Chemosphere 75 (2009) 1135–1143

Contents lists available at ScienceDirect

Chemosphere

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

Persistent organic pollutants in two fish species of *Percidae* and sediment from the Sulejowski Reservoir in central Poland

Ilona Waszak, Henryka Dąbrowska *

Sea Fisheries Institute in Gdynia, 81–332 Gdynia, Poland

ARTICLE INFO

Article history:
Received 3 December 2008
Received in revised form 9 February 2009
Accepted 1 March 2009
Available online 2 April 2009

Keywords:
PCBs
PCDD/DFs
Pesticides
Pikeperch
Perch
BSAFs

ABSTRACT

Two predatory fish species, pikeperch and perch, and sediment from the Sulejowski Reservoir in Poland were analyzed for several classes of persistent organic pollutants. Polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), heptachlor, and DDTs were measured in the fish muscles. In addition, the distribution and profile of PCBs in muscles, livers, and gonads was examined. In sediment, PCBs and polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs) were analyzed. The main contaminant in the muscles of both species was *p,p′*- DDE reaching an average of 1072 and 694 ng g^{-1} lipid in pikeperch and perch, respectively. ΣPCBs, with an average concentration of 454 and 261 ng g^{-1} lipid, respectively, were the second dominant contaminants. The two species differed in their PCB congener profile as a result of differences in feeding habits. Sediment PCDD/F concentrations ranged from 10.8 to 162.7 pg g^{-1} dry mass, $TEQ_{PCDD/Fs}$ from 1.13 to 4.13 pg g^{-1} dry mass, and the sum of indicator PCBs (ΣPCB_7) from 2.8 to 5.2 ng g^{-1} dry mass. Biota – sediment accumulation factors (BSAFs) for ΣPCB_7 were generally greater in pikeperch than in perch as a result of greater lipid content in the latter. Based on the contaminant levels in the sediment and fish, the Sulejowski Reservoir compares well with other, freshwater environments relatively uncontaminated with persistent organic pollutants.

1. Introduction

The occurrence of polychlorinated biphenyls (PCBs) and other halogenated organic pollutants in terrestrial and aquatic environments continue to be of concern due to persistence and potential hazard to wildlife and humans these compounds can pose. Their physical–chemical properties and mass production and use in the past have made them the most prevalent contaminants found in various biotic and non-biotic environmental compartments world – wide including remote regions of the globe (Meijer et al., 2003; Falandysz et al., 2004; Morrissey et al., 2005; Covaci et al., 2006; Hickey et al., 2006). In aquatic systems persistent organic pollutants (POPs) become distributed between water, particulate matter, sediment and biota and the main process that controls the distribution is sorption which governed by contaminant hydrophobicity and the lipid or organic carbon content of the particles (Stange and Swackhamer, 1994) in the end leads to their accumulation in biota and deposition in sediments. The accumulation in biota is related, in general, to sources and complex physical and biological processes in which the sediment serves both as a sink and source of contamination to the surrounding water and biota.

The EU legislative instruments i.e., the Water Framework Directive 2000/60/EC and Directive 2001/42/EC aim to protect and enhance the quality of aquatic ecosystems and shall ensure that all water bodies will have good ecological status by 2015. The legislation requires the member states to develop and implement management strategies to reach the goals through protection and restoration where necessary the surface waters. Assessment of current status is fundamental to reaching the goals. The extent of aquatic systems contamination by PCBs and other POPs has been only recently investigated in selected areas of Poland (Bojakowska and Gliwicz, 2005).

The Sulejowski Reservoir is one of the largest water areas in the central Poland. It is a shallow, eutrophic reservoir constructed in the middle course of the Pilica River in 1973, has a mean depth of 3.3 m, a maximum of 11 m, and at its full capacity covers an area of 22 km^2. For decades the reservoir served as a drinking water source for the city of Łódź, a second largest city in Poland. Currently it is used as an alternative source of drinking water and generally serves as a flood prevention measure and a research and recreation park. Over the last decades the water quality in the reservoir has deteriorated and periodical strong cyanobacterial blooms became a concern (Izydorczyk et al., 2008).

The purpose of this study was to assess the present status of the reservoir in respect to POPs contamination. PCBs and selected organochlorine pesticides were measured in two dominant, predatory fish species, and PCBs and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) were examined in the sediment. In addition, biota – sediment accumulation factors (BSAFs) for PCBs were

* Corresponding author. Tel.: +48 58 7356 205; fax: +48 58 7356 110.
E-mail address: dabrowska@mir.gdynia.pl (H. Dąbrowska).

0045-6535/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2009.03.001

determined. To our knowledge this is the first work to report on PCDD/Fs in a freshwater environment and on BSAFs - PCBs in predatory fish in Poland.

2. Material and methods

2.1. Sample collection

Sediment and fish were collected in late summer 2006. Sediment samples were taken from three sites (Fig. 1) along the reservoir length to include its front i.e. the Pilica River inflow (S1), the central (S2), and the outflow (S3) sub-basins. At each site three sediment samples within a radius of 10 m were taken to form a composite for a given site. Sediment samples were freeze-dried, passed through a 1 mm sieve and stored at −20 °C in brown glass jars until analysis. Two fish species, pikeperch (*Stizostedion lucioperca*) and perch (*Perca fluviatilis*) were collected by gill nets. The species differ in their feeding preferences i.e., perch feeds on invertebrates during early life stages and later becomes a piscivorous, whereas pikeperch is piscivorous from early on. Table 1 shows the biological characteristics including body mass and length of both species, and liver and gonad mass, hepato- and gonado – somatic indexes (HIS, GSI) of pikeperch. Muscles fillets with skin on were taken from both species for measurement of target contaminants and lipid content. In addition, livers and gonads of pikeperch females were collected and analyzed for PCB levels and profiles.

2.2. Sample processing and analyses

For PCB measurements sediment samples were processed and analyzed based on methods of Smedes and de Boer (1997) and Covaci et al. (2006) with some modifications. Freeze – dried samples (20–30 g) fortified with activated copper (5–8 g) were Soxhlet extracted with a mixture of hexane and acetone (3:1). Extracts were concentrated and cleaned up on a column packed with H_2SO_4 modified (40%) silica between layers of anhydrous sodium sulfate eluted with hexane, followed by column filled with alumina between layers of anhydrous sodium sulfate eluted with hexane. The extract was concentrated and further eluted through a silica-carbon column with hexane and hexane/toluene mixture, sequentially. The final extract was concentrated to near dryness by rotary evaporator and further by a gentle nitrogen stream, solvent exchanged to isooctane, and reconstituted to 0.5 mL. Analyses of PCDD/Fs in sediment samples were subcontracted to an accredited laboratory of the Nofer Institute of Occupational Medicine in Łódź, Poland. Freeze-dried sediments were extracted with toluene in an accelerated extraction system Dionex ASE 200 and cleaned up on a multilayer silica column packed from the bottom with basic silica, H_2SO_4 modified (44% and 22%) silica, and $AgNO_3$ in between layers of deactivated silica. The column was eluted with hexane. The final extract volume was 0.1 mL.

Fish samples were processed according to routinely performed procedures in the Sea Fisheries Institute laboratory. Muscle fillets were ground and freeze dried before extraction in an auto extraction unit (2050 Soxtec; Foss Tecator AB, Höganäs, Sweden) with a mixture of dichloromethane/*n*-hexane (1:1). Livers and gonads were ground with anhydrous sodium sulfate and extracted in a glass column with the same solvent mixture as the muscle tissue. Lipid content was determined gravimetrically on an aliquot of the extract for each sample. The extracts were concentrated by a rotary evaporator to about 2 mL and cleaned up on a multilayer column (anhydrous sodium sulfate, deactivated silica, H_2SO_4 modified (40%) silica, anhydrous sodium sulfate) eluted with 100 mL of hexane. The hexane extract, after concentration, was further processed in the same way as were the sediment extracts i.e. eluted through a silica – carbon column with hexane and hexane/toluene mixture, sequentially. Thereafter, the final extract was concentrated solvent exchanged to isooctane, and reconstituted to 0.5 mL.

2.3. Reagents and standards

Solvents, of high purity ENVISOLV®, were obtained from Riedel-de Haën, AG (Seelze, Germany). Silica gel, Davisil® grade 634, and anhydrous sodium sulfate were from Sigma Aldrich. The

Fig. 1. Location of the Sulejowski Reservoir.