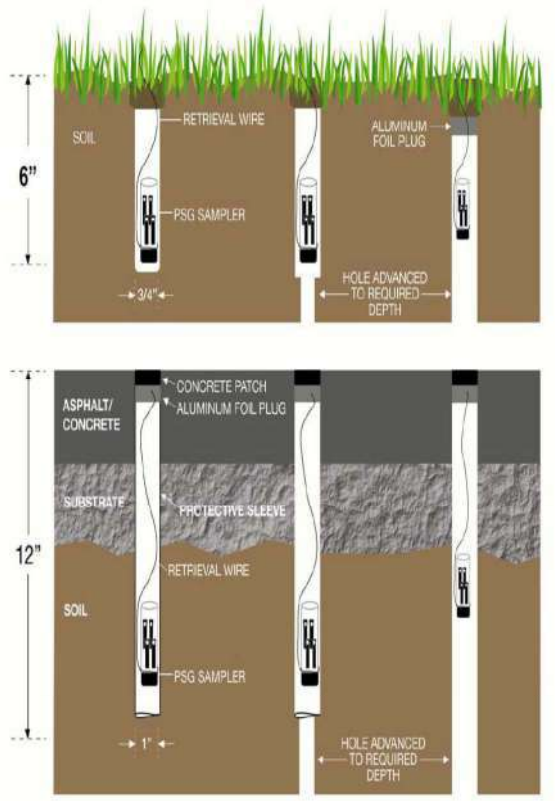
- Anaerobic reactions： CH_4
- Gasoline compounds： BTEX, MTBE
- Light alkane： C1~C6 compounds
- Diesel compounds：n-Decane

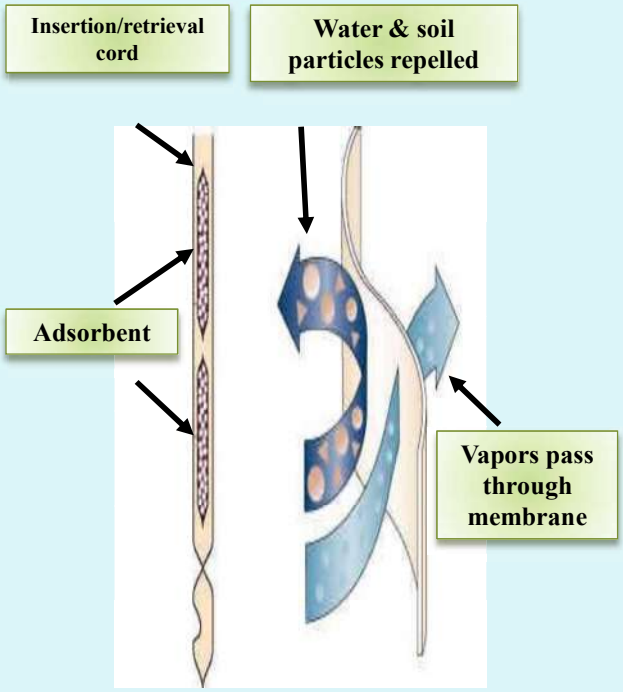
Contamination classified by parameters

GC Chromatogram	Grade	PID/FID	Recognition
	I	PID : background FID : low or medium	CH_4 detected meant probable diesel contamination or anaerobic reactions
		PID : background FID : background	No CH_4 detected meant no contamination potential
	II	PID : background or low FID : background or low	No CH_4 and MTBE detected usually indicates being remedied in the past but the some contaminants remained.
	III	PID : low or medium FID : low or medium	MTBE detected indicates recent contamination but far away the hot spot.

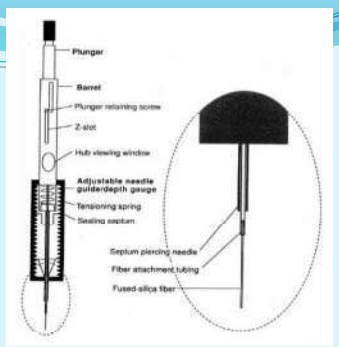
GC Chromatogram	Grade	PID/FID	Recognition
	IV	PID : medium or high FID : medium or high	Weathering contaminants and the site remained to be contaminated.
	V	PID : high FID : high	Newly contaminated gasoline and diesel
	VI	PID : high FID : high	Newly contaminated gasoline

Passive Monitoring of Soil Vapor





Sorbent Tubes Anasorb CSC®

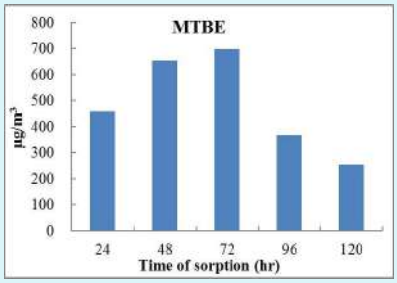


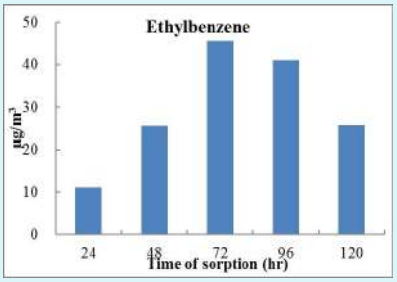
Solid phase microextraction SPME

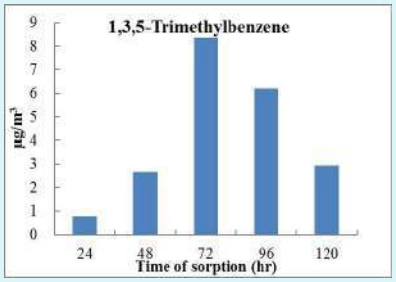
ULTRA sampler sorbe®

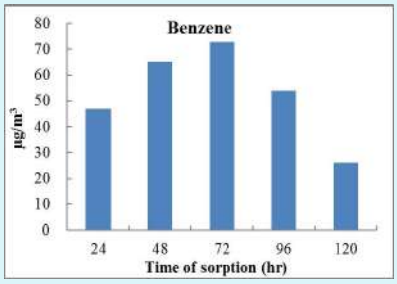
Tedlar® Sample Bag

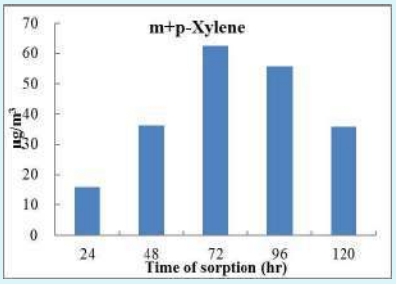
Sorption of VOCs vs. Time
Sorbent Tubes Anasorb CSC®

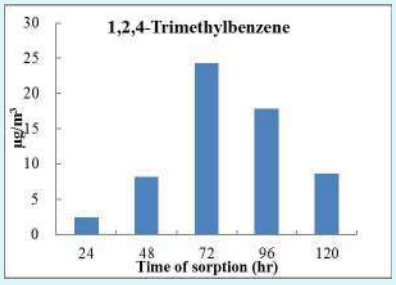


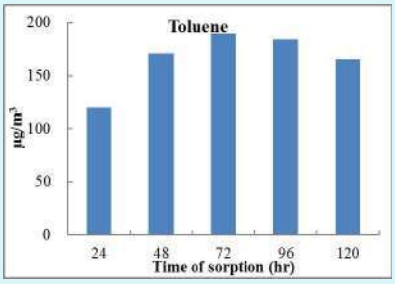


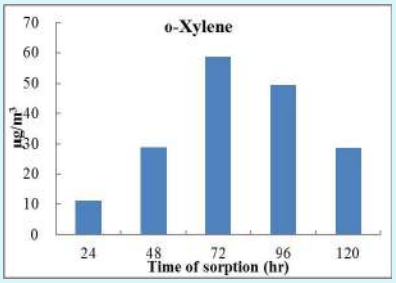


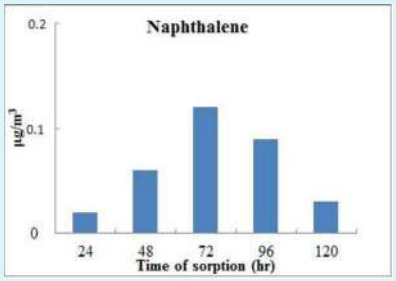










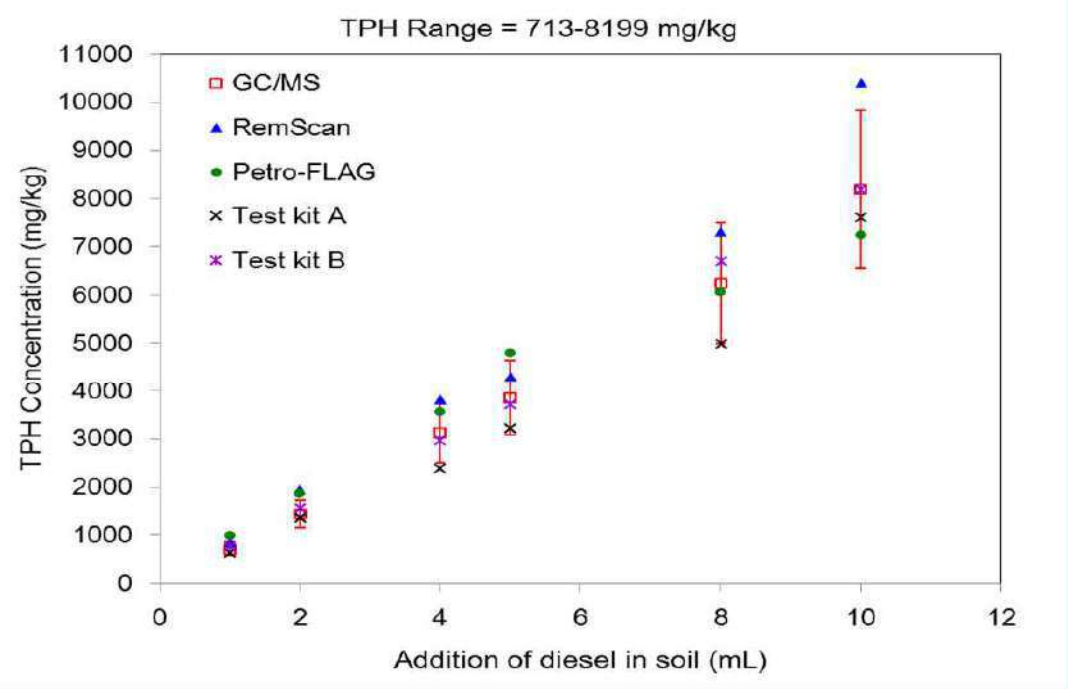


In-situ TPH Screening

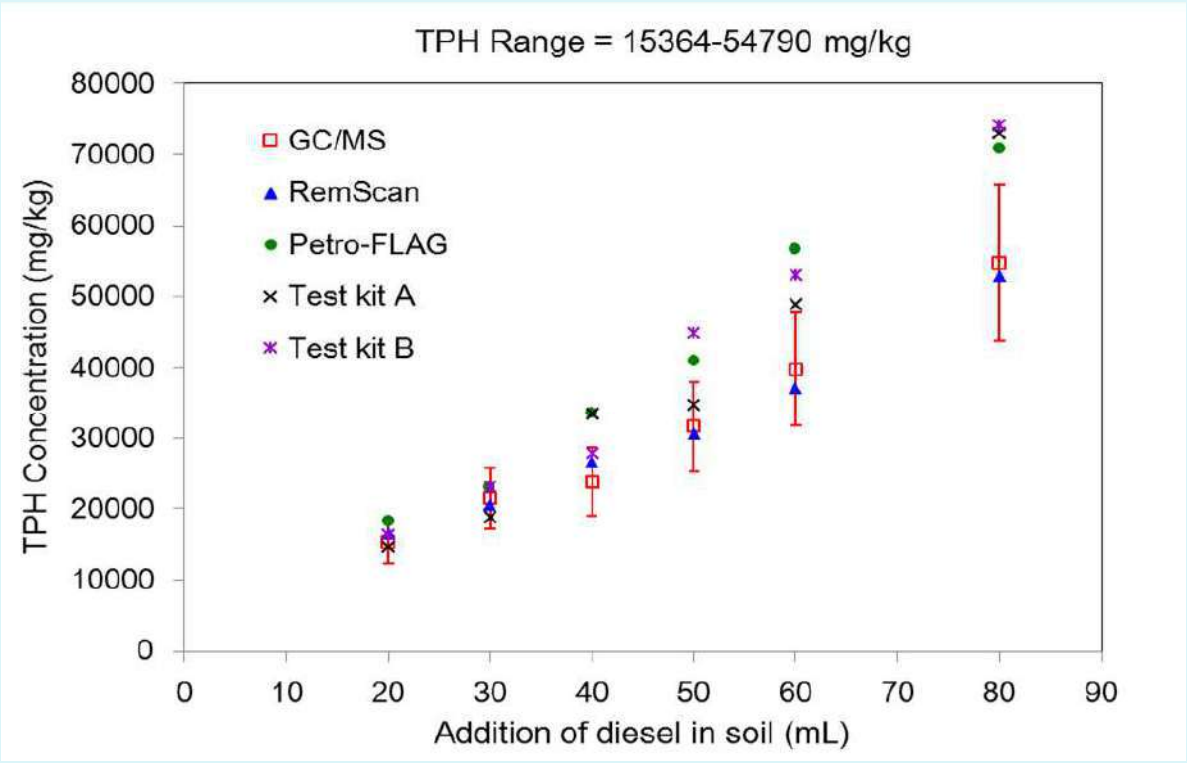
RemScan

TPH test kit

TPH measurement of reference soils by GC/MS and field methods



TPH measurement of reference soils by GC/MS and field methods



Diverse Nature of Soil Core Samples

		Sample	TPH by GC/MS (mg/kg)	RemScan TPH_d (mg/kg)	RSD	Water content
TPH by certified lab (mg/kg)	10900	1	9876	11900	4.0	0.04
		2	16117	17820	3.6	1.40
		3	6827	10260	4.4	4.52
		4	11.91	0	-	7.44
		5	9.349	0	-	7.10
		6	4.533	0	-	6.48

Average of 3 subsamples
10940 (GC/MS)
13327(RemScan)

The core sample at depth of 3.5-4 m was divided to 6 subsamples

		Sample	TPH by GC/MS (mg/kg)	RemScan TPH_d (mg/kg)	RSD	Water content
TPH by certified lab (mg/kg)	17400	1	17797	17420	3.0	1.00
		2	21815	14660	4.2	0.06
		3	10311	16500	3.0	4.94
		4	22547	18580	3.6	3.42
		5	8982	9680	4.8	4.70

Average of 5 subsamples
16290 (GC/MS)
12368 (RemScan)

The core sample at depth of 3.5 to 4 m was divided to 5 subsamples

		Sample	TPH by GC/MS (mg/kg)	RemScan TPH_d (mg/kg)	RSD	Water content
TPH by certified lab (mg/kg)	8720	PL5030005-1	5850	8100	5.2	5.30
		PL5030005-2	8225	13340	4.0	4.16
		PL5030005-3	5255	10680	4.6	5.16
		PL5030005-4	9059	11100	6.4	4.98
		PL5030005-5	5081	9580	6.2	4.96
		PL5030005-6	4472	7200	4.2	4.32
		PL5030005-7	2009	4200	4.8	4.90
		PL5030005-8	4016	6620	5.8	4.90
		PL5030005-9	156.6	0	-	5.66
		PL5030005-10	2.033	0	-	6.34

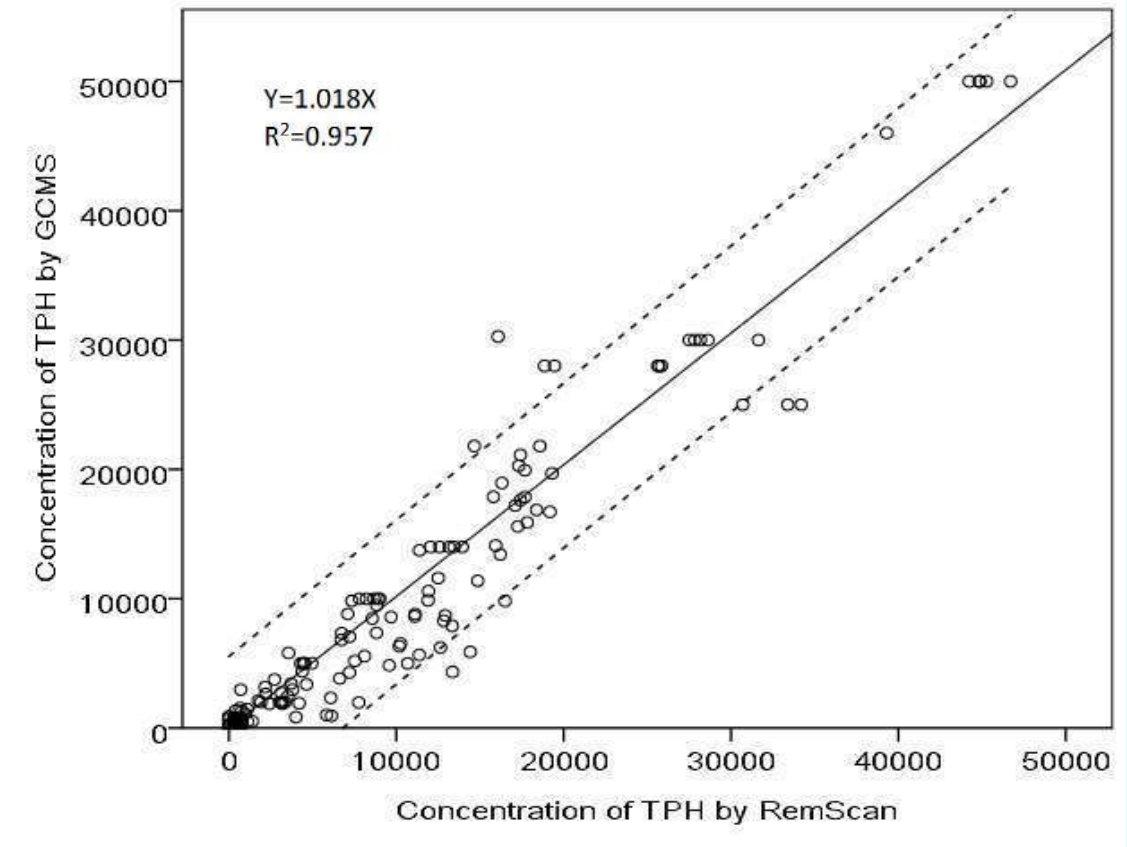
Average of 5 subsamples
6694 (GC/MS)
10560 (RemScan)

Sample at depth of 3.5-4 m was divided to 10 subsamples (sample at depth of every 5 cm)

		Sample	TPH by GC/MS (mg/kg)	RemScan TPH_d (mg/kg)	RSD	Water content
TPH by certified lab (mg/kg)	6960	PL5030009-1	2085	7760	5.4	5.64
		PL5030009-2	961.6	4920	7.0	2.22
		PL5030009-3	1028	3640	11	1.72
		PL5030009-4	868.0	2640	12	3.06
		PL5030009-5	116.1	1300	6.5	1.70

Sample at depth of 3.5-4 m was divided to 5 subsamples

RemScan predictions versus laboratory TPH analysis for soil samples



Implementation of Gas Station Investigation

The phase of investigation		2001	2002 -2004	2006 -2007	2007 -2009	2009 -2010	2010 -2011	2011 -2012	EPA	EPB	Total	
		Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6	Phase 7				
Sites Investigated		191	800	400	400	46	416	333	2,586	-	**2, 584**	
Total contaminated sites		10	32	18	14	22	29	9	134	76	**210**	
Listed	remediation sites	3	4	1	2	1	0	0	11	6	**17**	**125**
	controlled sites	2	7	7	4	5	18	4	47	15	**62**	
	taking the necessary response measures	0	0	0	2	5	9	5	21	25	**46**	
De-listed	remediation Sites	0	1	1	0	0	0	0	2	0	**2**	**85**
	control sites	5	11	3	1	0	0	0	20	7	**27**	
	taking the necessary response measures	0	9	6	5	11	2	0	33	23	**56**	

Updated on August 31st, 2013

216 sites (Dec, 2012)→ 84 sites (Feb, 2016)→ 68 sites (April, 2018)

Environmental Forensics

- Environmental forensics is defined as a scientific methodology developed for identifying potentially hazardous environmental contaminants and for determining their sources and time of release.

- Environmental forensics includes investigating, interpreting and presenting evidence of source, fate, transport, composition, age, and extent of or responsibility for contamination of all environmental media (i.e. air, soil, water or biota).

"The application of scientific methods used to identify the origin and timing of a contaminant release"

Disciplines in Environmental Forensics

- Chemistry
- Statistics
- Environmental Engineering
- Microbiology
- Hydrology
- Geology
- Soil Science
- Toxicology
- Ecology
- Litigation Experience
- And others…..

Questions Addressed in Environmental Forensic Studies

WHAT, WHERE & WHEN?

- Contaminant identification(s)
- Spatial extent of contaminant(s)
- Age-dating of contaminant(s)

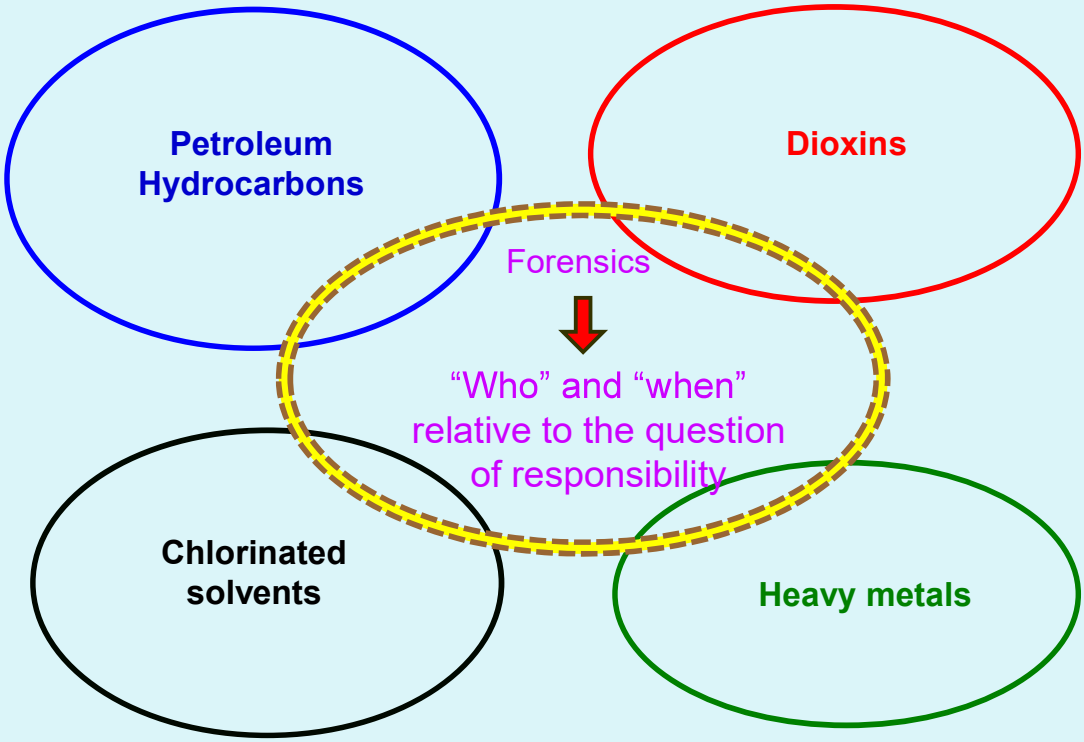
- **Detailed Site Assessments**
- **Remedial Design/Monitoring**
- **Risk Assessments**

WHO?

- Defensible Allocation of Responsibility

- **Due Diligence Investigations**
- **Spills & Leaks**
- **Assessment**

Need for Environmental Forensics in Soil and Groundwater Remediation



Major Issues

- Change of lease holders in state-owned highway service stations makes identification of potentially responsible party (PRP) very difficult
- Compensation of property damage due to petroleum hydrocarbon contamination
- The timing of the release and allocate of contamination is a challenging task

CPC Corporation (CPC)

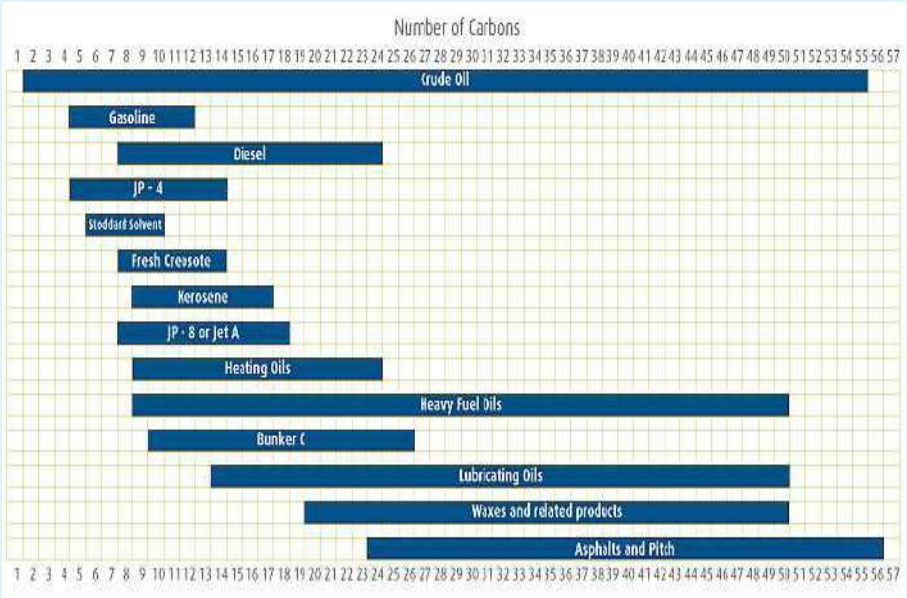
Formosa Petrochemical Corporation (FOR)

2002-2012 CPC → 2012-2018 FOR → 2018- present CPC

Forensic Tools for Petroleum Hydrocarbon Releases

- Petroleum carbon range
- Gas chromatogram pattern matching
- Discrete constituent analyses and constituent ratios
- Biomarkers
- Age-dating releases via “weathering ratios”

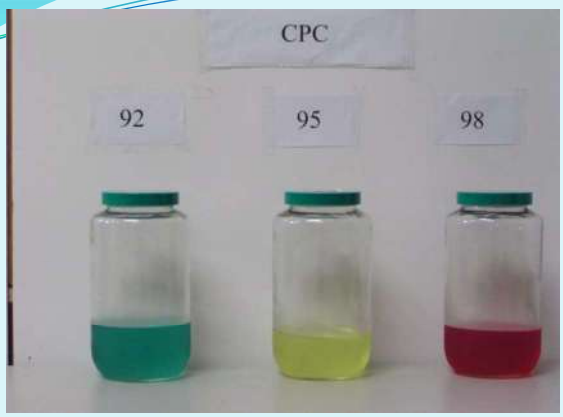
Carbon Ranges



General Characteristics of Individual Fuel Mixture

Petroleum Fuel Mixture	Density (g/mL)	Carbon Number	Distillate	Boiling point (℃)	Compound Classes
Gasoline	~0.73	C_4 ~ C_{12}	low-end	40~200	High concentrations of BTEXs, monoaromatics and branched alkanes. Low concentrations of n-alkanes, alkenes, cycloalkanes, and naphthalenes. Very low concentrations of PAHs.
Kerosene	~0.80	C_6 ~ C_{16}	middle	150~300	High concentrations of cycloalkanes and n-alkanes. Low concentrations of monoaromatics and branched alkanes. Very low concentrations of BTEXs and PAHs.
JP-fuel (4~7)	0.75~0.82	C_5 ~ C_{18}	middle	150~275	High concentrations of n-alkanes and cycloalkanes. Low concentrations of n-alkanes, BTEXs and monoaromatics. Very low concentrations of PAHs.
Diesel(＃2)	~0.83	C_8 ~ C_{21}	middle	200~325	High concentrations of n-alkanes. Low concentrations of branched alkanes, cycloalkanes, monoaromatics, naphthalenes and PAHs. Very low concentrations of BTEXs.
No.2 fuel oil	~0.90	C_8 ~ C_{21}	middle	200~325	High concentrations of n-alkanes. Low concentrations of branched alkanes, cycloalkanes, monoaromatics, naphthalenes and PAHs. Very low concentrations of BTEXs.
No.6 fuel oil	~0.95	C_{12}~C_{34}	Residual oil	350~700	High concentrations of n-alkanes and cycloalkanes. Low concentrations of naphthalenes and PAHs. Very low concentrations of BTEXs.
Lubricating and motor oil	~0.95	C_{18}~C_{34}	Heavy - end	325~600	Low concentrations of barium. High concentrations of branched alkanes and cycloalkanes. Very low concentrations of BTEXs and PAHs.
Crude oil	~0.94	C_1 ~C_{34}	Heavy - end	feedstock	High concentrations of n-alkanes, branched alkanes and cycloalkanes. Low concentrations of BTEXs, PAHs and naphthalenes. Variable concentrations of sulfur heterocyclics

Fuel Products



Fuel Products

CPC

Density (g/L) 740 741 748 831

FOR

Density (g/L) 733 742 754 835 838

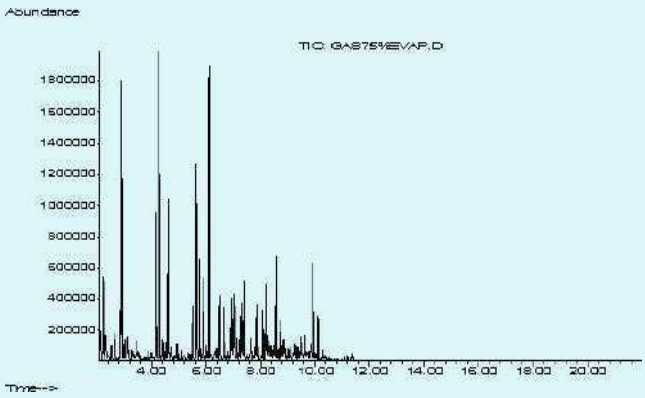
General Characteristics of Individual Petroleum Fuel Mixture

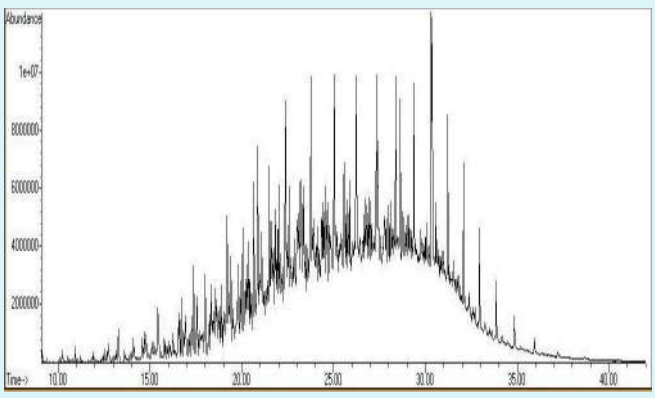
		2016		2014		2007	
Gasoline	Carbon number	MW (g/mole)	Density (g/L)	MW (g/mole)	Density (g/L)	MW (g/mole)	Density (g/L)
CPC92	C_4-C_{14}	118	740	116	732	131	730
CPC95	C_4-C_{14}	121	741	120	738	130	730
CPC98	C_4-C_{14}	124	748	123	750	123	740
FOR92	C_4-C_{14}	120	733	120	723	118	720
FOR95+	C_4-C_{14}	122	742	122	756	119	730
FOR98	C_4-C_{14}	124	754	128	746	120	740
E3				118	742	123	749

General Characteristics of Individual Fuel Mixture

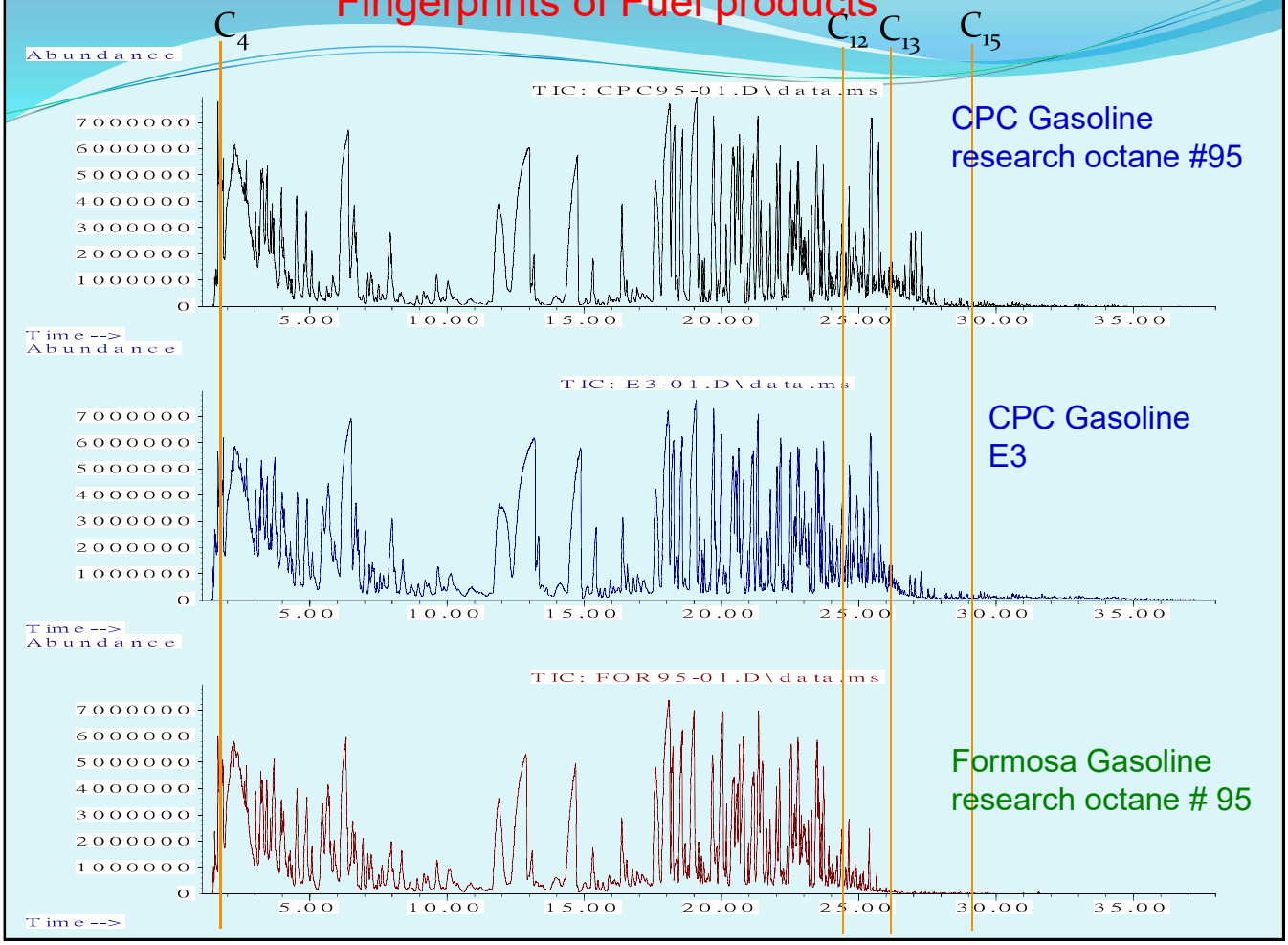
	Carbon number	MW (g/mole)	Density (g/L)
Diesel			
CPC	C_8-C_{26}	242	829
FOR	C_8-C_{26}	240	828
B1	C_8-C_{26}	249	829
CPC(B2)	C_8-C_{26}	227	840
FOR(B2)	C_8-C_{26}	234	834
Jet Fuel			
Jet A-1	C_7-C_{18}	161	786
JP-8	C_7-C_{16}	147	780

Gas Chromatogram Pattern Matching

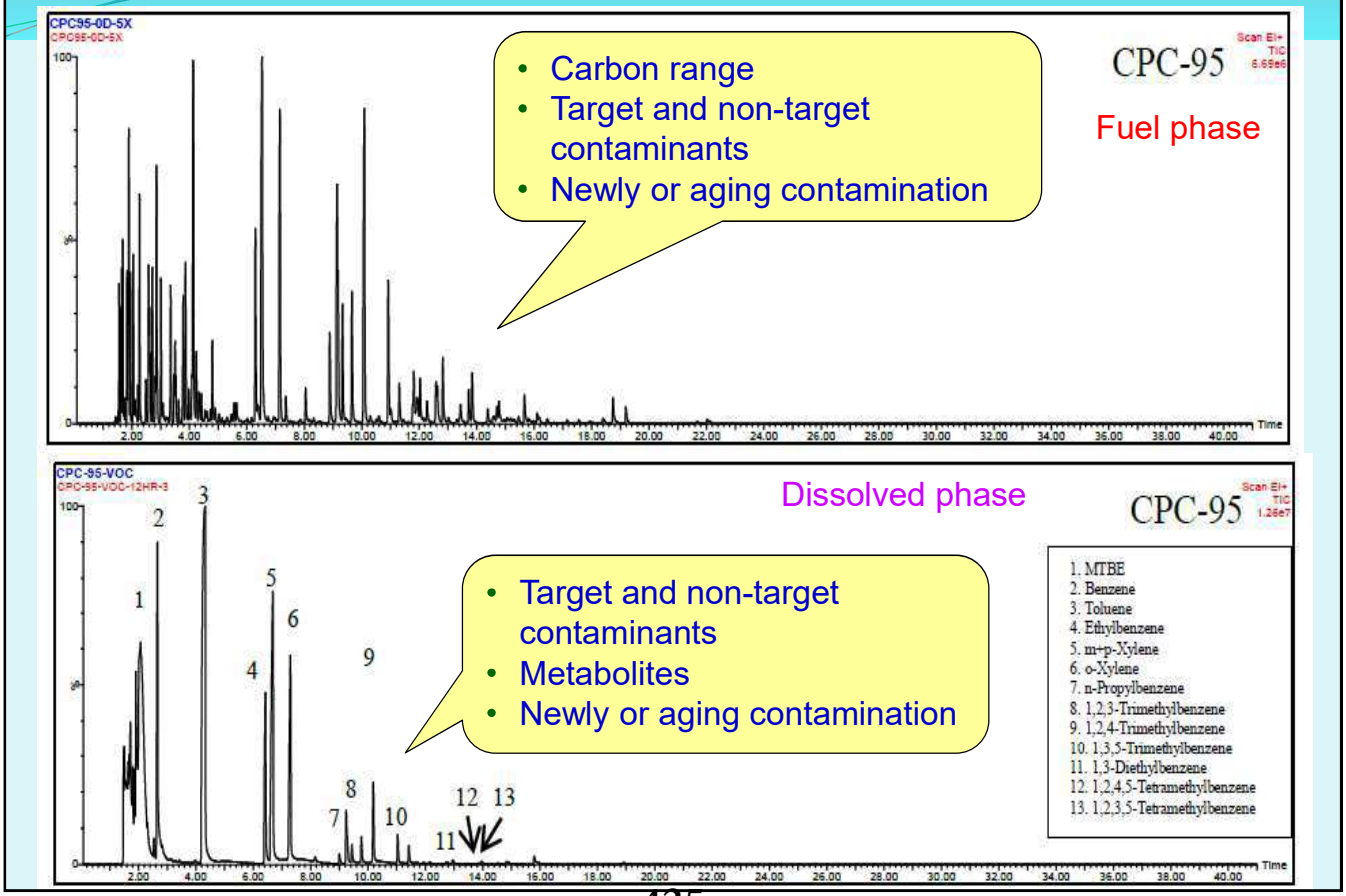




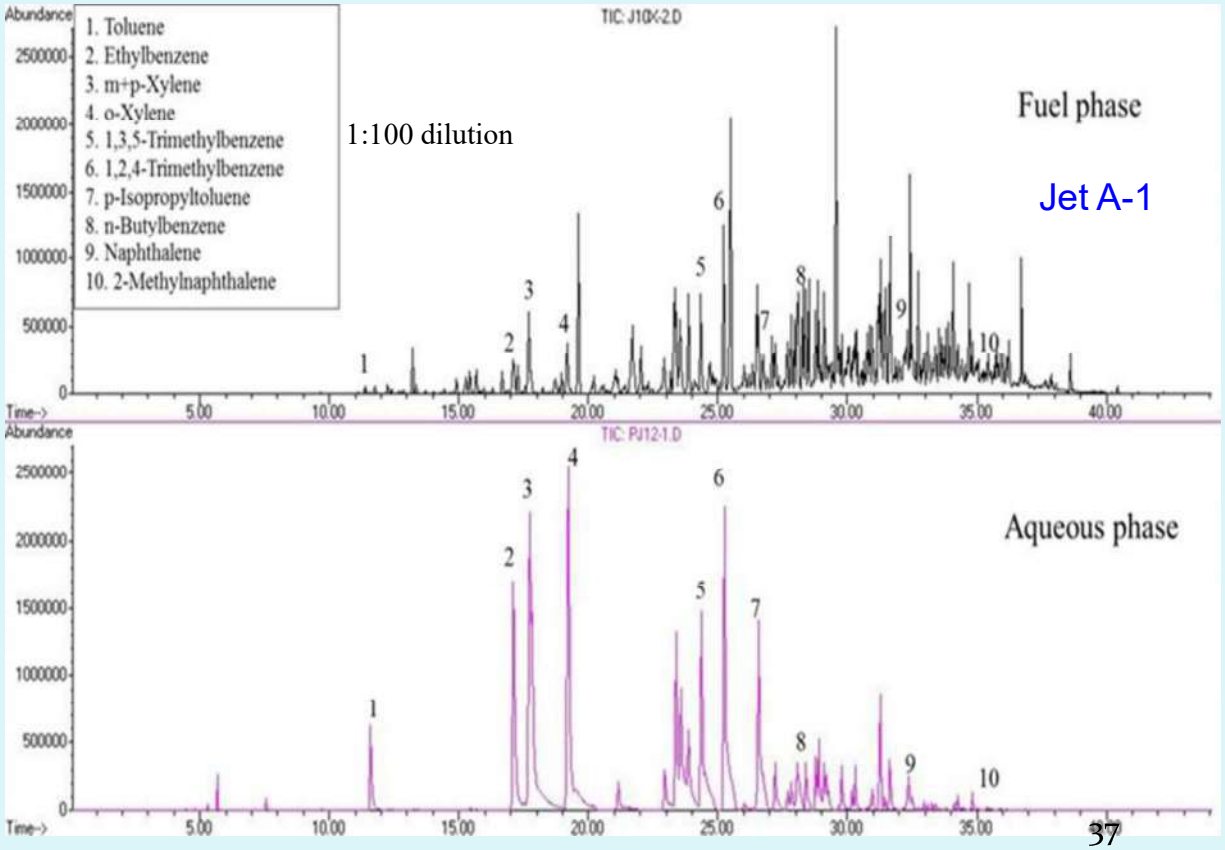
Fingerprints of Fuel products



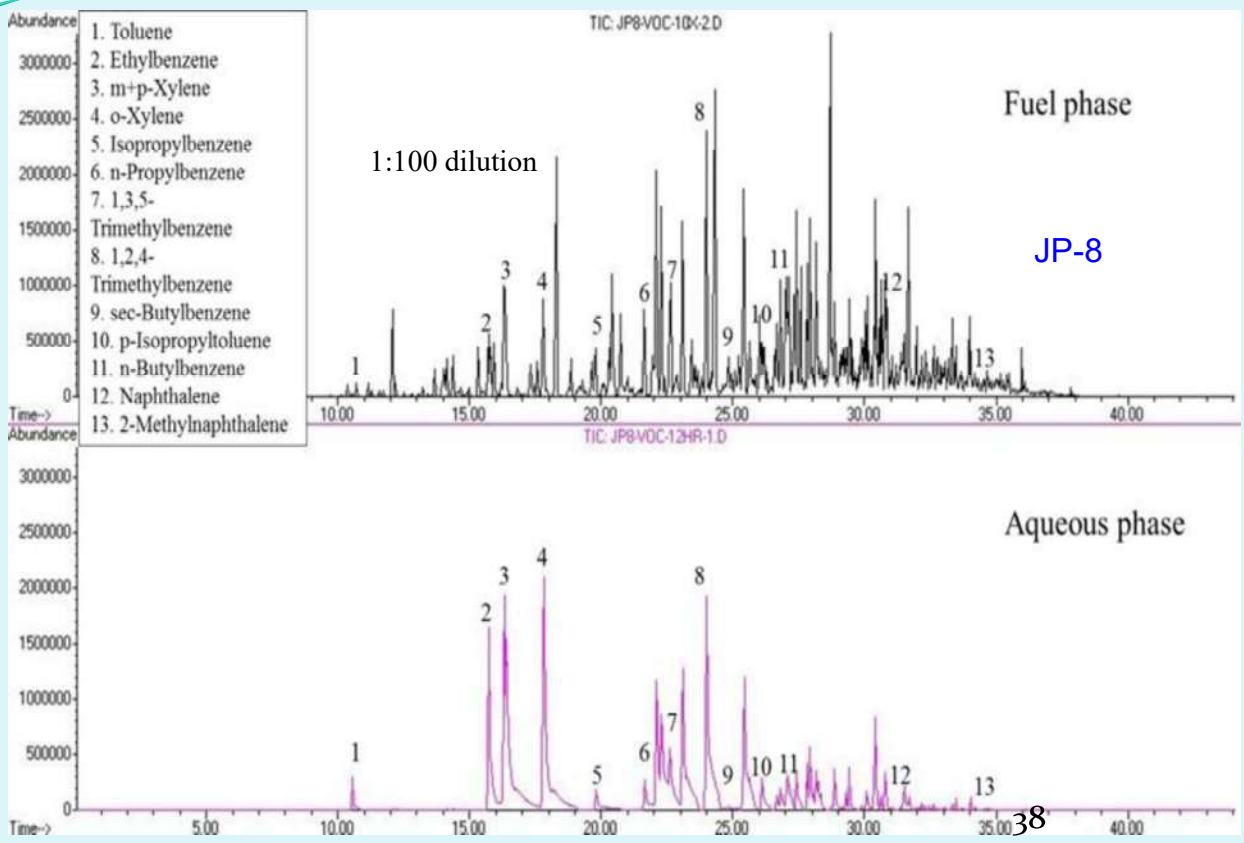
Chromatograms of gasoline in different phases

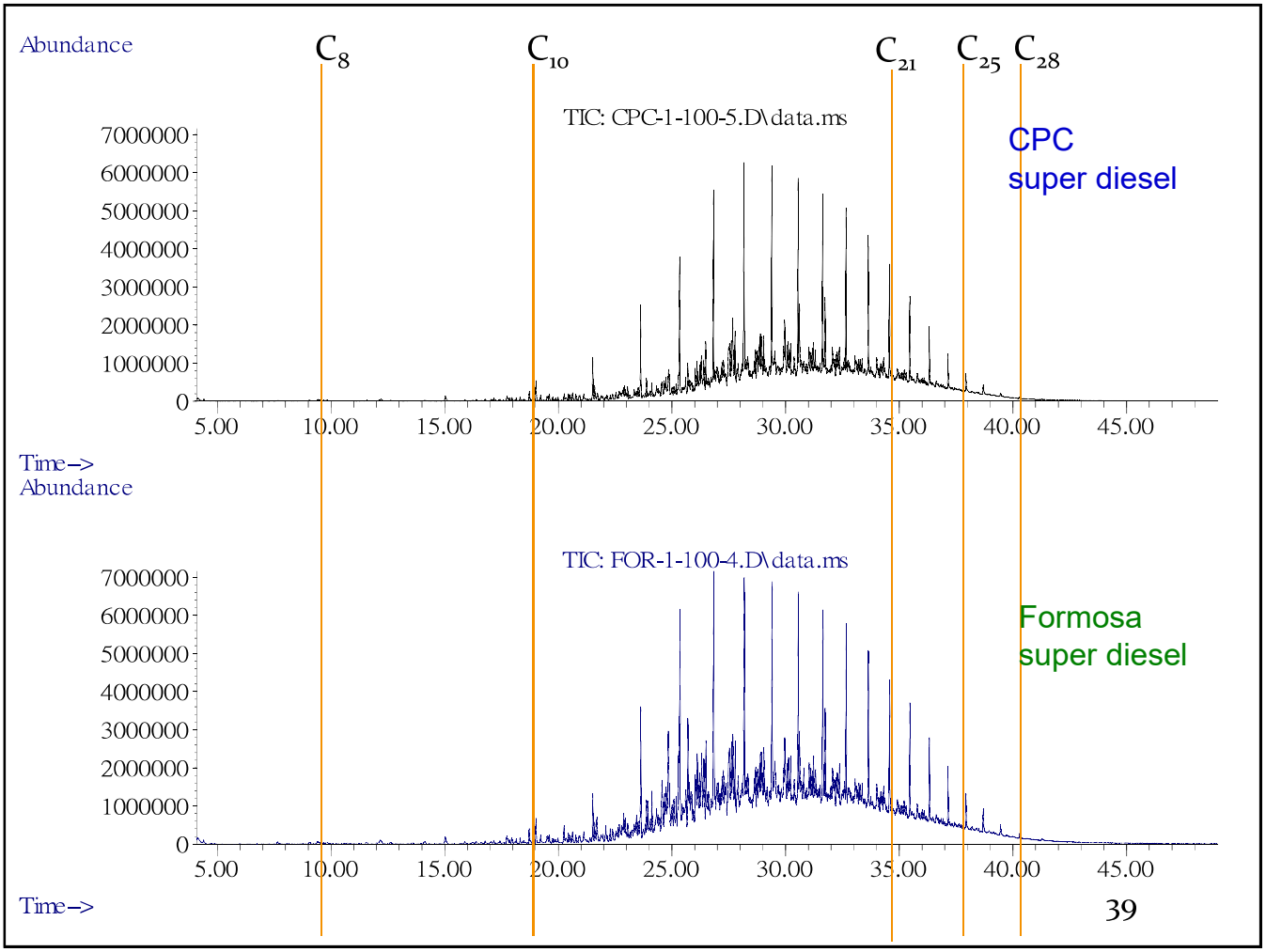


Chromatograms of Jet A-1 in different phases



Chromatograms of JP-8 in different phases





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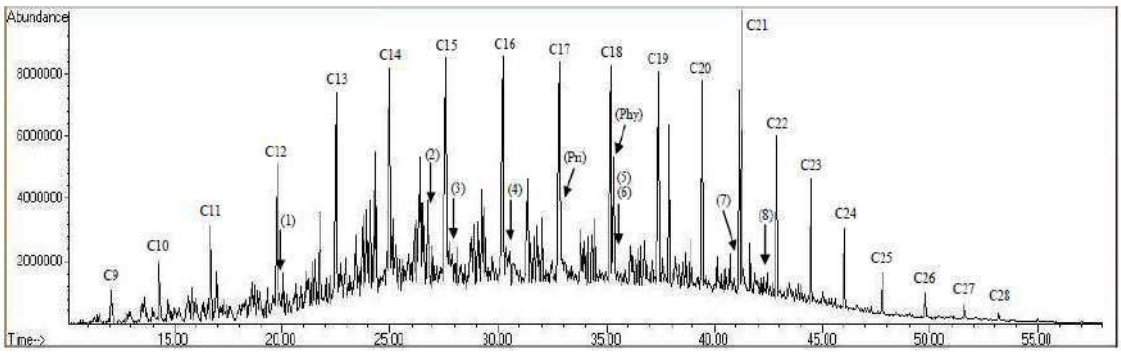
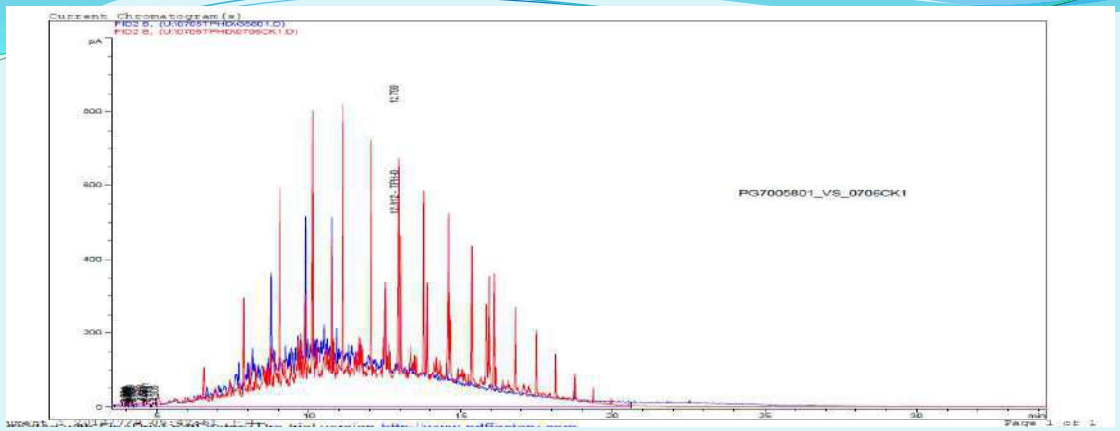
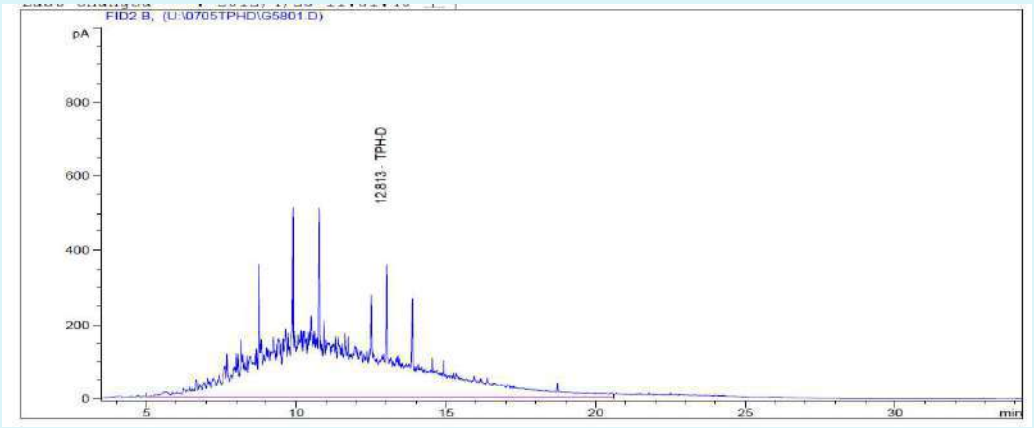
CPC Biodiesel (B2)



(20120131) CPC B2 1:100 dilution
(C9-C28) 直鏈烷
(1) Naphthalene (19.89 min)
(2) Acenaphthylene (26.90 min)
(3) Acenaphthene (27.91 min)
(4) Fluorene (30.55 min)
(5) Phenanthrene (35.48 min)
(6) Anthrancene (35.61 min)
(7) Fluoranthene (41.14 min)
(8) Pyrene (42.37 min)
(Pri) Pristane (32.857 min)
(Phy) Phytane (35.330 min)

Diesel Contaminated Groundwater





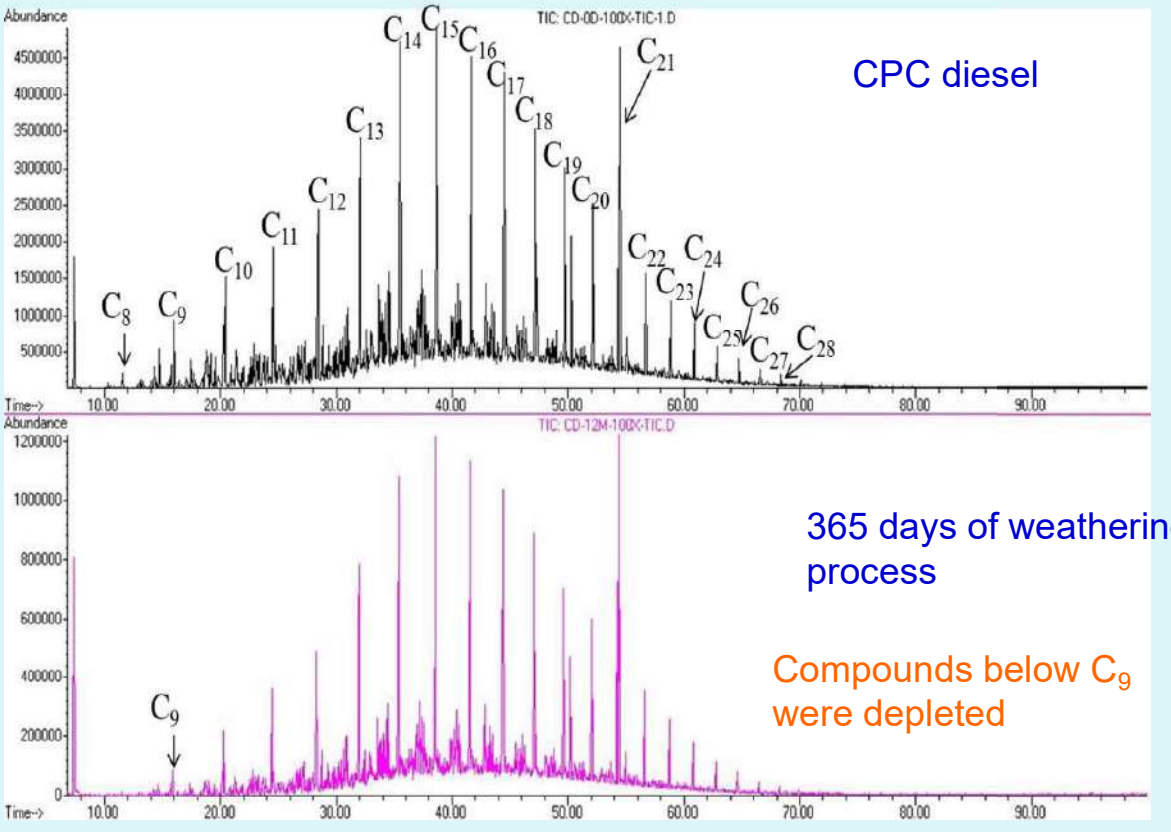
Less soluble compounds presented in groundwater

Discrete Constituent Analyses and Constituent Ratios

Alkane to Isoprenoid Ratio

- Alkanes to isoprenoids (Alk/Iso, defined as the ratio of the sum of *n*-C_{14} to *n*-C_{18} divided by the sum of farnesane, trimethyl-C_{13}, norpristane, pristane, and phytane; 2.4 and 2.4)
- C_{17}/pristane ($C_{19}H_{40}$, 2,6,10,14-tetra methyl pentadecane)
- C_{18}/phytane ($C_{20}H_{42}$, 2,6,10,14-tetra methyl hexadecane)

Assess the impact of weathering processes on chemical fingerprints of diesel fuel-CPC

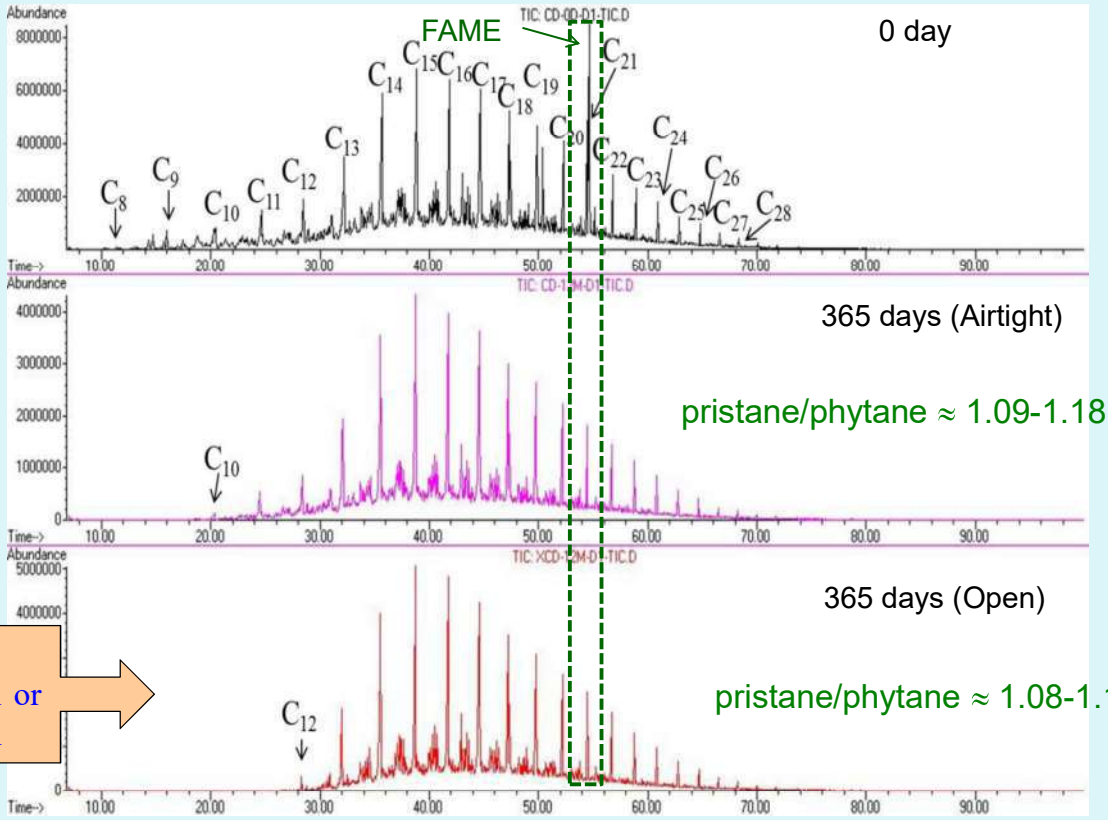


CPC diesel

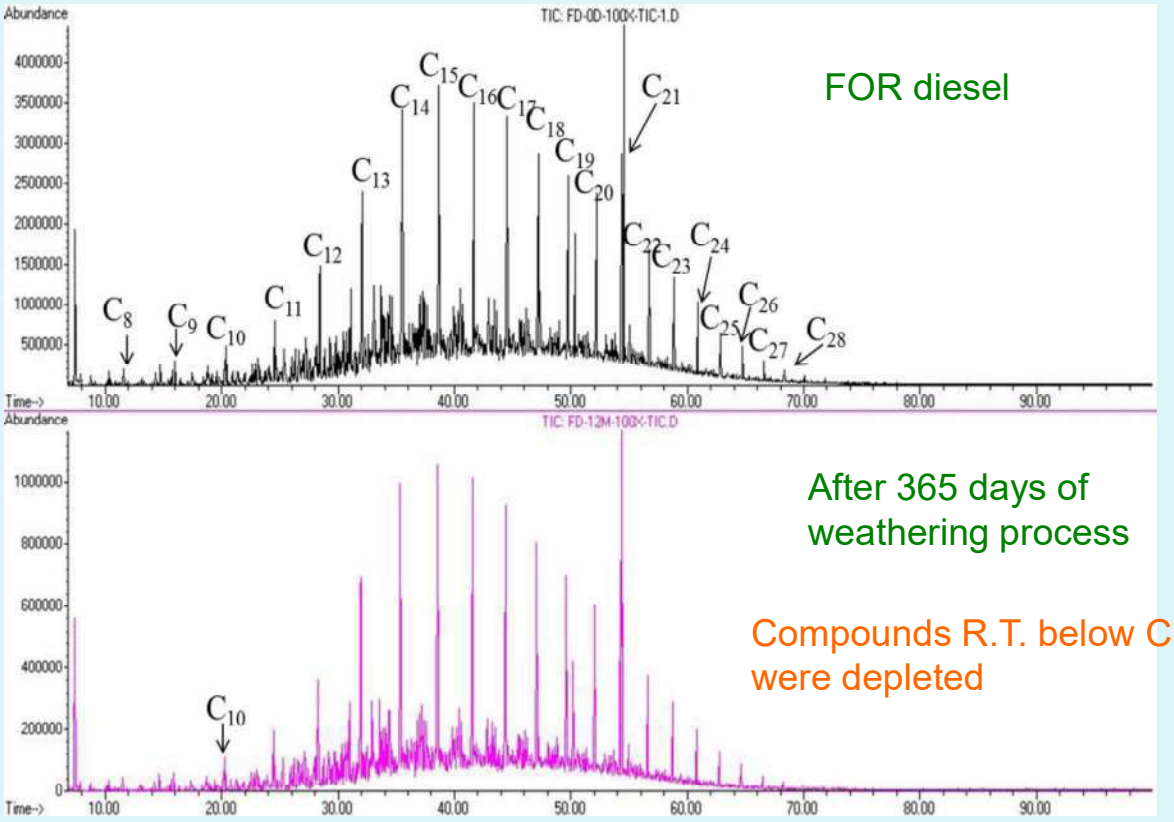
365 days of weathering process

Compounds below C_9 were depleted

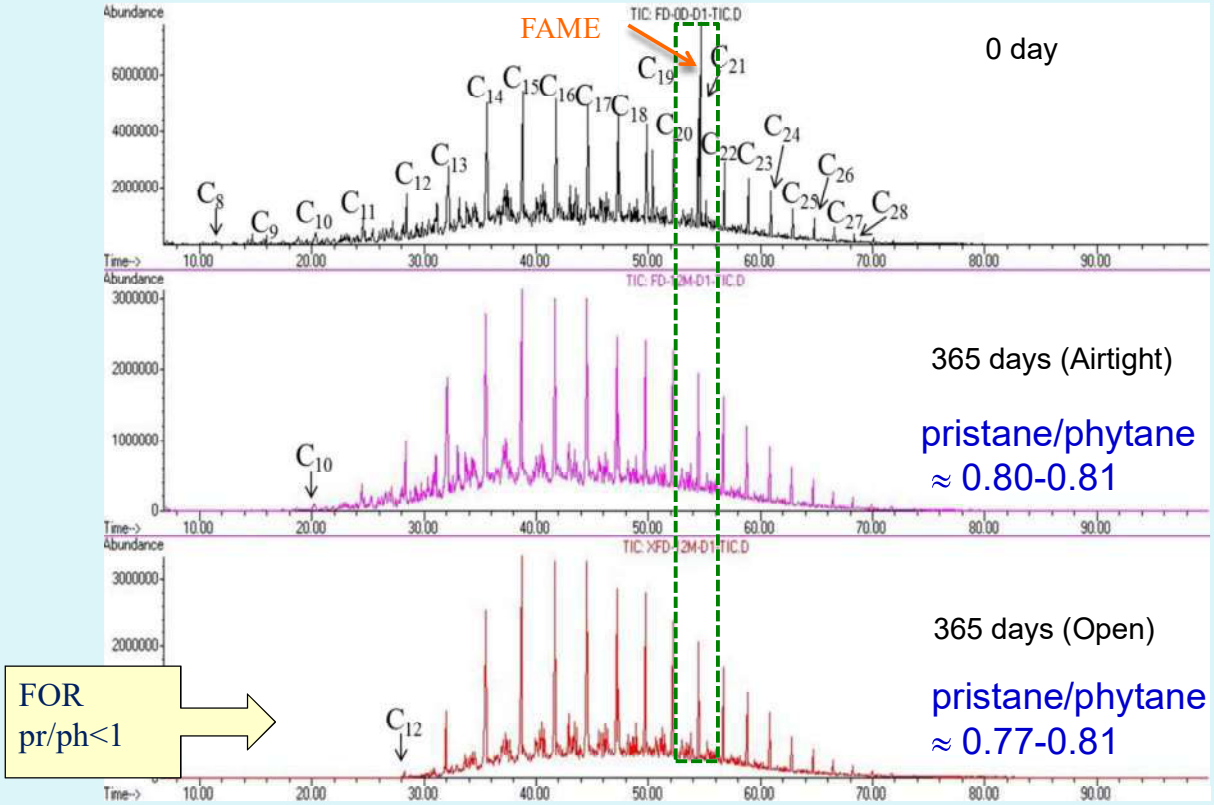
Diesel contaminated soils-CPC



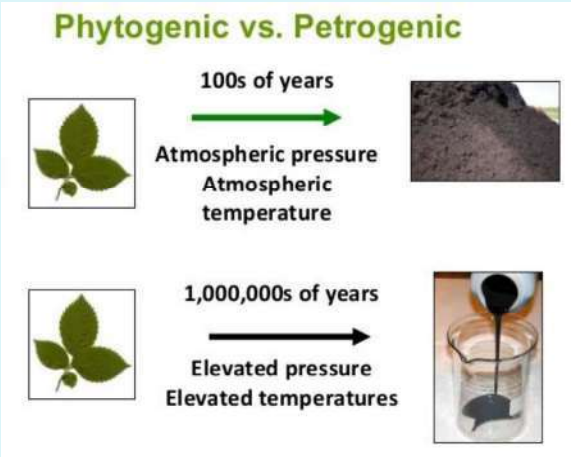
Assess the impact of weathering processes on chemical fingerprints of diesel fuel-FOR

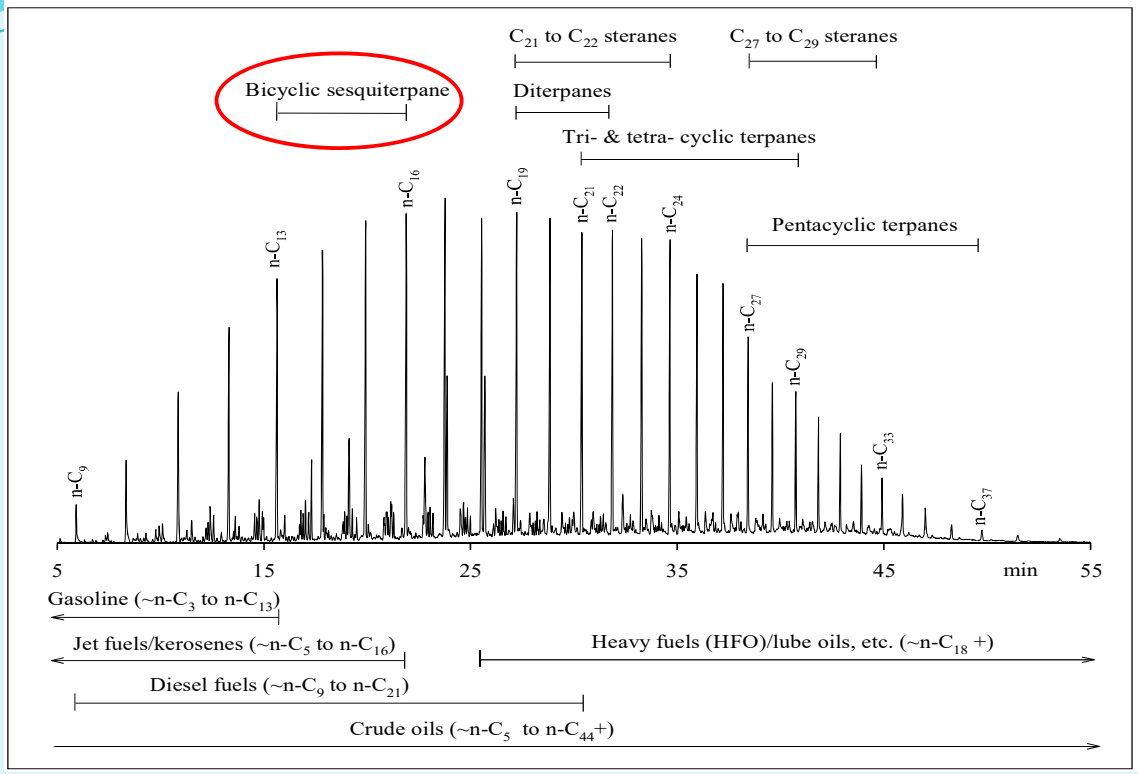


Diesel contaminated soil-FOR



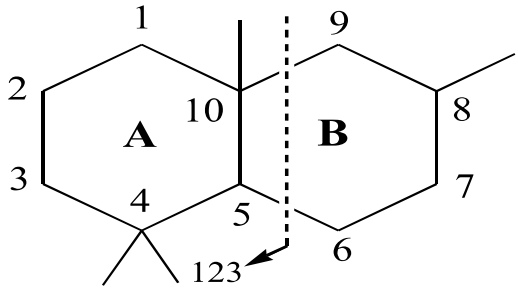
Biomarkers



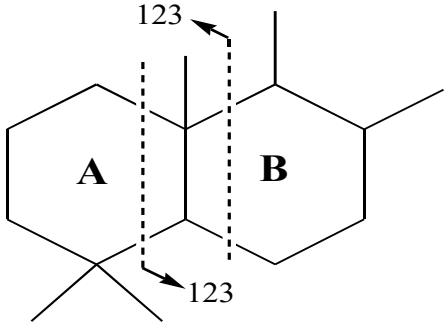


Carbon ranges of bicyclic sesquiterpanes and common tri- to penta-cyclic biomarkers in crude oils and petroleum products

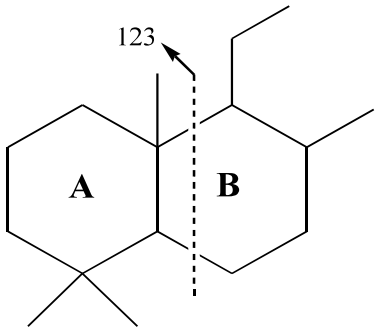
Sesquiterpanes



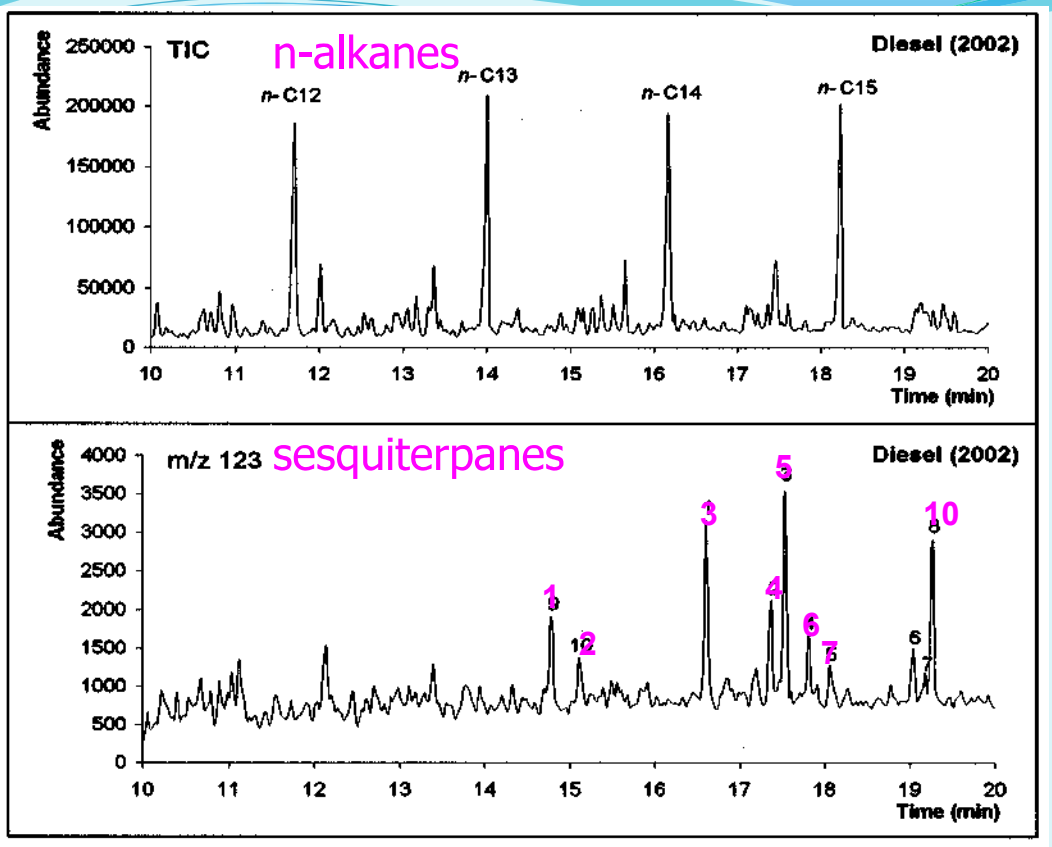
C_{14}: C_4-decalin (peak 1)



C_{15}: 8β(H)-drimane (peak 5)



C_{16}: 8β(H)-homodrimane (peak 10)

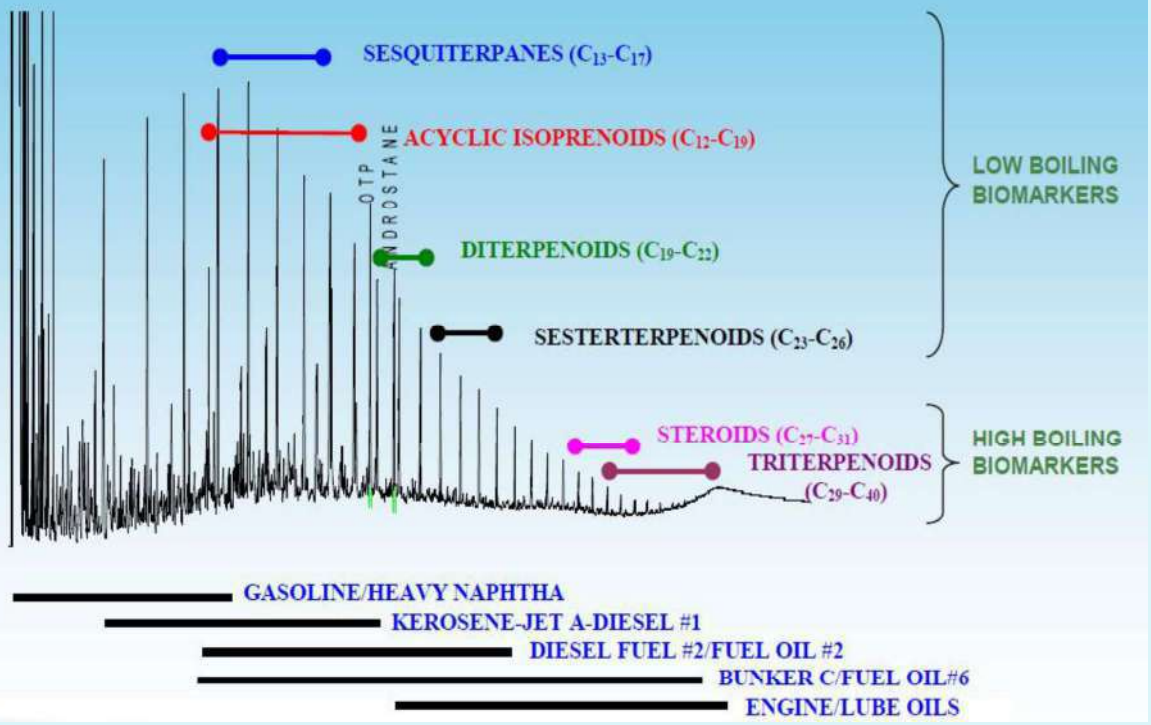


Sesquiterpane eluting carbon range: n-C_{13} – n-C_{16}

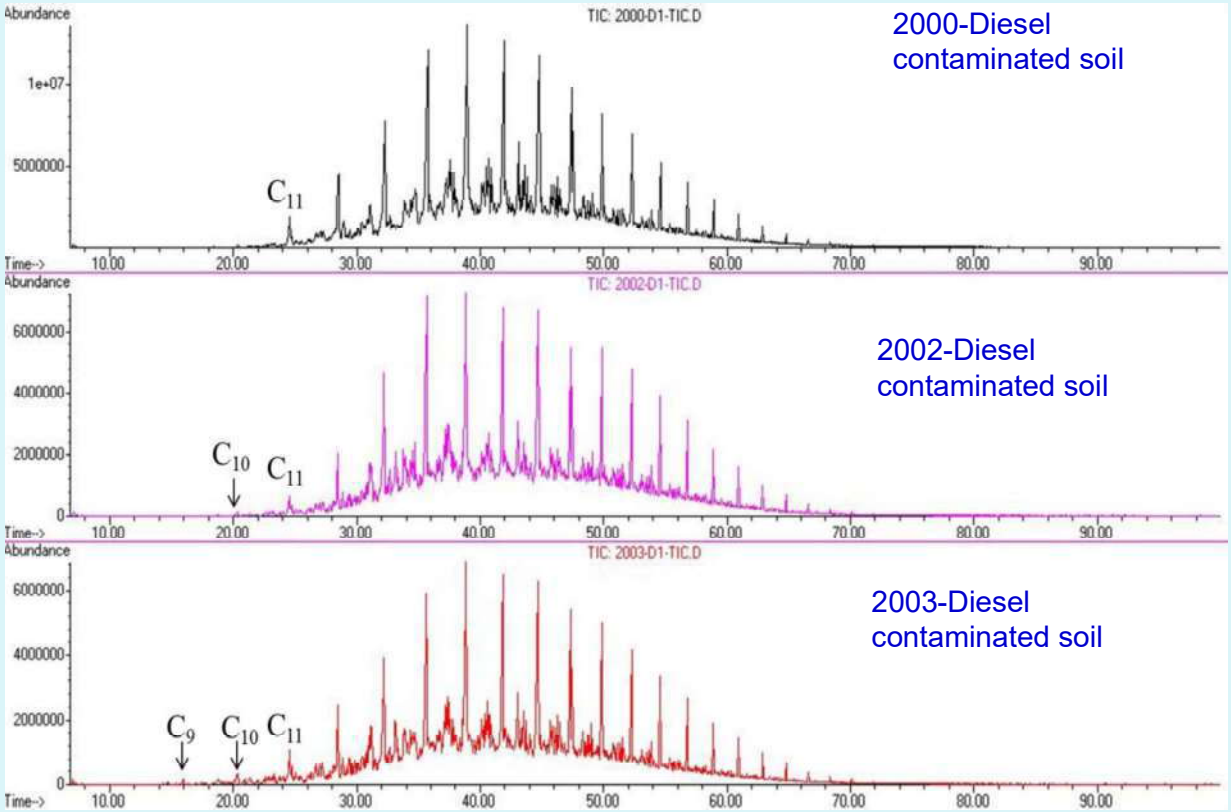
Bicyclic sesquiterpanes identified in crude oils and petroleum products by GC/MS

Peak No.	Compounds	Abbreviations	Formula	M^+ (m/z)	Base peak	I_A*
1	C_4-decalin	BS1	$C_{14}H_{26}$	194	179	1340
2	C_{14} sesquiterpane	BS2	$C_{14}H_{26}$	194	179	1353
3	C_{15} sesquiterpane	BS3	$C_{15}H_{28}$	208	193	1425
4	C_{15} sesquiterpane	BS4	$C_{15}H_{28}$	208	193	1461
5	8b(H)-drimane	BS5	$C_{15}H_{28}$	208	123	1470
6	C_{15} sesquiterpane	BS6	$C_{15}H_{28}$	208	123	1482
7	C_{16} sesquiterpane	BS7	$C_{16}H_{30}$	222	123	1494
8	C_{16} sesquiterpane	BS8	$C_{16}H_{30}$	222	193	1531
9	C_{16} sesquiterpane	BS9	$C_{16}H_{30}$	222	193	1536
10	8b(H)-homodrimane	BS10	$C_{16}H_{30}$	222	123	1539

Environmental weathering



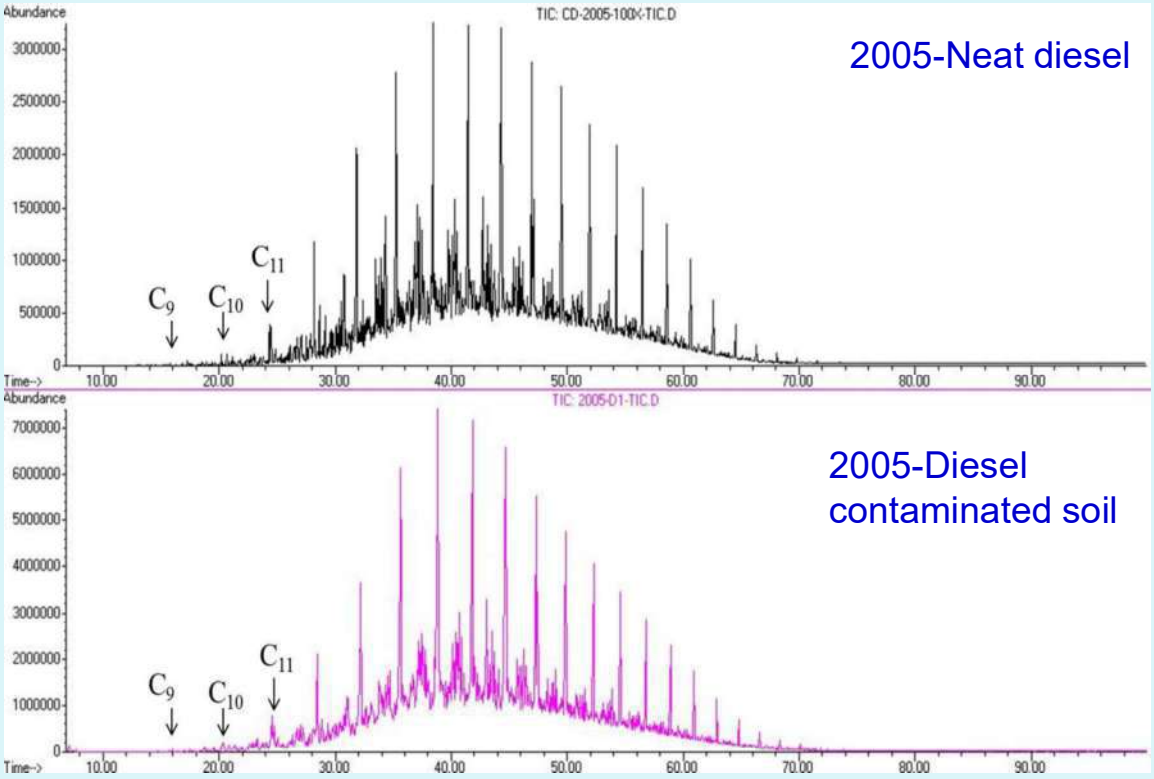
Assess the long term impact of weathering processes on chemical fingerprint change of diesel fuels



Diagnostic ratios for bicyclic sesquiterpanes (m/z=123) from soils contaminated by diesel fuel of 2000 to 2003

Diagnostic ratio	Diesel contaminated soil		
	2000	2002	2003
C_{14} group			
BS1/BS2	1.06	0.89	0.95
C_{15} group			
BS3/BS5	0.50	0.50	0.53
BS4/BS5	0.37	0.34	0.36
BS4/BS6	0.68	0.64	0.65
BS6/BS5	0.55	0.48	0.51
C_{16} group			
BS8:BS10	0.20	0.16	0.14
intergroup			
BS1/BS3	0.39	0.38	0.40
BS3/BS10	0.58	0.55	0.57
BS5/BS10	1.15	1.10	1.09
%C_{14} of Total	10	11	11
%C_{15} of Total	62	60	60
%C_{16} of Total	29	30	29

Assess the long term impact of weathering processes on chemical fingerprint change of diesel fuels



Diagnostic ratios for bicyclic sesquiterpanes (m/z=123) from diesel fuel and soil contaminated by diesel fuel in 2005

Diagnostic ratio	2005	
	Neat diesel	Diesel contaminated soil
C_{14} group		
BS1/BS2	1.29	1.31
C_{15} group		
BS3/BS5	0.95	0.93
BS4/BS5	0.63	0.72
BS4/BS6	1.36	1.41
BS6/BS5	0.25	0.28
C_{16} group		
BS8/BS10	0.18	0.14
intergroup		
BS1/BS3	0.58	0.48
BS3/BS10	0.57	0.61
BS5/BS10	1.03	0.97
%C_{14} of Total	14	10
%C_{15} of Total	53	60
%C_{16} of Total	33	30

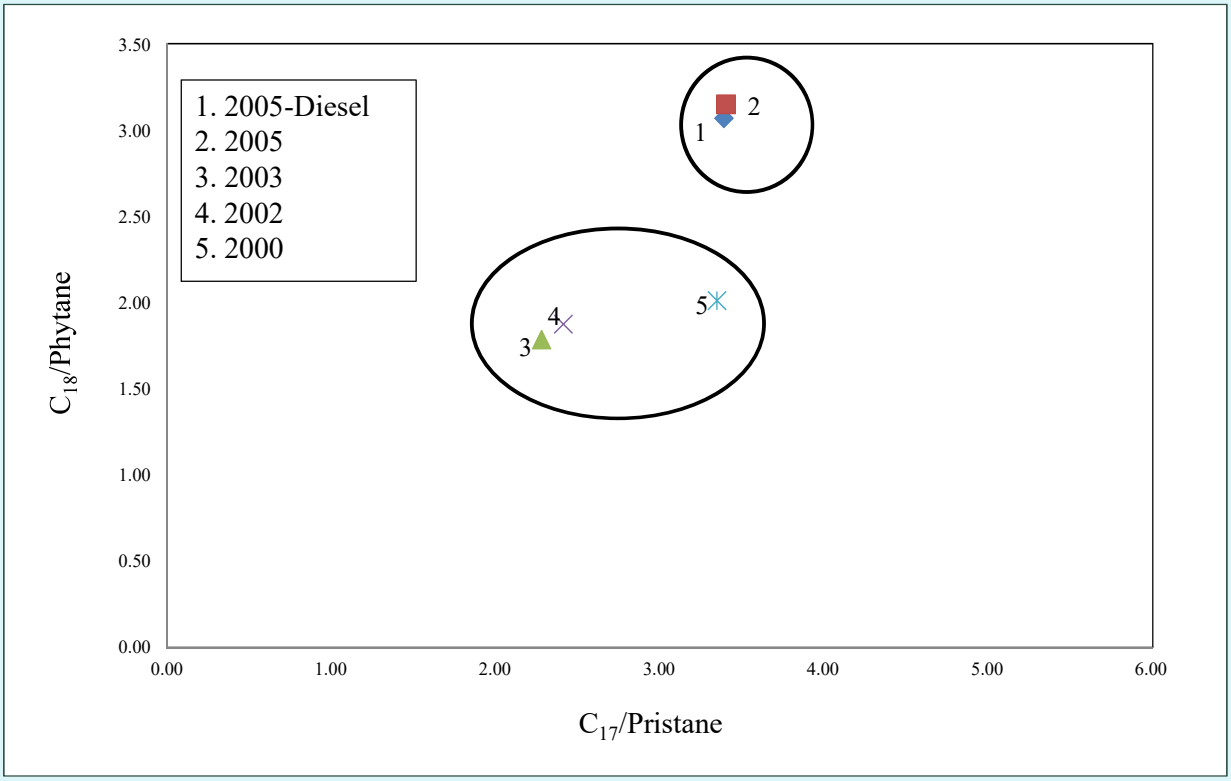
Analytical results of repeatability limit of diesel fuel and soil contaminated by diesel fuel in 2005

2005						
Diagnostic ratio	Neat diesel	Diesel contaminated soil	$\bar{X}$	CD	AD	Match
BS3/BS5	0.95	0.93	0.94	0.13	0.02	Match
BS4/BS5	0.63	0.72	0.67	0.09	0.08	Match
BS4/BS6	1.36	1.41	1.38	0.19	0.06	Match
BS3/BS10	0.57	0.61	0.59	0.08	0.04	Match
BS5/BS10	1.03	0.97	1.00	0.14	0.06	Match
C_{17}/Pr	3.39	3.40	3.40	0.48	0.01	Match
C_{18}/Ph	3.07	3.15	3.11	0.43	0.08	Match
Pr/Ph	1.30	1.31	1.31	0.18	0.01	Match
MNR	0.72	0.82	0.77	0.11	0.10	Match
MPR	1.46	1.62	1.54	0.22	0.16	Match
MPI 1	0.99	0.97	0.98	0.14	0.02	Match
MPI 2	1.14	1.10	1.12	0.16	0.03	Match

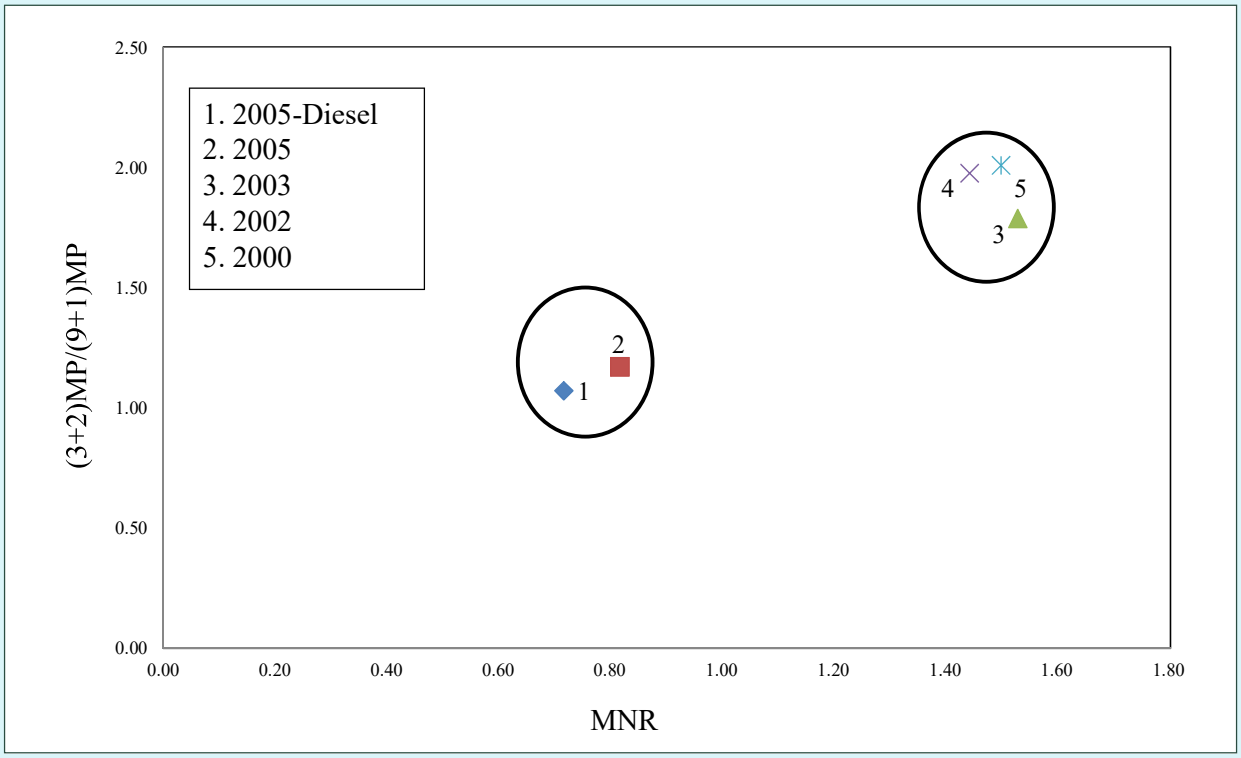
$$\text{MPI 1} = \frac{1.5(2\text{-MP}+3\text{-MP})}{\text{P}+1\text{-MP}+9\text{-MP}}$$

$$\text{MPI 2} = \frac{3(2\text{-MP})}{\text{P}+1\text{-MP}+9\text{-MP}}$$

Cross-plots of the diagnostic ratios of C_{17}/Pristane versus C_{18}/Phytane for diesel fuels



Cross-plots of the diagnostic ratios MNR versus (3+2)MP/(9+1)MP for diesel fuels



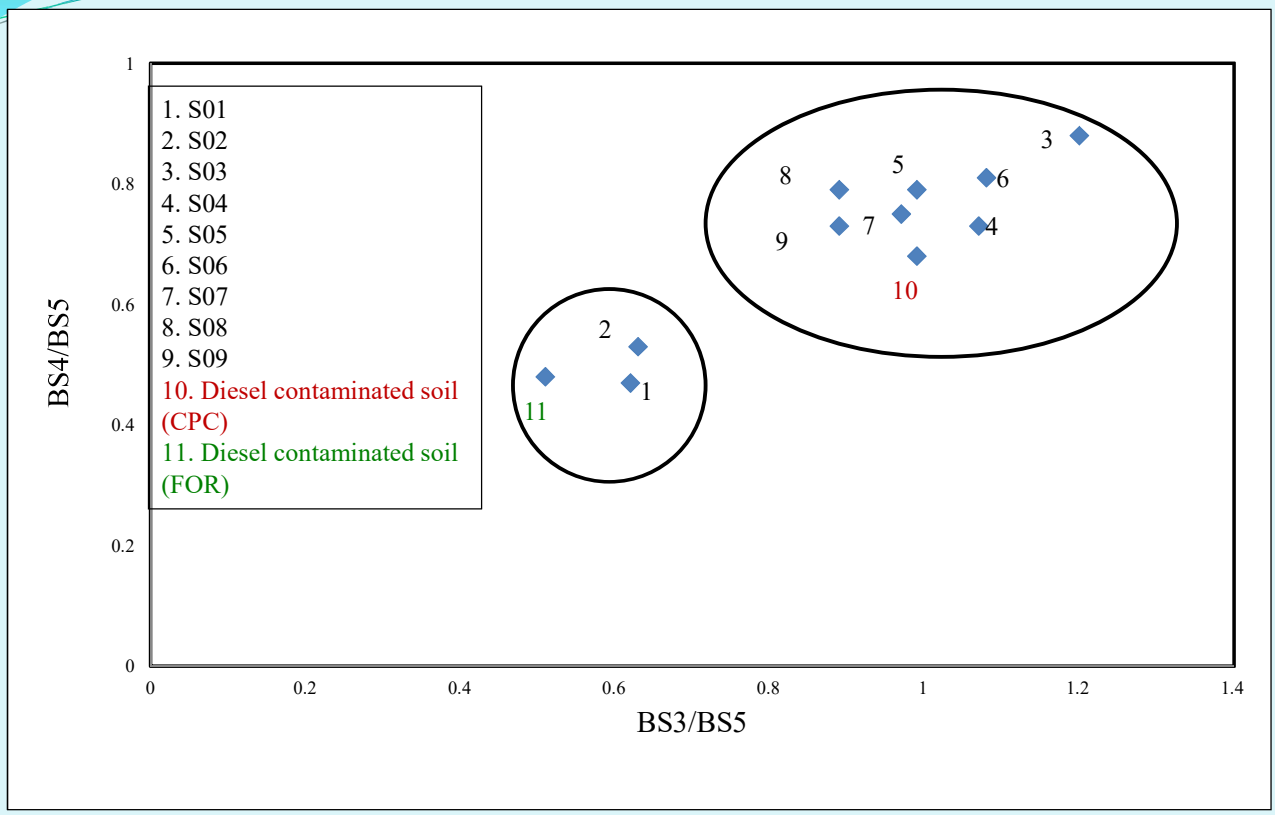
Validation of diesel contaminated soils

Sample	location	Sampling date (M/D/Y)	Potential contaminants
S01	Hsinchu	5/31/2011	gasoline, diesel
S02	Taoyuan	7/11/2011	gasoline, diesel
S03	Nantou	4/9/2012	diesel
S04	Changhua	5/21/2012	diesel
S05	Taichung	7/23/2012	Jet fuel, diesel
S06	Taichung	7/23/2012	Jet fuel, diesel
S07	Taichung	7/23/2012	diesel
S08	Chiayi County	7/9/2012	diesel
S09	Taoyuan	10/11/2012	gasoline, diesel

Characteristic ratios of diesel contaminated soils from 9 contaminated sites

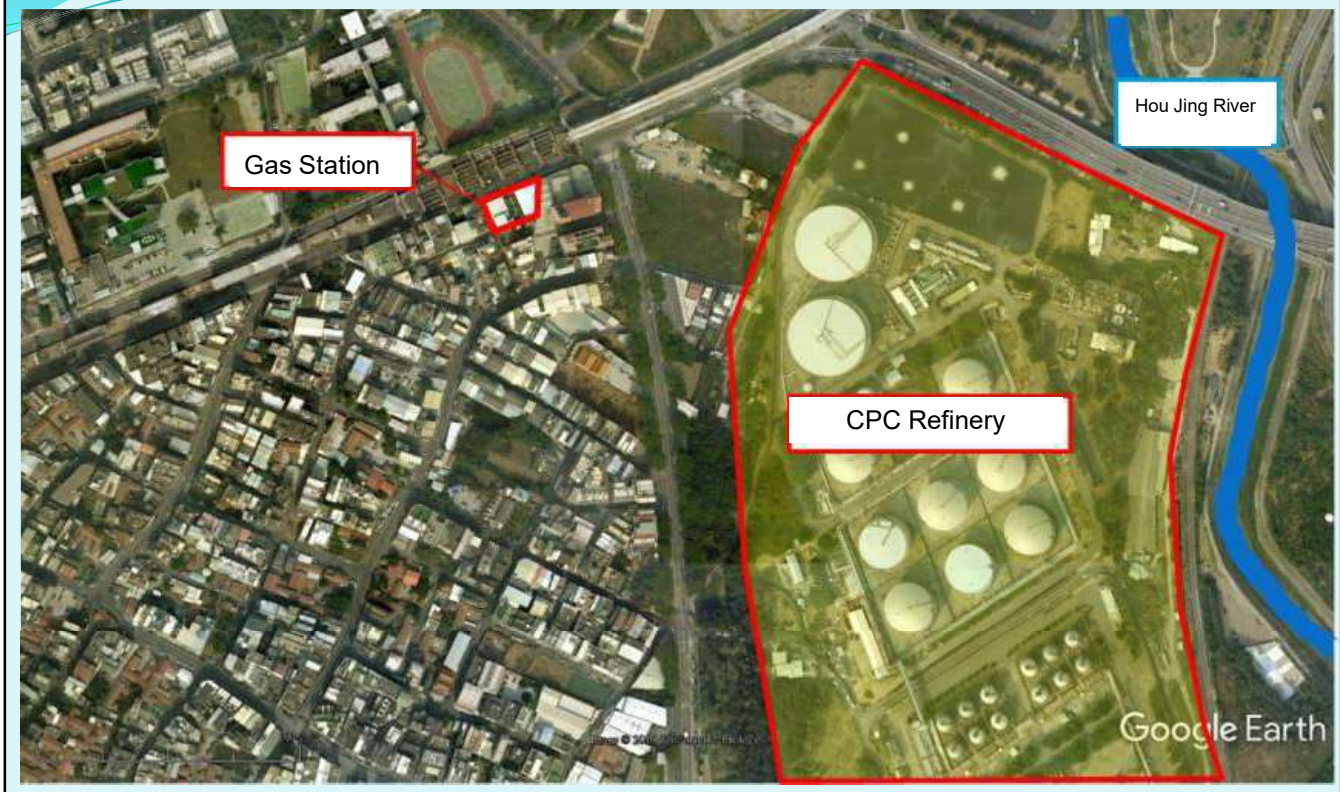
Contaminated soil	S01	S02	S03	S04	S05	S06	S07	S08	S09
TPH (mg/kg)	831.79	18283	2908.5	16636	73509	3640.3	15703	58343	6394.3
C_{17}/Pristane	-	0.26	-	0.36	2.17	-	-	0.05	0.84
C_{18}/Phytane	-	1.18	-	0.40	3.15	-	-	0.04	2.56
Pristane/Phytane	-	0.90	-	1.14	1.62	-	-	1.57	1.56
BS3/BS5	0.62	0.63	1.20	0.89	0.99	1.08	0.97	0.89	1.07
BS4/BS5	0.47	0.53	0.88	0.73	0.79	0.81	0.75	0.79	0.73
BS4/BS6	0.62	0.76	2.13	1.24	1.54	1.36	0.79	1.68	1.48
BS3/BS10	0.51	0.57	0.94	0.58	1.43	0.71	0.40	0.89	1.09
BS5/BS10	0.63	0.68	0.78	0.73	1.45	0.66	0.72	1.11	0.74
MNR	-	1.55	-	-	1.01	-	-	-	-
MPR	-	1.99	-	-	-	-	-	1.08	-
MPI 1	-	1.71	-	-	-	-	-	-	-
MPI 2	-	1.78	-	-	-	-	-	-	-

Cross-plots of the diagnostic ratios BS3/BS5 versus BS4/BS5 for diesel contaminated soils



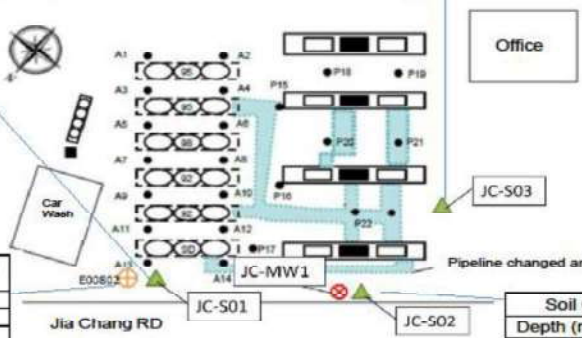
Gas Station (Jia Chung, Kaohsiung)

- Investigation was conducted by TEPA in November, 2015
- TPH contamination was found in soil and groundwater
- Both TPH_g and TPH_d were detected, it was suspected that leakage of gasoline and diesel may occur
- The owner claimed nearby CPC refinery caused the contamination
- Fuel products supplied by CPC during 1990 to 2010, then shifted to FOR in 2010



Soil Contamination (mg/kg)		
Depth (m)	5.5-6.0	6.0-6.5
TPH_g	149	11100
TPH_d	2580	17600

Soil Contamination (mg/kg)		
Depth (m)	6.0-6.5	6.5-7.0
TPH_g	2960	5
TPH_d	14400	38



Groundwater Contamination (mg/L)	
MTBE	<0.01
Benzene	0.045
Toluene	0.068
Ehylbenzene	0.411
Xylenes	0.881
TPH_g	8.9
TPH_d	5.2

Soil Contamination (mg/kg)		
Depth (m)	5.5-6.0	6.0-6.5
TPH_g	243	8440
TPH_d	2970	14000

Verification of Total Petroleum Hydrocarbon

- Concentration of TPH_d in S01 and S02 showed declined trend, TPH_d in S03 was not clear

Sample	S01			S02			S03		
Depth	5.0-5.5	6.0-6.5	6.5-7.0	5.5-6.0	6.0-6.5	6.5-7.0	4.0-4.5	6.0-6.5	6.5-7.0
1st TPH_d (mg/kg)	-	4,412	22,904	ND	1,414	-	113.4	-	1,011
2nd TPH_d (mg/kg)	1,558		2,916	ND	-	20,482	ND	-	ND
3rd TPH_d (mg/kg)	211.3	2,735	ND	ND	56.64	10,686	-	ND	3,672

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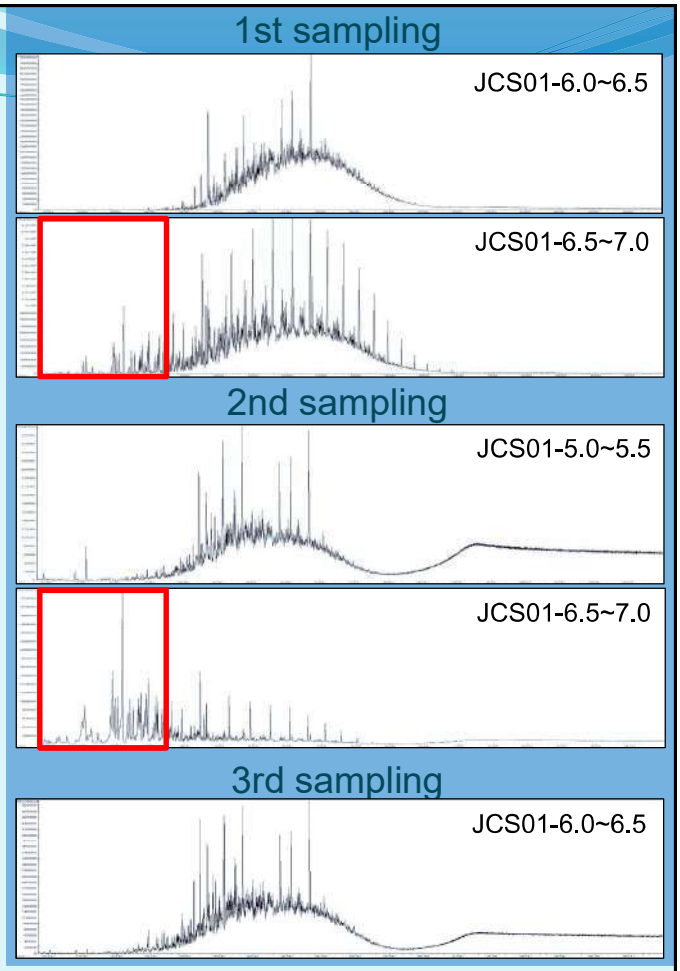
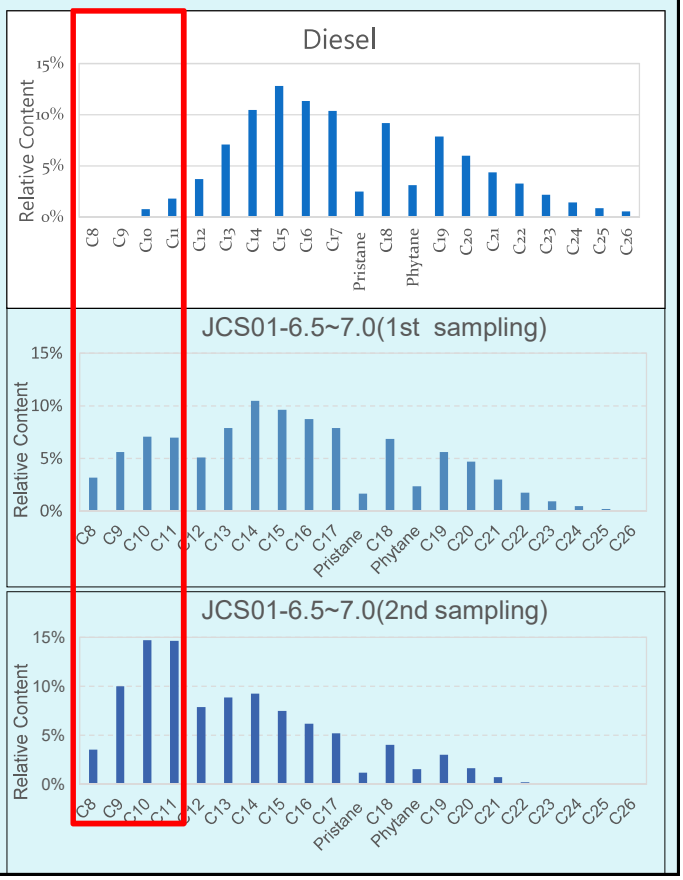
Total Ion Chromatograms

- Severe weathering effect in S01 at depth of 5.0-6.5 m was observed
- Apparent loss of alkanes was found
- Weathering effect was not obvious at the depth of 6.5-7.0 m
- Contamination by gasoline was observed at the depth of 6.5-7.0 m



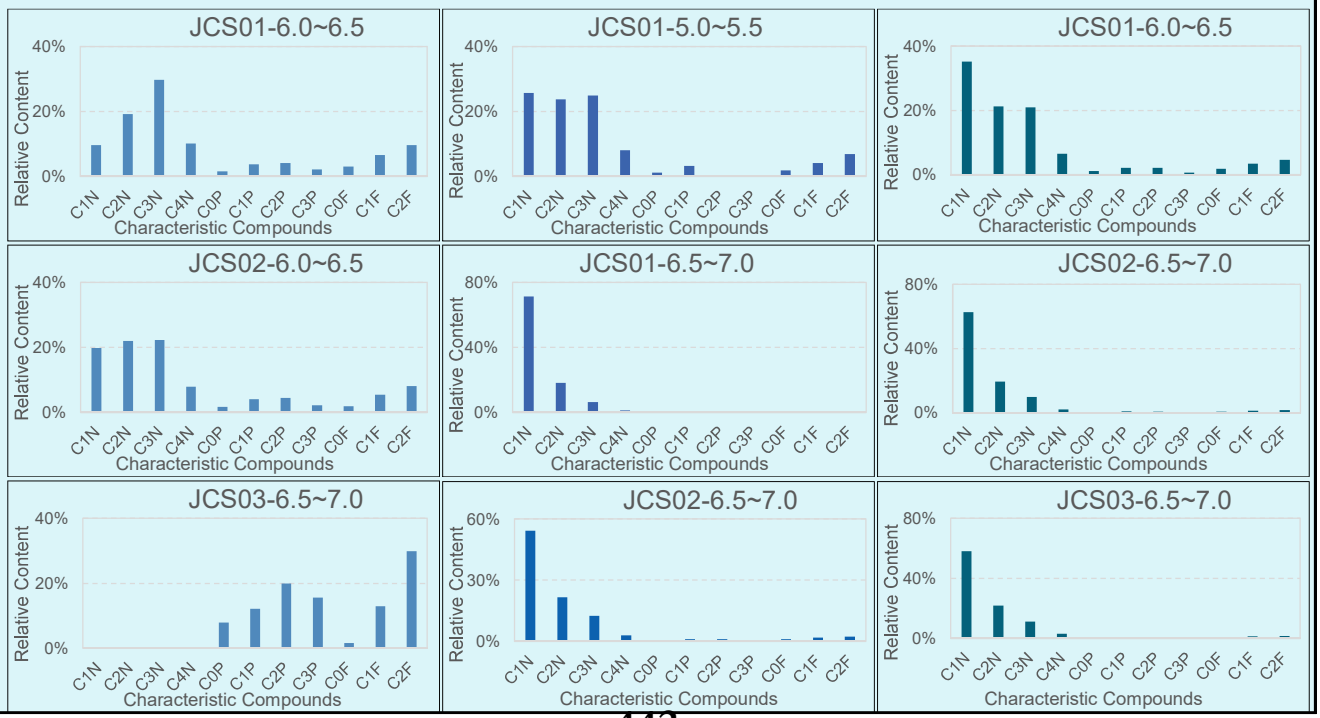
Alkane Distribution Patterns

- Alkane distribution is not similar to the pattern of diesel contamination
- The relative content of C_8 to C_{11} is higher in soil samples. It may be contributed by gasoline



PAHs Distribution

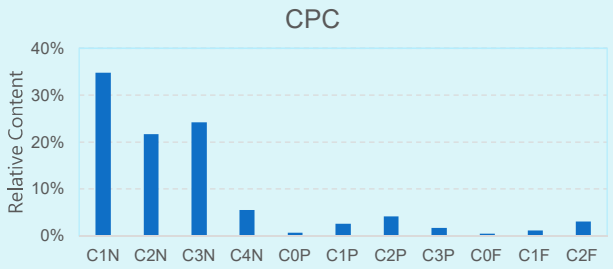
- Diverse distribution of PAHs in all three samples

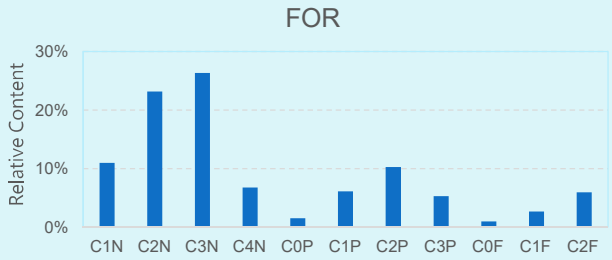


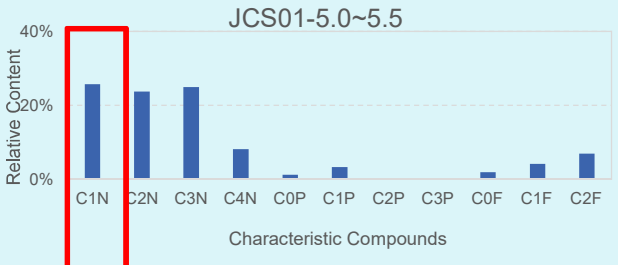
PAHs Distribution

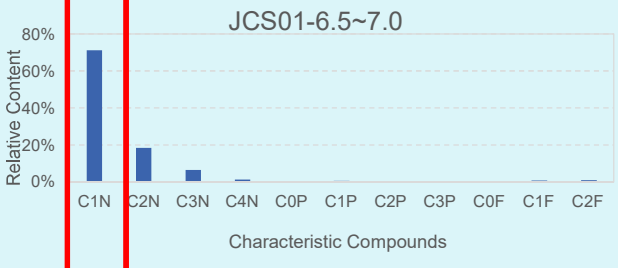
Source of C_1N?

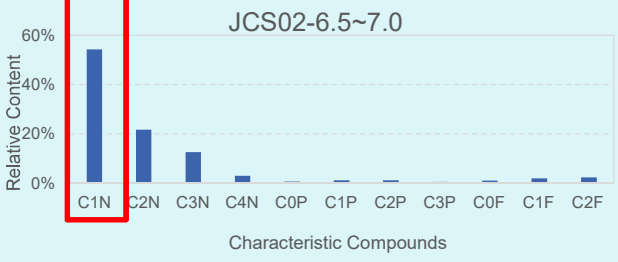
- The content of C_1N was high than other PAHs
- It may be contributed by contamination of CPC diesel





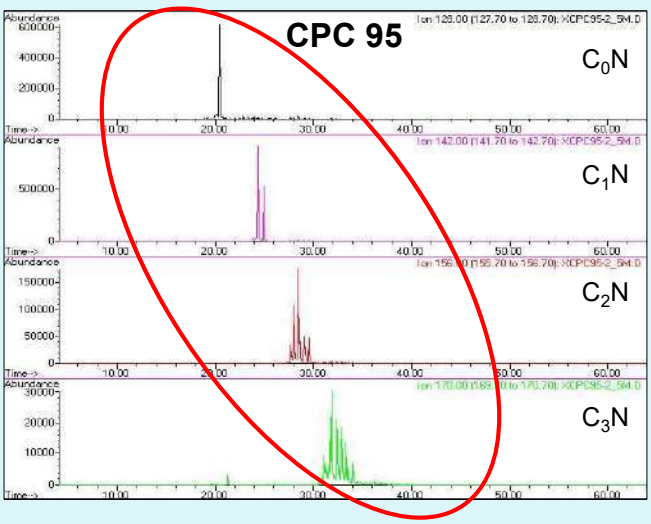


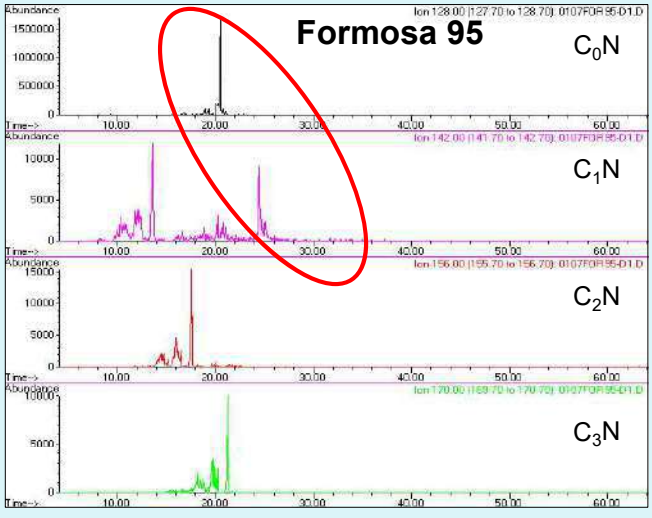




PAHs Distribution

- The ratio and distribution of naphthalene and methyl-substituted naphthalenes may be affected by gasoline but not diesel??
- CPC gasoline contains C_0N, C_1N, C_2N, and C_3N · FOR gasoline contains C_0N and C_1N





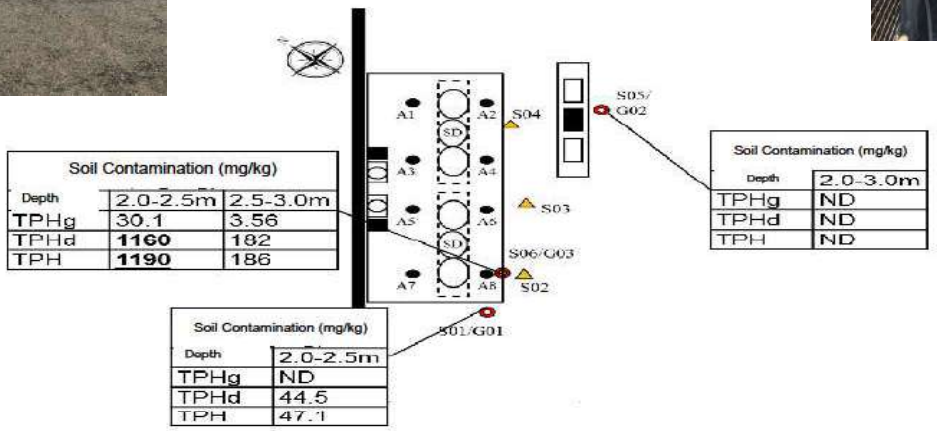
Diagnostic Ratio of Groundwater sample

- Comparing diagnostic ratio of 1st soil samples (S01 at 6.5 to 7.0m) with groundwater samples, contamination may originally come from the same source

		Soil sample			
		S01-6.0~6.5	S01-6.5~7.0	S02-6.0~6.5	S03-6.5~7.0
BS3/BS5	JC-MW1	match	match	not match	match
BS4/BS5		match	match	not match	match
BS4/BS6		match	match	match	match
BS3/BS10		not match	match	not match	not match
BS5/BS10		not match	match	not match	not match

Pier 121, Kaohsiung

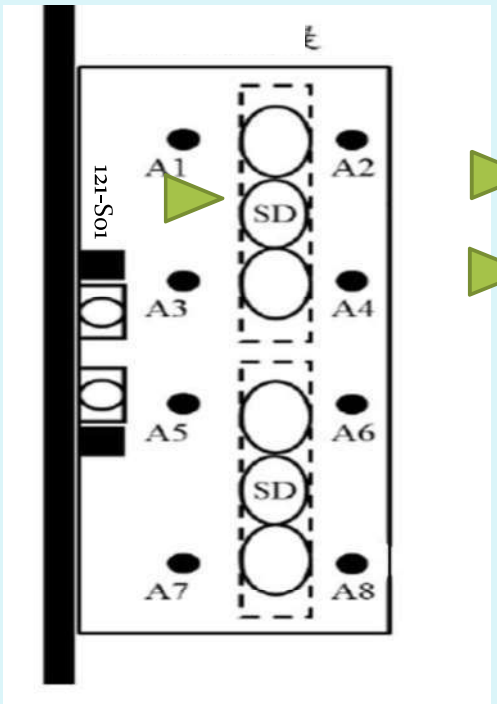
- Investigation was conducted by TEPA in October, 2015
- TPH contamination was found in soil
- Free product was found in soil monitoring wells A5 and A8
- Operation of station was stopped in July, 2016.
- Further investigation was conducted in 2017 by the owner

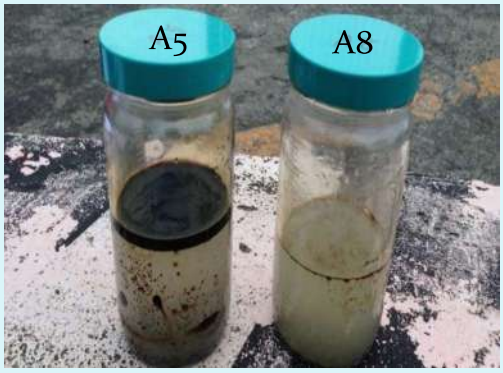


Soil Contamination (mg/kg)		
Depth	2.0-2.5m	2.5-3.0m
TPHg	30.1	3.56
TPHd	**1160**	182
TPH	**1190**	186

Soil Contamination (mg/kg)	
Depth	2.0-2.5m
TPHg	ND
TPHd	44.5
TPH	47.1

Soil Contamination (mg/kg)	
Depth	2.0-3.0m
TPHg	ND
TPHd	ND
TPH	ND





Free products found in Soil monitoring wells

Verification of Total Petroleum Hydrocarbon

- Concentration of TPH_d in S01 showed declined trend

Sample	S01			S02			S03		
Depth	2.0-2.5	2.5-3.0	3.0-3.5	2.5-3.0	3.0-3.5	3.5-4.0	2.5-3.0	3.0-3.5	3.5-4.0
1st TPH_d (mg/kg)	ND	-	17,160	-	3,737	ND	-	ND	ND
2nd TPH_d (mg/kg)	20,010	4614	-	ND	ND	-	-	-	ND
3rd TPH_d (mg/kg)	12,388	ND	ND	ND	ND	-	4,451	623.2	-

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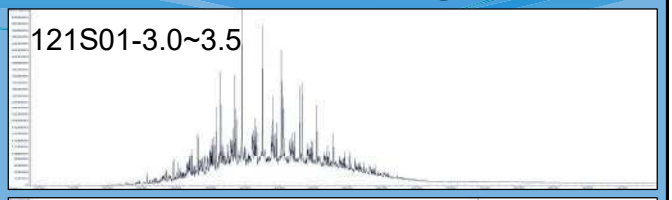
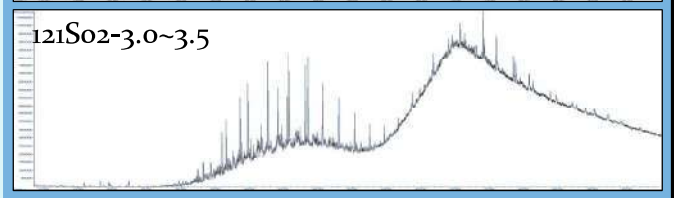
Total Ion Chromatograms

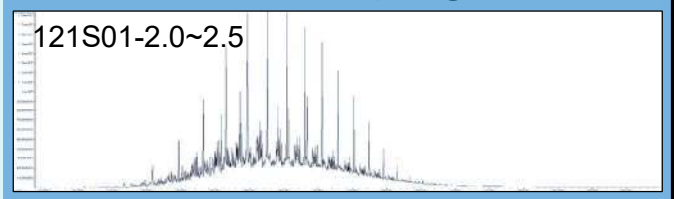
- Source of contamination in S02-at 3.0~3.5m may contains different fuel products
- The samples from the 2nd and 3rd sampling indicated the typical pattern of diesel contamination with low weathering effect (i.e., newly contaminated)

1st sampling

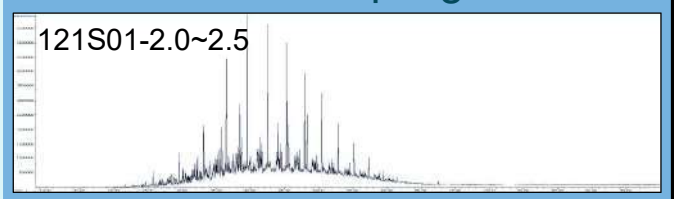




2nd sampling



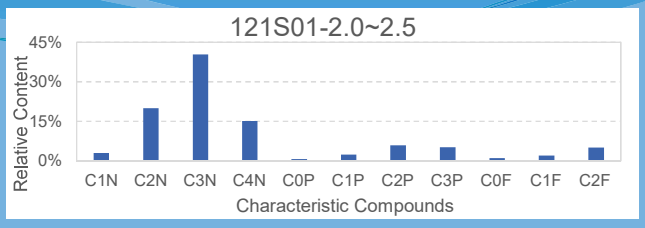
3rd sampling

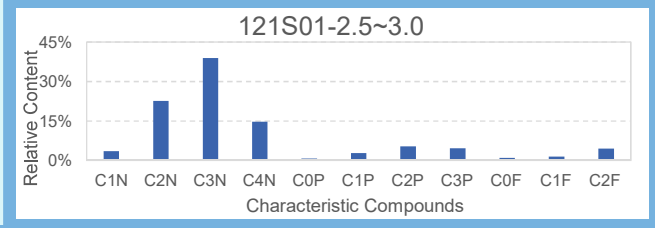


PAHs Distribution

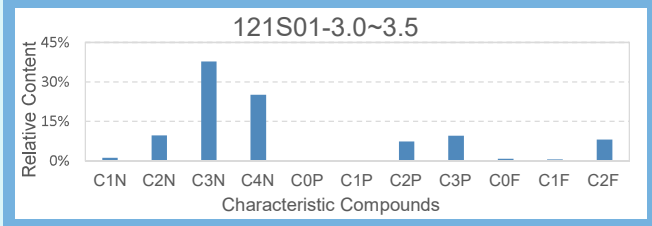
- Weathering effects of PAHs illustrated similar patterns during three times of sampling

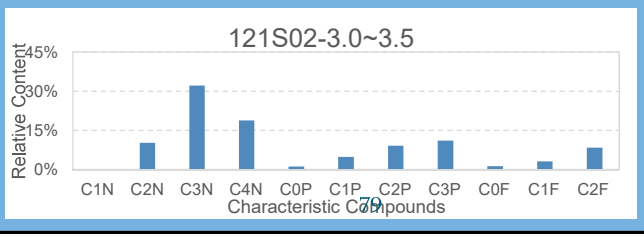
2nd sampling



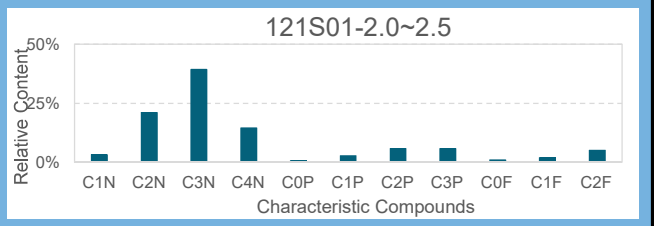


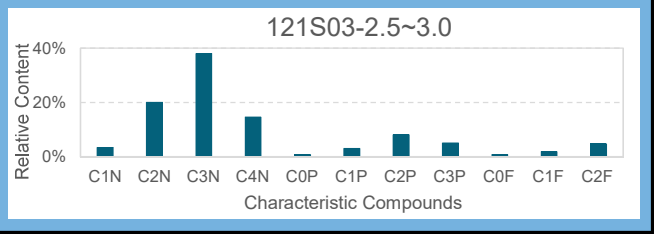
1st sampling





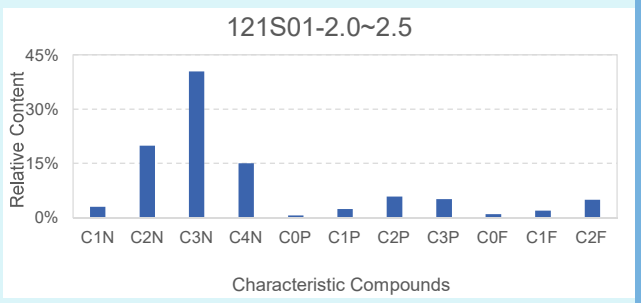
3rd sampling

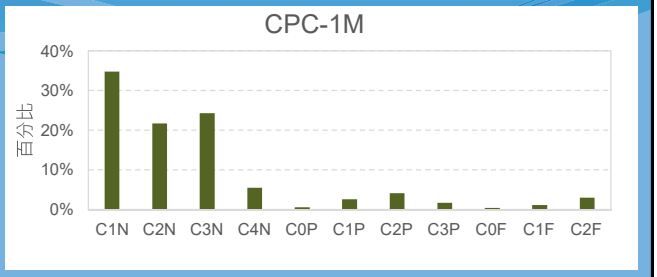


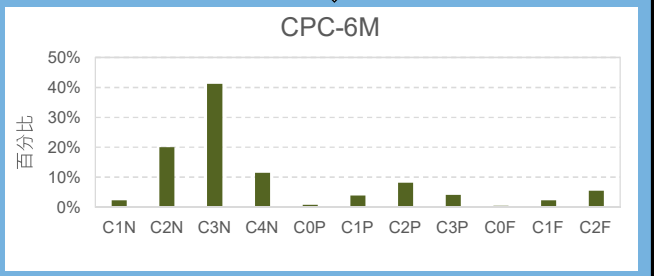


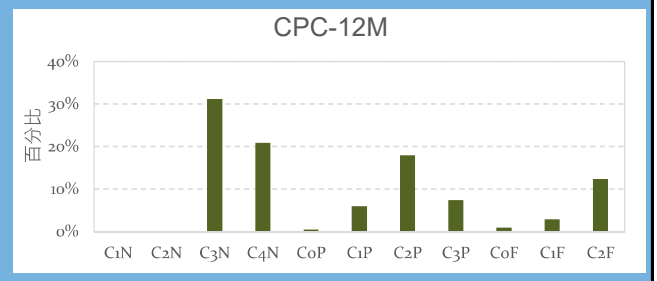
PAHs Distribution

- Comparing our laboratory studies, apparent degradation of PAHs was found in this site







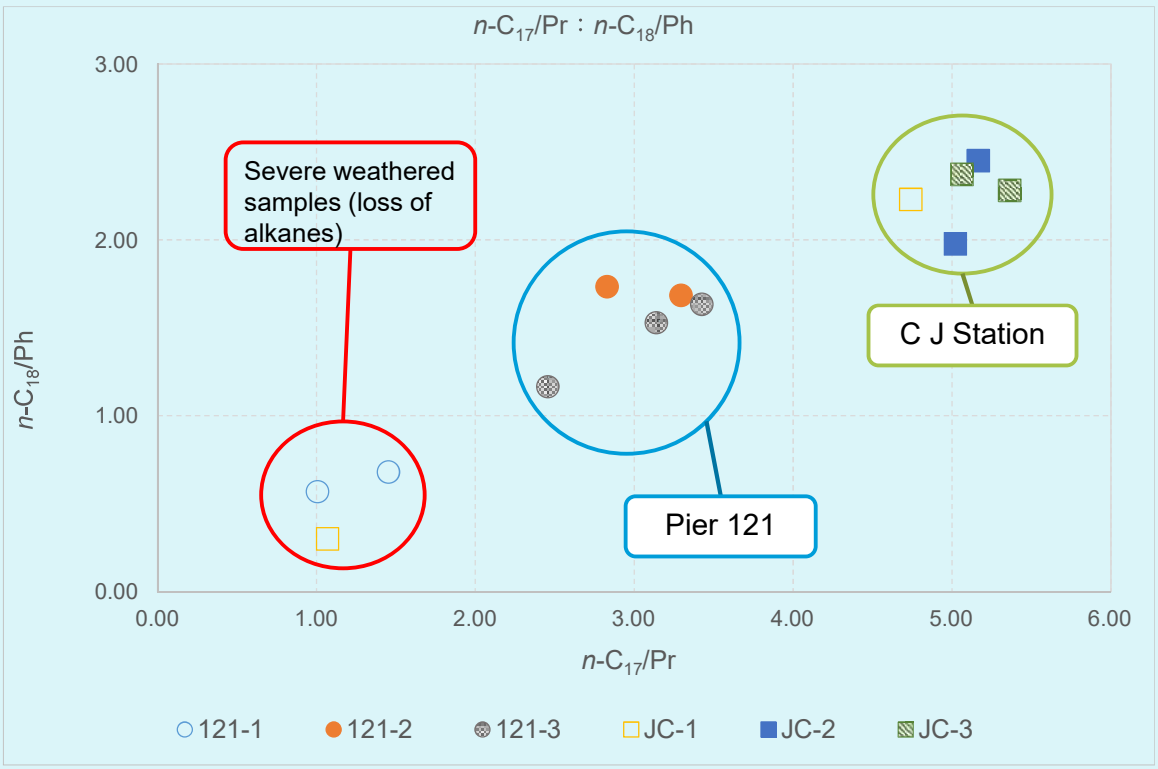


Diagnostic Ratio of Groundwater sample

- Comparing diagnostic ratio of 1st and 2nd soil samples (S01 and S02) with groundwater samples (121-GW2),most ratios match except BS4/BS5
- Contamination may originally come from the same source

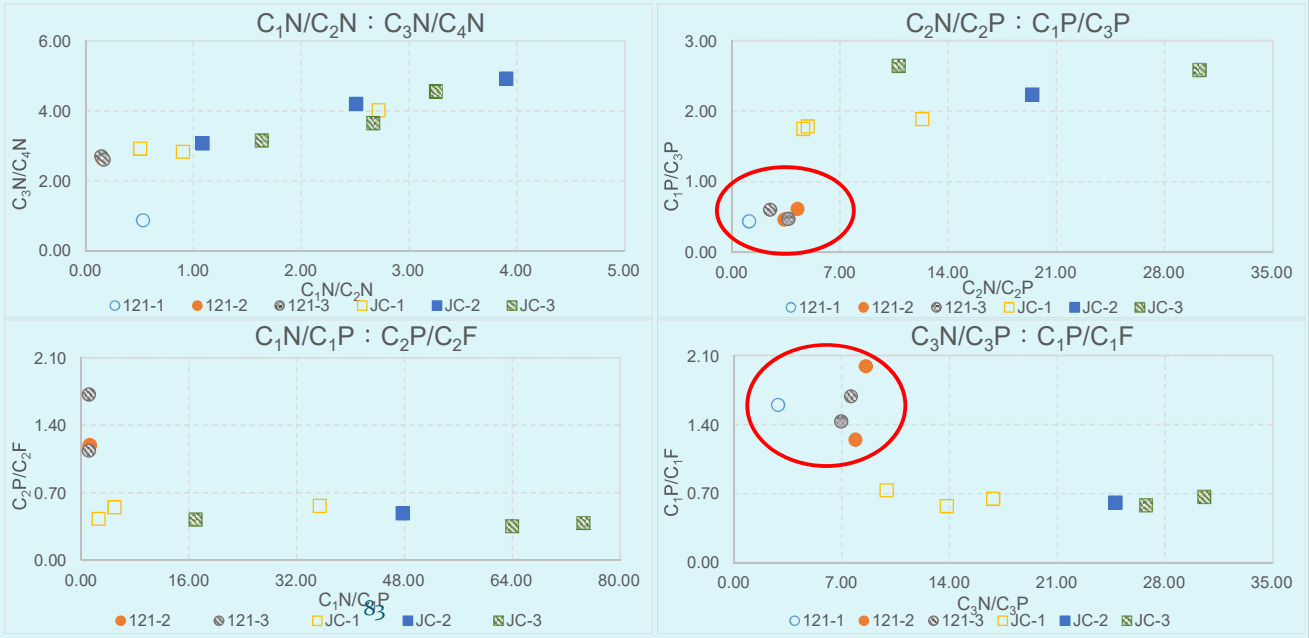
		Soil Sample			
		1st sampling		2nd Sampling	
		S01-3.0~3.5	S02-3.0~3.5	S01-2.0~2.5	S01-2.5~3.0
Pr/Ph	121-GW2	match	match	match	match
BS3/BS5		match	match	match	match
BS4/BS5		match	not match	not match	not match
BS4/BS6		match	match	match	match
BS3/BS10		match	match	match	match
BS5/BS10		match	match	match	match

Isoprenoid ratio

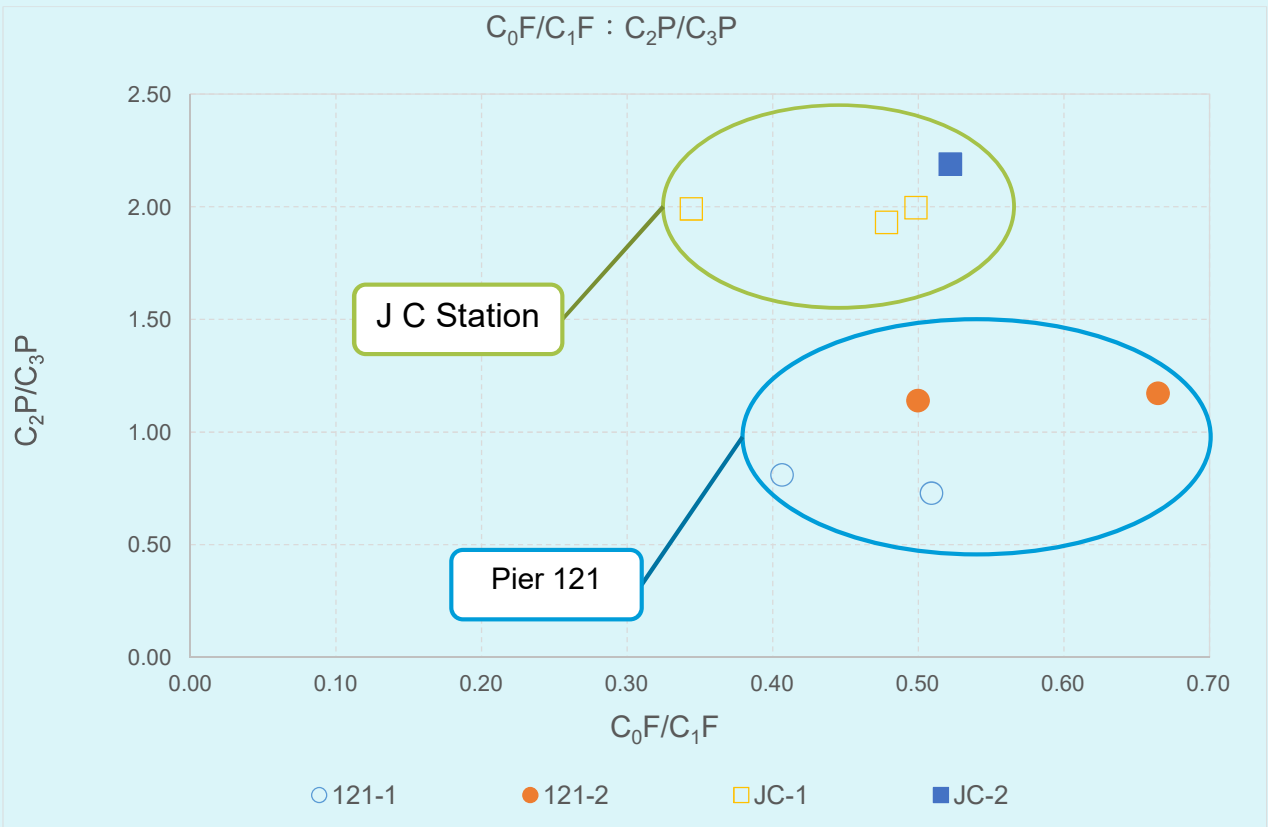


The Diagnostic Ratios of PAHs

- Cluster was grouped for Pier 121 but not Jia Chung Station due to naphthalene by gasoline contamination

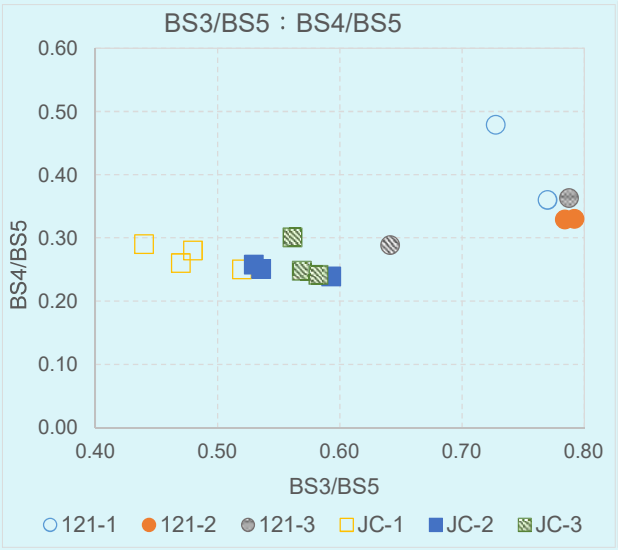


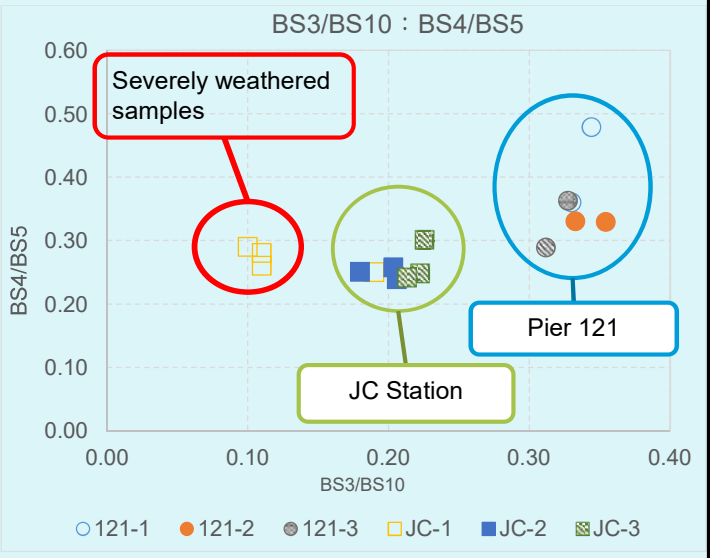
The Diagnostic Ratios of PAHs



Bicyclic Sesquiterpanes Ratio

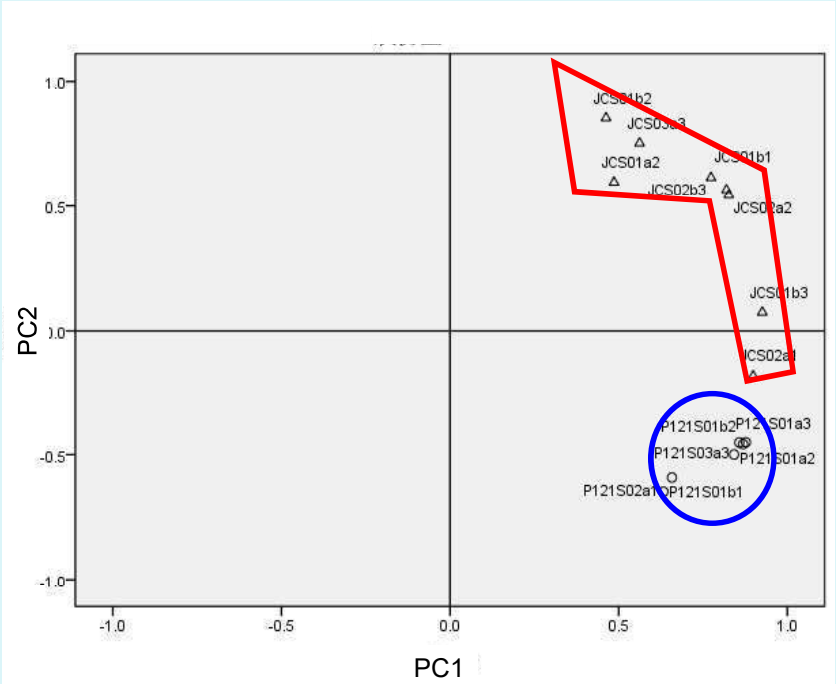
- The ratio of BS3/BS10：BS4/BS5 is more effective than BS3/BS5：BS4/BS5 to distinguish source of diesel fuel contamination





Principal Component Analysis

- Samples from Jia Chung Station and Pier 121 can be grouped to 2 clusters based upon 24 diagnotistic ratios to distinguish different fuel products



Empirical Equations to predict spill time

Prediction Model	Estimated contamination time (year)				
	min	max	average	median	n
C_3N/C_4N = 4.548 - 0.180 (Time) - 0.056 (water content) + 0.489 (organic carbon content)	1.46	5.35	3.48	3.90	5
C_1P/C_2P = 0.462 - 0.124 (Time) - 0.036 (water content) + 0.496 (organic carbon content) + 0.123 (Diversity)	0.24	3.84	2.53	3.52	3
C_1P/C_2P = 1.116 - 0.110 (Time) - 0.036 (water content) + 0.383 (organic carbon content)	2.10	3.07	2.58	2.58	2
C_2N/C_3N = 1.091 - 0.055 (Time)	1.25	8.75	3.59	2.17	4
C_2P/C_3P = 2.091 - 0.055 (Time)	1.97	3.15	2.47	2.38	4
C_{18}/Ph = 2.740 - 0.139 (Time)	2.43	19.02	8.16	4.28	7
Total PAH = 1.407 - 0.162 (Time)	1.19	8.98	5.04	5.11	6
C_2N/C_4N = 0.561 - 0.371 (Time) - 0.063 (water content) + 1.335 (organic carbon content) + 0.607 (Diversity)	2.97	7.21	4.96	4.71	3
C_2N/C_4N = 3.909 - 0.195 (Time)	3.68	11.22	6.42	5.39	4

Thank you for your attentions

Colin S. Chen, Ph.D.
Professor
cschen@nknu.edu.tw
Laboratory of Environmental Remediation
Department of Biotechnology
National Kaohsiung Normal University
Kaohsiung 824, Taiwan

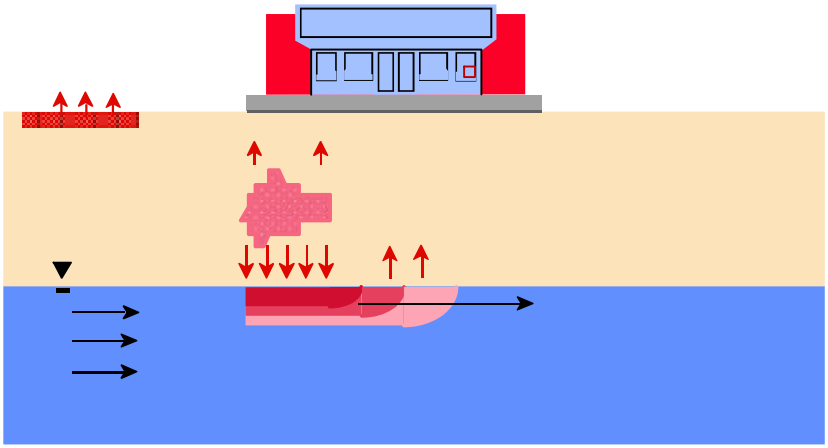
2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Remediation of Organic Contaminated Sites: Theories and Case Studies

Jimmy Kao
National Sun Yat-Sen University
Kaohsiung, Taiwan

Organic Contaminant Fate and Transport

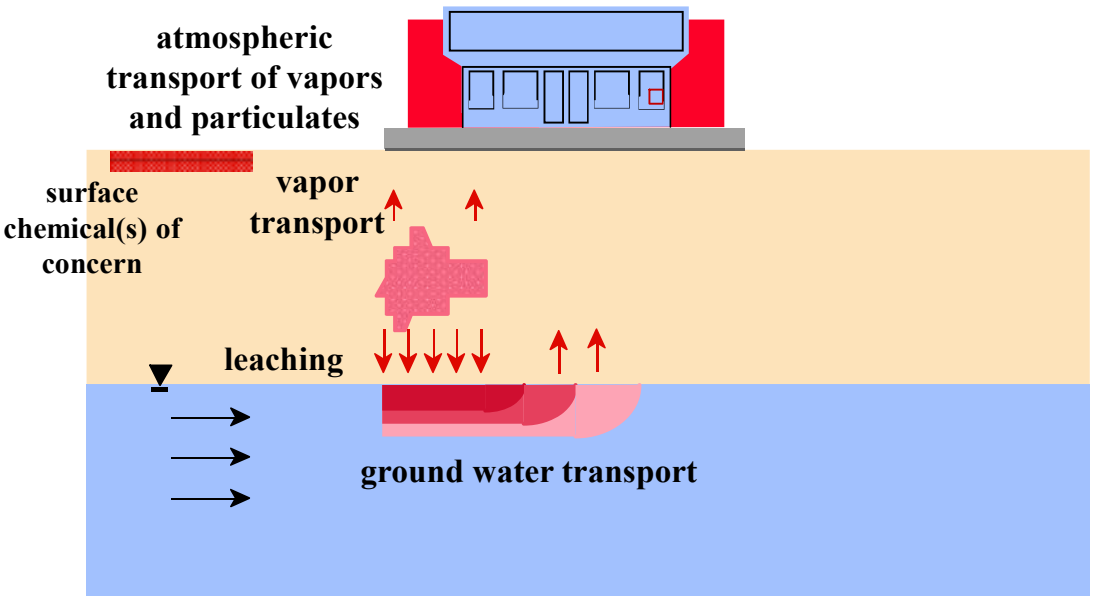


Jimmy Kao
National Sun Yat-Sen University
Kaohsiung, Taiwan

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 = $\alpha \times v_x + D_d$

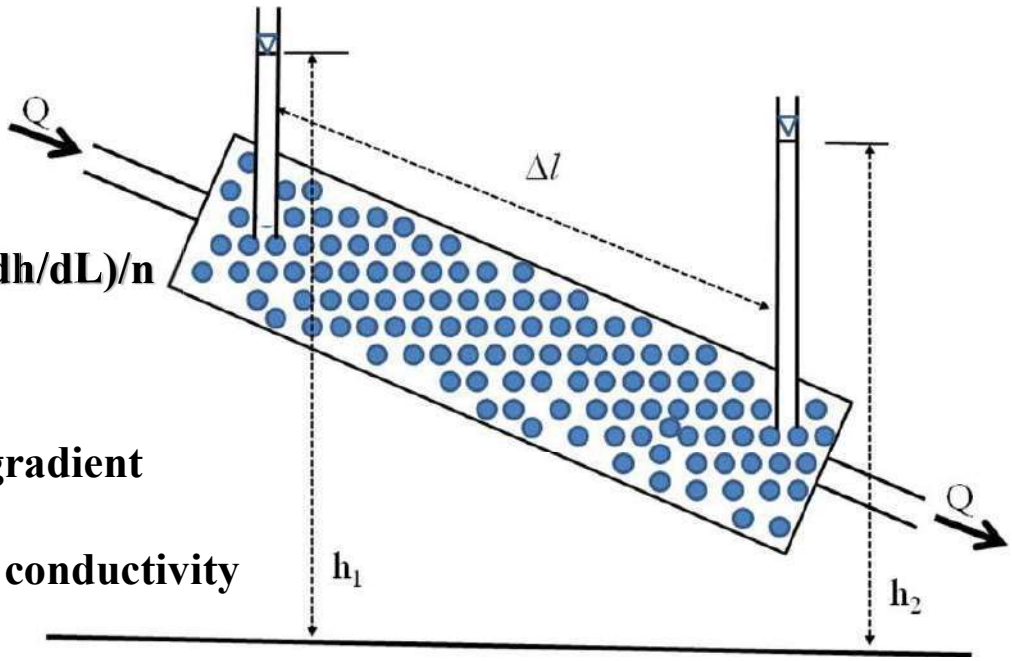
- **Adsorption Effects**
  Retardation factor (R) = $1 + K_d\ (\rho/n)$
  Distribution coefficient = K_d (mL/g) = $f_{oc}\ K_{oc}$
  $K_{oc} = 0.63\ K_{ow}$
  K_{oc} = soil water partition coefficient (mL/g)
  K_{ow} = octanol water partition coefficient (mL/g)
  f_{oc} = fraction of organic carbon

- **Biodegradation**

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

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

i = hydraulic gradient
n = porosity
K = hydraulic conductivity



Darcy's column experiment

soil particle density, ρs

$$\rho_s = W_s / V_s$$

bulk density, ρ_b

$$\rho_b = W_s / V_t$$

porosity, n

$$n = (V_a + V_w)/V_t = V_v / V_t$$

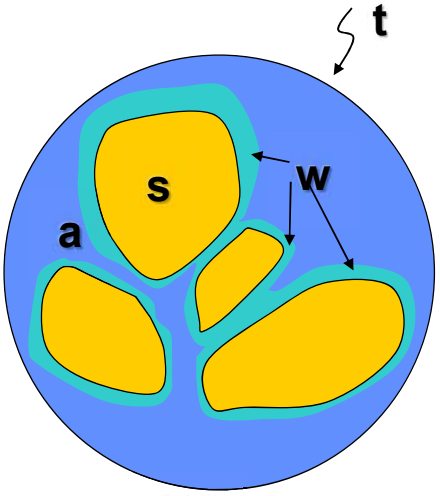
$$n = 1 - \rho_b / \rho_s$$

void ratio, e

$$e = V_v / V_s = (V_w + V_a)/V_s$$

$$e = n/(1-n)$$

$$n = e/(1+e)$$

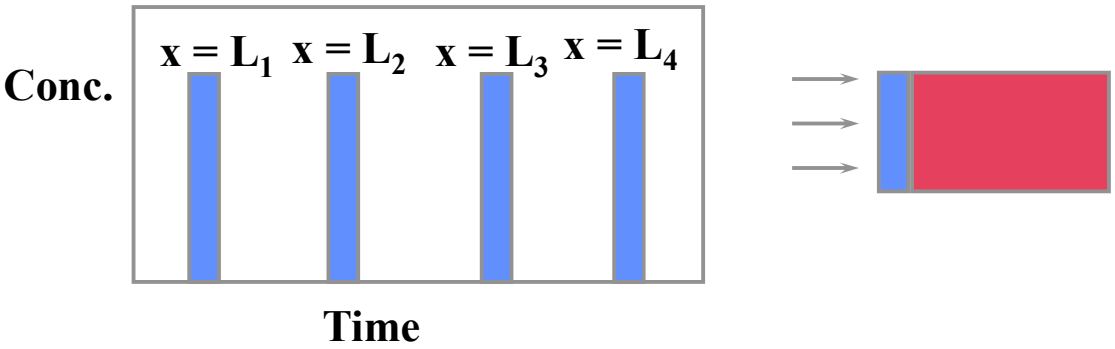


s: solid
a: soil air
w: soil water
t: total volume

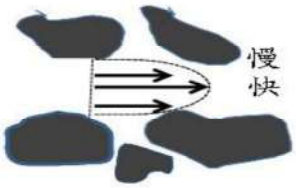
W: weight
V: volume

Advective Transport - Summary

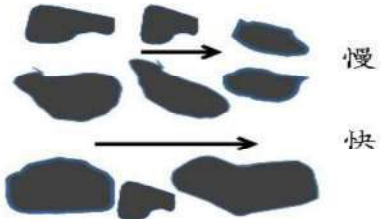
Advection moves dissolved hydrocarbons with the bulk fluid flow, but the dissolved concentrations are not expected to change.



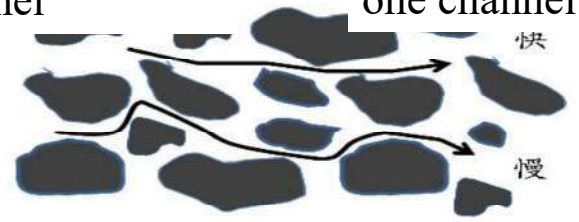
Advective rate estimates are affected most by uncertainties in the distribution coefficient and ground water velocity.



(a) friction within a single pore channel



(b) velocity differences from one channel to another

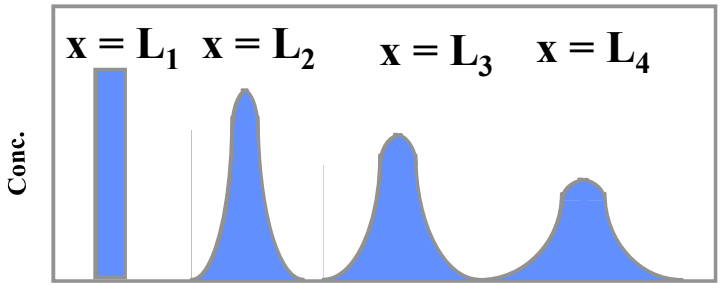


(c) variable path lengths

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.

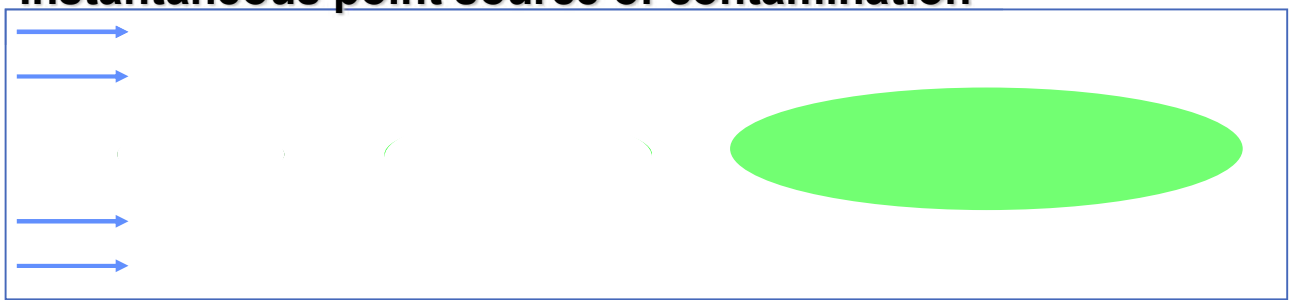
Dispersion

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.

Instantaneous point source of contamination



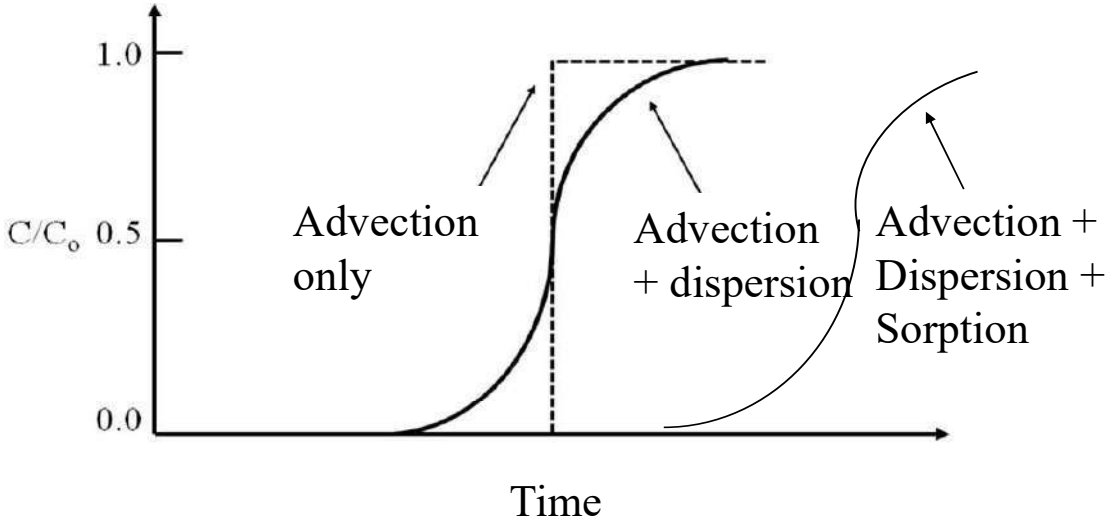
Continuous point source of contamination

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



Breakthrough Curve of a 1-D column experiment

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:

{ decay rate } **is proportional to** { concentration of hydrocarbon }

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

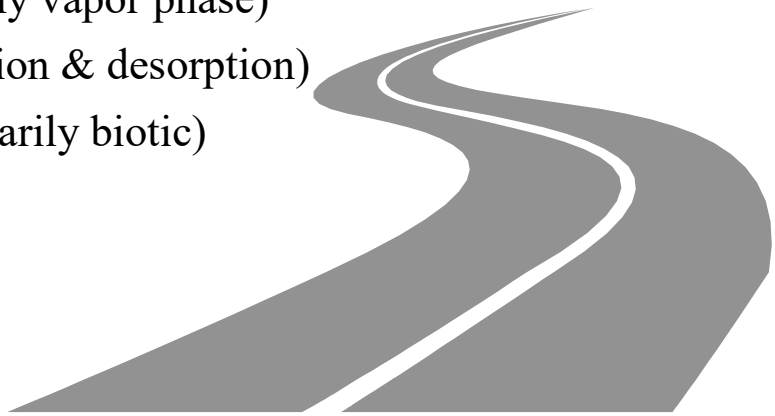
Contaminant Fate and Transport

- 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

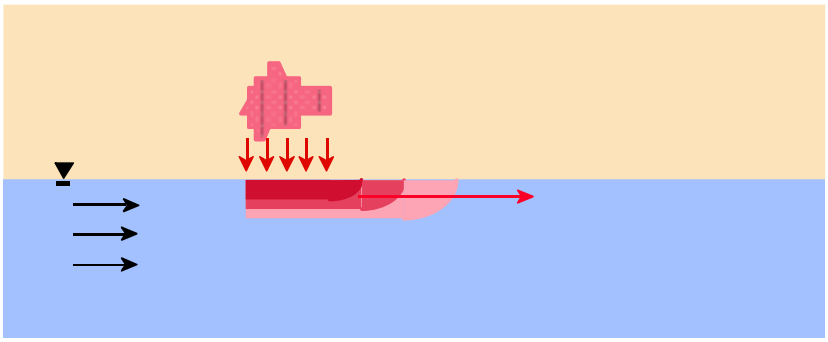
- advection (flow or movement in the media)
  - vapor
  - liquid
  - dissolved

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

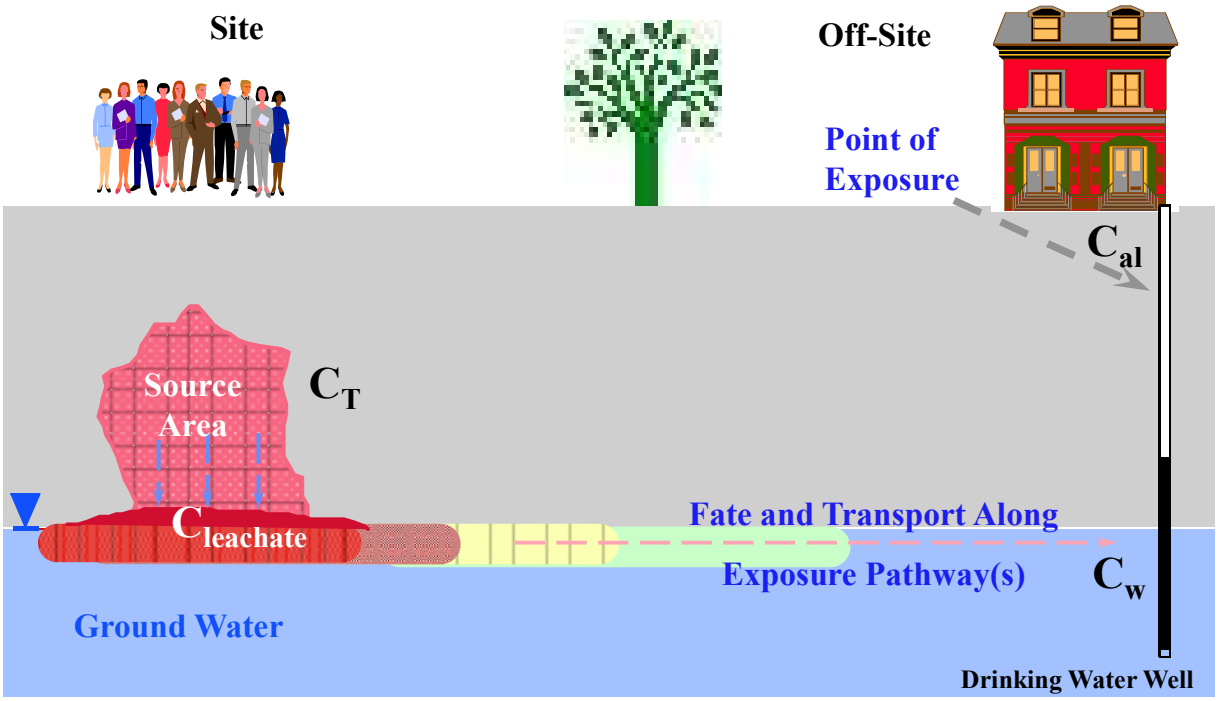
Fate & Transport

- 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



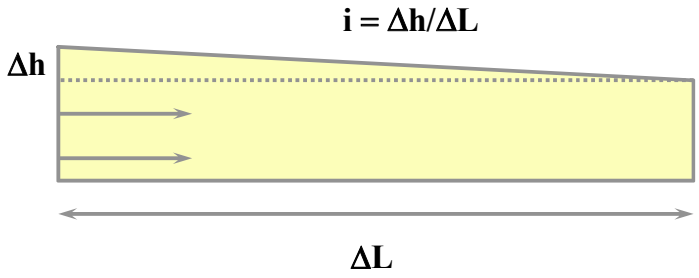
Ground Water Fate and Transport



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

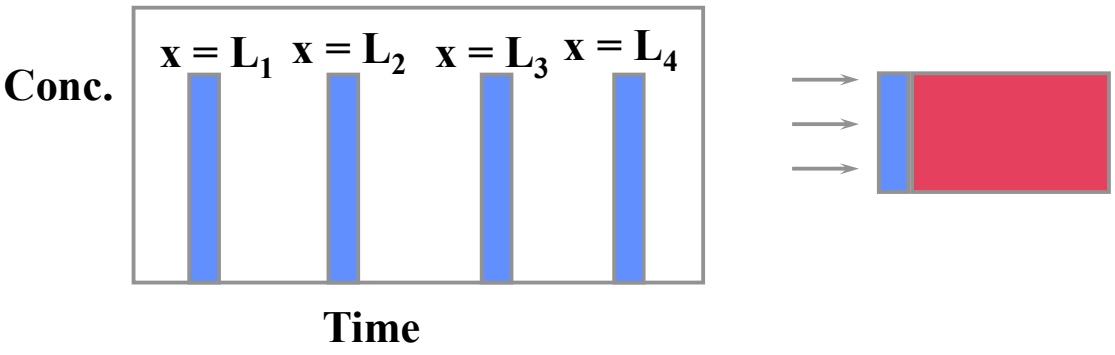
- Estimation of distribution coefficient (k_d)
  - laboratory experiments or
  - calculated for organic chemicals

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

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

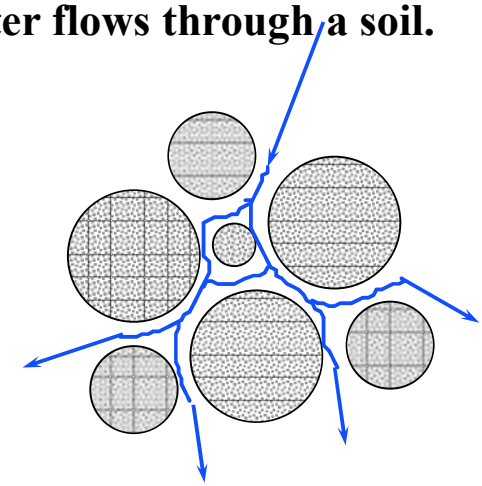
Fick's first law

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

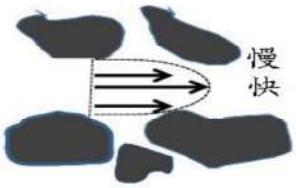
$\mathbf{D_d}$ is the coefficient of molecular diffusion for the solute in the porous medium.

Dispersion

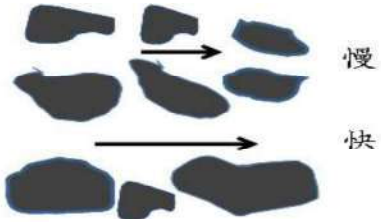
"Dispersion" refers to the in-situ mixing that results as a ground water flows through a soil.



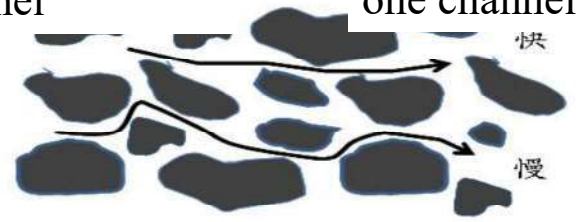
Hydrodynamic dispersion occurs as a result of mechanical mixing (mechanical dispersion) and molecular diffusion. The coefficient of hydrodynamic dispersion can be expressed in terms of the two components.



(a) friction within a single pore channel



(b) velocity differences from one channel to another

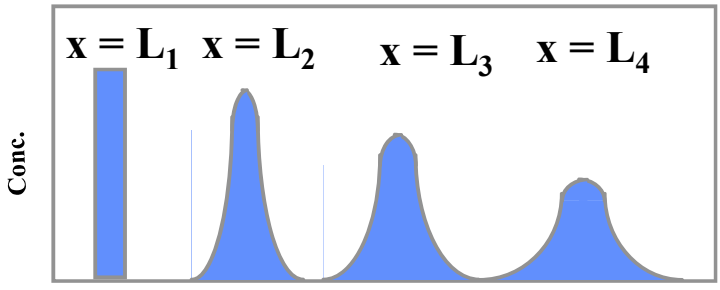


(c) variable path lengths

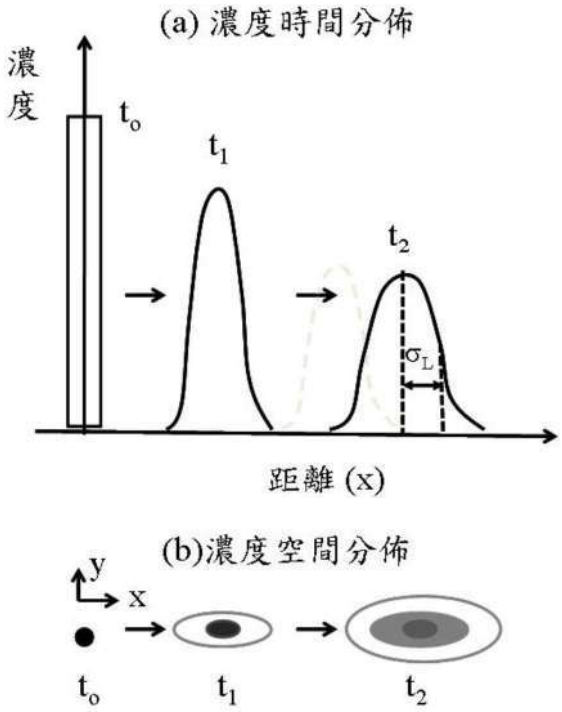
Hydrodynamic dispersion is caused by heterogeneities in the medium that create variations in flow velocities and flow paths. These variations can occur due to friction within a single pore channel, to velocity differences from one channel to another, or to variable path lengths.

Dispersion

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

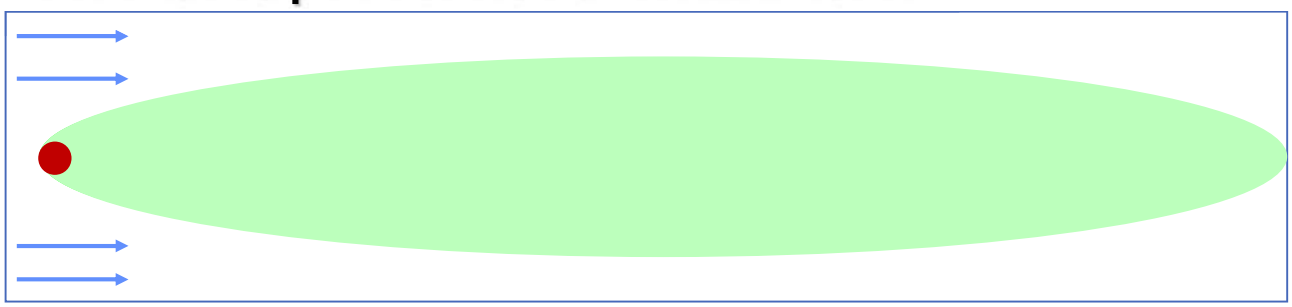


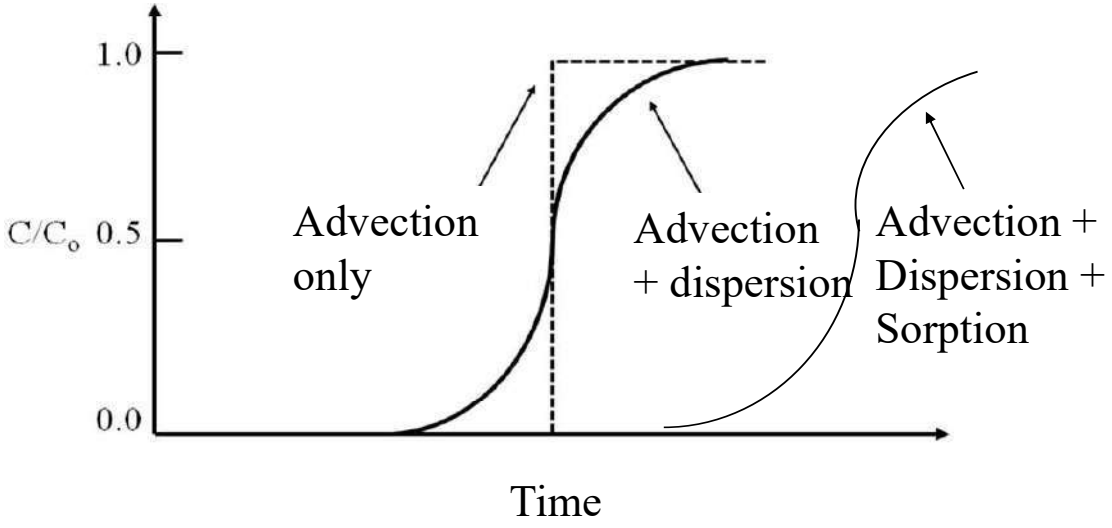
Dissolved concentrations generally decrease as the chemical moves away from a source.



Instantaneous point source of contamination

Continuous point source of contamination



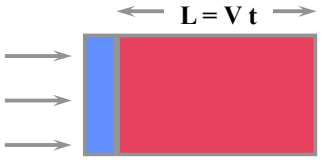


Breakthrough Curve of a 1-D column experiment

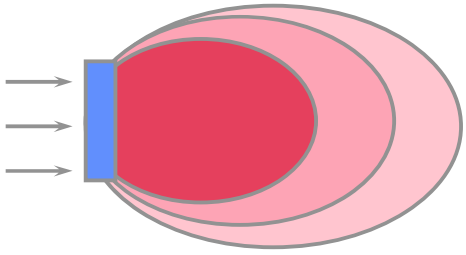
Hydrodynamic Dispersion

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

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



Transport at time t without dispersion



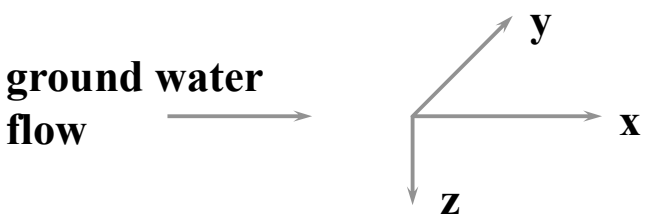
Transport at time t with dispersion

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]

$\alpha_x, \alpha_y, \alpha_z$ = dispersivities in x, y, and z direction [ft, m, cm]

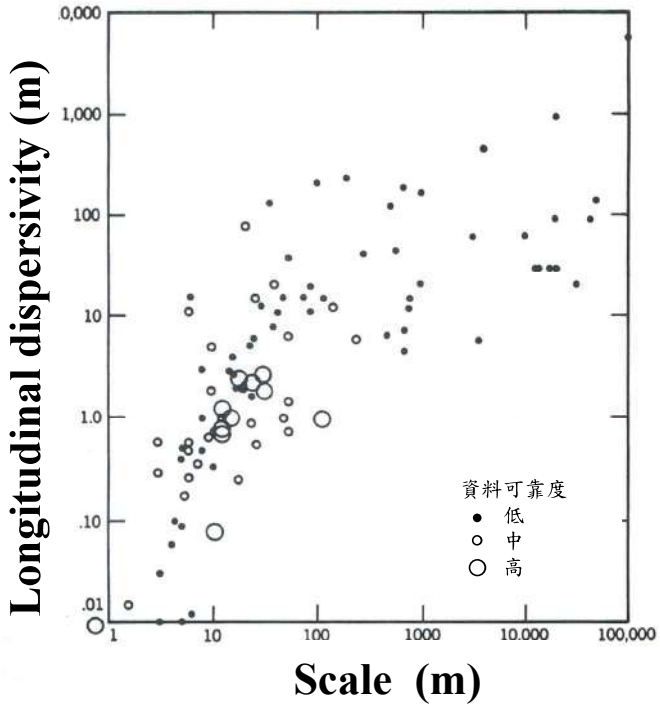


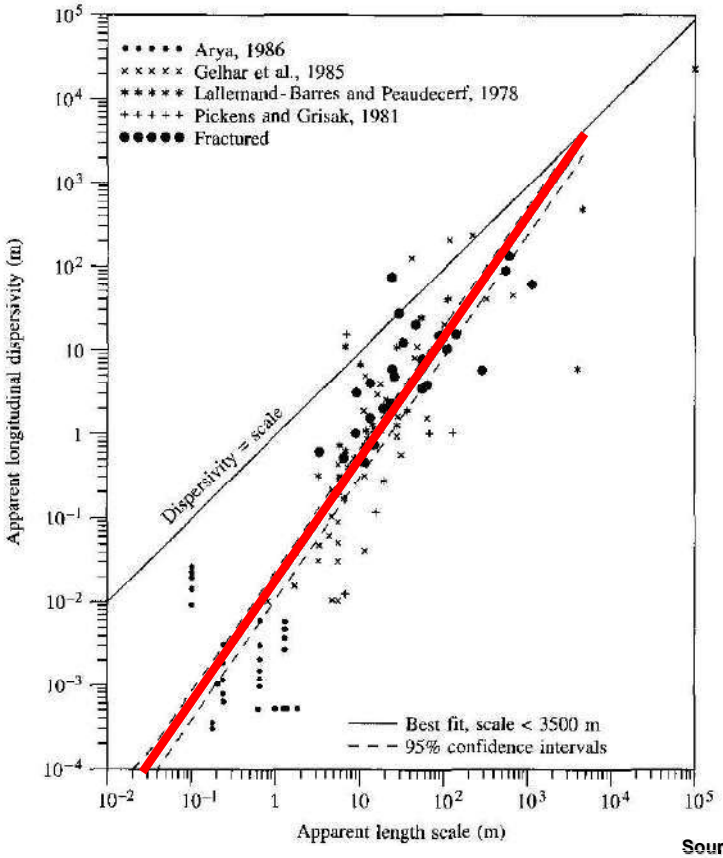
Hydrodynamic Dispersion

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:

$\alpha_x = L/10$
$\alpha_y = \alpha_x/3$
$\alpha_z = \alpha_x/20$
L = distance away from source





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:

{ decay rate } is proportional to { concentration of hydrocarbon }

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

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 ($\mu g/l$)
C_o = initial concentration ($\mu g/l$)

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

Biodegradation

Decay

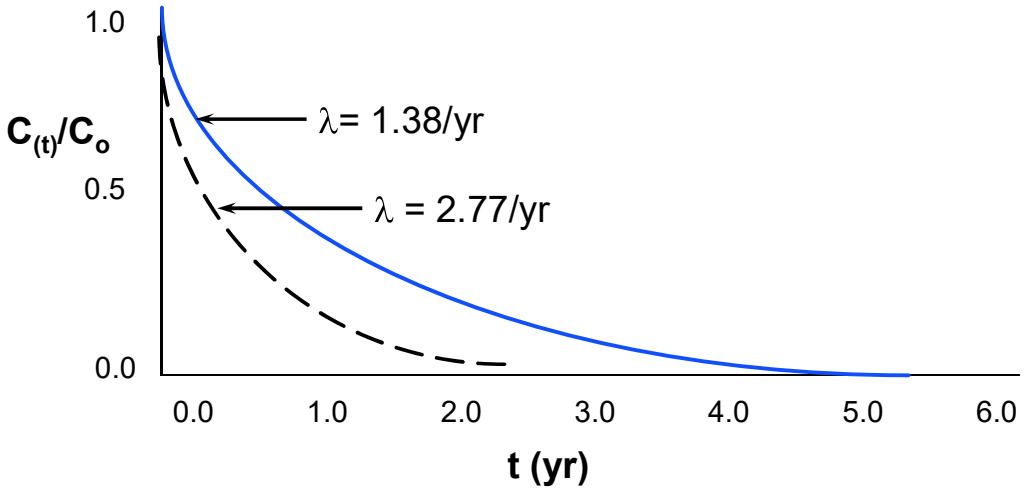
The half-life of a chemical is defined as the time it takes for the first-order reaction to transform half of the initial mass of the chemical. If $C_{(t)}/C_o$ is replaced with 0.5, then:

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

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

Biodegradation

Illustration of first-order decay

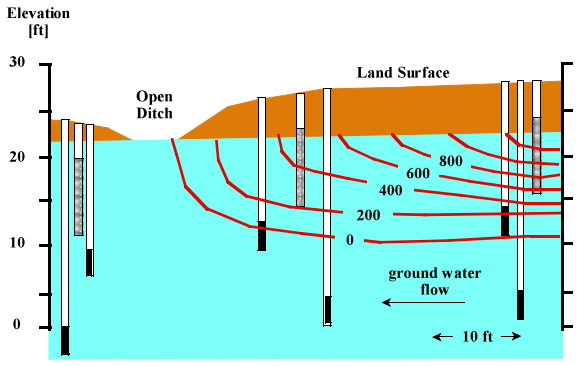


Natural Attenuation

"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 $= \bar{v}_x n C dA$

dispersion $= n D_x \frac{\partial C}{\partial x} dA$

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

Adsorption and Biodegradation effects

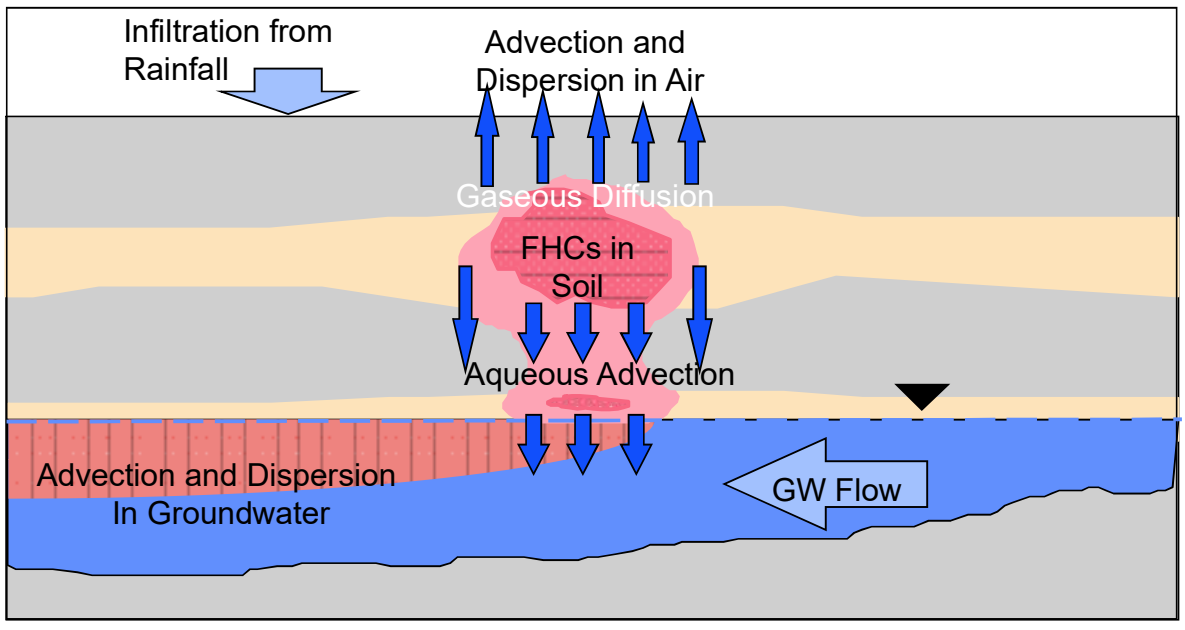
Sink/Source $$D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + \sum_{k=1}^{N} R_k = \frac{\partial C}{\partial t}$$

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]

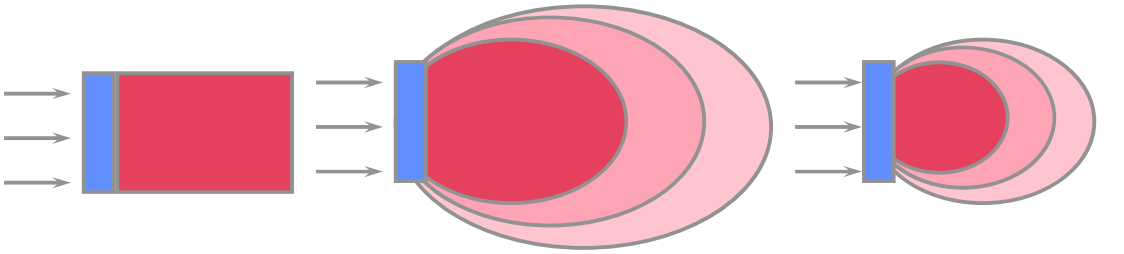
Example of a Conceptual Model, Showing Significant Transport Processes



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:

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

Concentration at Downgradient Distance x Away from Source — $C(x)$

Concentration at Source — C_0

Longitudinal Dispersivity — α_x

First-Order Decay Constant — λ

Ground Water Seepage Velocity — V

Error Function — erf

Ground Water Source Width and Depth — S_w, S_d

Transverse Dispersivity — α_y

Vertical Dispersivity — α_z

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

Hydraulic Conductivity — k

Hydraulic Gradient — i

Volumetric Water Content (Porosity) — θ

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

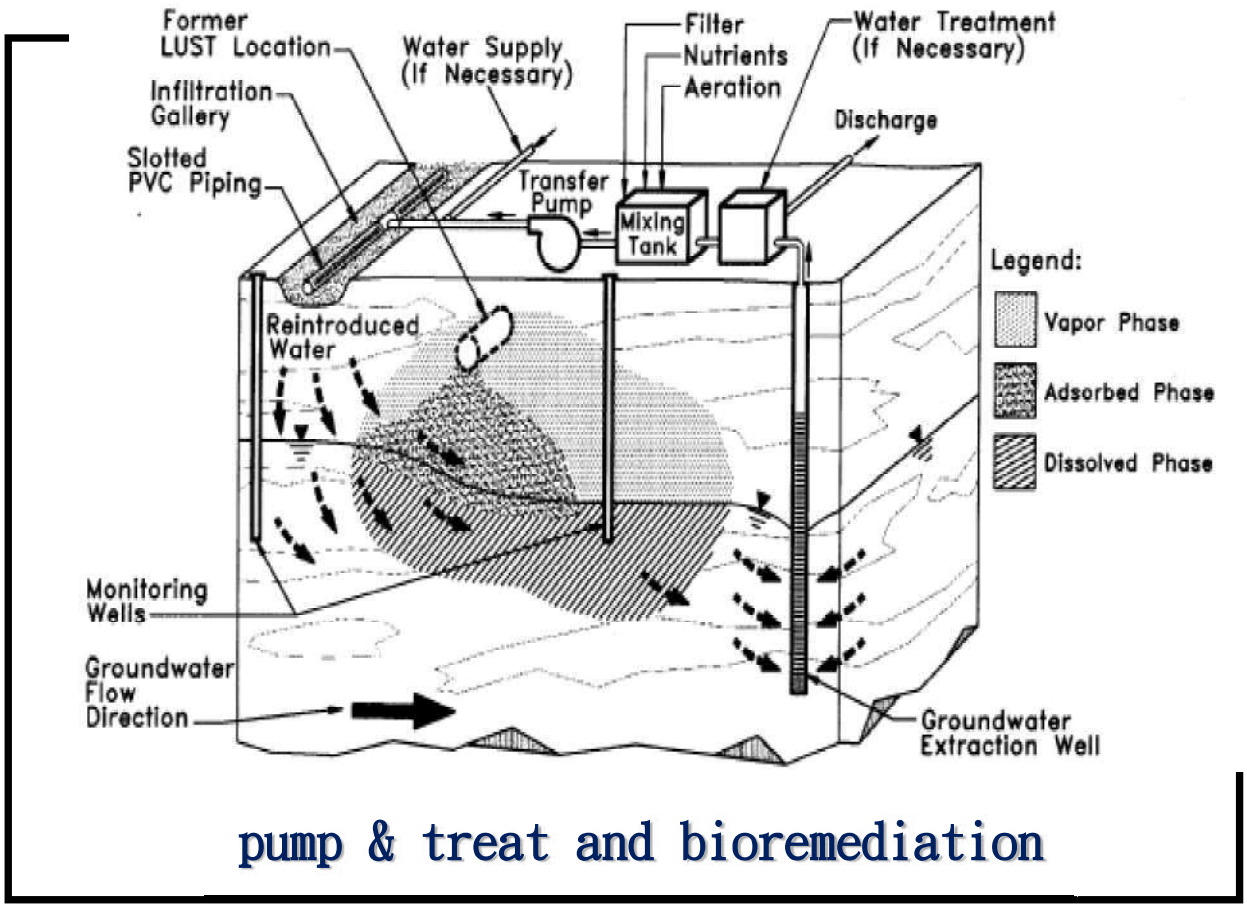
Available technology → applicable to site → feasible to implementation → societal acceptability → need new data → long term remediation → prospective technology → (remedy screening → potentially feasible technology) → treatability study → meet performance goal → remedy selection → meet remediation goal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

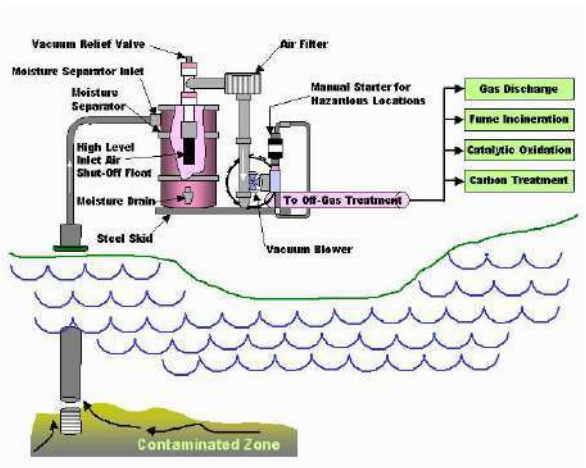
Trend of Groundwater Remediation Technology Development

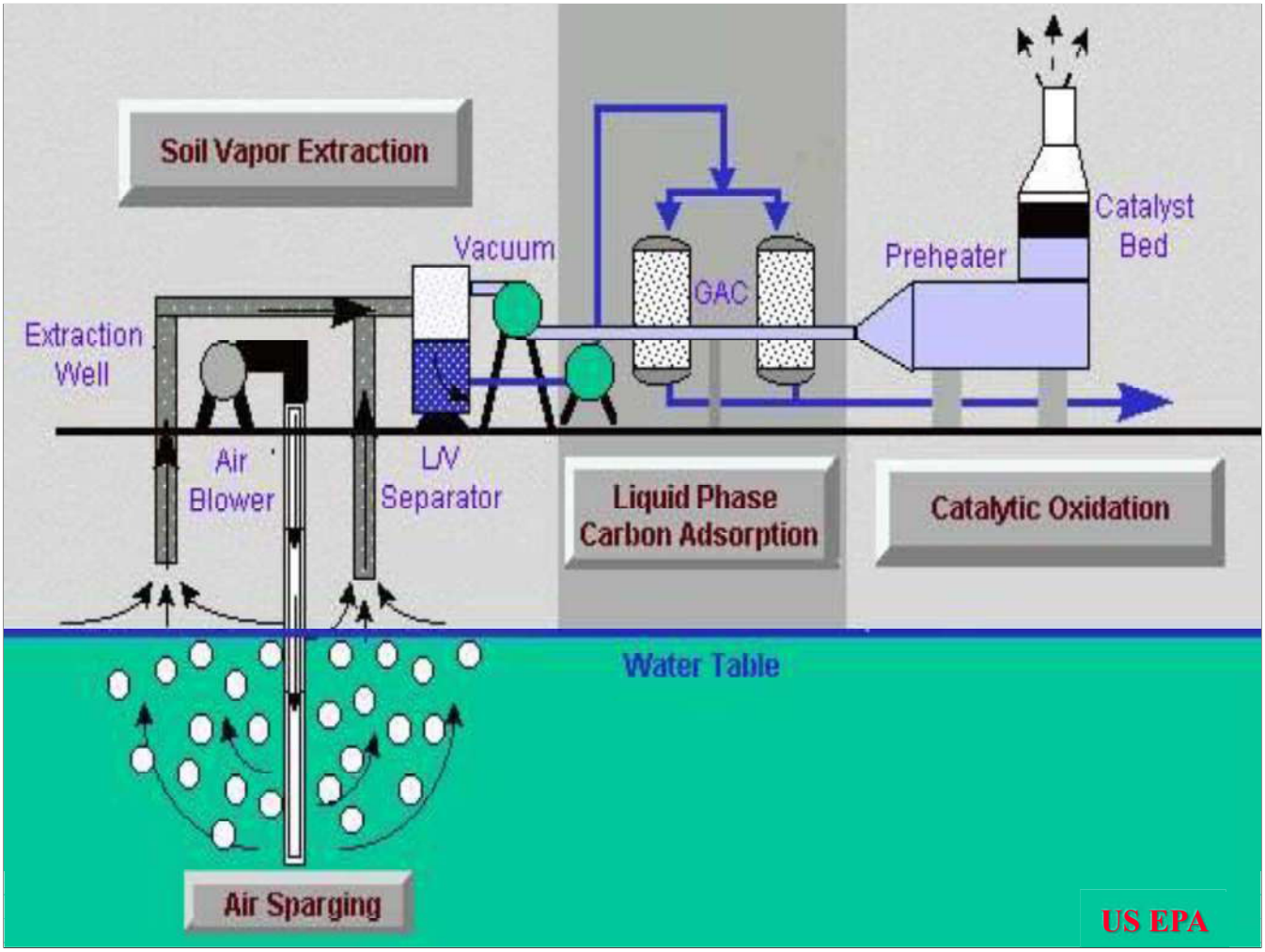
- Mid 1990s – present
  - in situ mass destruction
  - in situ reaction zone, IRZ
  - in situ chemical oxidation
  - in situ bioremediation
  - monitored natural attenuation, MNA
  - risk assessment
  - Brownfield
- Current
  - treatment train
  - life cycle design
  - natural treatment system
  - green remediation

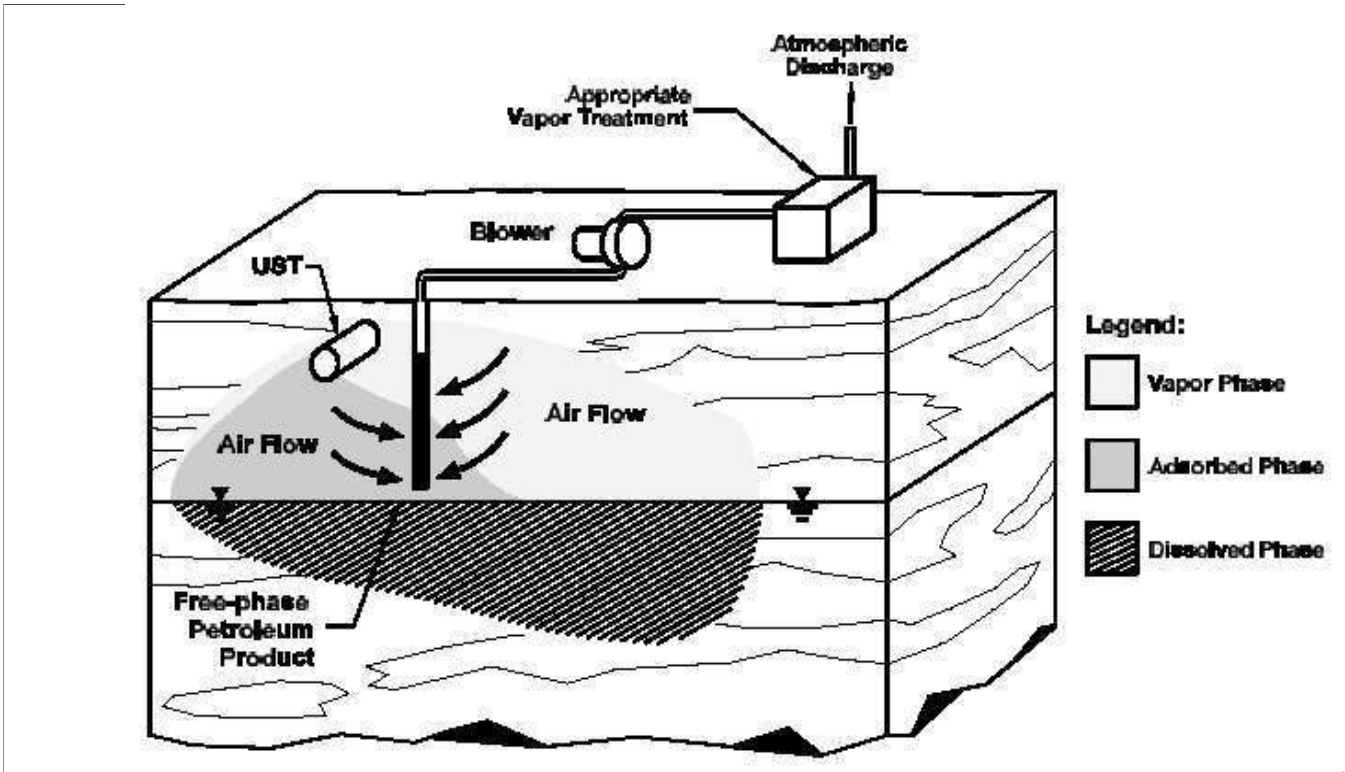


pump & treat and bioremediation

Soil Vapor Extraction



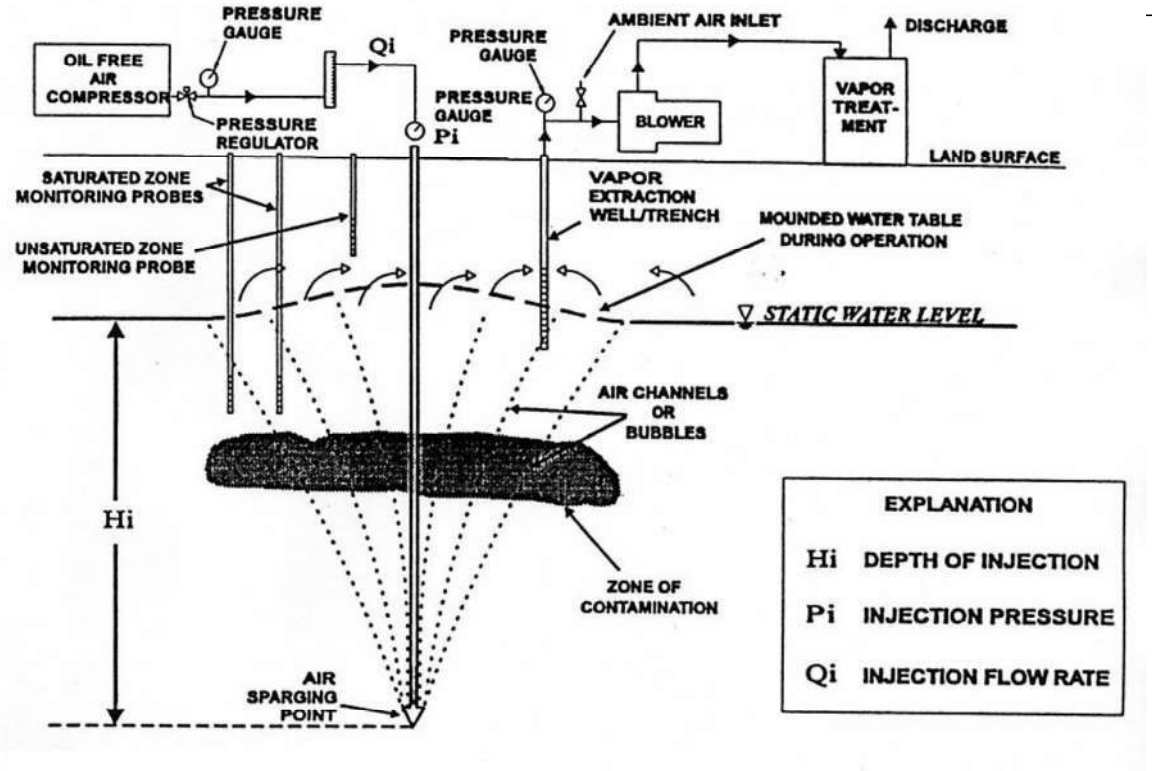

Soil Vapor Extraction
Vacuum
GAC
Preheater
Catalyst Bed
Extraction Well
Air Blower
L/V Separator
Liquid Phase Carbon Adsorption
Catalytic Oxidation
Water Table
Air Sparging
US EPA


Atmospheric Discharge
Appropriate Vapor Treatment
Blower
UST
Air Flow
Air Flow
Free-phase Petroleum Product
Legend:
Vapor Phase
Adsorbed Phase
Dissolved Phase

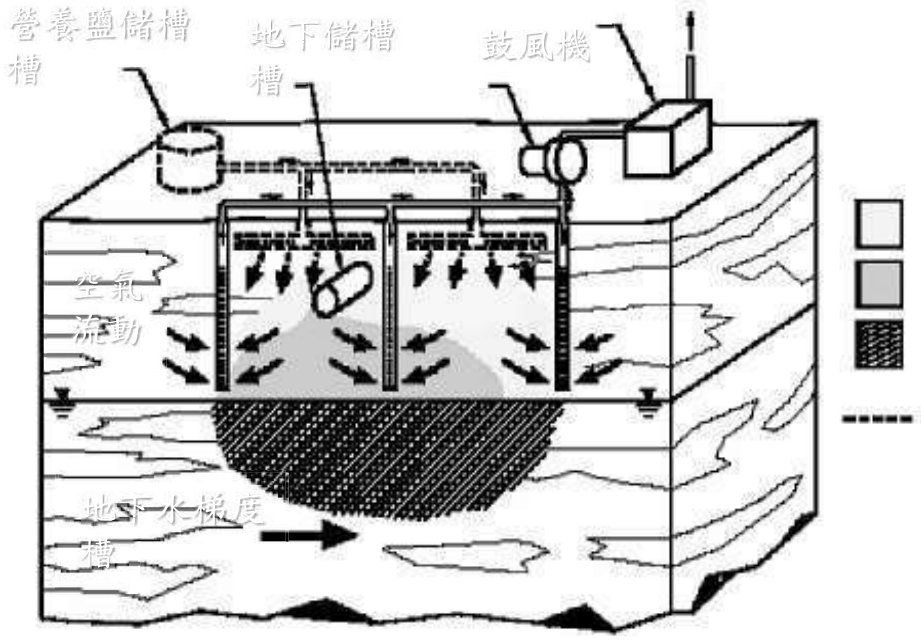
SVE

US EPA

air sparging

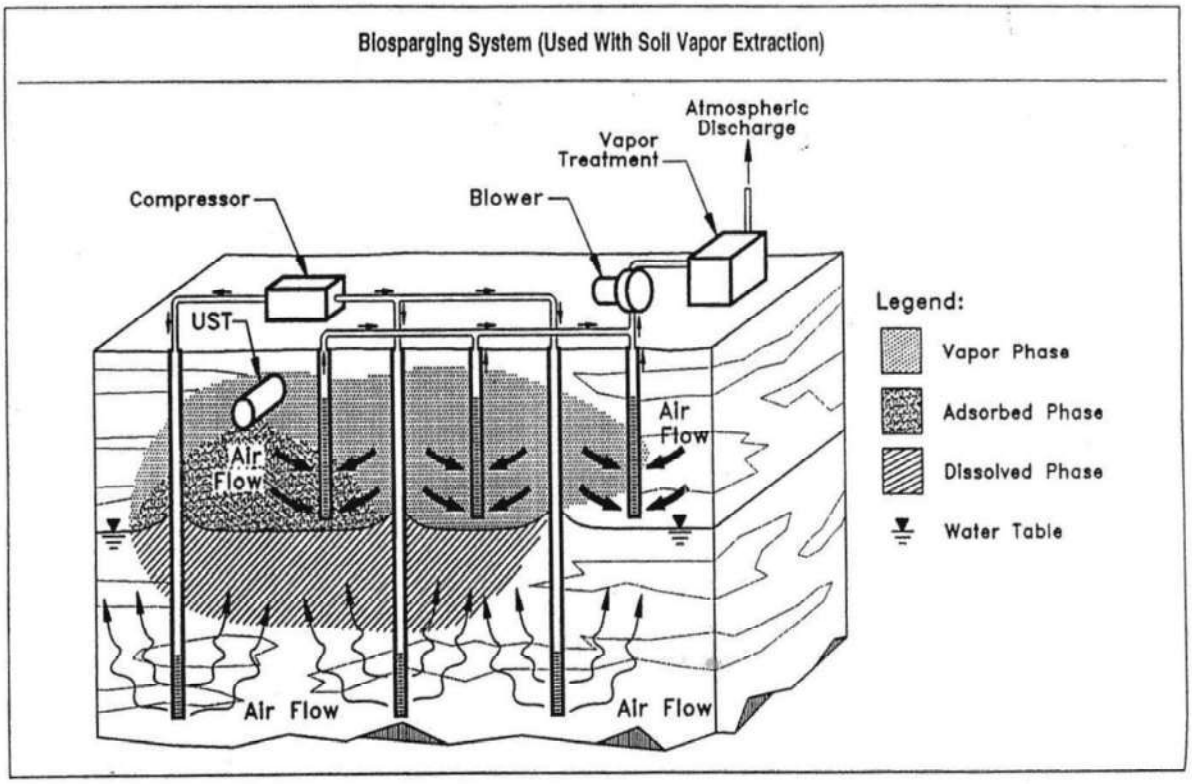


US EPA



bioventing

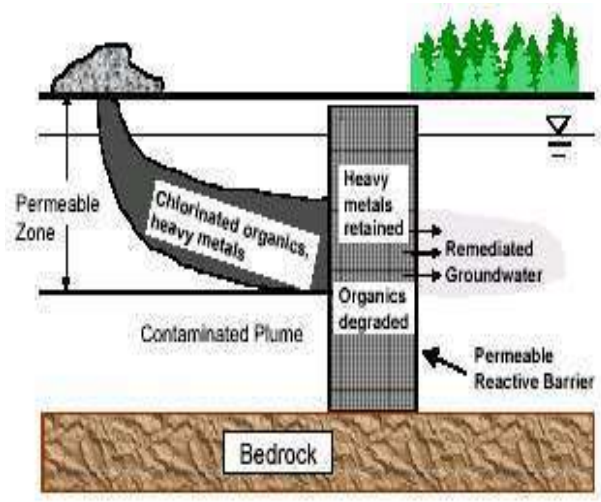
US EPA

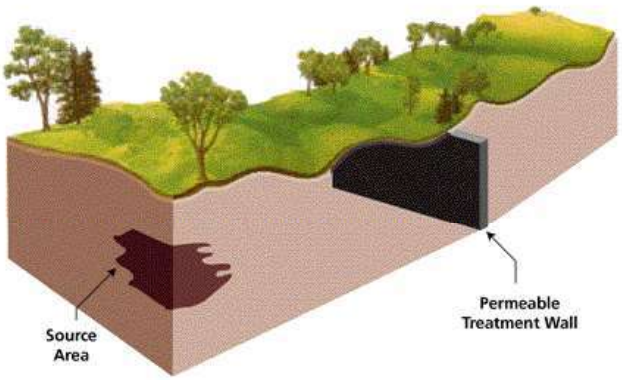


biosparging

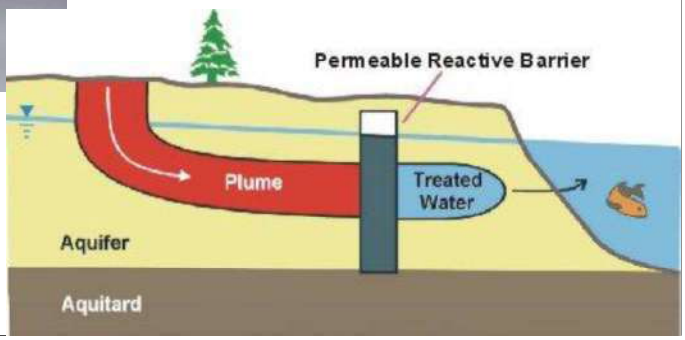
US EPA

permeable reactive barrier, PRB

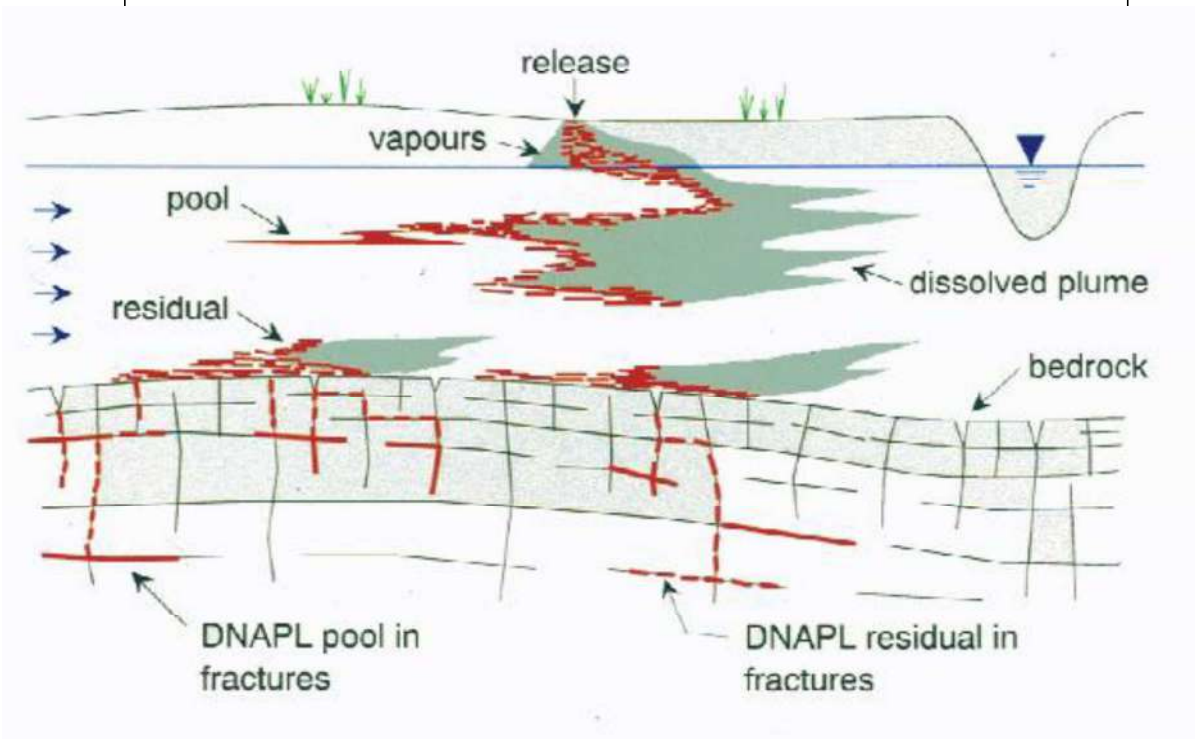




US EPA



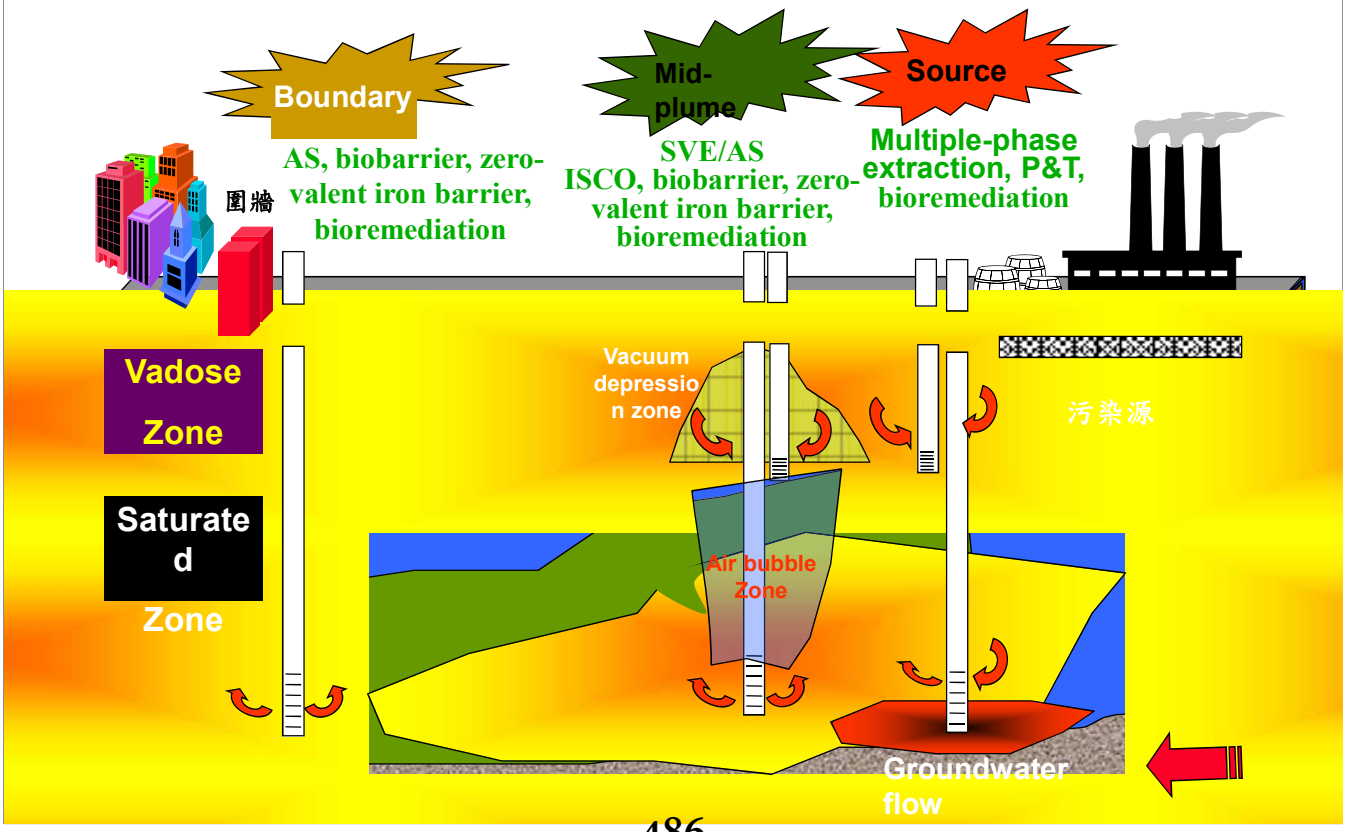
Dense non-aqueous phase liquid (DNAPL) Source Zone



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

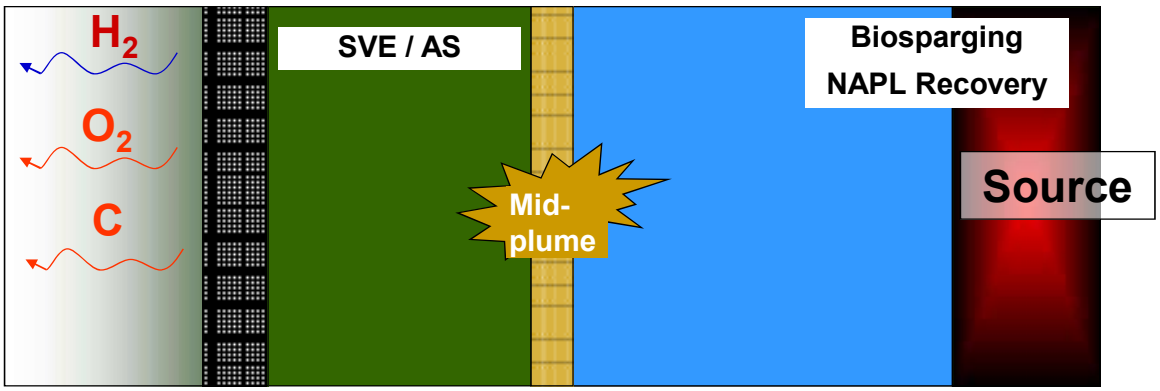


Biobarrier

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

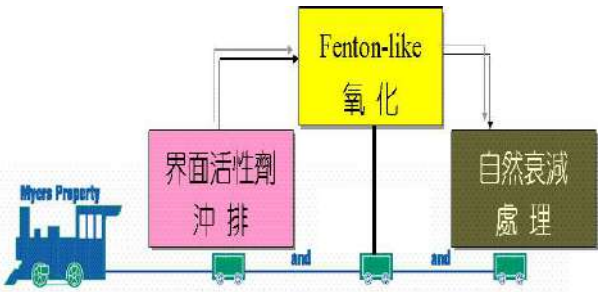
Oxygen Release Compound.

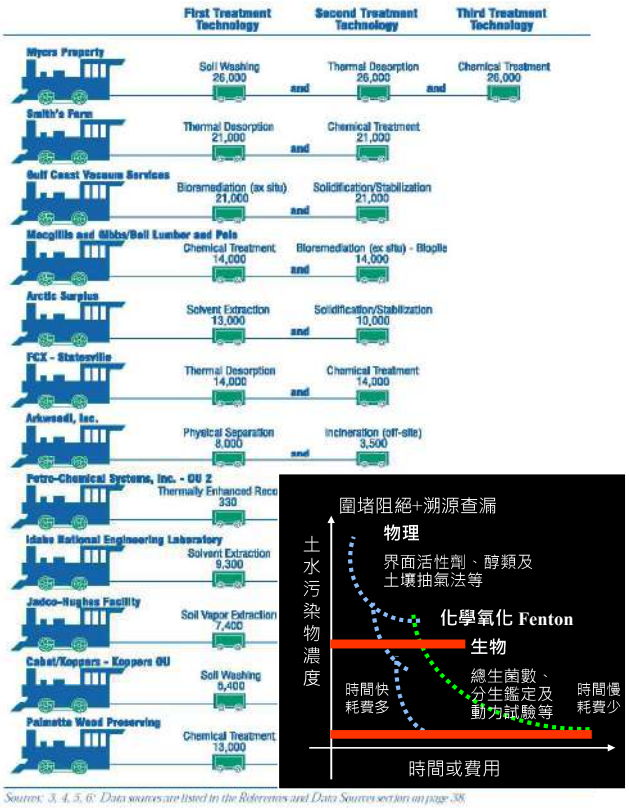
Biobarrier



Groundwater flow

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

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Protection of Farmland Contamination:
Investigation and Risk-based Approached Remediation Technology

Zueng-Sang Chen
Emeritus Professor
Department of Agricultural Chemistry, National Taiwan University
Tel: +886-2-2369-9677; soilchen@ntu.edu.tw
Website: http://lab.ac.ntu.edu.tw/soilsc/
ORCID: http://orcid.org/0000-0002-8499-4924

Contents

- A. Design the soil sampling projects.
- B. Select the soil sampling method to make the best survey report.
- C. How to map the high risk potential polluted area based on the general soil survey reports?
- D. Summary of soil remediation technologies of rural soils.
- E. Hypothesis and case studies to explain the relationships between heavy metals concentration in brown rice and in soils.
- F. Integrated experiences of remediation strategies by health risk assessment approaching technology for As, Cr, Ni-contaminated rural soils in Taiwan

Soil properties related to fates of soil pollutants

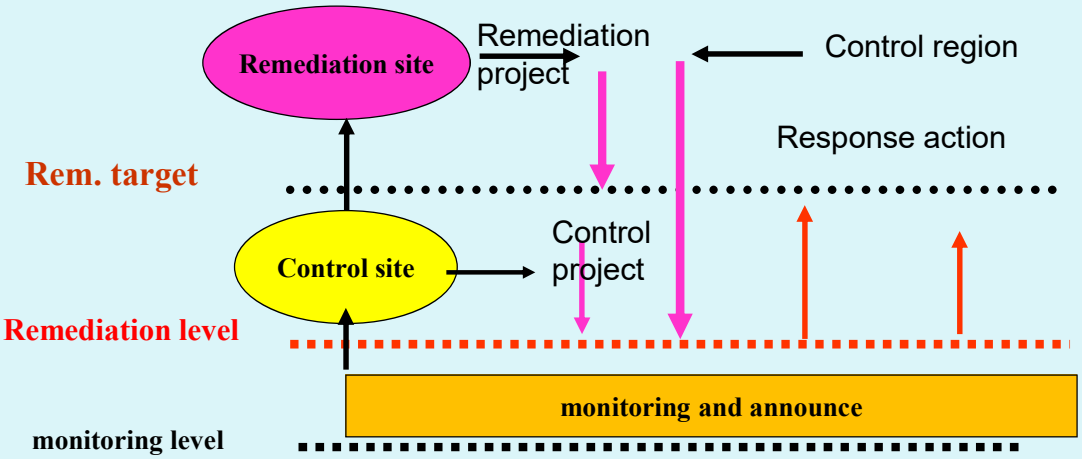
- pH: related to solubility of pollutants
- organic matter: absorption of pollutants
- clay%: absorption site and transformation
- soil texture classes: related to soil porosity, adsorption and transformation
- clay mineral composition: movement and adsorption of pollutants
- characteristics of soil pollutants and pollution status

Sampling time

- baseline survey
- Environ. Safety Assessment, ESA
- monitoring survey
- remedial investigation and feasibility study, RI/FS
- Delineation survey
- remedial action
- Validation after soil remediation
- Early warming system assessment

Soil remediation Act and Action in Taiwan

Pollution source is identified Pollution source is not identified



Part A
Design of soil sampling project

- Objectives
- Field investigation
- Proposal of sampling project and budget estimation
- Preparation of soil sampling
- Field sampling and pre-treatment
- Lab analysis
- Data treatment and analysis
- Write reports and make a evaluation of risk

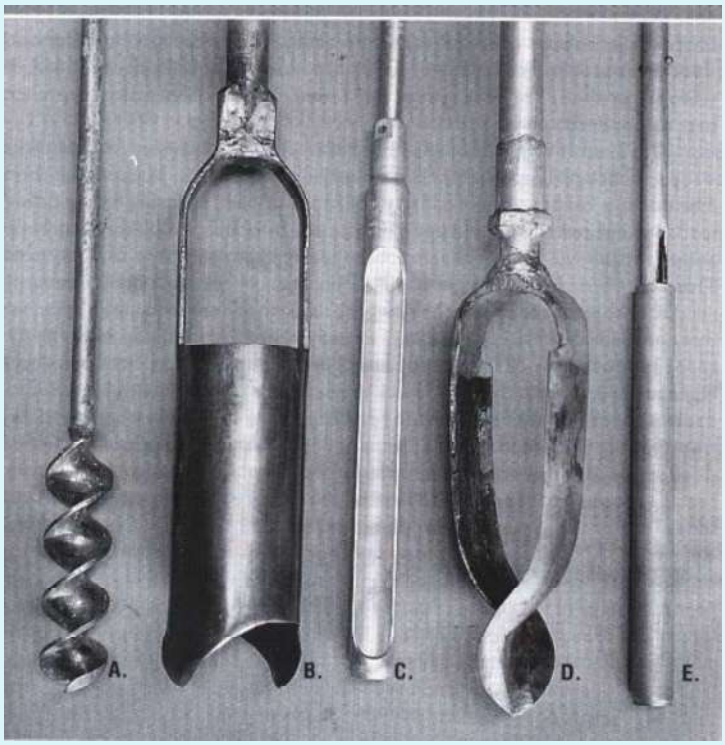
Selection of sampling tools

- Hand - held shovel
- Hand - held auger
- Split - barrel sampler
- Thin - walled tubes sampler
- Piston rod soil sampler
- Dual tube soil sampler

(NIEA-Taiwan EPA, 2001) **NIEA S102.60B**

sampling tools in shallow soils

- Auger: for heavy metals analysis
- Surface soil (0-15 cm)
- subsurface soil (15-30 cm) or deeper
- maximum reliable depth: 2 m
- soil was disturbed



(Soil Survey Staff, 1993)

Powerprobe or Geoprobe

- diameter 1.5～3 inches
- Suitable fore different geology layers
- depths：10 meter depth
- benefit：fast speed

Powerprobe or Geoprobe
Apollotech Company.

Selection of auger

- Hollow stem auger
- Geoprobe or power probe
- Hydraulic rotary
- Cable tool
- Air Harmber
- Hydraulic geology
- budget
- Space for operation

Part B

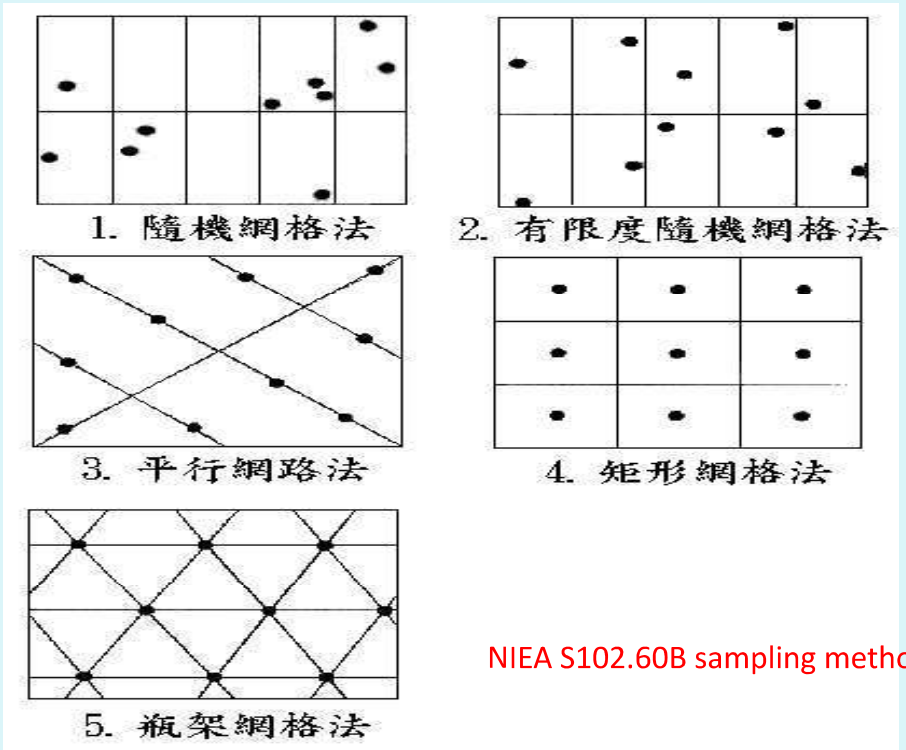
Location of sampling methods

- Judgmental sampling
- Simple random sampling
- Stratified sampling
- Systematic and grid sampling
- Adaptive cluster sampling
- Composite sampling

(NIAES, 2011)

Systematic and grid sampling

- Judgmental sampling
- Stratified sampling



- Judgmental sampling
- Systematic and grid sampling

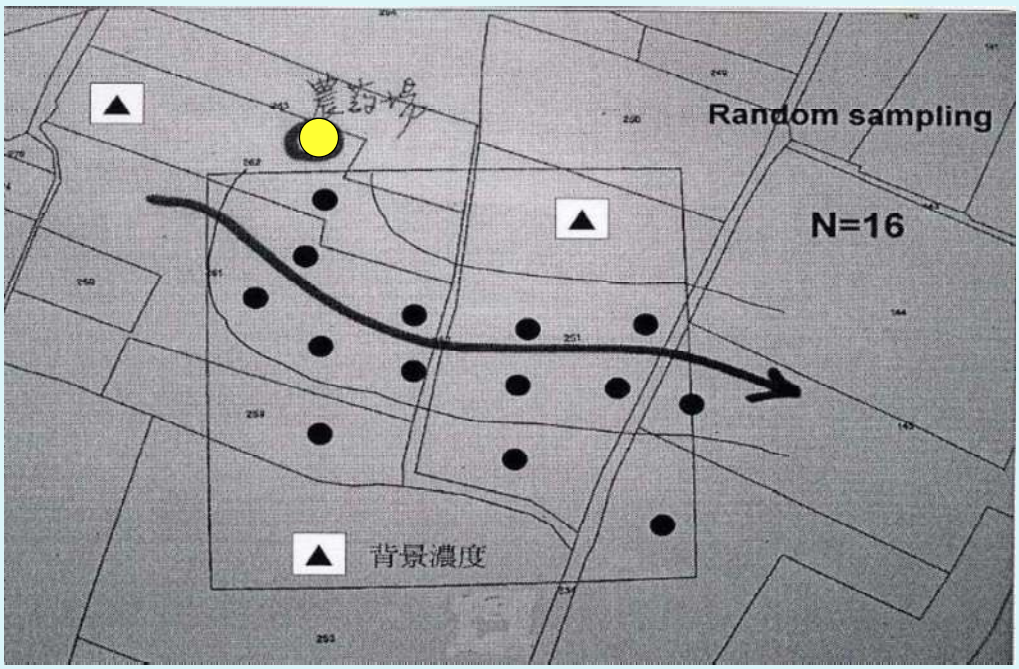
NIEA S102.60B sampling methods

Soil sampling and strategy

- USEPA soil sampling design
- http://www.epa.gov/swerust1/cat/mason.pdf

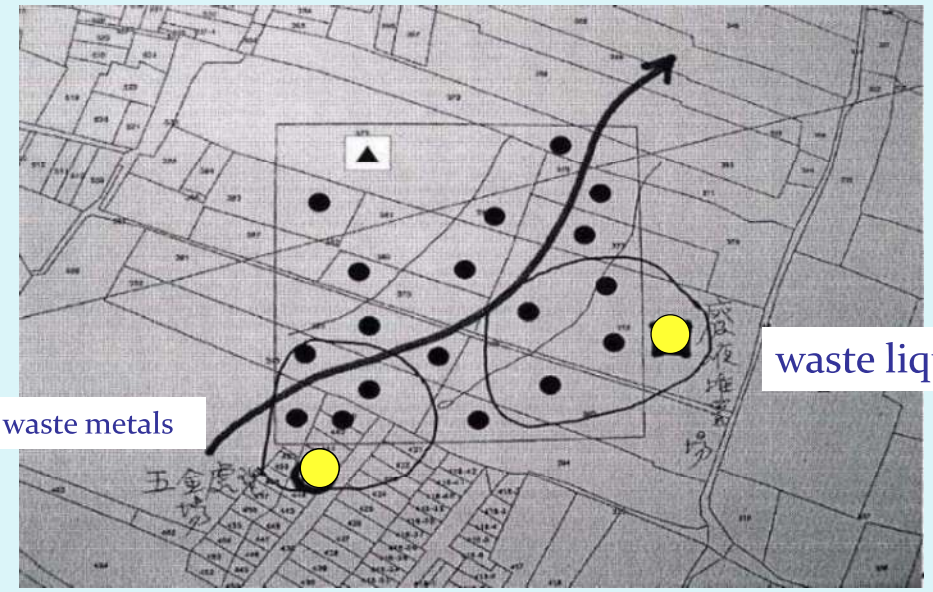
- USEPA soil sampling technology of verification report
- http://www.epa.gov/etvprgrm/pdfs/vrvs/01_vr_clement.pdf (not found, moved to other website)

Pesticides pollution



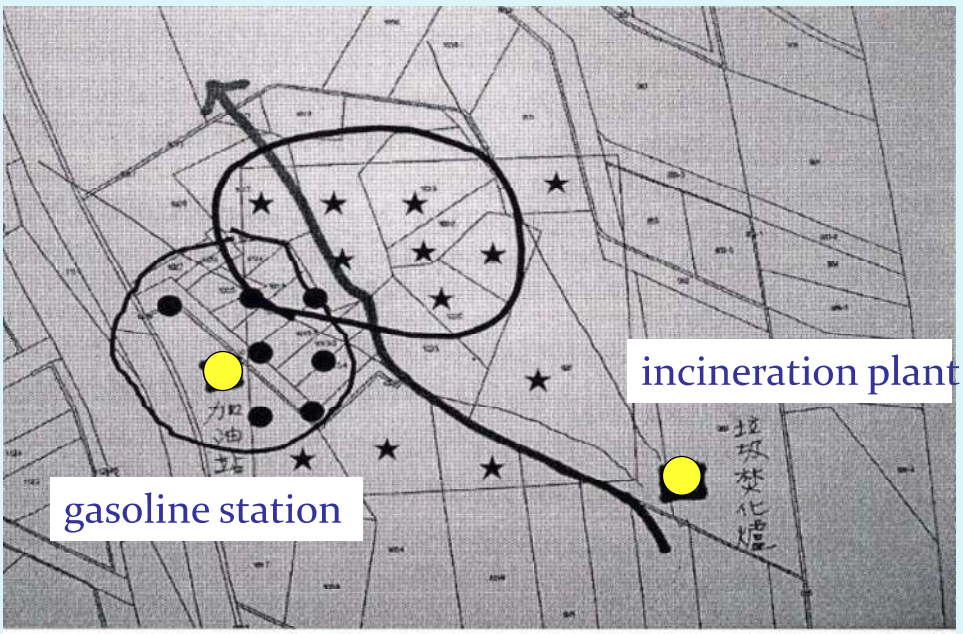
- Judgmental sampling
- Adaptive cluster sampling

Waste metals and liquid metals pollution



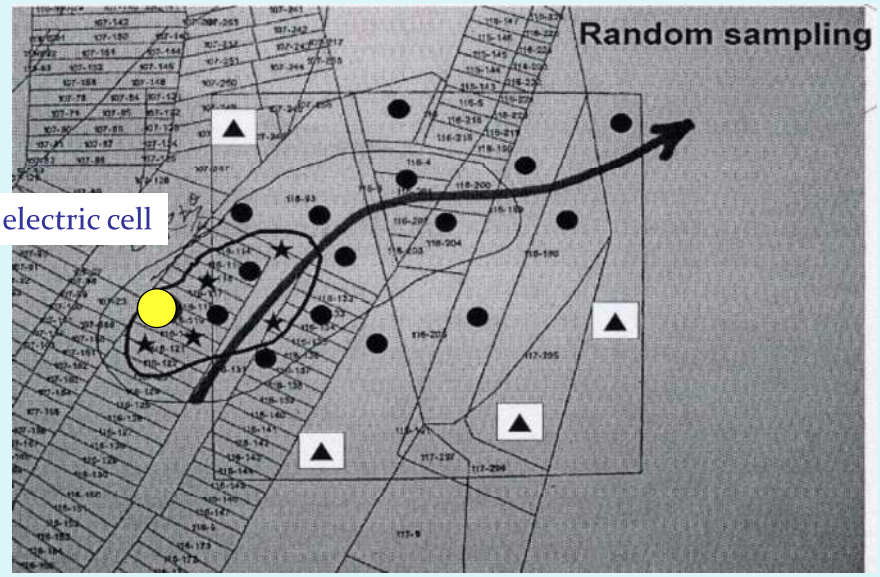
- Judgmental sampling
- Stratified sampling
- Adaptive cluster sampling

Gasoline station and incineration plant



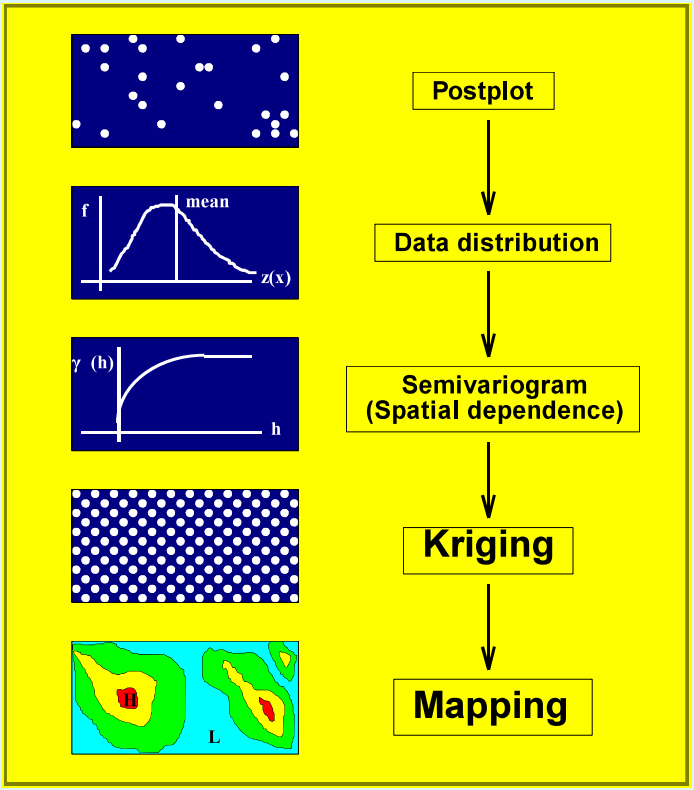
- (Judgmental sampling)
- (Stratified sampling)
- (Adaptive cluster sampling)

Electric cell site pollution



- (Judgmental sampling)
- (Stratified sampling)
- (Adaptive cluster sampling)

Geostatistics technology



Flow chart of geostatistics
(Dar-Yuan LEE, 2003)

Part C.
How to map the high risk potential polluted area based on the general soil survey reports?

Indicator of Nemelow pollution index (Pn)

- Consider the each metal's concentration and maximum concentration of pollution metals in soils

$$P_n = \sqrt{\frac{1}{2}\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{C_i}{C_{Si}}\right)^2 + \max\left(\frac{C_i}{C_{Si}}\right)^2\right]}$$

Pn：Nemelow pollution index

Ci：Real concentration of i pollution metal

Csi：the background concentration of i metal pollutant in rural soils

Based on the metal background concentration of metals of Taiwan rural soils (Chen et al., 2012)

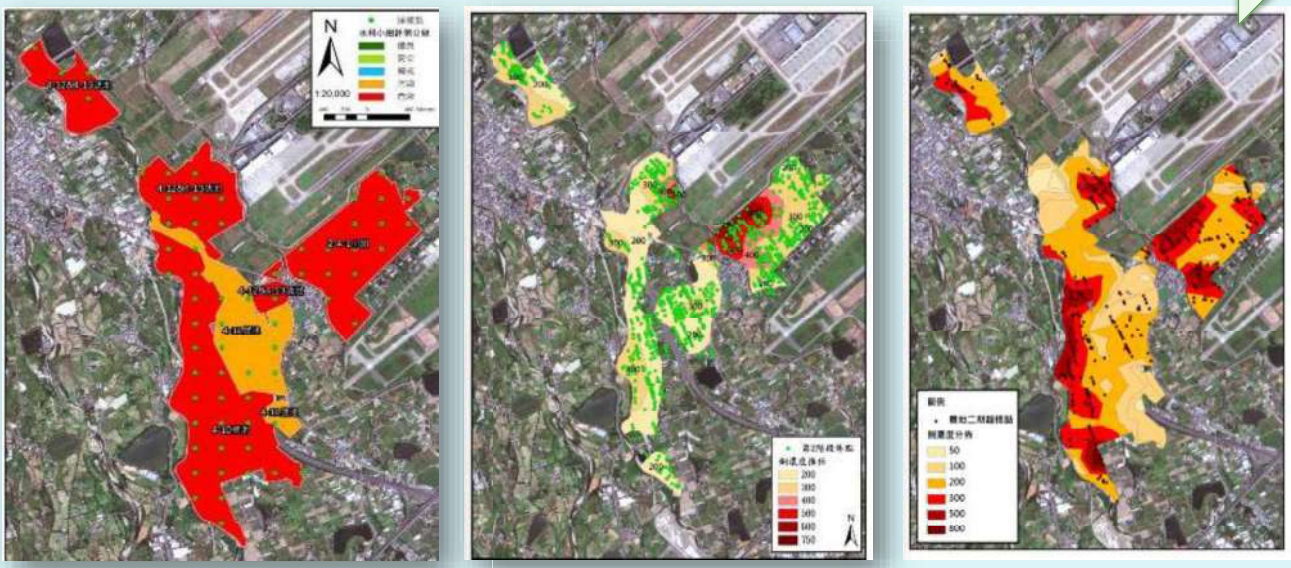
Key indicator for high potential pollution sites

- Ratio of metal concentration to the background concentration of metals in surface soils (0-15 cm)
- Nemelow's pollution ratio **(Pn) > 3**: high potential pollution
- Nemelow's pollution ratio **(Pn) > 2**: slight potential pollution
- Nemelow's pollution ratio **(Pn) > 1**: almost no pollution

Case study in northern Taiwan

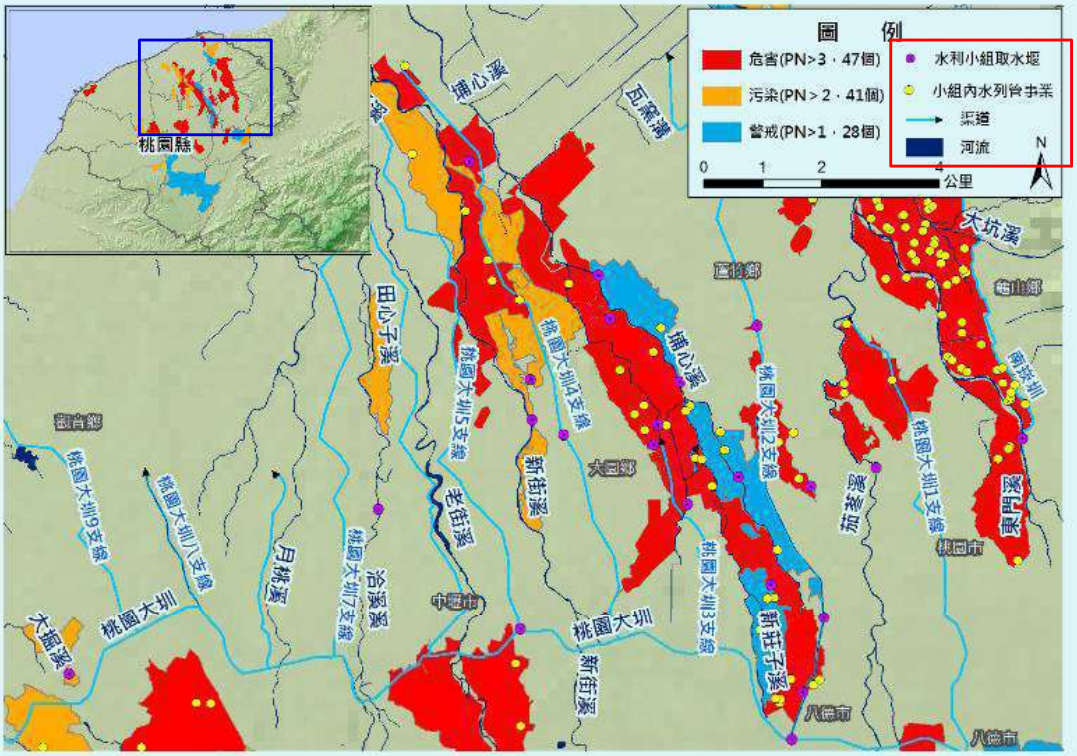
全國重金屬高污染潛勢農地之管制及調查計畫,2011

High potential sites → Screen by ratio of metal to background → Detailed survey for more sites



High pollution potential sites in Taoyuan

全國重金屬高污染潛勢農地之管制及調查計畫, 2015



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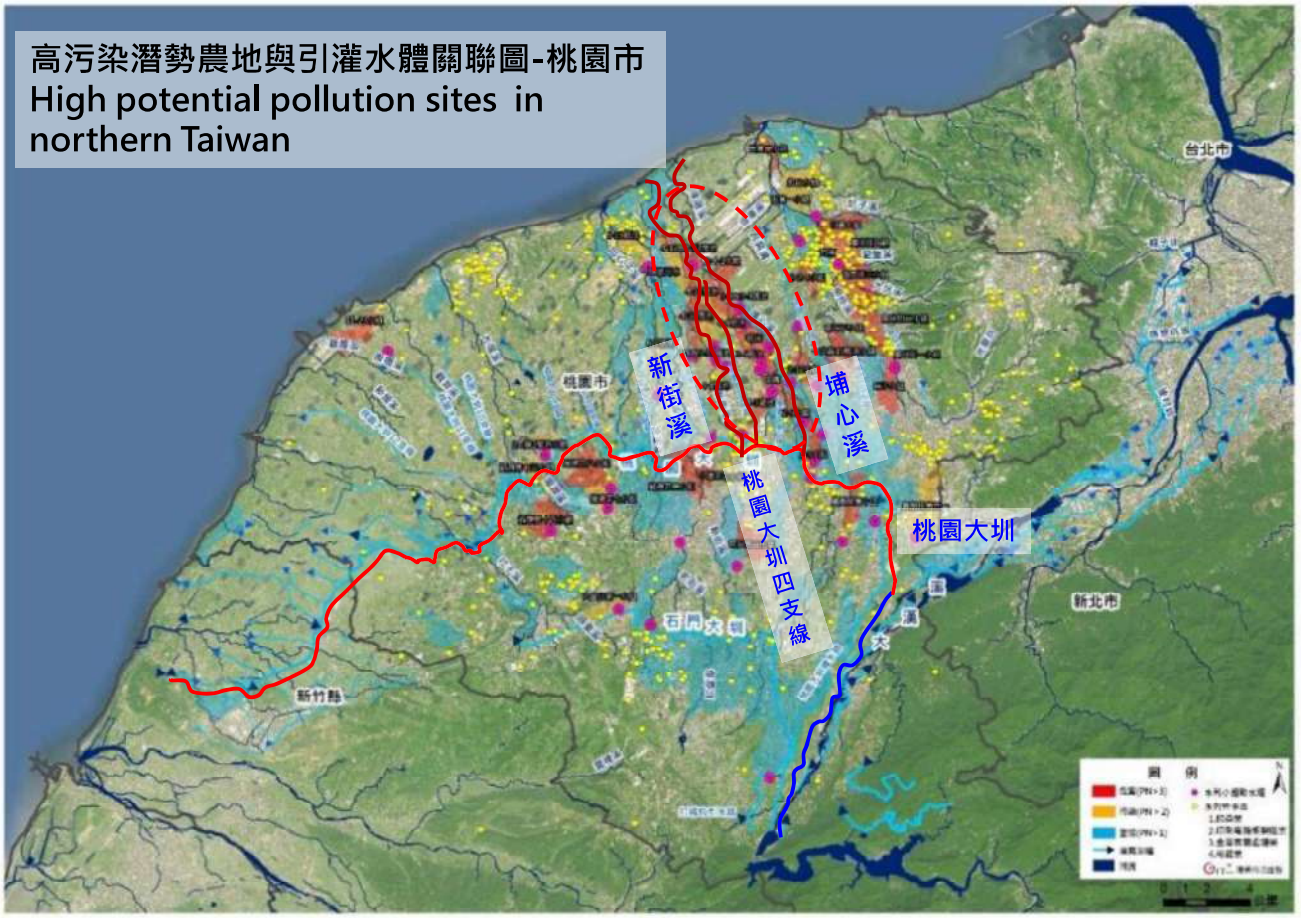
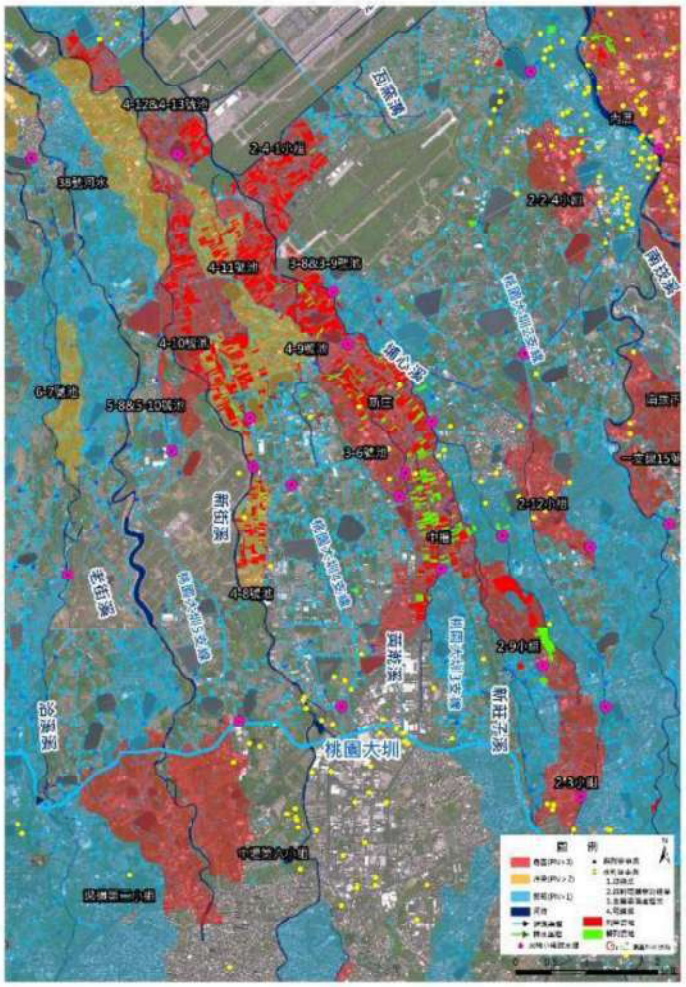
(動畫輔助說明)

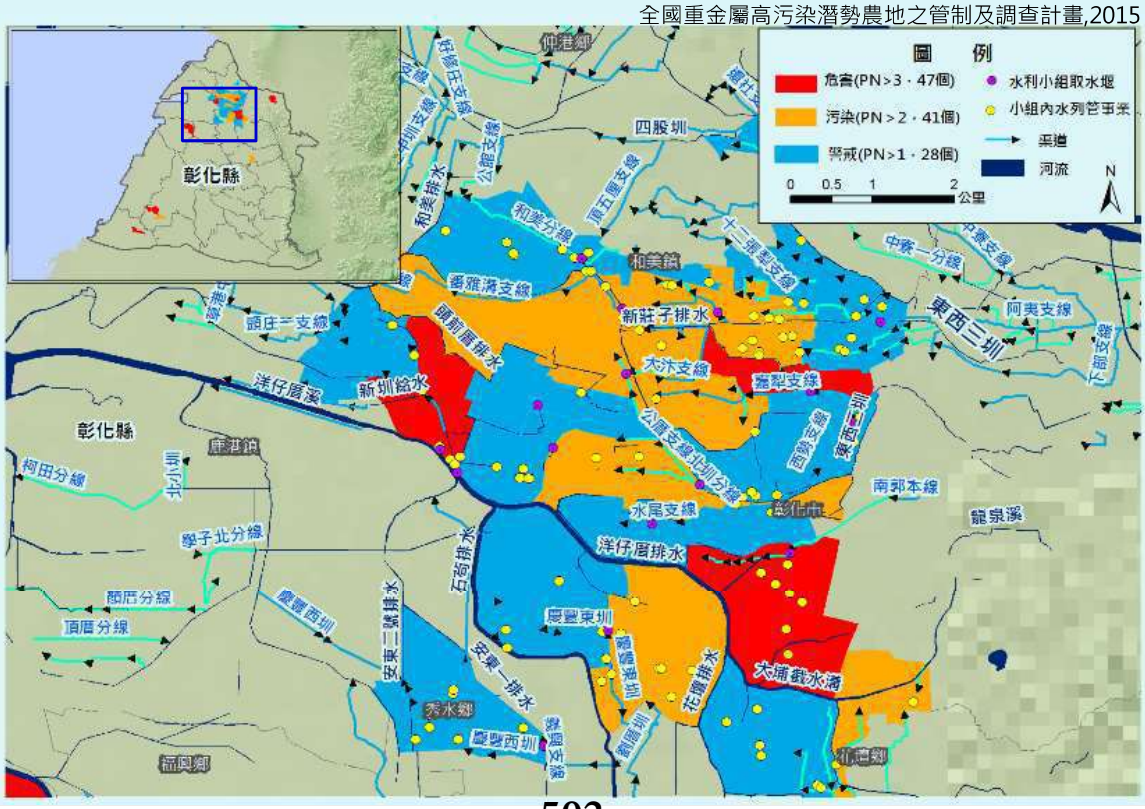


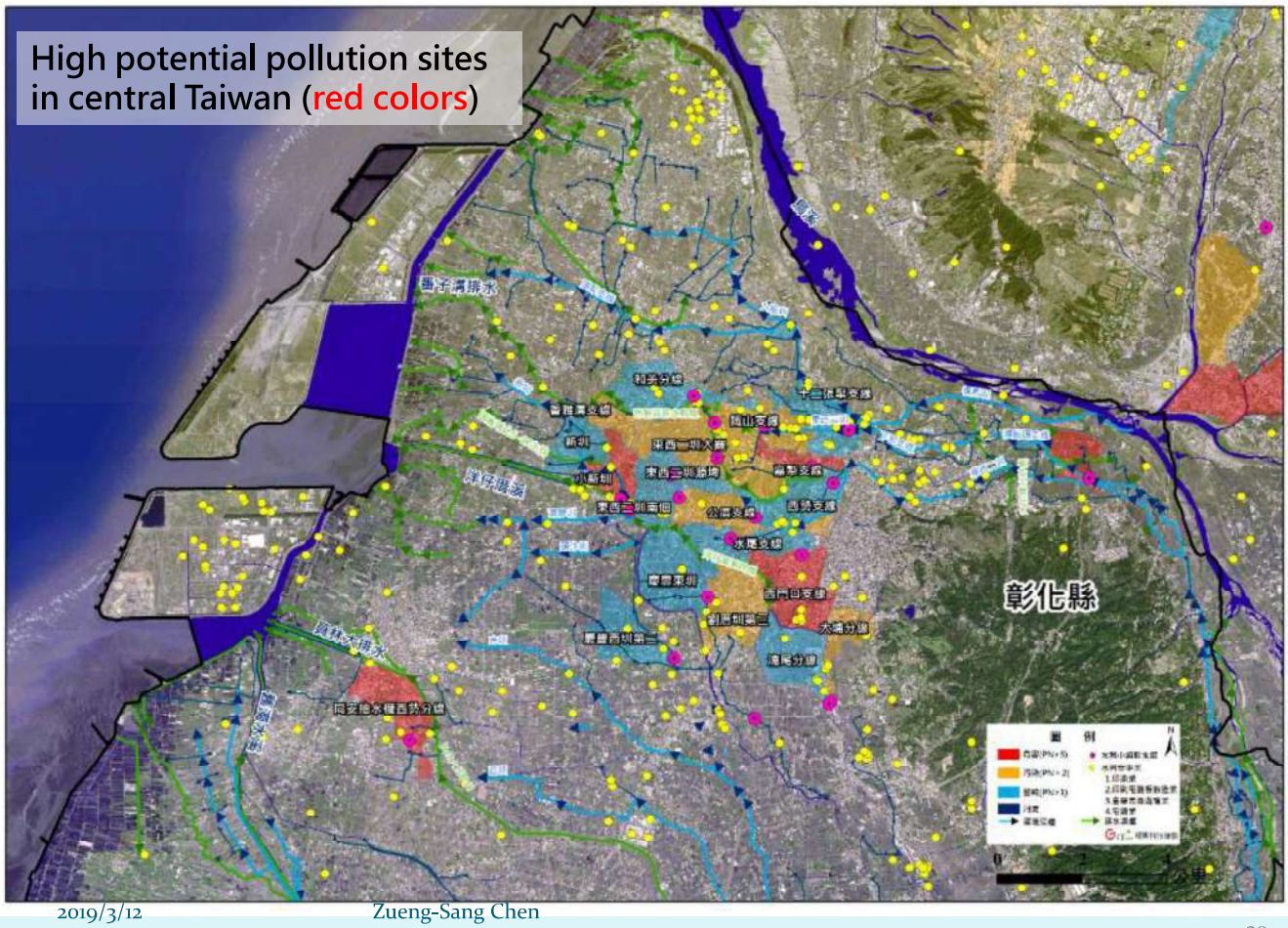
- Relations of high potential pollution sites and irrigation water quality
- Wastewater were illegally discharged from industrial park



High pollution potential sites of Central Taiwan

全國重金屬高污染潛勢農地之管制及調查計畫,2015





Part D.
Summary of soil remediation technologies for rural soils

- **Chemical methods**
  - a. extraction method
  - b. reduced condition
  - c. stabilization

- **Engineering methods**
  - a. removal contaminated soils and cover with clean soils
  - b. cover with clean soils
  - c. soil washing
  - d. electrokinetics

- **Biological methods**
  - a. phytoremediation
  - b. phytostabilization
  - c. microorganisms

In-situ physico-chemical method

Solidification

By adding the chemical materials to mix or react with the pollutants in the soil

To solid the contaminated soil as very low release material under natural raining system

To reduce the pollutants released from the solid materials.

Cost effective?

in-situ physico-chemical method

Soil amendments

To reduce the bioavailability of metals treated with different non-toxic materials as soil amendments

Reduce the bioavailability of metals in soils by addition of lime materials, phosphate materials, zeolite, hydrous metal oxides, or organic materials, etc.

Cost-effective?

Any other materials can be used?

in-situ physico-chemical method

Attenuation

To mixture and dilute the soils of whole soil depths

Dilution the surface contaminated soils by mixing with the subsurface clean soils by machines.

About 200 ha of Taiwan rural soils were cleaned up by this method.

How to approve it is effective?

What is the limit factor to apply this method? (soil depth)

in-situ physico-chemical method

Soil Washing

Treated with different acids including HCl, HNO_3, phosphoric acid, etc.

Must be recycled of the chemical acids to reduce the remediation cost

Need to treat the waste water to discharge into the environment

Need to recovery the soil characteristics and soil function for crop productivity.

Very high cost including remediation, waste water treatment and soil function recovery

in-situ physico-chemical method

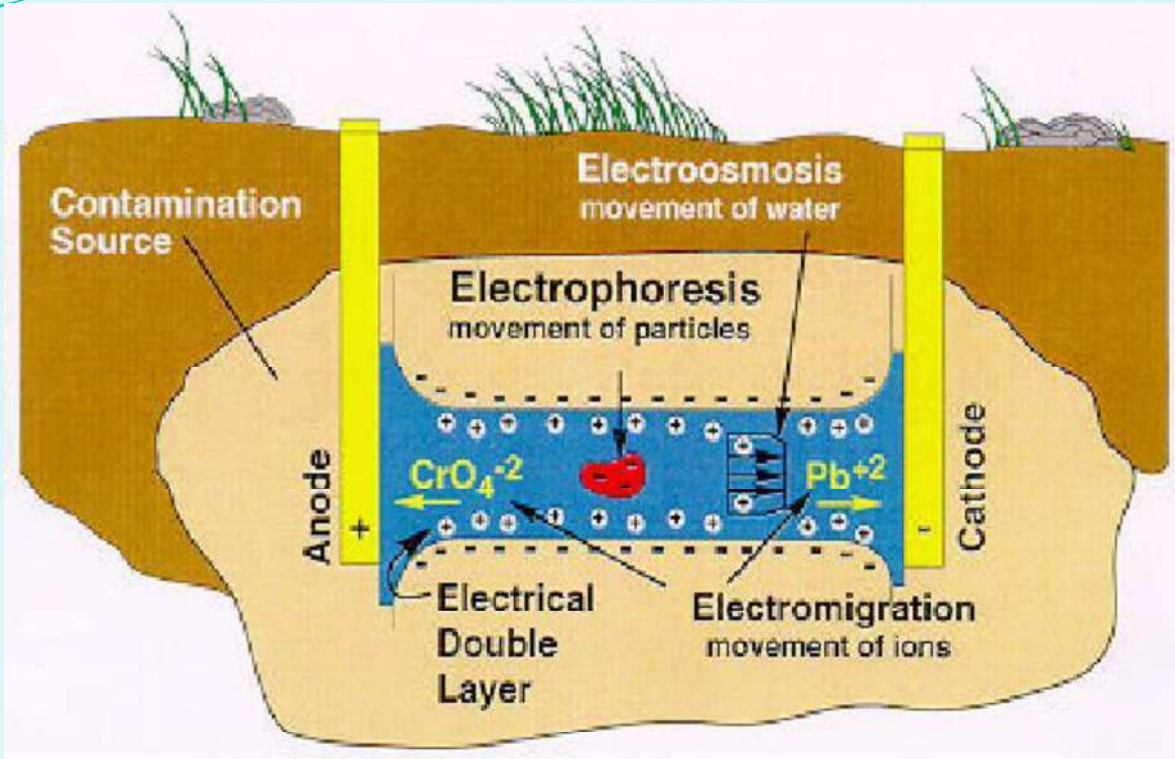
Electrokinetics (EK)

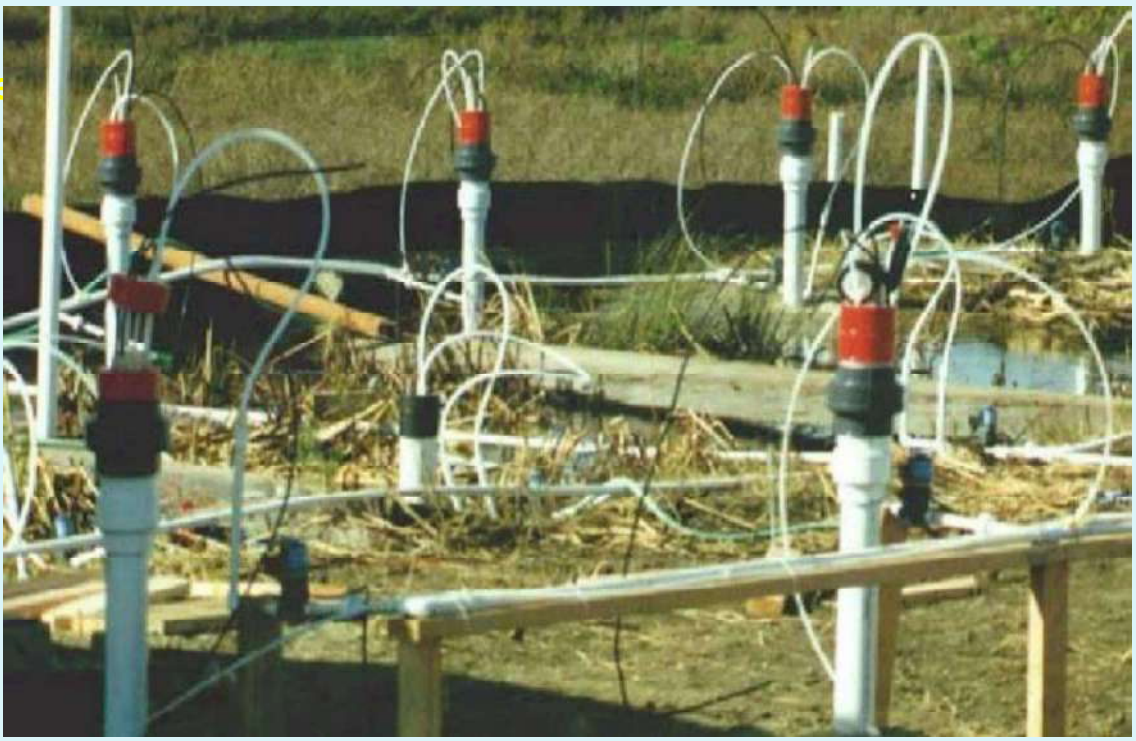
Electric current induced movement of ions to electrodes and to remove the pollutants.

Need to evaluate the efficiency to remove the pollutants

Cost-effective? High energy?

Why it is not successful in the field site?





In-situ: electrokinetics and heating

*V*itrification

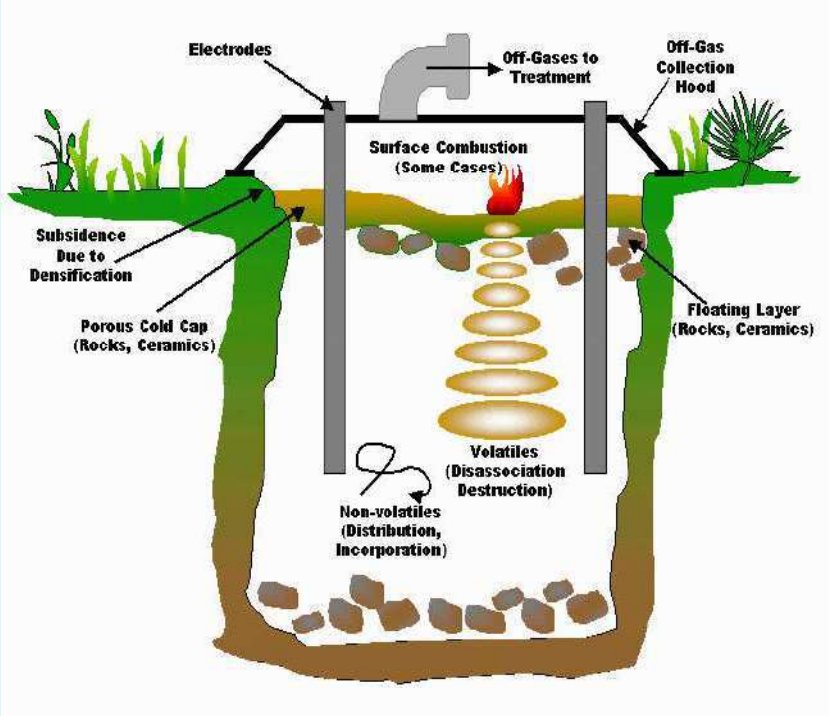
Heating to produce a glass-like, nonporous materials.

300-600 degree C for Hg sites and pesticides sites in Taiwan.

More than 1000 degree C for high concentration of Hg sites and dioxin sites

Very high cost techniques.

Vitrification



U.S. EPA TIO

In-situ: biological method

Phytostabilization

To promote vegetative growth to immobilize metals of contamination site (eg. vetiver grass)

To produce the green landscape and to stabilize the contaminated sites

Can not significant remove the pollutants from the sites

Very low cost (< US$ 10/ton soil)

ONLY recommendation for low contaminated sites

In-situ: biological method

Phytoremediation (or phytoextraction)

To significantly remove the metals by plants.

420 plant species found for different metals uptake

Higher than **100 times of general plant species** (>100 mg/kg for Cd, >1000 mg/kg for Cu, Cr, Ni, Pb, or >10000 mg/kg for Zn)

Highly accepted by the local community for low contamination sites, especially for European Union.

Very low cost **(< US$ 10/ton soil**)

ONLY recommendation for low contaminated sites

Cost-effective ?

Hyperaccumulator

Thlaspi caerulescens

Pb 8,500 mg/kg
Cd 164-2,800 mg/kg
Zn 27,000 mg/kg

Dr. Rufus L. Chaney

Phyto-stabilization

(42 species tested in the field of Taoyuan, Taiwan)

12 species (total 24,000 plants) were studied in 1.2 ha of Cu, Zn, Cr and Ni-contaminated soils

(Lai et al., 2010)

Chemical remediation techniques

- acid washing or extraction method
- Stabilization or solidification
- chemical oxidation, reduction or neutralization)
- Electrokinetics

Chemical Stabilization or solidification method

By adding the chemical materials (*liming materials*) to stabilize or react with the pollutants in the soil

To *solid the contaminated soil* as very low release material under natural raining system

To reduce the pollutants released from the solid materials.

Cost effective?

Case study for *stabilization technology* in USEPA

Case studies for stabilization technologies (modified from U.S. EPA.[10])

Site/ contractor	Contaminant (concentration)	Treatment volume	Physical form	Binder	Percentage binder(s) added	Treatment (batch/ continuous in situ)	Disposal (onsite/ offsite)	Volume increase, %	Scale of operation
Midwest, U.S. Plating Company, Envirite	Cu, Cr, Ni	16,000 yd^3	Sludge	Portland cement	20%	In situ	Onsite	> 0	Full scale
Marathon Steel Phoenix, AZ Silicate, Tech.	Pb, Cd	150,000 yd^3	Dry-landfill	Portland cement and silicates (Toxsorb)™	Varied 7–15% (cement)	Concrete batch plant	Landfill	NA	Full scale
N.E. Refinery ENRECO	Oil sludges, Pb, Cr, As	100,000 yd^3	Sludges, variable	Kiln dust (high CaO content)	Varied, 15–30%	In situ	Onsite	>Varied, ~ 20% average	Full scale
Amoco Wood River Chemfix	Oil/solids Cd, Cr, Pb	90,000,000 gallons	Sludges	Chemfix proprietary	NA, proprietary	Continuous flow (proprietary process)	Onsite	Average 15%	Full scale (site delisted 1985)
Pepper Steel & Alloy, Miami, FL VFL Technology Corporation	Oil sat: soil Pb (1000 ppm) PCBs (200 ppm) As (1–200 ppm)	62,000 yd^3 (plus 5000 tons of surface debris)	Soils	Pozzolanic and proprietary	~ 30%	Continuous feed (mixer proprietary) design	Onsite	~ 1%	Full scale
Vickery, OH Chemical Waste Management	Waste acid PCBs (< 500 ppm), dioxins	~235,000 yd^3	Sludges (viscous)	Lime and kiln dust	~ 15% CaO ~ 5% kiln dust	In situ	Onsite (TSCA cells)	>~ 9%+	Full scale
Wood Treating, Savannah, GA Geo-Con, Inc.	Creosote wastes	12,000 yd^3	Sludges	Kiln dust	20%	In situ	Onsite lined cells	>~ 14%	Full scale
Wyandotte, MI Treatment Plant Chem Met	Various/combined	20 million gal/yr	Various	Lime		Continuous	Offsite (secure landfill)		In-plant process
Chem Refinery, TX HAZCON	Combined metals, sulfur, oil sludges, etc.	90,000 gal. (445 yd^3)	Sludges (synthetic oil sludges)	Portland cement and proprietary	NA	Continuous flow	Onsite (secure landfill)	>Estimated 10%	Full scale
Metalplating, WI Geo-Con, Inc.	Al (9500 ppm) Ni (750 ppm) Cr (220 ppm) Cu (2000 ppm)	3000 yd^3	Sludges	Lime	10–25%	In situ	Onsite landfill	> 4–10%	Full scale

Summary of remediation techniques used for rural soils in Taiwan

- **Phytostabilization** (** field scale)
- **Dilution attenuation** (*field scale) : heavy metals pollution
- Soil amendments (soil addition) (pilot scale)
- **Soil washing** (by acidic solution) : (*field scale)
- **Soil vapor extraction** (SVE) (*field scale)
- **Thermal desorption** (*field scale) (pesticides)
- Solidification: heavy metals pollution (in pilot scale)
- **Chemical oxidation** (gas station pollution) (*field scale)
- Electrokinetics separation (EK) (field)
- **Bioremediation** (oil pollution) (*field scale)
- **Land farming** (oil pollution sites) (*field scale)

Part E.
Hypothesis and case studies to explain the relationships between heavy metals concentration in rice and in soils

Six Hypotheses to explain the relationships between metals in crops and in soils

- Hypothesis 1: Single-metal abrupt toxicity threshold **(Chang, 1992)**
- Hypothesis 2: Soil-plant barrier **(Chaney and Giordano, 1977)**
- Hypothesis 3: Clean sludge concept **(Chaney, 1989)**
- Hypothesis 4: Uptake plateau concept **(Corey et al., 1987)**
- Hypothesis 5: Aging effect **(Rundle et al., 1982)**
- Hypothesis 6: Absence of evidence **(USEPA, 1995)**

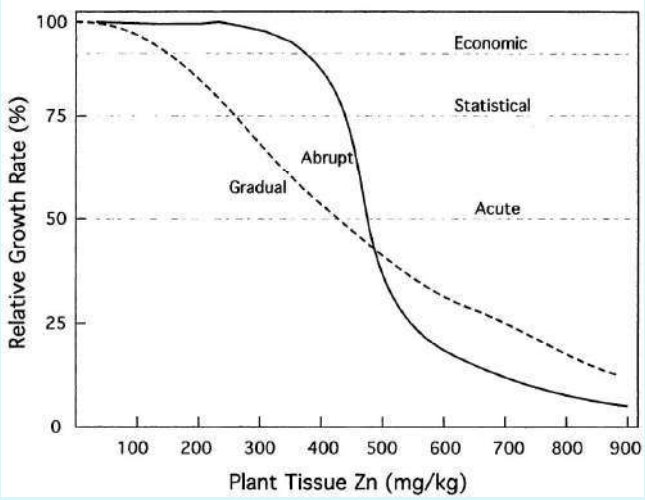
Key Concepts Governing Phytoavailability of Heavy Metals

1. Toxicity and bioavailability in metal spiked soil is greater than those in residual-treated soils. The salt effect overestimates metal bioavailability.
   - Salt Effects
2. Plant metal content plateaus at high residual loadings and the plateau is related to the residual's metal concentration and sorption capacity.
   - Plateau Effects
3. The soil-plant barrier limits transmission of many metals through food chain, either by soil barrier (chemical process limits metal solubility) or plant barrier (plant senescence from toxicity)
   - Soil-Plant Barrier

Cadmium, which has lower affinity for metal-sorbing phases (e.g., oxides, NOM), has the greatest potential for transmission through the food chain in levels that present risk to consumers (Chaney et al., 1987)

Hypothesis 1: Single-metal abrupt toxicity threshold

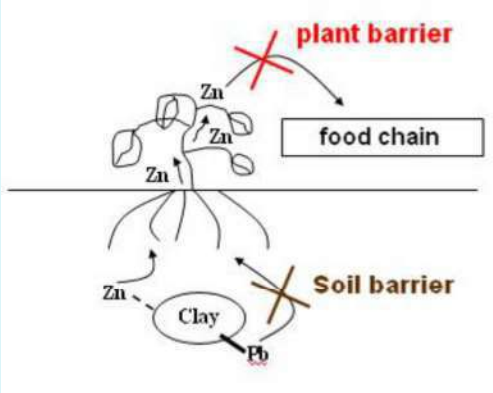
- The threshold concentration of economically significant crop yield loss (i.e. 10% reduction) is apparently smaller for **gradual** than for **abrupt** toxicity response.
- Not all plant species showed abrupt toxicity response pattern, some plant species exhibited gradual toxicity response pattern.
- The assumption, phytotoxic response in crops is an abrupt function of metal concentration in plant tissue, may underestimate the metal toxicity risks of some crops.



Schematic diagram of gradual and abrupt phytotoxic responses in a crop. (cited from McBride, 2003)

Hypothesis 2: Soil-plant barrier

- Assumption: The human health risk from food chain is negligible because the **soil-plant barrier** limits transmission of many toxic metals through the food chain.
- Some studies showed that the transfer of Cd from soil to seeds of wheat, corn, sunflower, flax, and palak tissue can be high enough to exceed health standards in some countries, even in slightly or moderately Cd contaminated land. **(Nan et al., 2002; Sharma et al., 2007)**
- It is doubtful to conclude that the barrier provides protection for the human food chain in all cases, especially for **Cd, Zn, Mo, and Se**.

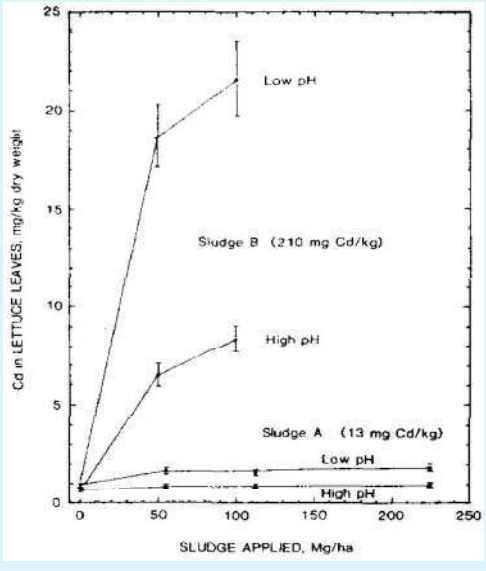


Schematic diagram of soil-plant barrier

Hypothesis 3: Clean sludge concept

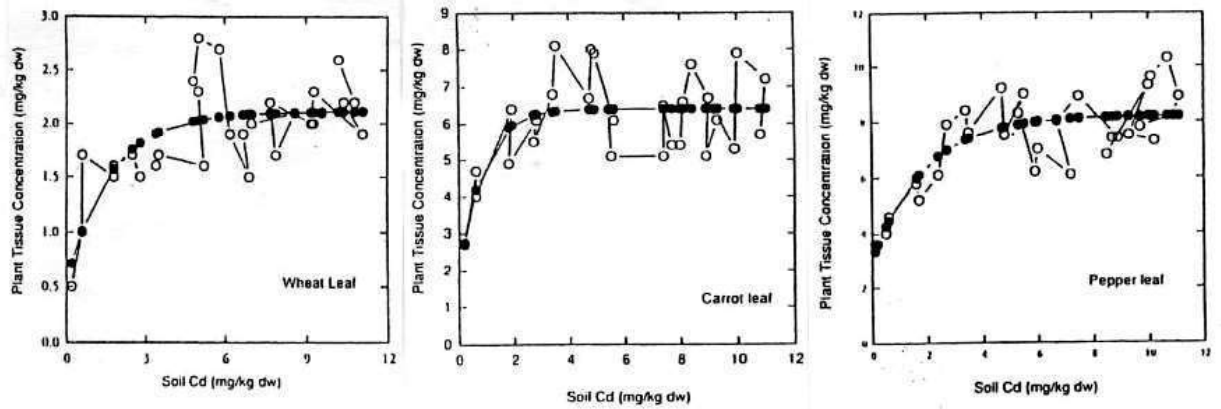
- Assumption: Crop uptake of soil Cd is determined solely by **sludge Cd total concentration**, when Cd input rate were fixed.
- Many researches have also **failed to support** the concept of "Clean Sludge". (Zarcinas et al.,2001; Whatmuff, 1999)
- It is clear that the **chemical forms of metals in sludge and soil and soil conditions** determines the solubility and toxicity of metals.

Lettuce response to two sludge applied and pH effect.
(cited from Chaney, 1990)



Hypothesis 4: Uptake plateau concept

- Assumption: The metal concentrations in plant tends to **reach a maximum** as the cumulative sludge application increases.
- The short-term sludge experiments with plateau effect may be caused by **temporary soil pH increases**, **growth dilution**, **ion competition effects**, or **root toxicity effects** that limit the crop's metal uptake ability. **(McBride, 2003)**
- The evidence of plateau phenomena under **field conditions** over **longer periods** is more reliable but rare.



Relationship between **Cd** concentration in plant leaf and soil, and the data were fitted by nonlinear regression. (cited from Chang et al, 1996)

Hypothesis 5: Aging effect (Time bomb)

- Fig. 21 shows that metals extracted by $CaCl_2$ (Cd, Zn, Ni), NaOH (Zn and Ni), and EDTA (all metals) increased within the first 10 years of sludge addition and then no further change.
- Assumption: The **permanent immobilization ability** of soil or sludge can reduce the opportunity of **"time bomb"** effect.
- However, some studies found the sludge-bound metals in soils may become more soluble or bioavailable after the long termination of sludge application.

(Walter et al., 2002; Antoniadis et al., 2007)

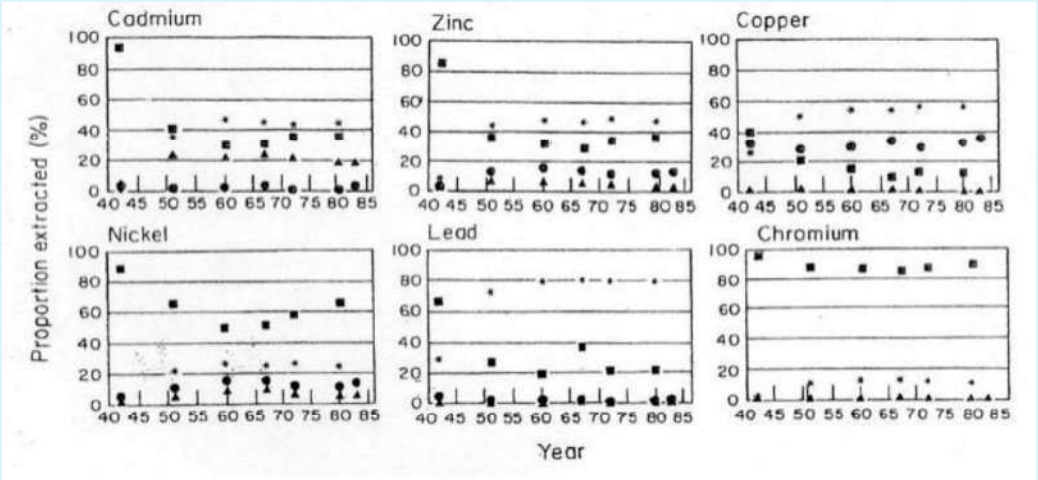


Fig. 21. Percentage extraction of six metals in four sequential extracts (▲ = $CaCl_2$; ● = NaOH; * = EDTA; ■ = aqua regia) The years referred to are 1940 to 1985. (extracted from McGrath and Cegarra, 1992)

Hypothesis 6: Absence of evidence

• Assumption: The **unregulated toxic metals** in sewage sludge will **not cause significant risks** to human and ecosystem because of **scare evidence.**

• After reviewing new information concerning Cr and the land application of sewage, USEPA decided to delete Cr limit from the land applied sewage sludge regulation.
(USEPA, 1995)

• However, in tropical area the organic matter in soil decomposes quickly, the risks will be higher in Cr-contaminated soil. In addition, soil organic matter shows weak capability to reduce Cr^{6+} under high pH condition.
(Bartlett and Kimble, 1976)

Heavy metals regulation of rural soils in Taiwan

- **As 60 mg/kg**
- **Cd 5 mg/kg** (20 mg/kg for general soils)
- **Cu 200 mg/kg** (400 mg/kg for general soils)
- **Cr 250 mg/kg**
- **Hg 5 mg/kg** (20 mg/kg for general soils)
- **Ni 200 mg/kg**
- **Pb 500 mg/kg** (2000 mg/kg for general soils)
- **Zn 600 mg/kg** (2000 mg/kg for general soils)

Based on Soil and Groundwater pollution and remediation Act of Taiwan EPA (2011)

Cited from Guo et al. 2007

panicle formation stage of rice at LuKang site

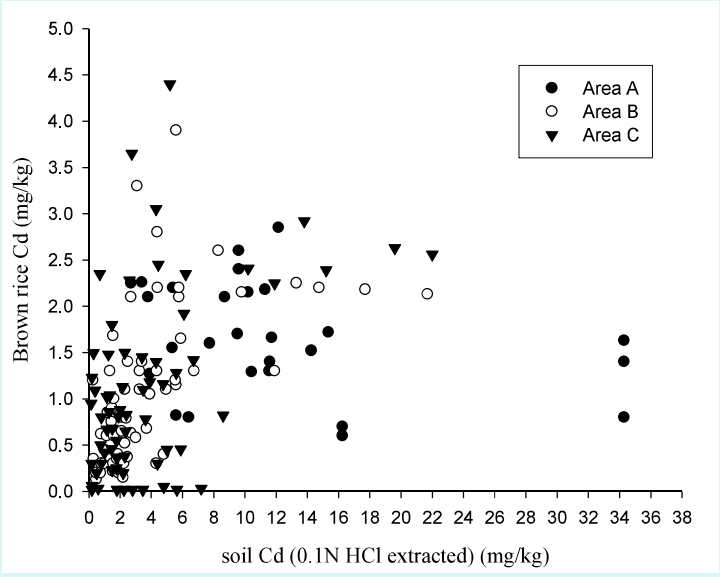
Cited from Guo et al. 2007

Different species of rice has its own growth stages

Field experiments

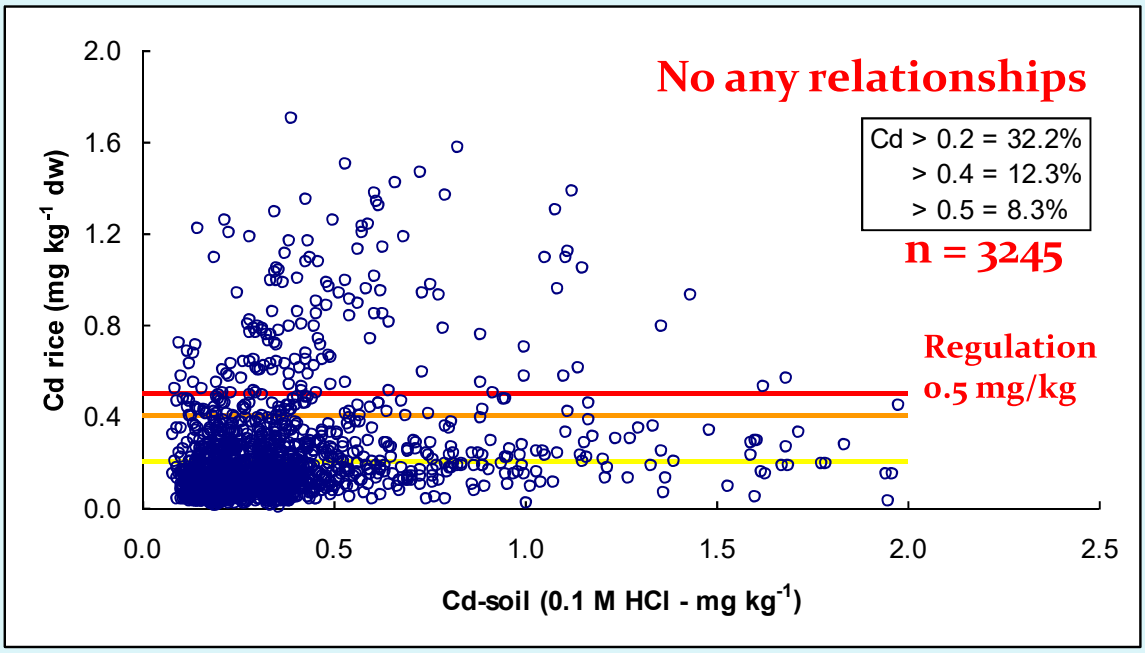
Cited from Guo et al. 2007

Cd concentration of brown rice of northern Taiwan



The relationship between **Cd** concentration in soils and brown rice grains in three Cd-contaminated areas of Taiwan. **(cited from Li et al., 1988 and Chen, 1991).**

Cadmium of brown rice in central Taiwan: relation with soil Cd?

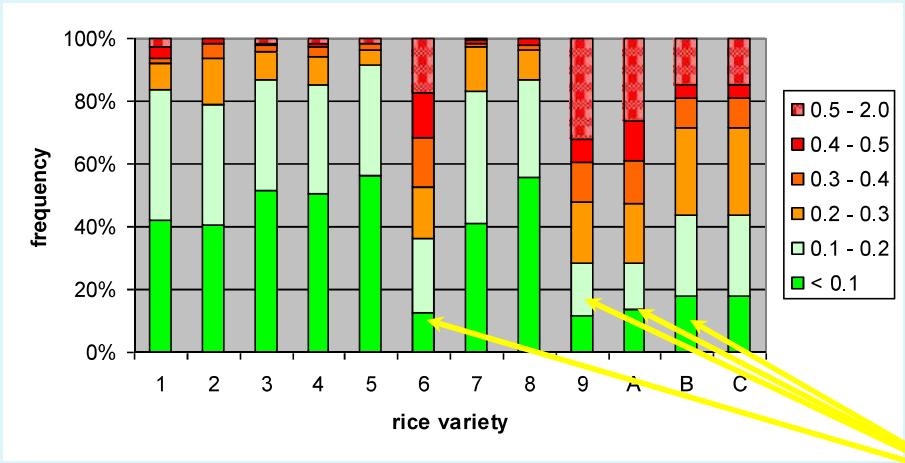


Note: Present action value of Cd in soil of Taiwan: 5 mg kg^{-1}

(Cited from Guo et al. 2006; 2007)

Cadmium in brown rice quality

Cadmium in rice (**mg/kg**) (8 locations; 12 varieties)



Indica species

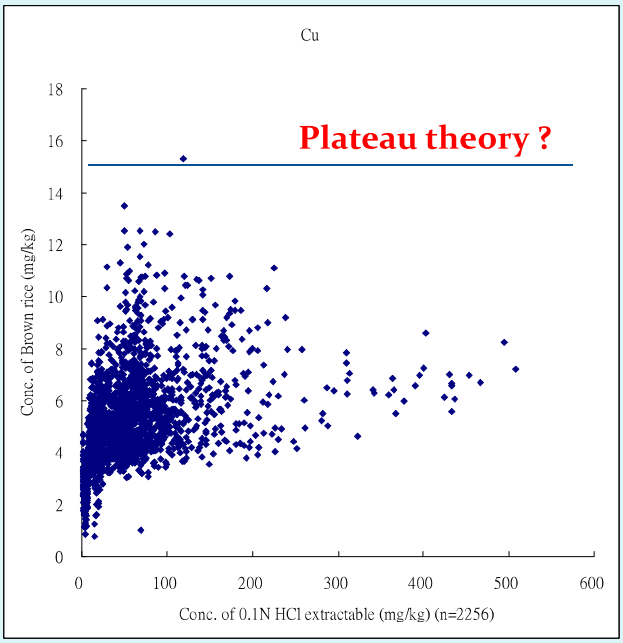
The others are Japonica species

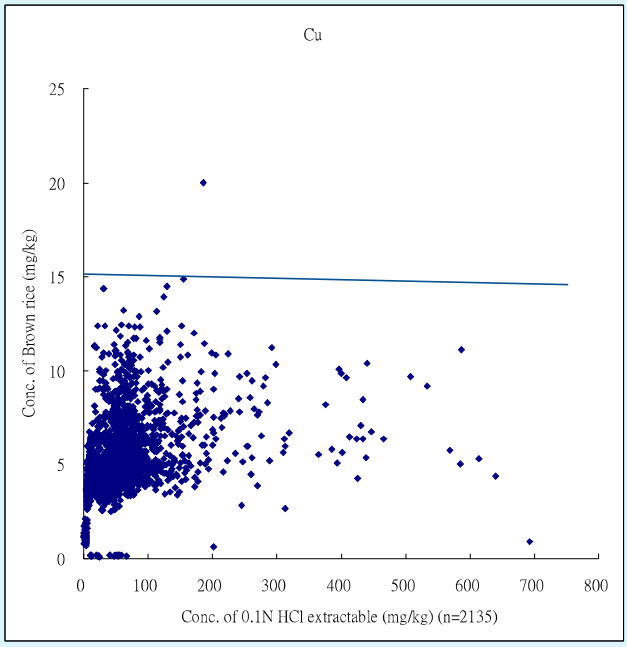
(Cited from Guo et al. 2006; 2007)

Cu in rice: relation with soil 0.1 N HCl extractable soil Cu?

First rice crop
(n= 2256)

Second rice crop
(n=2135)





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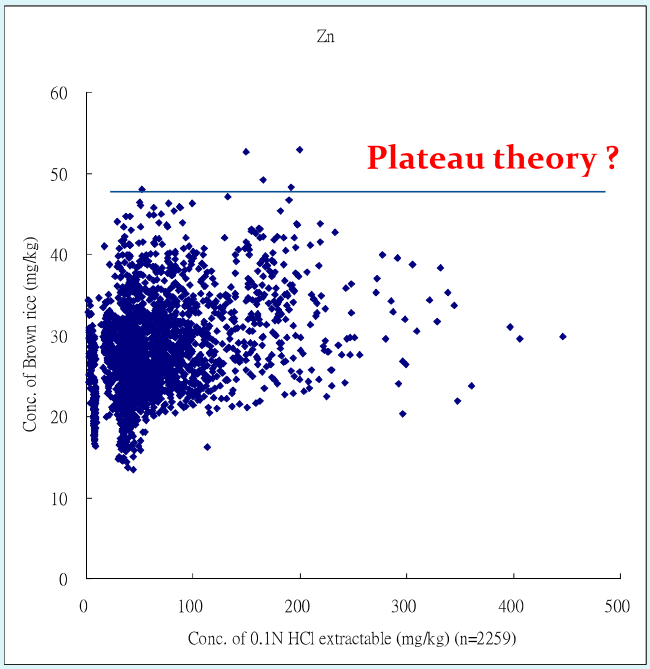
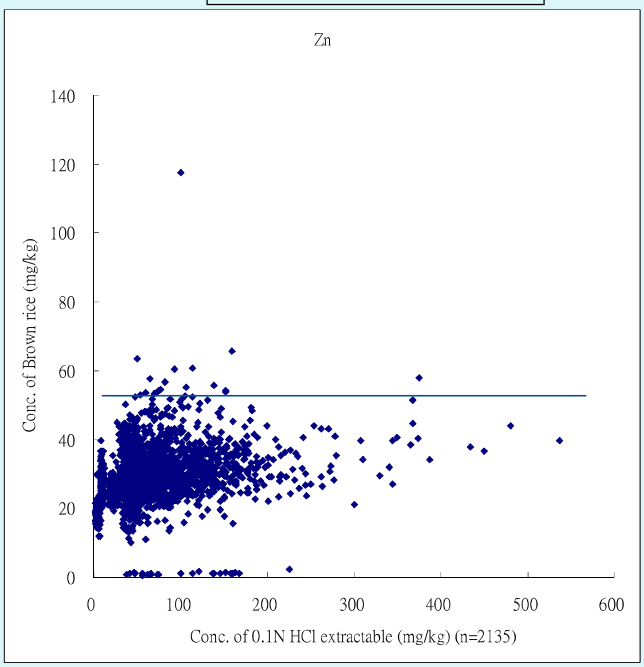
Zn in rice: relation with soil 0.1 N HCl extractable soil Zn?

First rice crop
(n= 2259)

Second rice crop
(n= 2135)





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Part F.
Integrated experiences of remediation strategies by health risk assessment approaching technology for As, Cr, Ni-contaminated rural soils in Taiwan

Key issues for soil quality evaluation and health risk assessment for soil remediation decision

- Soil quality was always changed after soil remediation.
- What's the differences between before and after soil remediation?
- Key issues are Environmental quality and health risk assessment.
- How to make the soil remediation decision for polluted soils with high concentration of heavy metals? To meet the regulation target?
- Risk-based approached remediation tech are key issues to save high cost.
- Risk communication and management are more important in the future.

Food safety on Cd, As, Cr and Ni-contaminated rural soils

- Food safety of Cd and As-polluted rural soils are still big issues in the world.
- Health risk-based remediation technology for Cd, As, Cu, Zn, Cr and Ni-polluted soils need more risk communication between governmental agencies (EPA, MOA, DOH), scientists and NGOs.
- Two successful cases of big area and high content of As, Cr, and Ni in the rural soils of Taiwan are released as normal and background soils and their agricultural products are evaluated as healthy and safety foods.

Food safety regulation of brown rice in Asian countries

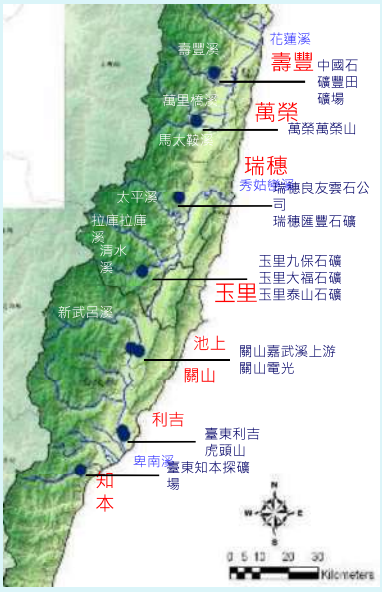
- Cd of brown rice in Taiwan and Japan: 0.4 mg/kg.
- Cd of brown rice in Korea and China: 0.2 mg/kg.
- As of brown rice in Taiwan and Japan: 0.2 mg/kg (As (III), arsenite ion for white rice) and 0.30 mg/kg for brown rice.
- Cd of brown rice can be reduced by flooding soil water management.
- As of brown rice can be reduced by drained or saturated soil water management.
- No any regulation of Cu, Zn, Cr and Ni of brown rice in Asian countries.

Part F.
1st successful story:

Geochemical background content and health risk assessment of Cr and Ni of serpentine soils

Properties and distribution of serpentine rock in Taiwan

- **Serpentine rocks formation**
  - Collusion of Euroasian Plate and Pacific Plate
  - Formed in the metamorphic rock region
- **Serpentine characteristics**
  - **Ultrabasic rock, SiO_2 <45% with high Fe and MgO (>30%)**
  - **High Cr and Ni > 2,000 mg/kg**
  - Dark green, gray green color rocks.
  - Major mineral composition are olivine, augite.
  - Major rocks are serpentine and meghemite.
- **Mining distribution area in Taiwan**
  - Central ridge and marine mountain region in Taiwan.
  - Major located at eastern Taiwan **(0.5 million tons per year)**



臺灣鑛業史編纂委員會，1984，臺灣鑛業史續一（1964-1980）

Serpentine rock of Eastern Taiwan

Very good crop production, but food safety?

Cr and Ni contents of serpentine soils of the world

Location	Cr (mg/kg)	Ni (mg/kg)
Taiwan	**3300**	**400-5800**
East coast, USA	6000	100-20000
West coast, USA	100-4200	100-4500
South Africa	500-2600	2000-5000
Canada	800-5500	200-1700
Italy	1000-8300	600-5100
Germany	700	500
France	100-3900	200-3600
Iran	200-400	800-1200
Costa Rita	1400-3600	3200-7200
Portugal	200-4300	<100-1600
Brazil	5100-17000	2300-6000
New Zealand	7900	6100
New Caledonia	17000-19000	7000-8500

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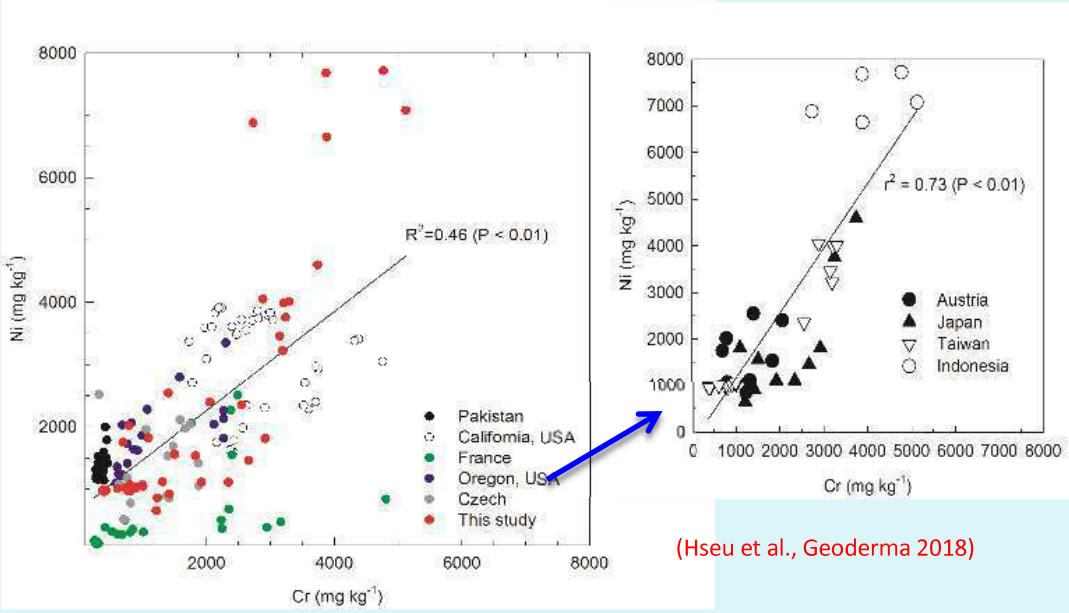
Good relations of Ni and Cr concentration of serpentine rural soils



(Hseu et al., Geoderma 2018)

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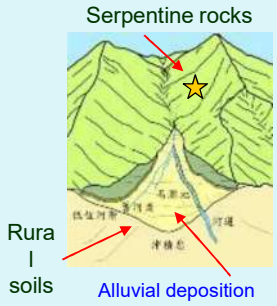
High Cr and Ni content of serpentine soils in Taiwan

- Geochemical anomaly

rocks	Cr (mg/kg)	Ni (mg/kg)
Andesite	13 - 342	11 ~ 115
Basalts	146 - 434	113 ~ 336
Serpentine	1,080 -2,880	1,450 - 2,300

Taiwan EPA (2013)

- **Alluvial deposits along the river**

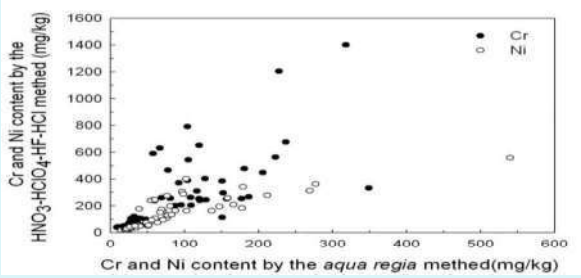


Rural soils

- Residual parent material

Weathering soils from serpentine in eastern Taiwan

Geochemical background Cr and Ni concentration



Taiwan SGS (2013-2015) by NIEA S321.63B/M104.01C methods

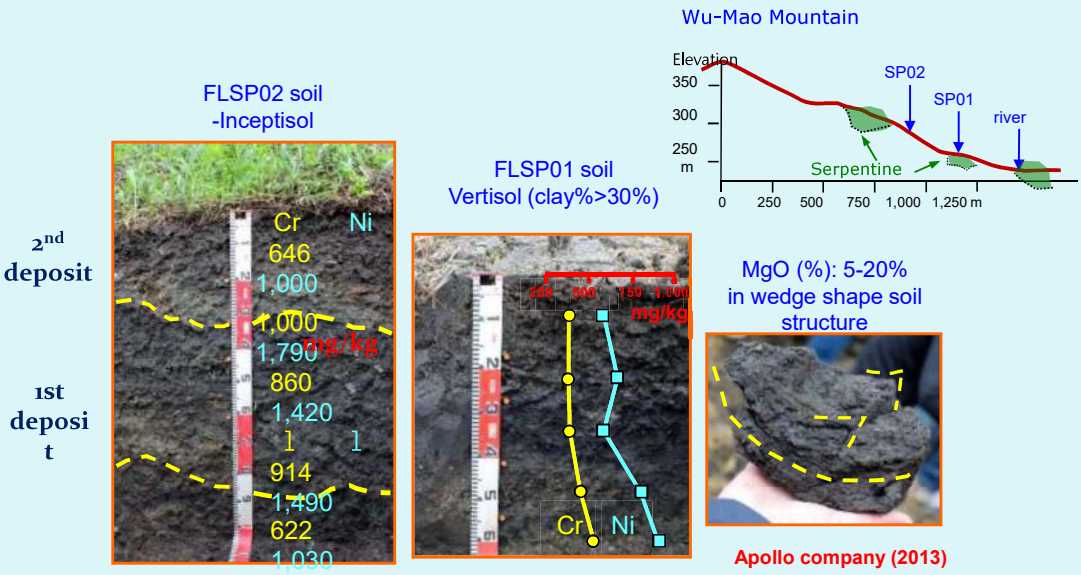
Survey region		numbers	Cr (mg/kg)	Ni (mg/kg)
Serpentine soils area	Central ridge	14	32 ~ 349 (129 ± 88.4)	29~179 (87.4 ± 50.1)
	Marine Mountains	**16**	**56 ~ 551 (154 ± 131)**	**56 ~ 825 (206 ± 205)**
Non-serpentine soils area	Central ridge	4	23 ~ 36 (28.6 ± 6.40)	22 ~ 51 (32.3 ± 11.6)
	Marine Mountains	**5**	**10 ~ 28 (18.4 ± 7.58)**	**20 ~ 40 (29.8 ± 9.18)**
	Lanhsu island	5	87 ~ 177 (138 ± 35.1)	48 ~ 64 (55.7 ± 6.82)
	Green island	2	25.3, 108	14.4 and 60.7

Apollo Company (2013-2015)

Objectives

- To understand the geochemical composition and processes,
- To understand the Cr and Ni content of serpentine soils,
- To develop the **relationships** between Soil Cr, Ni and crop Cr and Ni in rice and vegetables, and
- To evaluate the **health risk** of crops and risk management

Soil profile characteristics of Wu-Mao Mountain



Apollo company (2013)

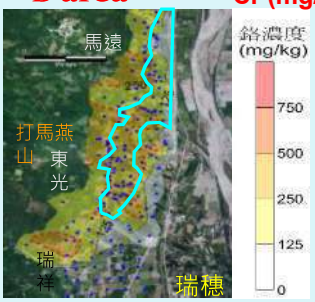
Soil quality survey and evaluation

■ Distribution of serpentine soils

Region	Survey area	Area (ha)	Rural soil (ha)	Rice production area (ha)
Wang-Rong	A	183	28	10
Jh-Swei	B	400	104	28
Kuangshan & Cheeshan	C	246	44	40
Total		829	176	76

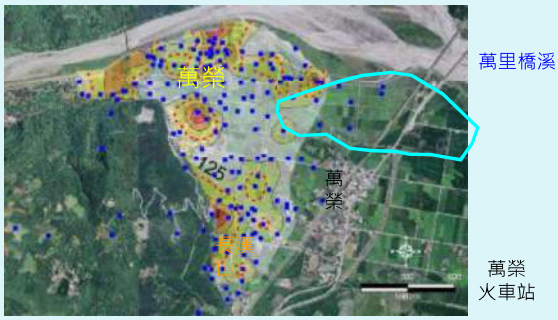
B area

Cr (mg/kg)



Apollo company (2013)

A area



C area

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Soil quality survey and evaluation

■ Distribution of serpentine soils

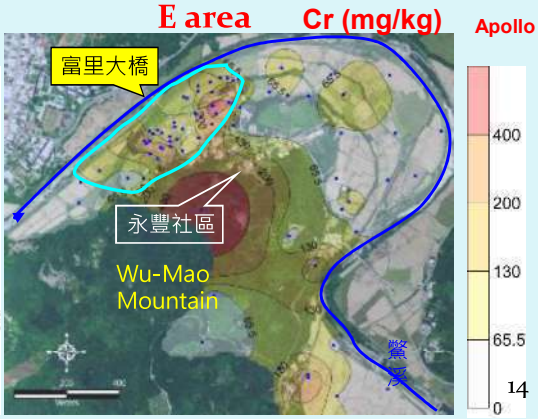
region	Survey area	Area (ha)	Rural soils (ha)	Rice production area (ha)
Yu-Li	D	84	84	36
Fu-Li	E	96	24	24
Total		180	108	60

D area

Cr (mg/kg)

E area

Cr (mg/kg)



Apollo company (2013)

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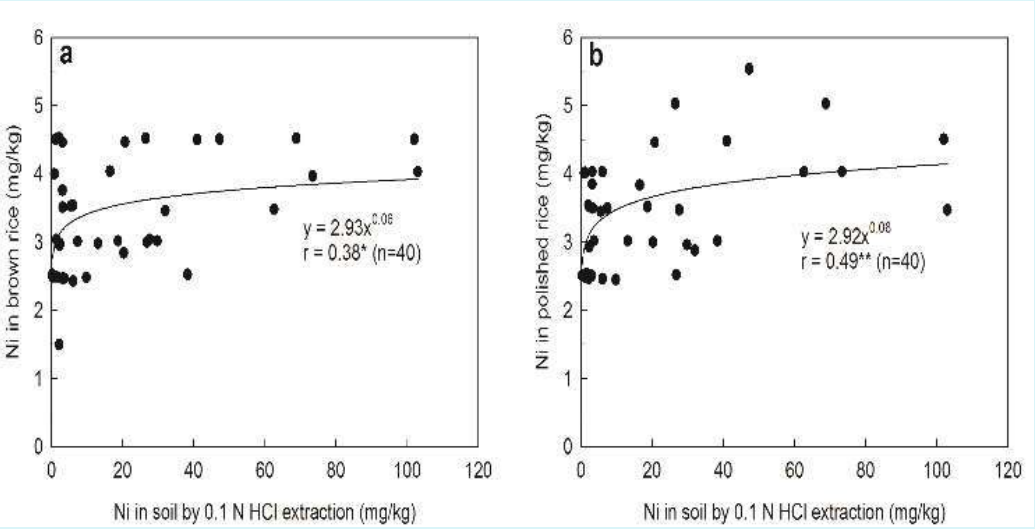
Ni of brown rice (a)

Ni of polished rice (b)



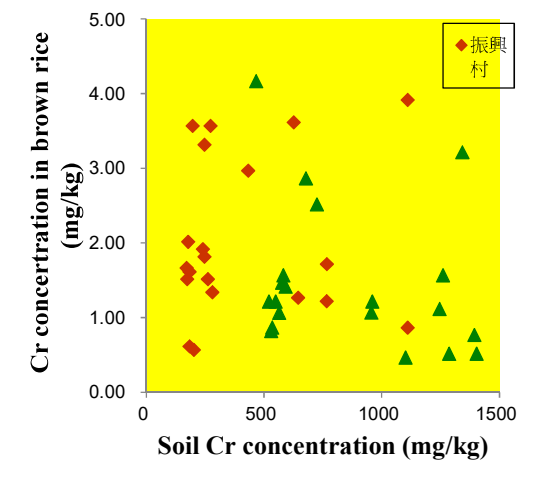
(ZY Hseu, 2014)

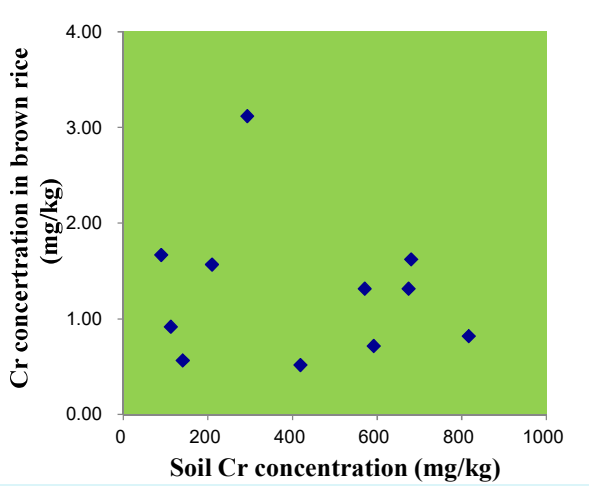
Relationship between available Ni with 0.1 N HCl extraction in soil and Ni in brown rice (a) and polished rice (b) (*: $p < 0.05$; **: $p < 0.01$).

Taitung region

Hwalien region

Relations between Cr in soil and Cr in brown rice





- There is no any relationships between soil Cr and brown rice, and
- The Cr of brown rice ranged 0.5-4.5 mg/kg.

(ZS Chen, 2014)

Bioavailable Cr evaluation of soils (<5 mg/kg in soil)

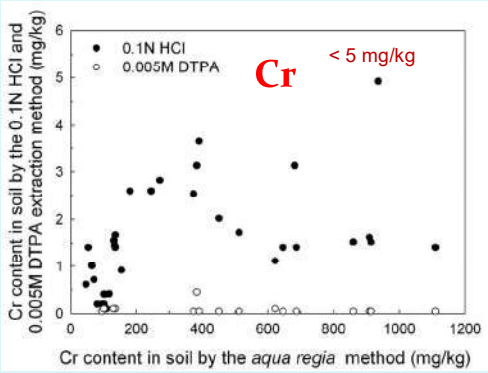
Bioavailable concentration

- 0.1 N HCl: Cr <1% & Ni <10% of total conc.
- 0.005 M DTPA: Cr <0.1% & Ni <10% of total conc.

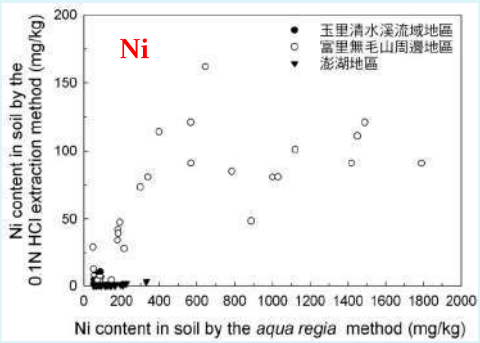
regions	N	Bioavailable conc. (mg/kg)	
		0.1 N HCl	0.005 M DTPA
Yu-Li (serpentine soil)	10	Cr : ND ~ 0.41 Ni : 2.53 ~ 11.1	Cr : ND Ni : 1.62 ~ 26.3
Fu-Li (serpentine soil)	26	Cr : ND ~ 3.64 **Ni : 3.64 ~ 162**	Cr : ND **Ni : 1.36 ~ 245**
Peng-Fu (Basalt soil)	38	Cr : ND Ni : 0.20 ~ 3.00	Cr : ND Ni : 0.27 ~ 0.97
Regulation of organic farming in Taiwan (mg/kg)		Cr : 10 Ni : 10	

Note: the MDL of 0.1 N HCl is 0.09 mg/kg and 0.005 M DTPA is 0.04 mg/kg

(Apollo company, 2013-2015)

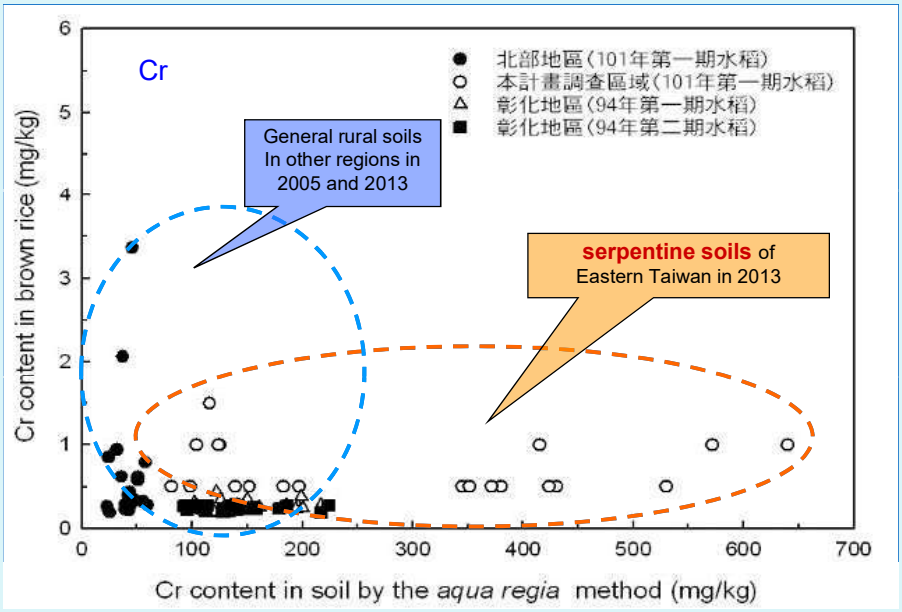


(Apollo company, 2013-2015)



Cr of brown rice in different regions of Taiwan

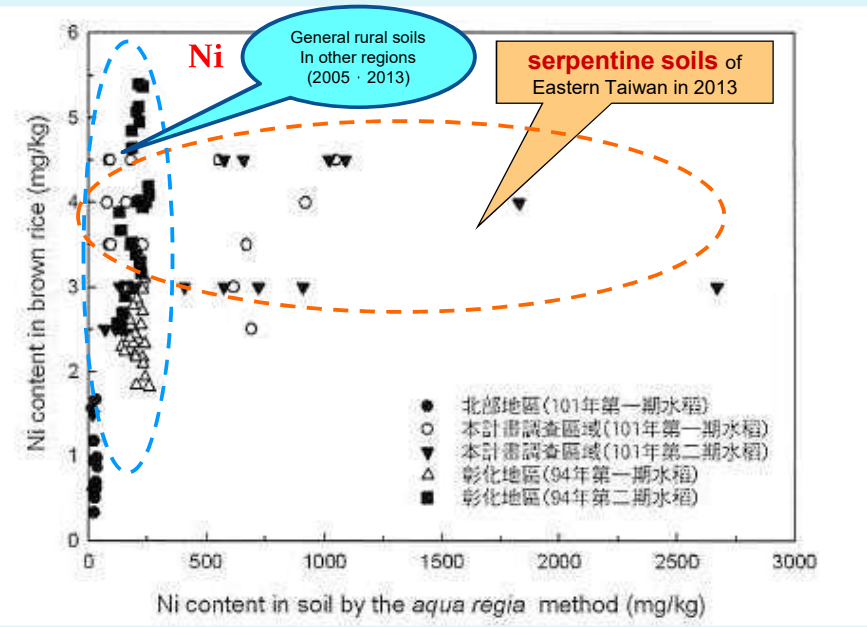
(1- 4 mg/kg)



Taiwan EPA project report (2013)

Ni of the brown rice in different regions of Taiwan

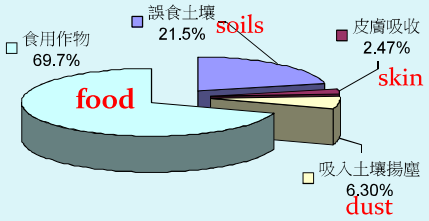
(1-6 mg/kg)



(環保署 計畫報告, 2013)

Risk assessment of brown rice and vegetables

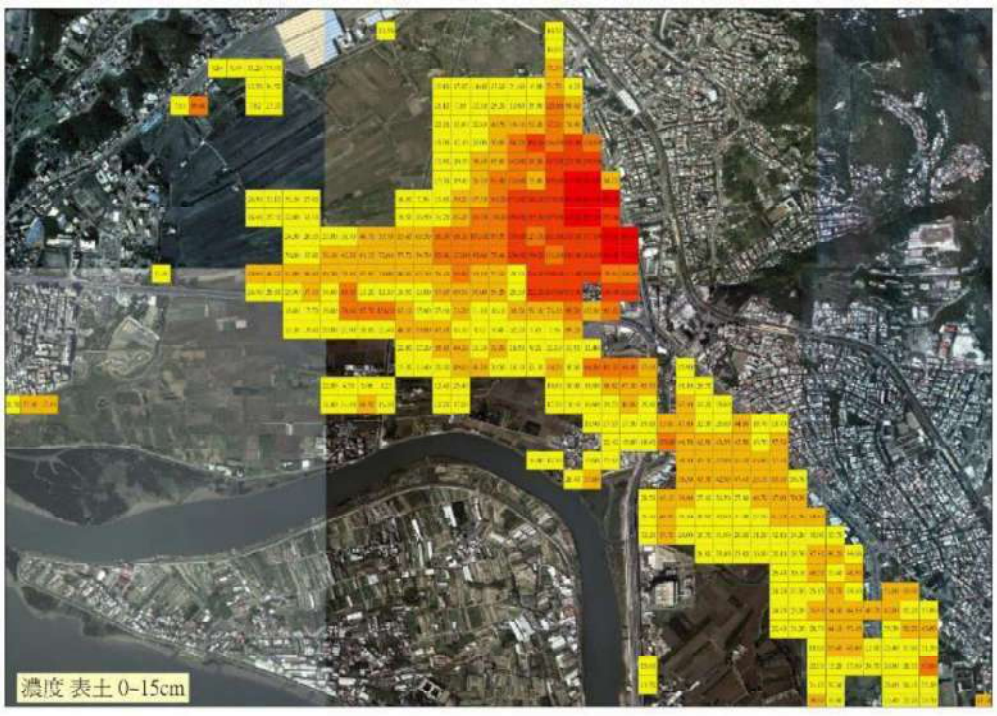
- Cr(III) is regarded as non-carcinogen risk and HQ is < 1,
- Cr (VI) was only found in the air and was evaluated as intake from the air dust,
- Totally, there is no any health risk.



Forms	risks	In Wang-Rong region		In Jae-Suwei region		In Chee-Shan and Cheng-Hsiung regions	
		Carcinogen risk	Non-carcinogen risk	Carcinogen risk	Non-carcinogen risk	Carcinogen risk	Non-carcinogen risk
Cr (III)	adult	-	2.24×10^{-2}	-	2.44×10^{-2}	-	2.82×10^{-2}
	children	-	1.77×10^{-2}	-	1.79×10^{-2}	-	2.22×10^{-2}
Cr (VI)	adult	1.86×10^{-7}	8.81×10^{-4}	1.38×10^{-7}	6.34×10^{-4}	2.11×10^{-7}	1.09×10^{-3}
	children	6.63×10^{-8}	6.93×10^{-4}	4.42×10^{-8}	4.62×10^{-4}	8.10×10^{-8}	8.46×10^{-4}

Part F.
2nd Successful story:

As polluted soils of Gangdu Plain soils and As speciation of brown rice of Pollution area



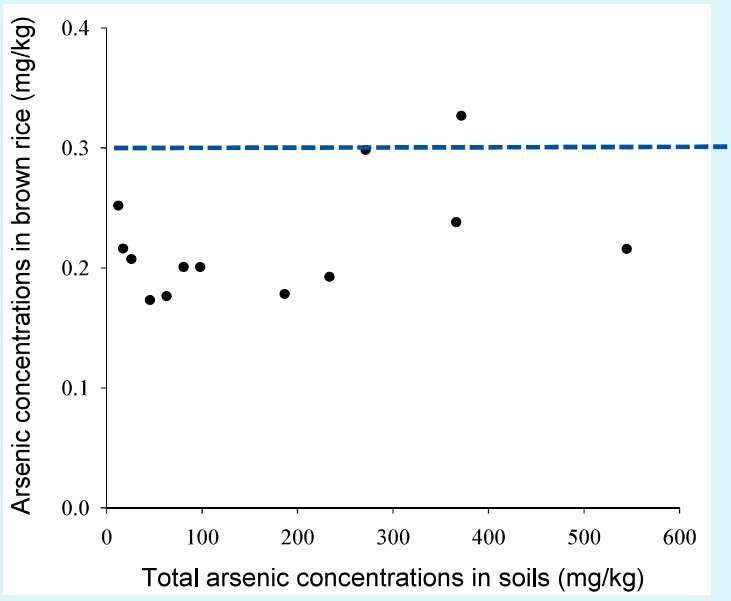
As: 60-500 mg/kg (brown and red color region

Total area : 200 ha

Crops: rice and vegetables

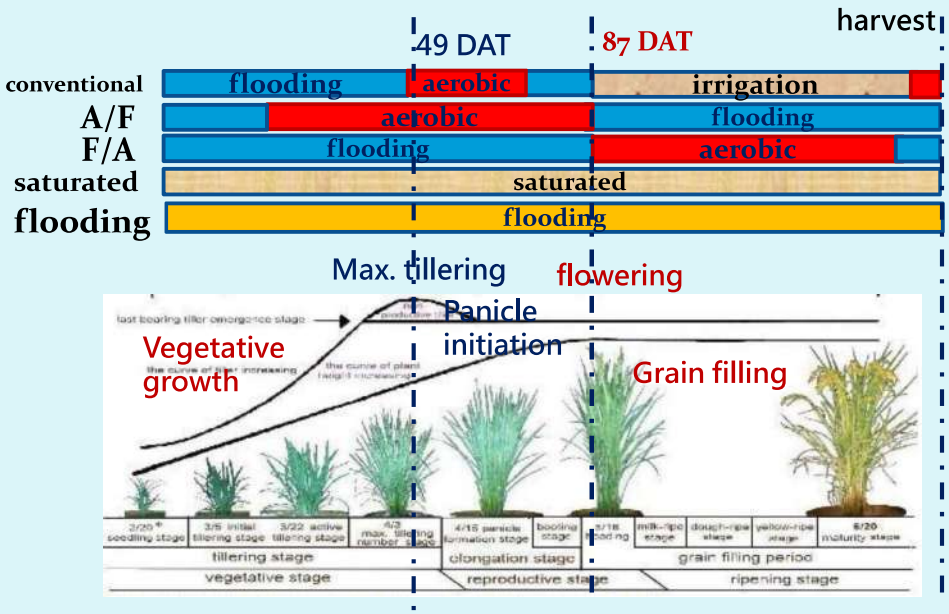
The sampling sites of soil and rice samples in Guandu Plain

Relations between As of brown rice and soil As concentration



Meet the regulation

Pot experiments by different soil water managements



Soil characteristics

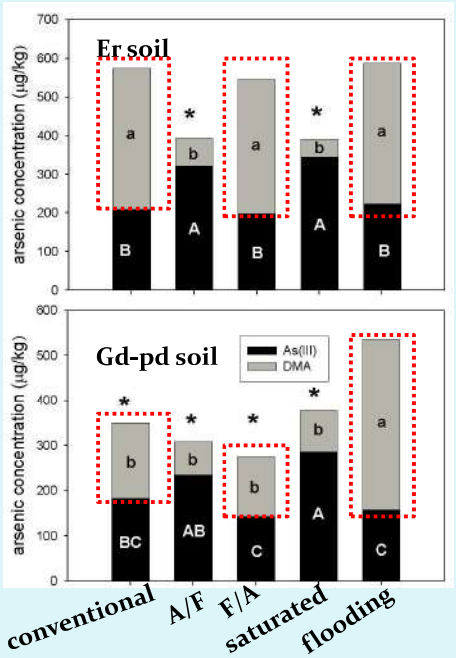
The basic physical and chemical properties of the studied soils.

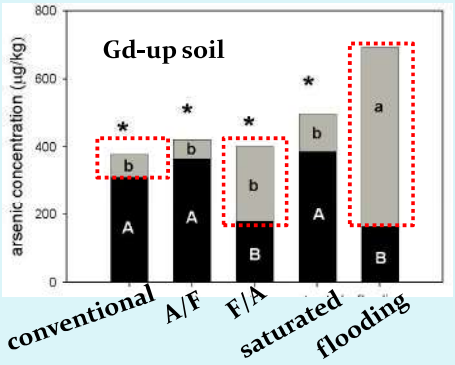
Soil characteristics	Er soil	Gd-pd soil	Gd-up soil
pH	7.7	5.8	5.7
OC(%)†	1.3 ±0.1	3.6 ±0.1	2.0 ±0.1
Texture	silt loam	silty clay	silty clay
amorphous Fe (g/kg)	4	18 ± 1	15.8
free Fe (g/kg)	8.4	27 ± 1	45 ± 3
Total Fe (g/kg)	35 ± 1	56 ± 2	75 ± 3
amorphous Mn (mg/kg)	205± 5	100 ± 1	393 ±3
free Mn (mg/kg)	222 ± 3	160 ± 1	576 ± 28
Total Mn (mg/kg)	425±10	265±9.5	719±13
Total As (mg/kg)	**35 ± 1**	**379 ± 1**	**531 ± 32**

† organic carbon. n = 2, mean ± std.
Crystalline Fe(%) = free Fe(100%) – amorphous Fe(%)

- **Organic carbon and oxide content are high in Gd soils, which are typical volcanic soils.**
- **The efficiency drainage in Gd soil increased the redox potential immobilized As in soil.**

Arsenic speciation of the brown rice





- Soil Eh is elevated in the soil water management and reduced the DMA in the soil and the pore water.
- As (III) of brown rice < 0.2 mg/kg
- The As(III) species in A/F and saturated treatment increased.

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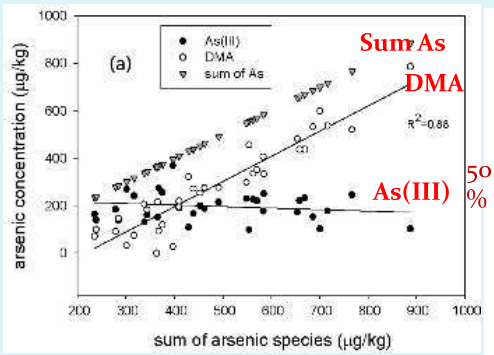
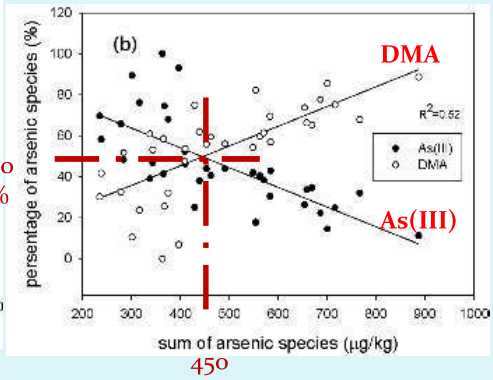
Flooding before flowering

(conventional, F/A and flooding treatment)



50 %



450

- The DMA concentration increased to 800 μg/kg with the arsenic concentration of the brown rice.
- The percentage of DMA in the brown rice increased from 20 to 80% between 200–900 μg/kg sum of arsenic.

(Chen et al., 2014, 2015)

Conclusion-1

- Sampling objectives and field investigation
- Cost-effective sampling number and location for soil survey quality and Pre-treatment quality.
- Different soil remediation techniques were developed for rural soil contaminated by heavy metals.
- Technical and non-technical factors to be considered.
- Risk-based approached regulations and technologies should be considered.

Conclusion-2

- High concentration of Cr and Ni in serpentine soils of Taiwan are evaluated as natural formation and regarded as background level.
- Cr and Ni concentration of serpentine soils are much higher than the regulation of Cr and Ni (250 mg/kg) of rural soils and are produced by natural geological formation.
- Cr and Ni concentration of brown rice and vegetables after the health risk assessment indicated brown rice grown in serpentine soils are safe and no health risk.
- The volcanic rural soils can fixed the bioavailability of high As concentration (60-500 mg/kg), which are regarded as no health risk region by more risk management.

Thanks for your attention.

Questions ?

2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Sediment Contamination: Protection and Remediation

Shu-Chi Chang, Ph.D., P.E.

Associate Professor

Dept. of Environmental Engineering,

National Chung Hsing University

Outline

- Introduction
- Sediment Protection
- Sediment contamination
- Sediment remediation
- Examples (3 cases)
- Conclusion

Introduction

Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

Introduction

- What is sediment
- A dynamic system
- Is it originally pristine?
- A status quo of Taiwan
- Why do we care about sediment?

What is sediment?

- Sediments are fragmented materials that originate from weathering and erosion of rocks or unconsolidated deposits and are transported by, suspended in, or deposited by water. (USEPA, 2014)
- 底泥：指因重力而沉積於地面水體底層之物質。

  Sediment: those substances, due to gravity, deposited at the bottom of a surface water body. (Taiwan EPA)

A dynamic system

- Erosion of the surface materials within a watershed
- Transport of suspended particles
- Deposition of suspended particles
- High flow velocity event can re-suspend the deposited particles and re-deposit
- During low flow rate period, some may be blown into air
- Water chemistry plays a big role at tidal-reach sections
- Contaminants in small and large quantities
- Microbes and benthic organisms

Is it originally pristine?

- Very hard to judge
- Initially eroded particle may be pristine
- Litters and organic matter may be present at the middle and downstream sections
- Human activities may cause higher BOD that exceeds the self purification capacity of the sediment ecosystem
- Farming and industrial activities may introduce persistent organic pollutants

A status quo in Taiwan

- Full survey is underway (mandatory)
- Selectively monitored heavily polluted rivers for specific contaminants for more than 10 years.
- Sediment research has been continuously funded for more than 20 years
- For the past 10 years, more funds have been provided by Soil and Groundwater Pollution Remediation Fund Management Board, Taiwan EPA.

Why do we care?

- An important link in food chain
- Estuary areas and continental shelve are traditionally important fishing areas
- Heavy metals can enter organismal body and accumulate (El-Moselhy et al., 2014)
- Hydrophobic organic compounds (HOCs) may also accumulated and biomagnified through food chain
- Cycle time could be shorter than other environmental matrices

Sediment protection

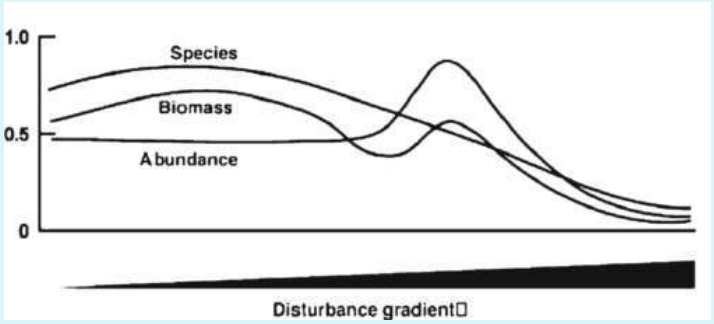
Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

Protection of sediment

- Administrative approach
  - Guidelines for sediment quality
  - Implement the guidelines
  - Review the results and revise the guidelines
- Scientific strategies
  - Risk assessment
    - Chemical
    - Physical
    - Biological
  - Toxicity evaluation

Scientific strategies

- Risk assessment
  - Physical: Total solids, PSD, specific gravity, acidity (pH), temperature, etc.
  - Chemical: heavy metals, xenobiotics, petroleum hydrocarbons, flame retardanta, microplastic, endocrine disrupting compounds, etc.
  - Biological



Sany et al., 2014., Environ Sci Pollut Res 21:813-833

Natural conc. of heavy metals

	Sedimentary rocks	Igneous rocks	Soil	Land plants	Land animals	Mean values from 10 lakes	Sea water (bowen 1966)	Fresh water
Ag	0.05	0.07	0.1	0.06	0.006	≤1		0.00013
Al	4,000–80,000	82,000	71,000	500	4–100	26,000		0.24
As	1–13	1.8	6.0	0.2	≤0.2	8.6	0.0026	0.0004
Cd	0.035–0.3	0.2	0.06	0.6	≤0.5	0.58	0.0001	<0.08
Co	0.1–20	25	8.0	0.5	0.03	18.5		0.0009
Cr	10–100	100	100	0.23	0.075	48.7	0.00005	0.00018
Cu	4–50	55	20	14	2.4	28.7	0.003	0.01
Fe	4,000–50,000	56,300	38,000	140	160	26.7		0.67
Hg	0.03–0.4	0.08	0.03–0.8	0.015	0.046	0.12	0.00003	0.00008
Mn	50–1,000	950	850	630	0.2	860		0.012
Mo	0.2–2.5	1.5	2	0.9	<0.2	≤10		0.00035
Ni	2–70	75	40	3	0.8	49.7	0.0054	0.01
Pb	7–20	12.5	10	2.7	2	34.9	0.00003	0.005
Sn	0.5–6	2	10	0.3	<0.15	<10		0.00004
V	20–130	135	100	1.6	0.15	≤150	0.0019	0.001
Zn	15–100	70	50	100	160	110.6		0.01

Sany et al., 2014., Environ Sci Pollut Res 21:813-833

Sediment toxicity assessment

- Nebeker et al (1984): Biological methods for determining toxicity of contaminated freshwater sediments to invertebrates (USA)
- Then Canada, Europe, Australia, and New Zealand
- Methods and Sediment quality guidelines
- Toxicity identification evaluation (USEPA)
- Benthic assessment of sediment toxicity (BEAST)
- Conceptual models and weight-of-evidence based approaches
- USNRC (2007): Sediment Dredging at Superfund Megasites: Assessing the Effectiveness

Burton, 2013, *ET&C* 32(7):1438-1440

Sediment toxicity assessment

- ASTM's sediment toxicity standard methods for mussels and amphibians
- Predicted no effect concentrations (PNECs or $PNEC_{sed}$): EC's Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) and Water Framework Directive programs
- Predicted Environmental Concentration in sediment (PEC_{sed})
- Risk Quotient Ratio (RQR) = PEC_{sed}/ $PNEC_{sed}$
- Emerging contaminants as well as engineered nanomaterials: no guidelines yet
- Sediment resuspension

Burton, 2013, *ET&C* 32(7):1438-1440 15

Sediment toxicity assessment

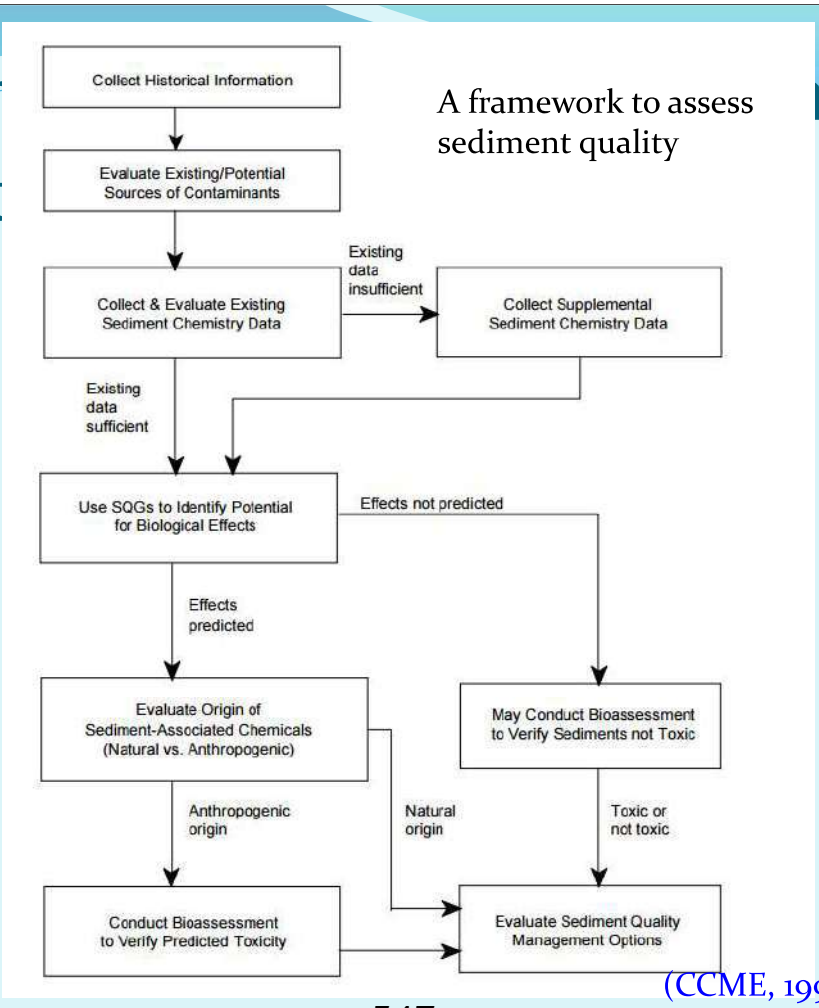
- Sediment quality guideline for multiple contaminants?
- Human dominated watersheds
- CECs?
- Remediation cost and magnitudes
- Harbor dredging problems
- More site-specific guidelines?
- species sensitivity distribution (SSD) and field-based SSD (f-SSD)
- SEDNET in Europe and SETAC Sediment Advisory Groups in USA. How about Asia?

Burton, 2013, *ET&C* 32(7):1438-1440
Kwok et al., 2014 Environ Sci Pollut Res 21(1):17-27 16

World perspective

- USA
  - US NOAA proposed screening values on 190 chemicals (1989)
  - USEPA's Contaminated Sediment Management Strategy (Farris et al., 1995)
- Canadian could be one of the leaders
  - *Protocol for the Derivation of Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.* (CCME, 1995)
- EU regulation seemed to be delayed. No legal guideline but has good risk assessment scheme.
- Australia and New Zealand: SQGs established in 2000 , then updated for some contaminants as well as the introduction of a numerical weight of evidence assessment scheme
- Taiwan
  - Included into the "Act for soil and groundwater remediation" in 2010
  - Specific guideline issued in 2012
  - In 2013, a specific regulation issued to require the government authority in charge of the relevant end-enterprise to finish a first-run sediment survey within 5 years

A fra… …ent qualit…



A framework to assess sediment quality

(CCME, 1995)

Protection of sediment

- Canadian approach as a model
  - The Sediment Quality Guidelines
  - How the guidelines work
    - The **No Effect Level**: the level of the chemicals in the sediment do not affect fish or the sediment-dwelling organisms..
    - The **Lowest Effect Level**: a level of contamination which has no effect on the majority of the sediment-dwelling organisms.
    - The **Severe Effect Level**: At this level, the sediment is considered heavily polluted and likely to affect the health of sediment-dwelling organisms.

Protection of sediment

- Guideline development
  - Sediment Background Approach
  - Equilibrium Partitioning Approaches
  - Apparent Effects Threshold Approach (AET)
  - The Screening Level Concentration Approach (SLC)
  - Spiked Bioassay Approach

ENVIRONMENTAL FACTOR	DIFFERENCE COMPARED TO TEMPERATE CLIMATES	ANTHROPOGENIC INPUT	ECOLOGICAL EFFECT
Light	More Intense		Increased eutrophication Photochemical alterations
Air, soil and water temperature	Higher		Lower productivity Higher BOD and COD potential Increased thermal stress
Salinity	Higher	Sewage Xenobiotic Waste	Increased salinity stress
Oxygen	Lower concentrations		Increase in community restructuring
Nutrients levels	Lower concentrations		Increased eutrophication
Surface Water Tubidity	Lower		Alterations of Benthic Biota (i.e. corals)
Community Structure	More Linear		Loss of diversity

Kwok et al., 2014 *Environ Sci Pollut Res* 21(1):17-27 21

OVERALL…

CHARACTERISTIC	TROPICAL AQUATIC ECOSYSTEMS RELATIVE TO TEMPERATE ECOSYSTEMS
Biological uptake rate	Higher
Biological release rate	Higher
Rate of Physiochemical degradation	Higher
Rate of biological degradation	Higher
Rate of oxygen depletion	Higher
Biological impact of nutrients	Higher
Biological impact of suspended solids	Higher
Solubility of liquids and solids	Higher
Solubility of gases	Lower
Toxicity thresholds	???

Kwok et al., 2014 *Environ Sci Pollut Res* 21(1):17-27 22

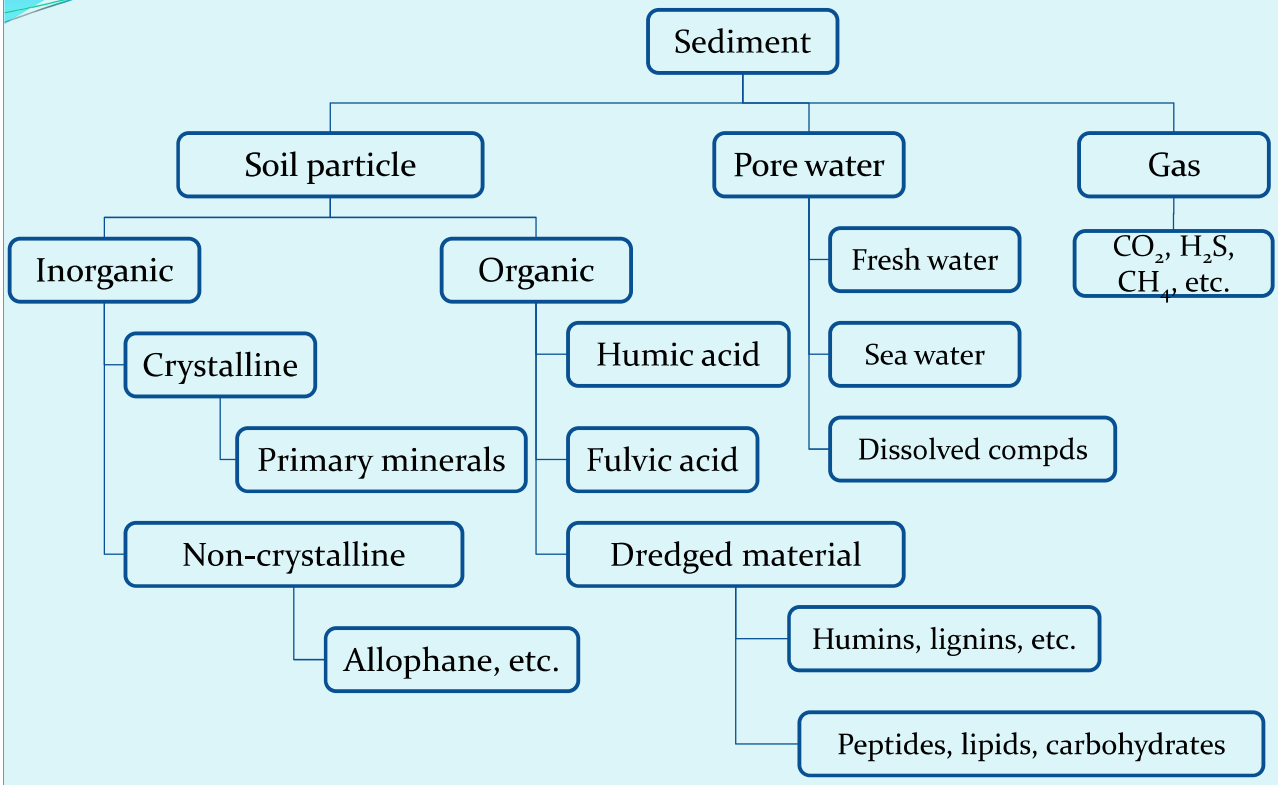
Summary for sediment protection

- More than 30 years of efforts
- Slow development in the past two decades
- Attracting more and more attention recently due to the fact that the pollution may significantly impact ecosystem and human health
- The challenging is enormous
  - Technology for toxicity evaluation
  - Legislation support
  - Public awareness: education and academic societies?
  - Remediation and monitoring technologies

Sediment contamination

Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

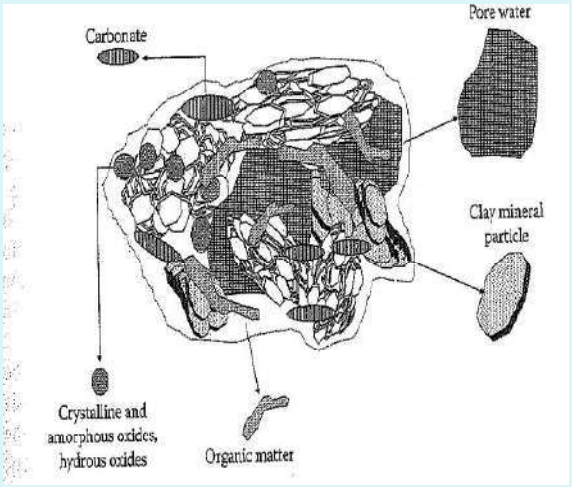
Sediment contamination



(Mulligan et al., 2010)

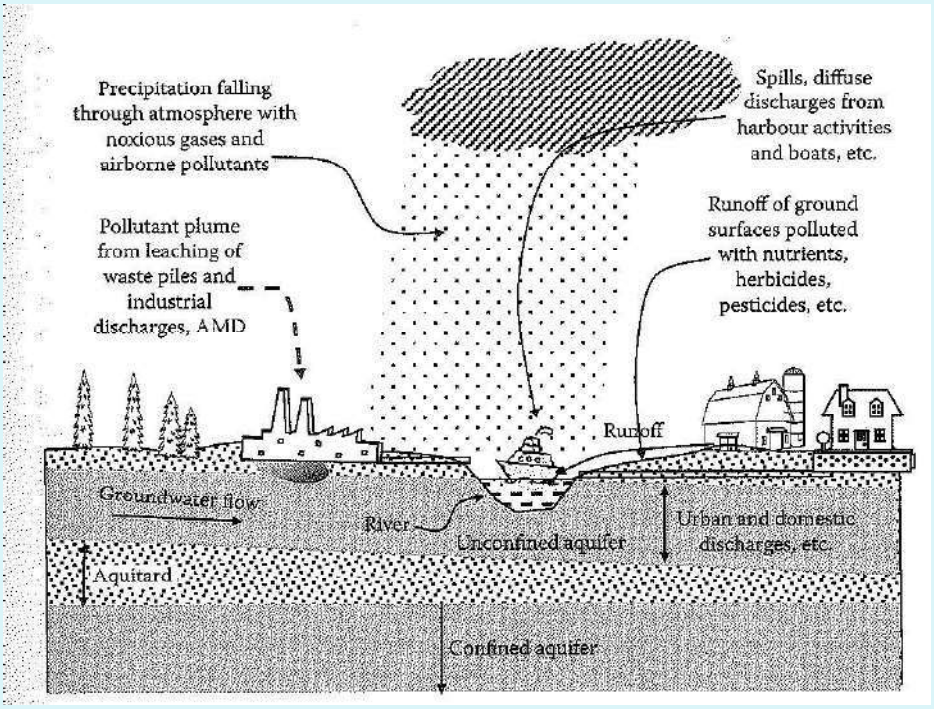
Sediment contamination

- Primary minerals
- Secondary minerals
- Organic matters
- Oxides and hydrous oxides
- Carbonates and sulfates



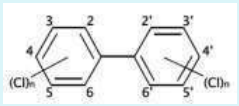
(Mulligan et al., 2010)

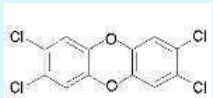
Sediment contamination

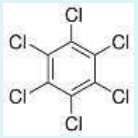


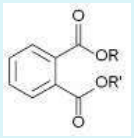
Sediment contamination

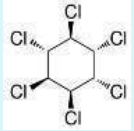
- Contaminants
  - Heavy metals
  - Organic pollutants
    - Grease and oils
    - PAHs
    - PCBs
    - PBDEs
    - BPA
    - Phthalates
    - Chlorobenzenes
    - Dioxin and furans
    - Herbicides and pesticides
    - etc.
  - Emerging contaminants

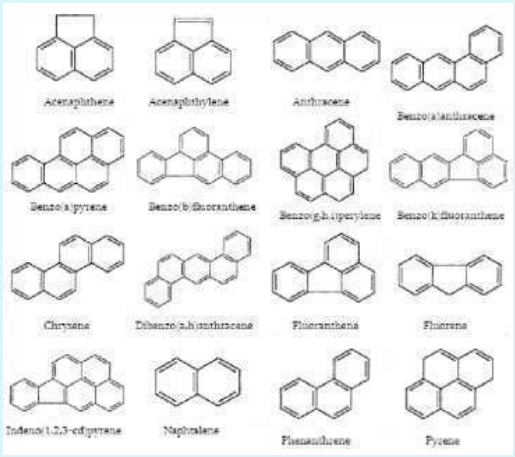


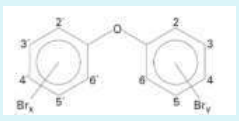


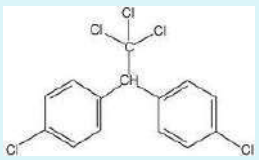








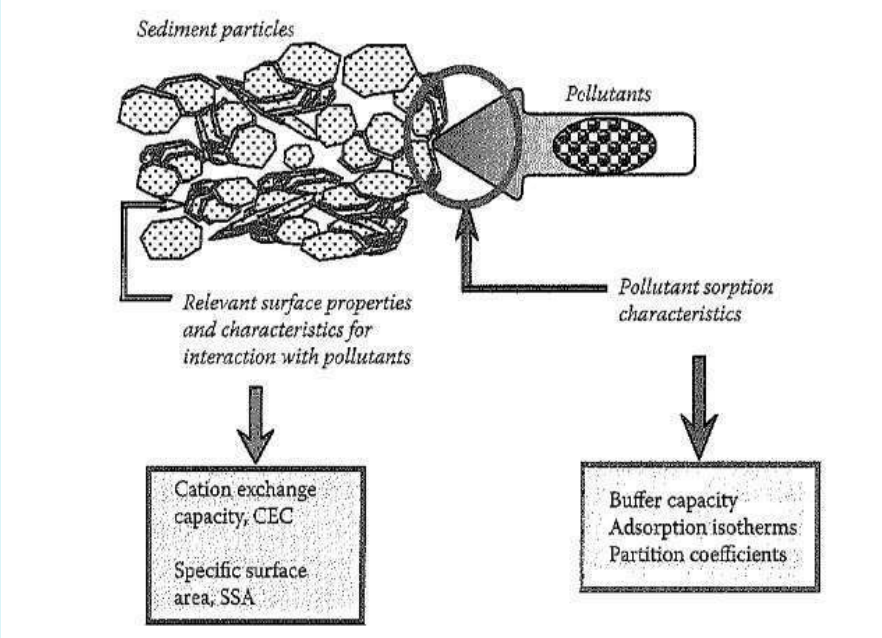




NAPL= non-aqueous phase liquid

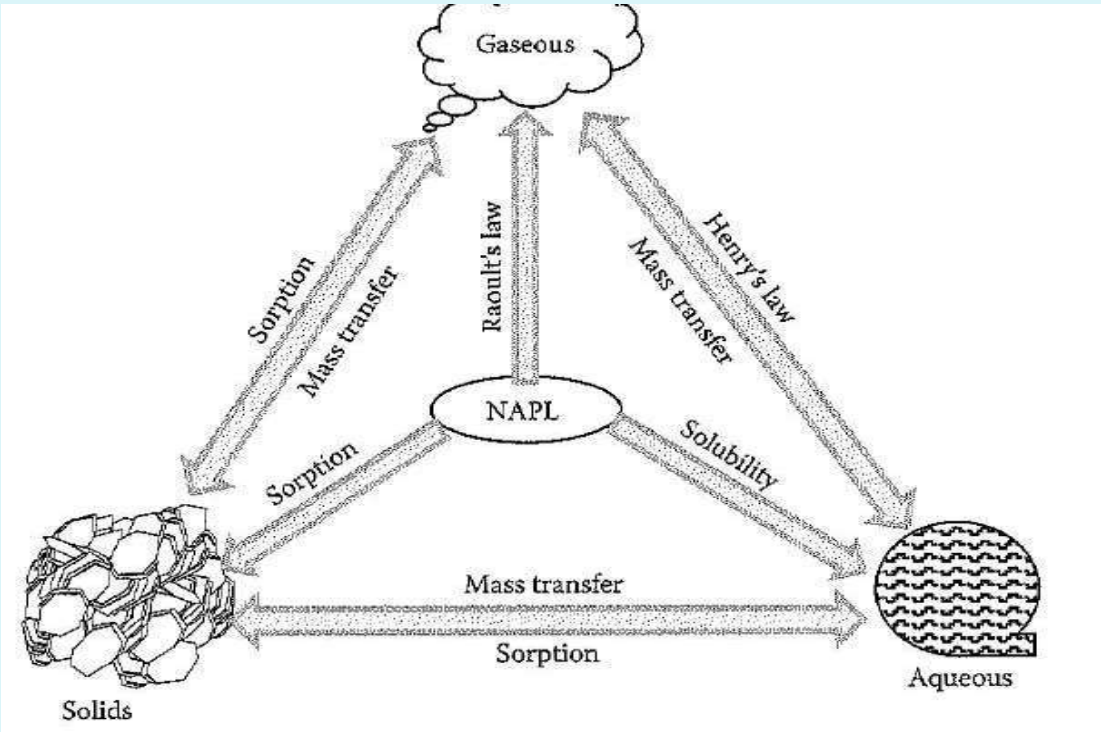
Sediment contamination

- Fate and transport



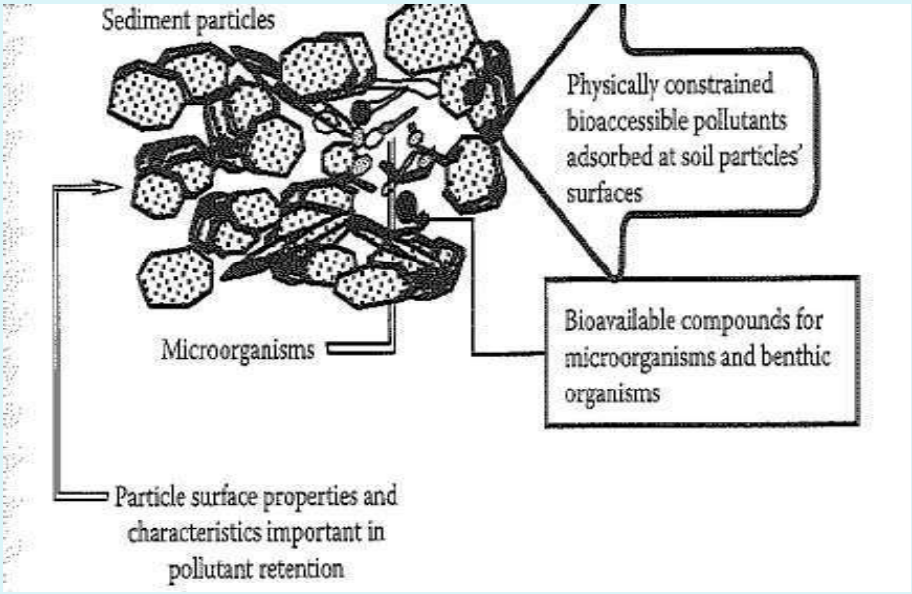
(Mulligan et al., 2010)

Sediment contamination



Sediment contamination

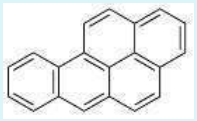
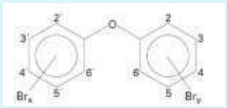
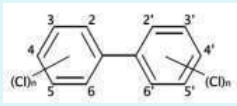
- Bio-attenuation and bioavailability



Properties of typical contaminants

- Molecular weight
- Density
- Water solubility
- K_{ow}
- K_{oc}
- K_H
- Vapor pressure
- Viscosity
- Biodegradability
- others

Examples

Congeners	MW（g/mole）	log K_{ow}	Vapor pressure（Pa, 25°C）	Water solubility（μg/L）
BaP	252.3	6.04	7.0×10^{-7}	3.8
HCB	284.8	5.73	1.45×10^{-3}	6
Aroclor 1254	328	6.5	1.03×10^{-2}	12-57
PentaBDE	564.8	6.5-7.0	4.69×10^{-5}	13.3
OctaBDE	801.5	8.4-8.9	6.59×10^{-6}	<1
DecaBDE	959.2	10.0	4.63×10^{-6}	<0.1

Compounds	MW（g/mole）	Log K_{ow}	Vapor pressure（Pa）	Water solubility（μg/L）
1,2-DCA	99	1.47	1.09E+04	8,500,000
CA	64.5	1.43	1.60E+04	5,700,000
TCE	**131.4**	**2.53**	**9.84E+03**	**1,100,000**
cis-DCE	96.9	1.86	2.70E+04	3,500,000
trans-DCE	96.9	1.93	4.43E+04	6,260,000
1,1-DCE	96.9	2.13	8.03E+04	3,344,000
VC	62.5	1.38	3.54E+05	2,763,000

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3-9

Sediment sampling

- Sediment sampling method（NIEA S104.31B）
  - Sediment: usually consists of clay, silt, sand, organic matters, and other mineral mixtures. After long term physical, chemical, and through biological reaction and aquatic transport process, then deposited on the bottom of water bodies.
  - Surface sediment: the sediment 0 to 15 cm below the surface
  - Deep sediment : the sediment more than 15 cm below the surface。
  - Sampling devices: trowel or scoop, grab sampler, or core sampler
  - Considering sampling objectives, sediment, contaminants, and the environments
  - Samples
    - Grab sampling
    - Composite samples
  - This method describes the apparatus, materials, sampling, sample preservation, safety, and quality controls.

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Samplers

Trowel

Ekman dredge

Gravity corer

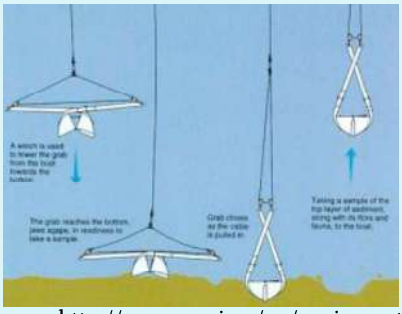
Sampling kit

Van Veen dredge

http://www.kc-denmark.dk/products/sediment-samplers/van-veen-grab/van-veen-grab-2500-cm%C2%B2.aspx

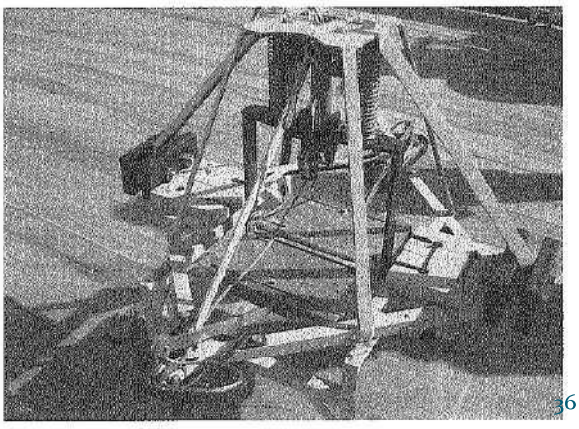
Other samplers

Open core sampler



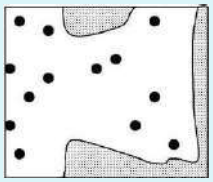
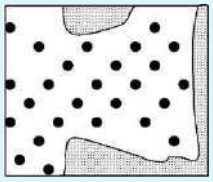
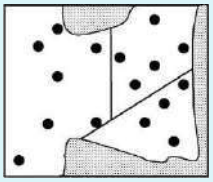
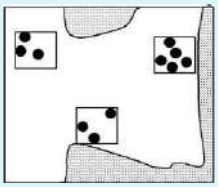
http://www.geosi.no/no/equipment/grabb.htm

Smith McIntyre sampler



(Mulligan et al., 2010)

Sampling points selection

Random	According to the random number table to locate different points	
Grid sampling	Fixed distance	
Zone sampling	Separate into several different homogeneous areas and allocate sample numbers according the weight of area size.	
Multistage sampling	Initially large area and then focused on heavily contaminated areas	

Others

- Weather
  - Temp, wind, tide, wave, storm?
- Transportation
  - Mass transport, rental cars, rental boats, rafts, or wading
- Special needs
  - Climbing
  - Taking boats
  - Diving?
- Safety
  - Insurance
  - safety rope
  - Life jackets
  - Physical training

QA/QC

- Blank samples
  - Field blank sample
  - Trip blank sample
  - Equipment blank sample

Blanks

- Field blank sample
  - Meaning：if contaminated during sampling process
  - Prep：

  - Amount：batch. One of twenty samples and if not

Air：filter paper
groundwater：reagent water or dilution water
sediment ：soils
❖ Without the target pollutant(s).

Blanks

- Trip blank sample
  - Meaning：To judge if the samples were contaminated
  - Prep

  - Amount：every batch and at least one per 20 samples

3-14
41

Blanks

- Equipment blank sample
  - Meaning：also called rinse blanks. To judge if samplers are contaminated
  - Prep：Collect the reagent water or solvent at the very last step of rinsing
  - Amount：every batch and at least one per 20 samples

3-15
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Method selection

- Analytes characteristics
- Feasibility
- Convenience
- Accuracy and precision
- Sensitivity
- Cost?

Methods and instruments

- Instruments
  - Gas chromatography
    - Suitable for chemicals that are thermally stable (will not decompose or change chemical structure). The boiling point should be lower than 350°C.
  - Liquid chromatography
    - Suitable for semi-volatile and non-volatile compounds and those thermally decomposable analytes but the analytes have to be dissolved in solvents.
    - Higher molecular weight
  - Ionic chromatography
  - Inductively coupled plasma optical emission spectrometry (ICP-OES) or ICP-MS
  - Atomic absorption spectroscopy

QA/QC for detection

- Surrogate Standard
- Method blank sample
- Quality check sample
- Duplicate sample
- Spiked sample

3-17

Pretreatment

- All samples have to be determined for their water contents
- Digestion
- Extraction

Extraction

Using accelerated solvent extraction to recover a 40-ml sample with solvent

圖5　Speed Extractor

(Speed Extractor E-916, BÜCHI Labortechnik AG, Switzerland)

Using GC for analysis
Column: depends定樣品
Injection: 1 μL
Carrier gas: Nitrogen

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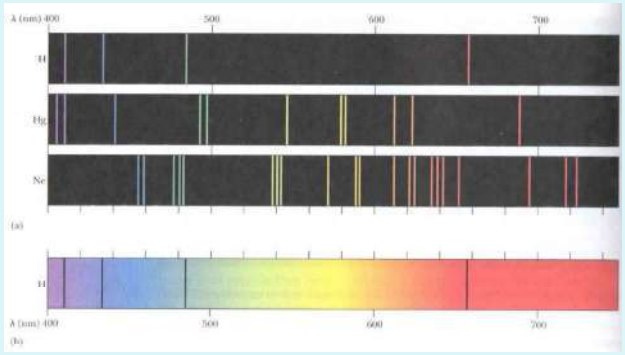
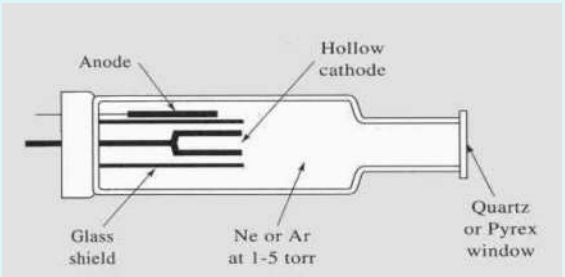
Heavy metal analysis (I)

- Atomic absorption spectrometry (AA)





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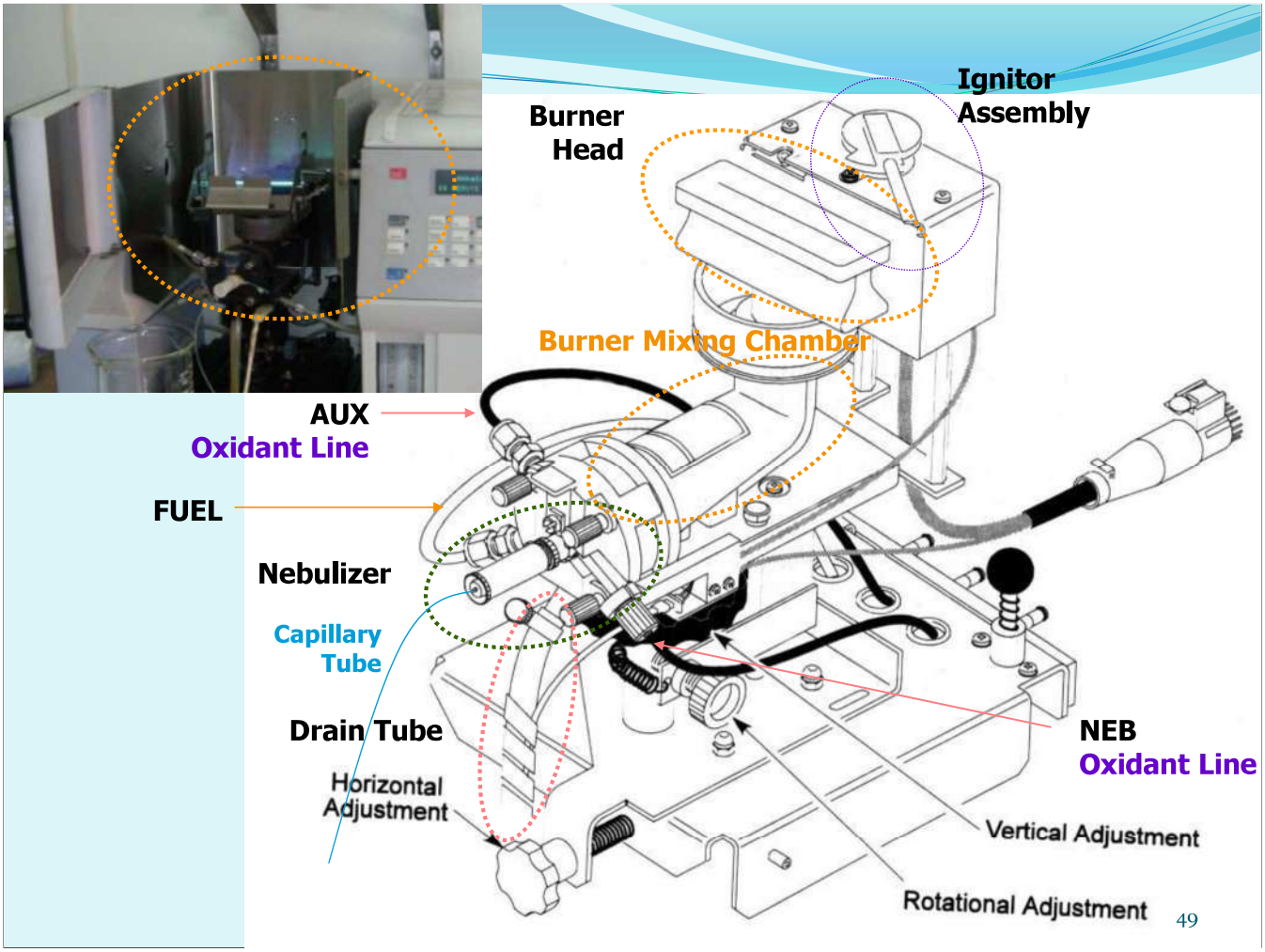
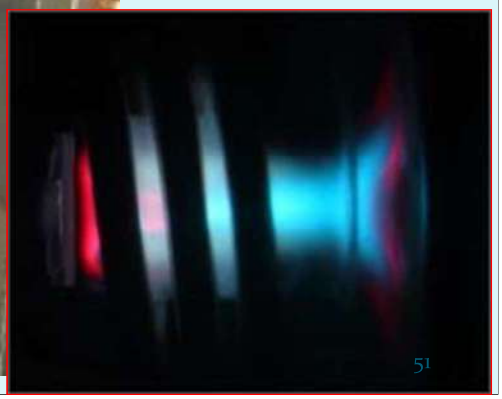


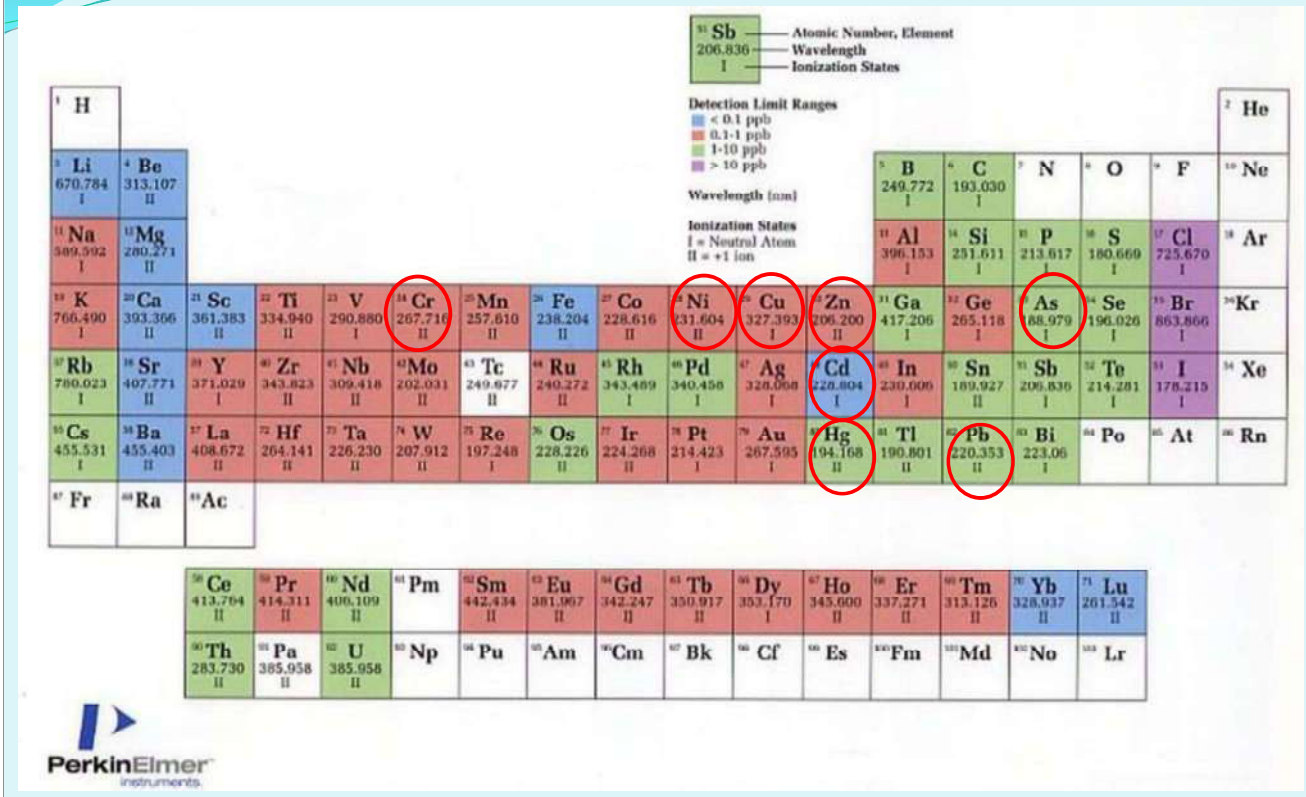
Heavy metals (II)

- Inductively coupled plasma- optical emission spectrometry
- Can quantify more than 60 different metals
- No need to change lamps
- Higher sensitivity (but not so for Hg, As, etc.)

ICP-OES



51


51 Sb
206.836
I
Atomic Number, Element
Wavelength
Ionization States
Detection Limit Ranges
< 0.1 ppb
0.1-1 ppb
1-10 ppb
> 10 ppb
Wavelength (nm)
Ionization States
I = Neutral Atom
II = +1 Ion
PerkinElmer
instruments

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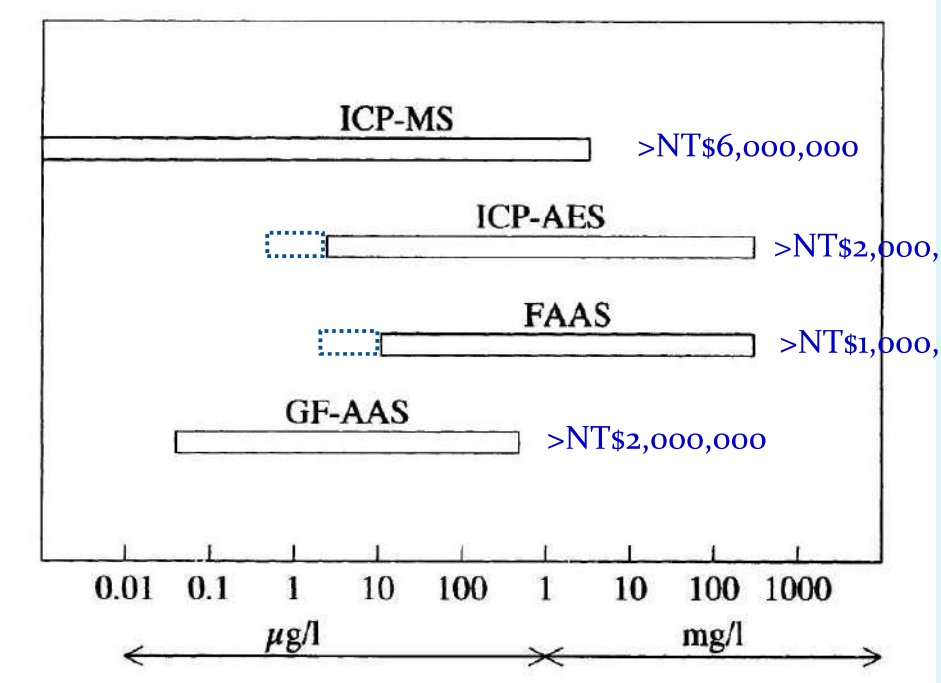
Dynamic range



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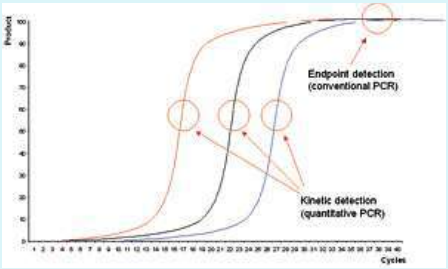
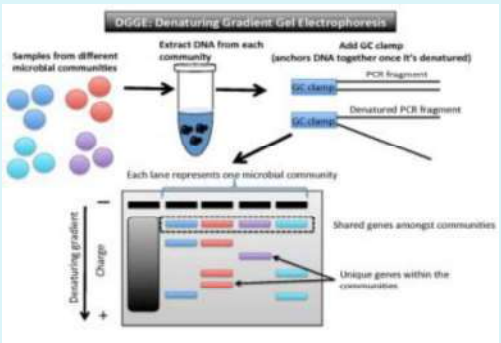
Biological analysis

- Total cell count and viability count
- Fluorescent in situ hybridization
- Polymerase chain reaction – denaturant gradient gel electrophoresis
- Real-time PCR or Q-PCR
- Stable isotope probing
- Flow cytometry and cell sorting
- Pyro-sequence and NGS





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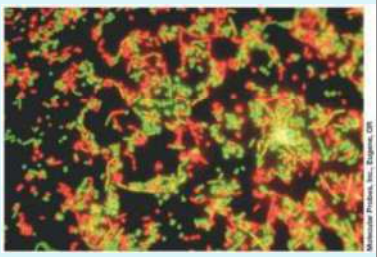
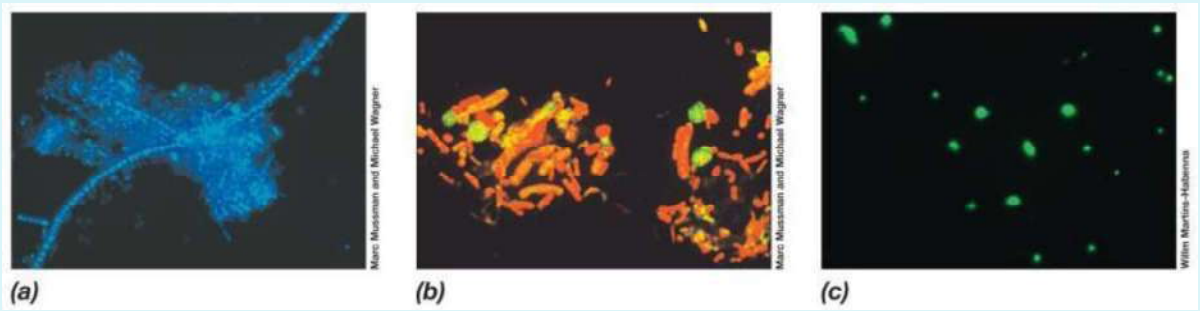
Total cell count

- Fluorescent staining using DAPI (a), acridine orange (b), or SYBR Green I (c). Cannot differentiate between live and dead cells
- Viability stains: differentiate between live and dead cells

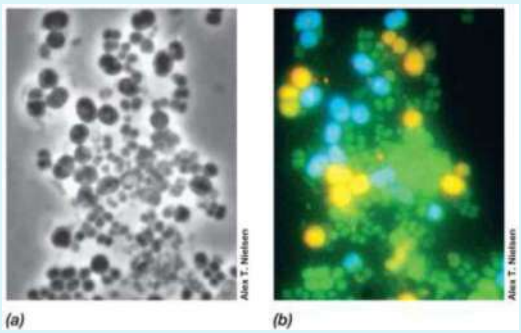


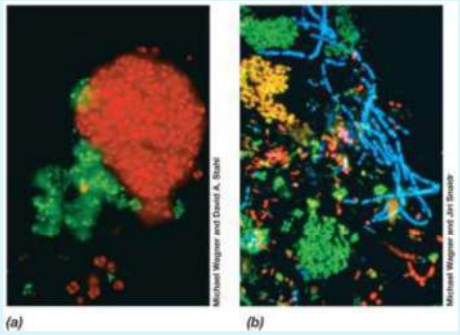


Photos are from *Brock Biology of Microorganisms* by Madigan et al., 2015

Fluorescent in situ hybridization (FISH)

- Nucleic acid probe is DNA or RNA complementary to a sequence in a target gene or RNA
- FISH: fluorescence in situ hybridization Phylogenetics of microbial populations
  - Fluorescing nucleotides complementary to rRNA sequence

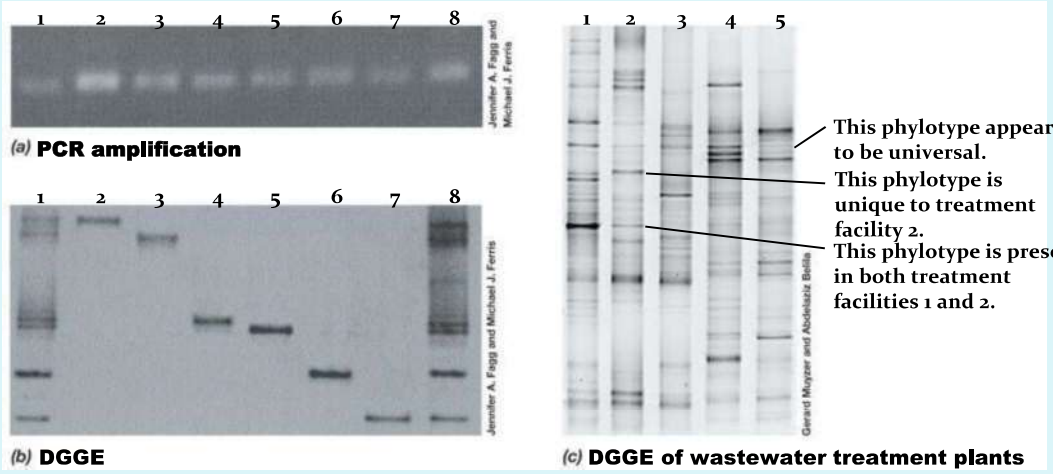




Photos are from *Brock Biology of Microorganisms* by Madigan et al., 2015

PCR-DGGE

- PCR : Polymerase chain reaction
- DGGE: denaturing gradient gel electrophoresis separates genes based on differences in base sequence.
  - Denaturant is a mixture of urea and formamide
  - Strands melt at different denaturant concentrations



Photos are from *Brock Biology of Microorganisms* by Madigan et al., 2015

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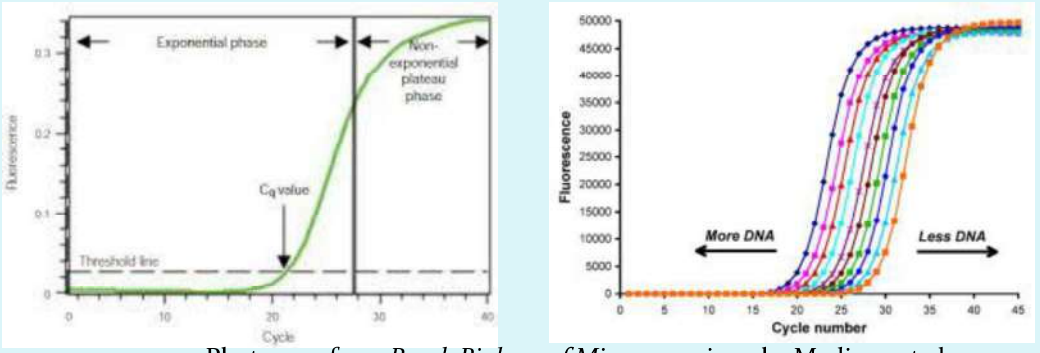
Real-time PCR or qPCR

- Purpose
  - Quantitative identification of specific microbes
  - Quantifying the expressed mRNAs
- Reverse transcriptase PCR (RT-PCR) to make cDNA
- Quantitative real-time PCR
  - Uses fluorescently labeled PCR products
  - Almost immediate results



Photos are from *Brock Biology of Microorganisms* by Madigan et al., 2015

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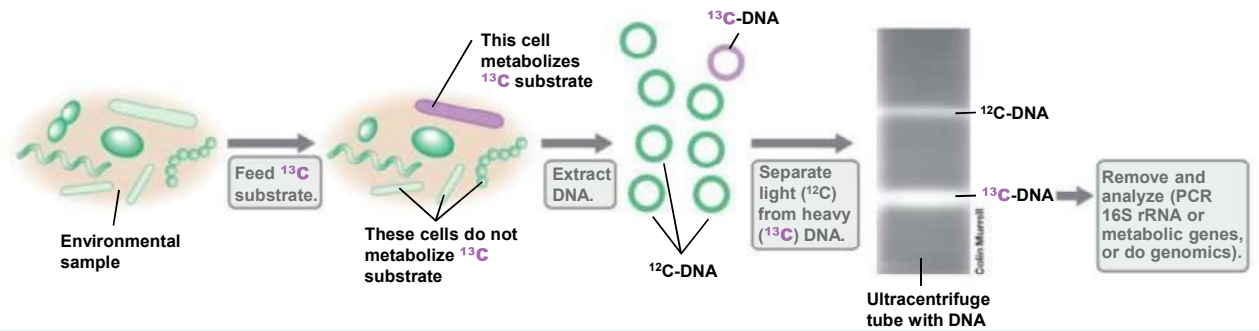
Stable isotope probing

- *Stable isotope probing (SIP)*: links specific metabolic activity to diversity using a stable isotope
  - Microorganisms metabolizing stable isotope (e.g., ^{13}C)
  - DNA with ^{13}C can then be used to identify the organisms that metabolized the ^{13}C
  - SIP of RNA also possible



Photos are from *Brock Biology of Microorganisms* by Madigan et al., 2015

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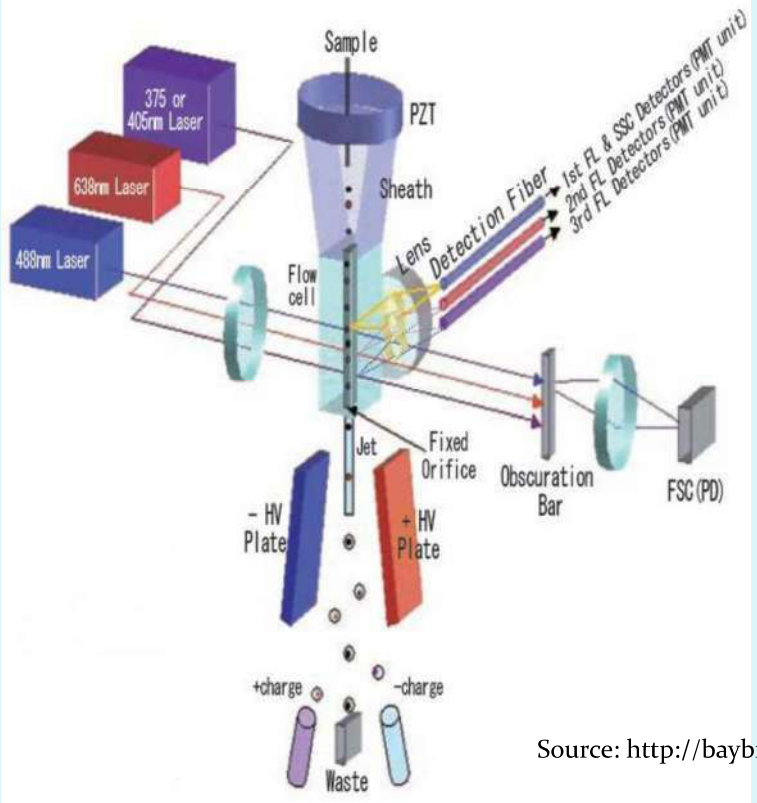
Flow cytometry



Source: http://baybio.co.jp/english/jsan/8.html

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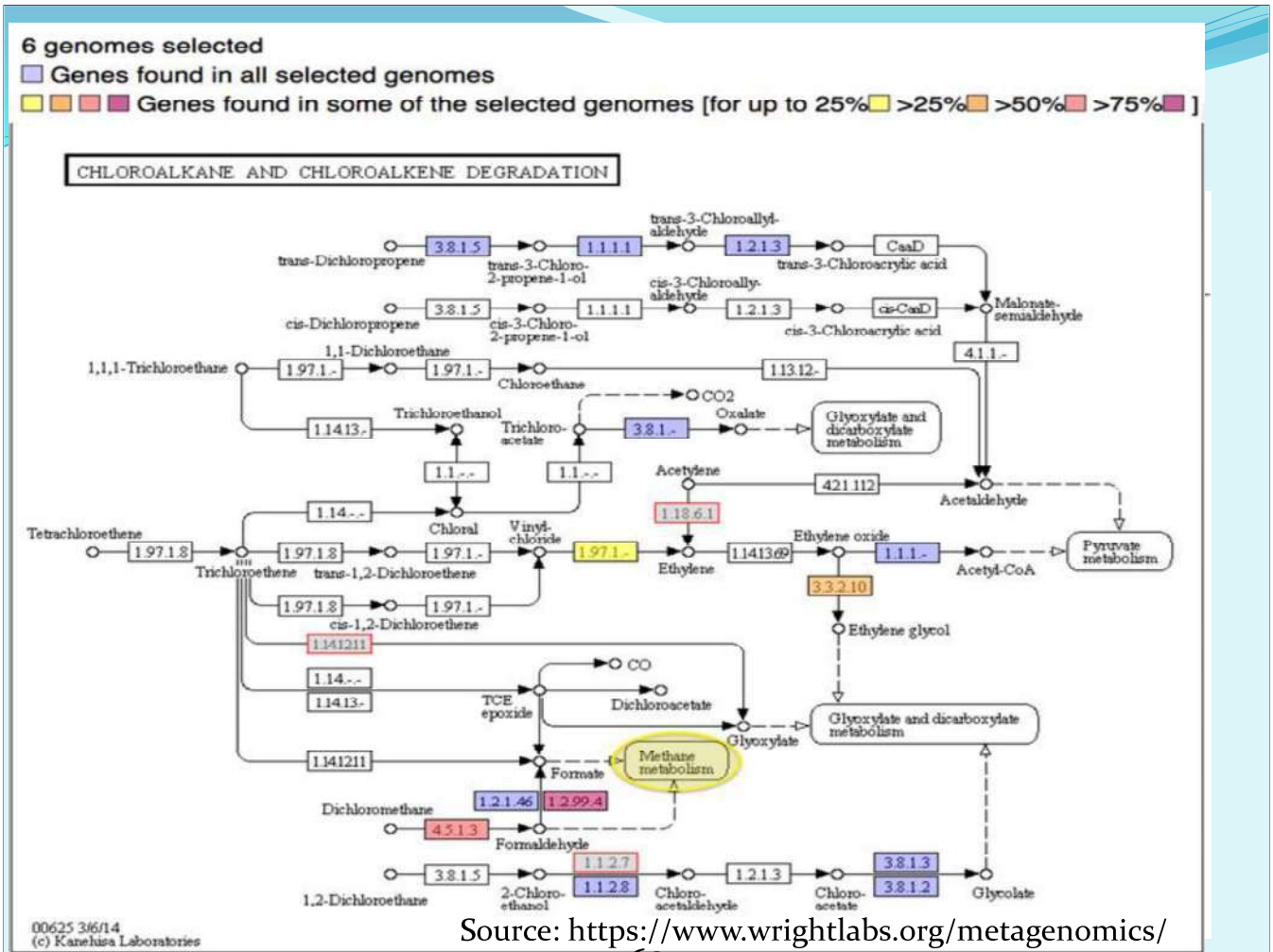
Pyro-sequence and NGS

- Sequencing: determining the precise order of nucleotides in a DNA or RNA molecule
- Sanger dideoxy method
- Second generation sequencing
  - Generates data 100x faster than Sanger method
  - Massively parallel methods
  - Large number of samples sequenced side by side
  - Uses increased computer power and miniaturization
    - 454 Life Sciences pyrosequencing
    - Illumina/Solexa sequencing https://www.youtube.com/watch?annotation_id=annotation_228575861&feature=iv&src_vid=womKfikWlxM&v=fCd6B5HRaZ8
    - SOLID/Applied Biosystems method
- Third generation sequencing
- Fourth generation sequencing



Source: https://www.wrightlabs.org/metagenomics/

Sediment remediation

Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

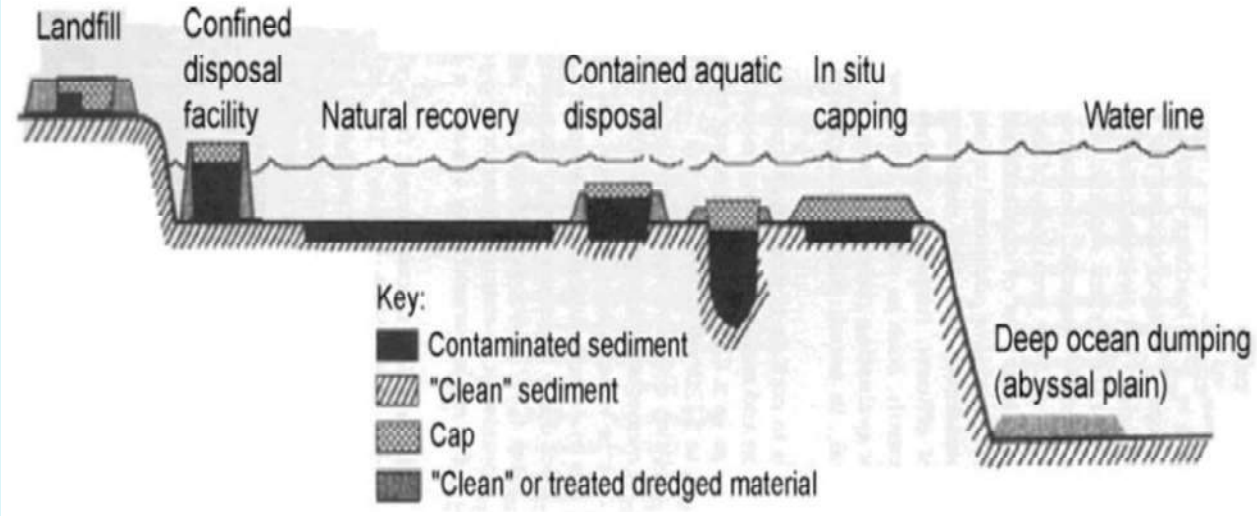
Remediation

- Remedial technologies
- Engineering practices
- Two cases
- Current research

Remedial technologies

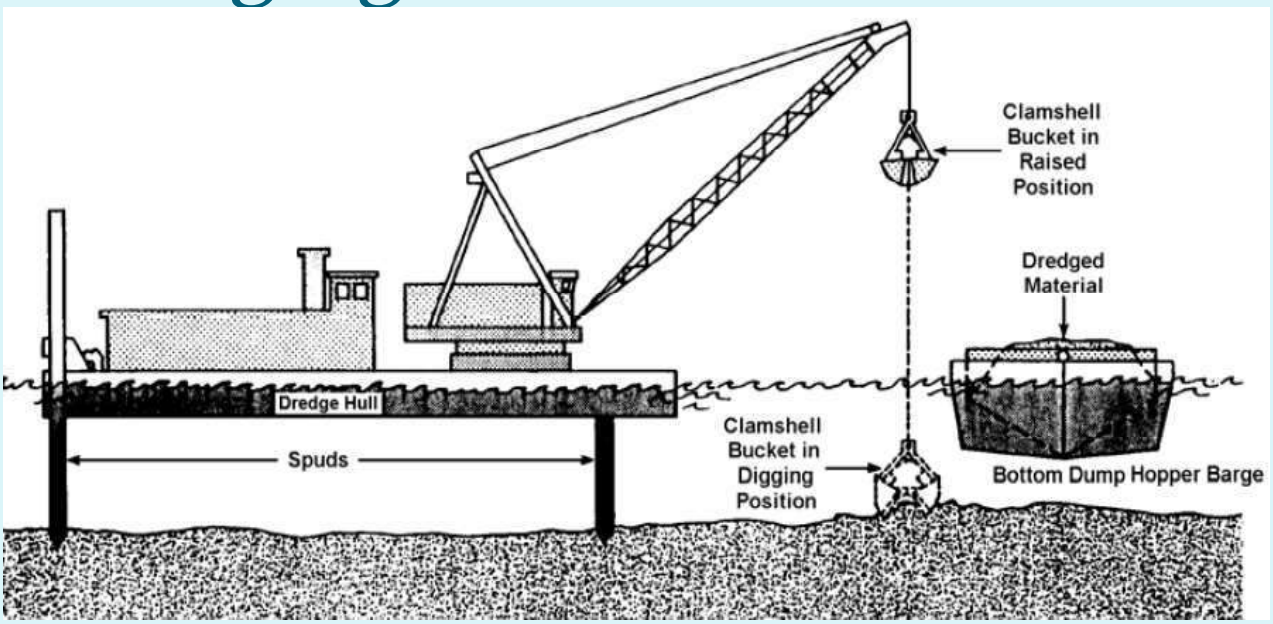
- Physical: separation, rinsing, floatation, ultrasonic
- Chemical/thermal treatment：oxidation, electrokinetic, solidification, plasma vitrification, thermal desorption
- Biological：Slurry reactor, land farming, compositing, bioleaching, biotransformation, phytoremediation

Engineering practices



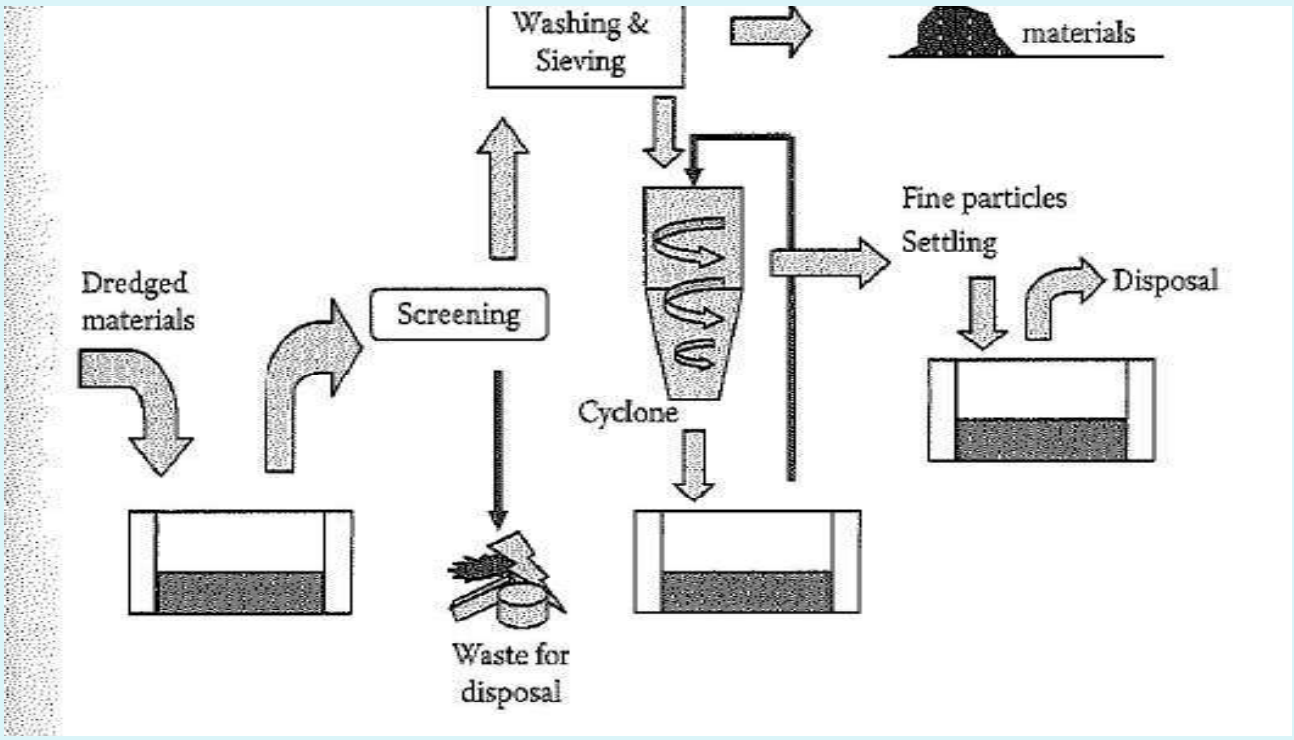
(Adriaens et al., 2006)

Dredging



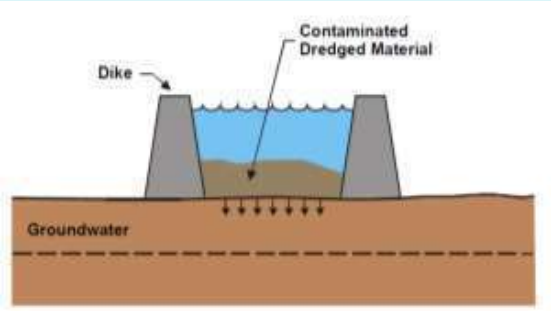
(Palermo et al, 2008)

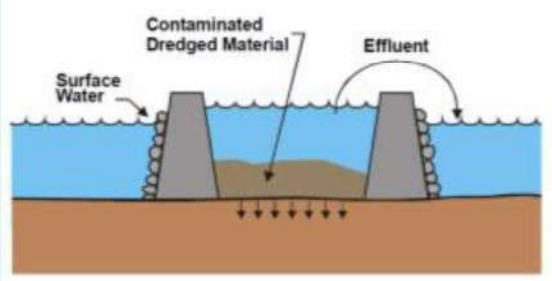
Treatment of dredged materials

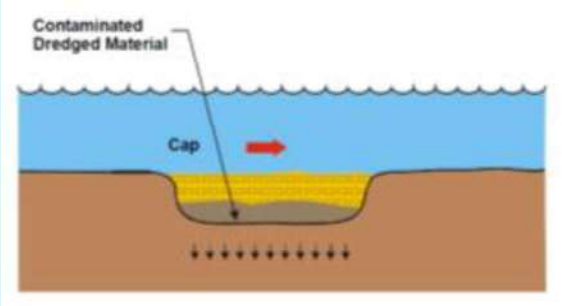


(Mulligan et al., 2010)

Confined disposal

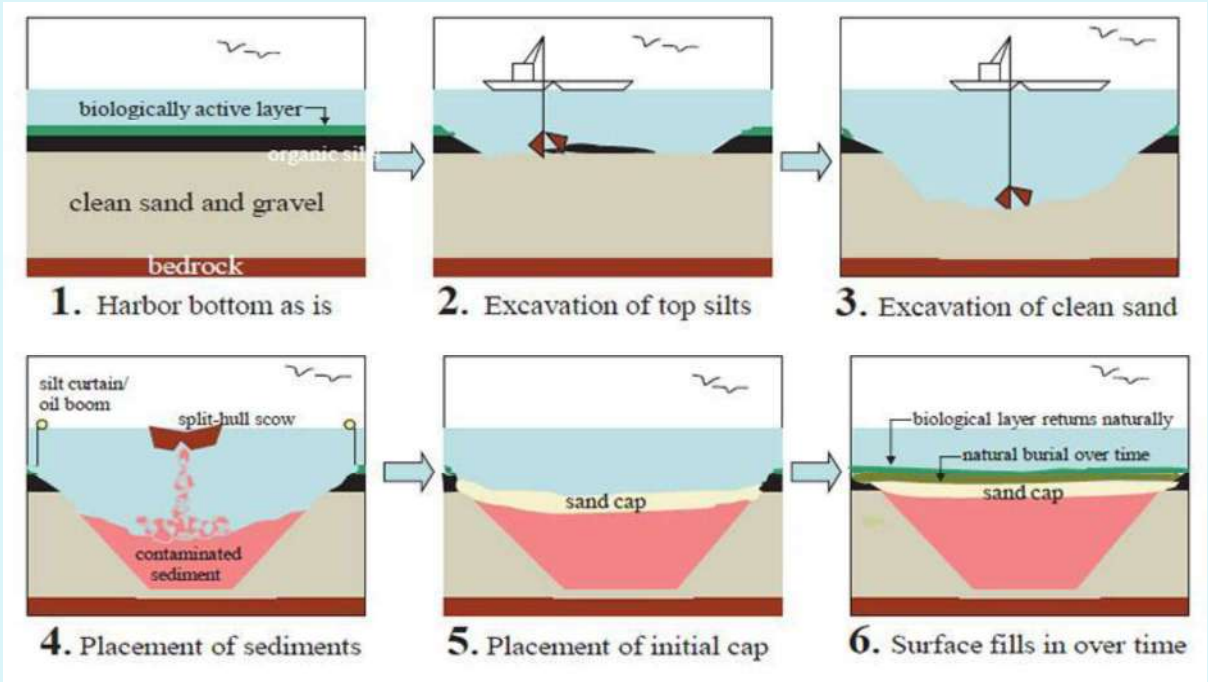






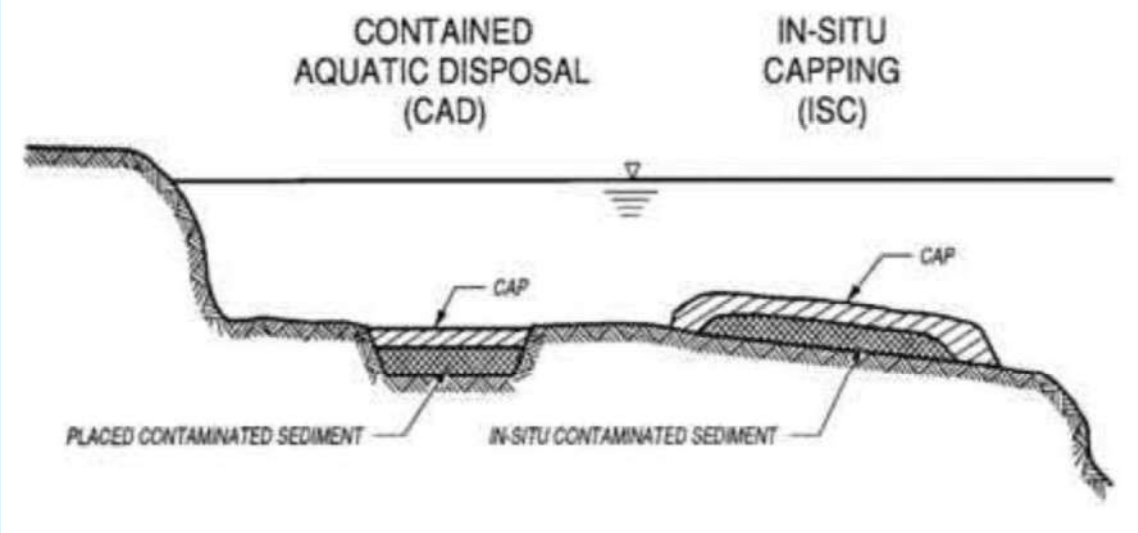
(Netzband, 2002)

Contained aquatic disposal



(Thomas and Concord, 2005)

Capping

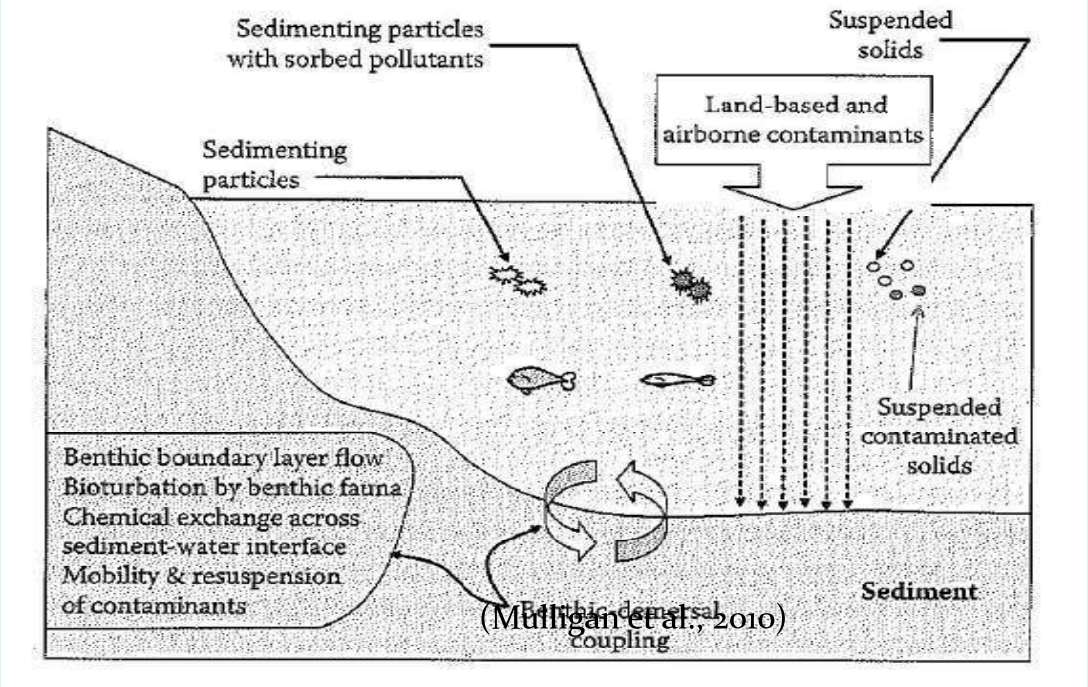


(Aldrich, 2010)

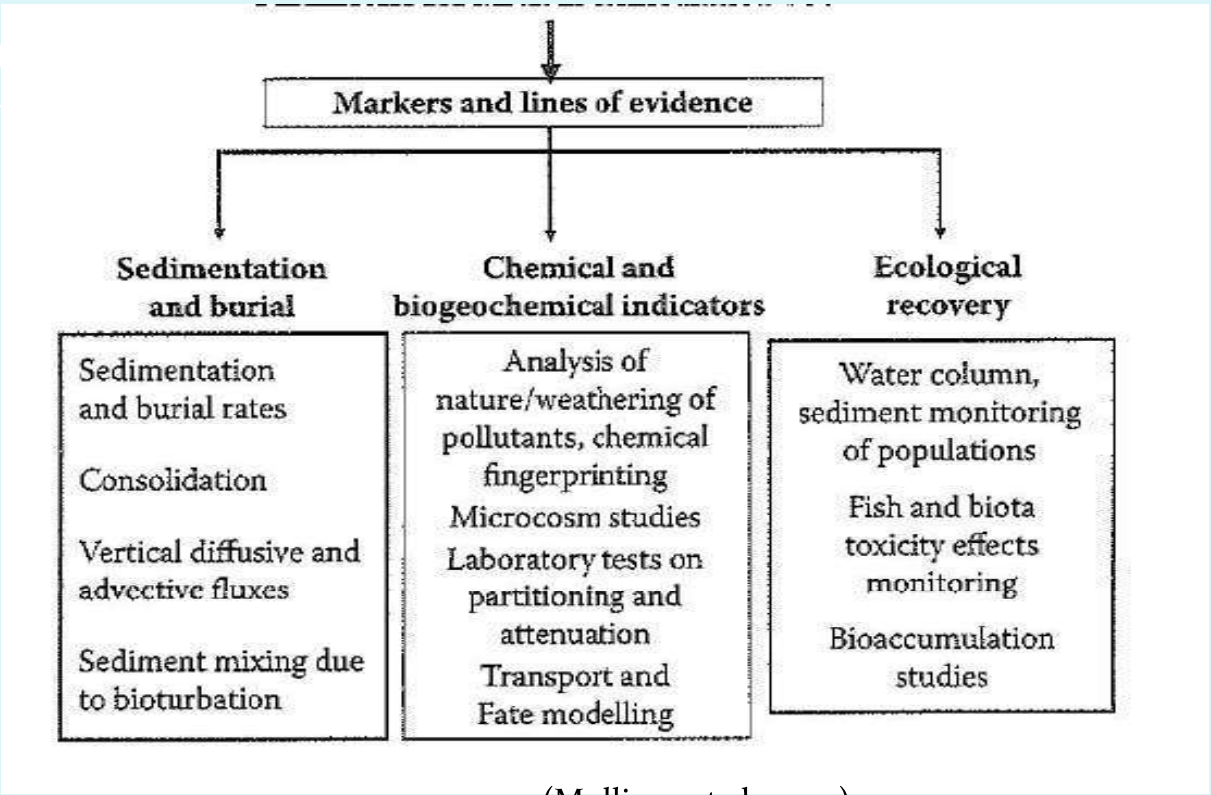
Active capping

- Organic clay
- Activated carbon
- Ash
- Apatite
- reactive mat

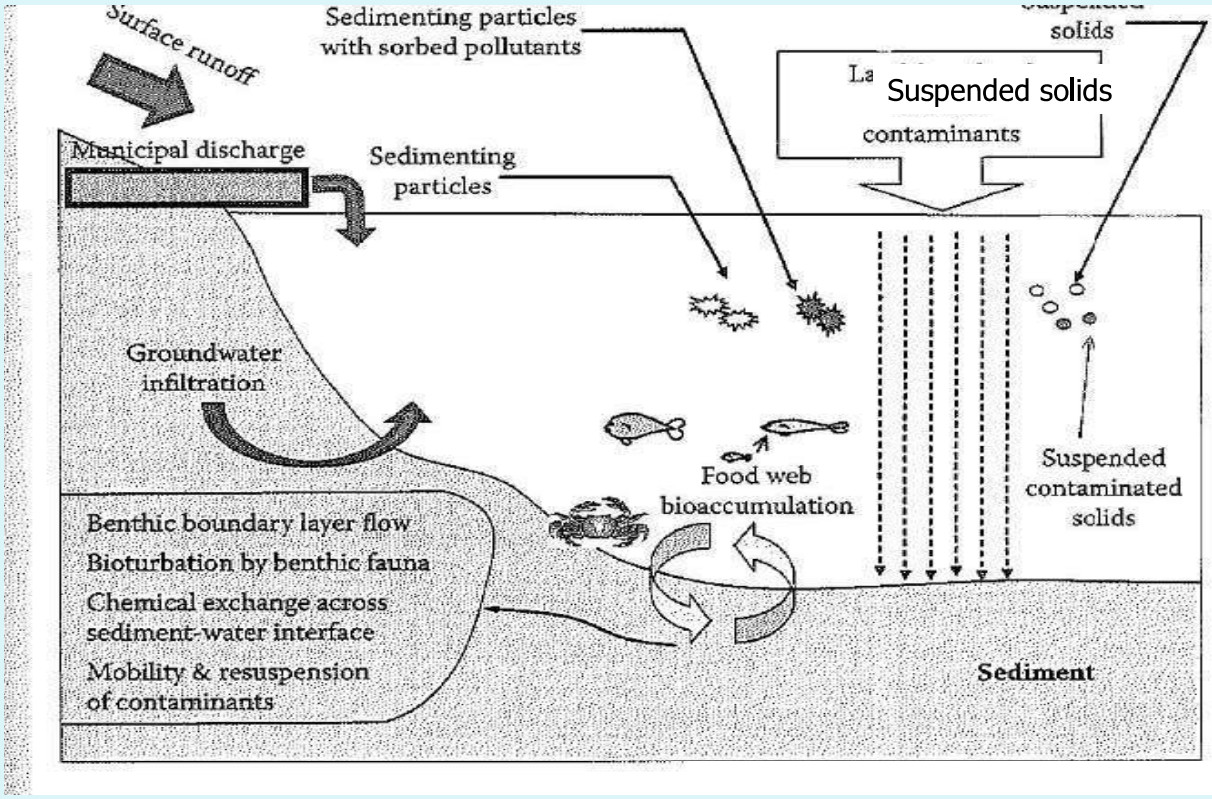
Monitored natural recovery (MNR)



(Mulligan et al., 2010)



(Mulligan et al., 2010)



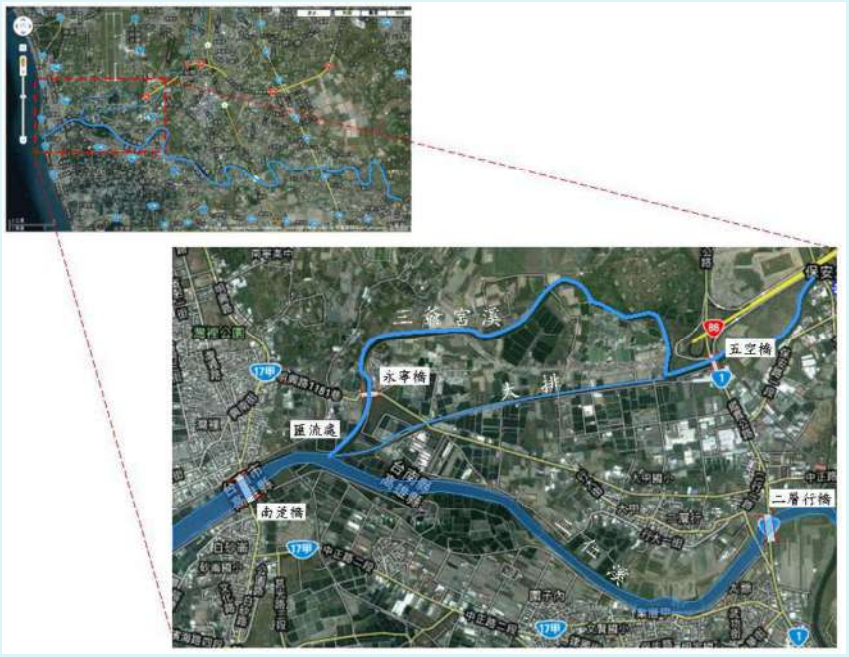
(Mulligan et al., 2010)

Case 1
Sediment remediation

Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

A pilot study on remediation

- Er-Ren River as an example
  - PAHs
  - PCBs
  - Dioxins
  - Heavy metals



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Initial conditions

- PAHs

PAHs	環數	二層行橋	永寧橋	匯流處	匯流下游	南萣(上游)	南萣(下游)	平均濃度/上限	平均濃度/下限
Naphthalene	2	ND	ND	ND	0.11	0.39	ND	0.15	1.19
Acenaphthylene	3	0.06	0.32	0.35	0.11	0.18	0.23	0.49	5.19
Aceaphthene	3	1.66	2.73	2.25	0.66	1.40	1.29	6.17	41.64
Fluorene	3	0.21	1.13	4.41	0.07	0.25	0.16	4.00	25.98
Phenanthrene	3	0.23	0.80	1.90	0.42	0.15	0.16	0.55	4.07
Anthracene	3	0.04	0.58	1.98	0.33	0.12	0.66	0.77	7.73
Fluoranthene	4	0.44	1.13	9.92	1.75	0.60	0.27	0.82	8.11
Pyrene	4	0.11	0.53	6.28	1.39	1.42	0.20	0.69	5.71
Benzo(a)anthracene	4	0.40	2.18	2.67	0.86	0.19	0.65	0.96	8.27
Chrysene	4	0.70	0.68	13.49	0.96	0.36	2.26	1.78	16.18
Benzo(b)fluoranthene	5	0.78	12.89	11.26	0.63	2.46	0.67	1.58	14.94
Benzo(k)fluoranthene	5	0.35	5.66	26.34	0.73	0.96	0.36	4.10	35.83
Benzo(a)pyrene	5	0.56	16.38	8.46	1.18	0.96	0.80	3.52	29.50
Indeno(1,2,3-cd)pyrene	6	0.19	5.86	2.92	0.22	0.77	0.32	1.39	10.71
Dibenzo(a,h)anthracene	6	0.31	7.70	4.03	0.39	0.61	0.36	8.58	55.79
Benzo(g,h,i)perylene	6	0.27	6.73	13.07	1.85	1.06	0.49	3.06	26.08

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Heavy metal and PCBs

Conta-minants	analytical results, mg/kg						value/reg.	value/ upper limit	value/ lower limit
	1	2	3	Mean	Stdev	CV			
Nap	<0.01	<0.01	<0.01	NA	NA	NA	NA	NA	NA
PCBs*	**0.369**	**0.155**	**0.209**	**0.244**	**0.111**	**45.50%**	**272%**	22%	**271%**
As	7.72	9.97	10.3	9.33	1.4	15.00%	16%	28%	85%
Cd	1.18	1.14	1.15	1.16	0.021	1.80%	6%	46%	**178%**
Cr	**352**	**360**	**354**	**355**	**4.16**	**1.20%**	**142%**	**152%**	**467%**
Cu	**648**	**641**	**640**	**643**	**4.36**	**0.70%**	**161%**	**410%**	**1286%**
Hg	0.378	0.274	0.304	0.319	0.054	16.80%	2%	37%	**139%**
Ni	167	166	164	166	1.53	0.90%	83%	**208%**	**692%**
Pb	194	193	196	194	1.53	0.80%	10%	**120%**	**404%**
Zn	818	796	830	815	17.2	2.10%	41%	**212%**	**582%**

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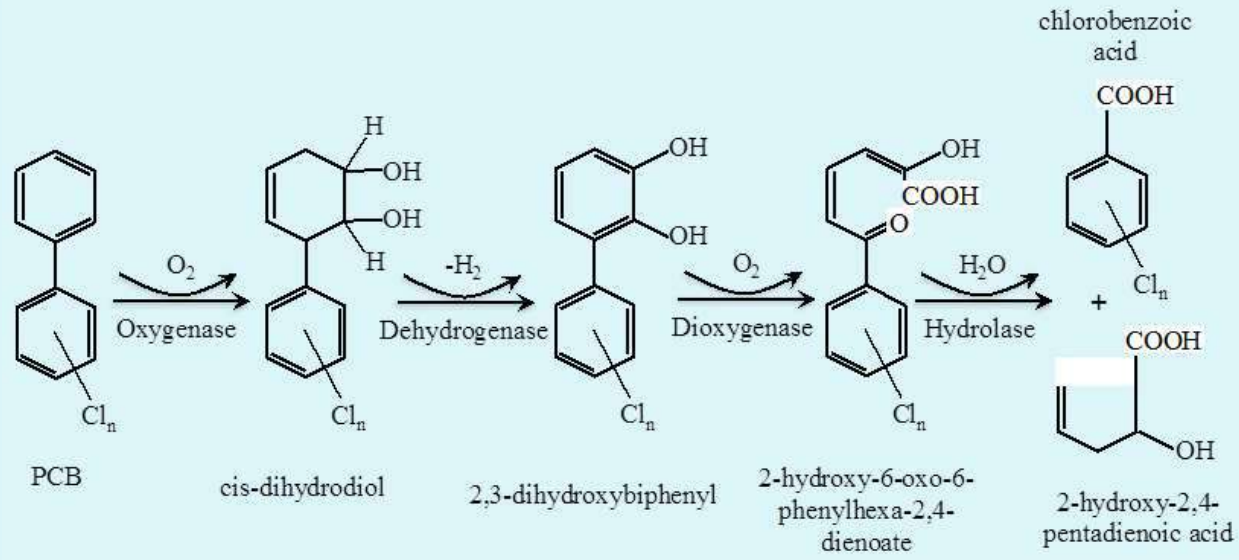
PCBs degradation pathway (1)



(Borja *et al.*, 2005)

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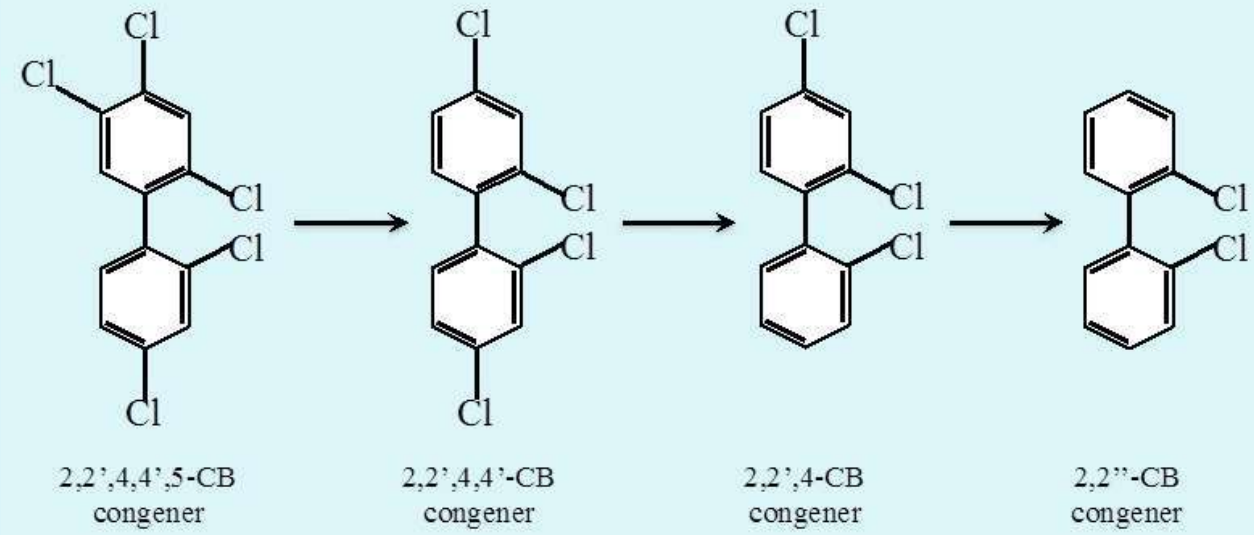
PCBs degradation pathway (2)



(Borja *et al.*, 2005)

Nanoemulsion in lab test

- Lab result
  - PCBs
  - As and Cr

組別	厭氧			好氧		
	k(day^{-1})	R^2	$k_{ave.}$ (d^{-1})	k(day^{-1})	R^2	$k_{ave.}$ (d^{-1})
NC	-0.0129	0.3020	-0.0099	-0.0166	0.3948	-0.0090
NE1	-0.0083	0.6022		-0.0121	0.4639	
NE2	-0.0089	0.5009		-0.0063	0.1643	
NE3	-0.0094	0.7803		-0.0010	0.1588	
NLC	-0.0217	0.7983	-0.0144	-0.0148	0.5210	-0.0113
NLE1	-0.0166	0.8869		-0.0183	0.7818	
NLE2	-0.0086	0.3953		-0.0106	0.6016	
NLE3	-0.0109	0.9407		-0.0014	0.0191	
NHC	-0.0125	0.5581	-0.0119	-0.0128	0.5470	-0.0075
NHE1	-0.0110	0.7064		-0.0067	0.2503	
NHE2	-0.0080	0.7902		-0.0052	0.1061	
NHE3	-0.0163	0.7975		-0.0052	0.6934	
TC	-0.0069	0.3256	-0.0058	-0.0080	0.1358	-0.0068
TE1	-0.0104	0.6774		-0.0047	0.1514	
TE2	-0.0020	0.1512		-0.0136	0.6769	
TE3	-0.0040	0.4612		-0.0009	0.0053	
TLC	-0.0079	0.8901	-0.0037	-0.0118	0.5510	-0.0069
TLE1	-0.0063	0.6287		-0.0055	0.0939	
TLE2	-0.0019	0.7942		-0.0068	0.1329	
TLE3	0.0014	0.2053		-0.0037	0.1148	
THC	-0.0075	0.4457	-0.0015	-0.0152	0.4245	-0.0079
THE1	0.0030	0.0618		-0.0040	0.0719	
THE2	0.0009	0.3027		-0.0083	0.2874	
THE3	-0.0025	0.5007		-0.0042	0.0551	

As Removal

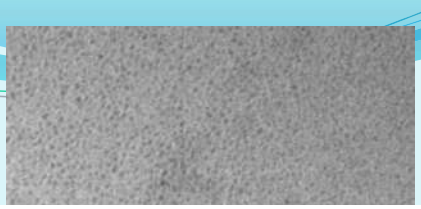
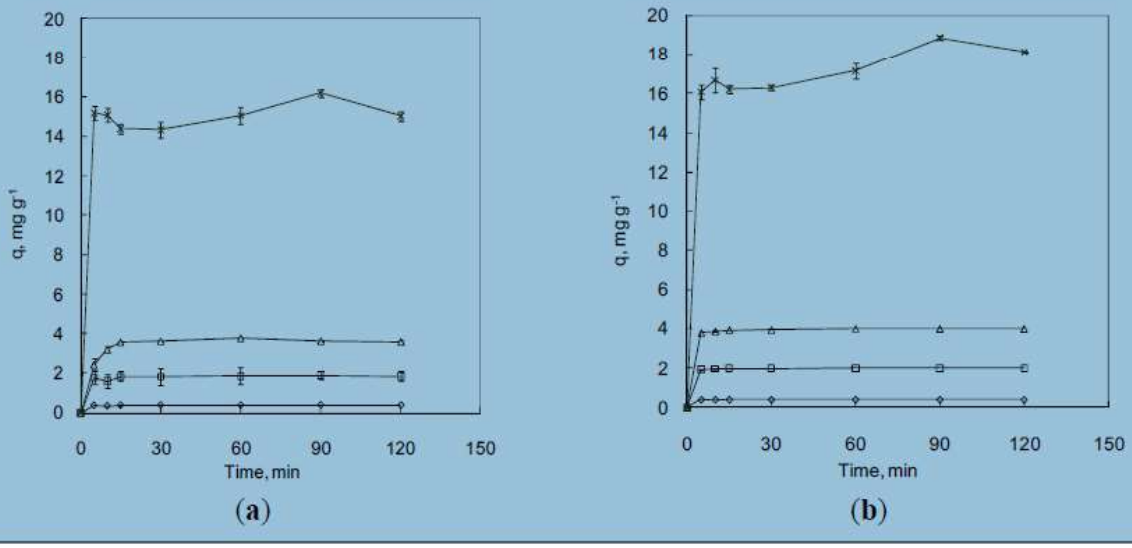


Figure 3. Adsorption of As(III) (**a**) and As(V) (**b**) by MNP under anaerobic condition. Rhombus, square, triangle, and cross represent initial concentrations of 10, 50, 100, and 500 $\mu g \cdot L^{-1}$, respectively. Error bars indicate CI 95%.



As removal

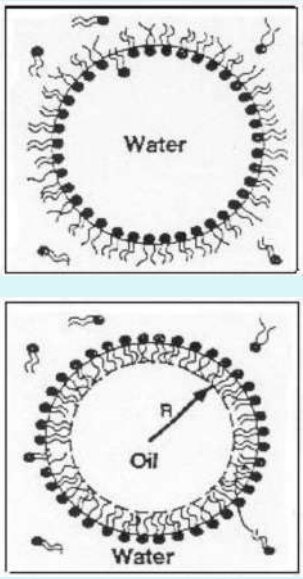
Table 1. Comparison of the adsorption capacity of different iron oxide on As(III) and As (V).

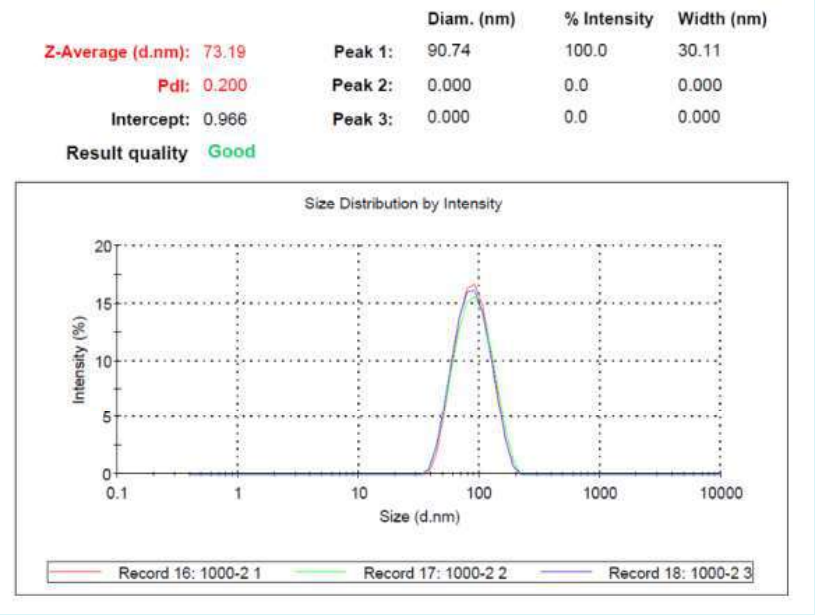
Adsorbent	Size (nm)	pH	SSA ($m^2 \cdot g^{-1}$)	q_e, max				References
				A(III) ($mg \cdot g^{-1}$)	As(V) ($mg \cdot g^{-1}$)	As(III) (nm^{-2})	As(V) (nm^{-2})	
MNP	3.02 ± 0.32	8.0	65.8	168.8	206.9	-	-	This study
				108.6	138.1	-	-	This study
MNPC	-	8.0	-	157.9	165.1	-	-	This study
Maghemite	6	7	174	172.5	-	8.1	-	[11]
Magnetite	12	8.0	-	-	~200 **	-	-	[14]
	11.72	8.0	98.8 *	114.9	172.5	9.3 *	14.0 *	
Magnetite	20	8.0	60	29.2	5.9	3.8 *	0.8 *	[13]
	300	6.1	3.7	1.5	0.75	3.3 *	1.6 *	
Maghemite	3.8 ± 0.8	7.0	203.2	-	20.0	-	0.04	[21]
		9.0			12.5	-	0.02	

* Calculated by Yean *et al.* [13]. ** Estimated by the authors.

Nanoemulsion

- 成分：大豆油、食品級界面活性劑、水

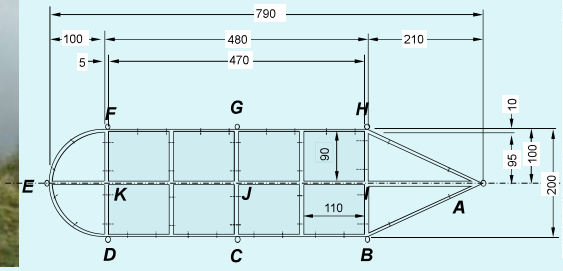


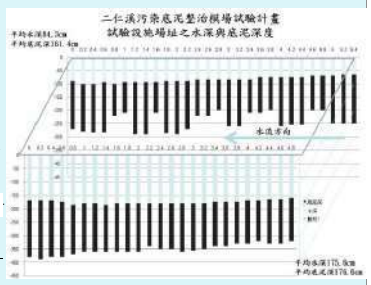


Experiments

Group	No.	MNP	MNP recovery	SONE
NR	1	0 mg/L	N	0
	2	0 mg/L	N	0
Adsorptin	3	0 mg/L	Y	0
	4	20 mg/L	Y	0
	5	1000 mg/L	Y	0
Bio-stimulation	6	0 mg/L	N	0.10%
	7	0 mg/L	N	1.00%
	8	0 mg/L	N	10.0%
Integrated	9	20 mg/L	Y	0.10%
	10	1000 mg/L	Y	0.10%
	11	20 mg/L	Y	1.00%
	12	1000 mg/L	Y	1.00%

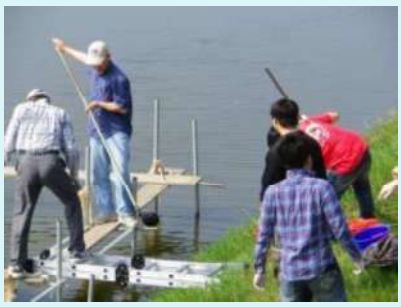
Process（1）





87

Process（2）



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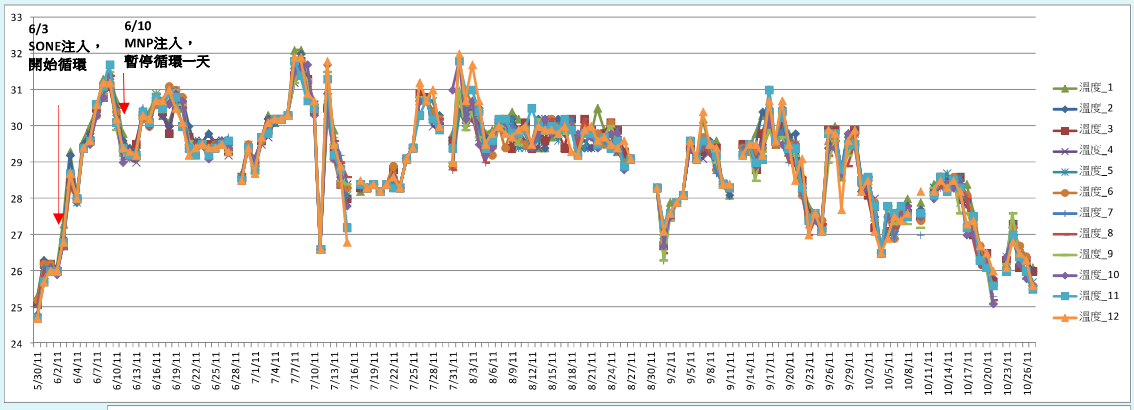
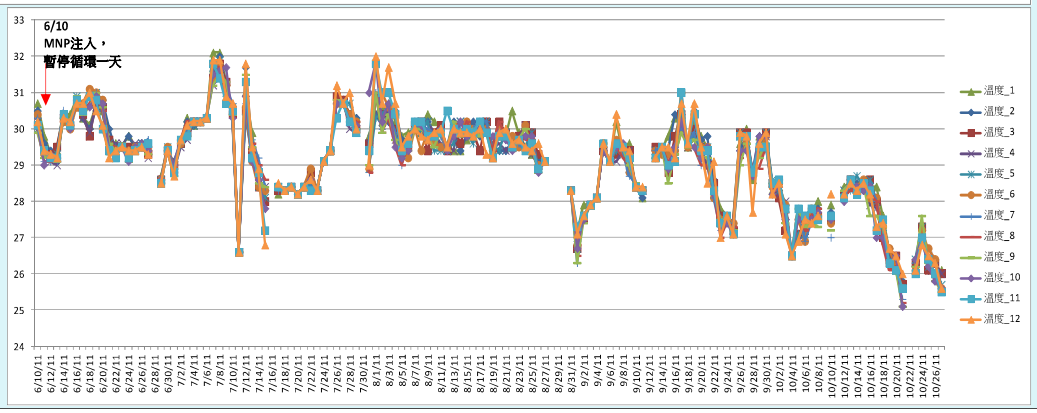
Field measurement

- Temp





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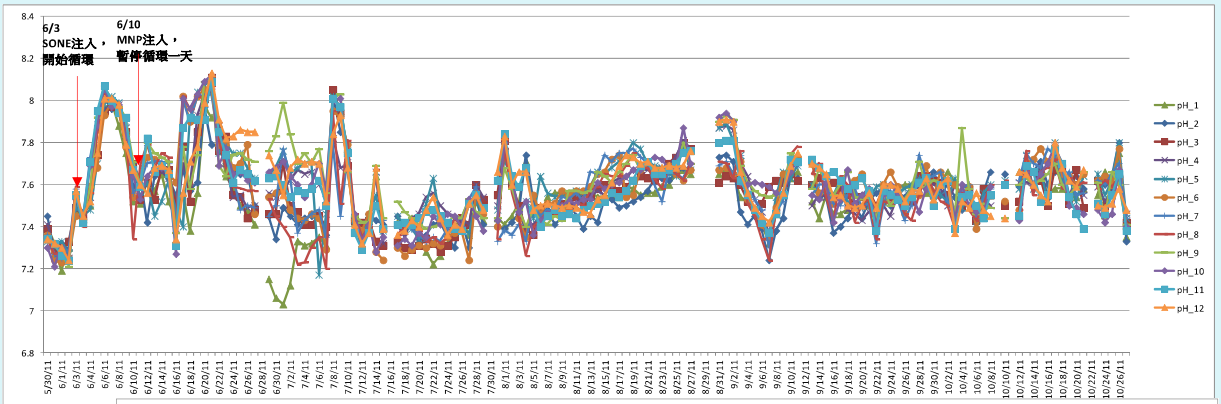
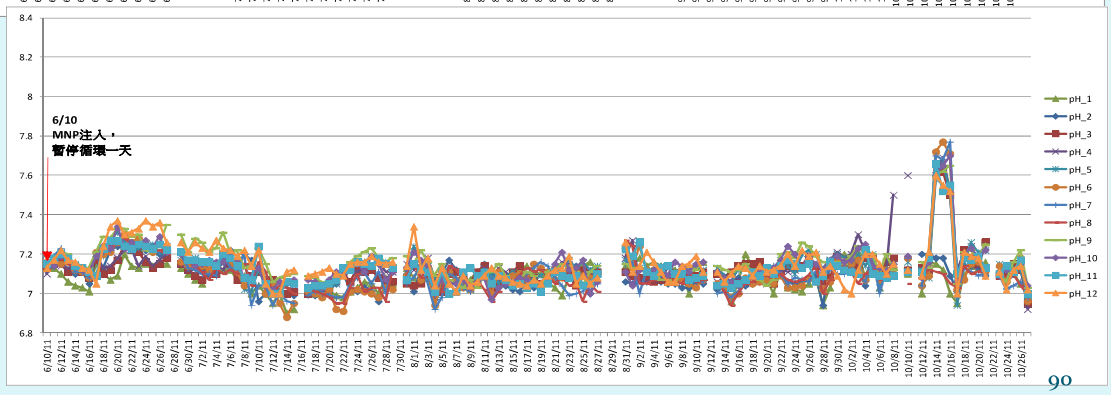
Field measurement

- pH

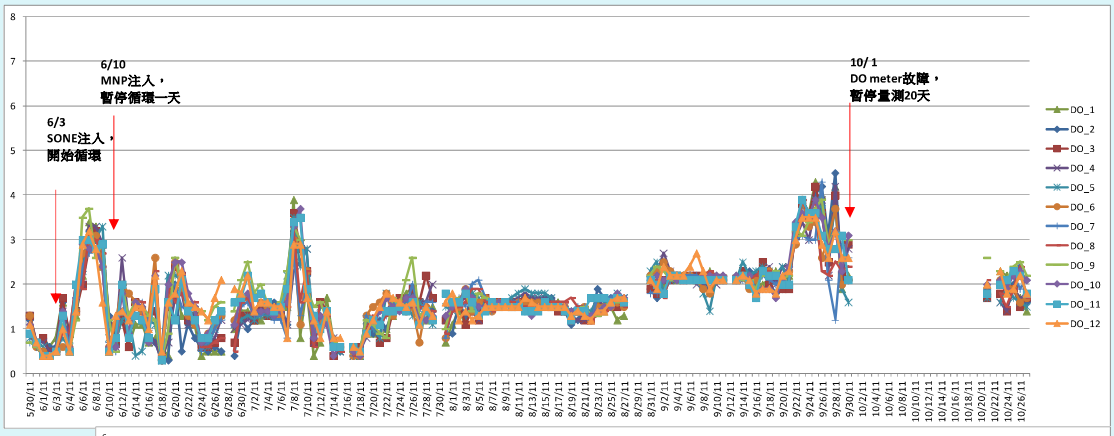


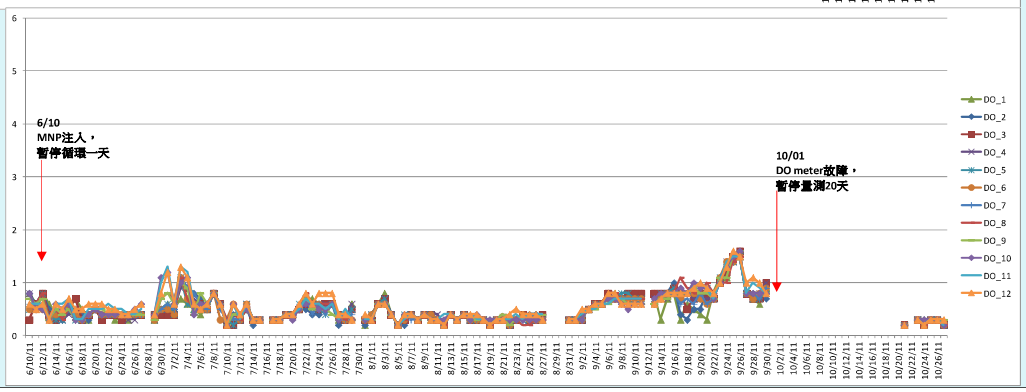


90

Field measurement

- DO





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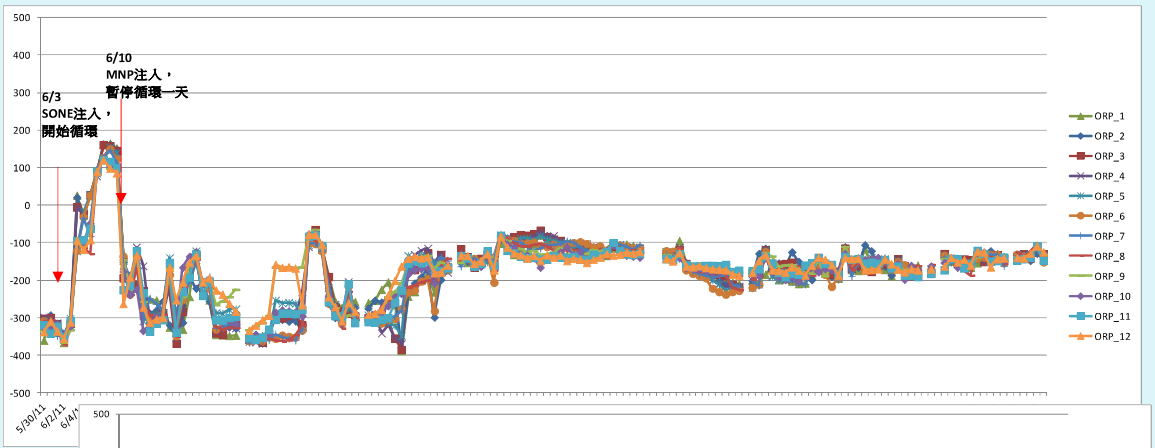
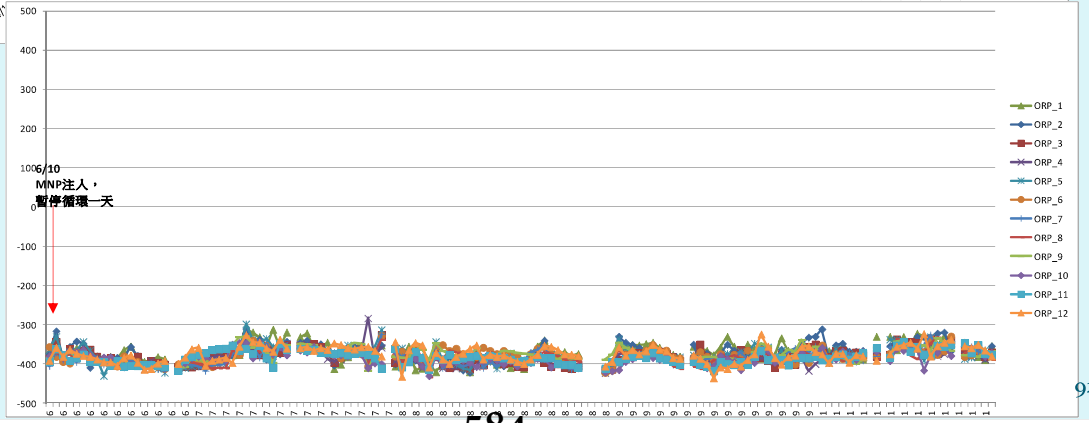
Field measurement

- ORP





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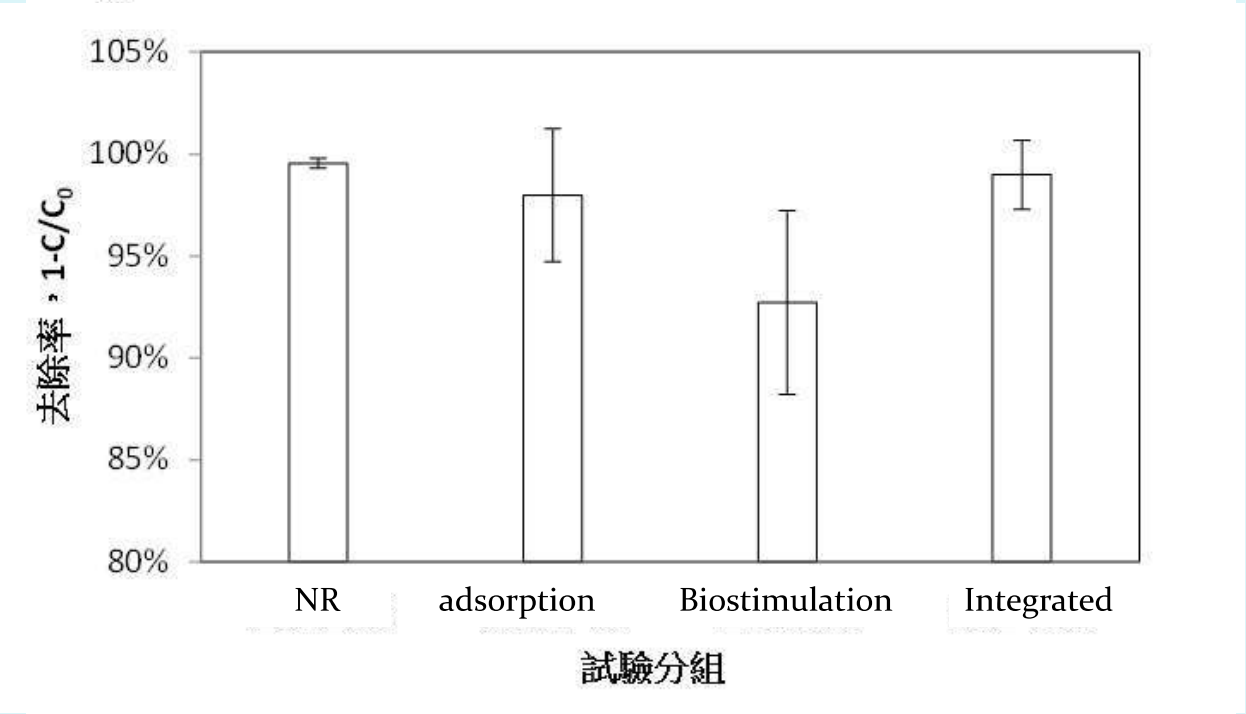
Nap removal



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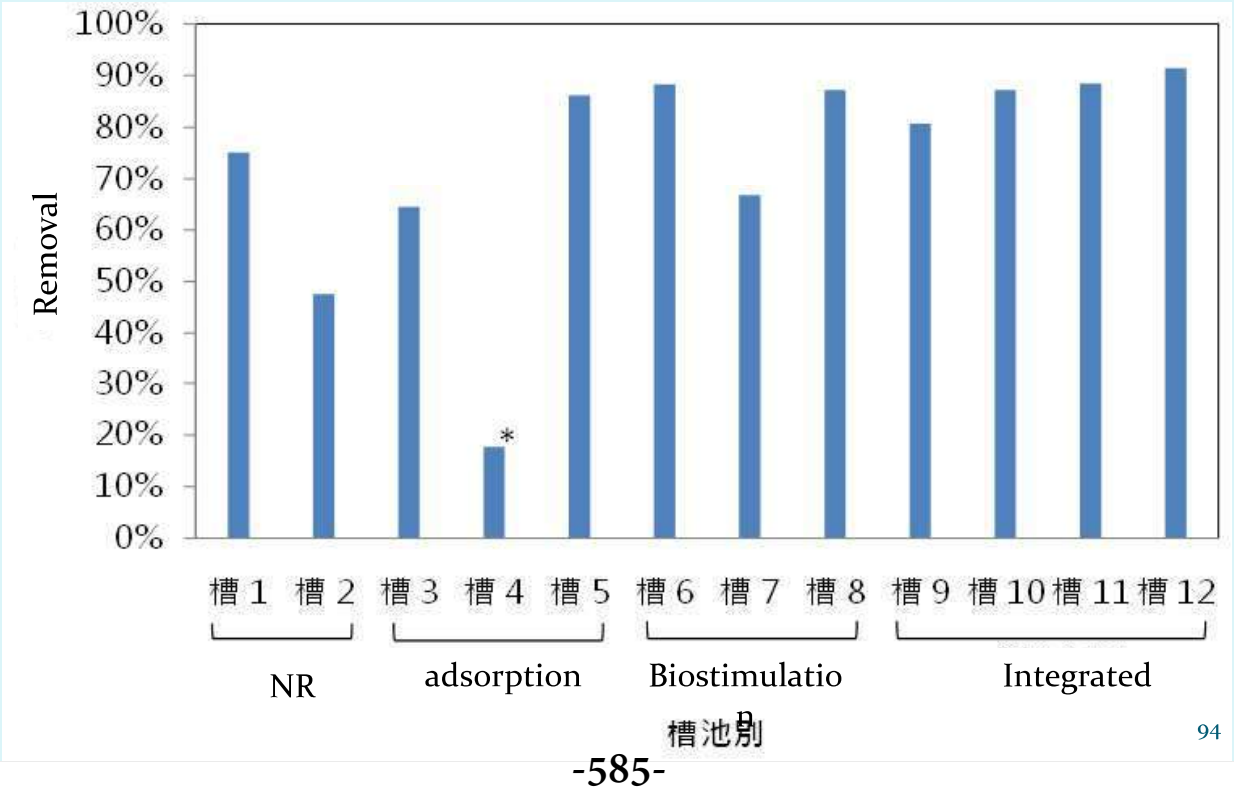
PCBs removal



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Evaluation

實驗組別	NR		Adsorption			Biostimulation			Integrated			
實驗條件	1	2	3	4	5	6	7	8	9	10	11	12
MNP 添加	0	0	0	低	高	0	0	0	高	低	低	高
回收作業	無	無	有	有	有	無	無	無	有	有	有	有
SONE 添加	0	0	0	0	0	0.10%	1.0%	10%	0.10%	0.10%	1.0%	1.0%
檢測項目	各該項目處理效果排序											
NAP	6	4	2	6	10	12	9	11	1	8	2	4
PCBs	8	11	10	12	6	3	9	4	7	4	2	1
砷	11	8	5	8	2	1	7	12	2	10	6	2
鉻	10	10	4	6	5	6	9	12	8	3	1	1
砷與鉻總計	21	18	9	14	7	7	16	24	10	13	7	3
排名	11	10	5	8	2	2	9	12	6	7	2	1
砷與鉻(1)+PCB(1)	19	21	15	20	8	5	18	16	13	11	4	2
排名	10	12	7	11	4	3	9	8	6	5	2	1
砷與鉻(1)+PCB(1)+NAP(1)	25	25	17	26	18	17	27	27	14	19	6	6
總排名	8	8	4	10	6	4	11	11	3	7	1	1
8 種重金屬總計	71	60	43	42	35	55	62	67	61	35	39	39
排名	12	8	6	5	1	7	10	11	9	1	3	3
8 種重金屬(1)+PCB(1)+NAP(1)	26	23	18	23	17	22	28	26	17	13	7	8
總排名	10	8	6	8	4	7	12	10	4	3	1	2

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Case 1 conclusion

- Could be used for removal of PCBs, naphthalene, and heavy metals。
- Adding small amount of nanoemulsion can enhance the removal of PCBs and adding small amount of magnetite nanoparticles can further improve the effects.
- Under aerobic conditions, it is not recommended to use nanoemulsion.

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Case 2
Sediment vitrification

Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

About a movie

- A romantic story: “Sweet Home Alabama”
- Lightening-made glass

Contaminated sediment?

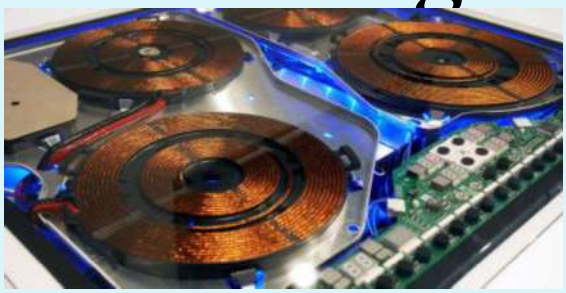
Rapid, cheap, and *in situ*!

Underwater heating?

Bingo!!

What is induction heating?

Zhongshan Aimore Electric Manufacturing Co., Ltd



Reviewed.com Ovens

http://www.dailymail.co.uk/sciencetech/article-3163614/Who-knew-frying-egg-blow-mind-Video-reveals-strange-electromagnetic-power-induction-HOB.html

賴小脆- 痞客邦PIXNET

How to get really high temp?

- Well-established heat treatment processes
- Nearby factory

Yes!

- Can they lend it to me? (380V and 65 A, budget…)
- Can I do some experiments there?

Research Objectives

- Can heavy metals be successfully fixed in the glassy matrix by induction heating?
- How fast?
- Adding some iron sand?
- Temperature matters?
- Water content?
- Cost?

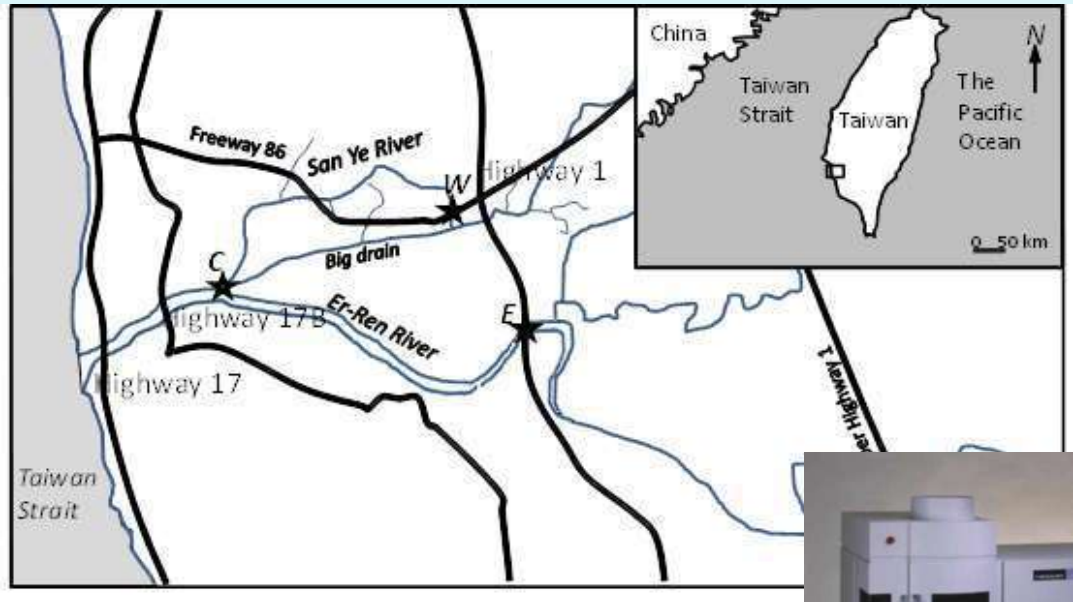
Materials and Methods

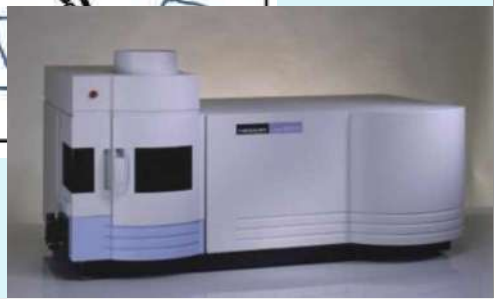
i
- Sediment sampling and anylsis

ii
- Experiments on vitrification

iii
- Other test?

Sampling and Instruments





Sampling and analysis results

Contaminant	Sampling location			Average	Regulated level		% of UL	% of LL
	C	E	W		AL	WL		
As	1.38	2.46	ND	1.92	33	11	6%	17%
Cd	ND	ND	ND	--	2.49	0.65	--	--
Cr	354.6	347.7	208.7	303.7	233	76	130%	400%
Cu	445.7	436.2	77.7	319.9	157.0	50	204%	640%
Hg	ND	ND	ND	--	0.87	0.23	--	--
Ni	162.9	160.4	58.6	127.3	80	24	159%	530%
Pb	104.0	102.4	49.9	85.4	161	48	53%	178%
Zn	888.5	825.9	281.1	665.2	384	140	173%	475%

Units: mg/kg, dry base

Oven heating

- Oven heating is not an effective way for vitrification because it needs at least **1.0 h** to finish
- Higher temperature will improve the vitrification of sediment particles
- Higher iron sand contents did improve the vitrification of sediment samples.

(a) (b)

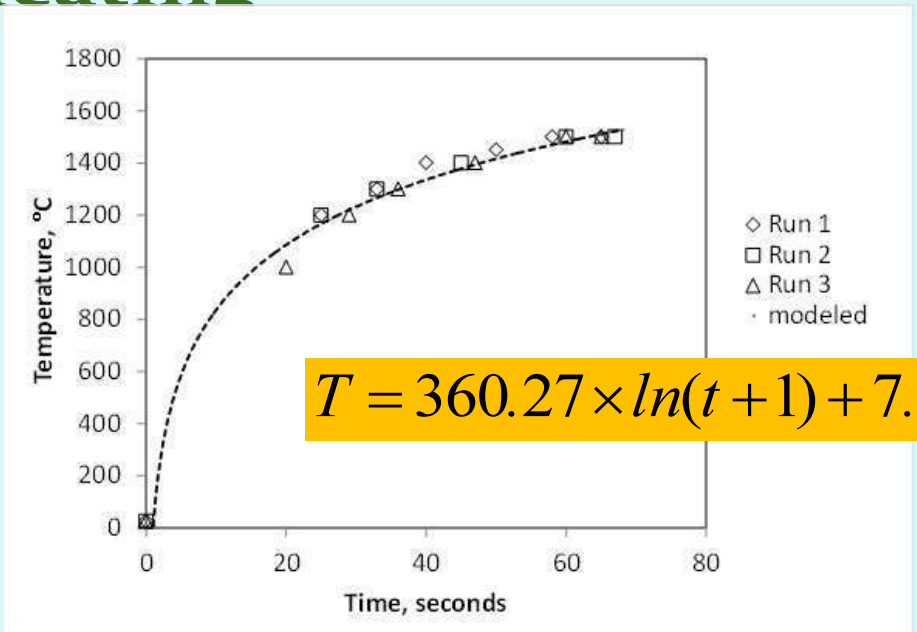
Figure 2. The appearance of the oven vitrification at 500 ℃ (a) and 1100 ℃ (b). For the samples appeared in both panels, from left to right, the iron sand contents are 0%, 1%, 2%, 5%, and 20%, respectively.

Ind

(a)

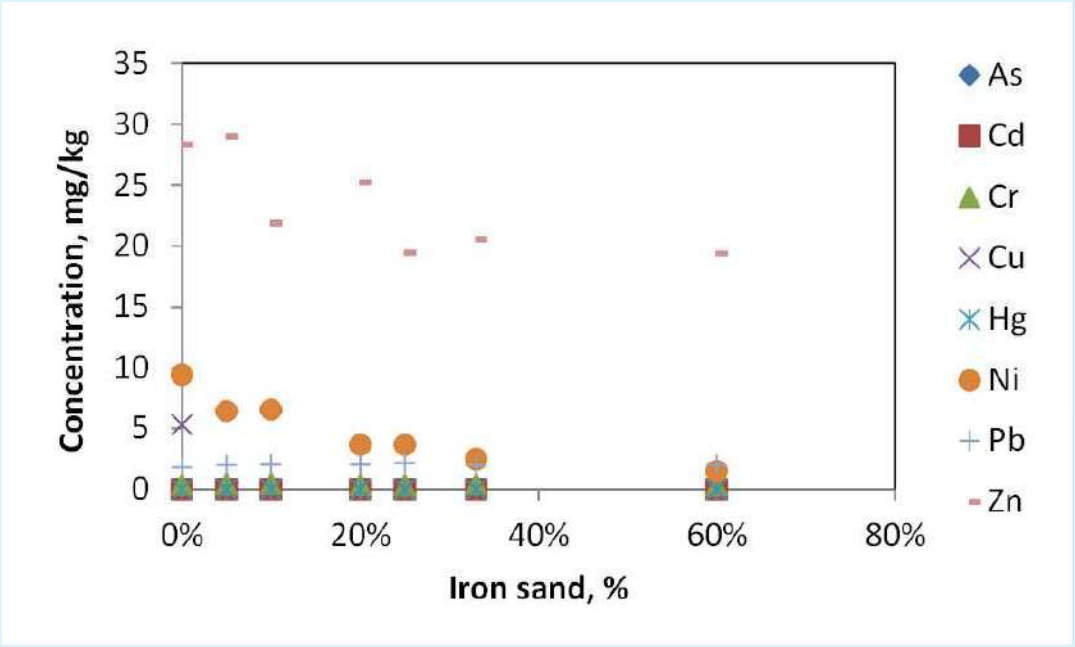
Figur *℃*
(b), a

Heating curve by induction heating



$$T = 360.27 \times ln(t+1) + 7.1218$$

TCLP results



TCLP results

Metal	Iron sand ratio							Ave.	Stailized	Complied
	0%	5%	10%	20%	25%	33%	60%			
砷 (As)	ND	ND	ND	ND	ND	ND	ND	ND	100.0%	Yes
鎘 (Cd)	ND	ND	ND	ND	ND	ND	ND	ND	NA	Yes
鉻 (Cr)	4.1	4.3	4.7	3.6	3.4	4.4	3.4	4.0	99.9%	Yes
銅 (Cu)	53	0	0	0	0	0	0	7.6	99.8%	Yes
汞 (Hg)	ND	ND	36	27	21	17	ND	25	NA	Yes
鎳 (Ni)	95	64	66	36	36	25	15	48	97.0%	—
鉛 (Pb)	18	20	20	20	21	20	20	20	98.1%	—
鋅 (Zn)	283	290	219	252	195	206	194	234	97.4%	Yes

Units: mg/L

Whole extraction results (HT)

No.	Additives	Temp	Location	Iron sand(%)
1-2	HTA	1400°C	C	0%
2-2	HTA	1400°C	C	20%
3-2	HTA	1400°C	C	60%
4-2	HTA	1400°C	ETB	0%
5-2	HTA	1400°C	ETB	20%
6-2	HTA	1400°C	ETB	60%
7-2	HTA	1400°C	WKB	0%
8-2	HTA	1400°C	WKB	20%
9-2	HTA	1400°C	WKB	60%

Whole extraction results (HT)

No.	Passed AL?								Passed WL?							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
2-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y		Y	Y
3-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y		Y	Y
4-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
5-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
6-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
7-2	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
8-2	Y	Y	Y	Y	Y	Y	Y		Y	Y			Y		Y	
9-2	Y	Y			Y		Y	Y	Y	Y			Y		Y	Y

Whole extraction results (MT)

No.	Additives	Temp (°C)	Location	Iron sand(%)
10-2	HTAGPL	800	C	0%
13-2	HTAGPL	900	WKB	20%
16-2	HTAGPL	1000	ETB	60%
17-2	HTAGPM	800	WKB	60%
11-2	HTAGPM	900	ETB	0%
14-2	HTAGPM	1000	C	20%
15-2	HTAGPH	800	ETB	20%
12-2	HTAGPH	900	C	60%
18-2	HTAGPH	1000	WKB	0%

Whole extraction results (MT)

Passed AL?

No.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1-2	Y	Y	Y	Y	Y	Y	Y	Y
2-2	Y	Y	Y	Y	Y	Y	Y	Y
3-2	Y	Y	Y	Y	Y	Y	Y	Y
4-2	Y	Y	Y	Y	Y	Y	Y	Y
5-2	Y	Y	Y	Y	Y	Y	Y	Y
6-2	Y	Y	Y	Y	Y	Y	Y	Y
7-2	Y	Y	Y	Y	Y	Y	Y	Y
8-2	Y	Y	Y	Y	Y	Y	Y	Y
9-2	Y	Y	Y	Y	Y	Y	Y	Y

Passed WL?

As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	Y	Y		Y		Y	Y
Y	Y	Y	Y	Y	Y	Y	Y
Y	Y	Y	Y	Y	Y	Y	Y
Y	Y	Y	Y	Y	Y	Y	Y
Y	Y	Y	Y	Y	Y	Y	Y
Y	Y	Y	Y	Y	Y	Y	Y
Y	Y		Y	Y		Y	Y
Y	Y	Y	Y	Y	Y	Y	Y
Y	Y	Y	Y	Y	Y	Y	Y

Whole extraction results (LT)

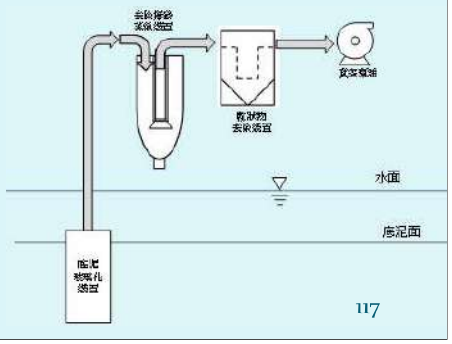
No.	Additives	Temp (°C)	Location	Iron sand(%)
10-2	HTAGPL	300	C	0%
13-2	HTAGPL	360	WKB	20%
16-2	HTAGPL	400	ETB	60%
17-2	HTAGPM	300	WKB	60%
11-2	HTAGPM	360	ETB	0%
14-2	HTAGPM	400	C	20%
15-2	HTAGPH	300	ETB	20%
12-2	HTAGPH	360	C	60%
18-2	HTAGPH	400	WKB	0%

Whole extraction results (LT)

No.	Passed AL?								Passed WL?							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1-2	Y		Y	Y	Y	Y					Y		Y			
2-2	Y	Y	Y	Y	Y	Y			Y	Y			Y			
3-2	Y	Y	Y	Y	Y	Y			Y	Y		Y	Y			
4-2	Y	Y	Y	Y	Y	Y			Y	Y		Y	Y			
5-2	Y	Y	Y	Y	Y	Y			Y	Y	Y	Y	Y	Y		
6-2	Y	Y	Y	Y	Y	Y			Y	Y	Y	Y	Y	Y		
7-2	Y	Y	Y	Y	Y	Y			Y	Y	Y	Y	Y	Y		
8-2	Y	Y	Y	Y	Y	Y			Y	Y	Y	Y	Y	Y		
9-2	Y	Y	Y	Y	Y	Y			Y	Y		Y	Y	Y		

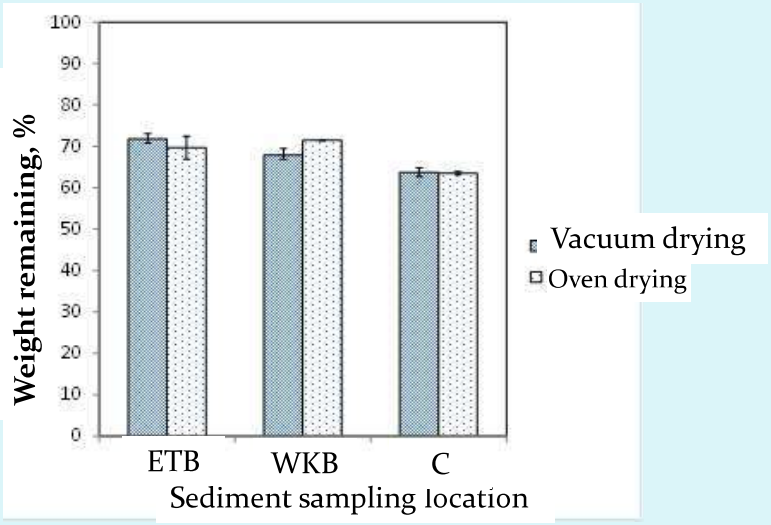
Air monitoring

- The heating time for 800-1000°C was about 8.0-14.7 seconds.
- All smoke collected for each sample during the heating period had been tested for PCB concentration and all of them were below detection limit.
- The heating time from 270°C to 360°C is so short (0.19 sec) that **polychlorodibenzofuran** may not be formed as byproducts.
- This method seemed to be quite robust to pass the most stringent standard. Thus, the treated sediment can be left in the river requiring no further disposal.



Drying in situ?

- Vacuum drying is comparable to oven drying



If not fully dried?

- It is still feasible for TCLP
- It passed all SQG levels for 30% water content but failed for 60% water content

Metals	40% H_2O	Compliance
As	71.4±14.9	Y
Cd	5.3±0.9	Y
Cr	33±13.3	Y
Cu	5.7±0.4	Y
Hg	ND	Y
Ni	194±75	—
Pb	1399±520	—
Zn	432±69	Y

Case 2 conclusion

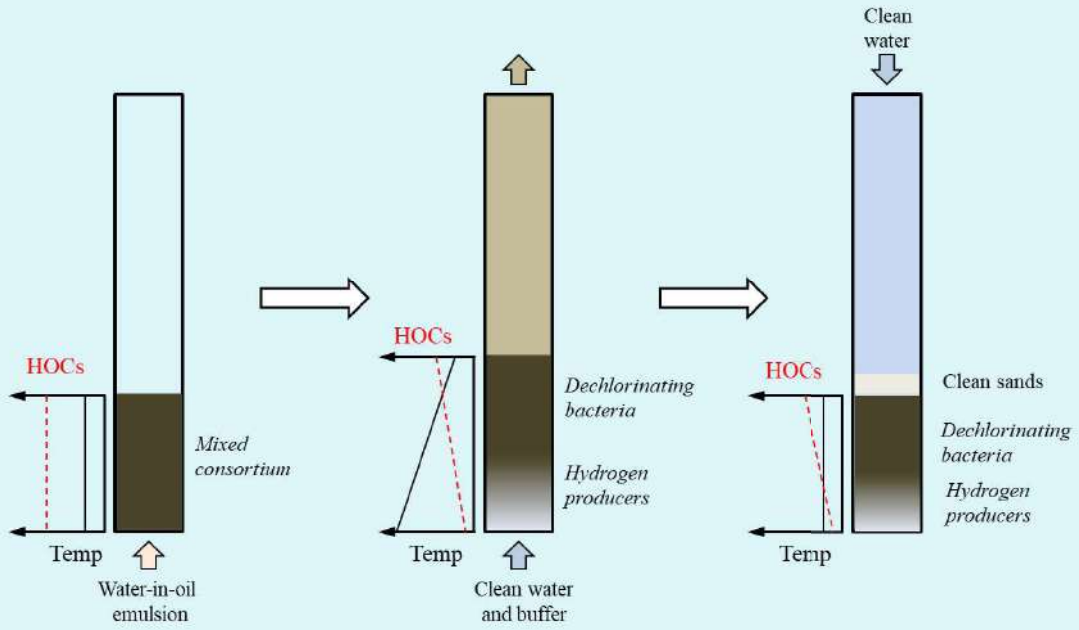
- The sediment in Er-Ren River in Taiwan is heavily polluted by heavy metals and PCBs.
- Oven heating up to 1100°C for 1.0 hour was not effective for sediment vitrification.
- Induction heating to 800-1000°C can finish sediment vitrification within 1.0 minute and the product passed both TCLP standards and almost all sediment quality standard regulated by Taiwan EPA.
- Iron sand seemed to improve the vitrification process showing less metals leaching out of the treated samples.
- Samples with typical water content (55%) can be effectively vitrified to pass TCLP standards.
- In-situ vitrification might be feasible since underwater induction heating welding has already been demonstrated.
- **Cost could still be a problem.**

Case 3
ISPIE/BiRD for Sediment remediation

Shu-Chi Chang, Ph.D., P.E.
Associate Professor
Dept. of Environmental Engineering,
National Chung Hsing University

Idea-

in situ phase inversion emulsification and biological reductive dechlorination



Innovations

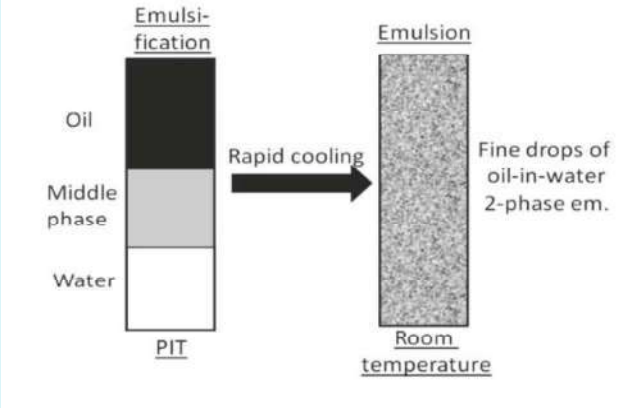
(1) Hot water-in-oil (W/O) emulsion injection to enhance HOCs desorption from sediment organic matter and partition in oil

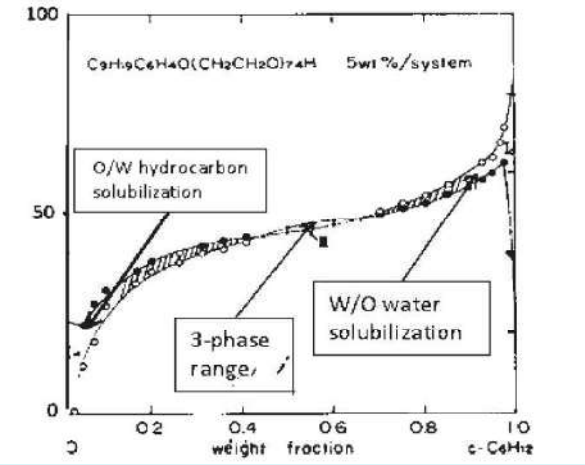
(2) Holding for a short period of time to encourage desorption and mass transfer of HOCs and simultaneous heat selection of microorganisms

(3) Cool water injection to induce phase inversion to form an oil-in-water (O/W) emulsion with much smaller HOC-rich oil droplets in water, which could be easily displaced by incoming water

(4) Accelerated biological reductive dechlorination using residual emulsion ingredients and HOCs as electron donors and acceptors

Phase inversion emulsification





Friberg, S.E., Corkery, R.W., Blute, I.A., 2011. Phase Inversion Temperature (PIT) Emulsification Process. Journal of Chemical & Engineering Data 56, 4282-4290.

Desorption

$$\frac{S_t}{S_0} = F_{rap}e^{-k_{rap}t} + F_{slow}e^{-k_{slow}t}$$

k_{slow} (h^{-1}) for HCB and selected PCBs at 60 ˚C was about 40 to 92 times larger than those at 20 ˚C. Thus, at 80 ˚C, the k_{slow} could be even larger and this is why the removal is much better than those tested at room temperature by using similar emulsion formulation.

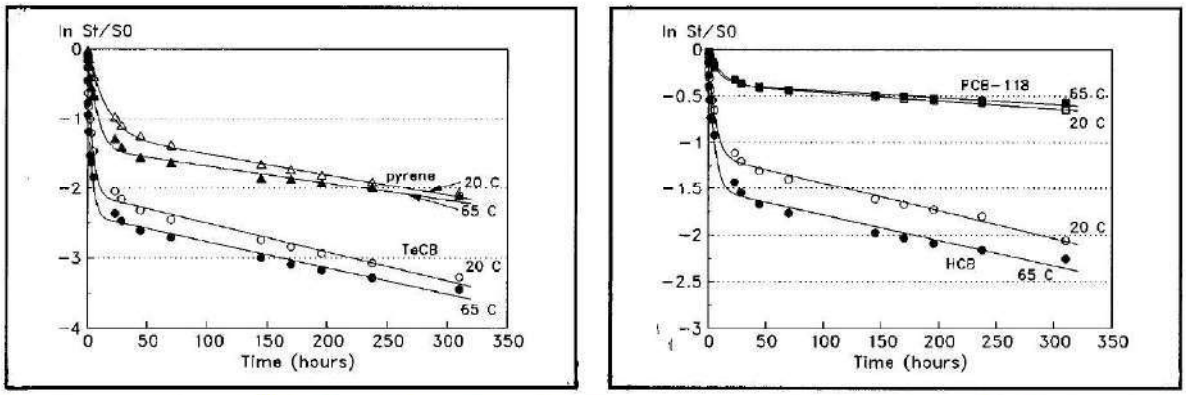


FIGURE 2. Desorption plots for OVP sediment equilibrated at 20 °C (open symbols) and 65 °C (solid symbols) for TeCB (circles), pyrene (triangles), HCB (circles), and PCB-118 (squares). Solid lines obtained by exponential curve fitting.

Cornelissen, G., van Noort, P.C.M., Parsons, J.R., Govers, H.A.J., 1997. Temperature Dependence of Slow Adsorption and Desorption Kinetics of Organic Compounds in Sediments. Environmental Science & Technology 31, 454-460.

Dissolution

- log K_{ow} of HCB decreases from 5.46 to 5.17 as temperature increased from 25 ˚C to 45 ˚C with a slope of d(log K_{ow})/dT = -0.0144.

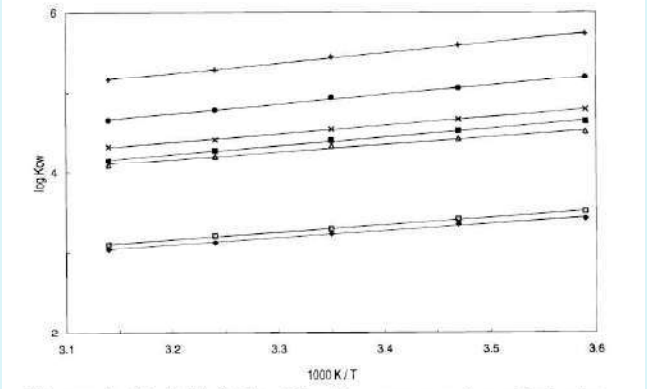


Figure 1. Van't Hoff plot of log K_{OW} versus reciprocal absolute temperature for 1,2-dichlorobenzene, □, 1,4-dichlorobenzene ◆, 1,3,5-trichlorobenzene △, 1,2,3,4-tetrachlorobenzene ■, 1,2,3,5-tetrachlorobenzene ×, pentachlorobenzene ●, and hexachlorobenzene +.

Bahadur, N.P., Shiu, W.-Y., Boocock, D.G.B., Mackay, D., 1997. Temperature dependence of octanol–water partition coefficient for selected chlorobenzenes. Journal of Chemical & Engineering Data 42, 685-688.

Heat selection on hydrogen production

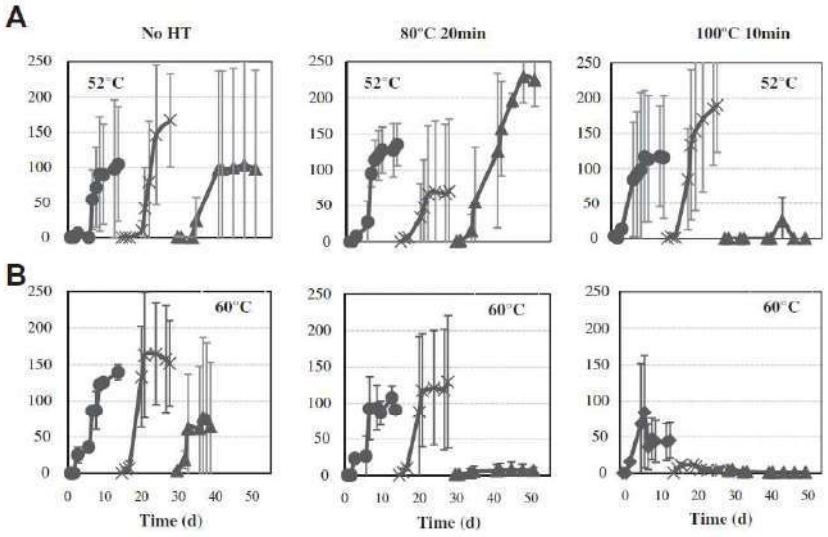
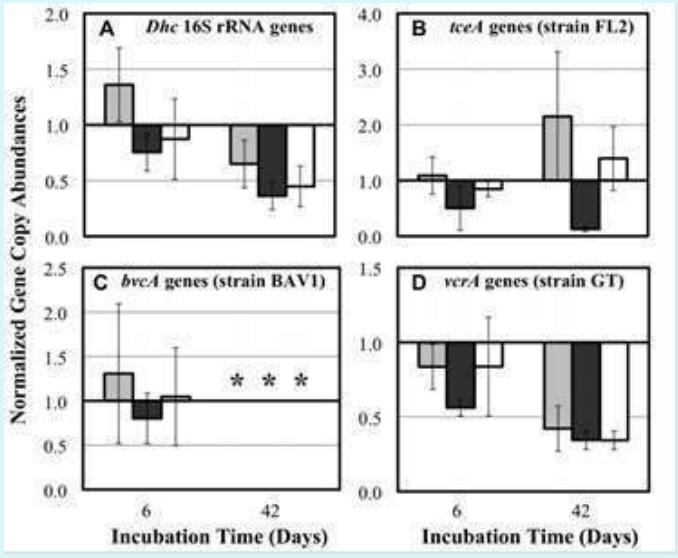


Fig. 1. Hydrogen production (mL-H_2 g-cellulose^{-1}) from cellulose with compost inoculum at 52 °C (A) and at 60 °C (B). Sphere (●): the 1st enrichment, cross (x): the 2nd enrichment, and triangle (▲): the 3rd enrichment phase. HT = heat-treatment.

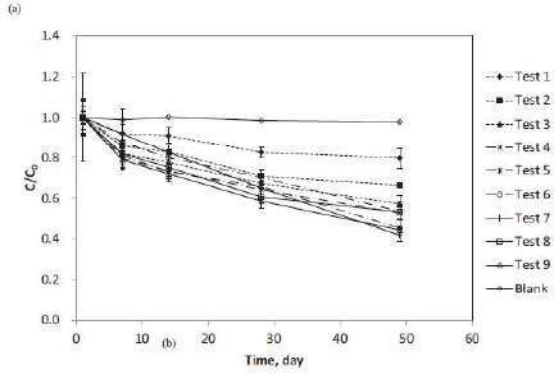
Nissilä, M.E., Tähti, H.P., Rintala, J.A., Puhakka, J.A., 2011. Effects of heat treatment on hydrogen production potential and microbial community of thermophilic compost enrichment cultures. Bioresource Technology 102, 4501-4506.

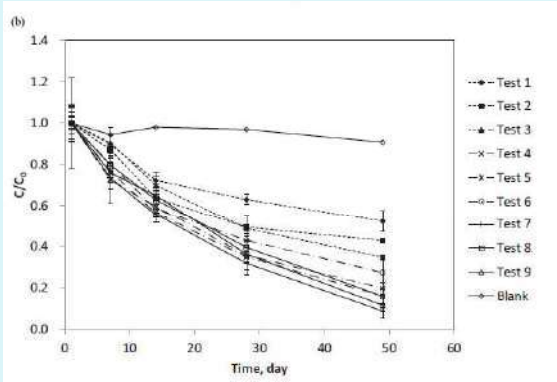
Optimal temp range

- For most anaerobes capable of reductive dechlorination, the range is around 30-37°C

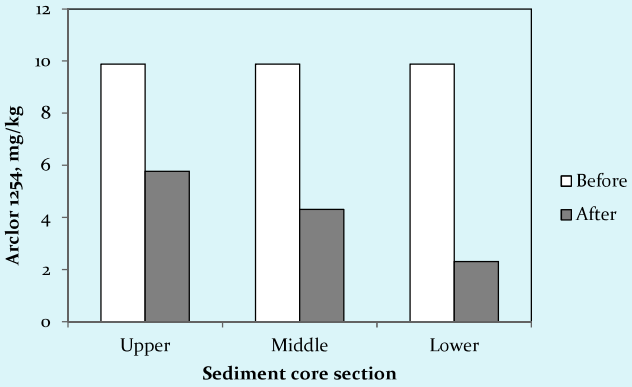


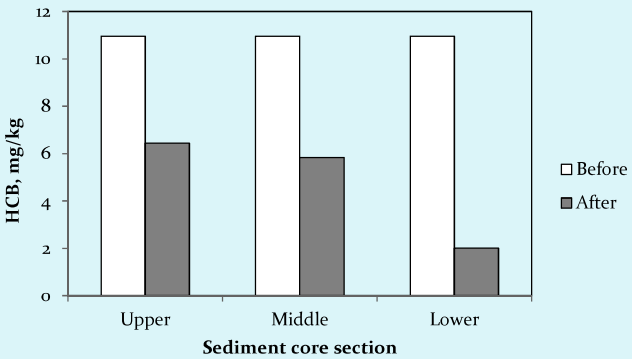
Batch study in the lab



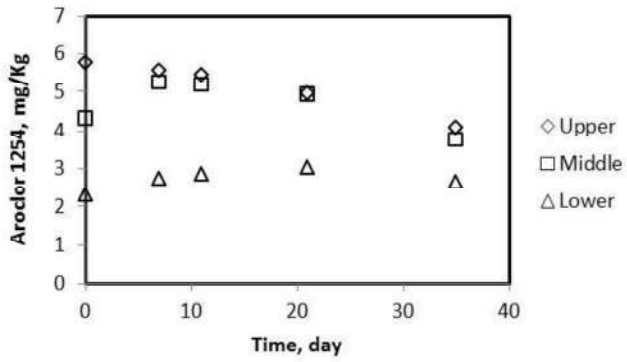


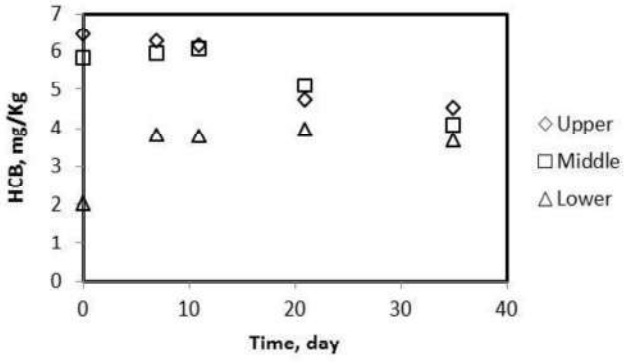
Column study - ISPIE





Column study - BiRD

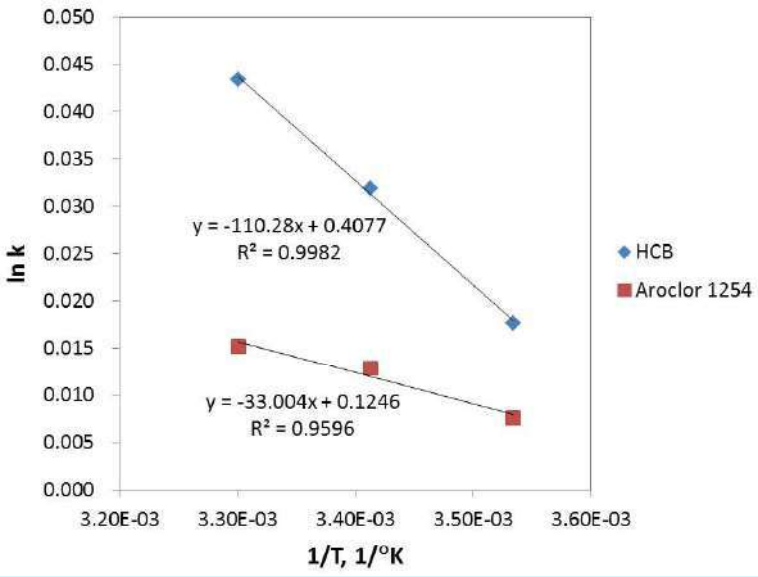




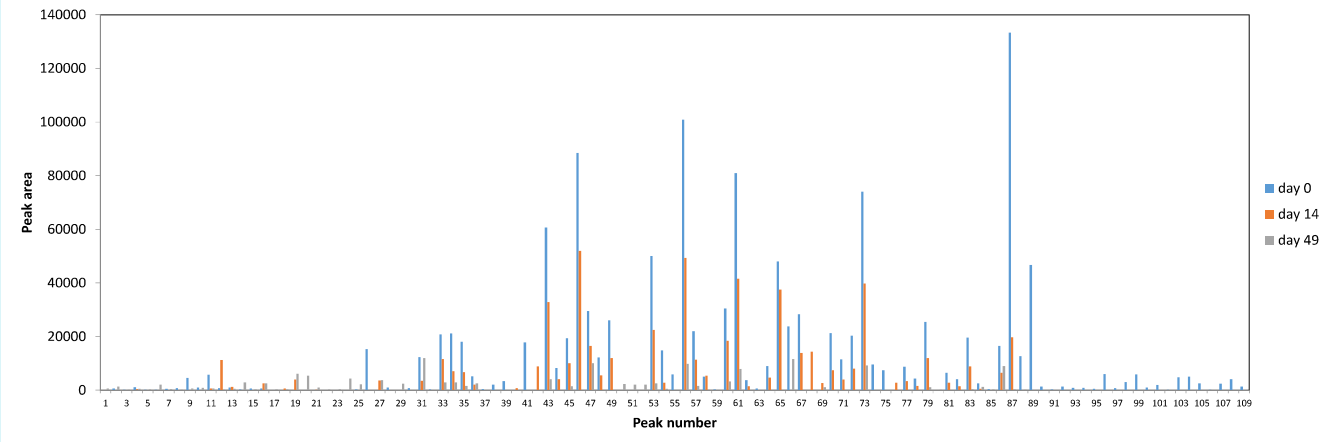
Kinetics

No.	HCB				Aroclor 1254				$\frac{t_{1/2,PCB}}{t_{1/2,HCB}}$ or $\frac{k_{HCB}}{k_{PCB}}$
	k (day^{-1})	R^2	$t_{1/2}$ (day)	rank	k (day^{-1})	R^2	$t_{1/2}$ (day)	rank	
1	0.0131	0.9435	52.9	9	0.0044	0.9053	156.9	9	2.97
2	0.0176	0.8985	39.4	8	0.0079	0.9005	87.5	8	2.22
3	0.0224	0.9806	30.9	7	0.0104	0.9377	66.3	7	2.15
4	0.0326	0.9941	21.2	5	0.0118	0.9316	58.5	6	2.76
5	0.0371	0.9990	18.7	4	0.0147	0.9669	47.0	3	2.51
6	0.0261	0.9797	26.6	6	0.0122	0.9910	56.9	5	2.14
7	0.0490	0.9884	14.1	1	0.0179	0.9921	38.7	1	2.74
8	0.0374	0.9951	18.6	3	0.0123	0.9291	56.5	4	3.04
9	0.0438	0.9846	15.8	2	0.0155	0.9702	44.6	2	2.82

The Arrhenius equation plot of HCB and Aroclor 1254



Dechlorination in process



Pilot study

- By using real contaminated sediment with weathered and freshly-added contaminants, a single ISPIE operation can remove about 60% of weathered Aroclor 1254 and HCB.
- For weathered HCB and Aroclor 1254, the total removal could reach 98% in 70 days.
- Instead, heat-tolerant archaea, e.g., *Methanosaeta* spp., may play much more important roles in the subsequent biological dechlorination.

Case 3 conclusion

- In this study, a new approach was successfully demonstrated for remediation of river sediments contaminated by two HOCs, Aroclor 1254 and HCB.
- This approach integrated ISPIE, heat selection of microbial populations, and BiRD. In a batch biodegradation test, within 49 days, the removals of Aroclor 1254 and HCB were 58% and 91% and half-lives were 38.7 and 14.1 days, respectively.
- Single operation of ISPIE can remove more than 56% of these contaminants and, within 35 days, subsequent BiRD further removed nearly 30% of the contaminants at the upper and middle sections of the tested sediment columns.
- However, when applying this technology to the field, temperature (an inherent field condition) and residual emulsion concentrations (an engineering controllable parameter) may heavily influence the results. Thus, site-specific characteristic is still an indispensable factor in sediment remediation design.

Research focus

- In situ
- No disturbance
- Fast (to finish the project within a 6-month dry season)
- No derived negative impact
- Low cost

Current research-sediment

- Emulsion-enhanced recovery and degradation of hydrophobic organic contaminants in river sediments (published in Soil and Sediment Research, 2017)
- Magnetic activated carbon for the removal of HOCs and heavy metals in river sediments
- Rapid vitrification of contaminated sediments (patent granted)
- Surface-enhanced Raman scattering for rapid contaminant identification and quantification (patent granted)
- Separation of smaller sediment particles using modified porous gel spheres (patent filed)
- Coupling in-situ phase-inversion emulsification and active capping for rapid sediment remediation (patent filed)

Current research- groundwater

- Pilot study of TCE-contaminated aquifer using different electron donors and carbon sources (Outstanding Paper Award in 2016 annual meeting of the institute of Chinese Environmental Engineering)
- Rapid biological reductive dechlorination of TCE by heat selected microbial consortia
- Biodegradation patterns of 1,2-DCA using different microbial consortia

Current research-eutrophication control

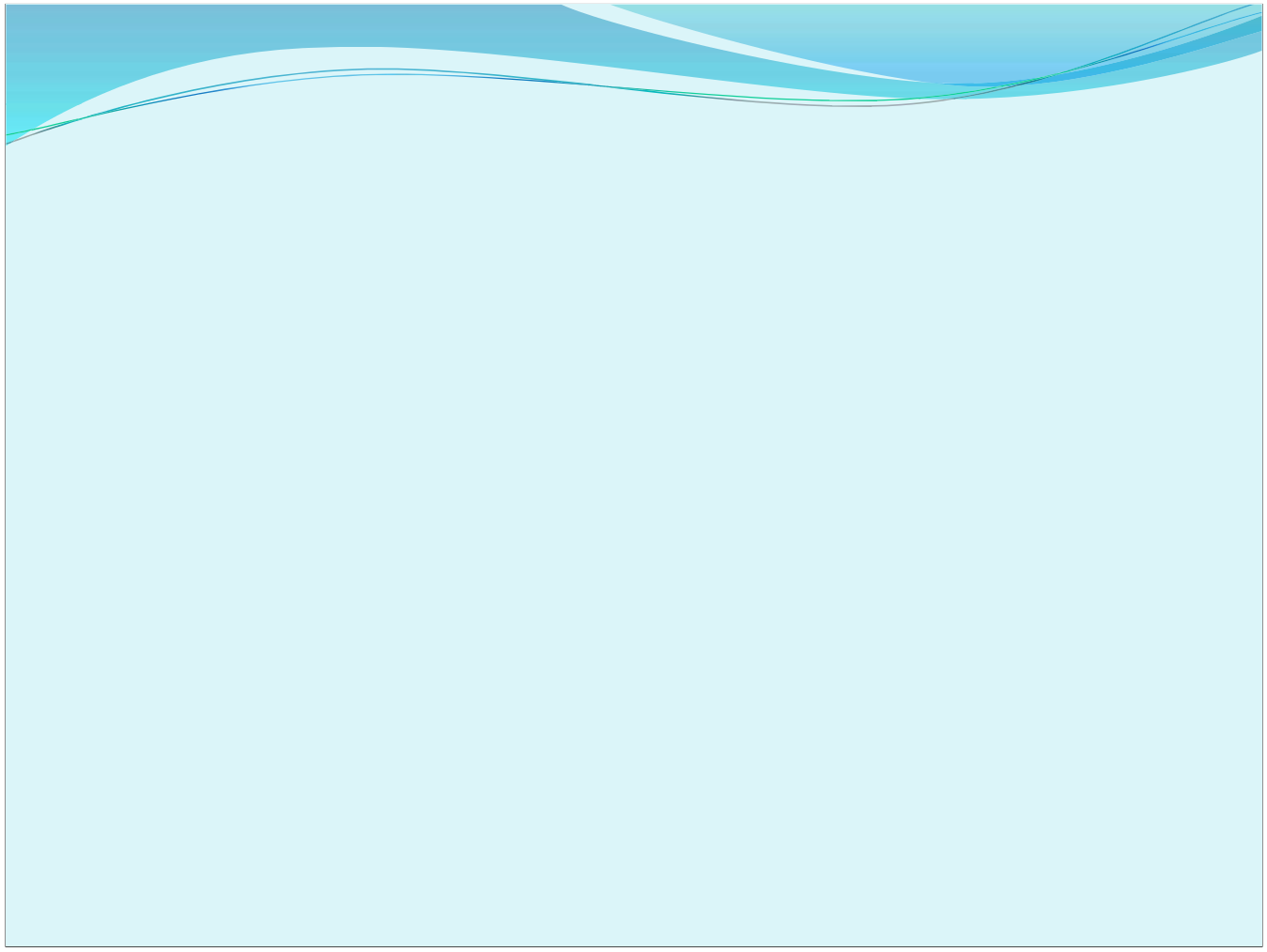
- Effective removal of Microcystis aeruginosa and microcystin-LR using nanosilicate platelets (published at Chemosphere, 2014)
- A method to prepare magnetic nanosilicate platelets for effective removal of *Microcystis aeruginosa* and microcystin LR (published as a chapter in Microbial Toxins: Methods and Protocols, 2017, Otto Holst (editor), Springer Science+Business Media, LLC, New York.)

Conclusion

- Sediment is very important environmental matrix that should be protected
- The regulation is still under development for most countries
- Methods for sampling and analysis are ready
- Risk assessment for local conditions and better remedial technology are in demand

Acknowledgement

- Financial support from Ministry of Sciences and Technology of Taiwan through a grant of NSC 98-2622-E-005-024-CC2
- Financial support from Taiwan Environmental Protection Administration through a grant of EPA-99-GA103-03-A236-17



2019 International Joint-Research and Training Program

International Workshop on Promoting Sustainable Protection and Restoration of Soil, Groundwater and Water Environment

Petrochemical Business Division, CPC Corporation, Taiwan

Introduction to the Remediation Works at Lin-Yuan Petrochemical Plant

Bing Nan Wang, Manager.

Sinotech Environmental Technology, Ltd.

March, 22, 2019

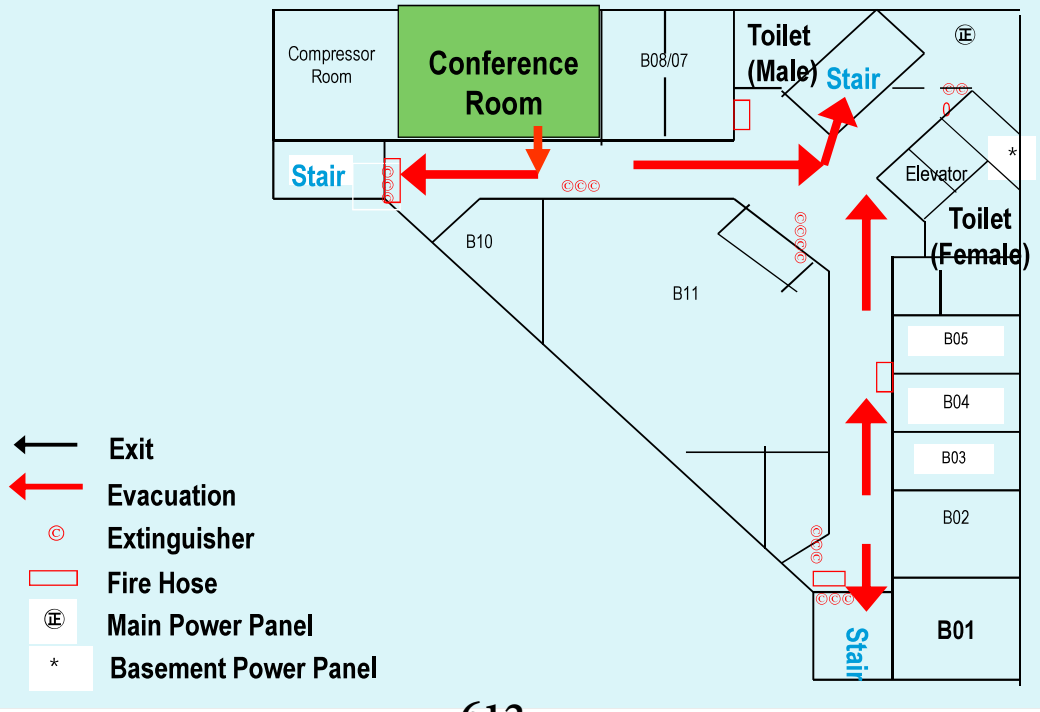
Schedule

Time	Issue	Speaker
10:00 – 10: 10	Welcome Remark	CPC
10:10 – 10:50	Introduction to the Remediation Works at Lin-Yuan Petrochemical Plant	Bing Nan Wang Sinotech Environmental Technology, LTD.
10:50 – 11:00	Move to tour bus	
11:00 – 12:00	Site Tour	Bing Nan Wang CKYan

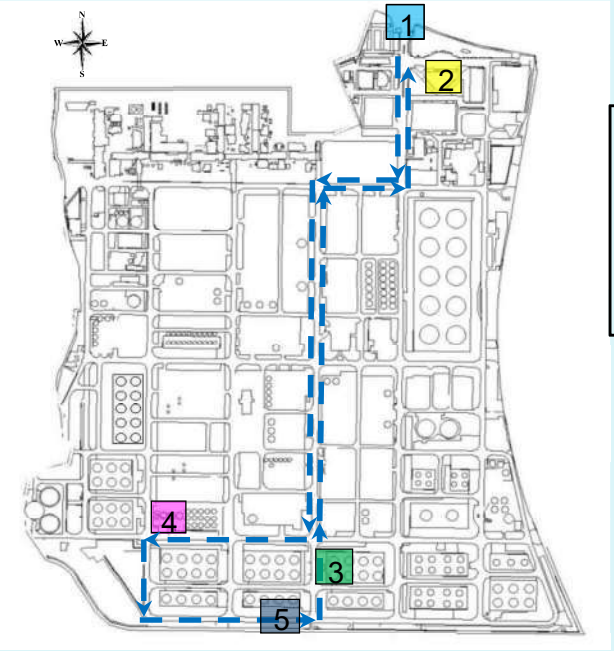
Safety Announcement

- No smoking in the plant site.
- Cellular phones are prohibited to use in the plant site.
- Take helmet tie up the straps and use personal protection equipment when entering the plant site.
- Following the direction of engineer. No entering factory area without permission.

Evacuation Guideline of Main Building



Site Visit Route



Remark :
1. : Main Entrance
2. : Conference Room
3. : Surfactant Flush and Free product recovery
4. : SVE/AS
5. : Air Curtain

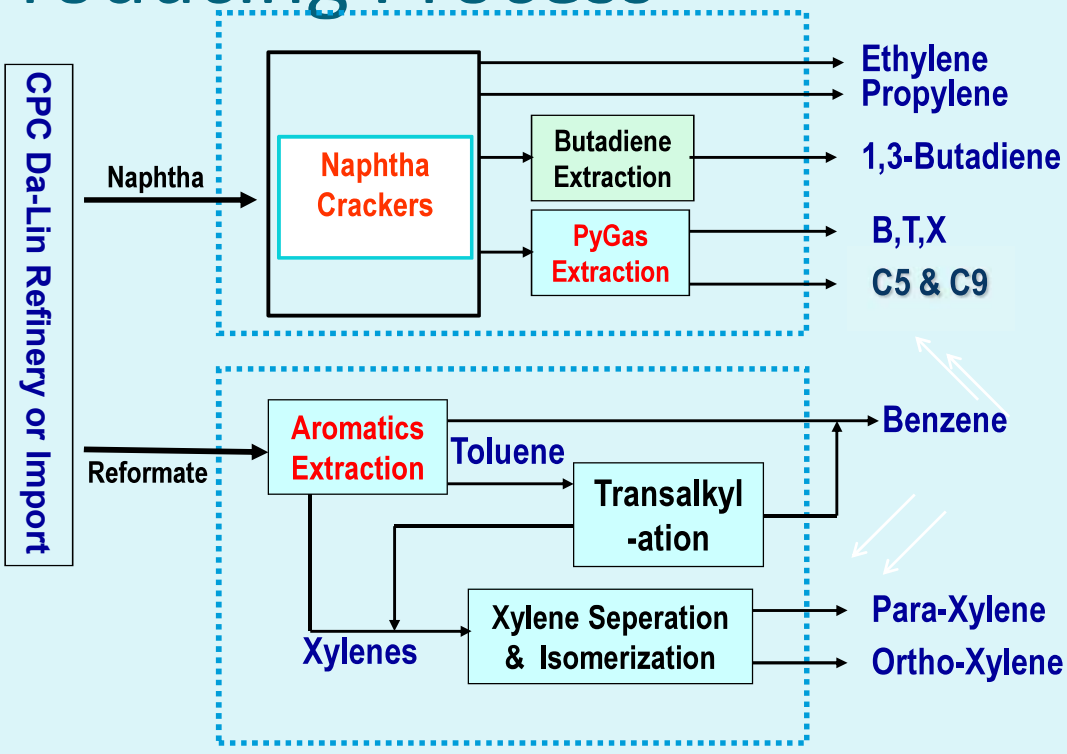
Outline

1. Background
2. Contamination
3. Remediation Works

Site Location and information

- Location
  - Lin-Yuan District, Kaohsiung City, Taiwan
- Site Area
  - 970,905 m²

Producing Process

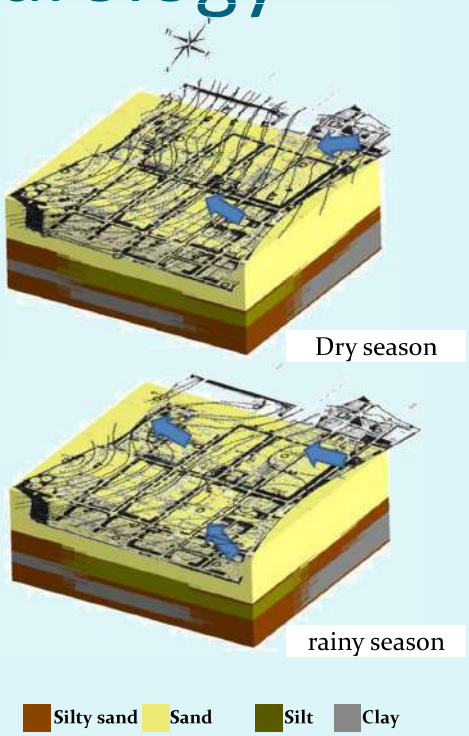


Site history

Jul 1976	Lin-Yuan Petrochemical Plant was founded.
Nov 2001	The benzene concentration in groundwater was found exceeding regulatory standard (0.05 μg/L) according to the investigation of Taiwan EPA.
Apr 2002	Lin-Yuan Petrochemical Plant was listed as Control Site by former Kaohsiung County EPB.
Jul 2012	After assessment, Kaohsiung City EPB proposed Lin-Yuan Petrochemical Plant as Remediation Site to EPA.
Dec 2012	Lin-Yuan Petrochemical Plant was listed as Remediation Site by EPA.
Mar 2013	The Soil and Groundwater Investigation Plan was submitted and reviewed, the following fieldwork will be processed soon.
May 2016	The remedial proposal was approved by EPA and the work of remediation was beginning
Mar 2017	The surfactant flushing was adopted for the hot spot zone as the major technology of remediation

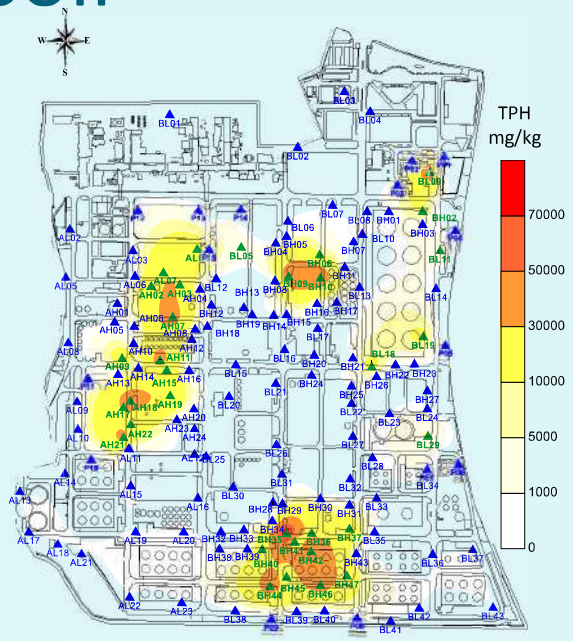
Site Geology and hydrology

- Geology
  - Shallow aquifer 0-20 m bgs
  - Primarily coarse sand and fine sand
  - Hydraulic conductivity (K): 1.37×10^{-4} -2.94×10^{-3} m/s
- Hydrology
  - GW Level
    - 3.0-5.0 m bgs, averagely 1.5 m difference between dry season and wet season
  - GW Flow
    - Direction: toward west
    - Velocity: 92 m/yr
  - Tide Effect on GW Level
    - Maximum difference is about 0.2 m, with 12-hour cycle



Contamination - Soil

- Major Contaminants
  - TPH, Benzene, Toluene, Ethyl-benzene and Xylene
- Hot Spots
  - Process Zone, Tank Farm.
  - The vertical distribution of high concentration region varies with GW surface variation.
  - The contamination still can be detected at 6 m (bgs) in certain area.

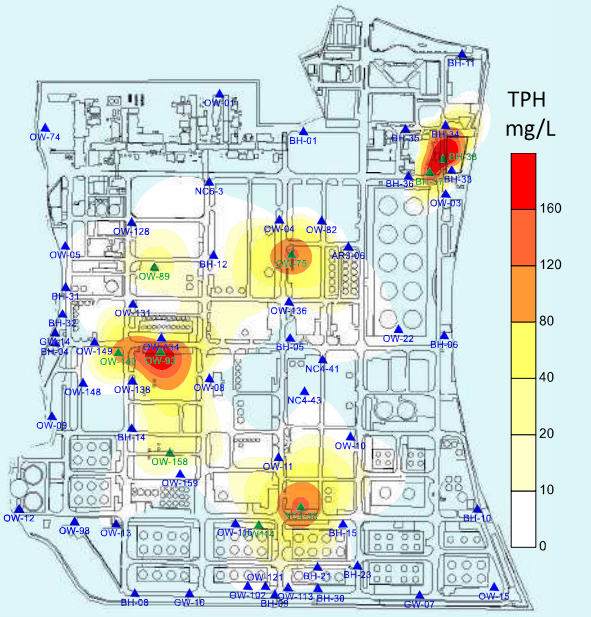


4.0-4.5 m TPH distribution in 2018

Contamination

Contamination - Groundwater

- Major Contaminants
  - TPH, Benzene, Toluene, Ethyl-benzene and Naphthalene.
- Hot Spots
  - Process Zone, Tank Farm.
  - The distribution of pollutants in GW is slightly bigger than soil contamination.
  - Free product was found in some area above GW surface.

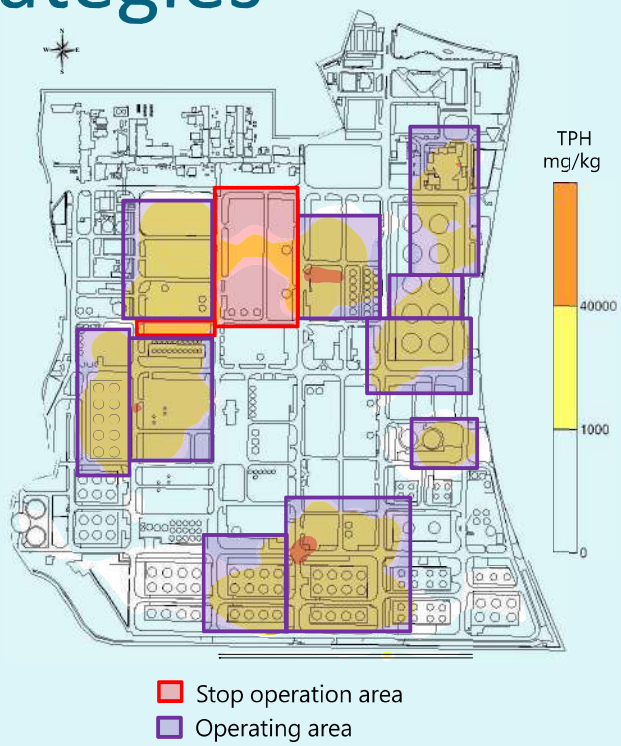


TPH distribution in GW in 2018

Remediation Works

Remediation Strategies

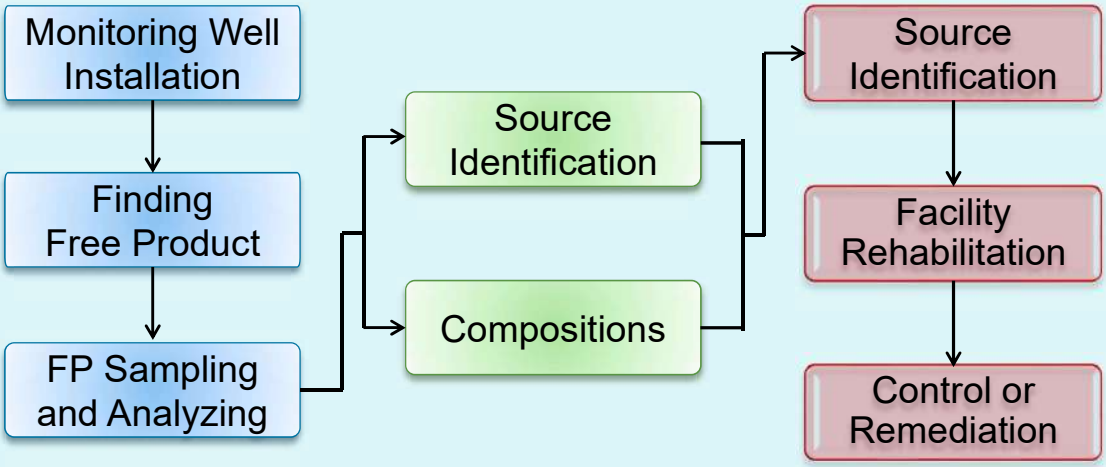
- Source Control
  - Finding leaking facilities and rehabilitation
- Remediation
  - High concentration area
    - Free-Product Recovery
    - Excavation (stop operation area)
  - Mid-to-Low concentration area
    - Surfactant flush
    - ISCO
    - ~~Groundwater circulation well (GCW)~~
    - Soil vapor extraction/air sparging (SVE/AS)
  - Containment (boundary)
    - ~~Oxygen release compound (ORC) injection~~
    - Bioventing/ Air current



Remediation Works

Source Control

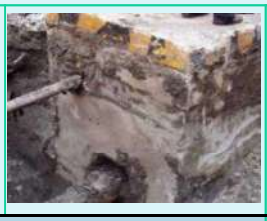
- Leaking Source Identification



Remediation Works

Source Control

- Renewed or fixed the pipelines



Underground sewer leaking (2003)

Recycled oil pipeline leaking (2011)

Basin joint leaking (2012)

Underground sewer repairing (2003)

Recycled oil pipeline replacing (2011)

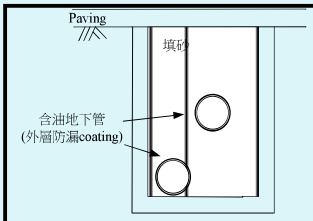
Basin joint repairing (2012)

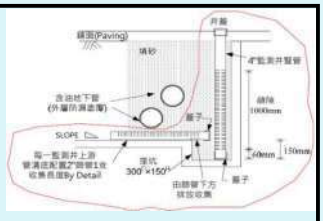
Remediation Works

Source Control

- All CPI/API applied protective coating
- All pipelines in newly constructed factories are above-ground or placed in lined trenches
- Base plates of the tanks were checked and applied with FRP coating in #100 Tank Farm

CPI coating was renewed



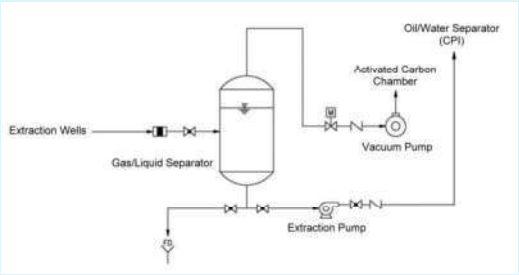


Underground pipelines were place in trenchs

Tank base plate check and FRP coating applied

High Conc. Area Remediation

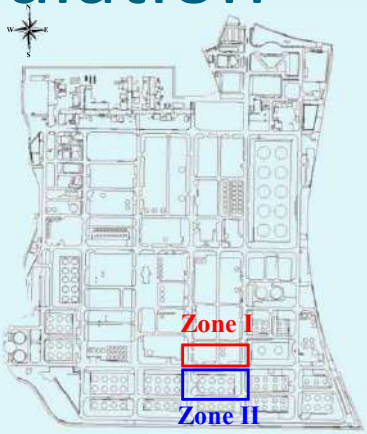
- Free Product Recovery
  - Principle
    - Using vacuum to extract free product (oil) and contaminated groundwater from aquifer
  - Contaminants Removal
    - Oil and water is first treated by CPI, treated GW will be discharged to WTP and the separated oil will be reused
    - Small volume of gas (treated by activated carbon) will be pumped out in order to maintain vacuum

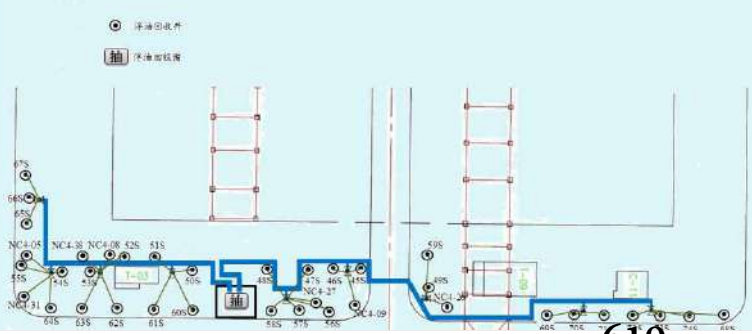


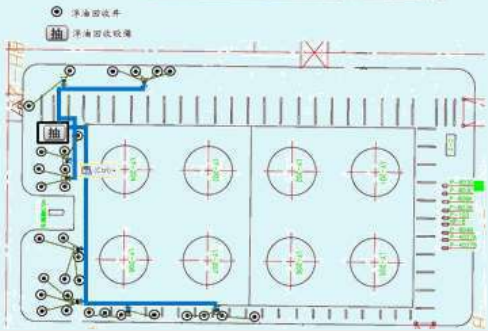
Remediation Works

High Conc. Area Remediation

- Free Product Recovery
  - Operation
    - Totally 68 extraction wells were installed wells, divided into 2 zones
    - Each zone is cyclically operated for 30 minutes and standby for 4 hours
    - Adjust extraction pipes daily
    - Replace activated carbon if necessary

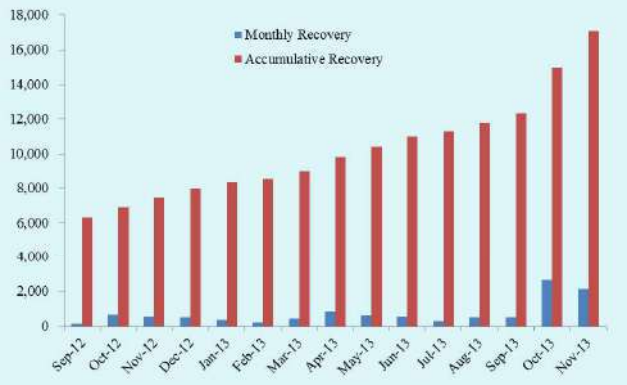






High Conc. Area Remediation

- Free Product Recovery
  - Results
    - Totally 17,091 L of free product were recovered in 15 months



Month	Monthly Recovery (L)	Accumulative Recovery (L)
2012/09	131	6,315
2012/10	621	6,936
2012/11	549	7,485
2012/12	511	7,996
2013/01	357	8,353
2013/02	209	8,562
2013/03	426	8,988
2013/04	832	9,820
2013/05	598	10,418
2013/06	564	10,982
2013/07	279	11,261
2013/08	531	11,792
2013/09	536	12,328
2013/10	2,642	14,970
2013/11	2,121	17,091

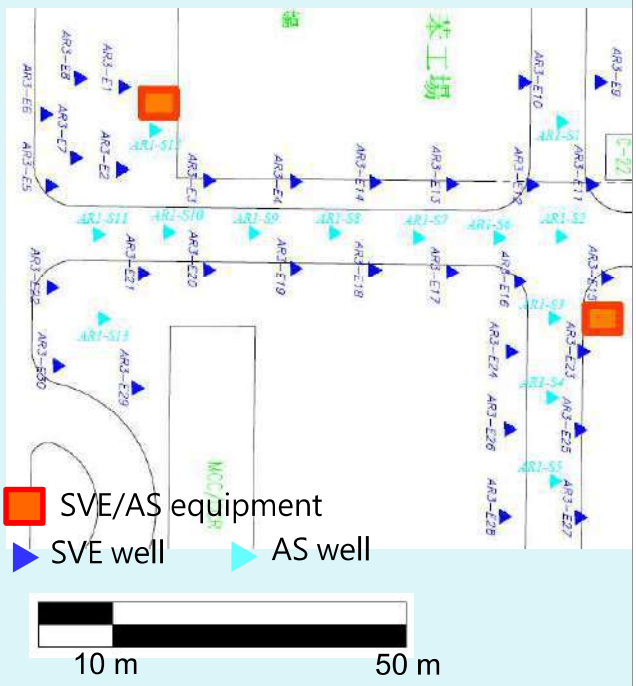
Mid-to-Low Conc. Area Remediation

- SVE/AS
  - Principle
    - Using vacuum to extract VOC laden gas from vadose zone (soil vapor extraction, SVE)
    - VOC in GW stripped by air sparging (AS) into vadose zone and then removed by SVE
  - Contaminants removal
    - The extracted vapor is treated in different ways (e.g. activated carbon extraction, concentration and condensation) before discharge

Mid-to-Low Conc. Area Remediation

Remediation Works

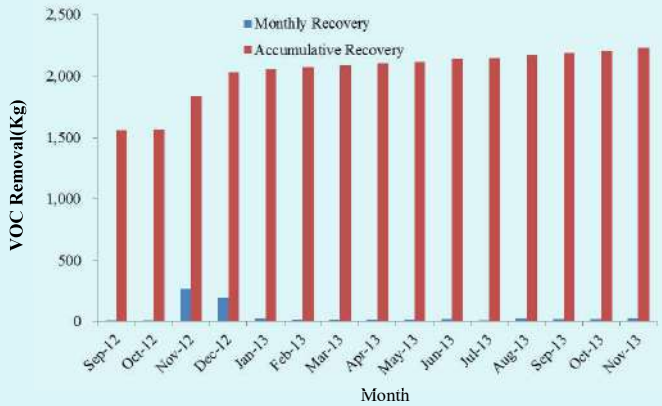
- SVE/AS
  - Operation
    - Soil vapor extraction wells
      - Flow rate: 250 L/Min each
      - Screen: 0-3.0 m bgs
      - ROI: 14 m
    - Air sparging wells
      - Flow rate: 200 L/Min each
      - Screen: 7.0-8.0 m bgs
      - Injection pressure 0.4 kg/cm²
      - ROI: 7.7 m



Mid-to-Low Conc. Area Remediation

Remediation Works

- SVE/AS
  - Results
    - Totally 2,232 kg of VOC were removed since year 2011

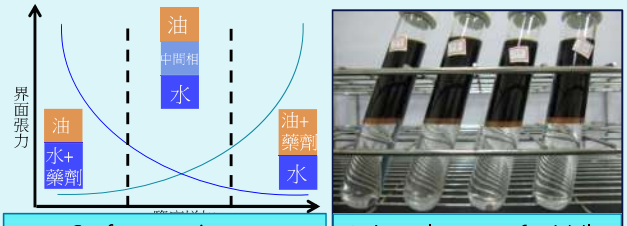


Month	Monthly Removal (kg)	Accumulative Removal (kg)
2012/09	2	1,563
2012/10	3	1,566
2012/11	274	1,840
2012/12	190	2,030
2013/01	28	2,058
2013/02	15	2,073
2013/03	16	2,089
2013/04	13	2,102
2013/05	14	2,116
2013/06	22	2,138
2013/07	7	2,145
2013/08	25	2,170
2013/09	21	2,191
2013/10	18	2,209
2013/11	23	2,232

CPC Corporation, Taiwan

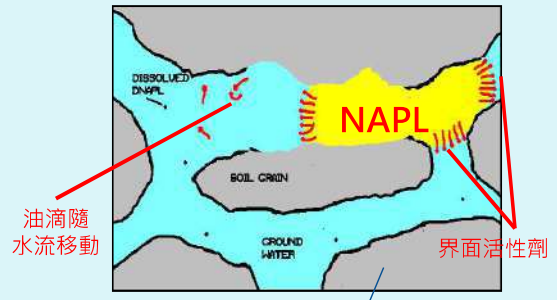
Surfactant flush

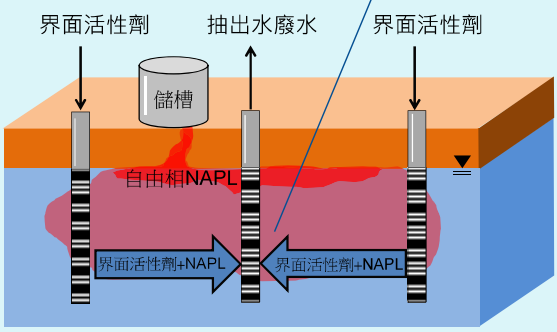
- Advantage of surfactant
  - Increasing NAPL solubility in water
  - Reducing surface tension of NAPL and increasing mobility
  - As carbon source of microbes



Surface tension vs Phase behavior of NAPL

Lab scale tests of middle phases



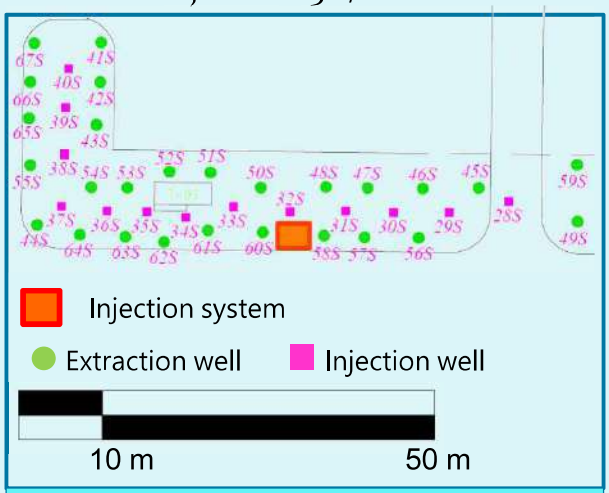


Surfactant flush

Remediation Works

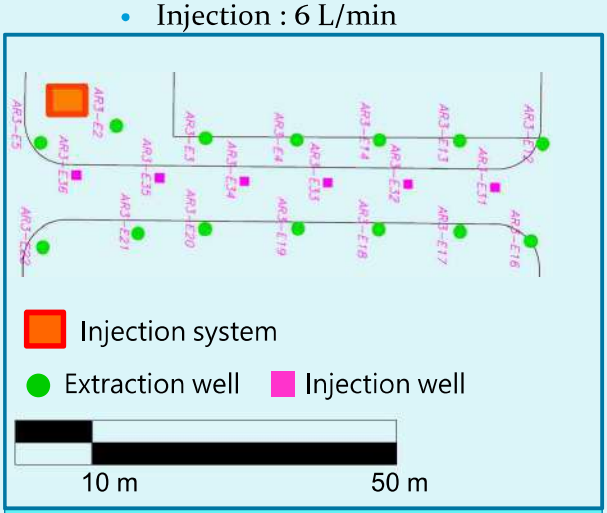
Surfactant flush

- Wells ： 40
- ROI：7 m
  - Extraction : 27 L/min
  - Injection : 13 L/min



四輕組沖排井場規劃

- Wells：20
- ROI：7 m
  - Extraction : 14 L/min
  - Injection : 6 L/min



芳三組沖排井場規劃

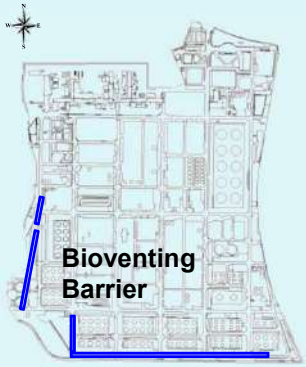
Boundary control

- ORC Dosing
  - Principle
    - Elevated dissolved oxygen in GW by dosing oxygen release compound (ORC) to enhance bioremediation
  - Operation
    - Period: year 2004-2009
    - Averagely 450 kg ORC was dosed into selected wells per month
    - Contaminant concentration was monitored regularly along the boundary

Remediation Works

Boundary control

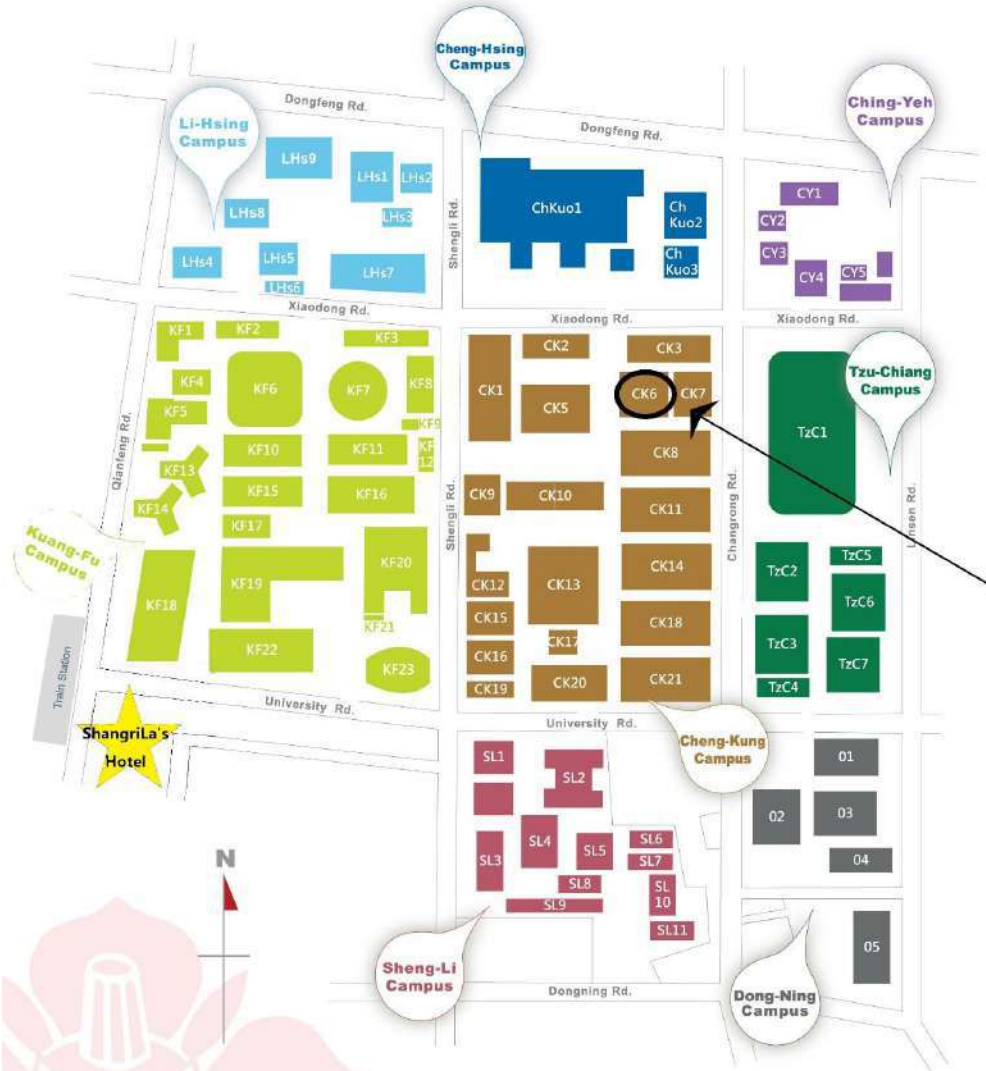
- Bioventing
  - Principle
    - Delivered oxygen into aquifer through sparing air and formed a barrier combined with the effects of bioremediation and VOC stripping
  - Operation
    - Period: year 2007-now
    - Totally 31 compressor sets were installed, each set covers 6 bioventing wells
    - Sparging pressure: 0.1-0.5 kg/cm²



Final Remark

- Since year 2001 the groundwater contamination was first revealed in Lin-Yuan Petrochemical Plant, CPC has continuously devoted into the plant facility rehabilitation and the remediation of contaminated soil and groundwater. The vast results of the past works are shown in this presentation.
- For Lin-Yuan Petrochemical Plant, the soil and groundwater remediation is not an easy task. However, the technologies applied in this site are continuously improved through the accumulation of operation experience.
- In recent years, new technologies of site investigation and remediation were introduced in Taiwan. CPC will continuously adjust remediation strategy and apply new technologies, thus the final goal of delisting can be achieved in the near future.

National Cheng Kung University
Campus Map



01 Aeronautical & Astronautical Eng. Dept.
SL1 Alumni Association Center
KF1 Architecture Dept.
02 Center for Micro/Nano Science & Technology
CK14 Chemistry Dept.
TzC2 Chemical Eng. Dept.
KF7 Chinese Lit. Dept.
CK8 Civil Eng. Dept.
ChKuo2 College of Bioscience & Biotech.
TzC7 College of Eng.
TzC3 College of Eng. & Computer Science
KF20 College of Management
ChKuo1 College of Medicine
KF1 College of Planning & Design
CK12 College of Sciences
LHs5 College of Social Sciences
KF3 College of Liberal Arts
CK18 Computer Science & Info. Eng. Dept.
CK15 Earth Sciences Dept.
TzC3 Electrical Eng. Dept.
CK21 Eng. Science Dept.
CK6 Environmental Eng. Dept.
CK17 Ge-Chi Hall
CK11 Geomatics Dept.
KF11 History Dept.
CK3 Hydraulics & Ocean Eng. Dept.
KF10 Industrial Design Dept.
KF5 Institute of Art Studies
CK2
CK11 Materials Science & Eng. Dept.
CK10 Mathematics Dept.
TzC6 Mechanical Eng. Dept.
LHs1 Medicine & Nursing Dept.
LHs3 Mental Health Center
CK1
ChKuo1 Nursing Dept.
ChKuo3 Occupational Therapy Dept.
ChKuo3 Physical Therapy Dept.
CK16 Physics Bldg. No.2
CK13 Physics Dept.
LHs4 R&D Foundation
CK14 Resources Eng. Dept.
TzC7 Systems & Naval Mechatronic Eng. Dept.
KF4
ChKuo2 University Center for Bioscience & Biotech.
KF2 Urban Planning Dept.

KF5 Architecture Research Bldg.
TzC4 Chi Mei Building
CK7 Geotechnical Eng. Bldg.
KF3 Hsiu-Chi Building
CK12 Info. Tech. Bldg.
TzC5 Instrumentation Equipments Bldg.
CK5 Main Library
ChKuo2 Medical Lab. Science & Biotech. Bldg.
CK19 Multi-Purpose Bldg.
CK12 Physics & Chemistry Bldg.
LHs4 Public Health Bldg.
02 Science & Tech. Bldg.
SL2 Students' Reading Hall
LHs2 The Uni President Health Research Building
KF15 Wei-Nong Building

ChKuo1 NCKU Hospital
LHs7 NCKU Hospital Bldg. No.2

KF17 Military Training Office
KF16 Yun-Ping Administration Bldg.

KF19 Art Center
ChKuo1 Cheng-Hsing Auditorium
KF19 Cheng-Kung Auditorium
CK13 Ge-Chi Auditorium
KF9 History Archives
KF19 International Conference Hall
LHs6 Magic School of Green Technology
KF19 Student Activity Center I
SL8 Student Activity Center II
LHs8 Taiwanese Lit. Dept.
LHs9 Life Sciences Dept.
KF6 Banyan Garden
KF8 Cheng Kung Lake
CK20 NCKU Museum
KF16 Phoenix Theater
KF12 Small West Gate
SL1 Zenda Suites

KF23 Chung Cheng Gym
KF22 Kuang-Fu Sports Court
KF18 Kuang-Fu Sports Field
SL3 Swimming Pool
TzC1 Tzu-Chiang Sports Field

03 Aeronautical & Astronautical Eng. Dormitory
CY4 Ching-Yeh Student Dorm No.1
CY3 Ching-Yeh Student Dorm No.2
CY2 Ching-Yeh Student Dorm No.3

KF14 Kuang-Fu Student Dorm No.1
KF13 Kuang-Fu Student Dorm No.2
CY5 Medical Doctor Dormitory
05 Scholar Dormitory
SL9 Sheng-Li Student Dorm No.1
SL7 Sheng-Li Student Dorm No 2
SL6 Sheng-Li Student Dorm No.3
SL5 Sheng-Li Student Dorm No.5
SL4 Sheng-Li Student Dorm No.6
SL10 Sheng-Li Student Dorm No.8
SL11 Sheng-Li Student Dorm No.9
04 Single Faculty Housing
CY1 Single Faculty Housing

CK9 Hsin Yuan
CK20 Mail Room
KF21 Post Office

- Centers & Dept.
- Buildings
- Hospital
- Administrations
- Auditorium
- Scenic Spots
- Sports
- Dorms & Lodgings
- Others