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## Hexachlorocyclohexanes in Arctic and Antarctic Marine Ecosystems

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### 1. Introduction

Pesticides are a group of chemicals made for the purpose of killing or otherwise deterring “pest” species. The word pesticides may refer to insecticides, fungicides, herbicides or other pest control formulations. Introduced in 1940s, organochlorine pesticides (OCPs) were widely used as insecticides in agriculture and pest control until research and public concern regarding the hazards of their use and adverse effects in the environment led to government restrictions and bans. Two International legally binding instruments have been negotiated and concluded: the Protocol to the regional United Nations Economic Commission for Europe Convention on Long Range Transboundary Air Pollution (CLRTAP) on Persistent Organic Pollutants (POPs), opened for signature in June 1998 and entered into force on 23 October 2003 and the Stockholm Convention on POPs, opened for signature in May 2001 and entered into force on 17 May 2004. Both these agreements identify POPs that should be banned and/or phased out or whose use or emissions should be restricted, they include industrial chemicals and by-products such as PCBs, hexachlorobenzene, dioxins and furans, and a number of OCPs such as aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. All together are often called the “dirty dozen” (Stockholm Convention, 2004). The hexachlorocyclohexanes (HCHs) are covered by the UNECE Protocol but not the Stockholm Convention. For several listed substances, some limited use is allowed, for example DDT for fighting malaria. Despite the actions of these two Conventions, POPs are still present at high levels in the polar regions and will require vigilant action in the continuing implementation of the Conventions to prevent further contamination of these rich and productive ecosystems.

OCPs are organic chemical substances which possess a particular combination of physical and chemical properties and once released into the environment they remain intact for long periods of time (from weeks to decades). They are persistent that is they resist to environmental degradation through chemical, biological and photolytic processes. They are toxic to both humans and wildlife and accumulate in the fatty tissue of living organisms (bioaccumulation), and are found at higher concentrations at higher levels of the food webs (biomagnification). They are subjected to long range transport (LRT) and can be found in remote regions, including Arctic and Antarctica, where they have never been used or produced (i.e.: Su et al., 2006; Bargagli, 2008; Corsolini, 2008; Rigét et al., 2010; Donaldson et al., 2010)

The transport of POPs in the Northern and Southern hemispheres is a well documented phenomenon. POPs are thought to be transported such long distances by a variety of processes including:

- a process known as global distillation (Wania and Mackay, 1993; 1996), according to which POPs with sufficiently high vapour pressure evaporate from the warmer regions, (where they are used or released), and then move through the atmosphere, condense at colder and high latitudes, finally concentrating in Arctic and Antarctic. According to this process, POPs of higher volatility like HCHs may migrate faster towards the poles than those of lower volatility such as DDTs;
- migration through ocean circulation;
- deposition by means of wet (snow, rain, mist) or dry depositions (i.e. atmospheric processes (particle settling)) onto terrestrial and aquatic surfaces;
- transport through migratory animals which are thought to offload their body burdens into polar ecosystems through their excretion and during body decomposition (Wania, 1998).

The fate and different transport routes of a POP are strongly influenced by its specific physical and chemical properties such as water solubility, vapour pressure (VP), Henry's law constant (H), octanol-water partition coefficient ( $K_{ow}$ ) and the carbon-water partition coefficient ( $K_{oc}$ ).

## 2. POPs in polar regions

The polar regions are of great intrinsic value and vital importance for the conservation of biological diversity.

Even though the Antarctic is still the region of the earth that is the least influenced by human activity, strict regulation is needed to maintain its untouched and pristine condition today. Most of the Antarctic region is situated south of 60°S latitude and is governed in accordance with the International legal regime of the Antarctic Treaty System. The Protocol on Environmental Protection to the Antarctic Treaty, which came into effect in 1998, designates Antarctica as an internationally important natural reserve devoted to peace and science, and provides a comprehensive environmental management regime. The Treaty area cover the continent itself as well as the archipelagos of the South Orkney Islands, South Shetland Islands, Peter Isalan, Scott Island and Balleny Island. Antarctica and the Southern Ocean are a remote region with no indigenous human population and no industrial and agriculture activities. Human impact is concerned largely with scientific investigations and the logistic operations in support of these. As a result of Antarctica's designation as a Special Conservation Area, many countries that maintain research stations in Antarctica have improved management practises and developed strategies to reduce environmental disturbances. The protection of the Antarctic Environment is the primary responsibility of the Antarctic Treaty Parties and the release of POPs into the Antarctic environment is incompatible with the comprehensive approach of the Protocol. Therefore, the obligation to monitor the introduction of these substances is vested upon the Parties to the Protocol and practices have been improved and importation of specific POPs has been prohibited. However, LRT remains an important process by which POPs contaminate the Antarctic environment.

In the last decades, extensive international cooperation has also been developed in several fields in the Arctic region as well. The Arctic Monitoring and Assessment Programme

(AMAP) is the first international programme to design and develop monitoring programmes to study the sources, transport mechanisms and pathways, levels, fate and behaviour of most of the groups of contaminants, including POPs, in the Arctic environment and its ecosystems (atmospheric, marine, terrestrial, humans). Further aims of the AMAP are to prevent releases of radioactive substances and emissions of other hazardous chemicals and provide scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions relating to contaminants. AMAP is one of the six scientific Working Groups of the Arctic Council (Arctic Contaminants Action Program - ACAP, AMAP, Conservation of Arctic Flora and Fauna - CAFF), Emergency, Prevention, Preparedness and Response - EPPR), Protection of the Arctic Marine Environment - PAME and SDWG) a forum of cooperation between the eight Arctic countries (Canada, Greenland (Denmark), Finland, Iceland, Norway, Russia, Sweden and United States), and also between national governments and indigenous peoples.

POPs are now distributed in the global environment and their accumulation of organochlorine pesticides in Northern and Southern latitudes has been extensively documented. In particular, HCHs have been extensively used throughout the world and this factor in combination with a relatively high vapour pressure, a low octanol-air partition coefficient, a low Henry's law constant and the highest water solubility of all organochlorines (Harner *et al.*, 1999, Brubaker and Hites, 1998, Gregor and Gummer, 1989, Kucklick *et al.*, 1991) is reflected in the relative abundance of these compounds in Arctic and Antarctic ecosystem compartments.

Most of the associated literature focuses on the occurrence and levels of HCHs in air and on the study of air/water exchanges fluxes (UNECE, 1998; Hargrave *et al.*, 1997), while only a little number of papers can be found dealing with water samples probably due to the difficulty involved in determination of very low concentrations of these contaminants in the Arctic and Antarctic seawaters. However seawater is an almost unique passage where pollutants transfer from the atmosphere or rivers to the shallow water. It is also a significant path way for OCPs accumulated in the plankton and therefore enter the terrestrial food webs of the polar regions (Cai *et al.*, 2010).

This review reports the levels, trends and distribution of HCHs in water and biota of both polar regions. The accumulation in marine organisms will be described; in particular, krill, fish, seabirds and seals will be considered. Moreover, the  $\alpha$ -HCH enantiomeric composition in the Arctic and Southern oceans will be reviewed in order to evidence the presence of environmental biochemical processes.

## 2.1 Hexachlorocyclohexanes

Hexachlorocyclohexane (HCH), also known as benzene hexachloride (BHC), is one of the most widely studied pesticides with respect to its environmental fate and effects (Breivick *et al.*, 1999). It is an organochlorine insecticide that is available in two commercial formulations: technical grade and lindane.

Technical HCH was heavily used and it is an ubiquitous pesticide introduced in world war II and consists of a mixture of different isomers  $\alpha$ -HCH (60-70%),  $\beta$ -HCH (5-12%),  $\gamma$ -HCH (10-15%),  $\delta$ -HCH (6-10%) and  $\epsilon$ -HCH (3-4%) (Kutz *et al.*, 1991). Because of its low cost and high effectiveness, HCH was one of the most widely used insecticides in the world (Li, 1998). The insecticidal properties of HCH were first discovered in Europe in 1941-1942,

however, in 1944 it was found that the  $\gamma$ -isomer is the only HCH isomer responsible for these properties (Hardie, 1964). Lindane is the  $\gamma$ -HCH (>99% pure) (UNEP, 2006). Lindane has been used as a broad-spectrum insecticide, which acts by contact, against a wide range of insects. Its main uses include treatment of seeds, on crops, in warehouses, in forestry, on domestic and agricultural animals, and for pest control of scabies and lice on humans (WHO, 1991).

	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH
Molecular weight	290.85	290.85	290.85
Structural code Axial/Equatorial	AAEEEE	EEEEEE	AAAE EE
Melting point (°C)	159.5	309.5	112.5
Boiling point (°C)	288 at 760 mmHg <sup>1</sup>	60 at 0.5 mmHg <sup>2</sup>	323.4 at 760 mmHg <sup>1</sup>
Vapour Pressure <sup>1</sup>	$4.5 \times 10^{-5}$ mmHg at 25°C	$3.6 \times 10^{-7}$ mmHg at 20°C	$4.2 \times 10^{-5}$ mmHg at 20°C
Henry's law constant <sup>3</sup>	$\text{LogH}_a = 10.13(\pm 0.29) - 3098(\pm 84)/T$	$\text{LogH}_b = 9.96(\pm 0.23) - 3400(\pm 68)/T$	$\text{LogH}_\gamma = 10.14(\pm 0.59) - 3208(\pm 161)/T$
Log K <sub>ow</sub> <sup>4</sup>	3.94	3.9	3.9
Log K <sub>oc</sub> <sup>5</sup>	3.57	3.57	3.57

Table 1. Physical and chemical properties of key HCHs (References: 1.HSDB, 2003; 2. Lide, 1991; 3. Sahsuvar et al., 2003; 4. Shen et al., 2004; Willett et al., 1998; 5. Weiss, 1986)

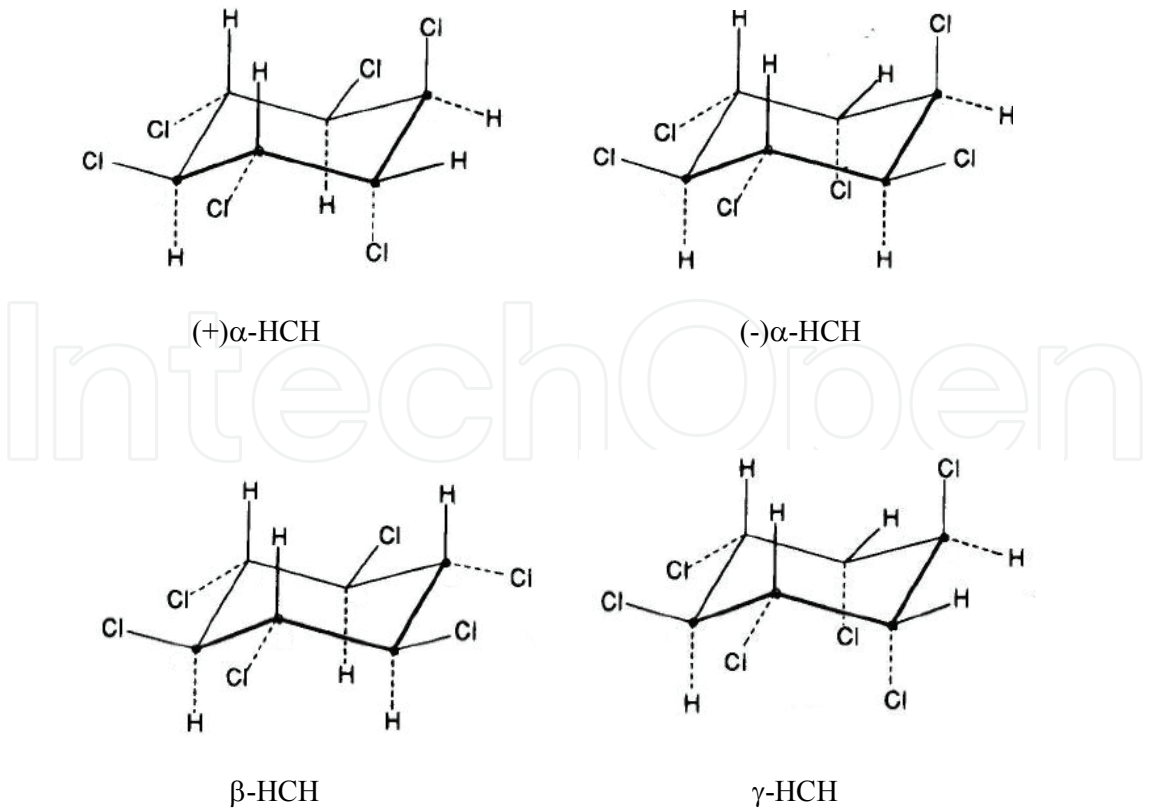


Fig. 1. Structure of the principal HCH isomers ( $\alpha$ ,  $\beta$  and  $\gamma$ )



Because of the environmental and biological persistence of HCHs, many developed countries banned or restricted technical HCH usage since 1970s, a ban followed by many developing countries in 1980s (Voldner and Li, 1993). In 2009, an International ban on the use of lindane in agriculture was implemented under the Stockholm Convention on POPs. A specific exemption allows for it to continue to be used in second-line treatments for the head lice and scabies for 5 more years.

Distribution, transportation and fate of HCHs in the environment is strongly influenced by the different physical and chemical properties of the various isomers and these are, to a great extent, responsible for the vast differences in the fates of the  $\alpha$ ,  $\beta$  and  $\gamma$ -isomers.

The chemical structures and chemical-physical properties of the key HCHs are reported in Table 1 and Figure 1.

## 2.2 Antarctica

### 2.2.1 The marine environment

The Southern Ocean occupies a belt between 55-70°S. The more southerly part of this zone is covered by sea ice for all or part of the year. Water temperatures vary very slightly in both time and space. Summer temperatures may be as high as 3-4°C in the northern part of the Southern Ocean, decreasing to slightly below zero close to the continent. The annual range of water temperature is typically only a few degrees. Despite this apparently hostile environment, the Southern Ocean supports a diverse biota, in strong contrast to Antarctic terrestrial ecosystems that is a cold desert. The region supports a number of fisheries, some of which are of global importance.

### 2.2.2 HCHs in Antarctic seawater

Relatively few investigations have been carried out to determine HCHs content in Antarctic seawater. The first HCHs data in seawater samples were reported by Tanabe et al. (1982a, b) who found the sum of HCHs ranging from 260 to 920 pg/L during an Antarctic supply voyage between Japan and the Syowa Research Station in 1980-1981. Similar total HCH concentrations (210-930 pg/L) were determined in seawater samples collected close to Syowa Station, not showing strong variations between samples collected under fast ice and at the outer margins of pack ice (Tanabe et al., 1983). Authors found mean  $\alpha$ -HCH concentrations of 3.2 pg/L in 2002 and 1.41 pg/L in 2003-2004, showing little spatial and temporal variability during each sampling period. These values were lower than those measured in 1989-1990 (18-43 pg/L) (Iwata et al., 1993), 1997 (3.6-15 pg/L), 1997-1998 (5.1-28 pg/L) (Jantunen et al., 2004), and 1999 (2-9.6 pg/L) (Lakaschus et al., 2002).

Desideri et al. (1991) and Cincinelli et al (2009) measured the concentrations of HCHs in surface seawater samples collected at Terra Nova Bay in the spring-summer periods 1988-1989 and 2003-2004, respectively. They found mean  $\alpha$ -HCH concentrations of 129 ( $\pm 42$ ) and 3.13( $\pm 0.89$ ) pg/L, and mean  $\gamma$ -HCH concentrations of 562 ( $\pm 335$ ) and 7.11 ( $\pm 1.22$ ) pg/L, respectively. Desideri et al. (1991) found a mean of 147 $\pm 25$  pg/L of  $\alpha$ -HCH and 470 $\pm 229$  pg/L of  $\gamma$ -HCH in sea-ice samples and these values were higher than those measured in seawater samples; they hypothesized that POPs are accumulated during winter in the sea ice and then released into the seawaters during the seasonal ice melting, which contribute to the Summer POP increasing concentration in the seawater. This hypothesis was also confirmed by Cincinelli et al. (2009), who found higher HCH concentrations in the seawater

samples collected at Terra Nova Bay than those measured later in the Ross Sea ( $\alpha$ -HCH  $1.08 \pm 0.40$  and  $\gamma$ -HCH  $2.12 \pm 1.08$ ), as well by Dickhut et al. (2005), who detected higher levels of  $\gamma$ -HCH in surface water collected during the early part of the summer in the vicinity of Palmer Station on the western Antarctic Peninsula in 2002. These authors found concentrations of  $\alpha$ -HCH ranging from 1.65 to 4.54 (mean value  $3.20 \pm 0.82$ ) pg/L, and concentrations of  $\gamma$ -HCH ranging from 0.90 to 10.6 (mean value  $4.09 \pm 4.08$ ) pg/L in seawater samples.

### 2.2.3 HCHs in Antarctic biota

The scientific literature on the presence of HCH isomers in Antarctic organisms is very scarce, owing to the difficulty of collecting biotic samples in such an extreme environment, the distance from any part of the world, the very high cost of scientific expeditions and the need to be part of one of those to be allowed to reach the continent and collect organism samples, whose collection need special internationally valid permits released by a commission of the Antarctic Treaty. Moreover, data are often reported in different ways and thus no comparisons are allowed owing to different tissues, unit of measures (on a lipid, wet, or dry wt), chemicals analyzed, and species. The presence of HCHs in Antarctic marine organisms has been reported in few articles since 1960s.

The presence of HCHs in krill (*Euphausia superba*) and in Emperor penguin (*Aptenodytes forsteri*) feathers was reported first by Sen Gupta et al (1996); they detected  $141.3 \pm 9.8$  -  $164 \pm 16.6$  pg/g dry wt of  $\alpha + \gamma$ -HCHs in krill, and  $108.7 \pm 7.6$  -  $112.5 \pm 8.6$  pg/g dry wt in penguin feathers collected in 1987 near the Indian Station Daksin Gangotri ( $70^{\circ}05'S$ ,  $12^{\circ}00'E$ ). They reported that the  $\gamma$ -isomer was the most abundant in both species. Twenty years later, Bengston-Nash et al. (2008) found 0.03 ng/g wet wt of HCHs; the most abundant isomers were  $\alpha$ -HCH >  $\beta$ -HCH >  $\delta$ -HCH (14.2, 9.3, and 6.9 pg/g wet wt, respectively). HCH concentrations in the Antarctic Peninsula were 0.009 ng/g lipid wt in samples collected in 2001 (Chiuchiolo et al. 2004) and 0.25 ng/g wet wt (0.14-0.35 ng/g wet wt) in samples collected in 2005 at King George Is. (South Shetlands). Concentrations in krill samples collected in the Ross Sea were reported by Corsolini et al. (2006) and Cincinelli et al., (2009) and they were  $0.28 \pm 0.04$  ng/g wet wt and  $0.11 \pm 0.07$  ng/g wet wt, respectively. Notwithstanding the difference in the unit of measure, samples collected in 1980s seems to be more contaminated than those collected in the 2000s; moreover, the Indian Sector of the Southern Ocean showed lower levels than the Ross Sea in 2000s.

Data in fish are very scarce. A paper reported  $1.35 \pm 0.72$  ng/g wet wt of  $\Sigma$ HCHs in the emerald rockcod (*Trematomus bernacchi*) muscle, where  $\gamma$ -HCH was the principal contributor ( $1.23 \pm 0.67$  ng/g) (Corsolini et al., 2006). Usually  $\beta$ -HCH is stable in animals, but it is less volatile than  $\alpha$ - and  $\gamma$ -HCH, thus it can reach the Polar Regions less easily than other HCH isomers, due to the global fractionation (Wania and Mackay, 1993).  $\beta$ -HCH concentration in Arctic atmosphere (Li et al., 2003) and in some species of seal and whale (Willett et al., 1998) is very low in comparison with the more volatile  $\alpha$ - and  $\gamma$ -HCHs. Several industrial countries such as Canada, European Countries and the U.S. have banned HCHs since the 1970s. However, a few developing countries from tropical belt continued to use Lindane (pure  $\gamma$ -HCH) until the 1990s (Li et al., 1996, 2003; Senthil Kumar et al., 2002); this would have influenced  $\gamma$ -HCH occurrence in Antarctic food webs.

The HCH contamination in seabirds will be discussed in reference to penguins; in fact, among seabirds, penguins spend all their life cycle in the Antarctic Ocean; other seabird species nest in Antarctica during Summer, but they overwinter northward, often in non-Antarctic seawaters. Thus they can accumulate higher burdens of contaminants and they do not reflect exactly the contamination status of the Antarctic ecosystems (Corsolini, 2009). Penguins feed mainly on krill and they are a good indicator of HCH contamination; many different chemical families have been studied in various species since 1960s (for a review see Corsolini, 2009). Data of HCH presence in their tissues were first reported in 1985: Schneider et al. (1985) detected  $\gamma$ -HCH in Adélie penguin fat (*Pygoscelis adeliae*) (73 ng/g lipid wt), and Emperor penguin fat (26 and 118 ng/g lipid wt). The figure 2 shows the  $\Sigma$ HCH concentrations in Adélie, Chinstrap (*Pygoscelis antarctica*) and Gentoo (*Pygoscelis papua*) penguins from different regions of Antarctica and collected from 1988 to 2005. Levels ranged between below the detection limit in Adélie penguin muscle from King George Island to 5 ng/g wet wt in blood of Gentoo penguin from the same area (Inomata et al., 1996). The minimum and maximum concentrations found ranged from 0.25 to 1.32 ng/g wet wt in Adélie penguin, from 0.17 to 2.28 ng/g wet wt in Chinstrap penguin, and from 0.1 to 5 ng/g wet wt in Gentoo penguin, showing a weak increase of concentration in Gentoo > Chinstrap > Adélie penguins. These penguin species nesting at King George Island share the same environment and have adopted a fine ecological segregation to reduce niche overlap and food competition (Trivelpiece et al., 1987). In fact, all the Pygoscelid species are usually very synchronous in nesting, while the breeding chronologies of these populations are asynchronous (Trivelpiece et al., 1987). Chicks hatched at approximately 2 week intervals, with Adélie penguin being the earliest and Chinstrap penguin the latest to hatch annually. Asynchronous breeding chronologies greatly reduce competition for food between species during chick rearing. At the same time, this asynchrony may affect the HCH accumulation;

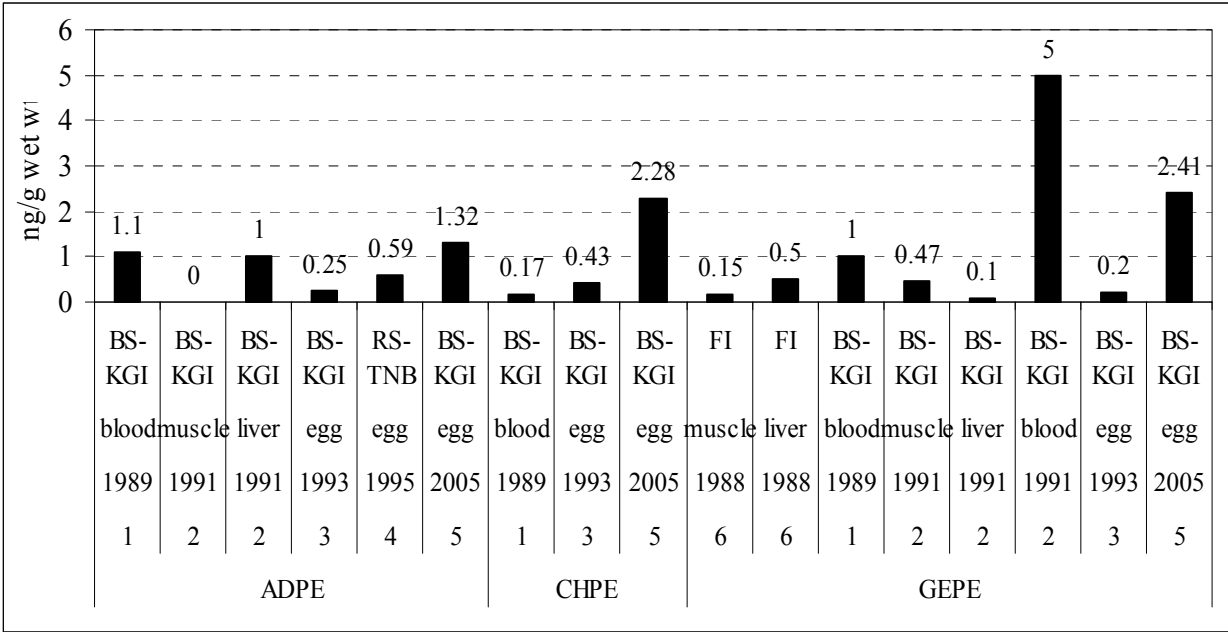


Fig. 2.  $\Sigma$ HCH concentrations (ng/g wet wt) in tissues of Adélie (ADPE), Chinstrap (CHPE), and Gentoo (GEPE) penguins from King George Island (BS-KGI) and Falkland Islands (FI) (YoS = year of sampling; Refs = references: 1. Lara et al., 1990; 2. Inomata et al, 1996; 3. Wanwimolruk et al., 1999; 4. Corsolini et al., 2006; 5. Cipro et al., 2010; 6. de Boer et al., 1991).



in fact, large amounts of HCH pesticides are used in tropical and temperate regions during Summer, with resulting HCH increasing levels in the Antarctic environment in Summer and Autumn (Larsson et al., 1992). The seasonality of HCH transport to Polar Regions has already been reported, and it affects also the accumulation in Antarctic organisms (Sen Gupta et al., 1996; Corsolini et al., 2000). Interestingly, the HCH concentrations in Adélie, Chinstrap and Gentoo penguin eggs increased from 1993 (Wanwimolruk et al., 1999) to 2005 (Cipro et al., 2010) (figure 3). This pattern may be due to the historical use of HCH-based pesticides worldwide and in particular in American, European and some Asiatic countries: after a massive use until the 1970s and 1980s, governments started to ban their use and production. First, levels continued to increase as a result of their global transport and dispersion, but then concentrations in biota showed a light decrease followed by the reduced use. The new increase observed at the end of 1990s can be as a result of a couple of reasons. The first reason can be the slow release of these chemicals from legal or illegal stocks. Secondly, the releases from the final sink as deep oceanic sediments and waters that may follow natural cycles in the marine ecosystems. Increasing concentration trends have been observed in other Antarctic species and also for other chemicals (Aono et al., 1997; Corsolini, 2009; Corsolini, 2011).

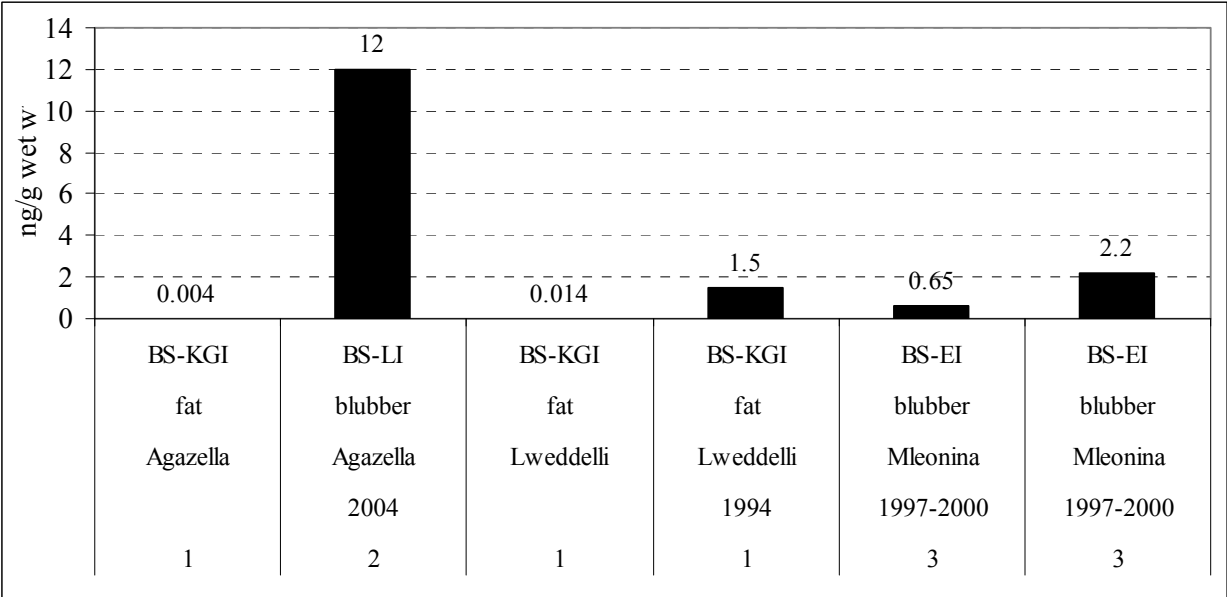


Fig. 3. ΣHCH concentrations (ng/g wet wt) in tissues of fur seal (*Agazella*), Weddell seal (*Lweddelli*), and elephant seal (*Mleonina*) from King George Island (BS-KGI), Livingston Island (BS-LI), and Elephant Island (BS-EI) (YoS = year of sampling; Refs = references: 1. Vetter et al., 2001; 2. Schiavone et al., 2009; 3. Miranda-Filho et al., 2007).

There are few articles that report HCH levels in Antarctic seals. HCH were very low in the fur seal (*Arctocephalus gazella*) from King George Island, 0.04 ng/g wet wt, and in the Weddell seal (*Leptonychotes weddelli*), 0.014 ng/g wet wt (Vetter et al., 2001). HCH higher concentrations were reported in specimens of Weddell seal and elephant seal (*Mirounga leonina*). Schneider et al. (1985) detected 13 and 20 ng/g lipid wt in the Weddell seal blubber, and 39 and 103 ng/g lipid wt in the Crabeater seal blubber (*Lobodon carcinophagus*), collected in 1981. The β-HCH prevailed in samples of fur seal from Livingstone island, where the

isomer pattern abundance was  $\beta\text{-HCH} > \alpha\text{-HCH} > \gamma\text{-HCH} > \delta\text{-HCH}$  (Schiavone et al., 2009). The pattern was  $\gamma\text{-HCH} > \alpha\text{-HCH} > \beta\text{-HCH}$  in the elephant seal (Miranda-Filho et al., 2007). A temporal trend of HCH concentration in Antarctic organisms is not evident mainly because of the paucity of data available. Extreme environments promote the selection of peculiar adaptations like the use of lipids to store energy, to protect against cold, to aid buoyancy in fish; the presence of this lipid component may affect the concentrations of lipophylic contaminants such as HCHs in relation to the season and period of the biological life cycle during which sampling is carried out. Therefore, HCH concentrations may vary depending on all such factors. Similar patterns have been reported also for other families of POPs in most of the species analyzed and collected in Antarctic seawaters (for a review see Corsolini et al., 2009).

## 2.3 Arctic

### 2.3.1 The marine environment

The Arctic region can be defined as the area north of the Arctic circle (63°33'N). It covers an area of approximately 13.4 million km<sup>2</sup> and large tracks of land are covered by glacial ice. The Arctic includes the Arctic Ocean and parts of Canada, Greenland, Russia, the United States (Alaska), Iceland, Norway, Sweden and Finland. The Arctic marine area includes the Arctic Ocean, the adjacent shelf seas (Beaufort, Chukchi, East Siberian, Laptev, Kara and the Barents Sea), the Northern Seas (Greenland, Norwegian and Iceland seas), the Labrador Sea, Baffin Bay, Hudson Bay, the Canadian Arctic Archipelago and the Bering Sea. The connection with the shallow Bering Sea occurs through the narrow Bering Strait, while the main connection with the Atlantic Ocean is via the deep Fram Strait and the Nordic Seas. The Arctic Ocean is divided into two deep basins, the Eurasian and the Canadian by the transpolar Lomonosov Ridge (AMAP 1998), extending as a submarine bridge about 1060 miles from Siberia to the northwestern tip of Greenland. Parallel to it there are two shorter ridges: the Alpha Ridge on the North American side, defining the Canada and Makarov basins, and the mid-ocean ridge on the Eurasian side, defining the Nansen and Fram basins. Due to ice coverage the temperature of the Arctic Ocean is close to freezing point year round. Surface water salinities vary between 30-33 in the Arctic Ocean. The salinity is lower in the summer due to the input of freshwater from rivers and terrestrial ice melting (AMAP, 1998).

The Arctic ocean is considered a sink for global pollution because of the flow of oceanic and atmospheric currents. It is a fragile ecosystem threatened by land-based sources of pollution particularly POPs and heavy metals (Lystsov, 2006). Principal loadings of HCHs to the Arctic Ocean during the last decades occurred by atmospheric transport and air-water exchange, precipitation and riverine input, and migration through north flowing ocean currents (Li et al., 2004). However the relative inputs by these pathways varied over time and differed for the eastern and western sides of the Arctic Ocean which have been termed the North American Arctic Ocean (NAAO) and Eurasian Arctic Ocean (EAO) (Bidleman et al., 2007).

### 2.3.2 HCHs in Arctic sea-water

Seawater samples were collected from a few limited number of cruises under taken throughout the 1980s to 2000s in different regions of the Arctic Ocean. The most extensive database on HCH concentrations in Arctic seawater samples belongs to the Bering and

Chukchi Seas where several cruise expeditions occurred, mainly organised by Japan, USA, Canada and former USSR.

An USSR/US investigation was begun in 1984 in the Bering and Chukchi Seas to study the transport of agricultural chemicals such as pesticides and other persistent pollutants (Chernyak et al., 1995). Results showed that  $\alpha$ -HCH concentrations ranged from 810 to 1220 pg/L on the transect from the Sea of Japan to the Bering Sea, and a trend of increasing concentration with increasing latitude was observed ( $r^2 = 0.88$ ). This correlation is proved to be even stronger when average concentrations and latitudes from the Bering and Chukchi Seas and the Chirikov Basin were included in the regression ( $r^2 = 0.99$ ) (Chernyak et al., 1992), an increasing of with  $\alpha$ -HCH concentrations from 800 pg/L in the South China Sea to 2500 pg/L in the Chukchi Sea. This trend for  $\alpha$ -HCH concentration may reflect the effect of much colder surface water temperatures in the polar seas, because the Henry's law constant of  $\alpha$ -HCH decreases with decreasing water temperature, thus favouring deposition to the water phase. However the same trend was not observed for the  $\gamma$ - and  $\beta$ - isomers which ranged from 770 to 1150 pg/L and from 80 to 740 pg/L, respectively.

Mean concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH of 7.1 and 0.8 ng/L, respectively, were reported by Patton et al. (1989) for four seawater samples collected over a depth of 1-10 m from the Ice island in the Beaufort Sea in June 1987. In the same area Hargrave et al. (1988) measured  $\alpha$ -HCH levels in seawater samples at different depths and found average values of 4249 pg/L at 0-60 m, 2030 pg/L at 75-200 m and 320 pg/L at a depth >200 m in May 1986, average values of 5430 pg/L at 0-60 m, 2230 pg/L at 75-175 m in August 1986 and average values of 2820 pg/L at 10 m and 1440 pg/L at 110 m in June 1987. In general, concentrations of HCHs were maximum in the upper 60 m layer with decreasing values towards greater depths. The observed vertical distribution of  $\alpha$ -HCH and other OCPs observed in this study indicated a source in the upper low salinity surface layer, probably a direct exchange between atmosphere and ocean (sea ice). In fact, most relevant inputs of pesticides into the Arctic marine environment may be atmospheric, riverine and oceanic transport even if the relative importance of each of these sources is difficult to assess.

Similar concentrations of  $\Sigma$ HCH (5-7 ng/L) in the Beaufort Sea were also reported by McDonald and McLaughlin (1993, 1994) for surface water samples collected between 1992 and 1993. Graphical presentation of data in Mc Donald et al. (2000) indicated levels for both isomers of 0.4-0.8 ng/L.

On the third Soviet-American Joint Ecological Expedition to the Bering and Chukchi Seas (August 1988), seawater samples were collected and analysed for OCPs. Average  $\alpha$ -HCH concentrations in surface water samples were 2.4 ng/L, and average  $\gamma$ -HCH concentrations were 0.6 ng/L (Hinckley et al., 1991). In the same seas, Iwata et al (1993) collected seawater samples during the period between April 1989 and August 1990 reporting no differences between the mean concentration values of  $\alpha$ -HCH (1.5 ng/L (range 1.2-1.9 ng/L) and 1.4 ng/L (range 1.3-1.6 ng/L)) and  $\gamma$ -HCH (0.190 ng/L (range 0.160-0.230 ng/L) and 0.180 ng/L (range 0.150-0.220 ng/L)), in the Bering and Chukchi Seas, respectively.

Paired air and water samples were collected at Resolute Bay (74°N, 95°W) in summer 1992 to estimate the direction of gas exchange of HCHs and investigate possible loss processes in the water column (Bidleman et al., 1995; Falconer et al., 1995). Average concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH in ocean surface water were  $4.75 \pm 0.9$  and  $0.44 \pm 0.11$  ng/L, respectively. Water/air fugacity ratios were 1.03 for  $\gamma$ -HCH and 1.57 for  $\alpha$ -HCH, indicating a slight potential for volatilization of  $\alpha$ -HCH. The average concentration of the sum of  $\alpha$ -HCH and

$\gamma$ -HCH (5100 pg/L) (Bidleman et al., 1995; Falconer et al., 1995) was higher than values from Bering Sea and Chukchi Sea (1600 -3400 pg/L) reported by Iwata et al.(1993) and Kawano et al.(1988) (mean  $\alpha$ -HCH 2800 pg/L,  $\gamma$ -HCH 610 pg/L).

During August-September 1993 a joint Russian -US expedition to the Bering Sea and Chukchi Sea took place and surface water samples (from 1 to 2 m) were collected from 21 sites. Highest water concentrations were observed for HCH in open waters north and south of the Bering strait, both regions being similar ( $\alpha$ -HCH 2.2 ng/L and lindane 0.35 ng/L) (Strachan et al., 2001). The water-air fugacity for the HCHs indicated that  $\alpha$ -HCH is degassing in both Bering and Chukchi Seas while  $\gamma$ -isomer is degassing in Bering Sea but it is close to equilibrium in the Chukchi Sea (Strachan et al., 2001).

In the summers of 1993 and 1994, seawater samples from the surface layer (40–60 m) were collected to determine the spatial distribution of organochlorine pesticides on expeditions that crossed the Arctic Ocean from the Bering and Chukchi Seas to the North Pole, to a station north of Spitsbergen, and then south into the Greenland Sea (Jantunen and Bidleman, 1998). In the upper 40 m of the northern Chukchi Sea,  $\alpha$ -HCH and  $\gamma$ -HCH averaged  $2.06 \pm 0.48$  ng/L and  $0.43 \pm 0.09$  ng/L. In the polar mixed layer (60 m) of the western Arctic Ocean  $\alpha$ -HCH and  $\gamma$ -HCH averaged  $2.42 \pm 0.23$  ng/L and  $0.47 \pm 0.11$  ng/L. Concentrations were 2–3 times lower than these means at two stations near Spitsbergen and one station in Greenland Sea, averaging  $0.87 \pm 0.22$  ng/L for  $\alpha$ -HCH and  $0.20 \pm 0.03$  ng/L for  $\gamma$ -HCH. Thus, HCHs in the upper 40–60 m increased from the Chukchi Sea to the pole, and then decreased toward Spitsbergen and Greenland Sea.

Similar results were found by Harner et al. (1999) who measured HCH concentrations in seawater samples collected during a cruise aboard the Swedish icebreaker “Oden” in July-September 1996 and found mean concentrations in surface water of 910 pg/L (range 350–1630 pg/L) for  $\alpha$ -HCH and 270 pg/L (range 120–400 pg/L) for  $\gamma$ -HCH. Both HCHs increased with latitude between  $74^\circ$ – $88^\circ$ N ( $r^2 = 0.58$  and  $0.69$  for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively). Same authors also observed that mean surface concentrations of HCHs in the eastern Arctic ocean were lower than those in the western Arctic.

Further water samples from the Bering and Chukchi Seas were collected and analysed by Yao et al. (2002) during the first Chinese Arctic Research Expedition from July to September 1999. They investigated the distribution and composition of organochlorine pesticides (including HCHs, heptachlor, heptachlor epoxide, aldrin, endosulfan I, p,p'-DDE, dieldrin, endrin, p,p'-DDD, endosulfan II, p,p'-DDT, endrin aldehyde, and endosulfan sulphate) and found that the most abundant pesticide in the Arctic seawater was  $\alpha$ -HCH, whose concentration was usually one or two magnitude grade greater than other contaminants.  $\alpha$ -HCH concentrations ranged between 156 and 683 pg/L and between 157 and 662 pg/L in the Bering Sea and Chukchi Sea, respectively. The average of  $\Sigma$ HCHs ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) was nearly equal in the Bering Sea (mean concentration 412.7 pg/L) and in the Chukchi Sea (mean concentration 445.8 pg/L), showing no latitudinal difference of these two regions. Compared with previously reported studies, concentrations of OCPs in these regions were much lower than the levels in the last decades. The  $\alpha/\gamma$ -HCH ratio was  $5.0 \pm 1.8$  and  $3.4 \pm 1.0$  for the Bering and Chukchi Seas, respectively, which indicated the different pesticide composition in these regions. The ratio of  $\alpha/\gamma$  in Bering Sea suggested a technical HCH mixture indicating that OCPs were mostly transported from the low latitude. However the observed low  $\alpha/\gamma$  ratio observed in the Chukchi Sea might imply the presence of a possible emission source of lindane nearby this region.



Hexachlorocyclohexanes (HCHs) in the surface water of the Canadian Archipelago and south Beaufort Sea were measured in summer 1999 (Bidleman et al., 2007). Overall concentrations of HCH isomers were in order of abundance:  $\alpha$ -HCH (ranging between 1.1 and 5.4, mean value  $3.5 \pm 1.2$  ng/L) >  $\gamma$ -HCH (ranging between 0.19 and 0.45, mean value  $0.31 \pm 0.07$  ng/L) >  $\beta$ -HCH (ranging between 0.056 and 0.16, mean value  $0.10 \pm 0.03$  ng/L). Concentrations also varied latitudinally for  $\alpha$ -HCH and  $\gamma$ -HCH ( $p < 0.002$ ) but not for  $\beta$ -HCH.

A recent study reports HCHs data collected on the FS Polarsten during the cruise ARKXX in the North Atlantic and Arctic Ocean in 2004 (Lohmann et al., 2009) and shows the  $\alpha$ -HCH concentrations near 1 pg/L in many samples < 80°N to mostly >20 pg/L above 80°N. The concentrations of  $\gamma$ -HCH were generally lower than  $\alpha$ -HCH ranging from <1 to 20 pg/L. These authors confirmed that concentrations of HCHs have continued to decline in the last few years.

The most recent data on HCHs concentrations in Arctic ocean are presented by Cai et al. (2010), who successfully applied the new analytical method developed by Qiu and Cai (2010) based on the combination of solid phase extraction and headspace solid phase microextraction (HS-SPME), for the determination of 17 ultra trace OCPs. Surface seawater samples were collected during the third Chinese Arctic expedition cruise from July to September 2008 on board the R/V "Xuelong". The track covered the Japan sea, Okhotsk sea, Bering sea and the zone to the North of the Bering Strait including the Chukchi sea, Canadian Basin and Arctic ocean. Cai et al. (2010) found that among the organochlorine pesticides, HCHs, especially  $\alpha$ -HCH and  $\gamma$ -HCH, were the most predominant in the Arctic surface water body as found by other authors (Iwata et al., 1993; Chernyak et al., 1995; Jantunen et al., 1995; Yao et al., 2002; Weber et al., 2006). This trend might be attributable to the higher historic usage of HCHs compared to the other investigated compounds (Li and McDonald, 2005). In the Bering Sea, the surface water concentrations were found to be 0.065-0.2671 ng/L for  $\alpha$ -HCH, 0.0775-0.8075 ng/L for  $\beta$ -HCH and 0.0725-0.7175 ng/L for  $\gamma$ -HCH. Respect to concentrations values reported earlier for this area,  $\gamma$ -HCHs values reported by Cai et al (2010) showed a level comparable to that reported in 1999, but a slightly decreasing trend was observed for  $\alpha$ -HCH. Water samples collected in the western Arctic Ocean presented concentrations of 2.07-2.63 ng/L and 0.33-0.70 ng/L for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively. Results for  $\alpha$ -HCH in the Chukchi Sea (0.0583-0.3926 ng/L) were slightly lower than those in 1999 (Yao et al., 2002) while  $\gamma$ -HCH concentration level were fairly comparable indicating that a state of equilibrium of  $\gamma$ -HCH was achieved recently.  $\beta$ -HCH showed higher concentrations respect to previous data in the Chukchi Sea and authors (Cai et al., 2010) attributed this result to the extremely low sensitivity of detection which could lead to higher error in the integration of the peak area.

### 2.3.3 HCHs in Arctic biota

The POP presence in Arctic organisms has been investigated during the last decades and many articles have been published in international scientific journals. The easier access to the area with respect to the Antarctic region is responsible of the high number of studies on Arctic biotic ecosystems. The interest in this polar region increased when the presence of very high concentrations of POPs was detected in those human populations that live the further north lands of Europe, Asia and America (for a comprehensive study see the AMAP Report 2009, AMAP, 2009). In the framework of the AMAP, many researches have been



carried out. Recently, reviews of POP presence and trends in the Arctic have been published (Muir et al., 2010). The occurrence of HCHs in the Arctic organisms will be examined in the same classes reported for the Antarctic organisms, that is pelagic crustaceans (krill), fish, seabirds, and seals, in order to allow a discussion.

Borgå et al. (2005) reported  $26.1 \pm 2.3$  ng/g lipid wt of  $\Sigma$ HCHs in the Arctic krill *Thysanoessa inermis*. The isomer abundance followed the pattern  $\alpha$ -HCH >  $\delta$ -HCH >  $\beta$ -HCH ( $\alpha$ -HCH made up more than 60% of the  $\Sigma$ HCHs); samples were collected in 1999 in the Greenland Sea and NW and NE of Svalbard Islands. The extracted organic matter in these samples was  $10.7 \pm 0.4$ . The comparison with concentrations in Antarctic krill showed a higher concentration in Arctic krill. These two species of Euphausiacea are important species in their trophic webs being food of many species of fish, seabirds, seals, and whales.

Fish species collected in the Arctic region and analyzed for HCHs were mostly the Arctic cod (*Arctogadus glacialis*), the Polar cod (*Boreogadus saida*), the Greenland halibut (*Reinhardtius hippoglossoides*), and others.  $\Sigma$ HCH concentrations in Polar cod muscle from the Canadian Arctic were  $90.2 \pm 13.7$  ng/g lipid wt (Moisey et al., 2001),  $40 \pm 3.2$  ng/g lipid wt (Hoekstra et al., 2003), and 10 ng/g lipid wt (Kelly et al., 2008); concentrations in the Greenland halibut muscle were as 81 ng/g lipid wt in (Fisk et al., 2002), and 53 ng/g lipid wt in Greenland shark (*Somniosus microcephalus*) liver (Fisk et al., 2002). Levels in Polar cod were of the same order of magnitude, but a decreasing trend can be observed during 2000s. Sinkkonen et al. (2000) analyzed Polar cod liver in specimens collected from 1987 to 1998 in the Norwegian Arctic and they detected 4-23.3 ng/g lipid wt of  $\alpha$ -HCH and 2.9-8.1 ng/g lipid wt of  $\delta$ -HCH. Their decreasing trend were very significant ( $p = 0.001$ ) during this time span; these Authors reported that  $\alpha$ -HCH concentrations declined faster than those of  $\delta$ -HCH, in agreement with observations for Arctic air and water (Li et al., 1998; Bidleman et al., 1995; Jantunen and Bidleman, 1995). The HCH isomer abundance were  $\alpha$ -HCH >  $\beta$ -HCH >  $\delta$ -HCH in Polar cod (Sinkkonen et al., 2000; Moisey et al., 2001) and  $\delta$ -HCH >  $\alpha$ -HCH >  $\beta$ -HCH in the Antarctic *T. bernacchi* (Corsolini et al., 2006). These patterns could be interpreted as an indication that the use of technical HCH (containing 60-70% of  $\alpha$ -HCH) has decreased faster than that of pure lindane (Li et al., 1998). Li et al. (1998) reported that there were two significant drops of HCH concentrations in the Arctic air: in 1982-1983 and in 1990-1992 and they followed the ban of technical HCH use in China (1983), India and ex-Soviet Union (1990). This decrease was not followed by a decrease of  $\alpha$ -HCH concentrations in Arctic seawater. These speculations might help to interpret the different patterns found in Arctic and Antarctic fish. In fact, chemical concentrations and patterns in the two polar regions might be influenced by the air mass movement and the different use of HCHs in the two hemispheres, in agreement with the model proposed by Wania et al. (1999), suggesting that levels in the Southern Ocean are higher than those in tropical seas. Anyway,  $\alpha$ - and  $\delta$ -HCH were reported to be decreasing in the Arctic (Rigét et al., 2010).

A study on the occurrence of HCH in several species of seabirds from the Northwater Polynia (NOW) reported  $\Sigma$ HCH concentrations in various species:  $222 \pm 19.9$  ng/g lipid wt in dovekie,  $84.5 \pm 9.6$  ng/g lipid wt in thick-billed murre,  $285 \pm 46.7$  ng/g lipid wt in black guillemot,  $47.3 \pm 6.3$  ng/g lipid wt in black-legged kittiwake,  $442.7 \pm 51.9$  ng/g lipid wt in glaucous gull,  $143.0 \pm 32.7$  ng/g lipid wt in ivory gull,  $65.1 \pm 5.8$  ng/g lipid wt in northern fulmar (Moisey et al., 2001). These Authors reported the  $\alpha$ ,  $\beta$  and  $\gamma$ -isomer patterns of abundance was  $\beta$ -HCH >  $\alpha$ -HCH >  $\delta$ -HCH in all these species.

Concentrations of  $\Sigma$ HCHs collected from 1975 to 2003 were  $2.0 \pm 0.4$  –  $5.7 \pm 0.7$  ng/g wet wt in northern fulmars,  $4.0 \pm 0.4$  –  $7.7 \pm 0.6$  ng/g wet wt in black-legged kittiwake, and  $9.2 \pm 1.3$  –  $18.6 \pm 2.0$  ng/g wet wt in thick-billed murre (Braune, 2007 a, b). The isomer abundance patterns were  $\alpha$ -HCH >  $\beta$ -HCH in northern fulmar and thick-billed murre collected from 1975 to 1993, and  $\beta$ -HCH >  $\alpha$ -HCH in northern fulmar and thick-billed murre collected in 1998 and 2003, and in black-legged kittiwake. Braune (2007 a, b) noted significantly increasing concentrations of  $\beta$ -HCH in northern fulmars and thick-billed murres, and  $\Sigma$ HCH in black-legged kittiwakes and northern fulmars; the increasing  $\Sigma$ HCH concentrations in the northern fulmars and black-legged kittiwakes were owed to  $\beta$ -HCH.

Other articles reported  $\Sigma$ HCH levels ranging from <1-170 ng/g lipid wt (white-winged scoter and common eider: Kelly et al., 2008; herring gull, common guillemot, Atlantic puffin, and black-legged kittiwake: Helgason et al., 2008; black guillemot: Vorkamp et al. 2004; northern fulmar: Knudsen et al., 2007; glaucous gull: Verrault et al., 2005; peregrine falcon: Vorkamp et al. 2009), and 24-80 ng/g wet wt (northern fulmar, glaucous-winged gull, and tufted puffin: Ricca et al., 2008). Concentrations exceeding 100 ng/g lipid were detected in black guillemot eggs from east Greenland (Vorkamp et al., 2004), glaucous gull plasma from Svalbard Islands (Verrault et al., 2005), and ivory gull eggs from Canada (Braune et al., 2007a, b). A decreasing or stable temporal trend of  $\Sigma$ HCHs,  $\alpha$ -,  $\beta$ -, and  $\delta$ -HCH concentrations during the last decade was reported in all these species except fulmar and thick-billed murre eggs, and the rate of decrease varied among species and geographical areas (Rig  t et al., 2010).

Pinnipeds may accumulate high amount of chemicals and different concentrations in their tissues are often evident and depending on their diet.  $\Sigma$ HCH concentrations in seal blubber were  $150.5 \pm 13.1$  ng/g lipid wt in ringed seal collected in the NOW in 1998 (Moisey et al., 2001), 145 ng/g lipid wt in specimens from the Canadian Arctic (Kelly et al., 2008), and  $190 \pm 50$  ng/g lipid wt in the same species collected in 1999-2000 (Hoekstra et al., 2003). Lower concentrations were detected in ringed seal from Greenland: 67 ng/g lipid wt (Vorkamp et al., 2004) and 40 ng/g lipid wt (Vorkamp et al., 2008). Vetter et al. (2001) reported  $\Sigma$ HCH concentrations in three species of Arctic seals and in three species of Antarctic seals: they were 659 ng/g wet wt in grey seal from the Baltic Sea, 5-11 ng/g wet wt in grey seal from Iceland, and 181 ng/g wet wt in harp seal from the North Sea. Values found in samples from Iceland were of the same magnitude than those found in Antarctic species (Weddell seal = 14 ng/g lipid wt, fur seal = 4 ng/g wet wt, elephant seal = not detected). The concentrations of  $\Sigma$ HCHs and HCH  $\alpha$ ,  $\beta$  and  $\gamma$ -isomers were reported to be decreasing in ringed seals (Rig  t et al., 2010). Rig  t et al. (2008) reported annual decreases in ringed seals from East and West Greenland from 1986 to 2006 that were 9.1–11.7%, 1.4–3.9% and 6.0–6.4% for  $\alpha$ ,  $\beta$  and  $\gamma$ -HCH, respectively.  $\delta$ -HCH was the less abundant isomer both in West Greenland juvenile seals (4.95 ng/g lipid wt in 1995 and 1.91 ng/g lipid wt in 2002) and in East Greenland juvenile seals (7.89 ng/g lipid wt in 1986 and 2.57 ng/g lipid wt in 2006); adult seals showed larger temporal variation (9.3 ng/g lipid wt in 1994 and 2.7 ng/g lipid wt in 2002).

## 2.4 Enantiomer fraction of $\alpha$ -HCH in Antarctic and Arctic marine environment

$\alpha$ -HCH is a chiral compound and thus exists in two enantiomers forms. Enantiomers are stereoisomers in which the atoms are arranged such that the molecules are mirror images of each other. The two enantiomers can rotate polarized light in different directions. Two

principal metrics are used for reporting enantiomer composition of chiral POPs. The enantiomer ratio (ER) and the enantiomer fraction (EF). Most earlier studies used ER, consisting in the separation of these enantiomers by GC and subsequent calculation of the peak area or height ratio of the (+) and (-) enantiomers. The ER ranges from zero to infinity, with a racemate having an ER of 1. The EF, now more commonly used, is defined as the ratio of the (+) enantiomer to the sum total enantiomer concentrations. EF ranges between zero to infinity with a racemic value of 0.5. EF are preferred to ER as the EF is bounded and a deviation from the racemic value in one direction is the same as in the other (Harrad, 2009).

Chirality has been used to detect, characterize and differentiate biotic and abiotic transformation processes. Biotic processes such as microbial degradation, enzymatic processes or biological uptake may be enantioselective, causing the observed ER or EF to vary from the racemic value of 1.0 or 0.5, respectively; while abiotic processes such as hydrolysis and photolysis are not enantioselective (Helm, 2000) and affect both enantiomers of achiral compound in the same way.

The enantiomer composition of  $\alpha$ -HCH in Antarctic seawater samples is not well documented; in fact only Jantunen et al. (2004) studied the influence of latitude on EF ratio on seawater samples collected during the South African National Antarctic Expedition (December 1997 – February 1998). Same authors reported EF values ranging from 0.477 to 0.515 and evidenced a significant regression of EF versus latitude ( $R^2=0.28$ ,  $p\leq 0.005$ ) with a slight preferential tendency to degrade of (-) enantiomer at the lower latitudes ( $EF \geq 0.500$ ), versus racemic or depletion of the (+) enantiomer ( $EF \leq 0.500$ ) at the higher latitudes.

Enantiomeric fractions of chiral  $\alpha$ -HCH in Antarctic biota were studied by Corsolini et al. (2006). They reported average EF values of  $0.44 \pm 0.01$ ,  $0.49 \pm 0.01$  and  $0.58 \pm 0.04$  in krill, emerald rockcod and Adélie penguin eggs, respectively. According to these results, these authors suggested enantioselective biotransformation at lower trophic animal, with a decrease in the (+) $\alpha$ -HCH enantiomer compared to the (-) $\alpha$ -HCH. The (+) $\alpha$ -HCH contribution increased by 14% from lower to the higher trophic level (from krill to penguin): the proportion of the (+) enantiomer increased from 44% to 58%, suggesting an enantioselective biotransformation up the food web. Accumulation of (+) $\alpha$ -HCH in the higher trophic levels was already reported for marine mammals and polar bear (Iwata et al., 1998; Wiberg et al., 2000; Kallenborn and Huhnerfuss, 2001).

There has been an extensive analysis of  $\alpha$ -HCH enantiomer composition in the Arctic Ocean. Falconer et al. (1995) found ER of  $0.93 \pm 0.06$  in Resolute Bay in August–September 1992, showing that the (+) enantiomer was depleted in seawater and suggesting a microbial degradation of HCHs. A microbial degradation was also observed in seawater samples collected on a cruise along the Eastern Arctic Ocean in July–September 1996 (Harner et al., 1999), where the ER values ranged between 0.72 to 0.94 (mean value  $0.87 \pm 0.06$ ) in surface water and decreased with depth.

The ER of  $\alpha$ -HCH ((+)- $\alpha$ -HCH / (-)- $\alpha$ -HCH) in Arctic seawater was reported by Jantunen and Bidleman (1996, 1997), who found ER generally  $> 1.00$  in the Bering-Chukchi Seas, indicating preferential degradation of (-) $\alpha$ -HCH, whereas depletion of the (+) $\alpha$ -HCH in the Arctic Ocean and Greenland Sea, with ERs  $< 1.00$ . One hypothesis to explain this different enantiomer depletions could be due to the different microbial populations in these regions. Although generally HCHs are measured in the dissolved fraction, levels of HCHs in water were high enough to allow ER values to be measured on the filters of the large volume samples. The results showed different enantioselective degradation in the dissolved and

particulate phase suggesting that different microbial populations are involved in these two phases. Authors also noted that ERs for  $\alpha$ -HCH decreased with depth (Jantunen and Bidleman 1996, 1997) as observed by Harner et al. (1999) in the Eastern Arctic ocean, where the ER ranged from 0.72 to 0.94 (mean  $0.87 \pm 0.06$ ) in 21 surface water samples indicating selective degradation of (+) $\alpha$ -HCH and microbial degradation was suggested as the major removal process of HCHs from the water column. The reversal of enantiomer preference observed respect to the early 1990s could be due to changes in microbial degradation in the water column with subsequent changes over time leading to consistent enrichment of the (-)enantiomer (Harrad, 2009).

Tracer studies have determined that the “ventilation age” of the 250-1000 m water in the Nansen Basin of the eastern Arctic Ocean is in the range of 12-20 years (Wallace et al., 1992). The ventilation age is the time since the water was at the surface and able to exchange gases with the atmosphere. This information, combined with measurements of HCH concentrations in 1996 (Harner et al. 1999) and 1979 (Gaul et al., 1992), allows us to estimate the removal rates from the water column, which are due to microbial degradation, hydrolysis and sedimentation. The latter is negligible, and microbial degradation is 3-10 times faster than hydrolysis (Harner et al. 1999).

In a recent paper, Lohmann et al. (2009) found depletion of the (+) enantiomer, with EFs ranging from 0.432-0.463, and increased from west to east in the Archipelago.

### 3. Conclusions

The concentration levels of  $\alpha$ - and  $\gamma$ -HCH in surface waters of Antarctica are much lower (by 1-2 orders of magnitude) than those in the Arctic, due to the remoteness of this continent from populated and industrial regions relative to the Arctic. A decreasing trend was observed for  $\alpha$ -HCH and  $\gamma$ -HCH concentration in both Arctic and Antarctic oceans, corresponding to the global bans on HCHs. However the recent declining usage and atmospheric inputs of  $\alpha$ -HCH isomer have caused the exchange to reverse, and made the Arctic ocean a source of  $\alpha$ -HCH to the atmosphere rather than the major sink for LRT of it.

A comparison between levels and trends in Arctic and Antarctic biota indicates higher contamination levels in the Arctic organisms in relation to the geographical isolation of the Antarctic continent and Southern Ocean, which make difficult for chemicals to reach this region. It might be that the global transport to Antarctica and equilibrium between phases of HCHs follow different mechanisms of time scale in the two Polar Regions; Antarctica could show a delay in the chronological steps that characterize the HCH distribution globally and in the marine ecosystems. The Arctic is showing a decreasing temporal trend of contamination followed the peak occurred in the past years and in relation to the great HCH use/production and following ban. Thus, a decreasing or stable temporal trend of  $\Sigma$ HCHs,  $\alpha$ -,  $\beta$ -, and  $\delta$ -HCH concentrations during the last decade was reported in seawater and most of the studied species, and the rate of decline varied among species and geographical areas.

By comparing available data, it emerges a different pattern in the Antarctica where a temporal trend is not clearly recognizable, owing to the paucity of data and unevenness of report features and style. In this regard, compared to the Arctic, it could be hypothesized a slight delay in the transport, accumulation, and decrease of HCH in the southern polar region, that can be an effect of the geography and of the chemical transport pathways, that affect the distribution on the marine ecosystems.



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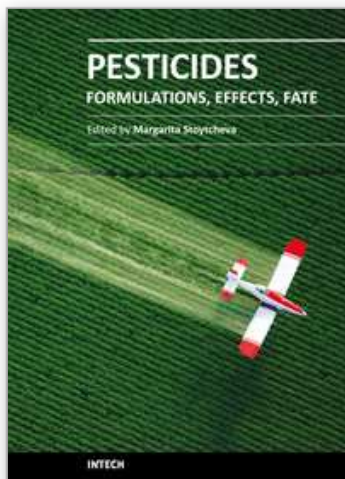


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### **Pesticides - Formulations, Effects, Fate**

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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