## Decision Rationale

## Total Maximum Daily Load for
## Total 2,3,7,8- TCDD ( Dioxin) for the Ohio River

### I. Introduction

This document will set forth the Environmental Protection Agency's (EPA) rationale for approving the Total Maximum Daily Load (TMDL) for Total Dioxin for the Ohio River which was sent out for public comment on July 5, 2000 and closed on August 18, 2000. Our rationale is based on the determination that the TMDL meets the following 8 regulatory conditions pursuant to 40 CFR §130.

1. The TMDLs are designed to implement applicable water quality standards.
2. The TMDLs include a total allowable load as well as individual waste load allocations and load allocations.
3. The TMDLs consider the impacts of background pollutant contributions.
4. The TMDLs consider critical environmental conditions.
5. The TMDLs consider seasonal environmental variations.
6. The TMDLs include a margin of safety.
7. The TMDLs have been subject to public participation.
8. There is reasonable assurance that the TMDLs can be met.

### II. Background

In 1997, the U.S. Environmental Protection Agency, Region 3, entered into a Federal Consent Order to complete a Total Maximum Daily Load (TMDL) for dioxin for the Ohio River by September, 2000. The Ohio River Valley Water Sanitation Commission is completing the monitoring, modeling and daily load analysis on behalf of Region 3. This effort has been coordinated and reviewed, on an ongoing basis, by the Commission's TMDL Work Group. This work group is composed of representatives from all mainstem states, and US EPA Regions 3, 4, 5 and headquarters.

TMDLs are required for waters not meeting applicable water quality standards after application of best practicable control technology. A TMDL must be designed to meet water quality standards, which is 0.013 pg/L for the Ohio River for 2,3,7,8-TCDD (dioxin). TMDLs must include allocations. TMDLs must consider background conditions, which are accounted for through the utilization of the dioxin sample data. TMDLs must consider critical conditions and seasonality, which are accounted for by utilizing harmonic mean flow (representative of a long-term average condition).

Section 303(d) of the Clean Water Act requires states to develop lists of waters still requiring total maximum daily loads (TMDLs). In 1997, U.S. EPA entered into a federal Consent Agreement obligating them to complete a TMDL for dioxin on the Ohio River from ORM 266 to ORM 312, per West Virginia's 1996 draft 303(d) List, by September, 2000. West Virginia's 1998 303(d) List includes the Ohio River for dioxin (2,3,7,8-TCDD) from Racine Dam at Ohio River mile (ORM) 237.5 to the West Virginia state line at ORM 317. The listing was based on West Virginia fish consumption advisories and "high volume" water column sampling for dioxin conducted by the Ohio River Valley Water Sanitation Commission (ORSANCO). Hence, the requirement for the Ohio River dioxin TMDL was extended to include the segments on the 1998 list (ORM 237.5 to ORM 317).

Figure 1 provides a map of the TMDL segment including important land marks and high volume sampling sites used in the TMDL analysis. The TMDL includes a 79.5 mile segment of the Ohio River from Racine Dam (ORM 237.5) to the West Virginia-Kentucky border (ORM 317). This segment forms a portion of the Ohio-West Virginia state border and ends immediately upstream of the Kentucky border. The RC Byrd Dam splits the TMDL segment at ORM 279.2. The Ohio River Basin drains approximately 40,000 square miles upstream of the TMDL segment.

Based on West Virginia's 1998 303(d) list, a dioxin TMDL is to be completed for the Ohio River segment from Ohio River Mile (ORM) 237.5 to ORM 317. This segment borders Ohio and West Virginia. "High Volume" dioxin sampling, a collection technique that effectively concentrates 1000 liters (L) into a single sample in order to achieve necessary detection levels, was conducted within the TMDL segment during 1997-1998. Multiple samples were collected over the period at various flows. The data are used to estimate TMDL segment boundary loads and to verify water quality modeling results. The SMPTOX4 water quality model was utilized to determine dioxin loads at various river flows. The model was run at three flows: seven day-ten year low flow, harmonic mean flow, and a one-year flood high flow. These flow regimes compare reasonably with flows at which monitoring data were collected.

## Model Selection and Segmentation

After reviewing several models for possible use in performing this TMDL analysis, SMPTOX 4 was selected. This model was selected because it has a sediment component which is critical to the transport of dioxin, because its complexity best matches the available data and current scientific knowledge of dioxin transport and fate mechanisms, and because the model is supported by the US EPA. SMPTOX is a steady-state flow model that simulates transport and fate of chemical pollutants and sediments. The primary purpose of the model is to determine the maximum dioxin loading within the TMDL segment at critical conditions. SMPTOX was determined to be the most appropriate model considering the transport and fate processes to be simulated, the available data for input to the model, and the most appropriate level of complexity. A comprehensive description of the modeling effort is attached in a separate report, Technical Support Document for the Development of an Ohio River Total Maximum Daily Load for 2,3,7,8-TCDD (Dioxin).

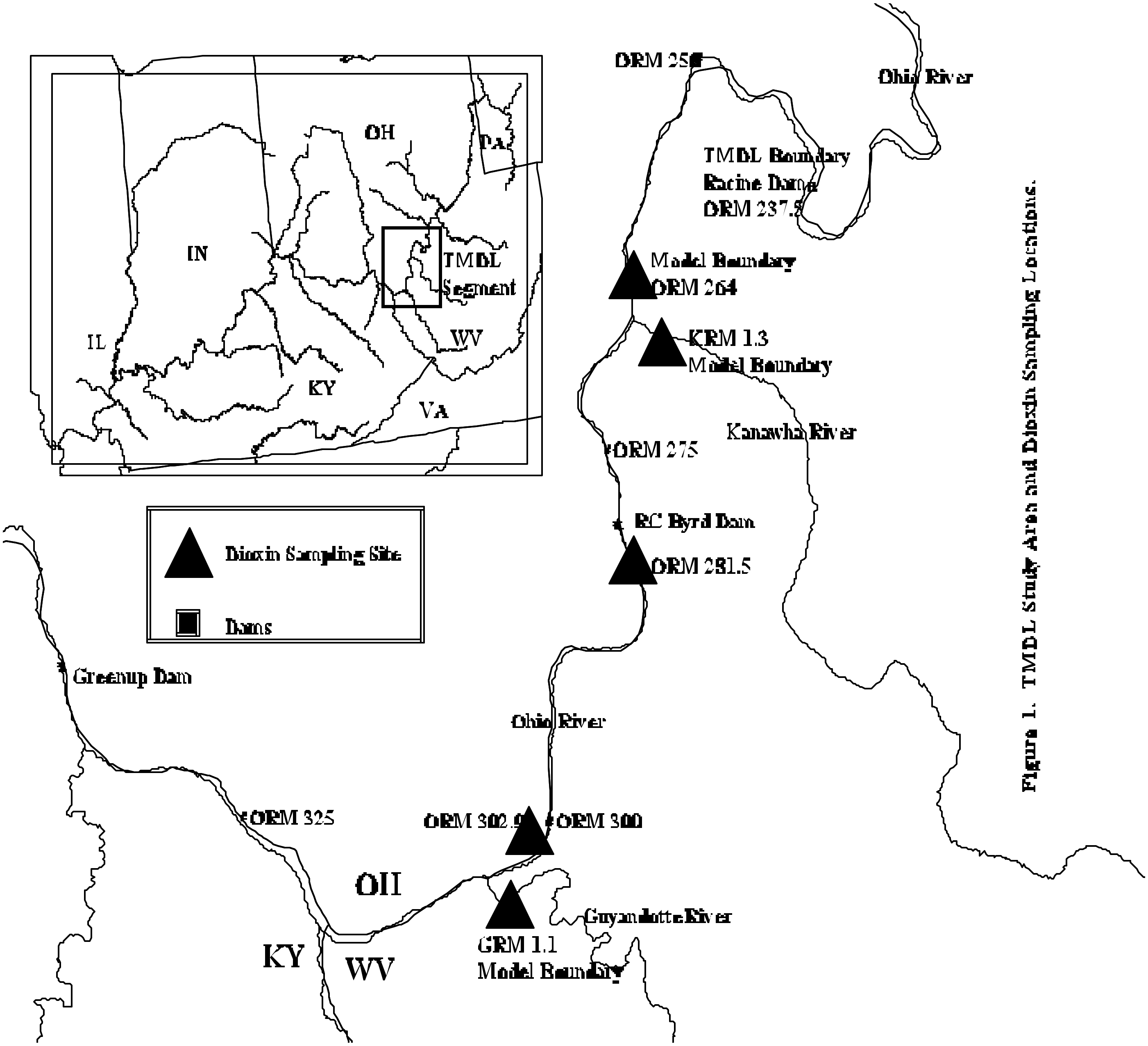



Figure 1. TMDL Study Area and Dioxin Sampling Locations.

## III. Discussion of Regulatory Conditions

EPA finds that sufficient information has been provided to meet all of the 8 basic requirements for establishing a dioxin TMDL on the Ohio River mainstem. EPA therefore approves this TMDL. Our approval is outlined according to the regulatory requirements listed below.

*1) The TMDL is designed to meet the applicable water quality standards.*

Since the portion of the Ohio River, for which this TMDL is being established, forms the boundary between Ohio and West Virginia, both states' Water Quality Standards for 2,3,7,8- TCDD (dioxin) must be considered in the development of this TMDL. The State of Ohio's Water Quality Standard for the Ohio River is 0.13 pg/L, to be applied at one- tenth the harmonic mean flow, at a cancer risk level (CRL) of $10^{-5}$. Surrounding States WQS also should be considered for consistency. Pennsylvania's Water Quality Standard for dioxin is 0.01 pg/L to be applied at harmonic mean flow, and Kentucky's Water quality standard is 0.013 pg/L at harmonic mean flow.

West Virginia's criteria for dioxin is 0.013 pg/L, however, West Virginia Water Quality Standards Regulations (WV-46-1-8-2.b) defer a final decision on critical flow for carcinogens, in order that the State may further study the issue. Presently, the West Virginia Water Quality Standards Regulations state -- " the regulatory requirement for determining effluent limits for carcinogens shall remain as they were on the date this Rule was proposed." WV 46-1-7.2.b states -- in the absence of any special application, numeric water quality standards shall apply at all times when flow is greater than 7Q10 flow.

In this TMDL application, where only load allocations will be developed, we believe that harmonic mean flow is not inconsistent with West Virginia Water Quality Standards Regulations 46 CSR 1. Because human health criteria assume long-term chronic exposure, harmonic mean flow is the most appropriate flow to describe the critical condition. A coordinated and consistent approach among bordering states has become more important, especially for waters like the Ohio River that are shared.

*2) The TMDL includes a total allowable load as well as individual waste load allocations and load allocations.*

<u>Total Allowable Loads</u>

### Source Loadings by Category

There is no net increase of dioxin within the TMDL segment itself (with the exception of the Kanawha River load) as model results demonstrate in Figure 6. Additionally, atmospheric deposition of 2,3,7,8-TCDD has been determined, based on a limited amount of sampling data, to be insignificant. Therefore, all important sources of dioxin that need to be accounted for are upstream of the TMDL segment, either in the Ohio River Basin upstream of ORM 264 or in the Kanawha Basin. Modeling results indicate that diffusion from pore water (water trapped in the pore spaces in the river bed) has been determined to be negligible. Low flow loads might typically be attributed to dry weather sources such as point sources and contributions from contaminated groundwater. Conversely, high flow loads might typically be attributed to wet weather sources such as resuspended bed sediments and contaminated runoff. High flow related sources are much greater than from low flow sources.

In order to illustrate the variation in dioxin at different flow conditions, the model was executed at three flows: seven-day/ten-year low flow, harmonic mean flow, and at the one-year flood.
These flows represent low, moderate, and high flow conditions respectively, with the harmonic mean flow being specified as the critical condition, or the condition under which allocations would be applied. Dioxin concentrations based on model results are presented graphically in Figure 6.

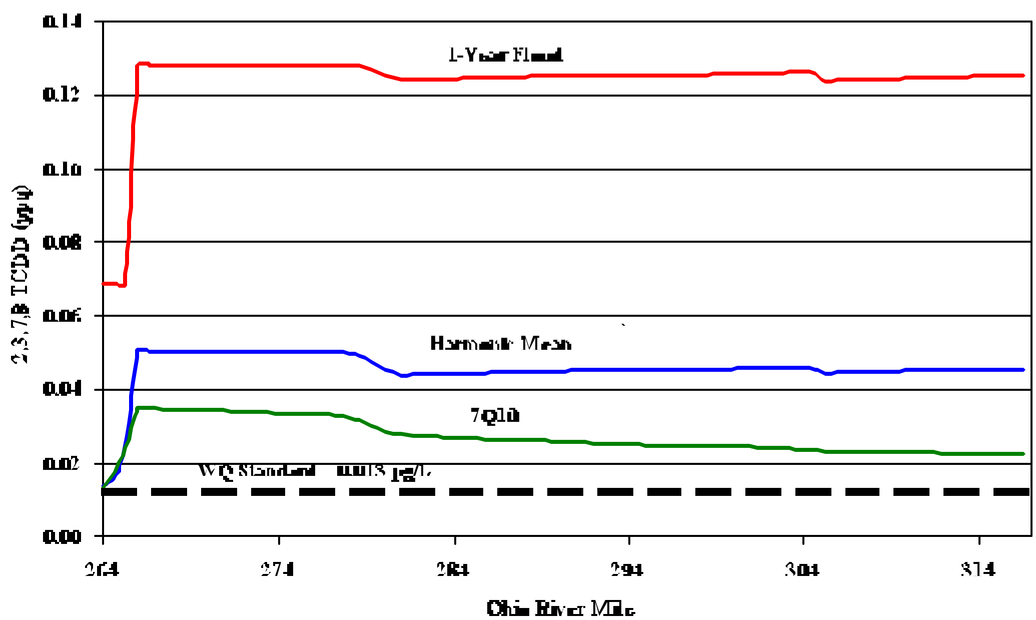



**Figure 6. SMPTOX4 Model Results at Various Flows.**

ORM 266 (critical river location) is the location on the Ohio River with the highest dioxin concentrations and loads, at all flow conditions modeled, and is positioned immediately downstream of the confluence with the Kanawha River. The water quality standard of 0.013 pg/L is violated at all three flows, at this critical river location, but are highest during the high flow, one-year flood. The maximum modeled concentration of total 2,3,7,8-TCDD is 0.128 pg/L (parts per quadrillion), which occurred immediately downstream of the Kanawha River at ORM 266, the critical location.

Figure 7 plots modeled dioxin loads at low, moderate and high flows at ORM 266. A best-fit power function trend line having an r-squared value of 0.9988 can be used to estimate Ohio River dioxin loads at flows other than those modeled. The equation for the best-fit power function trend line is $y=0.0023x^{1.3917}$ (y in pg/L; x in cfs) which can be used to calculate a predicted dioxin load for any flow. The total 2,3,7,8-TCDD load (modeled) at the critical location in the Ohio River (ORM 266), at the critical harmonic mean flow, is 4245 ug/day. The dioxin total maximum daily load, or the highest load that would not result in violation of the 0.013 pg/L water quality standard at the harmonic mean flow (listed as capacity in Table 2), is 1097 ug/day. Therefore, a 74 percent reduction would be needed to meet water quality standards at the critical harmonic mean flow condition. The Ohio River upstream of the Kanawha River accounts for approximately nineteen percent of the total dioxin load at the harmonic mean flow, while the Kanawha River accounts for the remaining 81 percent of the Ohio River dioxin load. Even though the Ohio River meets water quality standards at the harmonic mean flow, a proportionate reduction (19 percent or 152 ug/day) in its dioxin load will be required to assist in meeting the water quality standard downstream. The remaining reduction need to meet water quality standards, 3452 ug/day or 87 percent of the Kanawha's dioxin load at harmonic mean flow, will be obtained from sources within the Kanawha River Basin.

Waste Load Allocations

Very little is known about specific source contributions of dioxin to the Ohio River TMDL segment. Potential sources can be categorized as follows:

Sources within the Ohio River TMDL segment.
Sources upstream of the TMDL segment.
Point sources.
Nonpoint sources.
Surface runoff carrying contaminated sediment.
Resuspension of contaminated bed sediments.
Atmospheric deposition.
Groundwater infiltration.
Diffusion from bed sediment pore water

The TMDL for the Ohio River looked at all the point sources in the subwatershed for permitted sources of 2,3,7,8-TCDD or dioxin, which resulted at this time, in no point sources, thus no Waste Load Allocation for this segment.

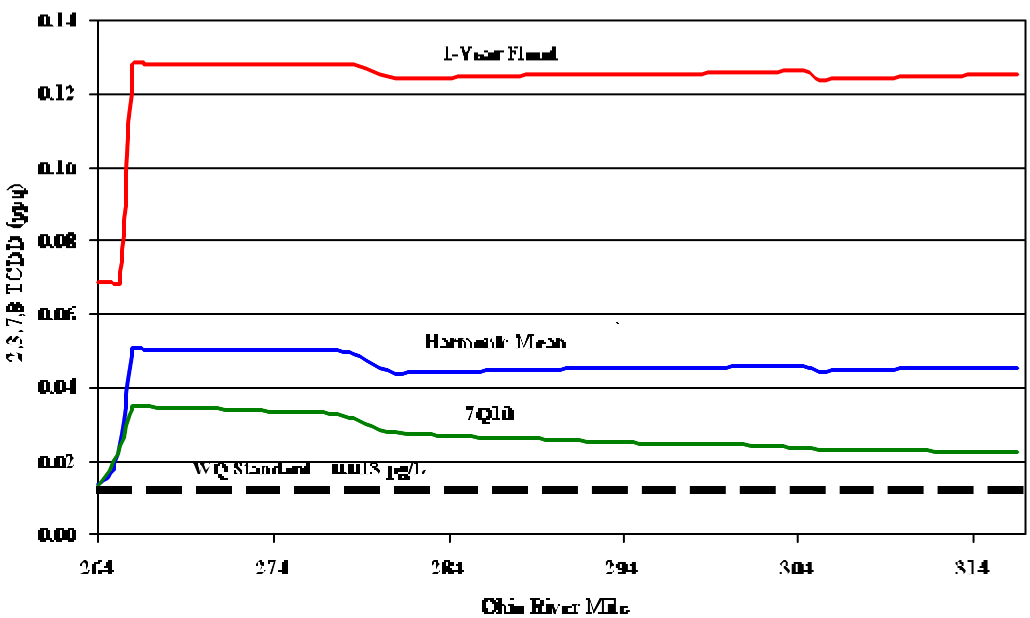
**Kanawha River Total Maximum Daily Load**

Certain sources in the Kanawha River Basin have been identified and are described in a June 2000 report, <u>Dioxin TMDL Development for Kanawha River, Pocatalico River, and Armour Creek, West Virginia</u> (Limno-Tech, Inc., Ann Arbor. MI). Allocations to Kanawha Basin sources will be addressed under the Kanawha River Dioxin TMDL.

<u>Load Allocations</u>

According to federal regulations at 40 CFR 130.2 (g), load allocations are best estimates of the loading, which may range form reasonably accurate estimates to gross allotments, depending on the availability of data and appropriate techniques for predicting loading. Wherever possible natural and nonpoint source loads should be distinguished. In this TMDLs, the data supported only gross load allocations. As mentioned earlier, the critical flow for this TMDL was considered to be harmonic mean flow, even though the modeling was completed for three flows, 7Q10, harmonic mean, and 1 year flood. Table 1. Summarizes the load allocation for the Ohio River.

In order to illustrate the variation in dioxin at different flow conditions, the model was executed at three flows: seven-day/ten-year low flow, harmonic mean flow, and at the one-year flood.
These flows represent low, moderate, and high flow conditions respectively, with the harmonic mean flow being specified as the critical condition, or the condition under which allocations would be applied. Dioxin concentrations based on model results are presented graphically in Figure 6.




ORM 266 (critical river location) is the location on the Ohio River with the highest dioxin concentrations and loads, at all flow conditions modeled, and is positioned immediately downstream of the confluence with the Kanawha River. The water quality standard of 0.013 pg/L is violated at all three flows, at this critical river location, but are highest during the high flow, one-year flood. The maximum modeled concentration of total 2,3,7,8-TCDD is 0.128 pg/L (parts per quadrillion), which occurred immediately downstream of the Kanawha River at ORM 266, the critical location.

The total 2,3,7,8-TCDD load (modeled) at the critical location in the Ohio River (ORM 266), at the critical harmonic mean flow, is 4245 ug/day. The dioxin total maximum daily load, or the highest load that would not result in violation of the 0.013 pg/L water quality standard at the harmonic mean flow (listed as capacity in Table 2), is 1097 ug/day. Therefore, a 74 percent reduction would be needed to meet water quality standards at the critical harmonic mean flow condition. The Ohio River upstream of the Kanawha River accounts for approximately nineteen percent of the total dioxin load at the harmonic mean flow, while the Kanawha River accounts for the remaining 81 percent of the Ohio River dioxin load. Even though the Ohio River meets water quality standards at the harmonic mean flow, a proportionate reduction (19 percent or 152 ug/day) in its dioxin load will be required to assist in meeting the water quality standard downstream. The remaining reduction need to meet water quality standards, 3452 ug/day or 87 percent of the Kanawha's dioxin load at harmonic mean flow, will be obtained from sources within the Kanawha River Basin.

| | **flow cfs** | **conc.,pg/l** | **capacity ug/day** | **loading ug/day** | **% reduction to meet WQS** |
|---|---|---|---|---|---|
| **harmonic mean flow** | | | | | |
| Ohio River upstream of Kanawha River | 26000 | 0.0126 | 827 | 801 | 152 ug/day (19%) |
| Kanawha River | 8500 | 0.1660 | 270 | 3452 | 2996 ug/day (87%) |
| Ohio River downstream of Kanawha R., ORM 266 | 34500 | 0.0503 | 1097 | 4245 | 3148ug/day (74%) |
| Guyandotte River | 1400 | 0.0011 | 45 | 4 | N/A |

*3) The TMDL considers the impacts of background pollution.*

The Ohio River upstream of the Kanawha River accounts for approximately nineteen percent of the total dioxin load at the harmonic mean flow, while the Kanawha River accounts for the remaining 81 percent of the Ohio River dioxin load. This upstream concentration was considered as background for this TMDL. Even though the Ohio River meets water quality standards at the harmonic mean flow, a proportionate reduction (19 percent or 152 ug/day) in its dioxin load will be required to assist in meeting the water quality standard downstream

*4) The TMDL considers critical environmental conditions.*

EPA regulations at 40 CFR 130.7 (c)(1) require TMDLs to take into account critical conditions for stream flow, loading, and water quality parameters. The intent of this requirement is to ensure that the water quality of the Little Kanawha River Watershed is protected during times when it is most vulnerable.

Critical conditions are important because they describe the factors that combine to cause a violation of water quality standards and will help in identifying the actions that may have to be undertaken to meet water quality standards[1]. Critical conditions are the combination of environmental factors (e.g., flow, temperature, etc.) that results in the attaining and maintaining the water quality criterion and has an acceptably low frequency of occurrence. In specifying critical conditions in the waterbody, an attempt is made to use the to use a reasonable "worst-case" scenario condition. For example, stream analysis often uses a low-flow (7Q10) design condition because the ability of the waterbody to assimilate pollutants without exhibiting adverse impacts is at a minimum.

Concurrently with selection of a numeric endpoint, in this case the Water Quality criteria, TMDLs need to define the environmental condition that will be used when defining allowable loads. TMDLs are usually designed around the concept of "critical condition". The critical condition is defined as the set of environmental conditions, which, if controls are designed to protect, will ensure attainment of standards for all other conditions.

Because 2,3,7,8-TCDD is defined as a carcinogen, harmonic mean flow has been specifically identified as the appropriate flow condition to use with the criterion (EPA Guidance 1991). Dioxin sources on the Ohio River are believed to arise from a mixture of sources. There may be no other single condition that is protective for all other conditions. For this reason, this TMDL does examine an entire range of

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[1]EPA memorandum regarding EPA Actions to Support High Quality TMDLs from Robert H. Wayland III, Director, Office of Wetlands, Oceans, and Watersheds to the Regional Management Division Directors, August 9, 1999.

flow conditions and can define a load allocation that will be protective for different flows. However, for this TMDL harmonic mean flow is the flow condition that will be used for setting allocations

*5) The TMDLs consider seasonal environmental variations.*

Seasonal variations involve changes in stream flow as a result of hydrologic and climatological patterns. In the continental United States, seasonally high flow normally occurs during the colder period of winter and in early spring from snow melt and spring rain, while seasonally low flows typically occurs during the warmer summer and early fall drought periods. The TMDL was developed to attain standards at harmonic mean flow therefore, seasonality is inherently accounted for in using this flow, since that harmonic mean flow theoretically accounts for conditions over a long period of time.

*6) The TMDLs include a margin of safety.*

This requirement is intended to add a level of safety to the modeling process to account for any uncertainty. Margins of Safety (MOS) may be implicit, built into the modeling process by using conservative modeling assumptions, or explicit, taken as a percentage of the wasteload allocation, load allocation, or TMDL.

The applicable ambient water quality criterion for 2,3,7,8-TCDD is 0.013 pg/L which is based on a $10^{-6}$ cancer risk level. This criterion is designed to protect human health from long-term (lifetime) exposure. The harmonic mean flow is theoretically representative of an average flow over a lifetime. The recommended use of the long-term harmonic mean flow for carcinogens has been derived from the definition of the human health criteria (HHC) for carcinogenic pollutants. The adverse impacts of carcinogenic pollutants is estimated in terms of life-time intake. Therefore, estimation of the load reduction necessary to achieve water quality standards for dioxin at the harmonic mean flow will be protective of human health and provide an intrinsic margin of safety. The estimated Ohio River reduction in loading of 2,3,7,8-TCDD, at 7Q10 flow, at the critical point downstream from the Kanawha River, based on the model is 63 percent. The estimated load reduction using the harmonic mean flow at the same location is 74 percent. Therefore, load allocations designed to meet this critical condition of harmonic mean flow would provide an increased margin of safety over 7Q10 for the protection of human health over a lifetime exposure.

*7) The TMDLs have been subject to public participation.*

An informational meeting to discuss the preliminary findings of the TMDL was held by EPA and ORSANCO in Huntington, Huntington Public Library on October 18, 2000. The public comment period for the TMDL was open on July 5, 2000 and closed on August 18, 2000. During the comment period, EPA held a public hearing to hear testimony from the citizens of the watershed as well as other stakeholders. The public hearing was held in Barburville, West Virginia from 6:00pm to 8:00pm on July 27, 2000.

*8) There is a reasonable assurance that the TMDL can be met.*

EPA requires that there be a reasonable assurance that the TMDL can be implemented. WLAs will be implemented through the NPDES permit process. According to 40 CFR 122.44(d)(1)(vii)(B), the effluent limitations for an NPDES permit must be consistent with the assumptions and requirements of any available WLA for the discharge prepared by the state and approved by EPA. Furthermore, EPA has authority to object to issuance of an NPDES permit that is inconsistent with WLAs established for that point source.

The reasonable assurance that this TMDL for the Ohio River can be met, will come from the commitment of EPA and ORSANCO to continue to search and to narrow its search for 2,3,7,8-TCDD in the Upstream Ohio River from this segment. The monitoring plan that follows, has started and the funding mechanism is in place for ORSANCO to continue its Pollution Reduction Activities in the Ohio River Watershed. The monitoring will definitely assist West Virginia, Pennsylvania and EPA controling any and all sources of 2,3,7,8-TCDD to this waterbody.

**Follow Up Monitoring Plan**

The purpose of the follow up monitoring plan is to identify and quantify if possible specific sources of dioxin contributing to the upstream load entering the TMDL segment from the upper-Ohio River Basin. While there are suspected sources contributing dioxin to the TMDL segment from the Kanawha River Basin, this monitoring plan only addresses Ohio River sources. A Kanawha River TMDL will address sources contributing dioxin to the Ohio River.

No specific sources of 2,3,7,8-TCDD have been identified to date in the upper Ohio river Basin, even though a number of sources are suspected. Funding for this monitoring has been provided through US EPA Region 3 as a grant to the Ohio River Watershed Pollutant Reduction Program. The monitoring effort will begin in 2000 and be completed by 2001. It is anticipated that an additional follow up monitoring plan may be necessary for 2001-2002 in order to complete a thorough investigation of dioxin sources in the upper Ohio River.

Design of the following monitoring plan is based on previous dioxin monitoring and modeling efforts and presented within this report previously. Specifically, Figure 10 identifies specific locations in the upper Ohio River that should be investigated further, areas targeted by this follow up monitoring plan. In addition, modeling results suggest resuspension of contaminated sediments as a potential major source in the upper Ohio River, so this monitoring plan addresses this source also.

**Monitoring to Identify Dioxin Sources in the Upper Ohio River Basin**

An Upper-Ohio River longitudinal survey of dioxin, utilizing the high-volume sampling technique, was conducted in 1998. Results of that survey suggest potential sources in the Pittsburgh area between

Ohio River Miles (ORM) 0 and 129, and the Marietta, OH area between ORM 129 and 175. However, no specific sources of dioxin to the Ohio River in these areas are known/quantified, even though dioxin-contaminated sites (having potential impacts) have been identified. In addition, there are a number of potential sources identified in a 1995 study conducted by ORSANCO (Figure 9). The focus of this objective is on narrowing the field of potential dioxin sources. Figure 11 is a map of high volume dioxin sampling locations discussed below which are to be included in the follow up monitoring plan.

**Task 1 - Pittsburgh-Area Dioxin Source Investigation**

This task involves narrowing the field of dioxin sources in the Pittsburgh area (ORM 0 to 129). There is one known dioxin-contaminated site along the Ohio River on Neville Island (ORM 10). In addition, there is a high density of direct discharges along the upper-Ohio River. Sampling locations are listed below and shown on Figure 11. Two rounds of high-volume sampling (at higher and lower flows) for dioxin will be completed including measurements of flow, total suspended solids (TSS), and TOC.

| **High-Volume Sampling Sites** | **Rationale** |
|---|---|
| Allegheny River (near mouth) | Upstream boundary |
| Monongahela River (near mouth) | Upstream boundary |
| 1. ORM 4 | Upstream of contaminated site |
| 2. ORM 10 | Downstream of contaminated site |
| 3. ORM 20 | Repeat site from 1998 survey |
| 4. Beaver River | Major trib w/potential sources |
| 5. ORM30 | Cover gaps |
| 6. ORM 40 | Repeat site from 1998 survey |
| 7. ORM 70 | Cover gaps |
| 8. ORM100 | Cover gaps |
| 9. ORM 129 | Repeat site from 1998 survey/downstream boundary |

**Task 2 - Marietta-Area Dioxin Source Investigation**

This task involves narrowing the field of dioxin sources in the Marietta area (ORM 129 to 207). There is one known dioxin-contaminated site at ORM 173 (at confluence with Muskingum River). Sampling locations are listed below and shown on Figure 11. Two rounds of high-volume sampling (at higher and lower flows) for dioxin will be completed including measurements of flow, total suspended solids (TSS), and TOC.

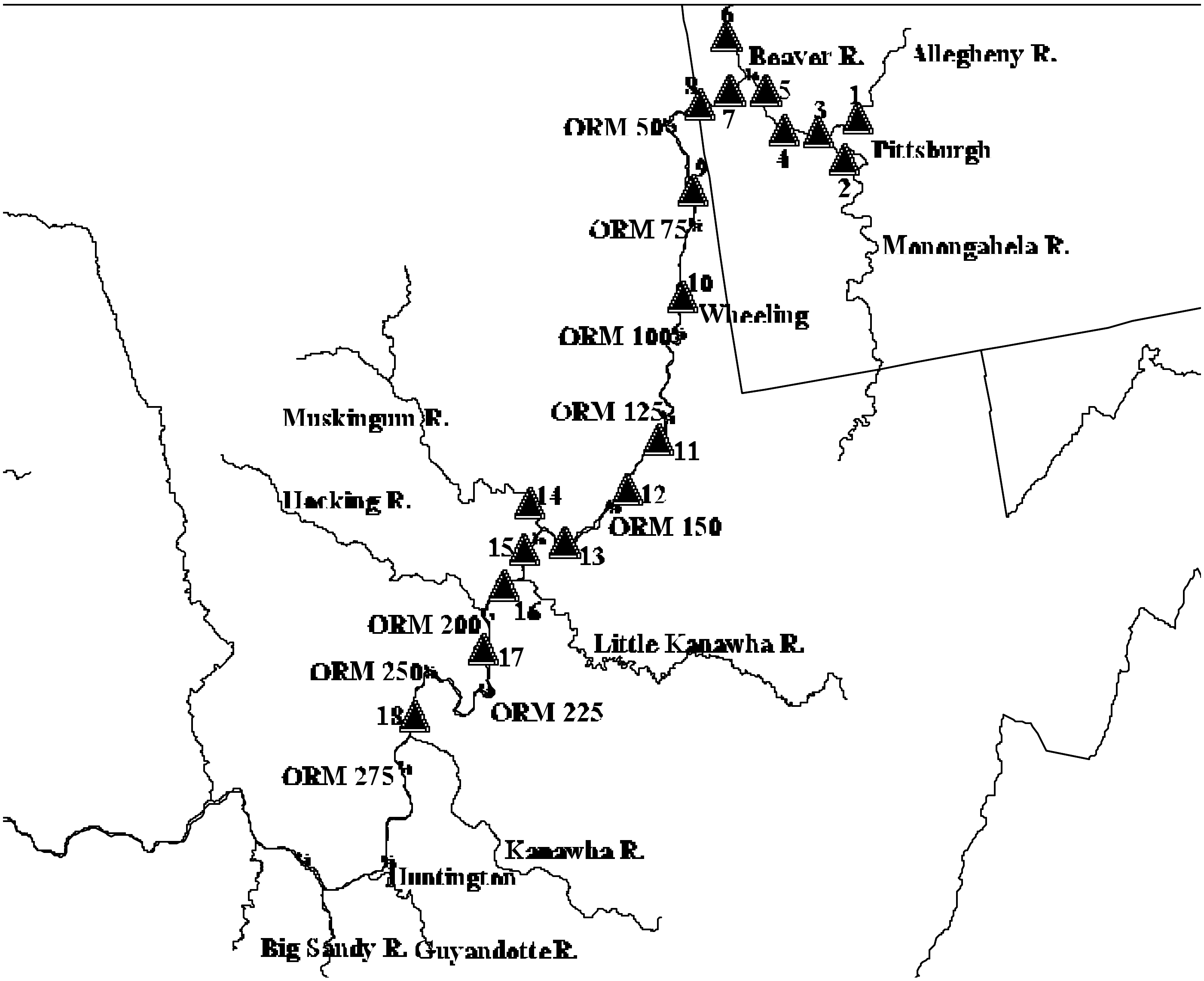
| **High-Volume** **Sampling Sites** | **Rationale** |
|---|---|
| 9. ORM 129 | Repeat site from 1998 survey/upstream boundary |
| 10. ORM 150 | Upstream Marietta urban area |
| 11. ORM 171 | Upstream contaminated site, downstream Marietta |
| 12. Muskingum River | Potential sources exist in Muskingum basin |
| 13. ORM 175 | Repeat site from 1998; downstream contaminated site |
| 14. ORM 185 | Further downstream of contaminated site |
| 15. ORM 207 | Repeat site from 1998 survey |
| 16. ORM 264 | Upstream TMDL boundary |

**Task 3 - Upper Ohio River Bottom Sediment Longitudinal Survey;**

This survey will characterize Ohio River bottom sediments from Pittsburgh through the TMDL segment (ORM 0 to ORM 317). It is suspected that much of the dioxin load results from resuspension of existing contaminated sediments. The data will be used to help determine whether this assumption is correct as well as to identify hot spots. One bottom sediment sample will be collected and analyzed for dioxin every five miles from ORM 0 to ORM 317.

**Task 4 - Atmospheric Dioxin Sampling**

Two stations in the Pittsburgh area and two stations in the Marietta area will be sampled four times (quarterly) for dioxin to determine atmospheric contributions to water.


6
Beaver R.
Allegheny R.
8
5
1
7
3
ORM 50
4
Pittsburgh
2
9
ORM 75
Monongahela R.
10
Wheeling
ORM 100
Muskingum R.
ORM 125
11
Hocking R.
14
12
ORM 150
15
13
16
ORM 200
Little Kanawha R.
17
ORM 250
ORM 225
18
ORM 275
Kanawha R.
Huntington
Big Sandy R.
Guyandotte R.

# Technical Support Document for the Development of an Ohio River Total Maximum Daily Load for 2,3,7,8 TCDD (Dioxin)

## *Final Report*

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September 2000

## TABLE OF CONTENTS

# 1.0 INTRODUCTION

## 1.1 History

Section 303(d) of the Clean Water Act requires states to develop lists of waters still requiring total maximum daily loads (TMDLs). The Act also requires the US EPA to develop TMDLs when the state fails to do so. In 1997, US EPA entered into a federal Consent Agreement obligating them to complete a TMDL for dioxin on the Ohio River, per West Virginia's most recent 303(d) List, by September 2000. West Virginia's 1998 303(d) List includes the Ohio River for dioxin (2,3,7,8-TCDD) from Racine Dam at Ohio River mile (ORM) 237.5 to the West Virginia state line at ORM 317. The listing was based on high-volume water column sampling for dioxin conducted by the Ohio River Valley Water Sanitation Commission (ORSANCO) in 1997.

## 1.2 Purpose

The purpose of this modeling effort is to simulate the fate and transport of dioxin within the study area in order to quantify the necessary reductions needed to meet water quality standards. This report provides the technical details associated with the model development process. Further discussion on the application of the model results to the TMDL development process is provided in a separate report, *Development of a Total Maximum Daily Load for Dioxin for the Ohio River*.

## 1.3 Background Information on Dioxin

### *1.3.1 Dioxin Characteristics*

There are 75 polychlorinated-dibenzo-dioxin (PCDD) congeners and 135 polychlorinated-dibenzo-furan (PCDF) congeners. Collectively, these compounds are referred to as dioxins. Seventeen of these congeners (seven PCDDs and 10 PCDFs) are toxicologically significant. The unifying characteristic of this group of 17 compounds is that they all elicit similar toxicological responses in humans and/or in wildlife. The actual toxicity of each of the congeners, however, varies greatly. The most toxic congener, 2,3,7,8 tetra-chloro-dibenzo-dioxin (TCDD), is 1000 times more potent than the least toxic congeners, octa-chloro-dibenzo-dioxin (OCDD) and octa-chloro-dibenzo-furan (OCDF).

Physical and chemical processes that affect the fate of dioxins, particularly the 2,3,7,8 TCDD congener, in the environment are well documented in the literature. Dioxins have a low water solubility, are very lipophilic, and readily bioaccumulate in humans and wildlife. These compounds strongly bind to particulate matter in all media (EPA 1994). Mobility through soil is believed to be extremely limited due to the strong sorptive nature of dioxins (EPA 1987). These compounds are very stable, and thus very persistent in the environment. Leaching and volatilization of particulate bound dioxins appear to be negligible (EPA 1994). Hydrolysis is also thought to be an insignificant transformation process for dioxins (EPA 1992a). Photodegradation of dioxins in the vapor phase, at the soil-air or water-air interface, appears to be the only significant decay process (EPA 1994). The chemical half-life for 2,3,7,8 TCDD in the top few inches of soil is estimated to be 1 to 3 years (EPA 1992a), while more deeply buried 2,3,7,8 TCDD could have a half-life greater than 10 years (USFWS 1986). The half-life of 2,3,7,8 TCDD in surface water is estimated to be 1 to 1.5 years (EPA 1992a).

In the atmosphere, dioxins are partitioned between the particulate and vapor phases. The more chlorinated congeners are typically found in the particulate phase. The less chlorinated species, such as the 2,3,7,8 TCDD congener, are predominately found in the vapor phase in the summer months, and more evenly distributed between the two phases during cooler periods (Eitzer and Hites 1989). Considering dioxins, in general, favor the particulate phase, and sorbed species do not readily undergo photodegradation, long range transport of dioxins does occur via the atmosphere. Dioxins emitted from a single atmospheric point source, such as an incinerator, could possibly travel hundreds of miles before being deposited to land or surface waters.

The ultimate fate of dioxins in the environment is to either be buried in soil or accumulate in aquatic sediments. Dioxins deposited to soil surfaces tend to bind to particulate matter, and are either buried in place, resuspended into the atmosphere, or are transported to surface waters through erosion. Once in water, whether from direct atmospheric deposition, effluent discharge, or soil erosion, dioxins primarily sorb to suspended solids. These particles can be transported considerable distances downstream before settling to the streambed (EPA 1987).

### *1.3.2 General Sources*

Dioxins are not intentionally produced, but are an unwanted by-product of various combustion and chemical processes. EPA and others have identified many different categories of potential dioxin sources. Many questions still remain about the impacts of these sources. Emission estimates for all source categories are highly uncertain and further research is needed to better characterize dioxin emissions. Most sources that have been identified are atmospheric in nature. Limited available data implicate municipal and hospital incinerators, and cement kilns burning hazardous waste as the largest producers of dioxins. Other potential producers of dioxins include industrial and residential wood burners, secondary metals industries such as copper smelters, chemical manufacturers of chlorinated compounds, sewage sludge and hazardous waste incinerators, wastewater treatment plants, PCB transformer fires, wood treating facilities, and pulp & paper mills. Automobiles have also been identified as a source, with diesel fuel combustion being the main contributor. The use of unleaded fuel is believed to have greatly curbed dioxin emissions from cars. Researchers have also suggested that forest fires are a source of dioxins, however, it is not conclusive whether the dioxins released from these fires are being produced by the forest fires or merely resuspended into the atmosphere.

*1.3.3 Water Quality Standards*

EPA's (1984) recommended ambient water quality criteria for dioxin are 0.13, 0.013, and 0.0013 pg/L, with an associated increase cancer risk level (CRL) of $10^{-5}$, $10^{-6}$, $10^{-7}$, respectively. These criteria are for the protection of human health from the consumption of contaminated water and aquatic organisms, and only apply to the 2,3,7,8 TCDD congener. The criteria document does not differentiate between dioxin in the particulate and dissolved phases, and as such, the criteria must be applied to total 2,3,7,8 TCDD concentrations.

Since the Ohio River forms the boundary between Ohio and West Virginia, both states' water quality standards for dioxin must be considered in the development of the TMDL. West Virginia applies human health criteria at a $10^{-6}$ CRL, while Ohio uses the less stringent $10^{-5}$ CRL. In cases where a discrepancy exists among states' criteria, the more stringent must be used. As a result, the TMDL analysis will be based on West Virginia's standard of 0.013 pg/L (or parts per quadrillion). This standard is written to apply to all times at which stream flows are equal to or greater than the minimum seven day, ten-year low flow (7Q10).

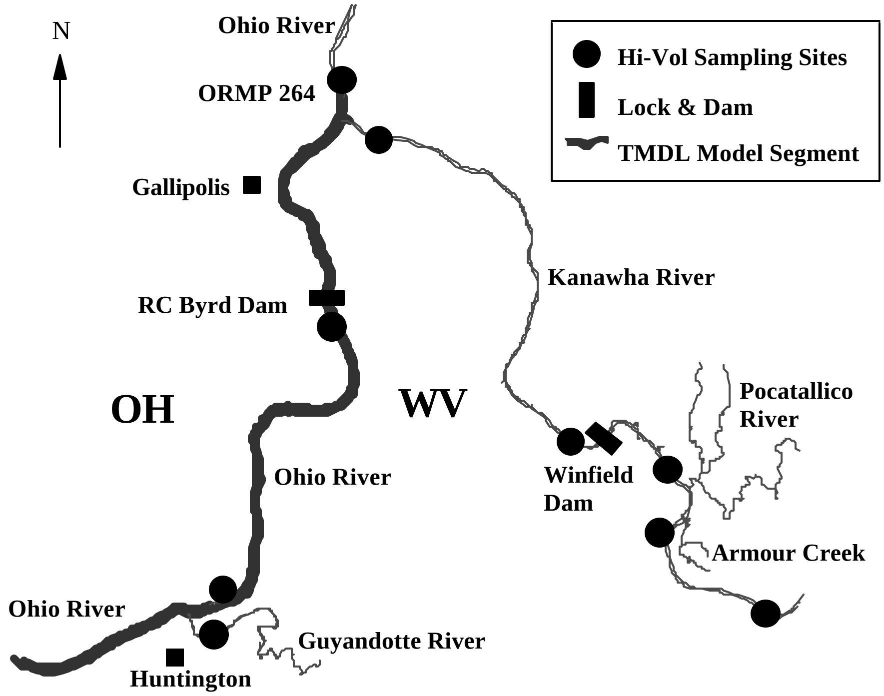
# 2.0 STUDY AREA DESCRIPTION

## 2.1 Physical Description

The dioxin TMDL must be developed for the Ohio River from Racine Dam (ORM 237.5) to the Big Sandy River at the WV / KY border (ORM 317). The model study area, however, begins at Point Pleasant, WV (ORM 264) and extends to the end of the TMDL segment at ORM 317. Figure 1 depicts the study area and includes high volume dioxin sampling locations and the segment being modeled. The study area lies in West Virginia and Ohio, and is immediately upstream of the Kentucky border.

There are two major tributaries in the study area: the Kanawha and Guyandotte Rivers entering the Ohio River at mile points 265.7 and 305.2, respectively. At their confluence, flows from the Kanawha River account for approximately one-fourth of the total flow in the Ohio River. The Guyandotte River contributes much lesser flows. Average monthly stream flows for the Ohio River at RC Byrd Lock and Dam range from 27,100 cfs in September to 149,200 cfs in March with an overall average of approximately 80,000 cfs (ORSANCO 1994). The 7-day, 10-year low flow (7Q10) for the Ohio River at RC Byrd is 9,120 cfs, and the harmonic mean flow is 34,500 cfs (ORSANCO 1997).

Figure 1. Ohio River TMDL model study area.




## 2.2 External Dioxin Sources to Study Area

Dioxin may enter the study area through several pathways involving atmospheric deposition, overland runoff, groundwater, point sources and tributary streams. These potential external sources of dioxin are discussed below.

1. *Ohio River mainstem upstream of the TMDL segment*.

   An inventory of dioxin sources in the Ohio River Basin was conducted in 1995 by ORSANCO. Thirty-five potential sources of dioxin were identified in the Upper Ohio River Basin, upstream of the study area. Only two direct potential sources to water were identified, a pulp and paper mill on the Clarion River (tributary to the Allegheny River) in Pennsylvania, and a wastewater treatment plant in Nitro, WV (on the Kanawha River) which treats runoff from a hazardous waste site with known dioxin contamination. The other 34 include four facilities with confirmed soil contamination, and 30 atmospheric sources. All of these sources may ultimately contribute to the dioxin loading observed at the upstream boundary of the study area.

2. *Tributaries:* Major tributaries include the Kanawha River and Guyandotte River.

   Kanawha River – The Kanawha River has the potential to contribute significant amounts of dioxin to the Ohio River considering the size of the tributary and the presence of several confirmed sources along its banks. ORSANCO's inventory of sources revealed 14 potential sources of dioxin to the Kanawha River. These

sources are concentrated along a 30-mile stretch of the river and its tributaries from Charleston, WV to Winfield Locks and Dam. All of these sources are linked to chemical manufacturing or chemical waste disposal. Ten of the 14 sites are potentially contaminated land sites, seven of which have confirmed soil contamination. Three of the potential sources are hazardous waste incinerators, which may contribute dioxin to the atmosphere. A wastewater treatment plant in Nitro, WV which treats runoff from a hazardous waste site with known dioxin contamination is the only potential point source identified in the Kanawha River Basin. In addition to the sources identified in ORSANCO's 1995 inventory, an additional seven hazardous waste sites were identified as potential dioxin sources in EPA's draft Kanawha River TMDL report (1999).
Guyandotte River – The potential contribution of dioxin to the Ohio River from the Guyandotte River is believed to be minimal, based on its relatively small drainage area and the lack of significant sources. Only two potential sources of dioxin to the Guyandotte River have been identified, a sewage sludge incinerator and a chemical manufacturer. These two facilities are listed as potential sources based solely on US EPA's (1994) listing of sewage sludge incinerators and chemical manufacturers in general as potential dioxin sources. No sampling, however, has been conducted to confirm whether or not these specific facilities are contributing to the dioxin load in the Guyandotte River.

3. *Point sources in the study area*

There are currently 20 active NPDES permitted dischargers on the Ohio River from river mile 265.7 (Kanawha River confluence) to river mile 317 (Big Sandy River confluence). None of these dischargers have been identified as potential point sources of dioxin to the Ohio River.

4. *Non-point sources in the study area*

Non-point sources enter the mainstem through overland flow, direct atmospheric deposition on the river surface, and groundwater inflow. Atmospheric deposition, however, is the only non-point source for which data are available to estimate the dioxin contribution in the study area. Dioxins deposited from the atmosphere enter surface waters via two different routes – direct deposition and run-off. Direct deposition occurs continuously through particle settling in dry periods and precipitation. Dioxins deposited to land can be transported to streams as a result of surface run-off. Considering dioxins have a strong affinity to bind to particulate matter, most dioxins entering surface waters via run-off are likely to already be in the particulate phase. Estimating the impact of atmospheric deposition of dioxins to surface waters is an extremely difficult task. Current sampling methods allow direct deposition to be estimated, but there is no reasonably accurate means of estimating the amount of dioxins deposited to land that enter surface waters through run-off. A discussion regarding the estimation of atmospheric deposition of dioxins in the Upper Ohio River Basin based on ambient air concentrations is included in Section 4.3 *Input Parameter Estimation*.

# 3.0 MODEL NEEDS AND SELECTION

## 3.1 Modeling Needs

Modeling is used in the development of the TMDL to determine a quantitative understanding of how dioxin behaves in the reaches of the Ohio River in the study area. With the model, we can estimate the fate of dioxin entering the study area, and when combined with the allowable dioxin concentrations, used to determine alternative loading combinations that will meet water quality standards.

## 3.2 Modeling Alternatives

Three categories of models were considered in the selection process: 1) a one-dimensional steady-state water quality model; 2) a one or two-dimensional water quality model with gradually changing flows; and 3) one or two-dimensional water quality models with fully dynamic flows and dynamic sediment routines. Each of these options is described below followed by the assessment and selection process.

### *3.2.1 Steady State Models*

In a steady state model, all flows and loadings are represented as constant over time. In doing TMDL assessment, a critical flow condition is selected and used as input to the model. Examples of commonly used steady state models include QUAL-2E (Brown and Barnwell, 1987; EPA, 1995a) and SMPTOX4 (EPA, 1995b). Because of its capability to simulate toxic pollutants, SMPTOX4 was evaluated as the candidate model in this category.

SMPTOX4 is a user-friendly model developed for US EPA for use in waste load allocation and TMDL development. Its origin is EPA's Simplified Method (EPA, 1980) with the later incorporation of toxic pollutant models and several other evolutionary steps. SMPTOX4 is a one-dimensional, steady state model of the fate and transport of toxic pollutants in a riverine environment. The primary processes represented in the model include:

(a) Mixing of effluent and upstream waters
(b) Partitioning of toxicant between the dissolved and particulate phases in both the water column and the bed
(c) Exchange between the water column and the bed
(d) Decay by irreversible chemical transformations
(e) Losses by burial and volatilization
(f) Downstream transport via stream flow

The processes represented in SMPTOX4 are illustrated in Figure 2 reproduced from the SMPTOX4 User's Manual.

Because SMPTOX4 is a steady-state model, it assumes that all inputs are constant over time and that all processes are in equilibrium. For example, this means that loadings and flow do not vary over time during a model run and the rates at which particulates settle (move from the water column to the bed) and the rate at which they are resuspended do not vary over time. The model is spatially variable so that flows and loads may be introduced along the river and parameters such as resuspension rate may vary from reach to reach.

In SMPTOX4, the river is represented as a series of reaches. A reach is a stretch of river with constant physical characteristics. The user must specify several hydraulic characteristics of the reach including the length, depth, width, bed depth, dispersion, lateral inflow, and sediment properties. Each reach is divided into several computational segments.

The chemical transformations and movement of chemicals between media (atmosphere, water column, active sediment, and deep sediment) are represented by a set of steady-state equations. Rate coefficients for these transformations are provided by the user.

The model calculates and reports concentrations for the various forms of each chemical (i.e., particulate, sorbed, dissolved) in each segment/reach.

Figure 2. Processes represented in SMPTOX4 (EPA 1995b).

### *3.2.2 Gradually Varying Flow Models*

In a gradually varying flow model, flows and loads may vary over time. However, due to the formulation of such models, the variation must be relatively gradual and the dynamic effects of such variation are not represented. WASP5 (Ambrose et al, 1995) is a popular model that fits into this category and was considered as a candidate.

The Water Quality Analysis Simulation Program--5 (WASP5), is an enhancement of the original WASP model (Ambrose et al, 1983; Di Toro et al., 1981; Connolly and Winfield, 1984). WASP5 is a dynamic compartment modeling program for aquatic systems. Compartments can be used to represent the epilimnion (surface water), the hypolimnion layers (subsurface), an upper benthic layer, and lower benthic layers. The time-varying processes of advection, dispersion, point and diffuse mass loading, and boundary exchange are represented in the program. This structure permits the modeler to structure one, two, and three dimensional models; allows the specification of time-variable exchange coefficients, advective flows, waste loads and water quality boundary conditions; and flexibility in representing the kinetic processes.

The WASP5 system consists of two stand-alone computer programs, DYNHYD5 and WASP5, that can be run in conjunction or separately. The hydrodynamics program, DYNHYD5, simulates the movement of water while the water quality program, WASP5, simulates the movement and interaction of pollutants within the water. While DYNHYD5 is delivered with WASP5, other hydrodynamic programs (such as RIVMOD and SED3D) can also be linked with WASP.

WASP5 is supplied with two kinetic sub-models to simulate the major classes of water quality problems: conventional pollution (involving dissolved oxygen, biochemical oxygen demand, nutrients and eutrophication) and toxic pollution (involving organic chemicals, metals, and sediment). The equations describing chemical transformations and exchanges between the layers are essentially the same as those used in SMPTOX4.

WASP5 reports the simulated chemical concentrations in each of the compartments and during each time step.

### *3.2.3 Fully Dynamic Flow and Sediment Models*

For the purpose of this study, this category includes a variety of models that simulate one or more of the following situations: unsteady flow, multi-dimensional situations, dynamic sediment and bed interactions. Examples of models in this category include: SERATRA (Onishi et al, 1982), SEDIMENT-4H (Ariathurai, 1980), FETRA (Onishi, 1981), HSCTM-2D (EPA, 1995c) and MIKE (DHI). These models all tend to be more complex than the steady-state and gradually varied flow models. Each has its own strengths in representing various aspects of the dynamic processes.

### 3.3 Model Selection

The general approach that was adopted in this study was to select the least complex model that would acceptably perform the required analyses. The basic objective of the modeling effort was the ability to represent the movement and transformations of dioxin within the study area under critical conditions. Following are some considerations in selecting a model for use in the study.

- The critical hydrologic condition that was identified was a high flow event, specifically the 1-year flood event. A constant flow condition corresponding to this event was selected. Thus, a steady-state flow model was deemed sufficient for use in the study in order to simulate the critical event.

- The high-volume dioxin sampling campaigns generally lasted several days with each sample taking approximately one day to collect. Since there were flow changes during the course of the sampling campaign, use of a gradually varying flow model could be advantageous in calibration. However, the flow changes were relatively minor in magnitude and the flow values provided by the National Weather Service are considered only to be estimates of the true values. Therefore, the use of the gradual flow model was not considered to be necessary.

- Based on discussions with Corps of Engineers' personnel, there appears to be significant temporal and spatial variation in bed load characteristics. Locations in the vicinity of dams and bends in the river are the most likely locations to experience significant variations. Additionally, it is likely that the sedimentation process (deposition and resuspension) is relatively dynamic and also quite variable in time and space. However, there are very few field measurements available on bed load conditions and even fewer on the dynamic processes associated with sediment movement. Therefore, though a fuller understanding of the dynamics and variation of sediment processes would be useful in predicting the fate and movement of dioxin, it is considered to be neither practical nor necessary to utilize models representing the dynamics of the sediment process in this study.

- The SMPTOX4 model has been successfully applied in the development of the TMDL for dioxin for the Columbia River.

Based on the above considerations, the decision was made to utilize the steady-state SMPTOX4 model for this Ohio River TMDL model application.

## 4.0 MODEL SETUP

### 4.1 Hydraulic Representation of the Ohio River

The SMPTOX4 model represents a river as a series of segments referred to as reaches. The primary factors affecting the selection of reaches are (1) the limitation that flow changes can only be introduced at the upstream end of a reach, and (2) the requirement for hydraulic homogeneity in a reach. The flow change limitation resulted in reaches being selected so that the entry of significant tributaries (Kanawha River and Guyandotte River) occurred at the upstream end of reaches.

Hydraulic homogeneity was assessed by using the HEC-2 water surface profile program. The Huntington District of the Corps of Engineers has modeled the Ohio River in the study area using HEC-2. They have divided the river in the vicinity of the study area into two sections: (1) from the Meigs County line (ORM 256) downstream to the RC Byrd Lock and Dam (ORM 279.2); and (2) from the RC Byrd Lock and Dam (ORM 279.2) downstream to the Big Sandy River (ORM 317). The HEC-2 representation includes geometric data on cross-sections at approximately quarter mile intervals. HEC-2 was applied to determine water surface profiles under three hydrologic conditions: (1) 7-day/10-year low flow; (2) harmonic mean flow; (3) 1-year flood conditions. Water level elevations at the downstream ends of the simulations (RC Byrd L&D and at the confluence with the Big Sandy River) were provided by the Corps of Engineers for each of the hydrologic conditions.

Based on the HEC-2 runs, longitudinal velocity profiles were prepared and used to subjectively select a common set of relatively homogeneous reaches for use in SMPTOX4. For each reach, average hydraulic characteristics (depth, top width, and velocity) were calculated for each hydrologic condition. This information is summarized in Table 1. Average velocity for each reach is also plotted in Figures 3 through 5.

Figure 3. Average reach velocities at 7Q10 flow conditions.

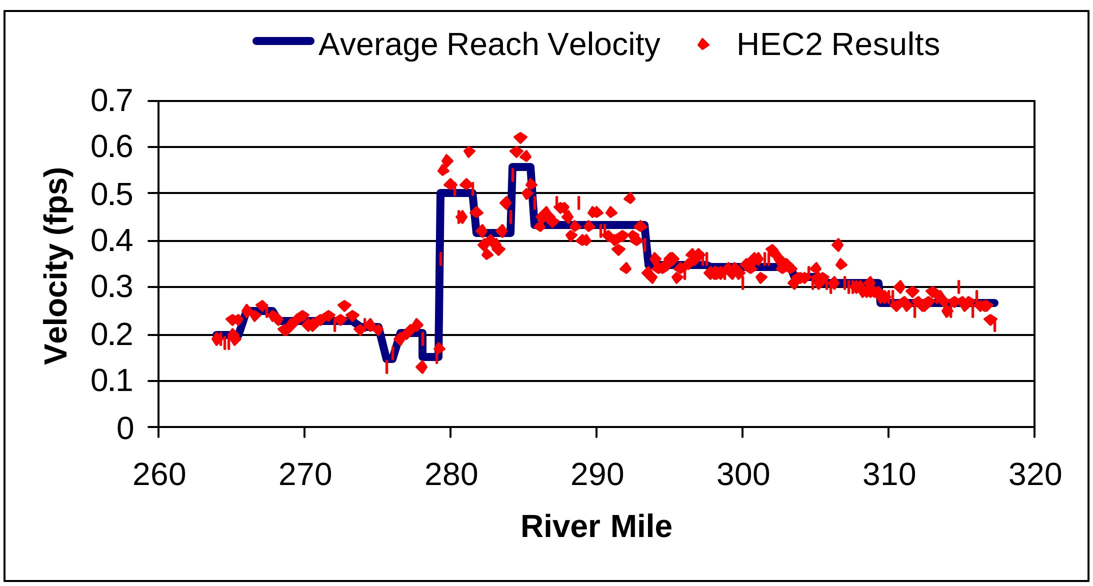


Figure 4. Average reach velocities at harmonic mean flow.

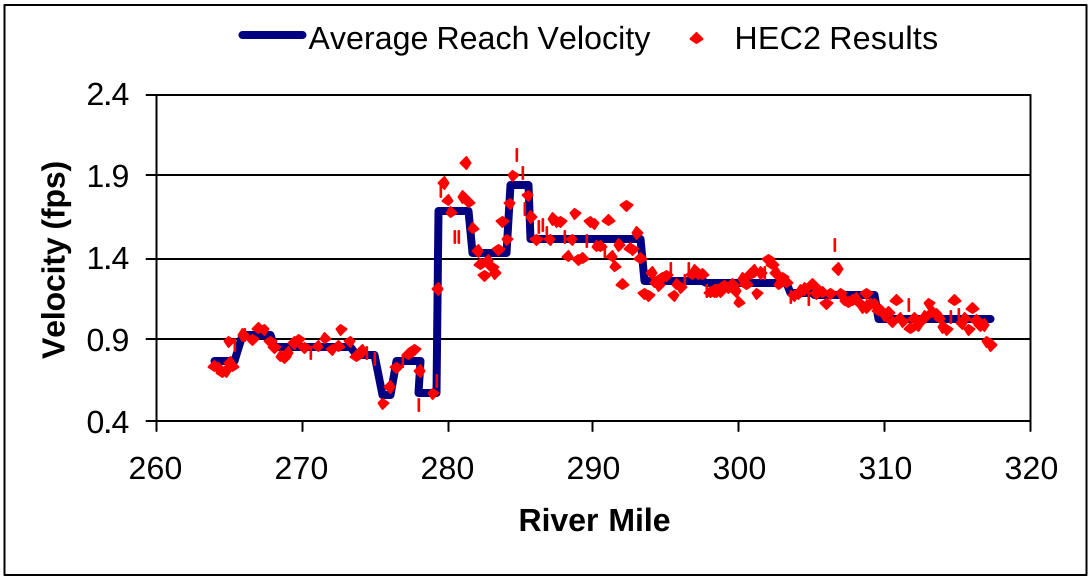
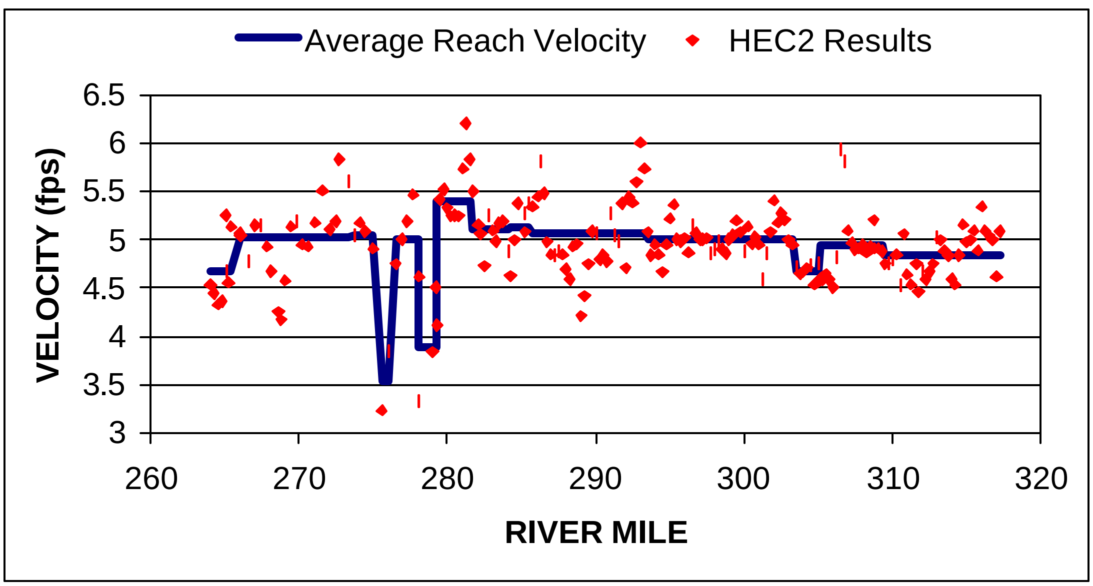



Figure 5. Average reach velocities at 1-year high flow.




## 4.2 Description of Parameterization Process

Models are approximations of processes that occur in the real world. In most models, there are parameters that must be set in order to tailor the model's use to a specific situation. The process of setting these parameters is known as parameterization.

The following steps were followed in parameterizing SMPTOX4:

For each parameter, a reasonable range of values was determined. A combination of literature values and/or values based on field measurements were used in determining this range. An initial best estimate was made for each parameter.

A sensitivity analysis was performed in order to determine the response of the model to variations in each parameter. The best estimate was used for each parameter during the sensitivity analysis and, one-by-one, each parameter was varied over the identified range and the resulting dioxin concentration determined using SMPTOX4.

For the more sensitive parameters, the best estimates were further refined. In some cases this involved collection of additional field data while in other cases, further literature investigation was performed. For those parameters that resulted in insignificant variation in predicted dioxin concentrations, the initial best estimate of the parameter value was adopted.

The details of parameterization are discussed in Section 4.3.

## 4.3 Input Parameter Estimation

SMPTOX4 requires input parameters to be defined for pollutant properties, boundary conditions, reach inputs, and tributary inputs. Below, each input parameter is listed along with an explanation as to how that parameter was defined.

- *Molecular Weight, g/mol*

The reported molecular weight for 2,3,7,8 TCDD is 321.96 g/mol (Windholz, 1983).

- *$K_p$ (partition coefficient)*

SMPTOX4 uses a partition coefficient ($K_p$) to represent the degree to which toxics adsorb to solids. High-volume water sampling results were used to calculate an average $K_p$ for the study area using the following equation:

$$K_p = \nu / C_d$$

where

$\nu$ is the particulate pollutant per unit solid = $C_p/SS$
$C_d$ = Dissolved pollutant concentration
$C_p$ = Particulate pollutant concentration
SS is the solids concentration

Partition coefficients were calculated for each high-volume water sampling event conducted within the study area, in which detectable concentrations of 2,3,7,8 TCDD were found in both the dissolved and particulate phases. Based on these calculations, the $K_p$ ranged from 157,000 to 928,000 L/Kg, with an average of 361,000 L/Kg.

The high-volume sampling data allowed for the partition coefficient to be directly calculated from field measurements. In most cases, however, this type of data is not available, which then makes it necessary to determine the $K_p$ indirectly. As a result, SMPTOX4 does not allow the user to directly input the $K_p$ into the model, but rather calculates the partition coefficient based on the $K_{oc}$ (organic carbon partition coefficient) and the $f_{oc}$ (fraction of organic carbon of the solids in the water column) values specified by the user. The model uses the following equation to calculate $K_{p.}$

$$K_p = K_{oc} * f_{oc}$$

where

$K_{oc}$ is the chemical-specific organic carbon partition coefficient
$f_{oc}$ is the fraction of organic carbon of solids

The SMPTOX4 manual states that for organic contaminants, the organic carbon partition coefficient can be estimated as equal to the chemical's octanol-water partition coefficient, or $K_{oc} = K_{ow.}$ A wide range of $K_{ow}$ values, from $1.4X10^6$ to $1.9X10^7$, has been reported for 2,3,7,8 TCDD (EPA 1992a). For this model application, $K_{ow}$ was assumed to be $10^{7.02}$ (approximately 10,000,000) as cited by EPA (1995d).

Since there were no data available regarding site-specific $f_{oc}$ values, the fraction of organic carbon in the water column was calculated using the above equation. The average partition coefficient based on the high-volume water sampling (361,000 L/Kg) was divided by the assumed $K_{ow}$ value ($10^{7.02}$), which resulted in an average $f_{oc}$ value of 0.034.

Sensitivity analysis indicated that the model results were very sensitive to changes in $K_{ow}$ and $f_{oc}$. However, considering that SMPTOX4 only uses the $K_{ow}$ and $f_{oc}$ values to calculate the $K_p$, the individual values for the two parameters are unimportant as long as the product of the two input parameters accurately represent the partition coefficient. Since the high volume water sampling data allows for the partition coefficient to be derived directly from measured field data, this minimizes any concern regarding the accuracy of the $K_{ow}$ and $f_{oc}$ values.

- *Henry's Constant, atm $m^3$/mol*

The reported value for the Henry's Law Constant for 2,3,7,8 TCDD is $2X10^{-6}$ atm $m^3$/mol (EPA 1992a).

- *Hydrolysis (acid, base, and neutral), 1/m/day*

Hydrolysis has been found to be an insignificant decay process for 2,3,7,8 TCDD, and as such, was assumed to be zero for this modeling effort. The same assumption was used in the development of a dioxin TMDL for the Columbia River (EPA 1992b).

Hydrolysis is independent of waterbody type, and the comparison to the Columbia River TMDL is provided simply as a reference to values used in other similar assessments.

- *Biodegradation (aerobic and anaerobic), 1/day*

Biodegradation has also been found to be an insignificant decay process for 2,3,7,8 TCDD, and as such, was assumed to be zero for this modeling effort. The same assumption was used in the development of a dioxin TMDL for the Columbia River (EPA 1992b). Biodegradation is independent of waterbody type, and the comparison to the Columbia River TMDL is provided simply as a reference to values used in other similar assessments.

- *Bed Depth, cm*

No site-specific data for active bed depth is available. For this model application, the bed depth was set at 5 cm as recommended by the SMPTOX4 User's Manual (EPA 1995b) for cases where there is insufficient data.

- *Settling Velocity and Resuspension (meters/day)*

SMPTOX4 represents the movement of suspended solids between the water column and the bed based on user defined values for the settling velocity and the resuspension velocity. In the model, these values are assumed to be constant within each reach. Factors that are known to affect the settling velocity and resuspension rate are particle size, river turbulence, and velocity. Stokes' equation relates the terminal velocity of a particle to particle size and density for the case of independent particles in a quiescent aquatic environment. Such conditions do not occur in the Ohio River nor does SMPTOX4 explicitly model particle sizes. Therefore, the user must implicitly assume some average particle size in defining settling and resuspension rates.

Sediment transport theory shows that settling and resuspension rates are dependent upon the velocity and turbulence in the river. As turbulence increases, the suspended solids tend to remain in the water column, thus resulting in a lower settling velocity. Similarly, as river velocity and turbulence increases, there is a greater degree of scour of the bed that results in a greater degree of resuspension and thus a higher resuspension velocity. Thus, based on sediment transport theory, it can be surmised that settling velocity will decrease under higher flow conditions (due to higher velocity and turbulence), and that resuspension rates will increase under higher flow conditions due to greater scour.

However, quantitative estimation of settling velocities and resuspension rates is difficult because these rates cannot be directly measured in the field. Therefore, they must be estimated based on field observations of the suspended loads in the river. In order to estimate rates for settling and resuspension, ORSANCO conducted two longitudinal total suspended solids (TSS) surveys throughout the study area. The first study was conducted under relatively low flow conditions (13,000 cfs at RC Byrd Dam), while the second survey saw Ohio River flows of 60, 000 cfs (nearly twice the harmonic mean flow). Inspection of the longitudinal TSS measurements from both surveys indicated the following: (1) average TSS concentrations on the Ohio River remained fairly constant from the Kanawha River confluence to RC Byrd Dam, and (2) there was a significant drop in TSS concentration between measurements made just upstream of RC Byrd Dam and immediately downstream of the structure. The behavior of solids from just downstream of the dam to the downstream end of the study area in Huntington, WV was different for the two surveys. During the low-flow sampling there was a slight gradual decrease in concentration longitudinally for reaches downstream of the dam, while during the second survey conducted under moderate flow conditions, TSS concentrations increased slightly in a downstream direction.

The SMPTOX4 model was used to estimate the settling and resuspension rates by running the model iteratively to determine the combination of settling and resuspension rates that resulted in a longitudinal suspended solids profile that best fit the observed data. In making these estimates, it was assumed that the resuspension velocity would be very low under the low-flow conditions, and slightly higher during moderate flow conditions. Resuspension rates were also assumed to be higher for the reaches below the dam, than those on the upstream side, based on swifter currents downstream of the structure.

For the low-flow TSS survey, a resuspension value of $1X10^{-7}$ m/day was selected for the reaches upstream of RC Byrd Dam and a rate of $1X10^{-6}$ m/day downstream of the dam. To simulate the TSS profile during the moderate flow survey, resuspension rates of $1X10^{-6}$ and $1.45 \times 10^{-5}$ m/day were used for the reaches upstream and downstream of the dam, respectively. Once the assumed resuspension rates were established, the settling velocities were adjusted until the SMPTOX4 model results simulated the observed suspended solids profile data. This process produced pairs of settling and resuspension rates for the three distinct segments of the study area (i.e. reaches upstream of the dam, reach representing the dam, and the reaches downstream of the dam). These estimated settling and resuspension rates are presented in Table 2. Reaches 1-7 represent the study area upstream of RC Byrd L&D, reach 8 is at the dam, and reaches 9-16 are downstream of the structure. The resulting best fit simulated suspended solids concentrations are compared to the observed suspended solids in Figures 6 and 7.

Table 2. Settling and resuspension rates that produce TSS longitudinal profiles that simulate observed TSS longitudinal survey data.

| | Low-flow TSS Survey | | | Moderate-flow TSS Survey | | |
|---|---|---|---|---|---|---|
| Reach #s | 1-7 | 8 | 9-16 | 1-7 | 8 | 9-16 |
| Settling, m/day | 0.2 | 11.5 | $1x10^{-6}$ | 0.74 | 14.5 | 0.639 |
| Resuspension, m/day | $1x10^{-7}$ | $1x10^{-7}$ | $1x10^{-7}$ | $1x10^{-6}$ | $1x10^{-7}$ | $1x10^{-6}$ |

**Figure 6. Low-flow TSS longitudinal survey and best fit SMPTOX results.**

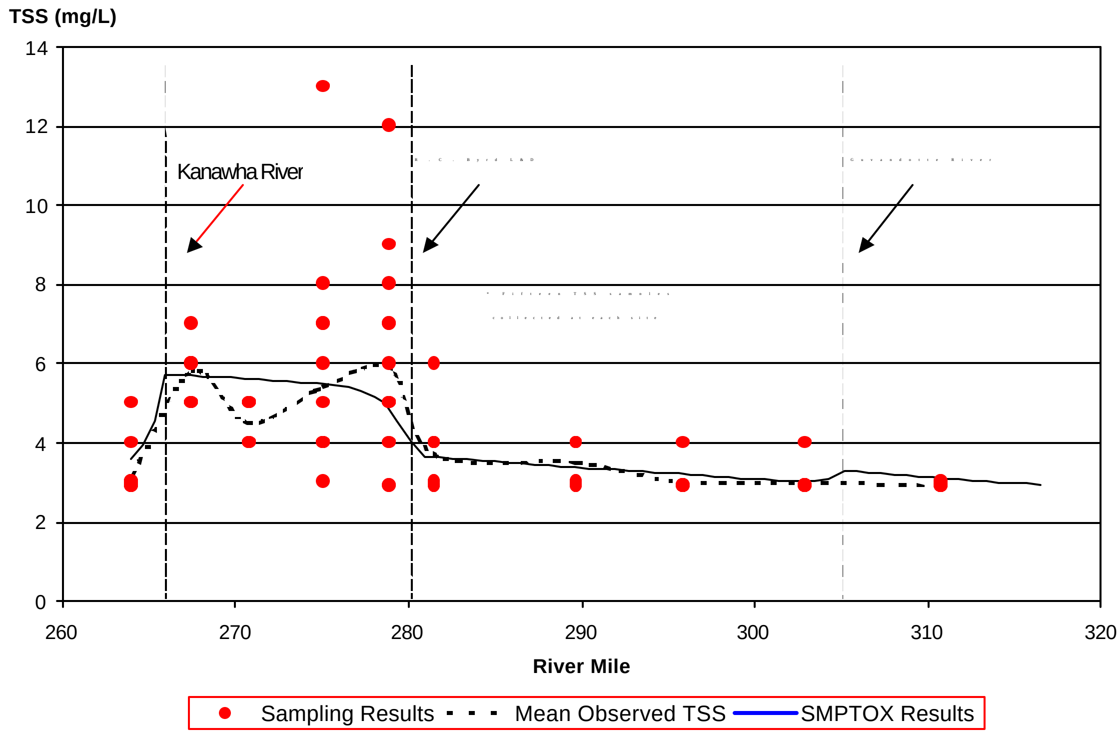
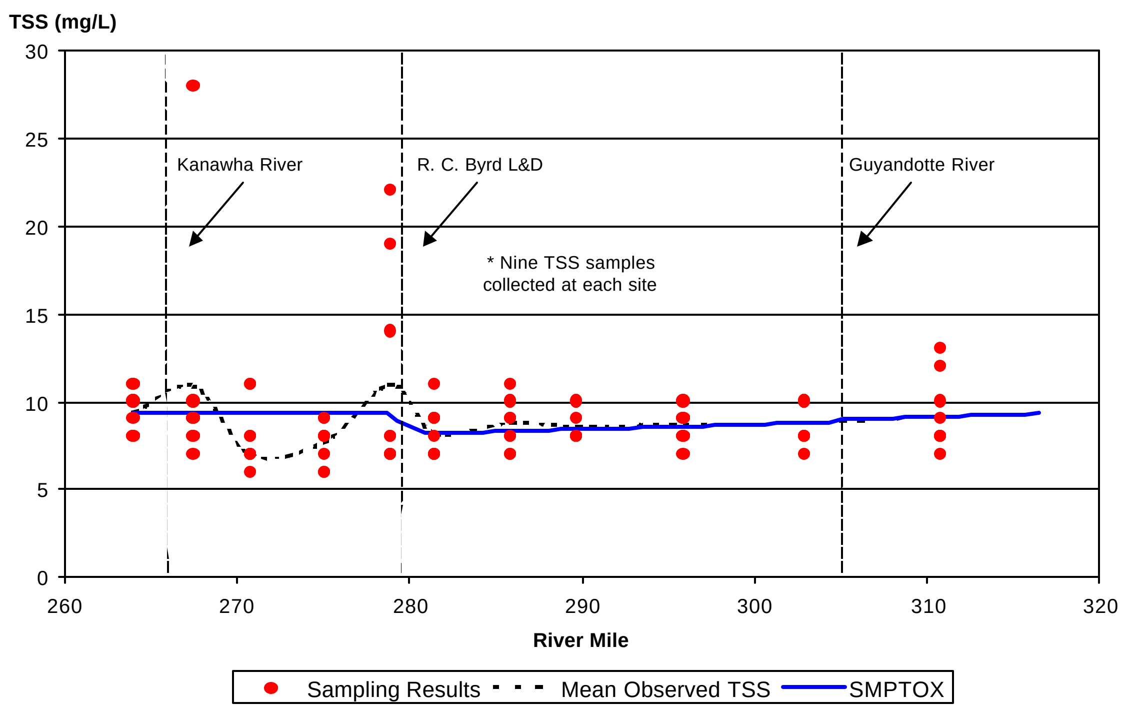
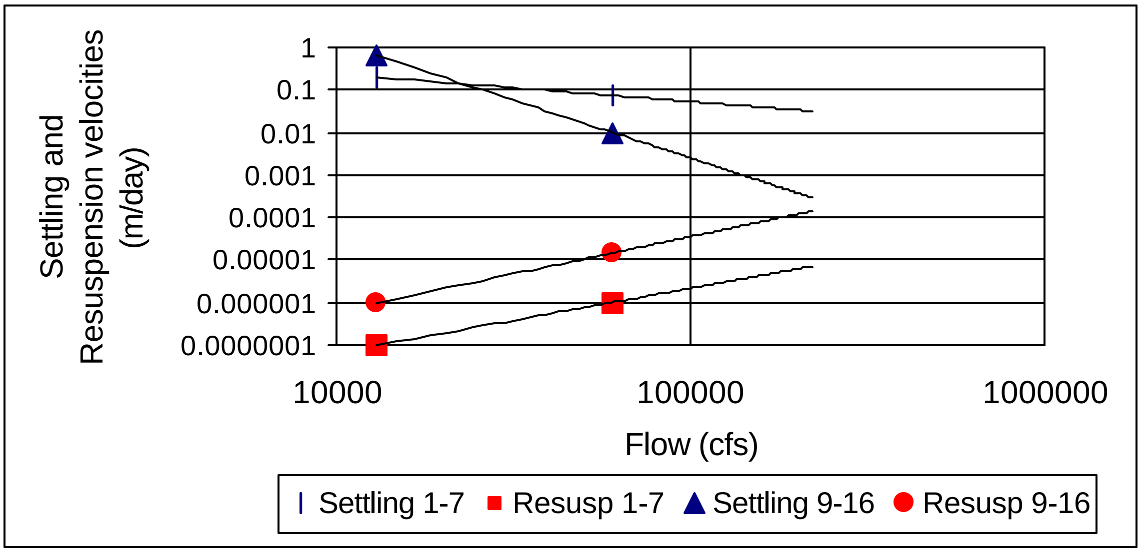



**Figure 7. Moderate-flow TSS longitudinal survey and best fit SMPTOX results.**



The estimated settling and resuspension rates that produced results that best fit the data from the two longitudinal TSS surveys were used to develop a relationship between stream flow to settling and resuspension velocities. This flow-correlated relationship (depicted in Figure 8) was used to predict the settling and resuspension velocities for each of the flow conditions at which the SMPTOX4 model was run.

Figure 8. Postulated relationship between settling and resuspension rates to flow.




- *Dispersion, m2/day*

In most rivers and streams, advection (net downstream flow) is the primary transport process. A secondary form of transport is longitudinal dispersion, which is the longitudinal “spreading out” of particles due to variations in velocity across the river width. The primary method of estimating dispersion is through a field tracer study using a conservative tracer.

Two dye tracer studies were conducted by ORSANCO in the Greenup Pool of the Ohio River in order to identify travel times and dispersion characteristics of the river. The Greenup pool extends from the RC Byrd Lock and Dam (river mile 279.2 downstream to the Greenup Lock and Dam (river mile 341.0). In both studies, Rhodamine WT dye was injected across the river in a short time period (< 0.5 hours) and the concentration of the dye traced downstream in the river over a period of several days. The first study was conducted from August 19 to August 23, 1996 when flow conditions were in the range of 37,000 cfs to 54,000 cfs based on National Weather Service estimates. The second study, conducted from December 9 to December 11, 1997 was performed under higher flow conditions (60,000 cfs to 80,000 cfs).

Fischer (1973) shows that for an instantaneous point injection that the downstream peak concentration ($C_p$) in a uniform channel can be estimated by the following equation:

$$C_p = W / [A (4\pi D_x t)^{0.5}]$$

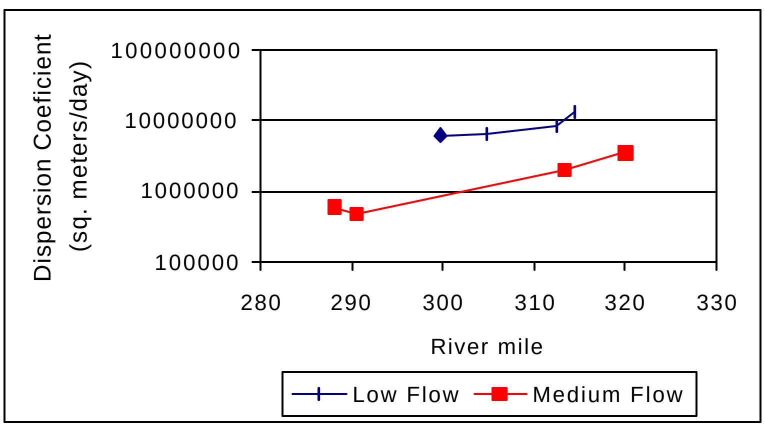
where

W is the mass discharged
A is the channel cross section area
$D_x$ is the longitudinal dispersion coefficient
T is time

For the two tracer studies, the longitudinal dispersion coefficient was calculated for different locations downstream of the tracer injection point using Fischer's equation. A constant cross-sectional area and constant stream flow rates were assumed. The results of these calculations are shown graphically in Figure 9. As illustrated, the calculated dispersion coefficients increase significantly as you move downstream. It is postulated that this variation is due to actual variations in cross-sectional area, in temporal variations in stream flow rate which differ from the assumption of constant values, and loss of dye during the studies.

A sensitivity analysis of SMPTOX4 indicated that modeling results are quite insensitive to dispersion rates. The analysis showed that there was no significant variation in predicted dioxin and solids concentrations when the dispersion coefficient was varied from 100,000 to 20,000,000 square meters per day (the range of calculated values based on the two tracer studies). Therefore, for the SMPTOX model, an average dispersion coefficient of 1,000,000 meters$^2$/day was assumed for all cases.

Figure 9: Calculated Dispersion Coefficients Based on Tracer Studies




- *Inflow, cfs/mile*

Inflow refers to the influx of pure water to the modeled area. This parameter was assumed to be 0 cfs/mile since the amount of water that enters the study area via runoff is minimal compared to the stream flow of the Ohio River, and as such would have a negligible impact.

- *Solids Load, kg/mile/day*

Solids load is the influx of solids to the modeled area via runoff. While there is no data to quantify this loading, the solids influx is believed to be negligible compared to the solids load entering the model study area at the upstream boundaries. Considering the minimal impact that the solids load would have on the model results, this parameter was assumed to be 0 kg/mile/day.

- *Bed $f_{oc}$*

The average weight fraction of bed solids consisting of organic carbon is referred to as bed $f_{oc}$ (EPA 1995b). There is no bed $f_{oc}$ data available for the Ohio River. A typical bed $f_{oc}$ value of 0.01 was used in this model application as suggested by LTI, the developers of the SMPTOX4 model. Sensitivity analysis indicated that the SMPTOX4 model results are very insensitive to bed $f_{oc}$, with no appreciable difference in the model results with bed $f_{oc}$ values ranging from 0.001 – 0.1

- *Bed Porosity and Density, g/cc*

The bed sediment solids concentration is the sediment parameter of ultimate interest to the SMPTOX4 model. This value is rarely measured, but can be calculated based on the bed porosity and density using the following equation:

$$m_2 = \rho_s(1 - \phi_2) \cdot 10^6$$

where

$m_2$ = bed sediment solids concentration (mg/L)
$\rho_s$ = porosity of bed solids
$\phi_2$ = density of bed solids (g/cc)

Sensitivity analysis revealed that the SMPTOX4 model results are moderately sensitive to the density and porosity of the bed solids. As density increases, the SMPTOX4 model results reflect an increase in the suspended solids concentration, and subsequently an increase in the concentration of particulate phase 2,3,7,8 TCDD. Conversely, an increase in bed porosity results in a decrease in suspended solids and particulate phase 2,3,7,8 TCDD concentrations. Data for both variables are lacking for the Ohio River. In the absence of site specific data, sediment characteristic values were estimated. A constant value of 2.5 g/cc was assumed for the density of the bed solids. This value was based on the density that was used in the development of a dioxin TMDL for the Columbia River (EPA 1992b). Bed porosity was assumed to be 0.8 based on discussions with LTI. A similar value of 0.9 was used in the Columbia River TMDL. It is acknowledged that there may be differences in the bed characteristics between the Ohio and Columbia Rivers, however, in the absence of site specific data, these values were deemed reasonable estimates.

- *Mixing Factor*

The mixing factor as applied by SMPTOX4 is a factor between 0 and 10, which represents enhanced diffusional exchange between the bed and water column due to effects such as bioturbation. The sensitivity analysis determined that this parameter has a negligible effect on the model results, and as such, was assumed to be zero for all model runs.

- *2,3,7,8 TCDD Load, g/mile/day*

The 2,3,7,8 TCDD load parameter refers to the influx of the pollutant to the model study area from nonpoint sources. There are two major nonpoint source routes to consider, runoff and atmospheric deposition. Considering that no 2,3,7,8 TCDD contaminated sites have been identified within the study area, the pollutant contribution from runoff is assumed to be zero. This assumption, however, is based solely on the absence of known contaminated sites and not on field measurements.

Atmospheric deposition has the potential to be a significant source of dioxins to surface waters. Many of the dioxin congeners have the ability to travel great distances through the atmosphere before depositing to the ground. The 2,3,7,8 TCDD congener, however, is less stable in the atmosphere than other congeners. As a result, the 2,3,7,8 TCDD congener is more likely to either be deposited near its source, or undergo photodegradation. Ambient air samples were collected at RC Byrd Locks & Dam (Ohio River mile 279.2) on five occasions in order to estimate the potential 2,3,7,8 TCDD loading to the Ohio River from atmospheric deposition. The 2,3,7,8 TCDD congener was not detected in any of the samples, while low-level concentrations were found for the other 16 congeners. Based on these findings, the 2,3,7,8 TCDD load from nonpoint sources was assumed to be zero.

- *Photolysis (Dissolved and Particulate), 1/day*

Photolysis is the chemical breakdown due to the action of light. It is believed that photolysis is the only potentially significant decay process for 2,3,7,8 TCDD in water. EPA’s Columbia River study (1992b) found photolysis rates to range from 0.00023 to 0.001/day. Rates for the Ohio River would differ from that of the Columbia River for a variety of reasons including differences in latitude, stream depth, and light attenuation. However, due to the lack of site specific data, the range of values reported for the Columbia River were used to evaluate the potential loss due to photolysis for the Ohio River. The sensitivity analysis revealed that even at the upper end value of 0.001/day, photolysis is a negligible decay process for 2,3,7,8 TCDD within the study. As a result, a conservative approach was taken with the model application, and photolysis rate was assumed to be zero.

## 4.4 Estimation of Boundary Conditions

The SMPTOX4 model calculates pollutant and suspended solids concentrations within the study area based on the upstream boundary conditions and tributary inputs specified by the user. These boundary inputs include stream flow, total suspended solids concentrations, and pollutant concentrations. The methods used to define each of these conditions are described below.

### *4.4.1 Stream Flow*

In applying the SMPTOX4 model, the user must specify the flows and loads entering the river at the upstream boundary and at tributary points along the river. Three separate flow conditions were selected for modeling: low flow (7Q10), harmonic mean flow, and one-year flood conditions. The stream flows for the Ohio, Kanawha, and Guyandotte Rivers corresponding to these three conditions are presented in Table 3. Tributary flows were calculated by subtracting the Ohio River flow upstream of the tributary's confluence from the Ohio River stream flow downstream of the tributary inflow. These stream flow values are based on critical Ohio River flows, and as such, the stream flows attributed to tributaries do not exactly reflect the critical flow conditions for the Kanawha and Guyandotte Rivers. For instance, the 7Q10 value for the Kanawha River is approximately 2,000 cfs; however, based on a comparison of Ohio River 7Q10 values upstream and downstream of the Kanawha River confluence, a stream flow of 2,420 cfs is assigned to the Kanawha River. This value, though greater than the Kanawha River 7Q10 value, represents the typical Kanawha River inflow when the Ohio River is at 7Q10 flow conditions.

Table 3: Stream flows for the Ohio, Kanawha, and Guyandotte Rivers used for SMPTOX4 model runs.

| **Flow Condition** | **Ohio River at upstream boundary (cfs)** | **Kanawha River (cfs)** | **Guyandotte River (cfs)** |
|---|---|---|---|
| 7Q10 (low flow) | 6,700 | 2,420 | 180 |
| Harmonic mean | 26,000 | 8,500 | 1,400 |
| 1 year flood | 225,000 | 42,700 | 6,000 |

### *4.4.2 Suspended Solids*

Total suspended solids data collected by ORSANCO at long term monitoring stations were used to predict TSS concentrations at the upstream boundaries of the study area. Data collected at Winfield Lock & Dam were used to estimate TSS loadings for the Kanawha River. Since Winfield is located 31 miles upstream of the mouth of the Kanawha River, some changes in solids could occur between the monitoring site and the mouth. However, it was judged that these changes would be relatively minimal, and that this data set would provide the best possible estimate of solids. Solids concentrations for the Ohio River upstream of the Kanawha River were estimated by subtracting the load contributed by the Kanawha River from the solids load at RC Byrd Lock & Dam on the Ohio River. Long term monitoring data collected by WV DEP, coupled with USGS stream flow data, were used to estimate TSS concentrations entering the study area from the Guyandotte River.

For each model run, the solids concentrations for the Ohio, Kanawha, and Guyandotte Rivers were predicted based on a positive correlation between stream flow and the historical TSS data. Figures 10-12 illustrate this relationship. For each of these cases, a best fit linear, exponential, logarithmic, and power function relationship were determined relating solids concentrations to flow. On the Kanawha River, a linear correlation resulted in a best fit (greatest $r^2$ value), while the power function produced the best correlation for the Ohio and Guyandotte Rivers. Based on this analysis, boundary TSS concentrations were calculated using the equation for the selected best-fit line and the stream flow corresponding to each model run (i.e. 7Q10, harmonic mean flow, and 1-year flood). These results are presented in Table 4.

Table 4. Predicted TSS concentrations based on historical data.

| | | **7Q10** | | **Harmonic Mean** | | **1-Year Flood** | |
|---|---|---|---|---|---|---|---|
| Boundary Site | Equation | Flow Cfs | TSS mg/L | Flow cfs | TSS mg/L | Flow cfs | TSS mg/L |
| Ohio R. upstream | $TSS = 0.000001Q^{1.5317}$ | 6700 | 0.7 | 26000 | 5.8 | 225000 | 157.7 |
| Kanawha R. | $TSS = 0.0006Q + 3.7101$ | 2420 | 5.2 | 8500 | 8.8 | 42700 | 29.3 |
| Guyandotte R. | $TSS = 0.2903Q^{0.531}$ | 180 | 4.6 | 1400 | 13.6 | 6000 | 29.4 |

Figure 10: Calculated TSS at Ohio River upstream boundary site (based on RC Byrd and Winfield historical TSS data 1/89 – 12-98).

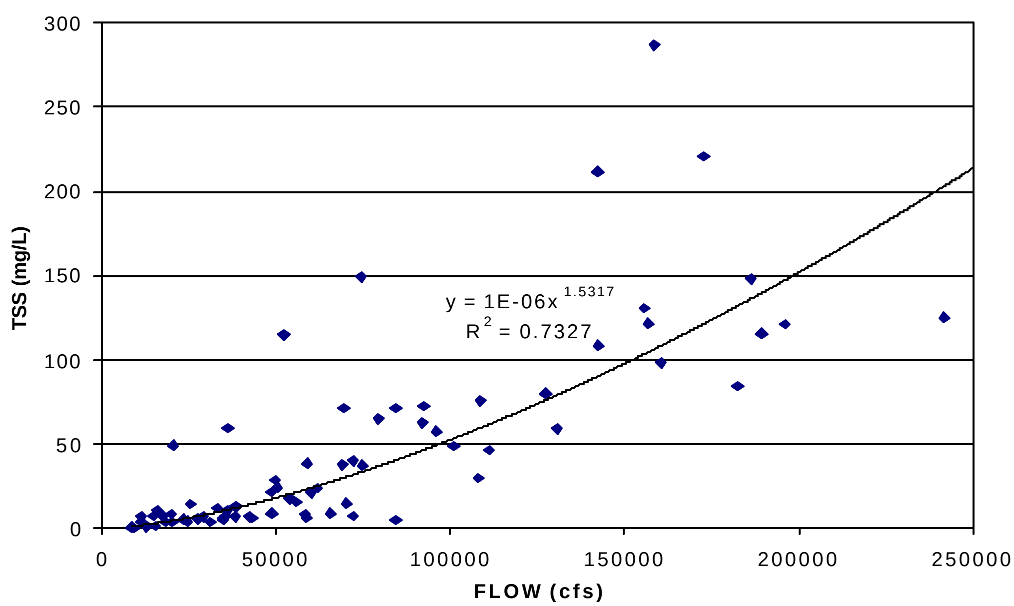


Figure 11: Total suspended solids on the Kanawha River at Winfield L&D (1/89 – 12-98)

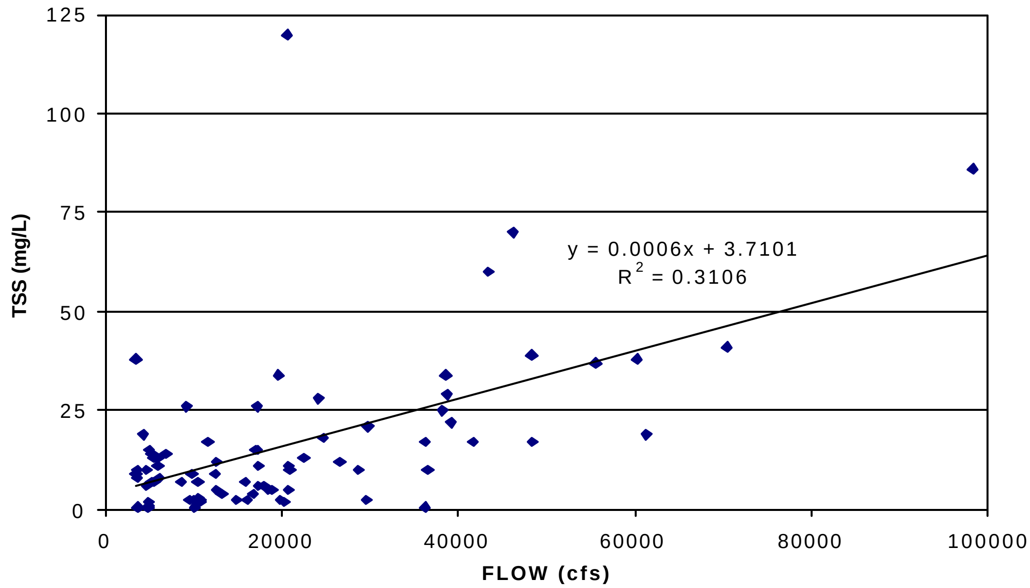
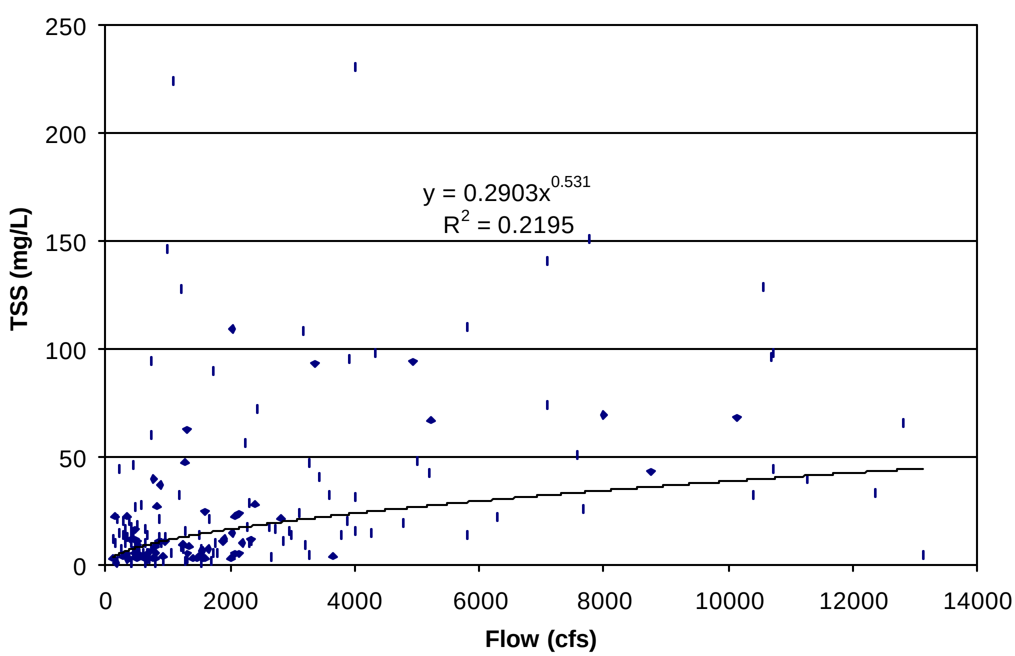



Figure 12: Total suspended solids on the Guyandotte River (1980-1995).




It should be noted that the weak correlation observed on the Guyandotte River in Figure 12 is likely the result of the method used to estimate stream flows at the TSS sampling points. The only daily flow data for the Guyandotte River is collected by the USGS 81 miles upstream of the mouth. Though the stream flow data was adjusted for the increase in drainage area at the TSS sampling location near the mouth, the range of uncertainty associated with this data is rather large. The ultimate effects of these inaccuracies; however, are of minimal concern considering that the potential TSS and dioxin loadings from the Guyandotte River are practically insignificant to the Ohio River merely due to the extreme size difference of the two rivers.

*4.4.3 Dioxin Loading*

Instream dioxin data was collected using high-volume water sampling. This sampling technique achieves detection limits of approximately 0.001 ppq by filtering and extracting dioxins from a large volume of water (i.e. 1000 liters). High-volume water sampling was conducted in 1997 and 1998 at three Ohio River locations within the study area: Pt. Pleasant, WV (ORM 264), Apple Grove, WV (ORM 281.5), and Huntington, WV (ORM 302.9). Sampling was also conducted on the Kanawha and Guyandotte Rivers approximately one mile upstream of their Ohio River confluences. Sampling results are included in *Appendix A*.

The high-volume water sampling data, though limited, indicate that the particulate phase 2,3,7,8 TCDD concentrations are positively correlated to stream flow and TSS. This relationship is not surprising considering that dioxins strongly bind to particulate matter, and suspended solids concentrations generally increase as stream flow increases. Dissolved concentrations, however, showed no consistent relationship with stream flow or TSS concentrations. Figures 13 through 15 illustrate the relationship of 2,3,7,8 TCDD concentrations to stream flow. Though SMPTOX4 requires the user to specify total 2,3,7,8 TCDD concentrations for the boundaries, these sampling results indicate the need to develop separate relationships for particulate and dissolved 2,3,7,8 TCDD concentrations.

Based on the relationships of particulate and dissolved concentrations of 2,3,7,8 TCDD to stream flow (as presented in Figures 13-15), it was concluded that the best means of predicting total 2,3,7,8 TCDD concentrations at the desired flow conditions was to estimate the concentration in each phase separately (using two different methods), and then add the two together. Particulate phase concentrations were predicted using a best-fit regression line for concentration versus stream flow. Because there were so few dioxin sampling data points, and since the addition or subtraction of only one or two data points could easily alter which type of regression produced the best correlation coefficient, the regression line that resulted in the greatest $r^2$ value was not automatically selected as the best-fit line to represent the relationship between the two parameters. Since particulate phase 2,3,7,8 TCDD is bound to solids in the water column, and there is an ample amount of historical TSS data available, the regression that produced the "best fit" between TSS and stream flow was also used to represent the relationship between particulate phase 2,3,7,8 TCDD and stream flow. As a result, the relationship between particulate phase dioxin and stream flow was determined to be linear for the Kanawha River, while the power function regression was used for the Ohio and Guyandotte Rivers. Particulate concentrations at the boundary sites were then calculated using the equation for the selected regression line.

Since no correlation to flow or TSS was apparent for dissolved concentrations, average dissolved 2,3,7,8 TCDD concentrations were used for each of the boundary sites. Two of the five rounds of sampling at the Ohio River upstream boundary, as well as, one of two rounds on the Guyandotte River resulted in undetectable dissolved concentrations. For these boundary sites, average concentrations were calculated by assuming the non-detects were equal to one-half of the detection limit (using ½ the detection limit is a common reporting practice for dioxin congeners). Considering dissolved concentrations are typically an order of magnitude less than the concentration in the particulate phase, the uncertainty involved with simply using an average dissolved concentration is of minimal concern. Once the average dissolved 2,3,7,8 TCDD concentrations and the predicted particulate concentrations were calculated (based on the selected regression) for each boundary site, total concentrations were calculated by simply adding the two phases together. The calculated concentrations used to define the boundary conditions for each model run are presented in Tables 5-7.

Table 5. Predicted 2,3,7,8 TCDD concentrations at boundary inputs for 7Q10 model run.

| **7Q10** | | | | | |
|---|---|---|---|---|---|
| Boundary Site | Regression Line Equation (particulate) | Flow cfs | Particulate ppq | Average Dissolved ppq | Total 2,3,7,8 TCDD ppq |
| Ohio River upstream | $2x10^{-6}Q^{0.8453}$ | 6700 | 0.0034 | 0.0018 | 0.0052 |
| Kanawha R. | $8x10^{-6}Q + 0.0842$ | 2420 | 0.1036 | 0.0138 | 0.1174 |
| Guyandotte R. | $5x10^{-11}Q^{2.2462}$ | 180 | 0.0000 | 0.0005 | 0.0005 |

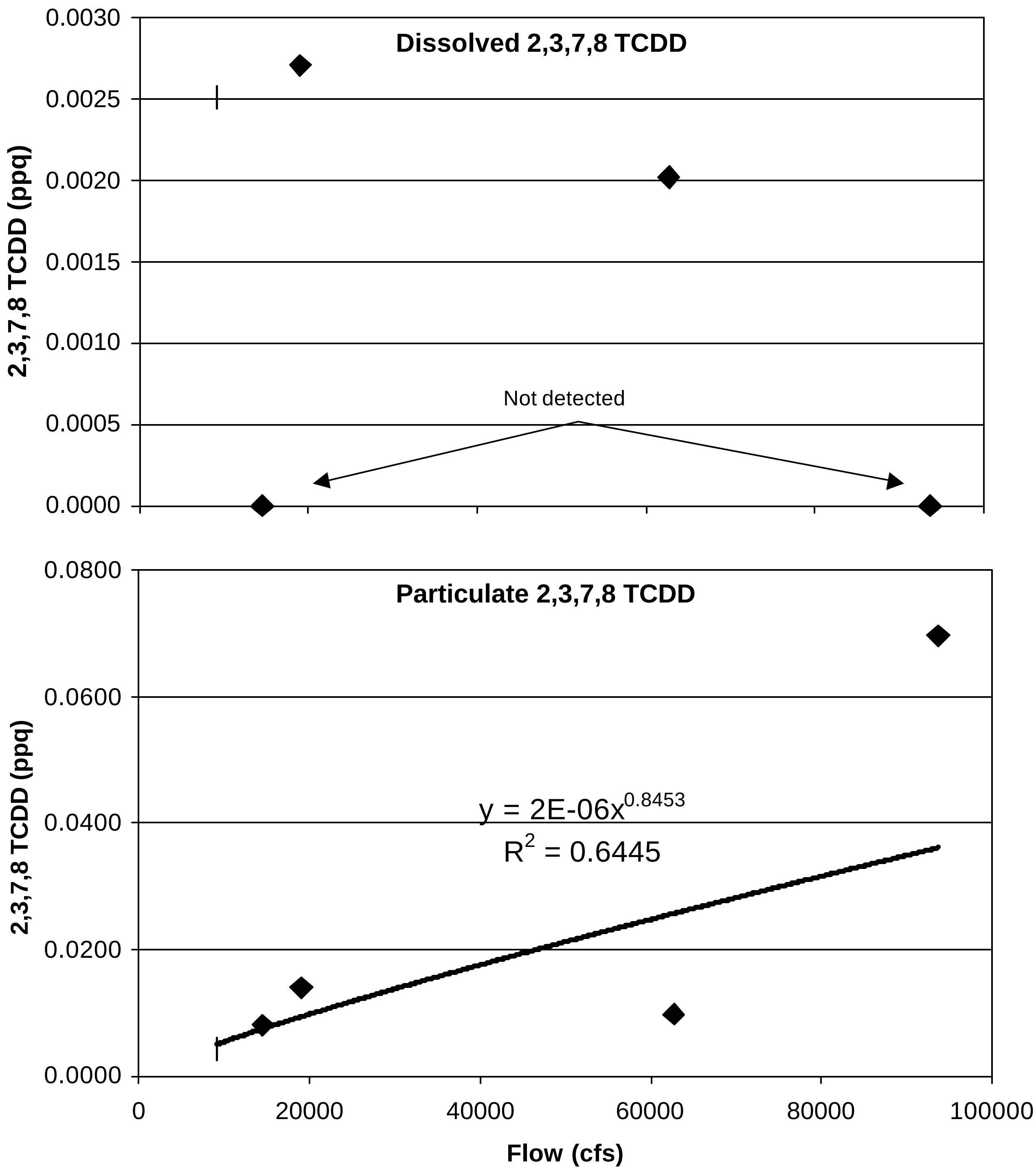
Table 6. Predicted 2,3,7,8 TCDD concentrations at boundary inputs for harmonic mean flow model run.

| **Harmonic Mean** | | | | | |
|---|---|---|---|---|---|
| Boundary Site | Regression Line Equation (particulate) | Flow cfs | Particulate ppq | Average Dissolved ppq | Total 2,3,7,8 TCDD Ppq |
| Ohio R. upstream | $2x10^{-6}Q^{0.8453}$ | 26000 | 0.0108 | 0.0018 | 0.0126 |
| Kanawha R. | $8x10^{-6}Q + 0.0842$ | 8500 | 0.1522 | 0.0138 | 0.1660 |
| Guyandotte R. | $5x10^{-11}Q^{2.2462}$ | 1400 | 0.0006 | 0.0005 | 0.0011 |

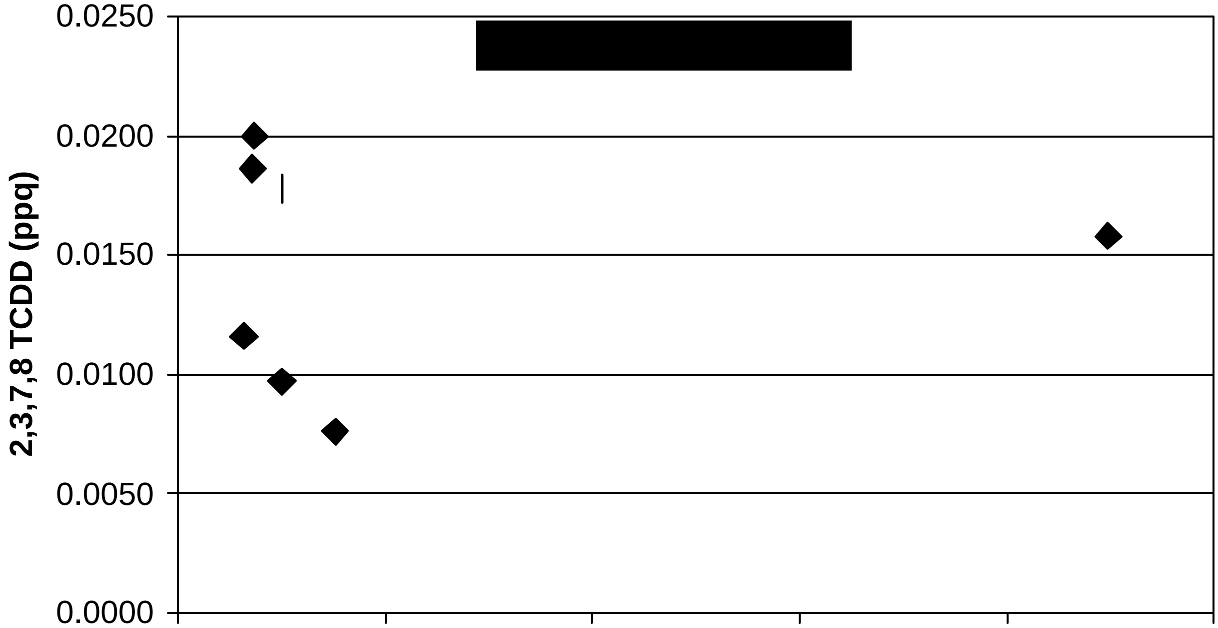
Table 7. Predicted 2,3,7,8 TCDD concentrations at boundary inputs for 1-year flood conditions model run.

| **1-Year Flood** | | | | | |
|---|---|---|---|---|---|
| Boundary Site | Regression Line Equation (particulate) | Flow cfs | Particulate Ppq | Average Dissolved ppq | Total 2,3,7,8 TCDD ppq |
| Ohio R. upstream | $2x10^{-6}Q^{0.8453}$ | 225000 | 0.0669 | 0.0018 | 0.0687 |
| Kanawha R. | $8x10^{-6}Q + 0.0842$ | 42700 | 0.4258 | 0.0138 | 0.4396 |
| Guyandotte R. | $5x10^{-11}Q^{2.2462}$ | 6000 | 0.0153 | 0.0005 | 0.0158 |

**Figure 13. Relationship between 2,3,7,8 TCDD concentrations and flow at Ohio River mile 264.**



[redacted]


[redacted]
0.0250
0.0200
0.0150
0.0100
0.0050
0.0000
2,3,7,8 TCDD (ppq)

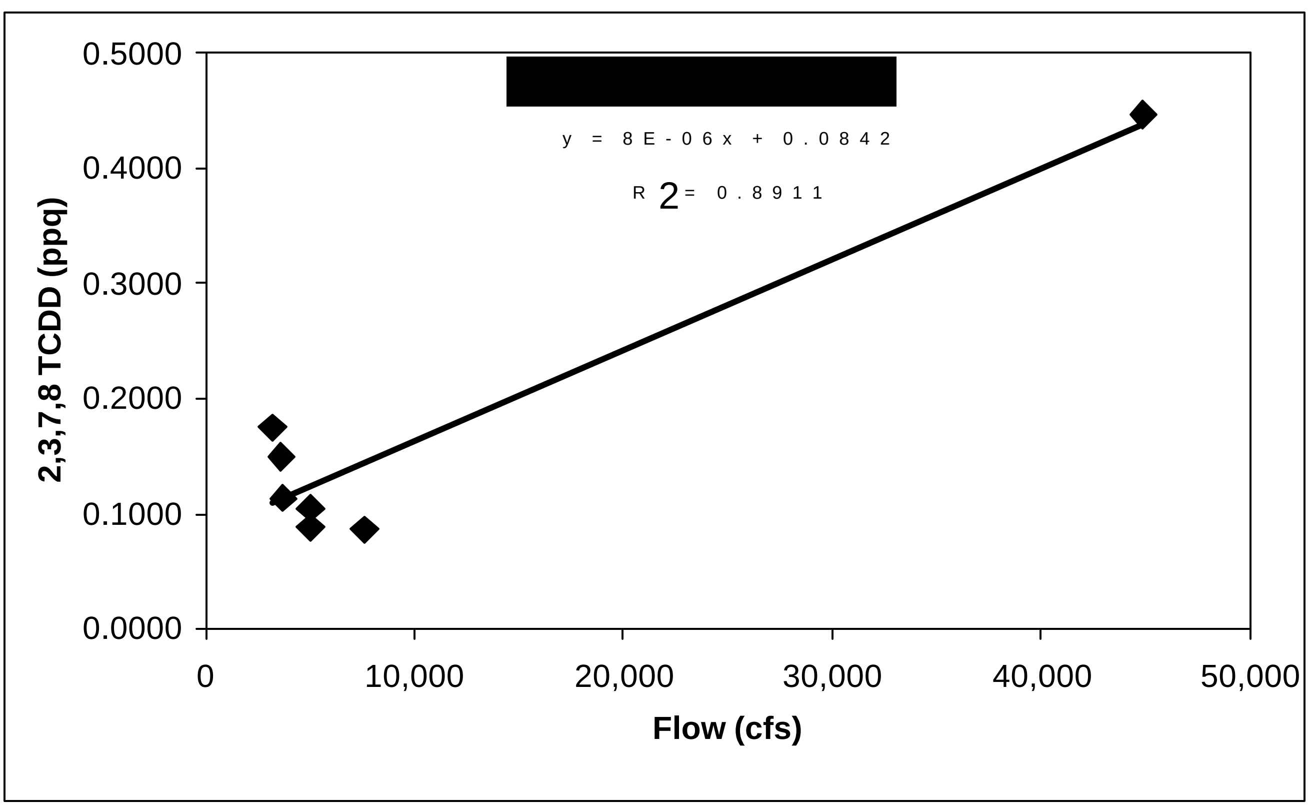
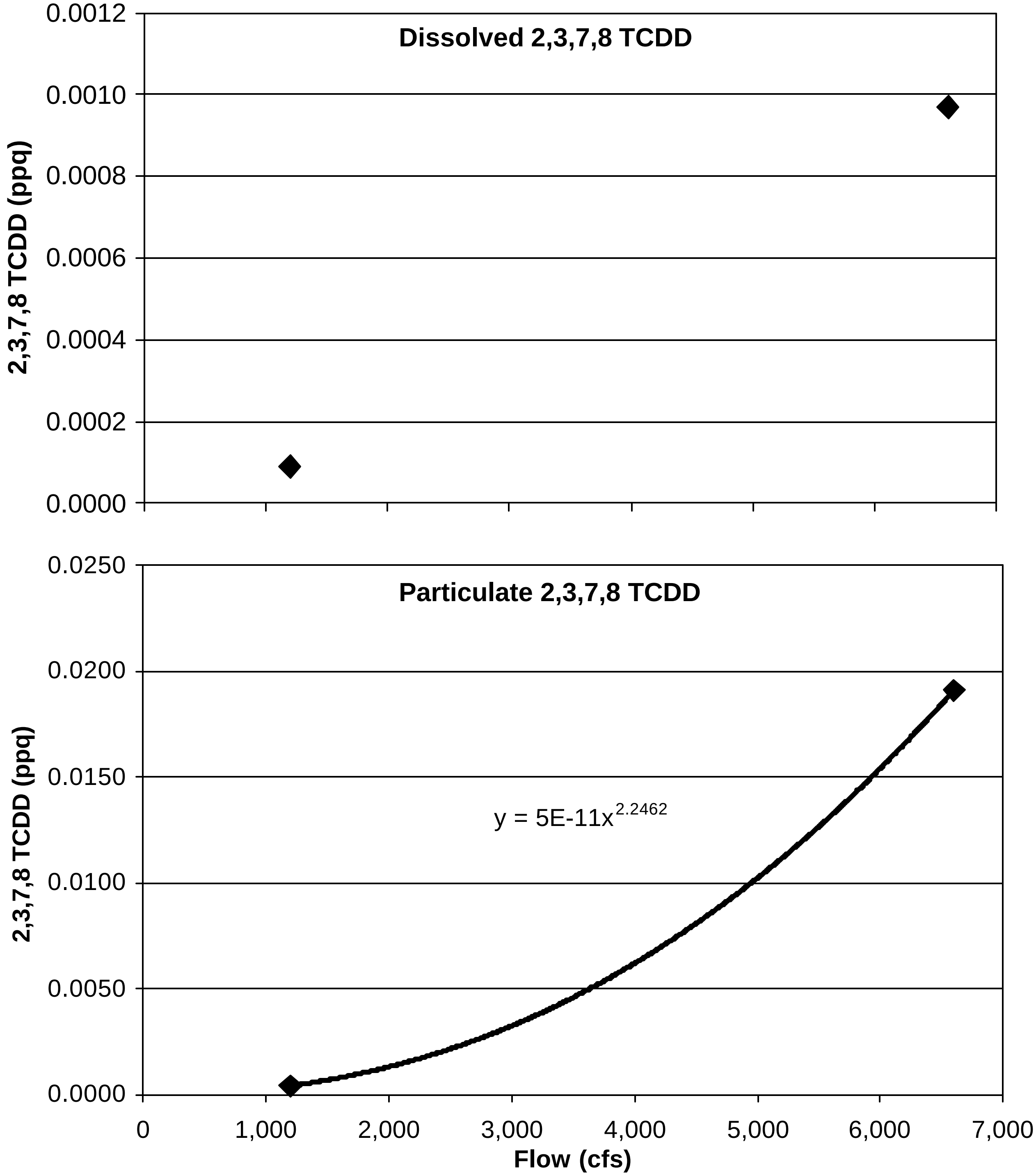

[redacted]
y = 8E-06x + 0.0842
R2 = 0.8911
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
2,3,7,8 TCDD (ppq)
0
10,000
20,000
30,000
40,000
50,000
Flow (cfs)

**Figure 15. Relationship between 2,3,7,8 TCDD concentrations and flow at Guyandotte River mile 1.1.**



### 4.5 Validation

When developing a model, a comparison of model results to measured field data is necessary to validate the model's ability to simulate real-world conditions. In order to perform a true validation, the data used to calibrate the model should not be used to also validate the model. As is the case in many studies where limited field data is available, there was insufficient field data available to perform a fully independent validation. In this case, dioxin sampling data collected at the boundary sites were used to predict boundary concentrations of 2,3,7,8 TCDD (as discussed in Section 4.4.2) at the various flow conditions corresponding to each model run. However, dioxin data collected at two points within the study area (ORM 281.5 and 302.9) were only used to estimate the partition coefficient for 2,3,7,8 TCDD. The partition coefficient only affects the distribution of dioxin between the particulate and dissolved phases, and has no impact on the total concentration. As a result, data for these two sampling points can be used for validation by comparing the model results to observed total 2,3,7,8 TCDD concentrations.

Five model validation runs were completed, one for each round of high-volume dioxin sampling data. For each run, observed total 2,3,7,8 TCDD and TSS concentrations, along with National Weather Service (NWS) flow estimates were used as boundary inputs for the Kanawha River and the Ohio River upstream of the study area. Predicted dioxin and TSS concentrations were used for the Guyandotte River using the method described in Section 4.4 since high-volume sampling was not conducted on this tributary at the same time that the other four sites in the study area were sampled. The boundary inputs for each validation run are included in Tables 8-12 and the results are presented in Figures 16-20.

Table 8. Boundary inputs for model validation run corresponding to November 1998 dioxin sampling.

| Boundary Site | 4-Day Avg. Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| Ohio R. (upstream) | 11025 | 10.8 | 0.0068 |
| Kanawha River | 3475 | 18.0 | 0.1686 |
| Guyandotte River | 375 | 6.8 | 0.0006 |

Figure 16. SMPTOX4 results corresponding to November 1998 dioxin sampling.

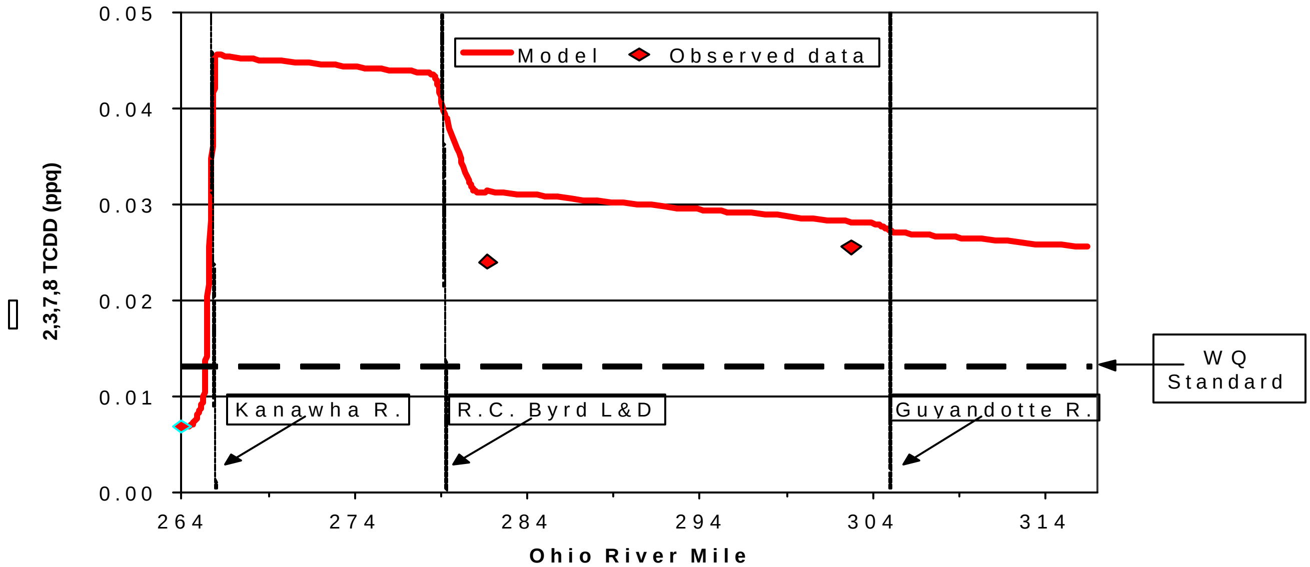



Table 9. Boundary inputs for model validation run corresponding to September 1997 dioxin sampling.

| Boundary Site | 4-Day Avg. Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD Ppq |
|---|---|---|---|
| Ohio R. (upstream) | 15850 | 9.0 | 0.0085 |
| Kanawha River | 3775 | 11.0 | 0.1340 |
| Guyandotte River | 1625 | 14.7 | 0.0014 |

Figure 17. SMPTOX4 results corresponding to September 1997 dioxin sampling.

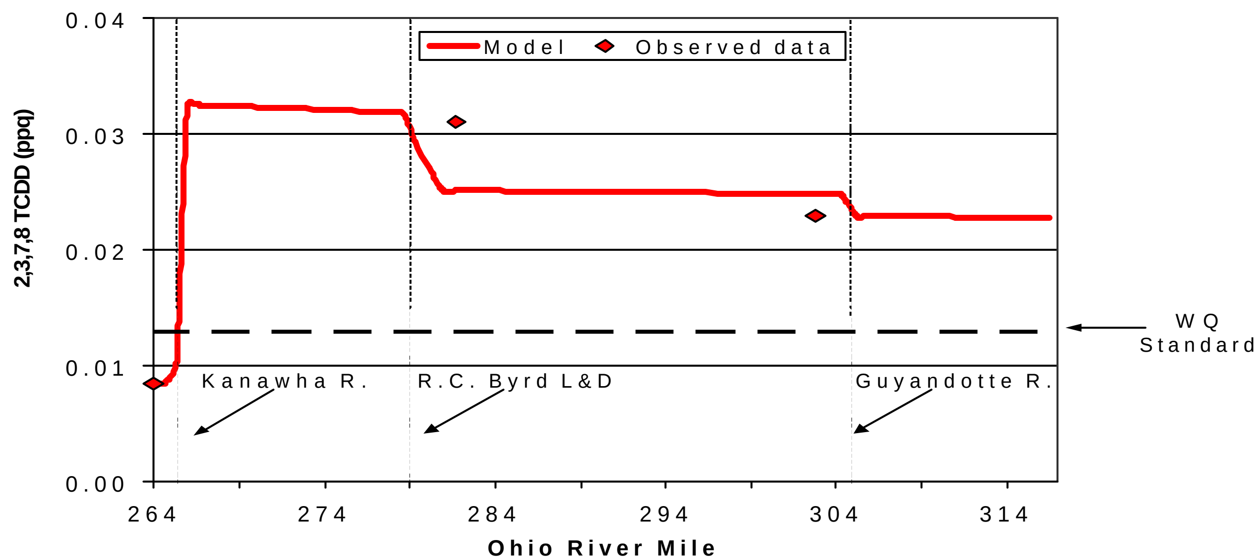


Table 10. Boundary inputs for model validation run corresponding to July 1997 dioxin sampling.

| Boundary Site | 4-Day Avg. Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| Ohio R. (upstream) | 18225 | 11.0 | 0.0167 |
| Kanawha River | 4650 | 14.0 | 0.0982 |
| Guyandotte River | 1075 | 11.8 | 0.0009 |

Figure 18. SMPTOX4 results corresponding to July 1997 dioxin sampling.

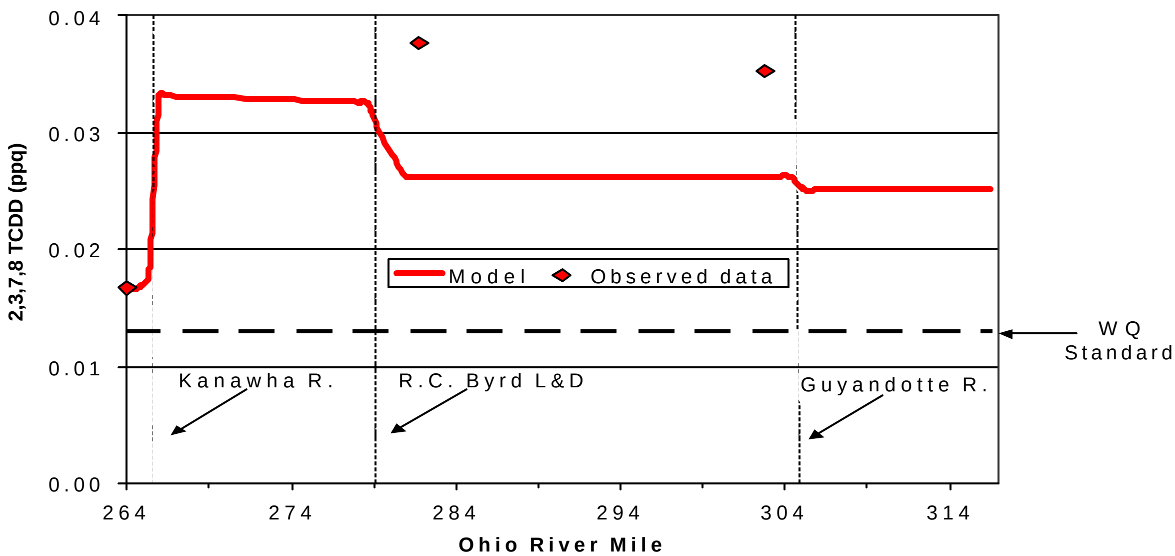



Table 11. Boundary inputs for model validation run corresponding to August 1997 dioxin sampling.

| Boundary Site | 4-Day Avg. Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| Ohio R. (upstream) | 64350 | 30.0 | 0.0118 |
| Kanawha River | 9650 | 20.0 | 0.1228 |
| Guyandotte River | 3450 | 21.9 | 0.0050 |

Figure 19. SMPTOX4 results corresponding to August 1997 dioxin sampling.

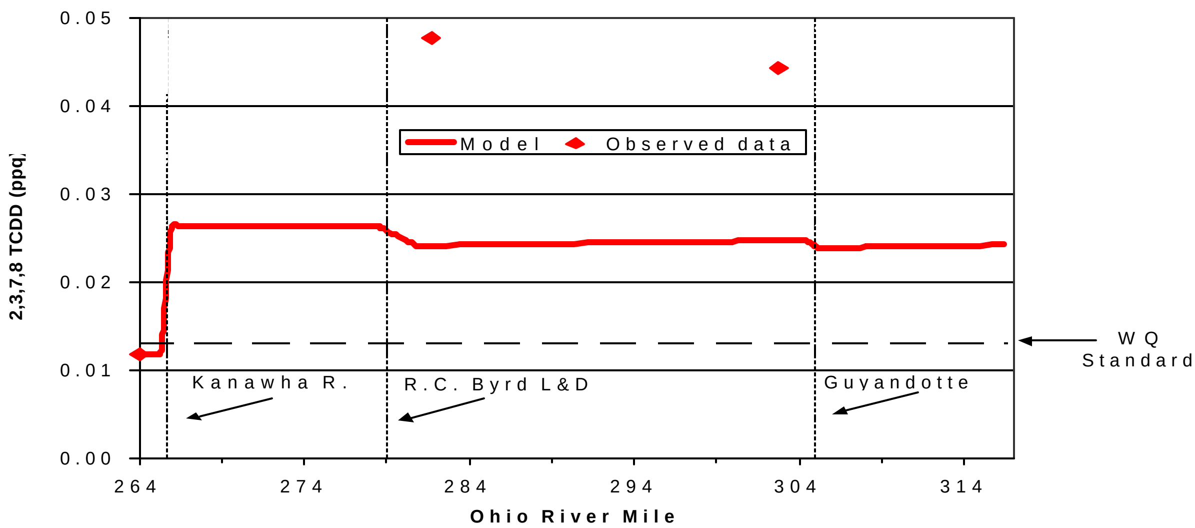
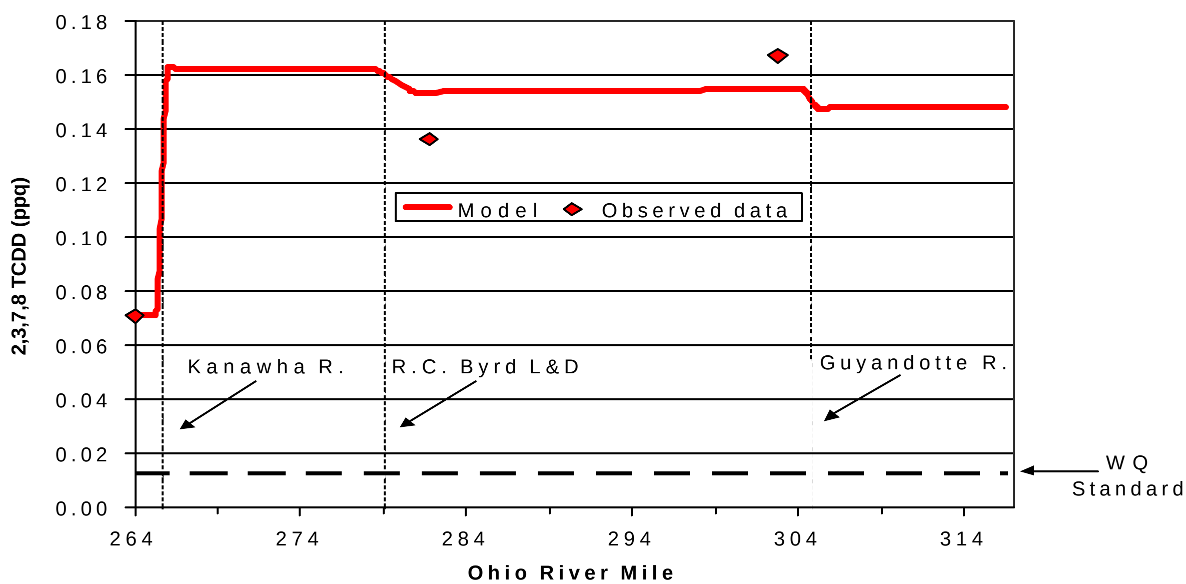



Table 12. Boundary inputs for model validation run corresponding to June 1998 dioxin sampling.

| Boundary Site | 4-Day Avg. Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| Ohio R. (upstream) | 107000 | 203.0 | 0.0710 |
| Kanawha River | 32400 | 209.0 | 0.4628 |
| Guyandotte River | 8200 | 34.8 | 0.0315 |

Figure 20. SMPTOX4 results corresponding to June 1998 dioxin sampling.



Three of the five validation runs showed good agreement. Predicted 2,3,7,8 TCDD concentrations for the September 1997 and June 1998 model runs were within the range of concentrations observed at the sampling sites located at Ohio River mile points (ORM) 281.5 and 302.9. The November 1998 model results were slightly higher than the observed concentrations, but were still quite reasonable. The September 1997 and November 1998 rounds of sampling were conducted during relatively low flow conditions with average stream flows at the upstream boundary of 19,600 and 11,025 cfs, respectively. The June 1998 sampling was conducted under much higher flow conditions with average stream flows of 107,000 cfs.

In the July and August 1997 validation runs, on the other hand, the predicted and observed dioxin concentrations showed greater deviation. In both cases, the model underestimated dioxin concentrations when compared to the high-volume sampling results. During both of these rounds of sampling, stream flows on the Ohio River were decreasing over the four-day sampling period. The discrepancy between the observed and predicted concentrations is believed to be a result SMPTOX4's inability to account for the unsteady flow conditions that were present during the sampling.

# 5.0 MODEL APPLICATION TO TMDL

## 5.1 Selection of Critical Conditions

The specific uses of a model are important factors in assessing and selecting the proper model. In the present study, the objective of the modeling is to simulate the behavior of 2,3,7,8 TCDD within the study area under situations that are determined to be the critical condition. The critical condition is the specific reasonable hydrologic event that results in the highest concentrations of dioxin in the study area.

As previously discussed, high-volume water sampling for dioxin was conducted on the Ohio, Kanawha, and Guyandotte Rivers. Sampling was conducted under different flow conditions (low, moderate, and relatively high flows) to determine if a relationship existed between flow and 2,3,7,8, TCDD concentration. Though the data is limited to five rounds of sampling, the concentration of 2,3,7,8 TCDD in the particulate phase did show a positive correlation with flow, and likewise with TSS concentrations. No correlation to hydrologic conditions was determined for the pollutant in the dissolved phase. Considering that more than 90% of the total 2,3,7,8 TCDD concentration resulted from the particulate phase, and the particulate concentration increases as flow increases, the critical condition for the pollutant was defined to be at high flow conditions. For modeling purposes, the one-year high flow condition, as defined by the USCOE, was arbitrarily selected as the specific critical condition to be used in the TMDL development. In addition to modeling under the defined critical condition, the model was also run at minimum 7-day, 10-year low flow and at the harmonic mean flow for comparison.

### 5.2 Model Results

Three separate model runs were completed at different flow conditions – 7Q10, harmonic mean flow, and the 1-year high flow. Figure 17 graphically displays the model results for each run, with numerical results at selected points along the Ohio River provided in Tables 13-15. All three runs indicate a significant increase in the 2,3,7,8 TCDD concentration at the confluence of the Kanawha River. The sudden drop in concentration near Ohio River mile 280 is due to the effects of RC Byrd L&D. As previously discussed, longitudinal surveys indicated TSS concentrations immediately below the dam were lower than that upstream of the dam. The dam acts as a barrier to suspended solids, which apparently causes a portion of the suspended solids load to settle out due to the decreased stream velocities upstream of the structure.

SMPTOX4 predicts that the instream water quality standard for 2,3,7,8 TCDD of 0.013 parts per quadrillion (ppq) will be exceeded in all three scenarios, with the greatest concentrations occurring immediately downstream of the Kanawha River. Of the three model runs, the 1-Year high flow run resulted in the highest predicted concentrations, which were approximately one order of magnitude above the standard. These results clearly illustrate that the critical condition for dioxin occurs under high-flow conditions.

Figure 21. SMPTOX4 model results for selected critical flow conditions.

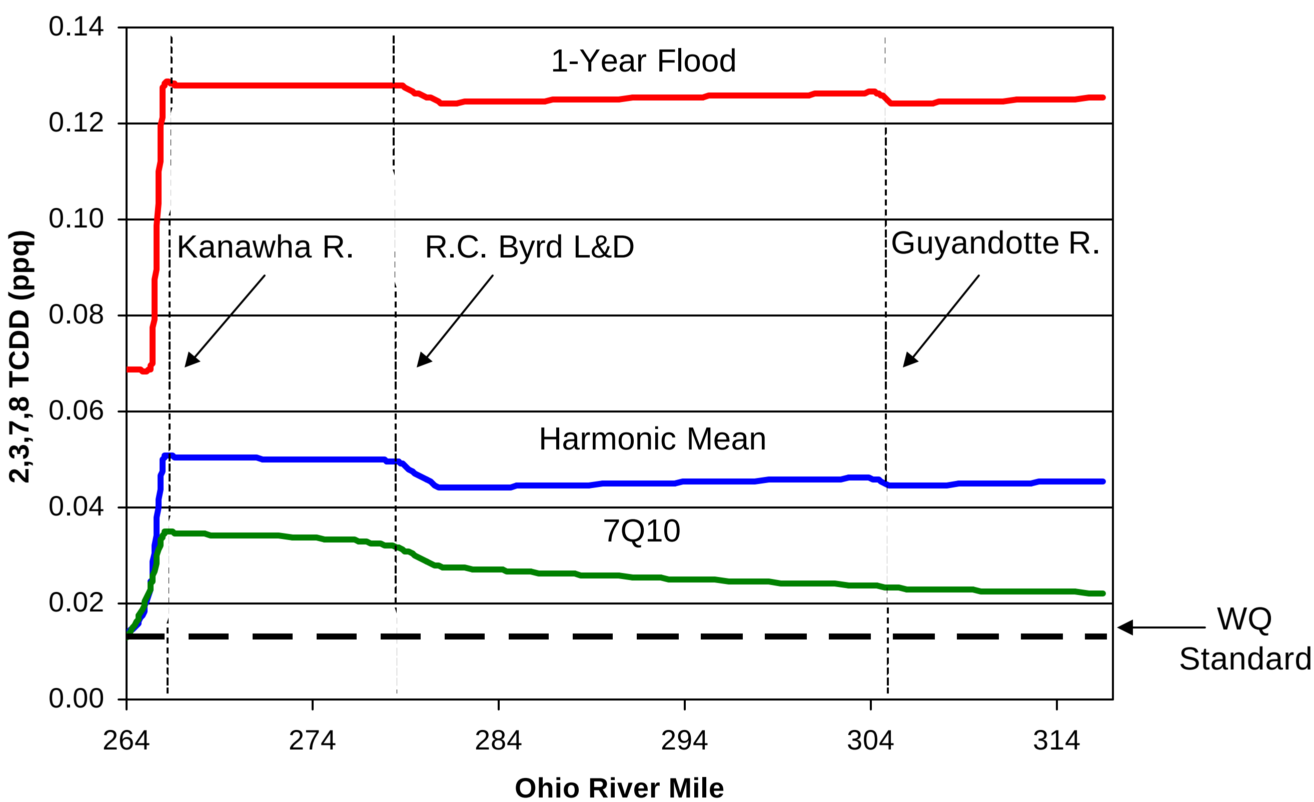


Table 13. One year flood SMPTOX4 model results at selected river mile points.

| Ohio River Mile | Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| 264.0* | 225,000 | 157.7 | 0.0687 |
| 266.0 | 267,700 | 137.2 | 0.1278 |
| 280.9 | 267,700 | 133.2 | 0.1241 |
| 316.5 | 273,700 | 134.6 | 0.1252 |

Table 14. Harmonic mean flow SMPTOX4 model results at selected river mile points.

| Ohio River Mile | Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| 264.0* | 26,000 | 5.8 | 0.0126 |
| 266.0 | 34,500 | 6.5 | 0.0503 |
| 280.9 | 34,500 | 5.4 | 0.0441 |
| 316.5 | 35,900 | 6.3 | 0.0456 |

Table 15. 7Q10 low flow SMPTOX4 model results at selected river mile points.

| Ohio River Mile | Flow cfs | TSS mg/L | Total 2,3,7,8 TCDD ppq |
|---|---|---|---|
| 264.0* | 6,700 | 0.7 | 0.0052 |
| 266.0 | 9,120 | 1.9 | 0.0347 |
| 280.9 | 9,120 | 0.9 | 0.0276 |
| 316.5 | 9,300 | 0.3 | 0.0223 |

* TSS and 2,3,7,8 TCDD concentrations at Ohio River Mile 264.0 are not SMPTOX4 model results, but rather model input values at the upstream boundary. These values are provided as a point of reference.

## 6.0 SUMMARY OF FINDINGS

The purpose of this modeling effort was to simulate the fate and transport of dioxin within the study area to support the development of an Ohio River dioxin TMDL. This effort resulted in the following conclusions.

- Sampling results indicate that concentrations of 2,3,7,8 TCDD increase with stream flow. This positive correlation with stream flow is likely due to the resuspension of contaminated sediments and possibly other non-point sources.
- While the ambient water quality criteria is exceeded throughout the study area at all flow conditions, the greatest exceedences occur at high flow conditions.
- Model boundary conditions were based on long-term TSS sampling data and limited high-volume water sampling results. Additional instream monitoring of dioxin is desired to better define the relationship between dioxin and stream flow. An emphasis should be placed on sampling under higher flow conditions.

- Sampling results indicate that the Kanawha River is a significant source of dioxin to the Ohio River. At the 1-year flood condition, the Kanawha River flow accounts for 16% of the total Ohio River flow just downstream of the Kanawha River confluence, but contributes a disproportionate 55% of the total 2,3,7,8 TCDD load.
- The only identified dioxin sources within the study area, excluding the boundary sites (Ohio River upstream of the study area, Kanawha River, and the Guyandotte River), are resuspension of contaminated sediments and pore water diffusion. The modeling results indicate that the contributions attributed to these sources are offset by the loss due to settling at RC Byrd L&D.
- Modeled dioxin concentrations exceed the water quality standard of 0.013 pg/L throughout the entire study area for all three flow conditions modeled (7Q10, harmonic mean, and 1-year flood). Model results indicate the highest 2,3,7,8 TCDD concentrations within the study area occur immediately downstream of the Kanawha River confluence. Load reductions necessary to meet the water quality standard should be based on the dioxin load predicted at this point.

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