Artificial Reefing

Ex-ORISKANY Artificial Reef Project

Time Dynamic Model (TDM) Documentation

SPAWAR
Systems Center
San Diego

January 2006
FINAL REPORT

PEO SHIPS

PROGRAM EXECUTIVE OFFICE SHIPS

Ex-ORISKANY
Artificial Reef Project

TIME DYNAMIC MODEL (TDM)

January 2006
FINAL REPORT

Prepared for:
Program Executive Office Ships (PMS 333)

Prepared by:
SPAWAR Systems Center, San Diego
Menzie-Cura Associations, Inc.
URS Corporation

List of Abbreviations, Acronyms, and Terms

Section 1. Introduction 1-1

1.0 Introduction 1-1
1.1 General Description of the Time Dynamic Model (TDM) 1-3
1.1.1 Input To the TDM 1-6
1.1.2 Model Construction and Assumptions 1-6
1.1.3 Model Issues 1-12
1.1.4 Model Algorithms 1-21
1.1.5 PCB Homolog Mass Budgets 1-25
1.2 TDM OUTPUT 1-25
1.2.1 Graphic Output in Appendices B and C 1-25
1.2.2 Data Input to PRAM 1-26
1.3 TDM Model UncertainTies 1-29
1.3.1 Vessel Geometry 1-29
1.3.2 Vessel Hull and Interior Compartments 1-30
1.3.3 Water Column Turbulence vs. Existence of a Pycnocline 1-31
1.3.4 Physical Properties of PCB and PCB Homologs (K_{ow} and K_{oc}) 1-31
1.3.5 Other Model Simplifications 1-31
1.4 REFERENCES 1-32

TABLES

Table 1-1. Grams PCB homolog and total PCB released per day. 1-6

Table 1-2. Homolog Koc values used in TDM and PRAM. 1-11

Table 1-3. Temporally and spatially averaged TDM output provided to PRAM 1-29

FIGURES

Figure 1-1. Random chords across ellipse representing the ex-ORISKANY 1-7

Figure 1-2. Assumed kinetics of PCB partitioning 1-8

Figure 1-3. Modeled vertical mixing of PCBs across the pycnocline with Kz = 0.1 cm2 sec-1 1-9

Figure 1-4. Bulk water (water +DOC+TSS) concentration of pentachlorobiphenyl in the ship as a function of internal water velocity. 1-14

Figure 1-5. November 1 degree modeled mixing depth from NOAA's World Ocean Atlas dataset http://www.nodc.noaa.gov/OC5/indprod.html 1-16

Figure 1-6. July 1 degree modeled mixing depth from NOAA's World Ocean Atlas dataset http://www.nodc.noaa.gov/OC5/indprod.html 1-17

Figure 1-7. Historical CTD casts in the vicinity of the ex-ORISKANY site at 30N 87W http://www.nodc.noaa.gov/OC5/indprod.html. 1-18

List of Abbreviations, Acronyms, and Terms

FIGURES (Continued)

Figure 1-8. Water Density with Depth, Derived from Temperature and Conductivity 1-19

Figure 1-9. Density profiles predicted by the U.S Navy's Global Digital Environmental Model (GDEM v3) at 30N/87W. http://128.160.23.42/gdemv/gdem_desc_v30.html 1-20

APPENDICES

Appendix A Computer Code for the Time Dynamic Model

Appendix B Time Dynamic Model Output Graphs – Homolog Concentrations Through Model Time and Space in all Abiotic Media

Appendix C Time Dynamic Model Output Graphs – Homolog Concentrations in Abiotic Media at Ranges of Maximum Concentration, and Homolog Mass Budgets.

Appendix D Response to Regulatory Comments on the First Draft of TDM Documentation

List of Abbreviations, Acronyms, and Terms

ACRONYMS AND ABBREVIATIONS

CFR	Code of Federal Regulations
CTD	conductivity, temperature and depth
Cw	PCB concentration in seawater
DOC	dissolved organic carbon
F_{oc}	fractional organic carbon
K_{oc}	water-organic carbon partitioning coefficient
km	kilometers
Kp	equilibrium partition coefficient
Kz	vertical eddy diffusivity
m	meters
mg	milligram
mL	milliliter
NAVSEA	Naval Sea Systems Command
NCCOSC	Naval Command, Control and Ocean Surveillance Center
NEHC	Navy Environmental Health Center
ng	nanogram
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
OPPT	Office of Pollution Prevention and Toxics
PCB	polychlorinated biphenyl
ppm	part per million
Px	PCB desorption isotherm
R_o	PCB concentration (irreversibly bound)
SHHRA	screening human health risk assessment
SINKEX	Deep-water Sinking Exercise
SSC-SD	Space and Naval Warfare System Center - San Diego
TDM	Time Dynamic Model
TOC	total organic carbon
TSS	total suspended solids
USEPA	U. S. Environmental Protection Agency
ZOI	Zone of Influence

SECTIONONE

1.0 INTRODUCTION

This document describes a mathematical model, the Time Dynamic Model (TDM), that supports the Naval Sea Systems Command's (NAVSEA) efforts to sink a decommissioned aircraft carrier, the ex-ORISKANY. The sunken vessel will be an artificial reef in shallow waters off the Florida coast. The vessel may release polychlorinated biphenyls (PCBs) to the environment after sinking because solid PCB-containing materials such as paints, bulkhead insulation, rubber products, and electrical cable insulation will remain onboard (CACI, 2004).

The ex-ORISKANY vessel is an Essex-class aircraft carrier. It is 888 feet (271 m) long, has an average beam (width) of 90 feet (27 m) (NEHC, July 2004), and is approximately 90 feet high to the flight deck. Superstructure, called the island, extends up approximately another 45 feet (14 m) above the flight deck. CACI (2004) estimated that 328 kilograms (722 pounds) of PCBs will remain onboard the ex-ORISKANY after the vessel has been prepared for sinking, calculated from mean PCB concentrations in source materials and estimated quantities of source materials remaining onboard. Using the 95% upper confidence limits on the mean PCB concentrations in source materials, one would estimate that 565 kilograms (1,243 pounds) of PCBs may remain onboard. This higher estimate was used in all modeling.[1]

The Space and Naval Warfare Systems Center – San Diego (SSC-SD) developed this model. It predicts concentrations of PCBs in abiotic media (water, sediment, total suspended solids, and dissolved organic carbon) in the marine environment that may result from PCB releases from the ex-ORISKANY during the first two years after sinking. This document describes model structure, input and output; the latter as temporal and spatial predictions of abiotic PCB concentrations. TDM output serves as input to the biological algorithms in the Prospective Risk Assessment Model (PRAM Version 1.4; NEHC/SSC-SD, 2005) when predicting PCB concentrations in marine organisms during the first two years.

Why did the Navy develop TDM subsequent to the application of another fate and transport model, Prospective Risk Assessment Model (PRAM)?

In July, 2004 the Navy submitted a draft Supplemental Human Health Risk Assessment (SHHRA) for the proposed ex-ORISKANY artificial reef to the U.S. Environmental Protection

---

[1] This estimate is based on the material sampling results (indicating the concentrations of PCBs in specific PCB-containing bulk product materials on the ex-ORISKANY) and estimates of the amount of PCB-containing bulk product materials that remain on the ex-ORISKANY after vessel preparations. The source term estimate report (CACI, 2004), presented in Appendix D, provides this information. 95% UCLs were estimated in CACI, 2004) assuming normally distributed data and again in documentation for PRAM (NEHC SSC-SD, 2006x) using USEPA's ProUCL software. The 95% UCL estimates from PRAM are more closely aligned with current USEPA guidance; therefore, 95% UCLs from PRAM are reported here instead of 95% UCLs from CACI (2004).

Agency (USEPA) Office of Pollution Prevention and Toxics (OPPT) to seek risk-based disposal of PCBs under the regulatory provision of 40 Code of Federal Regulations (CFR) 761.62(c) (NEHC, 2004). The USEPA invited the State of Florida to comment on the SHHRA. The SHHRA quantitatively evaluated the potential human health risks (cancer risks and non-cancer hazards) that would be associated with chronic human exposure to PCBs via a fish ingestion pathway. This risk assessment relied heavily on results of PRAM (Version 1.3, NEHC 2004), a multimedia environmental model. The Navy Environmental Health Center (NEHC), Portsmouth, VA, developed PRAM to predict steady-state abiotic and biotic PCB concentrations in various organisms that may reside on or near the ex-ORISKANY. PRAM models steady-state, long-term release of PCBs from a sunken vessel, distribution of released PCBs into abiotic media compartments in the marine environment surrounding the vessel, uptake and bioaccumulation of PCBs into representative biota living on or near the reef, and potential human health risks associated with chronically ingesting fish caught at the artificial reef. PRAM assumes that steady-state abiotic PCB concentrations occur beginning two years after vessel sinking. Documentation for a subsequent version of PRAM (1.4) justifies a two-year pre-steady state period for two reasons: (1) The authors maintain (NEHC/SSC-SD, 2005 subsection 2.2.1) that two years post-sinking is an appropriate pre-steady state period based on two assumptions: it will take two years for biota to colonize the sunken vessel; and, it will take at least two years for heavy PCB homolog groups to accumulate to maximum levels and (2) The Navy's laboratory PCB leach rate studies (SSC-SD, 2004) indicate that PCB homolog-specific and material-specific leach rates from bulk material are initially unstable and increasing, reach a maximum, and then stabilize to a lower asymptotic release rate, referred to as the stable release rate, within two years' time. PRAM originally used predicted release of PCBs occurring two years after the sinking of the ex-ORISKANY as input.

The USEPA and Florida reviewed the draft SHHRA document in July and August, 2004 and USEPA conducted an in-depth review of the PRAM (Version 1.3). Reviewers submitted written comments and recommendations to the Navy on both the SHHRA document and PRAM, then clarified their questions, concerns, and recommendations in technical working group[2] meetings with the Navy held in August, September, and November, 2004 (USEPA and Florida, 2004) and technical working group teleconferences between August 2004 and January 2005.

A major concern during the review was that the risk assessment evaluated potential human health risks associated with lifetime, chronic exposure (risks associated with lifetime ingestion of fish that are caught on the artificial reef), but did not evaluate potential acute or subchronic health risks for the first two years after sinking of the ex-ORISKANY (USEPA and Florida, 2004).

---

[2] The technical working group is comprised of representatives from the USEPA (Office of Pollution Prevention and Toxics, Office of Water, and Region 4), the State of Florida (Florida Fish and Wildlife Conservation Commission, the Escambia County Marine Resources Division, and other agencies), and the Navy and its subcontractors.

SECTIONONE

During the first two years after sinking, PCB release rates are higher, variable and non-monotonic. Reviewers were concerned that PRAM did not address potentially higher environmental PCB concentrations due to initially higher leach rates observed in the laboratory test. Ensuing corollary questions arose: Might not higher PCB concentrations in abiotic media, albeit transient, lead to higher PCBs concentrations in biota residing on or near the reef during this period? Could there be higher and/or unacceptable human health or ecological risks during this initial release period? The reviewers wanted the Navy to address implied uncertainties in the SHHRA with these questions.

In response, the Navy suggested addressing the initial PCB release period at the ex-ORISKANY reef with a model that SSC-SD had developed during its deep-water sinking exercise (SINKEX) program (NCCOSC, 1994). This model predicted released PCB concentrations in abiotic media in a marine environment. During a September, 2004 technical working group meeting, it was suggested that the model (which is now named the TDM) could predict abiotic PCB concentrations at various distances from the vessel and at various times after sinking. The Navy also suggested that these modeled concentrations could be inputs to PRAM's biouptake and bioaccumulation algorithms to estimate biota-specific tissue PCB concentrations at various spatial and temporal intervals. The tissue concentrations could then be used to evaluate ecological and human health risks during the initial two-year period.

TDM and PRAM are based on conservative assumptions that are not likely to under-predict PCB concentrations resulting from the sunken vessel. Coupled model results can help risk managers revaluate potential human health and ecological risks associated with the ex-ORISKANY reef. These evaluations will support 40 CFR 761.62 (c) disposal approval decisions about beneficial use of decommissioned vessels to create artificial reefs**.**

1.1 GENERAL DESCRIPTION OF THE TIME DYNAMIC MODEL (TDM)

This section describes the conceptual approach of TDM. Appendix A lists the computer code for the model. Appendix B contains graphs of modeled abiotic PCB homolog concentrations outside of the ship. Appendix C contains graphs of abiotic PCB homolog concentrations and mass inside the ship. Appendix D provides regulators' comments to earlier descriptions of TDM and Navy responses; all of which are incorporated into the body of this document.

TDM is written as a simple, two-dimensional abiotic box model that tracks adsorption/desorption of PCB homologs released into water inside the ship and moving into/out of dissolved organic carbon (DOC), total suspended solids (TSS) and sediment. TDM was designed to model a complex, three-dimensional problem applied at a screening assessment level and required appropriate simplifications. TDM links the following general assumptions together to predict

abiotic PCB homolog concentrations: complex, three-dimensional problem applied at a screening assessment level and required appropriate simplifications. TDM links the following general assumptions together to predict abiotic PCB homolog concentrations:

- The Navy's measured leach rates (SSC-SD, 2004) govern the initial release of PCB homlogs to water inside the sunken ship;
- PCBs approach equilibrium concentrations with dissolved organic carbon (DOC) and total suspended solids (TSS) within the ship in about four hours;
- PCBs then slowly leak from the ship, and are advected in the prevailing current;
- There is a pycnocline outside the ship that slows the vertical exchange of water, TSS, and DOC;
- Outside the ship, PCBs approach new equilibrium concentrations in water, DOC, TSS above and below the pycnocline, and sediment to a distance of 3000 m in all directions from the ship.

The over-arching model structure is as follows. The model proceeds forward in time at 1-minute intervals, making predictions of PCB concentrations from inside the ship to the model boundary 3000 m from the ship. Like PRAM, TDM assumes a prevailing 25 cm sec^{-1} current speed but not direction. The 1-minute time step was chosen to provide 15 m radial spatial resolution (1 minute*25 cm sec^{-1} =15 m) in model predictions. This resolution was felt necessary, particularly close to the ship where abiotic concentration gradients were expected to be very large. In each time interval, PCBs are released from solids inside the ship, assumed to mix instantaneously in the ship's internal volume and equilibrate instantaneously into water, DOC and TSS within the ship. Assumptions of instantaneous mixing and equilibrium partitioning within the ship were adopted from PRAM. Subsequently, PCBs in small volumes of water, DOC and TSS leave the ship and mix instantaneously into the first annular volume (first model bin) surrounding the ship.

TDM then assumes that the 25 cm sec^{-1} current external to the ship flows equally in all directions over time. Conceptually, ship PCB release is modeled similar to a pulsing, lawn sprinkler head releasing jets of PCBs in water, DOC and TSS at 25 cm sec^{-1} sequentially in a 360 degree pattern. The speed of the jet is maintained out to the model edge 3 km from the ship. This analogy was used because the ship is imagined as being engulfed by a current of constant speed that regularly shifts direction like the sprinkler head, Current is not modeled as truly radial, flowing in all directions simultaneously. Rather, over some short period of time, released PCBs sequentially (or randomly) flow in all directions equally. Radial advection of PCBs in all

directions is a modeling simplification to simulate random flow direction. Such a regular change in direction (though not in speed) is often measured at a site experiencing tidal currents.

Successive bins stretching from the ship to the model perimeter are not the same size, but rather are concentric annuli of increasing water, DOC, TSS and sediment volume. Each annulus is 15 m wide from the inside diameter to the outside diameter. PCBs, initially in water, TSS and DOC escaping the ship, are diluted in the larger water volume as they move outward from the ship into ever-larger annuli and are allowed to adsorb to ever-larger volumes of DOC, TSS and sediment. Movement of PCB in water, DOC and TSS to the next larger annulus proceeds in lockstep in all 200 annuli of the model per 1-minute interval. PCBs that exit from the 200th annulus leave the model domain.

PCBs adsorb/desorb from water to DOC, TSS and sediment in each annulus, partially approaching equilibrium concentrations in the 1-minute time step. The first order kinetics of PCB partitioning, particularly from water to sediment are kept fast (approximately 1 day to equilibrium, $C=C_0e^{-4.6t}$ where C is the PCB concentration in desorbing media, C_0 is the original PCB concentration, t is in days). This assumption is conservative and enhances PCB loading into the sediment during the 200-minute residence time (3000m/15 m min^{-1}) in the model.

PCBs in water TSS and DOC are released from the ship below the pycnocline. However, PCBs partition to DOC and TSS above and below a pycnocline which is set at 15 m below the surface. Mixing of PCB-laden water, TSS and DOC across the pycnocline and into the upper water column is controlled by a vertical dispersal rate much slower than the PCB partitioning rate. Vertical flux of PCBs across the pycnocline occurs within each annulus, but not into the volume directly above the ship. The water column directly above the ship is assumed to remain free of PCBs. TDM predicts radial isopleths of decreasing concentrations in all directions and decreasing concentrations upward across the pycnocline.

TDM predictions of abiotic PCB concentrations are input into PRAM for biotic predictions in the first two years (see section 1.2 below). PRAM predicts biotic PCB concentrations within two regions: zones of influence (ZOIs) equal to two and five times the areal footprint of the ship. For a ZOI=2, the areal, 2-dimensional footprint extends 14.8 m from the ship. TDM PCB concentrations in the first model bin (0 to 15 m [ZOI=2} from the ship) were input into PRAM's food web module to predict PCB concentrations in biota. For a ZOI=5, the areal footprint extends 48.7 m from the ship. Average TDM PCB concentrations for the first three bins (0 to 45 m from the ship) and first four bins (0 to 60 m from the ship) were themselves averaged together and input into PRAM for ZOI=5 biotic predictions.

SECTIONONE

1.1.1 Input To the TDM

The TDM uses empirical leach rate data obtained in the laboratory (SSC-SD, 2004). Table 1-1 is the input file accessed by the model code. Values under columns cl1, cl2 … to total (denoting homologs with one, two … chlorine atoms and total PCBs) are grams released day^{-1} from all shipboard material. Note that no release of cl8 – octachlorobiphenyl – was measured. This homolog is subsequently not represented in graphics of model output in the appendices.

Table 1-1. Grams PCB homolog and total PCB released per day. 'Days' column is release time period and reflects time between laboratory measurements.

days	cl1	cl2	cl3	cl4	cl5	cl6	cl7	cl8	cl9	cl10	total
0.007	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	5.5E-02	0.0E+00	0.0E+00	0.0E+00	5.5E-02
1.163	0.0E+00	0.0E+00	2.0E-02	4.8E-01	4.5E-01	0.0E+00	3.2E-01	0.0E+00	0.0E+00	0.0E+00	1.3E+00
5.906	6.1E-05	1.7E-01	6.4E-02	8.3E-01	7.9E-01	1.2E-01	6.7E-02	0.0E+00	0.0E+00	0.0E+00	2.1E+00
7.007	0.0E+00	6.4E-02	5.6E-02	1.1E+00	1.2E+00	1.4E-01	4.6E-02	0.0E+00	0.0E+00	0.0E+00	2.6E+00
7.015	3.9E-05	3.8E-03	5.2E-02	1.3E+00	2.3E+00	3.4E-01	1.6E-02	0.0E+00	0.0E+00	0.0E+00	3.9E+00
21.129	3.4E-05	5.8E-03	2.6E-02	6.0E-01	9.2E-01	1.4E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.7E+00
27.074	8.0E-06	3.7E-03	2.2E-02	7.8E-01	1.8E+00	4.2E-01	5.8E-04	0.0E+00	0.0E+00	0.0E+00	3.0E+00
13.838	2.7E-05	1.0E-02	2.7E-02	8.4E-01	2.1E+00	3.8E-01	3.6E-02	0.0E+00	0.0E+00	0.0E+00	3.4E+00
34.997	2.5E-05	2.8E-03	1.7E-02	4.3E-01	8.4E-01	1.9E-01	4.5E-04	0.0E+00	9.1E-04	5.1E-04	1.5E+00
48.969	2.1E-05	5.1E-04	1.2E-02	5.7E-01	1.6E+00	4.1E-01	2.8E-02	0.0E+00	1.6E-04	9.1E-05	2.6E+00
42.026	1.8E-05	4.0E-04	1.0E-02	3.2E-01	6.5E-01	1.4E-01	1.4E-02	0.0E+00	0.0E+00	0.0E+00	1.1E+00
42.061	1.9E-05	2.2E-06	1.2E-02	3.7E-01	7.6E-01	1.5E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.3E+00
34.958	2.1E-05	2.5E-06	8.9E-03	3.1E-01	4.4E-01	6.9E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	8.3E-01
41.942	1.9E-05	1.2E-05	8.9E-03	2.2E-01	4.5E-01	1.1E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	7.8E-01
42.024	1.9E-05	1.7E-05	9.6E-03	2.6E-01	4.0E-01	8.0E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	7.5E-01
27.963	1.7E-05	3.8E-05	1.9E-02	3.1E-01	5.5E-01	1.5E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.0E+00
56.240	1.5E-05	1.1E-05	1.1E-02	1.4E-01	2.4E-01	7.2E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	4.6E-01
275.681	1.4E-05	1.4E-01	1.0E-02	1.7E-01	3.2E-01	7.9E-02	7.3E-02	0.0E+00	1.1E-03	5.9E-04	8.0E-01

1.1.2 Model Construction and Assumptions

Model Geometry and Residence Time Inside the ex-ORISKANY

TDM assumes that the ex-ORISKANY is an elliptical volume 270 m by 36.5 m and 6.9 m high, sunk in 64 m of water. These dimensions match the estimated volume of the real ship and the geometry used in the PRAM (NEHC/SSC-SD, 2005). The model assumes that PCBs leach into this ship volume at 1-minute intervals, mix instantaneously into the interior water, and adsorb to DOC and TSS.

We estimated residence time within the ship as a function of advection of water from inside the ship and geometric path lengths. An assumed slow, internal current of 0.25 cm sec^{-1} releases water, DOC and TSS from the ship. Figure 1-1 shows estimated path lengths of DOC and TSS inside the vessel, based on random transects. The most common path length of approximately 37

m and a current of 0.25 cm per second results in an expected residence time of 247 minutes within the ship.

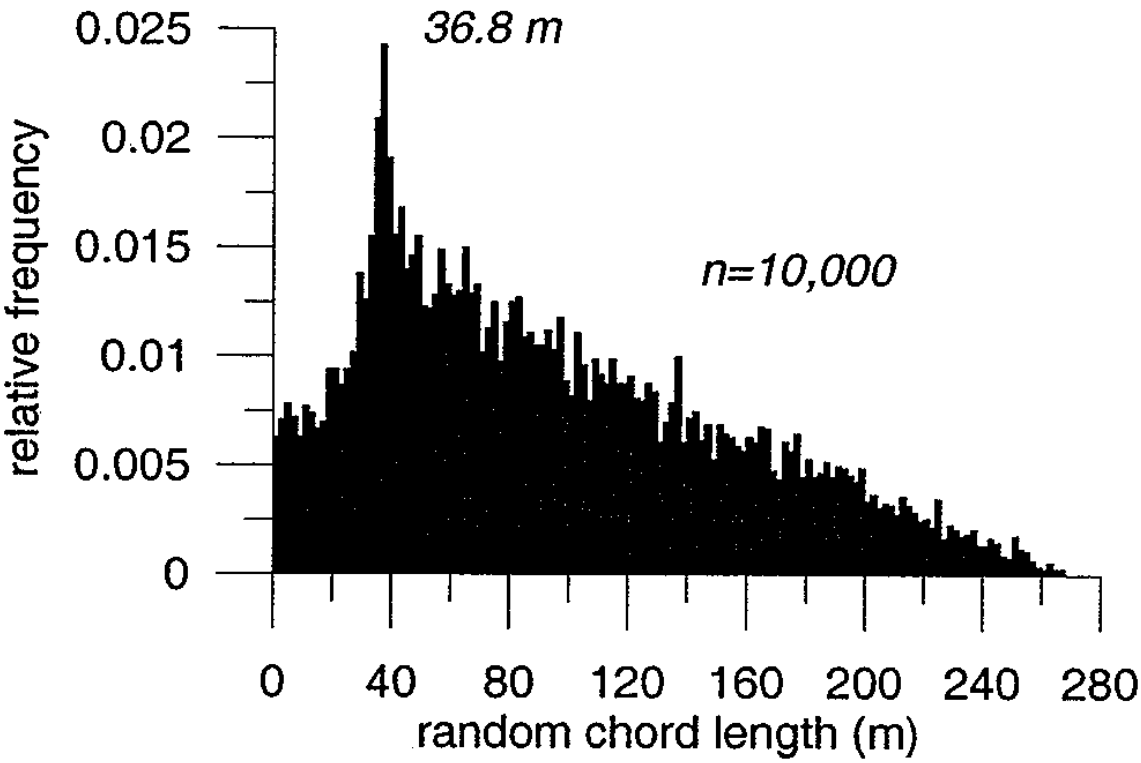

Figure 1-1. Random chords across ellipse representing the ex-ORISKANY.

Equilibrium Inside the ex-ORISKANY

We used the modeled first-order kinetics of PCB adsorption and desorption among water, DOC, TSS and sediment (Figure 1-2) to estimate percent equilibrium reached during residence time in the ship. Ninety-nine percent of equilibrium concentrations are assumed reached within 24 hours (Di Toro and Horzempa, 1982). These kinetics specify that 54.7% equilibrium is reached between water, DOC and TSS during the 247 minute residence time within the ship.

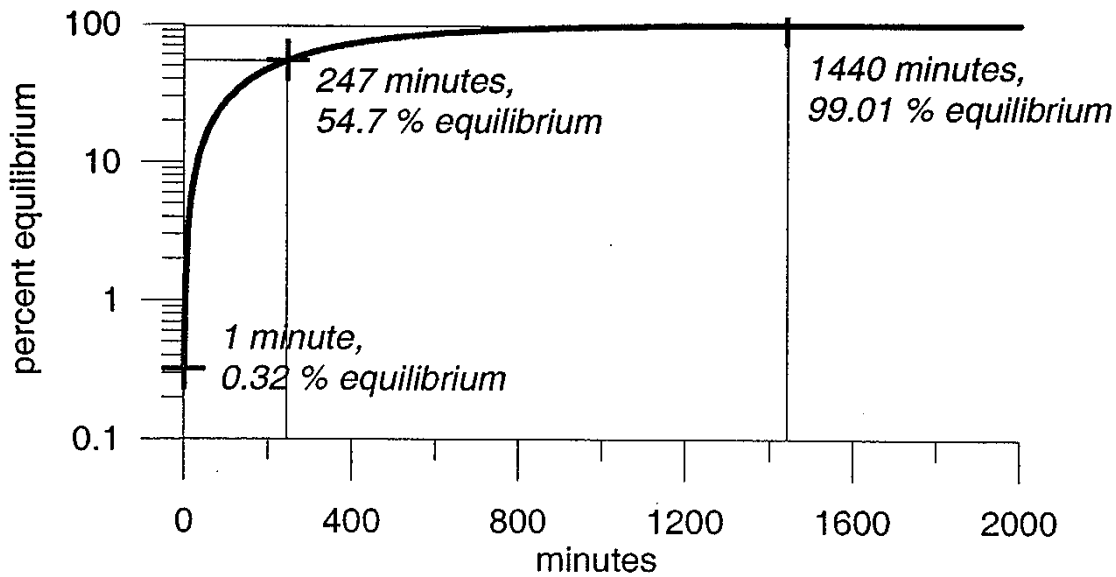

Figure 1-2. Assumed kinetics of PCB partitioning. Highlighted are percent equilibria at 1 minute, 247 minutes, and 1440 minutes.

Model Geometry Outside the ex-ORISKANY

The model calculates external PCB concentrations in concentric bins (elliptical annuli) 15 m wide, expanding away from the ship and extending to the surface. The 15 m matches the distance a 25 cm sec^{-1} current travels in the 1-minute model time step.

A pycnocline is fixed at 15 m, based on local diver experience (Turpin, 2004). The vertical division of the bins at 15 m simulates this pycnocline and provides an upper 15 m tall bin and a lower 49 m tall bin. The model extends outwards 200 bins (3000 m) from the ship. The model assumes that the entire volume of a bin (water, suspended solids and dissolved organics) moves to the next bin at each time step. Sediment is not transported between bins.

The only source of PCBs at the outer boundary are from the sunken ship. PCBs are assumed to be advected away from the ship and, over time, escape in all directions beyond the perimeter of the model 3 km from the ship. PCB concentrations at the outer boundary are functionally zero because PCBs are never allowed into the model domain from the outer boundary and they do not impact their advective removal from the ship. Water, DOC and TSS movement are not explicitly tracked in the model though they are assumed to carry PCBs away from the ship and out of the model domain at 25 cm sec^{-1}.

SECTIONONE

Equilibrium Outside the ex-ORISKANY

The 1-minute time step allows 0.32% equilibrium concentrations to be reached between water DOC and TSS and sediment below the pycnocline (Figure 1-2). Approach to equilibrium between water DOC and TSS above the pycnocline is slower and governed by vertical turbulent diffusion. We assumed an eddy diffusivity K_z of 0.1 cm^2 sec^{-1} to mix dissolved PCBs across the pycnocline (Toole et al, 1994; Law et al, 2003). Figure 1-3 plots the approach to equal PCB water concentrations above and below the pycnocline with a K_z=0.1 over time. Ninety-nine percent equal concentrations (99% equilibrium) was reached in 64.7 days. This period is the same in every model bin, regardless of size, because the area across the pycnocline grows at the same rate as the bin volume, which is essentially cylindrical. A larger K_z value denotes more energetic vertical mixing and shorter time to equilibrium. When K_z=0.1, a 1-minute time step allows time for only 0.0011% of equilibrium PCB concentrations between water, DOC and TSS to be reached above the pycnocline.

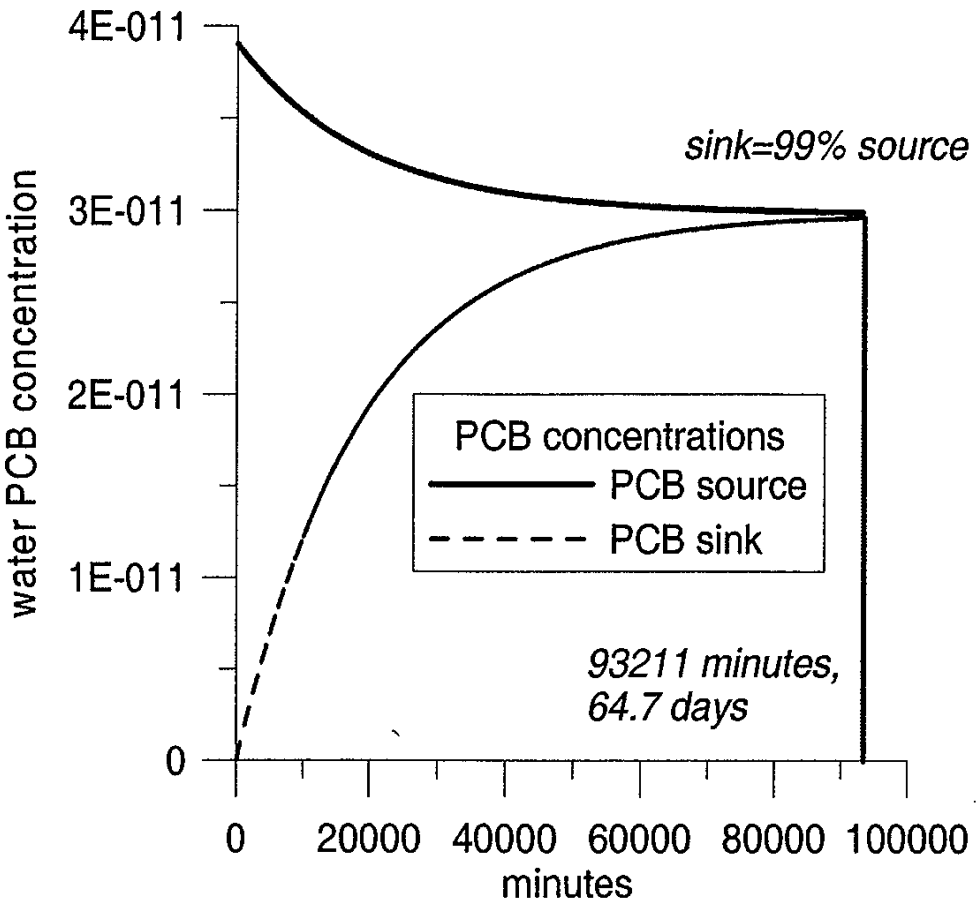

Figure 1-3. Modeled vertical mixing of PCBs across the pycnocline with Kz = 0.1 cm2 sec-1

SECTIONONE

Assumptions About Abiotic Media

The TDM adopted several assumptions from the PRAM food chain model about water and sediment to calculate PCB homolog concentrations. These assumptions are:

- The density of water is 1 g ml^{-1};
- The total organic carbon (TOC) in sediment is 1% (i.e. the model parameter f_{oc} in sediment equals 0.01);
- Sediment and adsorbed PCBs are mixed by infaunal organisms to a depth of 10 cm;
- The density of sediment is 1.5 g ml^{-1};
- The concentration of DOC is 0.6 mg $liter^{-1}$ and is composed of 100% organic carbon;
- The concentration of TSS is 10 mg $liter^{-1}$ and is 15% organic carbon;
- The ship has no internal structure or adsorptive sediment;
- Transfer or loss by evaporation at the water's surface is not modeled, nor are PCBs modeled as occurring in the water column directly above the ship.

Assumptions and Parameters to Describe the PCB Homologs

In TDM, concentrations are in units of mass fraction (mass of PCBs in media to total mass of the media), versus molar concentration or mass to volume. The homolog-specific **e**quilibrium partitioning coefficient $K_p=K_{oc}*f_{oc}*C_w$ where K_p is the ratio of the PCB homolog concentration in DOC, TSS, sediment to the PCB homolog concentration in water at equilibrium. (Fetter, 1999; Maidment, 1993). The partition coefficient is the product of the water-organic carbon partitioning coefficient K_{oc} and the fraction organic carbon f_{oc}. K_{oc} values specific for each homolog were taken from PRAM and listed in Table 1-2. F_{oc} is the mass fraction of organic carbon in DOC, TSS and sediment, equal to 1, 0.1, and 0.01 respectively. C_w is the water PCB homolog concentration. $K_{p,}$ K_{oc}, f_{oc}, and C_w are unitless. C_w is initially determined by the PCB release rate within the ship and is then usually reduced via volume dilution and partitioning into DOC, TSS and sediment. The equilibrium partition coefficient is also the slope of the initial sediment adsorption isotherm (Weber et al., 1991 Thibodeaux, 1996). Desorption of PCBs from sediment is assumed to follow a more shallow isotherm than adsorption and preserves a residual adsorbed fraction which cannot be reversibly desorbed (Di Toro and Horzempa, 1982).

The 24-hour time frame for PCB partitioning equilibrium was adopted from Di Toro and Horzempa (1982) who were studying adsorption and desorption of hexachlorobiphenyl between water and suspended sediments. The time frame is fast relative to more current literature, particularly when considering adsorption/desorption to bed sediment (Borglin et al, 1996; Lick et al, 1996; Valsaraj and Thibodeaux, 1998; Gess and Pavlostathis, 1997). Assumption of fast adsorption was considered conservative however, since laboratory-measured rapid release of PCBs was short-lived. Rapid adsorption would allow initially high water concentrations to be reflected in the sediment. The corollary assumption of fast sediment desorption was tempered by the conservative assumption of a large, irreversibly-bound fraction R_o, as described in the Di Toro and Horzempa (1982) paper. Assumption of a permanently-bound fraction is supported in more recent literature (McGroddy et al, 1995; Hunter et al, 1996; Kan et al, 1997; Kan et al, 1998). In summary, TDM assumes fast partitioning from the water to the sediment to capture early, large PCB releases from the ship in the first two years, then assumes that a large fraction can not desorb out of the sediment and this output is then provided as input into PRAM.

Table 1-2. Homolog Koc values used in TDM and PRAM.

PCB homolog	K_{oc}
monochloro	$4.61*10^3$
dichloro	$1.14*10^4$
trichloro	$4.22*10^4$
tetrachloro	$4.51*10^4$
pentachloro	$8.61*10^4$
hexachloro	$1.2*10^6$
heptachloro	$2.19*10^6$
octachloro	$2.85*10^6$
nonachloro	$9.24*10^6$
decachloro	$8.72*10^7$

Assumptions and Constructs Regarding Fate and Transport Outside the Ship

The model assumes that PCBs are released only down-current from the ship, but currents flow equally in all directions over time. As a result, PCB dispersal is assumed to be radially symmetric around the ship, and the PCB load is distributed in all directions in each one-minute time step. Mass of PCBs is the only parameter that is tracked and budgeted in TDM. TDM assumes that sequential flow of PCBs occurs in all directions during each time step. PCBs are modeled to move from inner to outer annuli, initially staying in the same medium as in the previous time step, but diluted in concentration by the larger mass of water, DOC and TSS of the outer annuli. If water, DOC, and TSS mass were similarly tracked, the mass of the material coming from the vicinity of the ship would need to be similarly divided by the respective mass in

each annulus. This would slow the average current considerably below 25 cm sec^{-1} , distorting and increasing the partitioning to the sediment. TDM assumes that PCBs are being advected away from the ship with a constant current flowing at 25 cm $sec^{-1.}$ Extending the analogy by averaging the current over time and increasing the period in which water-borne PCBs remain in the model domain was felt to lead to misleading results.

Simple geometry requires that the concentric bins increase in volume away from the ship. In the second and subsequent bins this larger volume dilutes the water PCB concentrations. There is more mass of DOC and TSS in each subsequently larger bin because the model assumes that their concentrations are constant.

To conserve PCB mass associated with DOC and TSS moving from an inner bin to the next outer bin, potential adsorption or desorption is calculated for only the DOC and TSS advected from the previous inner bin into the current bin. The current bin contains DOC and TSS advected into it from the previous bin, plus additional DOC and TSS to maintain a constant concentration. The new PCB mass adsorbed to DOC or TSS from the previous bin is divided by the mass of all the DOC or TSS in the current bin – effectively diluting it. This approach makes sense if one assumes that currents first advect particles in one direction, then another, making the average concentration equal to the incoming load averaged over all DOC or TSS mass at that range from the ship.

In the one-minute period within a particular annulus, PCB partitioning approaches equilibrium concentrations via flux from one medium to another. Total PCB mass released from the ship over time is distributed in the sediment, which stays in the model, and transiently in water, DOC and TSS in the annuli as it moves toward the model perimeter. Since water and entrained DOC and TSS are quickly advected away at 25 cm sec^{-1}, most PCB mass escapes from the model domain before it can adsorb to the sediment. Only the immobile sediment retains an irreversible fraction of its adsorbed PCB load.

1.1.3 Model Issues

This subsection discusses three model issues: equilibrium inside the ship; PCB flux across the pycnocline; and PCB desorption from DOC and TSS.

Issue 1: Equilibrium Inside the Ship

The first issue is the assumption that DOC and TSS inside the ship immediately reach their 247 minute, 54.7% approach to equilibrium PCB concentrations, regardless of how long the DOC and TSS were actually in the ship. This simplification eliminates the need to keep track of specific particle residence times, in keeping with the assumption of no internal ship structure. It has the effect of increasing the PCB load in these media and reducing it in water inside the ship.

SECTIONONE

As reviewers pointed out in comments regarding the TDM, release of PCBs outside of the ship will eventually match release of PCBs inside the ship if the ship hull is permeable. The degree of permeability, characterized as the current speed inside the ship, will determine the internal ship PCB concentrations. Current speed inside the ship was arbitrarily set at 1% of external current or 0.25 cm sec^{-1}. This assumption was first made in PRAM and adopted in the TDM. In PRAM, reef fish are assumed to stay inside the ship and be exposed to internal PCB concentrations 10% of the time. The 1% value for the current was felt to be a conservative compromise between very slow internal currents, which would elevate internal PCB concentrations, and faster internal currents that reflect accessibility of the inner ship to reef fish as assumed in PRAM. Figure 1-4 below, based on the maximum measured release of pentachlorobiphenyl at 2.3 g day^{-1}, illustrates the sensitivity of internal PCB concentration to internal current velocity. As internal velocity increases, internal concentration decreases in a non-linear fashion. The 1% internal current results in modeled exposure to 3.2 10^{-12} g pentachloro PCB in 1 g of water, organic carbon and total suspended sediments combined. The same general relationship holds for total PCBs. While a slower internal current could have been chosen, that option seemed less reasonable given the assumed accessibility of the ship interior to mobile reef organisms.

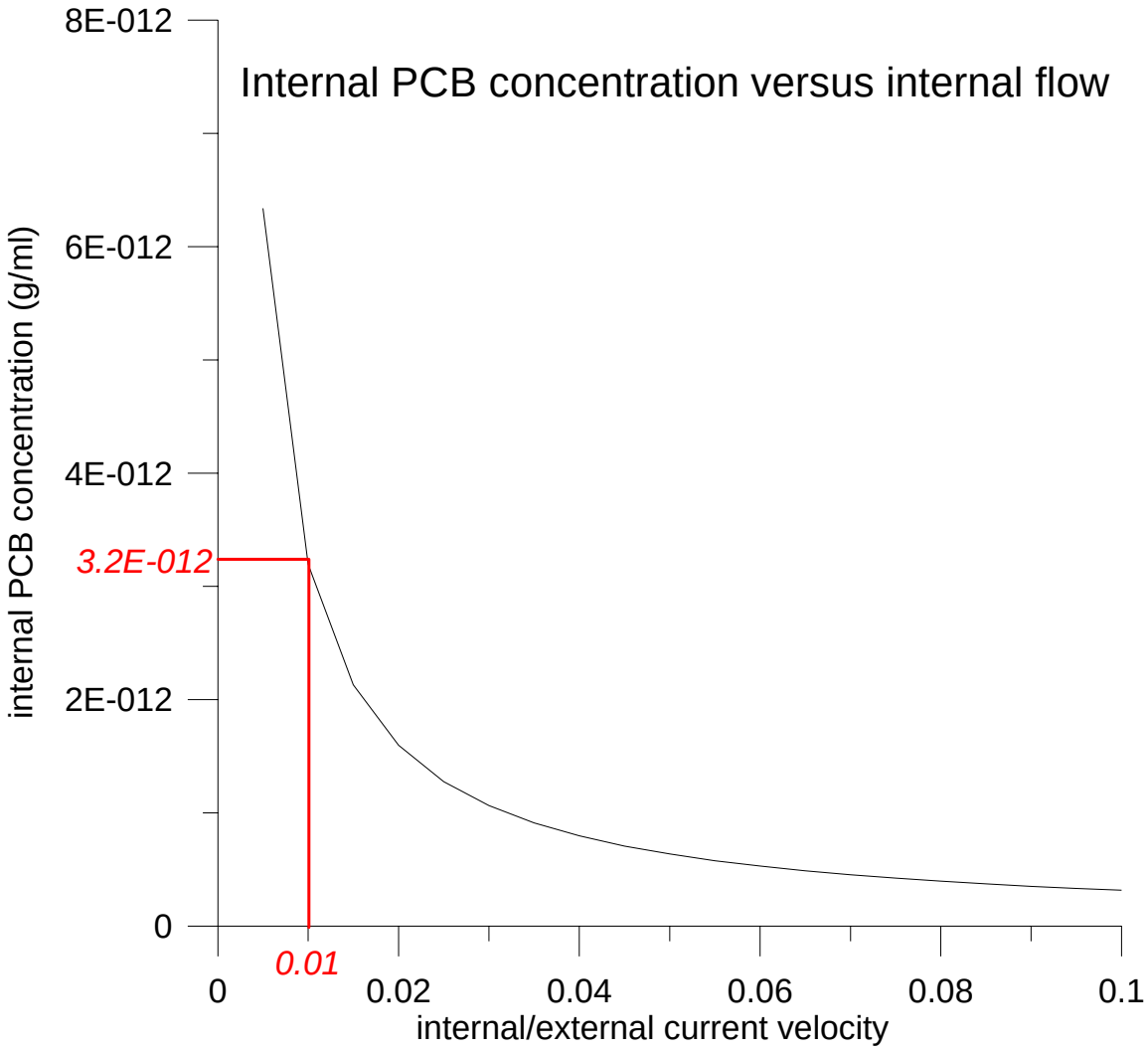

Figure 1-4. Bulk water (water +DOC+TSS) concentration of pentachlorobiphenyl in the ship as a function of internal water velocity. Internal water velocity is plotted as a fraction of the assumed external 25 cm sec^{-1} current. Maximum release of 2.3 g day^{-1} for pentachlorobiphenyl was modeled, but relationship applies to total PCBs as well.

Issue 2: PCB Flux Across the Pycnocline

The second issue(s) is the variability of the pycnocline, and that PCB flux across the pycnocline via turbulent mixing of water, DOC and TSS is handled implicitly by slowing the approach to equilibrium over 64.7 days. The pycnocline occurs at the depth of the maximum thermohaline density gradient in the water column that maintains vertical stability and arises from solar heating. Typically, water above or below the pycnocline is more easily mixed, while at the pycnocline vertical mixing is impeded. The pycnocline can be disrupted by strong mixing, typically from surface winds. In this case the pycnocline could also be disrupted by upwelling

resulting from the current deflecting off the ship's side. At the proposed ex-ORISKANY site at 30N/87W in the Gulf of Mexico, stormy cool winter weather conditions can break down the pycnocline, which is re-established in the late spring and deepens through the summer. Below, Figures 1-5 through 1-8 depict modeled and measured ocean density structure.

Figures 1-5 and 1-6 are comparisons of modeled mixed depth throughout the oceans at coarse resolution. Deep winter mixing (above the pycnocline) in the Gulf in November gives way to shallower mixing under stratified conditions in July. In these low resolution figures, 30N/87W is plotted as land. However, a mixed layer depth shoaling from 25 m in November to 0 m in July can be seen in the Gulf. Figure. 1-7 shows locations of CTD (conductivity, temperature, depth) casts from which density profiles can be calculated. The density profiles from the stations indicated in red and green in figure 1-7 are shown in figure 1-8. The green profiles in figure 1-8, taken at the stations denoted in green in figure 1-7, were measured in October, 1995. While ocean conditions at locations 1, 2, and 3 in figure 1-7 are not equivalent, a trend is seen. where the pycnocline is very shallow in the spring, deepens to around 5 m in early summer, deepens further to 40 m in the fall then suddenly disappears in the winter as the entire water column cools and is mixed. Figure 1-9 is the monthly density profile modeled at 30N/87W used in Navy sound propagation models in the Gulf. The maximum inflection point can be used to estimate depth of the pycnocline. Here more clearly than in the above figures, a weak or non-existent pycnocline exists in winter. Then in spring the pycnocline is seen to reestablish and strengthen throughout the summer, reaching a maximum depth of approximately 50 m in August or September, then disintegrating in late fall and early winter. The selection of a pycnocline at 15 m in the TDM was not based on the above information, but rather on diver experience at the proposed reefing site (Turpin, 2004). In view of the above figures, a 15 m pycnocline depth in the vicinity of the ex-ORISKANY sink site appears to be supported. The strength of the pycnocline, in terms of hindering vertical mixing, is described by turbulent vertical diffusivity (K_z). A K_z value of 0.1 cm sec^{-2} is used in the TDM, based on literature values referenced in the TDM documentation.

Rather than having fractional mixing occur across the pycnocline within the 1-minute time step and then allowing adsorption and desorption to occur above the pycnocline, TDM simply slows down the approach to equilibrium above the pycnocline. This simplification is justified because the K_z term dominates the apparent rate of adsorption of upper water media compared to the adsorption kinetics, and because calculated PCB flux across the pycnocline is always upward into those media (figures in Appendix B). Allowing K_z to control adsorption above the pycnocline however forces a small slowing in PCB flux rates, predicted from 24-hour kinetics, from media that release PCBs below the pycnocline. For example, predicted net PCB mass flux out of water, DOC and TSS into the sediment and into media above the pycnocline exceeds the net adsorptive capacity of those media to absorb it within the 1-minute time step. In this case, the

model reduces the PCB flux from the water to accommodate the adsorptive kinetics of those receiving media.

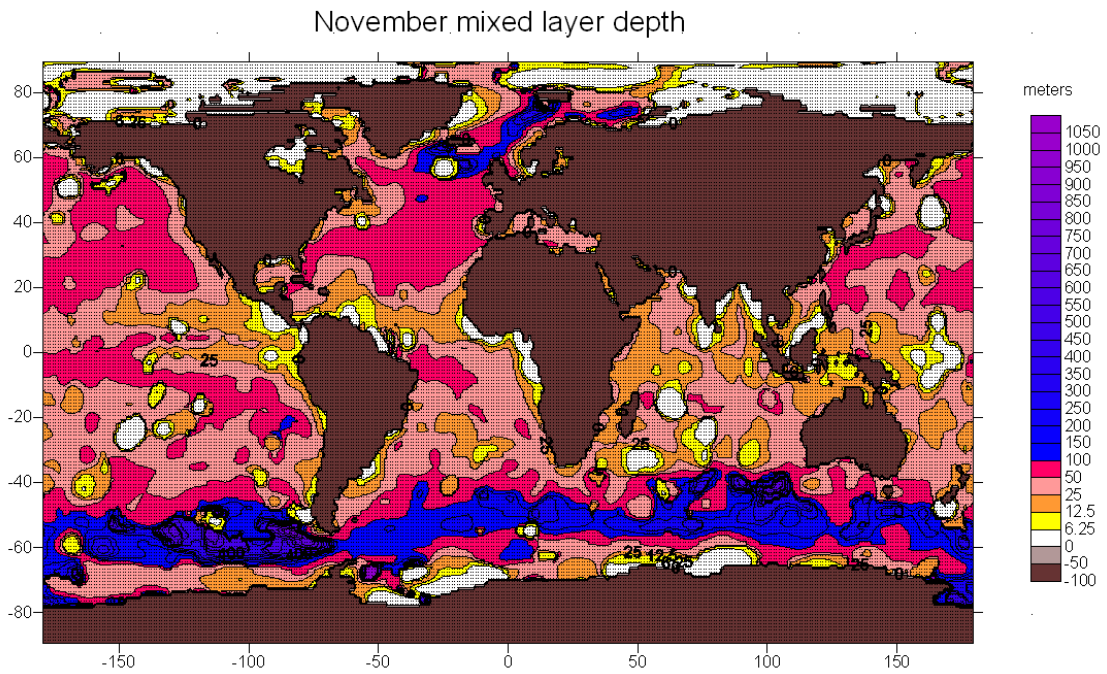

Figure 1-5. November 1 degree modeled mixing depth from NOAA's World Ocean Atlas dataset http://www.nodc.noaa.gov/OC5/indprod.html

SECTIONONE

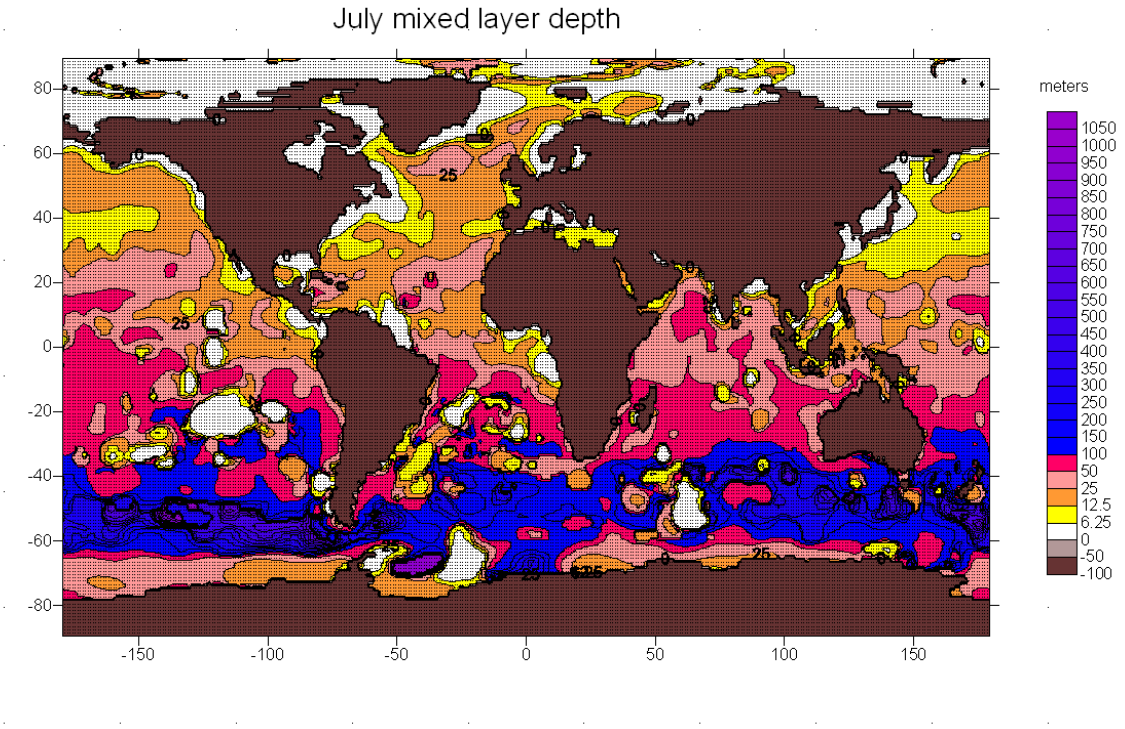

Figure 1-6. July 1 degree modeled mixing depth from NOAA's World Ocean Atlas dataset http://www.nodc.noaa.gov/OC5/indprod.html

SECTIONONE

CTD casts in vicinity of proposed REEFEX sinking at 30N 87W

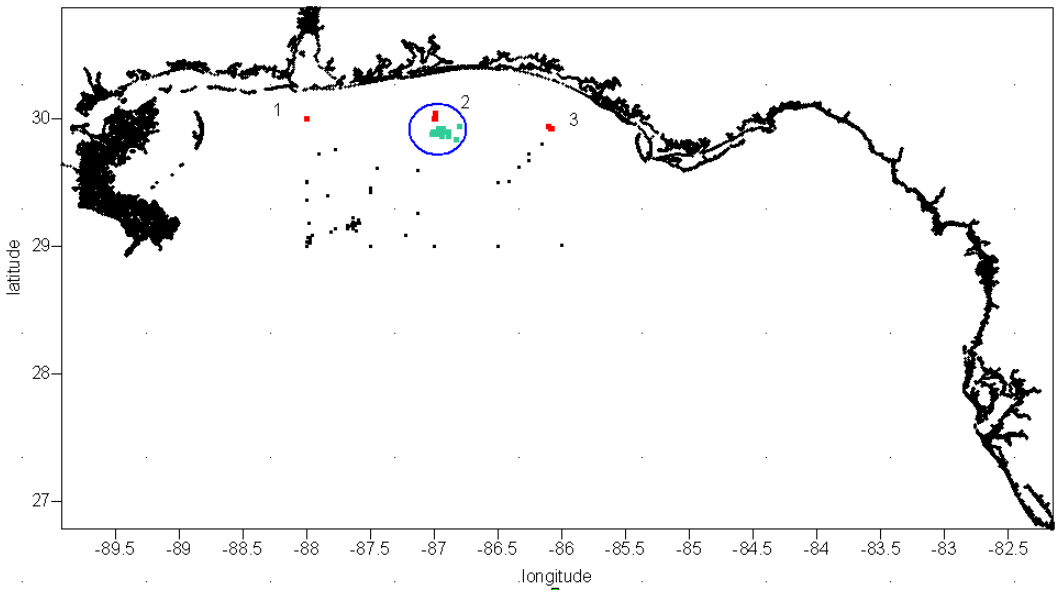

Figure 1-7. Historical CTD casts in the vicinity of the ex-ORISKANY site at 30N 87W http://www.nodc.noaa.gov/OC5/indprod.html. The stations denoted in green are from Naval Research Laboratory Stennis (Steve Crossland, pers. comm.)

SECTIONONE

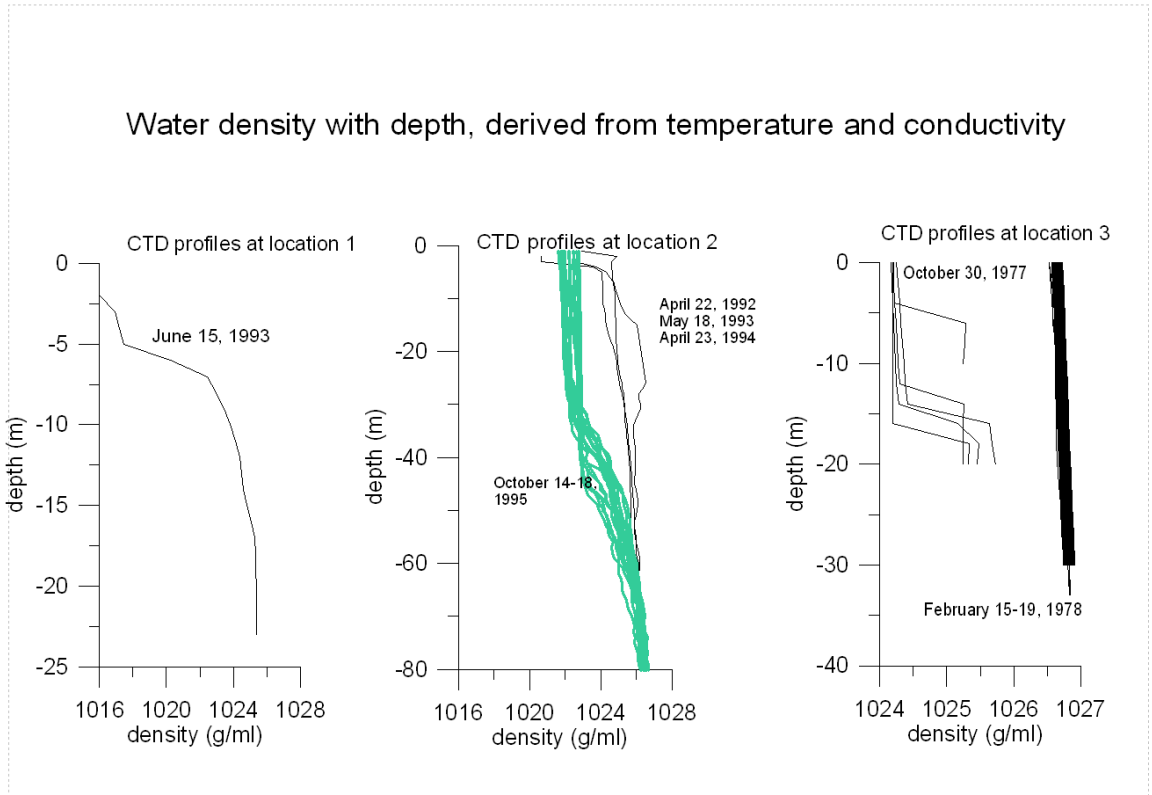

Figure 1-8. Water Density with Depth, Derived from Temperature and Conductivity. Profiles are from stations in Figure 1-7. The green profiles are from the Figure 1-7 stations, also indicated in green.

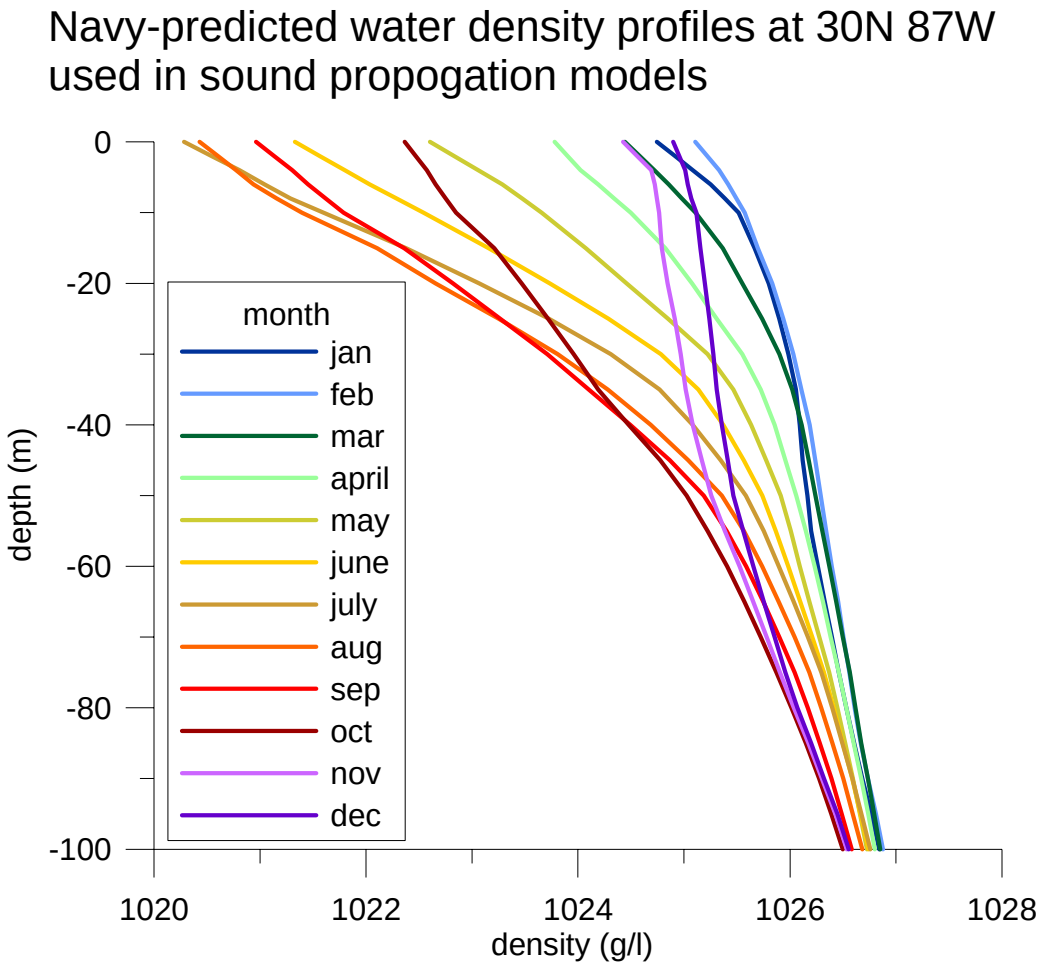

Figure 1-9. Density profiles predicted by the U.S Navy's Global Digital Environmental Model (GDEM v3) at 30N/87W. http://128.160.23.42/gdemv/gdem_desc_v30.html

Issue 3 PCB Desorption from DOC and TSS.

The third issue is that PCB desorption from DOC and TSS does not follow the same isotherm used for sediment. The shallower desorption isotherm was not implemented for DOC and TSS for computational simplicity, though Di Toro and Horzempas (1982) analyzed PCB adsorption from, and desorption to, suspended sediments. PCB concentrations in water-borne DOC and TSS below the pycnocline are maximum adjacent to the ship, then decrease by 100, well below the residual sediment concentration R_o (R_o is equal to 0.57*maximum sediment concentration). The apparent drop in concentration is due primarily to volume dilution. Volume from within the ship to the outermost bin below the pycnocline increases 183 fold, accounting for the apparent decrease in concentration. As a result, the net flux of PCBs out of DOC and TSS is reduced.

Calculation of net desorption of PCB homologs from TSS and DOC during their advection from

the ship to the model's perimeter at 3000 m, showed that desorption of more than 43% of the PCB mass occurred in only three instances in over nine million simulations (9 homologs*730 days*1440 minutes per day). PCB homolog loss from TSS and DOC that exceeded 43% of the original mass when these media escaped the ship was noted for hexachlorobiphenyl on day 1 in the 200th bin (43.6% lost), for nonachlorobiphenyl on day 83 in the 200th bin (45.1% lost), and for decachlorobiphenyl on day 83 in the 200th bin (45.4% lost). In addition, if the shallower desorption isotherm had been adopted for these particular simulations, the homolog mass that remained adsorbed to TSS and DOC would have been greater, resulting in concentrations that would probably stay above R_o in all cases.

The net effect of this simplification is that DOC and TSS release their PCB load into media closer to the ship. This is more important for the more-chlorinated homologs, for which DOC and TSS are important PCB transport vehicles from the ship (see relative mass in these media within the ship, Appendix C). If model currents were slower and residence times longer, Di Toro and Horzempas' (1982) desorption constraints probably should be implemented. Above the pycnocline, DOC and TSS always increase in PCB concentration as they are advected away from the ship, so desorption isotherms are not an issue (Appendix B).

1.1.4 Model Algorithms

The model has two calculation loops enclosing the adsorption and desorption code. The outer loop is a time loop that steps the model through the measured homolog release sequence over two years, one minute at a time. The inner loop calculates concentrations in a series of bins as concentric annuli around the ship. The inner spatial bins loop has three parts: inside the sunken ship, the first bin adjacent to the ship, and the remaining 199 concentric bins. Each bin is subsequently divided into a lower bin below the pycnocline and an upper bin above it. The following is a general set of steps that occur in most cells. The first bin (bin 1) adjacent to the ship is a little different in that it acquires PCB mass directly from the ship rather than an adjacent bin, and PCBs are not advected into bin l above the pycnocline. PCBs enter bin i from the inner, adjacent bin i-1, initially in the same media. PCB homolog concentration is immediately reduced by the larger media volume in the current bin. For example, for PCB in TSS below the pycnocline:

1a. input to bin i: $\mathbf{PCB_{lower\ TSS\ (i)} = PCB_{lower\ TSS\ (i-1)}}$

2a. PCB concentration in TSS in bin i: $\mathbf{PCB_{lower\ TSS(i-1)}/lower\ TSS_{(i)}}$

The same is true above the pycnocline for all but the first cell:

1b. input to bin i: $\mathbf{PCB_{upper\ TSS\ (i)} = PCB_{upper\ TSS\ (i-1)}}$

SECTIONONE

2b. PCB concentration in TSS in bin i: $PCB_{upper\ TSS(i-1)}$/upper $TSS_{(i)}$

In the first cell, PCBs enter water above the pycnocline only by mixing from below. PCBs in water and DOC are similarly advected into bin i and diluted. Total PCB mass in bin i in water, DOC, TSS and sediment above and below the pycnocline is calculated:

3. $\Sigma PCB(i)=PCB_{lower\ water(i)} + PCB_{upper\ water(i)} + PCB_{sediment(i)} + PCB_{lower\ TSS(i)} + PCB_{upper\ TSS(i)} + PCB_{lower\ DOC(i)} + PCB_{upperDOC(i)}$.

Total PCB is rewritten as a sum of products of PCB concentrations, denoted with brackets below, times the mass of water, DOC, TSS and sediment.

4. $\Sigma PCB(i)=[PCB_{lower\ water(i)}]$*lower water(i)

+$[PCB_{upper\ water(i)}]$ *upper water(i)

+$[PCB_{sediment(i)}]$*sediment(i)

+$[PCB_{lower\ TSS(i)}]$*lower TSS(i)

+$[PCB_{upper\ TSS(i)}]$*upper TSS(i)

+$[PCB_{lower\ DOC(i)}]$*lower DOC(i)

+$[PCB_{upperDOC(i)}]$*upper DOC(i).

Equilibrium concentrations for PCBs in the different media in the bin are next computed, all as functions of equilibrium water concentration. times First the equilibrium water concentration is calculated:

5a. Equilibrium $[PCB_{water(i)}] = \Sigma PCB(i)$/

(lower water(i)+ upper water(i)

+sediment(i)*K_{oc}*f_{oc}

+(lower TSS(i)+ upper TSS(i))*K_{oc}*f_{oc}

+(lower DOC(i)+ upper DOC(i))*K_{oc}*f_{oc})

When PCBs are modeled to desorb from the sediment, a small modification in equation 5a is needed to account for an irreversible PCB fraction adsorbed to the sediment, argued by DiToro

and Horzempa (1982). In equation 5b, R_o is the concentration of PCBs that resist desorption and P_x is a shallower linear adsorption desorption isotherm:

5b. Equilibrium [$PCB_{water(i)}$] = ΣPCB(i)-R_o*sediment(i)/

(lower water(i)+ upper water(i)

+sediment(i)*P_x

+(lower TSS(i)+ upper TSS(i))*K_{oc}*f_{oc}

+(lower DOC(i)+ upper DOC(i))*K_{oc}*f_{oc})

where R_o=0.57* maximum [$PCB_{sediment(i)}$]; P_x=(1/2.3)*K_{oc}*f_{oc}

The other equilibrium concentrations are again calculated as water equilibrium concentrations times K_{oc} and correct media f_{oc}.

6a. Equilibrium [$PCB_{lower\ water(i)}$] = equilibrium [$PCB_{water(i)}$]

Equilibrium [$PCB_{upper\ water(i)}$] = equilibrium [$PCB_{water(i)}$]

Equilibrium [$PCB_{sediment(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}

Equilibrium [$PCB_{lower\ TSS(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}

Equilibrium [$PCB_{upper\ TSS(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}

Equilibrium [$PCB_{lower\ DOC(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}

Equilibrium [$PCB_{lower\ DOC(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}

When sediment desorption occurs, the equilibrium sediment concentration equation is modified to account for the irreversible fraction:

6b. Equilibrium [$PCB_{sediment(i)}$] = R_o+ equilibrium [$PCB_{water(i)}$]* P_x

PCB flux between media follows first order kinetics, where existing concentrations approach equilibrium concentrations asymptotically. The flux is calculated as a difference between existing and equilibrium concentrations times the mass of the particular media. Rate constants are included to account for the 1 minute time step:

7. $Flux_{lower\ water(i)}$ = rate*((equilibrium [$PCB_{lower\ water(i)}$])-[$PCB_{lower\ water(i)}$])*lower water(i)

SECTIONONE

$Flux_{upper\ water(i)}$ = pycnrate*((equilibrium [$PCB_{upper\ water(i)}$])-[$PCB_{upper\ water(i)}$])*upper water(i)

$Flux_{sediment(i)}$ = rate*((equilibrium [$PCB_{sediment(i)}$])-[$PCB_{sediment(i)}$])*sediment(i)

$Flux_{lower\ TSS(i)}$ = rate*((equilibrium [$PCB_{lower\ TSS(i)}$])-[$PCB_{lower\ TSS(i)}$])*lower TSS(i)

$Flux_{upper\ TSS(i)}$ = pycnorate*((equilibrium [$PCB_{upper\ TSS(i)}$])-[$PCB_{upper\ TSS(i)}$])*upper TSS(i)

$Flux_{lower\ DOC(i)}$ = rate*((equilibrium [$PCB_{lower\ DOC(i)}$])-[$PCB_{lower\ DOC\{i)}$])*lower DOC(i)

$Flux_{upper\ DOC(i)}$ = pycnorate*((equilibrium [$PCB_{upper\ DOC(i)}$])-[$PCB_{upper\ DOC(i)}$])*upper DOC(i)

Rate constant ‘rate’ has a value of 0.0032 and corresponds to a 1 minute increment in first order kinetics reaching 99% equilibrium in 24 hours (see 1d. above) Rate constant ‘pycnorate’ has a much smaller value of 1.0728e-5, reflecting the much slower 64.7 day approach to 99% equilibrium across the pycnocline. The latter constant was based simulations using a vertical diffusivity K_z value of 0.1 $cm^2\ sec^{-1}$.

In model simulations, PCBs are observed to always move up across the pycnocline. The first flux term in equation 7, involving PCBs in the lower water, has a rate constant based on a 24-hour approach to equilibrium for all media above and below the pycnocline. PCB flux to water, TSS and DOC above the pycnocline is limited by the much smaller pycnocline rate constant. In order to accommodate the slower PCB mixing across the pycnocline, a correction is made to lessen PCB release from media below the pycnocline. The algebraic correction factor is a value less than 1.0, labeled as the variable ‘brake’ in the model code. It is calculated as the sum of the flux terms and absolute values of the flux terms in equation 7, divided by the difference between the sum of absolute fluxs and sum of fluxs in each cell:

8. Brake=($\Sigma abs(Flux_j)$+ $\Sigma Flux_j$)/($\Sigma abs(Flux_j)$-$\Sigma Flux_j$)

where the index j denotes the seven different media in each bin and abs denotes the absolute value.

This correction is applied to each flux calculation in equation 7 that has a negative value (i.e. the media is releasing PCBs) and maintains conservation of PCB mass in the model. The fluxes are then added to masses advected into the i bin from the i-1 bin and new concentrations are calculated:

9. $[PCB_{lower\ water(i)}] = (PCB_{lower\ water(i)} + Flux_{lower\ water(i)}) / \text{lower water}_{(i)}$

   $[PCB_{upper\ water(i)}] = (PCB_{upper\ water(i)} + Flux_{upper\ water(i)}) / \text{upper water}_{(i)}$

   $[PCB_{sediment(i)}] = (PCB_{sediment(i)} + Flux_{sediment(i)}) / \text{sediment}_{(i)}$

   $[PCB_{lower\ TSS(i)}] = (PCB_{lower\ TSS(i)} + Flux_{lower\ TSS(i)}) / \text{lower TSS}_{(i)}$

   $[PCB_{upper\ TSS(i)}] = (PCB_{upper\ TSS(i)} + Flux_{upper\ TSS(i)}) / \text{upper TSS}_{(i)}$

   $[PCB_{lower\ DOC(i)}] = (PCB_{lower\ DOC(i)} + Flux_{lower\ DOC(i)}) / \text{lower DOC}_{(i)}$

   $[PCB_{upper\ DOC(i)}] = (PCB_{upper\ DOC(i)} + Flux_{upper\ DOC(i)}) / \text{upper DOC}_{(i)}$

Appendix A provides the computer code for the TDM model (in C programming language).

1.1.5 PCB Homolog Mass Budgets

We tested conservation of PCB homolog mass with a mass budget calculation using two mass conservation algorithms. The first calculated the difference between the mass of each homolog released from the vessel and each homolog mass retained in the model domain among the different media. The second algorithm summed each homolog mass advecting from the model domain in water, DOC and TSS. The difference and sum converged within 24 hours after equilibrium sediment PCB concentrations were reached for all homologs except decachlorobiphenyl. The difference and sum remained less than homolog mass released, but approached the released mass as the percent retained in the model domain became insignificant. PCB masses in the different abiotic media over time are plotted in Appendix C.

1.2 TDM OUTPUT

1.2.1 Graphic Output in Appendices B and C

Appendix B provides three-dimensional, TDM output graphs of abiotic homolog and total PCB concentrations outside of the ship over all spatial and temporal scales. Seventy figures are presented in Appendix B. The following figures are sets of total PCB and nine homolog (cl1-cl7, cl9, and cl0) concentrations in the seven abiotic media. Cl8 or octachlorobiphenyl release was not measured, and subsequently not modeled. Data shown are daily mean concentrations. The abiotic media are water, TSS and DOC above and below the pycnocline; and sediment. In each set of concentrations per medium, the total PCB concentration is shown first to establish the color concentration scale. Concentration is shown on the vertical axis, while distance from the ship and time are shown in the horizontal axes. The same color scale is used on the nine

subsequent homolog concentration plots per media, while the numerical scale accommodates the range of values for that homolog. This allows quick detection by color of the most significant homolog to total PCB loading in the medium.

Appendix C provides output graphs detailing homolog and total PCB at ranges of maximum concentration. Appendix C is composed of 31 two-dimensional plots. The figures compare homolog and total PCB concentrations and mass in all the seven abiotic matrices, inside and outside of the ship over time. Concentration and mass values are daily means. Distance from the ship was fixed at the range where the total PCB and homolog concentrations were maximum. For instance, below the pycnocline; water, TSS, DOC, and sediment concentrations were greatest in the first bin, 15 m from the ship. Above the pycnocline: water, TSS and DOC concentrations were highest in the last bin, 3000 m from the ship (see Appendix B). Inside the ship, there is only one range, since the ship was considered non-compartmentalized and well-mixed.

The first 30 figures in Appendix C are divided into ten sets of three. The ten sets present data for each of the nine PCB homologs, plus total PCBs. No release of octachlorobiphenyl was measured and was not modeled in this study. The three figures per set show concentrations outside the ship, concentrations and mass inside the ship, and mass outside the ship. Concentration and mass inside the ship were not combined in the figures showing conditions outside the ship to maintain some clarity in the graphs. Each of the three figures per homolog requires a little explanation. The first figure shows only concentrations outside the ship and all units are g PCB/ g media. Concentrations below the pycnocline are shown as solid lines, concentrations above are shown as dashed lines. The second figure shows concentration and mass in the ship in water, TSS and DOC. Sediment was not assumed to occur in the ship. Concentrations are shown as dashed lines; units are g PCB/g media. Mass is shown as solid lines; units are g. Mass is plotted on the same vertical axis, so mass values are read as g PCB, not g PCB/g matrix. Total PCB mass inside the ship is shown also as a thick grey line. The third figure is the PCB mass outside of the ship. The upper red line is the total PCB released from the ship, the grey line is the total released minus the sum remaining in the model, and the black line is the total PCB leaving the model domain. The latter two plots were used as a check on model mass balance. The grey and black lines quickly converge and are offset from the red line by the PCB mass that remains in the model. The other solid lines represent PCB mass in matrices below the pycnocline, the dashed lines represent mass in matrices above the pycnocline. The final figure is the daily homolog release rates measured by Dr. Rob George and used as model input (SSC-SD, 2004).

1.2.2 Data Input to PRAM

This section describes TDM predictions used to derive PCB tissue concentrations in a variety of representative reef organisms likely found around the ex-ORISKANY during the transient release

period. Time-averaged TDM outputs are used as inputs to the PRAM's biotic food-web module to predict biotic tissue concentrations at discrete time and distance intervals. These biotic tissue concentrations may be used to assess ecological and human health risks associated with the artificial reef during the transient release period. To account for the change in community structure and dynamics during the initial 2-year period after the vessel is sunk, a food web scenario has been developed (see the sections on PRAM and Ecological Risk Assessment). The time-variable dietary composition for representative organisms is used to simulate the PCB exposures, via diet, that these organisms will experience. The progressive food web starts at day 1 after sinking and progresses through 1 week, 2 weeks, 1 month, 6 months, 1 year, and 2 years. It is assumed that the community structure and PCB release rates will reach a steady-state condition at day 730 (i.e, at the 2-year mark).

TDM outputs were provided as a series of files that provided time-averaged PCB concentrations in abiotic media at distance intervals of 0 to 15 meters, 0 to 45 meters, and 0 to 60 meters away from the sunken vessel. The fifteen meter distance correlates with a ZOI of 2, and the 45 and 60 meter distances were evaluated because they bracket the ZOI of 5 (approximately 50 meters) for evaluating PCB bio-uptake into the benthic and pelagic community organisms. TDM was constructed to estimate PCB concentrations in abiotic matrices at one-minute time intervals, over the entire time domain, and at 15 meter distance intervals, over the entire distance domain. However, for the human health and ecological risks assessments it was recognized that 24-hour time intervals would be the finest resolution needed for determining abiotic PCB concentrations, and that the distance intervals closest to the vessel would be most significant for determining exposures to reef-associated organisms. TDM outputs provided data for conducting the human health and ecological risk assessments for the following time-averaged intervals: daily (each 24-hour period, starting at day 1, through day 730); day 1 (24 hours), day 7 (the 6 days after day 1); day 14 (the 7 days after day 7); day 28 (the 14 days after day 14); 6 months (the 5 months after 28); 1 year (the 6 months after day 180); and 2 years (the 1 year period after day 365). TDM outputs (time-averaged PCB concentrations) were provided for each PCB homolog (mono- through decachlorobiphenyl), and for total PCBs (as the sum of PCB homolog concentrations) in each of the abiotic media compartments. Ten different sets of information were provided for each homolog:

- PCB concentration in the water in the upper water column
- PCB concentration in the total suspended solids in the upper water column
- PCB concentration in the dissolved organics in the upper water column
- PCB concentration in the water in the lower water column
- PCB concentration in the total suspended solids in the lower water column

- PCB concentration in the dissolved organics in the lower water column
- PCB concentration in the sediment
- PCB concentration in the water internal to the ship
- PCB concentration in the total suspended solids internal to the ship
- PCB concentration in the dissolved organics internal to the ship

These data (Table 1-3) were used in place of the PRAM's abiotic module output. To supplement the TDM data, it was assumed that the PCB concentration in sediment pore water was equal to the PCB concentration in the lower water column.

Table 1-3. Temporally and spatially averaged TDM output provided to PRAM

Time Increment	Distance from the Ship	PCB Homologs
Day 1	15	all PCB homologs (mono –deca)[14]
Day 1	45	all PCB homologs (mono – deca)
Day 1	60	all PCB homologs (mono – deca)
Day 7	15	all PCB homologs (mono – deca)
Day 7	45	all PCB homologs (mono – deca)
Day 7	60	all PCB homologs (mono – deca)
Day 14	15	all PCB homologs (mono – deca)
Day 14	45	all PCB homologs (mono – deca)
Day 14	60	all PCB homologs (mono – deca)
Day 28	15	all PCB homologs (mono – deca)
Day 28	45	all PCB homologs (mono – deca)
Day 28	60	all PCB homologs (mono – deca)
Day 180	15	all PCB homologs (mono – deca)
Day 180	45	all PCB homologs (mono – deca)
Day 180	60	all PCB homologs (mono – deca)
Day 365	15	all PCB homologs (mono – deca)
Day 365	45	all PCB homologs (mono – deca)
Day 365	60	all PCB homologs (mono – deca)
Day 729	15	all PCB homologs (mono – deca)
Day 729	45	all PCB homologs (mono – deca)
Day 729	60	all PCB homologs (mono – deca)

1.3 TDM MODEL UNCERTAINTIES

1.3.1 Vessel Geometry

We have used a simplified geometric shape to approximate the ex-ORISKANY's dimensions, as opposed to trying to derive a mathematical description that would account for the complex

contours of this ex-aircraft carrier. The vessel has a displacement of 27,100 tons, and thus it is assumed that it will sink into the sediment to some depth. We have calculated an "effective ship height" of 6.9 m, which was used in conjunction with a length dimension of 271 m and an average width of 36 m, to approximate the dimensions of the vessel's displacement in the marine environment. The vessel is not an exact elliptical shape, and its geometry is complex. Therefore, the ZOI or boundary conditions are approximate.

1.3.2 Vessel Hull and Interior Compartments

In TDM, the ship's hull is assumed to be porous, allowing PCBs released into the internal vessel compartment to freely move to the outside of the vessel, as a function of the external water current. This not does accurately reflect reality, since the ship's hull is actually constructed of thick steel plates. The model assumption of one interior compartment is obviously a simplification. Aircraft carriers such as the ex-ORISKANY may have 5,000 separate compartments within the structure of the ship. Reviewers have raised concerns whether one or more of the actual internal compartments could accumulate released PCBs because a hatch had not been removed, or had not remained open, etc. The question is whether or not this could pose a hazard if, in the future, there were a compartment structural failure, and the concentration of PCBs built up in this internal compartment are released in a bolus or "pulse" to the external environment, causing unexpected human health or environmental risks.

In 2001, the URS modeler conducted calculations to simulate this scenario and found that a limited internal-compartment buildup and catastrophic failure would have little impact on the environment, or risk to human health, as compared to long-term, chronic release of PCBs from the vessel because:

- the large volume of the vessel itself (53,800 cubic meters) will dilute sudden releases internally;
- the large dilution volume of water immediately external to the ship (for example, within a 15-meter standoff from all sides of the ship) will dilute external releases;
- a sudden and transient release and the time scales of biouptake and bioaccumulation in fish and other organisms are out of phase.

The time-dependence of biouptake and bioaccumulation, as compared with the relatively short time required for transport of solubilized PCB, indicated that a confined-space internal buildup of PCBs would have limited impact with regard to increasing overall PCB concentrations in the external environment should a catastrophic failure of the compartment occur.

1.3.3 Water Column Turbulence vs. Existence of a Pycnocline

There is uncertainty associated with the assumption of a pycnocline caused by a lack of knowledge concerning the behavior of currents and upwelled water around the ship (There probably is a pycnocline based on Escambia County divers' experience, as relayed in technical working group meetings).

The ex-ORISKANY's vertical profile will present a "wall" extending from the sea floor up to about 27 meters below the surface. Above that, the "island" portion of the vessel will extend up another 15 meters or so. If ocean currents run perpendicular to the sides of the vessel, they may lift , causing an upwelling of water that will mix the water above the vessel. If ocean currents are perpendicular to the bow or stern of the vessel, less turbulence could occur. Additionally, there is evidence that there is naturally occurring turbulence in offshore Florida waters that may be expected to occur in the LAARS where the ex-ORISKANY is proposed to be deployed.

1.3.4 Physical Properties of PCB and PCB Homologs (K_{ow} and K_{oc})

The organic carbon-water partition coefficient (K_{oc}) of hydrophobic organic compounds such as PCBs is a parameter that significantly affects partitioning and bioaccumulation properties. Most risk assessments rely on deterministic calculations with parameter values taken from tabulations compiled by the USEPA or other regulatory agencies, from literature sources, or from a combination of these. In TDM, the K_{oc} values for the PCB homologs were adopted from PRAM.

1.3.5 Other Model Simplifications

There are a number of simplifications and assumptions in TDM not identified in Section 2.2 (Model Issues) that result in uncertainties in model output:

- DOC, TSS and sediment are treated as bulk material with no internal structure or distinct chemical properties. For example, PCB flux through sediment pore water is not explicitly addressed, but is assumed to contribute to net sediment PCB flux. TSS settling and sediment resuspension are not modeled, primarily due to a lack of site-specific information on these processes.

- Independent adsorption and desorption processes are combined together to yield net PCB adsorption or desorption. Adsorption and desorption kinetics are assumed to be the same, reaching 99% equilibrium concentrations in 24 hours, though the Di Toro and Horzempa (1982) paper only addressed adsorption rates.

The same kinetics are also applied to all PCB homologs, though the same paper only studied a single hexachlorobiphenyl. Since the kinetics are fast relative to the release periods, modeled PCB concentrations in stationary sediment would not be impacted. However, the kinetics are short relative to water, DOC and TSS residence time in the model domain. Increasing or decreasing adsorption/desorption rates would increase or decrease the PCB load in DOC and TSS relative to water, respectively.

TDM is constructed to use individual PCB homologs to model abiotic transport and bioaccumulation. The K_{ow} and K_{oc} values from scientific literature for each PCB homolog (mono- through deca-) were found. Thus we have attempted to avoid the controversy associated with the wide range of K_{ow} and K_{oc} values that have been recommended to total PCBs.

1.4 REFERENCES

Borglin, S., A. Wilke, R. Jepsen, and W. Lick. 1996. Parameters affecting the desorption of hydrophobic organic chemicals from suspended sediments. *Environ. Toxic. Chem*. 15(10):2254-2262.

CACI. 2004. Final Report – Polychlorinated Biphenyls (PCB) Source Term Estimates for ex-ORISKANY (CVA34).

Di Toro, D.M. and L.M. Horzempa. 1982. Reversible and resistant components of PCB adsorption-desorption: isotherms. *Environ. Sci. Technol*. 16:594-602.

Fetter, C.W. Contaminant Hydrology Section Edition 1999. Prentice Hall, Inc. Upper Saddle River, New Jersey.

Gess, P and S. G. Pavlostathis. 1997. Desorption of chlorinated organic compounds from a contaminated estuarine sediment. *Environ. Toxic. Chem.* 16(8):1598-1605.

Hunter, M. A., A. T. Kan, and M. B. Tomson. 1996. Development of a surrogate sediment to study the mechanisms responsible for adsorption/desorption hysteresis. *Environ. Sci. Technol.* 30(7):2278-2285.

Kan, A. T., G. Fu, M. Hunter, W. Chen, C. H. Ward, and M.B. Tomson. 1998. Irreversible sorption of neutral hydrocarbons to sediments: experimental observations and model predictions. *Environ. Sci. Technol* 32(7):892-902.

Kan, A. T., G. Fu, M. Hunter, and M. B. Tomson. 1997. Irreversible adsorption of naphthalene and tetrachlorobiphenyl to Lula and surrogate sediments. *Environ. Sci. Technol*. 31(8):2176-2185.

Law C.S., E.R. Abraham, A.J. Watson, M.L. Liddicoat. 2003. Vertical eddy diffusion and nutrient supply to the surface mixed layer of the Antarctic Circumpolar Current. *J. Geographical Research* 108(C8):3272.

Lick, W. and V. Rapaka. 1996. A quantitative analysis of the dynamics of the sorption of hydrophobic organic chemicals to suspended sediments. *Environ. Toxic. Chem*. 15(7):1038-1048.

Maidment, D.R. Handbook of Hydrology. 1992. McGraw-Hill Inc. New York, New York.

National Marine Fisheries Services (NMFS). 1993. Data Tapes for the 1993 NMFS presented to USEPA, National Center for Environmental Assessments.

McGroddy, S. E., J. W. Farrington, and P. M. Gschwendl. 1995. Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environ. Sci. Technol*. 30(1):172-177.

NCCOSC 1994. Richter, K.E., a. Valkirs, C. Dooley, R. Gauthier, M. Stallard, and D.H. Rushworth 1994. Ecological analysis of deep sea sinking of Naval ships containing Polychlorinated Biphenyls (PCB) impregnated materials, White Paper. Naval Command, Control, and Ocean Surveillance Center, Research Development Test and Evaluation Division (NRaD), Environmental Sciences Division, Code 52, 4 March 1994, San Diego, CA

NEHC/SSC-SD 2005. Prospective Risk Assessment Model Version 1.4 Documentation. May

NEHC 2004. Supplemental Human Health Risk Assessment (SHHRA) for the ex-ORISKANY Artificial Reef (Draft), July, 2004. (Chapter 5 of SHHRA described the Prospective Risk Assessment Model).

PRAM. Version 1.3, 2004. Electronic copies of the Prospective Risk Assessment Model, Version 1.3, were provided to the Navy (NAVSEA), the USEPA and the State of Florida in July 2004.

SSC-SD 2004. Space and Naval Warfare Systems Center – San Diego. Draft Final Report: Investigation of polychlorinated biphenyl (PCB) release rates from selected shipboard solid materials under laboratory-simulated shallow ocean (artificial reef) environments, October, 2004.

Thibodeaux, L.J. *Environmental Chemodynamics: Movement of Chemicals in Air, Water, and Soil, Second Edition.* 1996. John Wiley & Sons, Inc. New York, New York.

Toole, J.M, K.L Polzin and R.W. Schmidt. 1994. Estimates of diapycnal mixing in the abyssal ocean. *Science*. 164:1120-1123

Turpin, R. 2004. Personal Communication from Captain Robert Turpin, Escambia County Marine Resources Division.

USEPA and State of Florida, 2004. Comments and responses to comments on the SHHRA, dated August 15, 2004.

SECTIONONE

Valsaraj, K. T. and L. J. Thibodeaux. 1999. On the linear driving force model for sorption kinetics of organic compounds on suspended sediment particles. *Environ. Toxic. Chem*. 18(8):1679-1683.

Weber, W.J. Jr., P.M. McGinley and L.E. Katz. 1991. Sorption phenomena in subsurface systems: concepts, models and effects of contaminant fate and transport. *Wat. Res*.25(5):499-52.

COMPUTER PROGRAMMING CODE FOR THE TIME DYNAMIC MODEL (TDM)

```
-
program;
set c:\pcb\simul\finalprephomologs;

create c:\pcb\simul\bigfiles\cl5ship (keep pulse release cumday cummin shippcb conc tssc docc)(buffer=65535); order pulse release cumday cummin shippcb conc tssc docc;
create c:\pcb\simul\bigfiles\cl5bud (keep pulse release cumday cummin shipmass cumrel cumwater upcumwat cumsed cumtss upcumtss cumdoc upcumdoc cumloss1
cumloss2)(buffer=65535); order pulse release cumday cummin shipmass cumrel cumwater upcumwat cumsed cumtss upcumtss cumdoc upcumdoc cumloss1 cumloss2;
create c:\pcb\simul\bigfiles\cl5sed (keep pulse release cumday cummin bconc1-bconc200)(buffer=65535); order pulse release cumday cummin  bconc1-bconc200;
create c:\pcb\simul\bigfiles\cl5wat (keep pulse release cumday cummin conc1-conc200)(buffer=65535); order pulse release cumday cummin conc1-conc200;
create c:\pcb\simul\bigfiles\cl5upperwat (keep pulse release cumday cummin uconc1-uconc200)(buffer=65535); order pulse release cumday cummin uconc1-uconc200;
create c:\pcb\simul\bigfiles\cl5tss (keep pulse release cumday cummin tssc1-tssc200)(buffer=65535); order pulse release  cumday cummin  tssc1-tssc200;
create c:\pcb\simul\bigfiles\cl5suppertss (keep pulse release cumday cummin utssc1-utssc200)(buffer=65535); order pulse release cumday cummin  utssc1-utssc200;
create c:\pcb\simul\bigfiles\cl5doc (keep pulse release cumday cummin docc1-docc200)(buffer=65535); order pulse release cumday cummin  docc1-docc200;
create c:\pcb\simul\bigfiles\cl5upperdoc (keep pulse release cumday cummin udocc1-udocc200)(buffer=65535); order pulse release cumday cummin  udocc1-udocc200;

array volume [200] vol(1-200);
array mass [200] mass(1-200);
array conc [200] conc(1-200);
array watfl[200] watfl(1-200);
array uvol [200] uvol(1-200);
array umass [200] umass(1-200);
array uconc [200] uconc(1-200);
array uwatfl[200] uwatf(1-200);

array bflux [200] bflx(1-200);
array bcum [200] bcum(1-200);
array bconc[200] bconc(1-200);
array bvol[200] bvol(1-200);
array bmax[200] bmax(1-200);
array area[200] area(1-200);

array tsscm[200] tsscm(1-200);
array tssc[200] tssc(1-200);
array tssvl[200] tssvl(1-200);
array tssfl[200] tssfl(1-200);
array utsscm[200] utsscm(1-200);
array utssc[200] utssc(1-200);
array utssvl[200] utssvl(1-200);
array utssfl[200] utssfl(1-200);


array doccm[200] doccm(1-200);
array docc[200] docc(1-200);
array docvl[200] docvl(1-200);
array docfl[200] docfl(1-200);
array udoccm[200] udoccm(1-200);
```

COMPUTER PROGRAMMING CODE FOR THE TIME DYNAMIC MODEL (TDM)

```
array udocc[200] udocc(1-200);
array udocvl[200] udocvl(1-200);
array udocfl[200] udocfl(1-200);

array pcbtot1[200] pcbtot1(1-200);
array flux[200] flux(1-200);
array abflx[200] abflx(1-200);
/*********************************************initialize variables ************************************************************/
pi=3.1415928;
bins=200;

rate=0.0032;                                /*accounts for 1 minute time step when 99% equilibrium reached in 24 hours */
pycnrate=1.0728e-5;                              /* 1 minute time step whn  99% equilibrium across pycnocline in 64.7 days  (Kz=0.1 cm^2/sec)  */
shiprate=0.547;                              /* fraction of equilibrium with 247 minute DOC and TSS in-ship residence time */

depth=64;
pycno=15;
height=depth-pycno;

volume=(pi/4)*270*36.5*6.91*1e6;                    /* these are ship related; length width and height of ellipse */
tssvl=volume*1e-5;                             /* internal to ship */
docvl=volume*6e-7;                             /* internal to ship */
freedvol=(pi/4)*(270+0.3)*(36.5+0.3)*6.91*1e6;        /* volume that escapes (is free) from inside to outside ship each minute */
freedvol=freedvol-volume;
freedtss=freedvol*1e-5;
freeddoc=freedvol*6e-7;

if _n_=1 then begin;
  initmass=5e5;                              /* place holder for calculating percentages later */
  start=1;
  pulse=0;
  cummin=0;
  cumrel=0;
  mass=0;                                  /* I use non-indexed variables inside the ship, indexed outside. The index denotes the bin number */
  tsscm=0;
  doccm=0;
  cumloss1=0;
  cumloss2=0;
end;



if _n_=1 then do i=1 to bins;
     m=i*15;
     bigarea=(pi/4)*(270+(2*m))*(36.5+(2*m));           /* these calculated sequential external bin volumes */
     prearea=(pi/4)*(270+(2*(m-15)))*(36.5+(2*(m-15)));
```

```
    area=bigarea-prearea;
    area[i]=area;

    volume[i]=area[i]*height*1e6;
    mass[i]=0;
    conc[i]=mass[i]/volume[i];
    watfl[i]=0;
    uvol[i]=area[i]*pycno*1e6;
    umass[i]=0;
    uconc[i]=0;
    uwatfl[i]=0;

    bflux[i]=0;
    bcum[i]=0;
    bconc[i]=0;
    bvol=area*1e4*1.5*10;
    bvol[i]=bvol;
    bmax[i]=0;

    tsscm[i]=0;
    tssc[i]=0;
    tssvl[i]=volume[i]*1e-5;
    utsscm[i]=0;
    utssc[i]=0;
    utssvl[i]=uvol[i]*1e-5;


    docvl[i]=volume[i] *6e-7;
    docc[i]=0;
    doccm[i]=0;
    udocvl[i]=uvol[i] *6e-7;
    udocc[i]=0;
    udoccm[i]=0;
    pcbtot1[i]=0;
    flux[i]=0;
    abflx[i]=0;
 end;


/******************************get release rate and period input data from Rob George ************************************************************/

release=cl5;
release=release/(24*60);
prevrel=lag1(release);
period=days*24*60;
```

COMPUTER PROGRAMMING CODE FOR THE TIME DYNAMIC MODEL (TDM)

```
koc=8.61e4;                    /* this is a literature value */

sedpart=0.01*koc;              /* the 0.1 and 0.15 are fractions of organic carbon in sediment and tts; doc is 100% organic carbon */
tsspart=0.15*koc;
docpart=koc;


/***********************************************program start ************************************************************/
do min=1 to period;
   if min=1 then start=1;                          /* this is a flag to keep concentrations 0 until PCB cloud arrives in the bin */
   if min=1 and prevrel<>0 and prevrel<>. then start=0;
   if min=1 then pulse=pulse+1;
   cummin=cummin+1;
   cumday=cummin/1440;
   cumday=int(cumday);                              /* I round here for daily mean calculations, otherwise I ran into a MALLOC memory bug */
/*********************************************inside the boat; variables lack index values ********************/
   cumrel=cumrel+release;
   mass=mass+release;
   conc=mass/volume;
   tssc=tsscm/tssvl;
   docc=doccm/docvl;

   shippcb=mass+tsscm+doccm;                            /* total mass released inside the ship */

    watequi=shippcb/ (volume+(tssvl*koc*0.15)+(docvl*koc*1));      /* equilibrium distributions of total mass released in ship */
    tssequi=watequi*koc*0.15;
    docequi=watequi*koc*1.0;

     watfl=shiprate*(watequi-conc)*volume;                  /* flux necessary to reach equilibrium conditions, but limited by what's allowed after 247 minutes */
     tssfl=shiprate*(tssequi-tssc)*tssvl;
     docfl=shiprate*( docequi-docc)*docvl;

     flux=watfl+tssfl+docfl;
     abflx=abs(watfl)+abs(tssfl)+abs(docfl);

     if flux<0 then begin;                          /*if desorption too fast, slow it down */
         brake=(abflx+flux)/(abflx-flux);                /* always the case */
         if watfl<0 then watfl=watfl*brake;               /* without this brake, water desorbs ~12% more Cl5 mass than can be adsorbed */
         if tssfl<0 then tssfl=tssfl*brake;
         if docfl<0 then docfl=docfl*brake;
    end;

    if flux>0 then begin;                           /*if adsorption too fast, slow it down - never seen to occur */
         brake=(abflx-flux)/(abflx+flux);
         if watfl>0 then watfl=watfl*brake;
         if tssfl>0 then tssfl=tssfl*brake;
```

```
        if docfl>0 then docfl=docfl*brake;
    end;

    mass=mass+watfl;                                /* calculate the new mass distribution and concentrations */
    conc=mass/volume;

    tsscm=tsscm+tssfl;
    tssc=tsscm/tssvl;

    doccm=doccm+docfl;
    docc=doccm/docvl;
/*********************** what leaves the ship at 0.15 m/min in water tss and doc ****************************/
    freedpcb=(conc*freedvol)+(tssc*freedtss)+(docc*freeddoc);   /*total pcbs freed from ship */

    mass=mass-(conc*freedvol);
    conc=mass/volume;

    tsscm=tsscm-(tssc*freedtss);
    tssc=tsscm/tssvl;

    doccm=doccm-(docc*freeddoc);
    docc=doccm/docvl;

/*************************************************first bin ***************************************************************/
    do i=1 to bins;
        m=i*15;
        if i=1 then begin;
        uconc[i]=0;
        udocc[i]=0;
        utssc[i]=0;
/*************************************************ship release  and dilution   ***************************************/
            mass[i]=conc*freedvol;
            conc[i]=mass[i]/volume[i];

            tsscm[i]=tssc*freedtss;
            tssc[i]=tsscm[i]/tssvl[i];

            doccm[i]=docc*freeddoc;
            docc[i]=doccm[i]/docvl[i];
/******************determine PCB mass in bin, above nd below pycnocline ******************************************/

mass[i]=conc[i]*volume[i];
umass[i]=uconc[i]*uvol[i];
tsscm[i]=tssc[i]*tssvl[i];
doccm[i]=docc[i]*docvl[i];
udoccm[i]=udocc[i]*udocvl[i];
```

COMPUTER PROGRAMMING CODE FOR THE TIME DYNAMIC MODEL (TDM)

```
utsscm[i]=utssc[i]*utssvl[i];
bcum[i]=bconc[i]*bvol[i];

pcbtot1[i]=mass[i]+bcum[i]+tsscm[i]+doccm[i]+umass[i]+utsscm[i]+udoccm[i];  /*this is the starting mass to be redistributed */

r0=0.57*bmax[i];                          /* these are Di Toro and Horzempa's (1982) retention terms */
px=(1/2.3)*koc*0.01;

/****************************************determine equilibrium concentrations ****************************************/


if bconc[i]>=bmax[i] then begin;
   watequi=pcbtot1[i]/ ((volume[i]+uvol[i])+bvol[i]*koc*0.01+((tssvl[i]+utssvl[i])*koc*0.15)+((docvl[i]+udocvl[i])*koc*1));
   sedequi=watequi*koc*0.01;
end;

if bconc[i]<bmax[i] then begin;
   watequi=(pcbtot1[i]-r0*bvol[i])/ ((volume[i]+uvol[i])+bvol[i]*px+((tssvl[i]+utssvl[i])*koc*0.15)+((docvl[i]+udocvl[i])*koc*1));
   sedequi=r0+watequi*px;
end;

tssequi=watequi*koc*0.15;
docequi=watequi*koc*1.0;
upwateq=watequi;
uptsseq=watequi*koc*0.15;
updoceq=watequi*koc*1.0;

/***********************determine fluxes occurring in 1 minute ****************************************************/


 watfl[i]=rate*(watequi-conc[i])*volume[i];
 bflux[i]=rate*(sedequi-bconc[i])*bvol[i];
 tssfl[i]=rate*(tssequi-tssc[i])*tssvl[i];
 docfl[i]=rate*(docequi-docc[i])*docvl[i];
 uwatfl[i]=pycnrate*(upwateq-uconc[i])*uvol[i];
 utssfl[i]=pycnrate*(uptsseq-utssc[i])*utssvl[i];
 udocfl[i]=pycnrate*(updoceq-udocc[i])*udocvl[i];

flux[i]=watfl[i]+bflux[i]+tssfl[i]+docfl[i]+uwatfl[i]+utssfl[i]+udocfl[i];
abflx[i]=abs(watfl[i])+abs(bflux[i])+abs(tssfl[i])+abs(docfl[i])+abs(uwatfl[i])+abs(utssfl[i])+abs(udocfl[i]);



if flux[i]<0 then begin;                          /*if desorption too fast, slow it down */
   brake=(abflx[i]+flux[i])/(abflx[i]-flux[i]);
   if watfl[i]<0 then watfl[i]=watfl[i]*brake;
```

```
    if bflux[i]<0 then bflux[i]=bflux[i]*brake;          /* flux (net flux) is <>0 except when there is no loading */
    if tssfl[i]<0 then tssfl[i]=tssfl[i]*brake;
    if docfl[i]<0 then docfl[i]=docfl[i]*brake;
    if uwatfl[i]<0 then uwatfl[i]=uwatfl[i]*brake;
    if utssfl[i]<0 then utssfl[i]=utssfl[i]*brake;
    if udocfl[i]<0 then udocfl[i]=udocfl[i]*brake;
end;

if flux[i]>0 then begin;                          /*if adsorption too fast, slow it down - not observed  */
    brake=(abflx[i]-flux[i])/(abflx[i]+flux[i]);
    if watfl[i]>0 then watfl[i]=watfl[i]*brake;
    if bflux[i]>0 then bflux[i]=bflux[i]*brake;
    if tssfl[i]>0 then tssfl[i]=tssfl[i]*brake;
    if docfl[i]>0 then docfl[i]=docfl[i]*brake;
    if uwatfl[i]>0 then uwatfl[i]=uwatfl[i]*brake;
    if utssfl[i]>0 then utssfl[i]=utssfl[i]*brake;
    if udocfl[i]>0 then udocfl[i]=udocfl[i]*brake;
end;

  mass[i]=mass[i]+watfl[i];                       /* calculate the new mass distribution and concentrations */
  conc[i]=mass[i]/volume[i];

  bcum[i]=bcum[i]+bflux[i];
  bconc[i]=bcum[i]/bvol[i];
  if bconc[i]>bmax[i] then bmax[i]=bconc[i];

  tsscm[i]=tsscm[i]+tssfl[i];
  tssc[i]=tsscm[i]/tssvl[i];

  doccm[i]=doccm[i]+docfl[i];
  docc[i]=doccm[i]/docvl[i];

  umass[i]=umass[i]+uwatfl[i];
  uconc[i]=umass[i]/uvol[i];

  utsscm[i]=utsscm[i]+utssfl[i];
  utssc[i]=utsscm[i]/utssvl[i];

  udoccm[i]=udoccm[i]+udocfl[i];
  udocc[i]=udoccm[i]/udocvl[i];

end;                                                  /* end of bins=1 loop */
/************************************************** all the other bins ****************************************************************/
/******************determine PCB mass in bin, above and below pycnocline ****************************************/
else begin;
```

```
            if i>min and start=1 then mass[i]=0;  else mass[i]=mass[i-1]; conc[i]=mass[i]/volume[i];
            if i>min and start=1 then umass[i]=0;  else umass[i]=umass[i-1]; uconc[i]=umass[i]/uvol[i];
            if i>min and start=1 then doccm[i]=0; else doccm[i]=doccm[i-1] ; docc[i]=doccm[i]/docvl[i];
            if i>min and start=1 then tsscm[i]=0; else tsscm[i]=tsscm[i-1] ; tssc[i]=tsscm[i]/tssvl[i];
            if i>min and start=1 then udoccm[i]=0; else udoccm[i]=udoccm[i-1] ;  udocc[i]=udoccm[i]/udocvl[i];
            if i>min and start=1 then utsscm[i]=0; else utsscm[i]=utsscm[i-1] ; utssc[i]=utsscm[i]/utssvl[i];

r0=0.57*bmax[i];
px=(1/2.3)*koc*0.01;

pcbtot1[i]=mass[i]+bcum[i]+tsscm[i]+doccm[i]+umass[i]+utsscm[i]+udoccm[i];

/****************************************determine equilibrium concentrations ****************************************/

if bconc[i]>=bmax[i] then begin;
   watequi=pcbtot1[i]/ ((volume[i]+uvol[i])+bvol[i]*koc*0.01+((tssvl[i]+utssvl[i])*koc*0.15)+((docvl[i]+udocvl[i])*koc*1));
   sedequi=watequi*koc*0.01;
end;

if bconc[i]<bmax[i] then begin;
   watequi=(pcbtot1[i] - r0*bvol[i]) / ((volume[i]+uvol[i])+bvol[i]*px+((tssvl[i]+utssvl[i])*koc*0.15)+((docvl[i]+udocvl[i])*koc*1));
   sedequi=r0+watequi*px;
end;

tssequi=watequi*koc*0.15;
docequi=watequi*koc*1.0;
upwateq=watequi;
uptsseq=watequi*koc*0.15;
updoceq=watequi*koc*1.0;

/***********************determine fluxes occurring in 1 minute ****************************************************/

  watfl[i]=rate*(watequi-conc[i])*volume[i];
  bflux[i]=rate*(sedequi-bconc[i])*bvol[i];
  tssfl[i]=rate*(tssequi-tssc[i])*tssvl[i];
  docfl[i]=rate*(docequi-docc[i])*docvl[i];
  uwatfl[i]=pycnrate*(upwateq-uconc[i])*uvol[i];
  utssfl[i]=pycnrate*(uptsseq-utssc[i])*utssvl[i];
  udocfl[i]=pycnrate*(updoceq-udocc[i])*udocvl[i];

flux[i]=watfl[i]+bflux[i]+tssfl[i]+docfl[i]+uwatfl[i]+utssfl[i]+udocfl[i];
abflx[i]=abs(watfl[i])+abs(bflux[i])+abs(tssfl[i])+abs(docfl[i])+abs(uwatfl[i])+abs(utssfl[i])+abs(udocfl[i]);


if flux[i]<0 then begin;                          /*if desorption too fast, slow it down */
   brake=(abflx[i]+flux[i])/(abflx[i]-flux[i]);
```

```
    if watfl[i]<0 then watfl[i]=watfl[i]*brake;
    if bflux[i]<0 then bflux[i]=bflux[i]*brake;
    if tssfl[i]<0 then tssfl[i]=tssfl[i]*brake;
    if docfl[i]<0 then docfl[i]=docfl[i]*brake;
    if uwatfl[i]<0 then uwatfl[i]=uwatfl[i]*brake;
    if utssfl[i]<0 then utssfl[i]=utssfl[i]*brake;
    if udocfl[i]<0 then udocfl[i]=udocfl[i]*brake;
end;

if flux[i]>0 then begin;                          /*if adsorption too fast, slow it down */
    brake=(abflx[i]-flux[i])/(abflx[i]+flux[i]);
    if watfl[i]>0 then watfl[i]=watfl[i]*brake;
    if bflux[i]>0 then bflux[i]=bflux[i]*brake;
    if tssfl[i]>0 then tssfl[i]=tssfl[i]*brake;
    if docfl[i]>0 then docfl[i]=docfl[i]*brake;
    if uwatfl[i]>0 then uwatfl[i]=uwatfl[i]*brake;
    if utssfl[i]>0 then utssfl[i]=utssfl[i]*brake;
    if udocfl[i]>0 then udocfl[i]=udocfl[i]*brake;
end;

  mass[i]=mass[i]+watfl[i];
  conc[i]=mass[i]/volume[i];

  bcum[i]=bcum[i]+bflux[i];
  bconc[i]=bcum[i]/bvol[i];
  if bconc[i]>bmax[i] then bmax[i]=bconc[i];

  tsscm[i]=tsscm[i]+tssfl[i];
  tssc[i]=tsscm[i]/tssvl[i];

  doccm[i]=doccm[i]+docfl[i];
  docc[i]=doccm[i]/docvl[i];

  umass[i]=umass[i]+uwatfl[i];
  uconc[i]=umass[i]/uvol[i];

  utsscm[i]=utsscm[i]+utssfl[i];
  utssc[i]=utsscm[i]/utssvl[i];

  udoccm[i]=udoccm[i]+udocfl[i];
  udocc[i]=udoccm[i]/udocvl[i];

 end;                                              /* end of the bins loop, out at 3 km */
/*****************************************************************budget stuff:  pickup at the edge of the world for cumloss 2  *******************/
        if i=bins then begin;
             watloss=mass[i];
```

```
            tssloss=tssc[i]*tssvl[i];
            docloss=docc[i]*docvl[i];
            uwatloss=umass[i];
            utssloss=utssc[i]*utssvl[i];
            udocloss=udocc[i]*udocvl[i];
        end;
   exitloss=watloss+tssloss+docloss+uwatloss+utssloss+udocloss;  /* this will leave the model in the next iteration */
   end;
/*****************************************************************more budget stuff, pickup load inside model domain ****************************/
   cumwater=0;
   cumsed=0;
   cumtss=0;
   cumdoc=0;
   upcumwat=0;
   upcumtss=0;
   upcumdoc=0;
   do i=1 to bins;
      cumwater=cumwater+mass[i];
      upcumwat=upcumwat+umass[i];
      cumsed=cumsed+bcum[i];
      upcumtss=upcumtss+utsscm[i];
      cumtss=cumtss+tsscm[i];
      cumdoc=cumdoc+doccm[i];
      upcumdoc=upcumdoc+udoccm[i];
   end;
   shipmass=initmass-cumrel;
   modelmass=mass+tsscm+doccm+
            cumwater+cumsed+cumtss+cumdoc+upcumwat+upcumtss+upcumdoc;  /* PCB mass in model domain */
   cumloss1=cumrel-modelmass;                                  /* one calculation of what's leaving */
   cumloss2=cumloss2+exitloss;                                 /* the other calculation of what's leaving - hopefully they're pretty close */
  output;
end;
run;

/************* calculate daily means and export for graphics. Bin 63 was a maximum range for tss in an earlier model, I keep it for reference now****/

unistat;
set c:\pcb\simul\bigfiles\cl5ship(buffer=65535);
var shippcb conc tssc docc;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5ship mean=shippcb conc tssc docc;
run;


compute;
in=c:\pcb\simul\bigfiles\cl5sed.dbs
```

```
   out=c:\pcb\simul\bigfiles\cl5sed.ascii2(buffer=65535);
order pulse release cumday cummin bconc1 bconc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5sed(buffer=65535);
var bconc1-bconc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5sed mean=bconc1-bconc200;
run;


compute;
in=c:\pcb\simul\bigfiles\cl5wat.dbs
   out=c:\pcb\simul\bigfiles\cl5wat.ascii2(buffer=65535);
order pulse release cumday cummin conc1 conc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5wat(buffer=65535);
var conc1-conc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5wat mean=conc1-conc200;
run;

compute;
in=c:\pcb\simul\bigfiles\cl5upperwat.dbs
   out=c:\pcb\simul\bigfiles\cl5upperwat.ascii2(buffer=65535);
order pulse release cumday cummin uconc1 uconc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5upperwat(buffer=65535);
var uconc1-uconc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5uwat mean=uconc1-uconc200;
run;

compute;
in=c:\pcb\simul\bigfiles\cl5tss.dbs
   out=c:\pcb\simul\bigfiles\cl5tss.ascii2(buffer=65535);
order pulse release cumday cummin tssc1 tssc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5tss(buffer=65535);
```

COMPUTER PROGRAMMING CODE FOR THE TIME DYNAMIC MODEL (TDM)

```
var tssc1-tssc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5tss mean=tssc1-tssc200;
run;


compute;
in=c:\pcb\simul\bigfiles\cl5uppertss.dbs
   out=c:\pcb\simul\bigfiles\cl5uppertss.ascii2(buffer=65535);
order pulse release cumday cummin utssc1 utssc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5uppertss(buffer=65535);
var utssc1-utssc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5utss mean=utssc1-utssc200;
run;

compute;
in=c:\pcb\simul\bigfiles\cl5doc.dbs
   out=c:\pcb\simul\bigfiles\cl5doc.ascii2(buffer=65535);
order pulse release cumday cummin docc1 docc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5doc(buffer=65535);
var docc1-docc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5doc mean=docc1-docc200;
run;


compute;
in=c:\pcb\simul\bigfiles\cl5upperdoc.dbs
   out=c:\pcb\simul\bigfiles\cl5upperdoc.ascii2(buffer=65535);
order pulse release cumday cummin udocc1 udocc63;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5upperdoc(buffer=65535);
var udocc1-udocc200;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5udoc mean=udocc1-udocc200;
run;
```

COMPUTER PROGRAMMING CODE FOR THE TIME DYNAMIC MODEL (TDM)

```
compute;
in=c:\pcb\simul\bigfiles\cl5bud.dbs
   out=c:\pcb\simul\bigfiles\cl5budget.ascii2(buffer=65535);
order pulse release cumday cummin shipmass cumrel cumwater upcumwat cumsed cumtss upcumtss cumdoc upcumdoc cumloss1 cumloss2;
run;

unistat;
set c:\pcb\simul\bigfiles\cl5bud(buffer=65535);
var shipmass cumrel cumwater upcumwat cumsed cumtss upcumtss cumdoc upcumdoc cumloss1 cumloss2;
class cumday _lowest_;
output c:\pcb\simul\daymean\cl5bud mean=shipmass cumrel cumwater upcumwat cumsed cumtss upcumtss cumdoc upcumdoc cumloss1 cumloss2;
run;


exit;
```

Figure B 1 - Total PCB in Water Below Pycnocline

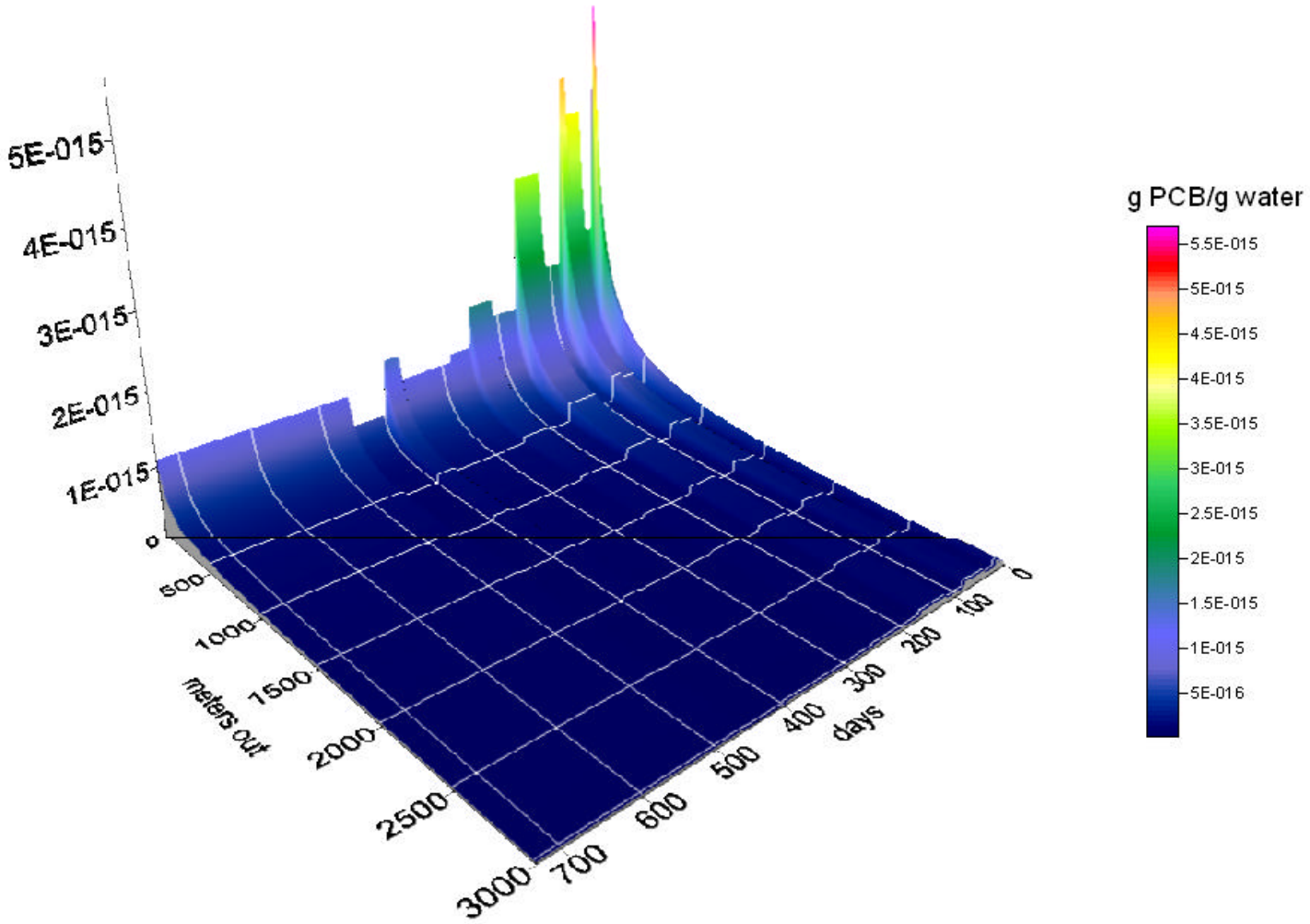

Figure B 2 - Monochlorobiphenyl in Water below Pycnocline

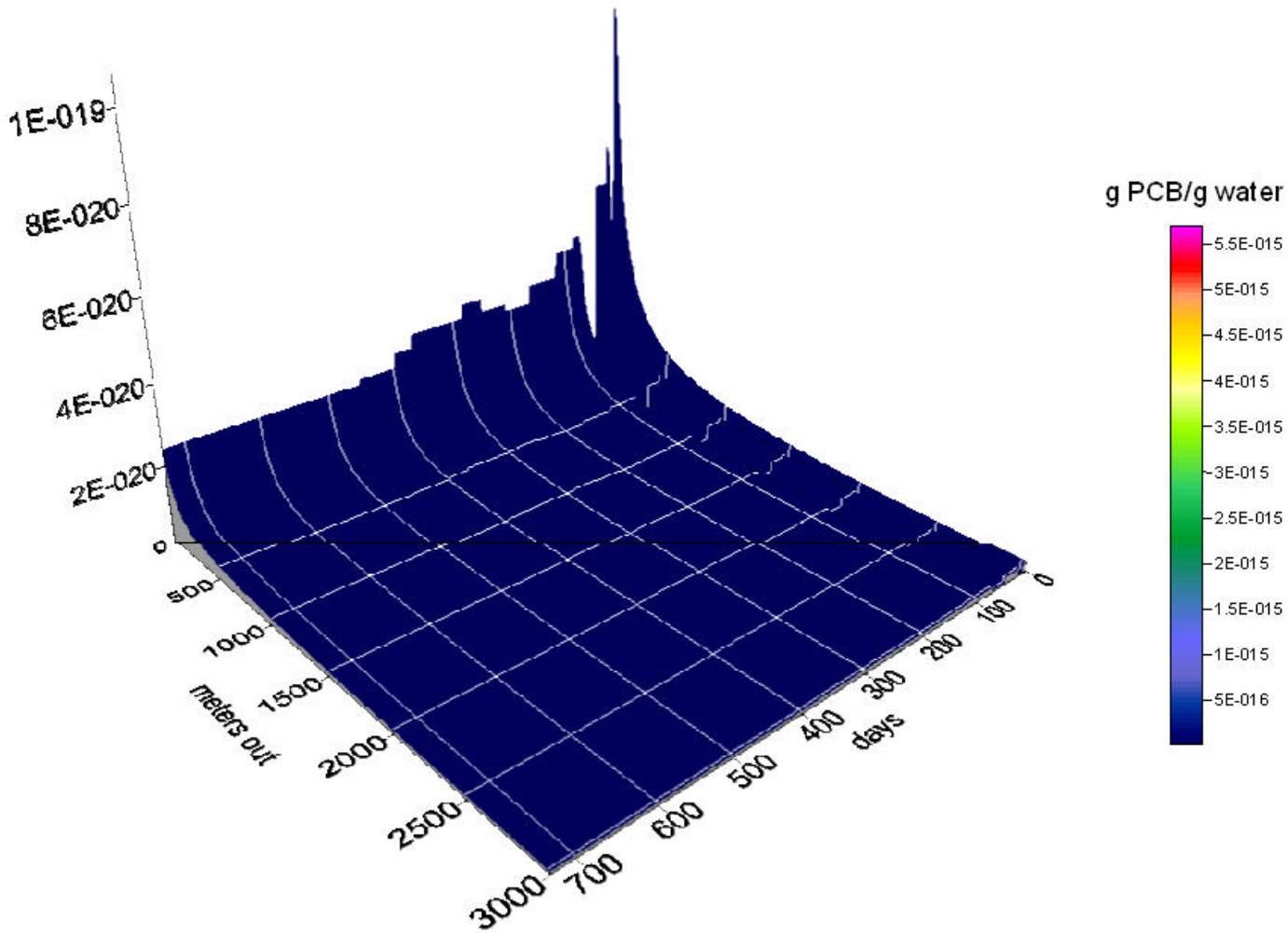

Figure B 3 - Dichlorobiphenyl in Water below Pycnocline

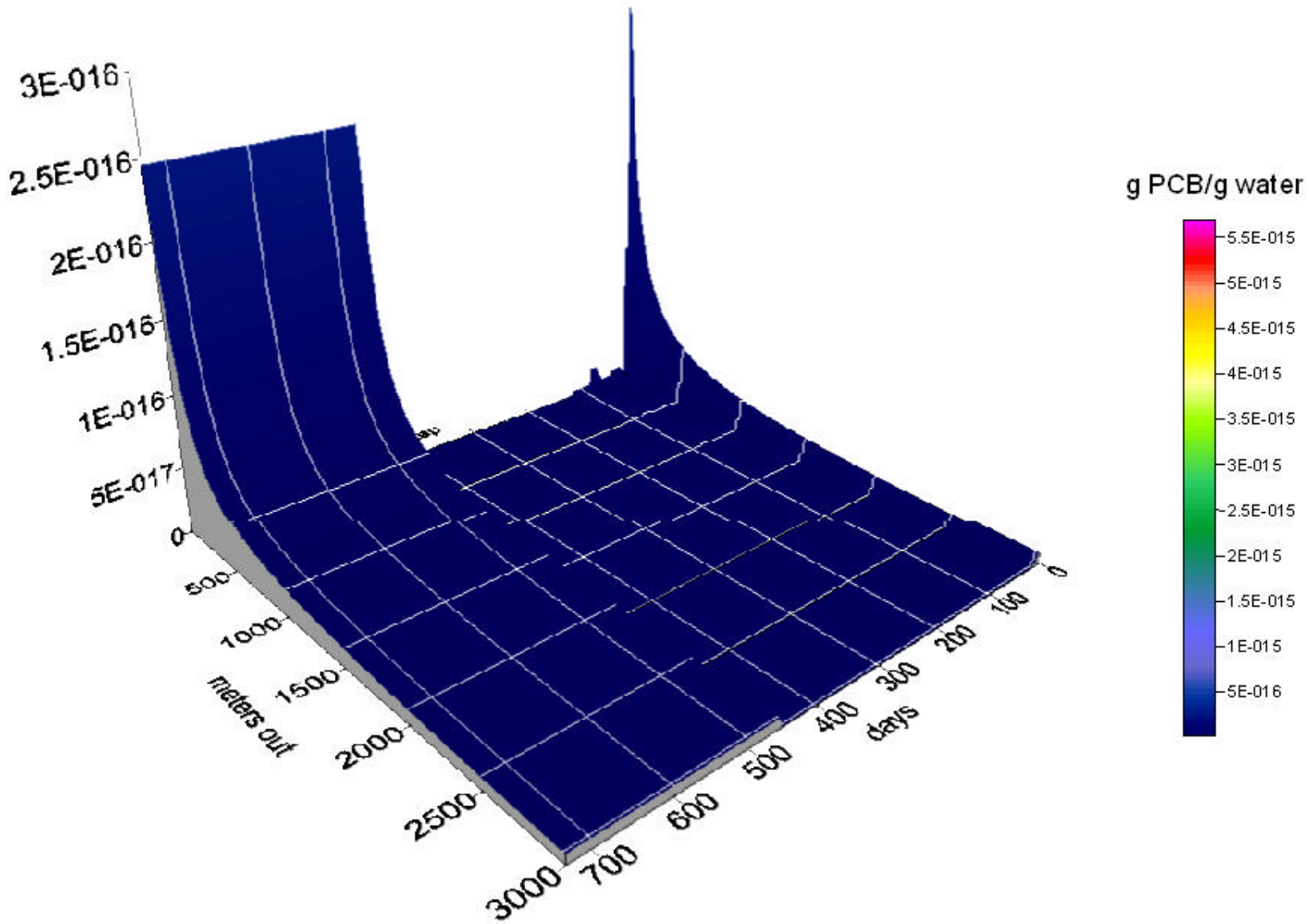

Figure B 4 - Trichlorobiphenyl in Water below Pycnocline

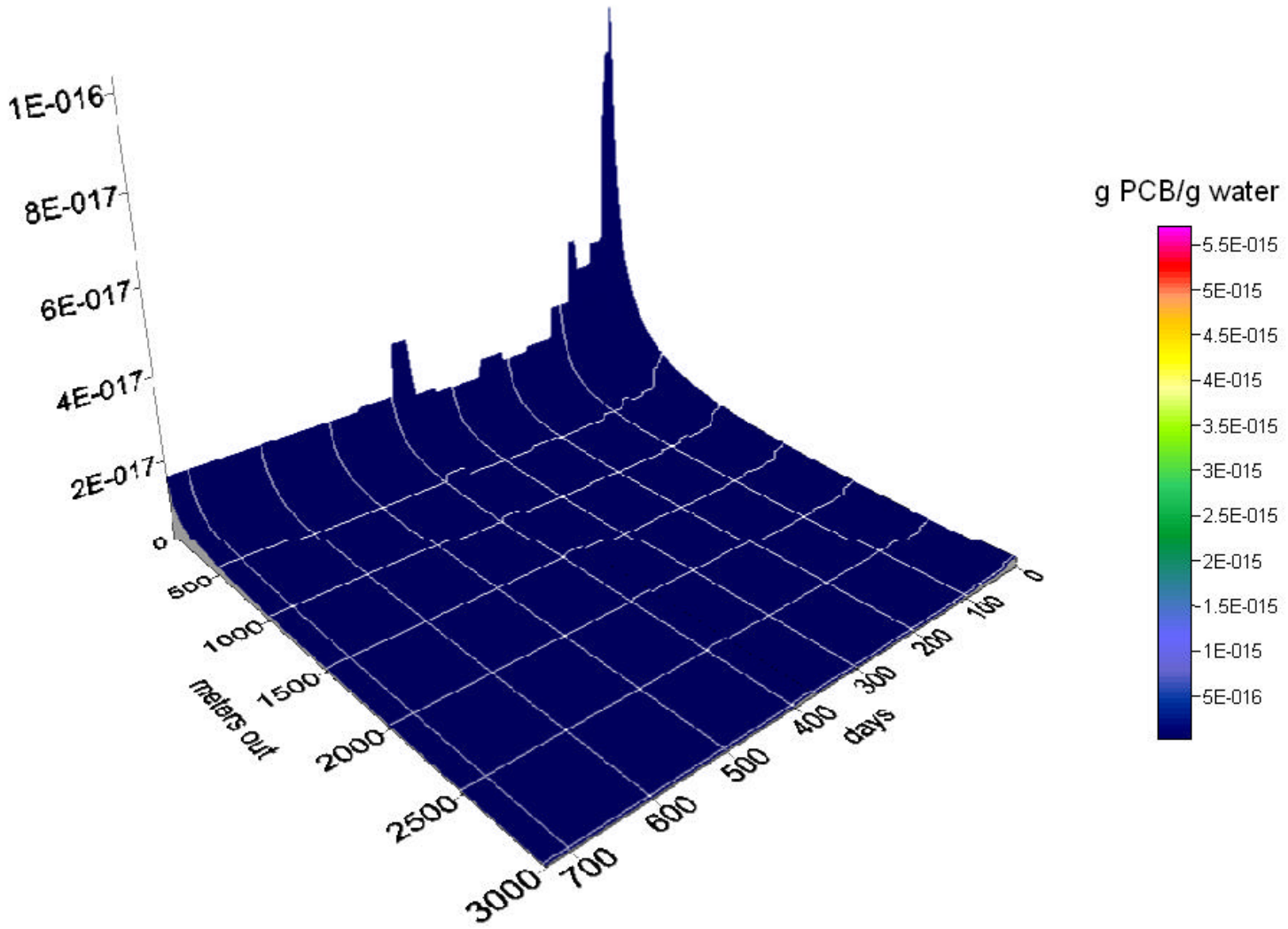

Figure B 5 - Tetrachlorobiphenyl in Water below Pycnocline

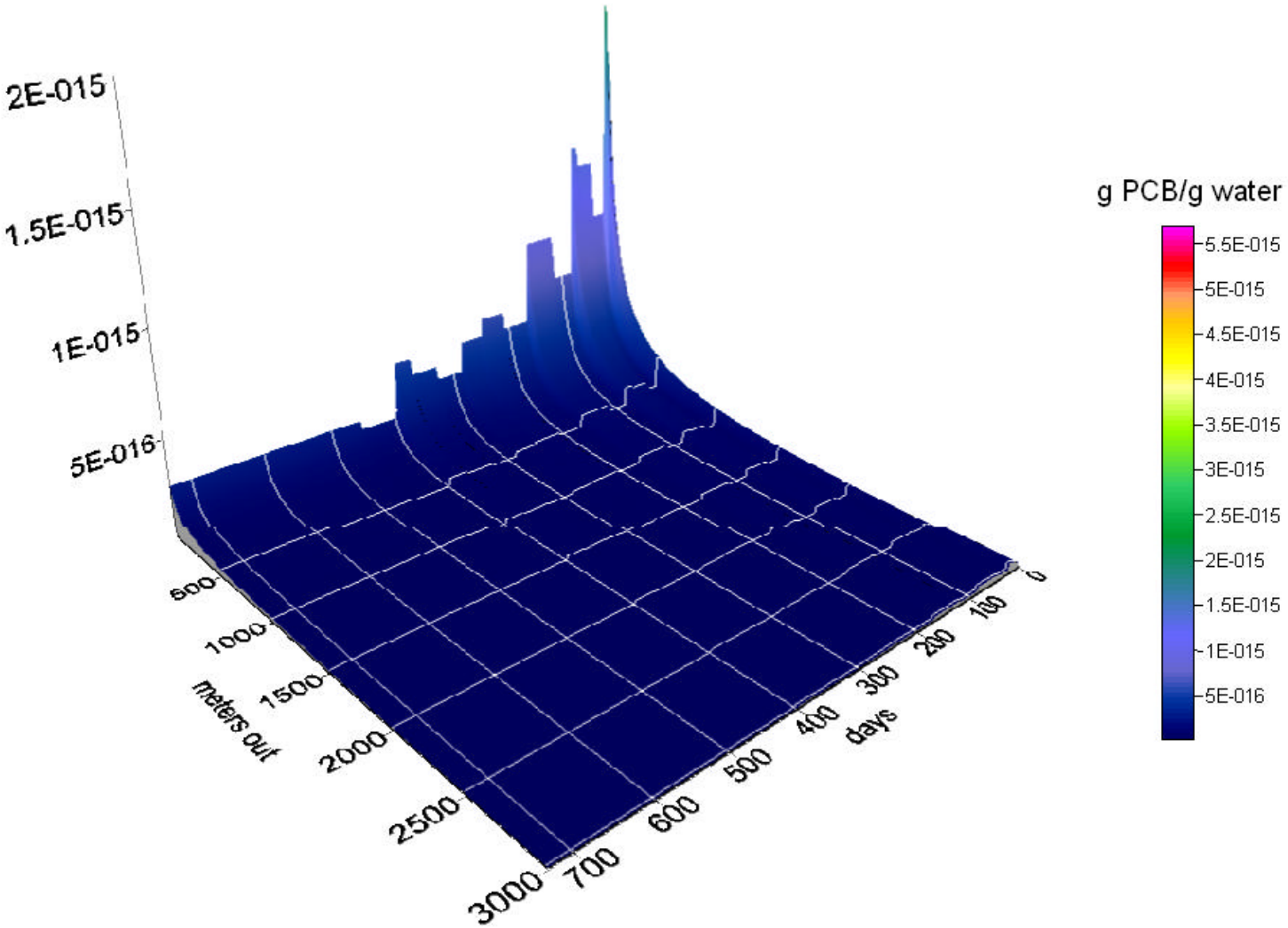

Figure B 6 - Pentachlorobiphenyl in Water below Pycnocline

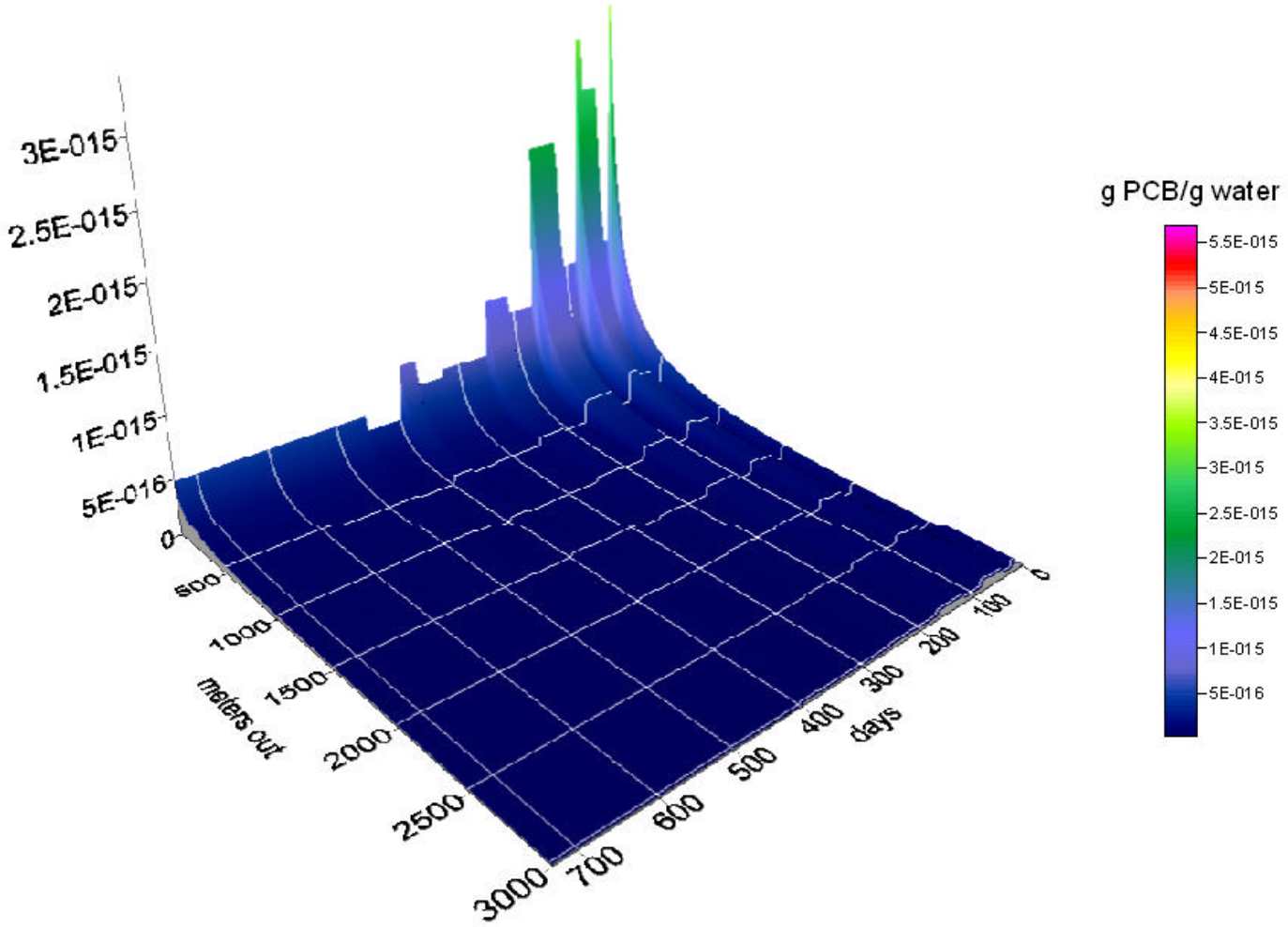

Figure B 7 - Hexachlorobiphenyl in Water below Pycnocline

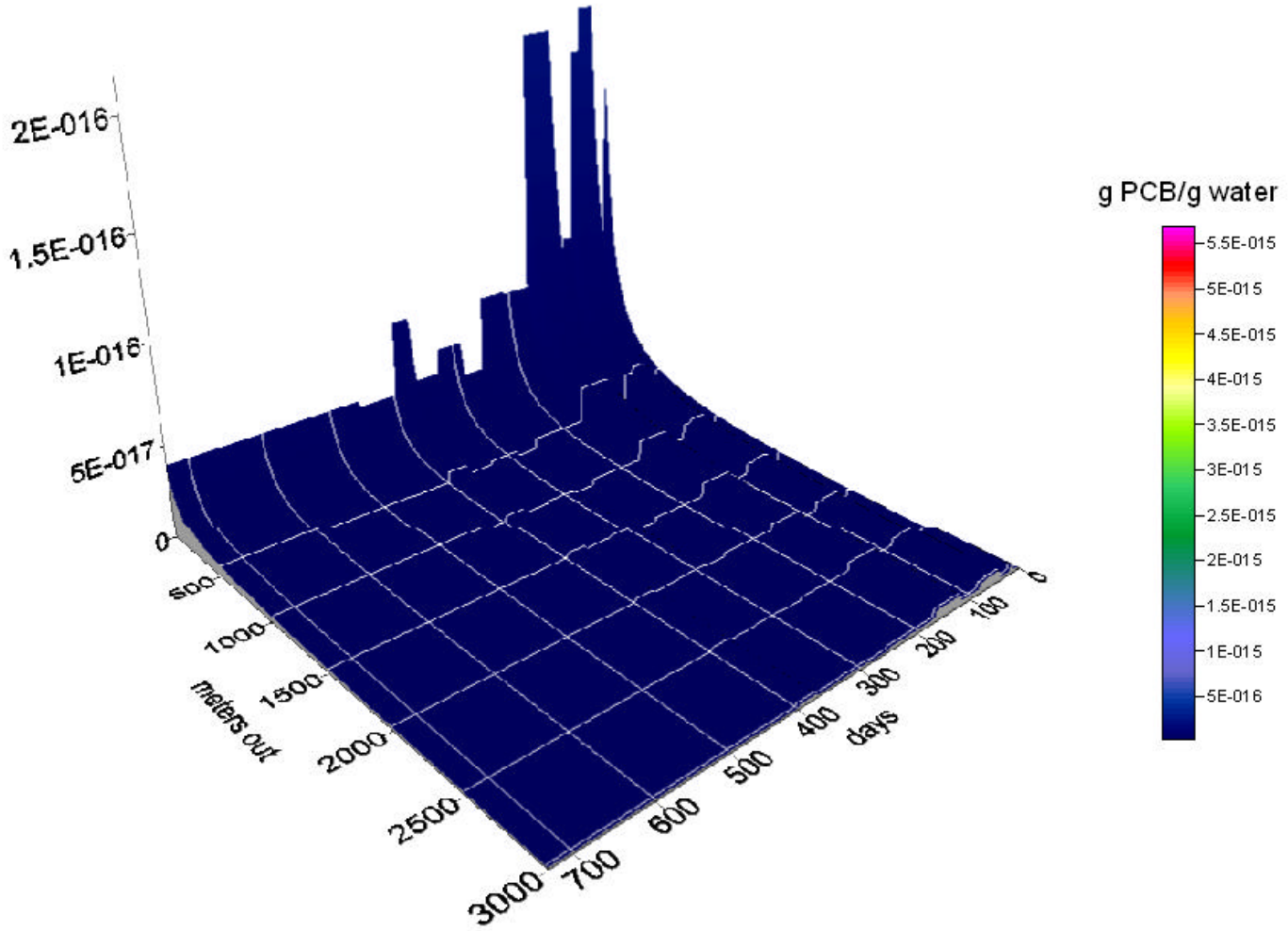

Figure B 8 - Heptachlorobiphenyl in Water below Pycnocline

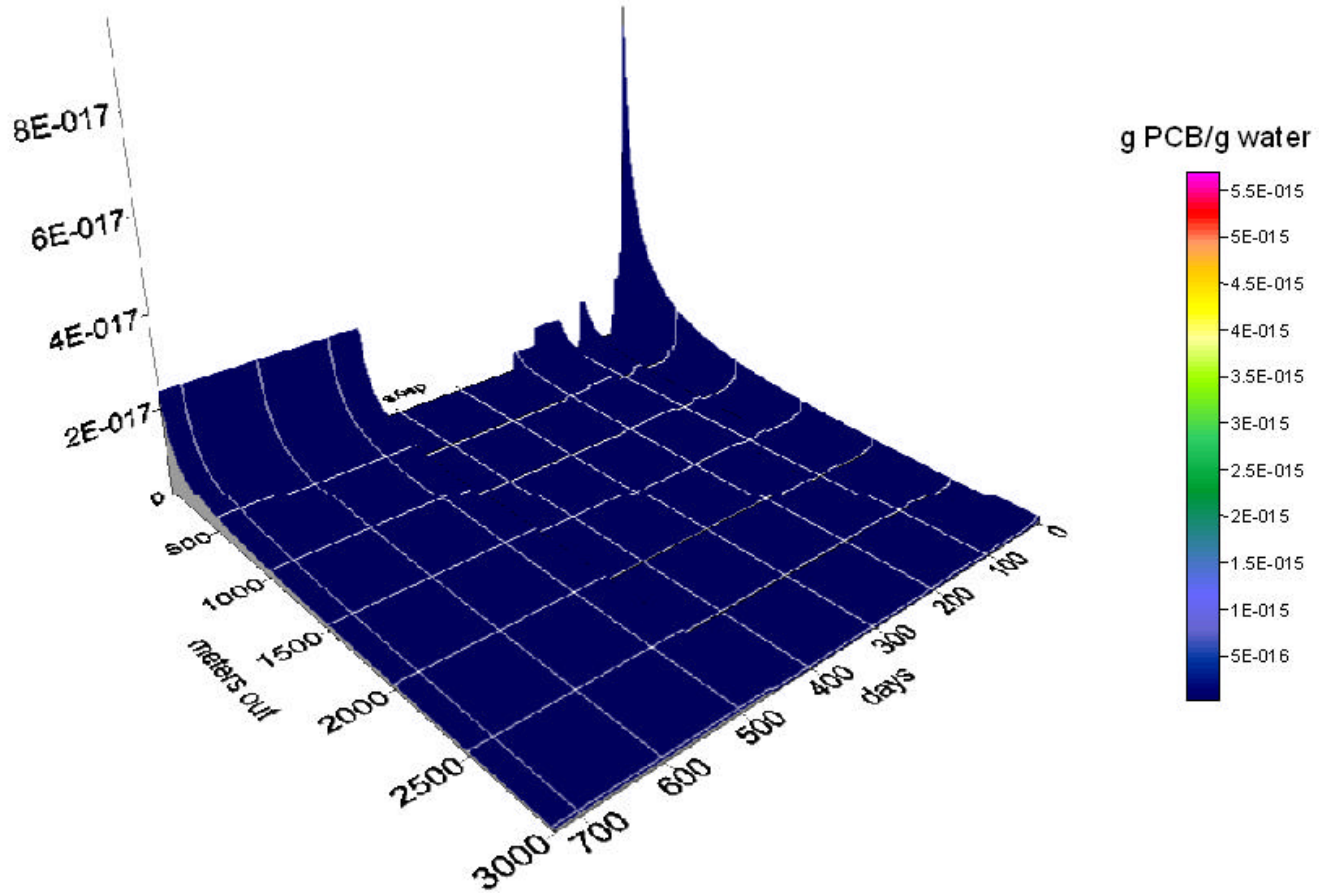

Figure B 9 - Nonachlorobiphenyl in Water below Pycnocline

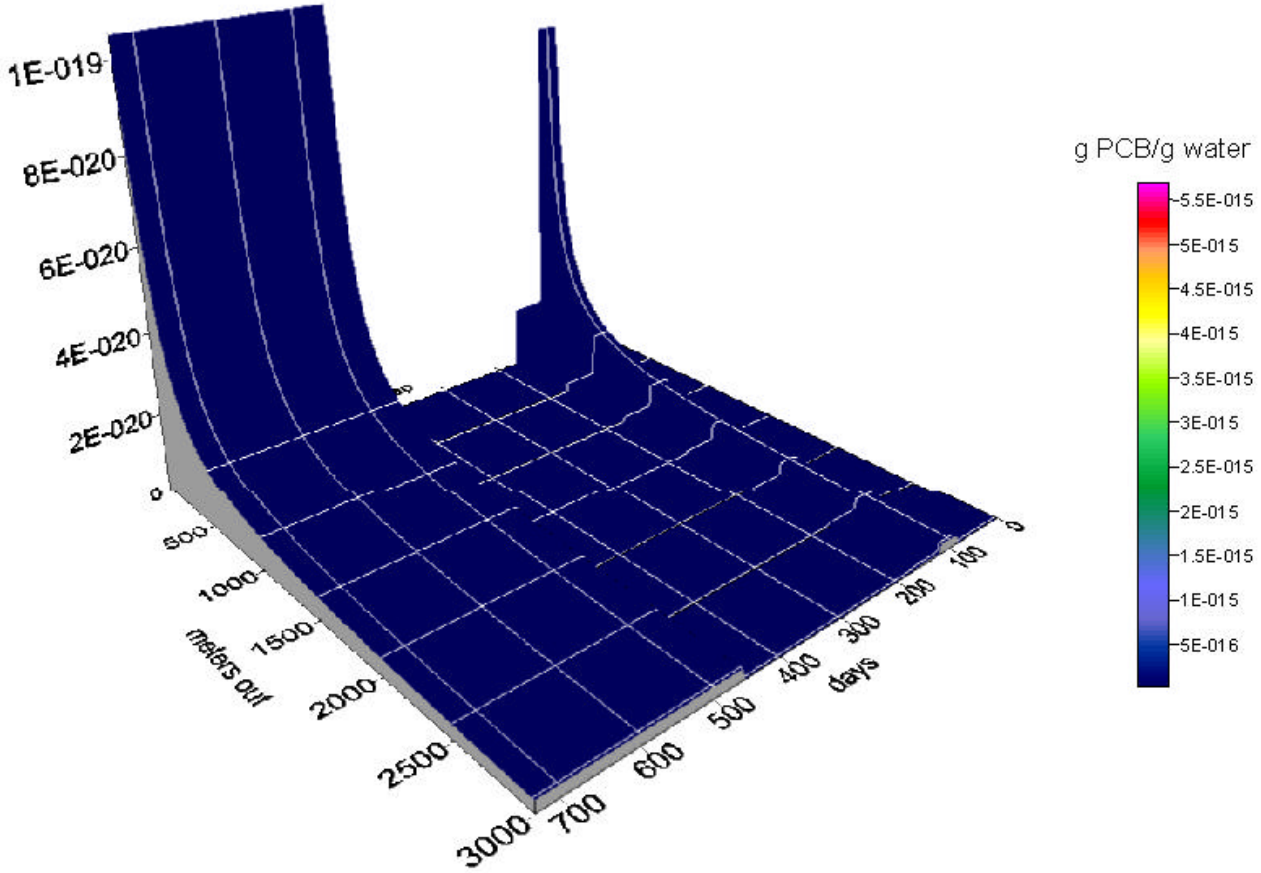

Figure B 10 - Decachlorobiphenyl in Water below Pycnocline

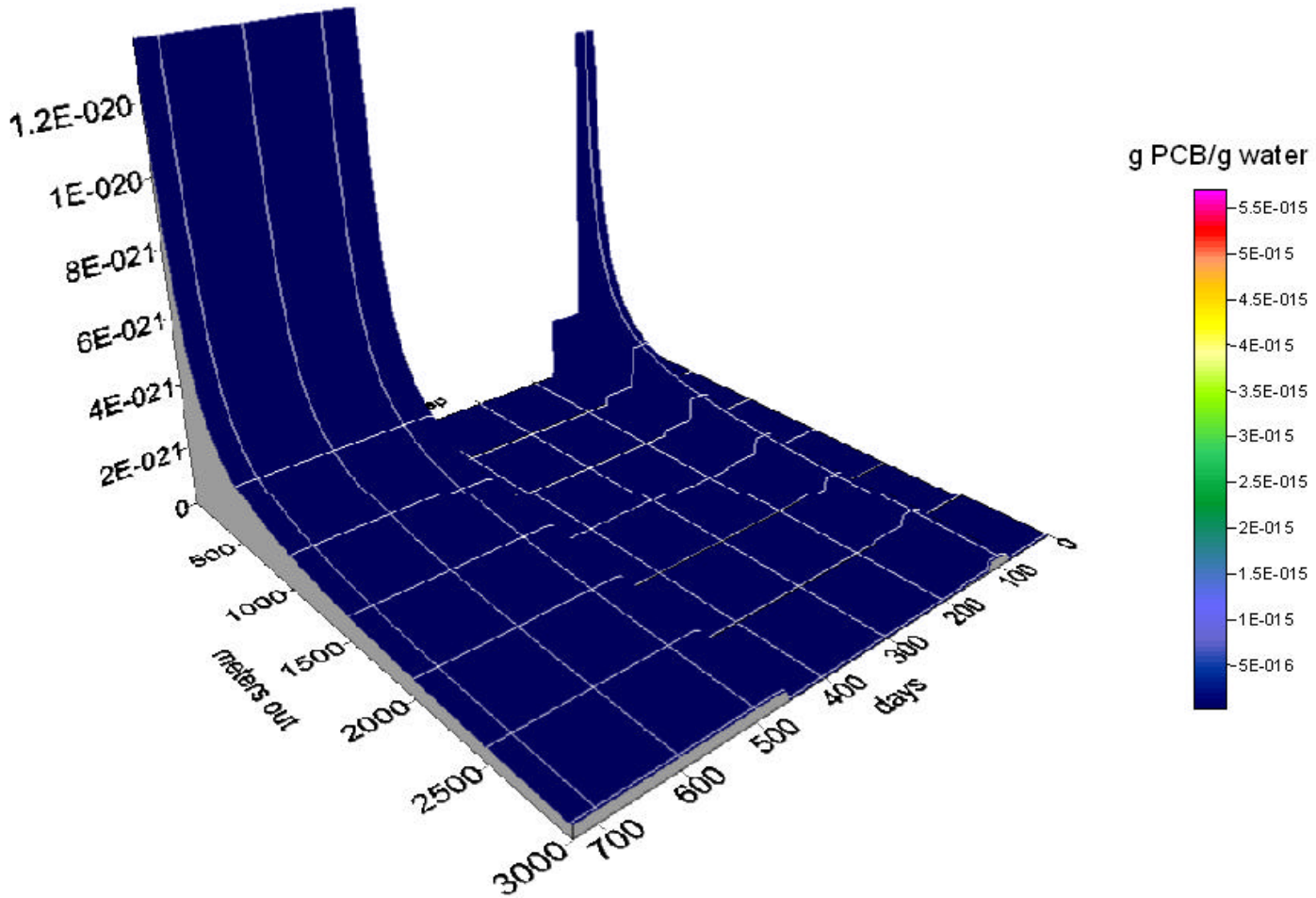

Figure B 11 - Total PCB in DOC below Pycnocline

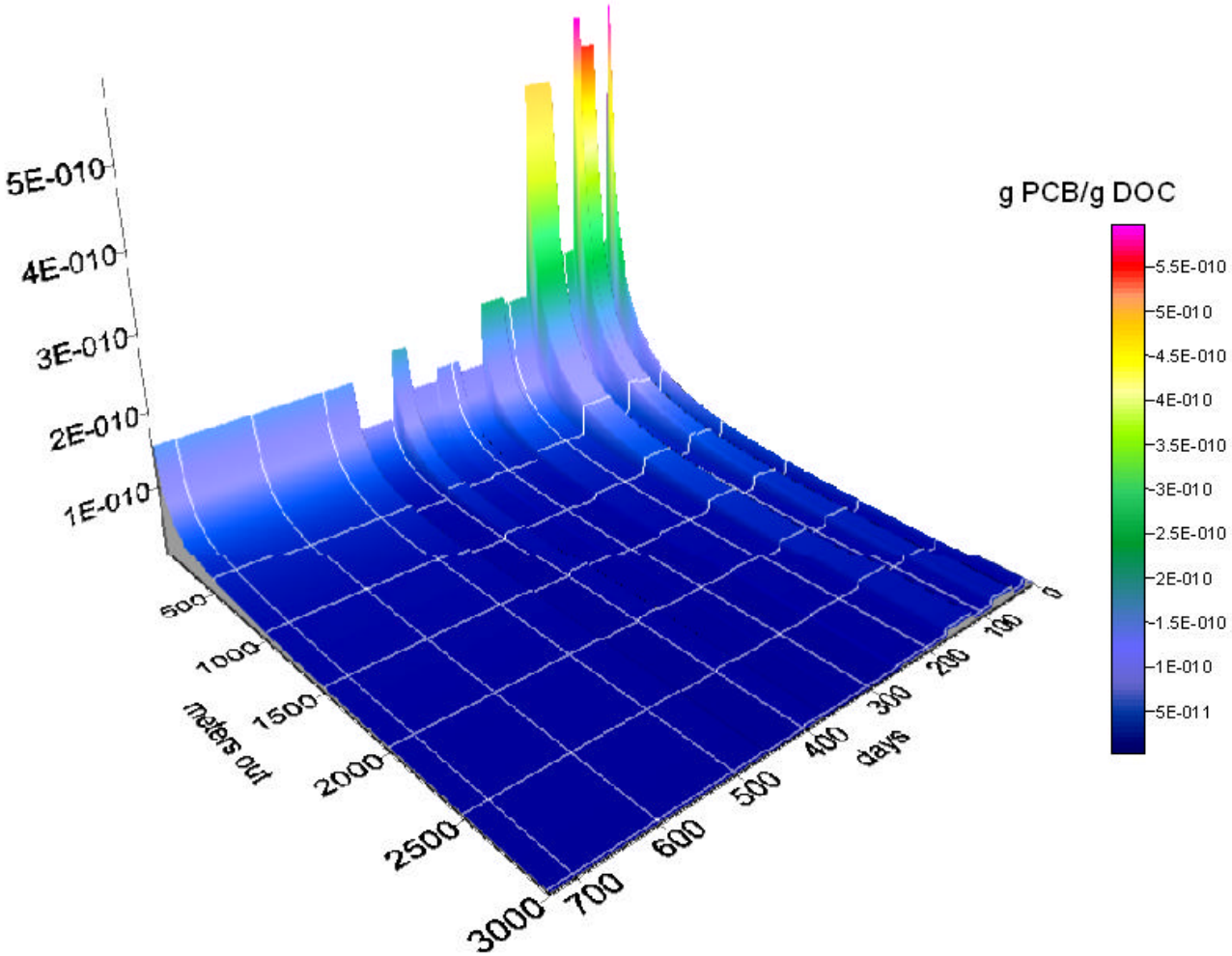

Figure B 12 – Monochlorobiphenyl in DOC below Pycnocline

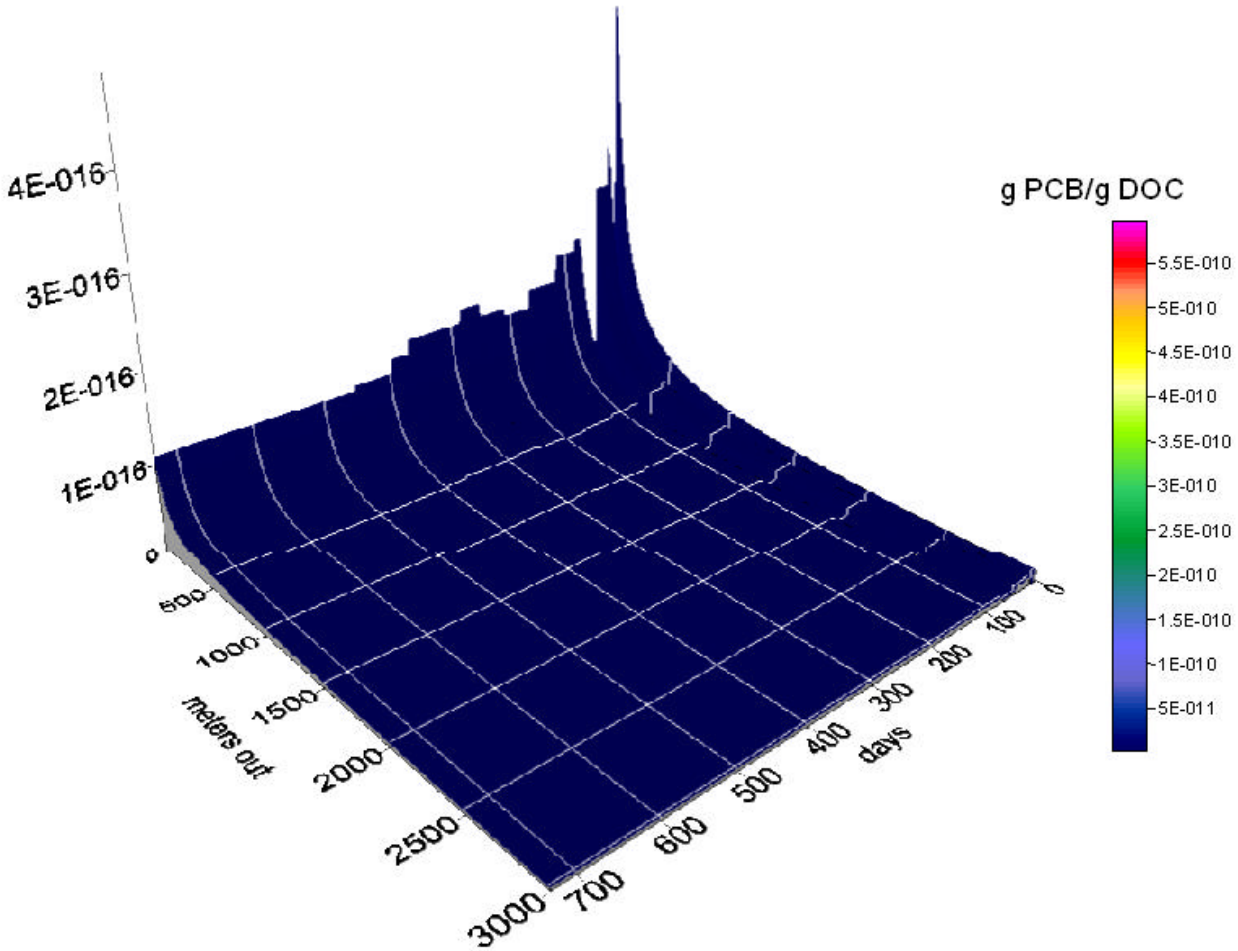

Figure B 13 - Dichlorobiphenyl in DOC below Pycnocline

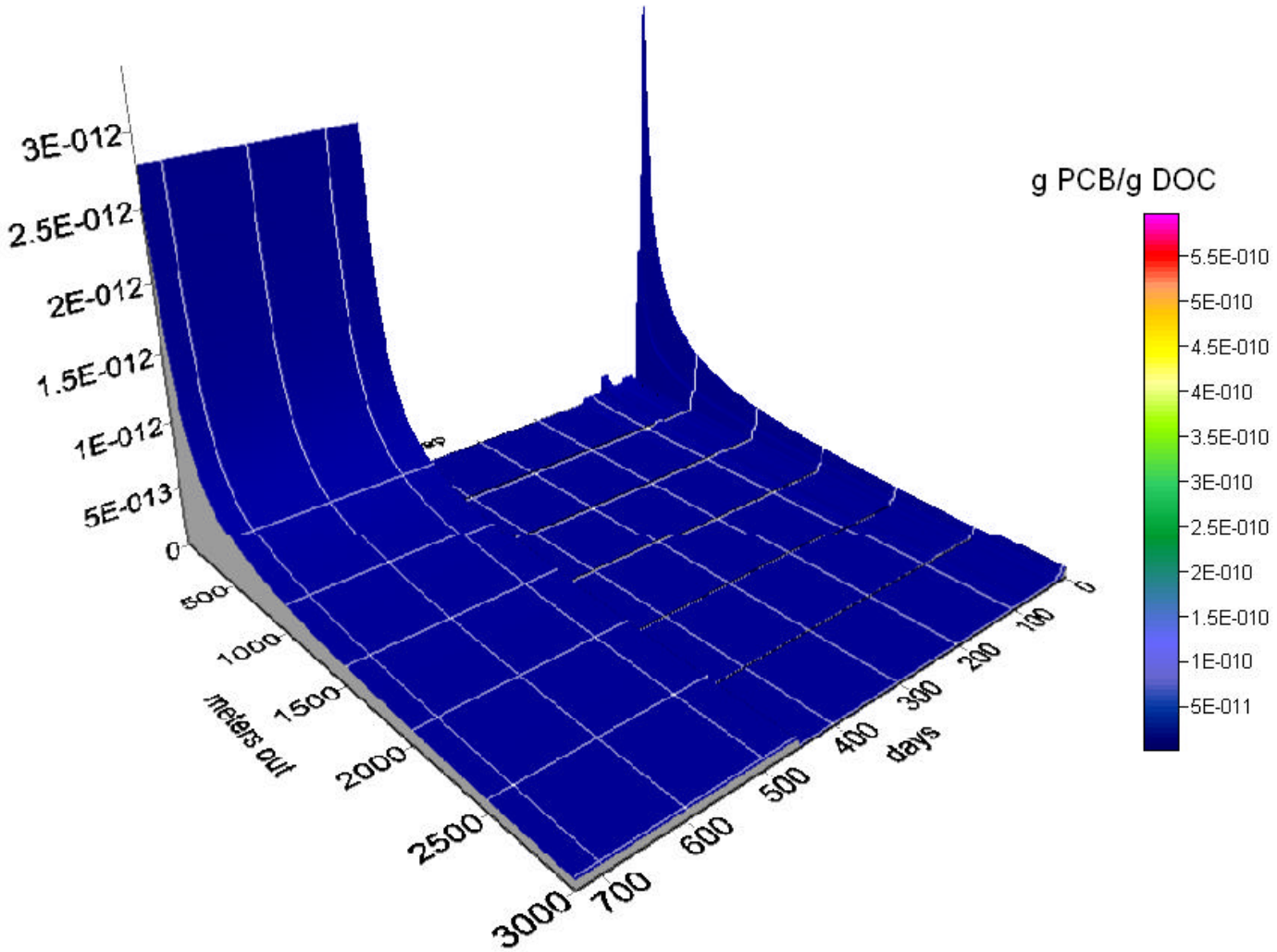

Figure B 14 - Trichlorobiphenyl in DOC below Pycnocline

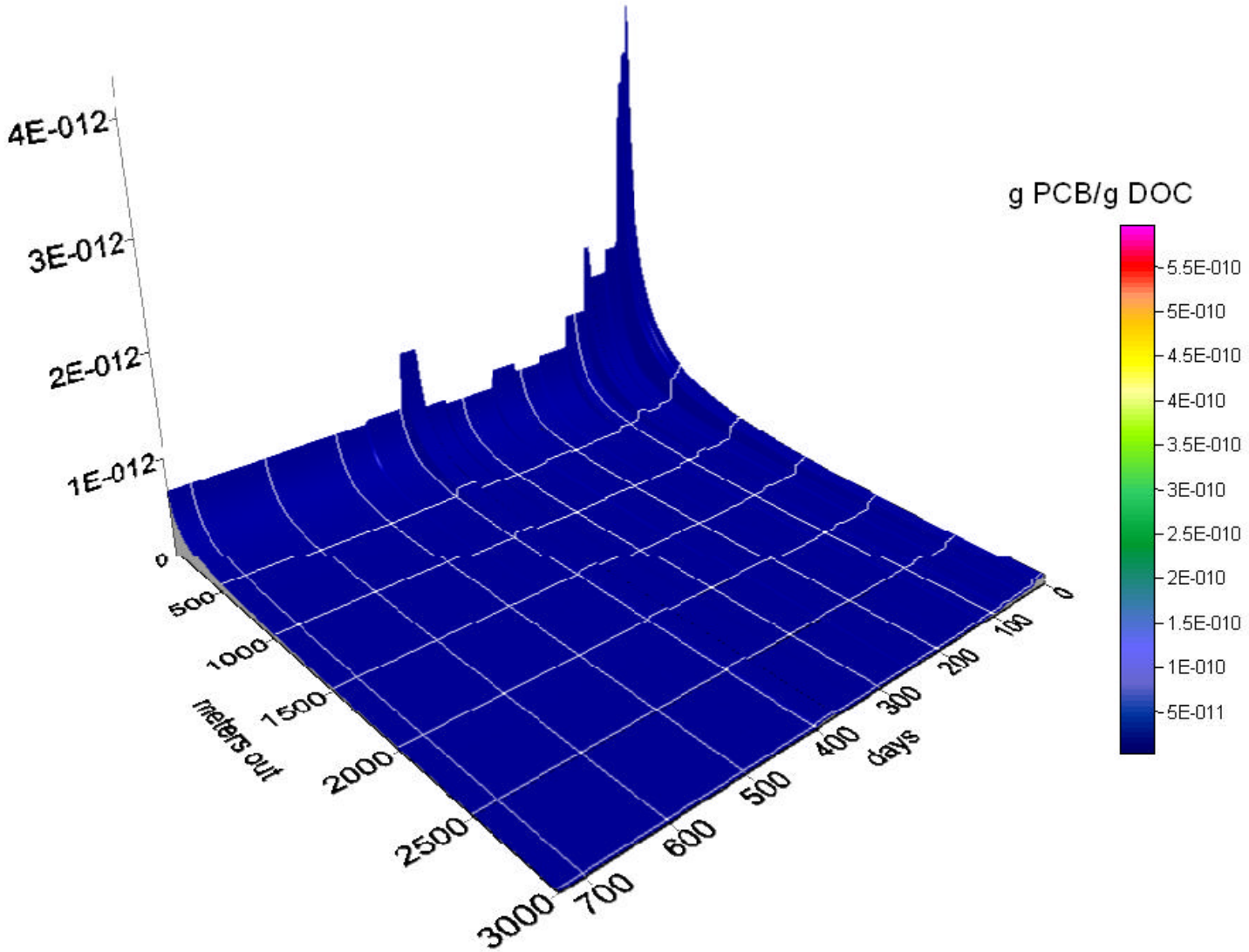

Figure B 15 – Tetrachlorobiphenyl in DOC below Pycnocline

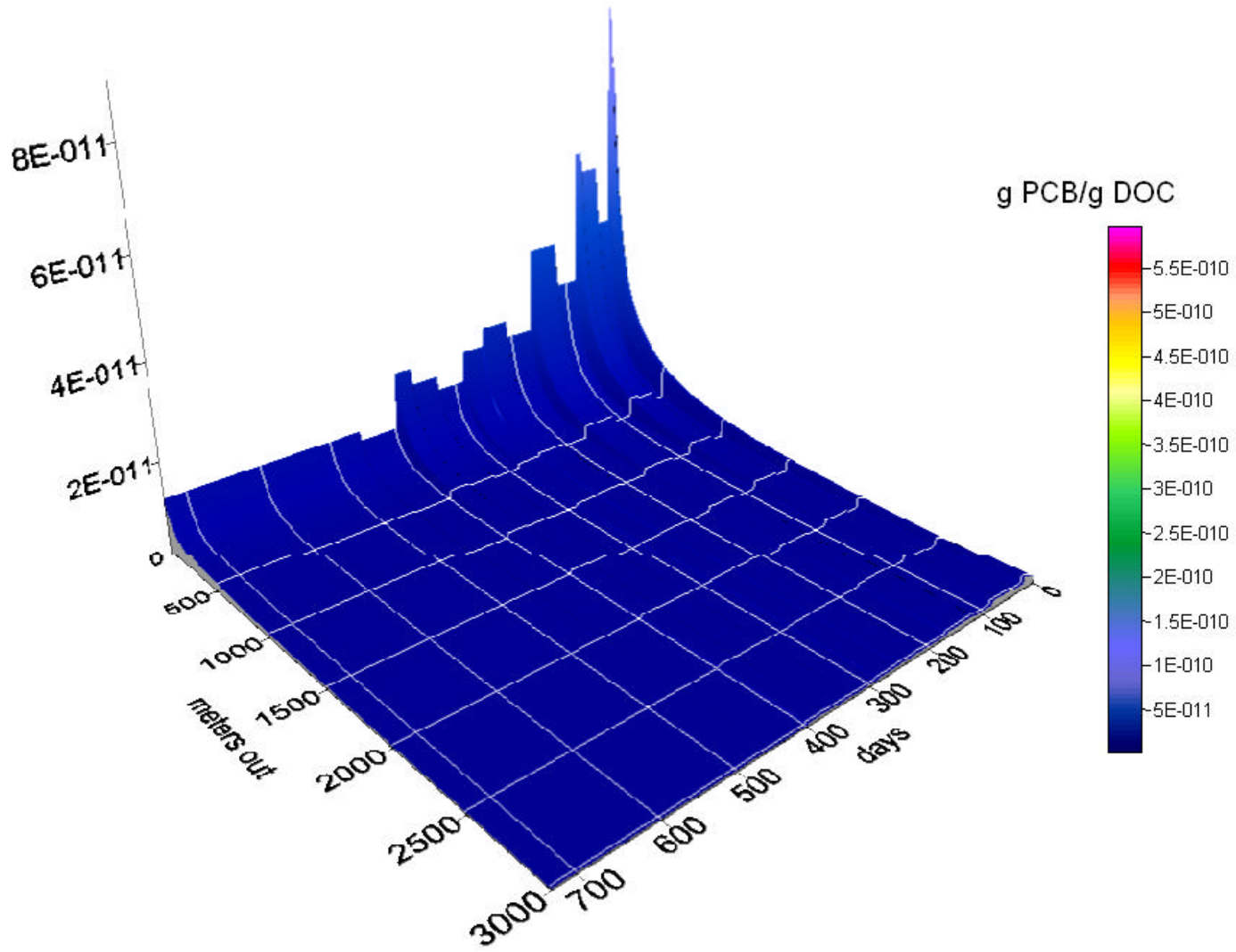

Figure B 16 – Pentachlorobiphenyl in DOC below pycnocline

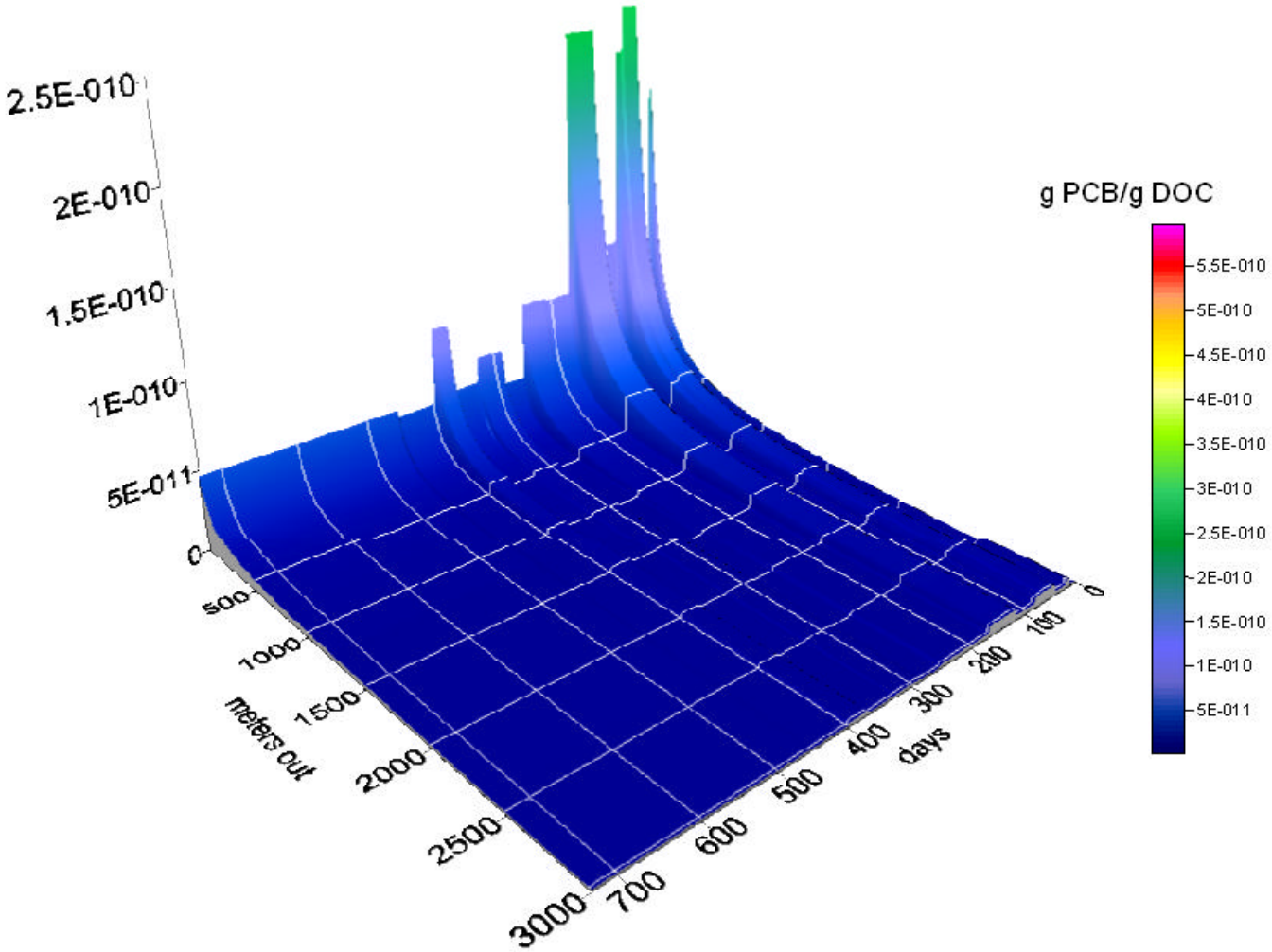

Figure B 17 - Hexachlorobiphenyl in DOC below Pycnocline

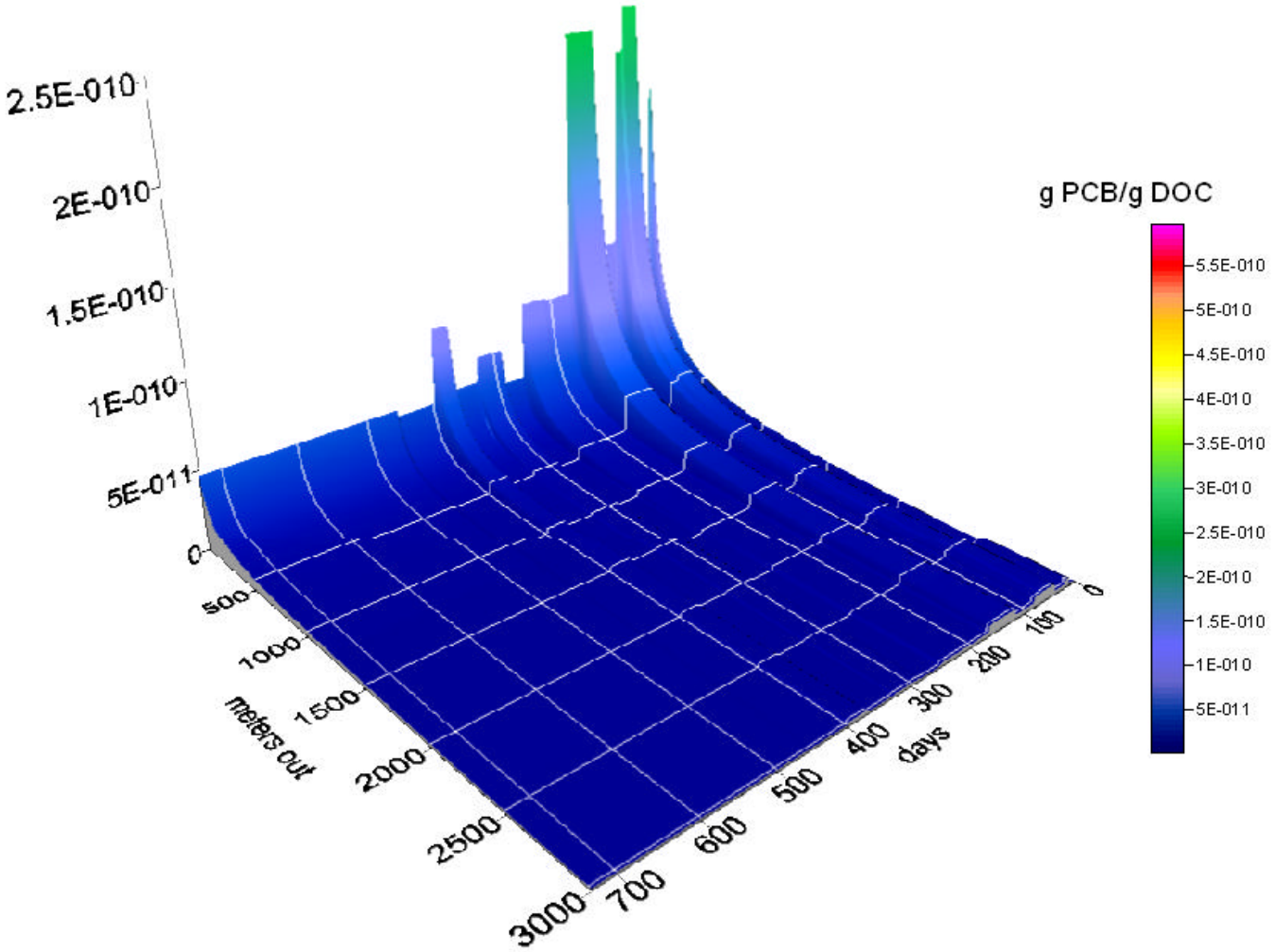

Figure B 18 - Heptachlorobiphenyl in DOC below Pycnocline

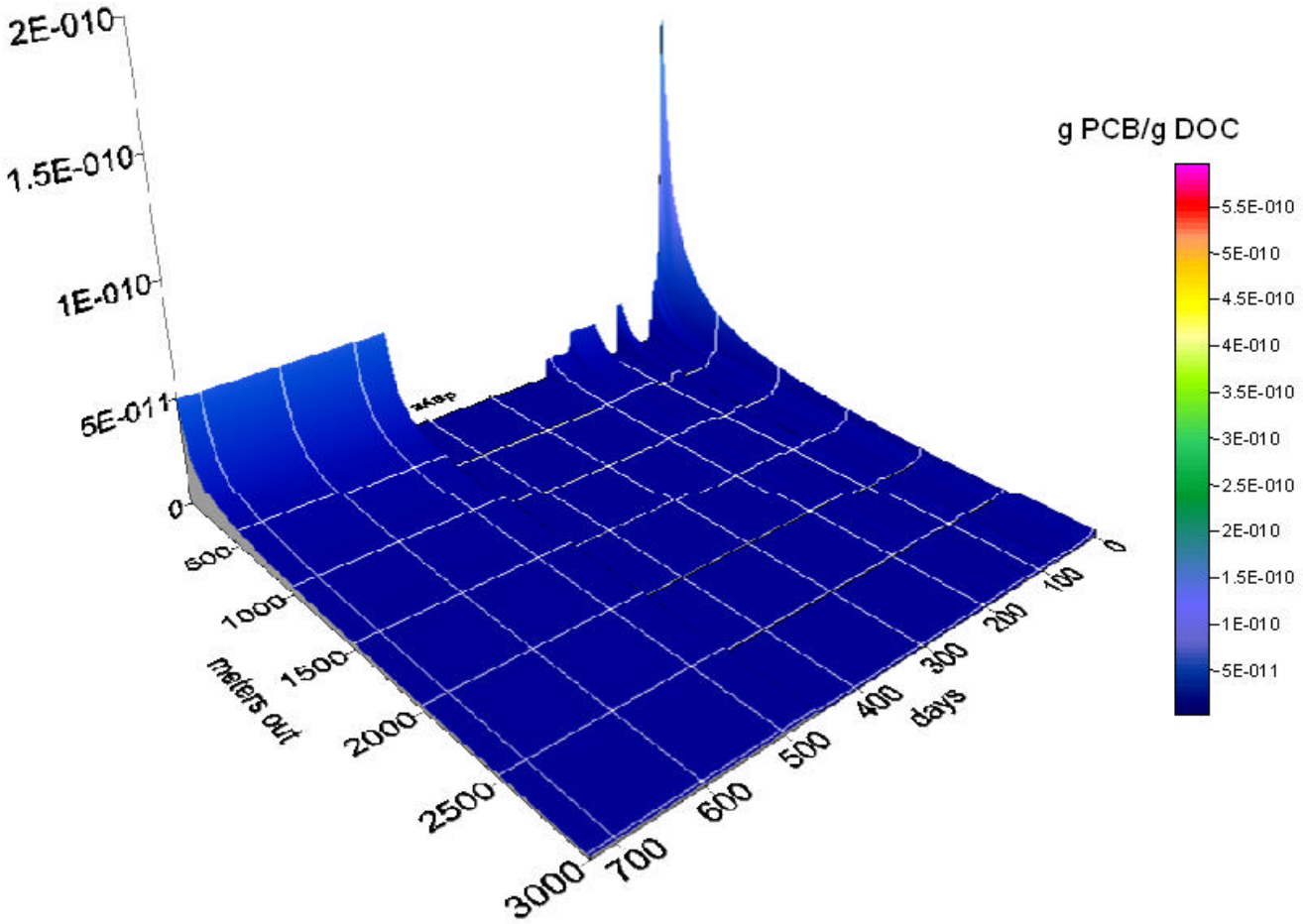

Figure B 19 – Nonachlorobiphenyl in DOC below Pycnocline

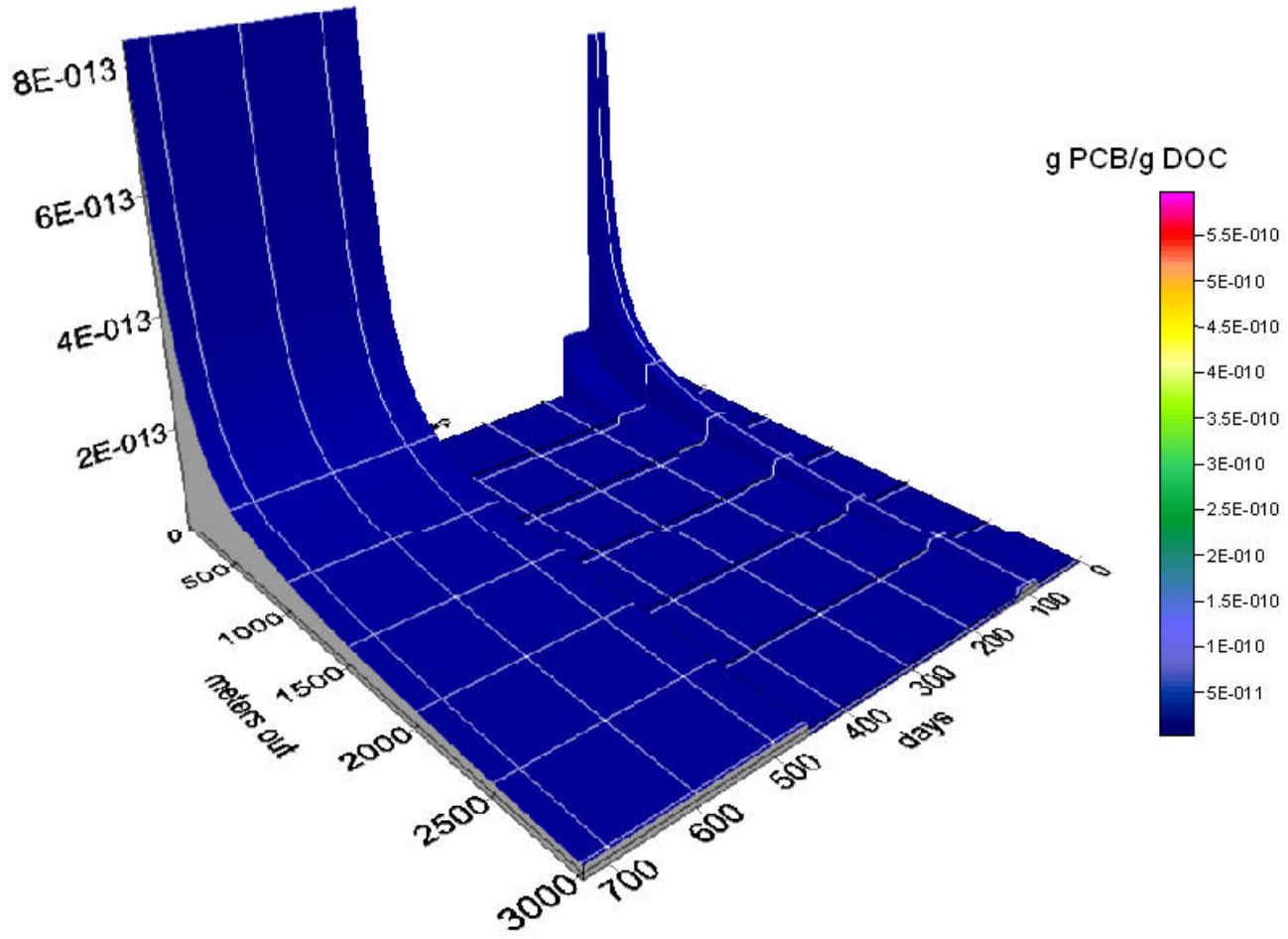

Figure B 20 - Decachlorobiphenyl in DOC below Pycnocline

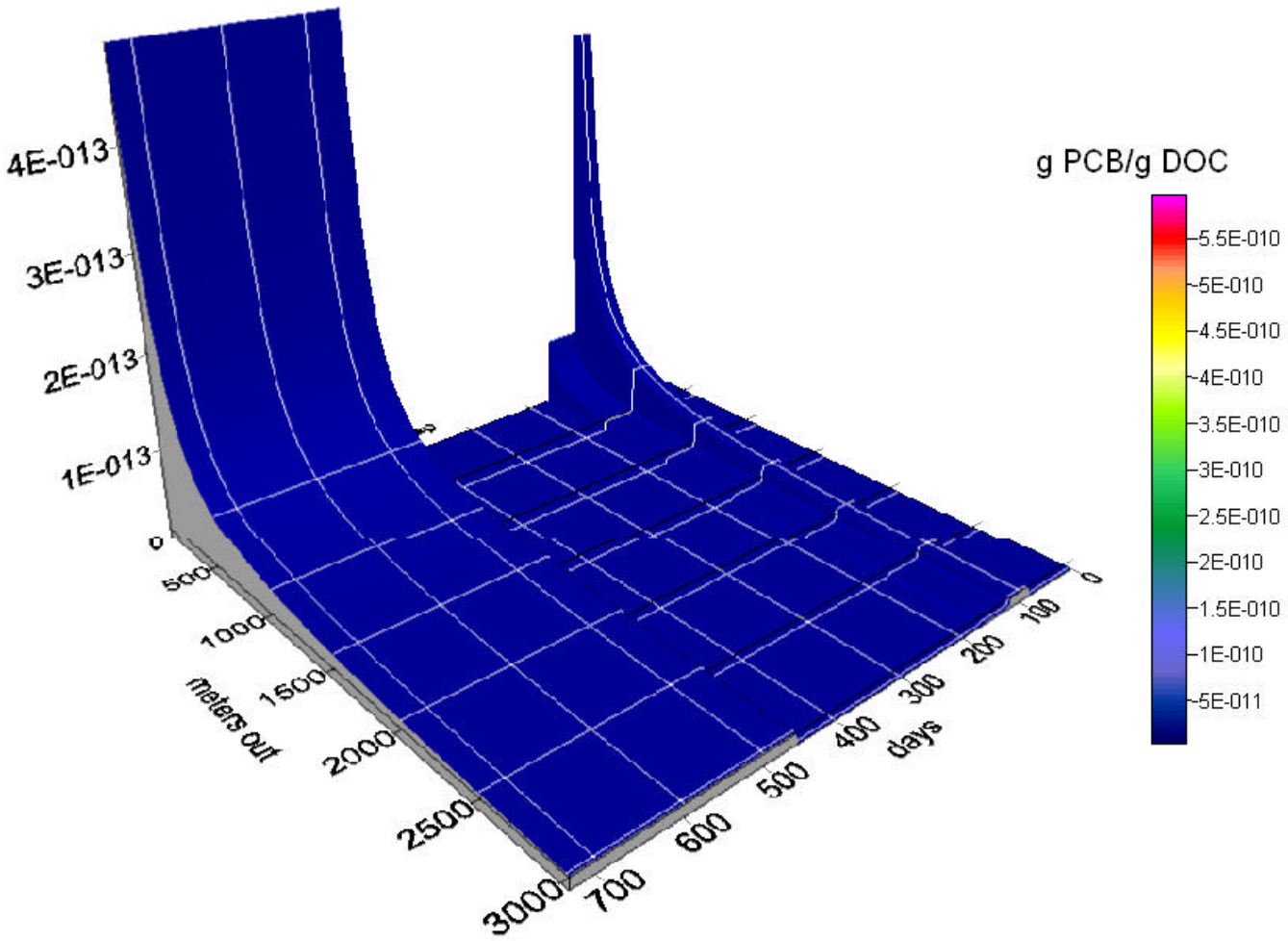

Figure B 21 - Total PCB in TSS below Pycnocline

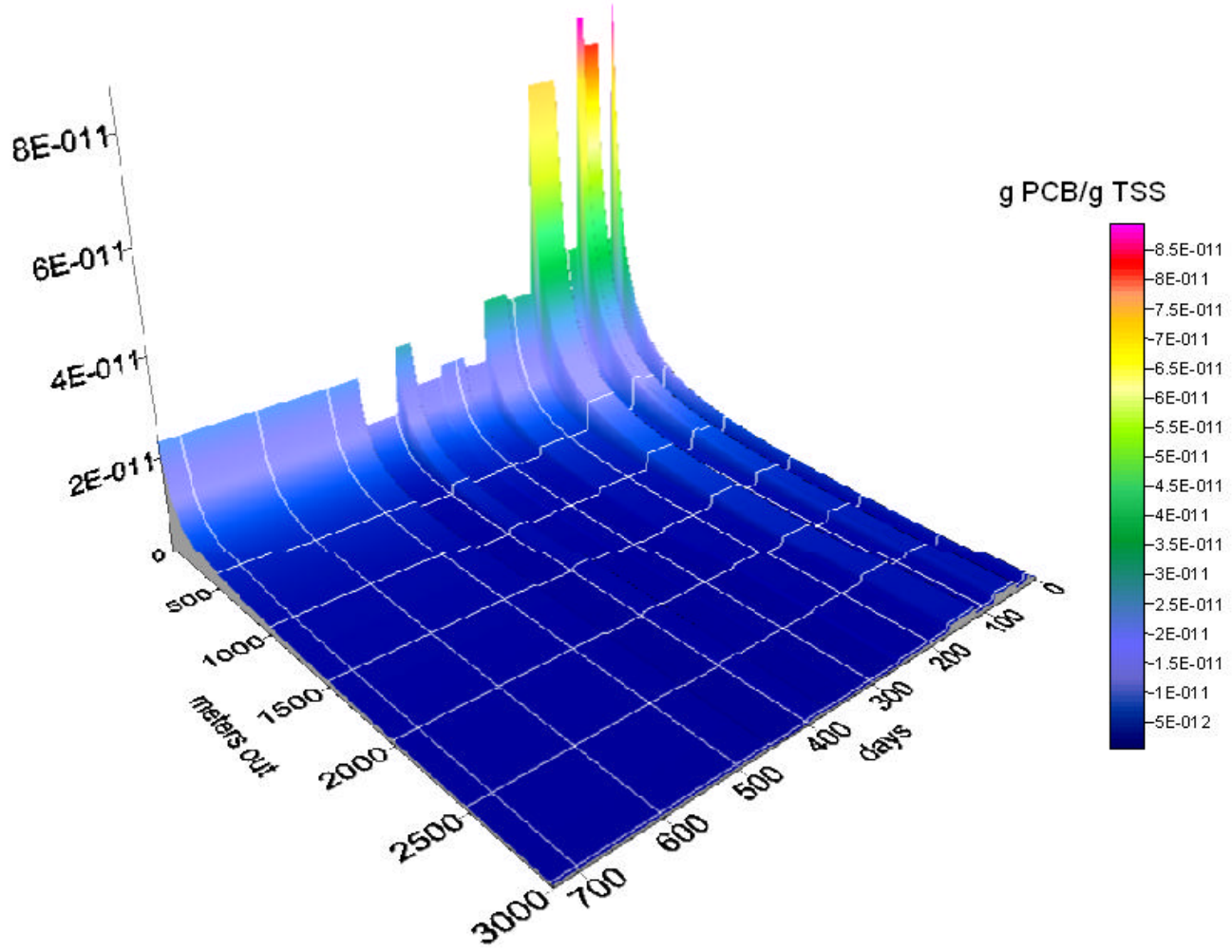

Figure B 22 – Monochlorobiphenyl in TSS below Pycnocline

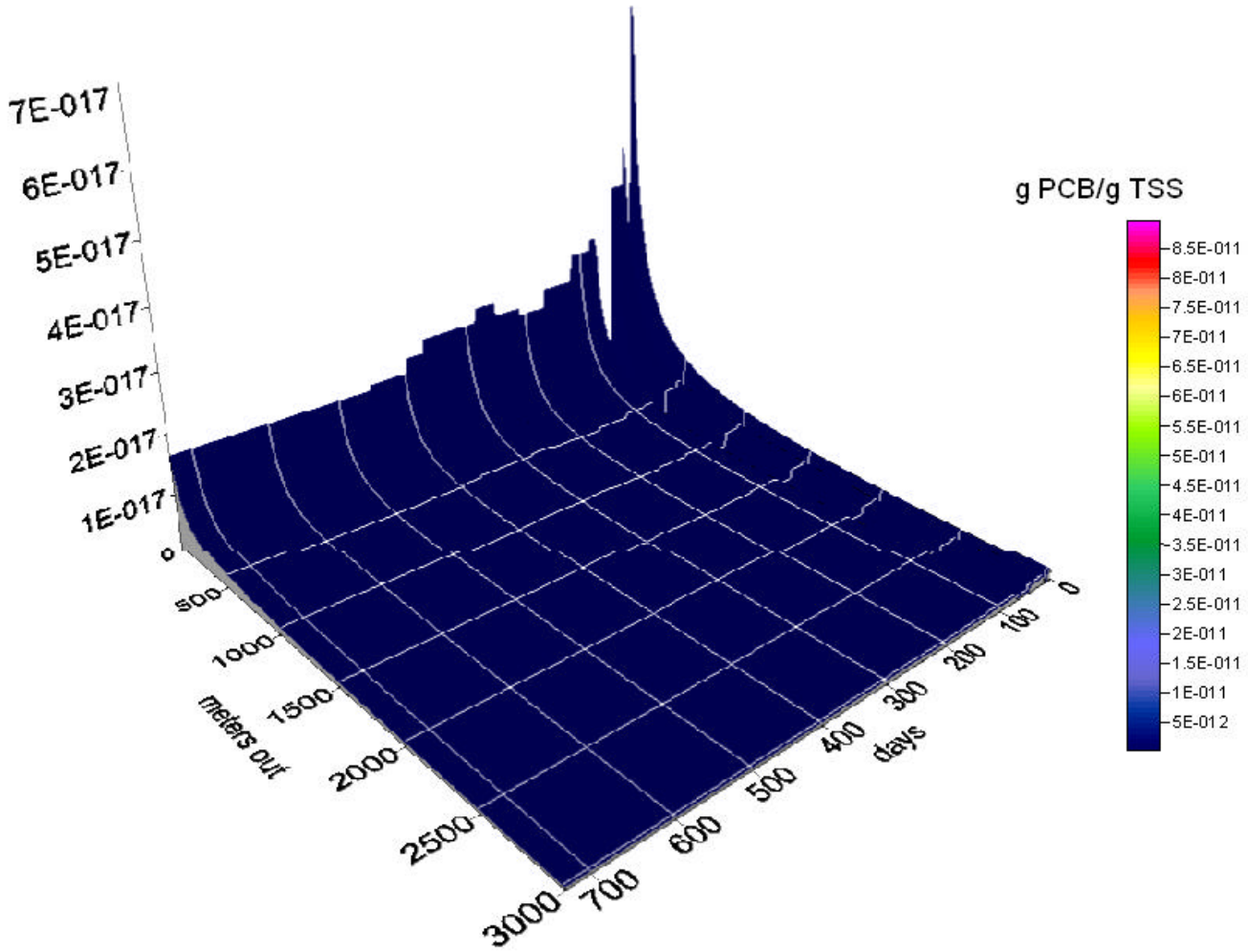

Figure B 23 - Dichlorobiphenyl in TSS below Pycnocline

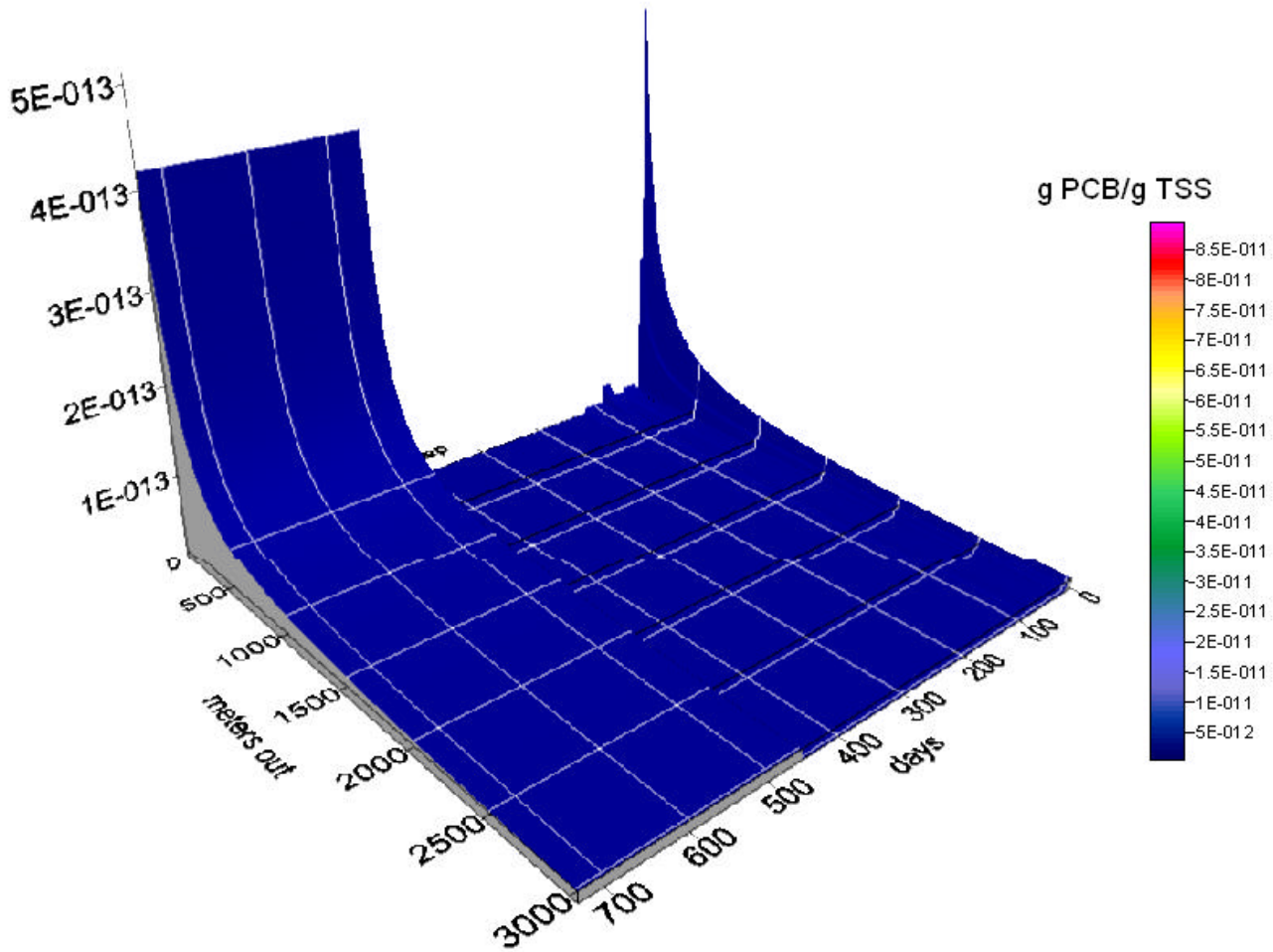

Figure B 24 - Trichlorobiphenyl in TSS below Pycnocline

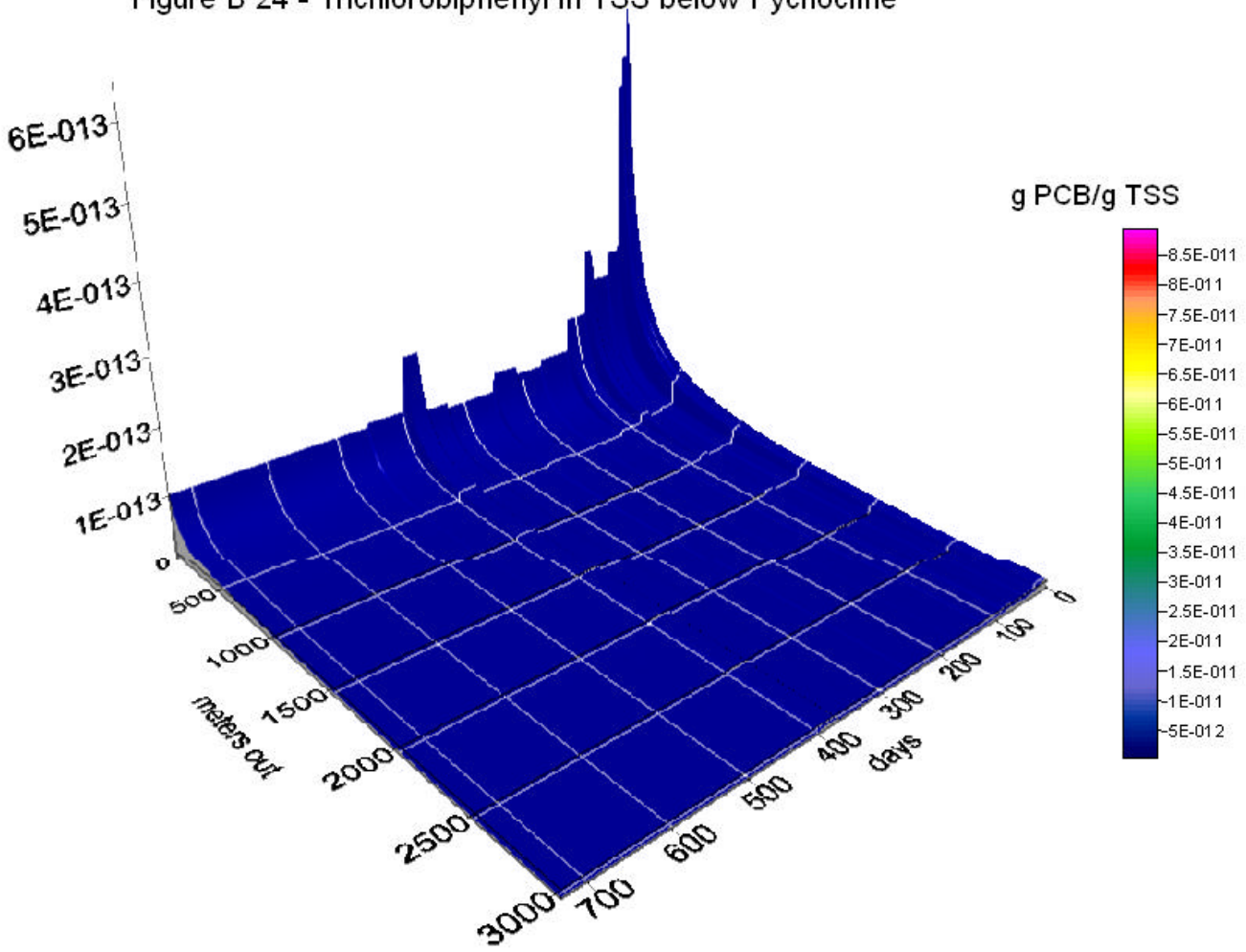

Figure B 25 - Tetrachlorobiphenyl in TSS below Pycnocline

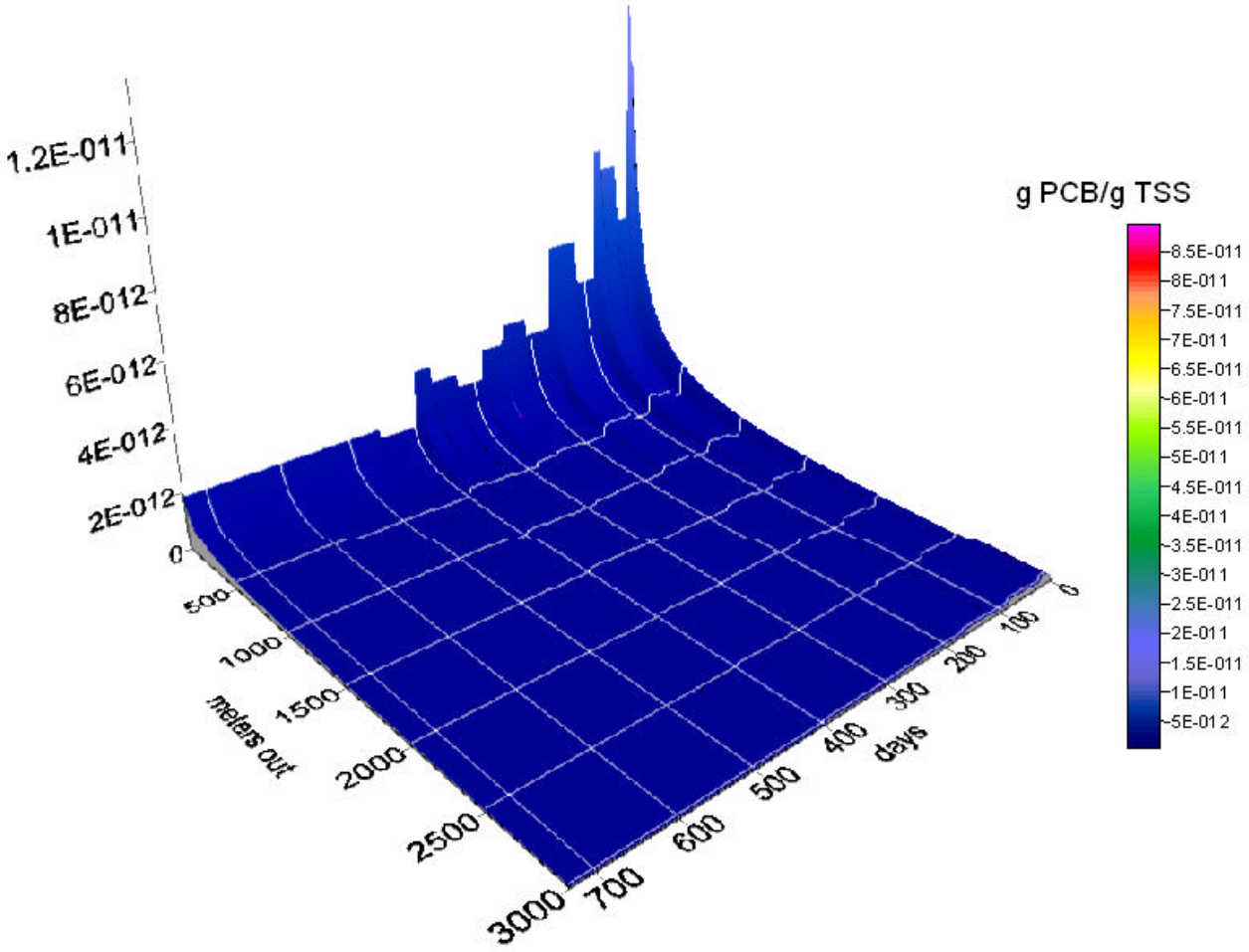

Figure B 26 - Pentachlorobiphenyl in TSS below Pycnocline

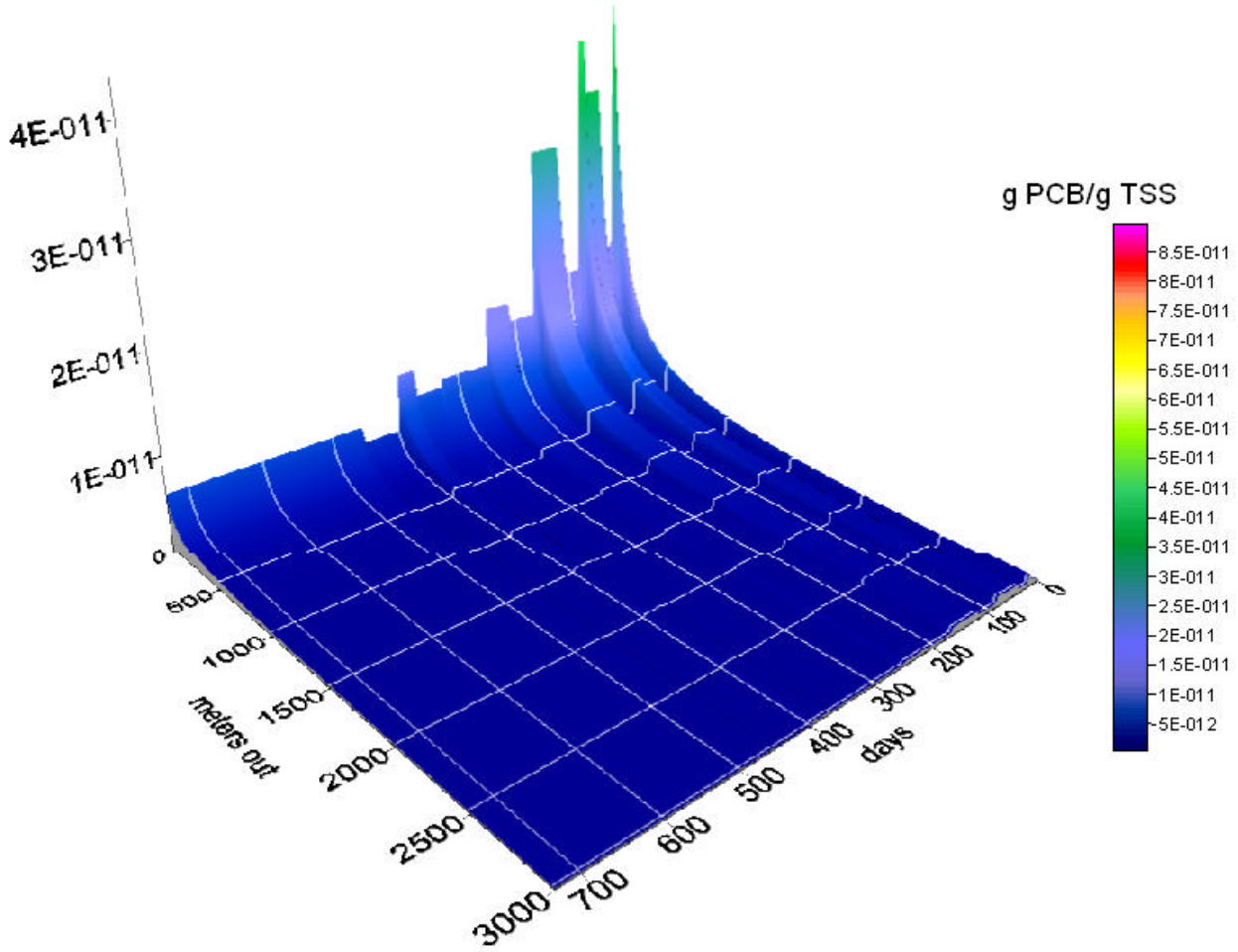

Figure B 27 - Hexachlorobiphenyl in TSS below Pycnocline

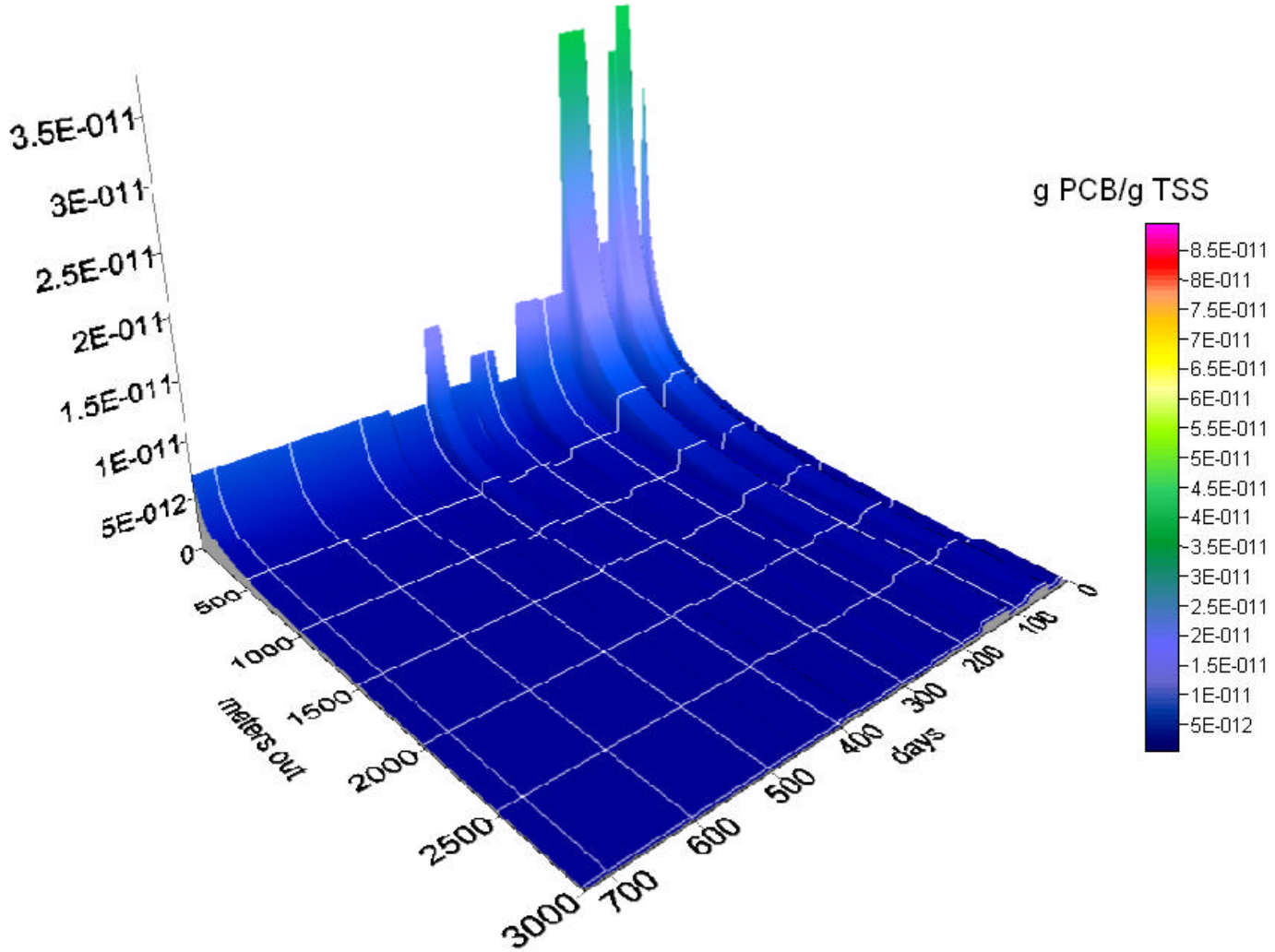

Figure B 28 - Heptachlorobiphenyl in TSS below Pycnocline

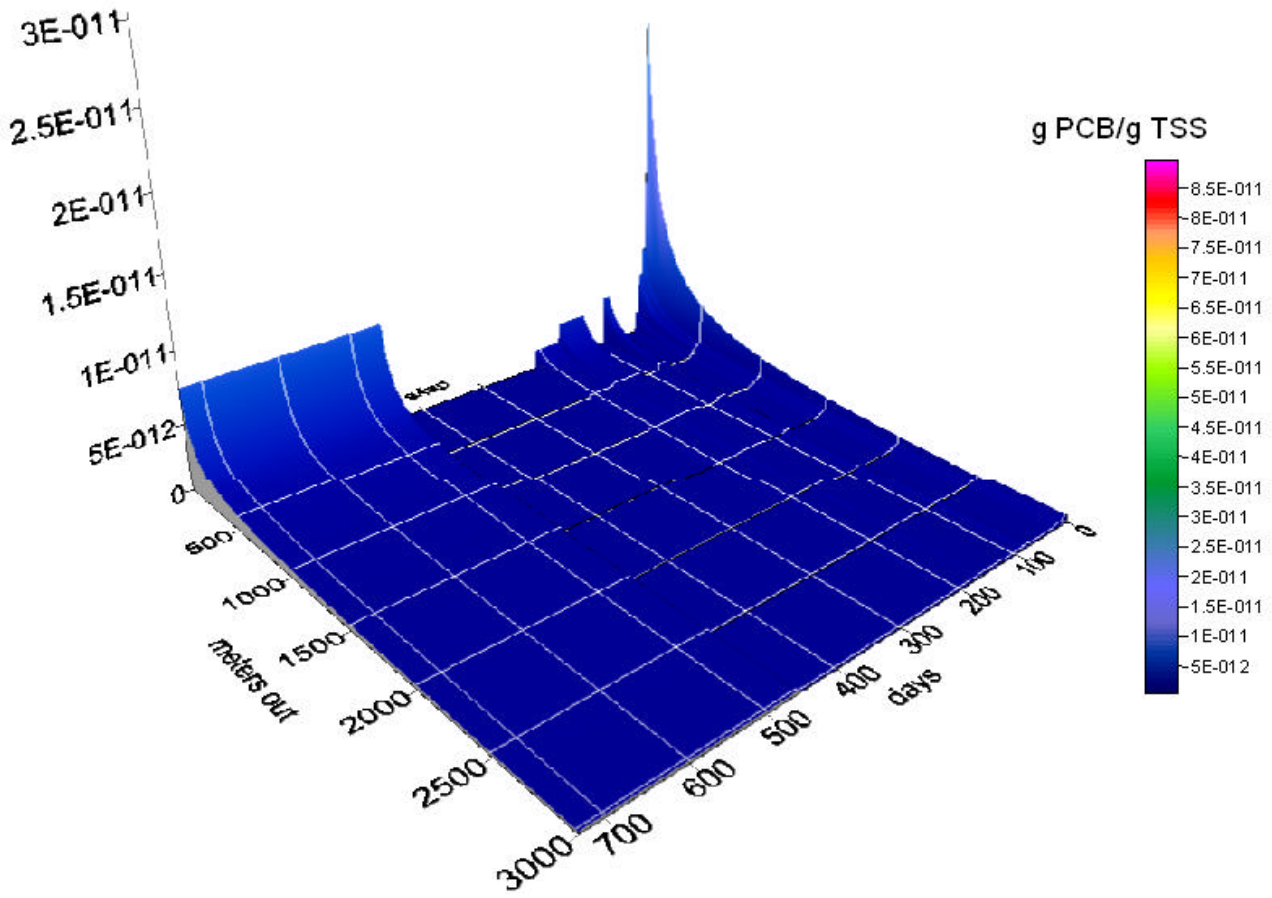

Figure B 29 - Nonachlorobiphenyl in TSS below Pycnocline

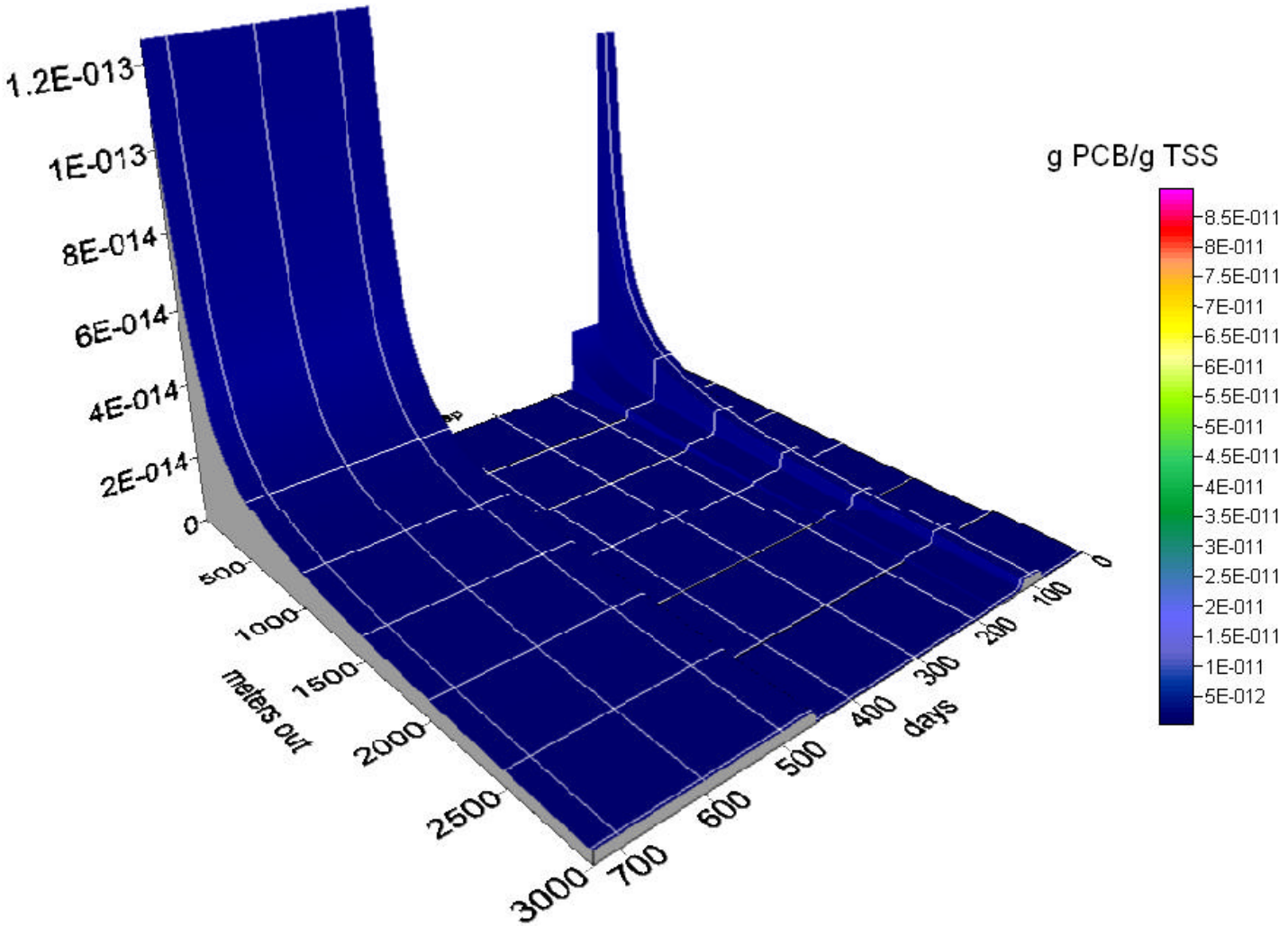

Figure B 30 - Decachlorobiphenyl in TSS below Pycnocline

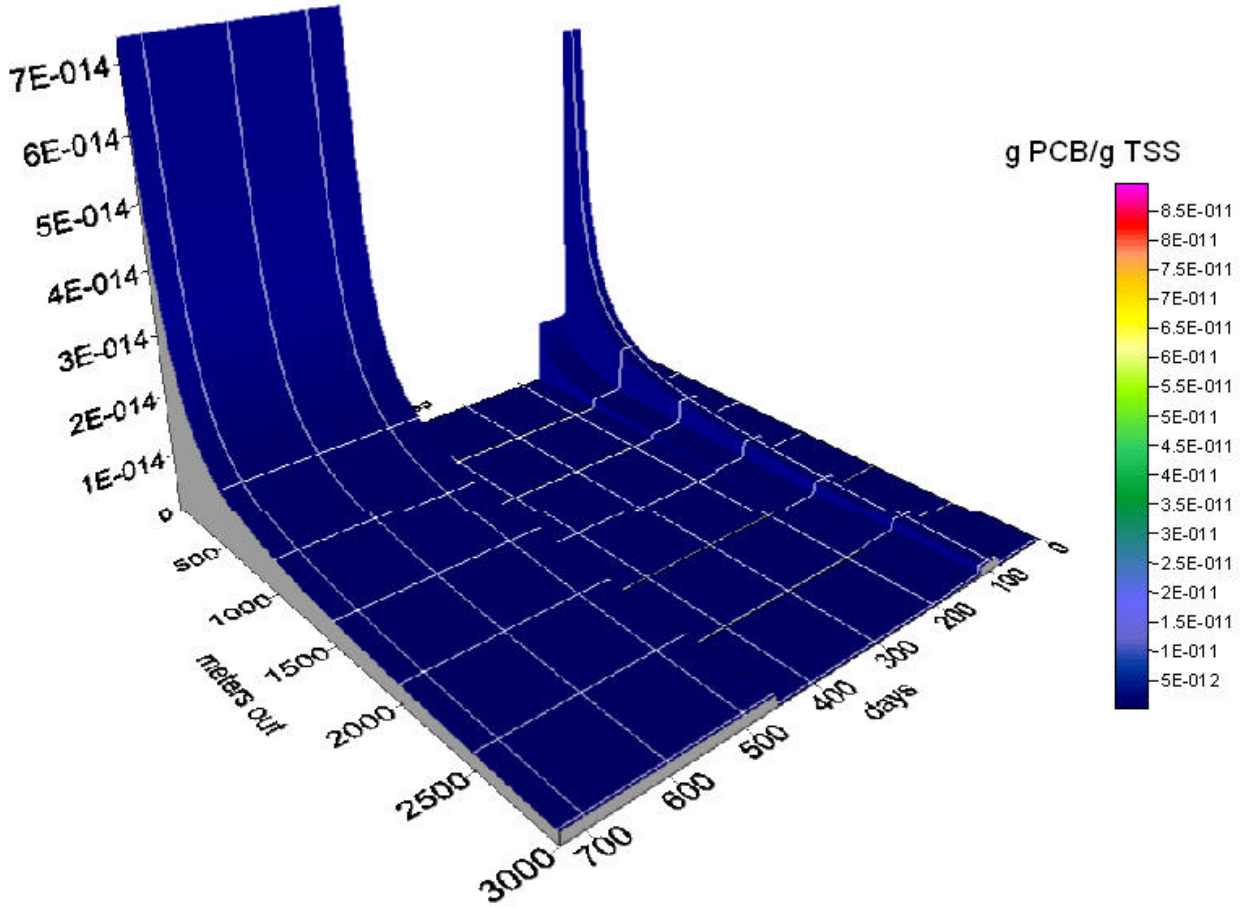

Figure B 31 - Total PCB in Sediment

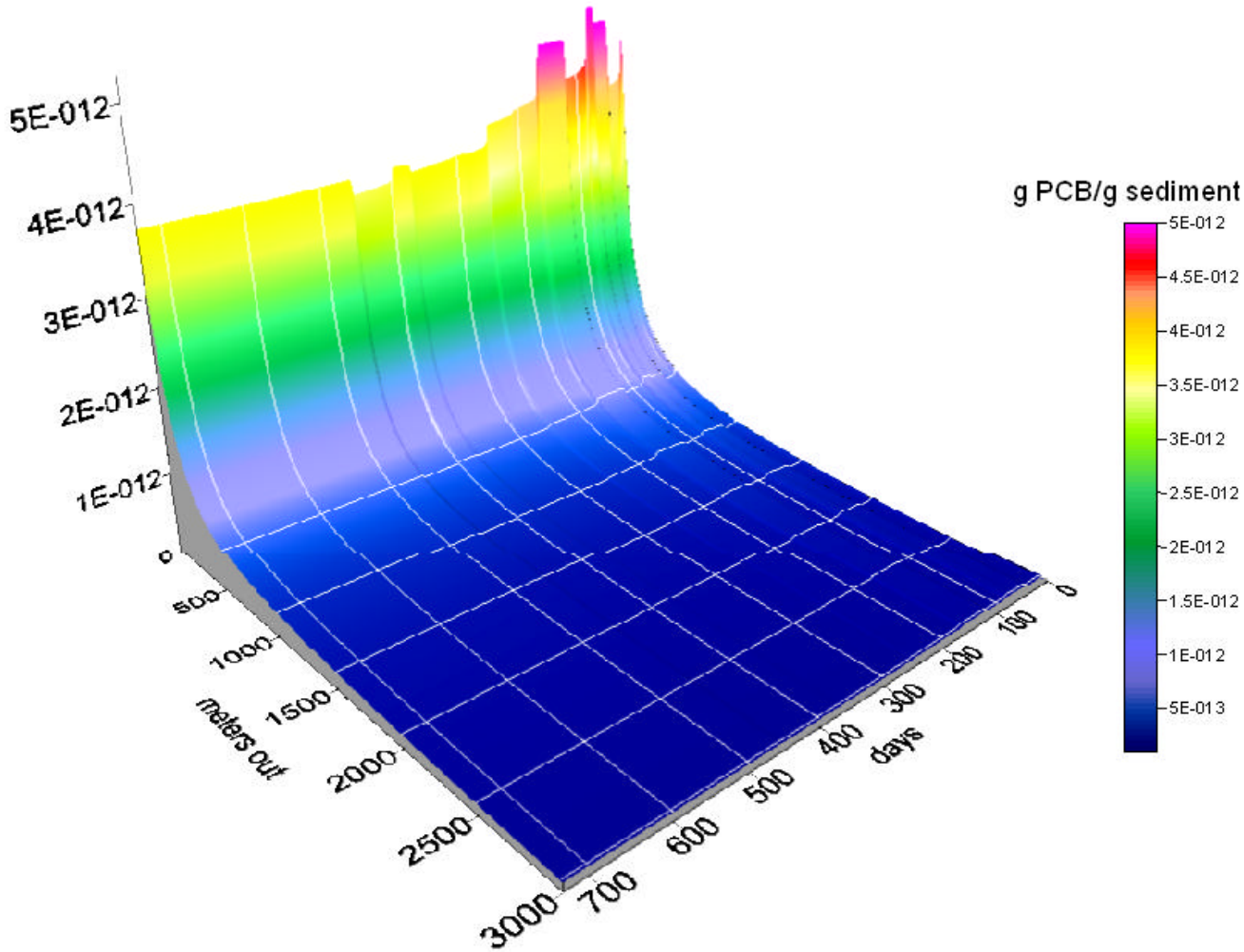

Figure B 32 – Monochlorobiphenyl in Sediment

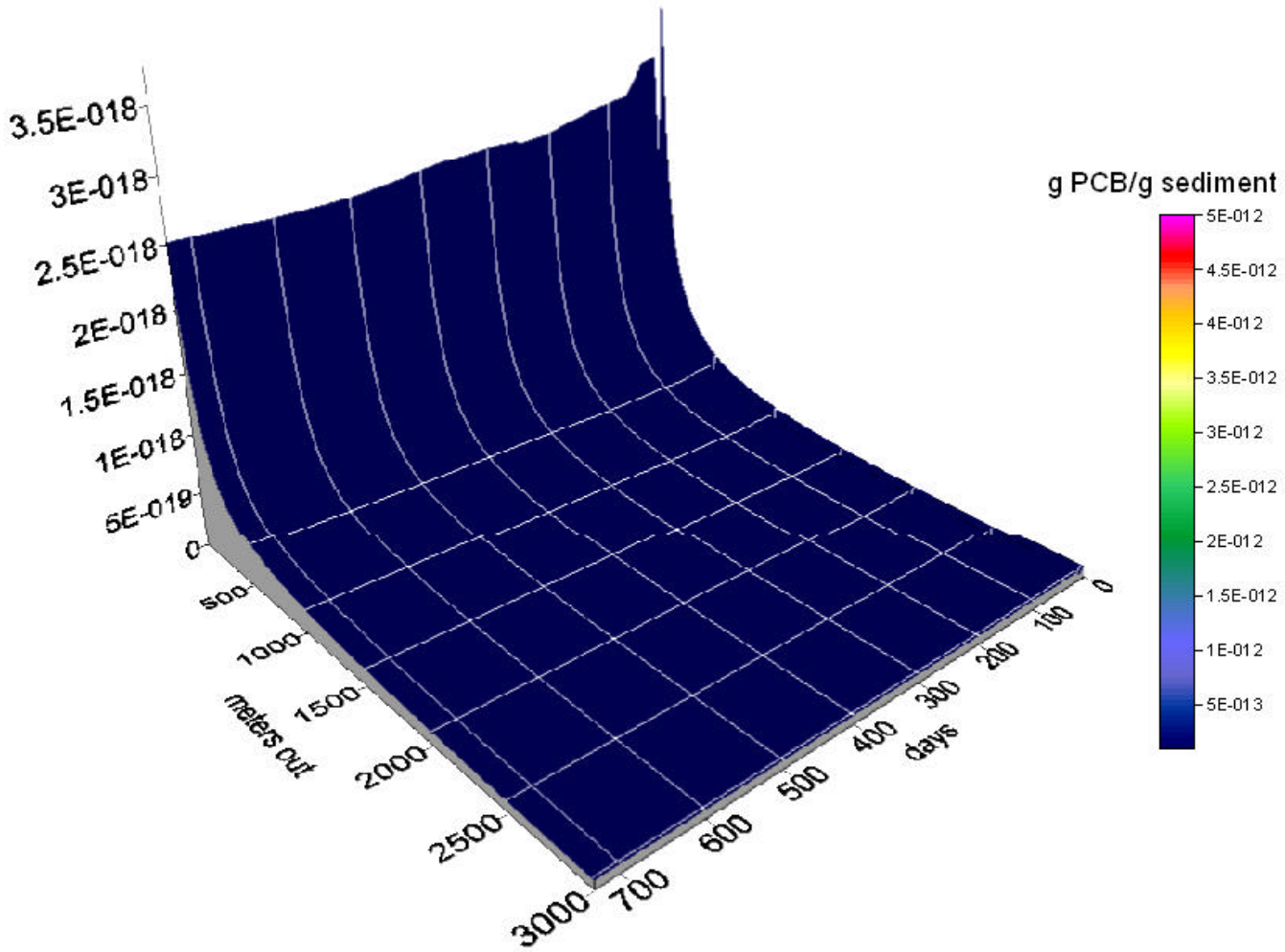

Figure B 33 – Dichlorobiphenyl in Sediment

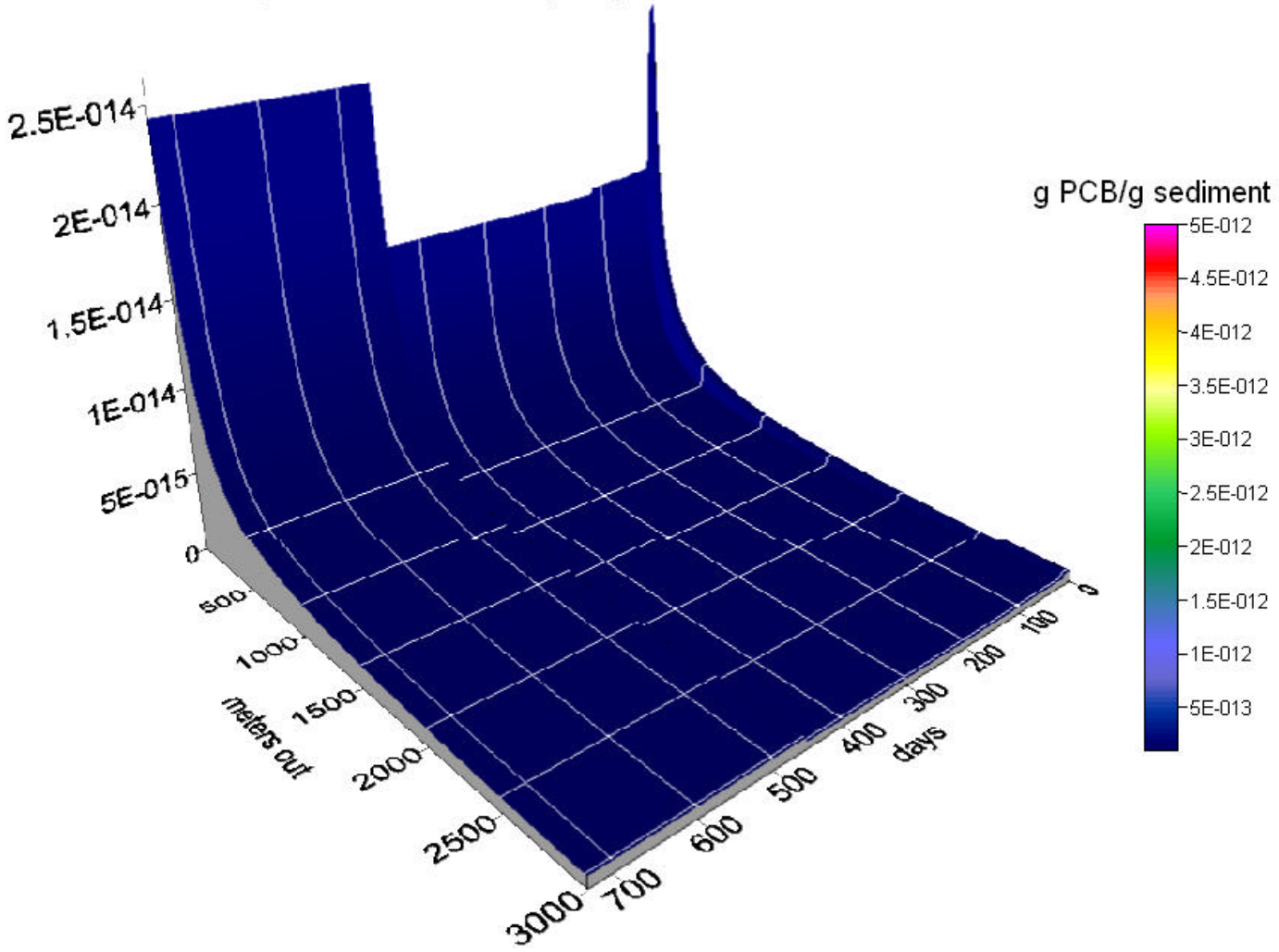

Figure B 34 – Trichlorobiphenyl in Sediment

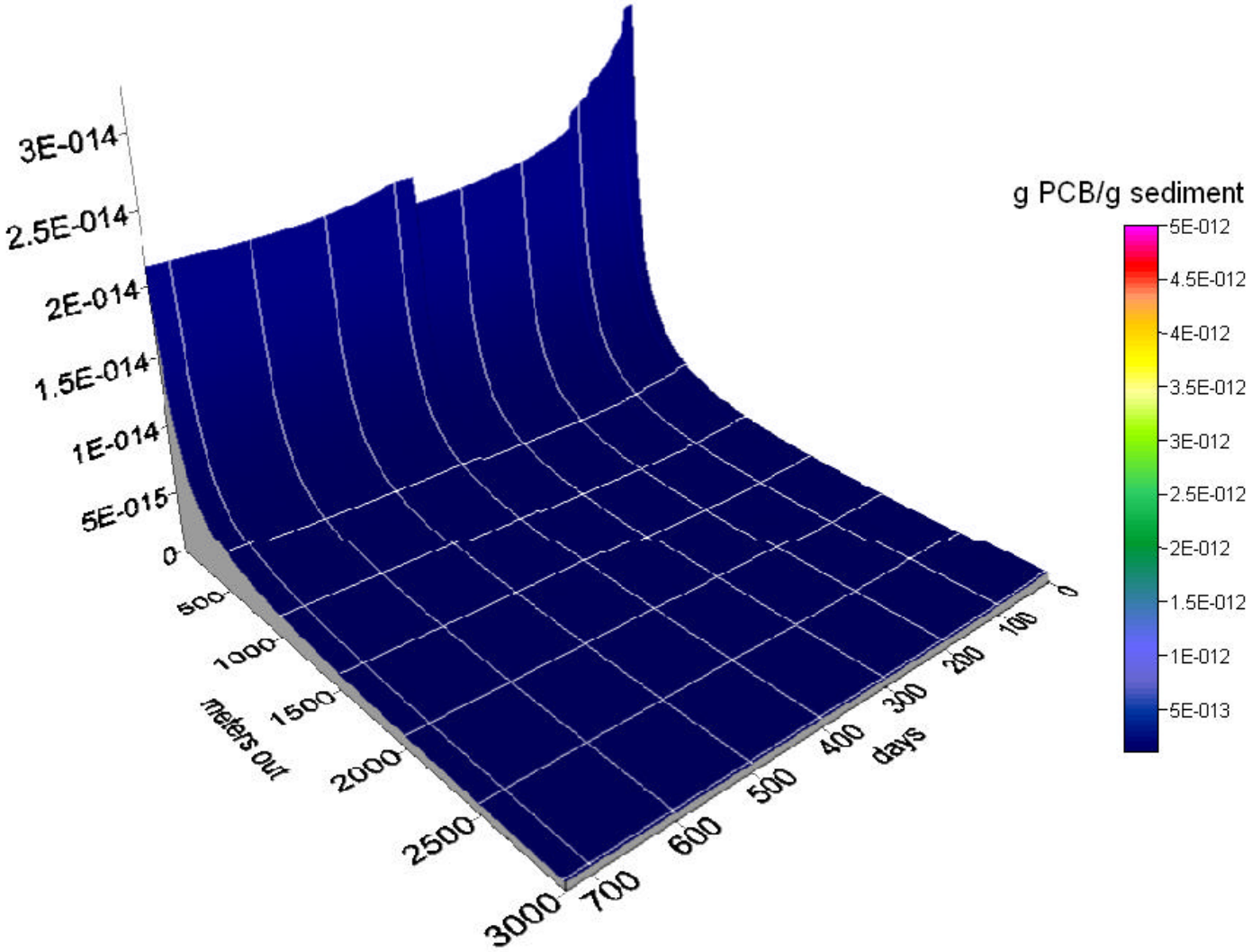

Figure B 35 - Tetrachlorobiphenyl in Sediment

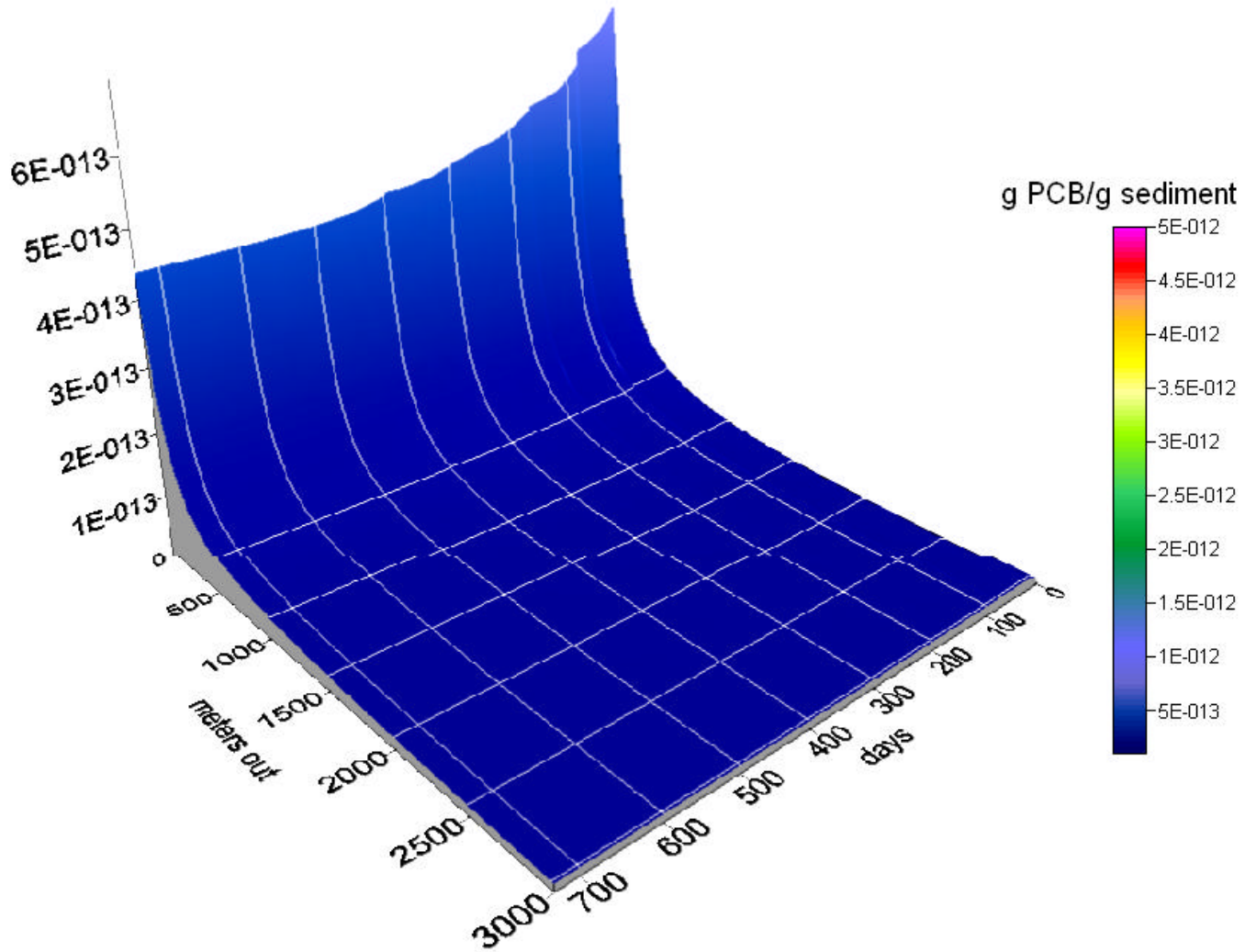

Figure B 36 – Pentachlorobiphenyl in Sediment

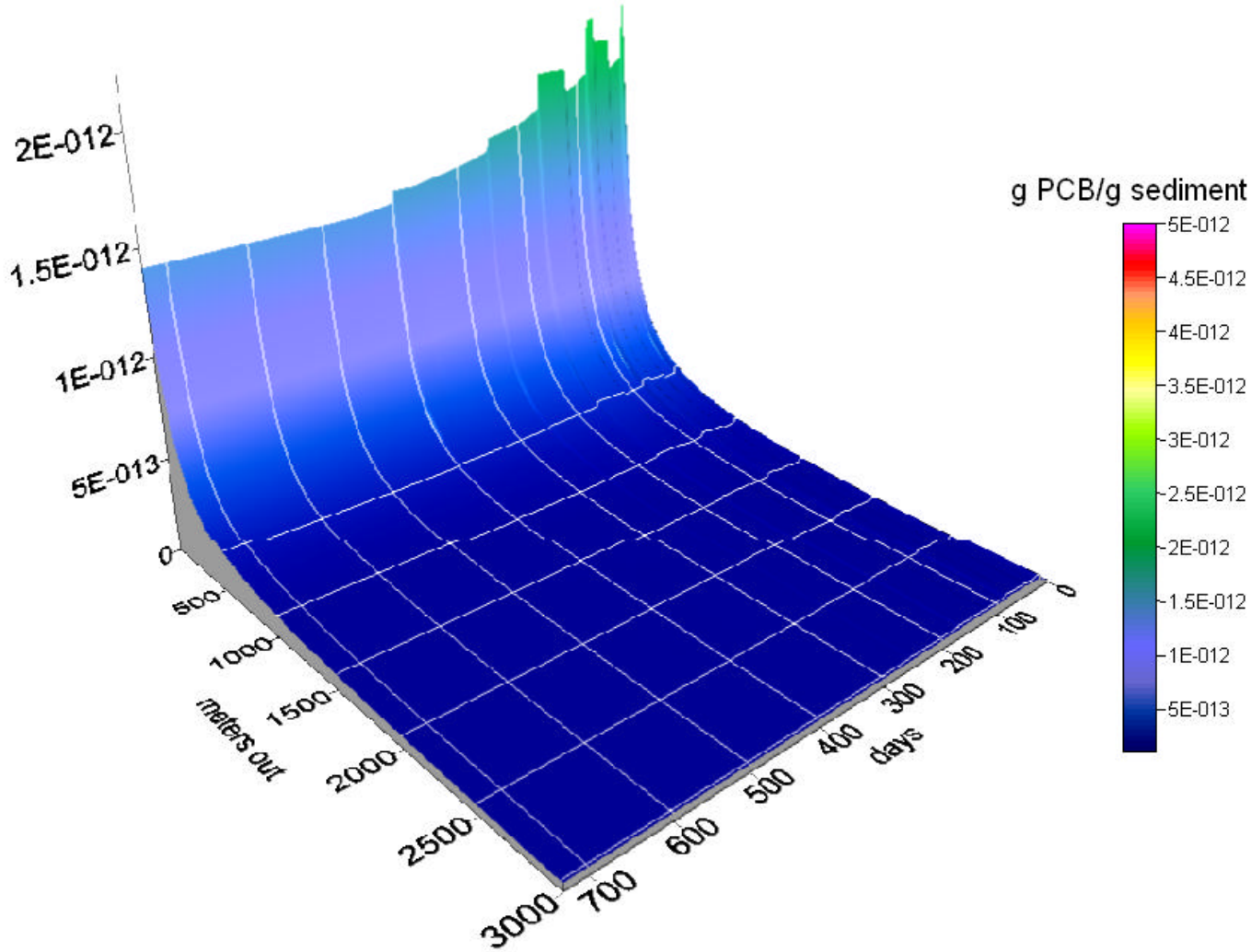

Figure B 37 – Hexachlorobiphenyl in Sediment

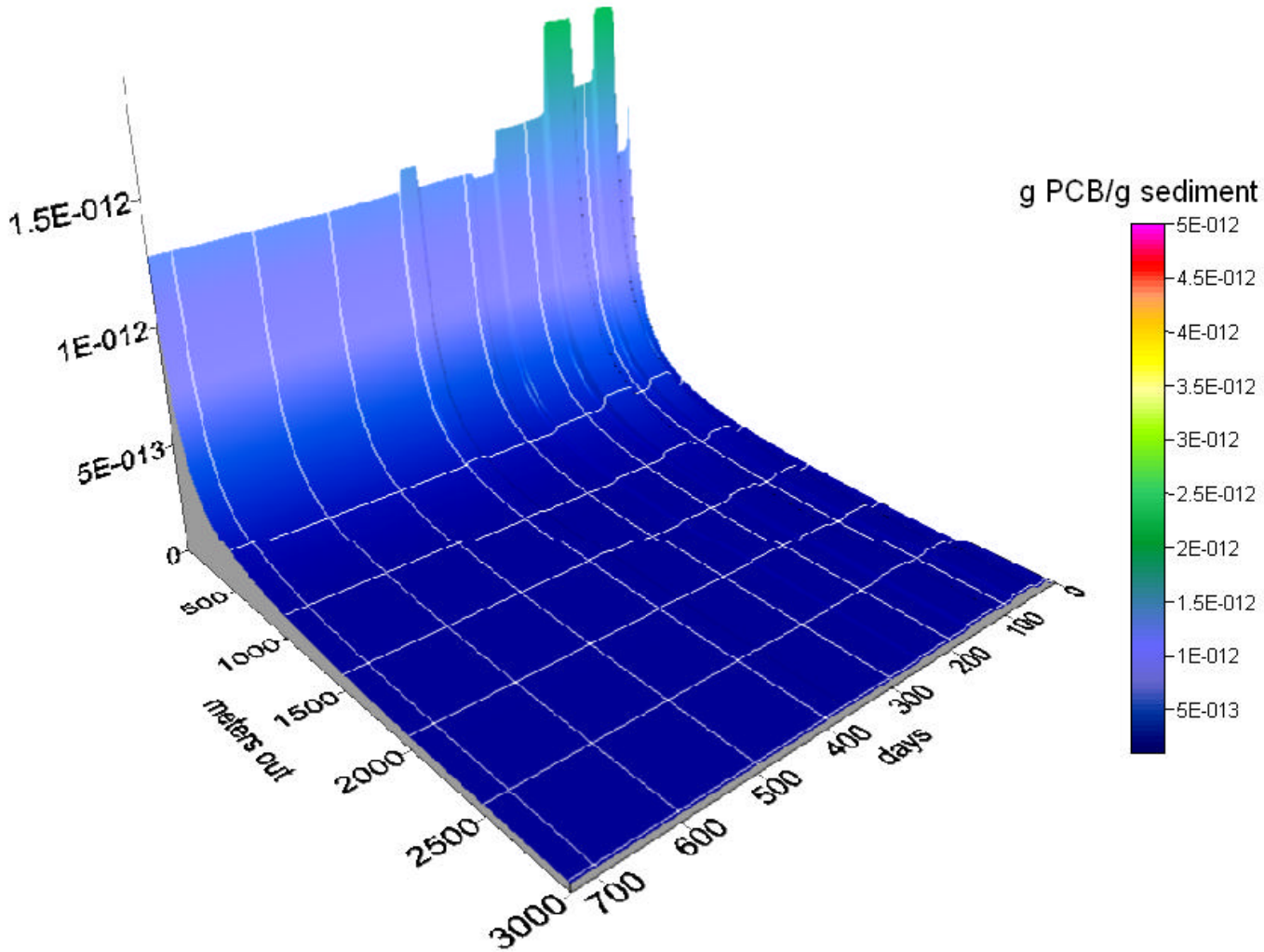

Figure B 38 – Heptachlorobiphenyl in Sediment

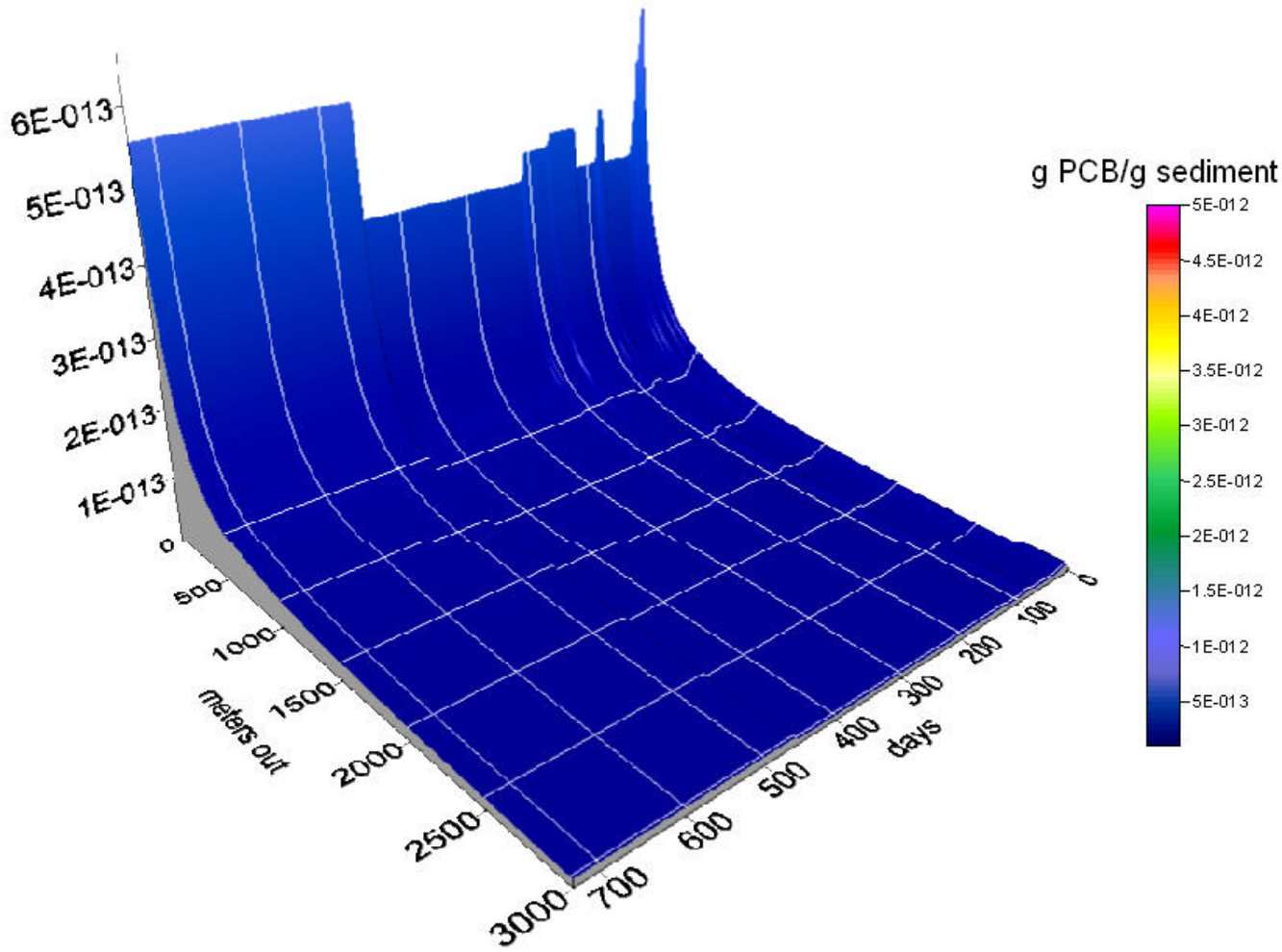

Figure B 39 – Nonachlorobiphenyl in Sediment

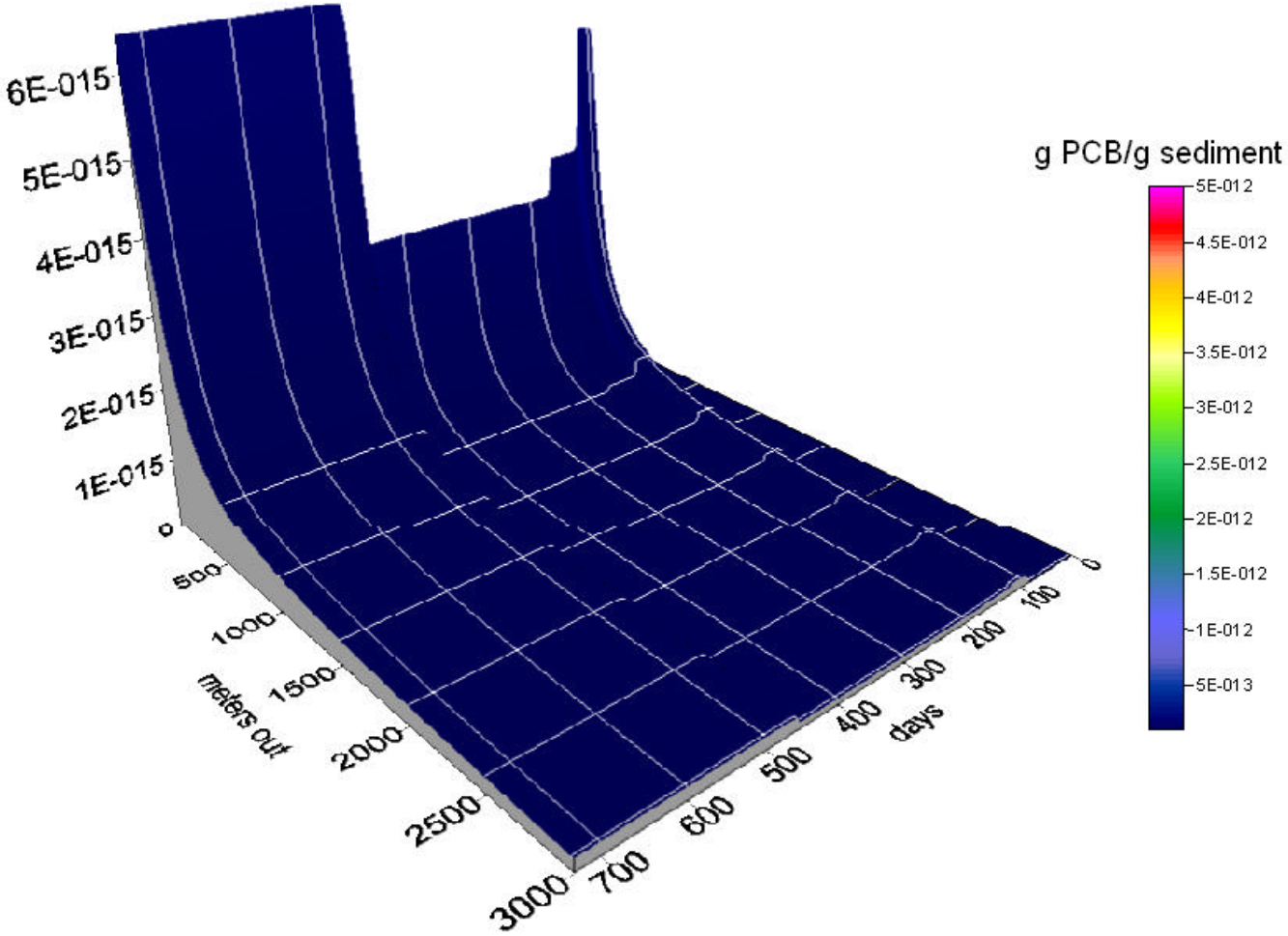

Figure B 40 – Decachlorobiphenyl in Sediment n

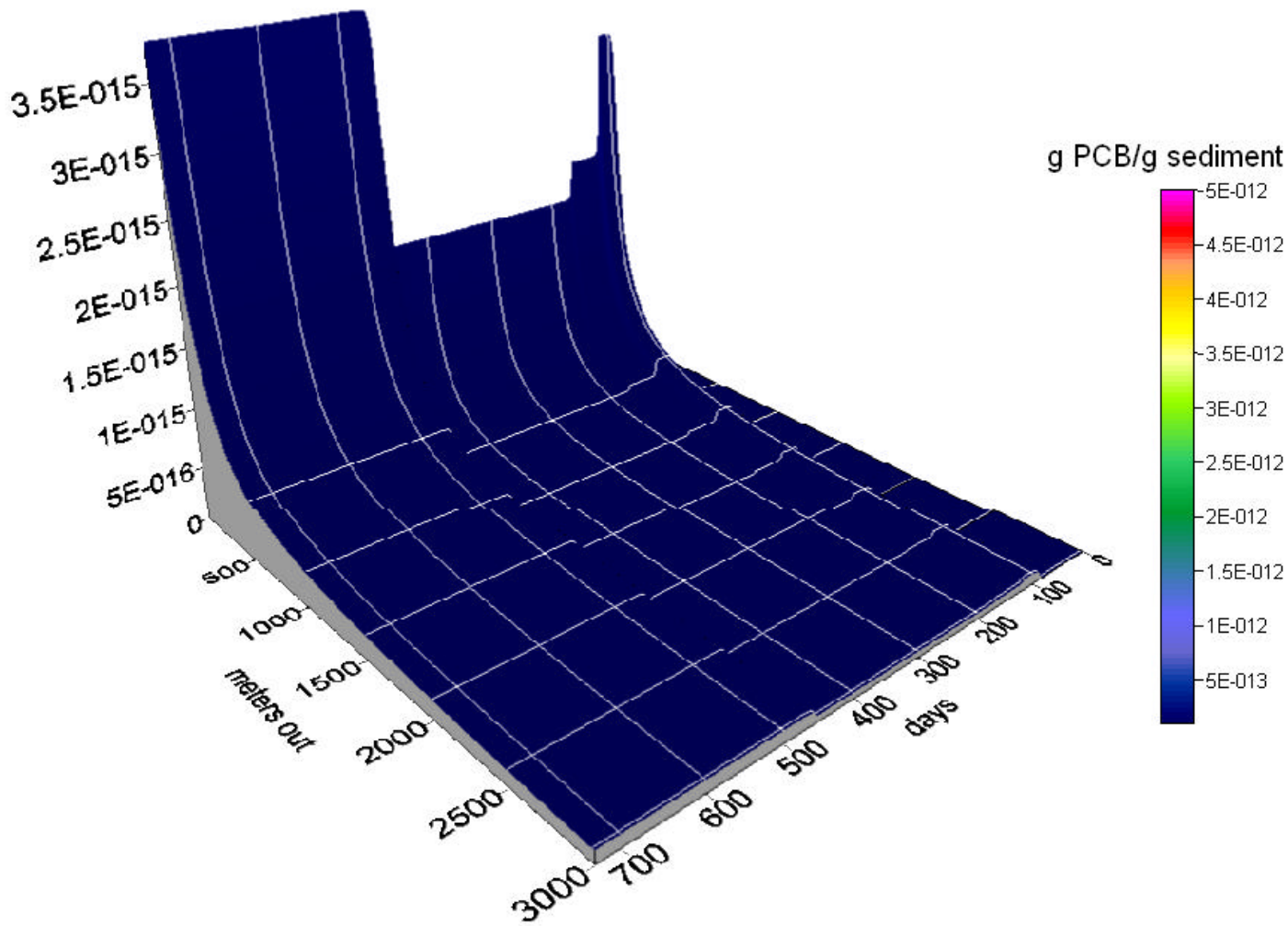

Figure B 41 - Total PCB in Water above Pycnocline

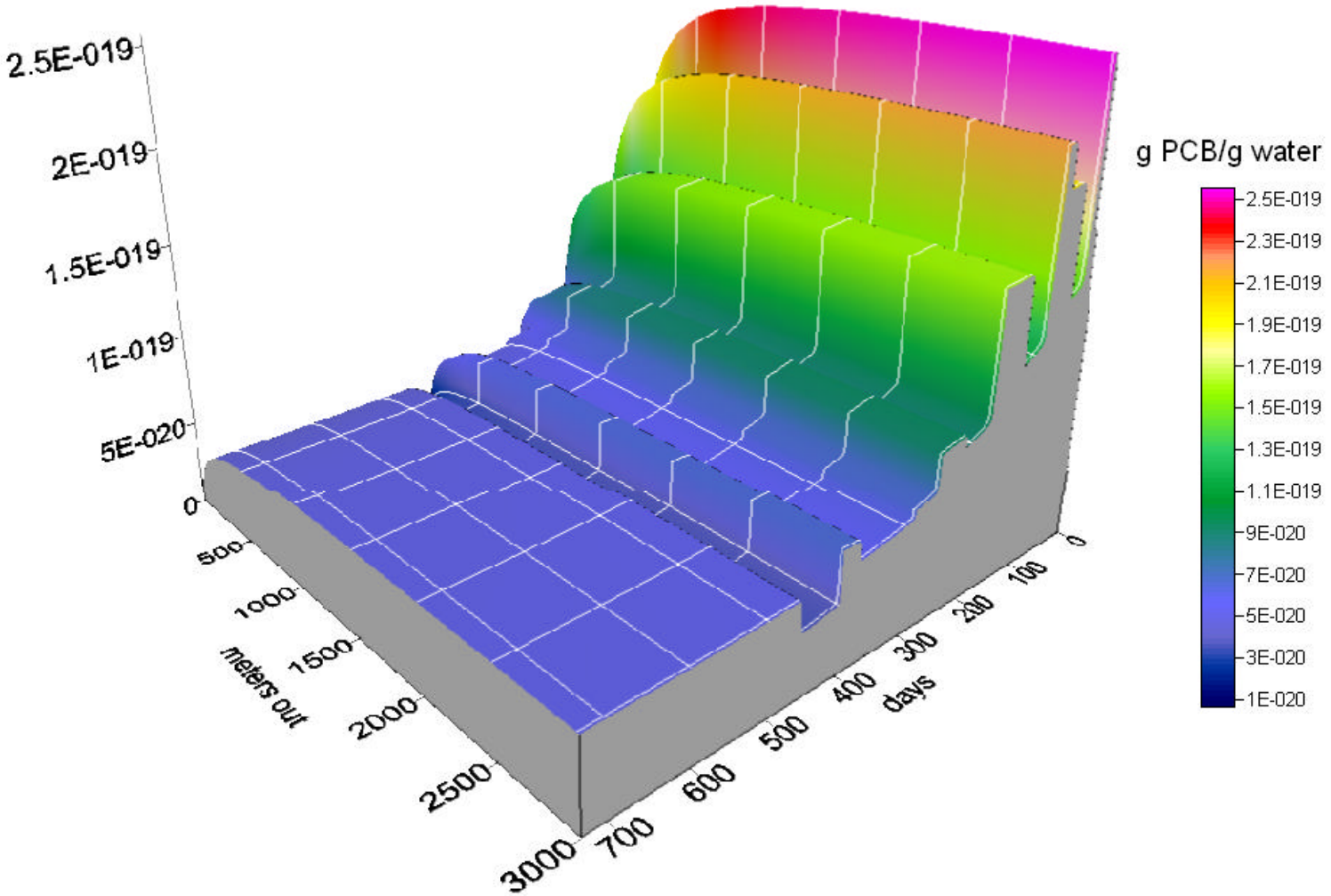

Figure B 42 - Monochlorobiphenyl in Water above Pycnocline

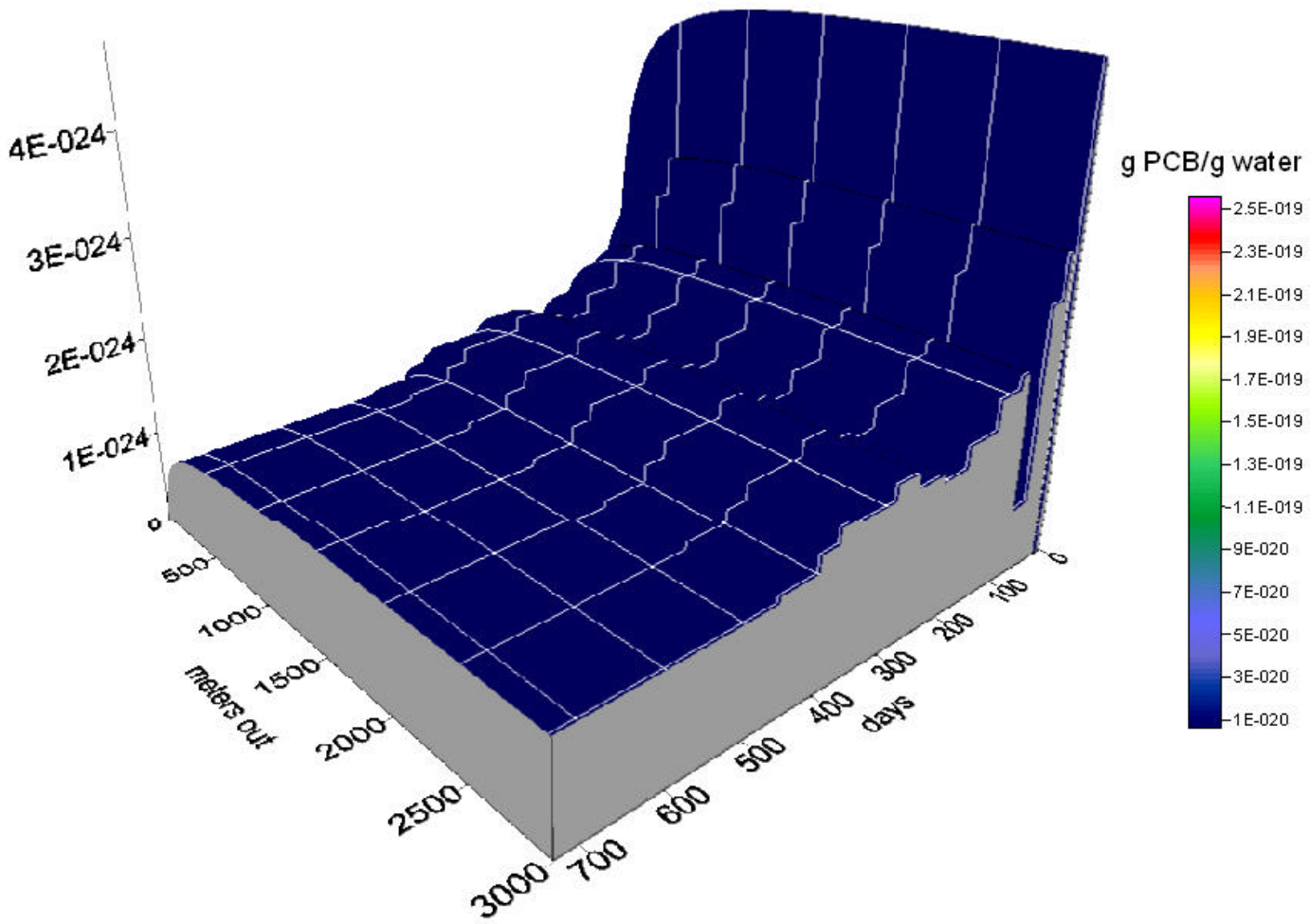

Figure B 43 - Dichlorobiphenyl in Water above Pycnocline

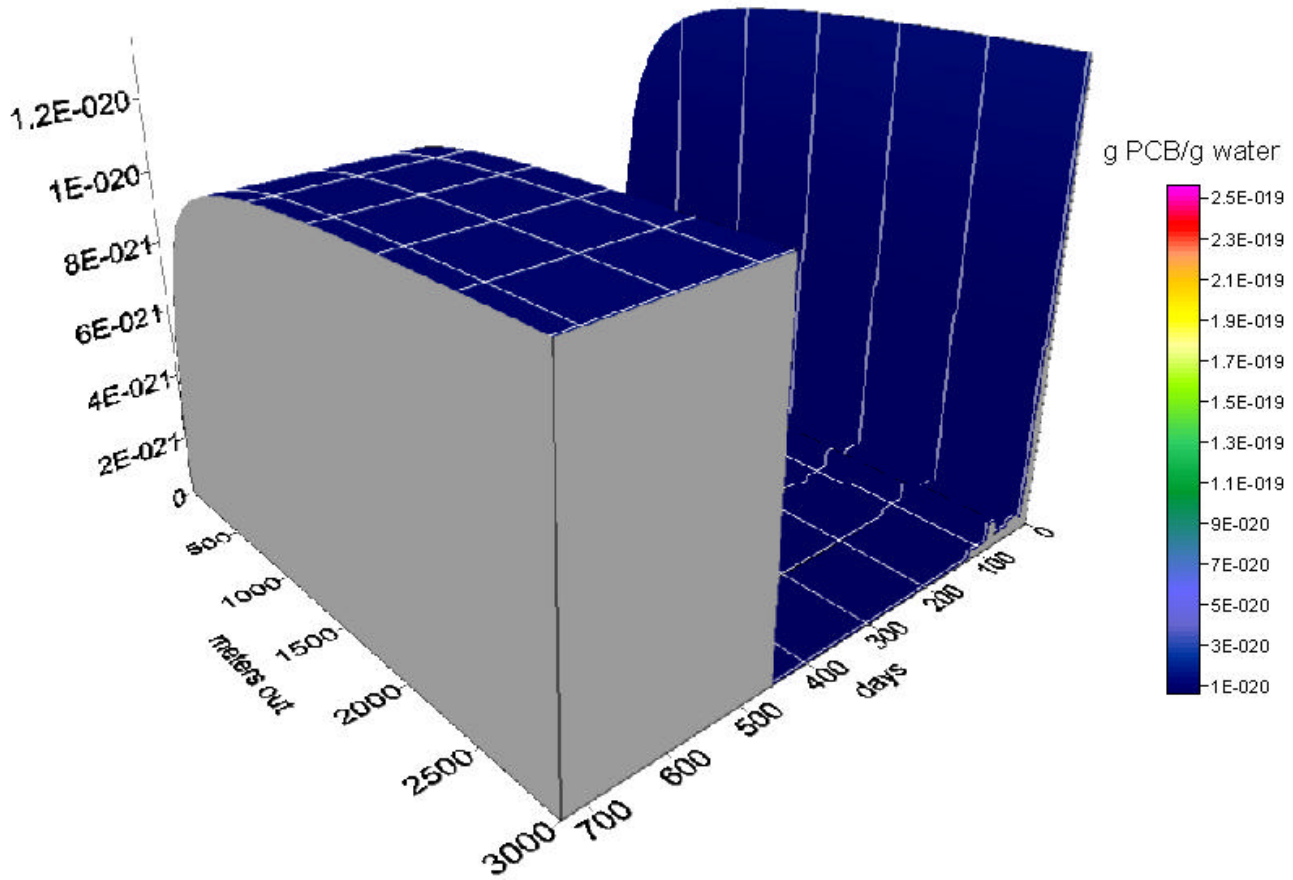

Figure B 44 - Trichlorobiphenyl in Water above Pycnocline

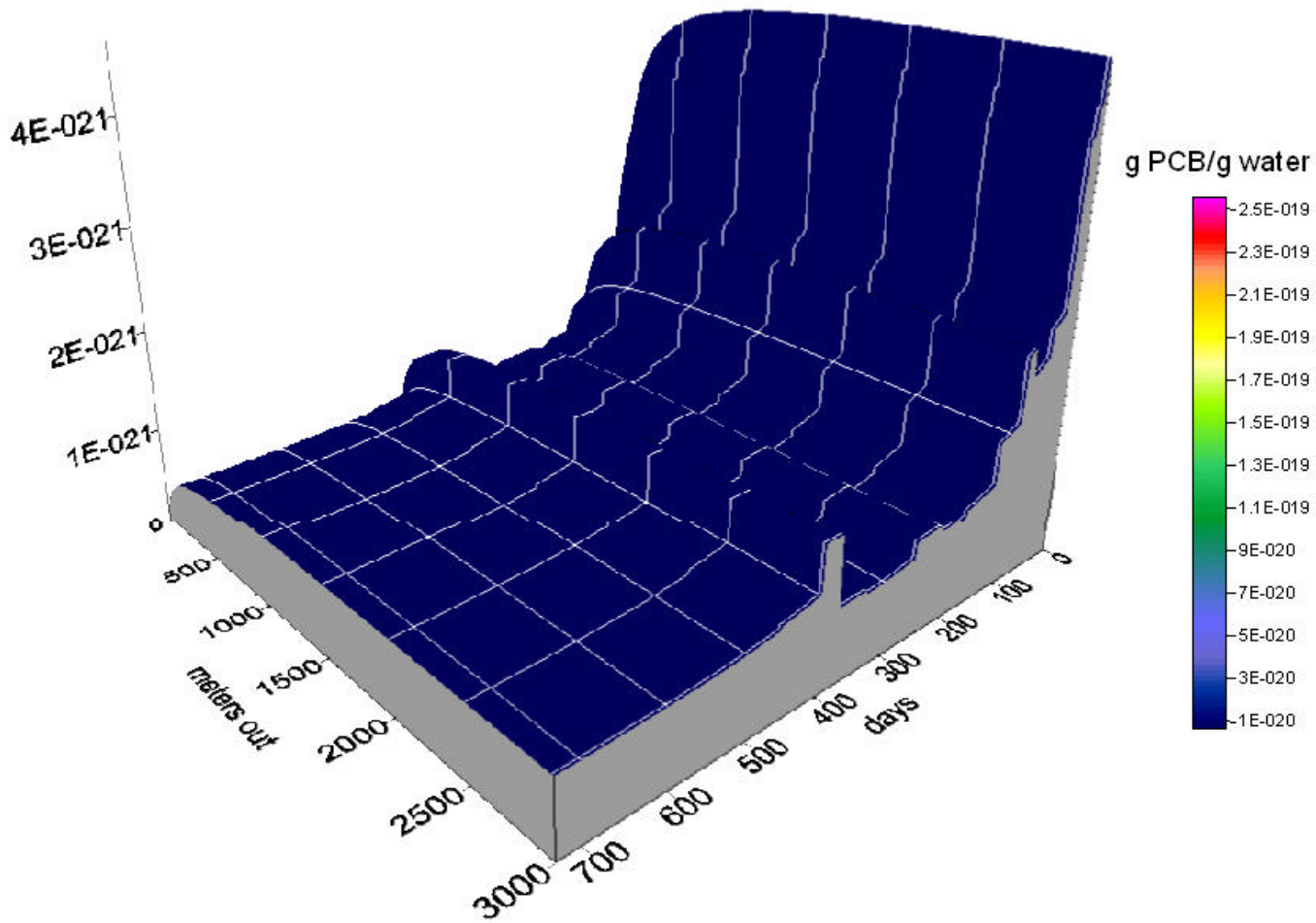

Figure B 45 - Tetrachlorobiphenyl in Water above Pycnocline

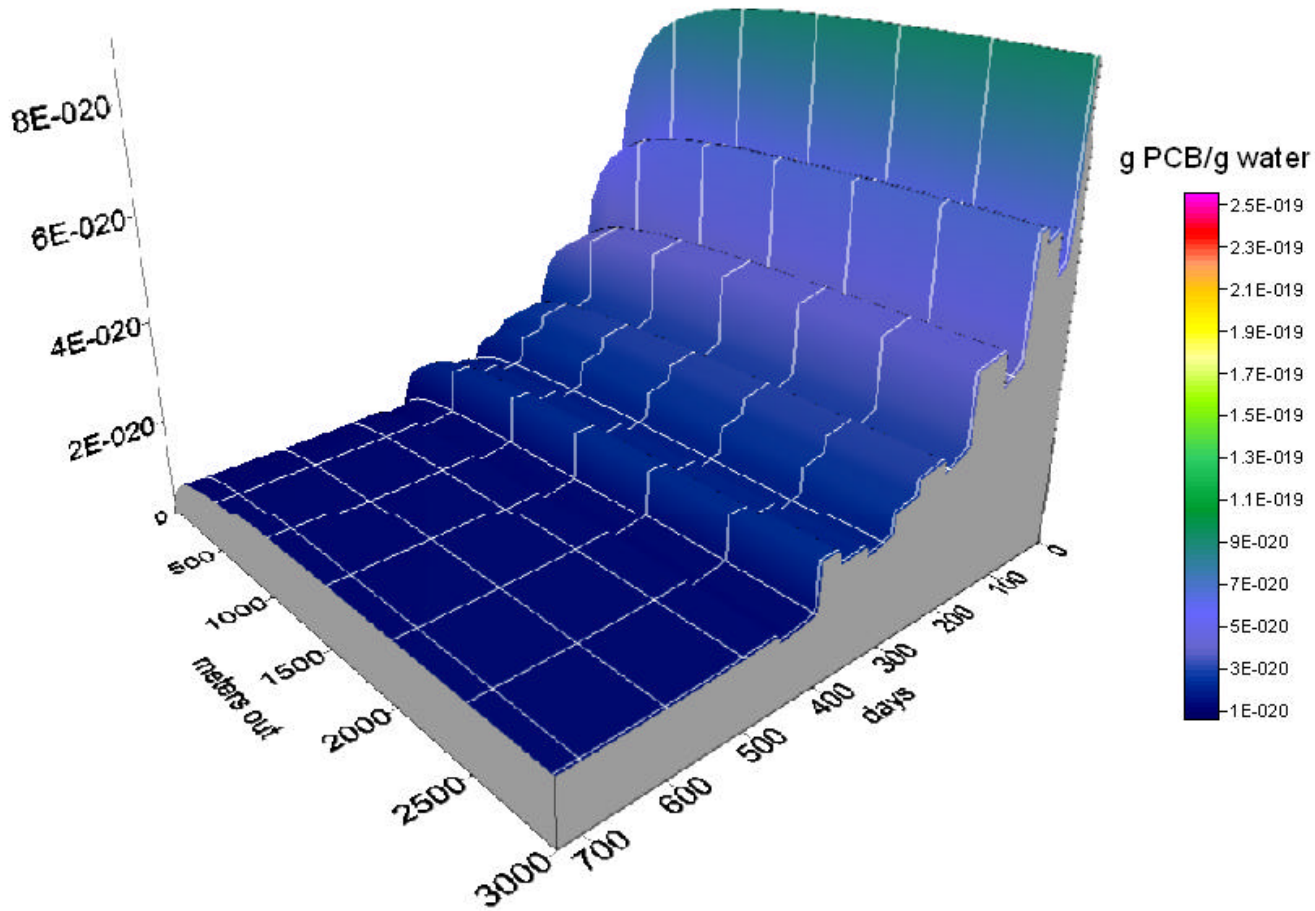

Figure B 46 – Pentachlorobiphenyl in Water above Pycnocline

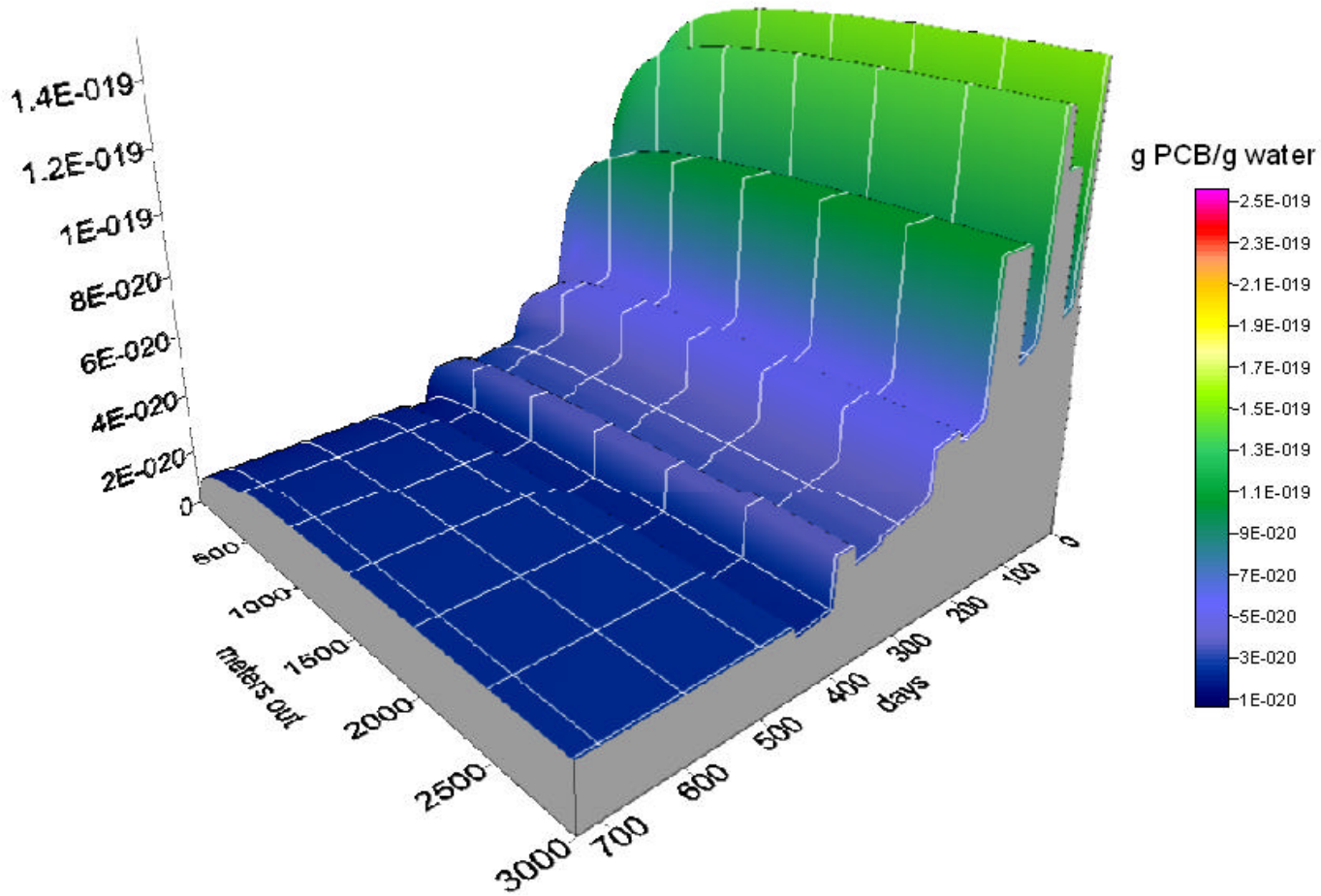

Figure B 47 - Hexachlorobiphenyl in Water above Pycnocline

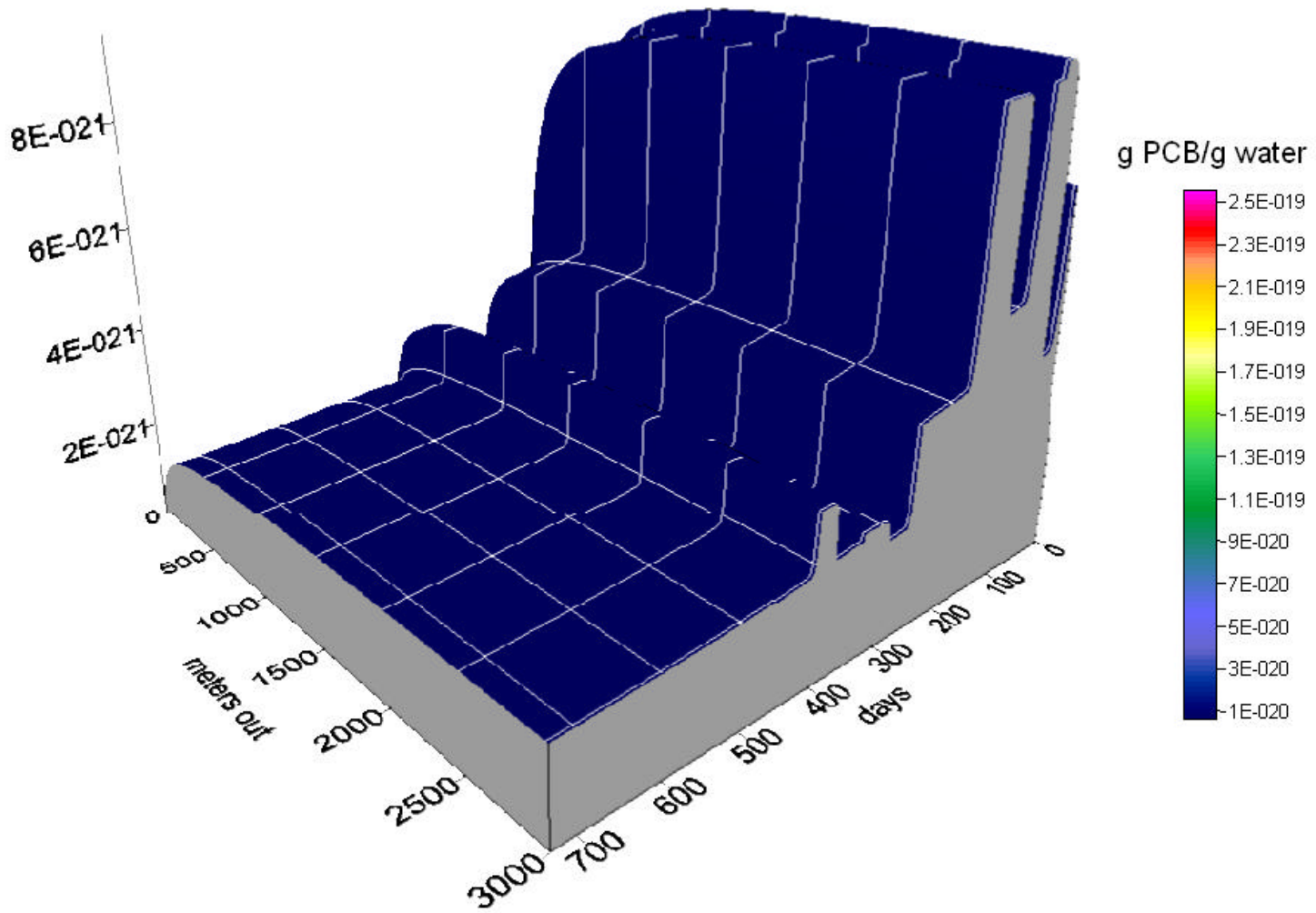

Figure B 48 - Heptachlorobiphenyl in Water above Pycnocline

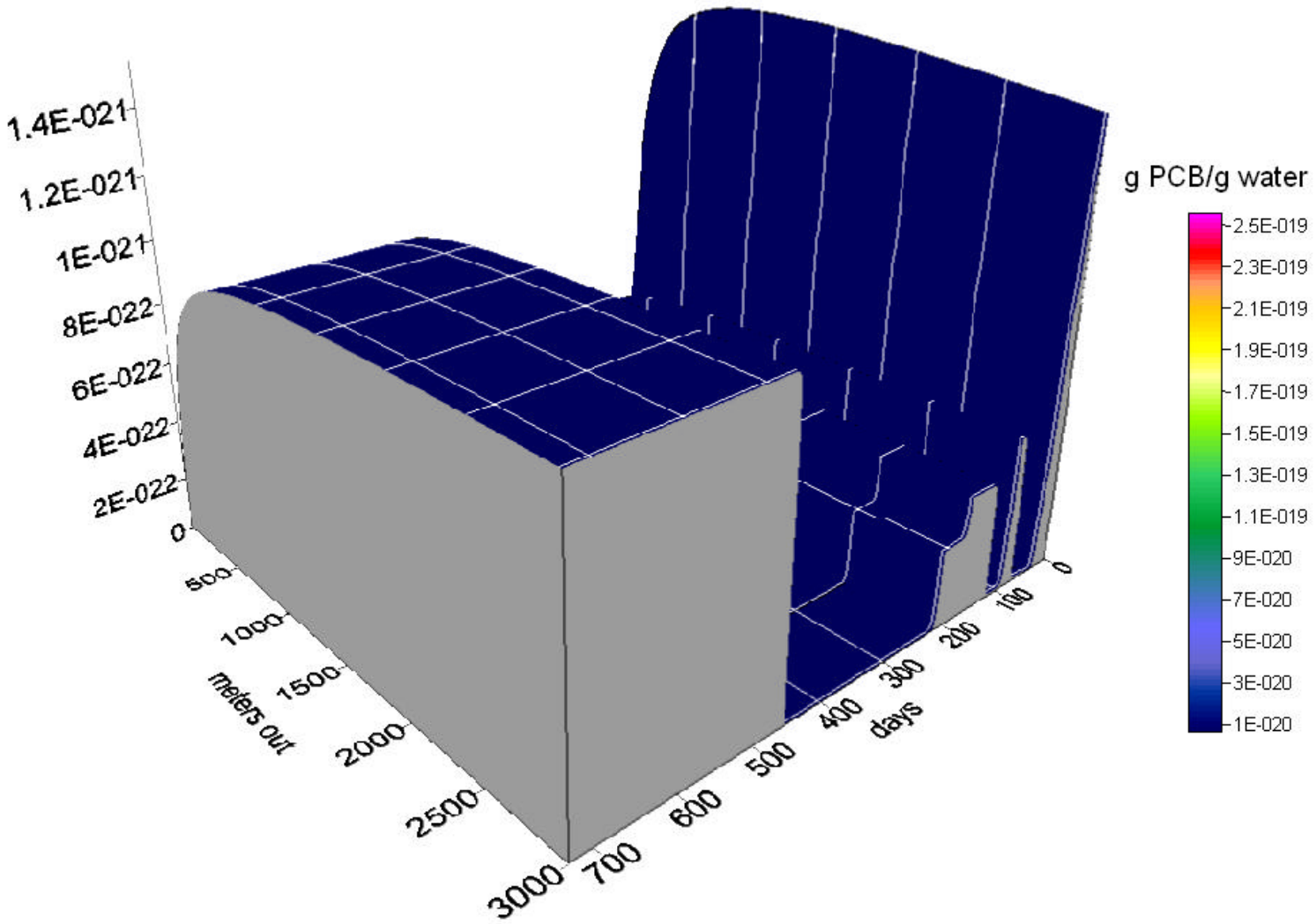

Figure B 49 - Nonachlorobiphenyl in Water above Pycnocline

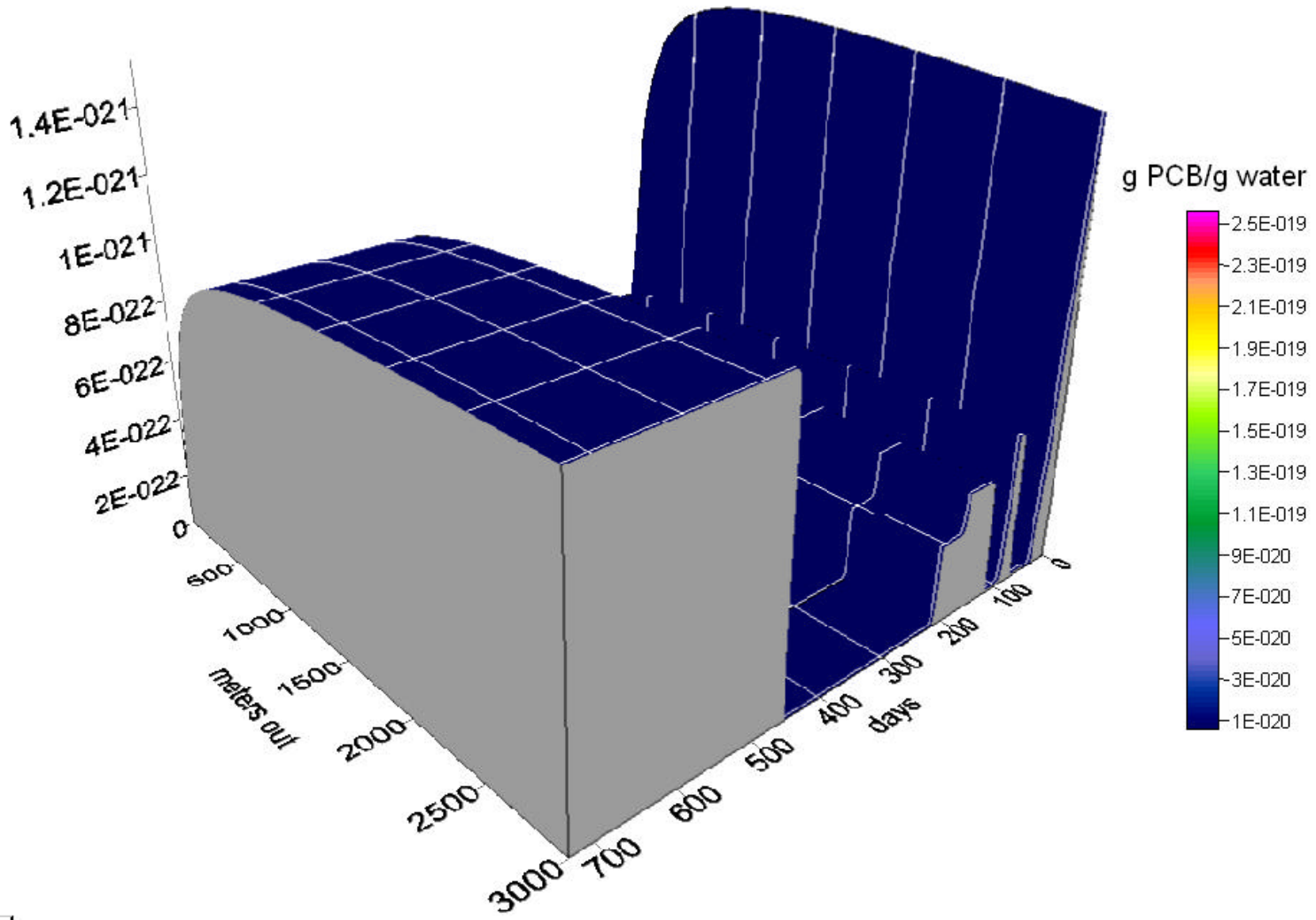

Figure B 50 - Decachlorobiphenyl in Water above Pycnocline

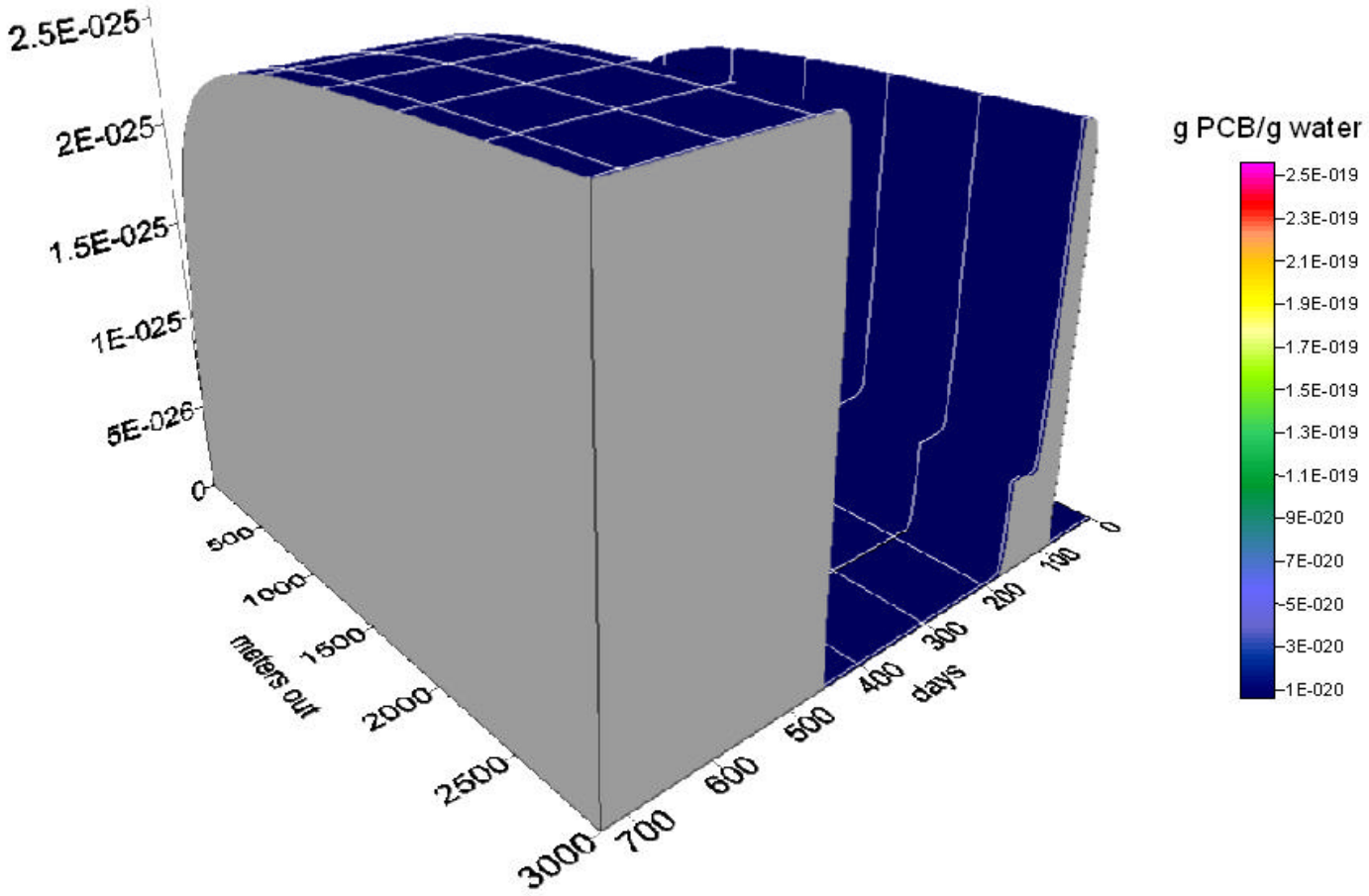

Figure B 51 - Total PCB in DOC above Pycnocline

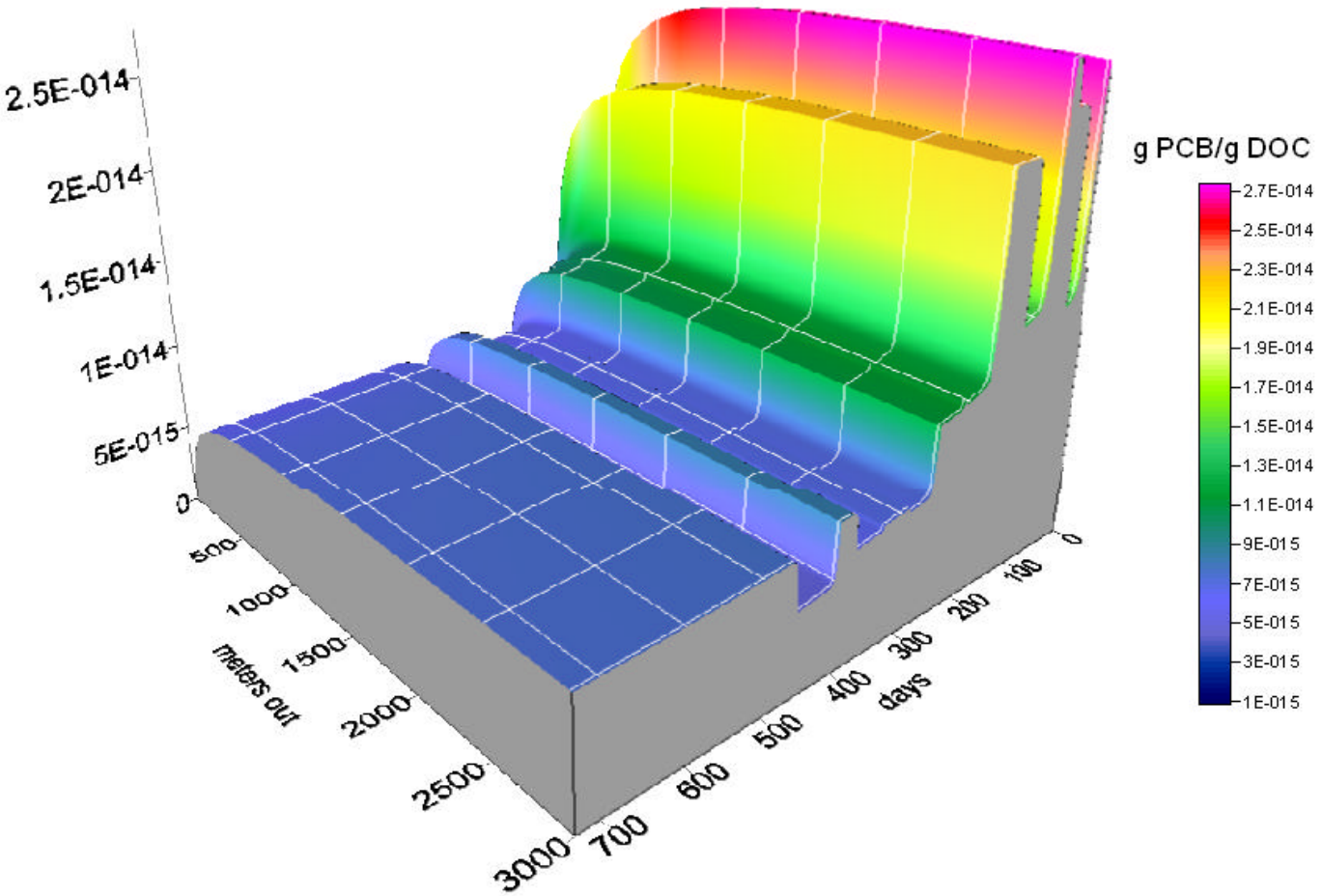

Figure B 52 - Monochlorobiphenyl in DOC above Pycnocline

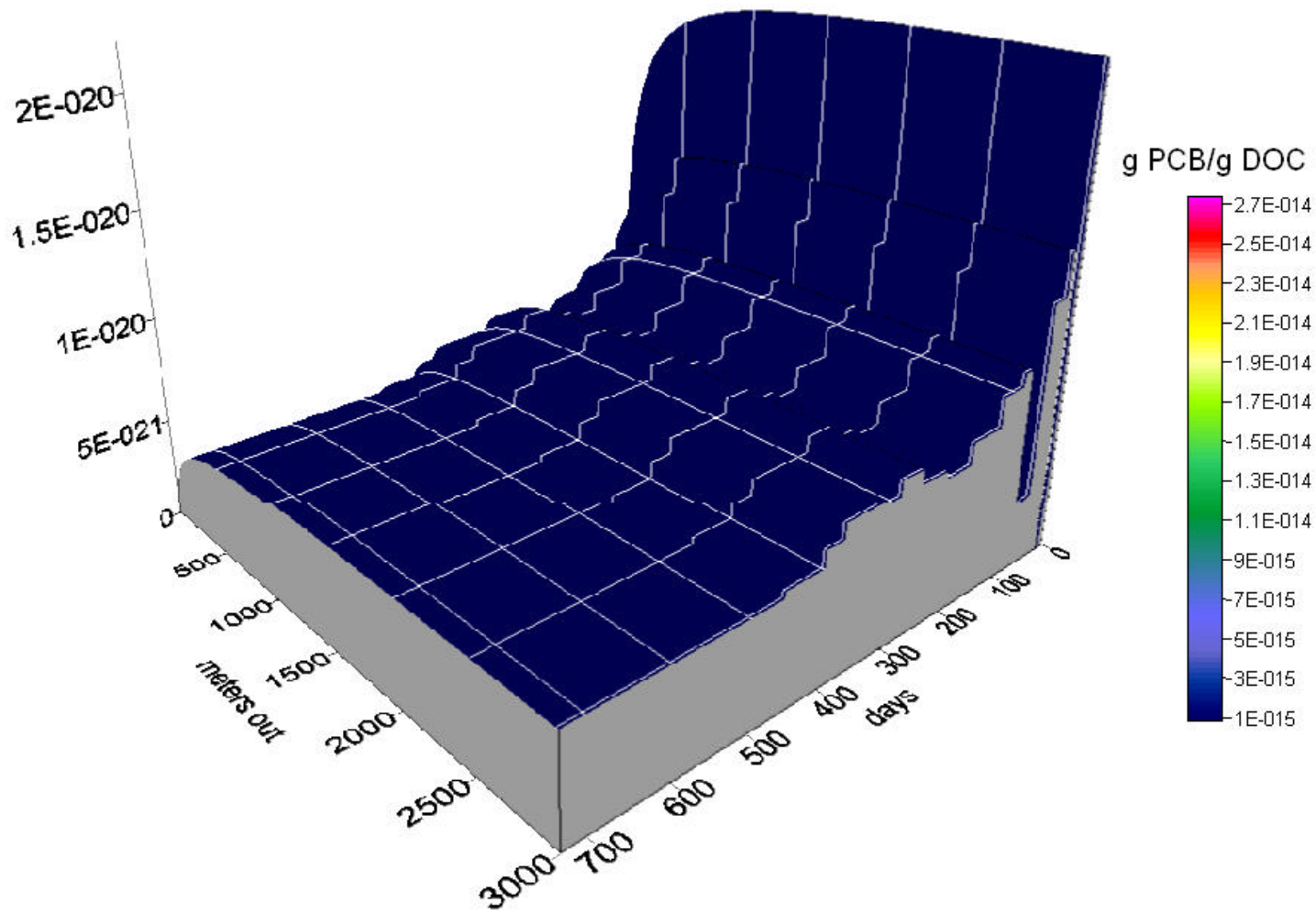

Figure B 53 – Dichlorobiphenyl in DOC above Pycnocline

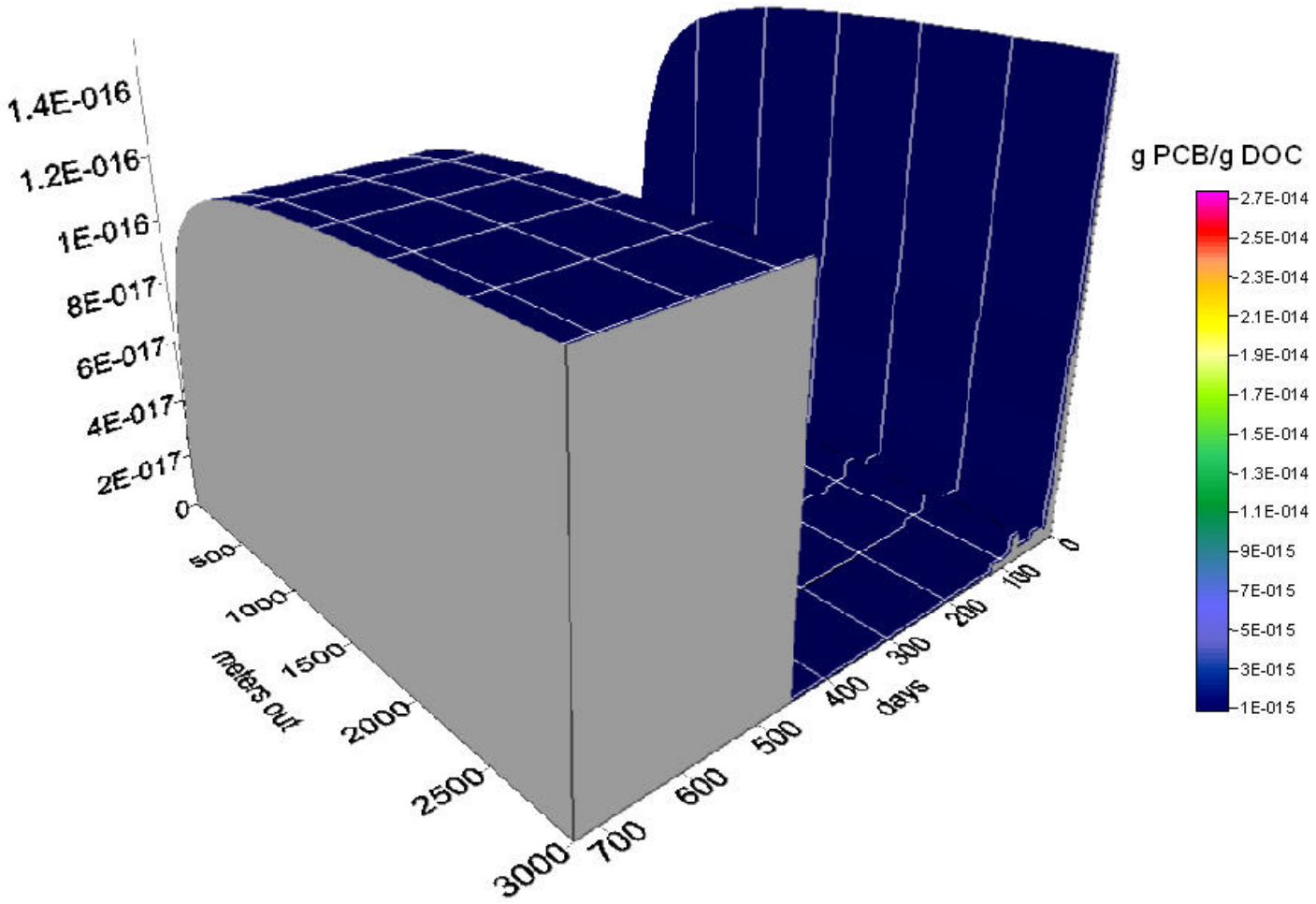

Figure B 54 - Trichlorobiphenyl in DOC above Pycnocline

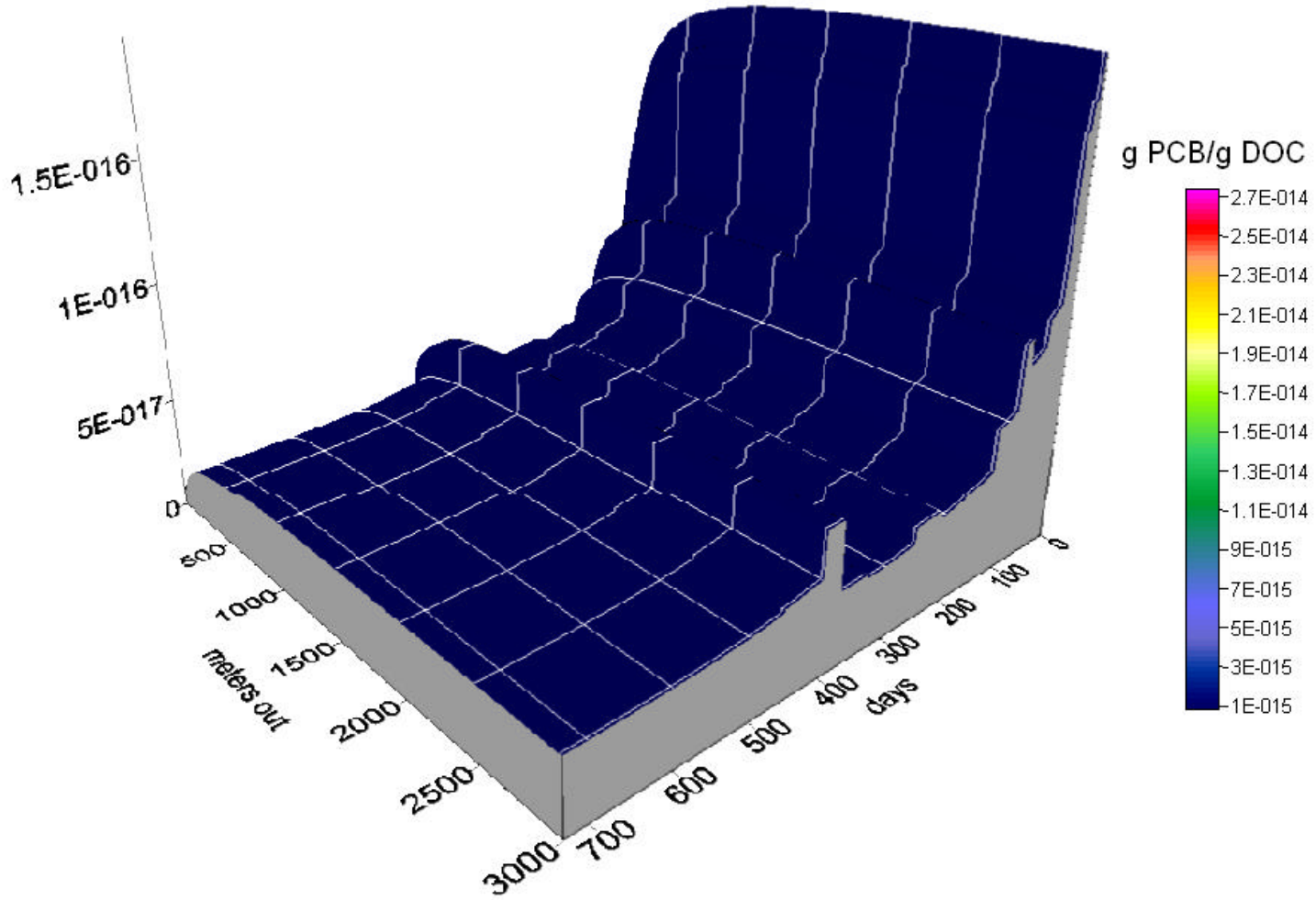

Figure B 55 - Tetrachlorobiphenyl in DOC above Pycnocline

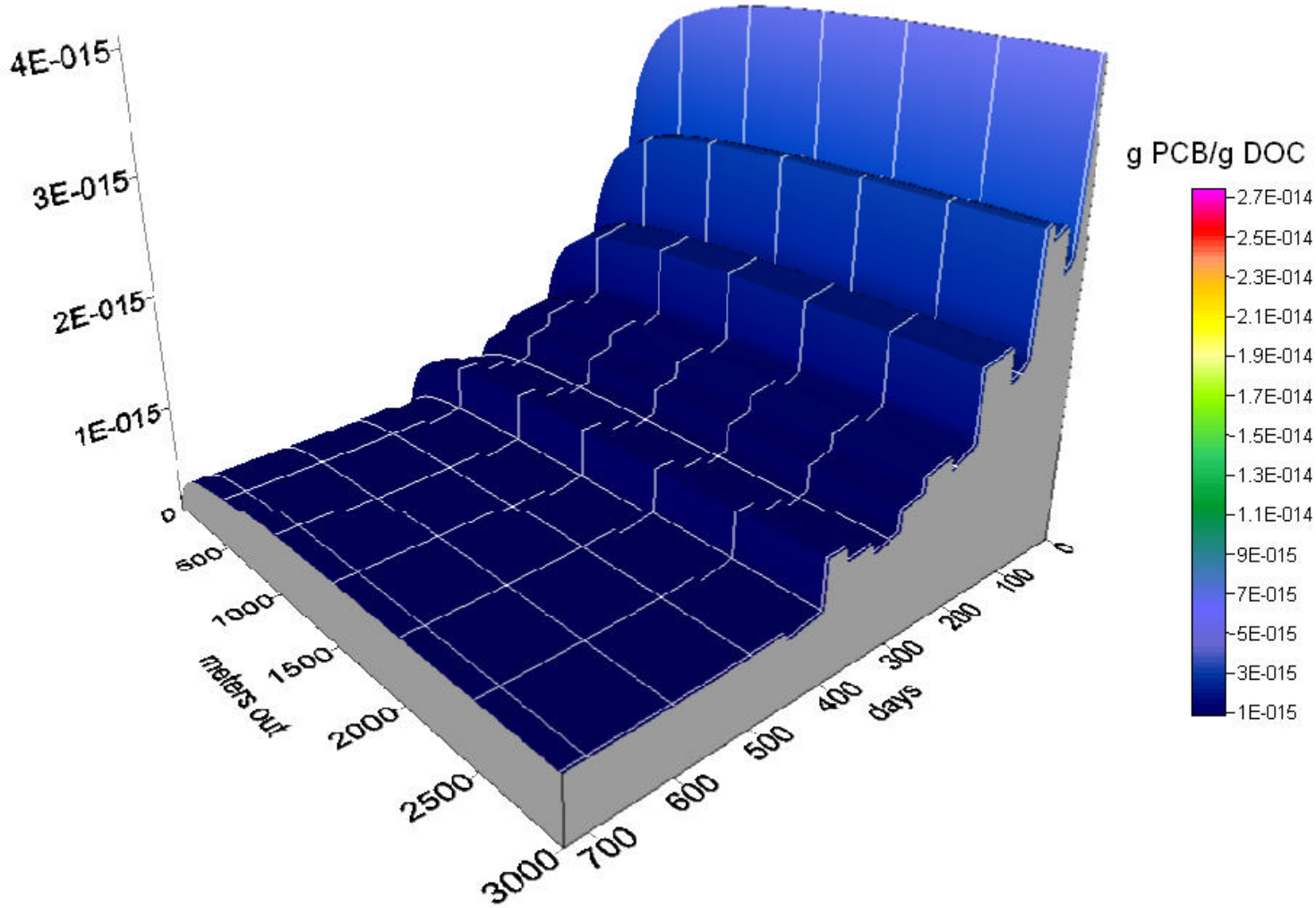

Figure B 56 - Pentachlorobiphenyl in DOC above Pycnocline

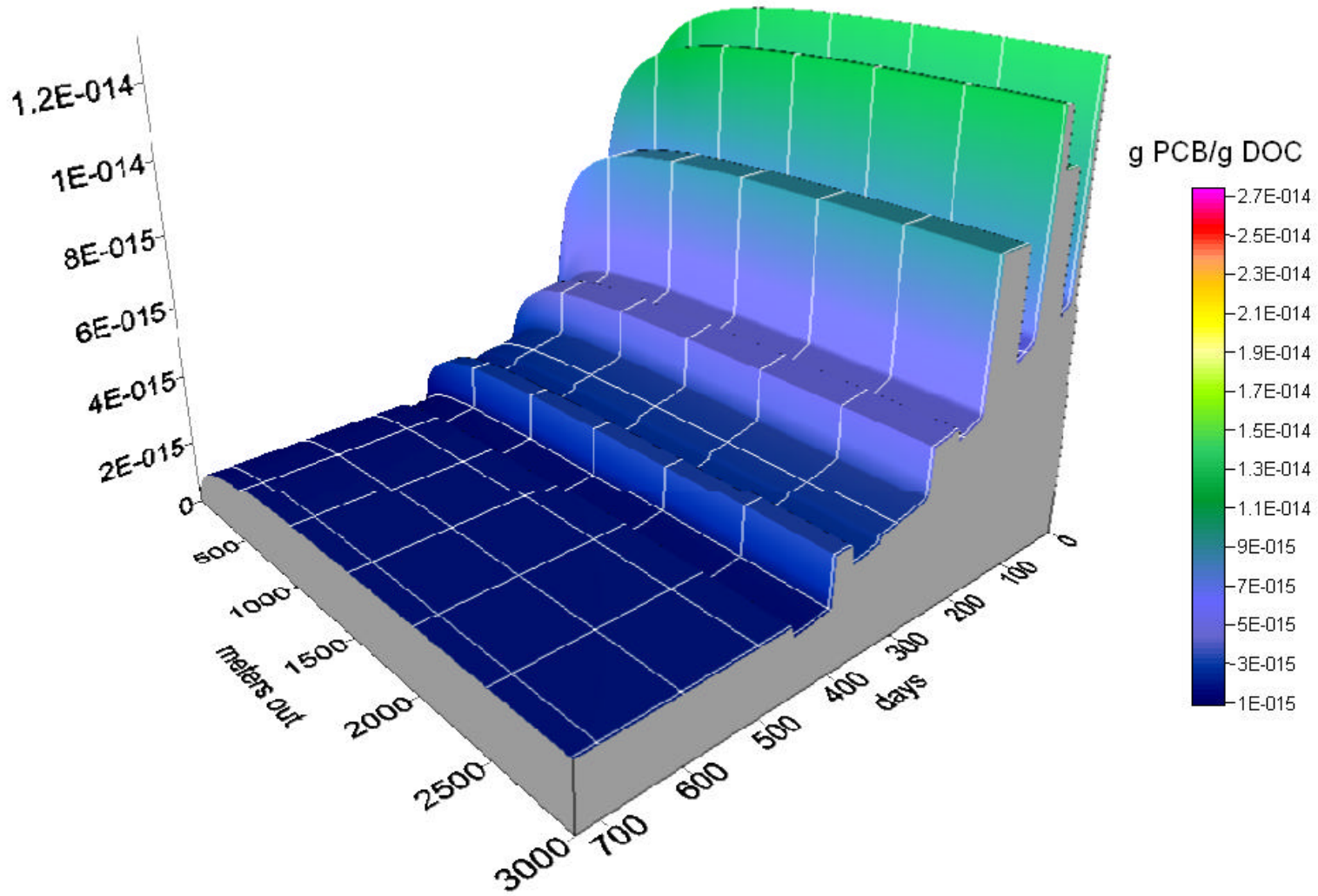

Figure B 57 - Hexachlorobiphenyl in DOC above Pycnocline

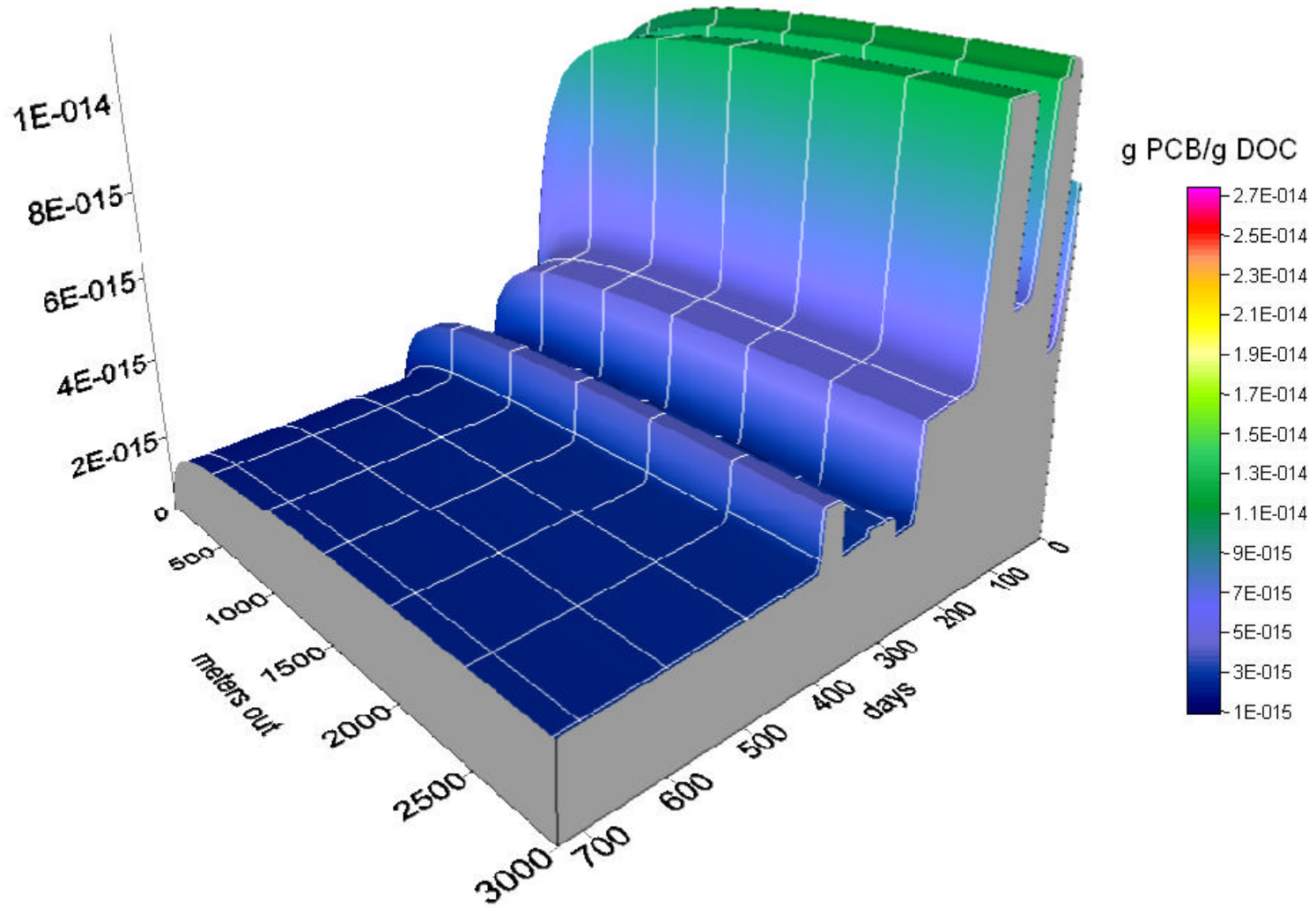

Figure B 58 - Heptachlorobiphenyl in DOC above Pycnocline

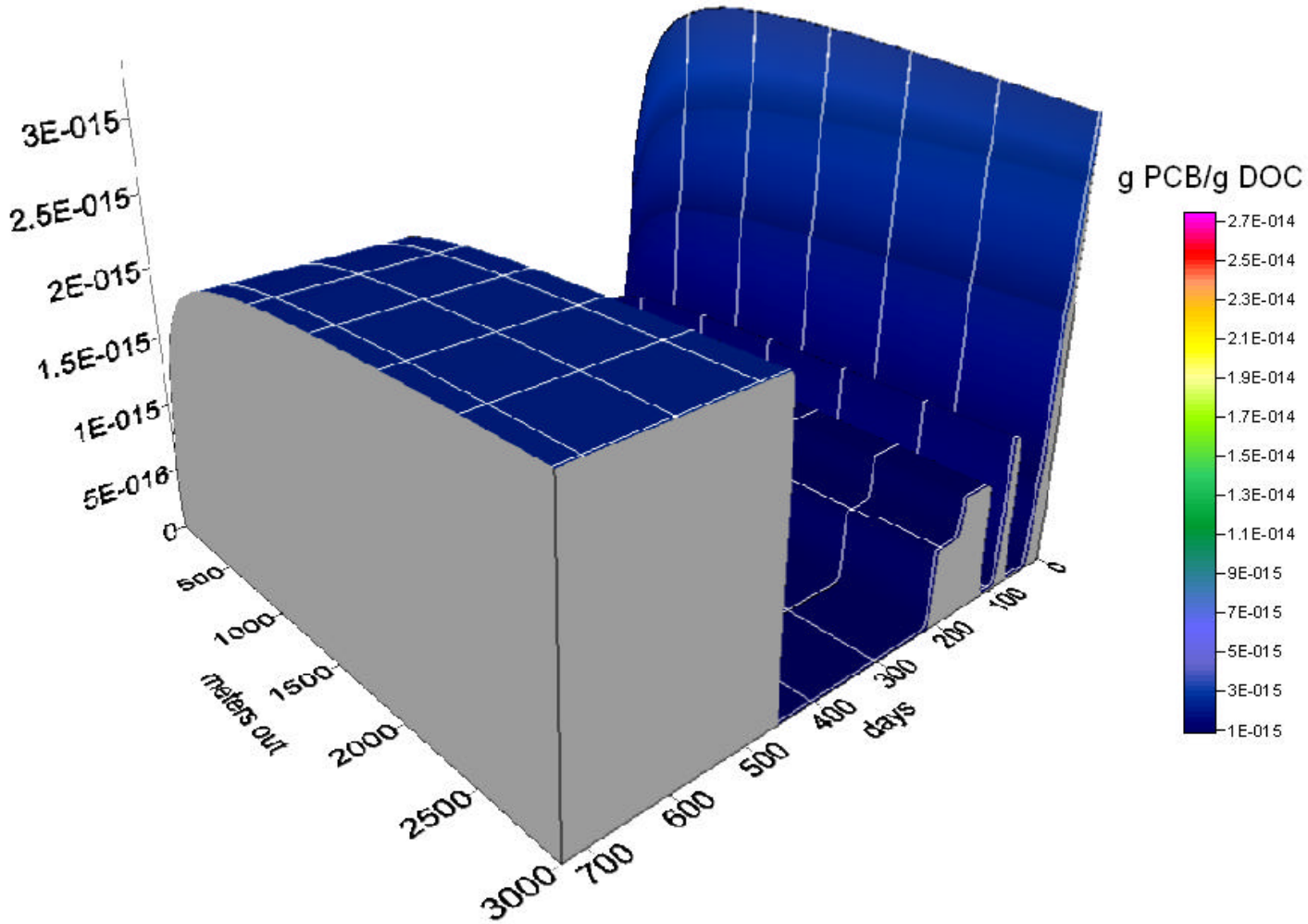

Figure B 59 – Nonachlorobiphenyl in DOC above Pycnocline

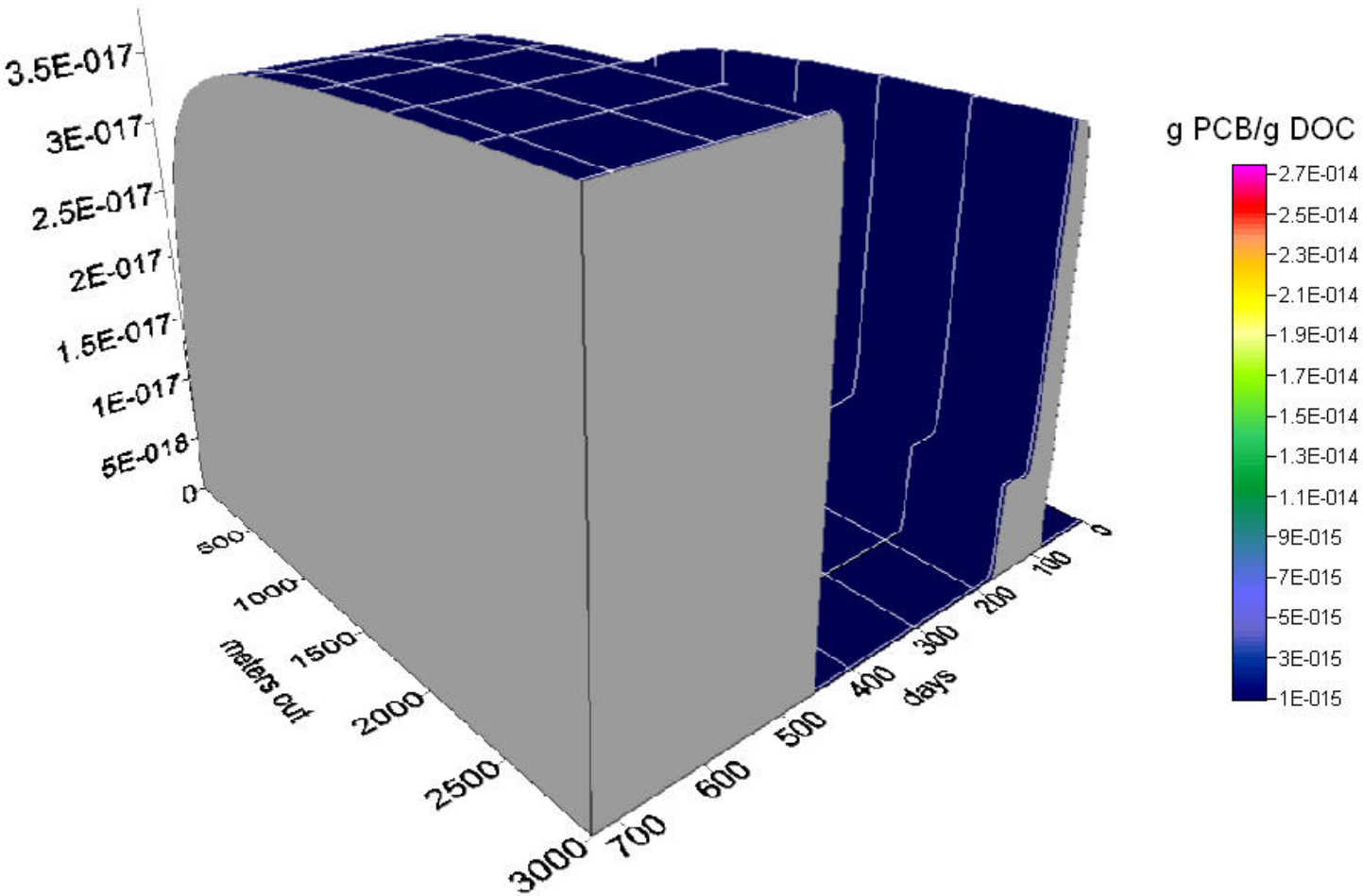

Figure B 60 - Decachlorobiphenyl in DOC above Pycnocline

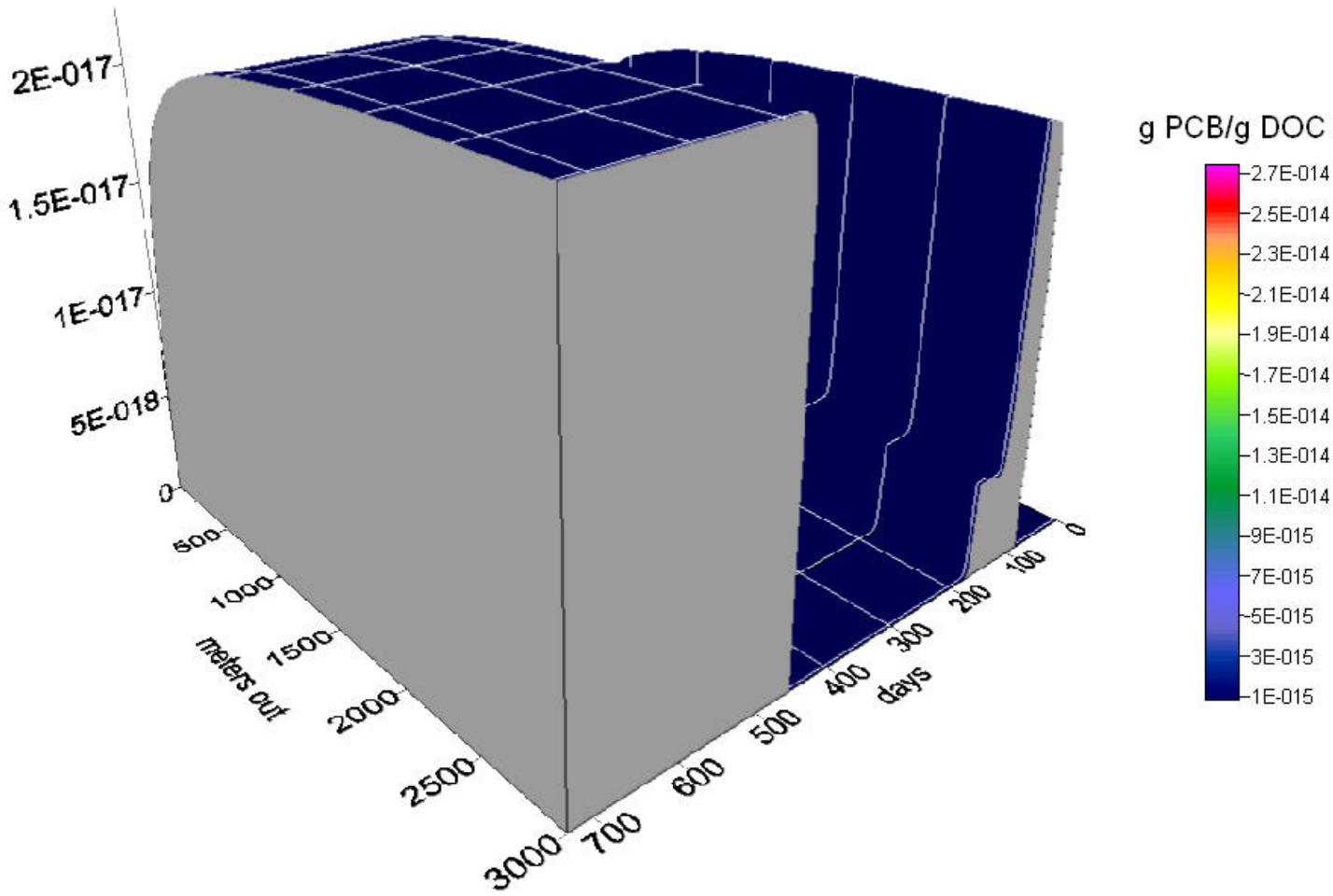

Figure B 61 - Total PCB in TSS above Pycnocline

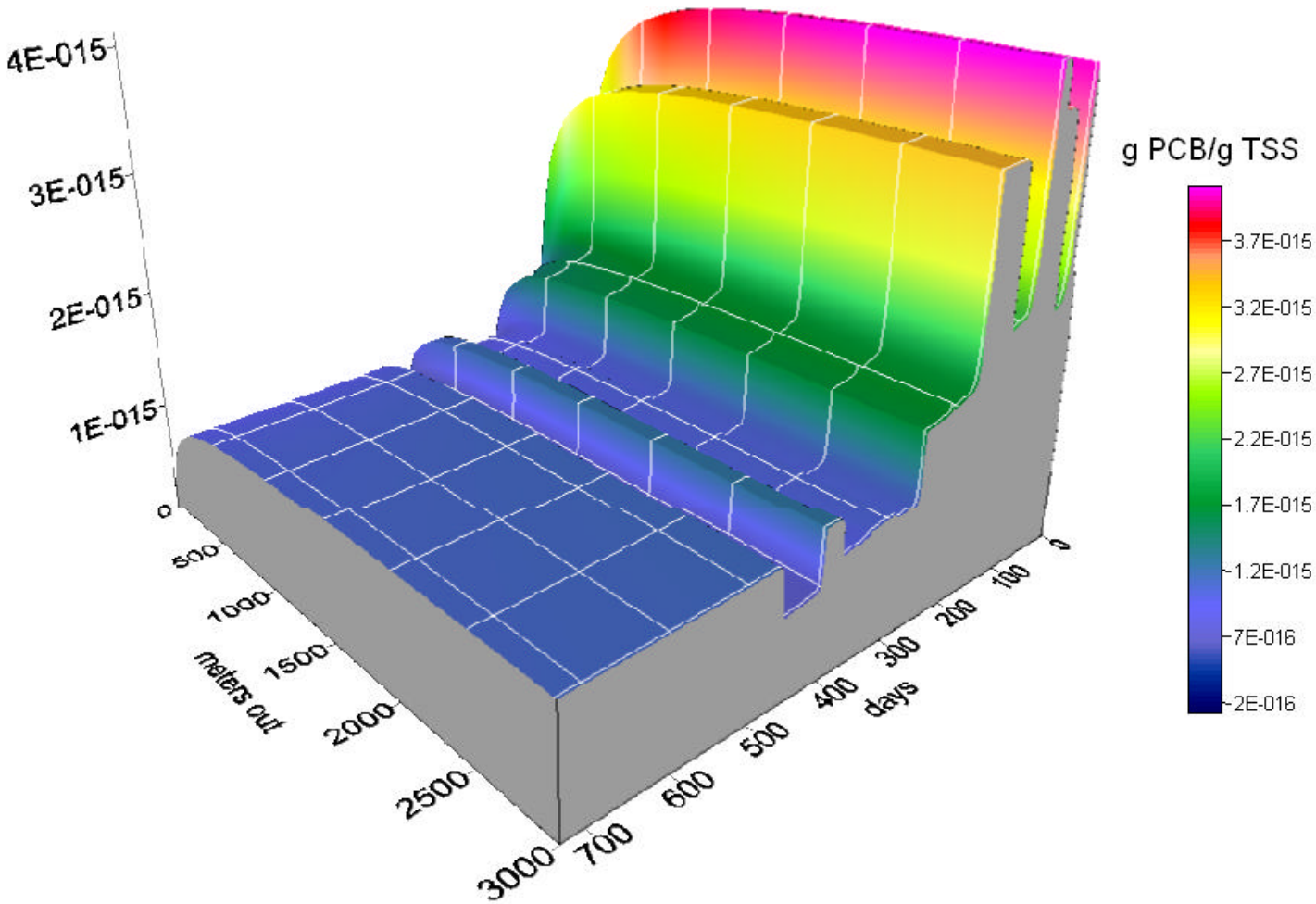

Figure B 62 - Monochlorobiphenyl in TSS above Pycnocline

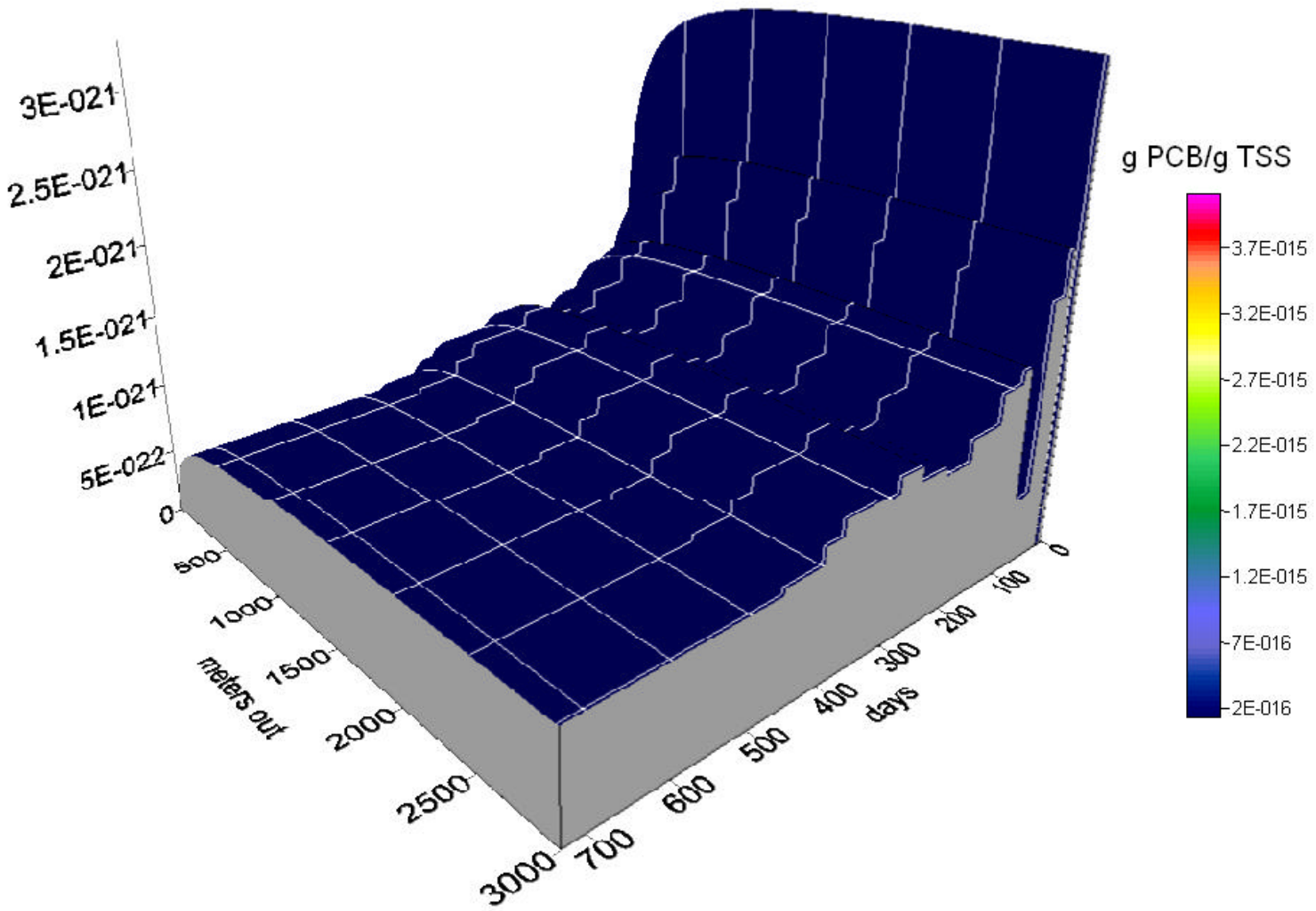

Figure B 63 - Dichlorobiphenyl in TSS above pycnocline

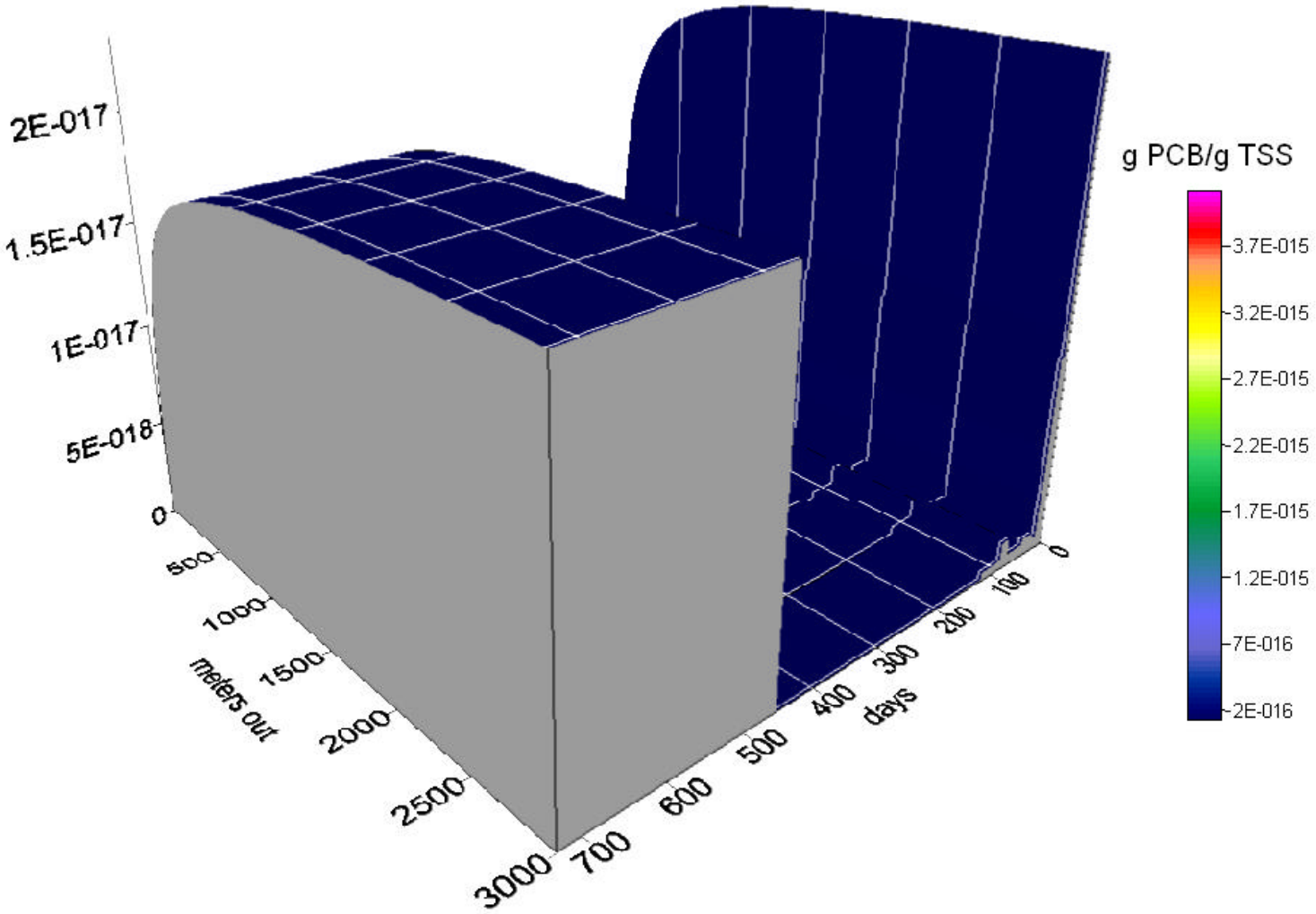

Figure B 64 - Trichlorobiphenyl in TSS above Pycnocline

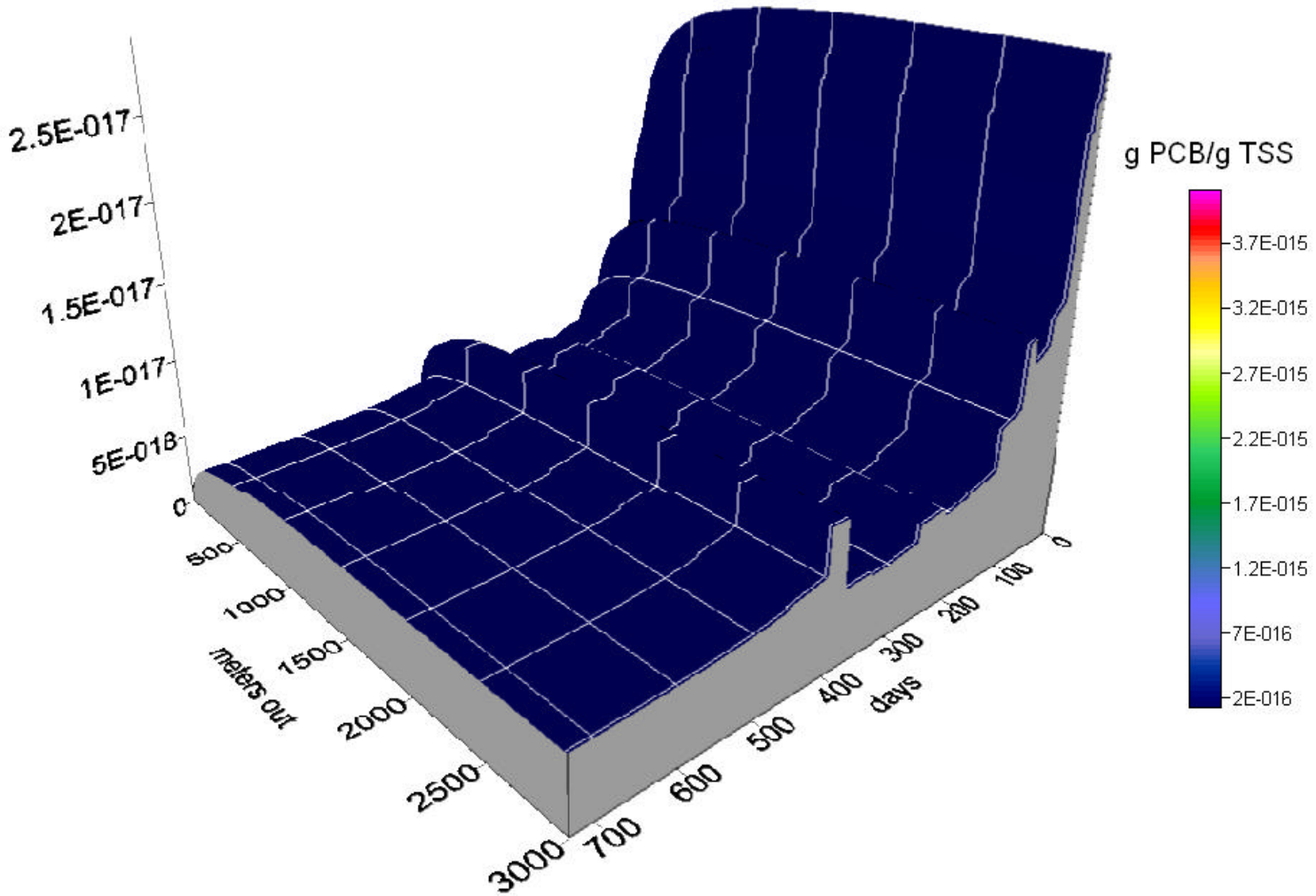

Figure B 65 - Tetrachlorobiphenyl in TSS above Pycnocline

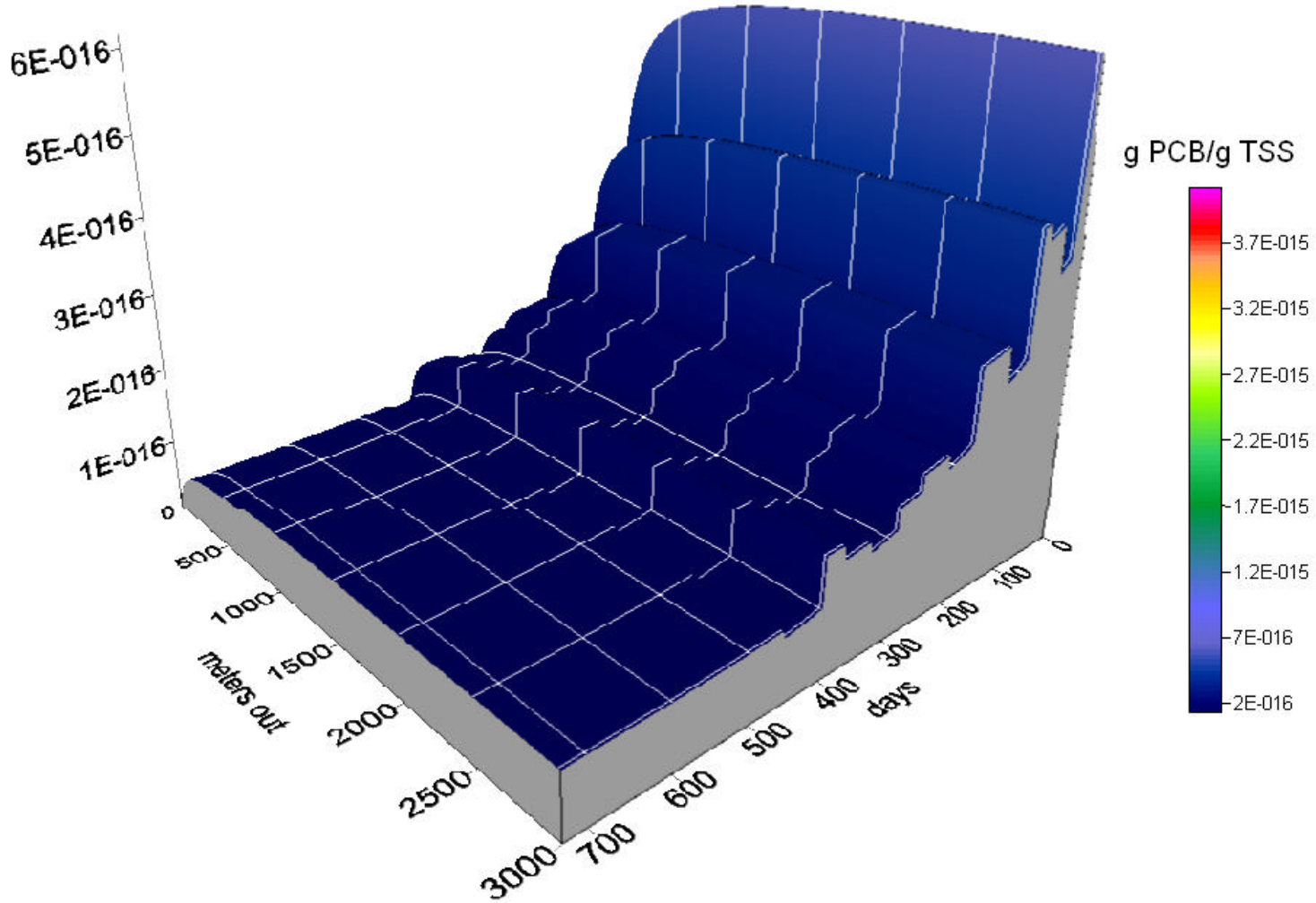

Figure B 66 - Pentachlorobiphenyl in TSS above Pycnocline

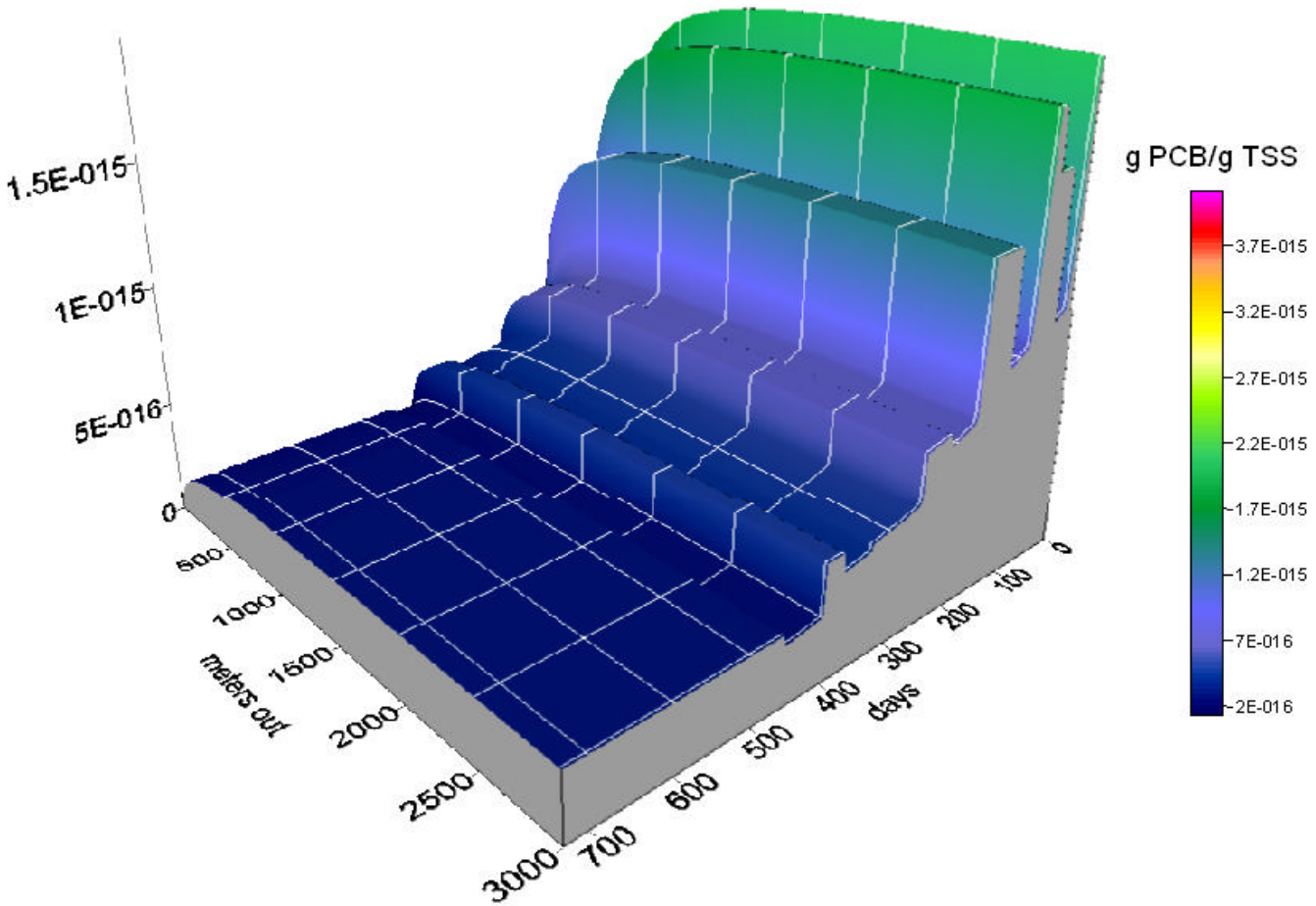

Figure B 67 - Hexachlorobiphenyl in TSS above Pycnocline

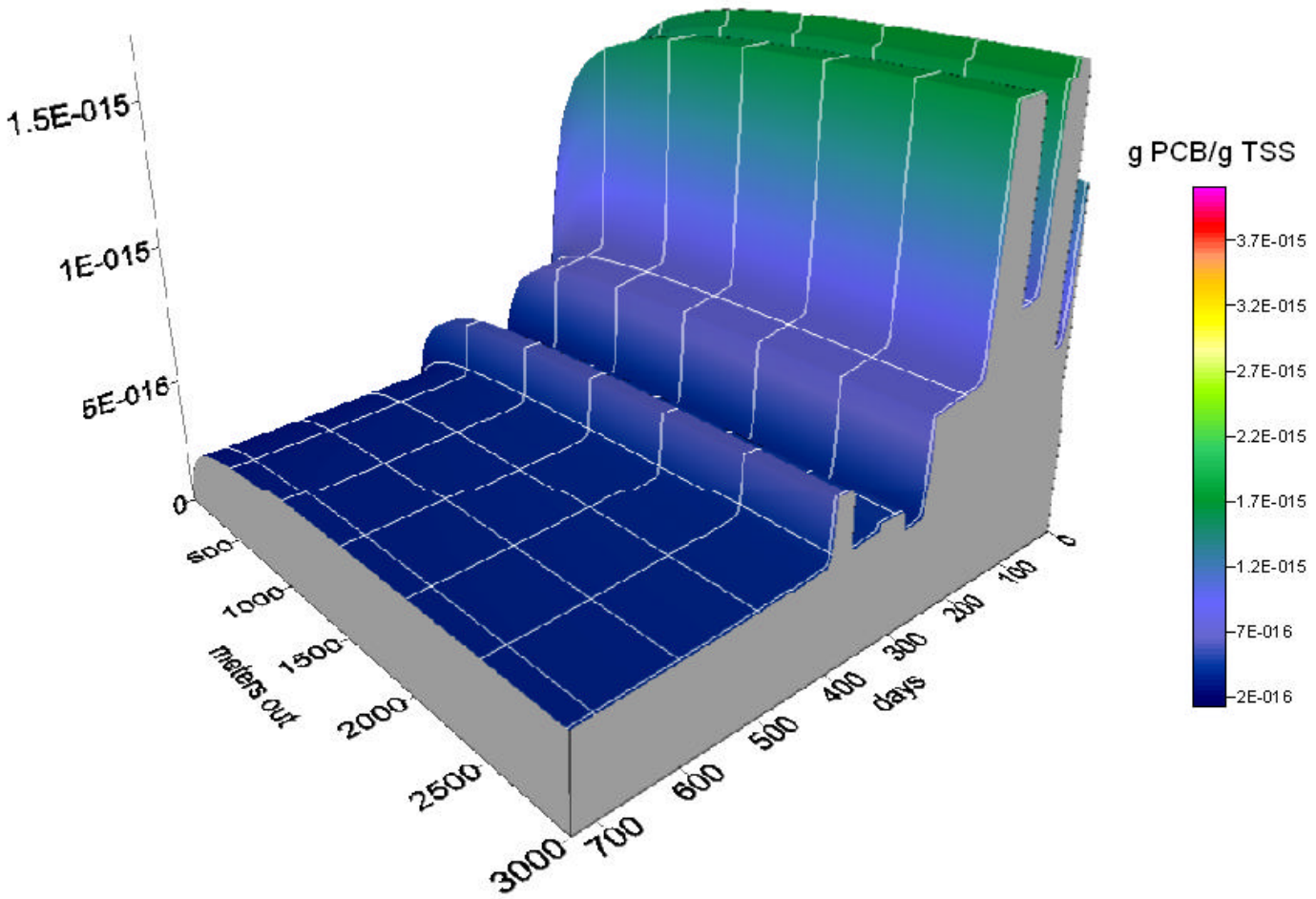

Figure B 68 - Heptachlorobiphenyl in TSS above Pycnocline

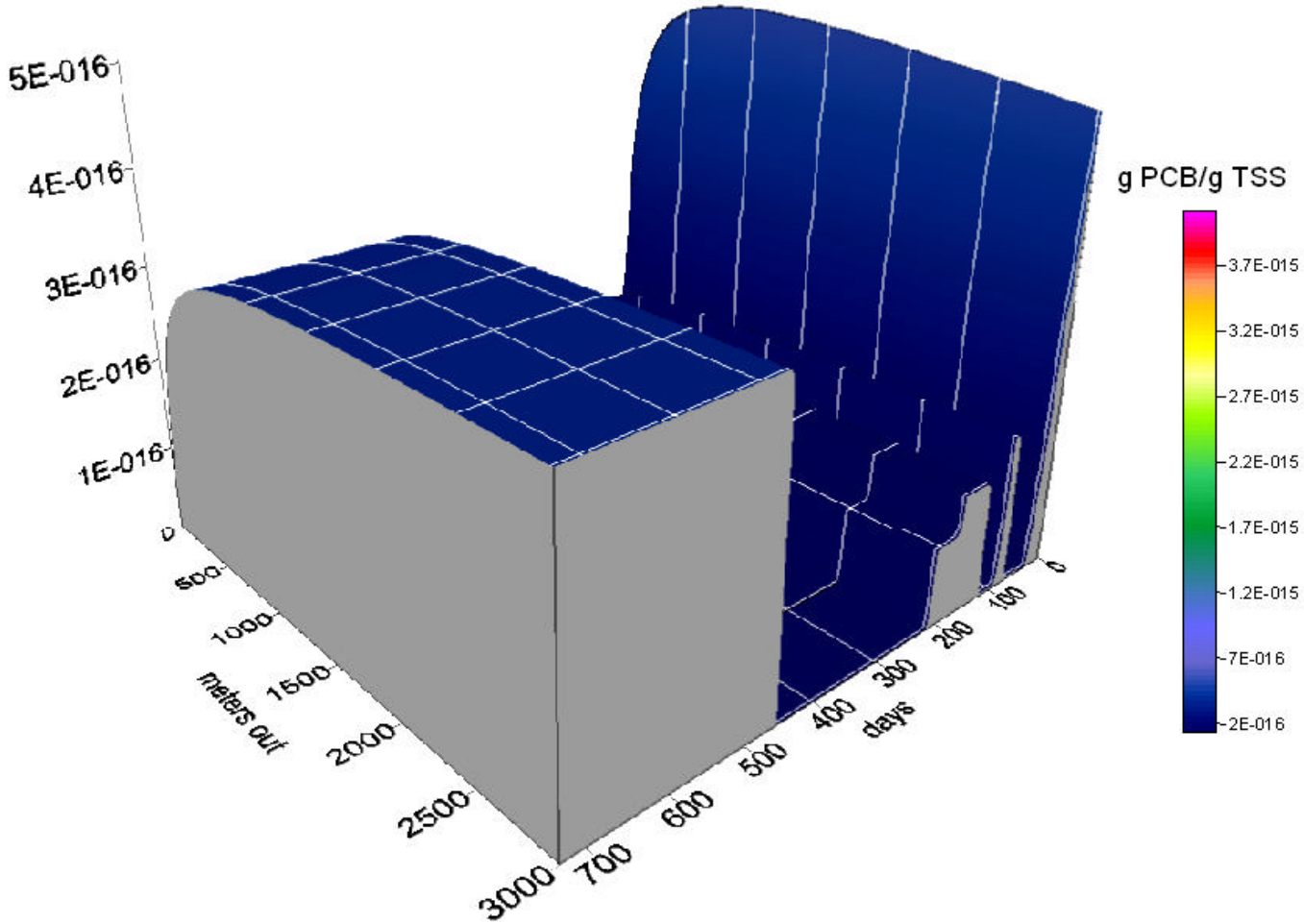

Figure B 69 - Nonachlorobiphenyl in TSS above Pycnocline

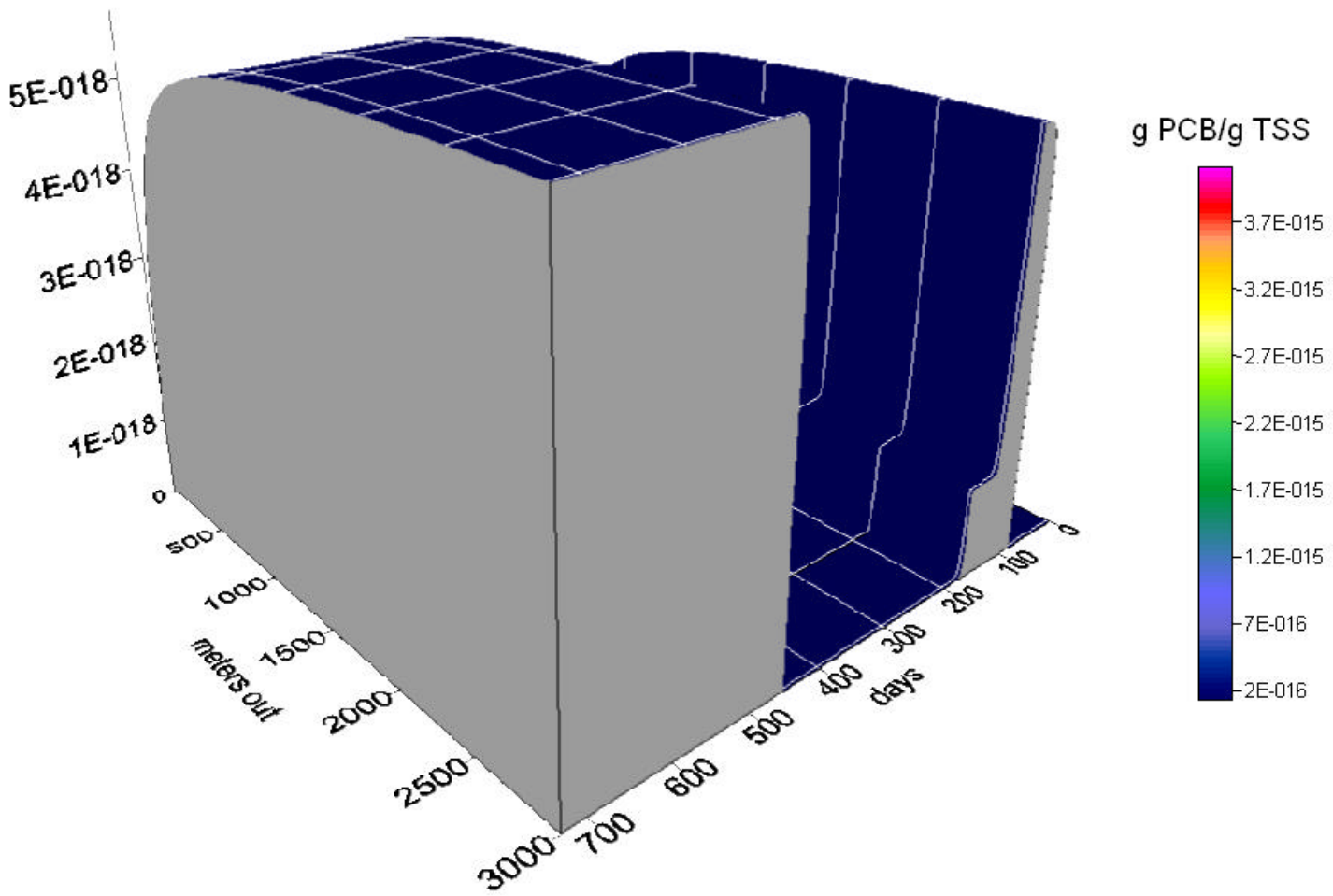

Figure B 70 - Decachlorobiphenyl in TSS above Pycnocline

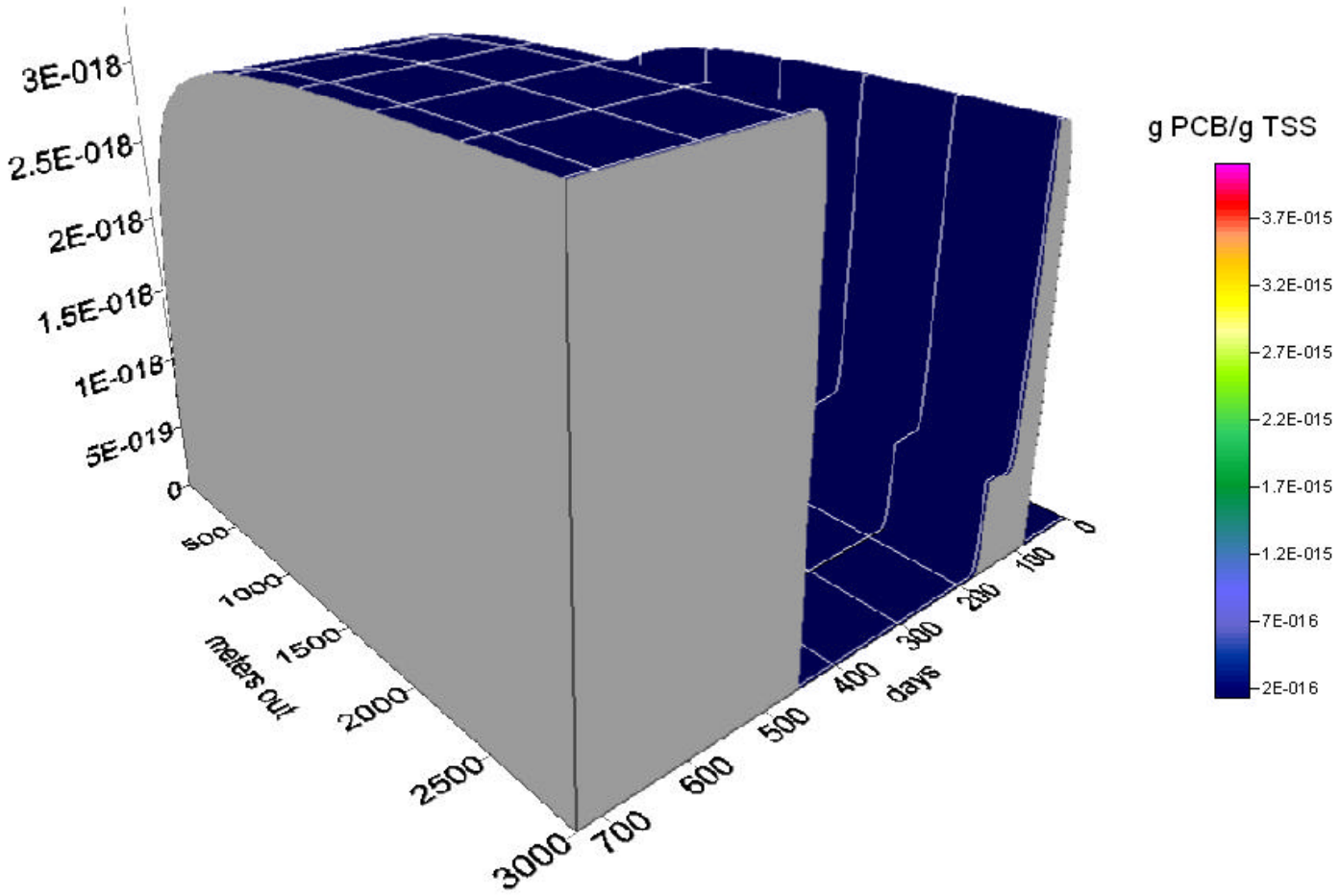

Figure C 1 – Monochlorobiphenyl Concentrations at Distances of Highest Concentrations

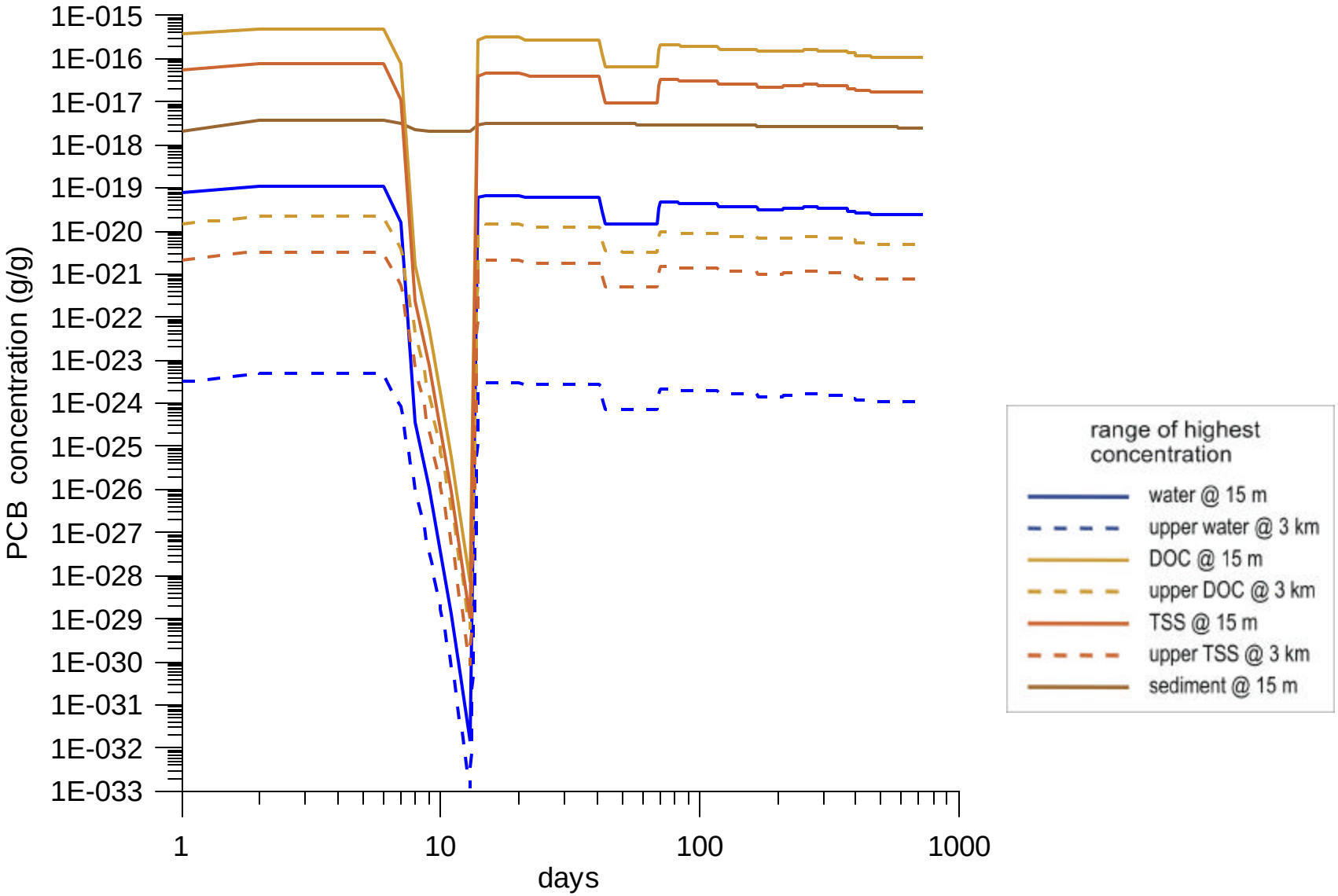

Figure C 2 – Monochlorobiphenyl Concentrations and Total Released Mass inside the Ship

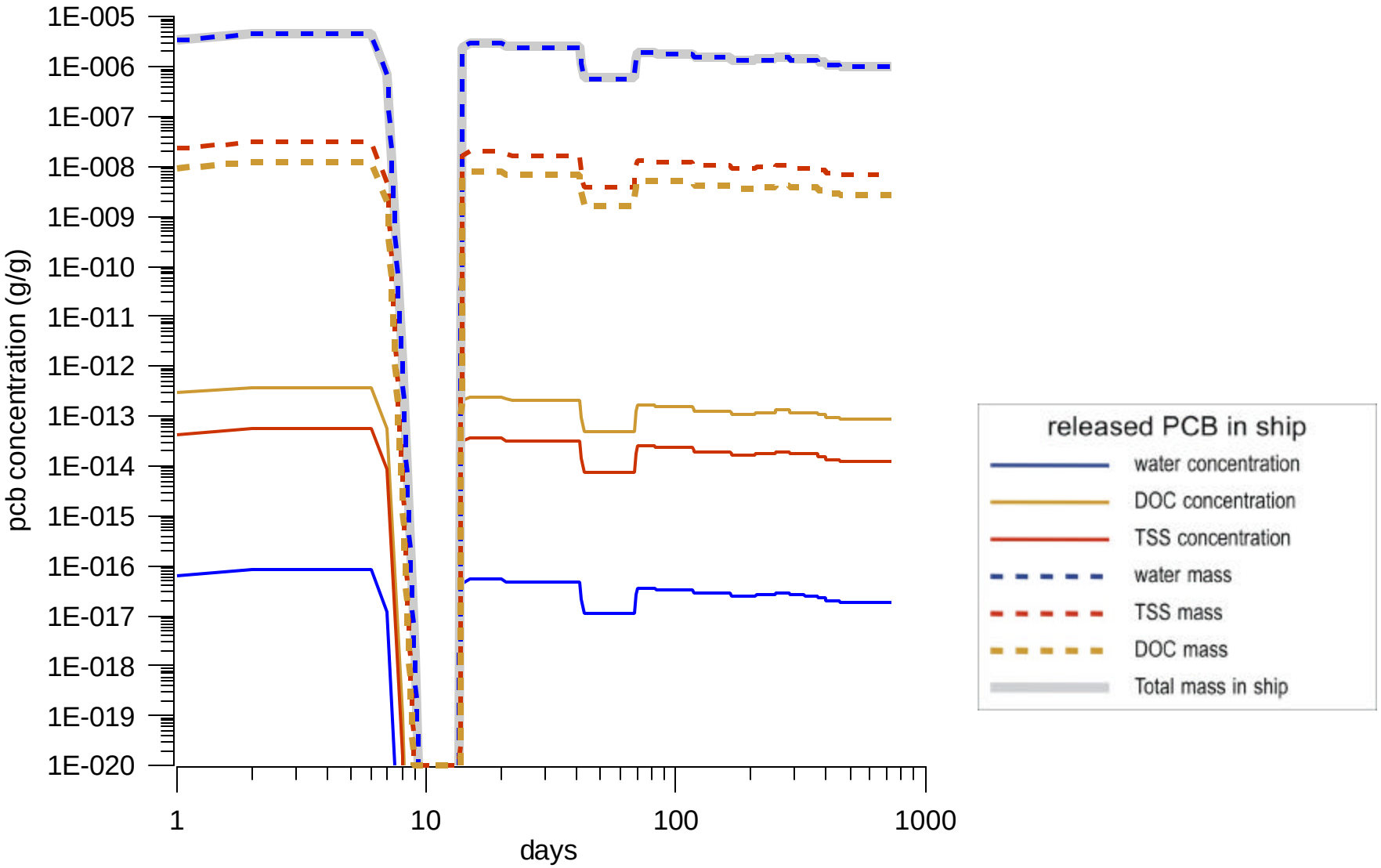

Figure C 3 – Monochlorobiphenyl Mass Budget

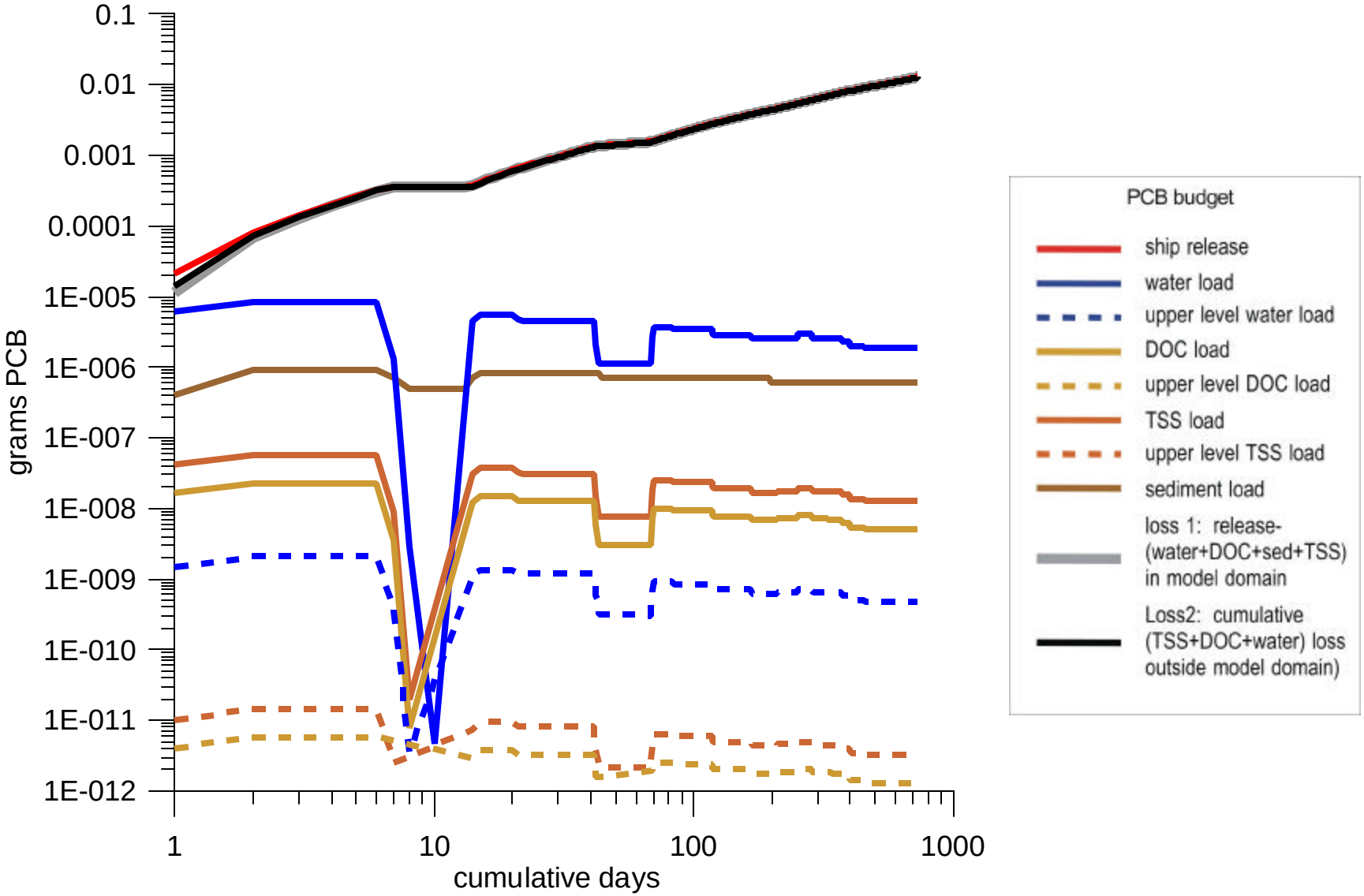

Figure C 4 –Dichlorobiphenyl Concentrations at Distances of Highest Concentrations

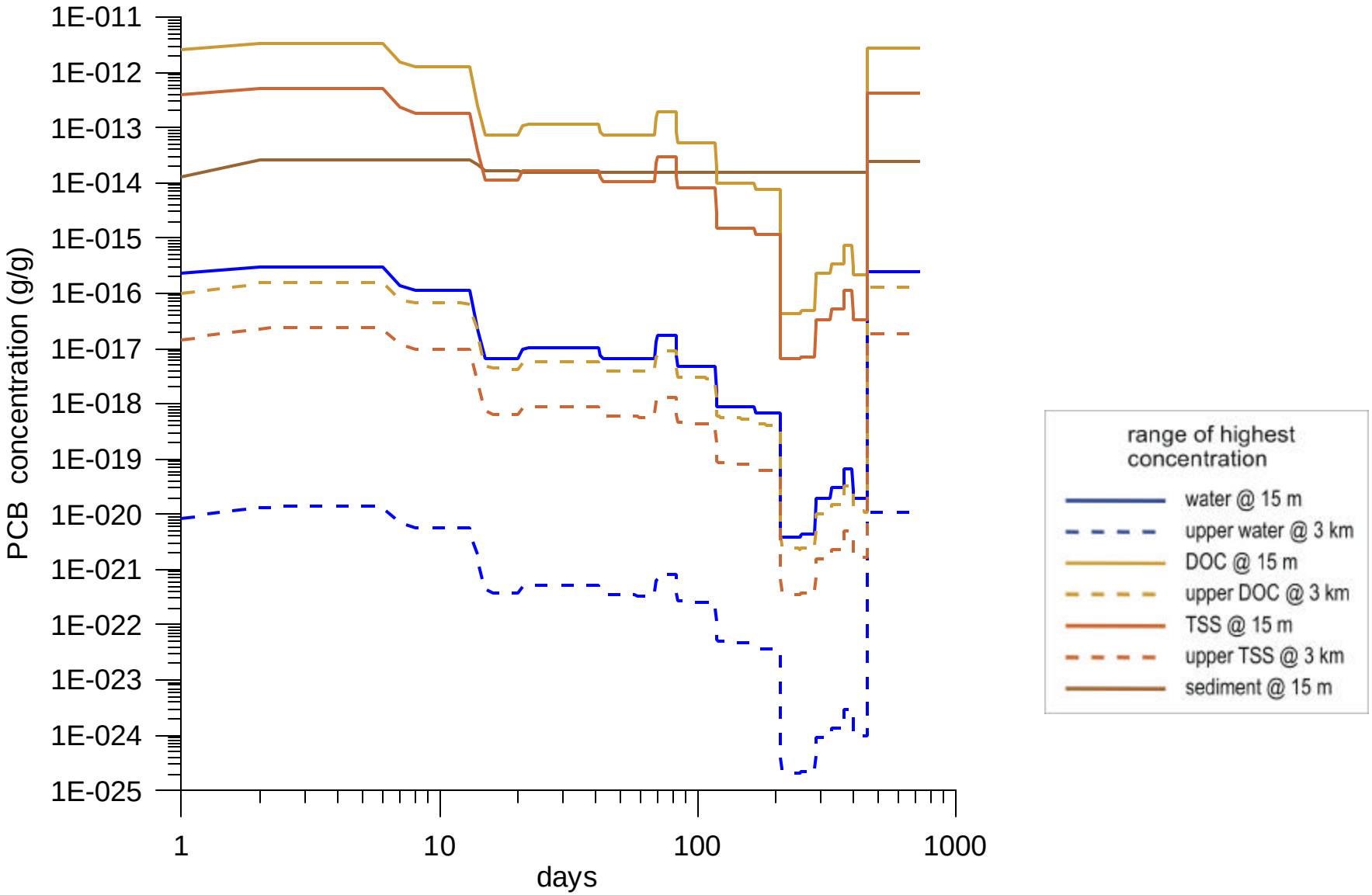

Figure C 5 – Dichlorobiphenyl Concentrations and Total Released Mass inside theShip

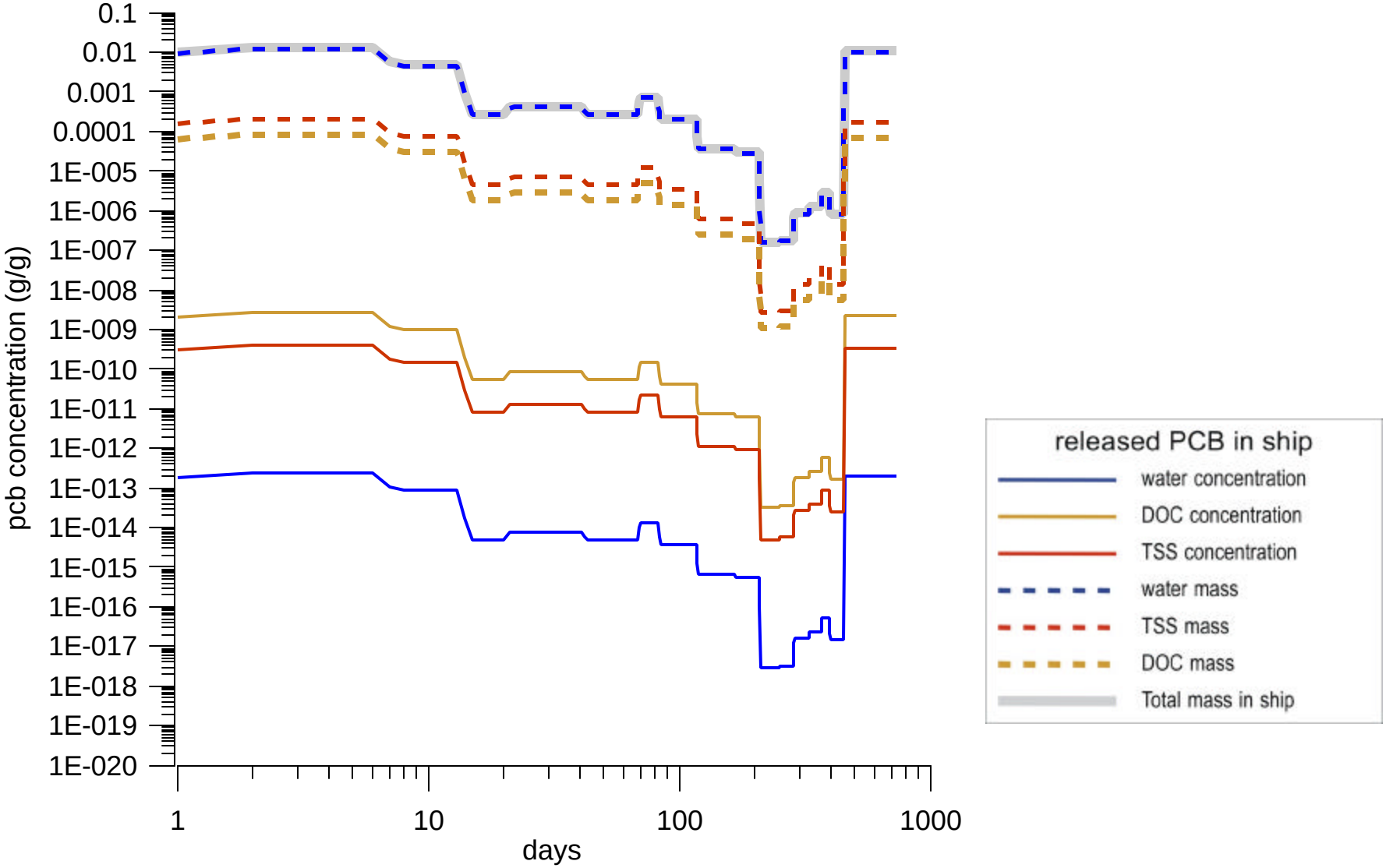

Figure C 6 – Dichlorobiphenyl Mass Budget

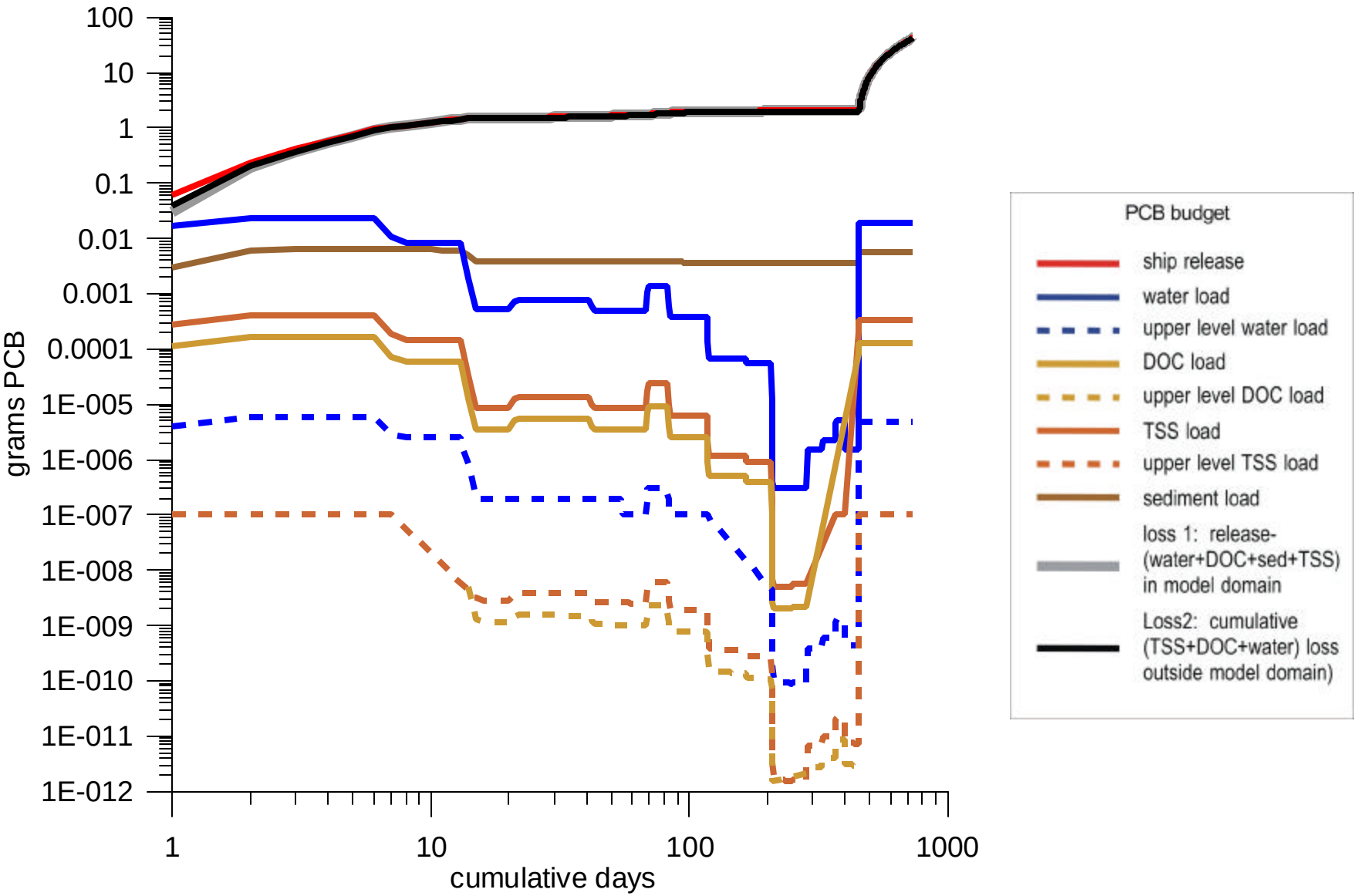

Figure C 7 – Trichlorobiphenyl Concentrations at Distances of Highest Concentrations

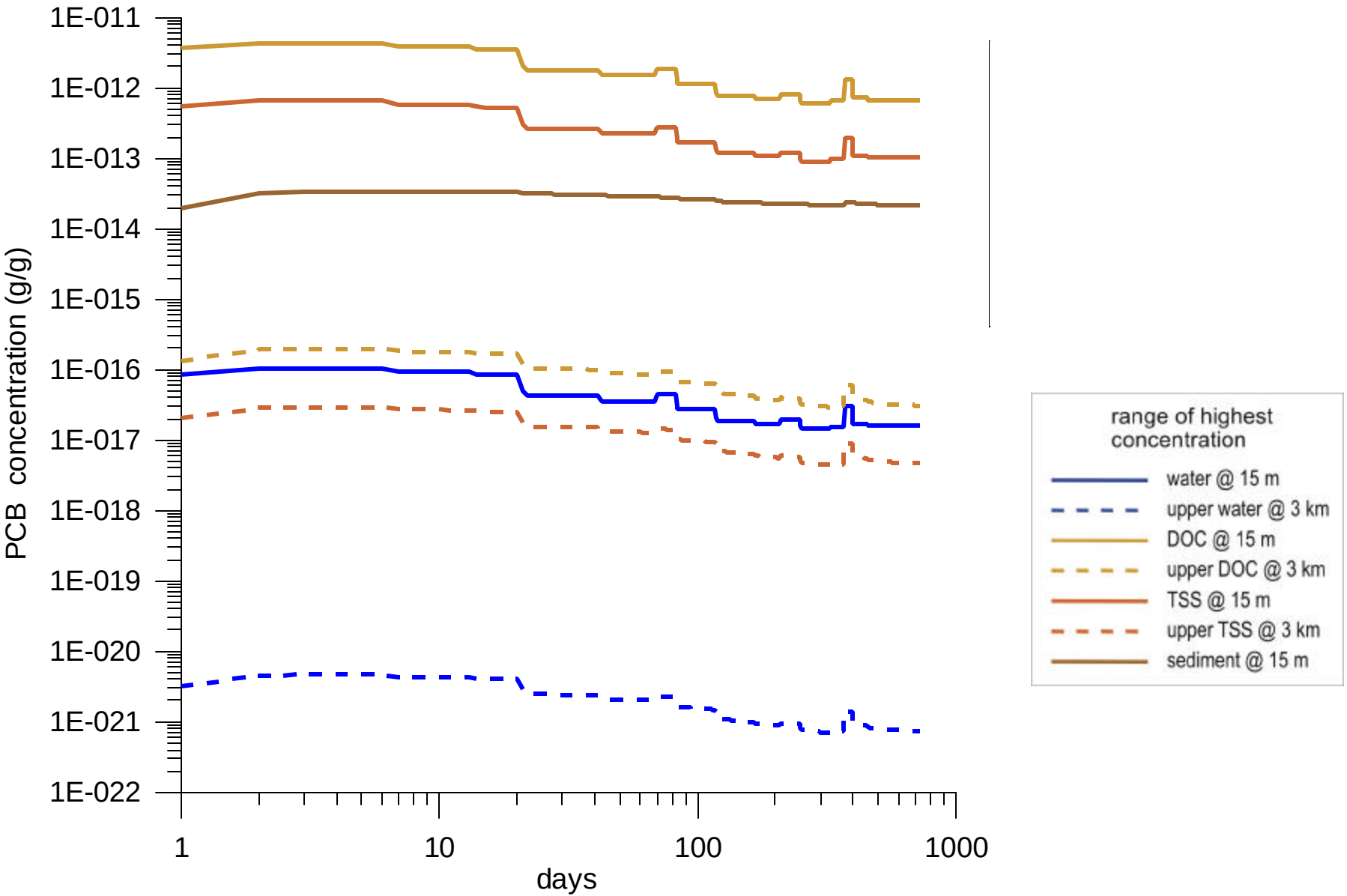

Figure C 8 – Trichlorobiphenyl Concentrations and Total Released Mass inside the Ship

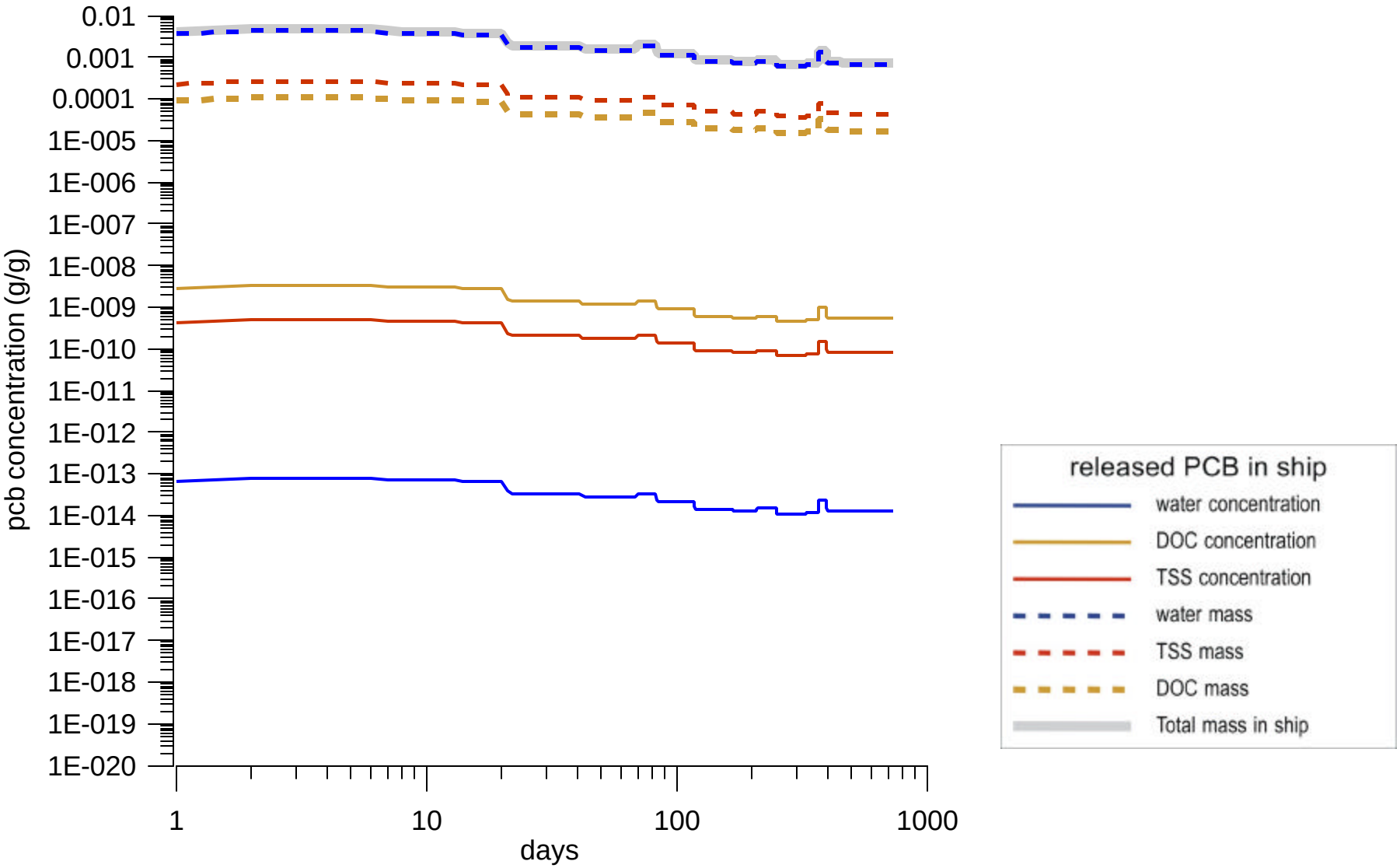

Figure C 9 – Trichlorobiphenyl Mass Budget

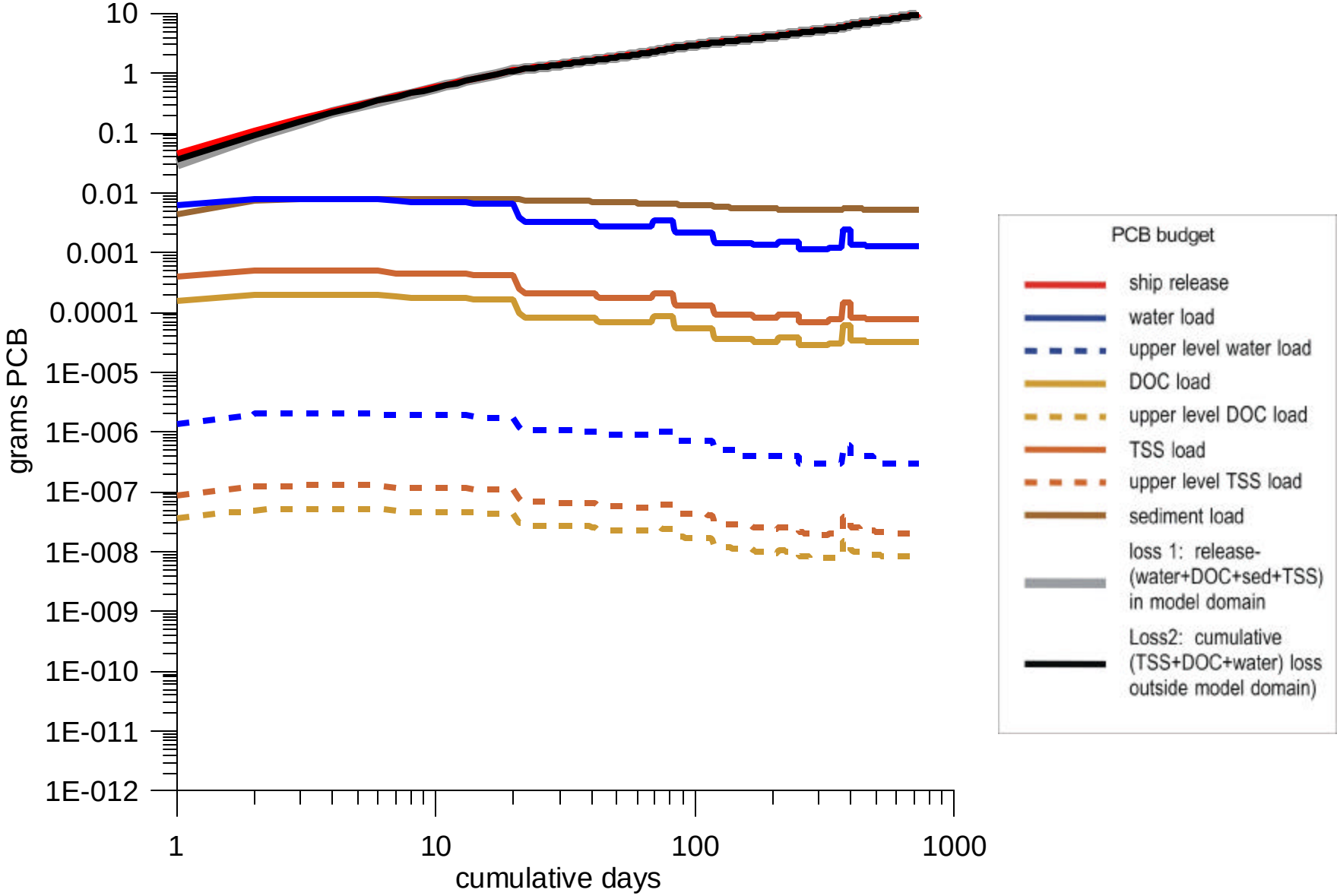

Figure C 10 – Tetrachlorobiphenyl Concentrations at Distances of Highest Concentrations

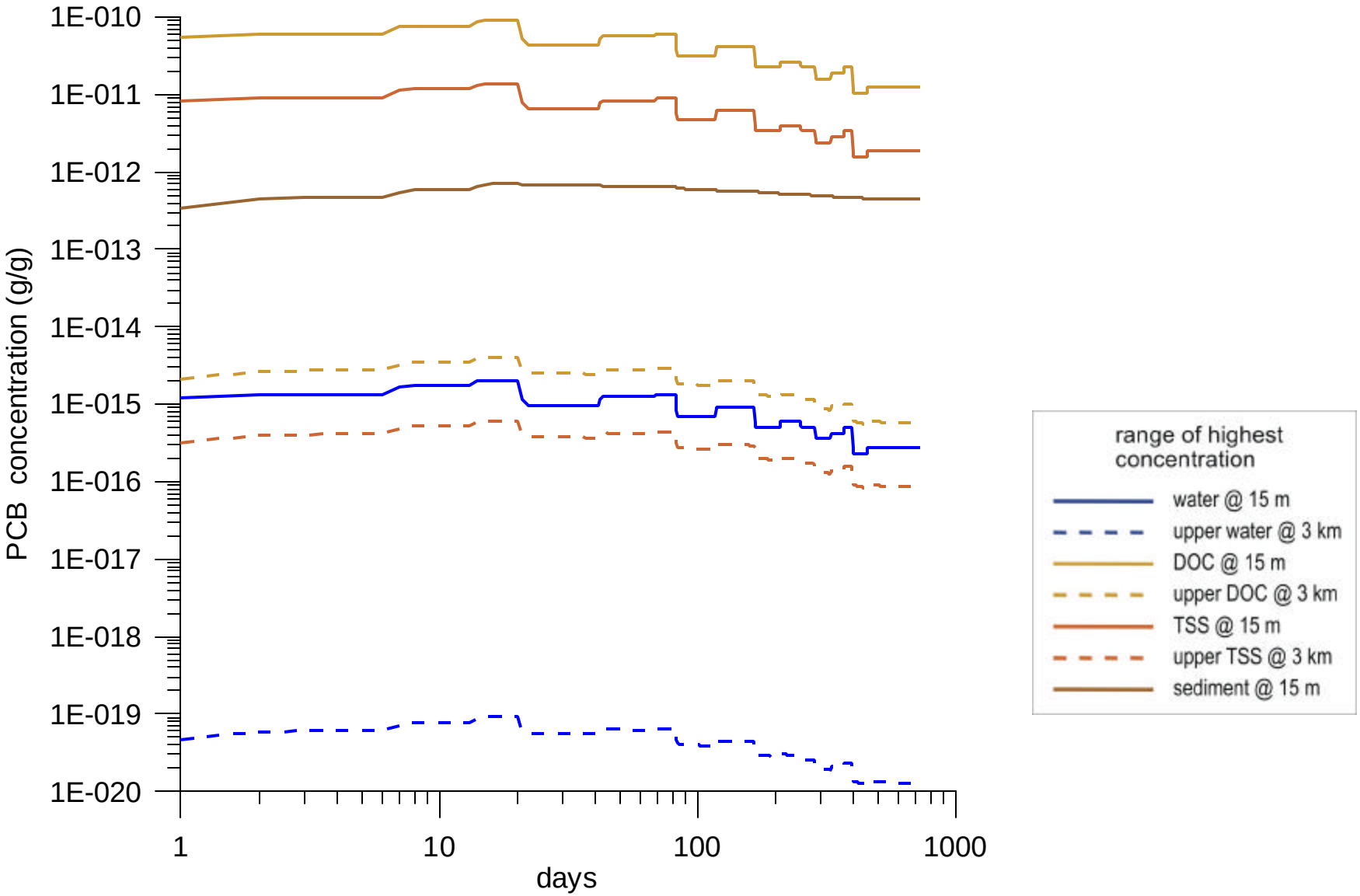

Figure C 11 – Tetrachlorobiphenyl Concentrations and Total Released Mass inside the Ship

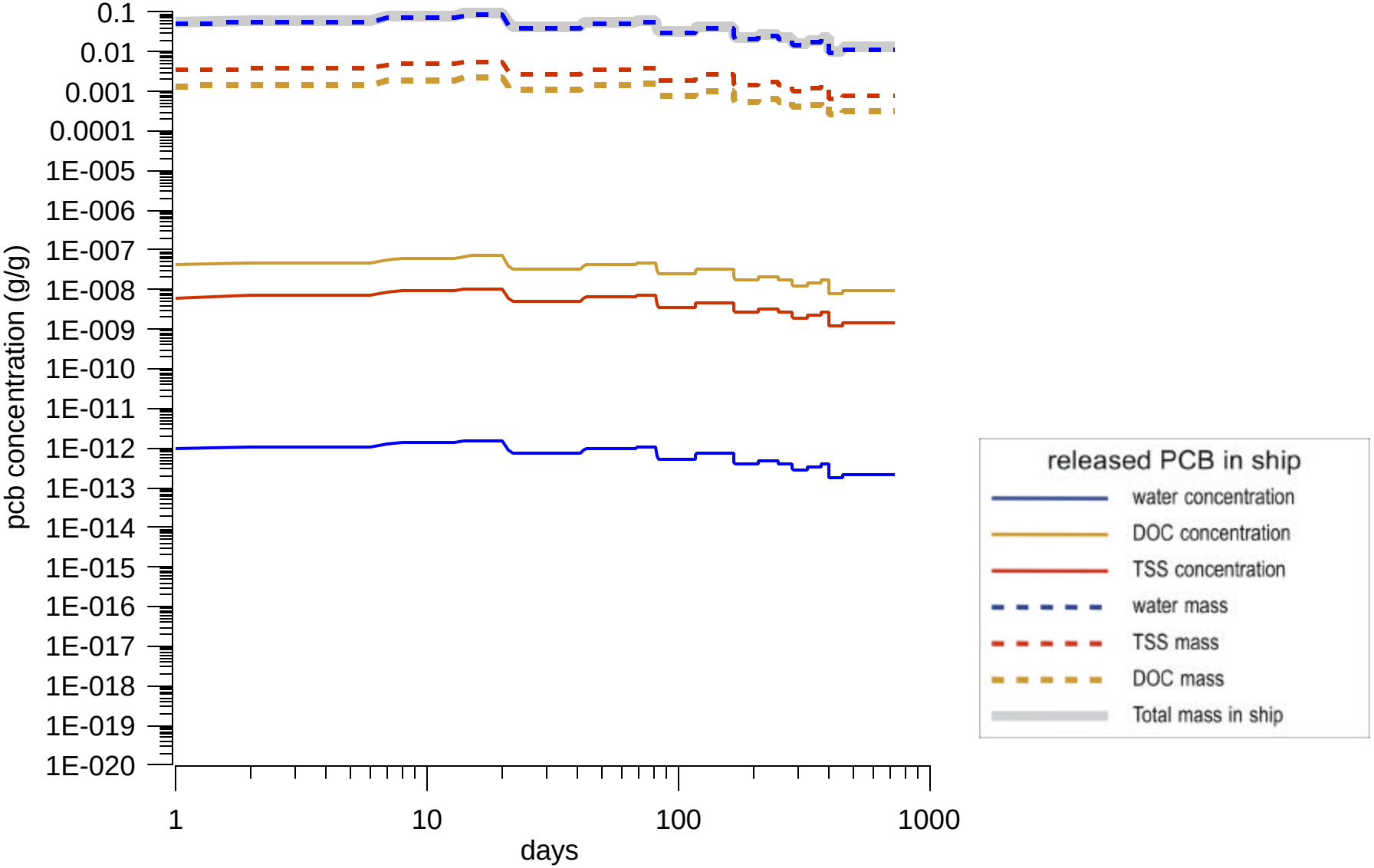

Figure C 12 – Tetrachlorobiphenyl Mass Budget

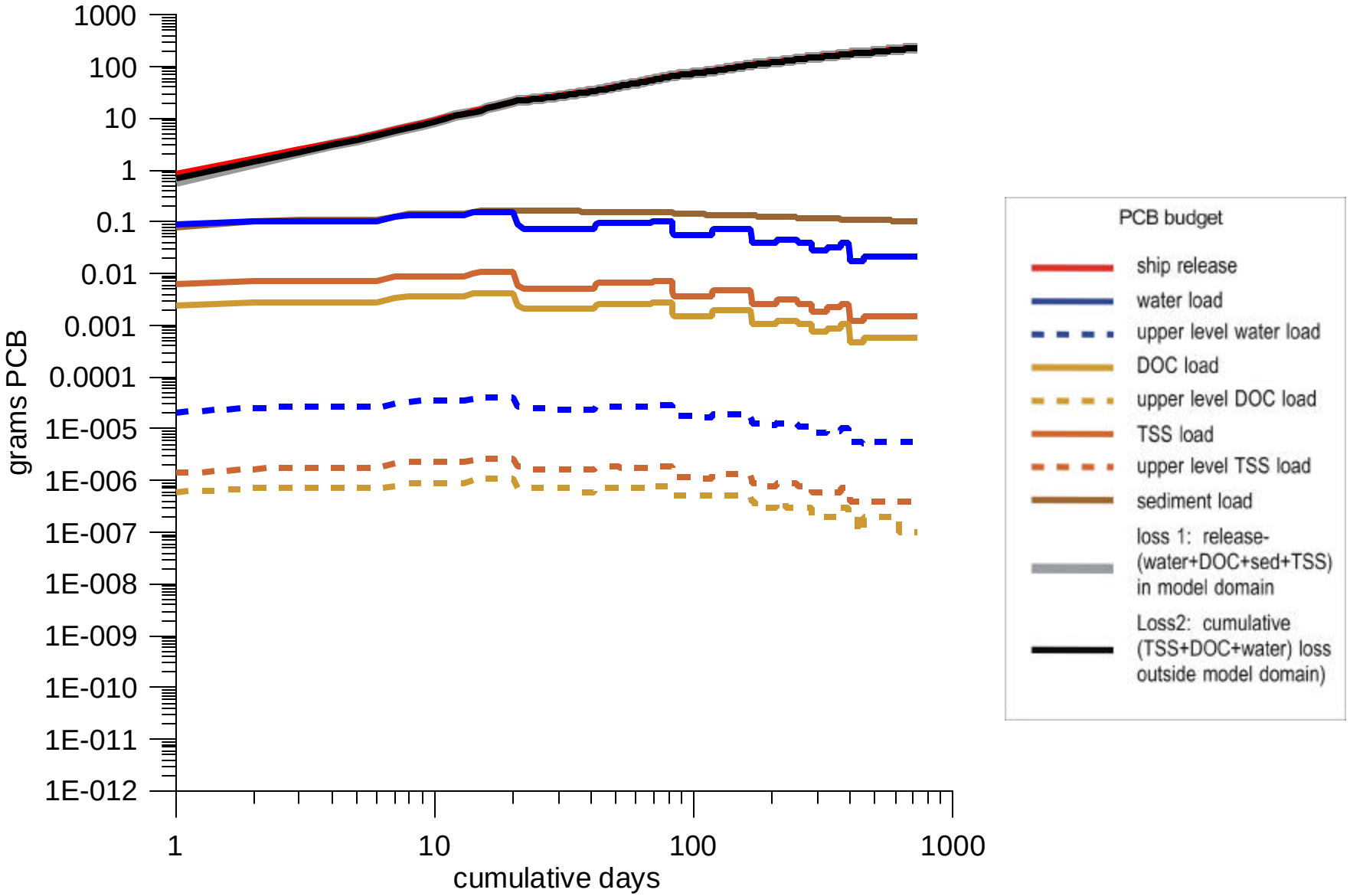

Figure C 13 –Pentachlorobiphenyl Concentrations at Distances of Highest Concentrations

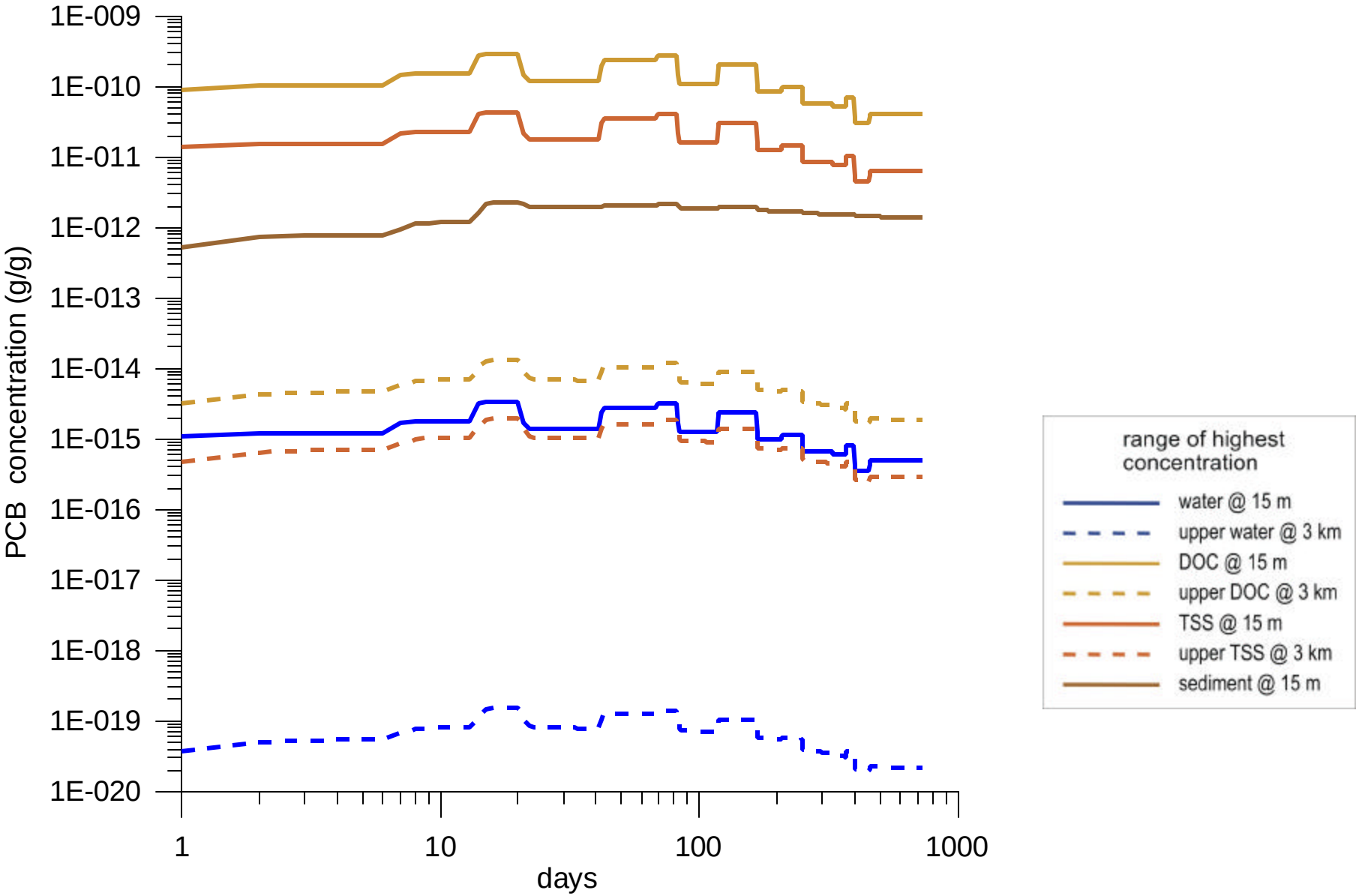

Figure C 14 – Pentachlorobiphenyl Concentrations and Total Released Mass inside the Ship

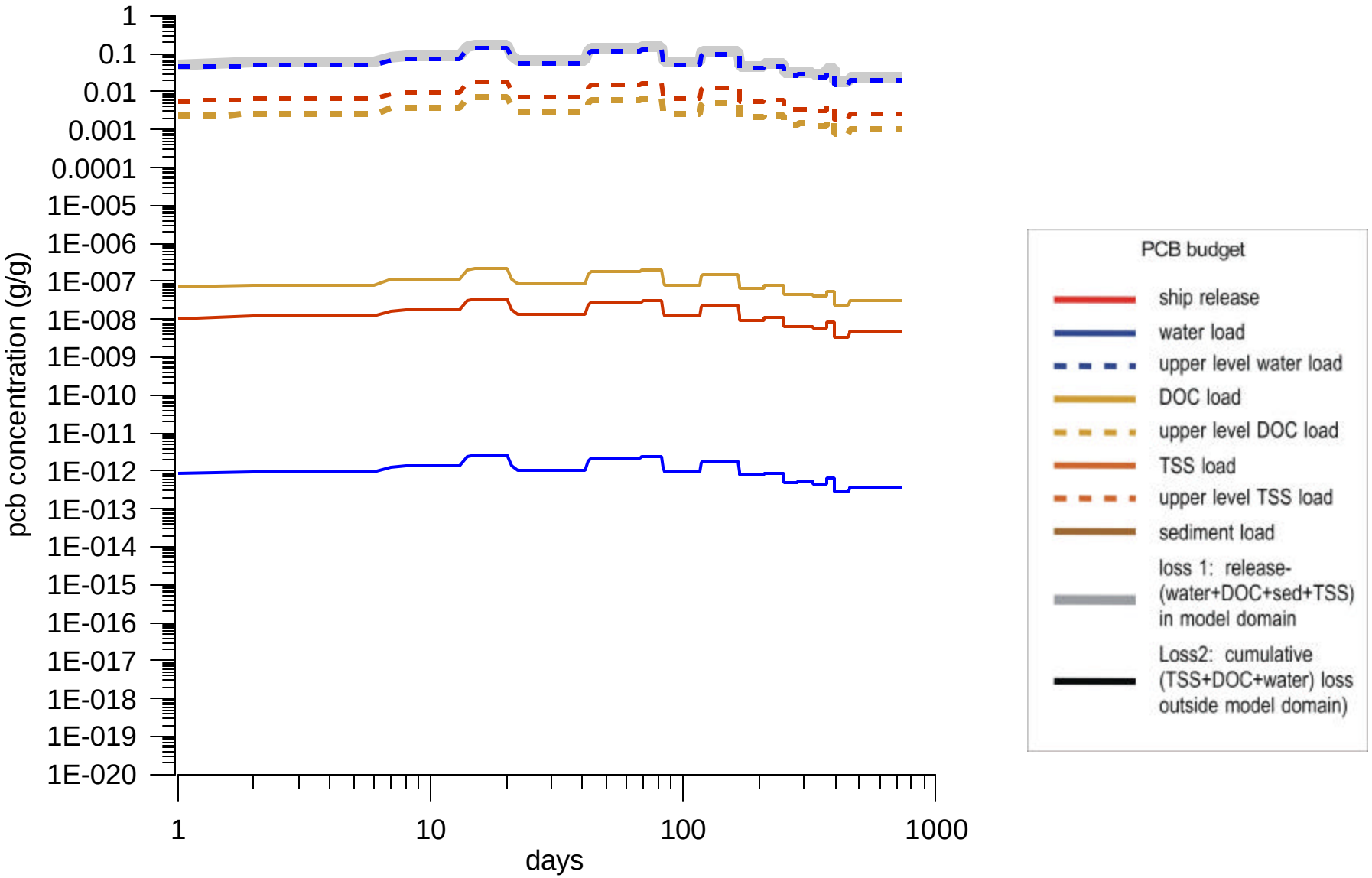

Figure C 15 – Pentachlorobiphenyl Mass Budget

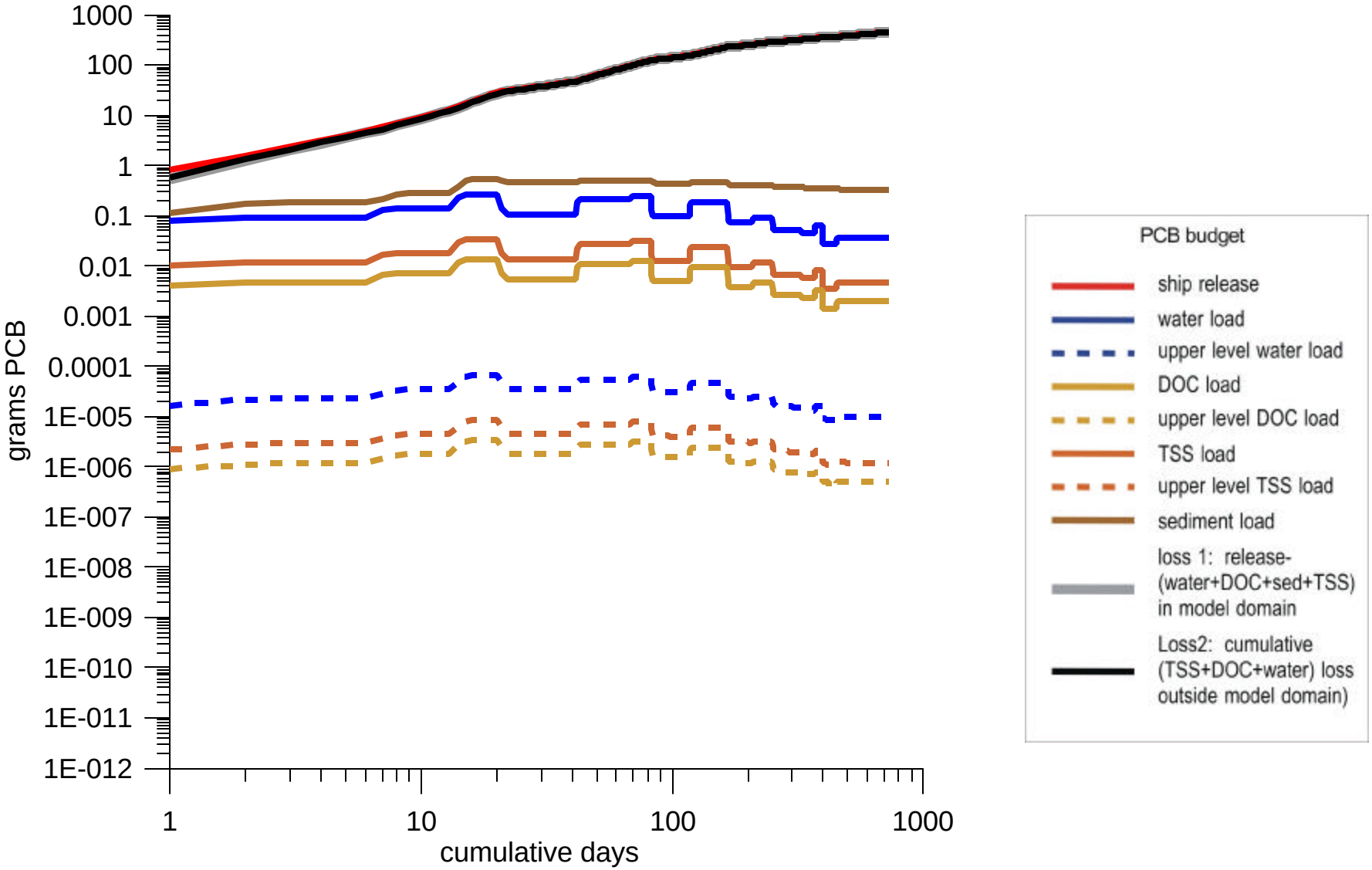

Figure C 16 – Hexachlorobiphenyl Concentrations at Distances of Highest Concentrations

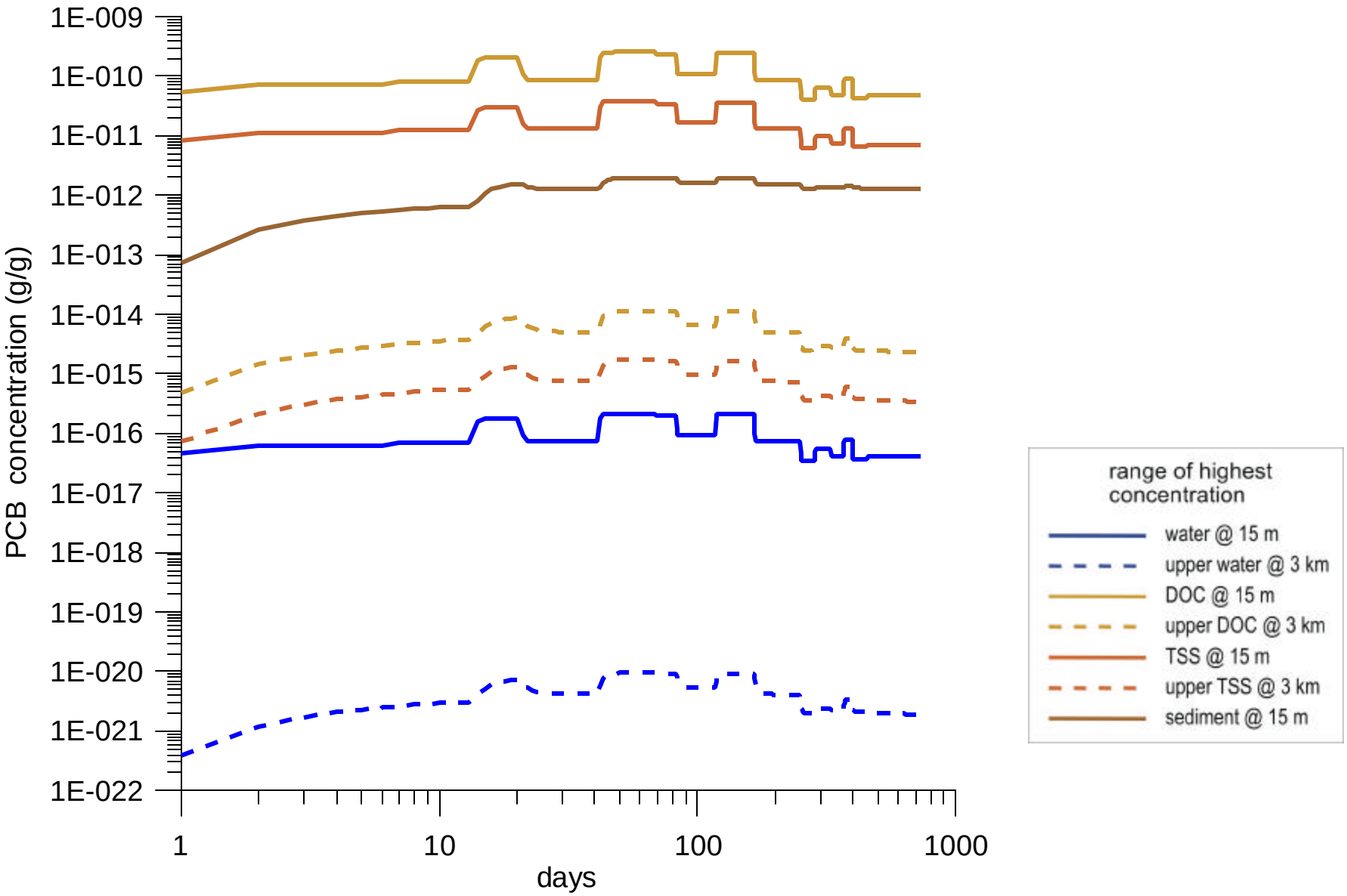

Figure C 17 – Hexachlorobiphenyl Concentrations and Total Released Mass inside the Ship

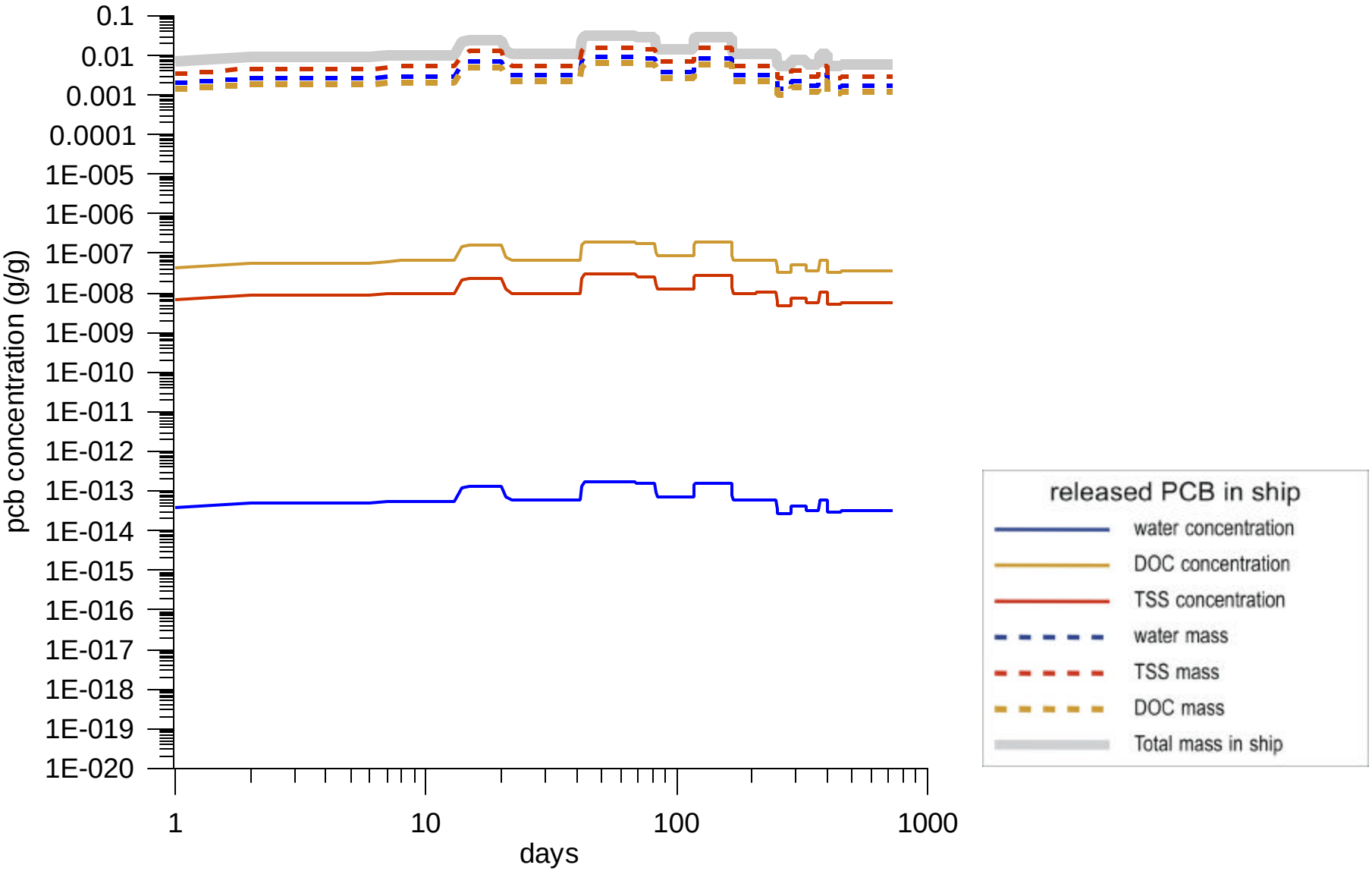

Figure C 18 – Hexachlorobiphenyl Mass Budget

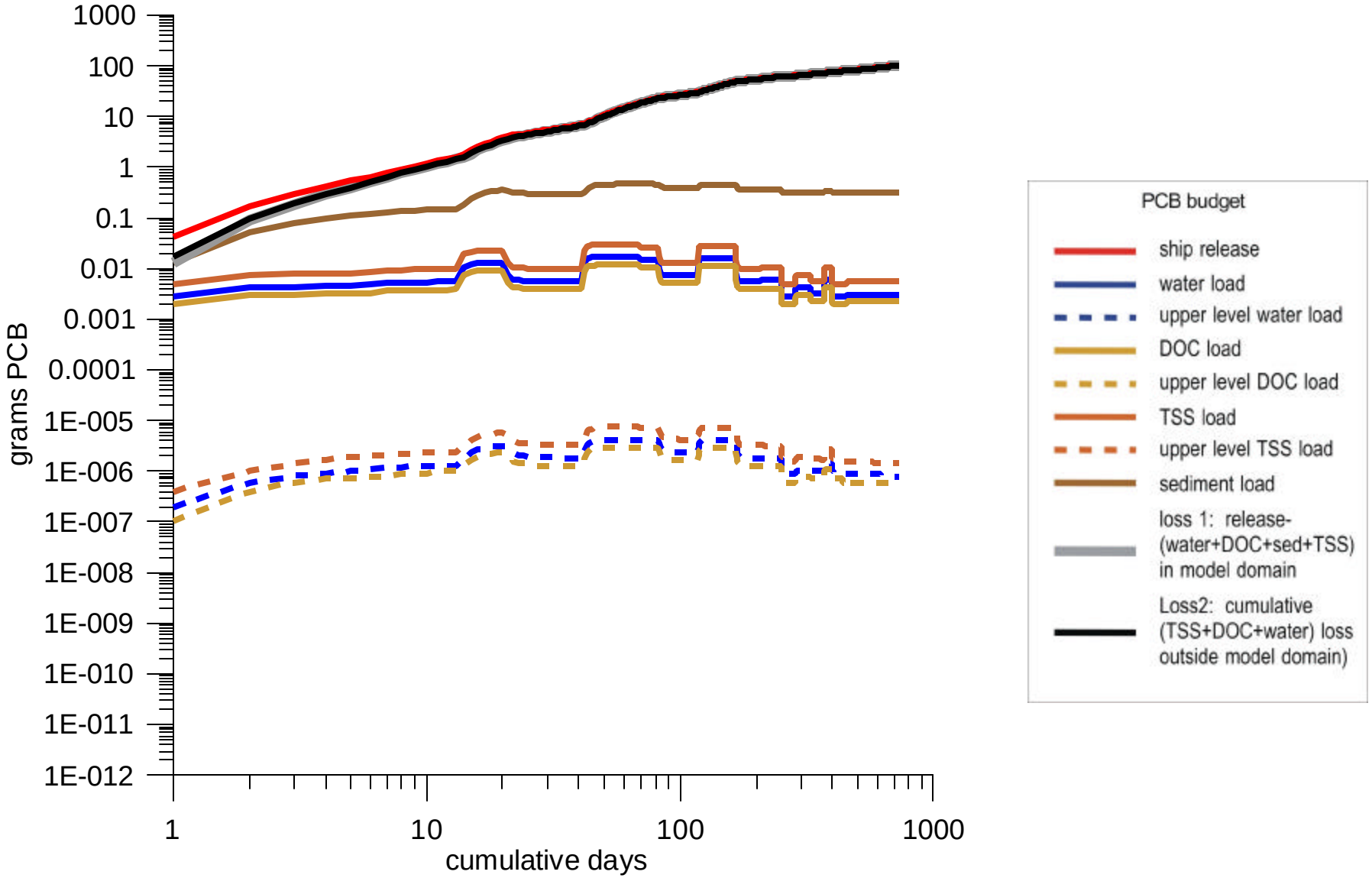

Figure C 19 – Heptachlorobiphenyl Concentrations at Distances of Highest Concentrations

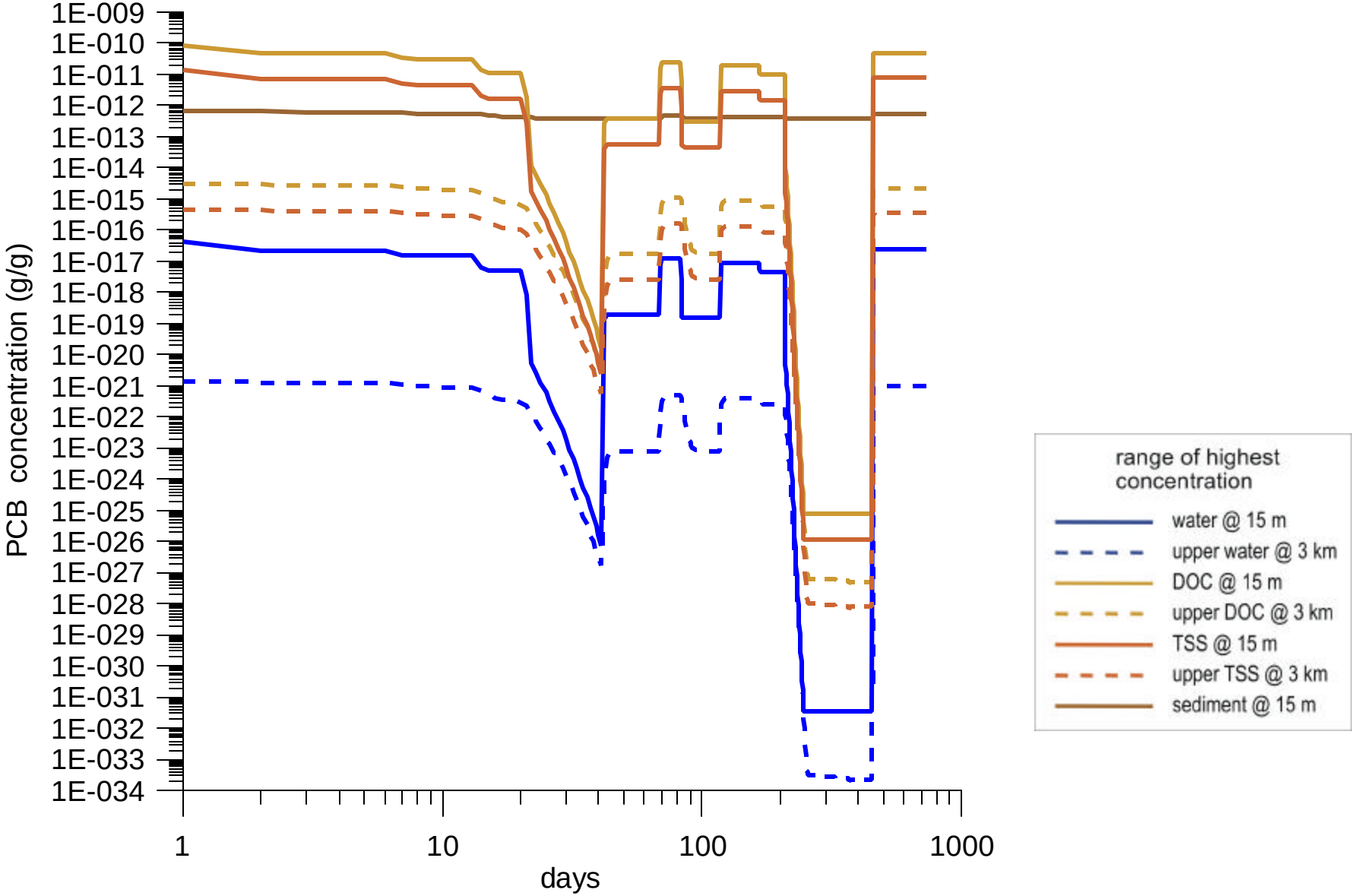

Figure C 20 – Heptachlorobiphenyl Concentrations and Total Released Mass inside the Ship

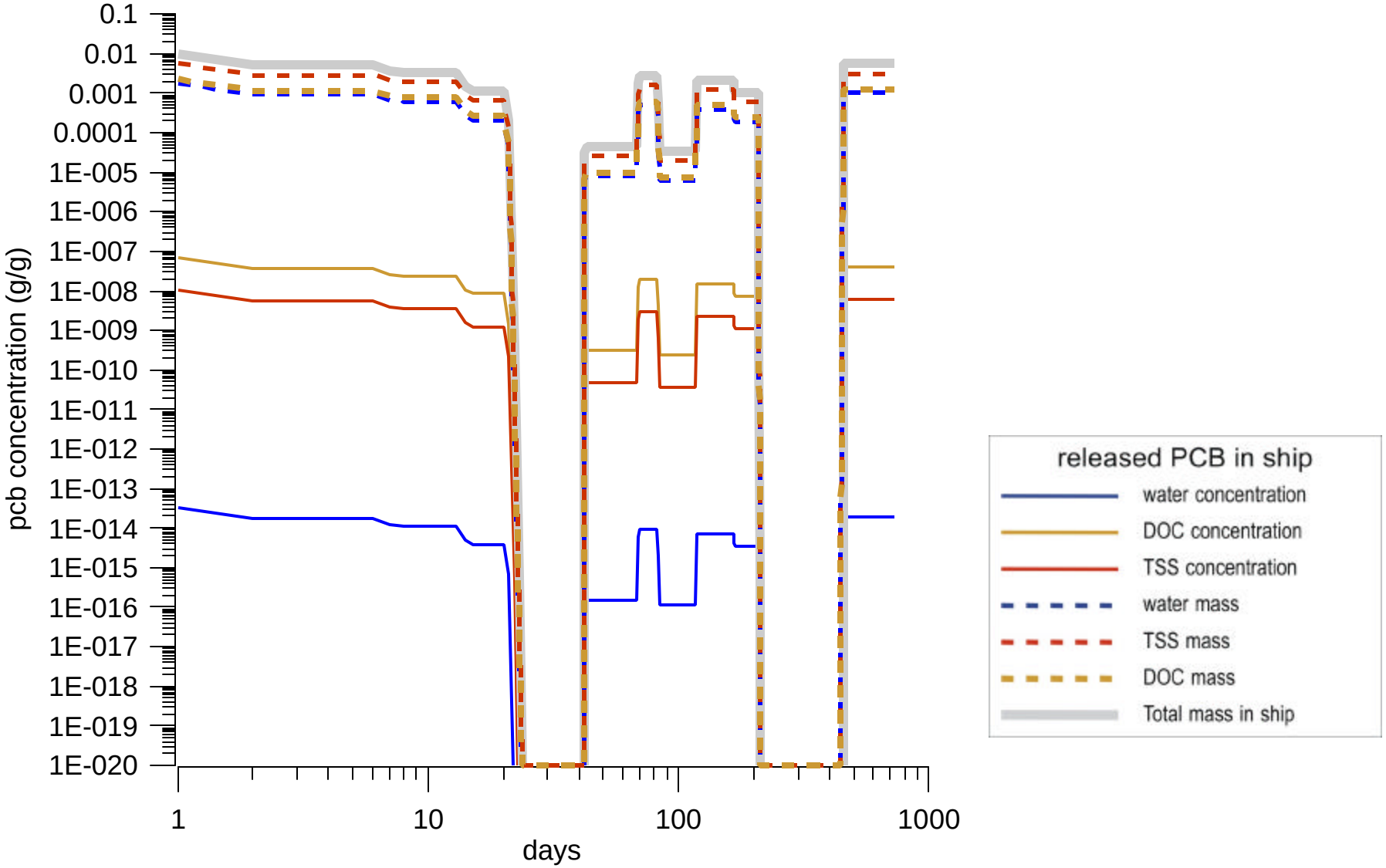

Figure C 21 – Heptachlorobiphenyl Mass Budget

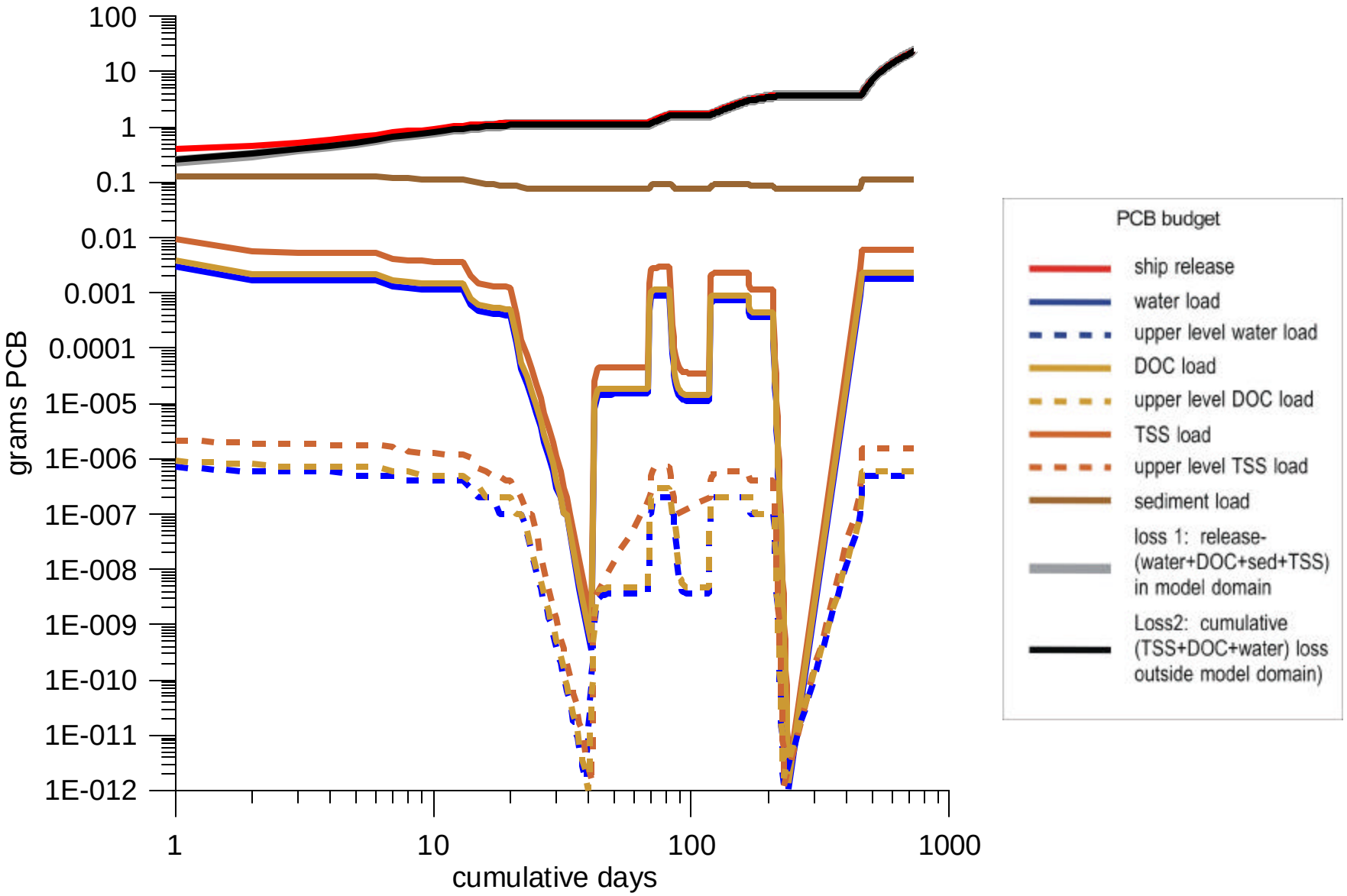

Figure C 22 – Nonachlorobiphenyl Concentrations at Distances of Highest Concentrations

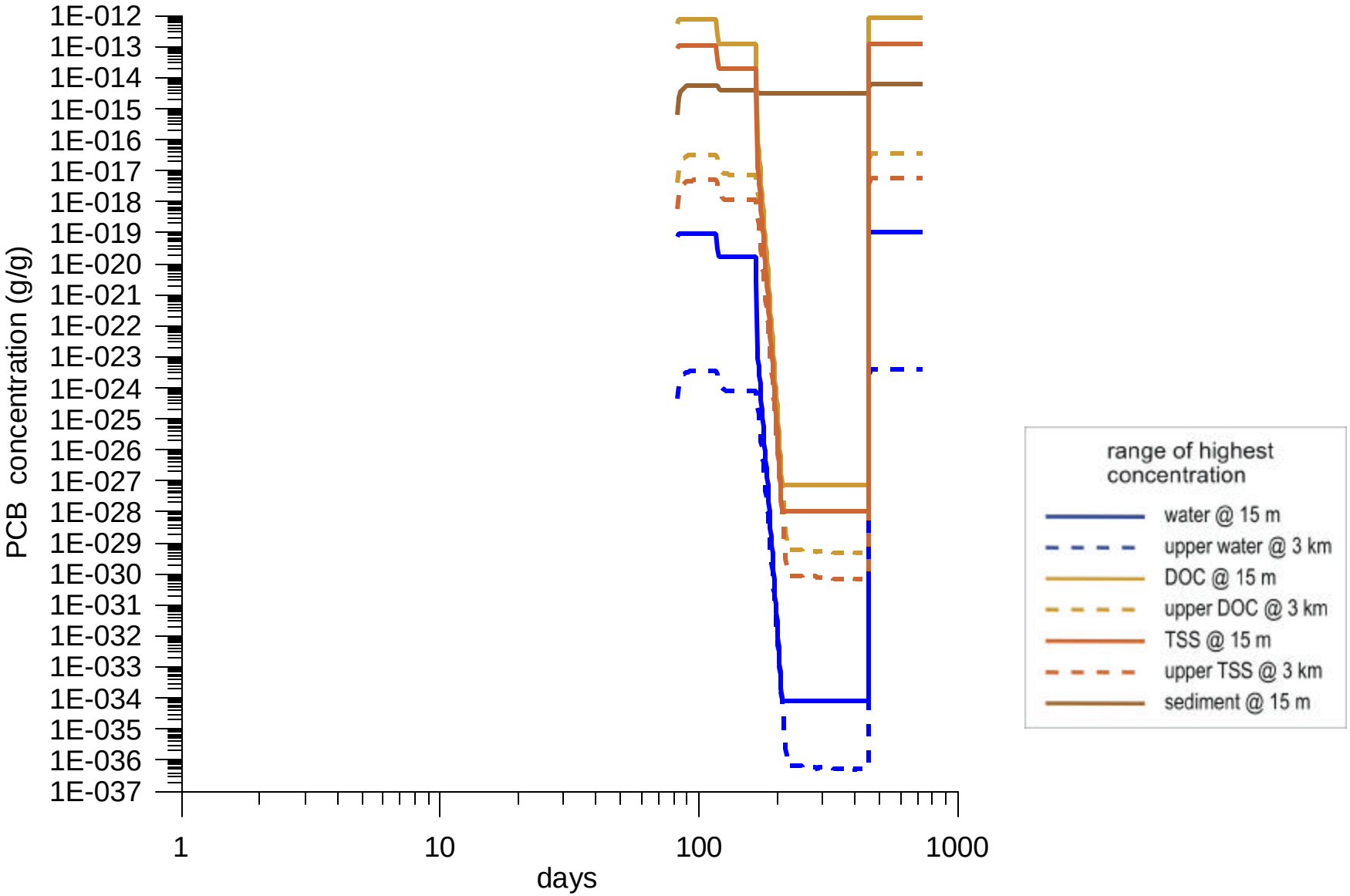

Figure C 23 –Nonachlorobiphenyl Concentrations and Total Released Mass inside the Ship

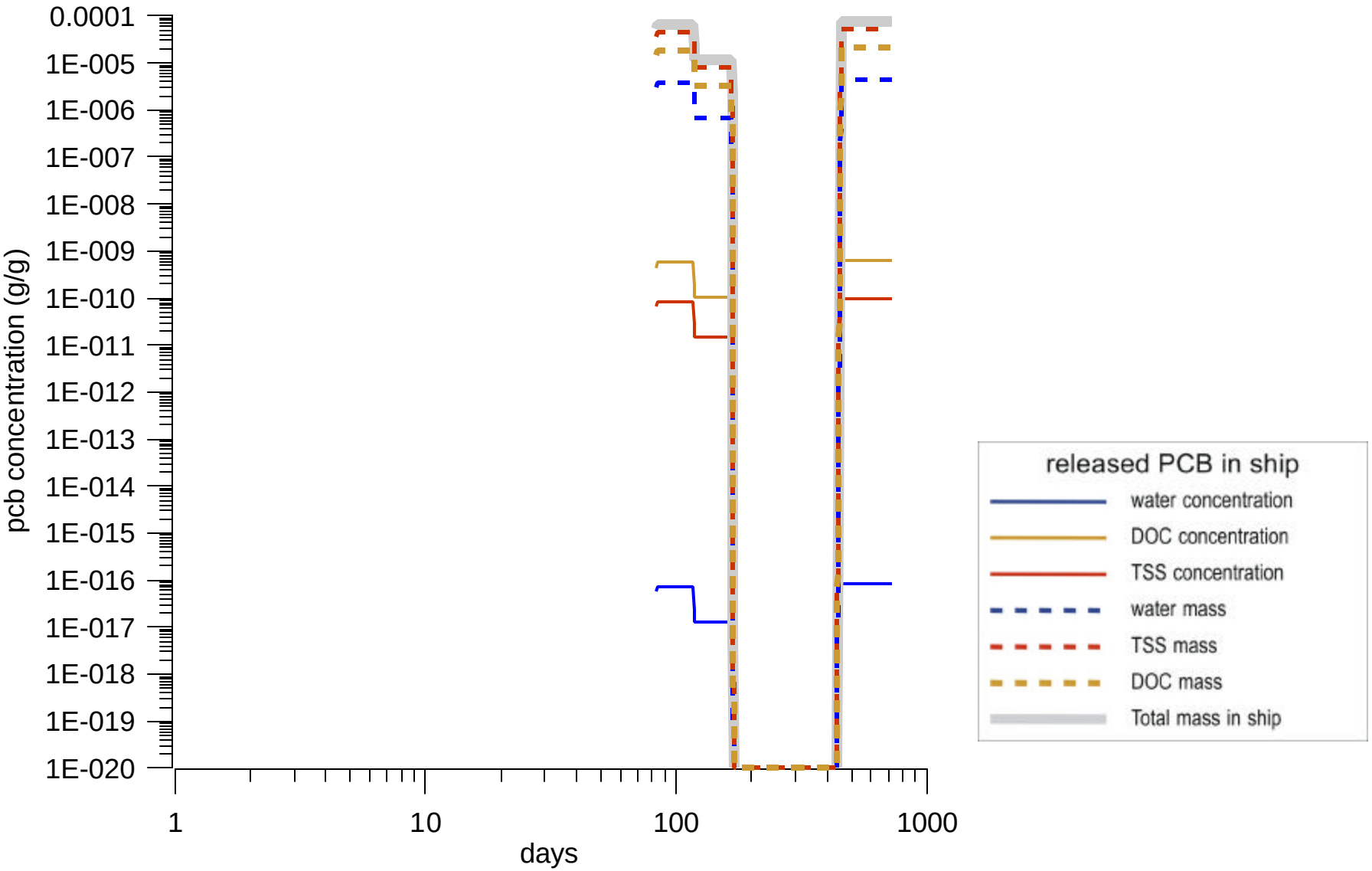

Figure C 24 – Nonachlorobiphenyl Mass Budget

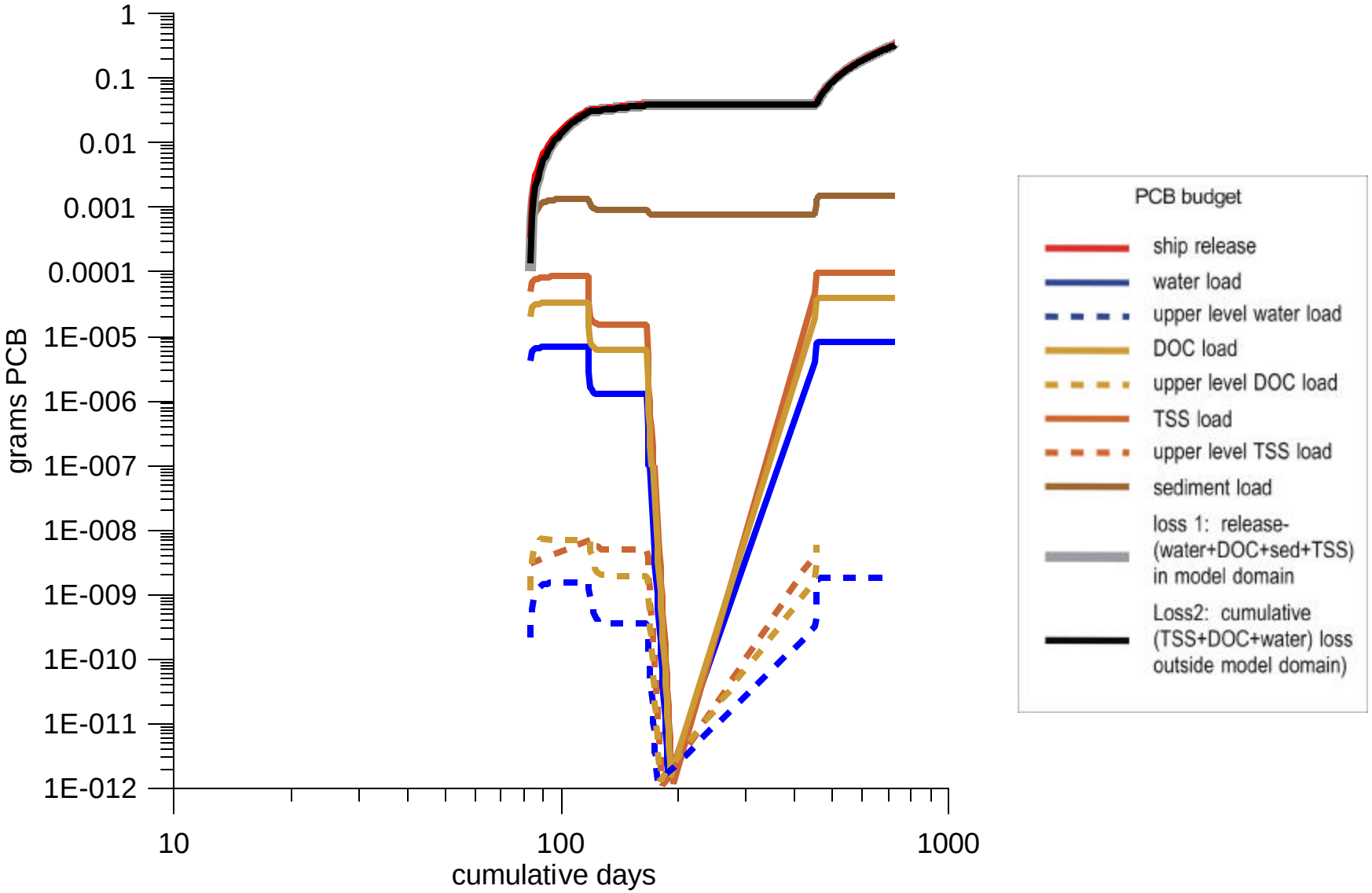

Figure C 25 – Decachlorobiphenyl Concentrations at Distances of Highest Concentrations

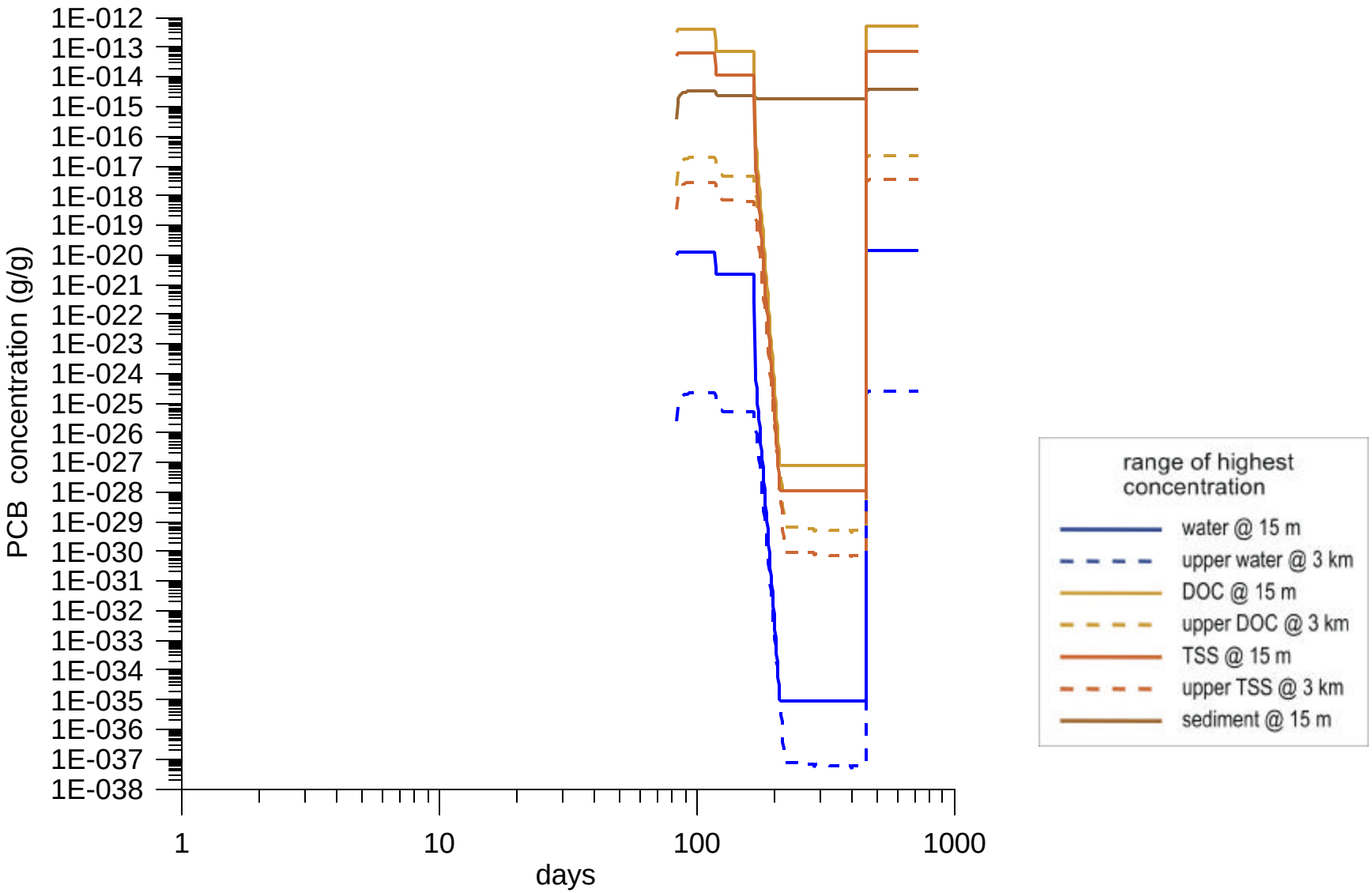

Figure C 26 – Decachlorobiphenyl Concentrations and Total Released Mass in the Ship

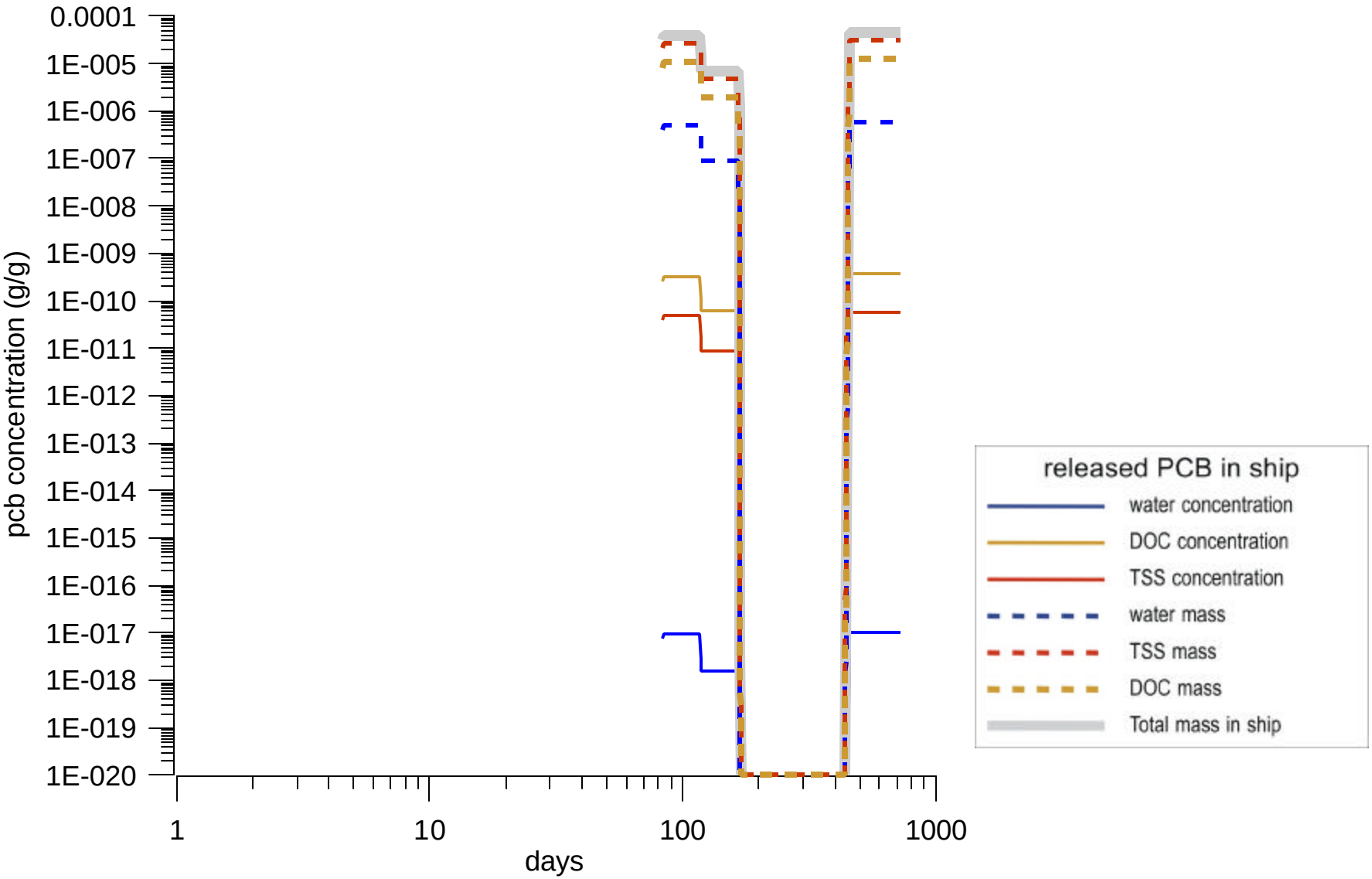

Figure C 27 – Decachlorobiphenyl Mass Budget

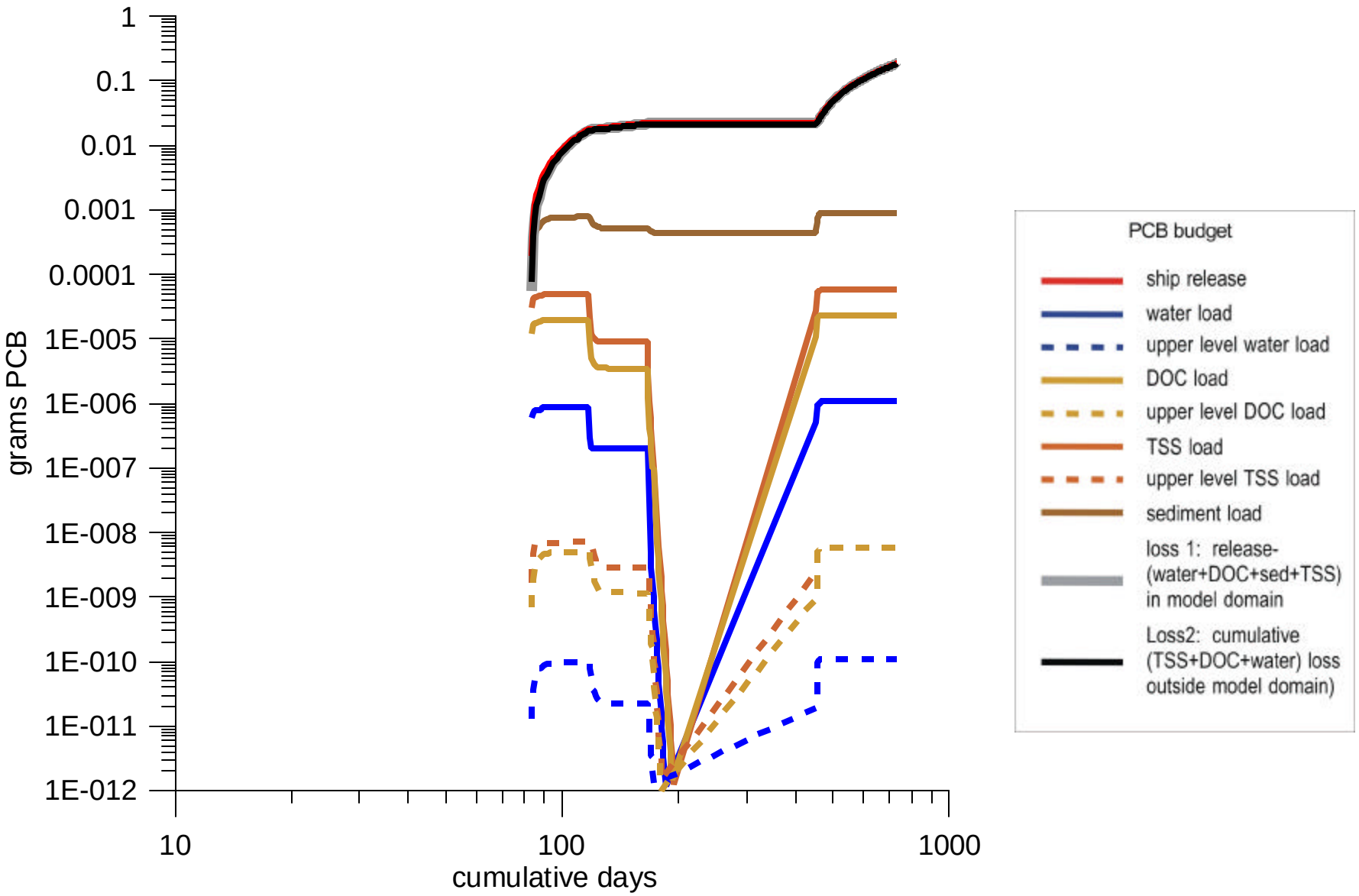

Figure C 28 – Total PCB Concentrations at Distances of Highest Concentrations

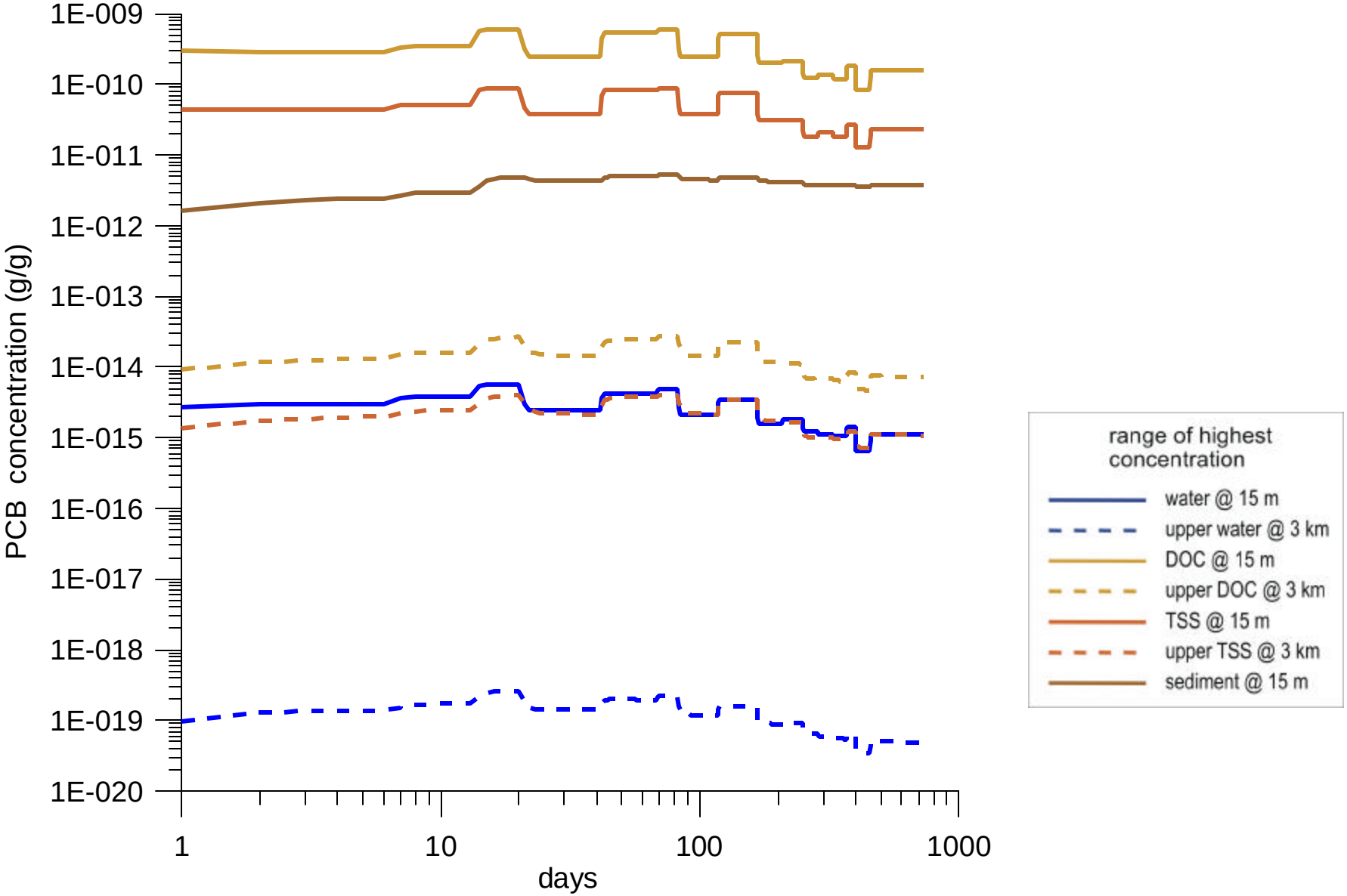

Figure C 29 – Total PCB Concentrations and Total Released Mass inside the Ship

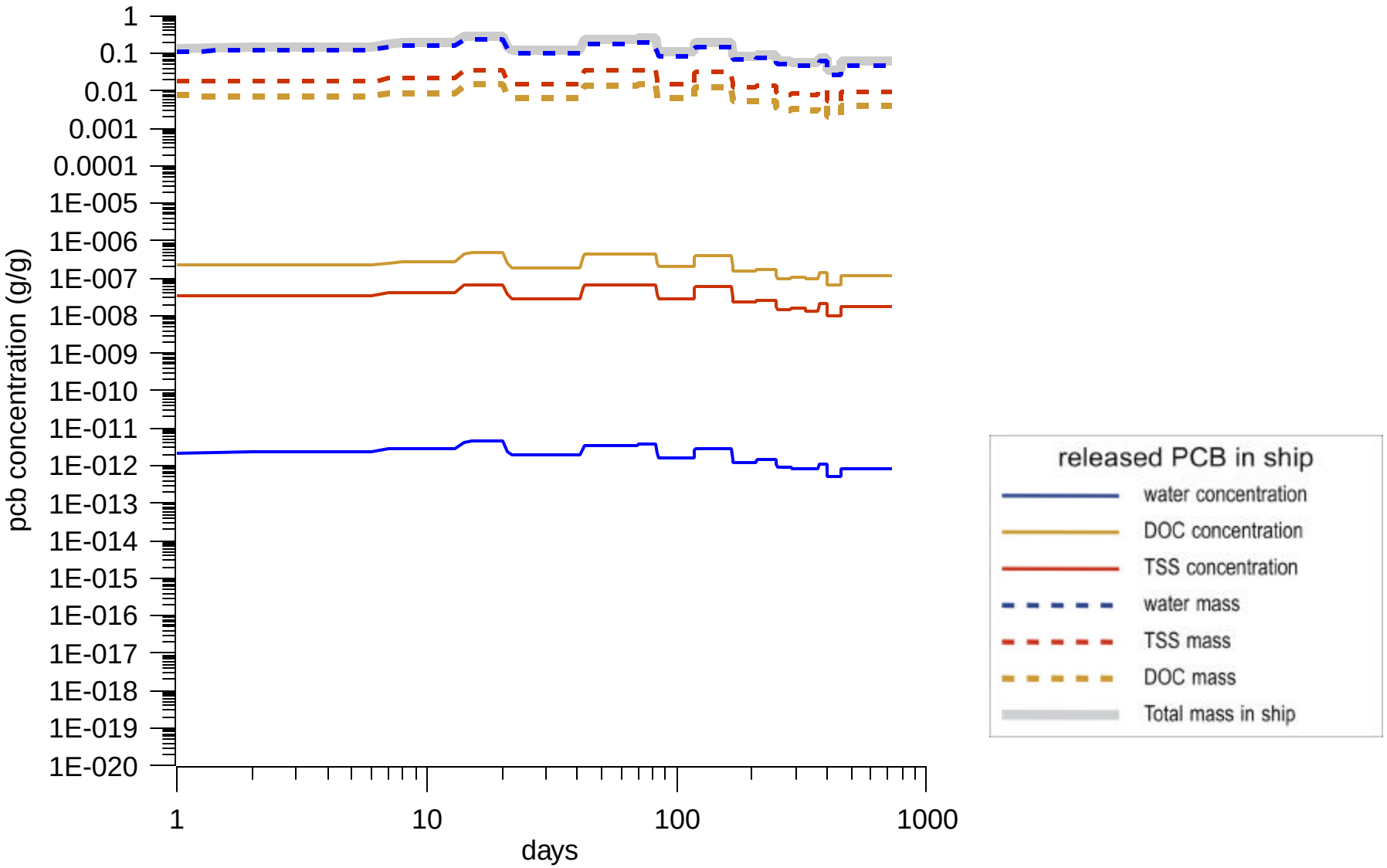

Figure C 30 – Total PCB Mass Budget

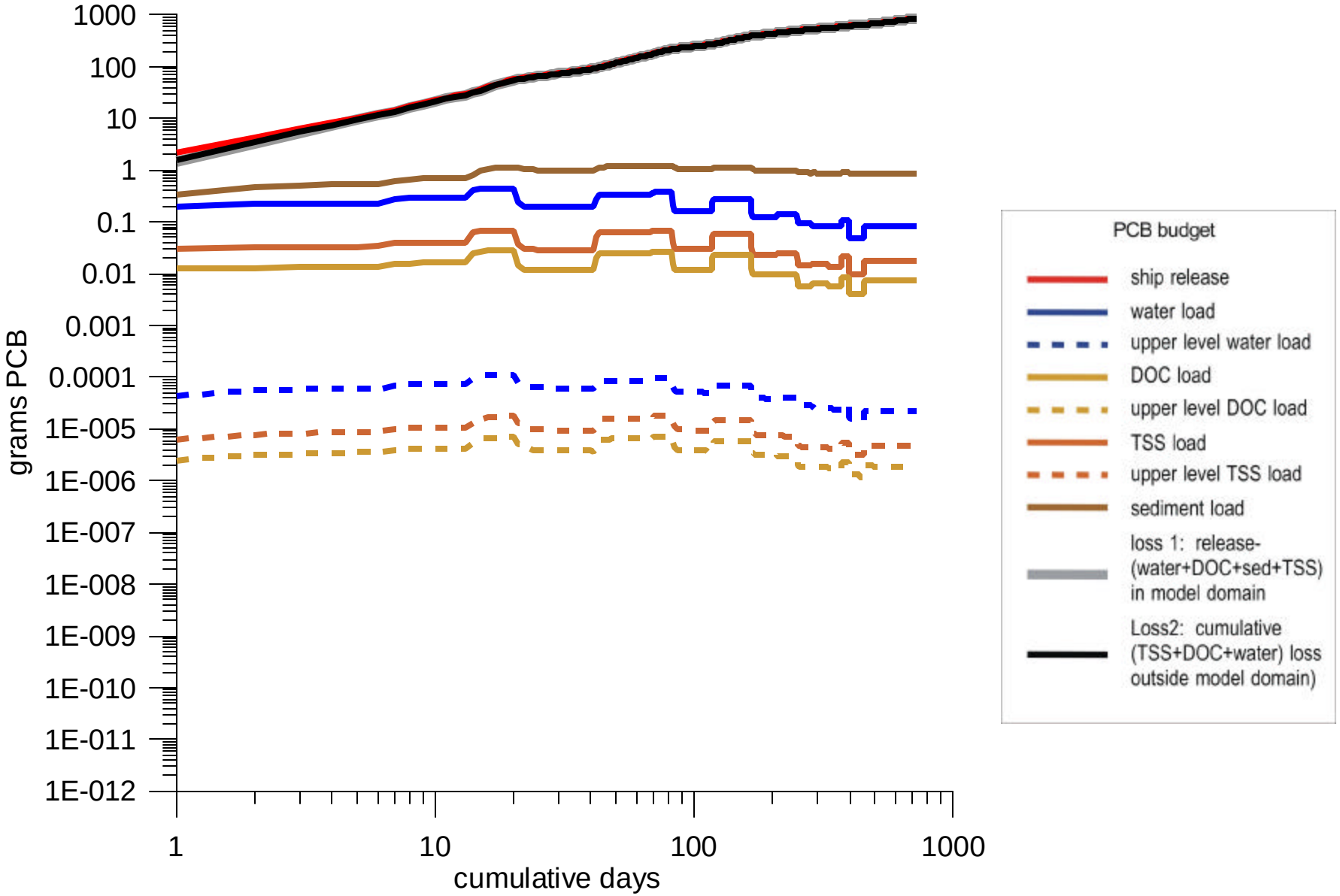

Figure C 31 –Table of PCB Homolog Release Rates used in the TDM

	Final Preparation Scenario, 72.6% BHI Removal	Sum of All Material Contributions Averaged over each Interval										
		ex-Oriskany 95% UCL Total Vessel Release Rate (g PCB/day)										
Leaching Time (days)	Leaching Interval (days)	Cl1-all	Cl2-all	Cl3-all	Cl4-all	Cl5-all	Cl6-all	Cl7-all	Cl8-all	Cl9-all	Cl10-all	tPCBs-all
0												
0.007	0.007	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	5.5E-02	0.0E+00	0.0E+00	0.0E+00	5.5E-02
1	1.163	0.0E+00	0.0E+00	2.0E-02	4.8E-01	4.5E-01	0.0E+00	3.2E-01	0.0E+00	0.0E+00	0.0E+00	1.3E+00
7	5.906	6.1E-05	1.7E-01	6.4E-02	8.3E-01	7.9E-01	1.2E-01	6.7E-02	0.0E+00	0.0E+00	0.0E+00	2.1E+00
14	7.007	0.0E+00	6.4E-02	5.6E-02	1.1E+00	1.2E+00	1.4E-01	4.6E-02	0.0E+00	0.0E+00	0.0E+00	2.6E+00
21	7.015	3.9E-05	3.8E-03	5.2E-02	1.3E+00	2.3E+00	3.4E-01	1.6E-02	0.0E+00	0.0E+00	0.0E+00	3.9E+00
42	21.129	3.4E-05	5.8E-03	2.6E-02	6.0E-01	9.2E-01	1.4E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.7E+00
69	27.074	8.0E-06	3.7E-03	2.2E-02	7.8E-01	1.8E+00	4.2E-01	5.8E-04	0.0E+00	0.0E+00	0.0E+00	3.0E+00
83	13.838	2.7E-05	1.0E-02	2.7E-02	8.4E-01	2.1E+00	3.8E-01	3.6E-02	0.0E+00	0.0E+00	0.0E+00	3.4E+00
118	34.997	2.5E-05	2.8E-03	1.7E-02	4.3E-01	8.4E-01	1.9E-01	4.5E-04	0.0E+00	9.1E-04	5.1E-04	1.5E+00
167	48.969	2.1E-05	5.1E-04	1.2E-02	5.7E-01	1.6E+00	4.1E-01	2.8E-02	0.0E+00	1.6E-04	9.1E-05	2.6E+00
209	42.026	1.8E-05	4.0E-04	1.0E-02	3.2E-01	6.5E-01	1.4E-01	1.4E-02	0.0E+00	0.0E+00	0.0E+00	1.1E+00
251	42.061	1.9E-05	2.2E-06	1.2E-02	3.7E-01	7.6E-01	1.5E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.3E+00
286	34.958	2.1E-05	2.5E-06	8.9E-03	3.1E-01	4.4E-01	6.9E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	8.3E-01
328	41.942	1.9E-05	1.2E-05	8.9E-03	2.2E-01	4.5E-01	1.1E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	7.8E-01
370	42.024	1.9E-05	1.7E-05	9.6E-03	2.6E-01	4.0E-01	8.0E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	7.5E-01
398	27.963	1.7E-05	3.8E-05	1.9E-02	3.1E-01	5.5E-01	1.5E-01	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.0E+00
454	56.240	1.5E-05	1.1E-05	1.1E-02	1.4E-01	2.4E-01	7.2E-02	0.0E+00	0.0E+00	0.0E+00	0.0E+00	4.6E-01
730	275.681	1.4E-05	1.4E-01	1.0E-02	1.7E-01	3.2E-01	7.9E-02	7.3E-02	0.0E+00	1.1E-03	5.9E-04	8.0E-01
	Total Mass Released over 730 days (g PCB)	1.3E-02	4.1E+01	9.7E+00	2.3E+02	4.6E+02	1.0E+02	2.4E+01	0.0E+00	3.3E-01	1.9E-01	8.7E+02
	At end of Pulse, rate used from regression analysis/PRAM is significantly higher than final empirical rate											
	Average based predominantly on PRAM rates from regression analysis, but slight overlap with final empirical pulse interval rate for some materials											
	ex-Oriskany Loading by Homologue (PCBs onboard using CACI Report and Homologue distributions from Leach Rate Study materials)											
		Cl1	Cl2	Cl3	Cl4	Cl5	Cl6	Cl7	Cl8	Cl9	Cl10	tPCBs
		2.4E-04	3.4E-03	3.0E-01	5.9E+01	2.8E+02	1.8E+02	4.8E+01	4.8E-01	5.9E-02	2.2E-02	5.6E+02
		Kg	Kg	Kg	Kg	Kg	Kg	Kg	Kg	Kg	Kg	Kg

Response to Appendix A of SAB Comments on Ex-ORISKANY Artificial Reef Project: Time Dynamic Model (TDM). June 2005 (Draft Final).

	COMMENT	RESPONSE
1	**Model documentation.** The documentation for the TDM is not sufficient to judge the science and the appropriateness. The hydrodynamic model employed in the TDM is unclear and appears to have problems in its formulation. A diagram showing the boundaries and spatial discretization of the flow domain needs to be provided, and the model details (differential equations, boundary conditions, initial conditions, solution technique) need to be provided. a. The structure of the model is difficult to understand. b. The description of the model needs to be improved in the document such as water mass transport and other parameters. c. The chemical equilibrium partitioning constants used are not clearly described. d. The 24 hour time frame for chemical reactions should be reviewed in regard to more recent publications and justification for the approach used for reaction rates in the model needs to be presented. (The consideration of instantaneous or rapid (within 24 hours) phase partitioning of PCBs in the model was surprising considering the objective to predict PCB concentrations as a function of time.)	**a. Model structure is difficult to understand.** The time dynamic model (TDM) is written as a simple 2-dimensional abiotic box model that tracks adsorption/desorption of PCB homologs released into water inside the ship and moving into/out of dissolved organic carbon (DOC), total suspended solids (TSS) and sediment. Like PRAM, TDM specifies a prevailing 25 cm sec^{-1} current speed but not direction. This effort was designed to describe a complex, 3-D problem applied at a screening assessment level and required appropriate simplifications. Output from TDM is input into PRAM in order to determine sub-chronic biotic concentrations. The over-arching model structure is as follows. The model proceeds forward in time at 1-minute intervals to the model boundary 3000 m from the ship. The 1-minute time step was chosen to provide 15 m radial spatial resolution (1 minute*25 cm sec^{-1} =15 m) in model predictions. This resolution was felt necessary particularly close to the ship, where abiotic concentration gradients were expected to be very large. In each time interval, PCBs are released from solids inside the ship, assumed to mix instantaneously in the ship's internal volume and equilibrate instantaneously into water, DOC and TSS within the ship. Assumptions of instantaneous mixing and equilibrium partitioning within the ship were adopted from PRAM. Subsequently, PCBs in small volumes of water, DOC and TSS leave the ship and mix instantaneously into the first annular volume surrounding the ship. TDM then assumes that the 25 cm sec^{-1}current external to the ship flows equally in all directions over time. Conceptually, ship PCB release is modeled similar to a pulsing, lawn sprinkler head releasing jets of PCBs in water, DOC and TSS at 25 cm sec^{-1} sequentially in a 360 degree pattern. The speed of the jet is maintained out to the model edge 3 km from the ship. This analogy is used because the ship is imagined as being engulfed by a current of constant speed that regularly shifts direction like the sprinkler head, The current is not modeled as truly radial, flowing in all directions simultaneously. Rather, over some short period of time, released PCBs sequentially (or randomly) flow in all directions equally. Radial advection of PCBs in all directions is a modeling simplification to simulate the

	COMMENT	RESPONSE
	e. The outer boundary of the flow domain, with specified boundary conditions, is not defined. f. The hydrodynamic model apparently used is not consistent with advection in a time-varying bottom current flow direction. g. The cell by cell equations should be included. h. The mass balance in the model needs to be addressed.	random flow direction. Such a regular change in direction (though not in speed) is often measured at a site experiencing tidal currents. Successive bins stretching from the ship to the model perimeter are not the same size, but rather are concentric annuli of increasing water, DOC, TSS and sediment volume. Each annulus is 15 m wide from the inside diameter to the outside diameter. PCBs, initially in water, TSS and DOC escaping the ship, are diluted in the larger water volume as they move outward from the ship into ever-larger annuli and are allowed to adsorb to ever-larger volumes of DOC, TSS and sediment. The first order kinetics of PCB adsorption, particularly from water to sediment are kept fast (approximately 1 day to equilibrium, $C=C_0e^{-4.6t}$ where t is in days) as a conservative assumption to maximize PCB loading into the sediment during the 200 minute residence time (3000m/15 m min^{-1}) in the model. PCB concentrations in water DOC and TSS are diluted by the larger water, DOC and TSS volume of the annulus. PCBs adsorb/desorb from water to DOC, TSS and sediment in this annulus, partially approaching equilibrium concentrations in the 1-minute time step. In the same time interval, PCBs dissolved in water and adsorbed to DOC and TSS (but not sediment) in the first annulus move outward to the second, larger annulus; are diluted in the larger volume of water, DOC and TSS and again partition partially to equilibrium. Movement of PCB in water, DOC and TSS to the next larger annulus proceeds in lockstep in all 200 annuli of the model per 1-minute interval. PCBs that exit from the 200th annulus leave the model domain. PCBs in water TSS and DOC are released from the ship below the pycnocline. However, PCBs partition to DOC and TSS above and below a pycnocline which is set at 15 m below the surface. Mixing of PCB-laden water, TSS and DOC across the pycnocline and into the upper water column is controlled by a vertical dispersal rate much slower than the PCB partitioning rate. Vertical flux of PCBs across the pycnocline occurs within each annulus, but not into the volume directly above the ship. The water column directly above the ship remains free of PCBs. TDM predicts radial isopleths of decreasing concentrations in all directions and decreasing concentrations vertically across the pycnocline.

	COMMENT	RESPONSE
		TDM predictions of abiotic PCB concentrations are input into PRAM. PRAM predicts biotic PCB concentrations within two regions: zones of influence (ZOIs) equal to two and five times the areal footprint of the ship. For a ZOI=2, the areal, 2-dimensional footprint extends 14.8 m from the ship. TDM PCB concentrations in the first model bin (0 to 15 m [ZOI=2} from the ship) were input into PRAM's food web module to predict PCB concentrations in biota. For a ZOI=5, the areal footprint extends 48.7 m from the ship. Average TDM PCB concentrations for the first three bins (0 to 45 m from the ship) and first four bins (0 to 60 m from the ship) were themselves averaged together and input into PRAM for ZOI=5 biotic predictions. **b. Description of water mass transport and other parameters needs to be improved.** Mass of PCBs is the only parameter that is tracked and budgeted in TDM. TDM assumes that sequential flow of PCBs occurs in all directions during each time step. PCBs are modeled to move from inner to outer annuli, initially staying in the same matrices as in the previous time step, but diluted in concentration by the larger mass of water, DOC and TSS of the outer annuli. If water, DOC, and TSS mass were similarly tracked, the mass of the material coming from the vicinity of the ship would need to be similarly divided by the respective mass in each annulus. This would slow the average current considerably below 25 cm sec^{-1} , distorting and increasing the partitioning to the sediment. TDM assumes that PCBs are being advected away from the ship with a constant current flowing at 25 cm $sec^{-1.}$ Extending the analogy by averaging the current over time and increasing the period in which water-borne PCBs remain in the model domain was felt to lead to misleading results. In the one minute period within a particular annulus, PCB partitioning approaches equilibrium concentrations via flux from one matrix to another. Total PCB mass released from the ship over time is distributed in the sediment, which stays in the model, and transiently in water, DOC and TSS in the annuli as it moves toward the model perimeter. Since water and entrained DOC and TSS are quickly advected away at 25 cm sec^{-1}, most PCB mass escapes from the model domain before it can adsorb to the sediment. Only the immobile sediment retains an irreversible fraction of its adsorbed PCB load (see response 1d).

	COMMENT	RESPONSE
		c. Equilibrium partitioning constants are not clearly described. In the TDM, concentrations are in units of mass fraction (mass of PCBs in matrix to total mass of the matrix), versus molar concentration or mass to volume. One ml of seawater is assumed to weigh one gram. Equilibrium PCB concentrations in DOC, TSS and sediment follow a simple linear isotherm, based on PCB concentrations in water. (Weber et al, 1991). Homolog-specific equilibrium partitioning constants $K_p=K_{oc}*f_{oc}*C_w$ where K_p is the ratio of the PCB homolog concentration in DOC, TSS, sediment to the PCB homolog concentration in water at equilibrium. K_{oc} is the organic carbon to water partitioning coefficient for each PCB homolog, taken from PRAM (listed in Table 1 below). F_{oc} is the mass fraction of organic carbon in DOC, TSS and sediment, equal to 1, 0.1, and 0.01 respectively. C_w is the water PCB homolog concentration. K_p, K_{oc}, f_{oc}, and C_w are unitless. C_w is initially determined by the PCB release rate within the ship and is then usually reduced via volume dilution and partitioning into DOC, TSS and sediment. **PCB homolog** / **K_{oc}** monochloro / $4.61*10^3$ dichloro / $1.14*10^4$ trichloro / $4.22*10^4$ tetrachloro / $4.51*10^4$ pentachloro / $8.61*10^4$ hexachloro / $1.2*10^6$ heptachloro / $2.19*10^6$ octachloro / $2.85*10^6$ nonachloro / $9.24*10^6$ decachloro / $8.72*10^7$ Table 1: Homolog K_{oc} values used in PRAM and TDM Reference: Weber, W. J., P. M. McGinley and L E Katz. 1991. Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport. Wat. Res

	COMMENT	RESPONSE
		25(5):499-528. **d. The 24-hour time frame for partitioning equilibrium is surprisingly fast and should be reviewed.** The 24-hour time frame for PCB partitioning equilibrium was adopted from Di Toro and Horzempa (1982) who were studying adsorption and desorption of hexachlorobiphenyl between water and suspended sediments. The time frame is fast relative to more current literature, particularly when considering adsorption/desorption to bed sediment (Borglin et al, 1996; Lick et al, 1996; Valsaraj and Thibodeaux, 1998; Gess and Pavlostathis, 1997). Assumption of fast adsorption was considered conservative however, since laboratory-measured rapid release of PCBs was short-lived. Rapid adsorption would allow initially high water concentrations to be reflected in the sediment. The corollary assumption of fast sediment desorption was tempered by the conservative assumption of a large, irreversibly-bound fraction, as described in the Di Toro and Horzempa (1982) paper. Assumption of a permanently-bound fraction is supported in more recent literature (McGroddy et al, 1995; Hunter et al, 1996; Kan et al, 1997; Kan et al, 1998). In summary, TDM assumes fast partitioning from the water to the sediment to capture early, large PCB releases from the ship, then assumes that a large fraction can not desorb out of the sediment and this output is then provided as input into PRAM. References: Di Toro D. M. and L. M. Horzempa. 1982. Reversible and resistant components of PCB adsorption-desorption: isotherms. Environ. Sci. Technol.16:594-602. Borglin, S., A. Wilke, R. Jepsen, and W. Lick. 1996. Parameters affecting the desorption of hydrophobic organic chemicals from suspended sediments. Environ. Toxic. Chem. 15(10):2254-2262. Lick, W. and V. Rapaka. 1996. A quantitative analysis of the dynamics of the sorption of hydrophobic organic chemicals to suspended sediments. Environ. Toxic. Chem. 15(7):1038-1048.

	COMMENT	RESPONSE
		Valsaraj, K. T. and L. J. Thibodeaux. 1999. On the linear driving force model for sorption kinetics of organic compounds on suspended sediment particles. Environ. Toxic. Chem. 18(8):1679-1683. Gess, P and S. G. Pavlostathis. 1997. Desorption of chlorinated organic compounds from a contaminated estuarine sediment. Environ. Toxic. Chem. 16(8):1598-1605. McGroddy, S. E., J. W. Farrington, and P. M. Gschwendl. 1995. Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. Environ. Sci. Technol. 30(1):172-177. Kan, A. T., G. Fu, M. Hunter, W. Chen, C. H. Ward, and M.B. Tomson. 1998. Irreversible sorption of neutral hydrocarbons to sediments: experimental observations and model predictions. Environ. Sci. Technol 32(7):892-902. Kan, A. T., G. Fu, M. Hunter, and M. B. Tomson. 1997. Irreversible adsorption of naphthalene and tetrachlorobiphenyl to Lula and surrogate sediments. Environ. Sci. Technol. 31(8):2176-2185. Hunter, M. A., A. T. Kan, and M. B. Tomson. 1996. Development of a surrogate sediment to study the mechanisms responsible for adsorption/desorption hysteresis. Environ. Sci. Technol. 30(7):2278-2285. **e. The outer boundary conditions of the flow field are not defined.** The only source of PCBs at the outer boundary are from the sunken ship. PCBs are assumed to be advected away from the ship and, over time, escape in all directions beyond the perimeter of the model 3 km from the ship. PCB concentrations at the outer boundary are functionally zero because PCBs are never allowed into the model domain from the outer boundary and they do not impact their advective removal from the ship. Water, DOC and TSS movement are not explicitly tracked in the model though they are assumed to carry PCBs away from the ship and out of the model domain at 25 cm sec^{-1}. □

	COMMENT	RESPONSE
		f. The hydrodynamic model is not consistent with advection and a time-varying current flow. TDM is not a hydrodynamic model. It employs water currents only as a transport mechanism, carrying PCBs away from the ship source. Water parcels are not tracked, water mass is not conserved and is only referenced as a diluting mechanism for PCB concentrations as PCBs move away from the ship. **g. The cell-by-cell equations should be included.** The following is a general set of steps that occur in most cells. The first bin (bin 1) adjacent to the ship is a little different in that it acquires PCB mass directly from the ship rather than an adjacent bin, and PCBs are not advected into bin l above the pycnocline. PCBs enter bin i from the inner, adjacent bin i-1, initially in the same media. The concentration is immediately reduced by the larger media volume in the current bin. For example, for PCB in TSS below the pycnocline: **1a. input to bin i: $PCB_{lower\ TSS\ (i)} = PCB_{lower\ TSS\ (i-1)}$** **2a. PCB concentration in TSS in bin i: $PCB_{lower\ TSS(i-1)}$/lower $TSS_{(i)}$** The same is true above the pycnocline for all but the first cell: **1b. input to bin i: $PCB_{upper\ TSS\ (i)} = PCB_{upper\ TSS\ (i-1)}$** **2b. PCB concentration in TSS in bin i: $PCB_{upper\ TSS(i-1)}$/upper $TSS_{(i)}$** In the first cell, PCBs enter water above the pycnocline only by mixing from below. PCBs in water and DOC are similarly advected into bin i and diluted. Total PCB mass in bin i in water, DOC, TSS and sediment above and below the pycnocline is calculated: **3. $\Sigma PCB(i)=PCB_{lower\ water(i)} + PCB_{upper\ water(i)} + PCB_{sediment(i)} + PCB_{lower\ TSS(i)} + PCB_{upper\ TSS(i)} + PCB_{lower\ DOC(i)} + PCB_{upperDOC(i)}$.** Total PCB is rewritten as a sum of products of PCB concentrations, denoted with brackets below, times the mass of water, DOC, TSS and sediment. **4. $\Sigma PCB(i)=[PCB_{lower\ water(i)}]$*lower water(i)**

	COMMENT	RESPONSE
		+[$PCB_{upper\ water(i)}$] *upper water(i) **+[$PCB_{sediment(i)}$]*sediment(i)** **+[$PCB_{lower\ TSS(i)}$]*lower TSS(i)** **+[$PCB_{upper\ TSS(i)}$]*upper TSS(i)** **+[$PCB_{lower\ DOC(i)}$]*lower DOC(i)** **+[$PCB_{upperDOC(i)}$]*upper DOC(i)**. Equilibrium concentrations for PCBs in the different media in the bin are next computed, all as functions of equilibrium water concentration: times the organic carbon/water partitioning coefficient K_{oc} and fraction organic carbon for that media f_{oc}.: **5a. Equilibrium [$PCB_{water(i)}$] = ΣPCB(i)/** **(lower water(i)+ upper water(i)** **+sediment(i)*K_{oc}*f_{oc}** **+(lower TSS(i)+ upper TSS(i))*K_{oc}*f_{oc}** **+(lower DOC(i)+ upper DOC(i))*K_{oc}*f_{oc})** When PCBs are modeled to desorb from the sediment, a small modification in equation 5a is needed to account for an irreversible PCB fraction adsorbed to the sediment, argued by DiToro and Horzempa (1982). In equation 5b, R_o is the concentration of PCBs that resist desorption and P_x is a shallower linear adsorption desorption isotherm: **5b. Equilibrium [$PCB_{water(i)}$] = ΣPCB(i)-R_o*sediment(i)/** **(lower water(i)+ upper water(i)** **+sediment(i)*P_x** **+(lower TSS(i)+ upper TSS(i))*K_{oc}*f_{oc}** **+(lower DOC(i)+ upper DOC(i))*K_{oc}*f_{oc})** **where R_o=0.57* maximum [$PCB_{sediment(i)}$]; P_x=(1/2.3)*K_{oc}*f_{oc}** The other equilibrium concentrations are again calculated as water equilibrium concentrations times K_{oc} and correct media f_{oc}.

	COMMENT	RESPONSE
		6a. Equilibrium [$PCB_{lower\ water(i)}$] = equilibrium [$PCB_{water(i)}$] **Equilibrium [$PCB_{upper\ water(i)}$] = equilibrium [$PCB_{water(i)}$]** **Equilibrium [$PCB_{sediment(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}** **Equilibrium [$PCB_{lower\ TSS(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}** **Equilibrium [$PCB_{upper\ TSS(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}** **Equilibrium [$PCB_{lower\ DOC(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}** **Equilibrium [$PCB_{lower\ DOC(i)}$] = equilibrium [$PCB_{water(i)}$]*K_{oc}*f_{oc}** When sediment desorption occurs, the equilibrium sediment concentration equation is modified to account for the irreversible fraction: **6b. Equilibrium [$PCB_{sediment(i)}$] = R_o+ equilibrium [$PCB_{water(i)}$]* P_x** PCB flux between media follows first order kinetics, where existing concentrations approach equilibrium concentrations asymptotically. The flux is calculated as a difference between existing and equilibrium concentrations times the mass of the particular media. Rate constants are included to account for the 1 minute time step: **7. $Flux_{lower\ water(i)}$ = rate*((equilibrium [$PCB_{lower\ water(i)}$])-[$PCB_{lower\ water(i)}$])*lower water(i)** **$Flux_{upper\ water(i)}$ = pycnrate*((equilibrium [$PCB_{upper\ water(i)}$])-[$PCB_{upper\ water(i)}$])*upper water(i)** **$Flux_{sediment(i)}$ = rate*((equilibrium [$PCB_{sediment(i)}$])-[$PCB_{sediment(i)}$])*sediment(i)** **$Flux_{lower\ TSS(i)}$ = rate*((equilibrium [$PCB_{lower\ TSS(i)}$])-[$PCB_{lower\ TSS(i)}$])*lower TSS(i)** **$Flux_{upper\ TSS(i)}$ = pycnorate*((equilibrium [$PCB_{upper\ TSS(i)}$])-[$PCB_{upper\ TSS(i)}$])*upper TSS(i)** **$Flux_{lower\ DOC(i)}$ = rate*((equilibrium [$PCB_{lower\ DOC(i)}$])-[$PCB_{lower\ DOC\{i)}$])*lower DOC(i)**

	COMMENT	RESPONSE
		$Flux_{upper\ DOC(i)}$ = pycnorate*((equilibrium [$PCB_{upper\ DOC(i)}$])-[$PCB_{upper\ DOC(i)}$])*upper DOC(i) Rate constant 'rate' has a value of 0.0032 and corresponds to a 1 minute increment in first order kinetics reaching 99% equilibrium in 24 hours (see 1d. above) Rate constant 'pycnorate' has a much smaller value of 1.0728e-5, reflecting the much slower 64.7 day approach to 99% equilibrium across the pycnocline, shown in Figure 2-2 of the original document. The latter constant was based simulations using a vertical diffusivity K_z value of 0.1 $cm^2\ sec^{-1}$. In model simulations, PCBs are observed to always move up across the pycnocline. The first flux term in equation 7, involving PCBs in the lower water, has a rate constant based on a 24-hour approach to equilibrium for all media above and below the pycnocline. PCB flux to water, TSS and DOC above the pycnocline is limited by the much smaller pycnocline rate constant. In order to accommodate the slower PCB mixing across the pycnocline, a correction is made to lessen PCB release from media below the pycnocline. The algebraic correction factor is a value less than 1.0, labeled as the variable 'brake' in the model code. It is calculated as the sum of the flux terms and absolute values of the flux terms in equation 7, divided by the difference between the sum of absolute fluxs and sum of fluxs in each cell: **8. Brake=($\Sigma abs(Flux_j)+\Sigma Flux_j$)/($\Sigma abs(Flux_j)-\Sigma Flux_j$)** where the index j denotes the seven different media in each bin and abs denotes the absolute value. This correction is applied to each flux calculation in equation 7 that has a negative value (i.e. the media is releasing PCBs) and maintains conservation of PCB mass in the model. The fluxes are then added to masses advected into the i bin from the i-1 bin and new concentrations are calculated: **9. [$PCB_{lower\ water(i)}$]= ($PCB_{lower\ water(i)}$+$Flux_{lower\ water(i)}$)/ lower $water_{(i)}$**

	COMMENT	RESPONSE
		$[PCB_{upper\ water(i)}] = (PCB_{upper\ water(i)} + Flux_{upper\ water(i)}) / upper\ water_{(i)}$ $[PCB_{sediment(i)}] = (PCB_{sediment(i)} + Flux_{sediment(i)}) / sediment_{(i)}$ $[PCB_{lower\ TSS(i)}] = (PCB_{lower\ TSS(i)} + Flux_{lower\ TSS(i)}) / lower\ TSS_{(i)}$ $[PCB_{upper\ TSS(i)}] = (PCB_{upper\ TSS(i)} + Flux_{upper\ TSS(i)}) / upper\ TSS_{(i)}$ $[PCB_{lower\ DOC(i)}] = (PCB_{lower\ DOC(i)} + Flux_{lower\ DOC(i)}) / lower\ DOC_{(i)}$ $[PCB_{upper\ DOC(i)}] = (PCB_{upper\ DOC(i)} + Flux_{upper\ DOC(i)}) / upper\ DOC_{(i)}$ **h. Mass balance of the model needs to be addressed.** The only mass explicitly tracked in the model is PCB released from the ship. Mass released equals mass calculated to reside in the model water, DOC, TSS and sediment; plus mass lost by advection across the model boundary. Since TDM is a PCB mass transport model and not a hydrodynamic model, movement of water, DOC and TSS are not explicitly modeled and mass balances are not tracked. Issues of bottom shear, TSS particle size, particle density and settling velocity are also not addressed or defined. Particle resuspension and settling was thus not included in calculating PCB loads.
~	**Ship integrity and internal flow rate assumptions**. The assumption about the vessel hull is not necessarily a conservative one. Given that the leach rates are set in Appendix C, there is no question that the same quantity of PCB will released no matter what the hull porosity assumptions are. However, a slower flow rate through the ship would result in a higher residence time and therefore higher concentrations coming out of the ship, but in less volume of water. So, it's not clear if the total mass released per day, say, would be more or less than is currently predicted with the model. The internal-ship flow velocity assumed	As reviewers pointed out in comments regarding the TDM, release of PCBs outside of the ship will eventually match release of PCBs inside the ship if the ship hull is permeable. The degree of permeability, characterized as the current speed inside the ship, will determine the internal ship PCB concentrations. Current speed inside the ship was arbitrarily set at 1% of external current or 0.25 cm sec^{-1}. This assumption was first made in PRAM and adopted in the TDM. In PRAM, reef fish are assumed to stay inside the ship and be exposed to internal PCB concentrations 10% of the time. The 1% value was felt to be a conservative compromise between very slow internal currents, which would elevate internal PCB concentrations, and faster internal currents that reflect accessibility of the inner ship to reef fish as assumed in PRAM. Figure 1 below, based on the maximum measured release of pentachlorobiphenyl at 2.3 g day^{-1}, an illustrates the sensitivity of internal PCB concentration to internal current velocity. As internal velocity increases, internal concentration decreases in a non-linear fashion. The

	COMMENT	RESPONSE
	(1/100 of external flow velocity) appears to have been selected rather arbitrarily. This really needs to be monitored and assessed for ships already in place.	1% internal current results in modeled exposure to 3.2 10^{-12} g pentachloro PCB in 1 g of water, organic carbon and total suspended sediments combined. The same general relationship holds for total PCBs. While a slower internal current could have been chosen, it seemed less reasonable given the assumed accessibility of the ship interior to mobile reef organisms.
5	**Pycnocline**. While there is information to indicate the existence of a pycnocline near the depth used in the model at various times of the year, the variation of the depth and existence of the pycnocline are not addressed.	The pycnocline occurs at the depth of the maximum thermohaline density gradient in the water column that maintains vertical stability and arises from solar heating. Typically, water above or below the pycnocline is more easily mixed, while at the pycnocline vertical mixing is impeded. The pycnocline can be disrupted by strong mixing, typically from surface winds. In this case the pycnocline could also be disrupted by upwelling resulting from the current deflecting off the ship's side. At the proposed ex-Oriskany site at 30N/87W in the Gulf of Mexico at a depth of 64 m of water, stormy cool winter weather conditions can break down the pycnocline, which is re-established in the late spring and deepens through the summer. Below, Figures 2-6 depict modeled and measured ocean density structure. Figures 2 and 3 are comparisons of modeled mixed depth throughout the oceans at coarse resolution. Deep winter mixing (above the pycnocline) in the Gulf in November gives way to shallower mixing under stratified conditions in July. In these low resolution figures, 30N/87W is plotted as land. However, a mixed layer depth shoaling from 25 m in November to 0 m in July can be seen in the Gulf. Figure. 4 shows locations of CTD (conductivity, temperature, depth) casts from which density profiles can be calculated. The density profiles from the stations indicated in red and green in figure 4 are shown in figure 5. The green profiles in figure 5, taken at the stations denoted in green in figure 4, were measured in October, 1995. While ocean conditions at locations 1, 2, and 3 in figure 4 are not equivalent, a trend is seen. The pycnocline is very shallow in the spring, deepens to around 5 m in early summer, deepens further to 40 m in the fall then disappears in the winter as the entire water column cools and mixes. Figure 6 is the monthly density profile modeled at 30N/87W used in Navy sound propagation models in the Gulf. The maximum inflection point can be used to estimate depth of the pycnocline. Here more clearly than in the above figures, a weak or non-existent pycnocline exists in winter. Then in spring the

	COMMENT	RESPONSE
		pycnocline is seen to reestablish and strengthen throughout the summer, reaching a maximum depth of approximately 50 m in August or September, then disintegrating in late fall and early winter. The selection of a pycnocline at 15 m in the TDM was not based on the above information, but rather on diver experience at the proposed reefing site (Rob Turpin pers, comm., 2004). In view of the above figures, a 15 m pycnocline depth in the vicinity of the ex-ORISKANY sink site appears to be supported. The strength of the pycnocline, in terms of hindering vertical mixing, is described by turbulent vertical diffusivity (k_z). A k_z value of 0.1 cm sec^{-2} is used in the TDM, based on literature values referenced in the TDM documentation.

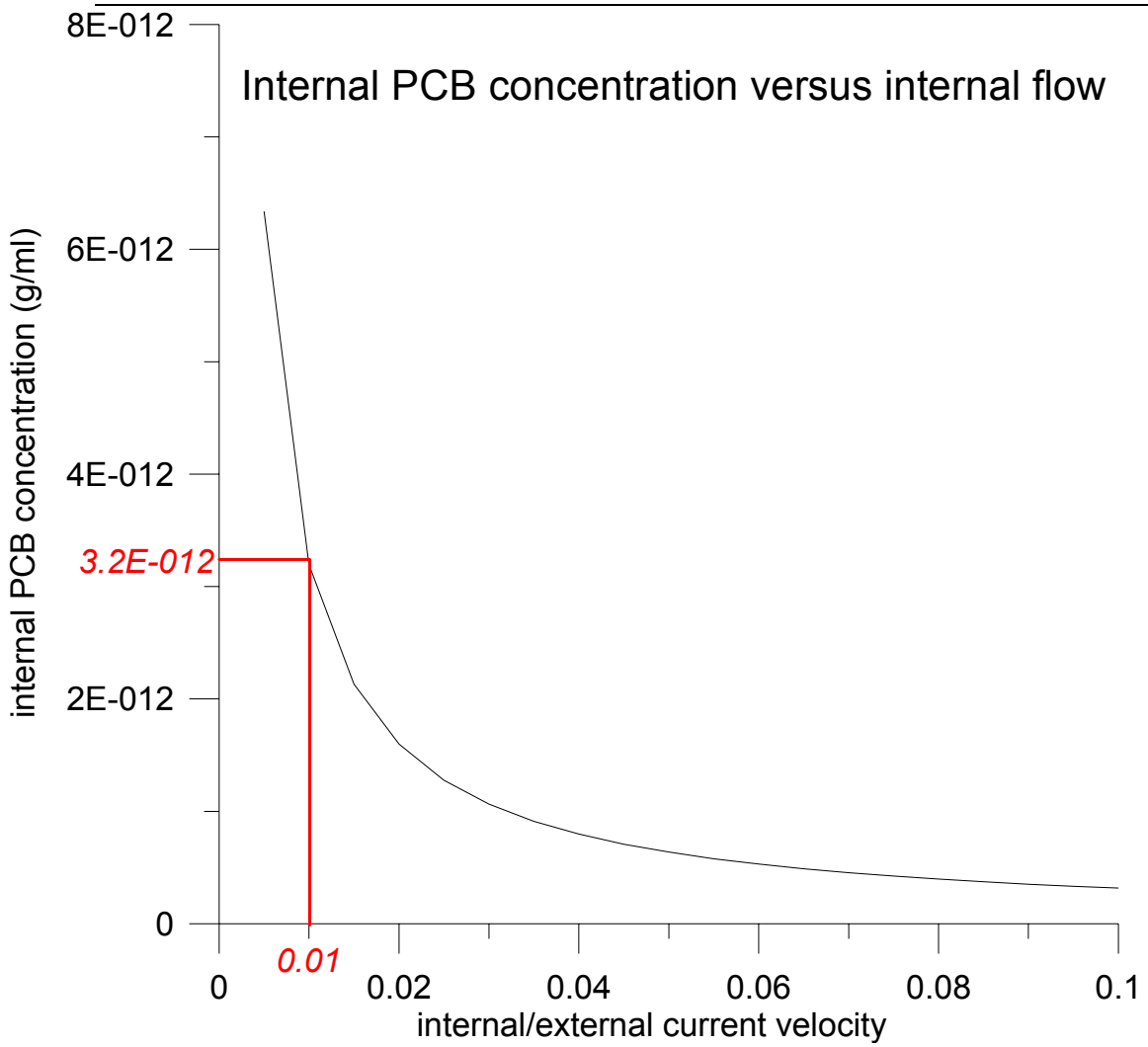

Figure 1: Bulk water (water +DOC+TSS) concentration of pentachlorobiphenyl in the ship as a function of internal water velocity. Internal water velocity is plotted as a fraction of the assumed external 25 cm sec^{-1} current. Maximum release of 2.3 g day^{-1} for pentachlorobiphenyl was modeled, but relationship applies to total PCBs as well.

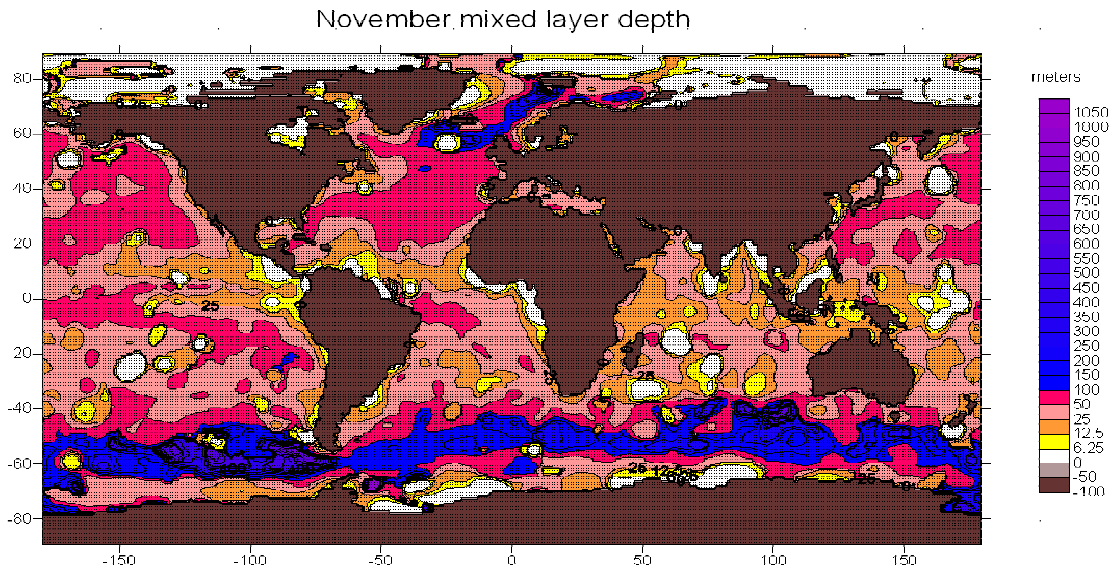

Figure 2: November 1 degree modeled mixing depth from NOAA's World Ocean Atlas dataset http://www.nodc.noaa.gov/OC5/indprod.html

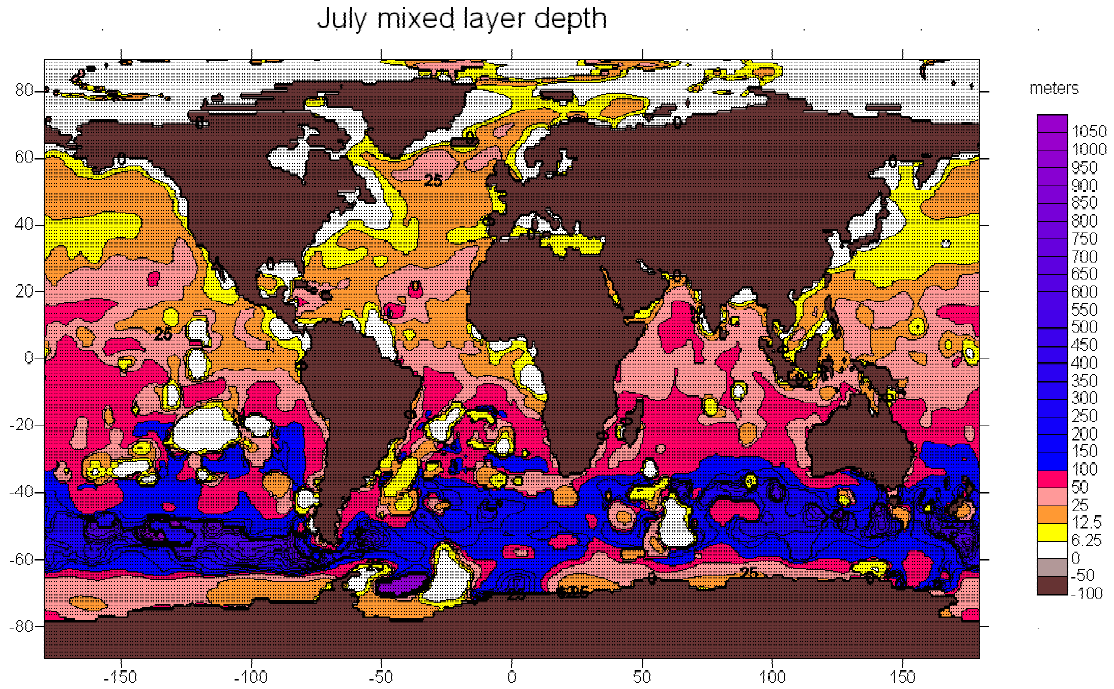

Figure 3: July 1 degree modeled mixing depth from NOAA's World Ocean Atlas dataset http://www.nodc.noaa.gov/OC5/indprod.html

CTD casts in vicinity of proposed REEFEX sinking at 30N 87W

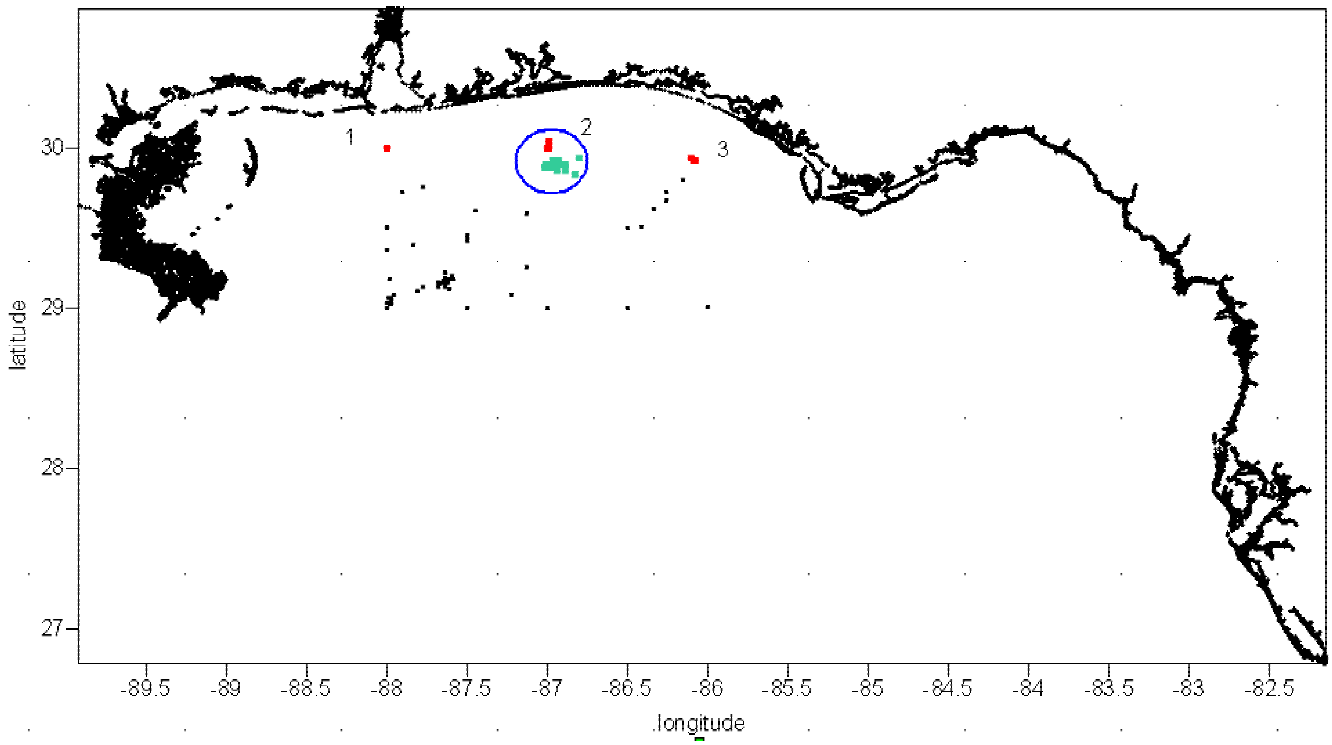

Figure 4: Historical CTD casts in the vicinity of the ex-Oriskany site at 30N 87W http://www.nodc.noaa.gov/OC5/indprod.html. . The stations denoted in green are from Naval Research Laboratory Stennis (Steve Crossland, pers. comm.)

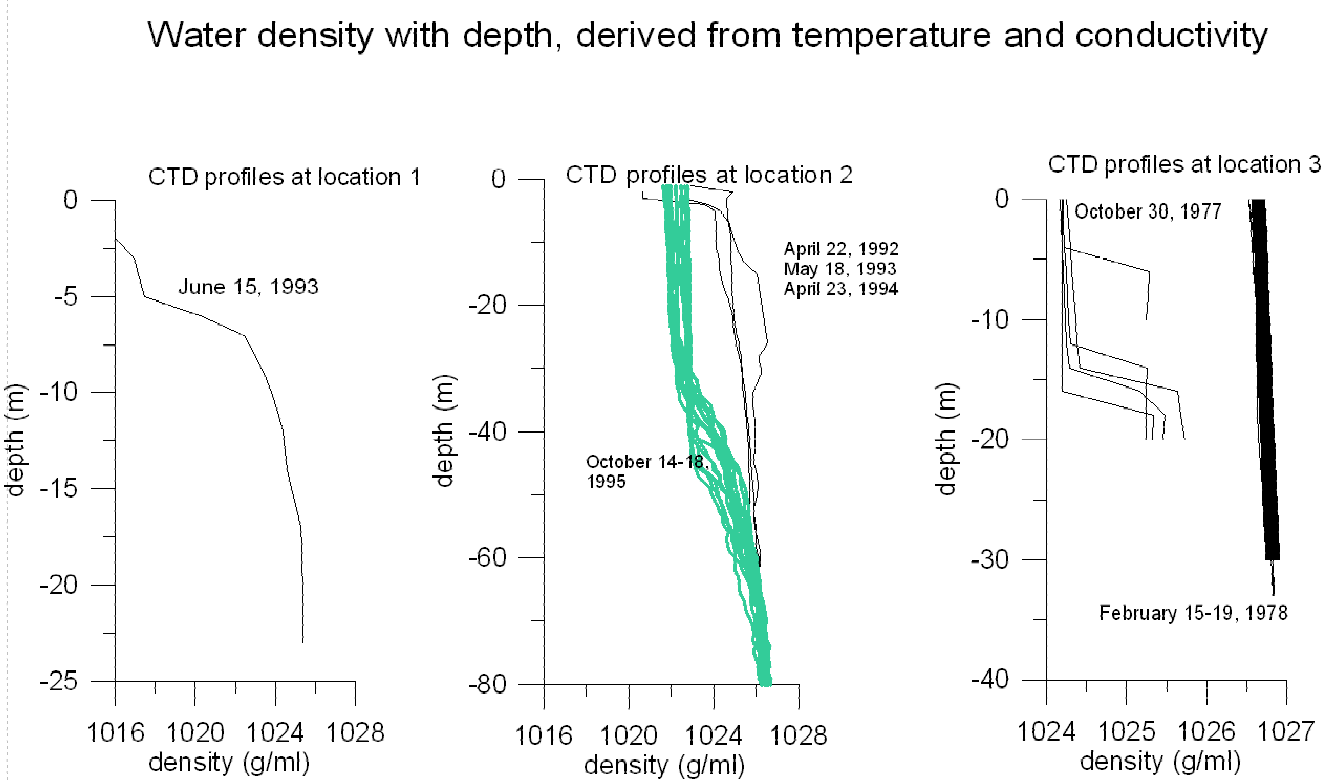

Figure 5: Water Density with Depth, Derived from Temperature and Conductivity. Profiles are from stations
in Figure 4. The green profiles are from the Figure 4 stations, also indicated in green.

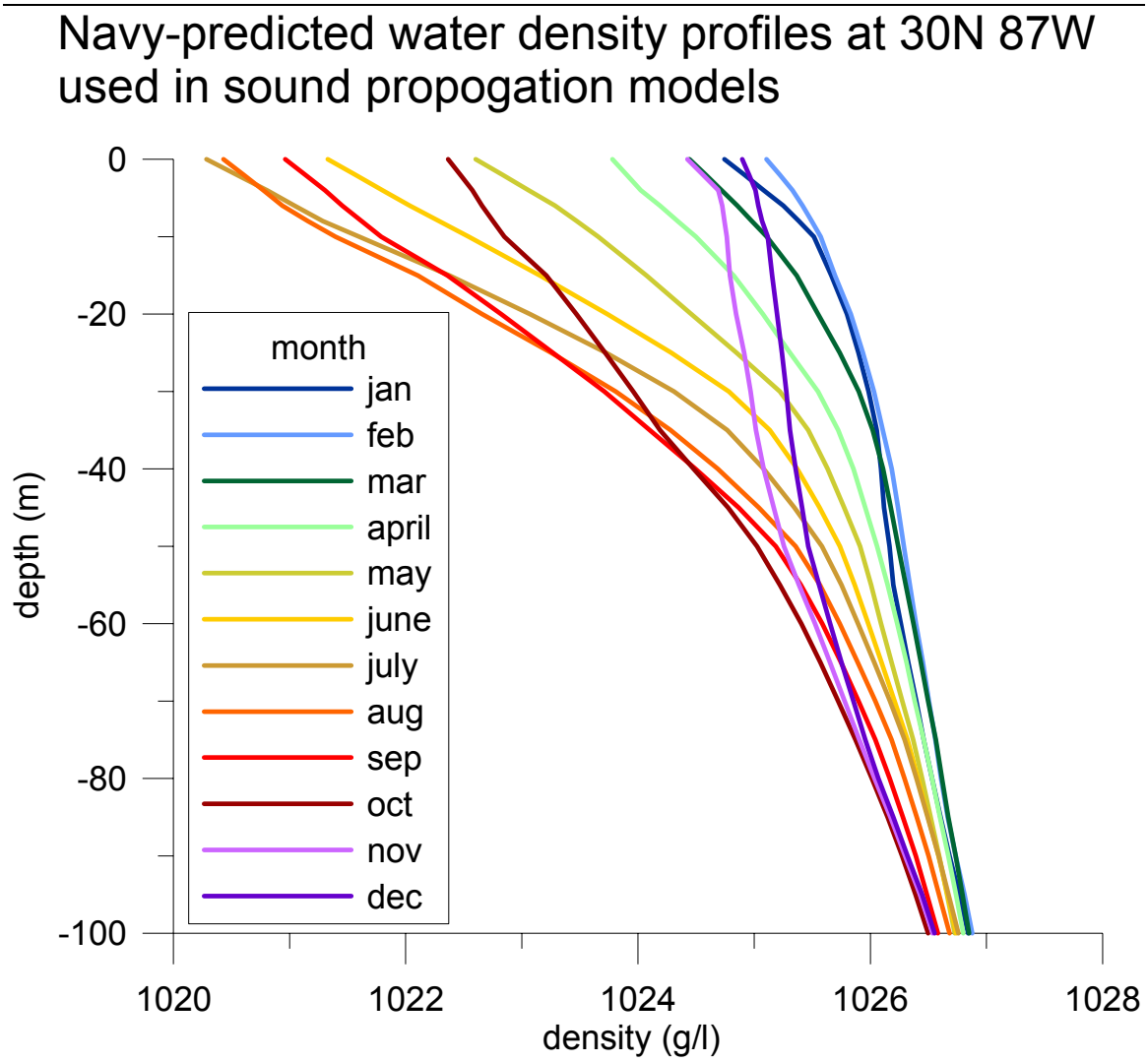

Figure 6: Density profiles predicted by the U.S Navy's Global Digital Environmental Model (GDEM v3) at 30N/87W. http://128.160.23.42/gdemv/gdem_desc_v30.html

Comment	COMMENT	RESPONSE
SC 4	Provide more details on ship preparation for scuttling--bulkhead doors open or closed, hull cut or not, etc. This may impact transport of PCBs. .	The TDM-modeled release of PCBs from ship was based on a hypothesized internal current speed that was 1% of the current speed outside of the ship. The hull was assumed permeable enough to allow the internal current to flush out released PCBs. No specific hull configuration was modeled. A description of ship preparation for scuttling can be provided in the text or an appendix.