



## **Sensitivity Analysis of Toxic Contaminant Levels in the NY/NJ Harbor Estuary to Particulate Organic Carbon (POC) from Tributary Headwaters**

May 31, 2010

### **Executive Summary**

For the NY/NJ Harbor Toxics TMDL purposes of addressing margin of safety, seasonal variation, and potential public comments, a CARP modeling sensitivity analysis of 2,3,7,8-TCDD concentrations in the NY/NJ Harbor to refractory organic carbon fraction in tributary headwaters has been completed. Two versions of sensitivity analysis were completed. The first version considers a hypothetical increase of the inert fraction of particulate organic carbon introduced by tributary headwaters. While this increases sediment organic carbon, the analysis assumed that the total contaminant mass in the bed initial condition would remain unchanged. The increase in inert fraction of particulate organic carbon introduced by tributary headwaters evaluated would be expected to change future water column concentrations of strongly particle bound contaminants, such as 2,3,7,8-TCDD, by -11.9% to +4.2%, with an overall average potential change in the water column concentration across HEP waters of -2.7%. There would be longer time horizons associated with the response of contaminant concentrations in the bed to contaminant loading changes. The second sensitivity analysis considered the potential increase in the inert fraction of particulate organic carbon introduced by tributary headwaters in an historical context whereby legacy contaminant mass in the sediment bed was also simultaneously increased (i.e., legacy measured contaminant per mass organic carbon sediment initial conditions were applied to a higher mass of organic carbon). The second sensitivity analysis conditions resulted in the calculation of an average increase in 2,3,7,8-TCDD water column concentration of 30.1% and range of 9.4% to 49.4% across the HEP waters. For TMDL calculations where the full removal of legacy contamination as a starting point is an assumption in the TMDL, the results of the first sensitivity analysis are more relevant. A hypothetical change in refractory organic carbon fraction in tributary headwaters would be acting on current loadings only.

### **Background Information**

Ongoing TMDL planning and development for toxics in the NY/NJ Harbor relies upon the previously developed and reviewed numerical models and data from the Contamination Assessment and Reduction Project (CARP). New data collection and numerical modeling activities are taking place independently in selected portions of the Harbor for purposes other than toxics TMDLs.

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A preliminary interim observation based on limited new data in a portion of the Harbor is that fraction organic carbon in the sediment bed of a selected segment of the Harbor might be anomalously higher (i.e., 5-6% or more) than typical for marine waters (2-3%). One possible explanation, if these data are in fact credible and representative of all of the headwater portions of the Harbor, could be that particulate organic carbon (POC) delivered to the Harbor via tributary headwaters is more refractory than previously modeled and supported by dissolved oxygen mass balance and CARP hydrophobic organic contaminants modeling.

Fraction organic carbon in the sediment bed influences how much of and for how long a contaminant remains in the sediment bed. The influence of fraction organic carbon would be most pronounced for those contaminants that are very strongly particle bound such as 2,3,7,8-TCDD.

Potentially for the toxics TMDL purposes of addressing margin of safety, seasonal variation, and potential public comments, a CARP modeling sensitivity analysis of 2,3,7,8-TCDD concentrations in the NY/NJ Harbor to refractory organic carbon fraction in tributary headwaters has been completed.

### **Sensitivity Analysis Approach**

A sensitivity analysis of the CARP model to particulate organic carbon input specifications was completed. Previously approved loading inputs of refractory particulate organic carbon loads were revised to a 50/50 split between refractory and inert POC for testing purposes, maintaining the same total organic carbon load as the CARP model calibration. The 50/50 split represents an overall increase in the inert carbon fraction and therefore the fraction of carbon and bound contaminants trapped in the sediment bed.

Both the organic carbon production and contaminant fate and transport portions of the CARP model were re-run for testing purposes. The organic carbon production portion of the CARP model was run for a 37 year period which allowed the model to reach equilibrium with the revised POC loads for testing. The final 4 years of the organic carbon production model results were used as inputs for the contaminant fate and transport portion of the CARP model. The final 4 years of the organic carbon production model results were cycled 8 times for a total of 32 years for the contaminant fate and transport model portion of the testing simulations. Results for both the organic carbon production and contaminant fate and transport models for the test conditions and previously approved conditions were compared to determine the impacts of the organic carbon sensitivity on projected 2,3,7,8-TCDD responses in the water column and the TMDL loads required to achieve water quality standards.

Two different CARP model simulations were completed to determine the impact of the POC change on calculations of 2,3,7,8-TCDD concentrations. In the first simulation, the CARP contaminant fate and transport model was run using all of the original inputs for 2,3,7,8-TCDD with the only exception being the information passed from the organic carbon production model (i.e., this simulation included the testing changes to splits between refractory and inert organic carbon inputs). In the second simulation, the first simulation conditions were repeated but the initial conditions for 2,3,7,8-TCDD concentrations in the sediment bed were also reassigned based on the revised sediment organic carbon calculated

for POC sensitivity analysis testing. Legacy measured contaminant per mass organic carbon sediment initial conditions were applied to a higher mass of organic carbon thereby increasing the inventory of 2,3,7,8-TCDD stored in the bed.

The data used to set 2,3,7,8-TCDD initial condition concentrations for the approved CARP model included both CARP and R-EMAP 1998 data sets with an average sediment percent organic carbon of 2.6% and a range of 0.05% to 10.3%. The average percent organic carbon in HEP waters from the approved CARP model was 2.4% and increased to 3.0% in the sensitivity testing runs.

### **Sensitivity Analysis Results**

Figure 1 shows calculated water column organic carbon concentration time series results for selected CARP model segments in the Passaic and Hackensack Rivers for sensitivity analysis testing conditions. Figure 1 also shows calculated fraction organic carbon for the sediment bed at these locations. After 37 years of sensitivity analysis test simulation, it appears that an equilibrium condition was reached in the sediment bed.

Across HEP waters, increasing the inert fraction of particulate organic carbon specified for the CARP model carbon loading forcing functions resulted in a calculated average increase as compared to the accepted CARP model by a ratio of 1.26, ranging from a ratio of 1.14 in Raritan Bay to 2.14 in the Passaic River as shown on the right side y-axis of Figure 2. The average calculated organic carbon fractions for each sub-region of HEP waters are also presented in Figure 2 as bar diagrams (see left side y-axis). Figure 2 includes results from the accepted CARP model and the results of the POC sensitivity testing simulation along with the ratio between the two. The sensitivity test with fraction of sediment organic carbon exceeding 4% gives an indication of how sensitive the contaminant portion of the CARP model is to changes in organic carbon.

The first simulation demonstrates the sensitivity of the calculated contaminant “response time” to the change in sediment organic carbon, and the second demonstrates the sensitivity of both the “response time” and the estimated initial conditions to the change in sediment organic carbon. What is meant by contaminant response time is the effect of trapping capacity of contaminant in the bed for a longer time by virtue of increased non-reactive bed organic carbon content. “Response time” specifically refers to how long it would take for an equilibrium concentration to be reached in the bed after a loading change.

The first simulation, where sediment contaminant initial conditions were left as previously approved, demonstrates the effect of the higher POC on the response time of the model alone. The first CARP sensitivity simulation and approved CARP model results have the same initial contaminant mass and are allowed to respond over time to the same set of contaminant loads and the differences in organic carbon. The higher levels of organic carbon in the bed result in less transfer of contaminant from the bed to the water column. Since the legacy contamination in the bed is the main source of contaminant in the case of TCDD, the calculated result is initially lower water column concentrations and slightly longer ‘response times’ in both the sediment and water column. Figures 3a through 3n show the time series responses to the sensitivity runs. The first two panels show the response in water column layers 1 and 10 over time respectively, and the third and fourth panels show the sediment responses for the top 10 cm, on a dry weight and organic carbon normalized

basis. On these figures, the blue line represents the approved CARP results and the red line represents the first organic carbon reactivity sensitivity simulation. The implications of the first sensitivity for the TMDL projections using the 28 to 32 year time horizon range from +4.2% to -11.9%, with an overall average change in the water column concentration across the HEP waters of -2.7%. The HEP waters average 2,3,7,8-TCDD concentrations for the final four years (i.e., years 28-32) along with the ratio of the sensitivity results to the approved CARP results are presented in Figures 4, 5 and 6 for water column, sediment dry weight and sediment organic carbon normalized results respectively. The figures show the approved CARP model concentration results, along with the results of the two sensitivity calculations, as bars. The ratio of the contaminant concentration results of the two sensitivities to the approved CARP contaminant concentration results are shown as lines.

The second sensitivity results in a far greater change in contaminant concentrations than the first simulation. Initial contaminant conditions in the bed were set in the approved CARP model based on organic carbon normalized sediment chemical measurements. The measured points were spatially interpolated over the model domain, and then multiplied by the organic carbon production model calculations of sediment organic carbon concentration to get the dry weight sediment concentrations for the contaminant model initial conditions. Using this same approach with the revised organic carbon model calculations for the sensitivity testing conditions, results in higher bed initial contaminant conditions. Although the overall average HEP waters organic carbon was only increased by 26%, the average initial concentration of 2,3,7,8-TCDD increased by 43%. This higher initial condition, along with the longer response times associated with the higher sediment organic carbon results in an average increase in 2,3,7,8-TCDD water column concentration of 30.1% with a range of 9.4% to 49.4% across HEP waters. Since this increase over the first sensitivity results is strictly related to an increase in legacy sediment contamination and the TMDL calculations have been done with legacy contamination set to zero, the impact on TMDL calculations should be the same as the first sensitivity. With the higher level of legacy contamination but the same loading conditions the model would ultimately reach the same equilibrium, it would just take a longer time. For example in Figure 3h, for the Passaic River, water column concentrations from the second sensitivity lag behind the first sensitivity by approximately 12 years with nearly the same behavior. The results of the second sensitivity are displayed along with the first sensitivity on Figures 3 through 6.

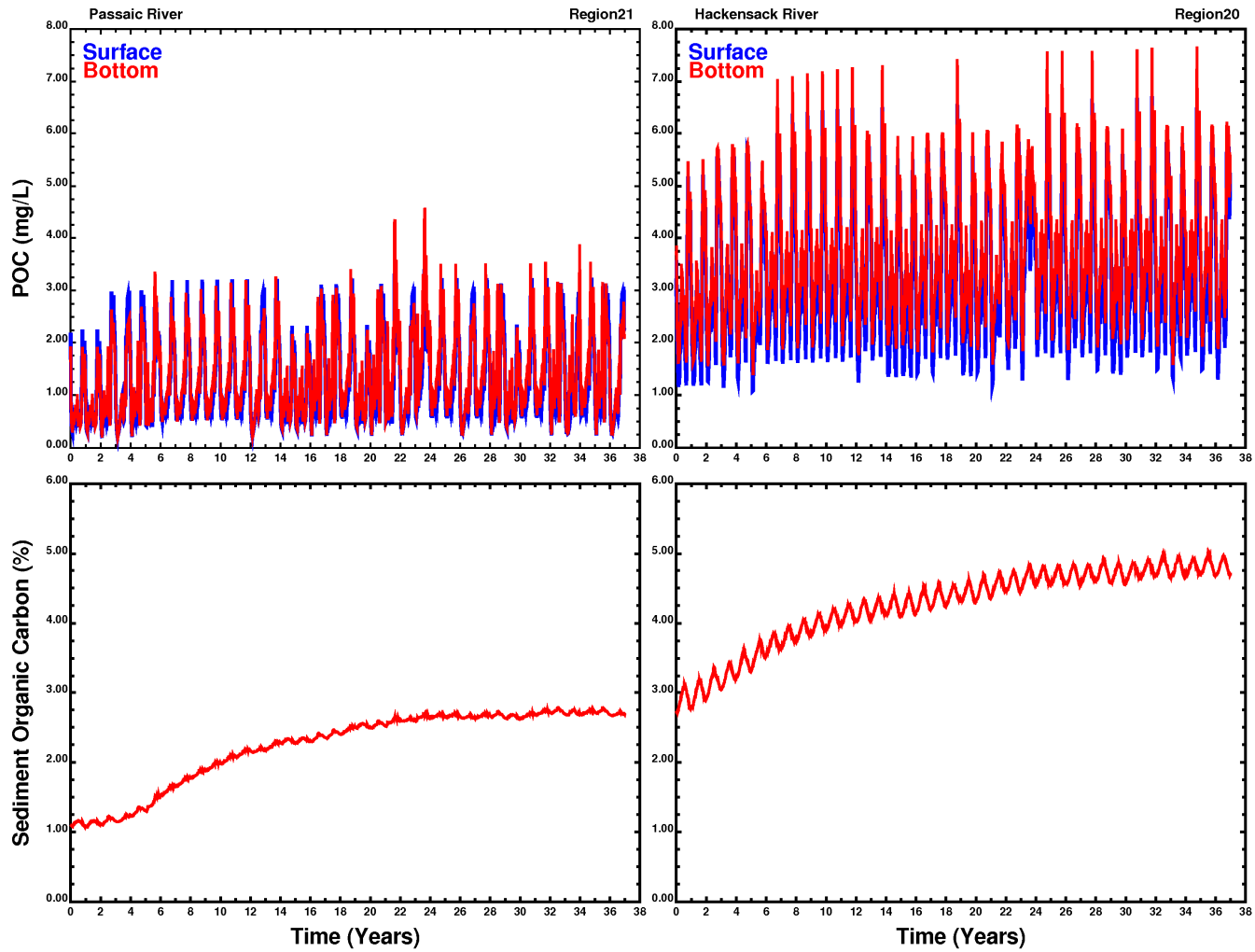
## Conclusions

The sensitivity analyses show that the higher levels of particulate organic carbon (2.4% vs. 3.0% on average) resulting from splitting refractory particulate organic carbon loadings between refractory and inert POC pools results in longer model contaminant response times throughout HEP waters. When applied to the sediment 2,3,7,8-TCDD initial conditions as in the second sensitivity simulation, the higher organic carbon also results in a larger initial mass of legacy contamination. Further effort and additional monitoring would be required to better understand the source of potentially locally high organic carbon concentrations observed recently in a specific sub-region of HEP waters as well as discrepancies between organic carbon concentrations measured during historical and new field studies.

Results of the first sensitivity analysis are most applicable to Harbor TMDLs which will mostly address managing ongoing rather than legacy contaminant sources. These results show modest decreases in projections of future water column contaminant concentrations

(see Figure 4) as legacy contaminant will remain associated with the bed over longer time horizons and contribute less to the water column in the future. The first sensitivity analysis suggests a slightly more optimistic picture for future management of water column concentrations than has been calculated for Harbor TMDLs to date. In this sense, the harbor TMDL analyses performed to date are more conservative than the results obtained in the evaluation of a hypothetical change in carbon reactivity.

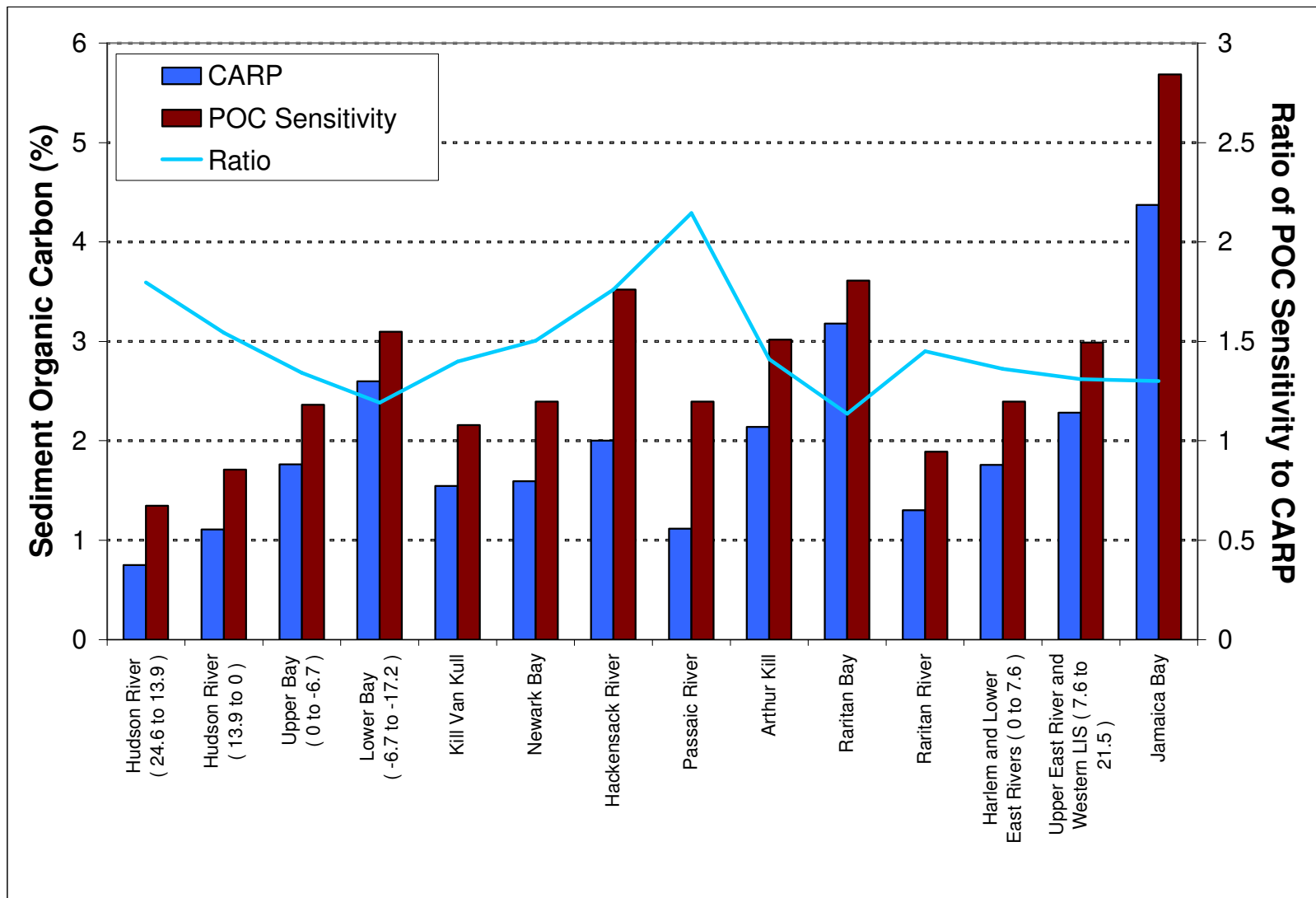
Figure 1. Organic Carbon Time Series



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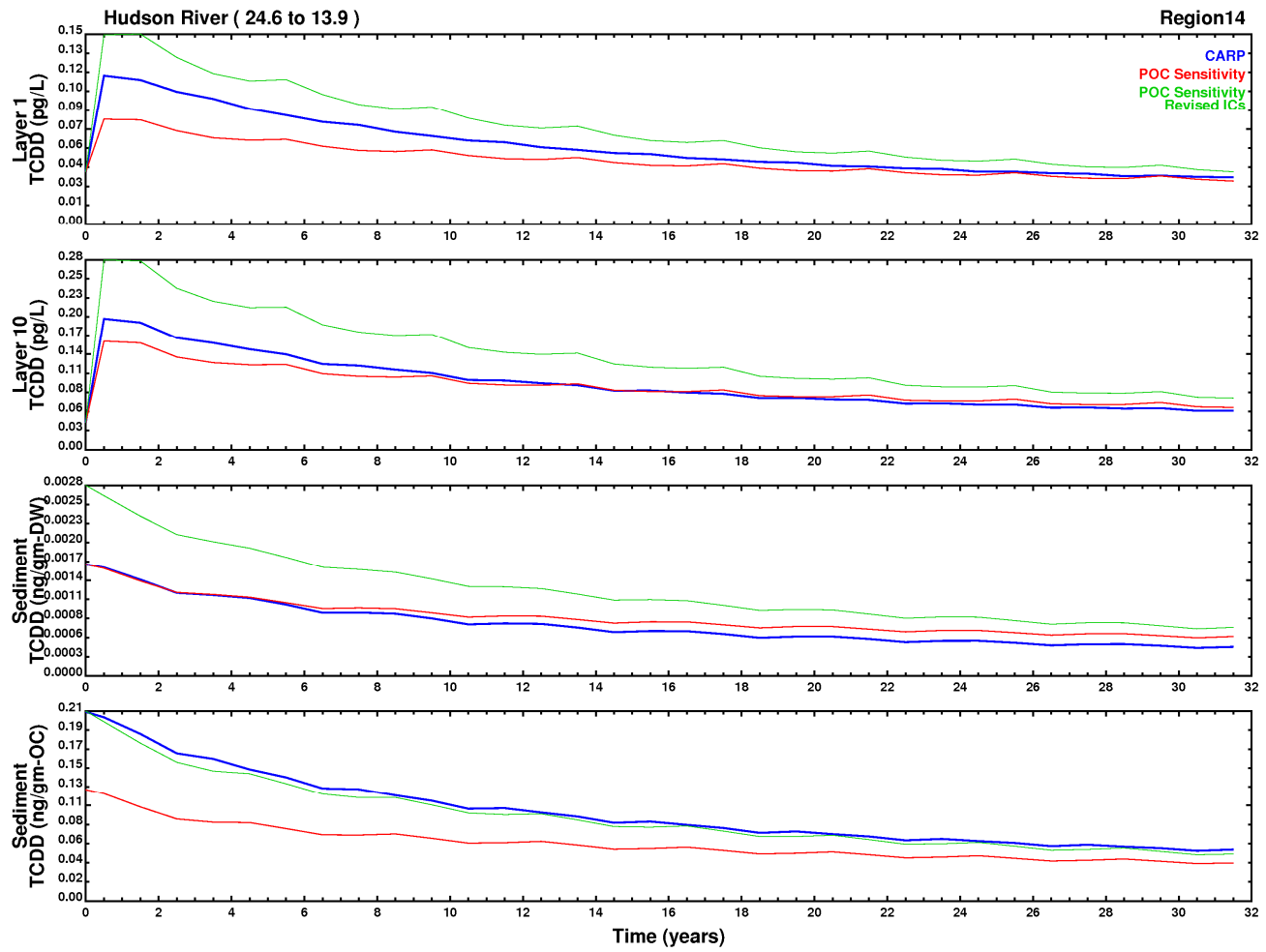
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Figure 2. Organic Carbon Sensitivity Responses by HEP Core Region



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Figure 3a. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions

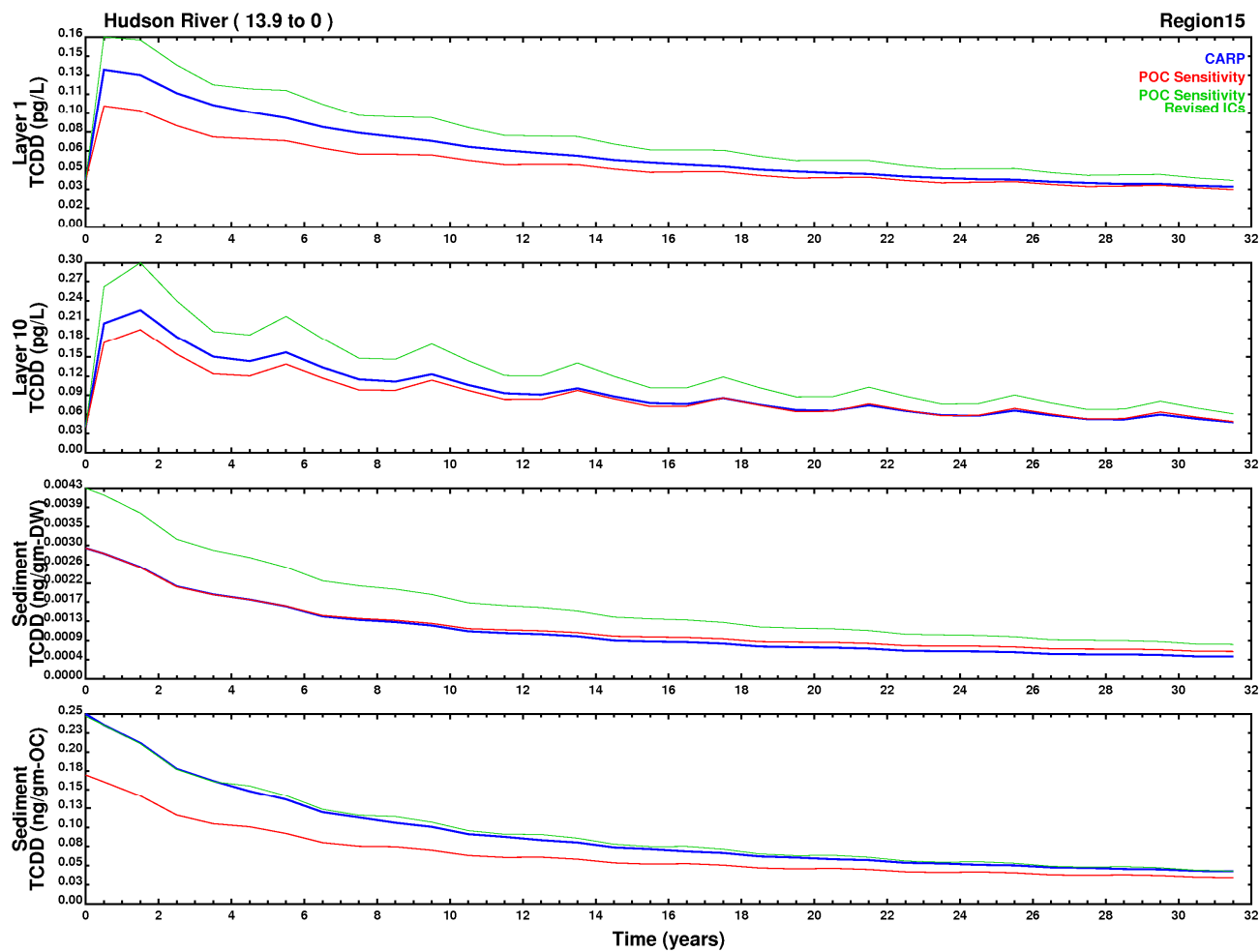


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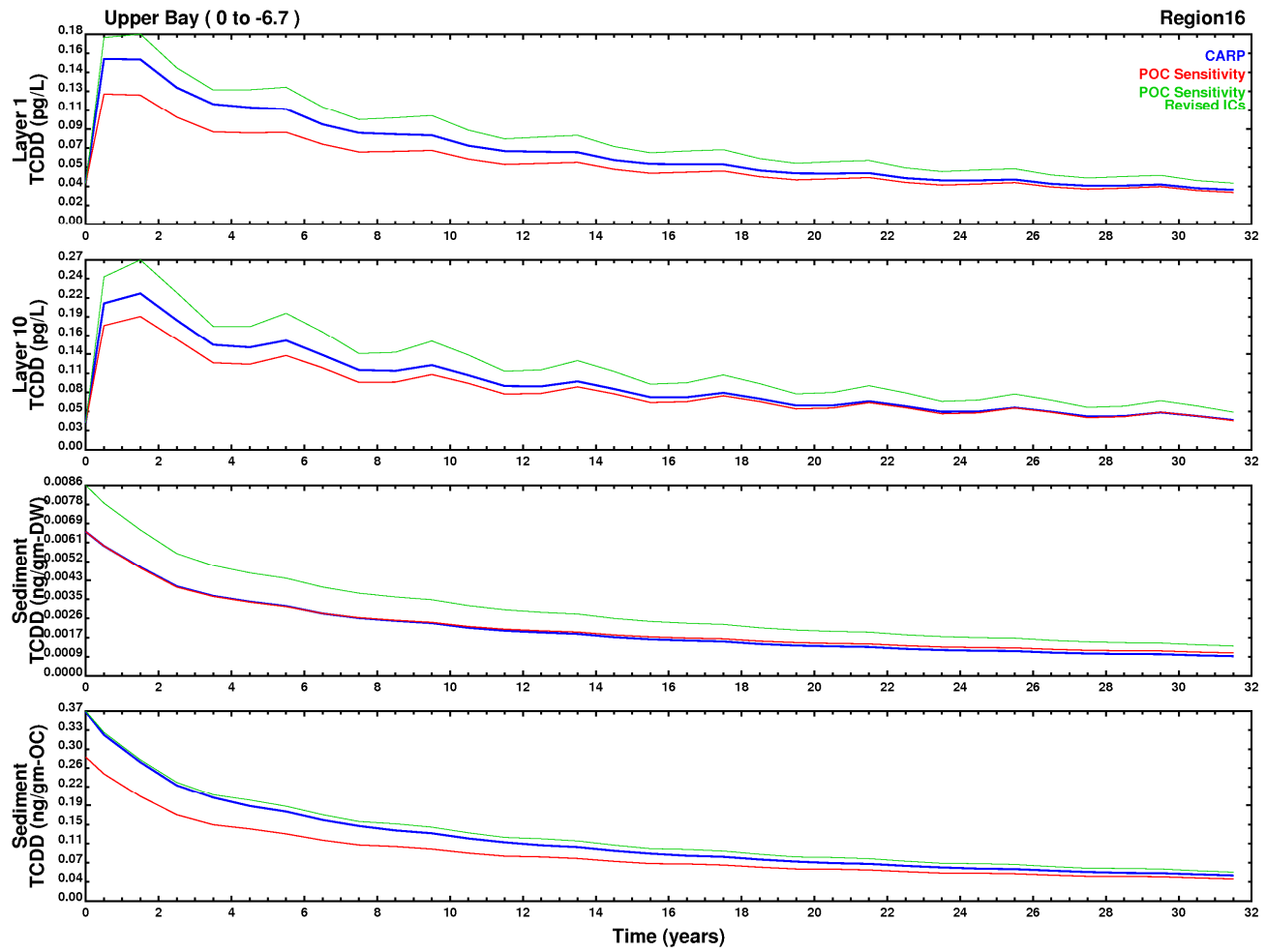
Figure 3b. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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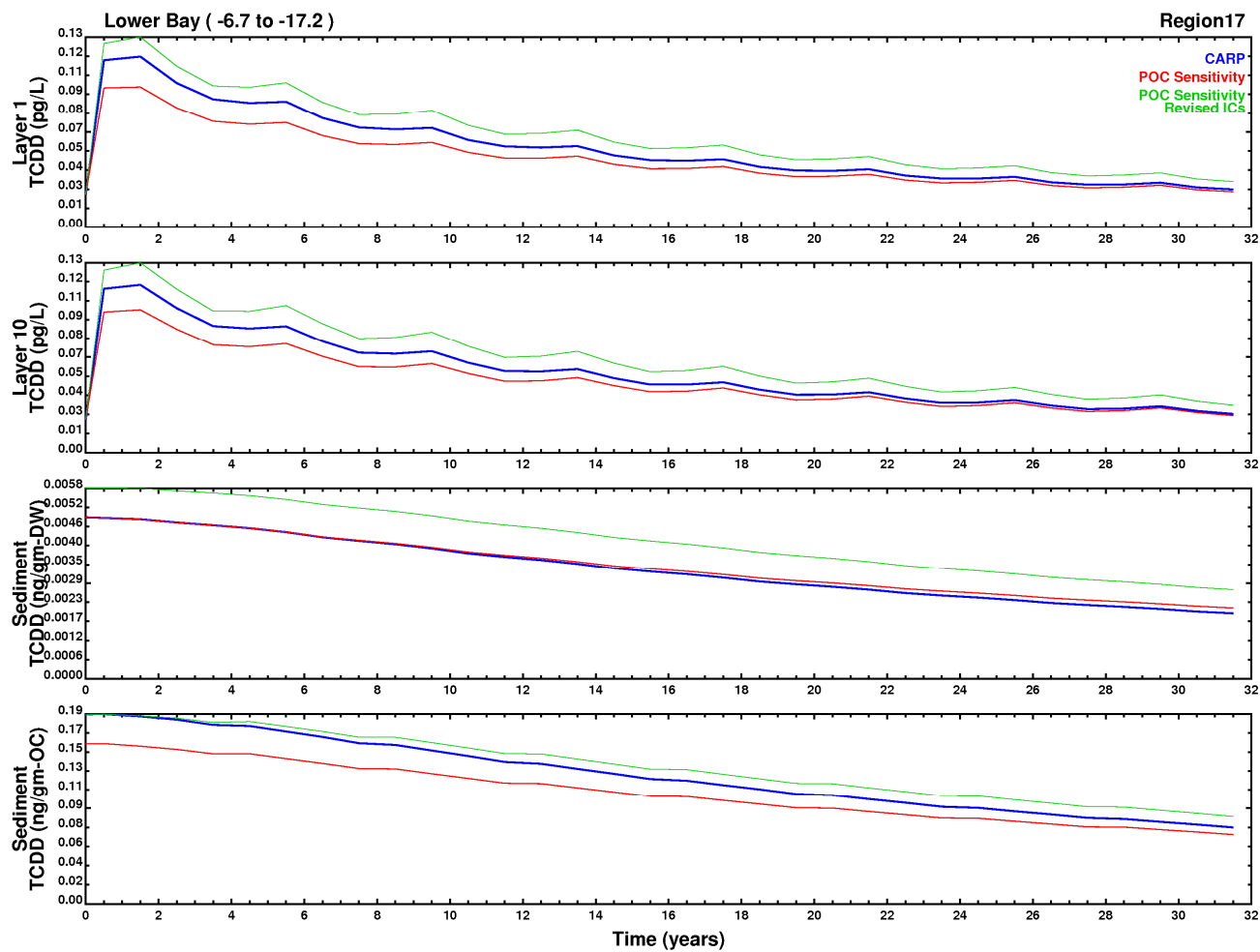
Figure 3c. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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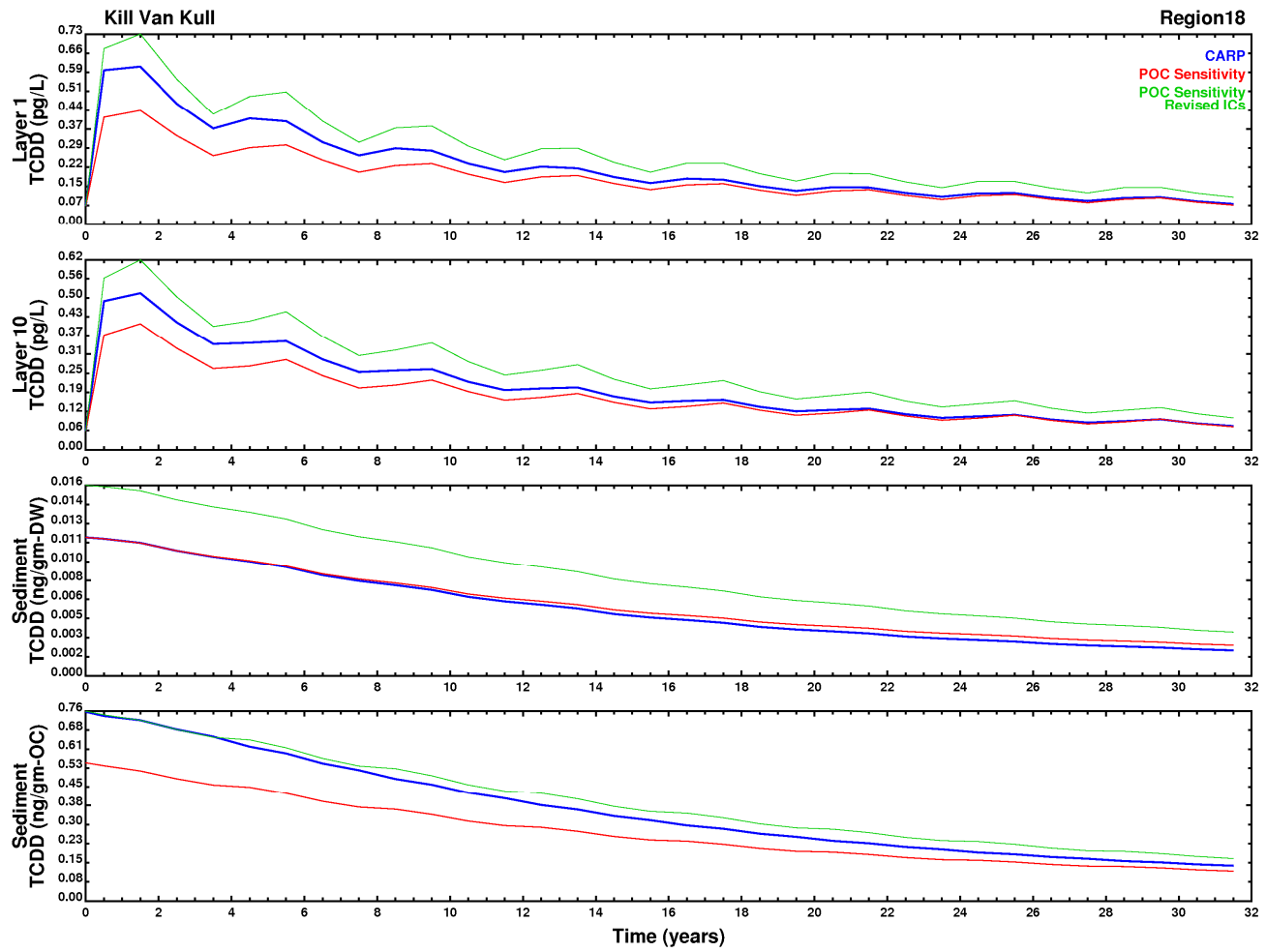
Figure 3d. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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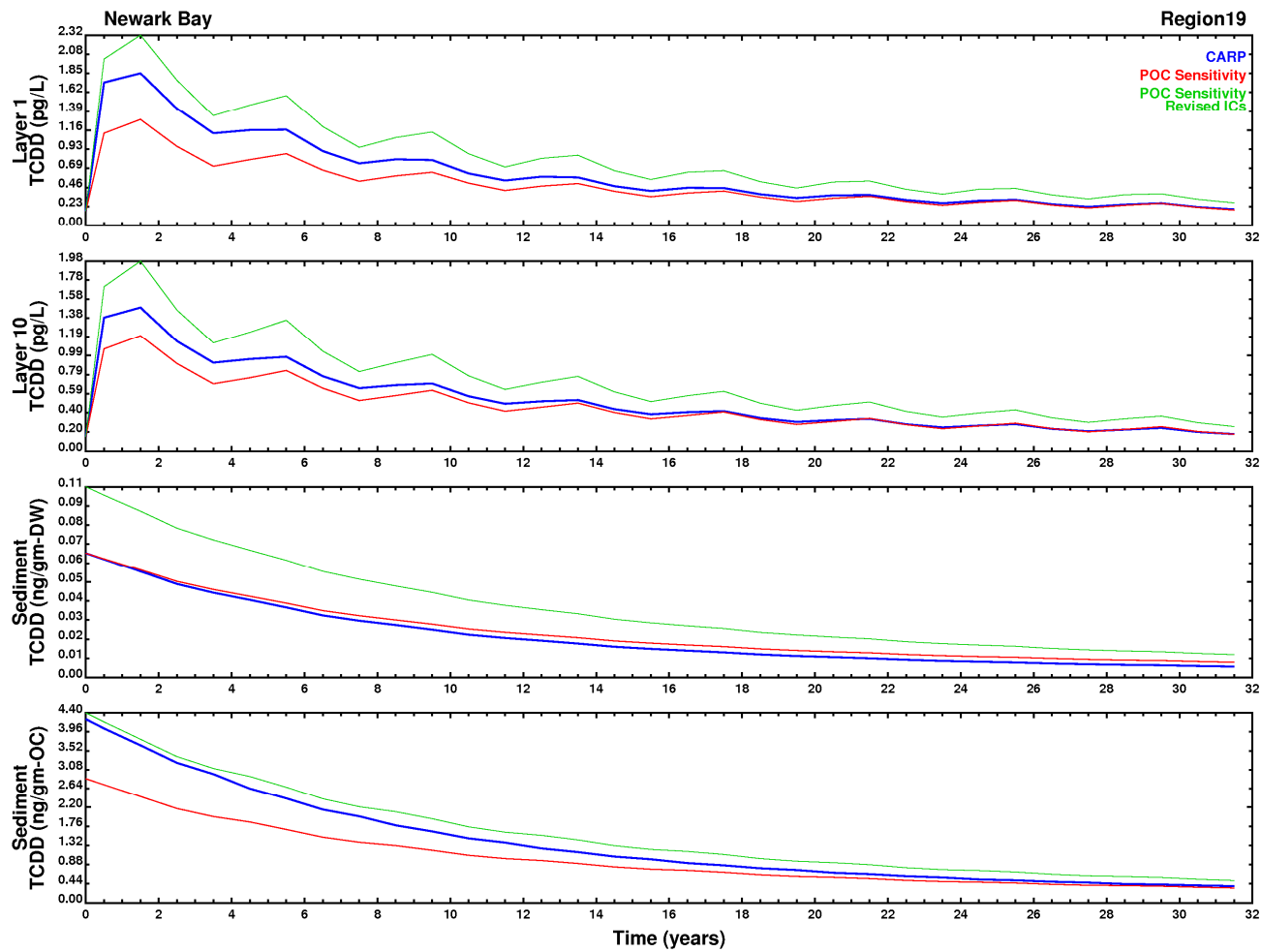
Figure 3e. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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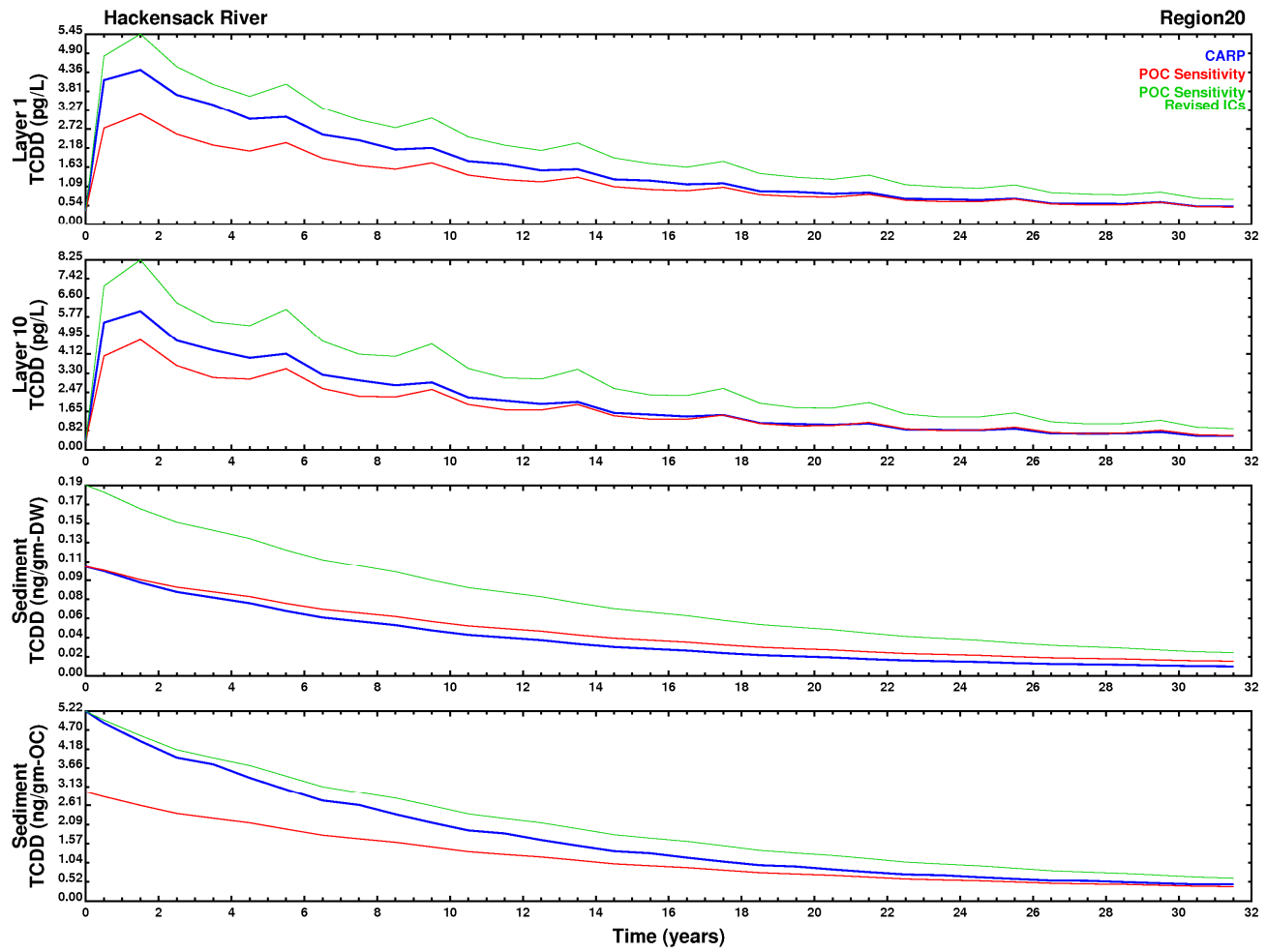
Figure 3f. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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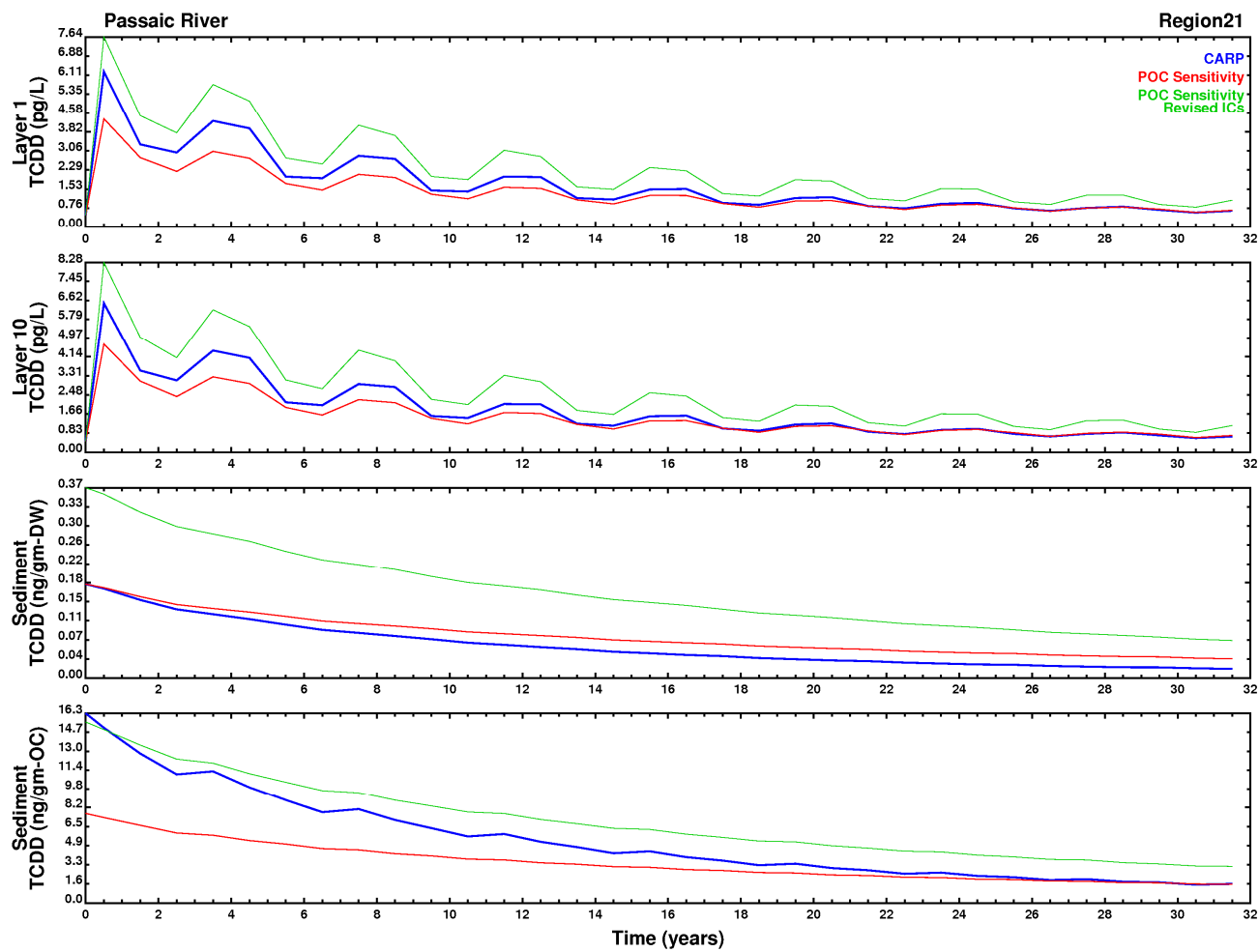
Figure 3g. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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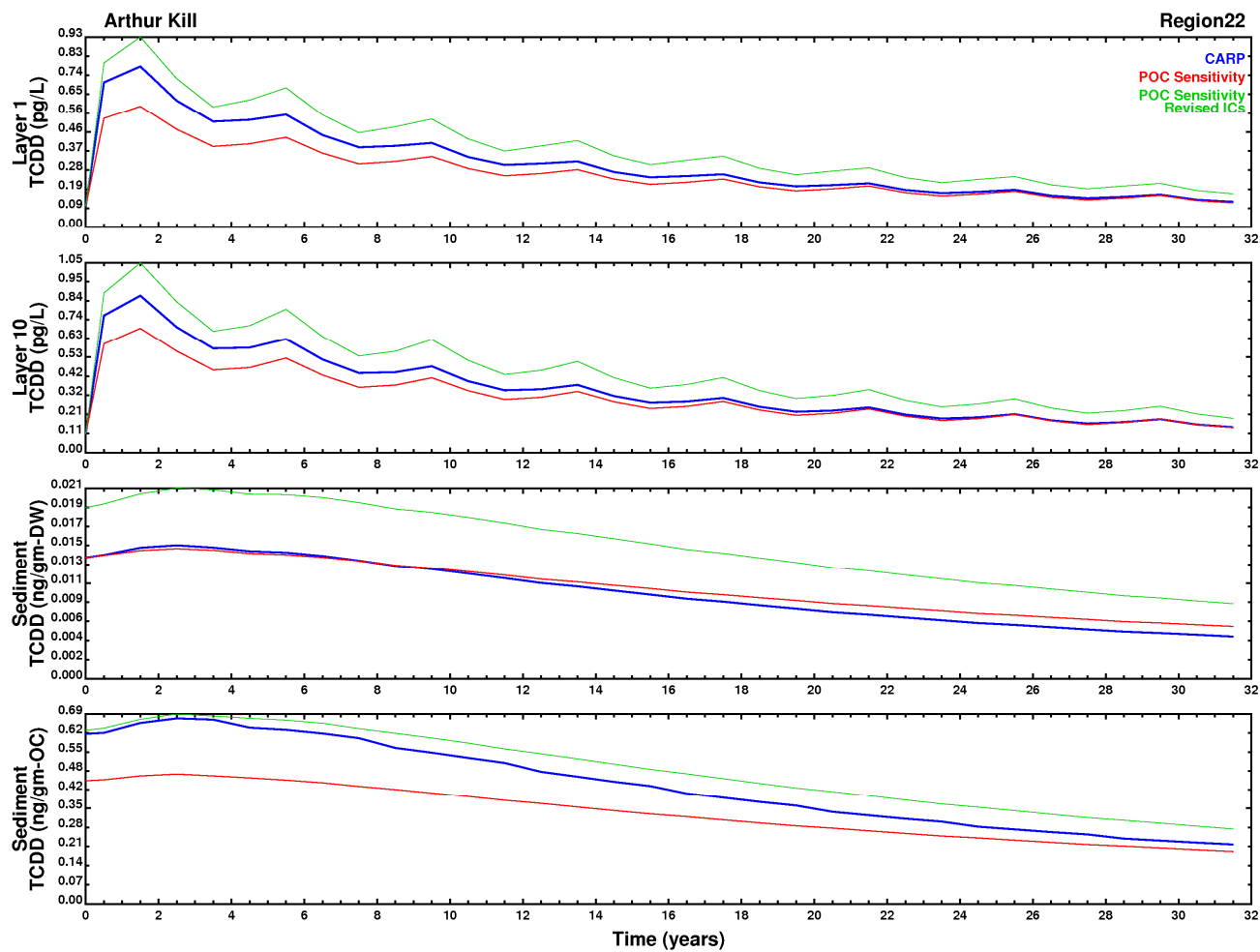
Figure 3h. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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Figure 3i. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions

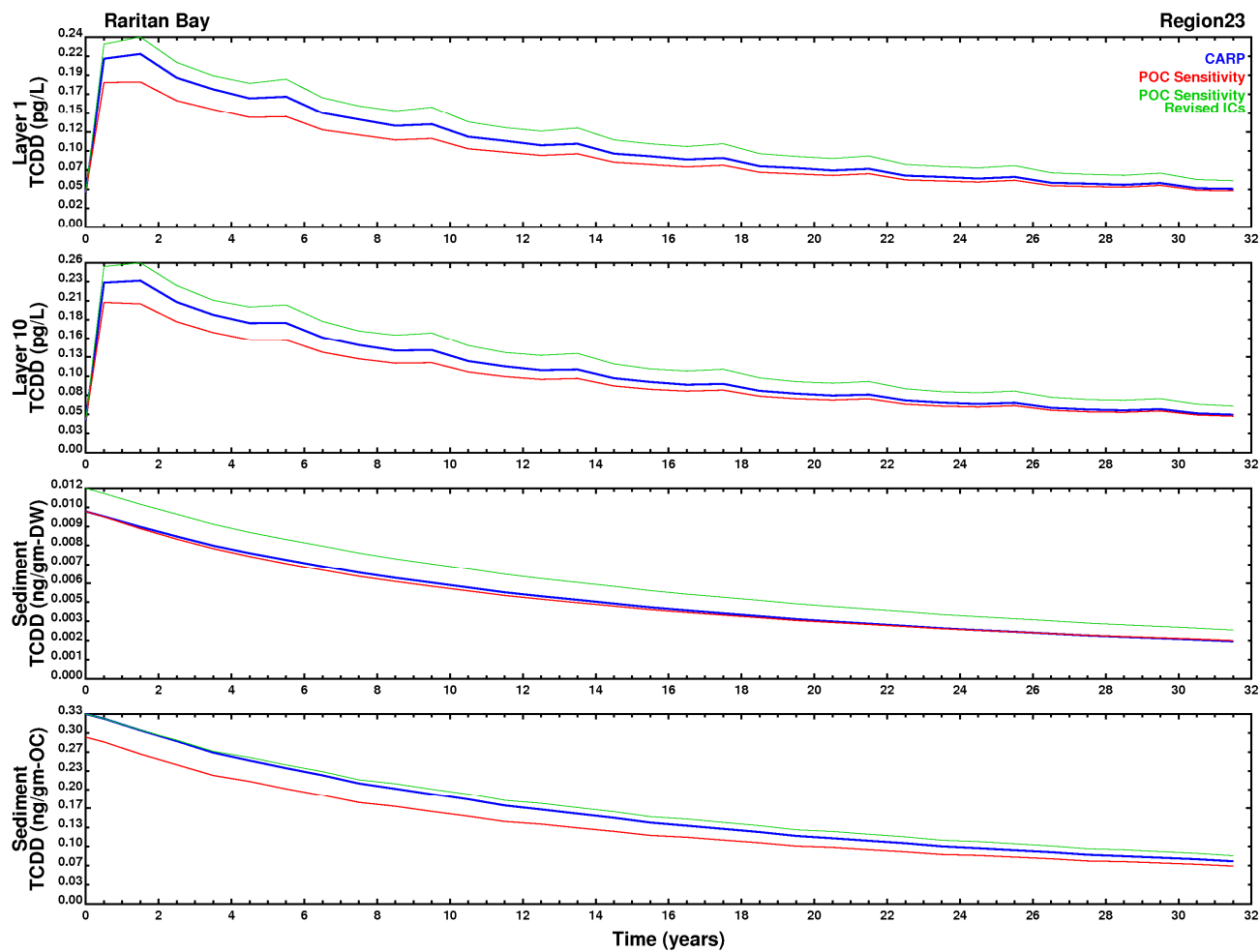


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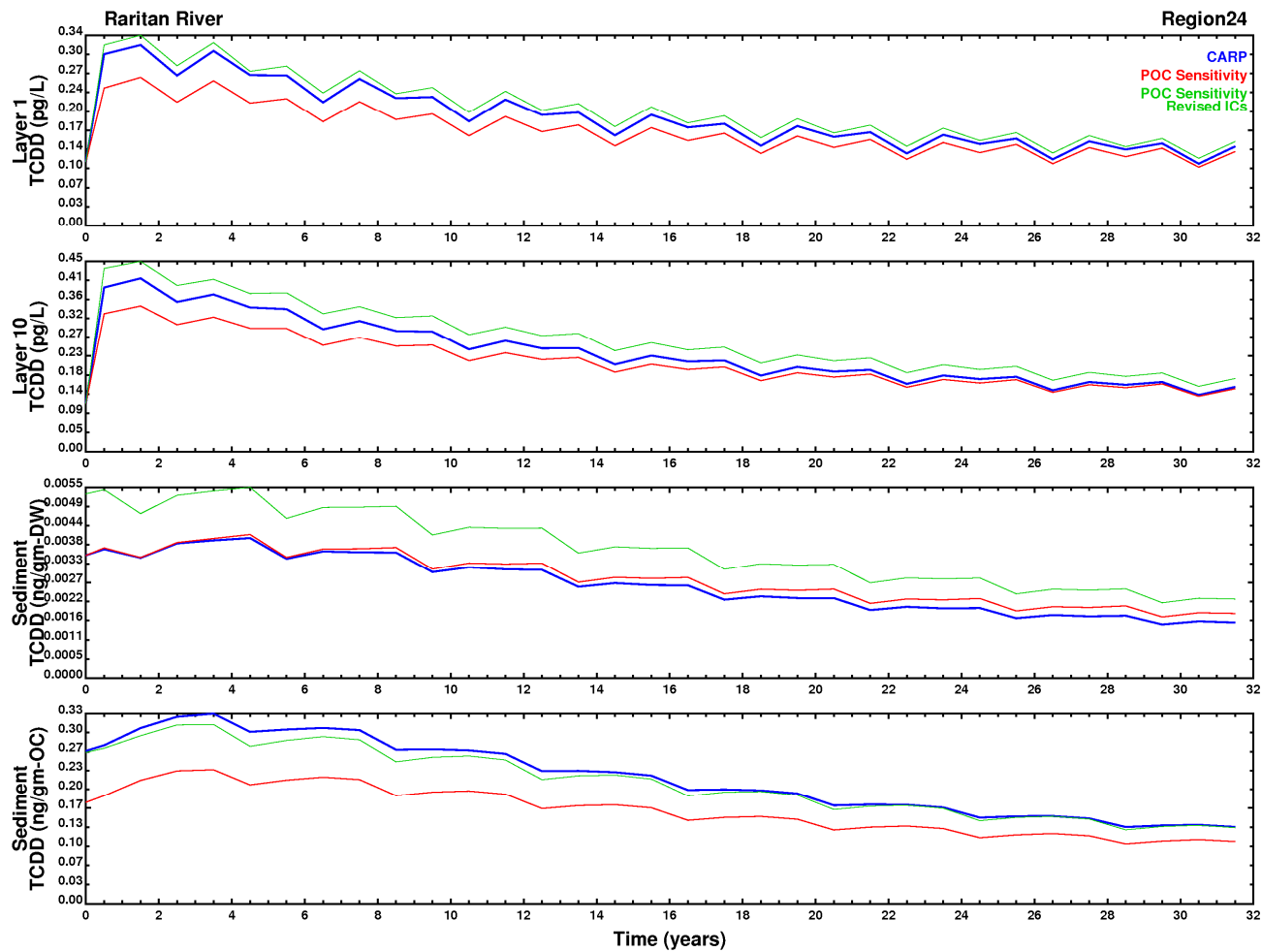
Figure 3j. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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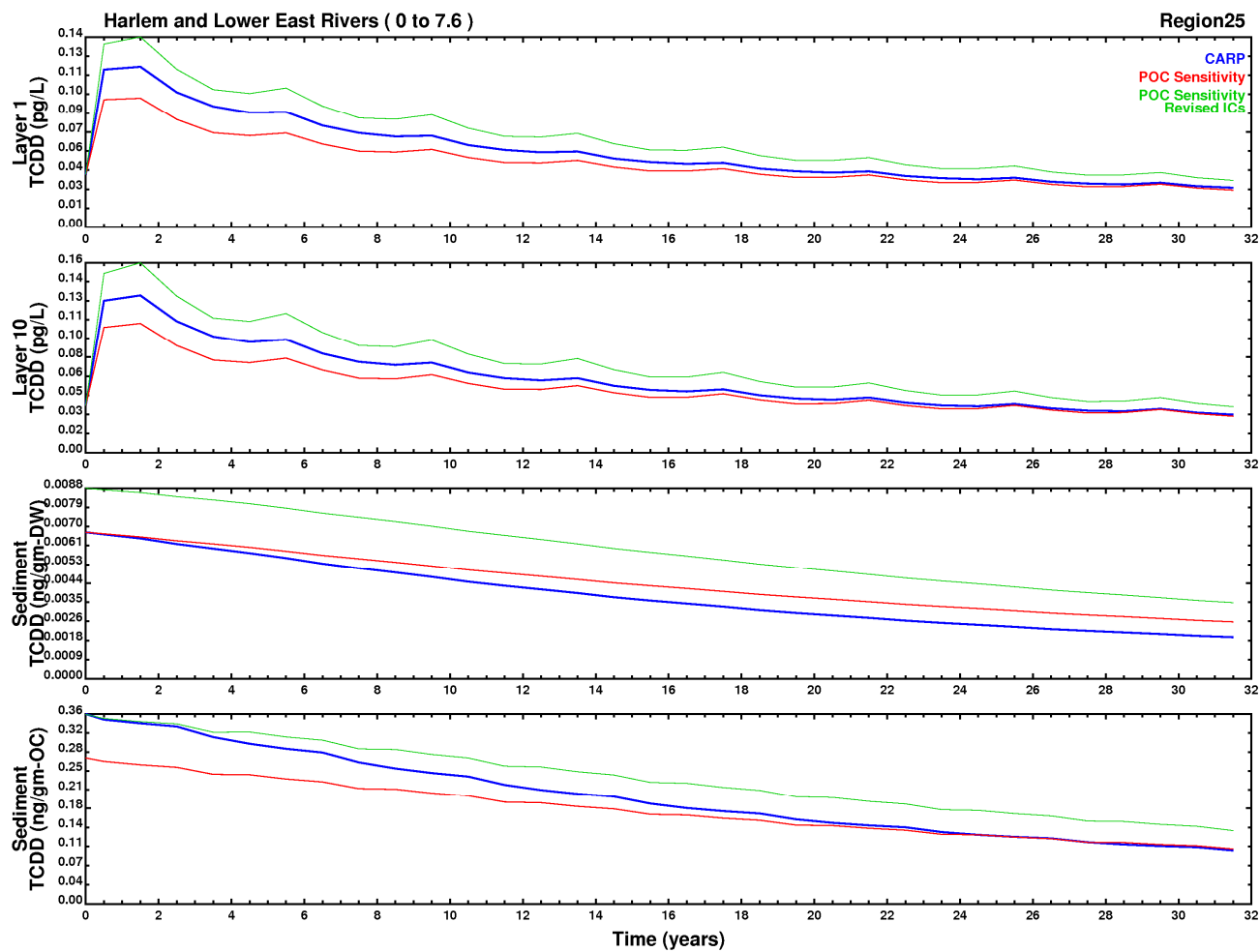
Figure 3k. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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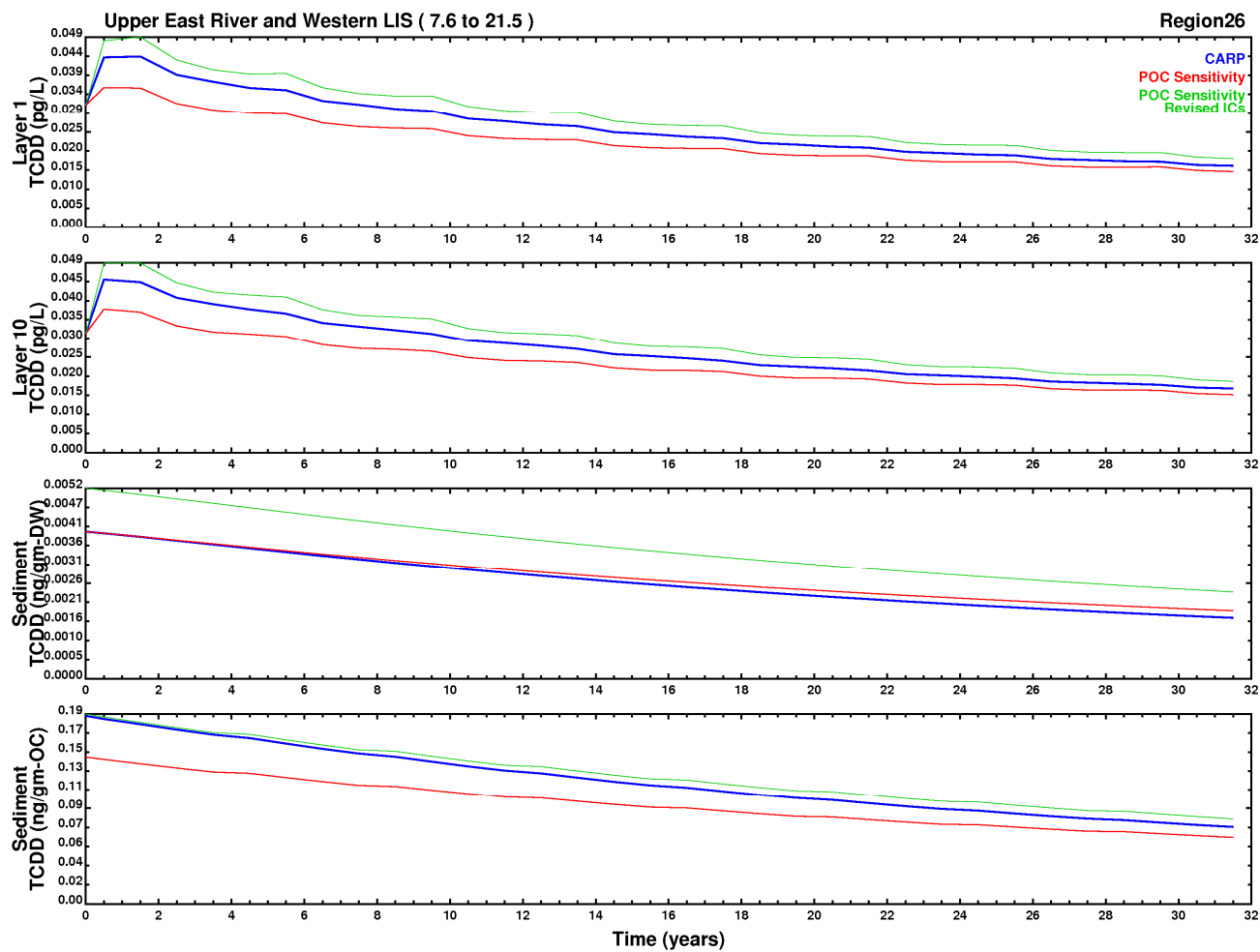
Figure 3l. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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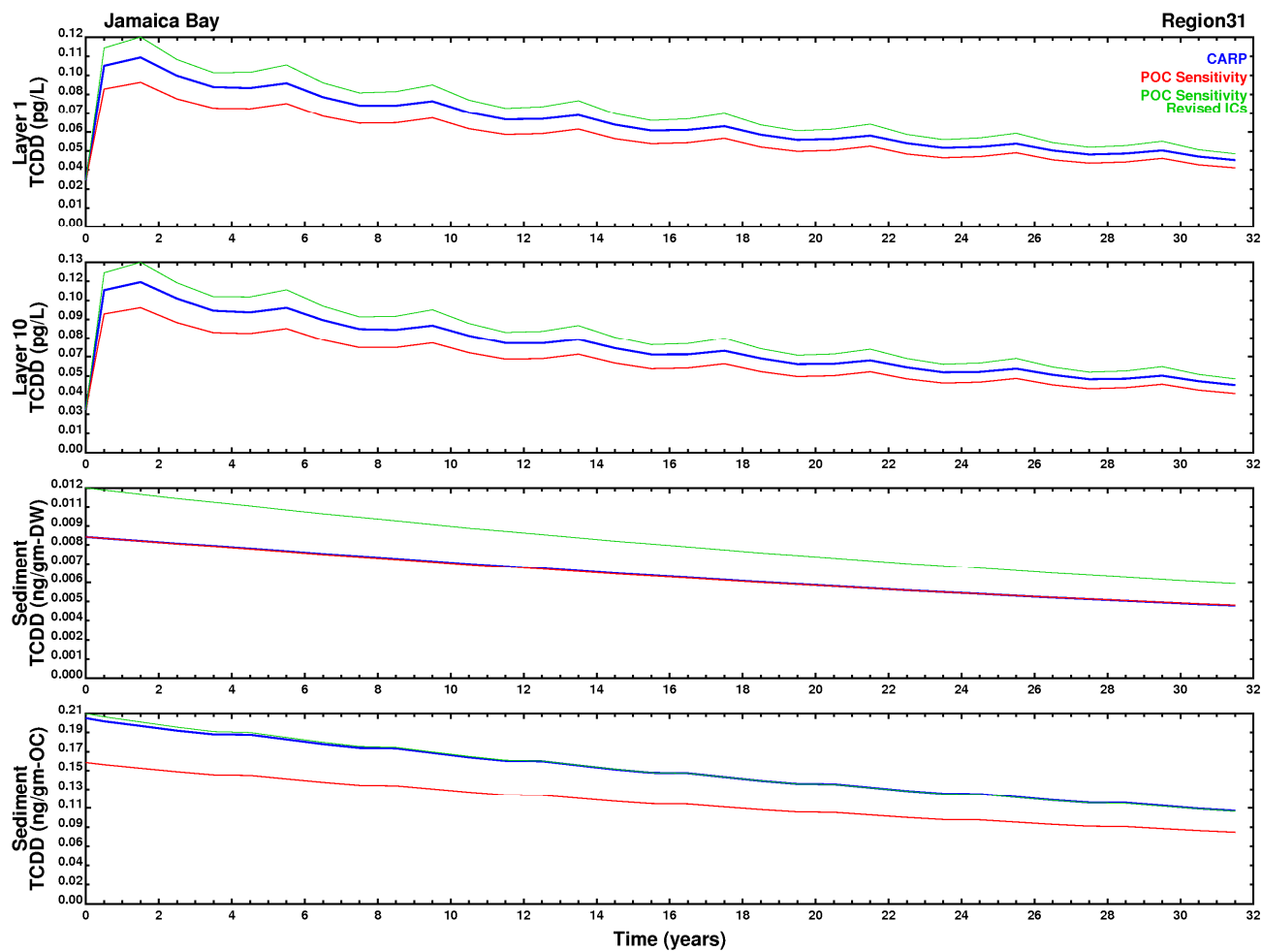
Figure 3m. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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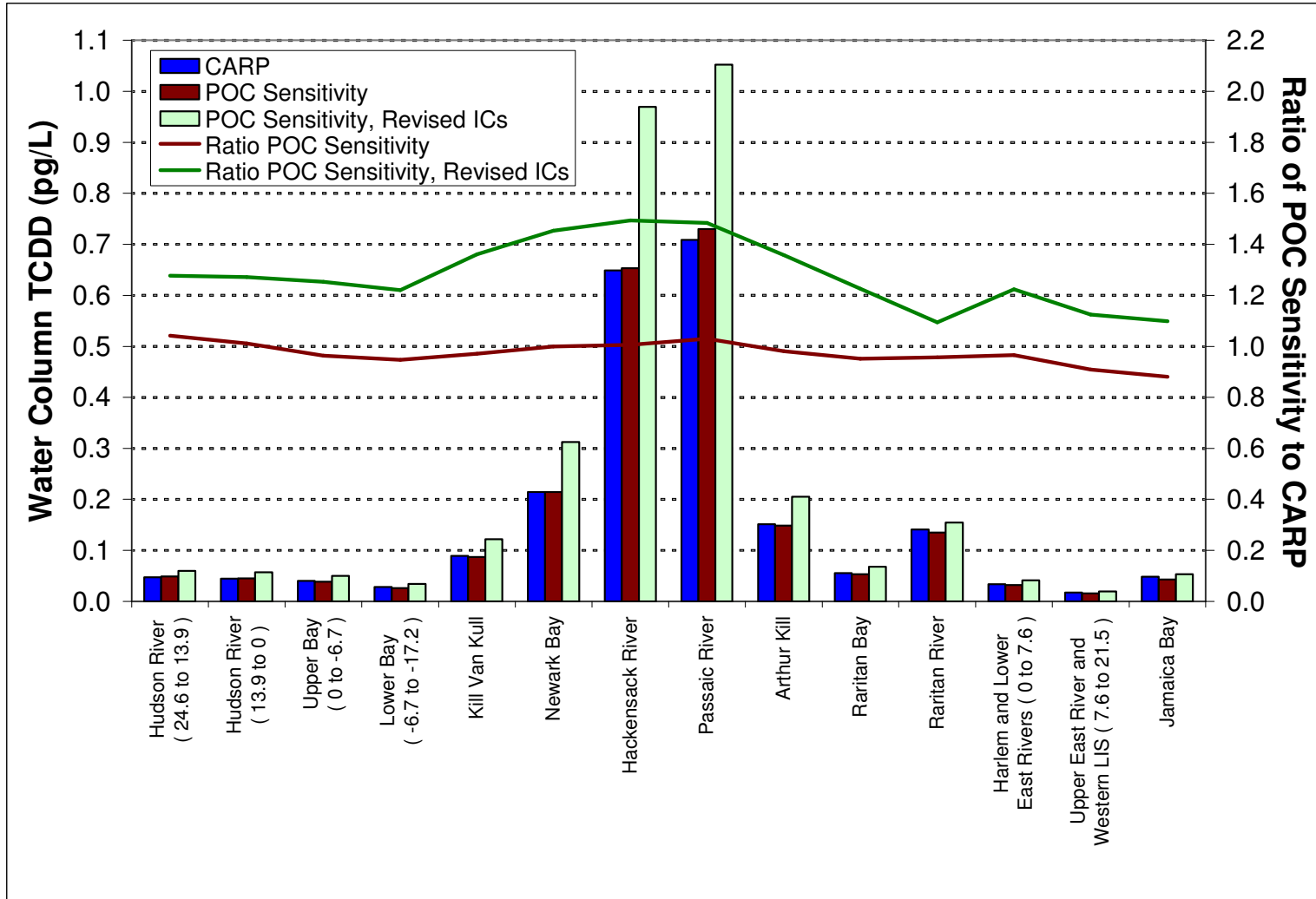
Figure 3n. 2,3,7,8-TCDD Time Series Response for CARP Matrix Regions



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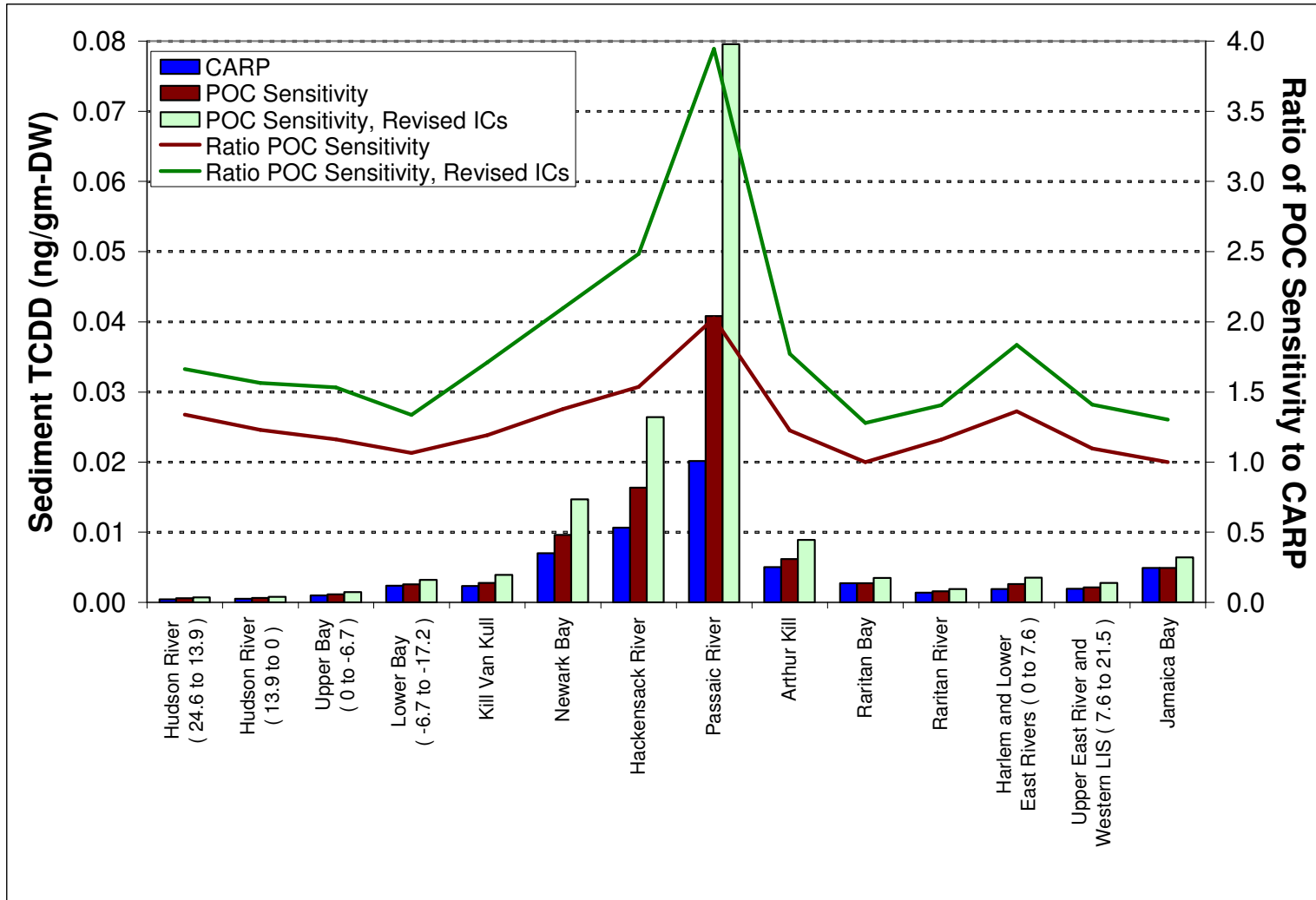
Figure 4. Water Column 2,3,7,8-TCDD Responses to Organic Carbon Sensitivity by HEP Core Region



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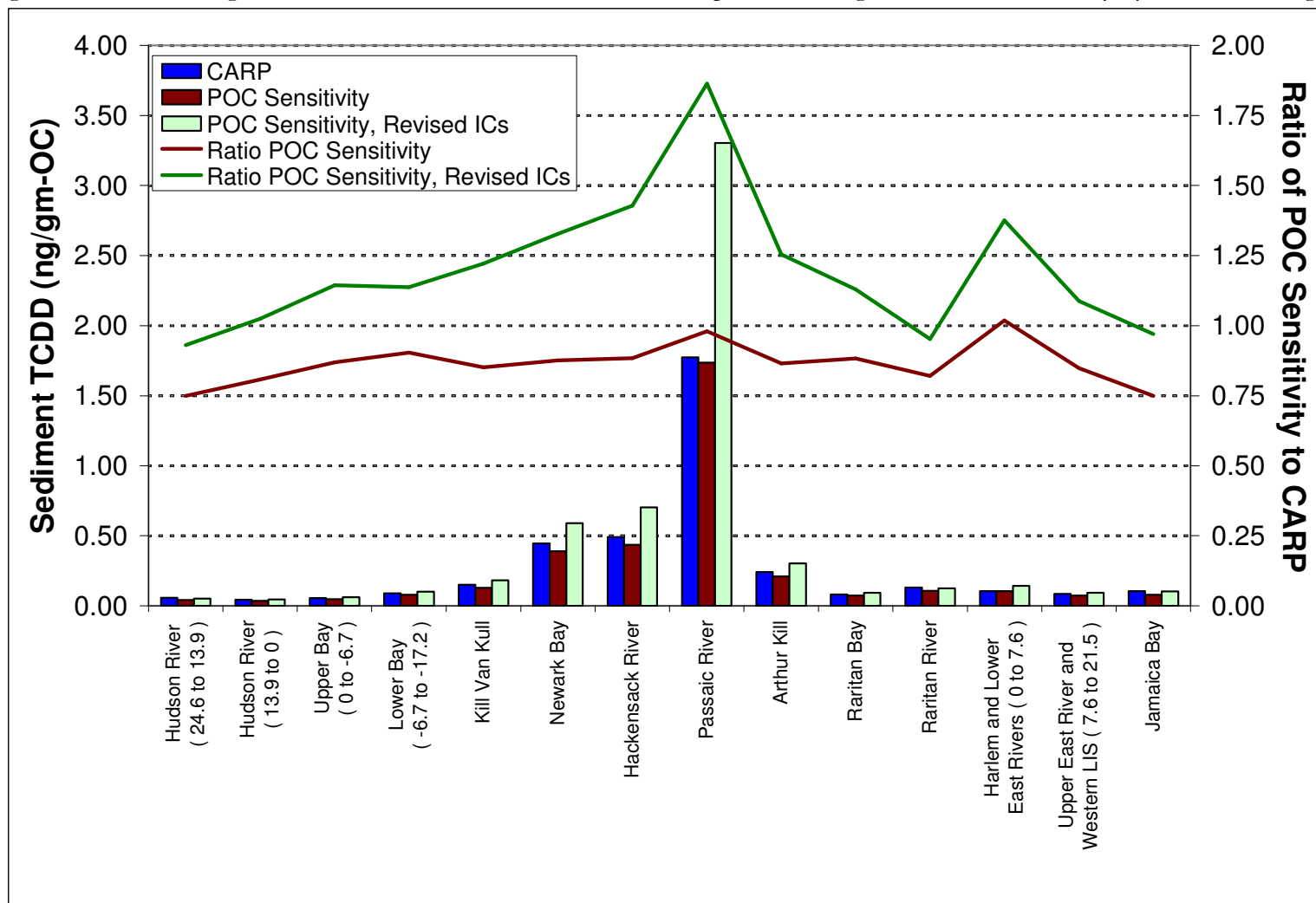
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Figure 5. Sediment Dry Weight 2,3,7,8-TCDD Responses to Organic Carbon Sensitivity by HEP Core Region



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Figure 6. Sediment Organic Carbon Normalized 2,3,7,8-TCDD Responses to Organic Carbon Sensitivity by HEP Core Region



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