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DEVELOPMENT OF AN ANALYTICAL METHOD TO MEASURE POLYBROMINATED DIPHENYL ETHERS IN ARCHIVED EXTRACTS OF AVIAN EGGS

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ABSTRACT

POLYBROMINATED DIPHENYL ETHERS (PBDEs) are part of a group of brominated flame retardants used in a wide range of commercial and domestic applications to reduce product flammability. Large scale production of PBDEs started in the early 1970s with their presence in the environment first measured in 1979. Production of PBDEs has increased steadily since then with global annual production in 2001 estimated at 67,000 metric tons. In order to properly assess the level of risk associated with PBDEs, accurate and sensitive methods are needed to measure these compounds. In this study we developed and validated an analytical procedure to measure 13 PBDE congeners in extracts of common (*Sterna hirundo*) and roseate (*Sterna dougalli*) tern eggs originally processed for polychlorinated biphenyl (PCB) analysis. Negative chemical ionization mass spectrometry (NCI-MS) was determined to have much lower detection limits for PBDEs than standard electron impact ionization (EI). Results are presented for eight environmentally ubiquitous congeners (PBDEs 17, 28, 47, 66, 99, 100, 153, 154). Provisional PBDE values from a NIST standard reference material (SRM1974b) compared well against our results, indicating excellent extraction recoveries and accurate analytical data. Reanalysis of selected samples for PCBs showed little change in concentrations over time, indicating that analyte loss during archival was not a factor. In addition, PBDE levels in the samples compared well with literature values, providing further evidence of the robustness of the methods used. Overall, results show that previously archived samples can be used to measure other classes of contaminants provided that methodologies and procedures are properly validated.

INTRODUCTION

POLYBROMINATED DIPHENYL ETHERS are currently used as additives in plastics, foam, textile products and other materials to reduce their flammability. PBDEs enter the environment during manufacture, leach from products during their use and when products are either recycled or disposed of. Production of PBDEs started in the 1970s, with a steady gain in global usage. One of the results of the growing use of PBDEs over time has been the presence and increasing levels of these compounds in environmental samples as well as both animal and human tissues.

PBDEs have physical and chemical properties similar to other persistent organic pollutants (POPs) (e.g., PCB, DDT) and have been found to be bioaccumulative and toxic. 209 PBDE congeners exist and are numbered using the IUPAC system applied to PCBs (Figure 1). PBDEs are extremely hydrophobic (log K_{ow} 5-10) with solubility and vapor pressure decreasing as the degree of bromination increases. A number of technical mixtures (e.g., Aroclor 1248, Aroclor 1254, Aroclor 1260, Aroclor 1268, Aroclor 1281, Aroclor 1282, Aroclor 1283, Aroclor 1284, Aroclor 1285, Aroclor 1286, Aroclor 1287, Aroclor 1288, Aroclor 1289, Aroclor 1290, Aroclor 1291, Aroclor 1292, Aroclor 1293, Aroclor 1294, Aroclor 1295, Aroclor 1296, Aroclor 1297, Aroclor 1298, Aroclor 1299, Aroclor 1300, Aroclor 1301, Aroclor 1302, Aroclor 1303, Aroclor 1304, Aroclor 1305, Aroclor 1306, Aroclor 1307, Aroclor 1308, Aroclor 1309, Aroclor 1310, Aroclor 1311, Aroclor 1312, Aroclor 1313, Aroclor 1314, Aroclor 1315, Aroclor 1316, Aroclor 1317, Aroclor 1318, Aroclor 1319, Aroclor 1320, Aroclor 1321, Aroclor 1322, Aroclor 1323, Aroclor 1324, Aroclor 1325, Aroclor 1326, Aroclor 1327, Aroclor 1328, Aroclor 1329, Aroclor 1330, Aroclor 1331, Aroclor 1332, Aroclor 1333, Aroclor 1334, Aroclor 1335, Aroclor 1336, Aroclor 1337, Aroclor 1338, Aroclor 1339, Aroclor 1340, Aroclor 1341, Aroclor 1342, Aroclor 1343, Aroclor 1344, Aroclor 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