
United Heckathorn Superfund Site, Richmond, California
DDT Fate and Transport Study

Final

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Contents

1. Introduction.....	1
2. Conceptual Site Model.....	3
2.1 Sources.....	3
2.2 Sediment Transport Process Summary.....	4
2.3 DDT Degradation.....	7
2.4 Dissolved-phase DDT transport	8
3. DDT Mass Analysis	9
4. DDT Mass Balance	13
4.1 Sources and Losses.....	13
4.2 Mass Balance Model	15
5. Summary	19
6. References	20

List of Figures

Figure 1. Location of the United Heckathorn Superfund Site.....	2
Figure 2. Multibeam bathymetry and delineation of the three characterization areas.....	6
Figure 3. Total DDT mass in the 2013 YBM.	12
Figure 4. Change in DDT mass over time with least squares linear regression and 95% confidence intervals (CI).....	13
Figure 5. Conceptual diagram of average yearly sources and losses of DDT mass to the Lauritzen Channel sediment.....	16
Figure 6. Change in total DDT mass as a result of all sources to and losses from the system. Sensitivity to ongoing source terms is included.....	16
Figure 7. Conceptual diagram of the sources and losses to the Lauritzen Channel sediment.	18
Figure 8. Change in bulk YBM DDT concentration. Sensitivity to the unquantified source terms is included.	18

List of Tables

Table 1. Conclusions from the United Heckathorn Source Identification Study (CH2MHILL, 2014).	4
Table 2. Transport quantities associated with vessel resuspension.....	5
Table 3. Average Composition of DDT and DDT Metabolites in Lauritzen Channel Surface Sediment.....	7
Table 4. Resultant sediment mass and deposition rates determined from the YBM analysis.	10
Table 5. Mass and volume calculations for the time period of evaluation.	11
Table 6. Estimates of DDT loss due to diffusion from the Lauritzen Channel sediment.	14
Table 7. Mass balance terms for DDT recovery assessment.	15

List of Appendices

Appendix A. Application of Polyethylene (PE) Passive Samplers to Assess DDTs in the Lauritzen Channel at the United Heckathorn Superfund Site in Richmond Harbor, San Francisco Bay	
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1. Introduction

The United Heckathorn Superfund Site is located in Richmond Harbor on the east side of San Francisco Bay in Richmond, California (Figure 1). The site includes the former United Heckathorn facility where organochlorine pesticides were processed, packaged, and shipped. As a result of these activities, the adjacent waterways were adversely affected by releases from the former facility. A Record of Decision (ROD) that presented the selected remedial action for the site was issued in 1994 (USEPA, 1994). Remediation activities for the upland portion of the site consisted of excavation and offsite disposal of contaminated soil (from 1982 to 1993) and placement of concrete and geotextile/gravel caps (from 1998 to 1999) over approximately 4.5 acres of Levin Richmond Terminal Corporation's (LRTC) upland soils to prevent erosion and collect surface runoff. Remediation activities for the waterways were performed in 1996 and 1997 and consisted of (1) dredging and offsite disposal of sediment from the Lauritzen Channel and Parr Canal and (2) placement of clean sand in the channels to promote the recovery of the benthic community. However, post-dredging monitoring of surface water and sediment has indicated that the remediation levels specified in the ROD have not been maintained (EPA, 2012). A focused feasibility study (FFS) is being performed to address residual contamination in the channel sediment.

This report presents the results of a DDT¹ fate and transport study that was performed for the Lauritzen Channel as part of the FFS. The objectives of the study were as follows:

- Calculate the mass of DDT resuspended by vessel movements
- Develop a quantitative contaminant fate and transport conceptual site model (CSM) and DDT mass balance for the Lauritzen Channel
- Use the mass balance model to assess trends in DDT mass and concentration in sediment

The report synthesizes results of previous studies conducted at the study site. Section 1 is an introduction. Section 2 summarizes the refined CSM that incorporates the results of the source identification study (CH2MHILL, 2014), Tier 2 sediment transport study (SEI, 2014) and passive sampler studies (P. Gschwend & Burgess, 2012; P. M. Gschwend, 2014). Section 3 develops and presents a DDT mass analysis and mass balance for the Lauritzen Channel. The summary and conclusions are provided in Section 4.

¹ Dichlorodiphenyltrichloroethane; for the purposes of this report, "DDT" refers to the sum of all 4,4'- and 2,4'- isomers of DDT, DDD, and DDE.

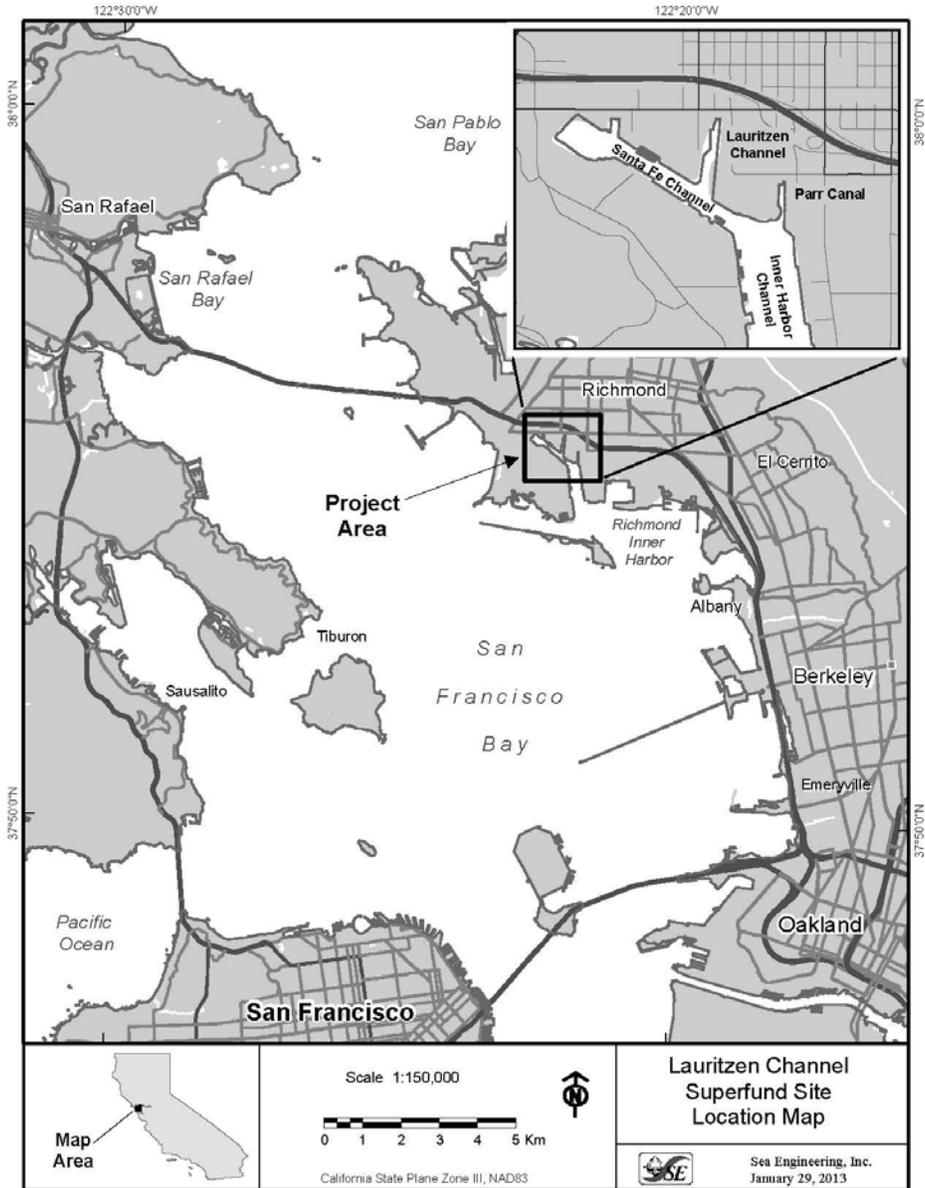


Figure 1. Location of the United Heckathorn Superfund Site.

2. Conceptual Site Model

The CSM provides the framework for evaluating DDT fate and transport. The CSM synthesizes available data, describes a mass balance (i.e., a simple representation of all inputs and outputs to a system), and describes inferred spatial and temporal transport patterns. The primary DDT sources and transport components are identified and described for the Lauritzen Channel in the source identification study and Tier 2 sediment transport study (CH2MHILL, 2014; Sea Engineering, 2014). The significant findings from these studies are summarized in the following sections.

2.1 Sources

The source identification study (CH2MHILL, 2014) characterized and quantified, to the extent possible, ongoing sources of contamination to the Lauritzen Channel. The study focused on identifying the sources of the DDT that have been consistently measured in sediment, surface water, and biota in the Lauritzen Channel since the remedy was completed in 1997. The potential ongoing sources of contamination that were evaluated included:

- Embankments (e.g., point source discharges from pipes, outfalls, and seeps; and/or erosion of DDT-contaminated embankment soils)
- Groundwater discharge from the upland portion of the site into the Lauritzen Channel
- DDT-contaminated wood pilings
- Storm water outfalls
- Sources outside of the Lauritzen Channel
- Dredging residuals (including both undisturbed [undredged] sediment, and material that was re-suspended during dredging, escaped from the dredge bucket, ran out of the scow, or sloughed into dredged areas); residuals also include contaminated embankment sediments that were not removed in either the upland or marine remedial actions)

The general conclusions for each potential source are listed in Table 1. Generally, while there are ongoing sources of DDT to the channel, they appear to be small relative to the mass of DDT in channel sediments. While some of the potential ongoing sources of contamination to the Lauritzen Channel could not be quantified, the mass balance analysis presented in Section 4 provides a suitable method for assessing their magnitude.

Important conclusions from the source identification study were drawn regarding the character of the primary source of sediment to the Lauritzen Channel (San Francisco Bay) and the primary source for the present day DDT in the channel. The available sediment chemistry data for areas outside of the Lauritzen Channel suggested that incoming material from the San Francisco Bay is a relatively clean source of sediment.² In light of the relatively small magnitude of the ongoing sources compared to the DDT mass currently found in the Lauritzen Channel sediments, the primary source to the sediment bed was concluded to be dredging residuals from the 1997 remedial efforts.

² The ambient threshold value for total DDT in San Francisco Bay sediments is 7 µg/kg for sediments with greater than 40% fines (Gandesbery and Hetzel, 1998).

Table 1. Conclusions from the United Heckathorn Source Identification Study (CH2MHILL, 2014).

Conclusions of Source Identification Study

United Heckathorn Superfund Site, Richmond, California

Potential Ongoing Source	Character of Potential Source
Embankment Areas	<p>Pipes and outfalls are unlikely to be significant sources of pesticides to the Lauritzen Channel during dry weather conditions because they do not convey dry weather flow. One seep that was sampled contained low levels of pesticides. Pipes and outfalls have not been inspected or sampled during wet weather conditions. Some of the identified and possible unidentified pipes and conveyances could have and may still act as preferential pathways for contaminant transport from upland areas with DDT-contaminated soil and groundwater to the Lauritzen Channel.</p> <p>DDT contamination above the remediation goal is widespread along the eastern, northern, and northwestern shorelines of the channel. Although the shoreline is largely armored with rip rap, concrete, and sheetpile, fine-grained sediments are present in pockets in the rip rap and soils are eroding from under the sheetpile in some areas.</p>
Groundwater Seepage	<p>Estimated contribution to channel is approximately 170 g DDT per year, which is not sufficient to account for concentrations currently observed in sediments but continues to impact channel sediments, surface water, and biota.</p>
Wood Pilings	<p>Desorption is not a significant source of DDT to surface water or sediment. Mechanical weathering of the pilings could result in incorporation of DDT-contaminated particles into the sediment bed and potentially into the food web.</p>
Stormwater Outfalls	<p>The municipal storm drain system cannot be fully evaluated as an ongoing source of contamination until DDT-contaminated residual sediments are removed from the system.</p> <p>The storm drain system that serves the upland cap on the Levin Richmond Terminal property is generally functioning as designed. Low levels of pesticides are periodically detected in stormwater samples.</p>
Source Material Outside of the Lauritzen Channel	<p>There were no sources of DDT outside of the Lauritzen Channel that were identified as having potential to act as an outside source to the site.</p>
Areas Not Previously Dredged	<p>Dredging residuals appear to be the primary source of present day contamination in the Lauritzen Channel.</p>

2.2 Sediment Transport Process Summary

The Lauritzen Channel is a low-energy, protected region with tidal velocities that are not likely to result in sediment resuspension. The low energy coupled with sediment input from San Francisco Bay result in a net sediment accumulation in the channel. Ongoing vessel operations in the channel are responsible for localized sediment bed resuspension (up to approximately 10 cm deep). The resuspended sediment is primarily deposited locally within the channel within a few 100 m from where it was resuspended. In

the Tier 2 study, it was found that, on average, approximately 3.5% of resuspended sediment may also be tidally dispersed into the Santa Fe Channel.

The largest amount of sediment accumulation is in the berth on the east side of the Lauritzen Channel. The accumulation is occurring in the deep dredged region where currents are likely the lowest, causing the berth to behave as a sediment trap. Conversely, the west side of the channel, which experiences the highest vessel activity in relatively shallow regions, exhibits generally low accumulation of YBM. Finally, the head of the channel with low energy shallow water and moderate barge activity shows a moderate YBM accumulation and a mix of potential erosion and deposition. The general boundaries of these three regions (northern, eastern, and western) are illustrated in Figure 2.

While vessel resuspension is not a source of DDT to the Lauritzen Channel, it is responsible for the mixing of surface sediment, redistribution within the channel, and loss of DDT to the Santa Fe Channel. The Tier 2 sediment transport analysis showed that vessel activity can lead to sediment suspension by increasing near-bottom velocity. Vessel scour depth averages about 1.4 cm, with a maximum depth of about 10 cm (Sea Engineering, 2014). The wake caused by a vessel also has the potential of mobilizing sediment near or under piers and in shoreline areas throughout the channel as a whole; however, the mass of sediment suspended along the shorelines is very low in comparison to the sediment suspended behind a vessel.

The modeling simulations in the Tier 2 sediment transport analysis indicated that sediment deposition was negligible outside of the Lauritzen Channel one day after resuspension due to vessel activity. The results indicated that on average 96.5% of the sediment was deposited within Lauritzen Channel, resulting in an average loss of 3.5 % of resuspended sediment mass (Sea Engineering, 2014). Table 2 shows the average transport quantities for the vessel operations simulated in the Tier 2 sediment transport analysis. An average of 142 kg of sediment is resuspended during a typical vessel operation in the channel. Assuming one operation per day with a 3.5% loss of sediment to the Santa Fe Channel, approximately 1,800 kg of sediment is lost from the Lauritzen Channel due to vessel operations each year.

Table 2. Transport quantities associated with vessel resuspension.

Vessel Resuspension	
Average Resuspension Mass (kg/event)	142
Average Percent Mass Lost (%/event)	3.5
Yearly Sediment Mass Lost (kg)	1800

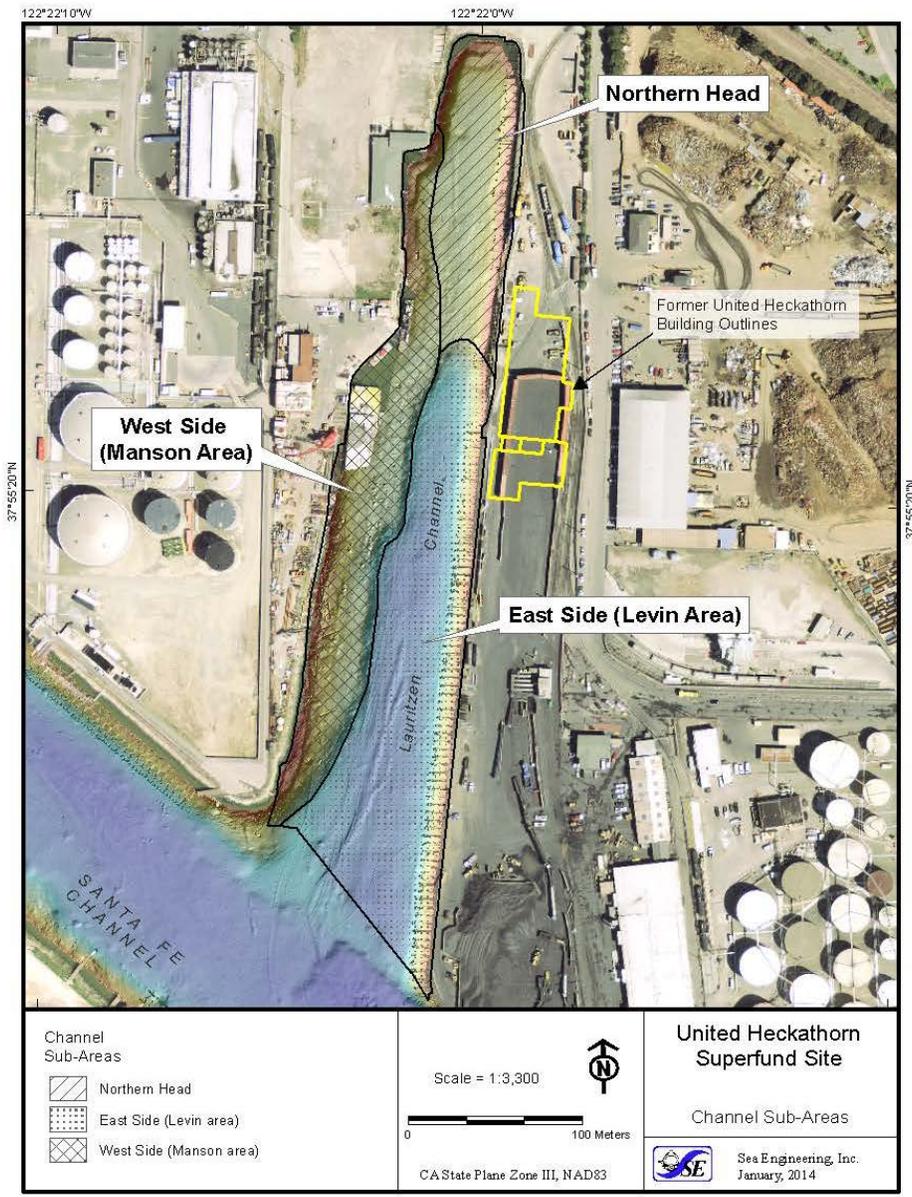


Figure 2. Multibeam bathymetry and delineation of the three characterization areas.

2.3 DDT Degradation

A long-term loss of DDT³ occurs through natural degradation. Natural degradation involves the breakdown of DDT through physical, chemical and biological processes (Horsak, Bedient, Hamilton, & Thomas, 2006). Degradation rates and pathways for DDT vary widely depending on environmental conditions such as pH, availability of various nutrients and oxygen, temperature, and nature of the microbial populations. DDT undergoes aerobic and anaerobic degradation. Under anaerobic conditions, DDT typically degrades to DDD and its breakdown products, whereas DDE and its breakdown products are more typically found in aerobic systems (Walker, Schrieir, & Pucik, 2004; Yu, Lian, Liang, & Zeng, 2011).

The degradation rates of DDT in the Lauritzen Channel sediments are not known and cannot be determined without additional site-specific studies. However, high concentrations of DDT and its metabolites persist in sediment even though the pesticide processing activities at the site ended in 1966. Table 3 summarizes the relative contributions of the 2,4' and 4,4' isomers of DDT, DDD and DDE in surface sediment samples collected in 2013 from the characterization areas shown in Figure 2. Samples from the former plant site were collected along the embankment adjacent to the former United Heckathorn buildings (shown in yellow in Figure 2). These samples have the highest proportions of 4,4'-DDT (approximately 65%), indicating relatively non-degraded DDT deposits. For comparison, technical grade DDT contains 65-80% 4,4'-DDT (Metcalf, 1995). The most abundant metabolite in the northern head and west side of the channel is 4,4'-DDD (approximately 50%), indicating a more degraded contaminant mix, with degradation occurring under mostly anaerobic conditions. Given the limited information on degradation rates and the presence of non-degraded DDT, no loss term for DDT due to degradation is incorporated into the DDT mass balance presented in Section 3.

Table 3. Average Composition of DDT and DDT Metabolites in Lauritzen Channel Surface Sediment

Area	Total DDT (µg/kg)	% 2,4'-DDD	% 2,4'-DDE	% 2,4'-DDT	% 4,4'-DDD	% 4,4'-DDE	% 4,4'-DDT
Former Plant Site	32,401	4%	0.5%	12%	14%	7%	64%
Northern Head ¹	12,873	10%	1%	3%	50%	7%	29%
West Side	7,104	7%	1%	5%	47%	3%	38%
East Side	969	5%	0.2%	6%	19%	5%	65%

¹ Excluding one sample from the northwest corner of the channel with a total DDT concentration of 298,290 µg/kg composed of 90% 4,4'-DDT.

³ Although the present report refers to DDT as the sum of all isomers, Sections 2.3 and 2.4 depart from this convention to discuss the individual isomers relevant to degradation.

2.4 Dissolved-phase DDT transport

The majority of the DDT in the Lauritzen Channel is associated with the particulate phase. However, adverse effects to biota from DDT may be more closely related to freely-dissolved concentrations in sediment porewater and surface water than to concentrations in bulk sediment. The freely-dissolved phase is the fraction of the total DDT load that is most available for exposure and uptake by aquatic organisms. Two passive sampler studies have been performed in the Lauritzen Channel to quantify the diffusive flux of DDT from the sediment bed to the overlying water column and infer dissolved DDT concentrations in porewater and surface water (P. Gschwend & Burgess, 2012; P. M. Gschwend, 2014). The results of the 2013 passive sampler study are provided in Appendix A. The key findings were as follows:

- Porewater and bottom water concentrations of DDT isomers and their degradation products in the Lauritzen Channel were found to be at similar levels in September 2013 as seen previously in March 2012, implying similar bed-to-water column diffusive fluxes.
- The 2013 water column data, inferred using passive samplers, could not be readily fit using a mass balance model that reflects only inputs via bed-to-water column diffusive fluxes and output via tidal flushing from a vertically well-mixed water column. The misfit between the measurements and this simple model suggests an important additional input of total DDT was occurring somewhere mid-channel or further south during the 2013 study. Such a source must be particularly enriched in non-degraded 4,4'-DDT relative to DDD and DDE and therefore cannot be explained by in-channel sediment resuspension.
- Comparison of water column concentrations inferred from passive samplers and mussel tissue suggests that mussels are accumulating DDT from both the seawater and resuspended solids in the water column. The results suggest that additional mussel accumulation is occurring due to resuspension from the sediment bed.

Overall the passive sampler study suggests that there is ongoing diffusion of DDT from the sediment, there is additional uptake of DDT from resuspended sediment, and that there is a source of non-degraded DDT from somewhere between the mid-channel and the mouth of the channel. The embankment adjacent to the former plant site is believed to be the source of the additional DDT. The low ratios of modeled to measured 4,4'-DDT (non-degraded DDT) surface water concentrations (Appendix A) correspond to the sections of the model that are adjacent to the former plant site. Although the mass balance model presented in Appendix A is relatively simple, the calculations are consistent with the observed sediment chemistry trends at the site. The 2013 sediment sampling data show that the embankment sediment adjacent to the former plant site has some of the highest total DDT concentrations in the Lauritzen Channel, and that 4,4'-DDT comprises the majority of the total DDT. The embankment is believed to be the source of the additional 4,4'-DDT seen in the surface water concentrations inferred from the passive samplers. As noted in the source identification study report (CH2M HILL, 2014), the previous removal actions along the embankment did not address sediment below about 0 feet mean lower low water (MLLW) or embankment soils with total DDT concentrations below 100 mg/kg. The dredging remedy extended only to the toe of the slope. Therefore, the high DDT concentrations that persist along the embankment adjacent to the former plant site appear to be

attributable to historical contamination that was not addressed in either the upland or the marine remedial actions.

3. DDT Mass Analysis

Hydrophobic contaminants, such as DDT, are strongly sorbed to sediment; therefore, the mass distribution of the contaminant in the sediment governs transport, both sorbed and dissolved phase. The highest DDT sediment concentrations in the Lauritzen Channel are under the Levin pier and along the shoreline by the former plant site, and at the head of the channel in an area that was apparently undredged during the 1997 remedial actions. Lower concentrations of DDT are present along the west side of the channel, consistent with the thinner YBM layer and higher potential for vessel resuspension in this region. Geophysical and chemical data in the Lauritzen Channel are available from coring efforts conducted in 1999, 2003, 2007, and 2013⁴. Geophysical properties and concentrations of DDT from the sediment core samples can be used to create interpolated distribution maps and enable calculation of the following parameters:

1. YBM thickness
2. Dry bulk density
3. YBM mass
4. DDT concentration and mass

These mass distributions can help elucidate patterns of long term sediment and contaminant fate and transport. The following sections outline the determination of DDT mass in the channel over the time periods for which adequate data are available.

The YBM thickness throughout the Lauritzen Channel was calculated in order to determine the volumes of sediment potentially containing DDT. Values for YBM thickness were determined from data supplied by CH2M HILL. YBM thickness values, determined from coring efforts and corrected for less than 100% core recovery, were manually contoured at 1 foot intervals and data were interpolated within the channel. The volume of YBM was calculated by multiplying total thickness by the area of each interpolated cell. The sediment accumulation results from the YBM core analysis are consistent with the Tier 2 sediment transport analysis. The highest accumulation is in the deep berth next to the Levin Terminal and the upper head of the channel. The western side next to the Manson facility has the lowest sediment accumulation consistent with areas of frequent vessel activity.

The sediment dry bulk density variation through the channel also was determined so that the YBM sediment mass could be determined. Sediment dry bulk density was directly measured for 10 Sedflume cores that were collected in summer 2013 (Sea Engineering, 2014). Bulk density analyses were performed at five depth intervals per core, within the top 30 cm of sediment. A depth-weighted average value was calculated for each of the cores by taking into account interval thickness variations. The mean weighted average of dry bulk density for the 10 Sedflume samples was 0.43 g/cm³. However, due to the

⁴ The 1999/2003 data were combined for analysis because the 2003 cores were intended to fill spatial data gaps in the 1999 core locations. The combined data set is referred to as 2001.

small number of cores and relatively shallow core depths (top 30 cm of sediment), these values could not be relied upon for accurate mass determination.

The CH2M HILL sediment chemistry cores from all previous sampling events penetrated through most or all of the YBM and were more spatially distributed than the Sedflume cores. Dry bulk density values were not directly measured from these chemistry cores, but were calculated using specific gravity and percent moisture data using a technique common for fine sediment (Roberts, Jepsen, Gotthard, & Lick, 1998). The overall weighted average value of dry bulk density determined from the CH2M HILL chemistry cores was 0.90 g/cm³. A bulk density interpolation was developed using isopach surfaces as with the YBM calculations and used in the determination of sediment mass.

The dry mass of YBM sediment for the entire Lauritzen Channel was calculated by multiplying the YBM thickness (cm) by bulk density (g/cm³). The product of area density of YBM (kg/cm²) and area of each interpolated cell resulted in total mass of YBM. The grid cell values were summed and with unit conversions, provide total mass of YBM in kilograms (Table 3). The average sediment accumulation rate from the 2001 to 2013 time period was also calculated in kg/yr (Table 4).

Table 4. Resultant sediment mass and deposition rates determined from the YBM analysis.

Sediment Mass	
Present Sediment Mass (kg)	45,478,880
Sediment Deposition (kg/yr)	2,480,400
Avg. Sediment Density (kg/m ³)	900

Total DDT concentration values from each sediment sampling effort were spatially interpolated over the entire Lauritzen Channel. Total DDT mass was calculated by multiplying the YBM mass (kg) and total DDT concentration (mg/kg) to derive mg/grid cell. The grid cell values were then summed to give total kilograms of DDT. The total DDT mass for the entire channel in 2013 was estimated to be 344 kg. The change in YBM and DDT mass over time is shown in Table 5. The spatial distribution of DDT mass in 2013 is shown in Figure 3.

There are two primary sources of uncertainty in these calculations. The first source is the variation in coring locations between the three time periods. Without collocated cores, uncertainty arises due to the inconsistent sampling of the sediment thickness and DDT concentration patterns in the sediment. The second source is due to the interpolation between the coring locations in each effort. Interpolating across heterogeneous gradients introduces errors in the interpolated surface. While uncertainty arises from each of these sources, it is nonetheless informative to show the channel-wide temporal changes in derived DDT mass (Figure 4). The analysis shows a trend of increasing mass over time. The regression of DDT mass versus time indicates a potential net source of DDT to the sediment of about 5 kg/yr (least squares linear regression slope of 5). Compared with source values from the source identification study (e.g. groundwater contribution of about 170 g/yr, this source is large; however, the value provides an estimate of the magnitude of unquantified ongoing sources for a DDT mass balance in the Lauritzen Channel. These sources include embankment erosion and potential seepage from preferential pathways

along the shoreline (Table 1). Additionally, the 2013 water column study (P. M. Gschwend, 2014) also suggested at least one additional input of DDT was occurring somewhere mid-channel or further south that could contribute to this ongoing source.

Table 5. Mass and volume calculations for the time period of evaluation.

Year	YBM Volume (m³)	YBM Mass (kg)	Total DDT Mass (kg)
2001	17,467	15,731,336	278
2007	29,255	26,319,230	379
2013	50,549	45,478,880	344

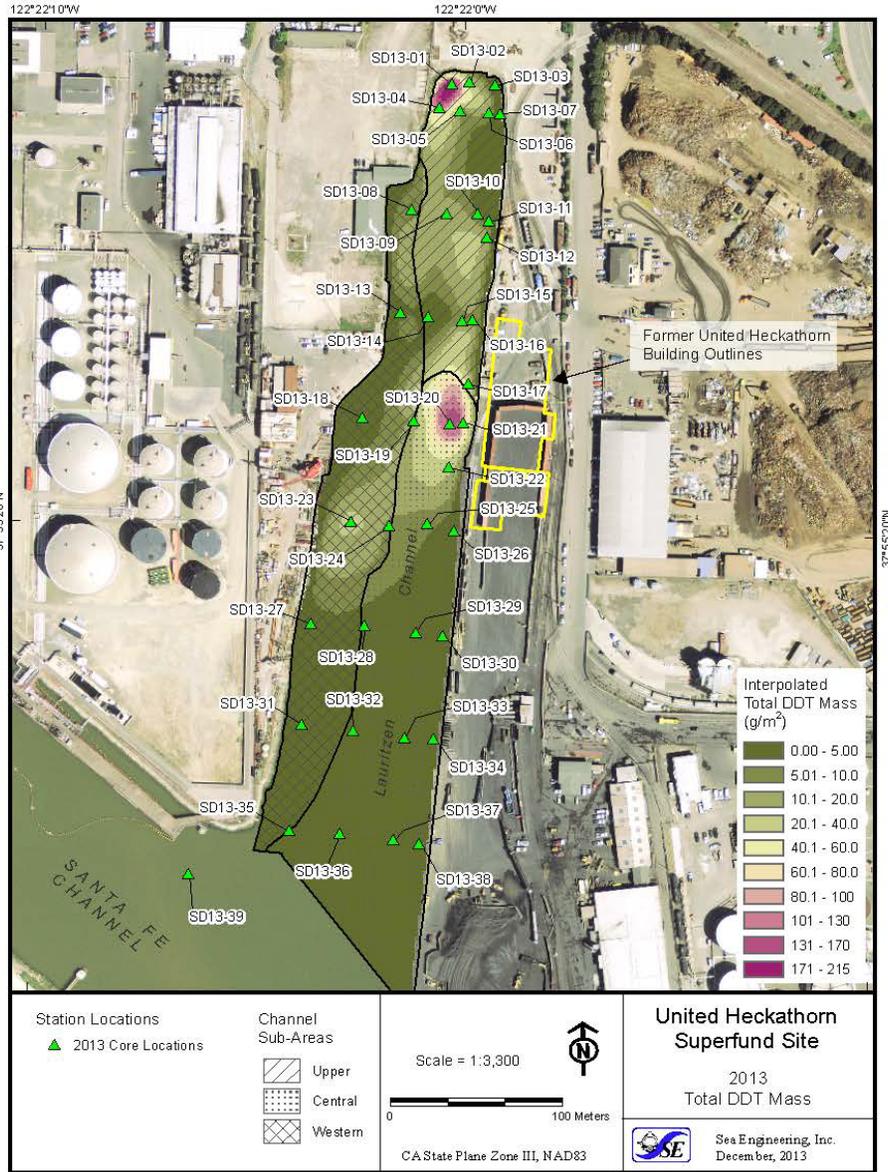


Figure 3. Total DDT mass in the 2013 YBM.

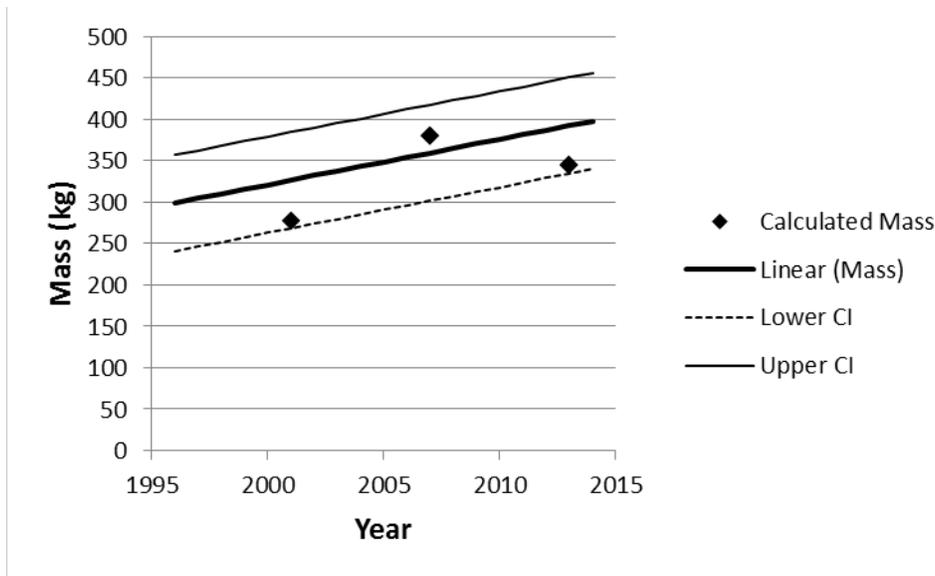


Figure 4. Change in DDT mass over time with least squares linear regression and 95% confidence intervals (CI).

4. DDT Mass Balance

A mass balance for DDT can be developed to account for the external inputs, outputs, and storage of DDT mass in the Lauritzen Channel due to the net effects of the transport processes discussed herein. The balance provides a useful tool for accounting for sources and evaluating the effects of any changes to the system. Essentially the balance can be described by:

$$DDT\ Mass\ Input - DDT\ Mass\ Output = \Delta DDT\ Mass$$

The goal of the DDT mass balance is to summarize the external inputs and outputs of DDT to the system and investigate the net result of these processes.

4.1 Sources and Losses

The source identification, passive sampler studies, and Tier 2 sediment transport studies provide information for the source and loss terms for the DDT mass balance. The source identification study identifies numerous sources of DDT, many of which are relatively small compared to the overall mass of DDT in the system (CH2MHILL, 2014). One notable input is from groundwater, which is an ongoing DDT source of 170 g/yr (0.17 kg/yr). Conservatively this can be assumed as a mass loading to the surface sediment. The sediment depositing in the Channel from San Francisco Bay also has an associated mass of DDT. Using the ambient threshold concentrations in the Bay from the Regional Water Quality Control Board (7 µg/kg) (Gandesbery & Hetzel, 1998), an ongoing source of 0.017 kg/yr was calculated.

One additional class of sources includes the municipal stormwater outfall and other pipe and embankment discharges, for which quantitative loading estimates are not available. While other lines of evidence (e.g. field observations) suggest that these inputs are not significant, they were included as a general category of other sources. Additionally, the 2013 water column study (P. M. Gschwend, 2014) also suggested at least one additional input of DDT was occurring somewhere mid-channel or further

south that could contribute to the channel DDT mass. The inclusion of these unquantified sources is discussed below.

The passive sampler analyses (P. Gschwend & Burgess, 2012; P. M. Gschwend, 2014) estimate the DDT flux from the sediment from a number of locations throughout the system, from the head to the mouth of the channel. By averaging the fluxes together and multiplying by the area of the channel, an estimate of average DDT diffusion from the channel can be made. Table 6 shows the result of these calculations and a diffusion loss of 0.15 kg/yr of DDT.

Table 6. Estimates of DDT loss due to diffusion from the Lauritzen Channel sediment.

DDT Diffusion	
Average Diffusion (ng/m ² /day)	9,647
Area (m ²)	42,142
DDT Diffusion (kg/yr)	0.15

The loss of DDT from the Lauritzen Channel due to vessel resuspension can be determined from the mass loss terms in Section 2.2. By multiplying the mass of sediment loss per year due to vessel resuspension (1,814 kg) by the average DDT concentration in surface sediment in the western region experiencing the loss (7,104 µg/kg), a loss term of 0.013 kg/yr from the channel sediment can be determined. While the resuspension and redistribution of sediment can increase diffusion from the sediment, this loss was assumed to be accounted for in the estimate of present day diffusion loss.

To account for the uncertainty in the inputs of DDT to the Lauritzen Channel sediment (e.g. from the embankments), the change in DDT mass over time (Figure 4) can be used. While the estimate of the change in DDT mass is uncertain, it shows a positive source of DDT to the system. The existence of the source is consistent with the unquantified sources from Table 1 and the 2013 water column study findings (P. M. Gschwend, 2014). The estimated load from the DDT mass analysis in Section 3 was about 5 kg/yr. This ongoing source is over an order of magnitude higher than all other sources and losses combined.

Table 7 presents a summary of all of the sources and sinks included in the mass balance analysis. It is important to note that the yearly magnitude of vessel resuspension loss, diffusive loss, and ground water sources are essentially insignificant when compared with the total mass of DDT remaining in the channel sediments. These values, even with associated uncertainty, support the conclusions in the source identification memo that ongoing sources are small and the majority of the mass of DDT in the channel sediments is from dredging residuals.

Table 7. Mass balance terms for DDT recovery assessment.

DDT Balance Terms	
Calculated 2013 DDT Mass (kg)	344
Calculated 2013 DDT Concentration (ug/kg)	7,564
Vessel Resuspension Loss (kg/yr)	0.013
GW Load (kg/yr)	0.17
Diffusion Loss (ky/yr)	0.15
Deposition Load (kg/yr)	0.017
Other Estimated Load (kg/yr)	5

4.2 Mass Balance Model

To determine the net effect of all of these terms, the mass balance as a function of time can be considered. The change in mass over time in the Lauritzen Channel sediment can be represented as:

$$\frac{dM_{DDT}}{dt} = S_{GW} + S_{dep} + S_{others} - L_{vessels} - L_{diff}$$

where S_{GW} is the groundwater source, S_{dep} is the source due to background DDT deposition from San Francisco Bay, S_{others} is other or unquantified ongoing sources (5 kg/yr), $L_{vessels}$ is the loss of DDT from the channel due to vessels, and L_{diff} is the loss due to diffusion. By integrating the above equation over time, the yearly change in total DDT mass in the Lauritzen Channel YBM can be calculated. Figure 5 presents a conceptual diagram of the yearly sources and losses of DDT mass to the Lauritzen Channel sediment. Figure 6 shows the results of the projected DDT mass as a result of the mass balance. The progression is linear due to the linearly increasing combination of constant source and loss terms.

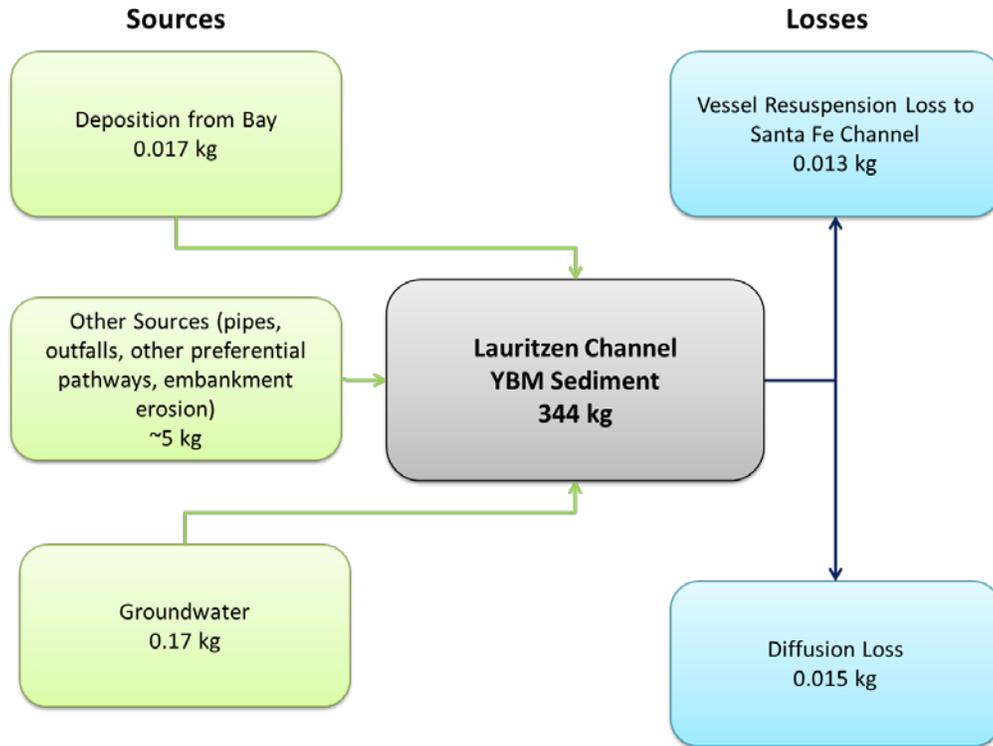


Figure 5. Conceptual diagram of average yearly sources and losses of DDT mass to the Lauritzen Channel sediment.

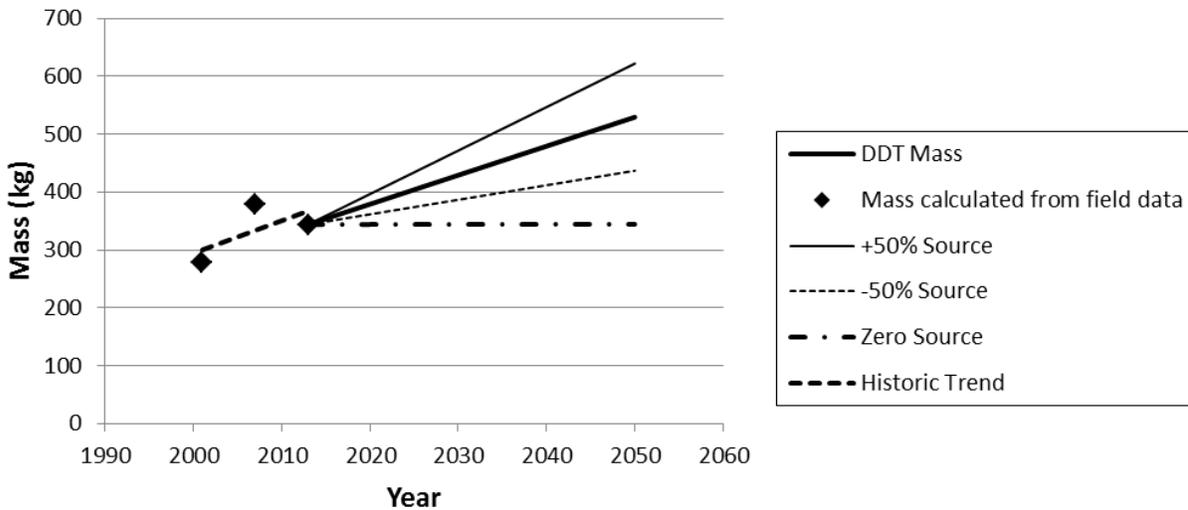


Figure 6. Change in total DDT mass as a result of all sources to and losses from the system. Sensitivity to ongoing source terms is included.

In the mass balance model, the mass of DDT increases primarily due to the other ongoing DDT sources of 5 kg/yr. Since this term is strictly derived from the DDT mass estimates, which have their own uncertainties, a sensitivity analysis was performed around these other ongoing DDT sources. For the sensitivity analysis the magnitude of the source was increased and decreased by 50% and was also set to

zero. As seen in Figure 6, the DDT mass projected for 2050 varies by almost a factor of two due to the +/- 50% change in mass due to the other sources.

As discussed, of primary interest for the FFS is the DDT concentration in sediment. To evaluate the net results of changing DDT mass and concentration from all sediment and DDT sources it was necessary to balance the sediment and DDT mass and then calculate the resulting DDT concentrations. The bulk contaminant concentration (C_{cs}) in terms of mass of DDT (M_{DDT}) divided by sediment mass (M_{sed}) can be expressed as:

$$C_{cs} = \frac{M_{DDT}}{M_{sed}}$$

The DDT mass values in sediment can be divided by the YBM mass to calculate a bulk DDT concentration in the YBM sediment. The sources and losses of sediment mass to the Lauritzen Channel sediment are shown in Figure 7 including upland sources of sediment determined in the Tier 2 investigation (Sea Engineering, 2014). Since these concentrations are bulk averages over the entire YBM they are different than the spatially interpolated concentrations in Section 3, but provide a representative comparison of mass and concentration. Figure 8 presents the computed bulk DDT concentration in the YBM for the Lauritzen Channel. It is important to note that the mass of the YBM also increases during time in these calculations, which dilutes the DDT mass. For all of the source sensitivity cases, the DDT concentrations continue to decrease due to a dilution from clean incoming sediment. The sensitivity analysis demonstrates that even with relatively large variations in the magnitude of the ongoing DDT source, the bulk concentrations of DDT in YBM are dominated by incoming sediment and continue to decrease. However, in all cases, the bulk DDT concentration remains above the sediment remediation goal from the 1994 ROD (USEPA, 1994) of 590 $\mu\text{g}/\text{kg}$ at year 2050.

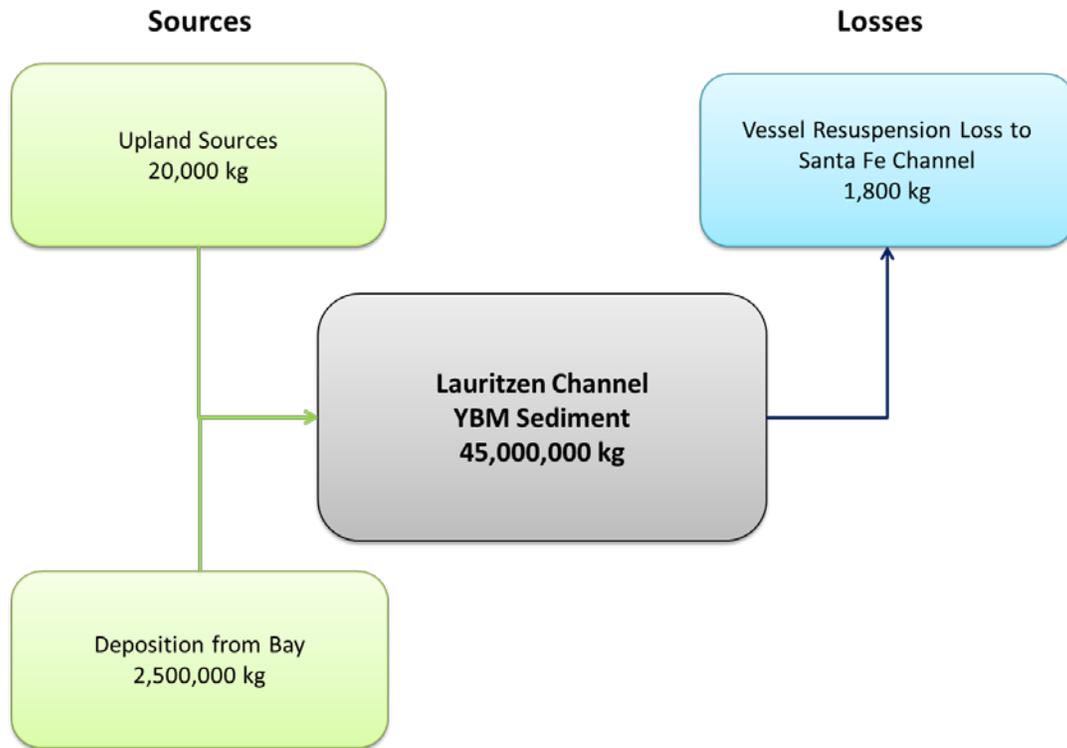


Figure 7. Conceptual diagram of the sources and losses to the Lauritzen Channel sediment.

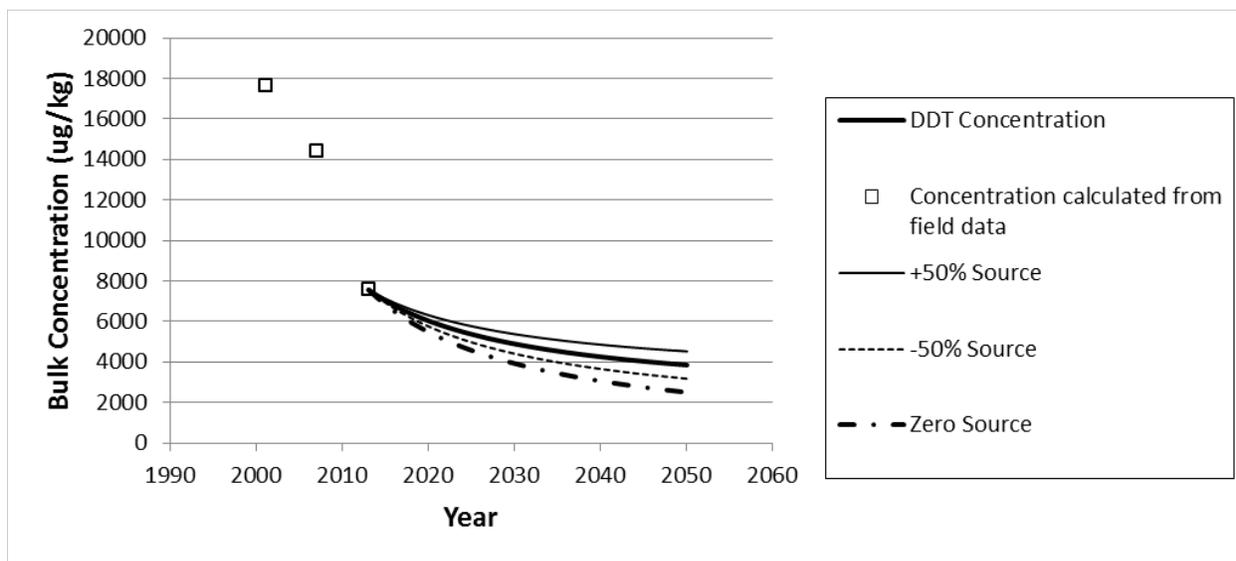


Figure 8. Change in bulk YBM DDT concentration. Sensitivity to the unquantified source terms is included.

5. Summary

This report presents the results of a DDT fate and transport study that was performed for the Lauritzen Channel as part of the FFS. The objectives were to develop a quantitative contaminant fate and transport CSM and DDT mass balance for the Lauritzen Channel based on available analyses and assess trends in DDT mass and concentration in the Channel.

Overall, the Tier 2 sediment transport analysis showed that the Lauritzen Channel is accumulating relatively clean sediment from San Francisco Bay. There are three distinct regions with different sediment transport and accumulation characteristics in the channel. The largest amount of sediment accumulation is in the deep dredged berth on the east side of the Lauritzen Channel. The west side of the channel, which experiences the highest vessel activity in relatively shallow regions, exhibits generally low sediment accumulation. The northern head of the channel has a moderate YBM accumulation and a mixed potential of erosion and deposition. The average DDT concentrations in the YBM sediment are decreasing in the channel.

Several passive sampler studies have been performed in the Lauritzen Channel to quantify the diffusive flux of DDT and infer dissolved DDT concentrations in porewater and surface water (P. Gschwend & Burgess, 2012; P. M. Gschwend, 2014). The results of the 2013 passive sampler study suggest that there is ongoing diffusion of DDT from the sediment, and that at least one important additional input of DDT is occurring mid-channel or further south, most likely along the embankment adjacent to the former plant site. The results also suggest that mussels are accumulating DDT from the water column and resuspended sediments in the water column.

The DDT mass balance model shows that bulk YBM DDT concentrations are projected to decrease, even when accounting for uncertainty in the magnitude of the ongoing sources to the system. The projected bulk YBM DDT concentrations remain over 2,000 $\mu\text{g}/\text{kg}$ in 2050 despite +/-50% variation in DDT mass input. The magnitudes of sources and losses of DDT investigated in the mass balance support the conclusions of the source identification study that ongoing sources are relatively small compared to the DDT mass in channel sediments. The findings lead to the conclusion that dredge residuals are responsible for primary DDT mass in the channel. Even with the uncertainty associated with each line of evidence, the conclusions are well supported by comparison of the order of magnitude of sources, losses, and sedimentation.

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Appendix A.

**Application of Polyethylene (PE) Passive Samplers to Assess DDTs in the
Lauritzen Channel at the United Heckathorn Superfund Site in Richmond
Harbor, San Francisco Bay**

Application of Polyethylene (PE) Passive Samplers to Assess DDTs in the Lauritzen Channel at the United Heckathorn Site in Richmond Harbor, San Francisco Bay

Report to US EPA, Region 9, Attn: Rachelle Thompson

May 27, 2014

Philip M. Gschwend, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge MA 02139

Summary

1. Porewater and bottom water concentrations of DDT isomers and their degradates (herein altogether referred to as DDx) in the Lauritzen Channel were found to be at similar levels in September 2013 as seen previously in March 2012, implying similar sediment bed-to-water column diffusive fluxes.
2. The 2013 water column data, inferred using PE samplers, could not be readily fit using a mass balance model that reflects only inputs via bed-to-water column diffusive fluxes and output via tidal flushing from a vertically well-mixed water column. The misfit between the measurements and this simple model suggests an important additional input of DDx was occurring somewhere mid-channel or further south during Sept 2013. Such a source must be particularly enriched in DDT, as opposed to DDD and DDE; and so episodic resuspension of Channel sediments and release of DDx, while a likely additional mechanism moving DDx into the overlying water, cannot explain the modeling misfit since this source would input DDE, DDD, and DDT at about the same ratios as bed-to-water diffusion.
3. The 2013 water concentration data, inferred using PE passive samplers deployed in the water column, were consistently lower (*ca.* 5x) than levels inferred by assuming that mussel tissues reflect equilibrium with water concentrations. It is noteworthy that DDx measurements using filtered water samples were also much lower than indicated by the mussels. This discrepancy may suggest that mussels were accumulating DDx from both the seawater and resuspended solids in the water column. Perhaps in support of this hypothesis, some of the sediment bed PE samplers were found to be almost completely buried after their month-long deployments (i.e., little of the sampler was in the water column), implying significant disturbance of the sediment bed during September 2013.

Introduction

DDT and its derivatives (herein collectively referred to as DDx) continue to cause human and ecosystem health concerns in the vicinity of Richmond Harbor, California. In order to improve our ability to remediate this situation, we need to identify the continuing source(s) of these contaminants to the surface waters of that system. In 2012, we used passive polyethylene samplers, deployed in both the water column and sediment bed of the Lauritzen Channel, to identify the site sediments with the highest DDx porewater concentrations. These plastic films absorb DDx in proportion to these compounds' availabilities: (a) to move in this system (e.g., from the sediment bed into the overlying water column) and (b) to bioaccumulate in biota living in the area. The following summarizes our findings from our earlier February - March 2012 field deployment campaign.

1. All eight Lauritzen Channel sediment locations exhibited DDx concentration gradients that imply diffusive fluxes from the sediment bed to the overlying waters. A control site located outside the Channel did not show such gradients.
2. Polyethylene samplers indicated similar porewater concentrations of DDx extending at least 30 cm into the sediment at several sites distributed along the length of the channel.
3. Freely dissolved DDx concentrations in the water column, determined using polyethylene samplers, correlated strongly with values inferred from transplanted mussel-tissue concentrations, although the mussel-based water concentrations averaged about 2x the corresponding PE-inferred values.
4. A 3-box model of the DDx concentrations in the Lauritzen Channel water column, reflecting only diffusive fluxes of DDx out of the sediments and tidal flushing to remove these contaminants, indicated that continuing inputs from the undisturbed sediment bed were sufficient at that time to explain the freely dissolved DDE and DDD concentrations in the Channel water column. However, the same model and assumptions under-estimated DDT in the middle and southern portions of the Channel, perhaps suggesting a second DDT source was present in addition to diffusive inputs from the sediment beds.

In light of these findings, certain questions remained. Firstly, we needed to better define the boundaries between sediment areas with high, medium, and low DDx porewater concentrations. Such data would substantially improve our understanding and modelling of the effects of the sediment bed conditions. Further, this result would give us a better tool with which we can evaluate various “what if” remediation scenarios. Secondly, as long term post-remediation monitoring will likely be required for this site, even after it is cleaned up, we need to continue to evaluate the utility of PE sampling in the water column with respect to the question: can we use PE passive sampler observations as surrogates for mussel-based monitoring?

Goals of the 2013 PE Passive Sampling

1. To better delineate the most problematic sediments releasing DDx at the United Heckathorn site, we deployed a second round of PE samplers in the sediments and water column to measure DDx concentrations in the pore waters, bottom waters, and surface waters.
2. To improve our understanding of the fate of DDx at that site, we collaborated with colleagues at CH2M-Hill and Sea Engineering to develop a mass balance model that uses more accurate physical dimensions (e.g., Channel depths) and tidal data to test the hypothesis that diffusive fluxes of DDx from the sediments to the tidally flushed water column of the Lauritzen Channel could explain the loads of DDx in that surface water. Then, to test the accuracy of this simple DDx modeling, we compared model predictions of DDx concentrations in the Lauritzen Channel water column to our independent PE-based measures of dissolved DDx in that water.
3. Finally, to assess the efficacy of using PE samplers in place of mussel-based biomonitoring, we co-deploy PE samplers alongside transplanted mussels and compared the PE-based measures of freely-dissolved DDx concentrations to values obtained using conventional mussel-based monitoring methods.

Methods

PE samplers were prepared as described previously (Gschwend et al. 2012a). Briefly, the PE is solvent cleaned, loaded with performance reference compounds (PRCs), and then mounted in aluminum sheet metal frames for deployment across the sediment-water interface or in aluminum mesh bags for water column sampling.

On September 10 and 11, 2013, working with EPA divers, we deployed polyethylene devices (PEDs) in the sediment bed at 10 stations located in the Lauritzen Channel (Figure 1). These sample locations were chosen to fill in the spatial coverage that had been acquired during our previous efforts in March 2012. At every site, a portion of the sampler was purposefully left sticking up above the sediment bed to enable that portion of the PE strip to sample the bottom water. At one of the locations (09), duplicate samplers were deployed beside each other.

During the same field campaign, water column PE samplers were also deployed (Figure 2). These PE samplers were placed at five sites along the eastern edge of the Lauritzen Channel, at a location to the northwest in the Santa Fe Channel ("floating dock"), at a location in Parr Canal, and at a background site near Ford Point. Many of these water column samplers were located at the same stations where cages of transplanted mussels were deployed.

One month later (October 10, 2013), the EPA divers retrieved all the samplers. That same evening, the samplers were taken to the EPA Region 9 laboratory, cleaned of adhering sediment or biofilms, photographed, and cut out of the aluminum sheet metal sampler frames. Each piece of PE was placed in a VOA vial and labeled for transport back to MIT to begin extraction and analysis on the next day.

Once back at MIT, each sample was processed as described previously (Gschwend et al. 2012b). First, each PE strip was soaked in organic solvent with surrogate (recovery) standards added. The solvent was replaced two more times and the extracts combined in each case. The solvent was blown down and exchanged into hexane. Finally, the hexane extracts were transferred into auto-injector sample vials, injection standards were added, and finally they were analyzed via GCMS. Polyethylene that had not been deployed was analyzed in the same manner to ascertain the initial PRC concentrations. Following analyses, data were corrected for surrogate recoveries. Then measured losses of the PRCs were used to extrapolate measured target DDx loads to equilibrated levels. Finally, these results were converted to corresponding water concentrations by dividing the PE concentrations by each compound's polyethylene-water partition coefficient (K_{pe-w} , Table 1).

compound	log K_{pe-w}	log K_{lip-w}
2,4'-DDE	5.2	5.6
4,4'-DDE	5.5	6.1
2,4'-DDD	5.1	6.0
4,4'-DDD	5.0	5.8
2,4''-DDT	5.7	6.4
4,4'-DDT	5.8	6.6

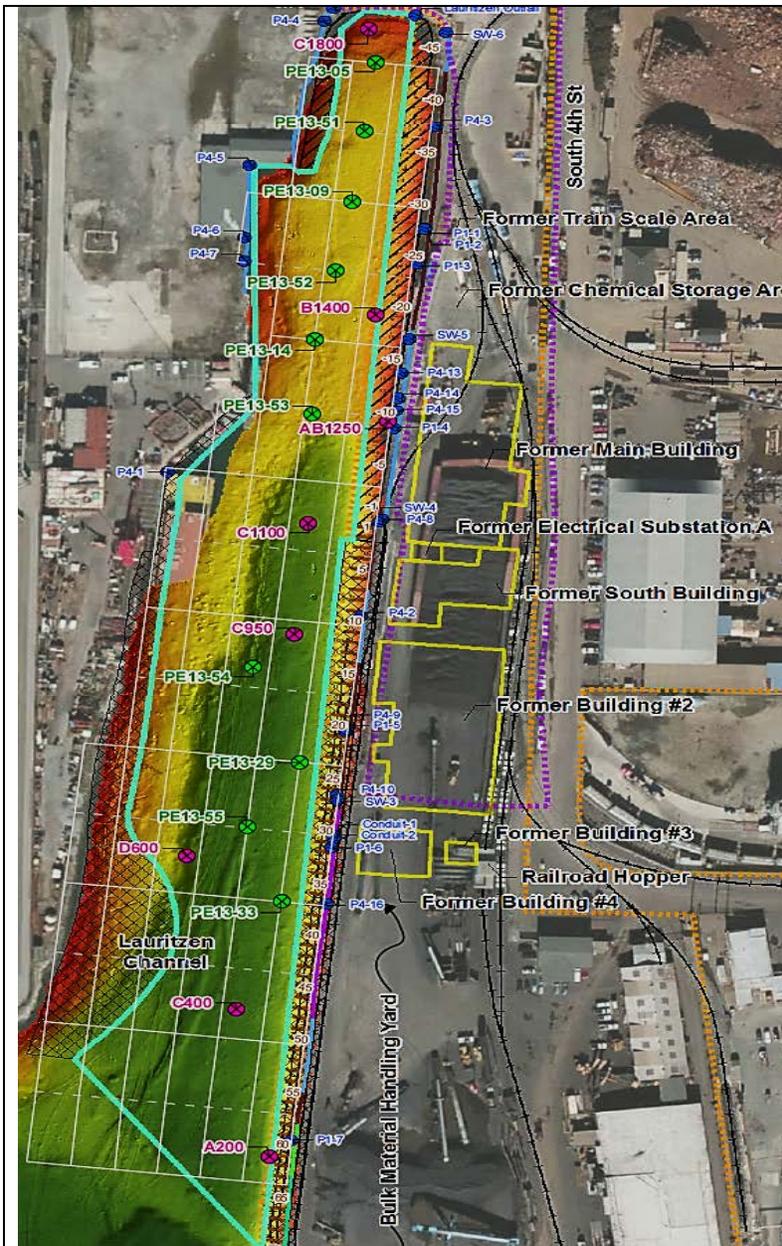


Figure 1. Map of the Lauritzen Channel showing both the 2013 sediment passive sampling sites (in green):

- PE13-05
- PE13-51
- PE13-09 (sampler buried)
- PE13-52 (sampler buried)
- PE13-14
- PE13-53
- PE13-54
- PE13-29
- PE13-55
- PE13-33

& the 2012 stations (in purple):

- C1800,
- B1400
- AB1250
- C1100
- C950
- D600
- C400
- A200.

Results

Porewater and Bottom Water DDX Concentrations

As seen in 2012, stations to the north in the Channel generally had higher porewater concentrations than stations to the south (Figure 3). Also as before, the two DDD isomers were most abundant (see Appendix A for all of the individual DDX concentrations). However, unlike 2012, the 2013 polyethylene sampler data did not always show elevated DDX porewater concentrations in the upper 5 cm of the bed (0-5 cm surface sediment), as compared to the bottom waters (0 to 5 cm bottom water) at all stations (Figure 3). This was particularly true for stations in the southern part of the Channel (stations 54, 29, and 55). Station D600, located near these three stations, previously showed a relatively weak bed-water gradient in 2012.



Figure 2. Stations at which PE passive samplers were deployed in the water column in September 2013 in the Lauritzen Channel: 303.7, 303.3, L02, L01, 303.2, in Parr Channel: 303.6, in the Santa Fe Channel: 303.4, and near Ford Point (not shown).

In light of these concentration data from 2012 and 2013 field campaigns, the Channel may be broken up into four sections based on each section's 4,4'-DDD porewater concentration (Appendix C):

- (1) a southernmost section of 900 ft in which porewater 4,4'-DDD is generally about 10 ng 4,4'-DDD/L,
- (2) a second portion (600 ft) in which porewater is between 10 and 100 ng 4,4'-DDD/L,
- (3) a third short section (200 ft) in which porewater exceeds 100 ng 4,4'-DDD/L, and
- (4) a short (100 ft) northernmost portion in which porewater exceeds 1000 ng 4,4'-DDD/L.

Dividing the Channel up this way, we made initial estimates of the bed-water fluxes for each section assuming a bottom water diffusive boundary layer thickness of 1 mm, consistent with relatively thick layers seen by others in lab studies (Steinberger and Honzo, 1999) and field work (Lorke et al., 2003). In so doing, one finds the northernmost section of the Channel has the largest local fluxes of all the DDx

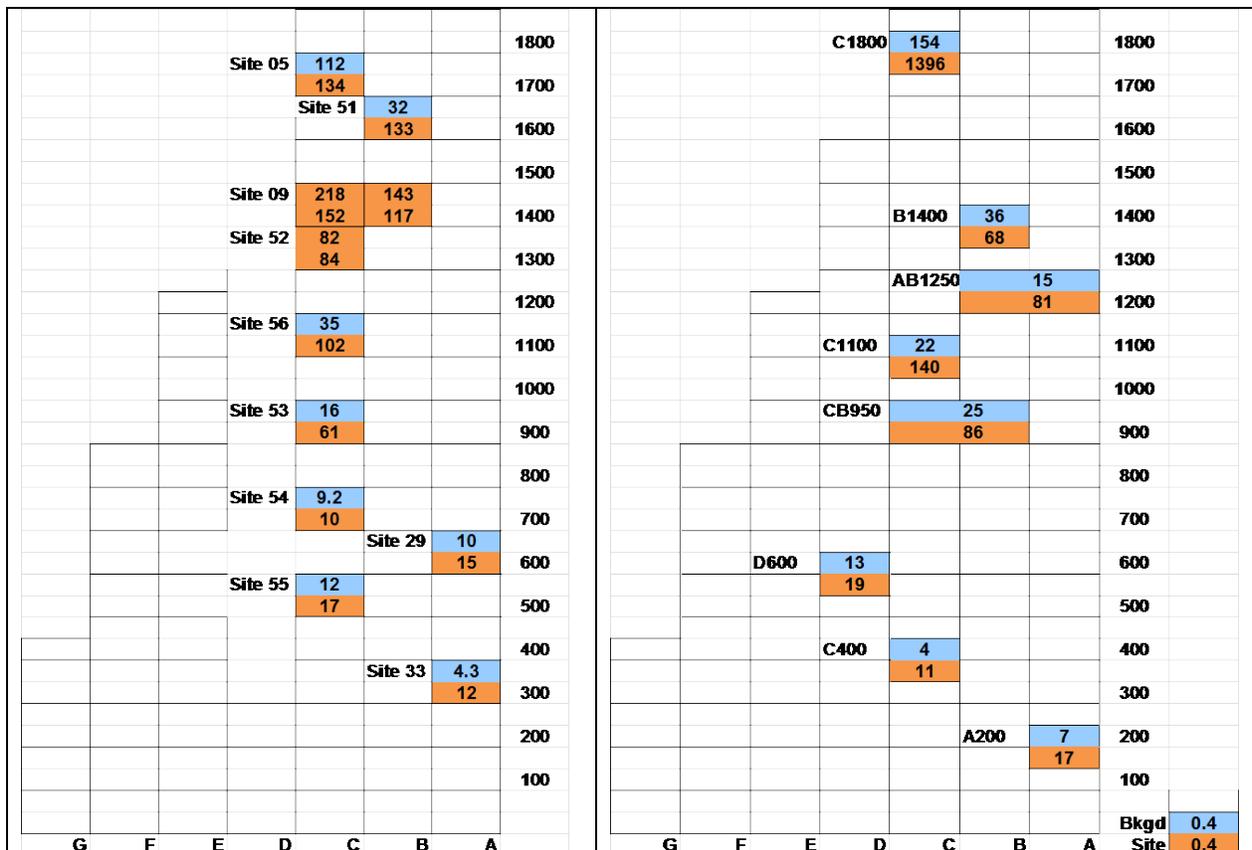


Figure 3. Porewater (brown) and bottom water (blue) concentrations of 4,4'-DDD (ng/L) , the most abundant DDX constituent, deduced using PE passive samplers in the field in September 2013 (left) and March 2012 (right). At sites 09 and 52 in 2013, PE samplers were found to have been fully buried in the sediment when the divers went to retrieve them, suggesting substantial sediment disturbance during their month-long deployment.

(Figure 4). If one multiplies each section's average local flux by the corresponding area of each section, then the greatest input of DDD is still in the northern part of the Channel ("section 4"), but the greatest DDE input is found in both section 4 and halfway down the Channel ("section 2"). Notably, the largest sediment bed-derived input of the parent DDX, DDT, is from section 2 (Figure 4, right panel). In all cases, fluxes into the water column on the order of milligrams/day are implied for each DDX; the absolute values could be higher (perhaps by as much as a factor of 10) if the assumed 1 mm diffusive boundary layer thickness was thinner at any places and times.

Surface Water Concentrations

Polyethylene samplers that were deployed in the upper water column at several sites (Figure 2) showed the freely dissolved DDX were individually present in the Lauritzen Channel water column at levels between 0.1 and 10 ng/L (Figure 5 and Appendix B). This range was also seen on the March 2012 sampling. As also found with the pore waters, the DDD isomers tended to occur at the highest concentrations of all the DDX. This implies that they were transported from sources in which the DDT isomers were reduced to the corresponding DDDs such as anoxic sediment beds.

Mass Balance Modeling of DDx in the Water Column of the Lauritzen Channel

To test the hypothesis that diffusion of DDx out of the sediments into the overlying water column is the main continuing source of those DDx to the Channel's water column, a mass balance model was set up to compare the expected water column concentrations with what was measured. In this model, DDx diffusion from the bed sediments to the overlying water column is the only source of DDx to the Lauritzen Channel water column, and tidal flushing is the only sink from a vertically well mixed water column. Given the dramatic changes in porewater concentrations down the Channel from north to south (Appendix C), the Channel was taken to have four sections or "boxes of water": a northernmost box of about 100 ft length (section 4), a neighboring box of 200 ft length (section 3), and mid-channel box of 600 ft length (section 2), and a southern box of 900 ft length (section 1). With the help of Craig Jones (Sea Engineering), the areas, volumes, and tides moving in and out for these four sections were obtained (Table 2) and used in the model.

	width (m)	length (m)	ave depth (m)	area (m ²)	low tide volume (m ³)	tidal volume (m ³)
section 1 (0-900 ft)	90	274	7.25	24,528	172,737	70,271
section 2 (900-1500 ft)	76	183	5.43	13,890	72,322	31,881
section 3 (1500-1700 ft)	64	61	4.23	3,887	15,548	9,153
section 4 (1700-head)	52	34	2.97	1,761	4,639	2,782

In the first step of the model (Figure 6), the tide is assumed to move a "tidal volume" of water (Table 2) from outside the Channel into the southernmost box (section 1), from the southern box to section 2, and so on. Water outside the Lauritzen Channel is assumed to have concentrations like those at the Floating Dock (303.4) station (Appendix B), although sensitivity analyses on this assumption was also performed (Appendix D). Then DDx are assumed to diffuse from the bed below each box into the overlying water for 6 h (Figure 6). At slack tide, the boxes are assumed to become completely mixed. Outgoing tides reverse the flow, thereby flushing a portion (= tidal volumes shown in Table 2) of each box to the neighboring box to the south. After the tide has gone out, a 6-hour diffusive flux of DDx from the bed below each compartment occurs and the water is assumed to become well-mixed before the sequence repeats itself. Given the volumes and fluxes involved, the water column concentrations no longer changed after about 1 month of simulation time, and so this was taken as the "steady state" condition. It is worth noting that the sediment concentrations were so high that there is insignificant depletion of the sediment DDx load by diffusive losses to the overlying water. Also, the offshore water concentrations were held constant at their initial measured levels. Finally, this model did not operate with temporally changing conditions such as neap and spring tides.

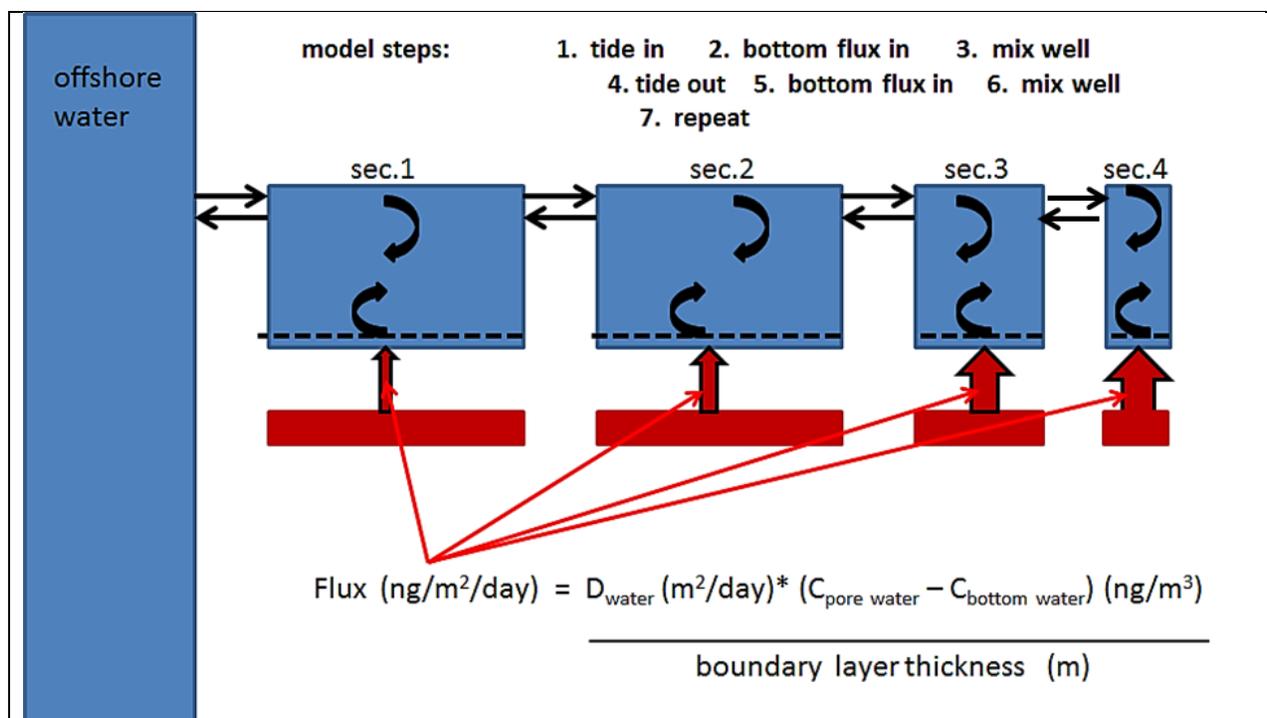


Figure 6. Depiction of mass balance model used to assess hypothesis that DDx diffusion out of sediment bed was primary source of those DDx to overlying water column. Tidal flushing to offshore water was assumed to be the only sink.

With bed-water fluxes (based on the PE data and an assumed 1 mm boundary layer thickness, after Steinberger and Hondzo, 1999; Lorke et al., 2003) and such tidal flushing, steady state water column concentrations were estimated for each section (Table 3). Not surprisingly, the northernmost box is estimated to have the highest DDx concentrations (e.g., 4,4'-DDD at about 24 ng/L), with more southerly boxes having somewhat lower levels. Given the pore water results, it is not surprising that the modeling results would cause us to expect water column DDD will be greater than water column DDE or DDT.

To evaluate the accuracy of this simple mass balance model, we contrasted the model-derived estimates with the PE-inferred truly dissolved concentrations (Table 4). In the "base case" (Table 3 and repeated in Table 4), DDx inputs are assumed to only occur by diffusion out of the sediment bed to the overlying

	4,4'-DDE	4,4'-DDD	4,4'-DDT	total 4,4'-DDx	Table 3. Modelled water column concentrations (ng/L) of three DDx and their sums assuming a 1 mm bottom boundary layer thickness everywhere in the Channel.
section 4	2.1	23.8	0.6	26.5	
section 3	1.3	9.6	0.4	11.3	
section 2	0.9	4.2	0.3	5.5	
section 1	0.8	2.0	0.3	3.1	
Santa Fe Channel (based on 303.4)	0.68	1.1	0.26	2.04	

water through a bottom water boundary thickness of 1 mm everywhere. In this case, ratios of model-based concentrations to measured concentrations (using PE samplers) indicate that the northern sections have too strong of a source and the southern sections have too little input, especially for 4,4'-DDT. We note that this discrepancy is exacerbated if one assumes the water outside the Channel has concentrations like those at Ford Point or an average of Floating Dock and Ford Point (Appendix D). This may mean that diffusive transfer of DDx out of the sediments was the major source of DDx to the overlying seawater in the northern portion of the Channel, but in the south a stronger DDx input must be considered.

One simple adjustment to the model would be to allow the bottom boundary layer thickness to vary along the Channel (Table 4 and Appendix D). In the more sheltered northern sections of the Channel, this thickness might be thicker than in the south. Hence the model was rerun using thicker boundary layer in sections 3 and 4, but still using a thinner layer in sections 1 and 2 (Table 4, middle panel). This approach certainly changes the ratio of modeled-to-measured concentrations in section 3 to be much closer to 1, implying this adjustment may be justified. Yet, this change does not correct the large model vs. measurement discrepancies in sections 1 and 2, especially for DDT.

The low model/measure ratios in sections 1 and 2 imply one of the following: (a) flushing is too strong in such a box model, especially in the southernmost sections (e.g., due to numerical dispersion), (b) the water column is inaccurately represented as well mixed in September 2013, or (c) there is an additional DDx source in this part of the Channel. To begin to test this latter prospect, the bottom boundary layer thicknesses were held at the same values used in the previous case, but now additional inputs of the DDx into only section 1 were allowed (Table 4, bottom panel). In particular, the sediment diffusive fluxes of 0.6 mg 4,4'-DDE/day, 4 mg 4,4'-DDD/day, and 0.2 mg 4,4'-DDT/day in section 1 were increased by factors of 100, 300, and 1000, respectively, to 60 mg 4,4'-DDE/day, 1200 mg 4,4'-DDD/day, and 200 mg 4,4'-DDT/day. In so doing, the model/measure ratios moved much closer to 1 for sections 1 and 2. However, this simultaneously caused the ratios in section 3 to move well above 1, especially for DDT. Note that such an added source must be enriched in DDT relative to DDE and DDD as compared to diffusive inputs from sediments in section 1. Thus additional inputs due to resuspension and desorption of the bed sediments cannot supply such an enrichment in DDT as compared to DDE and DDD.

It seems likely that model adjustments involving boundary layer thicknesses and inclusion of a significant additional source of DDx in the southern portion of the Channel could enable the model to fit the Sept 2013 data. But it is not the point of this mass balance modeling to "fit the data". Rather, this simple modeling is already sufficient to suggest two key outcomes concerning the dominant sources of DDx to the surface water in the Lauritzen Channel. First, as suggested by both the March 2012 and September 2013 data, the sediment bed with the highest porewater concentrations in the northern part of the Channel may well be the most important source of DDx, especially DDE and DDD, in the water column in that part of the Channel. However, the September 2013 data point to an important additional source besides the sediment bed of DDx, especially DDT, into the southern portion of the Channel. In addition

Table 4. Model predicted concentrations (ng/L) and corresponding ratios of modelled/measured (based on PE) found making various modeling assumptions. Ratios are not shown for section 4 because no PE sampler was deployed in the water column of section 4 in the 2013 field campaign. bbl=bottom boundary layer thickness. "Base case" assumes bbl is 1 mm everywhere. "Change bbl" case allows a 1 cm thick bbl in sections 4 and 3, but retains a 1 mm bbl for sections 2 and 1. Finally, "add source" case increases the inputs to section 1 by a factor of 100 for DDE, a factor of 300 for DDD, and a factor of 1000 for DDT.

base case	sec 4, bbl = 0.1 cm	sec 3, bbl = 0.1 cm	sec 2, bbl = 0.1 cm	sec 1, bbl = 0.1 cm
4,4'-DDE	2.1	1.3	0.9	0.8
4,4'-DDD	24	9.6	4.2	2.0
4,4'-DDT	0.6	0.4	0.3	0.3
		model/measure	model/measure	model/measure
4,4'-DDE		2.0	0.2	0.3
4,4'-DDD		1.9	0.2	0.3
4,4'-DDT		1.4	0.04	0.08

change bbl	sec 4, bbl = 1 cm	sec 3, bbl = 1 cm	sec 2, bbl = 0.1 cm	sec 1, bbl = 0.1 cm
4,4'-DDE	0.9	0.9	0.8	0.7
4,4'-DDD	4.3	2.9	2.3	1.5
4,4'-DDT	0.3	0.3	0.3	0.3
		model/measure	model/measure	model/measure
4,4'-DDE		1.4	0.2	0.3
4,4'-DDD		0.6	0.1	0.2
4,4'-DDT		1.1	0.04	0.08

add source	sec 4, bbl = 1 cm	sec 3, bbl = 1 cm	sec 2, bbl = 0.1 cm	sec 1, bbl = 0.1 cm
4,4'-DDE	1.4	1.4	1.3	1.2
4,4'-DDD	15	14	13	11
4,4'-DDT	2.1	2.1	2.1	1.9
		model/measure	model/measure	model/measure
4,4'-DDE		2.2	0.3	0.5
4,4'-DDD		2.7	0.6	1.8
4,4'-DDT		7.4	0.3	0.5

to comparing modeled and measured concentrations, one can contrast the total masses of DDx measured in the Lauritzen Channel assuming the near-surface deployed water column samplers reflect vertically well-mixed concentrations. This calculation implies one must introduce more than 10x more DDT to the southern part of the Channel than is diffusing out of the sediment bed there (factor depends on how close to the mouth of the Channel the input occurs), even assuming a thin diffusive boundary layer of 0.2 mm thickness. (The same calculation for DDE and DDD implies only an additional source about 1x and 3x greater than diffusion for the bed, respectively.) And if the model is inaccurately representing a stratified water column, the high relative concentration of DDT in sampler L01 still suggests a non-sediment bed input of this compound to this surface water.

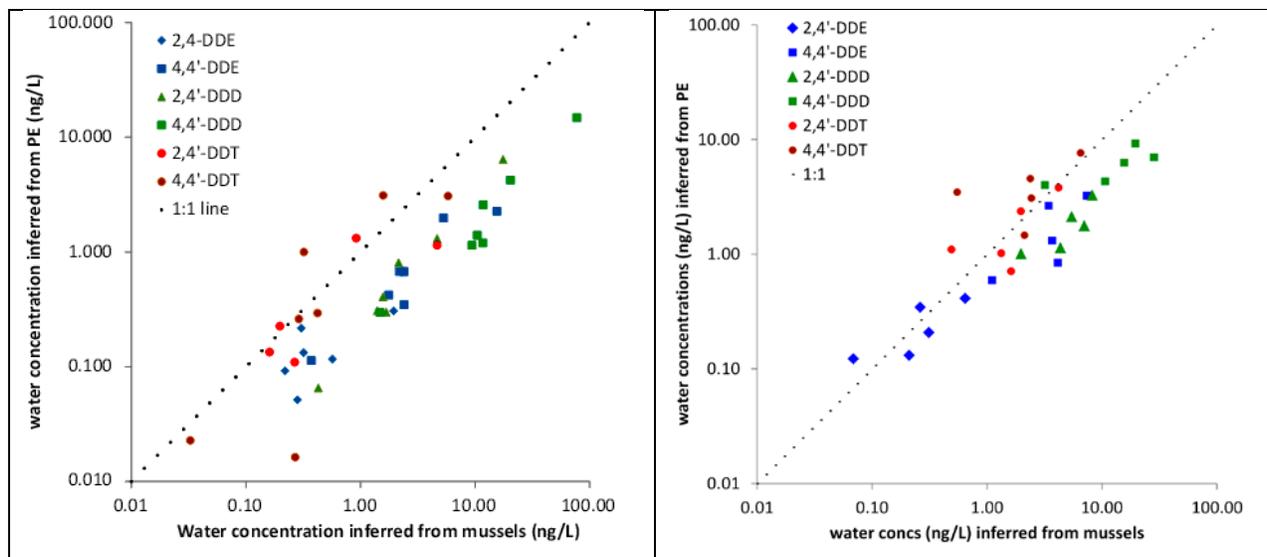


Figure 7. Comparison of water column DDX concentrations (ng/L) inferred from transplanted mussel tissues and from co-deployed PE samplers. (left) Data from September 2013 and (right) from March 2012.

This suggestion is supported by the particularly large discrepancy for DDT, seen in both the 2012 and 2013 data for the southern section, which implies a source of unreacted insecticide nearby. It is also noteworthy that the water column sampler deployed at the mid-Channel site, L02, exhibited the highest DDX concentrations. This sampler had a relatively low DDD-to-DDT ratio (about 2 to 1), especially compared to the water column sampler in the northern part of the Channel (station 303.7 had DDD-to-DDT at about 20 to 1). Finally, this water column sampler at L02 was the only one that did not become covered with a thick biofilm, perhaps implying that the DDX was at toxic at that location.

Potential for Use of PE Samplers as Surrogates for Mussels

Transplanted mussels, co-deployed with the PE samplers, also exhibited DDX levels in their tissues (CH2M-HILL, 2013a). Normalizing these tissue data to the mussels' lipid contents, and then dividing by each DDX's lipid-water partition coefficient (Table 1), allows a second independent estimate of the freely dissolved DDX at the site.

The mussel data suggest the dissolved DDX concentrations ranged from 0.1 to 100 ng/L, with DDD isomers predominating. On average, for the Sept. 2013 field observations, the total DDX based on the mussels was 5x larger than what was inferred from the PE data (Figure 7, left). Only a factor of 2x average offset was seen using the March 2012 data (Figure 7, right). The cause of these higher inferred water concentrations from the mussel data is unknown. It may involve inaccuracies in the K_{lip-w} values used (Table 1), as these values are somewhat uncertain. The values in Table 1 would have to be biased low. But it may also involve uptake of DDX as a result of mussel ingestion of resuspended sediment bed solids. If this is correct, the mussel might "overestimate" the truly dissolved water column concentrations if the resuspended bed particles did not have enough time to equilibrate in the overlying water column. Moreover, the mussel monitoring might be especially sensitive to temporally varying

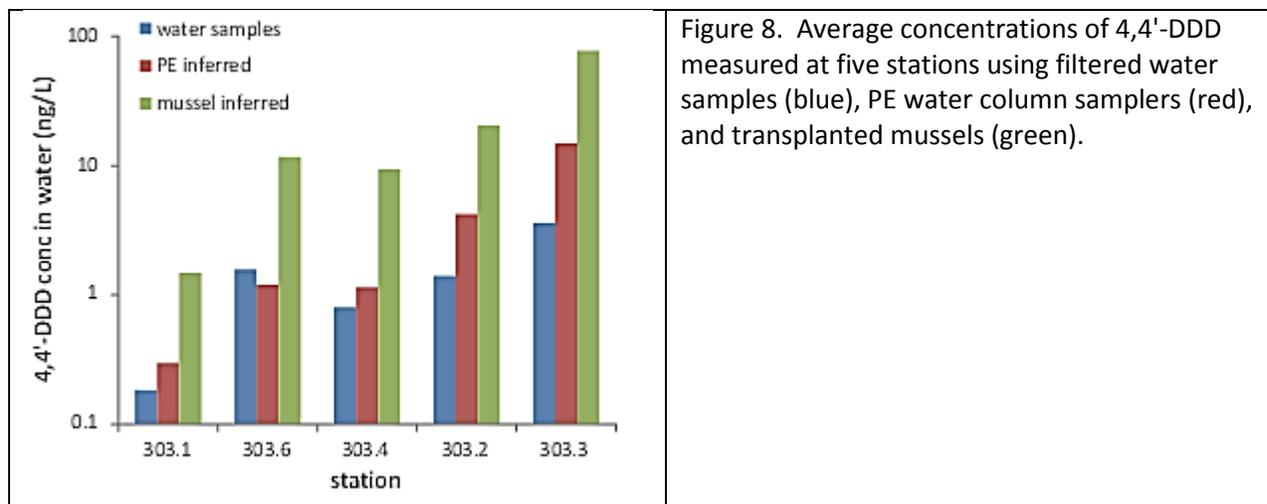


Figure 8. Average concentrations of 4,4'-DDD measured at five stations using filtered water samples (blue), PE water column samplers (red), and transplanted mussels (green).

intensities of sediment resuspension arising from changing tugboat activities in the Channel. We note that the samplers deployed at stations PE13-09 and PE13-52 in September 2013 had been substantially buried during that field campaign, perhaps also indicating the occurrence and importance of sediment disturbance during that period.

We also note that the average DDX concentrations in filtered water samples collected in September 2013 (CH2M_HILL, 2013b) were about half of the values inferred from PE and more than 10x less than mussel-inferred results (Figure 8). This trend was also seen in our first year of passive sampling at this Superfund site (September 2009) in which we reported: "Ratios of mussel-inferred concentrations to filtered water concentrations were 20 ± 13 (and mussel to SPME ratios were 11 ± 7). This may indicate that the mussels exhibit body burdens reflecting uptake from the frequently resuspended bed solids, and the DDT/DDD/DDE in those solids were not equilibrated with the water column." Burgess et al. (2010) have previously suggested this type of effect may explain the relationship between concentrations accumulated in transplanted mussels and passive samplers (e.g., PE) for PCBs at the New Bedford Harbor Superfund site.

Nonetheless, the PE data correlated well with the mussel data in both 2012 and 2013. Hence, if the goal is to monitor a site's changes over time, this result supports the suggestion that PE samplers can be substituted for mussels in future monitoring efforts. However, if one wants to accurately quantify the truly dissolved concentrations of hydrophobic substances like DDX, then we need a better understanding of the biases associated with (a) using single time point data from filtered water samples versus (b) time averaging with PE samplers and (c) inferences from filter feeding organisms like mussels as well as improved certainty with respect to their lipid-water partition coefficients.

Conclusions

The September 2013 data substantially filled in the map of DDX porewater concentrations in the Lauritzen Channel sediments. As a result, it appears that the heavily contaminated northern section of

the Channel has a much smaller footprint than thought based on only our 2012 data. This decreases its importance by about a factor of 2 as compared to the 2012 mapping. But since the most prominent DDX, 4,4'-DDD has about 90% of its flux into the water occurring in this very northernmost section, even more careful delineation of its extent may be merited.

The mass balance modeling supports the contention that diffusion out of the sediments is the dominant DDX source to the overlying water in the northern sections (sections 3 and 4). However, the same modeling points to at least one "missing source" of a DDT-rich DDX mixture somewhere mid-channel (section 2) or further south (section 1).

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Appendix A. Bottom water (blue) and pore water (brown) concentrations (ng/L) found using PE samplers at 10 sites in the Lauritzen Channel. Site 9 shows results for two samplers deployed beside each other.

	Site 51		Site 05	
	H2O 0-7cm	SED 0-5cm	H2O 0-1cm	SED 0-5cm
	piling -38		piling -43	
2,4'-DDE	0.32	1.2	1.1	1.3
4,4'-DDE	2.5	9.7	8.4	7.5
2,4'-DDD	8.4	38	33	38
4,4'-DDD	32	133	112	134
2,4'-DDT	0.29	< 0.1	< 0.1	< 0.2
4,4'-DDT	0.53	0.27	0.14	< 0.2
Σ DDx	44	182	155	181

	Site 52		Site 09-1		Site 09-2	
	SED 0-5cm	SED 5-10cm	SED 0-5cm	SED 5-10cm	SED 0-5cm	SED 5-10cm
	piling -24		piling -30			
2,4'-DDE	1.0	0.9	1.9	1.2	1.3	0.9
4,4'-DDE	7.8	9.3	27	11	23	7.8
2,4'-DDD	29	25	67	51	41	49
4,4'-DDD	82	84	218	152	143	117
2,4'-DDT	0.4	< 0.1	< 0.1	1.0	< 0.1	< 0.1
4,4'-DDT	< 0.1	0.20	2.02	< 0.1	< 0.1	< 0.1
Σ DDx	120	119	316	216	207	175

	Site 54		Site 53		Site 56	
	H2O 0-5cm	SED 0-5cm	H2O 0-5cm	SED 0-5cm	H2O 0-5cm	SED 0-5cm
	piling 15		piling -10		piling -16	
2,4'-DDE	0.20	0.18	0.27	0.74	0.49	1.3
4,4'-DDE	2.1	1.9	2.4	6.6	4.7	11
2,4'-DDD	2.9	3.3	5.0	21	10	32
4,4'-DDD	9.2	10	16	61	35	102
2,4'-DDT	0.13	0.16	< 0.1	< 0.1	0.65	< 0.1
4,4'-DDT	0.34	0.28	1.1	1.7	2.0	0.46
Σ DDx	15	15	25	92	53	147

	Site 33		Site 55		Site 29	
	H2O 0-5cm	SED 0-5cm	H2O 0-5cm	SED 0-5cm	H2O 0-5cm	SED 0-5cm
	piling 37		piling 30		piling 24	
2,4'-DDE	0.16	0.34	0.16	0.28	0.46	0.37
4,4'-DDE	1.3	3.6	1.6	2.0	3.2	3.1
2,4'-DDD	1.3	3.5	3.5	5.0	3.2	4.9
4,4'-DDD	4.3	12	12.1	17	10	15
2,4'-DDT	0.12	0.06	0.02	0.03	0.33	0.02
4,4'-DDT	0.31	0.5	0.13	0.06	0.5	0.19
Σ DDx	7.5	20	17	24	17	24

Appendix B. Water column concentrations (ng/L) found using PE samplers. Note: the sampler for site **L02** was found underneath the pier; this sampler was the only one to show no signs of biological colonization.

	Ford Pier 303.1	Parr Canal 303.6	floating dock 303.4	Floating dock 303.4 - Deep	outer channel 303.2	outer channel 303.2 - Deep
2,4'-DDE	< 0.003	0.22	0.09	0.05	0.12	0.13
4,4'-DDE	0.11	0.42	0.68	0.35	2.0	0.67
2,4'-DDD	0.07	0.30	0.31	0.41	1.3	0.81
4,4'-DDD	0.30	1.2	1.1	1.4	4.2	2.6
2,4'-DDT	< 0.001	0.11	0.13	< 0.001	1.3	0.23
4,4'-DDT	0.02	0.29	0.26	0.02	3.1	1.00
sum DDx	0.5	2.5	2.6	2.2	12.1	5.4

	inside channel L01	mid channel L02*	inner channel 303.3	inner channel 303.3 - Dupl.	hot spot 303.7
2,4'-DDE	0.19	0.13	0.31	0.32	0.10
4,4'-DDE	2.7	6.6	2.3	2.3	0.62
2,4'-DDD	2.8	9.6	6.4	5.5	2.1
4,4'-DDD	8.5	35	15	13	5.1
2,4'-DDT	1.6	8.4	1.1	2.1	0.15
4,4'-DDT	4.2	9.6	3.1	7.2	0.29
sum DDx	20.0	69.7	28.0	30.5	8.3

Appendix D. Modeling sensitivity studies to input parameters: (a) bottom boundary layer thickness held constant over the whole Channel, (b) bottom boundary layer thickness allowed to vary with position in the Channel, and (c) Santa Fe Channel concentrations set equal to those found at station 303.4 (Floating Dock), at station 303.1 (Ford Point), or an average of these two. Improvements in fits can be judged by looking at how close the ratios of model/measure approach the value, 1.0.

Sensitivity of Lauritzen Channel water column concentrations of specific 4,4' DDx isomers to the choice of bottom boundary layer thicknesses where all taken to be same.

	Modelled water		Modelled water		Modelled water		Modelled water	
	concs (pg/L)	Model/Measure						
	2 mm bbl		1 mm bbl		0.5 mm bbl		0.1 mm bbl	
4,4'-DDE	1399		2117		3555		15054	
4,4'-DDD	12466		23832		46564		228419	
4,4'-DDT	414		568		875		3337	
4,4'-DDE	969	1.56	1259	2.03	1838	2.96	6469	10.43
4,4'-DDD	5356	1.05	9611	1.88	18122	3.55	86211	16.90
4,4'-DDT	330	1.14	399	1.38	539	1.86	1654	5.70
4,4'-DDE	806	0.18	931	0.21	1182	0.27	3191	0.72
4,4'-DDD	2644	0.11	4187	0.17	7274	0.30	31972	1.33
4,4'-DDT	299	0.04	338	0.04	415	0.05	1036	0.12
4,4'-DDE	720	0.31	759	0.32	838	0.36	1472	0.63
4,4'-DDD	1574	0.25	2047	0.32	2995	0.47	10575	1.67
4,4'-DDT	272	0.07	285	0.08	310	0.08	509	0.14

Sensitivity of Lauritzen Channel water column concentrations of specific 4,4' DDx isomers to the choice of bottom boundary layer thicknesses where allowed to vary from north to south.

Measured water concs (pg/L)			Modelled water		Modelled water	
using PE (PRC corr'd) in fall 2013			concs (pg/L)	Model/Measure	concs (pg/L)	Model/Measure
			2, 1, 0.5, 0.1 mm bbls		10, 10, 0.1, 0.1 mm bbls	
section 4						
4,4'-DDE			1660		2155	
4,4'-DDD			14708		13771	
4,4'-DDT			516		872	
section 3						
4,4'-DDE	620		1229	1.98	2069	3.34
4,4'-DDD	5100		7564	1.48	12349	2.42
4,4'-DDT	290		432	1.49	855	2.95
section 2						
4,4'-DDE	6600	2300	1040	0.23	1953	0.44
4,4'-DDD	35000	13000	4519	0.19	11151	0.46
4,4'-DDT	9600	7200	396	0.05	812	0.10
section 1						
4,4'-DDE	2000	2700	821	0.35	1109	0.47
4,4'-DDD	4200	8500	2366	0.37	4467	0.70
4,4'-DDT	3100	4200	313	0.09	444	0.12

Sensitivity of Lauritzen Channel water column concentrations of specific 4,4' DDx isomers to assumed Santa Fe Channel concentrations: (a) using Floating Dock values, (b) using Ford Point values, (c) using average of Floating Dock and Ford Point values.

	Modelled water		Modelled water		Modelled water	
	concs (pg/L)	Model/Measure	concs (pg/L)	Model/Measure	concs (pg/L)	Model/Measure
	Floating Dock, 1 mm bbls		Ford Point, 1 mm bbls		ave Floating and Ford, 1 mm bbls	
4,4'-DDE	2117		1547		1832	
4,4'-DDD	23831		23031		23432	
4,4'-DDT	568		328		448	
4,4'-DDE	1259	2.03	689	1.11	974	1.57
4,4'-DDD	9610	1.88	8810	1.73	9211	1.81
4,4'-DDT	399	1.38	159	0.55	279	0.96
4,4'-DDE	931	0.21	361	0.08	646	0.15
4,4'-DDD	4186	0.17	3386	0.14	3787	0.16
4,4'-DDT	338	0.04	98	0.01	218	0.03
4,4'-DDE	759	0.32	189	0.08	474	0.20
4,4'-DDD	2047	0.32	1247	0.20	1647	0.26
4,4'-DDT	285	0.08	45	0.01	165	0.05