さまざまな災害による化学物質汚染

大阪大学環境安全研究管理センター　〇中野　武
兵庫県環境研究センター　羽賀雄紀、吉識亮介、松村千里
ベオグラード大学　Vladimir P. Beskoski

Disaster and chemicals contamination

Recently,
various disaster occurred over the world

Earthquake, Tsunami,
Mudslide, Landslide
Typhoon, Hurricane
Climate Change, abnormal weather
War, Bombing, Civil war
Hot summer heat, warm rain 44C
Floods with heavy rain, drought

POPs/PTS have accumulated in landfills, dumps, stockpiles contaminated sites and in soils and sediments mainly over the last century

Roland Weber et al. Organohalogen compounds (2012)

THE NEED FOR INVENTORIES OF RESERVOIRS OF PTS IN THE FACE OF CLIMATE CHANGE

豪雨、土砂崩れ、山崩れ


© AP

Hanshin-Awaji earthquake

1995.01.17

Second floor disappear

First floor of station disappear

Gone with Great Fire by earthquake

Gone with Great Fire by earthquake

Gone with Great Fire by earthquake

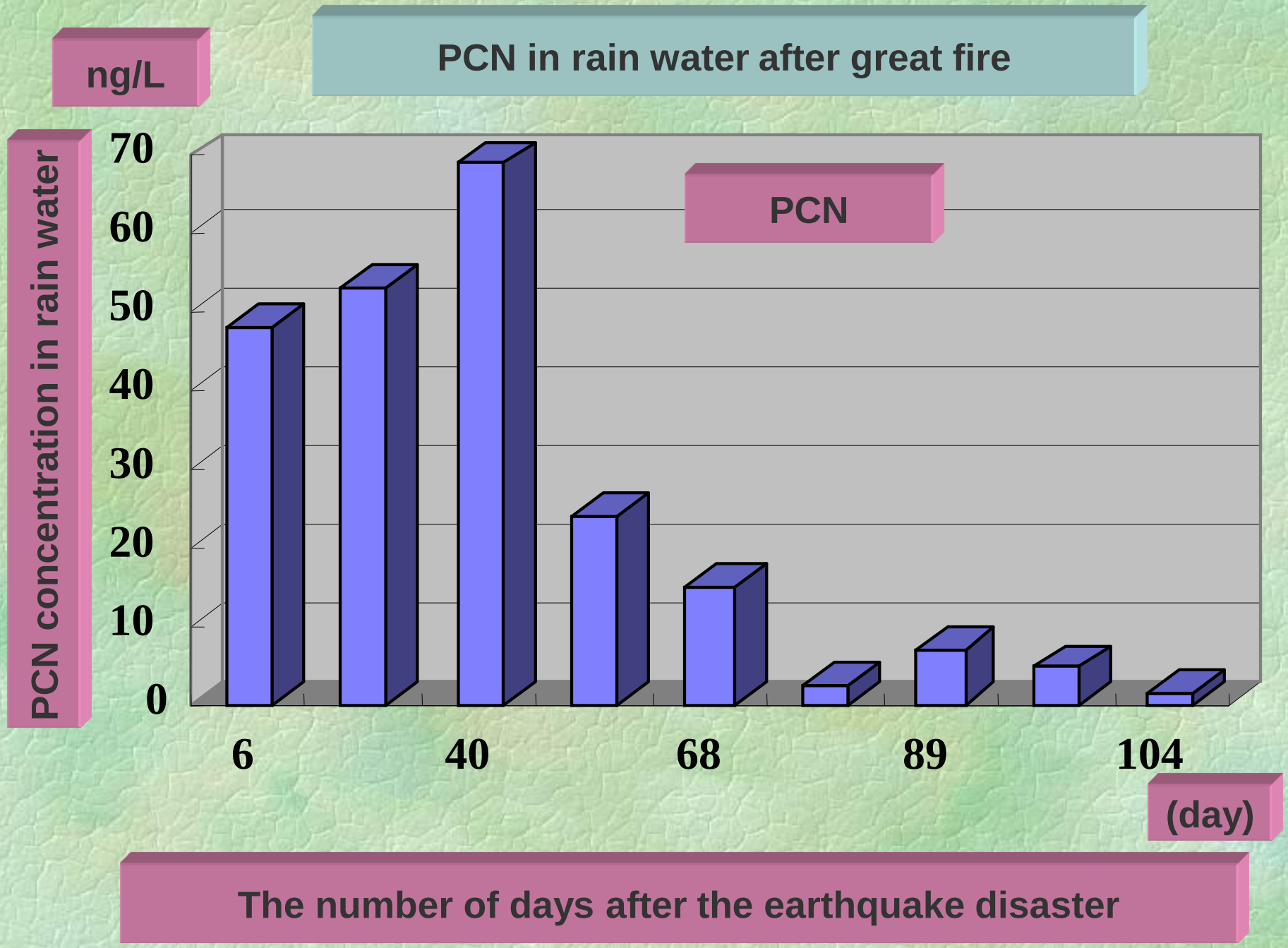
Gone with Great Fire by earthquake

1995.1.17 5:46am

Great Earthquake

Everything disappear with great fire

unintentional combustion product such as PCDD/PCDF/PCB/PCN formed


PCN in rain water after great fire
ng/L
PCN concentration in rain water
70
60
50
40
30
20
10
0
PCN
6
40
68
89
104
(day)
The number of days after the earthquake disaster

Railway damaged by earthquake

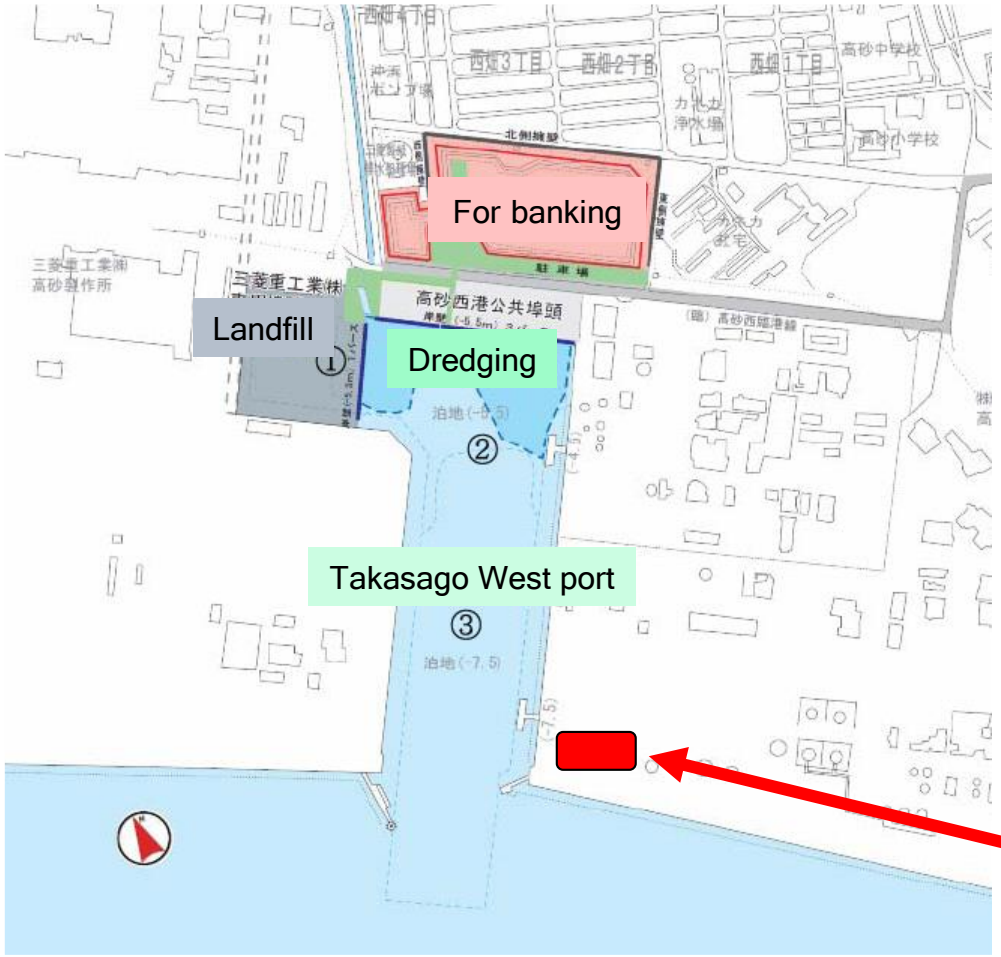
We have completely damaged by earthquake

and lost everything, but also fortunately

5500t liquid PCB waste completely destroyed

before great earthquake

PCB Survey for Bottom Sediments



All the survey points have shown PCB concentrations below tentative removal standards for PCB

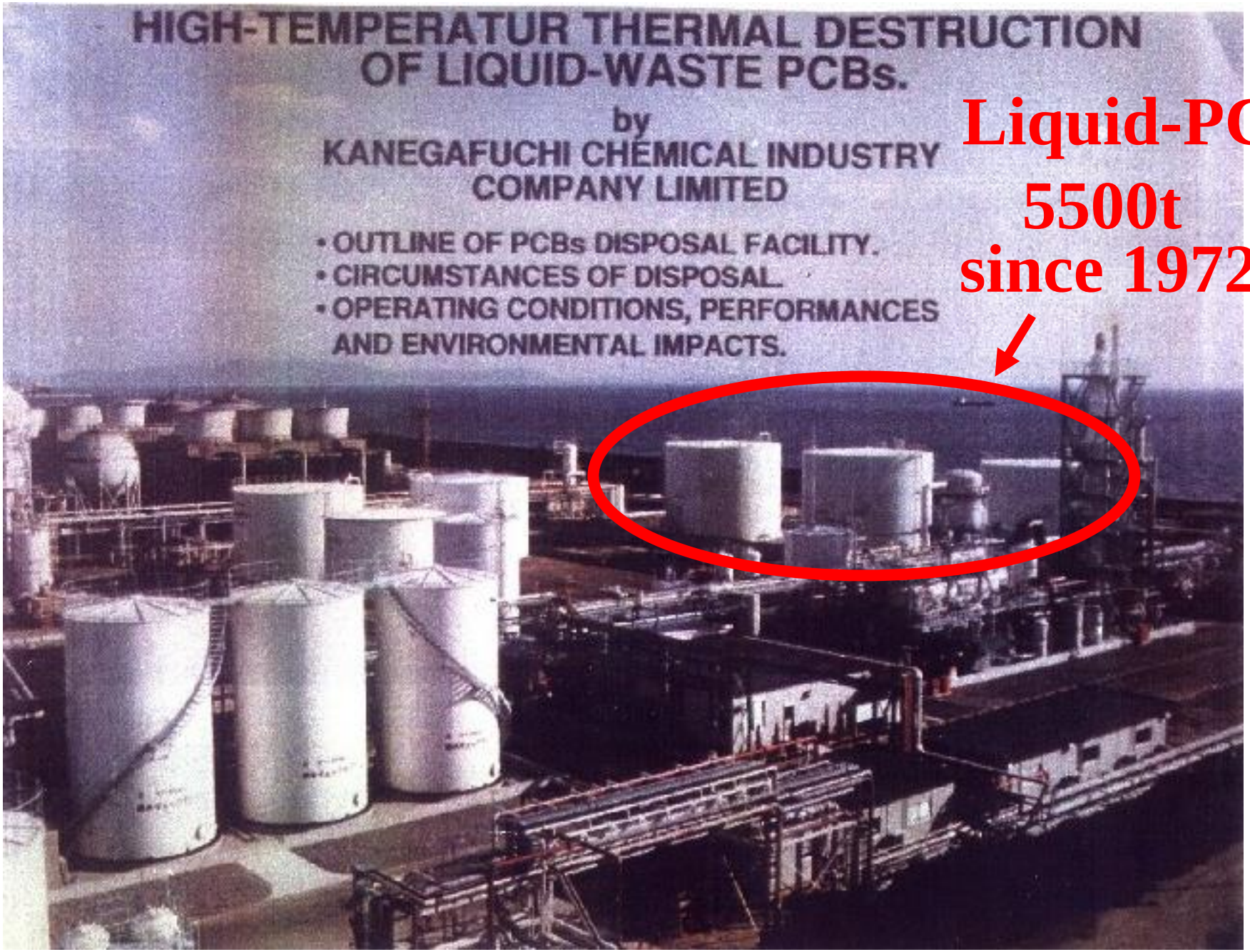
Liquid-PCB
5500t
since 1972

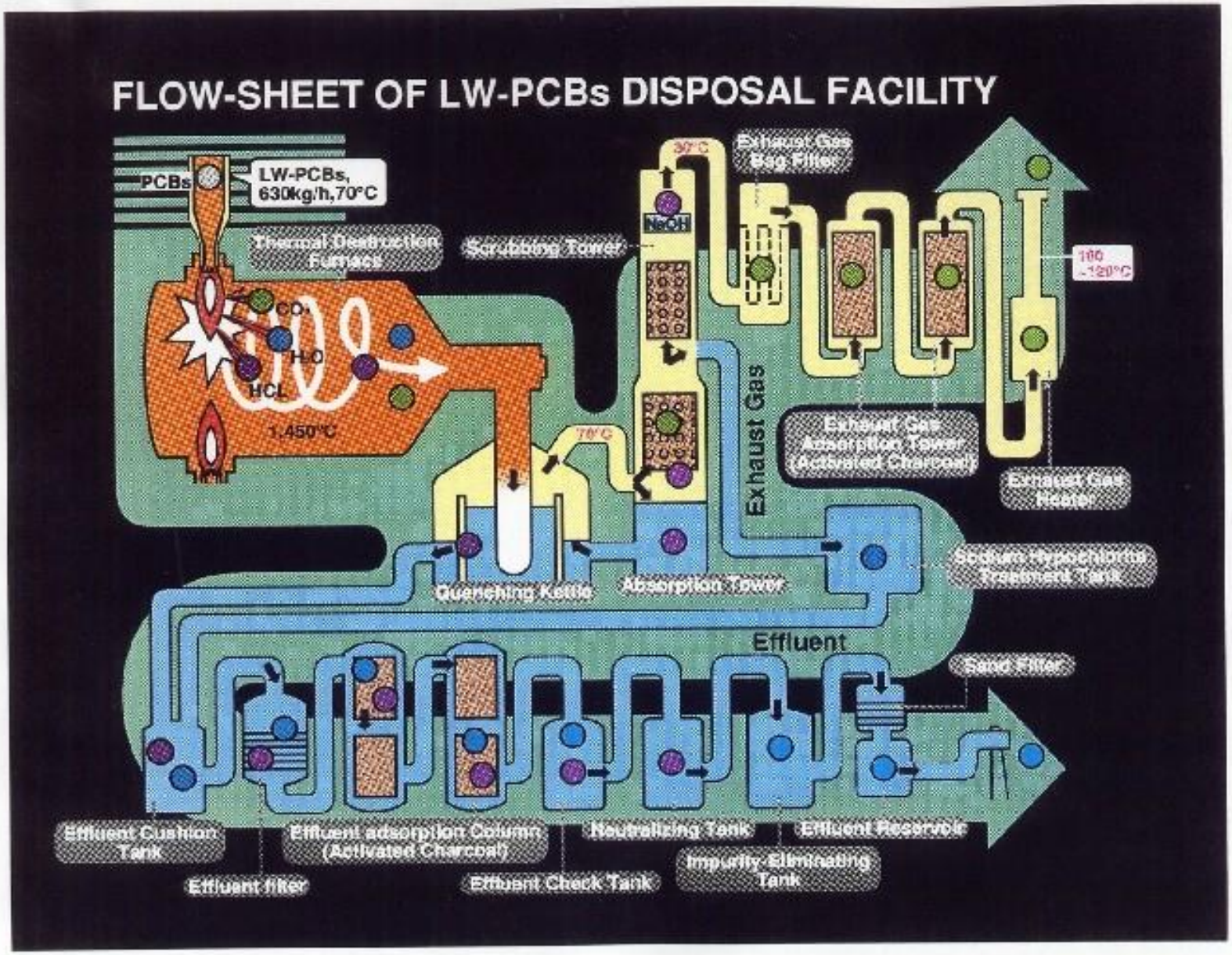
It was collected from all over Japan
stocked in the tank
tank degraded year by year

Environmental survey (Monitoring point)

図 8-2　環境モニタリング地点（対象施設周辺）(1)

5500t Liquid-PCB since 1972


HIGH-TEMPERATUR THERMAL DESTRUCTION
OF LIQUID-WASTE PCBs.
by
KANEGAFUCHI CHEMICAL INDUSTRY
COMPANY LIMITED
• OUTLINE OF PCBs DISPOSAL FACILITY.
• CIRCUMSTANCES OF DISPOSAL.
• OPERATING CONDITIONS, PERFORMANCES
AND ENVIRONMENTAL IMPACTS.
Liquid-PCB
5500t
since 1972


FLOW-SHEET OF LW-PCBs DISPOSAL FACILITY
PCBs
LW-PCBs, 630kg/h,70°C
Thermal Destruction Furnace
CO2
H2O
HCL
1,450°C
Scrubbing Tower
NaOH
37°C
Exhaust Gas Bag Filter
180 ~120°C
Exhaust Gas
Exhaust Gas Absorption Tower (Activated Charcoal)
Exhaust Gas Heater
78°C
Quenching Kettle
Absorption Tower
Sodium Hypochlorite Treatment Tank
Effluent
Sand Filter
Effluent Cushion Tank
Effluent adsorption Column (Activated Charcoal)
Neutralizing Tank
Effluent Reservoir
Effluent filter
Effluent Check Tank
Impurity-Eliminating Tank

Lesson 1 for us
If we didn't finish PCB treatment until 1995 as great earthquake

5500t PCB contaminated
our important environment

It was big national project
and completely destroyed liquid PCB

Disaster and chemicals contamination

The 2011 off the Pacific coast of Tohoku Earthquake and Tsunami

2011.03.11


青い海
守る思いやり


Sea water
Sea mud gets over the embankment with tsunami
Gone with tsunami


Iwate
M 9.0
A ship on the building

would like to propose
risk evaluation method
for environmental impact

How ?

Enantioselective Analysis of POPs

Enantioselective Analysis of PCB Congeners in Breast Milk

and

EF value of POPs in sea sediment around diaster area

Objectives

- To evaluate the impact of disaster
- Enantiomeric compositions of POPs in human and environmental samples were investigated

- The enantioselectivity of chiral POPs was shown by Enantiomer Fraction (EF),

  for the purpose of

  - ✓ tracking and apportioning chemical movement between environmental compartments
  - ✓ investigating the historical pollution(new/old) .

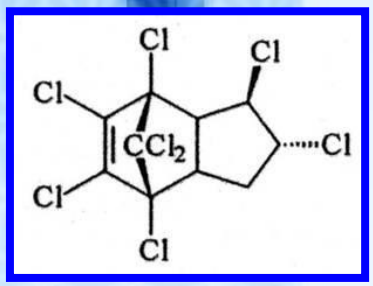
HRGC/HRMS conditions

GC	MS
Device：HP-6890N(HP) Column：BGB-172*(BGB Analytik) 30m, 0.25mm i.d. film thickness 0.25μm Carrier Gas：He 1.0 mL/min	Device：JMS-800D (JEOL) Ionization：EI Ion source temperature：260℃ Ionization volt : 38eV Accel volt :10kV Resolution : >10,000 Selected fragment (m/z) : [M]+, [M+2]+ or [M+2]+, [M+4]+
Temperature Program： 120℃ (2min) → 2℃/min →250℃ (3min) Injector temperature：230℃ Injection Volume：2μL	

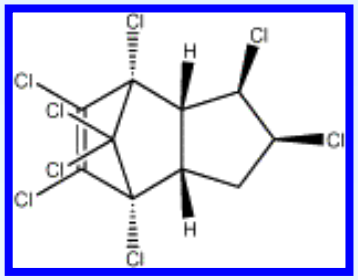
＊BGB-172（20% tert-butyldimethylsilyl-b-cyclodextrin dissolved in 15% diphenyl-polysiloxane and 85% dimethylpolysiloxane）

Target chemicals

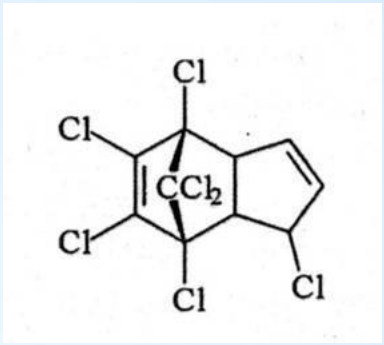
Technical compounds



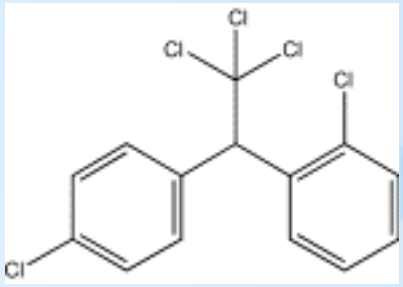
trans – Chlordane



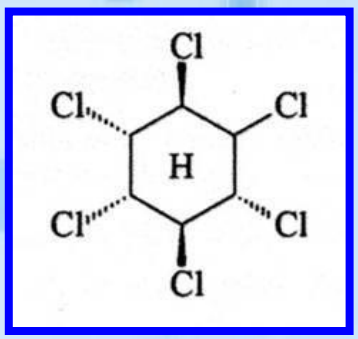
cis – Chlordane



Heptachlor

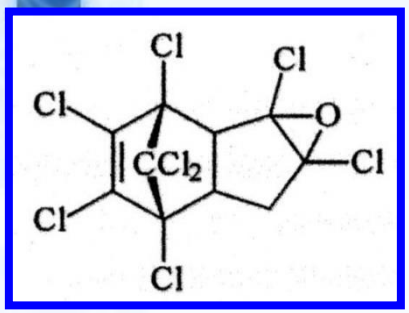


o,p' – DDT

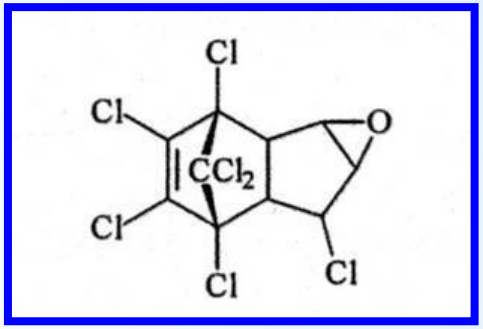


α – HCH

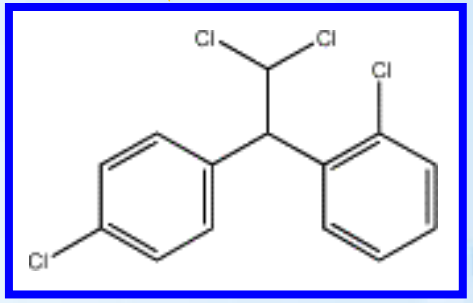
Metabolites



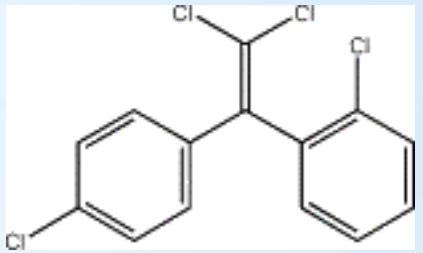
Oxychlordane



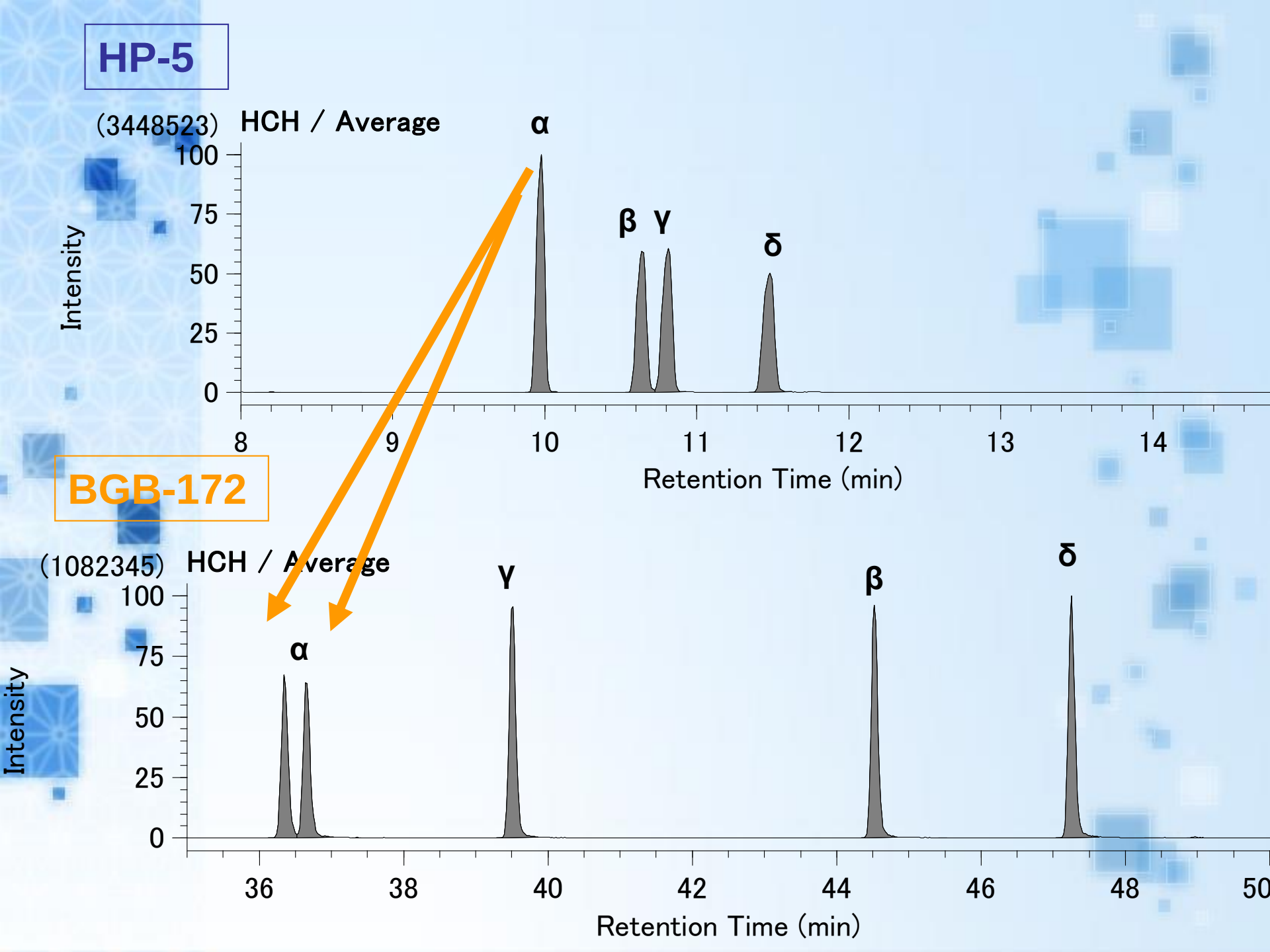
Heptachlor epoxide



o,p' – DDD



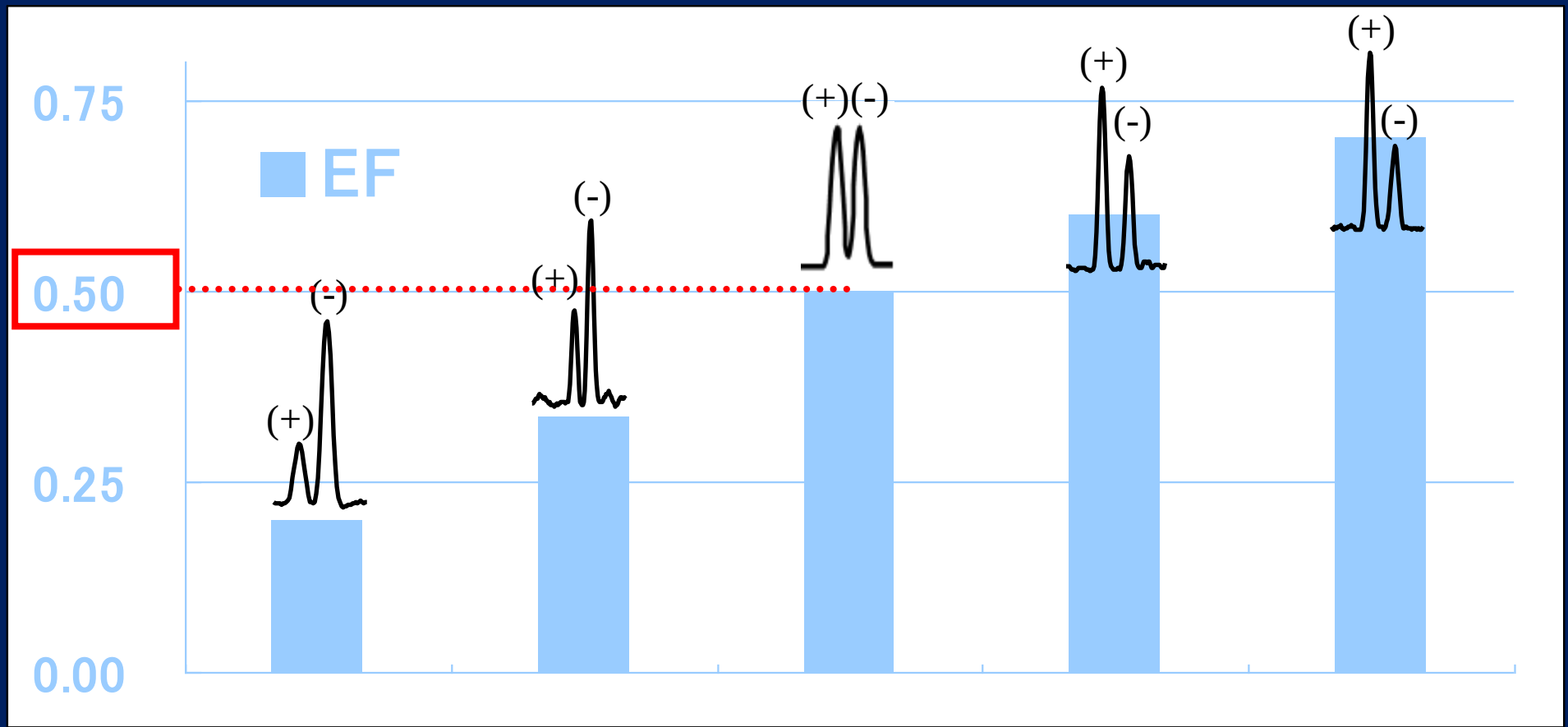
o,p' – DDE


HP-5
(3448523) HCH / Average
α
β γ
δ
100
75
50
25
0
Intensity
8
9
10
11
12
13
14
Retention Time (min)
BGB-172
(1082345) HCH / Average
α
γ
β
δ
100
75
50
25
0
Intensity
36
38
40
42
44
46
48
50
Retention Time (min)

Enantiomer Fraction(EF）

$$EF = \frac{E(+)}{E(+) + E(-)}$$

E(+): amount of (+)enantiomer
E(-) : amount of (-）enantiomer



Enantiomer Fraction(EF)

Changes in physicochemical process,

the EF value does not change.

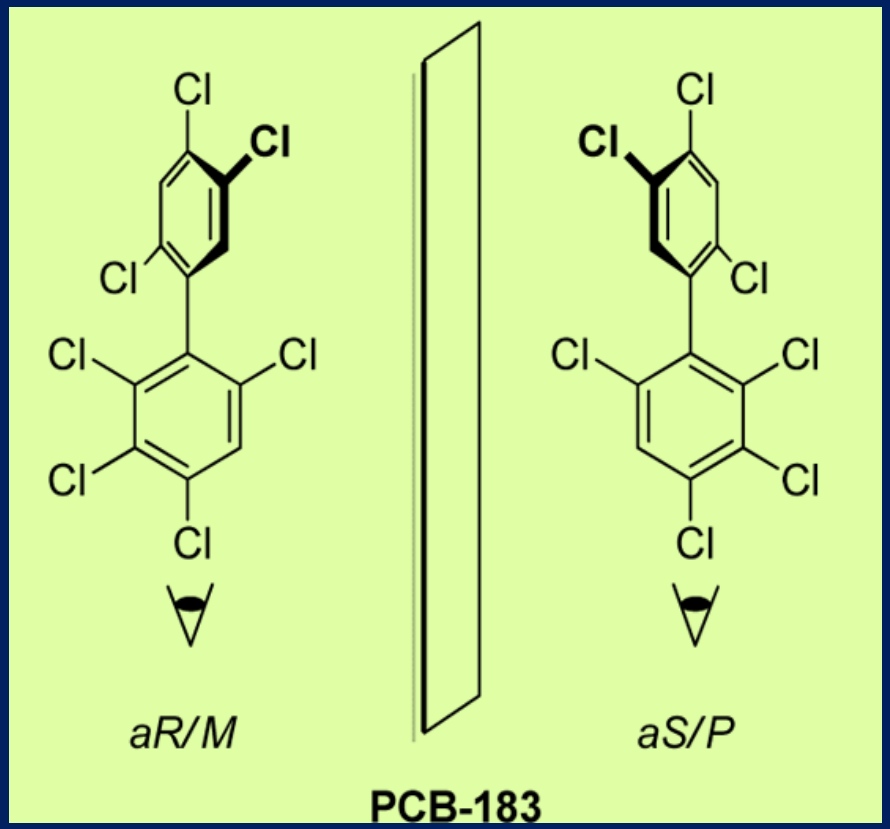
Changes in metabolic process,

the EF value changes.

We could estimate the historical trend of pollution occurred, past or present, by monitoring EF .

Enantioselective Analysis of PCB Congeners in Breast Milk

Chiral PCBs



Toda, M., Matsumura, C., Tsurukawa, M., Okuno, T., Nakano, T., Inoue, Y., Mori, T. 2012. Absolute configuration of atropisomeric PCB 183 enantiomerically enriched in human samples. *J. Phys. Chem. A.*, 116(37), p9340-9346 (2012)

- 19 PCB congeners contain 3 or 4 ortho- substituted chlorines and have high energy barriers that prevent rotation of the two rings.
- Technically called atropisomers instead of enantiomers.
- Selective metabolism in humans, wildlife, soils and sediments.

Time Trend of POPs Concentration in Breast Milk

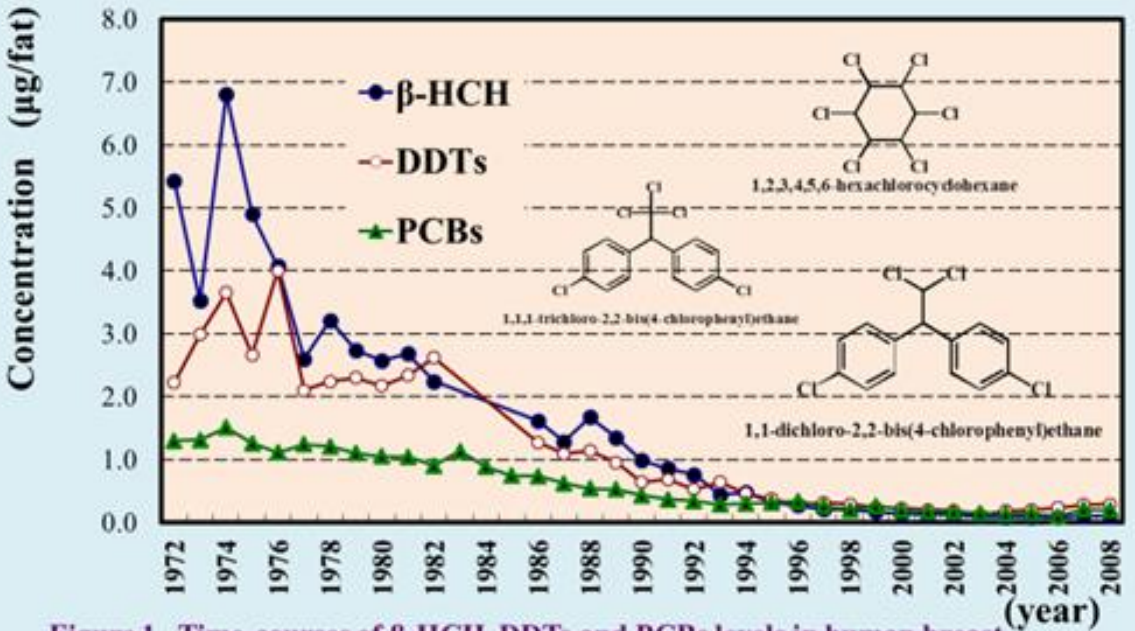
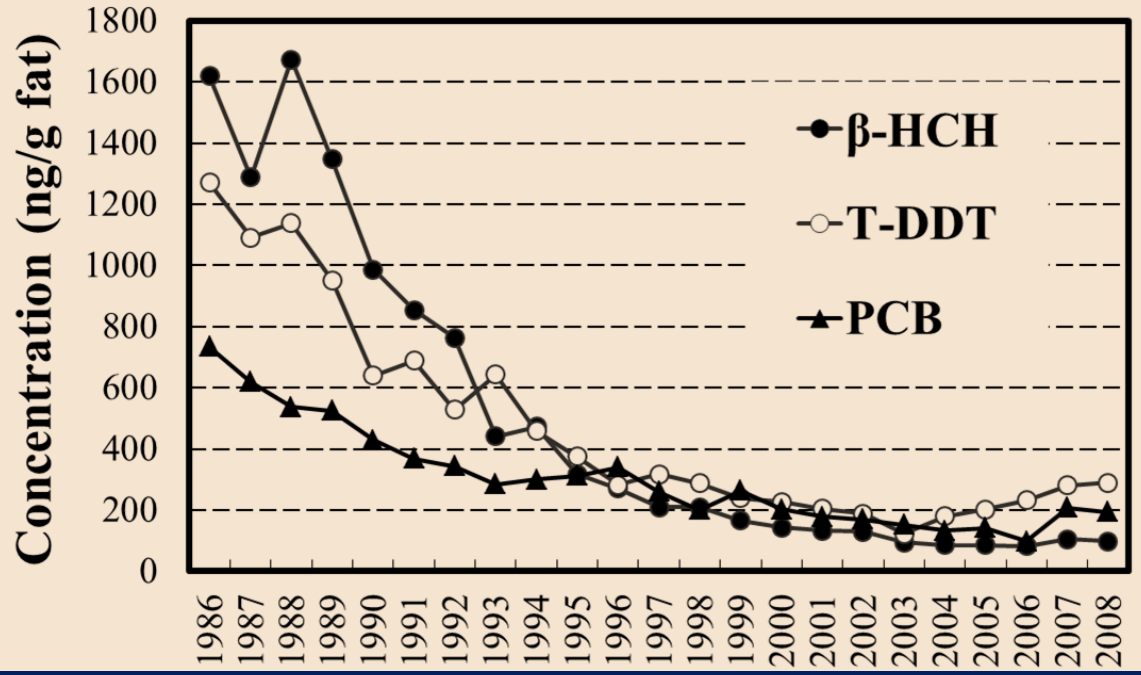
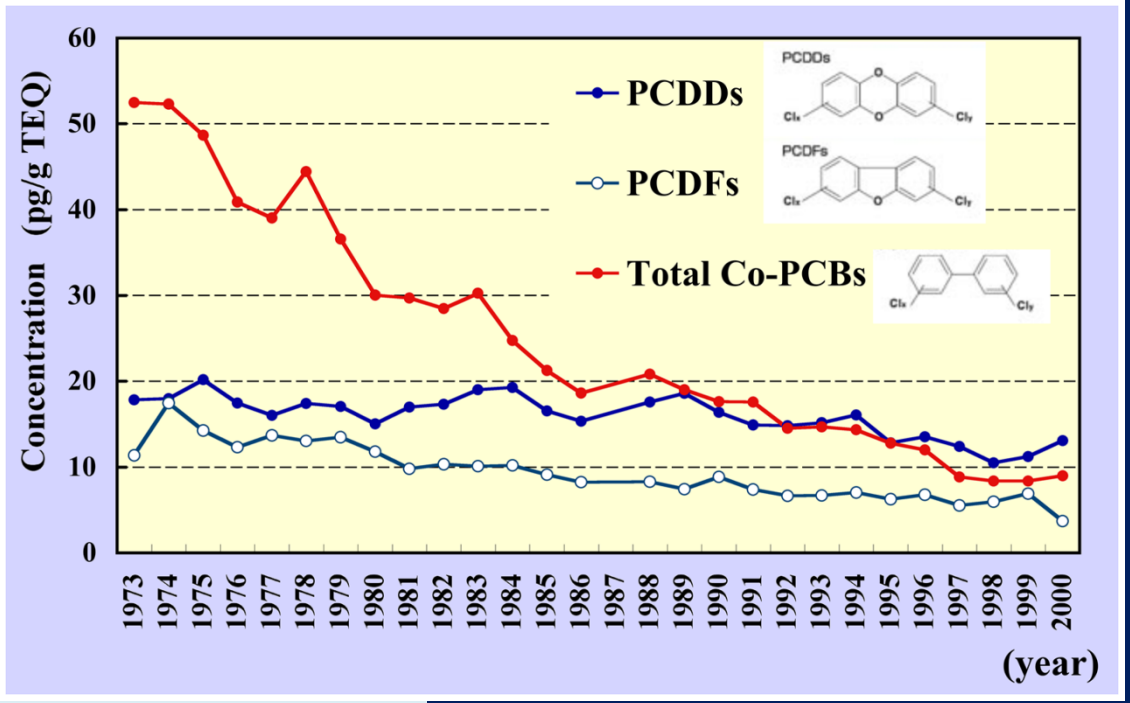


Figure 1. Time-courses of β-HCH, DDTs and PCBs levels in human breast milk from 1972 to 2008 fat basis



PCBs is considered to be the most stable compounds among these POPs in breast milk.
(Konishi et al.)

Time Trend of PCBs & Dioxins Concentration in Breast Milk



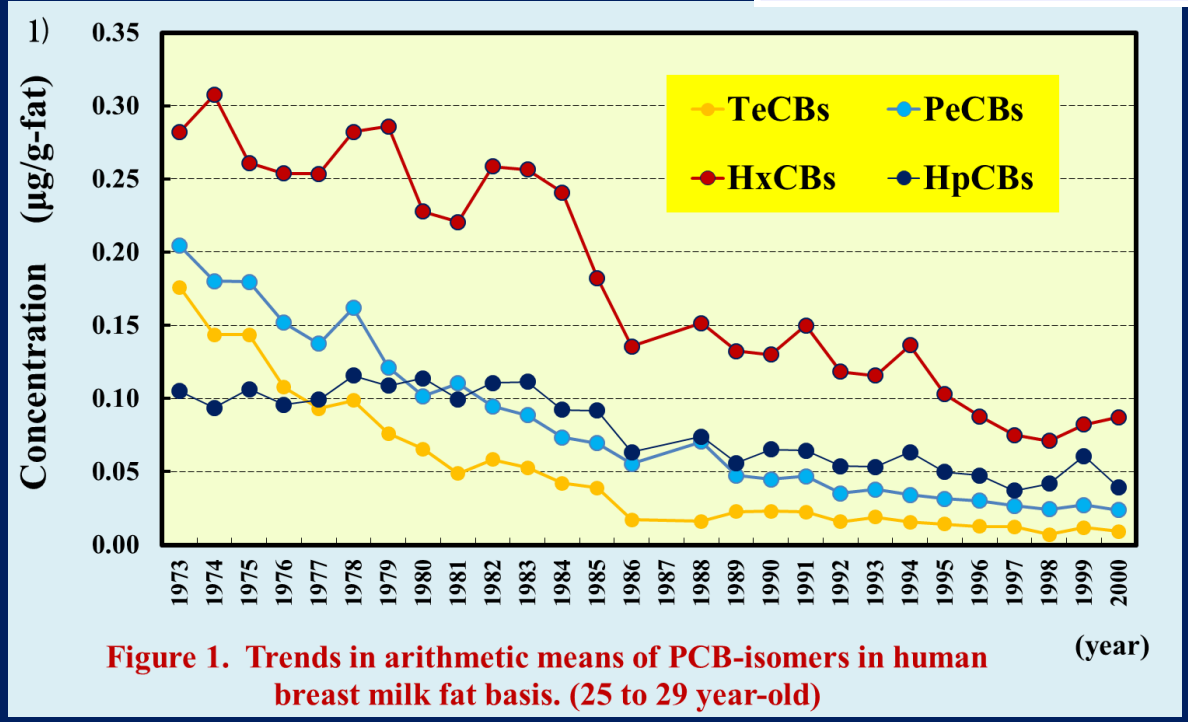


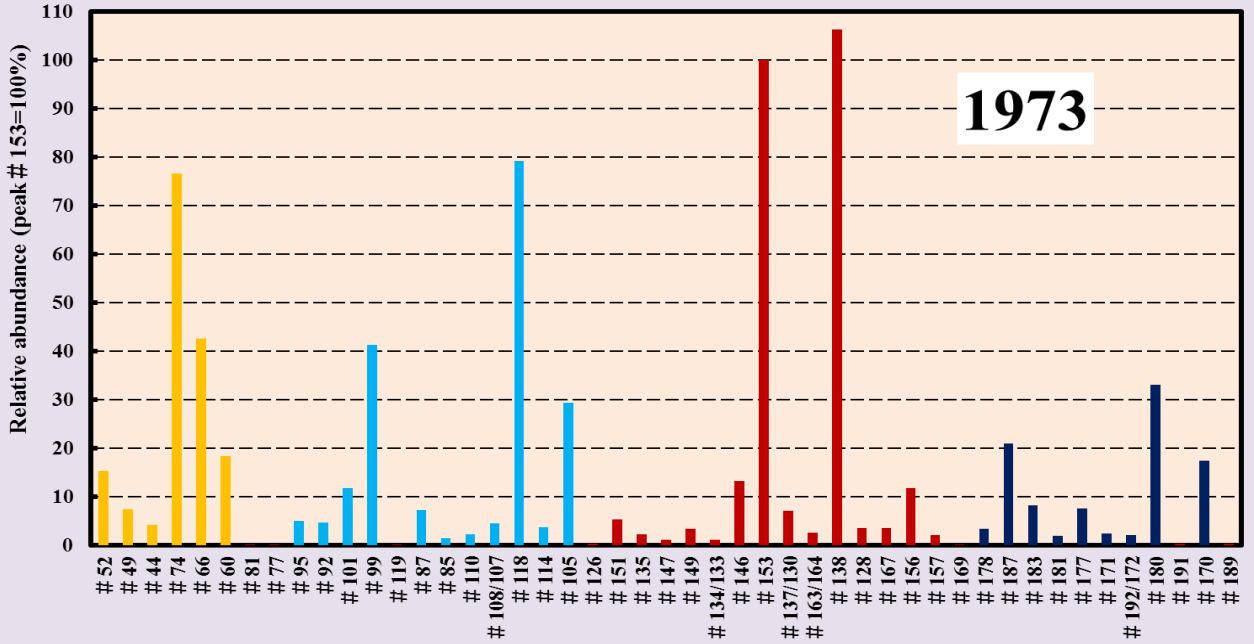
Figure 1. Trends in arithmetic means of PCB-isomers in human breast milk fat basis. (25 to 29 year-old)

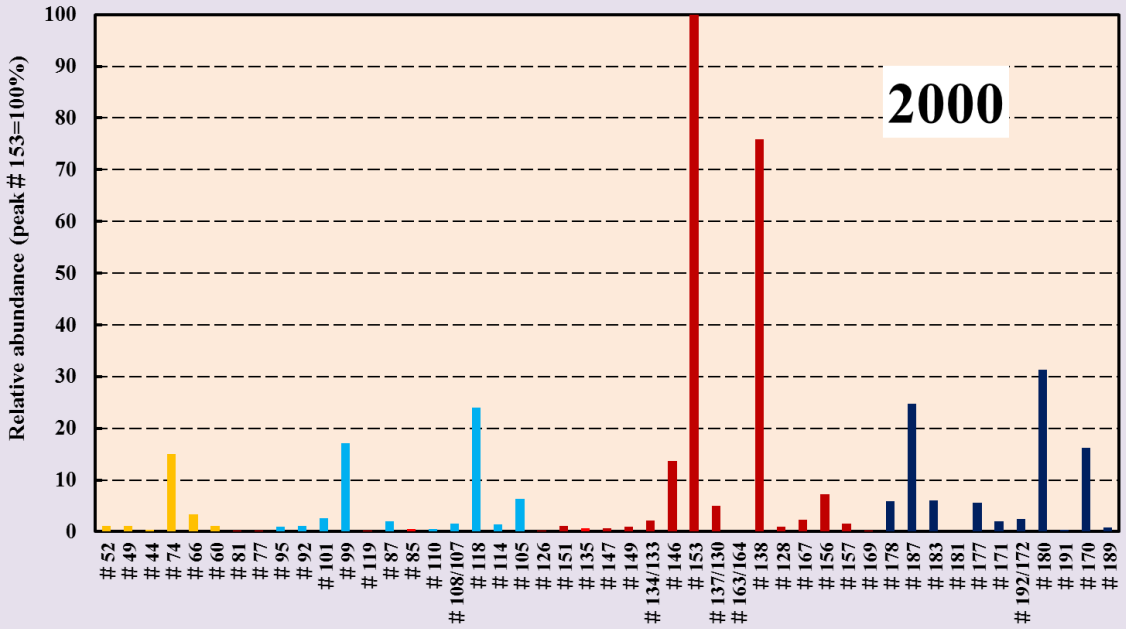
The declining rate of high chlorinated PCB congeners is slower than that of low chlorinated congeners in breast milk.

(Konishi et al.)

The Comparison of Congener distribution between 1973 & 2000 (30 years)

Human breast milk

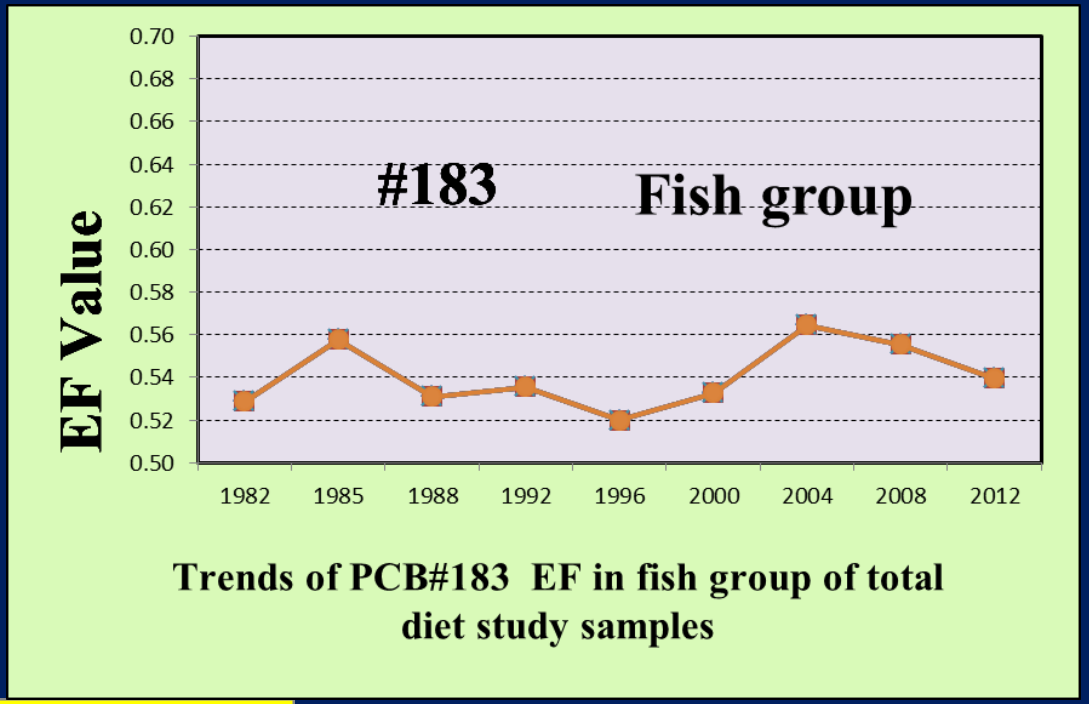


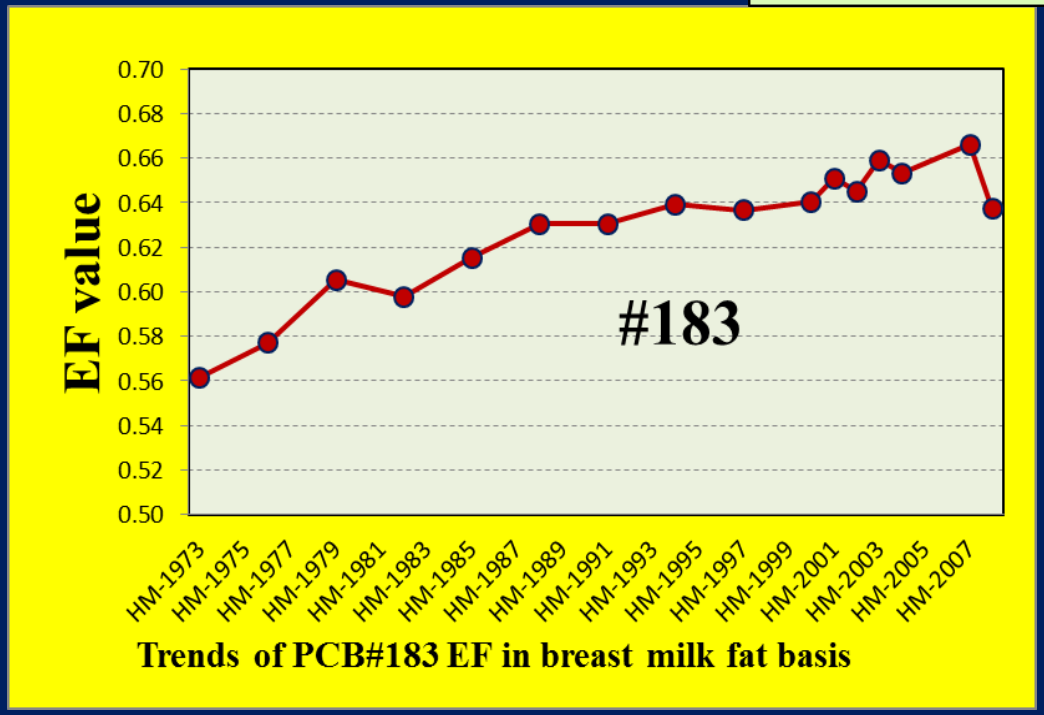


Chiral congeners, #183, #171 #149 and #135, were determined, but the proportion of these congeners was 2% or less of the total PCBs.

PCB #183 showed the highest concentration.

EF value of fish intake sustained close to racemate (EF = 0.5).





EF values of #183 in breast milk were elevated year by year .

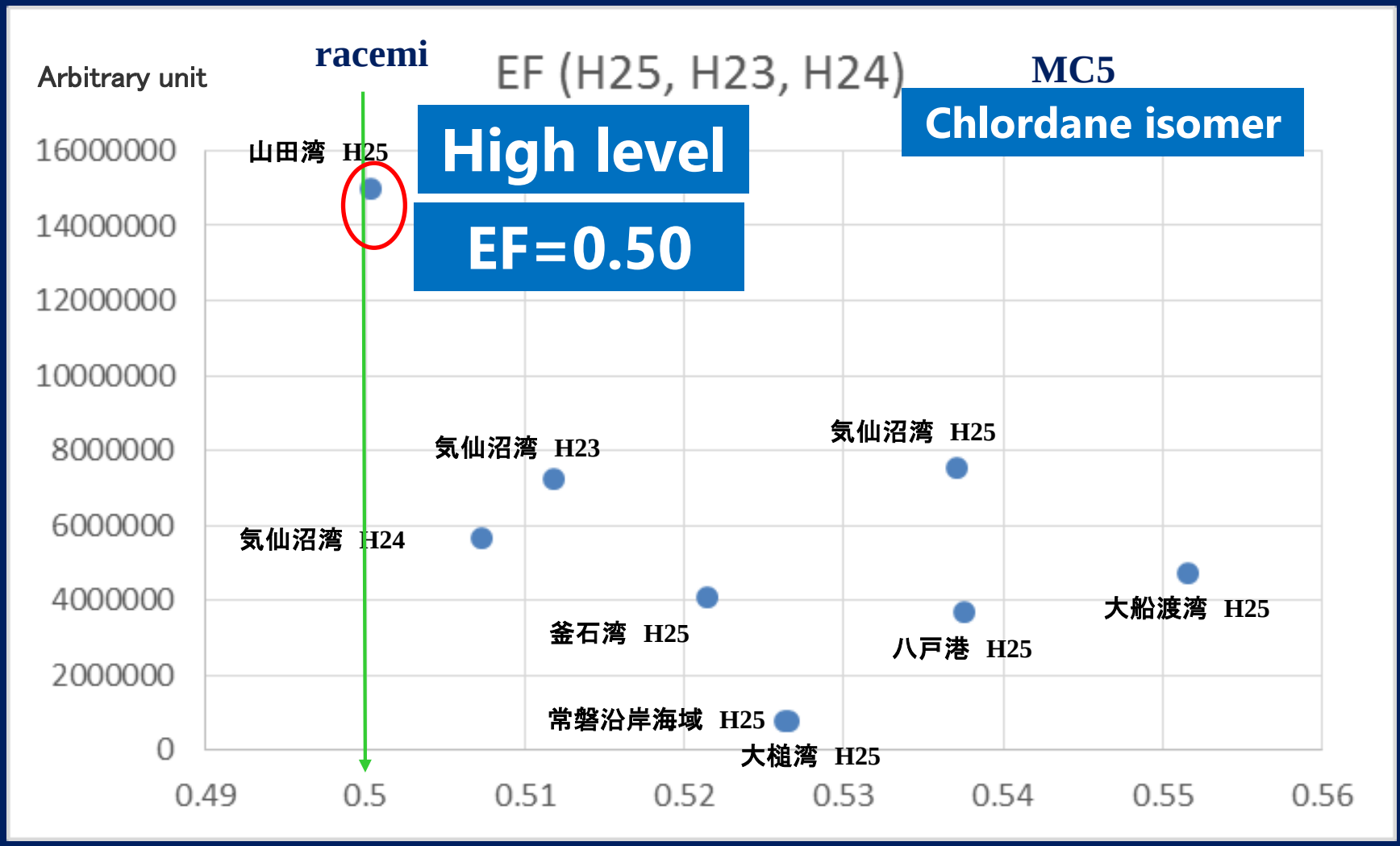
There are 154 congeners from HpCB to TeCB. 48 types of congeners were detected from a sample of 2000, although 51 types of congeners were detected from the sample of 1973.

Determined enantiomers in breast milk were #135, #149 (HxCB) and #171, #183 (HpCB). However, these congeners were 2% or less of the total PCBs. #183 showed the highest concentration among these congeners.

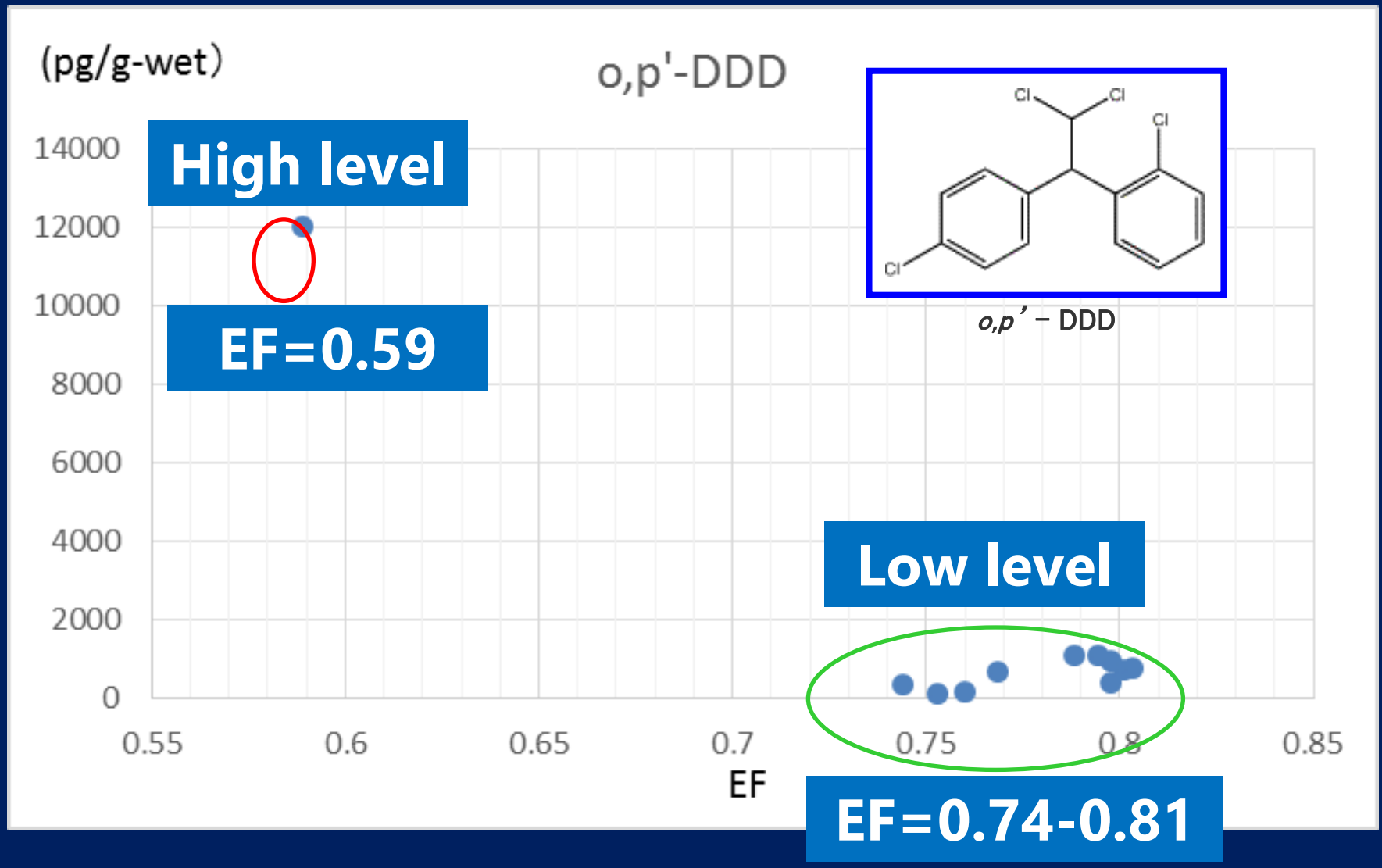
PCBs intake from seafood has been gradually decreased from the first half of the 1990s, but, EF value sustained a value close to the racemate.

On the other hand, EF values of #183 in breast milk were elevated, despite decreasing its concentration over the time. This fact indicated that (-)-PCB-183 would be metabolized more rapidly than (+)-PCB-183.

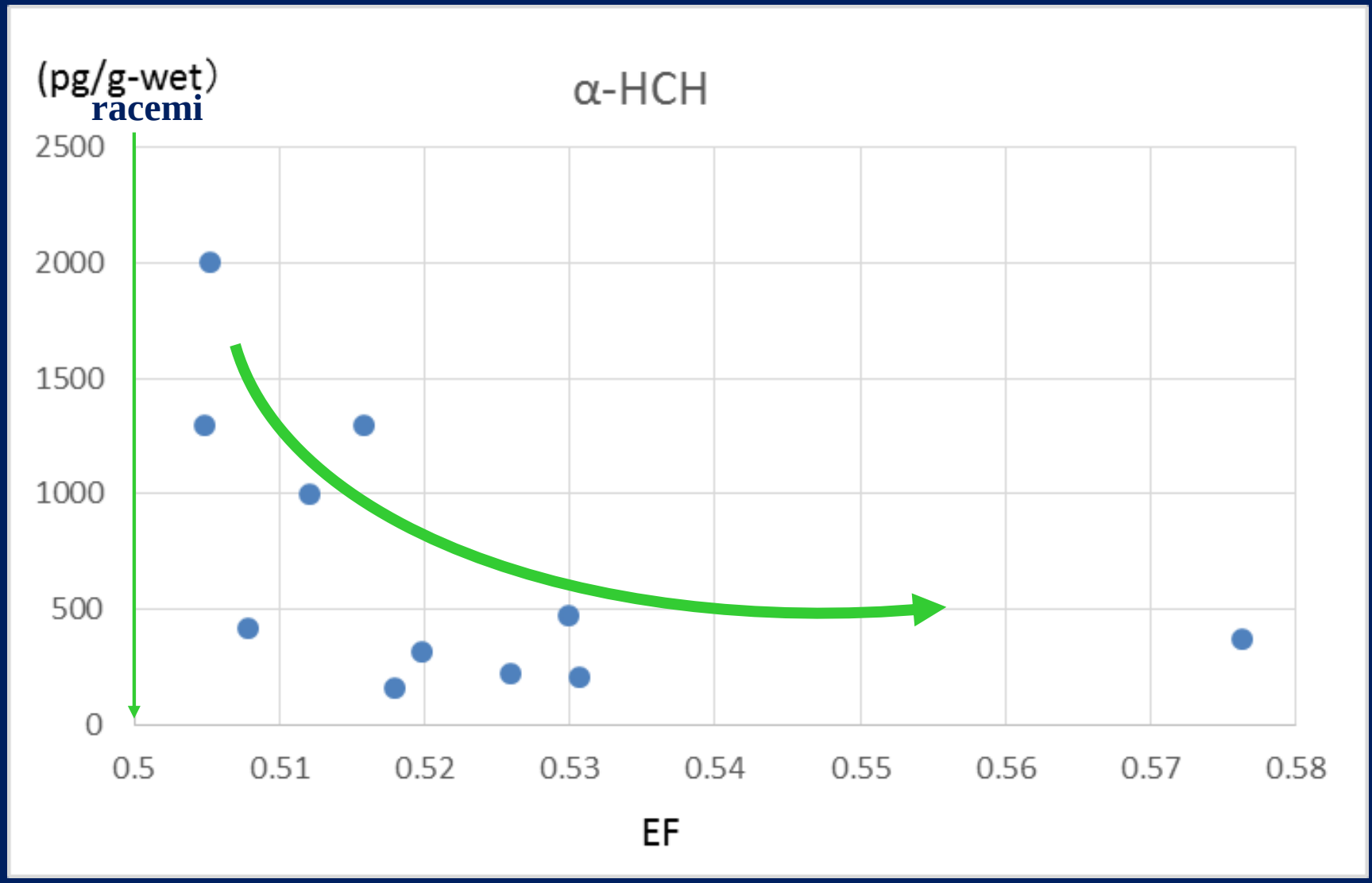
EF value of sea sediment



MC5 : one component of chemical product



***o,p´*– DDD : metabolite of *o,p´*– DDT**



alpha-HCH : one component of HCH

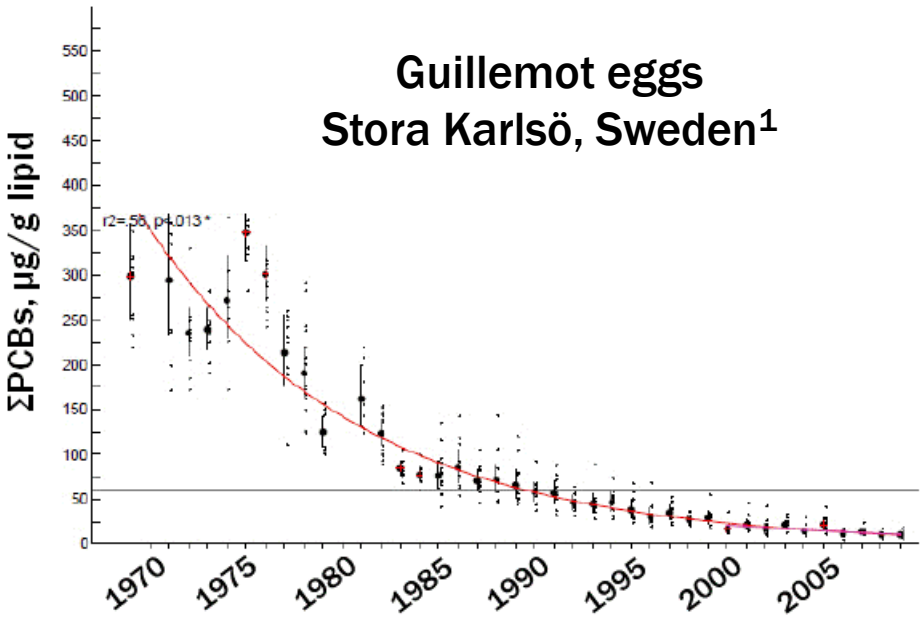
Lesson 2

possibility of evaluation for environmental impact

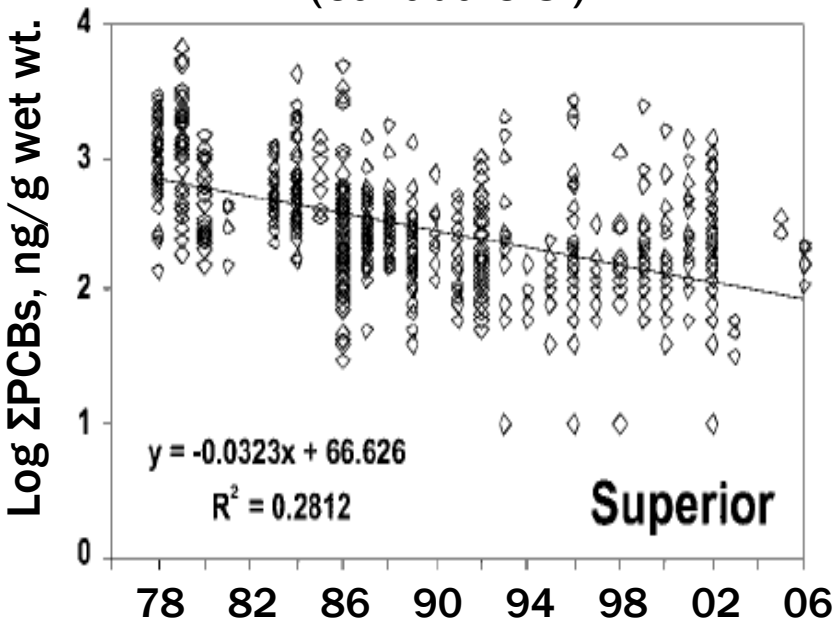
Climate change and POPs pollution

Some successes…

Guillemot eggs
Stora Karlsö, Sweden[1]



Lake trout, Lake Superior
(Canada-U.S.)[2]

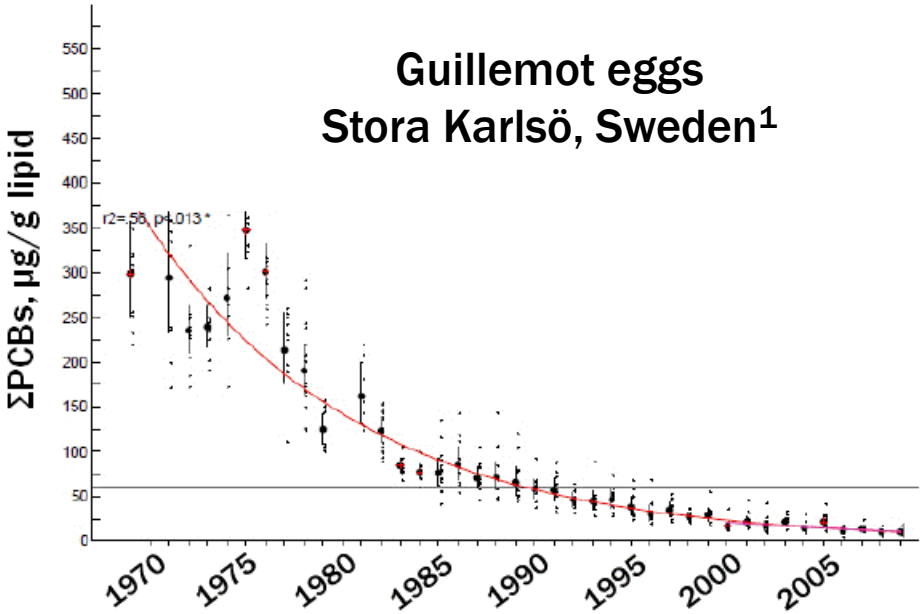


1. Swedish Environmental Protection Agency, 2012. *National Implementation Plan for the Stockholm Convention*, Report 6298.

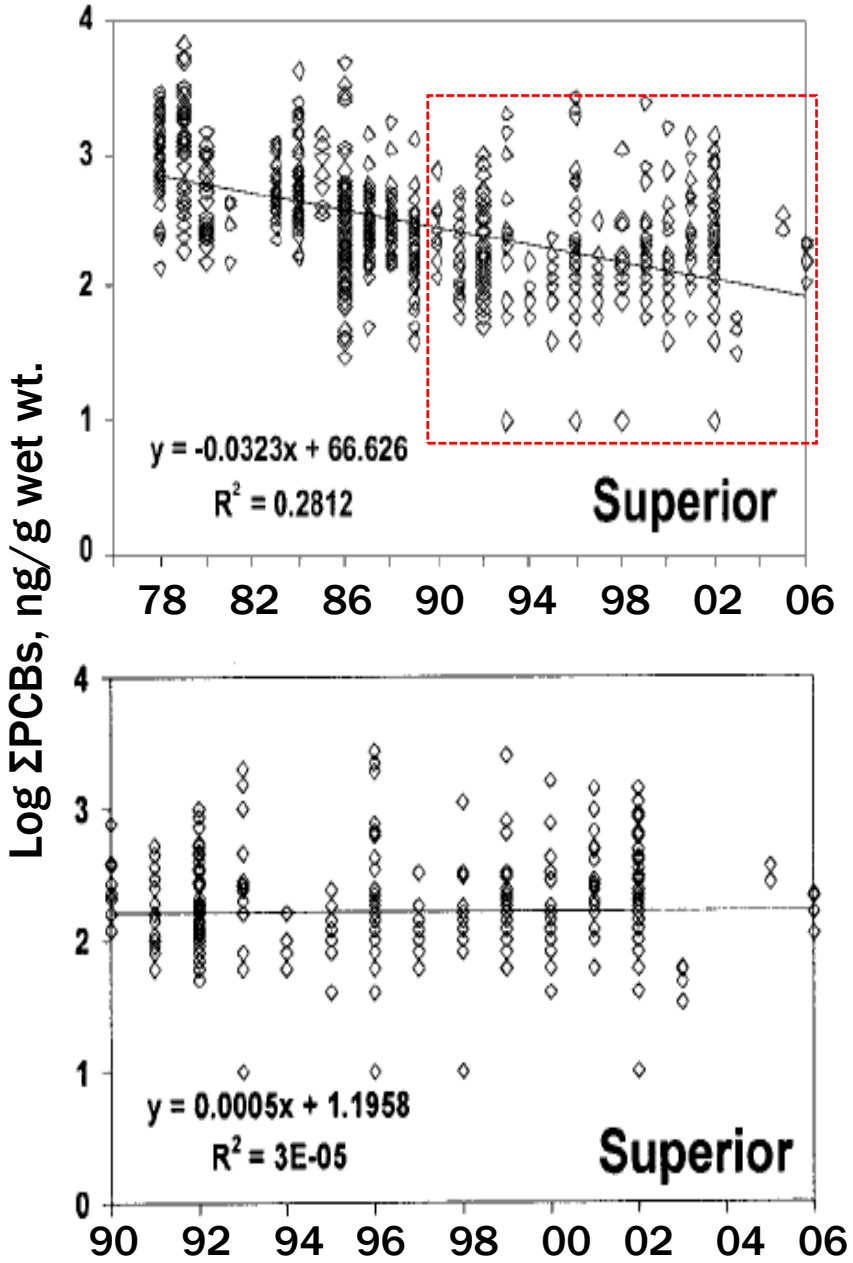
2. Bhavsar, S.P. et al., 2007. *J. Great Lakes Res.* 33, 592-605.

Some successes…but further to go

Guillemot eggs
Stora Karlsö, Sweden[1]



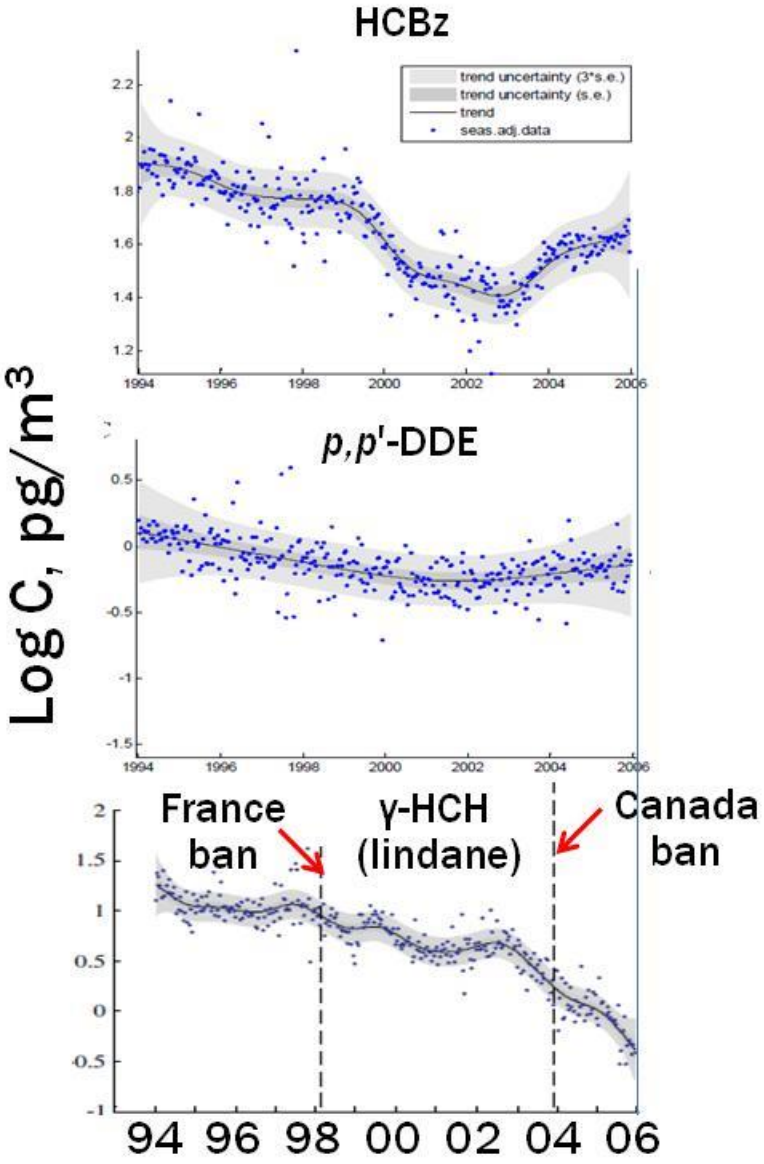
Lake trout, Lake Superior (Canada-U.S.)[2]



1. Swedish Environmental Protection Agency, 2012. *National Implementation Plan for the Stockholm Convention*, Report 6298.

2. Bhavsar, S.P. et al., 2007. *J. Great Lakes Res.* 33, 592-605.

POPs in arctic air at Zeppelin Mountain, Svalbard



Compound	Time for 50% decrease, years
γ-HCH	4.6
α-HCH	4.7
HCBz	18
cis-chlordane	16
trans-chlordane	9.3
p,p'-DDE	11
p,p'-DDT	4.1

Becker, S. et al., 2008. *Atmos. Environ.* 42, 8225-8233; Becker, S. et al., 2008. *Atmos. Environ.* 42, 8225-8233; Hung, H. et al. 2010. *Sci. Total Environ.* 408, 2854-2873.

Secondary Sources: “Recycled” POPs

GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L24602, doi:10.1029/2009GL041340, 2009

Cycling of DDT in the global environment 1950–2002: World ocean returns the pollutant

Irene Stemmler[1,2] and Gerhard Lammel[3,4]

nature climate change — LETTERS

PUBLISHED ONLINE: 24 JULY 2011 | DOI: 10.1038/NCLIMATE1167

Revolatilisation of POPs in the Arctic induced by climate change

Jianmin Ma, Hayley Hung, Chongguo Tian, Roland Kallenborn

Luca Nizzetto et al.

Environ. Sci. Technol. **2010**, *44*, 6526–6531

Environmental Science & Technology Feature

Past, Present, and Future Controls on Levels of Persistent Organic Pollutants in the Global Environment

Atmos. Chem. Phys., 11, 12799–12811, 2011

Soil-air exchange controls on background atmospheric concentrations of organochlorine pesticides

A. Cabrerizo, J. Dachs, K. C. Jones, and D. Barceló

Environ. Sci. Technol. **2009**, *43*, 8173–8177

Blast from the Past: Melting Glaciers as a Relevant Source for Persistent Organic Pollutants

CHRISTIAN BOGDAL,*,†,‡ PETER SCHMID,‡ MARKUS ZENNEGG,‡ FLAVIO S. ANSELMETTI,§ MARTIN SCHERINGER,† AND KONRAD HUNGERBÜHLER†

Environ. Sci. Technol. **2008**, *42*, 3958–3962

Melting Glaciers: A Probable Source of DDT to the Antarctic Marine Ecosystem

HEIDI N. GEISZ,* REBECCA M. DICKHUT, MICHELE A. COCHRAN, WILLIAM R. FRASER,† AND HUGH W. DUCKLOW‡

Environ. Sci. Technol. **2011**, *45*, 876–881

Air—Water Exchange of Anthropogenic and Natural Organohalogens on International Polar Year (IPY) Expeditions in the Canadian Arctic

FIONA WONG,†,‡ LIISA M. JANTUNEN,† MONIKA PUĆKO,§,∥ TIM PAPAKYRIAKOU,∥ RALF M. STAEBLER,⊥ GARY A. STERN,§,∥ AND TERRY F. BIDLEMAN*,†

Impacts of Climate Change on Environmental Fate and Long-Range Transport of POPs[1]

- Primary and secondary volatilisation sources
- Melting of polar ice caps and mountain glaciers
- Degradation and transformation
- Biomagnification (alteration of food webs)

Physical factors:

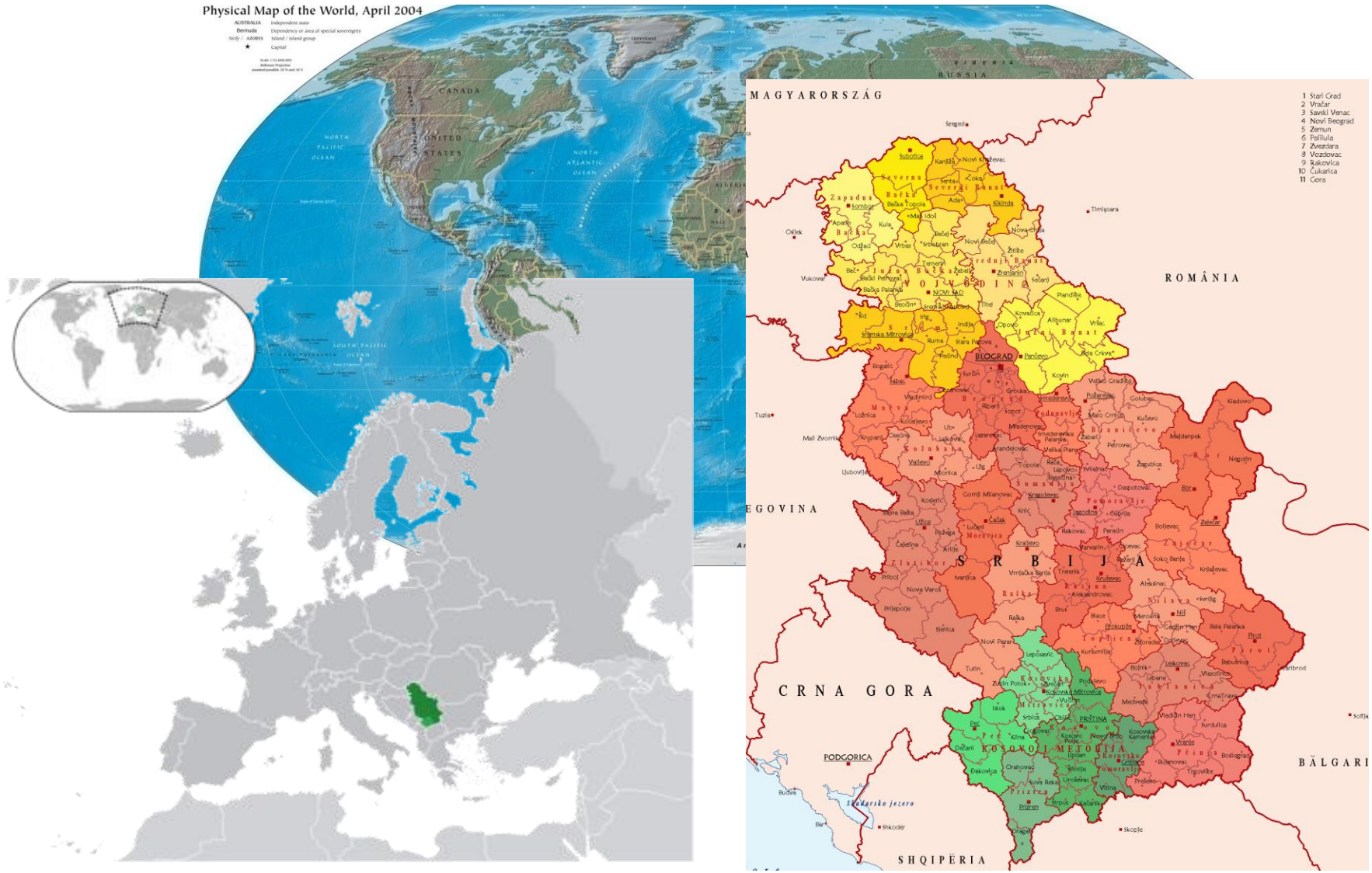
- Wind fields and wind speed
- Precipitation
- Ocean currents
- Frequency of extreme events – e.g., floods[2,3]

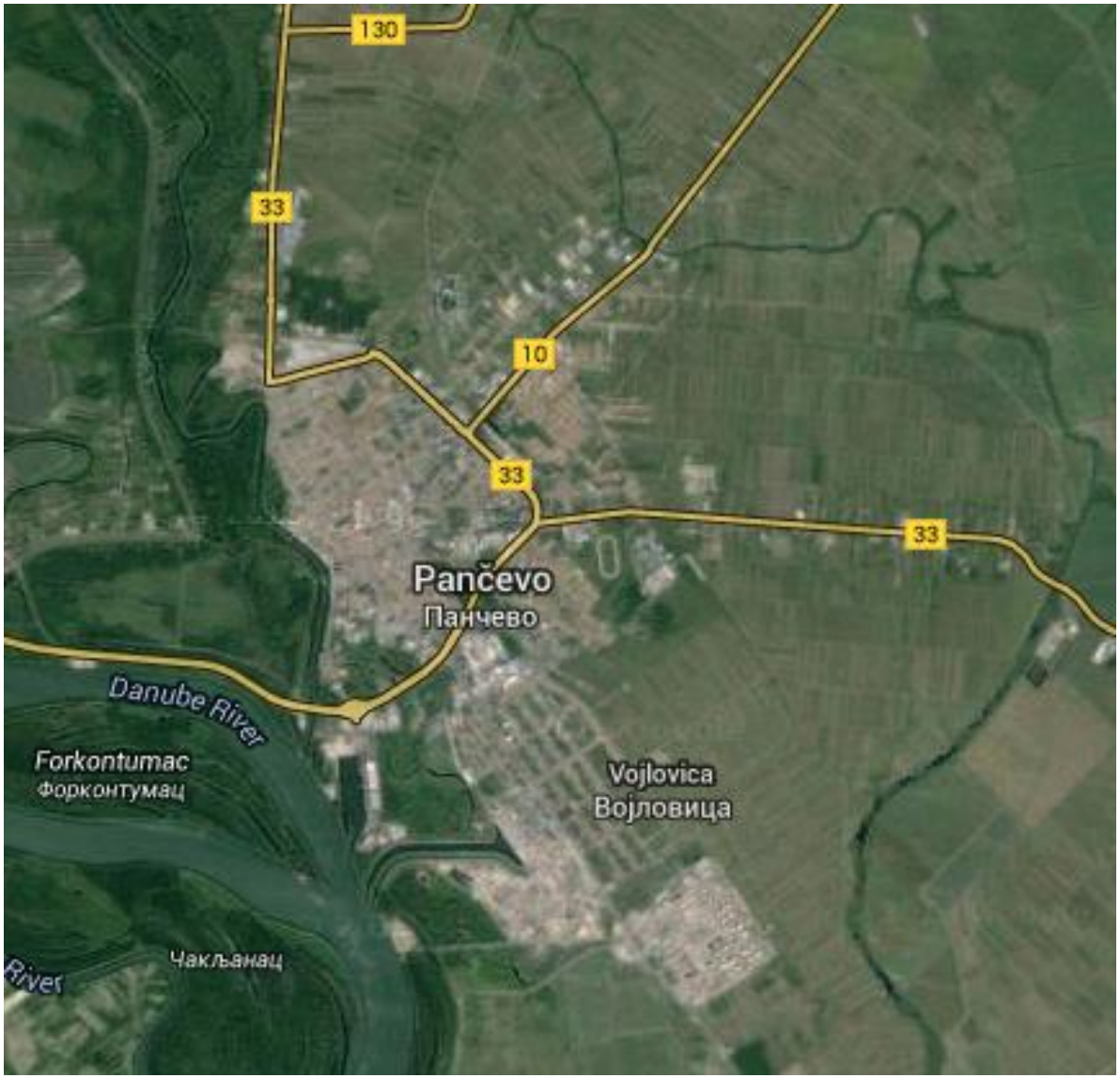
1. UNEP/AMAP 2011. *Climate Change and POPs: Predicting the Impacts.* Report of the UNEP/AMAP POPs Expert Group, Secretariat of the Stockholm Convention, Geneva, 62 pp. 2. Tysklind, M. et al., Dioxin-2012, Cairns, Australia. 3. Hilscherova, K. et al., 2007. *J. Soil Sed*. 7, 167-177.

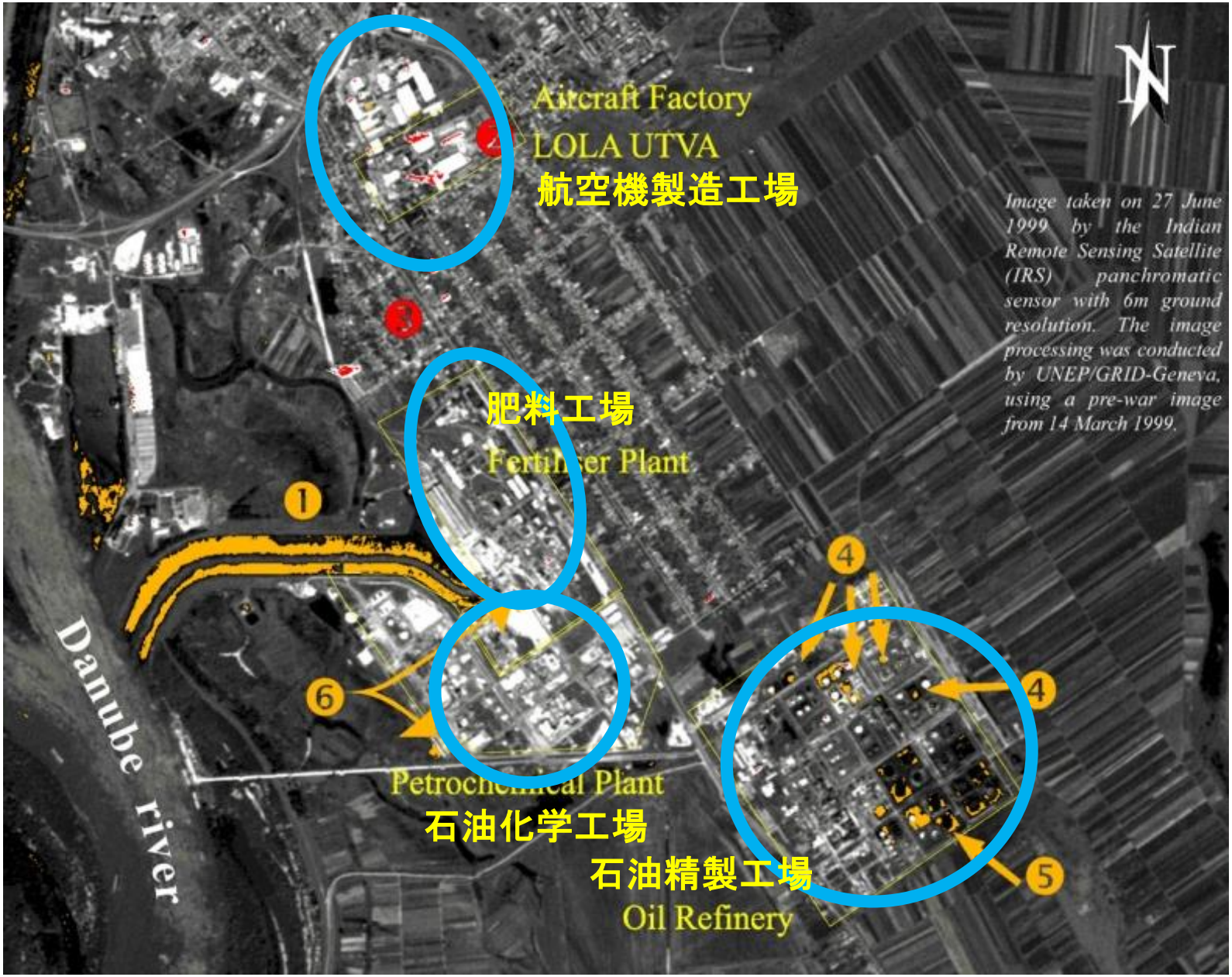
Civil war in Serbia
NATO bombing campaign

1999

Serbia - geography




130
33
10
33
33
Pančevo
Панчево
Danube River
Forkontumac
Форконтумац
Vojlovica
Војловица
Чакљанац
River


Aircraft Factory
LOLA UTVA
航空機製造工場
Image taken on 27 June 1999 by the Indian Remote Sensing Satellite (IRS) panchromatic sensor with 6m ground resolution. The image processing was conducted by UNEP/GRID-Geneva, using a pre-war image from 14 March 1999.
肥料工場
Fertiliser Plant
Danube river
Petrochemical Plant
石油化学工場
石油精製工場
Oil Refinery

NATO bombing in 1999

Bombings and Chemical Release at Pancevo

HIP Petrohemija

- **Vinyl chloride** storage tank was hit and the **440 tons** of material that was stored in it burned
- **2,100** tons of **1,2-dichloroethane** was spilled
- **8 tons** of metallic **mercury** was released into the environment (Most of the material that was spilled onto the soil was recovered, but that is not the case for the mercury that was spilled into the Channel)
- The **transformer station** at the factory was also damaged during this attack **polychlorinated biphenyls (PCBs)** were released from the transformer

NIS Oil Refinery

- Approximately **62,000 tons** of **crude oil and oil products** burned and **5,000 to 7,000 tons** leaked onto the soil and into the sewer system. The spills resulted in **100,000** square meters (10 hectares) of contaminated soil within the refinery complex.

HIP Azotara

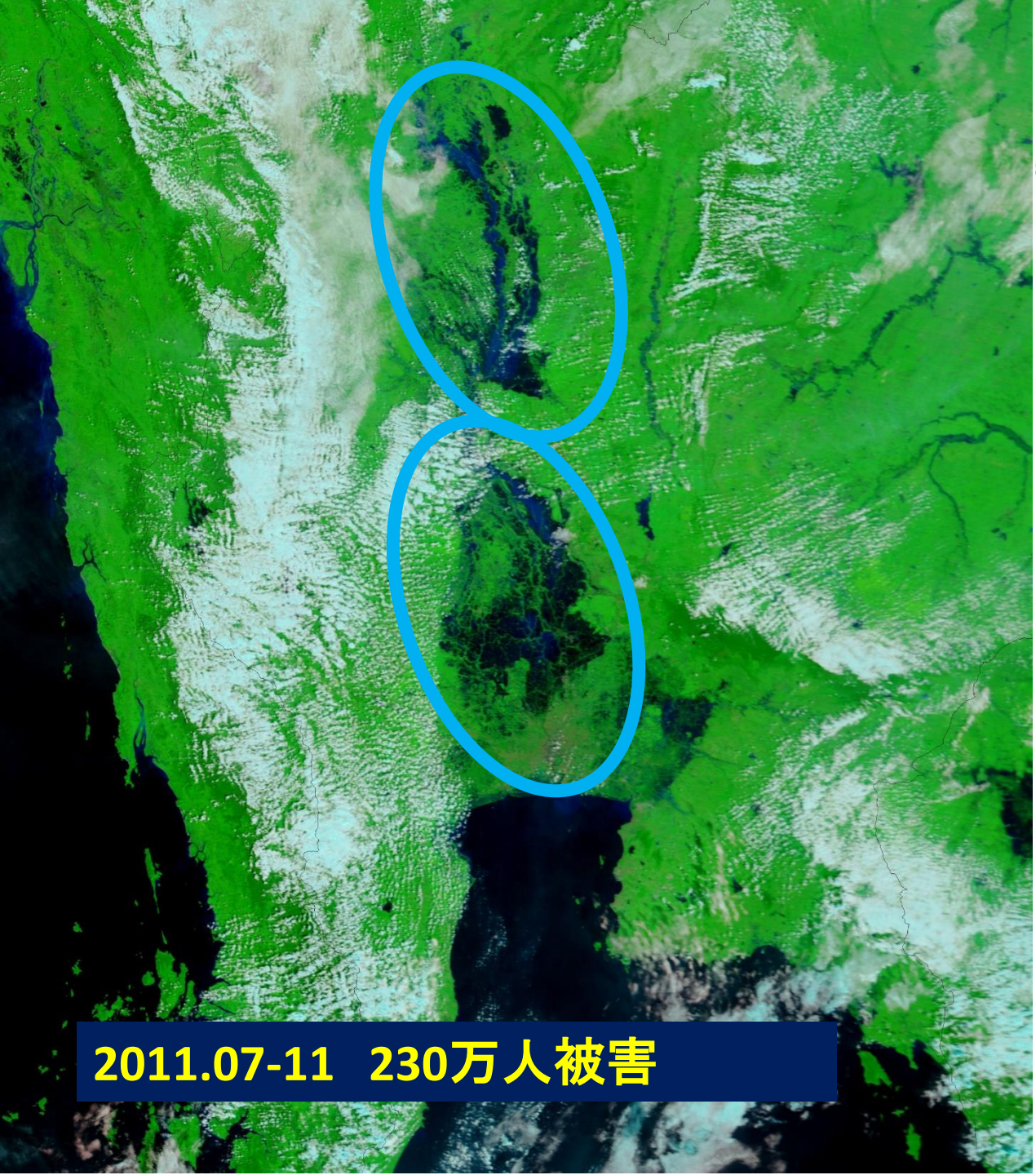
- **250 tons** of **ammonia** was intentionally dumped directly into the wastewater canal to prevent it from being released into the atmosphere after an explosion.

Sriram Gopal and Nicole Deller, *Precision Bombing, Widespread Harm Two Case Studies of the Bombings of Industrial Facilities at Pancevo and Kragujevac During Operation Allied Force, Yugoslavia 1999*

Table 2: Summary of pollutants released as a result of the 1999 bombings in Pancevo

Substance	Location	Amount Released (metric tons)	Emission Route
Ammonia	HIP Azotara	250	Waste channel
Calcium ammonium nitrate, phosphates, potassium chloride	HIP Azotara	250	Most burned, some into channel
Crude oil	HIP Azotara	150	Most burned, some into channel
Vinyl chloride	HIP Petrohemija	460	Burned
1,2-dichloroethane	HIP Petrohemija	2,100	50% to channel, 50% to soil
Mercury	HIP Petrohemija	8	7.8 metric tons to soil, remainder to channel
Sodium Hydroxide	HIP Petrohemija	100	Soil and waste channel
Ethyl-, propylene	HIP Petrohemija	1,900	Intentionally burned
Hydrochloric acid	HIP Petrohemija	130	Soil and waste channel
Crude oil and derivatives	NIS Oil Refinery	85,000	80,000 metric tons burned, remainder spilled onto soil

Floods



2011.07-11　230万人被害

2014.05
Serbia

Thank you for your attention

> PCDD/F in flyash, MS/MS : 17:10 (Mon) chamber-1

> Halogenated-PAH : 14:40 (Thr) conference-1

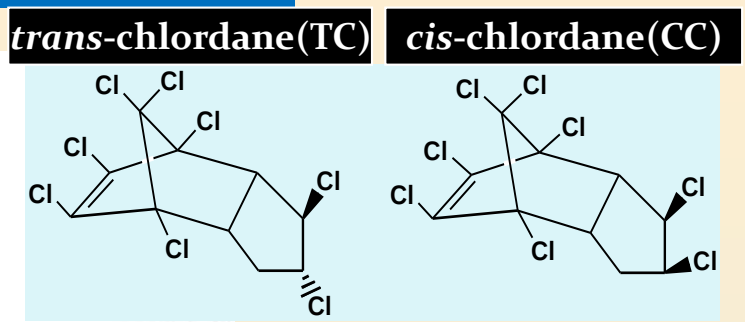
> OH-PCB in urine sample : 16:50 (Thr) chamber-2

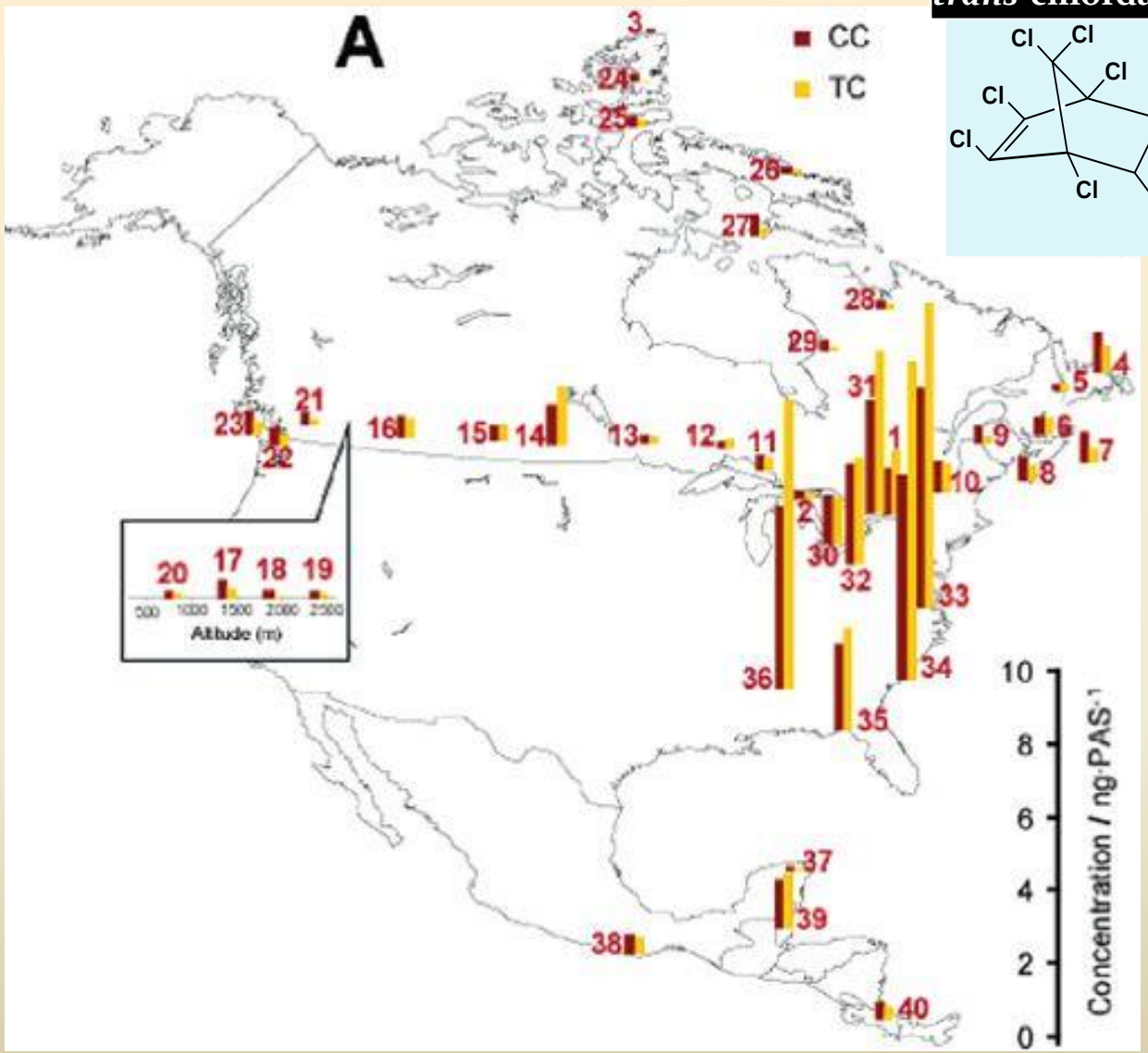
> POPs in soot from marine diesel engines : poster-101

> Benzotriazole in Environmental sample : poster-174

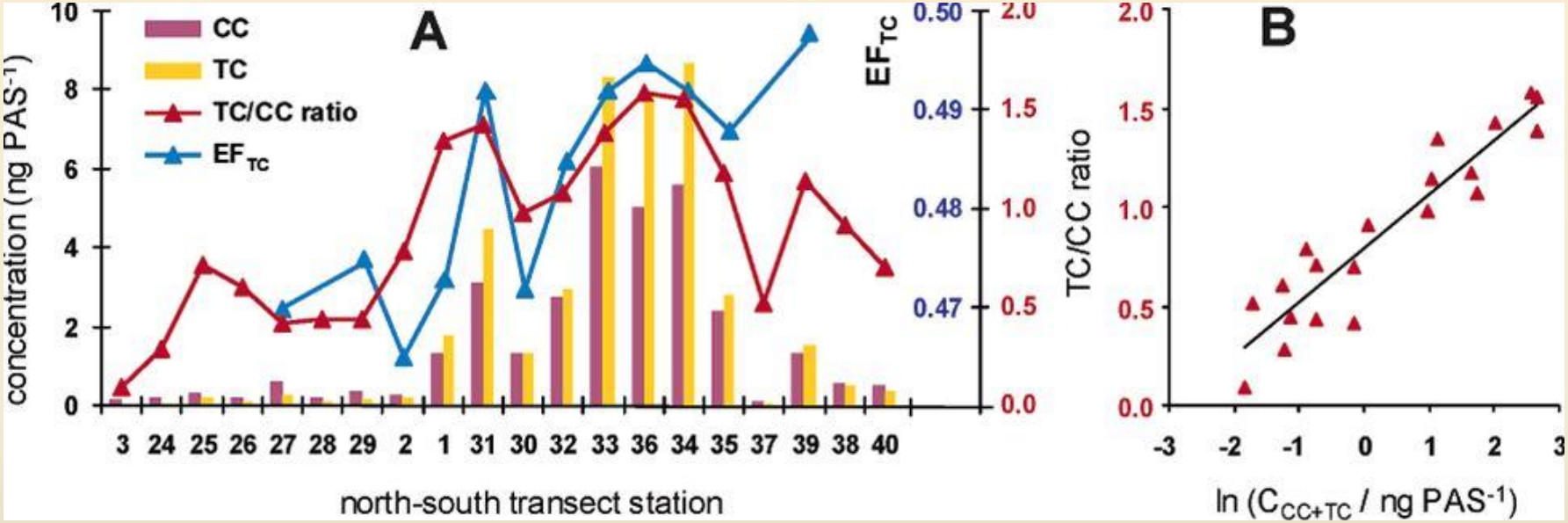
Welcome to dioxin 2019 in Kyoto

Chlordane level in ambient air





Shen et al (2005): Environ. Sci. Technol. 39(2)



Shen et al (2005): Environ. Sci. Technol. 39(2)