Transport of Particulate Pollutants in Lake Erie Tributaries:

The Role of Particle Size and Size-Specific Chemistry

Final Report for LEPF Grant 97-29

Submitted by:

R. Peter Richards and David B. Baker

Water Quality Laboratory
Heidelberg College
310 E. Market Street
Tiffin, OH 44883

April 26, 2000

INTRODUCTION

Sediment is a major pollutant in its own right, as the costs associated with dredging of harbors and shipping channels demonstrate. Sediment is also the most important carrier of many chemical pollutants, including phosphorus, the limiting nutrient for Lake Erie; many metals; and toxic organics such as PCBs and DDT (IJC, 1978, 1980). Most sediment which reaches Lake Erie is of non-point origin, and is transported through the tributaries primarily during periods of high flow following storms (Baker, 1988). The transport properties and many chemical properties of sediment in transport are strongly related to sediment mineralogy and particle size, which are influenced by many factors including the source of the sediment and the flow rate in the river (Culbertson, 1977).

Pre-existing storm runoff data, gathered for other purposes by the Water Quality Laboratory, showed that the suspended sediment is generally richer in phosphorus on the falling limb of the storm runoff hydrograph, as the flood stage decreases, than on the rising limb, and that it is richer in phosphorus in winter storms than in summer storms (Figure 1). We also showed that the difference related to hydrograph position is consistent in direction for four different Lake Erie tributaries, and that there are additional overall differences from river to river in phosphorus richness of suspended sediment (Figure 2).

We hypothesized that these differences are due to, or at least strongly influenced by, particle size effects on chemistry. We suggested that differences between rising and falling limbs of hydrographs might be due to differences in grain size distribution, with a greater percentage of clay-sized particles on the falling limb, coupled with preferential adsorption of phosphorus onto the clay particles. Differences between seasons might result from lower concentrations in winter storm runoff than in summer storm runoff. If lower sediment concentrations correspond with smaller particles on average, then the difference could be due to particle size differences.

The research carried out in this project was designed to gather information on chemical composition and particle size distribution of a number of samples from Lake Erie tributaries, and to use the resulting data to begin to assess these relationships.

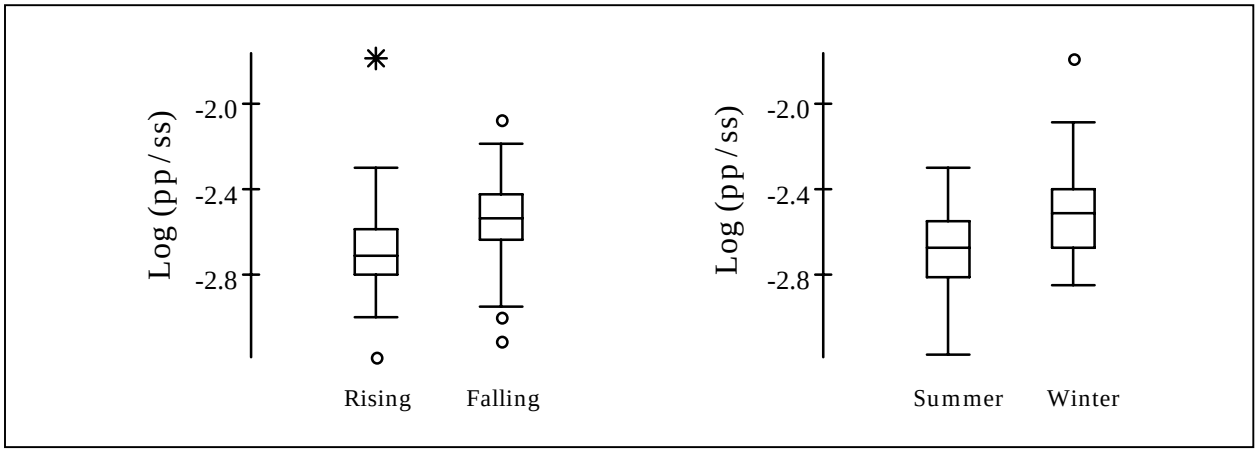

Figure 1. Box plots showing the distribution of phosphorus/sediment ratios for the Maumee River, 1989 through 1992. "Winter" represents the months December, January, and February; "Summer" represents April through July. The box plots show that there is more phosphorus per unit of sediment on the falling limb of the hydrograph than on the rising limb, and that winter storms carry sediment richer in phosphorus than summer storms.

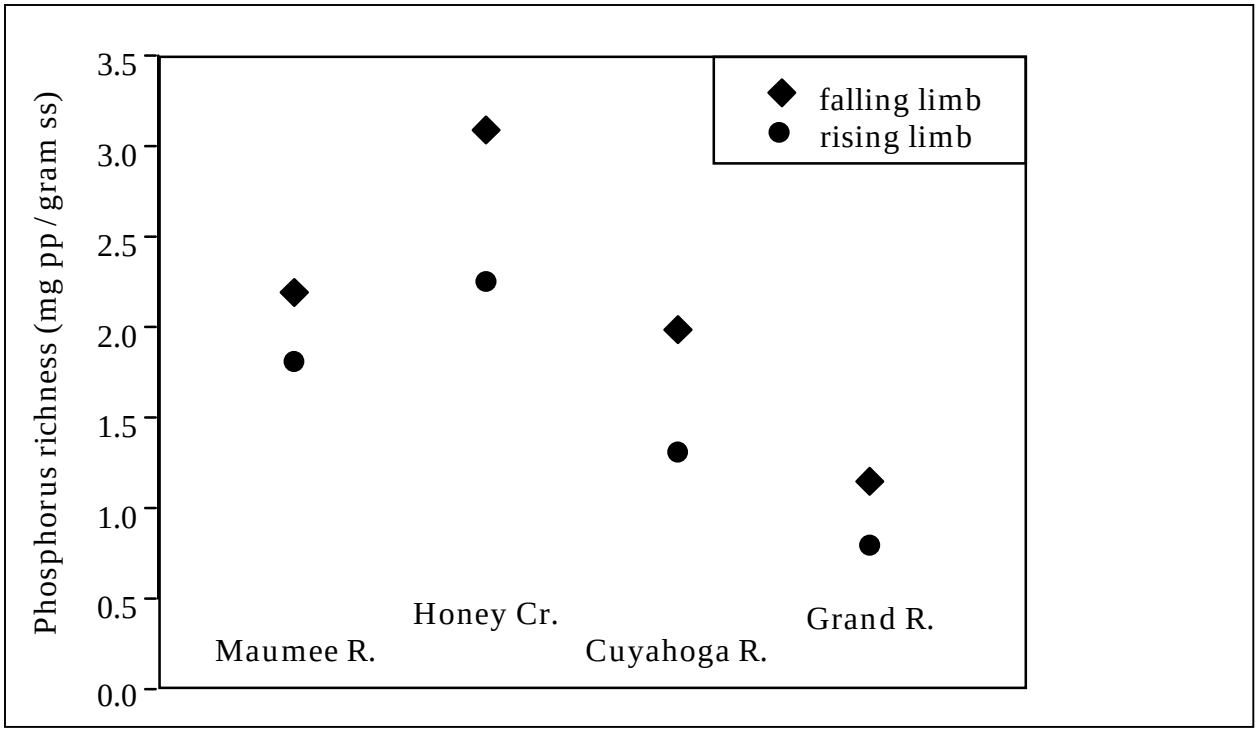

Figure 2. Phosphorus richness of suspended sediment collected on the rising and falling phases of storm runoff in four different watersheds. Data are median richness values for storm runoff samples collected from 1989 through 1992. Data were classified as rising limb or falling limb based on whether the flow for current observation was less than or greater than the preceding observation. Because of possible reversals within limbs, this is a screening-level separation technique.

PROJECT GOAL AND OBJECTIVES

The goal of the project was to seek a detailed understanding of the role played by sediment particle size in the transport of sediment-bound (particulate) pollutants through Lake Erie tributaries. The specific objectives of the project were to:

1. Characterize the particle size distribution of suspended sediment in samples collected during storm runoff.

2. Evaluate differences in aggregate and primary particle size distributions as a function of position in the storm runoff hydrograph, magnitude of the runoff event, season of the year, and basin land use and geology.

3. Characterize particulate pollutant content of suspended solids in storm runoff samples with respect to phosphorus, organic nitrogen, organic carbon, and the metals iron, aluminum, copper, lead, cadmiuum, and zinc.

4. Divide selected samples into five particle size classes within the silt-clay size range and characterize the particle size distribution and pollutant content of each size class.

5. Evaluate the importance of particle size distributions and size-specific chemistries for understanding the fate and transport of sediment and associated pollutants in the tributaries, bays, and nearshore areas of Lake Erie.

METHODS

Sampling and Chemical Analysis

Samples were collected from a number of storm runoff events in 199x – 199x at our autosampler-equipped water quality stations located at U.S. Geological Survey gages at Waterville (Maumee R.), Fremont (Sandusky R.), Tiffin (Rock Cr.), Independence (Cuyahoga R.), and Painesville (Grand R.), with up to 12 samples being collected over the duration of the storm runoff period. In addition, a few samples were obtained for reconaissance purposes from the Scioto River at Chillicothe and the Great Miami below Miamisburg. A major subset of the samples were characterized for the pollutants listed in objective 3 above, using standard methods

of automated chemical analysis (e.g Greenberg *et al.*, 1992) already in use in our lab. Particulate pollutant concentrations were calculated as the difference between the "total" analysis and the "dissolved" analysis for each parameter.

Particle Size Analysis

The sediment particle size distribution of each sample was measured with a Malvern Mastersizer Plus laser particle size analyzer, which resolved the distribution into 92 discrete size classes. Sediment often forms aggregates of individual "primary" particles, and the transport properties are related to the aggregate size, but the chemical properties are related to the primary particles (e.g. Tye *et al.*, 1996). For this reason, particle size distributions were measured in samples as collected, and also following sonication for six minutes to disaggregate flocculated particles into primary particles.

Water Elutriation

Selected samples were split into five size classes, using water elutriation (Walling and Woodward, 1993), and particle size and chemical analyses were performed on each size class as well as on an unelutriated aliquot.

RESULTS AND DISCUSSION

Data

Particle size analyses were completed for 372 samples; most samples were analyzed twice, once before and once after sonication to disaggregate floculated particles. A total of 726 particle size analyses were included in the data base. A number of additional particle size analyses were carried out for quality control purposes, for technique development, and for other purposes. Chemical analyses were performed for nearly all samples. The distribution of samples among stations is shown in Table 1, and the number of analyses for each parameter is shown later in Table 3.

Table 1. Number of samples analyzed, by station

Station	Number of Samples
Cuyahoga	75
Grand	54

Maumee	128
Great Miami	6
Rock Creek	258
Sandusky	196
Scioto	8

The Malvern particle size analyzer reports the percent of the sample in each of 92 different size ranges, which were set up as fractions of the standard phi scale for sediments. However, the resulting data are overly complex, and for reporting purposes these 92 classes were collapsed into seven broader classes, shown in Table 2.

Table 2. Particle size classes

Class	Diameter (microns)
Fine clay	<1
Clay	1-4
Fine silt	4-16
Coarse silt	16-63
Fine sand	63-250
Medium to coarse sand	250-1000

The data are included with this report as an Excel file on CD-ROM. Each data record consists of the following elements:

- Sediment Sample ID. The identifier assigned to the sample by the operator who performed the grain size analyses. This ID contains information which usually identifies the station, the date, and the sample code. For the latter, an SPT number indicates that the sample was collecte specifically for the project and was intended for the full set of chemical analyses, though these were not always completed due to shortage of sample or other problems. Other numbers usually refer to the bottle set in the autosampler which collected the sample. These samples were included in the particle size analysis program on an ad hoc basis, and did not receive a full program of chemical analysis. This Sediment Sample ID is included for completeness; it will not be needed by most future users of this data.

- Station name, date and time of the sample.
- Chemical Sample Code. Used to track the sample in the analytical laboratory. Included for completeness; it will not be needed by most future users of this data.
- Partical Size Record Number. Used to identify the results of the particle size analysis. Included for completeness; it will not be needed by most future users of this data.
- Sample Type. Normal or sonicated. With few exceptions, each sample was analyzed for particle size before and after sonication.
- Partical Size Data. Included are the 10th percentile size, the median size, and the 90th percentile size, in microns, and the percent of the sample falling into the sizes shown in Table 2.
- Chemical Parameters. The parameters included in the file are listed in Table 3. See methods section for further information on the chemical parameters.

Table 3. Chemical parameters and the number of analyses for each parameter. For conciseness, a short name starting with "T, D, P" refers to total, dissolved, and particulate components of the parameter listed under the full name.

Short Name	Full Name	Number of Analyses
SS	Suspended Solids	711
TP	Total Phosphorus	721
TSP	Total Soluble Phosphorus	546
PP	Particulate Phosphorus	546
TKN	Total Kjeldahl Nitrogen	711
S TKN	Soluble Kjeldahl Nitrogen	546
P TKN	Particulate Kjeldahl Nitrogen	546
T,D,P OC	Total (etc) Organic Carbon	546, 546, 542
T,D,P, Fe	Total (etc) Iron	593, 544, 490
T,D,P Al	Total (etc) Aluminum	597, 544, 494
T,D,P Cu	Total (etc) Copper	591, 544, 486
T,D,P Pb	Total (etc) Lead	593, 544, 488
T,D,P Cd	Total (etc) Cadmium	595, 544, 486
T,D,P Zn	Total (etc) Zinc	593, 544, 488

Findings

Objective 1: Particle size distributions

Particle size distributions are typically bimodal, but the particle size corresponding to the two modes varies from sample to sample. Sonication has a strong effect on the particle size distribution, shifting the distribution toward smaller particle sizes. This indicates that many particles are aggregates of smaller particles. These aggregates change size and shape with storage, and even during transport in the river. Thus distributions of particle size made without sonication to disperse aggregates are of uncertain value.

Objective 2: Causes of differences in particle size distributions

Position in the Hydrograph

Contrary to our initial expectations, the particle size distribution of sonicated samples did not change substantially with position in the storm runoff hydrograph. There is reason to suspect that the particle size distributions of the actual particles in transit in storm runoff change with position in the hydrograph, but because these size distributions are not stable even under brief storage, none of our data allows us to evaluate this.

The period of this project was a dry one, and we did not have very many ideal storms to sample. Consequently, we did not obtain enough data to adequately evaluate the relationship of particle size to magnitude of the runoff event.

Seasonal effects

Particle size and chemical parameters were examined for differences as a function of season, using sonicated samples only. Samples taken in January, February, and March were considered to be winter samples, while samples taken in May, June, July, and August were considered to be summer samples. No samples were obtained in other months. The number of samples taken in each month is shown in Table 4.

Table 4. Number of sonicated samples by month and station

Station	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
Maumee	16	5	5		8	22		8				
Sandusky	15	6	10		8	49	3	6				
Rock	18	6	7		11	48	28	4				
Cuyahoga	12	2	1		11	6	4					
Grand	16	1					8					

While many significant differences appear to exist between winter and summer samples, they are sometimes artifacts that reflect real differences between stations, which were not sampled with the same frequency in a given season. Analysis of variance (ANOVA) with interactions, using season and station as the independent variables, was used to cancel out the station effect and allow the pure seasonal effect to be examined. The station effect was highly significant in nearly every analysis, indicating that important differences between stations exist. These differences are discussed later.

The seasonal effects are shown in Table 5. Analyses were done for the grain size parameters, the suspended solids concentration, and the various ratios of chemical parameters to sediment concentration – the sediment "richness" for each chemical parameter. Because one or two extreme values can produce spurious differences or mask real ones, and because the ratios generally were not normally distributed as assumed, analyses were also done on the ranks of the data. Ranks are not normally distributed, but at least they are symmetrically distributed, and they are not strongly affected by outliers. Using the ranks of the data is a common approach when parametric statistics are applied to non-normal data.

Table 5. Differences between winter and summer values of different parameters.

Parameter	Difference, Values	Difference, Ranks
10th %ile size	None	None
Median size	S>W	S>W
90th %ile size	None	None
% fine clay	W>S	W>S
% coarse clay	S>W	S>W
% fine silt	None	S>W
% coarse silt	None	None
% fine sand	None	None
% med. sand	None	W>S
SS	S>W	None

Parameter Ratios	Difference, Values	Difference, Ranks
PP/SS	None	None
TKN/SS	S>W	S>W
OC/SS	None	W>S
Fe/SS	W>S	W>S
Al/SS	W>S	W>S
Cu/SS	None	None
Pb/SS	None	W>S
Cd/SS	None	W>S
Zn/SS	None	W>S

Median grain size suggests that particles are larger in the summer than in the winter, as does the greater percentage of fine clay in the winter. The greater percentage of coarse clay in the summer is enigmatic. When fine clay and coarse clay are combined, the seasonal effect is not significant. The greater percentage of the coarsest particle size (medium sand) range is not very meaningful, because this percentage is low in all samples and zero in more than 85% of samples. Suspended solids concentrations appear to be greater in summer than in winter – the difference in ranks is in the same direction and nearly statistically significant (p=.057) – however, the difference is not great. The significant differences in sediment chemistry are consistent in the sense that all metal parameters are greater in winter than in summer. TKN is greater in summer than in winter, and may reflect higher productivity in warmer months. Organic carbon is greater in winter than in summer, a finding which appears contrary to that for TKN. The reason for this difference is not clear. In general, these results suggest that an important seasonal difference is that suspended sediments are more mineral in nature in the winter, and more biological in nature in the summer.

Differences between Stations

Particle size distributions are summarized by station in the table below. Generally, the Maumee and Sandusky Rivers and Rock Creek have smaller particle sizes than the Cuyahoga and Grand Rivers. This is seen in the smaller median particle size and the much smaller 90th pecentile particle size. Clay-sized particles make up the majority of the particles in the western rivers, and particle sizes greater than fine silt constitute less than 10% of the particles. In the eastern rivers, silt and sand make up more than half of the particles.

Table 6. Median values for grain size parameters, by river.

Parameter	Maumee	Sandusky	Rock Cr.	Cuyahoga	Grand
10th %ile size (µ)	.27	.28	.29	.30	.28
Median size (µ)	2.02	2.15	1.54	7.53	5.35
90th %ile size (µ)	11.13	13.20	7.67	33.98	26.05
% fine clay	37.78	35.99	40.30	19.41	22.53
% coarse clay	29.16	28.44	31.63	17.06	20.08
% fine silt	25.81	27.24	21.5	35.02	36.19
% coarse silt	5.21	7.48	2.26	24.22	18.31
% fine sand	.08	.22	0	2.66	1.05
% med. sand	0	0	0	0	0

Objective 3: The distributions of the chemical constituents in this study are summarized in Table 7. Box plots of the log of concentration, by river, are shown in Figure 3 on the next pages.

Table 7. Chemical content of sediments, expressed as mg of chemical per gram of sediment.

Parameter	Minimum	Median	Mean	90th percentile	Maximum
PP	0.03	1.29	1.39	2.12	6.04
P TKN	0.00	3.67	4.16	6.33	42.39
POC	0.00	4.22	7.74	22.09	65.72
P Fe	0.34	32.26	35.75	49.44	245.90
P Al	0.00	18.50	21.05	35.94	110.02
P Cu	0.00	0.03	0.04	0.09	0.54
P Pb	0.00	0.03	0.00	0.08	0.42
P Cd	0.00	0.01	0.00	0.02	0.18
P Zn	0.00	0.14	0.15	0.23	1.19

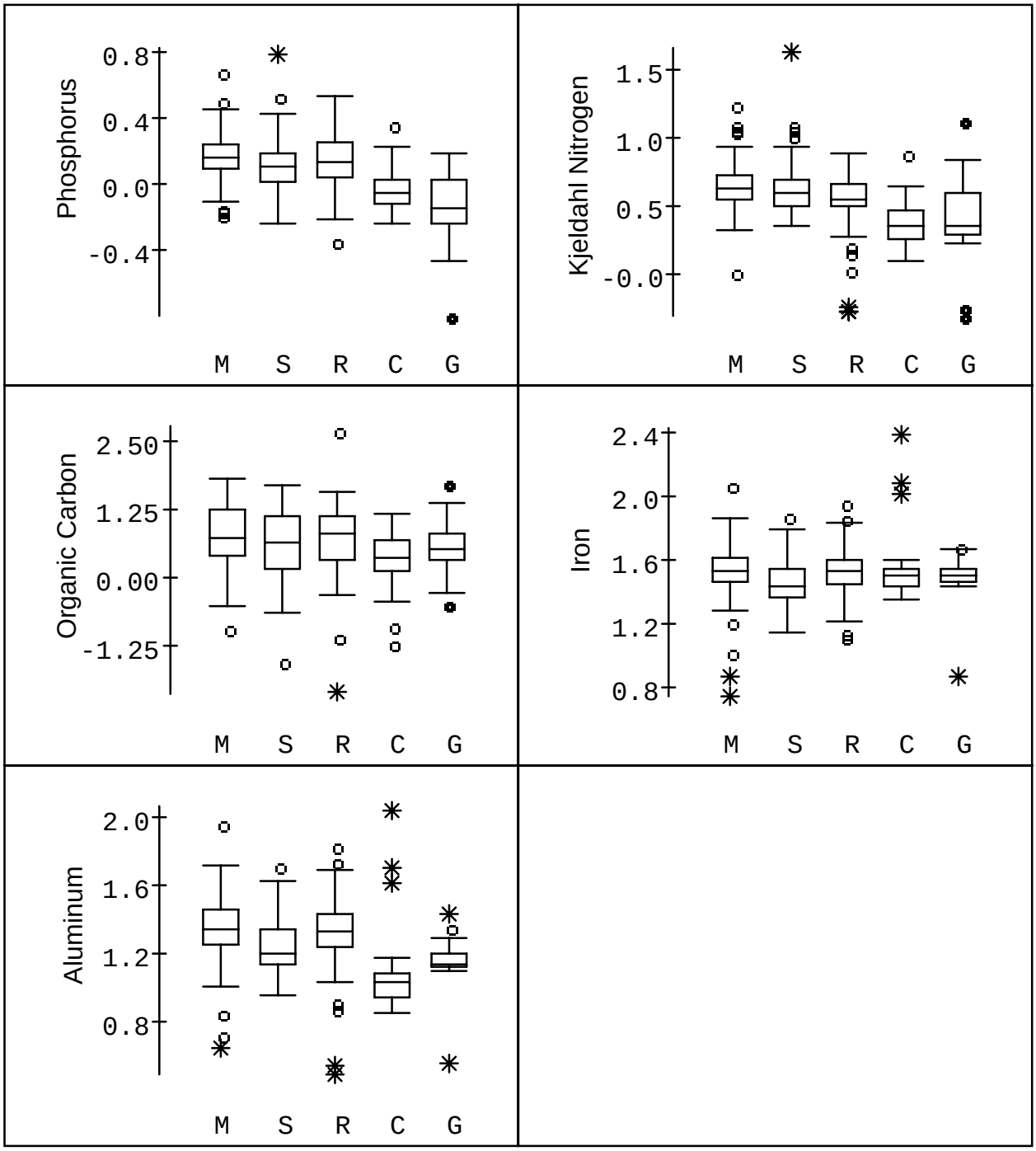

Figure 3. Boxplots of logs of chemical content of sediment, measured in milligrams chemical per gram of sediment. Part a: nutrients and major metals.

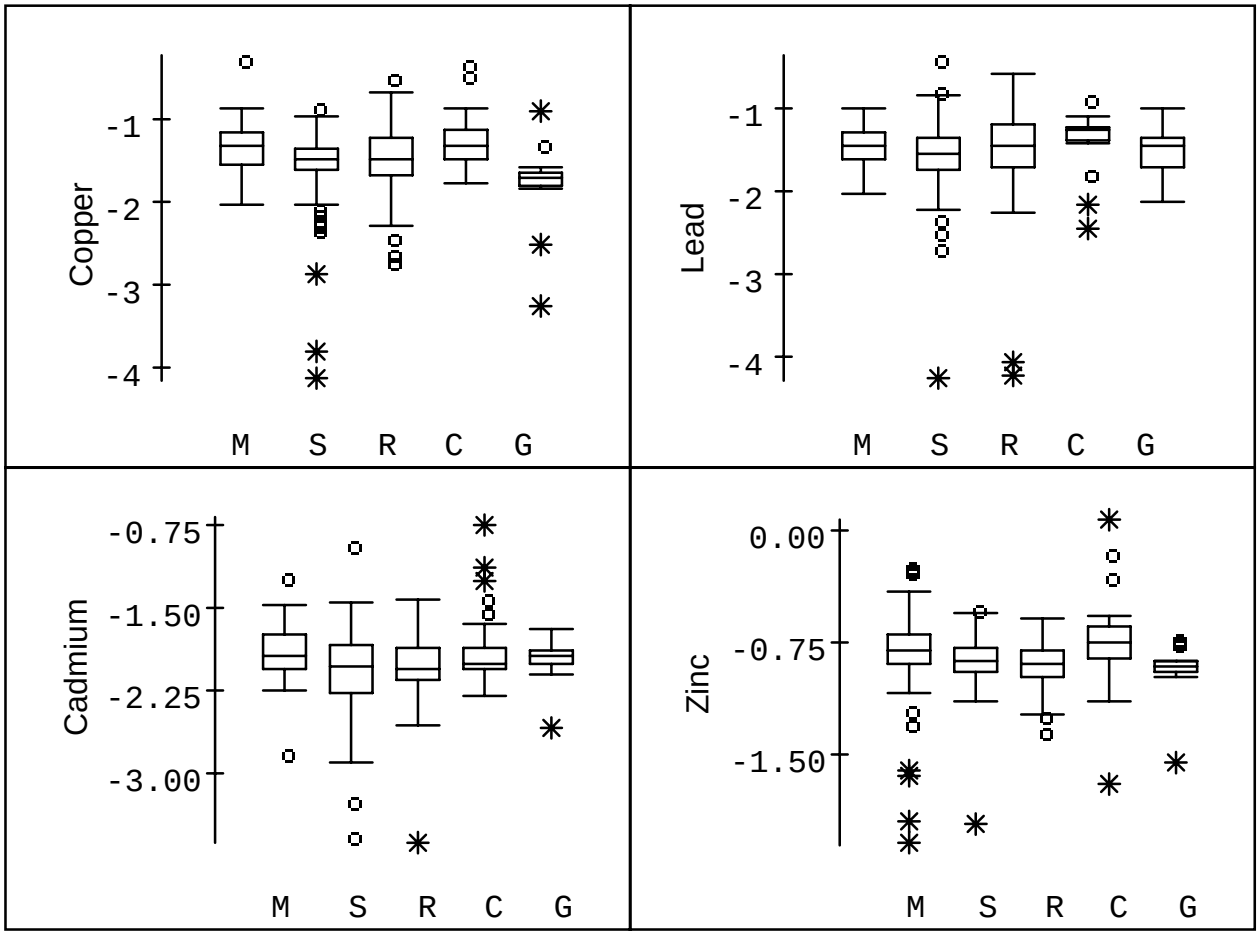

Figure 3, concluded. Boxplots of logs of chemical content of sediment, measured in milligrams chemical per gram of sediment. Part b: trace metals

Objective 4: Water elutriation successfully separated the particles by particle size, as judged by observing settling velocities in each chamber of the elutriation device. However, because of the dynamic nature of sediment floculation, there was considerable overlap in the particle size distributions of each elutriation fraction when the sediment was resuspended and evaluated with the particle size analyzer. After sonication, a substantial portion of each fraction was composed of clay-sized particles, reflecting disaggregation of floculates. This aspect of the project was not very succesful as a result of this problem of floculated sediments. Because there was so much overlap among the size distributions of the various fractions, there was also little difference between their chemistries.

Objective 5: We continue to believe that particle size distributions are important in understanding the transport of sediment and associated pollutants in the tributaries, bays, and nearshore areas of Lake Erie. We have gained a new awareness of the importance of floculation in producing aggregate particles whose behavior is different from primary particles of which they are composed, and from solid particles of comparable size. Floculation is a very complex and dynamic process, and trying to characterize the size distibution of sediment in transport is like trying to hit a moving target. No less an expert on sediment than Willi Lick has told us that he considers it a hopeless task. Techniques other than those available in this project will be needed to make progress in this area.

REFERENCES CITED

Baker, D.B. 1988. *Sediment, Nutrient and Pesticide Transport in Selected Lower Great Lakes Tributaries.* Great Lakes National Program Office, U.S. EPA, Chicago, IL. EPA-905/4-88-01

Culbertson, J. 1977. "Influence of flow characteristics on sediment transport with emphasis on grain size and mineralogy." In Shear, H. and A.E.P. Watson, eds., *The Fluvial Transport of Sediment-associated Nutrients and Contaminants*. International Joint Commission, Windsor, Ontario, Canada, pp. 117-136.

Greenberg, A.E.; Clesceri, L.S.; Eaton, A.D., eds. *Standard Methods for the Examination of Water and Wastewater, 18th Edition*; American Public Health Association: Washington, DC, 1992.

IJC. 1978. *Environmental Management Strategy for the Great Lakes System*. International Joint Commission, Windsor, Ontario, Canada.

IJC. 1980. *Pollution in the Great Lakes Basin from Land Use Activities*. International Joint Commission, Windsor, Ontario, Canada.

Tye, R., R. Jepsen, and W. Lick. 1996. "Effects of colloids, flocculation, particle size, and organic matter on the adsorption of hexachlorobenzene to sediments." *Environ. Sci. Technol.* 15: 643-651

Walling, D.E. and J.C Woodward. 1993. "Use of a field-based water elutriation system for monitoring the in situ particle size characteristics of fluvial sediment." *Water Research* 27: 1413-1421.