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PCDD/Fs, PBDEs IN ARCTIC BIRDS AND TERRESTRIAL ANIMALS

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Introduction

Arctic regions of Russia occupy vast areas where indigenous population use meat of reindeer, wild birds and hares for food. Consumption of reindeer meat is about 400 g per day. Analysis of wild animal meat pollution with POPs can help in risk assessment of exposure via the food chain.
Examination of sea animals permits assessment of global pollution and background levels whereas exposure of terrestrial animals may reveal local sources on land. Polar bear and reindeer/caribou served as PCDD/Fs bioindicators in arctic areas of Sweden, Norway and Canada (PCDD/F TEQs for reindeer range from 0.1 to 9.45 pg/g w.w.) [1,2]. Wild birds also were objects for PCDD/Fs monitoring in Arctic including Kola Peninsula in Russia. Thus in eggs of peregrine falcon and white-tailed eagle, 35 and 5.0 pg/g lw PCDD/F TEQs were found respectively[3]. Global BFRs pollution also resulted in PBDEs accumulation in biological objects[4]. Data on seabirds, belugas, seals indicate that levels of the brominated flame retardant PBDE are increasing for the last 20 years (from 0.5 to 4 ng/g lw in ringed seal blubber and from 3 to 16 ng/g lw in beluga whale blubber)[5]. Levels of sum PBDE are 0.47-1.7 ng/g l.w. in reindeer and moose from Sweden[6].

Method and materials

The objects for analysis were pooled samples of liver, muscles and kidney tissue of reindeer and mountain hare and also muscles of ptarmigan (*Lagopus lagopus and Lagopus mutus)* and duck *(Bucephala clangula, Anas acuta and Clangula hyemelis).*
In the places of biota sampling, soil, moss (*Pleurozium schreberi, Dicranum, Cetraria cuclata and Hilocomium splendens)* and lichen *(Cladina rangiferina)* were also sampled. Soil represented a long-term deposition of vegetation.
The areas of sampling included the main arctic regions of Russia: Kola Peninsula (region of Lovozero), the Pechora river basin (settlement of Oksino), Taimir Peninsula (settlements of Dudinka and Khatanga) and Chukotka Peninsula (settlements of Lavrentiya and Kanchalan).
Measurement of PCDD/Fs was carried out in compliance with the method 1613. Modification of the HR GC/MS method was used for determination of 2,2',4,4'-TBDE, 2,2',4,4',5-PnBDE.
The samples were thawed, skinned and the epaxial muscle homogenized before being subdivided into smaller replicate portions (100 g) and stored at –20°C prior to analysis. Soil, moss and lichen samples were preliminarily dried. Extraction of fat tissues was carried out with methylene chloride – hexane and 1%-ethyl acetate and enrichment by defatting followed by separation on modified SiO_2, activated Al_2O_3 and Carbopac C/Celite. PBDEs extraction from biosamples was made by the mixture of chloroform – hexane with addition of 1% - ethyl acetate, soil samples were extracted with mixture of methylene chloride – acetone (2/1) in an ultrasonic bath, vegetation samples were extracted with mixture of heptane-acetone (1/1) in ultrasonic bath after preliminary watering. Extracts purification was made on a column with activated Florisil. Measurement was made by gas chromatography - high resolution MS (Carlo-Erba 8035/Autospec-Ultima) in the EI mode.

Quantification was carried out by the isotope dilution internal standard method using carbon-13 PCDD/F congeners (CIL, EDF 8999-4), MBDE # 47 and 99 (Wellington). Registration of two molecular ions was carried out for native and labeled standards: 22'44-tetrabromdiphenyl ether- 483.7131; 485.711, 22'44'5 – pentabromdiphenyl ether - 563.6216; 565.6196.
The samples were analyzed for the following compounds: PBDEs (IUPAC # 47, 99), PCDD/Fs. Recoveries of internal carbon-13 BDEs (## 47, 99) standards (calculated based on 33'44'TCB (D6), added prior to injection) ranged between 67-91 %. Method limits of detection for PBDEs ranged between 0.05-0.1 ng/g lipids of tissue and 2 pg/g d.w. of vegetation. All values were adjusted to the lipid content of the tissue samples (table 1,3,4).

Results and discussion

Difference in PCDD/Fs and PBDE accumulation in reindeer tissue samples due to bioaccumulation was observed both depending on the area of sampling and on the type of tissue. Thus PCDD/Fs content in liver exceeds by several times the content in muscle samples of one and the same group of animals (figure 1). Relatively increased PCDD/Fs pollution levels were found in Kola Peninsula and in the sample from downstream water of the Pechora River.
Low levels of lipids in most of our samples (mean 5%) do not allow for correct comparison with available data on reindeer fat from Sweden, Norway and Canada, which were 0.2-3.1 pg/g reindeer fat from Canada and up to 11.4 pg/g l.w. in the sample from Ammarnas, Sweden[1].
Some data on Russian reindeer and mountain hare point to increased dioxin and furan levels on theKola Peninsula, probably due to local emissions from smelters. It is impossible to determine the pollution source more exactly because it was a pooled sample. The 2,3,7,8-TCDD content and especially the penta-CDD/F isomers and OCDD in the liver sample of reindeer exceeds by several times the levels in other arctic areas.
Moss and lichen are the main food for hare and reindeer and POPs traces were found in them (figure 2). The content of 2,2'4,4'-TBDE is 2 times higher in lichens as compared with moss samples. For 22'44'5-PnBDE this tendency is the same.
Total PBDEs (#47, 99) are 25-36 pg/g dry weight in all samples from the Arctic and probably represents the background level of the area due to transboundary transport. Soil levels range from 3.2 pg/g in the Pechora river basin to 7 pg/g w.w. in Kola Peninsula and in Chukotka (settlement of Kanchalan).
Hare liver and muscle samples also show geographic differences. The sample from Kola Peninsula is most polluted in the analyzed series of samples (figure 3). Liver also accumulates PCDD/Fs more than muscles and it is obvious that 22'44'-TBDE dominates (figure 2).
Muscles of duck from arctic areas contain PCDD/Fs at 2 times higher levels than muscles of ptarmigan (figure 4). Kola Peninsula and Taimir Peninsula are related to the areas with higher pollution level. According to the available limited information the type of duck does not matter much for levels.
If we consider the studied objects as elements of the human food chain then it should be noted that the allowable PCDD/F content in meat food adopted in Russia (3.2 pg/g lipids I-TEQ), is exceeded in all samples of reindeer liver and meat as well as hare and birds from Kola Peninsula. Probable pollution of water reservoirs of Taimir Peninsula is also reflected in increased PCDD/Fs content in duck tissues. Ptarmigan accumulates pollutants to a lesser extent apparently due to difference in food ration. The levels of PCDD/Fs found in biological samples of arctic areas in Russia point to the presence of local pollution sources and may be used for risk assessment concerning the indigenous population of the Russian Arctic.

Acknowledgment
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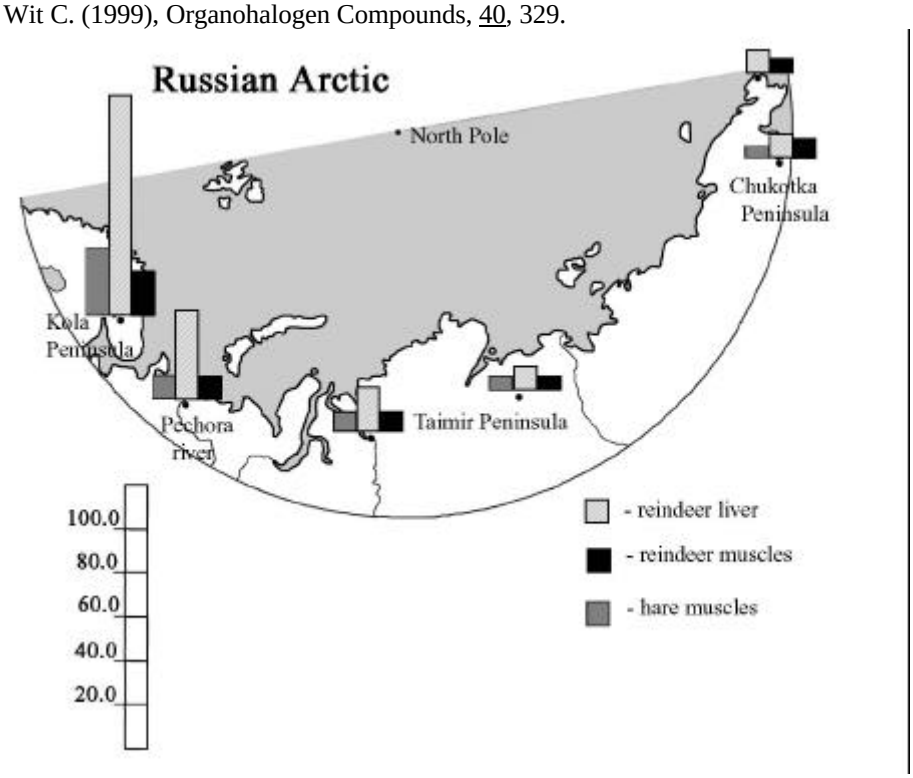

Figure 1. PCDD/Fs in reindeer and hare samples, WHO-TEQ, pg/g l.w.

Figure 2. PCDD/Fs in muscles samples of arctic wild birds

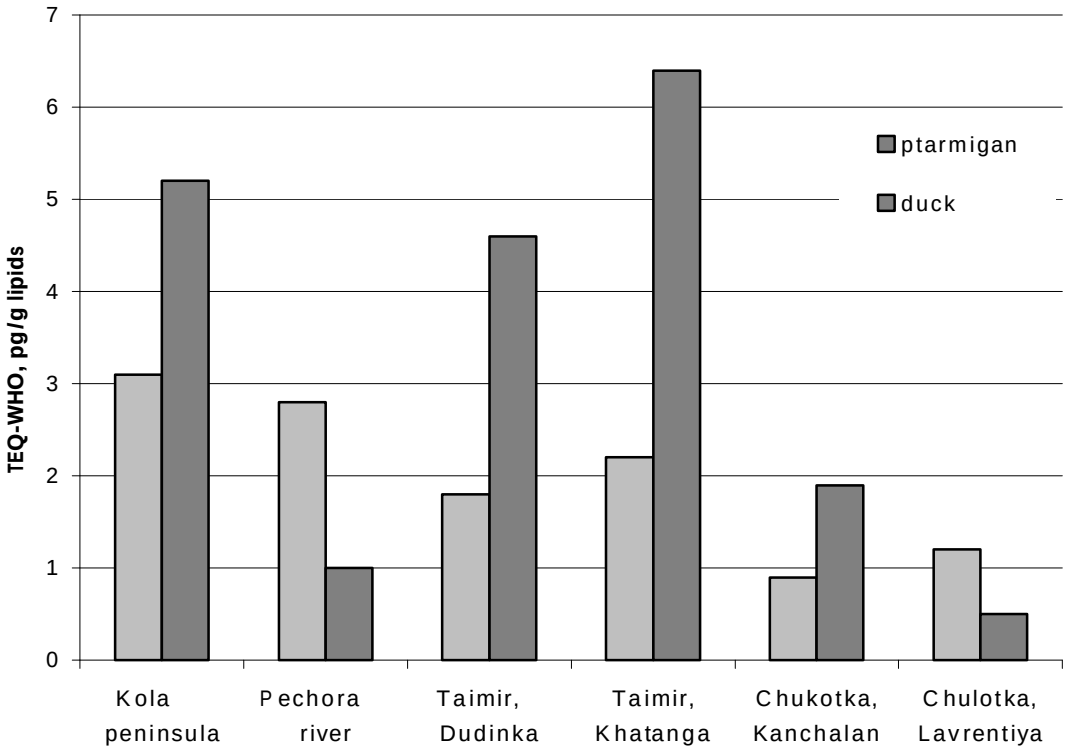

Figure 3. Sum of PBDE (##47,99) in samples from Russian Arctic, pg/g d.w. (soil, plants), pg/g l.w. (kidney, liver)