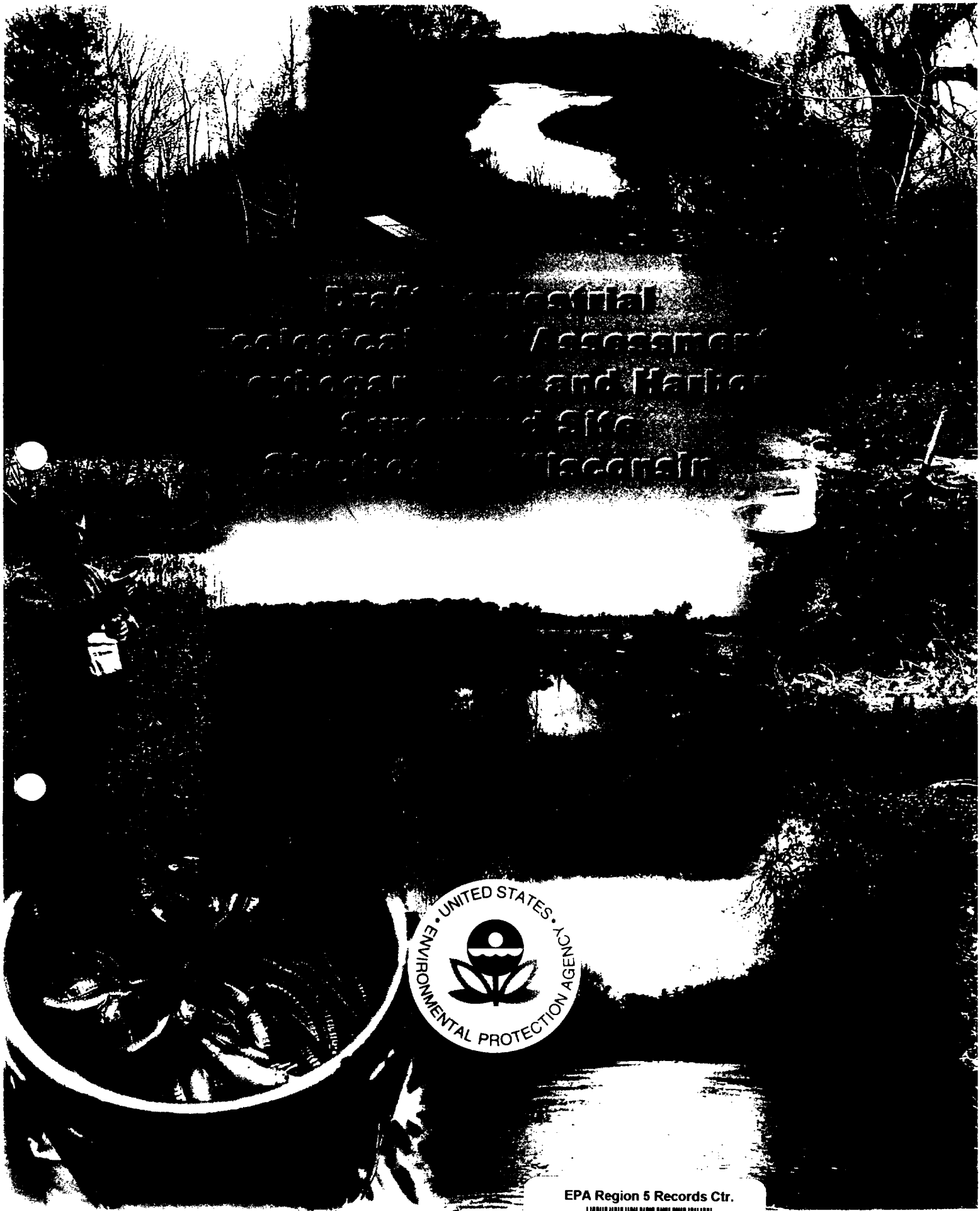

Sheboygan River and Harbor

Terrestrial (Floodplain) Ecological Risk Assessment

DRAFT

April 7, 1999

Prepared for

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List of Acronyms and Abbreviations

95%UCL - 95th percent upper confidence level
a - animal
AERA - aquatic ecological risk assessment
AHH - aryl hydrocarbon hydroxylase enzyme
AhR - aryl hydrocarbon receptor
Am - alluvial land
An - wet alluvial land
ARNT - AhR nuclear translocator
ASRI - alternative specific remedial investigation
BAF - bioaccumulation factor
Be - Bellevue silt loam
Bf - Bellevue fine sandy loam
BMF - biomagnification factor
BSAF - biota-soil accumulation factor
bw - bodyweight
BZ# - Ballschmiter and Zell PCB congener number
C - concentration
CYP1A1 - gene that controls the production of one of the P450 enzymes
d - day
D - dose
DL - detection limit
DNA - deoxyribose nucleic acid
dw - dry weight
E - analytical data exceeded calibration range and therefore required dilution
EPC - ecologically protective concentration
ERA - ecological risk assessment
EROD - 7-ethoxyresorufin-*o*-deethylase enzyme
ew - earthworms
f - fraction
fr - fruit
fd - fraction of diet
FPL - floodplain left
FPR - floodplain right
FS - feasibility study
ft - foot
fw - fresh weight (same as wet weight)
g - gram
GR - glucocorticoid receptor
hi - hard-bodied invertebrates (beetles)
HI - hazard index
HQ - hazard quotient
HSP - heat shock protein
i.p. - interperitoneal
IR - ingestion rate
IUPAC - International Union of Pure and Applied Chemistry

kg - kilogram
L - detected concentration less than minimum specified level
LOAEC - lowest observed adverse effect concentration
LOAEL - lowest observed adverse effect level
m - meter
Ma - made land
mc - moisture content
mg - milligram
NOAEC - no observed adverse effect concentration
NOAEL - no observed adverse effect level
P450 - an enzyme system that catalyzes oxidative reactions
PB-PK - physiologically-based pharmacokinetic
PB-TK - physiologically-based toxicokinetic
PCB - polychlorinated biphenyl
pH - measure of acidity
ppb - parts per billion
ppm - parts per million
PRG - preliminary remedial goal
QA - quality assurance
QSAR - quantitative structure-activity relationship
R - rejected data
REFL - reference location
RI - remedial investigation
RPD - relative percent difference
Ry - rough broken land
s - soil
SD - standard deviation
si - soft-bodied invertebrates (other than earthworms)
SOP - standard operating procedure
SWAC - surface-weighted average concentration
TCDD - 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin
TEF - TCDD (dioxin) toxic equivalency factor
TEQ - TCDD (dioxin) toxic equivalent
TERA - terrestrial ecological risk assessment
TOC - total organic carbon
TRV - toxicity reference value
U - not detected
USEPA - United States Environmental Protection Agency
WDNR - Wisconsin Department of Natural Resources
WHO - World Health Organization
wk - week
ww - wet weight
μg - microgram

Summary

The floodplain terrestrial ecological risk assessment (TERA), part of the risk assessment efforts at the Sheboygan River and Harbor Site, is a companion to the aquatic ecological risk assessment (AERA 1998) (the other component is human health). The TERA was based on PCB congener-specific analyses of co-located earthworm and soil samples collected November 3 - 5, 1997. The worm congener data were extrapolated to robin egg concentrations, which were compared with egg toxicity data on three bases: total PCBs, specific congeners, and dioxin toxic equivalents (TEQs). The egg hazard quotients (HQs), based on hatchability and malformations, ranged from 13 to 48 for no observed adverse effect concentrations (NOAEC), and from 6 to 22 for lowest observed adverse effect concentrations (LOAEC) for the central tendency scenarios of the various approaches. For the 95 percent upper confidence limit scenarios, NOAEC-HQs ranged from 22 to 80, and LOAEC-HQs ranged from 9 to 36. HQs were also developed on the basis of dose to adult birds, but the results varied by as much as an order-of-magnitude: central tendency 30 - 280 NOAEL-HQs and 3 - 120 LOAEL-HQs.

Since egg-based risk estimates were less variable than oral dose-based estimates, the egg bioaccumulation models were used to back-calculate ecologically protective earthworm concentrations separately for total PCBs and on a congener-specific basis. Ecologically-protective soil preliminary remedial goals (PRGs) were back-calculated from earthworms by use of site-specific soil-to-earthworm bioaccumulation factors (BAFs). Soil PRGs are 1 - 2 ppm total PCBs based on NOAECs, and 3 - 5 ppm based on LOAECs.

Area use effects were assessed by comparing robin foraging ranges (126 x 126 ft while caring for nestlings, and 295 x 295 ft for fledglings) with the horizontal distribution of PCBs in 1992 soil samples collected in floodplain sections with previously identified elevated levels (mean concentrations of 25 ppm at 0 - 100 ft from the nearest river bank, 3 ppm at >100 - 200 ft, and 0.3 ppm at >200 ft).

The nestling-stage foraging area fits almost within the 100-ft wide strips of elevated floodplain soil contamination. This means robins with nestling-stage foraging areas bordering the Sheboygan River are at risk of reproductive impairment where the floodplain soil mean PCB concentration exceeds 4 ppm. Adverse reproductive effects are unlikely where the floodplain soil mean PCB concentration is under 2 ppm.

Robins with nestling-stage foraging areas located further than 100 ft from the river, but with fledgling-stage foraging areas that extend to the river bank, are at risk of reproductive impairment where the 0 - 100-ft floodplain soil mean PCB concentration exceeds 9 ppm. Adverse reproductive effects are unlikely where the floodplain soil mean PCB concentration is under 2 ppm.

1.0 Site History and Floodplain Characteristics

1.1 General Site History

The Sheboygan River and Harbor Superfund site, Wisconsin, includes about 14 river miles from above Sheboygan Falls Dam to the harbor at Lake Michigan. PCB uptake by fish was first identified by the State of Wisconsin monitoring program in 1977, and the following year consumption advisories were issued. Waterfowl consumption advisories were issued in 1987. The river and harbor were designated as a Superfund site in 1986.

The main contaminant of concern has been PCB, found in highest concentrations in river sediments immediately downstream from the Tecumseh Products Company facility, and in harbor sediments. Tecumseh used PCB-containing hydraulic fluids from the mid-1960s to the early 1970s. Soil at the facility became contaminated with high levels of PCBs, 2050 m^3 of which was excavated in 1979. The most highly contaminated river sediments were excavated or armored in pilot and emergency removal actions between 1989 and 1991.

Other potential contributors to river contamination include Kohler Company (landfill), Thomas Industries (manufacture of paint spraying equipment), Diecast Corporation, and a former coal gasification plant operated by the Wisconsin Public Service Corporation. Kohler landfill was designated a Superfund site in 1984. Investigations have not revealed a pathway from the landfill to the river.

1.2 Floodplain History

Elevated PCB concentrations were detected in floodplain soils along the Sheboygan River in the remedial investigation (RI). Several additional rounds of soil sampling were performed for the Alternative Specific Remedial Investigation (ASRI 1995). Two rounds of composited soil samples were collected from depositional areas within the 10-year floodplain (Phase I, 7/90; and Phase II, 9/90). A later round of discrete soil samples was collected along transects located in floodplain sections previously identified as containing soil PCB concentrations greater than 10 ppm (post-Phases I and II, 6/92) (ASRI 1995). The discrete sampling revealed a pattern of elevated soil PCB concentrations within approximately 100 ft of the nearest river bank, and much diminished levels at greater distances (Appendix F.1).[1] The floodplain sections with elevated PCB levels mainly occur along 2 - 3 river miles between the Tecumseh facility (located below Sheboygan Falls Dam near the confluence of the Onion River) and upstream of Waelderhaus Dam, although an isolated floodplain deposit with elevated PCB levels was also reported further downstream along a golf course. These areas are well upstream of the Kohler landfill and the former coal gasification plant.

1.3 Floodplain Habitat

Only the approximately two-mile section of the floodplain sampled for the TERA is described because this includes the majority of the sections with soil PCB levels above 10 ppm (Appendix A.1). The river is bordered on both sides by strips of deciduous trees and shrubs for approximately the first one-half river mile downstream from the confluence of the Onion River. Grassy fields (some mowed or grazed) are beyond the wooded riparian corridors. The river loops clockwise for the next three-quarters of a mile around three sides of a mostly deciduous woods (approximately 35 acres), which is on the right side of the river facing downstream. On the left bank, the vegetation changes from a riparian wooded corridor with grassy fields for about one-quarter mile, to mixed trees and shrubs for one-quarter, to grassy fields for another quarter mile. The river then makes a counter-clockwise loop with steep slopes on the left side (outside bank) and scrub-shrub on the right (inside bank). Deciduous woods are on the right

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[1] The values under the heading "Approx. Distance from River Bank" in Table 7-21 of the ASRI (1995) are often not the distances from the nearest river bank. They are instead transect distances. Although the transect origins are near the river, the transect distances often do not reflect the distance to the nearest river bank either because the transects are not perpendicular to the river, or because the river bends such that the distal portion of a transect is closer to a different section of river. See figures 7K - 7 N of the ASRI.

bank and grassy fields on the left at River Bend Dam, the furthest floodplain sampling location for the ERA, almost 2 miles downstream from the Onion River confluence.

1.4 Floodplain Soils

Floodplain soil descriptions are based on the Soil Survey for Sheboygan County (USDA 1978). Most of the floodplain sections with elevated PCB levels occur on Bellevue silt loam (map symbol Be) or Bellevue fine sandy loam (Bf). Both are nearly level (0 - 2 % slopes), well drained and moderately well drained alluvial (deposited by running water) soils. Both are subject to flooding and streambank erosion. The soils are commonly 2 - 3 ft deep. For Be, the surface (A) horizon is a dark brown silt loam about 10 in deep, over a reddish brown silty clay loam subsoil (B) horizon. Be has moderate permeability and neutral pH (6.6 - 7.3). Bf differs in having a greater proportion of sand - dark grayish brown fine sandy loam surface horizon, over a dark brown fine sandy loam subsurface. Bf has moderately rapid permeability, greater than that of Be because of the increased sand, and mildly alkaline pH (7.4 - 8.4). The native vegetation on these soils was dominated by elm, basswood and maple.

A few floodplain sections with elevated PCB levels occur on Alluvial land (Am), characterized by layered loamy, sandy, and sometimes gravelly flood deposits. The soils are usually long and narrow, nearly level (0 - 2 % slopes), well drained to moderately well drained. Permeability varies depending on the nature of the deposits. The reference location for the TERA is on wet Alluvial land (An), which is poorly to very poorly drained. Other than drainage, An is similar to Am.

Other soils along the upper Sheboygan River downstream of the Tecumseh facility include Rough Broken land (Ry) on steep slopes (20 - 45 %), and Made land (Ma) comprised of fill (Rochester Park). PCBs at or above 10 ppm have not been reported for these soils.

1.5 Floodplain Wildlife

The terrestrial wildlife present along most of the upper Sheboygan River would be species adapted to mixed open, shrub, and wooded habitats that are tolerant of human disturbance. Species dependent on forested habitat may be present in the approximately 35-acre wooded "peninsula" formed by a clockwise loop of the river. This forested area is less disturbed by humans because it is surrounded by the river on three sides with no easily fordable approaches, and is backed by a steep slope on the fourth side.

Birds that include earthworms in their diets (vermivores) are of particular concern, since this is the probable pathway of greatest exposure to floodplain PCBs. Vermivorous robins and eastern bluebirds are present along the Sheboygan River in open and mixed habitats. Ovenbirds, another vermivorous species, nest in forested habitats. Ring-billed gulls also include worms in a highly varied diet, and forage far inland. Many species of birds feed on terrestrial invertebrates (beetles and other insects, spiders, etc.), such as brown thrashers, wrens, killdeer (especially beetles), young wood duck, blue jays, northern flickers (especially ants), common grackles (also steal food from robins), and spotted sandpipers (Bellrose 1976; Johnsgard 1981; Ehrlich, et al. 1988; Kaufman 1996). These species could be exposed to soil PCBs through their prey (although probably not as much exposure as vermivores), but also may opportunistically include earthworms in their diets when readily available.

Two highly vermivorous bird species, woodcock and snipe, are not likely to be present along the upper Sheboygan River because of habitat limitations.

Vermivorous species other than birds that have been recorded in Sheboygan County include short-tailed shrew, star-nosed mole, skunk, raccoon, opossum, fox, five species of salamanders, American toad, two species of frogs, four species of snakes, as well as ants, ground and rove beetles, and centipedes (Appendix B.1). Species recorded in Sheboygan County that feed on terrestrial invertebrates, but not usually worms, include six frog, two shrew, and four rodent species (Appendix B.2).

2.0 Ecological Risk Assessment (ERA) Introduction

There are two main goals of an ecological risk assessment (ERA): 1) to determine whether harmful effects are likely for wild animals or plants, and 2) if there is risk, to calculate a protective remedial goal that would reduce the risk to wild animals or plants. Only wildlife is considered, domesticated animals or plants are excluded from ERA. The process for performing an ERA is described in the Superfund guidance for ecological risk assessment (USEPA 1997). The main steps of an ERA are outlined below.

An initial step of an ERA is to decide which components of an ecosystem (the sum of the living organisms and physical factors in a particular area) should be protected, that is, which species should be the focus of the ERA. This is different from human health risk assessments in which the species is predetermined (human). The decisions of what to protect and how to measure it are made in the Problem Formulation step of the ERA.

Problem formulation begins with development of a conceptual model, which is a representation of how the particular contaminants at a site are expected to behave in the environment. The conceptual model is based on fate (e.g., does a contaminant break down in the environment or is it persistent?) and transport (how does a contaminant move through the environment and in which compartments does it reside?). The conceptual model is used to narrow attention to the animals and/or plants likely to be exposed to the contaminants at the site. In risk assessment language, the species that may be exposed to contaminants are called "receptors". The contaminants are called "stressors". Stressors may also be physical factors (e.g., temperature, water supply, light levels, storms, erosion, floods, fire, etc.) or biological factors (other species that compete with, prey on, parasitize, or cause disease in the receptor species).

It is not possible to evaluate every species that is potentially at risk at a site. In the Great Lakes region there are some 75 species of amphibians and reptiles, 80 species of mammals, over 200 species of breeding birds (and a nearly equal number of nonbreeding and accidental species), a couple of hundred species of fish, several thousand species of terrestrial plants, at least 20,000 species of insects, and so forth. The purpose of the problem formulation is to focus attention on a few species or groups of species that are appropriate for answering the question of whether an ecological risk exists at the site.

Different terms are used to refer to what should be protected (assessment endpoint) and what will be studied (measurement endpoint). Assessment endpoints are explicit expressions of the environmental value that is to be protected, that is, a short explanation of why anyone should be concerned about potential ecological impacts at a site. Measurement endpoints are measurable ecological characteristics that are related to the assessment endpoints, and

may include measures of effects (caused by a stressor) and/or measures of exposure (to a stressor). In other words, what will actually be investigated to determine the level of risk.

Assessment and measurement endpoints may be one and the same, or different but related to each other. For example, fish production could be an assessment endpoint. A possible measurement endpoint would be to perform a field study of fish productivity at the site (measurement and assessment endpoints are the same). Another approach would be to measure the impact of contaminants on benthic invertebrates (measurement endpoint), which are related to fish productivity (assessment endpoint) because benthic invertebrates (the insects and other small creatures that live on the bottoms of streams and other bodies of water) form the base of the food chain that supports freshwater fish populations. In this case, effects on benthic invertebrates are assessed for the ERA, but the reason for doing so is concern over potential impacts on fish.

An individual measurement endpoint is often described in terms of a single species, but it should be kept in mind that the measurement endpoint represents a larger group of species that would be expected to be exposed to contaminants in a similar fashion. For example, robin reproductive effects may be selected as a measurement endpoint for a site with contaminants that are known to bioaccumulate in earthworms. The resulting risk determinations should not be interpreted solely in terms of robins, but should also be considered indications of possible risks to other species at the site that include worms in their diets. If the measurement endpoint is at risk, then the other species represented under the assessment endpoint are also potentially at risk.

The next steps are Characterization of Ecological Effects and Characterization of Exposure.

In Characterization of Ecological Effects, the potential adverse effects of the contaminants are described. The information is taken from literature of field and laboratory studies performed for the particular contaminant, and, if available, from investigations of ecological impacts at the site. An important part of this section is to calculate the dose that is associated with adverse effects, that is, how much of a contaminant must be absorbed to cause an adverse effect?

Characterization of Exposure summarizes what is known of the extent of contamination at the site, and the measured or estimated uptake of the contaminants by the ecological receptors.

The next step is Characterization of Risk in which the amount of exposure of the ecological receptors to the contaminants is compared with the dose associated with adverse effects to determine whether the contamination at the site presents a potentially significant risk. If risk is indicated for the site, back-calculations are performed to determine ecologically protective cleanup goals, such that exposures would be reduced below levels of concern.

An Uncertainty section is included in risk assessments to describe the uncertainties associated with the assumptions, extrapolations, and limitations of knowledge, and the possible effects of these uncertainties on the outcome.

3.0 Problem Formulation

The terrestrial ecological risk assessment (TERA) was performed to assess the potential risks to terrestrial ecological receptors associated with the contaminated floodplain soils, and to calculate ecologically-protective preliminary soil remedial goals (PRGs).

3.1 Chemicals of Concern (COC)

The TERA focused solely on polychlorinated biphenyls (PCBs) because they were previously identified as a potential contaminant of concern in floodplain soils. Chlorinated dioxins and dibenzofurans were not included because they were shown to make only a minor contribution (less than 10 %) to the toxicity of fish contaminant loads in the Sheboygan River (AREA 1998). The PCBs in the upper river floodplain were deposited by floods, so the contaminant composition of the upper floodplain soils should be similar to that of the river sediments. Exclusion of dioxins and furans may result in a modest underestimation of floodplain contaminant risks.

3.1.1 PCB Structure and Names

PCBs refer to a class of chemicals comprised of two six-carbon rings attached together by a single carbon-carbon bond with various numbers of chlorine (Cl) atoms attached to the outside of the rings. There are 209 types of PCBs differentiated by the number of Cl atoms and their positions. The different types are referred to as "congeners". The congeners have been numbered for convenience, 1 through 209, according to a system described by Ballschmiter and Zell (1980). In the TERA, the numbers are referred to as congener or BZ numbers. In the literature, they are also called IUPAC numbers, for International Union of Pure and Applied Chemistry, or PCB numbers. The structures and numbers of the PCB congeners are presented in Eisler and Belisle (1996). Another term used in the literature is "homolog", which refers to the congeners with the same number of Cl atoms that differ only in the positions of the Cl atoms on the phenyl rings (e.g., all 46 five-chlorine congeners are homologs).

Commercial PCBs mixtures were marketed under several names, Aroclor is best-known in the U.S..[2] Aroclors are congener mixtures designated by four numbers - the first two are always "12" to indicate biphenyls, and the second two give the overall percentage by weight of Cl atoms in the mixture,[3] for example, Aroclor 1248 has 48 % Cl. Unfortunately, Aroclor batches with the same number may differ in the specific congener composition so long as the overall Cl percentage remains the same.

A small subset of PCB congeners cause dioxin-like toxicological effects because the geometry of these congeners is similar enough to that of dioxin so they behave the same at the sub-cellular level. An important characteristic for dioxin-like behavior is that the two phenyl rings orient in the same plane, referred to as planar or coplanar PCBs. The coplanar congeners that best mimic dioxin behavior have no Cl atoms attached to the closest positions on the phenyl rings to the bond holding the two rings together. This is called the *ortho* position, and congeners with no *ortho* Cl are called non-*ortho* (coplanar congeners 77, 81, 126, and 169). Another class of coplanar PCBs have one

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[2] Other names for commercial PCB mixtures include Clophen, Phenoclor, Pyralene, Kanechlor, and Fenclor.

[3] With the exception of Aroclor 1016, a PCB distillation product, for which "16" does not indicate Cl percentage.

Cl in the *ortho* position, and are called mono-*ortho* (coplanar congeners 105, 114, 118, 123, 156, 157, 167, and 189) (Van den Berg, et al. 1998). Each of the twelve non- and mono-*ortho* congeners listed here also possess the remaining characteristics required for dioxin-like activity: 2 Cl in the *para* positions (attached to the phenyl rings directly opposite from the point of attachment of the two rings) and 2 or more Cl in the *meta* positions (located between the *ortho* and *para* positions).

3.1.2 PCB Ecotoxicity

Recent reviews of the ecotoxicity of PCBs include Bosveld and Van den Berg (1994), Barron, et al. (1995), Eisler and Belisle (1996), and Hoffman, et al. (1996). Effects on birds are emphasized in this summary consistent with the selected assessment and measurement endpoints (Sections 3.3 and 3.4). See Sections 4.4.1 and 4.4.2 for detailed discussions of selected toxicological studies.

PCBs have been associated with a range of adverse effects in wildlife including growth, neurobehavioral, hormonal, reproductive, embryotoxic, immunotoxic, and lethal effects. Certain PCBs have been shown to be mutagenic and carcinogenic in laboratory studies, but cancers in wildlife have not been correlated with environmental PCB exposures. Many, but not all, adverse effects appear to be mediated through the same mode of action as for dioxins, and are therefore attributed to the dioxin-like coplanar congeners (Sections 3.1.1 and 4.2.5). However, non-dioxin-like congeners also may be responsible for toxic effects through different modes of action (Fisher, et al. 1998; Johansson, et al. 1998).

One of the most sensitive adverse effects in birds related to PCB exposure is reproductive. Reduced reproductive success results from increased embryo mortality (reduced hatchability), deformities, and chick mortality; delayed hatching; and reduced growth rates. These effects may occur at PCB doses less than the levels causing overt parental toxicity, however, sublethal neurobehavioral effects (parental inattentiveness) has been shown to contribute to the reduced reproductive success in addition to the direct effects on embryos and chicks. Common external deformities include beak, leg, toe and neck abnormalities. Internal effects include increased liver weight and abnormalities in thyroid, bursa of Fabricius (an organ in birds that functions similar to the thymus), and pituitary weights. Growth rates of chicks may also be depressed. Although PCBs may affect eggshell thickness at very high doses, this effect usually does not play a role in impaired reproductive success because the embryo and chick adverse effects occur at much lower doses. Edema (excessive accumulation of fluids) in embryos results in embryo or chick mortality, but there are questions whether this effect is caused by PCBs or by other environmental contaminants.

PCBs have also been associated with impaired immune functions, endocrine (hormonal) disruptions, and altered vitamin A regulation. PCBs have been shown to promote of hepatic (liver) cancers in rodents.

There are significant differences in PCB sensitivities between species. Of the bird species tested, chickens are the most sensitive, followed by pheasants/turkey, ducks, and gulls, in descending order.

3.2 Conceptual Model

PCBs are deposited in the floodplain during flood events. The possible environmental fates of soil PCBs are:

1) adsorption to soil organic matter, usually measured as total organic carbon (TOC), and other soil fractions
2) absorption by soil invertebrates through dermal and/or ingestion pathways
3) uptake by plant roots through adsorption to root surface and/or absorption into root tissue; and uptake by mushrooms
4) "incidental" soil ingestion by terrestrial vertebrates (inadvertent or intentional soil ingestion)
5) volatilization
6) leaching
7) erosion
8) degradation
9) formation of tightly-bound soil residues (not extractable with standard techniques)

Fates 1 and 2 are expected to predominate. Fate 3 is unlikely to be significant because soil PCBs are poorly taken up by plant roots (Puri, et al. 1997), but information on mushroom uptake of PCBs was not located. Fate 4 may be a significant exposure pathway, but is unlikely to appreciably reduce soil PCB levels. Fates 5 - 7 act to decrease local soil concentrations by redistributing PCBs to other environmental compartments and localities. They are significant for evaluating floodplain soils as potential sources of contaminants to other media and locations, but, over the past decades, these processes have not reduced the floodplain soil PCBs to acceptable levels.

Fate 8 represents a true decrease in PCB levels in the environment. Aerobic degradation appears to be limited to the lower-chlorinated PCB congeners, which are not associated with the main toxic effects of PCBs. Anaerobic (without oxygen) degradation preferentially targets many of the higher-chlorinated congeners (Unterman 1996), but sustained anaerobic conditions are unlikely to occur in surficial floodplain deposits, except for brief periods during flood events. In a study of bioremediation of soil PCBs at a racetrack in upstate New York, "There was no evidence of any PCB biodegradation in the soil samples from an adjacent control plot" (Unterman 1996), that is, natural rates of degradation of soil PCBs were too slow to be measured over the 4-month duration of the study.

Fate 9 is often overlooked. Over time, a portion of PCBs becomes tightly bound within the soil such that it is not extractable by standard analytical techniques. Possible mechanism include binding within cavities of organic molecules or within soil micropores (Alcock, et al. 1996). Although the tightly-bound fractions appear to have been "lost", their presence may be demonstrated by pretreating soil samples with acids (to disrupt organic molecules), or by crushing soil samples (to break down soil micropores). The long-term fate and availability of these fractions are poorly known.

Most investigations of biodegradation of PCBs have been short-term studies that did not distinguish between true degradation and other losses. Some research indicates that volatilization may be mainly responsible for most of the apparent degradation of soil PCBs (Alcock, et al. 1996). A long-term field study (>20 yr) of PCBs in sludge-amended soils (silt-loam with 2 % total organic carbon) showed half-lives of soil PCBs for all forms of loss ranging from 6.5 to 8.5 years on two plots, and 2 to 5.5 years on a third plot (Alcock, et al. 1996). These correspond to projected times for 99 % loss of soil PCBs of 43 to 56 years for the first two plots, and 13 to 37 years for the third. However, the loss was slower for higher chlorinated (and generally more toxic) congeners than for lower

chlorinated congeners. For example, the percentage of total PCBs contributed by the dioxin-like PCB congeners 77 and 118 approximately doubled over the two decades of the study.[4]

Terrestrial biota may be exposed to soil PCBs through the following pathways:

1) direct ingestion of soil (usually referred to as incidental soil ingestion in the case of vertebrate species)
2) indirect ingestion through feeding on soil invertebrates including worms (vermivory) and insects (insectivory)
3) dermal absorption, especially in soil invertebrates and in burrowing (fossorial) vertebrate species
4) indirect ingestion by predators feeding on vermivores/insectivores (potential prey for this pathway includes toads, salamanders, frogs, shrews, moles, or vermivorous birds, and their eggs)
5) adsorption/absorption of volatilized PCBs by above-ground plant tissues
6) indirect ingestion through feeding on plant tissues (herbivory) or mushrooms (fungivory)
7) absorption of volatilized PCBs through equilibrium partitioning between air, blood, and body fat compartments.

Pathways 1 - 3 are the primary exposure routes for soil invertebrates (worms, insects, spiders, centipedes, millipedes, etc.). Pathway 2 is the primary pathway for vertebrates (mammals and birds) because PCBs are lipophilic (fat-loving) and persistent, which mean they bioaccumulate through food-chain exposures. Pathways 1 and 3 also contribute to terrestrial vertebrate exposure, but less so than pathway 2 because of the associated bioaccumulation. However, pathway 1 may be significant in animals that eat soil for mineral nutrition, but do not have large foodchain exposures, for example, evening grosbeaks (Ehrlich, et al. 1988). Predators may be exposed through feeding on PCB-contaminated prey or their eggs (pathway 4). Some opportunists that feed on earthworms (pathway 2) may be additionally exposed by feeding on eggs (oophagy) laid by vermivorous birds (pathway 4) (e.g., raccoon, skunk, opossum).

Although pathway 5 is the primary route of exposure to terrestrial plants (Schwarz and Jones 1997), and therefore is the main route of exposure (pathway 6), along with pathway 1, to herbivores (Fries 1995), the exposures are usually much less than those occurring through pathway 2. For example, DDT accumulation (DDT bioaccumulation is similar to that of PCBs) has been shown to be as much as an order of magnitude greater in shrews (vermivores/insectivores) than in voles and mice (herbivores) (Talmage and Walton 1991). A potential pathway of unknown importance is mushroom uptake. Mushrooms were shown to be the main route of exposure for accumulation of radioactive cesium from the Chernobyl accident in the milk of grazing animals in Norway (Hove, et al. 1990). Information on bioaccumulation of PCBs by mushrooms was not located.

Pathway 7 is a postulated global equilibrium among PCBs in water, atmosphere, blood, and body fat (Duursma and Carroll 1996). The basis of this hypothesis is an exchange of inhaled and circulatory system PCBs, and exchange of PCBs between the circulatory system and body fats (equation 1).

$$PCBs_{\text{sediments or soil}} \rightleftarrows PCBs_{\text{surface water or pore water}} \rightleftarrows PCBs_{\text{atmosphere}} \rightleftarrows PCBs_{\text{blood}} \rightleftarrows PCBs_{\text{fat}} \quad [1]$$

[4] Congener 77 was co-eluted with congener 110. The soil PCB concentrations were low even at the on-set of the study: 0.2 to 0.4 ppm following sludge application in 1972, which declined to 0.02 to 0.05 ppm by 1990 (Alcock, et al. 1996).

If correct, this pathway may account for most or part of the "background" PCB levels in wildlife and humans throughout the world, but is not relevant to the present risk assessment which is concerned with the additional risks associated with foodchain and other local exposures above and beyond the globally distributed exposures. A possible exception may be inhalation exposure in burrowing animals in highly contaminated soils, however, even in this situation dermal and foodchain pathways are probably more significant, especially since the source of soil contamination is flood deposition which means that contaminants should be surficial.

3.3 Assessment Endpoint

The assessment endpoint for the TERA is reproductive performance in terrestrial vermivorous and insectivorous species (feeds on earthworms and insects, respectively). The endpoint selection was based on fate and transport of PCBs, bioaccumulation potential, and likely ecotoxicological effects.

3.4 Measurement Endpoint

The measurement endpoint is modeled reproductive performance in robins. Robins feed predominantly on insects, earthworms and other invertebrates during the breeding and nesting season, and therefore should be representative of a variety of birds that have similar diets (Section 1.5). Woodcock would be expected to show greater risk than robins since they feed almost exclusively on earthworms (earthworms accumulate higher levels of PCBs from soil compared with most insects). However, USEPA and WDNR biologists agreed that the habitats along the floodplain sections with elevated soil PCBs are not favorable for woodcock or snipe. Robins were selected as reasonably representative of potential avian receptors in the floodplain section under consideration.

Although mammals were not considered in this risk assessment, mammals that feed on worms for much (shrews, moles) or part (raccoons, skunks, opossum) of their diets may also be at risk (Whitaker and Hamilton 1998). Surprisingly, even fox may eat substantial numbers of worms when available (MacDonald 1980). The vermivorous northern short-tailed shrew and star-nosed mole are likely present at Sheboygan along with the remaining aforementioned mammals (Appendix B.1).

Examples of other earthworm consumers that may be at risk include garter snakes, salamanders, frogs, toads, larval and adult ground and rove beetles, centipedes, and ants (Edwards and Bohlen 1996; Curry 1998). Eight species of vermivorous amphibians are reported in Sheboygan County: four-toed, eastern tiger, blue-spotted, and red-backed salamanders, eastern newt efts, wood and northern leopard frogs, and American toads; as well as four species of vermivorous reptiles: eastern garter, brown, northern ring-necked, and northern red-bellied snakes (Appendix B.1).

Even species that do not feed on earthworms may be exposed by preying on vermivorous amphibians, mammals or birds that have accumulated PCBs in their tissues, or by feeding on vermivorous bird eggs. For example, earthworms are not a significant component of blue jay diets, but blue jays are well known nest robbers (Ehrlich, et al. 1988). Sharp-shinned hawks feed almost exclusively on birds, and robins are a favored prey (Johnsgard 1990). Kestrels prey on small mammals and birds, but insects, usually caught near the ground, may be seasonally important prey as well (Johnsgard 1990), any of which could serve as an exposure pathway for soil PCBs.

The measurement endpoint (robins) therefore serves as a proxy for a half-dozen or so additional bird species, a similar number of mammalian species, eight amphibian species, four reptilian species, and numerous vermivorous

invertebrate species (beetles, ants, centipedes). While no other species would have the same level of risk as robins; because of differences in dietary composition, foraging behavior, metabolism, susceptibility, and so forth; a finding of risk to robins would indicate that other vermivorous species may be potentially at risk as well.

4.0 Study Design

4.1 Overview

The basis of the TERA is reproductive effects in robins extrapolated from site-specific earthworm contaminant data. Reproductive effects are assessed both by modeled doses to adult robins, which are compared to the results of feeding studies; and by modeled robin egg concentrations, which are compared to the results of egg injection studies or to feeding studies in which egg concentrations were measured. The results of the risk assessment are translated to soil ecologically-protective preliminary remediation goals (PRGs) by use of site-specific soil-earthworm bioaccumulation factors (BAFs). The PRGs are then adjusted for area use by robins, based on robin foraging range and the horizontal delineation floodplain sample results (1992 post-Phases I and II) (ASRI 1995).

4.2 Field Samples

4.2.1 Field Sampling Objectives

The purpose of the floodplain soil and earthworm sampling effort was 1) to measure earthworm PCB levels in contaminated floodplain sections for use in robin dose calculations to determine the likelihood of adverse ecological effects, and 2) to derive a site-specific bioaccumulation factor (BAF) for PCB uptake by earthworms for use, if appropriate, in setting ecologically protective cleanup goals.

4.2.2 Field Sampling Design and Rationale

Co-located earthworm and soil sampling were collected 11/3 through 11/5/97 by USEPA, WDNR and NOAA personnel in the sections of Sheboygan River between Sheboygan Falls and Waelderhaus Dam that were previously shown to have high levels of floodplain PCB contamination (ASRI 1995). On-site samples were located in floodplain areas known to have elevated PCB levels in order to reduce the chances of having non-detections in either the soil or earthworm tissue, which would complicate or prevent calculation of site-specific BAFs. Although risk is therefore estimated for the floodplain sections with the highest known soil PCB levels, risk can be assessed for other less-contaminated sections (if soil data is available) by use of the site-specific BAFs.

In the previous sampling efforts, the floodplain along this section of river was divided into 9 segments in ascending order in the downstream direction, each of which was further separated into left and right portions corresponding to the riverbank while facing downstream. The segments were designated by FPR or FPL, for floodplain right or left, respectively, followed by the segment number (Figure 7J of ASRI). These designations were retained in the TERA sampling effort.

There were 8 sample locations for the TERA in floodplain segments previously shown to have total PCB soil concentrations greater than 10 ppm. One segment, FPL 11, downstream of Waelderhaus Dam but with PCB concentrations greater than 10 ppm, was excluded from the present sampling effort because of landscaping

changes (ASRI 1995). Another segment, FPL 8, above Walderhaus Dam with soil PCB levels greater than 10 ppm, was also excluded because of anticipated access difficulties. Each of the remaining floodplain segments with soil PCB concentrations greater than 10 ppm was sampled as follows:

Table 1. Earthworm and Soil Sample Locations, 11/3-5/97, Sheboygan River Floodplain, WI..

Floodplain Segment	Sample Number	Vegetation Type	Near Previous Floodplain Sample (ASRI 1995)
Reference	1	deciduous woods/grass edge	–
FPR 3	2 [a]	grass	B1/C1 [b]
FPL 4	3 and 10 [c]	deciduous woods/grass edge	B1/C2
FPL 4	4	deciduous woods/grass edge	D2
FPL 4	5	mixed grass and deciduous trees	D5
FPR 5	6	coniferous/deciduous woods edge	B1
FPR 6	7	deciduous woods	A2
FPR 6	8	deciduous woods	B2
FPR 7	9	deciduous woods	A1/B1

a) The matrix spike/matrix spike duplicate (MS/MSD) was collected for sample 2.
b) "/" indicates the sample was taken between 2 previous sample locations.
c) Sample 10 was a field duplicate sample.

The approximate on-site sample locations are shown in Appendix A.1.

The reference (background) location is in a wooded area on the left bank upstream of the reference location for the aquatic risk assessment (Appendix A.2). The reference area was accessed by heading west on Old Plank Road Trail (a bicycle path) from the parking lot southwest of the intersection of Rt. 23 and Meadowlark Road (neither the parking lot or the bicycle path are shown in the map). The woods are located near the river across a field south of the bicycle path before the trail goes under Rt. 23. The reference samples were composited from 9 pits dug within a 50-ft radius of the southern edge of the woods (the side nearest the river).

Field sample procedures are described in Appendix G.

Earthworm samples were not depurated, that is, gut contents were not expelled. Undepurated worm data may be considered more realistic for estimating exposure to higher trophic levels because vermivores consume undepurated worms (Beyer and Stafford 1993). An uncertainty with this approach is the bioavailability of the gut content contaminants is usually unknown. In contrast, depurated worm data is useful for estimating the bioavailable component, under the simplifying assumptions that tissue absorbed contaminants are bioavailable and gut content contaminants are unavailable (Stafford and McGrath 1986). Neither assumption holds in all cases - absorbed

contaminants may be sequestered in an unavailable form, and some studies have shown increased bioavailability of metals in earthworm casts, that is, following excretion from the worms (Ireland 1983).

4.2.3 Soil and Earthworm Tissue Chemical Analysis

PCB congeners were analyzed by Axys Analytical Services by two methods: high resolution for 3 non-*ortho*-substituted congeners (77, 126 and 169), 8 mono-*ortho*-substituted congeners (105, 114, 118, 123, 156, 157, 167, and 189), and 2 di-*ortho*-substituted congeners (170 and 180) (draft EPA Method 1668, 10/4/95, high resolution gas chromatography/high resolution mass spectrometry); and low resolution for 101 congeners, singly or in combination (5/8, 15, 16/32, 17, 18, 19, 22, 24/27, 25, 26, 28/31, 33, 40, 41/64/71, 42, 44, 45, 46, 47/48, 49, 52, 56/60, 66, 70/76, 74, 83, 84/92, 85, 87, 89/90/101, 91, 95, 97, 99, 105, 107, 110, 114, 118, 128, 129, 130, 131, 134, 135/144, 136, 137, 138/163/164, 141, 146, 149, 151, 153, 156, 157, 158, 170/190, 171, 172, 174, 175, 176, 177, 178, 179, 180, 182/187, 183, 185, 189, 191, 193, 194, 195, 196/203, 197, 198, 199, 201, 205, 206, 207, and 208) (Axys SOP PCB Congeners Analysis Methods CL-S-03/Ver. 1 for soil and CL-T-03/Ver. 1 for tissue, low resolution GC/MS). Six congeners were analyzed by both high and low resolution techniques, for a total of 108 congeners, singly or in combination, analyzed between the two techniques. This represents slightly more than one-half of the 209 different PCB congeners, but includes all but one of the 12 congeners with known dioxin-like activity (the non-*ortho*- and mono-*ortho*-substituted congeners in the high resolution method). The excluded dioxin-like congener is congener 81, which is non-*ortho*-substituted.

Soil concentrations were reported as ppb on a dry weight (dw) basis. Earthworm tissue concentrations were reported as ppb on a wet weight (ww) basis. The earthworm values are for undepurated worms, that is, inclusive of gut contents (soil and undigested organic matter).

Soil samples were also analyzed for total organic carbon (TOC), total solids, and moisture content. Earthworm samples were analyzed for lipid and moisture contents. All analyses were performed by Axys Analytical Services with the exception of soil TOC, which was performed by Analytical Resources, Inc..

4.2.4 Data Reduction

Laboratory duplicate analyses and field duplicate samples were separately averaged for single sets of data. When one of a pair of duplicate results was non-detect (U), the positive detection value was retained without averaging. If both of a pair of duplicate results were U, the respective detection limits (DL) were averaged. Prior to further data analysis, all non-detection values were converted to one-half DLs.

The results of the high resolution and low resolution analyses were combined in consolidated tables. The high resolution results took priority over the low resolution results for congeners with positive detections reported for both analytical techniques. If both the high and low resolution results were reported as non-detections for a particular congener, one-half of the high resolution DL was entered. In some cases the detected concentration was too high for the range of the high resolution method, in which case the corresponding low resolution value was retained in the consolidated tables. No means were calculated between high and low resolution results.

Congener 190 was reported in the consolidated tables as the difference between co-eluted 170/190 reported for the low resolution method and 170 reported for the high resolution method. Since the low resolution method is less

precise than the high resolution method, "190" includes both actual 190 and the fuzzy portion of the low resolution 170. However, the subtraction is necessary to avoid double-counting between the methods.

Ten congeners were not detected in any sample of either media (130, 169, 195, 197, 198, 201, and 205-208) and were deleted from the consolidated data tables. Congeners detected in soil, but not in earthworms (175, 191, 194, and 196/203), were retained in both tables. However, these congeners were excluded from the total PCB calculation for earthworms. R-flagged values, rejected because specific quality control limits were not met, were entered as 0 (only 4 entries). L-flagged (detected concentration < minimum level specified in Method 1668) and E-flagged (exceeded linear range of calibration series and required dilution) data were retained without modification.

Total PCBs for any given sample was calculated from the consolidated tables as the sum of all congeners with positive detections plus the sum of one-half of the detection limits for congeners not detected in that sample but with at least one positive detection in another sample of the same medium.

4.2.5 TCDD Toxic Equivalents (TEQ)

A select set of PCB congeners with dioxin-like activities were assessed on the basis of dioxin toxicity by calculating the TCDD toxic equivalent (TEQ). TEQ expresses the sum of the concentration of the dioxin-like PCB congeners in terms of the concentration of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (TCDD) that is expected to have the same level of toxic or cellular effects as the PCB congener combination in question. This approach applies only to the toxic effects mediated through (or otherwise correlated with) molecular binding of contaminants with the aryl hydrocarbon receptor (AhR). AhR is a ligand-induced nuclear transcription factor, which means that after a compatible contaminant (the ligand) binds with AhR, the receptor-ligand complex moves into the nucleus of the cell and attaches to DNA (forms a DNA adduct),[5] which in turn initiates production of specialized enzymes (Institute of Medicine 1994; Spitzer, et al. 1994; Segner and Braunbeck 1998). The amount of AhR activity can be quantified by directly measuring the amount of an enzyme (e.g., P450 isozyme CYP1A1, aka P4501A1) produced under control of an AhR-inducible gene (CYP1A1 also refers to the gene), or by measuring the effects of AhR-induced enzymes (e.g., aryl hydrocarbon hydroxylase (AHH) or 7-ethoxyresorufin *o*-deethylase (EROD) activities). Although the "mechanisms of AhR-mediated toxicity are unknown" (Safe 1998), the amount of AhR-mediated activity correlates with the severity of several toxic effects of dioxin-like chemicals.

An important caveat of the TEQ approach is that it only assesses the potential for dioxin-like effects. PCBs also have toxic effects unrelated to the Ah receptor (Fisher, et al. 1998). For example, gray and harbor seals in the Baltic Sea exhibit deformities, lesions, and immune suppression that appear to result from elevated levels of steroid glucocorticoid hormones. Laboratory studies demonstrated that methylsulfonyl metabolites of certain PCB congeners interfere with the glucocorticoid receptor (GR). The congeners that inhibited GR (methylsulfonyl congeners 91, 132, 149, 174) in one study (Johansson, et al. 1998) do not bind with AhR. The TEQ approach therefore would not indicate the potential for this type of effect.

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[5] The discussion is simplified by omitting some of the events such as dissociation of a heat shock protein (HSP 90) from AhR and the subsequent binding of the Ah receptor nuclear translocator (ARNT) to the receptor-ligand complex before it enters the nucleus. Activation of specific kinases may be necessary for receptor-ligand binding to occur.

TEQs were calculated by multiplying the concentration of each dioxin-like PCB congener by its toxic equivalency factor (TEF), and then summing the results for each sample. TEFs are the relative potency of PCB congeners (or other dioxin-like compounds) compared to 2,3,7,8-TCDD, which is the most toxic of the various dioxin congeners and therefore is assigned a TEF of 1.0. TEFs may be based on comparisons of 1) toxic effects in test animals, 2) various measures of AhR induction in animals (*in vivo*) or 3) in test tubes (*in vitro*), 4) AhR binding affinity for different chemicals, or 5) estimated toxicity derived from the molecular structure of the contaminant in question, formally called quantitative structure-activity relationship (QSAR). The approaches are listed in descending order of certainty, that is, direct comparison of toxic effects in animals is the preferred basis for deriving a TEF, but is also the most expensive and time-consuming to perform. QSAR is turned to only when no other studies have been performed for a chemical suspected of dioxin-like toxicity. Note that only method 1 results in actual toxic equivalency factors, the other approaches result in induction equivalency factors, which are assumed to be similar to true toxic equivalency factors because AhR induction and dioxin-like effects have been correlated in several studies (primarily in mammals) (Segner and Braunbeck 1998).

There are many sets of proposed TEFs in the literature, for example, seven are compared by Henshel, et al. (1997b). The TEFs used in this risk assessment are recommended by the World Health Organization for birds (Table 2). The WHO-TEFs were derived by consensus of experts from around the world., and therefore, in the absence of robin- or thrush-specific TEFs, are selected in preference to any single-species or single-assay derived set.

Table 2. World Health Organization Toxic Equivalency Factors for Birds (Van den Berg 1998).[a]

PCB Congener	WHO-TEF for Birds
77	0.05
105	0.0001
114	0.0001
118	0.00001
123	0.00001
126	0.1
156	0.0001
157	0.0001
167	0.00001
189	0.00001

a) Two remaining avian WHO-TEFs are not used in this risk assessment: congener 81 (TEF of 0.1) because it was not analyzed, and congener 169 (0.001) because it was not detected in any sample.

Some examples of the interpretation of TEFs are that congener 126 has one-tenth of the toxicity of TCDD, but congener 118 has one hundred-thousandth of the toxicity of TCDD in birds; or conversely, it takes 10 times more congener 126 and 100,000 times more congener 118 to produce the same level of dioxin-like effects associated with any given amount of 2,3,7,8-TCDD.

TEQs were calculated for earthworm tissue samples, robin dietary exposures, and modeled robin egg concentrations.

4.3 Modeling

4.3.1 Robin Dietary Composition and Ingestion Rate

The robin dietary composition presented in the Wildlife Exposure Factors Handbook (USEPA 1993b) was based on young (3 - 35 d) robin gut content analyses reported by Howell (1942). It included 19.5 % grass, which is probably not a food item (the author stated "its presence is accidental"). If grass is indigestible by robins, it should not be included in the dietary composition (unless the ingestion rate derivation includes non-food components). The robin ingestion value described below was based on laboratory feeding studies that did not include extraneous non-food items (Levey and Karasov 1989). So the grass component was subtracted from Howell's Table 8, and the percentage composition of the remaining dietary items were recalculated. "Traces of animal matter" (5 %) were added to the earthworm category (18.6 %) to partially compensate for the likely under representation of soft-bodied worms in gut analysis, for a final earthworm value of 23.6 % of the diet excluding grass. Similarly, the beetles category became 14.4 %. The percentage soft-bodied invertebrates (other than earthworms) was calculated by subtracting the earthworm and beetle values from the total animal matter (87.2 % excluding grass), for a value of 49.2 % (all wet weight (ww) percentages).

The ingestion rate was based on laboratory studies that determined robin ingestion rates separately for frugivory and insectivory, feeding on fruit and insects, respectively (Levey and Karasov 1989). The normalized ingestion rate for a diet of crickets (0.31 g/g_{bw}-d) is much lower than the frugivorous ingestion rates given in the Wildlife Exposure Factors Handbook (0.89-1.52 g/g_{bw}-d) (USEPA 1993b). An uncertainty associated with laboratory studies is that the ingestion rate may be lower than in wild birds because laboratory birds are less active. However, the ingestion rate in the Levey/Karasov study for a banana mash diet (0.99 g/g_{bw}-d) falls within the range of the other frugivorous studies (all wet weights), which lends credence to the approach and results of the Levey/Karasov study.

The details of Levey and Karasov (1989) were as follows: n = 10, initial robin bodyweight = 77.8 g, feeding period = 3 d (after acclimation), cricket ingestion = 6.8 g_{dw}/d, cricket moisture content (mc) = 72 %, banana mash ingestion = 11.6 g_{dw}/d, banana mash mc = 85 % (ingestion values are dry weight (dw)). On a ww basis, the ingestion values were: cricket = 24.3 g_{ww}/d and banana mash = 77.3 g_{ww}/d. The corresponding bodyweight-normalized ingestion rates were 0.31 and 0.99 g_{ww}/g_{bw}-d, respectively.

Note: the study also included a feeding trial with grape, viburnum and dogwood fruit, but the robins lost weight, so these results were not considered. In contrast, robins gained weight (1.9 g) on the cricket diet.

After removing the grass component from the robin dietary composition (Howell 1942), the overall diet was 13 % fruit and seeds, and 87 % animal matter. The overall ingestion rate based on Levy and Karasov (1989) was calculated as:

$$IR = (IR_a * fd_a) + (IR_{fr} * fd_{fr}) \quad [2]$$

where IR is the ingestion rate and fd the fraction of diet for animals (a) and fruit (fr).

Equation 2 is solved as (0.31 g_{ww}/g_{bw}-d) (0.87) + (0.99 g_{ww}/g_{bw}-d) (0.13) = 0.398 g_{ww}/g_{bw}-d, which should be reasonably representative for the breeding/nesting period.

4.3.2 Prey Contaminant Concentration Model

Undepurated earthworm concentrations were directly measured.

Concentrations of PCB congeners in soft-bodied invertebrates (other than earthworms) were estimated from the measured earthworm values using the ratio of soft-bodied invertebrate/earthworm concentrations of dioxin measured in field studies of paper sludge applications in pine plantations (equation 3). Martin, et al. (1987) reported undepurated earthworm concentration (mean 35.8 ppt), and Thiel, et al. (1988) reported undepurated soft-bodied invertebrate concentration (mean 2.7 ppt). The soft-bodied invertebrates included crickets, cockroaches, tent and other caterpillars, larvae, and spiders. Based on these studies, soft-bodied invertebrates are assumed to have 0.08 of the PCB concentration in earthworms at any particular sample location.

$$C_{si} = C_{ew} * CR_{si} \quad [3]$$

where C is the ww concentration in soft-bodied invertebrates (si) and earthworms (ew), and CR_{si} is the concentration ratio between earthworms and soft-bodied invertebrates (0.08).

The same approach was followed for estimating concentrations in hard-bodied invertebrates (beetles) (mean undepurated dioxin concentration of 6.2 ppt) (Thiel, et al. 1988). Based on these studies, hard-bodied invertebrates are assumed to have 0.17 of the PCB concentration in earthworms.

$$C_{hi} = C_{ew} * CR_{hi} \quad [4]$$

where C is the ww concentration in hard-bodied invertebrates (hi) and earthworms (ew), and CR_{hi} is the concentration ratio between earthworms and hard-bodied invertebrates (0.17).

These equations were applied to earthworm data for total PCBs, individual congeners, and TEQs to derive the respective soft- and hard-bodied invertebrate concentrations. The main uncertainty is to what degree relative dioxin bioaccumulation among different categories of terrestrial invertebrates reflects relative PCB bioaccumulation among the same groups. The estimates were based on dioxin studies because studies of relative PCB bioaccumulation were not located for terrestrial invertebrate exposures.

In aquatic systems, PCBs bioaccumulation is greater than that of dioxin (Suedel, et al. 1994; USEPA 1993a), but this may not hold true for terrestrial exposures. Comparison of published earthworm bioaccumulation studies is complicated by an often poor level of detail concerning the basis of the bioaccumulation calculation, specifically, whether the earthworm tissue concentrations are expressed as dry or wet weights, in addition to the usual difficulties in comparing field studies (e.g., differences in soil characteristics, contaminant levels, earthworm species, analytical methods, study length). Two studies of earthworm uptake of PCBs from soil showed dw/dw bioaccumulation of 11.5 (depurated) (Kreis, et al. 1987) and 1.8 - 3.4 (undepurated) [6] (Beyer and Stafford 1993). Three studies of earthworm uptake of dioxin from soil, apparently with ww earthworm concentrations, show ww/dw bioaccumulation of 14.4 (depurated) (Martinucci, et al. 1983), 4 - 9.4 (depurated) (Reinecke and Nash 1984), and 3.3 (undepurated) (Martin, et al. 1987). The corresponding dw/dw bioaccumulation values, assuming 80 % mc in earthworms, are 72, 20 - 47, and 16.5, respectively. These comparisons indicate that terrestrial earthworms may bioaccumulate dioxins to a greater extent than PCBs, however, the converse conclusion is indicated in another review (Jager 1998). Inter-study comparisons cannot be pushed too far because, in addition to the previous caveats, some studies have shown an inverse relationship between soil contaminant levels and bioaccumulation factors (e.g., Reinecke and Nash 1984) while others have not (e.g., Martinucci, et al. 1983).

The important question is not whether dioxins accumulate less or more in earthworms than do PCBs, but whether the ratio of bioaccumulation by earthworms compared to other soil invertebrates is similar for dioxins and for PCBs. There are apparently no studies that address this uncertainty. The choices for the risk assessment are 1) to apply the other invertebrates/earthworm ratios of dioxin bioaccumulation to relative PCB uptakes despite the uncertainty; 2) not to apply the ratios and assume that of the invertebrates living in and on soil, only earthworms bioaccumulate PCBs; or 3) assume all terrestrial invertebrates accumulate the same level of PCBs as earthworms. The two latter assumption are clearly inaccurate. For example, substantial bioaccumulation of congener 153 was demonstrated in great tits feeding on caterpillars. Congener 153 dry weight concentrations were two orders of magnitude greater in juvenile birds compared with the concentration in the oak leaves the caterpillars consumed (Winter and Streit 1992).

Since other invertebrates besides earthworms are likely to be exposed to soil PCBs and therefore will bioaccumulate PCBs to some extent, the dioxin relative bioaccumulation ratios were applied to estimate PCB uptake by other groups of invertebrates relative to the earthworm data. Since the dioxin bioaccumulation ratios show other invertebrates as having about an order-of-magnitude lower bioaccumulation compared to earthworms, inclusion of these bioaccumulation ratios is not likely to have a major impact on the outcome of the risk assessment. However, they were included for a more complete accounting of exposure pathways. It turns out that, under these assumptions, earthworm exposure alone accounted for nearly 80 % of the modeled dose to robins, the hard-bodied and soft-bodied invertebrates contributed about 20 % to the total dose.

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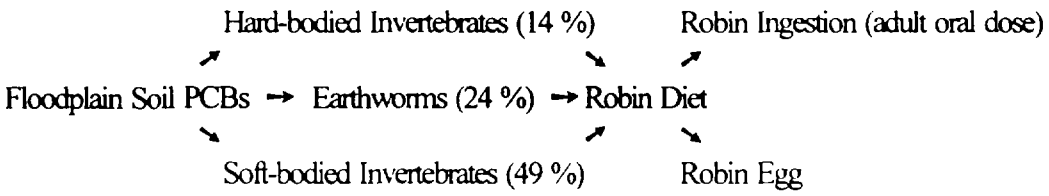
[6] The undepurated concentrations are lower than the depurated ones because of bioaccumulation. Earthworm tissue accumulates higher concentrations of chemicals such as PCBs compared with the soil concentration. Inclusion of the gut contents in the determination of undepurated earthworm concentrations therefore results in a lower combined concentration than if the gut contents are expelled and only earthworm tissues are analyzed.

4.3.3 Robin Contaminant Dose Model

The PCB dose to robins feeding in the contaminated floodplain was calculated for consumption of three broad categories of prey: earthworms, hard-bodied invertebrates (beetles), and soft-bodied invertebrates (other than earthworms) (Figure 1). Several other potential exposure pathways were not included in the model as discussed below.

Figure 1. Robin PCB Exposure Model, Sheboygan River Floodplain, WI.



Measured values: soil and earthworm PCB concentrations (congener-specific and total).
Modeled values: hard- and soft-bodied invertebrate, robin diet, and egg concentrations; and oral dose.
Contribution to robin diet in parentheses.

"Incidental" soil ingestion, the soil consumed along with prey, was not separately estimated because the earthworms were not depurated (gut contents were not emptied before performing chemical analyses). Earthworm gut contents account for roughly 30 % of the total undepurated dry weight (Stafford and McGrath 1986). The estimated fraction of soil in the diets of birds that feed on soil invertebrates range from 10.4 % in the highly vermivorous woodcock to 7 - 30 % in insectivorous sandpipers (Beyer, et al. 1994). Since these values are not higher than the gut content fraction of the earthworms analyzed for PCBs, the "incidental" soil term is already included in the earthworm data and therefore was not separately (and redundantly) estimated.[7]

Three potential exposure pathways were excluded from the dose model because they are expected to account for only a small fraction of the total dose: water ingestion, dermal uptake, and inhalation. PCBs are poorly soluble in water, therefore water ingestion exposures to terrestrial animals are minor in comparison to foodchain exposures in which PCBs bioaccumulate. The same is true for dermal exposures, especially since the feathers, beaks and claws of birds are not conducive to dermal absorption. Inhalation may play a role in the "background" exposure of wildlife to globally-distributed volatilized PCBs (Duursma and Carroll 1996), but is unlikely to significantly contribute to the increased exposure associated with contaminated floodplain soils, again because the pronounced tendency for bioaccumulation points to foodchain exposures as the predominant exposure pathway. Also, any

[7] It may be argued that since earthworms only comprise 24 % of the modeled robin diet, the worm gut contents alone are insufficient to account for the expected incidental soil ingestion for the total diet (7 % based solely on worm gut contents, calculated as 0.24 x 0.30 = 0.07). This would be a significant point except that the hard- and soft-bodied invertebrate concentrations were estimated as a fraction of the undepurated earthworm concentration, that is, the extrapolations resulted in undepurated concentrations in the hard- and soft-invertebrates as well. Since the combined dietary composition of earthworms and hard- and soft-bodied invertebrates was 87 % of the modeled robin diet, the expected contribution of incidental soil ingestion should be adequately covered.

attempt to model inhalation exposure would involve complex computations (air dispersion modeling) and highly uncertain assumptions (particularly the amount of time spent at different heights above the ground, that is, estimates of the 3-dimensional use of the habitat by robins would have to be coupled with 3-dimensional air dispersion modeling).

The overall concentration of PCBs in the robin diet was calculated as:

$$C_{diet} = (C_{ew} * fd_{ew}) + (C_{hi} * fd_{hi}) + (C_{si} * fd_{si}) \quad [5]$$

where C is the concentration and fd the fraction of diet for earthworms (ew), hard-bodied invertebrates (hi) and soft-bodied invertebrates (si).

The next step was to convert the concentration of PCBs in the robin diet to a dose, which is the amount of PCBs consumed per kg robin bodyweight per day (mg or $\mu g/kg_{bw}$-d). The dose (D) is calculated by multiplying the dietary concentration (C_{diet}) by the ingestion rate (IR).

$$D = C_{diet} * IR \quad [6]$$

This conversion allows comparison of modeled robin exposures with the results of toxicity tests performed with other species of birds with different bodyweights and ingestion rates than those of robins.

4.3.4 Robin Egg Contaminant Concentration Model and Diet-to-Egg Biomagnification Factor (BMF)

Two general approaches may be followed to model bioaccumulation in animals: 1) physiologically-based pharmacokinetic (aka toxicokinetic) models (PB-PK or PB-TK) and 2) empirical bioaccumulation factor (BAF) or biomagnification factor (BMF) extrapolations.[8] PB-TK models mathematically describe the uptake and internal distribution of chemicals within an animal's organ systems based on anatomical/physiological characteristics of the animal and physiochemical properties of the contaminant (e.g., Spacie, et al. 1995). The empirical approach does not attempt to model internal processes, but instead is based on measured ratios between dietary (or other environmental) concentrations and the concentration in the biological component of interest (tissue, organ, whole-body). For example, the empirical approach is used to estimate accumulation of contaminants in milk based on laboratory and field studies of the relationship between the concentrations in fodder and cow's milk (Fries 1995).

The empirical approach was used to estimate concentrations of PCBs in robin eggs. PCB diet-to-egg BMFs were taken from two sets of studies of piscivorous (fish-eating) birds and their prey in the Great Lakes: spottail shiner (*Notropis hudsonius*) to Forster's tern (*Sterna forsteri*) eggs (Kubiak, et al. 1989), and alewife (*Alosa pseudoharengus*) to herring gull (*Larus argentatus*) eggs (Braune and Norstrom 1989; Norstrom pers. comm. in Hoffman, et al. 1996). The values are listed in Table 3.

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[8] Bioaccumulation refers to accumulation of chemicals by living organisms from the environment through all routes of exposure. Biomagnification refers specifically to accumulation of chemicals by higher trophic level animals (predators) to concentrations greater than those in their prey. The distinction is not important for the purposes of this risk assessment. A third term, bioconcentration, refers to the limited case of an aquatic organism that accumulates a chemical by direct partitioning from water without foodchain exposures. Unfortunately, these terms are not consistently defined in the literature.

Table 3. PCB Diet-to-Egg Biomagnification Factors (BMF) (wet weight basis).		
PCB Congener	Alewife to Gull Egg[a]	Spottail Shiner to Tern Egg[b]
77	1.8	0.17
105	20	–
118	31	–
126	29	64
Total PCBs	31.7	–

a) Braune and Norstrom (1989); Norstrom pers. comm. in Hoffman, et al. (1996)
b) Kubiak, et al. (1989)

PCB congener-specific diet-to-egg BMFs were not located for wild terrestrial birds. Total PCB diet-to-egg BMFs have been reported for chickens (mean 3.2 - 5.9) (Summer, et al. 1996b), but there is a wide discrepancy with the gull value (31.7) (Braune and Norstrom 1989). As Summer, et al (1996b) point out, chickens lay eggs continuously in contrast to wild birds, which may explain the lower accumulation in individual eggs. Another factor is the feed in the Summer, et al. study is fairly dry (8 - 11 % mc) (Summer, et al. 1996a), so the chicken diet-to-egg BMF is really a dw-ww ratio, not a ww-ww ratio as are the gull and tern BMFs.

Both the gull and tern data show greater bioaccumulation for congener 126 than for congener 77, however, the BMF for 126 is three-times greater in terns than in gulls, and, conversely, the BMF for 77 is an order-of-magnitude greater in gulls than in terns. These differences are potentially significant because congeners 77 and 126 are likely to be responsible for most of the dioxin-like toxicity of the PCBs. Instead of attempting to chose between the BMFs, two egg bioaccumulation models were run: one with the gull BMFs only, the other with the two tern BMFs substituted for the corresponding gull values.

The BMF approach was not used to derive egg TEQ concentration from dietary TEQ s because BMFs were not located for TEQs. Egg TEQs were obtained by applying the WHO TEFs to the estimated congener concentrations in the eggs (congeners 77, 105, 118, and 126 only). The other congeners with WHO TEFs were not included because diet-to-egg BMFs were not available for estimating egg concentrations. These omissions should have only a minor effect on the results because the respective TEFs are several orders-of-magnitude less than those of congeners 126 and 77. For example, earthworm TEQs were based on the sum of all the dioxin-like congeners detected in the samples, but congeners 77, 105, 118, and 126 accounted for 99.4 - 99.8 % of the total TEQs (just congeners 77 and 126 accounted for 97.5 - 98.4 % of the total TEQs).

A potentially more problematic omission is congener 81, which was not analyzed in the soil or earthworm samples. Congener 81 is assigned an avian TEF of 0.1 by WHO, equivalent to the value for congener 126 and double the value for congener 77. The congener 81 TEF for birds is based on induction of enzyme activity (EROD) in liver cell cultures (chick embryo hepatocytes), but has not been investigated in egg injection studies (Van den Berg 1998). In a study of field-collected merganser eggs at Green Bay, WI, congener 81 concentrations were 40 % of the level of congener 126 (range 28 - 64 %) (Williams, et al. 1995). In contrast, congener 81 was not detected (< 1 ppb) in

common and Forster's tern eggs collected from Green Bay. Congener 81 was therefore less than 3 - 6 % of the levels of congener 77 in the tern eggs, and as little as 14 % of the congener 126 levels (Smith, et al. 1990). In an extensive study of snapping turtle eggs in the Great Lakes and the St. Lawrence River basin, congener 81 was 17 % (range 11 - 32 %) of congener 126 levels, but was 2.7 times greater (0.9 - 3.7) than congener 77 levels (Bishop, et al. 1998). These studies indicate that omission of congener 81 might, but not necessarily, result in a non-trivial underestimation of the potential toxic effects in eggs; however, there is large uncertainty regarding the actual toxicity of congener 81, the levels potentially present in Sheboygan floodplain soil and earthworms are not known, and a diet-to-egg BMF was not located for congener 81.

4.4 Characterization of Ecological Effects

4.4.1 Ingestion Toxicity Reference Values (TRVs)

4.4.1.1 Total PCB Ingestion TRV

The toxicity reference value (TRV) for total PCBs was based on a study of chicken (*Gallus domesticus*) fed naturally contaminated common carp (*Cyprinus carpio*) collected from the Saginaw River, Lake Huron, MI (Summer, et al. 1996a, b). The carp were analyzed for total PCBs on the basis of the sum of Aroclors 1242, 1248, 1254 and 1260, which should more closely approximate a congeners-based total PCBs than would any single Aroclor analysis. Different treatment doses were obtained by diluting the carp with chicken feed. Summer, et al. (1996a) reported mean bodyweight and daily PCB consumption (μg/hen) for biweekly intervals by treatment. For the purposes of this risk assessment, overall mean bodyweights and daily PCB consumption were calculated for the interval of weeks 1 through 8 following the onset of dietary exposure to contaminated carp (the duration of the experiment excluding the 2-week acclimation period),[9] and the resulting values were used to calculate bodyweight-normalized PCB ingestion rates for each of the treatments.[10] The results were checked by calculating PCB ingestion rates through a second procedure: the reported dietary PCB concentrations (single value for each treatment) were multiplied by the mean food ingestion rates for weeks 1 through 8 post-exposure.[11] The two approaches were in close agreement. The treatment doses by the first procedure are 0.0159, 0.0415, and 0.361 mg PCBs/kg_{bw}-d for control, low-, and high-doses, respectively.

The TRVs were selected on the basis of reproductive effects reported in Summer, et al. (1996b). Hatchability decreased by 18 % in the high-dose treatment relative to the control (weeks 4 - 8 post-exposure), and total embryo/chick deformities increased 2.3 times (over the entire experimental period including the 2-week

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[9] The designation of weeks differs in this ERA from the original study in which weeks were numbered from the beginning of the acclimation period. Weeks 1 - 8 post-exposure as described in this ERA correspond to weeks 3 - 10 in the original.

[10] Mean bodyweights of 1.690, 1.618 and 1.584 kg/hen for weeks 1 - 8 post-exposure in the control, low- and high-dose treatments, respectively; and mean daily PCB consumption of 0.0268, 0.0671 and 0.572 mg PCB/hen-d, respectively (calculated from Summer, et al. 1996a).

[11] Dietary concentrations of 0.3, 0.8 and 6.6 mg PCB/kg, for the control, low- and high-doses, respectively (Summer, et al. 1996a). Mean ingestion rates of 0.0511, 0.0553 and 0.0548 kg food/kg_{bw}-d for weeks 1 - 8 post-exposure in the control, low- and high-dose treatments, respectively (calculated from Summer, et al. 1996a).

acclimation). Deformities increased 1.4 times in the low-dose treatment relative to the control, but hatchability was unaffected. The overall deformity rates were 17, 24, and 40 % for the control, low-, and high-doses, respectively. The data were not statistically analyzed by the authors, but the increases in deformity rates are statistically discernible for both the low- and high-dose treatments (Kathy Patnode, WDNR, pers. comm.). For the purposes of the present risk assessment, the high-dose treatment was selected as the lowest observed adverse effect level (LOAEL), that is, the lowest dose in which a toxic effect was detected. This was based on the decrease in hatchability and the large increase in deformities. The low-dose treatment was selected as the no observed adverse effect level (NOAEL), the highest dose in which toxic effects were not detected. This was based on the lack of effect on hatchability and the comparatively low increase in deformities. In other words, despite the statistical "significance" of the low-dose deformity rate compared with controls, the effect was not considered to be biologically significant, especially since hatchability was unaffected. In contrast, the more than doubling of deformity rates accompanied by decreased hatchability in the high dose treatment was considered a biologically significant effect.

The main uncertainty with this study is that the carp absorbed their contaminant loads in nature (Saginaw Bay), so they may have accumulated other contaminants in addition to PCBs. This means that the observed adverse effects may not be solely due to PCB exposure. For example, PCB congeners 77 and 126 accounted for 87 % of the TEQ of carp samples collected from the Saginaw River in 1983, but 2,3,7,8-TCDD accounted for an additional 12 % (Smith, et al. 1990). Conversely, because carp absorbed PCBs in nature, the congener profile should accurately reflect the changes that occur when PCBs are passed through a food chain (environment → prey → predator). The congener patterns in the commercial PCB mixtures (Aroclors) commonly used in laboratory toxicity testing differ from the patterns found in living organisms, so laboratory feed spiked with an Aroclor may not have the same toxicity as bioaccumulated PCBs (Bush, et al. 1974).

4.4.1.2 PCB TEQ Ingestion TRV

The PCB TEQ TLVs were based on the same study (Summer et al. 1996a, b). Treatment doses were calculated from the reported dietary TEQs (measured by H4IIE rat hepatoma cell line EROD-induction bioassay) and the mean food ingestion rate for weeks 1 through 8 post-exposure (Summer, et al. 1996a).[12] The treatment doses were 0.00017, 0.00144 and 0.00323 μg TEQ/kg$_{bw}$-d for the control, low-, and high-doses, respectively. The high dose was selected for the LOAEL, and the low dose for the NOAEL, as described in the previous section.

4.4.1.3 Dioxin Ingestion TRV

A second approach for assessing the risk associated with exposure to PCB TEQs is to compare against the results of dioxin studies. The dioxin TRVs were based on fertility and embryo mortality in pheasants (*Phasianus colchicus*) given weekly interperitoneal (i.p.) injections of 2,3,7,8-TCDD (Nosek, et al. 1992, 1993). These studies were also the basis for TRVs in the USEPA assessment of dioxin risks to wildlife (USEPA 1993a) and the Great Lakes Water Quality Initiative (USEPA 1995). In both cases a subchronic to chronic extrapolation factor of 10 was applied because the study length (10 wk) was considered insufficient to attain steady-state dioxin accumulation.

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[12] Dietary concentrations of 3.3, 26 and 59 pg TEQ/g, for the control, low- and high-doses, respectively (Summer, et al. 1996a). Divide pg/g by 1000 to convert to μg/kg. Mean ingestion rates of 0.0511, 0.0553 and 0.0548 kg food/kg$_{bw}$-d for weeks 1 - 8 post-exposure in the control, low- and high-dose treatments, respectively (calculated from Summer, et al. 1996a).

This extrapolation factor was not included in the present risk assessment since the dioxin benchmark is being used to evaluate risk associated with PCB TEQ exposure, not dioxin exposure *per se* (the toxicokinetics of PCBs probably differ from that of dioxins), and because, as a migratory species, robins will have seasonal, not continuous, exposure to site contaminants.

The dioxin TRVs are derived as follows. Pheasants were injected with 0, 10, 100 or 1000 pg TCDD/g_{bw}-wk (Nosek, et al. 1992), which are equivalent to 0, 0.0014, 0.014 and 0.14 μg TCDD/kg_{bw}-d. The highest dose resulted in decreased hen bodyweight, reduced egg production, increased embryo mortality (all statistically discernible from controls), and substantial mortality (57 %) of adult hens. The only effect seen in the two lower doses was increased embryo mortality, however, it was not statistically discernible from controls for either treatment. The dioxin TRVs are therefore 0.14 and 0.014 μg TCDD/kg_{bw}-d for the LOAEL and NOAEL, respectively. An important uncertainty is the very steep dose-response curve between the highest and second highest doses. The actual LOAEL may be closer to 0.014 than to 0.14 μg TCDD/kg_{bw}-d. Another uncertainty concerns the extent to which i.p.-injected dioxin reflects the toxicokinetics of orally-ingested dioxin.

4.4.2 Egg Toxicity Reference Values (TRVs)

4.4.2.1 Total PCB Egg TRV

The aforementioned contaminated-carp chicken feeding study (Summer, et al. 1996a, b) was also used for deriving total PCB egg TRVs. Eggs were analyzed weekly for total PCBs (sum of Aroclors 1242, 1248, 1254 and 1260) for each treatment (Summer, et al. 1996b). The highest egg concentration of the last 3 weeks of the experiment (when levels appear to have reached a plateau) was selected for the no observed adverse effect concentration (NOAEC): 5 mg PCB/kg egg in the low-dose treatment. The lowest egg concentration of the last 3 weeks of the experiment was selected for the lowest observed adverse effect concentration (LOAEC): 24 mg PCB/kg egg in the high-dose treatment. Both concentrations are wet weight (ww). The effects associated with the treatments are described in Section 4.4.1.1.

The LOAEC is higher than the lowest egg PCB concentrations associated with the onset of reproductive impairment in field studies of bald eagles, and common and Forster's tern colonies, and onset of deformation in caspian terns (8 - 19 mg PCBs/kg egg), as reviewed in Bosveld and Van den Berg (1994). An uncertainty associated with field studies is to what extent contaminants besides PCBs, or other extraneous factors, contributed to the adverse effects. Regardless, the field results indicate that the LOAEC based on Summer, et al. is not overly conservative for several wild bird species.

4.4.2.2 Congener 126 Egg TRV

The apparent toxicity of congener 126 injected into chicken egg yolks was shown to be inversely related to the injection volume. The lethal concentration to 50 % of the embryos (LC_{50}) was 0.6 μg 126/kg egg (ww) for an injection volume of 1 μL/g egg (Powell, et al. 1996a), but was 2.3 μg 126/kg egg (less toxic) for an injection volume of 0.1 μL/g egg (Powell, et al. 1996b). The latter study was used for deriving the egg TRV. Nine doses were injected from 0 to 12.8 μg 126/kg egg. Statistically discernible increases in developmental abnormalities and in embryo mortalities occurred at 3.2 μg 126/kg egg (22 % abnormalities vs. 0 in controls, and 92 % mortality vs. 6

- 9 % in controls), which was selected for the LOAEC. The next lowest dose was selected for the NOAEC (3 % abnormalities and 22 % mortality).

Hoffman, et al. (1998) reported adverse effects at lower egg concentrations of congener 126 than the Powell, et al. (1996b) study, but the injection volume was not described. Since Powell, et al. have demonstrated an important effect of injection volume on the apparent toxicity, the results of their low-volume injection study was chosen for TRV selection.

4.4.2.3 Congener 77 Egg TRV

Powell, et al. (1996a) also investigated the effects of congener 77 in chicken eggs at the higher injection volume, but did not repeat the study with the lower injection volume. Six doses were injected from 0 to 81 μg 77/kg egg (ww). Embryo abnormalities increased 3-fold at 9 μg 77/kg egg, but were not statistically discernible from controls. Abnormalities increased 4-fold at 27 μg 77/kg egg compared with controls (a statistically discernible increase). Mortality was statistically elevated for doses 9 μg 77/kg egg (67 % mortality) and 27 μg 77/kg egg (100 %) compared with the vehicle control [13] (40 %). Under the assumption that the toxicity of congener 77 would have been lower if the study have been repeated with a smaller injection volume, as was shown for congener 126, the LOAEC was set at 27 μg 77/kg egg and the NOAEC at 9 μg 77/kg egg (shifted one dose level upwards from the results based on mortality).

4.4.2.4 Congener 105 Egg TRV

The congener 105 egg TRVs were based on the same study used for congener 77 (Powell, et al. 1996a). Six doses were injected from 0 to 8100 μg 105/kg egg (ww). Embryo abnormalities increased 4- to 7-fold at 8100 μg 105/kg egg, but were not statistically discernible from controls. Mortality was statistically elevated at 8100 μg 105/kg egg (84 %) compared with the vehicle control (40 %). The LOAEC was set at 8100 μg 105/kg egg and the NOAEC at 2700 μg 105/kg egg. The results were not shifted to account for the injection volume effect because the LOAEC was the highest dose in the study.

The relatively low reproductive toxicity of congener 105 was also demonstrated in feeding studies with pheasants (Hornung, et al. 1998).

4.4.2.5 Dioxin Egg TRV

The dioxin egg TRVs were based on the same low-injection study used for the congener 126 TRVs (Powell, et al. 1996b). Six doses of 2,3,7,8-TCDD were injected from 0 to 0.64 μg TCDD/kg egg (ww). Embryo abnormalities increased from 0 % in the vehicle control to 13 % at 0.16 μg TCDD/kg egg (a statistically discernible increase). Mortality was statistically elevated at 0.16 μg TCDD/kg egg (87 %) compared with the controls (23 %). The LOAEC was set at 0.16 μg TCDD/kg egg and the NOAEC at 0.08 μg TCDD/kg egg.

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[13] Vehicle control refers to eggs injected with the substance (the vehicle) used to dissolve congener 77 for injection by itself, that is, without the toxic chemical added to it.

Henshel, et al. (1997) also performed dioxin injections in chicken eggs. The NOAEC for mortality (0.1 μg TCDD/kg egg) was similar to the one based on Powell, et al. (1996b). The LOAEC was somewhat higher (0.3 μg TCDD/kg egg), but not markedly so. In contrast, a field study of wood ducks (*Aix sponsa*) and exposures to dioxins and polychlorinated dibenzofurans indicated an order-of-magnitude lower hatchability egg TRVs: means of 0.01 and 0.04 μg TEQ/kg egg, for NOAEC and LOAEC, respectively (White and Seginak 1994). A difficulty in interpreting these findings is that predation losses were assumed to be zero because the nest boxes were provided with conical predator guards. Therefore all egg losses were assumed to be caused solely by contamination. The validity of these assumptions is open to question, especially since the estimated effect levels are lower than the results obtained from egg injection studies, even those with chickens, which have the greatest sensitivity to dioxin-like effects of the species of birds used in toxicity tests.

4.4.3 Hazard Quotients (HQs) and Hazard Indices (HIs)

Risk to robins was evaluated by calculating hazard quotients (HQs) (equation 7).

$$HQ = \text{Modeled egg concentration} / TRV \quad [7]$$

where TRV is the toxicity reference value for either the NOAEC or LOAEC in eggs for the chemical under consideration (total PCBs, specific congeners, TEQ). HQs less than 1 indicate that modeled egg concentrations are below levels of concern, therefore adverse effects are considered unlikely. HQs equal or greater to 1 indicate that modeled egg concentrations are at or above levels of concern, therefore robins are at risk of adverse effects.

Three congener-specific risk estimates were made (congeners 77, 126 and 105). Under the assumption that the congener-specific effects are additive, the congener-specific HQs were summed to an overall hazard index (HI) (equation 8).

$$HI = HQ_{77} + HQ_{126} + HQ_{105} \quad [8]$$

Risk estimates on the basis of dioxin toxic equivalents (TEQs) were made by converting modeled egg concentrations of congeners 77, 126, 105 and 118 to a TEQ concentration, which was then divided by the dioxin TRV to calculate the HQ (equation 9).

$$HQ = \text{Modeled egg TEQ concentration} / \text{dioxin TRV} \quad [9]$$

4.5 Ecologically Protective Soil Preliminary Remedial Goals (PRGs)

4.5.1 Total PCB-based Soil PRGs and Soil-to-Earthworm Bioaccumulation Factor (BAF)

The procedure for calculating ecologically protective soil preliminary remedial goals (PRGs) on the basis of total PCBs began with the total PCB TRVs for eggs corresponding to the NOAEC and LOAEC (Appendix E). Ecologically protective robin dietary concentrations were calculated by dividing the egg PCB TRVs by the diet-to-egg biomagnification factor (BMF). Ecologically protective earthworm concentrations were calculated by combining and rearranging equations 3 through 6 (equation 10).

$$EPC_{ew} = EPC_{diet} / [fd_{ew} + (CR_{si} * fd_{si}) + (CR_{hi} * fd_{hi})] \quad [10]$$

where EPC is ecologically protective concentration, fd is fraction of robin diet, and CR is the concentration ratio between earthworms and other invertebrates, for earthworms (ew), robin diet (diet), soft-bodied invertebrates (si), and hard-bodied invertebrates (hi).

Ecologically protective soil PRGs were back-calculated from protective earthworm concentrations by dividing the earthworm concentration by the soil-earthworm bioaccumulation factor (BAF). The BAF, calculated from site-specific data, represents the ratio of earthworm wet weight concentration to soil dry weight concentration (equation 11).

$$BAF = C_{ew}\,(ww) / C_s\,(dw) \quad [11]$$

where C is the concentration of total PCBs or specific congeners in earthworms (ew) and soil (s).

An alternative to BAF is the biota-soil accumulation factor (BSAF), in which the earthworm concentration is lipid-normalized, and the soil concentration is total organic carbon (TOC)-normalized. Normalization is performed by dividing the respective concentrations by the lipid or TOC percentages (converted to fractions). This approach usually gives less variable results for chemicals that are poorly water soluble and consequently occur primarily in fats (lipids) and other forms of organic carbon. The BSAF approach was not implemented in this ERA because the earthworms were not depurated. Since the earthworm gut contents were not expelled, the distribution of lipids and TOC within the earthworm samples between tissue and gut soil is not known. In addition, the relationship between TOC-normalized gut content concentrations and lipid-normalized tissue concentrations within individual earthworm samples is not known. The meaning of "lipid-normalized" earthworm concentrations is unclear in undepurated samples, so the simpler BAF approach was used instead.

4.5.2 Congener-specific Soil PRGs and BAF

Soil PRGs were also back-calculated on a congener-specific basis. The procedure was similar to the one described for total PCBs with two modifications. First, the TRV of a designated congener had to be adjusted so that, after calculating the soil PRG, the sum of congener-specific HQs would sum to a HI equal to 1. Three congeners were included in the congener-specific HI (congeners 77, 126 and 105). If the TRV of one congener was used to back-calculate the soil PRG, the HQ for that congener would then equal 1, but the HI would be greater than 1 because of the contribution of the other two congener-specific HQs to the overall HI. To avoid this problem, the TRV of the congener making the greatest contribution to the HI was adjusted by multiplying the TRV by the ratio of that congener's HQ to the HI (equation 12).

$$TRV_{adj} = TRV * (HQ / HI) \quad [12]$$

where TRV_{adj} is the adjusted toxicity reference value of the congener making the greatest contribution to the HI. For example, if the congener 126 HQ accounted for 80 % of the HI, the adjusted TRV would be 0.8 times the TRV for congener 126. The adjusted TRV would then be used to back-calculate the soil PRG.

The second modification was to add an additional step to convert the back-calculated soil PRG from a congener concentration to a total PCB concentration. This was accomplished by dividing the back-calculated congener concentration by the site-specific ratio of that congener to the total PCB concentration in soil (equation 13).

Congener:PCB Ratio = Congener concentration / Total PCB concentration [13]

The results were checked by calculating the soil concentrations of the other two congeners corresponding to the total PCB PRG by use of their respective congener:PCB ratios, running the egg bioaccumulation model, calculating the three congener-specific HQs, and then summing to the HI, which should equal 1.

4.6 Area Use Adjustment to PRGs

The total PCB PRGs were adjusted for foraging area use based on the floodplain delineation sampling performed in 1992 ("post-phases I and II") (ASRI 1995). Two extrapolations were performed: 1) robin foraging range during the time they are feeding nestlings, and 2) the foraging range during the time they are caring for fledglings (the latter is a much larger area).

4.6.1 Robin Foraging Range

The foraging range of robins varies according to the life stage. Parental robins forage over a smaller area while feeding nestlings (1472 m^2) than while caring for fledglings (8080 m^2) (mean values, n = 24 pairs) (Weatherhead and McRae 1990). For the purposes of this risk assessment, the foraging range was assumed to be square (compare with Figure 3 of Weatherhead and McRae 1990). Converted to feet, the nestling and fledgling foraging ranges are 15844.5 and 86972.4 ft^2, respectively. For square ranges, this is equivalent to 126 x 126 ft for a nestling-stage range, and 295 x 295 ft for a fledgling-stage range. Note: the nestling-stage range refers solely to the adult foraging area, the fledgling-stage range refers to both adult and fledgling foraging area.

The nestling-stage and fledgling-stage foraging areas of a single breeding pair have been shown to overlap, that is, the fledgling-stage area is an expansion of nestling-stage area, not displaced to a different location (Weatherhead and McRae 1990). Robins have been reported to utilize different portions of their foraging area "on a fairly regimented schedule", roughly every hour in one example (Swihart and Johnson 1986). The investigators speculated that cyclic use of territory may be related to renewal of prey items. The main point for risk assessment purposes is that robins are expected to receive integrated exposures from throughout their foraging area (except for differences in habitat quality that markedly alter prey availability).

There are several uncertainties associated with the foraging area assumptions. Much smaller robin foraging areas (7900 ft^2) have been reported (Howell 1942) than the ones used in this ERA (about one-half and one-tenth of the aforementioned nestling-stage and fledgling-stage foraging areas, respectively), which, if applicable to the site, would increase exposure and risk estimates. The assumptions of square foraging geometry and equal use of all portions of the foraging area are also of uncertain applicability to the site. If robins preferentially forage closer to the river, the modeled area use adjustments would underestimate exposures and risks. Preferential foraging in floodplain areas closer to the river might occur because of differences in soil moisture, overstory vegetation, and/or soil organic matter accumulations that favor earthworms in comparison with more distant floodplain habitats, for example, under the tree line near the river bank compared with open fields further from the river. However, robin foraging

patterns have not been studied at the site, so the applicability of the foraging area and area use assumptions is not known.

4.6.2 PCB Distribution Pattern in the Sheboygan River Floodplain Soils

The distribution of PCB contamination in the floodplain soils was based on the 1992 floodplain delineation soil sample data set, referred to as "post-Phases I and II sampling" in the Sheboygan River and Harbor Alternative Specific Remedial Investigation Report (ASRI 1995). Seventy-seven discrete soil samples were collected to delineate the horizontal extent of PCBs in seven floodplain areas previously identified as having PCB soil levels at or above 10 ppm.

Before this data set could be used for area use purposes, the original distance values had to be corrected to reflect perpendicular distance from the nearest river bank. The distances to the nearest river bank reported in the present ecological risk assessment were measured from Figures 7K through 7N of the ASRI (1995). These distances often differed from the "Approx. Distance from River Bank" reported in Table 7-21 of the ASRI. The latter was actually the distance from the transect point of origin, which often was not the distance to the nearest river bank either because the transect was not perpendicular to the river, or because of river bends such that opposite ends of a transect were near different stretches of the river. The data base with the corrected distances to nearest river bank was used for the area use calculations in this ERA.

Mean PCB concentrations in floodplain soils were calculated for 50-foot intervals from the river bank: 0 - 50, >50 - 100, >100 - 150, >150 - 200, and >200 ft. Some of the intervals had similar mean PCB levels, so means were also calculated for consolidated intervals: 0 - 100, >100 - 200, and >200 ft.

4.6.3 Area Use Adjusted PRGs

Robin foraging areas were assumed to be square with one edge bordering the Sheboygan River, similar to the foraging areas shown bordering a lake (Weatherhead and McRae 1990). The soil PRG was adjusted to account for the portion of the foraging area that encompasses the less contaminated floodplain distance intervals from the river bank.

4.6.3.1 Nestling-stage Foraging Area PRG

Highly elevated floodplain soil PCBs were deposited within 100 ft of the Sheboygan River. For a square-shaped nestling-stage foraging area 126 ft on a side, the PRG should equal the area-weighted concentrations in the 0 - 100 ft and >100 - 150 ft intervals (equation 14).

$$PRG = (C_{0\text{-}100} * f_{0\text{-}100}) + (C_{>100\text{-}150} * f_{>100\text{-}150}) \quad [14]$$

where C is the mean soil PCB concentration for a distance interval from the river, and f is the fraction of the nestling-stage foraging area represented by a distance interval from the river (f = 0.794 and 0.206 for distance intervals 0 - 100 and >100 - 150 ft, respectively).

This was rearranged to calculate the protective level in the 0 - 100 ft distance interval (equation 15).

$$C_{0\text{-}100} = [PRG - (C_{>100\text{-}150} * f_{>100\text{-}150})] / f_{0\text{-}100} \quad [15]$$

4.6.3.2 Fledgling-stage Foraging Area PRG

For a square-shaped fledgling-stage foraging area 295 ft on a side, approximately one-third will be within 100 ft of the river, one-third between 100 and 200 ft, and one-third between 200 and 300 ft. The sum of the area-weighted concentrations should equal the soil PRG (equation 16).

$$PRG = (C_{0\text{-}100} * f_{0\text{-}100}) + (C_{>100\text{-}200} * f_{>100\text{-}200}) + (C_{>200} * f_{>200}) \quad [16]$$

This was rearranged to calculate the protective level in the 0-100 ft distance interval (equation 17).

$$C_{0\text{-}100} = [PRG - (C_{>100\text{-}200} * f_{>100\text{-}200}) - (C_{>200} * f_{>200})] / f_{0\text{-}100} \quad [17]$$

5.0 Characterization of Exposure

5.1 Quality Assurance Review

Data validation of the analytical results was completed to USEPA Level 2 QA review specifications by QA/QC Solutions (Appendix H). The results reported by the laboratory were considered acceptable, with the exception of soil total organic carbon (TOC). The relative percent difference (RPD) of 71 % for soil TOC did not meet the specified control limit of 80 - 120 %. However, since the recoveries of TOC from laboratory control samples and standard reference materials were within control limits, the variability of the sample TOC results appears to be related to variations in TOC content within the samples (sample heterogeneity) and not due to laboratory error. In the opinion of the QA reviewer, the RPD control limits are appropriate for TOC determination in water, but too strict for soil TOC analyses. In any case, the TOC results were not used for exposure characterization, bioaccumulation, or calculation of ecologically protective soil remedial goals, and therefore do not affect the results of the TERA.

Another issue is that nanogram quantities of some PCB congeners were detected in the cross contamination field blank. The field blank was obtained by swiping decontaminated sampling equipment with filter paper between collection of on-site soil samples. Unused filter paper showed fewer congeners at lower levels (picogram quantities). This indicates a potential for cross contamination between sample locations. However, the analytical data do not show a trend in soil PCB levels consistent with cross contamination. The lowest concentrations of the on-site soil samples occurred in samples 6 and 9 (numbered consecutively), while the highest concentrations occurred in samples 4, 5, and 8. Samples 2, 3, and 7 had intermediate concentrations (Appendix C.1). Additionally, the TERA soil PCB results were consistent with prior soil analyses, with the exception of sample 6 which was substantially lower than previously reported for that area.[14] This indicates that significant cross

[14] The TERA sample locations were only approximately located in the vicinity of prior floodplain sample locations, so exact comparison of results is unwarranted. However, TERA sample results that significantly exceeded prior soil data might have indicated possible cross contamination problems. Such was not the case.

contamination is unlikely. The reference location (sample 1) was sampled first specifically to avoid cross contamination issues.

The lab reported possible biases for some of the congeners in the standards used for calibration. The direction of the biases are unknown.

5.2 Floodplain Soils

Consolidated soil data are presented in Appendix C.1. The total PCB concentration in the on-site floodplain soil samples ranged from 0.045 - 85 ppm dw (mean 39 ppm). The total for sample 6 (segment FPR 5), 0.045 ppm, was much lower than those of the other on-site locations (30.5 - 85 ppm, mean 45 ppm). The total for the reference location was 0.006 ppm, four orders-of-magnitude less than the mean on-site concentration. The actual reference floodplain soil concentration was probably less than 0.006 ppm because three-quarters of the congener or congener combinations analyzed were non-detections (60 of 79) in the reference soil sample, but were assigned one-half the detection limit (DL) values. The total PCBs based only on congeners with positive detections in the reference location was 0.002 ppm.

The composition of selected PCB congeners in floodplain soil samples are given in Table 4.

Table 4. Composition of Selected PCB Congeners in Floodplain Soil Samples, Sheboygan River, WI, 11/4-5/97 (percent of total PCBs, dry weight).

Congener	On-site Mean Percentage [a]	On-site SD [a]	Percentage Range [a]	Sample 6 (FPR 5) Percentage	Reference Percentage
77	0.59	0.13	0.45 - 0.85	2.39	0.41
126	0.013	0.006	0.008 - 0.026	0.11	0.073
105	2.52	0.64	1.88 - 3.85	8.59	2.54
118	4.80	0.72	4.15 - 6.24	11.04	3.37
77 + 126	0.61	0.14	0.46 - 0.87	2.50	0.49

a) Excluding sample 6 (FPR 5).

The PCB congeners with the highest dioxin-like toxicity (congeners 77 and 126) accounted for less than 1 % of the total PCBs in the soil samples. Congeners 105 and 118 accounted for less than 10 % of the total PCBs. Sample 6 (segment FPR 5) had unusually high percentages of the aforementioned congeners. Since sample 6 also had the lowest total PCB concentration of the on-site floodplain soil samples, it appears that the lower-chlorinated PCB congeners were differentially diminished at the sample 6 location, resulting in an increase in the percentage of higher-chlorinated (and generally more toxic) PCB congeners.

The mean concentrations (and ranges) of selected dioxin-like congeners in on-site soil samples are given in Table 5. Although the percentage of higher chlorinated congeners was enriched in sample 6 compared with other on-site

samples, the concentrations were 1 to 2 orders of magnitude lower in sample 6 than in the next lowest on-site samples.

Table 5. Concentrations of Selected PCB Congeners in Floodplain Soil Samples, Sheboygan River, WI, 11/4-5/97 (ppb, dry weight).

Congener	On-site Mean [a]	On-site SD [a]	Range [a]	Sample 6 (FPR 5)	Reference
77	250	144	56 - 498	1	0.03
126	5	3	2 - 11	0.05	0.005
105	1035	568	253 - 2040	4	0.16
118	2060	1160	410 - 3985	5	0.22

a) Excluding sample 6 (FPR 5).

5.3 Earthworms

Consolidated earthworm data are presented in Appendix C.2. The total PCB concentration in the on-site floodplain earthworm samples ranged from 0.035 - 53.5 ppm ww (mean 25 ppm). The total for sample 6 (segment FPR 5), 0.035 ppm, was much lower than those of the other on-site locations (1.7 - 53.5 ppm, mean 29 ppm). The total for the reference location was 0.003 ppm, four orders-of-magnitude less than the mean on-site concentration. The actual reference earthworm concentration was probably less than 0.003 ppm because three-quarters of the congener or congener combinations analyzed were non-detections (55 of 75) [15] in the reference earthworm sample, but were assigned one-half the DL values. The total PCBs based only on congeners with positive detections in the reference location was 0.0014 ppm.

Earthworm PCB data were reported on a wet-weight basis to facilitate foodchain modeling. The moisture content ranged from 75 to 85 % (mean 82 %) (Appendix C.2). On a dry-weight basis, the on-site PCB concentrations in undepurated earthworms ranged from 0.2 to 268 ppm (mean 136 ppm), or, excluding sample 6, from 10 to 268 ppm (mean 155 ppm). The reference earthworms had 0.02 ppm PCBs dw.

The composition of selected PCB congeners in floodplain earthworm samples is given in Table 6.

[15] Four of the PCB congeners and congener combinations detected in soil samples were not detected in any earthworm samples.

Table 6. Composition of Selected PCB Congeners in Floodplain Earthworm Samples, Sheboygan River, WI, 11/4-5/97 (percent of total PCBs, wet weight, undepurated).

Congener	On-site Mean Percentage [a]	On-site SD [a]	Percentage Range [a]	Sample 6 (FPR 5) Percentage	Reference Percentage
77	0.27	0.05	0.19 - 0.36	0.56	0.15
126	0.006	0.003	ND [b] - 0.008	0.060	ND
105	1.97	0.31	1.72 - 2.65	4.10	1.51
118	4.38	0.52	3.69 - 5.30	5.71	4.37
77 + 126	0.27	0.05	0.19 - 0.36	0.62	0.15

a) Excluding sample 6 (FPR 5).
b) Not detected (ND).

The PCB congeners with the highest dioxin-like toxicity (congeners 77 and 126) accounted for less than 0.4 % of the total PCBs in the earthworm samples. Congeners 105 and 118 accounted for less than 10 % of the total PCBs.

The mean ww concentrations (and ranges) of selected dioxin-like congeners in on-site earthworm samples are given in Table 7. The concentrations on a dw basis are approximately 5.4 times greater than the Table 7 ww values.

Table 7. Concentrations of Selected PCB Congeners in Floodplain Earthworm Samples, Sheboygan River, WI, 11/4-5/97 (ppb, wet weight, undepurated).

Congener	On-site Mean [a]	On-site SD [a]	Range [a]	Sample 6 (FPR 5)	Reference
77	71	41	6 - 118	0.2	0.005
126	2	1	ND [b] - 3	0.02	ND
105	541	337	45 - 960	1.5	0.05
118	1223	762	89 - 2110	2	0.1

a) Excluding sample 6 (FPR 5).
b) Not detected (ND).

On-site earthworm TEQs ranged from 0.01 to 6.3 ppb ww (mean 3.3 ppb) (Appendix C.3). The range excluding sample 6 was 0.3 - 6.3 ppb (mean 3.8 ppb). The TEQ for the reference earthworms was 4 orders of magnitude lower (0.0003 ppb). The reference value was probably overestimated because 24 % of the TEQ was contributed by congener 126, which was not detected in the reference earthworms but was entered as one-half of the DL value.

Congener 77 accounted for 81 - 97 % of the total TEQ for on-site earthworms (92 - 97 % excluding sample 6). Congener 126 accounted for <1 - 17 % (<1 - 6 % excluding sample 6). Congeners 77 and 126 together accounted

for 98 % of the TEQ. Congener 105 accounted for 1 - 2 %. The rest of the dioxin-like congeners contributed less than 1 % of the TEQ in earthworms.

5.4 Other Invertebrates

Other invertebrate PCB, TEQ, and congener loads were modeled as constant proportions of the earthworm concentrations with factors of 0.17 and 0.08 for hard- and soft-bodied invertebrates, respectively. The modeled mean concentrations of total PCBs and TEQ were 4 ppm and 0.6 ppb, respectively, for hard-bodied invertebrates (beetles); and 2 ppm and 3 ppb, respectively, for soft-bodied invertebrates (Appendix D.1). Mean concentrations of congeners 77, 105, 118, and 126 were 11, 80, 182, and 0.3 ppb, respectively, for hard-bodied invertebrates; and 5, 38, 86, and 0.1 ppb for soft-bodied invertebrates (Appendix D.2). The extrapolations were based on mean earthworm concentrations inclusive of sample 6.

5.5 Robin Ingestion Dose

The modeled mean robin ingestion doses were 3 mg PCBs/kg_{bw}-d and 0.4 μg TEQ/kg_{bw}-d (Appendix D.1). Congener-specific ingestion doses were not estimated because congener-specific feeding studies were not located for evaluation of the toxicological significance of exposures to individual congeners.

5.6 Robin Eggs

The modeled mean robin egg total PCB concentration was 241 ppm ww (Appendix D.2). The modeled mean egg concentrations of congeners 105 and 118 were 2838 and 9947 ppb, respectively. Congeners 77 and 126 were modeled with two different diet-to-egg BMFs. Mean congener 77 concentrations were 3 to 33 ppb, and mean congener 126 concentrations were 14 to 31 ppb. The egg TEQs were calculated from the modeled egg congener concentrations. Mean TEQs ranged from 3.4 to 3.6 ppb. Egg TEQ values varied less than the concentrations of congeners 77 and 126 because the congeners fluctuated in opposite directions in the two scenarios such that the decrease in TEQ due to one congener was compensated by the increase in TEQ due to the other.

The relative contribution of congeners to the egg TEQ differed from that observed in earthworms because of the differential biomagnification of congeners from the diet to the eggs. Congener 126 accounted for 40 to 85 % of the total egg TEQ, depending on the BMF used, compared with 6 % or less of the earthworm TEQ. Congener 77 accounted for 4 to 49 % of the egg TEQ, compared with over 90 % of the earthworm TEQ. The combined contribution of congeners 126 and 77 to the egg TEQ was 89 % for either of the BMFs. Congeners 105 and 118 contributed 8 and 3 %, respectively, of the egg TEQ.

6.0 Risk Characterization

6.1 Robin Ingestion Dose

The on-site hazard quotients (HQs) for ingestion doses to adult robins varied by as much as an order of magnitude. The no observed adverse effect level (NOAEL)-based HQs ranged from 30 to 280 for the central tendency exposure concentrations. The corresponding lowest observed adverse effect level (LOAEL)-based HQs ranged from 3 to 120 (Appendix D.1). The highest risk estimates were based on comparison with the measured TEQs of

PCB-contaminated carp fed to chicken (Summer, et al. 1996a, b), and the lowest with dioxin injections in pheasants (Nosek, et al. 1992 and 1993). The reason for the order-of-magnitude differences in HQs between the two approaches for assessing risks based on TEQs is not obvious. One limitation is that bird TEFs are derived from cell culture and egg injection studies, but not from feeding studies (Van den Berg, et al. 1998). The avian TEFs therefore may be less appropriate for assessing risks associated with dietary exposures than for assessing risks on the basis of tissue or egg concentrations.

The reference location ingestion HQs are well below unity: 0.04 or less for NOAEL, and 0.4 or less for LOAEL TRVs.

The risk estimates based on total PCB ingestion dose were not affected by TEQ uncertainties. The central-tendency NOAEL-based HQ of 70 was higher than the robin egg HQs (20 - 50), but the central-tendency LOAEL-based HQ of 8 was reasonably consistent with the range of robin egg HQs (10 - 20) (see below).

6.2 Robin Eggs

The HQs for robin egg concentrations varied by a factor of 2 or 3, depending on the BMFs used for diet to egg extrapolations (Appendix D.2), which was much less variable than the range of ingestion HQs. In addition to total PCBs and TEQs, congener-specific risk estimates were also made for the sum of the HQs of congeners 77, 105 and 126. The central tendency NOAEC-based HQs of the three approaches ranged from 20 to 50 for combined tern and gull BMFs, and from 10 to 50 for gull only BMFs. The central tendency LOAEC-based HQs were 10 to 20, and 6 to 20, respectively.

Again, the reference location egg HQs were well below unity: less than 0.02 for NOAEC, and less than 0.01 for LOAEC TRVs.

6.3 Risk Summary

The results of the modeling and risk characterization approaches utilized in this ERA consistently indicated increased risks of adverse reproductive effects in robins foraging in contaminated sections of the Sheboygan River floodplain. Risk estimates for egg concentrations were less variable than for oral doses to adult robins. Egg NOAEC- and LOAEC-based HQs ranged from 10 to 50, and from 6 to 20, respectively, for central tendency exposure scenarios. HQs ranged as high as 40 and 80, based on NOAEC and LOAEC, respectively, for the 95 % upper confidence limit (95%UCL) exposure scenarios. In contrast, adverse effects are unlikely in the reference location where the egg HQs were two orders of magnitude less than the level of concern.

6.4 Ecologically Protective Soil Preliminary Remedial Goals (PRGs)

Egg-based risk estimates were much less variable than oral dose-based estimates, so the egg model was used to back-calculate soil ecologically protective remedial goals (PRGs) (Appendix E). PRGs were calculated on the basis of total PCBs, and two congener-specific models that differed in the biomagnification factors used to estimate egg congener concentration from the robin dietary concentration. TEQs were not used to back-calculate soil PRGs because congener-specific risk estimates were available for the congeners that predominantly contribute to the TEQ.

The risk estimates based on direct assessment of congener-specific toxicity were considered more reliable than risk estimates based on indirect assessment of the relative toxicities of PCB congeners compared to dioxin.

The following PRGs were calculated (Table 8).

Table 8. Ecologically Protective Soil Preliminary Remedial Goals (PRGs), Sheboygan River Floodplain, WI.

Toxicity Basis	NOAEC-based PRG	LOAEC-based PRG
	(ppm total PCBs)	
Total PCBs [a]	1	4
Congener-specific [b]	1.5	3
Congener-specific [c]	2	5
Area Use Adjusted [d]	no change	4 - 9

a) Modeled with gull diet-to-egg BMF (Braune and Norstrom 1989).
b) Modeled with tern BMF (Kubiak, et al. 1989).
c) Modeled with gull BMF (Norstrom pers. comm. in Hoffman, et al. 1996).
d) Combined results for nestling-stage and fledgling-stage foraging areas, respectively.

The total PCB-based and congener-specific-based PRGs indicate that adverse effects are unlikely where soil PCB concentrations are at or below 1 - 2 ppm. The congener-specific LOAEC-based soil PRGs range from 3 to 5 ppm, depending on the biomagnification model, but the results bracket the total PCB LOAEC-based PRG of 4 ppm. This indicates that adverse effects may occur where soil PCB concentrations exceed 3 - 5 ppm.

6.5 Area Use Adjusted Soil PRGs

The soil PRGs were adjusted for foraging area use based on the floodplain delineation sampling performed in 1992 ("post-phases I and II") (ASRI 1995). Two extrapolations were performed: one for the robin foraging range during the time they are feeding nestlings, and the second for the foraging range during the time they are caring for fledglings. The NOAEC-based PRG did not change, but the LOAEC-based PRG increased to 9 ppm for the fledgling-stage (Table 8). The calculations are described below.

Mean PCB concentrations in floodplain soils were calculated for 50-foot intervals from the river bank. Some of the intervals had similar mean PCB levels, so means were also calculated for consolidated 100-ft intervals (Table 9). The horizontal distribution of the individual 1992 floodplain samples are graphed in Appendix G.1.

Table 9. Mean Horizontal Distribution of Floodplain Soil PCBs, 1992, Sheboygan River, WI. [a]					
Distance from Nearest River Bank (ft) [b]	Number of Samples	Floodplain Soil PCBs (ppm)			
		Mean	Range	SD	95%UCL
0 - 50	26	22.8	0.3 - 150	33.3	36.3
>50 - 100	15	29.5	0.07 - 190	55.0	60.0
0 - 100	41	25.3	0.07 - 190	42.0	38.5
>100 - 150	10	2.4	0.07 - 16	4.9	5.9
>150 - 200	11	2.8	0.03 - 20	5.9	6.7
>100 - 200	21	2.6	0.03 - 20	5.3	5.0
>200	15	0.3	0.03 - 2.7	0.7	0.7

a) ASRI (1995).

b) Measured from Figures 7K through 7N (ASRI 1995). The values under the heading "Approx. Distance from River Bank" in Table 7-21 of the ASRI (1995) are often not the distances from the nearest river bank. They are instead transect distances. Although the transect origins are near the river, the transect distances often do not reflect the distance to the nearest river bank either because the transects are not perpendicular to the river, or because the river bends such that the distal portion of a transect is closer to a different section of river.

Robin foraging areas were assumed to be square with one edge bordering the Sheboygan River, similar to the foraging areas shown bordering a lake in Weatherhead and McRae (1990). Since the 0-100 ft interval mean PCB concentration exceeds the mean soil LOAEL-based PRG of 4 ppm, but the remaining interval means do not, the soil PRG was adjusted to account for the portion of the foraging area that encompasses the less contaminated intervals (i.e., robins may not be foraging exclusively in the most highly contaminated areas).

6.5.1 Nestling-stage Foraging Area PRGs

For a square-shaped nestling-stage foraging area 126 ft on a side, 79.4 % would be within 100 ft of the river, and 20.6 % would extent beyond. Since the mean soil PCB concentration in the >100 - 150 ft interval (2.4 ppm) is close to the NOAEC-based PRG (1 - 2 ppm), the area use adjustment would have no effect on the PRG for the 0 - 100 ft interval (calculations not shown).

The LOAEC-based PRG (mean of 4 ppm) was adjusted for nestling-stage foraging area use by solving equation 15.

$$C_{0\text{-}100} = [PRG - (C_{>100\text{-}150} * f_{>100\text{-}150})] / f_{0\text{-}100} \quad [15]$$

$$C_{0\text{-}100} = [4\ ppm - (2.4 * 0.206)] / 0.794$$

The adjusted PRG is equal to 4.4 ppm. The nestling-stage LOAEC-based PRG was barely changed by the area use factor calculation because the nestling-stage foraging area is small relative to the distribution of elevated contamination extending from the river bank.

6.5.2 Fledgling-stage Foraging Area PRG

For a square-shaped fledgling-stage foraging area 295 ft on a side, approximately one-third would be within 100 ft of the river, one-third between 100 and 200 ft, and one-third between 200 and 300 ft. The NOAEC-based PRG (mean of 1.5 ppm) was adjusted for nestling-stage foraging area use by solving equation 17.

$$C_{0\text{-}100} = [PRG - (C_{>100\text{-}200} * f_{>100\text{-}200}) - (C_{>200} * f_{>200})] / f_{0\text{-}100} \quad [17]$$

$$C_{0\text{-}100} = [1.5 \text{ ppm} - (2.6 * 0.33) - (0.3 * 0.33)] / 0.33$$

The adjusted NOAEC-based PRG is 1.6 ppm. It was barely changed by the area use calculation because the average soil PCB concentration of the 100 - 200 and >200 ft intervals combined is close to 1.5 ppm.

The LOAEC-based PRG (mean of 4 ppm) was adjusted for nestling-stage foraging area use by solving equation 17.

$$C_{0\text{-}100} = [4 \text{ ppm} - (2.6 * 0.33) - (0.3 * 0.33)] / 0.33$$

The adjusted LOAEC-based PRG is 9.2 ppm. The fledgling-stage adjusted LOAEC-based soil PRG was higher than the nestling-stage adjusted PRG because two-thirds of the fledgling-stage foraging area encompasses less contaminated floodplain intervals, but only one-fifth of the nestling-stage foraging area extends into a less contaminated interval.

6.6 PRG Summary and Discussion

Robins with nestling-stage foraging areas bordering the Sheboygan River are at risk of reproductive impairment where the soil mean PCB concentrations exceed 4 ppm. This includes robins nesting within about 130 ft of the river bank along contaminated (>4 ppm) floodplain sections. Adverse reproductive effects are unlikely where the floodplain soil mean PCB concentrations are less than 2 ppm.

Robins with fledgling-stage foraging areas bordering the Sheboygan River are at risk of reproductive impairment where the floodplain soil mean PCB concentration exceeds 9 ppm. The potential for reproductive impairment is still important during the fledgling stage because robins commonly produce second, and sometimes third, broods each season (Howell 1942; Weatherhead and McRae 1990). The second brood is more important for overall reproductive success because the "first nesting of the Robin is very often unsuccessful" (Howell 1942). In one study, the success rate (at least one fledgling leaving the nest) of first nestings was less than one-half that of second nestings (success rates of 33 and 75 %, respectively, n = 82 nests). The second nesting accounted for over 70 % of the successful nestings by the robin population (Howell 1942).

This means that in floodplain areas with elevated PCB levels, reproductive risk may occur not only in robin pairs that have nestling-stage foraging areas that border the river, but also in robin pairs that have nestling-stage foraging

areas set back from the river away from the elevated contamination, but then expand their fledgling-stage foraging areas to the river where floodplain PCB concentrations exceed 9 ppm. Any robins nesting within about 300 ft of the river along contaminated (>9 ppm) floodplain sections may be at risk for reproductive impairment.

The horizontal distribution of the 1992 floodplain samples and the ecologically protective soil concentrations are shown in Appendix F.2.

6.7 Feasibility Study (FS) Surface-weighted Average Concentration (SWAC)

The results and conclusions of the area-use calculation discussed above differ significantly from those based on the surface-weighted average concentration (SWAC) calculations for the Sheboygan River floodplain soils reported in the Feasibility Study (FS 1998). The FS results (Table D-4 of the FS) are summarized in Table 10. The FS is still under review by the agency. Inclusion of the FS SWAC in this risk assessment does not imply agency approval of the calculations or conclusions, but was done to address the large inconsistency between the approaches.

Table 10. Floodplain Soil Surface-weighted Average Concentration (SWAC) as Reported in the FS [a], Sheboygan River Floodplain, WI. (ppm total PCBs)

Floodplain Section	Floodplain Soil Remedial Option			Total Area
	no action	< 50 ppm remaining	<10 ppm remaining	(ft^2)
FPR-3	4.05	4.05	0.33	320,127
FPL-4	16.07	4.47	2.54	548,672
FPR-5	17.31	4.23	0.39	158,927
FPR-6 [b]	17.78	5.90	1.62	416,537
FPR-7	4.64	4.64	2.21	167,710
FPL-8	3.89	3.89	0.29	316,200
FPL-11 [c]	9.35	6.38	0.43	355,260

a) Feasibility Study (FS) (1998).

b) Sample FPR-6B-1 (12 ppm) was omitted from the SWAC calculation in the FS. The values shown here are not corrected for this omission.

c) The FS omitted the SWAC values for FPL-11. The values shown here are calculated from the FPL-11 data presented in Table D-4 of the FS.

Using 5 ppm as an upper bound PRG, the SWACs for removal of soils with 50 ppm total PCBs or more appears to be protective in most floodplain areas, with the exceptions of FPL-11 and FPR-6 (the <50 ppm remaining SWAC for FPR-6 is underestimated by the omission of sample FPR-6B-1). However, the areas over which the SWACs were calculated are much larger than robin foraging areas. The mean robin foraging area during the time they care for nestlings is 15,845 ft^2, which expands to 86,972 ft^2 while they care for fledglings (Weatherhead and McRae

1990). The FS included floodplain soil data in the SWAC calculation extending to approximately 300 ft from the river bank. Nestling-stage foraging areas are not likely to extend much beyond 130 ft from the river bank if approximately square in shape (such as shown in Weatherhead and McRae 1990), and each floodplain section used for the SWAC calculations potentially contains many such foraging areas. Although fledgling-stage foraging areas may extend as far as 300 ft from the river bank, each of the floodplain sections used for the SWAC calculations include a few to several of these larger foraging areas. This means that the SWACs reported in the FS are not realistic estimates of potential surface-area weighted exposures to foraging robins (or other earthworm-feeding species).

The foraging areas are assumed to be non-overlapping between different robin breeding pairs. There is evidence of exclusive territoriality in the vicinity of nests (Howell 1942), but overlap of territories often occurs as well (USEPA 1993b). The assumption of non-overlapping foraging areas is probably more valid for nestling-stage areas, when foraging occurs closer to the nest. The expanded fledgling-stage foraging areas probably result in significant overlap. Also, much smaller robin territories have been reported than those used in the risk assessment, for example, 7900 ft^2 (Howell 1942), which is one-half the size of the nestling-stage foraging area used in the risk assessment and less than one-tenth of the fledgling-stage foraging area. The numbers of potential foraging areas are therefore minimum estimates (Table 11).

Table 11. Number of Potential Robin Foraging Areas in SWAC [a] Areas as Reported in the FS [b], Sheboygan River Floodplain, WI.

Floodplain Section	Nestling-stage Areas	Fledgling-stage Areas
FPR-3	20	4
FPL-4	35	6
FPR-5	10	2
FPR-6	26	5
FPR-7	11	2
FPL-8	20	4
FPL-11	12	2
Total	134	25

a) Surface-weighted average concentration (SWAC).
b) Feasibility Study (FS) (1998).

SWACs are often greater when averaged on a scale consistent with robin foraging areas. For example, in FPR-3, where the FS-reported SWAC is 4 ppm, the areas allocated to the adjacent samples 3B-1 (35 ppm) and 3C-1 (12 ppm) sum to 51,460 ft^2. This is sufficient for 3 nestling-stage foraging areas, all of which would be at risk of reproductive impairment. When assessed on the basis of fledgling-stage foraging area, it accounts for 59 % of the required mean area. Including 41 % of 3B-2 (0.43 ppm) and 3C-2 (2.4 ppm) areas, the SWAC is 13.6 ppm, still well above protective levels, in contrast to the FS conclusion of no unacceptable risk for this floodplain segment.

The number of potential nestling-stage foraging areas at risk in each floodplain section under different remedial options is given in Table 12

Table 12. Number of Potential Nestling-stage Robin Foraging Areas Potentially at Risk Under Selected Remedial Options, Sheboygan River Floodplain, WI.

Floodplain Area	Floodplain Soil Remedial Option (total PCB)		
	no action	< 50 ppm remaining	<10 ppm remaining
FPR-3	3	3	0
FPL-4	11	5	2
FPR-5	2 - 3	2	0
FPR-6	6	4	0
FPR-7	3	3	1
FPL-8	5 - 6	5 - 6	0
FPL-11	7	6	0
Total	37 - 39	28 - 29	3
Risk reduction	0 %	25 %	92 %

The number of nestling-stage foraging areas at risk was determined for individual sample weighting areas as presented in Table D-4 of the FS, or, where appropriate, for combined adjacent sample weighting areas. For example, FPL-4B-1 (35 ppm, 15,707 ft^2) is equivalent to 1 nesting-stage foraging area (15,845 ft^2). An example of a combined area is FPL-4D-2 (120 ppm, 33,067 ft^2) and FPL-4D-1 (10 ppm, 13,950 ft^2), which together are equivalent to 3 nestling-stage foraging areas. Only samples exceeding an ecologically-protective PRG of 5 ppm were considered.

When assessed on a scale commensurate with robin foraging area, all of the floodplain sections included in the 1992 delineation sampling show risk to a few to many breeding robin pairs each. Remediation of floodplain PCBs equal or greater than 50 ppm results in only about a 25 % decrease in the total number of foraging areas at risk. In contrast, remediation of floodplain PCBs equal or greater than 10 ppm result in a 90% decrease in the number of foraging areas at risk. Note: although the risk assessment focuses on robins as the measurement endpoint, they are indicative of risks to a range of species that feed on earthworms and other soil-related invertebrates.

SWAC performed on a scale appropriate for robin foraging areas indicates that remediation of floodplain soil equal to or greater than 10 ppm PCB should be protective, that is, it should result in foraging SWAC at or below 5 ppm, with few exceptions. Remediation of floodplain soil PCB concentrations equal to or greater than 50 ppm may be appropriate in select areas of high quality forested habitat on the basis of a risk management decision to balance risk

reduction with habitat preservation, but it is not justifiable on the basis of SWAC when averaged over a scale appropriate for foraging robins.

7.0 Uncertainty

All risk assessments require that judgements be made on the choice of exposure pathways and species to evaluate, the studies to utilize, and the additional parameter values and extrapolations needed to calculate exposures and risks. The alternative would be to pursue open-ended investigations to reduce all uncertainties. At some point, cost, time and manpower constraints limit all such efforts. All risk assessments (and field investigations) therefore unavoidably have uncertainties, that is, unresolved questions that could be addressed with further research. The main uncertainties of the TERA are described below under three categories of how they might affect the risk estimate: overestimate, underestimate, and either.

7.1 Overestimate Risk

Several factors may have resulted in overestimation of risk. One is that the TRVs were mostly derived from studies of chickens. Chickens are the most sensitive to the reproductive effects of PCBs of the species of birds investigated. The sensitivity of robins, or other likely vermivorous species at Sheboygan, relative to chicken is unknown, but presumably less than for chickens. However, the egg LOAEC based on chicken used in the TERA is higher than those reported for bald eagles and several species of terns in field studies (Section 4.4.2.1), which indicates the value is not overly conservative.

Another issue is the Summer, et al. (1966a, b) studies relied on naturally contaminated Saginaw Bay carp for dosing chickens with PCBs. This means that other contaminants may have contributed to the observed toxicity in addition to PCBs. Again, the total PCB TRV from these studies is higher than those reported from field studies, but other contaminants may have also contributed to the effects observed in the field studies. This issue is unlikely to significantly bias the TERA because PCBs have been shown to account for most of the TEQ of Saginaw fish (Section 4.4.1.1), and because other contaminants (e.g., dioxins) probably are present in the Sheboygan floodplain at low levels, but were not included in the TERA.

Another issue concerns sampling cross contamination which potentially could increase contaminant levels in samples taken subsequent to a highly contaminated sample. Although nanogram quantities of certain PCB congeners were detected in the cross contamination blank, the sequence of floodplain soil samples does not show a pattern consistent with cross contamination problems. Conversely, the lowest on-site soil PCB concentrations were sampled immediately after the highest on-site concentrations. Also, no TERA samples significantly exceeded previous floodplain soil results in the near vicinity (Section 5.1).

The TERA risk estimates apply to vermivores feeding in the floodplain sections previously identified as having soil PCB concentrations at or above 10 ppm. Other floodplain sections have lower soil PCB levels so the risk estimates for vermivores in these sections would be corresponding lower. In other words, the risk estimates do not apply to the entire Sheboygan River floodplain. The back-calculated soil PRGs do apply to the entire floodplain, but most sections are below the LOAEC-based PRGs.

7.2 Underestimate Risk

Several factors may have resulted in underestimation of risks. Several potential COCs were not included, in particular, PCB congener 81 and chlorinated dioxins and dibenzofurans. Sheboygan River data indicates that the dioxins and dibenzofurans may contribute less than 10 % to the toxicity of biota contaminant burdens. The potential contribution of congener 81 is unknown.

The insectivorous robin ingestion value used in the TERA is much lower than the frugivorous ones reported in the Wildlife Exposures Factor Handbook (USEPA 1993b). The decrease is expected because insects are more nutritious than fruit, but part of the decrement may also be due to the fact that the study used for the insectivorous value was performed in a laboratory setting. Captive birds are less active than wild birds, and do not have to cope with weather extremes, and therefore require less food than wild birds to maintain bodyweight. However, captive birds might eat more than wild counterparts because of easy food availability and boredom.

Some potential exposure pathways were omitted: incidental soil ingestion, water consumption, and inhalation. The latter two were considered insignificant. The former was not modeled separately because the earthworm data were for undepurated worms. If any of these assumptions are incorrect, the exposures would be underestimated.

The TRVs were not always the lowest values reported in the literature, based on judgements regarding the quality or applicability of the studies (Sections 4.4.2.1, 4.4.2.2, and 4.4.2.5). Also, no uncertainty or conversion factors were used. These factors are often applied to decrease the TRVs to account for possible differences in species sensitivities, or to compensate for study limitations. Such factors were not applied in the TERA because most of the toxicological studies were performed with species known to be highly sensitive to PCBs.

The ecologically protective earthworm concentrations were back-calculated to soil PRGs by use of site-specific soil-to-earthworm BAFs. The BAFs used are central tendency values. The PRGs would have been lower if 95%UCL BAFs were used instead.

The sizes of the robin foraging areas used for area use adjustments of the soil PRGs are substantially larger than some of the other robin foraging areas reported in the literature. If Sheboygan robins utilize smaller foraging areas, their exposure and risk levels would be higher than estimated in the TERA.

7.3 Unknown Effect on Risk Estimate

Many factors have unknown effects on the risk estimates because the possible direction of bias is not known. The selection of TEFs, BMFs, and the extrapolations of hard- and soft-bodied invertebrate contaminant levels from earthworm data are notable examples.

The possible inaccuracies of the calibrating standards may have resulted in over- or underestimations of congener data. Congeners 77 and 118 may have been underestimated, which, if true, would result in underestimated risk, but the overall bias and its potential significance are not known.

The assumptions of square foraging geometry and equal use of all portions of the foraging area are also of uncertain applicability to the site. If robins preferentially forage closer to the river, the modeled area use adjustments

would underestimate exposures and risks. Preferential foraging in floodplain areas closer to the river might occur because of differences in soil moisture, overstory vegetation, and/or soil organic matter accumulations that favor earthworms in comparison with more distant floodplain habitats, for example, under the tree line near the river bank compared with open fields further from the river. Conversely, if robins preferentially forage away from the vicinity of the river, the area use adjustments would not sufficiently show the level of risk reduction. The latter seems unlikely since earthworms were plentiful and easily collected near the river; however, robin foraging patterns have not been studied at the site, so the applicability of the foraging area and area use assumptions is not known.

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Appendix A.1. On-site Floodplain Soil and Earthworm Sample Locations, Sheboygan River, WI, 11/4-5/97.

Appendix A.2. Reference Floodplain Soil and Earthworm Sample Location, Sheboygan River, WI, 11/3/97.

Appendix B.1. Terrestrial Vermivores Other Than Birds Potentially Present in the Sheboygan River Floodplain, WI.

Vermivorous Amphibians and Reptiles (Casper 1996; Harding 1997)

- Salamanders
  - Blue-spotted *Ambystoma laterale*
  - Central newt (efts) *Notophthalmus viridescens louisianensis*
  - Eastern tiger *Ambystoma tigrinum tigrinum*
  - Four-toed *Hemidactylium scutatum*
  - Red-backed *Plethodon cinereus*
- Eastern American Toad *Bufo americanus americanus*
- Frogs
  - Northern leopard *Rana pipiens*
  - Wood *Rana sylvatica*
- Snakes
  - Brown *Storeria dekayi wrightorum*
  - Eastern garter *Thamnophis sirtalis sirtalis*
  - Northern red-bellied *Storeria occipitomaculata occipitomaculata*
  - Northern ring-necked *Diadophis punctatus edwardsii*

Vermivorous Mammals (MacDonald 1980; Kurta 1995; Whitaker and Hamilton 1998)

- Northern short-tailed shrew *Blarina brevicauda*
- Star-nosed mole *Condylura cristata*
- Striped skunk *Mephitis mephitis*
- Raccoon *Procyon lotor*
- Opposum *Didelphis virginiana*
- Red fox *Vulpes vulpes*

Vermivorous Invertebrates (Edwards and Bohlen 1996; Curry 1998)

- Ants - Formicidae
- Beetles
  - Ground (larval and adult) - Carabidae
  - Rove (larval and adult) - Staphylinidae
- Centipedes - Chilopoda

Appendix B.2. Terrestrial Insectivores Other Than Birds Potentially Present in the Sheboygan River Floodplain, WI.

Terrestrial Insectivorous Amphibians and Reptiles (but not vermivorous) (Casper 1996; Harding 1997)

Frogs

- Bullfrog *Rana catesbiana*
- Gray tree *Hyla versicolor*
- Green *Rana clamitans melanota*
- Northern spring peeper *Pseudacris crucifer crucifer*
- Pickerel *Rana palustris*
- Striped chorus *Pseudacris triseriata*

Terrestrial Insectivorous Mammals (but not vermivorous) (Kurta 1995; Whitaker and Hamilton 1998).

Shrews

- Arctic *Sorex arcticus*
- Masked *Sorex cinereus*

Rodents

- Deer mouse *Peromyscus maniculatus*
- House mouse *Mus musculus*
- Meadow jumping mouse *Zapus husonius*
- White-footed mouse *Peromyscus leucopus*

Appendix C 1 Soil Data, High and low Resolution PCB Analysis, Sheboygan River Floodplain, WI, 11-3-5/97
dry weight concentrations

Station		REFL	FPR3	FPL4	FPL4	FPL4	FPR5	FPR6	FPR6	FPR7
Sample		1	2	3	4	5	6	7	8	9
Analyte	Units									
Total organic carbon	%	4 7	4 2	4.6	5 4	4 1	3 6	3 6	4 7	4 4
Total solids	%	81	87.5	79 1	78.8	84 1	83 3	79 9	76 2	74.9
Moisture content	%	21	13	22.5	21	12	18	20	24 5	25
PCB congener										
BZ#5 8	ppb	0 025 U	30	6.95	120	11	0 R	19	11	4
BZ#15	ppb	0 045 U	45	74	410	79	0 11	77	115	20
BZ#16/32	ppb	0.05 U	160	51.5	1000	120	0 025 U	300	650	3 4
BZ#17	ppb	0.05 U	52	23.5	330	38	0 025 U	68	94	5 5
BZ#18	ppb	0.05 U	37	22	98	42	0.05	44	94	4
BZ#19	ppb	0.05 U	18	8.6	220	11	0 025 U	51	90	2.2
BZ#22	ppb	0 03 U	100	57.5	240	130	0.06	100	200	7 9
BZ#24/27	ppb	0 05 U	46	31	300	57	0 025 U	110	230	4.4
BZ#25	ppb	0.03 U	31	49.5	210	74	0 015 U	72	140	12
BZ#26	ppb	0.03 U	52	83.5	170	96	0.04	76	175	18
BZ#28/31	ppb	0.03 U	1470	1685	2480	2080	0 61	1480	3680	260
BZ#33	ppb	0 03 U	25	20.5	89	36	0 04	43	86	2.4
BZ#40	ppb	0.07 U	110	44	240	110	0.035 U	100	215	1 4
BZ#41/71/64	ppb	0.075 U	2070	1440	4650	2950	1 1	2650	5225	200
BZ#42	ppb	0.075 U	510	300	1290	690	0 09	640	1290	27
BZ#44	ppb	0 075 U	1320	875	2940	1800	0 2	1600	3320	63
BZ#45	ppb	0.065 U	110	47	350	100	0 03 U	140	280	2 3
BZ#46	ppb	0 065 U	32	11 5	100	31	0.03 U	44	82	0 55 U
BZ#47/48	ppb	0.07 U	1080	765	2440	1420	0 28	1360	2590	67
BZ#49	ppb	0.07 U	1480	1130	3110	2050	0.62	1860	3745	220
BZ#52	ppb	0.065 U	2050	1475	3930	2740	0.57	2430	5085	260
BZ#56/60	ppb	0.045 U	1180	775	2070	1630	1.1	1330	2280	150
BZ#66	ppb	0.045 U	1990	1660	3390	3040	1.9	2380	4430	390
BZ#70/76	ppb	0.07 U	2170	2480	2230	3640	3.4	1930	3830	600
BZ#74	ppb	0.07 U	1890	1480	3090	2780	0.93	2120	4000	240
BZ#77	ppb	0.0266	182	177	298	349	1.08	194	498	55.7
BZ#83	ppb	0.065 U	110	110	220	180	0.03 U	140	295	23
BZ#84/92	ppb	0.05 U	580	565	1340	1010	0.44	780	1710	110
BZ#85	ppb	0.065 U	500	455	880	820	1.6	630	1270	130
BZ#87	ppb	0.065 U	920	920	1870	1650	0.98	1190	2615	200
BZ#89/90/101	ppb	0.13	1410	1495	3080	2630	1.6	1930	4185	330
BZ#91	ppb	0.05 U	250	235	580	410	0.14	340	690	55
BZ#95	ppb	0.05 U	970	1025	2250	1750	0.33	1370	3100	190
BZ#97	ppb	0.065 U	690	685	1460	1230	0.3	880	1935	130
BZ#99	ppb	0.14	870	875	1670	1480	1.4	1130	2415	240
BZ#105	ppb	0.164	754	785	1240	1340	3.885	836	2040	253
BZ#107	ppb	0.045 U	100	120	210	190	0.57	140	300	35
BZ#110	ppb	0.24	2550	2900	5660	5050	3.2	3750	7555	700
BZ#114	ppb	0.00977 L	78.3	70.4	123	146	0.2695	79.3	191	19 1
BZ#118	ppb	0.217	1340	1515	2730	2630	4 99	1810	3985	410
BZ#123	ppb	0.00875 L	35	28.1	34	66.9	0.21	35.3	89.6	11.4
BZ#126	ppb	0 00473 L	3.59	3.675	5.2	6.33	0.05195	4.25	10 5	1 68
BZ#128	ppb	0.095 U	200	280	440	470	1	280	715	75
BZ#129	ppb	0 055 U	32	45.5	78	80	0 R	47	110	8 5
BZ#131	ppb	0.06 U	8.8	10.45	24	23	0.045 U	16	34	2.8
BZ#134	ppb	0.06 U	37	55	91	77	0.045 U	52	135	13
BZ#135/144	ppb	0.06 U	96	125	220	190	0 17	140	330	36
BZ#136	ppb	0.06 U	86	125	230	190	0 045 U	150	340	25
BZ#137	ppb	0.055 U	38	52	91	96	0.26	58	135	13
BZ#138/163/164	ppb	0.55	700	955	1640	1750	3.7	1050	2555	270
BZ#141	ppb	0.055 U	77	110	180	190	0.32	110	290	25
BZ#146	ppb	0 05 U	55	82	140	130	0.35	86	195	27
BZ#149	ppb	0.17	460	625	1110	990	1	690	1645	190
BZ#151	ppb	0.06 U	83	115	200	180	0 25	130	285	32
BZ#153	ppb	0.33	370	515	910	950	2.4	600	1355	150
BZ#156	ppb	0.0483	92 6	137	180	208	0 4515	120	347	36 7
BZ#157	ppb	0 0127 L	18 6	27.8	37 1	37 8	0 10145	25 4	69 6	8 21
BZ#158	ppb	0.055 U	84	105	210	200	0 31	130	305	27
BZ#167	ppb	0 0182 L	24.2	35.6	50 9	58 4	0 152	34.1	93 2	10 6
BZ#170	ppb	0.0539	42.9	77.7	118	136	0 304	61.9	165	21 1
BZ#171	ppb	0.06 U	12	16 5	30	30	0 025 U	22	51 5	4 9

Appendix C 1 Soil Data, High and low Resolution PCB Analysis, Sheboygan River Floodplain, WI, 11/3-5/97
dry weight concentrations

Station		REFL	FPR3	FPL4	FPL4	FPL4	FPR5	FPR6	FPR6	FPR7
Sample		1	2	3	4	5	6	7	8	9
BZ#172	ppb	0.07 U	8.3	10.5	14	17	0.03 U	14	31.5	3.3
BZ#174	ppb	0.065 U	36	53.5	80	100	0.13	52	135	14
BZ#175	ppb	0.055 U	0.95 U	2.8	3.5	2.05 U	0.02 U	2 U	4.5	0.48 U
BZ#176	ppb	0.055 U	5.6	7.65	16	14	0.02 U	9.9	23	2.1
BZ#177	ppb	0.065 U	23	33	52	52	0.11	38	87.5	12
BZ#178	ppb	0.055 U	7.7	10.95	16	16	0.05	12	23.5	3.8
BZ#179	ppb	0.055 U	17	24	39	45	0.1	31	62	7.9
BZ#180	ppb	0.1	60.3	98.4	145	158	0.4155	88.7	224	30.4
BZ#182/187	ppb	0.055 U	32	43.5	81	79	0.25	56	115	16
BZ#183	ppb	0.065 U	18	25.5	51	47	0.11	32	67.5	6.4
BZ#185	ppb	0.065 U	5.9	6.5	11	14	0.025 U	9.3	14	1.4
BZ#189	ppb	0.00301 L	2.71	4.04	5.5	6.31	0.0138 L	3.74	10.1	1.26
BZ#190 (170/190 - 170)	ppb	0.04	26.1	27.3	42	64	0.096	48.1	95	7.9
BZ#191	ppb	0.07 U	3.4	3.8	7.9	5.9	0.03 U	0 R	9	0.6 U
BZ#193	ppb	0.07 U	4.8	6.3	12	15	0.03 U	9.6	21.5	2.1
BZ#194	ppb	0.4 U	20	26	52	70	0.22 U	14.5 U	53	8.2
BZ#196/203	ppb	0.255 U	13	18	33	45	0.12 U	31	46	6
BZ#199	ppb	0.27 U	15	19	0 R	40	0.13 U	10 U	47.5	8.1
Total PCBs	ppb	6.44696	32217.75	30475.515	65788.1	53469.69	45.2157	40532.09	85046	6566.68

NOTES:
U - one-half of the detection limit shown
L - detected concentration falls below the minimum levels specified in Method 1668
R - reported value rejected because specific quality control limits were not met, entered as 0

Appendix C.2. Earthworm Data, High and Low Resolution PCB Analysis, Sheboygan River Floodplain, WI, 11-3-5-97

wet weight concentrations

Station		REFL	FPR3	FPL4	FPL4	FPL4	FPR5	FPR6	FPR6	FPR7
Sample		1	2	3	4	5	6	7	8	9
Analyte	Units									
Lipids	%	1.2	0.88	0.885	0.9	0.98	0.97	1	1	0.88
Moisture content	%	83	75	81	82	81	84	80	85	83
PCB congener										
BZ#5/8	ppb	0.015 U	2.1	1.7	5.9	1.3 U	0.04	8.6	1.6	0.51
BZ#15	ppb	0.02 U	11	21.5	52	36	0.06	72	19	2.25
BZ#16/32	ppb	0.025 U	61	22.1	320	110	0.03 U	590	93	0.37 U
BZ#17	ppb	0.02 U	12	8.5	45	21	0.03 U	75	13	0.96
BZ#18	ppb	0.025 U	13	10.75	28	30	0.03 U	62	18	1.03
BZ#19	ppb	0.025 U	3.4	4.3	29	7.8	0.03 U	56	6.6	0.37 U
BZ#22	ppb	0.015 U	41	26.5	110	100	0.02 U	140	51	1.35
BZ#24/27	ppb	0.02 U	20	15.3	89	59	0.03 U	180	45	0.63
BZ#25	ppb	0.015 U	15	26	67	75	0.02 U	110	41	2.25
BZ#26	ppb	0.015 U	23	43.5	68	93	0.02 U	110	55	3.1
BZ#28/31	ppb	0.04	680	705	1470	1580	0.31	2270	1030	35.5
BZ#33	ppb	0.015 U	9.5	9.45	37	30	0.02 U	59	19	1.045
BZ#40	ppb	0.04 U	33	21.2	82	75	0.04 U	110	52	1.65
BZ#41/71/64	ppb	0.045 U	880	715	2420	2520	0.51	3420	1560	41.5
BZ#42	ppb	0.045 U	190	155.5	610	560	0.11	790	340	4.85
BZ#44	ppb	0.045 U	570	465	1550	1670	0.25	2170	980	13
BZ#45	ppb	0.035 U	41	20.6	120	76	0.035 U	150	48	0.39 U
BZ#46	ppb	0.035 U	11	5.5	36	2.4 U	0.035 U	52	9.2	0.39 U
BZ#47/48	ppb	0.04 U	460	345	1360	1110	0.38	1750	680	14
BZ#49	ppb	0.04 U	810	655	1940	2060	0.99	2780	1280	51
BZ#52	ppb	0.035 U	1240	925	2690	2930	1.2	3780	1880	70
BZ#56/60	ppb	0.025 U	420	345	1090	1140	0.39	1410	680	22
BZ#66	ppb	0.025 U	870	780	2120	2260	0.72	2720	1390	71.5
BZ#70/76	ppb	0.04 U	980	1210	2020	2630	1.8	2280	1440	120
BZ#74	ppb	0.04 U	870	780	1980	2280	0.34	2670	1430	39
BZ#77	ppb	0.00465	44.1	41.05	97.1	118	0.199	101	88.8	5.99
BZ#83	ppb	0.04 U	54	60.5	130	160	0.12	170	100	5.75
BZ#84/92	ppb	0.03 U	320	355	790	900	0.93	1070	650	35.5
BZ#85	ppb	0.04 U	220	245	570	650	1	730	430	25.5
BZ#87	ppb	0.04 U	400	485	1120	1320	0.69	1470	930	38
BZ#89/90/101	ppb	0.1	820	995	2250	2490	2.6	2760	1750	103.5
BZ#91	ppb	0.03 U	130	147.5	320	370	0.22	480	260	15
BZ#95	ppb	0.08	630	670	1420	1670	1.2	2010	1170	70
BZ#97	ppb	0.04 U	370	430	1010	1140	0.39	1260	790	34
BZ#99	ppb	0.03 U	500	590	1250	1440	1.5	1640	1000	70
BZ#105	ppb	0.0469 L	270	330	740	860	1.45	960	580	44.5
BZ#107	ppb	0.025 U	51	68.5	150	170	0.32	170	120	9.05
BZ#110	ppb	0.19	1260	1660	3710	4180	4.1	4730	2970	185
BZ#114	ppb	0.00311 L	24.5	26.6	52.3	69.7	0.0558 L	55.6	52.7	2.73
BZ#118	ppb	0.1355	580	800	1700	1990	2.02	2110	1290	89
BZ#123	ppb	0.003375 L	13.3	12.75	25	35.9	0.106	24.8	25.5	2.06
BZ#126	ppb	0.000775 U	1.25	1.302	2.22	3.06	0.0212	2.35	2.5	0.02615 U
BZ#128	ppb	0.045 U	82	135	210	290	0.47	280	220	15
BZ#129	ppb	0.025 U	18	30	51	63	0.03 U	56	46	3.95
BZ#131	ppb	0.035 U	2.6	8.8	11	14	0.04 U	13	9.6	0.5125 U
BZ#134	ppb	0.035 U	20	29	42	58	0.1	64	42	3.55
BZ#135/144	ppb	0.035 U	55	79	130	170	0.34	170	130	13
BZ#136	ppb	0.035 U	50	61.5	120	150	0.25	170	110	7.55
BZ#137	ppb	0.025 U	15	32.5	52	62	0.11	53	47	3.6
BZ#138/163/164	ppb	0.22	420	710	1140	1470	2.6	1520	1110	102.5
BZ#141	ppb	0.03 U	36	71	120	140	0.21	130	110	7
BZ#146	ppb	0.025 U	43	74	140	160	0.41	130	120	14
BZ#149	ppb	0.15	440	595	1050	1270	1.9	1500	980	104.5
BZ#151	ppb	0.11	77	101.5	170	210	0.47	240	150	15
BZ#153	ppb	0.1	210	385	660	740	1.9	780	570	62
BZ#156	ppb	0.01145 L	33.6	53.45	84.5	135	0.189	80	93.4	8.05
BZ#157	ppb	0.003445 L	6.53	10.555	17.1	26.3	0.0471	15.3	18.9	1.7
BZ#158	ppb	0.025 U	36	64	100	120	0.18	140	92	7.65
BZ#167	ppb	0.005055 L	8.81	15.305	24.7	36.8	0.0833	20.5	27.5	3.13
BZ#170	ppb	0.008705 L	13.2	22.85	37	52.8	0.0877	28.6	44	4.42
BZ#171	ppb	0.035 U	6.6	9.05	15	22	0.035 U	25	14	1.8
BZ#172	ppb	0.03 U	2.15 U	14	12	15	0.035 U	5.5 U	10	1.9

Appendix C.2 Earthworm Data, High and Low Resolution PCB Analysis, Sheboygan River Floodplain, WI, 11/3-5/97
wet weight concentrations

Station		REFL	FPR3	FPL4	FPL4	FPL4	FPR5	FPR6	FPR6	FPR7
Sample		1	2	3	4	5	6	7	8	9
BZ#174	ppb	0.035 U	20	24	41	55	0.14	59	44	4.6
BZ#175	ppb	0.03 U	1.65 U	2.7 U	2.6 U	3.8 U	0.035 U	4.25 U	2.05 U	0.725 U
BZ#176	ppb	0.03 U	1.65 U	2.7 U	6.8	3.8 U	0.035 U	4.25 U	6.5	0.725 U
BZ#177	ppb	0.035 U	13	19.5	30	34	0.04 U	45	26	3.3
BZ#178	ppb	0.03 U	5.4	12	12	16	0.07	16	13	2.2
BZ#179	ppb	0.03 U	11	12.6	20	25	0.08	33	20	2.5
BZ#180	ppb	0.026	20.5	35.2	64.7	76.7	0.199	43	67.4	8.54
BZ#182/187	ppb	0.13	77	108.5	150	190	0.63	220	140	29.5
BZ#183	ppb	0.035 U	8.3	14.5	26	33	0.04 U	24	23	2.7
BZ#185	ppb	0.035 U	1.9 U	3.075 U	6.4	4.35 U	0.04 U	4.9 U	6.3	0.825 U
BZ#189	ppb	0.00078 U	1.12	1.6095	2.39	3.86	0.0079 L	2.1	2.63	0.362
BZ#190 (170/190 - 170)	ppb	0.03	10.8	27.65	39	43.2	0.0923	48.4	29	3.73
BZ#191	ppb	0.03 U	2.15 U	3.525 U	3.5 U	5 U	0.035 U	5.5 U	2.7 U	0.95 U
BZ#193	ppb	0.03 U	4.6	10	12	14	0.035 U	14	10	2
BZ#194	ppb	0.08 U	8.5 U	17.25 U	13.5 U	27 U	0.09 U	19 U	12.5 U	3.825 U
BZ#196/203	ppb	0.08 U	4.55 U	9.5 U	7 U	14.5 U	0.09 U	10.5 U	6.5 U	2.1 U
BZ#199	ppb	0.085 U	12	10.25 U	23	16 U	0.095 U	26	20	4.1
Total PCBs (a)	ppb	3.10	15716.91	17018.70	40295.11	44742.97	35.3533	53518.9	29723.13	1680.15
TEQ	ppb	0.0003	2.37	2.23	5.18	6.34	0.01	5.42	4.78	0.31

NOTES:
U - one-half of the detection limit shown
L - detected concentration falls below the minimum levels specified in Method 1668
a - Total congeners excluding BZ#175, 191, 194, and 196/203, which were detected in soil, but not in earthworm tissue

Appendix C 3 Toxic Equivalents (TEQs) in Earthworms, Sheboygan River Floodplain, WI, 11/3-5/97.
wet weight concentrations

Station		WHO	REFL		REFL	REFL	FPR3	FPR3	FPR3	FPL4	FPL4	FPL4	FPL4	FPL4
Sample		Avian TEF	1		1	1	2	2	2	3	3	3	4	4
					TEQ	%TEQ		TEQ	%TEQ		TEQ	%TEQ		TEQ
Analyte	Units													
Lipids, percent	%		1.2				0.88			0.885			0.9	
Moisture, percent	%		83				75			81			82	
PCB congener														
BZ#77	ppb	0.05	0.00465		0.0002325	73.13	44.1	2.205	93.06	41.05	2.0525	91.91	97.1	4.855
BZ#105	ppb	0.0001	0.0469	L	0.00000469	1.48	270	0.027	1.14	330	0.033	1.48	740	0.074
BZ#114	ppb	0.0001	0.00311	L	0.000000311	0.10	24.5	0.00245	0.10	26.6	0.00266	0.12	52.3	0.00523
BZ#118	ppb	0.00001	0.1355		0.000001355	0.43	580	0.0058	0.24	800	0.008	0.36	1700	0.017
BZ#123	ppb	0.00001	0.003375	L	0.0000000338	0.01	13.3	0.000133	0.01	12.75	0.0001275	0.01	25	0.00025
BZ#126	ppb	0.1	0.000775	U	0.0000775	24.38	1.25	0.125	5.28	1.302	0.1302	5.83	2.22	0.222
BZ#156	ppb	0.0001	0.01145	L	0.000001145	0.36	33.6	0.00336	0.14	53.45	0.005345	0.24	84.5	0.00845
BZ#157	ppb	0.0001	0.003445	L	0.0000003445	0.11	6.53	0.000653	0.03	10.555	0.0010555	0.05	17.1	0.00171
BZ#167	ppb	0.00001	0.005055	L	0.0000000506	0.02	8.81	0.0000881	0.00	15.305	0.00015305	0.01	24.7	0.000247
BZ#189	ppb	0.00001	0.00078	U	0.0000000078	0.00	1.12	0.0000112	0.00	1.6095	0.000016095	0.00	2.39	0.0000239
Total TEQ	ppb				0.0003179376			2.3694953			2.233057145			5.1839109
TEQ/77,105,118,126	%					99.40			99.72			99.58		
TEQ/77,126	%					97.50			98.33			97.74		

NOTES:
U - one-half of the detection limit shown
L - detected concentration falls below the minimum levels specified in Method 1668

Appendix C.3. Toxic Equivalents (TEQs) in Earthworms, Sheboygan River Floodplain, WI, 11/3-5/97.

wet weight concentrations

Station		FPL4	FPL4	FPL4	FPL4	FPR5		FPR5	FPR5	FPR6	FPR6	FPR6	FPR6	FPR6	FPR6
Sample		4	5	5	5	6		6	6	7	7	7	8	8	8
		%TEQ		TEQ	%TEQ			TEQ	%TEQ		TEQ	%TEQ		TEQ	%TEQ
Analyte	Units														
Lipids, percent	%		0.98			0.97				1			1		
Moisture, percent	%		81			84				80			85		
PCB congener															
BZ#77	ppb	93.66	118	5.9	93.12	0.199		0.00995	81.12	101	5.05	93.21	88.8	4.44	92.93
BZ#105	ppb	1.43	860	0.086	1.36	1.45		0.000145	1.18	960	0.096	1.77	580	0.058	1.21
BZ#114	ppb	0.10	69.7	0.00697	0.11	0.0558	L	0.00000558	0.05	55.6	0.00556	0.10	52.7	0.00527	0.11
BZ#118	ppb	0.33	1990	0.0199	0.31	2.02		0.0000202	0.16	2110	0.0211	0.39	1290	0.0129	0.27
BZ#123	ppb	0.00	35.9	0.000359	0.01	0.106		0.00000106	0.01	24.8	0.000248	0.00	25.5	0.000255	0.01
BZ#126	ppb	4.28	3.06	0.306	4.83	0.0212		0.00212	17.28	2.35	0.235	4.34	2.5	0.25	5.23
BZ#156	ppb	0.16	135	0.0135	0.21	0.189		0.0000189	0.15	80	0.008	0.15	93.4	0.00934	0.20
BZ#157	ppb	0.03	26.3	0.00263	0.04	0.0471		0.00000471	0.04	15.3	0.00153	0.03	18.9	0.00189	0.04
BZ#167	ppb	0.00	36.8	0.000368	0.01	0.0833		0.000000833	0.01	20.5	0.000205	0.00	27.5	0.000275	0.01
BZ#189	ppb	0.00	3.86	0.0000386	0.00	0.0079	L	0.000000079	0.00	2.1	0.000021	0.00	2.63	0.0000263	0.00
Total TEQ	ppb			6.3357656				0.012266362			5.417664			4.7779563	
TEQ/77,105,118,126	%	99.69			99.62				99.75			99.71			99.64
TEQ/77,126	%	97.94			97.95				98.40			97.55			98.16

NOTES:

U - one-half of the detection limit shown

L - detected concentration falls below the minimum levels specified in Method 1668

Appendix C.3 Toxic Equivalents (TEQs) in Earthworms, Sheboygan River Floodplain, WI, 11/3-5/97.

wet weight concentrations

Station		FPR7		FPR7	FPR7
Sample		9		9	9
				TEQ	%TEQ
Analyte	Units				
Lipids, percent	%	0.88			
Moisture, percent	%	83			
PCB congener					
BZ#77	ppb	5.99		0.2995	97.00
BZ#105	ppb	44.5		0.00445	1.44
BZ#114	ppb	2.73		0.000273	0.09
BZ#118	ppb	89		0.00089	0.29
BZ#123	ppb	2.06		0.0000206	0.01
BZ#126	ppb	0.02615	U	0.002615	0.85
BZ#156	ppb	8.05		0.000805	0.26
BZ#157	ppb	1.7		0.00017	0.06
BZ#167	ppb	3.13		0.0000313	0.01
BZ#189	ppb	0.362		0.00000362	0.00
Total TEQ	ppb			0.30875852	
TEQ/77,105,118,126	%				99.58
TEQ/77,126	%				97.85

NOTES:

U - one-half of the detection limit shown

L - detected concentration falls below the minimum levels specified in Method 1668

Appendix D.1. Robin Ingestion Dose and Risk Estimate, Sheboygan River Floodplain, WI.
(all concentrations are wet weight (ww))

Component	Parameter	Units	Reference	On-site mean	n-site 95%UCL	Notes
Earthworm	fraction diet	proportion	0.236	0.236	0.236	a
	PCB conc	mg/kg worm	3.10E-003	25.34	42	b
	TEQ conc	ug/kg worm	3.00E-004	3.33	5.36	c
Invertebrates						
hard-bodied	fraction diet	proportion	0.144	0.144	0.144	d
	ratio worm conc	proportion	0.17	0.17	0.17	e
	PCB conc	mg/kg beetle	5.27E-004	4.31	7.14	f
	TEQ conc	ug/kg beetle	5.10E-005	0.57	0.91	f
Invertebrates						
soft-bodied	fraction diet	proportion	0.492	0.492	0.492	g
	ratio worm conc	proportion	0.08	0.08	0.08	h
	PCB conc	mg/kg soft inver	2.48E-004	2.03	3.36	i
	TEQ conc	ug/kg soft invert	2.40E-005	0.27	0.43	i
Robin diet	PCB conc	mg/kg food	9.30E-004	7.60	12.59	j
	TEQ conc	ug/kg food	9.00E-005	1.00	1.61	j
Robin dose	ingestion rate	kg food/kg bw-d	0.398	0.398	0.398	k
	PCB dose	mg/kg bw-d	3.70E-004	3.02	5.01	l
	TEQ dose	ug/kg bw-d	3.58E-005	0.40	0.64	l

Ingestion Toxicity Reference Value - No observed adverse effect level (NOAEL)						m
Basis	TRV	units	Hazard Quotients (HQ) (ratio)			n
PCB dose	0.0415	mg/kg bw-d	8.91E-003	72.87	120.77	o
TEQ dose	0.00144	ug/kg bw-d	2.49E-002	275.97	444.20	p
Dioxin dose	0.014	ug/kg bw-d	2.56E-003	28.38	45.69	q

Ingestion Toxicity Reference Value - Lowest observed adverse effect level (LOAEL)						r
Basis	TRV	units	Hazard Quotients (HQ) (ratio)			n
PCB dose	0.361	mg/kg bw-d	1.02E-003	8.38	13.88	s
TEQ dose	0.00323	ug/kg bw-d	1.11E-002	123.03	198.03	t
Dioxin dose	0.14	ug/kg bw-d	2.56E-004	2.84	4.57	u

Notes:

a) (Earthworms + traces of animal matter)/total robin diet excluding indigestible grass (Howell 1942).

b) Sum of measured congener concentrations in earthworms.

c) TEQs based on WHO avian TEFs for congeners 77, 105, 114, 118, 123, 126, 156, 157, 167, and 189.

d) Total coleoptera (beetles)/total robin diet excluding indigestible grass (Howell 1942).

e) Ratio of hard-bodied invertebrate concentration/earthworm concentration (based on the ratio of dioxin concentrations in beetles and earthworms (wet weights) from field studies of paper sludge applications in pine plantations) (Martin et al. 1987; Thiel et al. 1988).

f) Measured earthworm concentration x ratio of hard-bodied invertebrate concentration/earthworm concentration.

g) Total soft-bodied invertebrates/total robin diet excluding indigestible grass (Howell 1942).

h) Ratio of soft-bodied invertebrate concentration/earthworm concentration (based on the ratio of dioxin concentrations in soft-bodied invertebrates and earthworms (wet weights) from field studies of paper sludge applications in pine plantations) (Martin et al. 1987, Thiel et al. 1988). Soft-bodied invertebrates included crickets, cockroaches, caterpillars, insect larvae and spiders.

i) Measured earthworm concentration x ratio of soft-bodied invertebrate concentration/earthworm concentration

j) (Earthworm conc. x fraction of diet) + (hard-bodied invertebrate conc. x fraction of diet) + (soft-bodied invertebrate x fraction of diet)

k) Robin ingestion rate is based on feeding studies reported by Levey and Karasov (1989). Dry weight ingestion was 6.8 g/robin/d for a diet of crickets and 11.6 g/robin/d for a diet of fruit (banana mash). These are converted to wet weight (ww) ingestions of 24.3 and 77.3 g/robin/d for crickets (initial moisture content = 72%) and fruit (initial mc = 85%), respectively. Divided by the robin bodyweight (bw) of 77.8 g, the food ingestion rates are 0.31 and 0.99 g food/g bw-d, for insect and fruit diets, respectively. Based on a dietary composition of 87% invertebrates and 13% fruit and seeds (derived from Howell 1942 excluding the indigestible grass component), the overall ingestion rate is 0.398 g food/g bw-d [(0.31 x 0.87) + (0.99 x 0.13)]. Note: g/g bw-d is the same as kg/kg bw-d.

l) PCB or TEQ concentration in food x food ingestion rate. The dose units are milligrams or micrograms contaminant ingested per kilogram bodyweight per day.

m) No observed adverse effect level (NOAEL) is the highest dose that did not result in a measurable toxic effect.

n) Hazard quotient (HQ) = robin dose/benchmark dose. The benchmark dose is either the NOAEL or the LOAEL. HQ > 1 indicates potential risks to robins. HQ < 1 indicates that risk to robins is unlikely.

o) NOAEL for chicken based on mean bodyweight and PCB consumption for 1 through 8 weeks following onset of dietary exposure to PCBs in carp from Saginaw Bay, Lake Huron (Summer et al. 1996a and b). Total PCBs are the sum of Aroclors 1242, 1248, 1254 and 1260. The low-dose treatment is the NOAEL.

p) NOAEL for chicken based on mean food ingestion, bodyweight and food TEQ concentration (H4IIE rat hepatoma bioassay) for 1 through 8 weeks following onset of dietary exposure to PCBs in carp from Saginaw Bay, Lake Huron (Summer et al. 1996a and b). This is the same treatment as described in footnote o.

q) NOAEL for pheasant based on intraperitoneal (i.p.) injection of 2,3,7,8-TCDD (Nosek et al 1992, 1993). The middle dose is the NOAEL. This is compared to the TEQ robin dose.

r) Lowest observed adverse effect level (LOAEL) is the lowest dose that resulted in a measurable toxic effect.

s) LOAEL for chicken based on mean bodyweight and PCB consumption for 1 through 8 weeks following onset of dietary exposure to PCBs in carp from Saginaw Bay, Lake Huron (Summer et al. 1996a and b). Total PCBs are the sum of Aroclors 1242, 1248, 1254 and 1260. The high-dose treatment is the LOAEL. The effect is hatchability.

t) LOAEL for chicken based on mean food ingestion, bodyweight and food TEQ concentration (H4IIE rat hepatoma bioassay) for 1 through 8 weeks following onset of dietary exposure to PCBs in carp from Saginaw Bay, Lake Huron (Summer et al. 1996a and b). This is the same treatment as described in footnote s.

u) LOAEL for pheasant based on intraperitoneal (i.p.) injection of 2,3,7,8-TCDD (Nosek et al 1992, 1993). The high dose treatment is the LOAEL. This is compared to the TEQ robin dose. The effects are fertility and embryo mortality.

Appendix D.2 Modeled Robin Egg Concentration and Risk Estimates, Sheboygan River Floodplain, WI.
(all concentrations are wet weight (ww))

Component	Parameter	Units	Reference	On-site mean	On-site 95%aUCL	Notes	On-site mean	On-site 95%aUCL	Notes
Earthworm	fraction diet	proportion	0.236	0.236	0.236		0.236	0.236	a
	PCB conc	ppm	3.10E-003	25.34	42		25.34	42	b
	TEQ conc	ppb	3.00E-004	3.33	5.36		3.33	5.36	c
	BZ#77 conc	ppb	4.70E-003	62.03	99.85		62.03	99.85	d
	BZ#126 conc	ppb	8.00E-004	1.59	2.54		1.59	2.54	d
	BZ#105 conc	ppb	4.69E-002	473.24	779.16		473.24	779.16	d
	BZ#118 conc	ppb	1.36E-001	1070.13	1761.64		1070.13	1761.64	d
Invertebrates									
hard-bodied	fraction diet	proportion	0.144	0.144	0.144		0.144	0.144	e
	worm conc ratio	proportion	0.17	0.17	0.17		0.17	0.17	f
	PCB conc	ppm	5.27E-004	4.31	7.14		4.31	7.14	g
	TEQ conc	ppb	5.10E-005	0.57	0.91		0.57	0.91	g
	BZ#77 conc	ppb	7.99E-004	10.55	16.97		10.55	16.97	g
	BZ#126 conc	ppb	1.36E-004	0.27	0.43		0.27	0.43	g
	BZ#105 conc	ppb	7.97E-003	80.45	132.46		80.45	132.46	g
	BZ#118 conc	ppb	2.30E-002	181.92	299.48		181.92	299.48	g
Invertebrates									
soft-bodied	fraction diet	proportion	0.492	0.492	0.492		0.492	0.492	h
	worm conc ratio	proportion	0.08	0.08	0.08		0.08	0.08	i
	PCB conc	ppm	2.48E-004	2.03	3.36		2.03	3.36	j
	TEQ conc	ppb	2.40E-005	0.27	0.43		0.27	0.43	j
	BZ#77 conc	ppb	3.76E-004	4.96	7.99		4.96	7.99	j
	BZ#126 conc	ppb	6.40E-005	0.13	0.20		0.13	0.20	j
	BZ#105 conc	ppb	3.75E-003	37.86	62.33		37.86	62.33	j
	BZ#118 conc	ppb	1.08E-002	85.61	140.93		85.61	140.93	j
Robin diet	PCB conc	ppm	9.30E-004	7.60	12.59		7.60	12.59	k
	TEQ conc	ppb	9.00E-005	1.00	1.61		1.00	1.61	k
	BZ#77 conc	ppb	1.41E-003	18.60	29.94		18.60	29.94	k
	BZ#126 conc	ppb	2.40E-004	0.48	0.76		0.48	0.76	k
	BZ#105 conc	ppb	1.41E-002	141.90	233.62		141.90	233.62	k
	BZ#118 conc	ppb	4.06E-002	320.87	528.21		320.87	528.21	k
Diet-egg BMF	Total PCBs	ratio (ww/ww)	31.7	31.7	31.7		31.7	31.7	l
	BZ#77	ratio (ww/ww)	0.17	0.17	0.17	m	1.8	1.8	n
	BZ#126	ratio (ww/ww)	64	64	64	m	29	29	n
	BZ#105	ratio (ww/ww)	20	20	20		20	20	o
	BZ#118	ratio (ww/ww)	31	31	31		31	31	o
Robin egg	PCB conc	ppm	2.95E-002	240.85	399.21		240.85	399.21	p
	TEQ conc	ppb	1.59E-003	3.59	5.76		3.44	5.53	q
	BZ#77 conc	ppb	2.40E-004	3.16	5.09		33.48	53.89	r
	BZ#126 conc	ppb	1.54E-002	30.51	48.74		13.83	22.09	r
	BZ#105 conc	ppb	2.81E-001	2837.93	4672.47		2837.93	4672.47	r
	BZ#118 conc	ppb	1.26E+000	9946.90	16374.51		9946.90	16374.51	r
Egg Toxicity Reference Value - No observed adverse effect concentration (NOAEC)									s
Chemical	TRV	units			Hazard Quotients (HQ) (ratio)				t
PCB conc	5	ppm	5.89E-003	48.17	79.84		48.17	79.84	u
Dioxin conc	0.08	ppb	1.98E-002	44.91	72.00		43.00	69.18	v
BZ#77 conc	9	ppb	2.66E-005	0.35	0.57		3.72	5.99	w
BZ#126 conc	1.6	ppb	9.59E-003	19.07	30.46		8.64	13.80	x
BZ#105 conc	2700	ppb	1.04E-004	1.05	1.73		1.05	1.73	y
		HI (77,126, 105)	9.73E-003	20.47	32.76		13.41	21.52	z
Egg Toxicity Reference Value - Lowest observed adverse effect concentration (LOAEC)									aa
Chemical	TRV	units			Hazard Quotients (HQ) (ratio)				t
PCB conc	24	ppm	1.23E-003	10.04	16.63		10.04	16.63	ab
Dioxin conc	0.16	ppb	9.92E-003	22.45	36.00		21.50	34.59	ac
BZ#77 conc	27	ppb	8.87E-006	0.12	0.19		1.24	2.00	ad
BZ#126 conc	3.2	ppb	4.80E-003	9.53	15.23		4.32	6.90	ae
BZ#105 conc	8100	ppb	3.47E-005	0.35	0.58		0.35	0.58	af
		HI (77,126, 105)	4.84E-003	10.00	16.00		5.91	9.47	z

Notes

a) (Earthworms + traces of animal matter) total robin diet excluding indigestible grass (Howell 1942)

b) Sum of measured congener concentrations in earthworms

c) Dioxin toxicity equivalents (TEQs) based on World Health Organization (WHO) avian TEFs for congeners 77, 105, 114, 118, 123, 126, 156, 157, 167, and 189

d) Measured earthworm concentration.

e) Total coleoptera (beetles) total robin diet excluding indigestible grass (Howell 1942)

f) Ratio of hard-bodied invertebrate concentration/earthworm concentration (based on the ratio of dioxin concentrations in beetles and earthworms (wet weights) from field studies of paper sludge applications in pine plantations) (Martin et al 1987; Thiel et al. 1988).

g) Measured earthworm concentration x ratio of hard-bodied invertebrate concentration/earthworm concentration.

h) Total soft-bodied invertebrates/total robin diet excluding indigestible grass (Howell 1942).

i) Ratio of soft-bodied invertebrate concentration/earthworm concentration (based on the ratio of dioxin concentrations in soft-bodied invertebrates and earthworms (wet weights) from field studies of paper sludge applications in pine plantations) (Martin et al 1987; Thiel et al. 1988). Soft-bodied invertebrates included crickets, cockroaches, caterpillars, insect larvae and spiders

j) Measured earthworm concentration x ratio of soft-bodied invertebrate concentration/earthworm concentration.

k) (Earthworm conc x fraction of diet) + (hard-bodied invertebrate conc x fraction of diet) + (soft-bodied invertebrate x fraction of diet)

l) Diet to egg biomagnification factor (BMF) for PCBs = summed congener concentrations in herring gull egg/whole-body alewife (wet weights) in a Lake Ontario study (Braune and Norstrom 1989).

m) Diet-egg BMF for BZ#77 or 126 = congener 77 or 126 concentrations in Forster's Tern egg/whole-body spottail shiner (wet weights) in Green Bay, Lake Michigan (Kubiak et al. 1989).

n) Diet-egg BMF for BZ#77 or 126 = congener 77 or 126 concentrations in herring gull egg/whole-body alewife (wet weights) in Lake Ontario (Norstrom pers. comm. in Hoffman et al 1996).

o) Diet-egg BMF for BZ#105 or 118 = congener 105 or 118 concentrations in herring gull egg/whole-body alewife (wet weights) in Lake Ontario (Braune and Norstrom 1989).

p) Diet PCB concentration x total PCB diet-egg BMF.

q) TEQs are based on estimated robin egg concentrations of congeners 77, 105, 118 and 126, multiplied by the respective WHO avian TEFs: 0.05 0.0001, 0.00001 and 0.1. Other dioxin-like congeners are excluded because diet-egg BMFs are not available, however, the excluded congeners are unlikely to change the results by more than a few percent. Robin egg TEQ is not estimated directly from the dietary TEQ because a TEQ-based diet-egg BMF is not available.

r) Diet congener concentration x respective congener diet-egg BMF.

s) No observed adverse effect concentration (NOAEC) is the highest concentration that did not result in a measurable toxic effect.

t) Hazard quotient (HQ) = egg conc./benchmark conc. The benchmark conc. is either the NOAEC or the LOAEC. HQ > 1 indicate potential risks to robin embryos. HQ < 1 indicate that risk to robin embryos is unlikely.

u) NOAEC for mean total PCBs (Aroclors 1242, 1248, 1254 and 1260) (wet weight) measured in chicken eggs at week 7 following onset of dietary exposure to PCBs in carp from Saginaw Bay, Lake Huron (Summer et al. 1996b).

v) NOAEC for dioxin (2,3,7,8-TCDD) injected in chicken egg yolk (Powell, et al. 1996b).

w) NOAEC for congener 77 injected in chicken egg yolk (Powell et al. 1996a). This is the NOAEC for hatchability and deformity, the NOAEC for mortality is lower (3 ppb), however, the injection volume (1 uL/egg) was later shown to increase the adverse effects of congener 126 three-fold compared with an injection volume of 0.1 uL/egg (Powell et al. 1996b) The congener 77 study was not repeated with the lower injection volume, so the higher NOAEC was selected to account for the injection volume effect

x) NOAEC for congener 126 injected in chicken egg yolk (Powell et al 1996b)

y) NOAEC for congener 105 injected in chicken egg yolk (Powell et al 1996a)

z) Hazard Index (HI) = sum of HQs for congeners 77, 126 and 105. These HQs are summed because these congeners are expected to have similar effects mediated through the same physiological mode of action.

aa) Lowest observed adverse effect concentration (LOAEC) is the lowest concentration that resulted in a measurable toxic effect.

ab) LOAEC for mean total PCBs (Aroclors 1242, 1248, 1254 and 1260) (wet weight) measured in chicken eggs at week 7 following onset of dietary exposure to PCBs in carp from Saginaw Bay, Lake Huron. The effect is hatchability. (Summer et al. 1996b)

ac) LOAEC for dioxin (2,3,7,8-TCDD) injected in chicken egg yolk. The effects are mortality and deformity (Powell et al. 1996b).

ad) LOAEC for congener 77 injected in chicken egg yolk. The effects are hatchability and deformity (Powell et al. 1996a). See footnote w discussion on injection volume effect.

ae) LOAEC for congener 126 injected in chicken egg yolk. The effects are mortality and deformity (Powell et al. 1996b).

af) LOAEC for congener 105 injected in chicken egg yolk. The effects are mortality and abnormality (Powell et al. 1996a).

Appendix E. Soil Preliminary Remedial Goals (PRGs), Sheboygan River Floodplain, WI

Calculation of Ecologically Protective Earthworm Concentration

Chemical	Units	Toxicity Ref Value Basis	Egg conc. ww	Diet-Egg BMF ww/ww	Dietary Conc. ww	Soft-bodied Invert Conc. ratio ww/ww	Fract. diet	Hard-bodied Invert. Conc. ratio ww/ww	Fract. diet	Earthworm Fract. diet	Conc ww
PCB	ppm	NOAEC	5	31.7	0.16	0.08	0.492	0.17	0.144	0.236	0.53
	ppm	LOAEC	24	31.7	0.76	0.08	0.492	0.17	0.144	0.236	2.53
BZ#126	ppb	NOAEC	1.03	29	0.03552	0.08	0.492	0.17	0.144	0.236	0.12
	ppb	LOAEC	2.34	29	0.08069	0.08	0.492	0.17	0.144	0.236	0.27
BZ#126	ppb	NOAEC	1.49	64	0.02328	0.08	0.492	0.17	0.144	0.236	0.08
	ppb	LOAEC	3.05	64	0.04766	0.08	0.492	0.17	0.144	0.236	0.16

Calculation of Ecologically Protective Soil Concentration

Chemical	Units	Basis	Worm Conc. ww	Soil-Worm BAF ww/dw	Soil Conc. dw	126:PCB Ratio	Soil PCB ppm dw
PCB	ppm	NOAEC	0.526043	0.65	0.81		
	ppm	LOAEC	2.525006	0.65	3.88		
BZ#126	ppb	NOAEC	0.118454	0.4	0.30	0.00013	2.28
	ppb	LOAEC	0.269109	0.4	0.67	0.00013	5.18
BZ#126	ppb	NOAEC	0.077646	0.4	0.19	0.00013	1.49
	ppb	LOAEC	0.158939	0.4	0.40	0.00013	3.06

Notes:

Egg concentration for congener 126 was adjusted so that the sum of the hazard quotients (HQ) of congeners 126, 77 and 105 = 1.
Adjusted egg conc. = 126 benchmark * (126 HQ/HI), where HI is the hazard index (sum of 126, 77 and 105 HQs).

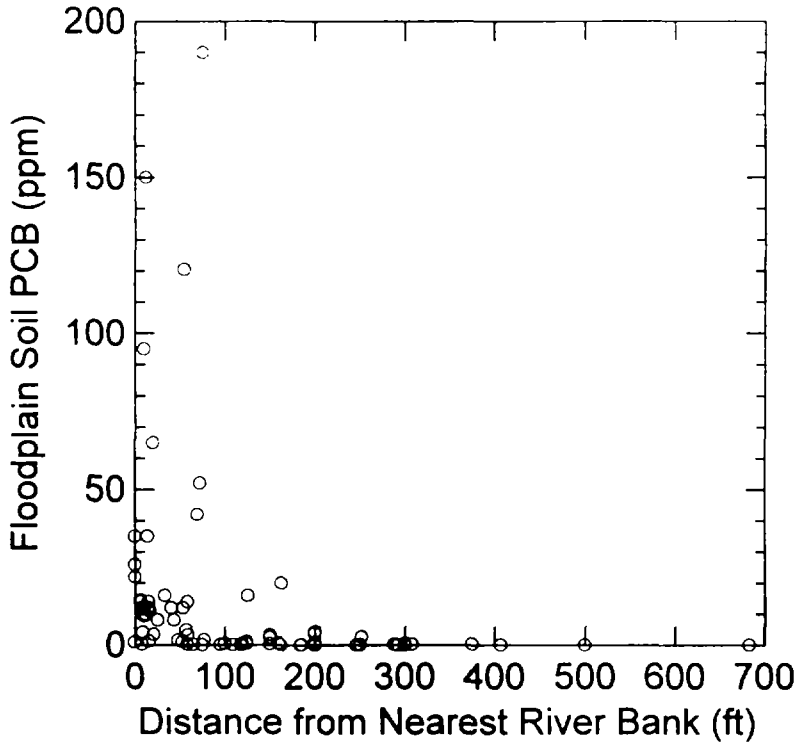
Diet-Egg BMF (biomagnification factor) = Egg conc. (ww)/Dietary conc. (ww) derived from field studies of gulls or terns.

Calculated earthworm conc. = Dietary conc./(worm fract. diet + (soft invert. conc. ratio * fract. diet) + (hard invert. conc. ratio * fract. diet))
where conc. ratio = invert. conc./earthworm conc. derived from field studies of paper sludge application in a pine forest

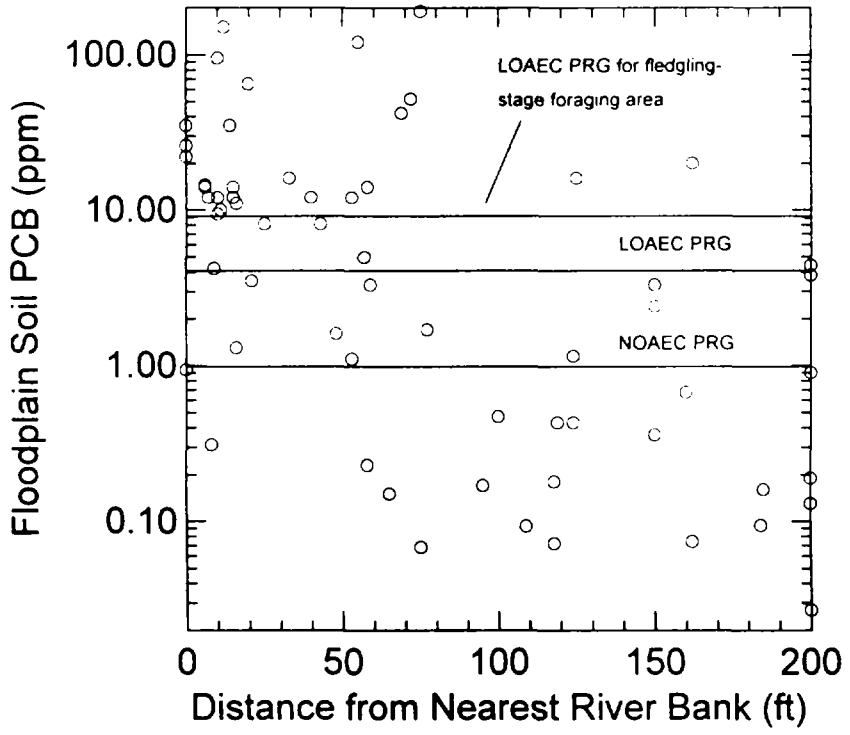
Soil-Worm BAF (bioaccumulation factor) = earthworm conc. (ww)/soil conc. (dw)
calculated from site-specific data (excluding reference datum)

126:PCB Ratio = soil BZ#126 conc. (dw)/soil total PCB conc. (dw)
calculated from site-specific data (excluding reference datum and sample 6 outlier)

Appendix F.1. Horizontal Distribution of Floodplain Soil PCB Concentrations, 1992 Data, Sheboygan River, Wisconsin.



Appendix F.2. Horizontal Distribution of Floodplain Soil PCB Contamination within 200 ft of Nearest River Bank, 1992 Data, Sheboygan River, Wisconsin.



Appendix G. Field Sampling Procedures, Sheboygan River Floodplain, WI.

Sample Size

Samples will only be taken from a given location if there are sufficient worms to provide the required sample size of 30 g. Based on a preliminary survey on 8/29/97, 30 g of earthworms is equivalent to 80 worms. The required soil sample size is 30 g.

Field Sampling Methods

The sequence within a given sample location will be to collect earthworms first and then collect the soil sample.

Earthworm Sampling Method

1) Clear an area of approximately 3 ft diameter of surface debris.
2) Dig up the upper 6-8 inches of soil over a 1-2 ft area with a spade. If the area is grassy, remove the sod first, then, if necessary, additional soil to a combined 6- to 8-inch depth.
3) Place the soil on stainless steel or aluminum trays and manually sort for worms. For sod, shake the soil out of the root mat over the trays and manually sort the loosened soil for worms.
4) Place the earthworms in a temporary glass sample jar, and the sorted soil in a stainless steel or aluminum mixing bowl.
5) Dig up deeper soil layers and repeat step 3. Use professional judgement for determining the appropriate depth to terminate excavation.
6) Place the earthworms in the temporary glass sample jar, but set the sorted deeper soil aside for refilling the hole after completion of sampling.
7) If insufficient worms are obtained (less than 80 worms), either extend the hole horizonally or dig new holes within 20 feet of the original and repeat steps 1-6.
8) When sufficient worms are obtained (80 worms), place the worms in 8 oz amber glass sample jars with teflon-coated lids; refill the hole(s) with the sorted deeper soil layer material; and retain the sorted upper soil layer for soil sampling.

Soil Sampling Method

1) Mix the surface soil (upper 6-8 inches) sample in a stainless steel bowl with a stainless steel spoon or trowel.
2) Spread the mixed soil out evenly and divide into quarters.
3) Sample consecutively from the quarters until two 8 oz amber glass sample jars with a teflon-coated lid are nearly filled (one jar is for PCB analyses, the other for TOC determinations).
4) Finish refilling the sample hole(s) with the remaining soil.

Field Equipment Decontamination

All sampling equipment will be decontaminated at the completion of sampling at each sample location before leaving that location.

1) Rinse with site water to remove any remaining soil.
2) Scrub with brushes using an Alconox ® solution.
3) Rinse and scrub with site water.
4) Rinse with distilled water.

The efficiency of the decontamination will be assessed by taking a wipe of the decontaminated sampling equipment after the third sample location. The wipe will be sealed in a sample jar and will serve as the field blank for the sampling effort.

Sample Identification, Labels, Documentation, and Custody

Sample Identification

Each sample will be assigned a unique indentifier according to the following code:

First two characters, "SR", for Sheboygan River, identify the project.
Next two characters identify the sample material - "EW" for earthworm, and "SS" for soil.
Next two digits identify the consecutive sample number (01 through 10). The sample numbers for earthworms and soil will be identical at the same location, with the exception of the duplicate sample location which will be assigned two sample numbers.

Next four characters indicate the floodplain segment (FPL or FPR followed by the segment number, see Table 1). REFL indicates the reference location.

Sample Labels

Sample labels are self-adhering and waterproof. Each sample label will contain the project number, sample identification number, date and time of collection in indelible ink. A completed sample label will be affixed to each sample container and clear tape will be wrapped over the label.

Documentation

The field coordinator will maintain a field logbook. See Aquatic ERA WP section 3.6.3

Chain of Custody

See Aquatic ERA WP section 3.6.4.

Shipping Requirements and Receipt

For shipping, sample containers will be wrapped in bubble wrap and securely packed inside the coolers with adequate ice packs to maintain the cooler temperature at 4° C. Chain-of-custody forms will be placed in zip-locked bags and taped to the inside lid of the cooler. Fiber tape will be wrapped completely around the cooler and it will be sealed with a chain-of-custody seal.

The coolers will be shipped by overnight mail to the appropriate laboratory. The point of contact and shipping information are given below.

PCB Analysis (Earthworms and Soil)

Georgina Brooks
Axys Analytical Services Ltd.
P.O. Box 2219
2045 Mills Rd.
Sydney, B.C., Canada V8L 3S8
tel: 250-656-0881

TOC Analysis (Soil)

Mark Harris
Analytical Resources, Inc.
333 Ninth Ave. N.
Seattle, WA 98109
tel: 206-621-6490

Sample Archiving

All samples will be held in deep freeze under appropriate chain-of-custody seal until analyzed.

APPENDIX H.1. QUALITY ASSURANCE REVIEW SUMMARY—
CHEMICAL ANALYSES OF SOIL SAMPLES

Prepared for EVS Consultants, Inc.
200 West Mercer Street, Suite 403
Seattle, Washington. 98119

Prepared by QA/QC Solutions
4714 West Bridges Road
Deer Park, Washington 99006

August 2, 1998

QUALITY ASSURANCE REVIEW SUMMARY— CHEMICAL ANALYSES OF SOIL SAMPLES

INTRODUCTION

This report documents the results of a quality assurance review of data reported for chemical analyses conducted on soil samples and associated field quality control samples collected in support of the Sheboygan River Floodplain Ecological Risk Assessment project conducted by EVS Consultants (Seattle, Washington). The results of the quality assurance review are presented herein. The chemical analyses completed included the analysis of polychlorinated biphenyl (PCB) congeners, total solids (percent moisture, and total organic carbon (TOC). Chemical analyses for PCB congeners using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for the toxic congeners and low resolution gas chromatography/mass spectrometry (LR GC/MS) for other PCB congeners and total solids were completed by Axys Analytical Services, Ltd. (Sidney, British Columbia, Canada). Total solids and TOC determinations were completed by Analytical Resources, Inc. (Seattle, Washington).

The quality assurance review was conducted to verify that the laboratory quality assurance and quality control (QA/QC) procedures were documented and that the quality of the data is sufficient to meet the project DQOs and support the use of the data for its intended purposes. Data validation procedures and qualifier assignments were generally based on U.S. Environmental Protection Agency (EPA) contract laboratory program national functional guidelines organic data review (U.S. EPA 1994), quality control criteria specified in the applicable analytical methods used by the laboratory, and n the context of the data quality objectives established for the project. Modifications of data validation procedures were made, as appropriate, to accommodate project-specific DQOs and quality control requirements for methods not specifically addressed by the national functional guidelines documents. The data validation review summary is included as an attachment to this report.

A summary of the data quality objectives (DQOs) established for the chemical analyses completed and the analytical methods used are provided in the quality assurance project plan (QAPP) and applicable laboratory statements of work prepared by EVS Consultants.

DATA VALIDATION PROCEDURES

Data validation was completed to EPA Level 2 QA review specifications, as modified by EVS Consultants. The level-of-effort contracted between EVS and QA/QC Solutions was to conduct 10 percent review and calculations checks for all calibration and quality control data, compound quantification and identification, 100 percent transcription checks, and calculation checks of 10

percent of positive identifications. All analytical data were validated in accordance with applicable guidance specified either by the referenced method-specific quality control criteria or in the context of the data quality objectives (DQOs) established by the client for this project.

The following laboratory deliverables were reviewed during the data validation process:

- Chain-of-custody documentation to verify completeness of the data
- The case narrative discussing analytical problems (if any) and procedures
- Sample preparation logs or data summary sheets to verify analytical holding times
- Instrument tuning, instrument calibration, and calibration blank results to assess instrument performance
- Column performance and RT Window data to assess reliability of analyte detection and identification
- Method blanks associated with each sample delivery group (SDG) to check for laboratory contamination
- Results for all applicable laboratory quality control check samples that included surrogate compound recoveries, laboratory control sample (LCS) recoveries, matrix spike recoveries, and internal standards to check analytical accuracy
- Duplicate sample results to check analytical precision
- Instrument and method detection limits for all target analytes
- Mass spectra to verify detection of analytes in the samples.

In addition, results for all applicable field quality control samples were reviewed. These results provide additional information in support of the quality assurance review.

SAMPLE DELIVERY GROUPS

The sample delivery groups (SDGs) contained all documentation and data necessary to conduct the level of effort required to complete the quality assurance review.

DATA QUALITY ASSESSMENT

The results of the quality control procedures used during sample analysis are discussed below. The laboratory data were evaluated in terms of completeness, holding times, instrument performance, accuracy, precision, method reporting limits, and field quality control samples.

During the quality assurance review, no data were qualified as estimated and no data were rejected.

COMPLETENESS

The results reported by the laboratory were 100 percent complete. No data were rejected during the quality assurance review.

HOLDING TIMES AND SAMPLE PRESERVATION

The analytical holding time constraints and sample preservation requirements specified in QAPP were met for all samples and analyses.

INSTRUMENT PERFORMANCE

The performance of the analytical instruments, as documented by the laboratory, was acceptable. No changes in instrument performance that would have resulted in the degradation of data quality were indicated during any analysis sequence.

Initial and Continuing Calibration

Initial and continuing calibrations were completed for all applicable target analytes and met the criteria for acceptable performance and frequency of analysis. Specific comments summarized in the SDGs are presented below.

The case narrative for analyses by HRGC/HRMS stated apparent inaccuracies with the chemical standards obtained by Cambridge Isotope Laboratories. Tests by the Axys indicated a significant overestimation of PCB 114 and an underestimation of PCB 170. Further, the standard solutions were compared to results obtained from the analysis of a certified reference material (CLB-1) obtained from the National Research Council of Canada. This comparison indicated an underestimation of PCB 77, PCB 118, and PCB 180, and an overestimation of PCB 114. One other comparison was made using a non-ortho substituted standard obtained from Environment Canada and the World Health Organization, which resulted in an underestimation of PCB 77 and PCB 169.

The laboratory apparently contacted Mr. Terry Grim at Cambridge Isotope Laboratories to discuss the issues discussed above. Apparently, Mr. Grim advised Axys that final validation of the standards had not been completed. Although there appear to be either an underestimation or an overestimation of the concentrations of specific PCB congeners, the sample results reported were not corrected for the observed apparent bias noted by the laboratory. Since the apparent bias in standard concentrations has not been verified at this time, no action was taken during the

data review; however, it should be noted that results reported for the PCBs listed above may exhibit either a negative or positive bias.

The case narrative also stated that the calibration verification acceptance criteria for analyses by HRGC/HRMS listed in Table 5 of Method 1668 are incorrect. The criteria appear to be based on concentrations in the precision and recovery (PAR) standard rather than n the concentrations in the calibration solutions. An interim acceptance criteria of 75-125 percent was used to assess the acceptability of the continuing verification standards. This control limit is considered acceptable; therefore, no action was taken during the quality assurance review.

Method Blank Analyses

No target analytes were detected in any applicable method blank at concentrations above applicable action limits specified by the analytical methods.

Some PCBs were detected in some of the filter blanks processed. The concentrations of the PCBs detected in the method blanks did not require the qualification of any sample results because the affected PCBs were present in the natural samples at concentrations significantly above the concentrations found in these blanks. The concentrations detected in the blanks are listed in the attached data review summary.

ACCURACY

The accuracy of the analytical results is evaluated in the following sections in terms of analytical bias (surrogate compound, matrix spike, LCS recoveries, and internal standards) and precision (duplicate sample analyses). Complete details of all surrogate compound, matrix spike, LCS recoveries, internal standards data, and duplicate or triplicate analytical data are presented in the attached data review summaries.

Surrogate Compound Recoveries

The recoveries reported by the laboratory for the applicable surrogate compounds added to all field and quality control samples met the criteria for acceptable performance.

Matrix Spike Recoveries

The recoveries reported by the laboratory for all applicable matrix spike analyses and the frequency of analysis met the criteria for acceptable performance, with the three exceptions.

For the LR GC/MS congener analyses, all recoveries met the control limit of 70-120 percent, with one exception. A recovery of 121 percent was reported for PCB 180, which is slightly

above the upper control limit of 120 percent. No data required qualification because the control limit was only slightly exceeded.

For the TOC analyses, a recovery of 57.8 percent was reported for the matrix spike and a recovery of 121 percent was reported for the matrix spike duplicate, resulting in a relative percent difference (RPD) of 71 percent. The matrix spike recoveries did not meet the specified control limit of 80-120 percent or RPD requirement of ±20 percent. No sample results were qualified for these exceedances because sample results are not qualified solely based on matrix spike results. Since the recovery of TOC in the LCS and standard reference material sample analyses were in control, it appears the recovery exceedances may be due to sample homogeneity issues. In addition, it is the opinion of the reviewer that the project-specific control limits are too tight for the analysis of soil samples; the control limits specified are more typical for water samples. A reasonable control limit of 50-150 percent should be used for assessing the accuracy, with ±50 RPD for precision, when solid samples are used for analysis.

For the HRGC/HRMS PCB congener analyses, matrix spikes were not conducted by the laboratory nor are they are required by the analytical method. The lack of matrix spike data does not affect the overall quality of the data set because the analytical method is an isotope dilution technique, and as such each sample is essentially a "matrix spike" (i.e., isotopically labeled surrogate compounds and internal standards are added to each sample).

Laboratory Control Sample Recoveries

The recoveries reported by the laboratory for all applicable LCS analyses (i.e. reference material samples, ongoing precision and recovery, and blank spike samples) and the frequency of analysis met the criteria for acceptable performance.

For analyses by LR GC/MS analyses, acceptable recoveries must meet the control limit of 70-120 percent. For this data set, the LCS was completed using the NIST 1588 standard reference material (cod liver oil) for 9 PCB congeners. Recoveries ranged from 87 percent to 105 percent and met the project-specific DQO of 70-120 percent recovery. Sample results did not require qualification based on LCS results.

For analyses by HRGC/HRMS, the concentrations of the ongoing precision and recovery (OPR) standards must be within the limits specified by the analytical method. The OPR is considered as the LCS, as specified by EPA Method 1668. The OPR is a laboratory blank spiked with known concentrations of target analytes. The OPR is processed and analyzed exactly like the samples to assess the adequacy of laboratory performance in the absence of potential matrix effects/interferences. Sample results did not require qualification based on OPR results.

Internal Standard Performance

Criteria for retention time and area count were met of all applicable internal standards added to all samples analyzed for organic target analytes.

Precision

The results reported by the laboratory for duplicate analyses and the frequency of analysis met the criteria for acceptable performance, with the exception of the RPD reported for the duplicate matrix spike analyses complete for TOC, as discussed in the matrix spike section above.

TARGET ANALYE IDENTIFICATION

All criteria for the identification of target analytes reported as detected or undetected, as specified in the applicable analytical methods, were met.

Based on pre-screen analyses, samples sizes were estimated to optimize the quantification of the data for analyses by HRGC/HRMS. Because many PCB congeners appeared to be present at very high concentrations action was required. The case narrative states that it was agreed between an EVS representative and Axys the higher level PCB congeners would be reported from the LR GC/MS analyses to avoid multiple dilutions. The proposed sample sizes, anticipated detection limits, and strategy were discussed with EVS and approval to proceed was granted.

In some instances some results reported for the analysis of PCB congeners by low resolution gas chromatography/mass spectrometry were flagged 'NDR' by the laboratory to indicate that the ion ratios failed method-specific criteria. None of these results were additionally qualified during the data review because other identification criteria were met, such as retention times and the actual presence of the appropriate ions.

The case narrative for analyses by HRGC/HRMS stated the relative retention time (RRT) of ^{13}C-PCB 77 (the isotopically labeled standard) was consistently lower than the lower control limit established. It is the opinion of this reviewer that although the RRT was low for this compound, it was consistent. Review of selected instrument printouts showed the characteristic ions were always present. Because the RRT was consistent and the ions were always present, no action was taken.

The case narrative for analyses by HRGC/HRMS also stated that following EPA Method 1668 protocols, where observed peaks failed the ion abundance ratio or other qualitative identification criteria the congener was reported as not detected. This convention could result in the reporting of a congener as a false negative, especially at very low concentrations. In instances where the ion abundance ratio was out based on the use of peak area, the ion ratio was recalculated using peak height. If this ion ration based on peak height was acceptable and all other criteria for

identification were met, the congener was reported as detected. This approach is considered as acceptable and no action was required during the data review.

METHOD DETECTION LIMITS

The method detection limits (MDLs) used by the laboratories met project DQOs; however, in some instances elevated MDLs/MRLs were reported for some samples and target analytes. Elevated MDLs/MRLs were reported because dilutions were necessary to conduct the analyses because elevated concentrations of target analytes, matrix interferences present in the samples, or both.

The laboratory completed a method detection limit study as described in Appendix B of 40 CFR Part 136 on the October 26, 1984 Federal Register. The method detection limits were calculated using a Student's t-value for six degrees of freedom and a 99 percent confidence level. The method detection limits (in ng/g) were based on a 10 gram volume. The calculated method detection limits for 32 PCB congeners (including co-eluting congeners) ranged from 0.02 ng/g to 0.15 ng/g.

FIELD QUALITY CONTROL SAMPLES

No field duplicate samples were known to this data reviewer. For analyses by HRGC/HRMS, the field blanks associated with the soil samples included a cross contamination that consisted of an ashless piece of filter paper that was used to wipe the sampling processing equipment after is has undergone decontamination procedures. The other field blanks consisted of filter blanks, used in conjunction with the cross contamination blanks to assist if verifying if any target analyte that may be found in the cross contamination blank was due to insufficient decontamination procedures or poor field technique.

Very low levels of few PCBs were detected in the filter paper blanks and did not require of qualification of the samples data because the concentrations of the affected PCBs in the samples were significantly above the concentrations found in the filter blanks.

REFERENCES

U.S. EPA. 1994. USEPA contract laboratory program national functional guidelines for organic data review. EPA 540/R-94/012. February 1994. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC.

APPENDIX H.2. QUALITY ASSURANCE REVIEW SUMMARY—
CHEMICAL ANALYSES OF EARTHWORM SAMPLES

Prepared for EVS Consultants, Inc.
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Prepared by QA/QC Solutions
4714 West Bridges Road
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August 2, 1998

QUALITY ASSURANCE REVIEW SUMMARY— CHEMICAL ANALYSES OF EARTHWORM SAMPLES

INTRODUCTION

This report documents the results of a quality assurance review of data reported for chemical analyses conducted on earthworm tissue samples and associated field quality control samples collected in support of the Sheboygan River Floodplain Ecological Risk Assessment project conducted by EVS Consultants (Seattle, Washington). The results of the quality assurance review are presented herein. The chemical analyses completed included the analysis of polychlorinated biphenyl (PCB) congeners using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for the toxic congeners, low resolution gas chromatography/mass spectrometry (LR GC/MS) for other PCB congeners, and percent lipids content. All analyses were conducted by Axys Analytical Services, Ltd. (Sidney, British Columbia, Canada).

The quality assurance review was conducted to verify that the laboratory quality assurance and quality control (QA/QC) procedures were documented and that the quality of the data is sufficient to meet the project DQOs and support the use of the data for its intended purposes. Data validation procedures and qualifier assignments were generally based on U.S. Environmental Protection Agency (EPA) contract laboratory program national functional guidelines organic data review (U.S. EPA 1994), quality control criteria specified in the applicable analytical methods used by the laboratory, and the context of the data quality objectives established for the project. Modifications of data validation procedures were made, as appropriate, to accommodate project-specific DQOs and quality control requirements for methods not specifically addressed by the national functional guidelines documents. The data validation review summary is included as and to this report.

A summary of the data quality objectives (DQOs) established for the chemical analyses completed and the analytical methods used are provided in the quality assurance project plan (QAPP) and applicable laboratory statements of work prepared by EVS Consultants.

DATA VALIDATION PROCEDURES

Data validation was completed to EPA Level 2 QA review specifications, as modified by EVS Consultants. The level-of-effort contracted between EVS and QA/QC Solutions was to conduct 10 percent review and calculations checks for all calibration and quality control data, compound quantification and identification, 100 percent transcription checks, and calculation checks of 10 percent of positive identifications. All analytical data were validated in accordance with

applicable guidance specified either by the referenced method-specific quality control criteria or in the context of the data quality objectives (DQOs) established by the client for this project.

The following laboratory deliverables were reviewed during the data validation process:

- Chain-of-custody documentation to verify completeness of the data
- The case narrative discussing analytical problems (if any) and procedures
- Sample preparation logs or data summary sheets to verify analytical holding times
- Instrument tuning, instrument calibration, and calibration blank results to assess instrument performance
- Column performance and RT Window data to assess reliability of analyte detection and identification
- Method blanks associated with each sample delivery group (SDG) to check for laboratory contamination
- Results for all applicable laboratory quality control check samples that included surrogate compound recoveries, laboratory control sample (LCS) recoveries, matrix spike recoveries, and internal standards to check analytical accuracy
- Duplicate sample results to check analytical precision
- Instrument and method detection limits for all target analytes
- Mass spectra to verify detection of analytes in the samples.

In addition, results for all applicable field quality control samples were reviewed. These results provide additional information in support of the quality assurance review.

SAMPLE DELIVERY GROUPS

The sample delivery groups (SDGs) contained all documentation and data necessary to conduct the level of effort required to complete the quality assurance review.

DATA QUALITY ASSESSMENT

The results of the quality control procedures used during sample analysis are discussed below. The laboratory data were evaluated in terms of completeness, holding times, instrument performance, accuracy, precision, method reporting limits, and field quality control samples. During the quality assurance review, no data were qualified as estimated and no data were rejected.

COMPLETENESS

The results reported by the laboratory were 100 percent complete. No data were rejected during the quality assurance review.

HOLDING TIMES AND SAMPLE PRESERVATION

The analytical holding time constraints and sample preservation requirements specified in QAPP were met for all samples and analyses.

INSTRUMENT PERFORMANCE

The performance of the analytical instruments, as documented by the laboratory, was acceptable. No changes in instrument performance that would have resulted in the degradation of data quality were indicated during any analysis sequence.

Initial and Continuing Calibration

Initial and continuing calibrations were completed for all applicable target analytes and met the criteria for acceptable performance and frequency of analysis. Specific comments summarized in the SDGs are presented below.

The case narrative for analyses by HRGC/HRMS stated apparent inaccuracies with the chemical standards obtained by Cambridge Isotope Laboratories. Tests by the Axys indicated a significant overestimation of PCB 114 and an underestimation of PCB 170. Further, the standard solutions were compared to results obtained from the analysis of a certified reference material (CLB-1) obtained from the National Research Council of Canada. This comparison indicated an underestimation of PCB 77, PCB 118, and PCB 180, and an overestimation of PCB 114. One other comparison was made using a non-ortho substituted standard obtained from Environment Canada and the World Health Organization, which resulted in an underestimation of PCB 77 and PCB 169.

The laboratory apparently contacted Mr. Terry Grim at Cambridge Isotope Laboratories to discuss the issues discussed above. Apparently, Mr. Grim advised Axys that final validation of the standards had not been completed. Although there appear to be either an underestimation or an overestimation of the concentrations of specific PCB congeners, the sample results reported were not corrected for the observed apparent bias noted by the laboratory. Since the apparent bias in standard concentrations has not been verified at this time, no action was taken during the data review; however, it should be noted that results reported for the PCBs listed above may exhibit either a negative or positive bias.

The case narrative also stated that the calibration verification acceptance criteria for analyses by HRGC/HRMS listed in Table 5 of Method 1668 are incorrect. The criteria appear to be based on

concentrations in the precision and recovery (PAR) standard rather than n the concentrations in the calibration solutions. An interim acceptance criteria of 75-125 percent was used to assess the acceptability of the continuing verification standards. This control limit is considered acceptable, therefore, no action was taken during the quality assurance review.

Method Blanks and Proof Blanks

No target analytes were detected in any applicable method blank at concentrations above applicable action limits specified by the analytical methods. In addition to the method blanks, an aqueous "Virtis" proof blank (i.e., a blank processed through the Virtis blender used to homogenize the tissue samples).

Some PCBs were detected in some of the filter blanks processed and no PCBs were detected in the "Virtis" proof blank. The concentrations of the PCBs detected in these method blanks did not require the qualification of any sample results because the affected PCBs were present in the natural samples at concentrations significantly above the concentrations found in these blanks. The concentrations detected in the blanks are listed in the attached data review summary.

ACCURACY

The accuracy of the analytical results is evaluated in the following sections in terms of analytical bias (surrogate compound, matrix spike, LCS recoveries, and internal standards) and precision (duplicate sample analyses). Complete details of all surrogate compound, matrix spike, LCS recoveries, internal standards data, and duplicate or triplicate analytical data are presented in the attached data review summaries.

Surrogate Compound Recoveries

The recoveries reported by the laboratory for the applicable surrogate compounds added to all field and quality control samples met the criteria for acceptable performance.

Matrix Spike Recoveries

For the HRGC/HRMS PCB congener analyses, matrix spikes were not conducted by the laboratory nor are they are required by the analytical method. The lack of matrix spike data does not affect the overall quality of the data set because the analytical method is an isotope dilution technique, and as such each sample is essentially a "matrix spike" (i.e., isotopically labeled surrogate compounds and internal standards are added to each sample).

Laboratory Control Sample Recoveries

The recoveries reported by the laboratory for all applicable LCS analyses (i.e. reference material samples, ongoing precision and recovery, and blank spike samples) and the frequency of analysis met the criteria for acceptable performance.

For analyses by LR GC/MS analyses, acceptable recoveries must meet the control limit of 70-120 percent. For this data set, the LCS was completed using the NIST 1588 standard reference material (cod liver oil) for 9 PCB congeners. Recoveries ranged from 87 percent to 105 percent and met the project-specific DQO of 70-120 percent recovery.

For analyses by HRGC/HRMS, the concentrations of the ongoing precision and recovery (OPR) standards must be within the limits specified by the analytical method. The OPR is considered as the LCS, as specified by EPA Method 1668. The OPR is a laboratory blank spiked with known concentrations of target analytes. The OPR is processed and analyzed exactly like the samples to assess the adequacy of laboratory performance in the absence of potential matrix effects/interferences. Sample results did not require qualification based on OPR results.

Internal Standard Performance

Criteria for retention time and area count were met of all applicable internal standards added to all samples analyzed for organic target analytes.

Precision

The results reported by the laboratory for duplicate analyses and the frequency of analysis met the criteria for acceptable performance.

For analyses by HRGC/HRMS, the tissue Sample SREW01REFL was analyzed in duplicate. The RPD results were calculated during the data review and entered on the hardcopy summary of results in the HRGC/HRMS data package. The RPDs of all target analytes detected in the duplicate sample analyses were less than the ±50 RPD control limit, with two exceptions.

An RPD of 89 percent (concentrations of 6.73 ng/kg and 2.57 ng/kg, with a detection limit of 0.82 ng/kg for the first sample and 2.12 ng/kg for the duplicate sample) was calculated for PCB 77 for the duplicate analyses completed on the tissue sample SREW01REFL. For the analysis of this sample using the DB-1 column, an RPD of 56.6 percent (concentrations of 4.42 ng/kg and 2.47 ng/kg, with a detection limit of 1.26 ng/kg for the first sample and 1.55 ng/kg for the duplicate sample) for PCB 157. No action was taken for this exceedance because the duplicate sample results were only slightly above the detection of 2.12 ng/kg for the duplicate analyses of Sample SRSS06FPR. Because the concentration of PCB 77 and PCB 157 in the duplicate sample analysis was near the detection limit, there is a much greater degree of uncertainty

associated with this result. It should be noted, however, results reported for PCB 77 and PCB 157 may exhibit a slight positive or negative bias.

TARGET ANALYE IDENTIFICATION

All criteria for the identification of target analytes reported as detected or undetected, as specified in the applicable analytical methods, were met. Complete details of target analyte identifications are presented in the attached data review summaries.

Based on pre-screen analyses, samples sizes were estimated to optimize the quantification of the data for analyses by HRGC/HRMS. Because many PCB congeners appeared to be present at very high concentrations action was required. The case narrative states that it was agreed between an EVS representative and Axys the higher level PCB congeners would be reported from the LR GC/MS analyses to avoid multiple dilutions. The proposed sample sizes, anticipated detection limits, and strategy were discussed with EVS and approval to proceed was granted.

In some instances some results reported for the analysis of PCB congeners by low resolution gas chromatography/mass spectrometry were flagged 'NDR' by the laboratory to indicate that the ion ratios failed method-specific criteria. None of these results were additionally qualified during the data review because other identification criteria were met, such as retention times and the actual presence of the appropriate ions.

The case narrative for analyses by HRGC/HRMS stated the relative retention time (RRT) of ^{13}C-PCB 77 (the isotopically labeled standard) was consistently lower than the lower control limit established. It is the opinion of this reviewer that although the RRT was low for this compound, it was consistent. Review of selected instrument printouts showed the characteristic ions were always present. Because the RRT was consistent and the ions were always present, no action was taken.

The case narrative for analyses by HRGC/HRMS also stated that following EPA Method 1668 protocols, where observed peaks failed the ion abundance ratio or other qualitative identification criteria the congener was reported as not detected. This convention could result in the reporting of a congener as a false negative, especially at very low concentrations. In instances where the ion abundance ratio was out based on the use of peak area, the ion ratio was recalculated using peak height. If this ion ration based on peak height was acceptable and all other criteria for identification were met, the congener was reported as detected. This approach is considered as acceptable and no action was required during the data review.

METHOD DETECTION LIMITS

The method detection limits (MDLs) used by the laboratories met project DQOs; however, in some instances elevated MDLs/MRLs were reported for some samples and target analytes. Elevated MDLs/MRLs were reported because dilutions were necessary to conduct the analyses because elevated concentrations of target analytes, matrix interferences present in the samples, or both.

The laboratory completed a method detection limit study as described in Appendix B of 40 CFR Part 136 on the October 26, 1984 Federal Register. The method detection limits were calculated using a Student's t-value for six degrees of freedom and a 99 percent confidence level. The method detection limits (in ng/g) were based on a 10 gram volume. The calculated method detection limits for 32 PCB congeners (including co-eluting congeners) ranged from 0.02 ng/g to 0.15 ng/g.

FIELD QUALITY CONTROL SAMPLES

No field duplicate samples were known to this data reviewer. Field blanks consisted of ashless filter paper that was used in conjunction with the cross contamination blanks (see soil report) to assist if verifying if any target analyte that may be found in the cross contamination blank was due to insufficient decontamination procedures or poor field technique. Very low levels of few PCBs were detected in the filter paper blanks and did not require of qualification of the samples data because the concentrations of the affected PCBs in the samples were significantly above the concentrations found in the filter blanks.

For the cross contamination blank, extremely high concentrations of PCBs were detected, as listed in the attached data review summary. No action was taken based on the detection of PCBs in this blank because the results could not be normalized to concentration units of ng/kg since the weight of the filters were not provided and no information was available on how this blank was collected, or after which natural sample it was collected. It should be noted, however, there is significant contamination of PCBs in this field blank that suggests the results reported as detected for the affected PCBs in the natural samples may exhibit a positive bias or be reported as false positives. Interpretation as to the impact of the field blank contamination on the sample results should be made by the data users. In terms of the data review, the results reported by the laboratory appear to be correct and the extremely high concentrations of PCBs detected in this field blank are not due to contamination issues at the laboratory because PCBs in all laboratory blanks were reported as not detected or at very low concentrations.

REFERENCES

U.S. EPA. 1994. USEPA contract laboratory program national functional guidelines for organic data review. EPA 540/R-94/012. February 1994. Office of Solid Waste and Emergency Response. U.S. Environmental Protection Agency. Washington. DC.

APPENDIX H.3. QUALITY ASSURANCE REVIEW SUMMARY—
CHEMICAL ANALYSES OF SOIL AND EARTHWORM SAMPLES

PREPARED FOR EVS CONSULTANTS, INC.
200 WEST MERCER STREET, SUITE 403
SEATTLE, WASHINGTON. 98119

PREPARED BY QA/QC SOLUTIONS
4714 WEST BRIDGES ROAD
DEER PARK, WASHINGTON 99006

AUGUST 2, 1998

PCB CONGENERS by HRGC/HRMS and LR GC/MS - DATA REVIEW SUMMARY

QA/QC Solutions Contract No.: 1197-5-EVS

Client: EVS Environmental Consultants
200 West Mercer Street, Suite 403
Seattle, Washington 98109

Contact: Ms. Julie Viveiros
Tel: 206/217-9337
Fax: 206/217-9343
e-mail: juliev@evs.wa.com

Client Project No.: 2/789-03

Analytical Laboratory:

Axys Analytical Services, Ltd.
P.O. Box 2219
2045 Mills Road
Sidney, British Columbia, Canada V8L 3SB

Contact: Ms. Georgina Brooks
Tel: 250/656-0881
Fax: 250/656-4511

Data Reviewer: James J. Mc Ateer Jr. of QA/QC Solutions

Level of QA Review: Level 2 (see *Comments* section for details)

Date of Data Review: July 24 to August 2, 1998

Lab Work Order No.	Matrix	No. Samples	Analysis
99805	Soil/Sediment	11 (10 + 1 dup)	Toxic PCB Congeners, PCB Congeners, solids, and TOC
99805	Tissue (earth worms)	11 (10 + 1 dup)	Toxic PCB Congeners, PCB Congeners, and lipids

Analytical Methods:

Draft EPA Method 1668 (October 4, 1995, Draft Revision) for the measurement of toxic PCB Congeners by isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for 13 PCB congeners (including co-elution PCB congeners 156 and 157).

Axys Analytical Services, Ltd. standard operating procedure (SOP): PCB Congeners Analysis, Methods CL-S-03/Ver. 1 for soil/sediment samples and CL-T-03/Ver.1 for tissue samples by Low Resolution GC/MS for 102 PCB congeners (including co-eluting PCB congeners) and total PCBs using low resolution gas chromatography/mass spectrometry (LR GC/MS). The MS was operated in the electron impact mode. Primary analyses were completed using a DB-5 fused silica column (60m x 0.25 mm i.d., 0.25 μm film thickness).

Note: The method references listed above do not coincide with those listed in Table 2 of the QAPP. Specifically, for the soil/sediment analyses, the QAPP references Axys CL-S-01/Ver. 2 and for tissues references Axys CL-T-02/Ver. 2.

COMMENTS

1. Data are acceptable as reported by the laboratory.

2. Data validation was completed to EPA Level 2 QA review specifications, as modified by EVS Consultants. The level-of-effort contracted between EVS and QA/QC Solutions was to conduct 10 percent review and calculations checks for all calibration and quality control data, compound quantification and identification, 100 percent transcription checks, and calculation checks of 10 percent of positive identifications. All analytical data were validated in accordance with applicable guidance specified either by the referenced method–specific quality control criteria or in the context of the data quality objectives (DQOs) established by the client for this project.

The following laboratory deliverables were reviewed during the data validation process:

- Chain-of-custody documentation to verify completeness of the data
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- Results for all applicable laboratory quality control check samples that included surrogate compound recoveries, laboratory control sample (LCS) recoveries, matrix spike recoveries, and internal standards to check analytical accuracy
- Duplicate sample results to check analytical precision
- Instrument and method detection limits for all target analytes
- Mass spectra to verify detection of analytes in the samples.

In addition, results for all applicable field quality control samples were reviewed. These results provide additional information in support of the quality assurance review.

3. Please note, discussion of analyses completed for total solids (percent moisture) and percent lipids are included in the *Assessment of Supplemental Information* section of this data review summary.

1. **Are all data acceptable for use as qualified?** Yes

2. **Are the data preliminary and pending action or verification?** No

3. **Is any action required by QA/QC Coordinator?** No

4. **Is any action required by Project Manager?** No

COMMENTS

All data are acceptable as reported by the laboratory. During the quality assurance review, no results were qualified as estimated and no results were rejected.

QUALIFIER CODES AND DEFINITIONS

U = The analyte was reported by the laboratory as not detected at a concentration above the reported method detection limit.

UB = The result reported by the laboratory was restated as undetected at the concentration found in the sample and reported by the laboratory because criteria for one or more blanks were not met.

J1 = The analyte was reported as detected, but the result was qualified as estimated because of method blank contamination. Results were qualified as estimated if the concentration of the analyte was greater than two times the concentration detected in the method blank.

J2 = The analyte was reported as either detected or undetected, but the result was qualified as estimated because percent recovery of the associated isotopically-labeled internal standard did not meet method-specific control limits.

NJ4 - The analyte was reported as detected, but the result should be considered as tentative (*N*) and estimated (*J4*) because all criteria for qualitative identification were not met. The concentration of the analyte was reported at an Estimated Maximum Possible Concentration (EMPC). EMPCs are reported by the laboratory if a GC/MS signal has eluted within the established PCDD/PCDF retention time window, but all criteria for qualitative identification were not met.

J4 - The analyte was reported as detected, but the result was qualified as estimated because of quantitative interferences associated with the isotopically labeled standard used for quantifying the target analyte. The recoveries of the associated isotopically labeled standard used for quantification (internal or recovery standard) exceeded the upper control limit. Elevated internal or recovery standard recoveries typically result from unknown quantitative interferences (e.g., co-elution of a non-target analyte) which effect QC ion stabilities. Qualitatively, the overall affect on the quality of the data is the sensitivity of the instrument may have been reduced, thus increasing the potential for reporting false positives. Quantitatively, the overall affect on the quality of the data is the concentrations of the target analytes may be under estimated (exhibit a negative bias) or overestimated (exhibit a positive bias). The degree of bias associated with the qualified result can not be determined because the presence of the quantitative interferences currently cannot be detected by other analytical techniques.

R = The detected or undetected result reported by the laboratory was rejected because specific quality control limits were not met.

DATA COMPLETENESS CHECK

1. **Are case narratives present?** Yes

2. Document control data:

   a. **Sample tracking information present?** Yes

   b. **Internal communication worksheet present?** Yes

   c. **Sample preparation data present?** Yes

   d. **HRGC/HRMS analysis data present?** Yes

   e. **Report generation and data review forms present?** Yes

   f. **Sample extraction logs present?** Yes

   g. **Sample analyses logs present?** Yes

   h. **Percent moisture/lipid calculations and forms present?** Yes

   i. **Miscellaneous information (e.g., faxs, correspondences)?** Yes

   j. **Chain-of-Custody documentation present?** Yes

   k. **Perfluorokerosene tuning data present?** Yes

   l. **Initial calibration (ICAL) data present?** Yes

   m. **Continuing calibration verification (CCV) data present?** Yes

   n. **GC Column Performance and RT Window data present?** Yes

   p. **Method blank data present?** Yes

   q. **Matrix spike (MS) data present?** Yes

   r. **Laboratory control sample (LCS) data present?** Yes

   s. **Sample data present?** Yes

3 Data Completeness Check

Completeness will be measured for each set of data received by dividing the number of valid measurements actually obtained by the number of valid measurements that were planned:

Equation for Completeness:

$$\text{Completeness} = \frac{\text{valid data points obtained}}{\text{total data points planned}} \times 100$$

COMMENTS

To be considered complete, the data set must also contain all quality control check analyses specified by the analytical method used in order to verify the accuracy (precision and bias) of the results. The sample results reported by the laboratory were 100 percent complete.

ASSESSMENT OF HOLDING TIMES

. HOLDING TIMES[3]. HOLDING TIMES[4]

Sample ID	Date Collected	Date Received	Date Extracted	Date Analyzed
Soil/Sediment Samples by HRGC/HRMS				
SRSS05FPL4	11/04/97	11/06/97	06/17/98	06/21/98
SRSS04FPL4	11/04/97	11/06/97	06/17/98	06/21/98
SRSS06FPR5	11/04/97	11/06/97	06/17/98	06/21/98
SRSS06FPR5 (dup)	11/05/97	11/06/97	06/17/98	06/21/98
SRSS07FPR6	11/03/97	11/06/97	06/17/98	06/21/98
SRSS01REFL	11/03/97	11/06/97	06/17/98	06/21/98
SRSS10FPL4	11/04/97	11/06/97	06/17/98	06/21/98
SRSS03FPL4	11/04/97	11/06/97	06/17/98	06/21/98
SRSS02FPR3	11/04/97	11/06/97	06/17/98	06/21/98
SRSS08FPR6	11/05/97	11/06/97	06/17/98	06/21/98
SRSS09FPR7	11/03/97	11/06/97	06/17/98	06/21/98
Tissue Samples by HRGC/HRMS				
SREW05FPL4	11/04/97	11/06/97	06/17/98	06/23/98
SREW04FPL4	11/04/97	11/06/97	06/17/98	06/23/98
SREW06FPR5	11/04/97	11/06/97	06/17/98	06/22/98
SREW07FPR6	11/05/97	11/06/97	06/17/98	06/23/98
SREW01REFL	11/03/97	11/06/97	06/17/98	06/22/98
SREW01REFL (dup)	11/03/97	11/06/97	06/17/98	06/22/98
SREW10FPL4	11/04/97	11/06/97	06/17/98	06/23/98
SREW03FPL4	11/04/97	11/06/97	06/17/98	06/23/98
SREW02FPR3	11/04/97	11/06/97	06/17/98	06/22/98
SREW08FPR6	11/05/97	11/06/97	06/17/98	06/23/98
SREW09FPR7	11/03/97	11/06/97	06/17/98	06/22/98
Cross Contamination Blank	11/04/97	11/06/97	06/17/98	06/21/98
Filter Blank	-	-	06/17/98	06/21/98

Holding Time Criteria:

No maximum holding times are associated with the analysis of PCB congeners using the methods. It is suggested that aqueous samples be stored at 4°C in the dark and solid samples be stored at <-10°C in the dark. If samples are stored in this manner, including the addition of any applicable preservatives, the samples may be stored for up to one year prior to extraction. In addition, sample extracts may be held for up to one year prior to analysis if stored at <-10°C in the dark.

Note: The holding time listed in the QAPP states 1 year for samples stored frozen.

ASSESSMENT OF HOLDING TIMES, continued

. HOLDING TIMES[4]. HOLDING TIMES[3]

Sample ID	Date Collected	Date Received	Date Extracted	Date Analyzed
Soil/Sediment Samples by LRGC/MS				
SRSS05FPL4	11/04/97	11/06/97	06/16/98	06/19/98
SRSS04FPL4	11/04/97	11/06/97	06/16/98	06/19/98
SRSS06FPR5	11/04/97	11/06/97	06/16/98	06/22/98
SRSS07FPR6	11/05/97	11/06/97	06/16/98	06/19/98
SRSS01REFL	11/03/97	11/06/97	06/16/98	06/19/98
SRSS10FPL4	11/03/97	11/06/97	06/16/98	06/19/98
SRSS03FPL4	11/04/97	11/06/97	06/16/98	06/19/98
SRSS02FPR3	11/04/97	11/06/97	06/16/98	06/19/98
SRSS08FPR6	11/04/97	11/06/97	06/16/98	06/19/98
SRSS08FPR6 (dup)	11/05/97	11/06/97	06/16/98	06/19/98
SRSS09FPR7	11/05/97	11/06/97	06/16/98	06/19/98
Tissue Samples by LR GC/MS				
SREW05FPL4	11/04/97	11/06/97	06/19/98	06/23/98
SREW04FPL4	11/04/97	11/06/97	06/19/98	06/23/98
SREW06FPR5	11/04/97	11/06/97	06/19/98	06/23/98
SREW07FPR6	11/05/97	11/06/97	06/19/98	06/23/98
SREW01REFL	11/03/97	11/06/97	06/19/98	06/22/98
SREW10FPL4	11/04/97	11/06/97	06/19/98	06/22/98
SREW03FPL4	11/04/97	11/06/97	06/19/98	06/22/98
SREW02FPR3	11/04/97	11/06/97	06/19/98	06/22/98
SREW08FPR6	11/05/97	11/06/97	06/19/98	06/22/98
SREW09FPR7	11/05/97	11/06/97	06/19/98	06/22/98
SREW09FPR7 (dup)	11/05/97	11/06/97	06/19/98	06/22/98

Notes: For analyses completed by LR GC/MS, a final extract volume of 100 μL was used prior to any dilutions that may have been required. Due to limited sample amounts available for extraction (per documentation by laboratory), a final extract volume of 30 μL was used for Sample SREW06FPR5, Sample SREW01REFL, and an associated procedural blank. The smaller extract volume was used to achieve lower detection limits. In addition, a final extract volume of 300 μL was used to complete the analysis of Sample SRSS08FPR6 due to high concentrations of some PCB congeners.

Holding Time Criteria:

No maximum holding times are associated with the analysis of PCB congeners using the methods. It is suggested that aqueous samples be stored at 4°C in the dark and solid samples be stored at <-10°C in the dark. If samples are stored in this manner, including the addition of any applicable preservatives, the samples may be stored for up to one year prior to extraction. In addition, sample extracts may be held for up to one year prior to analysis if stored at <-10°C in the dark.

Note The holding time listed in the QAPP states 1 year for samples stored frozen.

COMMENTS

1. All recommended analytical holding time constraints were met for analyses completed by LR GC/MS and HRGC/HRMS. In addition, all holding time constraints were met for the determination of total solids (soil/sediment only)., percent lipid content (tissues only), and total organic carbon (soil/sediment only).

2. The dates for sample extraction and analysis listed in the tables above represent the original dates of extraction and analysis of the samples. Some samples were diluted and reanalyzed within 1-2 weeks of the dates listed above.

ASSESSMENT OF INSTRUMENT TUNING

1. Was perfluorokerosene (PFK) used to tune the instrument and at the appropriate frequency for analyses completed using LR GC/MS and/or HRGC/HRMS? Yes

2. Was the minimum resolving power of ≥10,000 (10% valley) at m/z 304.9824 obtained? Yes

3. Verify that for each descriptor (Table 8 in EPA Method 1668), the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor must be monitored. Also, verify the resolution was ≥10,000 and the deviation between exact mass of m/z and the theoretical mass must be < 5 ppm? Acceptable

COMMENTS

The mass spectrometer tuning checks made by the laboratory were acceptable. No sample results required qualification based on instrument tuning.

ASSESSMENT OF INITIAL CALIBRATION VERIFICATION (ICV)

1. Instrument ID, Column, and Date of last ICAL prior to analysis of samples:

LR GC/MS: Finigan Incos 50 MS and a Varian 3400 GC equipped with a DB-5 fused silica column (60m x 0.25 mm i.d., 0.25 μm film thickness); MS operated in the electron impact mode using multiple ion detection. Initial calibration was conducted on June 2, 1998.

HRGC/HRMS: Initial analyses conducted using a VG 70 HRMS and a Hewlett-Packard HP-5890 GC. Dilutions analyzed using a VG Ultima HRMS. All primary analyses conducted using an SPB-Octyl column (30m x 0.25 mm i.d., 0.25 μm film thickness) and a DB-1 column (30m x 0.25 mm i.d., 0.25 μm film thickness) was used for resolving PCB 156/157 that co-elute on the SPB-Octyl column. The mass spectrometer was operated in the electron impact mode using selected ion monitoring. Initial calibration on the SPB-Octyl column (primary column) was conducted on June 15, 1998; initial calibration on the DB-1column was conducted on June 16, 1998.

2. Was an initial calibration verification completed using at least a 5-point curve for LR GC/MS and HRGC/HRMS analyses and was the initial calibration completed within 30 days from the date samples were analyzed? Yes. For analyses by LR GC/MS, the initial calibrations were completed using a 6-point curve. For analyses completed by HRGC/HRMS, the initial calibrations were completed using a 5-point curve.

The case narrative for analyses by HRGC/HRMS stated apparent inaccuracies with the chemical standards obtained by Cambridge Isotope Laboratories. Tests by the Axys indicated a significant overestimation of PCB 114 and an underestimation of PCB 170. Further, the standard solutions were compared to results obtained from the analysis of a certified reference material (CLB-1) obtained from the National Research Council of Canada. This comparison indicated an underestimation of PCB 77, PCB 118, and PCB 180, and an overestimation of PCB 114. One other comparison was made using a non-ortho substituted standard obtained from Environment Canada and the World Health Organization, which resulted in an underestimation of PCB 77 and PCB 169

The laboratory apparently contacted Mr. Terry Grim at Cambridge Isotope Laboratories to discuss the issues discussed above. Apparently, Mr. Grim advised Axys that final validation of the standards had not been completed. Although there appear to be either an underestimation or an overestimation of the concentrations of specific PCB congeners, the sample results reported were not corrected for the observed apparent bias noted by the laboratory. Since the apparent bias in standard concentrations has not been verified at this time, no action was taken during the data review; however, it should be noted that results reported for the PCBs listed above may exhibit either a negative or positive bias.

3. Are chromatograms, mass spectra, and/or selected ion current profiles (SICPs) present for all standards? Yes

4. For analyses completed using LR GC/MS,

A. Were relative responses factors (RRFs) and average RRFs calculated for all target PCB congeners and isotopically labeled PCBs and reported? RRFs were reported for all target analytes and isotopically labeled standards. RRFs calculated using internal standard technique.

1. Equation for RRF for target PCB congeners using calibration by internal standard:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = area of characteristic ion for applicable target analyte or surrogate compound
A_{is} = area of characteristic ion of applicable internal standard
C_{is} = concentration of applicable internal standard
C_s = concentration of applicable target analyte or surrogate compound

2. Equation for Average RRF:

$$\overline{RRF} = \frac{\sum_{j=1}^{n}}{n}$$

where n represents a particular target analyte and j is the calibration standard (i.e., 1 to 5)

Example Calculations for ICVs analyzed on June 2, 1998 for 1,3-DCB (RRF reported as 1.82 and the average RRF reported at 1.70)

$$RRF = \frac{471667 \times 384}{10144689 \times 9.8} = 1.82180556$$

$$\overline{RRF} = \frac{1.82 + 1.85 + 1.85 + 1.87 + 1.59 + 1.24}{6} = 1.703333$$

B. Were all percent relative standard deviations (%RSDs) of the average RRFs less than 20 percent? Yes

Equation for Percent relative standard deviation (%RSD):

$$\%RSD = \frac{\text{sdev of RRFs}}{\overline{RRF}} \times 100$$

where:

$\overline{RRF}$ = average relative response factor from ICAL
sdev = standard deviation of the five RRFs

Example Calculations for ICVs analyzed on June 2, 1998 for 1,3-DCB by LR GC/MS (laboratory reported a standard deviation of 0.25 and a %RSD of 14.76)

$$\%RSD = \frac{0.249773231}{1.703333} \times 100 = 14.66$$

note: slight difference in %RSD due to rounding

5. For analyses completed using HRGC/HRMS:

A. Were relative responses (RRs) and average RRs calculated for all target PCB congeners and isotopically labeled PCBs and reported? RRs were reported for all target analytes and isotopically-labeled standards. RRs calculated using internal standard technique.

1. Equation for RR for target PCB congeners using calibration by internal standard:

$$RR = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where:

A_x = sum of integrated ion abundances (primary and secondary m/z's) of target PCB
A_{is} = sum of integrated ion abundances (primary and secondary m/z's) of isotopically labeled PCB
C_{is} = concentration of PCB internal standard

C_x = concentration of unlabeled PCB target analyte

$$\text{Average RR} = \frac{\sum_{1}^{n}}{n}$$

2. Equation for Average RR:

where n represents a particular PCB
j is the calibration standard (i.e., 1 to 5)

Example Calculations for ICV (CS1) analyzed on June 15, 1998 using the SPB-Octyl column for 3,3',4,4'-TCB (PCB 77). RR reported as 0.92 and the average RRF reported at 0.92. Total area of PCB 77 at 124, 500 at a concentration of 0.5 ng/mL and Total area for isotopically labeled PCB 77 at 26,900,000 at 100 ng/mL. Average RR for PCB 77 reported at 0.92 using RRs of 0.92, 0.84, 1.03, 0.99, and 0.84

$$\text{Response Factor} = \frac{124{,}500 \times 100 \text{ ng/mL}}{26{,}900{,}000 \times 0.5 \text{ ng/mL}} = 0.9256$$

$$\overline{RR} = \frac{0.92 + 0.84 + 1.03 + 0.99 + 0.84}{5} = 0.9240$$

B. Were all percent relative standard deviations (%RSDs) of the average RRs less than 20 percent? Yes

Equation for %RSD of ICAL:

$$\%RSD = \frac{\text{sdev of RRs}}{\overline{RR}} \times 100$$

where:

sdev = standard deviation of the five RRs

$\overline{RR}$ = average relative response

Example Calculations for ICVs analyzed on June 15, 1998 using the SPB-Octyl column for 3,3',4,4'-TCB (PCB 77). Standard deviation of 0.086197448 with a mean RR of 0.92400000

$$\%RSD = \frac{0.086197448}{0.9240000} \times 100 = 9.3287$$

note: slight difference in %RSD due to rounding

C. For the isotopically labeled internal standards, were all %RSDs of the average RRs ≤20 percent if isotope dilution technique was used or ≤30 percent if internal standard technique was used? Yes

D. Was the absolute retention time of PCB 169 greater than 20 minutes on the SPB-Octyl column and the absolute retention time of PCB 157 greater than 25 minutes on the DB-1 column? Yes

6. Were all retention time criteria (as specified by the appropriate method) met? Yes

7. Were all ion abundance ratios (as specified by the appropriate method) within control limits? Yes.

COMMENTS

All criteria for acceptable instrument tuning and initial calibration were met. Sample results did not require qualification based on initial calibration. Ten percent of the data reported initial calibration data were verified during the data review.

ASSESSMENT OF CONTINUING CALIBRATION VERIFICATION (CCV)

1. Are CCV data present and analyzed at the appropriate frequency of within 12 hrs. of sample analysis? Yes

2. For analyses by LR GC/MS, were all of the percent differences (% D) of the RRFs compared to the average RRFs determined during the initial calibration less than 15 percent? Yes

Equation for Percent difference (%D), as an absolute value:

$$\%D = \left| \frac{\overline{RRF_{ical}} - RRF_{ccv}}{\overline{RRF_{ical}}} \right| \times 100$$

where:

$\overline{RRF_{ical}}$ = average relative response factor of analyte in initial calibration standard
RRF_{ccv} = relative response factor of analyte in associated CCV standard

2. For the target PCB congeners, were the concentrations found in the CCV analyses within the control limits specified by the method used? Yes, all concentrations reported for the CCVs were within the applicable concentration range of 75-125 percent.

The case narrative stated that the calibration verification acceptance criteria for analyses by HRGC/HRMS listed in Table 5 of Method 1668 are incorrect. The criteria appear to be based on concentrations in the precision and recovery (PAR) standard rather than n the concentrations in the calibration solutions. An interim acceptance criteria of 75-125 percent was used to assess the acceptability of the continuing verification standards.

3. Were all retention time criteria (within ±15 seconds of the retention times obtained during the calibration) met? Yes

4. Were all ion abundance ratios (as specified by the appropriate method) within control limits? Yes

5. Were all S/N ratios greater ≥10:1? Yes

COMMENTS

All criteria for acceptable continuing calibrations specified by the applicable methods were met. Sample results did not require qualification based continuing calibrations. Ten percent of the data reported initial calibration data were verified during the data review.

ASSESSMENT OF GC COLUMN PERFORMANCE AND RT WINDOWS

1. Are GC Column Performance and RT Window data present? Yes

2. Is resolution documentation present and acceptable? Yes

3. Were RT windows established and absolute RTs within ±15 seconds? Yes

4. Was the chromatographic resolution (i.e., valley height) between PCB isomers that most closely elute to PCB 126 and 169 <±25 percent? Yes

5. Was the valley height between PCBs 123 and 118 at m/z 325.8804 <10 percent on the SPB-Octyl column, and the valley height between PCBs 156 and 157 < 10 percent at m/z 359.8415 on the DB-1 column?

COMMENTS

All criteria for acceptable GC column performance and retention times were met. Sample results did not require qualification based on GC column performance and RT window data. Ten percent of the data reported for GC Column performance and RT windows were verified during the data review.

ASSESSMENT OF METHOD BLANKS

1. Were method blanks at the frequency 1 per 20 samples, or 1 per batch of <20 samples: Yes

2. Were results of all method blanks acceptable? Yes

If contamination is indicated, detected analytes may be reported as false positives. Use professional judgement to qualify any sample result. It is recommended that the 5x rule be used as an action limit (i.e., the concentration of any target analyte reported as detected in a sample must be ≤ 5 times the concentration present in the associated method blank) and applied for the presence of all PCB congeners. If the concentration of the affected analyte in the sample exceeds the action limit, sample results may need to be restated as undetected, qualified as estimated, or rejected.

3. Were all S/N ratios of all isotopically labeled standards ≥10:1? Yes

4. For analyses by LR GC/MS, were the recoveries of the isotopically labeled surrogate compounds within the control limits of 40-120 percent? Yes

5. For analyses by HRGC/HRMS, were the recoveries of the isotopically labeled surrogate compounds and recovery standards within control limits specified by the method? Yes

6. Were all ion abundance ratios (as specified by the appropriate method) within control limits? Yes

COMMENTS

1. All criteria were met for acceptable method blank analyses as specified by the methods. Sample results did not require qualification based method blanks.

2. For analyses by low resolution GC/MS, no PCB congeners were detected in any method blank (i.e., procedural blank, a filter blank, an aqueous equipment [Virtis] proof blank associated with either the soil/sediment samples or the tissue samples. The Virtis proof blank is a blank processed through the Virtis blender used to homogenize the tissue samples.

3. For analyses by soil samples by HRGC/HRMS some target analytes were detected, as summarized below:

Lab blank (filter paper, Lab ID CL-F-Blank 1378) associated with soil/sediment samples:

PCB 118 at 31.6 pg

Lab blank (filter paper, Lab ID CLS-BLK 1375) associated with soil/sediment samples

PCB 118 at 3.48 ng/kg
PCB 167 at 3.48 ng/kg
PCB 156/157 at 8.26 ng/kg
PCB 180 at 3.71 ng/kg

The concentrations of the PCBs detected in the method blanks did not require the qualification of any sample results because the affected PCBs were present in the natural samples at concentrations significantly above the concentrations found in the blanks.

4. For analyses by tissue samples by HRGC/HRMS some target analytes were detected, as summarized below:

Lab blank (tissue, Lab ID CL-T-1377):

PCB 118 at 69.0 ng/kg
PCB 105 at 29.8 ng/kg
PCB 167 at 3.64 ng/kg
PCB 157 at 21.4 ng/kg (DB-1 column)

Lab blank (solid, Lab ID CL-S-1375):

PCB 77 at 8.93.0 ng/kg

The concentrations of the PCBs detected in the method blanks did not require the qualification of any sample results because the affected PCBs were present in the natural samples at concentrations significantly above the concentrations found in the blanks.

Note, the bias of LCS measurements is calculated as the ratio of the measured concentration to the known concentration added.

Equation for LCS Recovery:

$$\text{Percent Recovery} = \frac{\text{measured concentration}}{\text{known concentration}} \times 100$$

1. Were the recoveries of all LCS analyses acceptable? Yes

A. For analyses by LR GC/MS analyses, acceptable recoveries must meet the control limit of 70-120 percent. For this data set, the LCS was completed using the NIST 1588 standard reference material (cod liver oil) for 9 PCB congeners. Recoveries ranged from 87 percent to 105 percent and met the project-specific DQO of 70-120 percent recovery. Sample results did not require qualification based on LCS results.

B: For analyses by HRGC/HRMS, the concentrations of the ongoing precision and recovery (OPR) standards must be within the limits specified by the analytical method. The OPR is considered as the LCS, as specified by EPA Method 1668. The OPR is a laboratory blank spiked with known concentrations of target analytes. The OPR is processed and analyzed exactly like the samples to assess the adequacy of laboratory performance in the absence of potential matrix effects/interferences. Sample results did not require qualification based on OPR results.

3. For analyses by HRGC/HRMS, were the concentrations of the ongoing precision and recovery (OPR) standards within the limits specified by the analytical method? Yes

4. Were all S/N ratios of all isotopically labeled standards ≥10:1? Yes

5. For analyses by LR GC/MS, were the recoveries of the isotopically labeled surrogate compounds within the control limits of 40-120 percent? Yes

6. For analyses by HRGC/HRMS, were the recoveries of the isotopically labeled surrogate compounds and recovery standards within control limits specified by the method? Yes

7. Were all ion abundance ratios (as specified by the appropriate method) within control limits? Yes

COMMENTS

All criteria for acceptable analysis of LCS and OPR samples were met.

ASSESSMENT OF MATRIX SPIKE RECOVERIES

Note, the bias of matrix spike measurements is calculated as the ratio of the measured quantity to the known quantity added

Equation for Matrix Spike Recovery:

$$\text{Percent Recovery} = \frac{\text{measured concentration}}{\text{known concentration}} \times 100$$

1. Were the recoveries for all matrix spikes within the project-specified control limits of 70-120 percent? Yes, with the exceptions noted below.

For analyses by LR GC/MS associated with the soil/sediment samples, a reference soil was used for the spike. Recoveries ranged from 94 percent to 121 percent for 12 PCB congeners and met the control limit of 70-120 percent recovery, with one exception. The 121 percent recovery (reported for PCB180) was above the upper control limit of 120 percent. No sample results were qualified because this exceedance was only slightly above the upper control limit. However, sample results could exhibit a slight positive bias for this PCB congener.

Example Calculation for PCB 180 (page 000104 in SDG); recovery of 121 percent reported:

$$\text{Percent recovery} = \frac{5.8\ \text{ng/g}}{4.8\ \text{ng/g}} \times 100 = 120.8$$

For analyses by HRGC/HRMS,

2. For analyses by LR GC/MS, were the recoveries of the isotopically labeled surrogate compounds within the control limits of 40-120 percent? Yes

3. Were all S/N ratios of all isotopically labeled standards ≥10:1? Yes, as applicable.

4. For analyses by HRGC/HRMS, were the recoveries of the isotopically labeled surrogate compounds and recovery standards within control limits specified by the method? Yes

5. Were all ion abundance ratios (as specified by the appropriate method) within control limits? Yes

COMMENTS

1. For analyses completed using LR GC/MS, the matrix spike was completed using a mixture of Aroclor® 1242, Aroclor® 1254, and Aroclor® 1260 for a PCB congener concentration of between 0.01 ng/g to 0.03 ng/g.

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2. Matrix spike recoveries ranged from 68 percent to 93 percent for low resolution GC/MS PCB congener analyses. The one recovery of 68 percent (for PCB 31/28) is slightly below the lower control limit of 70 percent. No data required qualification because concentration of PCB 31/28 in the natural sample was at a much greater concentration (180 ng/g) than the amount spiked (7.6 ng/kg) in to the sample. Sample results did not require qualification based on the matrix spike results.

3. For the HRGC/HRMS PCB congener analyses, matrix spikes were not conducted by the laboratory nor are they are required by the analytical method. The lack of matrix spike data does not affect the overall quality of the data set because the analytical method is an isotope dilution technique, and as such each sample is essentially a "matrix spike" (i.e., isotopically labeled surrogate compounds and internal standards are added to each sample).

ASSESSMENT OF DUPLICATE SAMPLE ANALYSES

Note. the precision of results reported for duplicate analyses is calculated as the relative percent difference (RPD) as an absolute value between the two reported results

Equation for RPD:

$$RPD = \pm \frac{abs[D_1 - D_2]}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = sample value
D_2 = duplicate sample value.

2. Were the relative percent differences (RPDs) for all target analytes reported as detected within the project-specific control limit of ±50 RPD? Yes

A. For analyses by LR GC/MS, the RPDs of all target analytes detected in both duplicate sample analyses were less than the ±50 RPD control limit. The soil/sediment Sample SRSS08FPR6 and the tissue Sample SREW09FPR7 were analyzed in duplicate. The RPD results were calculated during the data review and entered on the hardcopy summary of results in the LR GC/MS data package.

Example Calculation for Results Reported for PCB 107 (310 ng/g and 290 ng/g) for the LR

$$RPD = \pm \frac{abs[310 - 290]}{(310 + 290)/2} \times 100 = 6.7$$

GC/MS duplicate analysis of SRSS08FPR6:

B. For analyses by HRGC/HRMS, the soil/sediment Sample SRSS06FPR5 and the tissue Sample SREW01REFL were analyzed in duplicate. The RPD results were calculated during the data review and entered on the hardcopy summary of results in the HRGC/HRMS data package. The RPDs of all target analytes detected in the duplicate sample analyses were less than the ±50 RPD control limit, with two exceptions.

An RPD of 89 percent (concentrations of 6.73 ng/kg and 2.57 ng/kg, with a detection limit of 0.82 ng/kg for the first sample and 2.12 ng/kg for the duplicate sample) was calculated for PCB 77 for the duplicate analyses completed on the tissue sample SREW01REFL. For the analysis of this sample using the DB-1 column, an RPD of 56.6 percent (concentrations of 4.42 ng/kg and 2.47 ng/kg, with a detection limit of 1.26 ng/kg for the first sample and 1.55 ng/kg for the duplicate sample).

No action was taken for this exceedance because the duplicate sample results were only slightly above the detection of 2.12 ng/kg for the duplicate analyses of Sample SRSS06FPR. Because the concentration of PCB 77 in the duplicate sample analysis was so near the detection limit, there is a much greater degree of uncertainty associated with this result. It should be noted, however, results reported for PCB 77 may exhibit a positive or negative bias.

Example Calculation for Results Reported for PCB 77 (6.73 ng/kg and 2.57 ng/kg) for the

$$RPD = \pm \frac{abs[6.73 - 2.57]}{(6.73 + 2.57)/2} \times 100 = 89.46$$

HRGC/HRMS duplicate analysis of SREW01REFL:

COMMENTS

The results reported for the duplicate sample analyses and the resulting RPDs calculated during the data review are considered as acceptable. Although a few RPDs were above the DQO of ±50 percent, no action was taken as discussed above.

1. Are all sample data (e.g., chromatograms, mass spectra, SICPs, and/or instrument printouts present for all samples? Yes

2. For analyses by LR GC/MS, were the recoveries of the isotopically labeled surrogate compounds within the control limits of 40-120 percent? Yes

3. For analyses by HRGC/HRMS, were the recoveries of the isotopically labeled surrogate compounds and recovery standards within control limits specified by the method? Yes

4. Were all ion abundance ratios (as specified by the appropriate method) within control limits? Yes.

The case narrative for analyses by HRGC/HRMS stated that following EPA Method 1668 protocols, where observed peaks failed the ion abundance ratio or other qualitative identification criteria the congener was reported as not detected. This convention could result in the reporting of a congener as a false negative, especially at very low concentrations. In instances where the ion abundance ratio was out based on the use of peak area, the ion ratio was recalculated using peak height. If this ion ration based on peak height was acceptable and all other criteria for identification were met, the congener was reported as detected. This approach is considered as acceptable and no action was required during the data review.

5. Were all criteria for compound identification (as specified by the appropriate method) met? Yes, based on 10 percent verification

The case narrative for analyses by HRGC/HRMS stated the relative retention time (RRT) of ^{13}C-PCB 77 (the isotopically labeled standard) was consistently lower than the lower control limit established. It is the opinion of this reviewer that although the RRT was low for this compound, it was consistent. Review of selected instrument printouts showed the characteristic ions were always present. Because the RRT was consistent and the ions were always present, no action was taken.

6. Were all quantifications (as specified by the appropriate method) correctly performed? Yes, based on 10 percent verification

A. Equation for Analyses by LR GC/MS (corrected for surrogate recovery):

$$\text{Concentration of solid samples (ug/kg, dry wt. basis)} = \frac{A_s \times C_{is} \times V_{ext} \times D}{A_{is} \times \overline{RRF} \times V_i \times W_s}$$

where:

A_s = area (or height) of characteristic ion of target analyte in sample
C_{is} = concentration of characteristic internal standard (ng)
V_{ext} = volume of final extract (μL)
D = dilution factor, if required; if no dilution, then D = 1
A_{is} = area (or height) of characteristic ion of characteristic internal standard

$\overline{RRF}$ = average relative response factor for target analyte from applicable calibration
V_i = volume of extract injected (μL)

W_s = sample volume extracted (grams, dry weight basis)

NOTE: Other types of calculations (e.g., use of different concentration units) may be substituted so long as all factors affecting the final concentration reported are accounted for in the equation.

B. Equations for Analyses by HRGC/HRMS

1. Concentration of PCB in Extract (recovery corrected):

$$C_{ex}(ng/mL) = \frac{(A1_s + A2_s)\,C_i}{(A1_{is} + A2_{is})\,RR}$$

where:

C_{ex} = The concentration of the PCB in the extract
$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the PCB
C_i = T he concentration of the labeled compound in the calibration standard
$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard
RR = relative response (labeled to native) vs. concentration in standard solutions
m/z's = mass-to-charge ratio

2. Concentration of PCB in Solid Sample:

$$\text{Concentration in Solid (ng/g)} = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:

C_{ex} = The concentration of the PCB in the extract
V_{ex} = The volume of the extract in mL
W_s = Sample weight (dry wt. for soil/sediment and wet weight for tissue) in kg

NOTE: Other types of calculations (e.g., use of different concentration units) may be substituted so long as all factors affecting the final concentration reported are accounted for in the equation.

7. Were either method-specific or the project-specific DQO for detection limits met? In general, yes. Elevated detection limits were reported in several instances because either smaller sample volumes, dilutions, or both were required to complete the analyses due to high concentrations of the target analytes in the samples.

Note, project-specific detection limit goals are:

0.1 pg/g (dry wt) for soil/sediment using LR GC/MS for PCB congeners
0.2-1.5 pg/g (dry wt.) for soil/sediment using HRGC/HRMS for toxic PCB congeners
0.1 pg/g (wet wt.) for tissue using LR GC/MS for PCB congeners
0.1 ng/g (wet wt.) for tissue using HRGC/HRMS for toxic PCB congeners

The laboratory completed a method detection limit study as described in Appendix B of 40 CFR Part 136 on the October 26, 1984 Federal Register. The method detection limits were calculated using a Student's t-value for six degrees of freedom and a 99 percent confidence level. The method detection limits (in ng/g) were based on a 10 gram volume. The calculated method detection limits for 32 PCB congeners (including co-eluting congeners) ranged from 0.02 ng/g to 0.15 ng/g (see page 000008 in SDG for LR GC/MS analyses).

COMMENTS

1. All results reported by the laboratory for undetected and detected PCB congeners were acceptable. The results were recovery corrected based on the recoveries of the surrogate compounds added prior to extraction.

2. Results for sediment samples were reported on a dry weight basis and results for tissue samples were reported on a wet weight basis. In addition, percent moisture determinations were completed for all sediment samples and percent lipid determinations were completed for all tissue samples.

3. In some instances results reported by LR GC/MS PCB congener analyses were flagged 'NDR' to indicate that the ion ratios failed criteria. None of these results were additionally qualified during the data review because other identification criteria (e.g., retention times, presence of the appropriate ions) were met

4. For analyses by HRGC/HRMS, concentrations of some of the target analytes were present at concentrations significantly above the linear range of the calibration range and required dilutions. In addition, in other instances, if the concentrations were extremely large the results were reported for analyses completed using the LR GC/MS.

5. For analyses by LR GC/MS, a final extract volume of 100 μL was used prior to any dilutions that may have been required, with a few exceptions. Due to limited sample amounts for extraction, a final extract volume of 30 μL was used for Sample SREW06FPR5, Sample SREW01REFL, and an associated procedural blank. The smaller extract volume was used to achieve lower detection limits. In addition, a final extract volume of 300 μL was used to complete the analysis of Sample SRSS08FPR6 due to high concentrations of some PCB congeners. Some samples required dilutions or re-extractions using smaller sample sized due to high levels of the target analytes in the samples.

For analyses by HRGC/HRMS, a final extract volume of 20 μL was used prior to any dilutions that may have been required. Some samples required dilutions or re-extractions using smaller sample sized due to high levels of the target analytes in the samples.

6. Based on pre-screen analyses, samples sizes were estimated to optimize the quantification of the data for analyses by HRGC/HRMS. Because many PCB congeners appeared to be present at very high concentrations action was required. The case narrative states that it was agreed between an EVS representative and Axys the higher level PCB congeners would be reported from the LR GC/MS analyses to avoid multiple dilutions. The proposed sample sizes, anticipated detection limits, and strategy were discussed with EVS and approval to proceed was granted.

Field Duplicates

For field duplicates, compare the results reported for each sample, and recalculate the relative percent difference (RPD). Project DQO for precision is ±50 percent. If gross variation between duplicate results is identified, use professional judgement to assess the impact of the variation and apply qualifiers as necessary.

Precision for duplicate chemical analyses will be calculated as the relative percent difference (RPD):

$$RPD = \pm \frac{abs[D_1 - D_2]}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = sample value
D_2 = duplicate sample value.

Field Blanks

If contamination is indicated, detected analytes may be reported as false positives. Use professional judgement to qualify any sample result. There are no clear validation guidelines for assessing field quality control results.

COMMENTS

1. No field duplicate samples were known to this data reviewer.

2. For analyses by HRGC/HRMS, the field blanks associated with the soil/sediment samples included a cross contamination consisting of an ashless piece of filter paper that was used to wipe the sampling processing equipment after is has undergone decontamination procedures. The other field blank consisted of filter blanks, used in conjunction with the cross contamination blanks to assist if verifying if any target analyte that may be found in the cross contamination blank was due to insufficient decontamination procedures or poor field technique.

The PCBs detected in the field blanks are summarized below.

1. Cross Contamination Blank (filter, Lab ID 9805-21):

   PCB 77 at 1,530 pg
   PCB 123 at 286 pg
   PCB 118 at 10,000 pg
   PCB 114 at 702 pg
   PCB 105 at 6,500 pg
   PCB 126 at 46.9 pg
   PCB 167 at 302 pg
   PCB 156/157 at 1,230pg
   PCB 156 at 1,064 (DB-1)
   PCB 157 at 208 pg (DB-1)
   PCB 169 undetected
   PCB 180 at 872 pg
   PCB 179 at 544 pg
   PCB 189 at 33.8 pg

2. Filter blank (unused filter paper, Lab ID 9805-22):
   PCB 118 at 48.4 pg
   PCB 105 at 22.8 pg

No action was taken based on the detection of PCBs in the field blanks because these results could not be normalized to concentration units of ng/kg since the weight of the filters were not provided. It should be noted, however, there appears to be significant contamination based on the results reported for the cross contamination filter blank suggesting the associated results reported as detected for the affected PCBs in the natural samples may exhibit a positive bias or be reported as a false positive. Interpretation as to the impact of the field blank contamination on the sample results should be made by the data users. In terms of the data review, the results reported by the laboratory appear to be correct.

ASSESSMENT OF SUPPLEMENTAL INFORMATION

Analyses were completed for total solids (percent moisture) and total organic carbon (TOC) for soil/samples and percent lipids for tissue samples. Analytical Resources, Inc. (Seattle, WA.) completed total solids and TOC determinations. Axys Analytical Services, Ltd. (Sidney, British Columbia, Canada) completed total solids and percent lipids determinations. All results reported for these parameters are considered as acceptable as reported by the laboratory. All quality control measurements associated with these analyses are acceptable, except as note below.

For the TOC analyses, a recovery of 57.8 percent was reported for the matrix spike and a recovery of 121 percent was reported for the matrix spike duplicate, resulting in an RPD of 71 percent. The matrix spike recoveries did not meet the specified control limit of 80-120 percent nor the RPD requirement of ±20 percent. No sample results were qualified for these exceedances because sample results are not qualified solely based on matrix spike results. Since the recovery of TOC in the LCS and standard reference material sample analyses were in control, suggesting a sample homogeneity issue. In addition, it is the opinion of the reviewer that control limits are too tight for soil/sediment samples. It is more common for a control limit of 50-150 percent be used for accuracy and ±50 percent be used for precision.

ASSESSMENTOF SYSTEM PERFORMANCE

There are no specific criteria for system performance. Professional judgement should be used to assess the system performance. Discuss any analytical factors that may have been noted during data validation that may have had an affect on the analytical system that could result in the degradation of the quality of the data).

There were no signs of poor instrument performance identified during the data quality assessment that would appear to affect the overall quality of the data.

OVERALL ASSESSMENT

The results reported by the laboratory are considered as acceptable. No results were qualified or rejected during the quality assurance review; however, there were instances during the analysis of the samples that suggest selected sample results may exhibit a positive or negative bias. All information related to this uncertainty is discussed in the sections of the data review summary.

All work recorded herein has been completed in accordance with normal professional standards using accepted validation techniques and QA/QC procedures, except where otherwise requested by the client. All analytical data were validated in accordance with applicable guidance specified by either *Draft EPA Method 1668 (October 4, 1995)*, laboratory-specific SOPs; analytical method–specific quality control criteria; or, in the context of the data quality objectives established by the client for this project.

All information contained within this data review summary is intended to be used in its entirety and QA/QC Solutions is not responsible for use of less than the complete data review summary. There is no other warranty expressed or implied.

Respectfully Submitted by QA/QC Solutions:

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August 2, 1998