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LEVELS AND ENANTIOMERIC SIGNATURES OF ORGANOCHLORINE PESTICIDES (OCPs) AND POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN MARINE ORGANISMS FROM ANTARCTICA

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Introduction

The use of enantiomers to study sources, transport pathways and biological activity of persistent organic pollutants (POPs) has recently received increased importance. Once in the environment, a racemic mixture of pesticides may follow two ways: i) abiotic degradation, ii) biodegradation. In the first case, physical transport and abiotic chemical transformation does not affect the enantiomeric ratio (ER = (+)enantiomer/(-)enantiomer) that remain unchanged (1:1), while in the latter it varies as a consequence of biodegradation; in fact, metabolic processes may be selective. Moreover, enantiomers of a racemic pesticide mixture may have different toxic effects on organisms. For example, the (-) *o,p'*-DDT shows higher estrogenic activity than (+) *o,p'*-DDT[1]. Polybrominated diphenyl ethers (PBDEs) are a class of POPs used worldwide as flame retardants. They are hydrophobic, highly soluble in lipids and resistant to biodegradation depending on the level of bromination. Their bioaccumulation and biomagnification properties, as well their global and increasing presence, have already been reported by many authors[2-4].

Antarctica is a remote continent where volatile contaminants are transported mainly by air mass movements. Fractionation by condensation in cold environments has been proposed as a mechanism whereby POPs can reach polar regions[5]. There, due to the low temperatures and winter darkness, POP degradation is very slow, thus ice can entrap POPs and release them in the environment through ice melting[6], where they enter the trophic webs, bioaccumulate in the tissues of organisms and biomagnify[7].

The study of chiral compounds is proposed here to investigate on POP distribution in the Antarctic marine organisms. Due to the peculiar geography and ecosystems of the Antarctic continent, the use of enantiomeric chemicals may be a useful tool to assess: i) the fate of chiral pesticides in Antarctic trophic webs; ii) the transport pathway of racemic POPs to Antarctica; iii) the timing of contamination. To our knowledge, this is the first time that PBDEs and enantiomers of chiral pesticides are detected in Antarctic organisms.

Materials and Methods

Sampling. Homogenated whole body of Antarctic krill (*Euphausia superba*), homogenated whole body and muscle of emerald rockcod (*Trematomus bernacchii*) and homogenated unhatched eggs of Adélie penguin (*Pygoscelis adeliae)* were collected in the Ross Sea (74°04'S, 179°06'E), Terra Nova Bay (74°45'S, 164°06'E) and Edmonson Point (74°21'S, 165°08'E), respectively, during the XI (1994/95) and XVII (2001/02) Italian Expeditions, in the framework of the Italian Antarctic

Research Programme (PNRA). Penguins feed on krill and occasionally on emerald rockcod. Samples were kept at –30°C until laboratory analyses.

Analysis of contaminants. All samples were analyzed for hexachlorocyclohexane (HCHs), pentachlorobenzene (QCB), hexachlorobenzene (HCB), chlordanes (OXY, CC, TC), *trans*-nonachlor (TN), *p,p'*-DDE, *p,p'*-DDD, *o,p'*- and *p,p'*-DDT (Table 1) and seven PBDE congeners (Table 2). Moreover, we also reported PCBs nos. 99, 153 and 183 for comparison with PBDEs.

The method used for the determination of POPs in biota has been previously described and validated[8]. Briefly, after addition of internal standards (PCB46, PCB143, ε-HCH, BB103 and BB155), samples were Soxhlet extracted with Hexane/Acetone=3/1. After lipid determination, the remaining extract was cleaned-up on acidified silica. The final eluate containing PCBs, pesticides and PBDEs was concentrated to 80 µl iso-octane. PBDEs and organochlorine pesticides were measured by GC/MS operated in electron-capture negative ionization (ECNI) mode using a 25 m x 0.22 mm x 0.25 µm HT-8 capillary column. For PBDEs, ions m/z 79 and 81 were monitored for the entire run, while for pesticides, specific ions were acquired in defined time-windows.

For chiral analysis, extracts were fractionated on a silica SPE cartridge. The 1st fraction, containing all PCBs, DDTs and oxychlordane, was eluted with 4 ml hexane, and the 2nd fraction containing all HCH isomers and *p,p'*-DDD, was eluted with 3ml DCM. After concentration, the 1st fraction was analyzed by GC-ECD using a 30 m x 0.25 mm BGB172 column (BGB Analytik). The 2nd fraction was analyzed by GC/ECNI-MS using a 30 m x 0.25 mm Chirasil-Dex column (Chrompack). The enantiomeric ratio (ER) was defined as the ratio of peak area of the first to the second eluting enantiomer (E_1/E_2). A good reproducibility (RSD < 1.5%) for injections of standard solutions allowed the determination with sufficient significance of ER changes of even a few percentages. The enantiomeric fraction (EF) was defined as ER/(ER+1).

Quality assurance. The method performance was assessed through rigorous daily internal quality control and through regular participation in interlaboratory tests for PCBs and PBDEs.

Results and Discussion

The average concentrations of pesticides and PBDEs are reported in Tables 1-2. In general, concentration patterns reflected the organism positions in the trophic web (penguin > fish > krill). ΣHCHs and Σchlordanes were higher in fish muscle than in penguin eggs.

Mean PBDE concentrations were 0.05 ng/g wet wt, 0.16 ng/g wet wt, 0.2 ng/g wet wt and 0.29 ng/g wet wt in rockcod muscle, rockcod whole body, krill and penguin eggs, respectively. Most of the residue was due to BDE47 (50-70%). PBDE congener pattern was BDE47 > BDE28 > BDE100 > BDE99. Congeners BDE153, BDE154 and BDE183 were below the detection limit in all samples (Table 2). Presence of low-brominated congeners (tri-penta) might suggest that contamination is due to LRT (by air or water). BDE congener concentration was highest in the penguin eggs, followed by krill and fish samples (except BDE100). POP transfer from penguin female to eggs was already reported[9] and it could explain their higher values. While their lipid content was similar, the higher body surface/mass ratio in krill[7] can be responsible for the higher PBDE concentration with respect to the fish. The higher values found in the fish whole body homogenate respect to the muscle may be due to the lipid distribution in the body (preferential accumulation in the fish liver[4]). PBDE levels in organisms from the North Sea ranged 51-59.8 ng/g lipid wt in shrimp and 40.4-119.4 ng/g lipid wt in cod muscle[2]. In general, levels in the Antarctic organisms studied here were lower than those from other areas[10, 11]. The detection of BDEs 47, 99 and 100 in Antarctic organisms confirm the PBDE global distribution[4].

Enantiomeric ratios and fractions of chiral α-HCH and oxychlordane are showed in Figure 1. Average EF of α-HCH is 0.44 ± 0.01 in krill, 0.49 ± 0.01 in fish and 0.58 ± 0.04 in penguin eggs. The (+) α-HCH has increased with 13% from the lower trophic web (krill) to the higher level (penguin). Accumulation of (+) α-HCH in the higher trophic levels was already reported for marine mammals[12]. Average EF of oxychlordane is 0.61 ± 0.01 in fish and 0.62 ± 0.04 in penguin eggs. Similar EFs of oxychlordane could be observed for rockcod and penguin.

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References

1. McBlain W.A., Lewis V. and Wolfe F.W. (1976). Can J Physiol Pharmacol 54, 629-632
2. Boon J.P., Lewis W.E., Tjoen-A-Choy M.R., Allchin C.R., Law R.J., de Boer J., Ten Hallers-Tjabbes C and Zegers B.N. (2002) Environ Sci Technol 36, 4025-4032
3. Lebeuf M. and Trottier S. (2001) Organohalogen Compd 52, 13-17
4. de Boer J., Wester P.G., Klamer H.J.C., Lewis W.E., Boon J.P. (1998) Nature 394, 28-29
5. Wania F. and Mackay D. (1993) Ambio 22, 10-18
6. Fuoco R, Colombini M.P. and Abete C. (1991) Ann Chimica 81, 383-394
7. Corsolini S. and Focardi S. (2000) in Ross Sea Ecology (Faranda, F., Guglielmo, L. and Ianora, A., Ed.), Springer Verlag, Berlin Heidelberg, ISBN 3-540-65372-4
8. Jacobs M., Covaci A. and Schepens P. (2002) Environ Sci Technol 36, 2797-2805
9. Corsolini S., Ademollo N. and Focardi S. (2001) Proc VIII SCAR International Biology Symposium "Antarctic Biology in a Global context", Vrije Universiteit, Amsterdam, The Netherlands, August 27 – September 1, 2001, p. S6P04
10. Luross J.M., Alaee M., Sergeant D.B., Whittle D.M. and Solomon K.R. (2000) Organohalogen Compd 47, 73-76
11. **de Boer J. and Allchin C.R. (2001) Organohalogen Compd 52, 13-17**
12. Kallenborn R. and Hühnerfuss H. (2001). Chiral Environmental Pollutants. Springer, Berlin

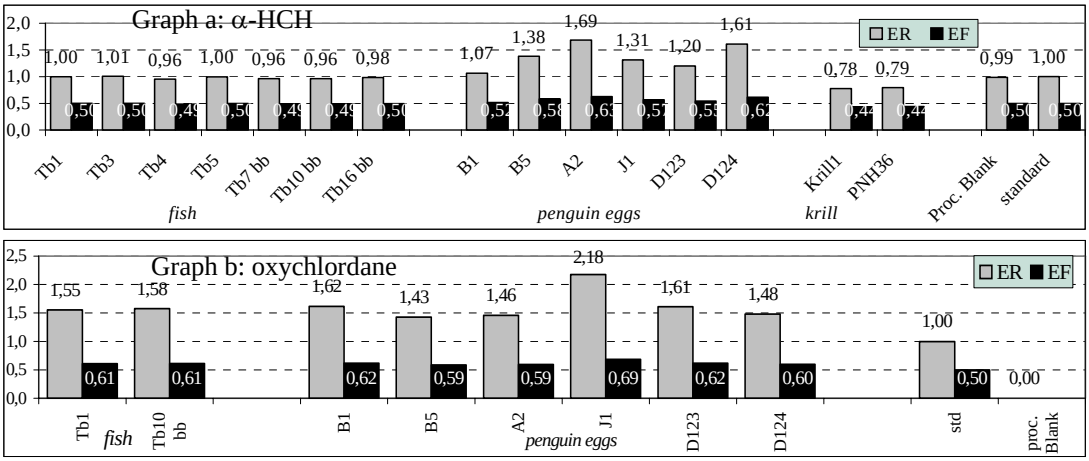

Figure 1: Enantiomeric ratios (ER) and enatiomeric fractions (EF) of chiral α-HCH (graph a) and oxychlordane (graph b).

Table 1: Pesticide concentrations (average ± SD, ng/g wet wt) in the analyzed Antarctic organisms (wb = whole body; nd = not detected (< 0.02 ng/g wet wt)).

	Krill (wb)	Rockcod	Rockcod (wb)	Penguin (eggs)
n	2	4	3	6
sample intake (g)	9.56 ± 0.75	6.12 ± 2.42	10.50 ± 2.39	4.50 ± 0.84
% lipids	3.57 ± 0.22	0.86 ± 0.12	3.50 ± 2.91	9.47 ± 5.47
α-HCH	nd	0.10 ± 0.04	0.03	0.05 ± 0.01
γ–HCH	0.28 ± 0.04	1.23 ± 0.67	0.17 ± 0.03	0.54 ± 0.20
β–HCH	nd	0.03 ± 0.01	nd	nd
ΣHCHs	*0.28 ± 0.04*	*1.35 ± 0.72*	*0.21 ± 0.03*	*0.59 ± 0.21*
QCB	0.05 ± 0.01	0.08 ± 0.02	0.09 ± 0.04	0.68 ± 0.6
HCB	0.23 ± 0.01	1.44 ± 0.45	1.35 ± 1.24	18.7 ± 8.0
OxC	nd	1.04*	0.13 ± 0.12	1.36 ± 0.63
TC	nd	nd	0.09	0.19 ± 0.09
TN	nd	1.23 ± 2.07	0.45 ± 0.36	0.24 ± 0.28
CC	nd	0.34*	0.23 ± 0.20	0.05 ± 0.01
Σchlordanes mix	nd	*2.61 ± 2.07*	*0.90 ± 0.67*	*1.83 ± 1.01*
p,p'-DDE	0.10 ± 0.01	2.53 ± 4.67	1.10 ± 1.04	20.7 ± 11.0
o,p'-DDT	nd	4.1*	0.11 ± 0.09	1.18 ± 0.65
p,p'-DDD	nd	1.38*	0.15 ± 0.14	0.31 ± 0.19
p,p'-DDT	0.07 ± 0.03	0.58 ± 1.01	0.40 ± 0.40	0.93 ± 0.54
ΣDDTs	*0.18 ± 0.03*	*8.60 ± 5.67*	*1.76 ± 1.67*	*23.0 ± 12.0*
PCB99	0.48 ± 0.01	0.32*	-	1.2 ± 2.0
PCB153	6.61 ± 3.54	0.42*	-	6.6 ± 12.0
PCB183	-	0.05*	-	2.7 ± 6.2

*detected in one sample only.

Table 2: BDE congener concentrations in the Antarctic samples (ng/g wet wt).

PBDE congener		28	47	100	99	154	153	183	ΣBDEs	ΣBDEs*
Krill	Krill1	0.05	0.18	nd	nd	nd	nd	nd	0.23	6.21
(whole body)	PHN	0.03	0.12	nd	0.02	nd	nd	nd	0.17	4.85
Rockcod	Tb7	0.02	0.06	0.07	0.01	nd	nd	nd	0.16	7.53
(whole body)	Tb10	0.01	0.08	0.02	0.05	nd	nd	nd	0.16	2.38
	Tb16	nd	0.1	0.03	0.02	nd	nd	nd	0.15	9.54
Rockcod	Tb1	nd	nd	nd	nd	nd	nd	nd	0.02	1.96
(muscle)	Tb3	0.02	0.04	nd	nd	nd	nd	nd	0.06	6.69
	Tb4	nd	0.05	nd	nd	nd	nd	nd	0.05	7.08
	Tb5	0.02	0.04	nd	nd	nd	nd	nd	0.06	7.11
Penguins	B1	nd	0.03	nd	nd	nd	nd	nd	0.03	1.94
(eggs)	B5	0.01	0.03	0.03	0.01	nd	nd	nd	0.07	0.91
	J1	0.01	0.05	0.01	0.03	nd	nd	nd	0.1	1.36
	D123	0.13	0.45	nd	0.03	nd	nd	nd	0.6	5.49
	D124	0.13	0.46	0.02	0.04	nd	nd	nd	0.65	6.00

* concentrations expressed in ng/g lipid weight