

# Water Quality Trends of the Upper Ohio River from 1977 to 1987<sup>1</sup>

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**ABSTRACT.** Water quality trends from 1977 to 1987 at four stations in the upper Ohio River were explored statistically by use of the seasonal Kendall test for trends and informally described by comparison with flow data and water quality criteria. Monthly data for eight chemical parameters were evaluated: cyanide, phenolics, copper, iron, lead, zinc, dissolved oxygen, and total suspended solids. Results indicated general improvements in the water quality, most notably in decreasing concentrations of cyanide, phenolics, lead, and zinc. The strongest trends were noted for cyanide. Flow adjustment of the data did not affect conclusions about concentration trends, and flow-concentration regressions were weak.

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## INTRODUCTION

The upper Ohio River historically has been the most heavily industrialized and polluted segment of the river. Over approximately the last decade, these characteristics have begun to change. The industrial economy of the upper Ohio River has been in transition to a more service-based economy and general improvements in the water quality of the upper Ohio River have been observed, largely because of a depression in steel manufacturing. Although water quality improvements have been generally noted in the river, few attempts have been made to statistically assess the changes.

The objective of this study is to explore trends of water quality over the past decade in the upper Ohio River. The formal research question was as follows: were the concentrations of certain chemical parameters in the upper Ohio River independent of time during the period 1977 to 1987? The chemical parameters chosen are known to be related to industrial pollution, and the area chosen is a highly industrialized reach of the upper Ohio River.

## Water Quality History of the Ohio River

When industrialization of the Ohio River Valley took place in the late Nineteenth and early Twentieth Centuries, the water quality of the river began to degrade because of the combination of wasteloadings from manufacturing processes and the increased population pressure that followed the industrial boom. The water quality of the Ohio River continued to deteriorate and was at its worst during the droughts that occurred in 1930-31 and 1934 (Pearson and Krumholz 1984). The first improvement in the water quality of the industrialized Ohio River came with the introduction of sewage treatment in the 1940s and 1950s. In the 1940s, mean monthly dissolved oxygen concentrations were recorded well below minimum accepted standards in low flow months. Beginning in the 1950s, the installation of primary and secondary sewage treatment plants in many locations caused improvement in dissolved oxygen levels. Most of the treatment facilities for point source pollutants to the Ohio River were built between 1953 and 1975 (Pearson and Krumholz 1984). The level of treatment provided today by municipal sewage treatment facilities in the Ohio River Basin is less than secondary

for 10%, secondary for 66% and advanced for 24% of facilities (Ohio River Valley Water Sanitation Commission [ORSANCO] 1986b). Low dissolved oxygen concentrations are now seen mostly as a result of temporary shut-down or breakdown of sewage facilities, or in areas where secondary treatment is inadequate.

Standards to control industrial pollution in the Ohio River were first adopted in 1955 (Vicory and Weaver 1984). The discharge of some toxic substances began to be restricted by law in 1958, and acid mine drainage was required to be treated beginning in 1960.

The passage of the Federal Water Pollution Control Act Amendments of 1972 set further standards to improve water quality nationwide. Operations of the navigation structures on the river and its tributaries have helped to increase low flow levels. Increased aeration provided by the structures may also improve dissolved oxygen concentrations (Ohio River Basin Commission 1978). The navigation dams also cause the river to move more slowly, allowing the settling of suspended material, thus lowering turbidity (ORSANCO 1986a). However, industry continues to be a source of some toxic pollution to the Ohio River and its tributaries (ORSANCO 1986b).

Few studies have documented changes in water quality or related parameters of the Ohio River. Van Hassel et al. (1988) found decreased numbers of pollution-tolerant fish species and increased numbers of more pollution-intolerant species, indicating improvement in the water quality and fishery of the Ohio River from 1973 to 1985. Ohio River sediment samples taken in 1987 generally had lower concentrations of cadmium, chromium, copper, iron, lead, nickel and zinc, and higher values for manganese than sediment samples taken in 1977. The 1987 levels were still well above background levels and could be a source for elevated instream concentrations of heavy metals (Youger and Mitsch 1989).

## Other Water Quality Trend Studies

Until recently, most river water quality data bases were not sufficient to support long-term statistical trend studies because of inconsistency in sampling methods and incomplete records. In addition, a lack of statistical methods suitable for use with water quality data presented problems (Wolman 1971). The existence of National Stream Quality Accounting Network (NASQAN),

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National Water Quality Surveillance System (NWQSS), and other new data bases was one motivation for Hirsch et al. (1982) to introduce a nonparametric (distribution-free) test suitable for use with monthly water quality time series data. The test was named the "seasonal Kendall" test and was described as a modified form of Kendall's rank order correlation (Kendall 1970). In addition, Hirsch et al. (1982) defined two other procedures: 1) the seasonal Kendall slope estimator for determining the magnitude of a trend; and, 2) flow adjustment procedures for determining the relationship between concentration of parameters and river flow. The authors compared these tests to other statistical methods and recommended them as exploratory tests for describing water quality trends. Smith et al. (1982) applied the seasonal Kendall test to monthly total phosphorus data collected at 303 NASQAN stations across the United States. Significant decreasing trends in phosphorus concentrations were found at 62 stations, while 38 showed significant increases. When the data were flow-adjusted, 45 stations showed decreasing trends and 40 showed increasing trends. Detailed statistical procedures were employed by Smith et al. (1987a, b) to determine and analyze water quality trends at nearly 400 NASQAN and NWQSS stations throughout the United States. Procedures used included the seasonal Kendall test for trend, seasonal Kendall slope estimator, flow-adjusted trend testing, and preliminary hypotheses testing for cause of observed trends. Among other analyses, these researchers found several trends for the Ohio River Basin, including upward trends in concentrations of chloride, nitrate, pH, suspended sediment and arsenic, and downward trends in concentrations of sulfate, dissolved oxygen deficit and lead. General national trends included widespread decreases in lead and fecal bacteria and increases in nitrate, arsenic and cadmium concentrations. Atmospheric deposition was suggested as an effect on water quality changes for nitrate, lead, arsenic and cadmium. Other significant influences on water quality changes were suggested to be municipal waste treatment, leaded gasoline consumption, use of highway salts and nitrogen fertilizer, and regional trends in coal combustion.

## MATERIALS AND METHODS

### Study Site

The focus of this study was on water quality trends at four Ohio River Valley Water Sanitation Commission (ORSANCO) manual sampling network stations on the upper Ohio River (Fig. 1). These sites, listed by river mile (RM) downstream of Pittsburgh, PA, are: East Liverpool, OH (RM 40.2); Pike Island Lock and Dam, Wheeling, WV (RM 84.2); Shadeyside, OH (RM 102.4); and Hannibal Lock and Dam, Hannibal, OH (RM 126.4) (Fig. 1). The river flows approximately north to south through this region with the State of Ohio on its western shore and the State of West Virginia on its eastern shore. This particular reach of the river was chosen for study for the following reasons: 1) it has historically been one of the most heavily industrialized areas of the river, primarily because of the number of steel mills in the region; and 2) this stretch of the river does not have major tributaries which would complicate analysis of water quality data (ORSANCO 1987a). There are eleven small tributaries to the Ohio River in the study region. Tributaries entering on the Ohio shore are Yellow Creek (RM 50.4), Cross Creek (RM 71.6), Short Creek (RM 81.4), Wheeling Creek (RM 91.0), McMahon Creek (RM 94.7), Captina Creek (RM 109.6), and Sunfish Creek (RM 118). Tributaries on the West Virginia side are Buffalo Creek (RM 74.7), Wheeling Creek (RM 91), Grove Creek (RM 102.5), and Fish Creek (RM 113.8) (ORSANCO 1986a). In the study area,

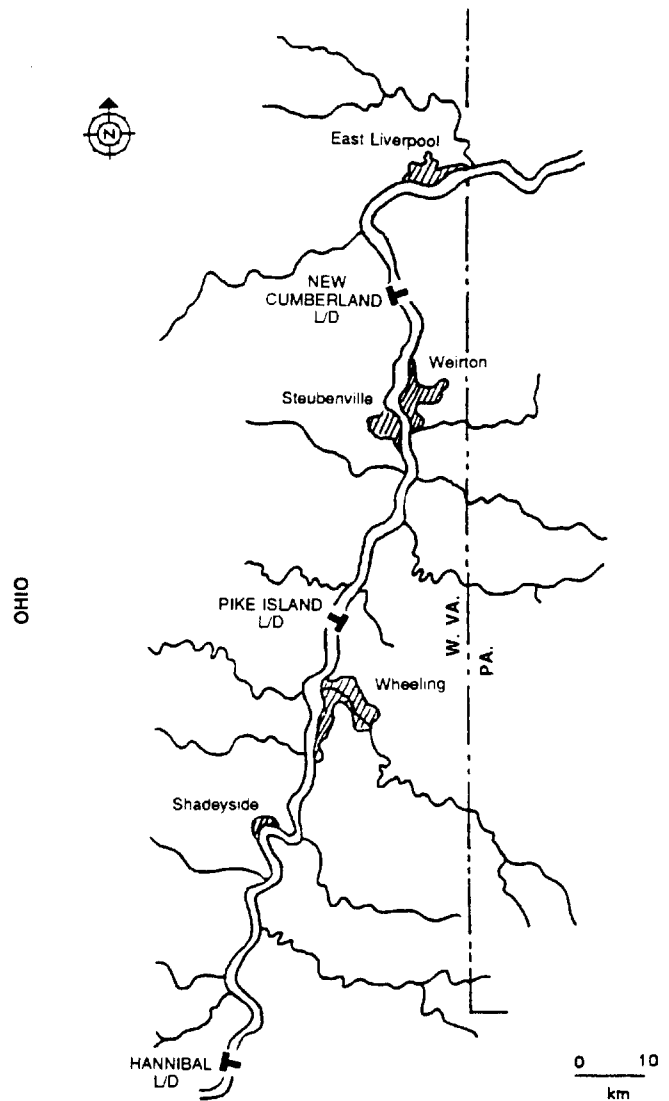


FIGURE 1. Map of study area showing sampling stations: East Liverpool, Ohio; Pike Island Lock and Dam, Wheeling, West Virginia; Shadeyside, Ohio; Hannibal Lock and Dam, Hannibal, Ohio; and surrounding areas.

there are five municipal water supply intakes, 39 industrial water supply intakes, seven power generating plants, 25 municipal dischargers (13 with primary treatment and 12 with secondary treatment), and 50 industrial wastewater dischargers (ORSANCO 1986a). The study area is within the Steubenville-Weirton and Wheeling Standard Metropolitan Statistical Areas (SMSA). The population residing within these SMSAs for the 1980 census was approximately 167,800 and 190,300 for Steubenville-Weirton and Wheeling, respectively (U.S. Dept. of Commerce 1982).

### Water Quality Data

The data used in this study were obtained from the ORSANCO manual sampling network, which provides monthly analysis of solids, nutrients, and metals. The sampling network began in 1975 and continues to the present. The data collected from this network are stored on STORET, a data base managed by the U.S. Environmental Protection Agency (USEPA). Data from specific years were not included in this study as follows: 1) data were not available for 1975 for the stations used in this study; 2) data from 1976 were not included because a full year of data was not available; 3) data from 1977 at Hannibal were not included because a full year of data was not available; and 4) data from 1988 were not included because a full year's data were not available at the time of this study.

The following water quality variables were examined: dissolved oxygen (DO), total suspended solids (TSS), phenolics, cyanide, cop-

per, iron, lead, and zinc. The metals, total suspended solids, phenolics and cyanide were chosen as variables because of the association of these pollutants with industrial effluents. The four metals were also chosen because relatively complete records were available for these metals. Dissolved oxygen was chosen as a variable to give some indication of the general health of the river. Flow data concurrent with concentration data were obtained from the manual sampling network. The flow values are provided to ORSANCO by the National Oceanic and Atmospheric Administration (NOAA) in Cincinnati, Ohio and are determined by use of a forecasting model. Field methods, operating procedures, and quality control measures followed by ORSANCO in obtaining the data are described in ORSANCO (1984). Laboratory methods followed standard procedures as described at the time of analysis by the USEPA and appropriate editions of Standard Methods (e.g. American Public Health Association 1980).

### Statistical Analysis

Simple descriptive statistics, including mean, standard deviation, standard error, and range were calculated. Although these statistics are usually used on data that are assumed to be normally distributed, they were used in this study to obtain a preliminary view of central tendencies and variations in the data. These descriptive statistics were computed separately for each parameter at each station and were reported as yearly summaries.

In this study a non-parametric trends analysis technique called the seasonal Kendall test was used to explore the following null hypothesis:

Ho: The concentration of the chemical parameters is independent of time.

The first step in the seasonal Kendall test was to nullify the effects of seasonality. For each month, differences ( $d_i$ ) were calculated only between other observations occurring in that same month of the year as follows:

$$d_i = x_{ij} - x_{ik} \quad (1)$$

where,

$x_{ij}$  = observation for the  $i$ th month of the  $j$ th year;

$x_{ik}$  = observation for the  $i$ th month of the  $k$ th year.

For example, a January observation occurring in 1978 would only be compared with January values for the other years. Once all of these differences were calculated, a score ( $S_i$ ) for that month was calculated as follows:

$$S_i = P_i - Q_i \quad (2)$$

where,

$P_i$  = number of positive differences ( $+d_i$ ) for the  $i$ th month;

$Q_i$  = number of negative differences ( $-d_i$ ) for the  $i$ th month.

The variance ( $v_i$ ) of the score was calculated as follows:

$$v_i = n_i(n_i - 1)(2n_i + 5)/18 \quad (3)$$

where,

$n_i$  = number of non-missing observations for the  $i$ th month.

Kendall's correlation coefficient (tau) was calculated as follows:

$$\text{tau} = S_i / (n_i(n_i - 1)/2) \quad (4)$$

A tau value equal to  $-1.0$  would indicate a perfect negative relationship between time and concentration. A tau value equal to  $+1.0$  would indicate a perfect positive relationship, and a tau equal to zero would indicate no relationship. Values of tau lying between these values were compared to a scale devised for this study which was based on a scale suggested for Pearson's sample correlation coefficient ( $r$ ) (Devore and Peck 1986). The scale is as follows: 1) a tau greater than 0.8 or less than  $-0.8$  indicated a strong trend; 2) a tau from 0.5 to 0.8 or from  $-0.5$  to  $-0.8$  indicated a moderate trend; 3) a tau between 0.0 and 0.5 or between  $-0.5$  and 0.0 indicated a weak trend; and, 4) a tau equal to 0.0 indicated no trend.

A continuity correction was then made so that the distribution of the test statistic ( $S$ ) could be approximated by the normal distribution as follows:

$$z_i = (S_i - 1)/s.d. \quad (5)$$

where,

$z_i$  = the standard normal deviate for the  $i$ th month;

s.d. = standard deviation (square root of  $v_i$ ).

The standard normal deviate was calculated using a confidence level of 90% (significance level of 0.1). Once  $z$  was calculated, the p-value was found by use of the standard normal table in Devore and Peck (1986). The p-value can be defined as the lowest significance level at which the null hypothesis can be rejected (Devore and Peck 1986).

Hirsch et al. (1982) also defined a technique for determining the magnitude of trends which they called the seasonal Kendall slope estimator. Both the seasonal Kendall test for trend and the slope estimator were compared by these authors with other statistical methods and were recommended as exploratory tests for describing water quality trends. The slope estimator does not assume a linear trend, rather the magnitude is expressed as change per year caused by the trend (Smith et al. 1982).

The first step in the seasonal Kendall slope estimator was calculated as follows:

$$d_{ijk} = (x_{ij} - x_{ik}) / (j - k) \quad (6)$$

where,

$d_{ijk}$  = differences calculated for month  $i$ , for years  $j$  and  $k$ .

The median of these differences for each month ( $x$ ) is then taken to be the seasonal Kendall slope estimate or the change in concentration per year resulting from a trend for that particular month.

### Flow Adjustment

In order to eliminate river discharge characteristics as a cause of a trend in chemical concentration, we explored the relationships between concentration ( $C$ ) and discharge ( $Q$ ) (Hirsch et al. 1982, Smith et al. 1982, Smith et al. 1987a,b). These authors suggest trying various regression models to find the best fit relationship, and then using the model with the highest  $R^2$  value to perform residual analysis. The models suggested by these authors use various functional forms of discharge ( $f(Q)$ ). The models attempted in this study were similar to those of Smith et al. (1982):

$$a) \text{ linear — } f(Q) = Q \quad (7)$$

$$b) \text{ log — } f(Q) = \ln Q \quad (8)$$

$$c) \text{ inverse — } f(Q) = 1/Q \quad (9)$$

### Data Preparation

Some manipulation of data was necessary to complete each of the methods described above. In calculating means, standard deviations, standard errors and ranges, all recorded values were used. Values reported below the level of detection were not included in those calculations.

For the seasonal Kendall test for trend and slope estimator, the data were prepared as follows: 1) missing values were not counted in the calculations; 2) values recorded as being below the level of detection were set to equal one-half the value of the detection level for that parameter (Crawford et al. 1983); and 3) whenever more than one observation per month was recorded, the median observation for that month was taken as the monthly observation (Crawford et al. 1983). Replacing values recorded below the detection level with one-half the detection limit presents no problem in interpretation of the seasonal Kendall trend test results; actual values of observations are not considered, but only whether they are smaller or larger in comparison to other values. Using one-half the detection level can lead to less reliable results from the seasonal Kendall slope estimator procedure.

## RESULTS

### Water Quality Trends

The seasonal Kendall test provided trend results for the four water quality sampling stations on the Ohio River (Table 1). The results are reported as the number of months showing a particular trend for each parameter and station combination. The seasonal Kendall test for the entire period was calculated separately for each

TABLE 1.  
Results from the Seasonal Kendall Test for Trend for 1977-87 water quality data for the Ohio River

Station/ Parameter	Trends Based on p-Value-Number of Months			Trends Based on Tau-Number of Months						
	Increase $p < 0.1$	Decrease $p < 0.1$	No Trend $p > 0.1$	Increase Weak $\tau = 0 \text{ to } 0.5$	Increase Mod. $\tau = 0.5 \text{ to } 0.8$	Increase Strong $\tau > 0.8$	Decrease Weak $\tau = -0.5 \text{ to } 0$	Decrease Mod. $\tau = -0.8 \text{ to } -0.05$	Decrease Strong $\tau < -0.8$	No trend $\tau = 0$
<u>E. Liverpool</u>										
Copper		5	7				11	1		
Iron		1	11	2			8	1		1
Lead		3	9				11	1		
Zinc		4	8	1			7	4		
Cyanide		11	1				1	10	1	
Phenolics			10	2			8	1		1
D.O.	1		11	5		1	6			
T.S.S.		1	11	1			5			6
<u>Pike Island</u>										
Copper			12	5	1		5			1
Iron			12	3			9			
Lead		5	7				9	2		1
Zinc		2	10	1			10	1		
Cyanide		11	1				1	10	1	
Phenolics			10	3			8	1		
D.O.	1	2	9	4	1		6	1		
T.S.S.			12	1	1		5	2		3
<u>Shadeyside</u>										
Copper		1	11	5			6	1		
Iron	1		11	7			5			
Lead		4	8	3			8	1		
Zinc		2	10	1			9	1		1
Cyanide		10	2				4	6	2	
Phenolics		3	9	2			6	2		2
D.O.	1	3	9	3	1		6	2		
T.S.S.			12	2			3	2		5
<u>Hannibal</u>										
Copper		5	7				10	2		
Iron	1	1	10	7			4			1
Lead		1	11	4			7			1
Zinc		2	10				11			1
Cyanide		11	1				3	7	2	
Phenolics		1	11	3			8	1		
D.O.	1	1	10	4	1		4	1		2
T.S.S.			12	2	1		6	1		2

month. Data in the first two columns report increasing and decreasing trends, defined here as when the p-value is less than 0.1 (Table 1). A p-value of 0.1 is considered to be the cut-off point for whether the trend is statistically significant (Smith et al. 1987a). The number of months showing an increasing or decreasing trend with a p-value greater than 0.1 or showing no trend ( $S_i = 0$ ) are reported in the third column, which is where the majority of the months appear (Table 1).

The results on the correlation coefficient (tau) provide more detail because all trends are reported and not just those above a certain significance level (right side of Table 1). The columns on this side of the table are broken down according to the strength of the correlation coefficient (tau). The majority of months showed decreasing trends with a tau between 0 and -0.5.

The changes per year of various chemical concentrations caused by trends are presented using the seasonal Kendall slope estimators (Table 2). The slope estimates

are also summarized as percentage change per year. There is a great range in percentage change from less than one percent to 10 percent. Almost all of the changes are negative, indicating trends of decreasing concentration.

Each of the chemical parameters investigated by these trend analyses is discussed below.

**CYANIDE.** Cyanide is the only parameter for which most months showed significantly decreasing trends ( $p < 0.1$ ) (Table 1). Most months showed decreasing trends in the moderate range ( $\tau = -0.8 \text{ to } -0.5$ ), and one to two months were in the strong decreasing range ( $\tau < -0.8$ ). There were no months which showed cyanide to be increasing based on p-values or tau. Cyanide showed percentage decreases in concentration of 8 to 14 percent per year at all sites (Table 2). The change was negative for all four stations. Patterns of annual mean concentrations and standard errors for cyanide indicate that cyanide generally decreased over time with

TABLE 2.  
Results from the Seasonal Kendall Slope Estimator for 1977-1987 water quality data for the Ohio River

Site/Parameter	Number of Samples	Average for Period	Average Change units/year*	Percent Change per year**
<u>E. Liverpool</u>				
Copper, $\mu\text{g/l}$	120	24	-1.2	-5
Iron, $\mu\text{g/l}$	120	2688	-125	-5
Lead, $\mu\text{g/l}$	120	16	-1.1	-7
Zinc, $\mu\text{g/l}$	120	68	-5.1	-8
Cyanide, mg/l	120	0.01	-0.00089	-9
Phenolics, $\mu\text{g/l}$	108	4.8	-0.36	-8
DO, mg/l	84	11	0.00022	0.002
TSS, mg/l	48	190	-7.1	-4
<u>Pike Island</u>				
Copper, $\mu\text{g/l}$	108	27	0.34	1
Iron, $\mu\text{g/l}$	108	2307	-75	-3
Lead, $\mu\text{g/l}$	108	16	-1.5	-9
Zinc, $\mu\text{g/l}$	108	54	-3.2	-6
Cyanide, mg/l	108	0.01	-0.0014	-14
Phenolics, $\mu\text{g/l}$	108	4.1	-0.37	-9
DO, mg/l	96	10	-0.039	-0.4
TSS, mg/l	60	216	-2.8	-1
<u>Shadeyside</u>				
Copper, $\mu\text{g/l}$	96	22	-0.31	-1
Iron, $\mu\text{g/l}$	96	2286	34	2
Lead, $\mu\text{g/l}$	96	16	-0.91	-6
Zinc, $\mu\text{g/l}$	96	68	-3.4	-5
Cyanide, mg/l	108	0.01	-0.0011	-11
Phenolics, $\mu\text{g/l}$	96	3.2	-0.23	-7
DO, mg/l	84	10	-0.076	-0.8
TSS, mg/l	48	220	-4.2	-2
<u>Hannibal</u>				
Copper, $\mu\text{g/l}$	120	15	-1.3	-9
Iron, $\mu\text{g/l}$	120	1008	1.6	0.2
Lead, $\mu\text{g/l}$	120	11	-0.28	-3
Zinc, $\mu\text{g/l}$	120	39	-2.4	-6
Cyanide, mg/l	120	0.01	-0.00083	-8
Phenolics, $\mu\text{g/l}$	120	3.5	-0.13	-4
DO, mg/l	84	10	-0.017	-0.2
TSS, mg/l	60	231	1.4	0.6

\* Average of Seasonal Kendall Slope Estimator (Values in  $\mu\text{g/l}$  except for Cyanide, DO, and TSS which are in mg/l).

\*\* (Average Change  $\div$  Average for Period)  $\times$  100

values in later years beginning to level off (Fig. 2). The plots for Pike Island (Fig. 2b) and Shadeyside (Fig. 2c) each show increases in mean concentration of cyanide in 1981 because of high concentrations during separate sampling periods at each site. These anomalies remain unexplained except that they may indicate accidental spills or other discharges.

**PHENOLICS.** The seasonal Kendall test results for phenolics (Table 1) show that most months had weak decreasing correlation coefficients. Each station had at least one month with a moderate decreasing correlation coefficient, and two months with weakly increasing coefficients. Only a few months showed decreasing trends with p-values less than 0.1. The percentage change per year in concentrations of phenolics were all negative. East Liverpool, Pike Island and Shadeyside each showed large percentage decreases, and Hannibal showed small percentage decreases relative to the other parameters

(Table 2). Mean concentrations of phenolics oscillated, but later values were generally lower than earlier values (Fig. 3). The plots for Pike Island (Fig. 3b) and Shadeyside (Fig. 3c) were most similar. These two stations also showed the largest decreases in concentration per year (Table 2). The smallest range in mean concentration occurred at Hannibal (Fig. 3d), which was also the station with the smallest percentage change per year (Table 2).

**COPPER.** Most months at each station showed no trend in copper concentrations based on p-values (Table 1). Based on correlation coefficients, most months showed weakly decreasing trends ( $\tau = -0.5$  to 0.0) in copper. A few months showed weak increases in copper ( $\tau = 0.0$  to 0.5). One month showed a moderate increasing trend ( $\tau = 0.5$  to 0.8) for copper, and one month showed no trend ( $\tau = 0$ ) for copper. Pike Island showed all twelve months with no trend based on p-value ( $p > 0.1$ ) and an even split between months showing increases and de-

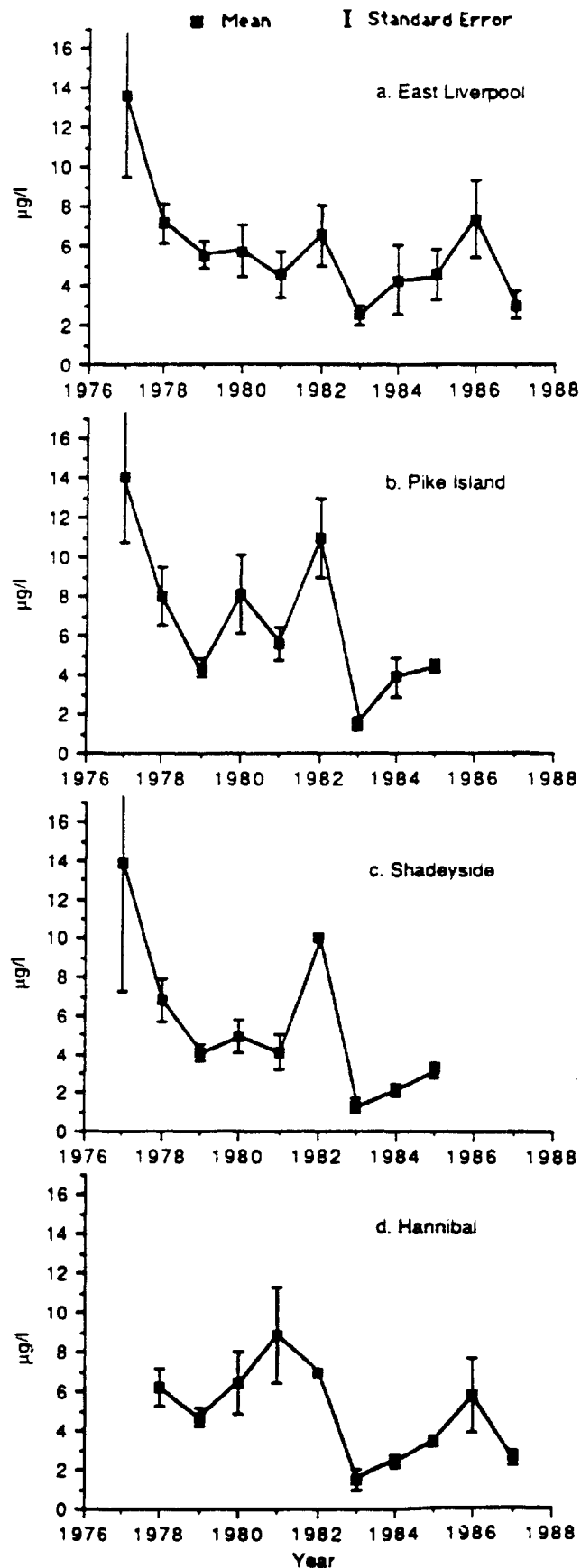
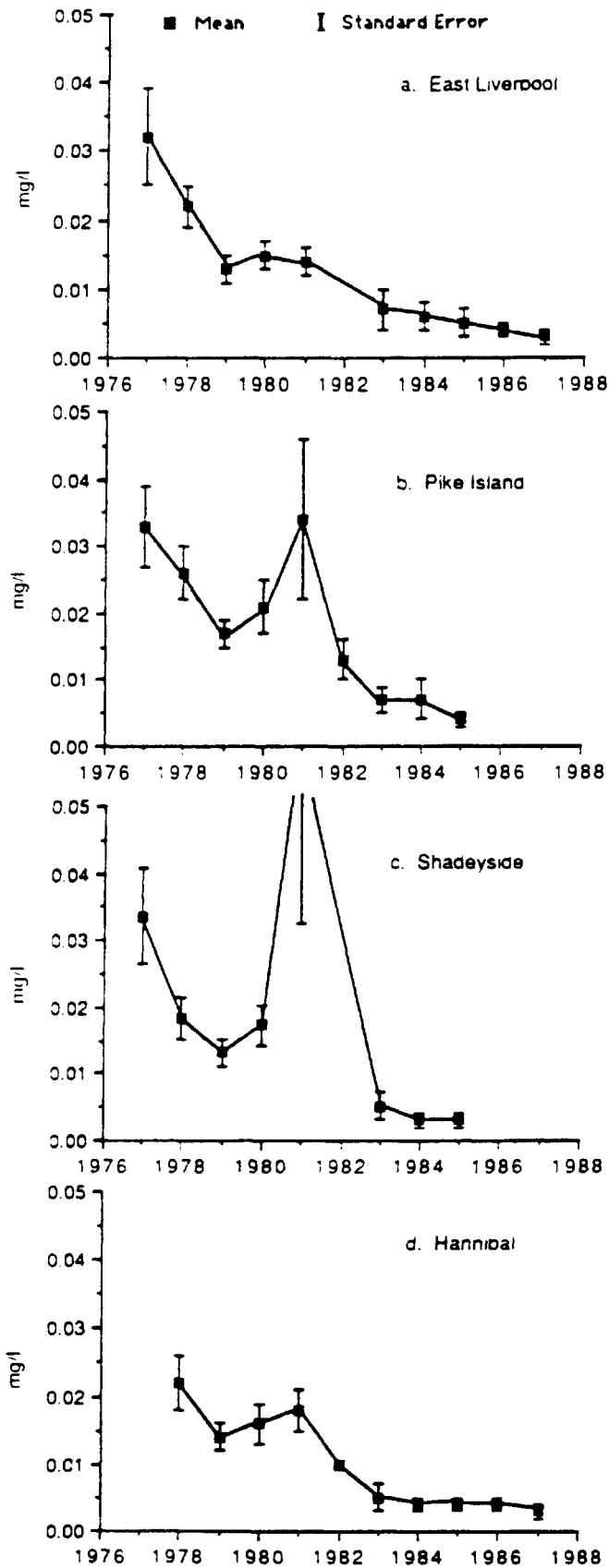


FIGURE 2. Mean concentrations and standard error bars of cyanide found in Ohio River samples from 1977-87 at: a) East Liverpool, Ohio; b) Pike Island Lock and Dam, Wheeling, West Virginia; c) Shadeyside, Ohio; and d) Hannibal Lock and Dam, Hannibal, Ohio.

FIGURE 3. Mean concentrations and standard error bars of phenols found in Ohio River samples from 1977-87 at: a) East Liverpool, Ohio; b) Pike Island Lock and Dam, Wheeling, West Virginia; c) Shadeyside, Ohio; and d) Hannibal Lock and Dam, Hannibal, Ohio.

creases in copper based on correlation coefficients. Pike Island was the only station to show a positive increase in copper (Table 2), and this was one percent. The largest change in copper was at Hannibal Lock and Dam.

**ZINC.** Most months showed no significant trend ( $p > 0.1$ ) for zinc (Table 1). A total of ten months showed significant decreasing trends ( $p < 0.1$ ) for all stations combined. The trends based on tau provided more detailed information on zinc trends. All stations except Hannibal showed one month with a weak increasing trend ( $\tau = 0.0$  to  $0.5$ ) and at least one month with a moderately decreasing trend ( $\tau = -0.8$  to  $-0.5$ ). Hannibal and Shadeyside each showed one month with no trend based on tau ( $\tau = 0.0$ ). The majority of the months for all stations had taus which fell into the range for weakly decreasing trends ( $\tau = -0.5$  to  $0.0$ ) for zinc. The changes per year in zinc concentration are all negative and are above five percent—high relative to other changes (Table 2).

**LEAD.** Most months showed no trend for lead based on p-value ( $p > 0.1$ ) and a few months showed significant decreases in lead based on p-value ( $p < 0.1$ ) (Table 1). The trends based on correlation coefficients showed most months with weakly decreasing trends ( $\tau = -0.5$  to  $0.0$ ) in lead concentrations. At least two months showed trends for lead in the following categories: weakly increasing trend ( $\tau = 0.0$  to  $0.5$ ); moderately decreasing trend ( $\tau = -0.8$  to  $-0.5$ ); and no trend ( $\tau = 0.0$ ). The largest percentage change in concentrations per year for any parameter was 9 percent for lead at Pike Island (Table 2).

**IRON.** Two months showed significantly increasing trends in iron concentrations based on p-values ( $p < 0.1$ ). The results for iron concentration trends based on tau fall into two groups: East Liverpool and Pike Island showed most months with decreasing trends; and, Shadeyside and Hannibal showed most months with increasing trends. Likewise, East Liverpool and Pike Island showed decreases in concentration, and Shadeyside and Hannibal showed increases in concentration per year although at Hannibal the increase is only 0.2 percent per year (Table 2).

**DISSOLVED OXYGEN.** Dissolved oxygen is the only chemical parameter examined for which an increase over time would be viewed as an improvement in water quality. More months showed significantly increasing trends ( $p < 0.1$ ) for dissolved oxygen than for any other pa-

rameter (Table 1). Only a few months showed significantly decreasing trends for dissolved oxygen based on p-value, and most months showed no significant trend. Dissolved oxygen was the only parameter to show a month with a strongly increasing trend based on the correlation coefficient ( $\tau > 0.8$ ). Most months had weak decreasing trends based on the correlation coefficient ( $\tau = -0.5$  to  $0.0$ ). The percentage changes in concentration of dissolved oxygen (Table 2) are the smallest for any parameter and are all less than one percent. East Liverpool is the only station which shows a positive increase, but it is extremely small.

**TOTAL SUSPENDED SOLIDS.** More months showed no trend for total suspended solids concentrations based on p-values and tau than for any other parameter (Table 1). Most months showed weakly decreasing trends ( $\tau = -0.5$  to  $0.0$ ) for total suspended solids. A few months showed weak ( $\tau = 0.0$  to  $0.5$ ) and moderate ( $\tau = 0.5$  to  $0.8$ ) increases in total suspended solids concentrations. Hannibal was the only station to show positive percentage changes for total suspended solids concentrations (Table 2). East Liverpool had the largest change at negative four percent.

### Flow Adjusted Trends of Water Quality

The importance of possible flow corrections for the trend analyses was investigated with regression analyses of chemical concentrations against various functions of flow (Table 3). The three regression models tested were: 1) concentration versus flow (Q); 2) concentration versus the natural log of flow ( $\ln Q$ ); and, 3) concentration versus the inverse of flow ( $1/Q$ ). Of the 96  $R^2$  values (Table 3), only six (approximately six percent) are above 0.5 or below  $-0.5$ , and five of these are for total suspended solids. Approximately 35% of the values are between 0.1 and 0.5 or  $-0.1$  and  $-0.5$ , 28 percent are between 0.01 and 0.1 or  $-0.01$  and  $-0.1$ , and 30 percent are less than 0.01 or greater than  $-0.01$ . Because most of these  $R^2$  values are not significantly different than zero, it did not seem necessary to do further analysis of the models such as using residual analysis procedures to flow-adjust concentrations, as suggested by Hirsch et al. (1982), Smith et al. (1982), and Smith et al. (1987a,b).

The regression models for cyanide at East Liverpool and total suspended solids at Shadeyside are illustrated to demonstrate two distinctly different situations (Figs. 4

TABLE 3.

*R<sup>2</sup> Values from regression of concentration of chemical parameters versus streamflow at upper Ohio River stations: East Liverpool, Ohio; Pike Island Lock and Dam, West Virginia; Shadeyside, Ohio; and, Hannibal Lock and Dam, Hannibal, Ohio*

	EAST LIVERPOOL			PIKE ISLAND			SHADEYSIDE			HANNIBAL		
	Q	lnQ	1/Q	Q	lnQ	1/Q	Q	lnQ	1/Q	Q	lnQ	1/Q
Cyanide	0.054	0.072	0.026	0.024	0.036	0.034	0.016	0.016	0.008	0.007	0.004	0.004
Phenolics	0.043	0.06	0.022	-0.0004	0.001	0.003	0	0.001	0.002	0.035	0.036	0.021
Copper	0.002	0.0002	0.001	-0.0005	0.003	0.005	0.001	0.001	0.006	0.012	0.009	0.009
Iron	0.216	0.18	0.122	0.517	0.346	0.169	0.302	0.249	0.175	0.436	0.314	0.15
Lead	0.03	0.005	0.00002	0.015	0.011	0.008	0.009	0.018	0.019	0.004	0	0.001
Zinc	0.069	0.067	0.053	0.274	0.179	0.091	0.05	0.058	0.056	0.149	0.119	0.063
D.O.	0.143	0.176	0.146	0.198	0.194	0.105	0.226	0.265	0.238	0.173	0.216	0.169
TSS	0.436	0.528	0.497	0.334	0.497	0.545	0.383	0.566	0.579	0.334	0.497	0.545

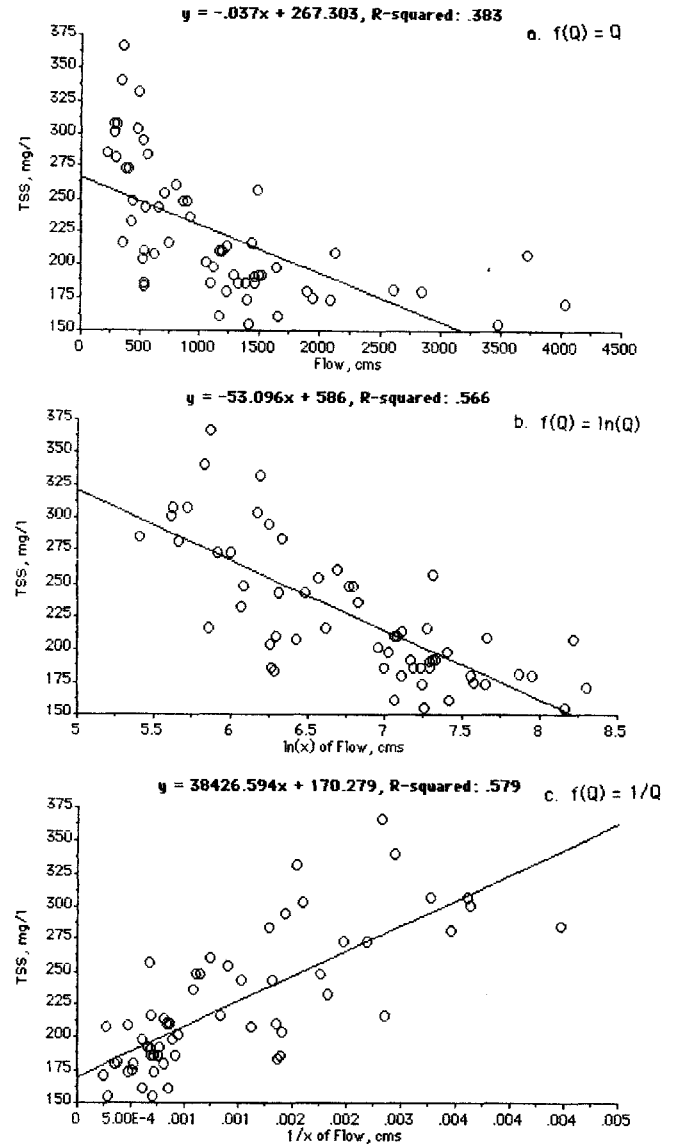
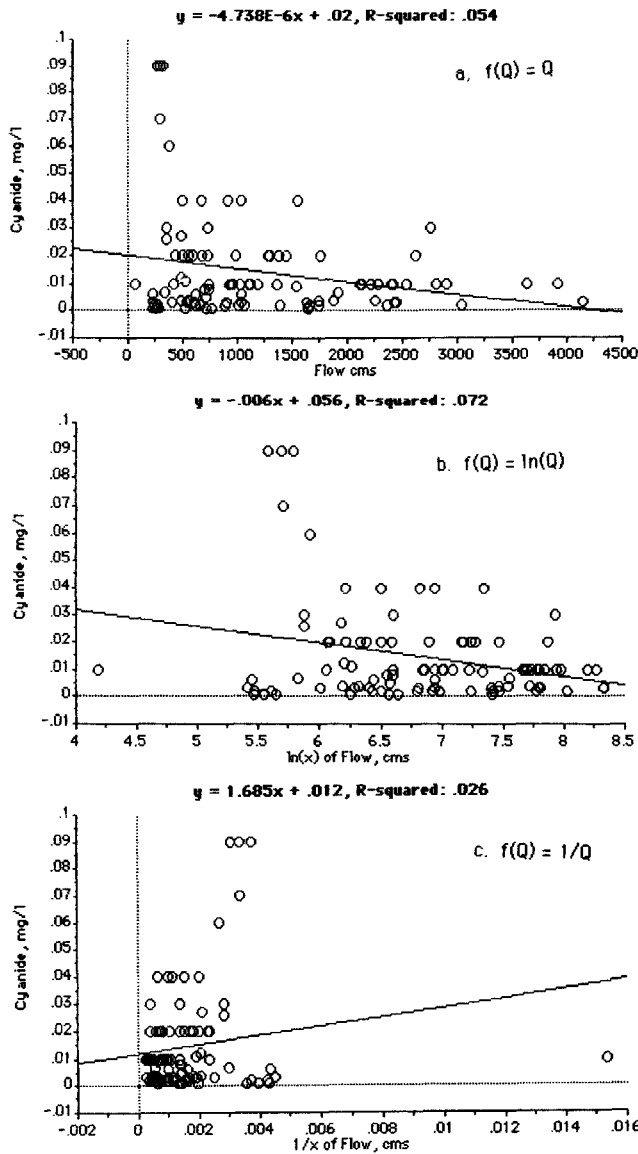


FIGURE 4. Regression of concentration of cyanide in mg/l versus streamflow (Q) in cubic meters per second (cms) in the Ohio River at East Liverpool, Ohio from 1977-87. Three functions of streamflow were used: a) linear,  $f(Q) = Q$ ; b) log,  $f(Q) = \ln Q$ ; and c) inverse,  $f(Q) = 1/Q$ .

FIGURE 5. Regression of concentration of total suspended solids in mg/l versus streamflow (Q) in cubic meters per second (cms) in the Ohio River at Shadeyside, Ohio from 1977-87. Three functions of streamflow were used: a) linear,  $f(Q) = Q$ ; b) log,  $f(Q) = \ln Q$ ; and c) inverse,  $f(Q) = 1/Q$ .

and 5). These two parameters were chosen for plots because of the differences in their seasonal Kendall trend results: cyanide concentrations showed the most significantly decreasing trends in the seasonal Kendall test and very weak negative correlation coefficients; total suspended solids showed the strongest no trend results in the seasonal Kendall test and the strongest negative correlation coefficients. The regression models for cyanide (Fig. 4) show essentially no relationships between concentration and flow. The regression plots for total suspended solids (Fig. 5) show an inverse relationship between flow and total suspended solids, a somewhat surprising result as high concentrations of sediments are usually associated with high concentrations of flow in rivers. The highest  $R^2$  value (0.58) of the entire data set is found in the relationship between total suspended solids concentration and the inverse of flow (Table 3 and Fig. 5c).

## DISCUSSION

### Summary of Water Quality Conditions

The most obvious conclusions from the seasonal Kendall results for trends based on p-values and those based on correlation coefficients are that most parameters did not appear to be significantly increasing, and most parameters that were significantly decreasing were not doing so in every month of the year. If only the trends based on p-values were considered, then the only conclusion of this study would be that there are few discernible trends for these parameters in the upper Ohio River.

That conclusion would be somewhat misleading. The use of correlation coefficients allowed recognition of all trends, even those that were weak. Based on correlation coefficients, and observing the data set as a whole, decreasing trends were most prominent, followed by no trend, then by increasing trends. It must be recognized,



however, that some departure from defining trend as a monotonic change is necessary.

The general trends of water quality parameters for the upper Ohio River have been summarized and put into categories ranging from strong decrease to no trend (Table 4). The placement in categories was determined by the seasonal Kendall trend test results based on tau. The strongest trend by far was for cyanide, which not only showed a strongly decreasing trend, but also showed a large rate of decrease per year at two stations. Cyanide was the only parameter which showed a strongly negative correlation coefficient and had the largest number of moderately negative correlation coefficients. The decreasing trend for cyanide is a significant finding for the Ohio River. High cyanide concentrations in the upper Ohio River have been a special concern since the mid-1970s (Weston, Inc. and HydroQual, Inc. 1986). Concentrations of phenolics have also been of concern since the mid-1970s, but these levels decreased less strikingly than cyanide. The magnitude of phenolic decreases, however, were consistently large at each station. Trends for phenol concentrations showed increases only in some summer and fall months. However, phenol concentrations were highest in winter months (from these data) and wasteloadings of phenols have historically been higher in winter months (Weston, Inc. and HydroQual, Inc. 1986). The increasing trends observed for phenols in summer months suggest that this constituent is being concentrated by the lower flows which occur then.

Of the heavy metals considered in this study, zinc, copper, and lead were detected more frequently in all Ohio River samples, and these substances were among those that most frequently exceeded criteria for aquatic life (ORSANCO 1987a). These metals are also on the USEPA's priority pollutant list. The concentrations of these metals decreased in the last decade on the upper Ohio River. Copper decreased less significantly than lead and zinc.

The two parameters which showed virtually no trend were iron and total suspended solids. In some instances iron showed a tendency to increase, and levels of iron remained high throughout the study period. Coal mine drainage, a major source of iron in tributary streams of the Ohio River in this region, may be the cause of this lack of a trend. After mine drainage is initiated by coal mining, it is very difficult to control, especially when the mined sites are abandoned.

Dissolved oxygen was the only parameter considered here that is not a contaminant and for which increasing trends in concentration would be a sign of improved water quality. Low dissolved oxygen levels do not appear to

be a problem in the study area. Although the predominant trend from the seasonal Kendall trend and slope estimator results showed dissolved oxygen to slightly decrease over the period of study, the magnitude of decrease was smaller than for any other parameter. Dissolved oxygen levels remained well above the minimum level required by ORSANCO and USEPA throughout the period of study.

#### Conditions by Station - Spatial Variability

Combined average concentrations of toxic pollutants considered here were generally lowest at Hannibal and highest at Pike Island. One exception for Hannibal was for total suspended solids for which it had the highest average concentration. In fact, average concentrations of total suspended solids were lowest at East Liverpool and increased at each successive downstream station in this study region. This suggests that total suspended solids increased as the water moved downstream, perhaps because of the high number of dischargers in the region. East Liverpool and Pike Island had more oscillation of concentrations from year to year than the other stations.

Based on seasonal Kendall test results, more decreasing trends were observed for East Liverpool, the most upstream site, than the other stations. This could be caused by an improvement in water quality occurring in the Pittsburgh region upstream of our study region. East Liverpool was followed by Pike Island, Hannibal, and, finally Shadeyside which showed the fewest decreasing trends. The order is exactly reversed for increasing trends.

#### Significance of Flow Adjustment

Flow adjustment of constituent concentrations helps to eliminate variations in streamflow as causes of trends or as confounding variables in the detection of trends. If a pollutant originates from non-point sources, then increased flow would tend to increase the concentration of that pollutant. Conversely, if a pollutant originates from a point source, then, barring unusual changes in discharge characteristics, increased flow would cause the contaminant to be diluted, and decreased flow would intensify its concentration.

Generally, significant relationships were not found between flow and concentration. The strongest statistical relationship between concentration data and flow was found for total suspended solids, but surprisingly, this was an inverse relationship. Direct correlations between streamflow and total suspended solids in the Ohio River have been found previously by ORSANCO (1986b).

The finding of no significant relationship between flow and concentration in the upper Ohio River may have resulted from one or more of the following: 1) measurement of flow only once per month may be inadequate to obtain reliable results (e.g. Yaksich et al. 1982); 2) with the exception of dissolved oxygen, the parameters analyzed in this study commonly originate from point sources, and therefore would not show a direct relationship with flow; 3) the tributaries to the Ohio River in the study area are small and may not contribute large amounts of nonpoint pollution such as total suspended solids to the Ohio River; and 4) ORSANCO's flow data are determined from forecasting models which may not

TABLE 4.

*Summary of water quality trends in the upper Ohio River, 1977-87*

Strong Decrease	Moderate Decrease	Minor Decrease	No Trend
Cyanide	Lead Zinc Phenolics	Copper*	Iron** TSS

\*showed some increasing trends

\*\*showed both some increasing and decreasing trends

be accurate enough to be considered as concurrent with the concentration data.

**Water Quality Criteria**

The percentage of samples each year which exceeded the most current water quality criteria were determined for five of the toxic chemicals, namely copper, zinc, cyanide, iron, and phenolics (Fig. 6). Present criteria, and not the criteria which were in place in earlier years, were used. ORSANCO criteria (ORSANCO 1987b) were used for all parameters except iron. Values reported below the level of detection were not included in the percentages. There were generally fewer criteria exceedences towards the end of the study period. It can be inferred that this decreasing trend was concurrent with downward trends observed for concentrations of the chemical constituents.

Lead concentrations exceeded the chronic criterion in 100 percent of the samples and did not exceed the acute criterion in 100 percent of the samples. Copper concentrations exceeded the chronic criterion most frequently in 1980, 1981 and 1986. Although at much lower percentages, the acute criteria violations for copper followed the same pattern as those for the chronic criterion, except in 1986. In that year, acute criterion exceedences for copper were at the lowest, but chronic criterion were violated frequently. There was little difference between the percentages of acute and chronic criteria for zinc because there is little difference in the two levels of criteria. The highest percent of exceedences of zinc criteria occurred in 1981 at 15 percent. The only year which showed any difference between the two criteria was 1982, where the acute criterion was exceeded four percent of the time and the chronic six percent of the time.

Cyanide concentrations exceeded the chronic ORSANCO criterion in at least 50 percent of the samples from 1977 to 1983. In three of those years, 100 percent of the samples exceeded chronic criterion. The chronic criterion for cyanide was exceeded in less than 25 percent of the samples from 1984 through 1987. The acute criterion for cyanide was exceeded much less frequently than the chronic criterion. The highest percentage of violations was near 30 percent in 1977 and 1978, but dropped off in subsequent years. Four years had no acute criterion exceedences for cyanide. The anomalous peaks in cyanide observed in 1981 data (Fig. 2b,c) and discussed above did not cause a concomitant increase in the number of violations of the acute standard for that year, as those peaks were caused by only two data points out of a total of 48.

There is no ORSANCO criterion for iron, so the USEPA (1986) criterion is used (Fig. 6c). Domestic water supply criterion was exceeded in at least 89 percent of the samples. Violations of freshwater aquatic life criterion averaged near 50 percent.

Results from flow adjustment suggest that the pollutants considered in this study originate from point sources. The decreasing trends in concentration and percent of criteria exceedences suggest that point-source contributions of these pollutants are decreasing as well. Several factors could cause point source contributions to lessen, but two are probable for the upper Ohio River: reductions in manufacturing activity in this area since the late 1970s,

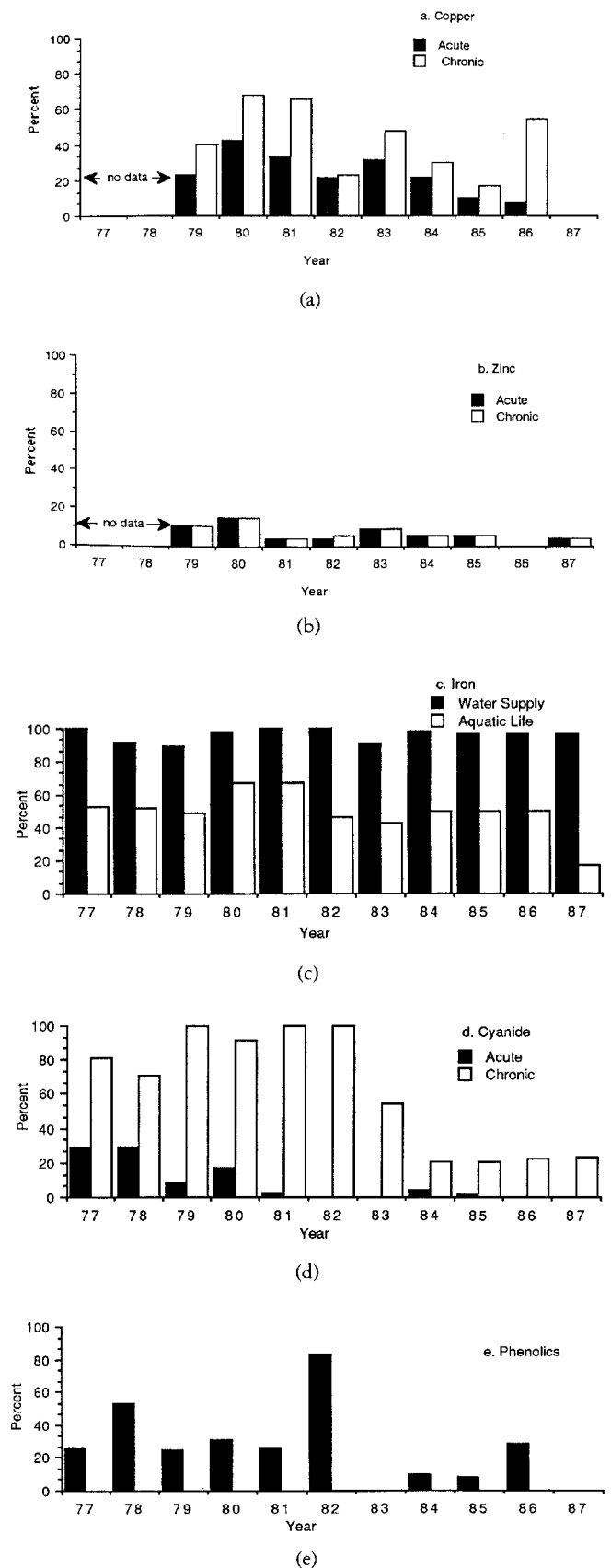


FIGURE 6. Exceedences of Ohio River Valley Water Sanitation Commission water quality criteria in the upper Ohio River, 1977-87 for: a) copper; b) zinc; c) iron (exceedence of USEPA water quality criterion for iron); d) cyanide; and e) phenolics. Criteria were not calculated for copper and zinc for 1977 and 1978 due to lack of hardness data.

especially in the steel industry; and, the implementation of point-source control and treatment technologies as a result of more stringent environmental regulations since the 1970s. Further study of the causes of the trends observed in this study would be appropriate to determine how much has been caused by economic downturn of the region and how much has been caused by effective water quality management strategies. However, the frequency of water quality criteria violations and the weak decreasing trends for many parameters observed in our study suggest that even further improvements are needed in the quality of the Ohio River.

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