Memo

Date: July 13, 2017

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From: Edward Garland, P.E.

Subject: Congener Analysis

Introduction

This memorandum summarizes analyses performed to assess potential links between concentrations of 2,3,7,8-substituted dioxins and furans measured in the Lower Passaic River (LPR) sediments and concentrations of those chemicals in the containment cells on the former Givaudan facility in Clifton and on the former Diamond Alkali facility on Lister Avenue in Newark.

Description of the Data Used

The data used in these analyses were collected by several groups. EPA collected samples from the former Givaudan and Diamond Alkali facilities in 2015 and from the river in 2013. The vast majority of the in-river data were collected by the Cooperating Parties Group (CPG) under EPA oversight between 2008 and 2013. Additional in-river data were collected by Tierra in 2009 in the Phase 1 removal area and in 2012 as part of their Focused Sediment Investigation. In 2011, in-river sediment data were collected at 15 locations by the Joint Defense Group.

Figure 1 presents concentrations of seventeen 2,3,7,8-substituted dioxin and furan congeners measured in three locations:

- Upstream of Dundee Dam (referred to as background);
- The containment cell on the former Givaudan facility in Clifton; and
- The containment cell on the former Diamond Alkali facility on Lister Avenue in Newark.

Gray shading identifies three congeners not included in the analysis; two because they are associated with combustion sources and are ubiquitous in the highly urbanized area surrounding the Lower Passaic River (1,2,3,4,6,7,8 HpCDD and OCDD), and the third (1,2,3,7,8,9-HxCDF) because a high proportion of the in-river data are non-detects.

For each of the three locations, data are shown as individual measurements (triangles), arithmetic averages (circles) and median concentrations (diamonds). Non-detected results are plotted as open symbols at the detection limit.

Individual measurements for any congener vary by more than an order of magnitude. For 2,3,7,8-TCDD, the mean concentration from the Lister Avenue cell is more than two orders of magnitude higher than the mean concentration from the Clifton cell, and the mean background concentration is lower than the Clifton cell mean concentration by over three orders of magnitude. For the penta- and hexa-dioxins, mean concentrations from the two containment cells differ by less than 35% and background concentrations average two to three orders of magnitude less than the containment cell means. For the furans, mean concentrations from the Lister Avenue containment cell are two to three orders of magnitude greater than mean concentrations from the Clifton cell for six of the nine furan congeners, and are a factor of approximately 20 to 60 times greater for the remaining three congeners. Background furan congener mean concentrations are generally one to 1.5 orders of magnitude lower than the mean Clifton concentrations. Congener concentrations were chosen to characterize the three source categories, rather than percentages of the sum of the 2,3,7,8-substituted dioxins and furans because concentrations are more appropriate in the mass balance type approach adopted for this analysis. Characterizing the congeners by percentage of the sum does not account for the order of magnitude differences in concentrations among the three sources.

Figure 1 also shows concentrations of three additional chemicals measured in the containment cells and a limited number of river sediment samples:

- Hexachlorophene (HCP)
- 1,2,4,5,7,8-Hexachloroxanthene (HCX)
- 2,4,6,8-Tetrachlorodibenzothiophene (TCDT)

Measured concentrations of HCX and HCP in the Clifton cell are approximately three orders of magnitude higher than either the Lister Avenue cell concentrations or background concentrations. Conversely, measured concentrations of TCDT in the Lister Avenue cell are approximately four orders of magnitude higher than either the Clifton cell concentrations or background concentrations. Based on these source-specific differences in concentrations, these three chemicals are referred to subsequently in this memorandum as markers.

Figures 2 and 3 present the cumulative frequency distributions of the 14 dioxin and furan congeners, and the three additional chemicals (HCP, HCX, and TCDT) used in the analysis. Each panel on Figures 2 and 3 presents data for an individual congener, named in the upper left-hand corner of the panel. The ratio of the Lister Avenue cell mean concentrations to the Clifton cell mean concentrations is printed in the lower right-hand corner of each panel. Because the background data contain a substantial number of non-detect results and the detection limits varied considerably for any giver congener, the mean and median concentrations for each congener for the background data were determined with a maximum likelihood estimator (MLE) method (Kmenta, 1986), using an assumption of a log-normal distribution. The MLE estimate of the distribution of each congener is indicated by the blue line and the horizontal purple line indicates the mean background concentration used in the analysis for each congener. The variability of the concentrations, indicated by the slope of the data on the cumulative frequency distributions is similar (in log space) and suggests that concentrations could have varied over time, which would result in variable contributions to in-river concentrations.

Approach

In order to assess potential links between the concentrations of 2,3,7,8-substituted dioxins and furans measured in LPR sediments and the concentrations of those chemicals in the Lister Avenue and Clifton cells, an equation was developed to describe the concentrations of those chemicals in the LPR sediments as a mixture of what was discharged from the former Diamond Alkali facility (as represented by the chemicals in the Lister Avenue cell), what was discharged from the former Givaudan facility (as represented by the chemicals in the Clifton cell) and what came into the LPR from over Dundee Dam (background). This equation assumes that there were no other major sources of 2,3,7,8-substituted dioxins and furans to the LPR sediments.

In this analysis, the concentrations in each of the three sources are specified as the arithmetic mean concentrations[1]. The approach adopted is to apply equation (1) to reproduce the mixture of fourteen 2,3,7,8-substituted dioxin and furan congeners in individual in-river sediment samples by blending the congener concentrations measured in the three sources. An optimization routine was used for individual in-river samples to determine values of the coefficients a_j, b_j and c_j that multiply the congener concentrations from each of the three sources to match the mixture of congeners in the in-river sample.

$$\boldsymbol{C_{i,j} = a_j C_{i,Lister} + b_j C_{i,Clifton} + c_j C_{i,background}} \quad (1)$$

[1] An alternate evaluation using median concentrations (rather than means) was investigated and the results were not sensitive to this change.

Where:

$C_{i,j}$	=	Concentration of congener (*i*) in in-river sediment sample (*j*)
a_j	=	Multiplier of Lister waste cell congener concentration for in-river sediment sample (*j*)
$C_{i,Lister}$	=	Lister waste cell concentration of congener (*i*)
b_j	=	Multiplier of Clifton waste cell congener concentration for in-river sediment sample (*j*)
$C_{i,Clifton}$	=	Clifton waste cell concentration of congener (*i*)
c_j	=	Multiplier of background (upstream) congener concentration for in-river sediment sample (*j*)
$C_{i,Background}$	=	Background concentration of congener (*i*)

The coefficients a_j, b_j and c_j, vary from in-river sample to in-river sample, but are applied to all 14 congeners to calculate concentrations of the 14 congeners for a single in-river sample. For each in-river sample (*j*), the attenuation or dilution of what was discharged from the former Diamond Alkali facility is described by the coefficient (a_j), which is multiplied by the concentrations of the congeners measured in the Lister Avenue cell ($C_{i,Lister}$) to calculate the concentrations in LPR sediment originating from the former Lister Avenue site. The attenuation or dilution of what was discharged from the former Givaudan facility is described as another constant (b_j) which is multiplied by the concentrations of the congeners measured in the Clifton cell ($C_{i,Clifton}$) to calculate the concentrations originating from the former Givaudan facility. Similarly the concentrations of the congeners measured in background sediments ($C_{i,background}$) are multiplied by a third constant (c_j) to calculate the concentrations originating from what flowed over Dundee Dam.

Figure 1 shows the concentrations of 2,3,7,8-substituted dioxins and furans that were measured in each containment cell: the arithmetic means shown in the figure are the C_1, C_2, C_3 and so on that were used in the equation. A program that solves many equations at once (Excel's Solver) was used to find the combination of a_j, b_j and c_j that, when applied to the group of fourteen congeners, would yield the best match of the pattern of 2,3,7,8-substituted dioxins and furans measured in a specific sample of LPR sediments.

The optimization of the coefficients, a_j, b_j and c_j, which multiply the Lister Avenue, Clifton, and background concentrations, was performed with Excel's Solver tool using an

objective function of the sum of the squares of the relative differences[2] between the calculated congener concentrations and data:

$$\boldsymbol{Diff_{Rel,j}}^2 = \sum_{i=1}^{14}\left(\frac{C_{i,j,Pred}-C_{i,j,Obs}}{C_{i,j,Obs}}\right)^2 \quad (2)$$

Where:

$Diff_{Rel,j}^2$ = Square of relative difference for in-river sediment sample (*j*)

$C_{i,j,Pred}$ = Predicted concentration of congener (*i*) for in-river sediment sample (*j*)

$C_{i,j,Obs}$ = Observed concentration of congener (*i*) for in-river sediment sample (*j*)

Comparison of Computed Congener Concentrations with Data

Predicted versus Measured

For each individual in-river sample, the combination of a_j, b_j and c_j, determined by the Solver optimization and the measured concentrations of each congener in the Lister Avenue and Clifton cells, plus background sediments, yields calculated concentrations of the 14 congeners in the LPR sediment sample. In order to test the results of the Solver optimization of equation (1), the calculated LPR sediment concentrations were compared to the measured LPR sediment concentrations (Figures 4 and 5). In each panel on Figures 4 and 5, a one-to-one line (perfect agreement between calculated LPR sediment concentrations and measured LPR sediment concentrations) is shown as a blue line, and a regression of predicted versus observed concentrations is indicated by the red line, with the slope and coefficient of determination (R^2) printed below the panel. Any non-detect data are plotted at half of the detection limit on these and subsequent figures[3].

The predicted concentrations are generally in good agreement with the data, with R^2 values greater than 0.9 in all but one of the regressions (the exception being 2,3,7,8-TCDF, with an R^2 of 0.82). Scatter around the regression line and differences between the regression and one-to one-line is expected given that only mean concentrations were used

[2] Alternate objective functions based on sum of 1) squares of model-data differences, 2) squares of log differences, absolute value of log differences, and maximum(model, data)/minimum(model, data). Only the use of the square of the model-data differences produced significantly different results and that option was rejected because it forced the results to be controlled by only the high concentrations.

[3] Alternate treatments of non-detects in model versus data comparisons were investigated (non-detect equals zero and non-detect equals the detection limit) and the results were not sensitive to these changes.

to characterize the three sources, and each showed variations in individual congener concentrations of more than an order of magnitude. For many of the congeners (e.g. 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, and the higher chlorinated furans), the tight cluster of points near the one-to-one line over four or more orders of magnitude means that the a_j, b_j and c_j, values found by the Solver do well in predicting measured LPR sediment concentrations. For other congeners (e.g. 2,3,7,8-TCDD, 1,2,3,6,7,8-HxCDD and 2,3,7,8-TCDF) the upper end of the concentration range is under-predicted, which could be caused by use of mean concentrations to characterize the three source terms.

Data for the marker chemicals were available for only a small fraction of the samples, and therefore, the marker chemicals were not included in the Solver optimization. The coefficients a_j, b_j and c_j, determined by the Solver optimization, are applied to each of the 14 congeners in the three sources, but can also be applied to the mean concentration of the marker chemicals from the three sources. Predicted versus measured marker chemical concentrations are presented on the last three panels of Figure 5 and show good agreement for the majority of the HCP data. Predictions for HCX show a fair amount of scatter and a bias toward over-prediction, while TCDT concentrations are generally under-predicted, although with less scatter than HCX. The predictions for the marker chemicals could also be affected by use of a mean concentration to represent variable concentrations. These comparisons of computed and measured marker chemicals can be thought of as a validation step, in that the coefficients aj, bj and cj determined by the Solver optimization for the dioxin and furan congeners were applied directly to the marker chemicals without including the agreement for the markers in the optimization.

Spatial Patterns

In addition to the previous evaluation of the agreement between predicted and observed congener concentrations (Figures 4 and 5) the results generated by the Solver optimization are evaluated further by assessing how the results vary in terms of spatial patterns of the contribution of a single source. Physical processes in the river are expected to influence spatial gradients in chemical concentrations discharged at different locations in a tidal estuary. This is evaluated by considering the calculated contribution of each source to the concentrations measured in river sediments, which can be calculated for each sample with the optimized coefficients, a_j, b_j and c_j, and source concentrations, as:

$$\boldsymbol{F_{Lister,i,j}} = \frac{\boldsymbol{a_j C_{i,Lister}}}{\boldsymbol{a_j C_{i,Lister} + b_j C_{i,Clifton} + c_j C_{i,Background}}} \quad (3)$$

$$F_{Clifton,i,j} = \frac{b_j C_{i,Clifton}}{a_j C_{i,Lister} + b_j C_{i,Clifton} + c_j C_{i,Background}} \quad (4)$$

$$F_{Background,i,j} = \frac{c_j C_{i,Background}}{a_j C_{i,Lister} + b_j C_{i,Clifton} + c_j C_{i,Background}} \quad (5)$$

The spatial variation in the contribution of each source to each of the 14 congeners and 3 markers is summarized by the mean (plus and minus 2 standard errors) over all depth intervals versus river mile, binned by one-mile intervals for the Lister (Figure 6 and 7), Clifton (Figures 8 and 9) and background (Figures 10 and 11) components. The ratio of the mean congener concentration in the Lister Avenue cell to the mean in the Clifton cell is printed in the upper left-hand corner of each panel on Figures 6 through 11.

Spatial patterns of the calculated Lister Avenue fractional contribution to in-river congener concentrations (Figures 6 and 7) follow two general patterns. For congeners with high ratios of concentrations in the Lister Avenue cell to the Clifton cell (e.g. 2,3,7,8-TCDD and more highly chlorinated furans), the calculated fractions are high downstream, decrease gradually in the upstream direction to approximately RM 12 or 13, and then decrease sharply upstream of RM 12 or 13. For congeners with ratios of concentrations in the two cells near 1.0 (i.e. penta- and hexa-dioxins) the Lister fraction at the downstream end of the river is approximately 10% to 15% and decreases gradually in the upstream direction.

Spatial patterns of the calculated Clifton fractional contribution to in-river congener concentrations (Figures 8 and 9) also show two general patterns. For congeners with cell concentration ratios (Lister/Clifton) near 1.0, computed fractional contributions peak at approximately 50 to 75% between RM 10 and 11 and decrease rapidly upstream and gradually downstream. For congeners with higher cell concentration ratios, peak Clifton fractional contributions are generally less than 15%. The mean Clifton contribution of 2,3,7,8-TCDD decreases from approximately 15% at RM 14 to less than 10% downstream of RM 6 (Figure 8). Mean contributions to penta- and hexa-dioxins are highest between RM 9 and RM 11, and decrease sharply moving upstream, and gradually moving downstream. Downstream of RM 11, mean contributions to 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD are in the range of 60% to 75%. In this same reach, mean contributions to 1,2,3,6,7,8-HxCDD are between 40% and 55% and mean contributions to 1,2,3,7,8,9-HxCDD are between 45% and 65%. Lower contributions are computed for the furan congeners, with maximum values between RM 8 to RM 10 of near 10% for the tetra- and penta-furans and near 5% for the more-highly chlorinated furan congeners (Figure 9) (with 2,3,4,6,7,8-HxCDF having a higher peak near 15%). Downstream of RM 8, the mean Clifton contributions of the hexa-, hepta, and octa-furans is generally less than 5%.

Spatial patterns of the calculated background fractional contribution to in-river congener concentrations (Figures 10 and 11) are highest upstream, above the influence of estuarine circulation and decrease to approximately RM 9 to 10. Between RM 9 and RM 7, the fractional contributions increase and then generally decrease downstream of RM 7, but with less variation than in the reach upstream of RM 10.

These spatial patterns are reasonable given the location of the Clifton and Lister Avenue sources. The higher computed Clifton contribution to in-river 2,3,4,6,7,8-HxCDF concentrations (relative to the other hexa-, hepta, and octa-furans) is also reasonable, given the Lister Avenue to Clifton cell concentration ratio of 42 for 2,3,4,6,7,8-HxCDF (compared to ratios for other hexa-, hepta, and octa-furans ranging from 414 to almost 3700). Lastly, the spatial pattern of the computed Clifton contribution to the three marker chemicals is reasonable, with Clifton dominating the HCP and HCX concentrations and having a mean contribution to TCDT of less than 5% at all locations.

Conclusions

The analysis described in this memorandum indicates that mixtures of fourteen 2,3,7,8-substituted dioxin and furan congeners measured in sediment of the LPR can be determined from blending the concentrations of the same 14 congeners measured in three sources: 1) the Lister Avenue cell of the former Diamond Alkali facility, 2) the Clifton cell of the former Givaudan facility, and background concentrations measured in sediments upstream of Dundee Dam. Concentrations of the 14 congeners predicted by applying Equation (1) to each in-river sediment sample fall reasonably tightly around regressions of computed versus measured concentrations (with the lowest R^2 of 0.83 and above 0.9 for the remaining 13 congeners). Multiple measurements of each congener in containment cells and upstream sediment show concentrations vary considerably about the mean concentrations used in this analysis, which leads to the expectation of variability in computed and measured concentrations in river sediments. For congeners more prevalent in the Clifton cell (e.g. 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD) and congeners more prevalent in the Lister Avenue cell (e.g. higher chlorinated furans), the predicted versus measured in-river concentrations form a tight cluster of points near the one-to-one line over four or more orders of magnitude, indicating that the Solver solutions for blending the three sources does well in predicting measured LPR sediment concentrations.

Given the relative magnitude of individual congener concentrations among the three sources and the location the sources, the results summarized as Clifton contribution are consistent with expected spatial patterns, considering how transport and fate processes affect discharges to a tidal estuary from spatially separated sources of different relative concentrations. For example, the Clifton contributions to congeners which represent a higher proportion of the Clifton cell data (e.g. penta- and hexa-dioxins), as compared to

the Lister Avenue cell data, are highest near the former Clifton facility and decrease gradually moving downstream.

The mean Clifton contribution of 2,3,7,8-TCDD decreases from approximately 15% at RM 14 to less than 10% downstream of RM 6. Mean contributions to penta- and hexa-dioxins are highest between RM 9 and RM 11, and decrease sharply moving upstream, and gradually moving downstream. Conversely, for congeners which represent a low proportion of the Clifton cell data (e.g. hexa- and hepta-furans), as compared to the Lister Avenue cell data, Clifton contributions of less than 10% are typically computed.

The spatial pattern of the computed Clifton contribution of the three marker chemicals, which is generated by using the coefficients a_i, b_i and c_i, derived from the dioxin and furan congeners, is also reasonable, with Clifton dominating the HCP and HCX concentrations and having a mean contribution to TCDT of less than 5% at all locations. This comparison serves as a validation rather than a calibration and lends additional support to the conclusion that the analysis approach produced reasonable results.

The analyses described in this memo were conducted with alternate selections of several inputs or data treatments, and regardless of choice, the overall conclusion did not change. While the exact magnitude of contribution from the Clifton source changed with assumptions, substantial non-zero contributions to more than 50% of in-river samples were computed for penta- and hexa-dioxins. Based on each iteration in the suite of analyses, the Clifton contribution was needed to explain in-river congener concentrations.

The power in the approach is in fitting the fourteen 2,3,7,8-substituted dioxins and furan congeners included in the analysis all at once. Concentrations of a single congener could be explained by various combinations of the three sources, however, the adjustment of one source versus another carries the effect to all 14 congeners. Improvements in the agreement with data for one congener in a specific sample could degrade the agreement for another congener, if the adjustment is made to the wrong source. The Excel Solver optimization tool is ideal for performing the adjustments by adjusting all fourteen congeners from a single source by the same factor and making the adjustments to the three factors for the three sources simultaneously. The comparisons of the computed and measured concentrations indicate that the blending calculations provide reasonable predictions of the in-river congener concentrations.

References

Kmenta, J., 1986. *Elements of Econometrics*, 2nd Edition, New York: Macmillan Publishing Company, pp. 176-187.

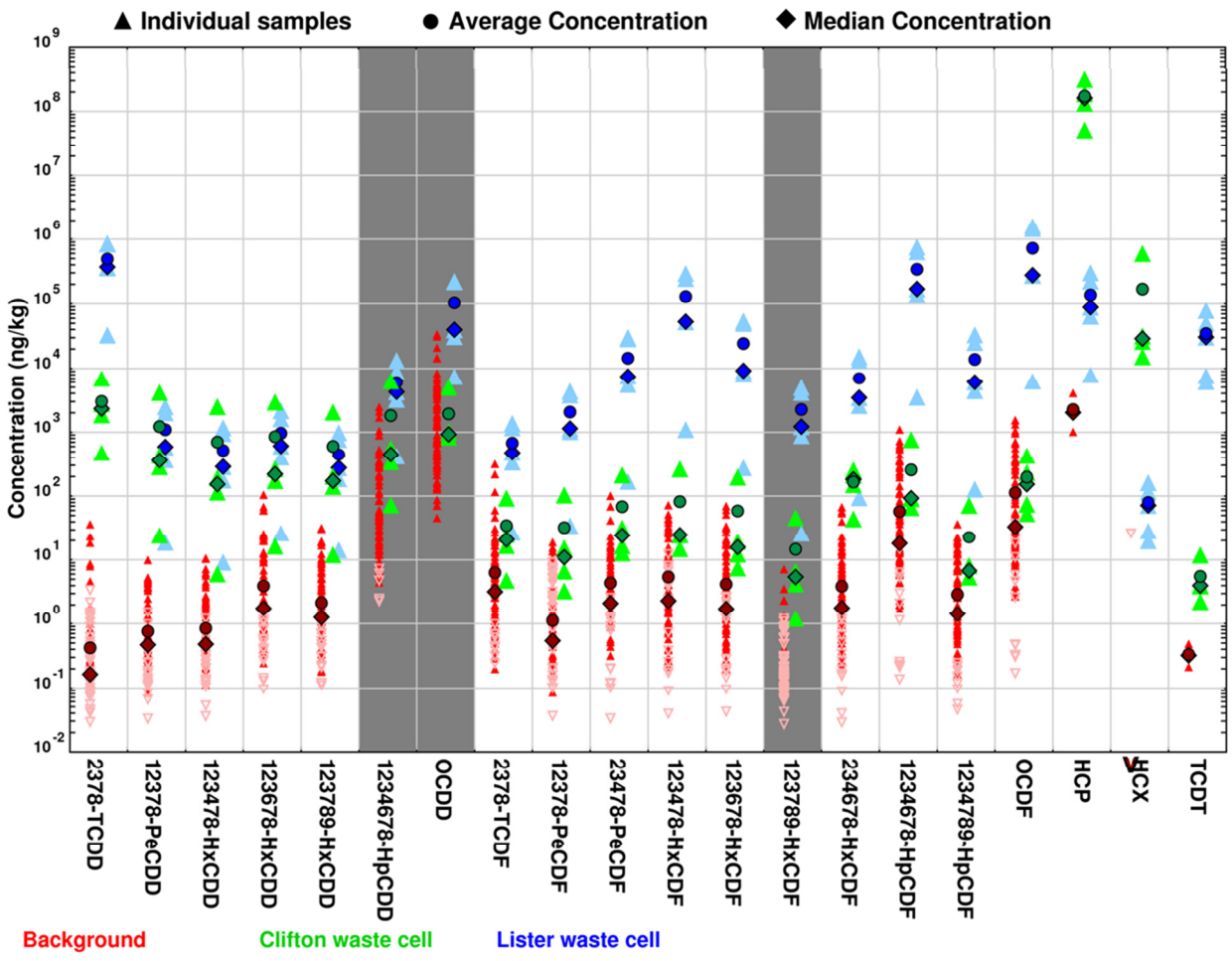

Figure 1. Concentrations measured in samples from upstream of Dundee Dam (background), and containment cells at Clifton and Lister Ave. sites.

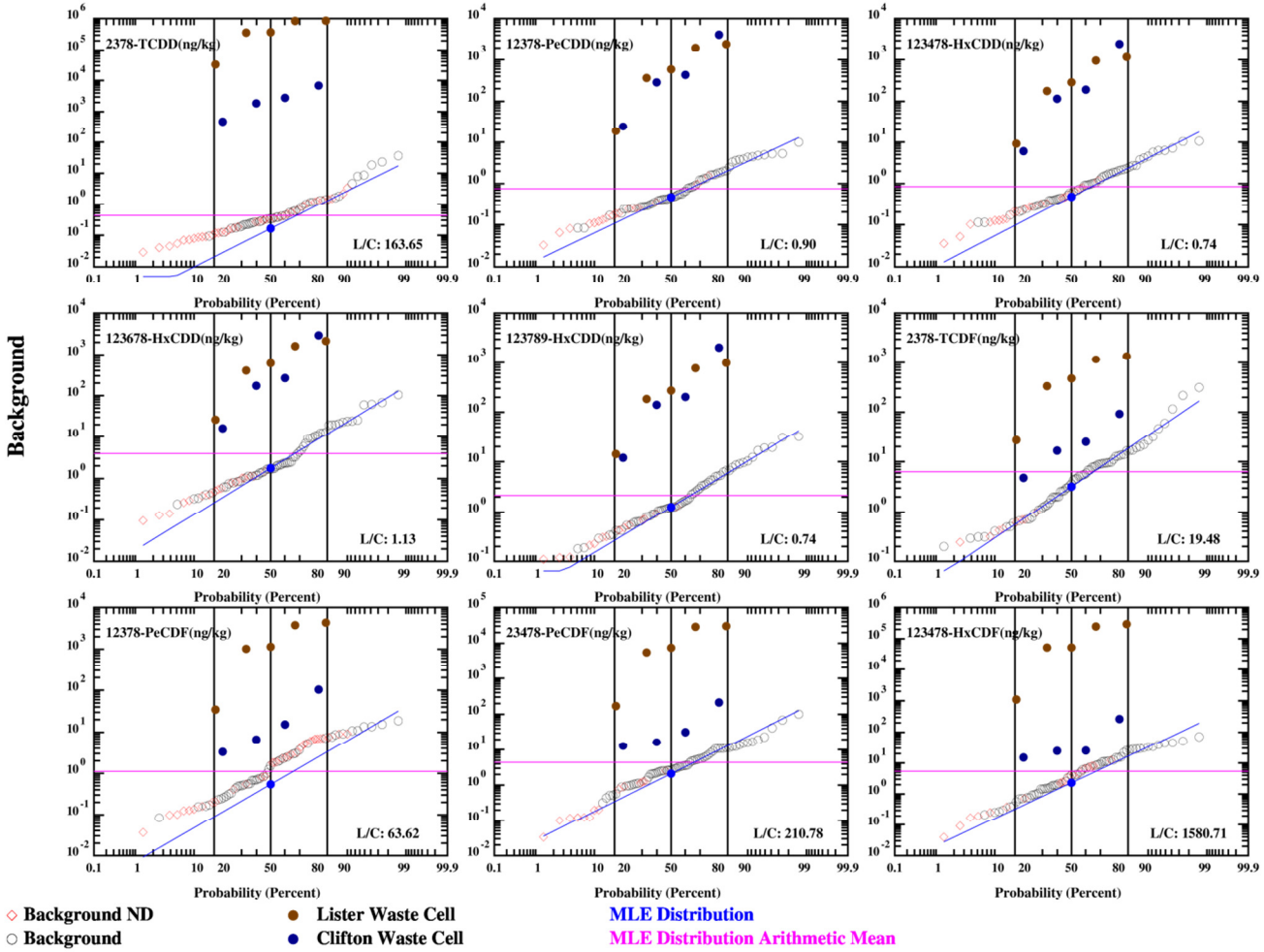

Figure 2. Cumulative frequency distributions of data from upstream of Dundee Dam (background), and containment cells at Clifton and Lister Ave. sites. Page 1 of 2 page set.

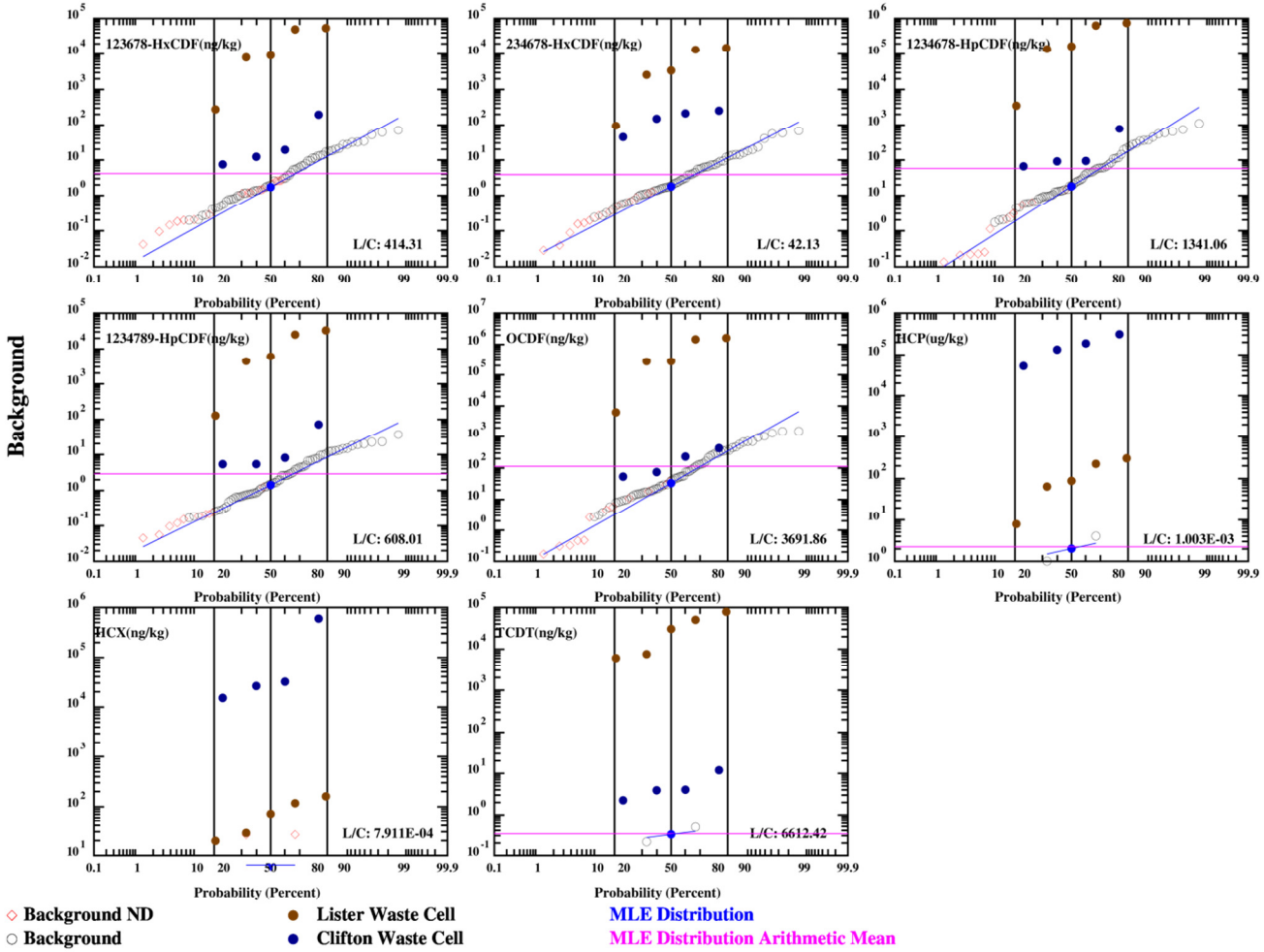

Figure 3. Cumulative frequency distributions of data from upstream of Dundee Dam (background), and containment cells at Clifton and Lister Ave. sites. Page 2 of 2 page set.

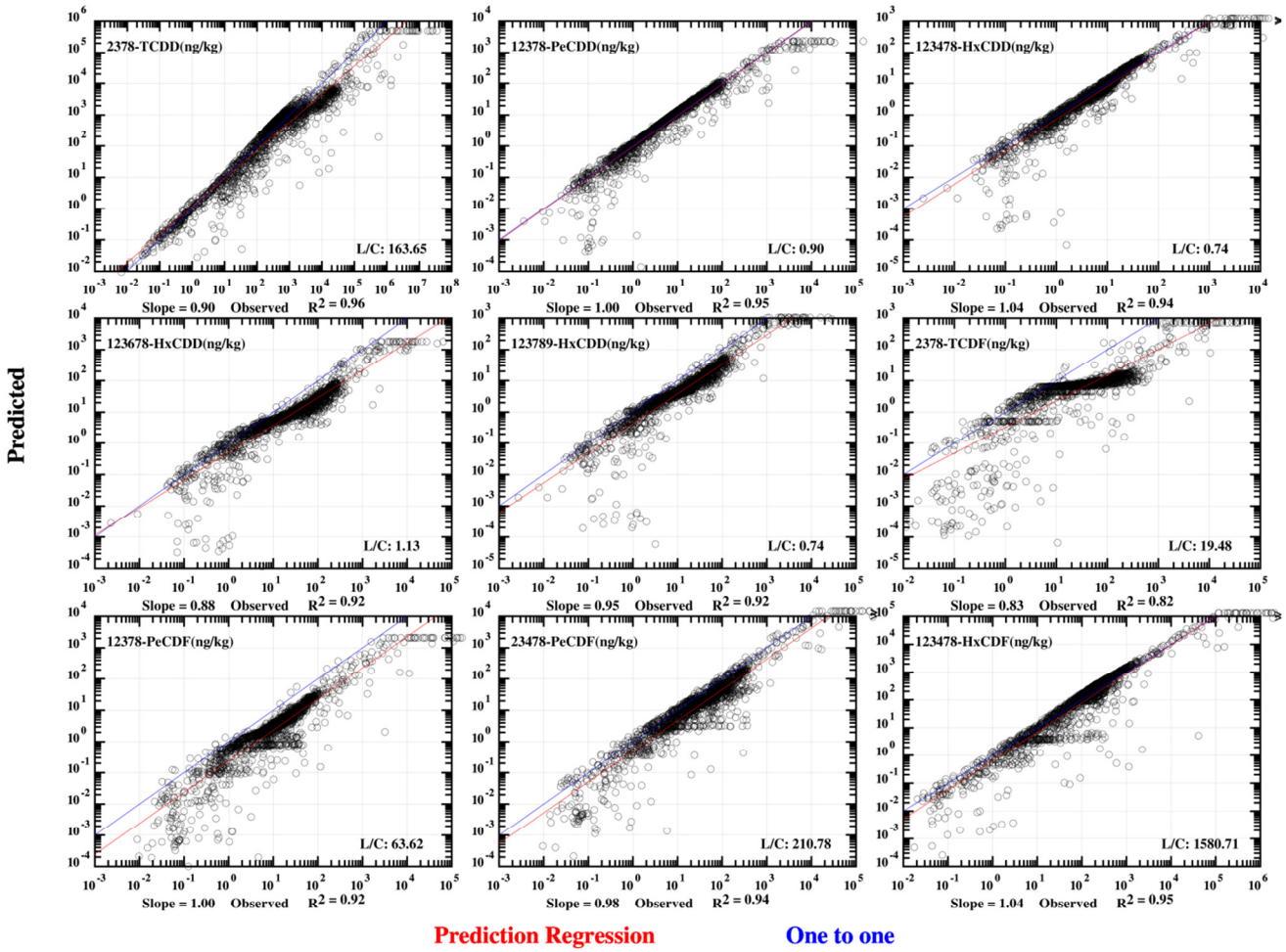

Figure 4. Cross-plot of predicted versus observed concentrations. Page 1 of 2 page set.

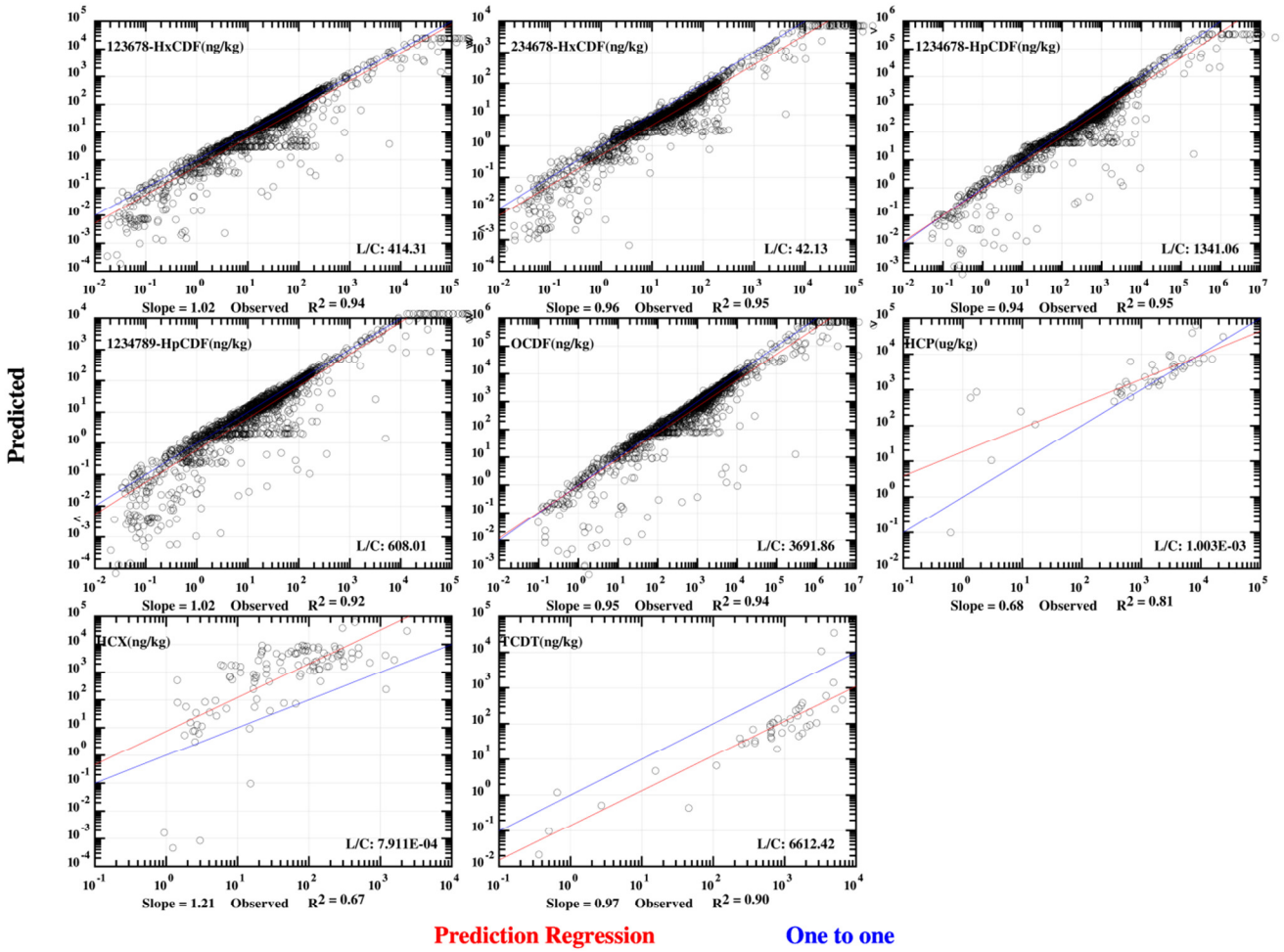

Figure 5. Cross-plot of predicted versus observed concentrations. Page 2 of 2 page set.

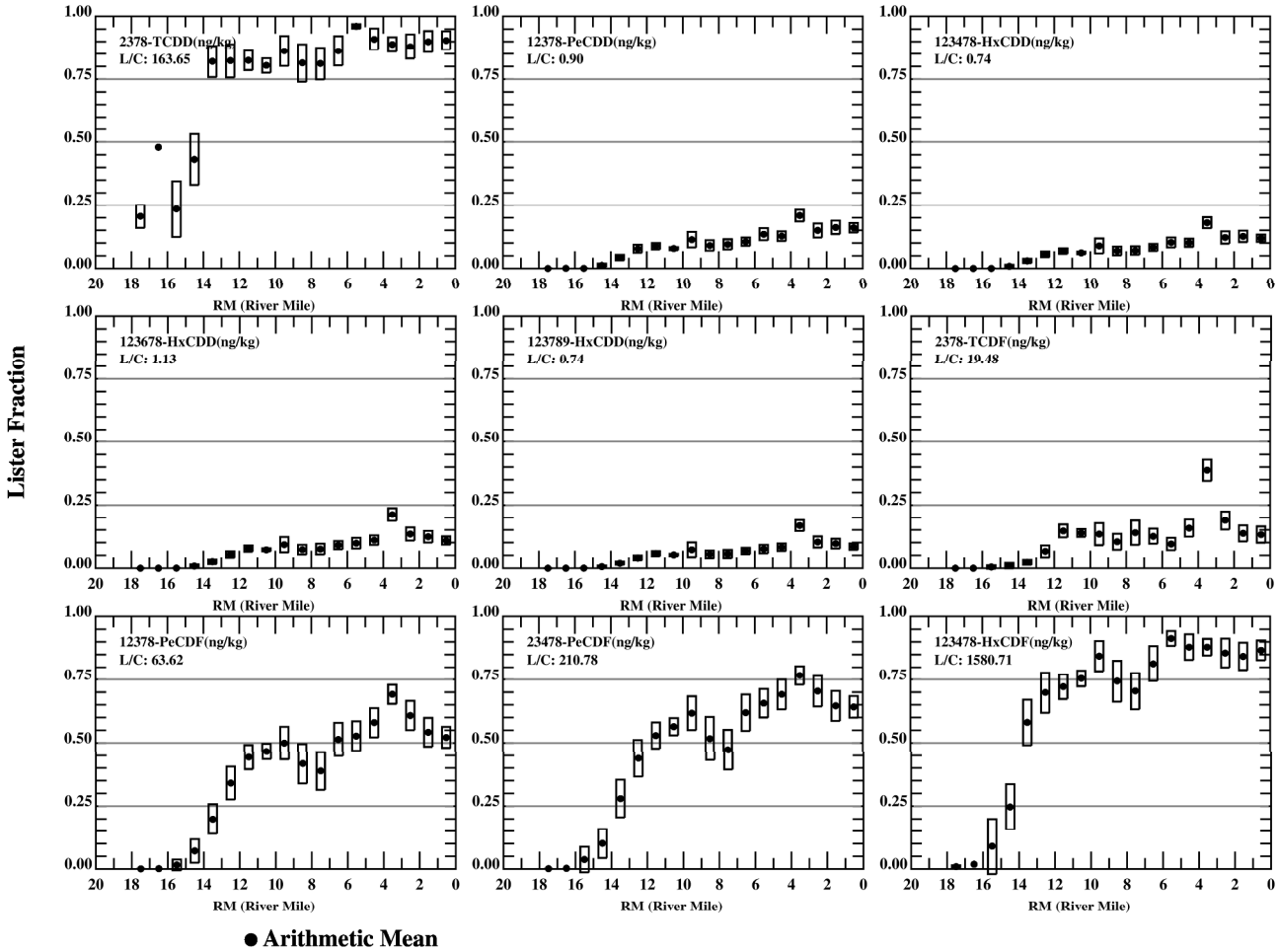

Figure 6. Mean +/- two standard errors of Lister fraction of in-river concentrations versus river mile, binned by one-mile intervals. Page 1 of 2 page set.

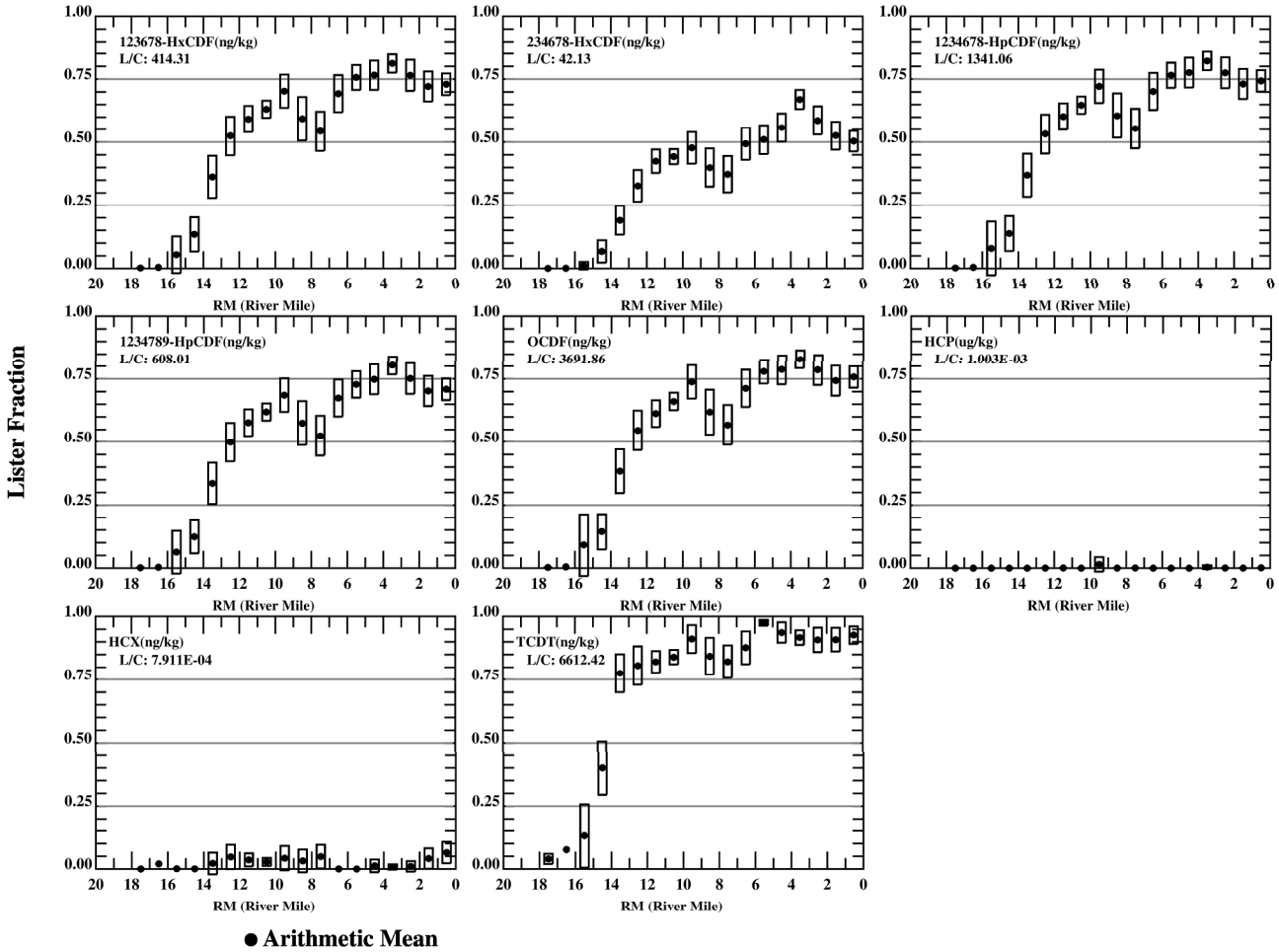

Figure 7. Mean +/- two standard errors of Lister fraction of in-river concentrations versus river mile, binned by one-mile intervals. Page 2 of 2 page set.

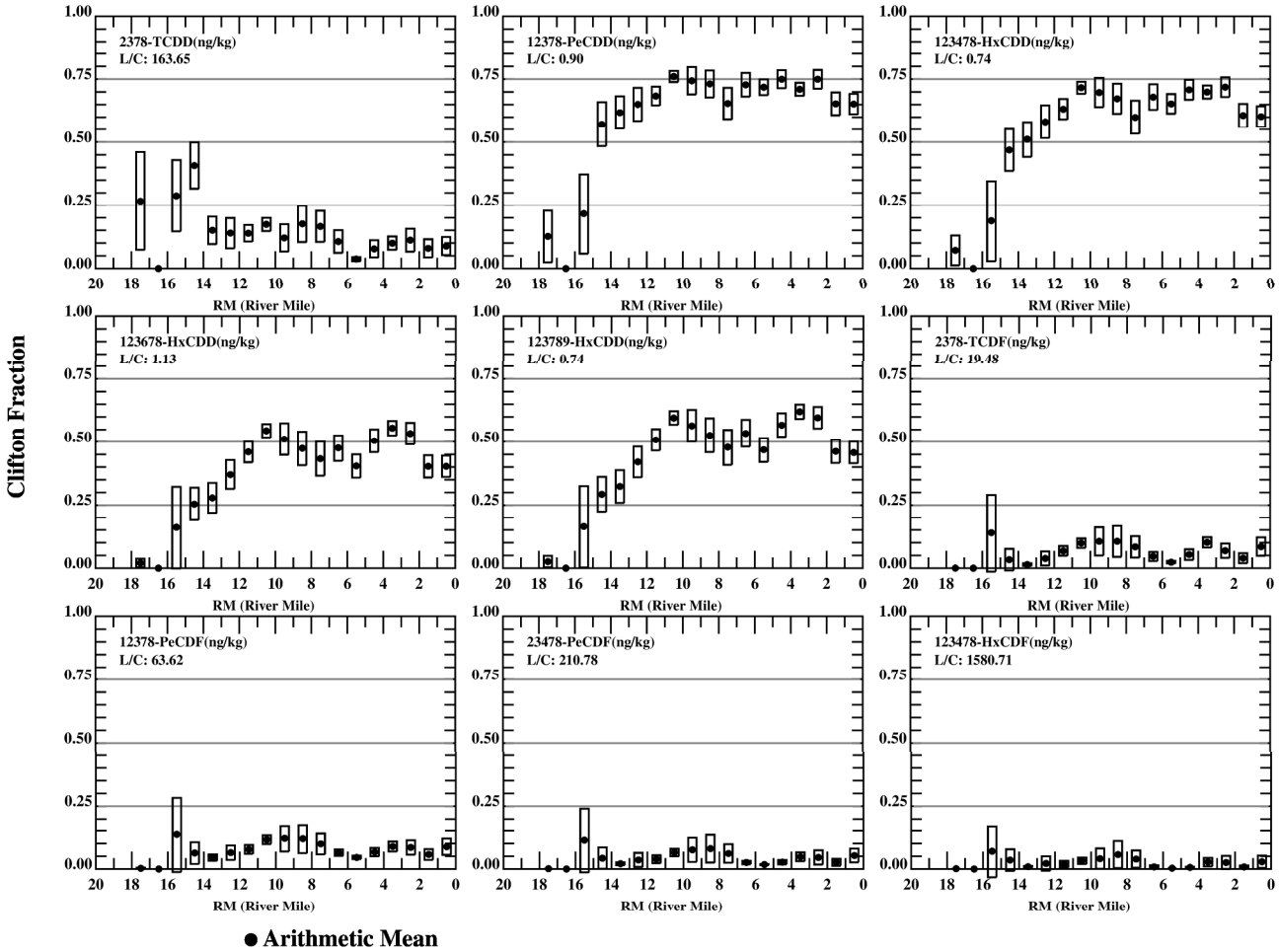

Figure 8. Mean +/- two standard errors of Clifton fraction of in-river concentrations versus river mile, binned by one-mile intervals. Page 1 of 2 page set.

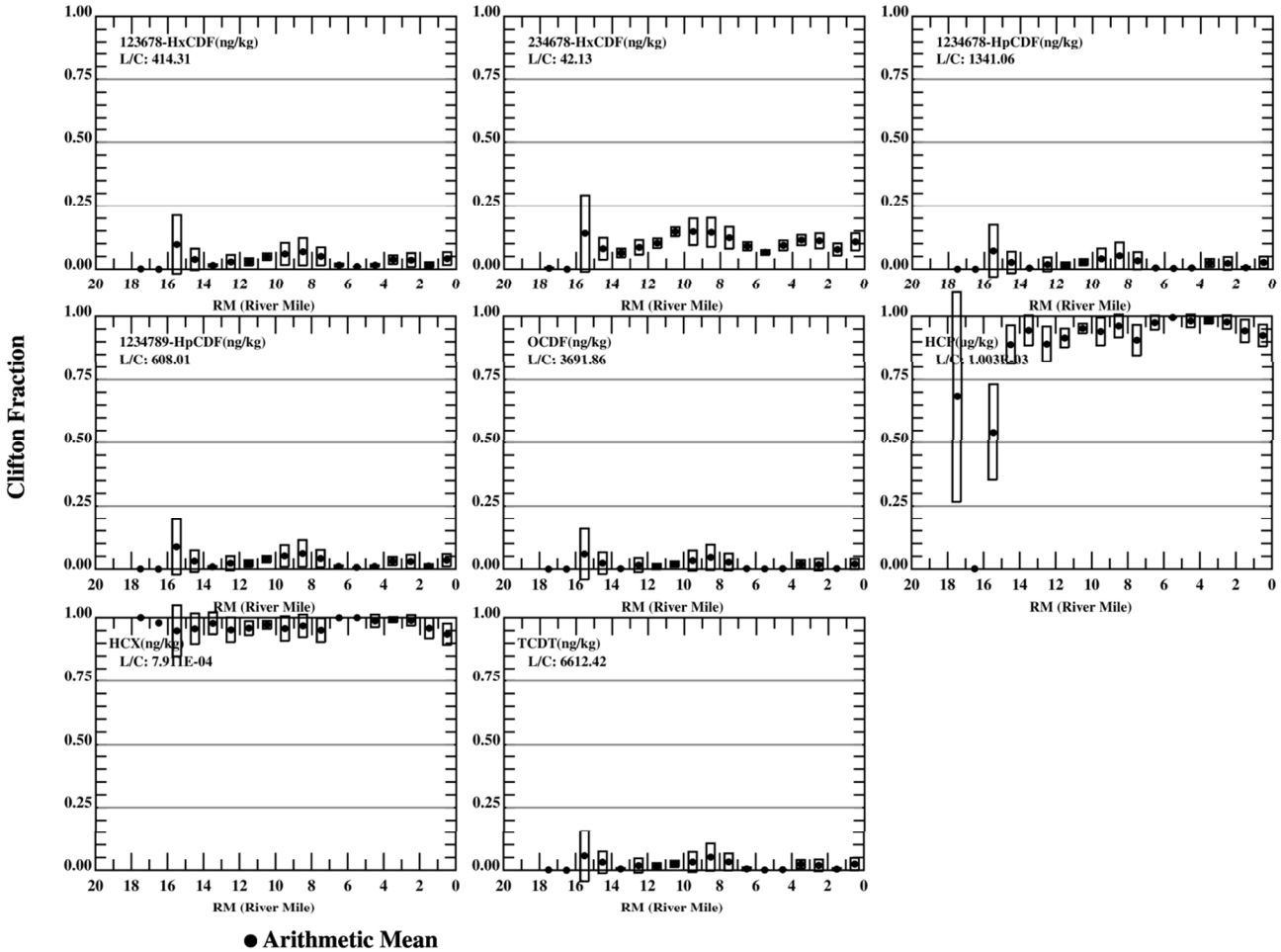

Figure 9. Mean +/- two standard errors of Clifton fraction of in-river concentrations versus river mile, binned by one-mile intervals. Page 2 of 2 page set.

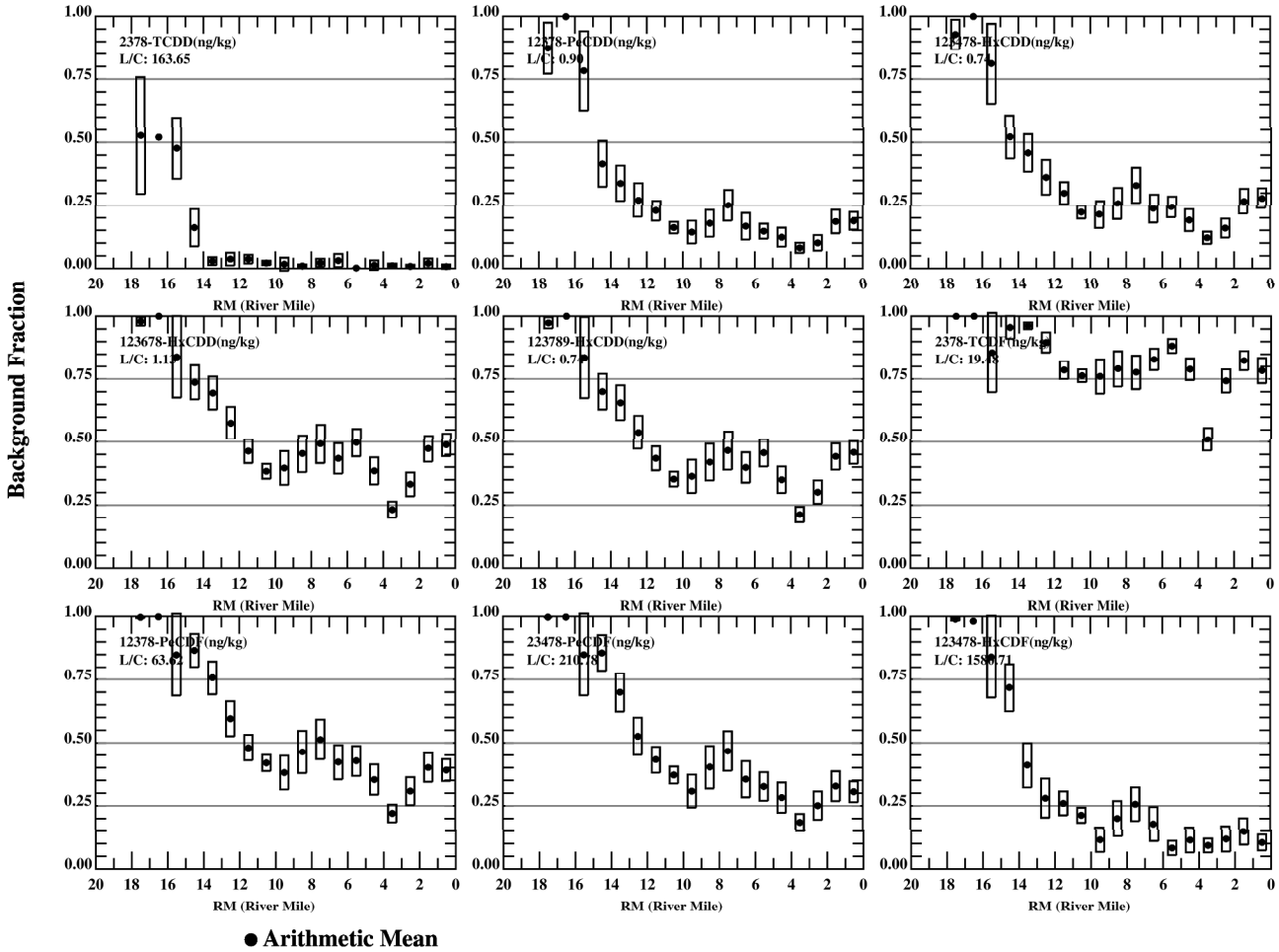

Figure 10. Mean +/- two standard errors of background fraction of in-river concentrations versus river mile, binned by one-mile intervals. Page 1 of 2 page set.

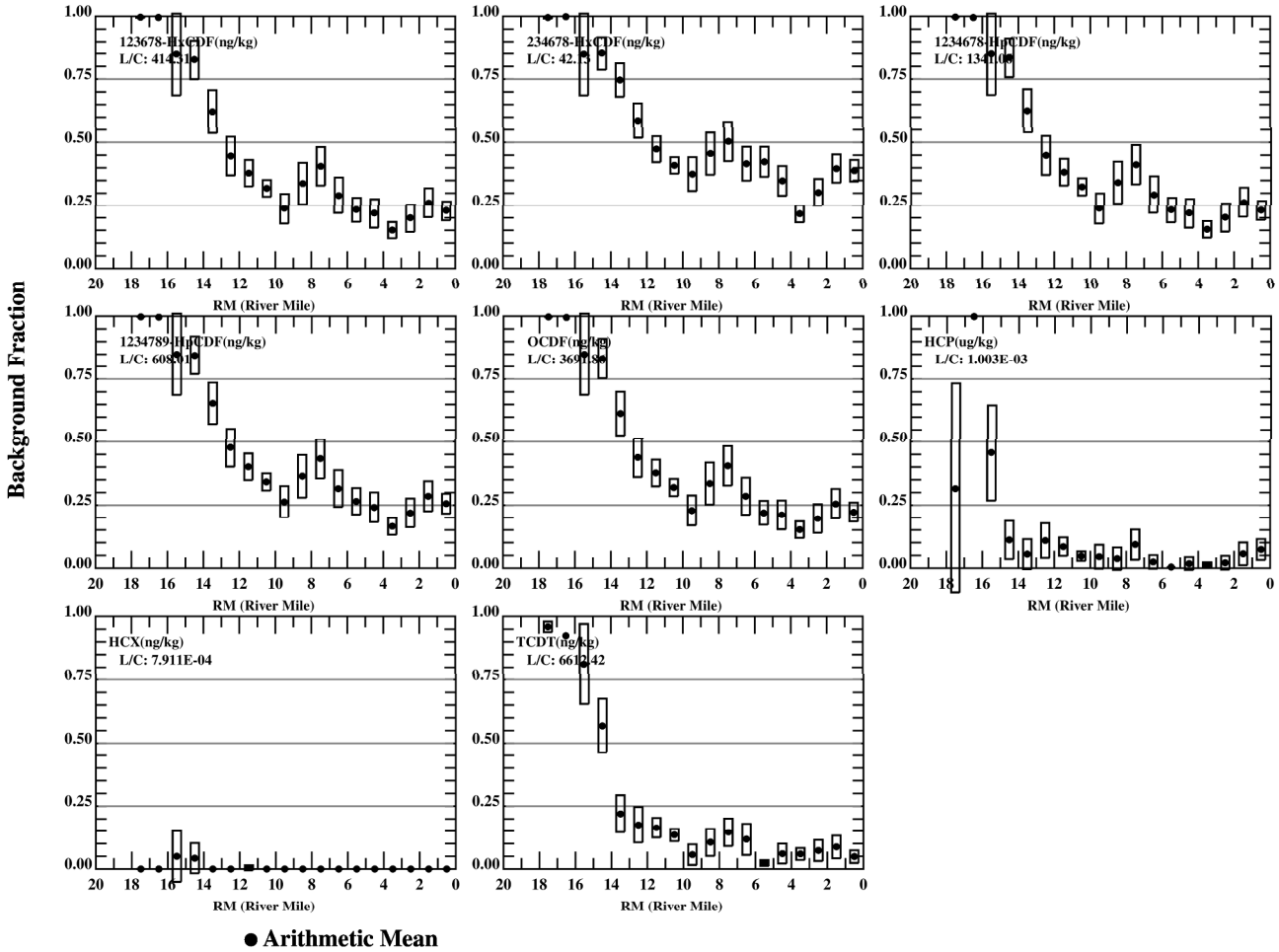

Figure 11. Mean +/- two standard errors of background fraction of in-river concentrations versus river mile, binned by one-mile intervals. Page 2 of 2 page set.