PCB-anomalies in the sediments of the harbour basin of Zadar (Croatia) as consequence of war action and /or industrial contamination

Martin Kralik[1], Edith Haslinger[1], Mladen Picer[2], Nena Picer[2], Franz Ottner[3]

[1]Umweltbundesamt, Spittelauer Laende 5, A-1090 Vienna, Austria
[2]Institute Ruđer Bošković, Bijenička cesta 54, HR-1000 Zagreb, Croatia
[3]Institute of Applied Geology, Univ. of Natural Resources and Applied Life Sciences, A-1190 Vienna, Austria

Phone: +43-(1)-31304-3530
E-mail: martin.kralik@umweltbundesamt.at

Introduction: A great part of the former Yugoslavia has recently been encompassed by warfare. Research on the environmental impact of warfare has shown that many sorts of highly stable organic contaminants have entered the environment. Karstic regions and in many cases urban karst regions of former Yugoslavia warrants particular attention because of its exceptional ecological vulnerability. Objective of the EU-Project APOPSBAL (Assessment of the selected POPs (PCBs, PCDDs/Fs, OCPs) in the atmosphere and water ecosystems from the waste materials generated by warfare in former yugoslavia,ICA2 – CT – 2002 – 10007) was to investigate the levels of POPs (with the special attention to PCBs) in various environmental matrices, their atmospheric and hydrogeological fate.

Methods: The marine sediments were sampled from a motor-boat by means of a gravity corer in the harbour of Zadar. Samples of two different depths (mostly 0 – 2 and 2 – 10 cm).were taken.

One representative PCB-contaminated harbour sediment sample was fractionated by wet-sieving using deionised water and sieves with mesh-sizes of 2000, 630, 200, 63, 40 and 20 µm. After the sieving, each complete sieve fraction was freeze-dried.

The mineralogy and the organic components (TOC) of the sediments were analysed by XRD, FTIR, STA. The PCB-content was analysed.

Results: The sediments of the Marina and harbour (Uvala Vrulje and Jazine) are characterised by the black (oxygen poor) very fine grained (silt) TOC rich (2.5-8 %) nature. The mineral phases are variable amounts of carbonate minerals as calcite and aragonite and silicates (quartz, illite-mica).

The harbour area of the *Marina (u. Vrulje) and the Jazine* is an large area of about 0.18 km^2 with a PCB-anomaly of 0.2-3 mg/kg (sum 7 cong.) in the fine fractions (<0.063 mm). The depth controlled sampling down to about 0.3 m indicate a decrease of PCB contamination towards the top. Analysing the size distribution of theses sediments showed the fraction (<0.063 mm) is the dominating one, however, the coarser fractions (0.2-2 mm) contain similar quantities of PCBs. The harbour sediment samples show a significant anthropogenic enrichment of phosphorous, arsenic, cadmium, chromium, copper, lead and zinc as well.

Discussion: Studies in other areas showed that these organic rich very fine grained sediments in a mixture zone of meteoric and sea water are particular prone to scavenge nearly all contaminants to the sediments including PCBs.

Considering the sediment-depth of 0.3 m only at least 54 000 m^3 or 75 000 t (1.4 t/m^3) of PCB contaminated sediment are deposited in the harbour area. At a mean PCB concentration of about 0.8 mg/kg about 60 kg (sum 7) PCBs were trapped in this harbour basin. As the action level of PCB-contamination of most European countries are in the concentration range of 0.1-2 mg (sum 6 or 7 PCBs) per kg dry sediment [1] further investigations of these sediments are strongly recommended.

The source of this contamination is not clear. Likely sources of PCBs are PCBs in ship paintings used as antifouling agent in former times or war induced contamination in the industrial recharge area of the harbour occurred.

The marine sediments south of the Zadar centre and west of this industrial area are not affected by any significant PCB-contamination. This is supported by the analysis of fish [2] around the Zadar area.

The missing correlation of TOC-content and PCB-concentration in the harbour basin sediments indicates that the mechanism of PCB fixation is different in the finer (<0.2 mm) than in the coarser fractions. The negative correlation with TOC and therefore a positive one with carbonate suggests a fixation in the carbonate pore space. The different distribution of the single congeners support a fixation of the lighter congeners to organic compounds whereas the heavier ones rather stick to the carbonates. Future measurements on the coarse carbonate fractions should test this hypothesis.

References: [1] OSPAR (2004): Publ. No. 211, 22 p. (www.ospar.org 4/11/2005), [2] Picer et al (2005): (187-192), Proc. Intern. Conf., 888 p.,13-19 Sept. 2005, Belgrade & Kotor.