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Distribution of dioxins and furans in size-fractionated suspended solids in Canagagigue Creek, Elmira, Ontario

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Abstract A study was conducted to examine the occurrence and concentration of dioxins and furans in separated size fractions of suspended sediment collected in Canagagigue Creek near Elmira, Ontario. Field-based water elutriation systems were used to collect a time-integrated sample of suspended solids from the creek during a spring storm event. The elutriation system hydraulically sorts suspended solids into five predetermined grain-size classes (<8, 8–16, 16–32, 32–63, >63 μm). Dioxin and furan compounds were detected in suspended sediment fractions at levels below the Ontario Ministry of the Environment and Energy (OMEE) Interim Sediment Quality Guidelines. Average concentrations of the most toxic compounds, 2,3,7,8 T_4CDD and 2,3,7,8 T_4CDF, were 20 ppt and 22 ppt, respectively. The data show no trend between grain size and pollutant concentration. Concentrations of dioxins and furans in suspended sediments are consistent with contaminant levels observed in river-bottom and downstream flood-plain sediments. Independent studies show that elevated levels of dioxins and furans in creek sediments accumulate in the tissues of aquatic organisms and may biomagnify through the food chain.

INTRODUCTION

Contamination of aquatic sediments can pose a significant and long-lasting threat to ecosystem health. The entry, distribution and fate of hydrophobic organic contaminants in aquatic systems is governed by several dynamic processes including sorption, advection, volatization and transformation processes (Karickhoff, 1984). The grain-size distribution of aquatic sediments is one important factor controlling pollutant sorption (Smith *et al.*, 1988) and downstream transport (Ongley *et al.*, 1992). Studies of riverbed sediment report increasing pollutant concentrations with increasing carbon content and decreasing grain size (Witkowski *et al.*, 1986). Consequently, higher contaminant concentrations are commonly found in fine-grained bed sediments that typically accumulate in low water velocity sections of streams (Wood & Armitage, 1997) or flood plains (Marcus, 1989).

Dioxins and furans are hydrophobic organic compounds with large partition coefficients (Table 1) that preferentially bind to fine-grained sediment and accumulate in animal body tissue in aquatic systems (Moore & Ramamoorthy, 1984; Smith *et al.*, 1988). Recent studies report the presence of dioxins and furans in bed sediments of Canagagigue Creek adjacent to the Uniroyal Chemical Ltd site in Elmira, Ontario (Jaagumagi & Townsend, 1996; Jaagumagi & Bedard, 1997) and in downstream flood-plain sediments (Jaagumagi & Bedard, 1997). While these studies have focused on

Table 1 Chemical characteristics and interim sediment quality guidelines for polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

	Compound	Partition coefficient log K_{oc}	I-TEF	Guideline
Dioxins	2,3,7,8-T_4CDD	6.83	1	25.7 ppt
	1,2,3,7,8-P_5CDD	7.27	0.5	354 ppt
	1,2,3,4,7,8-H_6CDD	7.67	0.1	1.8 ppb
	1,2,3,6,7,8-H_6CDD	7.58	0.1	14 ppb
	1,2,3,7,8,9-H_6CDD	6.69	0.1	186 ppt
	1,2,3,4,6,7,8-H_7CDD	7.86	0.01	27.5 ppb
	O_8CDD	8.06	0.001	436 ppb
Furans	2,3,7,8-T_4CDF	6.56	0.1	138 ppt
	1,2,3,7,8-P_5CDF	7.67	0.05	8.9 ppb
	2,3,4,7,8-P_5CDF	7.32	0.5	396 ppt
	1,2,3,4,7,8-H_6CDF	7.57	0.1	1.4 ppb
	1,2,3,6,7,8-H_6CDF	7.47	0.1	1140 ppt
	1,2,3,7,8,9-H_6CDF	6.88	0.1	285 ppt
	2,3,4,6,7,8-H_6CDF	6.88	0.1	285 ppt
	1,2,3,4,6,7,8-H_7CDF	8.28	0.01	72 ppb
	1,2,3,4,7,8,9-H_7CDF	6.78	0.01	2.3 ppb
	0_8CDF	8.2	0.001	602 ppb

I-TEF: International Toxic Equivalency Factor.

contamination of in-place sediments, little is known about processes governing the downstream dispersion of contaminated riverbed sediment and its biological availability in the creek.

The objective of this study was to investigate the occurrence and distribution of dioxins and furans in separated size fractions of fine-grained suspended solids (<63 μm) in Canagagigue Creek. Field-based water elutriation systems were used to collect and size-fractionate suspended solids from the creek for seven days during a spring storm event. Concentration of dioxins and furans in the time-integrated sediment size fractions are compared with data from contaminant studies on in-place river-bottom and downstream flood-plain sediments Jaagumagi & Bedard (1997) and related to the distributions of congener specific uptake by organisms following *in situ* exposure.

METHODS

Canagagigue Creek flows through Elmira Ontario and drains an area of 143 km^2 (Fig. 1). Land use in the watershed is agriculture (80%), wood lot (10%) and industry (10%), which is located primarily in or near the town of Elmira (Carey *et al.*, 1983). Creek-bottom sediments at the study site (site 4, Fig. 1) are fine-grained (sand: 10.1%; silt: 59.1%; clay: 30.2%) with relatively high organic content (LOI: 6.1%; TOC: 31 mg g^{-1}) (Jaagumagi & Beddard, 1997).

Three field-based water elutriation systems (Walling & Woodward, 1993; Lau & Krishnappan, 1994) were deployed at site 4 (Fig. 1). The elutriators were used to withdraw suspended solids from the river channel with *in situ* or *effective* particle size characteristics and sort the particles into representative effective size classes (<8, 8–16, 16–32, 32–63, >63 μm). The inlet of each system was fixed to a metal rod 35 cm

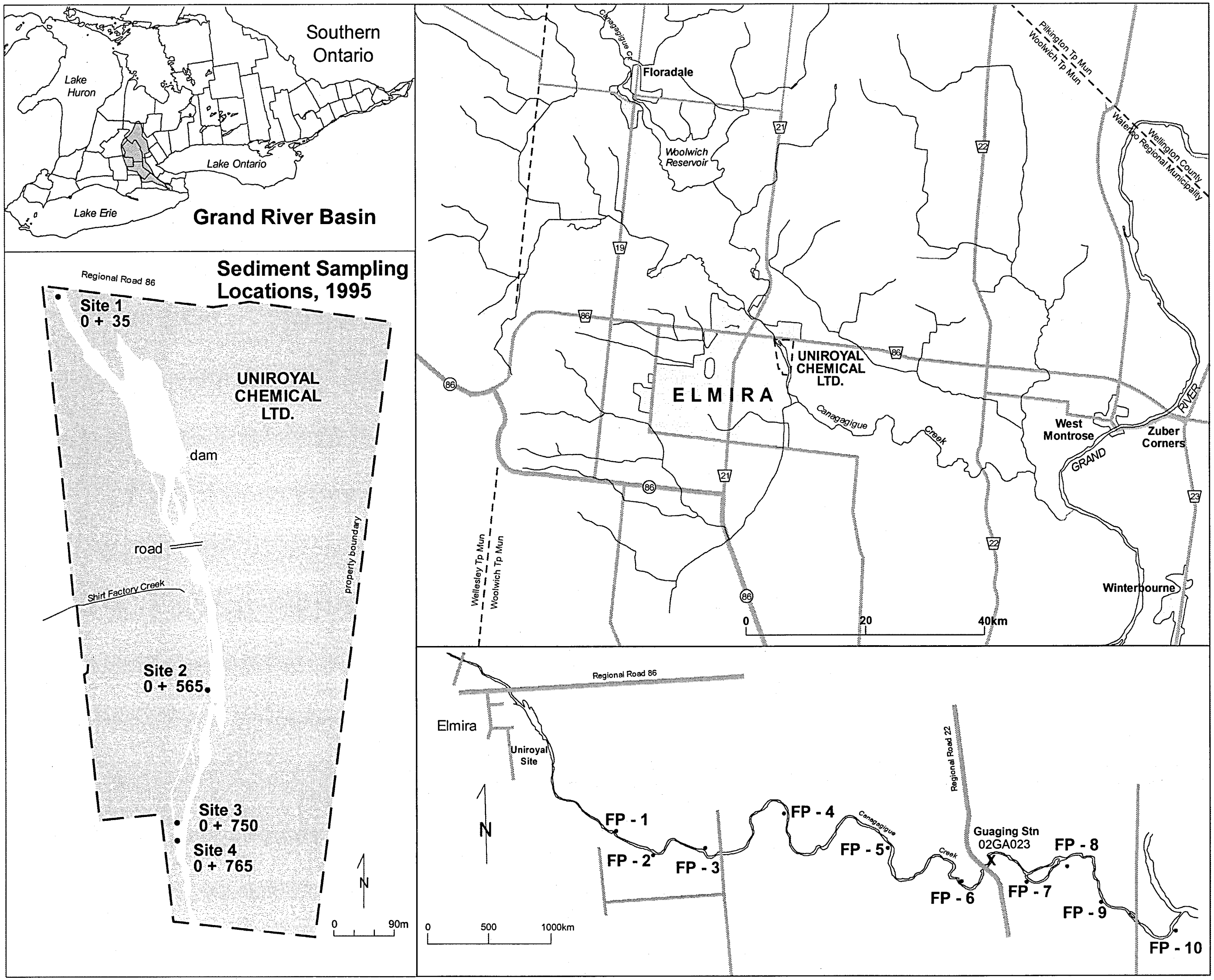

Fig. 1 Study area and sample location.

above the river bottom and oriented upstream in the centroid of flow. Elutriators were operated continuously at a sample rate of 105 ml min^{-1} for seven days (20–27 May 1996) during the storm event. Similar size classes from the elutriators were combined and submitted to Ontario Ministry of the Environment and Energy (OMEE) laboratories in Downsview, Ontario, for dioxin and furan analysis according to analytical procedures described in OMEE (1983).

Suspended solids were collected daily and the grain-size distribution of each sample was determined according to the method of Droppo & Ongley (1992). Samples were analysed using conventional light microscopy (COM) and imaged (sized) to a lower resolution of 2 μm (×10 objective) using a Zeiss Axiovert S100 microscope interfaced with an Image Analysis System (Northern Exposure™-Empix Imaging, Inc.). Grain-size data are presented as % in range by number and % in range by volume in Fig. 2. Suspended sediment concentrations were determined by membrane filtration. A Water Survey of Canada Gauging Station (no. 02GA023) is located 4 km southeast of Elmira (Fig. 1). For the period of record (1950 to present), the average daily discharge of the creek in the month of May is 0.83 m^3 s^{-1} and a maximum instantaneous discharge of 61.2 m^3 s^{-1} for this month was recorded on 17 May 1974. Instantaneous discharge was recorded every 15 min at the Water Survey of Canada gauging station no. 02GA023.

The toxicity of dioxin and furan mixtures in the environment can be assessed using an internationally accepted system of comparison known as toxic equivalency factors (TEF). The most toxic forms have chloride atoms in the 2,3,7 and 8 positions and TEF values for these compounds are listed in Table 1, where I-TEF refers to International Toxic Equivalency Factors. These congeners are used as the basis for a dioxin and furan toxic equivalency (TEQ) calculation. To obtain the TEQ value, the measured concentration of each dioxin or furan isomer for separated size fractions of suspended sediment was multiplied by the TEF value. The TEQ for suspended sediment size fractions was determined and compared with previously published TEQ data for bed and flood-plain sediments to assess the relative potency of dioxins and furans within the Creek.

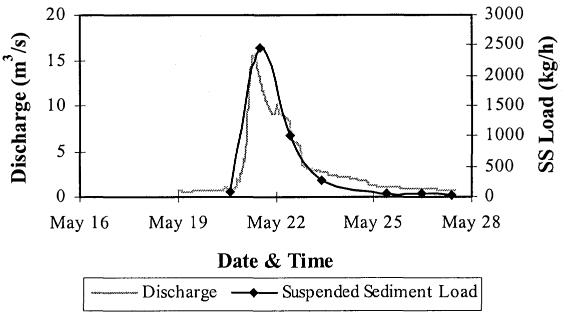

Fig. 2 Particle-size characteristics of suspended solids in Canagagigue Creek.

RESULTS AND DISCUSSION

Flow conditions and size characteristics of suspended solids

Flow conditions of the creek for the period 20–27 May 1996 are shown in Fig. 3. During the study period, a maximum instantaneous discharge of 15.5 m^3 s^{-1} was

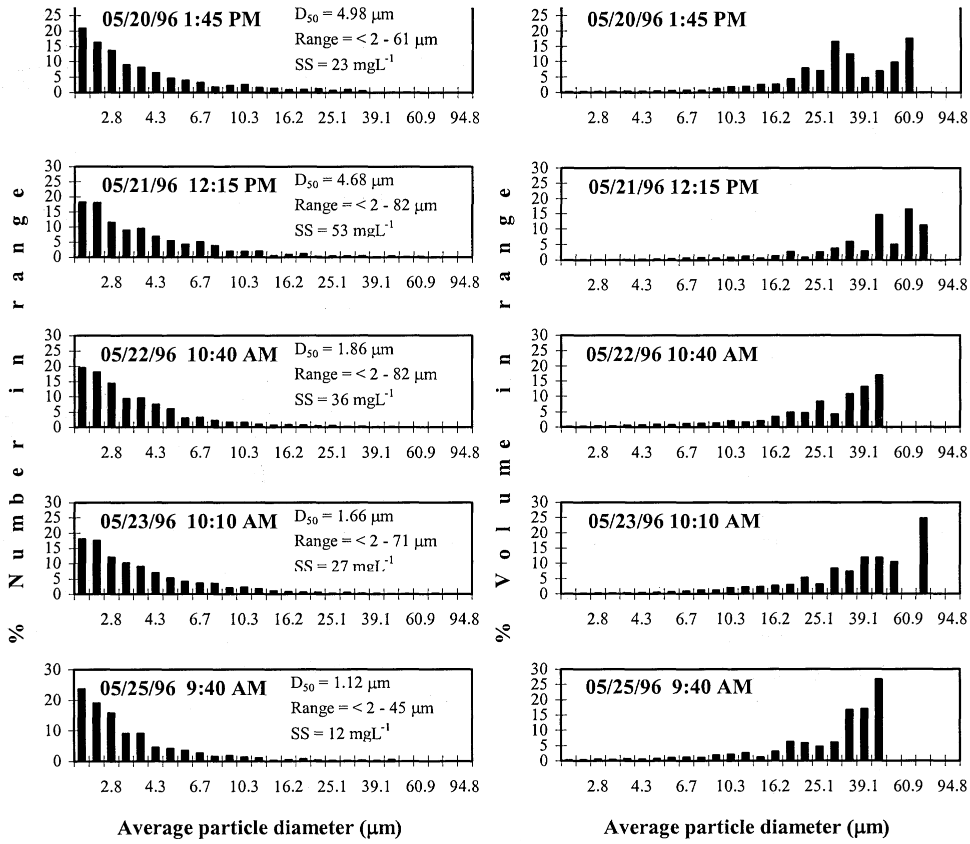

Fig. 3 Storm hydrograph.

recorded 21 May at 2:00 a.m. The recurrence interval for this flow is 13.3 years. The concentration of suspended solids prior to the storm was 23 mg l^{-1}. A maximum concentration of 53 mg l^{-1} was measured just after the peak of the hydrograph. With the return of baseflow on 25 May, sediment concentrations decreased to 12 mg l^{-1} (Fig. 3). Increases in the number of large flocculated particles were observed with increasing river discharge. During storm flow, the majority of particles in suspension were <20 µm in diameter, but particles >20 µm accounted for the largest % of particle volume. On the recessional limb of the hydrograph, the D_{50} decreased from 1.86 µm (22 May, 10:40 a.m.) to 1.12 µm (25 May, 9:40 a.m.).

Sediment chemistry

River-bottom and flood-plain sediment In 1995, OMEE conducted an environmental assessment of riverbed and flood-plain sediment in Canagagigue Creek (Jaagumagi & Townsend, 1996). They reported that 2,3,7,8-T_4CDD was the most prevalent dioxin compound in creek sediments adjacent to and downstream of the Uniroyal plant. Dioxin and furan levels upstream of the plant were below the detection level. In the following year, river-bottom and flood-plain samples were collected and further analysed for dioxins and furans (Jaagumagi & Beddard, 1997). Dioxin and furan levels for three river-bottom sample locations (Sites 1, 2 and 3, Fig. 1) adjacent to the Uniroyal plant and 10 flood-plain sites downstream (FP1–FP10, Fig. 1) are presented in Table 2. These data show a trend of increasing dioxin and furan levels in river-bottom sediments on the Uniroyal property from site 1 to site 3, then a decrease in levels in downstream flood-plain sediments. Data in Table 2 show that contaminated river sediments are being deposited in a number of flood prone areas. In flood-plain sediments, dioxin and furan compounds were detected at depths of 20–30 cm, which indicates a history of contaminant loading to these depositional areas (Jaagumagi & Beddard, 1997).

Suspended sediment The results of dioxin and furan analysis of suspended sediment size fractions are presented in Table 2 as totals for each congener group and for specific 2,3,7,8 substituted isomers. The data show that several furan and dioxin compounds including 2,3,7,8-T_4CDD and 2,3,7,8-T_4CDF were detected in suspended solids at comparable levels to those reported in previous investigations of creek bottom and flood-plain sediments (Jaagumagi & Beddard, 1997).

Hydrophobic organic contaminants tend to partition preferentially to fine-grained solids and several studies have reported increasing contaminant levels with decreasing grain size (Smith *et al.*, 1988). In the present study, this pattern of increasing contaminant levels with decreasing grain size was not observed (Table 2). Possible reasons for the apparent lack of correlation between grain size and contaminant levels are threefold. First, sufficient quantities of suspended solids were not collected for contaminant analysis in the < 8 μm size fraction, thus biasing possible trends between contaminant concentration and grain size. Second, water elutriators sort suspended particulate matter into representative *in situ* or *effective* size classes (Walling & Woodward, 1993). Solids observed by image analysis were highly flocculated and better correlations between contaminant concentration and grain size may result from contaminant analysis of sediment sorted by grain size after particle disaggregation and chemical dispersion. Third, sediment collected in the elutriators represents a time-integrated sample collected over several days. Contaminant concentrations may have been diluted in each size fraction as less contaminated materials from upstream were collected over time.

Dioxin and furan levels in size-fractionated suspended sediment are below the MOEE Interim Sediment Quality Guidelines (Table 1). Dioxin/furan TEQs for individual size fractions ranged from 27 to 39 and were similar for creek-bed and flood-plain sediments reported by Jaagumagi & Beddard (1997) and listed in Table 2. Independent studies using a three week *in situ* placement of mussels (*Elliptio complanata*) in Canagagigue Creek report that furans and dioxins bioaccumulate in these aquatic organisms at levels comparable to those found in creek sediments (Hayton & Petro, 1996). Consequently, an elevated dioxin and furan level in creek-bed sediments is of primary concern for the bioaccumulation and biomagnification of these compounds through the food chain. Given the concentrations of dioxins and furans in separated size fractions of suspended sediment, it is reasonable to suggest that resuspension of bottom sediments at the study site plays a significant role in the downstream transport and subsequent deposition of organic pollutants in flood-plain areas of Canagagigue Creek.

Table 2 Sediment dioxin and furan concentrations in Canagagigue Creek (all values in ppt).

	Suspended sediment size fraction (μm)				Riverbed sediment sampling station*			Floodplain sediment/soils (0–10 cm)*									
Dioxins:	8–16	16–32	32–63	>63	Site 1	Site 2	Site 3	FP-1	FP-2	FP-3	FP-4	FP-5	FP-6	FP-7	FP-8	FP-9	FP-10
2,3,7,8-T$_4$CDD	19	18	18	25	<	14	81	13	8.6	16	13	63	25	12	39	33	9.3
T$_4$CDD, total	52	47	43	44	4.3	26	140	29	23	63	66	150	71	49	110	89	41
1,2,3,7,8-P$_5$CDD	3	2.8	2.2	2.8	<	<	9.1	1.1	1.2	<	2.1	3.2	1.8	1.4	3.4	2.5	<
P$_5$CDD, total	9.7	13	11	6.6	<	1.8	46	2.7	4.4	13	18	37	17	13	33	24	7.1
1,2,3,4,7,8-H$_6$CDD	3.1	2.9	2.2	2.8	<	<	4.1	<	1.2	<	<	<	<	<	1.2	1.2	<
1,2,3,6,7,8-H$_6$CDD	8.2	7.6	5.9	8.3	1.3	2.8	14	2.5	3.3	3.6	5.2	7.6	3.2	2.1	6.5	5.5	1.9
1,2,3,7,8,9-H$_6$CDD	6.5	5.6	4.6	6.9	1.3	1.8	6.1	1.7	2.6	2.4	3.3	3.1	1.9	1.7	3.3	3.2	1.3
H$_6$CDD, total	67	59	49	65	9.7	18	70	16	26	31	52	57	24	20	50	46	13
1,2,3,4,6,7,8-H$_7$CDD	130	130	96	150	25	36	220	44	49	49	40	84	40	24	56	5.1	22
H$_7$CDD, total	260	240	180	280	43	66	370	76	88	83	75	150	70	44	95	89	38
O$_8$CDD	910	880	670	1100	150	250	1500	370	460	350	180	410	270	140	330	270	150
Furans:																	
2,3,7,8-T$_4$CDF	22	21	19	23	1.3	15	60	17	10	24	17	67	27	17	72	39	13
T$_4$CDF, total	160	170	150	130	7.9	89	470	150	95	240	190	320	250	170	440	320	140
1,2,3,7,8-P$_5$CDF	1	1	1	1	<	<	8.9	<	<	<	<	1.4	<	<	<	<	<
2,3,4,7,8-P$_5$CDF	2	2.1	1.7	2.3	<	1.5	7.4	<	<	1.1	1	2.7	1.1	<	2.4	1.6	<
P$_5$CDF, total	100	100	80	87	8.8	39	170	28	33	78	63	200	75	46	170	110	38
1,2,3,4,7,8-H$_6$CDF	5.8	5.1	4	5.7	<	2.3	7.1	1.4	1.8	2.9	2.8	6.5	2.5	1.9	5.2	3.9	1.5
1,2,3,6,7,8-H$_6$CDF	4.8	4.3	3.3	4.7	<	1.4	6.2	1.1	1.4	1.8	1.9	6.4	1.7	1.7	3.2	2.6	1.1
2,3,4,6,7,8-H$_6$CDF	8.7	7.3	5.4	8.6	<	2.9	6.4	1.2	1.6	2.9	2.4	9.8	2.4	1.8	5.5	4.1	1.4
H$_6$CDF, total	210	180	120	180	9.4	40	160	35	40	65	68	340	57	34	140	100	32
1,2,3,4,6,7,8-H$_7$CDF	490	430	260	490	9.8	42	290	68	46	82	86	920	76	36	170	120	41
1,2,3,4,7,8,9-H$_7$CDF	5.1	5.1	3.2	5.4	<	<	4.5	<	<	2	1.4	5.3	1.4	<	2.5	2.1	<
H$_7$CDF, total	1300	1100	640	1300	26	98	740	170	110	190	180	2200	180	84	380	300	110
O$_8$CDF	1800	1600	890	1500	26	120	900	240	93	220	200	3000	170	78	270	260	95
TEQ	32.7	30.5	27.2	38.8	0.5	17.8	103.2	16.8	11.9	21.2	18.7	85.3	31.1	15.7	53.3	42.2	11.8

<: below detection limit

* Data from Jaagumagi & Beddard (1997).

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REFERENCES

Carey, J. H., Fox, M. E., Brownlee, B. G., Metcalfe, J. L., Mason, P. D. & Yerex, W. H. (1983) *Fate and Effects of Contaminants in Canagagigue Creek. 1. Stream Ecology and Identification of Major Contaminants*. Environment Canada, Scientific Series no. 135. Canada Centre for Inland Waters, Burlington, Ontario.

Droppo, I. G. & Ongley, E. D. (1992) The state of suspended sediment in freshwater fluvial environment: a method of analysis. *Wat. Res.* **26**(1), 65–72.

Hayton, A. & Petro, S. (1996) Canagagigue Creek mussel and leech biomonitoring study. *A Report to the Uniroyal Public Advisory Committee.* Ontario Ministry of Environment and Energy, Toronto, Ontario.

Jaagumagi, R. & Townsend, J. (1996) *Initial Sediment Investigation of Canagagigue Creek at the Uniroyal Chemical Ltd Plant, Elmira, 1995*. Ontario Environmental Monitoring and Reporting Branch of the Standards Development Branch, Ontario Ministry of Environment and Energy, Toronto, Ontario.

Jaagumagi, R. & Bedard, D. (1997) *Sediment and Biological Assessment of Canagagigue Creek at the Uniroyal Chemical Ltd Plant, Elmira, Ontario, 1995–96*. Environmental Monitoring and Reporting Branch of the Standards Development Branch, Ontario Ministry of Environment and Energy, Toronto, Ontario.

Karickhoff, S. W. (1984) Organic pollutant sorption in aquatic systems. *J. Hydraul. Div. ASCE* **110**(6), 707–735.

Lau, Y. L. & Krishnappan, B. G. (1994) *Comparison of Particle Size Measurements Made with a Water Elutriation Apparatus and a Malvern Particle Size Analyzer*. NWRI Contribution no. 94–82, National Water Research Institute, Burlington, Ontario.

Marcus, A. (1989) Regulating contaminated sediments in aquatic environments: a hydrologic perspective. *Environ. Manage.* **13**(6), 703–713.

Moore, J. W. & Ramamoorthy, S. (1984) Organic chemicals in natural waters. In: *Polychlorinated Dibenzo-p-dioxins (PCDD)* (ed. by R. S. Santo), 192–212. Springer Series on Environmental Management, Springer-Verlag, New York.

OMEE (1983) *Handbook of Analytical Methods for Environmental Samples*, vols I and II. Ontario Ministry of the Environment and Energy, Toronto, Ontario.

Ongley, E., Krishnappan, B. G., Droppo, I., Rao, S. & Maguire, R (1992) Cohesive sediment transport: emerging issues for toxic chemical management. *Hydrobiologia* **235/236**, 177–187.

Smith, J. A., Witkowski, P. & Fusillo, T. (1988) Manmade organic compounds in surface waters of the United states—a review of current understanding. *US Geol. Survey Circ. 1007.*

Walling, D. E & Woodward, J. C. (1993) Use of a field-based water elutriation system for monitoring in-situ particle size characteristics of fluvial suspended sediment. *Wat. Res.* **27**(9), 1413–1421.

Wood, P. & Armitage, P. (1997) Biological effects of fine sediment in the lotic environment. *Environ. Manage.* **21**(2), 203–217.

Witkowski, P. J., Smith, J., Fusillo, T. & Chiou, T. (1986) A review of surface-water sediment fractions and their interactions with persistent man made organic compounds. *US Geol. Survey Circ. 993.*