LAKE SUPERIOR / DULUTH-SUPERIOR HARBOR TOXICS LOADING STUDY

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ACRONYMS and ABBREVIATIONS

AOC	Area of Concern
DDD/DDE	Degradation products of DDT
DDT	p,p'-dichlorodiphenyltrichloroethane
ΣDDT	Sum of o,p' and p,p' isomers of DDT + DDE + DDD
DL	Detection Limit
GC/ECD	Gas Chromatography/Electron Capture Detection
GC/MS	Gas Chromatography/Mass Spectrometry
Hg	Mercury
HRMS	High Resolution Mass Spectrometry
MDL	Method Detection Limit
MPCA	Minnesota Pollution Control Agency
ND	Non-detect
OPR	Ongoing Precision and Recovery Standard
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
ΣPCB	Sum of PCB congeners
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SDL	Sample Detection Limit
SOP	Standard Operating Procedure
TCDD	Tetrachlorodibenzo-p-dioxin
TSS	Total Suspended Solids
USGS	United States Geological Survey
USEPA	United States Environmental Protection Agency
WDNR	Wisconsin Department of Natural Resources
WSLH	Wisconsin State Laboratory of Hygiene

channel is greater than that through the Duluth Channel (Table 8). The two most significant sources of water to the Duluth Superior Harbor are the Nemadji and St. Louis Rivers. The St, Louis River has a higher flow rate that the Nemadji River (Table 8). Box plots of the distribution of mean daily discharge over the course of this study are presented in Figure 4.

Table 8. Average annual mean daily discharge in cubic feet per second at each site.

Year	Duluth Shipping Channel	Superior Shipping Channel	Nemadji River	St. Louis River
1995	1,106	2,490	428	3,027
1996	1,396	2,912	500	3,787
1997	1,031	2,692	342	2,983
1998	612	1,965	251	2,288

Table 9. Mercury concentrations* and associated flows‡.

Duluth Channel			Superior Channel			St. Louis River			Nemadji River		
Date	Hg (ng/L)	Flow (cfs)	Date	Hg (ng/L)	Flow (cfs)	Date	Hg (ng/L)	Flow (cfs)	Date	Hg (ng/L)	Flow (cfs)
970923	0.94	1150	970923	0.61	850	970923	1.46	1155	970923	1.48	67
971126	1.15	0	971024	1.59	1970	971211	1.74	1281	971024	2.25	97
971211	1.40	0	971126	1.65	2045	971229	1.86	960	971211	2.06	89
971229	1.25	261	971211	2.16	1470	980121	1.73	1050	971229	1.86	87
980122	1.31	0	971230	1.16	0	980202	1.55	1103	980122	1.68	73
980202	0.99	906	980121	1.81	910	980218	1.50	1407	980202	1.31	75
980219	0.90	0	980202	1.02	0	980303	4.50	5009	980223	4.00	343
980303	1.00	2180	980219	1.10	0	980430	3.10	1880	980302	11.00	832
980429	3.00	947	980302	5.20	5150	980506	2.60	1344	980430	2.40	166
980507	1.85	797	980428	3.20	1340	980514	2.77	1302	980507	1.80	115
980513	1.82	289	980507	1.90	541	980520	2.25	2100	980513	1.64	104
980519	1.90	0	980512	2.01	0	980610	4.33	1586	980519	3.53	150
980527	1.74	498	980519	2.59	4420	980615	6.45	5397	980611	4.23	180
980610	1.48	288	980528	1.36	4030	980714	3.63	1197	980715	2.64	111
980623	3.95	2100	980612	2.47	4170	980824	1.22	699	980825	0.88	69
980714	1.59	77	980617	3.01	2720	980909	1.28	327	980903	0.91	40
980721	1.61	0	980715	2.56	1579	980910	0.93	327	980904	1.19	40
980826	1.20	0	980826	0.52	0				980908	1.02	38
980901	1.28	0	980901	0.32	90						
980902	1.25	0	980908	0.96	193						
980904	1.13	0	980910	1.01	0						
980909	0.62	0									
980910	0.42	0									

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

The annual mercury load in the St. Louis and Nemadji Rivers averaged 4.9 ± 0.67 and 0.62 ± 0.05 kg respectively. Almost 90% of the measured mercury load to the Harbor originated in the St. Louis River and watershed. This is largely due to the larger watershed size and greater discharge volume of the St. Louis River. The St. Louis River accounts for approximately 90% of the combined water volume entering the Harbor from the St. Louis and Nemadji Rivers (Table 8). Normalized to the area of their respective watersheds, the mercury loads are very similar, with Nemadji:St. Louis unit area load ratios of 1.1 and 1.0 in 1997 and 1998 respectively. This indicates that there is not likely a significant point source or in-place pollutant source of mercury to either river, and mercury loads in these tributaries are highly influenced by atmospheric inputs to the watersheds.

A recent review of atmospheric loadings of toxics to Lake Superior (Hoff et al., 1996) estimated that the mercury load to Lake Superior from tributaries, wet and dry deposition and gas absorption is approximately 890 kg/yr with volatilization accounting for an annual loss of 240 kg/yr. Hoff et al. 1996 estimate tributary inputs of mercury to Lake Superior to be approximately 15 kg/yr, which may be low given the estimated loadings from the Duluth-Superior Harbor alone (approx. 5 kg/yr). Eisenreich and Strachan (1992) estimated that atmospheric deposition resulted in a load of approximately 2,181 kg/yr to Lake Superior.

Table 10. Average annual mercury loads (kg).

Year	Duluth Shipping Channel load (kg)	95% C.I. *	N	Superior Shipping Channel load (kg)	95% C.I.*	N	Average annual mercury loads to Lake Superior from the Duluth-Superior Harbor.
1995	NA			NA			NA
1996	NA			NA			NA
1997	0.91		4	3.9		5	4.8
1998	1.2		19	4.0		16	5.2

Year	St. Louis River load (kg)	95% C.I. *	N	Nemadji River load (kg)	95% C.I. *	N	Average annual mercury loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995	NA			NA			
1996	NA			NA			
1997	4.5		3	0.58		4	5.1
1998	5.4	20%	14	0.66	32%	14	6.1

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995	NA	NA
1996	NA	NA
1997	1.2	1.3
1998	1.5	1.5

* = No confidence intervals are reported for the Duluth or Superior channels because negative flows were modified in the flow file in a manner that results in an artificially low C.I. No confidence intervals are reported for loading estimates with $n < 8$. See Methods Section – Loading Estimation for details.

Table 11. Dissolved, particulate and whole water dieldrin concentrations*.

	Dissolved pg/L	Particulate pg/L	Whole Water pg/L	TSS mg/L	Mean Daily Flow (cfs)‡
Duluth					
19950518	60.0	3.5	63.5	NA	2910
19950613	50.0	4.0	54.0	NA	698
19950803	30.0	4.0	34.0	NA	0
19960416	80.0	8.0	88.0	NA	3840
19960513-19960515	20.0	2.0	22.0	NA	1368
19970825-19970829	47.7	0.5	48.2	2.18	338
19971016-19971021	46.3	0.5	46.8	2.67	688
19980212-19980216	60.0	2.0	62.0	5.75	0
19980429	60.4	3.1	63.4	4.73	947
19980527	69.6	4.7	74.2	5.00	498
19980623	24.2	1.8	26.0	5.10	2100
19980721	74.5	5.7	80.2	4.55	0
19980824	56.5	2.3	58.8	2.30	0
19980825	56.3	4.4	60.6	2.76	0
19980902	70.8	4.4	75.2	2.12	0
Superior					
19950518	40.0	15.0	55.0	NA	5335
19950613	40.0	10.0	50.0	NA	1164
19950803	50.0	NA	50.0	NA	3213
19960430-19960501	9.0	2.0	11.0	NA	11600
19970825-19970904	32.7	0.5	33.2	NA	1690
19971016-19971019	102.4	0.5	102.9	7.07	3212
19980127-19980130	60.0	0.7	60.7	4.38	881
19980428	65.5	3.3	68.8	14.57	1340
19980528	80.3	5.7	86.0	10.21	4030
19980611	63.2	2.9	66.1	9.55	1480
19980616-19980617	43.1	2.5	45.6	6.82	2720
St. Louis					
19950614	20.0	5.0	25.0	NA	1271
19960515	20.0	1.0	21.0	NA	4883
19970827	95.6	0.5	96.1	4.96	658
19971014	52.5	0.5	53.0	6.78	2898
19980218	30.8	1.2	32.0	2.43	1407
19980506	46.5	1.5	48.0	6.09	1344
19980909-19980910	17.6	1.6	19.2	3.3	327
Nemadji					
19950614	20.0	2.5	22.5	NA	296
19960516	40.0	2.5	42.5	NA	394
19970828	96.5	0.5	97.0	14.20	101
19971015	56.4	0.5	56.9	13.34	158
19980219	303.4	10.7	314.1	17.89	229
19980513	53.0	1.4	54.4	13.07	104
19980903-19980904	17.1	0.5	17.6	15.3	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

Table 12. Average annual dieldrin loads (kg).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual dieldrin loads to Lake Superior from the Duluth-Superior Harbor.
1995	0.07	3	0.11	3	0.18
1996	0.11	2	0.04	1	0.15
1997	0.04	2	0.22	2	0.26
1998	0.02	8	0.15	5	0.17

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual dieldrin loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995	0.07	1	Tr	1	0.07
1996	0.07	1	Tr	1	0.07
1997	0.15	2	0.04	2	0.18
1998	0.07	3	0.04	3	0.11

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995	0.02	<0.08
1996	0.02	<0.08
1997	0.04	0.08
1998	0.02	0.08

Table 17. Dissolved, particulate and whole water 2,3,7,8-TCDD concentrations*.

Collection Date (yyyymmdd)	Dissolved fg/L	Particulate fg/L	Whole water fg/L	TSS mg/L	Mean Daily Flow (cfs)‡
Duluth					
19950518	0.50	0.50	1.00	NA	2910
19950803	14.00	16.00	30.00	NA	0
19960416	27.50	28.00	55.50	NA	3840
19960513-19960515	4.00	6.00	10.00	NA	1368
19970825-19970829	2.08	1.68	3.76	2.18	338
19971016-19971021	3.56	0.64	4.20	2.67	688
19980212-19980216	1.45	5.60	7.05	5.75	0
19980429	7.09	7.70	14.78	4.73	947
19980527	0.50	5.69	6.19	5.00	498
19980623	7.71	6.42	14.13	5.10	2100
19980721	38.05	12.44	50.49	4.55	0
19980824	7.80	6.59	14.38	2.30	0
19980825	6.99	1.99	8.98	2.76	0
19980902	5.65	4.49	10.14	2.12	0
Superior					
19950518	0.50	0.50	1.00	NA	5335
19950803	10.00	NA	10.00	NA	3213
19960430-19960501	5.00	2.50	7.50	NA	11600
19970825-19970904	0.50	4.54	5.04	NA	1690
19971016-19971019	5.71	6.55	12.26	7.07	3212
19980127-19980130	1.65	2.50	4.15	4.38	881
19980428	6.46	11.83	18.29	14.57	1340
19980528	0.50	9.78	10.28	10.21	4030
19980611	15.34	22.59	37.93	9.55	1480
19980616-19980617	0.50	24.63	25.13	6.82	2720
St. Louis					
19960515	11.00	7.50	18.50	NA	4883
19970827	2.21	3.56	5.77	4.96	658
19971014	2.63	3.27	5.90	6.78	2898
19980218	3.08	2.09	5.17	2.43	1407
19980506	2.73	5.20	7.93	6.09	1344
19980909-19980910	4.29	5.22	9.51	3.34	327
Nemadji					
19960516	9.50	12.50	22.00	NA	394
19970828	0.50	3.33	3.83	14.20	101
19971015	0.50	1.35	1.85	13.34	158
19980219	2.40	8.41	10.81	17.89	229
19980513	6.16	6.59	12.75	13.07	104
19980903-19980904	6.36	4.44	10.79	15.34	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

St. Louis River concentrations were somewhat lower than those in the shipping channels with an average whole water 2,3,7,8-TCDD concentration of 8.8 ± 5.0 fg/L. An average of 53 ± 11% of total 2,3,7,8-TCDD was measured in the particulate phase. The dissolved and particulate phase concentrations averaged 4.3 ± 3.3 and 4.5 ± 1.9 fg/L respectively. One hundred percent (6 of 6) of the samples at this site exceeded the water quality standard for this chemical. The Nemadji River whole water 2,3,7,8-TCDD concentration averaged 10 ± 7.2 fg/L with average dissolved and particulate concentrations of 4.2 ± 3.7 and 6.1 ± 4.0 fg/L respectively. Eighty-three percent (5 of 6) of the Nemadji River samples exceed the water quality standard. The particulate phase accounted for 65 ± 17% of total 2,3,7,8-TCDD at this location.

Spearman rank order correlation analysis indicated that there was no significant (at $p = 0.10$) correlation between water discharge rate and 2,3,7,8-TCDD concentration at any of the sites. The Spearman's r coefficients for the Duluth, Superior, St. Louis and Nemadji sites are –0.10, -0.28, 0.14 and 0.48 respectively.

The AutoBeale model used to estimate contaminant loadings in this study did not have the ability to calculate loads less than 0.036 kg/year. Because the dioxin concentrations were so low, the AutoBeale model was not able to estimate a load, indicating only that there were trace loads at all sites (Table 18). A rough approximation of annual load can be estimated by multiplying the total annual discharge at each site and the average annual 2,3,7,8-TCDD concentration. Table 19 provides load estimates based on this approximation. This estimation results in an average load of 39 ± 16 mg/yr of 2,3,7,8-TCDD to Lake Superior from the Harbor. This is balanced by an estimated average flux to the Harbor of 36 ± 32 mg/y from the St. Louis and Nemadji Rivers. On a yearly basis, output from the Harbor exceeded input in 2 of the 3 years measured. For the one year in which the 2,3,7,8-TCDD flux to the Harbor exceeded the flux out of the Harbor, load estimates were based on only one or two samples per site. Based on the 1997-98 data for which there were more data points, it appears that there may be a net export of 2,3,7,8-TCDD out of the Harbor. On a mass-basis, loading from the St. Louis River exceeded that of the Nemadji by factors of 6 to 18. Normalized to watershed area, the loads were similar. The ratios of Nemadji to St. Louis unit area loads were 1.3, 0.46 and 1.4 in 1996, 1997 and 1998 respectively.

Loading data for 2,3,7,8-TCDD are scarce for Lake Superior. Our estimate of the average (± stdev) 2,3,7,8-TCDD annual loading rate was 0.000039 ± 0.000016 kg/yr. Eisenreich and Strachan estimated the loading rate for all tetra chlorinated dioxin congeners to Lake Superior via wet deposition to be 0.019 kg/yr.

Table 18. Average annual 2,3,7,8-TCDD loads (kg).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual TCDD loads to Lake Superior from the Duluth-Superior Harbor.
1995	Tr	2	Tr	2	Tr
1996	Tr	2	Tr	1	Tr
1997	0.0	2	Tr	2	Tr
1998	Tr	8	Tr	5	Tr

Year	St. Louis River load (kg)		Nemadji River load (kg)	N	Average annual TCDD loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996	Tr	1	Tr	1	Tr
1997	Tr	2	0.0	2	Tr
1998	Tr	3	Tr	3	Tr

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995	Tr	Tr
1996	Tr	Tr
1997	Tr	Tr
1998	Tr	Tr

Tr = trace amount below 0.036 kg/yr (which is the lowest load the Beale model can report)

Table 19. Estimates of 2,3,7,8-TCDD loads based on the product of average annual 2,3,7,8-TCDD concentration and total water discharge (note: loads are expressed as milligrams).

Year	Duluth Shipping Channel load (mg)	N	Superior Shipping Channel load (mg)	N	Average annual TCDD loads to Lake Superior from the Duluth-Superior Harbor.
1995	15	2	12	2	28
1996	41	2	20	1	60
1997	3.7	2	21	2	24
1998	8.6	8	34	5	42

Year	St. Louis River load (mg)	N	Nemadji River load (mg)	N	Average annual TCDD loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996	62	1	9.8	1	72
1997	16	2	0.87	2	16
1998	15	3	2.6	3	18

Watershed area-normalized tributary loads

Year	St. Louis River load (mg/mi^2)	Nemadji River load (mg/mi^2)
1995		
1996	0.017	0.023
1997	0.004	0.002
1998	0.004	0.006

Figure 16. Estimated whole water toxaphene concentrations, indicating exceedences of the Minnesota water quality standard.

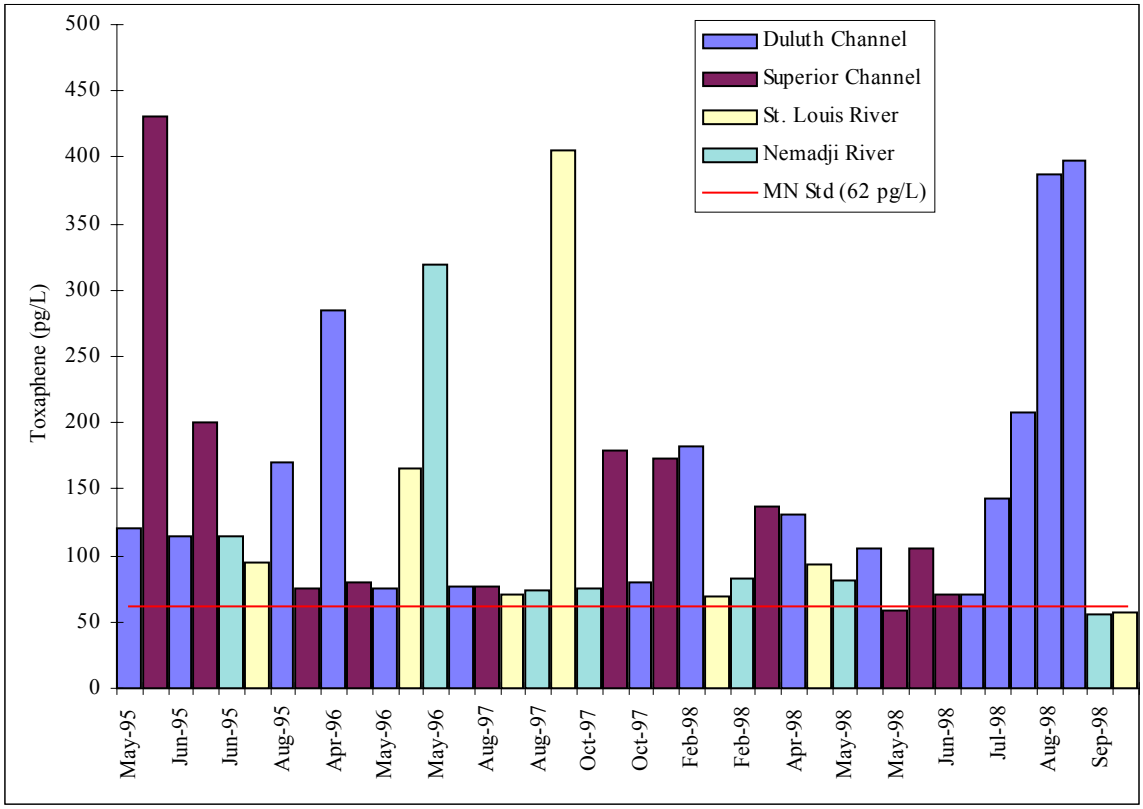


Table 20. Estimated dissolved, particulate and whole water toxaphene concentrations.

Collection Date yyyymmdd	Dissolved pg/L	Particulate pg/L	Whole Water pg/L	TSS mg/L	Mean Daily Flow cfs‡
Duluth					
19950518	60.0	60.0	120.0	NA	2910
19950613	90.0*	25.0	115.0	NA	698
19950803	95.0	75.0	170.0	NA	0
19960416	155.0	130.0	285.0	NA	3840
19960513-19960515	35.0	40.0	75.0	NA	1368
19970825-19970829	38.1	38.1	76.1	2.18	338
19971016-19971021	39.9	39.9	79.8	2.67	688
19980212-19980216	145.0*	37.5	182.5	5.75	0
19980429	65.6	65.6	131.2	4.73	947
19980527	63.6	42.4	106.1	5.00	498
19980623	42.2	28.1	70.4	5.10	2100
19980721	114.6*	28.7	143.3	4.55	0
19980824	178.5*	28.9	207.4	2.30	0
19980825	358.1*	28.4	386.5	2.76	0
19980902	368.7*	28.8	397.5	2.12	0
Superior					
19950518	160.0*	270.0*	430.0	NA	5335
19950613	90.0*	110.0	200.0	NA	1164
19950803	75.0	NA	75.0	NA	3213
19960430-19960501	45.0	35.0	80.0	NA	11600
19970825-19970904	38.3	38.3	76.5	NA	1690
19971016-19971019	89.3	89.3	178.6	7.07	3212
19980127-19980130	135.0*	37.5	172.5	4.38	881
19980428	68.3	68.3	136.5	14.57	1340
19980528	35.4	23.6	59.1	10.21	4030
19980611	63.2	42.1	105.4	9.55	1480
19980616-19980617	42.5	28.3	70.9	6.82	2720
St. Louis					
19950614	65.0	30.0	95.0	NA	1271
19960515	90.0	75.0	165.0	NA	4883
19970827	37.7	32.6	70.3	4.96	658
19971014	367.8*	37.2	405.0	6.78	2898
19980218	27.5	41.3	68.8	2.43	1407
19980506	46.5	46.5	92.9	6.09	1344
19980909-19980910	28.4	28.4	56.8	3.34	327
Nemadji					
19950614	80.0	35.0	115.0	NA	296
19960516	130.0	190.0	320.0	NA	394
19970828	40.2	34.2	74.4	14.20	101
19971015	38.4	36.2	74.6	13.34	158
19980219	33.4	50.1	83.4	17.89	229
19980513	40.5	40.5	81.1	13.07	104
19980903-19980904	28.0	28.0	56.1	15.34	40

* = Sample was above detection limit.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

The St. Louis River had only one detectable dissolved phase and no detectable particulate phase toxaphene concentrations. The average whole water concentration was 140 ± 120 pg/L with dissolved and particulate averages of 95 ± 120 and 42 ± 16 pg/L respectively. There were no detectable toxaphene concentrations in any sample from the Nemadji River. Substituting values for ND as described in the Methods Section results in average whole water, dissolved and particulate samples of 110 ± 92, 56 ± 37 and 59 ± 58 pg/L respectively.

Due to the large percentage of ND values, analyses of flow-concentration correlation were not conducted.

Treating ND as described in the Methods Section, the average annual load of toxaphene to lake Superior from the Harbor was 0.50 ± 0.24 kg. This was balanced by inputs to the Harbor from the St. Louis and Nemadji river which averaged 0.55 ± 0.41 kg. Two years (1995 and 1998) showed a net flux of toxaphene out of the Harbor to Lake Superior, and two years (1996 and 1997) showed a net flux to the Harbor from the tributaries. Over the four years in this study, there was a positive annual net input to the Harbor of 0.04 kg. The average annual toxaphene load in the St. Louis River (0.49 ± 0.39 kg) was approximately 7 times the average annual load in the Nemadji River (0.07 ± 0.06 kg). Normalized to watershed area, the relative tributary loads were similar, with the Nemadji load exceeding the loads from the St. Louis River by factors of 1.2 and 2.4 in 1995 and 1996 respectively. The unit area load of the St. Louis River exceeded that of the Nemadji in 1997 by a factor of three, and in 1998 when the Nemadji load was too low to be estimated by this model. A comparison of the relative loadings of the St. Louis and Nemadji Rivers is not reliable due to the significant number of non-detects at both locations. The loadings described in this section, are our best estimates of loads in this area. The upper and lower bound estimates are described below.

Substituting zero for all ND in the data set results in a similar trend but of a lower magnitude. With this substitution, the average annual load of toxaphene to Lake Superior from the Harbor was 0.17 ± 0.30 kg. The annual load to the Harbor from the St. Louis and Nemadji Rivers averaged 0.24 ± 0.47 kg. In the lower bound estimate, the Nemadji River carried no load of toxaphene to the Harbor (all values were ND). The lower-bound load estimate results in an average net input to the Harbor of 0.07 kg/yr.

Substituting the detection limit for all ND in the data set again results in net flux of toxaphene to the Harbor. With this substitution, the average annual load of toxaphene to Lake Superior from the Harbor was 0.84 ± 0.31 kg. The annual load to the Harbor from the St. Louis and Nemadji Rivers averaged 0.89 ± 0.50 kg. The upper-bound estimate results in an average net accumulation of 0.05 kg/yr in the Harbor from the tributaries.

This study estimated the average annual load of toxaphene to Lake Superior to be between 0.17 ± 0.30 and 0.84 ± 0.31 kg/yr. Reliable loading estimates for toxaphene in Lake Superior are also scarce. Eisenreich and Strachan (1992) estimated wet and dry deposition of toxaphene to Lake Superior at 17 kg/yr.

Table 21 (a). Average annual toxaphene loads (kg). In this table, non-detects are substituted as described in the Methods Section.

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual toxaphene loads to Lake Superior from the Duluth-Superior Harbor.
1995	0.11	3	0.69	3	0.80
1996	0.33	2	0.22	1	0.55
1997	0.07	2	0.36	2	0.44
1998	0.06	8	0.17	5	0.22

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual toxaphene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995	0.26	1	0.04	1	0.29
1996	0.55	1	0.15	1	0.69
1997	1.0	2	0.04	2	1.1
1998	0.15	3	Tr	3	0.15

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995	0.07	0.08
1996	0.15	0.34
1997	0.28	0.08
1998	0.04	Tr

* = No confidence intervals were reported for the Duluth or Superior channels because negative flows were modified in the flow file in a manner that results in an artificially low C.I.

Table 21 (b). Lower-bound estimate of average annual toxaphene loads (kg). In this table, non-detects are replaced by zero concentration.

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual low toxaphene loads to Lake Superior from the Duluth-Superior Harbor.
1995	Tr	3	0.62	3	0.62
1996	0.00	2	0.00	1	0.00
1997	0.00	2	0.00	2	0.00
1998	0.01	8	0.04	5	0.05

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual low toxaphene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995	0.00	1	0.00	1	0.00
1996	0.00	1	0.00	1	0.00
1997	0.95	2	0.00	2	0.95
1998	0.00	3	0.00	3	0.00

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995	0.00	0.00
1996	0.00	0.00
1997	0.26	0.00
1998	0.00	0.00

Table 21 (c). Upper-bound estimate of average annual toxaphene loads (kg). In this table, non-detects are replaced by the detection limit.

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual upper estimate of toxaphene loads to Lake Superior from the Duluth-Superior Harbor.
1995	0.22	3	0.77	3	0.99
1996	0.66	2	0.40	1	1.06
1997	0.15	2	0.77	2	0.91
1998	0.10	8	0.28	5	0.38

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual upper estimate of toxaphene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995	0.51	1	0.073	1	0.58
1996	1.13	1	0.292	1	1.42
1997	1.13	2	0.036	2	1.17
1998	0.33	3	0.036	3	0.36

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997	0.31	0.08
1998	0.09	0.08

Table 22. Dissolved, particulate and whole water acenaphthene concentrations*.

Collection Date yyyymmdd	Dissolved ng/L	Particulate ng/L	Whole water ng/L	TSS mg/L	Mean Daily Flow cfs‡
Duluth					
19950518	1.40	0.05	1.45	NA	2910
19980212-19980216	2.20	0.12	2.32	5.75	0
19980429	4.64	0.12	4.76	4.73	947
19980527	1.95	0.15	2.10	5.00	498
19980623	1.18	0.16	1.35	5.10	2100
19980721	1.38	0.04	1.41	4.55	0
19980824	1.67	0.04	1.71	2.30	0
19980825	1.82	0.05	1.86	2.76	0
19980902	0.92	0.01	0.94	2.12	0
Superior					
19950518	1.70	0.03	1.73	NA	5335
19980127	2.00	1.51	3.51	4.38	881
19980428	4.19	0.14	4.32	14.57	1340
19980528	1.46	0.15	1.61	10.21	4030
19980611	0.93	0.12	1.05	9.55	1480
19980616-19980617	2.27	0.13	2.40	6.82	2720
St. Louis					
19980218	0.72	0.04	0.76	2.43	1407
19980506	1.18	0.06	1.24	6.09	1344
19980909-19980910	0.47	0.01	0.49	3.34	327
Nemadji					
19980219	58.74	0.21	58.94	17.89	229
19980513	3.62	0.11	3.73	13.07	104
19980903-19980904	4.62	0.05	4.68	15.34	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

Whole water acenaphthene concentrations in the Nemadji River averaged 22 ± 32 ng/L with an average of 2% associated with the particulate phase. The dissolved and particulate phase concentrations were 22 ± 32 and 0.12 ± 0.08 ng/L respectively. The relatively high dissolved-phase value was measured in February 1998, and is approximately 13 times higher than the next highest concentration measured at this site. Without this value the average whole water concentration is 4.2 ± 0.67 ng/L. Acenaphthene loads from the Nemadji River will be estimated with and without this value.

There were no statistically significant correlations between water flow rate and acenaphthene concentration. The Spearman's r coefficient for the Duluth, Superior, St. Louis and Nemadji sites are 0.02, -0.54, 0.50 and 0.50 respectively.

Tables 23 (a) and (b) provide load estimates for acenaphthene with and without the high acenaphthene value in the Nemadji River. There was only one year (1998) in which PAH data were available for both the shipping channels and the tributaries. In this year, the acenaphthene load to Lake Superior from the Duluth-Superior Harbor was 6.3 kg. When all data are included in the load calculations (Table 23 (a)), the estimated load to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers is 12 kg, resulting in a net accumulation of 5.5 kg of acenaphthene in the Harbor. The annual load from the Nemadji River (9.9 kg) exceeded that from the St. Louis River (2.0 kg) by a factor of five. Normalized to the size of their respective watersheds, the load per unit area from the Nemadji exceeded that from the St. Louis by a factor of 42.

While the high concentration measured in the Nemadji River may be a valid measure, it may not be representative of typical conditions. Given that there are only three concentration values used for the 1998 load estimate, this high value may result in an over-estimation of the average annual load. Table 23 (b) provides load estimates for acenaphthene excluding the highest Nemadji River concentration. In this case, the 1998 load from the Harbor to the lake remains the same at 6.3 kg. The load to the Harbor from the tributaries decreases to 2.8 kg, resulting in a net loss from the harbor of 3.4 kg in 1998. This indicates that sediments with elevated PAHs may be contributing significantly to the load of acenaphthene to Lake Superior. In terms of absolute load, the St. Louis River exceeded the Nemadji River by a factor of two with average loads of 2.0 and 0.88 kg respectively. However, even with the highest value removed the Nemadji unit area load was 3.7 times greater than that from the St. Louis River, indicating that PAH-contaminated sediments in the Nemadji River watershed may be a source of acenaphthene to the Harbor.

Our estimate of the average (± stdev) annual loading rate to Lake Superior from the Duluth-Superior Harbor is 5.5 ± 1.05 kg/yr (average of 1995 and 1998 annual loads). Acenaphthene atmospheric load estimates for Lake Superior are reported as 62 kg/yr from wet deposition (Eisenreich and Strachan, 1992).

Table 23(a). Average annual acenaphthene loads (kg).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual acenaphthene loads to Lake Superior from the Duluth-Superior Harbor.
1995	1.4	1	3.4	1	4.8
1996					
1997					
1998	1.7	8	4.6	5	6.3

Year	St. Louis River load (kg)	N	Nemadji River load (kg) (with high value)	N	Average annual acenaphthene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996					
1997					
1998	2.0	3	10	3	12

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997		
1998	0.55	23

Table 23(b). Average annual acenaphthene loads (kg), excluding the highest Nemadji River value (see text for explanation).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual acenaphthene loads to Lake Superior from the Duluth-Superior Harbor.
1995	1.4	1	3.4	1	4.8
1996					
1997					
1998	1.7	8	4.6	5	6.3

Year	St. Louis River load (kg)	N	Nemadji River load (kg) (high value excluded)	N	Average annual acenaphthene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996					
1997					
1998	2.0	3	0.88	2	2.8

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997		
1998	0.55	2.0

However, the Nemadji River contributed a load 12 times that from the St. Louis when normalized to watershed area. As with acenaphthene, this may indicate a significant contribution of PAH from the wood preservative-contaminated site in the Nemadji watershed. This study estimated that the average annual loading rate of anthracene to Lake Superior was 1.39 ± 0.16 kg/yr (average of 1995 and 1998). A search of the literature failed to find any estimates of anthracene loadings for Lake Superior.

Table 24. Dissolved, particulate and whole water anthracene concentrations* (lab blank-corrected).

Collection Date (yyyymmdd)	Dissolved (ng/L)	Particulate (ng/L)	Whole water (ng/L)	TSS mg/L	Mean Daily Flow (cfs)‡
Duluth					
19950518	0.41	0.07	0.48	NA	2910
19980212-19980216	0.38	0.32	0.70	5.75	0
19980429	0.54	0.26	0.80	4.73	947
19980527	0.20	0.27	0.47	5.00	498
19980623	0.13	0.28	0.41	5.10	2100
19980721	0.24	0.00	0.24	4.55	0
19980824	0.95	0.00	0.95	2.30	0
19980825	0.28	0.00	0.29	2.76	0
19980902	0.14	0.00	0.14	2.12	0
Superior					
19950518	0.26	0.10	0.36	NA	5335
19980127	0.22	0.00	0.22	4.38	881
19980428	0.22	0.16	0.37	14.57	1340
19980528	0.59	0.31	0.89	10.21	4030
19980611	0.77	0.22	0.99	9.55	1480
19980616-19980617	0.20	0.20	0.40	6.8	2720
St. Louis					
19980218	0.04	0.01	0.05	2.43	1407
19980506	0.02	0.27	0.29	6.09	1344
19980909-19980910	0.16	0.00	0.17	3.3	327
Nemadji					
19980219	2.58	0.19	2.77	17.89	229
19980513	0.18	0.07	0.25	13.07	104
19980903-19980904	0.42	0.00	0.42	15.3	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

Table 25. Average annual anthracene loads (kg).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual anthracene loads to Lake Superior from the Duluth-Superior Harbor.
1995	0.47	1	0.80	1	1.3
1996					
1997					
1998	0.33	8	1.2	5	1.5

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual anthracene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996					
1997					
1998	0.33	3	0.47	3	0.80

Watershed area-normalized tributary loads		
Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997		
1998	0.09	1.1

Table 26. Dissolved, particulate and whole water benzo(a)pyrene concentrations*.

Collection Date (yyyymmdd)	Dissolved ng/L	Particulate ng/L	Whole water ng/L	TSS mg/L	Mean Daily Flow (cfs)‡
Duluth					
19950518	0.18	0.24	0.42	NA	2910
19980212-19980216	0.10	0.95	1.05	5.75	0
19980429	0.06	0.96	1.02	4.73	947
19980527	0.02	1.10	1.12	5.00	498
19980623	0.06	1.18	1.24	5.10	2100
19980721	0.00	0.41	0.42	4.55	0
19980824	0.01	0.58	0.58	2.30	0
19980825	0.00	0.46	0.46	2.76	0
19980902	0.00	0.15	0.15	2.12	0
Superior					
19950518	0.11	0.39	0.50	NA	5335
19980127	0.00	0.02	0.03	4.38	881
19980428	0.04	0.67	0.71	14.57	1340
19980528	0.02	1.04	1.06	10.21	4030
19980611	0.00	0.78	0.78	9.55	1480
19980616-19980617	0.03	0.79	0.82	6.82	2720
St. Louis					
19980218	0.00	0.17	0.17	2.43	1407
19980506	0.01	0.16	0.17	6.09	1344
19980909-19980910	0.00	0.04	0.04	3.34	327
Nemadji					
19980219	0.00	0.29	0.30	17.89	229
19980513	0.01	0.12	0.13	13.07	104
19980903-19980904	0.00	0.11	0.11	15.34	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

In 1998, 2.1 kg of benzo(a)pyrene were loaded into Lake Superior through the Duluth and Superior shipping channels (Table 27). This load is five times greater than the mass of benzo(a)pyrene loading into the harbor from the combined input of the St. Louis and Nemadji Rivers (0.40 kg), indicating that the Harbor is serving as a significant source of this contaminant to Lake Superior. In terms of absolute mass of benzo(a)pyrene loaded to the Harbor, the St. Louis contributed 4.5 times the mass contributed by the Nemadji River in 1998. When normalized to watershed size, the Nemadji contributed 1.8 times the load as the St. Louis River. This is lower than the ratio of unit area loads for acenaphthene (42) and anthracene (12). It appears that either benzo(a)pyrene is not associated with the source contributing elevated PAHs in the Nemadji watershed, or there may be a difference in transport of particle-associated PAHs (benzo(a)pyrene) vs. predominantly dissolved-phase PAHs (acenaphthene, anthracene, fluoranthene and phenanthrene) in the Nemadji watershed.

This study estimated the average (± stdev) annual loading rate of benzo(a)pyrene to Lake Superior to be 1.8 ± 0.43 kg/yr. Atmospheric loading of benzo(a)pyrene to Lake Superior has been estimated to be 115 kg/yr due to wet and dry deposition (Eisenreich and Strachan, 1992), 298 kg/yr due to wet deposition, dry deposition and gas absorption (Hoff et al., 1992). Hoff et al., also estimated that there was a loss of benzo(a)pyrene from Lake Superior estimated at 17 kg/yr resulting in a net load of 281 kg/yr.

Table 27. Average annual benzo(a)pyrene loads (kg).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual benzo(a)pyrene loads to Lake Superior from the Duluth-Superior Harbor.
1995	0.40	1	1.1	1	1.5
1996					
1997					
1998	0.61	8	1.5	5	2.1

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual benzo(a)pyrene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996					
1997					
1998	0.33	3	0.07	3	0.40

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997		
1998	0.09	0.17

The average (± stdev) annual loading rate of fluoranthene to Lake Superior in this study (average of 1995 and 1998 data) was 14 ± 4.6 kg/yr. Eisenreich and Strachan (1992) estimated that the atmospheric load of fluoranthene to Lake Superior due to wet and dry deposition was 455 kg/yr.

Table 28. Dissolved, particulate and whole water fluoranthene concentrations*.

Collection Date (yyyymmdd)	Dissolved ng/L	Particulate ng/L	Whole water ng/L	TSS mg/L	Mean Daily Flow (cfs)‡
Duluth					
19950518	4.40	0.66	5.06	NA	2910
19980212-19980216	1.40	2.80	4.20	5.75	0
19980429	6.91	3.15	10.06	4.73	947
19980527	1.61	2.04	3.65	5.00	498
19980623	2.98	2.08	5.07	5.10	2100
19980721	0.97	0.75	1.72	4.55	0
19980824	2.92	1.16	4.07	2.30	0
19980825	2.56	0.85	3.41	2.76	0
19980902	1.67	0.36	2.03	2.12	0
Superior					
19950518	4.40	1.20	5.60	NA	5335
19980127	1.00	0.18	1.18	4.38	881
19980428	4.19	2.28	6.46	14.57	1340
19980528	1.32	2.08	3.40	10.21	4030
19980611	1.18	1.52	2.70	9.55	1480
19980616-19980617	3.17	1.73	4.90	6.8	2720
St. Louis					
19980218	0.72	0.72	1.43	2.43	1407
19980506	1.12	0.61	1.72	6.09	1344
19980909-19980910	0.94	0.15	1.09	3.3	327
Nemadji					
19980219	9.34	3.07	12.41	17.89	229
19980513	2.49	0.97	3.46	13.07	104
19980903-19980904	2.50	0.53	3.03	15.3	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

Table 29. Average annual fluoranthene loads (kg).

Year	Duluth Shipping Channel load (kg)	N	SuperiorShipping Channel load (kg)	N	Average annual fluoranthene loads to Lake Superior from the Duluth-Superior Harbor.
1995	5.0	1	12	1	17
1996					
1997					
1998	4.1	8	6.8	5	11

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual fluoranthene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996					
1997					
1998	3.1	3	2.2	3	5.4

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997		
1998	0.87	5.1

with acenaphthene, anthracene and fluoranthene, the PAH-contaminated wetland on Crawford Creek may be serving as a source of elevated phenanthrene in the Nemadji River.

This study estimated the average loading rate of phenanthrene to Lake Superior from the Duluth-Superior Harbor to be 13 ± 3.9 kg/yr. Atmospheric loads of phenanthrene to Lake Superior have been estimated at 339 kg/yr from wet and dry deposition (Eisenreich and Strachan (1992), 8160 kg/yr from wet and dry deposition and gas absorption (Hoff et al., 1996) and 5400 kg/yr from wet and dry deposition and gas absorption (Hillery, et al., 1998).

Table 30. Dissolved, particulate and whole water phenanthrene concentrations*.

Collection Date (yyyymmdd)	Dissolved ng/L	Particulate ng/L	Whole water ng/L	TSS mg/L	Mean Daily Flow (cfs)‡
Duluth					
19950518	3.00	0.36	3.36	NA	2910
19980212-19980216	3.25	1.65	4.90	5.75	0
19980429	13.12	1.40	14.52	4.73	947
19980527	5.77	1.36	7.13	5.00	498
19980623	3.32	1.35	4.67	5.10	2100
19980721	5.56	0.80	6.36	4.55	0
19980824	5.59	0.81	6.40	2.30	0
19980825	5.17	0.74	5.91	2.76	0
19980902	3.51	0.37	3.89	2.12	0
Superior					
19950518	2.90	0.51	3.41	NA	5335
19980127	2.85	0.24	3.09	4.38	881
19980428	7.01	1.27	8.28	14.57	1340
19980528	5.67	1.56	7.23	10.21	4030
19980611	3.03	1.18	4.21	9.55	1480
19980616-19980617	4.71	0.99	5.70	6.82	2720
St. Louis					
19980218	1.54	0.83	2.37	2.43	1407
19980506	3.84	0.87	4.71	6.09	1344
19980909-19980910	2.98	0.36	3.34	3.34	327
Nemadji					
19980219	26.70	3.87	30.57	17.89	229
19980513	5.35	1.13	6.48	13.07	104
19980903-19980904	6.73	1.01	7.74	15.34	40

* = Precision is to 2 significant digits.

‡ = A flow rate of zero is used in the shipping channels when the mean daily discharge for that day is negative.

Table 31. Average annual phenanthrene loads (kg).

Year	Duluth Shipping Channel load (kg)	N	Superior Shipping Channel load (kg)	N	Average annual phenanthrene loads to Lake Superior from the Duluth-Superior Harbor.
1995	3.3	1	7.6	1	11
1996					
1997					
1998	5.3	8	11	5	16

Year	St. Louis River load (kg)	N	Nemadji River load (kg)	N	Average annual phenanthrene loads to the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers
1995					
1996					
1997					
1998	7.1	3	5.4	3	12

Watershed area-normalized tributary loads

Year	St. Louis River load (g/mi^2)	Nemadji River load (g/mi^2)
1995		
1996		
1997		
1998	2.0	12

Summary and Conclusions

Figure 28 (a and b) presents the median concentrations of contaminants from the four sampling sites in this study (1995-1998). Figure 29 presents the estimated average annual contaminant loading rates calculated for each of the sampling sites in this study.

Mercury occurred at concentrations exceeding the MN chronic standard for class 2B waters in the Lake Superior Basin at all sites in this study. Sixty-six percent of all samples exceeded the standard of 1.3 ng/L. Water concentrations in both the St. Louis and Nemadji Rivers tended to be higher than concentrations in the shipping channels. Mass loadings from the tributaries were also slightly higher than loading through the shipping channels, resulting in an average net accumulation of 0.5 kg/yr in the Harbor between 1997 and 1998. The St. Louis River contributed a greater mass of mercury to the Harbor relative to the Nemadji River. However, when loads were normalized to the area of the watershed, contributions from the Nemadji and the St. Louis were similar, indicating that the mercury inputs from these two watersheds may be largely influenced by the size of the drainage area rather than point sources or in-place pollutants in either watershed. Between 1997 and 1998, an average of 5.0 kg/yr of mercury was loaded into Lake Superior from the Duluth-Superior Harbor.

Dieldrin was measured in all samples at concentrations exceeding the Minnesota chronic standard for class 2B waters in the Lake Superior Basin (6.5 pg/L). There was a net flux of dieldrin out of the Harbor, indicating that contaminated sediments or current discharges to the Harbor are a source of dieldrin to Lake Superior in addition to tributary inputs. While the St. Louis River delivered a greater mass of dieldrin to the Harbor, the Nemadji contributed 2 to 4 times the unit area load. An average of 0.19 kg/yr of dieldrin was loaded to Lake Superior from the Harbor between 1995 and 1998.

Ninety-three to 100% of the ΣDDT samples in this study exceeded the water quality standard of 11 pg/L. The average load of ΣDDT to Lake Superior was approximately twice that of the combined load from the Nemadji and St. Louis Rivers entering the Harbor, indicating that the Duluth-Superior Harbor may be serving as a source of this chemical to Lake Superior. Between 1995 and 1998, an average of 0.60 kg/yr ΣDDT were transported into Lake Superior from the Duluth-Superior Harbor. The St. Louis River contributed a greater mass of ΣDDT to the Harbor than did the Nemadji River. However, when normalized to watershed area, the Nemadji load was slightly (by a factor of 1.2 to 2.4) but consistently greater than the St. Louis River.

The Minnesota water quality standard for PCBs in class 2B waters in the Lake Superior basin is 25.2 pg/L. All samples in this study exceeded the water quality standard. In three of the four years measured in this study there was a net flux of PCBs out of the harbor, indicating that the Harbor may be serving as a source of PCBs to Lake Superior. The exception to this was in 1996, when the annual loads in the St. Louis River and Nemadji Rivers were estimated from a single spring sample from each site. The ΣPCB concentration in both spring samples were high relative to other measurements and may not have been representative of the average annual load at these sites. This resulted in a net flux of PCBs into the Harbor for 1996. The ΣPCB load carried by the St. Louis River was greater than that in the Nemadji River. However, the unit area loads were quite similar, indicating that there probably is not a significant non-ambient source of

Figure 28. Median whole water concentrations of mercury, chlorinated organics and PAHs between 1995 and 1998 in the Nemadji River (NR), St. Louis River (SL), Superior Entry (SE) and Duluth Entry (DE).

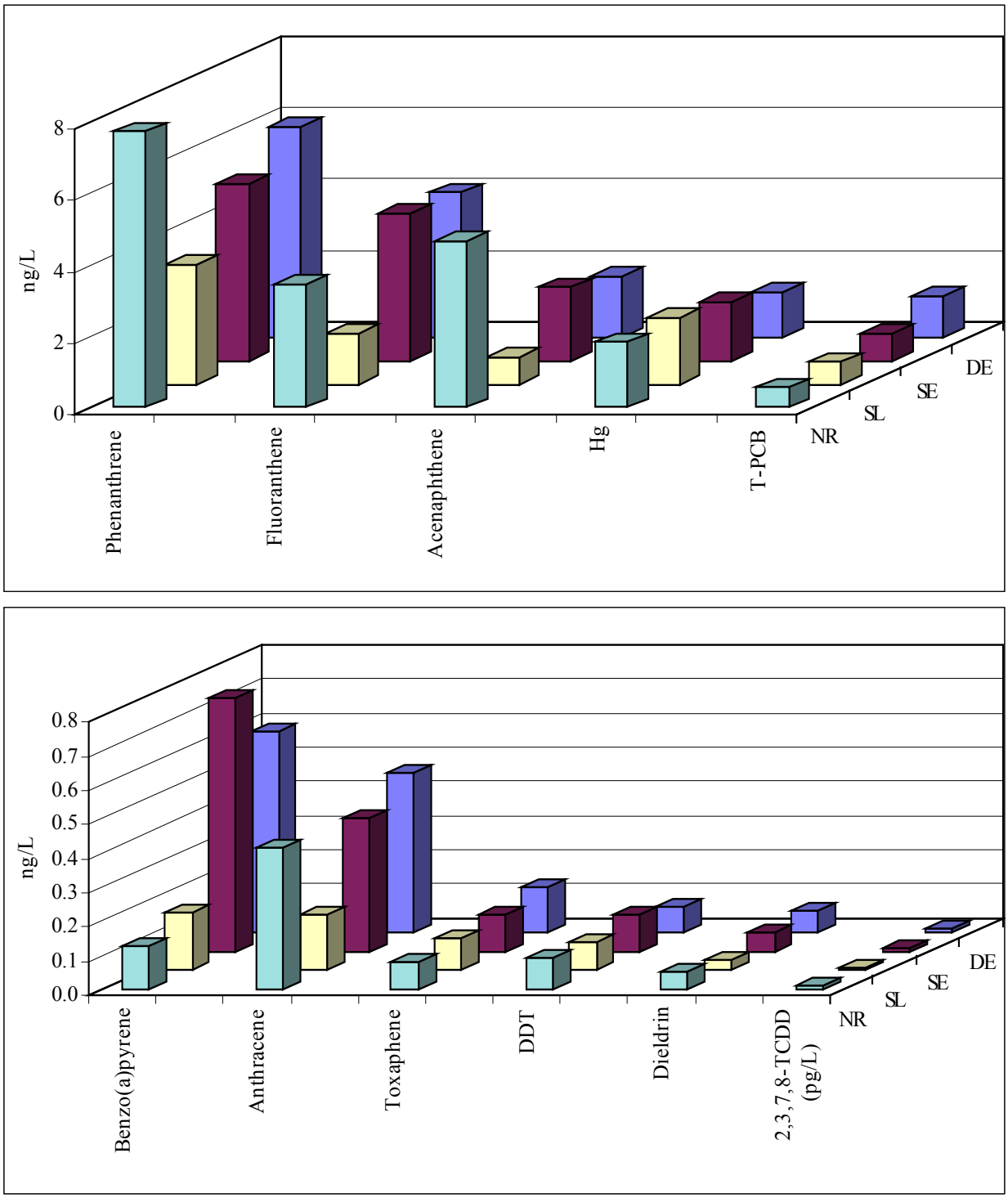
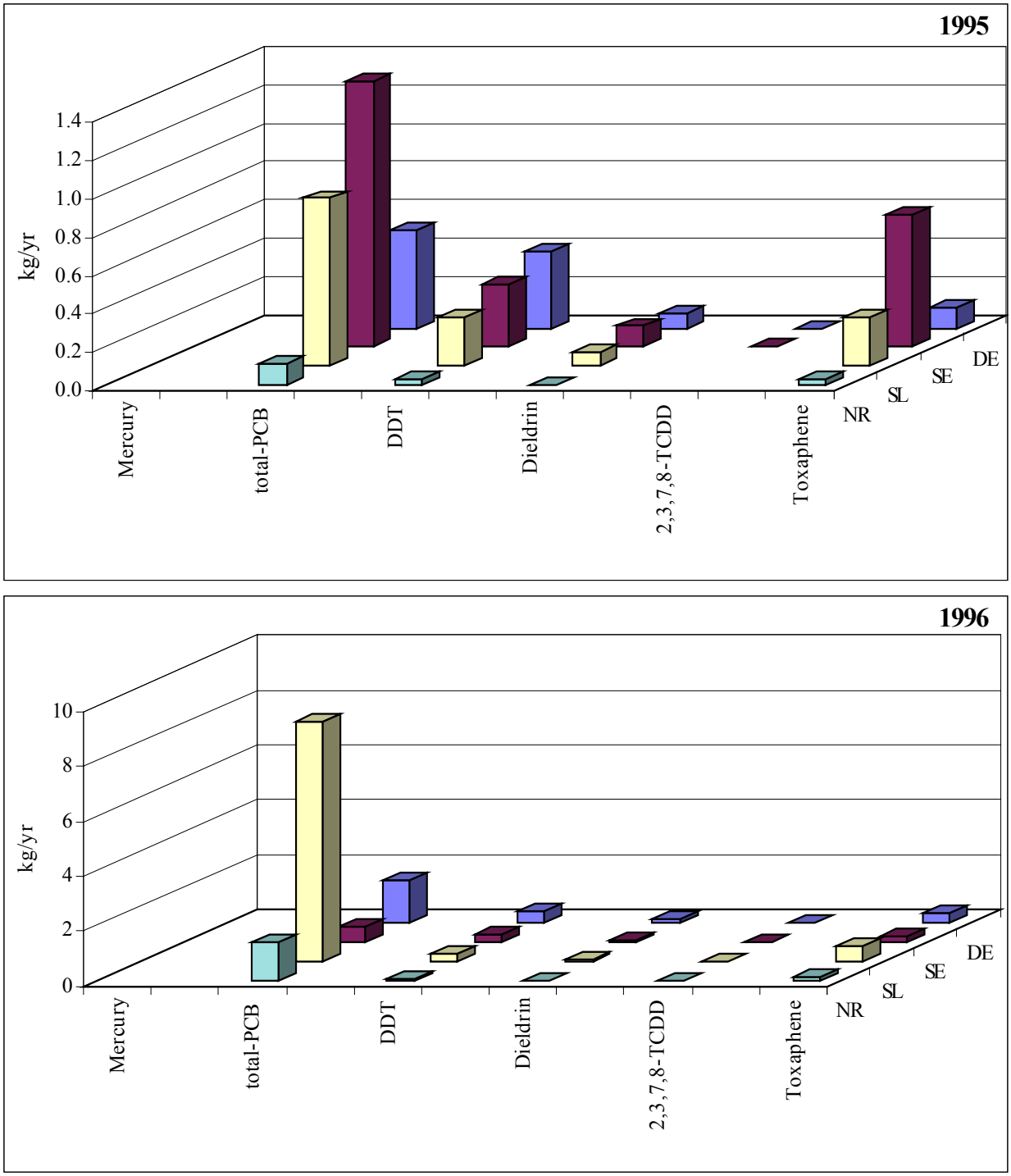
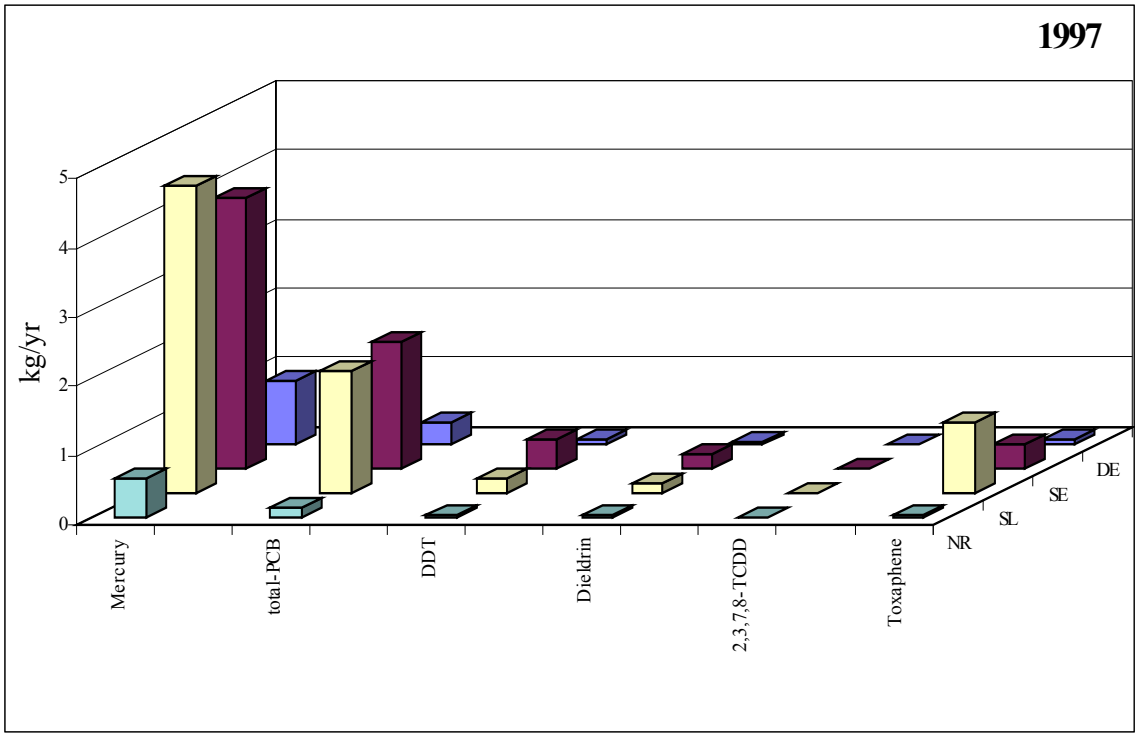


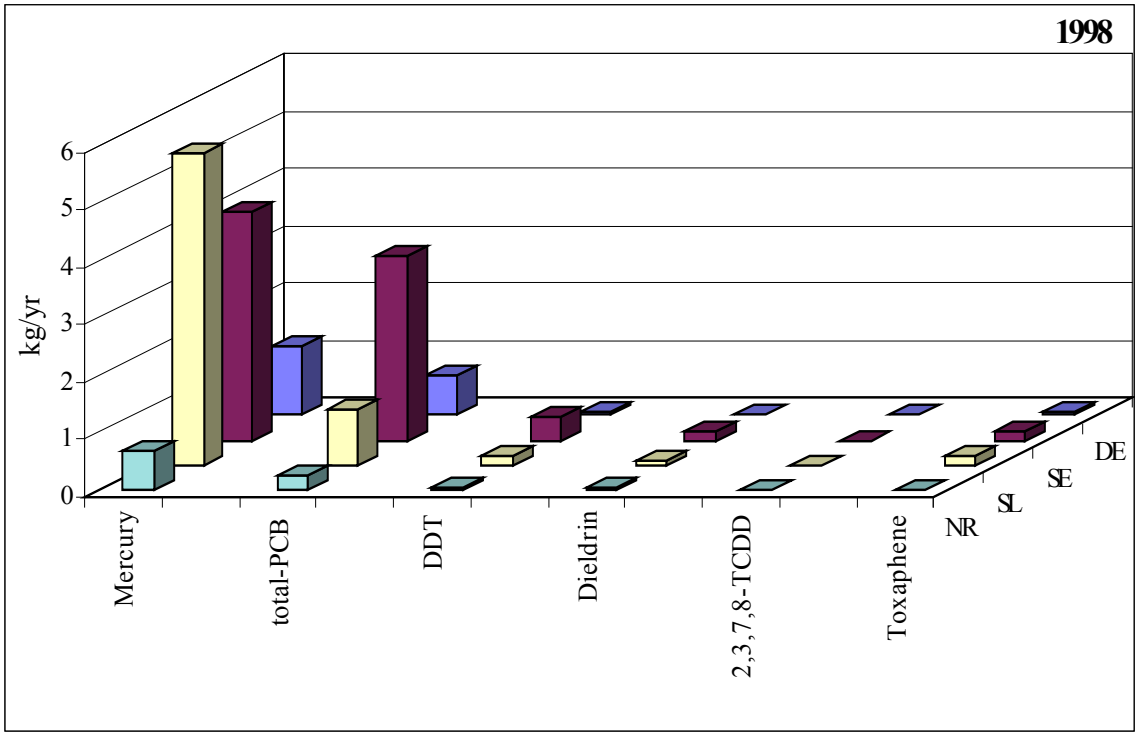
Figure 29. Average annual loading rates of mercury, chlorinated organics* and PAHs in the Nemadji River (NR), St. Louis River (SL), Superior Entry (SE) and Duluth Entry (DE) 1995-1998.



*= Quantitative estimates of toxaphene loads are unreliable due to the high number of non-detects (especially in the tributaries).

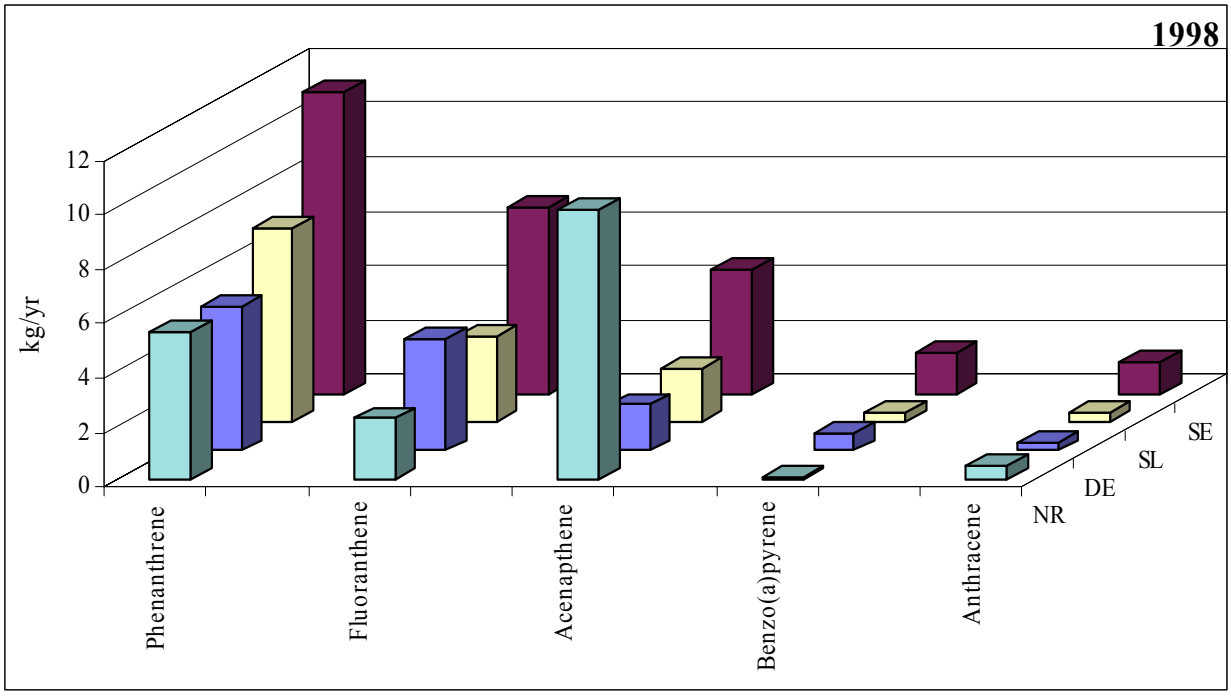
Figure 29(cont.).





*= Quantitative estimates of toxaphene loads are unreliable due to the high number of non-detects (especially in the tributaries).

Figure 29 (cont.).



PCBs in either watershed. The relative congener distributions in samples from the Harbor and the tributaries indicated that there might be a different source of PCBs to the Harbor relative to the tributaries. The average loading rate of ΣPCBs to Lake Superior from the Duluth-Superior Harbor in this study was 2.5 ± 0.93 kg between 1995 and 1998.

The water quality standard for 2,3,7,8-TCDD in class 2B waters in the Lake Superior Basin is 3.1 fg/L. Approximately 90% of the samples in this study exceeded this standard. The Stratified Beale Ratio Estimator model used to estimate loads in this study was not able to calculate loads less than 0.036 kg/yr. The low concentration of dioxin in this study precluded the use of this model. Therefore, loads were estimated by multiplying the average concentration of 2,3,7,8-TCDD in a given year by the total discharge for that year. Based on this rough approximation, the average load from the Harbor appears to be balanced by the average load to the Harbor between 1996 - 1998. On a yearly basis, 2,3,7,8-TCDD mass loading from the Harbor exceeded inputs from the tributaries in 2 of the three years measured. The St. Louis River load of 2,3,7,8-TCDD exceeded that of the Nemadji River. On a unit area basis, the Nemadji and St. Louis loads were quite similar indicating that 2,3,7,8-TCDD loads are dominated by atmospheric inputs to both watersheds. The average 2,3,7,8-TCDD load to Lake Superior from the Duluth-Superior Harbor was estimated to be 0.04 ± 0.02 g/yr. However, loading rates should be considered highly tentative given the low concentrations of 2,3,7,8-TCDD and the crude method of load calculation.

The majority of toxaphene samples at all sites were below the detection limit. Most samples with detectable levels of toxaphene were collected in the shipping channels. There was only one sample with detectable toxaphene collected in the St. Louis River. There were no samples with detectable toxaphene in the Nemadji River. Depending on what value is substituted for the non-detect values (ranging from zero to 1/2 the detection limit) 25 to 92% of the samples exceed the state water quality standard for toxaphene. Load estimates were significantly influenced by the values substituted for ND in the samples. Therefore, upper and lower bound estimates of loading rates were calculated in addition to the load estimate based on substituting for ND as described in the Methods Section. The latter calculation was considered our best estimate of loading in this area. This method results in an estimated average annual toxaphene load to Lake Superior of 0.50 ± 0.24 kg. The significant number of non-detects (especially in the tributaries) precludes reliable comparisons of relative loadings among the sites in this study except to observe that most detectable values were measured in water discharging from the Harbor.

There were no exceedences of the acenaphthene water quality standard in this study. There was only one year in which there are data for both the tributaries and the Harbor (1998). Loads were calculated with and without a very high acenaphthene concentration measured in the Nemadji River in February 1998. Both estimates are described in the Results Section. Because there were only three data points used to estimate the loading from the Nemadji River, the elevated concentration probably biased the average load high. Excluding the high acenaphthene value in the Nemadji River resulted in a net flux of acenaphthene out of the Harbor and an average annual load from the St. Louis River that was twice that from the Nemadji River. When the loads were normalized to the area of the watersheds, the Nemadji River load was 3.5 times that of the St. Louis River, indicating that there may be an additional source of acenaphthene in the Nemadji River watershed. The estimated average annual load of acenaphthene to Lake Superior is 5.5 ± 1.05 kg/yr.

All anthracene values were below the Minnesota water quality standard. The data were corrected to their associated laboratory blanks due to background contamination. Although not as extreme as the acenaphthene value, the February 1998 anthracene value was also relatively high. In 1998, the flux of anthracene out of the Harbor was twice that coming into the Harbor from the tributaries, indicating that the Harbor is also serving as a source of anthracene to Lake Superior. The average load from the Nemadji River exceeded the average load from the St. Louis River on an absolute mass and unit-area basis by factors of 1.4 and 12 respectively, indicating that there may be an additional source of anthracene in the Nemadji River watershed. This study estimated that the average annual loading rate of anthracene to Lake Superior was 1.39 ± 0.16 kg/yr.

While there is no Minnesota water quality standard for benzo(a)pyrene, there was a site-specific criterion developed for a contaminated site in the Duluth-Superior Harbor which can be used for comparison to the values in this study. Forty-three percent of the samples exceeded this criterion. All exceedences occurred in samples collected from the Duluth (56% exceeded) and Superior (67%) shipping channels. There were no exceedences in the tributaries. The 1998 load from the Harbor was five times greater than the load entering the Harbor from the tributaries, indicating that the Harbor is serving a significant source of benzo(a)pyrene to Lake Superior. On an absolute mass basis, the load in the St. Louis River exceeded that of the Nemadji River. Normalized to watershed size, the Nemadji load was greater but within a factor of two of the St. Louis River load. The average (± stdev) annual loading rate of benzo(a)pyrene to Lake Superior was estimated at 1.8 ± 0.43 kg/yr.

There were no exceedences of the fluoranthene water quality standard. The 1998 fluoranthene loading from the Harbor was twice that of the load entering the Harbor from the St. Louis and Nemadji Rivers. The St. Louis contributed 1.4 times the mass of fluoranthene as the Nemadji River. However, the Nemadji River contributed almost six times the load of the St. Louis River when compared on a unit area basis, indicating the possible presence of an additional source of fluoranthene in the Nemadji watershed. The average (± stdev) annual loading rate of fluoranthene to Lake Superior in this study was 14 ± 4.6 kg/yr.

There were no exceedences of the phenanthrene water quality standard in this study. Phenanthrene loads from the Duluth-Superior Harbor were 1.3 times the load into the Harbor in 1998. The St. Louis River loading was 1.3 times the load from the Nemadji River. However, the Nemadji River contributed 6 times the load when normalized to watershed area, indicating a potential source of phenanthrene in the Nemadji watershed. This study estimated the average loading rate of phenanthrene to Lake Superior from the Duluth-Superior Harbor to be 13 ± 3.9 kg/yr.

Annual net fluxes into and out of the Harbor were calculated as the difference in mass of contaminant leaving the Harbor through the two shipping channels and mass of contaminant entering the Harbor from the St. Louis and Nemadji Rivers (Table 32). A net flux out of the Harbor indicated that the Harbor is likely serving as a source of the contaminant in addition to tributary contributions. A net flux into the Harbor indicates that the tributaries may be serving as a more significant source and the contaminant may be accumulating in the Harbor. The direction and magnitude of the net flux are used to assess the significance of tributary and Harbor contributions of these contaminants to Lake Superior.

Mercury was the only contaminant which consistently (2 annual load estimates) had a net flux into the Duluth-Superior Harbor from the St. Louis and Nemadji Rivers, resulting in a net accumulation

of mercury in the Harbor. The Duluth-Superior Harbor appeared to be source of dieldrin, ΣDDT, anthracene, benzo(a)pyrene, fluoranthene and phenanthrene (and possibly PCBs and acenaphthene, depending on treatment of outlying values). The source of these contaminants in the Harbor may be contaminated sediments and / or current discharges to the Harbor. The concentrations of 2,3,7,8-TCDD were too low to estimate loads using the stratified AutoBeale Ratio Estimator Model. A rough estimate of 2,3,7,8-TCDD loadings (discussed in the Results Section) indicated that the average loads into and out of the Harbor were similar, although the mass flux out of the Harbor exceeded the mass flux into the Harbor in two of the three years measured. Due to the high number of non-detects in the data set, the relative loadings of toxaphene are highly dependent on the values substituted for non-detects in the load calculations. Because of this, quantitative estimates of loads are unreliable.

The loads from the St. Louis and Nemadji Rivers were compared to assess the relative significance of these watersheds as sources of pollutants to the Harbor. In terms of absolute contaminant loadings, the St. Louis River contributed a greater mass of all contaminants except acenaphthene and anthracene. For these two PAHs, high concentrations in the February 1998 sample resulted in the average Nemadji River load exceeding that of the St. Louis River. The significant number of samples in which toxaphene was not detected, precludes assessing the relative loadings of this contaminant. Since contaminant loads are partially driven by the area of the watershed draining into each tributary, loads were also calculated as mass per unit area of watershed for each tributary. On a unit area basis, the Nemadji River contributed a greater mass of all PAHs, dieldrin and possibly ΣDDT. There is a known area of PAH contamination in a wetland draining into a tributary of the Nemadji River that may explain the greater loading of PAHs. However, we are unaware of any sites in the Nemadji watershed with elevated dieldrin or DDT. The unit area loads of mercury, PCBs and 2,3,7,8-TCDD were similar (within a factor of two) between the St. Louis and Nemadji Rivers. This indicates that there probably are not any significant in-place pollutant sources or point sources of these contaminants in either watershed, and loadings are primarily influenced by ambient inputs.

With the exception of the 1998 mercury data set, the number of samples used in the tributary load calculations was too small to allow reporting of reliable confidence intervals for the loading estimates in this study. In addition, confidence intervals were not reported for the estimated loading rates from the Harbor Entries because the data correction required to account for flow reversals in the shipping channels resulted in artificially low estimates of the confidence intervals for the load estimates. Quantitative comparisons of loadings should be done with this in mind. Confidence in any particular load estimate should consider the number of samples involved, analyte precision measured by analyses of duplicates and any QA issues involving that analyte.

Table 32. Average annual loads of contaminants from the Duluth and Superior shipping channels, total load to Lake Superior (sum of Duluth and Superior loads), average annual loads from the St. Louis and Nemadji Rivers, total load to the Harbor (sum of St. Louis and Nemadji loads) and the net flux from the Harbor (load to Lake Superior minus load to the Harbor). Negative flux indicates a net accumulation in the Harbor.

		Duluth shipping channel (kg)	Superior shipping channel (kg)	Loads to Lake Superior (kg)	St. Louis River (kg)	Nemadji River (kg)	Loads to Duluth-Superior Harbor (kg)	Net flux from Harbor (kg)
Mercury	1995							
	1996							
	1997	0.91	3.90	4.82	4.45	0.58	5.04	-0.22
	1998	1.22	3.99	5.21	5.41	0.66	6.07	-0.86
Dieldrin	1995	0.07	0.11	0.18	0.07	Tr	0.07	0.11
	1996	0.11	0.04	0.15	0.07	Tr	0.07	0.07
	1997	0.04	0.22	0.26	0.15	0.04	0.18	0.07
	1998	0.02	0.15	0.17	0.07	0.04	0.11	0.06
DDT	1995	0.40	0.33	0.73	0.26	0.04	0.29	0.44
	1996	0.44	0.29	0.73	0.26	0.07	0.33	0.40
	1997	0.07	0.44	0.51	0.22	0.04	0.26	0.26
	1998	0.04	0.40	0.45	0.15	0.04	0.18	0.26
Total PCB	1995	0.51	1.39	1.90	0.88	0.11	0.98	0.91
	1996	1.53	0.55	2.08	8.72	1.39	10.11	-8.03
	1997	0.33	1.82	2.15	1.75	0.15	1.90	0.26
	1998	0.68	3.21	3.90	0.95	0.22	1.17	2.73
2,3,7,8-TCDD	1995	Tr	Tr					NA
(grams)	1996	Tr	Tr		Tr	Tr		NA
	1997	0.00	Tr		Tr	0.00		NA
	1998	Tr	Tr		Tr	Tr		NA
2,3,7,8-TCDD*	1995	0.015	0.012	0.028				
(grams)	1996	0.041	0.020	0.060	0.062	0.010	0.072	-0.012
	1997	0.004	0.021	0.024	0.016	0.001	0.016	0.008
	1998	0.009	0.034	0.042	0.015	0.003	0.018	0.024
Toxaphene	1995	Tr	0.62	0.62	0.00	0.00	0.00	0.62
(lower estimate)	1996	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1997	0.00	0.00	0.00	0.95	0.00	0.95	-0.95
	1998	0.01	0.04	0.04	0.00	0.00	0.00	0.04
Toxaphene	1995	0.11	0.69	0.80	0.26	0.04	0.29	0.51
	1996	0.33	0.22	0.55	0.55	0.15	0.69	-0.15
	1997	0.07	0.36	0.44	1.02	0.04	1.06	-0.62
	1998	0.06	0.17	0.22	0.15	Tr	0.15	0.08
Toxaphene	1995	0.22	0.77	0.98	0.51	0.07	0.58	0.40
(upper estimate)	1996	0.66	0.40	1.06	1.13	0.29	1.42	-0.36
	1997	0.15	0.77	0.91	1.13	0.04	1.17	-0.26
	1998	0.10	0.28	0.38	0.33	0.04	0.36	0.02

* = 2,3,7,8-TCDD loads based on the product of average annual 2,3,7,8-TCDD concentration and total water discharge.

Table 32(cont.). Annual loads of contaminants from the Duluth and Superior shipping channels, total load to Lake Superior (sum of Duluth and Superior loads), annual loads from the St. Louis and Nemadji Rivers, total load to the Harbor (sum of St. Louis and Nemadji loads) and the net flux from the Harbor (load to Lake Superior minus load to the Harbor). Negative flux indicates a net accumulation in the Harbor.

		Duluth shipping channel (kg)	Superior shipping channel (kg)	Loads to Lake Superior (kg)	St. Louis River (kg)	Nemadji River (kg)	Loads to Duluth-Superior Harbor (kg)	Net flux from Harbor (kg)
Acenaphthene	1995	1.42	3.38	4.81				
	1996							
	1997							
	1998	1.69	4.60	6.29	1.97	9.86	11.83	-5.53
Anthracene	1995	0.47	0.80	1.28				
	1996							
	1997							
	1998	0.33	1.17	1.50	0.33	0.47	0.80	0.70
Benzo(a)pyrene	1995	0.40	1.10	1.50				
	1996							
	1997							
	1998	0.61	1.50	2.11	0.33	0.07	0.40	1.71
Fluoranthene	1995	5.00	12.45	17.45				
	1996							
	1997							
	1998	4.08	6.82	10.91	3.14	2.23	5.36	5.54
Phenanthrene	1995	3.32	7.59	10.91				
	1996							
	1997							
	1998	5.32	11.06	16.38	7.12	5.40	12.52	3.86

Recommendations

This project provided contaminant concentration data and estimated contaminant loading rates for the Duluth-Superior Harbor, the St. Louis River and the Nemadji River. Given the limited number of samples collected at each site, the results of this study should be interpreted and used carefully as indicators of general trends and as a guide to future contaminant assessment activities. The following recommendations are based on the results of this project.

- Those chemicals and associated waterbodies found to exceed their respective Minnesota water quality standards should be assessed for inclusion in the Clean Water Act 303d list of impaired sites based on exceedences of specific water quality standards. These chemicals are mercury, dieldrin, ΣDDT, ΣPCB, 2,3,7,8-TCDD and benzo(a)pyrene.
- Chemicals for which data are deemed uncertain but suggestive of water quality standard exceedence (e.g. toxaphene) should be re-sampled at volumes large enough to accurately quantify concentrations.
- For most contaminants, the St. Louis River had a greater contaminant loading rate than the Nemadji River. For those chemicals that exceed the Minnesota water quality standard, the MPCA should assess whether the higher load is due to the larger drainage area of this stream or potential areas of elevated contamination (sediments, landfills etc.). Normalization to watershed area suggests that the higher loading may be due to a larger watershed. However, this normalization procedure is complicated by the existence of several reservoirs on the St. Louis River where particle-associated contaminants may settle out. Additional sampling should be done above the most upstream reservoir and below each depositional reservoir to assess contaminant transport from the watershed and additional loading from sediments accumulated behind the dams.
- The Nemadji River contributed relatively high loads of PAHs. The PAH-contaminated wetland in the Nemadji River watershed has been listed on the Wisconsin 303d list of impaired waters due to sediment contamination. Continued remediation efforts at this location should result in reduced loadings of PAHs from this tributary.
- For those contaminants identified as having a net loading from the Harbor, loading rates into the Harbor from current point-source discharges should be estimated to help assess the relative significance of discharges and contaminated sediments as sources of these contaminants.
- Future work of this type may benefit by the following suggestions:
  - Ensure that adequate numbers of samples are collected each year of sampling to allow for statistical testing and to provide reliable estimates of loading and associated error.
  - Ensure adequate sample volume is collected if analytes are measured at or near the detection limit.
  - Avoid splitting the sample extracts in the laboratory for analyses of different classes of chemicals as this lowers the apparent sample volume.
  - Have all instrumental responses reported, regardless of whether they are below the detection limit (they must be flagged as below the detection limit).

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In order to minimize paper consumption, the data appendices were not printed with every report. If you would like a copy of the Appendices (70 pages), please contact the Patti King at the MPCA (651) 296-8723 or patricia.king@pca.state.mn.us.