カワウにおけるダイオキシン類曝露と生存リスク評価

Dioxin and Dioxin-like PCB Exposure and Their Risk Estimation: Survival Rate of Common Cormorant in Japan

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背景（Backgrounds）

わが国における対応 *A countermeasures in Japan*

環境庁：’78よりPCBや有機塩素系農薬のモニタリング調査

Environ. Agency Govement Japan: Since 1978, Monitoring chemicals total PCB and organochlorine compounds in a few bird species and fish.

＝総濃度（PCB）としての表示，環境安全点検という前提

= Showing as total concentration for indicator of environmental safety check.

→生物個体への曝露（毒性）評価としては，不十分

→It is insufficient as exposure (toxic) evaluation to the wildlife.

’98野生生物のダイオキシン類汚染状況調査

Since 1998, Monitoring of PCDDs, PCDFs and dioxin-like PCBs in wildlife.

→モニタリング中心，体内挙動などの解明が必須

→It is indispensable that not only monitoring but resolution such as mechanism of action within body.

目的:化学物質による野生鳥類への毒性影響を定量的に評価する

Objectives: Quantitative estimation of toxic effect by chemicals to wildbird

▽有害となる化学物質

The peculiarity of the chemical which becomes harmful

1. 生産量および発生量
   Amount of produce and occurrence
2. 使用量, 使用形態
   Using form and volume
3. 残留性 Persistency in environment
4. 生物濃縮性 Bioaccumulation
5. 毒性 Toxicity

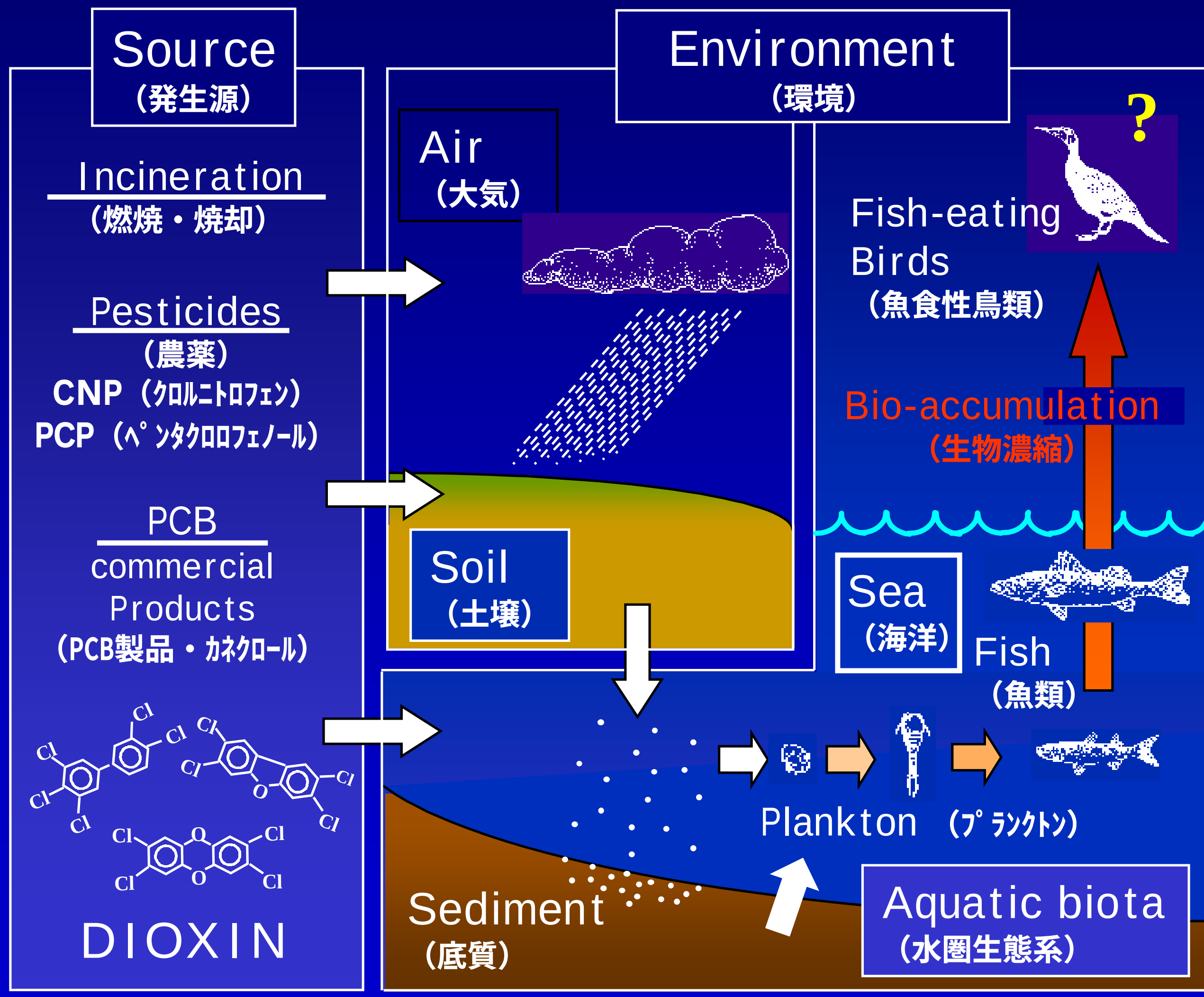
▽対象生物(カワウ)

Target (Cormorant)

1. 大型 Big body size
2. 魚食性 Fish eating nature
3. 定住性 Residential
4. 長寿命 Long life

Cormorant

ダイオキシン類の環境挙動
(Environmental fate of PCDD, PCDF and dioxin-like PCBs)



野生鳥類にみられた化学物質による毒性影響
Observed toxicity by chemicals in wildbirds

皮下水腫
Subcutaneous edema

胚の死亡
Embryo mortality

卵殻の薄化(DDE)
Egg shell thickness

アメリカ五大湖で観察された
ミミヒメウ幼鳥の嘴の奇形

嘴や足の奇形
Deformity;
Cross-bill, Club-feet

免疫毒性
Immuno toxicity

生殖低下
Reduced reproduction

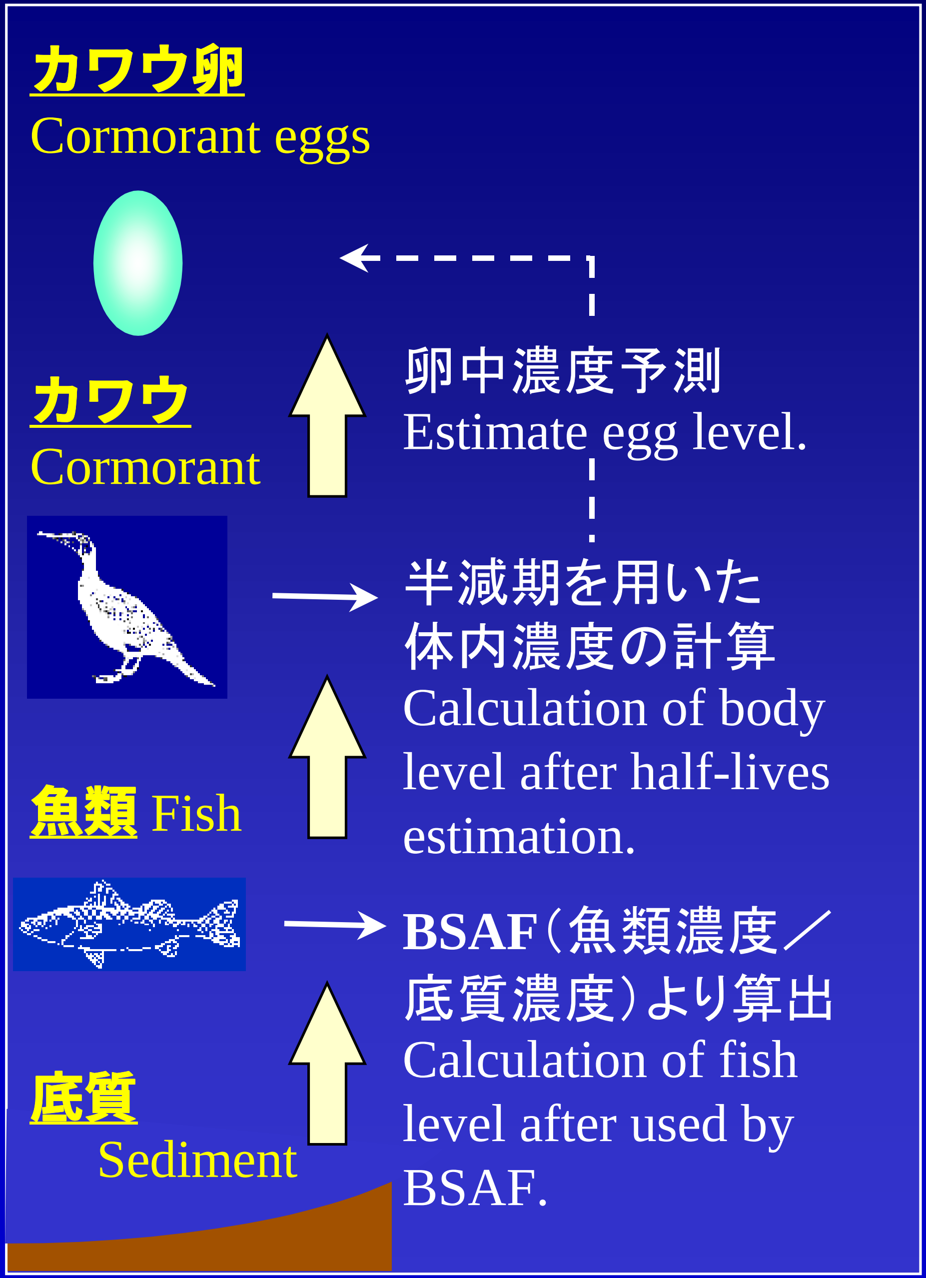
本研究の構成
Scheme of this study

1.**カワウ肝臓および卵，魚類中レベル（**BMF,TEQ**による異性体の特徴）**
Levels in the liver, egg of cormorant’s and fish (Conc., BMF, TEQ).

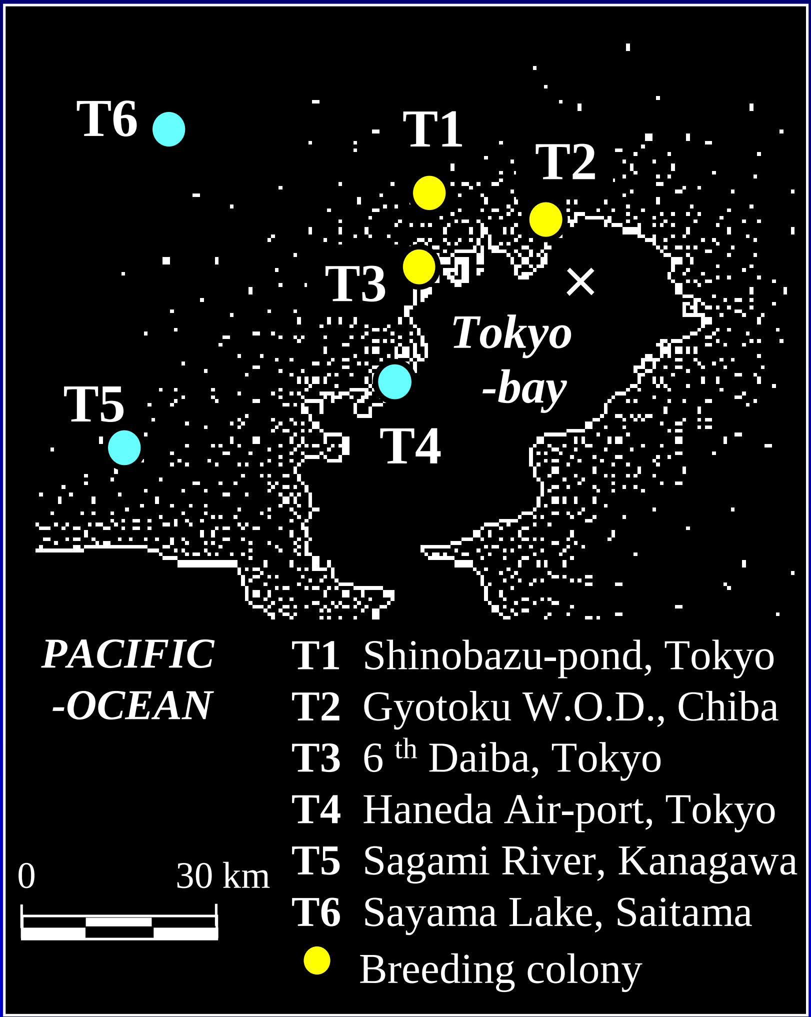
2.**体内分布**
Body distribution.

3.**半減期の推定**
Estimation of half-lives.

4.**底質コア濃度からの卵中濃度変遷の推算**
Trend of TEQ in the egg.

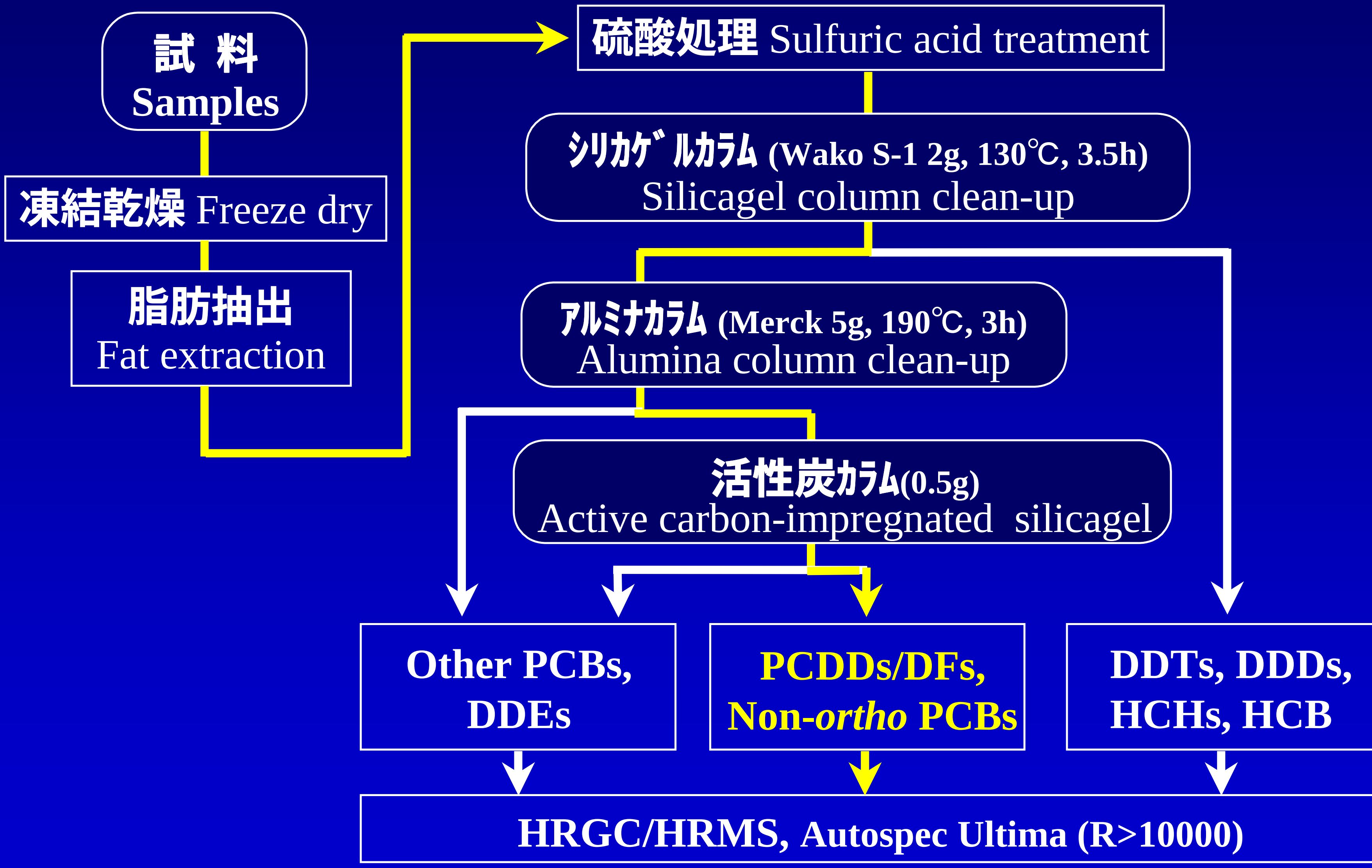


分析試料 Sampling locations

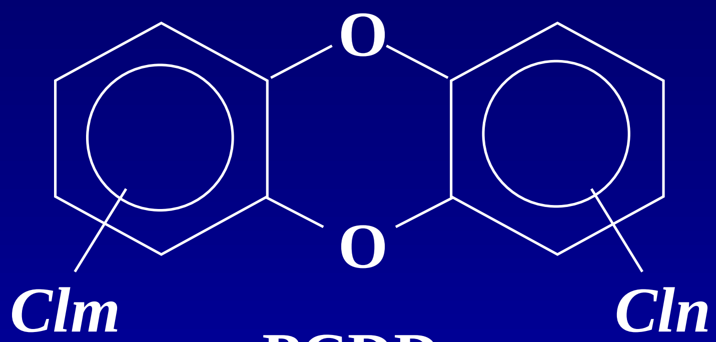


種　類 Species	*n*	場　所 Locations
カワウ **Cormorant**	*16*	上野不忍池, **T1**
雛 Chick	*1*	行徳, **T2**
幼鳥 Juv.	*10*	狭山湖, **T6**
成鳥 Adult	*5*	相模川, **T5**
フクロウ **Owl**	*1*	行徳, **T2**
カルガモ **Duck**	*1*	行徳, **T2**
トビ **Kite**	*1*	羽田空港, **T4**
ユリカモメ **Gull**	*1*	行徳, **T2**
チュウシャクシギ **Whimbrel**	*1*	羽田空港, **T4**
アオサギ **Blue heron**	*1*	行徳, **T2**
カラス **Crow**	*1*	羽田空港, **T4**
キジ **Pheasant**	*1*	行徳, **T2**
ドバト **Pigeon**	*1*	行徳, **T2**
ウコッケイ **Silky**	*1*	**Nihon-Univ.**

化学分析のフローチャート
Schematic diagram of chemical analysis

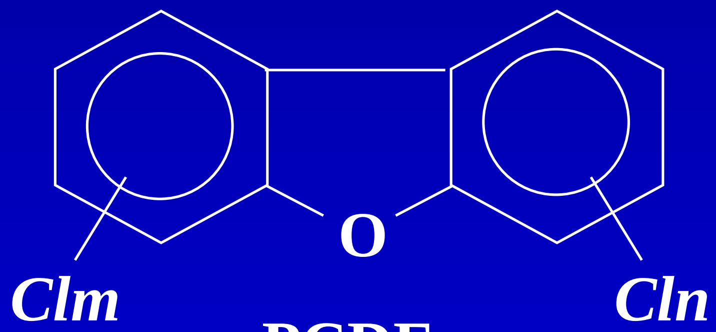


測定物質 Analyzed dioxin and its related compounds



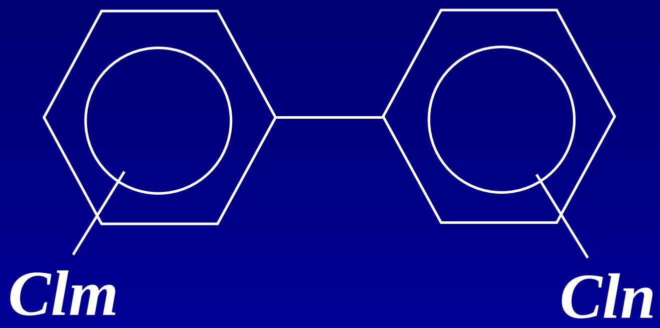
PCDDs

$m+n = 4 \sim 8$



PCDFs

$m+n = 4 \sim 8$



PCBs

$m+n = 4 \sim 7$

Dioxin-like PCBs

non-*ortho* PCBs

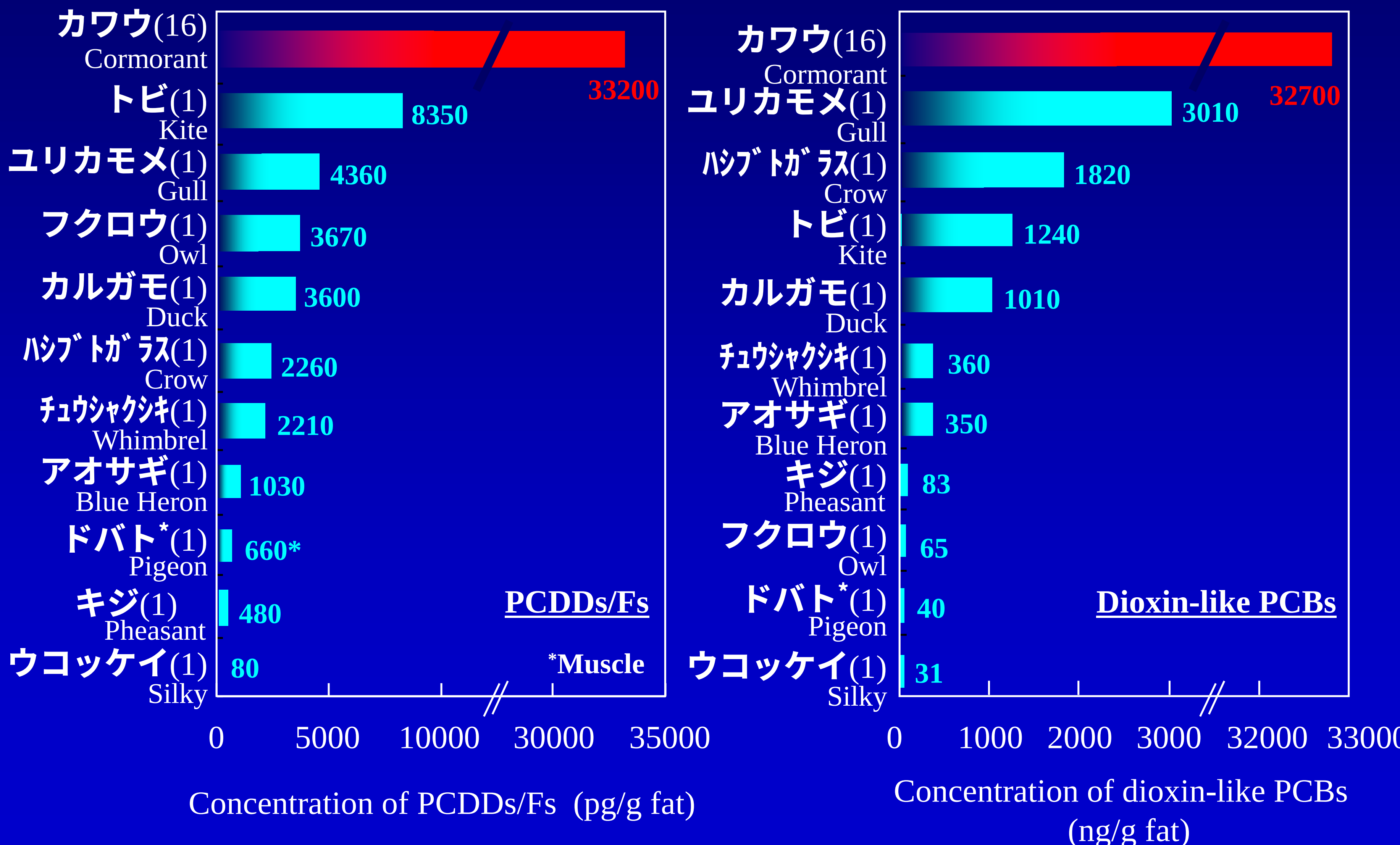
CB81, CB77, CB126, CB169

mono-*ortho* PCBs

CB105, CB114, CB118, CB123, CB156, CB157, CB167, CB189

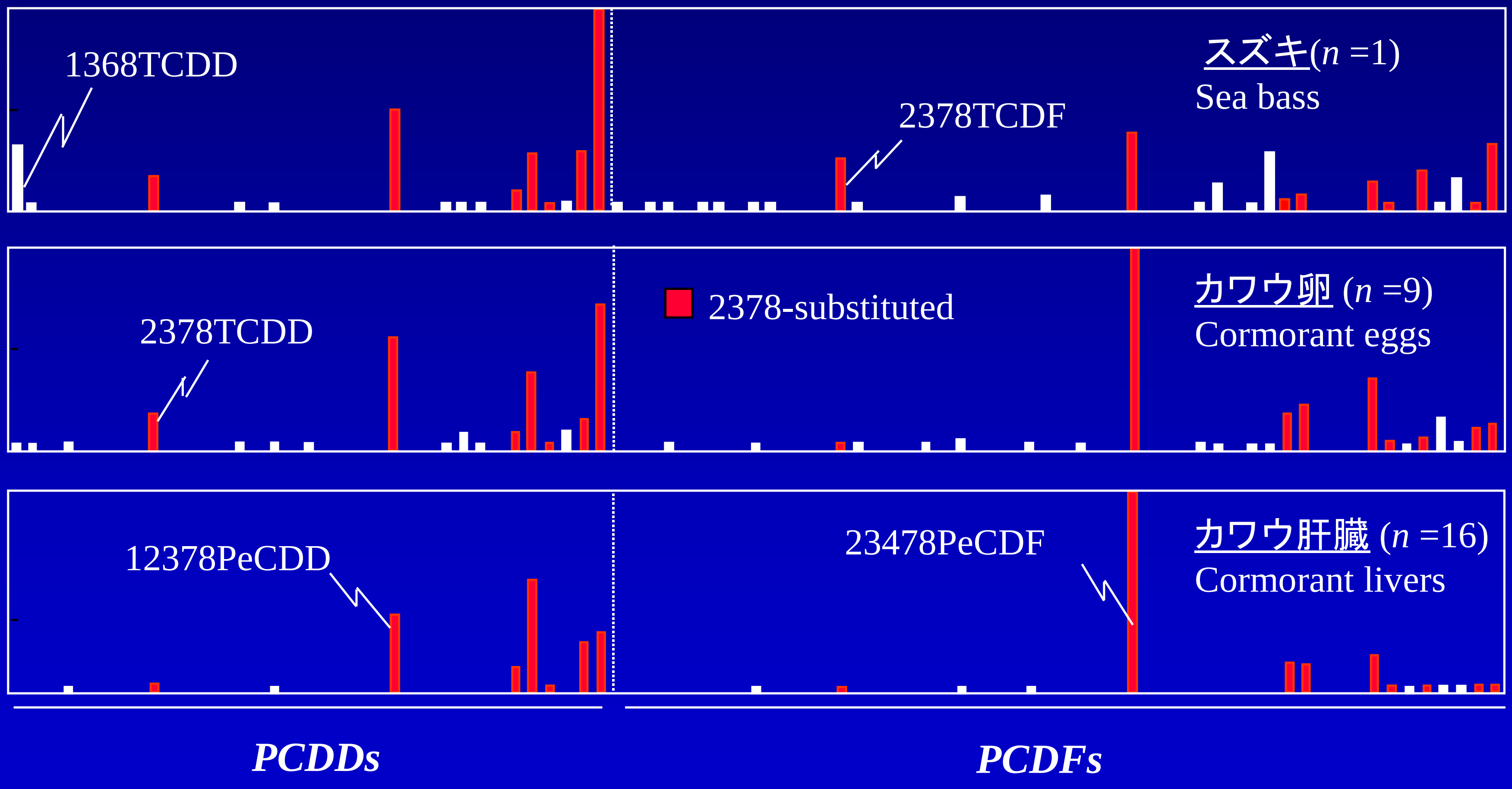
肝臓中PCDDs/DFsとdioxin-like PCBs総濃度の種間比較

Comparison of PCDD/Fs and dioxin-like PCBs concentrations in the liver among bird samples.



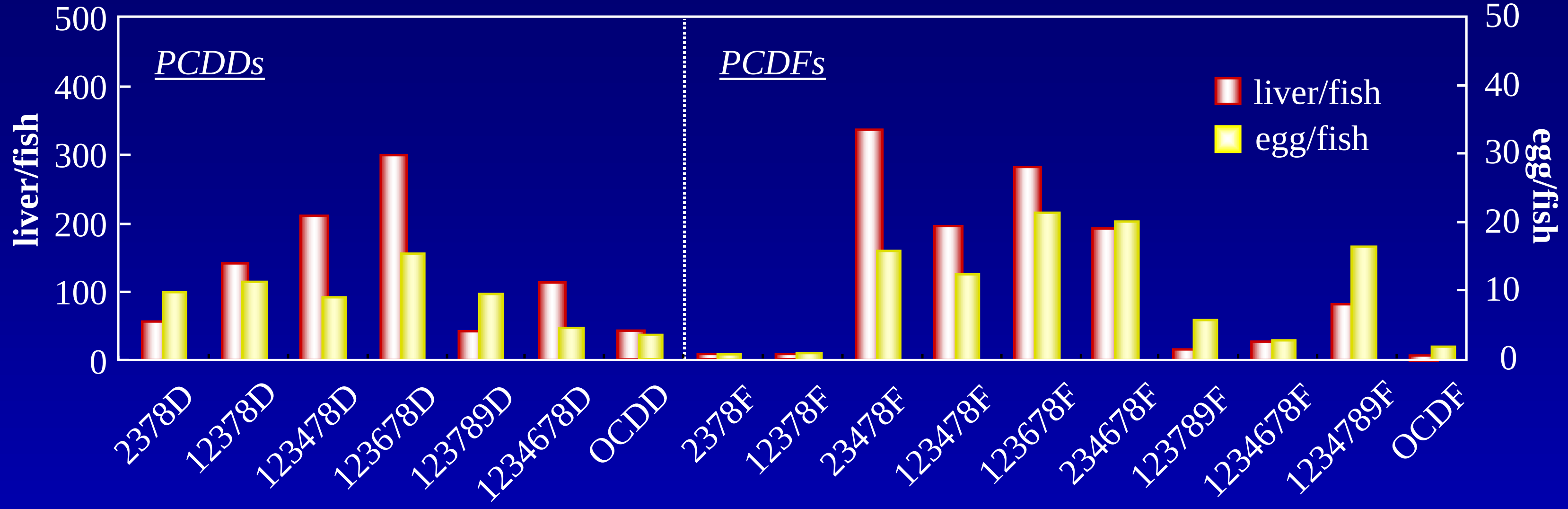
カワウ肝臓，卵および魚類中の異性体プロファイル

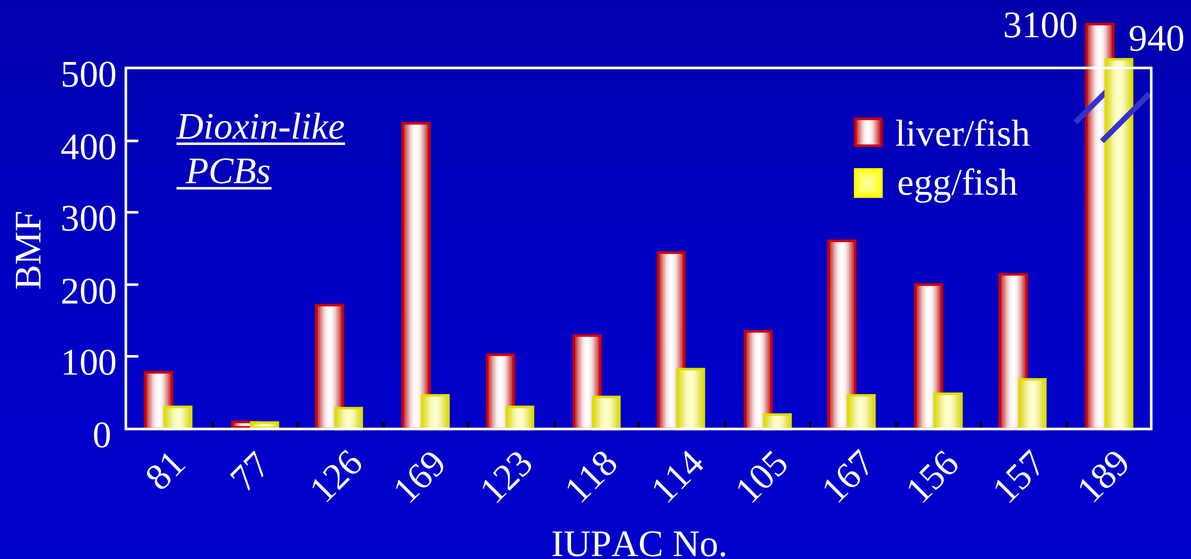
Congener profiles of PCDDs and PCDFs in the liver of cormorants and in whole fish.



カワウ肝臓および卵におけるダイオキシン類の生物濃縮係数（BMF）

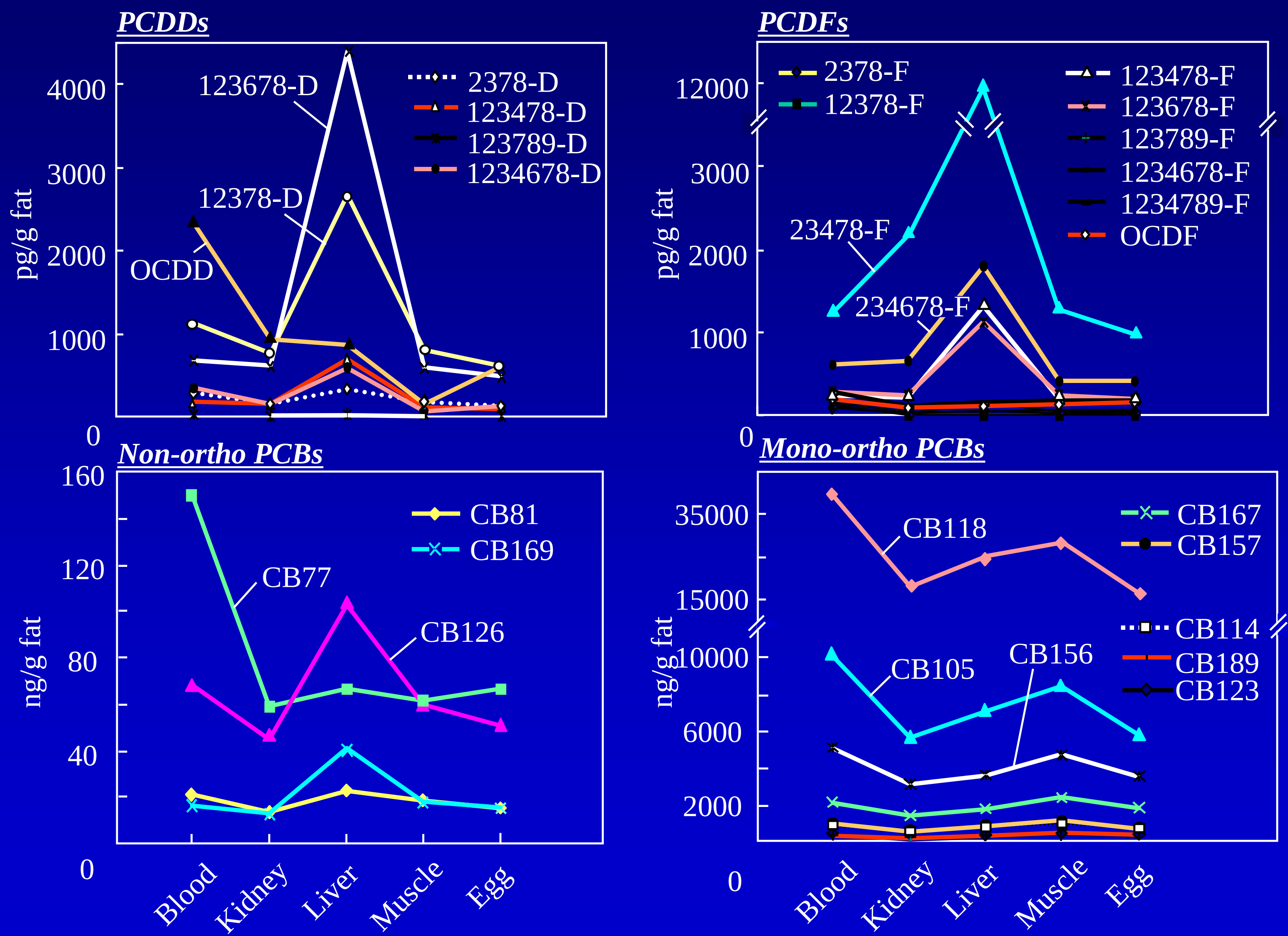
Biomagnification factor of common cormorant liver and egg /fish collected from Tokyo Bay, Japan





カワウ組織・器官中PCDD/Fs, dioxin like PCBs濃度

Distribution of PCDD/Fs and dioxin like PCBs in cormorant



毒性等価係数 TEF: Toxic equivalent factor

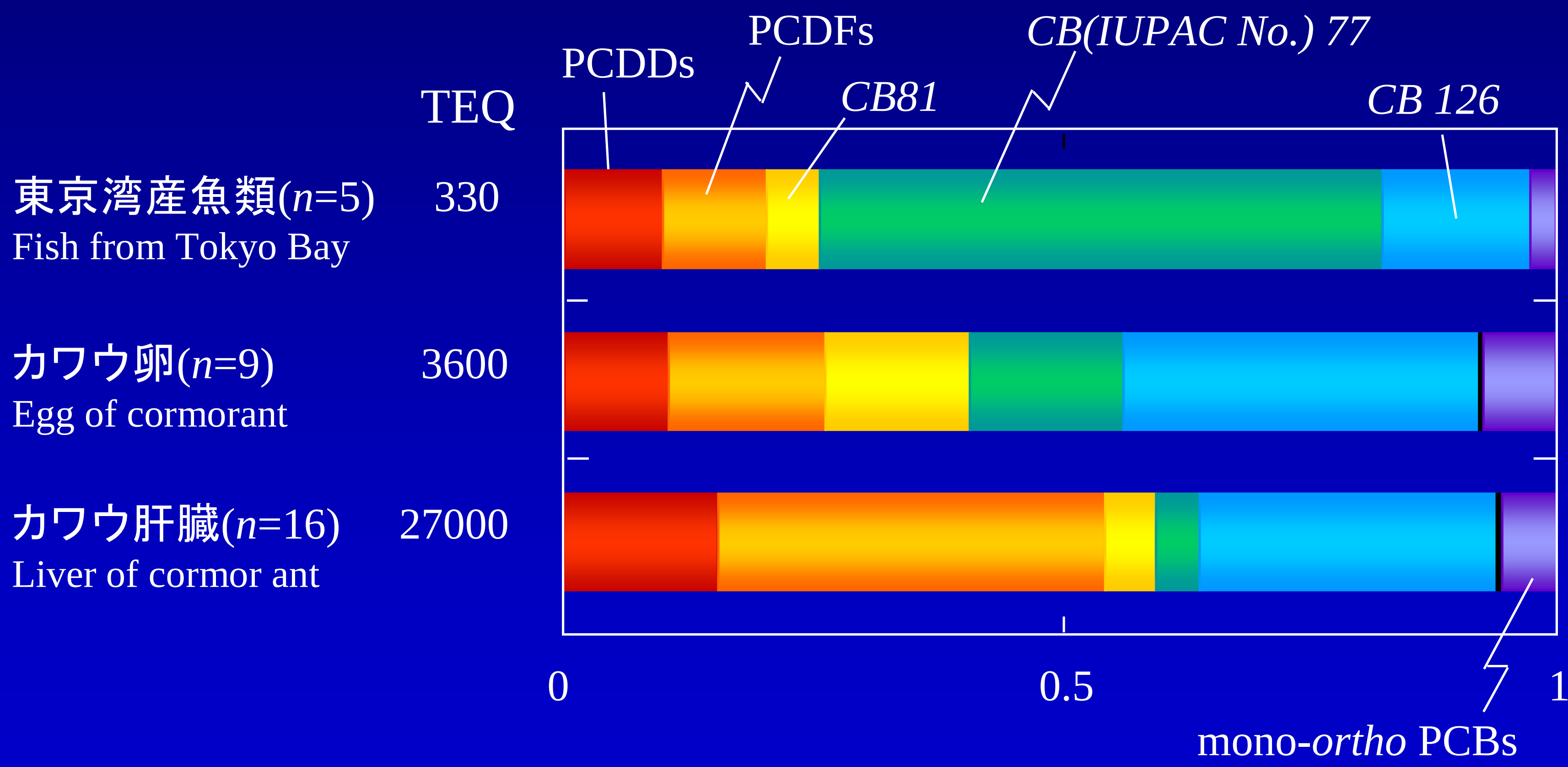
Congener	WHO-TEF (Human/ mammal)	WHO-TEF (Birds)
PCDDs		
2,3,7,8-D	1	**1**
1,2,3,7,8-D	1	**1**
1,2,3,4,7,8-D	0.1	0.05
1,2,3,6,7,8-D	0.1	0.01
1,2,3,7,8,9-D	0.1	0.1
1,2,3,4,6,7,8-D	0.01	0.001
OCDD	0.0001	-
PCDFs		
2,3,7,8-F	0.1	**1**
1,2,3,7,8-F	0.05	**0.1**
2,3,4,7,8-F	0.5	**1**
1,2,3,4,7,8-F	0.1	0.1
1,2,3,6,7,8-F	0.1	0.1
2,3,4,6,7,8-F	0.1	0.1
1,2,3,7,8,9-F	0.1	0.1
1,2,3,4,6,7,8-F	0.01	0.01
1,2,3,4,7,8,9-F	0.01	0.01
OCDF	0.001	0.0001

Congener	WHO-TEF (Human/ mammal)	WHO-TEF (Birds)
Non-*ortho* PCB		
CB81	0.0001	**0.1**
CB77	0.0001	**0.05**
CB126	0.1	0.1
CB169	0.01	0.001
Mono-*ortho* PCB		
CB105	0.0001	0.0001
CB114	0.0005	0.0001
CB118	0.0001	0.00001
CB123	0.0001	0.00001
CB156	0.0005	0.0001
CB157	0.0005	0.0001
CB167	0.00001	0.00001
CB189	0.0001	0.00001

TEQ（**毒性等価量**）
= Σ Conc. × TEF（**毒性等価係数**）

TEQ寄与割合の比較

Toxic equivalent contribution (Birds-TEF) of PCDDs, PCDFs and dioxin-like PCBs in cormorant and fish.



まとめ 1（Summary-１）

1. カワウは他鳥種と比較してダイオキシン類の高い曝露をうけている種である.
Cormorants are significantly exposed to dioxin and its related compounds with comparison to those of other species.

2. カワウ肝臓および卵中**PCDD/Fs**は, **2,3,7,8-**置換体が優占的であり, その組成は餌である魚類中のものと類似していた.
2,3,7,8-substituted PCDD/Fs comprised 97% and 90% in the liver and egg, respectively, these profile is similar to fish from same location in Tokyo Bay.

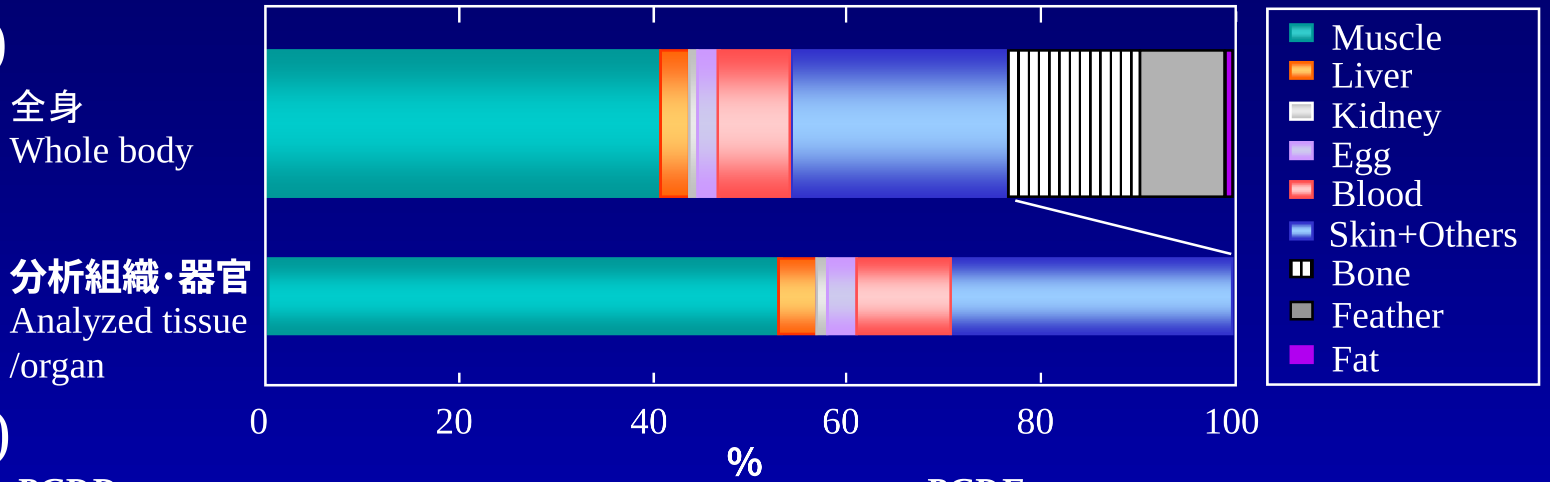
3. 肝臓および卵中**BMF**（生物蓄積係数）を比較したところ, 肝臓で**1,2,3,6,7,8-HxCDD**（**300**）や**2,3,4,7,8-PeCDF**（**340**）, **CB169**（**424**）などが特に高い値を示した. 一方, **2,3,7,8-TCDF**（**1.9**）や**CB77**（**6.9**）は非常に小さい値となった.
High bio-magnification found for 1,2,3,6,7,8-HxCDD（300）, 2,3,4,7,8-PeCDF（340）and CB169（424）, while 2,3,7,8-TCDF（1.9）and CB77（6.9）found to lower.

4. **2,3,7,8- PCDD/Fsの肝臓への特異的な蓄積がみられた. またTEQ寄与は, 肝臓（50%）と卵（25%）で大きく異なった.**
Specific accumulation of 2,3,7,8-substituted PCDD/Fs were found in the liver, and these TEQ contribution is different between liver (50%) and egg (25%).

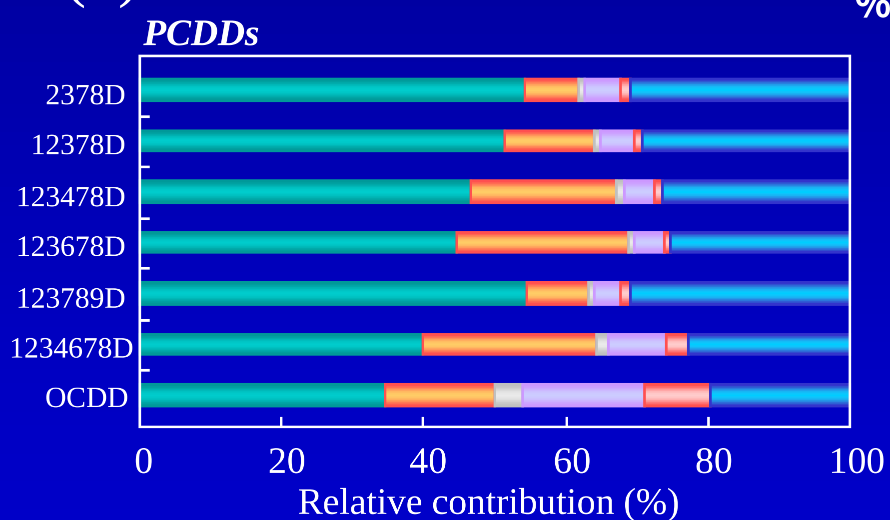
カワウ組織・器官の重量割合(a)とPCDDs/DFs負荷割合(b)

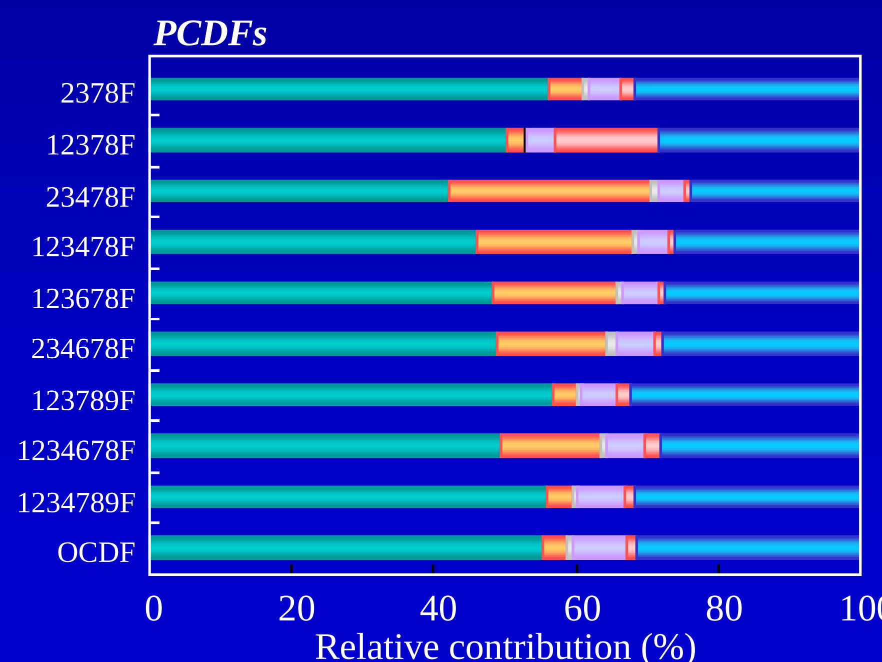
(a)Percentage body weight of target organ and (b) burden of 2,3,7,8-substituted PCDD/Fs in the tissue/organ.

(a)



(b)





→ $Ratio_{liver}$を決定

体内半減期の推定 Estimation of half-lives

定常状態にある体内濃度の計算式：
The formula for concentration within body in static state:

$$\frac{C_{Fish} \times AD \times f}{Fat_{liver}} \times \frac{T_{1/2}}{Log_e 2} \times Ratio_{liver} = C_{liver}$$

where, C = Concentration, AD =Administered dose,
f = Absorption ratio, $Log_e 2$ = 0.693,
$Ratio_{liver}$ = Burden of liver among analyzed tissue.

$$T_{1/2} = \frac{C_{liver} \times Log_e 2 \times Fat_{liver}}{C_{fish} \times AD \times f \times Ratio_{liver}}$$

計算に用いた各パラメーター
Parameters used to calculate half-lives in common cormorant.

Symbols			Ratio $_{liver}$	
[1] *Weight ratio in whole body*			2,3,7,8-TCDD	*0.075*
Muscle	W_M	*0.41*	1,2,3,7,8-PeCDD	*0.13*
Liver	W_L	*0.029*	1,2,3,4,7,8-HxCDD	*0.21*
Kidney	W_K	*0.0090*	1,2,3,6,7,8-HxCDD	*0.24*
[2]Egg	W_E	*0.021*	1,2,3,7,8,9-HxCDD	*0.09*
[3]Blood	W_B	*0.074*	1,2,3,4,6,7,8-HpCDD	*0.24*
Others	W_O	*0.23*	OCDD	*0.15*
[4] *Fat ratio in the tissues/organs*				
Muscle	F_M	*0.036*	2,3,7,8-TCDF	*0.048*
Liver	F_L	*0.037*	1,2,3,7,8-PeCDF	*0.026*
Kidney	F_K	*0.028*	2,3,4,7,8-PeCDF	*0.28*
Egg	F_E	*0.060*	1,2,3,4,7,8-HxCDF	*0.22*
Blood	F_B	*0.0034*	1,2,3,6,7,8-HxCDF	*0.17*
Parameters			2,3,4,6,7,8-HxCDF	*0.15*
Administrative dose	*AD*	$BW \times 0.26$	1,2,3,7,8,9-HxCDF	*0.031*
[5]Absorption ratio	f	*0.94*	1,2,3,4,6,7,8-HpCDF	*0.14*
Body weight	*BW*	*1885*	1,2,3,4,7,8,9-HpCDF	*0.036*
$Log_e 2$		*0.693*	OCDF	*0.033*
Fish fat%		*0.07*		

[1]Assumption from real value of female (n =4), [2]Egg data measured in this study.
[3]Blood data is value from other study, unpublished, [4]Fat ratio is value of analyzed sample in this study.
[5]Absorption ratio is using fat ratio of fecal matter/ fish.

推定に用いた魚類中およびカワウ肝臓中濃度と推定された体内半減期（$T_{1/2}$）

Concentration used to calculate half-lives in common cormorant and estimate half-lives ($T_{1/2}$).

Congener	Concentration (pg/g fat)		$T_{1/2}$
	Fish (*n* =5)	Liver (*n* =6)	
PCDDs			
2,3,7,8-TCDD	9.5	703	43
1,2,3,7,8-PeCDD	26	4464	59
1,2,3,4,7,8-HxCDD	5.4	1307	51
1,2,3,6,7,8-HxCDD	16	5565	61
1,2,3,7,8,9-HxCDD	1.5	57	19
1,2,3,4,6,7,8-HpCDD	20	1949	17
OCDD	88	4472	14
PCDFs			
2,3,7,8-TCDF	23	66	2.6
1,2,3,7,8-PeCDF	5.6	13	3.9
2,3,4,7,8-PeCDF	32	14859	72
1,2,3,4,7,8-HxCDF	8	1906	47
1,2,3,6,7,8-HxCDF	4.8	1534	79
2,3,4,6,7,8-HxCDF	10	2566	73
1,2,3,7,8,9-HxCDF	2.6	46	24
1,2,3,4,6,7,8-HpCDF	13	322	7.8
1,2,3,4,7,8,9-HpCDF	2.2	220	122
OCDF	28	297	14

動物種における2,3,7,8-TCDDの生物学的半減期
2,3,7,8-TCDD half-lives ($T_{1/2}$) of other animals and humans

種 Species	半減期($T_{1/2}$) Half-lives($T_{1/2}$)
カワウ Cormorant	31～69day
マウス* Mouse	11～24day
ラット* Rat	17～31day
モルモット* Guinea pig	30day
魚* Fish	52～83day
アカゲザル* Monkey	1year
ヒト* Human	6～10year

eit *et al.* , 1992

非定常における肝臓中濃度の計算式：
The formula for concentration within body in unstatic state:

$$\frac{C_{Fish} \times AD \times f}{Fat_{liver}} \times \frac{T_{1/2}}{Log_e 2} \times Ratio_{liver/target} \times \left[1 - \exp\left(- Log_e 2 / T_{1/2}\right) \times t\right] = C_{liver}$$

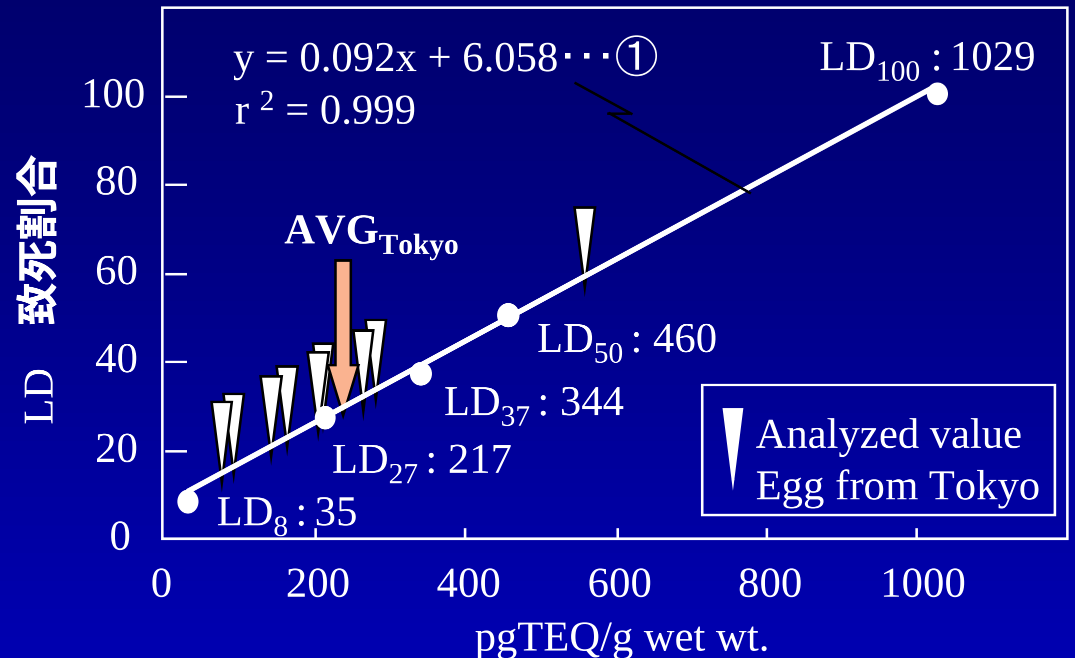
where, C = Concentration, AD =Administered dose, f = Absorption ratio, $Log_e 2 = 0.693$

カワウ5歳齢の実測値と非定常（5年）を仮定した計算値の比較
Comparison between anlyzed level of PCDD/Fs in the liver of cormorant (5 years old) and calculated value from assumed in unstatic state.

Congener	Concentration		Congener	Concentration	
	5year	Calculated		5year	Calculated
PCDDs			*PCDFs*		
2,3,7,8-TCDD	692	701	2,3,7,8-TCDF	52	66
1,2,3,7,8-PeCDD	4763	4449	1,2,3,7,8-PeCDF	17	13
1,2,3,4,7,8-HxCDD	2380	1303	2,3,4,7,8-PeCDF	20124	14810
1,2,3,6,7,8-HxCDD	8000	5547	1,2,3,4,7,8-HxCDF	2440	1900
1,2,3,7,8,9-HxCDD	83	57	1,2,3,6,7,8-HxCDF	1992	1529
1,2,3,4,6,7,8-HpCD	3877	1943	2,3,4,6,7,8-HxCDF	3204	2558
OCDD	12347	4457	1,2,3,7,8,9-HxCDF	70	46
			1,2,3,4,6,7,8-HpCD	548	321
			1,2,3,4,7,8,9-HpCD	280	219
			OCDF	322	296

カワウ卵における毒性影響濃度と計算式の補正

Toxic effected levels of cormorant egg and compensation of formula



Analyzed value (Tokyo)：226pgTEQ/g wet wt.＝LD_{27}

Caluculated (5yr old)　：1181pgTEQ/g wet wt.＞LD_{100}

補正値(Revised value)　0.2

<u>**考えられる要因**　Conciderinq reason</u>

魚類中濃度，採食量，吸収率，分配比

Fish level, Intake volume, Absorption ratio, Distibution ratio

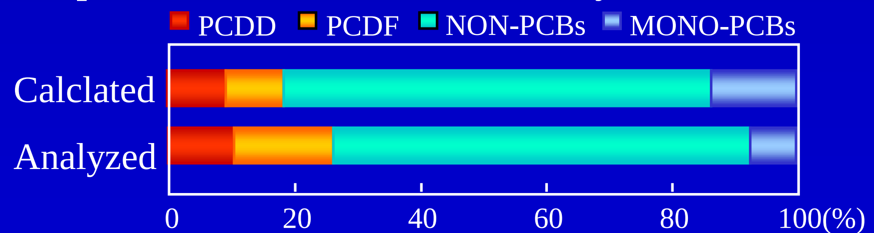
$$\frac{C_{Fish} \times AD \times f}{Fat_{egg}} \times \frac{T_{1/2}}{Log_e 2} \times Ratio_{egg/target} \times \left[1 - \exp\left(-Log_e 2 / T_{1/2}\right) \times t\right] = C_{egg}$$

カワウ卵PCDD/Fs, dioxin like-PCB濃度の計算（補正）値と実測値の比較
Comapison of concentration of PCDD/Fs, dioxin like-PCB between calculated and analyzed value

Congener	Calculated	Analyzed
PCDDs		
2,3,7,8-TCDD	82	94
1,2,3,7,8-PeCDD	274	290
1,2,3,4,7,8-HxCDD	45	56
1,2,3,6,7,8-HxCDD	162	250
1,2,3,7,8,9-HxCDD	4.2	9.3
1,2,3,4,6,7,8-HpCD	109	92
OCDD	855	310
PCDFs		
2,3,7,8-TCDF	11	11
1,2,3,7,8-PeCDF	3.3	5.6
2,3,4,7,8-PeCDF	330	500
1,2,3,4,7,8-HxCDF	63	99
1,2,3,6,7,8-HxCDF	74	100
2,3,4,6,7,8-HxCDF	151	15
1,2,3,7,8,9-HxCDF	13	11
1,2,3,4,6,7,8-HpCD	21	36
1,2,3,4,7,8,9-HpCD	71	36
OCDF	113	51

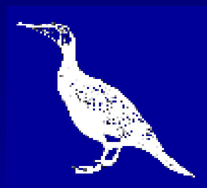
Congener	Calculated	Analyzed
Dioxin-like PCBs		
CB81	3.0	5.4
CB77	13	12
CB126	17	13
CB169	5.7	3.9
CB123	180	100
CB118	7102	6800
CB114	294	240
CB105	2912	1000
CB167	851	320
CB156	1099	570
CB157	253	200
CB189	146	80

Comparison with calculated and analyzed TEQ



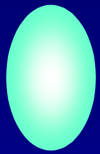
	Calculated	Analyzed
TEQ (pg/g fat)	3935	3600

底質コア濃度からの卵中濃度変遷の推算
Estimation to egg level from sediment core



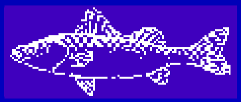
半減期を用いたカワウ体内濃度の計算
Calculation of bodylevel used by half-lives.

卵
Eggs

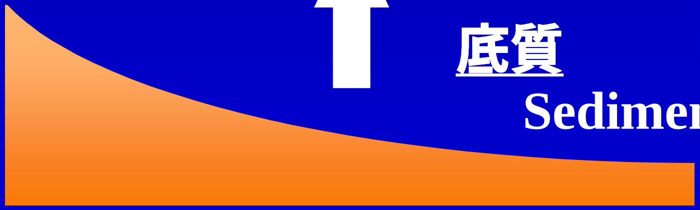


$$\frac{C_{Fish} \times AD \times f}{Fat_{egg}} \times \frac{T_{1/2}}{Log_e 2} \times Ratio_{egg/target} \times \left[1 - \exp\left(- Log_e 2 / T_{1/2}\right) \times t\right] = C_{egg}$$

魚類 Fish

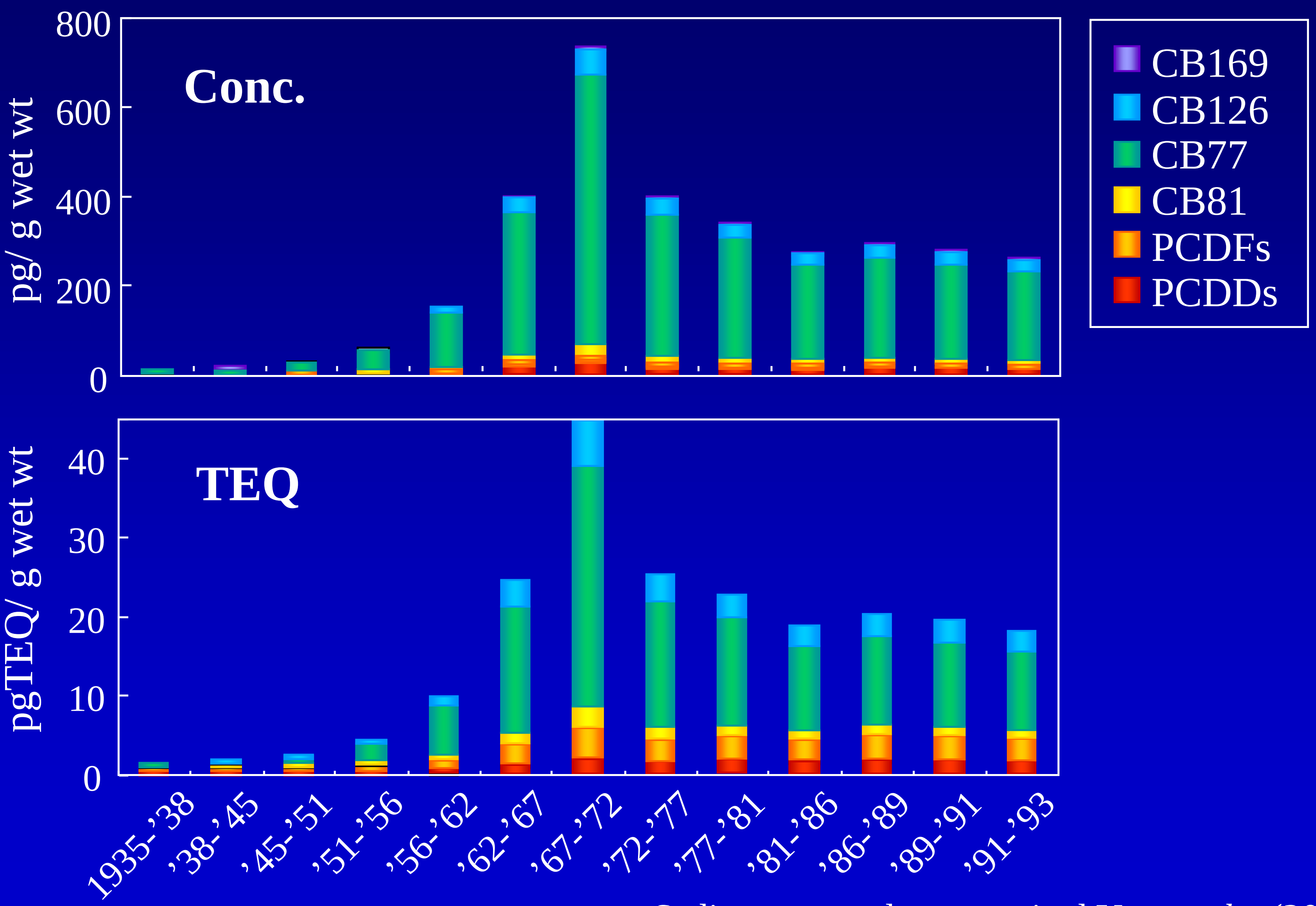


BSAF（魚類／底質）より魚類中濃度を算出
Calculation of fish level used by BSAF.



底質
Sediment

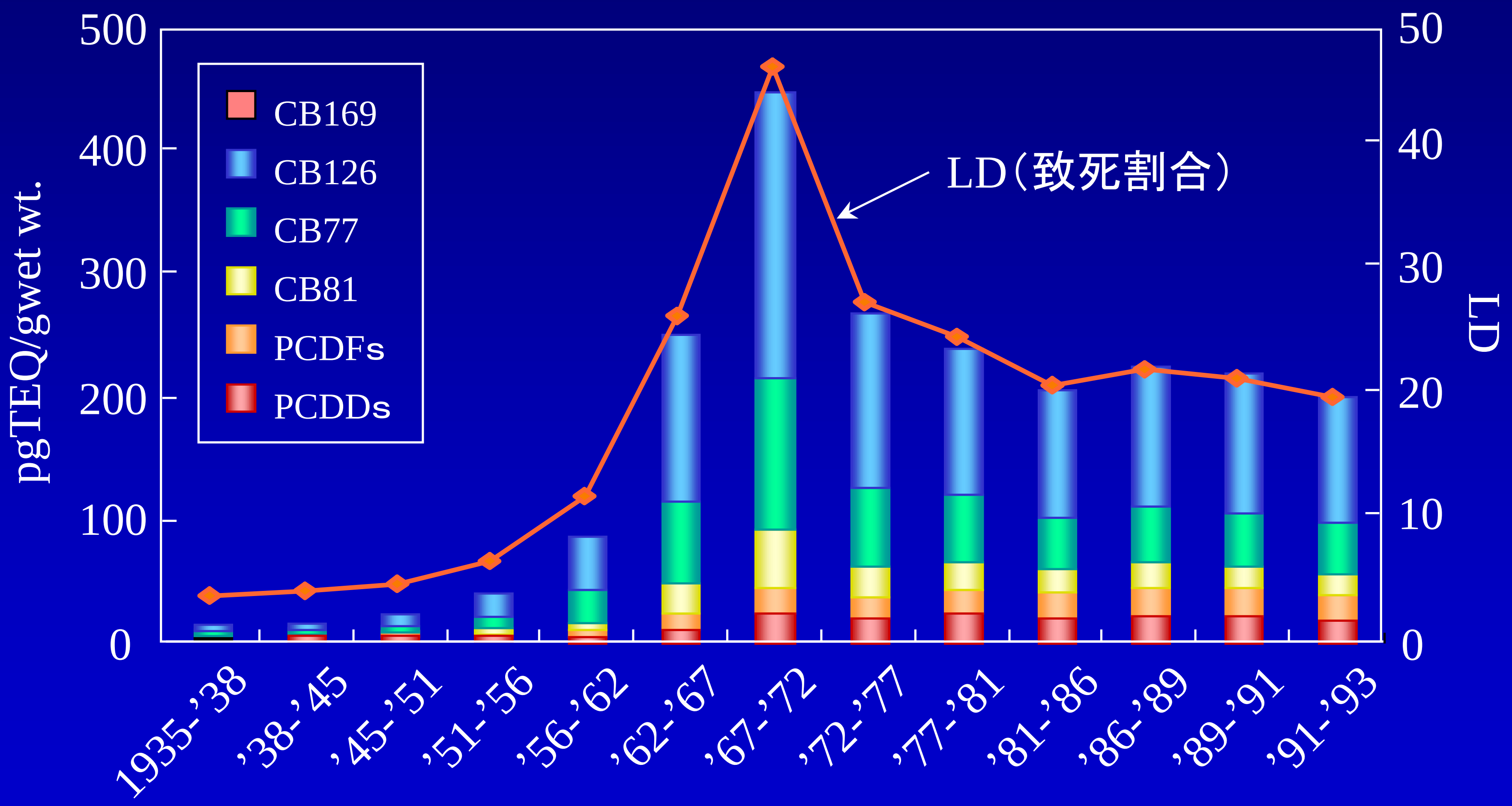
BSAFより推算された魚類中レベルとその変遷
Trend of estimated fish level used by BSAF.



Sediment core data was cited Yao *et al.*, (2000)

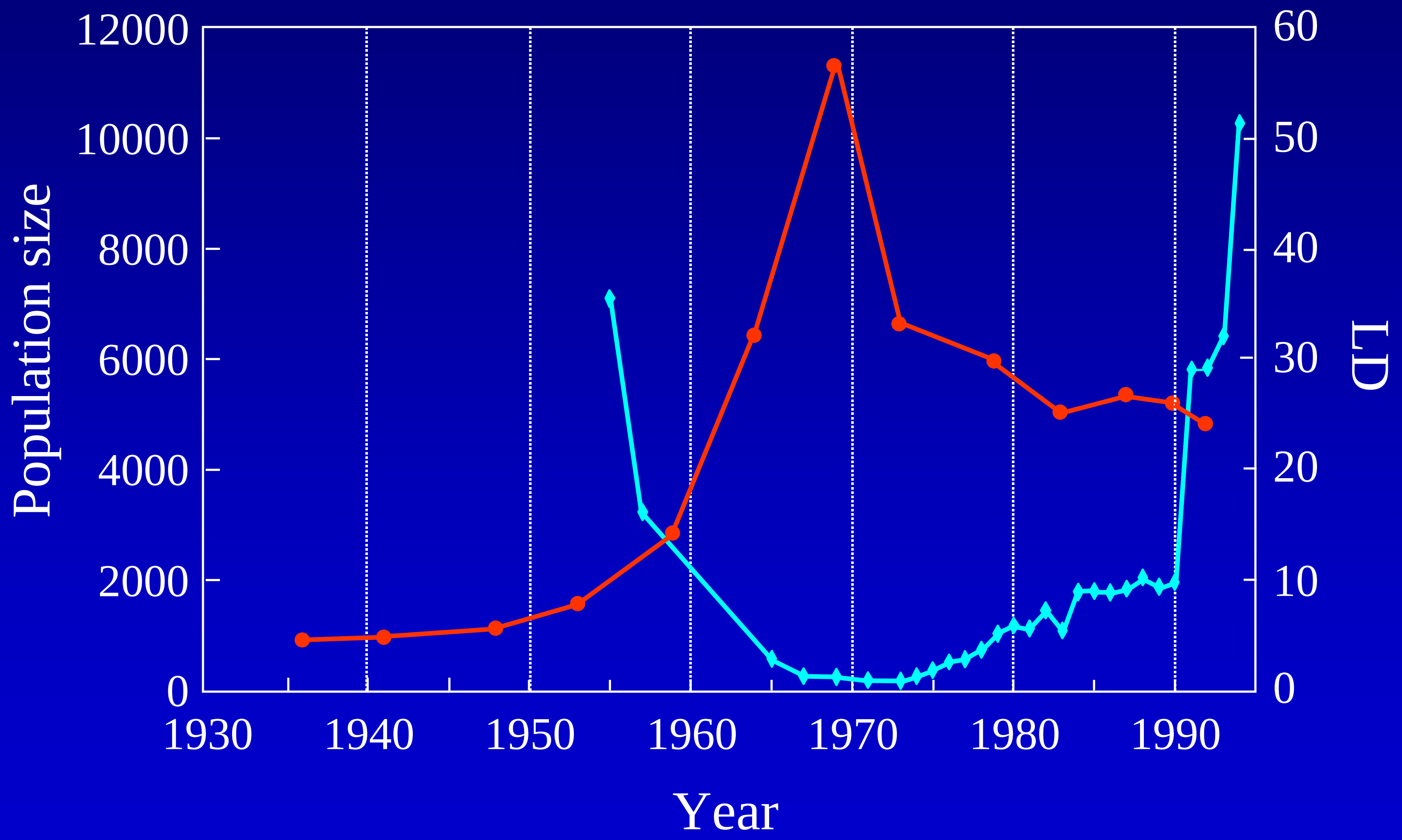
試算されたカワウ卵中TEQとリスク変遷

Trend of TEQ in the egg and its effect in mortality of common cormorant from Tokyo.



関東におけるカワウ個体数と致死割合の推移

The transition of the population size and lethal dose of common cormorant in Kanto region.



まとめ 2（Summary-2）

5. 東京産魚類の平均濃度（*n*=5）と成鳥（*n*=6）の肝臓中平均濃度から定常状態を仮定した半減期を算出した結果，2,3,7,8-TCDDでおよそ31～69日と推定された.
   Half-lives of 2,3,7,8-TCDD were estimated for 31～47 days, after calcuated under assumed stable state used by fish and liver of adult cormorant levels.

6. 卵への曝露影響は，加齢よりも餌濃度に大きく左右されることが明らかとなった.
   It is clear that exposure effect to egg is more sensitive depend on diet fish level than age differences of cormorant.

7. 東京湾における胚発生のリスク変遷では，1970年にピークとなり，その後減少した. これらの毒性へはCo-PCBが大きく寄与していた.
   Trend of dioxin exposure risk and its effect on mortality of cormorant was estimated and maximum increase until 1970, then declined.