POPs Contamination in the Korean Coastal Environment and its possible sources

Sang Hee Hong

Korea Ocean Research and Development Institute

KORDI 한국해양연구원

MERL
Marine Environmental Research Laboratory

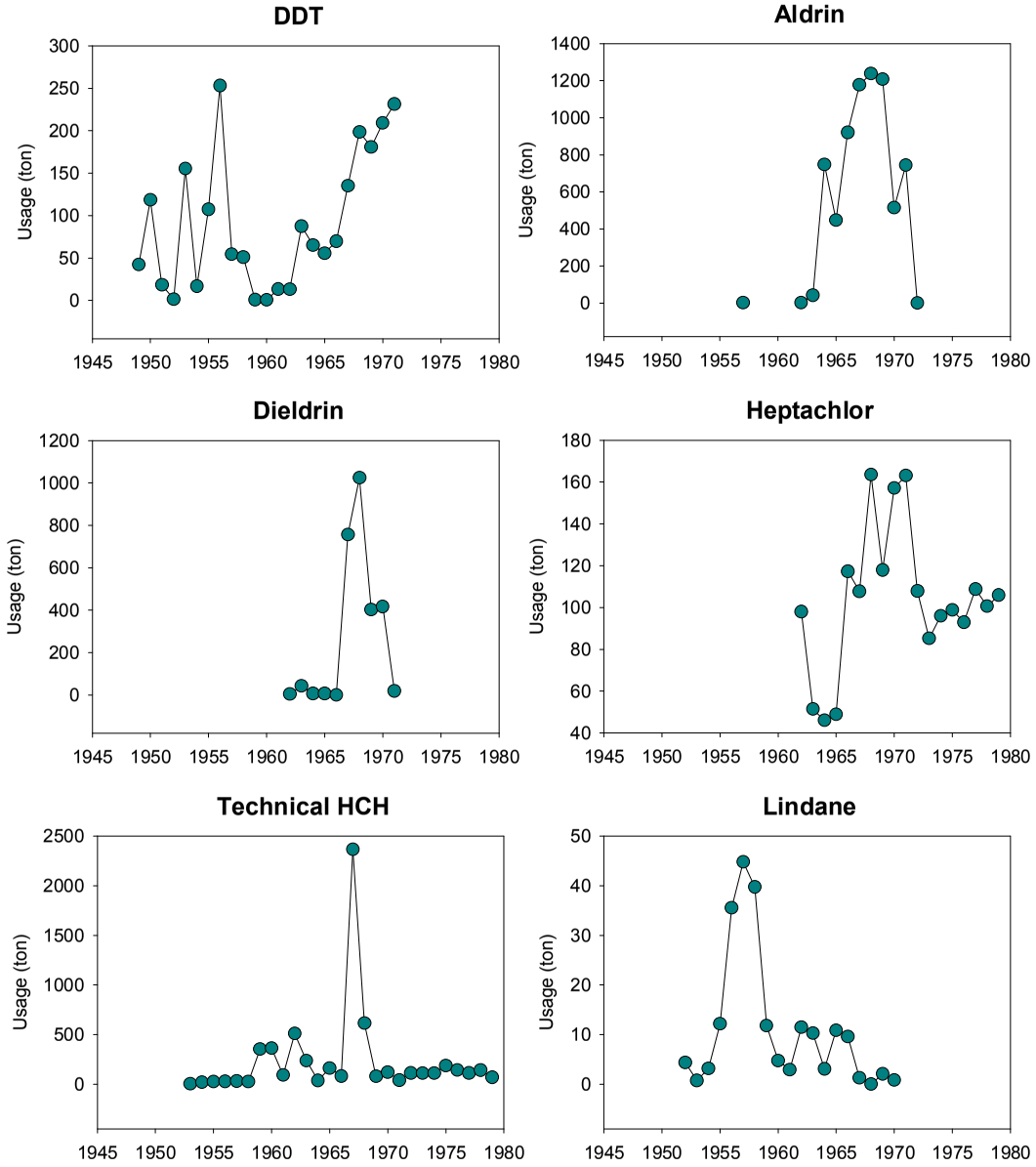
Stockholm Convention

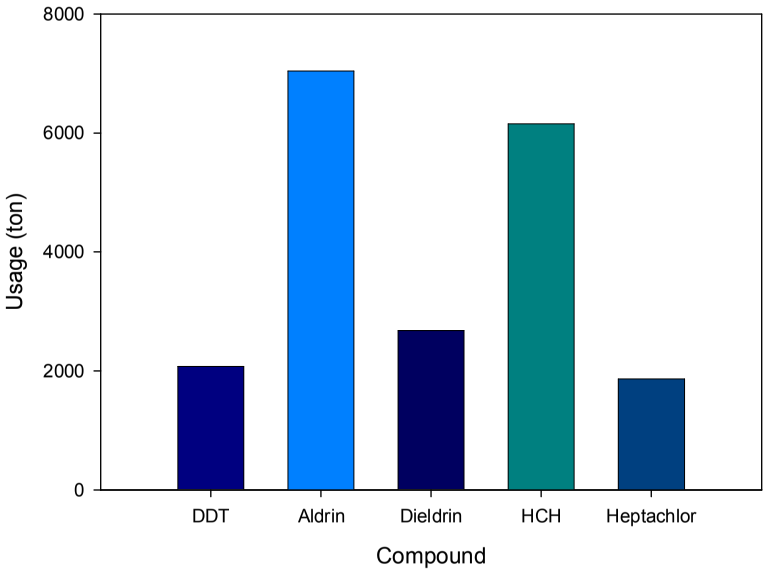
- The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (POPs).
- The Convention was adopted on 22 May 2001.
- The Convention enter into force on May 2004.
- Republic of Korea ; signature - 4 Oct 2001
  ratification - 25 Jan 2007

POPs Regulation in Korea

POPs	Related Act	Regulation	Year
Aldrin	Toxic Chemicals Control Act	Banned	1999
	Agrochemicals Management Act	Banned	**1969**
Dieldrin	Toxic Chemicals Control Act	Banned	1999
	Agrochemicals Management Act	Banned	**1970**
Endrin	Toxic Chemicals Control Act	Banned	1999
	Agrochemicals Management Act	Banned	**1969**
Chlordane	Toxic Chemicals Control Act	Banned	1999
	Agrochemicals Management Act	Banned	**1969**
Heptachlor	Toxic Chemicals Control Act	Banned	1999
	Agrochemicals Management Act	Wettable: Banned	**1970**
		Emulsion: Banned	**1979**
DDT	Toxic Chemicals Control Act	Banned	1991
	Agrochemicals Management Act	Wettable: Banned	**1969**
		Emulsion: Banned	**1971**
Toxaphene	Toxic Chemicals Control Act	Banned	1991
	Agrochemicals Management Act	Banned	**1982**
PCBs	Toxic Chemicals Control Act	Banned	1996
	Electrical Installation and Inspection Act	Banned	**1979**
Hexachloroben zene	No regulation; This chemical has never been manufactured, imported or used in Korea.		
Mirex	No regulation; This chemical has never been manufactured, imported or used in Korea.		
Dioxins/Furans	Waste Management Act	restricted emission	**1997**

POPs usage in Korea

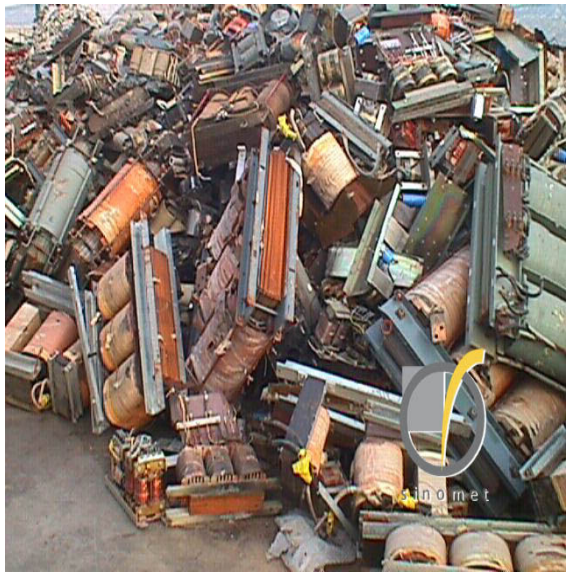




The danger is not over

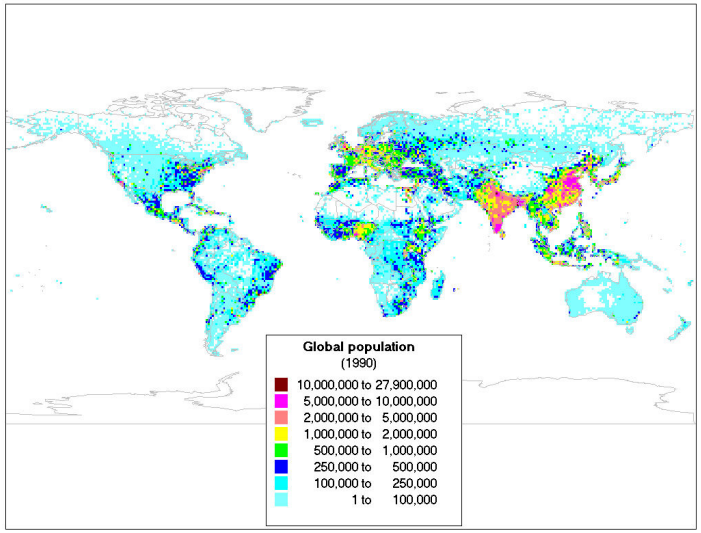
There are many hundreds of tonnes of PCBs ‘stockpiled’ in the world, for example in transformer and capacitor.

Toxic chemicals, including dioxins, furans and PCBs, can form as by-products when chlorinated compounds are manufactured or burned.

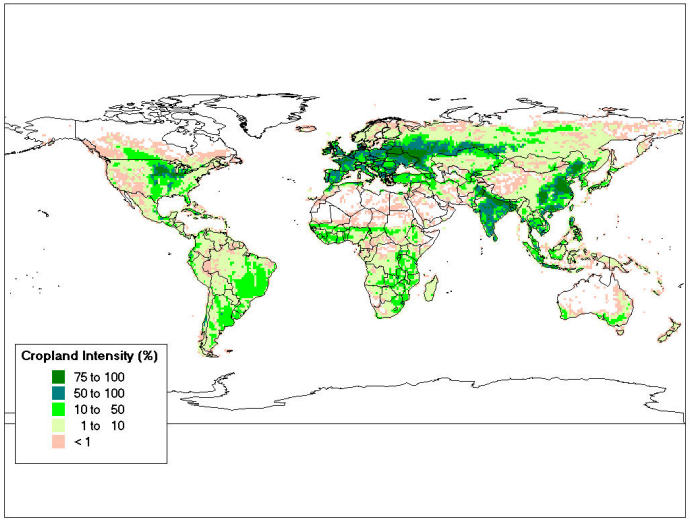


Usage and Ban for HCH and DDT

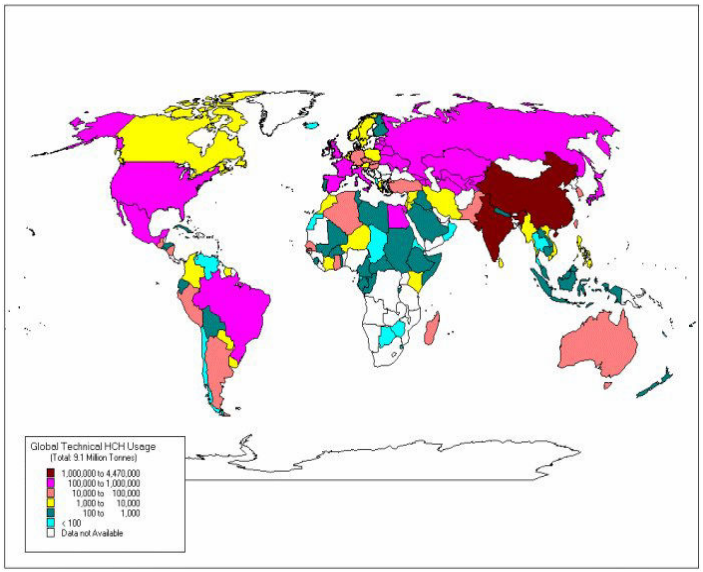
Global population



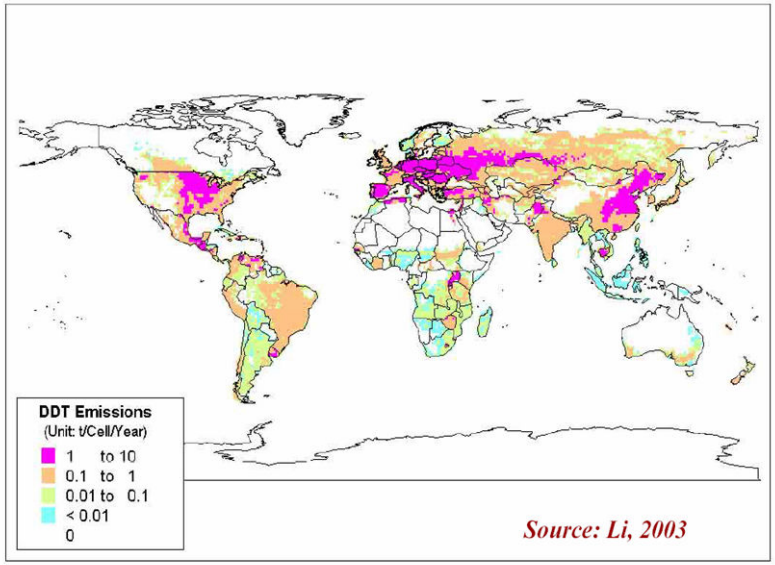
Cropland Intensity



Global technical HCH usage



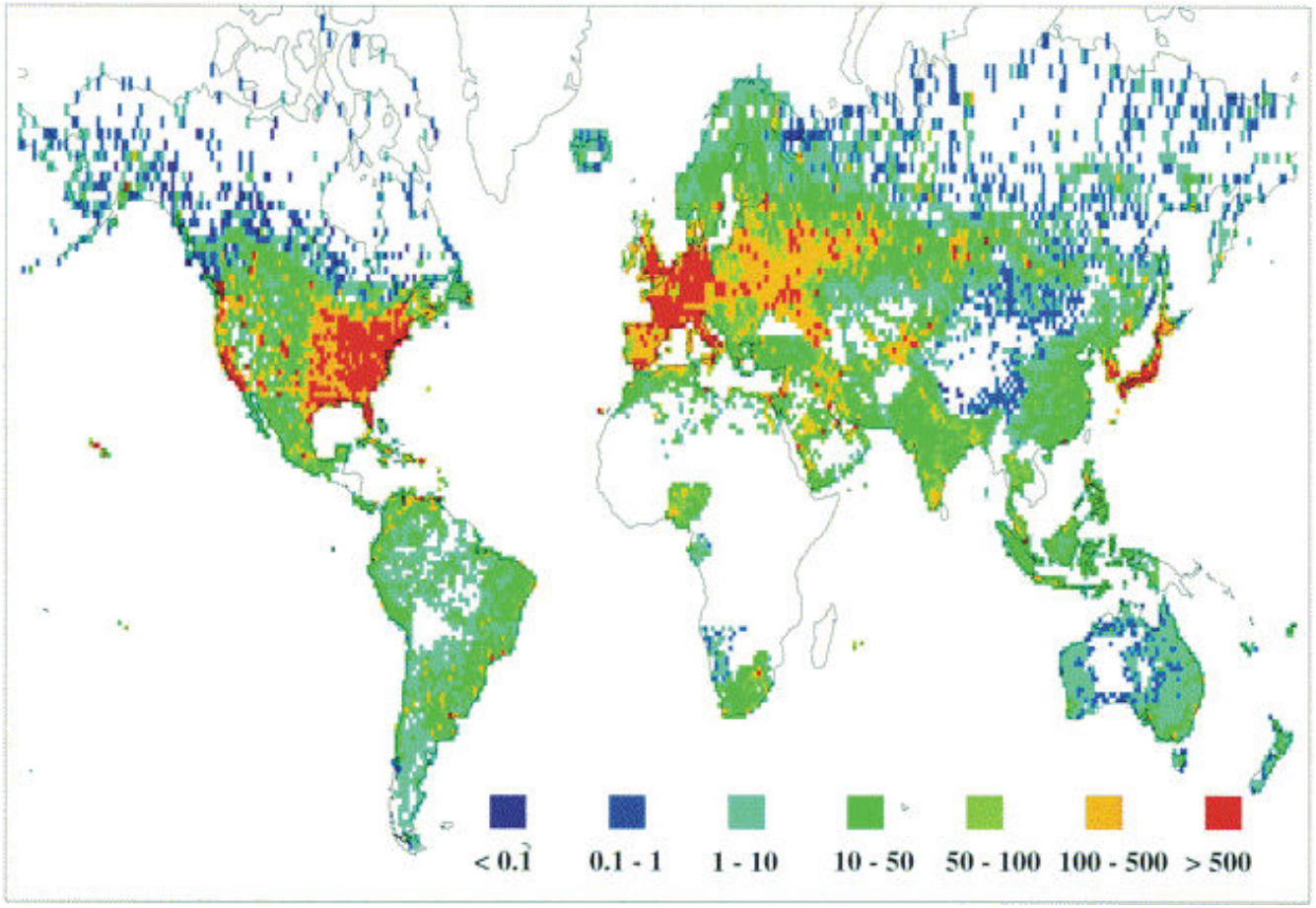
Global DDT Emission in 2000



http://www.msc-smc.ec.gc.ca/data/gloperd/EmissionInv_e.cfm

Estimated cumulative global usage of PCBs

- ***Estimated global production*** **:** 1.3 million tons (1930 – 1993)
- ***Usage of PCB in Korea*** **:** 560 tons (1975 - 1984)



Breivik et al. (2002) Sci. Total Environ. 290(1-3), 199-224

Content

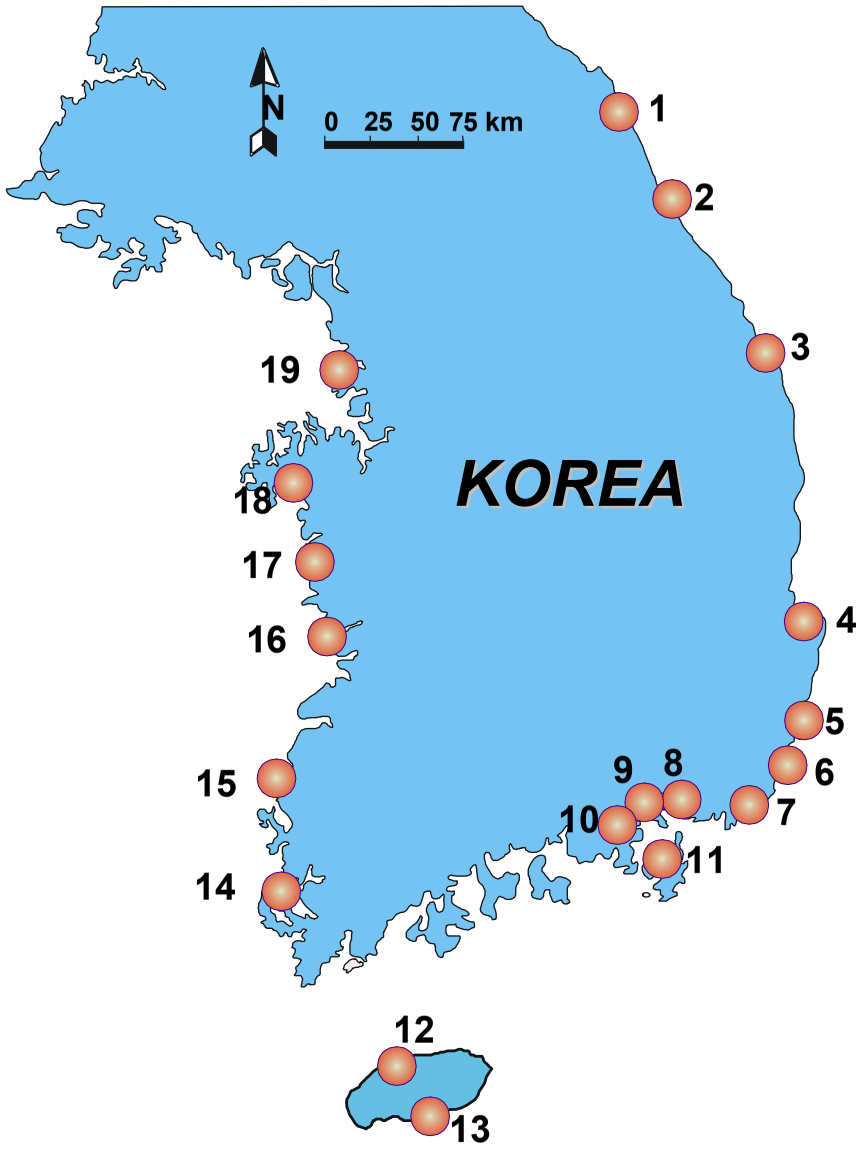
Case study I.

Fish monitoring study on POPs in the Korean Coastal regions

Case study II.

Possible point source of POPs in the Korean Coastal regions

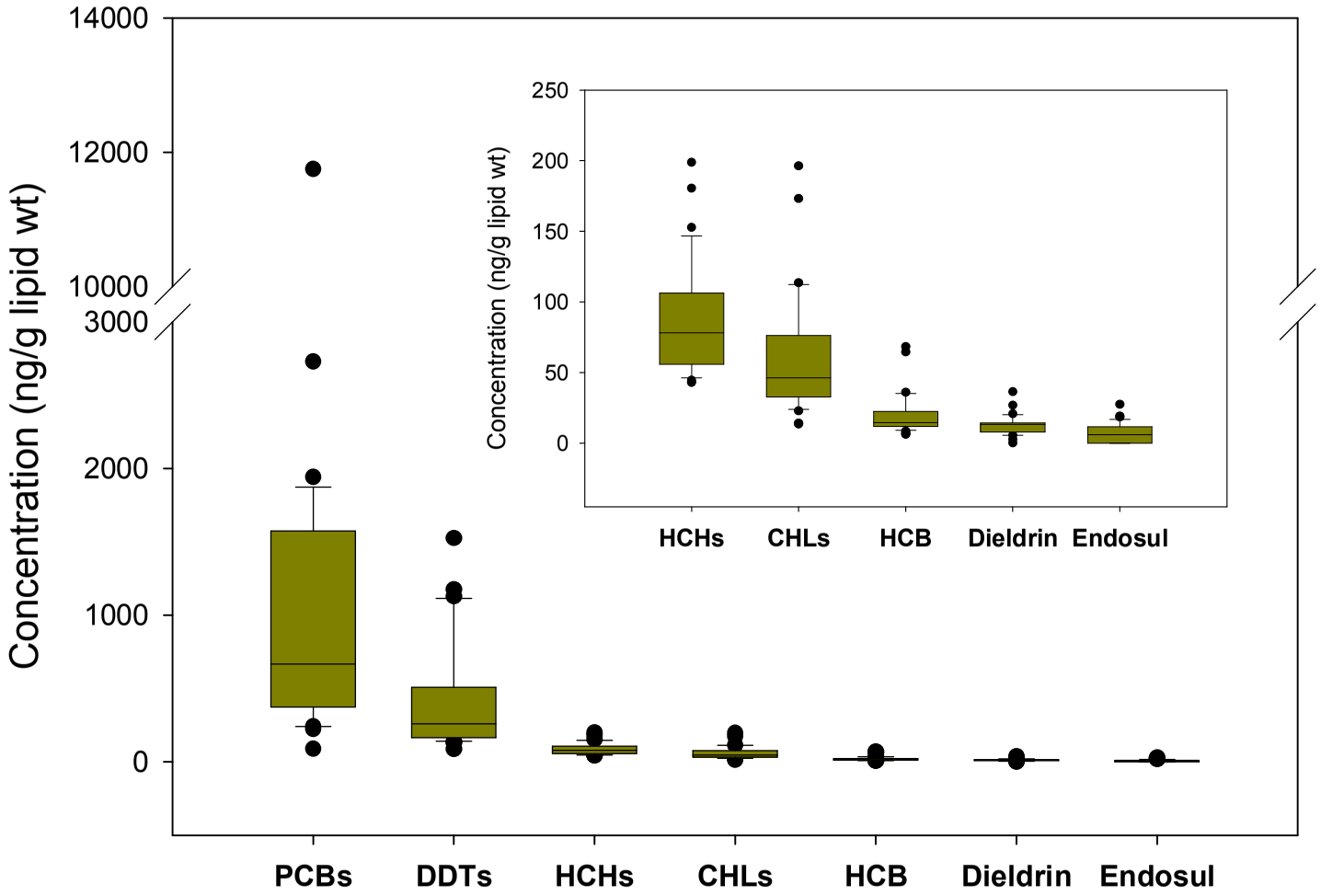
Location map of fish sampling and purchasing sites



Elknorn sculpin (*Alcichthy alcicornis*) *(1-1)*
Browen sole (*Limanda herzensteini*) *(1-2)**
Elknorn sculpin (*A. alcicornis*) *(2-1)*
Elknorn sculpin (*alciornis*) *(2-2)**
Elknorn sculpin (*A. alcicornis*) *(3-1)**
Whip sculpin (*Gymnocanthus intermedius*) (3-2)*
Greenling (*Hexagrammos otakii*) *(4-1)*
Elknorn sculpin (*A. alcicornis*) (4-2)*
Marbled sole (*Limanda yokohamae*) *(5-1)*
Willowy flounder (*Tanakius kitaharai*) *(5-2)**
Greenling (*H. otakii*) *(6-1)*
Striped mullet (*Mugil cephalus*) *(7-1)*
Willowy flounder (*T. kitaharai*) *(7-2)**
Finespotted flounder (*Pleuronichthys cornutua*) *(8-1)*
Greenling (*H. otakii*) *(8-2)*
Stone flounder (*Kareius bicoloratus*) *(9-1)*
Striped mullet (*M. cephalus*) *(9-2)**
Greenling (*H. otakii*) *(10-1)*
Nake-headed goby (*Favonigobius gymnauchen*) *(11-1)*
Dusky spinefoot (*Siganus fusceesens*) *(12-1)*
Silvery pomfret (*Pampus argenteus*) *(12-2)**
Striped mullet (*M. cephalsus*) *(13-1)*
Bartail flat head (*Platycephalus indicus*) *(14-1)**
Browen sole (*L. herzensteini*) *(14-2)**
Striped mullet (*M. cephalus*) *(14-3)**
Yellow drum (*Nibea albiflora*) *(15-1)**
Greenling (*H. otakii*) *(16-1)**
Silvery pomfret (*P. argenteus*) *(16-2)**
Browen sole (*L. herzensteini*) *(16-3)**
Greenling (*H. otakii*) *(17-1)**
Mud Hopper (*Periopthalmus sp.*) *(18-1)*
Striped mullet (*M. cephalsus*) *(18-2)*
Black rockfish (*Sebastes schlegeli*) *(19-1)**

*** Fish purchased at local market**

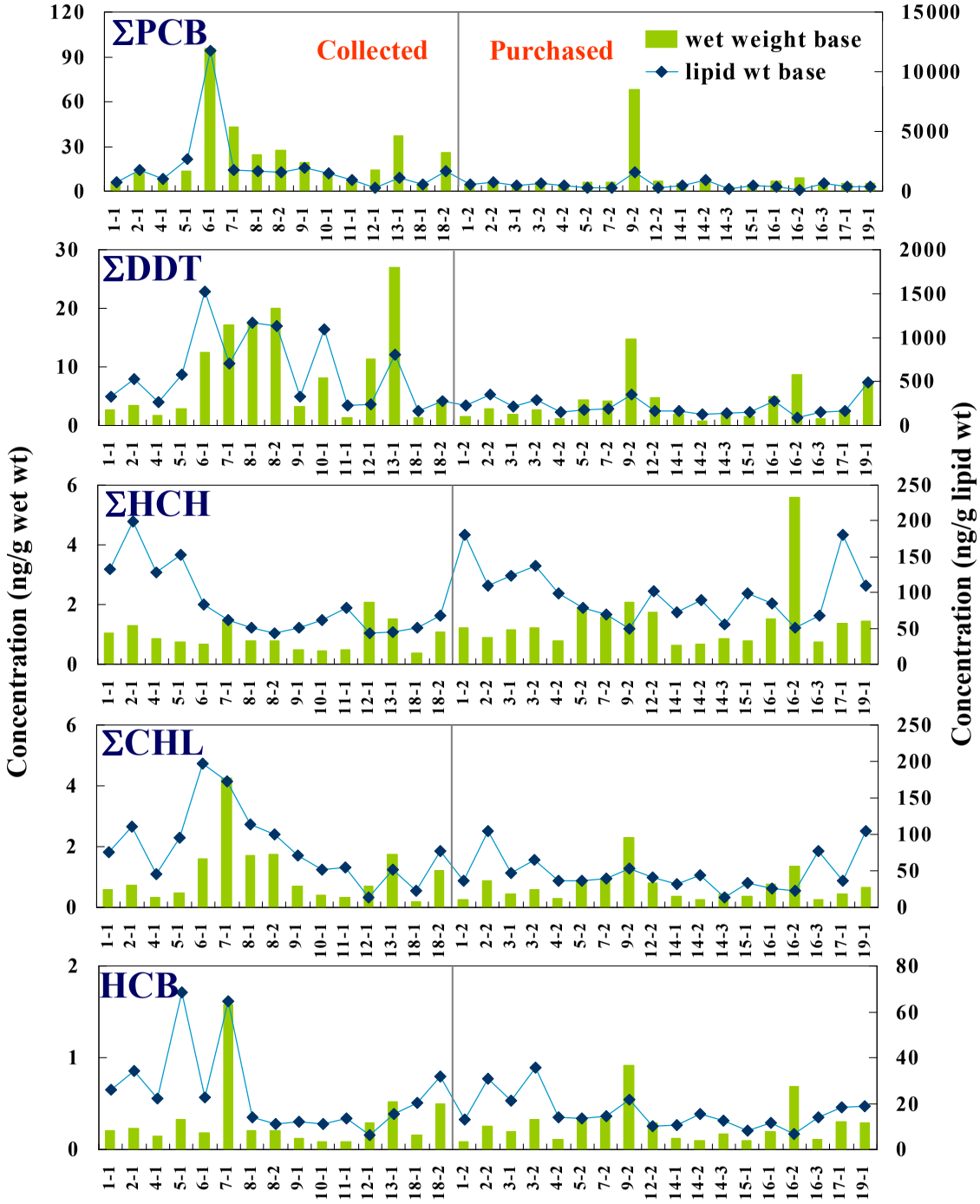
Contamination Status of POPs in fish from the Korean coastal regions



KORDI 한국해양연구원

MERL Marine Environmental Research Laboratory

Distribution of organochlorines in fish muscle samples



Screening value of organochlorines (using the EPA approach)

For noncarcinogens: $SV = (RfD \cdot BW)/CR$

For carcinogens: $SV = [(RL / CSF) \cdot BW] / CR$

SV = Screening Value (mg kg^{-1}; ppm)
BW = Body weight (kg), 70 kg
CR = Consumption rate of fish (g d^{-1}), 58.9 g d^{-1}
RfD = Oral reference dose (mg kg^{-1} d^{-1})
RL = Maximum acceptable risk level (dimensionless), 10^{-5}
CSF = Oral cancer slope factor (mg kg-1 $d^{-1})^{-1}$

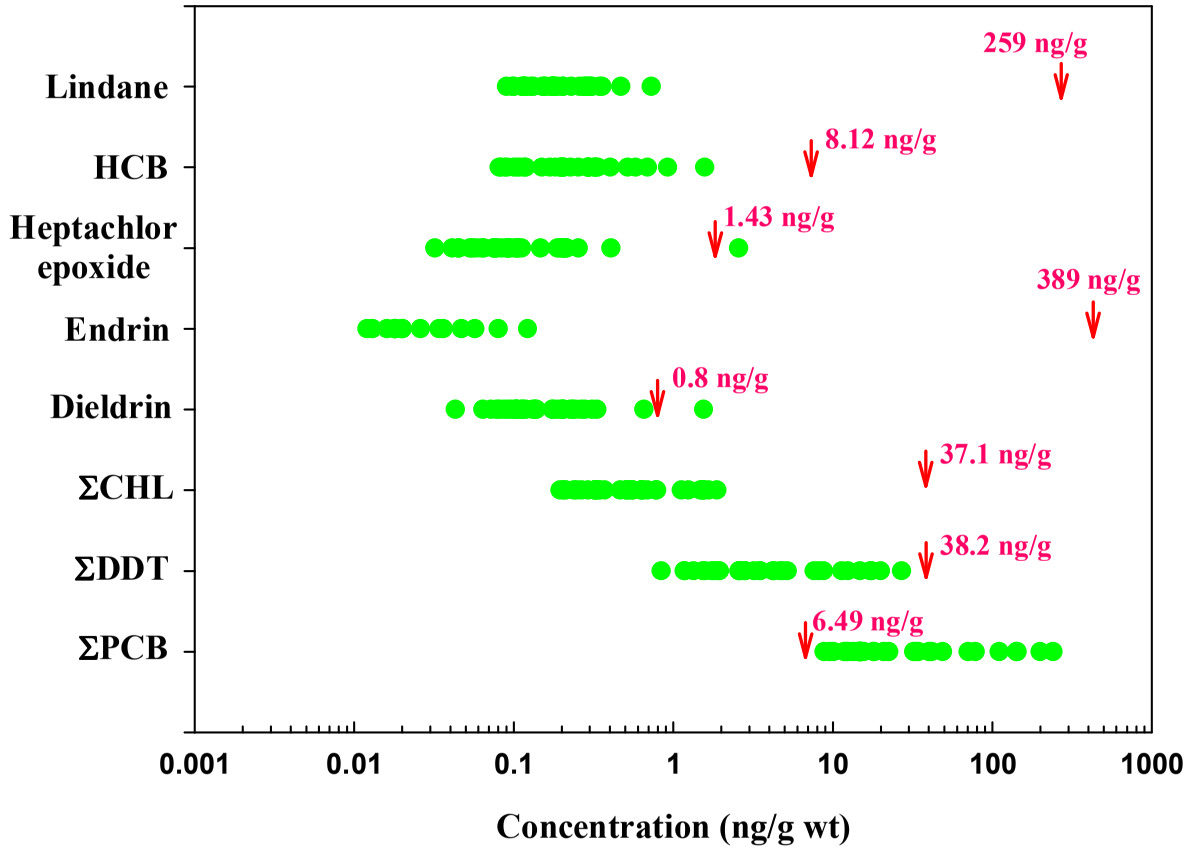
Comparison of estimated screening value screening values (SVs) in this study and US EPA SVs for organochlorines

Compounds	SV in this study[a] (ppm)	EPA SV for Recreational Fishers[b] (ppm)
PCBs	0.00504	0.02
DDTs	0.02966	0.117
CHLs	0.02881	0.114
Dieldrin	0.00063	0.0025
Endosulfan I and II	3.02513	24
Endrin	0.30251	1.2
Heptachlor Epoxide	0.00111	0.00439
HCB	0.0063	0.025
Lindane	0.00776	0.0307
Mirex	0.20168	0.8

[a]Pilot Study Screening Values developed using EPA Guidance document approach. Values reported are for carcinogens or non-carcinogens. Values based on 59.7 g day^{-1} of fish for a 60.2 kg adult.

[b]US EPA (2000a). Values based on consumption of 17.5 g day-1 of fish for a 70 kg adults.

Comparison of organochlorine concentrations in fish muscle from the coast of Korea with estimated screening values (SV) for fish consumption risk

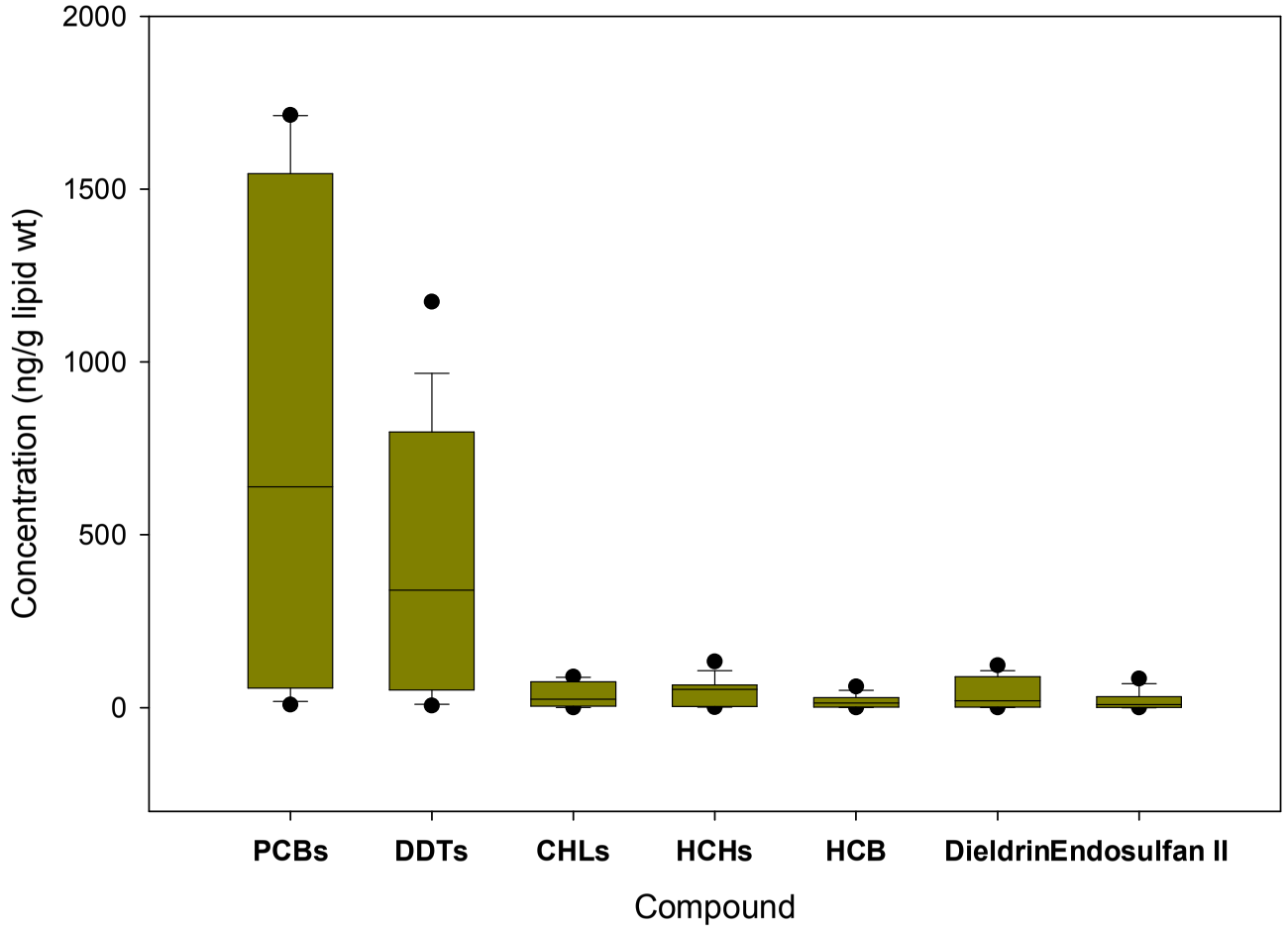


Fish Sampling in Han River Estuary

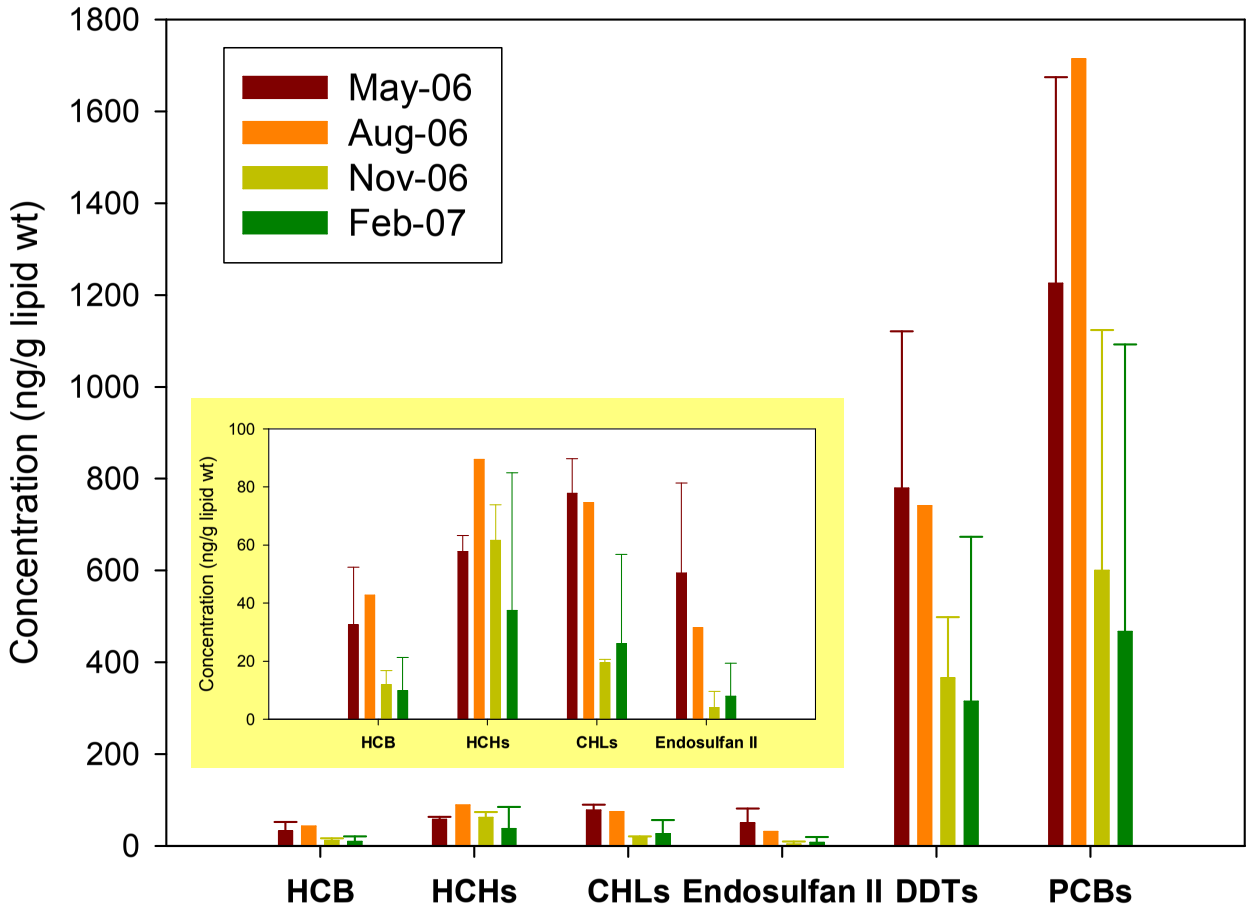
Fish Sampling in Han River Estuary

Date	Site	Species	Length (cm, mean±SD)	Weight (g, mean±SD)
06/5/25	C/B-1	crucian carp (*Carassius auratus*)	30.0 ± 0	407 ± 0
		striped mullet (*Mugil cephalus*)	44.5 ± 7.07	754 ± 207
		korean anchovy (Coilia ectens Jordan et Seale)	18.1 ± 2.81	15.8 ± 9.7
	C/B-3	striped mullet (Mugil cephalus)	45.2 ± 0	867 ± 0
06/8/24	C/B-3	carp (Cyprinus carpio)	44.3 ± 0	988 ± 0
06/11/9	C/B-1	striped mullet (Mugil cephalus)	12.4 ± 1.4	16.4 ± 3.6
	C/B-3	mud hopper (Periopthalmus cantonensis)	8.3 ± 2.41	5.87 ± 2.78
07/2/23	C/B-1	striped mullet (Mugil cephalus)	37.5 ± 1.39	506 ± 53.4
	C/B-3	striped mullet (Mugil cephalus)	11.7 ± 0.81	12.42 ± 2.35
		blak mouth goosefish (Lophiomus setigerus)	12.5 ± 1.99	32.1 ± 13.5
		korean anchovy (Coilia ectens Jordan et Seale)	16.1 ± 1.73	10.3 ± 2.65
		mud hopper (Periopthalmus cantonensis)	14.6 ± 1.76	17.4 ± 2.32
		mud hopper (Periopthalmus cantonensis)	9.62 ± 1.21	16.3 ± 8.19
		red tongue sole (Cynoglossus joyneri)	19 ± 0	34 ± 0
		chinese mitten crab (Eriocheir sinensis)	2.18 ± 0.46	5.05 ± 3.09

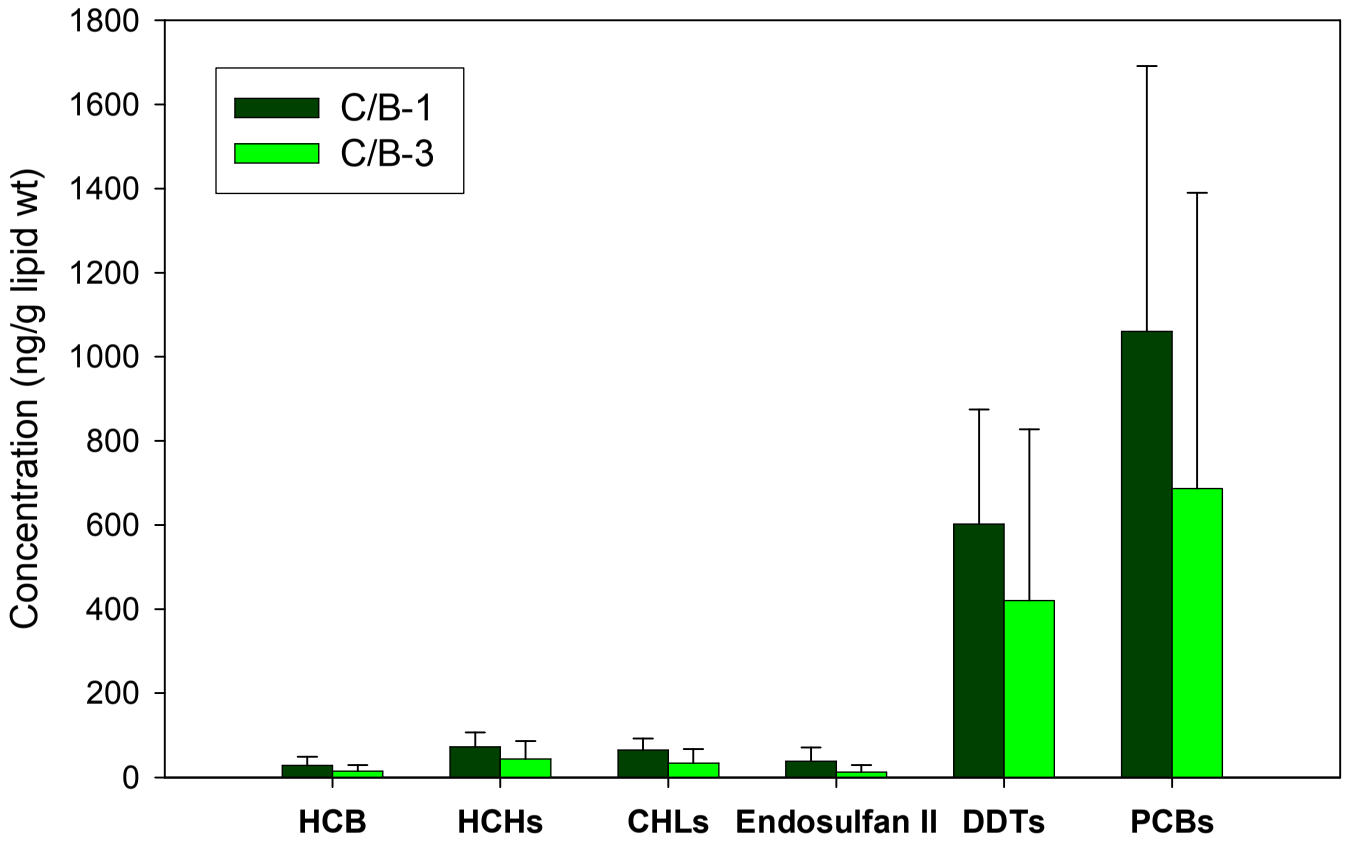
Contamination Status of POPs chemicals



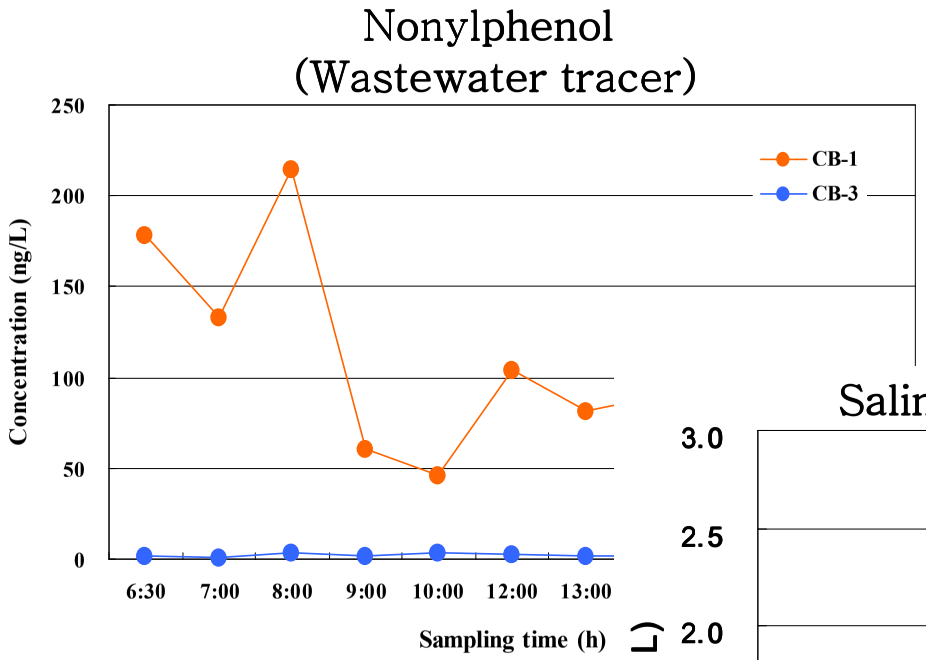
Seasonal Variation of POPs in Fish Muscle

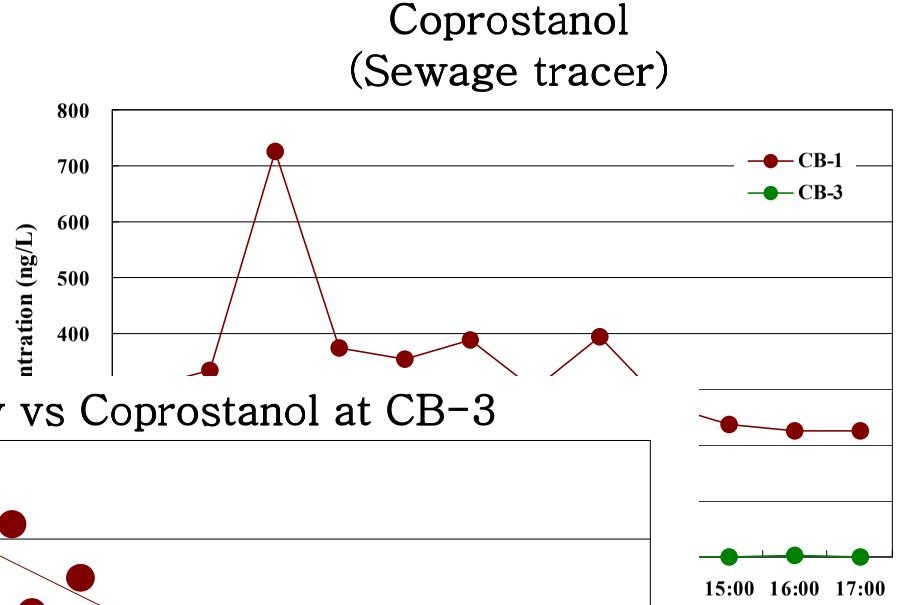


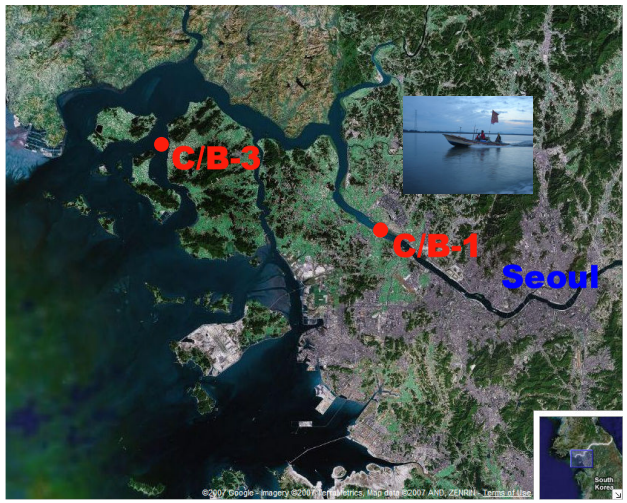
Spatial Distribution of POPs in Fish muscle

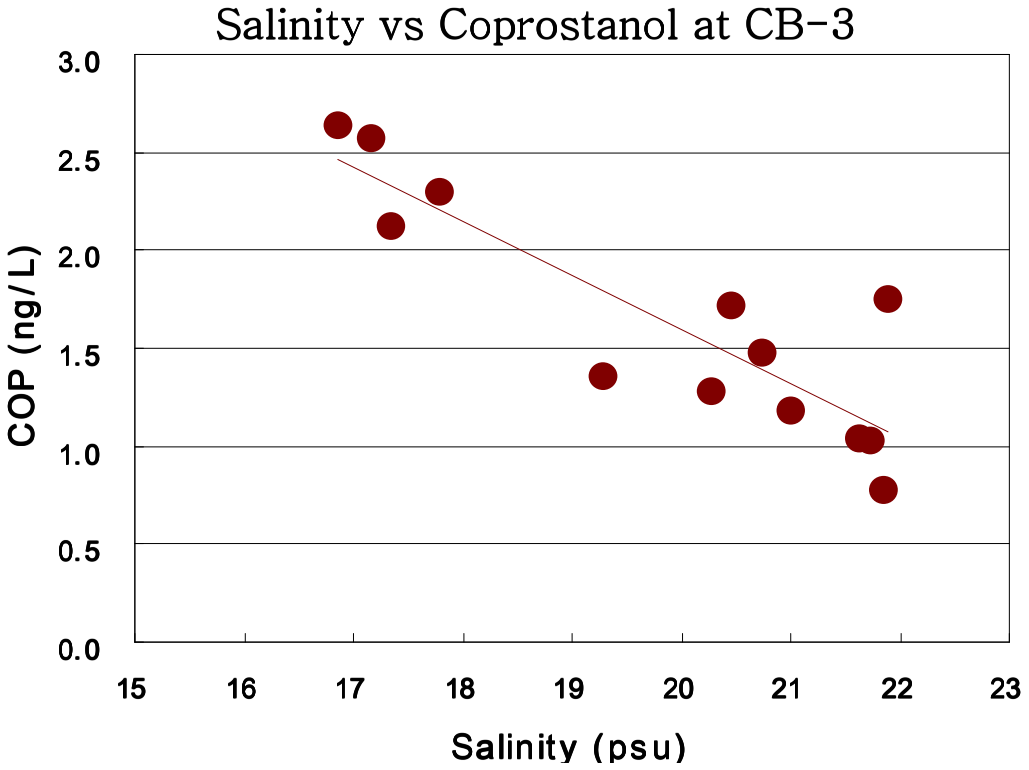


Wastewater / Sewage Tracer in the Water column

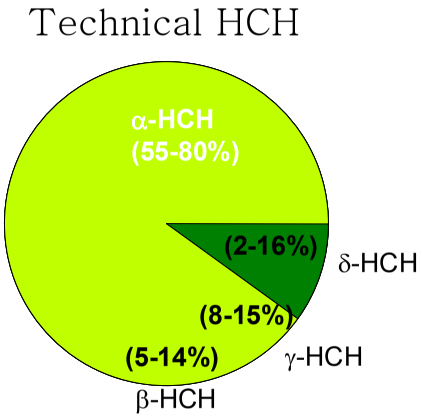


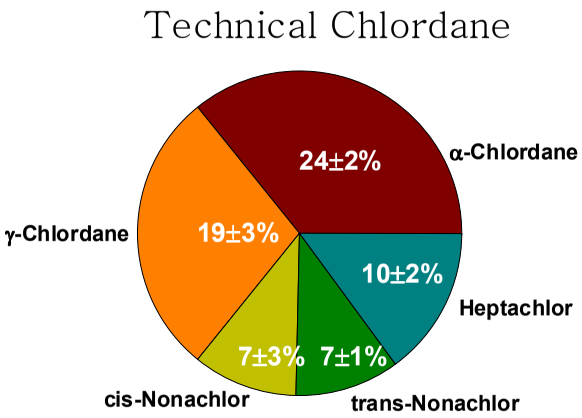


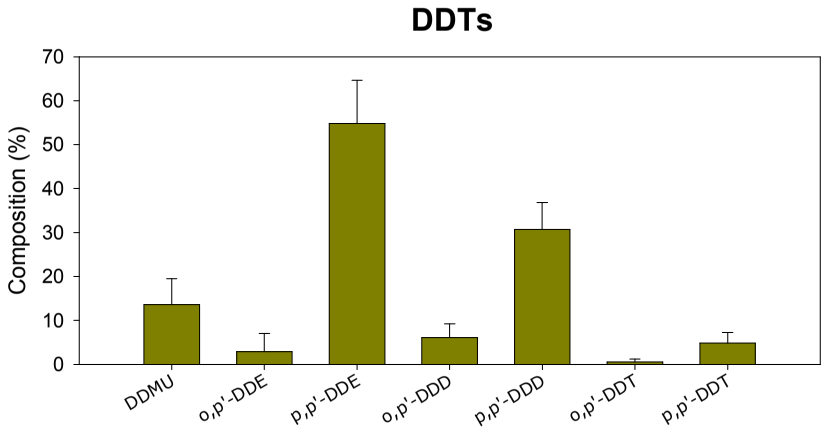


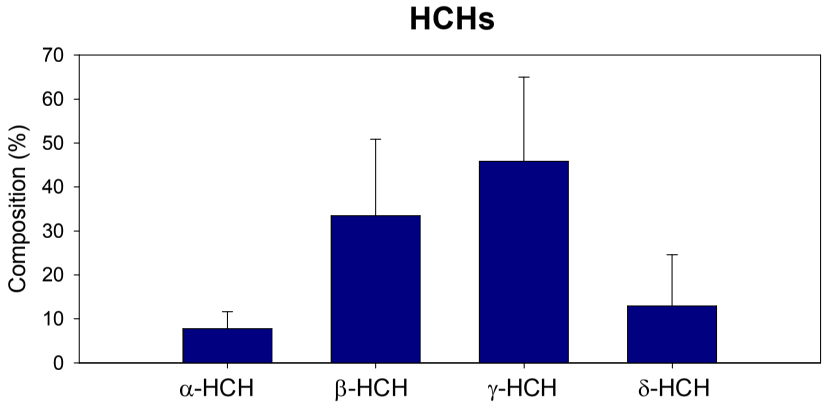


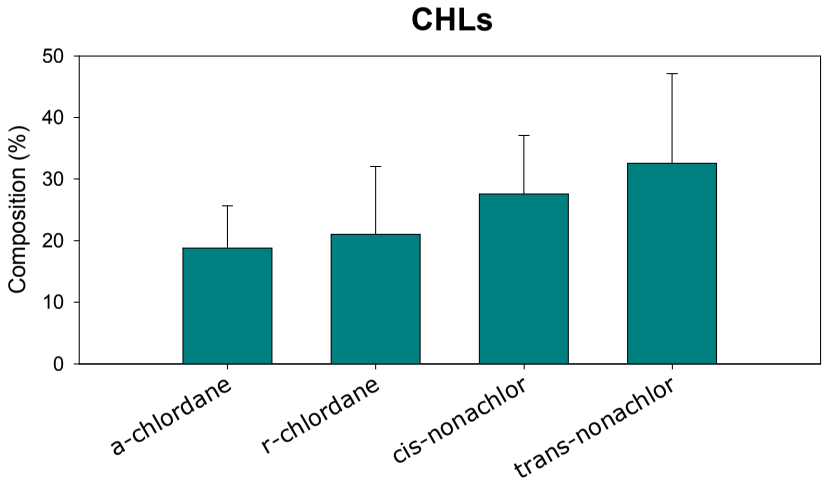
Relative composition of OCPs in fish muscle



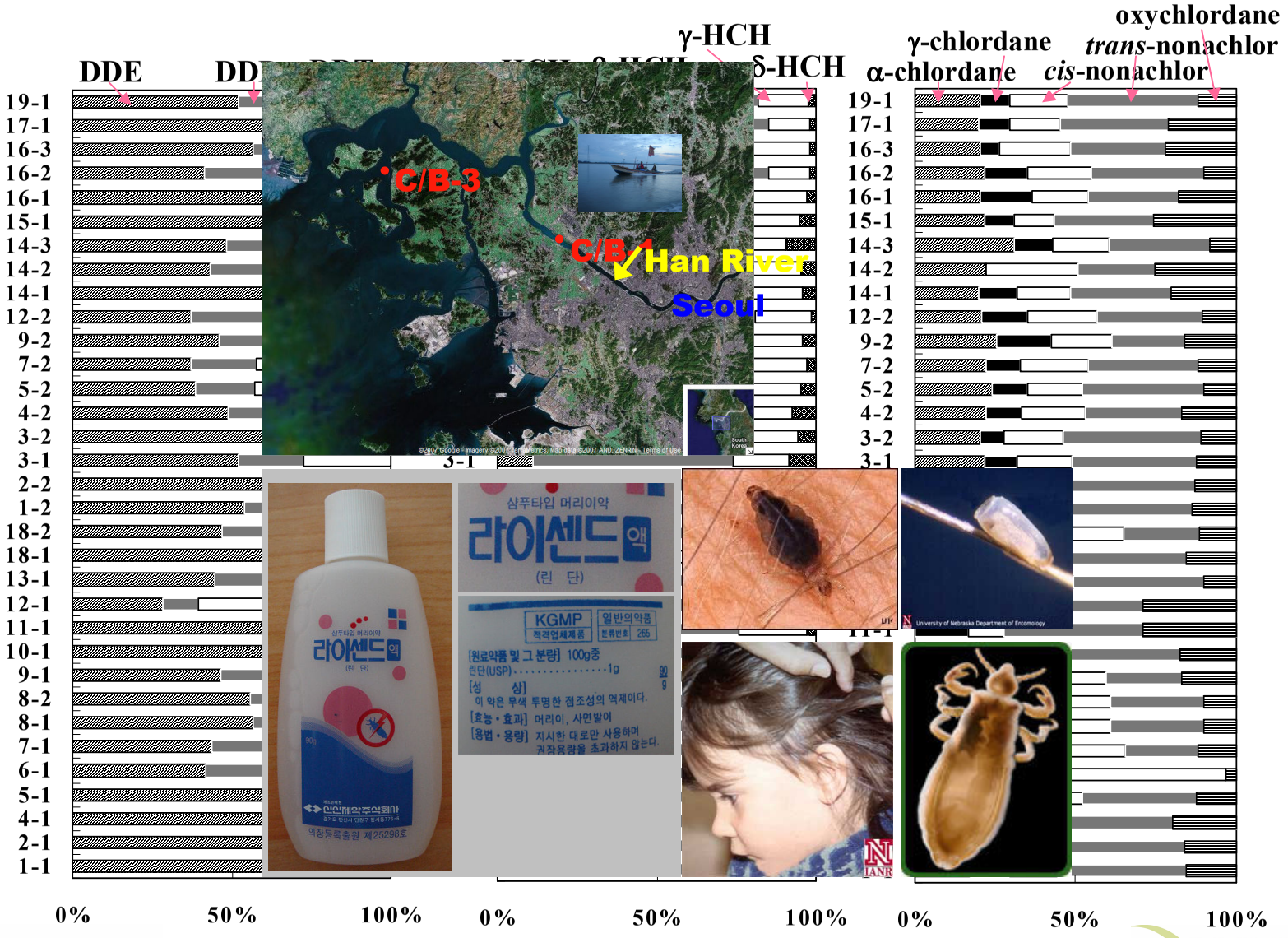








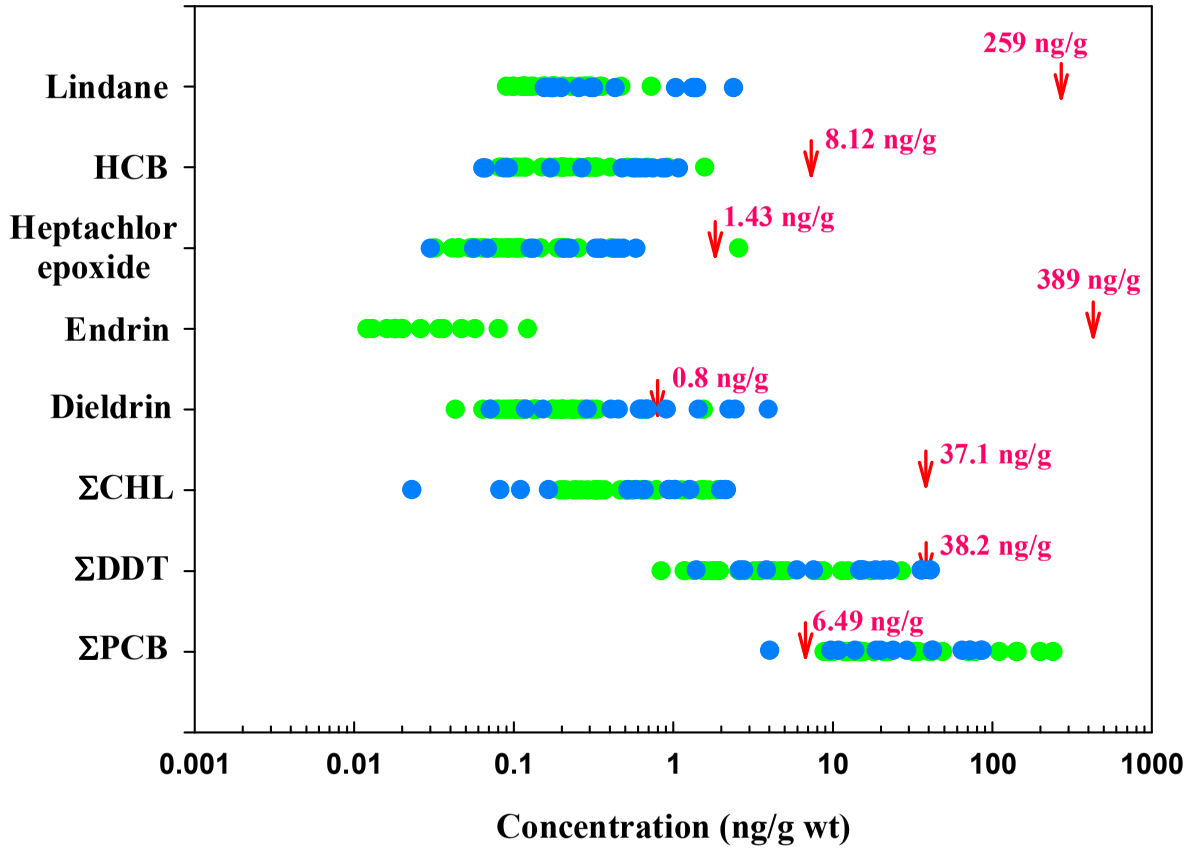
Relative composition of OCPs in fish muscle from the Korean coastal regions



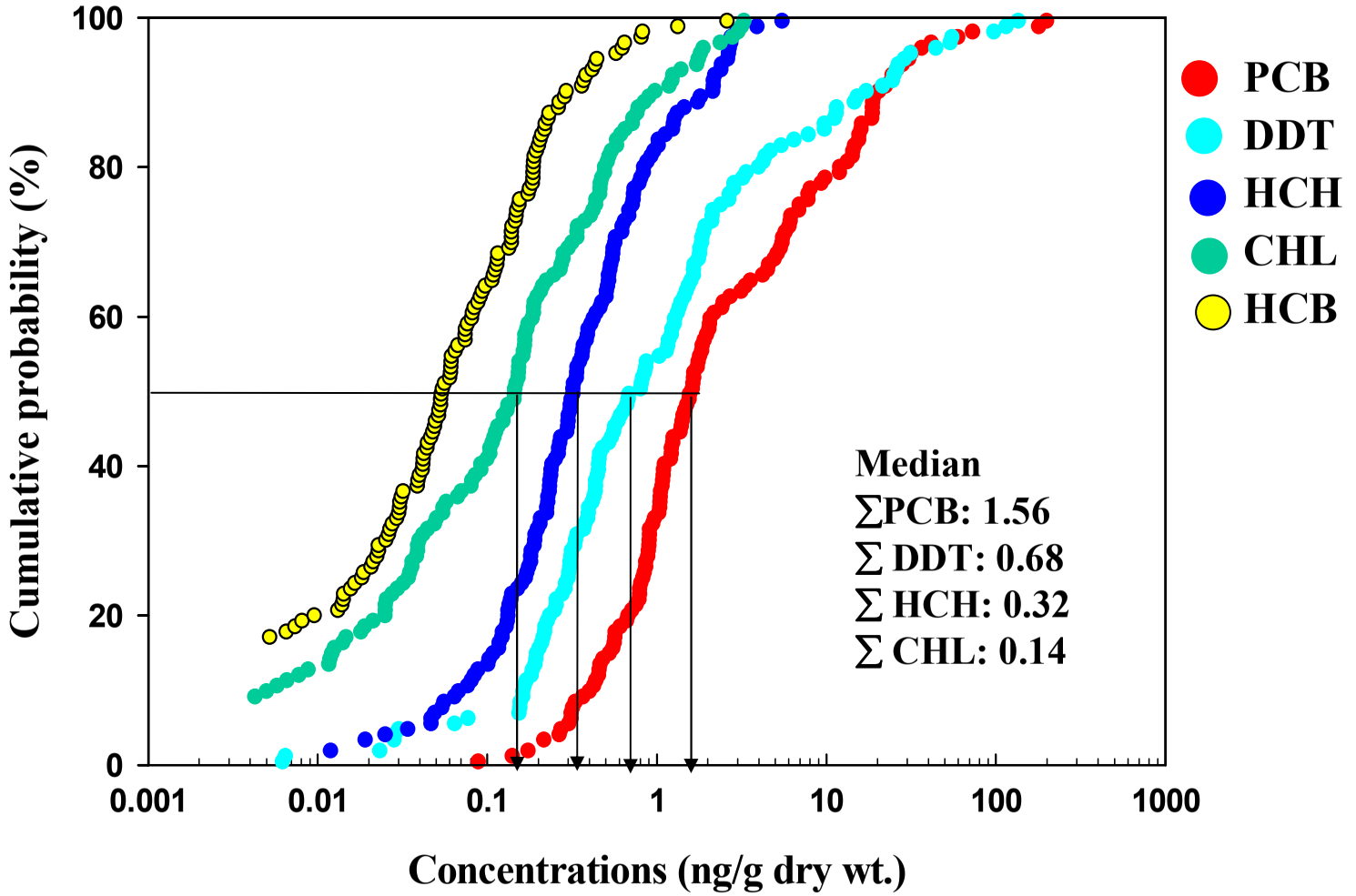
KORDI 한국해양연구원

MERI Marine Environmental Research Laboratory

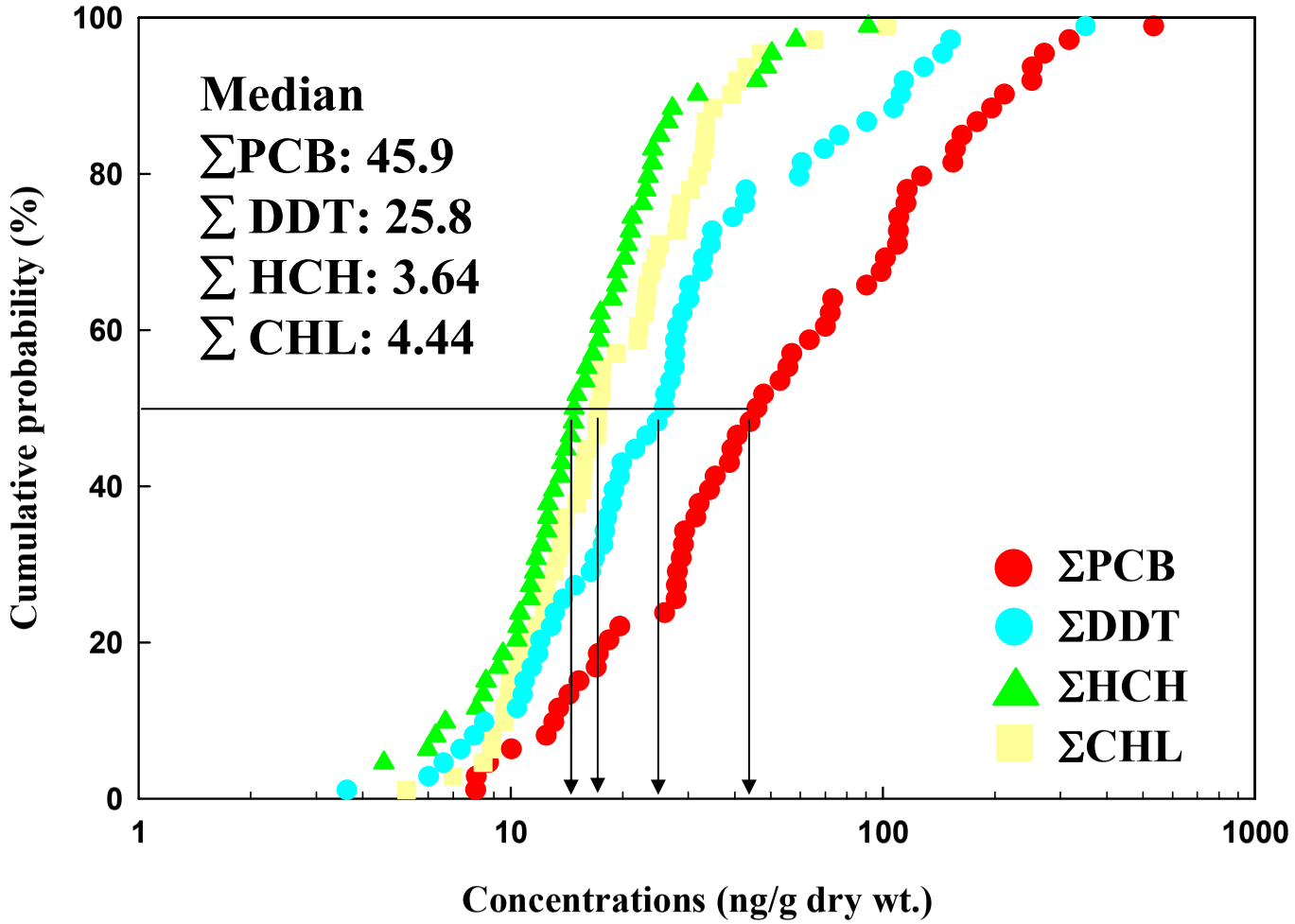
Comparison of organochlorine concentrations in fish muscle from the coast of Korea and Han River estuary with estimated screening values (SV) for fish consumption risk



Cumulative probability of OC concentrations in surface sediment from the coast of Korea



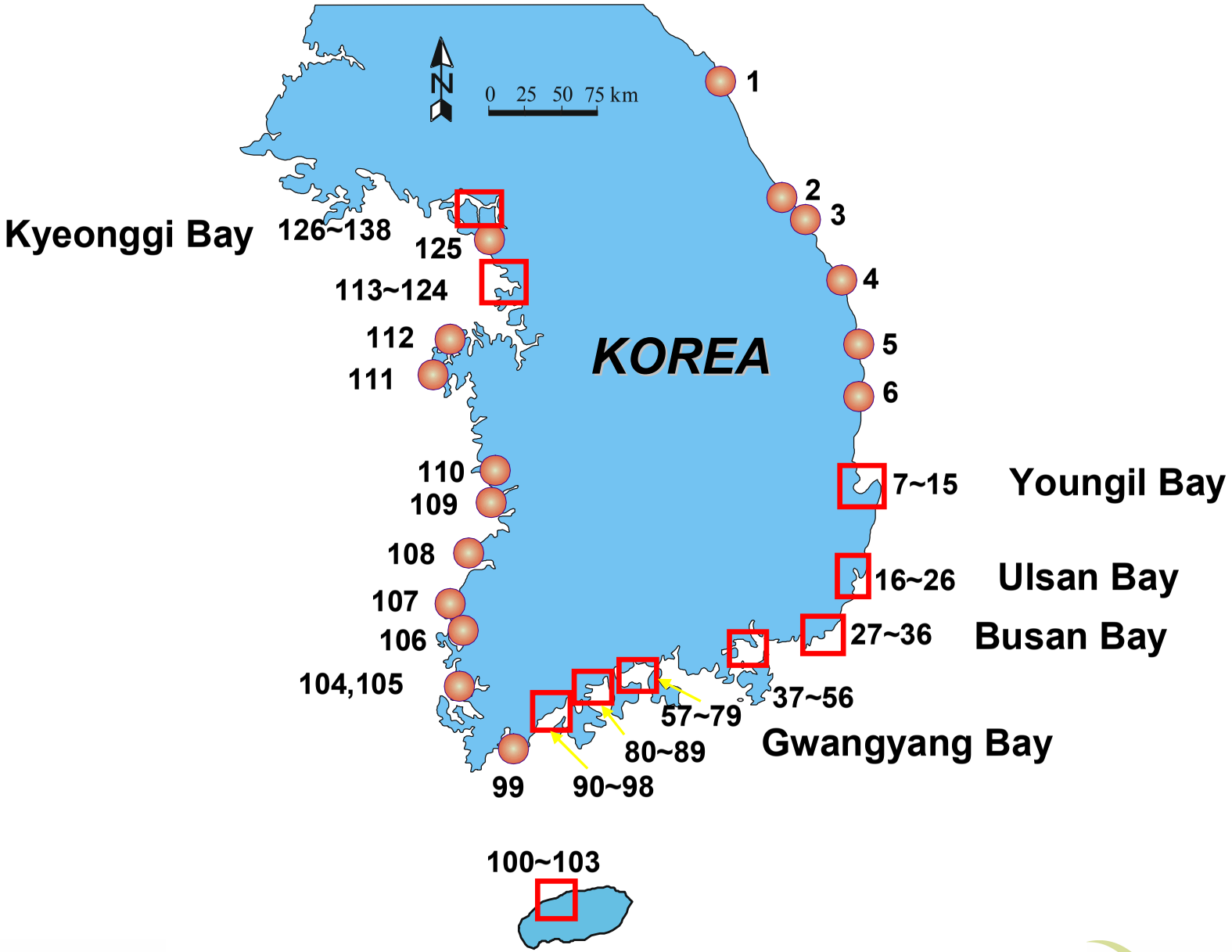
Cumulative probability of OC concentrations in bivalves from the coast of Korea in 2000



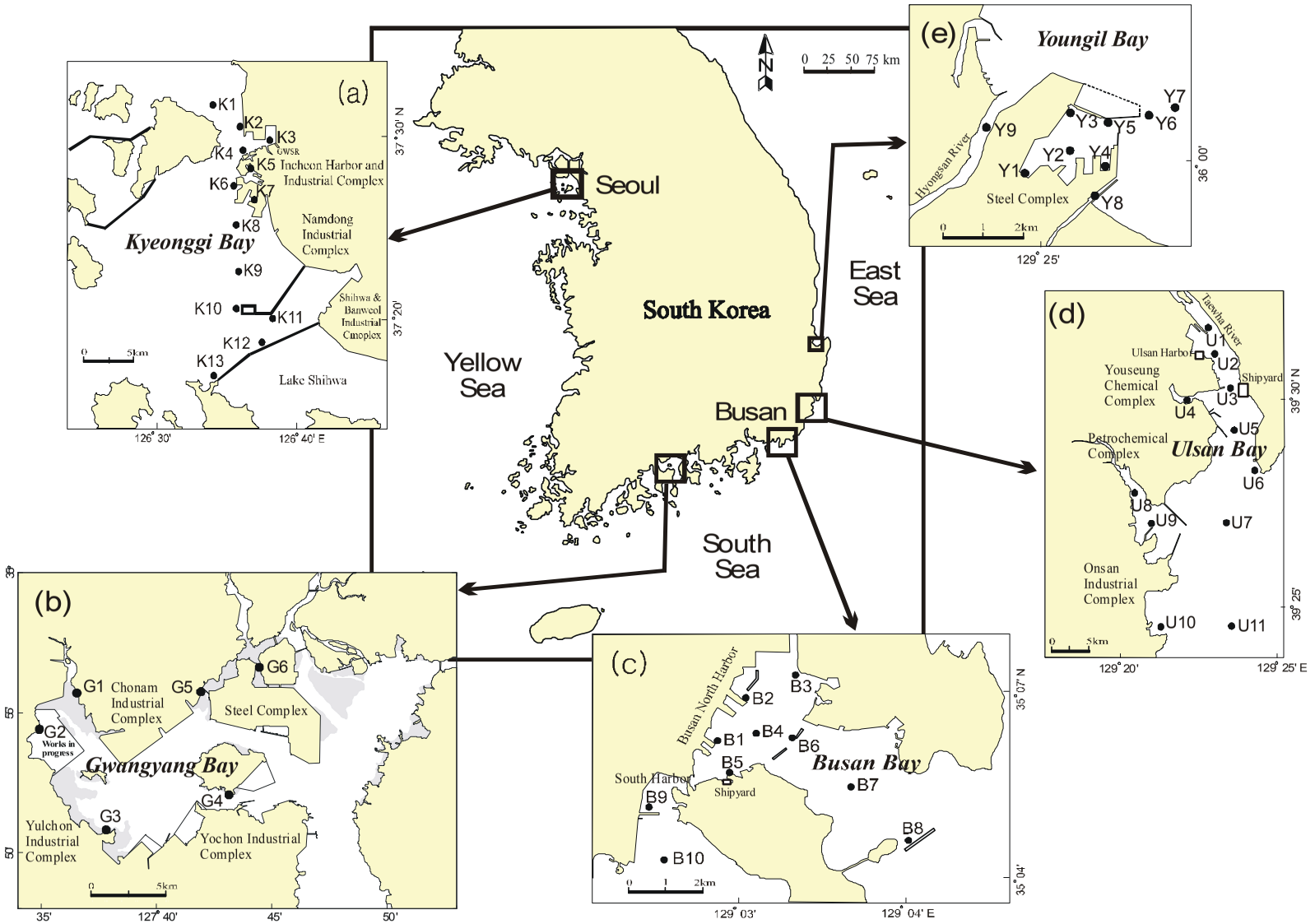
Case study II.

Possible point source of PCBs in the Korean Coastal regions

Surface sediment sampling sites

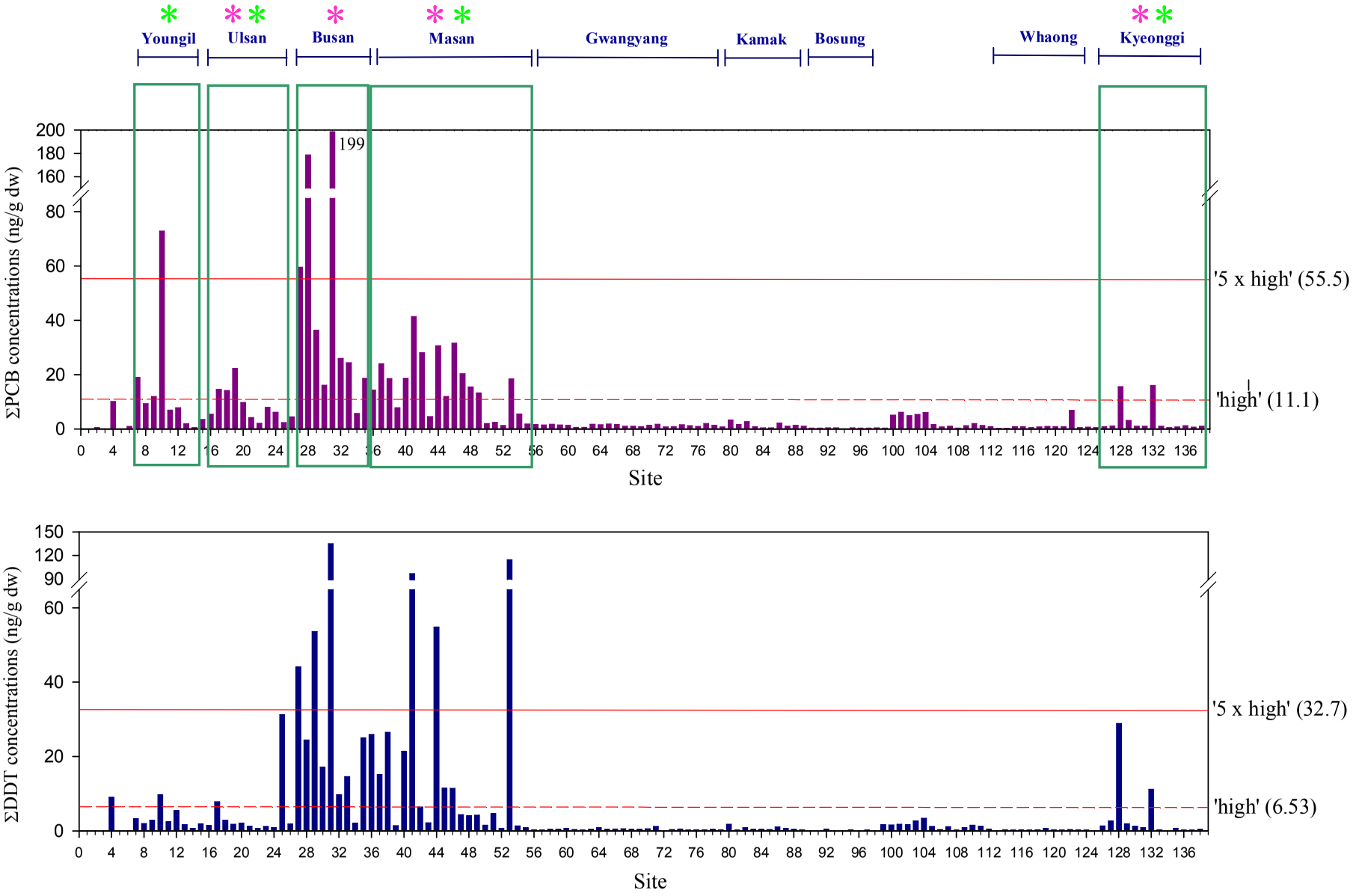


Sampling stations in five major industrialized bays

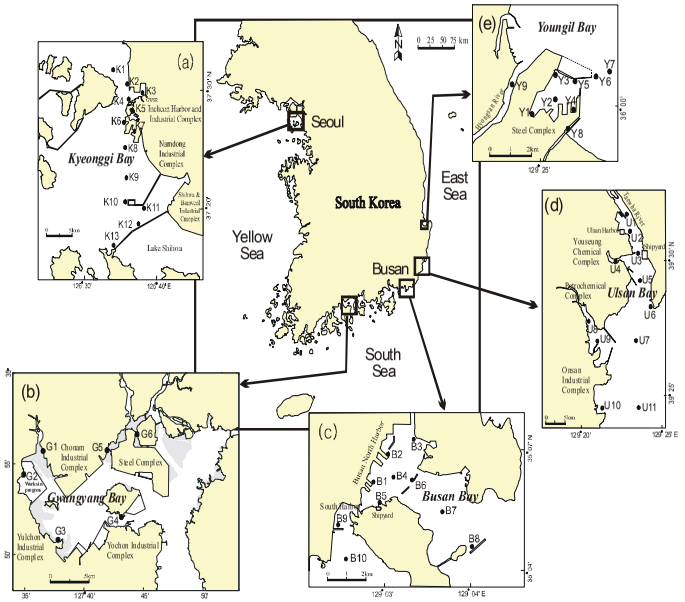


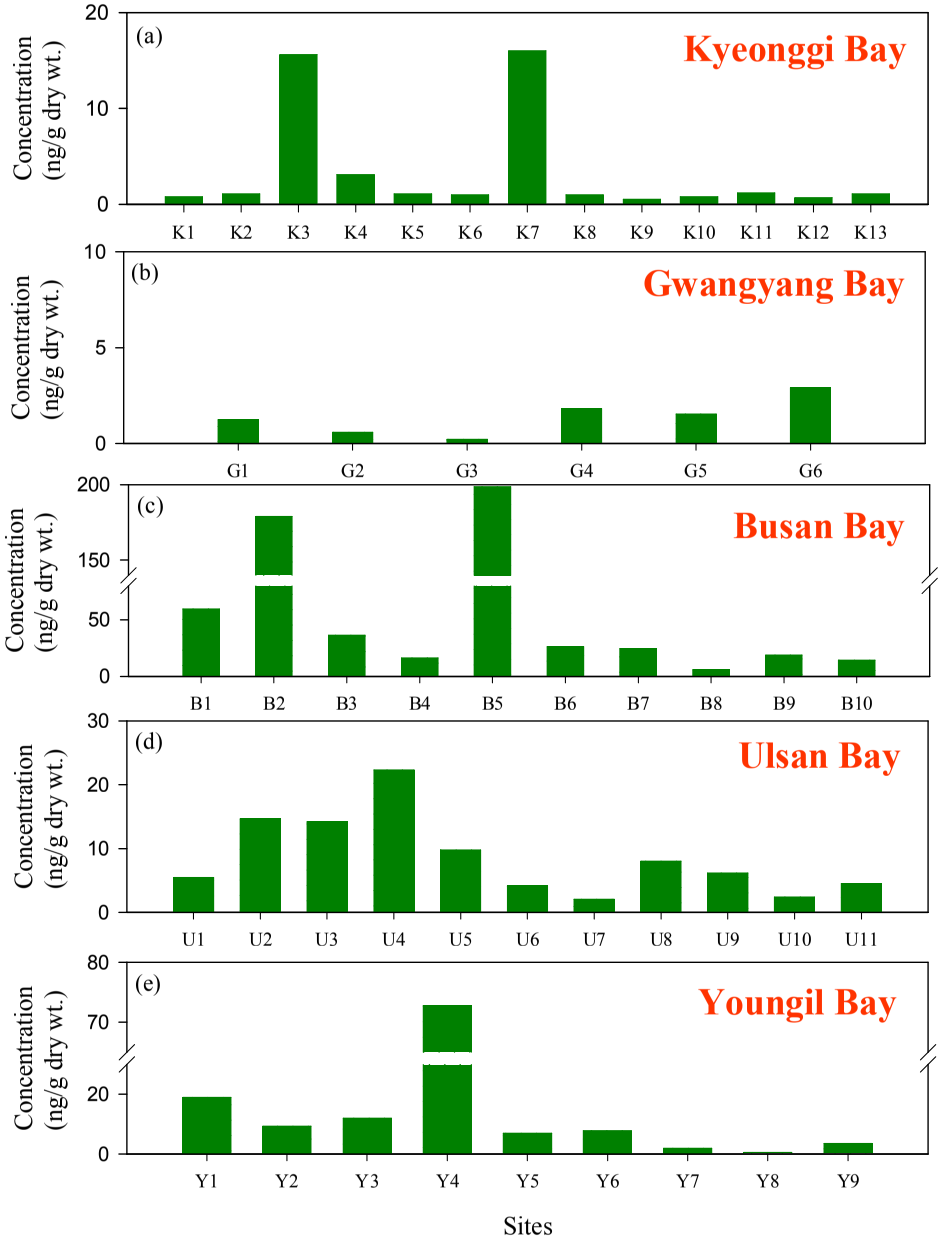
Spatial distribution of PCBs and DDTs

* Harbor area
* Industrial Complex area

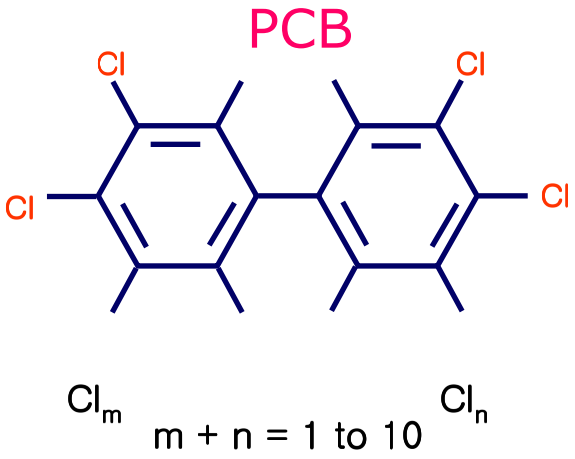


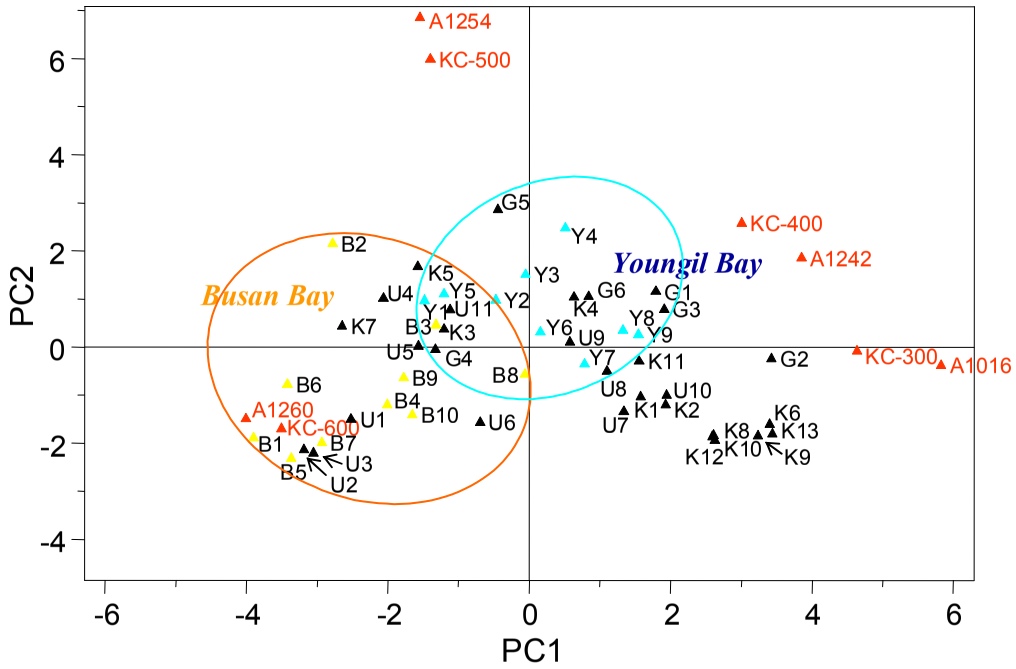
Spatial distribution of PCB concentrations in sediments from industrialized bays

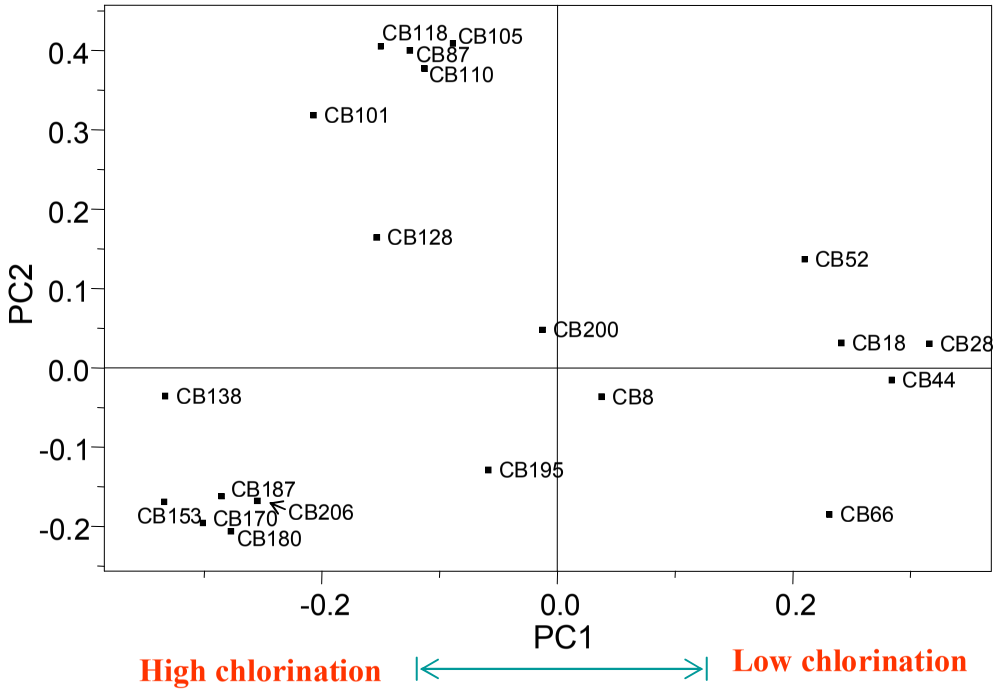




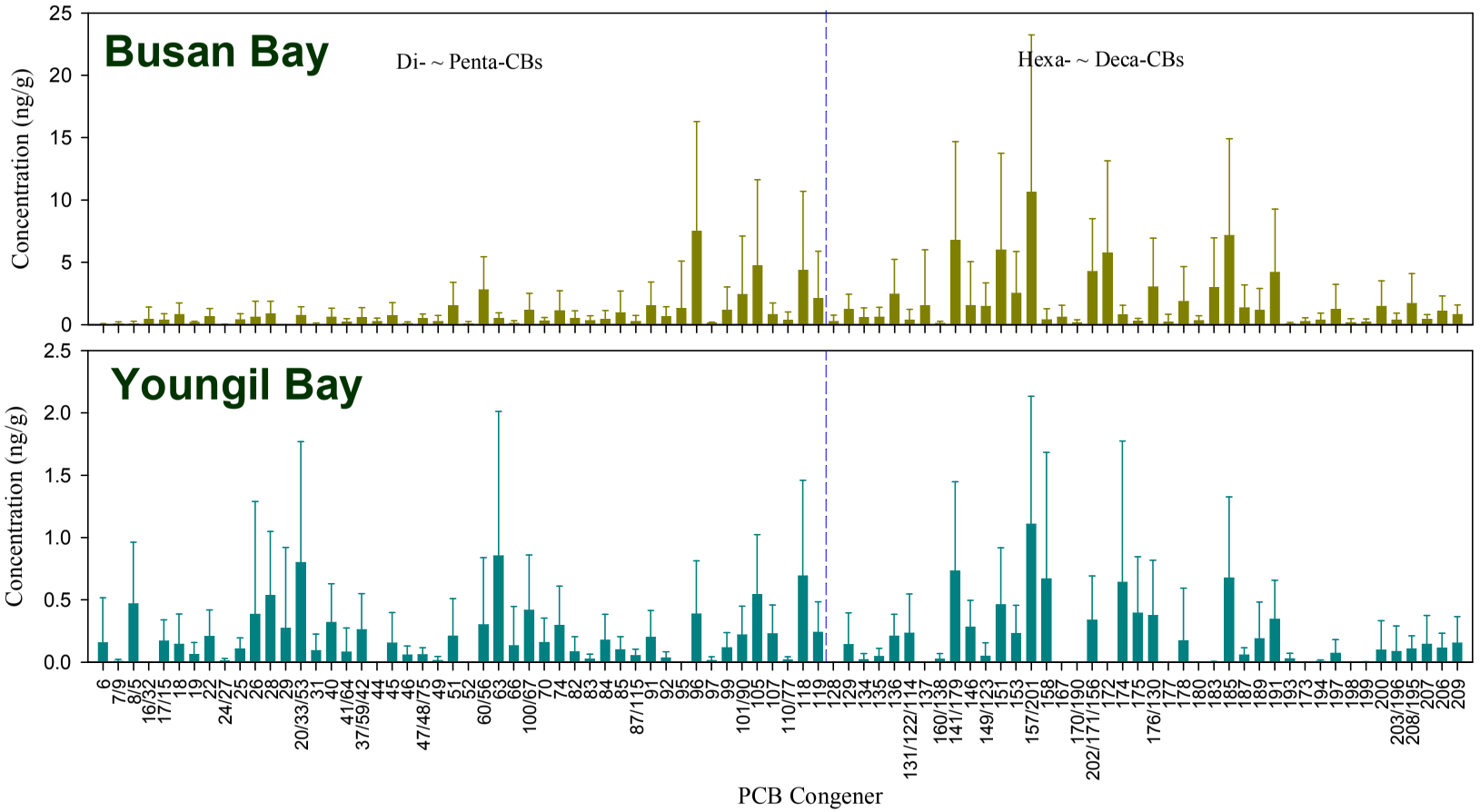
Principle component analysis score plot and loading plot of PCB congener pattern in five major bays







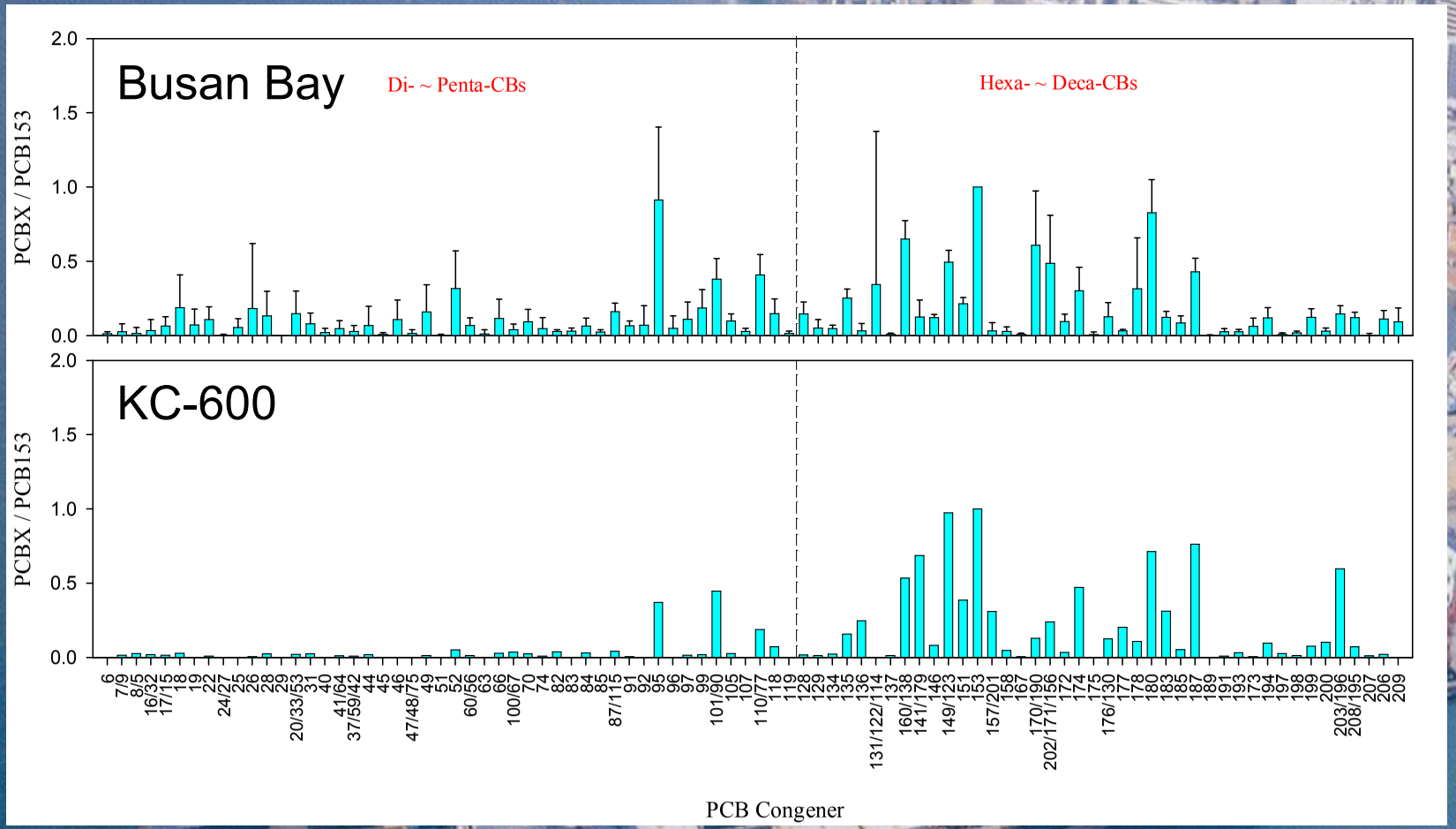
Congener profiles in Busan Bay and Youngil Bay (ng/g dw)



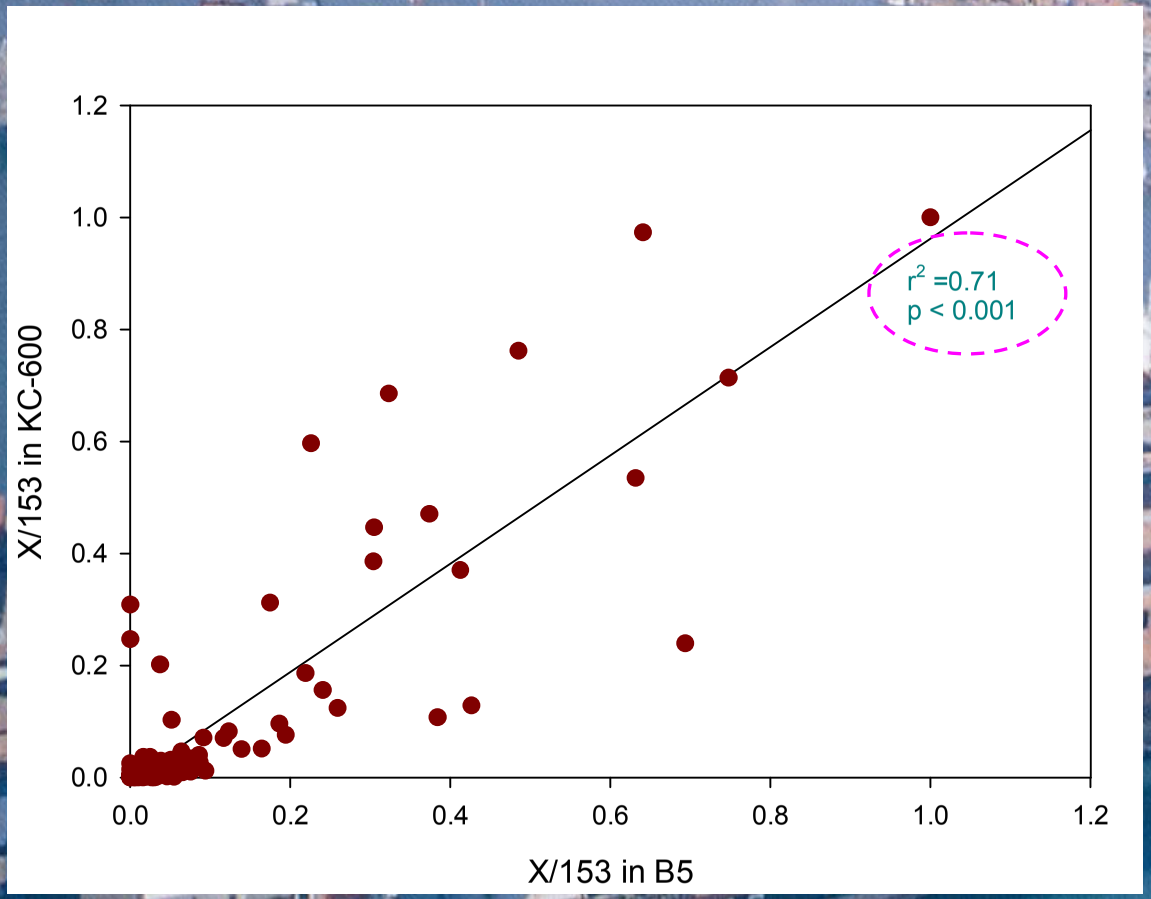
MERL
Marine Environmental Research Laboratory


Harbor Region
(Busan Bay)
MISC

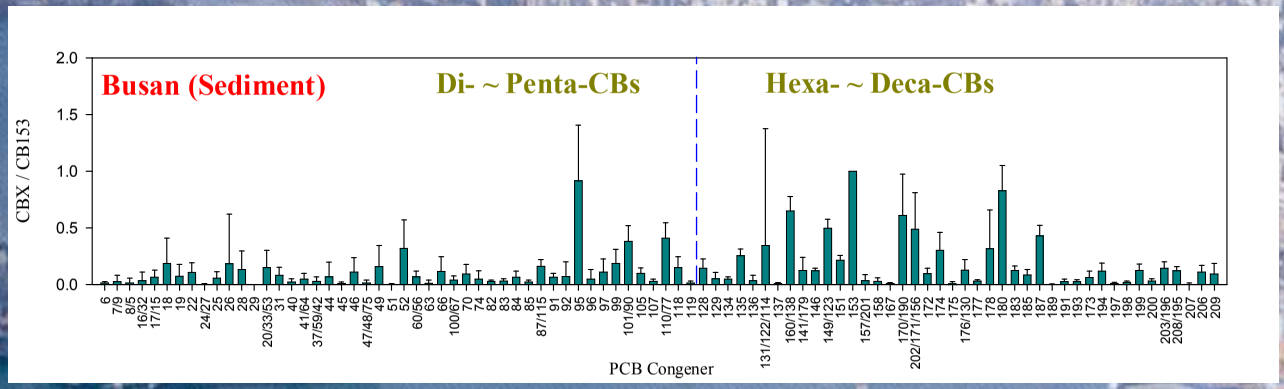
Congener profiles in Busan Bay and KC-600

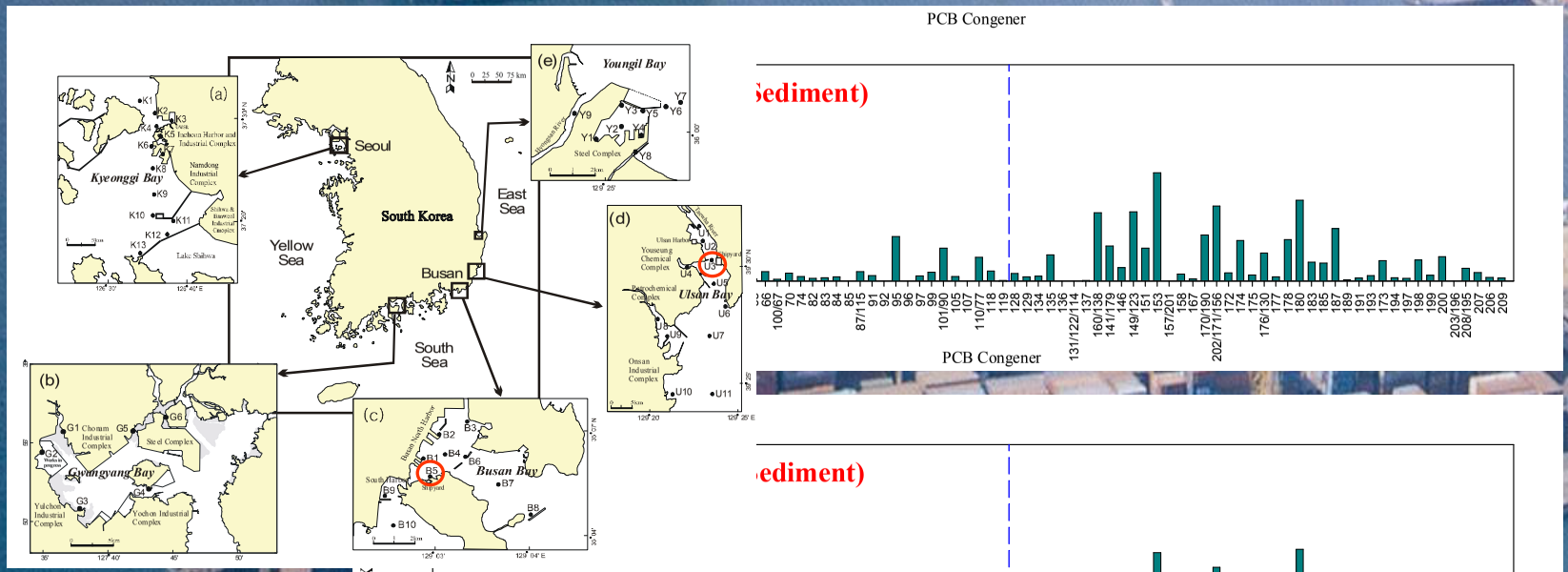


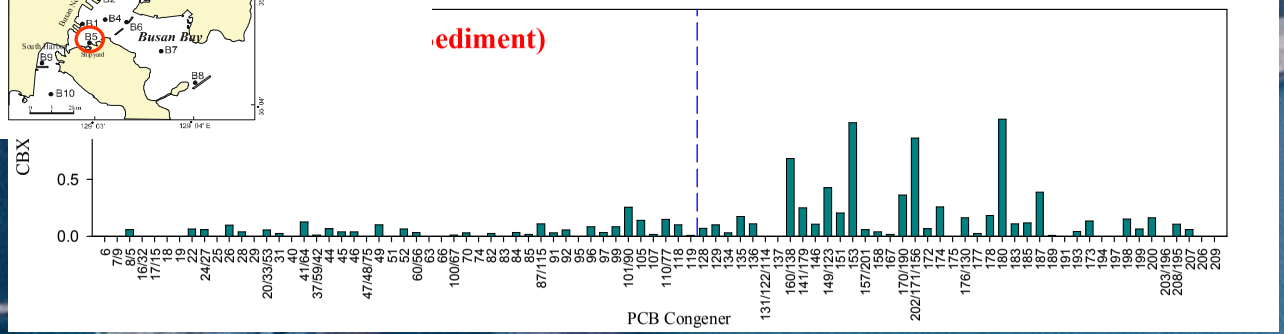
Correlation of congener composition between B5 and KC-600



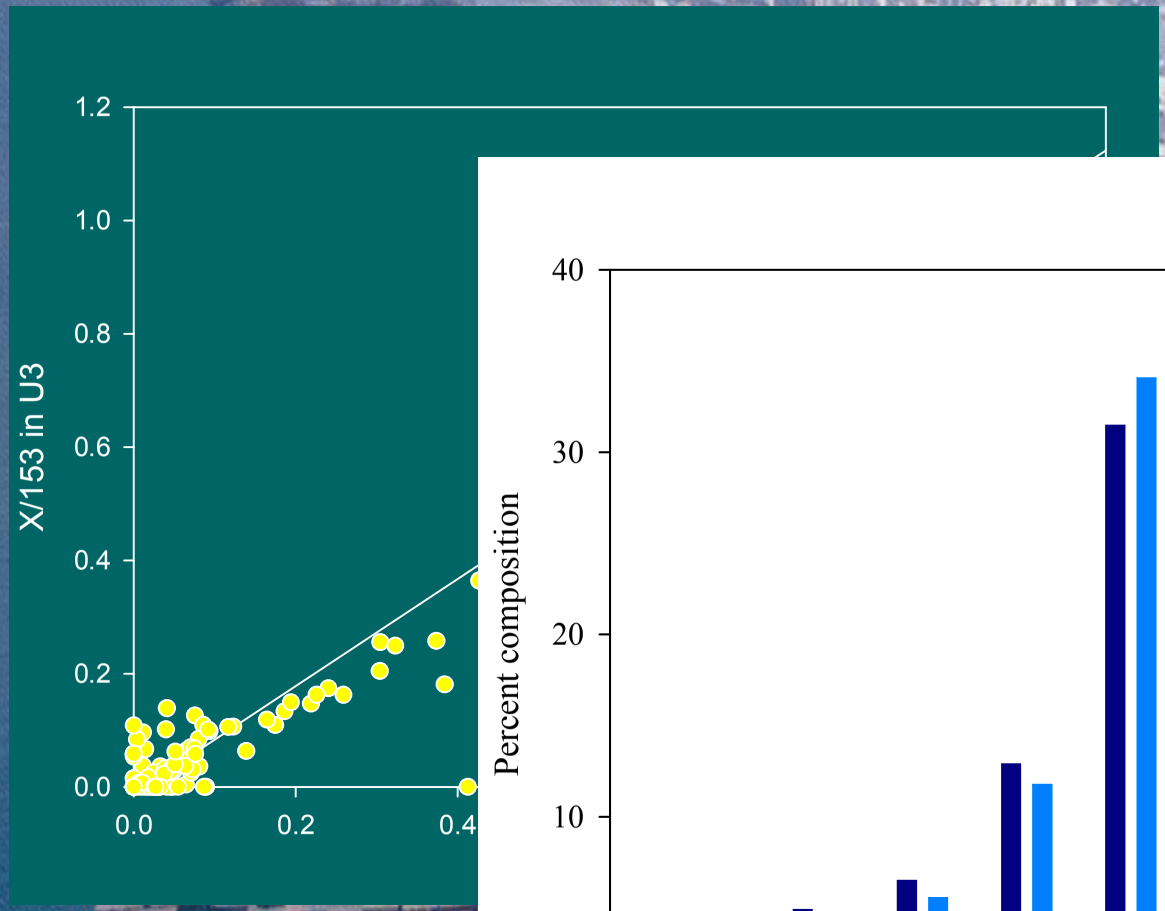
Congener profiles at shipyards

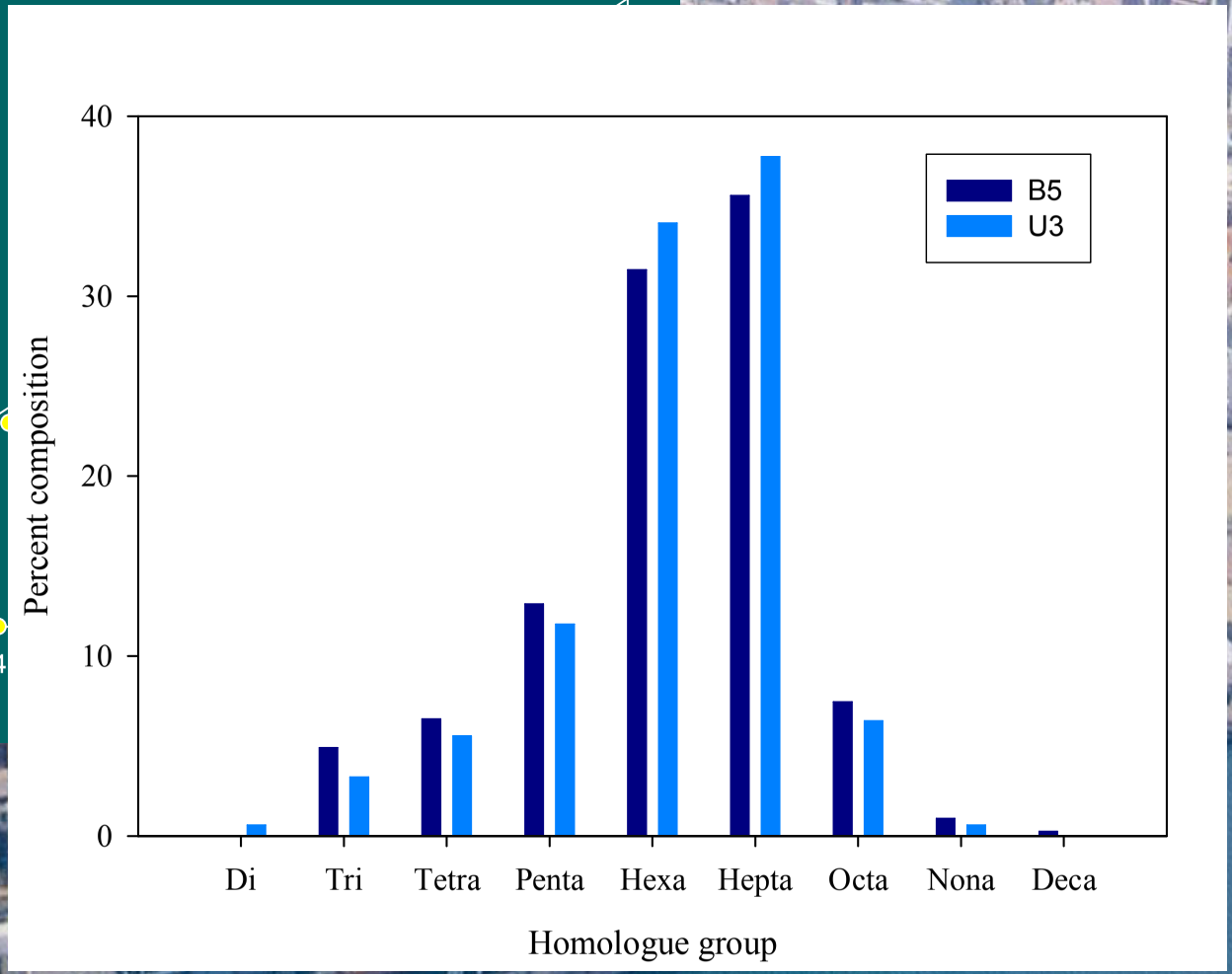






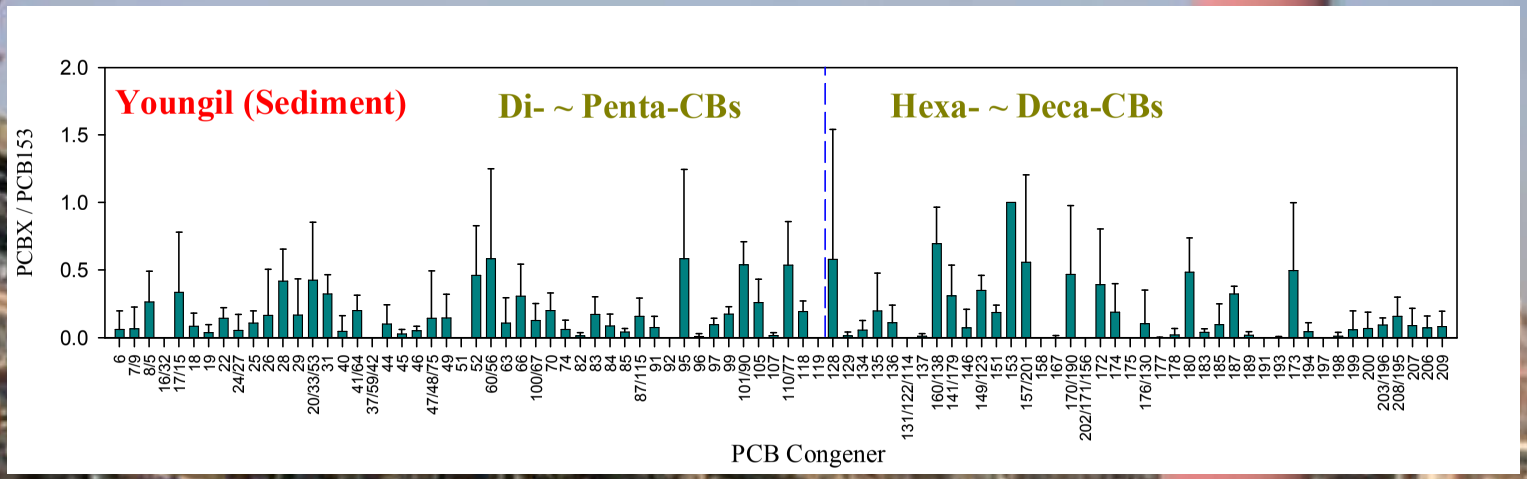
PCB homologue pattern near shipyards

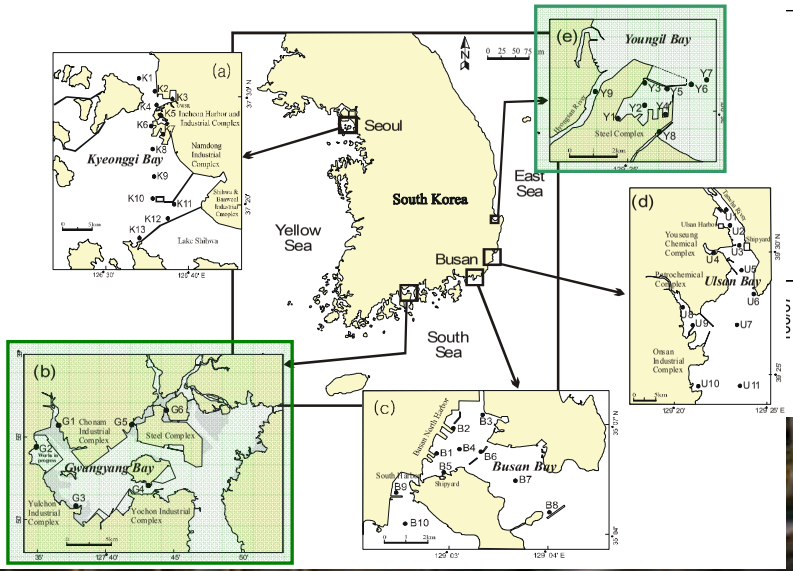


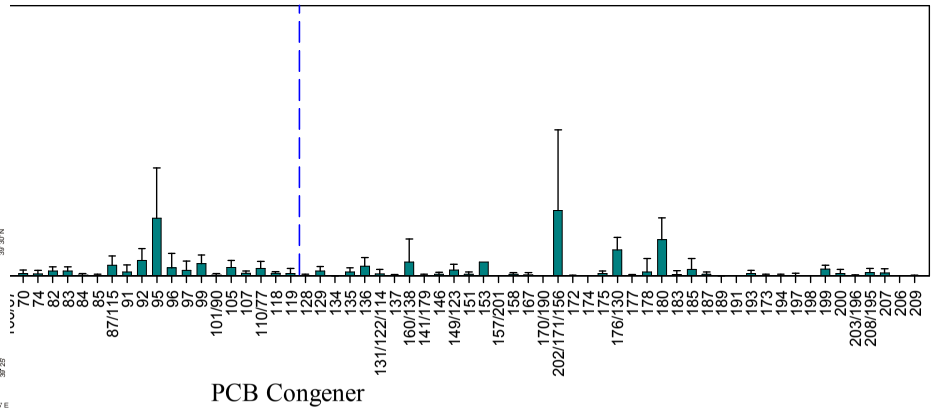



Steel Works Region

Congener profiles at Steel Works Region







Steel Works Region

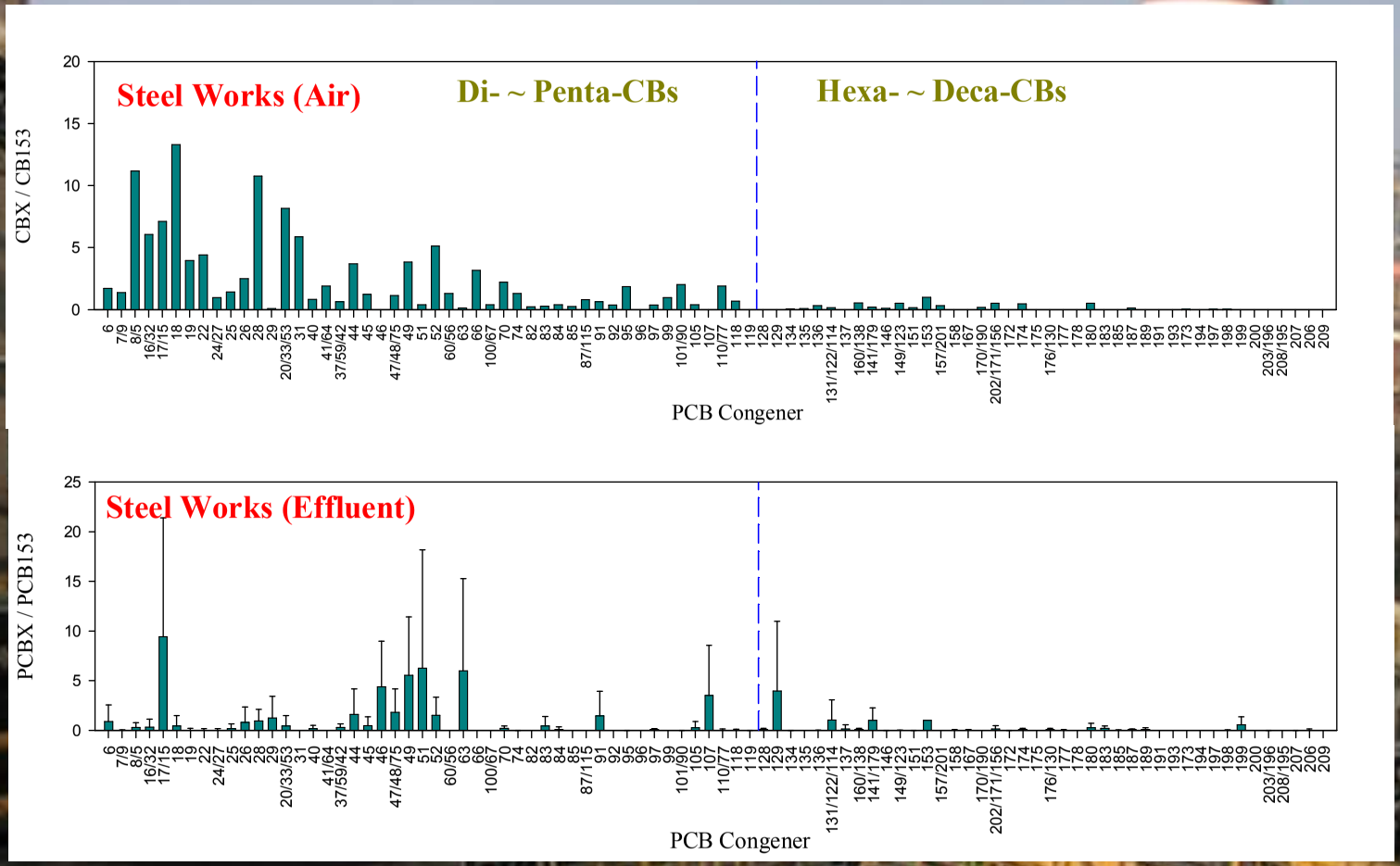
High Volume Sampler

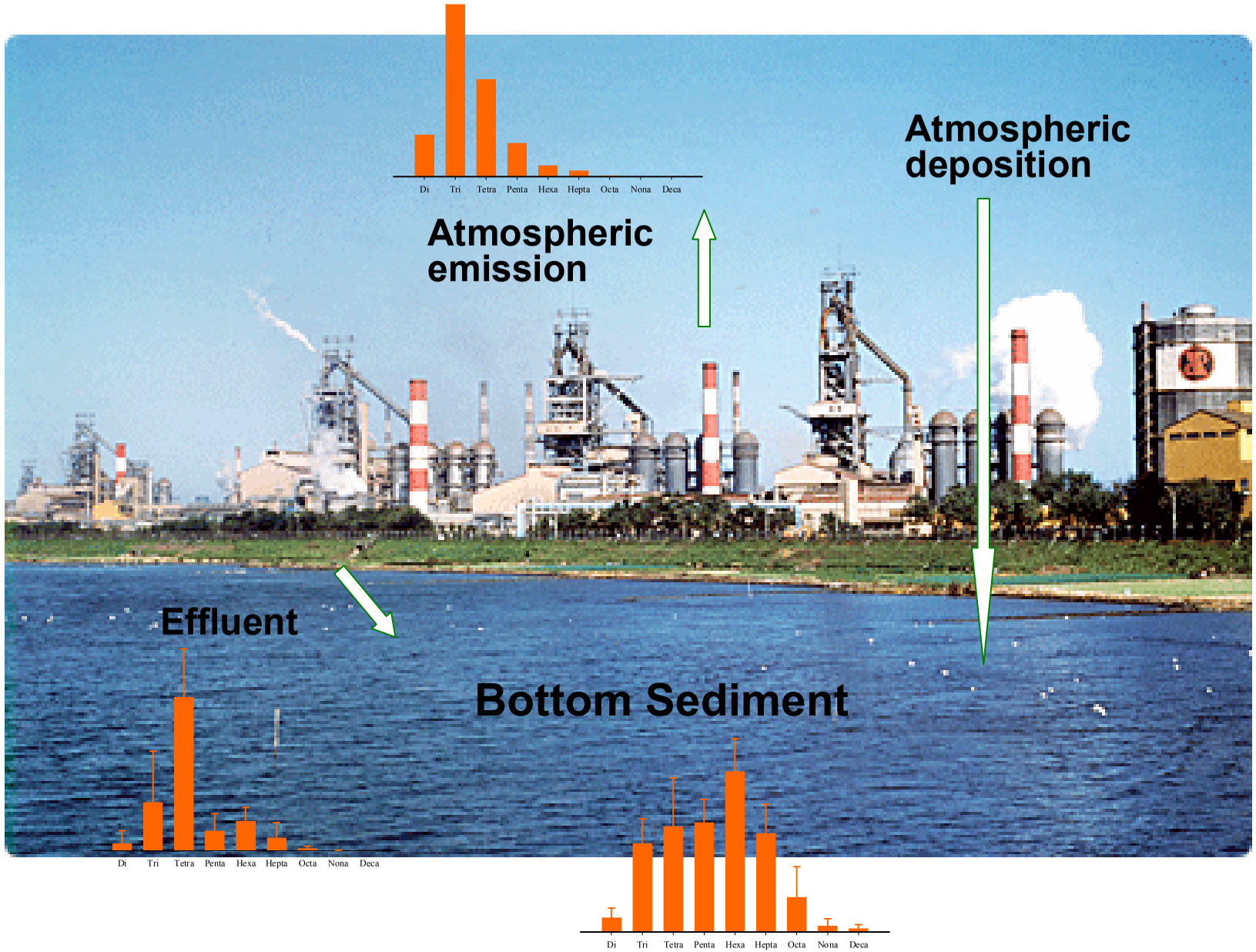
Glass fiber filters

PUF (polyurethane foam)

Soxhlet apparatus for PUF cleanup & extraction

Congener profiles at Steel Works Region




Di Tri Tetra Penta Hexa Hepta Octa Nona Deca
Atmospheric deposition
Atmospheric emission
Effluent
Bottom Sediment
Di Tri Tetra Penta Hexa Hepta Octa Nona Deca
Di Tri Tetra Penta Hexa Hepta Octa Nona Deca

Summary

- Polychlorinated biphenyls and organochlorine pesticides are widely distributed in the Korean coastal environment.
- Organochlorine compounds are widely distributed in the coastal environment of Korea and PCBs and DDT compounds are dominant organochlorines.
- Based on the estimated screening values, PCB compounds were identified as potential chemical of concern throughout the coast of Korea.
- Organochlorine contamination are closely related to industrial activity and shipping activity

Summary

- High PCB accumulation in harbor stations in comparison to industrial ones indicates the significance of ship-related activities such as mooring and repairing in Korean coastal environment for PCB contamination.

- Principal component analysis (PCA) reveals that each bay has its own pattern. Interestingly, samples from harbor region and steel complex region showed different distributions on PCA plot.

- Low chlorinated congeners with up to five chlorines are significantly abundant in steel complex region in comparison to those of harbor region (Student t-test, $p < 0.001$).

- The abundance of tri-, tetra, and penta-CBs in steel complex sediment resembles the PCB emission pattern in air and effluent discharged from Steel plant.


Thank you for
your attention!