

Appendix G

Evaluation of Contaminant Water Column Partitioning

TABLE OF CONTENTS

1	Introduction	1
2	Chemical Water Column Monitoring Programs	3
2.1	High Volume Program	3
2.2	Small Volume Program	4
3	Equilibrium Partitioning	6
4	Kinetic Sorption.....	9
4.1	Overview of Kinetic Sorption Framework	9
4.1.1	Parameterization of the Kinetic Framework with Empirical Data.....	12
4.2	Sorption Parameterization for Primary Calibration COPCs.....	14
4.3	Sorption Parameterization for Secondary Calibration COPCs	15
4.3.1	PCB-167, PCB-126, 1,2,3,7,8-PeCDD, and 2,3,4,7,8-PeCDF.....	15
4.3.2	Total 4,4'-DDx	16
4.3.3	Mercury	16
4.4	Model Application and Uncertainty	18
5	References	19

TABLES

Table 1-1	Timing of Sampling Events in the sv-CWCM and hv-CWCM Programs
Table 1-2	Summary of hv-CWCM Sampling Events
Table 1-3	Summary of sv-CWCM Sampling Events
Table 4-1	Octanol-Water Equilibrium Partition Coefficient (K _{ow}) Values Applied in Partitioning Analyses
Table 4-2	Measured POC and Chlorophyll-a Concentrations During the sv-CWCM Events that Best Match the hv-CWCM Events Spatially and Temporally
Table 4-3	Average Algal Carbon to Total POC Ratios Used in the hv-CWCM Sorption Analysis
Table 4-4	Calculated Fraction Equilibrium (fE) Values for Primary COPCs for Each hv-CWCM Station and Event
Table 4-5	Summary of Fraction Equilibrium (fE) Values Estimated for Primary COPCs from hv-CWCM Data
Table 4-6	Summary of Fraction Equilibrium (fE) Estimated for Secondary COPCs
Table 4-7	Calculated Fraction Equilibrium (fE) Values for Select Secondary COPCs for Each hv-CWCM Station and Event

Table 4-8 Mercury Algal Partitioning Data and Estimated Organic Carbon Partition Coefficients

Table 4-9 Calculated Fraction Equilibrium (f_E) Values for Mercury for Each sv-CWCM Station and Event

FIGURE

Figure 4-1 Distribution of Mercury f_E Estimates from sv-CWCM Measurements in Lower Passaic River/Newark Bay

ABBREVIATIONS

4,4'-DDx	sum of 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT
μm	micrometer
C_D	freely dissolved chemical concentration
C_{DOC}	chemical concentration associated with DOC
cfs	cubic feet per second
CFT	contaminant fate and transport
COPC	chemical of potential concern
C_P	total particulate contaminant concentration
C_{POC}	concentration associated with POC
C_T	total chemical concentration
C_{TD}	total dissolved chemical concentration
$C_{T,E}$	total chemical concentration in the Equilibrium Domain
$C_{T,R}$	total chemical concentration in the Resistant Domain
CWCM	chemical water column monitoring
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DDx	sum of DDD, DDE, and DDT
DOC	dissolved organic carbon
f_D	fraction dissolved
f_E	fraction Equilibrium
FFS	Focused Feasibility Study
f_P	fraction particulate
f_R	fraction Resistant
g	gram
HxCDD	hexachlorodibenzo-p-dioxin
HpCDF	heptachlorodibenzofuran
hv	high volume
K_{DOC}	dissolved organic carbon referenced sorption partition coefficient
kg	kilogram
K_{oc}	organic carbon referenced sorption partition coefficient
K_{ow}	octanol-water equilibrium partition coefficient
L	liter
LISST	Laser In Situ Scattering and Transmissometry
LPR	Lower Passaic River
LPRSA	Lower Passaic River Study Area

mg/L	milligrams per liter
NB	Newark Bay
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
PeCDD	pentachlorodibenzo-p-dioxin
PeCDF	pentachlorodibenzofuran
POC	particulate organic carbon
PUF	polyurethane foam tube
QAPP	Quality Assurance Project Plan
RI/FS	Remedial Investigation/Feasibility Study
SSC	suspended sediment concentration
sv	small volume
TCDD	tetrachlorodibenzo-p-dioxin
tetra-CB	tetrachlorobiphenyl
USEPA	U.S. Environmental Protection Agency
VCF	volume concentration factor

1 Introduction

The kinetic partitioning approach implemented in the Lower Passaic River (LPR) Study Area (LPRSA) Remedial Investigation/Feasibility Study (RI/FS) Contaminant Fate and Transport (CFT) model was parameterized using data from the high-volume (hv) chemical water column monitoring (CWCM) program and the small-volume (sv)-CWCM program.

Between August 2011 and June 2013, eight sampling events were conducted for the sv-CWCM program and two sampling events were conducted for the hv-CWCM program (Table 1-1). Samples were collected during the hv-CWCM program from above Dundee Dam, in the mainstem LPR, and in Newark Bay (NB; Table 1-2). This program was designed to characterize concentrations of polychlorinated biphenyls (PCBs) congeners and homologs as well as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs) on the separated solids and dissolved phase fractions¹ (AECOM 2012a, 2014a). High sample volumes were needed to reduce detection limits for the determination of the dissolved phase concentrations.

Samples were collected during the sv-CWCM program from above Dundee Dam, in the mainstem LPR, in major tributaries to the LPR, and in NB (Table 1-3). This program was designed to characterize chemical concentrations of contaminants and solids under a range of flow and tidal regimes to support calibration and validation of the CFT model (AECOM 2012b, 2014b). Included in the dataset is information on the partitioning of mercury and other metals (AECOM 2014b).

These programs provided sufficient data to parameterize partitioning for the modeled primary calibration chemicals of potential concern (COPCs): 2,3,7,8-tetrachlorodibenzodioxin (TCDD), tetrachlorobiphenyl (tetra-CB), and 1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF). They also provided data to parameterize partitioning for four of the six secondary calibration COPCs: 2,3,4,7,8-pentachlorodibenzofuran (PeCDF), PCB-167, PCB-126, and mercury. The remaining secondary calibration COPCs, 1,2,3,7,8-pentachlorodibenzo-p-dioxin (PeCDD) and total sum of 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT (4,4'-DDx),² were parameterized using estimates drawn from literature.

This appendix briefly describes the partitioning data provided by the hv-CWCM and sv-CWCM programs (Section 2) and presents the partitioning evaluation applied to parameterize the CFT model. First, traditional equilibrium partitioning is discussed as a foundation (Section 3). Building on this foundation, kinetic sorption is developed in Section 4 along with the associated

¹ The dissolved phase was operationally defined as concentrations in water passing through a 0.7 micrometer (µm) pore size filter in the hv-CWCM program.

² Total DDx refers to the sum of dichlorodiphenyltrichloroethane (DDT) and its breakdown products dichlorodiphenyldichloroethylene (DDE) and dichlorodipenyldichloroethane (DDD). Total 4,4'-DDx restricts this sum to include only the 4,4' isomers.

parameterizations for the CFT model's primary (Section 4.2) and secondary (Section 4.3) calibration COPCs.

2 Chemical Water Column Monitoring Programs

2.1 High Volume Program

Large volumes of water are needed to measure the particulate and dissolved phases of hydrophobic organic chemicals in the LPR and NB. The setup of a hv pumping system, the PR2900 developed and operated by Gravity Environmental, Inc., was tested and optimized during a field trial performed in May 2012 (AECOM 2014a). Sample collection involved the following series of separations meant to segregate the dioxin/furan and PCB homologs/congeners associated with suspended particles and filtered water:

1. Glass wool was used as a pre-filter to capture neutrally buoyant suspended matter, including algae and amorphous flocculent material, and to prevent clogging of the subsequent filter.
2. A vortex separator unit designed to trap larger suspended particles.
3. A 0.7-micrometer (μm) glass fiber filter to trap smaller suspended particles. Chemical mass on solids captured in the glass wool, the vortex separator, and the 0.7- μm filter were summed to represent the particulate chemical mass.
4. Two polyurethane foam tubes (PUFs) were arranged in series to trap the chemical dissolved in the water and attached to dissolved organic matter.
5. At two select monitoring stations, 10-liter (L) glass jars captured post-PUF filtrate to assess potential "breakthrough" chemical mass (to gauge the effectiveness of the PUFs in sorbing dissolved chemical mass).

Flow rates through the filter system were set to approximately 1.5 L/minute, optimized to avoid backpressure, to effectively separate solids in the vortex separator, and to provide sufficient sorption time for dissolved chemicals in the PUF series. The sorption efficiency of PUFs and the breakthrough of PCDD/PCDF and PCB from the first PUF to the second PUF and out in the effluent was assessed in several ways. Known quantities of spiked compounds ("dynamic spikes"; isotopically labeled PCDD/PCDFs and PCBs) were injected into the PR2900 sampler's inflow stream at a point after the filter but before the PUF to assess the PUF's sorption efficiency for hydrophobic organic compounds (AECOM 2014a). Mean recovery of the labeled PCDDs was 95% (range: 78% to 127%), and 99% of the dynamically-spiked compounds were sorbed to the first PUF; mean recovery of the isotopically labeled PCBs was 81% (range: 44% to 112%), and 98% of the dynamically-spiked PCBs were sorbed to the first PUF (AECOM 2014a). Other spiked compounds ("static spikes") were added to the PUF in the laboratory before shipping to the field for sampling. These compounds showed similarly high recoveries, indicating that the PUFs effectively sorbed and retained the target chemicals (AECOM 2014a). Most of the target analytes, approximately 80% of the total mass, were sorbed onto the first PUF (AECOM 2014a). Lastly, post-PUF filtrate was analyzed for breakthrough of PCDD/PCDF and PCB from samples taken at two locations (a freshwater station in the Passaic River [T042], and a saltwater

location in NB [TNBS]) during two sampling events. While there was detectable mass in the filtrate, this was similar to detections in laboratory method blanks. Although the post-filtrate samples were not validated, these detections were likely an artifact and not indicative of breakthrough (AECOM 2014a). Based on evaluations of the dynamic and static spikes and of the mass of target analytes on the second PUF and in post-PUF filtrate relative to total mass captured, sorption efficiency, and retention of the target analytes by the PUFs indicate that the flow rate allowed for adequate sorption of dissolved dioxin/furan and PCB congeners, and that the data met performance criteria described in the hv-CWCM Quality Assurance Project Plan (QAPP; AECOM 2012a).

Sample water volumes were determined by a flow meter integrated with the sampling device and the duration of pumping. The flow meter was calibrated periodically during operation by collecting water with a graduated cylinder (AECOM 2012a). The sample volumes, representing water that has passed through the filters and the PUFs, ranged from 100 to 775 L. Four time-weighted, composite, whole water samples were also collected at each station and analyzed for particulate organic carbon (POC), dissolved organic carbon (DOC), suspended sediment concentration (SSC)³, and salinity.⁴ Details on sampling dates and methodology can be found in the hv-CWCM sampling QAPP and data report (AECOM 2012a, 2014a).

2.2 Small Volume Program

The sv-CWCM program collected samples from eight locations in the LPRSA, including five locations in the main-stem LPR, one location in each of the LPR tributaries (Second River, Third River, and Saddle River), and one location above Dundee Dam. Sampling events covered a range of flow conditions (Table 1-3; AECOM 2014b). Routine events were conducted at freshwater flows ranging from 400 cubic feet per second (cfs) to 3,000 cfs measured at Dundee Dam and various tide conditions. Two high flow events were performed during flows of greater than 3,000 cfs. Lastly, one event was performed during simultaneous low flow and spring tide conditions. Two sampling locations, TTR1 and TTR2, were not fixed, and instead were located according to prevailing flow and tidal conditions. When flows exceeded 1,000 cfs at Dundee Dam, TTR1 and TTR2 were positioned at RM 6.7 and RM 4.2, respectively. When flows at Dundee Dam were less than 1,000 cfs, the position of the salt wedge dictated the sampling locations: TTR1 was located approximately 1 mile downstream of the salt wedge; TTR2 was located downstream of TTR1. In addition, eight locations were sampled

³ It is noted that one of the individual suspended solids samples at the Newark Bay (NB) Northeast station during the June 2013 event had a notably higher SSC (34.7 milligrams per liter [mg/L]) than the three other samples (ranging from 8.3 to 13.4 mg/L) that comprise the time-averaged result for this station. This is a validated result. The high concentration is within the variability of SSC observed in the sv-CWCM events at this station. Evaluation of field notes and contemporaneously taken turbidity and Laser In Situ Scattering and Transmissometry (LISST) data did not provide evidence to reject this result.

⁴ A 20-L carboy was filled using a separate peristaltic pump set at a flow rate that would fill the carboy as the hv sample was being collected. Upon completion of the hv sampling, the 20-L carboy sample was homogenized on a stir plate using a magnetic stir bar and sub-sampled four times to obtain four samples of SSC, DOC, and POC. The individual sub-sample results were averaged to obtain the SSC, POC, and DOC representative of the water that comprised the hv sample.

in NB, Hackensack River, Arthur Kill, and Kill van Kull (Table 1-3). These were sampled during the same events as for the LPRSA locations, except for the low-flow/spring-tide event that excluded the Newark Bay Study Area locations.

Water samples in the LPR were collected using a peristaltic pump from 3 feet below the water surface and 3 feet above the bottom. A single mid-depth sample was taken at stations above Dundee Dam and in the three tributaries, or if the water depth at other stations was less than 7 feet. Whole-water and filtered water samples were collected simultaneously by using a y-fitting with an inline 0.45- μm filter in one of the lines.

During routine and low-flow events, LPR samples were collected in a time series, capturing slack low tide, flood tide, slack high tide, and ebb tide conditions while only one sample each was collected above Dundee Dam and in the LPR tributaries (Table 1-3). During the high-flow events, the location above Dundee Dam was sampled six times to capture three rising limb, one peak flow and two falling limb samples, while the remaining locations were sampled four times to capture two rising limb, one peak flow and one falling limb samples (Table 1-3).

3 Equilibrium Partitioning

In systems like the LPRSA, organic matter is considered the principal sorbent for hydrophobic organic chemicals (Karickhoff 1984). As a background to the kinetic framework applied to the LPRSA CFT model (Section 4), this section derives a three-phase partitioning model that assumes chemical equilibrium among the sorbents POC and DOC and the dissolved phase. The units of the various parameters in this discussion are expressed on a dimensional basis—length is denoted by L (volume is thus denoted by L^3) and the mass of a parameter is represented by $M_{parameter}$.

At equilibrium, the total chemical concentration, C_T , is distributed between the freely dissolved concentration, C_D , the concentration associated with POC, C_{POC} , and the concentration associated with DOC, C_{DOC} (all with units $[M_{chemical}/L^3]$):

Equation 1

$$C_T = C_D + C_{DOC} + C_{POC}$$

The equilibrium ratio between a chemical sorbed to POC and a dissolved chemical is denoted by the organic carbon referenced sorption partition coefficient (K_{OC}):

Equation 2

$$K_{OC} = \frac{C_{POC}}{\frac{[POC]}{C_D}}$$

where:

$[POC]$ = concentration of POC $[M_{OC}/L^3]$

$\frac{C_{POC}}{[POC]}$ = carbon-normalized particulate contaminant concentration $[M_{chemical}/M_{OC}]$

The partition coefficient between the chemical sorbed to DOC and the freely dissolved chemical is termed K_{DOC} $[L^3/M_{DOC}]$ and is by analogy to Equation 2 expressed as:

Equation 3

$$K_{DOC} = \frac{C_{DOC}}{\frac{[DOC]}{C_D}}$$

The value of K_{DOC} is typically less than K_{oc} as well as K_{ow} , the octanol-water equilibrium partition coefficient. K_{DOC} is typically expressed as a fraction of K_{ow} (a), representing the lower binding affinity of contaminants to DOC .

Equation 4

$$K_{DOC} = a * K_{ow}$$

Combining Equations 1 through 4, the freely-dissolved concentration under the assumption of three-phase equilibrium partitioning can be expressed as⁵:

Equation 5

$$C_D = \left(\frac{C_T}{1 + K_{oc} * [POC] + a * K_{ow} * [DOC]} \right)$$

Because freely dissolved concentration (C_D) is not distinguished from the total dissolved concentration (C_{TD}) in the experimental methods used in the hv-CWCM and sv-CWCM programs, the preceding equations are rewritten as:

Equation 6

$$C_{TD} = C_D + C_{DOC} = \left(\frac{(1 + a * K_{ow} * [DOC])C_T}{1 + K_{oc} * [POC] + a * K_{ow} * [DOC]} \right)$$

⁵ Assuming a porosity of 1 for the water column when expressing the freely-dissolved concentration.

The chemical partitioning described by Equation 6 can be expressed in terms of K_{oc} in the following manner, for use with empirical data:

Equation 7

$$\log K_{oc} = \log \left(1 + (a * k_{ow} * [DOC]) - \left(\frac{C_{TD}}{C_T} \right) - \left(\frac{C_{TD}}{C_T} \right) * (a * k_{ow} * [DOC]) \right) - \log \left([POC] * \frac{C_{TD}}{C_T} \right)$$

A partition coefficient calculated from empirical data in this manner is here termed an apparent partition coefficient, where the term "apparent" is added because it is unknown whether the sampled chemical phases are at equilibrium. Such coefficients are not used in the LPR RI/FS CFT model because a kinetic sorption framework was implemented. That framework and its parameterization are described in the next section.

4 Kinetic Sorption

Several studies have characterized desorption of hydrophobic contaminants as taking place in three phases: rapid, slow, and very slow (Cornelissen et al. 2000, 2001; Ten Hulscher et al. 1999); others have distinguished only fast and slow phases, which are sometimes referred to in the literature as the “reversible” or “labile” and “resistant” phases, respectively (e.g., Pignatello and Xing 1996; Chai et al. 2006; Birdwell et al. 2007; and Schneider et al. 2007). The desorption rates observed by Sormunen et al. (2009; 2,3,7,8-TCDD desorption for four separate lake sediments) and by Carroll et al. (1994; PCB desorption in the Upper Hudson River) suggest that only the carbon (sorption sites) characterized by the fast desorption rate (time scale of a few days) could approach equilibrium over the time scales that particles are in suspension. Conversely, the carbon characterized by the very slow or resistant rates (time scales of hundreds of days) would not exchange significant chemical mass with the water column while in suspension. In these studies, approximately 40% to 70% of the chemical mass was observed in the latter category, which indicates that desorption limitations may cause a significant divergence between the apparent and true equilibrium K_{oc} .

The CFT model accounts for sorption kinetics in a simplified manner using the partitioning framework of DiToro (1985) (see Appendix O, Section 2.1.2.1). An overview of this framework, and its parameterization is provided below. Additional discussion of the framework and the motivation for including it in the CFT model as an alternative to equilibrium partitioning are presented in Appendix O (Section 2.1.2).

4.1 Overview of Kinetic Sorption Framework

In the DiToro (1985) framework, the slow and fast desorption phases are accounted for by dividing detrital carbon into two fractions termed the “Resistant Domain” (f_R) and the “Equilibrium Domain” (f_E). The Equilibrium Domain desorption is assumed fast enough to be approximated as instantaneous partitioning. The relationship between the two is:

Equation 8

$$f_E = 1 - f_R$$

The total contaminant concentration is represented as the sum of a Resistant Domain concentration ($C_{T,R}$, the chemical mass resistantly sorbed to the detrital carbon) and an Equilibrium Domain concentration ($C_{T,E}$, the chemical mass that is available to instantaneously distribute between the freely dissolved phase, DOC, and the remaining POC):

Equation 9

$$C_T = C_{T,R} + C_{T,E}$$

The latter term includes the chemical mass sorbed to the portion of the detrital carbon in the Equilibrium Domain ($f_E * [\text{detrital POC}]$) and the mass sorbed to algal carbon, which is treated separately here because it is explicitly represented in the CFT model. DOC and algal carbon are assumed to have 100% of their carbon masses in the Equilibrium Domain as it is unknown if they have a Resistant Domain component and presumably algal particles have on average not been exposed to contaminants long enough assuming Resistant Domain equilibration timescales of hundreds of days. This assumption allows $C_{T,E}$ to be expressed as:

Equation 10

$$C_{T,E} = C_D + C_{DOC} + C_{dPOC,E} + C_A$$

where:

$$\begin{aligned} C_{dPOC,E} &= \text{detrital particulate chemical concentration in the Equilibrium Domain} \\ &\quad [M_{\text{chemical}}/L^3], \text{ which corresponds to the mass sorbed to } f_E * [\text{detrital POC}] \\ C_A &= \text{concentration sorbed to algal carbon } [M_{\text{chemical}}/L^3] \end{aligned}$$

In contrast, $C_{T,R}$ is assumed to be entirely particulate as it is bound to the resistant carbon, that is:

Equation 11

$$C_{T,R} = C_{dPOC,R}$$

where:

$$\begin{aligned} C_{dPOC,R} &= \text{detrital particulate chemical concentration in the Resistant Domain} \\ &\quad [M_{\text{chemical}}/L^3], \text{ which corresponds to the mass sorbed to } f_R * [\text{detrital POC}] \end{aligned}$$

It is noted that when $f_E = 1$, this framework collapses to the standard equilibrium partitioning framework presented in Section 3. When $f_E < 1$, there exists resistantly sorbed mass that the dissolved phase is “blind” to.

By analogy to Equation 6, Equation 10 can be rearranged to express the total dissolved concentration:

Equation 12

$$C_{TD} = C_D + C_{DOC}$$

$$= \left(\frac{1 + a * K_{ow} * [DOC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) C_{T,E}$$

where [POC] in Equation 6 has been replaced by ($f_E * [detrital\ POC] + [algal\ POC]$), and an algal carbon binding affinity (a_{phy} , analogous to a for DOC) is added for consistency with the CFT model's convention. Also, for the organic chemicals the K_{oc} in Equation 6 is here replaced with the K_{ow} ; consistent with DiToro (1985), it is assumed that K_{oc} is mainly a property of the chemical and is equal to K_{ow} . This parameter dictates the partitioning behavior of the Equilibrium Domain. Site-specific sorption influences are embodied in f_E , reflecting both the nature of the solids and the mean extent of equilibration by the fast desorbing phase within the water column.

Likewise, the particulate contaminant concentration in the Equilibrium Domain, $C_{P,E}$, can be expressed as:

Equation 13

$$C_{P,E} = C_{dPOC,E} + C_A$$

$$= \left(\frac{f_E * K_{ow} * [detrital\ POC] + a_{phy} * K_{ow} * [algal\ POC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) C_{T,E}$$

Because the Resistant Domain concentration $C_{T,R}$ is assumed bound to the resistant carbon (Equation 11), it is 100% in the particulate phase and can be added to the particulate fraction in the Equilibrium Domain to yield the total particulate contaminant concentration, C_P :

Equation 14

$$C_P = C_{P,E} + C_{T,R}$$

$$= \left(\frac{f_E * K_{ow} * [detrital\ POC] + a_{phy} * K_{ow} * [algal\ POC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) C_{T,E} + C_{T,R}$$

Equations 12 and 14 may also be expressed as a fraction dissolved (total), f_D , and a fraction particulate, f_P , when normalized by total concentration:

Equation 15

$$f_D = \left(\frac{1 + a * K_{ow} * [DOC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) \frac{C_{T,E}}{C_T}$$

Equation 16

$$f_P = \left(\frac{f_E * K_{ow} * [detrital\ POC] + a_{phy} * K_{ow} * [algal\ POC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) \frac{C_{T,E}}{C_T} + \frac{C_{T,R}}{C_T}$$

It is noted that $f_D + f_P = f_E + f_R = 1$, and if $f_E = 1$, this framework collapses to the standard equilibrium partitioning approach. The f_D and f_P fractionations partition C_T and thereby influence the predicted dissolved (e.g., diffusion, volatilization) and particulate (e.g., deposition) contaminant fluxes, respectively.

4.1.1 *Parameterization of the Kinetic Framework with Empirical Data*

The hv-CWCM and sv-CWCM data were analyzed to derive site- and contaminant-specific values of the Fraction Equilibrium, f_E . Following DiToro (1985), this fraction embodies site-specific influences such as the nature of the solids (fraction of sorption sites in the Equilibrium Domain) and the extent of equilibration within the water column.

A key assumption in this and other partitioning frameworks is that a single partitioning value is adequate to model the chemical distribution between the aqueous and particulate phases. Using a single value of f_E is necessary as the limited site-specific data, particularly in the case of the hv-CWCM program, precludes the ability to derive reliable spatial and temporal functions. Paired dissolved and particulate data are analyzed as independent measurements of f_E , the equation for which is derived from the following sequence:

Equation 17

$$C_{T,R} = (1 - f_E)C_T$$

Equation 18

$$C_{T,E} = f_E C_T$$

These relationships allow Equations 15 and 16 to be simplified to:

Equation 19

$$f_D = \left(\frac{1 + a * K_{ow} * [DOC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) f_E$$

Equation 20

$$f_P = \left(\frac{f_E * K_{ow} * [detrital\ POC] + a_{phy} * K_{ow} * [algal\ POC]}{1 + f_E * K_{ow} * [detrital\ POC] + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]} \right) f_E + f_R$$

Equation 20 can be solved for f_E as a function of the observed operationally dissolved fraction f_D from the empirical measurements:

Equation 21

$$f_E = \left(\frac{1 + a * K_{ow} * [DOC] + a_{phy} * K_{ow} * [algal\ POC]}{1 + a * K_{ow} * [DOC] - K_{ow} * [detrital\ POC] * f_D} \right) f_D$$

It is noted that the f_E derived in this manner from water column measurements may be regarded as an “apparent” f_E (analogous to apparent partition coefficients derived by Equation 7; Section 3), as the extent to which the Equilibrium and Resistant Domains are equilibrated (i.e., reached their steady-state mass fractions) in the sample data is unknown. Such estimates are influenced both by the nature of the solids and the mean extent of equilibration by the fast desorbing phase within the water column. Analyzing across a range of samples is assumed to average out the influences of variations in sediment type, origin, and time histories, such that the central tendency of resistant desorption effects for sediments interacting with the water column may be reasonably captured with a sufficient number of observations.

4.2 Sorption Parameterization for Primary Calibration COPCs

In using Equation 21 to calculate f_E values from the hv-CWCM data, the K_{ow} values were taken from the U.S. Environmental Protection Agency (USEPA) Focused Feasibility Study (FFS) model (Table 4-1). Data treatments and additional assumptions are described below.

The total (or operational) dissolved chemical concentration (C_{TD}) was defined as the sum of chemical mass captured in PUF1 and PUF2 divided by the volume of the sample. The total chemical concentration (C_T) was the sum of the particulate concentration (C_{POC} ; the total chemical mass captured in the glass wool, vortex-separated solids, and solids trapped on the 0.7- μm filter divided by the volume of the sample [AECOM 2014a]) and C_{TD} . The reported mean POC and DOC concentrations from the whole water samples were used directly. Values of f_E were not computed for samples with non-detect POC, DOC, dissolved or particulate chemical concentrations.

Because the mass captured by PUF1 and PUF2 comprises both the freely dissolved and DOC-bound chemical phases, assumptions about sorption to DOC are required. The binding affinity of DOC (a) was set to 0.08 (Burkhard 2000), consistent with the settings in the USEPA FFS model (LBG 2014; USEPA 2016) and used in conjunction with the K_{ow} values in Table 4-1.

Assumptions about algal carbon concentration were also needed because it was not measured explicitly in the hv-CWCM program (rather, total POC was measured). Algal carbon was assumed to be a spatially varying function of POC defined by data collected in the sv-CWCM program. As noted in Section 1, eight sv-CWCM sampling events were conducted between 2011 and 2013 with samples collected from the near-surface and near-bottom waters at stations throughout the LPR and NB. The sv-CWCM events in December 2012 and June 2013 best match the timing of the hv-CWCM events (see Table 1-1). These sv-CWCM data were queried for the stations and depth that best matched the hv-CWCM data (Table 4-2). Chlorophyll-a was converted to algal carbon using a conversion factor of 100 mg C/mg Chlorophyll-a, consistent with the value used for the summer assemblage of algae in the USEPA ST-SWEM model for the LPR FFS (USEPA 2016). Algal carbon to POC ratios were computed for each sample in which both chlorophyll-a and total POC were detected. If chlorophyll-a data were unavailable at a station, ratios were calculated by linearly interpolating data from the nearest upstream and downstream station or assigned based on the nearest station when interpolation was not possible. The resulting station and event-specific ratios (Table 4-3) were then used to split the total POC measured in the hv-CWCM samples into detrital and algal carbon concentrations.

Individual f_E values were calculated from each set of hv-CWCM measurements, bounded at 1, and averaged over the sampling events and all stations. The individual f_E estimates for 2,3,7,8-TCDD, tetra-CB, and 1,2,3,4,6,7,8-HpCDF for each station and event are listed in Table 4-4, along with the physical parameters applied. The corresponding mean f_E values are listed in Table 4-5 along with

reference values from desorption study literature; these are the values selected for CFT model input (Appendix O, Section 3.5).

The mean f_E value for tetra-CB (0.55) is slightly above the range inferred from the Carroll et al. (1994) desorption experiments (0.31 to 0.49) based on the fraction of rapidly desorbing contaminant), while the mean f_E value for 2,3,7,8-TCDD (0.10) is lower than the range inferred from Sormunen et al. (2009; 0.27 to 0.42). The mean f_E value for 1,2,3,4,6,7,8-HpCDF (0.008) is lower than the single value inferred from Van Noort et al. (2014; 0.032), but is consistent in that the f_E is much lower than the other two contaminants. The lower TCDD value may reflect the bed being the primary source location and particle residence time in the water column being too short for the fast desorbing phase to completely desorb to equilibrium. Differences between f_E derived from hv-CWCM measurements and laboratory estimates of the fast desorbing phase are not surprising given potential differences in the origin of the sediment and the desorption timescales studied. For example, Sormunen et al. (2009) noted that their measured fractions of the rapidly desorbing phase may be elevated due to their use of spiked sediment samples, citing earlier work with in situ sediments where lower fractions of rapidly desorbing chemicals were observed for similar compounds (Sormunen et al. 2008; 0.19 and 0.06 for 2,3,7,8-TCDF and TCDFs, respectively). More generally, as controlled experiments the desorption literature will be less prone to disequilibrium effects than estimates derived from water column data, and thus f_E estimates derived from literature provide reference on expectations for a given COPC (ignoring potential site-specific influences such as the nature of the solids and their time history). Given the limited hv-CWCM dataset available to perform the analyses reported in Tables 4-4 and 4-5, the estimated f_E values are reasonably consistent with values inferred from literature described above and summarized in Table 4-5.

4.3 Sorption Parameterization for Secondary Calibration COPCs

The f_E values selected for parameterizing the CFT model's secondary calibration COPCs are listed in Table 4-6 along with the basis for the values. Unlike the primary calibration COPCs, the basis for the selected f_E values varied among the secondary COPCs due to data availability, as described below.

4.3.1 PCB-167, PCB-126, 1,2,3,7,8-PeCDD, and 2,3,4,7,8-PeCDF

The hv-CWCM data were analyzed to derive f_E estimates for PCB-167, PCB-126, 1,2,3,7,8-PeCDD, and 2,3,4,7,8-PeCDF using the same framework and assumptions as the primary calibration COPCs (see Section 4.2, above). The resulting f_E values for each station and event for these COPCs are listed in Table 4-7, along with the physical parameters applied. For PCB-167, PCB-126, and 2,3,4,7,8-PeCDF the means of the available f_E estimates were used: 0.25, 0.21, and 0.07, respectively (Table 4-6). The selected values are roughly consistent with expectations from literature (also in Table 4-6). For 1,2,3,7,8-PeCDD, there was only a single hv-CWCM sample with detected concentrations and it was outside of the LPR (at Dundee Dam). Consequently an f_E value derived from desorption studies

compiled in Van Noort et al. (2014) was used (0.06), specifically the sum of the reported “rapid” and “slow” desorbing fractions averaged for the two closest available congeners (1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin [HxCDD] and 1,2,3,7,8,9-HxCDD) (Table 4-6).

4.3.2 *Total 4,4'-DDx*

Site-specific partitioning values could not be derived for total 4,4'-DDx from the hv-CWCM and sv-CWCM program because dissolved and particulate phase concentration measurements of DDx isomers were not available. Instead, published studies were reviewed for relevant parameters, and an f_E value of 0.67 was taken as the sum of the “rapid” and “slow” desorbing fractions averaged across the available values for the 4,4' dichlorodiphenyldichloroethane (DDD), dichlorodiphenyldichloroethylene (DDE), and dichlorodiphenyltrichloroethane (DDT) isomers from Van Noort et al. (2014) (Table 4-6).

4.3.3 *Mercury*

Although mercury differs from the other modeled COPCs as the only metal, its sorption was also modeled with the DiToro (1985) framework. Mercury has a strong affinity for particulate organic matter (Benoit et al. 1998; Wallschlager 1998), dissolved organic carbon and sediment sulfur (Shartup et al. 2014), and biomagnifies like hydrophobic organic chemicals at all levels of the food chain (Mason et al. 1996). As a result, it has been suggested that the nature and extent of sediment-water partitioning of mercury is governed by its affinity for organic matter (Turner et al. 2001). Furthermore, mercury has been shown to quasi-irreversibly sorb (Le Roux et al. 2001). The combination of these properties makes the DiToro (1985) framework suitable.

Because mercury partitioning is not typically characterized in terms of a K_{ow} , a K_{oc} for the Equilibrium Domain was derived from literature (in the case of the hydrophobic organics, the K_{ow} was taken as the relevant K_{oc} for the Equilibrium Domain based on DiToro [1985], as noted previously). A mercury K_{oc} was established using the results of radioisotopic mercury accumulation in algal culture experiments to several species of phytoplankton with water from two mercury-contaminated water bodies in the San Francisco Bay watershed (Pickhardt and Fisher 2007). Pickhardt and Fisher (2007) present each observed partition coefficient as a volume concentration factor (VCF), representing the mass of sorbed mercury per unit volume of cells divided by the mass of dissolved mercury per unit volume of water (column 2 in Table 4-8). The factor has units of volume of water per volume of cells (e.g., L water/L cells). The authors of this study reported that their results were comparable to previously reported values.

The Pickhardt and Fisher (2007) study results are valuable for parameterizing partitioning for the Equilibrium Domain because they are unlikely to be confounded by resistant phase sorption, which can be dominant in field measurements of mercury on water column particulates or sediment (e.g.,

Le Roux et al. 2001). They are also useful in characterizing sorption to the algal organic matter that forms the base of the water column component of the food chain characterized in the bioaccumulation modeling that is driven by the CFT model results. The CFT model assumes that sorption to algae is entirely in the Equilibrium Domain, given that the residence times of algal particles limit the extent to which equilibration with resistant sorption sites may occur (unlike detrital carbon in the sediments), as noted in Section 4.1.

To establish K_{oc} values from Pickhardt and Fischer's VCFs required estimates of carbon content of the phytoplankton (i.e., g C/L cells). These values were specified using measurements reported by Moal et al. (1987; summarized in Table 4-8). Estimated mercury K_{oc} values are shown in Table 4-8. The range of estimated mercury K_{oc} values in Table 4-8 is less than a factor of 3, which provides confidence in choosing a value for the modeling. For simplicity, a mercury K_{oc} of 10^5 L/kg C was selected for use in the model from this analysis (reported in Table 4-1), which is approximately the central tendency of the results (the overall mean of the estimates in Table 4-8 is 1.2×10^5 L/kg C).

Using a K_{oc} of 10^5 L/kg C, the approach described in Section 4.2 for the primary COPCs was applied to calculate f_E values for mercury using data from the sv-CWCM program. Similar to the hv-CWCM analysis, calculations were only conducted with samples that contained detectable levels of POC, DOC, total mercury, and dissolved mercury. Algal carbon was estimated from chlorophyll-a using a conversion factor of 100 mg C/mg chlorophyll-a. If calculated algal carbon was greater than measured POC, algal carbon was set equal to POC. If calculated f_E values were greater than 1, they were set equal to 1 (13 out of 579 calculated values were greater than 1). If calculated f_E values were less than 0, they were ignored (16 out of 579 calculated values were less than 0). No temperature or salinity adjustments were made to the mercury K_{oc} . The resulting estimates of f_E are shown on a sample-specific basis in Table 4-9 and as a frequency distribution in Figure 4-1.

Mercury is unique among COPCs in the CWCM datasets in that it has a large number of partitioning data pairs, which allows for evaluation of f_E distributional properties. The distribution in Figure 4-1 is highly skewed, with a mean of 0.18, a median of 0.09, and a maximum likelihood (mode) estimate of <0.04. Low values of f_E (i.e., a low degree of reversible sorption) are consistent with the findings of Le Roux et al. (2001) and references therein (e.g., Le Roux et al. (2001) reported >80% "quasi-irreversible sorption" onto estuarine particles spiked with dissolved mercury). A CFT model input value of 0.04 (i.e., approximately the maximum likelihood value; Table 4-6) was chosen based on a combined assessment of these data, literature, and model performance in predicting the observed water column partitioning.

4.4 Model Application and Uncertainty

The application of the partitioning parameters derived above for the CFT model is described in Appendix O Sections 2.1.2 and 3.5.1, and an evaluation of model sensitivity to the Fraction Equilibrium setting is presented in Section 6.1 for two COPCs (2,3,7,8-TCDD and tetra-CB).

There is uncertainty in the partitioning parameters derived for the CFT model for all COPCs, and two sources of uncertainty are noted here. The first source of uncertainty is the limited data density. With the exception of mercury, the number of samples available to determine f_E was fairly small (9 or less; Tables 4-5 and 4-6) and in some cases literature was used due to a lack of data (1,2,3,7,8-PeCDD [only one detected value] and total 4,4'-DDx [not measured]). The small sample count does not allow evaluation of spatial or temporal trends in the partitioning behavior of the COPCs. Even when hv-CWCM data were available, the lack of data to estimate the fraction of algal carbon required assumptions which influence the f_E estimate. The second source of uncertainty noted is the framework itself. Although the adopted DiToro (1985) framework has the benefit of explicitly representing resistantly bound contaminant, it is a simplified framework in that it does not explicitly resolve the sorption/desorption process but rather lumps their net effect into a single parameter, f_E . Moreover, in the case of mercury, it does not account for speciation dynamics, which may influence partitioning. Although the simplifications made herein are considered reasonable assumptions for representing the LPR given the goals of the modeling effort, their potential effects on model metrics of interest should be considered during application as should the uncertainty of the input parameterization.

5 References

- AECOM, 2012a. *Quality Assurance Project Plan, Lower Passaic River Restoration Project. RI Water Column Monitoring/High Volume Chemical Data Collection*. Revision 2. Prepared for the Lower Passaic River Cooperating Parties Group. December 2012.
- AECOM, 2012b. *Quality Assurance Project Plan, Lower Passaic River Restoration Project. RI Water Column Monitoring/Small Volume Chemical Data Collection*. Revision 3. Prepared for the Lower Passaic River Cooperating Parties Group. July 2012.
- AECOM, 2014a. *High Volume Chemical Water Column Monitoring Sampling Program Characterization Summary – Draft Lower Passaic River Study Area RI/FS*. November 2014.
- AECOM, 2014b. *Small Volume Chemical Water Column Monitoring Sampling Program Characterization Summary – Draft Lower Passaic River Study Area RI/FS*. February 2014.
- Benoit, J.M., C.C. Gilmour, R.P. Mason, G.S. Riedel, G.F. Riedel, 1998. "Behavior of mercury in the Patuxent River estuary." *Biogeochemistry* 40(2-3): 249-265.
- Birdwell, J., R.L. Cook, and L.T. Thibodeaux, 2007. "Desorption kinetics of hydrophobic organic chemicals from sediment to water: A review of data and models." *Environ. Toxicol. Chem.* 26:424-434.
- Burkhard, L.P., 2000. "Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals." *Environmental Science & Technology* 34(22):4663-4668.
- Carroll, K.M., M.R. Harkness, A.A. Bracco, and R.R. Balcarcel, 1994. "Application of a permeant/polymer diffusional model to the desorption of polychlorinated biphenyls from Hudson River sediments." *Environmental Science & Technology* 28:253-258.
- Chai, Y., A.K. Kochetkov, and D.D. Reible, 2006. "Modeling biphasic sorption and desorption of hydrophobic organic contaminants in sediments." *Environmental Toxicology and Chemistry* 25(12):3133-3140.
- Cornelissen, G., K.A. Hassell, P.C.M. Van Noort, R. Kraaij, P.J. Van Ekeren, C. Dijkema, and H.A.J. Govers, 2000. "Slow desorption of PCBs and chlorobenzenes from soils and sediments: relations with sorbent and sorbate characteristics." *Environmental Pollution* 108(1):69-80.
- Cornelissen, G., H. Rigterink, D.E. ten Hulscher, B.A. Vrind, and P. Van Noort, 2001. "A simple Tenax® extraction method to determine the availability of sediment-sorbed organic compounds." *Environmental Toxicology and Chemistry* 20(4):706-711.

- DiToro, D.M., 1985. "A Particle Interaction Model of Reversible Organic Chemical Sorption." *Chemosphere* 14(10):1503–1538.
- Karickhoff, S.W., 1984. "Organic pollutant sorption in aquatic systems." *Journal of Hydraulic Engineering* 110(6):707–735.
- Le Roux, S.M., A. Turner, G.E. Millward, L. Ebdon, and P. Appriou, 2001. "Partitioning of mercury onto suspended sediments in estuaries." *Journal of Environmental Monitoring* 3:37–42.
- LBG (Louis Berger Group), 2014. *Remedial Investigation Report for the Focused Feasibility Study of the Lower Eight Miles of the Lower Passaic River*. Appendix BIII: Lower Passaic River Contaminant Fate and Transport Model. Prepared for U.S. Environmental Protection Agency, Region 2, and the U.S. Army Corps of Engineers, Kansas City District. 2014.
- Mason, R.P., J.R. Reinfelder, and F.M.M. Morel, 1996. "Uptake, Toxicity, and Trophic Transfer of Mercury in a Coastal Diatom." *Environmental Science and Technology* 30(6):1835–1845.
- Moal, J., V. Martin-Jezequel, R.P. Harris, J-F. Samain, and S.A. Poulet, 1987. "Interspecific and intraspecific variability of the chemical composition of marine phytoplankton." *Oceanologia Acta* 10(3):339–346.
- Pickhardt, P.C. and N.S. Fischer, 2007. "Accumulation of Inorganic and Methylmercury by Freshwater Phytoplankton in Two Contrasting Water Bodies." *Environmental Science and Technology* 41:125–131.
- Pignatello, J.J., and B. Xing, 1996. "Mechanisms of slow sorption of organic chemicals to natural particles." *Environmental Science & Technology* 30:1–11.
- Schneider, A.R., E.T. Porter, and J.E Baker, 2007. "Polychlorinated Biphenyl Release from Resuspended Hudson River Sediment." *Environmental Science & Technology* 41(4):1097–1103.
- Shartup, A.T., P.H. Balcom, and R.P. Mason, 2014. "Sediment-Porewater Partitioning, Total Sulfur, and Methylmercury Production in Estuaries." *Environmental Science & Technology* 48(2):954–960.
- Sormunen, A.J., J Koistinen, M.T. Leppanen, and J.V.K. Kukkonen, 2008. "Desorption of sediment-associated polychlorinated dibenzo-p-dioxins, dibenzofurans, diphenyl ethers and hydroxydiphenyl ethers from contaminated sediment." *Chemosphere* 72:1–7.
- Sormunen, A.J., M.T. Leppanen, and J.V.K. Kukkonen, 2009. "Desorption and bioavailability of spiked pentabromo diphenyl ether and tetrachlorodibenzo(p)dioxin in contaminated sediments." *Archives of Environmental Contamination and Toxicology* 56:670-679.

- Ten Hulscher, T.E., B.A. Vrind, H. Van den Heuvel, L.E. Van der Velde, P.C.M. Van Noort, J.E.M. Beurskens, and H.A.J. Govers, 1999. "Triphasic desorption of highly resistant chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in field contaminated sediment." *Environmental Science & Technology* 33(1):126–132.
- Turner, A., G.E. Millward, and S.M. Le Roux, 2001. "Sediment—Water Partitioning of Inorganic Mercury in Estuaries." *Environmental Science & Technology* 35(23):4648–4654.
- USEPA (U.S. Environmental Protection Agency), 2016. Record of Decision. Lower 8.3 Miles of the Lower Passaic River. Part of the Diamond Alkali Superfund Site. Essex and Judson Counties, New Jersey. March 2016.
- Van Noort, P.C.M., A. Poot, and A.A. Koelmans, 2014. "Analysis of organic contaminant desorption kinetic data for sediments and soils: Implications for the Tenax extraction time for the determination of bioavailable concentrations." *Science of the Total Environment* 490:235–238.
- Wallschlager D., M.V.M. Desai, M. Spengler, C.C. Windmoller, and R.D. Wilken. "How Humic Substances Dominate Mercury Geochemistry in Contaminated Floodplain Soils and Sediments." *Journal of Environmental Quality* 27(5):1044–1054.