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Arnold Schwarzenegger
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11 October 2010

To: Interested Parties

SUPPLEMENTAL INFORMATION FOR THE STAKEHOLDER MEETING FOR A PROPOSED BASIN PLAN AMENDMENT TO ADDRESS ORGANOCHLORINE PESTICIDES IN SEVERAL CENTRAL VALLEY WATERBODIES

This letter provides an overview on what has been done thus far for the Organochlorine TMDL/BPA, current TMDL efforts and the anticipated steps for the TMDL/BPA. The attached document provides supplemental information for the upcoming stakeholder meeting on 18 October 2010 at the Regional Board offices in Rancho Cordova for a proposed Basin Plan Amendment (BPA) to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins. The proposed Amendment will develop Total Maximum Daily Loads (TMDLs) for Organochlorine (OC) pesticides in several waterbodies located in the Sacramento River basin, San Joaquin River basin and Sacramento-San Joaquin Delta.

This supplemental packet provides a detailed discussion on the linkage analysis for the BPA/TMDL. This information is provided to encourage early stakeholder discussion about potential alternatives and approaches for the OC TMDL and no policy or regulation is either expressed or intended.

Overview of OC BPA/TMDL Development Efforts
The proposed TMDL/BPA covers several waterbodies located in the Sacramento River Basin, San Joaquin River Basin and the Sacramento-San Joaquin Delta for the control of Organochlorine (OC) pesticides in these Central Valley watersheds. A CEQA Scoping Meeting/Public Workshop was held in July 2009. At the meeting, Staff gave a presentation and sought public input on the range of alternatives the project needed to consider, the potentially significant environmental impacts of the project and the measures needed to mitigate any significant environmental impacts of the proposed amendment.

Subsequent to that, a series of public meetings with stakeholders in the form of Modules were planned to be held between June 2010 through February 2011. Three of these stakeholder meetings will have been conducted towards development of the TMDL/BPA thus far (including the 18 October meeting). These stakeholder meetings provide a forum for public consultation in an informal setting and are meant to encourage early involvement and offer an opportunity to discuss potential approaches that staff will consider during development of the TMDL. The stakeholder meetings will be followed by the formal BPA process, for example formal comment periods on the Public Review Draft and revised Final Draft Staff Report (including draft BPA text) prior to Regional Board adoption hearing. Staff encourages comments on additional options or any other relevant information that should be considered during the BPA process.

On 17 June, TMDL Staff held a public stakeholder meeting and provided an update on the overall status and schedule of the project. In addition, watershed descriptions, applicable OC impaired waterbodies and preliminary work products regarding potential TMDL targets were discussed. Preliminary BPA text associated with this Module was also released and discussed at the meeting. Stakeholders shared their comments verbally at the meeting and also submitted written comments which are currently posted on the OC TMDL web page.

On 19 August, TMDL Staff held a public stakeholder meeting and presented an overview of the preliminary source analysis. Stakeholders shared their comments verbally at the meeting and also submitted written comments that are available on the OC TMDL web page.

On 18 October, Staff will give a presentation on the linkage analysis for the BPA/TMDL. No BPA text has been released for the two meeting cycles (Module 2 and Module 3) as this is still in the development phase.

The next steps for development of the TMDL include drafting Preliminary BPA text related to Linkage Analysis and Allocations. Additional modules for discussion with stakeholders are anticipated to include Implementation (Part 1), Implementation (Part 2) and a Synthesis of all previous Modules. Development of the TMDL Staff Report will rely on previous discussions from Modules 1 through Module 3 as well as the pending future Modules. The next public meeting was tentatively scheduled for mid-December 2010. However, the Staff Lead on the Project will be leaving the Regional Board in late October 2010. This will result in a delay for all scheduled Module meeting dates. As soon as a revised schedule of overall project, including future meetings, is determined it will be shared via the Lyris List and posted on the project website at:
http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/central_valley_organochlorine_pesticide/index.shtml

Please bring this information to the attention of anyone you know who would be interested in this matter. Until further notice, the Public is requested to submit any questions regarding the Organochlorine Pesticide TMDL/BPA to the Pesticide TMDL Unit Senior, Amanda Montgomery at: 916-464-4716 or email her at: amontgomery@waterboards.ca.gov.

Thank you for your interest.

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1.0 Linkage Analysis
Linkage analysis relates loads of OC pesticides (OCs) to beneficial uses. The beneficial uses of Central Valley waterbodies most applicable to OCs are based on the protection of human health (MUN), and aquatic life in the water column, sediment and tissue. Further details on beneficial uses were covered in Module 1. Protection of beneficial uses from impairment by OCs is fundamentally about reducing OC concentrations in aquatic biota to acceptable levels, which necessitates reductions in water and sediment. The numeric targets for OCs in fish tissue define acceptable levels for protection of human health and wildlife, while numeric targets for water and sediment protect lower trophic level organisms and help trace impairment in biota back to sources.

1.1 Conceptual Model / Fate and Transport
A general conceptual model for OC fate, transport and effects in Central Valley watersheds is shown in Figure 1. This conceptual model, supported by the physical and chemical properties of the OCs, is necessary to understand the central role of sediments as a storage compartment and conveyance mechanism. The conceptual model helps support the basic assumption of this TMDL analysis, which is that actions to reduce OC concentrations in sediments will reduce OC concentrations in fish tissue and in the water column.

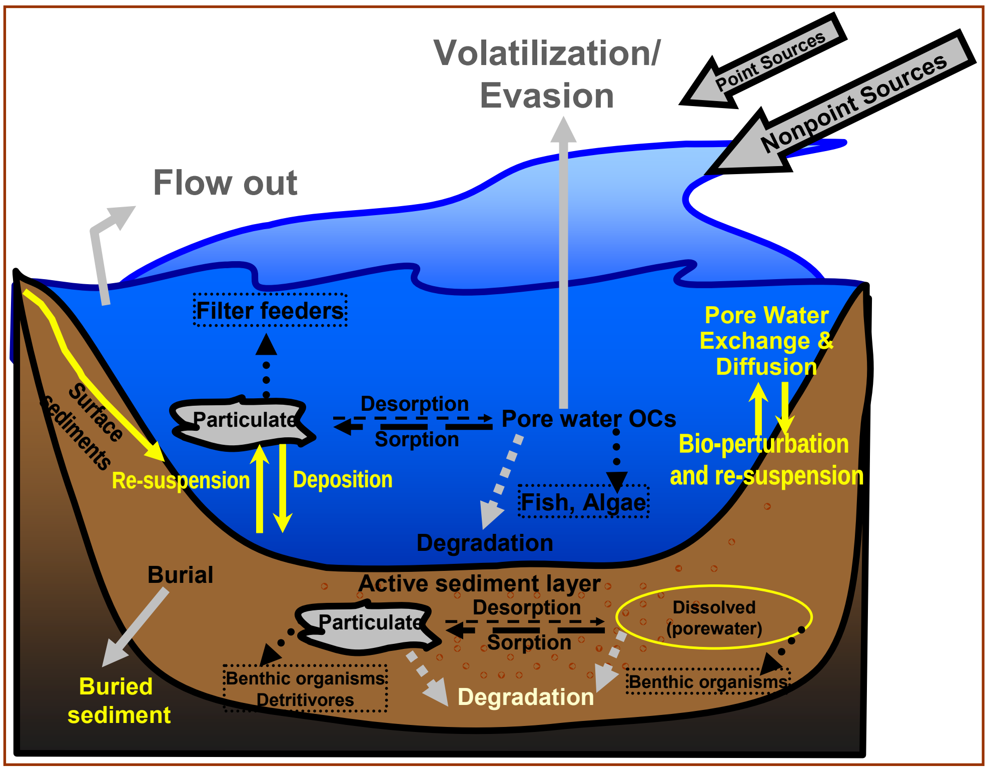

Fig. 1. Conceptual model of key transport and transformation processes of OCs in surface waters of the Central Valley watersheds and entry points to the food chain.

Figure 1 illustrates bio-availability, fate and transport. These are important processes because where given pollutants such as OC pesticides are in the environment affects their bioavailability. Bioavailability is the degree to which the contaminant is free to be taken up and to cause an effect at the site of action or on an organism at a higher trophic level. Fate in Figure 1 illustrates where a pollutant is stored in an environment (e.g. bioaccumulates, sorbs to soils, dissolved in pore water etc.) while transport is how the pollutant moves through the environment.

The size of the arrows for each process indicates the relative importance. As shown in the Sources Analysis Module, the dominant source of OCs is nonpoint source runoff from areas with high OC concentrations, resulting primarily from historic uses of OCs in these areas. Nonpoint source runoff also includes the load from atmospheric deposition, which is a much smaller contribution compared to the legacy load. As discussed in the Source Analysis (Module 2: Attachment 1), point source inputs from NPDES plants are a much smaller fraction of the overall load.

OC pesticides are no longer legally sold or used but they remain ubiquitous in the environment, bound to fine-grained particles. As such, there are no new sources in the watershed. When these fine-grained particles further up in the watershed become waterborne, the chemicals are ferried to new downstream locations and streams from point sources and nonpoint sources. Additionally, contaminated historically deposited open channel sediment contributes to the OCs loads in the rivers. The re-suspension of sediments from the aforementioned sources contributes to the waterbody impairment (Figure 1). Further details on this are discussed in the Source Analysis Module (Attachment 1).

With OC pesticides accumulating in the sediments, the constituents are available to migrate to the water column and ultimately to the food web. Through bioturbation and feeding processes, the contaminants may be taken up by benthic organisms. Once the sediment-bound OC pesticides contaminate benthic organisms, the contaminants may move out of the river sediments through each trophic layer. It is expected that if the concentrations of OCs in sediments loaded to the waterbodies and those within the waterbodies are reduced, then both water column and fish tissue targets will be met as well. A monitoring program consisting of water, sediment, and fish tissue monitoring should be considered as part of the implementation provisions to assess this assumption.

A portion of the sediment-bound contaminants may be carried out of a given waterbody through flushing to downstream locations while another portion remains within the waterbody. As the OCs settle into the sediments, some loss may occur through the slow decay and breakdown (degradation) of these organic compounds (Figure 1). Concentrations in surface sediments may also be reduced through the mixing with cleaner sediments. However these processes occur slowly and may take many years for the OCs to breakdown naturally.

Gaseous evasion and degradation (discussed below) are removal mechanisms, but also act on much slower timescales than hydraulic inputs and outputs. The OCs of concern in this TMDL all sorb strongly to particles. Thus, the gross movement of OCs through the watershed can be modeled as transport on the particulate phase. Although this simplifying assumption helps model watershed loads, site-specific factors that can enhance solubility (especially in pore waters) do need to be considered with regards to effects on beneficial uses.

The linkage of OCs in water and sediment to some applicable beneficial uses is uptake by organisms. As shown in Figure 1, uptake by filter feeders depends on their exposure to suspended particulate OCs while uptake by benthic detritivores is influenced primarily by OC concentrations in sediments. Dissolved OC concentrations in the interstitial waters of sediments (pore waters) may also be an important factor affecting OC uptake by benthic organisms. Fish may acquire dissolved OCs from the water column passing directly across the gills, as well as from consumption of contaminated organisms. Humans and wildlife are in turn susceptible to consumption of organisms contaminated with OCs.

Sediment OC concentrations are important to all of the bio-uptake pathways shown in Figure 1. Filter feeders and benthic detritivores are directly affected by the OC concentrations of bottom and suspended sediments in the active sediment layer. OC concentrations in sediments indirectly affect organisms whose primary route of exposure is dissolved OCs. Higher OC concentrations in sediments drive the adsorption-desorption equilibrium towards higher dissolved concentrations. In addition, bio-perturbation and re-suspension between the active sediment layer and pore water through exchange and diffusion contributes fluctuating levels of OCs between the two dynamic compartments (Figure 1).

1.2 Chemical Properties and Partitioning of OCs

In general, the fate, transport and bioavailability are dependent upon properties of the pollutant (does it volatilize, sorb to soil, and is it soluble in water or in lipids?), properties of the environment (percent organic carbon in sediment, temperature, salinity etc.) and properties of the organism (lipid content and size). For this section, emphasis is placed on properties of pollutants in order to better understand their environmental persistence. The section discusses relevant chemical properties for the 303(d) listed OCs applicable for this BPA and TMDL as shown in Table 1, followed by a description of their physical and chemical characteristics.

The likelihood of volatilization is measured using Henry's Constant (K_H)

Equation 1:

$$K_H = C_a / C_w$$

Where:

K_H = Henry's Constant; Ca = Concentration in air; Cw = Concentration in water

The lower the C_a/C_w ratio, the greater the likelihood of finding a constituent in water. Conversely, the higher the ratio (Equation 1), the higher the volatilization potential of a constituent. For example, based on data provided in Table 1, p,p'-DDT will have a higher likelihood of being found in water compared to p,p'-DDE which has a higher volatilization potential.

Table 1. Chemical properties of OC pesticides addressed by BPA/TMDL.

Constituent	Molecular Weight [1]	Water Solubility (mg/L) at 25°C [2]	Henry's Law Constant [2] (atm-m^3/mole)	Log K_{ow} [2]	Log K_{oc} [2]	Log BCF [2]	Half Life in Soil, Low (days) [1]	Half Life in Soil, High (days) [1]
DDT and its isomers								
DDTs (total)*	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	320.05	0.090	4.0x10-5	6.02	5.18	0.090	730	2190
p,p'-DDT	354.49	0.025	8.3x10-6	6.91	5.18	0.025	1,460	5,330
p,p'-DDE	318.03	0.120	2.1x10-5	6.51	4.70	0.120	1,000	5,475
Group A Pesticides								
Aldrin	N/A	0.017	1.7x10-4	5.52	4.69	3.500	N/A[3]	N/A[3]
Dieldrin	380.93	0.195	1.5x10-5	4.55	3.92	3.650	109	4,560
Endrin	380.92	0.250	7.5x10-6	4.56	4.06	3.170	60	5,110
Heptachlor	N/A	0.180	1.5x10-3	4.27	3.54	3.980	180	1,200
Heptachlor epoxide	389.20	0.200	9.5x10-4	5.40	1.02	4.160	N/A	N/A
Chlordane (total)**	409.80	0.056	4.9x10-5	N/A	3.09	4.270	350	7,300
Hexachlorocyclohexane								
gamma-BHC (Lindane)	290.85	7.300	1.4x10-5	3.61	3.03	3.100	3	1,095
alpha-BHC	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
beta-BHC	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
delta-BHC	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Endosulfan (total)								
Endosulfan (total)	406.95	0.450-0.510	1.1x10-5	3.83	3.82	3.020	5	150
alpha-Endosulfan	406.92	0.51	1.1x10-5	3.83		3.020		
beta-Endosulfan	406.92	0.450	1.31x10-5	3.83	3.82	3.020	5	150
Endosulfan Sulfate	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Toxaphene	414.00	0.740	6.0x10-6	4.68	5.32	3.490	9	5,110

Kow = octanol-water partitioning coefficient, Koc = organic carbon-normalized distribution coefficient, BCF = bioconcentration factor

[1] Sources: ATSDR website (www.atsdr.cdc.gov/toxfaq.html), EXTOXNET website (http://pmep.cce.cornell.edu/profiles/index.html)

[2] Source: Syracuse Research Corporation (http://www.syrres.com/what-we-do/databaseforms.aspx?id=381)

[3] Aldrin rapidly degrades to dieldrin in the environment (ATSDR, 2002), thus half life of dieldrin is representative.

N/A = information not available.

Lipophilicity of a constituent refers to its ability to dissolve in fats, oils, lipids, and non-polar solvents such as hexane or toluene. The octanol-water partition coefficient (K_{OW}) is used to determine a constituent's lipophilicity. The partition coefficient is the ratio of concentrations of un-ionized compounds between two solutions as presented in Equation 2.

Equation 2:

$$K_{OW} = C_O / C_W$$

Where:

K_{ow} = Octanol-water partition coefficient; C_o = Concentration in octanol;
C_w = Concentration in water

The greater the K_{OW}, the greater the lipophilic nature of the constituent. If the log K_{OW} is between 3 and 6, then the chemical will be predicted to bioaccumulate (Harper, 2008).

For example, DDT has a higher K_{OW} than gamma-BHC and has a higher potential to bioaccumulate in fatty tissue of a given organism.
The ratio of a chemical's concentration in the tissue of an organism (C_T) to the chemical's concentration in water (C_W) is referred to as the bioconcentration factor (BCF). This is often in L/kg.

Equation 3:

$$BCF = C_T \ / \ C_W$$

Where:
BCF = bioconcentration factor; C_T = chemical's concentration in the tissue of an organism; C_w = chemical's concentration in water

The BCF can be an observed value or the prediction of a partition model. This assumes that the pollutant partitions passively between water and aquatic organisms and that a chemical equilibrium exists between the organism and water. The previously described octanol: water partition coefficient (K_{OW}) is often used as a surrogate for the BCF with octanol acting as lipids (fat) and water acting as the aquatic environment.

Due to the hydrophobic nature of OCs they are strongly adsorbed onto silt, sediment particles, and organic matter within a water body. However, the dissolved fraction (operationally defined as the portion of a sample that passes a 1.2-µm filter) (Calleguas Creek TMDL, 2006) is of potential significance since it is sometimes more toxic and bioavailable. The organic carbon fraction of sediments is most commonly correlated with sorption of OCs.

The distribution coefficient (K_d) of a compound describes the partitioning of the compound between the solid and liquid phase, assuming equilibrium conditions. The organic carbon-normalized distribution coefficient (K_{OC}) is a related value that accounts for the fact that partitioning to sediments by hydrophobic compounds will increase with increasing amounts of organic carbon on sediments. The relationship between K_d and K_{OC} is as follows:

Equation 4:

$$K_d \cong f_{oc} * K_{oc}$$

Where:
K_d = distribution coefficient; f_{OC} = fraction of organic carbon in soil or sediment; K_{OC} = organic carbon-normalized distribution coefficient

The approximate symbol is used because other sediment textural factors (e.g., surface area to volume ratios) can affect the site-specific distribution coefficient. The K_d can also vary with site-specific factors such as pH, temperature, and the concentration of the adsorbing pollutant. The distribution coefficient is a useful property for ranking the relative affinity of different compounds for particles..

1.2.1 Gaseous Evasion

Evasion means the escape of OC pesticides into the atmosphere. Evasion is generally considered to be significant for compounds that have Henry's Law constants (K_H values) greater than 10^{-4} atm-m^3/mole, although other factors such as wind speed, atmospheric concentration, and temperature also affect evasion rates. Evasion of most OCs from soil and water bodies is not considered to be a major loss mechanism. Heptachlor, heptachlor epoxide, and Aldrin all have H values equal to or above 10^{-4}, so gaseous evasion could be an important removal process for those constituents.

1.2.2 Degradation

Degradation of OCs can proceed by both biologically mediated and abiotic processes. Abiotic degradation mechanisms include hydrolysis and photolysis. Hydrolysis is the chemical reaction that uses water to break down a molecular bond, is not a very important degradation pathway for most legacy OC pesticides (Mackay et al., 1997). However, the solubility properties of OCs in water are important because this determines their bioaccumulation potential. A more water soluble constituent is less likely to bioaccumulate and can easily move in surface water and subsequently to groundwater. For example, DDT has an aqueous solubility of 0.025 mg/L while gamma BHC has an aqueous solubility of 7.3 mg/L, implying that DDT has lower solubility than gamma BHC and has a higher bioaccumulation potential (Table 1), making it less likely to be found in surface water and groundwater but rather bound to sediment or in fish tissue compared to gamma BHC.

Photolytic degradation can proceed directly when a molecular bond absorbs light, or indirectly, when photolytically produced reactive substances (e.g., hydroxyl radical) attack molecular bonds. The mechanism and relative importance of photolysis (direct or indirect) depends on many factors, including the OC compound in question, the presence or absence of light-absorbing compounds (chromophores) that can produce reactive intermediates, and the degree of light penetration (in water) due to water depth and turbidity (Kulovaara et al., 1995; Calleguas Creek TMDL, 2006). The rate of photodegradation depends on the intensity and wavelength spectrum of light. It typically happens in chemicals with double bonded carbons such as alkenes and aromatics (Harper, 2008). An example of an OC constituent that undergoes photolysis with its corresponding half life is DDE – 22 hours (Hemond and Fechner-Levy, 2000).

Biologically mediated degradation is generally a more important degradation pathway than hydrolysis or photolysis for OC pesticides, especially DDT and DDE (Aislabel et al, 1997). For DDT and DDE, the distribution of intermediates formed in the biotransformation process is sensitive to redox conditions. Under anaerobic conditions, microbial transformation of DDT occurs primarily by reductive dechlorination to produce DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane). Under aerobic conditions, DDT dechlorination produces primarily DDE and DBP (Perieira et al., 1996). In soil conditions, DDT will anaerobically undergo biodegradation at a rate of 0.0035 ug/kg per day, Endrin 0.03 ug/kg per day and Lindane (gamma-BHC) at a rate of 0.0046 ug/kg per day (Hemond and Fechner-Levy, 2000).

The range in reported degradation rates for OCs in soils are reported as “half life” in Table 1. These values take into account all degradation reactions. Environmental monitoring data tend to indicate that degradation rates reported from controlled laboratory studies are generally faster than what is actually observed under natural conditions (Spencer et al., 1996; Zepp and Cline, 1977). Persistent chemical are of concern to regulators and toxicologists due to the impact on terrestrial life. Several OCs belong to the specific list of 12 compounds that US EPA considers as Persistent, Bioaccumuative and Toxic (PBT). These OCs include aldrin/dieldrin, , chlordane, octachlorostyrene, DDT and its metabolites (4,4’ DDT, DDD, DDE) (US EPA, 2010)

Volatilization, bioaccumulation, sorption to sediment and/or soil particles and water solubility are all in competition. Depending on the properties of the chemical and of the environment itself, the chemical will partition differently into each of these phases (i.e. air, water, lipids, sediment or soil) (Harper, 2008).

1.3 Using DDE as a Representative OC Pesticide

The use of DDE as a representative constituent for OC pesticides was based on its high detection frequency in Central Valley watersheds. This allows for analysis at varied spatial and temporal scales. One additional benefit of using DDE as a representative constituent is that it is one of the most persistent OCs, which means that implementation measures and timescales set for achieving DDE targets will facilitate achievement of targets for the other OCs. This holds true because OC pesticides possess similar physical and chemical properties that influence their fate and transport in the environment. There are instances in this discussion where Staff used data from OC pesticides other than DDE e.g. for temporal variation of OC pesticides in fish tissue. In order to evaluate attenuation of OCs, Staff opted to complement DDT data by including more OC constituents (chlordane and dieldrin) to compare temporal trends. These OCs were chosen because they were frequently detected in fish tissue.

1.4 Seasonal variations in DDE Concentration

Staff relied on data monitored within the Central Valley waterbodies as well as previous data monitored in the San Joaquin River Basin (USGS, 1998) to evaluate seasonal variations of DDE. Data monitored within the Central Valley were obtained from numerous sources that were listed in Table 1 of the Module 2 Attachment 1

Results from previous data monitored by USGS (Figure 2) indicate that DDE concentrations for Orestimba Creek at River Road were higher with the higher river discharge (referred to as “discharge” by USGS in Figure 2) from the rain season flushes (January – February) and during the irrigation season (May- October) with most of the other data remaining as non-detects (Figure 2). The DDE data for Salt Slough at Highway 165 Road and Merced River at River Road indicates that most of the data is non-detect with some detects in the months of February for both sites probably resulting from the higher flushes in the rain season.

There were numerous detections at the integrator site (San Joaquin River near Vernalis) with higher concentration also noted around the time of the winter rainfall flushes in January which is likely attributable to transport of DDE-laden sediments. Correlations between DDE and seasonality in Central Valley waterbodies suggests presence of DDE loading from various land use categories. The magnitude of the concentrations is likely related to precipitation and runoff conditions (as shown by river discharge in Figure 2).

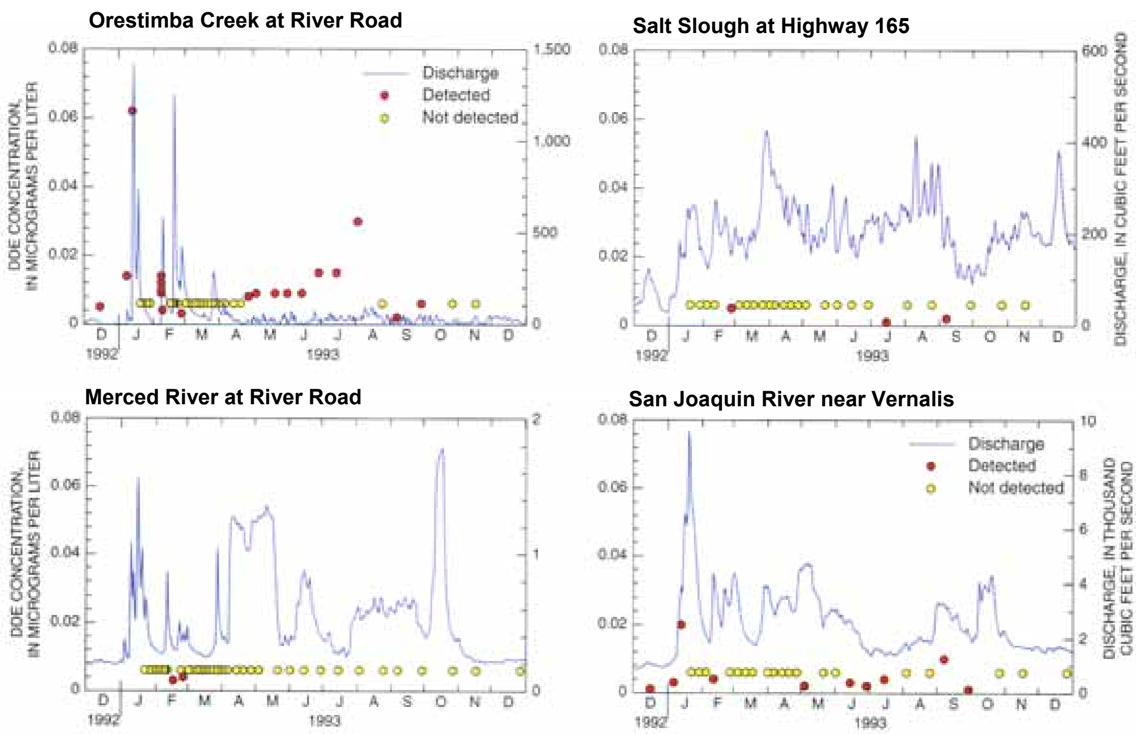

Figure 2. Time Series plots of OC pesticide concentration and stream discharge in the San Joaquin River Basin (Data graphs extracted from USGS, 1998).

Based on data monitored from selected Central Valley waterbodies, water column data (Figure 3) indicate that higher DDE concentrations were detected between April and August for Orestimba Creek (Below Kilburn Road) and DWW (Central Portion) potentially resulting from irrigation flows in this season. For the lower Merced River reach, consistently higher DDE levels were noted from December 2002 through June 2003 suggesting a combination of rainstorm flush events and irrigation flows. With the exception of a spike in July 2007, the Stanislaus to Delta Boundary registered consistently low values of DDE. This may be due to dilutions from upstream tributaries of the Merced, Toulumne and Stanislaus Rivers in this downstream reach. Rainfall data in Figure 3 were obtained from the National Climatic Data Center (NCDC) and California Irrigation Management Information System (CIMIS) as indicated for each impaired reach. For the Lower Merced River (Merced C, NCDC Station #5532), Orestimba Creek (Newman C, NCDC Station #6168), SJR, Stanislaus to Delta Boundary (Modesto A, CIMIS Station #71), and Delta Waterways (Central Portion) (CIMIS Station # 47).

Pesticide concentrations in stream water have been reported to vary through the year, and are usually characterized by long periods with low or undetectable concentrations of most pesticides, punctuated by seasonal pulses of much higher concentrations (USGS, 2007) as evidenced by Figures 2 and 3 (USGS, 1998). The timing and magnitude of seasonal pulses shown in Figures 2 and 3 are correlated with the timing and magnitude of runoff from rainstorms, and the timing and distribution of land-management practices such as irrigation and artificial drainage within the project area.

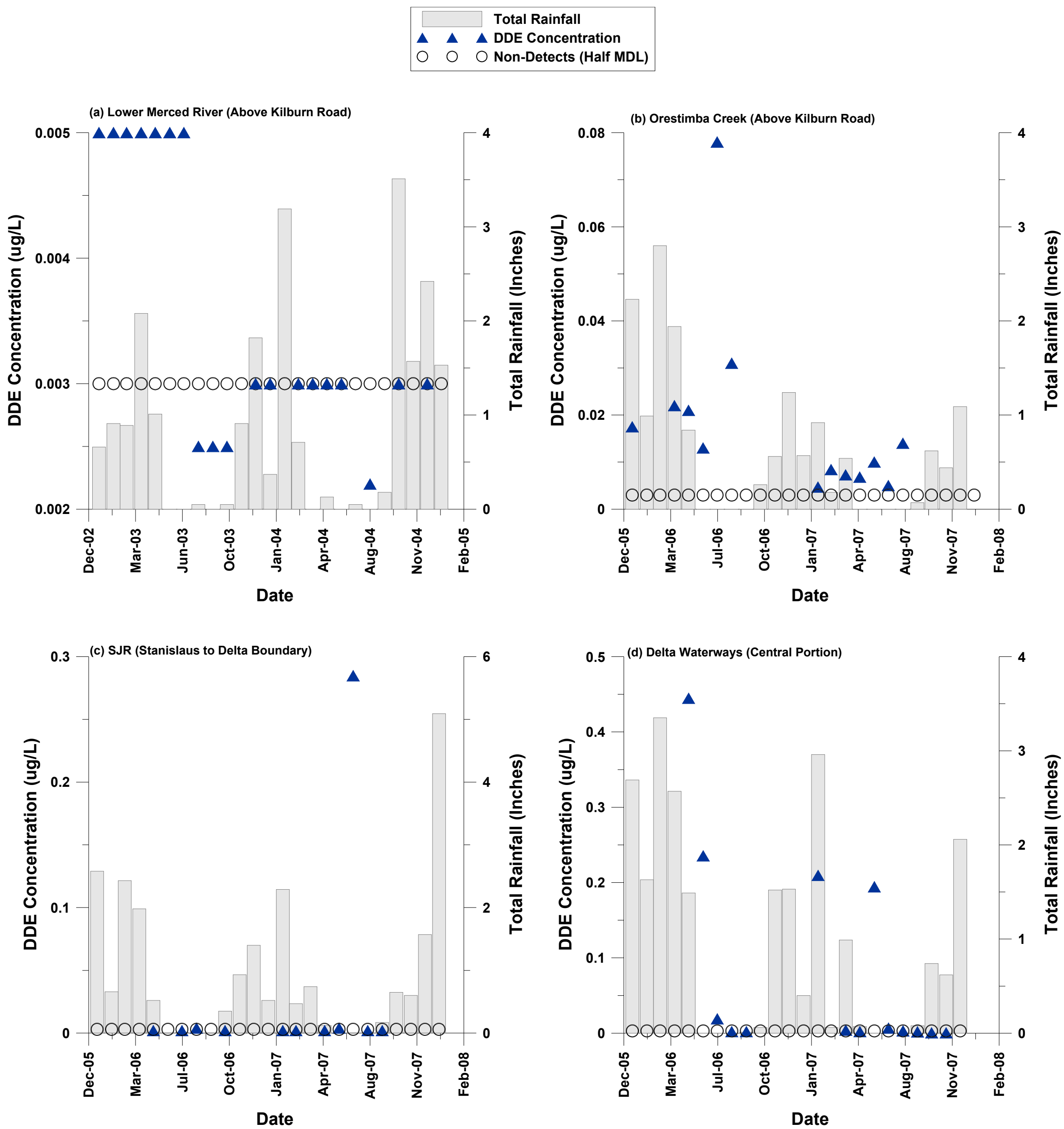

Figure 3. Time Series plots of OC pesticides from selected Central Valley waterbodies from multiple data sources listed in Table 1 (Module 2 Attachment 1)

1.5 Attenuation of OCs in the Central Valley Watersheds

Banned OC pesticides generally show a loss of concentration over time, due to a sum total effect of all the loss terms (balanced by residual legacy loads), as illustrated by the conceptual model (Figure 1). The best example of this can be seen in the OC concentrations of fish tissue samples from Central Valley watersheds (Figure 4). With the exception of DDT in Channel Catfish in the Stanislaus River to Delta Boundary (Fig. 4a), which had a relatively low Spearman's correlation coefficient of 0.25, all other plots shown in Figure 4 had significantly high correlation coefficients and showed fairly smooth exponential fits to the data. The various empirical relations for each time series are shown in Figure 4. The strongest exponential decay fits were for Channel Catfish in the Colusa Basin Drain for DDT and Dieldrin (Figs. 4d, 4f).

The temporal trends in Figure 4 also depict pollutant concentration differences in fish tissue with DDT having an order of magnitude higher than chlordane and an extra order of magnitude higher in dieldrin. Watershed differences are also apparent in this illustration with the SJR basin having higher concentrations of fish OC pesticides than the Sacramento River basin at Colusa Basin Drain and least amounts noted in the Sacramento-San Joaquin Delta for Delta waterways Northern portion.

The rates of decline seem to differ and appear to be lower in the Delta waterways portion with a less steep gradient (Fig. 4g and 4i) suggesting that the rate of decline could vary among locations. Reasons for this phenomenon are currently unknown to Staff. This could also explain why episodes of higher OC concentrations are observed in some recent sampling (Figure 4i) compared to data elsewhere (Figure 4c and 4f) indicating that the rate of decline might be much slower at some locations. Summarily, present findings still indicate that there are significant concentrations which persist in numerous locations within the Central Valley watersheds.

The exponential model curve fits were projected to the year 2020 to observe the fate and gradual natural attenuation of OC constituents in fish tissue if no remediation action were taken. The data indicates an apparent decline to near non-existance by the year 2020. However, it should be noted that this is based on the assumption that other variables that could re-introduce OC constituents such as re-excavation, re-suspension or atmospheric deposition do not occur in these watersheds. However, Staff feels these processes are likely to occur so levels of low levels of OCs may still be present after 2020.

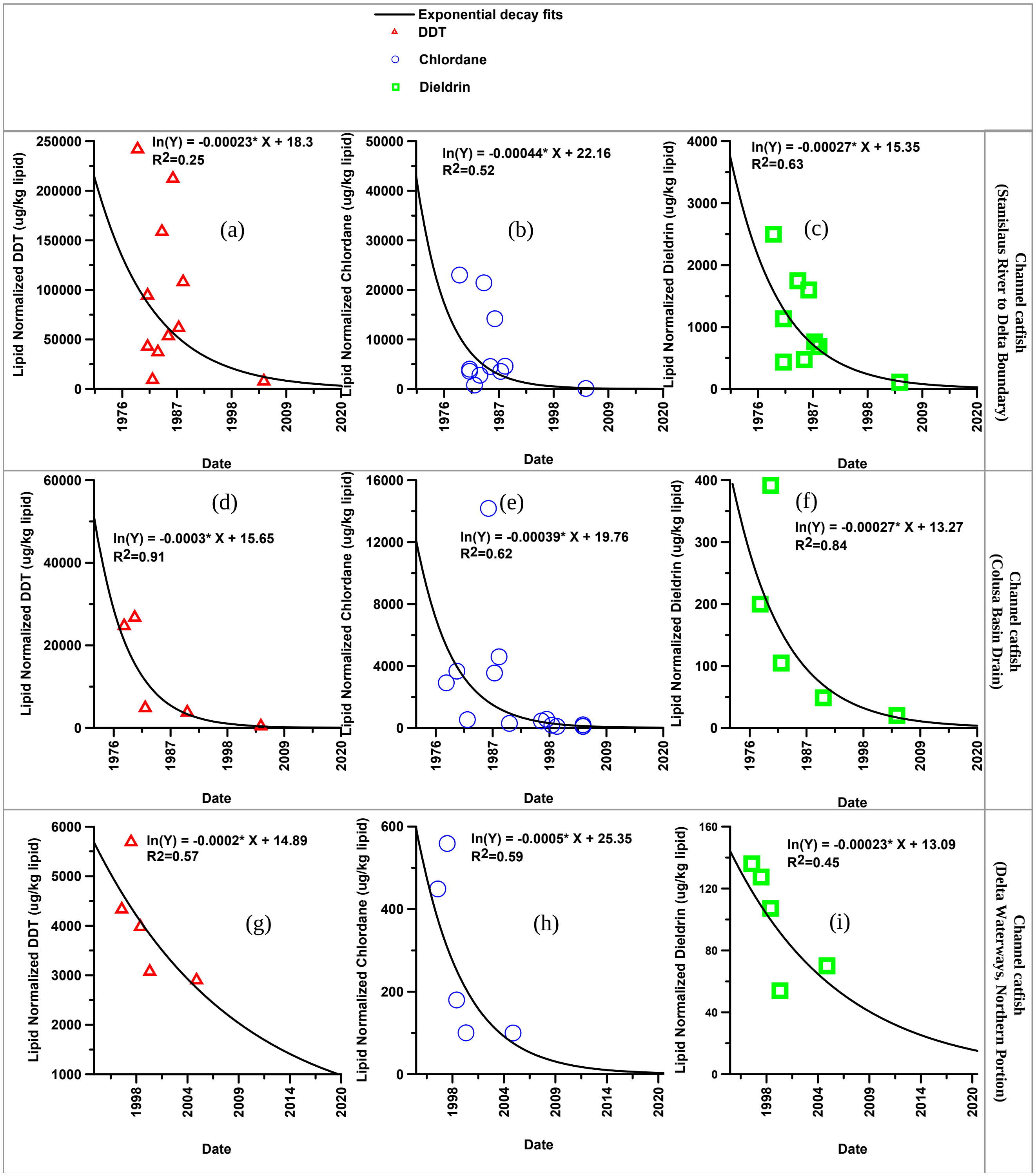

Fig. 4 Temporal Variation of OC Pesticides in Central Valley Fish (1978-2007) – Multiple data sources listed in Table 1 (Module 2 Attachment 1)

Previous research has documented similar results for temporal trends in OC pesticides. Contaminant concentration in fish within the lower SJR and Sacramento-San Joaquin Delta (Davis et al., 2000), simple fate models for the Bay (Connor et al. 2007) and sport fish monitoring data (SWAMP, 2007) have all indicated declining trends in OC pesticides in the Central Valley. The decreases in OC concentrations of biota emphasizes that natural attenuation of OCs is occurring already, due to processes such as degradation, burial, flow-out, volatilization and evasion (Figure 1). A primary goal of this TMDL and BPA is to augment natural attenuation through implementation actions. The conceptual model in Figure 1 shows the action most likely to result in progress towards that goal is reduction of inputs from point and nonpoint source loads of OC pesticides.

As shown in Figure 5, there was no clear correlation between DDE and seasonality for fish tissue data. Data from Toxic Substances Monitoring Program (TSMP) for the time period 1978-2000 was mainly collected between August and October of each year making it increasingly difficult to assess comparative temporal trends for different months of the year. On an annual scale, data shown in Figure 5 shows a decline in DDE levels. No temporal trends were conducted for sediment due to insufficient data.

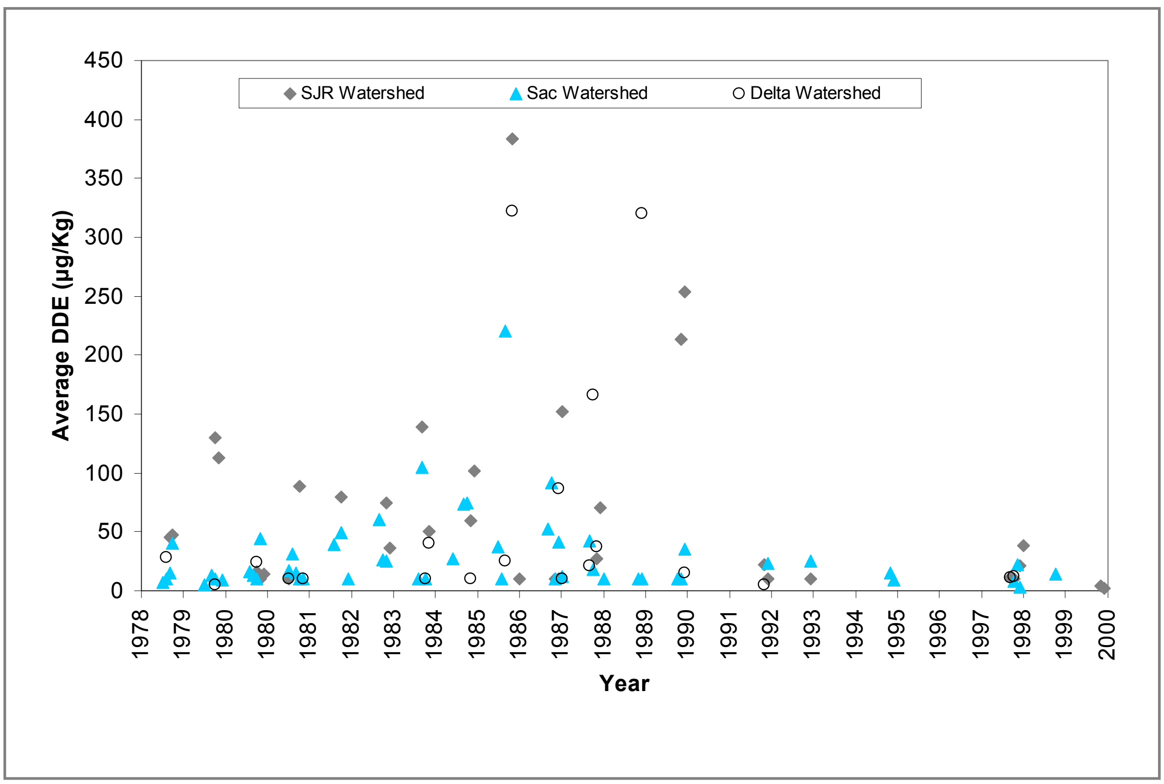

Figure 5. Variation of DDE in Central Valley Fish Tissue (1978-2000). Data from Toxic Substances Monitoring Program (State Water Board, 2002)

1.6 Linkage between OC Loads, Targets, and Beneficial Uses

The conceptual model for OC fate, transformation and uptake supports four basic linkages in this TMDL Analysis, shown in Figure 6. These linkages are 1) that risk is proportional to pollutant concentrations in fish times consumption rates; 2) OC concentrations in tissue are proportional to OC concentrations in sediments; 3) OC concentrations in water are a function of OC concentrations in sediment; 4) OC concentrations in sediment are a function of OC loading and sediment transport. A detailed explanation of these linkages follows below.

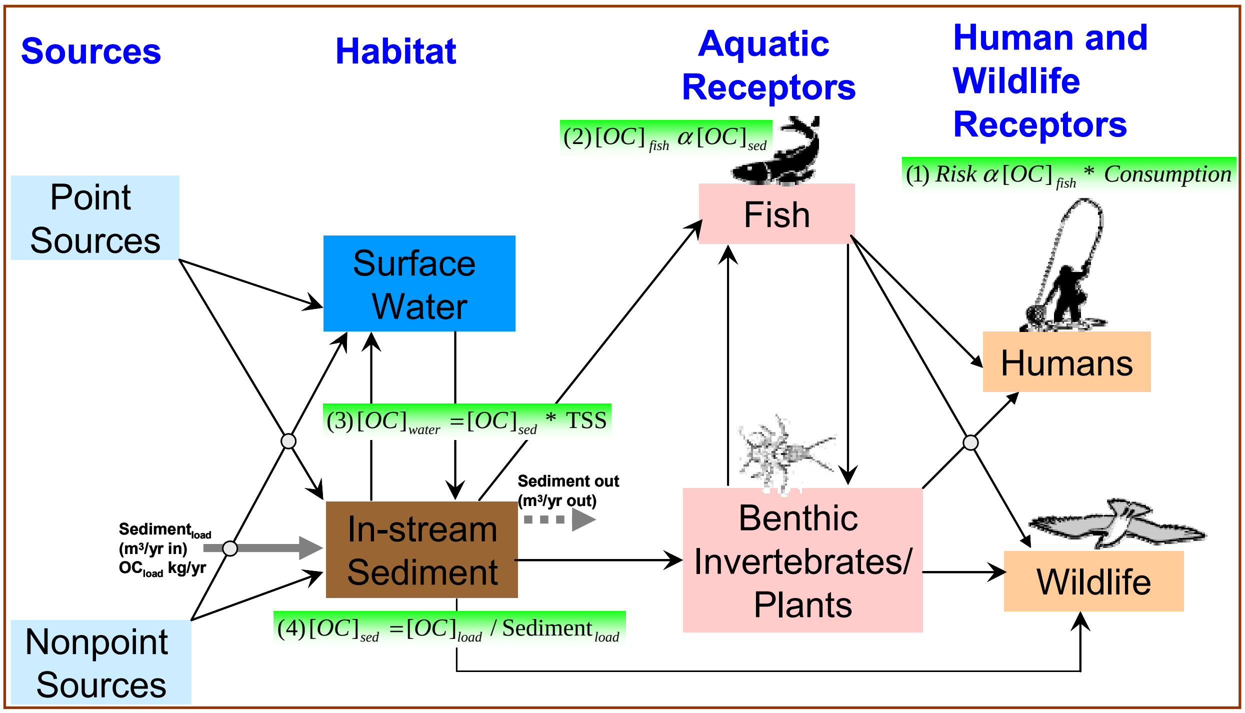

Figure 6. Conceptual illustration of linkage between OC loads, targets, and beneficial uses (Modified after Bridges et al., 2005).

1.6.1 OC Concentrations in Tissue are proportional to OC concentrations in sediments.

The basic premise underlying this linkage is explained in the conceptual model presented above: OCs in sediments are taken up directly by filter feeders and benthic feeders. Organisms taking up dissolved OCs are still affected by OCs in sediment, because of adsorption-desorption equilibria (Figure 1). When the OC concentration of sediments in Central Valley watersheds approaches zero, the OC concentration in the water column, interstitial waters, and the food chain will also approach zero.

This TMDL analysis makes the simplifying assumption that the relationship between OC concentrations in fish and sediments is linear, with the slope of the line being the overall sediment–organism bioaccumulation factor (BAF) (Fig. 7).

In Module 1, Staff proposed a number of options for sediment targets. For the case where we do not use an explicit sediment target, in order to translate required reductions in fish tissue and water column concentrations into sediment concentration reductions, it is assumed that BAFs for fish tissue to sediment and water to sediment are linear, and that a given percent reduction in fish tissue or water concentration results in an equal percent reduction in sediment concentration (Figure 7).

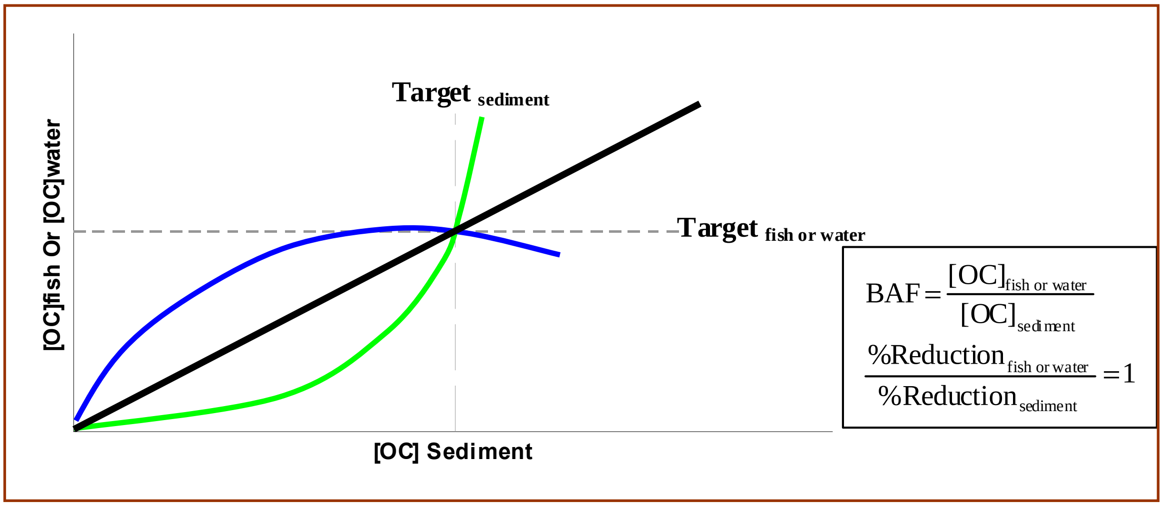

Figure 7. Assumptions for translation of reduction in concentration of fish tissue and water to sediment reductions

It is possible that a non-linear relationship between sediments and fish tissue may exist as indicated by the green and blue curves (Figure 7). This is an acknowledged uncertainty in the TMDL analysis. However, it is important to note that this uncertainty should not prevent action, because there is reasonable certainty that lower OC concentrations in sediments will lead to lower OC concentrations in the food chain.

Previous work conducted in Upper Newport Bay (Santa Ana Regional Water Board, 2006) illustrated the existence of a linear relationship (R^2=0.768) between DDE concentration in a benthic organism (*Macoma nasuta*) and in Newport Bay sediments. Santa Ana Regional Board Staff analysis surmised that by reducing the OC concentrations in sediment, the concentrations in aquatic food webs should likewise be reduced (Figure 8).

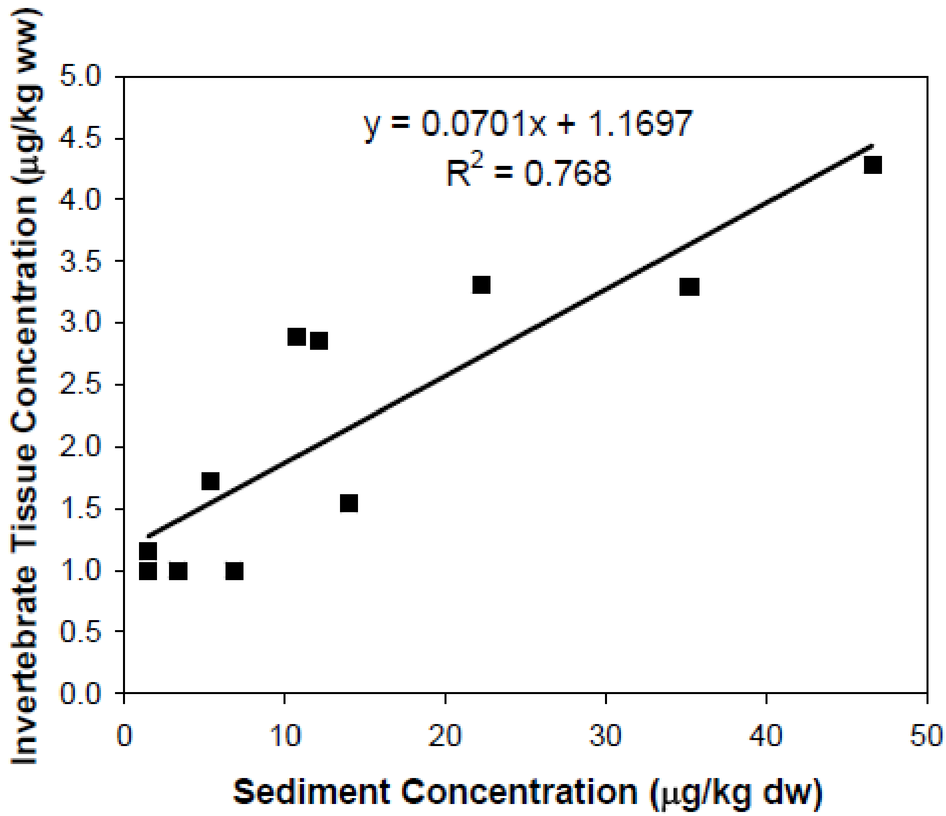

Figure 8. Relationship between sediment 4,4-DDE concentrations and *Macoma nasuta* 4,4-DDE concentrations in Upper Newport Bay (Santa Ana Regional Water Board, 2006).

To better predict the expected relationship between OC concentration in sediments and OC concentrations in fish tissue, it is important to develop and populate a food web model such as the one shown in Figure 9. An assessment of all organisms present in the food web for Central Valley watersheds has not been conducted, but extensive monitoring information (1978 through 2000) is available from the Toxic Substances Monitoring Program (TSMP) database (State Water Board, 1986; Rasmussen 1995). Staff relied on the TSMP database for fish tissue data and on studies conducted by Pauly and Palomares (2005) for identification of fish trophic levels. DDE concentrations in organisms found in Central Valley watersheds are shown in Table 2 for marine organisms and Table 3 for freshwater organisms. The TSMP data is available for public download at:
http://www.waterboards.ca.gov/water_issues/programs/swamp/mussel_watch.shtml

Many of the highest concentrations might be associated with specific locations where species reside (e.g., herbivores and/or detritivores living in or near runoff/discharge areas).

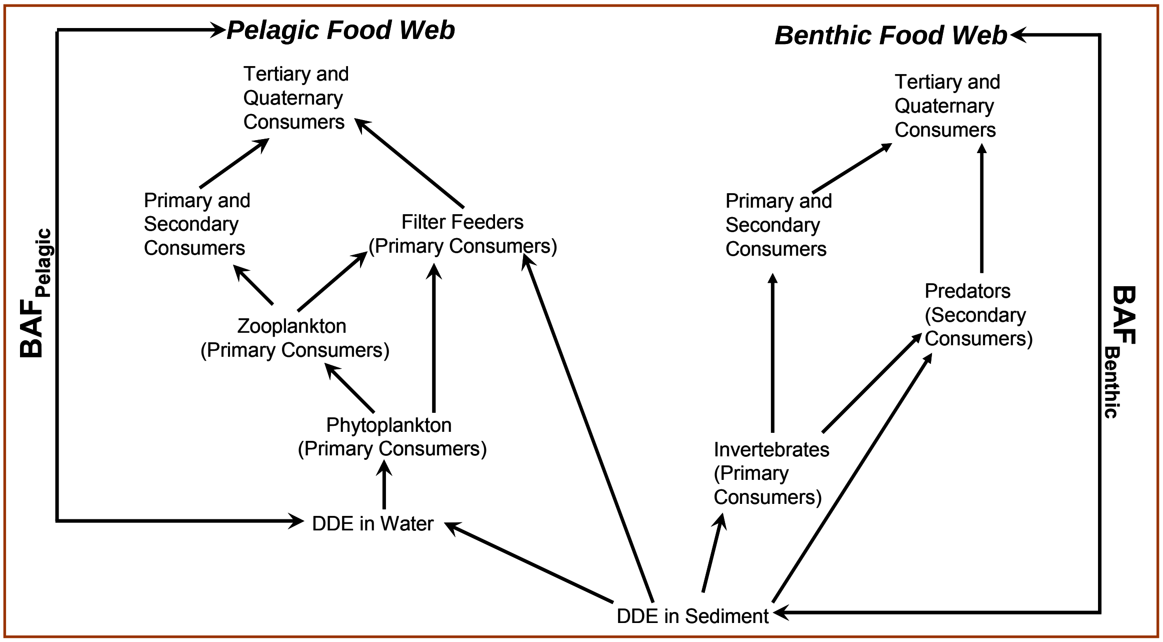

Figure 9. Basic food web model for Central Valley watersheds for freshwater and marine organisms (Adapted from Calleguas Creek TMDL, 2006)

In the absence of a complete assessment on organisms in the food web and OC bioaccumulation processes, proportionality between sediments and fish is assumed. Development of a detailed food web model and population of the model with matched predator-prey-sediment data could verify or refute that assumption. If a non-linear model applies, then the resulting TMDL may be lower or higher than that which is calculated by assuming a linear sediment-organism BAF.

Some of the common organisms identified from the TSMP database in the Central Valley watersheds include:

- Trophic Level 4 fish: bass (largemouth and striped), channel and white catfish, crappie, and Sacramento pikeminnow.
- Trophic Level 3 fish: black bullhead, bluegill, carp, redear sunfish, Sacramento sucker, and crayfish.
- Small (<50 mm) fish: primary prey species consumed by wildlife in Central Valley fish may include the species listed above, as well as juvenile bluegill, mosquitofish, red shiner, or other fish less than 50 mm.

Using DDE as a representative OC pesticide (see Section 1.3), Staff opted for selected river reaches in Central Valley watersheds. For the San Joaquin River watershed, the Stanislaus to Delta Boundary (San Joaquin River at Vernalis) was chosen as an integrator site for all upstream inputs from the San Joaquin Valley before discharging to the Delta. For the Sacramento River watershed, Staff chose the Colusa Basin Drain because this reach represents a man-made conveyance (unlike most reaches in the Project Area which are Rivers) that delivers runoff and agricultural return flows from about 1 million acres of watershed and discharges to the Sacramento River at Knights

Landing. A representation of organisms from the Drain helps contrast with organisms sampled from natural rivers and streams. For the Sacramento-San Joaquin Delta, Staff chose the Central Delta waterways. The Central Portion receives inputs from the Eastern, Southern, Stockton Deep Water Ship Channel and the Northern Portions. The Central Portion also receives flow inputs from the lower Sacramento Valley Basin as well flow inputs from the upper San Joaquin Basin above Vernalis which include inflows from the Stanislaus, Tuolumne, Merced as well as other upper San Joaquin Rivers downstream of New Melones, Don Pedro, McClure and Millerton Lakes.

No inference of DDE levels was made for marine organisms in the San Joaquin and Sacramento River watersheds due to absence of data, which is expected since these are freshwater waterbodies (Table 2). Though crayfish are known to be marine organisms, there are exceptions e.g. some crayfish were found in freshwater in the San Joaquin Valley (Table 2). It has been reported that some superfamilies namely Astacoidea and Parastacoidea are freshwater crustaceans that mostly reside in brooks and streams with fresh water running, and which have shelter against predators (Hart, 1994). This may be the case for crayfish found in the San Joaquin Valley. The average concentrations of DDE for marine organisms in Delta waterways, Central Portion generally increased with trophic level as would be expected for bioaccumulative substances. A similar trend was also observed for freshwater organisms (Table 4) in the San Joaquin and Sacramento River watersheds.

However, not all components of the food web reflect these trends as some do not generally increase with trophic level. This likely reflects the complexity of food web dynamics. For example, the channel catfish and largemouth bass in the SJR at Vernalis (TL 4) are not necessarily feeding on an exclusive diet of carp (TL3), and both organisms are free to forage outside of this reach. Additionally, largemouth bass are known feed in the water column while white catfish are more bottom-oriented foragers (Davis et al., 2000). These two species may exhibit different routes of exposure and bioaccumulation (US EPA, 1995). Thus, observations in Table 3 may have species-related trends even for fish within the same trophic level.

Table 2. Marine organisms[1] found for selected river reaches in Central Valley watersheds and average DDE tissue concentrations according to trophic level (Data from the TSMP Database)

Trophic Level	Trophic Level Description	Organism	Genus *(Species)*	n	Mean DDE Concentration (ug/g)	
					Filet/ Muscle	Whole Organism
San Joaquin Watershed (Stanislaus River to Delta Boundary: SJR at Vernalis)						
1	Primary Consumer (Herbivore)	-	-	-	-	-
2	Secondary Consumer (Primary Carnivore)	-	-	-	-	-
3	Tertiary Consumer (Secondary Carnivore)	Crayfish	Pacifastacus *(leniusculus)*	20	N/A	ND
4	Quaternary Consumer (Tertiary Carnivore)	-	-	-	-	-
Sacramento River Watershed (Colusa Basin Drain)						
1	Primary Consumer (Herbivore)	-	-	-	-	-
2	Secondary Consumer (Primary Carnivore)	-	-	-	-	-
3	Tertiary Consumer (Secondary Carnivore)	-	-	-	-	-
4	Quaternary Consumer (Tertiary Carnivore)	-	-	-	-	-
Delta Waterways, Central Portion*						
1	Primary Consumer (Herbivore)	-	-	-	-	-
2	Secondary Consumer (Primary Carnivore)	Golden shiner	Notemigonus *(crysoleucas)*	19	7.8	N/A
3	Tertiary Consumer (Secondary Carnivore)	Redear sunfish	Lepomis *(microlophus)*	17	17	N/A
		Black crappie	Pomoxis *(nigromaculatus)*	6	21	N/A
		Cray fish	Pacifastacus *(leniusculus)*	9	N/A	ND
4	Quaternary Consumer (Tertiary Carnivore)	-	-	-	-	-

1 = When referring to the term "marine", Staff recognizes that these waterbodies are either freshwater or tidally influenced, and thus not actual marine waterbodies but form estuarine environments with brackish water, a condition which commonly occurs when fresh water meets sea water. For example, the confluence of the Sacramento and San Joaquin River within the Sacramento-San Joaquin Delta. This type of ecological succession from a freshwater to marine ecosystem is typical of river estuaries which form important staging points during the migration of anadromous fish species (Moustakas and Karakassis, 2005).

* Sampling sites considered for Delta Waterways Central Portion included the following:
San Joaquin River around Turner Cut, San Joaquin River near Potato Slough, Mokelumne River/Lodi Lake, Mokelumne River near Woodbridge and Old River.

Acronynms used: n = Number of samples ; N/A = Not Analyzed; ND = Non-Detect

Table 3. Freshwater organisms for selected reaches in the Central Valley and average DDE tissue concentrations according to trophic level (Data from the TSMP Database)

Trophic Level	Trophic Level Description	Organism	Genus *(Species)*	n	Mean DDE Concentration (ug/g)	
					Filet/ Muscle	Whole Organism
San Joaquin Watershed (Stanislaus River to Delta Boundary: SJR at Vernalis)						
1	Primary Consumer (Herbivore)	Asiatic clam	Corbicula *(fluminea)*	2	N/A	480
2	Secondary Consumer (Primary Carnivore)	-	-	-	-	-
3	Tertiary Consumer (Secondary Carnivore)	Carp	Cyprinus *(carpio)*	9	580.7	N/A
4	Quaternary Consumer (Tertiary Carnivore)	Red swamp crayfish	Procambarus *(clarki)*	9	N/A	28.5
		White catfish	Ameiurus *(catus)*	46	8,006	N/A
		Channel catfish	Ictalurus *(punctatus)*	44	1,520	N/A
		Large-mouth bass	Micropterus (salmoides)	20	119	N/A
Sacramento River Watershed (Colusa Basin Drain)						
1	Primary Consumer (Herbivore)	Asiatic clam	Corbicula *(fluminea)*	-	N/A	19.5
2	Secondary Consumer (Primary Carnivore)	-	-	-	-	-
3	Tertiary Consumer (Secondary Carnivore)	Carp	Cyprinus *(carpio)*	21	332.5	N/A
		Sacramento sucker	Catostomus *(occidentalis)*	5	ND	N/A
		Sucker	Catostomus spp.	1	39	N/A
		Brown bullhead	Ameiurus *(nebulosus)*	11	450	N/A
4	Quaternary Consumer (Tertiary Carnivore)	White catfish	Ameiurus *(catus)*	12	830	N/A
		Channel catfish	Ictalurus *(punctatus)*	44	1754	N/A
Delta Waterways, Central Portion*						
1	Primary Consumer (Herbivore)	Asiatic clam	Corbicula *(fluminea)*	285	N/A	23.6
2	Secondary Consumer (Primary Carnivore)	Golden shiner	Notemigonus *(crysoleucas)*	2	7.80	N/A
3	Tertiary Consumer (Secondary Carnivore)	Carp	Cyprinus *(carpio)*	4	21	N/A
4	Quaternary Consumer (Tertiary Carnivore)	White catfish	Ameiurus *(catus)*	16	70.67	N/A
		Channel catfish	Ictalurus *(punctatus)*	4	190	N/A
		Large-mouth bass	Micropterus (salmoides)	18	25.5	N/A

* Sampling sites considered for Delta Waterways Central Portion included the following: San Joaquin River around Turner Cut, San Joaquin River near Potato Slough, Mokelumne River/Lodi Lake, Mokelumne River near Woodbridge and Old River

Acronynms used: n = Number of samples ; N/A = Not Analyzed; ND = Non-Detect

1.6.2 OC Concentrations in Water are a Function of OC Concentrations in Sediment

A conceptual model similar to the one presented in Figure 6 was examined to see if the approach is sufficient to justify linkage between suspended sediment and OC concentrations. This was the case for the Santa Ana Regional Water Board's Organochlorine pesticides TMDL in San Diego Creek and Newport Bay (Santa Ana Regional Water Board, 2006). For this case, Staff justified their rationale for using the conceptual model as sufficient because it demonstrated that: (1) the potential risk to human health and/or wildlife is proportional to the OC concentration in fish multiplied by the consumption rate; (2) the OC concentration in the tissue of fish and benthic invertebrates is proportional to the OC concentration in the sediments to which the organisms (or prey organisms) are exposed.

For this Central Valley TMDL /BPA, Staff proposes to use a combination of a conceptual model and other studies conducted elsewhere. Staff looked at three case studies (2 within California and one in Washington State) to see if a general trend between concentration of DDE and total suspended solids (TSS) could be found, which could be assumed to also occur in the Central Valley Waterbodies. For particle-associated pollutants, the pollutant concentration in water is the TSS concentration of the water multiplied by the pollutant concentration on the TSS.

This simplifying assumption is fundamental to many particle-associated TMDLs, such as work conducted in Los Angeles Regional Water Board's Calleaguas Creek for OC pesticides (Calleguas Creek TMDL, 2006) (Figure 10), For the Calleguas Creek TMDL, DDE concentrations in water increased with increasing TSS in agricultural drainage of the Calleguas Creek watershed (Figure 10). Studies on pesticides associated with suspended sediment in San Francisco Bay following the first major storm of water year 1996 showed a linear trend between concentration of DDE and total associated pesticide (Bergamaschi et al., 2001) (Figure 11). Findings related to suspended sediment and DDT in the Lower Yakima River TMDL demonstrated that DDT and suspended sediment concentrations in the Yakima River basin were highly related. Using 1995 monitoring data, a regression was developed of t-DDT (t-DDT = DDD+DDE+DDT) as a function of TSS (Figure 12). The best linear regression equation with a coefficient of determination (R^2) of 0.747 was based on 71 data pairs from river and tributary sites with detectable t-DDT concentrations (Yakima River TMDL, 1997) (Figure 12).

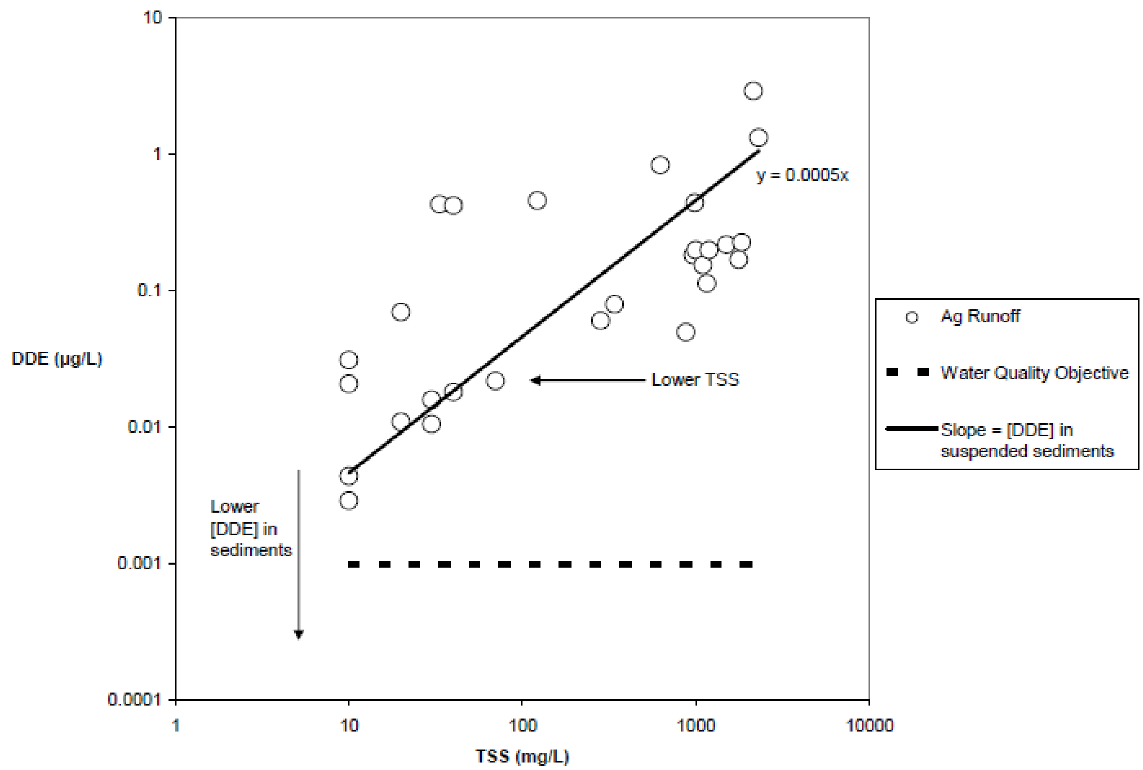

Figure 10. DDE concentrations in water increase with increasing TSS in agricultural drainage of the CCW. Note that the slope of the line gives the DDE concentration of suspended particulate matter (= 0.0005 µg DDE /mg sed or 500 ng/g). (Adapted from Calleguas Creek TMDL, 2006)

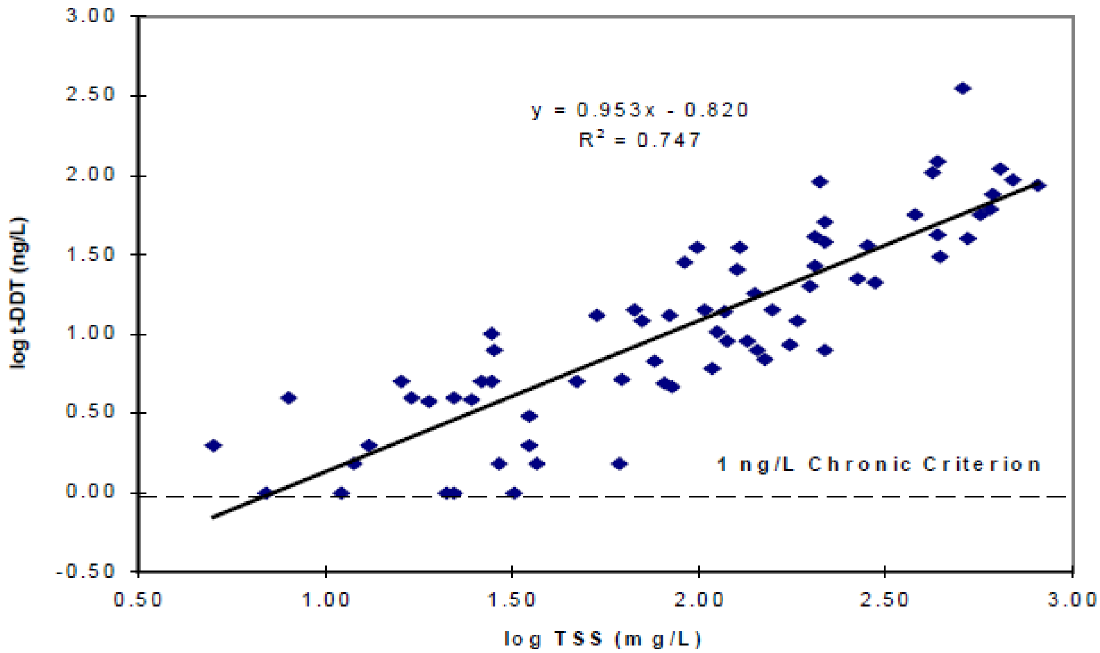

Figure 11. Regression of t-DDT as a function of TSS for water samples collected from the lower Yakima River basin canals, tributaries, drains and main stem river. (Adapted from Yakima River TMDL, 1997)

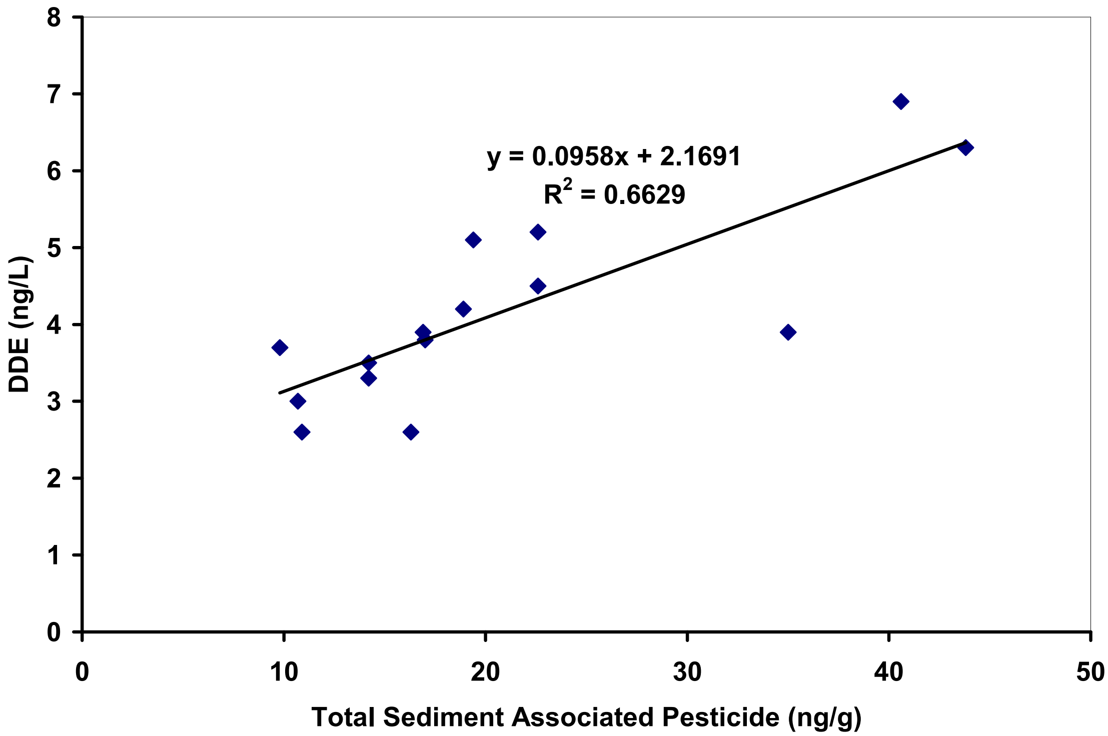

Figure 12. Pesticides associated with suspended sediments entering San Francisco Bay following the first major storm of water year 1996. (Adapted from Bergamaschi et al., 2001)

Though conducted in fairly different environmental conditions, the above three case studies indicate that the relationship between suspended sediment and OC pesticides is positively linear. The common aspect among the three studies is particle-associated pollutants and sediment transport. This suggests that the relationship between the concentration of a pollutant is highly dependent on the TSS. Other related critical variables may include soil type, topography and rainfall intensity (all of which determine erosion potential). Staff concludes that even though there is no paired TSS and fish tissue data for the Project Area, based on the aforementioned reasons, Staff assumes that similar trends would be observed for Central Valley watersheds. The results portrayed in the above case studies show that the linear relationship is central to understanding how reducing OC concentrations in sediments will not only lead to lower pollutant concentrations in the water column and sediment but will result in reduced concentrations in fish

1.6.3 OC Concentrations in Sediment are a Function of OC Loading and Sediment Transport

Pollutant concentration in sediments is the master variable for attainment of beneficial uses in this TMDL analysis. OC loads are related to OC concentrations in sediment via a simple, one-box mixing model (Figure 5). In reality, multi-box sediment transport dynamic models are more accurate representations, but the one-box approach is sufficient for the purposes of this BPA/TMDL, and will help to identify the most logical next steps in TMDL implementation.

Based on illustration shown in Figure 5, the sediments in any reach of the Central Valley watersheds, could be considered to be a well-mixed “reservoir” of a defined mass. Sediments enter from upstream, these deposits are mixed by winds, currents, tides, and organisms, and then re-suspended. OC pollutants adsorb on sediments or, if in the dissolved phase, are scavenged onto sediments. Sediments leave the box representing a reach by the “sediment out” arrow either through current flow or tidal action (Figure 5).

The long-term average concentration of OC pollutants in any given reach will simply be the long-term annual average of resident fish species or benthic organisms. This is in turn related to the sediment loading rate for that reach. Thus a reasonable basis for attaining fish tissue target concentration is reduction of sediment loads.

The importance of this concept is that it leads directly to the implementation actions needed to augment the effects of natural attenuation. The fastest way to attain the target concentrations of OCs in sediments, and therefore attain beneficial uses, is to address the largest controllable OC loads. In general, this will mean assessing OC concentrations in different land use types, and implementing management practices to reduce soil erosion, and sediment transport from areas with the highest OC concentrations in sediments.

1.7 Site Specific Data Challenges
Although the basic mechanisms that transport terrestrial soils are understood (i.e., erosion from agricultural and urban soils with historic OCs), more specific information about the concentrations and quantities of sediment transported by runoff and erosion are not currently available.

The proposed BPA/TMDL is based on the best available information at this time. For the Central Valley waterbodies, in some circumstances there is an absence of site specific and/or paired data. Reference to paired data is where data for multiple media types (such as sediment OC, water OC, and/or fish tissue OC concentrations) or constituents (such as TSS and fish tissue OC concentrations) are collected at the same location and time. Where there is an absence of such data, Staff has examined work done in other geographic areas to see if there is a generalized trend that can be applied to the Central Valley waterbodies.

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