

Revised Final Draft

**Milwaukee Harbor  
Sediment Oxygen Demand Study 2004  
MMSD Contract # M03006P01**

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## 1. Purpose:

The Milwaukee Metropolitan Sewerage District (MMSD) and the Southeastern Wisconsin Regional Planning Commission (SEWRPC) are currently developing plans essential for the improvement of water quality in the Greater Milwaukee Metropolitan area, including the Milwaukee Harbor Estuary. The MMSD's 2020 Facilities Planning Program and SEWRPC's Regional Water Quality Management Plan are both utilizing a comprehensive watershed-based approach to evaluate questions and provide answers with regards to water quality impacts and the benefits of potential improvements to the MMSD's wastewater collection, conveyance, treatment and watercourse systems. These two planning effort will need to answer questions which deal with a broad range of water quality issues, including those of in-place sediment influences on overlying water quality.

Under these two planning efforts, water quality models for the Milwaukee Harbor Estuary are being developed to understand sediment/water interactions. It is important to obtain recent sediment data for modeling purposes in order to properly simulate current Estuary conditions that reflect the impacts of pollution control measures put into place in the 1990s, most importantly the reduction of combined sewer overflows (CSO's). Modeling conducted in 1987 (Milwaukee Harbor Estuary Study) predicted significant positive changes in sediment quality due to these pollution abatement measures. What impacts in-place sediments still exert on water quality remains to be determined.

This study collected sediment samples from the Milwaukee, Menomonee and Kinnickinnic rivers within the Milwaukee Harbor Estuary and the Outer Harbor. Laboratory experiments were conducted to quantify the amount of organic carbon present, identify amount of nutrients released from the sediment samples (ammonium-nitrogen and soluble phosphorus) under anaerobic conditions, and determine the rate of dissolved oxygen depletion due to sediment oxygen demand (SOD). Data collected as part of this effort will be utilized as inputs (sources and sinks) into dissolved oxygen, diagenesis, and eutrophication models ultimately being developed for the Regional Water Quality Management Plan and MMSD's 2020 Facilities Plan to determine how in-place sediment processes affect water quality.

## 2. Methods:

### a. Sample collection

Cores were collected with a Benthos 3 inch gravity corer deployed from the R/V Neeskay or a small (18') Johnboat fit with coring davit and winch. Cores were collected at 3 stations on each of five sampling dates (see e.g. Table 1) using coordinates supplied by the District and located via dGPS (see <http://waterbase.glwi.uwm.edu/mmsd/sites.html>, and figure 1). Four cores were collected from each station on each sampling date. Cores were returned to the laboratory and 3 of the 4 cores were extruded hydraulically into 6.7 cm ID core liners. The fourth core was reserved as a backup in the event of a problem with the extrusion or set up. These were allowed to come to room temperature (~23 C.) overnight.



#### b. Core incubation and flux measurements

Each core was fit with an air and water tight end cap into which an oxygen electrode (TRACEABLE DIGITAL Oxygen Meter model # 06-662-66), two sampling ports and a stirring mechanism were mounted (see photographs). Fresh overlying water was replaced in the core immediately prior to commencing the time course experiment. Stirring was carried out at 21 rpm, sufficient to mix the overlying water and move water past the oxygen electrode without resuspending any sediment or disturbing the sediment-water interface. Cores were kept in the dark via coverage with aluminum foil. The oxygen concentration and temperature were recorded continuously at 1-second intervals. Data from the electrodes were recorded on a computer with 9 RS-232 ports (MOXA Technologies multi port serial card) – one for each electrode. Data was captured using a Visual basic program written by Tom Hansen (IT Consultant, WATER Institute). Periodically, 10 mL of overlying water was removed with a disposable plastic syringe for nutrient analysis and filtered through a 25 mm, 0.2  $\mu\text{m}$  Acrodisc<sup>®</sup> membrane syringe filter. This water was replaced simultaneously with 10 mL of fresh water via a second sampling port. No corrections for dilution have been applied to the flux calculations, as this dilution would have <5% effect, well within the variability observed. The volume of overlying water was measured for each core at the completion of the experiment (Table 6). These cores have a surface area of 35.32  $\text{cm}^2$ .

The oxygen data were averaged over 10 second intervals and plotted as shown in the figures given in Appendix B. Fluxes were estimated approximately every 30 minutes until oxygen reached zero via the change in concentration over the time interval. This flux was plotted as a function of time as shown in the figures given in Appendix B. Mean fluxes were calculated from these data over the entire experiment, during four hour intervals: 1-4 hrs, 5-8 hrs, 9-12 hrs, and for the eight hour interval, 1-8 hrs (see Table Z and Excel spreadsheets in the Appendix). The initial ~30 minutes were highly variable and not used in the calculation. On three occasions one individual replicate was significantly different than the two companion replicates and these were excluded from calculation of the mean oxygen demand as noted on the figures and in the tables. Mean sediment oxygen demand for each station is summarized in Table 1 below. Conversion units are 1  $\mu\text{mol O}_2 = 32$   $\mu\text{g}$  oxygen by weight.

Dissolved ammonium and soluble reactive phosphorus (SRP) fluxes were estimated from the measured change in concentration over time during the initial phase of the experiment, usually over the first 4-8 hours. These results are plotted in the figures given in the Appendix and summarized in Table 2 below. The anaerobic phosphorus flux was estimated from the increase in SRP following oxygen depletion and is summarized in Table 3. SRP and dissolved ammonium were analyzed by modifications of the methods for seawater analysis as given in Strickland and Parsons (A Practical Handbook of Seawater Analysis, Fisheries Res. Bd. Can. Bull 167, 1972).

c. Solid phase analysis

Following completion of the flux experiments, 1 cm was removed from the top of each core via hydraulic extrusion into 4 oz. tared plastic jars. Sediments were weighed wet, dried at 60 C. and reweighed to determine percent water. Porosity was estimated assuming a dry sediment density of  $2.45 \text{ g cm}^{-3}$  (Table 6).

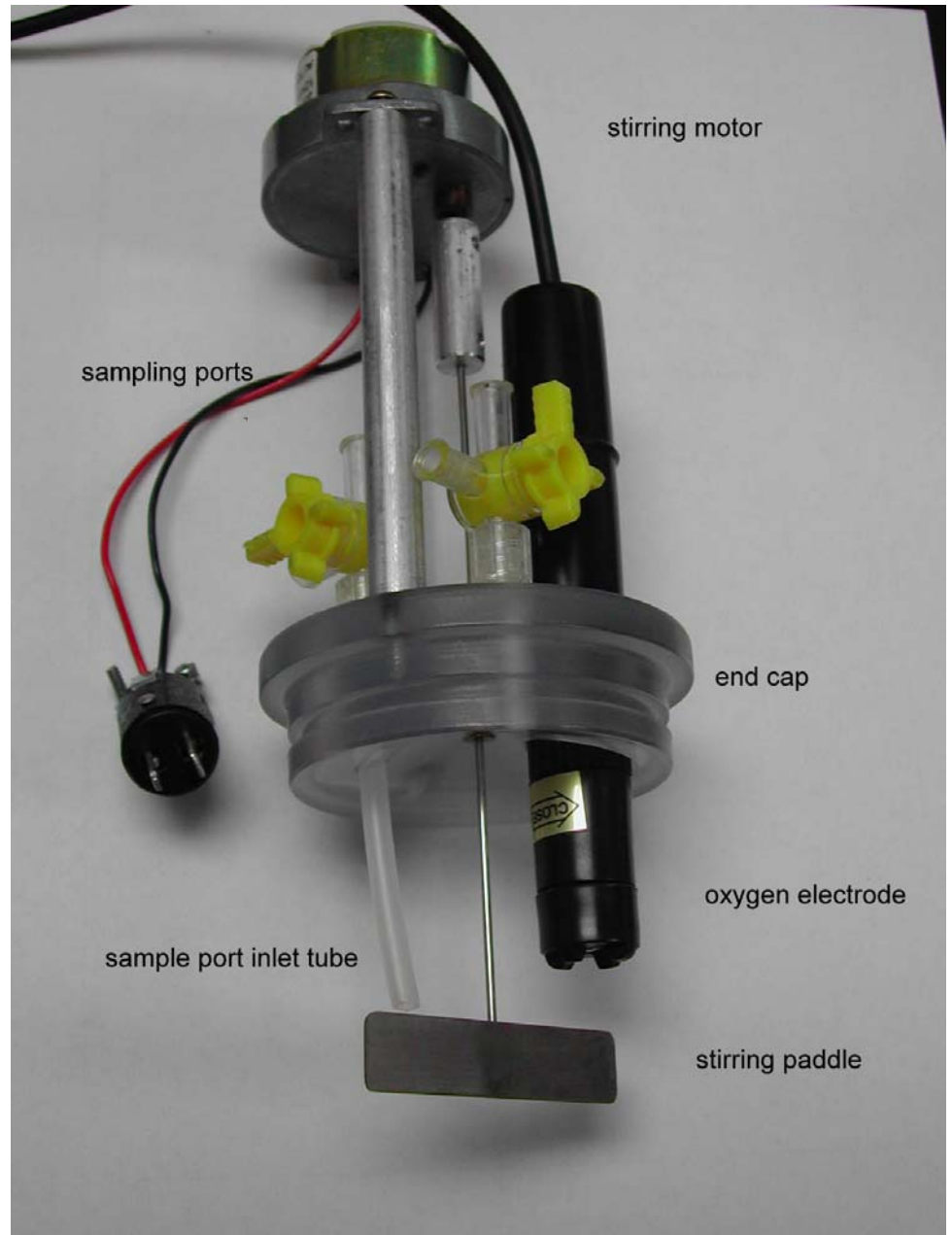
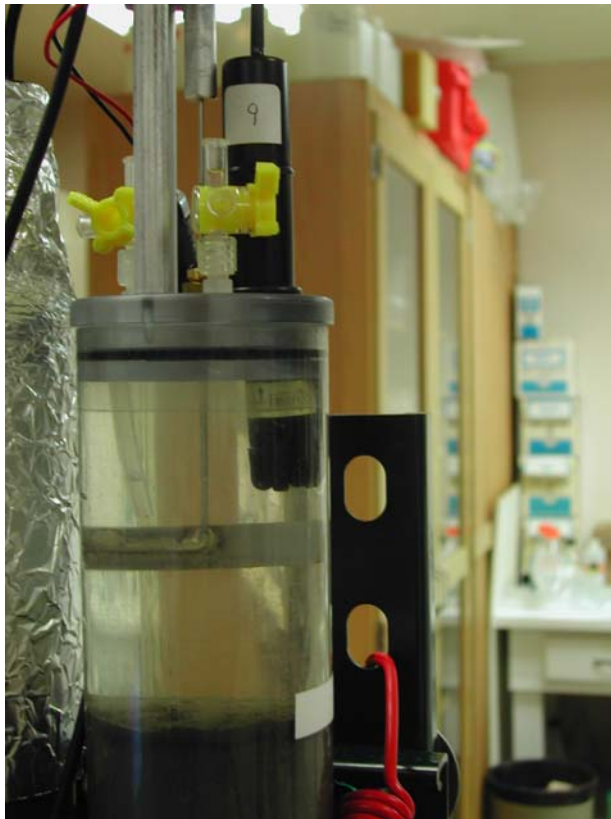
Total sediment nitrogen and total sediment organic carbon were measured via combustion on a Carlo Erba 1108 CHN analyzer following removal of carbonate via extraction with 3N phosphoric acid (Table 4).

Inorganic and organic sediment phosphorus (Table 5) were analyzed via the method of Ruban, et al [Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment, J. Environ. Monit. 1999, 1, 51-66. Appendix: Protocol for the phosphorus sequential extraction scheme according to Williams, as modified (SMT, 1998) part C. IP (inorganic phosphorus) and OP (organic phosphorus)]. Briefly, inorganic phosphorus is extracted with 1N hydrochloric acid. Organic phosphorus is determined via combustion of the residue at 450 C, for 3 h. and reextracted with 1N hydrochloric acid. Dissolved phosphate is analyzed via a modification of the Strickland and Parsons (1972) method.

One replicate core from station RI-14 from each sampling date deviated significantly in sediment properties from the other four replicates from both sampling dates. These two outliers were low in carbon, nitrogen and phosphorus content. These replicates also demonstrated anomalously low oxygen uptake rates. Values for all parameters in these two replicates were excluded in calculating the means shown in Tables 4, 5 and 6.

d. Photographs of experimental setup

- i) end cap showing oxygen electrode, stirring motor, stirring paddle, sampling ports (yellow luer fit stopcocks), and sample withdrawal tube. [right]
- ii) core with end cap in place prior to initiation of experiment. During experiment core is rapped in aluminum foil. [below]



- iii) Setup for simultaneous run of 9 cores. Cores are covered with aluminum foil during incubation.



- iv) Oxygen electrode meters. These are connected to an RS-232 port on a PC for continuous logging of dissolved oxygen concentration and temperature. Raw data are logged as \*.csv files given in Appendix.



### 3. Results (Tabular data):

**Table 1.1 Mean estimated sediment oxygen demand (see Table Z appendix for replicate data)**

Station	Date	All data less initial 1/2 hr	Mean Results - all values in $\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$								Notes
			+/-	%	4 hour flux	+/-	%	8 hour flux	+/-	%	
OH-4 Outer Harbor (North)	21-Jul-04	1211			1498			1369			
	05-Aug-04	754			1199			883			
	09-Sep-04	619			987			835			
	<b>Mean</b>	<b>861</b>	310	36%	<b>1190</b>	313	26%	<b>989</b>	339	34%	
OH-11 Outer Harbor (South)	21-Jul-04	1276			1464			1380			
	05-Aug-04	788			1402			1074			
	09-Sep-04	758			1074			1023			
	<b>Mean</b>	<b>941</b>	291	31%	<b>1314</b>	209	16%	<b>1159</b>	193	17%	
RI-19 Kinnickinnic River	21-Jul-04	1402			1697			1540			
	05-Aug-04	1505			1713			1130			
	09-Sep-04	1107			1694			1307			
	<b>Mean</b>	<b>1338</b>	207	15%	<b>1701</b>	10	1%	<b>1325</b>	206	16%	
RI-7 Milwaukee River	27-Jul-04	634			996			808			
	10-Aug-04	513			934			705			
	<b>Mean</b>	<b>573</b>	86	15%	<b>965</b>	44	5%	<b>757</b>	73	10%	
RI-11 Menomonee River	27-Jul-04	850			1147			999			
	10-Aug-04	949			1460			1063			
	<b>Mean</b>	<b>900</b>	70	8%	<b>1304</b>	222	17%	<b>1031</b>	46	4%	
RI-14 Kinnickinnic River	27-Jul-04	1507			1840			1507			A+B only
	10-Aug-04	1398			1822			1398			B+C only
	<b>Mean</b>	<b>1452</b>	77	5%	<b>1831</b>	13	1%	<b>1452</b>	77	5%	

**Table 1.2 Mean estimated sediment oxygen demand (g oxygen m<sup>-2</sup> day<sup>-1</sup> )**

Station	Date	All data less initial 1/2 hr	Mean Results - all values in g oxygen m <sup>-2</sup> day <sup>-1</sup>						Notes		
			+/-	%	4 hour flux	+/-	%	8 hour flux		+/-	%
OH-4 Outer Harbor (North)	21-Jul-04	0.93			1.15			1.05			
	05-Aug-04	0.58			0.92			0.68			
	09-Sep-04	0.48			0.76			0.64			
	<b>Mean</b>	<b>0.66</b>	0.24	36%	<b>0.94</b>	0.20	21%	<b>0.79</b>	0.23	29%	
OH-11 Outer Harbor (South)	21-Jul-04	0.98			1.12			1.06			
	05-Aug-04	0.60			1.08			0.82			
	09-Sep-04	0.58			0.83			0.79			
	<b>Mean</b>	<b>0.72</b>	0.22	31%	<b>1.01</b>	0.16	16%	<b>0.89</b>	0.15	17%	
RI-19 Kinnickinnic River	21-Jul-04	1.08			1.30			1.18			
	05-Aug-04	1.16			1.32			0.87			
	09-Sep-04	0.85			1.30			1.00			
	<b>Mean</b>	<b>1.03</b>	0.16	15%	<b>1.31</b>	0.01	1%	<b>1.02</b>	0.16	16%	
RI-7 Milwaukee River	27-Jul-04	0.49			0.77			0.62			
	10-Aug-04	0.39			0.72			0.54			
	<b>Mean</b>	<b>0.44</b>	0.07	15%	<b>0.74</b>	0.03	5%	<b>0.58</b>	0.06	10%	
RI-11 Menomonee River	27-Jul-04	0.65			0.88			0.77			
	10-Aug-04	0.73			1.12			0.82			
	<b>Mean</b>	<b>0.69</b>	0.05	8%	<b>1.00</b>	0.17	17%	<b>0.79</b>	0.04	4%	
RI-14 Kinnickinnic River	27-Jul-04	1.16			1.41			1.16			A+B only
	10-Aug-04	1.07			1.40			1.07			B+C only
	<b>Mean</b>	<b>1.12</b>	0.06	5%	<b>1.41</b>	0.01	1%	<b>1.12</b>	0.06	5%	

**Table 2. Mean estimated dissolved nutrient fluxes**

Station	Date	Ammonium Flux [ $\mu\text{mol m}^{-2} \text{hr}^{-1}$ ]					Phosphorus [SRP] Flux [ $\mu\text{mol m}^{-2} \text{hr}^{-1}$ ]				
		Replicate			Mean	+/-	Replicate			Mean	+/-
		1	2	3			1	2	3		
OH-4	8/5/2004	218	180	96	<b>165</b>	62	5.9	7.3	0.2	<b>4.5</b>	3.8
N. Outer Harbor	9/9/2004	87	319	75	<b>160</b>	138	7.4	-0.7	-7.4	<b>-0.3</b>	7.4
OH-11	8/5/2004	298	98	176	<b>191</b>	101	11.0	17.4	12.4	<b>13.6</b>	3.4
S. Outer Harbor	9/9/2004	19	118	126	<b>88</b>	59	5.8	5.0	5.1	<b>5.3</b>	0.5
RI-7	7/27/2004	351	177	131	<b>220</b>	116	20.7	16.8	4.2	<b>13.9</b>	8.7
Milwaukee R.	8/10/2004	256	173		<b>215</b>	59	13.4	11.0	2.3	<b>8.9</b>	5.9
RI-11	7/27/2004	448	347	538	<b>445</b>	96	25.6	16.0	23.2	<b>21.6</b>	5.0
Menomonee R.	8/10/2004	143	200	238	<b>194</b>	48	37.8	21.7	18.4	<b>25.9</b>	10.4
RI-14	7/27/2004	435	1003	185	<b>541</b>	419	-3.2	43.5	-2.9	<b>12.5</b>	26.8
Kinnickinnic R.	8/10/2004	237	223	223	<b>227</b>	8	2.9	4.6	5.3	<b>4.3</b>	1.2
RI-19	8/5/2004	380	302	370	<b>351</b>	42	86.8	66.2	17.4	<b>56.8</b>	35.7
Kinnickinnic R.	9/9/2004	204	155	242	<b>201</b>	43	-1.2	10.6	-0.7	<b>2.9</b>	6.7

**Table 3. Mean estimated anaerobic phosphorus fluxes**

Station	Date	Phosphorus flux [ $\mu\text{mol m}^{-2} \text{hr}^{-1}$ ]			Mean	+/-
		Replicate				
		1	2	3		
OH-4	8/5/2004	12	60	3	<b>25</b>	31
N. Outer Harbor	9/9/2004	51	6	2	<b>20</b>	27
OH-11	8/5/2004	51	18	5	<b>25</b>	24
S. Outer Harbor	9/9/2004	4	6	27	<b>12</b>	13
RI-7	7/27/2004	6	-4	5	<b>2</b>	5
Milwaukee R.	8/10/2004	9	0	3	<b>4</b>	5
RI-11	7/27/2004	110	56	60	<b>75</b>	30
Menomonee R.	8/10/2004	113	105	74	<b>97</b>	20
RI-14	7/27/2004	26	73	<b>3</b>	<b>49</b>	33
Kinnickinnic R.	8/10/2004	84	70	<b>15</b>	<b>77</b>	10
RI-19	8/5/2004	136	126	89	<b>117</b>	25
Kinnickinnic R.	9/9/2004	44	46	60	<b>50</b>	8

Values in **red** not included in calculation of mean

**Table 4. Sedimentary organic carbon and total nitrogen content @ 0-1 cm depth**

Station	Date	Sedimentary Organic Carbon Content % by weight					Sedimentary Total Nitrogen Content % by weight				
		Replicate			Mean	+/-	Replicate			Mean	+/-
		1	2	3			1	2	3		
OH-4	8/5/2004	6.51	6.68	6.63	<b>6.60</b>	0.09	0.275	0.270	0.230	<b>0.258</b>	0.024
N. Outer Harbor	9/9/2004	6.32	6.19	6.39	<b>6.30</b>	0.10	0.296	0.228	0.219	<b>0.247</b>	0.042
OH-11	8/5/2004	6.85	6.65	6.38	<b>6.63</b>	0.23	0.377	0.348	0.260	<b>0.329</b>	0.061
S. Outer Harbor	9/9/2004	6.69	6.67	6.85	<b>6.74</b>	0.10	0.338	0.345	0.353	<b>0.345</b>	0.007
RI-7	7/27/2004	7.04	5.78	6.22	<b>6.35</b>	0.64	0.323	0.223	0.314	<b>0.287</b>	0.055
Milwaukee R.	8/10/2004	7.09	7.64	7.45	<b>7.39</b>	0.28	0.339	0.376	0.387	<b>0.367</b>	0.025
RI-11	7/27/2004	7.16	7.29	7.76	<b>7.41</b>	0.31	0.374	0.372	0.371	<b>0.373</b>	0.002
Menomonee R.	8/10/2004	7.70	7.66	7.77	<b>7.71</b>	0.05	0.386	0.391	0.376	<b>0.384</b>	0.008
RI-14	7/27/2004	6.30	7.07	<b>3.57</b>	<b>6.69</b>	0.55	0.247	0.314	<b>0.090</b>	<b>0.280</b>	0.048
Kinnickinnic R.	8/10/2004	3.66	6.29	<b>2.43</b>	<b>4.98</b>	1.86	0.099	0.231	<b>0.029</b>	<b>0.165</b>	0.093
RI-19	8/5/2004	7.59	7.41	7.49	<b>7.49</b>	0.09	0.513	0.503	0.510	<b>0.508</b>	0.005
Kinnickinnic R.	9/9/2004	7.55	7.72	7.35	<b>7.54</b>	0.19	0.489	0.505	0.462	<b>0.486</b>	0.022

Values in red not included in calculation of mean

**Table 5. Sedimentary organic and inorganic phosphorus content @ 0-1 cm depth**

Station	Date	Sedimentary Organic Phosphorus Content					Sedimentary Inorganic Phosphorus Content				
		ug/g			Mean	+/-	ug/g			Mean	+/-
		Replicate	1	2			3	Replicate	1		
OH-4 N. Outer Harbor	8/5/2004	81	112	134	<b>109</b>	26	976	423	584	<b>661</b>	284
	9/9/2004	103	117	103	<b>108</b>	8	609	828	800	<b>746</b>	119
OH-11 S. Outer Harbor	8/5/2004	264	222	112	<b>199</b>	78	1414	1397	1453	<b>1421</b>	29
	9/9/2004	203	214	216	<b>211</b>	7	1343	1345	1357	<b>1348</b>	7
RI-7 Milwaukee R.	7/27/2004	142	87	167	<b>132</b>	41	926	644	808	<b>792</b>	142
	8/10/2004	156	167	203	<b>176</b>	24	869	923	943	<b>912</b>	38
RI-11 Menomonee R.	7/27/2004	288	306	299	<b>298</b>	9	1060	1091	1023	<b>1058</b>	34
	8/10/2004	288	281	272	<b>280</b>	8	1003	1018	978	<b>1000</b>	20
RI-14 Kinnickinnic R.	7/27/2004	173	224	<b>23</b>	<b>198</b>	36	793	964	<b>425</b>	<b>878</b>	121
	8/10/2004	100	142	<b>26</b>	<b>121</b>	30	572	759	<b>366</b>	<b>665</b>	133
RI-19 Kinnickinnic R.	8/5/2004	350	331	332	<b>338</b>	11	1152	1042	1054	<b>1083</b>	60
	9/9/2004	285	312	304	<b>300</b>	13	1119	1073	1037	<b>1076</b>	41

Values in red not included in calculation of mean

**Table 6. Milwaukee River/Estuary Sediment samples: Water content & porosity, 0-1 cm layer**

date	station	tare wt (g)	wet wt (g)	dry wt (g)	water vol (mls)	DO data file #	% H2O	porosity	ave porosity	+/-
7/20/2004 Neeskay	RI19A	37.67	76.7	46.96	317	4	0.7620	0.566		
	RI19C	38.17	82	51.62	317	5	0.6931	0.480		
	RI19D	37.3	85.15	49.21	317	6	0.7511	0.552	0.533	0.046
	OH4A	38.51	76.86	51.21	317	1	0.6688	0.452		
	OH4C	37.51	90.94	57.14	317	4	0.6326	0.413		
	OH4D	38.24	81.79	53.98	317	3	0.6386	0.419	0.428	0.021
	OH11B	37.7	77.85	47.99	317	7	0.7437	0.542		
	OH11C	38.02	82.25	50.98	317	8	0.7070	0.496		
	OH11D	37.76	87.69	50.42	317	9	0.7464	0.546	0.528	0.028
7/26/2004	RI 11A	37.56	93.72	52.49	229	7	0.7342	0.530		
	RI 11B	37.48	84.03	49.86	174	8	0.7340	0.530		
	RI 11C	38.01	75.45	48.11	220	9	0.7302	0.525	0.528	0.003
	RI 14A	38.36	86.17	54.79	202	1	0.6563	0.438		
	RI 14B	38.11	87.22	53.39	180	2	0.6889	0.475		
	RI 14D	38.16	106.26	77.1	214	3	<b>0.4282</b>	<b>0.234</b>	0.456	0.026
	RI 7A	38.16	92.03	56.8	211	4	0.6540	0.435		
	RI 7B	37.99	98.57	66.83	211	5	0.5239	0.310		
	RI 7D	37.58	80.02	51.25	211	6	0.6779	0.462	0.403	0.081
8/3/2004	RI19A	38.28	69.84	45.23	220	1	0.7798	0.591		
	RI19B	37.55	80.54	47.17	200	3	0.7762	0.586		
	RI19D	37.32	72.58	45.7	212	2	0.7623	0.567	0.581	0.013
	OH4A	37.86	89.5	53.11	228	4	0.7047	0.493		
	OH4B	38.09	105.9	59.67	240	5	0.6818	0.466		
	OH4C	38.15	80.69	52.81	225	6	0.6554	0.437	0.466	0.028
	OH11A	38.17	83.63	48.66	220	7	0.7692	0.576		
	OH11C	38.22	84.6	49.55	230	8	0.7557	0.558		
	OH11D	38.42	95.61	60.51	218	9	0.6137	0.393	0.509	0.101

date	station	tare wt (g)	wet wt (g)	dry wt (g)	water vol (mls)	DO data file #	% H2O	porosity	ave porosity	+/-
8/9/2004	RI 7A	38.52	86.74	55.42	219	5	0.6495	0.431		
	RI 7C	37.21	81	51.02	205	4	0.6846	0.470		
	RI 7D	37.45	70.72	46.14	204	6	0.7388	0.536	0.479	0.053
	RI 11A	37.81	69.36	45.12	169	7	0.7683	0.575		
	RI 11C	37.04	72.34	45.58	180	8	0.7581	0.561		
	RI 11B	38.31	74.69	47.85	187	9	0.7378	0.535	0.557	0.021
	RI 14B	37.89	97.7	70.92	186	1	0.4478	0.249		
	RI 14C	37.59	87.43	58.22	186	2	0.5861	0.366		
	RI 14D	38.09	113.63	91.16	211	3	<b>0.2975</b>	<b>0.147</b>	0.307	0.083
9/8/2004 Neeskay	RI19A	38.27	85.02	49.89	215	3	0.7514	0.552		
	RI19B	37.53	78.74	46.73	231	2	0.7768	0.587		
	RI19C	37.46	81.51	48.07	221	1	0.7591	0.563	0.567	0.018
	OH4A	37.86	108.81	61.79	242	5	0.6627	0.445		
	OH4C	37.89	91.16	56.87	235	6	0.6437	0.424		
	OH4D	38.31	98.81	60.14	233	4	0.6392	0.420	0.430	0.014
	OH11A	37.78	91.38	52.14	217	8	0.7321	0.527		
	OH11C	38.56	80.37	48.84	233	7	0.7541	0.556		
	OH11D	38.12	86.73	50.63	220	9	0.7426	0.541	0.541	0.014
<b>porosity summary</b>										
	OH 4								0.441	0.021
	OH 11								0.526	0.016
	RI 7								0.441	0.054
	RI 11								0.543	0.020
	RI 14								0.382	0.105
	RI 19								0.560	0.025

Values in red not included in calculation of mean

#### 4. Summary conclusions:

The principle results of this study are summarized in Figure 1 below, showing mean fluxes and sediment organic carbon, nitrogen and phosphorus content for each of the six stations sampled. In general, riverine stations exhibited higher fluxes of oxygen uptake and ammonium ( $\text{NH}_4^+$ ) and soluble reactive phosphorus (SRP) release than stations in the outer harbor. In particular, stations in the Kinnickinnic and Milwaukee Rivers (RI-11, RI-14, and RI-19) are probably anoxic at a shallower depth than the other stations. This results in a more pronounced phosphorus release following depletion of oxygen in the overlying water, as the entire sediment column goes anaerobic, releasing dissolved inorganic phosphorus adsorbed under oxidized sediment conditions. Outer harbor stations are probably more energetic environments that receive lower inputs of labile organic matter, but these inputs are likely to be episodic in nature. Physical mixing may also produce oxidized conditions at a greater depth at these stations.

Seasonal differences in fluxes appear slight with the exception of the outer harbor stations (Figure 2). In the outer harbor, oxygen demand decreased slightly from July to September. This could result from changes in inputs, changes in reactivity, or temperature effects, although all cores were incubated at room temperature and there was no significant change from August to September in organic carbon or total nitrogen content at these two stations.

The mean 4-hour oxygen consumption rate for all stations and dates was  $44 \pm 11 \text{ mg m}^{-2} \text{ h}^{-1}$ . The relative standard deviation about the mean is small, only 24%, and within the variability expected at a single station for this type of measurement. The largest variation occurred in phosphorus release rates, probably a function of redox conditions prevailing in the sediments during the time period (days to weeks) immediately prior to sampling, and the patchy nature of the bottom in areas, which, undoubtedly, are scoured nearly daily by ship and barge traffic. In some instances, replicate cores were clearly different, e.g. the third replicate at station R-14 for both sampling dates, and results from these outliers were excluded from calculation of the means, as noted.

Conclusions about the correlation between the C,N,P concentration in surface sediments and fluxes are difficult to make, and not necessarily expected. Fluxes are driven by the rate of input of labile organic matter to the sediment deposit, a function of both sedimentation rate and organic matter content. Hence, solid phase concentrations are only indirectly related to flux. Inputs are likely to be highly time dependent.

The average water content in the surface sediments was  $\sim 70\% \pm 7\%$ , translating to a mean porosity of  $\sim 0.5 \text{ cm}^3_{\text{H}_2\text{O}} \text{ cm}^{-3}_{\text{wet sed}}$ , indicating relatively well sorted, fine grained silty material. Carbon to nitrogen ratios for surface sediments are relatively high, ranging from 18-31. River and harbor sediments undoubtedly contain a higher proportion of terrestrial material with a higher content of refractory carbon than typical planktonically dominated lacustrine sediments in Lake Michigan with C:N ratios of  $\sim 6$ -10. Mean total sediment phosphorus content was  $\sim 1170 \pm 300 \text{ ppm}$  (26%), similar to most lacustrine deposits in the Great Lakes. Organic carbon averaged  $6.8 \pm 0.7\%$ , high for lake sediments, but well within the expected range for a eutrophic system. In short, in terms of these simple parameters, these sediments do not appear unusual, are remarkably similar for most of the measured parameters, and may be characterized as fairly typical, organic rich riverine-harbor deposits.

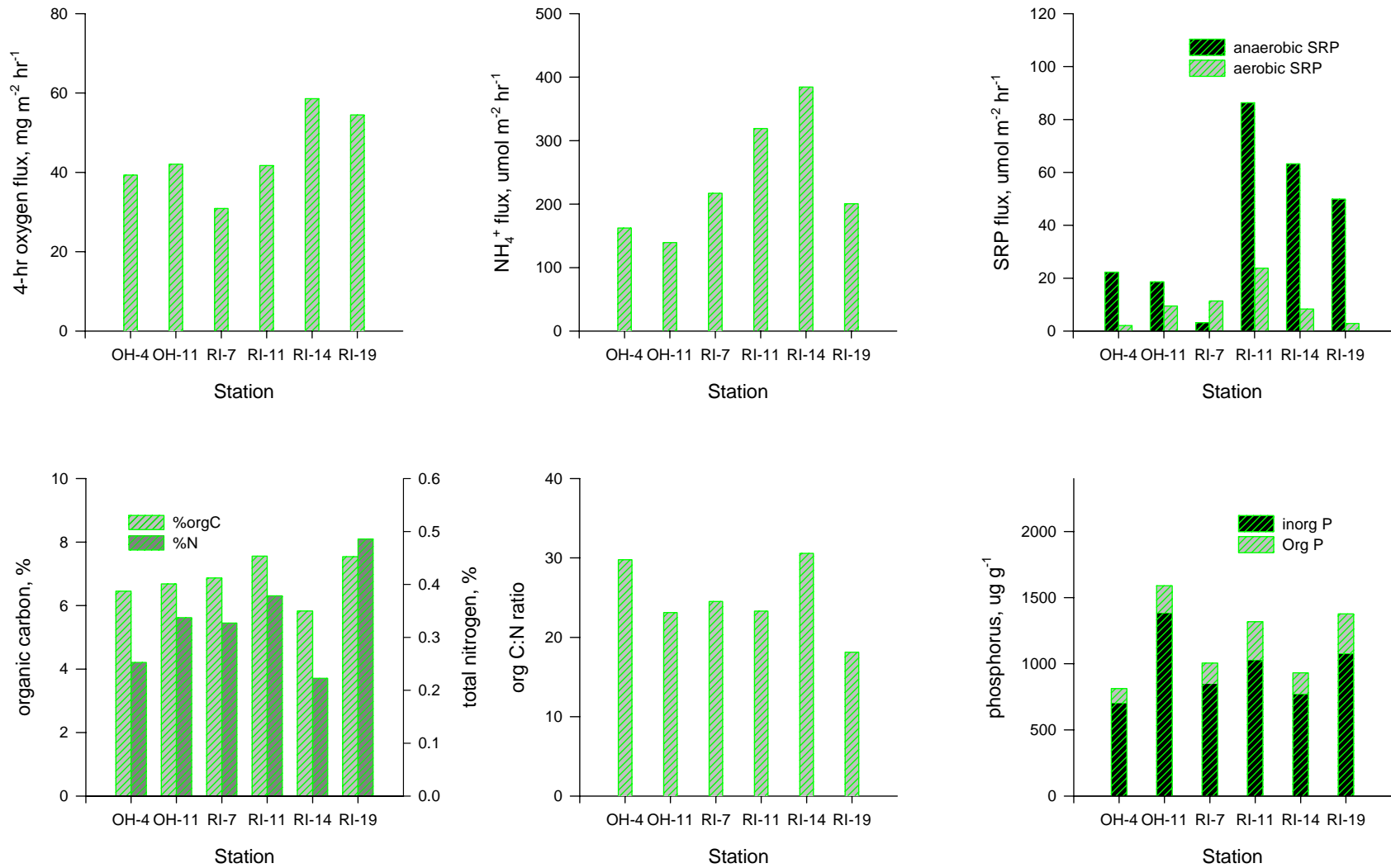


Figure 1. Mean values for measured parameters for all dates and replicates at each of the 6 stations sampled.

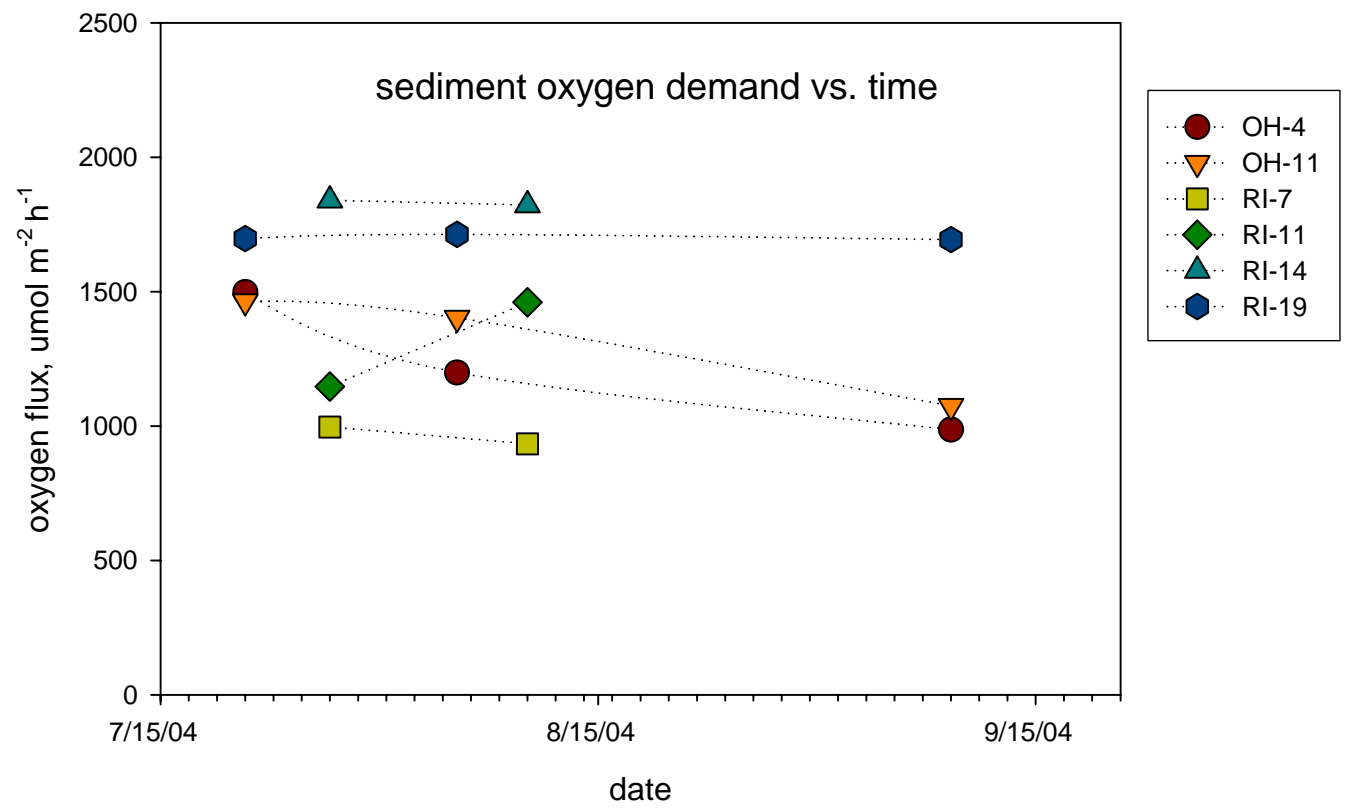


Figure 2. Sediment oxygen demand as a function of date of collection.

**Appendices: See attached CD**

1. Table Z. Summary of sediment oxygen demand in replicate cores (Table Z/ Table Z v2.pdf)
2. Table A. Sediment oxygen demand figures (figures/ SOD figures v3.pdf)
3. Table B. Sediment dissolved nutrient release figures (figures/ nutrient figures.pdf)
4. Data files:
  - i. raw data: Raw oxygen electrode data files [ \*.csv] – refer to DO file # for station location (Table 6).
  - ii. excel O2 files: Excel computational files [\*.xls]
  - iii. graphics files: SigmaPlot Graphics files [\*.jbn]
  - iv. core and nutrient data: core & nutrient data.xls