Ohio River Metals Translators

Development of Ohio River Translators for Estimating Total Recoverable Permit Limits from Dissolved Metal Criteria

Ohio River Valley Water Sanitation Commission
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Abstract

The Ohio River Valley Water Sanitation Commission (ORSANCO) has developed metals translators for the Ohio River using methods specified by United States Environmental Protection Agency (USEPA) Guidance (USEPA, 1996a). Translators can be applied to constant and one-time discharges as well as the ambient surface water of the Ohio itself. Metals translators estimate the dissolved concentration of a metal in the Ohio River resulting from a discharge when only the total recoverable concentration is known.

Metals translators are proposed in this document for aluminum, arsenic, barium, calcium, chromium, copper, magnesium, manganese, nickel, and zinc. These are ten of eighteen metals quantified since 1998 by the ORSANCO Clean Metals Program. Samples for the program are collected and analyzed using ultra-clean techniques specified by USEPA Method 1638. Low detection rates are the primary reason translators are not recommended for eight species monitored by ORSANCO. Periods of record for the Clean Metals Program at Ohio River sampling stations differ widely, small sample populations (less than twenty) eliminated five stations from this analysis except where data indicated aggregation of adjacent stations was appropriate.

This report is intended as a framework for future additions to and revisions of ORSANCO metals translators. The document establishes the appropriate translator calculation method for ten metals in the Ohio River. The analysis also illustrates for ORSANCO and similar data sets statistical methods to employ in the development of translators for other metals as data becomes available. This document includes both a detailed case study for the selection of an aluminum translator at one sampling station and a discussion of the analysis performed for each metal on all stations. A table of all currently proposed Ohio River translators completes the Recommendations section.

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The Metals Translator

A numerical translator is required to estimate a total recoverable permit limit from a dissolved criterion. The translator in its simplest form is a ratio of a metal in dissolved and particulate-adsorbed form. Changing hydrologic conditions and site-specific factors for the Ohio River require a more dynamic assessment of the translator; primarily recognition of the availability of metal adsorption sites. Site-specific metal translators for the Ohio River are of two basic types:

- the geometric mean of paired observations of dissolved and total recoverable concentrations allowing direct calculation of fraction dissolved.
- a linear regression of dissolved fraction and total suspended solids to arrive at site-specific partition coefficients

This document illustrates the process of determining appropriate translators for the Ohio River as set forth in the USEPA guidance, *The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion* (USEPA, 1996a). In addition to proposing translators for inclusion in ORSANCO Pollution Control Standards, this report is intended as an agency specific framework for the institution of translators for other metals. The selection and defense of translator calculation methods for ten metals in the Ohio River also provides a basis for periodic revision of those translators in the future.

ORSANCO Clean Metals Program

Historical ORSANCO metals data, collected by standard grab sample techniques for total recoverable metals analysis, in the past indicated violations of Aquatic Life Use Criteria[1]. In October 2000 the Commission adopted dissolved metals criteria as a better indicator of aquatic life impairment since the dissolved portion of metal contaminants is the more toxic and bioavailable component. A sampling plan was implemented to characterize dissolved metals concentrations in the Ohio River to support dissolved metals criteria and the development of numeric translators for dissolved metals.

The ORSANCO Clean Metals Program now samples at all 17 of its Ohio River main stem Bimonthly Sampling Program locations for dissolved and total recoverable metals. The Program uses a modification[2] to the clean technique devised by the Virginia Department of Environmental Quality for laboratory analysis by EPA method 1638. Sampling data from the Clean Metals Program, collected since 1998 at three stations and at all Ohio River stations since 2003, has indicated no violations of dissolved criteria.

Clean Sampling Technique

The clean technique for dissolved and total recoverable metals is based around non-contact collection of stream water through a peristaltic pump and Teflon® tubing approved by USEPA for the collection of metals samples. Use of this equipment eliminates a sampler's direct contact with the containers and stream sample itself and minimizes exposure of the sample and container to ambient air. All tubing and containers used for collection are cleaned, rinsed, and double-bagged by the laboratory to prevent contamination during transport and storage. Sampling equipment is manipulated with gloved hands only. The modified one-person method used by

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[1] Cd, Cu, Pb, Zn were the cause of "partially supporting" (>10% criteria violations) designations, 305b assessments 1990-1991, 1992-1993, 1994-1995, 1996-1997.

[2] Procedure modification allows a two-person technique to be performed by an individual sampler

ORSANCO designates one gloved hand “dirty hand” and the other “clean hand” in place of segregating clean and dirty tasks to a two-person team. Standard operating procedures for the ORSANCO modified method are available on the ORSANCO website (ORSANCO, 1998).

Grab sample collection for the ORSANCO Clean Metals Program begins by submerging a laboratory pre-cleaned 4-liter bottle. The bottle is kept sealed in two layers of plastic until the time of collection. Grab sample bottles are filled and emptied using pre-attached tubes to prevent outside contamination. Sample bottles are filled from the 4-liter grab by a peristaltic pump and pre-attached tubes. The dissolved portion of the sample is passed through a disposable 0.45 micron filter; while the total recoverable portion is pumped directly, without a filter.

One blank sample is collected with each stream sample. Prior to filtering the sample the filter is rinsed in the field with one-liter of blank water provided by the laboratory. The rinsed filter is used to collect a one-liter blank. The filter is then purged of blank water using water from the grab sample. Following the filter purge one liter of stream water is filtered from the constantly agitated sample to represent the dissolved portion. One liter of sample water is also transferred to a sample container with the filter removed; this sample represents the total recoverable portion. The filter is discarded after collection of each stream water sample. Samples are held on ice for overnight delivery to the laboratory.

Laboratory Analysis

All ORSANCO Clean Metals Program samples are analyzed by the Virginia Department of General Services, Division of Consolidated Laboratory Services (DCLS) in Richmond, Virginia. DCLS is equipped to prepare and analyze water samples by USEPA *Method 1638, Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma – Mass Spectrometry* (USEPA, 1996b) This method details rigorous quality assurance procedures to eliminate contamination of water samples in the field and once received for analysis by the laboratory.

Available Data

ORSANCO began its clean and dissolved metals program in January 1998 with a demonstration study at several sample locations near Cincinnati, Ohio. In July 1999 the program was expanded to five Ohio River sample locations. Five more sample locations were added in July 2000 and three each of the following years in July of 2001 and 2002. Greenup Lock and Dam, near Ashland, Kentucky was the last of the seventeen Ohio River sample locations to be included in January 2003.

Differing periods of record for each station and the varying rates of dissolved metal detections (see Appendix A, Tables 1 and 2) do not allow the calculation of translators for all metals at all Ohio River stations. Ohio River bimonthly Clean Metals Program grab samples are analyzed for concentrations of eighteen metals:

- Aluminum
- Antimony
- Arsenic
- Barium
- Cadmium
- Calcium
- Chromium
- Copper
- Iron
- Lead
- Magnesium
- Manganese

- Mercury
- Nickel
- Selenium
- Silver
- Thallium
- Zinc

Data used for translator development (collected through July 2005) met or exceeded the minimum data requirements for ten metal species at eleven stations, with a very few exceptions. Site-specific translators have been developed for the following Ohio River stations:

- Anderson Ferry, Ohio
- R.C. Byrd Lock and Dam
- Belleville Lock and Dam
- Pike Island Lock and Dam
- Smithland Lock and Dam
- J.T. Myers Lock and Dam
- New Cumberland Lock and Dam
- Hannibal Lock and Dam
- Willow Island Locks and Dam
- Louisville, Kentucky
- West Point, Kentucky

Some translators proposed are the result of aggregated data sets and will cover stations not named above. Translators have been determined for ten metals: aluminum, arsenic, barium, calcium, chromium, copper, magnesium, manganese, nickel, and zinc.

Too few data points exist for chromium at three stations: New Cumberland, R.C. Byrd, and Louisville; and zinc for three stations: Louisville, J.T. Myers, and Smithland. The sampling station at West Point, Kentucky downstream of Louisville is the only station with enough detections (*n*=36) of selenium to calculate a translator. A single-station translator cannot be evaluated against other Ohio River location-specific data; therefore a West Point selenium translator has not been pursued.

Censoring of Data

Translator guidance requires pairs of detections for both dissolved and total recoverable metals to calculate the fraction dissolved. Therefore all data sets are censored by those cases in which there was a non-detect for a dissolved metal or a data pair compromised by a contaminated blank. When Total Suspended Solids (TSS) has been included in the calculation of a translator a non-detect or absent analysis for TSS also eliminates a data pair.

Data sets for direct-calculated translators were censored as follows: dissolved concentration results higher than the total result for that sample were set equal to the value of the total result. This prevents any C_D/C_T ratio greater than one (100%) from being reported. Censoring of data in this manner resulted in small changes to summary statistics for three parameters: arsenic, calcium, and magnesium. This manner of censoring endorsed by the USEPA Guidance prevents the calculation of artificially high fraction dissolved due to errors in measurement.

Non-detect rates for each metal are presented in Appendix A, Table 2. The non-detect rate for TSS is 2% in this data set and has occurred at only four stations. Lack of paired TSS data does not reduce data pairs below the 20-pair minimum for any station. Contaminated blanks have reduced data sets negligibly with zinc contamination responsible for the rejection of 3% of zinc analyses and aluminum accounting for 1% rejection of aluminum analyses among all events (*N*=485).

Minimum Data Requirements
USEPA guidance (1996) was specific to developing metals translators for discharges and downstream surface waters. ORSANCO's study of Ohio River metals is analogous to the downstream surface water calculation guidance; allowing the estimation of resulting dissolved concentrations from a discharge of a known total recoverable concentration.

The USEPA Guidance document recommends the collection of at least twenty pairs of dissolved and total recoverable observations at all flows or ten pairs of data at low flow. Low flow data are used to create translators applicable to critical conditions only, i.e.: when TSS is low the fraction of dissolved metal is higher and therefore more toxic.

ORSANCO has opted to create translators applicable to all conditions. When data is restricted to pairs collected at low flows (< harmonic mean) only, the locations with sets of data meeting the minimum requirement of ten pairs drops considerably. Expanded applicability of the translator from critical conditions to all flow conditions when using data from all conditions, and the increased number of stations for which translators could be calculated was the deciding factor in the data set used for translator calculation.

Translator Calculation Methods

Site-specific metal translators for the Ohio River are of two primary types:

- Direct-Calculated Translators: the geometric mean of available observations of paired dissolved and total recoverable concentrations allowing direct calculation of fraction dissolved.
- Site-Specific Partition Coefficients: based on a linear regression of dissolved fraction and total suspended solids to arrive at partition coefficients

These primary calculation methods have been applied to individual station data as well as aggregated data sets from General Ohio River regions in order to improve confidence in the estimation of means (direct-calculated) and regressions (partition coefficient).

For metal species that do not display correlation between fraction dissolved and TSS the direct-calculation of translators is most appropriate. Translators have been calculated by this method for all species without fraction dissolved correlation with TSS and those for which the regression-based partition coefficient was unsatisfactory (regressions examined by various diagnostics discussed below).

Direct-Calculated Translators
The direct-calculated translator is simply the best measure of central tendency for the sample population of observed dissolved fractions. Determination of the appropriate measure (arithmetic mean, geometric mean) is made by selection of a transformation that normalizes the data. In most cases that measure is the first recommended by USEPA, the geometric mean of the fraction dissolved. Twenty-fifth and seventy-fifth percentiles of fraction dissolved are also provided in Appendix B, Table 1 for basic reference points indicating the variance of fractions observed. Cases in which the quartiles are disparate indicate the varying conditions during sampling events have had an impact on the dissolved portion of the metal. This indicator is used largely as an impetus to further examine the partition coefficient method.

Various tests for normality were employed to satisfy the assumption of the geometric mean as a measure of central tendency and the normality requirements of regression analysis. Primary confirmation of normality was provided by visual inspection of probability plots and histograms of untransformed and log-transformed raw data and regression residuals[3]. A skewness test of both populations and of predicted and observed residuals provided the numerical basis for selecting transformed or untransformed populations to meet the required assumptions of normality.

Skewness measures a distribution's asymmetry as a difference from the normal distribution. The farther a mark from zero, the less like a normal distribution it is. The skewness numbers in Table 1 show that for barium, nickel, and copper the untransformed population better fits the normal distribution than the transformed data set. Further transformation (arcsine square root) and more powerful tests (Shapiro-Wilks and Kolmogorov-Smirnov with Lillefors) were pursued to explore these three cases. Due to minor improvements afforded by the alternate transformation and the increased complexity of using multiple transformations for a set of translators the untransformed data (arithmetic mean) was used for the translator. In Table 1 bold type indicates the transformation used for analysis.

Table 1. Skewness of Dissolved Fraction ($F_D = C_D/C_T$) Distributions

	Ba	Ni	Cu	Mn	Zn	Cr	As	Al	TSS	Ca	Mg
C_D/C_T	**-0.85**	**-0.08**	**-0.12**	1.04	2.58	1.72	1.81	2.50	2.98	4.51	8.94
$\ln (C_D/C_T)$	-1.78	-1.12	-1.05	**-0.58**	**-0.45**	**-0.41**	**-0.41**	**-0.16**	**0.30**	**1.35**	**2.50**
$Sin^{-1}\sqrt{(C_D / C_T)}$	-0.42	-0.03	-0.09								

Site-Specific Partition Coefficients

Site-specific partition coefficients are the preferred basis of calculating the dissolved metal translator when the fraction dissolved demonstrates a correlation with TSS. Site-specific partition coefficients (K_P) are developed using the three equations below from the 1996 EPA guidance:

$$C_P = C_T - C_D \tag{1}$$

$$K_p = C_P /(C_D \bullet TSS) \tag{2}$$

$$f_d = (1 + K_p \bullet TSS)^{-1} \tag{3}$$

Where: C_P = adsorbed metal concentration
C_T = total recoverable metal concentration
C_D = dissolved metal concentration
K_P = partition coefficient
f_d = fraction dissolved

With Equation 3, an estimated dissolved concentration of a metal from the concentration of total recoverable metal can be calculated given a site-specific partition coefficient and the concentration of total suspended solids at the time of interest.

Assumptions required by the selection of the partition coefficient method are that a significant correlation of a dissolved fraction with TSS is determined, the normality of the data set, and normality of linear regression residuals is established. Fraction dissolved correlation with TSS

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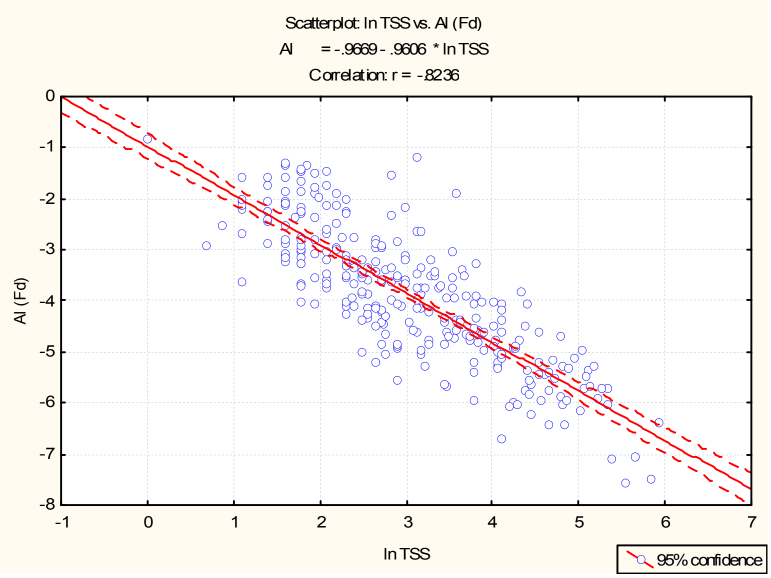
[3] Regression residuals here are measurements in the y-direction from an observation to the regression line

and slope of correlation were found to be significant for nine of the ten metals species for which minimum data requirements were met.

Test for Correlation of Dissolved Fraction with TSS

Correlation of aluminum with TSS is apparent in Figure 1. A clear decline in fraction dissolved with increasing TSS is evident from the negative slope (-0.96) and high R-value (0.8). Similar scatter plots for each metal, associated correlation values and p-scores are presented in Appendix C. It is apparent from the correlation values in Table 1 that dissolved fractions of Calcium and Magnesium have the weakest correlations with TSS, however due to the large sample sizes (*n*=288) the correlation of magnesium with TSS is considered very significant (p<0.025) despite its weak R value.

Figure 1. Aluminum fraction dissolved (Fd) Correlation with TSS



The slope of the regression directly relates to the impact the TSS value will have on the calculated fraction dissolved. The calcium translator has been pursued without the inclusion of TSS in the regression analysis due to its insignificant correlation and very low slope (0.001). A partition coefficient for magnesium based on TSS was unlikely to prove more reliable than the simple geometric mean of the fraction dissolved but the analysis has been examined as dictated by the significance (p<0.05) of the correlation (Pearson R).

Table 2. Correlation (Pearson R) of Dissolved Ratio with TSS

	Al	As	Ba	Ca	Cr	Cu	Mg	Mn	Ni	Zn
R	-.8236	-.6462	-.7209	.0112	-.5432	-.8143	-.1476	-.5263	-.8586	-.7483
p-score	**p=0.00**	**p=0.00**	**p=0.00**	p=.850	**p=.000**	**p=0.00**	**p=.012**	**p=0.00**	**p=0.00**	**p=0.00**
slope	-0.961	-0.327	-0.161	0.001	-0.415	-0.358	-0.022	-0.731	-0.435	-0.597

Selection of Site-Specific Partition Coefficients

With the data to support the inclusion of TSS development of the translator can continue with calculation of a site-specific partition coefficient. The partition coefficient is obtained by least-squares linear regression (Shi, et. al. as cited by Kinerson, et. al., EPA823-B-96-007, 1996). After algebraic rearrangement of the equation for fraction dissolved (Equation 3) the slope (b_1)of the resulting line becomes the calculated partition coefficient (b_1=K_P):

$$(Ct/Cd)-1 = Kp \bullet TSS \qquad (4)$$

In determining the line of TSS vs. (Ct/Cd)-1 with slope Kp it is important to note that the intercept of the line must be set to zero. This requirement is due to the intercept being the intersection of two real places in the relationship: that of zero suspended solids and zero particulate metal (100% dissolved metal). Equation 4 equals zero when TSS is zero or when *Cd* accounts for 100% of total concentration. Therefore the slope of Kp cannot include an intercept that violates this assumption.

On a site-specific basis, beyond the basic significance test for if a slope is different from zero, the translator must be tested for a slope that matters in real-world conditions. That is, in the normal range of TSS conditions and metal concentrations, does the Kp slope indicate differing dissolved fractions in the range of water quality criteria? If a regression slope does not indicate important differences in dissolved fraction then further pursuit of that regression is unwarranted.

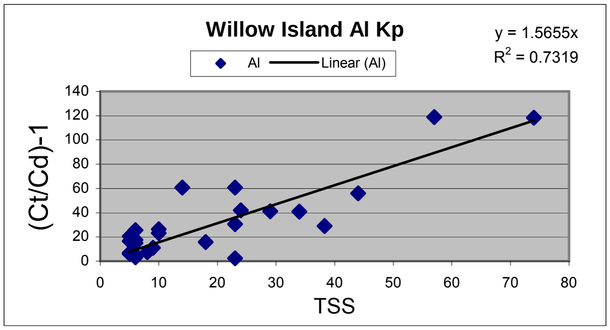
A detailed example of a site-specific regression calculated partition coefficient and the corresponding direct-calculated translator follows for the case of aluminum at Willow Island Lock and Dam, an Ohio River sampling station at mile 161.8, near Wheeling, WV.

Case Study: Aluminum Translator for Willow Island Lock and Dam

Of the seventeen ORSANCO Clean Metals Program stations, the period of record at Willow Island Lock and Dam is the median: five years, 31 sample events prior to this study. For this reason it will serve as a good example, typical of a site for which both site-specific partition coefficient and direct-calculated translators can be evaluated.

The quality of the regression of (C_T/C_D)-1 vs. TSS is integral to the efficiency of the partition coefficient-based translator. Forcing the intercept to zero always reduces the ability of a line to fit the data. For the regression to have strength the intercept should be at or near zero when unforced. A smaller shift when the intercept is forced allows for higher r-square values and greater normality in the residuals. At Willow Island when the intercept is included in the line equation improvement in Pearson R is minor: R-square at intercept 2.7 is 0.74 vs. at forced intercept zero R-square is 0.73.

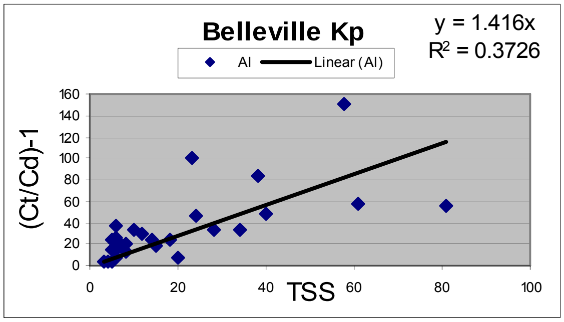
Figure 2



Site	Willow Island
N	26
Slope (kp)	1.49
r-square	0.7355
Intercept	2.7
Residual Mean	-2.7
Residual Skew	-0.2
RMSE	16.0
PRESS	8103
# Residual Outliers	0
High leverage, high influence	0

At Belleville Lock and Dam (Figure 3), one station downstream from Willow Island, the unforced intercept is 4 times as great: 12.7 on the y-axis. The shift in R-square for Belleville is also greater; from r-square 0.45 at intercept 12.7 to r-square 0.37 at intercept 0. Willow Island compares favorably to Belleville and other stations as well in residual skewness and mean. This strength in the Willow Island regression encourages the use of the site-specific partition coefficient.

Figure 3



All partition coefficient regression diagnostics (Appendix D offers narrative explanation of regression diagnostics) for aluminum at Willow Island Lock and Dam describe a strong relationship. The Willow Island table of regression diagnostics included with Figure 2 shows no residual outliers are present, and RMSE and PRESS statistics are in line with other strong aluminum regressions. Diagnostics for all aluminum regressions are shown in Appendix E, Table 1.

Once regression diagnostics are approved, the slope of the line (b_1 = 1.57) of TSS vs. (Ct/Cd)-1 is the regression-based partition coefficient (K_p=1.57) for aluminum at Willow Island Lock and Dam. This site-specific partition coefficient is used in Equation 3 to provide the fraction dissolved (F_D) at representative TSS conditions for the site. The regression based translator is then compared to the direct-calculated translator for a point of reference.

An important factor in deciding to use a site-specific translator with a regression-based partition coefficient is the significance of the Kp slope. Regression analysis would not have been made where a parameter's dissolved fraction did not show dependence on TSS. However, it is apparent from the weakness of some aluminum regressions that dividing sample populations by location restricts the range of TSS and metal concentrations observed and results in a deterioration of the relationship between TSS and dissolved fraction.

Evaluation of Willow Island Translator Types

The translator comparison provides a confirmation of the site-specific partition coefficient's ability to predict fraction dissolved at representative conditions. If the direct-calculated translator (the geometric mean) was selected it would have no ability to respond to different conditions. Table 1 compares translator values (F_D) at three representative TSS conditions. The fraction dissolved at the 25th percentile of TSS vs. the 75th has Relative Percent Difference (RPD) of 112% one of the largest found in the Ohio River data set.

Table 3. Comparison of Site-specific Aluminum Translators for Willow Island Lock and Dam

Method 1: Site-specific K_p K_p = 1.5655 $F_d = (1+K_p*TSS)^{-1}$	**F_d**		**Method 2: Direct Calculated** Statistics from Observed Fraction Dissolved (*n*=29)	**F_d**
TSS 75th percentile (23 mg/L)	2.7%		F_d 25th percentile	2.4%
TSS Geometric mean (10mg/L)	**6.0%**		F_d Geometric mean	**5.0%**
TSS 25th percentile (6 mg/L)	9.6%		F_d 75th percentile	8.5%

In this case the partition coefficient translator is considered superior to the geometric mean because it is known the geometric mean does not accurately represent all conditions. Indeed if the population is reasonably represented by the quartiles half of all observations made would fall outside these ranges and the error produced by the static geometric mean translator could over or underestimate the concentration of dissolved aluminum by more than 50%.

Ohio River Metals Translators

Translators have been proposed for ten metals at eleven Ohio River sampling stations. Regression-based site-specific partition coefficients have been examined for all metals which show a significant correlation with TSS (Table 1) and which have available data sets with TSS meeting the twenty pair requirement. Stations not meeting the required TSS data set are Hannibal, Louisville, J.T. Myers, and Smithland. For these stations only the direct-calculated translator could be used. Seven stations are examined for the site-specific partition coefficient. A table of all recommended translators by location and type is presented later under the heading Recommendations.

Aggregated data sets comprised of all stations in three river segments have also been examined. By aggregating data sets we are able to include stations with shorter periods of record; those that have been eliminated from other translator calculation methods because of a lack of data. Aggregation of data allows the proposal of translators that cover the entire river. Three river segments: upper, middle, and lower, were selected for comparable length, homogeneity of observations, and hydrologic considerations including the location of major tributaries. Translators proposed on an individual site-specific basis will exclude river segments and stations without enough data to avoid the complication of selecting a method for interpolation or the aggregation of different segments.

River segments selected are as follows: miles 0-265 are upper river, represented by five sample points from mile 54 to mile 204. The downstream end of this segment, mile 265, is the confluence of the Ohio River with the Kanawha River, a major tributary contributing on average one-quarter the combined downstream discharge. The middle river, miles 266 to 630 is represented by six sample points from R.C. Byrd Locks and Dam at mile 279 to Louisville, Kentucky at mile 600. The start of the lower river segment is the confluence of the Salt River at mile 630; this segment is represented by a nearby sample location at West Point, Kentucky and five more stations ending at mile 940 with Lock and Dam 52.

In the following parameter-specific tables of proposed translators an inverse relationship is often seen in comparing direct-calculated and site-specific partition coefficient dissolved fractions (columns four and five of the respective tables). This is because the representative TSS value used for the fraction dissolved calculation is based on an aggregated data set while the site-specific TSS values can show a small increasing trend over the aggregated segment. Partition coefficients are calculated using site-specific data reflecting that increasing trend within the segments. The benefits of station aggregation are often seen in the elimination of residual outliers as shown in Appendix F.

Aluminum Translators

Aluminum's strong correlation with TSS, second highest r^2 and greatest slope, makes it a good candidate for regression-based partition coefficients. Aluminum fraction dissolved observed throughout the entire data set for the Ohio River varies more in the upper river than across the lower river sampling stations. Extreme observations have been noted at percentages upward of 50% dissolved, however the geometric mean and median fraction dissolved observed is at or below 10% for all stations. The fraction dissolved observed in the upper river is generally greater, most likely due to the lower TSS concentrations observed over the sample period.

Table 4: Aluminum Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	7.3%	5.2%	5.5%
Pike Island			8.0%	5.1%	
Hannibal			5.1%		
Willow Island			4.6%	6.2%	
Belleville			4.4%	6.8%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	3.0%	2.0%	1.7%
Anderson Ferry			1.4%	1.2%	
Louisville			1.1%		
West Point	Lower (630-940)	35.3 mg/L	1.4%	1.6%	0.9%
J.T. Myers			0.8%		
Smithland			0.5%		
Entire River		19.9 mg/L			1.9%

There is agreement in aluminum translators between the direct-calculated method and the partition coefficient methods. Aggregation of stations into river segments has eliminated residual outliers present in the individual station data sets. Aggregated partition coefficients also closely follow the actual fractions observed as indicated by the direct-calculated method. The recommendation for aluminum translators is for site specific partition coefficients based on all stations aggregated into river segments.

Arsenic Translators

Observations of dissolved and total recoverable arsenic show that the element is readily dissolved, median dissolved fractions are greater than 50% for all stations. Arsenic is the only nonmetal (a metalloid) included in this analysis, it shows a solubility similar to that of the alkaline earthmetals, calcium and magnesium. Unlike the alkaline earthmetals dissolved arsenic shows correlation (slope -0.33, r-sq 0.42) with TSS concentrations. This correlation forces us to examine partition coefficients towards the goal of a translator adaptable to varying TSS conditions.

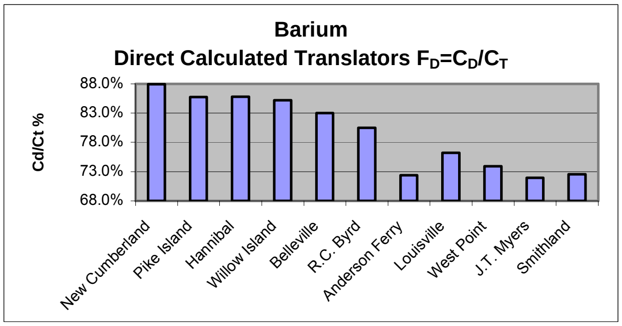
Direct calculated and site-specific translators for arsenic vary over the length of the river from about 55% dissolved at river mile 477 to more than 70% at mile 54. Site specific partition coefficients yield similar results, however the locations of the extremes are disparate. For this reason the recommended translators for arsenic are derived from the aggregated river segment data sets. Because the correlation with TSS is strong the partition coefficient produces the most appropriate translator.

Table 5: Arsenic Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	71.3%	63.9%	72.5%
Pike Island			68.4%	61.0%	
Hannibal			67.7%		
Willow Island			63.8%	74.8%	
Belleville			62.2%	77.3%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	62.1%	60.5%	61.6%
Anderson Ferry			55.7%	57.0%	
Louisville			60.9%		
West Point	Lower (630-940)	35.3 mg/L	61.9%	76.5%	69.1%
J.T. Myers			56.3%		
Smithland			60.9%		
Entire River		19.9 mg/L			74.1%

Barium Translators

Figure 4



The first alkaline earthmetal of three to be examined here is barium. All three earthmetals show weak correlation with TSS and a high solubility of the mineral forms. Geometric means of observed barium dissolved fractions are 70% or greater in all cases. A F_D/TSS slope near zero with a strong r-sq lends strength to the proposed use of direct-calculated translators. Due also to that low slope the 25th and 75th percentiles of observed fractions dissolved have a low relative percent difference of just 23% supporting the geometric mean as a reasonable translator. The magnitude of differences between dissolved fraction geometric means across stations, however, indicates the need to use site-specific geometric means as translators.

A clear trend (see figure 6) is seen in direct translators between the uppermost river station at mile 54 (88%) and the most downstream station at Smithland Lock and Dam, mile 918 (70%) with all but two stations lower than the closest upstream station. The translators proposed result from direct calculation and will be applied on a site specific basis. A good dissolved detection rate (>99%) for barium indicates that stations not meeting the required data set currently should gain it soon, at that time barium translators can be proposed for all Ohio River stations.

Table 6: Barium Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	87.9%	88.6%	91.4%
Pike Island			85.8%	89.3%	
Hannibal			85.8%		
Willow Island			85.2%	93.1%	
Belleville			83.0%	92.4%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	80.5%	82.2%	82.9%
Anderson Ferry			72.4%	80.9%	
Louisville			76.2%		
West Point	Lower (630-940)	35.3 mg/L	73.9%	86.3%	82.5%
J.T. Myers			72.0%		
Smithland			72.6%		
Entire River		19.9 mg/L			88.1%

Calcium Translators

Another alkaline earthmetal, common in it's mineral form ($CaCO_3$) in the Ohio River basin, elemental calcium is abundant in the Ohio River and heavily in a dissolved form. Despite their large fractions calcium and magnesium have the smallest standard deviations among the metals examined here, using the standard deviation divided by the mean expressed as a percent, a measure of relative variance, calcium and magnesium again show the least relative variance at 2% each.

A F_D/TSS slope near zero is partly responsible for the lack of variance among sample locations, however it is clear that the alkaline earth metals in general will be best represented by a river-wide translator based on the geometric mean of all fraction observed. The geometric mean of all calcium fraction dissolved observations (*n*=368) is 90.7%. The proposed dissolved metal translator for calcium at all sampling points is 91% dissolved in all conditions.

Figure 5

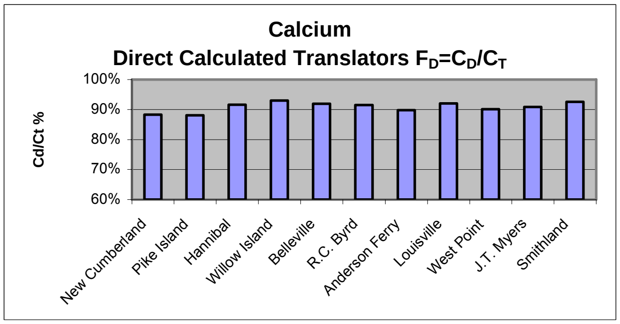


Table 7: Calcium Translators: Fraction Dissolved (Fd) by Direct Calculation Method

Site	River Sections	Direct Calculated $F_D = C_D/C_T$
New Cumberland	Upper (0-204)	88.2%
Pike Island		88.1%
Hannibal		91.6%
Willow Island		92.9%
Belleville		91.9%
R.C. Byrd	Mid (279-600)	91.4%
Anderson Ferry		89.8%
Louisville		92.0%
West Point	Lower (630-940)	90.0%
J.T. Myers		90.8%
Smithland		92.5%
Entire River Geometric Mean		90.7%

Chromium Translators

A lack of detections for chromium with paired TSS data contributes to little confidence in proposing partition coefficient-based translators river-wide for this metal. Given the information currently available, 20 dissolved and total detection pairs for eight of seventeen stations, the direct calculation method is the best choice. A good correlation with TSS (slope -0.42, r-sq 0.65) slope indicates that a single translator for the entire length of the river may not be a good choice. The variability of the direct calculated translators available confirm multiple translators will be necessary.

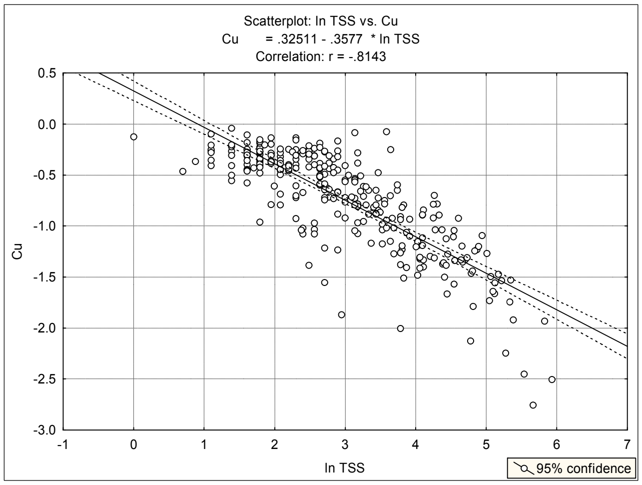
Table 8: Chromium Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L			43.8%
Pike Island			31.0%		
Hannibal					
Willow Island			24.8%		
Belleville			25.0%	52.2%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	20.6%		19.9%
Anderson Ferry			15.6%		
Louisville					
West Point	Lower (630-940)	35.3 mg/L	18.1%	11.6%	21.9%
J.T. Myers			17.9%		
Smithland			13.0%		
Entire River		19.9 mg/L			30.6%

In this case a direct-calculated translator by aggregated data set is the best choice. The stations with sufficient data sets available hint that the upper, middle, lower segments align with the arithmetic average of their geometric means at 27%, 18%, and 16% respectively. A separate calculation of geometric means using all data in each segment was performed with similar results and the three recommended translators: upper river 28%, middle river 18%, and lower river 16%.

Copper Translators

Figure 6



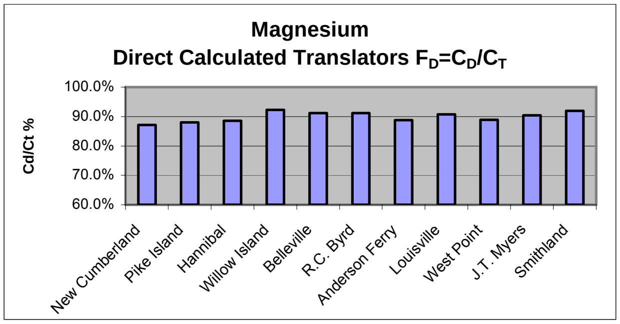
Though copper has a flatter slope in its dissolved fraction correlation with TSS than aluminum (-0.36 vs. -0.96 for Al) it is like aluminum in the tightness of that regression (Figure 6) with an r-sq of 0.66 (*n*=289) the third highest in the group. Another consideration is the increasing importance of including TSS in the translator in the downstream direction. The 25th and 75th percentiles of the fractions observed at mile 54 are 0.58 and 0.75 respectively (RPD = 25.2%), while at mile 918 they are 0.30 and 0.64 respectively (RPD = 71.4%). The high variance of the fractions observed in the lower river indicates the best translator will account for the role of particulate adsorbents (TSS). For this reason the partition coefficient-based translator derived from aggregated river segments is recommended here.

Table 9: Copper Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	66.1%	63.7%	68.0%
Pike Island			63.4%	57.1%	
Hannibal			60.7%		
Willow Island			62.4%	73.6%	
Belleville			61.5%	70.3%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	54.5%	47.2%	52.9%
Anderson Ferry			47.8%	49.4%	
Louisville			48.5%		
West Point	Lower (630-940)	35.3 mg/L	47.5%	58.8%	55.6%
J.T. Myers			46.7%		
Smithland			46.5%		
Entire River		19.9 mg/L			64.6%

Magnesium Translators

Figure 7



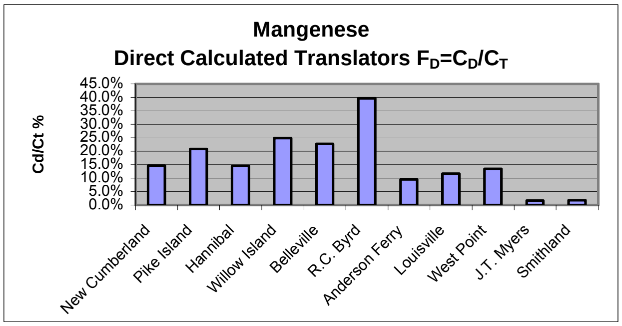
An alkaline earth metal with 90% of observed dissolved fractions greater than 80% of total concentration and very little correlation with TSS, the magnesium translator proposed is based on the direct calculation method. Dissolved fractions of magnesium are similar to that of calcium and encourage the use of all available data to arrive at the best measure of central tendency. The proposed translator for magnesium is the geometric mean of all dissolved fractions observed (*n*=288) on the Ohio River: 90%.

Table 10: Magnesium Translators: Fraction Dissolved (Fd) by Direct Calculation Method

Site	River Sections	Direct Calculated $F_D = C_D/C_T$
New Cumberland	Upper (0-204)	87.1%
Pike Island		88.0%
Hannibal		88.6%
Willow Island		92.3%
Belleville		91.1%
R.C. Byrd	Mid (279-600)	91.1%
Anderson Ferry		88.8%
Louisville		90.7%
West Point	Lower (630-940)	88.9%
J.T. Myers		90.4%
Smithland		91.9%
Entire River Geometric Mean		89.9%

Manganese translators

Figure 8



One of the highest variability by station is for fraction dissolved of manganese. The standard deviation of station observed fraction geometric means divided by their mean is greater than 60%, second only to aluminum. This could be related to dissolved manganese's low, yet still significant (p=0.00) correlation with TSS (slope -0.73, r-sq 0.28) however a declining longitudinal trend reflective of the higher TSS levels observed in the lower river is not apparent.

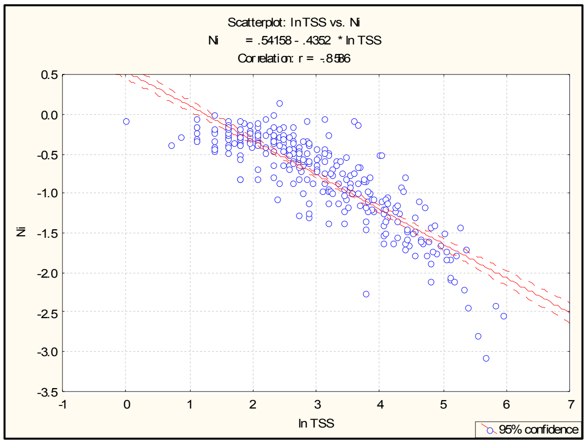
Site specific partition coefficients are weak for manganese because each regression with the exception of Willow Island has at least one residual outlier. Willow Island's regression-based Kp yields a fraction dissolved very close to that observed at the station, the relative percent difference between the methods is just 6%. Kp based on aggregated data sets are only slightly better, confirmed by low r-square values and residual means far from zero. The high variability in dissolved fractions observed and the lack of quality in the Kp regressions leave the site-specific direct calculated method the preferred translator. High variability, in excess of confidence limits for the mean ($\alpha=0.05$), also prohibits the use of aggregated data sets to cover sections of the river that do not have enough data pairs. Recommended translators are site-specific direct-calculated geometric means.

Table 11: Manganese Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	14.6%	6.9%	13.6%
Pike Island			20.9%	12.5%	
Hannibal			14.5%		
Willow Island			24.9%	23.5%	
Belleville			22.8%	10.6%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	39.7%	33.3%	6.2%
Anderson Ferry			9.5%	7.6%	
Louisville			11.7%		
West Point	Lower (630-940)	35.3 mg/L	13.4%	7.3%	3.1%
J.T. Myers			1.7%		
Smithland			1.8%		
Entire River		19.9 mg/L			6.2%

Nickel Translators

Figure 9



The correlation of dissolved nickel with TSS is the strongest of the group with an r-square of 0.74 and a slope of -0.44 (see figure 9). Observed dissolved fractions vary by an average 54% RPD (see Appendix B, Table 2). This average discrepancy between the 25th and 75th percentile fractions observed combined with the clear TSS correlation shown at right is likely due to varying TSS conditions.

Partition coefficient regressions for nickel were worse than expectations based on the high correlation with TSS. Regression weakness is indicated by residual outliers for most stations and outliers with high leverage at three of seven candidate stations. Aggregated data sets yield better results for Kp regressions. A single high-leverage residual outlier is found the in mid-river segment, a regression based on 116 data points that is more resistant to such outliers.

The tendency for the Kp to overestimate the geometric mean of observed fractions dissolved is less important than its ability to predict fractions dissolved at higher and lower TSS conditions. Due to strong correlation with TSS and strong regressions based on aggregated data sets the translators proposed are partition coefficients based on those aggregated sets.

Table 12: Nickel Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	74.1%	73.8%	74.8%
Pike Island			72.8%	76.2%	
Hannibal			66.9%		
Willow Island			67.4%	73.3%	
Belleville			66.1%	74.9%	
R.C. Byrd	Mid (279-600)	26.8 mg/L	57.4%	47.8%	48.8%
Anderson Ferry			44.9%	41.7%	
Louisville			41.8%		
West Point	Lower (630-940)	35.3 mg/L	46.1%	54.7%	47.0%
J.T. Myers			40.8%		
Smithland			40.4%		
Entire River		19.9 mg/L			59.1%

Zinc Translators

Development of translators for zinc is hampered by a low detection rate, 67% dissolved detection, about the same as for chromium. Low detection rates reduce the number of stations with sufficient data sets and the number of data points in each possible partition coefficient analysis.

Dissolved zinc's correlation with TSS is strong however (*n*=194, slope -0.6, r-square 0.56); absolute slope of that relationship is the third highest in the group of metals. Kp regressions were also fairly strong with no residual outliers. Use of the partition coefficient based on aggregated data sets is recommended to fill the gaps between stations with sufficient data and to account for changing TSS conditions.

Table 13: Zinc Translators: Fraction Dissolved (Fd) by Direct Calculated and Site-Specific Partition Coefficients

Site	River Sections	Representative TSS Condition (geometric mean)	Direct Calculated $F_D = C_D/C_T$	Fd at Site-Specific K_P $F_D = (1+K_P*TSS)^{-1}$	
				F_D at Rep. River Section TSS	Fd by Aggregated Data Set K_P
New Cumberland	Upper (0-204)	9.7 mg/L	41.9%	32.2%	33.4%
Pike Island			34.4%	39.7%	
Hannibal					
Willow Island			28.4%	27.7%	
Belleville			28.6%		
R.C. Byrd	Mid (279-600)	26.8 mg/L	30.2%		19.9%
Anderson Ferry			21.2%	20.6%	
Louisville					
West Point	Lower (630-940)	35.3 mg/L	19.2%	27.8%	25.4%
J.T. Myers					
Smithland					
Entire River		19.9 mg/L			29.5%

Conclusions and Recommendations

The development of Ohio River translators is not complete. Sites with insufficient data still exist. Translators for the ten metals examined in this document are likely to be developed for other sites in the future because the ORSANCO Clean Metals Program continues to gather data. Detection rates of these ten metals are sufficient to expect complete data sets after two more years of data collection. Greenup Lock and Dam, the final station to be included in the program, will be the last to gain the required set of twenty paired detections. This is estimated to occur by the summer of 2007. Laboratory data from samples collected July 2007 should be available for analysis late in the fall of 2007.

The ten metals that translators have been proposed for have dissolved detection rates better than 60% while most top 98% detection rates. Selenium is unique with a detection rate of 43%; other metals not included here have detection rates less than 5% (see Appendix A, Table 2). Translators for Selenium can be expected, however a timetable is not clearly foreseen. Chromium and zinc, both metals employing aggregated data sets for this analysis, have 64% and 67% detection rates. A review of translators in the future with extended data sets should improve confidence in these two metals as well as the entire set of translators proposed at this time. A triennial review of translators is recommended and could be scheduled to coincide with triennial revisions of the ORSANCO Pollution Control Standards.

Table 15, Proposed Metals Translators for the Ohio River, summarizes proposed translators for the length of the Ohio River. Translators are shown as they should be applied, with their numerical values truncated to two significant figures. Two significant figures is the lowest common denominator of data provided by the laboratory responsible for Method 1638 analysis.

The method of calculation for each translator presented in Table 15 is indicated as follows: Direct-calculated translators are shown as a factor to be applied to the total concentration (C_T) resulting in an estimated concentration of the metal in dissolved form. For partition coefficient-based translators only the coefficient itself (K_P) is given. The coefficient is applied in Equation 3 to arrive at a fraction dissolved (F_D) for a specific level of suspended solids (TSS). The fraction dissolved at that TSS level is then multiplied by the total concentration to generate an estimated concentration of the metal in dissolved form.

When site-specific translators are proposed, shaded boxes represent sites currently with insufficient data for translator calculation. Direct-calculated translators that do not include shaded locations are the result of calculations on aggregated data sets. Summary numbers of translator types proposed are shown in Table 14.

Table 14: Translator Calculation Method	Number
Direct-Calculated Site-Specific	2
Direct-Calculated Aggregated River Segments	1
Direct-Calculated Entire River Aggregated	2
Partition Coefficient Site-Specific	-
Partition Coefficient Aggregated River Segments	5
Partition Coefficient Entire River Aggregated	-
Total	10

Table 15: Proposed Metals Translators for the Ohio River

Direct-calculated translators shown as a percentage of total concentration (C_T)
Partition coefficients (K_P) given directly, to be applied to any TSS condition*

Site Name (Ohio River Mile)	River Segments	Al	As	Ba	Ca	Cr
New Cumberland (54)	Upper (0-265)	$K_P = 1.8$	$K_P = 0.040$	$0.88*C_T$	$0.91*C_T$	$0.28*C_T$
Pike Island (84)				$0.86*C_T$		
Hannibal (126)				$0.86*C_T$		
Willow Island (162)				$0.85*C_T$		
Belleville (204)				$0.83*C_T$		
R.C. Byrd (279)	Middle (266-629)	$K_P = 2.2$	$K_P = 0.023$	$0.81*C_T$		$0.18*C_T$
Greenup (341)						
Meldahl (436)						
Anderson Ferry (478)				$0.72*C_T$		
Markland (532)						
Louisville (601)				$0.76*C_T$		
West Point (626)	Lower (630-981)	$K_P = 3.0$	$K_P = 0.013$	$0.74*C_T$		$0.16*C_T$
Cannelton (721)						
Newburgh (776)						
J.T. Myers (846)				$0.72*C_T$		
Smithland (918)				$0.73*C_T$		
L&D 52 (939)						

Site Name (Ohio River Mile)	River Segments	Cu	Mg	Mn	Ni	Zn
New Cumberland (54)	Upper (0-265)	$K_P = 0.04$	$0.90*C_T$	$0.15*C_T$	$K_P = 0.035$	$K_P = 0.21$
Pike Island (84)				$0.21*C_T$		
Hannibal (126)				$0.15*C_T$		
Willow Island (162)				$0.25*C_T$		
Belleville (204)				$0.23*C_T$		
R.C. Byrd (279)	Middle (266-629)	$K_P = 0.03$		$0.40*C_T$	$K_P = 0.039$	$K_P = 0.15$
Greenup (341)						
Meldahl (436)						
Anderson Ferry (478)				$0.10*C_T$		
Markland (532)						
Louisville (601)				$0.12*C_T$		
West Point (626)	Lower (630-981)	$K_P = 0.02$		$0.13*C_T$	$K_P = 0.032$	$K_P = .083$
Cannelton (721)						
Newburgh (776)						
J.T. Myers (846)				$0.017*C_T$		
Smithland (918)				$0.018*C_T$		
L&D 52 (939)						

*K_P is applied to this equation: $F_D = (1+K_P*TSS)^{-1}$ to derive fraction dissolved at a given TSS

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Appendix A

Table 1. Period of Clean Metals Record at Ohio River Sample Locations

Site Name	Station Inception	Continued Through	Number of Samples
Anderson Ferry	January-98	Present	41
R.C. Byrd	January-98	Present	42
Belleville	January-98	Present	42
West Point	July-99	Present	37
Pike Island	July-99	Present	38
Smithland	July-00	Present	30
J.T. Myers	July-00	Present	30
New Cumberland	July-00	Present	33
Hannibal	July-00	Present	20
Willow Island	July-00	Present	31
Meldahl	July-01	Present	19
Louisville	August-01	Present	21
Markland	August-01	Present	19
L&D 52	November-02	Present	17
Cannelton	November-02	Present	17
Newburgh	November-02	Present	17
Greenup	January-03	Present	14

Table 2. Dissolved Metal Detection Rates by Parameter

Parameter	Number of Analyses	Percent Dissolved Detections
Al	458	99.56%
Ba	458	99.56%
Ca	458	99.56%
Cu	458	99.56%
Mn	458	99.56%
Mg	458	99.34%
Ni	458	99.34%
As	458	98.91%
Zn	458	67.25%
Cr	458	64.85%
Se	458	43.23%
Fe	458	4.59%
Pb	458	4.15%
Hg*	100/358	2.84%
Ag	458	1.53%
Tl	458	1.09%
Cd	458	0.66%
Sb	458	0.22%

* Hg RDL changed from 0.2 ug/L to 1.5 ng/L in July 2001, detections have increased from 0% to 3.6%

Appendix B, Table 1: Direct Calculated Translators

25th and 75th Percentile and Geometric Mean of Direct-Calculated Translators $F_D = C_D/C_T$

Site Name	Parameter	Al	As	Ba	Ca	Cr	Cu	Mg	Mn	Ni	Zn
New Cumberland	25th percentile	4.7%	54.7%	81.3%	86.3%		58.3%	84.7%	3.1%	66.1%	28.6%
	75th percentile	12.5%	100.0%	95.8%	96.5%		75.1%	96.6%	70.6%	83.9%	68.4%
	geomean*	**7.3%**	**71.3%**	**87.9%**	**88.2%**		**66.1%**	**87.1%**	**14.6%**	**74.1%**	**41.9%**
	count	32	32	32	32	17	32	32	32	32	27
Pike Island	25th percentile	4.3%	62.7%	80.8%	82.7%	21.8%	54.5%	83.1%	8.8%	66.8%	24.8%
	75th percentile	16.8%	98.7%	95.4%	96.4%	51.4%	76.9%	97.3%	65.7%	84.3%	53.9%
	geomean*	**8.0%**	**68.4%**	**85.8%**	**88.1%**	**31.0%**	**63.4%**	**88.0%**	**20.9%**	**72.8%**	**34.4%**
	count	38	38	38	38	23	38	38	38	38	32
Hannibal	25th percentile	2.1%	65.5%	80.5%	88.4%		56.4%	85.7%	3.7%	58.7%	
	75th percentile	13.3%	100.0%	96.1%	100.0%		72.9%	100.0%	56.2%	77.6%	
	geomean*	**5.1%**	**67.7%**	**85.8%**	**91.6%**		**60.7%**	**88.6%**	**14.5%**	**66.9%**	
	count	20	20	20	20	15	20	20	20	20	15
Willow Island	25th percentile	2.4%	44.9%	74.8%	89.8%	16.3%	48.9%	87.0%	14.4%	55.0%	16.9%
	75th percentile	8.4%	92.9%	94.2%	98.5%	40.4%	78.0%	97.8%	63.5%	86.3%	51.4%
	geomean*	**4.6%**	**63.8%**	**85.2%**	**92.9%**	**24.8%**	**62.4%**	**92.3%**	**24.9%**	**67.4%**	**28.4%**
	count	34	34	34	34	22	34	33	34	33	28
Belleville	25th percentile	2.6%	45.7%	77.8%	88.1%	17.3%	46.5%	87.9%	16.7%	51.5%	16.3%
	75th percentile	8.2%	95.0%	92.3%	99.1%	43.4%	76.4%	97.3%	48.8%	78.2%	41.7%
	geomean*	**4.4%**	**62.2%**	**83.0%**	**91.9%**	**25.0%**	**61.5%**	**91.1%**	**22.8%**	**66.1%**	**28.6%**
	count	45	45	45	45	31	45	45	45	45	33
R.C. Byrd	25th percentile	1.8%	52.9%	75.5%	87.0%	12.1%	39.0%	87.5%	36.1%	41.8%	17.3%
	75th percentile	5.6%	77.2%	86.3%	98.1%	31.5%	69.8%	96.0%	64.9%	72.7%	53.7%
	geomean*	**3.0%**	**62.1%**	**80.5%**	**91.4%**	**20.6%**	**54.5%**	**91.1%**	**39.7%**	**57.4%**	**30.2%**
	count	41	39	41	41	20	41	41	41	41	26

Appendix B, Table 1 (cont.): Direct Calculated Translators

Site Name	Parameter	Al	As	Ba	Ca	Cr	Cu	Mg	Mn	Ni	Zn
Anderson Ferry	25th percentile	0.7%	40.0%	65.8%	83.4%	5.6%	34.1%	81.6%	4.0%	29.2%	9.8%
	75th percentile	3.3%	87.8%	87.0%	98.0%	46.0%	67.2%	99.1%	22.6%	66.0%	47.0%
	geomean*	**1.4%**	**55.7%**	**72.4%**	**89.8%**	**15.6%**	**47.8%**	**88.8%**	**9.5%**	**44.9%**	**21.2%**
	count	41	41	41	41	21	41	41	41	41	32
Louisville	25th percentile	0.7%	42.5%	68.9%	85.8%		34.6%	87.0%	4.5%	30.0%	
	75th percentile	2.0%	83.3%	87.4%	100.0%		62.2%	98.6%	26.4%	52.2%	
	geomean*	**1.1%**	**60.9%**	**76.2%**	**92.0%**		**48.5%**	**90.7%**	**11.7%**	**41.8%**	
	count	21	21	21	21	16	21	21	21	21	12
West Point	25th percentile	0.7%	50.5%	67.9%	84.9%	12.1%	29.6%	85.5%	5.5%	26.7%	11.7%
	75th percentile	2.8%	93.5%	88.1%	96.3%	35.1%	64.9%	97.5%	48.6%	64.9%	36.6%
	geomean*	**1.4%**	**61.9%**	**73.9%**	**90.0%**	**18.1%**	**47.5%**	**88.9%**	**13.4%**	**46.1%**	**19.2%**
	count	37	37	36	37	31	37	37	37	37	25
J.T. Myers	25th percentile	0.4%	37.0%	59.7%	85.0%	14.5%	26.6%	87.0%	0.5%	20.6%	
	75th percentile	1.5%	82.1%	88.2%	99.2%	29.6%	69.6%	99.2%	4.8%	62.3%	
	geomean*	**0.8%**	**56.3%**	**72.0%**	**90.8%**	**17.9%**	**46.7%**	**90.4%**	**1.7%**	**40.8%**	
	count	30	30	30	30	21	30	30	30	30	13
Smithland	25th percentile	0.2%	44.5%	56.5%	87.8%	7.9%	30.2%	87.4%	0.7%	20.4%	
	75th percentile	0.7%	88.5%	87.8%	100.0%	22.1%	63.7%	100.0%	4.4%	54.5%	
	geomean*	**0.5%**	**60.9%**	**72.6%**	**92.5%**	**13.0%**	**46.5%**	**91.9%**	**1.8%**	**40.4%**	
	count	29	29	29	29	21	29	29	29	29	12

* Arithmetic means shown for Ba, Cu and Ni

Appendix B, Table 2: Relative Percent Difference in Fraction Dissolved Quartiles

Relative Percent Difference between quartiles of Observed Fraction Dissolved (F_D)

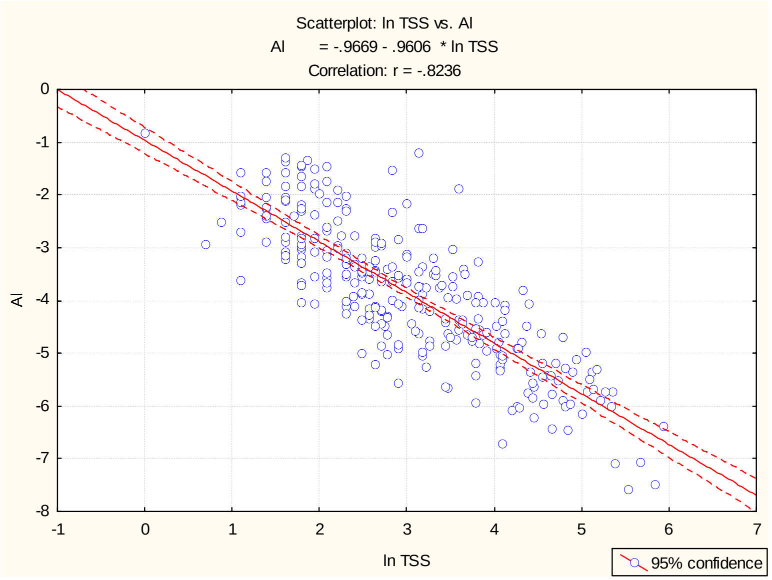
Site Name	Al	As	Ba	Ca	Cr	Cu	Mg	Mn	Ni	Zn
New Cumberland	90.4%	58.5%	16.4%	11.2%	95.2%	25.2%	13.1%	183.2%	23.7%	82.0%
Pike Island	117.9%	44.5%	16.6%	15.3%	81.0%	34.0%	15.7%	152.9%	23.1%	73.9%
Hannibal	146.0%	41.7%	17.7%	12.3%	85.3%	25.6%	15.4%	175.6%	27.7%	61.3%
Willow Island	112.0%	69.6%	23.0%	9.2%	84.8%	45.8%	11.8%	126.2%	44.2%	101.0%
Belleville	104.5%	70.2%	17.0%	11.8%	85.8%	48.7%	10.1%	98.2%	41.2%	87.7%
R.C. Byrd	103.9%	37.3%	13.3%	12.0%	89.1%	56.7%	9.3%	57.1%	54.0%	102.4%
Anderson Ferry	133.9%	74.8%	27.7%	16.1%	156.4%	65.3%	19.4%	140.0%	77.4%	130.9%
Louisville	90.0%	64.9%	23.6%	15.3%	102.3%	57.1%	12.4%	141.7%	54.1%	116.3%
West Point	120.7%	59.8%	25.9%	12.7%	97.2%	74.7%	13.2%	159.0%	83.4%	102.9%
J.T. Myers	109.3%	75.8%	38.5%	15.4%	68.7%	89.5%	13.1%	165.0%	100.7%	76.9%
Smithland	110.8%	66.1%	43.5%	13.0%	94.8%	71.4%	13.5%	145.8%	91.0%	117.1%
Average RPD	**112.7%**	**60.3%**	**23.9%**	**13.1%**	**94.6%**	**54.0%**	**13.4%**	**140.4%**	**56.4%**	**95.7%**

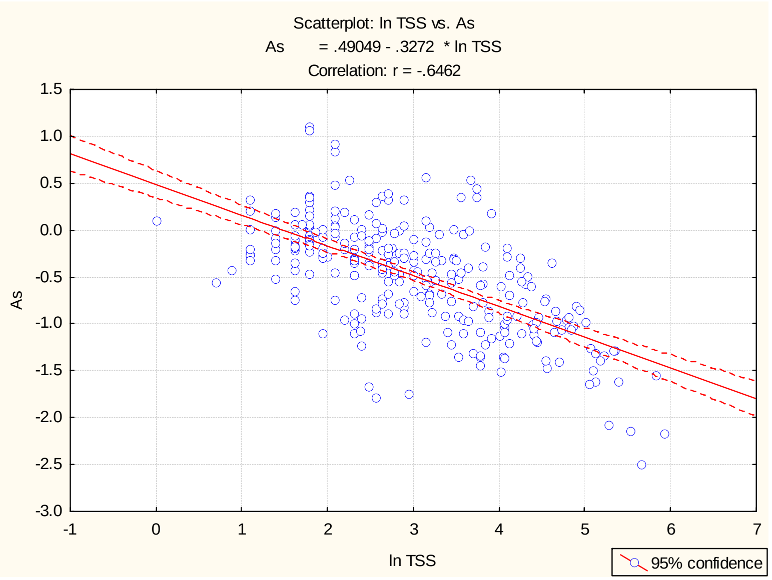
Appendix C.

Table 1. Correlation (Pearson R) of Dissolved Ratio with TSS

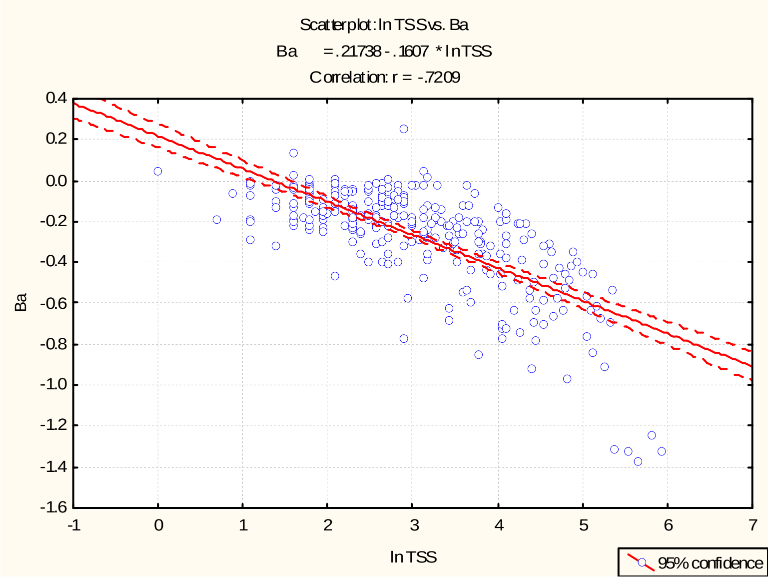
	Al	As	Ba	Ca	Cr	Cu	Mg	Mn	Ni	Zn
R	-.8236	-.6462	-.7209	.0112	-.5432	-.8143	-.1476	-.5263	-.8586	-.7483
N	N=289	N=285	N=289	N=289	N=189	N=289	N=288	N=289	N=288	N=194
p-score	p=0.00	p=0.00	p=0.00	p=.850	p=.000	p=0.00	p=.012	p=0.00	p=0.00	p=0.00
slope	-0.9606	-0.3272	-0.1607	0.0014	-0.4152	-0.3577	-0.0218	-0.7308	-0.4352	-0.5969

Figures 2- 12 Scatterplots log-transformed Dissolved Ratio and TSS



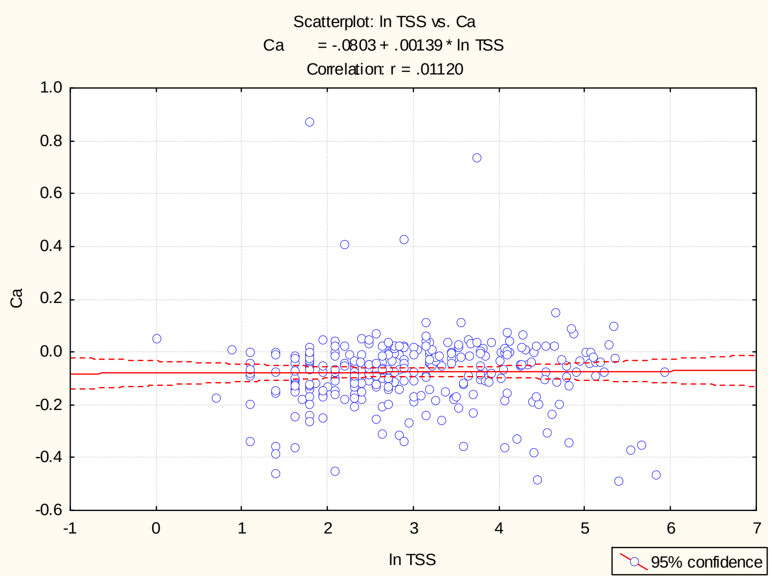


Appendix C.


Scatterplot: ln TSS vs. Ba

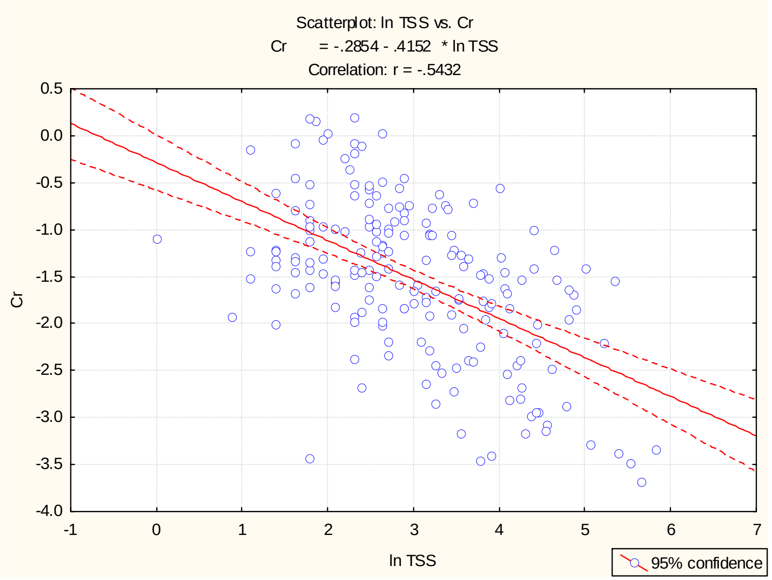
Ba = .21738 - .1607 * ln TSS

Correlation: r = -.7209


Scatterplot: ln TSS vs. Ca

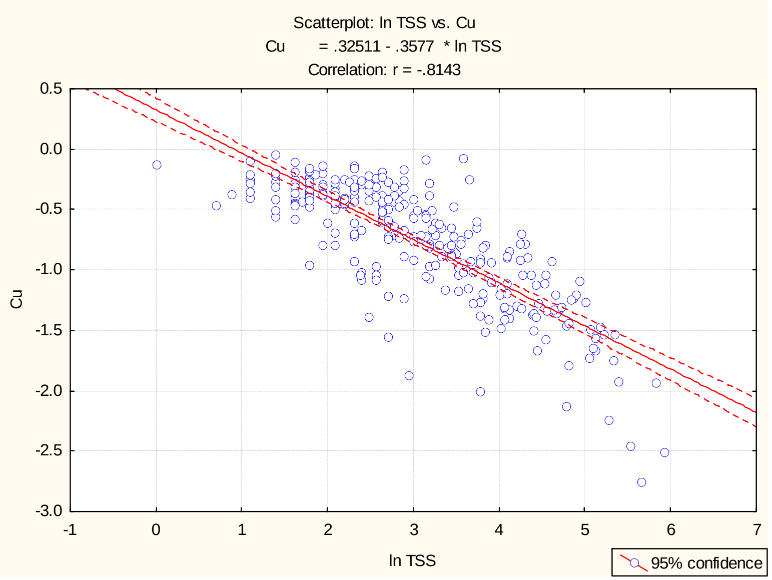
Ca = -.0803 + .00139 * ln TSS

Correlation: r = .01120


Scatterplot: ln TSS vs. Cr

Cr = -.2854 - .4152 * ln TSS

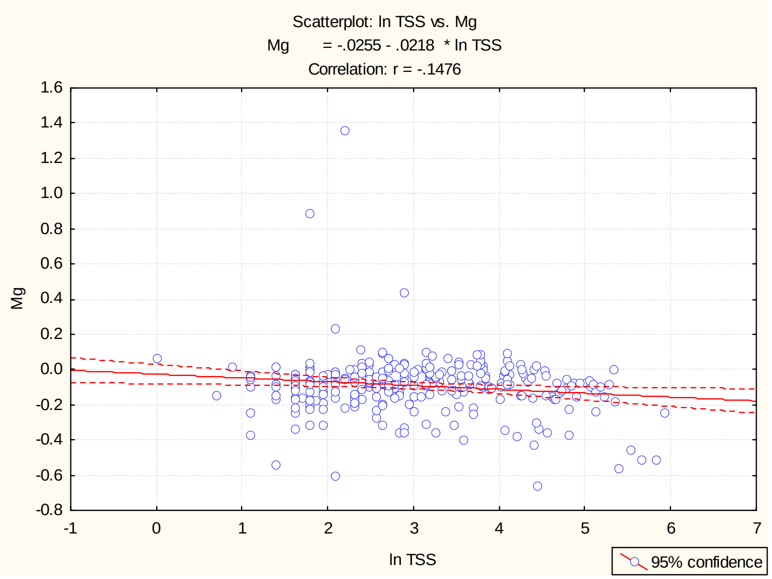
Correlation: r = -.5432


Scatterplot: ln TSS vs. Cu

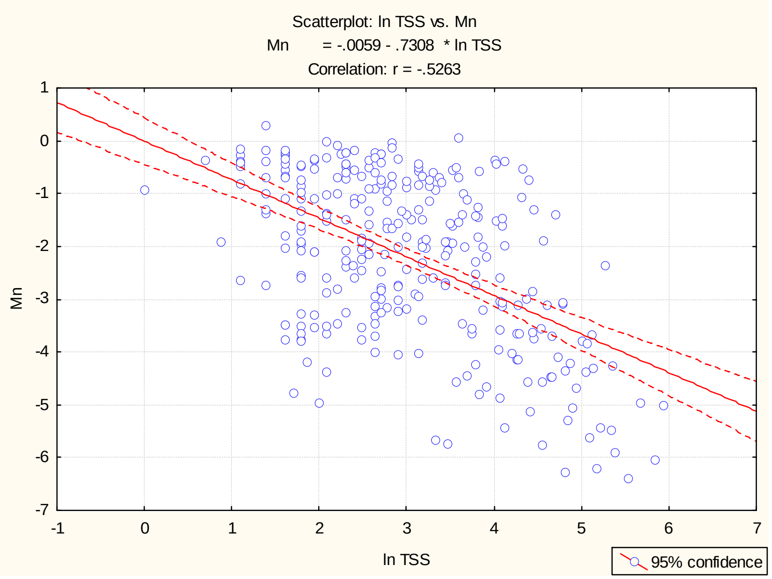
Cu = .32511 - .3577 * ln TSS

Correlation: r = -.8143

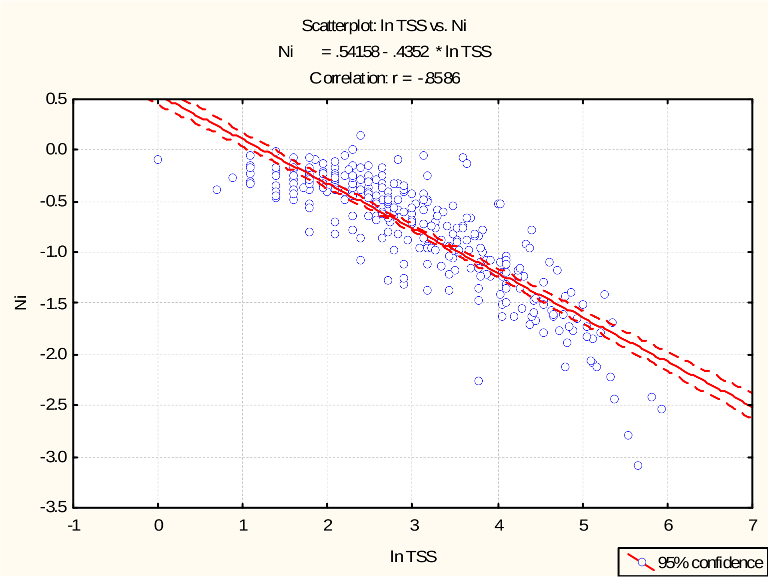
Appendix C.



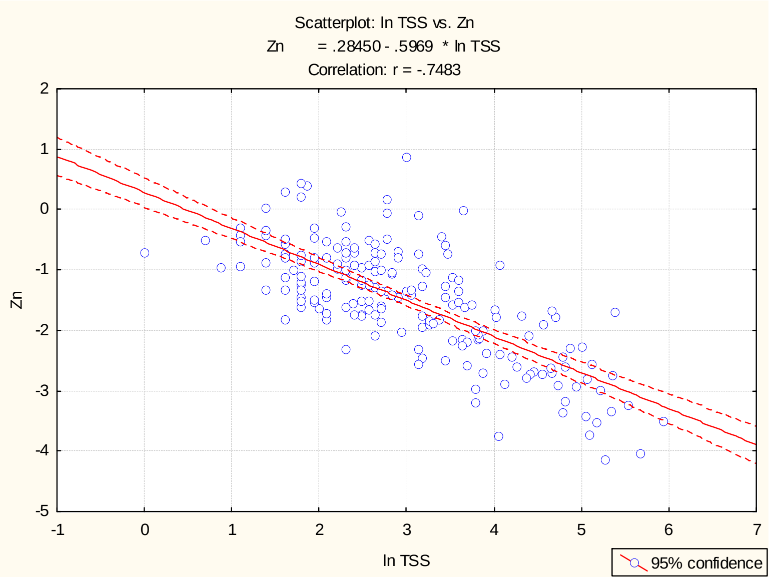
Scatterplot: ln TSS vs. Mg
Mg = -.0255 - .0218 * ln TSS
Correlation: r = -.1476
Mg
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1
0
1
2
3
4
5
6
7
ln TSS
95% confidence



Scatterplot: ln TSS vs. Mn
Mn = -.0059 - .7308 * ln TSS
Correlation: r = -.5263
Mn
1
0
-1
-2
-3
-4
-5
-6
-7
-1
0
1
2
3
4
5
6
7
ln TSS
95% confidence



Scatterplot: ln TSS vs. Ni
Ni = .54158 - .4352 * ln TSS
Correlation: r = -.8586
Ni
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-1
0
1
2
3
4
5
6
7
ln TSS
95% confidence



Scatterplot: ln TSS vs. Zn
Zn = .28450 - .5969 * ln TSS
Correlation: r = -.7483
Zn
2
1
0
-1
-2
-3
-4
-5
-1
0
1
2
3
4
5
6
7
ln TSS
95% confidence

Appendix D: Regression Diagnostics Narrative

Several regression diagnostics have been used to evaluate the quality of site-specific partition coefficient regressions. Statistics employed for regression diagnostics are largely those suggested by Helsel and Hirsh in their text "*Statistical Methods in Water Resources*" (USGS, 2002). Frequently Pearson R (or r-square) is relied upon as the primary diagnostic in regression analysis, however the various sample sizes and importance of regression strength make r-square inadequate for selection of appropriate partition coefficients.

The requirement of zero intercept (which reduces R values) in the regression analysis of Kp increases the importance of the test for normality of residuals as a benchmark for a valuable regression model. The residuals of the regression model are simply the differences between the model-predicted values and the observed values (y predicted for given x minus y observed at x). Residuals of a good regression model should be both normally distributed around zero and of minimum magnitude. Residuals are denoted "e_i" as is useful when including the term in further equations.

Several indicators of the adequacy of regression have been employed. These are the Pearson r and its square, the Root Mean Squared Error (RMSE) and the Prediction Error Sum of Squares (PRESS). R-square is a coefficient of regression commonly used to indicate the portion of variability in y explained by the independent variable x. Slopes highly influenced by one point are indicative of weak regressions regardless of their sometimes high Pearson correlation coefficient (R or R^2). Unfortunately r-square is easily affected by data points toward the high end of the x-axis, this is referred to as "leverage"; is quantified by Equation 1 and denoted h_i.

Points with large residuals, negative or positive, are also considered points with high influence. Standardized residuals, denoted e_{si}, have been used to identify observations with high influence. Equation 2 details the calculation of standardized residuals. It is the combination of these two conditions that contribute to misleading r-square values and resulting slopes.

$$h_i = \frac{1}{n} + \frac{(x_i - \bar{x})^2}{SS_x} \tag{1}$$

$$e_{si} = \frac{e_i}{s\sqrt{1-h_i}} \tag{2}$$

Where: SS_x - Sum of Squares of x
e_i – Residual, (predicted – observed)
s - standard deviation of the residuals

If an observation has high leverage (h_i > 3p/n) and is an extreme outlier as quantified by the standardized residual (e_{si} >3) but it cannot be discounted for any other reason, the translator partition coefficient regression has been abandoned until further data collection can improve the regression. Data points with high leverage and high influence (e_{si} > 2.5) are also noted for their influence on the regression slope. The number of observations meeting the above criteria has been provided for each regression in Appendix E, Tables 1-8.

To avoid the selection of site-specific partition coefficients based on weak relationships each regression has also been scored with two summary statistics, the RMSE and PRESS. The root mean squared error is a measure of the overall goodness of fit the regression line provides, yet is comparable only among models with identical units and transformations. The PRESS statistic is similarly a measure of the whole model, not a measure of individual observations, and is comparable only among data of the same type. The advantage of the PRESS statistic is that it computes the summed error of the regression as if each observation had been left out of the equation before its residual is calculated. This is indicated by the symbol (*i*) added to that of the residual ($e_{(i)}$).

As stated above the RMSE and PRESS statistics can only be compared within metal species among the other stations. Root mean square error is calculated with Equation 3 while prediction error sum of squares is calculated by Equations 4 and 5. These statistics are also provided for each regression in Appendix E, Tables 1-8.

$$RMSE^2 = \sum_{i=1}^{n} e_i^2 /(n-2) \tag{3}$$

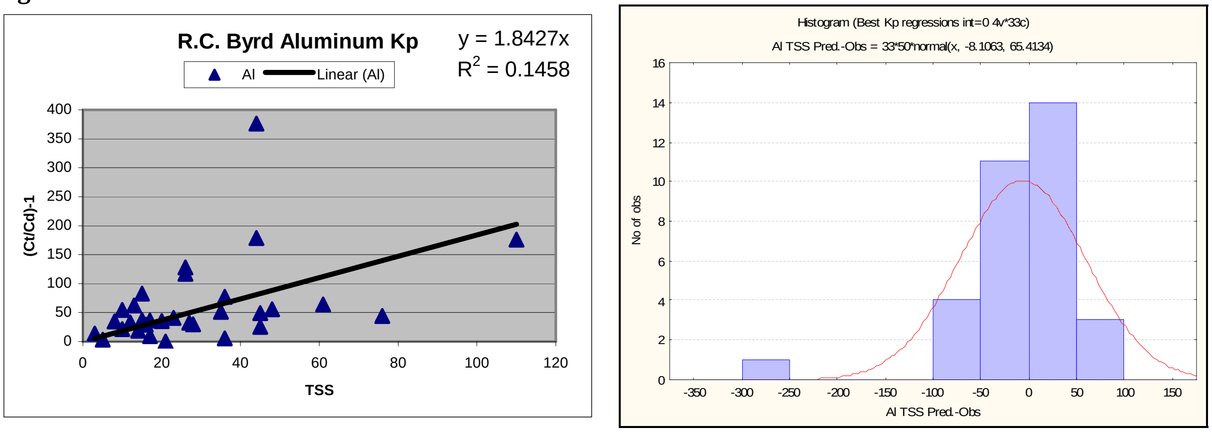
$$e_{(i)} = e_i /1 - h_i \tag{4}$$

$$PRESS = \sum_{i=1}^{n} e_{(i)}^2 \tag{5}$$

In the translator analysis weaker correlations with TSS result in lower confidence in the regression analysis for site-specific partition coefficients. When the regression of TSS and (Ct/Cd)-1 produced an intercept far from zero, a poor correlation coefficient, residual outliers, or relatively high PRESS or RMSE scores the site-specific partition coefficient was set aside to be used in the aggregated data sets or revisited only when more data has been collected. The direct-calculated translator has been proposed in each case where regression-based partition coefficients have failed.

Figure 2, a Kp regression and residual histogram of aluminum at R.C. Byrd Lock and Dam demonstrates a weaker relationship (r-square 0.17, 3rd highest PRESS and RMSE, residual skewness of -3.2). This data set illustrates the regression diagnostics selected for calculation of site-specific partition coefficients. It is apparent from both the residual histogram and the scatter plot itself that the data set includes one outlier, a sample collected at a TSS of 44 mg/L.

Figure 1



The presence of residual outliers contributes to the non-normality of the residuals and indicates a weak regression. An effort should be made to remove outliers from the data set but only if a reason can be found which justifies its removal. For the sample collected at R. C. Byrd Lock and Dam May 15, 2003 (TSS 44mg/L, dissolved Al 7.37ug/L, total Al 2780 ug/L) no field notes or quality assurance data can justify the point's exclusion and it must remain until supported by further data or until more data minimizes its influence on the regression. It is, however, possible to use the data immediately as part of the aggregated data sets for Ohio River segments that include multiple sampling stations.

Regional segments of the river with similar partitions have been identified using comparative plots of site-specific partition coefficients for all stations, including those with weaker relationships. A partition coefficient, often with increased strength of regression, was then calculated from the aggregated data set. Regression statistics for aggregated data sets are included in Appendix F, Tables 1-9.

For a complete discussion of these and other regression diagnostics the reader is referred to the Helsel and Hirsch text "*Statistical Methods in Water Resources*" (USGS, 2002).

Appendix E: Partition Coefficient (K_P) Regression Diagnostic Tables

Table 1: Aluminum K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	29	28	27	30	32	33	26	29
Slope (kp)	3.10	1.09	1.70	1.88	1.34	1.39	1.49	1.71
r-square	0.7406	0.4524	0.3318	0.8047	0.1786	0.2577	0.7355	0.5002
Intercept	-2.7	12.7	2.3	1.1	23.9	62.9	2.7	14.7
Residual Mean	-0.4	-12.7	-2.3	-1.1	-22.4	-62.9	-2.7	-14.9
Residual Skew	0.4	-1.6	-1.6	0.1	-3.2	-2.8	-0.2	-1.3
RMSE	106.7	26.7	15.0	12.1	67.4	218.2	16.0	66.0
PRESS	414369	26265	7430	5796	166406	1887528	8103	359414
# Residual Outliers (e_{si}>3)	0	0	1	0	1	1	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	2.97	0	0	0	

Table 2: Arsenic K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	29	28	27	30	30	33	26	29
Slope (kp)	0.03	0.03	0.05	0.07	0.02	0.01	0.03	0.03
r-square	0.7609	0.5758	0.1033	0.5688	0.4109	0.3555	0.3023	0.4396
Intercept	-0.4	0.1	0.1	0.0	0.1	0.4	0.1	0.0
Residual Mean	0.3	-0.1	-0.1	0.0	0.0	-0.4	-0.1	0.0
Residual Skew	0.1	-0.9	-3.0	-3.4	-1.3	-0.6	-0.1	-1.3
RMSE	1.1	0.5	1.0	0.8	0.6	0.9	0.8	0.8
PRESS	41	8	30	20	15	31	26	24
# Residual Outliers (e_{si}>3)	0	0	1	1	1	0	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	0	0	0	0	

Appendix E (cont.): Partition Coefficient (K_P) Regression Diagnostic Tables

Table 3: Barium K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	29	28	27	30	32	32	26	29
Slope (kp)	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01
r-square	0.7279	0.4996	0.0779	0.2206	0.2421	0.2147	0.3143	0.3282
Intercept	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.1
Residual Mean	-0.1	-0.1	-0.1	-0.1	-0.1	-0.3	-0.1	-0.1
Residual Skew	-0.9	-0.5	-0.2	-1.1	-3.2	-2.7	-0.6	-1.3
RMSE	0.3	0.1	0.2	0.2	0.2	0.6	0.2	0.3
PRESS	3	1	1	2	2	13	1	3
# Residual Outliers (e_{si}>3)	1	0	0	0	1	1	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	0	0	0	0	

Table 4: Chromium K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	15	20	16	19	19	27	17	19
Slope (kp)	0.13	0.00	-0.18	0.06	0.25	0.10	0.22	0.08
r-square	0.7273	0.0003	0.0271	0.0815	0.2758	0.0741	0.5513	0.2482
Intercept	2.3	4.0	5.7	2.6	0.1	4.8	0.1	2.8
Residual Mean	1.2	-2.8	-4.0	-1.4	3.5	-1.8	0.8	-0.6
Residual Skew	0.1	-1.3	-4.2	-2.2	0.2	-4.5	-0.7	-1.8
RMSE	7.2	4.3	7.0	3.3	8.5	26.3	3.6	8.6
PRESS	733	596	1563	406	843	27099	383	4425
# Residual Outliers (e_{si}>3)	1	0	1	0	0	1	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	0	0	0	0	

Appendix E (cont.): Partition Coefficient (K_P) Regression Diagnostic Tables

Table 5: Copper K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	29	28	27	30	32	33	26	29
Slope (kp)	0.04	0.04	0.03	0.07	0.03	0.01	0.03	0.04
r-square	0.8080	0.8557	0.1674	0.5507	0.2542	0.1467	0.3819	0.4521
Intercept	0.0	0.1	0.4	0.2	0.6	1.1	0.4	0.4
Residual Mean	0.0	-0.1	-0.4	-0.2	-0.5	-1.1	-0.4	-0.4
Residual Skew	0.1	-0.7	-1.6	-4.1	-2.4	-4.6	-0.1	-1.9
RMSE	1.1	0.4	0.6	0.8	1.3	3.2	0.7	1.1
PRESS	46	4	10	24	58	388	16	78
# Residual Outliers (e_{si}>3)	1	0	0	1	1	1	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	3.01	0	0	0	0	0	0	

Table 6: Manganese K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	29	28	27	30	32	33	26	29
Slope (kp)	0.45	0.61	-1.35	0.05	-0.10	0.37	0.10	0.02
r-square	0.5379	0.0447	0.0436	0.0004	0.0188	0.4115	0.0092	0.1523
Intercept	3.7	10.1	37.3	17.6	7.8	-1.9	8.5	11.9
Residual Mean	-2.1	-10.1	-37.3	-17.6	-7.7	1.9	-8.5	-11.6
Residual Skew	-1.9	-3.9	-2.5	-2.3	-5.1	-0.8	-2.3	-2.7
RMSE	25.0	56.3	54.0	38.9	16.9	39.5	19.5	35.7
PRESS	21490	104247	89340	52228	11215	81989	12101	53230
# Residual Outliers (e_{si}>3)	1	1	1	1	1	1	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	0	0	3.04	0	

Appendix E (cont.): Partition Coefficient (K_P) Regression Diagnostic Tables

Table 7: Nickel K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	29	28	27	30	32	33	25	29
Slope (kp)	0.06	0.03	0.01	0.02	0.03	0.02	0.03	0.03
r-square	0.8146	0.4712	0.0882	0.4226	0.2135	0.2981	0.5060	0.4020
Intercept	-0.2	0.2	0.3	0.2	0.4	1.1	0.2	0.3
Residual Mean	0.3	-0.2	-0.3	-0.2	-0.4	-1.1	-0.2	-0.3
Residual Skew	-0.2	-1.7	-1.9	-0.8	-4.1	-2.8	-1.3	-1.8
RMSE	1.6	0.6	0.4	0.4	1.4	2.6	0.6	1.1
PRESS	95	17	5	7	73	269	11	68
# Residual Outliers (e_{si}>3)	0	1	0	0	1	1	1	
High Leverage, High influence (h_i>3p/n, esi>2.5)	2.90	3.32	0	2.78	0	0	0	

Table 8: ZInc K_P Regression Diagnostics

	Anderson Ferry	Belleville	New Cumberland	Pike Island	R.C. Byrd	West Point	Willow Island	Average
N	22	18	22	26	18	23	20	21
Slope (kp)	0.16	0.14	0.20	0.11	0.09	0.05	0.28	0.15
r-square	0.8374	0.4610	0.2691	0.4579	0.1528	0.3695	0.3191	0.4095
Intercept	-1.2	2.0	0.3	1.4	2.3	3.2	-0.4	1.1
Residual Mean	2.0	-0.4	0.2	-1.0	-0.2	-0.8	0.8	0.1
Residual Skew	0.1	-0.3	-0.5	-0.5	-2.5	0.7	-1.9	-0.7
RMSE	4.8	3.6	2.1	2.0	4.6	6.5	6.9	4.3
PRESS	688	357	111	139	707	967	2200	714
# Residual Outliers (e_{si}>3)	0	0	0	0	1	0	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	0	0	0	2.70	

Appendix F: River Segment Partition Coefficient (K_P) Regression Diagnostic Tables

Table 1: Aluminum Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	126	116	96	338
Slope (kp)	1.70	1.98	2.84	2.61
r-square	0.6412	0.6031	0.4458	0.5239
Intercept	2.1	19.2	29.5	4.8
Residual Mean	-2.9	-22.3	-26.6	-16.3
Residual Skew	-0.4	-0.5	-1.0	-1.7
RMSE	50.3	201.5	543.6	582.0
PRESS	55450	848767	4258078	7788023
# Residual Outliers (e_{si}>3)	0	0	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	2.76	2.95	0	

Table 2: Arsenic Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	126	112	96	334
Slope (kp)	0.03	0.02	0.01	0.02
r-square	0.3009	0.7088	0.5220	0.4640
Intercept	0.2	0.0	0.2	0.3
Residual Mean	-0.1	0.1	-0.1	0.0
Residual Skew	-2.4	0.3	-0.7	-0.9
RMSE	2.1	2.1	1.9	3.5
PRESS	92	79	57	282
# Residual Outliers (e_{si}>3)	0	0	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	

Table 3: Barium Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	126	116	95	337
Slope (kp)	0.01	0.01	0.01	0.01
r-square	0.3643	0.6872	0.4544	0.5641
Intercept	0.1	0.1	0.1	0.1
Residual Mean	-0.1	-0.1	-0.1	-0.1
Residual Skew	-0.5	-1.4	-2.2	-2.4
RMSE	0.4	0.8	1.0	1.4
PRESS	4	10	19	43
# Residual Outliers (e_{si}>3)	0	0	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	

Appendix F (cont.): River Segment Partition Coefficient (K_P) Regression Diagnostic Tables

Table 4: Chromium Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	84	69	72	225
Slope (kp)	0.06	0.14	0.08	0.09
r-square	0.0688	0.5489	0.1059	0.1776
Intercept	2.7	1.3	3.6	2.6
Residual Mean	-1.8	3.0	-1.2	0.0
Residual Skew	-3.0	1.6	-6.4	-6.4
RMSE	12.8	12.4	33.2	37.7
PRESS	2512	1905	25024	35726
# Residual Outliers (e_{si}>3)	0	0	1	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	

Table 5: Copper Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	126	116	96	338
Slope (kp)	0.04	0.03	0.02	0.02
r-square	0.5201	0.7280	0.3632	0.5183
Intercept	0.3	0.3	0.6	0.5
Residual Mean	-0.3	-0.3	-0.5	-0.4
Residual Skew	-3.0	-0.9	-6.8	-7.5
RMSE	1.5	2.6	3.8	4.9
PRESS	55	138	393	693
# Residual Outliers (e_{si}>3)	0	0	1	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	

Table 6: Manganese Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	126	116	96	338
Slope (kp)	0.17	0.55	0.85	0.72
r-square	0.0051	0.2509	0.3494	0.3019
Intercept	16.6	1.2	4.9	4.8
Residual Mean	-18.5	-4.3	0.6	-8.2
Residual Skew	-3.2	-1.6	-1.5	-1.7
RMSE	100.2	166.4	171.2	258.9
PRESS	249937	271525	419791	1463755
# Residual Outliers (e_{si}>3)	0	0	0	
High Leverage, High influence (h_i>3p/n, esi>2.5)	0	0	0	

Appendix F (cont.): River Segment Partition Coefficient (K_P) Regression Diagnostic Tables

Table 7: Nickel Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	125	116	96	337
Slope (kp)	0.03	0.04	0.03	0.03
r-square	0.5268	0.7078	0.5589	0.6588
Intercept	0.2	0.2	0.7	0.3
Residual Mean	-0.2	-0.2	-0.6	-0.3
Residual Skew	-1.2	-1.1	-3.1	-3.1
RMSE	1.2	3.0	4.0	5.1
PRESS	35	205	324	692
# Residual Outliers ($e_{si}>3$)	0	1	0	
High Leverage, High influence ($h_i>3p/n$, esi>2.5)	0.00	3.48	0	

Table 8: Selenuim Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	39	44	64	147
Slope (kp)	0.00	0.00	0.00	0.00
r-square	0.0023	0.0457	0.0006	0.0153
Intercept	0.3	0.2	0.1	0.2
Residual Mean	-0.2	0.1	-0.1	-0.1
Residual Skew	-1.9	2.9	-0.5	2.2
RMSE	1.1	0.6	0.7	1.4
PRESS	7	2	3	14
# Residual Outliers ($e_{si}>3$)	0	0	0	
High Leverage, High influence ($h_i>3p/n$, esi>2.5)	0	0	0	

Table 9: Zinc Kp Regression Diagnostics

	Upper (0-204)	Mid (279-600)	Lower (630-940)	Entire River
N	97	77	51	225
Slope (kp)	0.18	0.15	0.07	0.11
r-square	0.3378	0.6889	0.5020	0.5387
Intercept	0.8	0.4	2.5	1.6
Residual Mean	-0.2	1.3	0.0	0.4
Residual Skew	-1.5	-0.3	0.3	-0.3
RMSE	9.8	12.9	15.1	22.2
PRESS	1877	1890	1511	7305
# Residual Outliers ($e_{si}>3$)	1	0	0	
High Leverage, High influence ($h_i>3p/n$, esi>2.5)	3.14	2.58	0	