Sources and Behavior of Dioxins in Japan

わが国におけるダイオキシンの源と挙動解析

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科学技術振興事業団 戦略的基礎研究推進事業

Human Health Related Research

I. Monitoring of chemicals in various environmental media

1. Levels of dioxin in the environment and biota.
2. Levels of benzene in air.
3. Levels of indoor air pollutants.

II. Behaviors of chemicals in the environment

1. Transport of dioxins in the environment.
2. Degradation of halogenated compounds in aquatic environment.
3. Heterogeneous reaction of air pollutants in atmosphere.

III. Development and validation of chemical fate models

1. Watershed model supported by Geographical Information System.
2. Characterization of uncertainty in multimedia fate models.
3. Transportation of pollutants near the incinerators.

IV. Development of chemical distribution model in the body

1. Model based on PBPK.

V. Human health risk evaluation

1. Population risk assessment of benzene
1. Exposure and risk assessment of dioxins

Dioxin related research in the project

Dioxin monitoring

1. Soil and Sediment
2. Atmospheric deposition
3. Aquatic biota
4. Dioxin profile at the emission source
5. Distribution in the body <-- birds

Environmental Behavior of dioxins

1. Origin estimation
2. Atmospheric transport & deposition
3. Bioaccumulation via food chain
4. Accumulation in the body: birds
5. Historical dioxin load: sediment core

Model estimation of dioxin exposure

1. Model calculation near the incinerator
2. PBPK (physiologically based pharmaco-kinetic) model

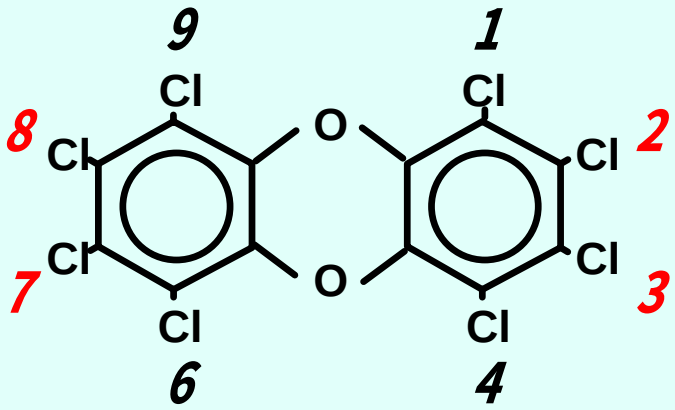
Risk assessment of dioxins

1. Risk of different sub population
2. Avian risk study

Basic Approach

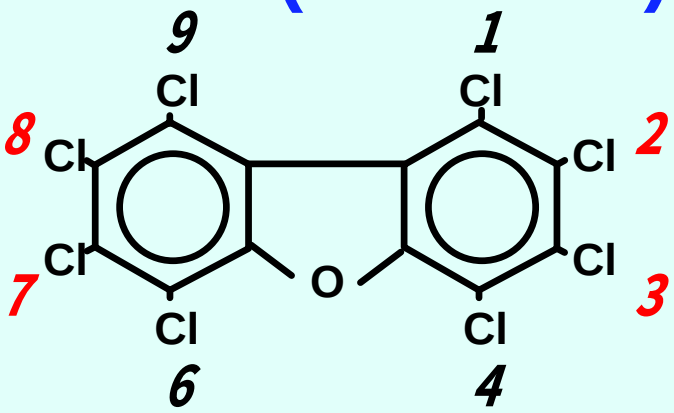
Isomer specific analysis. Quantitative risk evaluation.

Dioxins (PCDD/Fs)



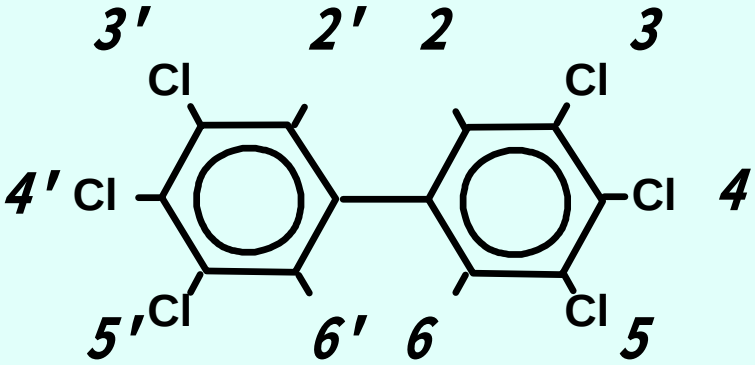
Polychlorinated dibenzo-*p*-dioxin (PCDD)

ポリ塩素化ジベンゾ-*p*-ダイオキシン



Polychlorinated dibenzofuran (PCDF)

ポリ塩素化ジベンゾフラン



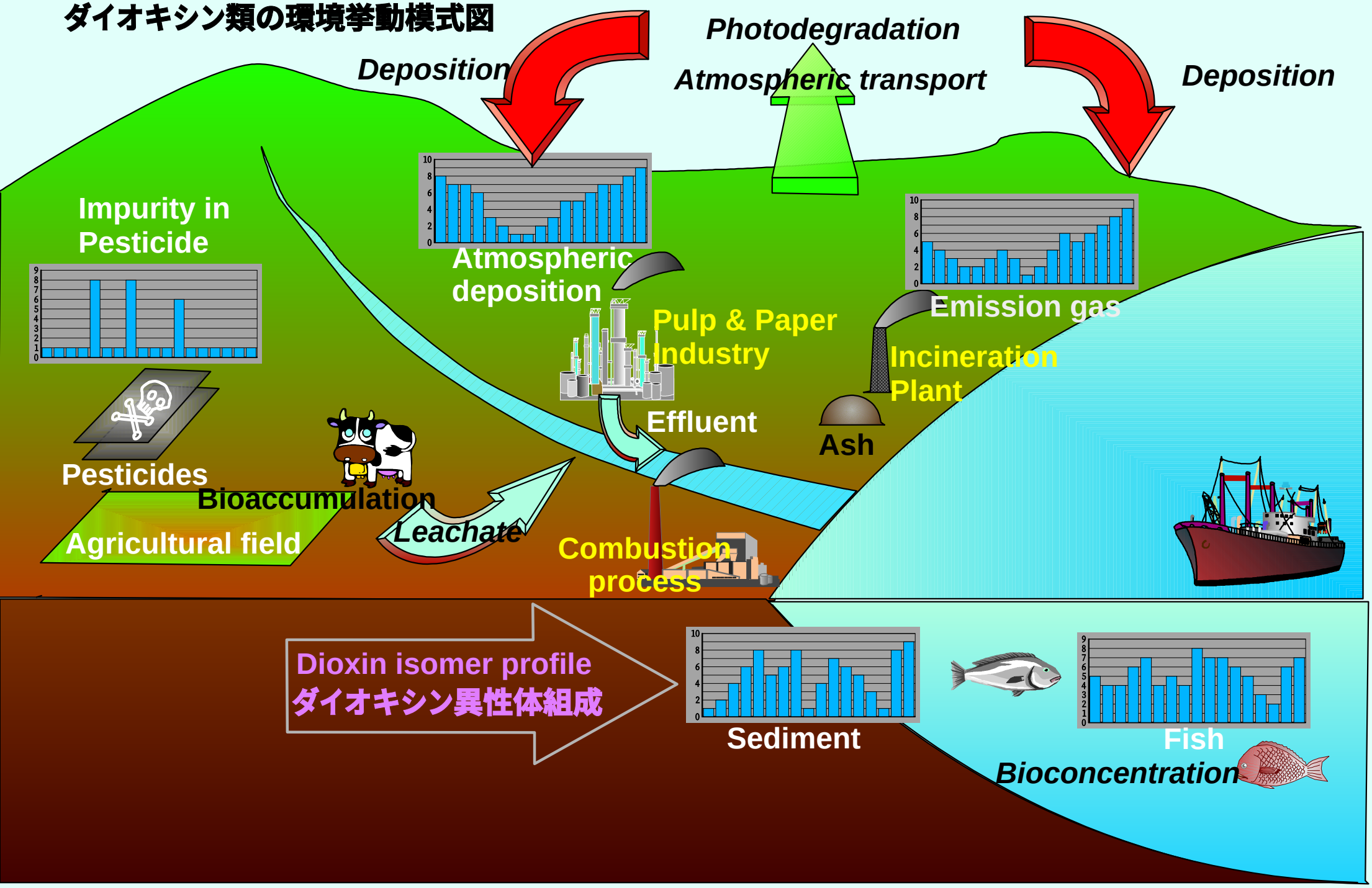
Polychlorinated biphenyl (PCB)

ポリ塩素化ビフェニール

No. of Cl	Dioxin	Abbr.	No. of Isomers	Dibenzofuran	Abbr.	No. of Isomers
1	monochlorodibenzo-p-dioxin	MCDD	2	monochlorodibenzofuran	MCDF	4
2	dichlorodibenzo-p-dioxin	DCDD	10	dichlorodibenzofuran	DCDF	16
3	tirchlorodibenzo-p-dioxin	TrCDD	14	trichlorodibenzofuran	TrCDF	28
4	tetrachlorodibenzo-p-dioxin	TCDD	22	tetrachlorodibenzofuran	TCDF	38
5	pentachlorodibenzo-p-dioxin	PCDD	14	pentachlorodibenzofuran	PCDF	28
6	hexachlorodibenzo-p-dioxin	HxCDD	10	hexachlorodibenzofuran	HxCDF	16
7	heptachlorodibenzo-p-dioxin	HeCDD	2	heptachlorodibenzofuran	HeCDF	4
8	octachlorodibenzo-p-dioxin	OCDD	1	octachlorodibenzofuran	OCDF	1
	Total		75	Total		135

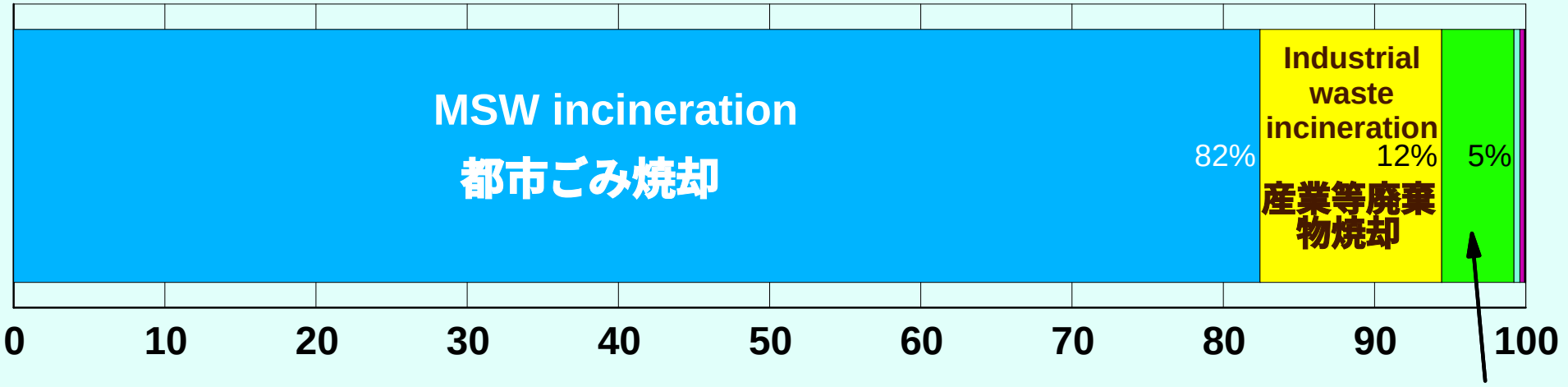
Schematics of PCDD/F behavior in environment

ダイオキシン類の環境挙動模式図



Inventory of Dioxin Sources in Japan (TEQ base, early 1990s)

Estimation by Environment Agency and Prof. Hiraoka

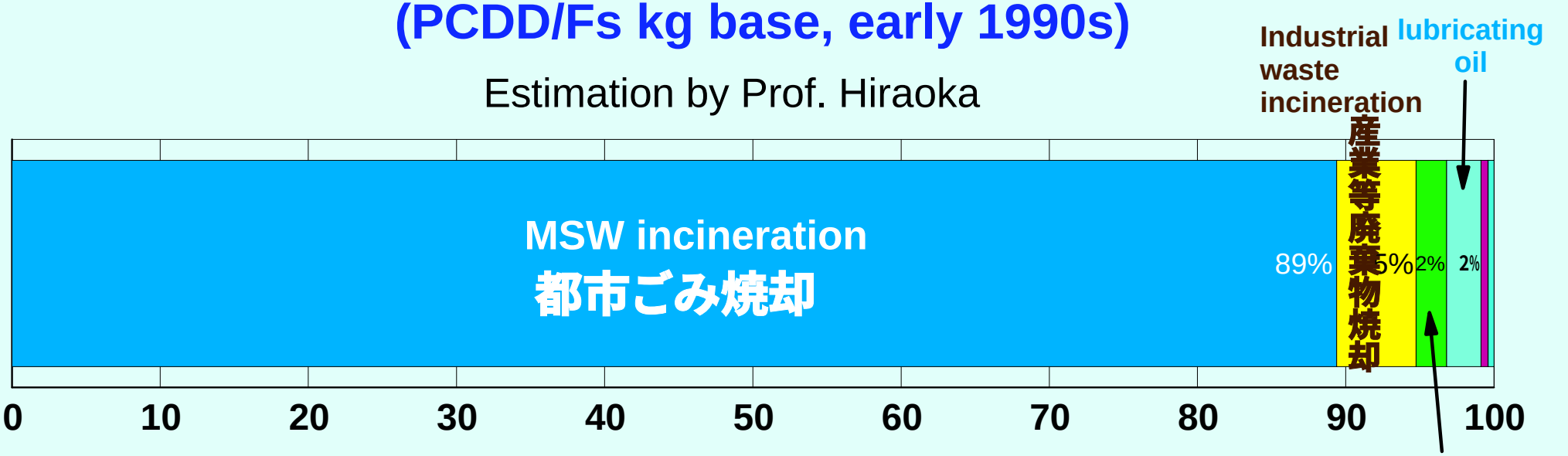


	Sources	g TEQ/year
	MSW incineration	4300 (3100 - 7400) ('96)
	Industrial waste incineration	627 (547 - 707)
	Metal production	250
	lubricating oil	20
	Cigarette smoke	16
	Black liquor recovery boiler	3
	Incineration of wood & waste wood	0.2
	Automobile exhaust	0.07
	Paper & pulp bleaching	0.7
	Pesticide (PCNB)	0.06

Inventory of Dioxin Sources in Japan

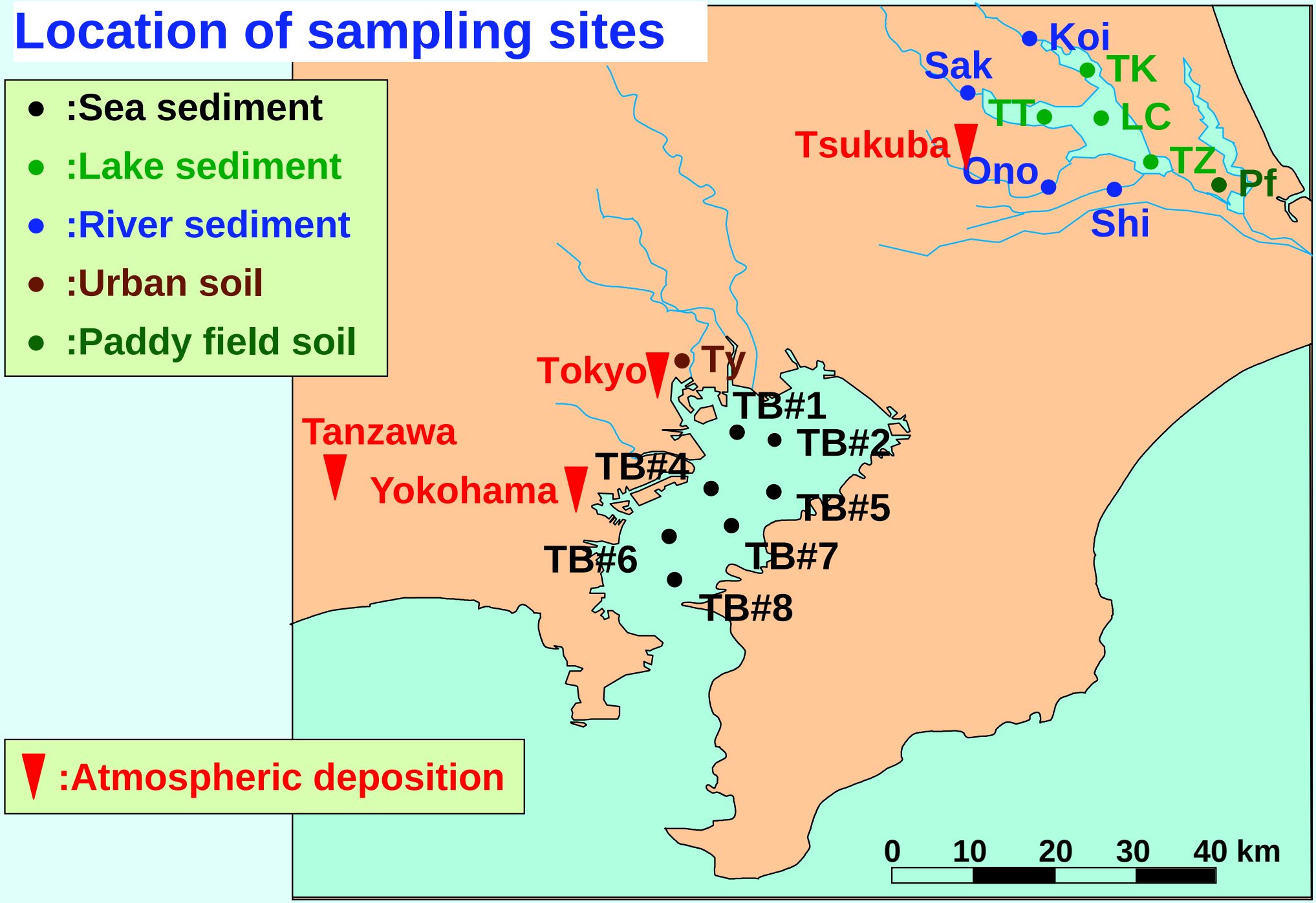
(PCDD/Fs kg base, early 1990s)

Estimation by Prof. Hiraoka

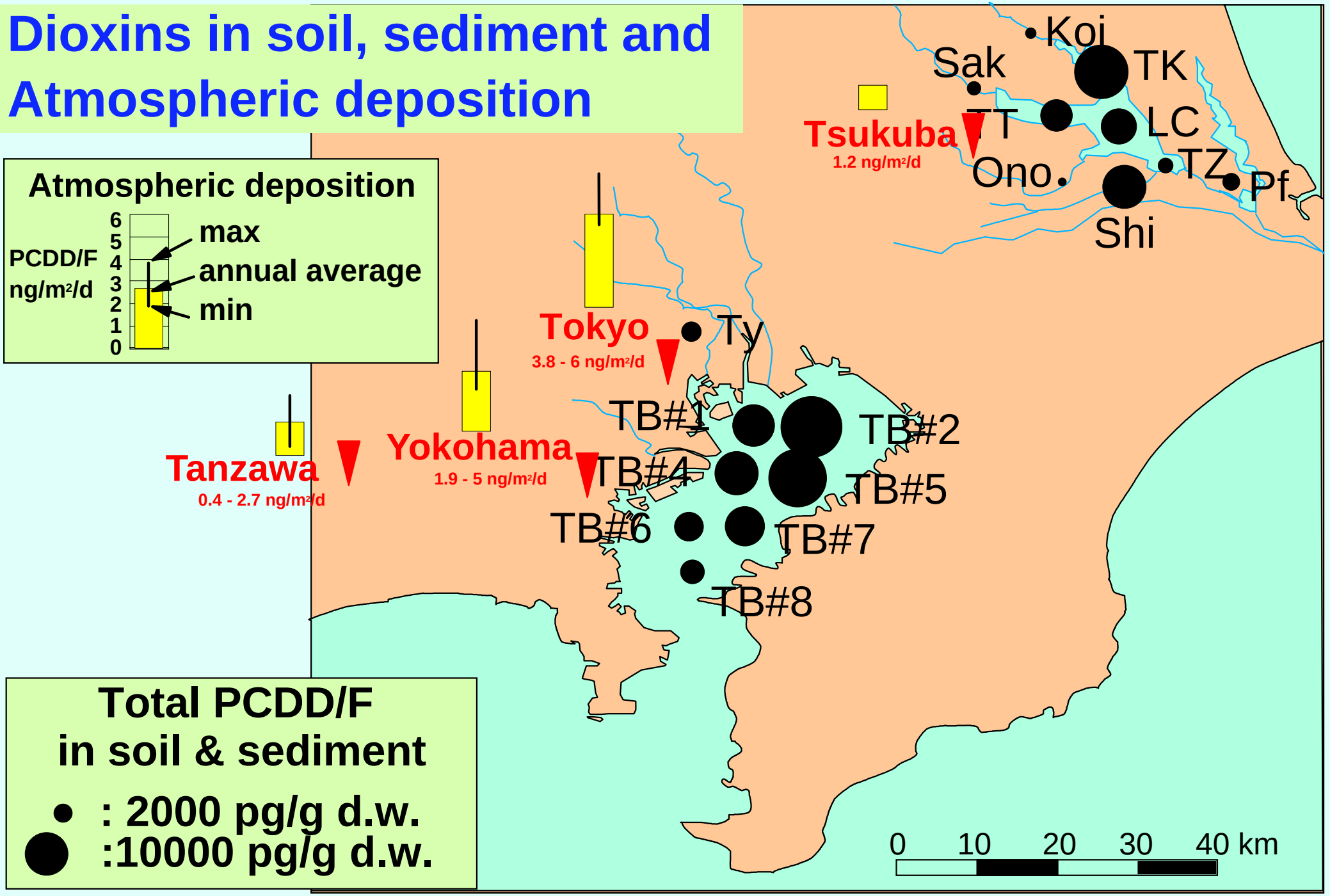


	Sources	kg/year
	MSW incineration	600 (173 - 1060)
	Industrial waste incineration	37 (32 - 42)
	Metal production	14.2
	lubricating oil	16
	Cigarette smoke	3.2
	Black liquor recovery boiler	0.140
	Incineration of wood & waste wood	0.008
	Automobile exhaust	0.007
	Paper & pulp bleaching	2.61
	Pesticide	?

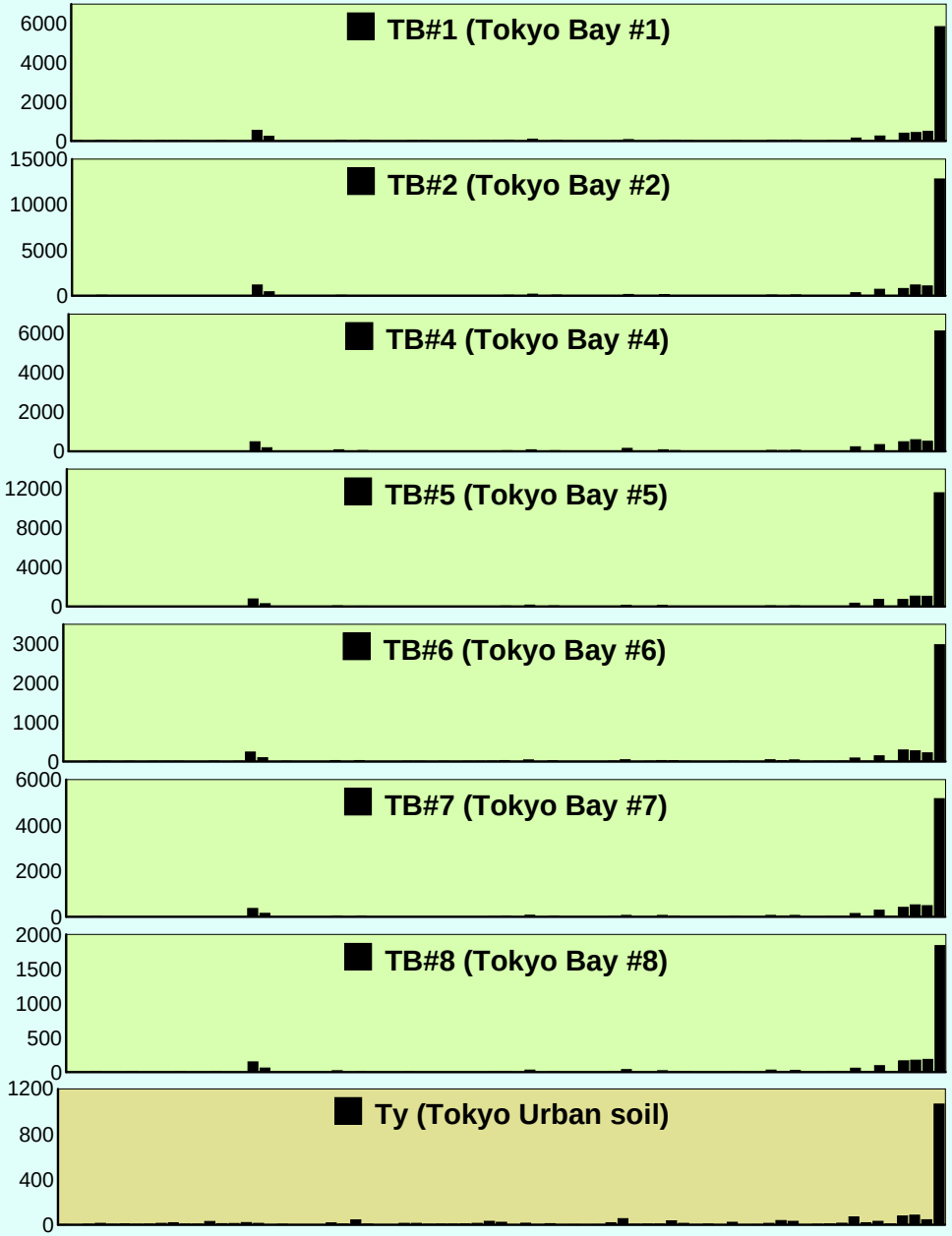
Location of sampling sites

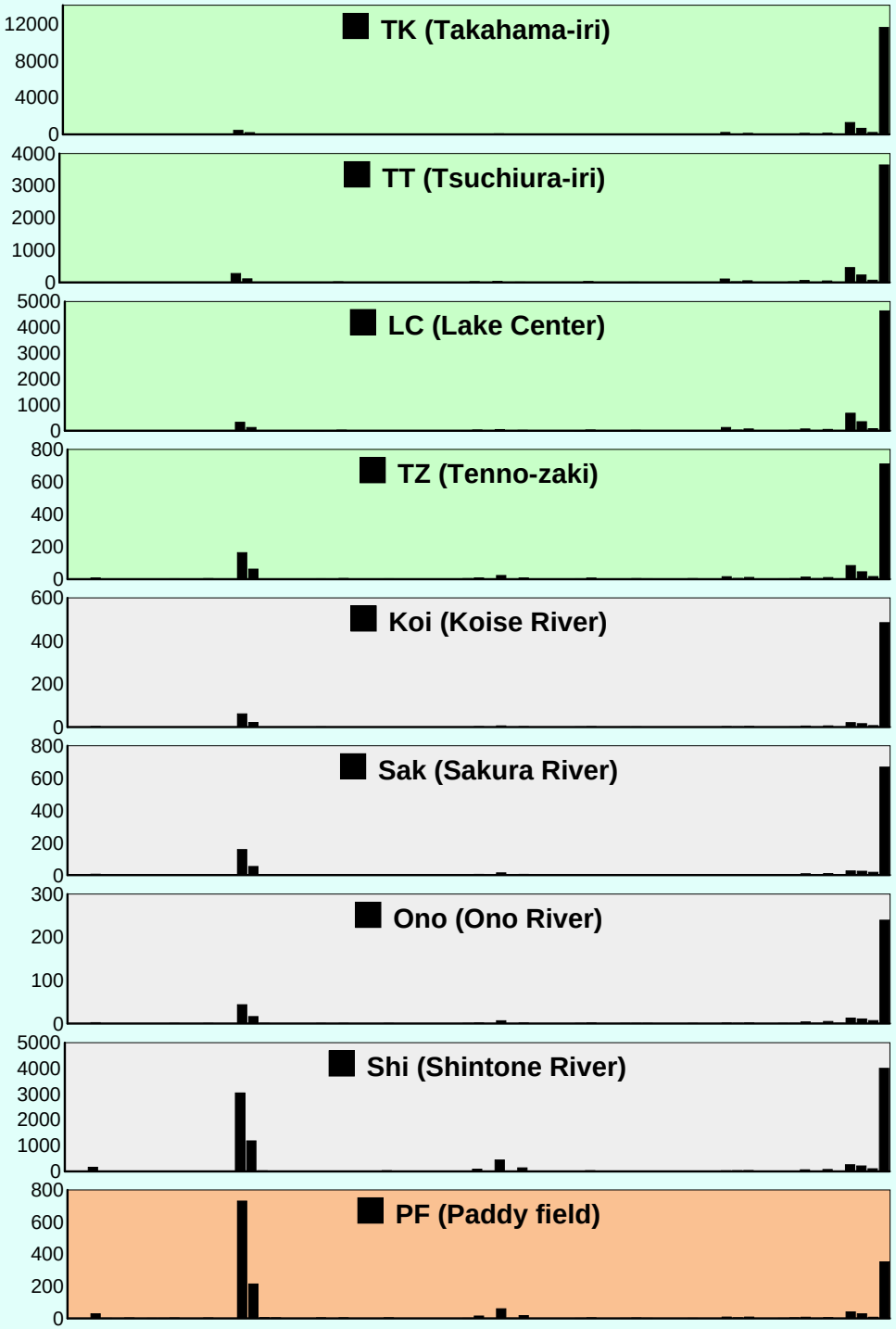


Dioxins in soil, sediment and Atmospheric deposition

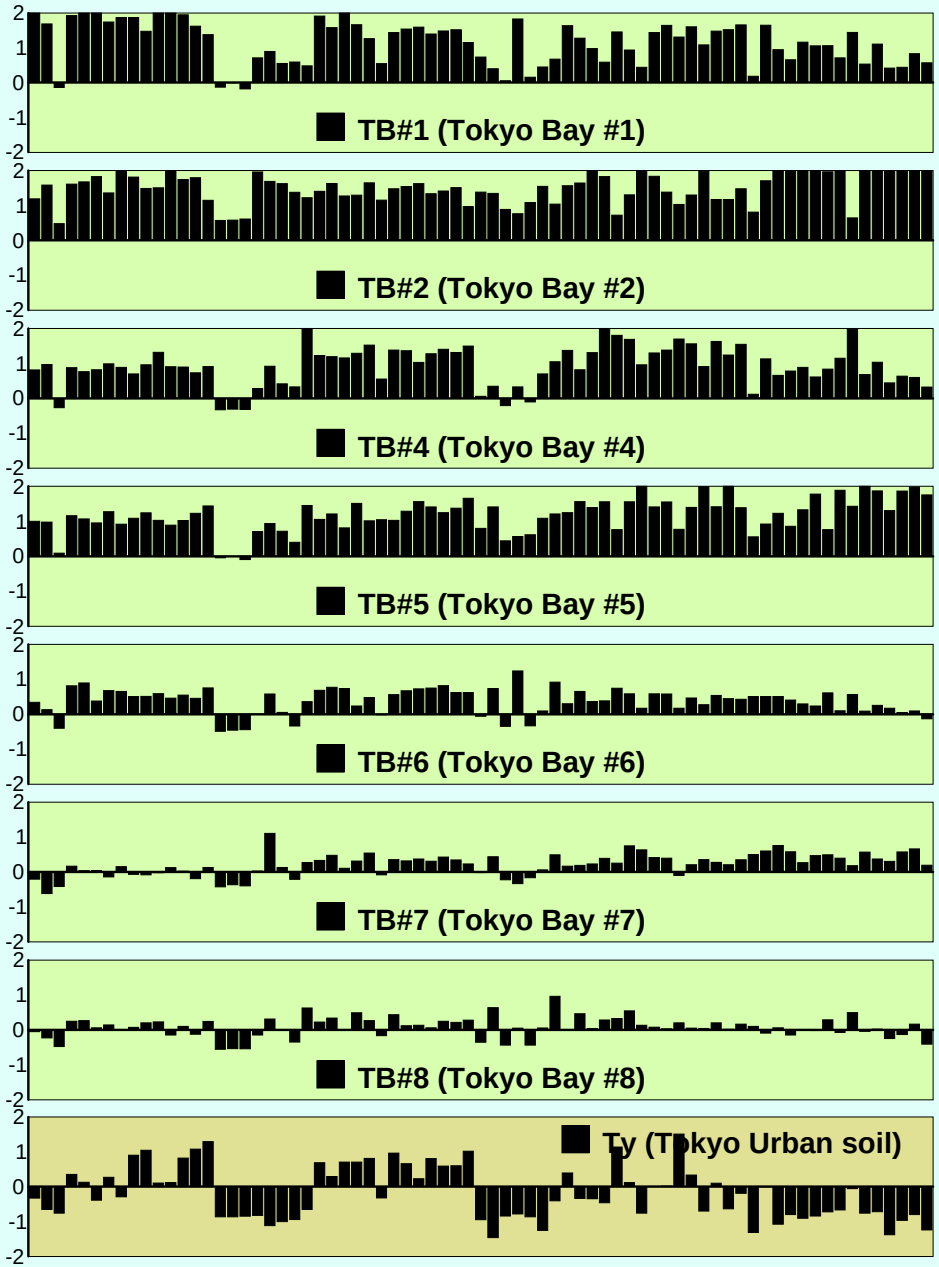


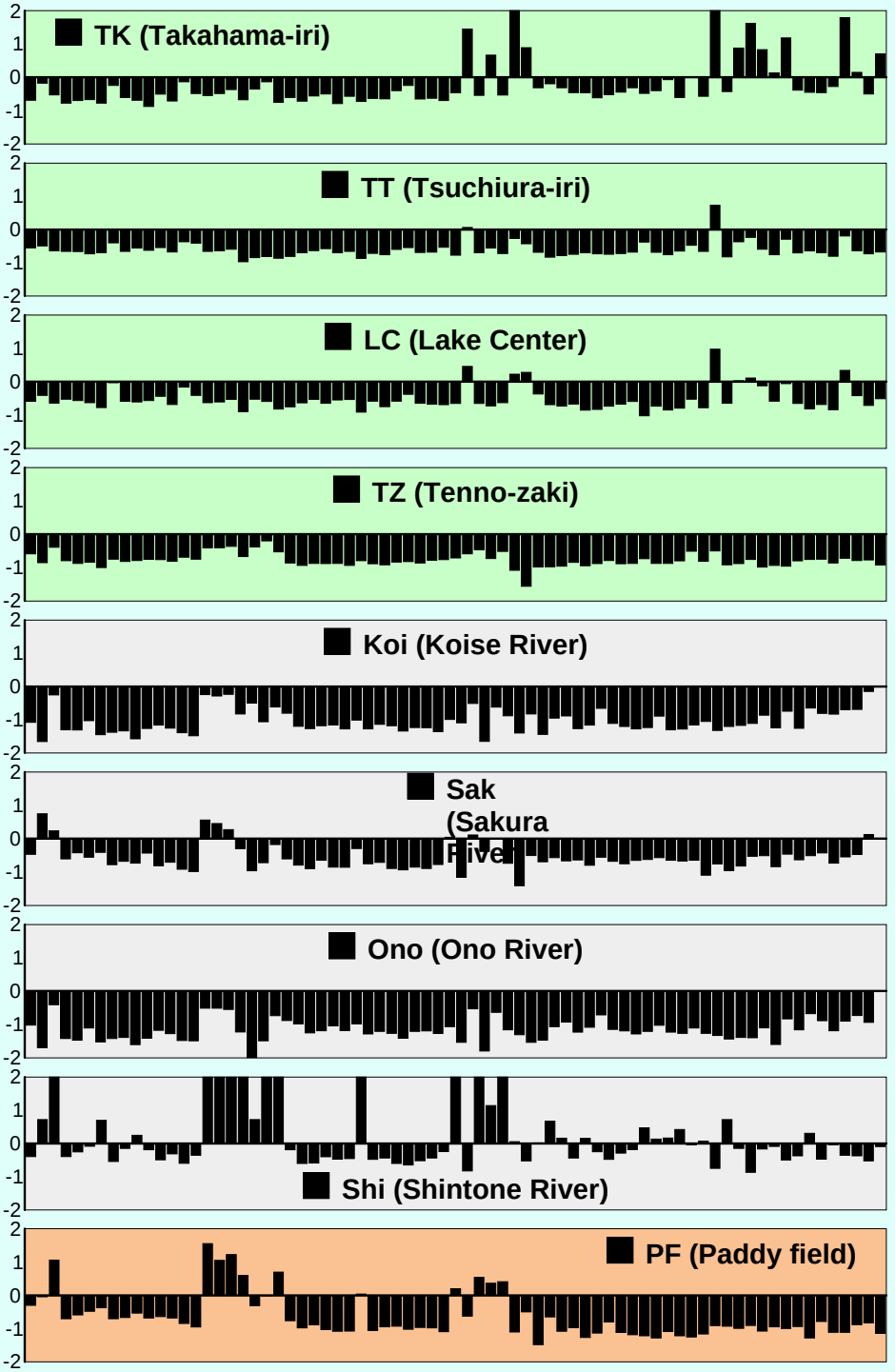
Dioxin isomer profiles (Actual concentration)





Dioxin isomer profiles (Normalized data)





Procedure of principle component analysis

主成分分析の手順

Dioxin concentration in 17 soil and sediment samples
(Isomer specific data: over 80 peaks. Ignition loss base)

↓

Excluding peaks with ND value in any one of the samples
(Variables: 73 peaks)

↓

Normalize for each peak (variance = 1)

↓

Calculate correlation matrix

↓

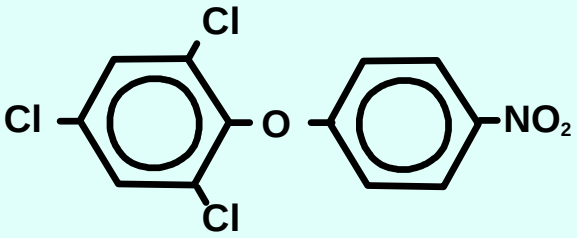
Principle component analysis with normal varimax rotation

Results of the principle component analysis

PCs	Contribution	Characteristic compounds [1)]	Origin attribution
PC-1	52 %	most of the tetra- to hexa-CDFs	Atmospheric deposition
PC-2	17 %	penta- to hepta-CDDs with 1269-Cl substitution	Unknown
PC-3	16 %	tetra- to penta-CDD/Fs, especially with 1368- or 1379-Cl substitution	CNP [2)]
PC-4	9 %	some of the hexa- to octa-CDD/Fs	PCP [3)]

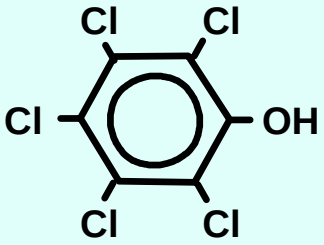
[1)] **Isomer or isomer-cluster peaks with high loading values (r>0.7).**

[2)] **CNP**



1,3,5-trichloro-2-(4-nitorphenoxy)benzene

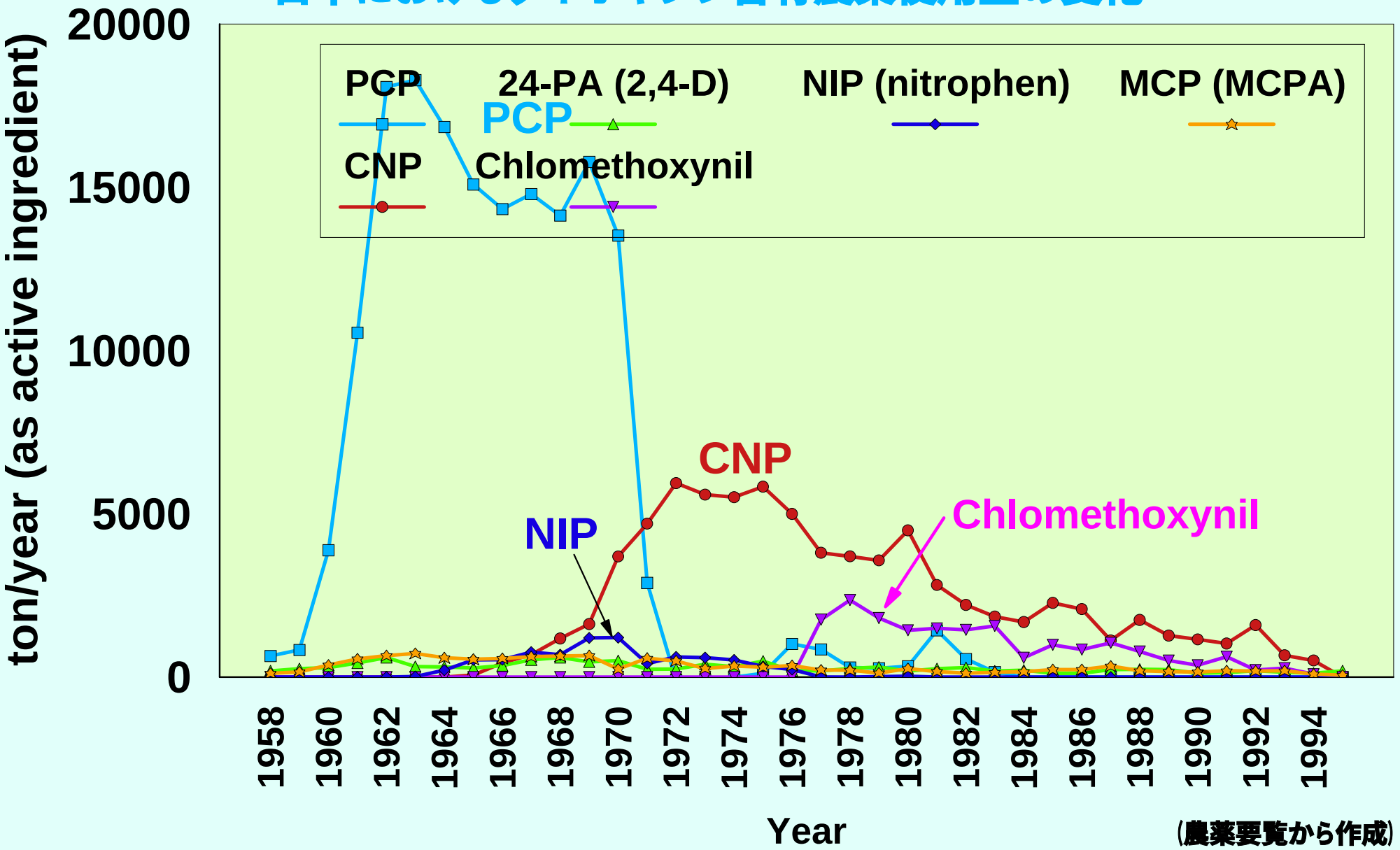
[3)] **PCP**



pentachlorophenol

Pesticide use in Japan

日本におけるダイオキシン含有農薬使用量の変化

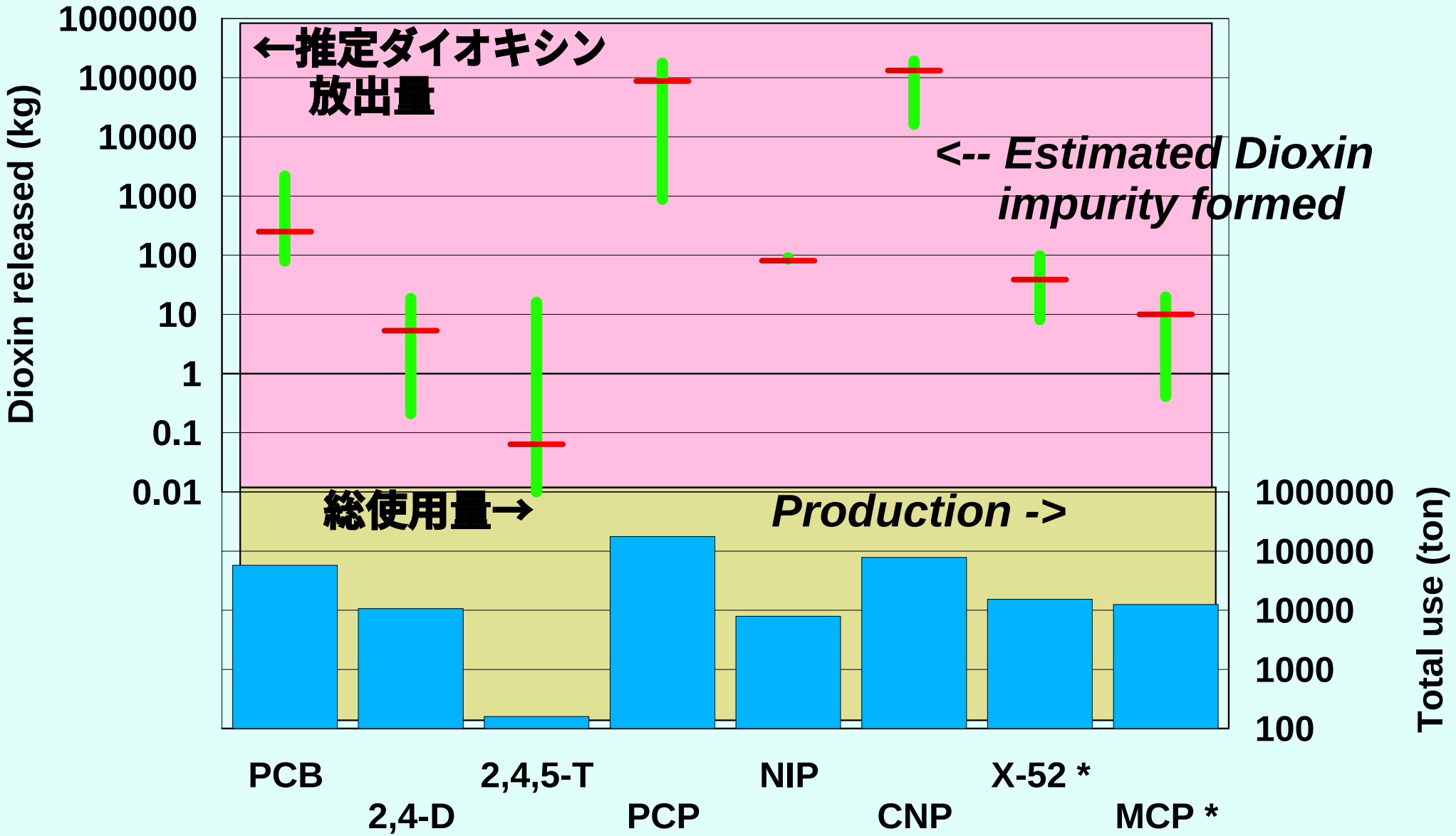


(農薬要覧から作成)

* 2,4-PA (2,4-D): 2,4-dichlorophenoxyacetic acid, MCP: 4-chloro-2-methylphenoxyacetic acid

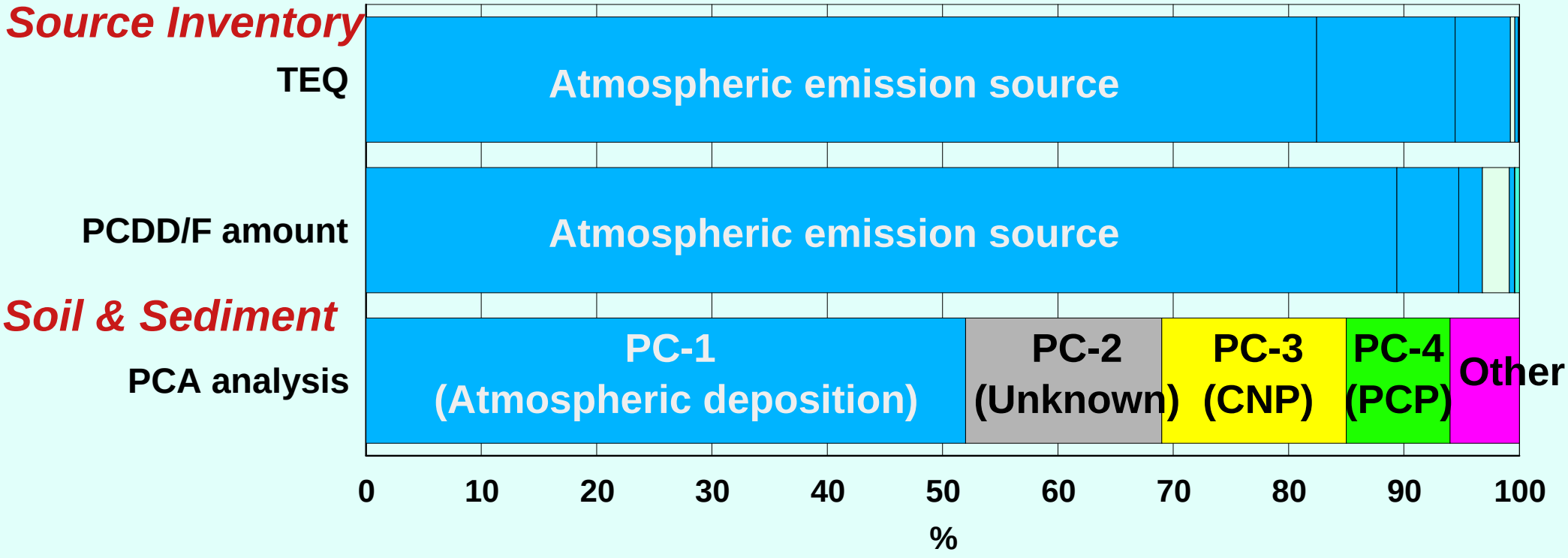
日本で使用された有機塩素化合物量とそれによるダイオキシンの推定放出量

Amount of organochlorine compound used and their dioxin impurities released in Japan



* X-52: chlomethoxynil, MCP: 4-chloro-2-methylphenoxyacetic acid

Dioxin source inventory and results of PCA analysis

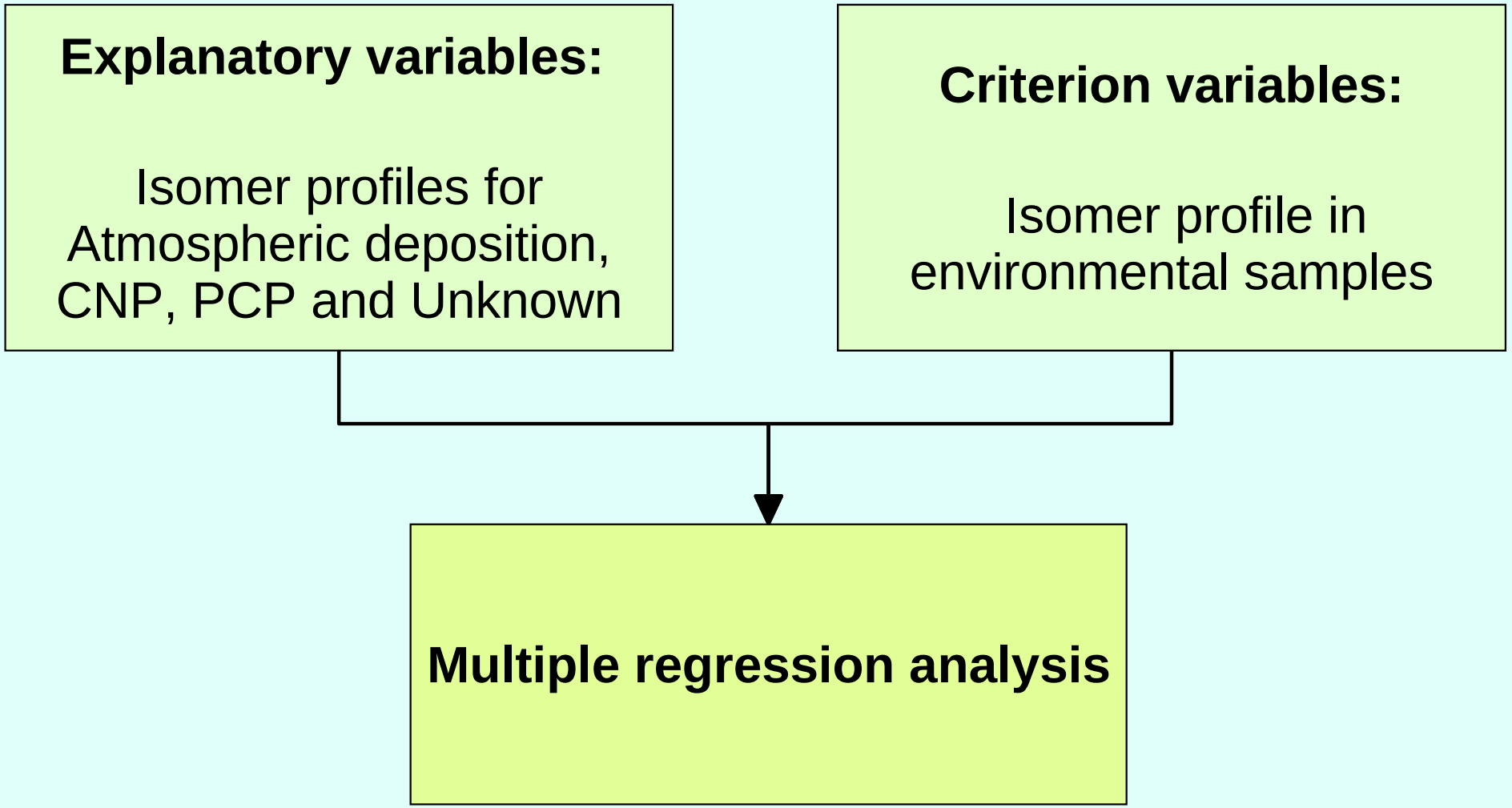


Possible cause of the discrepancy

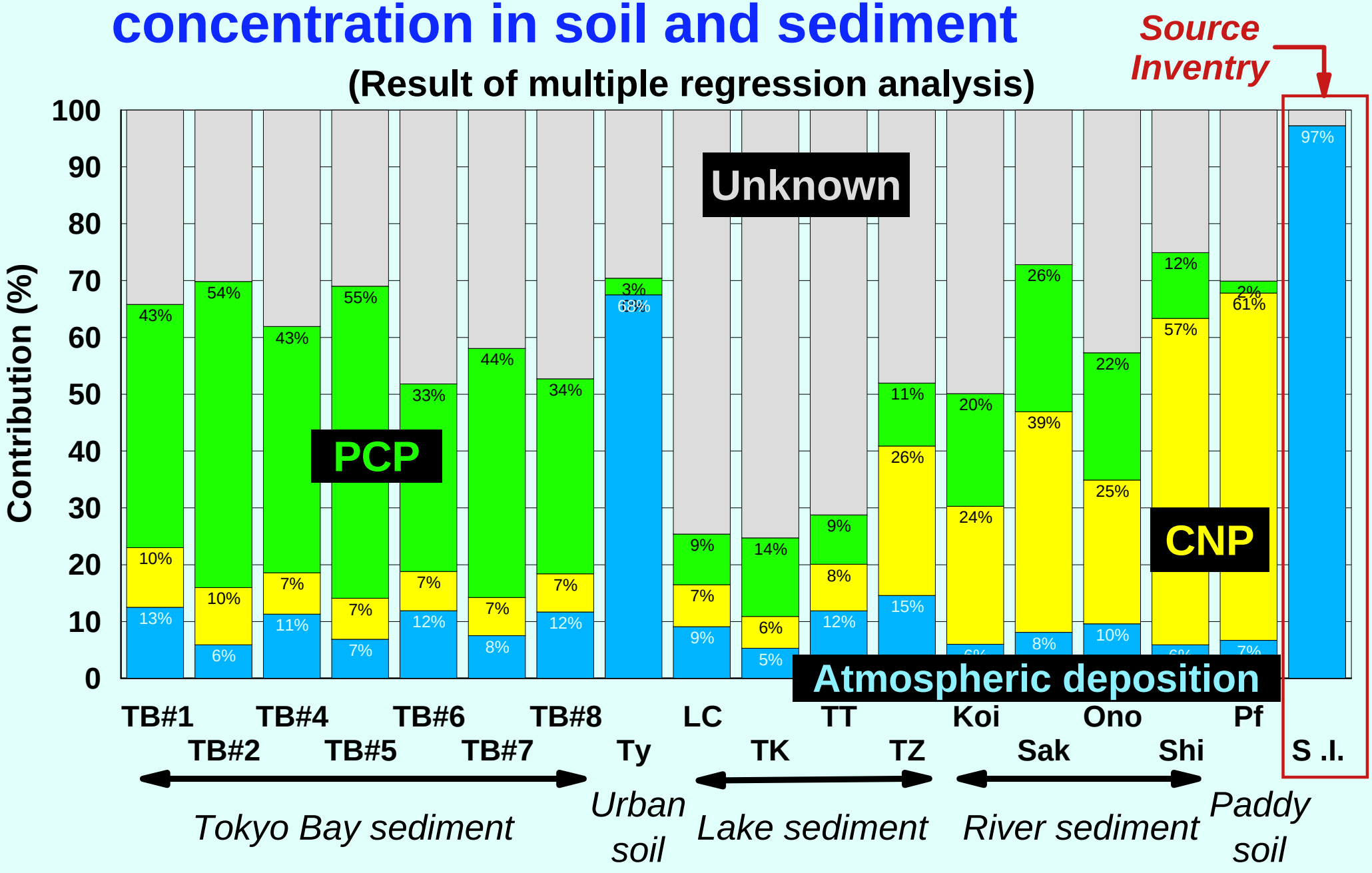
1. Contribution based on "Amount of dioxins" vs. "Variance of samples".
2. "Present emission" vs. "Accumulated pollution caused by past as well as present emission".

Procedure of Multiple Regression Analysis (MRA)

重回帰分析の手順

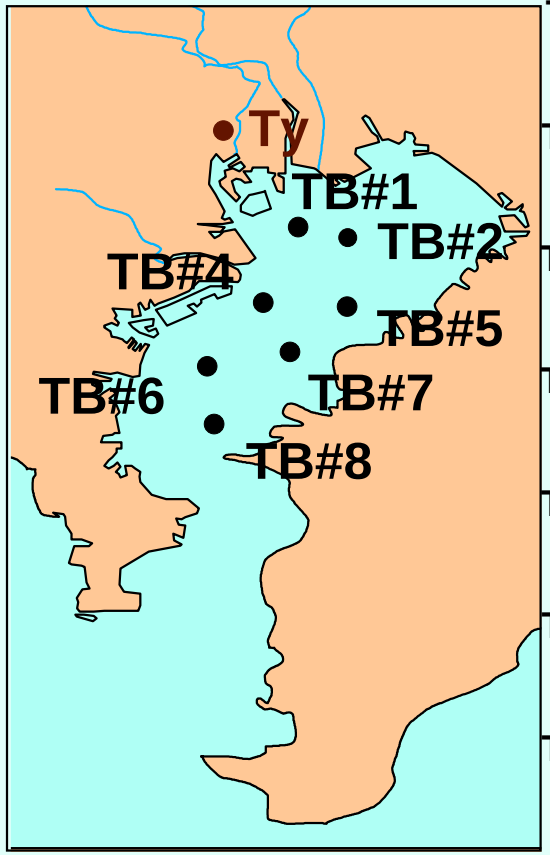


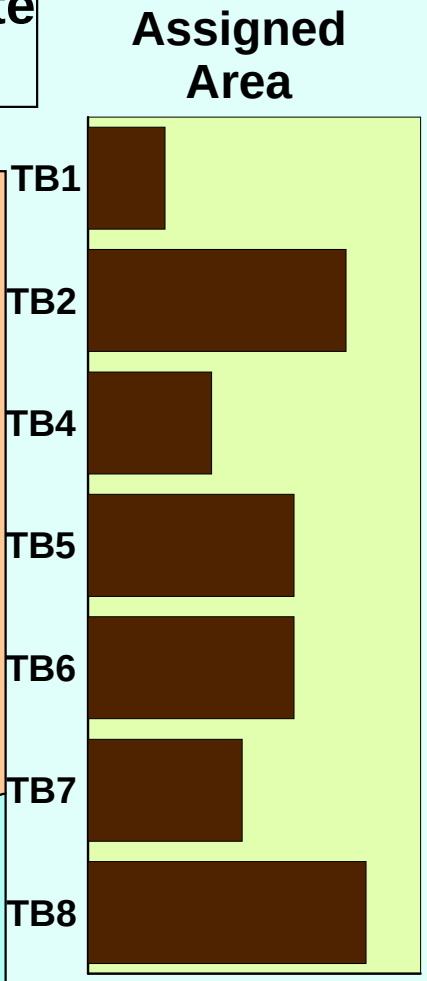
Contribution of different origins to the dioxin concentration in soil and sediment

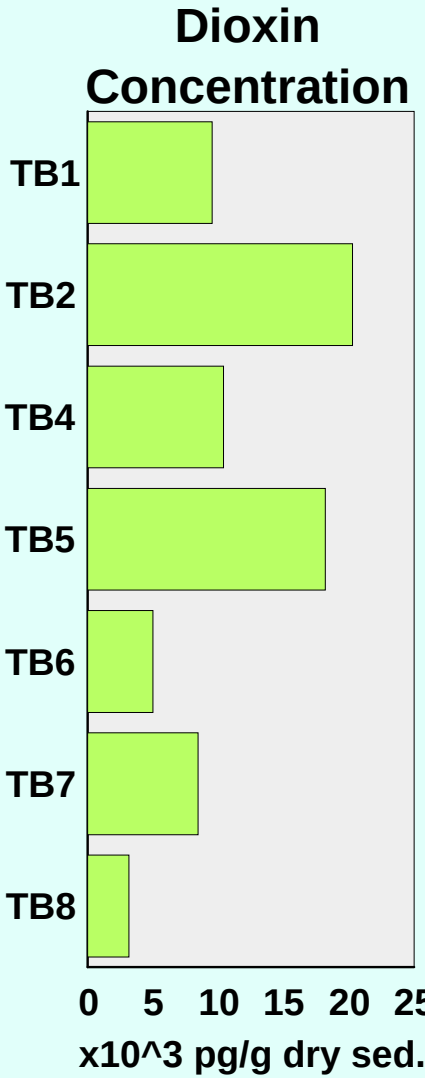


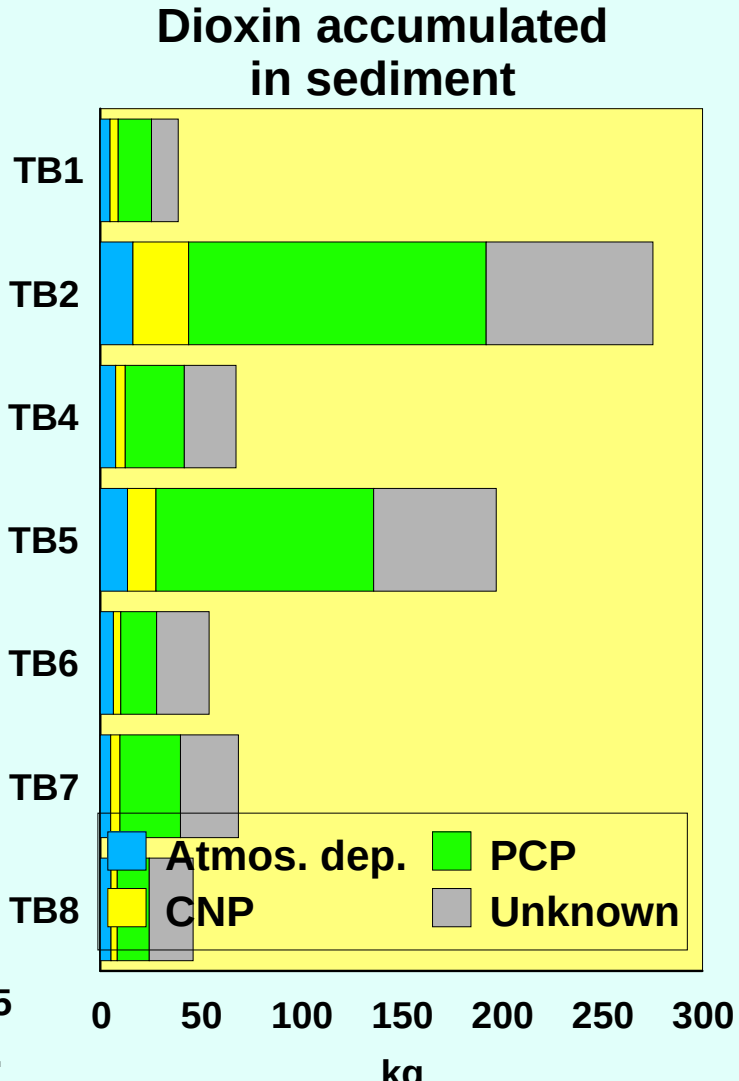
Dioxins accumulated in Tokyo Bay sediment over the past 35 years

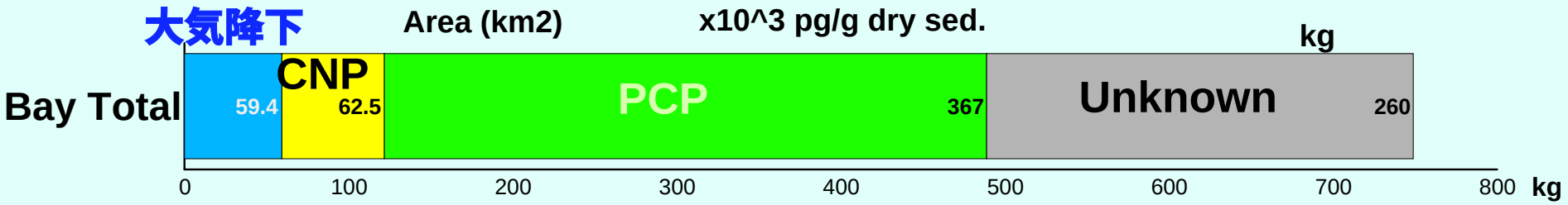
Sedimentation rate
= 0.2 g/cm²/y





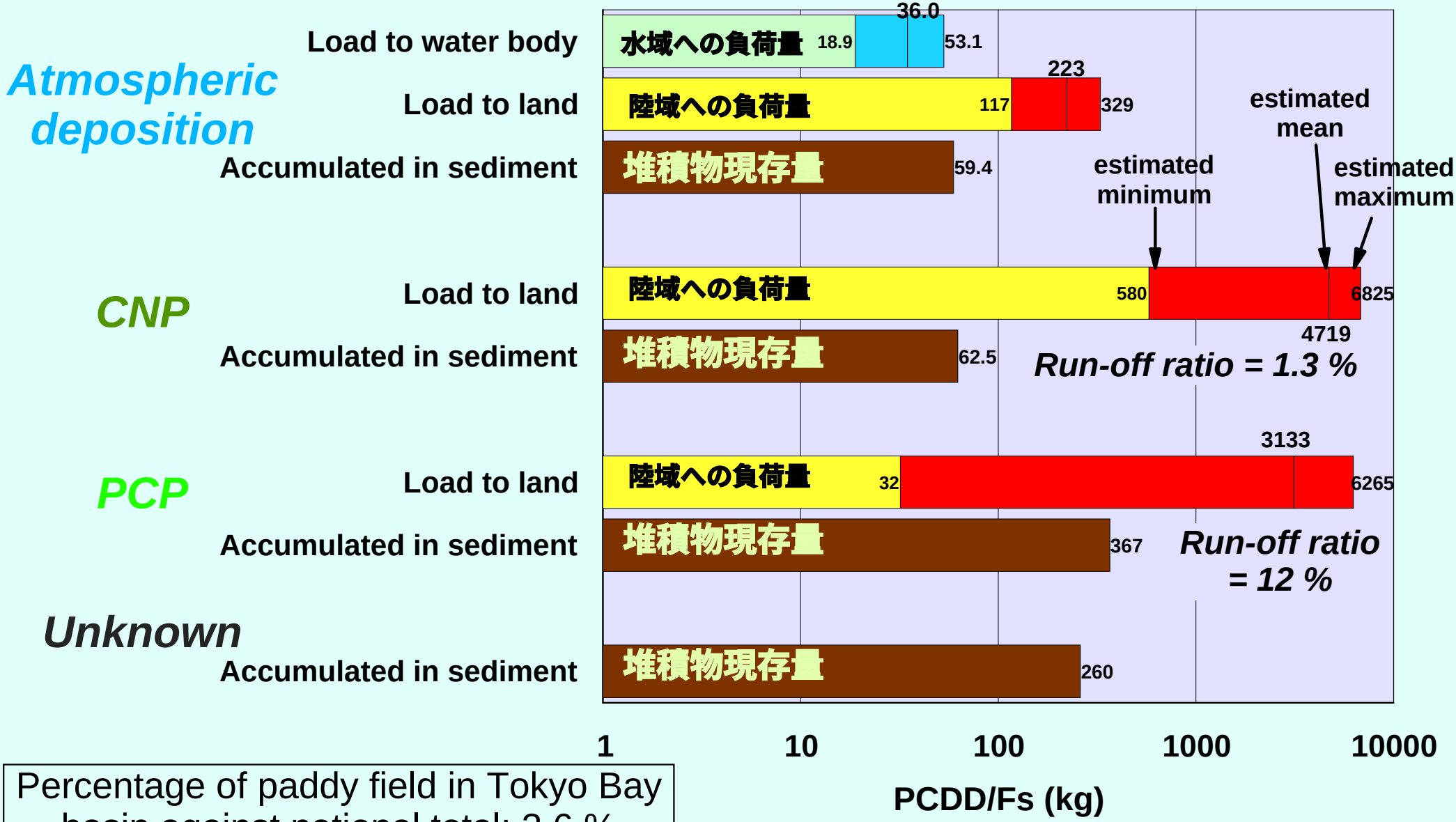






Dioxin load to Tokyo Bay basin over the past 35 years

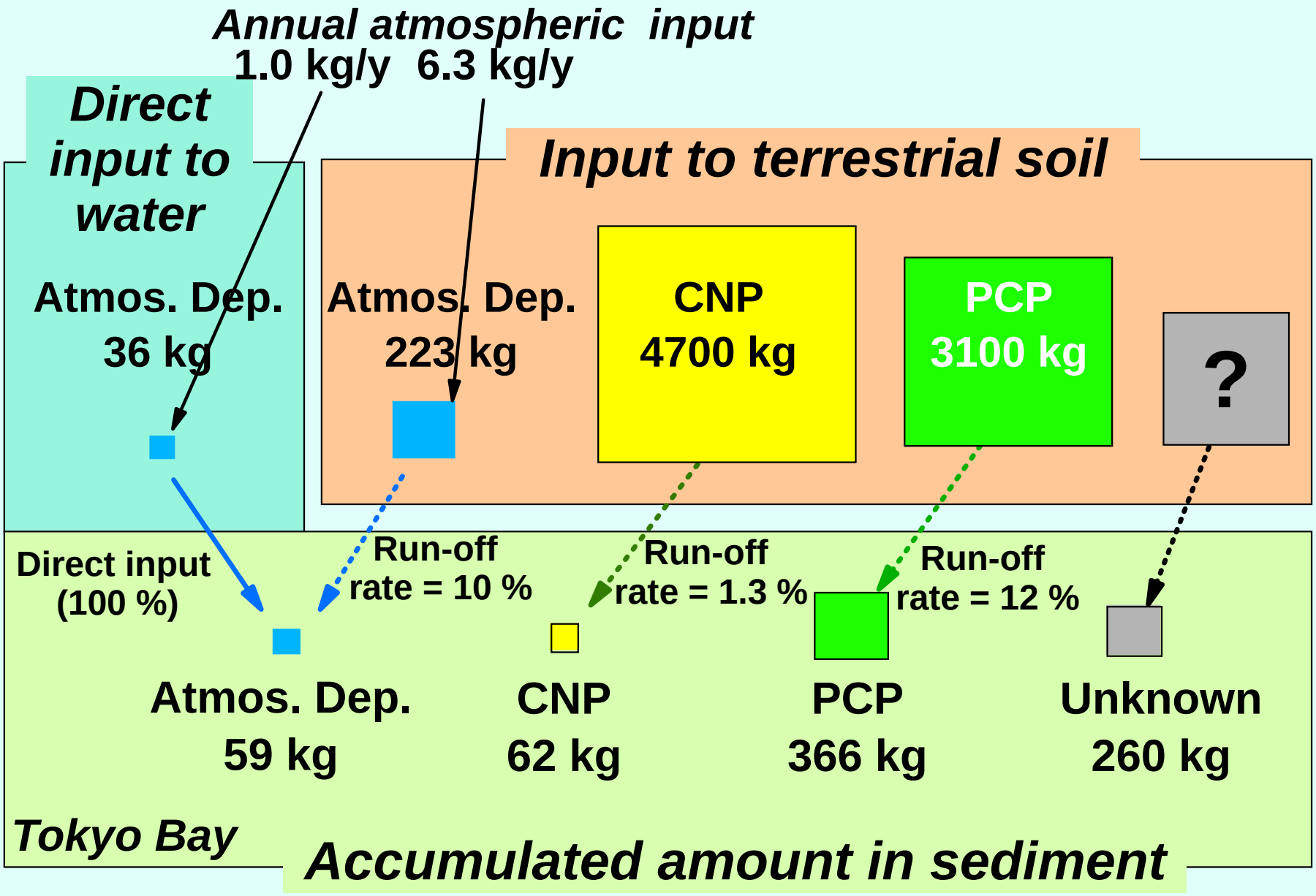
東京湾流域への過去35年間のダイオキシン負荷量と現存量



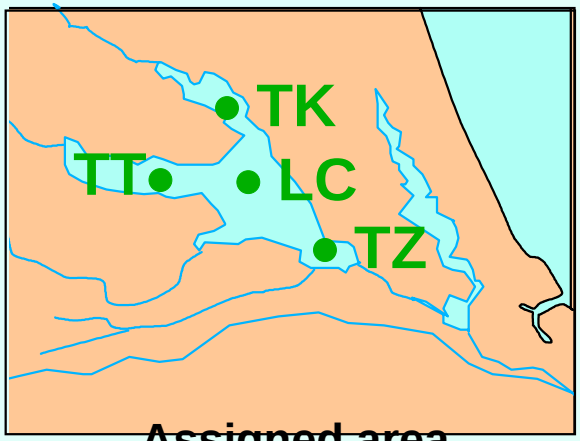
Percentage of paddy field in Tokyo Bay basin against national total: 3.6 %

Dioxin balance in Tokyo Bay basin

東京湾流域のダイオキシン収支（過去35年間）

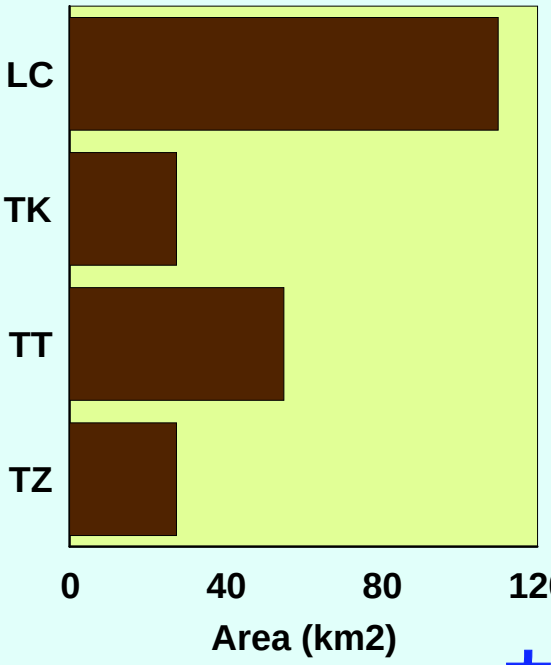


Dioxins accumulated in Kasumigaura Lake sediment over the past 35 years

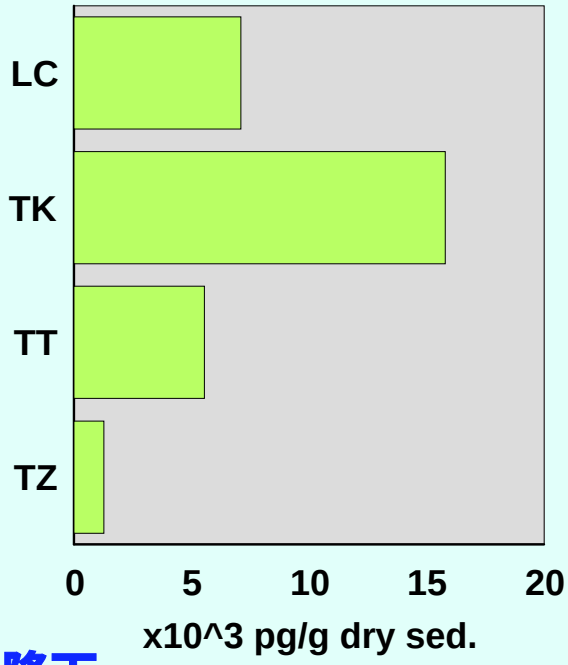


Sedimentation rate = 0.2 g/cm²/y

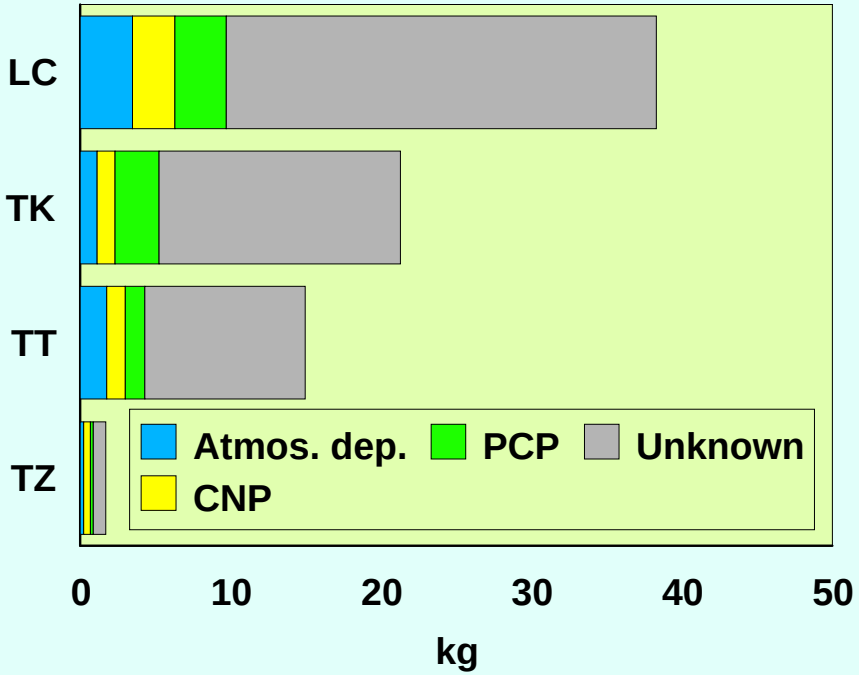
Assigned area

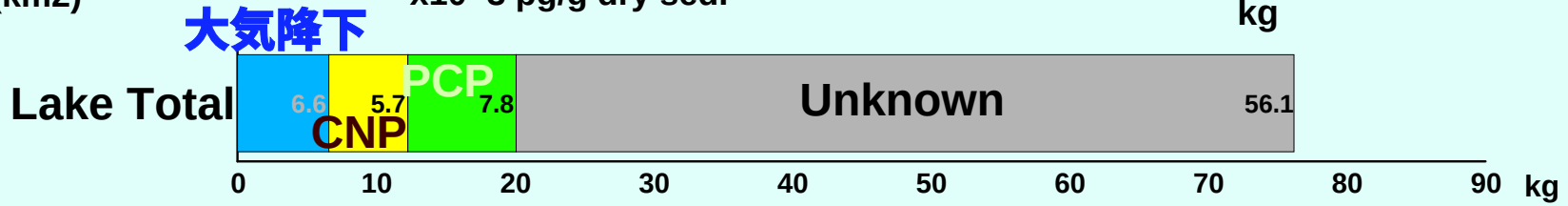


PCDD/F concentration

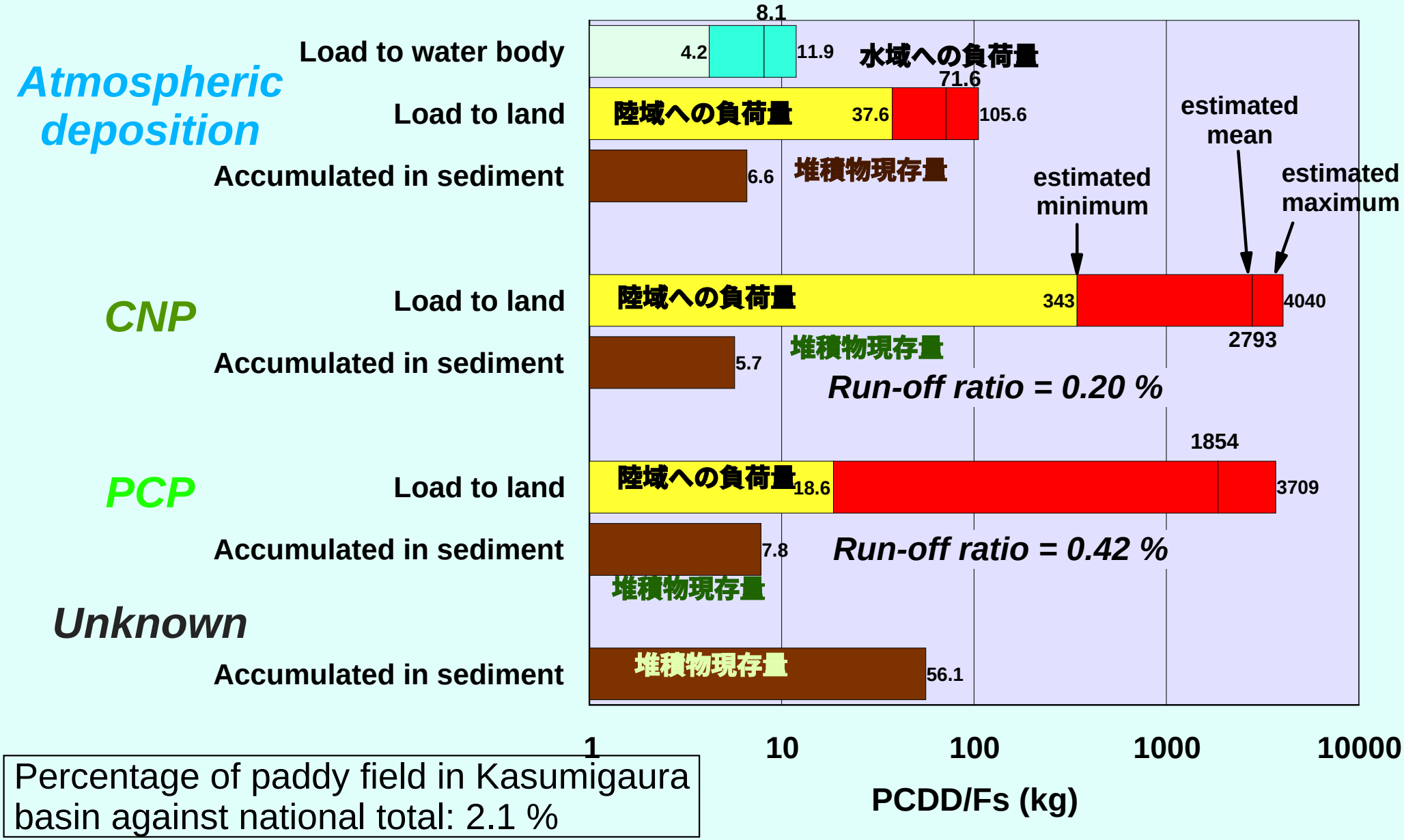


PCDD/F accumulated





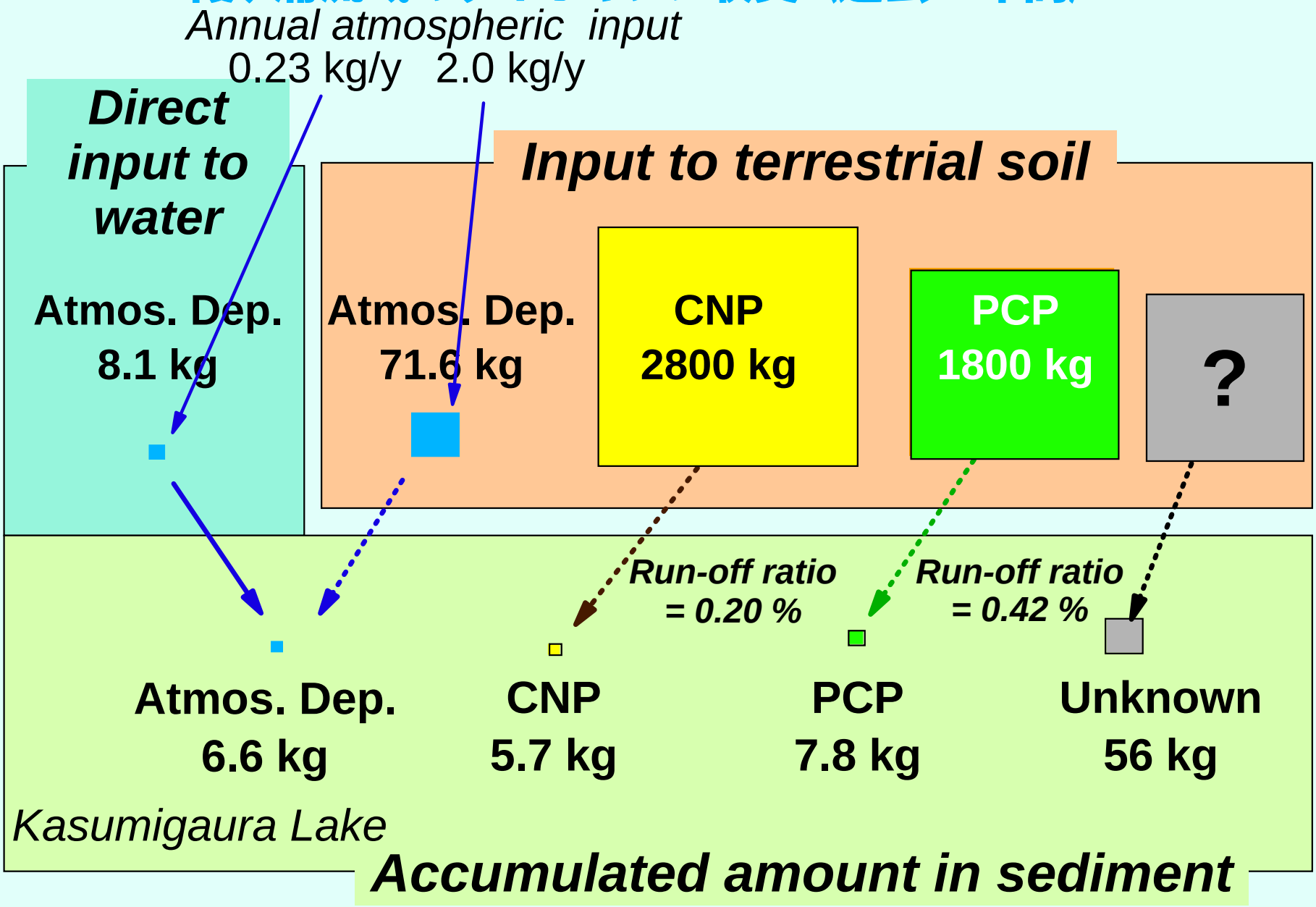
Dioxin load to Kasumigaura Lake basin over the past 35 years



Percentage of paddy field in Kasumigaura basin against national total: 2.1 %

Dioxin balance in Kasumigaura Lake basin

霞ヶ浦流域のダイオキシン収支（過去35年間）



Limitations of the current estimation

Hypothesis:

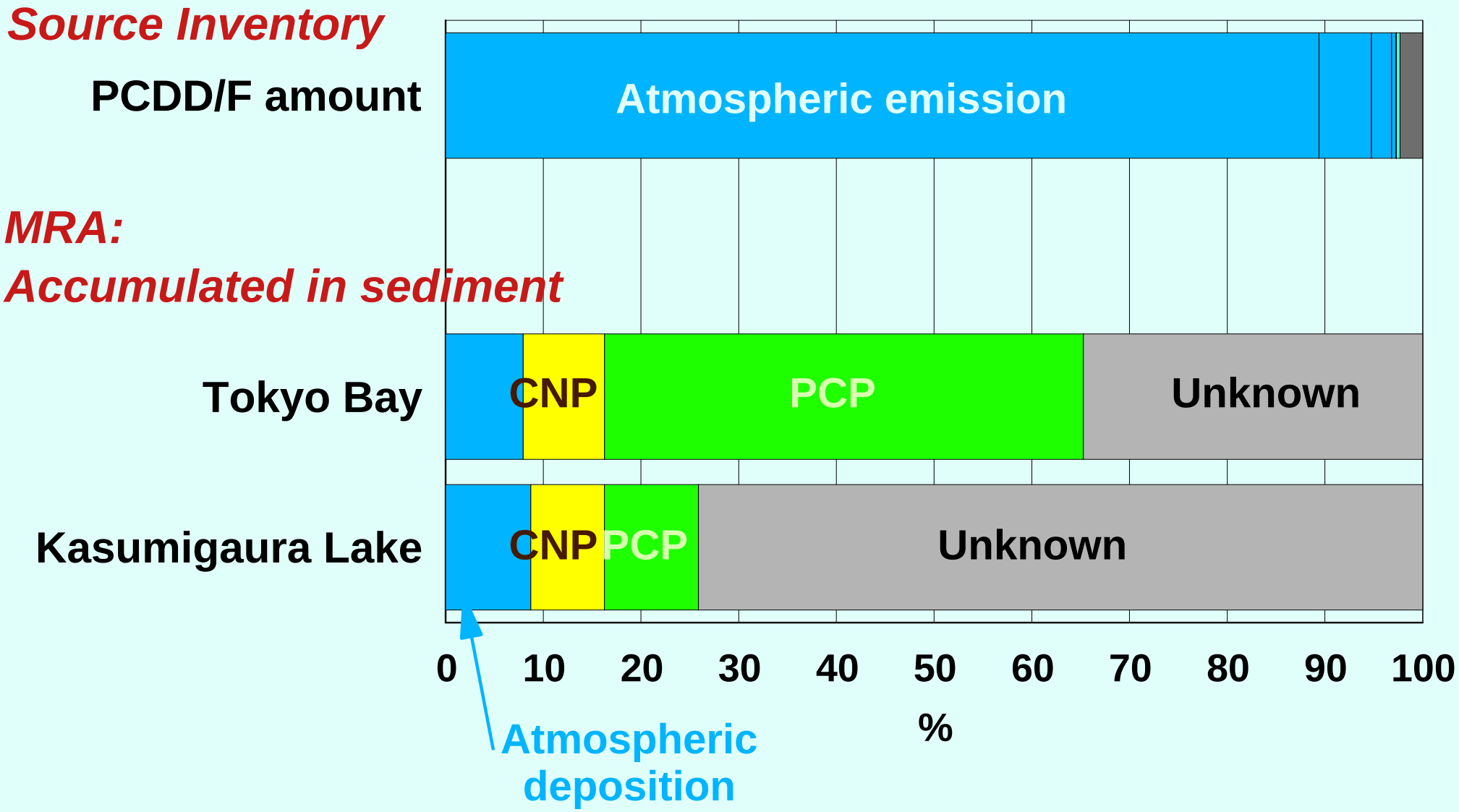
1. Measured dioxin concentration in surface sediment represents the past 35 years of sediment.
2. Atmospheric deposition flux constant for the past 35 year.
3. All the dioxin load entering into the water body accumulates in sediment.
4. No transformation nor volatilization of dioxin.

Uncertain data:

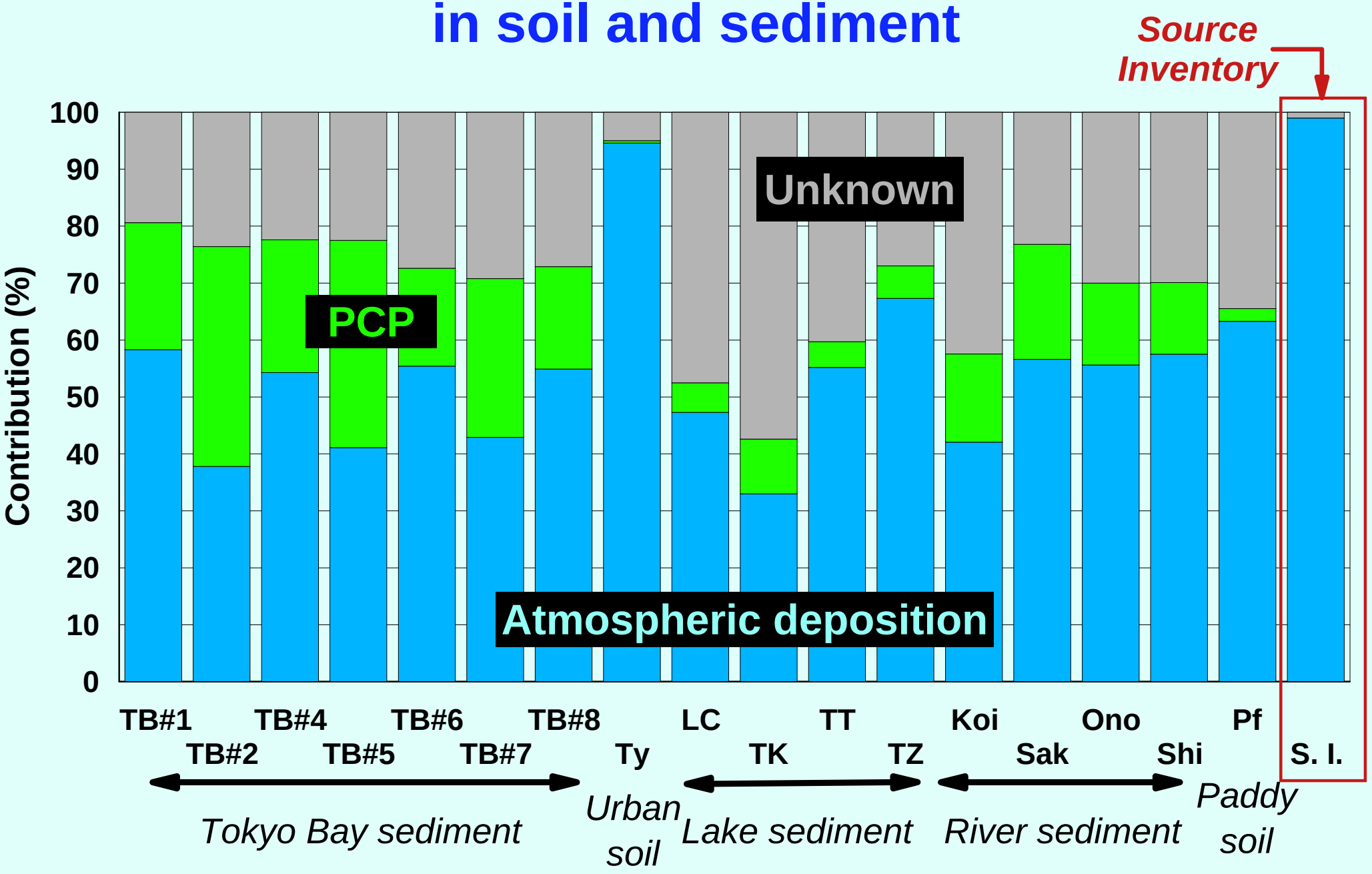
1. Dioxin impurity concentration in pesticides.
2. Pesticide use in the basin.

Dioxin source inventory and results of MRA analysis

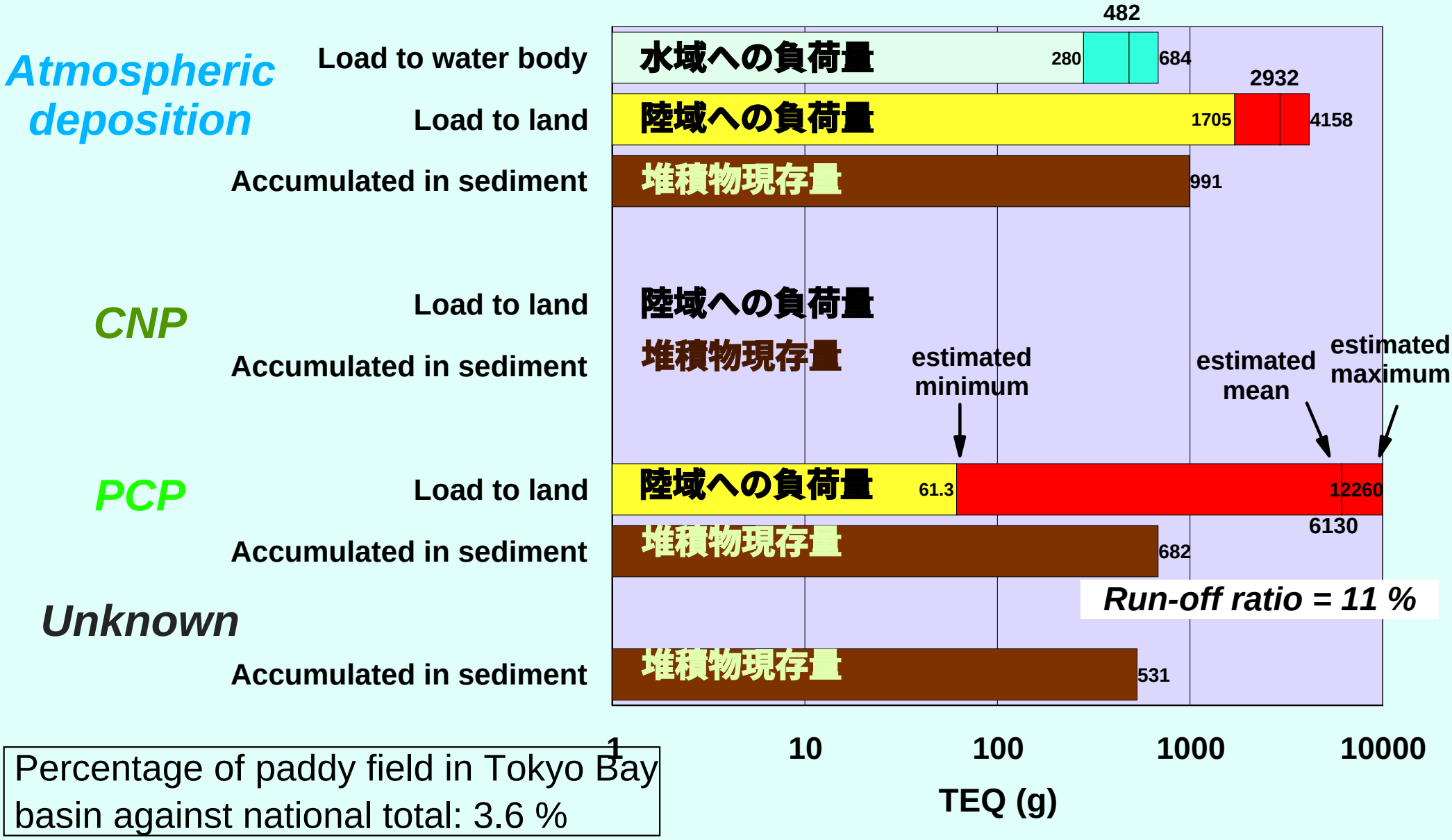
発生源インベントリーとMRAによる東京湾･霞ヶ浦における汚染源寄与率推定結果の比較



Contribution of different origins to the TEQ in soil and sediment

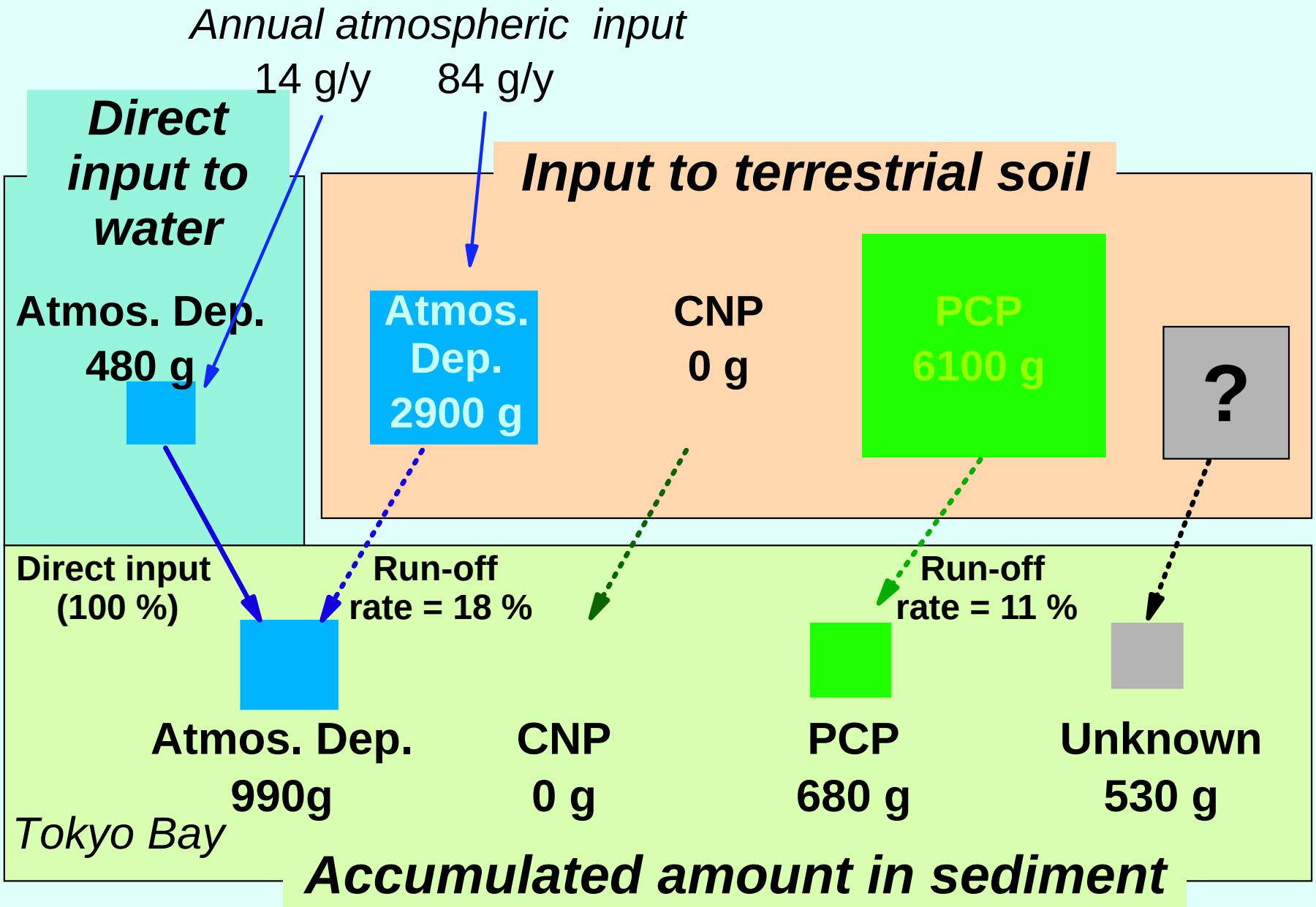


Dioxin TEQ load to Tokyo Bay basin over the past 35 years

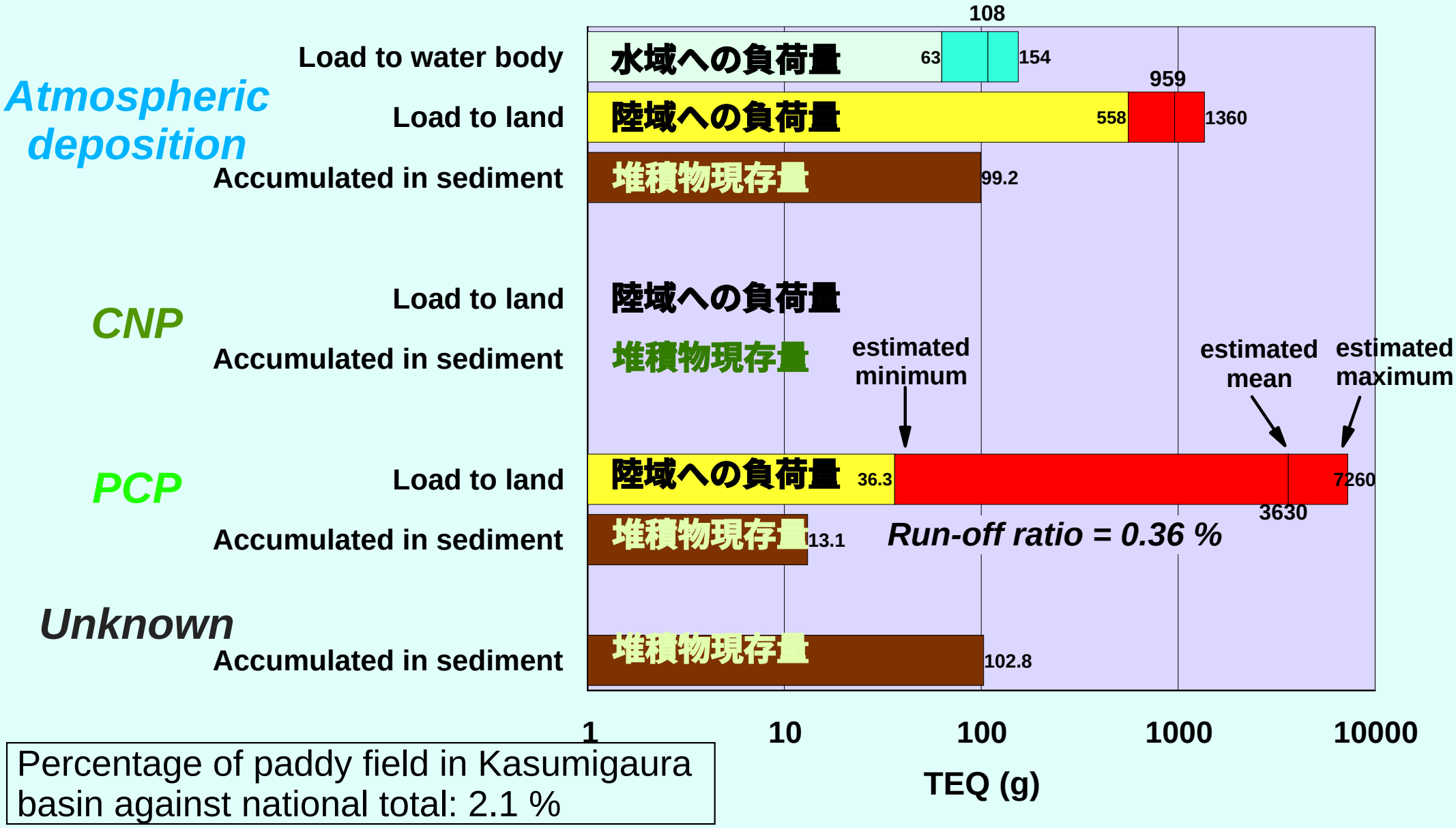


Percentage of paddy field in Tokyo Bay basin against national total: 3.6 %

Dioxin TEQ balance in Tokyo Bay basin

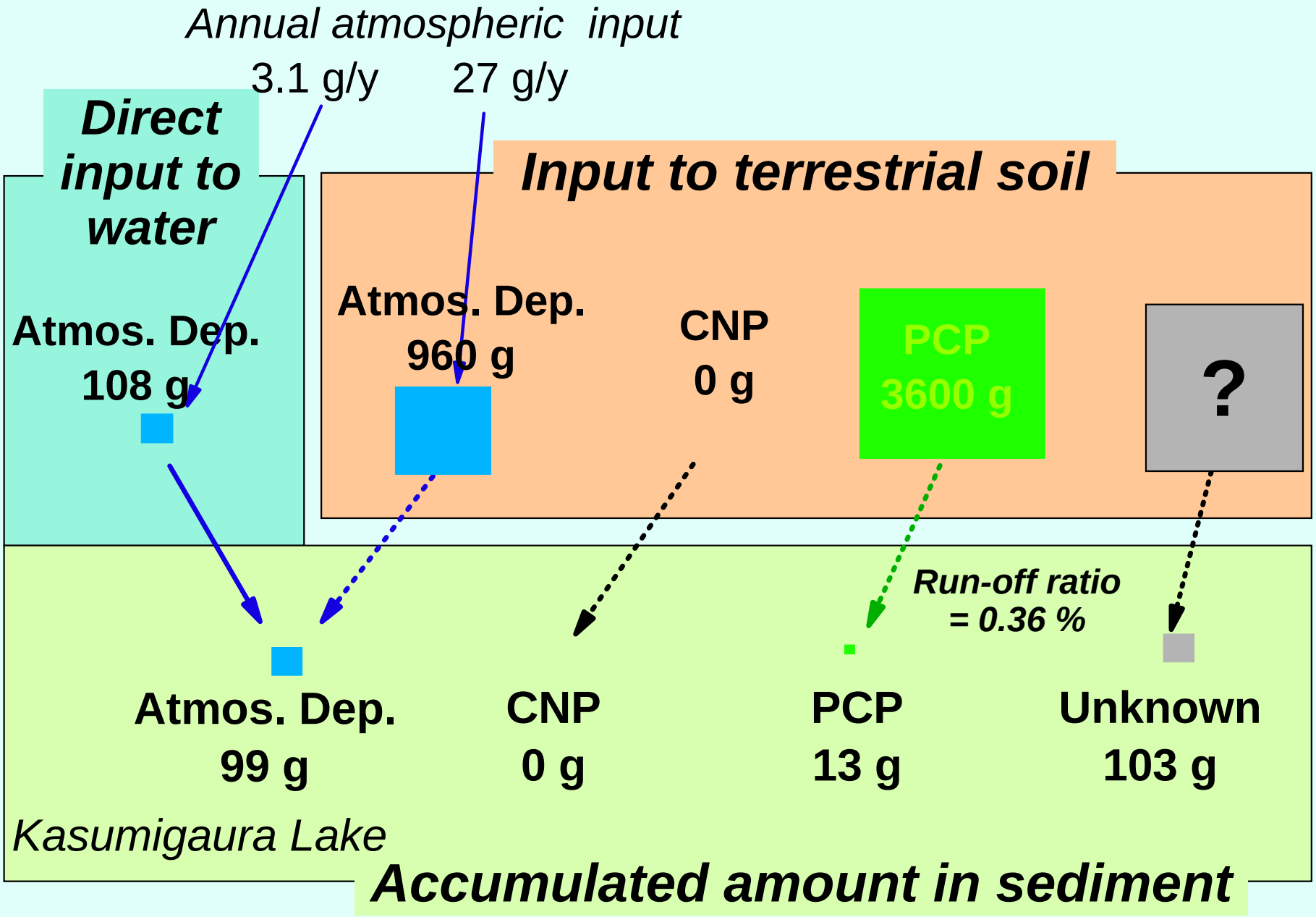


Dioxin TEQ load to Kasumigaura Lake basin over the past 35 years

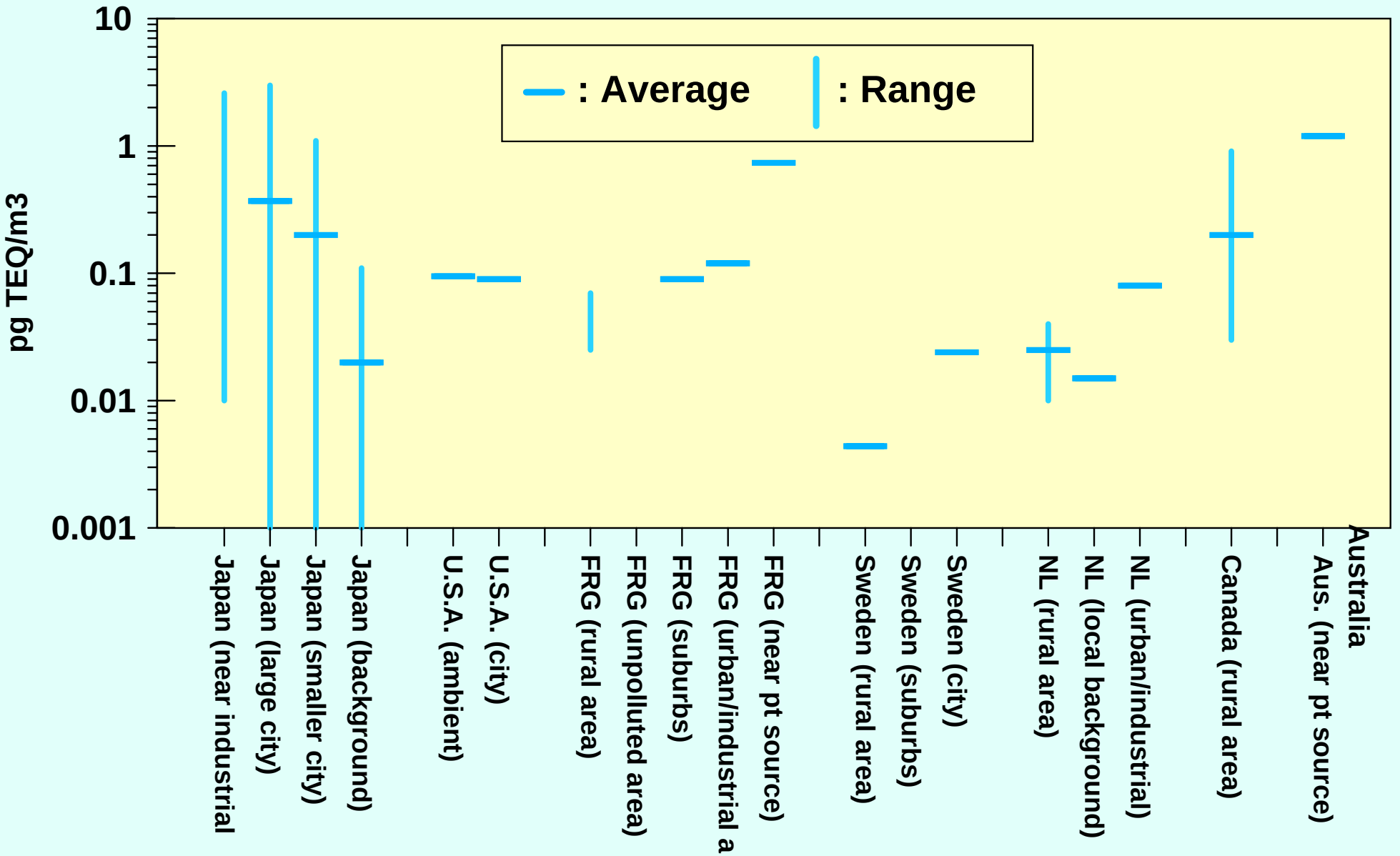


Percentage of paddy field in Kasumigaura basin against national total: 2.1 %

Dioxin TEQ balance in Kasumigaura Lake basin



Comparison of dioxin concentration in air



Japanese data from Environment Agency. Foreign data from Leam & Zorge and Leam et al.

Effect of dioxin emission reduction by the control of incinerators

Reduction of human dioxin uptake may take time in Japan because:

1. **Current dioxin pollution in aquatic environment is a result of past pesticide use.**

2. **Major dioxin uptake route from food:**

   Japan: fish <- aquatic environment

   European countries: meat and daily product
   <-grass <- atmospheric deposition

Conclusions

1. **Detailed isomer specific analysis of dioxins served to reveal the cause of dioxin pollution in the environment. Popular analytical procedure of quantifying 2378-isomers only is not sufficient for detailed analysis of dioxin behavior.**
2. **There is a great discrepancy between the widely acknowledged dioxin source inventory and current contamination in aquatic sediment.**
3. **Current dioxin contamination in aquatic environment is mainly a legacy of past pesticide use. In terms of TEQ, however, the importance of this legacy becomes smaller and comparable to that of atmospheric deposition.**
4. **More time may be required to reduce the human dioxin exposure in Japan than in European countries by atmospheric emission control.**