Environmental Pollution 200 (2015) 140–148

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Toxaphene in the aquatic environment of Greenland

Katrin Vorkamp [a, *], Frank F. Rigét [b], Rune Dietz [b]

[a] Aarhus University, Department of Environmental Science, Arctic Research Centre, Frederiksborgvej 399, DK-4000 Roskilde, Denmark
[b] Aarhus University, Department of Bioscience, Arctic Research Centre, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ARTICLE INFO

Article history:
Received 25 November 2014
Received in revised form
4 February 2015
Accepted 5 February 2015
Available online 26 February 2015

Keywords:
Arctic char
Bioaccumulation
Black guillemot eggs
Ringed seal
Shorthorn sculpin
Trends

ABSTRACT

The octa- and nonachlorinated bornanes (toxaphene) CHBs 26, 40, 41, 44, 50 and 62 were analysed in Arctic char (*Salvelinus alpinus*), shorthorn sculpin (*Myoxocephalus scorpius*), ringed seal (*Pusa hispida*) and black guillemot eggs (*Cepphus grylle*) from Greenland. Despite their high trophic level, ringed seals had the lowest concentrations of these species, with a Σ_6Toxaphene median concentration of 13–20 ng/g lipid weight (lw), suggesting metabolisation. The congener composition also suggests transformation of nona- to octachlorinated congeners. Black guillemot eggs had the highest concentrations (Σ_6Toxaphene median concentration of 971 ng/g lw). Although concentrations were higher in East than in West Greenland differences were smaller than for other persistent organic pollutants. In a circumpolar context, toxaphene had the highest concentrations in the Canadian Arctic. Time trend analyses showed significant decreases for black guillemot eggs and juvenile ringed seals, with annual rates of −5 to −7% for Σ_6Toxaphene. The decreases were generally steepest for CHBs 40, 41 and 44.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Originally used as a trademark by the US manufacturer Hercules Incorporated, “toxaphene” is now generally used for complex insecticidal mixtures of polychlorobornanes and camphenes. Depending on the manufacturing process, products likely differ in chlorination degree and congener composition, leading to a theoretical number of ten thousands of congeners (Vetter, 1993). The former Soviet Union produced a similar product called polychloropinene in an estimated quantity of 160 000 tons (Trukhin et al., 2007). The US production peaked in 1975, at an annual production of at least 27 000 metric tons, registered for three manufacturers in 1975 (ATSDR, 2010).

An accountable cumulative toxaphene usage of 450 000 tons was calculated in a global inventory, with an interpolated total usage from 1950 to 1993 of 1.33 million tons (Voldner and Li, 1993). This would place toxaphene in the same production volume category as polychlorinated biphenyls (PCBs), which had a cumulative production of 1.3 million tons (Breivik et al., 2002), and DDT, which was produced at 2.6 million tons (Voldner and Li, 1995). The highest usage of >100 000 tons of toxaphene was documented for the USA, while >10 000 tons were registered for the former Soviet Union, Germany, Brazil, Colombia, Egypt and possibly other countries (Voldner and Li, 1995). The use of toxaphene has also been reported for Sudan, Algeria and other African countries, causing runoff into the river Nile (de Geus et al., 1999; Voldner and Li, 1995). According to Voldner and Li (1995), >1000 tons were used in India and China and minor amounts in many other countries.

Toxaphene was mainly used for pest control on cotton crops in the Southern United States, with minor applications (<15%) on other crops and livestock. A source in the Northern United States and Canada might have been the use in sport fishing to control fish stocks (ATSDR, 2010). Toxaphene is highly toxic to aquatic organisms, in particular marine fish (de Geus et al., 1999), and has been classified as possibly carcinogenic to humans by the International Agency for Research on Cancer (IARC, 2001). The USA banned toxaphene in 1982, however, according to ATSDR (2010), several US facilities still handled toxaphene in 2008. Toxaphene was among the initial 12 compounds listed by the Stockholm Convention on Persistent Organic Pollutants (POPs), which entered into force in 2004 and aims to achieve a global phase out of persistent, bioaccumulative and toxic compounds transported over long distances.

The North American Great Lakes are probably the best studied region with regard to the environmental accumulation of toxaphene (e.g. Muir et al., 2004). Time trends have shown decreases of toxaphene in fish of the Great Lakes since the early 1980s, with a slightly lagged decrease in Lake Superior (e.g. Glassmeyer et al., 1997; Hickey et al., 2006). Despite its primary use in North

* Corresponding author.
E-mail address: kvo@envs.au.dk (K. Vorkamp).

http://dx.doi.org/10.1016/j.envpol.2015.02.014
0269-7491/© 2015 Elsevier Ltd. All rights reserved.

America, toxaphene has also been detected in the European environment, including fish in the North Sea (de Boer and Wester, 1993) and sediment cores in a remote Scottish lake, showing a steep increase of toxaphene in the 1960s (Rose et al., 2001). Time trends extending to recent years, e.g. in eggs of tawny owl (*Strix aluco*) from Norway, showed a decrease of toxaphene from the 1980s (Bustnes et al., 2007). Toxaphene is also present in Arctic air and water (Bidleman et al., 1995) as well as fish and wildlife (Muir et al., 1988; Vorkamp et al., 2004a, 2008, 2014; Wolkers et al., 1998).

Despite its significance as an insecticide and obvious ubiquitous distribution, information on toxaphene in the environment is sparse. This might be related to difficulties in analysing the complex mixture of congeners, which nowadays usually is based on specific individual standards (Braekevelt et al., 2001). This article presents results from ongoing studies in Greenland, including temporal trends in marine and freshwater species, circumpolar geographical trends and considerations on food web bioaccumulation and biomagnification.

2. Materials and methods

2.1. Sample collection

The marine samples were obtained from local hunters at Qeqertarsuaq in Central West Greenland (69°14′50″N 53°32′00″W) and Ittoqqortoormiit in Central East Greenland (70°29′07″N 21°58′00″W) between 1986 and 2012. The samples of landlocked Arctic char originate from a lake near Isortoq in Southwest Greenland (61°58′50″N 47°30′10″W). A map with the sampling locations is shown in the Supporting Information (Fig. S1). Shorthorn sculpin were caught by jigs and packed whole in polyethylene plastic bags for subsequent storage in a freezer. Only female sculpins were collected. The age of seals was determined according to Dietz et al. (1991). While only juvenile seals (≤4 years of age) were analysed from West Greenland, separate time trends were established for juvenile and adult seals in East Greenland. Detailed information on sample collection has been published previously (Rigét et al., 2010; Vorkamp et al., 2004b). An overview of the biota samples and their biological characteristics is given in Tables S1–S3 of the Supporting Information.

2.2. Chemical analysis

The analytical method was described in detail by Vorkamp et al. (2004a) and has not been changed significantly. The analytical standards of the octa- and nonachlorinated bornanes CHBs 26, 40, 41, 44, 50 and 62 were originally purchased from LGC Standards (former Promochem, Wesel, Germany), but discontinued production required a change of manufacturer in 2012. For the quantification of the 2012 samples, CHBs 26, 50 and 62 were purchased from Cambridge Isotope Laboratories (CIL, Tewksbury, MA, USA), CHBs 40 and 41 were purchased from Wellington Laboratories (Guelph, Ont., Canada) and CHB 44 was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Alternative nomenclatures of the target analytes are given in Table S4 of the Supporting Information.

The samples were homogenised, dried with sodium sulphate or diatomaceous earth and spiked with PCB-198 (LGC Standards) for recovery determination. The compounds were Soxhlet extracted, using 350 ml of a mixture of n-hexane:acetone (4:1). The extracts were reduced in volume and cleaned up on a multilayer column packed bottom-to-top with 5 g aluminium oxide (10% water), 1 g activated silica (24 h at 160 °C), 5 g activated silica (with sulphuric acid) and 1 cm anhydrous Na_2SO_4. The columns were eluted with 250 ml *n*-hexane, which subsequently was evaporated to <1 ml by rotary evaporation and under nitrogen. ^{13}C-*trans*-chlordane (CIL) was added as a syringe standard for quantification, and the samples were adjusted with iso-octane to a precise volume of 1 ml.

The extracts were analysed by gas chromatography–mass spectrometry (GC–MS) with electron capture negative ionisation (ECNI) on an Agilent GC HP6890 and MS HP5973. Methane was used as the ionisation gas at a pressure of 1.9 10^{-4} torr. The transfer line was at 280 °C and the ion source temperature was kept at 150 °C. The capillary column was a 60 m DB-5 (J&W Scientific; 0.25 mm inner diameter; 0.25 μm film thickness). The temperature programme was as follows: 90 °C (1 min), increase to 220 °C at a rate of 50 °C min^{-1}, increase to 260 °C at rate of 5 °C min^{-1}, isotherm for 9.3 min, increase to 310 °C at a rate of 50 °C min^{-1}, 18.1 min at 310 °C.

The samples were processed in batches of 12–19 individual samples, 1–2 duplicate analyses, a procedural blank and 2 samples of an internal reference material (sand eel oil). Recovery correction was not performed as only samples with recoveries >80% were accepted. Blanks were below the limits of detection in all batches. Duplicates generally showed good agreement (Table S5 of the Supporting Information). Detection limits for each species are summarised in Table S6 of the Supporting Information. Although detection limits were higher in early than in more recent analyses, only few samples were below detection limits (Table S7 of the Supporting Information). Precision was monitored by plotting the concentrations of the internal reference material in control charts with warning and action limits (two and three times the standard deviation, respectively). The laboratory participated in the QUASIMEME proficiency testing scheme for toxaphene until it was discontinued in 2007.

2.3. Data analysis

Σ_6Toxaphene is the sum of the individual CHBs 26, 40, 41, 44, 50 and 62. Concentrations below detection limits were set to zero in calculations of Σ_6Toxaphene. Prior to the statistical analyses, the concentrations were log-transformed to reduce skewness and thereby meet the assumption of normal distribution and homogenous variances. Analyses of variance (ANOVA) and Tukey's *post hoc* test were applied to test for differences between species and age groups. Linear mixed effect analyses (LME) with location as factor and sampling year as random (nested) factor were performed to test differences in log-mean concentrations between West and East Greenland in cases of shorthorn sculpin and juvenile ringed seals.

The analyses of temporal trends followed the procedure used in temporal trend assessments of the International Council for the Exploration of the Sea (ICES). The method is a robust regression-based analysis to detect temporal trends (Nicholson et al., 1998). The median concentration is used as yearly contaminant index value and was chosen instead of the mean concentration because it is less influenced by concentrations below detection limits and possible outliers. The total variation over time is divided into a linear and a non-linear component. Log-linear regression analysis was applied to describe the linear component and a three year running mean smoother was applied to describe the non-linear component. The linear and non-linear components were tested by means of an ANOVA. The statistical trend analyses were performed using the free software R version 2.15.2 (R Core Team, 2012).

3. Results and discussion

3.1. Bioaccumulation of toxaphene

As sampling of shorthorn sculpin was discontinued in 2004, this is the last year with data for all sample types, as specified in

Download English Version:

https://daneshyari.com/en/article/4424299

Download Persian Version:

https://daneshyari.com/article/4424299

Daneshyari.com