PCB LEVEL IN FISH OF ZADAR AREA, CROATIA AND ESTIMATION ITS INTAKE BY CRITICAL POPULATION

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Introduction

Even though there are no large urban centers in the Croatian karst area, it deserves special attention because of its high ecological sensitivity and unfortunately unscrupulous destruction of natural resources, infrastructure, homes, and enterprises during 1991-1995 warfare. There are great fears and concrete evidence these significant quantities of polychlorinated biphenyls (PCB); various flame-retardants, explosives, and their by-products were released in the environment during warfare. During uncontrolled combustion of PCB and other organohalogens, even more dangerous polyhalogenated dibenzofurans and dibenzodioxins are formed, so the area under warfare operations was under even greater jeopardy[1]. In Croatian karst area encompassed by warfare, several cases show reasonable doubt resulting with underground water contamination. Beside roads, airports, waste landfills or large industrial plant which are typical possible contamination sources for underground waters in karst, whose damage or destruction during warfare increases contamination hazard, it is necessary to exclude damaged transformer stations, and the use of non-sanitary waste landfills. Furthermore it is necessary to give notice that inappropriate waste or contaminated soil disposal, for example in karst valley (which happens occasionally in contamination remediation purposes), may multiply underground water contamination hazard in karst terrain. Taking into account location of destroyed Zadar Electrical Transformer Stations, there is some speculation regarding the potential hazard from organohalogenated toxicants to the coastal sea around the Zadar. DDT levels in coastal sediment of the investigated area during 1997 are mostly lower, compared with results obtained in Mediterranean, the Adriatic, and Rijeka bay[2]. However, PCB levels are significantly higher compared to DDT, and it could be said they are comparable with more contaminated areas of the Mediterranean, such as coast of Spain and France, Italy and Greece[3]. Epibenthic fish, and even more benthic fish, do not move through wide areas, so their contamination can better indicate the level of contaminants in some narrow area. On the other hand, contaminants in those fish do not depend much on relatively small distances from a dotted source of contamination (as is the case with mussels and sediment), thus better "integrating" contamination status of a site. This paper shows data on PCBs detected in fish of the territorial sea ecosystem in the area of Zadar, Croatia.

Area of investigation and methodology

Characteristics of the coastal area of Zadar are a relatively low shore with lots of bays, coves and small coves, islands and small islands and creeks and small creeks instilling superficially or underground into the sea. A portion of municipal wastewater is collected by drainage system and drained into the sea in Kolovare area by an underground pipe 1.5 km long. There are a number of smaller urban and industrial water inputs that are deposited on a relatively small distance from the coastline. Figure 1 shows position of the transformer station TS 110/35 kV, Zadar, and locations of stations where fish samples were collected by local sports fishermen and analysed in 1997.

Fish fillets were extracted by using high revolution blender with n-hexane. The analytical method used for the analysis of extracts included filtration through a column of Na_2SO_4 anh. cleaning on an alumina column and the separation of the PCB's from organochlorine insecticides on a miniature silica gel column. After concentration down to 1 cm^{-3}, elutes were analyzed by EC gas chromatography. During all the analytical procedures, the Mirex standard was used as the internal standard. More circumstantially details of used methods were described in numerous published papers[2,4,5].

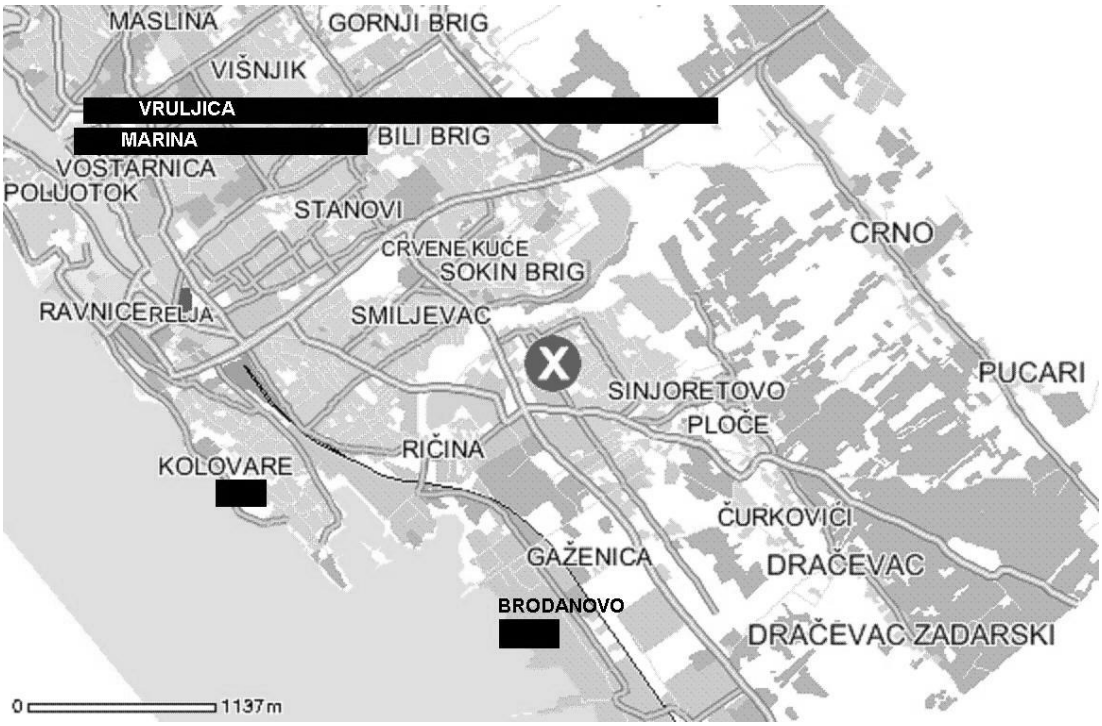

Figure 1 Level of PCBs (ng/g f.w.) in fish collected 1997 from Zadar area

Results and discussion

Fish collected for PCBs analysis during 1997 and 1999 from Zadar area are present on Table 1. There are benthic and epibenthic fishes which do not move through wide areas, so their contamination can better indicate the level of contaminants in some narrow area. Levels of PCBs (as equivalents of Aroclor 1254) in fish sampled during spring and autumn 1997 are presented as histograms on Figure 1. It has to be stressed that fish were collected very close to shore line. Cross on the Figure 1 show position of the destroyed Electro Transformer Station during the war. During February 1999 fish samples were collected at least more than 100 meters from the shore line and results are present on Figure 2.

Table 1 Fish collected for PCBs analysis during 1997 and 1999 from Zadar area

Year of collection	Fish species (Croatian name)	Fish species (English name)	Fish specie (Latin name)
1997	Špar	Annular sea bream	Diplodus annularis
	Lumbrak	Peacock wrasse	Crenilabrus tinca
	Vučić	Brown comber	Serranus hepatus
	Glavoč pločar	Giant goby	Gobius cobitis
	Babica balavica	Red-speckled blenny	Parablennius sanguinolentus
	Cipal zlatac, skočac	Golden grey mullet	Liza aurata
1999	Knez, cincela, libo	Rainbow wrasse	Coris julis
	Gira oštrulja, lužina	Picarel	Maena chryselis
	Gira menula	Picarel	Maena smaris
	Glavoč pločar	Giant goby	Gobius cobitis
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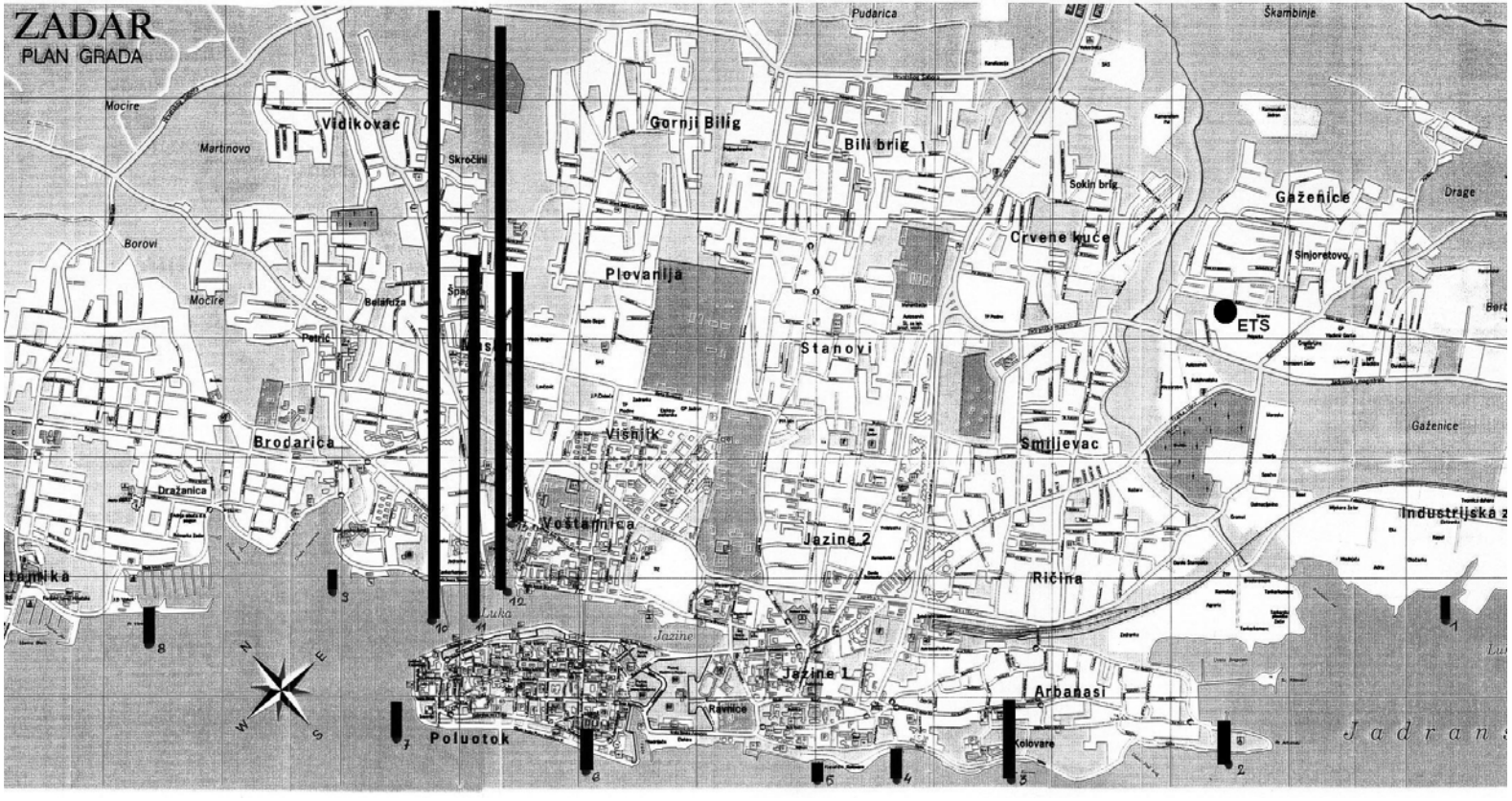


Figure 2 Level of PCBs (ng/g f.w.) in fish collected 1999 from Zadar area

On Figure 3 are present average and median of PCBs levels in fish sampled 1997 and 1999. The levels of PCBs in fish from local market collected in autumn 2003 are also present. Fish samples collected 1999 from station 1 are presented as Brodanovo station; from stations 2, 3, 4 and 5 are present as Kolovare station; from stations 6 and 7 as Centre station; from 8, 9, 10, 11 and 12 as Marina station and from station 13 as Vruljica station. As is seen levels of PCBs in fish samples collected 1999 are lower in comparison with samples collected 1997. Certainly levels of PCBs in fish from market are significantly lower in comparison with levels of PCBs in fish sampled from sea close to shore line of town Zadar.

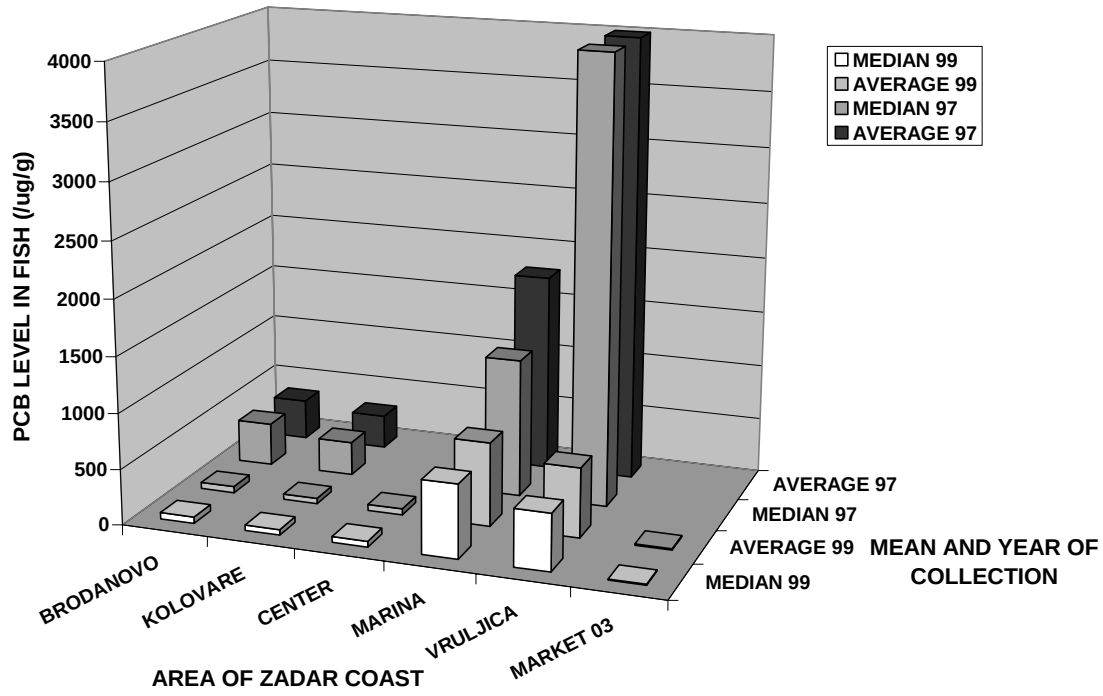
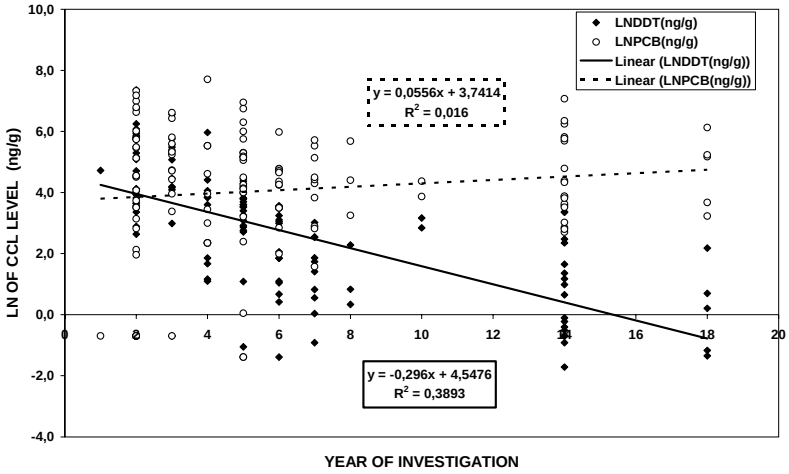


Figure 3 Average and median levels of PCBs (ng/g f.w.) in fish collected 1997 and 1999 from sea around Zadar and from market 2003.

Monitoring of DDTs and PCBs in fish samples from eastern coast of the Adriatic Sea have been performed since 1973[2] and trend lines of DDTs and PCBs levels present as natural logarithmic values are present on Figure 4a for period until 1991. As is seen levels of DDTs significantly diminished but levels of PCBs do not followed any significant trend. When the results of investigation DDTs and PCBs levels in fish samples collected 1997 from Zadar, Šibenik and Dubrovnik area are included (Figure 4b) the trend of PCBs levels are increasing. For only Zadar area, trend of PCBs and DDTs levels are present on Figure 4c. As is seen fish samples were

collected and analysed for chlorinated only sporadically in earlier years, but even that, the levels of PCBs increased significantly though levels of DDTs diminished.

The migration of PCBs from a waste dump into the karstic ground water and source water of the Kupa River in Slovenia has been established. An investigation of the levels of chlorinated hydrocarbons in tap water and water and fish samples collected from 1985 to 1988 from the Kupa River in the region of Petrinja and Sisak (about 200 km downstream from the primary contaminated area) was performed. Daily PCB and DDT intake was studied among sports fishermen and their families who consume fish from the Kupa River in significant quantities [2] .



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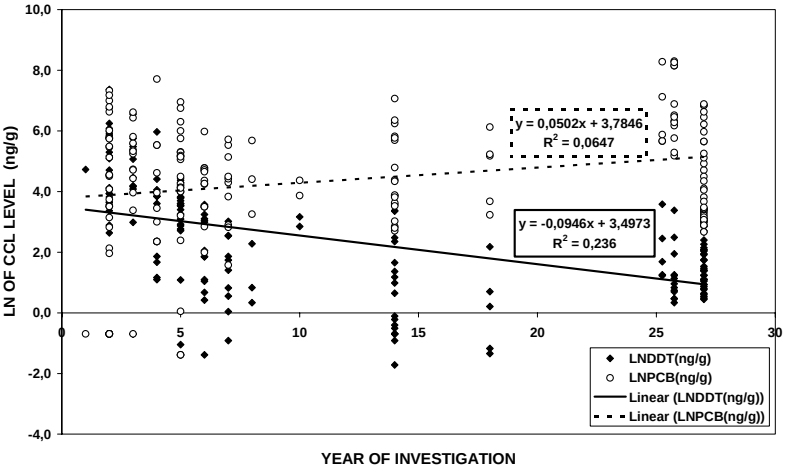

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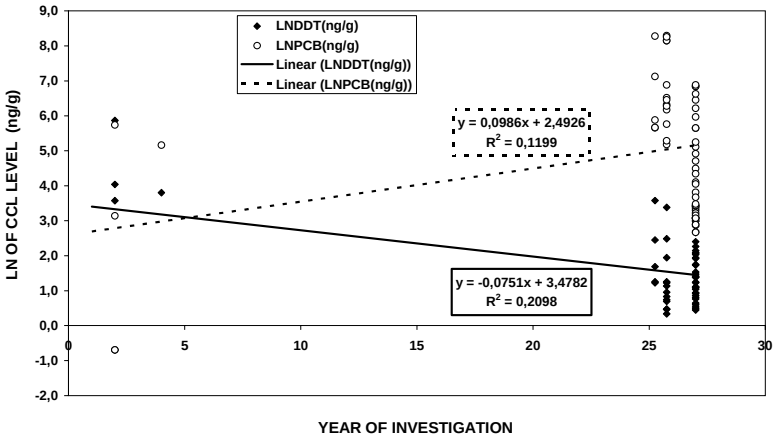

Figure 4 a) Yearly trend of CCl level in fish of Croatian eastern Adriatic coast until 1991; b) Yearly trend of CCl level in fish of Croatian eastern Adriatic coast until 1999; c) Yearly trend of CCl level in fish of Zadar area until 1999

The same calculations of PCBs intake were performed for sports fishermen and their families in the Zadar area. In Figure 5 daily intake of PCBs by sports fishermen and their family members in the Zadar area according to age is presented. There are four intake lines. RCM. M. D. INT. (recommended mean of daily intake); estimated daily intake in case of consuming fish which have mean level of PCBs collected 1997 and 1999 (INT. ZAD. 97/99). As is seen only in one case intake of PCBs will be just in range of acceptable level. The intake line where levels of PCBs in fish is present as average of level in fish from market, intake line is very low and the maximum intake is 0.045 μg/kg per day – it is more than twenty times less than recommended intake value. In case when this "critical" group of people from Zadar will consume fish with levels of PCBs as was found in the fish from harbour and marine samples, in several cases they will consume more PCBs in comparison with recommended value. In one case (for child in the group of 0-10 years range) even 5.9 times will be higher intake of PCBs than recommended.

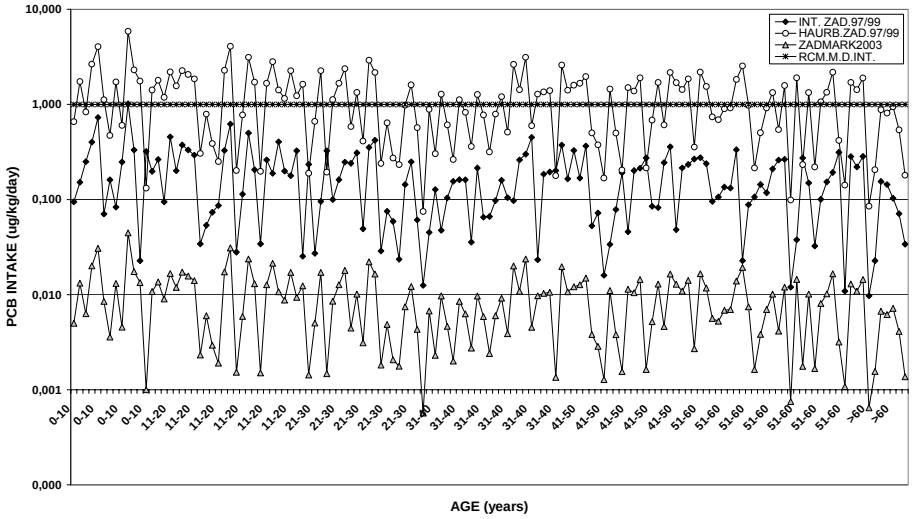

Figure 5 Estimated distribution of the daily input of PCB into critical population of Zadar from fish catched from total coastal area and only from harbour area (1997 and 1999) and fish from local market.

Conclusion

Levels of PCBs in fish samples collected 1999 are lower in comparison with samples collected 1997. Certainly levels of PCBs in fish from market are significantly lower in comparison with levels of PCBs in fish sampled from sea close to shore line of town Zadar. DDTs and PCBs in fish samples from eastern coast of the Adriatic Sea have been monitored since 1973 and for period until 1991 levels of DDTs significantly diminished but levels of PCBs do not followed any significant trend. When the results of investigation DDTs and PCBs levels in fish samples collected 1997 from Zadar, Šibenik and Dubrovnik area are included, the trend of PCBs levels are increasing. In case when "critical" group of people from Zadar will consume fish with levels of PCBs as was found in the fish from harbour and marine samples of Zadar, in several cases they will consume more PCBs in comparison with recommended value.

Acknowledgements

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