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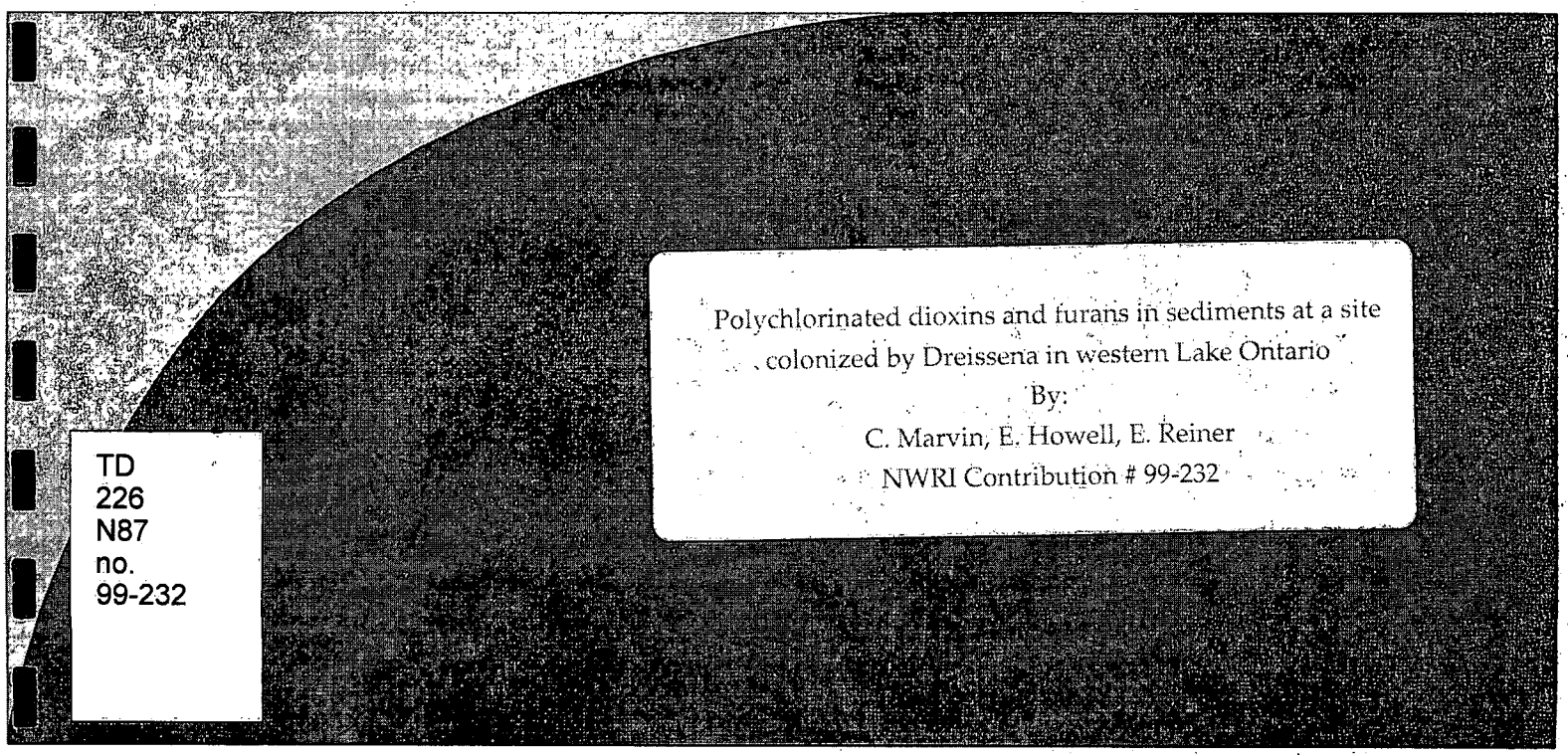

Polychlorinated dioxins and furans in sediments at a site colonized by Dreissena in western Lake Ontario

By:
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MANAGEMENT PERSPECTIVE

- **Title:** Polychlorinated dioxins and furans in sediments at a site colonized by Dreissena in western Lake Ontario.

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- **NWRI Publication #:** 99-232
- **Citation:**

- **EC Priority/Issue:** Lake Ontario LaMP, Great Lakes 2000, fisheries

- **Current Status:** Dreissena have extensively colonized nearshore areas of western Lake Ontario, much to the same extent as heavily colonized areas of Lake Erie. This work is an investigation of the potential impacts of Dreissena on the physical and chemical characteristics of nearshore sediments, with emphasis on polychlorinated dioxins and furans. Data show that Dreissena are capable of promoting the accumulation of fine particulate in the benthos and bioaccumulating dioxins and furans. Dreissena are capable of significantly elevating levels of dioxins and furans in sediments they colonize, relative to areas in close proximity that are not colonized. In comparing dioxin and furan burdens in biomass and sediments on an areal basis, the sediments remain the primary sink for these contamintants.

- **Next Steps:** Publish in a scientific journal and communicate to LaMP process. Any continuation of this work is contingent upon funding.

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POLYCHLORINATED DIOXINS AND FURANS IN SEDIMENTS AT A SITE COLONIZED BY *DREISSENA* IN WESTERN LAKE ONTARIO, CANADA

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Abstract—Potential impacts of *Dreissena* on polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) levels in sediment were investigated by comparing PCDD/PCDF levels in colonized sediment with levels in sediment in the same area that was not colonized but that was exposed to similar environmental conditions. Levels of PCDDs/PCDFs were also determined in *Dreissena* tissues. The particle size distribution of colonized sediment was characterized by silt-size material with peak abundance in the range of 7.5 to 20 μm, whereas noncolonized sediment was coarser in nature (30–60 μm). Total organic carbon (TOC) and concentrations of the PCDD/PCDF congener groups and individual 2,3,7,8-substituted isomers were greater in colonized sediment. A trend was observed toward decreasing concentrations of PCDF congener groups with increased chlorine substitution in mussel tissues in contrast to increasing concentrations of PCDF congener groups with increased chlorination in sediments. The trend in the PCDD congener group profile in mussel tissues appeared more similar to the profile in sediments. Areal estimates of toxicity equivalents (TEQ) in *Dreissena* biomass at Port Dalhousie, Ontario, Canada (approx. 1,300 pg/m²) were about 0.9% of the TEQ in the top 3 cm of sediment (approx. 135,000 pg/m²). Differences in particle size distribution and PCDD/PCDF levels between colonized and noncolonized sediment suggest that *Dreissena* may influence chemical and physical properties of sediment they colonize.

Keywords—Zebra mussel *Dreissena* Polychlorinated dibenzo-*p*-dioxins Polychlorinated dibenzofurans Lake Ontario

INTRODUCTION

The exotic mussels *Dreissena polymorpha* (zebra mussel) and *Dreissena bugensis* (quagga mussel) have established prolific populations in many areas of the Great Lakes. Impacts attributed to filtration of suspended particulate from the water column by *Dreissena* include increases in water transparency [1–3], decreases in mean chlorophyll *a* concentrations [2], and declines in phytoplankton densities [3,4]. Annual monitoring (1988–1992) of a site in eastern Lake Erie showed increases with time in water clarity and decreases with time in chlorophyll *a* concentrations that coincided with colonization of the site by *Dreissena* [5]. In addition, there was an increase in sediment total organic carbon (TOC), an increase in sediment concentrations of polycyclic aromatic hydrocarbons (PAH) and metals, and a transition in the particle size distribution of surficial sediment from sand-size particles to mainly silt-size particles. On the basis of these observations, it was inferred that after 1990 an increase occurred in the rate of accumulation of silt-size particles in the sediment, possibly as a result of cycling of suspended particulates by *Dreissena*.

To date, few investigations have addressed the potential consequences of the *Dreissena* invasion on contaminant burdens in the benthic zone. We recently reported the results of a study to investigate potential impacts of *Dreissena* on physical and chemical characteristics of sediments at near-shore sites in western Lake Ontario and eastern Lake Erie [6]. The particle size distributions, TOC, nutrient, and contaminant burdens of sediments colonized by *Dreissena* were compared with sediments in close proximity that were not colonized but that were exposed to similar environmental conditions. Colonized sediments were characterized by finer particle size distributions, higher TOC, and higher concentrations of metals compared to noncolonized sediments. The greater metal concentrations in colonized sediments was attributed to potentially increased accumulation and retention of silt-size particles as a result of particulate cycling and benthic layer alteration by *Dreissena*. *Dreissena* may also be a vector for the transfer of contaminants to other trophic levels by increasing the rate of movement of contaminants through the detrital food chain to benthic invertebrates, such as gammarid amphipods, that are important food sources for higher trophic levels [7]. *Dreissena* in the Great Lakes have the ability to accumulate contaminants in their tissues [8,9] and serve as prey for crayfish, some fish, and waterfowl [10,11]. Thus, *Dreissena* may potentially promote the movement of contaminants through both the detrital and the pelagic food chain.

In this study, the particle size distribution, TOC, and polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) burdens of sediment colonized by *Dreissena* at a site in western Lake Ontario were compared with sediment in close proximity that was not colonized but that was exposed to similar environmental conditions. The PCDDs and PCDFs are groups of persistent chlorinated organic compounds containing some isomers that exhibit strong toxicological properties. The most toxic of these compounds, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, and some other 2,3,7,8-substituted PCDD and PCDF isomers have been linked to a number of deleterious health effects in mammalian systems, including carcinogenicity [12] and teratogenicity [13,14]. Limited data

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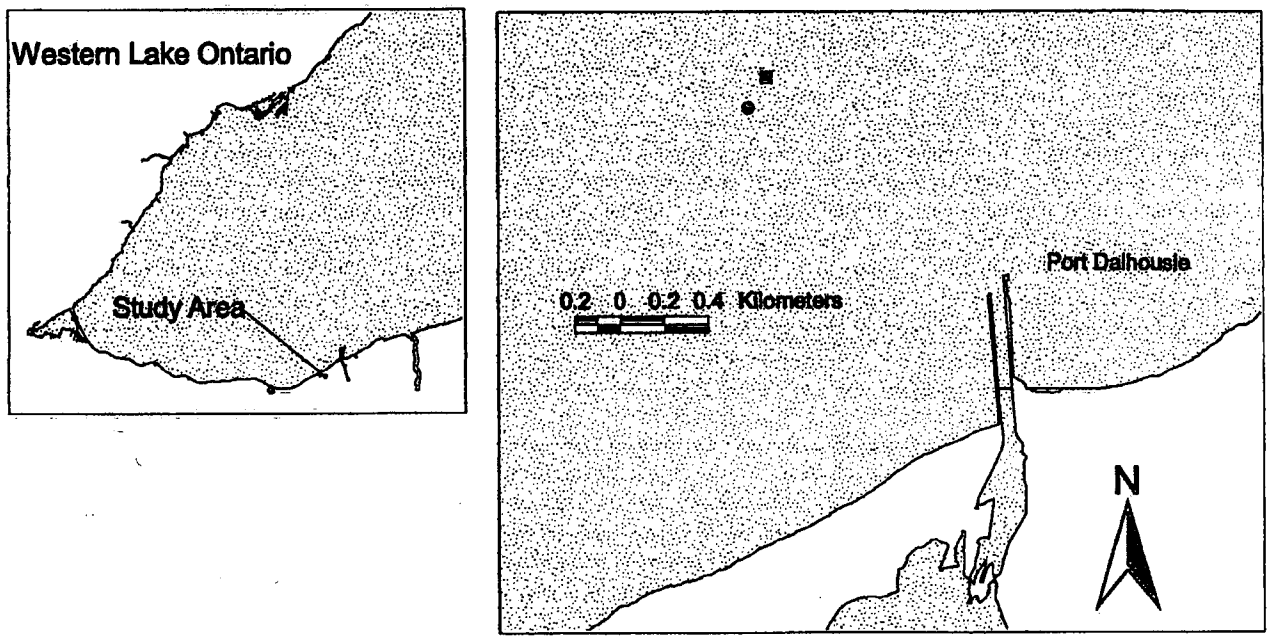

Fig. 1. Map of study area showing the colonized (●) and noncolonized (■) sampling sites.

are available on PCDD and PCDF levels in aquatic biota in the Great Lakes, but generally low levels of PCDDs and PCDFs have been detected in tissues of fish from Lake Ontario. Concentrations of 2,3,7,8-tetraCDD of Lake Ontario fish are typically less than 20 pg/g [15,16].

The levels of PCDDs and PCDFs were also determined in tissues of *Dreissena*, and the biomass burden of PCDDs/PCDFs was compared with the PCDD/PCDF burden in the sediment. The PCDD and PCDF congener profiles in *Dreissena* tissues and sediment were compared to investigate the possible mechanisms of bioaccumulation of PCDDs/PCDFs by *Dreissena*.

EXPERIMENTAL METHODS

Sediment and *Dreissena* samples were collected in May 1995 near Port Dalhousie in western Lake Ontario (43°13′09″N, 79°16′36″W; Fig. 1). A general reconnaissance of the area was undertaken to target sampling locations for sediment colonized by *Dreissena* and sediment devoid of mussels. The colonized and noncolonized sites were separated by a distance of 165 m. Three replicate Ponar dredge samples of each sediment type were collected, and the top 3-cm layer was removed for subsequent analyses. At both the colonized and the noncolonized site, the Ponar dredge penetrated to a depth of 10 to 12 cm; sediments exhibited firm consistency, and the top 3-cm layer was readily measured and removed. In addition, eight random grab samples were collected within a 50-m radius of the colonized sediment sample site for estimation of *Dreissena* population density, size distribution, and biomass. Depth of water for all samples ranged from 12.0 to 12.8 m. Aggregates of mussels were separated from the sediment, and particulates rinsed from the aggregates were retained and added to the sediment sample. Wet weights of sediment and mussels were recorded. Mussel samples were immediately stored on dry ice. *Dreissena* samples were characterized according to species, size distribution, and population density. The mussel samples were then shucked and the tissues freeze-dried in preparation for analysis of PCDDs and PCDFs.

Characterization of Sediments

Sediment samples were analyzed for TOC [17] and particle size classes less than 2 mm [18]. Sediments for total organic carbon analysis and particle size analysis were air-dried, disaggregated, put through a 2-mm sieve, and then ground to a fine powder using a mechanical grinder. An aliquot of the sediment powder was combusted using a Leco CR-12 Carbon Analyzer (Leco, Denver, CO, USA) at 1,370°C. The CO_2 evolved was measured by infrared detection; total organic carbon was calculated as total carbon minus total carbonate. An aliquot of sediment powder for particle size analysis was suspended in water and sonicated prior to particle size analysis with a Coulter Model LS130 Particle Size Analyser (Coulter Electronics, Toronto, Ontario, Canada) using laser light at 750 nm to size particles based on light diffraction.

Analysis of Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans

The sample preparation/cleanup procedure for PCDDs and PCDFs in sediment and tissue samples has been described in detail elsewhere [19–22]. Sediment and tissue samples were spiked with a standard solution containing ^{13}C-labeled standards for each of the individual 2,3,7,8-substituted isomers except 1,2,3,7,8,9-hexaCDD and octaCDF.

Mussel tissue was acid digested for 16 h in HCl and then extracted with hexane. The hexane extracts were then passed through a cylindrical funnel containing a 2-cm layer of anhydrous sodium sulfate over a 4-cm layer of 44% (w/w) sulfuric acid/silica gel. The combined hexane extract was reduced in volume under a gentle stream of nitrogen in preparation for normal-phase HPLC separation. The semiautomated HPLC procedure employed a primary separation using a 4.6-mm-i.d. × 25-cm Spherisorb 5-μ alumina column (Capital HPLC Limited, Broxburn, West Lothian, UK) followed by a secondary separation on a 4.6-mm-i.d. × 3-cm guard column packed with a 5% (w/w) mixture of Amoco PX-21 carbon and 70- to 230-mesh silica gel (BP, Amoco, Decatur, AL, USA). Two four-

port pneumatically actuated valves enabled enrichment of the PCDDs/PCDFs on the carbon–silica column after primary separation on the alumina column using a hexane/dichloromethane gradient program. The carbon–silica column was then back-flushed with toluene to yield a PCDD/PCDF-rich fraction that was reduced in volume under nitrogen prior to analysis by gas chromatography/mass spectrometry (GC-MS).

Sediment samples were extracted using a Soxhlet apparatus with toluene for 16 h. Sediment extracts were subjected to an open column chromatographic procedure. The first column contained the following: 1.5 g 10% silver nitrate, 1.0 g activated silica, 2.0 g 33% sodium hydroxide/silica, 1.0 g activated silica, 4.0 g sulfuric acid/silica, 2.0 g activated silica, and 2.0 g anhydrous sodium sulfate. The column containing the sample extract was eluted with hexane that was reduced in volume by rotary evaporation. The extract was transferred to a column containing 5.0 g of activated alumina and 2.0 g of anhydrous sodium sulfate. The column was eluted with dichloromethane that was reduced in volume, and the solvent was exchanged into hexane. The extract was then loaded onto a column with glass-wool plugs and ground-glass joints at both ends containing 3.0 g activated silica and 3.0 g Carbopack C. The column was rinsed with 15 ml of 25% dichloromethane/hexane (discarded) and then inverted and eluted with 70 ml of toluene to isolate a PCDD/PCDF-rich fraction. The extract was then reduced in volume under nitrogen prior to GC-MS analysis.

Sample extracts were analyzed by gas chromatography/tandem mass spectrometry in selected ion monitoring mode on a Finnigan MAT TSQ 70 triple quadrupole mass spectrometer (Finnigan, San Jose, CA, USA) interfaced with a Varian 3400 GC (Varian, Walnut Creek, CA, USA) equipped with splitless injection [20] or by gas chromatography/high-resolution mass spectrometry in selected ion monitoring mode on a Fisons/VG Autospec mass spectrometer (Micromass, Manchester, UK) operated at 10,000 (10% valley) resolution. The gas chromatograph was a Hewlett-Packard 5890 II (Hewlett-Packard, Avondale, PA, USA) equipped with a splitless injection system and a 60-m fused silica 0.25-mm-i.d. DB-5 capillary column with a 0.25-μ stationary-phase thickness. The carrier gas was helium at 30 psi, and the injector temperature and transfer line temperature were maintained at 280° and 300°C, respectively. The following temperature program was used: 100°C for 1 min, 100° to 200°C at 30°C/min, 200° to 235°C at 3°C/min, 235°C for 10 min, 235° to 300°C at 6°C/min, and 300°C for 17 min. Procedural blanks and precision and recovery samples (17 2,3,7,8-substituted native dioxins and furans spiked into cod liver oil) were processed with each set of eight samples analyzed.

RESULTS AND DISCUSSION

Population Structure

Dreissena colonies offshore of Port Dalhousie (western Lake Ontario) carpeted large tracts of sediment to a maximum depth of about 12.5 m. The estimated mean population density at the study site was 11,800 individuals/m² (Table 1). The mussel population was comprised of roughly equal numbers of *Dreissena polymorpha* (zebra mussels, 48%) and *Dreissena bugensis* (quagga mussels, 52%). Three distinct zebra mussel cohort classes were identified: less than 10 mm, 10 to 20 mm, and 20 to 30 mm. The smallest quagga mussel size class was less than 10 mm, but we were unable to accurately distinguish larger cohorts ranging in size from 12 to 30 mm. *Dreissena* were found mainly as druses with maximum lengths of about 7 cm. Most Ponar dredge samples containing mussels exhibited complete coverage of the sediment.

Table 1. *Dreissena* biomass and population estimates for eight Ponar dredge samples collected in the area of *Dreissena* colonized sediment at Port Dalhousie, western Lake Ontario

Population density (m²)	Weight/1,000 mussels (dry wt, g)	Biomass/m² (dry wt, g)
12,770	417	6,063
12,615	382	5,225
14,860	363	5,387
13,010	365	4,742
14,550	343	4,990
14,170	374	5,306
770	21	284
11,808	428	5,056
Mean 11,800	340	4,600

Physical character of sediment

The top 3-cm layer of sediment from the Ponar dredge samples was analyzed for particle size classes less than 2 mm; contrasting results were obtained for the colonized and noncolonized sediments. Silt-size particles dominated the unimodal particle size frequency distributions, but the mode for the noncolonized sediment was in the range of 40 to 60 μm (Fig. 2A) compared with a mode of 10 to 20 μm for colonized sediment (Fig. 2B). The dominance of 10- to 20-μm silt-size particles in the colonized sediment is within the size range reported for zebra mussel pseudofaeces [23]. The TOC level in colonized sediment (28.0 ± 13.2 mg/g dry wt.) was significantly higher ($p < 0.05$) than in sediment without colonization (13.3 ± 0.6 mg/g dry wt.). Zebra mussel pseudofecal material is reported to be lower in TOC than prefiltered particulate in the water column [23]; however, pseudofecal material is also generally higher in TOC than the top 3 cm of lake sediments. Increased roughness of the benthic layer may have resulted in retention of fine material deposited from the water column that had previously been removed through wave action. In addition, silt-size particles deposited in the benthic layer by *Dreissena* as pseudofaeces and faeces may have been trapped as a result of mussel colonies acting as physical barriers to resuspension and transport. In support of the mechanism of particle retention, mean particle size distributions of particulates associated with *Dreissena* druses we sampled from bedrock substrate in eastern Lake Erie were characterized by a dominance of silt-size particles in the range of 1 to 10 μm (data not shown).

Polychlorinated dioxins and furans in sediment

Low concentrations of PCDDs and PCDFs were detected in both sediment types at Port Dalhousie. However, the concentrations of all PCDD/PCDF congener groups were greater in colonized sediment compared to noncolonized sediment (Table 2). Figure 3 shows the PCDD/PCDF congener profiles from the two sediment types. The comparison of the profiles revealed similarities between the two sediment types as well as a similarity to profiles observed by Czuczwa and Hites [24] in sediments from other areas of the Great Lakes. The congener profiles were dominated by octaCDD and reflected the general environmental dominance of this compound as a result of its chemical stability and increased binding to suspended particulates and benthic sediments relative to other PCDDs/PCDFs. The concentrations of the tetra-, penta-, hexa-, and heptaCDF

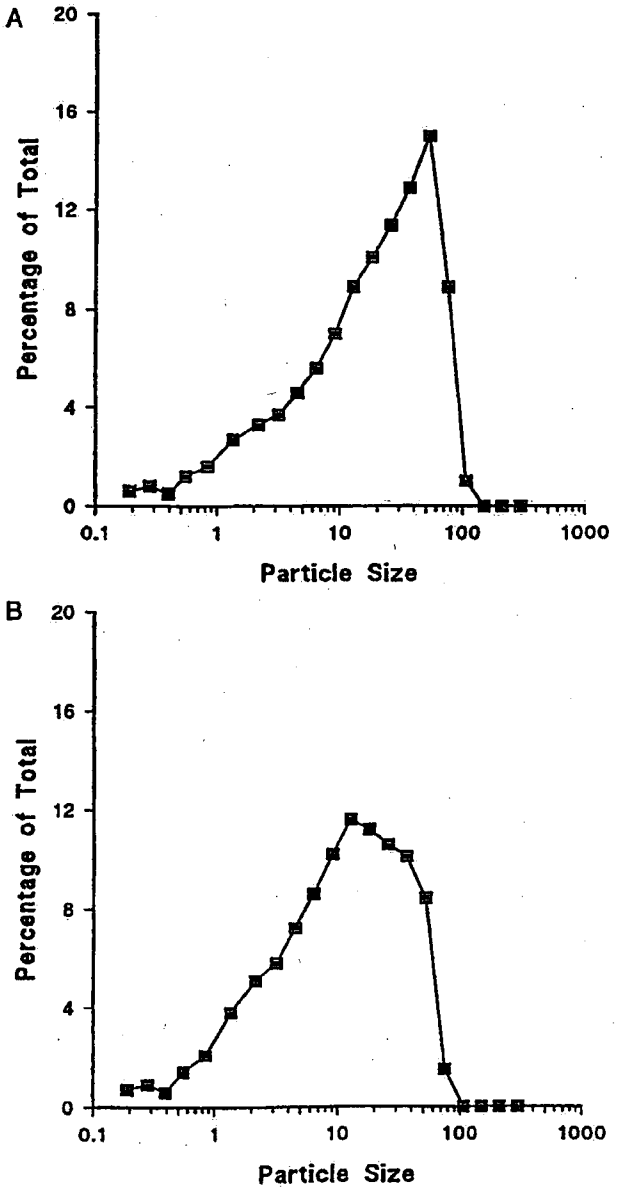

Fig. 2. Mean particle size distributions (<2000 μm) from three replicate samples of sediment at the Port Dalhousie site without *Dreissena* colonization (A) and at the Port Dalhousie site with colonization (B). Relative standard deviations for each particle size class ranged from 1.5 to 4.7% for colonized sediment and from 1.0 to 6.6% for noncolonized sediment.

congener groups were slightly but significantly greater in the colonized sediment (t test, $p < 0.05$; Table 2). The concentrations of the hexa-, hepta-, and octaCDD congener groups were also significantly greater in the colonized sediment. With the exceptions of 1,2,3,7,8-pentaCDF, 1,2,3,7,8,9-hexaCDF, 2,3,7,8-tetraCDD, and octaCDF, the concentrations of the 2,3,7,8-substituted congeners were significantly greater in the colonized sediment. Toxic equivalents (TEQ) were calculated using the International Toxicity Equivalency Factor (ITEF) method [25]; the TEQ was significantly greater in the colonized sediment (Table 2). The greater burden of PCDDs/PCDFs in colonized sediment was complementary to the observation of the greater number of fine particles in the particle size distribution and higher organic carbon, as adsorption of PCDDs/

Table 2. Comparison of concentrations of polychlorinated dibenzodioxins and dibenzofurans in sediment samples with and without colonization by *Dreissena* at Port Dalhousie, western Lake Ontario[a]

	Concentration (pg/g)	
	With mussels	Without mussels
Congener group		
TetraCDF*	50 ± 6 (12)	32 ± 3 (11)
PentaCDF*	43 ± 3 (11)	29 ± 7 (12)
HexaCDF*	57 ± 3 (8)	44 ± 2 (6)
HeptaCDF*	88 ± 2 (4)	70 ± 2 (4)
OctaCDF	91 ± 8	81 ± 6
TetraCDD	11 ± 1 (5)	9 ± 3 (4)
PentaCDD	16 ± 2 (6)	13 ± 4 (6)
HexaCDD*	51 ± 3 (6)	41 ± 4 (6)
HeptaCDD*	180 ± 6 (2)	140 ± 6 (2)
OctaCDD*	1,700 ± 100	1,300 ± 58
2,3,7,8-Substituted isomers		
2,3,7,8-TetraCDF*	7.4 ± 0.5	5.2 ± 0.1
2,3,4,7,8-PentaCDF*	4.0 ± 0.2	2.8 ± 0.2
1,2,3,7,8-PentaCDF	1.7 ± 0.1	1.4 ± 0.4
1,2,3,4,7,8-HexaCDF*	14 ± 1.0	12 ± 0.6
1,2,3,6,7,8-HexaCDF*	3.7 ± 0.1	3.0 ± 0.1
2,3,4,6,7,8-HexaCDF*	3.5 ± 0.1	2.6 ± 0.2
1,2,3,7,8,9-HexaCDF	<1.0	<1.0
1,2,3,4,6,7,8-HeptaCDF*	51 ± 1.7	40 ± 1.7
1,2,3,4,7,8,9-HeptaCDF*	2.9 ± 0.2	2.1 ± 0.2
2,3,7,8-TetraCDD	2.6 ± 0.2	2.5 ± 0.4
1,2,3,7,8-PentaCDD*	1.5 ± 0.1	1.1 ± 0.1
1,2,3,4,7,8-HexaCDD*	1.8 ± 0.2	1.4 ± 0.1
1,2,3,6,7,8-HexaCDD*	4.7 ± 0.2	4.0 ± 0.4
1,2,3,7,8,9-HexaCDD*	4.8 ± 0.2	3.6 ± 0.3
1,2,3,4,6,7,8-HeptaCDD*	78 ± 2	62 ± 3
Total 2,3,7,8-TetraCDD TEQ*	11.3 ± 0.5	8.7 ± 0.5

[a] Mean concentrations from three replicate samples (± SD) are expressed in picograms per gram (ppt) of dry sediment and are corrected for the recovery of ^{13}C-labeled standards. Numbers in brackets indicate the average number of isomers from the three replicate samples detected within the congener group. Asterisks denote a significant difference at the 95% probability level (t test, $p < 0.05$).

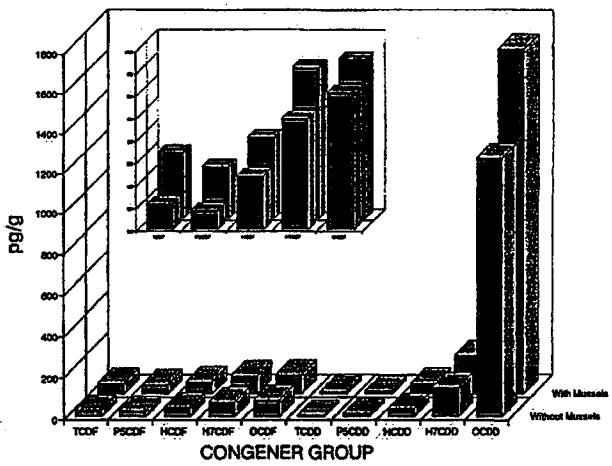

Fig. 3. Congener profiles of polychlorinated dibenzodioxins and dibenzofurans from surficial sediment with and without colonization by *Dreissena* at Port Dalhousie, western Lake Ontario. The insert to the figure shows the expanded dibenzofuran congener profile.

Table 3. Concentrations of polychlorinated dibenzodioxins and dibenzofurans in tissues of *Dreissena* sampled at Port Dalhousie, western Lake Ontario[a]

	Concentration (pg/g)	No. isomers
Congener group		
TetraCDF	58	15
PentaCDF	46	4
HexaCDF	28	4
HeptaCDF	17	2
OctaCDF	16	
TetraCDD	11	4
PentaCDD	1.5	1
HexaCDD	6.8	3
HeptaCDD	19	2
OctaCDD	160	
2,3,7,8-Substituted isomers		
2,3,7,8-TetraCDF	7.9	
2,3,4,7,8-PentaCDF	1.5	
1,2,3,7,8-PentaCDF	<1.0	
1,2,3,4,7,8-HexaCDF	2.5	
1,2,3,6,7,8-HexaCDF	<1.0	
2,3,4,6,7,8-HexaCDF	2.2	
1,2,3,7,8,9-HexaCDF	<1.0	
1,2,3,4,6,7,8-HeptaCDF	12	
1,2,3,4,7,8,9-HeptaCDF	<1.0	
2,3,7,8-TetraCDD	1.5	
1,2,3,7,8-PentaCDD	<1.0	
1,2,3,4,7,8-HexaCDD	<1.0	
1,2,3,6,7,8-HexaCDD	<1.0	
1,2,3,7,8,9-HexaCDD	<1.0	
1,2,3,4,6,7,8-HeptaCDD	7.8	
Total 2,3,7,8-tetraCDD TEQ	3.7	

[a] All concentrations are expressed in picograms per gram (ppt) of dry tissue and are corrected for the recovery of ^{13}C-labeled standards.

PCDFs increases with decreasing particle size and increasing organic carbon. *Dreissena* may have contributed to the greater PCDD/PCDF levels in sediment through a number of processes, including the creation of physical conditions conducive to retention of fine particulates and deposition of pseudofaeces and faeces with PCDDs/PCDFs.

The comparison of concentrations of PCDDs/PCDFs normalized to TOC in sediment (Table 4) contrasted with the comparison of concentrations based on dry weight of sediment. Concentrations normalized for TOC were greater in the noncolonized sediment for all PCDD/PCDF congener groups and 2,3,7,8-substituted isomers compared with the colonized site. Given the coarser particle size and lower TOC in sediment at the noncolonized site, it is unlikely that physical differences in sediment accounted for the observed variance in TOC-normalized PCDD/PCDF concentrations between the two sites.

Polychlorinated dioxins and furans in Dreissena

Low concentrations of PCDDs/PCDFs were detected in tissues of *Dreissena* (Table 3). The data presented in Table 3 are the result of a single analysis of a 21-g freeze-dried mussel tissue sample. The dry tissue was equivalent to about 515 g of wet tissue, or 780 g of whole wet mussels. Previous analyses of replicate samples of about 50 g of wet mussel tissue yielded no detectable concentrations of PCDDs/PCDFs (method detection limit, 1 pg/g).

With the exception of the tetraCDFs and tetraCDDs, lesser numbers of isomers were detected in the PCDD/PCDF congener groups from the mussel tissue analysis (Table 3) when compared to the sediment data (Table 2). Figure 4 shows the congener profile from the mussel tissue analysis. The insert to Figure 4 shows the PCDF congener profile, which stands in contrast to the profiles observed in the sediment samples (insert to Fig. 3). A trend was observed toward decreasing concentrations of the PCDF congener groups with increased chlorine substitution in mussel tissues, whereas a trend was observed toward increasing concentrations of PCDF congener groups with increased chlorination in the sediments. The trends in PCDD congener group concentrations were more difficult to interpret, but the congener profile in mussel tissues appeared similar to the profiles observed in the sediments (Fig. 3), with the exception of an increased concentration of the tetraCDD

Table 4. Biota–sediment accumulation factors (BSAFs) for polychlorinated dibenzodioxins and dibenzofurans calculated as ratios of concentrations in *Dreissena* tissues normalized for lipid content (10.7% of dry wt) to the mean concentrations (± SD) in colonized sediment normalized to organic carbon (2.8% of dry wt). Mean concentrations are also shown for noncolonized sediment normalized to organic carbon (1.3% of dry wt)

	Colonized sediment (pg/g carbon)	Noncolonized (pg/g carbon)	*Driessena* tissue (pg/g lipid)	BSAF
Congener group				
TetraCDF	1,780 ± 120	2,430 ± 140	542	0.30
PentaCDF	1,550 ± 70	2,210 ± 300	430	0.28
HexaCDF	2,020 ± 60	3,380 ± 80	262	0.13
HeptaCDF	3,130 ± 50	5,360 ± 90	159	0.05
OctaCDF	3,260 ± 160	6,260 ± 240	150	0.05
TetraCDD	405 ± 25	675 ± 130	103	0.26
PentaCDD	560 ± 40	1,030 ± 190	14	0.02
HexaCDD	1,830 ± 50	3,180 ± 180	178	0.05
HeptaCDD	6,550 ± 120	11,000 ± 260	178	0.03
OctaCDD	60,700 ± 2,060	97,400 ± 2,560	1,490	0.02
2,3,7,8-Substituted isomers				
2,3,7,8-TetraCDF	266 ± 10	400 ± 4	74	0.28
2,3,4,7,8-PentaCDF	143 ± 4	218 ± 7	14	0.10
1,2,3,4,7,8-HexaCDF	500 ± 20	897 ± 26	23	0.05
2,3,4,6,7,8-HexaCDF	125 ± 2	192 ± 8	21	0.16
1,2,3,4,6,7,8-HeptaCDF	1,820 ± 40	3,080 ± 80	112	0.06
2,3,7,8-TetraCDD	93 ± 4	192 ± 16	14	0.15
1,2,3,4,6,7,8-HeptaCDD	2,790 ± 40	4,540 ± 160	73	0.03
2,3,7,8-TetraCDD TEQ	122 ± 5	147 ± 7	35	0.11

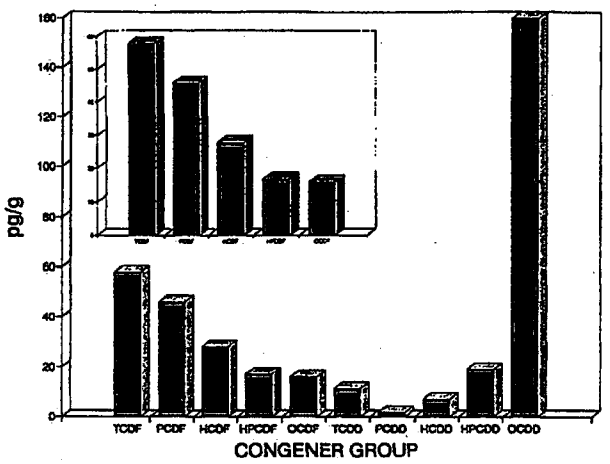

Fig. 4. Congener profile of polychlorinated dibenzodioxins and dibenzofurans from tissues of *Dreissena* sampled at Port Dalhousie, western Lake Ontario. The insert to the figure shows the expanded dibenzofuran congener profile.

congener group relative to the pentaCDD congener group in the mussel tissues.

The relationship between PCDDs/PCDFs in sediment and *Dreissena* was explored by calculating the biota–sediment accumulation factors (BSAFs; Table 4). The BSAFs are defined as the ratios of lipid-normalized tissue concentrations to TOC-normalized sediment concentrations and have been used in the assessment of sediment-associated contaminant bioavailability [26,27]. The BSAFs for the PCDF congener groups showed a trend toward decreasing values with increased chlorine substitution. No trend was apparent in BSAF values for the PCDD congener groups, but the value for the tetraCDD group was about five- to 10-fold greater than for the greater substituted dioxin groups. The highest BSAFs for individual 2,3,7,8-substituted compounds were generally exhibited by the tetra- and penta-substituted compounds, but a relatively high value was also calculated for one of the hexa-substituted compounds (2,3,4,6,7,8-hexaCDF).

The lesser chlorinated PCDDs/PCDFs generally have higher vapor pressures and lower log K_{ow} values but are more susceptible to biological or chemical degradation than the higher-chlorinated isomers [24,28]. The results of some studies show that freely dissolved PCDDs/PCDFs have short residency times in the aqueous phase and are rapidly partitioned to suspended particulates and dissolved organic material in the water column [29,30]. Servos et al. [30] reported half-lives in the aqueous phase of 2.6 d for 2,3,7,8-tetraCDD and 4.0 d for octaCDD in a study using lake enclosures. Thus, *Dreissena* sampled during this study at a site removed from active sources of PCDD/PCDF loadings to the water mass may have been exposed mainly to compounds that were particulate bound. Generally, a positive correlation is seen between the degree of bioaccumulation and log K_{ow} for benthic organisms [31–33]. Other factors that influence bioaccumulation of xenobiotics by *Dreissena* include body size and lipid content [33] and characteristics of the particles processed during filtration [7,34,35]. Bioaccumulation of PCDDs/PCDFs in aquatic organisms is reported to vary with degree of chlorination, but the rates for individual compounds cannot always be accurately predicted solely on the basis of their physical and chemical properties [36,37]. The rates and extent of PCDD/PCDF bioaccumulation in aquatic organisms have been shown to depend on factors such as chlorine substitution pattern and rates of depuration [38–41]. We are unaware of other data regarding PCDD/PCDF levels in *Dreissena* in the Great Lakes, but Hayton et al. [42] showed that the mussel *Elliptio complanata* rapidly bioaccumulated tetraCDDs and tetraCDFs after placement in a creek downstream of a wood-waste disposal site.

Both the mussel tissue PCDF congener profile (insert to Fig. 4) and the BSAFs indicated a decrease in bioaccumulation with increasing chlorination by congener class of PCDFs. The PCDD congener profile was more difficult to interpret, but the BSAF values for the PCDDs were much greater for the tetra compounds than for all other congener groups (Table 4). A parabolic relationship between bioaccumulation and log K_{ow} of hydrophobic organochlorine compounds has been reported [31,43,44]. Decreased bioaccumulation of compounds with higher degrees of chlorination and greater log K_{ow} values has been reported to be influenced by slow kinetics due to extreme hydrophobicity and steric factors [36,44–47]. Log K_{ow} values for congener classes of both PCDDs and PCDFs generally increase with degree of chlorination; the values for 2,3,7,8-TCDD and 2,3,7,8-TCDF (6.64 and 5.82, respectively [48,49]) fall roughly within the range of values for PCBs reported to exhibit positive linear bioaccumulation dependence with log K_{ow} [31]. On the basis of a comparison with PCBs, higher-chlorinated congener classes of PCDDs/PCDFs with log K_{ow} values greater than 7 could exhibit decreased bioaccumulation relative to the tetra-substituted compounds.

The TEQ was calculated for the mussel tissue sample and compared with the values obtained from the sediments. The TEQ for *Dreissena* was 3.7 pg/g of dry mussel tissue (Table 3), which was equivalent to 0.10 pg/g of whole wet mussels based on a conversion of dry-weight tissue to whole-wet-weight mussel of 2.7% calculated for these samples. The average wet areal mussel biomass of *Dreissena* at Port Dalhousie was estimated to be 12.5 kg/m^2. This resulted in a TEQ estimate of 1,300 pg/m^2 in the wet mussel biomass. The TEQ for the colonized sediment was 11 pg/g dry-weight sediment (Table 2), which was equivalent to 4.1 pg/g of wet sediment based on a conversion of dry-sediment weight to wet-sediment weight of 36%. The estimated average wet surficial sediment (top 3 cm) mass at the colonized site was 34.0 kg/m^2, which resulted in a TEQ estimate of 136,000 pg/m^2. Thus, it was estimated that the TEQ in *Dreissena* biomass at Port Dalhousie was equivalent to only roughly 0.9% of the TEQ in the surficial sediment layer.

CONCLUSIONS

The *Dreissena* population at the colonized site exhibited almost complete coverage of sediment and was comprised of roughly equal numbers of quagga mussels and zebra mussels. The particle size distribution of colonized and noncolonized sediment was characterized by an abundance of silt-size material; the particle size was finer at the colonized site. Total organic carbon was twofold greater in the colonized sediment compared to the noncolonized sediment.

Concentrations of PCDDs/PCDFs in colonized sediment were greater than in noncolonized sediment. Concentrations of the tetra-, penta-, hexa-, and heptaCDF and the hexa-, hepta-, and octaCDD congener groups were significantly greater in the colonized sediment ($p < 0.05$). The concentrations of most 2,3,7,8-substituted isomers were significantly greater ($p < 0.05$) in the colonized sediment. The greater PCDD/PCDF bur-

dens in the colonized sediment resulted in part from increased accumulation and retention of silt-size particles through mussel pseudofecal production and benthic layer alteration by *Dreissena*. These data suggest that *Dreissena* may mediate changes in sediment PCDD and PCDF concentrations at sites they colonize.

The PCDD/PCDF congener profiles were similar for both sediment types. With the exception of the tetraCDDs and tetraCDFs, lower numbers of PCDD/PCDF isomers were detected in mussel tissue compared to the sediments. A trend was observed toward decreasing BSAFs and decreasing concentrations of PCDF congener groups with increased chlorine substitution in mussel tissues, whereas a trend was observed toward increasing concentrations of PCDF congener groups with increased chlorination in the sediments. With the exception of the tetra-substituted congener group, the PCDD congener profile from the mussel tissues showed a trend toward increasing concentrations with increased chlorination that was similar to the profile observed in the sediment. The BSAFs for PCDDs were highest for the tetra-substituted compounds. The TEQ calculated for areal *Dreissena* biomass at Port Dalhousie was estimated to be equivalent to 0.9% of the TEQ in the surficial sediment (top 3 cm). These data showed that, compared to *Dreissena* biomass, the sediment at the study site was the major sink for PCDDs/PCDFs.

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