POLYCHLORINATED NAPHTHALENES AND COPLANAR PCBS IN SEDIMENT AND TISSUE ENVIRONEMNTAL REFERENCE MATERIALS.

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Introduction

PCNs are a class of halogenated aromatic compounds that had applications similar to PCBs. PCNs were used in capacitors, as dielectrics, flame retardants, wood preservatives and as water repellent waxes[1]. While PCN production was only 10% that of PCBs, their recalcitrant and toxic nature (some PCN congeners have comparable toxicity to coplanar PCBs) has led to recent efforts directed towards understanding their fate and distribution. For instance, PCNs have been recently measured in Arctic air[2], central Pacific Ocean seabirds[3], the Baltic Sea ecosystem[4] and the U.S. Great Lakes[5]. In some environmental samples, PCNs contribute as much or more to the total toxic equivalency factors than do PCBs[5]. Since PCNs are now more routinely measured in environmental samples, there is a need to provide reference values in control materials. The goal of this investigation, therefore, was to refine methodology for PCN measurement then apply these techniques to the determination of PCNs in two sediment and two tissue reference materials.

Materials and Methods

PCNs were determined in two candidate and two reference materials. The candidate reference materials were NIST Standard Reference Material (SRM) 1946 "Organics in Lake Superior Fish Tissue," which consists of cryohomogenized Lake Superior lake trout filets and SRM 1941b "Organics in Marine Sediment," which was a freeze-dried material. The reference materials were NIST SRM 1941a "Organics in Marine Sediment" and NRC Canada's Carp I. Three aliquots of each material were first dried with Na_2SO_4 then each aliquot was added to a 33 mL pressurized fluid extractor cell (PFE, Dionex). Six calibration solutions were prepared by weighing portions of SRMs 2261 (Chlorinated pesticides in hexane), 2262 (Chlorinated biphenyl congeners in 2,2,4 trimethylpentane), 2274 (Chlorinated biphenyl congeners in 2,2,4 trimethylpentane II) and 2275 (Chlorinated pesticides in hexane II) into weighed portions of isooctane. A mixed internal standard solution containing 4,4'-DDT-d_8, 4,4'-DDE-d_8, 4,4'-DDD-d_8, Endosulfan I-d_4, PCB 103 and PCB 198 was then added to each PFE vial, by weighing approximately 1 mL of the solution. The samples were extracted with CH_2Cl_2 using the PFE. The conditions were as follows: the cell

temperature was 100 °C, equilibration 5 min, static time 5 min, cell pressure was 2000 psi and there were three cycles. The sample extracts were then reduced to between 0.5 mL to 1 mL by evaporation in a stream of purified N_2 using a Turbovap II (Zymark). Elemental sulfur was removed from the sediment extracts by treatment with activated Cu powder.

Several HPLC techniques were used to isolate the compounds of interest. High molecular weight compounds, including lipids, were removed from the sample extracts by size exclusion chromatography (PLgel, Polymer Labs) using CH_2Cl_2 as the mobile phase. The extract was then fractionated using a semi-preparative aminopropylsilane column (μBondapak NH_2, Waters) into relatively lower and higher polarity fractions (F1 and F2, respectively). Compounds contained in the lower polarity fraction included PCBs, heptachlor, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, hexachlorobenzene, mirex and oxychlordane. Analytes in F2 included 4,4'-DDT, *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, α- β-, and γ-hexachlorocyclohexane, heptachlor epoxide, 2,4'- and 4,4'-DDD, and dieldrin.

Polychlorinated biphenyl congeners and organochlorine pesticides were initially quantified using GC with dual micro-electron capture detectors (Hewlett Packard 6890). Organochlorines in F1 and F2 obtained using the NH_2 column were separated using a 60 m DB-5 (J&W Scientific) with 0.25 mm interior diameter and a 0.25 μm film thickness and a 60 m DB-XLB (J&W Scientific) with 0.25 mm interior diameter and a 0.25 μm film thickness. The injector and detector temperatures were 220 °C and 325 °C, respectively; the carrier and makeup gasses were H_2 (constant velocity of 30 cm/s) and N_2 (30 mL/min), respectively. Samples were injected into the GC (2 μL, splitless injection), and the oven was programmed from 90 °C initially (1 min hold) to 170 °C at 18 °C/min, then 1 °C/min to 260 °C then ramped to 300 °C at 1.5 °C/min (107 min run time).

Planar compounds including PCNs and coplanar PCBs were separated from other compounds in the F1 using a Cosmosil PYE column (Phenomenex) to separate coplanar PCBs and PCNs from ortho-substituted PCBs[6]. PCNs and coplanar PCBs were analyzed by NCI-LRMS using either a 60 m or a 30 m DB-5MS columns. Coplanar PCBs were further quantified using EI-LRMS (Hewlett Packard 5973) in the selected ion monitoring mode with a 60 m DB-XLB column and EI-HRMS (JEOL, JMS-700) using a 30 m DB-5MS. ^{13}C labeled PCB 77, 126 and 169 were used as internal standards. For the PCN analysis, PCB 204 was used as a to quantify the recovery of the internal standards added just prior to extraction. Three concentrations of a solution of Halowax 1014 with known percent contributions of PCN congeners were used as a calibration standards[7].

Results and Discussion

PCNs were detected in all four of the materials examined. The total PCN concentrations (tPCN) measured in the four materials were 116 (2.8, SD, n=3) ng/g dry mass, 9.53 (1.9) ng/g dry mass, 0.30 (0.04) wet mass and 0.11 (0.02) ng/g wet mass for SRM 1941a, SRM 1941b, Carp I and SRM 1946, respectively. There was a different PCN congener distribution in the sediment relative to the fish materials. PCN congeners 73 and 75 were the dominant congeners in the sediment

materials comprising 29% and 24% in SRM 1941b and 20% and 23% in SRM 1941a, respectively. The most toxic PCN congeners[5], PCNs 66/67 were the next most abundant PCN congeners in the sediment materials comprising 14% and 9% of the tPCNs in SRM 1941b and SRM 1941a, respectively. However in Carp 1, PCN congeners 66/67 PCN were the most abundant PCN congeners comprising 64% of the total PCNs present in that material, although the tPCNs concentration was low in this material (0.30 ng/g wet mass). PCNs 42 and 47 were the next two most abundant congeners in the fish materials averaging 24% to 12% in Carp I and 47% and 36% in SRM 1946, respectively.

Coplanar PCBs were also present in all the materials. The dry mass based concentrations of PCB congeners 77, 126 and 169 in SRM 1941a were 0.88 (0.02) ng/g, 0.07 (0.001) ng/g mass, and 0.02 (0.003) ng/g and in SRM 1941b, 0.31 (0.03) ng/g, 0.029 (0.01) ng/g and 0.02 (0.003) ng/g, respectively. In the fish materials, the wet mass based concentrations of PCB congeners 77, 126 and 169 were 1.05 (0.12) ng/g, 0.310 (0.04) ng/g and 0.30 (0.006) ng/g in Carp I and 0.33 (0.03) ng/g, 0.38 (0.01), and 0.10 (0.001), respectively. PCNs were higher in concentration relative to coplanar PCBs in the sediment material, whereas the reverse was true in the fish materials. The occurrence of PCNs in measurable quantities in these reference materials indicates that they would be useful control materials, especially SRMs 1941a and 1941b, when analyzed alongside environmental samples with unknown quantities of PCNs.

References

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