Bull. Environ. Contam. Toxicol. (2005) 74:1084–1091
DOI: 10.1007/s00128-005-0692-1

Bulletin of Environmental Contamination and Toxicology

Bioaccumulation and Bioavailability of Mirex from Lake Ontario Sediments

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Received: 30 December 2004/Accepted: 11 March 2005

Mirex®, also known as dechlorane, is an extremely stable chlorinated hydrocarbon that is a major contaminant of concern in Lake Ontario bottom sediments. Primary anthropogenic sources to Lake Ontario include past effluent and air-borne emission deposition from pesticide manufacturing plants and facilities where it was employed as a fire-resistant additive to polymers, and waste site leachate from former producers and processors via the Niagara and Oswego Rivers (Oliver et al. 1989). Mirex is highly persistent and generally resistant to biological or chemical degradation. It is strongly hydrophobic (log octanol-water partition coefficient [log K_{ow}] = 7.13; Halfon and Allan 1995), readily partitioning from the water column to sediment and sorbing tightly to organic matter. Therefore, bottom and resuspended sediments function as both an environmental sink and source.

Contemporary environmental levels of mirex in surficial sediments have been shown to range from non-detectable (<4.5 μg/kg) to 260 μg/kg (Swart et al. 1996). Such concentrations at the sediment-water interface are present for uptake by aquatic organisms. Due to its lipophilic nature, mirex is stored in adipose tissue, and appears to resist biotransformation in animals (International Program on Chemical Safety [IPCS] 1984). Laboratory studies have demonstrated mirex toxicity to invertebrates (Ludke et al. 1971) and fish (Hyde et al. 1974).

A major pathway for mirex food web transfer in aquatic ecosystems is from sediments to scavengers, to predatory invertebrates, and to vertebrates (IPCS 1984). Therefore, the typically low and persistent levels of mirex in Lake Ontario sediments, combined with its propensity to bioaccumulate and potentially elicit chronic toxicity, signal long-term environmental risk. Although bioaccumulation of mirex around Lake Ontario has reached high levels in consumers and higher predators, it does appear to be declining over time (Fox et al. 2002; Suns et al. 1993). However, no published studies have focused on the bioaccumulation of mirex directly from freshwater sediments to benthic invertebrates, either for Lake Ontario, other field-collected sediments, or in spiked-sediment studies. Such information is valuable because sediments are the contemporary source of mirex contamination in aquatic systems, and the tendency of mirex to biomagnify accentuates the need to accurately assess its bioavailability at the benthic level.

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The objective of this study was to assess the bioavailability of mirex in surface sediments from a contaminated area of Lake Ontario using a standard freshwater bioaccumulation test with the aquatic oligochaete worm, *Lumbriculus variegatus*. This species is a surficial sediment deposit feeder used in prescribed Great Lakes sediment bioaccumulation tests (US Environmental Protection Agency [USEPA]/US Army Corps of Engineers [USACE] 1998).

MATERIALS AND METHODS

The sediment samples for this study were collected in 2003 at a 20-m deep open-lake area off the south shore of Lake Ontario near Rochester Harbor in Rochester, Monroe County, NY, USA (Figure 1). Surface grab sediment samples were collected using a Ponar/Peterson dredge sampler from four sites within the lake area, for a total volume of at least 6 L per site. Sediment samples were gathered in a stainless steel pan and homogenized. Equal volumes of the four discrete samples were combined and thoroughly mixed into a single sample for the bioaccumulation testing. The four discrete and composite samples were analyzed for mirex concentrations, total organic carbon (TOC), and grain size.

The *L. variegatus* 28-d bioaccumulation test for sediments was conducted according to guidelines provided in the USEPA/USACE Great Lakes Dredged Material Testing and Evaluation Manual ("the Manual") (USEPA/USACE 1998). Worms were exposed to test and control (Browns Lake, Vicksburg, MS) sediments in 6-L box aquaria (31.5 x 18 x 10.5 cm) using five replicates per treatment. Adequate exposure conditions were maintained using an intermittent flow system for overlying water renewal. At exposure termination, worms were recovered from the sediment, placed in water for gut purging (12 h), blotted dry and frozen at –20°C.

USEPA SW-846 Method 8081A was used for mirex sediment and tissue analyses, and Method 9060 was used for TOC analysis (USEPA 1996). Total tissue lipid content was determined using chloroform/methanol extraction and colorimetric analysis according to Van Handel (1985). Sediment samples including method blank, laboratory control spike (LCS), and laboratory control spike duplicate (LCSD) were extracted using pressurized fluid extraction. Extracts were concentrated and cleaned up using florisil and tetrabutylammonium sulfite reagent. Tissue samples including method blank, LCS, matrix spike and matrix spike duplicate were extracted using sonication and cleaned up using florisil. Concentrated extracts were analyzed for organochlorine pesticides using a Hewlett-Packard 5890 (Avondale, PA) gas chromatograph with dual capillary columns equipped with dual electron capture detectors. Average percent spike recovery for mirex was 97% (range 90-105%) for sediments and 95% (range 64-112%) for tissues.

Figure 1. Sampling area in US Lake Ontario waters near Rochester, NY

Biota-Sediment Accumulation Factors (BSAFs) were calculated from the bioaccumulation data to quantify and express the bioavailability of sediment-associated mirex (Ferraro et al. 1990):

$$BSAF = \frac{C_t / L}{C_s / TOC}$$

where C_t is the concentration of mirex in tissue (μg/kg wet weight), L is the concentration of lipid in *L. variegatus* tissue (percent of wet weight), C_s is the concentration of mirex in sediment (μg/kg dry weight) and TOC is the total organic carbon concentration in sediment (percent of dry weight).

A mean mirex BSAF was calculated based on the five replicate BSAFs. Uncertainty for the BSAF was estimated using standard error-based propagated error (PE) calculations for C_s, TOC, lipid and C_t (Clarke and McFarland 2000).

RESULTS AND DISCUSSION

Concentrations of mirex in discrete and composite sediment samples ranged from below laboratory reporting limit (LRL) (2.84 μg/kg) to 27.7 μg/kg (Table 1). The average (±1 Standard Error [SE]) of the mirex concentrations in discrete samples was 17.5±5.4 μg/kg and was consistent with the concentration in the composite sediment used in the bioaccumulation experiments. The physical characteristics of the samples were similar, with 80.2 to 88.8% silt/clay (average of 86.4%), and the remainder sand. TOC ranged from 1.9 to 2.2% and averaged 2.0±0.06%.

Table 2 summarizes the results of the bioaccumulation experiments, and the associated replicate and mean BSAFs. The bioaccumulated levels of mirex across

the five replicates ranged from 3.99 to 4.42 μg/kg and averaged 4.17±0.07 μg/kg. Two of the mirex levels in *L. variegatus* were non-detectable at the LRL. All non-detects were valued at the LRL in order to produce a maximum and most conservative BSAF. The lipid content ranged from 0.55 to 0.67% and averaged 0.60±0.02%. The mean mirex BSAF±PE was 0.83±0.28. The largest contributor to uncertainty associated with the mean BSAF was the LRL used for non-detectable mirex concentration in discrete sediment sample RR-4.

Table 1. Chemical and physical characteristics of sediments collected from the Rochester lake area

Sediment sample	Mirex (μg/kg-dry weight)	TOC (% of dry weight)	Particle size distribution (%)		
			Gravel	Sand	Silt/Clay
RR-1	22.8	1.9	0	13.1	86.9
RR-2	16.7	2.0	0	19.8	80.2
RR-3	27.7	2.2	0	10.3	89.7
RR-4	<2.84*	2.0	0	11.2	88.8
Composite	16.7	2.0	0	13.4	86.6

*Below laboratory reporting limit

Table 2. Results of 28-d mirex *L. variegatus* bioaccumulation experiments on Rochester lake area sediments and associated BSAFs

Replicate	Tissue concentration (μg/kg-wet weight)	Lipid (% of wet weight)	BSAF*
A	<4.19**	0.64	0.78
B	<4.19**	0.58	0.85
C	4.07	0.55	0.87
D	4.42	0.56	0.95
E	3.99	0.67	0.71
		Mean BSAF	0.83

*Based on composite sediment mirex and TOC data contained in Table 1
**Below laboratory reporting limit

The 28-d exposure period used in this study likely was sufficient to allow tissue concentrations of mirex to approach steady state in *L. variegatus*. Ingersoll et al. (2003) demonstrated that 14- to 28-d exposure periods for *L. variegatus* to field sediments contaminated with highly hydrophobic compounds, such as 4,4'-dichlorodiphenyldichloroethane (DDT), its metabolite 4,4'-dichlorodiphenyldichloroethylene (DDE) and benzo(a)pyrene, which have log K_{ow}s similar to mirex, reflected steady-state tissue concentrations. No further increase in the body residue of those compounds was observed in exposure periods greater than 28 days. In addition, the polychlorinated biphenyl (PCB) 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP), another highly hydrophobic

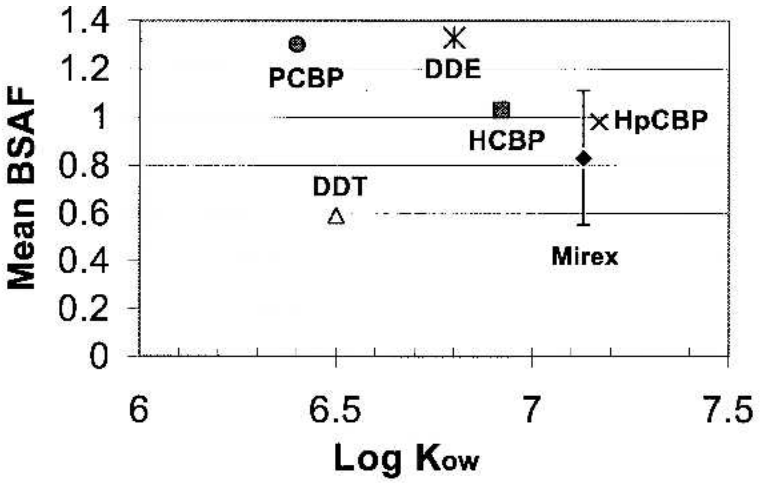

Figure 2. Comparison of the mean mirex BSAF, with uncertainty limits, to BSAFs for other chlorinated compounds with similar log K_{ow}s (average log K_{ow}s were used for PCB homologue groups).

compound (log K_{ow} = 6.92 [Hawker and Connell 1988]), is expected to approach steady-state concentrations in *L. variegatus* in less than 18 days (Schuler et al. 2003). Ankley et al. (1992) reported good correspondence in PCB BSAFs between laboratory-exposed *L. variegatus* and field oligochaetes, suggesting that steady-state tissue concentrations were achieved during the 28-d laboratory exposure period. Therefore, the BSAF determined in this study is expected to be representative of the *in-situ* bioavailability of mirex in Lake Ontario sediments within a reasonable degree of confidence.

No published information was found regarding the bioaccumulation of sediment-associated mirex by benthic organisms, and no BSAF values were found in the available literature or a BSAF database (US Army Engineer Research and Development Center, http://el.erdc.usace.army.mil/bsaf). However, published BSAFs based on comparable benthic organisms are available for several persistent organic compounds with similar log K_{ow}s, including DDT, DDE and several PCBs. For the marine polychaete *Heteromastus filifomus*, Mulsow and Landrum (1995) calculated mean DDT BSAFs that ranged from 0.40 to 0.80, for a grand mean of 0.59. Mean BSAFs for DDE using the marine hardshell clam *Macoma nasuta* ranged from 0.65 to 2.8, for a grand mean of 1.33 (Ferraro et al. 1990). Based on 28-day *L. variegatus* bioaccumulation experiments, Ankley et al. (1992) reported mean BSAFs of 1.30, 1.03 and 0.98 for the pentachlorobiphenyl (PCBP), HCBP and heptachlorobiphenyl (HpCBP) homologues, respectively. The mirex BSAF calculated in this investigation is in the same range as the BSAFs calculated for these other highly hydrophobic chlorinated compounds (Figure 2).

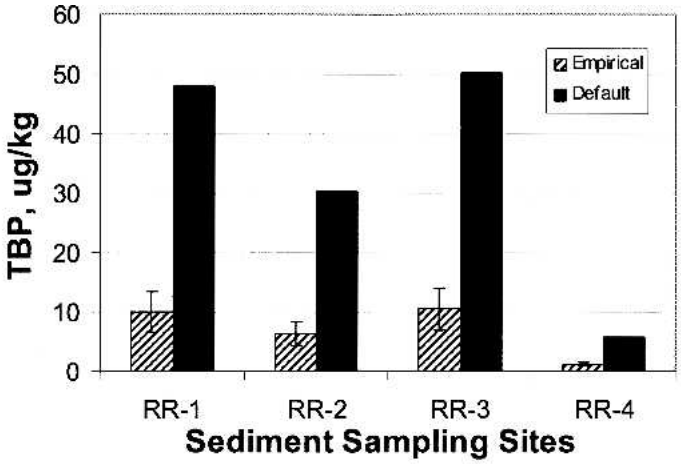

Figure 3. Mirex TBP predictions for Rochester lake area sediments using empirical (0.83) versus default (4.0) BSAFs. Error bars for empirical TBP estimates were calculated from upper and lower BSAF uncertainty limits.

The Manual (USEPA/USACE 1998) currently endorses the use of a default BSAF value of 4.0 in the theoretical bioaccumulation potential (TBP) model, an equilibrium theory-based algorithm used to predict the potential bioaccumulation of neutral, organic compounds in sediments (McFarland 1984). The empirical BSAF determined from the present study is markedly less than 4.0, and its use would yield more precise predictions and realistic assessments of mirex uptake.

The TBP model is expressed as:

$$TBP = BSAF\,(L)\ (C_s/TOC)$$

where TBP is the predicted whole body tissue concentration (µg/kg wet weight), L is the concentration of lipid in target animals (percent of wet weight), C_s is the concentration of mirex in sediment (µg/kg dry weight) and TOC is the total organic carbon concentration in sediment (percent of dry weight).

This model is employed as a tool to make regulatory determinations concerning the suitability of dredged sediments for open-water placement. Sediment data in Table 1 were used to estimate the TBP of mirex in aquatic oligochaetes in sediments from the Rochester lake area. The estimations assumed a 1% lipid content, an average characteristically representative of oligochaete worms (e.g., Ankley et al. 1992, Pickard et al. 2001). Figure 3 compares the TBPs using the empirical vs. default BSAFs. Use of the default value yields an 8-fold overestimation (TBP = 35.6±0.11 µg/kg) of actual bioaccumulation in *L. variegatus* (mean of 4.17±0.07 µg/kg), whereas the empirical value yields overestimates of actual bioaccumulation by less than a factor of two (TBP = 7.0±0.43 µg/kg).

The estimation of TBP is highly dependent on the quality of the BSAF due to the uncertainty associated with the four BSAF components. The PE for the mean mirex TBP was computed as ±5.26 and indicates that the TBP uncertainty range was less than a factor of two of the mean. While TBP is not a precise estimator of bioaccumulation, its predictive capabilities are comparable with alternative, more complex, multi-variable bioaccumulation models (e.g., Morrison et al. 1996). Therefore, the use of TBP estimated from empirically derived BSAFs provides a simple, cost-effective, screening tool for estimating the bioaccumulation of sediment-associated mirex and other non-polar organic compounds from sediments.

Acknowledgments. We thank USACE (Buffalo District) colleagues David Melfi, Dennis Rimer, William Butler, Ryan Lenihan and Steven Metivier for their support on this work.

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