

**Sacramento-San Joaquin Delta  
Regional Ecosystem Restoration Implementation Plan  
Ecosystem Conceptual Model**

**Chemical Stressors in the Sacramento-San Joaquin Delta**

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## PREFACE

This Conceptual Model is part of a suite of conceptual models which collectively articulate the current scientific understanding of important aspects of the Sacramento-San Joaquin River Delta ecosystem. The conceptual models are designed to aid in the identification and evaluation of ecosystem restoration actions in the Delta. These models are designed to structure scientific information such that it can be used to inform sound public policy.

The Delta Conceptual Models include both ecosystem element models (including process, habitat, and stressor models); and species life history models. The models were prepared by teams of experts using common guidance documents developed to promote consistency in the format and terminology of the models  
[http://www.delta.dfg.ca.gov/erpdeltaplan/science\\_process.asp](http://www.delta.dfg.ca.gov/erpdeltaplan/science_process.asp) .

The Delta Conceptual Models are qualitative models which describe current understanding of how the system works. They are designed and intended to be used by experts to identify and evaluate potential restoration actions. They are not quantitative, numeric computer models that can be “run” to determine the effects of actions. Rather they are designed to facilitate informed discussions regarding expected outcomes resulting from restoration actions and the scientific basis for those expectations. The structure of many of the Delta Conceptual Models can serve as the basis for future development of quantitative models.

Each of the Delta Conceptual Models has been, or is currently being subject to a rigorous scientific peer review process. The peer review status of each model is indicated on the title page of the model.

The Delta Conceptual models will be updated and refined over time as new information is developed, and/or as the models are used and the need for further refinements or clarifications are identified.

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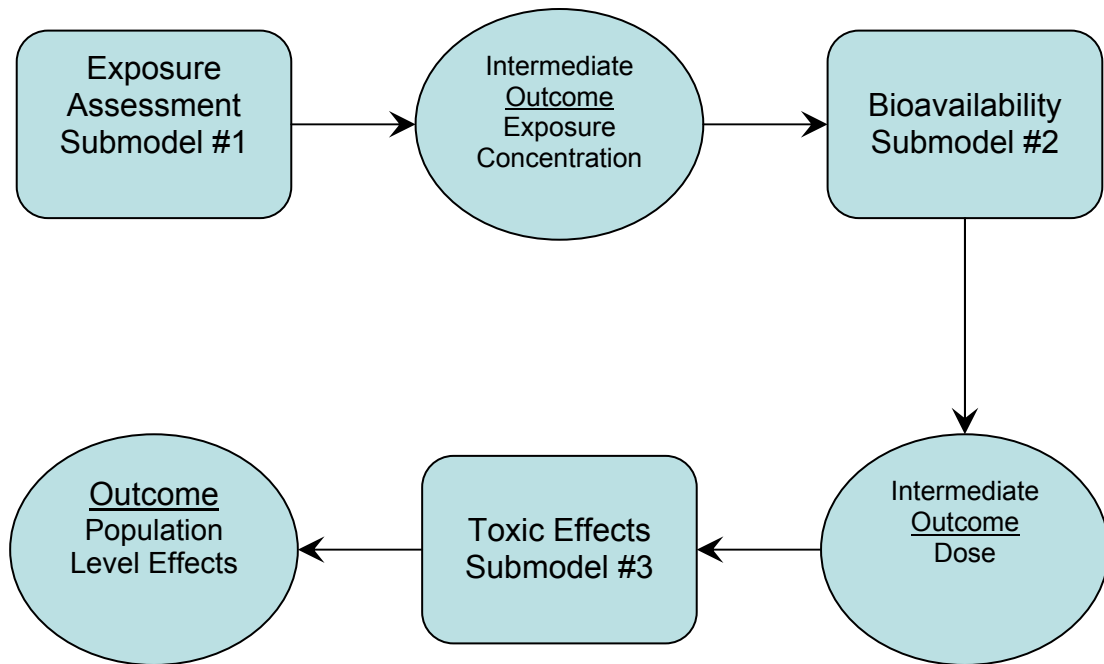
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# 1. Overview

The Sacramento-San Joaquin Delta ecosystem comprises many different habitat types, and is home to a large number of species. Thousands of chemical contaminants have been or are being introduced into the Delta. The conceptual model presented here is therefore general in nature, and is intended to provide a framework for more refined models for individual species, habitats and, in particular, contaminants of interest, for example selenium, mercury and pyrethroids.

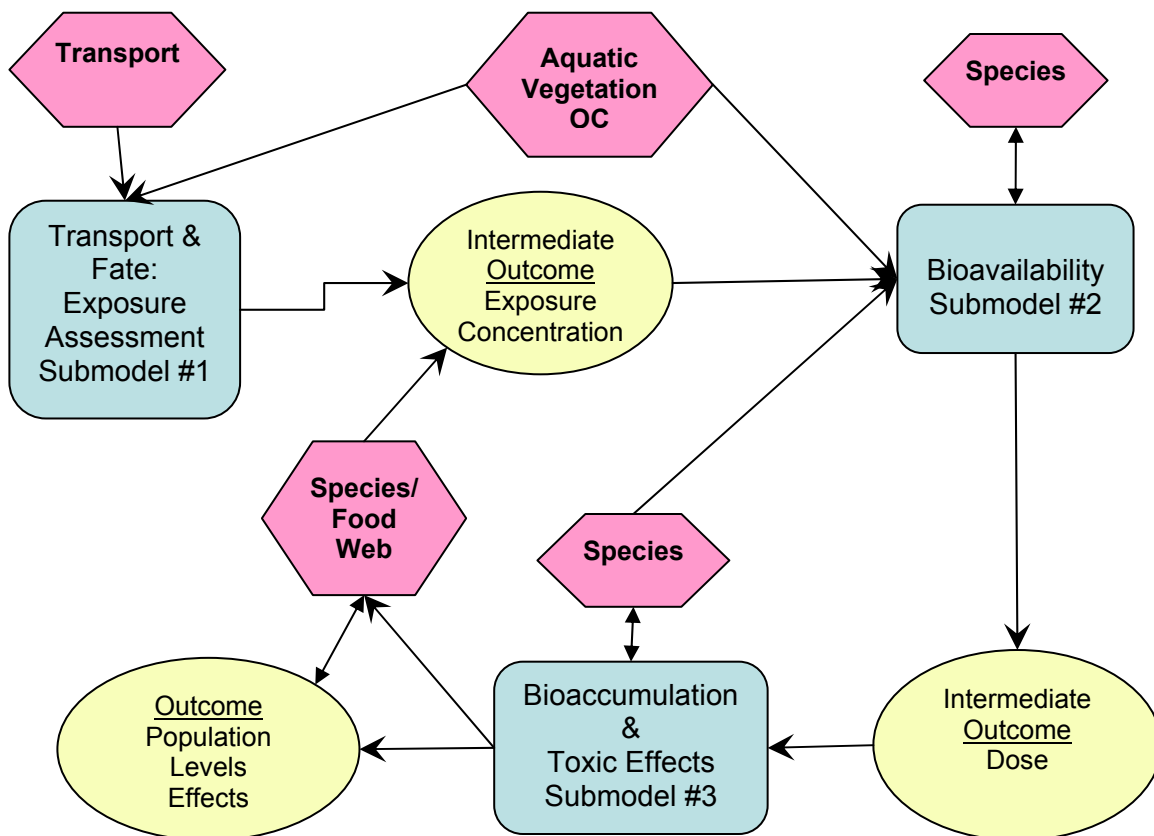
The model consists of three major submodels (Figure 1). Submodel 1: Exposure assessment which includes fate and transport of contaminants and the co-occurrence of chemicals with Delta organisms; the intermediate outcome of this submodel is “Exposure Concentration”. Submodel 2: Bioavailability of contaminants to Delta organisms; the intermediate outcome of this submodel is “Bioavailable Concentration” or “Dose”. Submodel 3: Toxic effects assessment with the final model outcome “Population Level Effects”.

In the following narrative, we provide a description for each submodel, its parameters, and linkages to other models. We discuss the model’s limitations and provide recommendations for its application in management.



*Figure 1. Main components of the general model; oval shapes are intermediate or final outcomes of submodels.*

The general contaminants model requires data input from a number of other DRERIP models and will feed back into several of these as outlined in Figure 2.



*Figure 2. The diagram outlines the interaction of individual submodels of the general contaminant model (rounded squares), outcomes (ovals) and other Delta conceptual models (hectagonal shapes).*

Most contaminants in the environment occur in complex mixtures. Appendix A describes potential approaches to the assessment of mixtures. Also, recognizing that not all contaminants can or should be addressed, Appendix B describes a process for identifying priority chemicals of concern.

The applicability of the general model is illustrated in the conceptual model for , synthetic pyrethroid insecticides (Werner and Oram, 2008). Although many different pyrethroids exist, the members of this group share many chemical and toxicological characteristics.

## 2. Problem Formulation and Overview

The general contaminants model described here focuses on the transport, fate and toxic effects of chemical contaminants in the aquatic environment. The number of chemical contaminants of potential concern is large. Nearly 23 million organic and inorganic compounds have been indexed by the American Chemical Society's Chemical Abstracts Service (CAS) in their Registry (CAS, 2004). Over seven million of these are commercially available, while the US Environmental Protection Agency (EPA) "Priority Pollutant List" contains a mere 126 compounds for which receiving-water benchmarks exist. An unknown number of these chemicals are introduced into the Delta from a multitude of sources. These include point sources such as effluents from municipal and industrial wastewater treatment plants, as well as urban, agricultural and industrial non-point sources. Chemical contaminants, in particular insecticides and metals have in the past been shown to be present in the Delta at toxic concentrations, but the lack of a comprehensive monitoring program presently precludes an assessment of contaminant impacts on the Delta ecosystem. Contaminants can negatively affect organism survival and compromise ecological fitness of individual species, consequently altering food webs and ecosystem dynamics, as well as represent hazards for public health, most prominently via drinking water and fish consumption

Contaminant effects are species-specific. Many contaminants, in particular pesticides and heavy metals, are more likely to directly affect lower trophic levels, with potential negative effects on species composition and food web dynamics. At higher trophic levels, toxic effects are less likely to be lethal (i.e. no fish kills), but sublethal toxicity may reduce ecological fitness through impaired growth, reproduction, or behavior, or increase the organism's susceptibility to disease.

Land use, pest control practices, and urban development largely determine non-point source input of contaminants within the delta, while population size, and the number and type of industrial facilities in nearby cities determine composition and volume of point-source effluents (industrial and municipal wastewater treatment plants). Rivers are important sources of contaminants. In addition to contaminants from urban areas, they carry mercury-enriched runoff from historic mining activities, as well as pesticides and selenium into the delta. In addition, herbicides and insecticides are applied directly to the water surface for aquatic plant and mosquito control. This is very important for migratory species that spend part of their life-cycle in rivers.

*Current-Use Pesticides:* Both winter storm runoff and irrigation return water from agricultural areas can contain fertilizer, current-use pesticides and other chemicals (so-called inert ingredients in pesticide formulations). While little is known about the potential effects of herbicides on phytoplankton, insecticides, in particular organophosphates (e.g. chlorpyrifos, diazinon) have been shown to be present at acutely toxic concentrations in tributaries and the delta (Kuivila and Foe, 1995; Werner et al., 2000; California Regional Water Quality Control Board Agricultural Waiver Program, 2007). The US EPA's decision to phase out certain urban uses of organophosphate insecticides because of their potential for causing toxicity in humans has led to their

gradual replacement by pyrethroids, a class of synthetic insecticides applied in both urban and agricultural areas. In recent years, pyrethroids at toxic concentrations have been detected in the majority of sediment samples collected from water bodies draining agricultural areas in the Central Valley (Weston et al., 2004; California Regional Water Quality Control Board Agricultural Waiver Program, 2007), as well as from urban creeks in the Bay/Delta region (Amweg et al., 2006; Woudneh and Oros, 2006a & b). Dissolved pyrethroid concentrations toxic to aquatic life were detected in water samples from Central Valley agricultural drains and creeks (Central Valley Regional Water Quality Control Board, 2007; Bacey et al., 2005), and tributaries to San Francisco Bay (Woudneh and Oros, 2006a & b).

*Legacy Pesticides:* Residues of legacy pesticides, primarily organochlorine (OC) pesticides including DDTs, chlordanes and dieldrin, remain high. These chemicals were used 30-40 years ago and are highly persistent. In San Francisco Bay, the compounds and their breakdown products occur at concentrations high enough to contribute to advisories against the consumption of sport fish from the Bay (Connor et al., 2007). Connor et al. (2007) report that these legacy pesticides continue to enter San Francisco Bay through runoff from California's Central Valley, from dredging and disposal of dredged material and other sources. Recently, the California Regional Water Quality Control Board Agricultural Waiver Program (2007) reported detection of DDT and other OC pesticides in agricultural irrigation ditches and drainage canals of the Delta region.

*Mercury:* The Delta and many of its tributaries are on the State Water Quality Control Board's 303 (d) list of impaired water bodies because of mercury contamination. Mercury contamination in the area has predominantly been attributed to historic gold and mercury mining in the watershed (Conaway et al., 2007 and cited references therein). However, despite reductions in mercury input to the system, mercury remains a persistent contaminant in the sediments of the estuary, and concentrations in some fish are still elevated, exceeding human health screening values. Mercury has also been measured at potentially toxic concentrations, and associated with detrimental effects in some waterbirds in the San Francisco Bay area (Conaway et al., 2007 and cited references therein). The most bioavailable and therefore toxic form of mercury is methylmercury. Many factors are involved in the transformation and biomagnification of inorganic mercury to methylmercury, and while wetlands are environments where mercury is methylated, recent studies show that not all wetlands are the same (Alpers et al., 2008). Some produce ten times more mercury than others, and some wetlands even appear to reduce methylmercury concentrations.

*Selenium:* Selenium in agricultural drainage that affected aquatic ecosystems at Kesterson National Wildlife Refuge in the western San Joaquin Valley in the 1980s remains a threat because drainage problems are unresolved. Loading of selenium to the refuge through the San Luis Drain from Westlands Water District caused massive bird deformities and fish extinctions (Presser and Luoma, 2006). Loading of selenium to the San Joaquin River through a portion of the San Luis Drain and Mud Slough was authorized in 1995. This regulated discharge of agricultural drainage to the river is from approximately 100,000 acres of the western San Joaquin Valley (Presser et al., in prep.).



Monitoring of selenium loads at other sites in the drain, slough, and river ecosystems show variability due to biological uptake in particulate matter and biota (in-transit loss) (Presser and Piper, 1998). Monitoring of the San Joaquin River at Vernalis at the entrance to the Delta is minimal and therefore selenium is extrapolated with some uncertainty. No further downstream monitoring of selenium takes place in the Delta. Other sources of selenium are refineries and wastewater treatment plants. In 1995, oil refineries reduced their selenium inputs to the estuary by about half, in response to court-ordered mandates. Wastewater treatment plants are a minor source of selenium compared to the refineries.

Selenium is a reproductive toxicant. Selenate, the form of selenium most common in agricultural drainage, can be converted to selenite in chemically reducing environments, such as wetlands and organic-rich, stagnant waters. Selenite is bioaccumulated much more readily than selenate. In the San Francisco Bay-Delta, selenium concentrations in white sturgeon are just above the monitoring threshold of 5.9 µg/g. While these concentrations are below the current USEPA standard of 7.9 µg/g, there is substantial scientific evidence indicating that this standard is not protective enough and more stringent standards for the Bay-Delta are being considered.

*Other Heavy Metals:* Buck et al. (2007) report that dissolved copper concentrations remain elevated in the farthest reaches of the San Francisco Bay at the Delta and Estuary interface, where the toxic effects of copper may not be buffered by organic ligands like in the more saline waters of the Bay. The Regional Monitoring Program for Water Quality in the San Francisco Bay (RMP) also identified nickel as an important water pollutant in the estuary due to watershed geology and inputs from wastewater treatment plants as well as urban runoff (Yee et al., 2007).

Organometallic compounds are either synthetic (e.g. tributyltin) or the products of microbial transformations that occur in the environment (e.g. methylmercury). Organotins have been used as polymer stabilizers, catalysts, wood preservatives and antifouling agents. Tributyltin (TBT), in particular, is widely used in antifoulant paints for boats. TBT is very stable and highly toxic to non-target invertebrate organisms.

*PCBs:* Polychlorinated biphenyls (PCB) are industrial legacy contaminants, i.e. chemicals no longer in use but ubiquitous in the environment. They are very persistent, and their bioaccumulation potential in aquatic organisms is high. Contamination of water bodies and wildlife with PCBs is therefore widespread. Although PCBs were banned in the late 1970s, PCB concentrations in some San Francisco Bay sport fish today are more than ten times higher than the threshold of concern for human health (Davis et al., 2007 and cited references therein). From 1993 to 2003, the PCB water quality criterion was exceeded in 325 of 361 (90%) of samples collected at all San Francisco Bay monitoring stations. Three monitoring stations had typical concentrations that were more than ten times higher than the water quality objective. PCB contamination is generally associated with industrial areas along shorelines and urban runoff in local watersheds. Although Davis et al. (2007) report that significant PCB loads enter San Francisco Bay through Delta outflow, no such monitoring data are available for the Delta.

PCB concentrations in San Francisco Bay and the Delta may be high enough to adversely affect wildlife, including rare and endangered species (Davis et al., 2007 and cited references therein). Fish-eating species at the top of the food web generally face the greatest risks. Populations residing in PCB-contaminated sites also face relatively high risks from direct exposure.

*PAHs*: Polycyclic aromatic hydrocarbons (PAH) are generated by the incomplete combustion of organic matter and enter the aquatic environment through atmospheric deposition or stormwater runoff from roads, urban and industrial areas. Another potential source for PAH contamination is from creosote, which has been used to impregnate wood products such as pier pilings. Creosote can contain up to 90% PAH by weight. Stormwater runoff from urban and industrialized areas, and inflow from tributaries (including the Delta) are the major sources of polycyclic aromatic hydrocarbons (PAHs) in San Francisco Bay (Oros et al., 2007). Oros et al (2007) report relatively low PAH concentrations in the Sacramento/San Joaquin Rivers and the Delta during the 1993-2001 monitoring period.

*“Emerging Pollutants”*: Effluents from municipal wastewater treatment plants are significant sources of ammonium as well as complex mixtures of contaminants that affect reproductive endocrine function (Kidd et al., 2007; Huang and Sedlak, 2001 and references therein). A growing number of organic compounds ranging from flame retardants, pesticides, plasticizers, and water repellents to fragrances, pharmaceuticals and personal care product ingredients have been shown to mimic the actions of natural hormones. Very few of these are presently monitored in San Francisco Bay and the Delta. A recent study by the San Francisco Estuary Institute (Hoenicke et al., 2007) detected high concentrations of flame retardants (polybrominated diphenyl ethers, PBDE) in clam (*Corbicula fluminea*) tissue from the Sacramento and San Joaquin Rivers. Tissue concentrations in striped bass and halibut showed significant increases in PBDE concentrations between 1997 and 2003, and these compounds were also found in Least Tern and California Clapper Rail eggs.

Endocrine disrupting chemicals (EDCs) can interfere with the hormonal systems in humans and wildlife, and act at extremely low concentrations resulting in negative effects on reproduction and development. Exposure of fish populations to low concentrations of such compounds can have dramatic effects. In a multi-year field study, Kidd et al (2007) showed that chronic exposure of fathead minnow to 5-6 ng/L 17alpha-ethynylestradiol (EE<sub>2</sub>, a synthetic estrogen used in birth-control pills) led to near extinction of this species from the experimental lake. Huang and Sedlak (2001) measured concentrations of up to 4.05 ng/L 17beta-estradiol (E<sub>2</sub>, the natural estrogen) and 2.45 ng/L EE<sub>2</sub> in treatment plant effluent after secondary treatment/chlorination, while concentrations were mostly below 1 ng/L in effluents treated with more sophisticated methods.

The complexity of evaluating the effects of contaminants on key species and foodwebs in the Bay and Delta has been daunting. However, numerous toxicologists

agree that approaches exist to answering priority resource management questions. For example, we can evaluate whether contaminants are involved in the decline of certain species in the Delta, and how restoration activities mobilize contaminants such as mercury. What is needed is a framework that bridges ecological and toxicological perspectives, making the science relevant to managers. The Delta conceptual modeling effort can provide tools and a framework for this next generation of indicator implementation and provide focus in assessing tradeoffs among alternative strategies. An iterative approach and varying strategies can be used to assess problems associated with both individual chemicals and chemical mixtures.

### 3. General Conceptual Model

#### 3.1 Submodel 1: Transport and Fate of Contaminants - Exposure Assessment

Submodel 1 consists of 1) the modeling of transport and fate of contaminant(s), and 2) an estimation of the degree of contact with specific Delta species and life-stages (link with *Species Life History* conceptual models) that co-occur with specific chemical(s).

Input of chemical stressors into the Delta occurs from a vast variety of sources including old mines, agricultural irrigation return water, industrial point-sources, sewage treatment plants, stormwater runoff, direct application to the water surface, chemical spills and atmospheric input (drift, rain). These sources can be outside the Delta, in which case chemicals are transported to the Delta via rivers and their tributaries or groundwater and subsurface flow, or they can be located directly within the Delta. The combined chemical load entering the Delta is a result of their use patterns (human activities), climatic and hydrologic factors and the physical-chemical properties of the chemicals themselves. Habitat structure within the receiving water body and hydrodynamic factors such as flow and sediment transport, are important drivers of how chemicals partition between sediments, plants and water, and where they will accumulate in the system.

The fate and transport submodel integrates these elements into a framework that allows for the spatially and temporally explicit assessment of substrate-specific concentrations of chemical stressors.

##### 3.1.1 Chemical Use

Sources of contaminants can be natural or anthropogenic. How a given chemical stressor is transported into the Delta is a function of where (spatial use pattern), when (temporal use pattern), and how (causal use pattern) that chemical is used or released into the environment. For example, chemical stressors associated with agricultural use (e.g., pesticides such as pyrethroid insecticides, selenium) are delivered to Delta waters in a way that is completely different than chemical stressors associated with municipal wastewater (e.g. metals, pharmaceuticals) or direct application of pesticides for aquatic plant and mosquito control. Thus, it is critical to obtain information on the spatial,

temporal, and causal patterns of use quantitative information for each chemical stressor of interest. Fortunately, much of this information already exists for pesticides (e.g., pesticide use patterns in the Sacramento River watershed were documented by U.S. EPA (2006) and pyrethroid use patterns in the Central Valley were documented by Oros and Werner (2005)). Generalizations can be made from chemical use patterns that describe the relative transport potential of a given contaminant. For example, a pesticide with high dry season use is likely to have a lower transport potential than a pesticide with high wet season use because of the increased potential for storm driven runoff during the wet season to wash the pesticide off the agricultural field into adjacent surface waters. However, irrigation return water as well as discharges from wastewater treatment plants and industrial operations can transport contaminants into the Delta during the summer and fall when river flows and therefore dilution potential is minimal. Unfortunately, a large data gap exists for loads of substances that are not analyzed for and may have substantial detrimental effects.

### **3.1.2 Climate and Watershed Hydrology**

The hydrology of the Sacramento-San Joaquin River Delta watershed is likewise important to understanding the fate and transport patterns of chemical stressors in the Delta. Two aspects of the Delta's hydrology are crucial to the transport and fate submodel: 1) temporal and spatial patterns of precipitation and 2) freshwater flow. Information regarding when and where precipitation occurs (October-May in Northern California) can be combined with information regarding chemical use patterns to estimate wash-off loads of chemical stressors into small tributaries (i.e., stormwater runoff loads from urban lands to creeks and storm drains and wash-off loads from agricultural lands). Freshwater flows are important for estimating dilution and transit times of these loads to the Delta. Depending on the desired level of model sophistication, ancillary data regarding riparian areas, watershed soils, slope, and land cover may also be important for determining chemical loads to the Delta. Although major chemical releases associated with agricultural return water have been studied (e.g. Kuivila and Foe, 1995), other hydrologic modifications such as the Vernalis Adaptive Management Plan (VAMP), and flooding of major bypasses have unknown effects on contaminant distribution in the system. The detrimental effects of using irrigation return water to create wildfowl habitat at Kesterson Reservoir with resulting selenium toxicity is an example of the need to integrate ecological and toxicological principles.

### **3.1.3 Factors Affecting Fate and Transport**

#### *3.1.3.1 Contaminant Properties*

The physical-chemical properties of chemicals directly influence their transport potential (behavior) and spatial and temporal distribution in the system. The physical – chemical properties of chemical stressors that determine their fate and transport are: speciation, lipophilicity (generally expressed as the  $k_{oc}$  or  $k_{ow}$ ), solubility in water,

volatility (Henry's law coefficient), and degradation half-life, which is substrate-dependent.

Speciation is important for understanding the solubility, sorption, and volatility of metals and metalloids. For example, speciation is a critical factor in understanding the potential of mercury to form the bioavailable and toxic methyl-mercury (see Mercury Model (Alpers et al., 2008)). Parameters that affect speciation are ionic strength, temperature, pH, Eh, concentrations of competing cations, and ligand concentrations. Organic compounds (DOC) are good chelating agents and will form complexes with metals in solution rendering them less bioavailable and less toxic.

The fate and transport of organic compounds is controlled largely by the selective partitioning between water and sediment. Partitioning of organic compounds is based mainly on their ability of a chemical to adsorb to soil and sediment, its organic carbon adsorption coefficient ( $K_{oc}$  or  $\log K_{oc}$ ) or the octanol-water partition coefficient ( $K_{ow}$  or  $\log K_{ow}$ , Table 1), solubility in water, volatility (Henry's law coefficient), and half-life (substrate-dependent). Measurements of these parameters can vary widely. Software programs and databases for estimating environmental and physical/ chemical property parameters of chemicals are available at: [http://www.syrres.com/esc/est\\_soft.htm](http://www.syrres.com/esc/est_soft.htm) and <http://logkow.cisti.nrc.ca/logkow/search.html>. In general, the  $K_{ow}$  and  $K_{oc}$  of a chemical are inversely proportional to its solubility in water, and solubility increases with increasing water temperature. Many organic compounds, including pyrethroid and organochlorine pesticides, PCBs, and PAHs, are relatively hydrophobic and thus tend to preferentially partition to sediment particles (both suspended and bedded). Sediment transport processes therefore often determine the overall fate and transport of organic contaminants in environmental systems, making development of a sediment budget essential to predicting the ultimate fate of these contaminants.

Table 1. Examples of physical-chemical properties for select organic contaminants. Unless otherwise noted, values are from Mackay et al (2006).

Chemical/ Group	<sup>1</sup> Log $K_{ow}$	Log $K_{oc}$	Solubility	Half-Life in Water
PCBs	4 - 8	4 - 7	$10^{-5} - 10^0$	> 6 yrs; 56 yrs <sup>2</sup>
Dioxin	4.01 - 4.65	4.01 - 4.34	0.8 - 0.9	?
Benzo-a-Pyrene (PAH)	5.12 - 6.78	6.74	$10^{-3}$	1 - 13 d
Pyrene (PAH)	4.88 - 5.22	4.92	$10^{-1}$	1 - 6 d
DDT(Organochlorine)	3.98 - 6.94	3.90 - 6.59	$10^{-3} - 10^{-2}$	8 - 52.5 yrs; 10 yr avg.
DDE (Organochlorine)	4.28 - 6.96	3.7 - 6.0	$10^{-3} - 10^{-2}$	6.9 days - 120 yrs
DDD (Organochlorine)	4.82 - 6.33	4.91 - 5.89	$10^{-3} - 10^{-1}$	2 - 15.6 yrs
Permethrin (Pyrethroid)	6.5 <sup>3</sup>	5.36	0.07	14 - 259 d
Esfenvalerate (Pyrethroid)	6.22 <sup>3</sup>	5.4	0.004	
Bifenthrin (Pyrethroid)	6.0 <sup>3</sup>	3.80 - 5.37	0.1	
Chlorpyrifos (Organophosphate)	4.96 <sup>3</sup>	4.13	1.39	7 - 120 d
Diazinon (Organophosphate)	3.81 <sup>3</sup>	2.28 - 3.20	40 - 60	13 - 80 d
Carbofuran (Carbamate)	2.32 <sup>3</sup>	1.45	351	2 - 864 hrs

<sup>1</sup>Values based on Aroclor mixtures

<sup>2</sup> Davis (2004)

<sup>3</sup> from <http://logkow.cisti.nrc.ca/logkow/search.html>.

Degradation half-lives of organic contaminants span many orders of magnitude (from days to centuries). Chemicals of most concern have degradation half-lives longer than the time scales of water and sediment transport (e.g. PCBs, DDT/DDD/DDE). These chemicals tend to persist in receiving waters (and sediments) for periods long enough to be a risk to resident biota. The distribution of in-place contaminants is often poorly characterized and fate and transport of substances locked in sediment may impact important management considerations such as the proposed TMDL for PCBs. At the other end of the spectrum, pyrethroid insecticides have half-lives on the order of days-weeks, but degradation time can vary widely and strongly depends on the presence of UV-light (see Pyrethroid Model [Werner and Oram, 2008]).

Volatility of a chemical determines the degree of transport out of a surface (soil, water) into the atmosphere. The process of volatilization is a function of the chemical-specific Henry's law constant (H), which is temperature dependent. When  $H < 3 \times 10^{-7}$  atm m<sup>3</sup>/mol, a chemical is less volatile than water. When  $H > 10^{-5}$ , volatilization of a chemical is significant in all surface waters.

### 3.1.3.2 Habitat Properties

[→ Links to/Input of Data from Aquatic Vegetation/Organic C Models]

The dominant properties of the aquatic habitat directly influence sequestration, degradation and compartmentalization of chemicals within the system. They are water chemistry (pH, conductivity, hardness and temperature), turbidity (amount and particle size distribution of suspended sediments), organic carbon (DOC, POC), microbial activity and UV-light intensity.

Temperature is one of the most important factors influencing the fate of chemicals. It generally enhances the degradation (half-life) of organic chemicals, but also affects the speciation of metals e.g. enhanced transformation of Hg to Methyl-Hg through bacterial activity (Benoit et al, 1998; Mason et al, 1995; Alpers et al., 2008). High water temperature also encourages plant growth (see Aquatic Vegetation models (Anderson, in prep.)), which, in turn, reduces light penetration and can lead to slower breakdown of chemicals.

Turbidity is of importance for the sequestration of hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and pyrethroids (see Pyrethroid Model (Werner and Oram, 2008)), which tend to bind quickly to suspended organic (phytoplankton) and inorganic (suspended sediment) particles (Oros and Ross, 2004; Oros and Werner, 2005). High turbidity also reduces light penetration and therefore UV-light intensity in the water column and benthic habitats, and will therefore influence plant/phytoplankton growth as well as photodegradation of chemicals. In the case of

PAHs UV-light can lead to photo-activation, and thus increased toxicity of chemicals (Monson et al, 1999).

Water chemistry parameters, salinity, pH, hardness, organic carbon concentration and – for sediments – the redox potential, are important factors affecting the complexation and speciation of hydrophobic chemicals, and metals such as mercury, copper and selenium (see Mercury (Alpers et al. 2008), Pyrethroid (Werner and Oram, 2008) and Selenium (Presser et al., in prep) models). These factors influence contaminant bioavailability, uptake and toxicity to aquatic life. For example, ammonia toxicity is greatly reduced at low pH, because the ionized form of ammonia,  $\text{NH}_4^+$ , which is favored at low pH, is considerably less toxic than the unionized form,  $\text{NH}_3$ . The solubility of inorganic Hg is enhanced by higher concentrations of chloride and/or higher pH (Alpers et al., 2008). Generally, toxicity of metals is reduced as salinity and hardness increase. Similarly, organic carbon forms complexes with hydrophobic compounds and metals, and thus reduces bioavailability and toxicity.

→ Data input from the *Transport (Burau et al., in prep.)* and *Sediment (Schoellhammer et al., 2007) Models* will provide information on the movement of water and sediment within the Delta, and will therefore be key to determining the spatial and temporal distribution of chemical stressors within the system.

### 3.1.3 Chemical Distribution – Partitioning

Biological, environmental and chemical factors described above will determine which matrix within the aquatic system a specific contaminant will partition into. Hydrophobic contaminants such as pyrethroids will partition mainly to the particulate/sediment/organic carbon compartment or adsorb to plants and detritus, while polar forms of Hg and Se will remain in the aqueous phase.

### 3.1.4 .Loss

Loss of contaminant can occur due to volatilization (e.g. organic solvents), degradation or transformation due to microbial activity, hydrolysis or photolysis, storage in sediments or export from the Delta.

→ *Data input from Species Life History Models* will provide information on the co-occurrence of contaminants and organisms in the Delta. Given the estimated contaminant levels in various media, it must be determined which species and life-stage, and by what route organisms are exposed to a contaminant. For example, early life stages of many Delta fish species are in the system during late winter and spring, a time when stormwater runoff from agricultural and urban areas can transport contaminants such as dormant spray pesticides and PAHs/metals into the Delta. Such early life stages are generally far more sensitive to contaminants than adults, and the toxic effects of these contaminants may be far more serious than if the same concentrations are present in the fall. Similarly,

fish species, that spend their whole life in the Delta are likely to be exposed to different contaminants and exposure regimes than juvenile salmonids who migrate through the system within a relatively short period of time. Bottom-feeding fish or sediment-dwelling invertebrates are likely to be exposed to sediment-associated contaminants (via diet and interstitial water), while pelagic organisms are mostly exposed to dissolved and suspended particle-associated contaminants in the water column.

Determining the likely co-occurrence of contaminants with certain life-stages and/or Delta species will help prioritize the species and life-stages at highest risk of contaminant exposure in the Delta. It is also important to take into account how prior exposures modify subsequent exposures through avoidance, attraction or modification of consumption rates. In addition, an organism may be exposed via multiple routes such as diet, respiration and direct contact.

### **3.1.5 Intermediate Outcomes:**

#### *3.1.5.1 Exposure of Aquatic Organisms*

*Exposure* signifies the degree of contact of an organism with a chemical. This takes into account the spatial and temporal distribution of chemical within the Delta system, and whether the chemical is deposited in sediments, adsorbed to plant/detritus material, suspended sediments or remains in solution. The most significant factors related to exposure are the pathway, magnitude (i.e. chemical concentration), duration, and frequency of exposure. Aquatic organisms may be simultaneously exposed to chemicals present in water, sediment, and/or food depending on the species, life stage, life history, trophic level, and feeding strategy.

#### *3.1.5.2 Contamination of Drinking Water – Human Exposure*

The Delta is used as a drinking water supply, either solely or partially, for over 23 million Californians. The Delta periodically contains significant concentrations of precursors – bromide and organic carbon – that can lead to the formation of regulated disinfection byproducts.

#### *3.1.6 Limitations and Recommendations*

Information on the sources and quantities of chemical stressors introduced into the Delta system is required (see *Chemical Use Patterns*). However, quantitative data for most chemical stressors is relatively scarce. Furthermore, there are many chemicals in the environment for which we do not have analytical methods that can detect them at toxicologically relevant concentrations.

In March 2006 the USEPA issued an analysis of pesticide loads in the Sacramento River Watershed. Estimated loads of five pesticides (chlorpyrifos, diazinon, diuron, paraquat dichloride, and permethrin) to the Sacramento River will be valuable to the Delta restoration planners. Valuable information for pyrethroid use patterns were



reported by Oros and Werner (2005). Some information on pharmaceuticals, hormones and other organic wastewater contaminants, albeit not Delta specific, has been summarized by Kolpin et al. (2002). A major management need is to utilize GIS techniques to create visual depictions of the spatial and seasonal patterns of contaminant distribution. This should be a targeted assessment addressing only times and places that are related to evolved management questions. An example would be to depict contaminant distribution during the periods of unexplained mortality for the delta smelt. A second management need is to support the development of analytic techniques for compounds that are not being measured but should be including numerous emerging compounds that may cause endocrine disruption and other reproductive harm.

Human Health: Drinking water guidelines and maximum contaminant levels (MCL) have been established by the US EPA for many (among them Hg, Se, Cu) but not all contaminants (e.g. many pesticides) potentially present in Delta water (see [www.epa.gov/safewater/mcl.html](http://www.epa.gov/safewater/mcl.html)).

### **3.2 Submodel 2: Bioavailability**

The extent to which a contaminant in a specific matrix (water, sediment, food) is free for uptake by an organism depends on 1) the physical-chemical properties of the chemical, 2) a number of organism-specific biological and ecological properties, and 3) biological and physical-chemical habitat properties. Chemicals may enter an organism through the body surface (dermal), the gills (respiratory) or via ingestion (dietary). In general, water-soluble (hydrophilic) chemicals or their soluble species (see Mercury (Alerps et al., 2008) and Selenium (Presser et al., in prep) Models) are more readily available to organisms than water-insoluble (lipophilic) chemicals (e.g. pyrethroid insecticides, HgS), which are often tightly adsorbed to suspended particles, organic matter or sediments. However, lipophilic chemicals adsorbed to suspended particles or sediments may enter an organism when they are in direct contact with gills, body surfaces or intestinal membranes.

#### **3.2.1 Contaminant Properties That Determine Bioavailability**

The steric conformation, lipo-/hydrophilicity, solubility in water, molecular size, and ionization (speciation) of chemicals determine how much of a chemical in a given environmental matrix is available for uptake by an organism.

For nonpolar organic chemicals, such as pyrethroids, PAHs, PCBs and organochlorines, the lipophilicity (generally expressed as the  $k_{oc}$  or  $k_{ow}$ ) is the major driving force for their distribution in the environment and uptake by organisms. Equilibrium partitioning models are generally applied to model the behavior of such chemicals and their relative distribution between dissolved and sediment phase. Many environmentally important, organic chemicals are found in the moderate to high  $\log k_{ow}$  range of 2 to 6, sorb well to organic particles, and tend to bioaccumulate in organisms

unless organisms are capable of metabolizing and excreting the contaminant. Methyl mercury is an exception, where the relatively low  $k_{ow}$  does not reflect the chemical's high potential for bioaccumulation or partitioning potential to biological tissues. On the other hand, organic chemicals with relatively high  $k_{ow}$ , such as pyrethroid insecticides, are generally readily metabolized after uptake and tend not to bioaccumulate or biomagnify in the food chain (see Pyrethroid (Werner and Oram, 2008) and Mercury (Alpers et al., 2008) Models). Other models use quantitative structure-activity relationships or QSARs that use molecular qualities of the organic compound to predict bioavailability or toxicity. A QSAR is a quantitative, often statistical, relationship between molecular qualities and bioavailability or toxicity (Spacie et al. 1995).

The bioavailability of metal ions to aquatic organisms depends strongly on the chemical form in which the metals occur (speciation), which, in turn, depends on solution conditions, especially pH (Brezonik et al., 1991). For example, fish in low-alkalinity lakes having pH of 6.0-6.5 or less often have higher body or tissue burdens of mercury, cadmium, and lead than do fish in nearby lakes with higher pH. The greater bioaccumulation of these metals in such waters seems to result partly from the greater aqueous abundances of biologically available forms ( $CH_3Hg^+$ ,  $Cd^{2+}$ , and  $Pb^{2+}$ ) at low pH (Spry & Wiener, 1991; Alpers et al., 2008).

### **3.2.2 Physical-Chemical Habitat Properties That Determine Bioavailability**

*[→Input from Organic C/Aquatic Vegetation Models]*

Besides pH, which plays a major role in the speciation of metals (see above), turbidity (suspended sediment), temperature, salinity, and – for sediments – redox potential are dominant factors determining the bioavailability of contaminants. Turbidity is of importance for the sequestration of hydrophobic chemicals such as PAHs, PCBs and pyrethroids, which tend to bind quickly to suspended particles and thus become less bioavailable to aquatic organisms. If already bound to particulate matter, sediment particle size and organic matter content influence their bioavailability. Contaminant uptake is most closely associated with fine organic-rich deposits. For metals, the redox potential and sulfide concentration of sediments are important factors influencing bioavailability (but see below). Higher salinity and alkalinity/hardness leads to the complexation of metals, which generally renders them less bioavailable to aquatic organisms. For example, the ultimate toxicity of copper applications to the Delta for the purposes of weed control will be substantially affected by these types of physical and chemical processes.

### **3.2.3 Biological Habitat Properties**

*[→Input from Aquatic Vegetation/Species Models]*

Microbial communities affect the breakdown as well as the speciation of contaminants. For example, microbial activity is crucially important in the conversion of

inorganic mercury and selenium to their bioavailable and biologically active forms (see Alpers et al (2008) and Presser et al. (in prep) for details). This can be an important factor to consider in habitat restoration. For example, changes in bioavailability of mercury and mercury speciation associated with wetland modifications have driven many management discussions and could thwart significant efforts to restore habitat. On the other hand, hydrophobic contaminants can adsorb to phytoplankton, detritus and submerged aquatic vegetation, where they can be taken up, broken down or ingested by aquatic planktivores and herbivores. Wetlands can therefore be beneficial where such biodegradable, hydrophobic contaminants are present, whereas their influence on mercury cycling could be detrimental. In addition, the structure and activity of the animal community (benthic or pelagic) will affect how and where contaminants are sequestered, ingested and released.

### 3.2.4 Organism Properties (I)

[→Input from Species Models]

Understanding how animals are exposed to the large repository of pollutants in the aquatic environment is complicated. A species' trophic level, and associated feeding behavior, diet and digestive processes, are major factors contributing to bioavailability and uptake of contaminants. For example, in a study by Lee et al. (2000), experiments with four types of invertebrates showed that feeding behavior and dietary uptake controlled bioaccumulation of cadmium, silver, nickel, and zinc. Metal concentrations in animal tissue correlated with metal concentrations extracted from sediments, but not with metal in porewater, across a range of reactive sulfide concentrations, from 0.5 to 30 micromoles per gram. This disputes the general assumption that bioavailability of metals is primarily related to their concentration in porewater. It is therefore important to consider different pathways of contaminant exposure and uptake. In the Delta, green and white sturgeon, as well as diving ducks feed on abundant, exotic clams (*Corbula amurensis*, *Corbicula fluminea*) that have been shown to be highly efficient accumulators of selenium and other metals. Clams and other mollusks also tend to bioaccumulate organic contaminants, and are therefore likely to be a major source of contaminants for benthic feeders.

Life-stage specific behavior and other features also need to be taken into account when assessing contaminant bioavailability and uptake. For example, fish embryos are protected by their chorion, and may not take up as much of a dissolved contaminant as juvenile or adult fish whose gills and body surfaces are directly exposed. Conversely, returning mature salmon that do not feed, will be unaffected by contaminants that have accumulated in their natural diet. Free-swimming clam larvae will behave very differently from their benthic adult form with regard to exposure and uptake of contaminants. In addition, seasonal cycles and the overall physiological condition can influence organism behavior, which will in turn affect their exposure and uptake of contaminants. It is critical to link contaminant exposure to the most vulnerable life-stages by connection with species-specific models

### **3.2.5 Intermediate Outcome 2: Bioavailable Concentration/Dose**

“Bioavailable Concentration = Dose” is the result of exposure concentration and bioavailability and constitutes the concentration of contaminant that is transported through biological membranes of the gut (dietary), gills (respiratory) or skin and cell walls (dermal) into the organism. Bioaccumulation and toxicity of chemicals is driven by bioavailability. For persistent chemicals, bioavailability determines the extent of how much contaminant is transferred and concentrated through the foodchain, including human consumption of fish and wildlife (see below, and mercury/selenium models).

### **3.2.6 Limitations and Recommendations**

As is evident from the previous chapter, the determination of how much of a given contaminant is bioavailable to and taken up by a given organism depends on a multitude of factors. To circumvent the complexity of modeling the bioavailability of contaminants, several models have been developed for metals which directly link environmental concentrations of individual compounds to toxic effects on organisms. The biotic ligand model (BLM) assesses acute toxicity of individual metals to aquatic organisms based on the dissolved metal concentration measured in the environment (Di Toro et al., 2001; Santore et al., 2001). Another model, the free-ion activity model (FIAM) assumes a direct correlation between bioavailability and toxicity with the free-metal concentration. Other, more general effect assessments establish the direct relationship between exposure and the toxic effects, using LC50s (= concentration lethal to 50% of exposed organisms) as the principal input (Rand, 1995).

These approaches are limited in their ability to predict toxic effects in the field. The existing models do not include species-specific characteristics such as feeding strategies to predict toxicity. In addition, toxicity data is lacking for most aquatic species, and information on the sensitivity of different life stages is limited. However, such effects assessments can be useful for identifying priority pollutants and species at highest risk in a given ecosystem.

## **3.3 Submodel 3: Bioaccumulation and Toxic Effects**

Bioavailable concentration (dose) and route of exposure, organism properties (II), physical-chemical properties of the contaminant, and temperature are the major drivers for whether a chemical is stored in tissues (bioaccumulation), excreted (transformation and elimination), or exerts toxicity (biologically effective concentration) after being taken up by a given organism.

### 3.3.1 Metabolism

#### 3.3.1.1 Transformation and Elimination

Transformation and potential elimination of chemicals after uptake by an organism can occur through excretion or sequestration (metals and metalloids) or metabolization then excretion (organic compounds). Some chemicals, e.g. organophosphate and carbamate insecticides, are transformed into toxic metabolites during this process, while others such as pyrethroid insecticides are rendered less or non-toxic. All transformation and many elimination processes occur through enzymatic reactions. Enzymatic activity in ectothermic organisms (fish, invertebrates) is strongly dependent on environmental temperature. It is important to note that some highly toxic compounds, such as many current-use pesticides, are rapidly metabolized and do not bioaccumulate; hence it is not feasible to use tissue burdens as a definitive indicator of the effects of such contaminants.

#### 3.3.1.2 Bioaccumulation

Bioaccumulation is the net accumulation of a contaminant in and on an organism from all sources (water, air, food, sediment, maternal transfer, suspended sediment, detritus). This is the most important process for evaluating the ecological and human health effects of mercury, selenium and other heavy metals (see Mercury (Alpers et al., 2008) and Selenium (Presser et al., in prep.) models for details). Bioaccumulation is determined by the exposure time and the metabolism (enzymatic activity) of a species, and often dependent on the gender, age, life-stage and physiological condition of the organism. Generally, body burden increases with size and weight of the organism, which is often a function of its age and/or trophic level. In general, the higher the trophic level of an organism the higher its contaminant body burden (biomagnification). Bioaccumulation can also differ between sexes often associated with gender-specific differences in lipid content. Females can eliminate body burdens of bioaccumulated contaminants when spawning or giving birth, which is then accompanied by “maternal transfer” of contaminants to the offspring or embryo. The physiological condition of an organism, food source, food quality and prey availability will also influence bioaccumulation of contaminants. Thus changes in the structure of the Delta food web from pelagic to benthic have profound effects on contaminant transfer and effects (see also Mercury (Alpers et al., 2008) and Selenium (Presser et al., in prep.) models).

For persistent organic chemicals such as PCBs and organochlorine pesticides, the equilibrium partitioning model describes the partitioning of chemicals into living tissues. Correlations using the  $k_{ow}$  have been successful at predicting bioaccumulation in organisms exposed mainly through water (Newman and Unger, 2003; Table 2). However, this assumption is only applicable to  $\log k_{ow}$  values of approximately 3 to 6 (Connell and Hawker, 1988). Above a  $\log k_{ow}$  value of 6, the rate of increase slows and eventually uptake begins to decrease with increasing  $k_{ow}$  as the large molecular size of the most lipophilic compounds begins to impede diffusion.

Many environmentally important chemicals are found in the moderate to high log  $k_{ow}$  range of 2 to 6, sorb well to organic particles, and tend to bioaccumulate in organisms. Methyl mercury is an exception, where the relatively low  $k_{ow}$  does not reflect the chemical's high potential for bioaccumulation or partitioning potential to biological tissues. This model also does not apply to organic contaminants that are readily biotransformed and excreted as is the case for PAHs and organophosphate, carbamate and pyrethroid insecticides. An evaluation of a variety of bioaccumulation models can be found at <http://hspf.com/pdf/FinalReport218.pdf>.

Table 2. Examples of physical-chemical properties and bioconcentration factors (BCF) for select organic contaminants. Unless otherwise noted, values are from Mackay et al (2006).

Chemical/Chemical Group	<sup>1</sup> Log $K_{ow}$	Log $K_{oc}$	Log BCF (for fish)
PCBs	4 - 8	4 - 7	5 - 6.5
Dioxin	4.01 - 4.65	4.01 - 4.34	4.49 - 4.68
Benzo-a-Pyrene (PAH)	5.12 - 6.78	6.74	1.09 - 6.95
Pyrene (PAH)	4.88 - 5.22	4.92	2.66 - 4.65
DDT(Organochlorine)	3.98 - 6.94	3.90 - 6.59	3.0 - 6.0
DDE (Organochlorine)	4.28 - 6.96	3.7 - 6.0	3.3 - 5.3
DDD (Organochlorine)	4.82 - 6.33	4.91 - 5.89	2.85 - 4.92
Permethrin (Pyrethroid)	6.5 <sup>3</sup>	5.36	1.08 - 4.83
Esfenvalerate (Pyrethroid)	6.22 <sup>3</sup>	5.4	
Bifenthrin (Pyrethroid)	6.0 <sup>3</sup>	3.80 - 5.37	
Chlorpyrifos (Organophosphate)	4.96 <sup>3</sup>	4.13	2.67 - 3.20
Diazinon (Organophosphate)	3.81 <sup>3</sup>	2.28 - 3.20	1.24 - 3.20
Carbofuran (Carbamate)	2.32 <sup>3</sup>	1.45	0.6 - 2.1

<sup>1</sup> Values based on Aroclor mixtures

<sup>2</sup> Davis (2004)

<sup>3</sup> from <http://logkow.cisti.nrc.ca/logkow/search.html>.

### 3.3.1.3 Biologically Effective Concentration and Toxic Effects

Toxicant effects begin by the interaction of contaminants with biomolecules. Effects then cascade through the biochemical, subcellular, cellular, tissue, organ, individual, population, community, ecosystem, landscape and biosphere levels of organization. The chemical may be present at acutely toxic concentrations leading to significant mortality in individuals or it may exert sublethal effects potentially resulting in mortality and/or reduced reproductive success in a population. Continuous exposure to a chronic dose of a chemical stressor can also act as a selective force leading to stressor-resistant populations. Changes in population structure or abundance may lead to indirect effects of the contaminant on species at a higher or lower trophic level thus affecting community structure and ultimately leading to ecosystem changes (Newman and Unger, 2003; Rand, 1995).

### 3.3.2 Temperature

Water temperature is perhaps the most important factor affecting biochemical and physiological processes of individual organisms. It affects contaminant transformation and excretion rates. Generally, increases in temperature within normal physiological ranges have been shown to increase bioaccumulation and toxicity of metals, but the effect is more complex for organic contaminants (Newman and Unger, 2003). For example, higher temperature increases the toxicity of organophosphate insecticides, because metabolic transformation is needed to render them toxic; contrarily, high temperature will decrease the toxicity of pyrethroid insecticides due to enhanced breakdown of the toxic parent compound (Oros & Werner, 2005, see Pyrethroid model (Werner and Oram, 2008)).

### 3.3.3 Organism Properties II

*[→Input from Species Models]*

The way chemical contaminants are metabolized or accumulated in biological tissues is highly dependent on the species, the size of the organism, its life stage, gender, digestive processes, its physiological condition, and its body temperature. Body temperature in most aquatic organisms is directly linked to water temperature.

### 3.3.4 Factors Affecting Toxicity

The toxic effects of a given contaminant as well as the effective contaminant concentration are highly dependent on the susceptibility of the species and life-stage. The mechanism of toxic action of a contaminant determines which species are most susceptible (e.g. herbicides disrupt cellular processes in plants; insecticides target processes in insects), but it is important to recognize that deleterious effects on non-target species are common. For examples, many insecticides are also highly toxic to fish and crustaceans, and several herbicides have been shown to disrupt the endocrine system of fish. Gender and reproductive stage will notably influence the effects of substances that interact with the endocrine system, many of which are not yet identified. An organism's trophic level will determine its susceptibility to predation after being negatively affected by contaminants, and behavioral characteristics (e.g. complex reproductive strategies) can modify the effects of toxic chemicals on the individual. The length of the life cycle can influence toxicity; generally, longer-lived species will accumulate higher contaminant body burdens and are less able to genetically adapt and build resistance. Species with short life cycles tend to recover more quickly after a toxic insult.

#### *3.3.4.1 Mechanism of Action of the Contaminant*

The mechanism through which a contaminant exerts toxicity is called the mechanism of action. It determines which cellular components, cells, and target organ(s) is (are) affected by the contaminant, how it will affect an organism, and which

species/life-stage/gender is susceptible. The toxic effects of contaminants are not limited to their primary mechanism of action. Many “side effects” may occur. It has been shown, for example, that neurotoxic insecticides and some metals can also negatively affect the immune system, and thus render the organism more susceptible to disease. Numerous contaminants that are otherwise unrelated to hormones have been shown to act as endocrine disruptors (or “pseudo-hormones”).

#### *3.3.4.2 Exposure Regime*

The exposure regime (magnitude (concentration), duration and frequency) is an important factor affecting toxicity. Multiple brief exposures within a given time period to a specific contaminant concentration may not have the same toxic effect as one continuous exposure over the same time period. High magnitude exposures of short duration may be enough to cause population level impacts, while low magnitude long duration exposures may have little or no impact.

#### *3.3.4.3 Mixture Effects*

Pre-exposure or simultaneous exposure to multiple contaminants, disease, or stressful environmental conditions such as unfavorable salinity and/or temperature may considerably alter the physiological condition and therefore susceptibility of the organism, as well as modify the toxicity of a given contaminant (see Appendix A: Mixture Effects). Contaminants occurring as complex mixtures, which is the norm in the Delta, can render each other more toxic (synergistic effects), less toxic (antagonistic effects) or their toxicity may simply be additive, depending on alterations in absorption, protein binding, biotransformation, excretion, and other physiologic processes (Rand, 1995).

#### *3.3.4.4 Organism Properties III*

*[→Input from Species Models]*

An organism’s sensitivity to toxic chemicals is species, life stage and gender dependent, and is a function of its size, behavior, reproductive stage, trophic level, physiological condition and generation time.

### **3.3.5 Individual Toxic Effects**

A contaminant may exert acutely toxic effects leading to mortality in individuals or it may exert sublethal effects. Sublethal toxic effects can occur at exposure levels far below the concentrations that cause lethality, and can have severe consequences for the fitness, reproductive success and survival of aquatic organisms, ultimately leading to population-level effects (Carson, 1962). Sublethal biological responses include altered behavior, reduced growth, immune system effects, reproductive/endocrine effects, histopathological effects as well as genetic effects. Direct links of these responses to higher-level effects are often difficult to establish. Nevertheless, sublethal toxic effects



can have far-reaching consequences in the aquatic environment, especially where organisms are exposed to many different stressors. Both simple and complex techniques exist for assessing biological responses to contaminant stressors and often the simplest techniques can reap substantial rewards. Careful development of portfolios of biological indicators can make investigations practical and cost effective.

#### 3.3.5.1 DNA Alteration

Genotoxicity is the damage by a physical or chemical agent to genetic materials such as DNA resulting in changes in hereditary characteristics or DNA inactivation. Genotoxic chemicals have common chemical and physical properties that enable them to interact with DNA. Genotoxic effects can have mutagenic (causing mutations), carcinogenic (causing cancer) and teratogenic (causing developmental malformations) consequences (Jones and Parry, 1992; Shugart, 1995) and affect fecundity as well as reproductive success (Anderson et al., 1994).

Metals can bind to DNA and change its stability and normal functioning. For example, mercury forms strong crosslinks between the two strands of the DNA molecule, and high mutation rates can result. Polycyclic aromatic hydrocarbons (PAHs), nitrosamines, aromatic amines, mycotoxins, halogenated aliphatic compounds and hydrazines are some well-known classes of chemical carcinogens.

In some cases, DNA alterations in the form of mutations may also lead to adaptation and increased resistance to environmental contaminants (Di Giulio et al., 1995). Normally, genetic adaptation to contaminants and formation of resistance tends to develop by natural selection in species with short life-cycles and large progenies.

#### 3.3.5.2 Tissue and Organ Damage:

Histopathology, the study of changes at the cellular and tissue level, can provide information on the health and functionality of organs (Hinton et al. 1992). These techniques integrate damage done at the molecular and cellular levels, and can assist in identifying target organs of specific toxicants and diagnose disease. Organ damage can result in reduced growth and fitness, decreased reproductive success or disease. Many contaminants cause specific or non-specific histopathologic lesions. For example, histopathologic lesions in the liver were observed in Sacramento splittail (*Pogonichthys macrolepidotus*) (Teh et al. 2005) shortly (1 wk) after 96-h exposure to sublethal concentrations of organophosphate and pyrethroid insecticides. Fish recovered from these lesions, but later showed high mortality rates, grew slower and showed signs of cellular stress even after a 3 month recovery period. Methyl mercury causes cellular damage to the brain, including lesions and nerve demyelination. Inorganic mercury has been shown to cause liver damage (see Mercury Model [Alpers et al., 2008]).

### 3.3.5.3 Abnormal Development

Some contaminants can adversely impact the developing embryo. Exposure can occur across the placenta (mammals), from contaminants deposited in the egg yolk (maternal transfer), from egg or sperm exposure before fertilization, and before or after elevation of the embryonal chorion in fish (Weis and Weis, 1989). Often there are critical periods in embryo development when a particular developmental effect can occur. Developmental toxicants act by disrupting and interfering with cellular processes (Weis and Weis, 1987). In general, effects early in development tend to be more deleterious than those occurring later.

Exposure during development can result in death, anatomical malformation, functional deficiencies, or slowing of growth. Behavioral abnormalities, such as the decreased ability to capture prey after hatching, were observed in mummichog (*Fundulus heteroclitus*) exposed as embryos to methyl mercury (Weis and Weis, 1995), and impaired neurological development and learning have been related to mercury in mammals and birds (Alpers et al., 2008). Lordosis (the extreme forward curvature of the spine) in fish larvae has been observed after exposure of embryos to high temperature (Van Eenennaam et al. 2005) or lead (Newman and Unger, 2003).

### 3.3.5.4 Reproductive Toxicity and Endocrine Disruption

Sublethal concentrations of contaminants can impede gonadal function via organ damage (Hinton et al., 1992), directly reduce fertilization success (Moore and Waring, 2001) via effects on sperm or oocytes, delay spawning and reduce larval survivability (Tanner and Knuth, 1996), and decrease fecundity (Werner et al., 2002; Day, 1989; Barry et al., 1995) in aquatic animals. Reproductive failure can also occur due to indirect effects, as in the case of DDT/DDE inhibition of Ca-dependent ATPase in the eggshell gland (Kolaja and Hinton, 1979), and consequent eggshell thinning.

Endocrine disrupting chemicals (EDC) interfere with the normal functioning of the endocrine system in animals; this system is responsible for the release of sex hormones and directs sexual differentiation, sexual development (gender reversal), fertility and mating behavior. EDCs can have estrogenic or androgenic effects, but considerably more research has been devoted to estrogenic chemicals with vitellogenin being a reliable biomarker for such effects in male and juvenile fish. One of the more potent synthetic estrogens found in surface waters is 17 alpha-ethynylestradiol (EE<sub>2</sub>), a biologically persistent analogue of estradiol that is widely used in oral contraceptives, which is not completely removed by sewage treatment plants (Newman and Unger, 2003). Both methyl mercury and selenium have been associated with impaired reproduction in wildlife (see Mercury (Alpers et al., 2008) and Selenium (Presser et al., in prep) Models).

Some EDCs include industrial waste products such as polychlorinated dibenzo dioxins (TCDDs) and furans, industrial chemicals such as polychlorinated biphenyls

(PCBs) and organometals, pesticides such as organochlorines (e.g., DDT) and their degradation products, surfactants such as nonylphenol polyethoxylates and their transformation product (p-nonylphenol) used in pesticide formulations, phthalates in plastic products, and steroidal hormones used by humans and in animals. For many contaminants their potential endocrine activity is yet unknown. The aquatic concentrations of these EDCs generally fall below U.S. EPA established water quality criteria ([www.epa.gov/waterscience/criteria/wqcriteria.html](http://www.epa.gov/waterscience/criteria/wqcriteria.html)); there are presently no water or sediment quality criteria for protecting humans and aquatic life against endocrine system disruption and its related effects, which can include reproductive defects or diseases, thyroid dysfunctions, and infertility. While there are no numeric water quality objectives or criteria for EDCs, the Regional Water Quality Control Board can apply the narrative toxicity objective if there is enough evidence of toxic effects.

#### *3.3.5.5 Behavior*

Abnormal behaviors produced by contaminants include changes in preference or avoidance, activity level, feeding, performance, learning, predation, competition, reproduction and species-specific social interaction such as aggression. Such changes can have significant consequences for fitness, survival and reproductive success of an individual. For example, many neurotoxic compounds (mercury, many insecticides including pyrethroids) cause abnormal swimming behavior or compromise swimming ability in fish and other aquatic animals (Christensen et al., 2005; Heckmann et al., 2005, Geist et al., 2007; see Mercury (Alpers et al., 2008) and Pyrethroid (Werner and Oram, 2008) Models). In the field, such changes can directly translate into increased vulnerability to predation or decreased food intake. Impairment of the olfactory function in salmon has been demonstrated after exposure to the organophosphate insecticide diazinon and copper (Moore and Waring, 1996). Copper concentrations of 2 ug/L completely eliminated the avoidance response of juvenile salmon to a predator cue (Sandahl et al., 2006). Male fathead minnows were less competitive in defending their nest and securing reproductive success after exposure to effluent from a municipal sewage plant (Martinovic et al., 2007).

#### *3.3.5.6 Growth*

Growth integrates a suite of biochemical and physiological effects into one endpoint that can often be associated with individual fitness. Many contaminants and other environmental stressors such as temperature result in a) increased energy use and/or b) decreased food intake, or c) decreased photosynthesis, ultimately reducing the organism's ability to grow and reproduce.

The “scope for growth” can be calculated from an energy budget of exposed individuals. The scope for growth is the amount of energy taken up by the organism minus the energy used for respiration, and excretion. The resulting value reflects the energy available for growth and reproduction. Scope-for-growth measurements have successfully been used in field monitoring using mussels (Widdows et al., 1990, 1995).

### 3.3.5.7 Immune System Effects

The immune response of fish and invertebrates plays a key role in the control of aquatic diseases, fitness and reproductive success. Toxicological assessments have identified the immune system as a frequent target of contaminants (Luster et al. 1988; Luster and Rosenthal 1993; Arkoosh et al. 1991, 1998 a, b, 2001; Zelikoff 1994). Contaminants may alter the function of the immune system and result in immunosuppression, uncontrolled cell proliferation, and alterations of the host defense mechanisms against pathogens. Pesticides including pyrethroids (Werner and Oram, 2008), metals, in particular copper, and polychlorinated biphenyls (PCBs) are among those identified to cause immunosuppressive effects in fish (Anderson and Zeeman 1995; Banerjee 1999; Austin 1999). Zelikoff et al. (1998) found reduced disease resistance in fish exposed to the pyrethroid permethrin. The susceptibility of juvenile Chinook salmon and rainbow trout to infectious hematopoietic necrosis virus (IHNV) was dramatically increased in juvenile fish exposed to sublethal concentrations of esfenvalerate (Clifford et al. 2005) and copper (Hetrick et al. 1979). On the other hand, selenium may actually increase disease resistance where this micronutrient is naturally deficient (Anderson and Zeeman 1995).

### 3.3.6 Population Level Effects

The focus of this discussion and model is on linkages of toxic effects in individuals to toxicity populations because many authors have noted that effects of contaminants are more frequently observed first on populations of sensitive species (Clements, 1997). It is important to note that the level of our observations is limited to the level of our monitoring efforts, which are almost always performed at the population level. Nevertheless, it is vital to note that diverse aspects of ecotoxicology have addressed ecosystem and foodweb effects of contaminant exposure. Processes of interest are numerous and have included foodweb structure and dynamics, energetics, community metabolism, nutrient cycling (Cairns et al., 1995) and, of course, biomagnification. Many sublethal effects will have lethal consequences in an ecological context, where the individual must successfully compete with other species, avoid predation, find a mate, and cope with multiple stressors. A reduction in swimming performance can directly lead to increased vulnerability to predation; a compromised immune system will negatively affect survival through the increased risk of disease; altered reproductive behavior can directly reduce reproductive success; decreased functionality of vital organs or a reduction in growth will lead to reduced fitness and susceptibility to disease and predation, and thus a reduction in survival. Genetic mutations can help a population adapt to environmental stressors (resistance), or lead to cell death, tissue damage and reduced survivability (DNA damage).

Approaches to examine changes in foodwebs and communities are diverse and include: 1) ecological simulation modeling (Bartell et al., 1992). 2) large and small scale field experiments, 3) multispecies toxicity tests (Lewis, 1995), 4) mesocosm research, 5) benthic community assessment, 6) community development assays using microbial

biofilms, settling plates and larger scale systems (e.g. Ward, 1995 for discussion). Evaluation of effects of contaminants on processes in the foodweb such as energy flow among various compartments of the Bay-Delta would be intriguing but research-oriented at this time. To our knowledge, nobody has tried to adapt theoretical studies, or some of the more applied work described above to the Bay Delta foodweb. A practical first step would be to analyze lists of contaminants of concern for the Bay and Delta and to prioritize further studies based on a ranking relative toxicities to various compartments of the foodwebs (primary producers, consumers, etc) and relating time and place of discharge to habitat for species of concern. The section provided below (Appendix A) may provide a basis for this next step. In addition, linkage with the Delta foodweb model (Durand, in review) could be achieved by a more detailed study of mixtures and a single chemical. Further dialogue is needed to recommend the most fruitful theoretical approach to achieve practical goals.

### **3.3.7 Limitations and Recommendations**

Bioaccumulation: Characterizing and understanding the processes controlling bioaccumulation is important to interpreting the environmental significance of bioaccumulation data. Due to the interaction between chemical and biological factors and inherent differences among species, environmental conditions and exposure regimes in laboratory and field testing, there are many pitfalls in attempting to make generalizations about specific biological factors controlling bioaccumulation. Knowledge of metabolic rates of individual aquatic species is limited, and more information is needed about the specific physiological and behavioral patterns of organisms.

Toxic Effects: In general, little is known about the toxic effects of contaminants known to be present in the Delta on resident Delta species. Even less is known about the sublethal toxic effects of contaminants. Although it is difficult to model sublethal responses to toxicants and predict ecotoxicological impact or risk, measures of sublethal effects are likely to be as important, or more important, than the measures of acute or chronic lethal effects to accurately assess the consequences of contaminant exposure.

The primary mechanism of toxic action is often not the only toxic effect a chemical can exert on target and non-target species. For example, neurotoxic pesticides may impair the immune system or exhibit hormonal effects, or can alter behavior with negative effects on predator avoidance or reproductive success (see above). Many of these chemical side effects are poorly understood or unknown.

Mixtures: In the Delta, organisms are likely to be simultaneously exposed to multiple chemical stressors in addition to potential physical and biological stressors. To date, the effects of multiple stressors and chemical mixtures are poorly understood. Approaches to assess the effects of mixtures are discussed below (Appendix A).

Our model provides focus for an iterative environmental management approach that links the toxicologic paradigm of exposure and effects to specific population declines

and other resource management goals such as habitat restoration. It is vital to note that steps of the model should not be viewed as a linear or stepwise process when the model is implemented for study design. Rather the model is used to stimulate thinking so that integrative investigations can be devised in a cost-effective and iterative manner.

Through integrated investigation portfolios of indicators can be derived because extraneous variables are filtered out. For example, a team of scientists working on a specific chemical pollution problem can use the model to focus their thinking and ensure that key steps are not eliminated or “pet projects” allowed to side-track goals. Factors that are known or determined to be insignificant do not require further study. When single chemical stressors have been identified, chemical bioavailability and fate often become the most significant issues. Whereas, when chemical stressors are unknown and mixtures are under investigation, investigations of biological effects are emphasized initially to better characterize the issues. An iterative process allows the most important components of the model to be assembled. Such an approach has been used and shown to be feasible by the Pacific Estuarine Ecosystem Indicator Research (PEEIR) consortium (<http://www-bml.ucdavis.edu/peer/index.htm>) and will have utility in Bay-Delta management.

In the PEEIR Consortium, an integrated and iterative approach was used to evaluate effects of contaminants on resident species. Using this method, a portfolio of several indicators is adapted for each species. The concept of this “Resident Species Portfolio” approach is to utilize indicators of fish condition, chemical and physiologic response, and analytical chemistry in varying proportions to diagnose potential effects of contaminants (Anderson et al., 2006). Studying effects in resident species in the field can be valuable in many circumstances and particularly where chronic effects are integrated over time. Because it is an iterative approach, the relative emphasis on any one of the three categories of indicators above would depend on the problem under investigation. For example, when the potential contaminants of concern are not well characterized, initial emphasis would be on improving the state of knowledge of fish condition and then employing a limited number of chemical and physiologic markers and analytical chemistry to characterize the extent of potential concerns. A sophisticated archiving plan is used to preserve tissues for more extensive follow-up. In contrast, when a chemical hazard has been well characterized, focused chemistry and diagnostic physiologic responses would be emphasized to confirm exposure and response. In addition, integration of laboratory and field studies would be undertaken to increase the scope of inference regarding the role of chemical contaminants. This approach was used successfully to uncover and confirm occurrence of endocrine disruption in a native fish (*Gillichthys mirabilis*) in Stege marsh in San Francisco Bay and to ascribe the response to the presence of chemical contamination in the sediment. Because standard toxicity tests were inadequate to characterize the chemical hazards at this site, it served as an interesting example of the need for Resident Species Portfolios that complement standard methods in management, such as toxicity testing and chemical analysis.

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## APPENDIX A

### Approaches to Quantify the Toxicity of Chemical Mixtures

#### Outcomes- Assessing Effects of Chemical Mixtures

Effects of chemical mixtures are more difficult to assess than are responses to individual toxic substances; however, options for analyzing these effects include both standardized and emerging techniques. One of the key issues in dealing with complex mixtures is that the toxicologic interactions among chemicals may be unknown. Effects may be additive, synergistic, or antagonistic, depending on alteration in absorption, protein binding, biotransformation, excretion, and other physiologic processes (Rand, 1995).

When only a few toxic substances (of similar or well-known modes of action) are presumed to be the cause for concern, a well established approach is frequently adequate to determine safe levels for the target chemicals. This method compares concentration levels observed in water or sediment to toxic levels for the organism of concern and then the toxicity of each compound is added to derive a summary statistic. Although a variety of statistical approaches exist to examine concentration response relationships, aquatic toxicologists generally use the term toxic unit (TU):

Toxic units = actual concentration in solution/ lethal threshold concentration

The TU for each component of the mixture is calculated and summed. Solutions with toxic unit values > 1 are expected to kill 50% of the organisms of concern within 96 hours. Higher TU values would be much more rapidly lethal. Use of this approach requires available data on toxic values or further empirical testing of the chemicals of concern using target species, and it assumes that toxic effects are additive rather synergistic or antagonistic. This approach can also be applied to unknown chemical mixtures (i.e. field samples) thus providing a quantifiable unit for chemical mixtures of unknown composition. Sometimes, Quantitative Structure Activity Relationships (QSAR) can be invoked to refine estimates of toxic levels when few data are available or to reexamine the assumption of additivity, which is often overly conservative (Calabrese and Baldwin, 1993) QSARs are based on mode of action of the chemical and an assumption that there are a finite number of ways that toxicants interact. The principle drawbacks of this approach are that chronic effects in resident species are not assessed and that effects of poorly characterized and highly complex mixtures cannot be examined.

There are three approaches to dealing with more complex mixtures; two have been used for a few decades and the third is an emerging approach based on in situ evaluation of chronic effects in resident species. The first approach is Toxicity Identification Evaluation (TIE), and it is based on the TU concept (above) and the use of aquatic toxicity testing. For a TIE, bioassay directed fractionation is used to discern what chemical fraction of a complex mixture (metals, polar organics, nonpolar organics

etc.) is the most likely cause of toxicity. Frequently, toxicity is observed in multiple fractions, and a mass balance is derived by determining what percentage of the toxicity is attributed to specific classes of chemicals. Detailed chemical characterization can follow on the individual chemical fractions to identify the chemicals of concern and recommend management actions. The principle disadvantages of this approach are that sediment TIEs are often fraught with artifacts, and that chronic effects on resident species are not assessed.

The second key approach is to employ an integrative assessment that combines toxicity testing with chemical analysis, as above, but also includes community or some type of ecosystem survey. The most well known of these is the Sediment Quality Triad which is comprised of sediment toxicity testing, sediment chemical analysis, and benthic community surveys. Different regulatory entities employ different decision criteria; but generally, when two legs of the triad show toxic hits, the sediment is considered impacted. Levels of contaminants known to be toxic in sediment in other systems are used as a reference for the benthic invertebrate data, but the further development of reasonable reference levels are still under debate as are rigorous decision criteria for triad data. While this approach takes into account effects on resident species, it is often difficult to discern why a particular benthic community appeared impacted and whether other confounding variables are of concern.

The third key approach is the emerging Resident Species Portfolio (RSP) method. This method has the potential to fill the gaps described above by creating techniques that can be used to discern chronic effects of complex mixtures on resident species. The RSP concept was developed and tested for California salt marsh species (Anderson et al., 2006), but initial data indicate that portfolios can be created for any aquatic habitat. RSPs involve the development of a nested portfolio of indicators for resident species in the ecosystem of concern. RSPs generally employ physiologically-based indicators (e.g. biomarkers) that can often be linked to selected modes of action of chemicals, which helps in identifying chemicals of concern. Integrative sampling is conducted such that all biochemical indicators are measured in the same fish (or invertebrate) allowing multivariate statistics to be utilized to discriminate among stressors. This is similar to the more innovative approaches also emerging from European monitoring programs. In the near future, toxicogenomic techniques will be an essential aspect any biomarker portfolio developed for resident species, and the potential power of these methods is already being demonstrated in management (Ankley et al. 2006).

Additionally, techniques exist for a variety of concerns that are beyond the scope of this discussion. For example, summation of the bioaccumulation of multiple compounds can be conducted for some chemical classes, and methods specifically evaluating bioaccumulation and bioavailability in sediments have been delineated (see general model).

The concerns regarding contaminant mixtures described above have important implications relative to our model of toxicant fate and effects. For many “real life” scenarios contaminant mixtures are more the rule than the exception, and detailed data

are often not available to complete an analysis of the factors in Submodels 1 and 2 of the general model. Frequently, resource management questions begin with a broad issue such as a population decline, and we cannot presume that only one contaminant or stressor is acting. In this case, we contend it is best to use toxicity tests as a screening tool but to then “ask the fish” what is wrong by moving to a combination of toxicity tests and analysis of effects in resident species using the RSP approach. Essentially, this means beginning any evaluation at the level of Submodel 3 and working backwards to identify chemicals of concern once toxicant effects are documented. The recently coined term “environmental forensics” might adequately describe this approach.

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## APPENDIX B

### Relative Risk and Priority Evaluation for Pesticides in the Central Valley: Summary

Agricultural and commercial applications of more than three hundred pesticides are reported annually for the Sacramento River watershed (DPR, 2003a). Several of these pesticides are included in the Clean Water Act Section 303(d) list for California waterways (SWRCB, 2003) and, therefore, are scheduled for total maximum daily load (TMDL) development.

In the 1980s, the State Water Resource Control Board (SWRCB) and the Central Valley Regional Water Quality Control Board (CVRWQCB) reviewed the existing monitoring data, evaluated toxicity data for aquatic species, determined the water quality criteria for the rice pesticides molinate and thiobencarb, and recommended control measures for reducing pesticide discharges from rice fields to the Sacramento River water system.

In 2004, Kuivila (USGS, Sacramento, unpublished data) assessed the risk of 160 pesticides to the Sacramento-San Joaquin Delta by identifying the risk of pesticides used or detected in the study area. Two methods were used to rank the risk of surface water contamination. Pesticides that had observed concentration and toxicity values were ranked to three levels according to the ratio of their observed concentration to their reported toxicity. Higher ratios meant higher risk to surface waters. Pesticides that had no analytical data were ranked based on agricultural use, water solubility, hydrolysis rate, and volatility.

Over the past decade, the California Department of Pesticide Regulation (DPR) has reported on the evaluations of the environmental fate of 35 pesticides (DPR, 2004). The reports describe the chemical and physical properties of the pesticides and their concentrations in air, soil, and water.

The California Department of Fish and Game (CDFG) assessed the risks of 20 pesticides to both fresh and saltwater aquatic organisms (CDFG, 2003). CDFG evaluated the available toxicity data and proposed water quality criteria (WQC) based on guidelines prepared by the United States Environmental Protection Agency (USEPA). However, CDFG proposed WQC for only a few pesticides because of insufficient information for the majority of the pesticides evaluated.

There has not been a comprehensive evaluation of pesticide risk for the Sacramento River watershed. It is very difficult to evaluate all pesticides used in the Sacramento River watershed because of the lack of information for most of them. This study is an initial screening of pesticides that pose a potential risk to surface water quality by occurring in either the water or associated sediments. The objective of the study is to determine the relative risks for the selected (target) pesticides to impact the water quality of surface waters in the Sacramento River watershed. Target pesticides were selected

that had the highest use in the study area for a relatively long period of time. Pesticides identified as high risk may require development of WQC and implementation programs.

Ranking of targeted high relative risk pesticides (Source: K. Larsen, Central Valley Regional Water Quality Control Board).

Chemical Name	Chem Code	Pesticides Type	Toxicity (ug/L)	Rank of Toxicity	Water Solubility (mg/L)	Log(water solubility)	Rank of Water solubility	Soil Koc	Rank of Koc	Soil half-life (day)	Rank of half-life	Rank of Sediment Contamin. Risk
(S)-METOLACHLOR	5133	Herbicide	8	High	480	2.68	High	185	Moderate	38.4	Moderate	Possible
ABAMECTIN	2254	Insecticide	0.022	Very high	5	0.70	Low	5000	High	28	Low	Potential
BIFENTHRIN	2300	Insecticide	0.00397	Very high	0.1	-1.00	Very Low	2.37E+05	Very High	26	Low	Potential
CHLOROTHALONIL	677	Fungicide	26.3	High	0.6	-0.22	Very Low	5000	High	48	Moderate	Potential
CHLORPYRIFOS	253	Insecticide	0.035	Very high	1.18	0.07	Low	9930	High	43	Moderate	Potential
CYFLUTHRIN	2223	Insecticide	0.002	Very high	0.02	-1.70	Very Low	31,000	Very High	22	Low	Potential
CYPERMETHRIN	2171	Insecticide	0.0047	Very high	0.004	-2.40	Very Low	6.10E+04	Very High	27	Low	Potential
DELTAMETHRIN	3010	Insecticide	0.0017	Very high	0.0002	-3.70	Very Low	6291	High	23.5	Low	Potential
DIAZINON	198	Insecticide	0.2	Very high	60	1.78	Moderate	1520	High	7	Very Low	Potential
DIURON	231	Herbicide	2.4	High	42	1.62	Moderate	477	Moderate	90	Moderate	Possible
ESFENVALERATE	2321	Insecticide	0.07	Very high	0.004	-3.40	Very Low	5273	High	42	Moderate	Potential
FIPRONIL	3995	Insecticide	0.056	Very high	22	1.34	Moderate	749	Moderate	366	High	Possible
HEXAZINONE	1871	Herbicide	6.8	High	29800	4.47	Very high	54	Low	79	Moderate	Unlikely
LAMBDA-CYHALOTHRIN	2297	Insecticide	0.0041	Very high	0.006	-2.22	Very Low	2341	High	61.8	Moderate	Potential
MALATHION	367	Insecticide	0.5	Very high	130	2.11	High	1200	High	9	Very Low	Potential
MANCOZEB	211	Fungicide	9.5	High	6.2	0.79	Low	6000	High	43	Moderate	Potential
MANEB	369	Fungicide	33	High	6	0.78	Low	240	Moderate	30	Moderate	Possible
OXYFLUORFEN	1973	Herbicide	0.29	Very high	0.116	-0.94	Very Low	100,000	Very High	30	Moderate	Potential
PARAQUAT DICHLORIDE	1601	Herbicide	0.55	Very high	6.20E+05	5.79	Very high	162,000	Very High	1067	Very High	Potential
PENDIMETHALIN	1929	Herbicide	5.2	High	0.225	-0.65	Very Low	13,400	Very High	174	High	Potential

PERMETHRIN	2008	Insecticide	0.018	Very high	0.006	-2.22	Very Low	39,300	Very High	42	Moderate	Potential
PROPANIL	503	Herbicide	16	High	152	2.18	High	400	Moderate	1	Very Low	Possible
PROPARGITE	445	Insecticide	31	High	0.6	-0.22	Very Low	5578	High	84	Moderate	Potential
PYRACLOSTROBIN	5759	Fungicide	4.16	High	19	1.28	Moderate	93	Low	105	High	Unlikely
SIMAZINE	531	Herbicide	36	High	6.2	0.79	Low	140	Moderate	89	Moderate	Possible
TRIFLURALIN	597	Herbicide	8.4	High	0.32	-0.49	Very Low	7200	High	81	Moderate	Potential
ZIRAM	629	Fungicide	8	High	65	1.81	Moderate	400	Moderate	30	Moderate	Possible

## REFERENCES APPENDIX B

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