Dynamics of PCDD/Fs and Coplanar-PCBs in Aquatic Food Chains from Lake Shinji and Tokyo Bay

宍道湖及び東京湾の食物連鎖における ダイオキシン類の動態について

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BACKGROUNDS 研究背景

- **Fish and shellfish consumption is a significant cause of exposure of PCDD/Fs and coplanar-PCBs in Japanese populations.**
  ダイオキシン類暴露における魚介類摂取の重要性

- **Adequate understanding of the contamination state and bioaccumulation pathways in aquatic biota is of major concern.**
  水圏生物の汚染状況及び生物濃縮経路把握

STUDY OBJECTIVES　研究目的

- **Contamination status and characterization**
  汚染状況及び特徴の把握
  - Quantification for the residue levels of PCDD/Fs and coplanar-PCBs
  - Characterization and accumulation profiles
- **Bioaccumulation trend in aquatic environment**
  水圏環境での生物濃縮現象
  - Biota-Sediment Accumulation Factor (BSAF)
  - Stable nitrogen isotope ratio ($\delta^{15}N$)

SAMPLE COLLECTION

Sampling location ; Lake Shinji（宍道湖） Tokyo Bay（東京湾）

Sampling date ; November 1994 〜 December 1995 November 1998

SAMPLE LIST

	Species	Common name	*n*	Analyzed tissue	Lipid content (% of dry wt.)
Shinji Lake	Waterfowl	キンクロハジロ(Tufted duck)	5	Muscle	12.7
	Fish (4)	スズキ(Sea bass)	3	Whole	28.8
		コノシロ(Gizzard shad)	2	Whole	30.7
		サッパ(Large-eyed herring)	1[*2*]	Whole	15.2
		マハゼ(Goby)	1[*2*]	Whole	10
	Bivalve	シジミ(Shijimi clam)	3[*10*]	Soft tissue	5.8
Tokyo Bay	Fish (6)	スズキ(Sea bass)	2	Whole	23.9
		コノシロ(Gizzard shad)	2	Whole	22.7
		イシガレイ(Stone flounder)	2	Whole	11.6
		マコガレイ(Dab)	1	Whole	9.8
		アカエイ(Stingray)	2	Whole	13.3
		アナゴ(Eel)	1	Whole	40.1
	Bivalve (3)	アサリ(Littleneck clam)	1[5]	Soft tissue	10.0
		ミドリイガイ(Hard-shell clam)	1[12]	Soft tissue	11.8
		バカガイ(Mactridae)	2[6]	Soft tissue	5.2
	Polychaeta	多毛類	1	Whole	5.2
	Plankton	プランクトン	1	Whole	7.9

CHEMICAL ANALYSIS

Sample

Freeze dry

Fat extraction

↓

Sulfuric acid treatment

Silica gel column

Alumina column

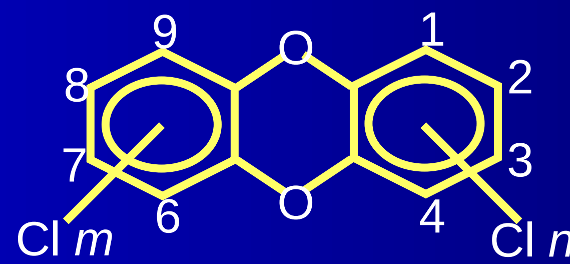
Active carbon column

↓

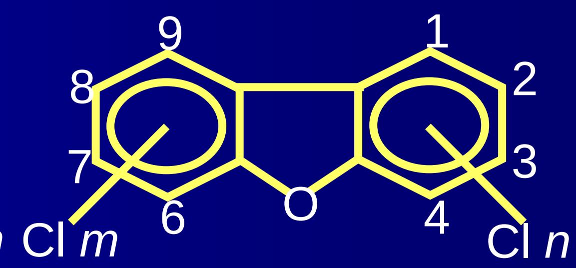
Other PCBs & **Mono-*ortho* PCBs**

PCDD/Fs & **Non-*ortho* PCBs**

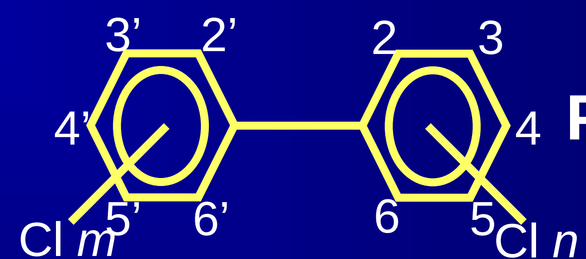
→ **HRGC-HRMS**



PCDDs ; 36 peak



PCDFs ; 51 peak



PCB

Non-*ortho* PCBs ; 4 isomer

Mono-*ortho* PCBs ; 8 isomer

STABLE ISOTOPE ANALYSIS

Sample

Freeze dry　凍結乾燥

Removal of fat　脱脂処理
(with 50% ethanol in benzene)

Elemental Analyzer 元素分析系
(combusted at 650℃)

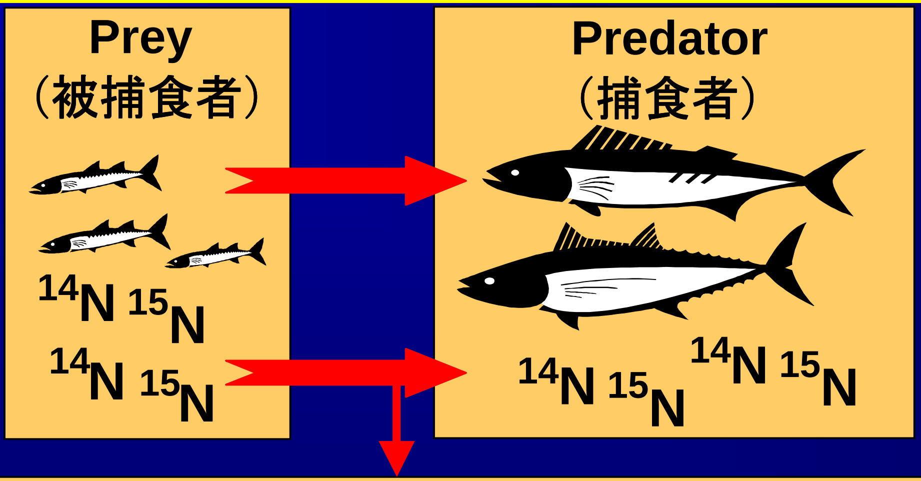
Isotope-ratio Mass Spectrometer
(Delta plus, Finnigan MAT)

Nitrogen stable isotope ratio
窒素安定同位体比 ($\delta^{15}N$, ‰)

$\delta^{15}N$ = [(R(sample) / R(standard) –1] × 1000

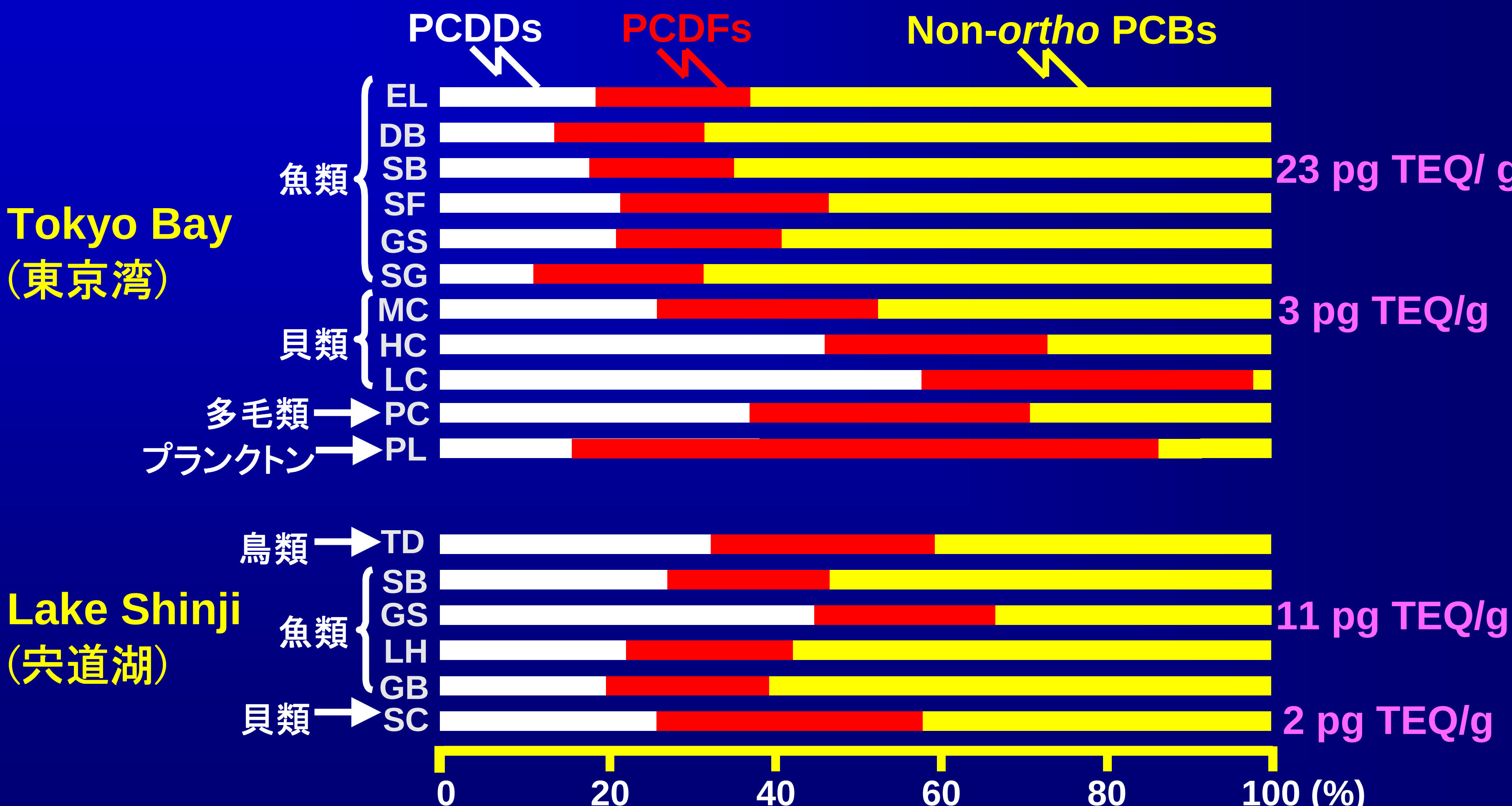
R ; $^{15}N/^{14}N$

Standard ; Atomospheric N (大気中窒素ガス).



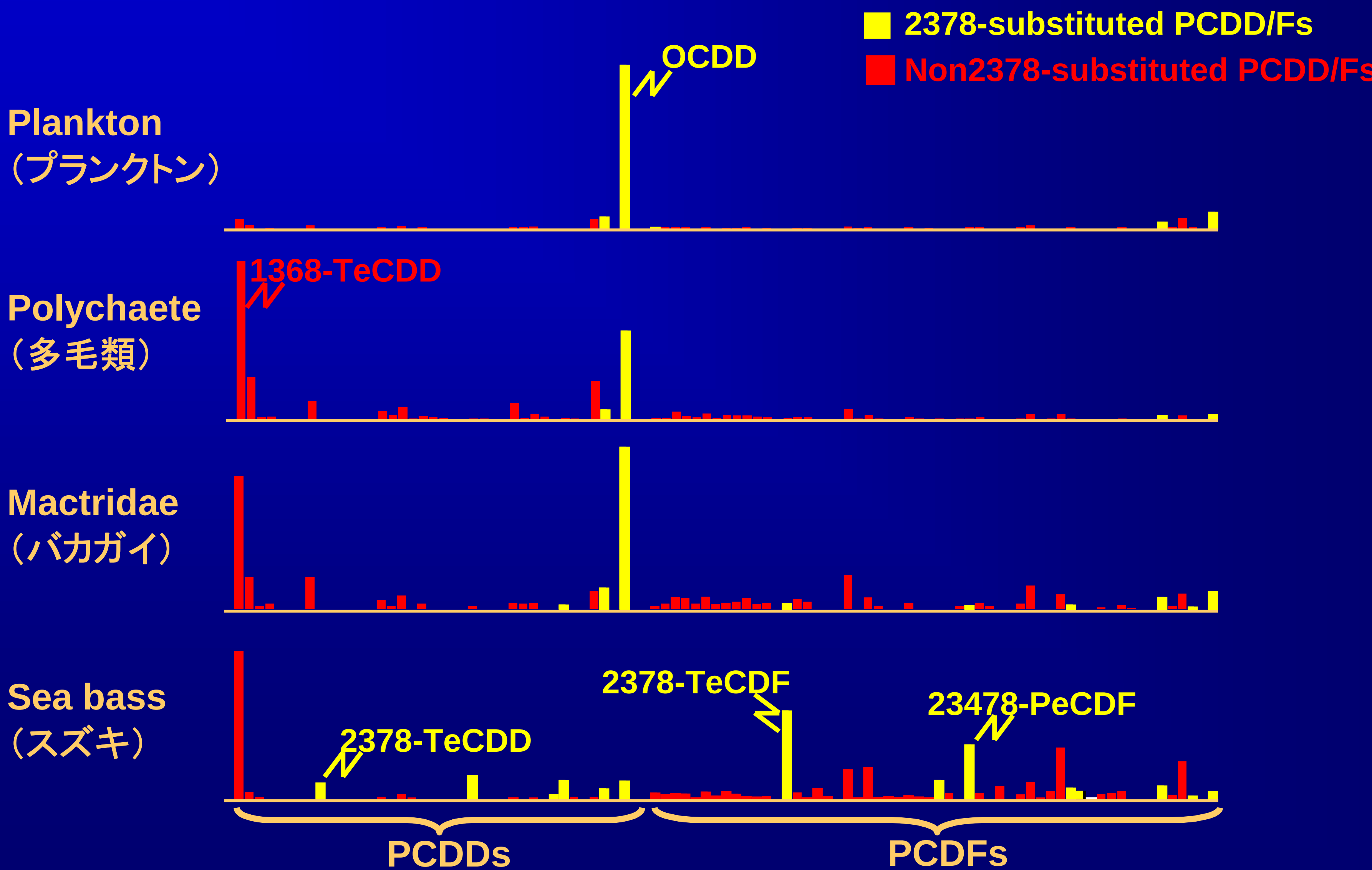
The $^{15}N/^{14}N$ ratio increases by 3 to 5 ‰.
(窒素安定同位体比の増加)

Composition of Total TEQ in aquatic organisms
(各生物種における総TEQの組成)



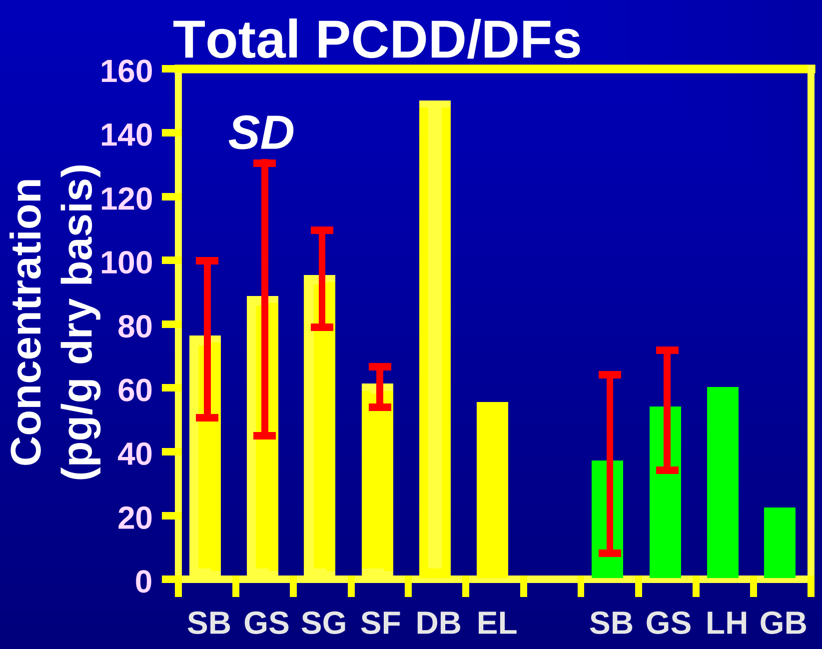
毒性等価量(TEQ)の換算
TEQ = ([PCDD/F*i* × TEF*i*]n) + ([Non-ortho PCB*i* × TEF*i*]n)
TEF(毒性等価係数)はWHO-TEF(Humans)を用いた。

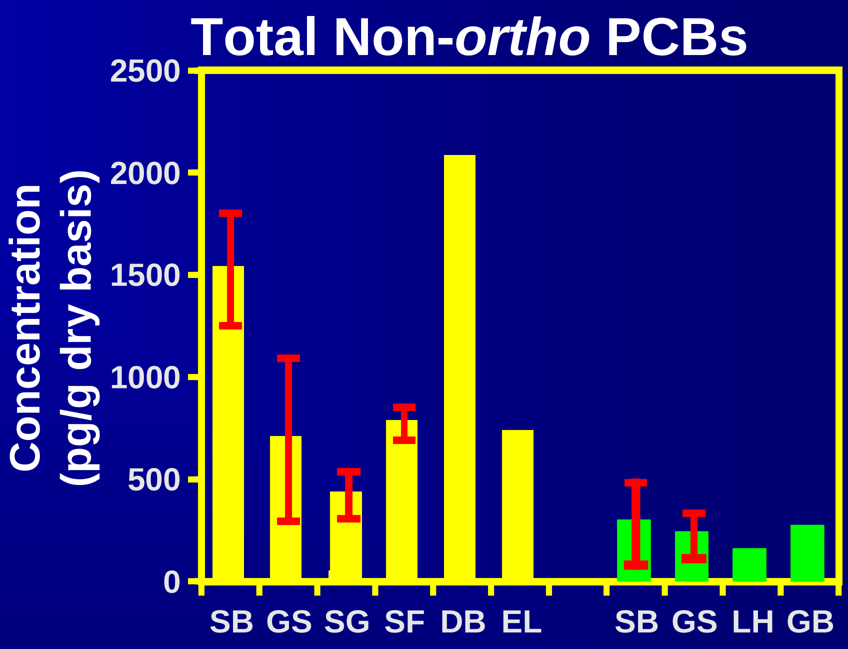
Congener-profiles of PCDD/F in aquatic organisms
（各生物種におけるPCDD/Fs異性体の組成）



Residue levels of PCDD/Fs and Non-*ortho* PCBs in Fish (魚類中ダイオキシン類の残留レベル)

Tokyo Bay (東京湾)
Lake Shinji (宍道湖)



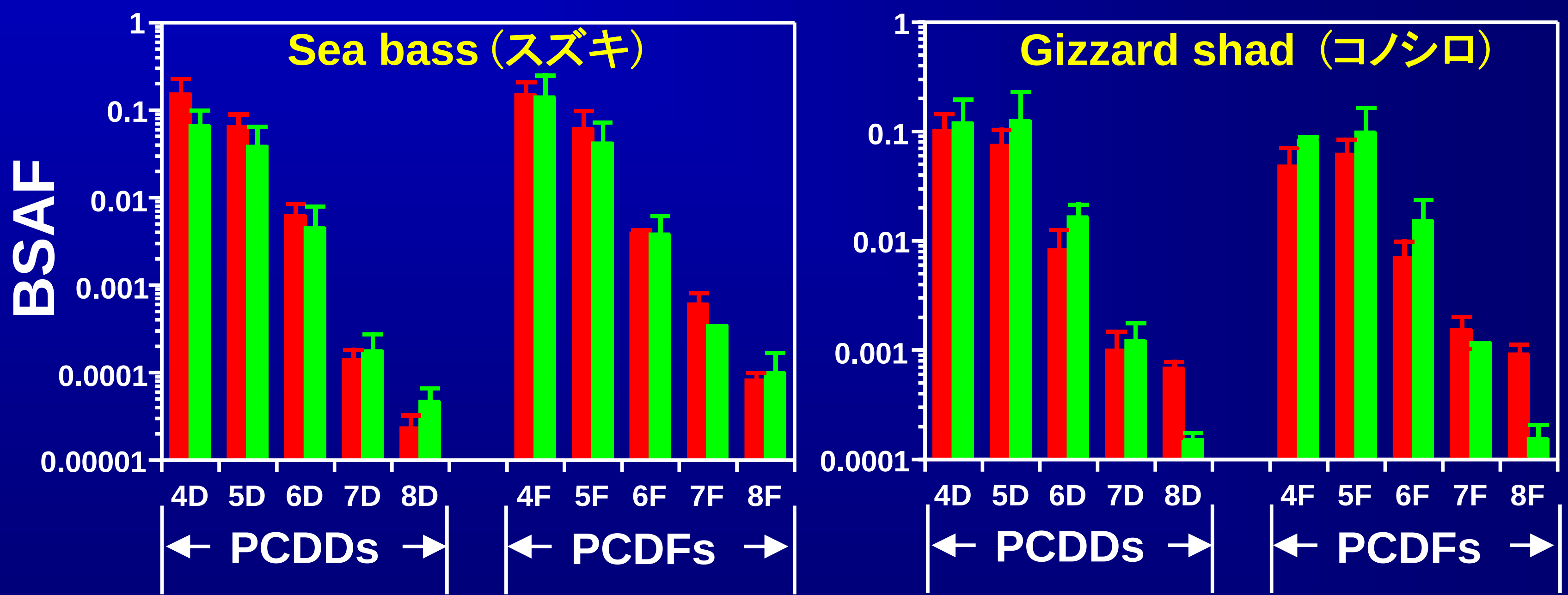


SB : Sea bass（スズキ）, GS : Gizzard shad（コノシロ）, SG : Stingray（アカエイ）, SF : Stone flounder（イシガレイ）, DB : Dab（マコガレイ）, EL : Eel（アナゴ）, LH : Large-eyed-herring（サッパ）, GB : Goby（マハゼ）

Comparison of PCDD/Fs BSAF
（生物-底質濃縮係数の比較；PCDD/Fs）

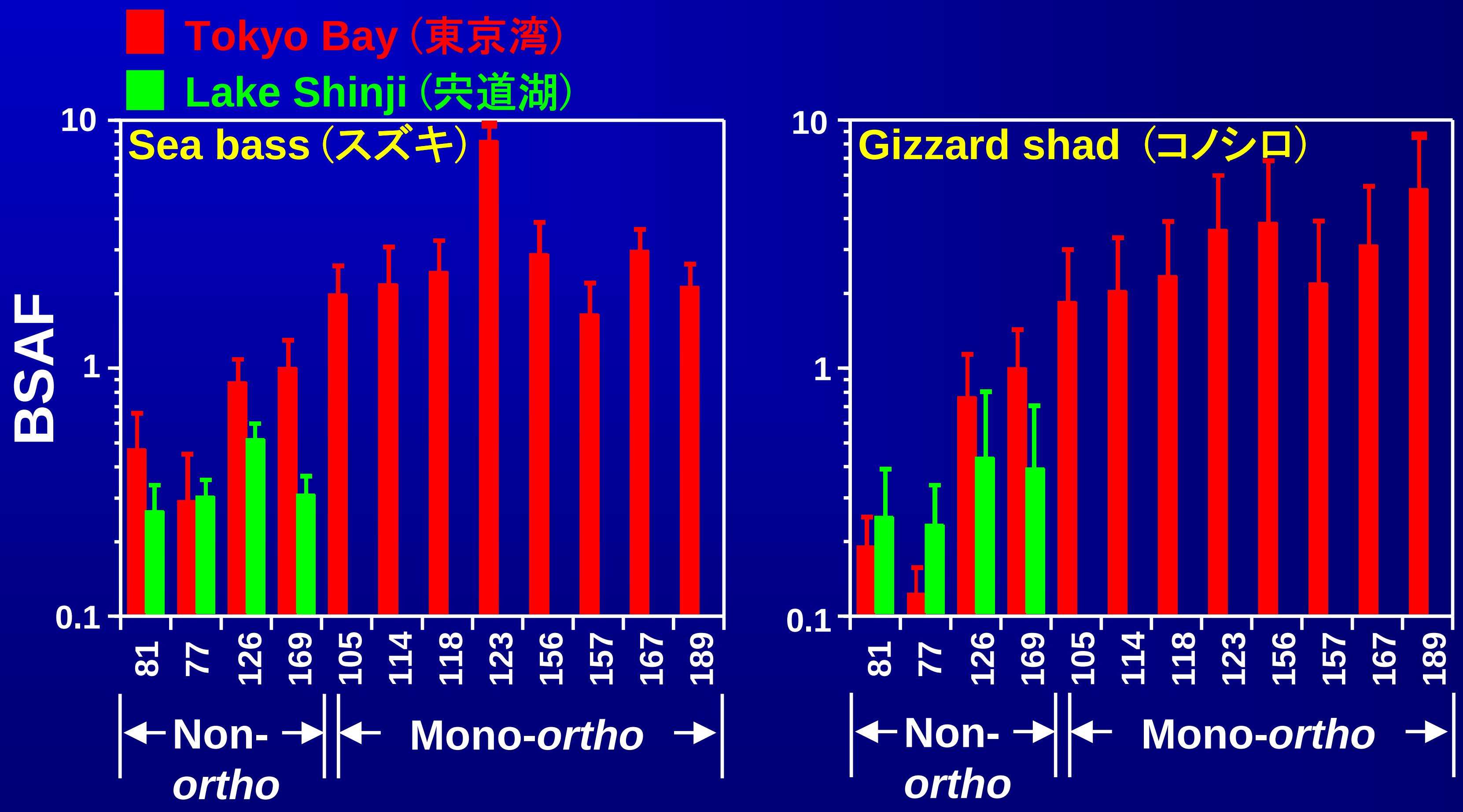
BSAF = Biota (pg/g lipid) / Sediment (pg/g carbon)

Tokyo Bay（東京湾）
Lake Shinji（宍道湖）

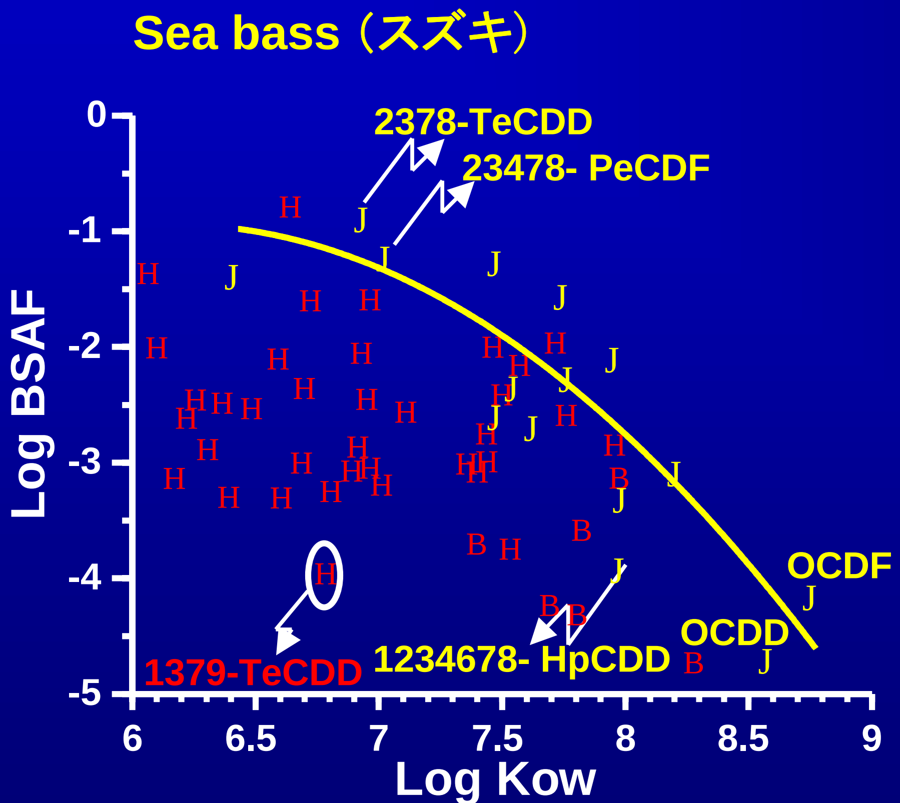


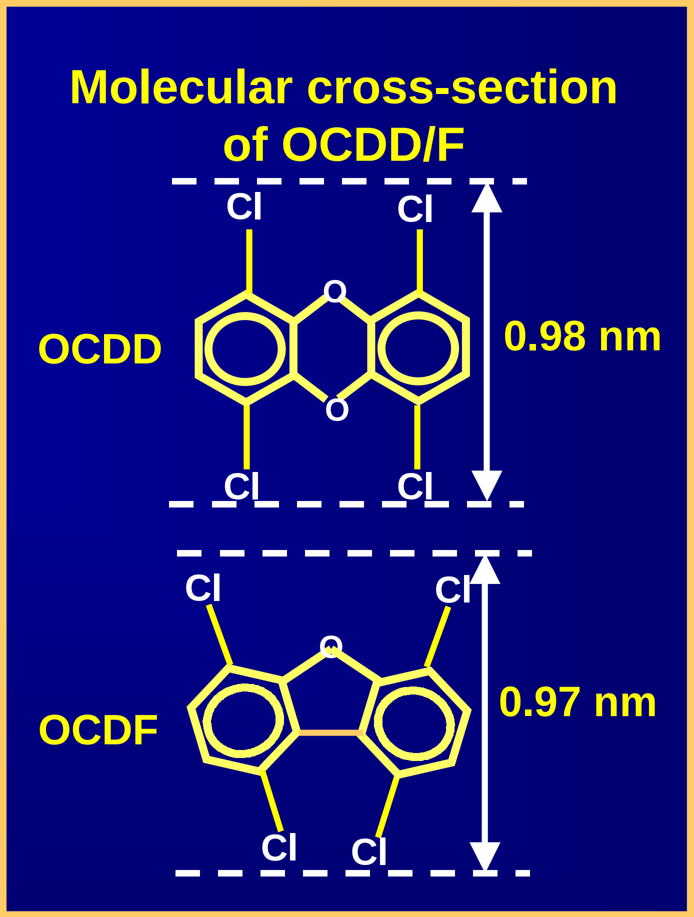
4D, 4F : 2,3,7,8-substituted TeCDD/Fs
5D, 5F : 2,3,7,8-substituted PeCDD/Fs
6D, 6F : 2,3,7,8-substituted HxCDD/Fs
7D, 7F : 2,3,7,8-substituted HpCDD/Fs
8D, 8F : 2,3,7,8-substituted OCDD/Fs

Comparison of Coplanar-PCBs BSAF
（生物-底質濃縮係数の比較；コプラナーPCBs）

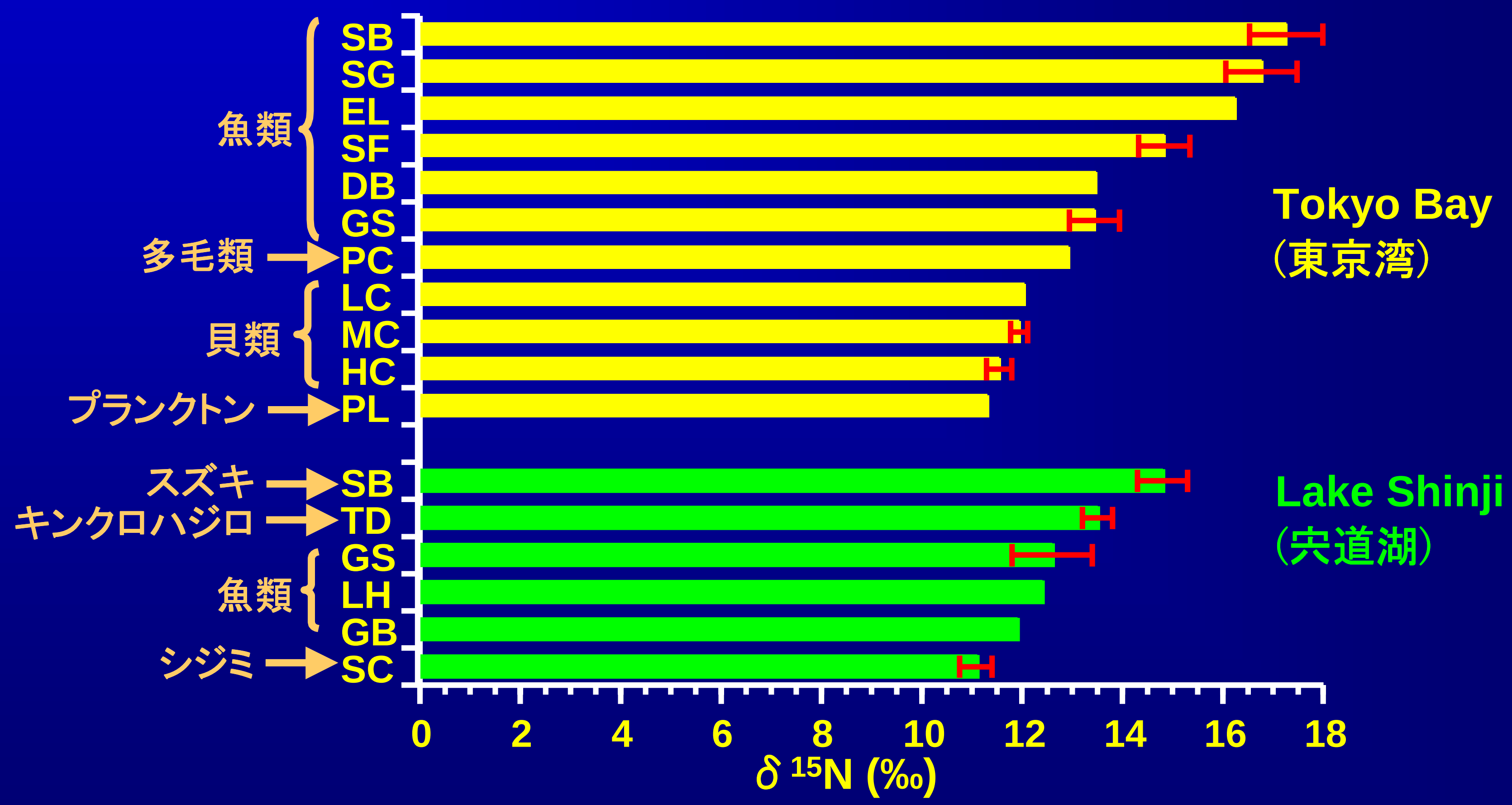


Log BSAF of 2378-substituted and Non 2378-substituted PCDD/Fs
（2378置換体及び非2378置換体PCDD/FsのLog BSAF比較）





Stable nitrogen isotope ratios in aquatic food chain
（水圏食物連鎖における窒素安定同位体比）

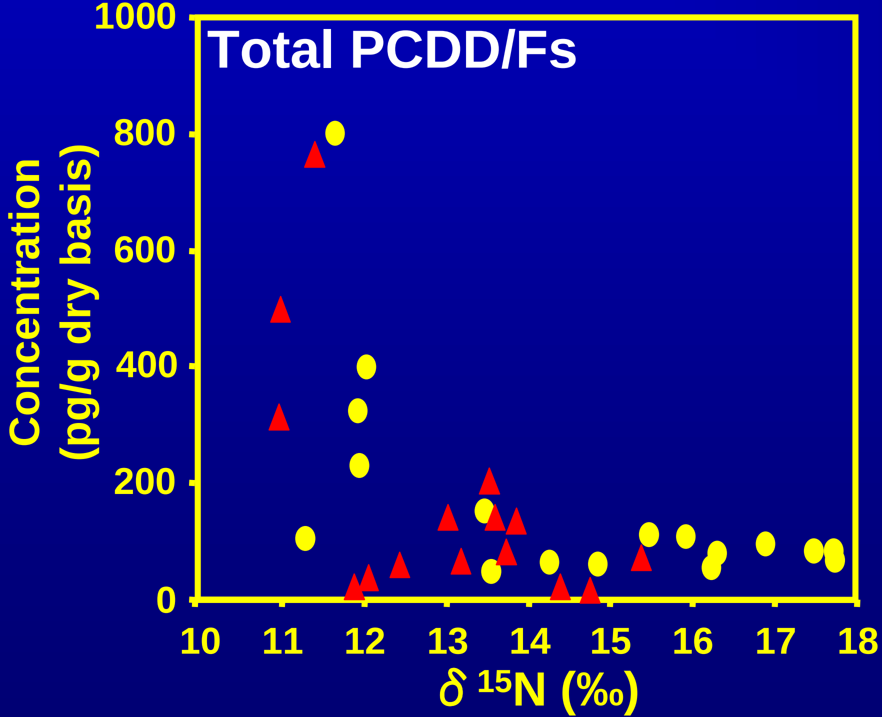


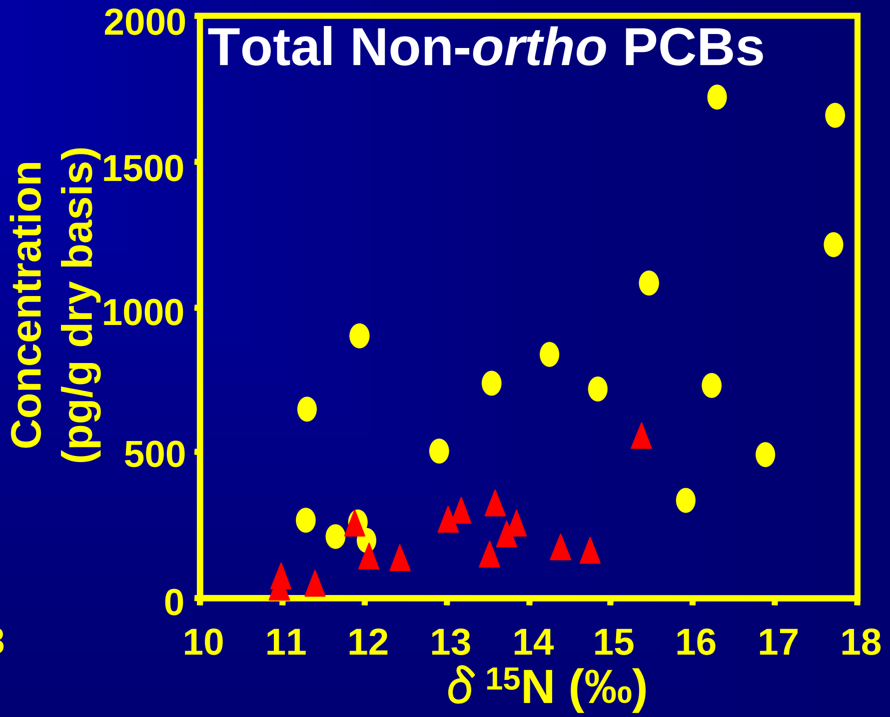
Relationship between PCDD/Fs and Non-*ortho* PCBs and δ ^{15}N in aquatic food chain

（水圏食物連鎖における総PCDD/Fs及びCoplanar-PCBsとδ ^{15}N の関係）

● Tokyo Bay（東京湾）

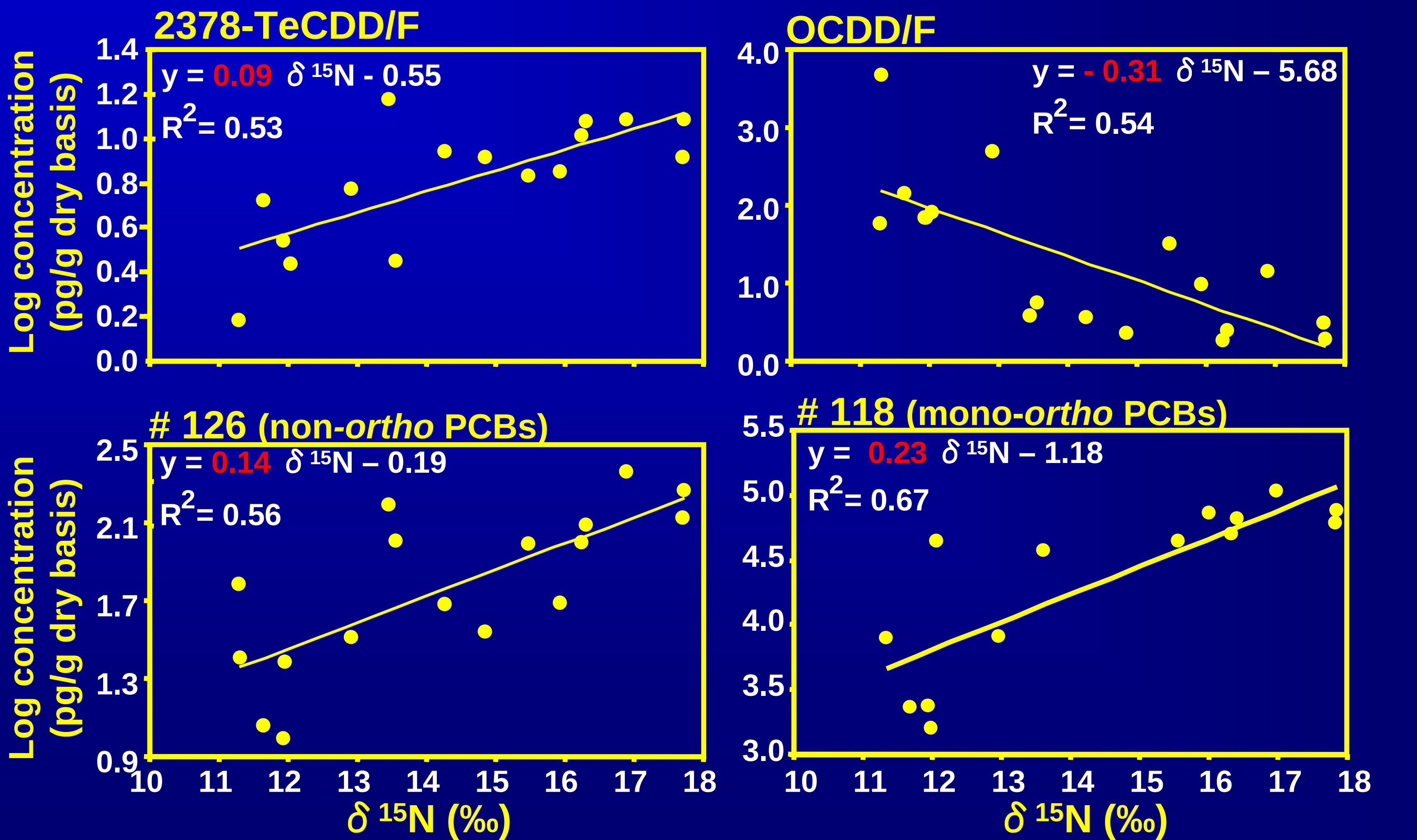
▲ Lake Shinji（宍道湖）



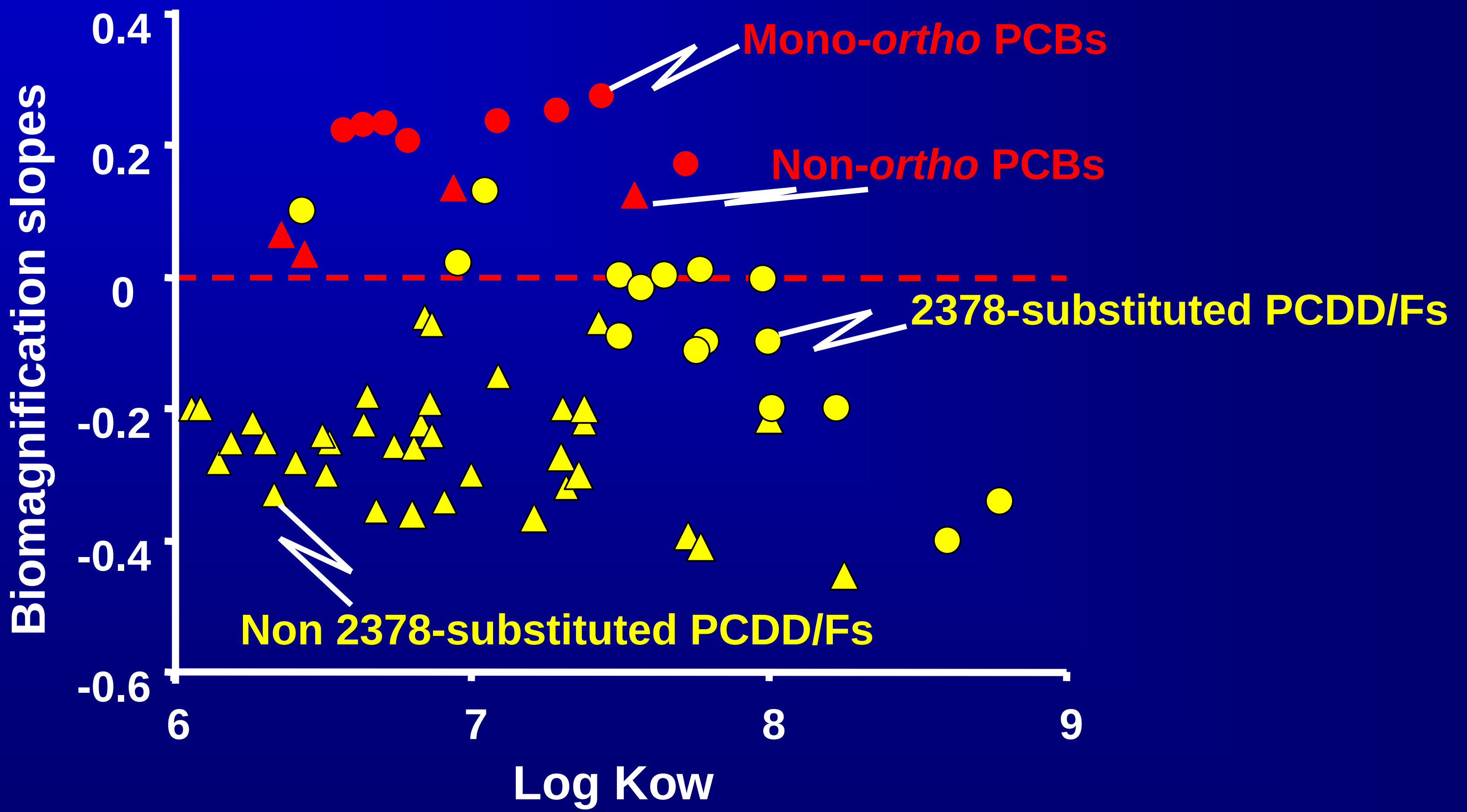


Biomagnification slopes of some congeners

（2378-TeCDD/F, OCDD/F, #126及び#118の生物濃縮スロープ）



Relationship between biomagnification slopes and Log Kow （生物濃縮スロープとLog Kowの関係）



CONCLUSIONS

- **The contamination status of PCDD/Fs and coplanar PCBs in aquatic organisms from Tokyo bay found to be higher than those from Lake Shinji.**
  The contributions of coplanar-PCBs-TEQ to the total TEQ were increased with increasing trophic levels in aquatic food chain.
  ダイオキシン類による汚染状況は宍道湖より東京湾のほうが高かった。
  総TEQ濃度に対するコプラナーPCB-TEQの寄与は高次栄養段階にいくほど増加していた。

- **The BSAFs of PCDD/Fs and coplanar-PCBs in the fish samples collected from Lake Shinji and Tokyo Bay recorded in the same order and showed similar trends in both area.**
  PCDD/F BSAFs were estimated to be lower and tended to decrease as the number of chlorines increased on homologus of PCDD /Fs.
  東京湾と宍道湖で観察されたダイオキシン類のBSAF値は同レベルであり、類似した傾向を示した。
  PCDD/FsのBSAFは塩素置換数の増加によって減少していた。

- **In the aquatic food chain, the total concentrations of coplanar-PCBs increased with increasing trophic levels estimated with stable nitrogen isotope ratios.**
  On the whole, the relationship between the PCDD/F concentrations and trophic level was not clear. Almost all PCDD/F congeners were negatively correlated with trophic levels.
  Altogether, the results suggested that the biomagnification of PCDD/Fs is not efficient when compared with coplanar-PCBs in the aquatic food chain.
  水圏食物連鎖上の栄養段階の増加に伴いコプラナーPCBsの濃度は増加傾向を示した。反面、PCDD/Fsの場合はいくつかの毒性が強い異性体を除いて大部分の異性体が栄養段階と逆相関を示していた。
  PCDD/Fsの生物濃縮効率はコプラナーPCBsと比べ低いと判断される。

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