

Polychlorinated Biphenyls in Fish from Black Sea

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Persistent organic pollutants

- Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world.
- In may 2001 was endorsed the Stockholm Convention on POPs to reduce or eliminate their production and use.
- POPs - organochlorine pesticides (like DDT), **polychlorinated biphenyls (PCBs)**, dioxins and furans can accumulate through the food chain.

- Fish are an excellent indicator for pollution in aquatic ecosystems, where trace contaminants are difficult to analyze directly.
- Fish consumption is one of the main source of human exposure to different organochlorine pesticides like **PCBs**.

The PCBs were determined in Black Sea fish in reference to their safety as food and the assessment of Black Sea contamination.

PCBs were determined in muscle tissue of ten most consumed marine fish species:



Goby
(*Neogobius cephalargoides*)



Sprat
(*Spratus spratus sulinus*)



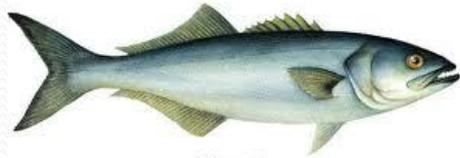
Horse mackerel
(*Trachurus Mediterraneus ponticus*)



Shad
(*Alosa pontica pontica*)



Grey mullet
(*Mugil cephalus*)



Bluefish
Pomatomus saltatrix

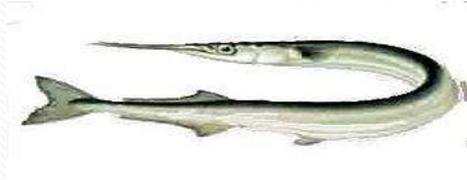
Bluefish

(Pomatomus saltatrix)



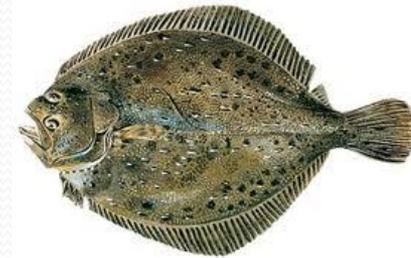
Bonito

(Sarda sarda)



Garfish

(Belone belone)



Turbot

(Psetta maxima)

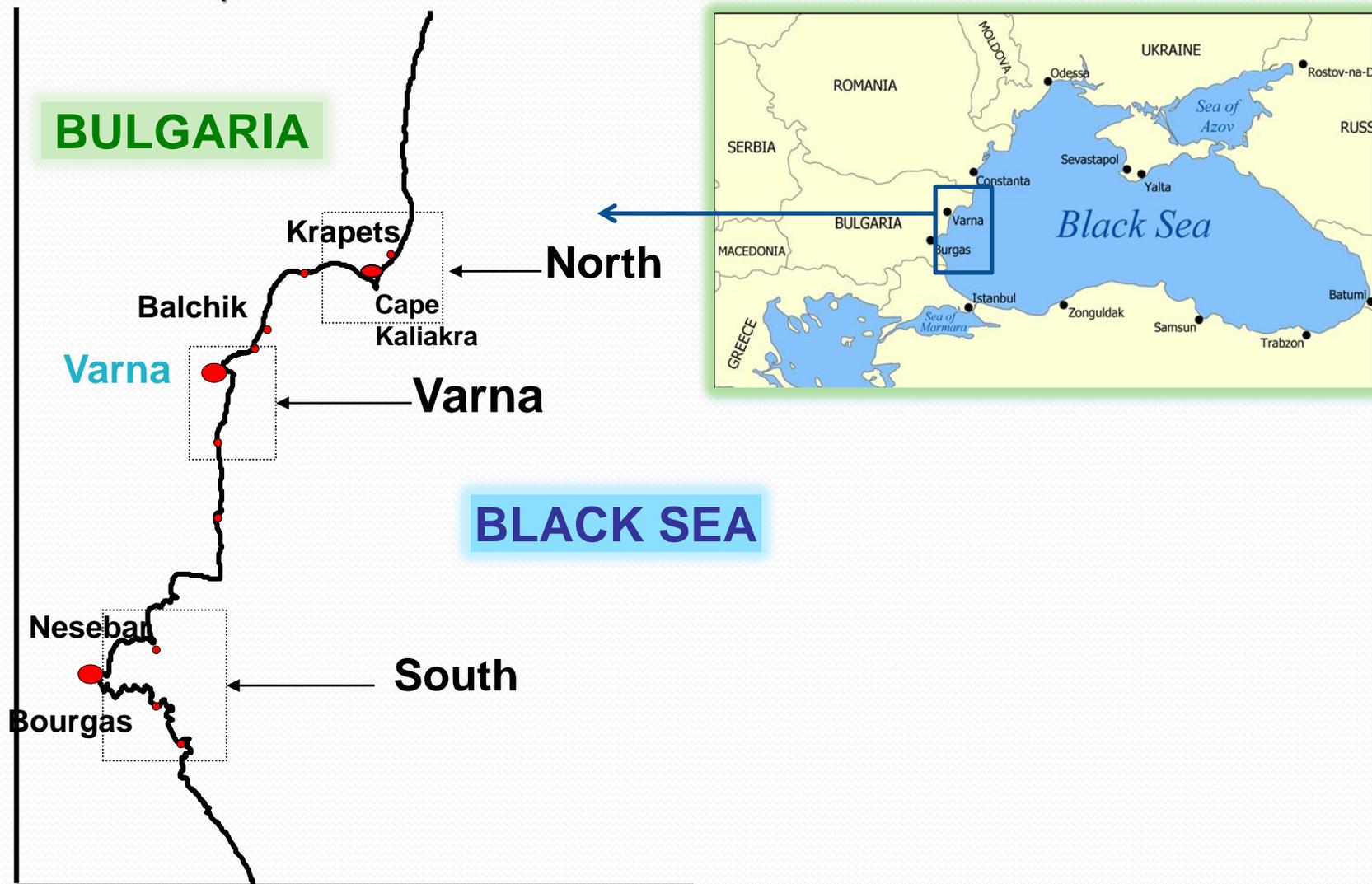


Red mullet

(Mullus barbatus)

SAMPLING AREA

Samples were collected from different parts of Bulgarian Black Sea coast in the period of 2007 – 2011.



Analytical method

Based on Method US EPA 1668a - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS*

1. Sample preparation

- **Homogenisation** of edible fish tissue - 20 g were taken for extraction
- **Soxhlet extraction** - hexane/dichloromethane (3/1; v/v)
- **Lipid determination**, gravimetrically
- **Extract clean up** - glass column packed with neutral and acid silica - eluent 80 ml n-hexane, 50 ml n-hexan/dichloromethane (80:20)

Analytical method

2. GC-MS determination:

- Gas chromatography system FOCUS (Thermo Electron Corporation, USA) using POLARIS Q Ion Trap mass spectrometer
- Capillary column TR-5ms - length 30 m, 0.25 mm ID and a film thickness of 0.25 μm .
- Pure reference standard solutions (PCB Mix 20 - Dr. Ehrenstorfer Laboratory and EPA 625/CLP Pesticides Mix 2000 $\mu\text{g}/\text{ml}$ – Supelco)
- Analytical parameters: LOQ – from 0,1 to 0,6 ng/g ww, Recovery – 85 - 108%

Analytical method

3. The quality control was performed by:

- Internal standards PCB 30 and PCB 204
- Certified reference material (CRM):
 - BB 350 (PCBs in Fish oil)

4. **Statistical analysis** were performed using SPSS 16 software.

PCBs

15 PCB congeners

IUPAC № 28, 31, 52, 77, 101, 105,
118, 126, 128, 138, 153, 156, 169,
170, 180

Indicator PCB

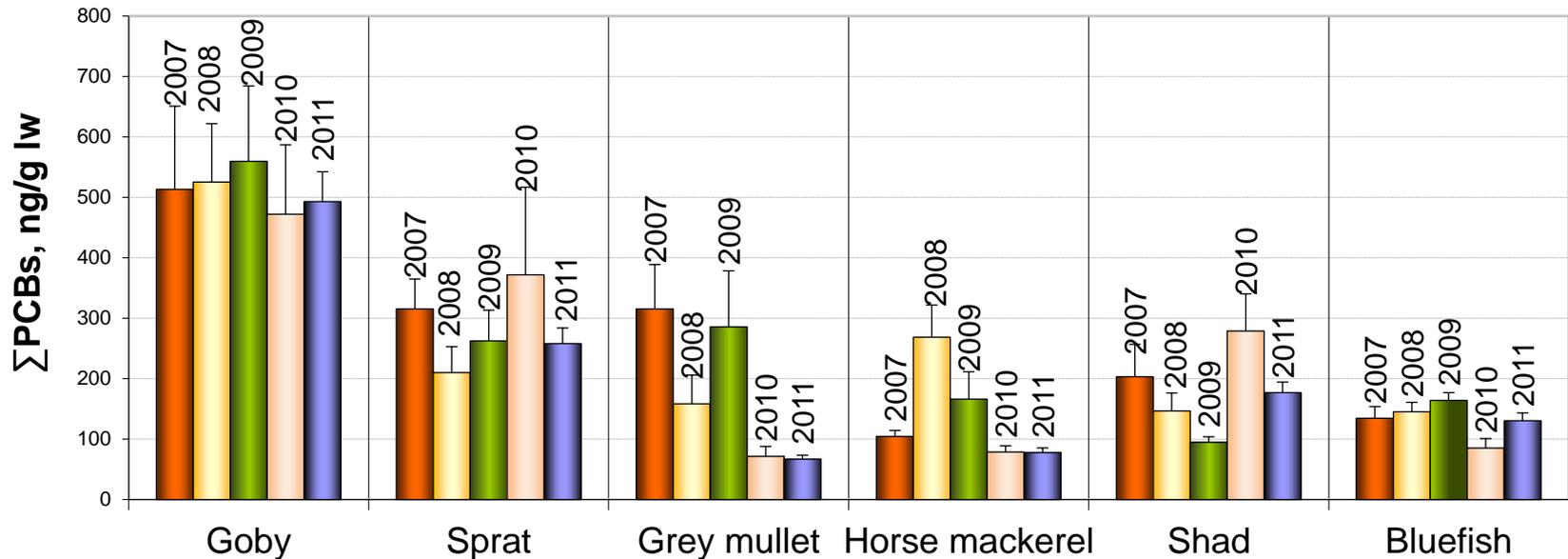
28, 52, 101, 138, 153, 180

Dioxin – like PCB

77, 105, 118, 126, 156, 169

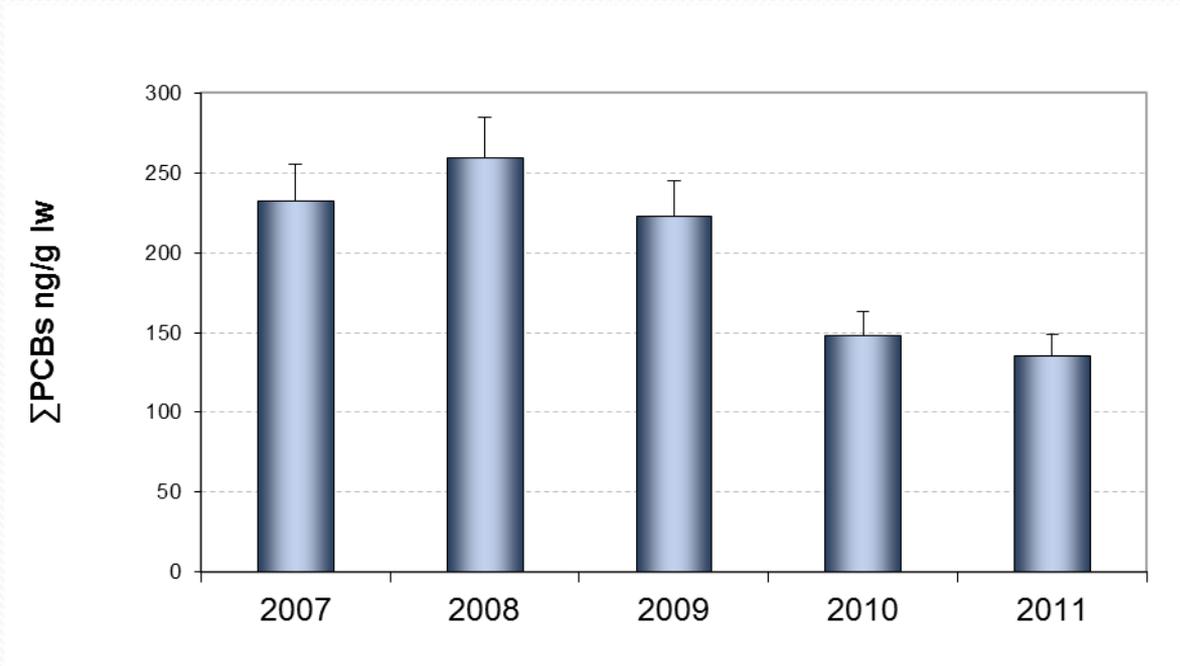
RESULTS

Σ PCBs, ng/g lipid weight, 2007-2011



- Concentrations of Σ PCBs in grey mullet and horse mackerel decrease in 2010 – 2011.
- The highest concentration of Σ PCBs were found in goby.

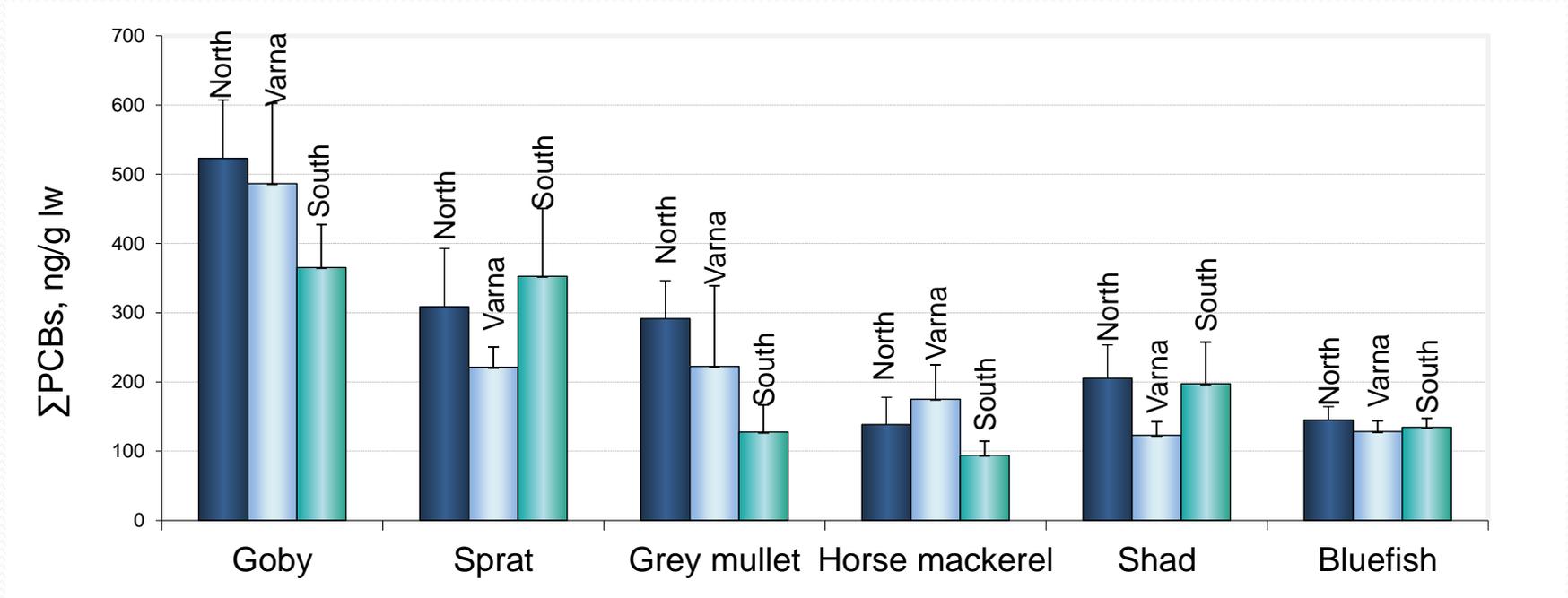
Σ PCBs, ng/g lw, 2007 - 2011



- The differences among mean annual concentrations of Σ PCBs were not statistically significant ($p > 0.05$).
- A relative decrease is observed in 2010 and 2011.

Σ PCB, ng/g lw

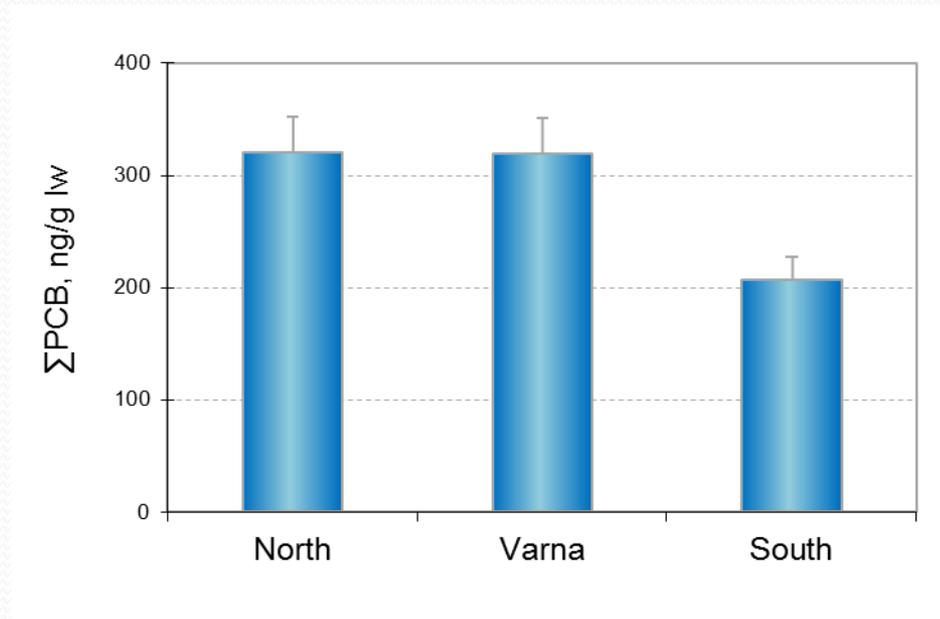
Sampling area



- The highest concentrations of Σ PCBs were found in goby from North sampling area.

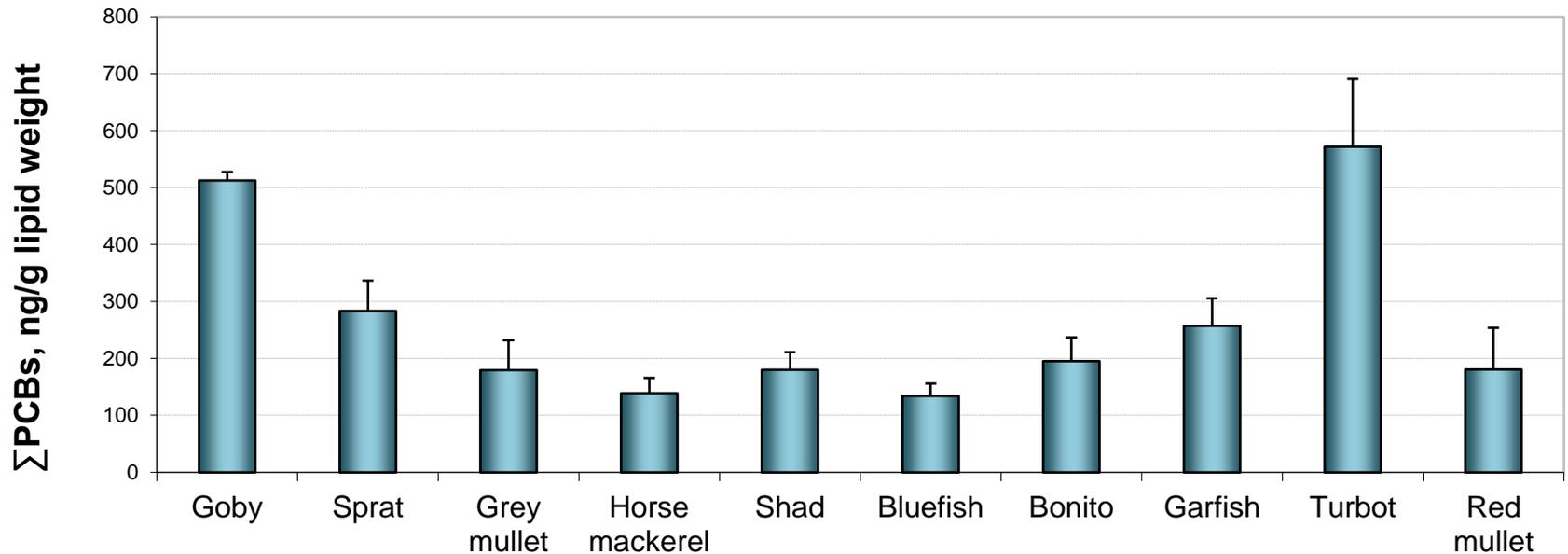
Σ PCB, ng/g lw

Sampling area



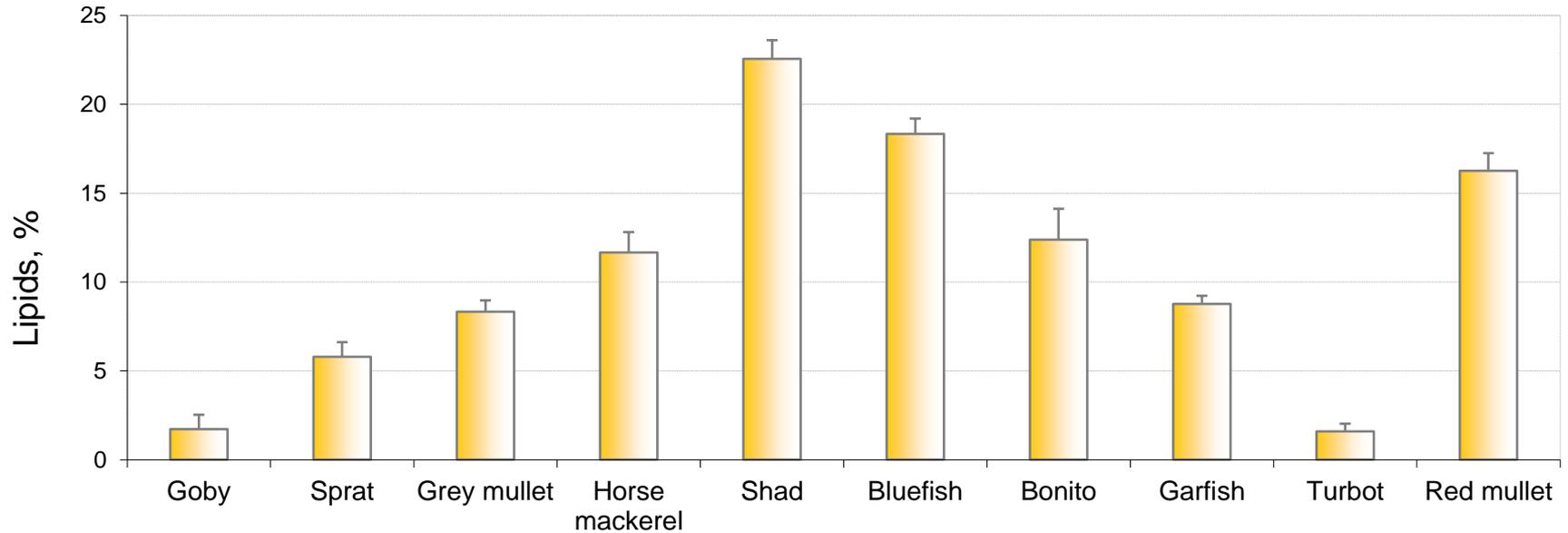
- The experimental results for Σ PCBs in fish species from different sampling sites showed no significant differences between the Northern, Varna and Southern coast sampling area.

Σ PCBs, ng/g lw



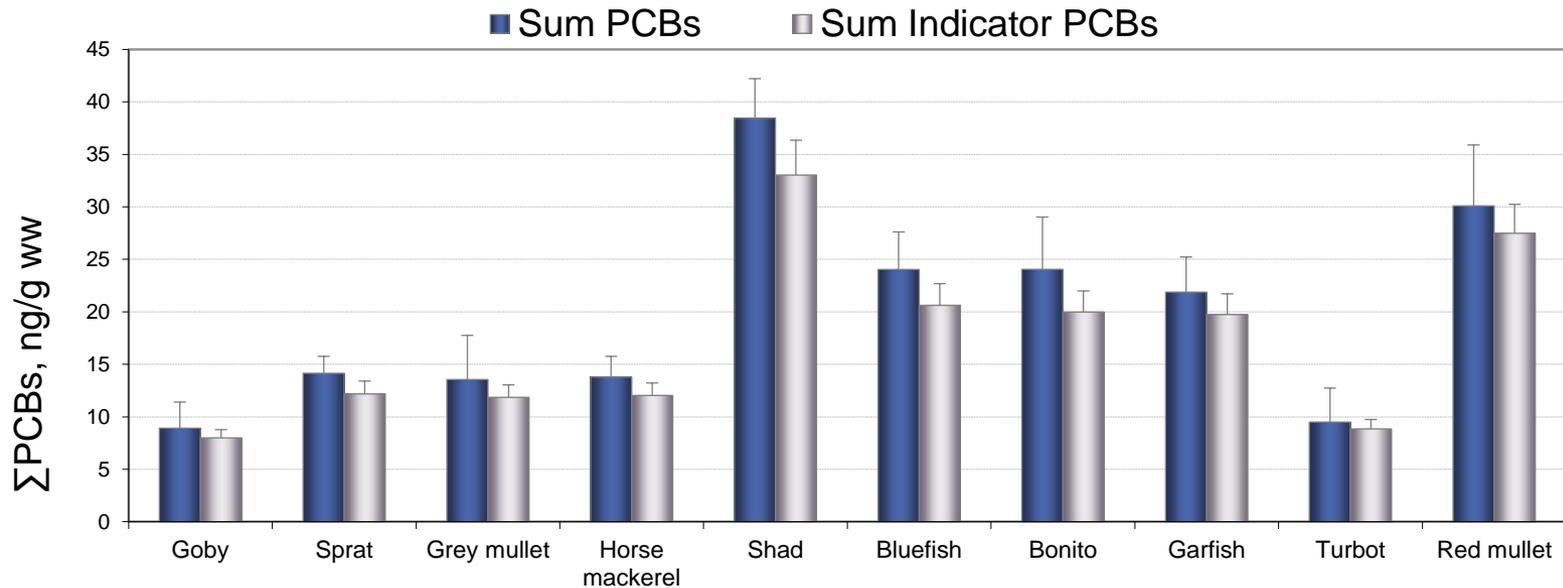
- Statistical data analysis indicates the presence of statistically significant difference in the results about total PCB provided by fish species ($p < 0,01$).
- The PCB content in goby and turbot is relatively high than other fish species.

Lipid content, %



- The lipid percentage ranged from 1.6% in turbot to 22.5% in shad.
- Fish with lower lipid content: goby, sprat, grey mullet and turbot.
- The lipid content in shad, bluefish and red mullet is relatively high.

Σ PCBs and Indicator PCBs, ng/g wet weight



- The sum of the indicator PCBs constituted from 81% to 95% of the total PCBs.
- The European Union has recommended a Maximum level of **75 ng/g wet weight** as sum of Indicator PCBs in fish (COMMISSION REGULATION (EU) No 1259/2011).
- Our results in all fish species did not exceed this limit.

CONCLUSIONS

- The systematic study of 10 fish species was made for five years - from 2007 to 2011.
- The concentrations of 15 PCB congeners, among them important indicator and dioxin-like PCBs were determined.

The results are summarized:

- **by areas of the catch** - no significant difference between the values of Σ PCBs in fish samples from three regions of sampling.
- **in years of sampling** - there was observed a slight decrease in the concentrations of PCBs in 2010 and 2011.
- **by fish species** - there is a significant difference between the different fish species such as average concentrations Σ PCBs for the entire period ranged from **20.8 ng / g ww to 208.5 ng / g WW**.

CONCLUSIONS

- The sum of the indicator PCBs constituted 81% to 95% of the total PCBs.
- The results for Indicator PCBs in all fish species did not exceed the EU limit of 75 ng/g ww.
- The experimental results showed that the concentrations of PCBs are lower or comparable with levels in fish from other investigation about fish species from other marine ecosystems.



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THANK YOU FOR YOUR ATTENTION!