POP LEVELS IN TWO SPECIES OF ANTARCTIC INVERTEBRATES: THE SEA STAR (*Odontaster validus*) AND THE SEA URCHIN (*Sterechinus neumayeri*)

Borghesi Nicoletta[1], Corsolini Simonetta[1], Focardi Silvano[1]

[1]Department of Environmental Science "*G. Sarfatti*", University of Siena, via P.A. Mattioli, 4, I-53100 Siena, Itlay, E-mail address: borghesi2@unisi.it

Introduction

In the 1960s the first scientific studies reported the presence of contamination in Antarctic ecosystems[1]. Many Persistent Organic Pollutants (POPs) are transported globally from the areas in which they are produced and released in the environment and they are expected to be transported to polar regions. POPs are carbon-based compounds that include industrial chemicals and combustion by-products. They are persistent in the environment, tend to accumulate trough the food webs and adversely affect ecosystems and human health. Nowadays there is continuing and growing concern about the potential effects of POPs in polar environments[2].

The lipophilic nature of these compounds allows them to be accumulated in the adipose tissues of organisms and subsequently to be biomagnificated trough the food webs. Many researches in Antarctic region have detected POP concentrations in fish and in high top predator such as penguins and seals[3,4] and only few studies have evaluated POPs in lower trophic levels of Antarctic marine food webs[5,6].

Since Antarctic marine food webs are relatively simple and short, a decline in the population of a species can affect the entire marine ecosystem. Moreover, POP accumulation in Antarctic organisms is affected by their low metabolic rate. This means that they need a longer time to metabolize chemicals and to excrete them; consequently they may have a longer time to bioaccumulate POPs. This is important above all for organisms at the lower trophic levels of the Antarctic marine food web, since they represent the first step in pollutants transport up the food chain. In this study POP levels were determined in two species of echinoderms: the sea star *Odontaster validus* and the sea urchin *Sterechinus neumayeri*, in order to evaluate the POP accumulation in species low the food chain. In particular, this research aims to evaluate the presence of polychlorobiphenyls (PCBs) and chlorinated pesticides (hexachlorobenzene, HCB, hexachlorocyclehexane, HCH, dichlorodiphenyldichloro ethane DDT), polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); all these compounds are known to elicit toxic effects in organisms. To our knowledge, this is the first time that a wide set of compounds are evaluated in these two species of Antarctic invertebrates.

Materials and Methods

Collection of Samples. Samples of *O. validus* (n=10) and *S. neumayeri* (n=12) were collected in January-February 2005. The fishing area was the Ross Sea, south of the Italian "Mario Zucchelli" scientific station (74° 42' 00''S 164° 08' 40''E). The organisms were taken to the laboratory where they were measured and weighed and then they were kept at -20°C until analysis.

Chemical analysis. PCBs, pesticides, PBDEs, PCDDs and PCDFs were analysed following a method described elsewhere, with some modifications[3,7]. Samples were homogenized with sodium sulphate; they were Soxhlet extracted and the extracts were rotary evaporated. Interfering substances were removed by fractionation on a multilayer silica gel column. Samples were then eluted with 200 mL of hexane and rotary evaporated to 1 mL for GC analysis of PCBs and pesticides and GC/MS analysis of PBDEs. The samples were then cleaned up through a glass column (10 mm i.d.) packed with 1 g of carbon impregnated silica gel (Wako Pure Chemical Industries, Tokyo, Japan). This fraction was rotary evaporated to 1 mL for GC/MS analysis of non-ortho- PCBs, PCDDs and PCDFs. Blanks were analyzed throughout the analytical procedure to check for interference and laboratory contamination. PCB, PBDE, PCDD and PCDF congeners are represented by their IUPAC numbers throughout the text. ΣPCBs, ΣPBDEs, ΣPCDDs and ΣPCDFs were calculated as the sum of the principal congeners identified (23, 9, 7 and 10 congeners, respectively). Results are given on a wet weight basis (wet wt).

Results and Discussion

Results are shown in Table 1. ΣPCBs were the most abundant class of POPs in both species (3.62 ng/g wet wt in *O. validus* and 1.96 ng/g wet wt in *S. neumayeri*), while the accumulation pattern of chemicals was ΣPCBs > ΣDDTs > ΣPBDEs > HCB > ΣHCHs > Σnon-orthoPCBs > ΣPCDFs > ΣPCDDs in the sea star and ΣPCBs > ΣPBDEs > ΣHCHs > ΣDDTs > HCB > Σnon-orthoPCBs > ΣPCDDs > ΣPCDFs in the sea urchin. These differences may be attributable to the different metabolism of species[8] or at the different diet of organisms. In fact, the sea urchin is mainly herbivorous, while the sea star is omnivorous (filter feeder and predator)[9]. PCB levels were higher in *O. validus* than in *S. neumayeri*, while Σnon-orthoPCBs were similar (16.10 pg/g wet wt in *O. validus* and 16.74 pg/g wet wt in *S. neumayeri*). The PCB fingerprints showed different patterns in the two species (Figure 1). The most abundant congeners were PCB8 > PCB44 > PCB138 in *O. validus*, and PCB18 > PCB189 > PCB52 in *S. neumayeri*. The class of isomer accumulation patterns were tetra-CBs > hexa-CBs > bi-CBs > hepta-CBs > penta-CBs > tri-CBs > octa-CBs > nona-CBs in the sea star, and tri-CBs > hepta-CBs > tetra-CBs > di-CBs > penta-CBs > hexa-CBs > octa-CBs > nona-CBs in the sea urchin. In general, low chlorinated congeners were more abundant than high chlorinated congeners in both species. This pattern is due to the global transport mechanism of these compounds. In fact, because of their volatility, low chlorinated PCBs can reach the polar regions faster than heavier molecules (such as high chlorinated PCBs) that tend to remain more in mid-latitudes[10].

Among pesticides, ΣDDTs were the most abundant in both species (1.03 ng/g wet wt in O. validus and 0.06 ng/g wet wt in *S. neumayeri*). These data were lower than those reported for other benthic species from Antarctic[11] and Arctic[12,13] regions and from other areas of the world[14]. In both species, *p,p'*-DDE was the most abundant metabolite of DDT and its contribution to the ΣDDT was more than 60%. In fact, *p,p'*-DDE was the most stable and persistent metabolite of DDT. This compound was the most abundant pollutant in other Antarctic organisms[3]. The *p,p'*-DDT/*p,p'*-DDE ratio was evaluated in order to assess the time of exposure, a value below 1.0 suggesting an old DDT contamination event[15]. The ratio value was 0.002 in *O. validus* and 0.014 in *S. neumayeri*, suggesting that DDT in Antarctic echinoderms derives from old contamination events.

HCH concentrations were higher in the sea urchin than in the sea star (0.10 and 0.04 ng/g wet wt, respectively). In both species, γ-HCH was the most abundant isomer, but the accumulation pattern was different (γ-HCH > β-HCH > α-HCH=δ-HCH in *O. validus* and γ-HCH > δ-HCH > α-HCH > β-HCH in *S. neumayeri*). These differences can be due to the different metabolism of these compounds in these species[16]. The ratio between the α- and γ-isomers can be used to monitor the global transport of HCHs[17]. The ratio α-HCH/γ-HCH was 2.08 in *O. validus* and 2.17 in *S. neumayeri* and so these data confirm that γ-HCH was transported in Antarctica from other areas of the world[15].

HCB concentrations were higher in *O. validus* than in *S. neumayeri* (0.14 and 0.04 ng/g wet wt, respectively). These data were lower than those reported for the same species[6] and similar to those reported for invertebrates collected in Belgium[18].

The ΣPBDE concentrations were similar in both species (189.68 pg/g wet wt in *O. validus* and 180.22 pg/g wet wt in *S. neumayeri*) and the congener accumulation pattern was PBDE100 > PBDE 153 > PBDE99. This pattern may be attributable to the dietary habits of these organisms, that are benthonic and feed on sediments. In fact, some studies carried out in different regions of the world reported that the most abundant PBDE congeners in sediments were PBDE47, PBDE99, PBDE100 and PBDE153[19,20,21].

PCDD and PCDF concentrations were higher in the sea urchin than in the sea star. In both species the isomers with six chlorine atoms prevailed, but the congener accumulation patterns differed between the two species. Even if these samples were collected near a permanent scientific station, combustion processes should be a minor source of dioxins and furans in Antarctica[3].

In general, POP levels in Antarctic invertebrates were lower than those reported for other marine species from other areas of the world[13,14,22]. The data reported in this study confirm the presence of POP in Antarctic organisms and above all in species at the bottom of the food chain. The differences between the two species may depend on the different physiological characteristics of the organisms and the different lipid content of the tissues. Anyway the extreme weather conditions and the low temperatures of the Antarctic region affect the physiology and ecology of organisms. It is important to monitor the trend of POP levels in Antarctic organisms, since the accumulation of pollutants in invertebrates may be of concern for the organisms themselves and also for the biomagnification processes through the food webs.

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Table 1. Concentrations of ΣPCBs, HCB, ΣHCHs, ΣDDTs (ng/g wet wt) and Σnon-orthoPCBs, ΣPBDEs, ΣPCDDs and ΣPCDFs (pg/g wet wt) in *O. validus* and *S. neumayeri* (average concentrations ± standard deviation).

	O. validus	***S. neumayeri***
n	10	12
ΣPCBs	3.62±1.88	1.96±2.04
HCB	0.14±0.14	0.04±0.07
ΣHCHs	0.04±0.04	0.10±0.04
ΣDDTs	1.03±1.32	0.06±0.09
Σnon-orthoPCBs	16.10±14.57	16.74±18.62
ΣPBDEs	189.68±52.64	180.22±50.37
ΣPCDDs	4.60±2.73	7.80±3.34
ΣPCDFs	6.77±6.75	7.29±6.33

Figure 1: PCB fingerprints in O. validus and S. neumayeri.