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## Amelioration of storm-water quality by a freshwater estuary

By DAVID M. KLARER and DAVID F. MILLIE<sup>1</sup>

With 4 figures and 3 tables in the text

### Abstract

The role of Old Woman Creek estuary, Lake Erie (U.S.A.) in ameliorating the quality of storm-water flow was investigated. Chemical parameters in water samples collected immediately following three distinct storm events displayed one of three patterns: 1) decreasing concentrations due to dilution by storm-water runoff, 2) increasing concentrations due to sediment input and/or surface runoff, and 3) increasing concentrations attributed to storm interflow. Outflow/inflow ratios of chemical concentrations indicated that up to 60 % of the metals and up to 80 % of the biologically-important nutrients were retained within the estuary. Amelioration of storm-water quality was attributed to sedimentation, biological uptake, and geochemical processes.

### Introduction

Of the Laurentian Great Lakes, Lake Erie has exhibited the greatest impact of increased nutrient inputs. This accelerated eutrophication led to a comprehensive study of nutrient inputs into the lake during the early 1970's (U.S.A.C.E., 1975). Although point source pollution was noted as the most obvious problem, non-point agricultural sources were determined to be a major cause of nutrient enrichment. More recently, researchers (BAKER, 1984, 1985; BAKER et al., 1985; RICHARDS & BAKER, 1985) have documented the importance of storm water in transferring nutrients and pollutants from the watershed to the receiving waters.

Amelioration processes in brackish-water estuaries remove particulate and dissolved matter and pollutants during moderate or low riverine flow (SCHEMEL et al., 1984). The major physical process, sedimentation, removes coarse particulate matter and is dependent on tidal mixing patterns and estuary morphometry (SCHUBEL & CARTER, 1984). The geochemical processes, adsorp-

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tion, flocculation, and precipitation, and biochemical processes remove dissolved chemicals from the water column (SHARP et al., 1984). Biological processes, such as filter feeding by benthic fauna, also remove fine sediment particles and their associated contaminants (BIGGS & HOWELL, 1984). However, these amelioration processes can be overwhelmed in periods of high flows (SCHEMEL et al., 1984).

The term "estuary" has been applied to the drowned portion of rivers and streams entering the Laurentian Great Lakes (BRANDT & HERDENDORF, 1972; BATES & JACKSON, 1980; HERDENDORF & KRIEGER, 1989). Although these freshwater estuaries are believed to be functionally similar to their marine counterparts, little evidence is available to support this. A previous study in a Lake Erie estuary noted the impact of storm-water inflow on the water chemistry of the estuary (O.D.N.R., 1981). However, the role of the estuary in ameliorating the quality of storm-water flow was not addressed. The intent of this study was to examine the role of that Lake Erie estuary in ameliorating the chemistry of storm water passing through it. Functional similarities between this freshwater estuary and brackish-water estuaries were also examined.

### Site description

Old Woman Creek (OWC) is a second-order stream which drains 78.7 km<sup>2</sup> of primarily agricultural lands in Huron and Erie Counties, Ohio (U.S.A.) before flowing into Lake Erie. The estuarine portion of OWC extends 2.1 km southward from the confluence of the creek and the lake (Fig. 1). The land bordering the estuary is composed of undisturbed hardwood forest and prairie.

The estuary is divided into distinct upper and lower reaches which have characteristics of riverine and lacustrine wetlands respectively (after COWARDIN et al., 1979). While the upper estuary is confined to a narrow deep channel, the lower estuary has an average depth of less than 1 m outside of the channel proper and extends over 0.3 km<sup>2</sup>. A small island is located in the center of lower estuary. The large surface area to depth ratio ( $3 \times 10^5 : 1$ ) of the lower estuary ensures that bottom sediments are easily suspended in the water column by moderate winds (KRIEGER, 1984). Water volume of the entire estuary is approximately  $3.7 \times 10^5$  m<sup>3</sup> with a retention time between 24 (maximum flow) and 114 hrs (mean flow) (WOODS, 1986). The location and size of the drowned creek mouth are continually modified by a shifting-sand, barrier beach which can isolate OWC from the lake for portions of each year. Seiches and storm surges in Lake Erie can rapidly change the water level of the estuary during times the creek mouth is open.

### Methods

Sampling sites were established in the creek proper (site A), the upper estuary (sites B, C), the lower estuary (sites D–H), and the nearshore zone of the lake (site I) (Fig. 1). Water samples were collected in polyethylene bottles immediately following two spring storms (13–20 April, 1984 and 13–27 May, 1985) and an autumn storm (1–7 October, 1984). For the spring storm events, samples were also collected on the day prior to the storm. Samples were analyzed within 12 to 24 hours after collection.

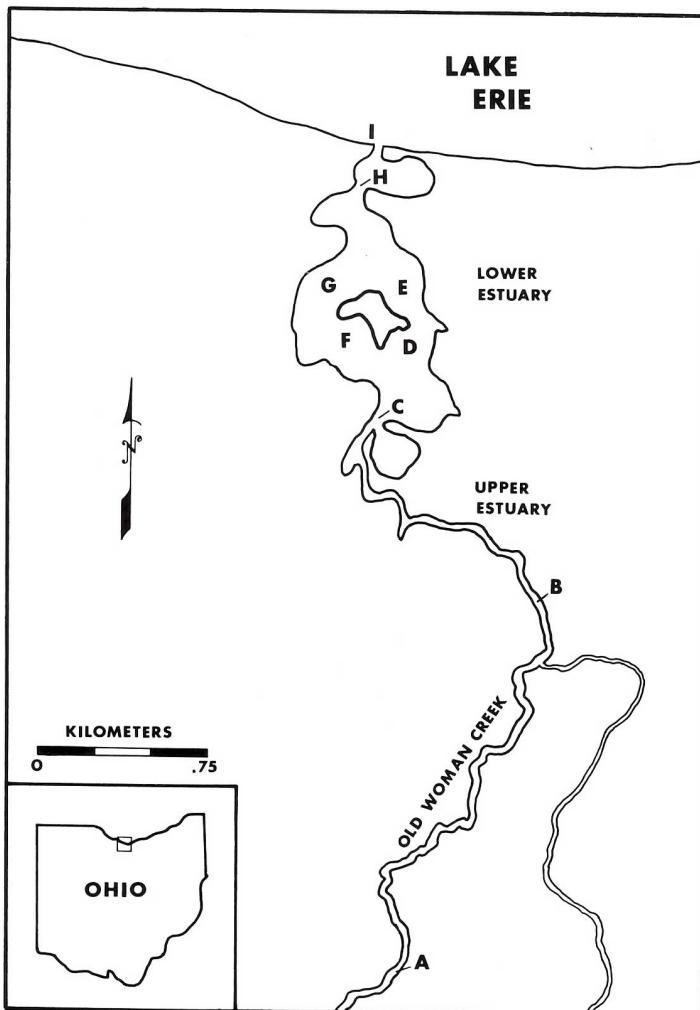


Fig. 1. Location of sampling sites in Old Woman Creek.

Alkalinity, specific conductance, pH, suspended sediments, turbidity, and chloride (Cl), nitrate ( $\text{NO}_3$ ), nitrite ( $\text{NO}_2$ ), orthophosphate ( $\text{PO}_4$ ), silicon (Si), and sulfate ( $\text{SO}_4$ ) concentrations were determined using methods outlined in Standard Methods (A.P.H.A., 1975). Ammonia ( $\text{NH}_3$ ) concentration was determined using the procedure described by ZADOROJNY et al. (1973). Iron (Fe), manganese (Mn), calcium (Ca), magnesium (Mg), copper (Cu), and zinc (Zn) concentrations were determined by atomic absorption while sodium (Na) and potassium (K) concentrations were determined by atomic emission, both on a IL451 AA/AE Spectrophotometer. Correlation coefficients (SNEDECOR & COCHRAN, 1980) of mean chemical values with turbidity values for the 3 storm events were determined for all sampling sites.

Outflow/inflow (O/I) ratios of chemical concentrations were used as estimates of the estuary's relative effectiveness to modify waters passing through it. O/I ratios for the upper, lower, and entire estuary were determined as the ratio of chemical concentrations at site C to site B, site H to site C, and site H to site B respectively (see Fig. 1). If the estuary had no effect on the chemical concentration of the waters, a value of 1.0 resulted. Removal from or additions to the chemical concentrations of the waters resulted in values less than or greater than 1.0 respectively. O/I ratios were calculated using mean chemical concentrations for each spring storm. The October storm event was not included for analysis of O/I ratios because the closing of the creek mouth during this time resulted in no visible interchange of water between the estuary and the lake.

## Results

The range of values observed for chemical parameters at inlet and outlet sampling sites within the upper and lower estuary (Table 1) were very similar to previously reported values for OWC estuary and other Lake Erie wetlands (see O.D.N.R., 1981; KRIEGER, 1984; HEATH, 1986; FRIZADO et al., 1986; HERDENDORF, 1987). Complete profiles of chemical parameters at all sites during the study period are presented in, and discussed by, KLARER (1988).

Chemical parameters displayed three distinct relationships with turbidity throughout the study (Table 2). PO<sub>4</sub>, NH<sub>3</sub>, K, Fe, Cu, and Zn concentrations exhibited positive correlations ( $P \leq 0.05$ ) with turbidity at all, or almost all, sampling sites. Si, NO<sub>2</sub>, and NO<sub>3</sub> concentrations exhibited positive correlations ( $P \leq 0.05$ ) with turbidity only at isolated sites. Si, NO<sub>2</sub>, and NO<sub>3</sub> con-

Table 1. Chemical profile of water at selected sites in the upper and lower estuary. Data are the lowest and highest values observed over all sampling dates. Refer to Fig. 1 for location of sampling sites.

Chemical Parameter	Sampling Site			
	B	C	H	
Turbidity (NTU)	13	-310	28	-210
Conductivity ( $\mu\text{mhos}/\text{cm}$ )	220	-617	239	-524
pH	7.5	- 8.2	7.4	- 8.1
Alkalinity (mg CaCO <sub>3</sub> /l)	67	-160	74	-128
Orthophosphate ( $\mu\text{g/l}$ )	6	-283	3	-104
Silica (mg/l)	1.3	-11.7	0.03	- 9.8
Nitrite (mg/l)	0.8	-12.4	0.1	-10.1
Nitrate (mg/l)	0.3	-180.0	1.0	-212.0
Ammonia (mg/l)	0.2	- 0.3	0.02	- 2.1
Chloride (mg/l)	19.9	-46.4	23.0	-44.3
Sulfate (mg/l)	32	- 76	35	- 66
Calcium (mg/l)	14.6	-62.0	24.2	-63.9
Magnesium (mg/l)	8.6	-22.1	8.9	-21.3
Potassium (mg/l)	3.0	-26.4	3.5	-12.7
Sodium (mg/l)	14.3	-36.2	15.2	-28.0
Iron (mg/l)	0.6	-33.6	1.5	-11.4
Copper (mg/l)	0.002	- 0.04	0.001	- 0.01
Manganese (mg/l)	0.04	- 0.3	0.006	- 0.2
Zinc (mg/l)	0.01	- 0.08	0.002	- 0.06

Table 2. Correlation coefficients of chemical parameters with turbidity at sampling sites in Old Woman Creek. Refer to Fig. 1 for location of sampling sites.

Chemical Parameter	Sampling Sites								
	A	B	C	D	E	F	G	H	I
Silica	.10	.15	.28	.18	.42	.54**	.42	.61**	.39
Nitrate	.49*	.33	.12	.48*	.24	.40	.22	.55**	.31
Nitrite	.43*	.37	.07	.31	.10	.21	.08	.24	.34
Orthophosphate	.46*	.24	.69**	.73**	.61**	.70**	.63**	.76**	.18
Potassium	.88**	.78**	.79**	.80**	.73**	.78**	.67**	.79**	.80**
Ammonia	.65**	.56**	.42**	.71**	.53**	-.07**	.64**	.82**	.56**
Iron	.91**	.93**	.97**	.85**	.83**	.83**	.83**	.81**	.90**
Copper	.82**	.93**	.91**	.72**	.55**	.67**	.70**	.70**	.63**
Zinc	.77**	.91**	.94**	.73**	.51**	.71**	.71**	.64**	.65**
Calcium	-.72**	-.74**	-.60**	-.41*	-.42*	-.39	-.51*	-.28	-.06
Magnesium	-.60**	-.60**	-.64**	-.38	-.46*	-.42	-.49*	-.13	.40
Alkalinity	-.64**	-.51**	-.60**	-.60**	-.57**	-.46*	-.58**	-.38*	.34
Sodium	-.26	-.26	-.12	-.02	-.15	-.10	-.28	-.08	.35
Chloride	-.42	-.40	-.32	-.15	-.33	-.36	-.42	-.47*	-.45
Sulfate	-.44*	-.53**	.06	.17	.09	.16	.03	.23	.23
pH	-.48*	-.27	-.60**	-.68**	-.58**	-.56**	-.63**	-.67**	-.20
Manganese	.75**	.52**	.05	.00	-.24	-.03	-.05	.15	.52*
Conductivity	-.25	-.30	-.18	-.01	-.18	-.14	-.23	-.03	.38

\* , \*\* indicate significance at the 95 and 99 % probability level respectively.

Table 3. Outflow/Inflow ratios of mean, post-storm chemical concentrations for the upper, lower and entire estuary. Methods for determining ratios and designation of sites in the upper and lower estuary are described in the text.

Chemical Parameter	April Storm			May Storm		
	Upper	Lower	Entire	Upper	Lower	Entire
Turbidity	1.04	0.64	0.67	0.89	0.92	0.82
Conductivity	1.03	0.92	0.95	0.96	0.74	0.71
Orthophosphate	1.36	0.36	0.49	0.61	0.33	0.20
Silica	1.00	0.50	0.50	0.82	0.34	0.28
Nitrate	0.99	0.66	0.65	0.84	0.34	0.29
Nitrite	1.09	1.00	1.09	1.40	0.50	0.70
Ammonia	0.87	1.36	1.18	1.52	0.53	0.81
Chloride	1.02	0.85	0.92	—	—	—
Sulfate	0.97	0.90	0.87	0.79	0.62	0.49
Calcium	0.99	0.99	0.98	0.91	0.80	0.73
Magnesium	0.96	1.00	0.96	0.99	0.75	0.74
Sodium	1.00	0.95	0.95	0.85	0.79	0.67
Potassium	0.96	0.70	0.67	0.85	0.65	0.55
Iron	1.02	0.64	0.65	0.70	0.66	0.46
Copper	0.74	0.64	0.47	0.70	0.71	0.50
Manganese	1.06	1.26	1.34	1.23	0.72	0.88
Zinc	0.72	0.69	0.50	0.73	0.55	0.40

centrations increased following all storm events, but only after the turbidity peak. Ca and Mg concentrations and total alkalinity exhibited negative correlations ( $P \leq 0.05$ ) at all, or almost all, sites. Na, Cl and  $\text{SO}_4$  concentrations, spe-

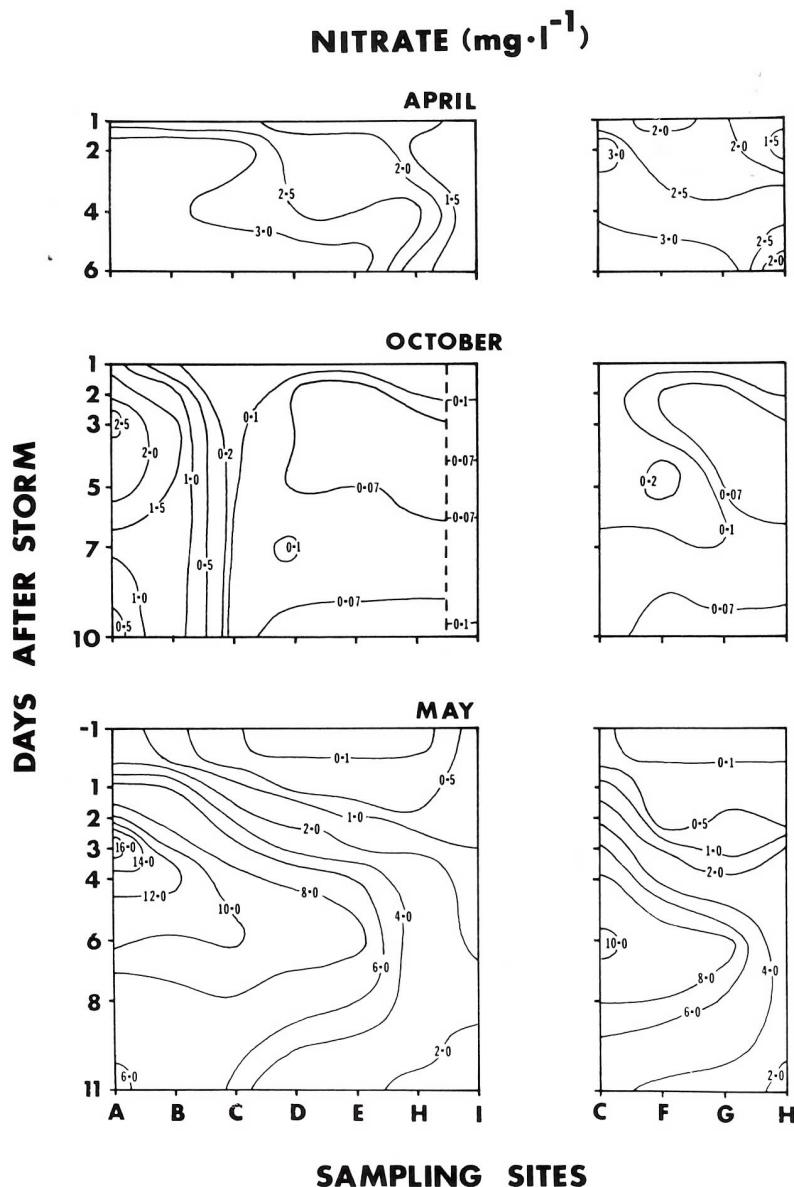


Fig. 2. Profiles of nitrate concentrations in flow for the April and October (1984) and May (1985) storm events. Profiles indicating sites D and E and sites F and G represent flow to the east and west of the island in the lower estuary respectively. The dashed line indicates the point at which flow ceased due to closure of the creek mouth.

cific conductance, and pH exhibited negative correlations ( $P \leq 0.05$ ) with turbidity only at isolated sites.

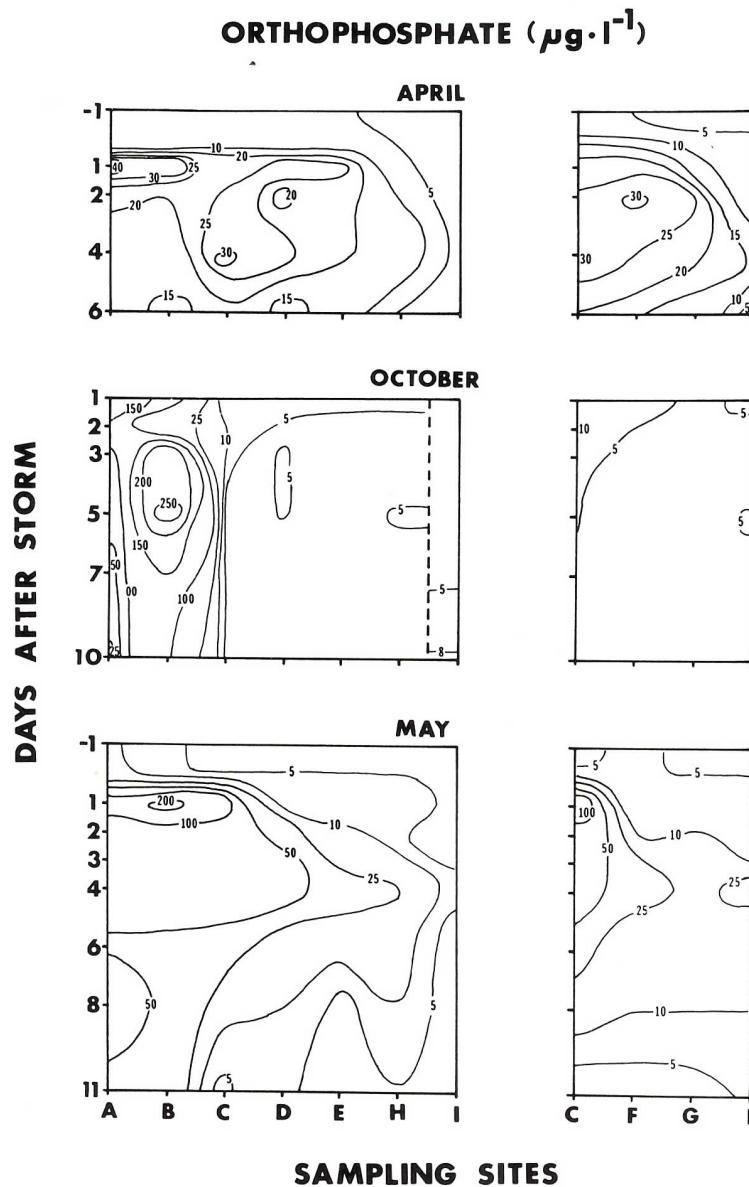


Fig. 3. Profiles of orthophosphate concentrations in flow for the April and October (1984) and May (1985) storm events. Profiles indicating sites D and E and sites F and G represent flow to the east and west of the island in the lower estuary respectively. The dashed line indicates the point at which flow ceased due to closure of the creek mouth.

O/I ratios of mean chemical concentrations for the upper, lower and entire estuary are presented in Table 3. For calculation of O/I ratios, it was as-

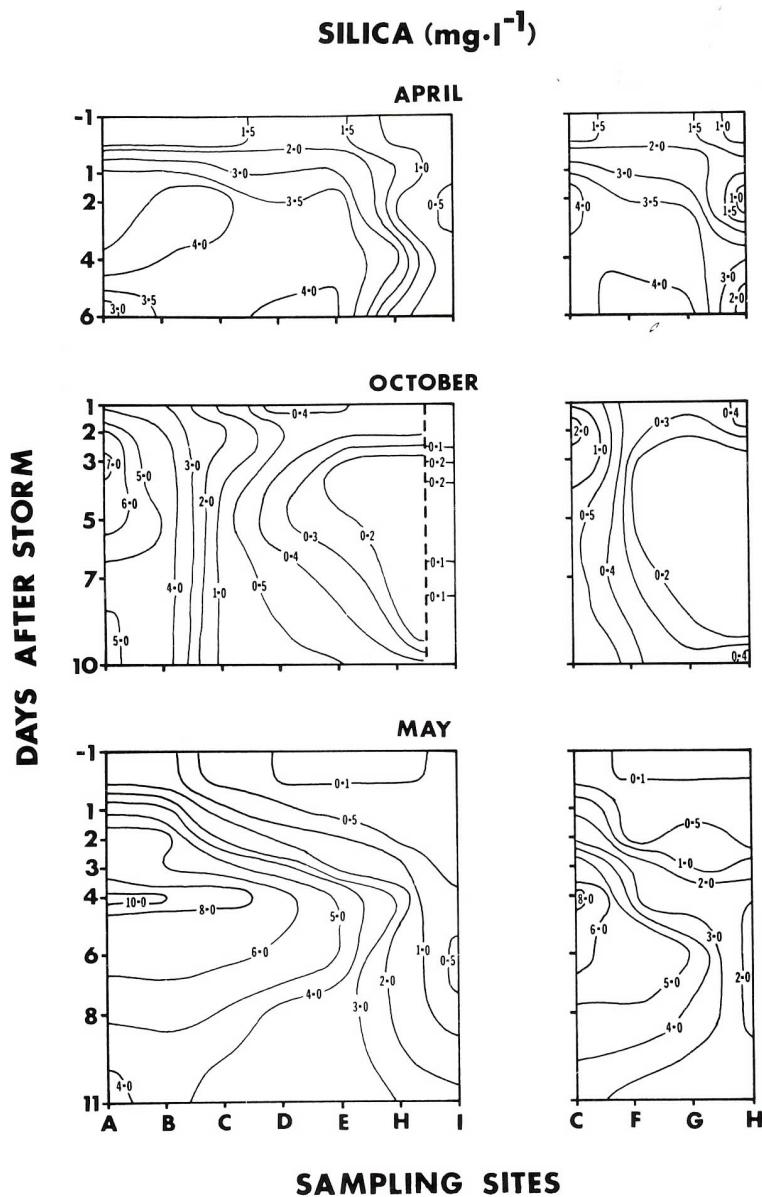


Fig. 4. Profiles of silica concentrations in flow for the April and October (1984) and May (1985) storm events. Profiles indicating sites D and E and sites F and G represent flow to the east and west of the island in the lower estuary respectively. The dashed line indicates the point at which flow ceased due to closure of the creek mouth.

sumed that 1) all storm-water flow passed through OWC estuary into Lake Erie, 2) storm-water flow was equally sampled at all sites, and 3) storm-water flow through the estuary was unidirectional. Turbidity,  $\text{NO}_3$ ,  $\text{PO}_4$ , Si, K, Fe, Cu, and Zn were substantially reduced in the estuary, particularly during the May storm event. Concentrations of the biologically-important nutrients,  $\text{NO}_3$ ,  $\text{PO}_4$ , and Si, exhibited marked increases at upstream sites immediately following all storm events (Figs. 2–4). Thereafter, outflow concentrations of  $\text{NO}_3$ ,  $\text{PO}_4$ , and Si were 35 to 71 (Fig. 2), 51 to 80 (Fig. 3), and 50 to 72 (Fig. 4) % less, respectively, than inflow concentrations. Outflow concentrations of Fe, Cu, Mn, and Zn were 35 to 54, 50 to 53, 12 (May storm event), and 50 to 60 % less, respectively, than inflow concentrations. During the April storm event, outflow concentrations of  $\text{NO}_2$ ,  $\text{NH}_3$ , and Mn were greater than their respective inflow concentrations. Comparison of O/I ratios also showed the greatest reduction of all chemical parameters occurred within the lower reaches of the estuary.

### Discussion

High correlations of storm-water runoff with suspended sediments have been observed in selected rivers of northwestern Ohio (BAKER, 1984, 1985; BAKER et al., 1985). While not routinely determined in this study, selected samples were analyzed for suspended sediments to determine the relationship between sediment concentrations and turbidity. The observed high correlation ( $r = 0.97$ , 40 D.F.) indicated that turbidity was a good indicator of storm-water flow in OWC estuary. KRIEGER (1984) also reported a significant relationship between suspended sediments and turbidity in OWC estuary.

The impact of storm-water inflow on the chemistry of receiving streams is not just a simple process of dilution. If a chemical's input is constant, regardless of the receiving stream's flow rate, the concentration would be inversely related with inflow (GOLTERMAN, 1975). Initial surface runoff, caused by rainfall exceeding the infiltration capacity of the watershed, culminates in maximum flow rates within receiving streams (CLEAVES et al., 1970). If a chemical is bound to sediments or is insoluble, the concentration would increase with increasing surface runoff. Input through storm interflow results from the discharge of water by percolation through soils. If a chemical is soluble, its concentration would increase with increasing interflow.

BAKER (1984) noted that the highest suspended sediment loads are frequently recorded immediately prior to maximum flow rates. The negative correlation of Ca and Mg concentrations and total alkalinity with turbidity at all sites indicated that these parameters were diluted by storm water in OWC estuary. Previous researchers (WAGNER et al., 1976; BOYDEN et al., 1978; PEVERLY, 1982; MANNY & OWENS, 1983) also attributed decreases in Ca, Mg,

and alkalinity to storm-water dilution. Na, Cl, and SO<sub>4</sub> concentrations and specific conductance were negatively correlated with turbidity, although correlations were not significant at all sites. Values of pH also were negatively correlated with turbidity. This occurrence was attributed to acidic rain within the Great Lakes basin and dilution by surface runoff (A.C.S. Ltd., 1977; MANNY & OWENS, 1983).

The significant, positive correlations of PO<sub>4</sub>, NH<sub>3</sub>, Fe, Cu, and Zn concentrations with turbidity indicated that these compounds entered the estuary in the sediment fraction and surface runoff during storm events. Other researchers also have reported increases in NH<sub>3</sub> (COOTE & DEHAAN, 1978), PO<sub>4</sub> (BAKER, 1984), and various trace metals (WILLIAMSON, 1985) with sediment loading following storm events.

Concentrations of K were significantly correlated with turbidity at all sites. Previous researchers, however, reported that K concentrations either decreased (WAGNER et al., 1976) or remained fairly constant (JOHNSON et al., 1969; MANNY & OWENS, 1983) during storm flow periods. Since these researchers analyzed streams draining forested rather than row-crop watersheds, K inputs during storm inflows may be influenced by land-use practices within the watershed. COOTE & DEHAAN (1978), noting that K concentrations in agricultural runoff were correlated with the number of rural residences and the clay content of the soil, suggested that septic tank leachate was a major source of K. Data from the present study does not support this contention. If septic tanks were a major input source, then the greatest K concentrations would occur during storm events after long dry periods. The greatest increase in K and NH<sub>3</sub> concentrations in OWC estuary occurred immediately after the May storm event, which closely followed planting of row crops in the drainage basin. Since both K and NH<sub>3</sub> are routinely applied in agricultural fertilizers during spring planting (Erie County Extension Service; per. comm.), the high concentrations observed suggest that fertilizers were a major source of these compounds in the watershed.

Concentrations of Si, NO<sub>2</sub>, and NO<sub>3</sub> increased following all storm events, but only after the turbidity peak. This delayed increase might be explained by interflow water passing through near-surface soil and "picking up" these compounds for subsequent transport to OWC. BAKER (1984) attributed NO<sub>3</sub> enrichment in other Lake Erie tributaries to storm interflow.

The primary intent of this study was to determine the effectiveness of OWC estuary in ameliorating the quality of storm water. To effectively determine chemical flux within the estuary, the entire hydrologic cycle, including inflow and outflow rates, evapotranspiration, gas exchange, and subsurface flows, should be quantified. Since quantification of the hydrologic cycle within the estuary was beyond the scope of this study, comparisons of chemical concentrations in inflow and outflow waters were used as estimates

of amelioration processes. KLOPATEK (1978) compared inflow and outflow concentrations to the flow of Cl, a biologically conservative element, to measure a wetland's effectiveness in regulating nutrient concentrations. In OWC estuary, all chemical O/I ratios after correction to Cl were not significantly different from uncorrected ratios (KLARER, 1988).

Retention rates of biologically-important nutrients estimated for the estuary were similar to those observed in other wetlands in the Laurentian Great Lakes region (see FETTER et al., 1978; KLOPATEK, 1978; MACCRIMMON, 1980; RICHARDS & BAKER, 1985). Concentrations of PO<sub>4</sub> at the creek mouth varied from 51% to 80% of the inflow concentration. Similar retention rates were also observed for NO<sub>3</sub> (35 to 71%) and Si (50% to 72%). HEATH (1986) determined that water leaving OWC estuary (site H) contained 77% less soluble, reactive phosphorus than it contained upon entering (site B).

The general physical sedimentation, geochemical, and biological reduction processes appear to be similar between OWC estuary and brackish-water estuaries. Although the estuary acts as a net sink for sediments (BUCHANAN, 1982), the amount trapped varied greatly among individual storms. Brackish-water estuaries often contain a specific area of "turbidity maximum" where geochemical amelioration is most effective (SHARP et al., 1984). Such a turbidity maximum does not exist within OWC estuary. Rather, the lower estuary may serve as a generalized area of turbidity maximum since its great surface area to depth ratio allows moderate winds to easily resuspend bottom sediments.

Although the presence of geochemical processes was difficult to verify in OWC estuary, the data presented here suggests that such processes are occurring. The decline in Cu, Zn, and Fe when compared to the decline in turbidity was greater than would be expected from sedimentation alone. Under pre-storm conditions, interstitial waters and sediments in the estuary contain greater concentrations of metals and act as a source for overlying waters (FRIZADO et al., 1986). During storm events, however, these areas may act as sinks for metals since concentrations in storm waters are greater than that in sediments and interstitial waters. ANGINO et al. (1974) suggested that strong correlations of Zn with Fe and/or Mn may indicate a coprecipitation of this element with Fe and/or Mn oxides. The significant correlations of Zn with Fe at all but one site suggested that Zn may be co-precipitated with Fe oxides (KLARER, 1988). The decline in the relative percentage of dissolved to total Fe from 20% in waters of the creek proper to 6% in waters at the creek mouth also suggested the occurrence of geochemical processes within the estuary.

The decline of PO<sub>4</sub>, NO<sub>3</sub>, and Si when compared to the decline of Fe, Cu and Zn was much greater than would be expected from sedimentation and geochemical processes alone. However, high uptake rates of these biologically-important nutrients would be expected in highly-productive, shallow-water habitats such as the lower reaches of OWC estuary. HEATH (1986) attributed

the decline of PO<sub>4</sub>, concentrations in OWC estuary to biological uptake. SHARP et al. (1984) noted that the removal of dissolved chemicals was most evident in the lower reaches of estuaries, attributing their decline to increased primary productivity.

OWC estuary plays an important role in ameliorating the chemistry of storm water passing through it, acting as both a sediment and a chemical sink. There are indications that the estuary also serves as a source for selected chemicals in some portions of the year. The data presented here indicates that OWC estuary acts as a chemical processor and filter and, therefore, is functionally similar to its brackish-water counterpart. Chemical processing and cycling within this, and other freshwater estuaries of the Laurentian Great Lakes system, however, are poorly understood and worthy of further research.

### Summary

The role of Old Woman Creek estuary, Lake Erie (U.S.A.) in ameliorating the quality of storm-water flow was investigated. Water samples were collected at selected intervals immediately following two spring storms and an autumn storm. Using changes in turbidity as estimates of storm-water flow rates, chemical parameters followed three distinct patterns. Significant, negative correlations of calcium and magnesium concentrations and total alkalinity with turbidity indicated that these parameters were diluted by storm-water runoff. Significant, positive correlations of orthophosphate, iron, copper, zinc, potassium, and ammonia concentrations with turbidity indicated that these parameters were associated with sediment input and surface runoff. Silica, nitrate, and nitrite concentrations increased following storm events but much later than the turbidity peak, indicating that these parameters were associated with storm interflow. Outflow/inflow ratios of chemical concentrations, used as estimates of the estuary's relative effectiveness to modify waters passing through it, indicated that 12 to 60 % of the metals and 35 to 80 % of the biologically-important nutrients were retained within the estuary. Amelioration of storm-water quality was attributed to sedimentation, biological uptake, and geochemical processes. Old Woman Creek estuary acted as a chemical processor and filter of storm-water flow and, therefore, demonstrates functional similarity to brackish-water estuaries.

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