PCB CONTAMINATION OF MARINE SEDIMENT SAMPLES IN COASTAL WATERS OF ZADAR TOWN, CROATIA

Hodak Kobasić V[1] , Picer M. [1], Picer N.[1], Haslinger E.[4] Kralik M. [2] Kodba-Cenčič Z[3] , Čalić V [1]

Institute " Ruđer Bošković", Bijenička cesta 54, 10000 Zagreb, Croatia[1]
Federal Environment Agency and University of Vienna, Spittelauer Laende 5, Vienna, Austria[2]
Environmental Protection Institute, Prvomajska 1, 2000, Maribor, Slovenia[3]
Geological Survey of Austria, Neulingg. 38, 1030 Vienna, Austria [4]

Introduction

In the last twenty years in the karst area of Slovenia and Croatia there were two serious incidents where significant amounts of PCB inflow into the bioecological cycles of the karst environment[1]. Some natural resources, infrastructure, homes, and enterprises during 1991-1995. warfare in the Croatian karst area has been unscrupulously destroyed. During 1996, waste oil and soil samples near damaged transformer stations were collected in Delnice, Zadar, Šibenik, Split, and Dubrovnik areas and analyzed on PCBs. Significant levels of PCBs (the highest at the "Bilice" E.T.S. over 2000 mg/kg PCBs in dry soil samples) were found in Šibenik, Zadar and Dubrovnik areas [2]. In the period from 1997 to 2007 numerous soil, marine biota and sediment samples were collected from various places in Croatia and Bosnia and analysed for PCBs and DDTs in areas close to the military conflict [3-9]. Beside this, various characteristics of sediment samples collected from the Zadar area were also determined[10]. The aim of this work is to investigate the influence of various soil and sediment characteristics on the level of chlorinated hydrocarbons present in samples.

Materials and methods

Characterisation of sediments

The content of total carbon was determined using a Coulomat (Stroehlein 702; EN 13137). The inorganic carbon was determined gas volumetrically using the Scheibler-apparatus (DIN 18129). The organic carbon content (TOC) was calculated by subtraction of inorganic carbon (TIC) from total carbon (TC). The size fractions were gained by wet sieving and subsequent drying at 40° C.

PCBs and DDTs analysis

The air dried sediment samples were sieved to 0.063 mm and extracted 24 hours with n-hexane by Soxhlet extraction. The method used for the analysis of extracts included filtration through a column of anhydrous Na_2SO_4 cleaning on an alumina column and the separation of the PCBs from organochlorine insecticides on a miniature silica gel column. Elutes were analyzed by gas chromatography. During all the analytical procedures, the Mirex standard was used as the internal standard. Details of used methods were described in numerous published papers[11,12,13] .

Results and disucssion

So far no linear relation between organic carbon in the analyzed sediments have been found (Fig 1). Sediment samples marked with Marina 03 were collected inside the local marina in 2003. All other sediments samples marked as sediments 04 were collected around Zadar town coastal waters and many of them inside the local harbor are heavily polluted with various organic and inorganic wastes. This supports the evidence that the source of PCB is or was in or around the Zadar harbor basin. However, the nearly exponential increase of PCB in the harbor basin sediments indicates that the character of these organic rich sediments are more prone to sequester higher quantities of PCBs than other marine sediments around Zadar. The PCB analyses of the sediment-fractions will help to identify sediment qualities, which are prone to PCBs sorption.

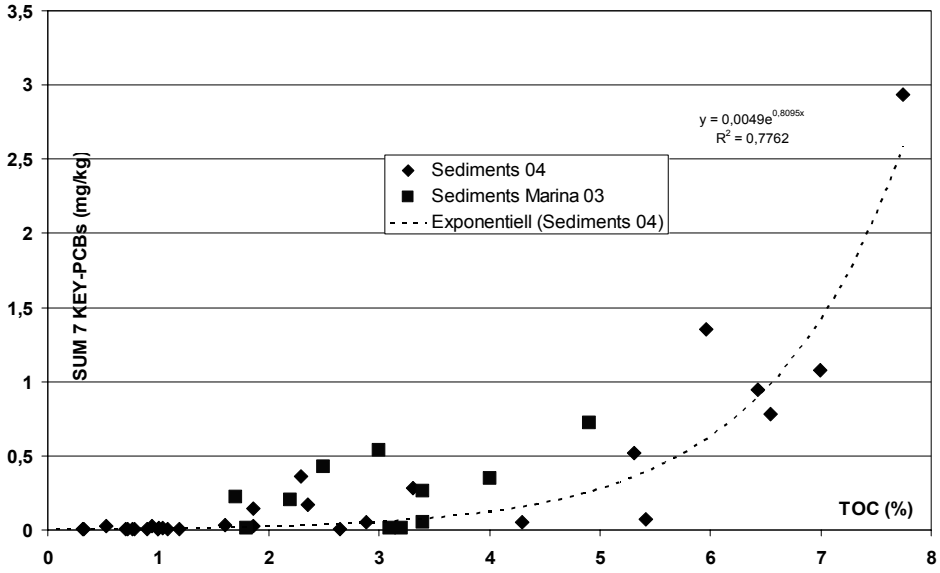

Figure 1: Organic carbon (TOC) versus PCB-content in the sediments (<0.063 mm) around Zada

Table 1. Levels of PCBs and OCPs (ng g^{-1} d.w.) in the size fractions of sea sediment collected from the Zadar harbor

Granulation	< 20 µm	≥ 20 µm	≥ 40 µm	≥ 63 µm	≥ 200 µm	≥ 630 µm	≥ 2 mm
Sample name	**ZDSED37-F1**	**ZDSED37-F2**	**ZDSED37-F3**	**ZDSED37-F4**	**ZDSED37-F5**	**ZDSED37-F6**	**ZDSED37-F7**
Collection date	6.8.2004	6.8.2004	6.8.2004	6.8.2004	6.8.2004	6.8.2004	6.8.2004
Sample size (g)	2.1	2.0	1.4	1.6	0.8	0.5	0.5
Dilution	1	1	1	1	1	1	1
PCB 28	11	4	4	5	11	17	18
PCB 52	9	5	8	11	41	26	25
PCB 101	36	38	51	100	420	201	135
PCB 118	363	83	124	271	905	670	270
PCB 138	31	146	209	414	1573	1071	402
PCB 153	58	161	225	560	1850	1419	434
PCB 180	48	178	304	632	1576	1956	427
TOTAL	556	615	925	1992	6376	5359	1710
PCB 8	2	2	3	3	6	10	5
PCB 18	8	3	4	5	14	13	8
PCB 44	9	2	4	4	11	13	12
PCB 66	16	26	5	59	234	123	107
PCB 77	524	37	49	96	449	193	159
PCB 105	<1	<1	<1	<1	<1	<1	<1
PCB 126	<1	15	27	61	159	161	45
PCB 128	176	11	15	36	167	85	33
PCB 170	0	98	170	344	966	999	226
PCB 187	<1	81	138	298	695	868	190
PCB 195	<1	17	36	63	122	194	35
PCB 206	<1	6	15	25	41	78	12
PCB 209	<1	<1	<1	<1	<1	<1	<1
TOTAL	737	300	467	994	2864	2737	833
Σ ALL CONGENERS	1293	915	1391	2986	9240	8095	2543
ΣPCB as Aroclor 1248+1254	5635	1359	1924	3931	11852	11747	4093
alpha-HCH	1.0	0.3	<0.1	0.6	1.3	1.2	1.4
beta-HCH	2.3	0.4	0.5	<0.1	2.8	<0.1	1.4
gamma-HCH	<0.1	0.6	0.1	0.7	1.6	2.8	1.6
TOTAL	3	1	1	1	6	4	4
p, p'-DDE	15.9	4.8	<0.1	0.8	1.2	2.7	27.1
p, p'-DDD	0.5	1.8	<0.1	4.4	12.7	46.1	26.5
p, p'-DDT	8.5	<0.1	0.2	2.8	11.4	39.4	<0.1
TOTAL	25	7	0	8	25	88	54

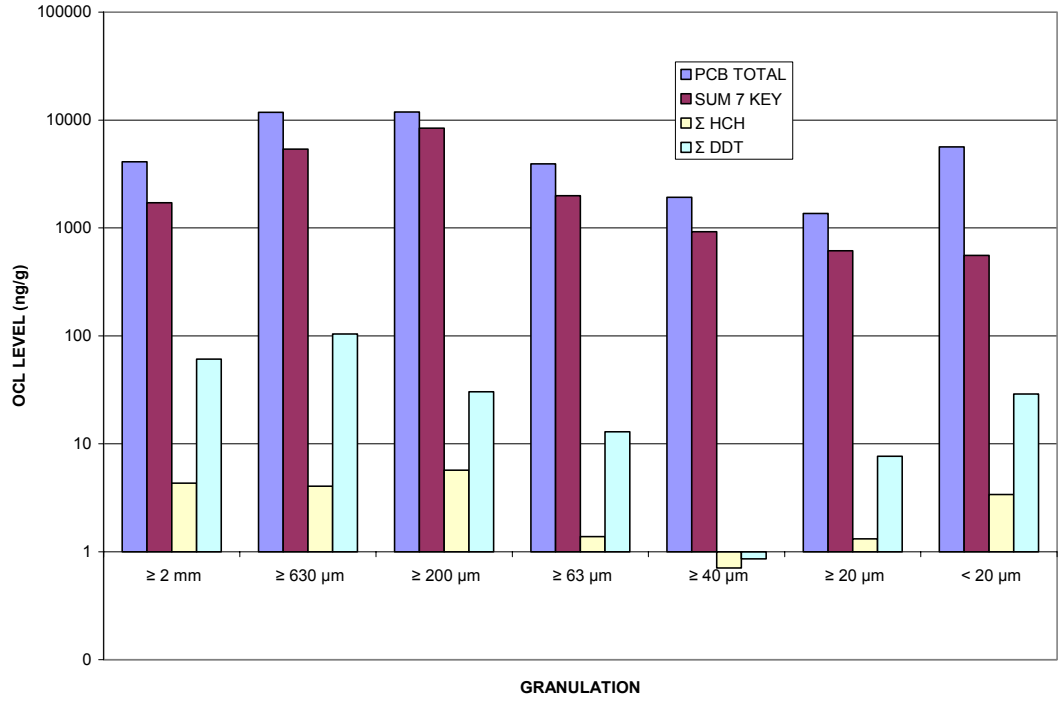

Figure 2 Dependence of organochlorine pollutants levels in marine sediment collected from Zadar harbor about granulation

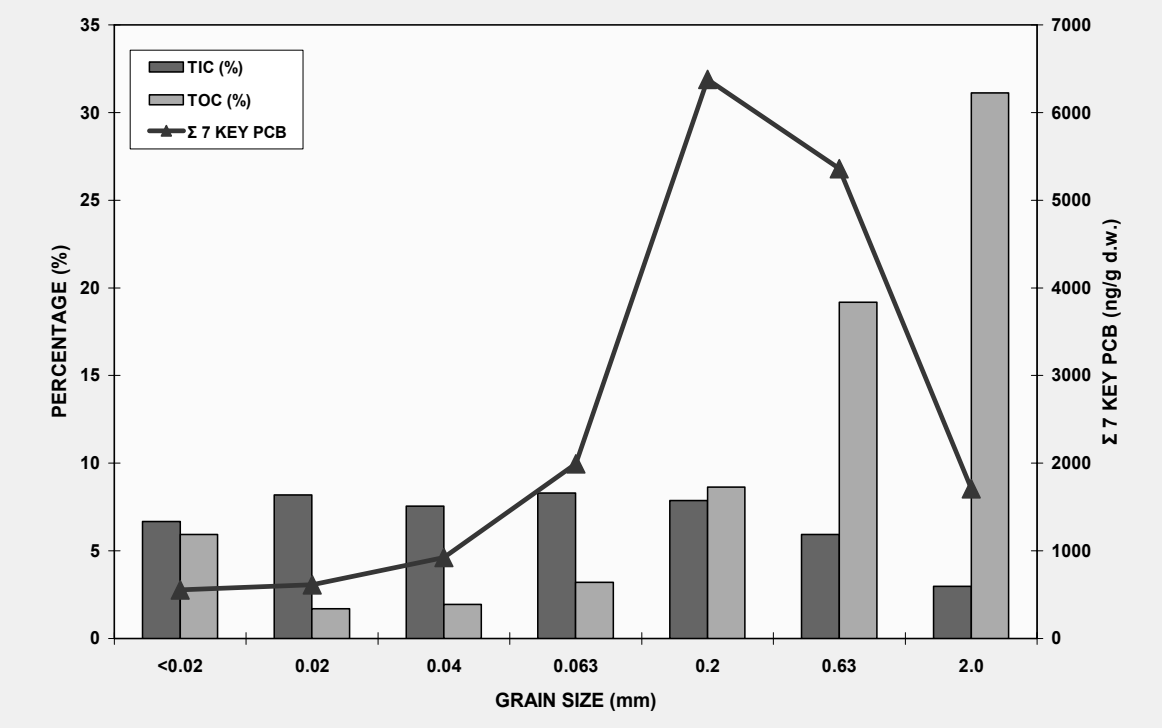

Figure 3. The distribution of level of sum of 7 key PCB congeners in fractions of sea sediment collected in Jazine , Zadar close to the diving club (TIC - total inorganic carbon, TOC - total organic carbon)

The level of PCBs and OCPs in different size fractions of one surface sediment sample were analyzed by the Environmental Protection Institute in Slovenia (Table 1 , Figure 2 and Figure 3). The distribution of of the sum of 7 key congeners of PCB was interesting (Figure 2). The highest levels of PCBs have been found in the fraction between 0.2 to 0.63 mm, while in the largest size fraction (> 2mm), the level was lower. It is interesting that levels of the PCB in fractions which smaller than 0.063 mm (which have been otherwise analyzed for contents of the organic and inorganic micropollutants in sediments) were lower compared to the larger size fractions.

Acknowledgements

The authors express their gratitude to the Ministry for Science and technology of Republic Croatia for financial support. This work has been carried out as part of the Contract ICA2- CT-2002-10007 (APOPSBAL) between the European Commission and Rudjer Boskovic Institute, Zagreb, Croatia and Federal Environment Agency Vienna, Austria and Environmental Protection Institute, Maribor, Slovenia.

References

1. Picer M and Holoubek I. 2003. *Fresenius environmental bulletin* 2003, 12: 86-93.

2. Picer M., Picer N. *Croatian Water Management* 1998, 7: No. 73, 10. (in Croatian).
3. Picer M., Picer N., Hodak Kobasic V. *Organohalogen compounds* 2003, 62: 472.
4. Picer, M., Picer N. *Periodicum Biologorum* 2003, 105 : 345.

5.Kovač T., Picer M., Picer N., Hodak Kobasić V. *Organohalogen compounds* 2004, 66: 1959.

6. Picer M., Kovač T., Kodba Cencič Z. *Organohalogen compounds* 2004, 66: 1569.

7. Picer M., Kovač T., Picer N., Čalić V., Miošić N., Cencič Kodba Z., Rugova A.. *Organohalogen compounds* 2005, 67: 2048

8. Čalić V., Miošić N., Cencič Kodba, Z. Picer M., Picer N., Rugova A., Arbneshi T. *Organohalogen compounds* 2005, 67: 2052.

9. Čalić V., Picer M., Kovač T., Hodak Kobasić V.. *Croatian Water Management* 2005, 14 (148): 59. (*in Croatian*)

10. Kralik M., Haslinger E.; Picer M., Picer N.; & Ottner F. *Chinese Journal in Geochemistry* 2006, 25: 159.
11. Picer M. *Croatica Chemica Acta* 2000, 73: 123. (review paper)
12. Picer M., Ahel M. *J. Chromatogr* 1978, 150: 119.
13. Picer M., Picer N. *Water, Air and Soil Pollut.* 1993, 68: 435.