EXTRACTABLE ORGANOHALOGENS (EOX) IN SEDIMENT AND MUSSEL TISSUES FROM THE KENTUCKY LAKE AND KENTUCKY DAM TAILWATER, USA

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Introduction

Persistent, bioaccumulative and toxic (PBT) organochlorine compounds are considered the most unwanted organic pollutants and powerful threats to wildlife and human health[1]. Some of the well-known PBTs are agricultural (DDTs and other chlorinated pesticides) and industrial chemicals (Polychlorinated biphenyls and dioxins). In the natural environment such as rivers and/or lakes, fish and other wildlife are often exposed to PBTs, from both natural as well as man-made sources[2,3]. Harmful biological effects of pollutants reported in fish, shellfish and higher trophic level animals were attributed largely to chlorinated organic compounds. Until the early 1980s, contaminant measurements in environmental and biological samples focused mainly on the levels of compounds such as chlorinated hydrocarbon pesticides and/or polychlorinated biphenyls (PCBs). Occurrence of brominated and iodinated compounds in the environment was largely ignored; however, recent studies have emphasized the need for understanding the levels of total organic halogens (EOX) including extractable, organically bound chlorine (EOCl), bromine (EOBr) and iodine (EOI) in environmental and biological samples[4-6] in order that meaningful risk estimates can be made for these contaminants. The EOCl, determined by neutron activation analysis (NAA), has been used as a measure of pollution by chlorinated organics[5].

Kentucky Lake is one of the major human-constructed lakes in the U.S. It covers an area of 65,000 ha and constitutes the northernmost end of a major shipping route for large ships and barges and small ships between the Gulf of Mexico and the Ohio River (Figure 1). The Kentucky Dam tailwater including the lowermost Tennessee River receives industrial wastewater from several industries including mercury cell chlor-alkali factories located in the Calvert city Industrial Complex (CCIC). During the past two decades, mass mortality of mussels has been frequently encountered in these regional waters, the causes of these extirpations have not been elucidated. In addition, the quality and quantity of cells harvested for pearl industry also were substantially reduced. Although a few studies have examined the levels of chlorinated organics in the locations of lowermost TN River and KY Lake[7,8], there have been no reports on the distribution of total halogenated organics found in sediment and/or biota from this region. The EOX include extractable organic chlorine (EOCl), extractable organic bromine (EOBr) and extractable organic iodine (EOI). These groups of compounds are quantified in sediment and biota by extracting with organic solvents followed by neutron activation analysis. In this study, the concentrations and distribution of extractable organohalogens (EOX = EOCl + EOBr + EOI) were measured in

sediment and mussel tissues collected at selected locations in the lowermost Tennessee River and Kentucky Lake (USA) in order to understand the status of contamination by chlorinated organic pollutants.

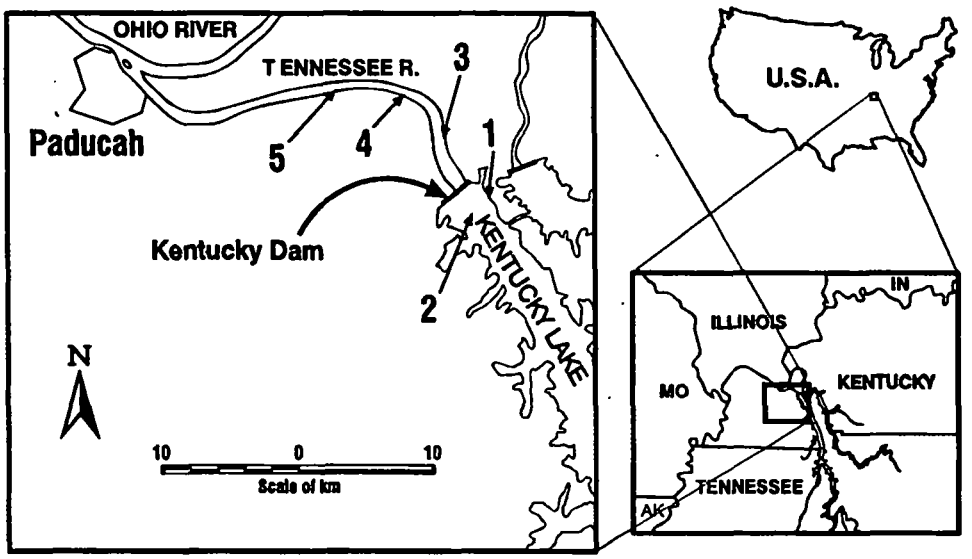

FIGURE 1. Map showing sediment and mussel sampling locations in the Kentucky Lake and Kentucky Dam Tailwater, U.S.A.

Materials and Methods

Figure 1 shows the sampling locations in the Kentucky Lake and KY Dam Tailwater. Surface sediment (0-5 cm) and mussel samples were collected on May 21, 1997. Ponar Grab sampler was used to collect sediments and mussel samples were collected by SCUBA diving. The mussels were measured, identified; wet weight and age were determined. The mussels were separated from shells. The individuals of the same species and age were pooled and transferred to pre-cleaned glass jars and stored under -20 °C until analysis. About 40 g wet sediment was extracted three times with 60 ml acetone each time in a using automatic shaker and combined acetone extract was K-D concentrated and exchanged to hexane prior to neutron activation analysis. An aliquot of sediment sample was dried in a hot air oven to calculate moisture content. Mussel samples were freeze-dried. About 3 to 5 g of dry mussel tissue was Soxhlet extracted for 16 h using 3:1 mixture of methylene chloride and acetone and the extract was transferred to hexane. The concentrations of EOCl, EOBr and EOI were determined by neutron activation analysis[4-6, 9]. Ammonium chloride, ammonium bromide and ammonium iodide of known concentrations dissolved in water, were used as standards. Sodium sulfate (100g) was Soxhlet extracted with methylene chloride and hexane and the extract was used as a procedural blank to check impurities and to correct sample values. Details of the polychlorinated biphenyls (PCBs) and chlorinated hydrocarbon pesticide analysis in the above samples were described elsewhere[7].

Results and Discussion

Table 1 and 2 show the concentrations of EOCl, EOBr, EOI and EOX in sediment and mussel tissues. Among the organohalogens measured (EOCl, EOBr, EOI), EOCl was the greatest in both sediment and mussel tissues. EOBr and EOI concentrations were relatively low and found in the same order of magnitude. EOCl accounted for over 90% of the EOX measured in sediment and mussel tissues. The concentration of organohalogens measured in mussel tissues were in the order of EOCl >> EOBr > EOI (Table 2).

TABLE 1. EOX concentrations (μg g^{-1} dry wt.) in sediment samples from the Kentucky Lake and KY Dam Tailwater, U.S.A. Values in parenthesis indicate percent composition.

Site No.	Location	EOCl	EOBr	EOI	EOX
1	TRM 23.1/R	0.19	ND	0.028	0.22
2	TRM 22.9/L	0.37	0.052	0.01	0.43
3	TRM 20.9R	0.32	ND	0.20	0.52
4	TRM 17.7/L	1.44	0.02	0.052	1.51
5	TRM 15.2/L	0.86	0.012	0.018	0.89
	Mean	0.64 (90)	0.017 (2.4)	0.062 (8.7)	0.71

TRM: Tennessee River Mile; L: Left bank; R: Right bank

TABLE 2. EOX concentrations (μg g^{-1} dry wt.) in mussel tissue samples from the Kentucky Lake and KY Dam Tailwater, U.S.A.

Site No.	Species	Age (yr)	EOCl	EOBr	EOI	EOX
1	*Q. quadrula(1)*	6	35.0	0.45	0.10	35.55
1	*A. plicata(1)*	7	33.2	0.98	0.06	34.24
1	*F. ebena(1)*	13	15.6	1.93	0.16	17.69
2	*NC*		NA	NA	NA	NA
3	*Q. quadrula(4)*	11-12	27.7	0.78	0.10	28.58
4	*A. plicata(5)*	8-11	42.8	0.45	0.10	43.35
5	*A. plicata(6)*	8-10	29.0	0.27	0.15	29.42
5	*Q. quadrula(5)*	8-10	20.3	0.71	0.10	21.11
	Mean (percent)		29.09 (96.9)	0.796 (2.65)	0.11	29.99

Values in parenthesis in associated with species in the column 2 indicate number of specimens pooled for analysis. *NC*: Not collected for safety reasons. NA: Data not available.

The concentrations of EOCl observed in sediments was comparatively lower (0.64 μg g^{-1} dry wt.) than the reported values of 822 (μg g^{-1} dry wt.) from an estuarine marsh near a chlor-alkali plant [5], and sediments from the vicinity of bleached pulp and paper mills in the Baltic sea and Jackfish Bays in Canada[10-12]. Lower concentrations of EOCl in sediments in Kentucky Lake and the KY Dam tailwater may be attributable to shorter hydraulic retention times of the river and the Lake, resulting in downstream transport of these compounds. In mussel tissues, EOCl concentrations were remarkably high ranging from 15.6 to 42.8 μg g^{-1} dry wt (Table 2). The highest concentration was found in *A. plicata* (5 specimens pooled) at site #4. Site #4 receives wastewater from several

industries including mercury cell chlor-alkali factories. Greater concentrations of EOCl in mussels may be due to long-term accumulation when Aroclor 1268 or other PCBs were in use in the mercury cell electrodes in the chlor-alkali factories. Legal use of PCBs in electrodes would have ended in 1979, unless the concentration was less than 50 ppm. Kannan *et al.*[5] attributed elevated concentrations of EOCl in biota from an estuarine marsh for the wastes from a former chlor-alkali plant and naturally occurring brominated and iodinated organics as the major sources of EOBr and EOI found in biota. Considering the percent composition of EOBr and EOI observed in the present study, it is possible that the sources for EOBr and EOI in sediment and mussels could be natural sources. Percent composition of EOCl measured in majority of sediment and mussel tissues were over 90%. Similar, compositions were also evident from carp from Buffalo River, Biota from Brunswick, GA, Harbor porpoise from Baltic Sea[4,5,10]. The measured concentration of known (identified) organochlorines such as PCBs and chlorinated hydrocarbon pesticides in sediment and mussel tissues were also examined. PCBs and chlorinated pesticides constituted only a minor part (<7.35%) of the EOCl, indicating the presence of additional, unknown organochlorine residues in sediments and mussel tissues from Kentucky Lake and KY Damtailwater. Elevated concentrations of EOCl and the proportions relative to the concentrations of EOBr and/or EOI in freshwater mussel tissues suggest that historical contamination as well as recent organic contamination may be possible source of organic halogens in the environment.

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