

SEASONAL VARIATIONS IN THE CONGENER COMPOSITION AND PHASE DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN SURFACE WATERS OF UKRAINE

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BACKGROUND:

Total PCB concentrations alone do not fully describe their transport and accumulation in aquatic systems. Seasonal changes in congener composition and partitioning between water and suspended particles must also be considered. Congeners with the same degree of chlorination may exhibit different phase distributions.

Aim: To analyse an existing dataset on PCBs in Ukrainian surface waters to identify seasonal differences in congener composition and phase distribution, with particular attention to the behaviour of individual congeners.

SEASONAL CHANGES IN CONGENER COMPOSITION

The dominant congener shifted from PCB-153 in autumn ($45.2 \pm 6.6\%$) to PCB-49 in spring ($33.6 \pm 7.5\%$). The contribution of PCB-153 decreased to $4.3 \pm 3.7\%$ in spring. The ratio of lower-chlorinated (2–4 Cl) to higher-chlorinated (5–7 Cl) PCBs increased 2.0–4.4-fold across water bodies with data available for both seasons.

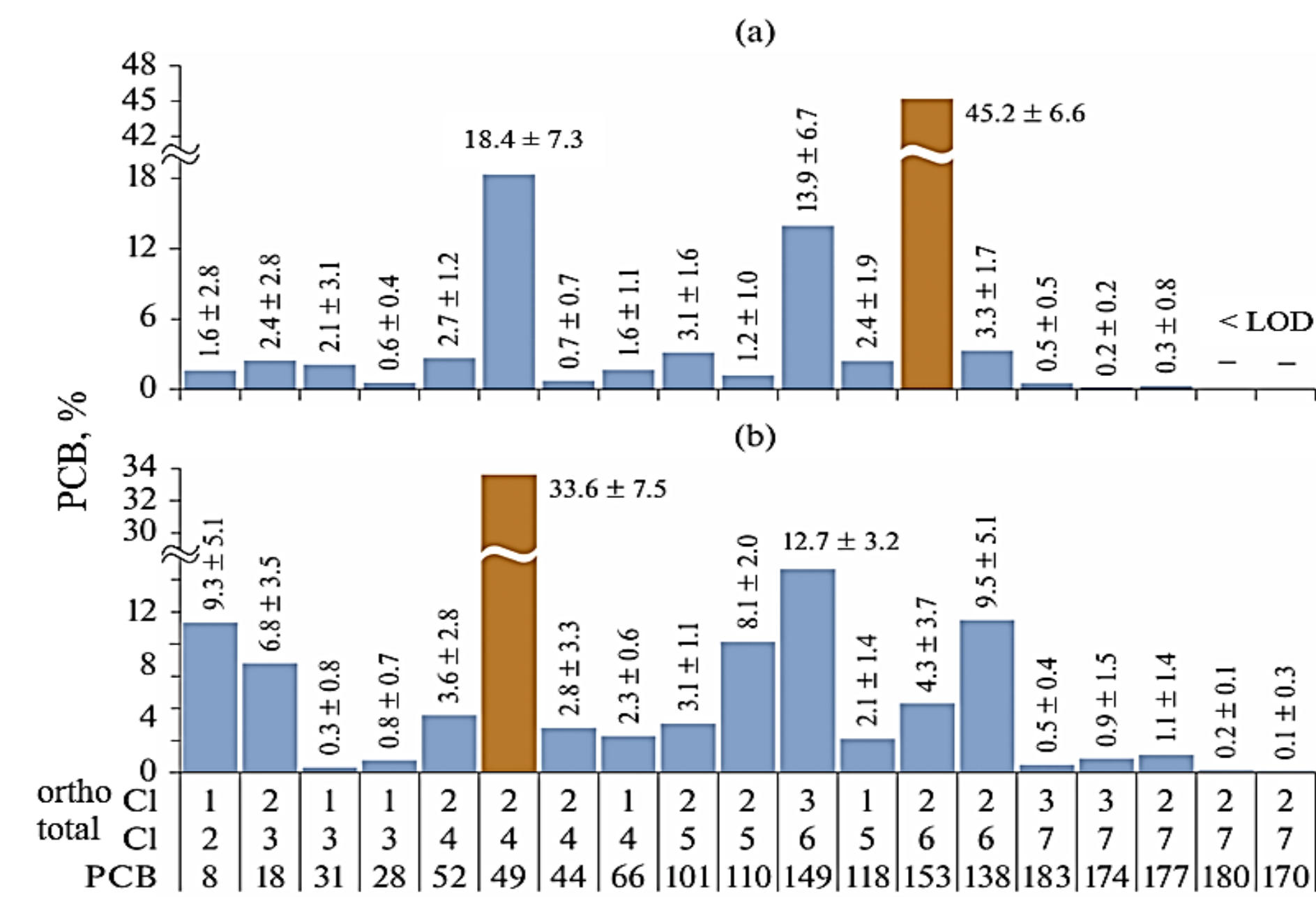


Fig. 1. Mean PCB congener profiles in surface waters of Ukraine: (a) autumn 2012; (b) spring 2013. Values are mean $\pm$ SD across sampling stations ($n = 9$ and 7 , respectively). Highlighted bars indicate the dominant congeners. Ortho Cl and total Cl denote the numbers of ortho-positioned and total chlorine atoms, respectively. <LOD — below the limit of detection.

HYDROPHOBICITY AND CONGENER-SPECIFIC PARTITIONING

In spring, the mean dissolved fraction decreased with increasing $\log K_{ow}$ ($r = -0.790$; $p = 0.001$; Fig. 3). A stronger correlation was observed for congeners with two ortho-chlorine substituents ($r = -0.866$; $p = 0.005$), although individual deviations persisted. Hydrophobicity alone therefore did not fully describe congener-specific phase distribution.

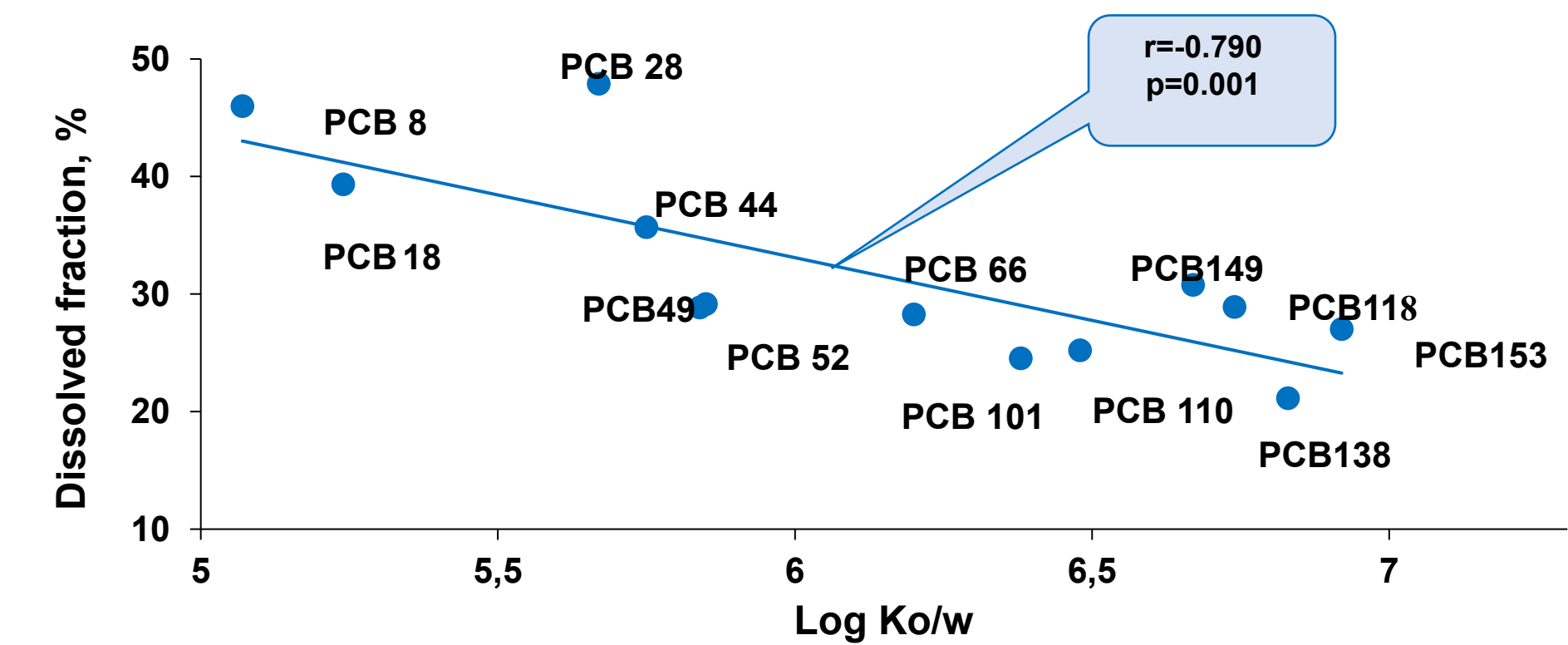


Fig. 3. Relationship between the mean dissolved fraction of individual PCB congeners and $\log K_{ow}$ in spring. The straight line represents the linear regression.

CONCLUSIONS

- The dominant congener shifted from PCB-153 in autumn to PCB-49 in spring, accompanied by an increased contribution of less chlorinated PCBs.
- PCBs remained predominantly particle-bound, while the mean dissolved fraction was higher in spring (28.6%) than in autumn (22.2%).
- Hydrophobicity explained the overall spring trend, but congener-specific deviations, particularly the autumn behaviour of PCB-149, show the need to consider individual congeners and seasonal conditions when assessing PCB phase distribution.

DATA AND ANALYTICAL APPROACH

Data source: Previously obtained results for 19 PCB congeners in Ukrainian riverine and estuarine waters, sampled in autumn 2012 and spring 2013. The original sampling and chemical analyses were performed by the late M.V. Milyukin.

The present study focused on:

- Comparing seasonal PCB concentrations and congener profiles.
- Assessing PCB distribution between dissolved and particle-bound fractions.
- Examining relationships with hydrophobicity and molecular structural characteristics.
- Identifying distinctive patterns in the behaviour of individual congeners.

The dissolved fraction refers to PCBs measured in the filtrate after $0.45 \mu\text{m}$ filtration.

SEASONAL CHANGES IN PHASE DISTRIBUTION

PCBs were predominantly associated with suspended particles in both seasons. The mean dissolved fraction increased from 22.2% in autumn to 28.6% in spring, while the contribution of the coarse particle fraction decreased from 63.8% to 56.7%. The fine particle fraction accounted for similar proportions in both seasons (13.9% and 14.7%, respectively).

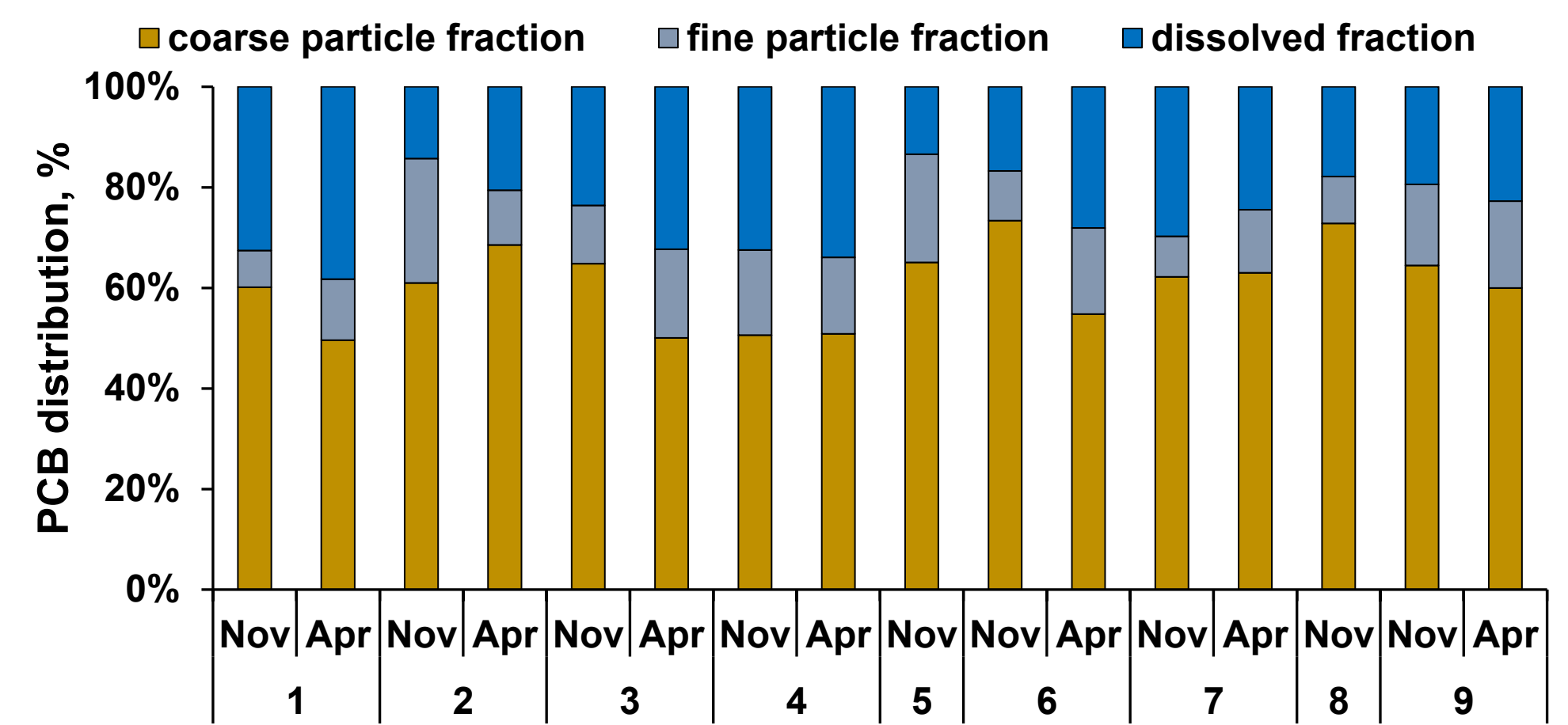


Fig. 2. Distribution of total PCBs among dissolved, fine and coarse particle fractions in November 2012 (Nov) and April 2013 (Apr). Sampling sites: 1 — Danube Estuary; 2 — Dniester Estuary; 3 — Dniester River; 4 — Muksha River; 5 — Poltava River; 6 — Bug Estuary; 7 —Southern Bug River; 8 — Viriovchyna River; 9 — Dniro River. Spring data were unavailable for sites 5 and 8.

CONGENER-SPECIFIC BEHAVIOUR: PCB-149

Despite having the same degree of chlorination, PCB-138, PCB-149 and PCB-153 exhibited different phase distributions in autumn. PCB-149 showed a higher dissolved fraction than the other two hexachlorinated congeners.

These differences indicate that the degree of chlorination alone is insufficient to describe PCB partitioning. Molecular structure, including ortho substitution, may contribute to the observed behaviour.

Table 1. Autumn $\log K_d$ values for three hexachlorinated PCB congeners.

Congener	Total Cl	Ortho Cl	Autumn $\log K_d$, mean $\pm$ SD
PCB-138	6	2	1.192 ± 0.469
PCB-149	6	3	-0.416 ± 0.327
PCB-153	6	2	2.037 ± 0.236