Concluding comments on the peer review of "Draft Bioaccumulation Model Report Greater Los Angeles and Long Beach Harbor Waters"

Jon Arnot ARC Arnot Research and Consulting Inc. December 27, 2016

Overview

This report summarizes my peer review of the document "Draft Bioaccumulation Model Report Greater Los Angeles and Long Beach Harbor Waters" (August 2016) prepared by Anchor QEA, LLC. My role was to conduct an independent review of the draft report and provide comments. I did not review the food web bioaccumulation model code and calculations; only the materials presented in the draft report and discussed with the authors throughout the review process including WebEx meetings (9/28; 10/26) and a meeting in Long Beach (12/8).

There have been productive discussions on the TMDL project and the bioaccumulation model report on the WebEx teleconferences and during the in person meeting in Long Beach. My review comments sent to the bioaccumulation report authors via AMEC Foster Wheeler on November 24, 2016 are presented as an appendix to this report. This appendix also includes the response to those comments provided by Anchor QEA representatives (received 12/6). I trust these revisions will be carried out as described in the responses in the appendix and as discussed at the Long Beach meeting (see meeting minutes provided elsewhere). I have not been asked to review the final revised report. In addition to providing a technical review of the model report, I have also provided some over-arching comments on the TMDL project as summarized below and in the appendix.

Based on the response to comments and the planned revisions discussed during the Long Beach meeting, the proposed bioaccumulation modelling report is considered sufficient to satisfy the current project objectives.

Final summary comments

The fate and bioaccumulation models used in this study are sensitive to calculations that describe and quantify chemical partitioning between the water phase and organic compartments such as sediment (i.e., fate calculations) and lipids (i.e., in the bioaccumulation calculations). The octanol-water partition coefficient (K_{OW}) is commonly used as a surrogate to quantify the chemical partitioning between the water and biota for neutral hydrophobic organic chemicals like PCBs and DDX. This physical-chemical property is a common bioaccumulation model input parameter and is a key determinant of PCB and DDX bioaccumulation in aquatic organisms [1-7]. Typical measured Biota-Sediment Accumulation Factors (BSAFs) and Bioaccumulation Factors (BAFs) for a range of PCB congeners show a non-linear relationship with K_{OW} , e.g., [4, 5, 7, 8]. K_{OW} , or the closely related property, the organic carbon-water partition coefficient (K_{OC}), are commonly used as input parameters for aquatic

fate model calculations as a surrogate for partitioning between aqueous and organic phases including particulates and dissolved organic carbon and bottom sediments [3, 9, 10].

There are 209 PCB congeners exhibiting approximately a 5,000-fold range of K_{OW} values (log K_{OW} range ~ 4.5 to 8.2 [11]). One of the major comments discussed in the appendix and at the in person meeting is the concern of using a "single Kow" value to represent the fate and bioaccumulation modelling for a mixture of PCBs with wide-ranging partitioning and degradation properties. Additionally, the calibration and model performance evaluations against measured data use total PCBs, where the predicted PCB values are based on a "single K_{OW} ", i.e., log $K_{OW} \sim 6.9$. Thus, possible errors outside of this relatively narrow K_{OW} range may exist and propagate into model interpretation and remediation (management) strategies. Congener-specific fate and bioaccumulation processes are expected to influence details of possible remediation strategies. It is difficult to ascertain the possible errors in congenerspecific PCB bioaccumulation that may occur in the currently linked fate and bioaccumulation model calculations. I encourage the project to consider using congener-specific data and model simulations in future model development (calibration), evaluation (performance) and application (remediation strategies). The bioaccumulation report should consider a case study to examine the uncertainties and errors that may result using the current assumptions in the model parameterization (i.e., using a single K_{ow} for total PCBs), calibration and evaluation.

The issue of using a "single K_{OW} " for DDX is not as much of a concern because the range of K_{OW} values for the different DDX chemicals is not very large; however, differences in biotransformation and possibly biodegradation rates between the different DDX chemicals are recognized [7].

The appendix (comment 44) includes a series of "back of the envelope" calculations to highlight the role of chemical exposure and bioaccumulation as a result of bioconcentration from the water only. The main point of these simpler calculations is to illustrate that the body burdens of PCBs and DDX in the fish are a result of sources in the water and the sediment. The emerging tools and models in this project can be used to more explicitly examine and quantify the relative flux of chemicals in the fish from the water and the sediment and source contributions. Congener-specific fate and bioaccumulation simulations may be particularly useful at that time.

Collectively, the two aforementioned comments seek to strengthen and improve the current linked modelling approach by more completely considering the unique fate and bioaccumulation of the individual chemicals in multi-media environments (multiple sources, water and sediment interaction and multiple exposure routes to organisms) to foster confidence in proposed remediation strategies for the system.

References

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- 9. Mackay, D.; Paterson, S.; Joy, M., Application of Fugacity Models to the Estimation of Chemical-Distribution and Persistence in the Environment. *ACS Symp. Ser.* 1983, *225*, 175-196.
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- 11. Hawker, D. W.; Connell, D. W., Octanol-Water Partition Coefficients of Polychlorinated Biphenyl Congeners. *Environ. Sci. Technol.* 1988, *22*, (4), 382-387.

Appendix:

See Below

	COMPENTS ON						
	HARBOR IOXICS IMDL PEEK KEVIEW						
			MODEL REPORT REVIEW CO	OMMENTS			
Corr	ments by [.] Io	n Arnot	Responses by:				
con	intents by: 50	in i ninot	Anchor QEA, LLC, and Everest on behalf of Port of Long Beach and	Port of Los Angeles			
Page Section			Comments	Responses			
1	General		Thank you for initial response to comments and for addressing these				
			additional comments provided below. These suggestions and				
			comments seek to provide clarifications and improve the report.				
2	7	1 st para	Change "Aqueous update" to "Aqueous uptake"	We will fix the typo.			
3	7	Last	Figure 2-1 indicates plankton are a part of the food web model, but	We will add a footnote to indicate that the model relies on			
		para	there are no plankton in the food web model.	water column particulate concentrations to represent			
				phytoplankton.			
4	8		Accumulation in invertebrates: Since the same BSAF is assumed for	Agreed. We will add a statement to clarify that the			
			each chemical (e.g., SUM PCBs and SUM DDX), and for all	accumulation in invertebrates is represented in the model			
			benthic invertebrates there should be a statement clarifying that all	as the same mix of trophic levels.			
			benthic invertebrates are assumed to be at the same trophic level.				
			Likewise, since the same AF is assumed for each chemical (e.g.,				
			SUM PCBs and SUM DDX), and for all water column invertebrates				
			there should be a statement clarifying that all water column				
			invertebrates are assumed to be at the same trophic level.				
5	8	Last	smaller fish that in turn accumulate from the water <i>and diet</i> .	We will make the suggested edit.			
		para					

	COMMENTS ON				
	HARBOR TOXICS TMDL PEER REVIEW				
			MODEL REPORT REVIEW CO	OMMENTS	
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Com	ments by: J	on Arnot	Responses by: Anchor OFA LLC and Everest on behalf of Port of Long Beach and	Port of Los Angeles	
	Page	Section	Comments	Responses	
6	8-11	2.1.2	Initial comments on the fish model formulation were sent	Thank you for the comment. We are on the same page; the	
			previously "Depuration Rate" (Eq'n 7). A response to those	report will be modified as suggested (but no additional	
			comments provided some clarification into the undocumented	simulations will be performed concerning this issue).	
			assumptions in the report (e.g., 1 g-blood = 1 mL water); however,		
			there is a need to revise the report. To avoid confusion, there is a		
			need to (i) provide consistent reporting of units, (ii) clearly state		
			assumptions, and (iii) clarify terminology. The rate constant for		
			respiratory uptake (Ku) is L/g(w)/d in Eq'n 2 on page 9, but		
			apparently $cm^3/g(w)/d$ in Eq'n 3 on page 10 and then switches back		
			to $L/g(w)/d$ in Eq'n 6 on page 11. Many details in the response to		
			the initial comments on Equation 7 are unnecessary. Conceptually,		
			and as described throughout Section 2 and in Equation 2 of the		
			report, the fish bioaccumulation model treats the fish as 1		
			compartment. The chemical is at equilibrium within the fish		
			compartment, i.e., "well-mixed box assumption"; blood and lipid		
			are at equilibrium. Therefore the model does not need to, and		
			cannot, explicitly consider the transfer of chemical from exposure		
			water to blood and blood to storage lipid, the model simply		
			quantifies chemical exchange between the water and the whole fish.		
			There is uptake into the single fish compartment from the water and		
			from food. For example, uptake from water is a product of the		
			uptake rate constant (Ku; L-water/g-fish(w)/d)) and the water		
			concentration (c; µg/L-water).		

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6	Cont'd		The loss depuration (excretion) rate from the single fish		
			compartment to the water is a product of the depuration rate		
			constant (Kdep; d^{-1}) and the concentration in the fish (v; $\mu g/g$ -		
			fish(w)). The current model is derived from Thomann and Connolly		
			(1984), which does not explicitly describe the excretion rate		
			equation (however, mentions it as a function of the uptake rate		
			constant and fish-water partitioning). As more explicitly described		
			in Thomann (1989):		
			$Kdep = Ku / K_{OW}$		
			where K _{OW} is a surrogate for lipid (fish) and exposure water		
			partitioning, i.e., $K_{LW} \cong K_{OW}$. In the 1989 equation Ku is expressed		
			on a lipid weight basis, rather than a wet weight basis, whereas the		
			TMDL model report is wet weight. However, the main point as		
			described by Thomann 1989 is "Mechanistically this equation		
			implies that the same mechanisms that hinder or enhance transport		
			into the organism are operative in the transport of lipid pools across		
			lipoprotein membranes and into the excretory systems." Because the		
			current report formulates uptake on a wet weight basis, rather than a		
			lipid weight basis, the denominator in the depuration rate equation		
			needs to consider the partitioning of the chemical between the		
			exposure water and the whole body (wet weight) compartment i e		
			$f_{Water} + K_L w f_{Linid}$. Because $K_L w$ (Kow) is so large for PCBs the last		
			term is a simpler first approximation		
			term is a simpler mist approximation.		

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6	Tage	Section	The source of confusion on this tonic lies in the use of the "linid	Responses	
0	Cont d		head partition acefficient" rather than the linid water partition		
			blood partition coefficient, rather than the hpid-water partition		
			Coefficient, for which octanol is the assumed suffogate for lipid.		
			the same as shamical dissolved in water. A significant volume		
			fraction of fish blood is water (0.82), but blood is comprised of		
			then constituents including red blood cells proteins linearesteins		
			other constituents including red blood cells, proteins, inpoproteins,		
			etc. Notably lipid volume fractions in blood are on the order of the shout 0.005 on shout $1/10^{th}$ the sub-la hady lipid fraction if 0.05		
			about 0.005 of about $1/10^{44}$ the whole body lipid fraction if ~0.05,		
			1.e., $K_{LB} \cong 0.1 K_{LW}$. The authors need to stop referring to blood as		
			water, particularly if they are using K_{OW} and assuming blood =		
			water. The statement "dissolved in blood" is not accurately		
			reflective of the surrogate partition coefficient (i.e., octanol-		
			WATER) because (i) the actual fraction of PCB in blood that is		
			dissolved in the pure water phase is on the order $\sim 10^{-5}$ to 10^{-6} and		
			(ii) the underlying mechanistic principle of the 1-compartment		
			model – partitioning between the whole fish and the exposure water.		
			One simple solution to this issue is to change, the "fBlood in the		
			fish" parameter to "fWater in the fish" and "K _{LB} " to "K _{LW} " (lipid-		
			water). Then the use of K _{OW} as a surrogate is appropriate. The		
			difference (error) in the calculations between the actual fraction of		
			blood (~0.03) and the fraction of water in the fish (~0.75) is		
			insignificant because the value for the partition coefficient is so		
			large $> 10^6$. Not worth updating any calculations.		

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7	12		What is the value for the activity multiplier?	The value for the activity multiplier is 2. We will add the values of the activity multiplier and coefficients that determine the respiration rate for each species in the			
0	10			revised report.			
8	12	6.2.2	Isn't fp = fd - fl instead of fp = fl - fd?	Y ou are correct; we will correct the text.			
9	16	8.3.2	"PV shelf exposure concentrations were based on <i>measured</i> data." (?)	We will make the suggested clarifying edit.			
10	Text and tables	Section 3.2.1; Tables 3-2 and 3-3	Ensure that sum of the proportions of days in different zones = 1, this is not always the case, perhaps due to rounding. If due to rounding mention this to avoid confusion.	We will clarify the text to indicate rounding affects the proportions in Tables 3-2 and 3-3.			
11	30	Bullet points	Clarify: "If all were non-detect" Does this mean that there were no detects for all PCB congeners? Does this mean that there were no detects for all DDX?	For a particular sample, yes.			
12	30	Bullet points	Please clarify in the report what is meant be duplicate results were averaged with parent sample results.	Field duplicates were collected for approximately 5% of samples from each field program; for these samples, total PCB and total DDX concentrations represent an average of the duplicate and parent sample concentrations.			
13	30	Bullet points	Please clarify in the report what is meant by excluding Aroclor results	Total PCB concentrations based on congener analysis were included, while the total PCB concentrations based on Aroclor measurements were excluded, for samples with both congener and Aroclor results.			
14	30	3 rd para	Why arithmetic averages? Were they normally distributed?? Or arithmetic averages of the log values? Please clarify in the report.	There was insufficient data available outside of the Harbor to compute spatially weighted averages.			

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15	31	1 st para and Figures 3-10 and 3-11	"Recent rain events" are discussed as a possible explanation for overprediction of the water column concentrations in certain zones. The overprediction of water concentrations and underprediction of sediment concentrations in Consolidated Slip <i>may</i> reflect slight parameterization error in the WRAP model.	The WRAP model was calibrated to the SPME data location during the deployment periods, while the figure represents an average of the model results for the entire fish movement zone over the simulation period. The water column figures are used to demonstrate that model and data are in same range but it is a bit of an apple and oranges comparison. Sediment PCB and DDX concentrations based on measured data were set as initial conditions for the WRAP model. During the calibration period, changes in sediment concentrations were minor. Therefore, differences between model and data do not reflect model dynamics, but rather setting of initial conditions. The differences between the model and data averaged shown in Figures 3- 10 and 3-11 may reflect differences in organic carbon normalization; the spatial-averages of the data were based on OC-normalized sediment concentrations while the WRAP model used spatial-averages of the dry-weight sediment concentrations. These differences are within a factor of 2 and are evaluated in the sediment bed concentration sensitivity.		
16	32	Bullet points	"surfperchesopportunistic feeding on benthos"	Surfperch opportunistic feeding on benthos was represented as 10% of their diet.		

COMMENTS ON HARBOR TOXICS TMDL PEER REVIEW MODEL REPORT REVIEW COMMENTS

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	Page Section		Comments	Responses
17	33	3.2.4.2	Arnot and Gobas 2004 should be Gobas and Arnot 2010	We will make the correction.
18	34	3.2.4.4	Were water column particulates sampled at the same location as the	Yes, with the exception of Inner LB, water column and
			bivalves? Were the water column particulates and bivalves sampled	bivalve sampling locations were collocated. The bivalves
			over the course of the year or at a particular season? Given what is	were collected during a single collection in October, and
			known about temporal variability in water concentrations and	the water column data were collected over the months of
			particulate concentrations, what are possible implications of	December and February. The SPME data show that water
			selected and applied sample dates?	column concentrations integrated over the month did not
				vary between December and February (see Figure 8.16
				from WRAP model report); thus, it is expected that the
				average exposure in October would be similar.
19	35	1 st para	Please include the range of accumulation factors from the Morrison	Water column accumulation factors based on water
			and Lamoureux studies. A congener-specific analysis here may	column invertebrates and water column particulate data
			provide insights for apparent discrepancies, i.e., potential errors in	from the Hudson River ranged between 0.5 and 10
			AFs as a function of Kow.	(Lamoureux et al. 2011). The Morrison reference was
				incorrect and will be removed from the text.
20	35	1 st para	Discussion on comparison of accumulation factors and BSAFs is	We will revise the text so that accumulation factors and
			presented before a presentation of the BSAFs. Present then BSAFs,	BSAFs are presented prior to discussion of them.
			then the comparison to the water column factors.	

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21	35		Non-lipid organic matter, i.e., protein, can be a relatively significant	Lipid contents of invertebrates ranged between 0.6 and		
			phase for hydrophobic chemical partitioning/sorption, particularly	2%; we will revise the accumulation factors and BSAF		
			when the lipid contents in a compartment are low, i.e., ~<2%. What	tables to include invertebrate lipid contents. Given that		
			are the lipid and protein contents of the invertebrates?	future changes in invertebrate body composition are		
				unknown and will not be incorporated into the model,		
				incorporation of protein would likely have very little effect		
				on the relationship between sediment and wet-weight-		
				based concentrations, which is what is needed for the		
				model.		
22	35	2 nd para	Were the surface sediments and benthic invertebrate samples co-	Yes, benthic and surface sediment samples were		
			located? If so, maybe mention this fact.	paired; we will make this clarification in the report.		
23	35	Near	USEPA 1699, "1996"?	This is correct as is. USEPA Method 1699 is the method		
		bottom		for evaluating pesticides including DDTs in water, soil,		
				sediment, and tissue using high-resolution GC/MS		
				techniques. We will add "Method" for clarity. The method		
				was published in 2007. We can also add a reference		
				(https://www.epa.gov/sites/production/files/2015-		
				10/documents/method_1699_2007.pdf).		
24	36	Тор	"were used for where available" – please clarify.	We will clarify that DDX BSAFs based on the three		
			Do these statements also mean that a BSAF of 0.56 was used for	reanalyzed samples were used. Yes, DDX BSAFs of 0.56		
			DDX throughout the modelling? Confusing. Please clarify in the	were used in the modeling instead of low results from low		
			rerport.	resolution data; we will clarify the text.		
25	36	3.2.5.5	Good!			

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26	37	3.3	Is it possible to move this section earlier? We are back talking about	Thank you for the comment. We will revise the text to			
			details of the model and I found myself flipping back to the	include the bioenergetics discussion at the beginning of			
			beginning of the report (Section 2), to follow the discussion. Maybe	Chapter 3 (but after the food web introduction) and			
			this section could go at the start of Section 3? Also note, not all of	separate the mass transfer discussion.			
			the discussion on this section relates to bioenergetics, i.e., mass				
			transfer.				
27	39	3.3.3	Maybe mention if the fillet are skin on or skin off here. I see it is	We will identify the type of fillets in this section in the			
			mentioned as a footnote in one of the Tables.	revised report.			
28	40	3.3.4	See major comments on Kow and model formulation. Kow does not	" K_{ow} " values were calculated as means of the K_{ow} values			
			change for each species and FMZ. Blood does not equal water.	for each congener, weighted by the concentration of that			
			How were the Kow values adjusted (footnote 9)?	congener in the fish. We will change reference to the term			
				used to describe partition between fish and water to a K_{fw} :			
				fish-water partition coefficient. The Kow values used to			
				calculate K_{fw} values were used as reported in (Hawker and			
				Connell 1988 and De Bruijn et al. 1989 or for 2 4'-DDE, 2			
				4'-DDD and 2 4'-DDT, estimated with the cLogP model);			
				the footnote makes reference to the most updated estimates			
				for these values.			
29	40	Footnote	What are the measured congener compositions? Are they the same	The measured congener compositions of the fish are the			
		10	in water, sediment and different biota? Please see major comment	distribution of congener concentrations measured in the			
			below.	2014 data. These distributions are similar to the sediment			
				composition. The composition in water contains a higher			
				proportion of lower molecular weight congeners for PCBs,			
				as would be expected.			

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30		Table 3-	Why are the ratios different for lipid (10) and PCBs/DDX (15) for	For white croaker, the average whole body to fillet ratios	
		2	halibut but not for croaker (all 4)?	calculated from the paired offal fillet samples collected in	
				the Ports' 2014 food web study were 4 for both lipids and	
				total PCBs, and 2 for total DDX. However, the lipid and	
				contaminant ratios for halibut calculated from this study	
				were very different for lipids and contaminants (30, 19,	
				and 6, for lipids, total PCB and total DDX, respectively).	
				The ratios for lipids and total PCB seemed high, so for the	
				contaminants, we calculated a ratio from a log-log	
				regression of the individual PCB and DDX congeners that	
				were detected, resulting in a ratio of 15. We have revised	
				our approach to use the same ratio of 15 for lipid.	
31		Table 5-	For the WCAFs – are the upper and lower bound values switched?	The values in Table 5-12 were not switched; the lower-	
		2		bound water column accumulation factors are combined	
				with the upper-bound BSAFs to produce an upper-bound	
				sediment contribution.	

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32		Figure 3-17	The model growth rate for halibut does not seem to be a very good fit to the measured data. Since the growth rate is largely determining the total elimination rate (and half-life), is this error/uncertainty appropriately addressed? Please clarify in the report.	The California halibut collected during the Ports' 2014 food web study were primarily juveniles (5-year-olds and younger), so there are only a few older fish. Thus, we relied on the more extensive data sets from the referenced studies to use as the growth rate. A slower (and faster) growth rate was included as a sensitivity (Figure 5-3). As shown in Figure 5-5, halibut tissue concentrations are not sensitive to these alternative growth rates. This result demonstrates that for the halibut, growth dilution is less important than elimination.		
33	General		Initial comments on " Modeling Mixtures " were sent and a response to those comments provided some clarification into the rationale for the model simulations for total PCBs and DDX. The fate and transport and bioaccumulation of these chemicals are a function of their unique chemical properties, i.e., partition coefficients and degradation rate constants are chemical specific. For example, at a fixed temperature, the K _{OWS} for PCBs span almost 4 orders of magnitude. Bioaccumulation factors in fish for different PCB congeners can also span a few orders of magnitude (Arnot and Gobas, 2006). The environmental fate (intermedia transport and biodegradation) is also a function of the unique congener and chemical-specific properties, e.g., DDT degrades to DDE. The toxicity of these chemicals is also chemical-specific. Furthermore, loading rates to the system are chemical specific; chemicals are not entering the system as total PCBs and total DDX. The current	 The primary concerns associated with modeling a mixture are whether the key properties of the mixture can be realistically represented and whether the composition of the mixture is likely to vary significantly over time or space. First, representation of the key properties: The K_{fw} values used in the model are means of the values for the individual congeners; thus, we are representing the actual congener composition of the LA/LB Harbor fish. 		

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	approach essentially models a single chemical with a single chemical property, i.e., K _{OW} , rather than each chemical individually. Cumulative exposure to the mixtures is highly relevant and appropriate, i.e., using SUM PCBs and SUM DDX; however, a more explicit treatment of the individual chemicals is recommended. Total exposures and TMDLs can be determined for the total PCBs and total DDX by summation of the concentrations determined for the individual congeners (e.g., Gobas and Arnot, 2010).	 Second, variation in composition of the mixtures: The 2014 high resolution data show fairly consistent PCB and DDX composition in sediments and fish. The PCB composition in NOAA mussel watch data are consistent over time. Finally: The TMDL is based on total PCB and total DDX, so this is the appropriate metric. Historical data used to develop input parameters and for model-data comparison are primarily Aroclor-based, so development of a congenerbased suite of models would have prevented us from using a significant amount of data. 	

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33	Cont'd		The current approach loses important information on the fate and			
			bioaccumulation (exposure) of the chemicals. I recognize this is a			
			"project-wide" subject matter (i.e., the numerical targets are set for			
			total PCBs (a mixture) and DDX (a mixture)) and this comment is			
			not strictly an issue with the bioaccumulation model report;			
			however, given the current state of the science the report should			
			provide more rationale (support) for modelling total PCBs and total			
			DDX as "single chemicals" and include some discussion on			
			possible implications on the assumptions. Please provide some			
			(additional) support in the report to justify the current modelling			
			approach that uses total concentrations, rather than an explicit			
			simulation for the individual chemicals. Perhaps the material			
			provided in response to the initial major comments can be used to			
			show congener profiles in various media to support the assumptions			
			made when using a "single K_{OW} for all PCB congeners" and a			
			"single K _{OW} for all DDX"?			

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34	Table 3-8		Please clarify in the report what this means "calculated from solid- phase microextraction data from the Low Detection Limit Water Column Study (Event 1 and Event 2 in 2014) using site-specific partition coefficients."	The solid-phase micro-extraction (SPME) freely dissolved concentration (C _{diss}) data were used to estimate water column particulate concentrations (C _{POC}) through the following equation: WC Particulate [µg/kg OC] = C _{diss} [µg/L]*K _{POC} [L/kg OC] The particulate organic carbon (POC) data were collected via grab samples that were collected at the beginning of the SPME deployment, from the same locations. Organic carbon partition coefficients (K _{POC}) were calculated from the particulate phases of paired high volume samples (C _{part}) that were also collected through the Low Detection Limit Water Column Study, and the freely dissolved concentrations measured from the SPME data: $K_{POC} = \frac{C_{part} \left[\frac{\mu g}{kgdry}\right]}{POC} \left[\frac{kg0C}{kgdry}\right]$		

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35	Table 3-8		The invertebrate measurements for mussels and oysters are from	The data for bivalves used to compute the water column			
			2002 to 2014. The water particulate concentrations "were calculated	accumulation factors are from 2014 for all stations, with			
			from solid-phase microextraction data from the Low Detection	the exception of a few additional samples from 2002 to			
			Limit Water Column Study (Event 1 and Event 2 in 2014) using	2010 from Zone 1; this was done to increase sample size.			
			site-specific partition coefficients." Please clarify in the report why				
			this was done.	SPME data are the only water column data available for			
				both sampling events and all stations in the Harbor. Given			
				these data provide only freely dissolved concentrations,			
				particulate concentrations needed to be estimated.			
36 Table 3-8 For water column particulate accumulation factors: Can the nature			For water column particulate accumulation factors: Can the nature	Yes, the particulate concentrations are a surrogate for			
	and		of the particulates be clarified? Are they phytoplankton? Are they	phytoplankton.			
elsewhere zooplankton? Other?							

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37	General		Initial comments on "Calibration" were sent and a response to	We will include model results before and after migration			
			those comments provided some clarification. It would be good to	adjustments, as well as using alternate versions of the			
			include those clarifications in the final report. To summarize the	BSAF and water column accumulation factors using the			
			concerns: The food web model is calibrated using 5 different	same site-specific data but based on different calculations			
			parameters to the relatively limited measured data. It appears as if	(i.e., Harbor-wide BSAF values).			
			the WRAP model is also calibrated. Calibrating the models in this				
			manner increases the statistical fit of the models to the measured				
			data ("model calculations are within a factor of 2 of measured data				
			in many cases"); however, model errors become difficult to				
			understand. Over-fitting models reduces the transparency of the				
			model and its calculations and may limit the forecasting (predictive)				
			capacity of the model.				
			To help convey the degree to which the model results are changed				
			as a result of the calibrations (greater transparency), it is				
			recommended that the model performance results against the				
			measured data before calibration also be shown in the final report.				

								
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37	Table 3-		Although not explicitly stated in the report, the methods also seem	Please see the response to comment 28. K_{fw} (formerly				
	13 and		to fit Kow for each fish, zone and mixture, see Table 3-13. I am	known as K _{ow} in the report) values were not fit, but were				
elsewhere			confused on this topic. Could the authors please explain how a	calculated from site data. As shown in Table 3-13, these				
			physical-chemical property changes from fish-to-fish and from	values are very similar across species and fish movement				
			zone-to-zone? There can be temperature and salinity affects, but this	zones.				
			does not seem to be the issue here. Changing the physical-chemical	These values were not used as calibration parameters				
			property for each fish and zone is also a "calibration". Do the	These values were not used as canoration parameters.				
			authors really mean there are measured water-fish partition					
			coefficients used as input in the model? Or water-fish lipid partition					
			coefficients? If the authors choose to maintain the calibration of					
			Kow in their methods, this calibration should be included in the list					
			of calibrated parameters. If the parameter in question is not really					
			Kow, then please clarify what this parameter is and how it is being					
			used.					
38	38 42		States that the "primary parameters adjusted during calibration were	These were the only parameters varied during calibration.				
			accumulation at the base of the food web (i.e., BSAFs), fish diets,	We will make this clarification in the text.				
			and the white croaker and California halibut migration patterns."					
			Were there other "secondary parameters adjusted"?					

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39	General		Due to the heterogeneity of the sediment contamination	Comment noted.			
			concentrations, the issue of fish migration is a crucial source of				
			uncertainty relating exposure concentrations with fish tissue				
			concentrations and possible exposure to fish consumers (humans,				
			birds, marine mammals). Tracking fish movements is a challenge				
			and there have been significant and impressive efforts				
			summarized in the report to address this uncertainty, i.e., there				
			are 13 of about 40 written pages devoted to describing the research				
			efforts to address fish migration in the report (Section 3.2.1). Please				
			ensure that this challenge and uncertainty is clearly communicated				
			when discussing the report and the overall project.				
40			It is not clear how fish migration is actually treated in the food web	Migration in the model is accomplished by "migrating" the			
			model calculations. Are ingestion rates based on a proportion of	fish to fish movement zones for the average proportion of			
			time in each zone and the subsequent relative ingestion of	time the subpopulations spend in each zone based on the			
			invertebrates in that specific zone? Are there differences in the	fish tracking data. In other words, the fish subpopulations			
			water concentrations between the zones? Is that difference included	are exposed to the water, sediment, and prey			
			based on "proportion of time"? Please clarify in the final report.	concentrations for each of the movement zones for the			
				proportion of time (days of a year) they are there			
				according to the fish tracking studies.			
4.1							
41	General		The uncertainty analysis is difficult to understand. Please try to	I he revised report will include a full description of the			
			clarify the objectives and approach in the revised report.	Uncertainty analysis included in our presentation from			
				October 28, rather than the limited approach described in			
				the draft report.			

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42	General		This comment is for the TMDL project, not just the food web	Data are not available within the Harbor to define the				
			modelling report. The sediment is a target for remediation. The	gradient in PCB and DDX concentrations within the top 16				
			modelling and decision-making are highly dependent on the	cm (or deeper) if it exists. Gradients seen within the				
			sediment concentration data. There is significant heterogeneity in	regions, but outside the Harbor, are not relevant because				
			the sediment concentrations across the region. The models seem to	the Harbor is such a well-mixed system (see				
			assume that the "active" and bioaccessible sediment compartment is	geochronology profiles).				
			a depth of 16 cm. An average concentration is being calculated for					
			each sample and the average concentration is a function of the	We used the best available data set to represent the spatial				
			volume. For example, if the sediments are more contaminated at the	variability of PCB and DDX concentrations within the				
			surface (e.g., 0-5 cm) then they are at the bottom (e.g., 12-16 cm) of	Harbor without significant bias. While this data-set may				
			the sample, then the average concentration over the 16 cm will be not capture isolated gradients in very limited un					
			lower than the top layer. Are the contaminants homogeneously	deposition areas, it has been determined to be accurate on				
			distributed throughout a sediment depth of 16 cm? Can more	a Harbor-wide basis by state agencies and local peer				
			supportive evidence be provided for the concentrations throughout	reviewers.				
t			the sediment column? Any additional evidence to support the 16 cm					
			sediment depth for the calculation of the BSAFs and for the	For most areas of the Harbor, it is unlikely that there is a				
			subsequent calculation of the worm concentrations would be	significant gradient in contamination with increasing depth				
			valuable.	for several reasons:				
				• Most of the Inner Harbor area and some of the				
				Outer Harbor area has been dredged (one or more				
				times) or filled at some point over the last 10 to 30				
				years. See Dredge and Fill maps in presentation.				
				• In addition, this is a very active harbor; it				
				represents the largest Port complex in the United				
				States and the ninth largest Port complex in the				

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		 world. Within the LA/LB Harbor itself, most of the "shoreline" is made up of shipping berths for loading and offloading cargo. Furthermore, because of the ever increasing size of cargo ships, the channels make up a large portion of the open waterway areas and are very deep (-55 to -80 feet MLLW in POLA navigational channels and -75 feet MLLW in POLB). See Ports Cargo/Berth maps. Consequently, the main ship channels are well mixed because of ship movement and maintenance/ construction dredging, while the berths are well mixed because of tugs/ships propeller wash stirring up sediments during anchoring, berthing, and loading/offloading. Much of the remaining portion of the open portion of the Harbor serves as anchorage areas for the container and cargo ships waiting to berth (see NOAA Nautical Chart). Therefore, even these areas are subject to constant and repeated anchoring disturbance and tug positioning. These non-empirical data are supported by geochronology core study was conducted to evaluate sediment depositional rates and patterns 							

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	Imments by: Jon Arnot Responses by: Anchor QEA, LLC, and Everest on behalf of Port of Long Beach an Page Page Section		 and estimate the rate of recovery throughout the Harbor. Cores were collected as ten locations that were strategically placed in depositional (non-erosional) areas, based on preliminary WRAP model simulations and other supporting data, and in non-navigational or recently dredged areas (these target areas were limited; See figure showing strategic core placement in depositional areas outside of navigation channels and recently dredged/filled areas). Cores were evaluated at multiple horizons in the top 40 cm for Cesium-137 peaks or Lead-210 increases (toward the surface); however, no consistent or significant depositional patterns were found, likely due in part to the high degree of mixing in the Harbor, combined with the large portion of the surface area that has been dredged or filled in recent years. See geochronology core profiles. The areas of the Harbor where higher concentrations of contaminants may exist at deeper sediments is limited to a few dead end slips, Dominguez Channel Estuary, and Consolidated Slip. 				

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43	General		Can the potential bias in the treatment of sediment concentration	Section 3.2.2 describes the sediment data treatment,			
			data (non-detects) be discussed or mentioned?	including that total PCB and DDX concentrations based on			
				congeners that were all non-detect were set to half the			
				maximum detection limit of the individual congeners. We			
				can include a discussion regarding potential bias			
				introduced by representing non-detect concentrations in			
				this manner. In brief, sediment total PCB and total DDX			
				concentrations below detection represent a small			
				percentage of the samples in each fish movement zone.			
				Thus, representing concentrations of these samples at half			
				the detection limit versus some other method, such as			
				regression on order statistics, is not anticipated to change			
				the area-weighted average concentrations estimated for			
				each fish movement zone.			
44	General		Please see below. This comment is for the TMDL project, not just				
			the food web modelling report.				

My understanding is that the TMDL project targets are:

Mixture	Fish Tissue	Sediment	
Total PCB	3.6 ppb (ug/kg)	3.2 ppb (ug/kg)	
Total DDX	21 ppb (ug/kg)	1.9 ppb (ug/kg)	

Simple models for bioconcentration factors (BCFs) that quantify exposure from the water only, not the diet, for persistent hydrophobic neutral organic chemicals like PCBs and DDX have existed for decades. There is a strong theoretical, thermodynamic basis for these models – chemical equilibrium partitioning between the exposure water and the lipid phases of the fish. The octanol-water partition coefficient (Kow) is shown to be a reasonable surrogate for lipid-water partitioning for these chemicals. At steady state, the BCF is Cfish/Cwater; hence, **Cfish can be calculated from the BCF and Cwater as Cfish = BCF.Cw**. A simple calculation for the BCF is the product of the whole body lipid fraction of the fish (Lf) and Kow, or **BCF = Lf.Kow**. Now, assuming the following:

- only exposure to the fish from the water in the harbor
- no dietary exposures (an additional exposure route that raises concentrations in fish for most PCBs and DDX); <u>hence, these "back of the envelope"</u> <u>calculations below will underestimate actual exposures for the vast majority of PCBs and DDX for fish in the harbor because they do not include dietary</u> <u>exposure and contamination from the sediment</u>
- the dissolved water concentrations measured in the study are accurate
- the "harmonized Kow values" selected in the report are reflective of water-fish partitioning (BCFs)

Some estimates of the fish tissue concentrations can be made from the measured water concentrations in the harbor as:

			PCB f	3.6		
				DDX f	ish Target (μg/kg)	21
Chemical	Location	Water column - dissolved (ng/L)	log Kow	BCF ¹ (L/kg)	Concentration in fish (µg/kg)	Factor over target
РСВ	DCE	11.95	6.9	3.97E+05	4746	1318
РСВ	Con Slip	1.8	6.9	3.97E+05	715	199
РСВ	LA Inner	0.51	6.9	3.97E+05	203	56*
РСВ	Ocean	0.18	6.9	3.97E+05	71	20
РСВ	PV shelf	0.14	6.9	3.97E+05	56	15
DDX	DCE	11.6	6.9	3.97E+05	4607	219
DDX	Con Slip	1.42	6.9	3.97E+05	564	27
DDX	LB inner north	0.43	6.9	3.97E+05	171	8*
DDX	Ocean	0.21	6.9	3.97E+05	83	4
DDX	PV shelf	0.48	6.9	3.97E+05	191	9

¹ assuming 5% lipid content; *Median water concentration within Harbor boundary

These calculations are presented to illustrate the challenges for meeting the current targets of the TMDL, particularly for PCBs.