New Technologies for Site Measurement and Remediation

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Tokyo University of Agriculture and Technology

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  Nakashima et al. (Kokusai Kogyo Co. Ltd.)

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Ground Air System (GAS)
~ Non-drilling Soil Gas Survey ~

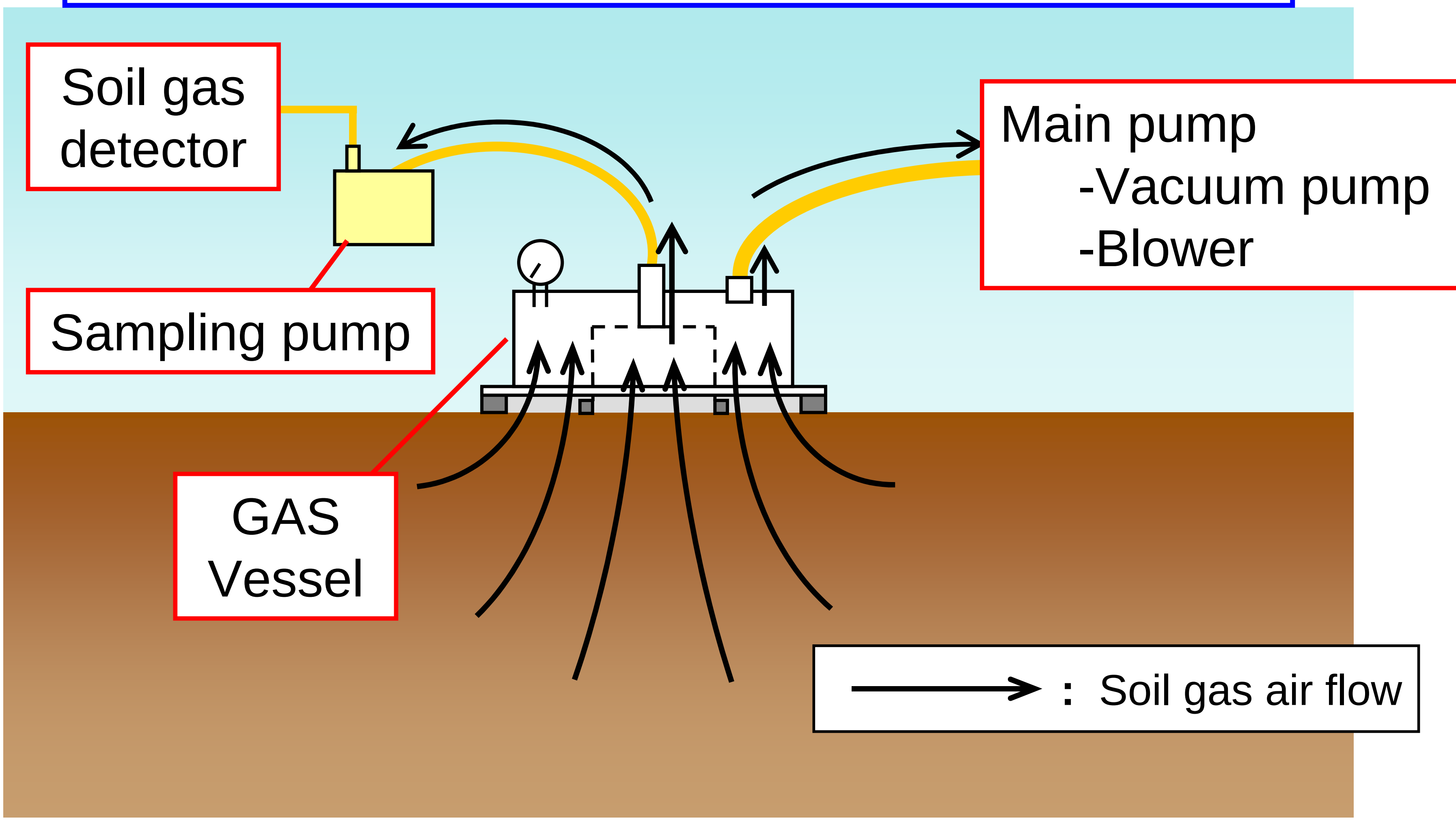
http://www.gass.jp/index.html
http://gass.jp/index_kaimei.html
http://www.kimitsu-system.com/

International Patentee:
Suzuki　Yoshikazu

(e-mail:info@kimitsu-system.com)

Ground Air System (GAS)

The soil-gas is extracted by the vacuumed pressure inside the GAS vessel.



Soil-gas survey

Drilling system	Non-drilling system
The sampling pipe is set up under the soil.	The device is set up on the ground level.

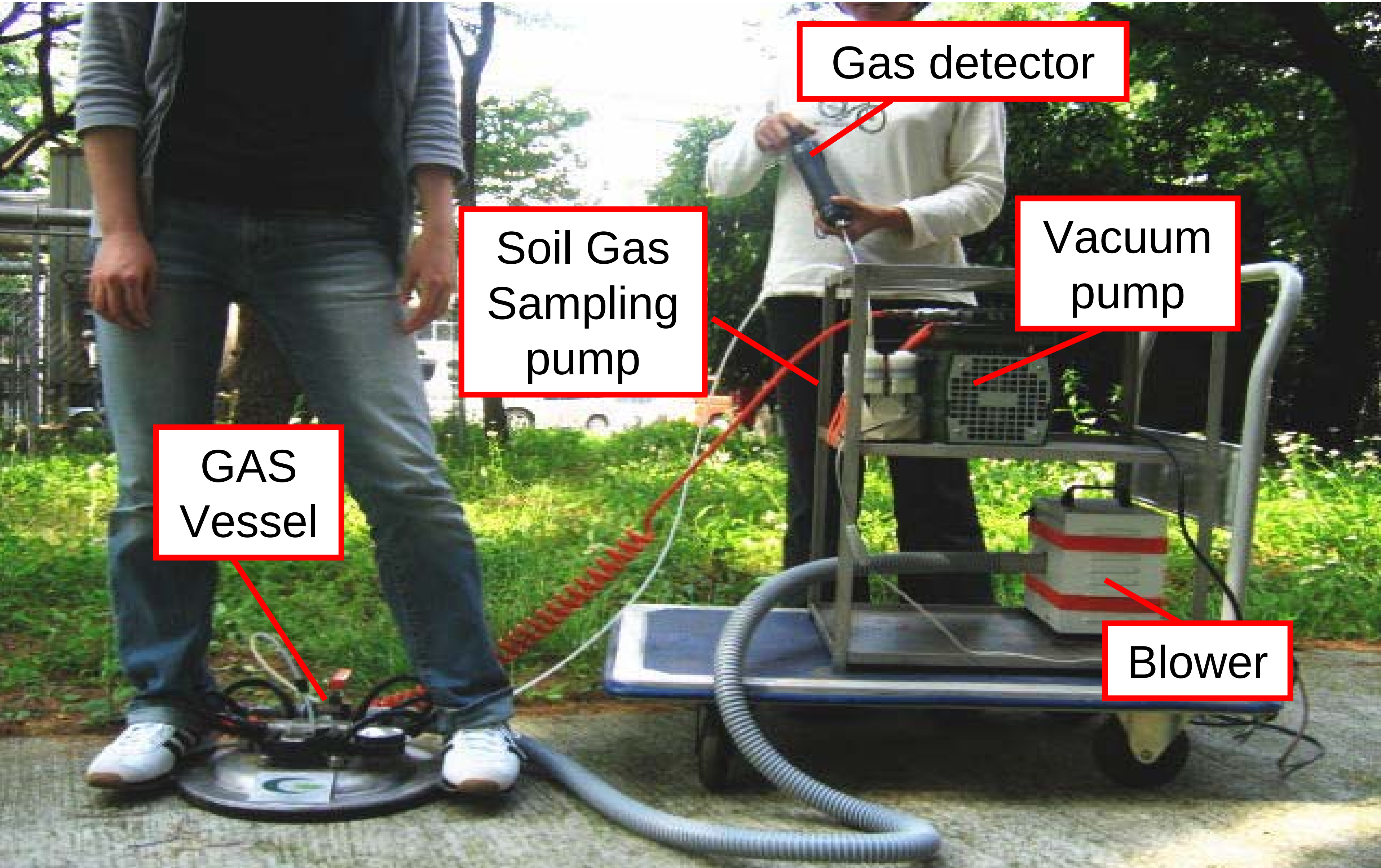
High — Cost — Low

difficult — Floor inside of factories and buildings under operating; Ground covered with concrete — Possible

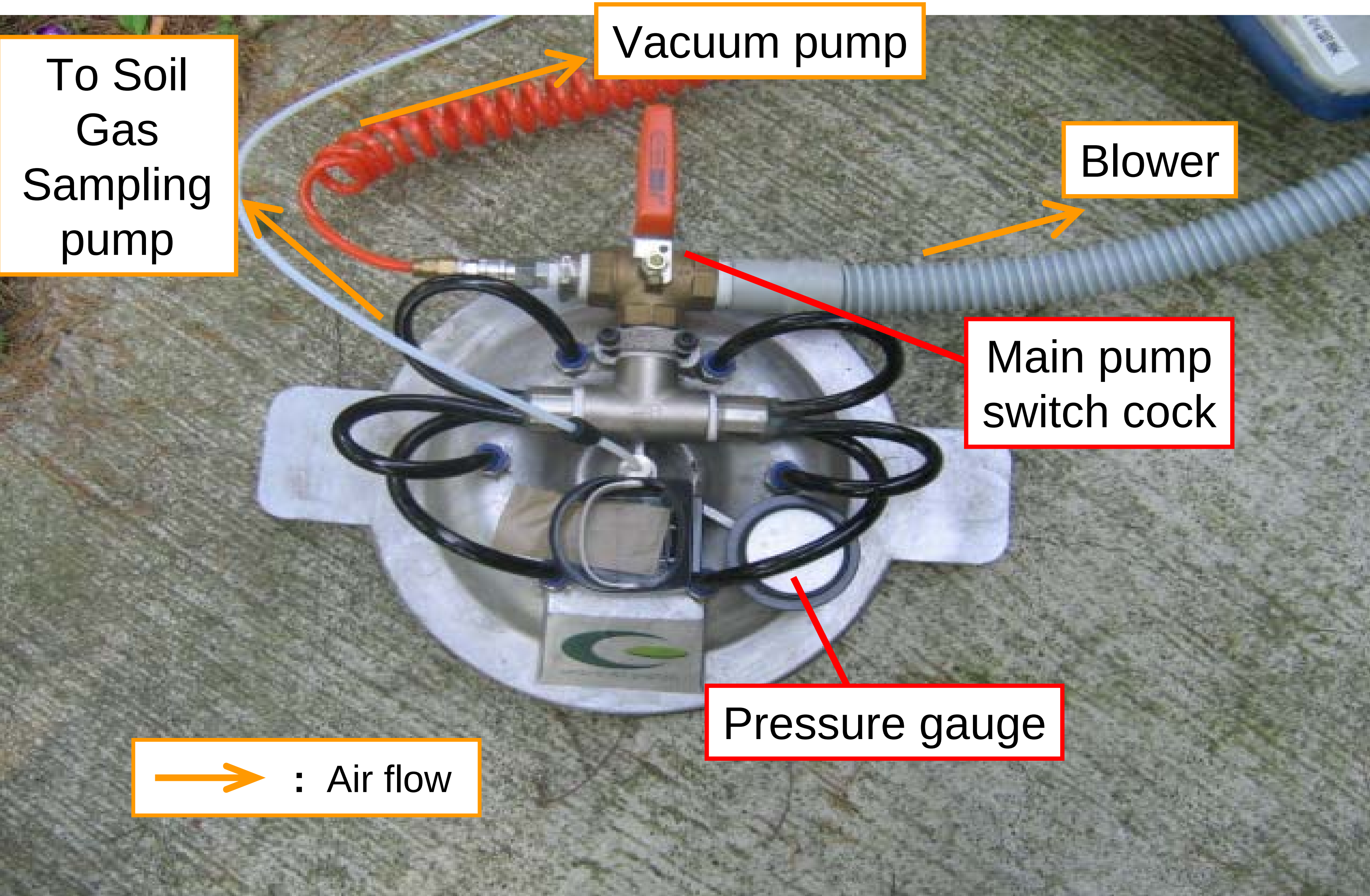
Searching hot-spot
(a heavily polluted area)
by GAS

- High-efficiency
- Low cost

Overview of soil gas survey by GAS

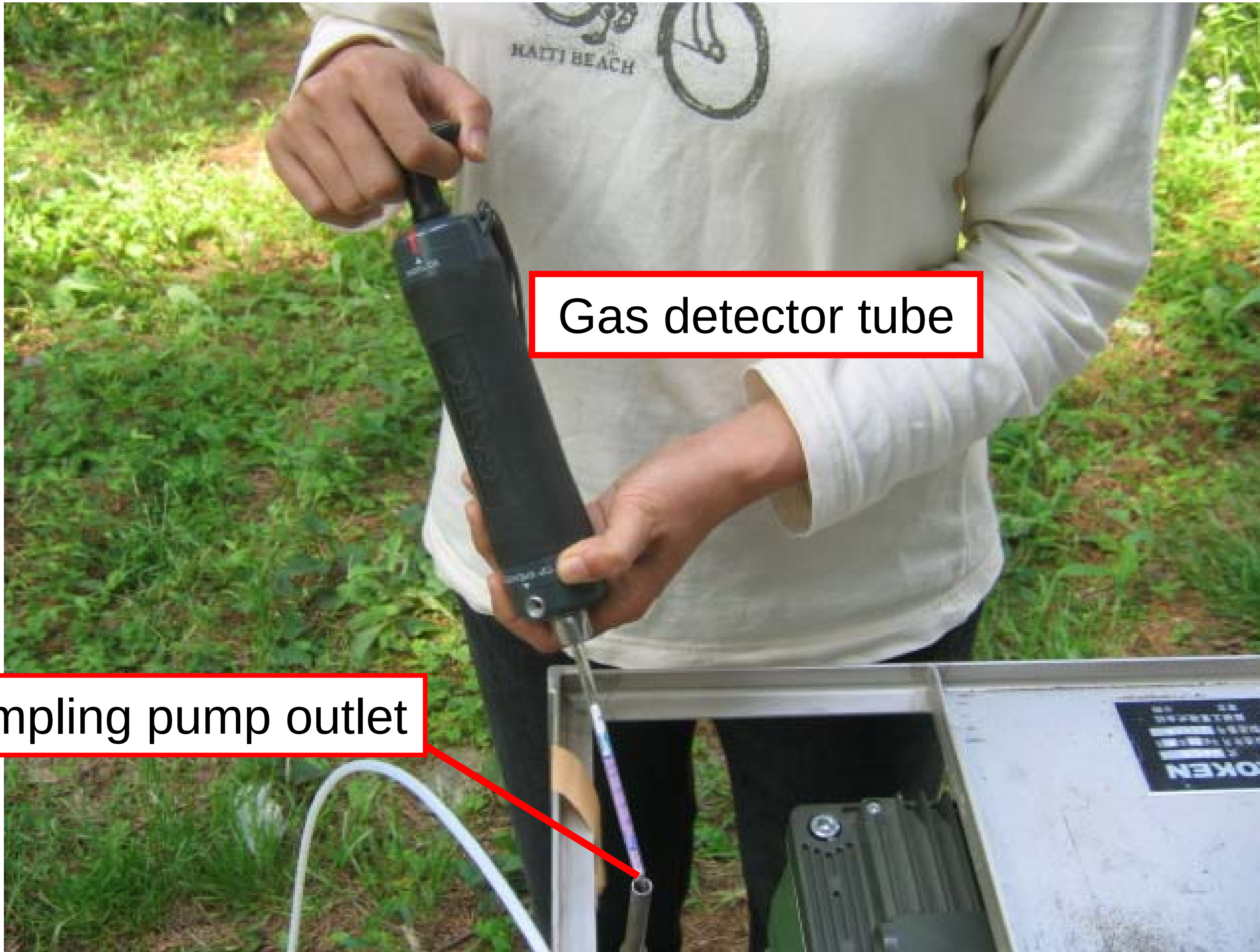


GAS Vessel



To Soil Gas Sampling pump
Vacuum pump
Blower
Main pump switch cock
Pressure gauge
: Air flow

Sampling and Measuring by Gas Detector Tube



Connecting sampling port from GAS vessel and tetra-bag for soil gas sampling

Joint Research between GAS and my Laboratory

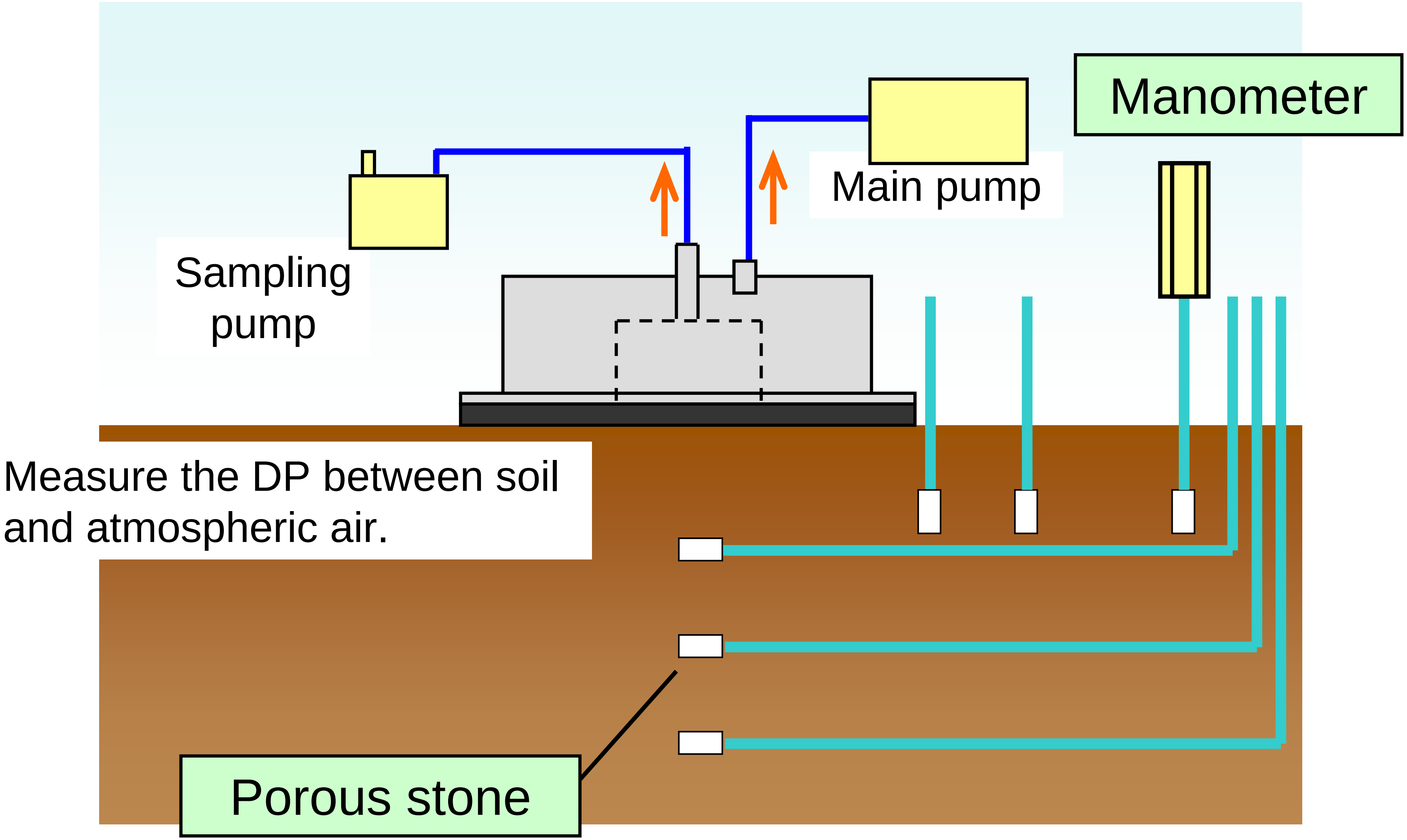
Extracted area of the soil-gas has not been understood with accuracy.

Estimate extracted area of the soil-gas by the GAS.

- Differential pressure (DP) test
- Tracer test

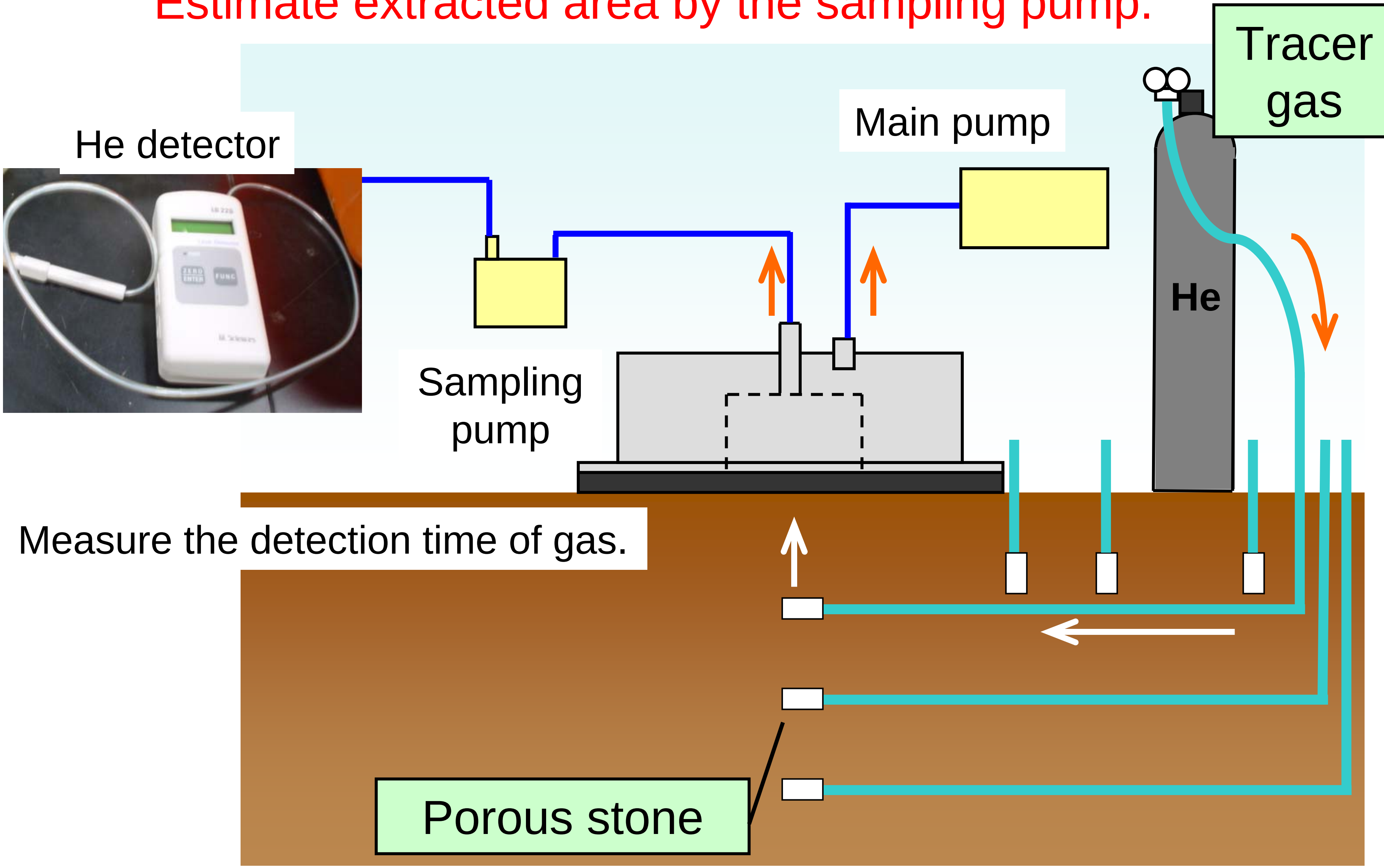
Differential pressure (DP) test

Estimate extracted area by the main pump.

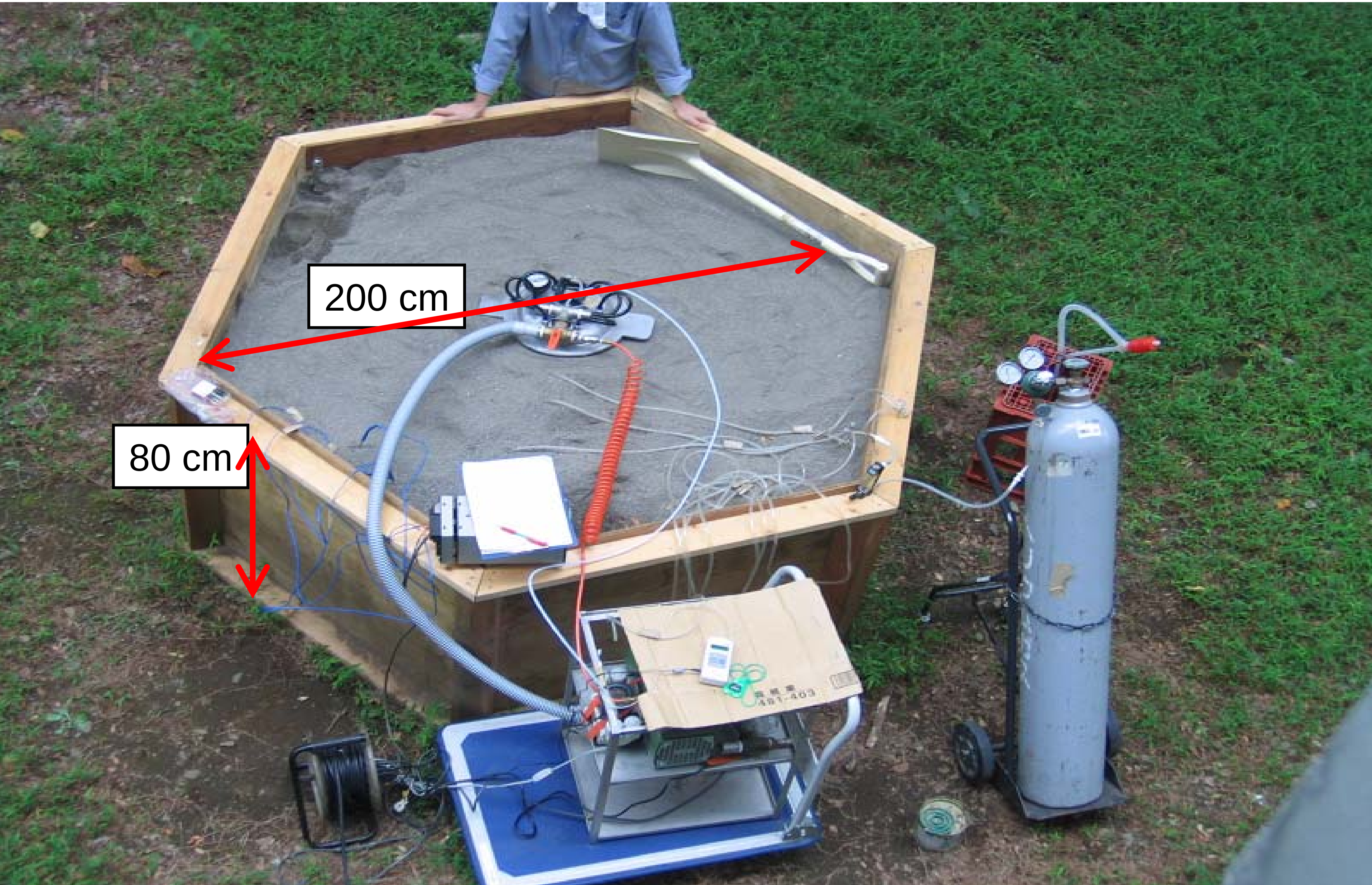


Tracer test

Estimate extracted area by the sampling pump.

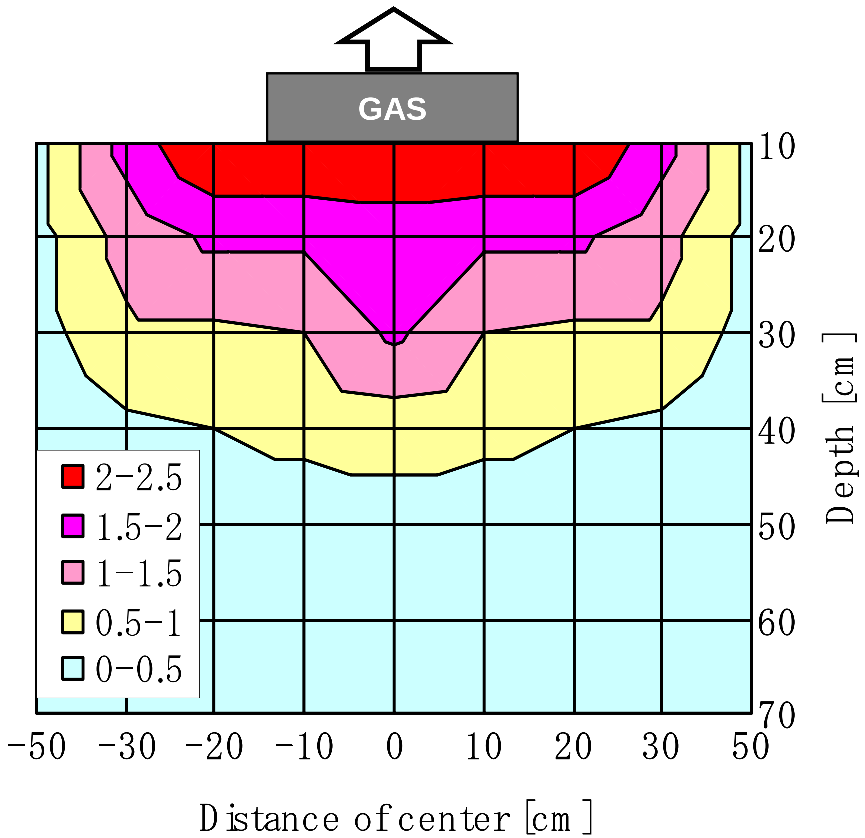


Sandpit

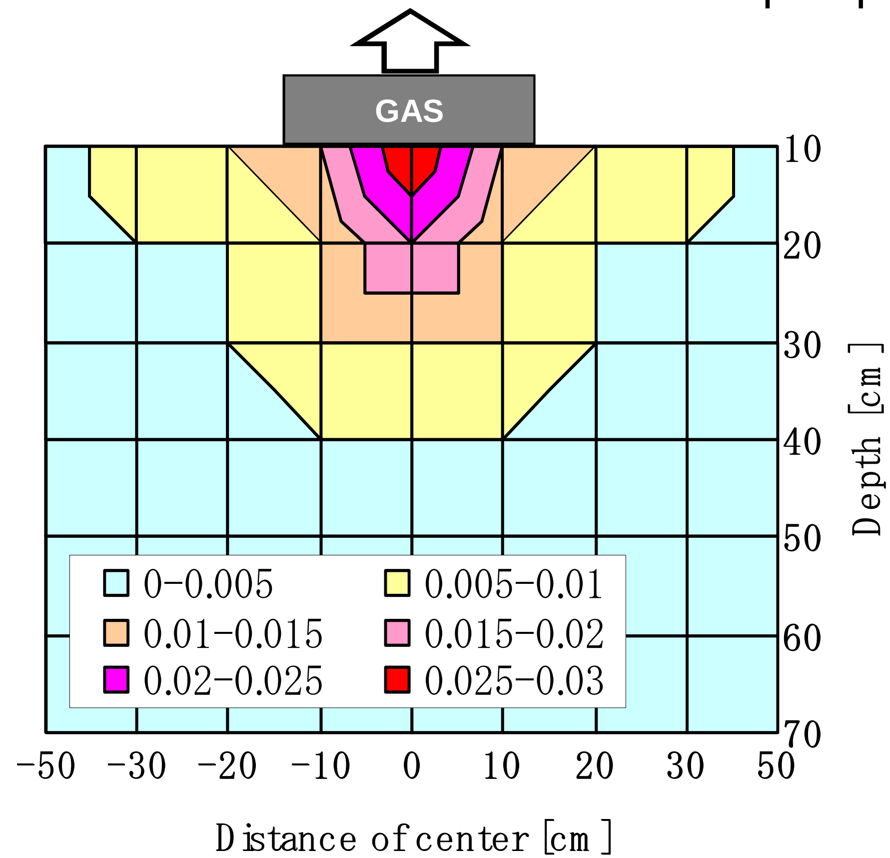


Map of extracted area

Main pump : Vacuum pump



Distribution of DP [kPa]



Distribution of average transfer speed of tracer gas [cm/s]

Extent of the impact of GAS is about 40-50 cm vertical under GAS vessel.

Measurement of GAS in a Factory under Operation

（MOE：Demonstration Program for Low-cost and loading type
soil monitoring and remediation technologies

Photo:Provided by Mitsuya Industrial Co. Ltd. (2003-2004)

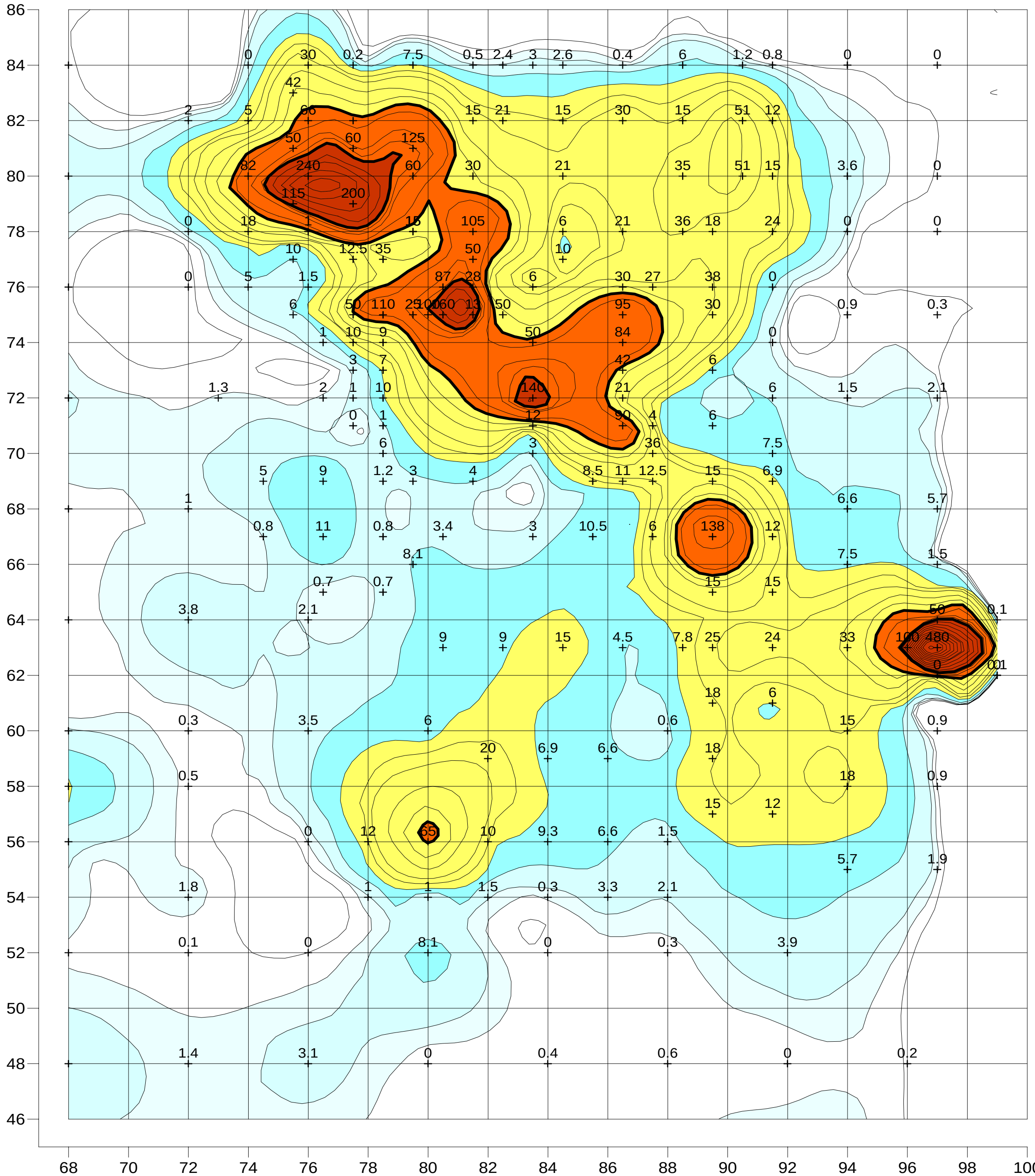
Measurement of GASS outside a Factory under Operation
（MOE：Demonstration Program for Low-cost and loading type
soil monitoring and remediation technologies
Provided by Mitsuya Industrial Co. Ltd. (2003-2004)

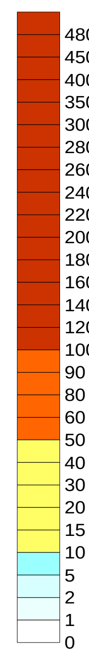
1 m-depth Core Boring for Soil Gas Investigation Following the Soil Investigation Manual in a Factory under Operation （MOE：Demonstration Program for Low-cost and Low-loading type Soil Monitoring and Remediation Technologies Provided by Suzuki (2003-2004)

1 m-depth Core Boring for Soil Gas Investigation Following the Soil Investigation Manual (Provided by Mr. Kamisuna)

Measurement of GAS in a Factory under Operation
（MOE：Demonstration Program for Low-cost and loading type soil monitoring and remediation technologies
Provided by Suzuki (2003-2004)

Horizontal distribution of TCE in soil gas determined by GAS without core boring（MOE：Demonstration Program for Low-cost and loading type soil monitoring and remediation technologies Provided by Suzuki (2003-2004)





Soil-gas survey by GAS

- System of searching a heavily polluted area

- Survey on floor inside of buildings and ground covered with concrete is possible.

- High-efficiency and low-cost system

- Rapid measurement (a few minutes)

Development of Real-Time PCR Techniques Targeting 16S rDNA of *Dehalococcoides* for Bioremediation *of* Chlorinated ethenes-contaminated Sites

Kanji Nakamura (Tohoku Gakuin University)*
Hiroaki Ishida (Kurita Water Industries Ltd.**)**
Masahiro Mizumoto (Kurita Water Industries Ltd.**)**

How to manage and control bioremediation

Field: Bioremediation of contaminated soil

Contaminants: Chlorinated ethenes

Tetrachloroethene (PCE)
Trichlororethene (TCE)
Dichloroethene (DCE)
Vinyl chloride (VC)

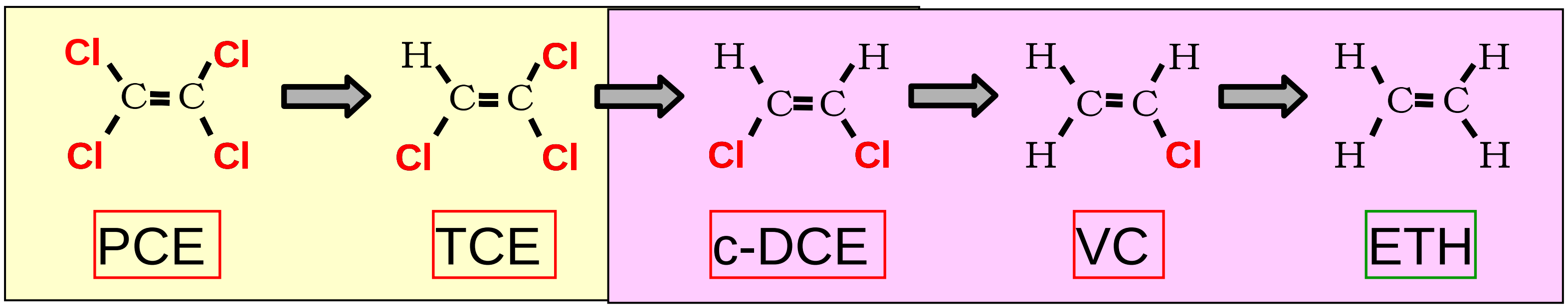
Microbe: *Dehalococcoides* bacteria

Technology: Biostimulation

Pathway of anaerobic dechlorination

Electron Donor：H_2 → Produced from added organics

Electron Acceptor: PCE, TCE, c-DCE, VC



Proceed easily

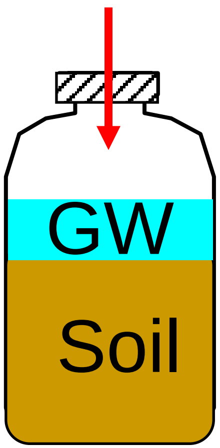
Dehalococcoides is needed

Maymo-Gatell et al. (1997) : *Dehalococcoides ethenogenes*

Hendrickson et al. (2002): Classification of *Dehalococcoides*

TCE degradation in vials with soils from 14 different contaminated sites in Japan

TCE with Na-acetate, N, P



Incubated 60 days at 30℃

Soil Sample	Final Product	Detection of *Dehalococcoides* 16S rDNA
A	**ETH**	**Detected**
B	**ETH**	**Detected**
C	**ETH**	**Detected**
D	**ETH**	**Detected**
E	**ETH**	**Detected**
F	**ETH**	**Detected**
G	**ETH**	**Detected**
H	**c-DCE**	**Not detected**
I	**c-DCE**	**Not detected**
J	**c-DCE**	**Not detected**
K	**c-DCE**	**Not detected**
L	**c-DCE**	**Not detected**
M	**TCE**	**Not detected**
N	**TCE**	**Not detected**
	7/14	**7/14**

Dehalococcoides 16S rDNA cloned from 7 vials

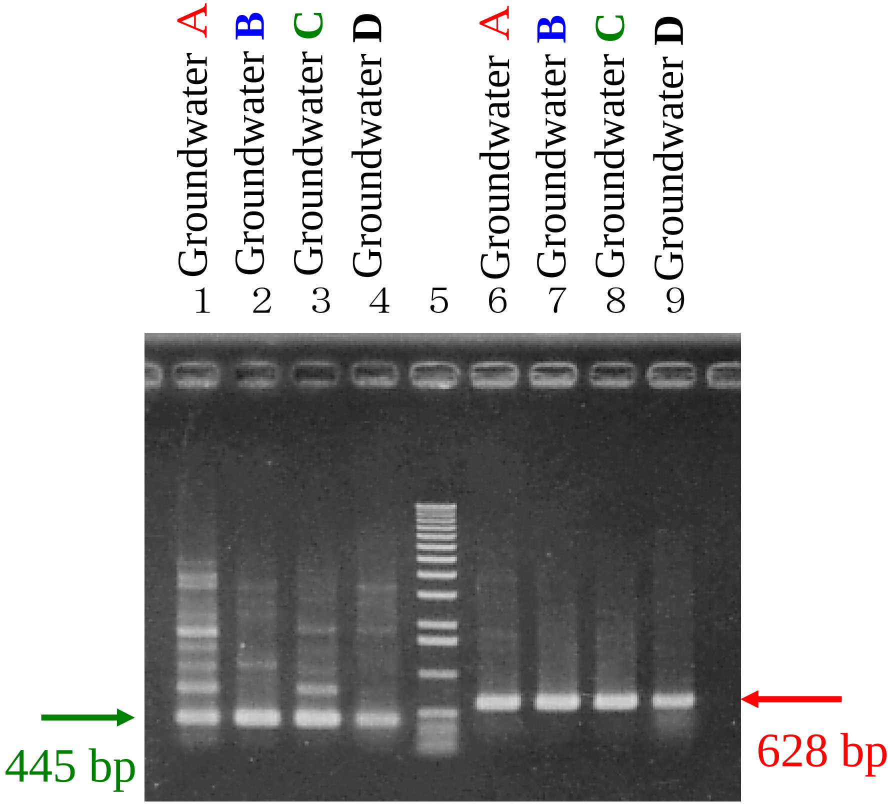
（PCR amplified w/ Bact27f/1492r）

GATGAACGCTAGCGGCGTGCCTTATGCATGCAAGTCGAACGGTCTTAAGCAATTAAGATAGTGGCGAACGGGTGAG
TAACGCGTAAGTAACCTACCTCTAAGTGGGGGATAGCTTCGGGAAACTGAAGGTAATACCGCATGTGGTGGRCCGA
CATATGTTGGTTCACTAAAGCCGTAAGGCGCTTGGTGAGGGGCTTGCGTCCGATTAGCTAGTTGGTGGGGTAATGGC
CTACCAAGGCTTCGATCGGTAGCTGGTCTGAGAGGATGATCAGCCACACTGGGACTGAGACACGGCCCAGACTCCT
ACGGGAGGCAGCAGCAAGGAATCTTGGGCAATGGGCGAAAGCCTGACCCAGCAACGCCGCGTGAGGGATGAAGGC
TTTCGGGTTGTAAACCTCTTTTCATAGGGAAGAATAATGACGGTACCTGTGGAATAAGCTTCGGCTAACTACGTGCC
AGCAGCCGCGGTAATACGTAGGAAGCAAGCGTTATCCGGATTTATTGGGCGTAAAGTGAGCGTAGGTGGTCTTTCA
AGTTGGATGTGAAATTTCCCGGCTTAACCGGGACGAGTCATTCAATACTGTTGGACTAGAGTACAGCAGGAGAAAA
CGGAATTCCCGGTGTAGTGGTAAAATGCGTAGATATCGGGAGGAACACCAGAGGCGAAGGCGGTTTTCTAGGTTGT
CACTGACACTGAGGCTCGAAAGCGTGGGGAGCGAACAGAATTAGATACTCTGGTAGTCCACGCCTTAAACTATGGA
CACTAGGTATAGGGAGTATCGACCCTCTCTGTGCCGAAGCTAACGCTTTAAGTGTCCCGCCTGGGGAGTACGGTCGC
AAGGCTAAAACTCAAAGGAATTGACGGGGGCCCGCACAAGCAGCGGAGCGTGTGGTTTAATTCGATGCTACACGA
AGAACCTTACCAAGATTTGACATGCATGTAGTAGTGAACTGAAAGGGGAACGACCTGTTAAGTCAGGAACTTGCAC
AGGTGCTGCATGGCTGTCGTCAGCTCGTGCCGTGAGGTGTTTGGTTAAGTCCTGCAACGAGCGCAACCCTTGTTGCT
AGTTAAATTTTCTAGCGAGACTGCCCCGCGAAACGGGGAGGAAGGTGGGGATGACGTCAAGTCAGCATGGCCTTTA
TATCTTGGGCTACACACACGCTACAATGGACAGAACAATAGGTTGCAACAGTGCGAACTGGAGCTAATCCCCAAAG
CTGTCCTCAGTTCGGATTGCAGGCTGAAACCCGCCTGCATGAAGTTGGAGTTGCTAGTAACCGCATATCAGCATGGT
GCGGTGAATACGTTCTCGGGCCTTGTACACACCGCCCGTCACGTCATGAAAGCCGGTAACACTTGAAGTCGATGTG
CCAACCGCAAGGAGGCAGTCGCCGAGGGTGGGACTGGTAATTGGGACG

（Position １４８：ＡorＧ）

A dominant type of *Dehalococcoides* existing in Japan

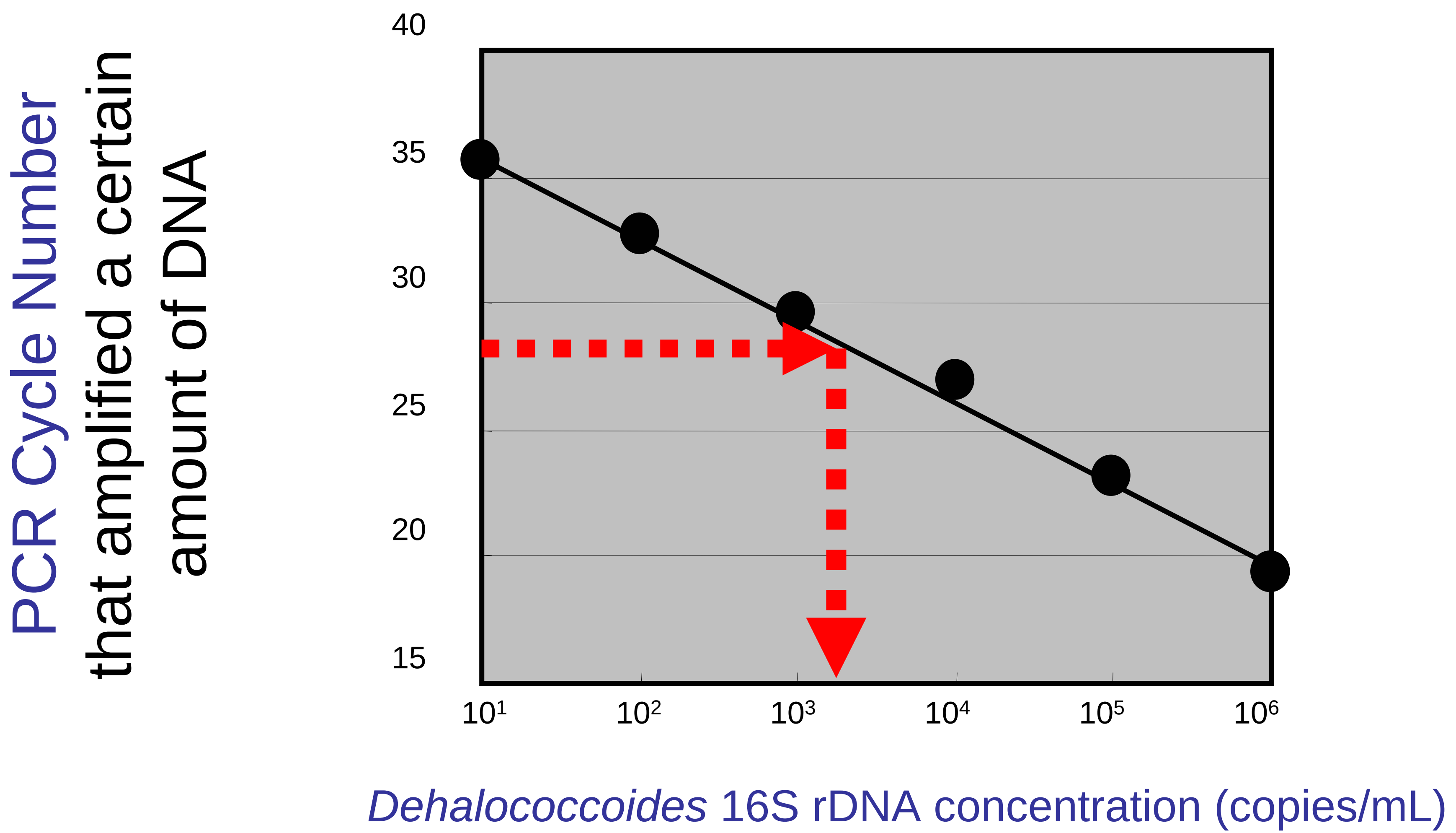
Detection of *Dehalococcoides* 16S rDNA by block PCR



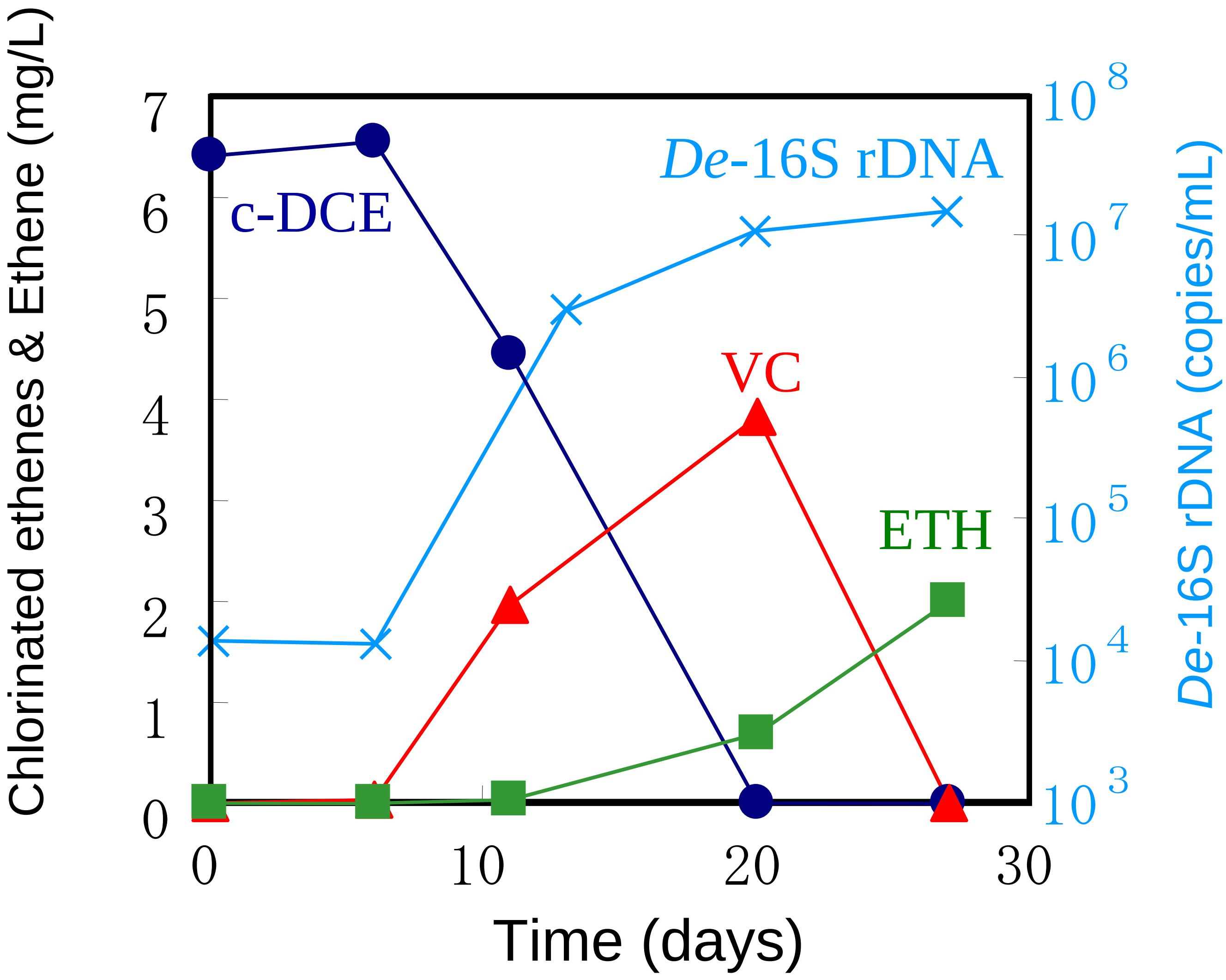
Primer pair A
Loffler et al. (2000)

Primer pair B (De624f and De1232r)
This study

Real-Time PCR by LightCycler



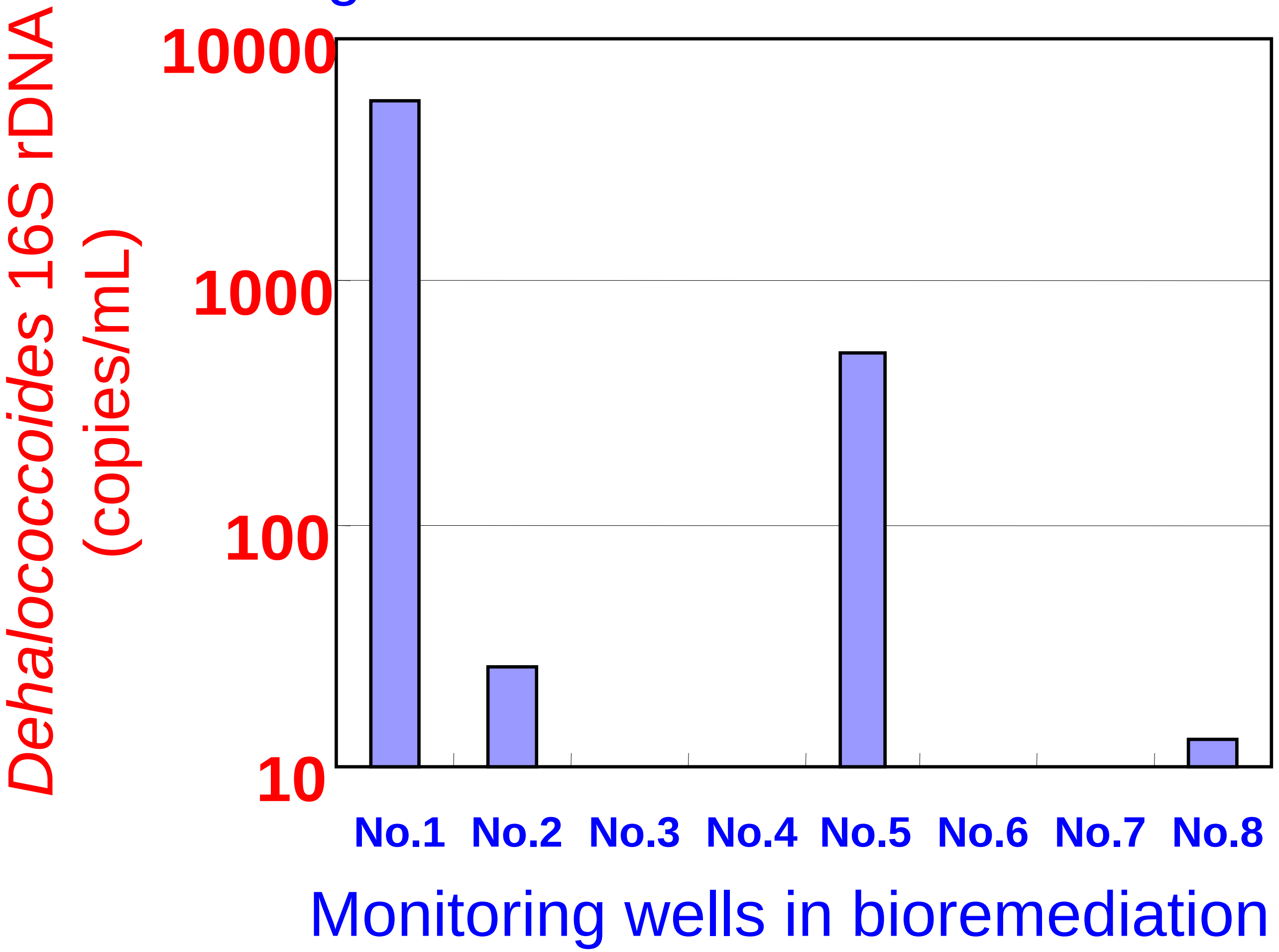
Detection of *Dehalococcoides* 16S rDNA by Real-Time PCR




Auto Core

Full scale biostimulation

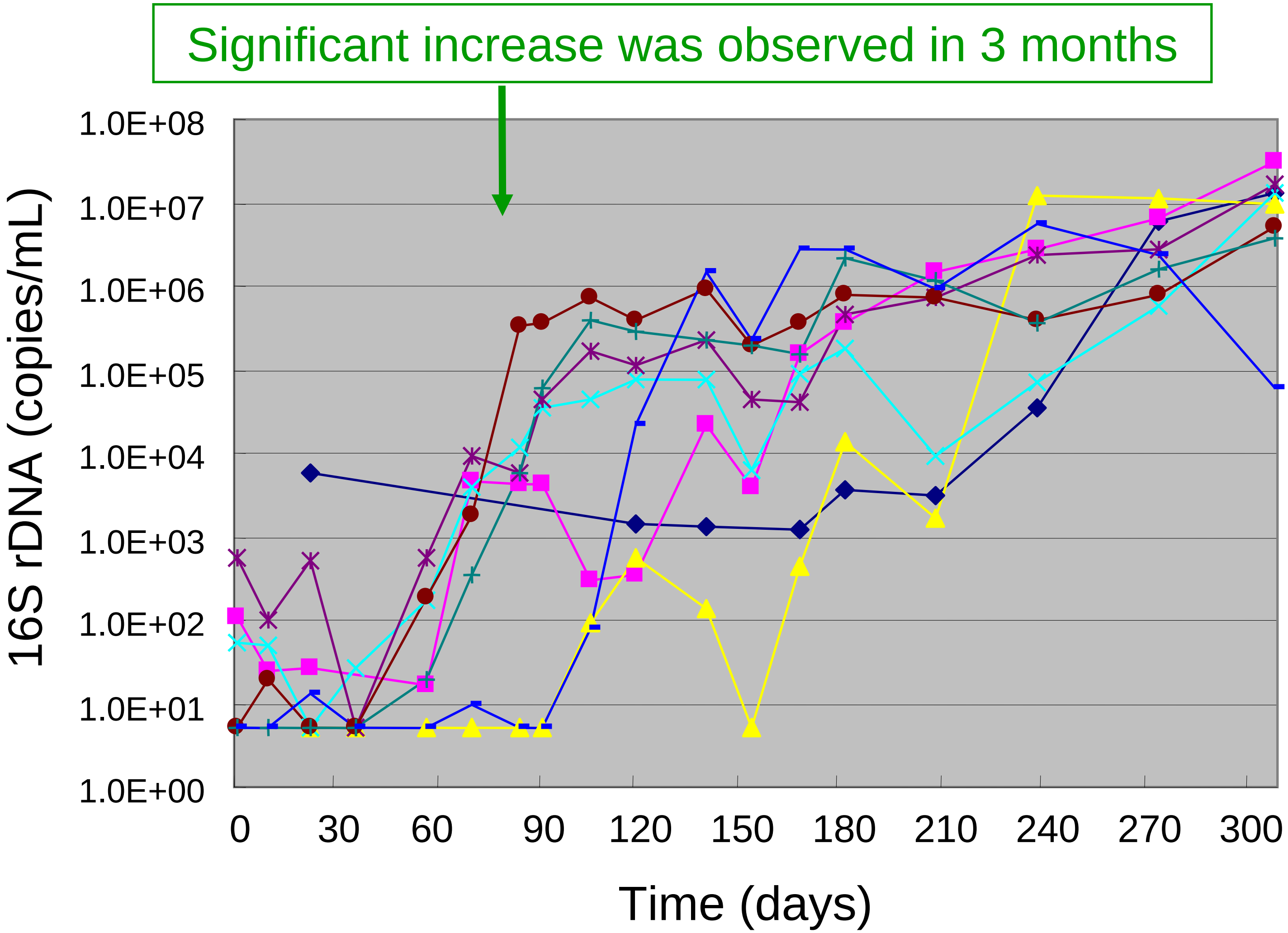
Initial *Dehalococcoides* 16S rDNA concentrations
in groundwater at a contaminated site



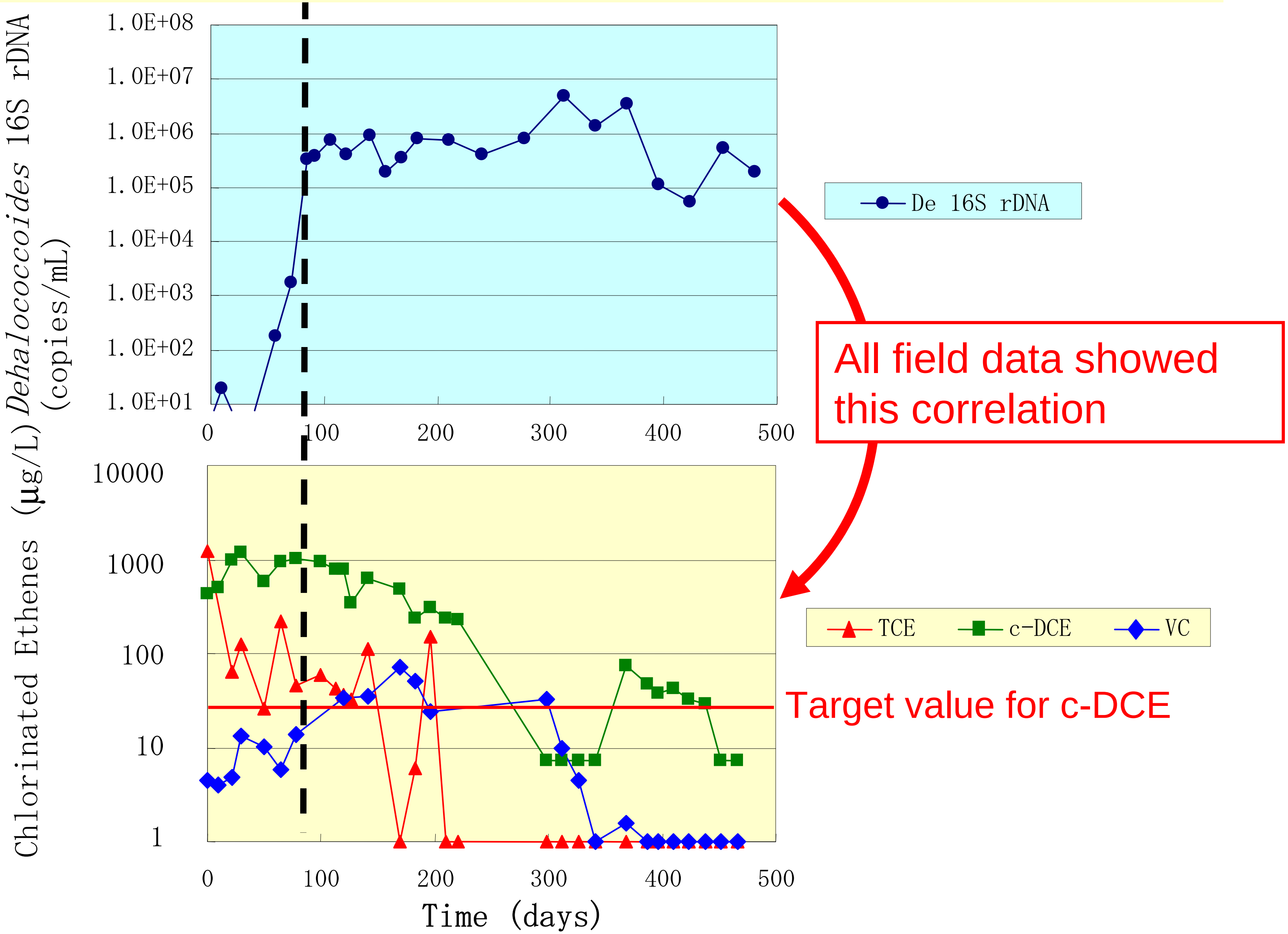
The result showed the feasibility of biostimulation

Change of *De*-16S rDNA concentrations in groundwater

Intermittent addition of organics and nutrients from multiple wells w/o circulation



The increase of *Dehalococcoides* population led the decrease of chlorinated ethenes in the field



Conclusions

1. *Dehalococcoides* population was needed for complete dechlorination.

2. A certain type of *Dehalococcoides* was dominant in Japan.

3. Real-Time PCR targeting 16S rDNA of *Dehalococcoides* was successfully used to manage the full scale biostimulation.

Non-combustion technology for dioxin, PCB and POPs pesticides: Mechanochemical Process (MC)

Radicalplanet Research Institute Co. Ltd.
& Hosomi Laboratory

Background for Non-combustion Technologies

- POPs Convention requires disposal techniques to be in environmentally sound manner and not produce other POPs by-products in the national implementation plan.
- Environmental and health concerns about release of POPs by-products like dioxins from incineration plants have triggered the development of alternative destruction technologies.

PCB problems in Japan

- PCB wastes including transformers, capacitors and carbonless copy paper have been stored for about 30 years because construction of incineration plant as PCB disposal facility has not been accepted publicly.

- In order to manage the risk of PCB release into the environment during long-term PCB storage, the central government established the evaluation system of emerging and alternative destruction technologies in 1996, i.e., non-combustion technologies.

Development of non-combustion technologies

- Private sectors have demonstrated the performance and effectiveness of non-combustion technologies for destruction of PCB wastes.

- Most of non-combustion technologies include chemical dehalogenation process with liquid phase reaction. (i.e., minimization of off-gas generated and easiness of verification of PCB degradation)

Definition of non-combustion technologies: alternative destruction technologies of incineration

Approval of non-combustion technologies

- The committees organized by the central government have reviewed these demonstration data in terms of treatment performance, by-products, final products, operation conditions and environmental concerns and confirmed several alternative technologies as officially approved PCB-disposal technologies.

Approved PCB Treatment Technologies

Decomposition technologies of liquid PCB waste

- Chemical dehalogenation
  - -Base catalyzed decomposition
  - -Metallic sodium dispersion process
  - -UV irradiation
  - -Pd/C catalytic hydrogenation reduction
  - -t-C_4H_9OK chemical extractive decomposition
- Molten metal decomposition
- Plasma decomposition
- Hydrothermal decomposition and Supercritical water oxidation
- Mechanochemical process

  (officially granted by the notification (No.25, April 1, 2004))

Washing and separation technologies of PCB waste

- Vacuum thermal separation
- Solvent/oil washing

Why do we focus on MC process?

Non-heating process

Closed system

High Safety

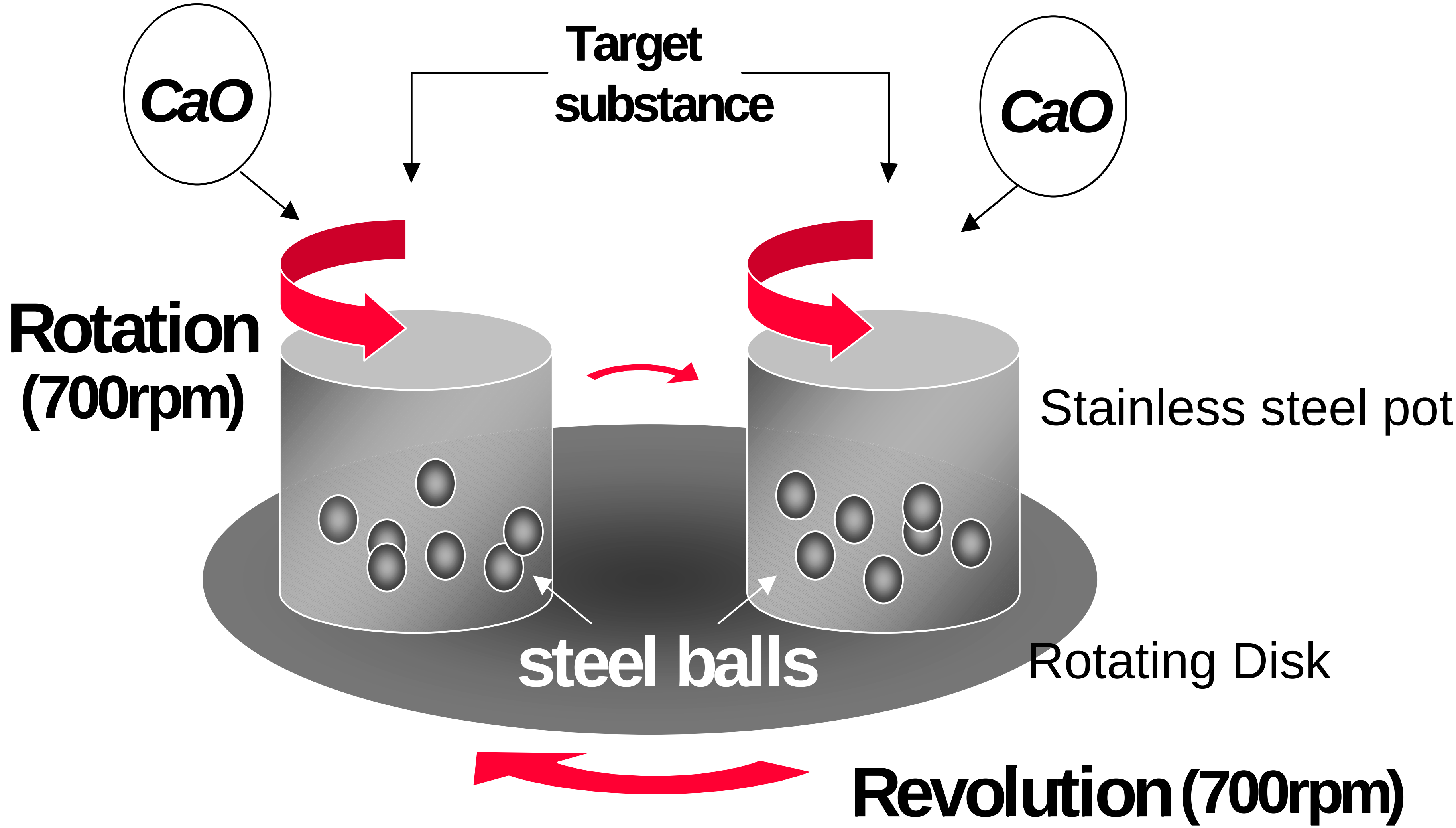
+

On-site treatment by mobile equipment

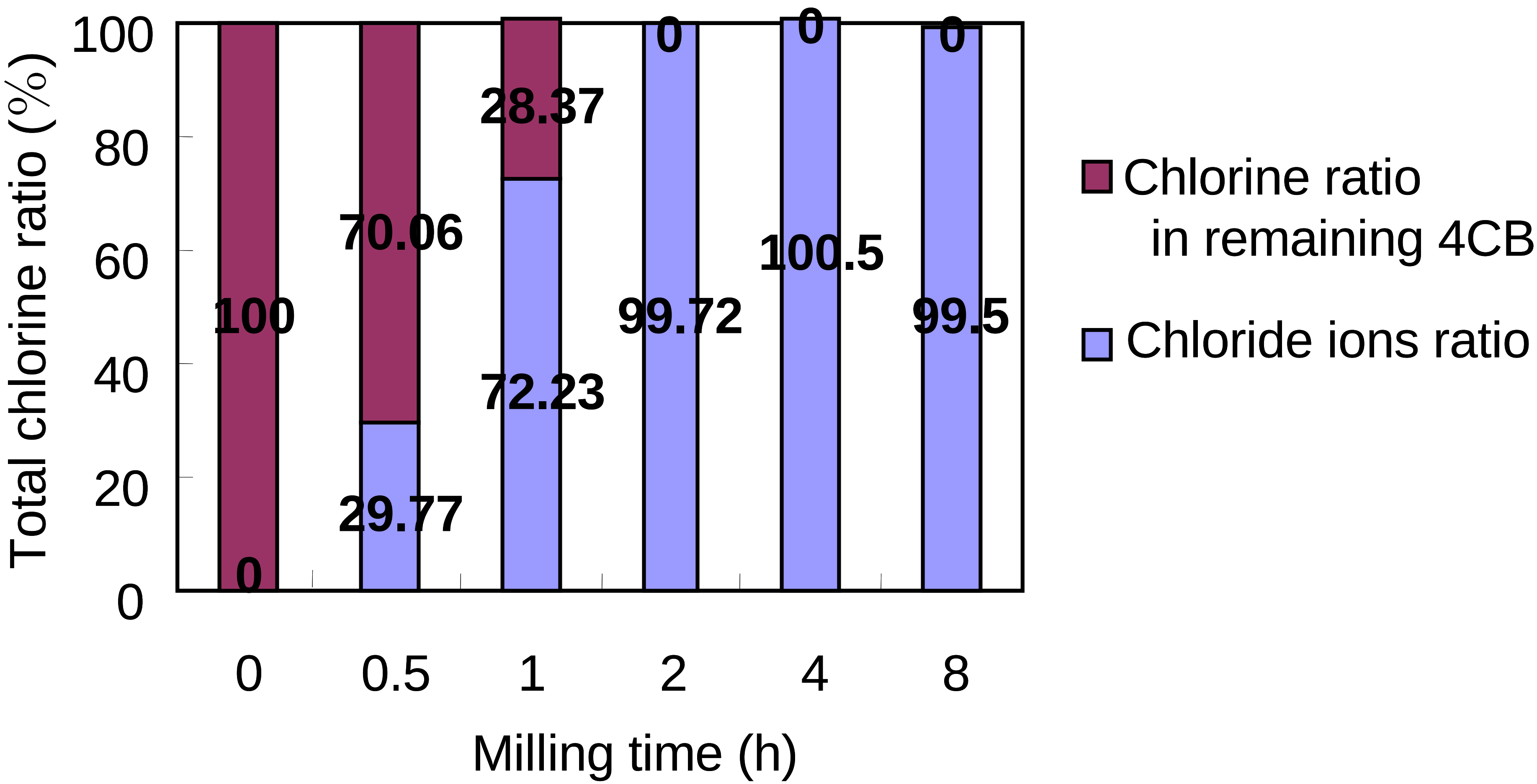
Lower cost and remove anxiety
without transfer of pollutants

Community and Public acceptance

MC is applicable to remediation of small site

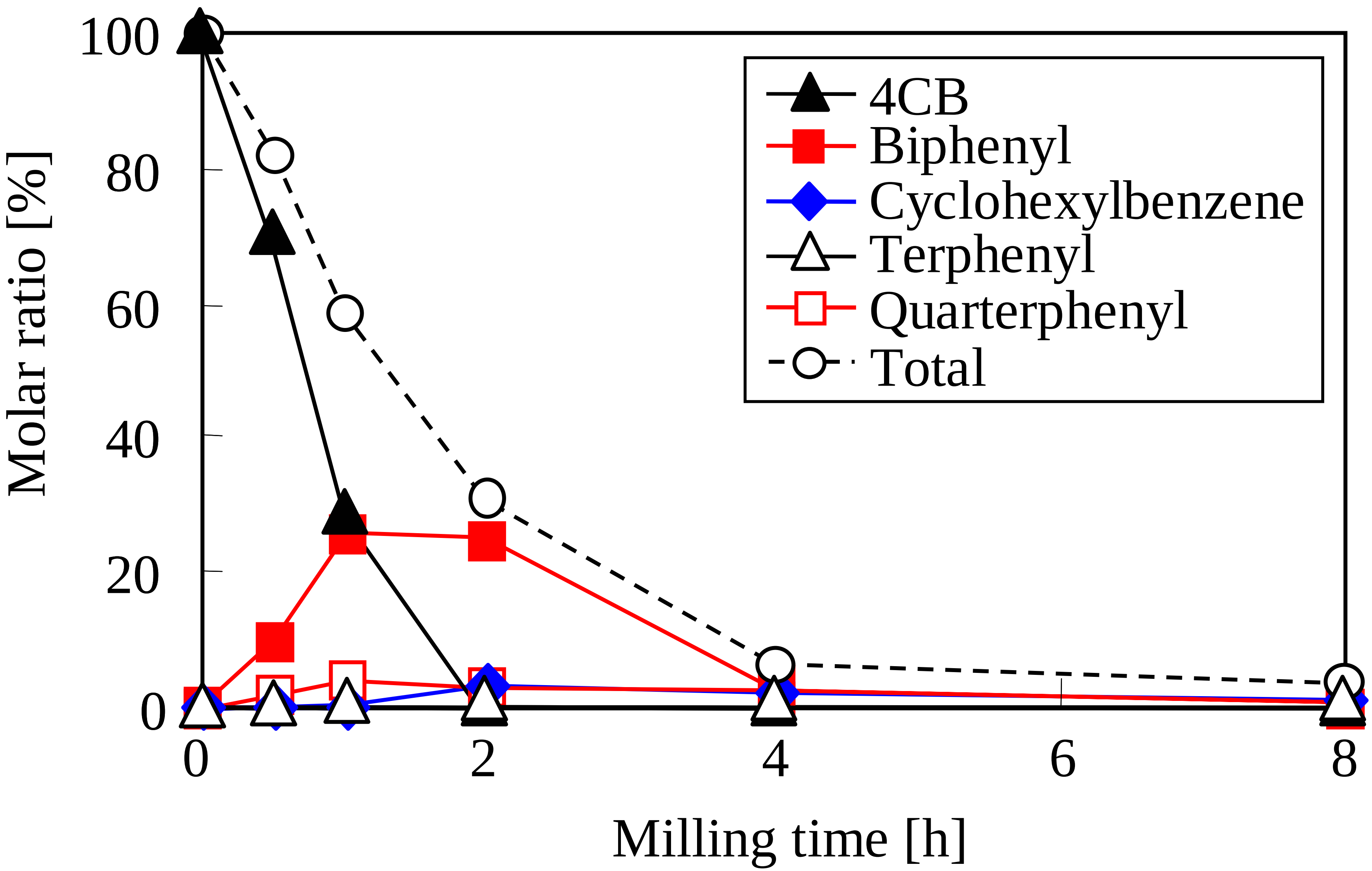


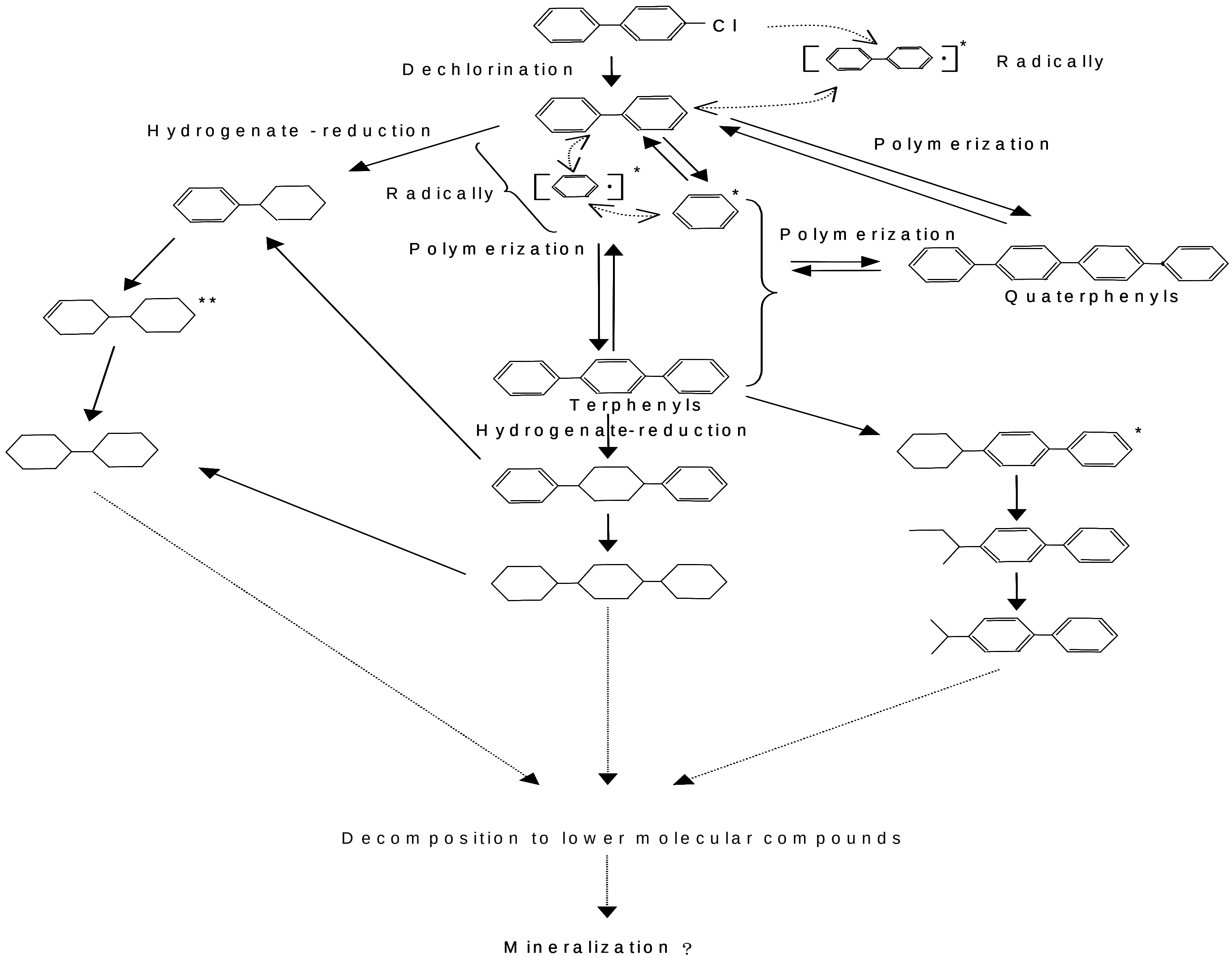
Mechanochemical (MC) treatment with a planetary ball mill



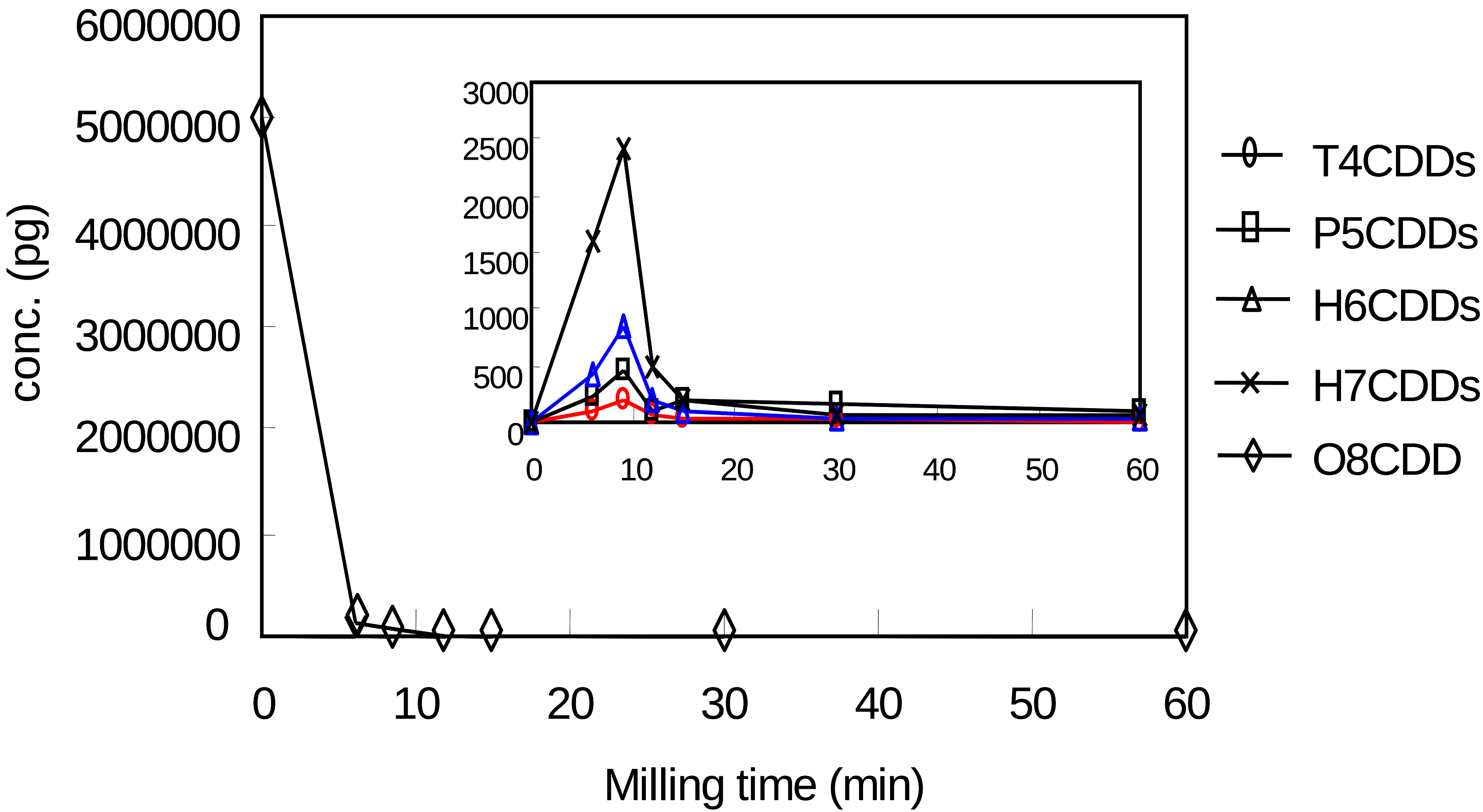
Chlorine balance during MC treatment of 4-chlorobiphenyl (4CB)

Time dependence of the molar ratio of degradation products during MC treatment of 4CB.

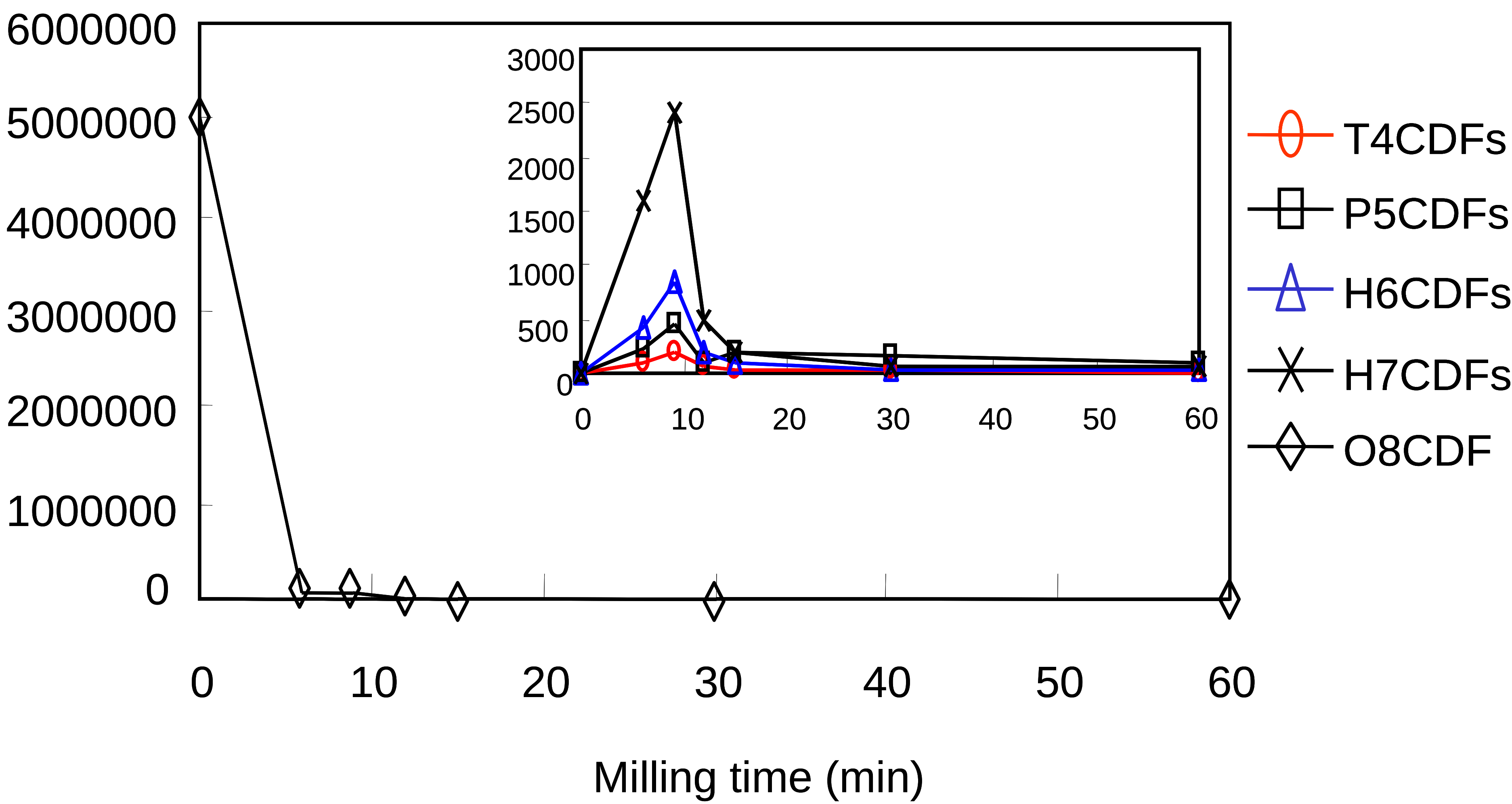




Proposed degradation pathways of 4CB by the MC treatment.
(*, not detected; **, detected, but not confirmed by spike test



Degradation of OCDD and by-products during MC treatment of OCDD



Degradation of OCDF and by-products during MC treatment of OCDF

Dechlorination rates [%] based on analyses of chloride ions after MC treatment of OCDD and OCDF for 2 h showed 99.9% and 99.3%, respectively.

Nomura and Hosomi (2005) Elucidation of degradation mechanism of dioxins during mechanochemical treatment, Env. Sci. Tech., 39, 3799-3804.

Note that this is the first study to demonstrate 100% dechlorination of dioxins by measuring the amount of chloride ions produced during the MC treatment of OCDD/OCDF.

No remaining dioxins or no other organochlorine compounds were detected, which confirms the complete dechlorination of OCDD/F.

What is Japanese Stockpile?

MOAFF put out the notice of collecting unused POPs pesticides in shed of end users through NOKYO and burying collected pesticides underground in 1972 because of their toxicity and adverse effects on human health.

Buried POPs pesticides are defined as Japanese Stockpile.

MOAFF has started to identify quantity and location of buried POPs pesticides since adoption of POPs convention and reported that total amount of buried POPs is about 4000 t and there are about 200 sites through sending out questionnaires to local governments and NOKYO.

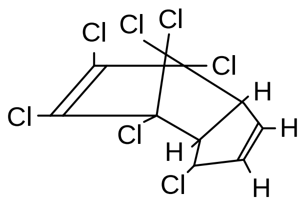
Buried POPs pesticides mainly consist of BHC, DDT, Chlordane, Dieldrin, End r in, Aldrin, and Heptachlor.

Employed Technologies in MOAFF's Project

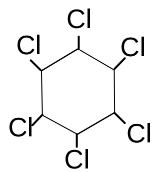
- 2000 fiscal year
  - Mechanochemical process
- 2001 fiscal year
  - Hydrothermal decomposition
  - Vacuum thermal decomposition
  - Geo-Melt vitrification
- 2002 fiscal year
  - Metallic sodium dispersion process
  - Base catalyzed decomposition
  - Supercritical water oxidation

Feasibility of treating POPs Pesticides using MC process

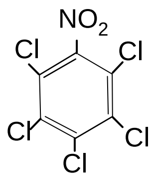
Target compounds for treatment



Heptachlor



γ -HCH



PCNB

additives CaO:2 g
target compound: 50 mg
Rotational speed:700 rpm
Milling time :2 h

Chloride ions extracted by hot water and ultrasonic cleaning for milled mixtures were measured by ion chromatography.

Target compound	Heptachlor	γ -HCH	PCNB
Dechlorination ratio（%）	**99.4**	**99.4**	**100.8**

(Dechlorination ratio: the amount of chloride ions / chlorine in a target compound added to the system)

- Dechlorination ratio reached 100 % in treatment of target compounds
- No organochlorine compound was detected as degradation products by the GC-MS analysis

Degradation mechanism of γ -HCH during MC treamtment

Experimental condition

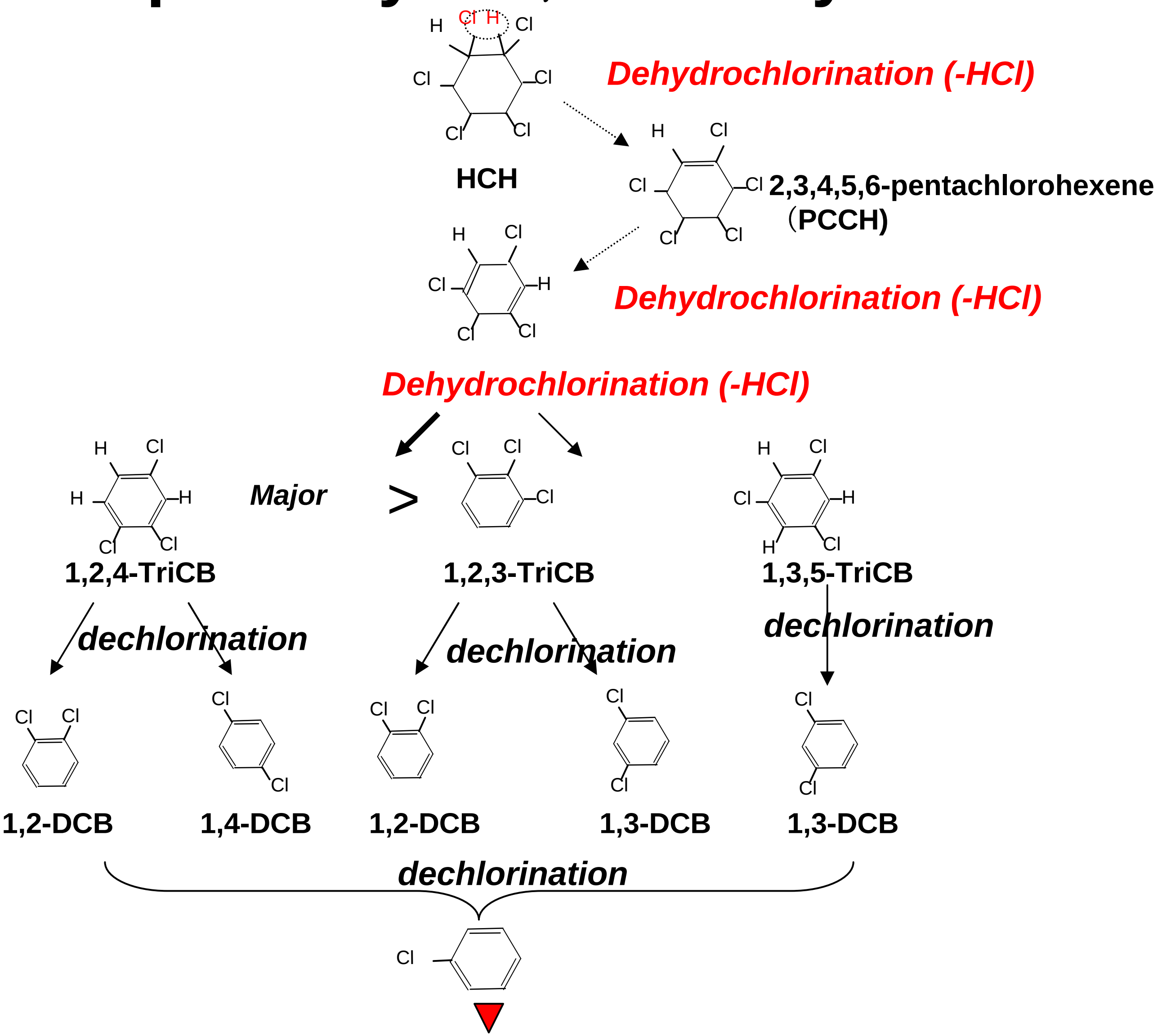
Additives :	**HCH and CaO**
Amounts :	**1:10 molar ratio with respect to chlorine bound γ - HCH to calcium as CaO**
Milling time :	**120 min**

Toward to elucidate the degradation behavior of γ - HCH

Ion chromatograph for analysis of chloride ions in milled mixtures

GC-MS for analysis of HCH and the degradation products in milled mixtures

Degradation pathway of γ -HCH by MC treatment



<u>100% dechlorination accomplished, and</u>

<u>Degraded to lower molecular compounds including Carbon !</u>

Conclusions

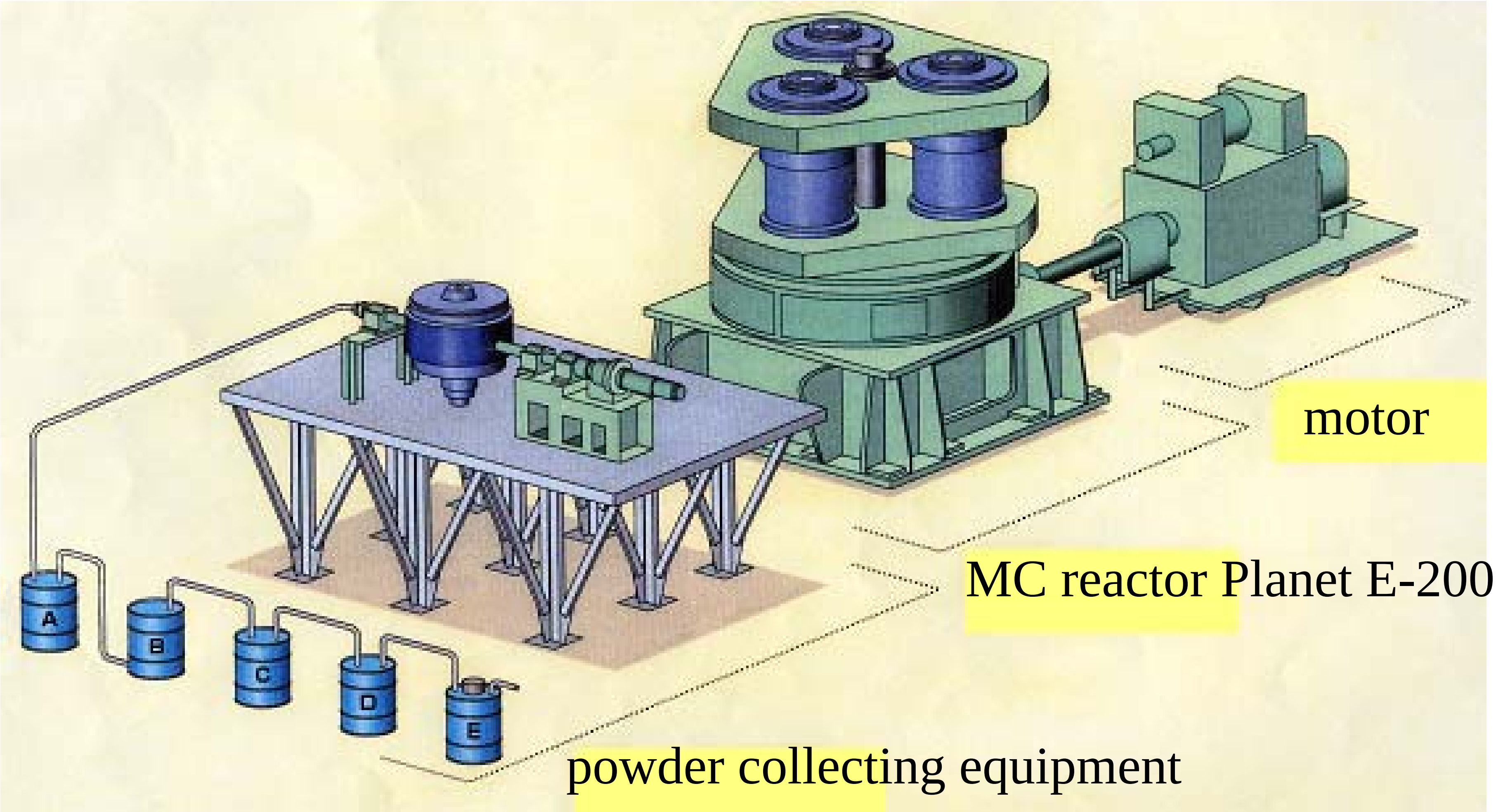
・Dechlorination ratio reached 100 % in treatment of heptachlor, HCH and PCNB, and no organochlorine compound was detected by GC-MS analysis. These results confirmed the feasibility of treating POPs pesticides.

・Dechlorination ratio in the MC treatment of HCH increased with milling time, and reached 100 % in 120 min.

・Chlorobenzenes and 2, 3, 4, 5, 6-pentachlorocyclohexene (PCCH) were identified as the major degradation products of the MC treatment of HCH.

・The degradation of HCH proceeds via dehydrochlorination
and the dechlorination of degradation products .

Schematic Profile of Commercial MC plant



Commercial MC plant owned by

Radicalplanet Research Institute Co. Ltd.

Produced by Sumitomo Heavy Industries Techno-Fort Co.,Ltd.

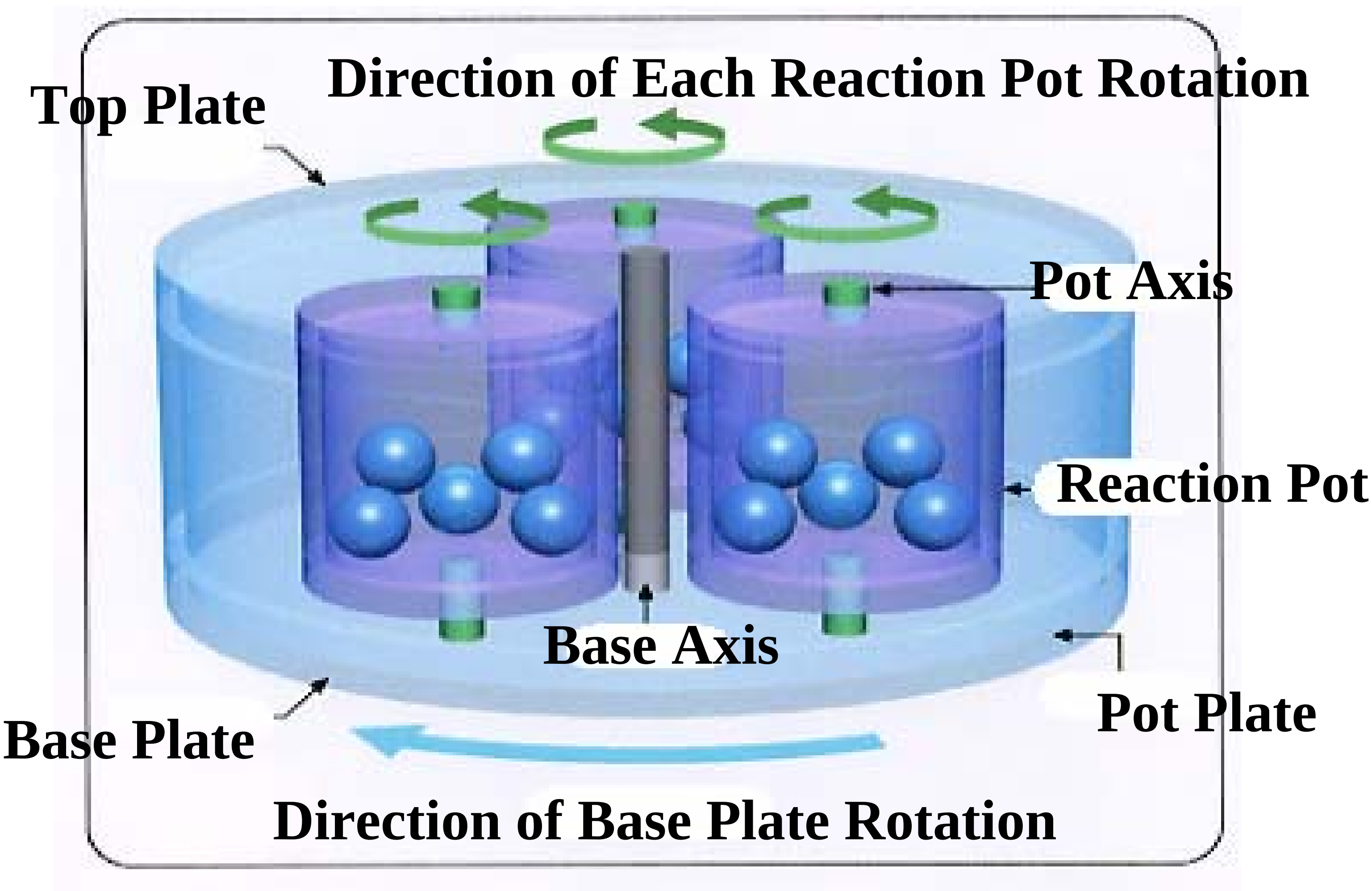
Transportability of MC Plant (Planet E-200)

"Radicalplanet process" consists of the Planet E-200, a motor and powder collecting equipment.

These equipments are simple, compact , separated and are transportable by trailers.

Skematic Mechanochemical Plant

by Radicalplanet Research Institute Co. Ltd.



PCB-contaminated Soil Destruction Treatments

PCB-contaminated soil

PCB oil and mixed oil

Time (hrs)	PCB (mg/kg)
0	1,283
16	1.5
32	0.12
64	ND (<0.01)

DXNs (pg-TEQ/g)		
PCDDs+PCDFs	Co-PCB	Total
0.00037	0.0041	0.0045

PCB（Fluorescent Ballast containing PCB Oil） Destruction Treatments

Fluorescent Ballast

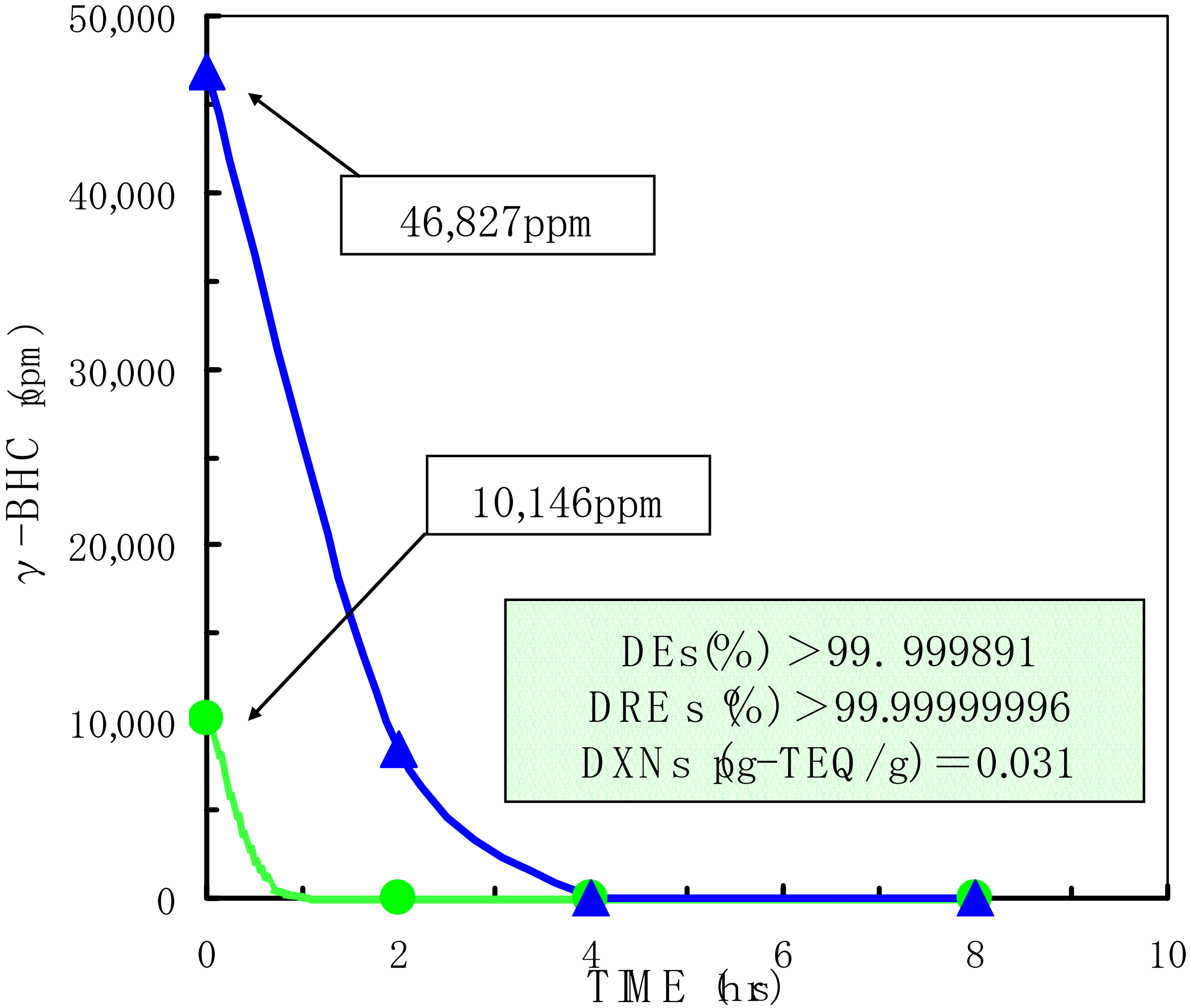
PCB oil and mixed oil

Time (hrs)	PCB (mg/kg)
0	1,263
16	ND (<0.01)
32	ND (<0.01)
64	ND (<0.01)

DXNs (pg-TEQ/g)		
PCDDs+PCDFs	Co-PCB	Total
0	0.00027	0.00027

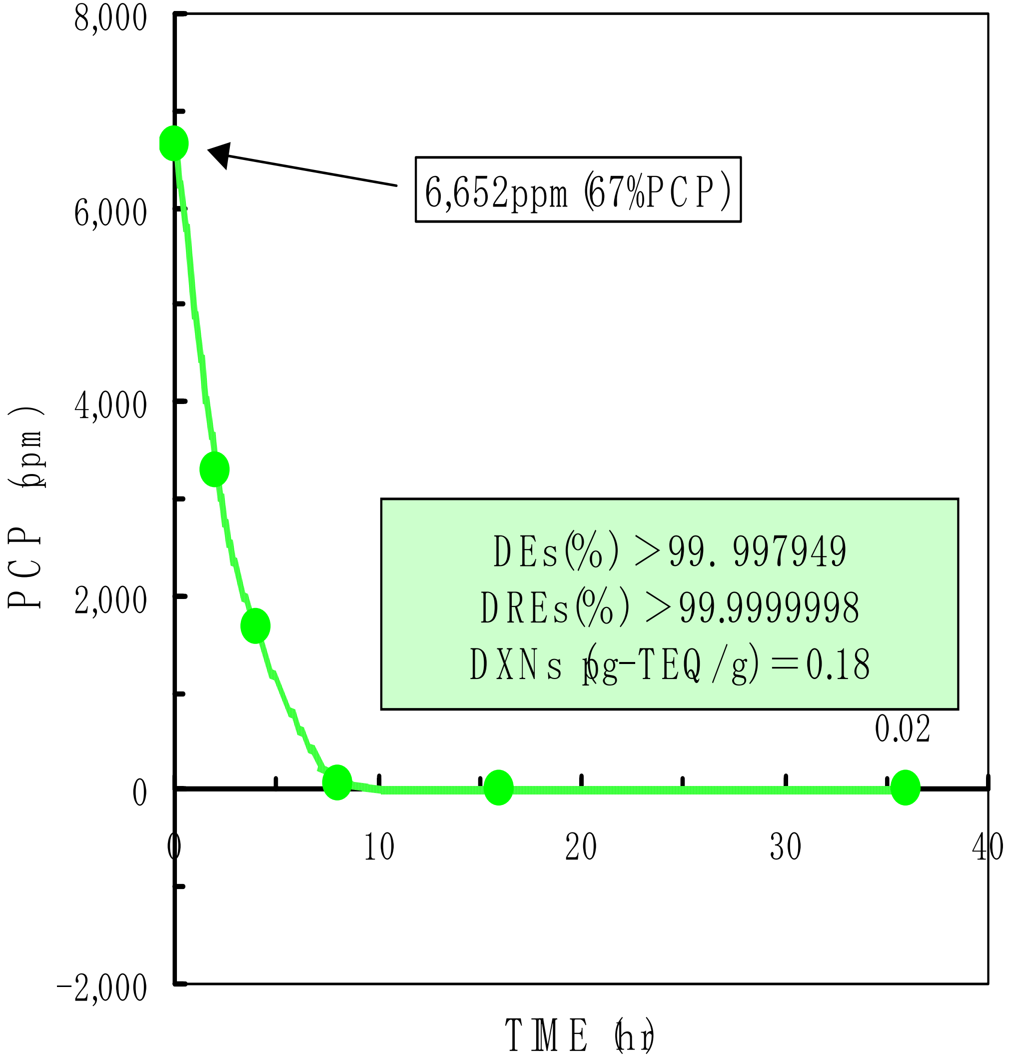
γ -BHC Destruction by MC Treatments

γ -BHC (liquid)



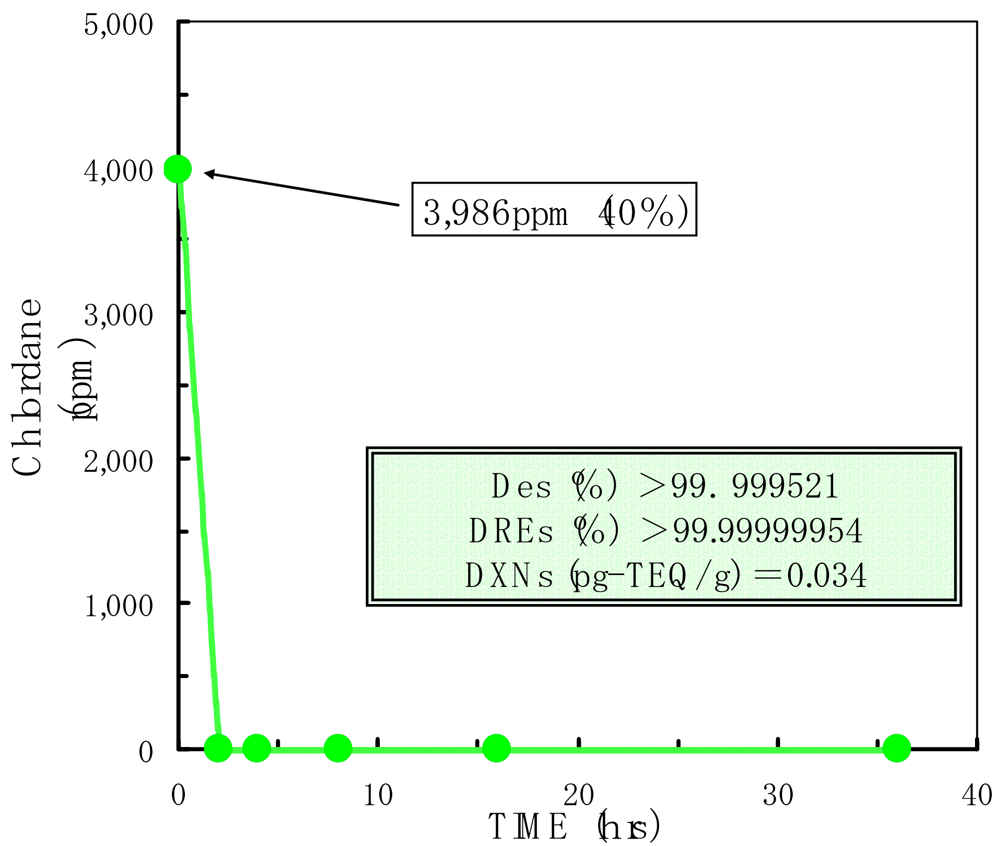
PCP Destruction by MC Treatments

PCP (Pentachlorophenol)



Chlordane Destruction by MC Treatments

Chlordane



MC Destruction of Mixed Agricultural Chemicals

DDT Powder

BHC Powder

Endrin Powder

Admixture of Powder

Results of Distruction

(Unit :mg/ kg)

		8Hrs After
DDT	op'DDT	<0.001
	pp'DDT	<0.001
	pp'DDD	<0.001
	pp'DDE	0.003
BHC	α BHC	<0.001
	β BHC	<0.001
	γ BHC	<0.001
	δ BHC	<0.001
Endrin		<0.001

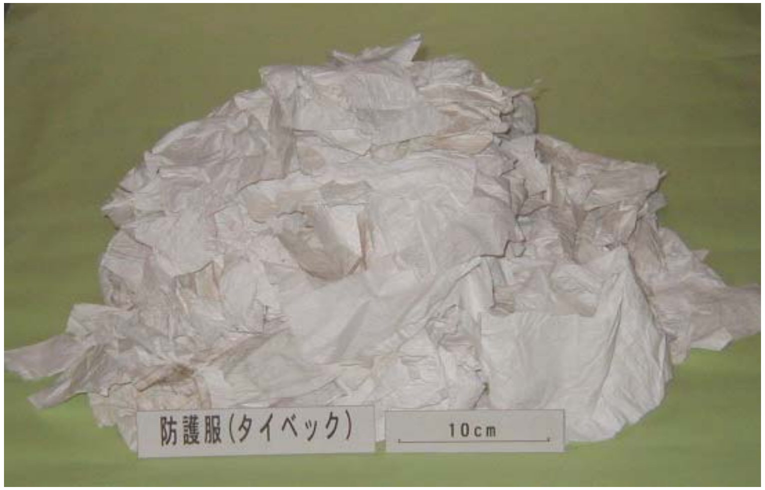
POPs Wastes Weights : 20~80kg / Charge

POPs Wastes Treated by MC (1)

Concrete and Soil

Plastic Masks

Clothe and Work Gloves



Protective clothing (Tyvex)

POPs Wastes Treated by MC (2)

Chipped Wood

Cardboard

Pieces of PP and PVC

Pipes and Can made of Metal

Destruction Treatment of Mixed Wastes

Mixed Wastes
in Reaction Pot

MC
Destruction

Powder after MC Treatment

Summary

- GAS is very promising and time- and cost-saving technology for soil gas survey in urban area including operating factory with concrete floor.
- High-sensitive real-time PCR techniques targeting 16S rDNA of *Dehalococcoides* give valuable information on applicability of biostimulation in small sites.
- MC process is applicable to remediation in small sites contaminated by pretty high-strength POPs.