Workshop LNR-II.ZZ.SS: Diossine e PCB in alimenti e mangimi.
9-10 Dicembre 2010, Teramo

PCBs' dynamic in *Tapes philippinarum* studied by combining detoxification experiment and ecotoxicological model

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The Venice Lagoon

Total surface of 550 km^2, made up of islands (44 km^2), wetlands ("barene") and tidal flats ("velme")

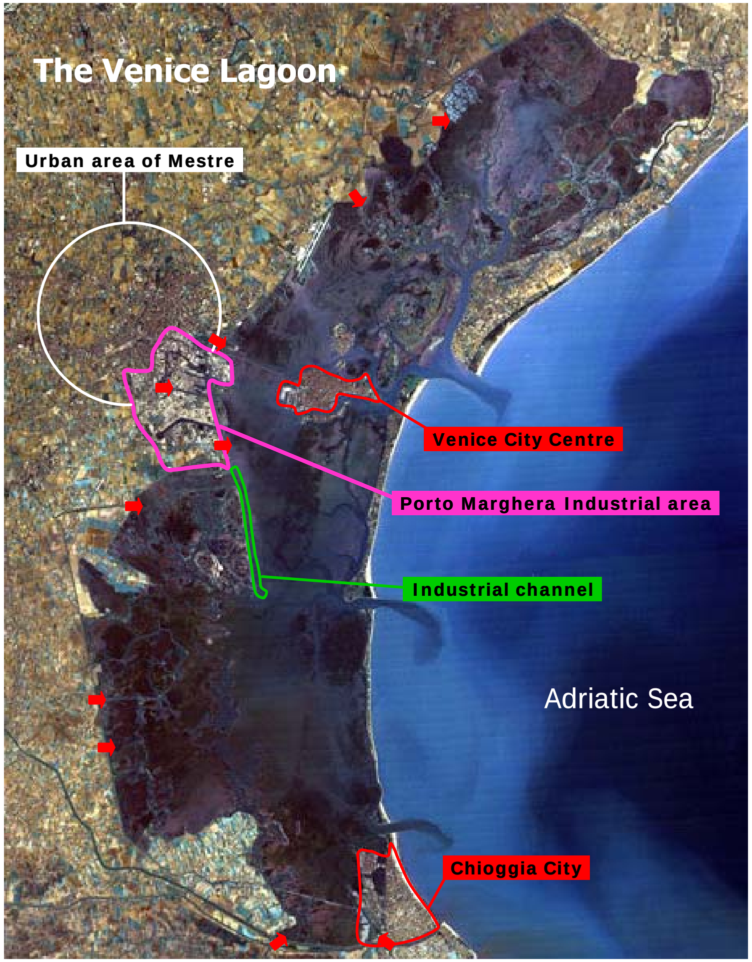
average depth 1m; deep channels allow navigation (65 km^2).

➡ 11 tributaries: average freshwater discharge ≈ $3x10^6$ m^3 day^{-1}

⇔ 3 inlets: ≈ $3.85x10^8$ m^3 day^{-1} of water are exchanged through the inlets with the sea.

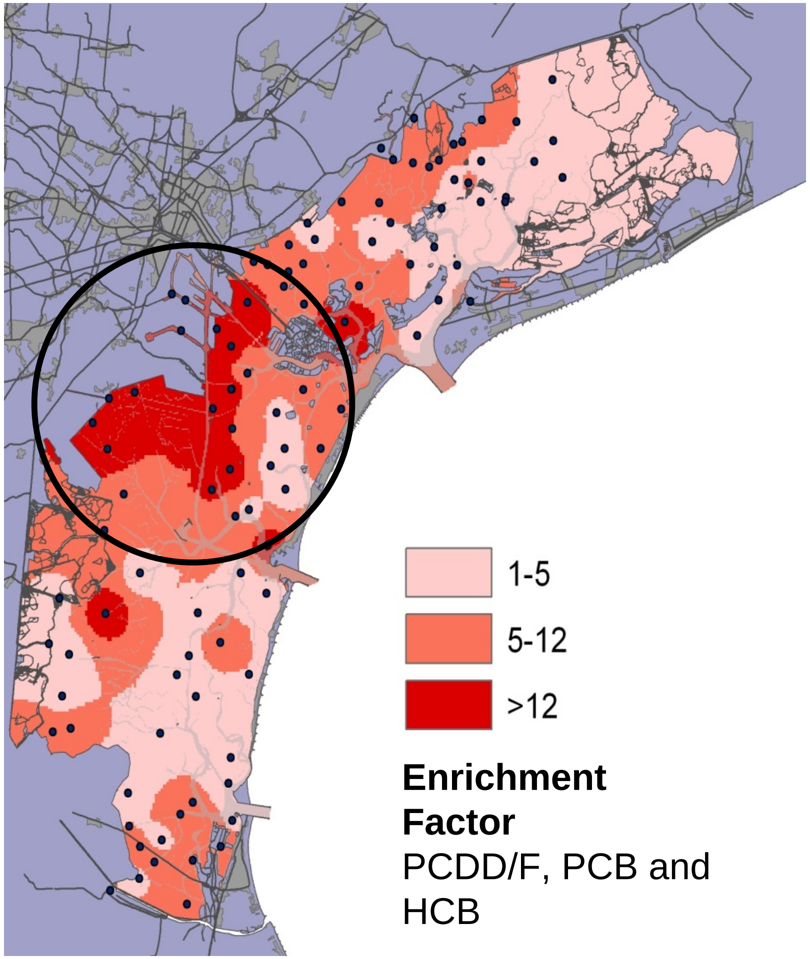
Persistant Organic Pollutants (POPs) in the Venice Lagoon

Sources of POPs



- Cities of Venice and Chioggia
- Hurban areas mainland
- Industrial area

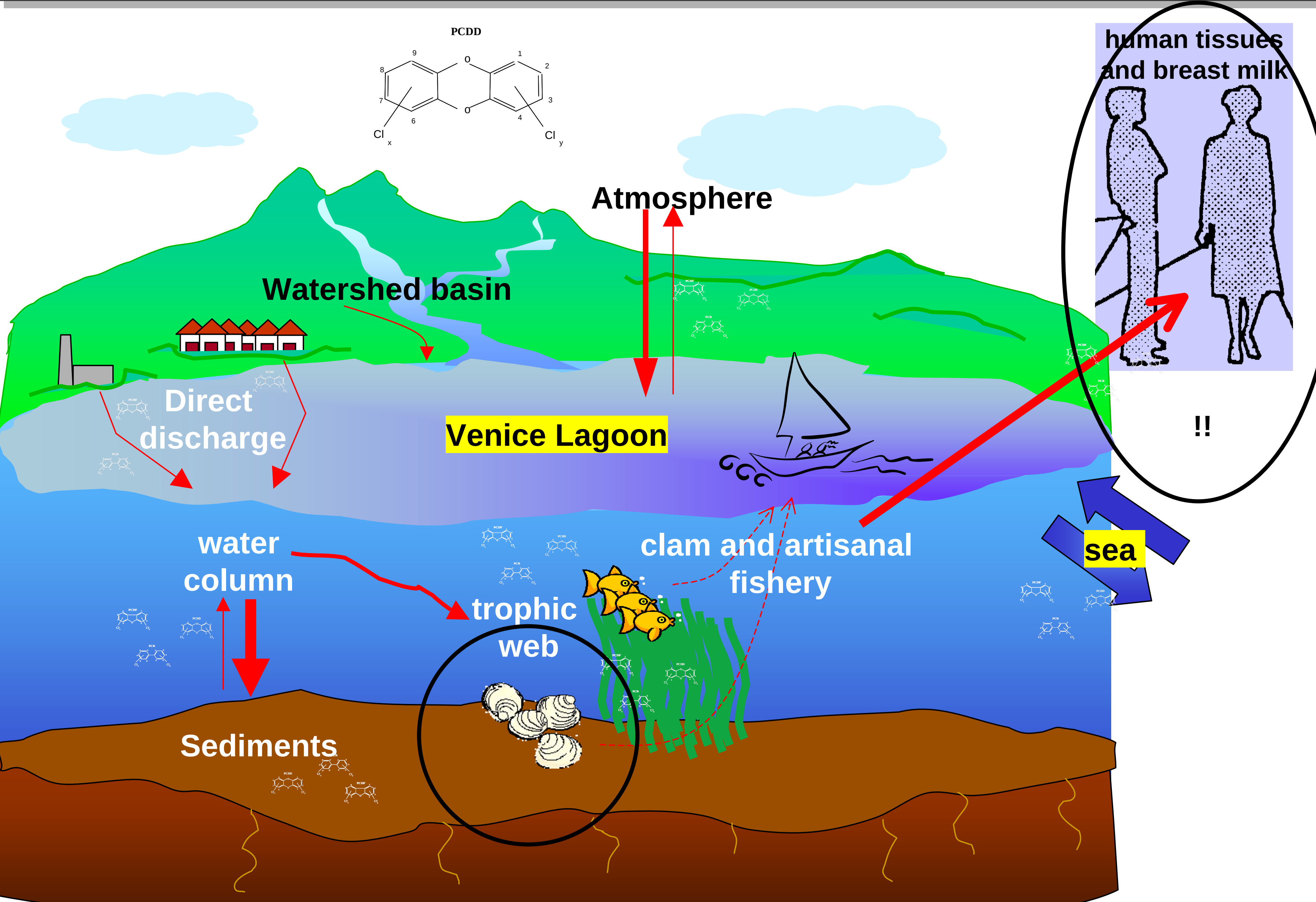
Sediment Contamination



- **Dioxins and other POPs are accumulated in the sediments**

Guerzoni et al., Chemosphere, 2007

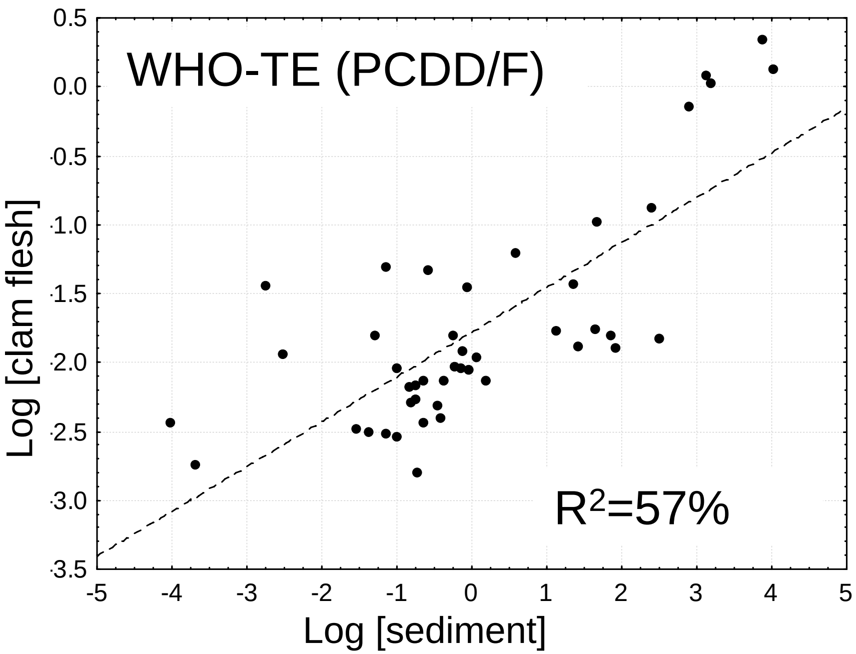
Fate of POPs in the Venice Lagoon



Clam contamination

Tapes philippinarum

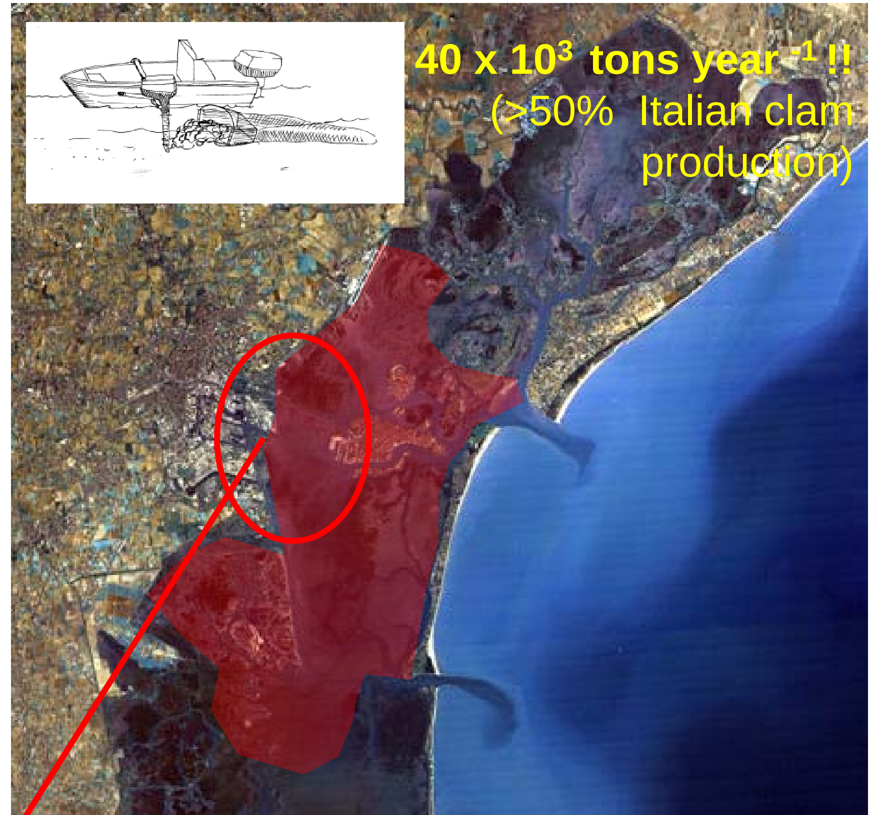
Manila clam



- **Clams can be very contaminated**
- **high correlation between clam and sediment contamination**

Raccanelli et al., Chemosphere, 2007

Clam fishery

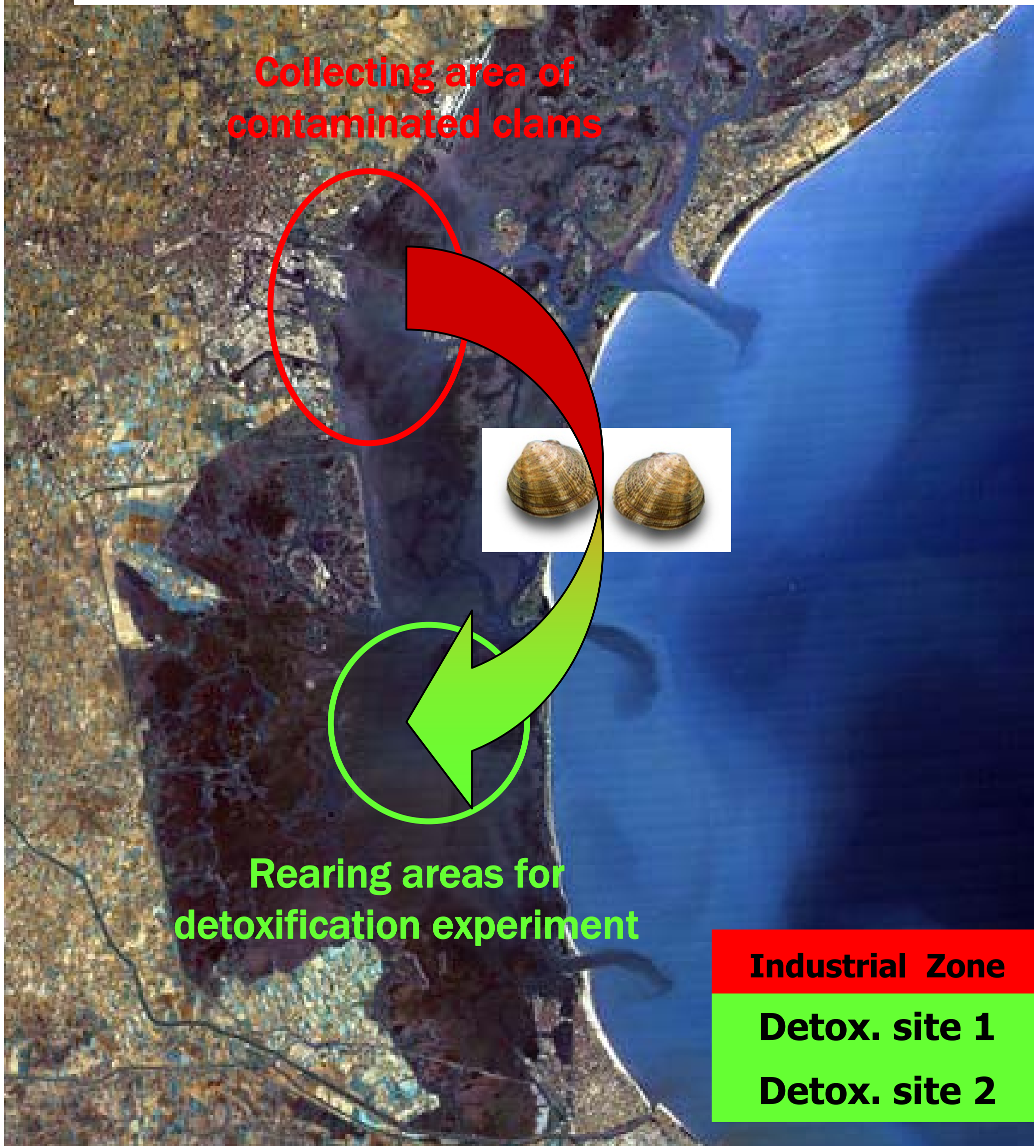


- **POPs concentrations in sediments up to 2500 ng I-TE kgdw^{-1}**
- **Industrial channels are important recruitment & growth areas for clam.**
- **Although banned clam harvesting is conducted illegally (2000€/day) .**

Detoxification experiment

The Venice Lagoon

In order to discourage illegal fishing & maintain exploitation opportunities, **detoxification experiments** were prompted by the local Administrative Council, i.e. the *Regione Veneto*



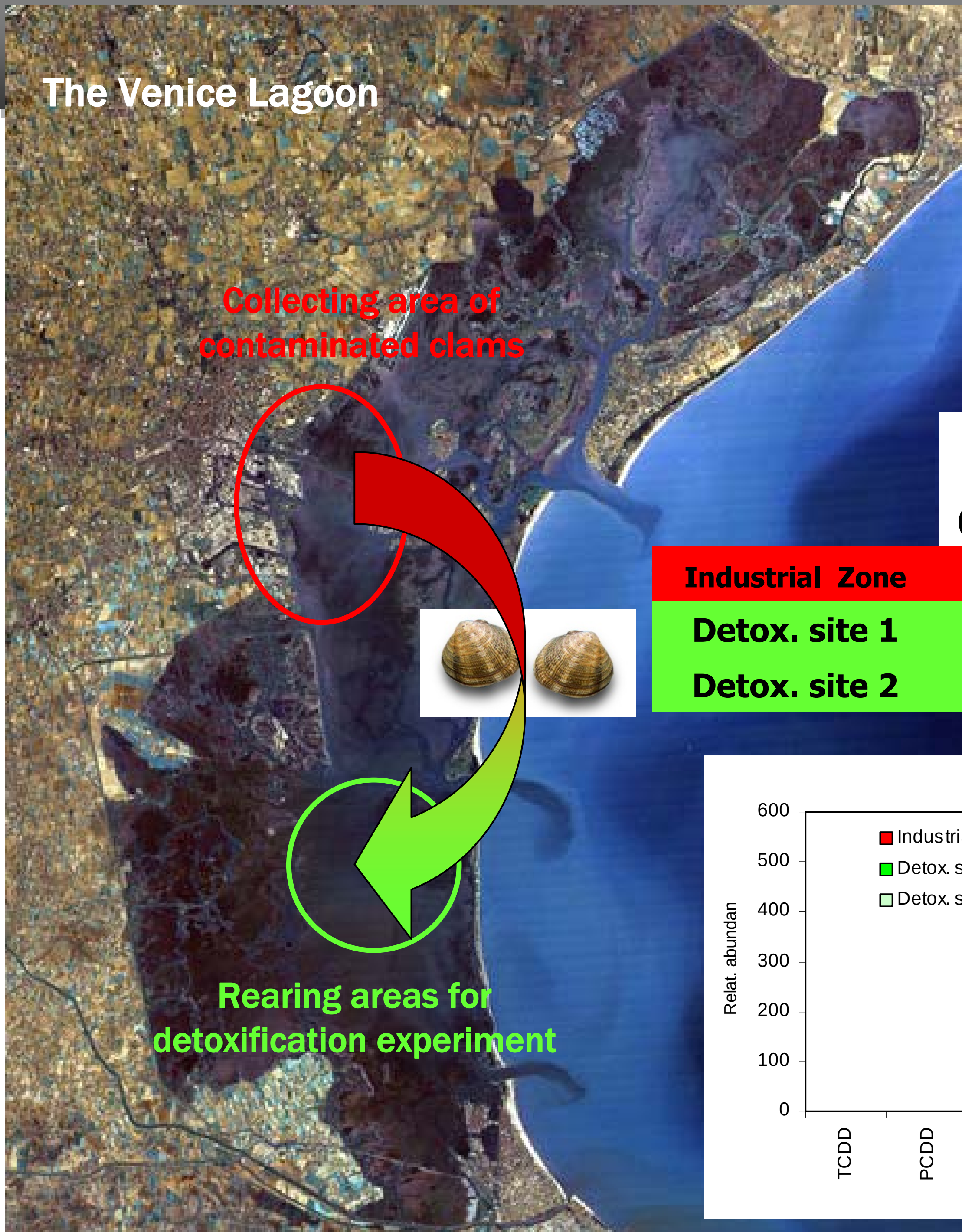
The experiments:

- SUMMER 2004 and WINTER 2006

- detoxification in natural conditions
- two detoxification areas (site 1 and site 2)
- samples of superficial sediments
- detoxification: 120 days long
- monitoring of PCB, PCDD/F, HCB concentrations in biota
- high frequency of sampling of biota (every 5 days) for measuring POPs on flesh and lipid basis

	PCDD/F WHO-TE (ng/kg dw)	PCB WHO-TE (ng/kg dw)	OCDF/ OCDD	HCB (µg/kg dw)
Industrial Zone	37.063	2.99	4.692	7.28
Detox. site 1	0.24	0.006	0.395	0.05
Detox. site 2	0.437	0.021	0.304	0.06

POPs in sediments



Superficial sediments (0-10 cm) of collecting site and detoxification sites. Dioxins fingerprints highlighted indutrial contamination of sediments of collecting site (high OCDF/OCDD ratio).

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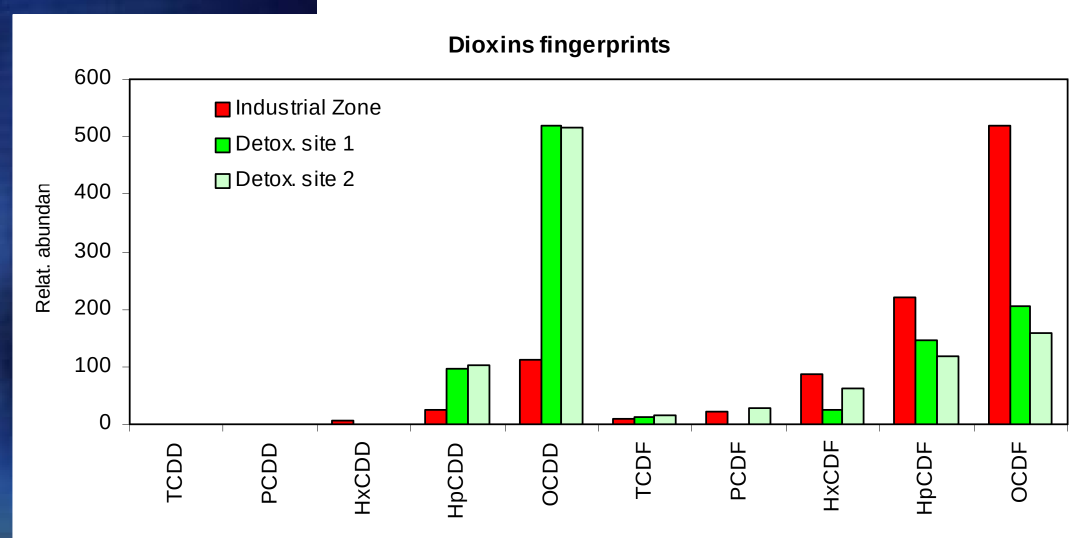
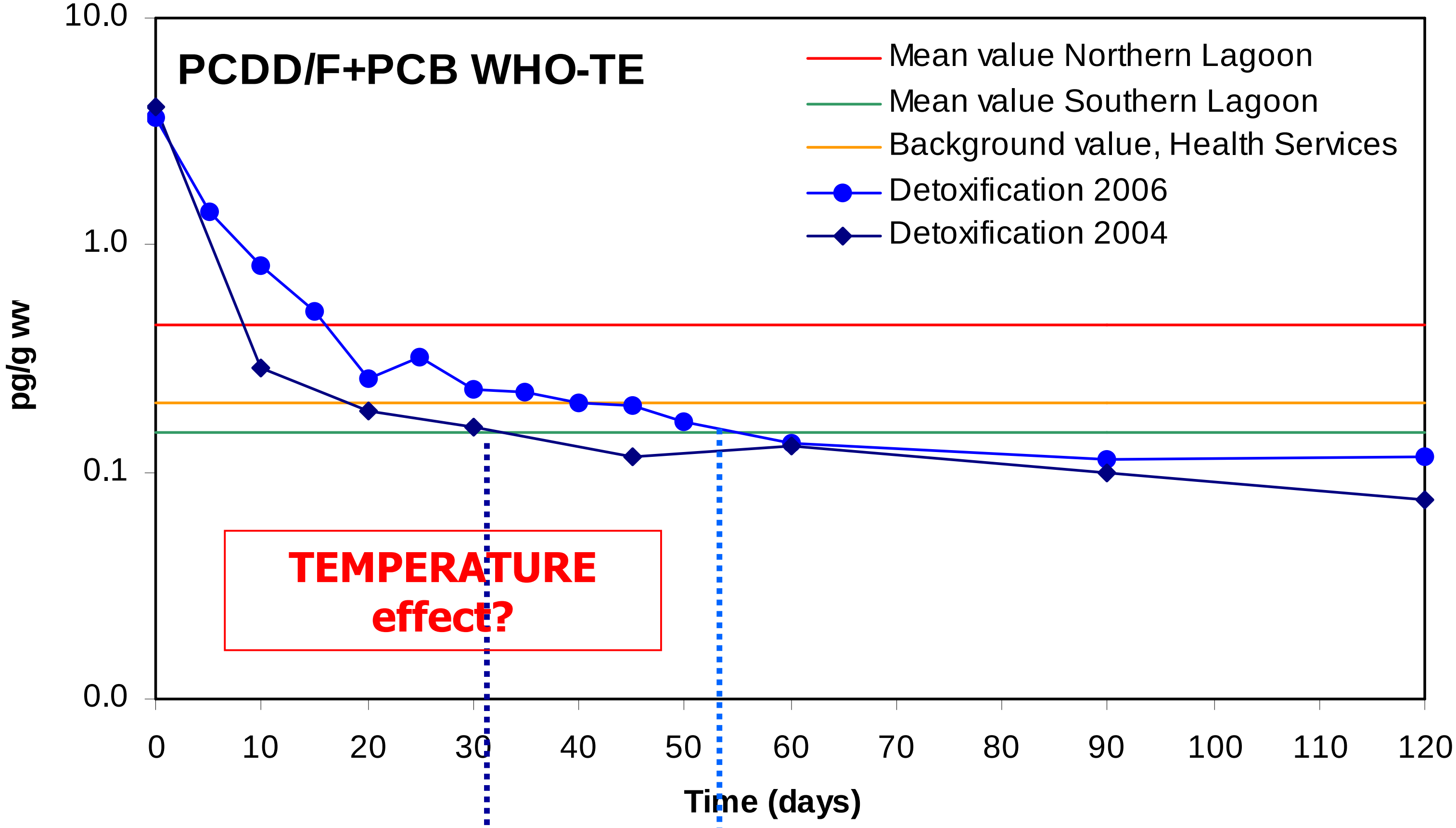


Detoxification of POPs in clam flesh

Total toxicity of Dioxins and PCB over time (on wet weight basis) and comparison with references

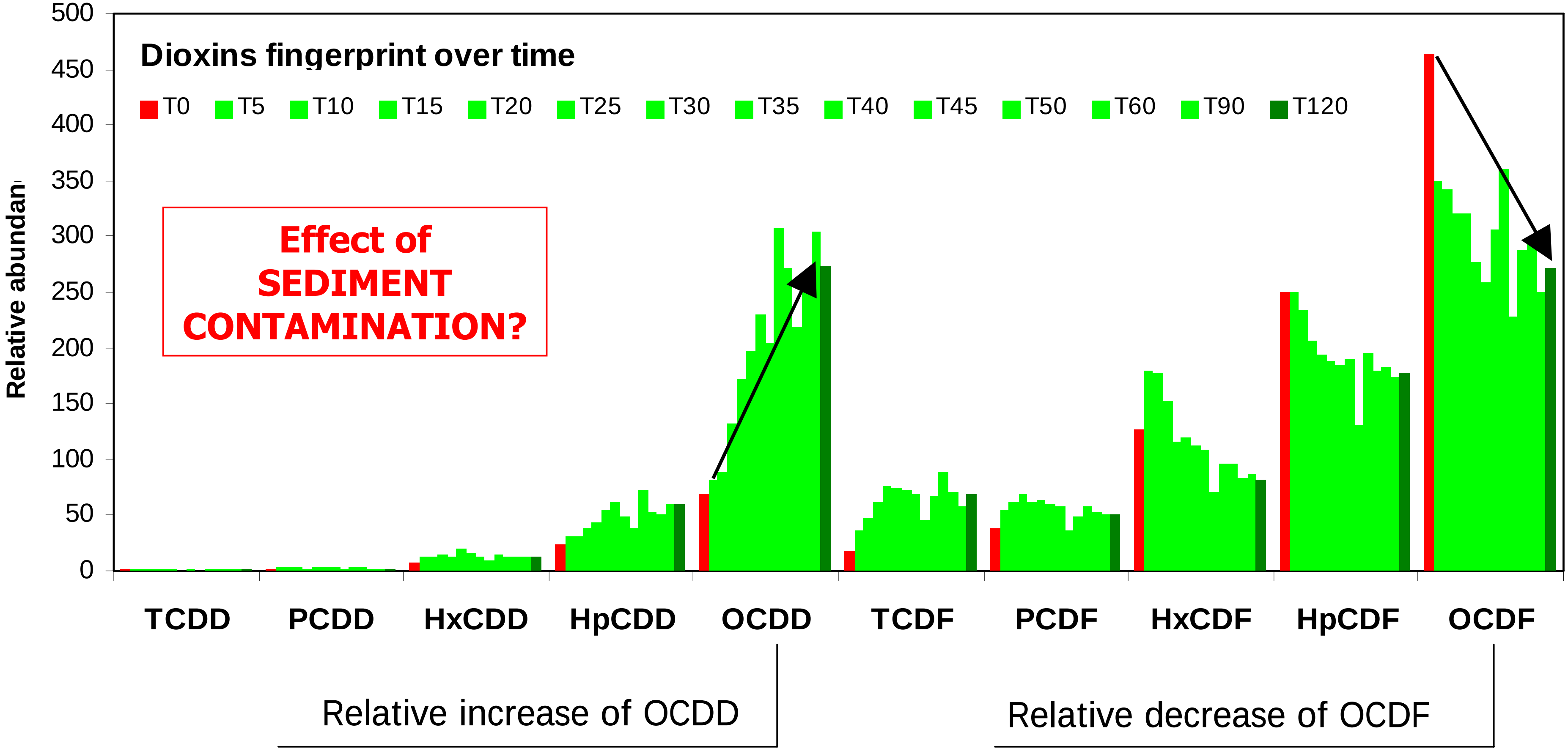


Summer 2004 experiment: Substantial decrease of toxicity: after 30 days TE reaches background values

Winter 2006 experiment: detoxification takes much longer, after 60 days TE still significantly decreasing, takes 50-60 days to reach background values

Dioxin fingerprint in clam flesh

During detoxification significant changes of the dioxin fingerprint over time



Dioxin fingerprints changed according with sediment supporting the strong relationship already found between sediment and clam contamination and **highlighting detoxification of clam from industrial contamination**

Raccanelli et al., Env. Chem. Letters, 2008

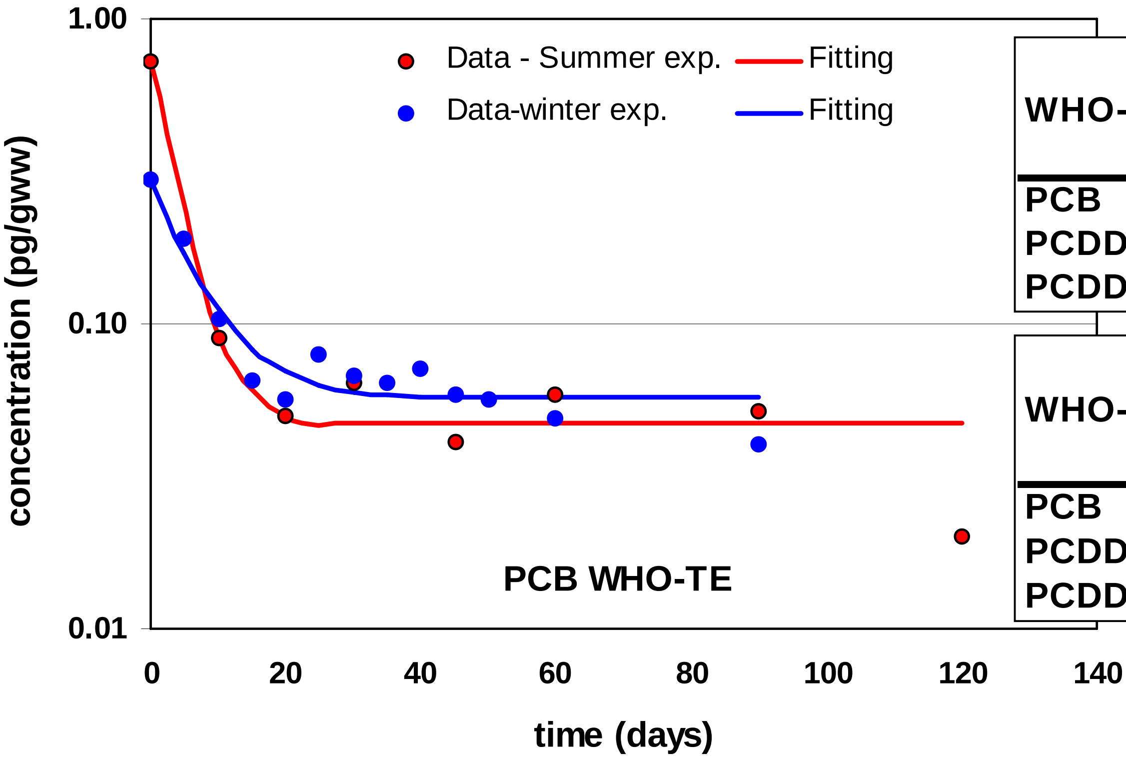
Apparent detoxification rate

Assuming that concentration of a generic POP (**C_B**) in bivalve depends on:

apparent bioaccumulation from sediments (**C_S**)

apparent detoxification

$$\frac{dC_B}{dt} = K_1 \cdot C_S - K_2 \cdot C_B$$



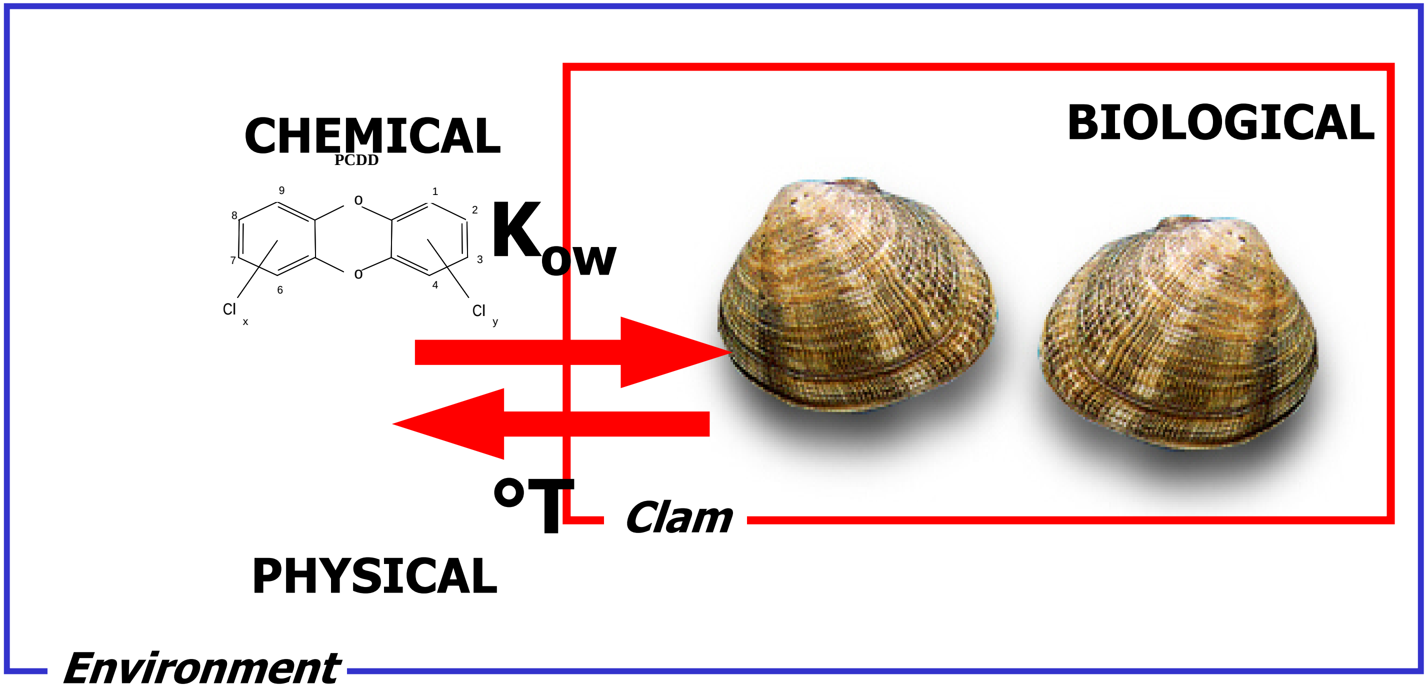
2006 (winter)				
WHO-TE	C_B^0 [pg/g]	K1 [days-1]	K2 [days-1]	half-life [days]
PCB	0.297	0.5956	0.1443	**4.80**
PCDD/F	3.361	0.1572	0.1943	**3.57**
PCDD/F+PCB	3.658	0.1972	0.1892	**3.66**

2004 (summer)				
WHO-TE	C_B^0 [pg/g]	K1 [days-1]	K2 [days-1]	half-life [days]
PCB	0.725	0.7601	0.2761	**2.51**
PCDD/F	3.365	0.1002	0.3289	**2.11**
PCDD/F+PCB	4.090	1.1852	0.3175	**2.18**

Modelling detoxification

The detoxification is a complex process that is influenced by the SEASON and DETOXIFICATION SITE (sediment).

More generally clam detoxification is a resulting from a set of different processes

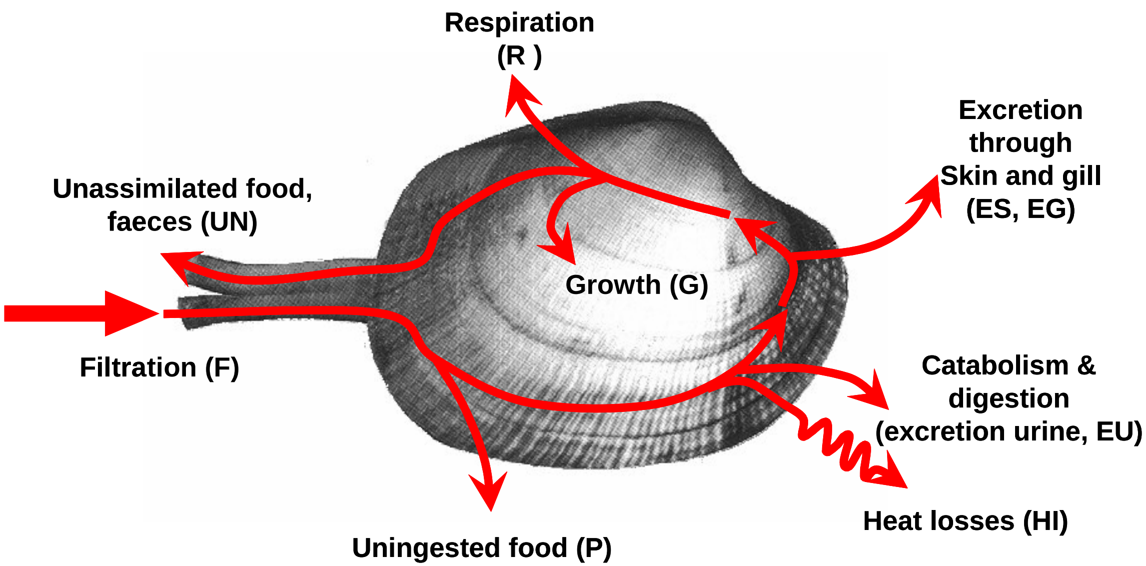


An ecotoxicological modelling approach allows for an explicit representation of these processes, thus it permits for **extending** and **broadening** the findings of detoxification experiments, exploiting at best the information carried out by costly field measurements: **DESCRIBE, UNDERSTAND and FORECAST**.

Bioenergetic growth model

Represents dynamically (in time) the different physiological processes

Growth = **Gross anabolism** - **Feeding catabolism** - **Basal Metabolism**

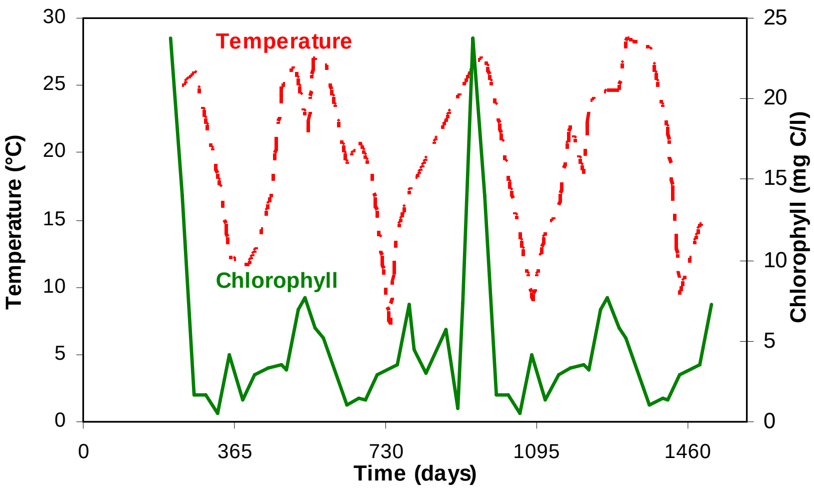


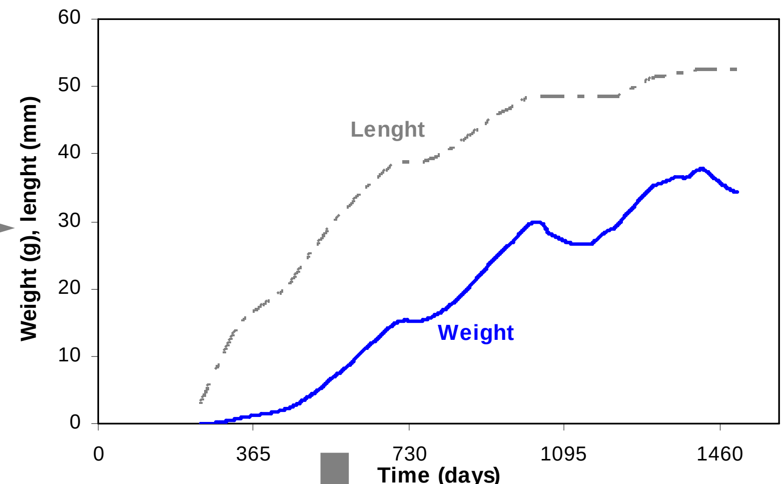
$$\frac{dw}{dt} = G_{max} \cdot f(T) \cdot f(Chla) \cdot w^m - \alpha \cdot G_{max} \cdot f(T) \cdot f(Chla) \cdot w^m - R_{max} \cdot f_T(T) \cdot w^n$$

Growth result from an energy balance function of **water temperature (T), shellfish size (w), food available (Chla)**

Bioenergetic growth model

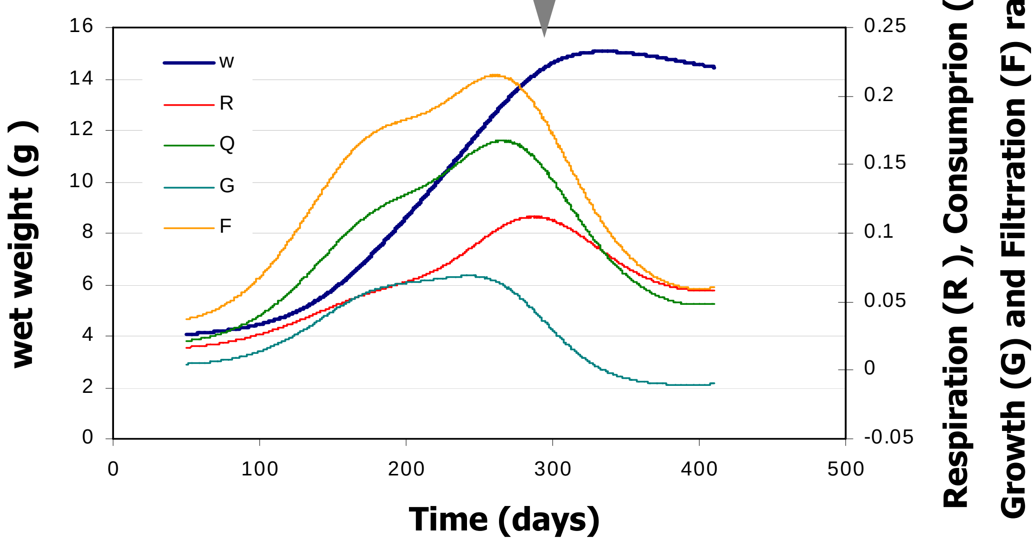
A bioenergetic growth model for *Tapes philippinarum* has been already identified, calibrated and validated for the Venice Lagoon (see. Solidoro et al., 2000)





Giving measured evolution of temperature and chlorophyll the model predict clam growth…

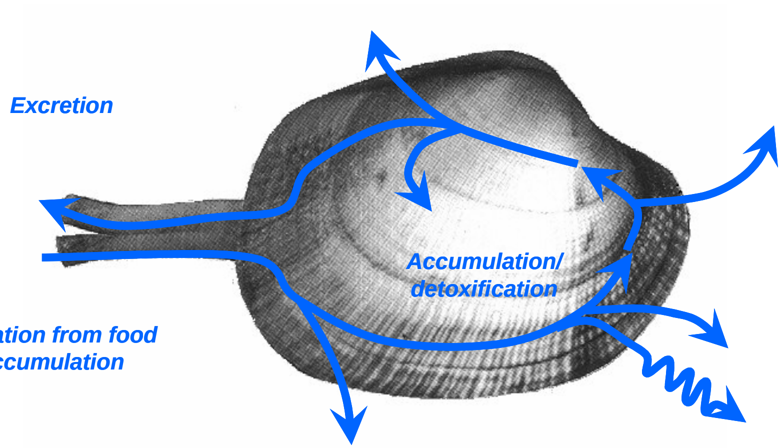
..and all the dynamics through time of the physiological processes involved in living clam



Bioaccumulation model

Represents a balance between processes of uptake and cleaning of pollutant in clam flash

Toxicant concentration in clam = Uptake from water + Uptake from food - Excretion of unasimilated - Metabolic detoxification - Dilution



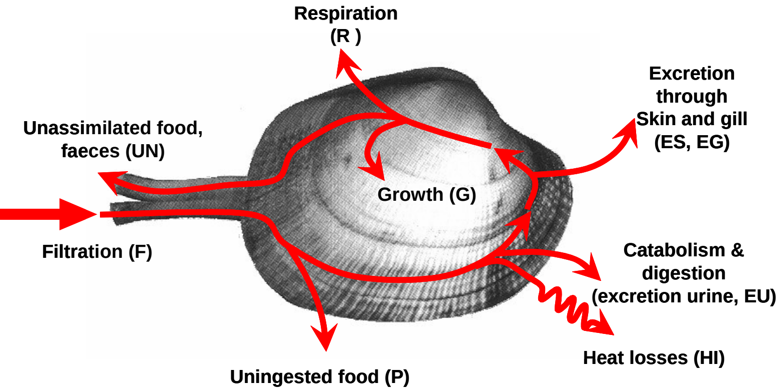
$$\frac{dC_B}{dt} = k_1 \cdot C_S + k_D \cdot C_D - \left[k_E + k_M + k_G\right] \cdot C_B$$

Concentration of pollutant in clam (C_B) is varying according to sediment (C_S) and food (C_D) concentration; it is depending on chemical properties of the pollutant (k_1, k_D, k_E are function of K_{ow}) and is influenced by temperature (T)....

Ecotoxicological model

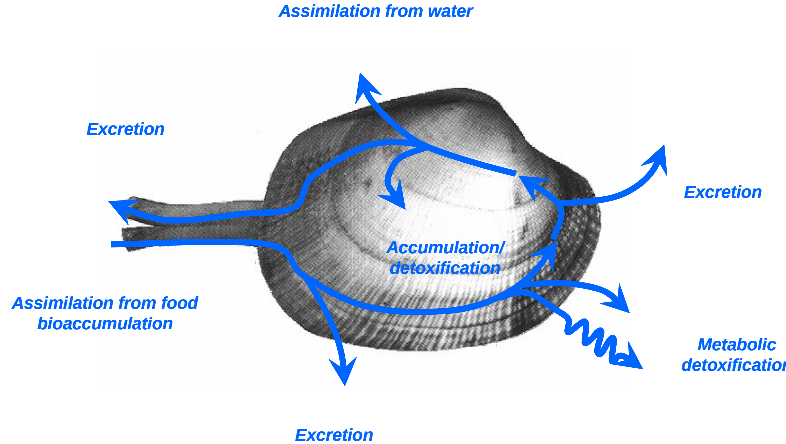
TEMPERATURE (°T)
FOOD (Chlorophyll)

BIOENERGETIC GROWTH MODEL



TEMPERATURE (°T), AFFINITY (K_{OW})
FOOD concentration (C_D)
Sediment concentration (C_S)

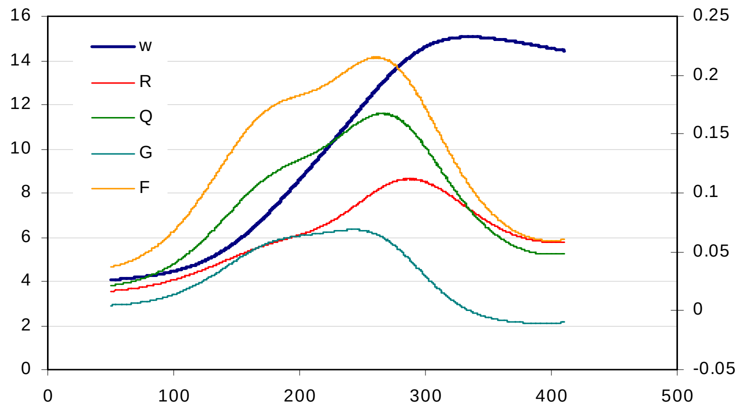
BIOACCUMULATION MODEL



Physiological processes

POPs dynamics

We applied to 2 sites, using measured °T, Chla

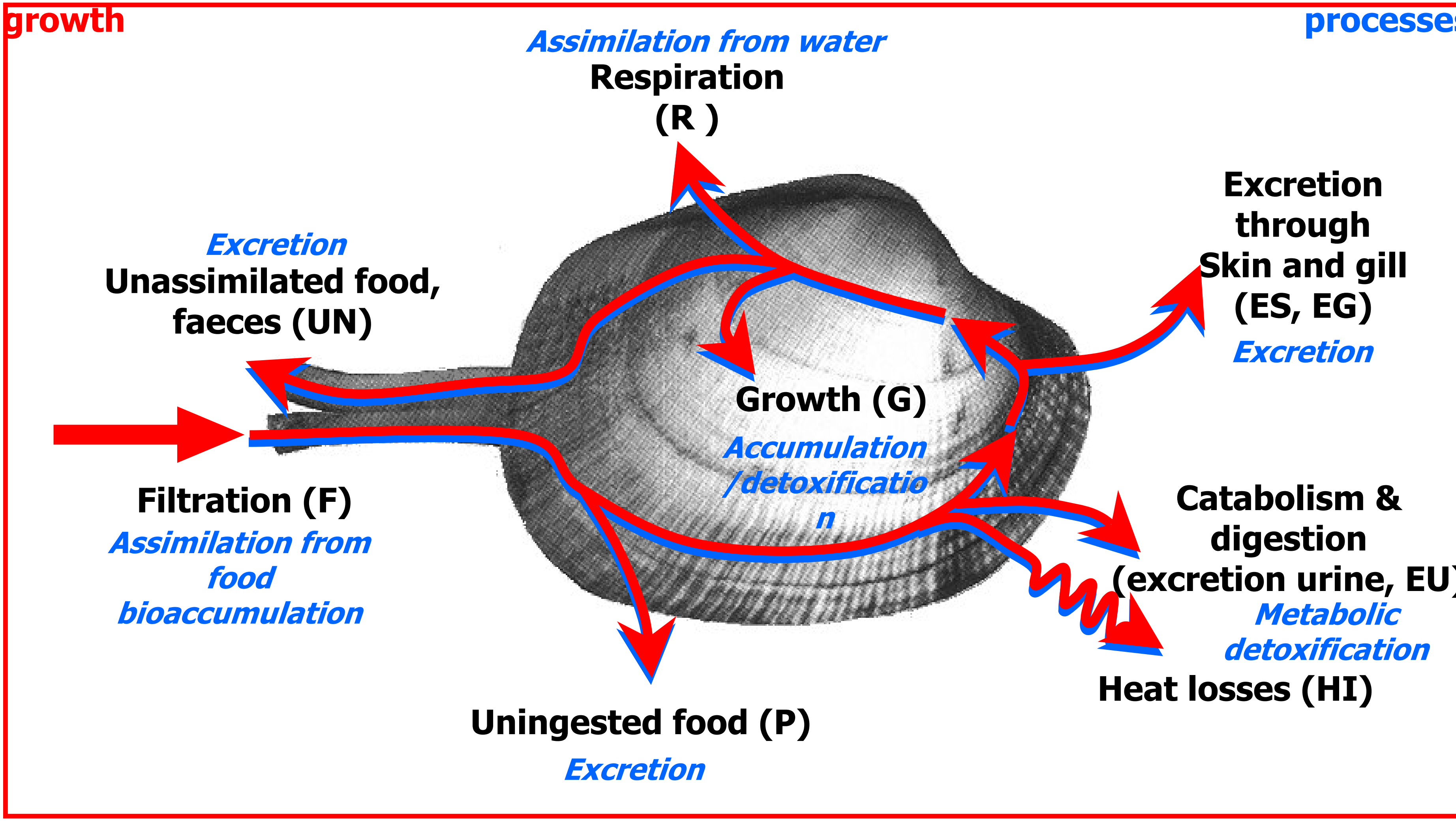


Applied to 2 sites, for 12 PCBs dioxin-like and 17 dioxins congeners

Ecotoxicological model

BIOLOGICAL PROCESSES: Flow of energy >> feeding, respiration, catabolism & growth

ECOTOX PROCESSES: bioaccumulation, bioconcentration & detoxification processes



TEMPERATURE (°T), FOOD, SIZE

TEMPERATURE (°T), LIPIDIC AFFINITY (Kow, Koc)

Bioaccumulation model

Moreover, each process is also depending on a correspondent physiological process derived from the bioenergetic model.

The coupling of the two models allow for the implicit representation of the dilution.

$$\frac{dC_B}{dt} = k_1(R)\cdot C_S + k_D(Q)\cdot C_D - \left[k_E(UN) + k_M(R) + k_G(G)\right]\cdot C_B$$

Uptake from water

function of respiration (R) and of the sediment concentration (Cs)

Uptake from food

Function of food ingested (Q) and of the food concentration (CD)

Excretion of unassimilated

Function of unassimilated food (UN)

Metabolic detoxification

Function of metabolic activity (R) - Capability of species to metabolize specific contaminant

UNKNOWN

Dilution due to growth

Function of growth rate (G)

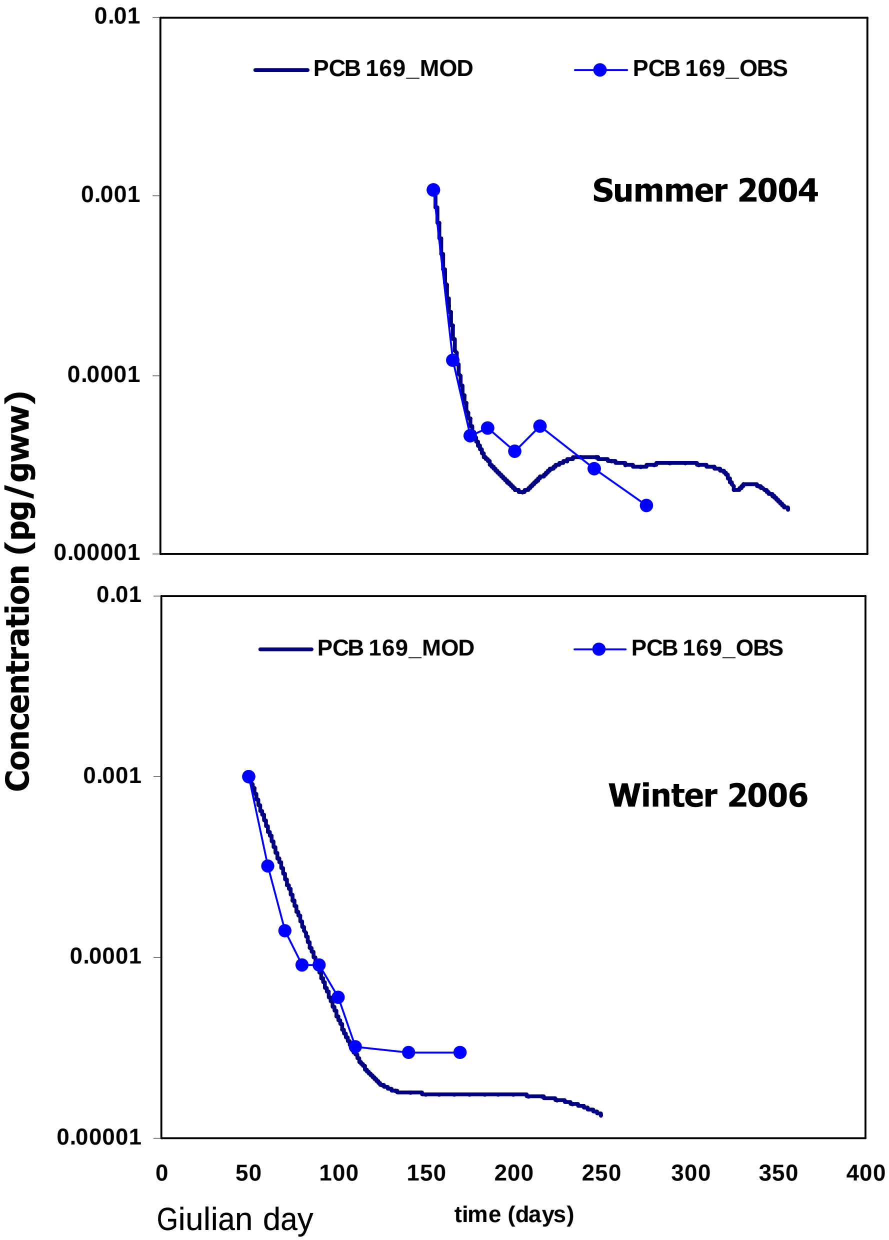
Estimation of dioxins half-lives

Specific half-life for each dioxin congener in clam flash

Congeners	K_M (days^{-1})	Half life (days)	Calibration R^2	Validation R^2
2,3,7,8-TCDD	0.0867	**7.99**	97.1%	97.9%
1,2,3,7,8-PCDD	0.0654	**10.59**	93.0%	91.9%
1,2,3,4,7,8-HCDD	0.0542	**12.80**	83.2%	82.1%
1,2,3,6,7,8-HCDD	0.0514	**13.48**	85.9%	83.2%
1,2,3,7,8,9-HCDD	0.0533	**13.00**	84.2%	83.8%
1,2,3,4,6,7,8-HpCDD	0.0385	**17.98**	69.6%	69.5%
1,2,3,4,6,7,8,9-OCDD	0.0339	**20.47**	63.3%	62.5%
2,3,7,8-TCDF	0.0250	**27.72**	78.9%	73.6%
1,2,3,7,8-PCDF	0.0471	**14.73**	83.9%	83.7%
2,3,4,7,8-PCDF	0.0381	**18.19**	71.2%	72.6%
1,2,3,4,7,8-HCDF	0.0626	**11.07**	84.5%	86.1%
1,2,3,6,7,8-HCDF	0.0534	**12.97**	82.3%	82.6%
2,3,4,6,7,8-HCDF	0.0454	**15.26**	80.0%	78.7%
1,2,3,7,8,9-HCDF	0.0946	**7.33**	95.2%	98.6%
1,2,3,4,6,7,8-HpCDF	0.0573	**12.09**	75.2%	79.6%
1,2,3,4,7,8,9-HpCDF	0.0832	**8.33**	86.2%	91.1%
1,2,3,4,6,7,8,9-OCDF	0.0578	**12.00**	70.7%	77.8%

Range from a minimum of 7 to a maximum of 28 days for 1,2,3,7,8,9 HCDF and 2,3,7,8 TCDF, respectively. These values, not surprisingly, are larger than those estimated from apparent detoxification rates

Calibration and validation (some examples)

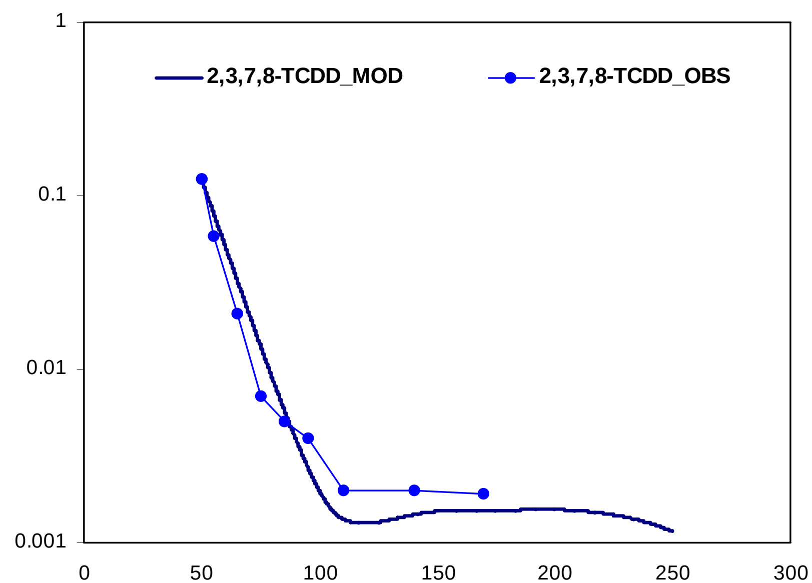


Calibration and validation for some PCB congeners and 17 PCDD/F congeners

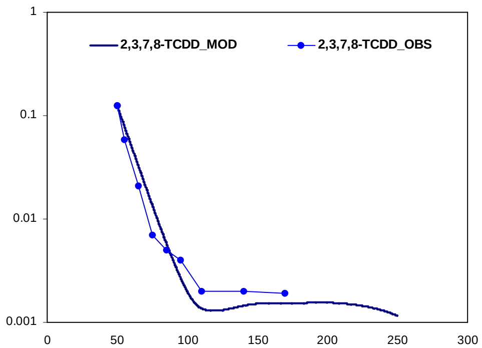
Using environmental conditions of two experiments (winter and summer)

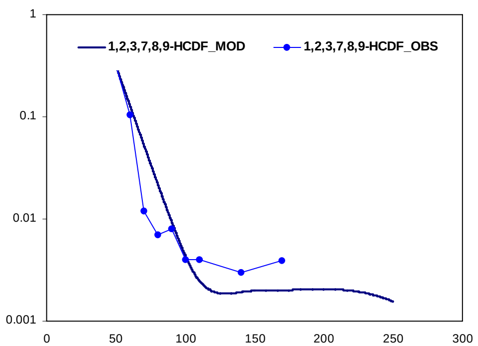
High level of agreement between model and data

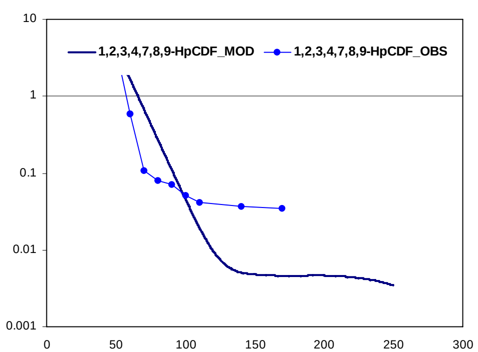
(note the log scale!)



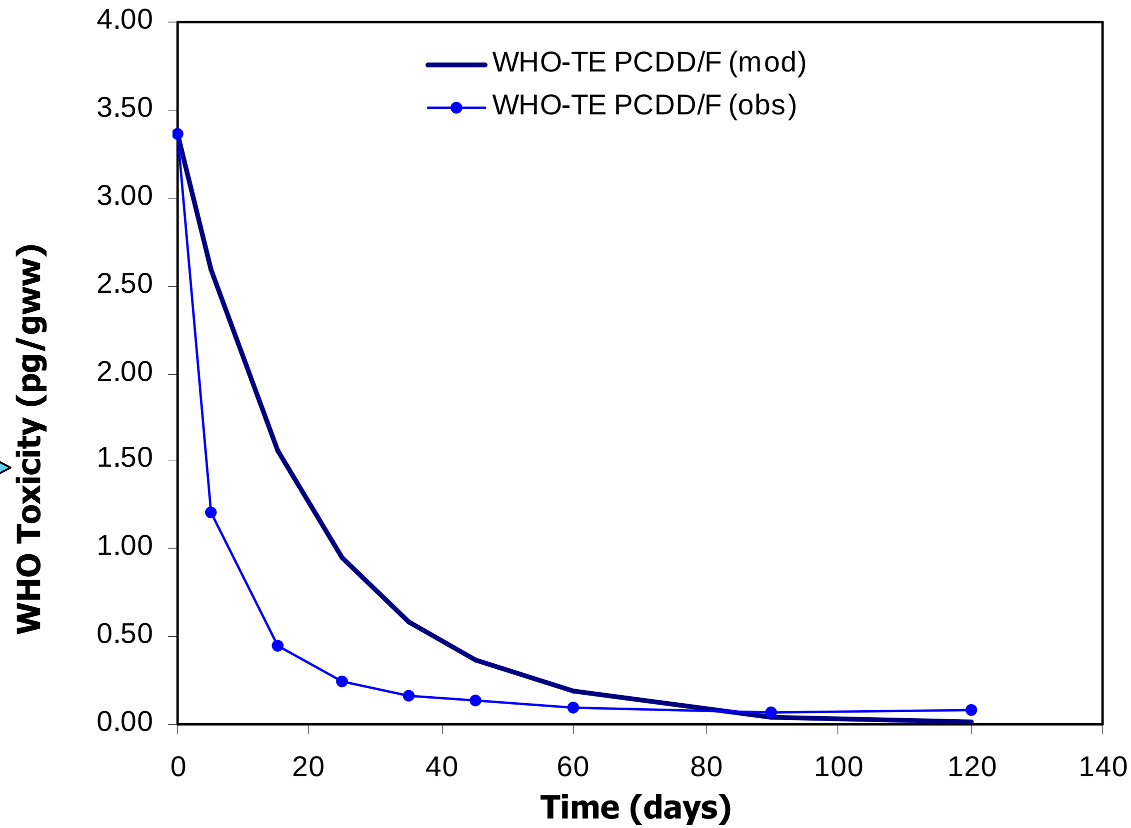
Estimation of dioxins half-lives







Dynamic simulation of all congeners for dioxins allows representing the dynamics of toxicity during time



represents quite well the final toxicity level due to dioxins observed in the field experiment

Represents roughly the first phase of sharp decreasing toxicity, evidencing the need for further analysis.

Conclusions and future directions

Sediments in areas surrounding the Industrial areas of the Venice Lagoon are still highly contaminated by POPs. Products/yields of illegal fishing for clams represent an important risk for human health both directly and indirecly.

The possibility to subtract clams from the industrial area and detoxify them naturally for consumption represent a valuable possibility for eliminating illegal fishing and preserve human health.

This work demonstrates the high potential of a coupled bioenergetic and biaccumulation model for describing the dynamics of POPs in clam flash.

This model can be applied to different areas of the lagoon (different sediment contamination) for estimating specific safe detoxification times, accounting for sediment, environmental conditions, food uptake and all detoxification processes

The model supports the possibility (proposed by local authority) for eliminating illegal fishing and reducing human heath risks.

For details and questions on the modelling approach, please write to:

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Istituto Nazionale di Oceangrafia e di Geofisica Sperimentale - OGS
Dept. Oceanography, Trieste, Italy

Thank you!


שלום
Paix
Hasîtî
Peace
평화
Barış
शांति
Friede
سلام
和平
Мир
Paz

“Uniformare raccolta dei dati e i metodi di trasmissione”

G. Migliorati 2009

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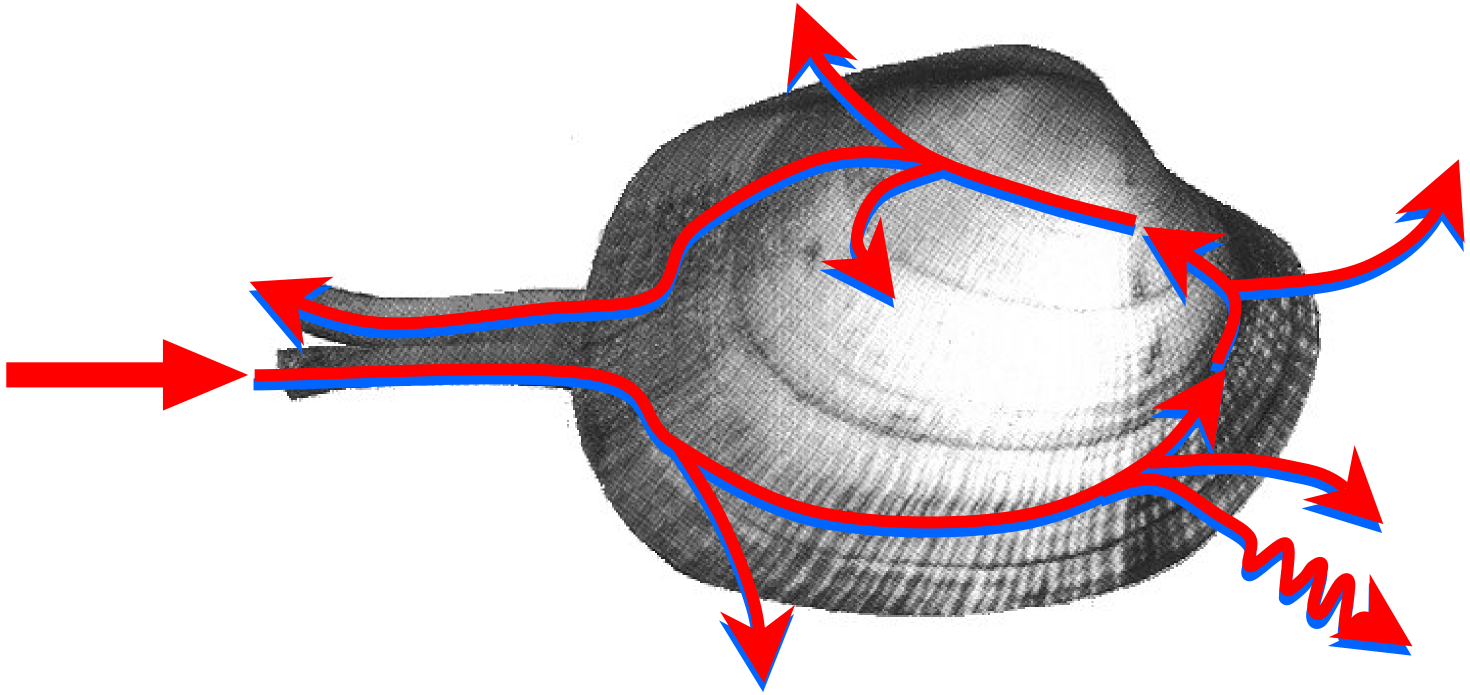
Da
Filosofia delle Nuvole, Luca Mercalli
e
NIMBUS, n° 5:11-20 1994

Ecotoxicological model

BIOLOGICAL PROCESSES: Flow of energy >> feeding, respiration, catabolism & growth

ECOTOX PROCESSES: bioaccumulation, bioconcentration & detoxification processes

ECOTOXICOLOGICAL MODEL FOR CLAM =



BIOENERGETIC GROWTH MODEL + BIOACCUMULATION/DETOXIFICATION MODEL

TEMPERATURE (°T), FOOD, SIZE

TEMPERATURE (°T), LIPIDIC AFFINITY (Kow, Koc)