AN ASSESSMENT OF CONTAMINATION STATUS OF SURFICIAL SEDIMENTS IN A FLOODED COASTAL AREA, VIBO MARINA (SOUTHERN ITALY)

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Abstract
A Tyrrhenian coastal area in southern Italy was flooded on July 2006. This event caused the spread of mud, detritus and the spill of industrial wastes into the sea water. Surficial sediment samples were collected and analysed for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polychlorinated dibenzo-*p*-dioxins and –furans (PCDD/Fs) in order to evaluate current contamination status and risk assessment by means of Toxic Equivalency Factors (TEF). Data analysis showed that PCBs and OCPs levels were low and homogeneous in the three areas while PCDD/F fingerprint showed an heterogeneous distribution, suggesting for these molecules different sources of pollution.

Introduction
In 2006, a Tyrrhenian coastal area in southern Italy (Vibo Marina) characterized by high industrial and commercial activities was flooded. This event severely damaged the coast and caused the release of industrial wastes mixed with mud and detritus in the near coastal area. The flooded factories caused the spread of organic contaminants as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polychlorinated dibenzo-*p*-dioxins and –furans (PCDD/Fs) which are persistent, ubiquitous, toxic contaminants in the environment. Due to their high persistence, hydrophobic nature and low solubility in water, they are adsorbed on particulate organic matter and accumulated in sediment. The Stockolm Convention on Persistent Organic Pollutants (POPs) nominated 12 chemicals, including OCPs, PCBs and PCDD/Fs, as high priority POPs.
Since contaminant concentrations in surficial sediments provide information about recent deposits and their distribution, 45 surficial samples were collected (Fig. 1) from three sites (A-low affected area; B-affected area; C-tourist area) and analysed for PCBs, OCPs and PCDD/Fs, in order to evaluate current contamination status and the risk assessment by means of Toxic Equivalency Factors (TEF)[1] .

Fig. 1. Study Area: site A-low affected area; site B-affected area; site C-tourist area.

Material and Methods

Seven polychlorbiphenyl congeners (PCB-28, -52, 101, -118, -153, -138, -180), nine OCPs (HCB, α-HCH, β-HCH, γ-HCH (lindane), δ-HCH, *pp*'-DDT, *op*'-DDT, *pp'*-DDE, *op'*-DDE), seventeen PCDD/F and four non-*ortho* PCBs (PCB-77, -81, -126, -169, Wellington Laboratories Inc.) were extracted from lyophilised sediment samples with an Accelerated Solvent Extractor (ASE 200, Dionex), using toluene as extraction solvent (US EPA 3545 A revision B method)[2]. A mix of PCB-30 and -209 was added as recovery standard before extraction. The extract was purified on multilayer silica columns (PCBs and OCPs fractions) and on carbon columns (fraction containing PCDD/Fs and non-*ortho* PCBs). The final solutions containing PCBs and OCPs were concentrated, injected in a gas chromatograph with electron capture detector (Mod. AutoSystem, PerkinElmer) and confirmed with an ion trap mass spectrometer (Mod. *Polaris* MS). Analytical conditions are reported in Pozo *et al.*[3]. For determination of PCDD/F we used isotopic dilution according to US EPA 1613 revision B method[4] with PCDD/F standard specific for that method ($^{13}C_{12}$, 99% Cambridge Isotope Laboratories). Two µL of extract was injected in a gas chromatograph (Mod. Trace™ GC 2000 with AS3000 autosampler, ThermoFinnigan) coupled with a *Polaris* MS ion trap. The six-point calibration curve was provided by the Cambridge Isotope Laboratory. Limits of detection (LOD) for non-*ortho* PCBs and PCDD/Fs were 2 and 0.4-1 pg/g d.w., respectively. Element analysis of total organic carbon (TOC) was performed using a CHNS analyzer with a TCD (Mod. NA 1500, Carlo Erba) by preliminary acid digestion with HCl and total flash combustion.

Results and discussion

TOC

TOC levels were similar to oligotrophic marine sediments from Mediterranean coastal areas. Since TOC did not correlate with contaminants and did not vary substantially between sampling sites (mean ± standard deviation: 0.19 ± 0.12 % d.w. site A; 0.25 ± 0.21 % d.w. site B; 0.26 ± 0.29 % d.w. site C), contaminant levels were not expressed in relation to TOC.

PCBs

The highest PCB levels were found in sediments from site A (mean value ± S.D. : 2.3 ± 4.8 ng/g d.w.), and were only slightly different from those found in sediments from site B (mean value ± S.D.: 1.8 ± 1.3 ng/g d.w.) (Fig. 2). PCB fingerprint showed a predominance of PCB-138 and –180 in sediments from all sampling sites.

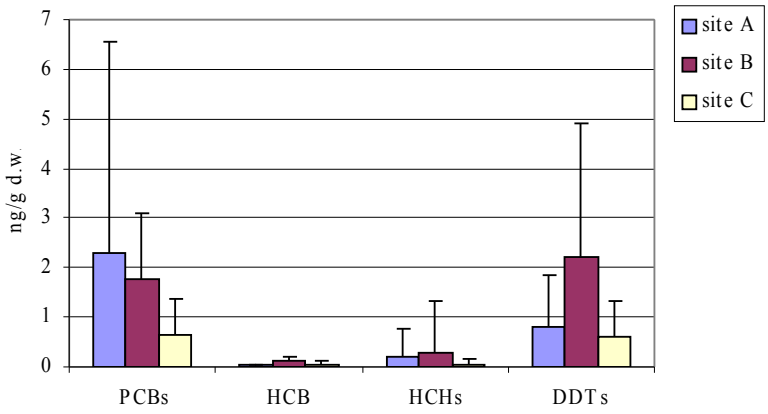

Fig. 2: PCB and OCPs levels.

PCBs levels in the three study areas were low compared to those reported in other monitoring studies of coastal areas and harbours[5,6]. This indicates neglegible recent PCBs input affected the coastal area of Vibo Marina, as PCBs are known to persist in aquatic environments due to their low rates of degradation and vaporization, low water solubility and partitioning to particles and TOC.

OCPs

The highest HCB, HCHs and DDTs levels were recorded in sediment from the affected site (B) as showed in Figure 2. In all study areas were observed a DDTs predominance followed by HCHs and HCB. Levels were low compared with concentrations in sediments from other monitoring studies in marine areas[5,7] probably reflecting limited past use of these pesticides in the study area and also the widespread ban on most of them.

PCDD/Fs, non-ortho PCBs and Toxicity Equivalents (TEQs)

Mean concentrations of PCDD/F were heterogeneous: site C > site B > site A (Table 1). PCDD/F fingerprint suggested different sources of pollution.: sediments from site B were characterized by a high percentage of OCDD (Fig. 3), usually found in sediments acting as a main sink for PCDD/Fs. This could be due to the low solubility of OCDD in water, atmospheric input from a variety of combustion processes and photochemical synthesis of pentachlorophenol. In the site C sediments tetrachlorodibenzofuran (TCDF) predominated. This type of contamination is probably associated with steel production which releases lightly chlorinated furans (TCDF e PeCDF)[8] (Fig. 3). Non-*ortho* PCBs were higher in samples from sites B and C than from site A (Tab. 1) and PCB-77 and –169 were the prevalent congeners.

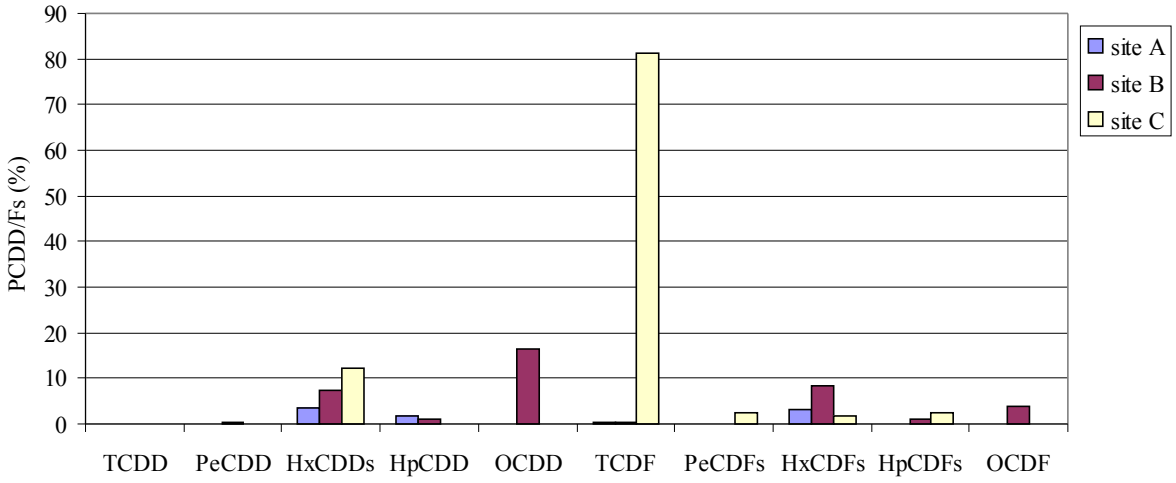

Fig. 3: Distributions of PCDD/Fs in surficial sediments in the three study areas.

Table 1 shows TEQs calculated for non-*ortho* PCBs and PCDD/F. The former were less abundant, contributing in a minor way to total TEQ. Total TEQs obtained by summing non-*ortho* PCBs and PCDD/Fs were higher in samples from area C. Overall, the concentrations recorded and TEQs calculated for sediments from the three areas indicate these areas as "not at risk" according to US EPA risk levels[9].

Tab. 1: Concentrations of PCDD/Fs, non-*ortho* PCBs and TEQs (mean ± S.D. pg/g d.w.) in sediments from the three study areas. n.d. = not detected

	site A		site B		site C	
PCDD/Fs	**Mean conc. pg/g d.w.**	**TEQs**	**Mean conc. pg/g d.w.**	**TEQs**	**Mean conc. pg/g d.w.**	**TEQs**
2,3,7,8-TCDD	n.d.	-	0.004 ± 0.02	0.004 ±0.015	n.d.	-
1,2,3,7,8-PeCDD	n.d.	-	0.07 ± 0.23	0.032 ± 0.112	n.d.	-
1,2,3,4,7,8-HxCDD	0.70 ± 1.03	0.07 ± 0.10	1.25 ± 3.69	0.125 ± 0.369	1.42 ± 2.96	0.142 ± 0.296
1,2,3,6,7,8-HxCDD	< 0.5	-	0.10 ± 0.33	0.010 ± 0.033	0.95 ± 2.32	0.095 ± 0.232
1,2,3,7,8,9-HxCDD	n.d.	-	0.07 ± 0.23	0.007 ± 0.023	n.d.	-
1,2,3,4,6,7,8-HpCDD	0.37 ± 0.67	0.004 ± 0.007	0.23 ± 0.55	0.002 ± 0.006	n.d.	-
OCDD	n.d.	-	3.18 ± 3.99	0.003 ± 0.004	n.d.	-
PCDDs	**1.07 ± 0.95**	**0.074 ± 0.109**	**4.94 ± 5.40**	**0.183 ± 0.562**	**2.36 ± 5.27**	**0.236 ± 0.528**
2,3,7,8-TCDF	0.08 ± 0.20	0.008 ± 0.020	0.04 ± 0.14	0.004 ± 0.014	15.60 ± 38.22	1.56 ± 3.822
1,2,3,7,8-PeCDF	n.d.	-	n.d.	-	0.29 ± 0.71	0.014 ± 0.035
2,3,4,7,8-PeCDF	n.d.	-	n.d.	-	0.18 ± 0.29	0.092 ± 0.143
1,2,3,4,7,8-HxCDF	0.52 ± 0.68	0.052 ± 0.068	1.28 ± 3.41	0.128 ± 0.341	0.32 ± 0.50	0.032 ± 0.050
1,2,3,6,7,8-HxCDF	0.07 ± 0.18	0.007 ± 0.018	0.24 ± 0.70	0.024 ± 0.069	n.d.	-
1,2,3,7,8,9-HxCDF	n.d.	-	n.d.	-	n.d.	-
2,3,4,6,7,8-HxCDF	n.d.	-	0.06 ± 0.19	0.006 ± 0.020	n.d.	-
1,2,3,4,6,7,8-HpCDF	n.d.	-	0.20 ± 0.46	0.002 ± 0.005	0.45 ± 1.09	0.004 ± 0.011
1,2,3,4,7,8,9-HpCDF	n.d.	-	n.d.	-	n.d.	-
OCDF	n.d.	-	0.75 ± 1.58	0.001 ± 0.002	n.d.	-
PCDFs	**0.67 ± 0.83**	**0.067 ± 0.105**	**2.57 ± 3.75**	**0.164 ± 0.450**	**16.84 ± 37.63**	**1.703 ± 4.061**
PCDDs + PCDFs	**1.74 ± 1.16**	**0.141 ± 0.215**	**7.52 ± 5.98**	**0.347 ± 1.011**	**19.21 ± 36.79**	**1.940 ± 4.589**
PCB-77	1.19 ± 3.16	0.0001 ± 0.0003	1.77 ± 2.60	0.0002 ± 0.0003	2.18 ± 3.56	0.0002 ± 0.0004
PCB-81	n.d.	-	0.01 ± 0.03	0.000001 ± 0.000003	n.d.	-
PCB-126	n.d.	-	n.d.	-	n.d.	-
PCB-169	n.d.	-	3.82 ± 4.29	0.038 ± 0.043	2.13 ± 3.20	0.021 ± 0.032
non-*ortho* PCBs	**1.73 ± 3.36**	**0.0001 ± 0.0003**	**5.61 ± 5.90**	**0.039 ± 0.043**	**4.60 ± 3.29**	**0.021 ± 0.032**
PCDD/Fs + non-*ortho* PCBs	**3.47 ± 4.52**	**0.141 ± 0.215**	**13.13 ± 11.88**	**0.386 ± 1.055**	**23.81 ± 40.08**	**1.961 ± 4.622**

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