Case Study: USEPA Benthic Invertebrate Risk Assessment for Endosulfan

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1. Background and Purpose

This case study was prepared upon the request of the organizing committee of the European Chemicals Agency (ECHA) Topical Scientific Workshop*: Risk Assessment for the Sediment Compartment*, held 7-8 May, 2013 in Helsinki, Finland. Its primary purpose is to illustrate the methods and data considered by the U.S. Environmental Protection Agency's (USEPA), Office of Pesticide Programs (OPP) in assessing pesticide risks to benthic invertebrates based on its recent environmental fate and ecological risk assessment for the insecticide, endosulfan (USEPA 2010).[1] Using this case study, various benthic invertebrate risk assessment issues are explored, including: (1) the choice of exposure media for expressing risk (pore water vs. bulk sediment); (2) the selection of invertebrate species for characterizing toxicological effects; (3) the role of monitoring data in benthic invertebrate risk assessment; and (4) the major sources of uncertainty encountered in the risk assessment.

It should be recognized that endosulfan is considered a "data rich" chemical with regard to the availability of ecological exposure and effects information relevant to benthic invertebrates. While the breadth and depth of information available for endosulfan is not expected to be available for most other chemicals of concern (especially industrial chemicals), this case study provides an opportunity to evaluate the utility and robustness of various risk assessment decisions and assumptions that must be made under "data poor" situations. It should also be understood that the benthic invertebrate risk assessment was only one component of the USEPA 2010 environmental fate and ecological risk assessment for endosulfan. Other components included an evaluation of risks to birds, mammals, amphibians, pelagic invertebrates, and plants in the context of both "near field" and "far field" (long range transport) exposures. The USEPA 2010 endosulfan environmental fate and ecological risk assessment was also part of a broader re-evaluation of the risks and benefits associated with registered uses of endosulfan in the U.S., and therefore also included evaluation of health effects, economic benefits, and available pesticide substitutes. Currently, endosulfan is being voluntarily phased out from use in the U.S., with a permanent phase out expected over the next several years.

[1] available at: http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2002-0262-0162;oldLink=false

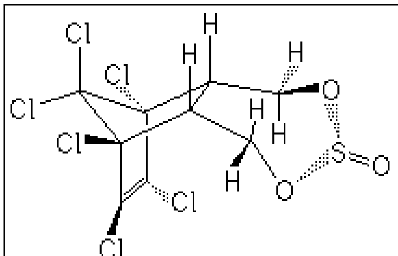
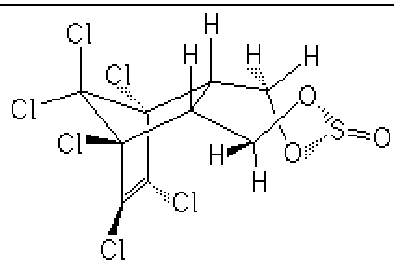
The following case study is organized by the main components considered in OPP ecological risk assessments: Problem Formulation, Exposure Assessment, Effects Assessment and Risk Characterization (USEPA 1998; USEPA 2004). Where appropriate, additional analyses have been conducted in this case study to illustrate specific issues associated with assessing risks to benthic invertebrates. In other cases, certain aspects of the risk assessment process are not presented or are condensed for the purpose of brevity.

2. Problem Formulation

Problem formulation provides a strategic framework for the risk assessment. It sets the objectives for the risk assessment, evaluates the nature of the problem, and provides a plan for analyzing the data and characterizing the risk (US EPA 1998). Main components of the problem formulation phase illustrated in this case study include: 1) defining the nature of the chemical stressor, 2) developing the conceptual model, 3) selecting assessment and measurement endpoints and 4) formulating the analysis plan.

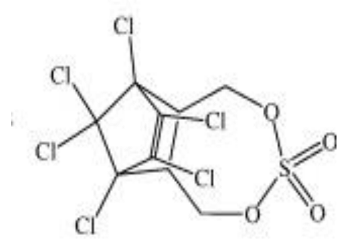
2.1 Nature of the Chemical Stressor

Endosulfan (6,7,8,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzadioxathiepin 3-oxide) is a dioxathiepininsecticide and acaricide (broadly classified as an organochlorine). The chemical is a 70:30 mixture of two biologically-active isomers (α and β) and it acts as a contact poison to a wide variety of insects and mites through blockage of GABA-(gamma amino butyric acid) gated chloride channels affecting nerve signals. Chemical structures of α and β endosulfan and its major degradate, endosulfan sulfate, are shown in **Figure 1**.

(the wedge bonds are used to indicate direction, not stereo-isomerism)

α-endosulfan (959-98-8) **β-endosulfan** (33213-65-9)



Endosulfan Sulfate (1031-07-8)

Figure 1. Chemical stressors of ecological concern for agricultural applications of endosulfan

Stressor sources include foliar application of endosulfan formulated products prepared from wettable powders and emulsifiable concentrates by air, ground and airblast application methods. In an agricultural setting, major quantities of the applied pesticide active ingredient reach target foliage and eventually end-up in the soil system. Smaller quantities of the applied pesticide reach nearby field or water bodies initially by drift and then by runoff/erosion and by volatilization. Based on submitted environmental fate data, biologically-mediated transformation of α and β-endosulfan is expected to occur in the soil system producing endosulfan sulfate (maximum observed levels ≅52% of applied material) which is a major degradate of toxicological concern. Endosulfan sulfate is included with its two parents α and β-endosulfan due to its similar toxicity as parent isomers and its formation as a "major" degradate (e.g., > 10%) in aquatic and terrestrial systems. Endosulfan sulfate is also more persistent than the parent isomers (α and β-endosulfan) and tends to be a major component of total endosulfan residues found in biologically active environmental media (e.g., aerobic soil, water, and sediments). Other degradates (endosulfan diol, endosulfan lactone and endosulfan ether) were considered but ultimately excluded from the risk assessment in part because they form in low quantities in the aquatic and terrestrial environment and available data suggest they are less toxic[2]. For the purpose of this case study, the term "endosulfan" refers to the technical grade active ingredient (TGAI), i.e. the combination of the **α-endosulfan** and **β-endosulfan** isomers only, unless otherwise indicated. The term "**total endosulfan**" or "**endosulfans**" refers to the combination of **α-endosulfan, β-endosulfan and endosulfan sulfate** unless otherwise noted.

Relevant physical-chemical and environmental fate properties of the endosulfan stressors of concern are summarized in **Table 1**. Based on its vapor pressure, endosulfan is considered a semi-volatile chemical and as a result, volatilization and atmospheric transport are potential environmental exposure pathways of concern. The α and β isomers show high hydrophobicity (log K_{OW} ~ 4.7), while endosulfan sulfate is less hydrophobic (log K_{OW} 3.7). The K_{OC} for α and β isomers are 10,600 and 13,500 L/kg$_{-OC}$, respectively. All three chemical components of the stressor are therefore expected to partition extensively to organic phases of aquatic ecosystems (sediments, dissolved and particulate organic carbon, and lipid phases of biota).

[2] A complete discussion of the degradates of interest for endosulfan is found in Section 3.2.1 of USEPA (2010).

The dominant degradation process in aquatic systems for the parent isomers is hydrolysis and microbial-mediated metabolism while that for endosulfan sulfate is metabolism only.

Table 1. Physical-chemical and fate properties of endosulfan stressors

Property	*α -endosulfan*	*β-endosulfan*	*Endosulfan sulfate*
Formula	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6SO_4$
Molecular Weight	406.9 g/mole	406.9 g/mole	422.9 g/mole
CAS Number	959-98-8	33213-65-9	1031-07-8
Water Solubility	530 µg/L	280 µg/L	330 µg/L
Vapor Pressure (torr @ 25 °C)	**4.6×10^{-5}**	**2.4×10^{-5}**	**9.75×10^{-6}**
Henry's Law Constant (atm-m^3 mol^{-1} *@ 25 °C)*	3.03×10^{-6}	1.38×10^{-6}	1.64×10^{-5}
Log K_{aw} (air/water)	-3.56	-4.75	-4.78
Log K_{ow} (octanol/water)	4.74, (4.93);	4.79, (4.78)	(3.71)
K_{ow}:	54,954; (95,499)	60,159 (60,256)	(5,129)
Log K_{oa}	6.41 & 8.64	6.41 & 8.64	8.45 & No value
Koc (L/kg-OC; Avg. n=4)	10,600	13,500	n/a
Hydrolysis half life	pH 5: >200 d pH 7: 11 d	pH 5: >200 d pH 7: 19 d	pH 7: 184 d
Aquatic photolysis	Stable	Stable	stable
Aerobic soil metabolism half life (n=4)	35-67 d	104-265 d	Stable
Anaerobic soil metabolism half life (n=2)	105-124 d	136-161 d	125-165 d
Data sources are provided in Tables 3.5 and 3.6 of USEPA (2010)			

At the time of the USEPA assessment in 2010, endosulfan was registered on a wide variety of food crops, non-food crops and ornamentals. Selected examples include tree nuts, non-bearing citrus trees, cotton, apples, cherries, pears, leafy vegetables, cucurbits, potatoes, beans and peas. Single application rates generally ranged from 0.5 to 2.0 pounds of active ingredient per acre (lb a.i./A) with maximum seasonal rates of 3.0 lb ai/A or less. Application frequencies ranged from 1 to 6 times per season depending on the crop and target pest.

2.2 Assessment Endpoints and Conceptual Model

Assessment endpoints represent the actual environmental components that are to be protected, defined by an ecological entity (species, community, or other entity) and its attribute or characteristics (US EPA, 1998). For the purpose of this case study, the ecological entities include benthic aquatic invertebrates that live in (infaunal) and on (epibenthic) benthic sediments in freshwater and saltwater ecosystems. The attributes considered for protection of benthic aquatic invertebrates include survival, growth, development and reproduction of benthic invertebrates. These assessment endpoints were selected because of their relationship to population level effects. Measures of ecological effects for benthic invertebrates include LC_{50}/EC_{50} and NOAEC values based on endpoints of survival, growth (dry weight, length), development (development rate) and reproduction (fecundity, emergence rate).

A conceptual model provides a written and visual description of the predicted relationships between the stressor (total endosulfan), potential routes of exposure, and the predicted effects for the assessment endpoint. The overall conceptual model used in the 2010 endosulfan ecological risk assessment is shown in **Figure 2**. Since benthic invertebrates are the focus of this case study, a more detailed discussion of stressor sources, exposure routes and predicted effects on benthic invertebrates is provided below.

Routes of entry for endosulfans to aquatic ecosystems include: 1) direct deposition of pesticide droplets from spray drift, 2) inflow of pesticide contaminated runoff, 3) influx of erosion of contaminated soil, 4) leaching to groundwater and subsequent input (likely limited to highly porous soils with low organic content), and 5) wet and dry deposition from atmospherically-transported chemical. Once in the waterbody, endosulfans are expected to predominately sorb onto suspended sediment and other organic matter present in the water column with subsequent deposition onto bed sediments via sedimentation. Benthic aquatic invertebrates may be exposed to endosulfans primarily through respiration of interstitial (pore) water, respiration of overlying water, ingestion of sediment particles and aquatic prey, and dermal absorption.

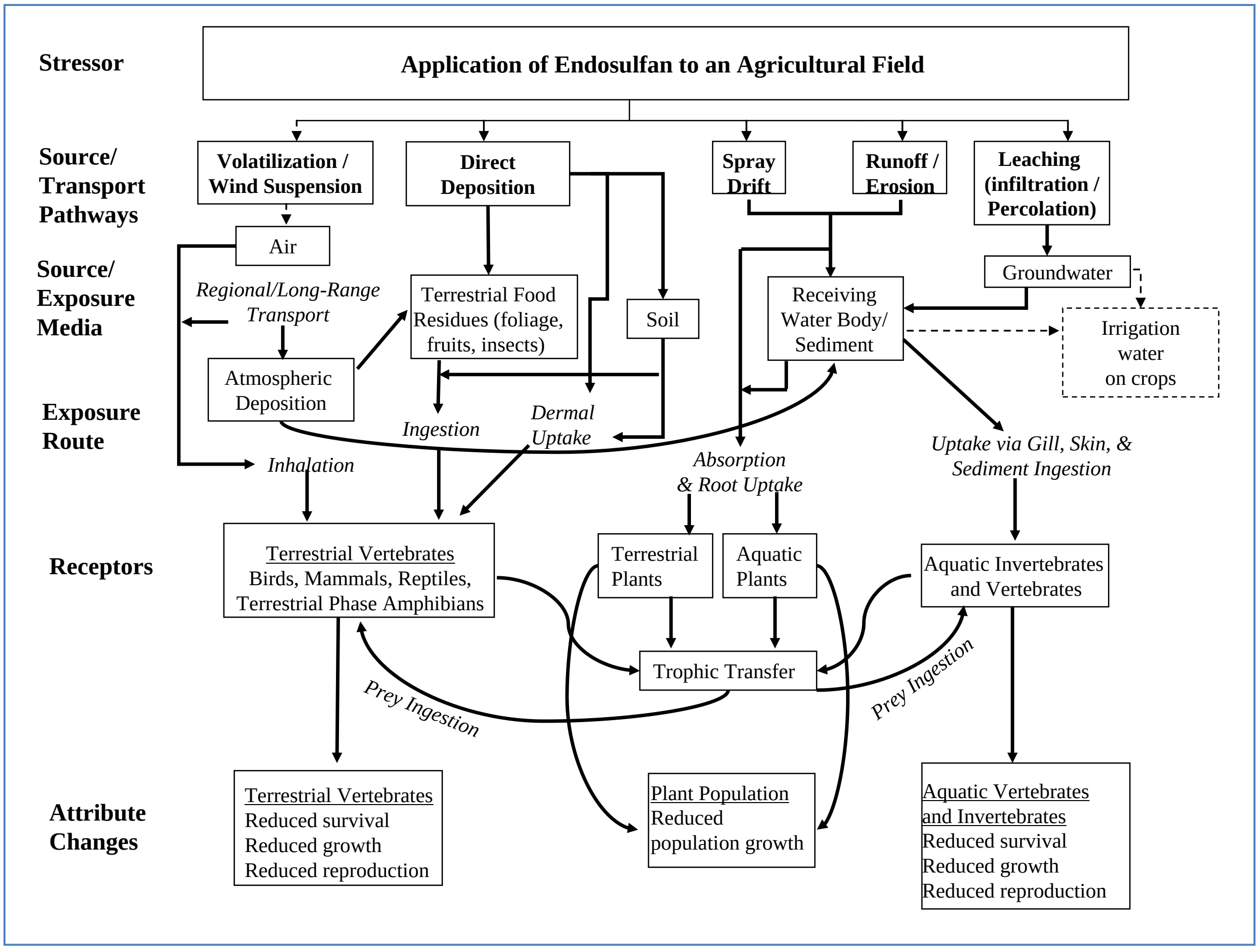


Figure 2. Conceptual model for agricultural uses of endosulfan.

2.3 Analysis Plan

The primary method used to assess ecological risk by OPP is the risk quotient (RQ). The RQ is the result of comparing measures of exposure to measures of effect:

$$RQ = \text{exposure concentration} / \text{effect concentration}$$

Risk quotients are determined separately for acute (short-term) and chronic (long-term) exposures and associated effect concentrations. For endosulfan, multiple methods were used for estimating the exposure concentration for benthic invertebrates. These include:

- Modeled concentrations in sediment pore water,
- Modeled concentrations in bulk sediment (normalized for OC), and

- Monitored concentrations in bulk sediment.

Since the 2010 endosulfan ecological risk assessment was a "screening-level" assessment, "high-end" estimates of exposure were developed for comparing to effect concentrations. For modeled concentrations, an estimated environmental concentration (EEC) was developed for pore water and bulk sediment. The EEC has two components: a return frequency and an averaging period. For OPP screening-level assessments, a 1-in-10 year return frequency is selected from a 30-year time series of daily concentrations of pesticides in surface water, pore water and bulk sediment. The averaging period (i.e., the time period over which the pesticide concentrations are averaged for comparing with the effect concentration) varies depending on the taxa and type of risk being evaluated (acute vs. chronic). For aquatic invertebrates, acute risk is determined from daily (peak) concentrations while chronic risk is determined from 21-d moving average concentrations that correspond to the aforementioned return frequency. For monitored concentrations, data are usually much less abundant compared to model-derived estimates and therefore, upper bound (e.g., maximum) values are typically selected.

Measures of effect (i.e., the denominator of the RQ) also vary depending on the type of risk being evaluated (acute vs. chronic). For acute risks to *pelagic* invertebrates, toxicity values such as the 48-h or 96-h LC_{50} (lethal concentration to 50% of test organisms) or the 48-h or 96-h EC_{50} (effect concentration to 50% of test organisms) are typically selected. For chronic risk to invertebrates, the NOAEC (No Observed Adverse Effect Concentration) is selected from a standard life cycle toxicity test (e.g., 21 days for *Daphnia magna*; 28 days for *Americamysis bahia*). For deterministic risk assessments, these acute and chronic effect endpoints are selected from the *most sensitive* species for which valid toxicity data are available.

With sediment toxicity tests of benthic invertebrates, standard exposure durations do not conform to those used in water column tests of pelagic invertebrates. Typically, subchronic sediment toxicity tests required by OPP include 10-day subchronic exposures to selected species (e.g., *Chironomus dilutus*, *Hyalella azteca*, *Leptocheirus plumulosus*) in which effects on survival and growth are measured. Chronic sediment toxicity tests include 28 to 65-day life cycle exposures in which effects on survival, growth, reproduction and development are measured. As a matter of current practice[3], measures of chronic risk are determined from the

[3] Formal guidance on selecting toxicity endpoints and EECs for benthic invertebrates risk assessment are currently under development in OPP.

pore water and/or bulk sediment NOAEC for the most sensitive species available from subchronic and chronic sediment toxicity testing. This NOAEC is used to compare with the 21-d EEC for calculating the chronic sediment RQ. For estimating acute risks to benthic invertebrates, current practice involves selecting the most sensitive LC_{50} or EC_{50} available from the *water column* acute toxicity tests for aquatic invertebrates (**Table 2**).

Table 2. Assessment endpoints, measures of effect, and measures of exposure used for assessing risk to pelagic and benthic aquatic invertebrates

Taxa	Assessment Endpoint	Type of RQ	Measures of Ecological Effect[1]	Measures of Exposure[2]
Freshwater invertebrates **(pelagic)**	Survival	Acute	Acute (48-96 h) LC_{50} or EC_{50}	Peak water column EEC
	Survival, growth, reproduction and development	Chronic	Chronic (21-d) NOAEC	21-day average water column EEC
Freshwater invertebrates **(benthic)**	Survival	Acute	Acute (48-96 h) LC_{50} or EC_{50} (from water column test)	Peak EEC for pore water
	Survival, growth, reproduction and development	Chronic	Subchronic (10-d) or chronic (28-65-d) NOAEC	21-day average EEC for porewater and/or bulk sediment
Estuarine/marine invertebrates (**pelagic**)	Survival	Acute	Acute (48-96 h) LC_{50} or EC_{50}	Peak water column EEC
	Survival, growth, reproduction and development	Chronic	Chronic (28-d) NOAEC	21-day average water column EEC
Estuarine/marine invertebrates (**benthic**)	Survival	Acute	Acute (48-96 h) LC_{50} or EC_{50} (from water column test)	Peak EEC for pore water
	Survival, growth, reproduction and development	Chronic	Subchronic (10-d) or chronic (28-d) NOAEC	21-day average EEC for porewater and/or bulk sediment

[1] Toxicity test durations in parentheses reflect those from typical test species
[2] Based on a 1-in-10-year return frequency for model-derived exposure estimates. For monitored exposure concentrations, upper bound (e.g., maximum) concentrations are typically selected.

Following the calculation of the applicable RQs, comparisons are then made to the established "Level of Concern" (LOC). If the RQ values exceed the LOC, risk is presumed. For acute risks to non-listed[4] aquatic invertebrates, an LOC of 0.5 is used while for chronic risks, an LOC of 1.0 is used. A more detailed discussion of the basis of the LOCs is found in USEPA (2004).

[4] The term "non-listed" refers to species that are not considered "threatened or endangered" under the US Endangered Species Act (ESA). For ESA listed species, different LOC values are used.

3. Exposure Assessment

Two different methods were used for assessing exposure of benthic invertebrates to endosulfans. The first method used modeled chemical concentrations in pore water and bulk sediment. The second method used measured endosulfan concentrations in sediment. Each of these methods is summarized below.

3.1 Modeled Sediment Concentrations

The USEPA Pesticide Root Zone Model (PRZM) and the Exposure Analysis Modeling System (EXAMS) models were used to estimate concentrations of endosulfans in bulk sediment and in pore water. The PRZM model is simulation model that calculates the fate of a pesticide in treated fields on a day-to-day basis. It considers how factors such as climatic conditions, evapotranspiration of plants, soil physicochemical and hydrological characteristics, crop-specific management practices, pesticide applications and pesticide fate parameters affect the degree to which a pesticide is taken up in the plant, leaches through the soil, volatilizes into the atmosphere, and is transported off site via runoff and soil erosion. Simulations are run with over 30 years of climate data for crop scenarios that vary by crop and region of the country.

Daily estimates of pesticide runoff and erosion from PRZM are then used as input to the EXAMS model, along with estimates of pesticide spray drift. The EXAMS model is parameterized for a "standard agricultural pond" 20 million liter pond of approximately 2 meters depth that is surrounded by an agricultural field. The EXAMS model accounts for volatilization, sorption, hydrolysis, biodegradation, and photolysis of the pesticide in the aquatic environment. The standard pond is represented by two compartments (water column and sediment layers). A conceptual representation is shown in **Figure 3**. Bioavailability of a nonionic organic pesticide like endosulfan is modeled in water based on equilibrium partitioning between the freely dissolved, DOC and POC-sorbed phases. Sediments are typically assumed to contain 4% organic carbon.

The end result of the PRZM and EXAMS model simulations is a 30-year time series of daily pesticide concentrations in overlying water, pore water and bulk sediment for each crop exposure scenario. Based on these 30-year time series, EECs were calculated for specified averaging periods (peak for acute exposures and 21-d for chronic exposures) that correspond to a 1-in-10 year return frequency. Predicted EECs for endosulfans in surface water, pore water and bulk sediment (dry weight) are shown in **Figure 4** for selected crop scenarios.

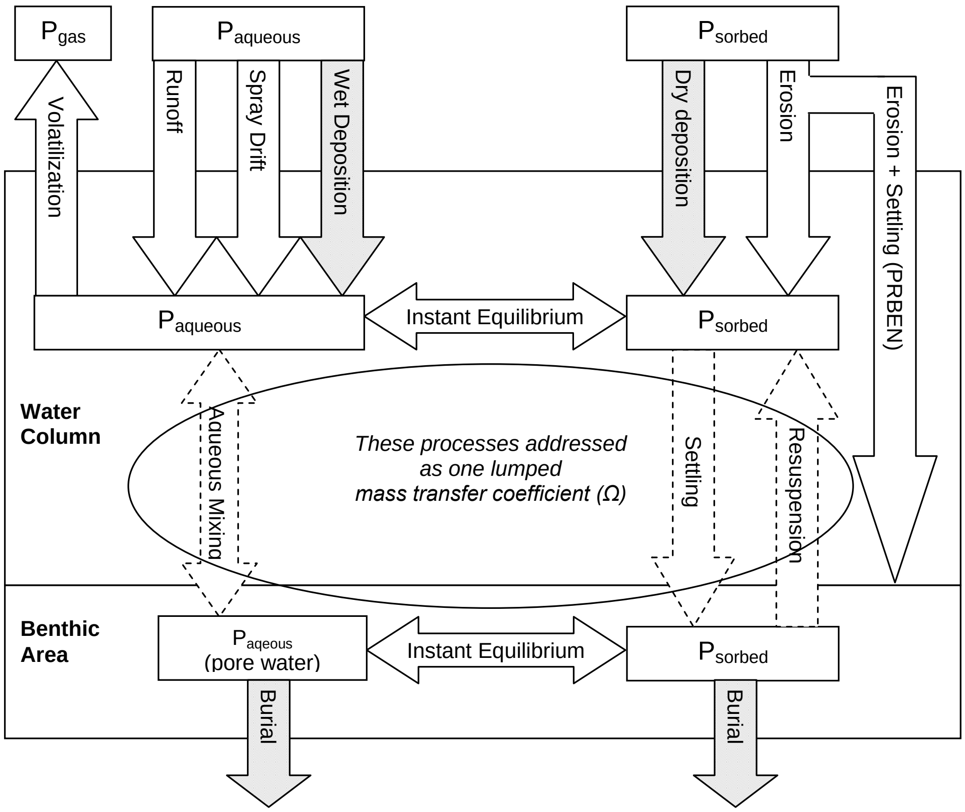


Figure 3. Conceptual model of OPP Standard Pond Scenario for Depicting Pesticide Transport

Arrows represent movement of pesticide mass from one phase (*i.e.,* sorbed or aqueous) or compartment to another. In this figure, P_{aqeous}=aqueous mass of pesticide; P_{sorbed}= sorbed mass of pesticide; and P_{gas}= gaseous mass of pesticide. Grey arrows are pathways not routinely simulated.

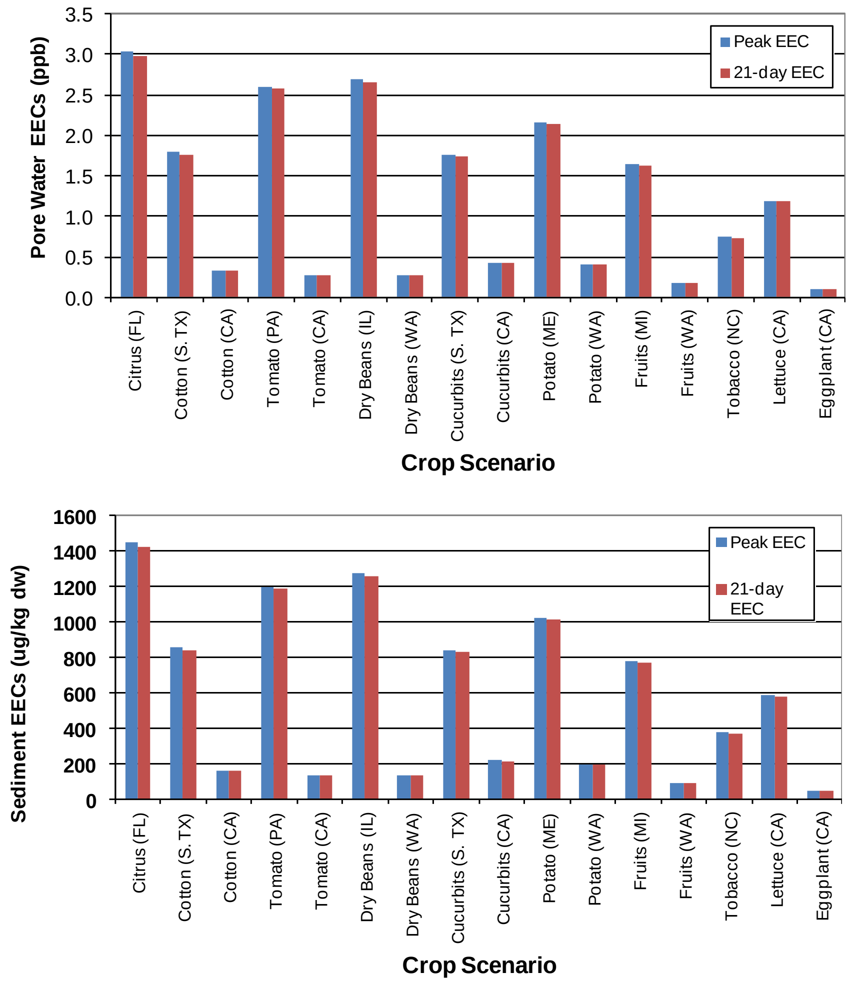


Figure 4. Predicted EECs of total endosulfan in pore water and sediment.

3.2 Monitored Sediment Concentrations

An extensive array of monitoring data was available for endosulfans measured in sediments across the U.S. The three main data sources are included in this case study:

- The US Geological Survey the North American Water Quality Assessment program (NAWQA) database[5];
- The National Sediment Quality Survey[6] (NSQS) database; and
- The South Florida Water Management District (SFWMD)[7] database (1992-2008).

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[5] NAWQA data was obtained on January 17, 2008: URL: http://infotrek.er.usgs.gov/traverse/f?p=NAWQA:HOME:3748645897450568

[6] http://epa.gov/waterscience/cs/library/nsidbase.html

[7] Detailed maps of station locations can be found at: http://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_era/pg_sfwmd_era_hydrometmonlocations

A brief summary of each of these databases is provided below. Additional details are found in USEPA (2010).

NAWQA Database. The NAWQA monitoring program represents a national scale network of numerous sites throughout the US that is intended for evaluation of broad spatial and temporal trends in contaminant concentrations. Sampling in regions alternate among different years. With respect to endosulfan in sediments, data were available from 1992-2007 and only the α endosulfan isomer was measured (not the β isomer or endosulfan sulfate degradate).

NSQI Database. The NSQI database reflects a compilation of sediment contaminant information from a wide variety of sources in the US, many of which are monitoring programs established at the State and local levels. For endosulfan, information was available from 1990 to 1998 and analyses were conducted on the parent isomers but not the endosulfan sulfate degradate. The spatial distribution of detections and non-detect from the NAWQA and NSQI databases for endosulfan is shown in **Figure 5**. A summary of the frequency of detection of endosulfan isomers and overall maxima is shown in **Table 3** and the overall distribution of detected endosulfans (α + β) is provided in **Figure 6**.

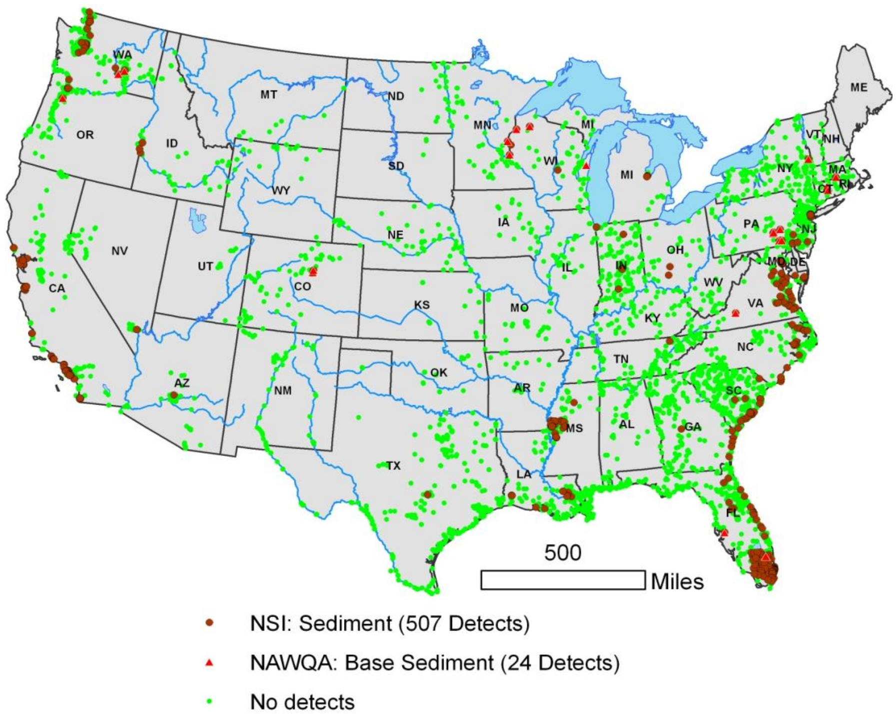

Figure 5. A map showing spatial distribution of endosulfans monitored in sediments from NAWQA (alpha endosulfan) and the NSQI (alpha & beta)

Table 3. Detection frequency and maximum sediment concentrations for endosulfan isomers

Data Source	*Monitoring Period*	*Number of Samples*		*Total*	*Detects %*	*Maximum Reported Concentration (µg/Kg)*		
		Detects	*No detects*			*Alpha*	*Beta*	*SO4*
NAWQA	*1992- 2001 & 2007*	**24**	**1,249**	**1,273**	**2%**	**8.8**	**ND**	**ND**
NSQI	1990-1998	**507**	**8,218**	**8,725**	**6%**	**430**	**192**	**ND**

ND= Not determined

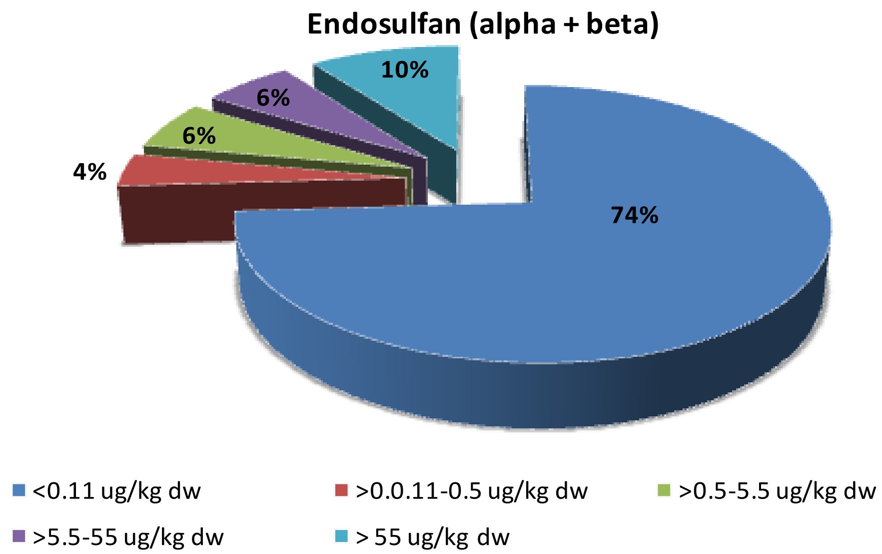

Figure 6. Frequency distribution of endosulfan detections (alpha + beta) in U.S. sediments from the NAWQA and NSQI databases

SFWMD Database. An extensive water quality monitoring network was available from the South Florida Water Management District's (SFWMD) that included sampling for pesticides in surface water and benthic sediment from numerous sites in South Florida. The data described herein represent endosulfans measured in sediment twice a year from 1992 – 2008 as reported in the SFWMD DBHYDRO database.[8] Data were reported for the α and β isomers and endosulfan sulfate. A map of the station locations is shown in **Figure 7**. Results for each of the SFWMD stations over this time period are provided in **Table 4** and those for the most contaminated station (S-178) are provided in **Figure 8**. An important limitation with these data is the lack of available information on the organic carbon content in sediment.

[8] Download date: Feb 6, 2009. Available at: https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_era/pg_sfwmd_era_dbhydrobrowser

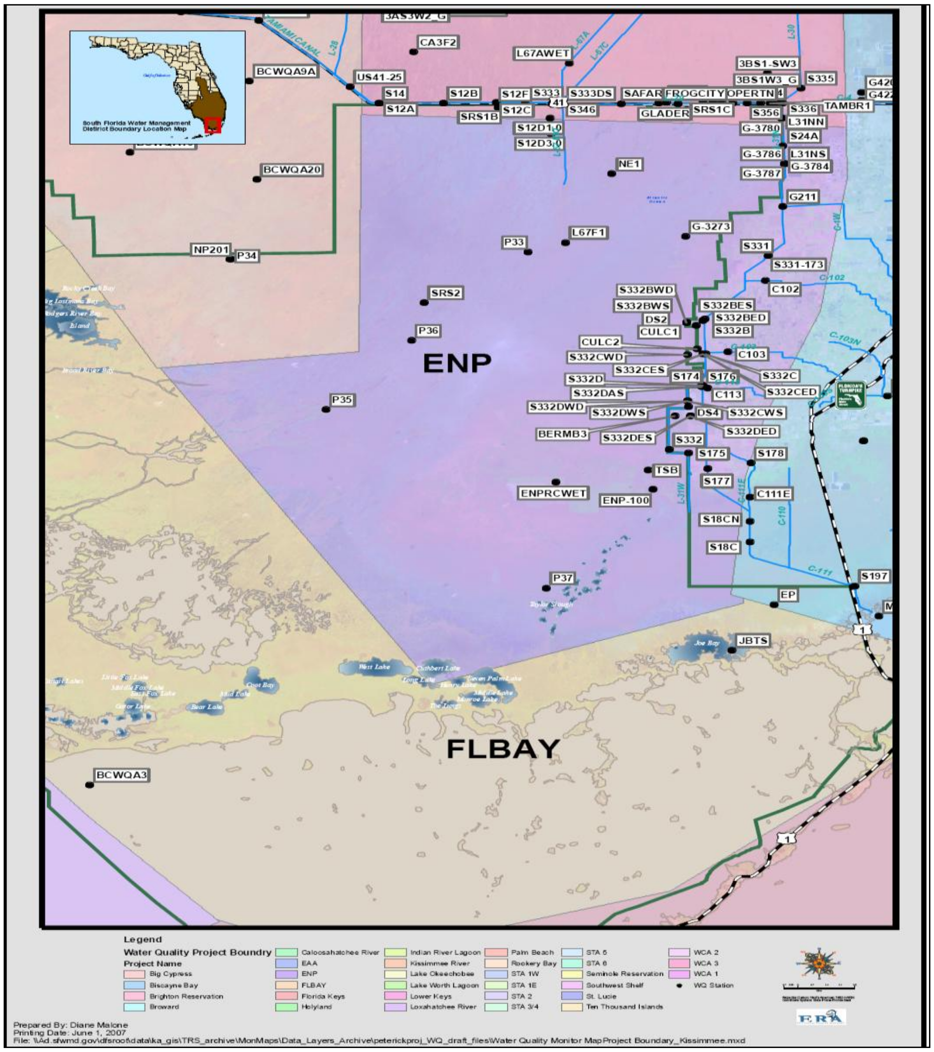

Figure 7. Sampling Locations of SFWMD water quality monitoring stations associated with the Everglades National Park (ENP) and Florida Bay (FLBAY) project areas

Table 4. Concentrations of endosulfans in sediment at SFWMD sampling sites with at least one reported detection (data source: SFWMD)

Station ID	No. Samples	No. Detects	Detection Frequency (1)	Total Endosulfans (µg/kg dw) Min.	Average (2)	Max.
C-111 Canal System						
S177	32	10	**31%**	bdl	2.9	55
S178	33	23	**70%**	bdl	39.4	152
S18C	35	1	3%	nd	nd	6.3
Subtotal	*100*	*34*	***34%***			
L-31 Canal System						
S331	23	1	4%	nd	nd	4.1
Other Stations						
C25S99	32	1	3%	nd	nd	1
G354C	1	1	**100%**	nd	nd	2.6
G393B	1	1	**100%**	nd	nd	5
G600	1	1	**100%**	nd	nd	1.3

Station ID	No. Samples	No. Detects	Detection Frequency (1)	Total Endosulfans (µg/kg dw) Min.	Average (2)	Max.
L3BRS	1	1	**100%**	nd	nd	0.9
S5A	32	1	3%	nd	nd	6.5
S6	27	1	4%	nd	nd	111
S79	31	1	3%	nd	nd	9.2
S80	33	1	3%	nd	nd	6.6
Subtotal	*190*	*9*	*4.7%*			

(1) Frequencies of detection of 0.1 (10%) or higher are highlighted in bold.
(2) Averages in µg/L calculated assuming that concentrations reported as being below the limit of analytical detection (bdl) contained 0 µg/L endosulfans.
(3) Total endosulfans = sum of alpha, beta and endosulfan sulfate analytes. bdl = below method detection limit (typically from 0.001-0.02 ppb). nd = not determined.

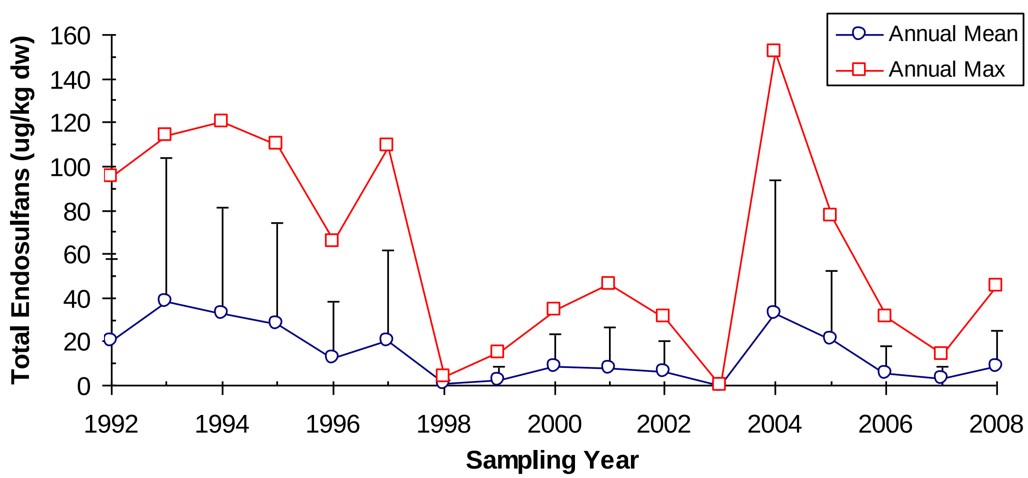

Figure 8. Annual Average and maximum concentrations of total endosulfans in sediment from the C-111 canal stations with at least one detection (1992-2008; source: SFWMD, error bars = 1 std. dev.)

4. Effects Assessment

4.1 Sediment Toxicity Data

The USEPA's 2010 ecological risk assessment for benthic invertebrates was based on registrant-submitted sediment toxicity data on the primary degradate, endosulfan sulfate. From an environmental fate perspective, endosulfan sulfate is the dominant form of endosulfan expected in sediments due to its higher persistence relative to the parent isomers. From a toxicological perspective, past studies indicate similar toxicity of endosulfan sulfate and the parent isomers (USEPA, 2007). For freshwater benthic invertebrates, two studies were submitted on the toxicity of endosulfan sulfate to the freshwater midge, *Chironomus dilutus.* The first study involved a 10-day subchronic exposure to sediments spiked with endosulfan sulfate (MRID 46382605; **Table 5**). The 10-d EC_{50} values for survival and growth determined from this study are 10.0 and 6.4 µg a.i./L-pw, respectively. The 10-d NOAEC for midge survival is 0.63 ug a.i./L-pw which is about 4X more sensitive than the NOAEC based on growth (NOAEC = 2.7 µg a.i./L-pw). The 10-d NOAECs for survival and growth in bulk sediment are 0.13 and 0.56 mg a.i./kg-dw, respectively. When normalized to 100% organic carbon, the 10-d NOAECs for survival and growth are 4.2 and 18.1 mg a.i./kg-OC, respectively. Examination of the statistical comparisons indicated hypothesis testing of survival and growth endpoints has similar statistical power (e.g., MSD= 15% and 23%, respectively).

The second sediment toxicity study with *C. dilutus* consisted of a 50-d exposure to endosulfan sulfate from which effects on survival, growth and reproduction were assessed (MRID 47318101). A NOAEC of 0.35 µg a.i./L-pw and 0.17 mg/kg dw are derived from this study based on survival (20-d) and emergence (50-d). The corresponding LOAEC values are 1.2 µg a.i./L-pw and 0.4 mg/kg-dw). Statistically significant adverse effects on growth (20-d dry weight) and reproduction (# eggs/female, % hatch) were not observed at the highest test concentration (1.2 µg a.i./L-pw and 0.4 mg/kg-dw).

Two toxicity studies were also available on the effects of endosulfan sulfate on the estuarine amphipod, *Leptocheirus plumulosus* via sediment exposure (**Table 5**). In the first study (MRID 46382606), a 10-day subchronic test was conducted which produced a NOAEC and LOAEC of 27 and 45 µg a.i./L-pw, respectively, based on mortality. Effects on growth were not determined. In a chronic 28-day test, the most sensitive NOAEC and LOAEC were determined as 1.58 and 4.0 µg a.i./L-pw, respectively based on growth and reproduction (MRID 46929001).

Table 5. Toxicity of Endosulfan Sulfate to Benthic Invertebrates Via Sediment Exposure.

Test Species	Exposure Duration	Endpoint [a]	Pore Water (µg ai/L)	Bulk Sediment (mg ai/kg dw)	Sediment OC Normalized (mg a.i./kg-OC)
Freshwater midge, *Chironomus dilutus* (3.1% TOC, MRID 46382605)	10-d	*Survival:*			
		EC_{50}	10.0	3.1	100
		NOAEC	0.63	**0.13**	4.2
		LOAEC	1.7	0.25	80.6
		Growth:			
		EC_{50}	6.4	1.9	61.3
		NOAEC	2.7	0.56	18.1
		LOAEC	3.8	1.2	38.7

Test Species	Exposure Duration	Endpoint [(a)]	Pore Water (µg ai/L)	Bulk Sediment (mg ai/kg dw)	Sediment OC Normalized (mg a.i./kg-OC)
Freshwater midge, *Chironomus dilutus* (9.3% TOC; MRID 47318101)	50-d	*Survival & Emergence:*			
		NOAEC	**0.35**	0.17	**1.8**
		LOAEC	1.2	0.4	4.3
		Growth:			
		NOAEC	1.2	0.4	4.3
		LOAEC	>1.2	>0.4	>4.3
		Reproduction:			
		NOAEC	1.2	0.4	4.3
		LOAEC	>1.2	>0.4	>4.3
Estuarine Amphipod, *Leptocheirus plumulosus* (1.6% TOC; MRID 46382606)	10-d	*Survival:*			
		EC_{50}	74	2.3	144
		NOAEC	27	0.86	53.8
		LOAEC	45	1.6	100
Estuarine Amphipod, *Leptocheirus plumulosus* (4.7% TOC MRID 46929001)	28-d	*Survival:*			
		EC_{50}	>4.0	>1.2	>25.5
		NOAEC	4.0	1.2	25.5
		LOAEC	>4.0	>1.2	>25.5
		Growth:			
		EC_{50}	>4.0	>1.2	>25.5
		NOAEC	**1.58**	**0.48**	**10.2**
		LOAEC	4.0	1.2	25.5
		Reproduction:			
		NOAEC	**1.58**	**0.48**	**10.2**
		LOAEC	4.0	1.2	25.5

(a)The lowest NOAEC values within freshwater and saltwater taxa are presented in **bold**.

4.2 Water Column Toxicity Data

Information from water column toxicity tests of invertebrate species can also provide useful information for assessing risks to benthic invertebrates. Specifically, toxicity to aquatic invertebrates can be assumed equivalent between exposures via the water column and pore water. Under the assumption of equilibrium partitioning (EqP) of a non-ionic organic chemical among the pore water and sediment organic carbon phases, risk can then be assessed by comparing water column toxicity values to predicted or measured concentrations in pore water. Although this approach was not used in the 2010 endosulfan ecological risk assessment due to the availability of sediment toxicity data, the EqP approach has been historically used by OPP for benthic invertebrate risk assessment in the absence of sediment toxicity data. It is also the basis of USEPA sediment quality benchmarks (USEPA 2002). With endosulfan, the breadth of water column-based toxicity data available for invertebrates provides an opportunity to compare the results of the EqP-based approach with those obtained from use of the set of whole sediment toxicity tests described previously. Therefore, a brief description of the applicable endosulfan water column toxicity tests for aquatic invertebrates is provided below.

The most sensitive freshwater aquatic invertebrate for which registrant-submitted acute toxicity data were available at the time of the 2010 risk assessment was for the stonefly, *Pteronarcys californica*, with a 96-h LC_{50} of **2.3 µg a.i./**L (MRID 40094602). However, much more information on the acute toxicity of endosulfan was available in the open literature. Specifically, applicable acute LC/EC_{50} values USEPA's ECOTOX database were identified and reviewed for their acceptability for pesticide risk assessment. These acute toxicity data range in exposure durations from 0.5 to 4 days and are shown in **Figure 9**. If values for multiple durations were available from a single test, then only the value from longest duration (up to 48-96 hours, depending on species) was used to make the comparison with the lowest registrant-submitted toxicity reference value of 2.3 µg a.i./L. There were 89 LC/EC_{50} values from 37 open literature studies representing 42 freshwater invertebrate species. Twenty-one of these values were below the registrant-submitted 2.3 µg a.i./L toxicity reference value (shown in red in **Figure 9**). A detailed review of these data for their suitability in USEPA pesticide risk assessment indicated the most acutely sensitive species for which acceptable data were available was for the mayfly, *Jappa kutera* (Leonard et al., 2001). Specifically, Leonard et al. (2001) compared the sensitivity of different forms of endosulfan to the freshwater mayfly, *J. kutera*. These forms included α and β endosulfan, a technical grade mixture (7:3 ratio of α and β), and endosulfan sulfate. The 96-h LC_{50} values were 0.7, 2.3, 1.8 and 1.2 µg a.i./L, respectively. The lowest of these values (**0.7 µg a.i./L** for α endosulfan) was selected for use in the 2010 risk assessment for freshwater (pelagic) invertebrates (**Table 6**). This 96-h LC_{50} value is about an order of magnitude lower than the 10-d LC_{50} value of 10 µg a.i./L-pw available for the midge, *C. dilutus*, despite the 2-fold longer duration of the midge study.

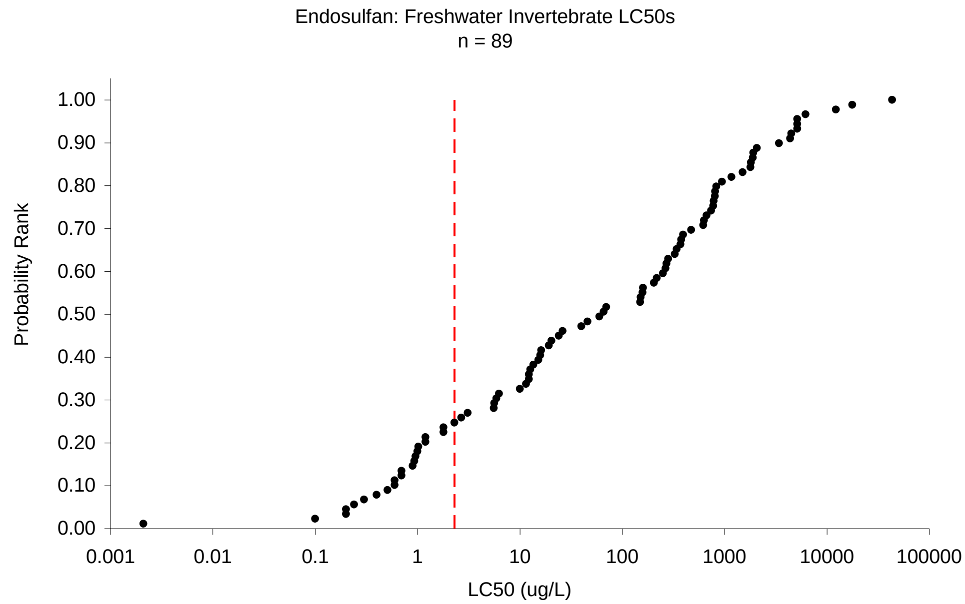

Figure 9. Freshwater invertebrate endosulfan acute toxicity data from ECOTOX (USEPA 2010). Red line denotes the lowest available LC_{50} value from registrant-submitted data (2.3 µg a.i./L)

Table 6. Acute and chronic toxicity reference values used for assessing endosulfan risk to water column invertebrates (USEPA 2010)

Species	Most Sensitive Toxicity Value Considered Acceptable for Risk Assessment (µg a.i./L)	Effects	Reference/Acceptability
Freshwater Invertebrates			
Mayfly *(Jappa kutera)*	96-h LC_{50} = 0.7 Chronic NOAEC = 0.011	Mortality Not Available	Leonard, et al. 2001; (ECOTOX 62479)/ Estimated [1]
Estuarine/Marine Invertebrates			
Pink shrimp *(Penaeus dourarum)*	96-h LC_{50} = 0.04 Chronic NOAEC = 0.013	Mortality Not Available	MRID 5005824 Estimated[2]

[1] The daphnid (*Daphnia magna*) acute-to-chronic ratio (ACR = 61.5) was used to estimate a freshwater mayfly chronic toxicity value because it is the most acutely sensitive freshwater invertebrate species and no chronic toxicity data are available for it.

[2] The mysid shrimp (*Americamysis bahia*) acute-to-chronic ratio (ACR = 3.1) was used to estimate pink shrimp chronic toxicity value because it is the most acutely sensitive saltwater invertebrate species and no chronic toxicity data are available for it.

A chronic NOAEC of **0.011 µg a.i./L** was estimated for the mayfly, *J. kutera*, by dividing its acute LC_{50} of 0.7 µg a.i./L by an endosulfan-specific acute to chronic ratio of 61.5 derived for *D. magna*. Although measured chronic toxicity data were available for *D. magna* (21-d NOAEC = 2.7 µg a.i./L), it is higher than the acute LC_{50} value for *J. kutera* (0.7 µg a.i./L) which indicates it is not among the more sensitive aquatic invertebrates to endosulfan.

For saltwater invertebrates, acute toxicity values were available from registrant-submitted studies for four species that had 96-h LC_{50} values ranging from 0.04 to 790 µg a.i./L. The most sensitive 96-h LC_{50} value of **0.04 µg a.i./L** (MRID 5005824) for pink shrimp (*Penaeus dourarum*) was considered acceptable for estimating acute risks to estuarine/marine invertebrates. No other acceptable acute toxicity values from the open literature were found to be lower than this value for pink shrimp at the time of the 2010 risk assessment. A chronic NOAEC of **0.013 µg a.i./L** was estimated for the pink shrimp (*P. dourarum*) by dividing the acute LC_{50} of 0.04 µg a.i./L by an endosulfan-specific acute to chronic ratio of 3.1 derived for *Americamysis bahia*. Although measured chronic toxicity data were available for *A. bahia* (28-d NOAEC = 0.14 µg a.i./L), it is higher than the acute LC_{50} value for *P. dourarum* (0.04 µg a.i./L) which indicates it is not among the more sensitive aquatic invertebrates to endosulfan.

5. Risk Characterization

In the USEPA 2010 assessment, risk to benthic invertebrates was determined based on comparisons of the EEC (described in Section 3) to the appropriate sediment toxicity endpoint (Described in Section 4). For the purposes of this case study, risks are also estimated based on comparisons of the EECs in pore water to the appropriate toxicity endpoints derived from water column toxicity tests. Risks were also estimated based on monitored concentrations of endosulfans in sediment. The results from each of these risk comparisons are summarized in the following sections.

5.1 Predicted EECs vs. Sediment Toxicity Endpoints

With the predicted EECs, risk quotients (RQs) for benthic invertebrates were estimated based on comparison with the sediment toxicity endpoints estimated in pore water and those estimated on a sediment organic carbon basis. Specifically:

$$\textit{Pore water RQ} = \frac{\textit{21-d EEC } (\mu g \textit{ a.i./L-pw})}{\textit{NOAEC } (\mu g \textit{ a.i./L-pw})}$$

$$\textit{Sediment RQ} = \frac{\textit{21-d EEC (mg a.i./kg-OC)}}{\textit{NOAEC (mg a.i./kg-OC)}}$$

Chronic RQ values derived for selected endosulfan crop exposure scenarios are provided in **Table 7.** These RQ values are based on modeled total endosulfan EECs in pore water compared to lowest available chronic sediment NOAEC measured in pore water. The pore water-based sediment RQs exceed the chronic risk LOC of 1.0 in **11 of the 16** crop scenarios modeled for freshwater benthic invertebrates and **7 of the 16** crop scenarios modeled for estuarine/marine benthic invertebrates. These results suggest that invertebrates are at risk of chronic effects on survival and reproduction from prolonged exposure to endosulfans in sediment.

Table 7. Chronic Risk Quotients for Benthic Aquatic Invertebrates Based on Modeled EECs and Measured Sediment Toxicity in Pore Water

Crop Use Category	EEC Range	Crop Scenario	21-day EEC (µg/L-p.w.)	RQ (fw)[1]	RQ (sw)[2]
Citrus-nb	Overall Maximum	FL Citrus-nb	2.99	**8.5**	**1.9**
Cotton	High	S. TX Cotton	1.76	**5.0**	**1.1**
	Low	CA Cotton	0.32	0.9	0.2
Tomato	High	PA Tomato	2.57	**7.3**	**1.6**
	Low	CA Tomato	0.27	0.8	0.2
Beans & Peas (dry)	High	IL Beans	2.66	**7.6**	**1.7**
	Low	WA Beans	0.28	0.8	0.2
Cucurbits	High	S. TX Melon	1.73	**5.0**	**1.1**
	Low	CA Melon	0.42	**1.2**	0.3
Potatoes	High	ME Potato	2.13	**6.1**	**1.4**
	Low	WA Potato	0.40	**1.2**	0.3
Fruits	High	MI Cherry	1.63	**4.7**	**1.0**
	Low	WA Orchards	0.18	0.5	0.1
Lettuce	n.a.	CA Lettuce	1.18	**3.4**	0.7
Tobacco	n.a.	NC Tobacco	0.73	**2.1**	0.5
Eggplant	Overall Minimum	CA Eggplant	0.09	0.3	0.1

[1] RQs based on the 50-d NOAEC of 0.35 µg/L porewater reported for survival and emergence of *C. dilutus* (MRID 473181-01)
[2] RQs based on the 28-D NOAEC of 1.58 µg/L porewater reported for growth of *L. plumulosus* (MRID 469290-01)
RQ values in bold and shaded exceed or meet the chronic risk LOC of 1.0.

Chronic RQ values expressed on the basis of sediment organic carbon are provided in **Table 8**. The sediment OC-based RQs exceed the chronic risk LOC of 1.0 in **15 of the 16** crop scenarios modeled for freshwater benthic invertebrates and **8 of the 16** crop scenarios modeled for estuarine/marine benthic invertebrates. Furthermore, it is evident that the magnitude of the chronic sediment OC-based RQ values is approximately a factor of 2 higher than the corresponding pore water-based RQ values.

The higher RQ values on the basis of sediment OC appears to reflect differences between the organic carbon partitioning assumed in modeling the sediment EECs compared to that which actually occurred in the sediment toxicity test. Specifically, K_{OC} values ranging from **10,600 to 13,500 L/kg-OC** were used in the derivation of the pore water and sediment-based EECs using the PRSM and EXAMS models. These K_{OC} values are based on standard sorption/desorption studies conducted using various soils of α and β endosulfan. By comparison, the "sediment " K_{OC} values[9] that correspond to the NOAECs from the sediment toxicity tests in **Table 5** range from approximately **2,000 to 6,700 L/kg-OC**. The lower "sediment" K_{OC} values relative to those measured from the soil-based sorption/desorption studies are consistent with the lower hydrophobicity of endosulfan sulfate (log K_{OW} =3.7) compared to the α and β isomers (log K_{OW} = 4.7 and 4.8, respectively). It may also be possible that greater amounts of dissolved endosulfan sulfate are present in pore water of the sediment toxicity tests due to sorption with DOC which may result in lower sediment K_{OC} values. However, the log K_{OW} of endosulfan sulfate (3.7) suggests that the concentration of DOC in pore water would have to be relatively high in order to substantially reduce the freely dissolved concentrations in pore water. Differences in the sorptive capacity of organic carbon underlying the soil- and sediment-based K_{OC} values may also be a factor that contributes to the observed differences in K_{OC} values. ***Thus, it appears from this case study that evaluating risks to benthic organisms on the basis of both porewater and sediment concentrations is beneficial to the risk assessment process*** because different sources and levels of uncertainty may exist among predicted (or measured) pesticide concentrations in porewater vs. bulk sediment.

Table 8. Chronic Risk Quotients for Benthic Aquatic Invertebrates Based on Modeled EECs and Measured Sediment Toxicity Normalized to Organic Carbon

Crop Exposure Scenario	EEC Range	Crop Scenario	21-day EEC (mg/kg-OC)	RQ (fw)[1]	RQ (sw)[2]
Citrus-nb	Overall Maximum	FL Citrus-nb	35.6	**19.5**	**3.5**
Cotton	High	S. TX Cotton	20.9	**11.5**	**2.0**
	Low	CA Cotton	3.9	**2.1**	0.4
Tomato	High	PA Tomato	29.7	**16.2**	**2.9**
	Low	CA Tomato	3.3	**1.8**	0.3
Beans & Peas (dry)	High	IL Beans	31.5	**17.2**	**3.1**
	Low	WA Beans	3.3	**1.8**	0.3
Cucurbits	High	S. TX Melon	20.7	**11.3**	**2.0**
	Low	CA Melon	5.3	**2.9**	0.5
Potatoes	High	ME Potato	25.3	**13.8**	**2.5**

[9] These sediment Koc values were determined by dividing each sediment OC normalized NOAEC (ug/kg-oc) by its corresponding porewater NOAEC (ug/L).

Crop Exposure Scenario	EEC Range	Crop Scenario	21-day EEC (mg/kg-OC)	RQ (fw)[1]	RQ (sw)[2]
	Low	WA Potato	4.8	**2.6**	0.5
Fruits	High	MI Cherry	19.3	**10.5**	**1.9**
	Low	WA Orchards	2.2	**1.2**	0.2
Lettuce	n.a.	CA Lettuce	9.3	**5.1**	0.9
Tobacco	n.a.	NC Tobacco	14.5	**7.9**	**1.4**
Eggplant	Overall Minimum	CA Eggplant	1.1	0.6	0.1

[1] RQs based on the 50-d NOAEC of 1.83 mg/kg-OC reported for survival & emergence of *C. dilutus* (MRID 47318101)
[2] RQs based on the 28-D NOAEC of 10.2 mg/kg-OC reported for growth & reproduction of *L. plumulosus* (MRID 46929001)
Bold and shaded RQs exceed the acute risk to non-listed species LOC of 0.5.

5.2 Monitored EECs vs. Sediment Toxicity Endpoints

Data on concentrations of endosulfans in sediments (µg/kg dry wt) were summarized earlier in Section 3.2. These data sets included two that were national in scope (NSQI, NAWQA) and one that focused on the South Florida region. Since porewater concentrations were not available from field monitoring surveys, evaluation of these data in relation to toxicity to benthic invertebrates was conducted on a sediment basis. Ideally, the fraction of organic carbon would be known from the monitored sediment samples, and the sediment NOAEC could be adjusted directly to match this OC value. However, such data were not readily available at the time of the 2010 risk assessment. Therefore, comparisons of the maximum measured concentration of endosulfans in sediment were made to the NOAEC adjusted to reflect low (2%), moderate (5%) and high (10%) organic carbon content of sediments. Specifically, the NOAEC value of 0.17 mg/kg dw for the most sensitive invertebrate (*C. dilutus*, MRID 47318101) was adjusted to reflect different fractions of organic carbon assumed in sediment (2%, 5% and 10%).

Results from this comparison (**Table 9**) indicate that maximum concentrations reported by the NSQI and SFWMD studies approach or exceed the freshwater NOAEC for *C. dilutus* as adjusted to all three values of sediment organic carbon. These results suggest that concentrations of endosulfans in monitored sediments can reach levels that would be of concern for the protection of freshwater benthic invertebrates for sediments that span a reasonably wide range of total organic carbon. In contrast, concentrations of α endosulfan reported by the NAWQA program are much lower and do not exceed any of the OC-adjusted NOAEC values. The NAWQA program is much broader in spatial scale and is designed to evaluate long-term trends in chemical concentrations rather than targeting particular sites or time periods that may be particularly vulnerable to pesticide runoff. That program also measured only α endosulfan which likely substantially under represents the concentration of total endosulfans in sediment.

Table 9. Comparison of Maximum Concentrations of Endosulfans Reported in U.S. Sediments with the Organic Carbon-Adjusted NOAEC for Freshwater Invertebrates

Study[1]	Location	Analyte	Max. Conc. (ug/kg dry wt)	RQ (Conc./NOAEC)[2]		
				2% OC	5% OC	10% OC
NAWQA	USA	α- isomer	8.8	0.2	0.1	0.0
NSQI	USA	α- isomer	430	**11.8**	**4.7**	**2.4**
SFWMD	S. Florida	α + β + SO_4	152	**4.2**	**1.7**	0.8

[1] Data sources are described in **Section 3.2. Bold and shaded** RQs exceed the chronic LOC of 1.0
[2] RQ values determined by adjusting the NOAEC of 0.17 mg/kg dry wt (MRID 47318101; 9.3% OC) to reflect 2%, 5% and 10% organic carbon in sediments (i.e., 0.037, 0.091, and 0.183 mg/kg dw, respectively).

5.3 Pore Water EECs vs. Water Column Toxicity Endpoints

Although risks to benthic invertebrates were not estimated on the basis of pore water EECs and water column toxicity values in the 2010 USEPA risk assessment, they are provided here for illustrative purposes. Acute and chronic risks are estimated according to the following:

$$\text{Acute RQ} = \frac{\text{Peak EEC } (\mu g \text{ a.i./L-pw})}{\text{Acute } LC_{50}/EC_{50} \text{ from water column test } (\mu g \text{ a.i./L})}$$

$$\text{Chronic RQ} = \frac{\text{21-d EEC } (\mu g \text{ a.i./L-pw})}{\text{Chronic NOAEC from water column test } (\mu g \text{ a.i./L})}$$

In each case, comparisons are made to the lowest acceptable acute or chronic toxicity value available for endosulfan on a deterministic basis. However, such comparisons could be made on a probabilistic basis using the distribution of pore water EECs and the distribution of species sensitivity presented earlier. Using the deterministic method, acute risks to freshwater and saltwater benthic invertebrates are shown in **Table 10**. Since the pore water EECs do not differ substantially between daily peak and 21-d average concentrations (**Table 10 vs. Table 7)**, differences in the sediment toxicity and water column toxicity-based RQ values is nearly entirely due to the use of different toxicity endpoints for different species. This difference is most apparent with the acute RQ values calculated for saltwater benthic invertebrates where the acute (96-h) water column LC_{50} value of 0.04 µg a.i./L for pink shrimp is 1/40th the pore water chronic (28-d) NOAEC of 1.58 µg a.i./L-pw *for L. plumulosus*, despite its much shorter exposure duration and consideration of effects only on survival.

Table 10. Acute risks to benthic invertebrates based on modeled EECs in pore water and water column toxicity endpoints

Crop Use Category	EEC Range	Crop Scenario	Peak EEC (µg/L-p.w.)	Acute RQ (fw)[1]	Acute RQ (sw)[1]
Citrus-nb	Overall Maximum	FL Citrus-nb	3.04	**4.3**	**75.9**
Cotton	High	S. TX Cotton	1.80	**2.6**	**44.9**
	Low	CA Cotton	0.33	**0.5**	**8.1**
Tomato	High	PA Tomato	2.61	**3.7**	**65.1**
	Low	CA Tomato	0.28	0.4	**6.9**
Beans & Peas (dry)	High	IL Beans	2.70	**3.9**	**67.4**
	Low	WA Beans	0.28	0.4	**7.0**
Cucurbits	High	S. TX Melon	1.76	**2.5**	**43.9**
	Low	CA Melon	0.42	**0.6**	**10.6**
Potatoes	High	ME Potato	2.16	**3.1**	**54.0**
	Low	WA Potato	0.41	**0.6**	**10.2**
Fruits	High	MI Cherry	1.65	**2.4**	**41.3**
	Low	WA Orchards	0.18	0.3	**4.6**
Lettuce	n.a.	CA Lettuce	0.74	**1.1**	**18.5**
Tobacco	n.a.	NC Tobacco	1.19	**1.7**	**29.8**
Eggplant	Overall Minimum	CA Eggplant	0.09	0.1	**2.3**

[1] Acute RQ values calculated using the peak EEC for total endosulfan (ά + β + sulfate) in pore water divided by the acute LC_{50} of 0.7 µg a.i./L for freshwater invertebrates based on mayfly (Leonard, et al. 2001; ECOTOX 62479) and the acute LC_{50} of 0.04 µg a.i./L for estuarine/marine invertebrates based on pink shrimp (MRID 5005824)
RQ values **bold and shaded** exceed the acute risk to non-listed species LOC of 0.5.

A more appropriate comparison can be made between chronic risks to benthic invertebrates determined using sediment toxicity and water column toxicity endpoints. Chronic RQ values calculated based on the most sensitive estimated NOAECs for freshwater and saltwater invertebrates exposed in the water column are shown in **Table 11**. Compared to chronic RQ values derived using sediment toxicity test NOAECs (**Table 7**), chronic RQ values calculated using water column toxicity test data for invertebrates are much larger (by an order of magnitude). These larger RQ values reflect the much greater number of aquatic invertebrate species represented in the water column toxicity database compared to the sediment toxicity database and consequently, the greater likelihood of capturing sensitive aquatic taxa in the water column toxicity database.

Table 11. Chronic risks to benthic invertebrates based on modeled EECs in pore water and water column toxicity endpoints

Crop Use Category	EEC Range	Crop Scenario	21-day EEC (µg/L-p.w.)	RQ (fw)[1]	RQ (sw)[1]
Citrus-nb	Overall Maximum	FL Citrus-nb	2.99	**272**	**230**
Cotton	High	S. TX Cotton	1.76	**160**	**135**
	Low	CA Cotton	0.32	**29**	**25**
Tomato	High	PA Tomato	2.57	**234**	**198**
	Low	CA Tomato	0.27	**25**	**21**
Beans & Peas (dry)	High	IL Beans	2.66	**242**	**205**
	Low	WA Beans	0.28	**25**	**22**
Cucurbits	High	S. TX Melon	1.73	**157**	**133**
	Low	CA Melon	0.42	**38**	**32**
Potatoes	High	ME Potato	2.13	**194**	**164**
	Low	WA Potato	0.40	**36**	**31**
Fruits	High	MI Cherry	1.63	**148**	**125**
	Low	WA Orchards	0.18	**16**	**14**
Lettuce	n.a.	CA Lettuce	1.18	**107**	**91**
Tobacco	n.a.	NC Tobacco	0.73	**66**	**56**
Eggplant	Overall Minimum	CA Eggplant	0.09	**8**	**7**

[1] Chronic RQ calculated using the 21-d EEC for total endosulfan (ά + β + sulfate) in pore water divided by the estimated chronic NOAEC of 0.011 µg a.i./L for mayfly and the estimated chronic NOAEC of 0.013 µg a.i./L for pink shrimp. **Bold and shaded** RQs exceed the chronic LOC of 1.0

6. Discussion and Conclusions

As of 2007, whole sediment toxicity testing (subchronic and chronic) have been conditionally required as part of pesticide registration actions in the U.S. under the Federal Insecticide, Rodenticide and Fungicide Act (FIFRA). Conditions for requiring sediment toxicity data depend on chemical properties and the expected use pattern for the pesticide. For example, sediment toxicity test are typically required for pesticides with high partitioning potential to sediment (e.g., K_d > 50, Koc > 1000, Log K_{OW} >3) and a use pattern that is likely to result in exposure in aquatic ecosystems. Typically, sediment toxicity tests are required for two species of freshwater invertebrates (e.g., *C. dilutus* and *H. azteca*) and one species of estuarine/marine amphipod (e.g., *L. plumulosus*). Inclusion of these species is designed to reflect differences in sensitivity and exposure potential that are expected among the diverse array of species that form the benthic invertebrate community. Distinctions are made between requiring a 10-d (subchronic) and a 28-65-d (chronic) test based on the expected persistence of the pesticide in sediments.

The preceding summary of the endosulfan risk assessment for benthic invertebrates is primarily intended to illustrate how these recently required sediment toxicity tests are being used by the USEPA in pesticide ecological risk assessments. Currently, risks are determined using multiple methods that include consideration of sediment pore water and bulk sediment exposure and toxicity. In concept, differences in chemical partitioning between that assumed in pesticide aquatic modeling and that observed in the conduct of sediment toxicity tests appears to support evaluation of benthic invertebrate risk on the basis of pore water and bulk sediment, especially for highly hydrophobic chemicals where subtle differences in organic carbon quality may result in large differences in bioavailability. In addition, analytical error and uncertainty associated with pore water analytical measurements tends to increase as the hydrophobicity of the chemical increases due to ever smaller pesticide concentrations being present in pore water. Thus, expressing risks on the basis of sediment concentrations may also avoid complications associated with analytical uncertainty in pore water concentrations.

This case study also illustrates the strengths and limitations associated with evaluating benthic invertebrate risk on the basis of monitored sediment concentrations. With endosulfan, an extensive database of measured sediment concentrations was available. Including monitored sediment concentrations within the risk assessment process can provide a valuable line of evidence in support of model-derived estimates of risk, as was the case with endosulfan. However, limitations associated with using sediment monitoring data also should be recognized and clearly communicated in the risk assessment. In the case of endosulfan, absence of important ancillary information (e.g., sediment TOC) contributed to uncertainty in the benthic invertebrate risk assessment using sediment monitoring data. Furthermore, interpretation of monitoring data should take into account the context of the monitoring program itself. Often, such monitoring programs do not target areas of frequent pesticide use and thus may not represent the true distribution of pesticide concentrations over space and time in areas that are vulnerable to pesticide exposure.

Finally, use of water column toxicity data as a basis of estimating benthic invertebrate risks may provide significant value by capturing a greater range of species sensitivity compared to the amount of sediment toxicity data that is typically available. Experience with OPP ecological risk assessments with pesticides has also demonstrated value in the use of sediment toxicity test endpoints for under-represented taxa in water column invertebrate tests (e.g., aquatic insects). In some case, such experience has led to requirements of water column toxicity testing of specific taxa which are known to be particularly sensitive to certain classes of pesticides (e.g., *H. azteca* with pyrethroids). As additional sediment toxicity studies are received by OPP, further analysis of the sediment toxicity database can be conducted to evaluate and further refine pesticide risk assessment for benthic invertebrates.

7. Cited Literature

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