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HAVE THE ICEBERG B15 AFFECTED THE POPS BIOACCUMULATION IN THE ROSS SEA? THE CASE OF TREMATOMUS BERNACCHII

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Introduction

Atmospheric long range transport is the major responsible for advection of Persistent Organic Pollutants (POPs) as gases and aerosols to the polar regions. Cold condensation and subsequent bioaccumulation has led to their occurrence in polar animals, with consequent effects, ranging from interference with sexual characteristics to dramatic population losses. In the last decades, various studies have shown the presence and bioaccumulation of POPs in Antarctic fishes with concentrations sometimes higher than those found in more industrialized part of the world. Among the pollutant of greatest concern are organochlorine pesticides (i.e. DDTs, DDE, HCB, HCHs, CHLs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxins and –furans (PCDDs/Fs) and polybrominated diphenyl ethers (PBDEs). The Stockholm Convention (www.chm.pops.int) considers reducing/banning, future production, and use of these chemicals as a top priority.

Due to global warming, melting glaciers could affect not only the sea level but also represent a secondary, likely important, source of POPs in the sea waters. In fact, glaciers represent a cold trap for atmospherically-derived POPs and provide records of the deposition of POPs over time. Due to their remobilization from these reservoirs, POPs are available to enter in the Antarctic food web and thus biomagnify from the low trophic levels (e.g. larvae, krill) to the higher ones.

In March 2000, iceberg B-15, the world's largest recorded iceberg measuring about 295 km large and 37 km wide with a surface area of 11000 square kilometers, calved from the Ross Ice Shelf of Antarctica. It broke up into smaller icebergs, the largest of which was named B-15A and travelled in the open waters of the Ross Sea.

The T. bernacchii is a Antarctic fish with a widespread distribution and high abundance in near-shore seawaters; thus it is considered a good bio-indicator for contamination study, assessment of changes in Antarctic ecosystem quality (1), and temporal trend evaluation.

In this study, levels of various POPs were evaluated in Trematomus bernacchii. POP concentrations determined in different years (data from the literature) were analyzed in order to investigate their concentration trends and the possible influence of iceberg melting.

Materials and methods

In order to select the species and POPs to be used for the temporal trend evaluation, more than 300 articles were studied. The following data were taken into account for the selection of those papers reporting data on Trematomus bernacchii: year of sampling, unit of measure, species, tissue analyzed, and area of sampling. The year of sampling may be very different from the year of publication; the unit of measure can be on a wet, lipid or dry weight. Same tissues can be excised from different regions of the body; however they were recorded as muscle, liver, or whole body. Sampling areas were referred as Terra Nova Bay (TNB), Syowa Station, McMurdo Station (McM).

Results and Discussion

Table 1 shows the concentration of various POPs in T. bernacchii collected in Antarctic seawaters in the last 30 years. A decreasing temporal trend from early 1980s to 2010s can be noted (Table 1). HCB and HCHs were one and two orders of magnitude higher in 2001 with respect to 2010, respectively. The DDT concentrations were of the same order of magnitude in the years, except in 2005. After the DDT ban in 1980s, DDTs have decreased worldwide (i.e. 2; 3), but its levels remained stable in the Antarctic fish (4; 5; 6); in fact, it can still be used in some countries to control the malaria-infected mosquitos, as allowed by the Stockholm Convention.

Besides a decreasing from the late 1980s, two higher peaks of PCB concentrations were reported in 2001 and 2005 in the Ross Sea and they may reflect the ice melting of glaciers, which are known to accumulate atmospherically derived contaminants (7). Global warming is speeding the melting process of glaciers, and increasing the contaminant flow from glaciers to seawater (7). Thus, ice layers contaminated in the past may contribute to higher concentrations of organic compounds in the seawater, which become bioavailable to marine organisms. Despite the negligible iceberg activity recorded between 1992-1999 in the Ross Sea (8), a very huge iceberg (B15) calved from the Ross Ice Shelf at the beginning of 2000. The iceberg B15, the world's largest iceberg (295 km long, 37 km wide, surface area of 11000 Km2), broke up in 2000, 2002 and 2003 into more pieces, the largest of which was the B15A (9). These icebergs interacted with the polynyas during their slow movements northward the Ross Sea and they could have been important contributors of POPs to surface seawaters. In fact, the ice melting of layers contaminated in the past, could remobilize POPs and justify the PCB peak concentrations found in T. bernacchii samples in 2001 and 2005; highest concentrations were also reported in 2005 for p,p'-DDE and PBDEs (Table 1). Even if icebergs melting may be one reason of the increased POP concentrations in fish, other sources cannot be excluded: the release from old stocks, the resurfacing from deep waters and sediments, the volatilization from soils, and illegal use could contribute to a higher concentration of these pollutants. Moreover, POPs can be transported from far regions and reach Antarctic seawaters. In particular, climate change may play a key role, because warmer temperatures promote the volatilization of semi-volatile contaminants from surface water and soil, which is the first step of the long-range transport of POPs. A combination of all these processes may have affected the higher concentrations observed in 2001 and 2005.

A contribution of global warming and long-range transport is highly probable. It should be also taken into account that persistent congeners as PCB 180 and 138 did not show a similar temporal trend, and thus other congeners, i.e. lower chlorinated PCBs, may be responsible of the concentration increase. This hypothesis is also supported by Szlinder-Richert et al. (10), who reported that high- and low-chlorinated PCBs follow different accumulation features in fish species from the Baltic Sea, and suggest that PCBs 28 and 52 may accumulate through different mechanisms than high-chlorinated PCBs. In other words, PCBs 138 and 180 are persistent and not easily metabolized by fish; PCBs 28 and 52 are easily transported from the surface to the deep sea and are more volatile, thus their global mobilization and dispersion can be affected by global warming. Szlinder-Richert et al. (10) observed a decline in the high-chlorinated PCBs in herring, sprat, flounder, and salmon samples but not in cod; this declining trend was statistically significant in herring and sprat from 1997 to 2001, but they did not observe further decrease to levels lower than those from 2001. This observation agrees with our findings and might confirm a new global PCB increase at the beginning of 2000s.

Because fire risk is very high in Antarctica due to the very dry air, a large use of flame retardants in buildings and furniture of stations is highly probable; moreover, many stations were built when there were no restrictions on flame retardants use. Notwithstanding the short time span (10 years), the Figure 1 shows an increasing trend until 2005 followed by a decreasing trend from 2005 to 2011. These tendencies may be related to the reduced use and production of BDE-based flame retardant, but the influence of the B15 iceberg on the POP release of in the seawater column cannot be excluded. If we hypothesize to exclude the PBDE release from the melting icebergs, the trend could be different and two scenarios should be taken into account: stable concentrations over this decade or a slight increase of concentrations. Both these alternatives can be plausible and related to the same reasons: the continued use of BDE technical mixtures and their global transport mechanisms to Antarctica (11). A clear global trend is not evident likely because some PBDEs have been banned only recently in some countries and other technical formulations are still in use.

de Wit et al. (12) reported a temporal trend of concentrations for the lower brominated BDEs that indicates a continued increase or a tendency to levelling off or possible declines, depending on the matrix studied and the geographic location. All these considerations suggest that a clear temporal trend is not detectable worldwide because PBDE technical formulations are still in use in many countries.

The T. bernacchii can be considered a good bioindicator of the bioaccumulation processes in the Antarctic seawaters for its ecological features; due to its widespread distribution and easy collection, it is among the most studied fish species. The data published in the scientific literature seem to confirm a concentration increase of some POPs after 2000. It may be ascribed to a combination of factors including the global warming that can affect the ice melting and the global transport of POPs, resulting in a re-distribution and new availability of contaminants for bioaccumulation.

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References

1. Bargagli R., Corsolini S., Focardi S., Fossi M.C., Sanchez-Hernandez J.C., 1998. Memories of National Institute of Polar Research, 52, 220-230.
2. Corsolini S., Sarà G., Borghesi N., Focardi S., 2007. Environmental Science & Technology, 41(12), 4227-4233.
3. Eqani, SAMAS, Cincinelli, A., Mehmood, A., Malik, R.N.,Zhang, G., 2015. Environmental Pollution, 2006, 688-695.
4. Borghesi, N., Corsolini, S., Focardi, S., 2008. Chemosphere, 73, 155-160
5. Corsolini, S., A. Covaci, N. Ademollo, S. Focardi and P. Schepens. 2006. Environmental Pollution, 140, 371-382.
6. Cincinelli A., Martellini T., Pozo K., Kukučka P., Audy O., Corsolini S., 2016. Environmental Pollution. Available on line 14 January 2016, ISSN 0269-7491.
7. Geisz H.N., Dickhut R., Cochran M.A., Fraser W.F., Ducklow H.W., 2008. Environmental Science & Technology, 42 (11), 3958–3962
8. Martin, S., Drucker, R.S., Kwok, R., 2007. Journal of Marine System, 68, 201-214.
9.NASA, 2014. Available online at http://www.natice.noaa.gov/doc/NATICE_Press%20Release_Ant%20Iceberg_9_16_2014_released.pdf, 25 September 2015).
10. Szlinder-Richert, J., Barska I., Mazerski, J., Usydus, Z., 2009. Marine Pollution Bulletin, 58, 85–92.
11. Wania F., 2003. Environmental Science & Technology, 37, 1344- 1351.
12. de Wit, C.A., D. Herzke and K. Vorkamp. 2010. Science of Total Environment, 408 (15) 2885-2918.

Table 1: Concentration of POPs in the tissues of *Trematomus Bernacchii* (TNB = Terra Nova Bay, McM = McMurdo).

YoS	wt basis (ng/g)	Tissue	Site	p,p'-DDE	SD/range	DDTs	SD/range	HCB	SD/range	HCHs	SD/range	PCDDs	SD/range	PCDFs	SD/range	References
1981	wet wt	whole	Syowa			0.7	0.5-0.7									Subramanian, 1983
1981	wet wt	muscle	Syowa			0.63										Hidaka et al., 1984
1989	dry wt	muscle	TNB	2.24	1.15	4		0.27	0.2							Focardi et al., 1992
1989	dry wt	liver	TNB	52.7	23.5-75.6	67		3.4	1.3							Focardi et al., 1992
1992	wet wt	liver	TNB													Focardi et al., 1995
1995	wet wt	muscle	TNB									0.08		0.14		Kumar et al., 2002
1999	wet wt	muscle	TNB	0.16	0.09			2.6	3.5			0		0		Corsolini et al., 2003
2001	wet wt	muscle	TNB	2.53	4.67	8.6	5.67	1.44	0.45	1.35	0.72					Corsolini et al., 2006
2003	lipid wt	whole	McM													Hale et al., 2008
2005	wet wt	muscle	TNB									0.0061	0.003-0.0095	0.019	0.0093-0.039	Borghesi et al., 2008
2005	wet wt	liver	TNB									0.013	0.0028-0.0019	0.026	0.011-0.038	Borghesi et al., 2008
2010-11	wet wt	muscle	TNB			0.43	0.11-1.17	0.12	0.003-0.37	0.036	0.018-0.061					Cincinelli et al., 2016

YoS	wt basis (ng/g)	Tissue	Site	CHLs	SD/range	PBDEs	SD/range	BDE47	PCBs	SD/range	PCB180	SD	PCB138	SD	PCB153	
1981	wet wt	whole	Syowa						0.18	0.12-0.24						Subramanian, 1983
1981	wet wt	muscle	Syowa	0.43					0.25							Hidaka et al., 1984
1989	dry wt	muscle	TNB						12.8							Focardi et al., 1992
1989	dry wt	liver	TNB						186		19.7	12.4	32.7	20.8		Focardi et al., 1992
1992	wet wt	liver	TNB						21	15-44	2.44		0.5			Focardi et al., 1995
1995	wet wt	muscle	TNB						0.15		0.07 – 0.17					Kumar et al., 2002
1999	wet wt	muscle	TNB						6.35	4.5						Corsolini et al., 2003
2001	wet wt	muscle	TNB	2.61	2.07	0.05	0.02	0.043	6.35	4.8	0.0951		0.34		0.42	Corsolini et al., 2006
2003	lipid wt	whole	McM			0.17	0.115-0.18									Hale et al., 2008
2005	wet wt	muscle	TNB			0.35	0.220-0.530		1.65	0.35-4.20	0.056		0.068			Borghesi et al., 2008
2005	wet wt	liver	TNB			0.79	0.005-1.100		15	5.20-28	1.2		0.054			Borghesi et al., 2008
2010-11	wet wt	muscle	TNB			0.075	0.02-0.137		0.084	0.001-0.01						Cincinelli et al., 2016

YoS = Year of sampling
wt = weigth
SD = standard deviation

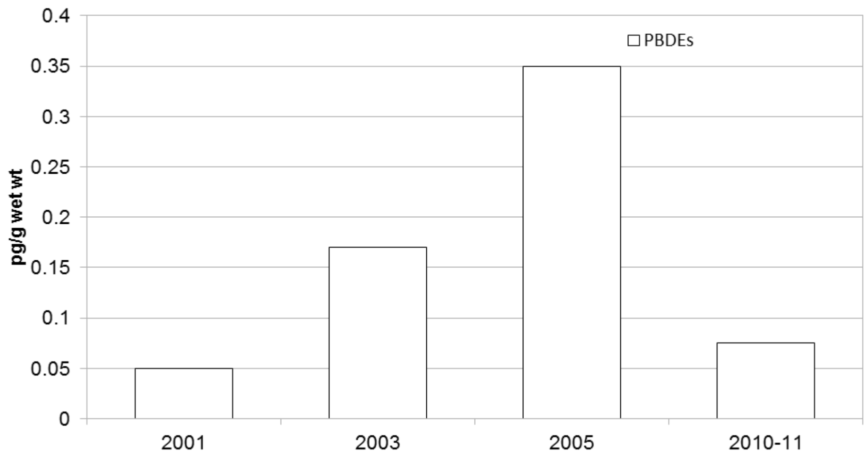

Figure 1: Concentration of PBDEs (pg/g wet wt) in the muscle tissues of the *T. bernacchii* (see Table 1 for references).