Removal Standards and Control Measure for Bottom Sediments Contaminated by Toxic Substances in Japan

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- Development of Sediment Criteria
- Removal Standards for Mercury and PCB in sediment and Control Measures
- Environmental Quality Standards for Dioxins in sediment and Control Measures

Development of Sediment Criteria

- Background based approach
- Pore water quality based approach: comparison of pore water and water quality criteria
- Bioassay based approach: how to select biota for bioassay? How long?
- Equilibrium Partition based approach
  - between sediment and water
  - between sediment and biota

$$K_D = \frac{C_s}{C_W}$$

C_S : concentration of the substance in water

C_W : concentration of the substance in sediment

K_D : Partition coefficient the substance

$$K_{OC} = \frac{C_{S/OC}}{C_{IW}} = \frac{C_S}{C_{IW}} \times \frac{1}{TOC} = K_D \times \frac{1}{TOC}$$

K_{OC} : partition coefficient between water and carbon

$C_{S/OC}$: concentration of the substance per unit organic carbon

C_{IW} : concentration of the substance in pore water

TOC : organic carbon content in sediment

C_{IW} = water quality criteria $C_{W/CRI}$ $C_{S/CR}$: sediment criteria

$$C_{S/CR} = TOC \times K_{OC} \times C_{W/CRI}$$

Determination of Removal Standard for Mercury

ADI: 0.17 mg methyl mercury/50 kg BW/week

↓

Acceptable Hg concentration in fish: 0.4 mg Hg/kg wet weight of fish

↓

Acceptable Hg in water: 0.0004 mg Hg/L
Based on overall bioconcentration factor: 1,000

↓

Acceptable Release flux of Hg from sediment
Based on mass balance of Hg in the target water body with tidal exchange

↓

Determination of Hg concentration in pore water
Based on Fick's diffusion law and acceptable Hg release flux

↓

Determination of acceptable Hg concentration in sediment
Based on elution test

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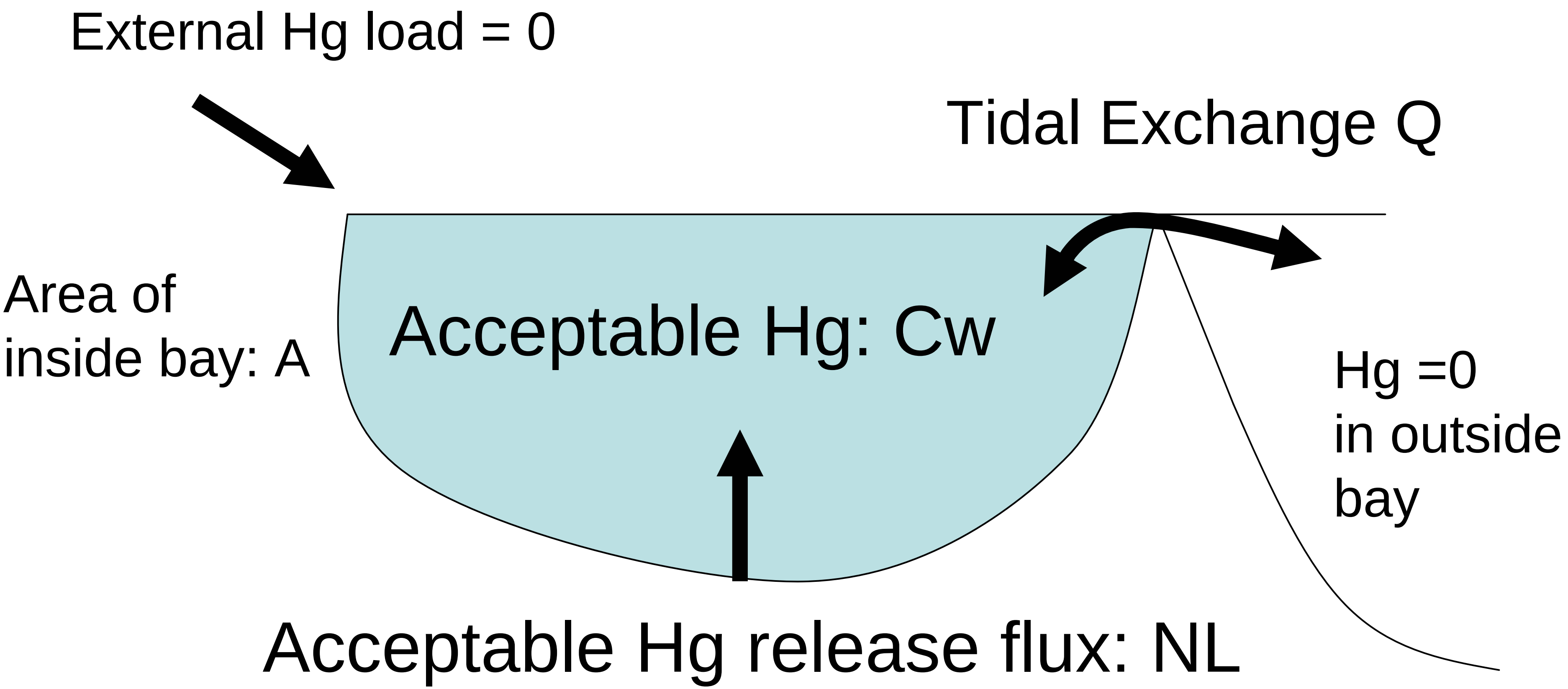
Mercury Balance in Targeting Water Body



$$NL\ (\mathrm{mgHg/m^2/day}) = Cw\ Q/A$$

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Determination of Hg concentration in pore water
Based on Fick's diffusion law and acceptable Hg release flux

Determination of acceptable Hg concentration in sediment
Based on elution test (leaching test) with safety factor

How to determine the relationship between Hg concentration in sediment and Hg concentration in pore water?

- Direct measurement of Hg concentration in pore water and sediment
- Elution test (Leaching test) leads modified equilibrium partition coefficient Kd’=Hg in sediment/ soluble Hg (in pore water)
- Removal Standard of Hg in sediment Cd:

Cd=acceptable Hg in pore water/Kd’/safety factor

Safety factor:

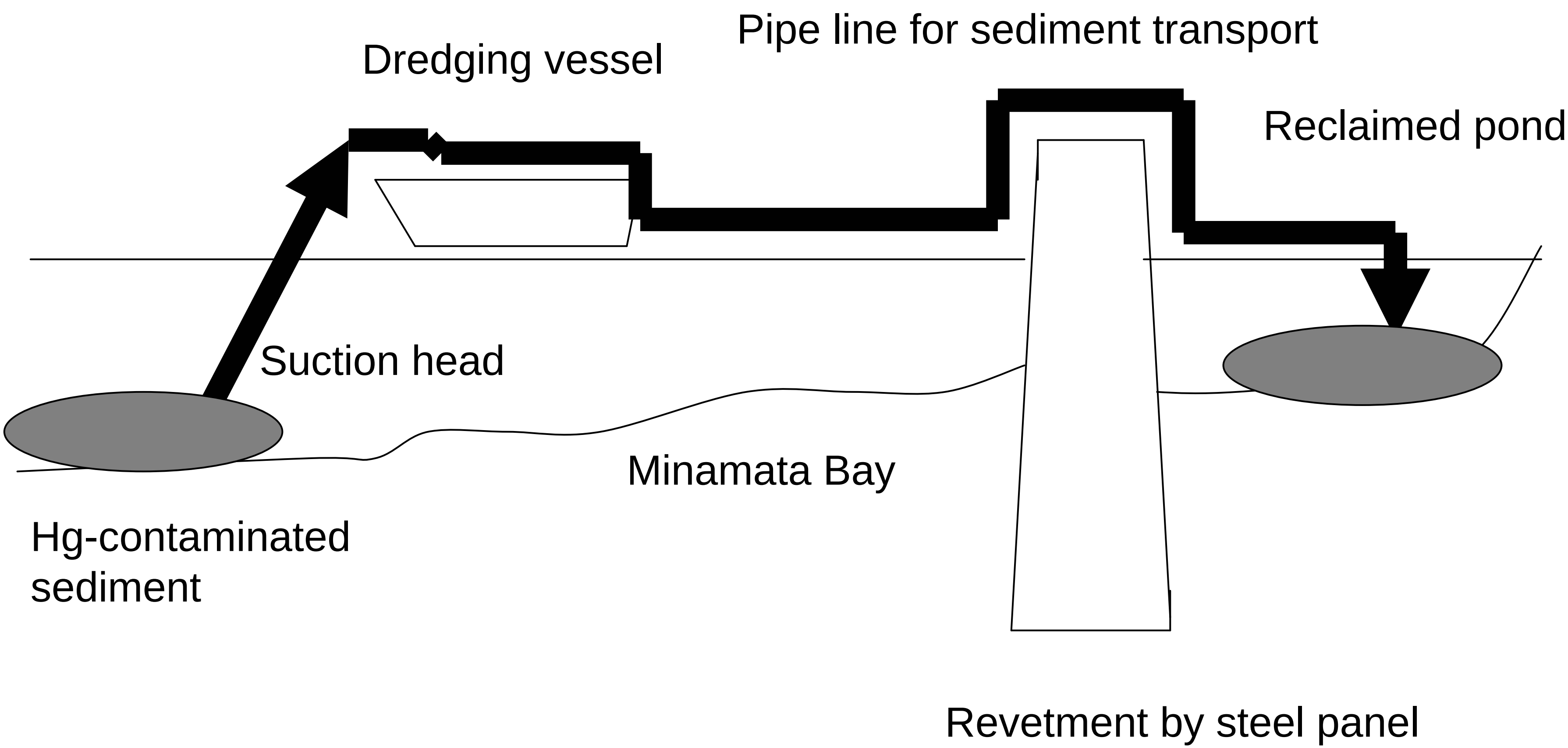
- No fisheries activity: 10
- Catch of benthic fish is less than 50% of total catch of fish: 50
- Catch of benthic fish is more than 50% of total catch of fish: 100

Ex. Minamata Bay: Cd = 25 mg Hg/kg

Hg-contaminated sediment: Pollution extent and control-measured sediment

Prefecture	Region or port	Pollution	Removal standard	Measured Volume	
		Min.- Max average		Area (m^2)	Volume (m^3)
Kumamoto	**Minamata Bay**	0.04 ~ 744 ppm 53.43 ppm	25 ppm	2,090,000	**2,506,000**
Mie	**Yokkaichi**	0.07 ~ 105 ppm 9 ppm	6 ppm	1,190,000	**1,800,000**
Fukuoka	Omuta River	0.03 ~ 86.6 ppm 16.1 ppm	25 ppm	165,390	1,024,310
Chiba	Chiba Port	0.07 ~ 181.69 ppm 25.06 ppm	10 ppm	501,000	460,000
Yamaguchi	Tokuyama Port	0.04 ~ 31.59 ppm 4.22 ppm	15 ppm	800,000	362,000

Illustration of sediment treatment/transport flow to confined pond



Determination of Removal Standard for PCB

ADI: 250 ug PCB/50 kg BW

↓

Acceptable PCB uptake from fish and shellfish: 180 ug PCB/50 kg BW

↓

Acceptable PCB concentration in fish and shellfish caught in inland water: 3 mg PCB/kg wet weight of edible part of fish

↓

Removal standard of PCB in sediment:

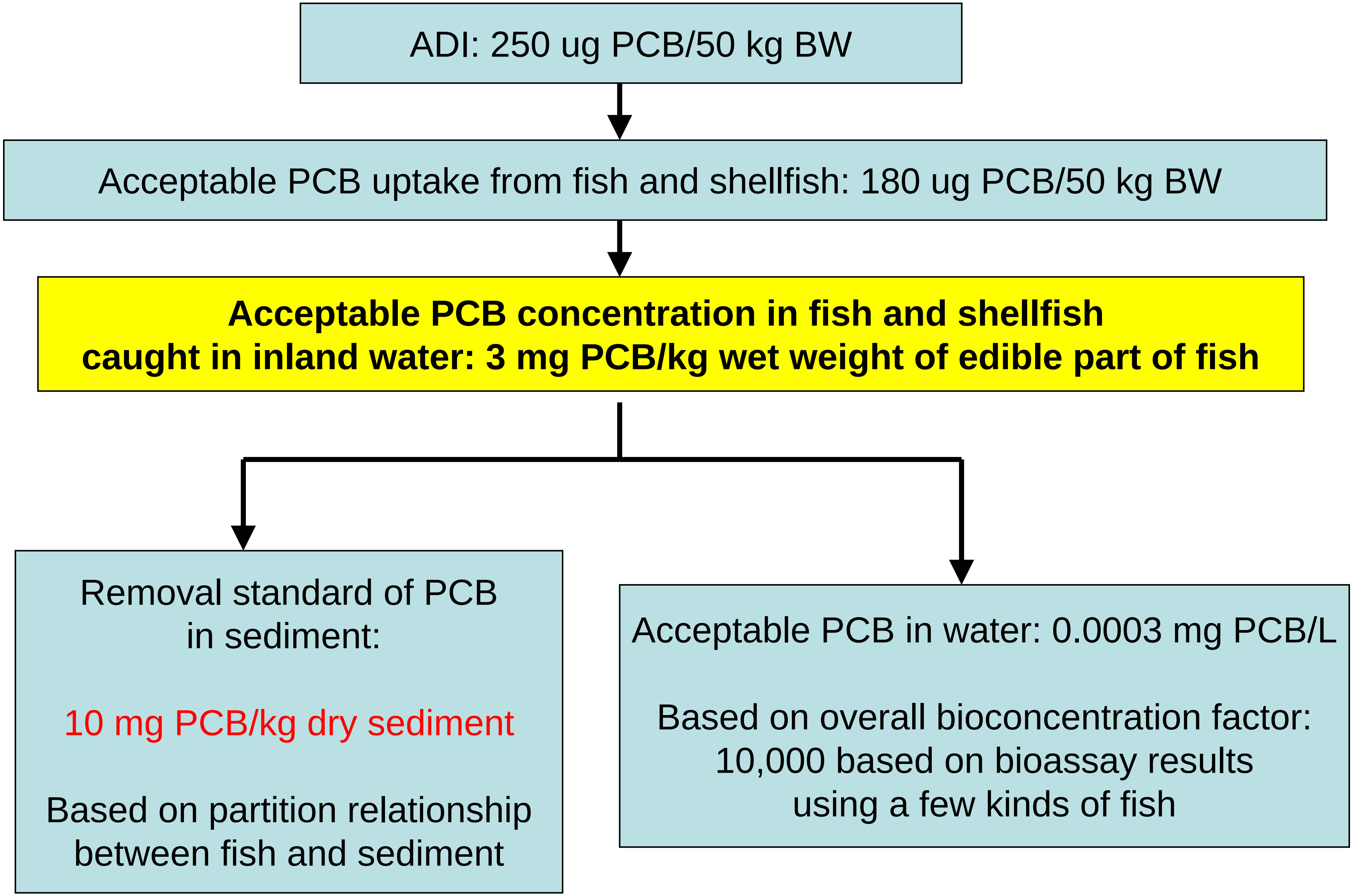
10 mg PCB/kg dry sediment

Based on partition relationship between fish and sediment

Acceptable PCB in water: 0.0003 mg PCB/L

Based on overall bioconcentration factor: 10,000 based on bioassay results using a few kinds of fish

Determination of Removal Standard for PCB



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Bioconcentration factor of PCB into edible part of fish obtained from the continuous bioassay experiment using seawater containing

Fish	Bioconcentration factor	PCB concentration in seawater (ppb)	Provided	Remarks
Croaker	7,600	1.00	Hansenn	10 samples
Young yellowtail	8,582	5.43	Tokai-region Fisheries Experiment Station	Calculated from the report on PCB pollution control in 1972
Yeel	7,592	1.30	Hyogo Prefectual Fisheries Experiment Station	6 samples
Yeel	5,667	0.96	Hyogo Prefectual Fisheries Experiment Station	6 samples

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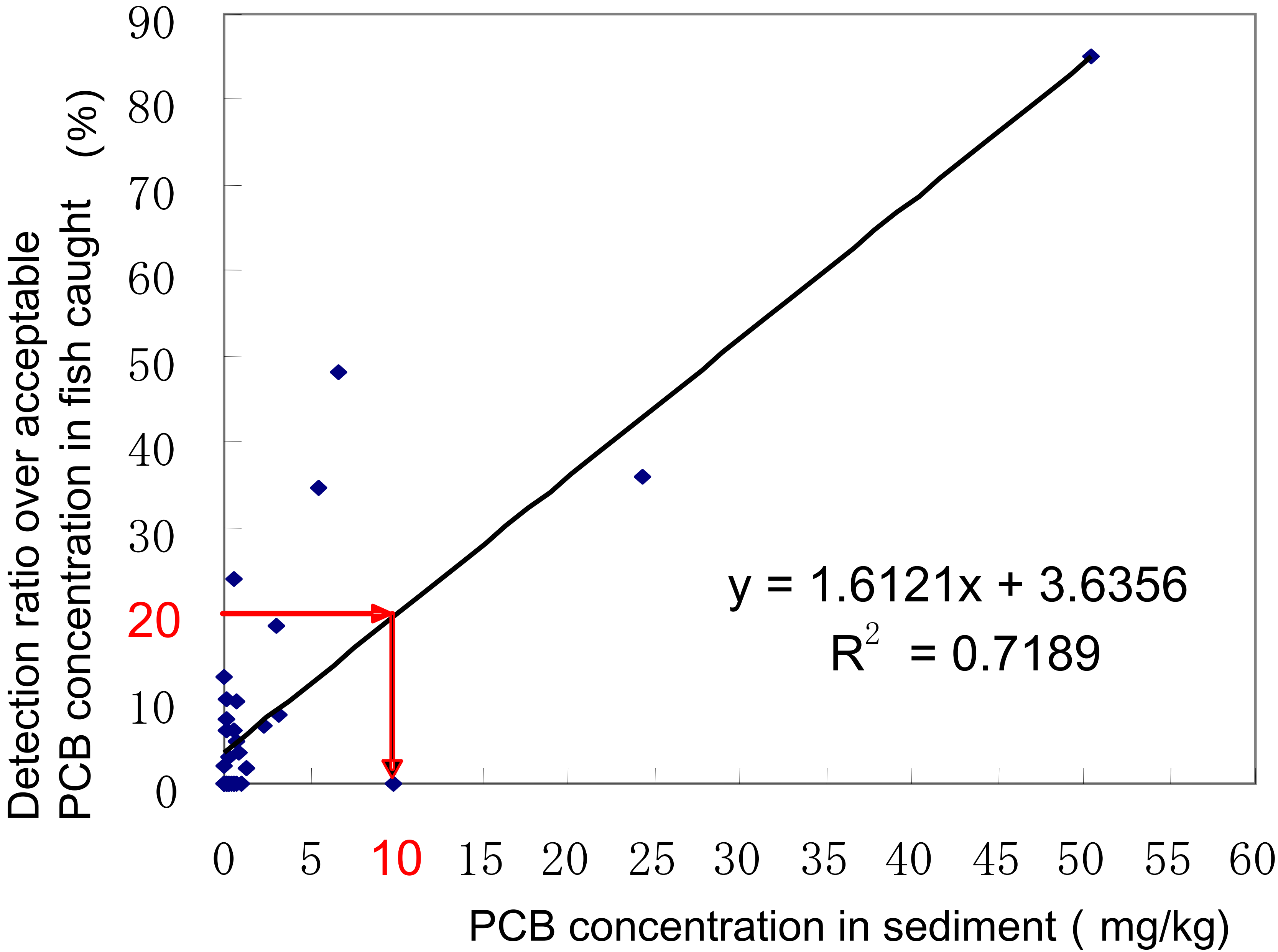


Detection ratio over acceptable PCB concentration in fish caught (%)
90
80
70
60
50
40
30
20
10
0
y = 1.6121x + 3.6356
$R^2 = 0.7189$
0
5
10
15
20
25
30
35
40
45
50
55
60
PCB concentration in sediment (mg/kg)

PCB-contaminated sediment: pollution extent and control-measured sediment

Prefecture	Region or port	Pollution Min.- Max average	Removal standard	Measured Volume Area (m^2)	Volume (m^3)
Ehime	**Iyo-Mishima Kawanoe**	0.29 ~ 12.2 ppm 0.87 ppm	10 ppm	860,000	**3,546,000**
Shizuoka	**Tagonoura**	0.084 ~ 79 ppm 53 ppm	10 ppm	-	**1,833,725**
Nagoya	Ohe River	ND ~ 145 ppm 15.1 ppm	10 ppm	184,000	350,000
Osaka	Kizu River	4.4 ~ 15.9 ppm 25.06 ppm	10 ppm	12,800	307,000
Hyogo	Tkasago Port	20 ~ 3,300 ppm 3.9 ppm	10 ppm	194,000	301,000

Law Concerning Special Measures against Dioxins

(Law No.105 of 1999.

Promulgated on July 16,1999)

Law Concerning Special Measures against Dioxins

(promulgated on July 16, 1999)

Dioxins: polychlorinated dibenzofurans (PCDFs), Polychlorinated dibenzo-para-dioxins (PCDDs), and co-Planar PCBs

Outline of law:

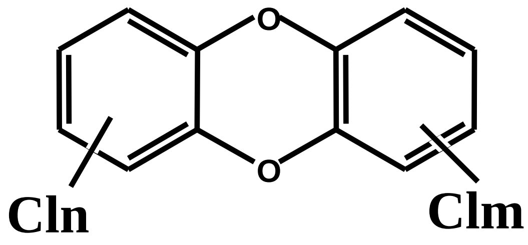
-To set environmental standards based on TDI (4 pg-TEQ/kg BW/day) ; air, water, soil, bottom sediment

-To set effluent standard and emission gas standards

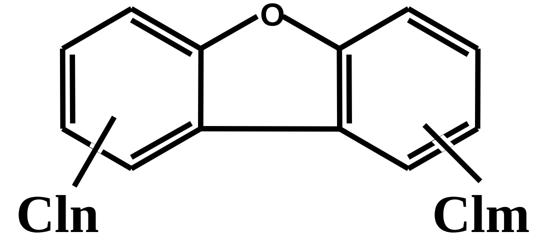
-To set management standard of the final disposal landfill site

-Investigation and monitoring obligation of pollution situation of dioxins (air, water, soil, bottom sediment)

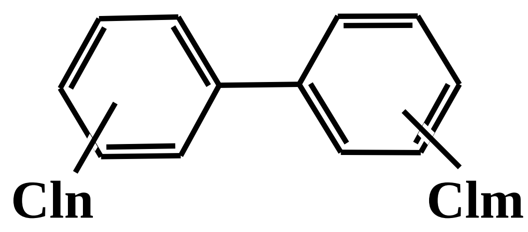
DIOXINS



Polychlorinated Dibenzo-p-dioxin (PCDD) (m+n=1-8)



Polychlorinated Dibenzofuran (PCDF) (m+n=1-8)



Coplanar Polychlorinated Biphenyl (Co-PCB) (m+n=4-7)

Tolerable Daily Intake (TDI)

- Daily dose of 2,3,7,8-tetrachlorodibenzo-para-dioxin which is assumed to have no adverse effects on human health if taken constantly over a lifetime
- The TDI of dioxins is set at 4 pg-TEQ/kg/day

  (4 picograms per kilogram of body weight per day)
- The TDI is set based upon effects due to exposure during the fetal period that is the most sensitive period.

  Manifestation of effects such as carcinogenicity would occur as a result of higher exposure than the set TDI

Environmental Quality Standard

• Ambient air	0.6 pg-TEQ/m^3
• Water (River, Lake, Coastal area)	1 pg-TEQ/L
• Soil	1000 pg-TEQ/g

Environmental standard for soil is an intervention value.

Emission Standard

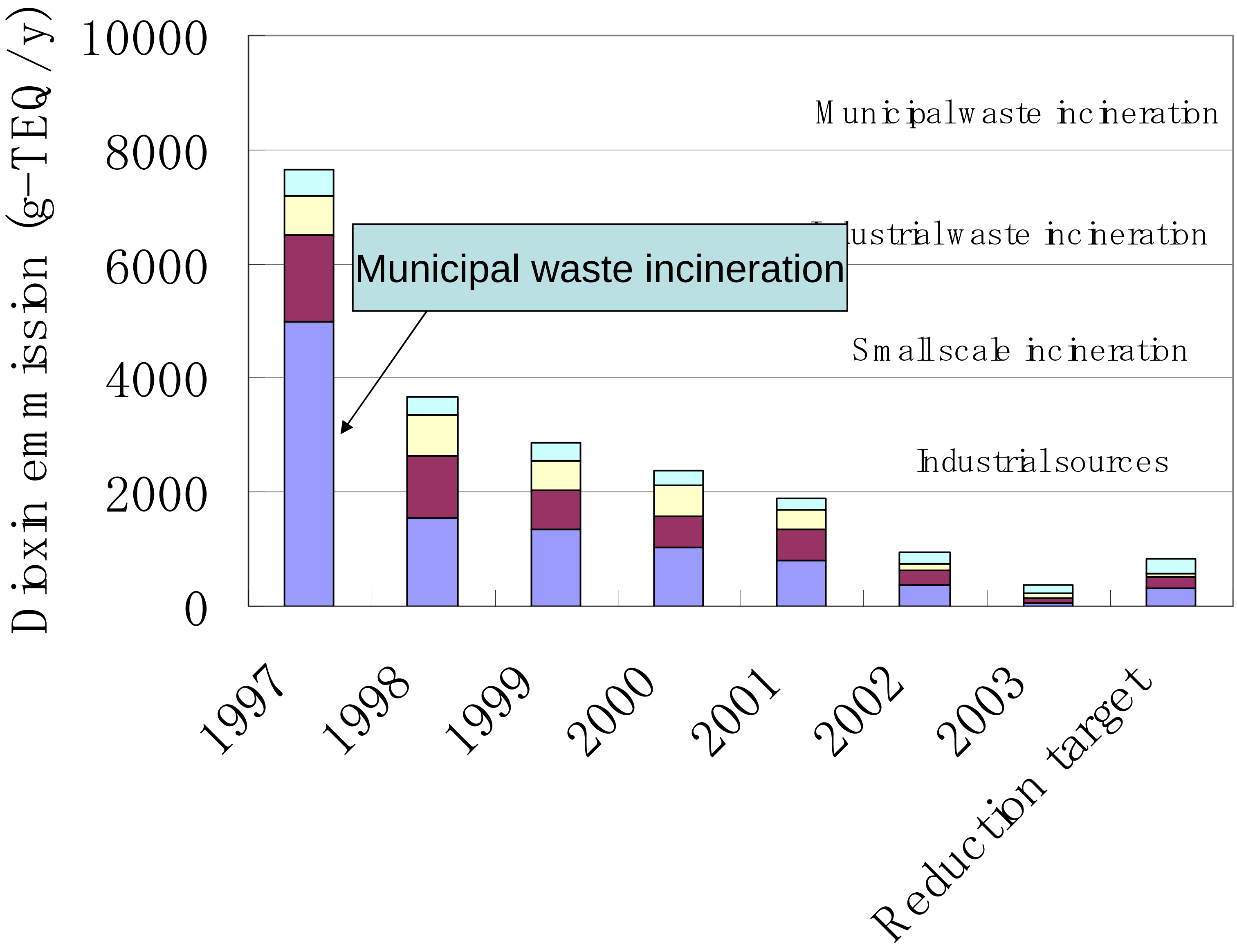
• **Effluent Water**	**10 pg-TEQ/L**
• **Off-gas from Waste Incineration**	**0.1 ng-TEQ/m^3N**

Emission Standards for Dioxins

Types of Specified Facilities	Standards for new facilities
Waste Incinerators More than 4t/h 2 t/h – 4 t/h Below 2 t/h	 0.1 ng-TEQ/m3N 1 ng-TEQ/m3N 5 ng-TEQ/m3N
Electric steel-making furnaces	0.5 ng-TEQ/m3N
Sintering facilities for steel industry	0.1 ng-TEQ/m3N
Facilities for collecting Zinc	5 ng-TEQ/m3N
Facilities for manufacturing Al base alloy	5 ng-TEQ/m3N

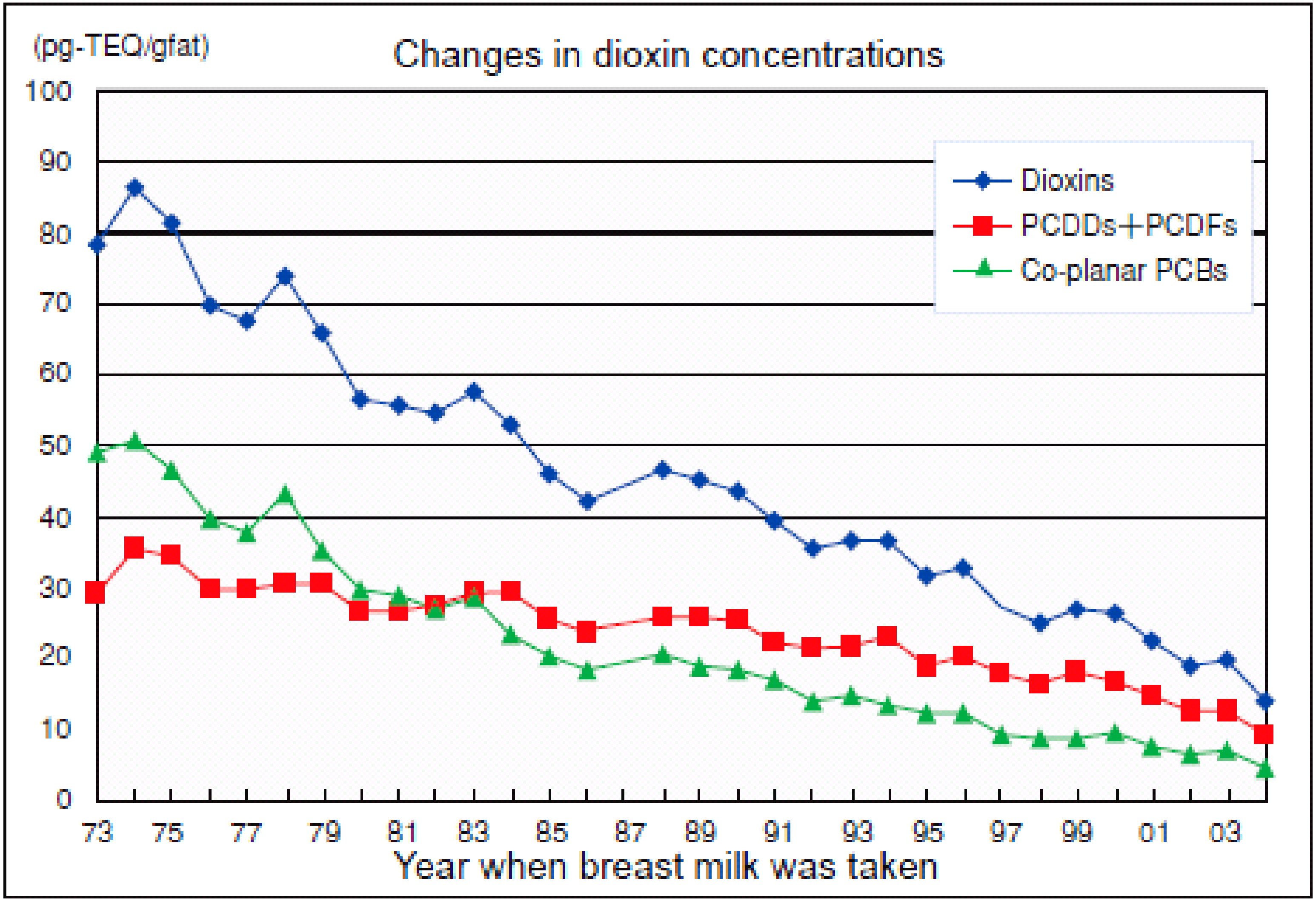
Effluent Standards for Dioxins

Specified Facilities -Bleaching facilities using chlorine or chlorine compounds used for manufacturing sulfate pulps (Kraft pulps) or sulfite pulps - Cleansing facilities for waste gas used for manufacturing potassium sulfate, etc.	10 pg-TEQ/L



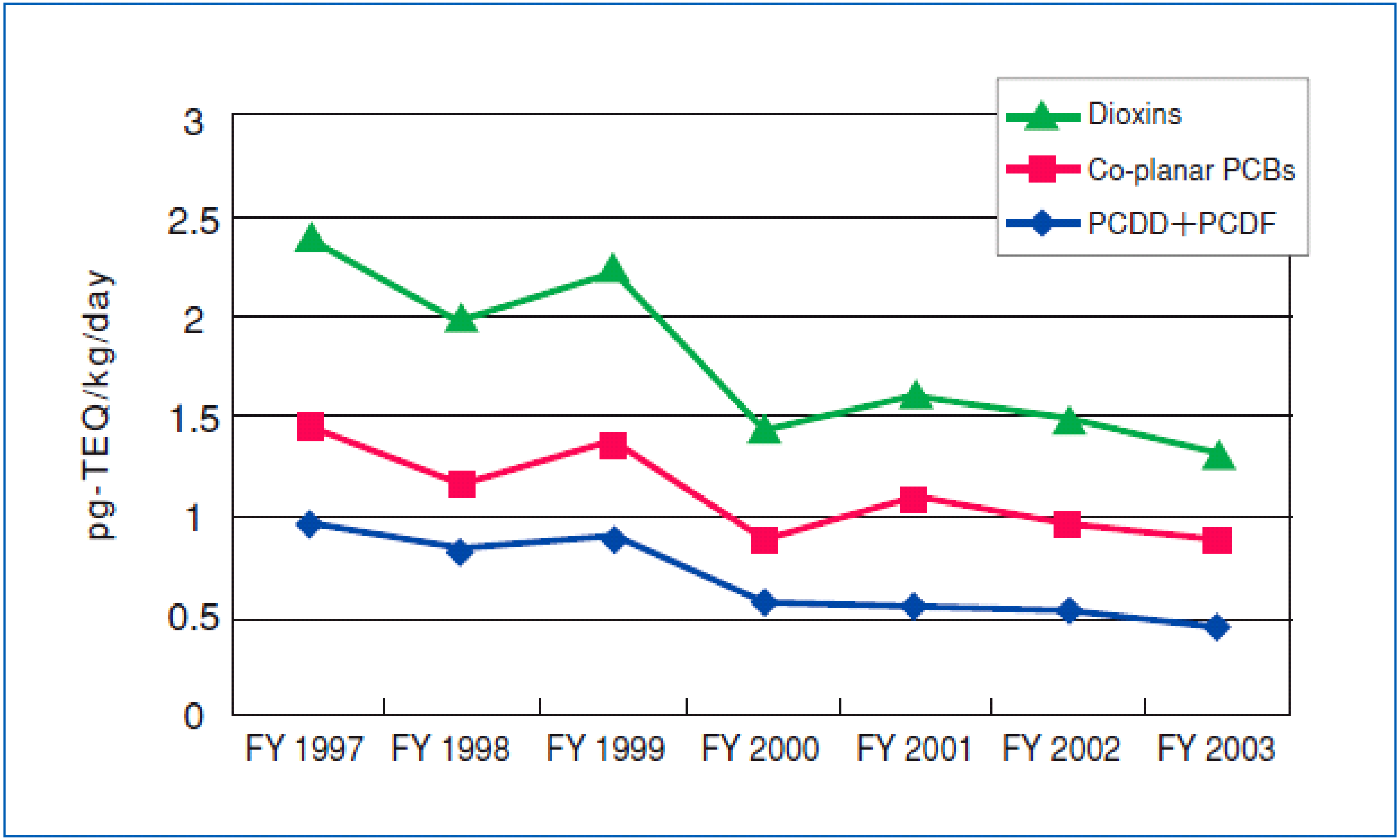
Dioxin emmission (g-TEQ/y)
10000
8000
6000
4000
2000
0
Municipal waste incineration
ustrial waste incineration
Small scale incineration
Industrial sources
Municipal waste incineration
1997
1998
1999
2000
2001
2002
2003
Reduction target

Figure 5 Dioxins concentrations in breast milk



Source: FY 2004 Health and Labour Science Research Grants
"Studies on Dioxins in Breast Milk"

Figure 4 Chronological Change in Daily Intake of Dioxins from Food



Source: Ministry of Health, Labour and Welfare: Total Diet Study for Dioxins

Figure 3 Daily Intake of Dioxins in Japan

Converted to amounts per kg of body weight

Total approx. 1.35 pg-TEQ/kg/day

Ambient air	0.019 pg-TEQ/kg/day	0.02pg-TEQ/kg/day	Ambient air
Soil	0.0052 pg-TEQ/kg/day		Soil
Seafood	1.15 pg-TEQ /kg/day	1.33 pg-TEQ/kg/day	Food
Meat and eggs	0.14 pg-TEQ /kg/day		
Milk and dairy products	0.032 pg-TEQ /kg/day		
Grain and potatoes	0.0014 pg-TEQ /kg/day		
Highly pigmented vegetables	0.0018 pg-TEQ /kg/day		
Others	0.007 pg-TEQ /kg/day		

Actual intake

Tolerable daily intake(TDI) 4pg-TEQ /kg/day

Basic Framework for Development of Sediment Quality Standard for Dioxin

Exposure route of contaminated sediment to human health is via consumption of contaminated fish and/or shellfish and drinking water.

①Based on bioaccumulation of dioxin into fish/shellfish:

Dioxin exposure via consumption of contaminated fish/shellfish is much larger than that of contaminated drinking water.

Dioxin concentration in fish/shellfish significantly correlated with dioxin concentration in sediment.

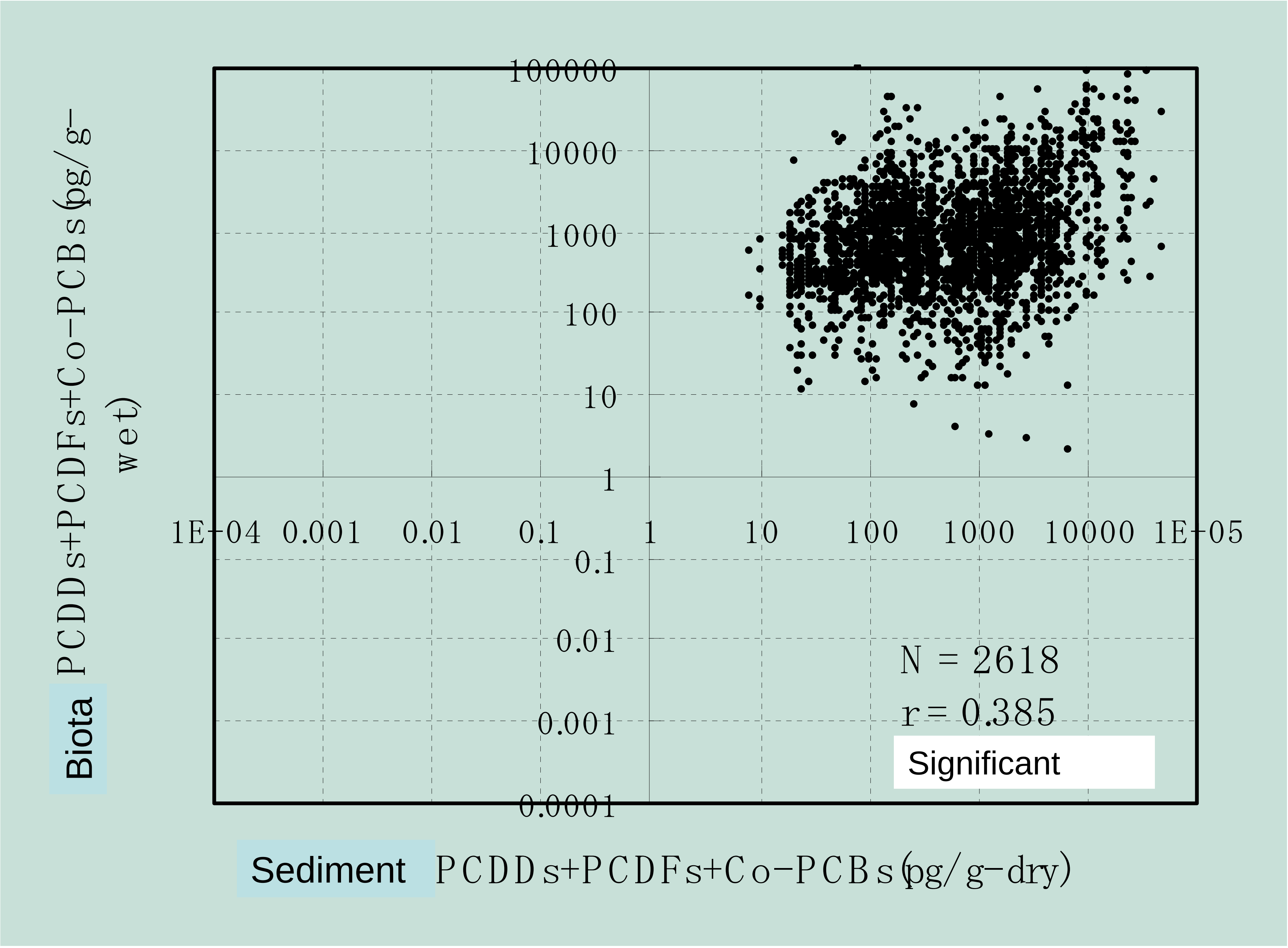
No acceptable dioxin levels in fish/shellfish has not established.

②Based on water quality standard for dioxin: 1 pg-TEQ/L

Dioxin in sediment is a source of dioxin in water.

Dioxin concentration in pore water is equivalent to water quality standard.

Sediment quality standard was derived from dioxin partition equilibrium between pore water and sediment.



100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
1E-04
0.001
0.01
0.1
1
10
100
1000
10000
1E+05
N = 2618
r= 0.385
Significant
Biota
PCDDs+PCDFs+Co-PCBs(pg/g-wet)
Sediment
PCDDs+PCDFs+Co-PCBs(pg/g-dry)

Basic Framework for Development of Sediment Quality Standard for Dioxin

Human route of exposure to contaminated sediment is via consumption of contaminated fish and/or shellfish and drinking water.

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②Based on water quality standard for dioxin: 1 pg-TEQ/L

Dioxin in sediment is a source of dioxin in water.

Dioxin concentration in pore water is equivalent to water quality standard.

Sediment quality standard was derived from dioxin partition equilibrium between pore water and sediment.

Sediment Quality Standard Derived from Partition Equilibrium Coefficient between Pore water and Sediment

$$\log Koc = 1.03 \times \log Kow - 0.61 \quad \text{(Eq.1)}$$

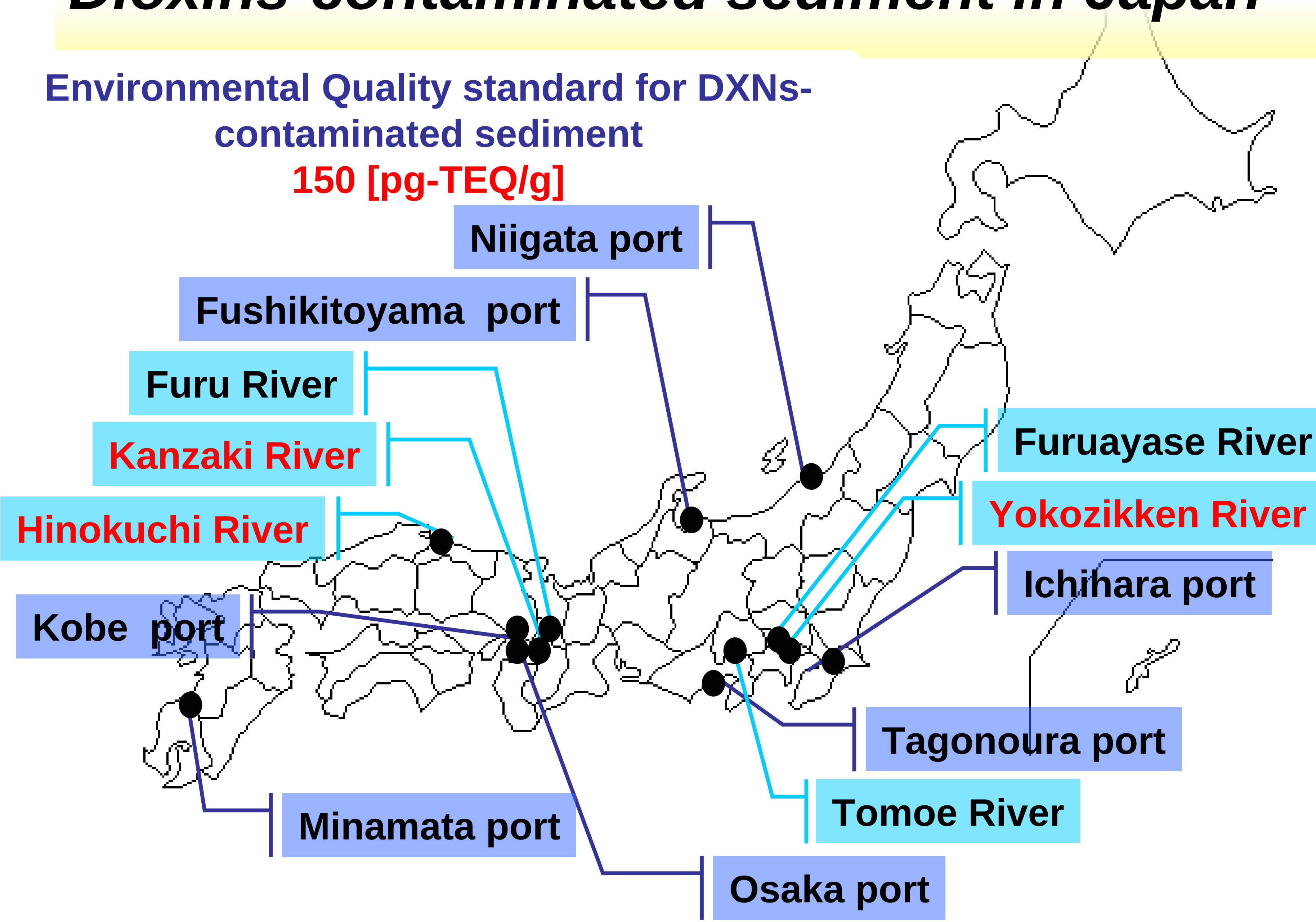
- Wide range of log Kow (n-octanol/water partition coefficient) for dioxins: 6 to 8
  log Kow=6.9 for dioxin which has the largest bioconcentration factor in US Federal Register (3/23/1995) was adopted.

- Substitution of log Kow=6.9 in Eq.1 leads log Koc: 6.50.
- TOC (Organic carbon content）: 5 %　（Germany and Italy）
- Water Quality Standard： 1 pg-TEQ/L

$$\text{Sediment Quality Standard} = Koc \times TOC \times 1 \ \text{pg-TEQ/L}$$
$$= 158 \ \text{pg-TEQ/g}$$
$$\fallingdotseq 150 \ \text{pg-TEQ/g}$$

Dioxins-contaminated sediment in Japan

Environmental Quality standard for DXNs-contaminated sediment
150 [pg-TEQ/g]



Removal Standard of Mercury and PCB vs. Environmental Quality Standard of Dioxins

Removal standard of PCB and mercury: we have to remove contaminated sediment by sediment dredging and dispose of dredged materials.

Dioxin Law requires to do any control measures for dioxin-contaminated sediment to protect human health risk.

Environmental sediment quality standard of dioxin: we can choose risk-based countermeasures, that is, we can choose removal by sediment dredging as well as sediment capping and in-situ containment including solidification/immobilization.

Demonstration Program of Clean-up Technologies for dioxin-contaminated soil and sediment

・1999-2001: Emergent technologies for dioxin-contaminated soil (by Environment Agency)

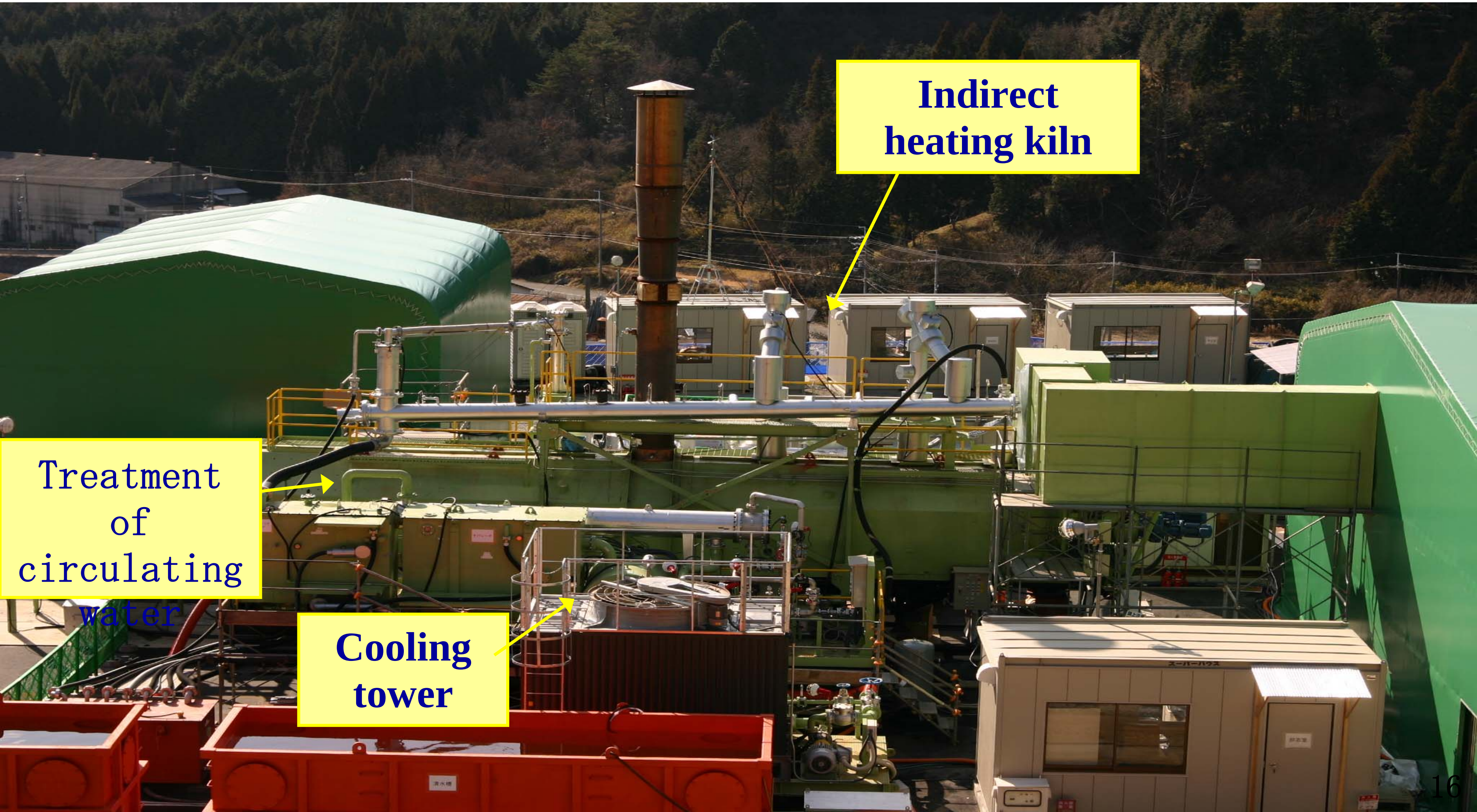
・ 2003-2004: Low-cost Clean-up technologies for dioxin-contaminated-soil (by Ministry of the Environment)

・ 2005-2006: Low-cost Clean-up technologies for PCB-contaminated-soil (by Ministry of the Environment)

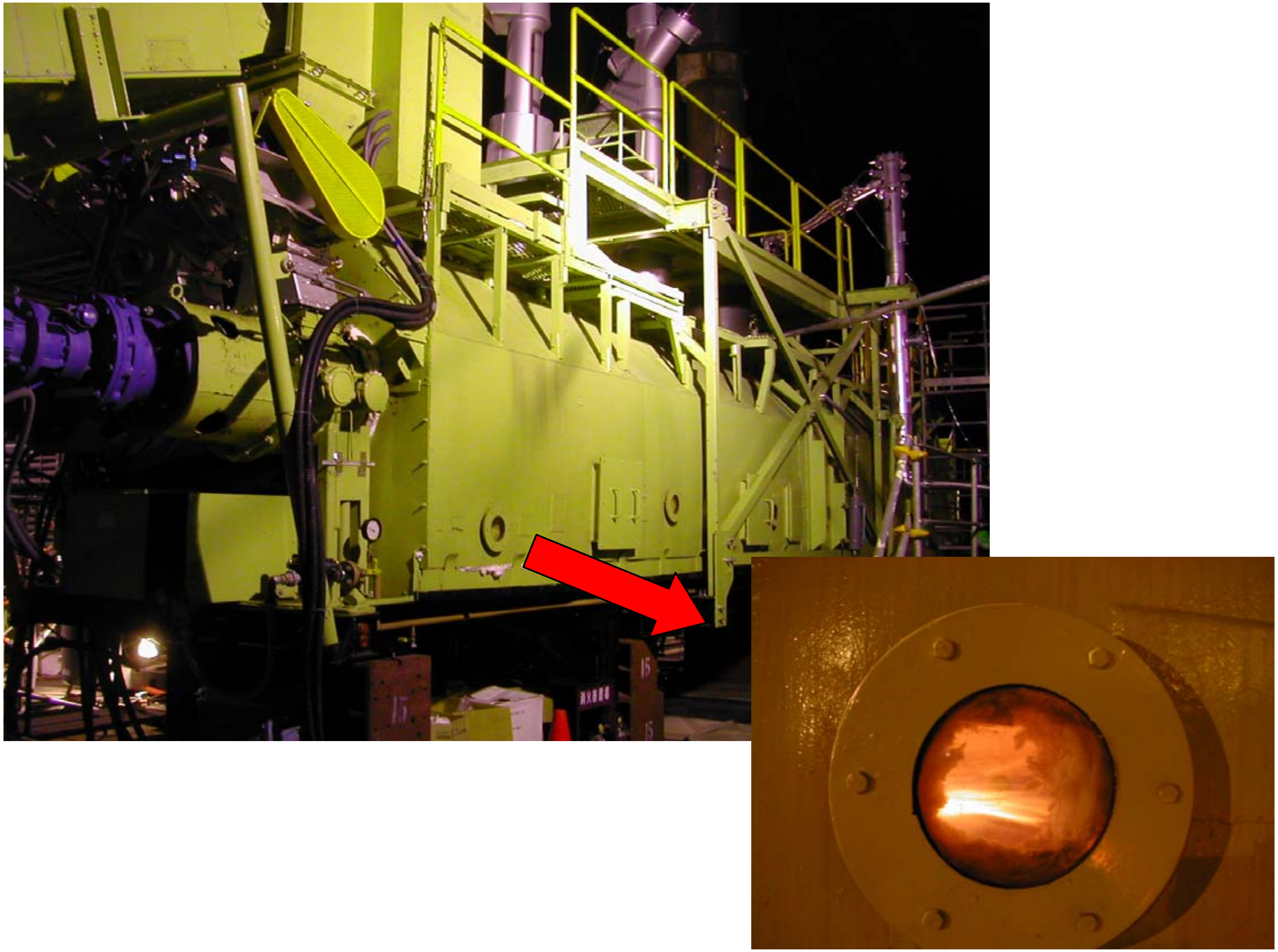
・ 2003-2004: Clean-up technologies for dioxin-contaminated-harbor sediment (by Ministry of Land, Infrastructure and Transport)

・ 2004-2006: Clean-up technologies for dioxin-contaminated-river sediment (by Ministry of Land, Infrastructure and Transport)

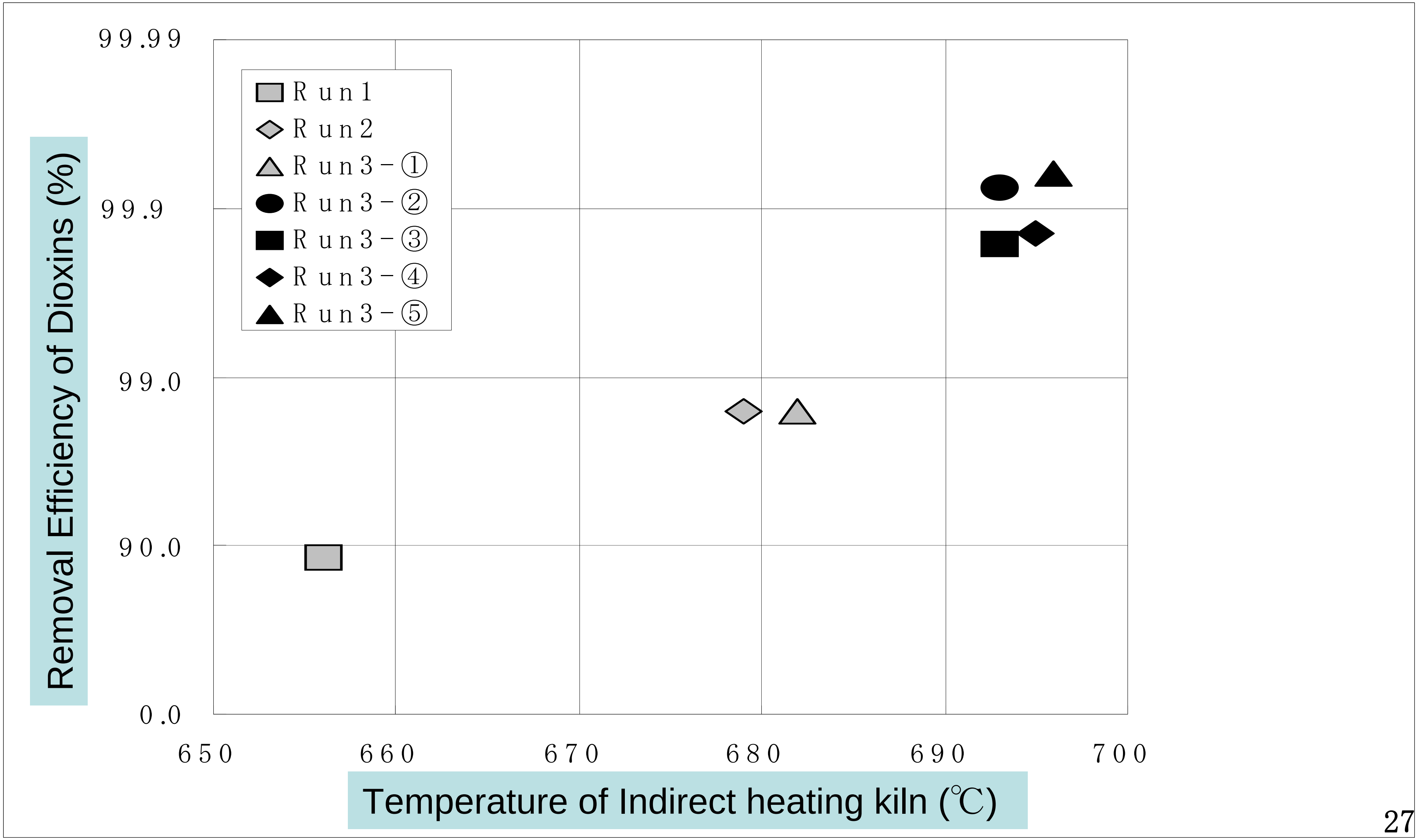
Demonstration site for Dioxin-contaminated soil by Thermal Phase Separation (indirect heating desorption process) in 2002



Indirect Heating Kiln



Relationship between heating temperature (℃) and dioxin removal efficiency （%）



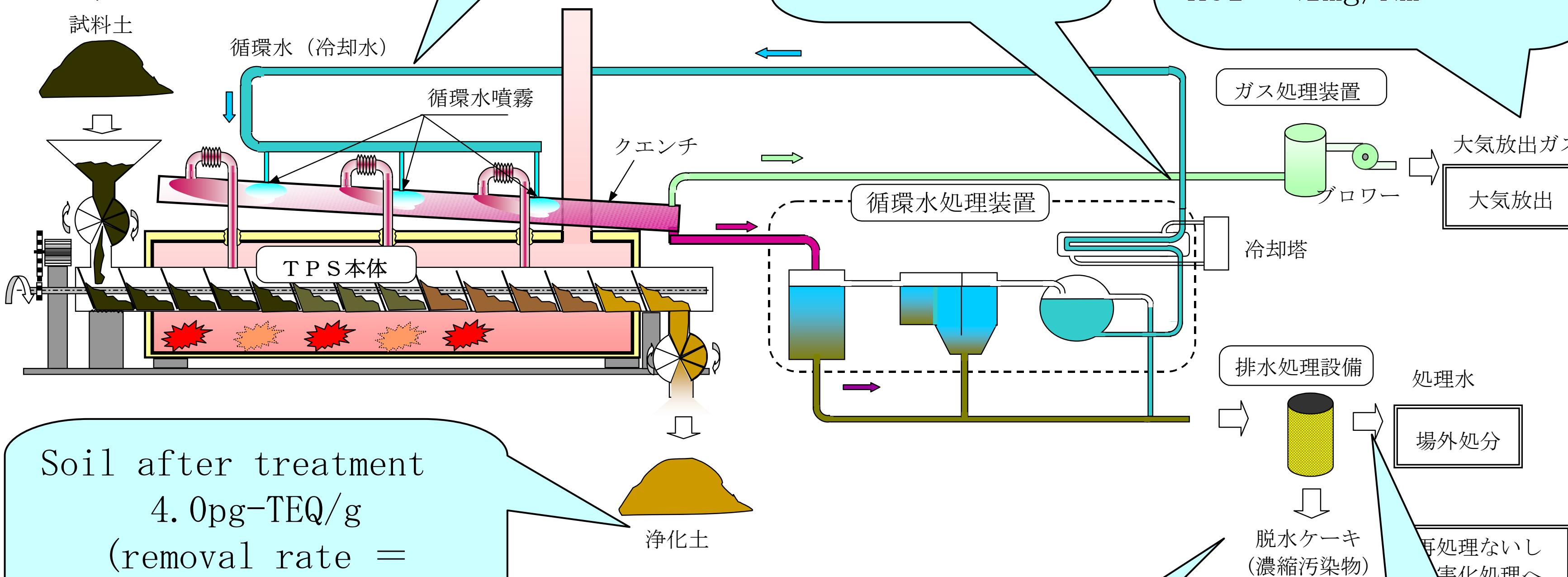
Dioxin balance in thermal separation process

Soil before treatment
6,400pg-TEQ/g

Circulation water
15,000pg-TEQ/L

Off-gas before treatment
0.31ng-TEQ/Nm^3

Off-gas after treatment
0.0000024ng-TEQ/Nm^3
SOx <0.001Nm^3/hr
NOx <10ppm
HCl <1mg/Nm^3



Soil after treatment
4.0pg-TEQ/g
(removal rate = 99.94%)

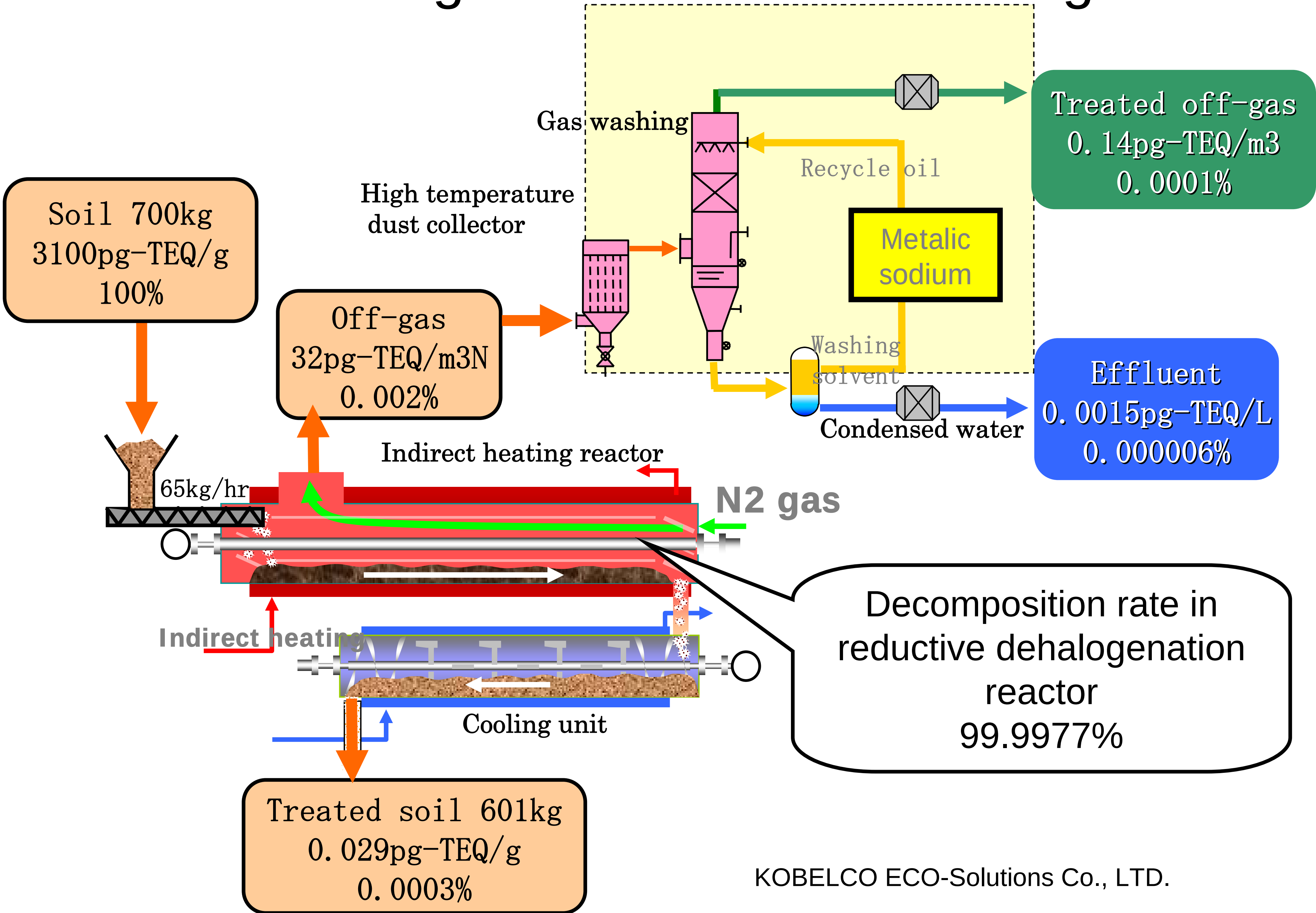
Dehydrated sludge cake
2,900pg-TEQ/g

Effluent
0.074pg-TEQ/L

Demonstration Plant of Thermal Reductive Desorption Process

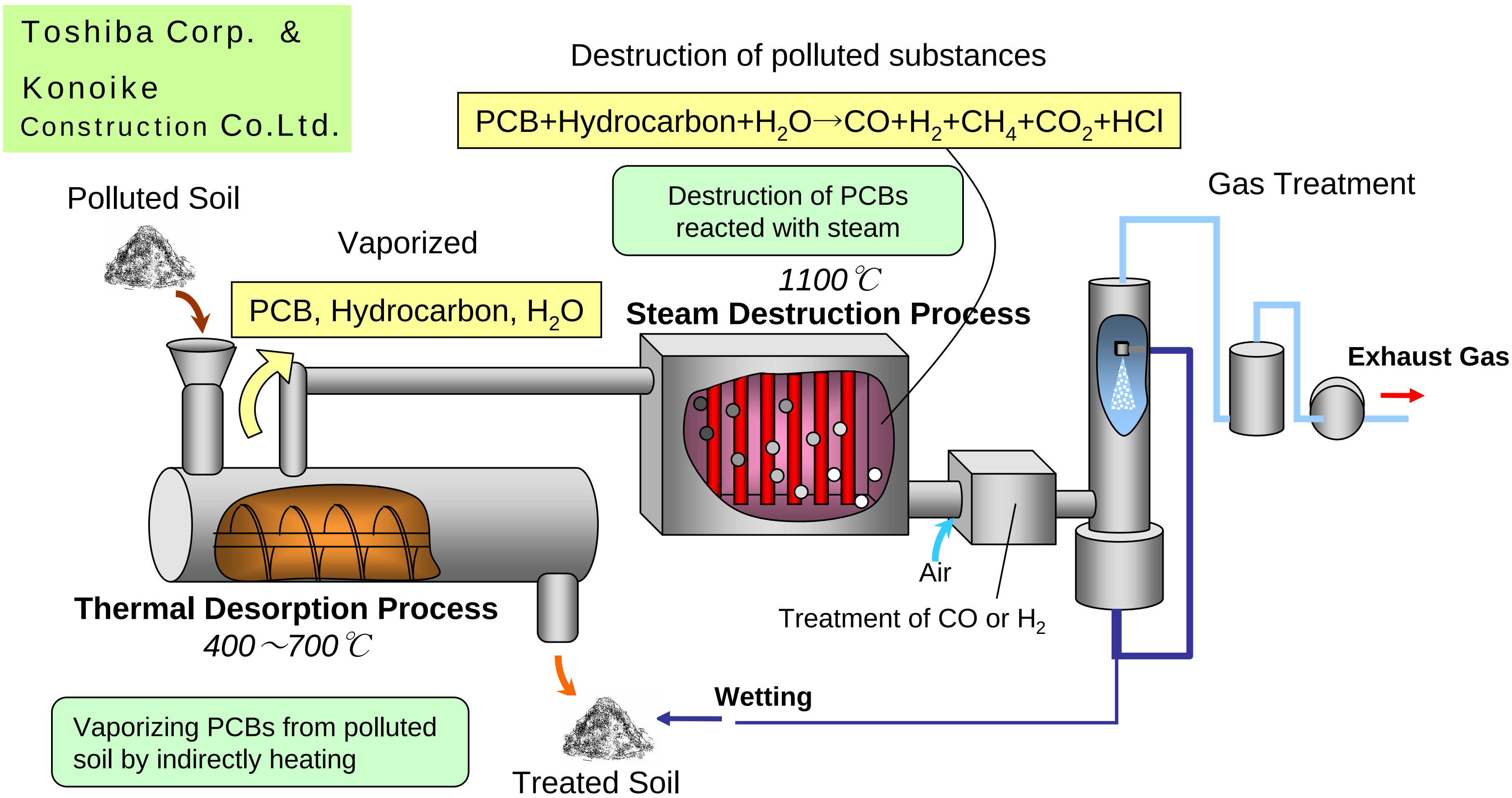
KOBELCO ECO-SOLUTIONS Co., LTD.

Indirect Heating with Reductive Dehalogenation



KOBELCO ECO-Solutions Co., LTD.

Indirectly Heated Thermal Desorption and Steam Destruction Technology



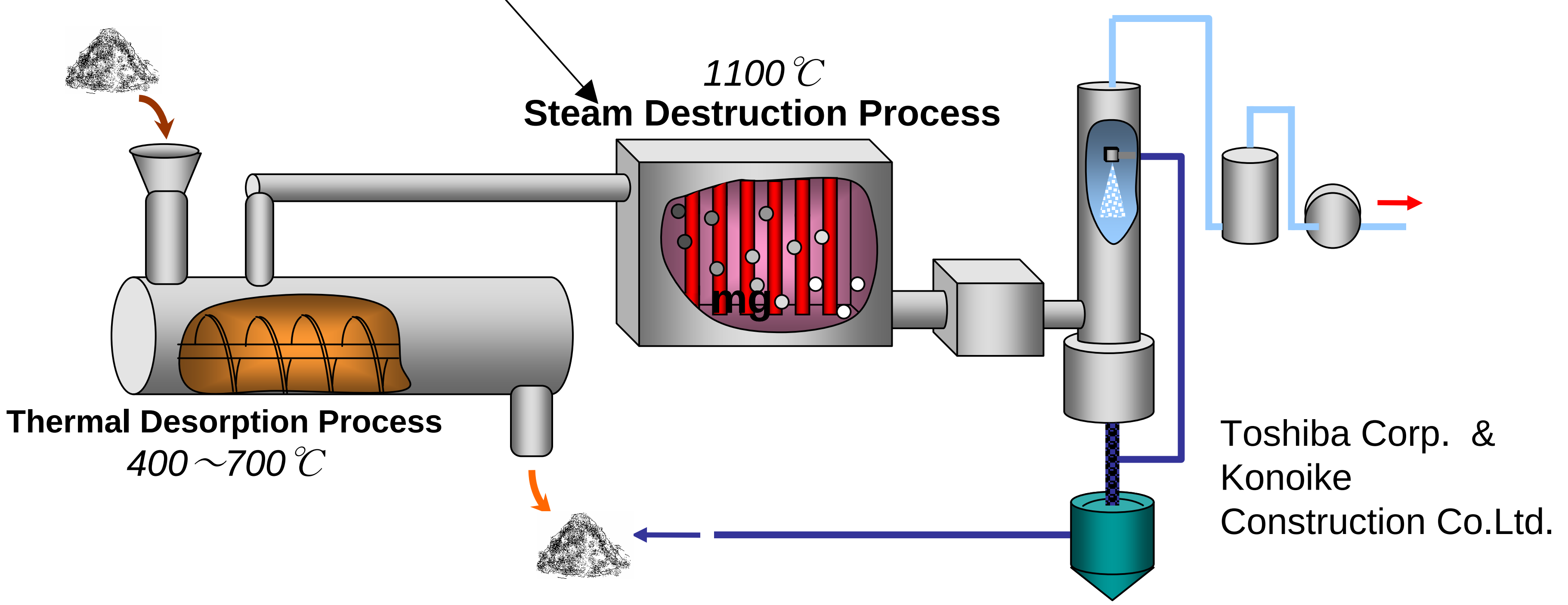
・PCBs are vaporized and removed by heating polluted soil in indirectly heated thermal desorption (1 hour, 600℃)

・PCBs are destructed by reaction with steam in steam destruction process (>3 sec, 1100℃)

Good points

Steam Destruction Process

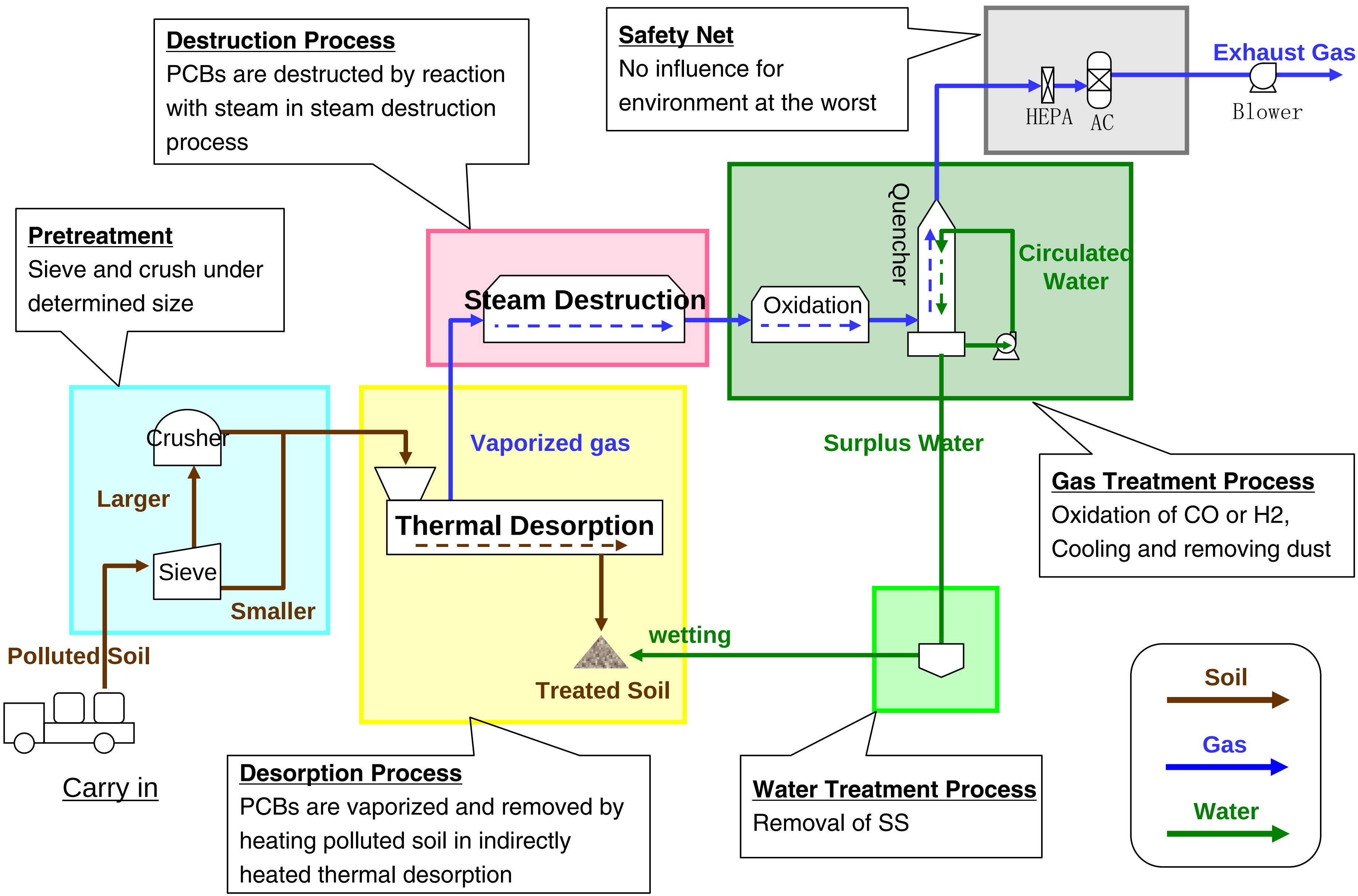
- **Indirectly heating of gas; little volume of exhaust gas, no NOx, soots in treated gas**
- **Stability of temperature distribution and residence time**
- **Simple operation**



Desorption and Destruction through One Plant

- **Stability of PCBs destruction**
- **No polluted water, sludge and activated carbon from the plant**
- **No concentrated pollutants**
- **No problem with tar or wax because of hydrocarbon destruction in steam destruction process**

System Flow


Destruction Process
PCBs are destructed by reaction with steam in steam destruction process
Safety Net
No influence for environment at the worst
Exhaust Gas
HEPA
AC
Blower
Pretreatment
Sieve and crush under determined size
Steam Destruction
Oxidation
Quencher
Circulated Water
Crusher
Larger
Sieve
Smaller
Vaporized gas
Thermal Desorption
Surplus Water
Gas Treatment Process
Oxidation of CO or H2, Cooling and removing dust
wetting
Treated Soil
Polluted Soil
Carry in
Soil
Gas
Water
Desorption Process
PCBs are vaporized and removed by heating polluted soil in indirectly heated thermal desorption
Water Treatment Process
Removal of SS

Commercial Scale Plant; 300 kg/hr

Thermal Desorption (Screw Conveyer)

Steam Destruction (Indirectly heating furnace)

Commercial Scale Plant

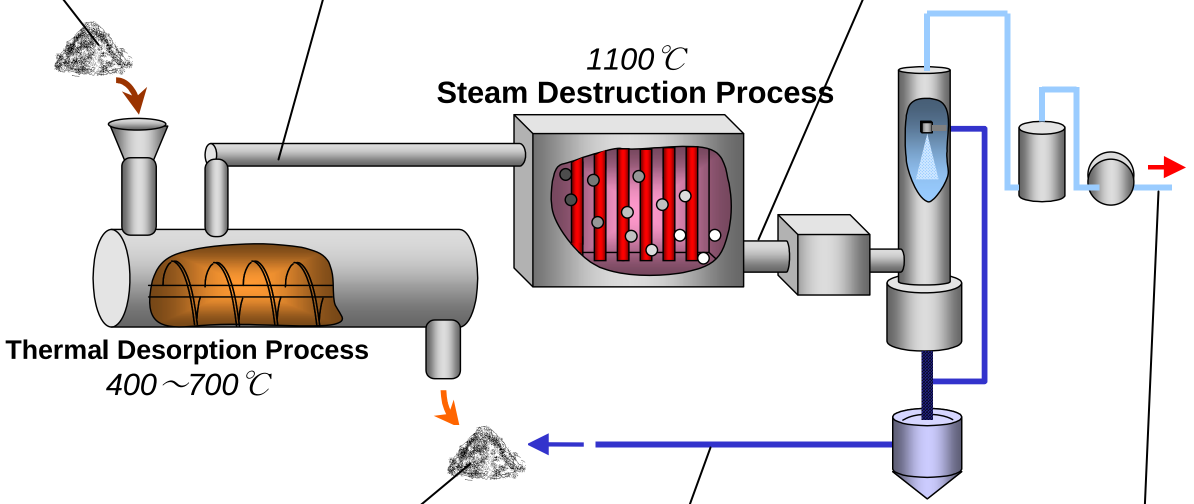
Toshiba Corp. & Konoike Construction Co.Ltd.

Test Data ; Remediation of PCB-polluted-soil in Commercial Scale Plant

Polluted Soil
PCB:11,000 mg/kg

Vaporized Gas
PCB:24,000 mg/m3

Steam Destruction Gas
PCB:0.0021 mg/m^{3}N



Treated Soil
PCB:0.03 mg/kg
Regulation for Sediment in Japan:10 mg/kg

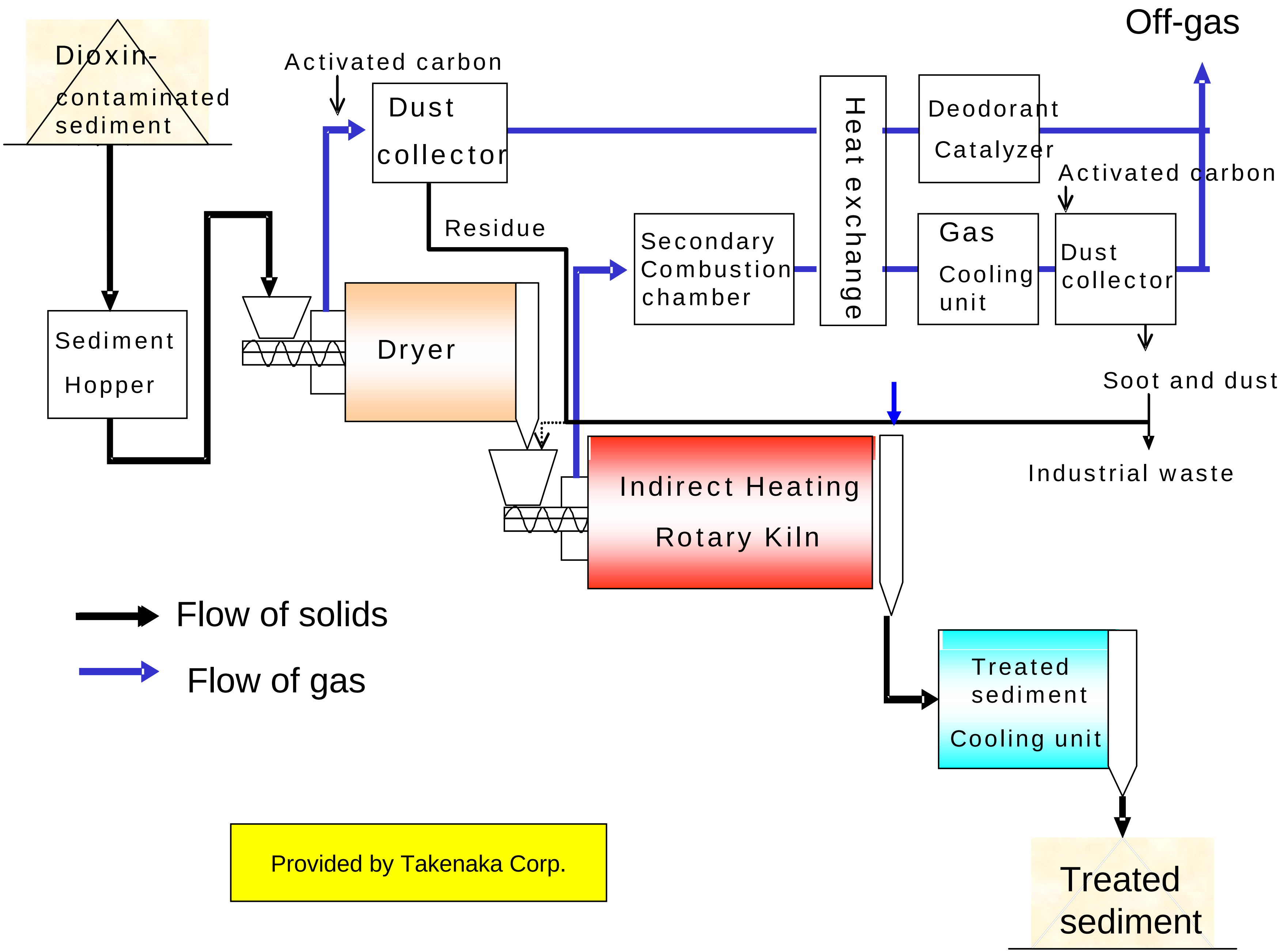
Exhaust Gas
PCB:0.00017 mg/m^{3}N
Regulation in Japan:0.1 mg/m^{3}N

Treated Water
PCB:<0.0005 mg/L
Regulation in Japan:0.003 pg-TEQ/L

Remediation of dioxin-contaminated sediment in the Hinokuchi River

- Clean-up of dioxin-contaminated sediment (360 m^3) by Indirect Heating Treatment Process (polluter-pay principle)

- Stabilization/immobilization by cement of dioxin-contaminated sediment as one part of river improvement project by local government



Provided by Takenaka Corp.

Clean-up of dioxin-contaminated sediment (Hinokuchi River)

Target amount of dioxin-contaminated sediment	360 m3 (including 66% water) before treatment → 54 t (dehydrated cake) after filter press → 94 t (separated sand) after sieving
Dioxin concentration in dehydrated sediment cake	200 - 480 pg-TEQ/g
Goal for dioxin concentration	<150 pg-TEQ/g (Environment Standard) (target in this site: <100 pg-TEQ/g)
Dioxin concentration in treated sediment	0.0044 - 0.7 pg-TEQ/g

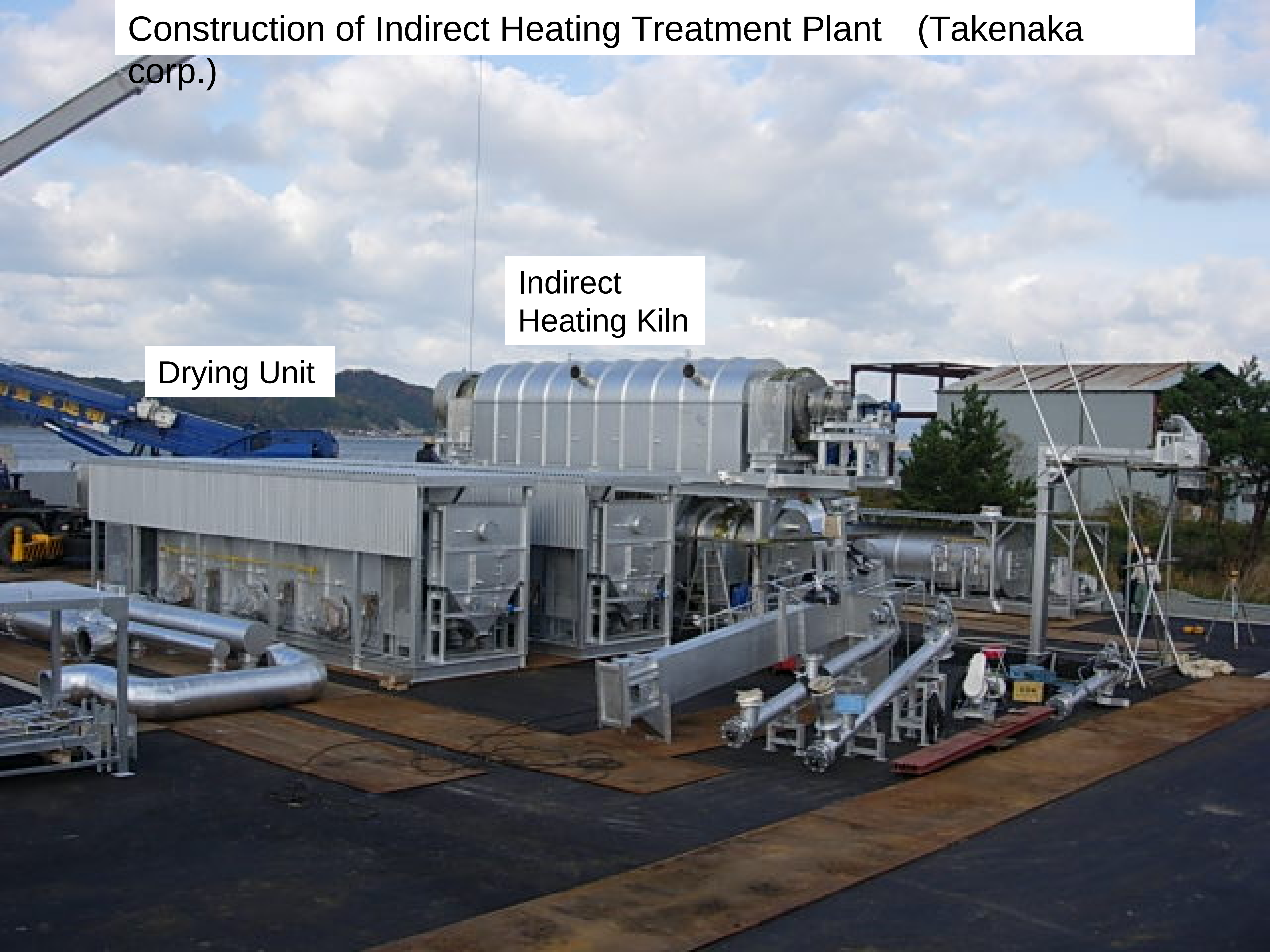
Clean-up of dioxin-contaminated sediment (Hinokuchi River)
Performance data on environmental impact

Target value of dioxin in off-gas	1 ng-TEQ/m3
Measured values	0.0045 - 0.31 ng-TEQ/m3
Target value of dioxin in wastewater	1 pg-TEQ/L
Measured values	0.00055 - 0.0071 pg-TEQ/L
Target value of dust concentration	1.0 mg/m3
Measure values	0 - 0.95 mg/m3
Target values of toxic substances in sediment	Values of Soil Pollution Control Law
Measured values	Below the values descibed by Soil Pollution Control Law
Target waste derived from treatment process	Standard for specially controlled waste
Measured waste	Below the standard value for specially controlled waste


Sediment Dredging
using Vacuum Pump
Hinokuchi River

On-site storage pit for
dredged sediment

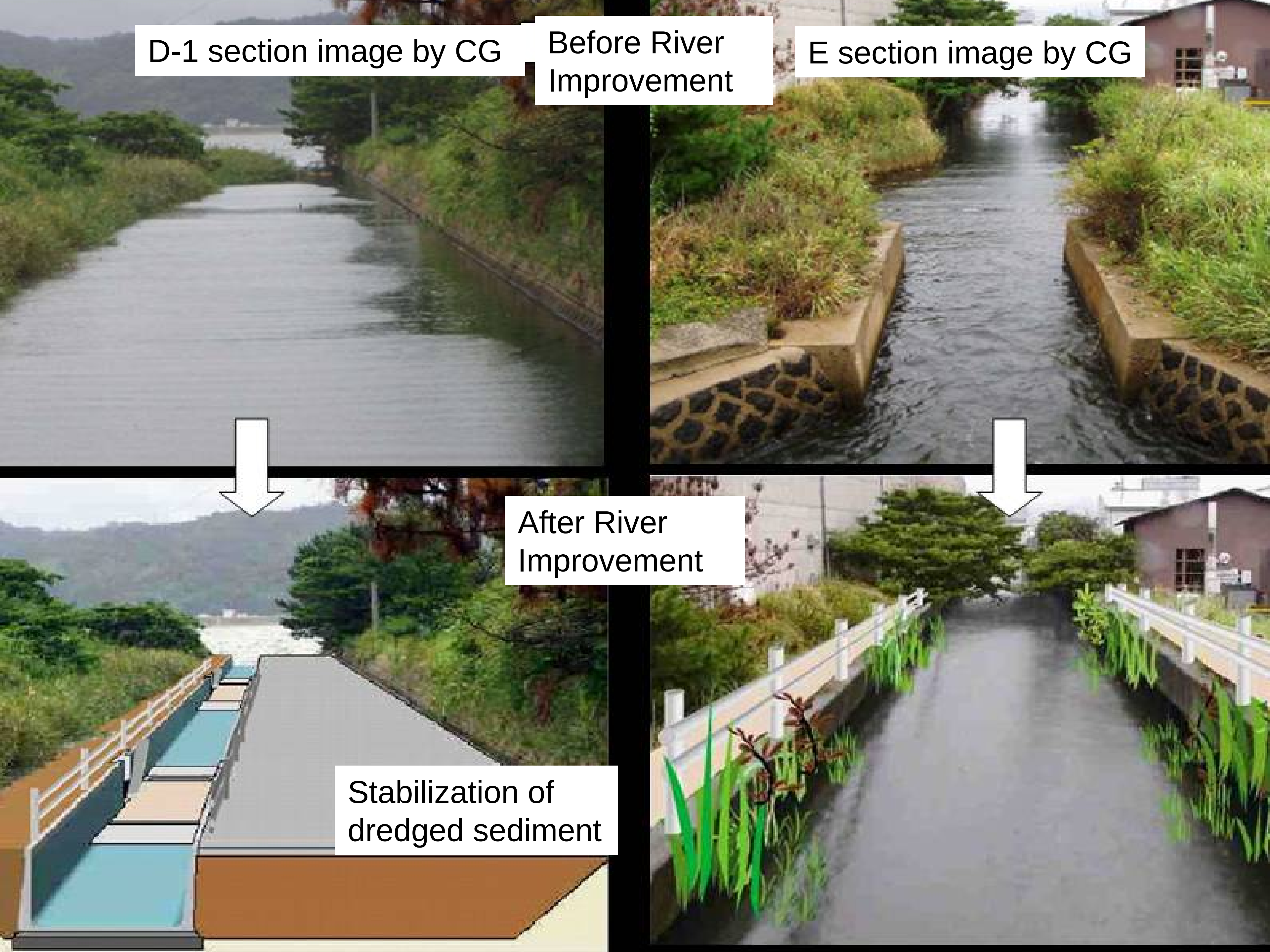
Construction of Indirect Heating Treatment Plant (Takenaka corp.)



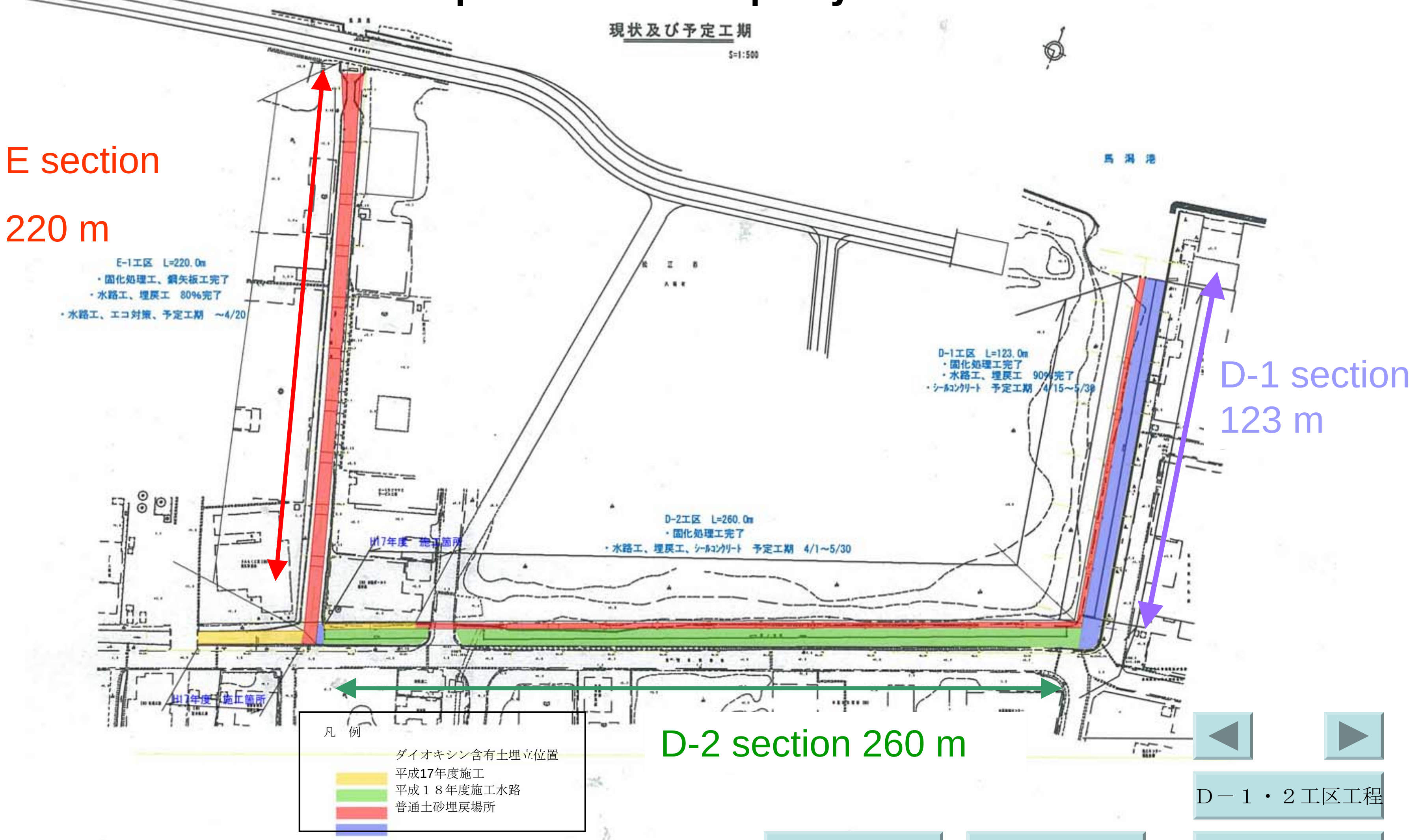

Temporary housing for drying unit and Indirect heating unit
Storage pit
Control office
On-site wastewater treatment unit


(Takenaka corp.)
Indirect Heating Kiln Unit with negative pressure control
無害化処理機


(Takenaka corp.)
Off-gas Treatment Unit


D-1 section image by CG
Before River Improvement
E section image by CG
After River Improvement
Stabilization of dredged sediment

Remediation project of dioxin-contaminated sediment in the Hinokuchi River through river improvement project



土砂仮置状況　仮締切排水工

Ｄ－１・２工区工程

Ｅ工区工程

Rotary Mixing Machine for cement stabilization/immobilization

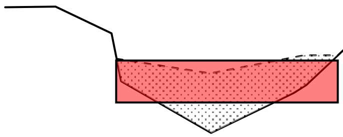
Ｄ工区攪拌へ

Ｅ工区攪拌へ

Ｄ－１・２工区工程

Ｅ工区工程

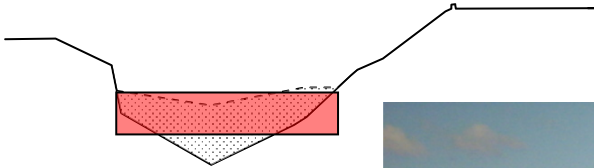
Cement Stabilization/Immobilization by Rotary Mixing Machine in D section



D－１・２工区工程

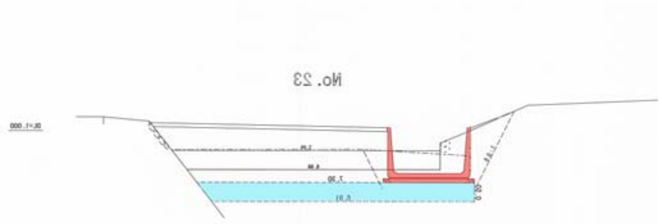
E工区工程

Outline of stabilization using RM machine in D section



D－１・２工区工程

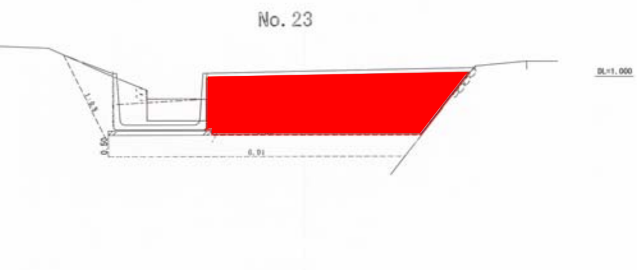
Ｅ工区工程



Installation of Precast box culvert

D－１・２工区工程

Containment by stabilized dioxin-contaminated sediment in D section



Ｄ－１・２工区工程

Stabilization/Immobilization Demonstration Project by Cement for dioxin-contaminated sediment in the Yokojikken River (Tokyo)

January 2006


105


420ml

Capping Demonstration Project for Dioxin-contaminated Sediment in the Kanzaki River (Osaka)

May 2007


CAT
320D
DSK
67


CAT
DSK

Future Problems to be solved

- Development of low-cost clean-up technologies for dioxin-contaminated sediment (Target: $400-500/m^3)
- Risk assessment of highly contaminated sediment in 50 cm more depth
- Long-term monitoring program for stabilization/immobilization of contaminated sediment
- Who should pay remediation cost?