# DEVELOPING TMDLs FOR ORGANOCHLORINE PESTICIDES AND PCBs[1]

**G. Fred Lee, PhD, PE, DEE and Anne Jones-Lee, PhD**
**G. Fred Lee & Associates, El Macero, California**
**Email: gfredlee@aol.com – Website: www.gfredlee.com**

Fish and other aquatic life in some agricultural and urban areas contain concentrations of organochlorine pesticides, such as DDT, dieldrin, chlordane, toxaphene and PCBs, which can be a human health threat to those who consume these organisms as food (Davis, *et al.*, 2000). Also in some urban industrial areas such as San Francisco Bay, edible fish have bioaccumulated dioxins to levels that are a threat to the use of the fish as food. Excessive bioaccumulation of organochlorines can lead to a 303(d) listing of the waterbody in which the fish with excessive edible tissue concentrations are located as an "impaired" waterbody. In 1998 the California Regional Water Quality Control Boards listed 60 waterbodies as "impaired" by PCBs. In that same year, there were over 160 California waterbodies listed as "impaired" due to the organochlorine pesticides (DDT, aldrin, dieldrin, chlordane, endrin, heptachlor, heptachlor epoxide, hexachlorocyclohexane (including lindane), endosulfan and toxaphene). The 303(d) listing results in the need for the regulatory agency responsible for the waterbody to develop a total maximum daily load (TMDL) to control the concentrations of the organochlorine pesticides and PCBs (OCls) so that the concentrations in the edible fish tissue are less than those that are considered a threat to human health. The authors are involved in the review of several situations of this type. This paper presents an overview of the approach that we feel should be used to establish TMDLs and their implementation to control excessive bioaccumulation of OCls.

**303(d) Listing**

The first step in developing a TMDL for organochlorine pesticides and PCBs is a reliable assessment of excessive concentrations of these types of pesticides and PCBs within edible fish tissue. In order to make this assessment, it is necessary to assume a fish consumption rate for those in the area who use fish from the waterbodies of concern. While the US EPA uses 6.5 g of fish per person per day as the national average consumption rate (which translates to about one meal per month), it is generally agreed that that consumption rate is not normally appropriate for protecting some of those who utilize local fish as a source of food. More frequently, one meal per week or even several meals per week is the rate of consumption of fish that is used to evaluate potential hazards of bioaccumulation of organochlorine pesticides and PCBs. The US EPA (2000a, b) has provided guidance on a risk-based consumption rate which will be protective of those who consume fish with regulated hazardous chemicals in the edible tissue.

Table 1 presents a summary of the California Office of Environmental Health Hazard Assessment (OEHHA) 1999 fish tissue screening values for selected OCls. These values are based on a cancer risk of $1 \times 10^{-5}$ and a fish consumption rate of 21 g/day.

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The US EPA draft consumption criteria for DDT and other chlorinated pesticides provide a recommended risk-based consumption limit that is related to the fish tissue concentration. For example, if the fish tissue concentration of DDT is 0.2 mg/kg, the US EPA recommends that no more than twenty-three 8-oz. meals or eleven 16-oz. meals per month be consumed. These rates of consumption are significantly different from the Food and Drug Administration (FDA) DDT Action Level of 5 mg/kg.

**Table 1**
**OEHHA Fish Tissue Contamination Screening Values**

| Chemical | OEHHA Screening Values (µg/kg) |
|---|---|
| Chlordane | 30 |
| Total DDT | 100 |
| Dieldrin | 2 |
| Endrin | 1,000 |
| Toxaphene | 30 |
| PCBs | 20 |
| Dioxin TEQ | 0.3 picograms/kg |

Source: SAWRCB (2000)

At that Action Level, the US EPA would recommend no more than one 4-oz. meal per month, six to eight 12-oz. meals per year, and no 16-oz. meals. It is evident that far greater attention needs to be given to the amount of fish consumed by those in a region who depend on local fish as a substantial part of their diet, where the concentrations of the chlorinated hydrocarbon pesticides and PCBs in the fish are above US EPA recommended risk-based levels.

Once the concentration of chlorinated hydrocarbon pesticides and PCBs in fish tissue that represents a threat to public health has been determined for a particular waterbody, considering local fish consumption rates, then detailed sampling of the fish is necessary to reliably assess whether the concentrations of OCls in each of the major types of edible fish exceed the critical concentrations. It has been found that various types of fish bioaccumulate hazardous chemicals to varying degrees. Also larger, higher trophic level fish tend to have higher concentrations of OCls than smaller fish. Further, fish with a higher body fat content tend to accumulate OCls to a greater degree. It is therefore, important to representatively sample the fish that are used as food in the region of concern. This may require a creel census. If the fish used as food contain OCls that exceed the critical concentrations, then the waterbody may be listed (if it is not already) as a 303(d) “impaired” waterbody, which requires that a TMDL be developed to control the excessive bioaccumulation of OCls in edible fish tissue.

While there are higher trophic level impacts of OCls, at this time, except for PCBs in the Great Lakes region, there are no national water quality criteria for protection of aquatic life. Generally, it is assumed that aquatic life will be protected if humans are protected, especially if the consumption rate is based on one meal per week.

In addition to concern about excessive bioaccumulation of the OCls as a human health threat, there is also increasing concern about the body burdens of these chemicals being adverse to the host organism. There are two publications (Jarvinen and Ankley, 1999, and US COE, 1987) which provide information on the concentrations of various chemicals, including several of the OCls, that have been found to be adverse to the host aquatic organism.

It should be noted that GC or GC/MS organochlorine pesticide and PCB scans of fish tissue from some areas show that there are unidentified, apparently anthropogenic chemicals in fish tissue that potentially could be a threat to those who use the fish as food. While this situation has been known for over 35 years, thus far, federal and state regulatory agencies and others, such as the USGS, are largely ignoring it. At this time, there is no effort to systematically investigate the chemicals responsible for the unidentified peaks in the GC or GC/MS scans for organochlorine pesticides and PCBs, as well as once they are identified, determine their hazard to human health and higher trophic level organisms.

**Developing TMDL Goals for OCls**

Normally the TMDL goal is the state water quality standard, which is based on the US EPA water quality criterion for the constituent of concern. These criteria are typically based on a worst case (greatest) bioaccumulation of the chemical in laboratory or field conditions. The US EPA, as part of promulgating the California Toxics Rule (US EPA, 2000c), has developed updated recommended water quality criteria for several organochlorine pesticides. Table 2 presents these criteria.

It is the authors’ experience that, occasionally, the concentrations of total DDT in runoff from some agricultural areas, where DDT has not been used for many years, can exceed the drinking water maximum contaminant level (MCL) (Domagalski, 1997; Panshin, et al., 1998). Generally, the MCL is much higher than the water quality criterion for prevention of bioaccumulation under worst-case conditions. Under those conditions, high levels of bioaccumulation would be expected.

The criteria presented in Table 2 could be used as TMDL goals to protect against excessive bioaccumulation ("organisms only" column in Table 2) or to protect against adverse impacts to aquatic life (the "CCC" columns in Table 2).

Lee and Jones-Lee (1996) have discussed the problems of trying to use water column-based bioaccumulation water quality criteria to predict fish tissue concentrations. The basic problem is that the sediments of a waterbody act as an additional sink for the constituent of concern. Therefore, there is a partitioning between the organism tissue, the sediments and water. The distribution of a chemical like DDT into these compartments depends to a considerable extent on the characteristics (TOC content) and amounts of sediment. This situation leads to a significant overestimation of the amount of bioaccumulation that will occur in a waterbody based on a measured concentration of the constituent in the water column relative to the US EPA worst case-based water quality criterion.

The US EPA senior staff (Pendergast, 2000) has indicated that the Agency is proceeding toward addressing the problem of not being able to reliably use US EPA water quality criteria to predict bioaccumulation of hazardous chemicals in fish tissue. Eventually, the US EPA may adopt a much more technically valid approach of basing TMDL goals on an allowable fish tissue residue, considering appropriate local fish consumption rates. For now, it appears that the Agency may allow this approach, provided that a site-specific water column constituent concentration be used to estimate the bioaccumulation that is occurring between the water column concentrations and the organisms. This site-specific bioaccumulation factor is a pseudo-bioaccumulation factor that ignores the role of the sediments in controlling tissue residues. While this approach will allow the Agency to continue to use a numeric chemical concentration as a TMDL goal, it should be understood that this pseudo-bioaccumulation factor has no predictive capabilities that can be used to estimate the amount of bioaccumulation that will occur if the magnitude of the sediment reservoir of the available forms of the constituent of concern is altered, such as through sediment remediation programs.

**Table 2**
**Selected National Recommended Water Quality Criteria for**
**Priority Toxic Pollutants-Pesticides**

| Priority Pollutant | Freshwater | | Saltwater | | Human Health For Consumption of: | |
|---|---|---|---|---|---|---|
| | CMC (: g/L) | CCC (: g/L) | CMC (: g/L) | CCC (: g/L) | Water + Organism (: g/L) | Organism Only (: g/L) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Chlordane | 2.4 | 0.0043 | 0.09 | 0.004 | 0.0021 | 0.0022 |
| 4,4'-DDT | 1.1 | 0.001 | 0.13 | 0.001 | 0.00059 | 0.00059 |
| 4,4'-DDE | – | – | – | – | 0.00059 | 0.00059 |
| 4,4'-DDD | – | – | – | – | 0.00083 | 0.00084 |
| Dieldrin | 0.24 | 0.056 | 0.71 | 0.0019 | 0.00014 | 0.00014 |
| Endrin | 0.086 | 0.036 | 0.037 | 0.0023 | 0.76 | 0.81 |
| Polychlorinated Biphenyls PCBs | – | 0.014 | – | 0.03 | 0.00017 | 0.00017 |
| Toxaphene | 0.73 | 0.0002 | 0.21 | 0.0002 | 0.00073 | 0.00075 |

Source: US EPA (1999)

In summary, there are a variety of approaches for establishing TMDL goals for OCls to prevent their excessive bioaccumulation. The most reliable approach is the development of an appropriate allowable fish tissue residue that will be protective of those who use fish from a waterbody as a source of food, considering the local fish consumption rate from the waterbody. The implementation of this TMDL goal should be based on a phased approach, in which readily-controllable sources of available forms of the constituent of concern are controlled to the extent technically and economically feasible during Phase I. After five years or so following sediment remediation to the extent possible during Phase I and it is found that the desirable fish tissue residue has not been achieved, then a Phase II sediment remediation program should be undertaken and the system be allowed to equilibrate for a number of years following the sediment remediation program. There is no need to invoke the technically invalid approach of establishing a TMDL goal of a single chemical water column concentration to appropriately implement a TMDL for controlling excessive bioaccumulation of OCls and, for that matter, other hazardous chemicals.

**Defining the Source of Bioaccumulatable Chemicals**

The next step in developing an appropriate TMDL-based control program for organochlorines that bioaccumulate to excessive levels in aquatic life is to define the location(s) where they occur to the greatest extent in the waterbody of concern. Ordinarily, in a TMDL, the focus of the control programs is on identified, currently-discharging sources of the constituents to be controlled. However, with the organochlorine pesticides and PCBs, since these chemicals have not been sold in the U.S. for many years and, therefore, should not ordinarily be present in wastewater discharges or runoff from current use, the TMDL must focus on identifying and controlling reservoirs of these chemicals associated with former use/discharge. The most likely reservoirs for these chemicals are terrestrial soils and/or aquatic sediments. The identification of the source(s) of the OCls that have bioaccumulated to excessive levels within edible organisms will require the use of techniques designed to assess bioavailable forms of the chemical(s) of concern within a waterbody and its watershed.

While some attempt to make an assessment of the sources of OCls based on concentrations of organochlorines in sediments and water, usually today the concentrations in water are below detection limits. Water concentrations should be determined in various parts of the watershed to determine if, in fact, there are sufficient concentrations to be measured using highly sensitive, reliable analytical methods. The focus should be on both total and dissolved forms, with care exercised in determining the dissolved forms to insure that the separation process, such as filtration, does not bias the results through sorption on the filters. In some instances it is necessary to use high-speed, large-volume centrifugation to properly separate dissolved from particulate forms of pesticides and PCBs.

With respect to determining bioaccumulatable organochlorines in sediments, it is important not to equate concentrations in sediments to the sediments being a source of the OCls that are bioaccumulating to excessive levels in fish or other aquatic life. The bioaccumulation process is based on both a food web uptake and a partitioning between the sediments, the associated interstitial water and aquatic organisms. The availability of OCls for partitioning is dependent on the organic carbon content of the sediments. The OCls sorb onto organic carbon particles and thereby reduce their availability for partitioning with the interstitial water associated with the sediment particles. This partitioning, however, may not prevent uptake of the OCls by sediment-ingesting benthic organisms.

In order to assess where elevated concentrations of organochlorines present in sediments are a bioaccumulation source, it is necessary to do some forensic bioaccumulation evaluation using caged organisms. It may also be possible to use natural organisms to detect sources of bioaccumulatable chemicals. The key to reliably implementing this approach is the availability of aquatic life with limited mobility such as freshwater clams and, in marine waters, mussels, throughout the waterbody of concern and its tributaries. Through gradient analysis of aquatic organism tissue, it may be possible to identify toxic “hot spots” of the chemicals that are bioaccumulating to excessive levels in higher trophic level organisms.

The US EPA (2000d) has developed a procedure involving the use of *Lumbriculus variegatus* to assess bioaccumulation. The sediments are incubated in the presence of these organisms, and the tissue concentrations are assessed. The US EPA has recently expanded this testing procedure to include the testing of the sediments for aquatic life toxicity using *Hylella*, a freshwater amphipod. The toxicity of sediments would not likely be due to the organochlorines, but to other constituents in the sediments. Also, the US EPA and the Corps of Engineers (US EPA/COE 1991, 1998) have bioaccumulation testing procedures that can be used to assess bioaccumulatable chemicals in sediments.

**Control of Bioaccumulatable Hazardous Chemicals**

If the forensic studies identify areas where there are substantial concentrations of bioaccumulatable chemicals of concern in the waterbody sediments, then sediment remediation techniques can be used to remove the contaminated sediments from the waterbody. The approach that is followed in sediment remediation would, in general, be similar to that being used today at Superfund sites where contaminated sediments are part of the site. Through a phased approach, after remediation of contaminated sediments that are likely to be the most significant source of the bioaccumulatable chemicals that are leading to excessive edible tissue residues, it may be necessary to conduct a Phase II evaluation of potential sources if the remediation of the "hot spots" does not reduce the constituents of concern in the edible organism tissue to acceptable concentrations.

It should also be understood that if the source of the bioaccumulatable chemicals is widespread throughout the sediments, then it may not be possible to eliminate the exceedance of the tissue residue. Under these conditions, it may be necessary to change the designated beneficial uses of the waterbody through a Use Attainability Analysis to restrict consumption of fish or some types of fish from the waterbody with excessive tissue residues.

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