ATTACHMENT E

A Preliminary Evaluation of the Application of USEPA's National Bioaccumulation Methodology in the Derivation of Human Health-Based Surface Water Quality Criteria for Florida

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Florida Pulp & Paper Association
Environmental Affairs

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EVALUATION OF BAF METHODOLOGY

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CONTENTS

Acronyms and Abbreviations i

Executive Summary 1

Introduction 1

Background: Derivation of Surface Water Quality Criteria for Protection of Human Health 2

FDEP's Derivation of BCFs and BAFs for Florida Surface Waters 3

Review of the Florida BAF for BaP 8

Applicability of National FCMs to Florida Surface Waters and Food Webs 11

Sediment-Water Concentration Quotient 11

Chemical Concentrations in Sediment and Water Column 12

Organic Content of Water 12

Rate of Metabolism in Forage and Piscivorous Fish 12

Additional Environmental Parameters and Conditions 13

Food Web Structure 13

Summary 14

References 14

TABLES

1. Comparison of Florida BAFs and National BAFs and Derivation Methods
2. Geometric Mean of Original and Corrected Baseline BAF Values (L/kg-lipid)
3. Geometric Mean of Original and Corrected Final BAF Values (L/kg-tissue)
4. Comparsison of Gobas Speadsheet Results and USEPA Published Values
5. Sensitivity of Various Gobas Model Parameters With Respect to Calculated Food Chain Multipliers
6. Comparison of FCMs and BAFs Calculated With and Without Metabolism
7. Lake Ontario Based Food Web Model Used to Derive National Food Chain Multipliers Adopted by FDEP
8. Hypothetical Florida-Based Food Web Model Parameters
9. Comparison of FCMs Calculated With Great Lakes and Hypothetical Florida Food Web Parameters

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ACRONYMS AND ABBREVIATIONS

AWQC	ambient water quality criteria
BAF	bioaccumulation factor
BaP	benzo(a)pyrene
BCF	bioconcentration factor
BSAF	biota-sediment accumulation factor
Cwfd	concentration of chemical freely dissolved in the water column
DOC	dissolved organic carbon
DOM	dissolved organic matter
FCM	food chain multiplier
FDEP	Florida Department of Environmental Protection
f_{fd}	fraction of total concentration freely dissolved
f_l	fraction of tissue that is lipid
HHC	human health-based criteria
HHWQC	Human Health Water Quality Criteria
Π_{socw}	sediment-water concentration quotient
k_d	dietary uptake rate constant
k_m	metabolic transformation rate constant
K_{ow}	n-octanol-water partition coefficient
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyls
POC	particulate organic carbon
SWQC	surface water quality criterion
TL	trophic level
USEPA	United States Environmental Protection Agency

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EXECUTIVE SUMMARY

This white paper presents preliminary findings of a review and evaluation of the methods used by the Florida Department of Environmental Protection (FDEP) to estimate bioaccumulation of compounds from Florida surface waters into fish and shellfish consumed by Floridians. The estimation of such bioaccumulation is a key component in developing the human health-based surface water quality criteria (HHC) proposed by FDEP in May 2016. FDEP relied primarily, with exceptions noted in the white paper, on the methods and models developed and used by United States Environmental Protection Agency (USEPA) to derive the national 2015 Human Health Water Quality Criteria (HHWQC).

It is important to understand that USEPA has an expressed preference for developing HHC based on bioaccumulation factors (BAFs) rather than bioconcentration factors (BCFs) because BAFs account for exposure of fish and shellfish from all exposure pathways (e.g., water, diet, sediment) while BCFs account for exposure from only water. When measured BAFs are available USEPA's procedure uses those to estimate bioaccumulation. When measured BAFs are not available USEPA estimates BAFs by multiplying either measured or modeled BCFs by a food chain multiplier (FCM). The FCM is intended to account for exposure of fish and shellfish from the non-water exposure pathways.

This white paper focuses on two aspects of USEPA's procedure as it was used by FDEP. The first is the process and data used to develop measured BCFs for compounds that do not have field measured BAFs. This white paper uses an example compound and focuses on the process and data used to estimate the BCF for benzo(a)pyrene (BaP) a polycyclic aromatic hydrocarbon (PAH) that is used as a surrogate by USEPA and FDEP to estimate the bioaccumulation of six other PAHs. The second aspect of USEPA's process addressed in this white paper is the applicability of national FCMs to surface waters in Florida. The FCMs used by USEPA (and FDEP) are based on a model developed to estimate bioaccumulation of compounds in a food web representative of the Great Lakes. This white paper examines some of the assumptions used by USEPA to characterize surface water and food webs in the Great Lakes and compares them to surface waters and food webs in Florida to determine the applicability of the FCMs to Florida surface waters.

Review of the approach used by USEPA (and FDEP) to develop the BAF for BaP identified three key concerns that affect the final BAF (or in the case of FDEP, the BCF) used to derive the proposed HHC.

- The USEPA database includes three invertebrate species that are not representative of shellfish consumed by Floridians (i.e., the water flea (*Daphnia magna*), an amphipod (*Pontoporeia hoyi)*, and a mayfly (*Hexagenia limbata*). Whether the accumulation of BaP in typically consumed shellfish is well represented by BCFs from amphipods, mayflies and water fleas is unknown. What is known is that these three organisms are very different from those that are regularly consumed. Until it has been shown that their BCFs are representative of regularly consumed species, it might be best to exclude them when estimating the BCFs of regularly consumed shellfish species. Excluding these three species causes the final BCF for BaP to increase.
- USEPA's (and FDEP's) BAF derivation process includes establishing something USEPA refers to as a baseline BAF. A baseline BAF is expressed on a 100% lipid basis and assumes that all of a compound is dissolved in water (i.e., none of the compound in the water column is bound to organic carbon, so all of the compound is available to be accumulated). Most studies reporting

ED_002388_00000424-00006

BCFs do not provide information on the fraction of BaP dissolved in the water column versus the fraction sorbed to organic carbon suspended in the water column. To estimate the fraction of BaP dissolved in the water column USEPA needed to make assumptions about how much organic carbon was present in the experiments reporting BCFs. USEPA assumed all of those experiments had organic carbon equal to the median measured in U.S. surface waters. However two thirds of the BaP BCF studies used filtered water. Such water will likely have a much lower organic carbon concentration than that assumed by USEPA. When an organic carbon concentration more representative of filtered water is used to derive baseline BAFs, the baseline BAF for BaP decreases by about 40%.

- For compounds that do not have measured BAFs, a key step of USEPA's process for deriving a baseline BAF is multiplying a BCF by a FCM. USEPA's guidance lists certain characteristics of a compound that preclude the application of a FCM. One of those characteristics is "high metabolism" which is how USEPA classified BaP. Thus, USEPA should not have multiplied the BaP BCFs by FCMs to derive a baseline BAF. FDEP recognized this incorrect application of a FCM and did not apply a FCM to the BCF of BaP when developing the proposed HHC. The effect of not including the FCM is substantial, baseline BAFs decrease by several-fold.

When all of the above factors are accounted for, the Florida-specific BAF for BaP becomes 484 kilograms per liter (L/kg); lower than the BAF of 600 L/kg used by FDEP in the proposed HHC and lower than USEPA's national BAF for BaP of 3,900 L/kg.

Review of the applicability of national FCMs to Florida surface waters and food webs revealed numerous reasons to believe the national default assumptions used by USEPA to derive national FCMs are unlikely to be representative of Florida conditions.

- The model used by USEPA to derived national FCMs is based on and calibrated for a Great Lakes food web using PCB data. A Florida based food web will have substantially different inputs and structure and could result in a very different FCMs. For example Florida waters do not support alewives, smelt or salmonids and the lipid content of many fresh water species appears to be lower in Florida than in the Great Lakes. At this point it is unknown whether food webs more representative of Florida surface waters will have higher or lower FCMs than those derived for the Great Lakes but the components and structure will clearly be very different.
- USEPA's model assumes that surface waters have had a long history of loading of compounds followed by a relatively recent reduction in such loading (such as PCBs in the Great Lakes and Hudson River in the 1980's and 1990's). That scenario of high historic loading leads to a high proportion of a compound in sediments compared to conditions closer to equilibrium. The effect of that high proportion of a compound in sediments is to increase FCMs. FCMs decrease substantially when compound loadings expected to be representative of most waters in the U.S. and Florida are employed in the FCM model.
- The FCMs developed by USEPA assume no metabolic transformation of a compound by fish and shellfish. Yet USEPA (and FDEP) are using the FCMs developed using the assumption of no metabolic transformation to derive HHC for many compounds that are likely to be metabolized to some degree by fish or shellfish or both. The potential effect on FCMs of incorporating metabolism was investigated for pentachlorophenol, heptachlor, and 1,3-dichlorobenzene. When

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the compound-specific metabolic transformation rate constants were incorporated into the FCM model, the FCMs dropped substantially for all three chemicals.

- Finally, the temperature used in the USEPA model is much cooler than might be expected in Florida waters. Use of a higher temperature in the FCM model increases FCMs because the higher temperature results in an increase in dietary intake in the model. Because the model assumes no metabolic transformation, the increased dietary intake is not balanced by what one might expect to be an increased rate of metabolic transformation as temperature increases.

In summary, the preliminary evaluations presented in this white paper provide several lines of strong evidence that the application of USEPA's national BAF procedure to estimate bioaccumulation in Florida surface waters is premature and does not represent good science. Additional evaluation is necessary to identify those aspects of USEPA's national BAF methodology that are applicable to Florida and those that need Florida-specific modification before they can be used to derive human health-based criteria for Florida surface waters. While the preliminary evaluation of some of the individual parameters of the FCM model suggest that BAFs in Florida may be lower than estimated by USEPA for the Great Lakes, the combined effect of all such modifications, and whether those will lead to higher or lower estimates of bioaccumulation, is unknown at this time.

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Introduction

To estimate the bioaccumulation of substances from surface water into fish and shellfish the Florida Department of Environmental Protection (FDEP) relied primarily, with exceptions as noted below, on the methods and models developed and used by United States Environmental Protection Agency (USEPA) to derive the national 2015 Human Health Water Quality Criteria (HHWQC) and as further explained by USEPA in their January 2016 supplemental information for development of national bioaccumulation factors (USEPA 2016). See Table 1 for a comparison of Florida and National bioaccumulation factors (BAFs).

USEPA's process has an expressed preference for basing HHWQC on BAFs rather than bioconcentration factors (BCFs) because BAFs account for exposure of fish and shellfish from all exposure pathways (e.g., water, diet, sediment) while BCFs account for exposure from only water. When measured BAFs are available USEPA's procedure uses those to estimate bioaccumulation. When measured BAFs are not available USEPA estimates BAFs by multiplying either measured or modeled BCFs by a food chain multiplier (FCM). The FCM is intended to account for exposure of fish and shellfish from the non-water exposure pathways. Exceptions to this process include inorganic compounds that are not expected to biomagnify, ionized organic compounds, organic compounds with log K_{ow} of less than 4, and organic compounds that are highly metabolized. For compounds that fall into either of these four categories USEPA's procedure suggests using a field measured BAF and if such is not available, a laboratory derived BCF.

This white paper focuses on two aspects of USEPA's procedure as it was used by FDEP to estimate bioaccumulation of substances from Florida surface waters into fish and shellfish. The first is the process and data used to develop measured BCFs for compounds that do not have field measured BAFs. Measured BCFs are used to estimate accumulation of 20 of 88 compounds for which revised HHC are proposed. This white paper focuses on the process and data used to estimate the BCF for benzo(a)pyrene (BaP) a polycyclic aromatic hydrocarbon (PAH) that is used as a surrogate to estimate the bioaccumulation of six other PAHs (benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene). Whether the comments presented below for the derivation of the BCF for BaP apply to all the other compounds for which measured BCFs are used is not known; what is known is that they do apply to a total of seven PAHs, which represents slightly more than a third of the compounds for which measured BCFs were used.

The second aspect of USEPA's process to estimate bioaccumulation that is addressed in this white paper is the applicability of the FCMs to surface waters in Florida. A FCM is used by FDEP to estimate the accumulation of 60 of 88 compounds for which revised HHWQC are proposed. The FCMs used by USEPA (and FDEP) to adjust BCFs to account for exposures other than water, are based on a model adopted by USEPA in 1993 (Gobas 1993). That model was developed to estimate bioaccumulation of compounds such as polychlorinated biphenyls (PCBs) in a food web representative of the Great Lakes. This white paper examines some of the assumptions used by USEPA to characterize surface water and food webs in the Great Lakes and compares them to surface waters and food webs in Florida to determine the applicability of the FCMs to Florida surface waters. For some model parameters, the white paper also presents a sensitivity analysis demonstrating whether FCMs specific to Florida surface waters

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would be different (either higher or lower) from Great Lakes-based FCMs. The sensitivity analysis does not address all parameters used in the Great Lakes FCM model. Thus, it remains unknown whether FCMs based on a model that truly represents Florida surface waters and food webs, would be higher or lower than the FMCs used to derive the currently proposed HHWQC.

Background: Derivation of Surface Water Quality Criteria for Protection of Human Health

FDEP used USEPA guidance (USEPA 2000) to derive surface water quality criteria (FDEP 2016). The equation for non-carcinogenic compounds for consumption of water and organisms is as follows:

$$SWQC(\mu g/L) = \frac{\left[RfD\left(\frac{mg}{kg \cdot d}\right) \times RSC\right] \times BW\,(kg) \times 1{,}000\,(\mu g/mg)}{DI\,(L/d) + \Sigma_{i=2}^{4}\left[FCR_i\left(\frac{kg}{d}\right) \times BAF_i\left(\frac{L}{kg}\right)\right]}$$

Where:

SWQC = surface water quality criterion (µg/L);

RfD = compound-specific reference dose (mg/kg-d);

RSC = Relative source contribution factor to account for non-water sources of exposure (not used for linear carcinogens);

BW = body weight (kg);

DI = drinking water intake (L/d);

FCR_i = fish consumption rate for aquatic trophic levels (TLs) 2, 3, and 4 (kg/day);

BAF_i = bioaccumulation factor for aquatic TLs 2, 3, and 4 (L/kg); and

$\Sigma^4_{i=2}$ = summation of values for aquatic TLs, where the letter i stands for the TLs to be considered, starting with TL2 and proceeding to TL4.

For carcinogenic compounds, the reference dose term in the denominator is replaced by [Target Risk/CSF (mg/kg-d)] where:

CSF = Cancer slope factor (mg/kg-d); and

Target Risk = Allowable incremental life-time increased cancer risk (usually either $1x10^{-6}$ of $1x10^{-5}$).

For SWQC developed to protect human health from exposures associated with consumption of organisms only, the drinking water intake term is removed from the equation.

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FDEP used a probabilistic approach (Monte Carlo simulation) to solve these equations and calculate HHC[1]. This was accomplished by specifying a distribution for some of the parameters (e.g. body weight, fish consumption rate, drinking water rate) rather than using a point estimate for that parameter, randomly choosing from that distribution and solving the equation in multiple iterations to ensure that specific segments of the population are protected at specified target risk levels. Other parameters were characterized using point estimates (e.g. bioaccumulation factors, reference doses, cancer slope factors, relative source contribution (RSC)). The general categories of parameters are summarized briefly below.

Toxicity Parameters – FDEP used values from the IRIS database and alternative sources for reference doses and cancer slope factors similar to the approach used by USEPA in the calculation of their 2015 HHWQC. These were entered as point estimates in the equations. FDEP used a default value of 0.2 for the RSC.

Exposure Parameters – FDEP developed state specific probability distributions for exposure parameters for the probabilistic approach. The distributions for drinking water intake and body weight are based on national recommendations from the 2011 USEPA Exposure Factors Handbook. The fish consumption rate (FCR) distribution is based on USEPA's 2014 Estimated Fish Consumption Rates for the U.S. Population and Selected Subpopulations. FDEP created FCR distributions for the probabilistic analysis based on the geographic regions representative of Florida, Atlantic Coast, Gulf Coast, and Inland South.

Bioaccumulation Parameters – In general, FDEP's approach followed the methodology described by USEPA (2003) but used Florida-specific values for lipid content of fish species and organic carbon content in surface waters. Other critical parameters used in the BAF calculations, particularly food chain multipliers (FCMs), were not Florida-specific and were based on the national default values. The final calculated BAFs were entered as point estimates in the HHC equations. A detailed analysis of the methodology used by FDEP to calculate BAFs is described below and includes a comparison of Florida-specific and National BAFs.

FDEP's Derivation of BCFs and BAFs for Florida Surface Waters

In general FDEP followed the USEPA methodology to derive BCFs/BAFs for use in WQC calculations (USEPA, 2000, 2003, 2016) and used the same methods and the same studies to derive BCFs/BAFs as USEPA. For most compounds[2] the methodology involves estimating a baseline BAF (i.e. a BAF based on the dissolved fraction and adjusted for lipid concentration) based on field or laboratory studies if available. If field or laboratory studies are not available, the baseline BAF is estimated from a compound's n-octanol-water partition coefficient. The baseline BAFs are averaged by species and trophic level (geometric mean) and a food chain multiplier (FCM) is applied to each trophic level for chemicals classified as non-metabolized. With the exception of PAHs, FDEP used the baseline BAFs provided in the supplemental information provided by USEPA (USEPA, 2016). The baseline BAFs were then converted to Florida BAFs using state specific assumptions about the concentration of dissolved organic carbon (DOC) and particulate organic carbon (POC) is surface water, parameters used to calculate the freely

[1] The May 2016 FDEP technical support document refers to the proposed criteria as HHC. These are the same as the SWQC referred to in the formula above. USEPA refers to such criteria as ambient water quality criteria (AWQC). Such criteria have also been referred to as HHWQC. Depending upon citation, all of these terms may appear in this white paper and refer to surface water quality criteria for protection of human health.
[2] BCFs and not BAFs were developed and used to derive the proposed HHC for some compounds.

ED_002388_00000424-00011

dissolved fraction in Florida waters, and Florida-specific assumptions for the lipid content in each trophic level. FDEP assumed lipid contents of 1.8%, 1.5% and 2% for TL2, TL3 and TL4 respectively. For PAHs, FDEP determined that USEPA (2015a) failed to correctly account for high metabolic transformation rates. Specifically, USEPA calculated the BAFs for 12 PAHs by multiplying laboratory BCFs by FCMs. FDEP noted that this is not consistent with USEPA guidance for highly metabolized compounds and therefore they recalculated the baseline BAFs for 12 PAHs based on the laboratory BCF results provided by USEPA (2016) but without applying FCMs. There was another inconsistency with guidance on the part of USEPA's baseline BAF calculations. Baseline BAFs are supposed to be calculated based on the study specific measurements of the freely dissolved fraction of a chemical during the experiment. However, USEPA used default values of DOC and POC to calculate baseline BAFs from field or laboratory based BAFs or BCFs. FDEP did not recognize this departure from guidance in USEPA's calculations and used the baseline BAFs as presented in the supplemental material (USEPA 2016). A discussion of the potential implications of this departure from guidance is further discussed below.

The USEPA methodology prescribes four methods for deriving BAFs presented below in order of preference given the amount of available information from literature.

1. Measured BAFs derived from data obtained from a field study (i.e., field measured BAFs).
2. BAFs predicted from biota-sediment accumulation factors (BSAFs) obtained from a field study (i.e., field-measured BSAFs).
3. BAFs predicted from laboratory-measured BCFs, with or without adjustment by a FCM.
4. BAFs predicted from a compound's n-octanol-water partition coefficient (K_{ow}), with or without adjustment by a FCM.

The methods are to be chosen preferentially in the order shown depending on the amount of information available in the literature and based on the properties of the compound and whether or not the compound is metabolized as shown in the flow chart below. BAFs and BCF were not combined in calculations. Each method results in an estimate of a baseline BAF for each trophic level using one of the following equations:

$$(\text{Baseline BAF})_{TL\ n} = [BAF_T^t/f_{fd} - 1] \cdot 1/f_l$$

$$(\text{Baseline BAF})_{TL\ n} = (FCM)_{TL\ n} \cdot [BCF_T^t/f_{fd} - 1] \cdot 1/f_l$$

$$(\text{Baseline BAF})_{TL\ n} = K_{ow} \cdot (FCM)_{TL\ n}$$

Where:

$(\text{Baseline BAF})_{TL\ n}$ = baseline BAF for TL "n" (L/kg-lipid);

BAF_T^t = total BAF from field sample (i.e., total concentration of chemical in tissue / total concentration of chemical in water [L/kg-tissue]);

BCF_T^t = total BCF from laboratory measure (i.e., total concentration of chemical)

in tissue / total concentration of chemical in water [L/kg-tissue]);

f_{fd} = fraction of the total concentration of chemical in water that is freely dissolved (in field or laboratory sample);

f_l = fraction of tissue that is lipid (in tested species);

FCM = FCM for TL “n”; and

K_{ow} = n-octanol-water partition coefficient.

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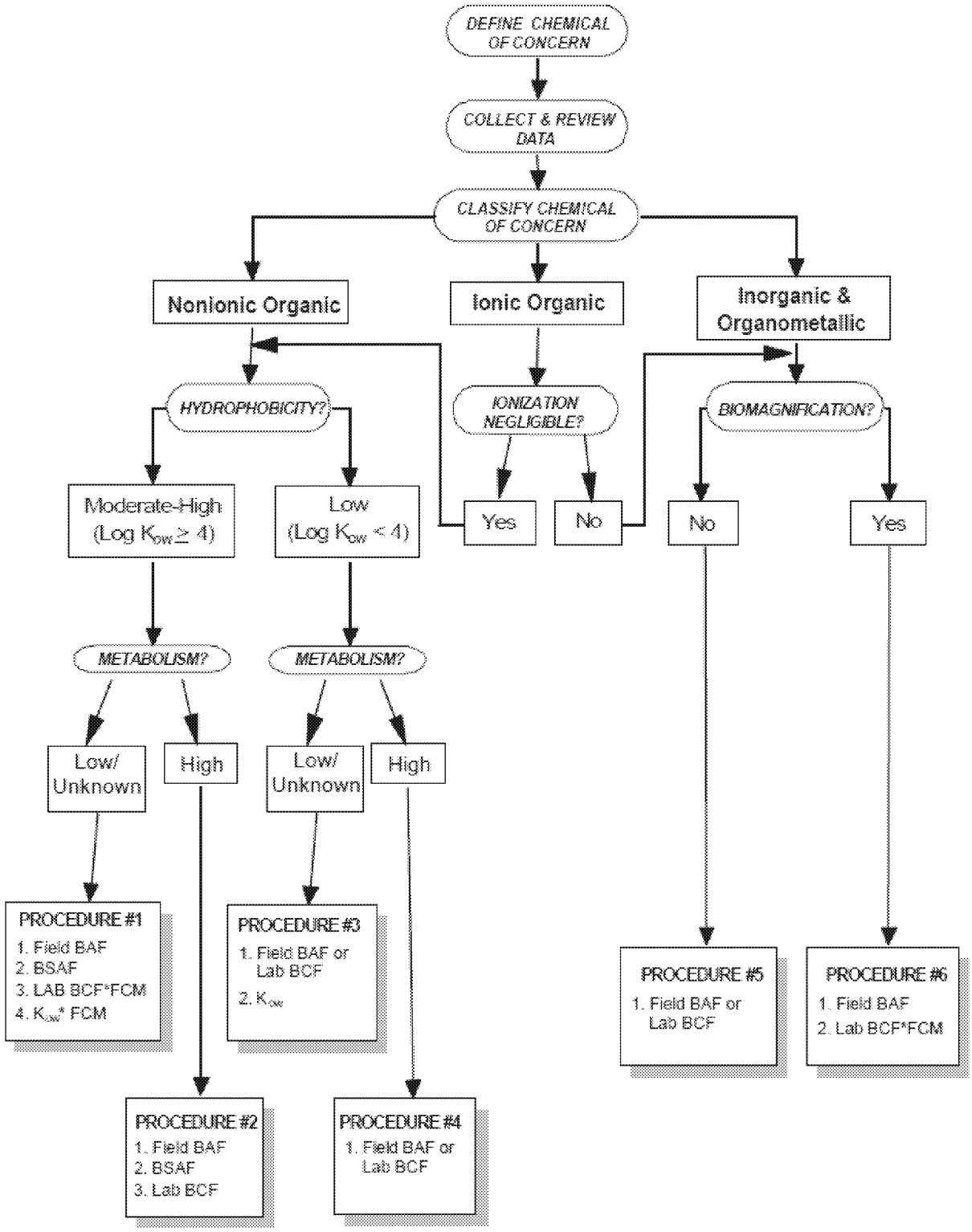
DEFINE CHEMICAL OF CONCERN
COLLECT & REVIEW DATA
CLASSIFY CHEMICAL OF CONCERN
Nonionic Organic
Ionic Organic
Inorganic & Organometallic
HYDROPHOBICITY?
IONIZATION NEGLIGIBLE?
BIOMAGNIFICATION?
Moderate-High (Log $K_{ow} \geq 4$)
Low (Log $K_{ow} < 4$)
Yes
No
No
Yes
METABOLISM?
METABOLISM?
Low/ Unknown
High
Low/ Unknown
High
PROCEDURE #1
1. Field BAF
2. BSAF
3. LAB BCF*FCM
4. K_{ow}* FCM
PROCEDURE #3
1. Field BAF or Lab BCF
2. K_{ow}
PROCEDURE #5
1. Field BAF or Lab BCF
PROCEDURE #6
1. Field BAF
2. Lab BCF*FCM
PROCEDURE #2
1. Field BAF
2. BSAF
3. Lab BCF
PROCEDURE #4
1. Field BAF or Lab BCF

For compounds that fall under procedures #1 and #6 and when the log K_{ow} is greater than or equal to 4, the species is assigned to a particular TL (i.e., 2, 3, or 4) and an FCM is applied. For other cases, the FCM is dropped from the equation (or equivalently set to 1.0). FCMs were developed by USEPA using a food web model further described below. FDEP applied the USEPA-derived FCMs where appropriate to calculate baseline BAFs (i.e. all baseline BAFs used by FDEP are the same as USEPA baseline BAFs with the exception of the 12 PAHs mentioned above).

Multiple baseline BAFs, either from laboratory or field studies (but not both), are averaged by species and then by trophic level using the geometric mean to calculate a final baseline BAF for each TL. For study-based baseline BCFs/BAFs, estimates of f_{fd} and f_l are supposed to be study specific. However, in the Excel spreadsheet provided by USEPA as part of the supplemental information, it is clear that USEPA did not enter f_{fd} from the specific studies but rather estimated it using the national default values for DOC and POC and the following equation:

$$F_{fd} = 1 / [1 + POC \cdot K_{ow} + DOC \cdot 0.08 \cdot K_{ow}]$$

This departure by USEPA from their own guidance calls into question the validity of all the study-based baseline BAFs. Potential implications of this departure from guidance are further discussed below.

The final Florida BAFs were calculated in the same way as national BAFs except with Florida specific assumptions as follows:

$$\text{Florida BAF} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_l)_{TL\ n} + 1] \cdot (f_{fd})$$

Where:

Florida BAF = final Florida BAF (L/kg-tissue);

Final Baseline $BAF_{TL\ n}$ = mean baseline BAF for TL "n" (L/kg-lipid);

$(f_l)_{TL\ n}$ = Florida specific estimate of lipid fraction at TL "n", assumed to be 1.8%, 1.5% and 2.0% for TLs 2, 3, and 4, respectively, compared to the national lipid contents assumed by USEPA 1.9%. 2.6% and 3.0%, respectively; and

f_{fd} = fraction of total concentration freely dissolved based on Florida specific estimates of DOC and POC, assumed to be 12 mg/L and 0.6 mg/L, respectively, compared to the national concentrations assumed by USEPA of 2.9 mg/L and 0.5 mg/L, respectively.

Table 1 shows a comparison of the Florida derived BAFs and the USEPA derived national BAFs and which of the above four methods was used in the derivation. There are a total of 88 compounds for which Florida used BCFs/BAFs. The following methods were used: Log K_{ow}*FCM (n=54); Field BAFs (n=6); BCF*FCM, (n=3); Alternative BAF/(BCF*FCM)" (n=3); Alternative BAF (n=5); BCF (n = 12 PAHs); 1980 BCF for beryllium; and 2002 BCF (n=4). Alternative BAFs refer to a method of calculating one BAF to represent all three trophic levels. This is applied when data are not available to estimate BAFs for all 3 TLs. In general, FDEP used the same methods, field studies, and assumptions as USEPA. However, as noted above, unlike USEPA, FDEP did not apply FCMs when calculating baseline BAFs for 12 PAHs, ((Acenaphthene, Anthracene, Benzo (a) Anthracene, Benzo (a) Pyrene, Benzo (b) Fluoranthene, Benzo (k) Fluoranthene, Chrysene, Dibenzo (a,h) Anthracene, Fluoranthene, Fluorene, Indeno (1,2,3-cd) Pyrene, and Pyrene)). FDEP's approach is correct because these compounds have been classified by USEPA as highly metabolized and, therefore, FCMs should not have been applied by USEPA.

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For all other compounds FDEP used the same methodology as USEPA and for methods 1 through 3, FDEP used the same set of field BAFs or laboratory BCFs as USEPA to derive baseline. In these cases the differences between Florida BAFs and National BAFs are wholly attributable to the differences in Florida's assumptions for lipid content at each trophic level (which are lower than the national default assumptions) and their assumptions of POC and DOC of Florida surface waters (which are higher than the national default assumptions and result in lower estimates of the dissolved fraction). Florida's assumptions for both lipid and organic carbon concentration result in lower final BAF calculations as compared to national final BAFs. The degree of difference depends on hydrophobicity for organic compounds. Florida TL2 BAFs are about half as large as national BAFs when log K_{ow} > 6.5 but are not much different when log K_{ow} < 5.

Review of the Florida BAF for BaP

As noted above, this white paper focuses on the process and data used to estimate the BCF for BaP as an example of some of the short comings in that process and those data. Whether the shortcomings described below for the derivation the BCF for BaP apply to all the other compounds for which measured BCFs are used is not known. Arcadis has not review the underlying data and publications for the other compounds for which revised HHC are proposed. What is known is that the shortcomings do apply to a total of seven PAHs (BaP and the six PAH for which BaP is used as a surrogate (i.e., benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene). These seven PAH represent slightly more than a third of the compounds for which measured BCFs were used.

The general process that USEPA followed to estimate a national BCF for a specific species from a specific study had four steps. FDEP adopted most of these steps when estimating accumulation of BaP in fish and shellfish (and the other six PAHs for which BaP is assumed to be a surrogate) with a very important exception. As a final step, USEPA multiplied the trophic level 2 and 3 BCFs for BaP by FCMs of 1 and 10.2, respectively to derive a BAF of 3900 for BaP even though USEPA classified BaP as having "high metabolism" (USEPA 2015). According to USEPA's supplemental information released in January 2016 (USEPA 2016), and consistent with the text describing the derivation of the BAF for BaP in USEPA (2015a), the BCF for BaP should not have been multiplied by a FCM because of the high metabolism classification. Use of FCMs is inappropriate for metabolized compounds because USEPA's FCM model assumed compounds are not metabolized[3]. Such an assumption does not apply to BaP or to the other PAHs. FDEP recognized this incorrect application of a FCM and did not apply a FCM to the BCF of BaP when developing the proposed HHC.

[3] According to USEPA (2016) other chemical characteristics also preclude the use of FCMs when using BCFs to derive baseline BAFs. One such characteristic is ionization. If a compound is expected to be ionized, an FCM should not be applied to a BCF to derive a baseline BAF. USEPA classified pentachlorophenol as an "ionic organic chemical, with ionization not negligible" (USEPA 2015b). Nevertheless, when deriving the baseline BAF for pentachlorophenol, and contrary to their guidance, USEPA used FCMs.

ED_002388_00000424-00016

The first step in deriving a BCF for BaP was identifying and summarizing the BCFs reported in peer-reviewed literature for BaP[4]. At this point Arcadis has not conducted a comprehensive review of the available literature on BaP BCFs and, therefore, this white paper is not commenting on the completeness of the data set used by USEPA to derive the BCF for BaP. Other peer-reviewed studies reporting valid BCFs for BaP may be available. As part of the review of the peer-reviewed studies included in the USEPA database, Arcadis identified one study that reported a BCF that appears to have been entered incorrectly in the database. Jimenez et al. (1987) report a BCF of 608 L/kg but the database lists a BCF of 842 mg/L[5]. Arcadis was not able to identify an explanation for the discrepancies between the BCF reported by the study and the BCF listed in the database. The BCFs for BaP reported by the other studies agree with the database entries.

Of note regarding the 26 measured BCFs for BaP included in the database is a BCF for a water flea (*Daphnia magna*), a BCF for an amphipod (*Pontoporeia hoyi)*, which is close relative of beach lice, and a BCF for a mayfly (*Hexagenia limbata*). These species are used to estimate the accumulation of BaP into shellfish that Floridians regularly consume (e.g., crabs, shrimp, lobster, clams) but these species are very different from shellfish regularly consumed by Floridians. Whether the accumulation of BaP in typically consumed shellfish is well represented by BCFs from water fleas, amphipods and mayflies is unknown. What is known is that these three organisms are very different from those that are regularly consumed and until it has been shown that their BCFs are representative of regularly consumed species, it might be best to exclude them when estimating the BCFs of regularly consumed shellfish species. Other species for which BCFs are reported include three for Bluegill sunfish (*Lepomis marochirus*), one for shrimp (*Mysis relicta*), and 19 for zebra mussels (*Dreissena polymorpha).*

The second step in deriving a BCF for BaP is converting the BCFs reported for each species in each of the studies to what USEPA refers to as a baseline BAF[6]. The baseline BAF is expressed on a freely dissolved and 100% lipid basis. Some peer-reviewed studies report the lipid content of the species for which a BCF is presented, precluding the need to make assumptions about the lipid content of the test organisms. Other studies do not report the lipid contents and a default national species-specific lipid content (USEPA 2003) is used.

In almost all cases, the peer-reviewed study does not measure or estimate the freely dissolved concentration of a BaP in the setting from which the BCF was derived. The study simply reports the nominal concentration of BaP in the setting and reports the BCF on the basis of the nominal concentration. One exception to this is Landrum and Poore (1988). Landrum and Poore (1988) correct BaP uptake by mayflies for the fraction of the BaP that was bound to dissolved organic matter (DOM) in the test setting, recognizing that the increase in DOM can ultimately reduce the bioavailability of non-polar organics such as BaP measured in water. Thus, the BCFs for BaP reported by Landrum and Poore

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[4] The database upon which USEPA and FDEP rely to develop BCFs/BAFs for BaP report both measured BCFs and measured BAFs from peer-reviewed literature for BaP. Because many more peer-reviewed BCFs are reported than are BAFs, USEPA relies on the reported BCFs and not the reported BAFs to derive a baseline BAF. Hence, the BaP example refers to peer-reviewed literature reporting BCFs.

[5] During Arcadis's review of the BaP dataset we also identified a discrepancy for one of the studies reporting a BAF for BaP. Frank et al. (1986) report a BAF of 676 mg/L, however a BAF of 3,236 mg/L is listed in USEPA's database.

[6] To be consistent with the terminology used by USEPA and FDEP this white paper uses the term "baseline BAF" when referring to either literature-derived BCFs or BAFs, even though in the case of BaP (and other chemicals as well) that baseline BAF is based on BCFs reported in the literature.

ED_002388_00000424-00017

(1988) are expressed on based on a freely dissolved basis and, therefore, the fraction freely dissolved factor should not be applied. USEPA (and FDEP because they used the USEPA BCF) incorrectly applied a fraction freely dissolved correction factor to the BCF reported by Landrum and Poore (1998). The effect of removing the fraction freely dissolved correction factor of the BCF for BaP is discussed at the end of this section.

The freely dissolved fraction depends upon chemical-specific characteristics (log K_{ow}) as well as characteristics unique to the setting in which the BCF was measured (concentration of dissolved organic carbon (DOC) and particulate organic carbon (POC)). One can imagine that in a laboratory setting, using synthetic or filtered water, the amount of organic material in the water is much lower than it would be in a naturally occurring surface water. Additionally, and as USEPA (2000) states, POC is eliminated from the laboratory test water that is filtered prior to use in BCF and BAF experiments. Three of the five studies that report BaP BCFs used filtered lake waters: Gossiaux et al. (1996) and Landrum and Poore (1988) used water from Lake St. Clair, and Murray et al. (1991) used water collected from sites in Port Phillip Bay, Victoria , Australia. Assuming that the concentration of DOC in these filtered lake waters would be comparable to the national median DOC used by USEPA for all waters (i.e., 2.9 mg/L) does not seem unreasonable as the mean DOC concentration in lake waters was 2.9 mg/L as well (USEPA 2003). However, assuming that the concentration of POC in filtered lake water is the same as that present in ambient waters (i.e., 0.5 mg/L) is unlikely to be appropriate given that the filtering of lake water would remove most if not all of the POC present in ambient lake water. A POC concentration of 0 mg/L might be more appropriate for studies using filtered lake water. The effect of such an assumption on the BCF for BaP is discussed at the end of this section.

The third step in deriving a BCF for BaP is converting the national baseline BCFs reported for each species in each of the studies to a Florida-specific BCF. The process entails adjusting the baseline BCF which assumes all of the BaP is freely dissolved and is expressed on a 100% lipid content-basis to account for the amount of BaP that is expect to be freely dissolved in Florida surface water and for the lipid content of fish in Florida surface water. In developing its updated 2015 HHWQC USEPA used national DOC and POC concentrations and national lipid contents for fish in each of the three trophic levels. FDEP correctly recognized that the national averages were not appropriate for Florida surface waters and Florida fish and utilized Florida-specific DOC/POC and lipid concentrations. The Florida-specific DOC and POC concentrations were 12 mg/L and 0.6 mg/L, respectively, compared to the national median of 2.9 mg/L and 0.5 mg/L, respectively. The Florida-specific lipid content was 0.018, 0.015, and 0.02 in trophic levels 2, 3 and 4, respectively, compared to national average lipid contents of 0.019, 0.026, and 0.03.

USEPA's fourth step for deriving a BAF for BaP was to multiply the national BCF by a FCM. As described above, FDEP correctly recognized that application of a FCM to BaP (and to the other PAHs) is inappropriate and did not adjust the BaP BCFs beyond accounting for Florida-specific DOC and POC concentration and lipid content.

The effect of making the corrections described above (i.e., estimating fraction freely dissolved using a POC concentration of 0 mg/L, assuming the mayfly BCF reported by the study is on a freely dissolved basis) on the baseline BAF calculated by USEPA and FDEP for each species is presented in Table 2 and for the BAFs for each trophic level and the final BAF for combined trophic levels in Table 3. When all adjustments are applied, the Florida-specific BCF for BaP decreases from 596 L/kg (rounded to 600 L/kg by FDEP) to 383 L/kg. The national BAF developed by USEPA, which included the incorrect application

ED_002388_00000424-00018

of FCMs, decreases from 3,875 L/kg (rounded to 3,900 L/kg by USEPA) to 2,483 L/kg. The largest contributor to the decrease in Florida-specific BCFs and the national BAFs is correcting the assumption about the concentration of POC in filtered lake water. If the three invertebrate species that are not representative of shellfish consumed by Floridians (i.e., water flea (*Daphnia magna*), amphipod (*Pontoporeia hoyi)*, and mayfly (*Hexagenia limbata*) are removed from the derivation of the Florida-specific BCF, the corrected Florida specific BCF increases from 383 L/kg (Table 2) to 484 L/kg, which is still less than the Florida-specific BCF of 600 used in the proposed HHC for BaP and the other six PAH to which the BaP BCF was applied.

Applicability of National FCMs to Florida Surface Waters and Food Webs

USEPA used a food web model (Gobas 1993) parameterized to a Great Lakes food web and fish tissue data to calculate FCMs for TLs 2, 3, and 4 (USEPA 2003). USEPA (2003) defines food chain multipliers as "a measure of the chemical's tendency to biomagnify in aquatic food webs" and provides the following equation:

$$FCM = \frac{Baseline\ BAF}{K_{ow}} \approx \frac{Baseline\ BAF}{Baseline\ BCF}$$

USEPA considered the models of both Gobas (1993) and Thomann et al. (1992) for development of FCMs, ultimately deciding to use the Gobas (1993) model for reasons described in USEPA (2003). Many of the values and assumptions used to parameterize the model for the Great Lakes are likely very different from the values and assumptions that would be used to represent surface waters and food webs in Florida.

The key input parameters are described below. Arcadis input the values and assumptions for these key parameters as described in Gobas (1993) into the spreadsheet model which is available online in an effort to reproduce the FCMs published by USEPA (USEPA 2016). Arcadis was not able to reproduce all of the FCMs and it is unclear why. Table 4 shows a comparison of the FCMs calculated using the spreadsheet model vs. those published by USEPA. In general the agreement is very close (within 5%) at log K_{ow}s less than 7, but the difference increases at higher K_{ow}s.

Sediment-Water Concentration Quotient

USEPA describes the sediment-water concentration quotient ($\prod_{socw}$) as "the ratio of the chemical concentrations in the sediments (expressed on an organic carbon basis) to those in the water column (expressed on a freely dissolved basis)". USEPA reviewed data sets from Lake Ontario, Hudson River, and Green Bay in the Lake Michigan ecosystem to determine $\prod_{socw}$. This review concluded that $\prod_{socw}$ is strongly dependent on the K_{ow} and calculated an average value of 23 for the $\prod_{socw}/K_{ow}$ ratio.

USEPA acknowledges there is very large variability in $\prod_{socw}$ across ecosystems. USEPA also presents simulations showing that constant loading results in a maximum $\prod_{socw}/K_{ow}$ of 4.9 (see Figure 4-5 of USEPA (2003)). USEPA also states that with continued loading, sediment concentration will increase until a steady state condition is reached with a $\prod_{socw}/K_{ow}$ in the 2 to 10 range. It would seem that the $\prod_{socw}/K_{ow}$ estimate of 23 is only applicable to chemicals that have high historic loading followed by a large reduction

in loading (e.g., PCBs in the Hudson River). Therefore, it is likely not applicable to most Florida waters. The Π_{socw}/K_{ow} ratio has a substantial effect on the FCMs (Table 5) because the increase in benthic tissue concentrations from sediment cause an increase in tissue concentrations that cascade up the food web.

Chemical Concentrations in Sediment and Water Column

In deriving the FCMs, 1 ng/L (concentration of chemical freely dissolved in the water column, C_w^{fd}) is used. USEPA (2003) states that the corresponding chemical concentration in the sediment is calculated by using the Π_{socw}/K_{ow} = 23 relationship, or C_s (ng/kg) = 23 (L/kg oc) * K_{ow} * (1 ng/L) * f_{oc} (kg oc/kg) * 0.001 (kg/g). The parameter is not affected by the Florida-specific values.

Organic Content of Water

To avoid using the Gobas (1993) model's method of accounting for bioavailability, USEPA (2003) set the concentration of the DOC in the model to an extremely small number, 1.0×10^{-30} kilograms per liter. The Gobas (1993) model takes the total concentration of the chemical in the water that is input to the model and, before doing any predictions, performs a bioavailability correction by calculating the C_w^{fd}. The C_w^{fd} is then used in all subsequent calculations by the model. By setting the concentration of the DOC to 1.0×10^{-30} kilograms per liter, the total concentration of the chemical input into the model becomes essentially equal to the C_w^{fd}, because the bioavailability correction employed by the method of Gobas (1993) becomes extremely small.

Rate of Metabolism in Forage and Piscivorous Fish

The FCMs developed by USEPA (USEPA 2003, 2016) assume no metabolic transformation of a compound by fish and shellfish. That is, the metabolic transformation constant (k_m) is set to zero in the model when FCMs are calculated in part because information on metabolic transformation was lacking for many compounds when the model was parameterized (i.e., in the early 1990's) and also because the model was parameterized for PCBs which are assumed to have relatively low metabolic transformation so the assumption of zero for the metabolic transformation rate constant is not unreasonable (Gobas 1993). However USEPA and FDEP are using the FCMs developed using the assumption of zero for the metabolic transformation constant to derive HHC for many compounds that differ from PCBs and are likely to be metabolized by fish or shellfish or both. Additionally a great deal more information on metabolic transformation rate constants is now available than was in the early 1990's. Arnot et al. (2008) produced a database of metabolic transformation rate constants for organic chemicals. Therefore the assumption of zero metabolism is not only incorrect, but data are available to make more appropriate assumptions, including for halogenated organics, phenyls, dioxins, and furans, hydrocarbons, amines, imides, alcohols, phenols, ethers, ketones, and esters.

To evaluate the effect of incorporating metabolism into the Gobas (1993) model used to calculate FCMs, metabolic transformation rate constants (k_m) were obtained for pentachlorophenol, heptachlor, and 1,3-dichlorobenzene (see footnotes to Table 6 for source of transformation rate constants). When the compound-specific k_ms are incorporated into the Gobas (1993) model, the FCMs for trophic levels 3 and 4 drop substantially for all three chemicals (Table 6). For pentachlorophenol and heptachlor, FDEP used FCMs greater than 1 for trophic levels 3 and 4. Because 1,3-dichlorobenzene has a log K_{ow} less than 4, FDEP defaulted to FCMs of 1 for all trophic levels. In reality, many (if not most) chemicals undergo

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transformation. When transformation is accounted for and is substantial, it appears that FCMs can be less than 1.0, as demonstrated for the above three compounds.

When the FCMs calculated with metabolism are incorporated into the FDEP derivation of Florida-specific BAFs, the resulting trophic level 3 and 4 BAFs drop substantially for all three compounds (Table 6), demonstrating that incorporating metabolism, even for those chemicals that are not flagged as "highly metabolized", has a notable effect on the Florida-specific BAFs.

Additional Environmental Parameters and Conditions

USEPA (2003) used the following environmental parameters and conditions to determine FCMs:

- Mean water temperature: 8° C
- Organic carbon content of the sediment: 2.7%
- Density of lipids: 0.9 kg/L
- Density of organic carbon: 0.9 kg/L

The water temperature used by USEPA (8° C) is substantially cooler than all Florida waters. Water temperature is used in an equation that calculates the dietary uptake constant (kd) in the model. The effect of increasing temperature tends to increase the FCMs because it increases the dietary uptake (Table 5). Sediment organic carbon does not affect FCMs. Density of lipids and density of organic carbon are not water body specific assumptions and are not expected to vary between the Great Lakes and Florida surface waters.

Food Web Structure

USEPA (2003) uses the mixed food web structure from the Lake Ontario ecosystem (Flint 1986; Gobas 1993) as the representative food web for determining FCMs for the national methodology. USEPA notes that there are large differences in food webs across the country and for this reason, strongly encourages States and Tribes to make site-specific modifications to USEPA's national BAFs (USEPA 2000). Table 7 summarizes some of the key inputs used by USEPA to parameterize the food web of the Great Lakes.

Table 8 summarizes hypothetical inputs that are likely to be more representative of a food web in a Florida freshwater lake or river. Ideally, a Florida-specific food web would be calibrated to measured data. However, this hypothetical food web is presented to evaluate the potential effect of alternate food web parameters on calculated FCMs.

When the Gobas model is parameterized with assumptions and values representative of a hypothetical Florida food web rather than a Great Lakes food web, and a water temperature and sediment-water concentration quotient more representative of Florida surface waters but still assuming no metabolic transformation, the calculated FCMs increase for trophic level 3 and decrease for trophic level 4, particularly at higher K_{ow} (Table 9). Note that all of the hypothetical more Florida-specific FCMs are substantially lower than the national FCMs developed by USEPA using assumptions and values representative of surface water and food webs of the Great Lakes. While the hypothetical Florida food web and associated FCMs are presented herein purely for illustrative purposes, the results indicate that

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developing a food web structure representative of Florida lakes and streams has the potential to substantially alter the calculated FCMs.

In summary, the national default assumptions used by USEPA to derive FCMs are unlikely to be representative of Florida conditions. The model is based on and calibrated for a Great Lakes food web using PCB data. As indicated above, a Florida based food web will have substantially different inputs and structure and could result in a very different outcome. In addition, assumptions of sediment contamination are based on areas that have a high historic loading followed by substantial reduction (e.g. PCBs in the Hudson River). The parameter that estimates sediment concentrations from water concentrations, Π_{socw}/K_{ow}, is, therefore, higher than what would be expected in Florida waters resulting in larger FCMs than are representative of conditions in Florida. Of the parameters evaluated in the preliminary sensitivity analysis, the Π_{socw}/K_{ow} ratio has the most substantial effect of all the parameters evaluated to date (Table 5). Finally, the temperature used in the USEPA model is much cooler than might be expected in Florida waters. Inputting a higher temperature, however, tends to increase FCMs because the higher temperature results in an increase in dietary intake in the model. This increased dietary intake is not balanced by what one might expect to be an increased rate of metabolism because metabolism is assumed to be zero in USEPA's FCM model.

Summary

In summary, the preliminary evaluations presented in this white paper provide several lines of strong evidence that the application of USEPA's national BAF procedure to estimate bioaccumulation in Florida surface waters is premature and does not represent good science. Additional evaluation is necessary to identify those aspects of USEPA's national procedure that are applicable to Florida and those that need Florida-specific modification before they can be used to derive human health-based criteria for Florida surface waters. While the preliminary evaluation of some of the individual parameters of the FCM model suggest that BAFs in Florida may be lower than estimated by USEPA for the Great Lakes, the combined effect of all such modifications, and whether those will lead to higher or lower estimates of bioaccumulation, is unknown at this time.

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TABLES

Table 1. Comparison of Florida BAFs and National BAFs and Derivation Methods

CAS Number	Chemical Name	Mean Log K_{OW}	Derivation Method (for baseline BAF/BCF)	Florida BAF/BCF (L/kg-tissue)				National BAF/BCF (L/kg-tissue)			
				TL2	TL3	TL4	Alternative	TL2	TL3	TL4	Alternative
71-55-6	1,1,1-Trichloroethane	2.49	Log Kow*FCM	6	5.6	7.2	ND	6.9	9	10	ND
79-34-5	1,1,2,2-Tetrachloroethane	2.39	Log Kow*FCM	5	4.7	5.9	ND	5.7	7.4	8.4	ND
79-00-5	1,1,2-Trichloroethane	2.42	Log Kow*FCM	5.7	4.9	6.3	ND	6	7.8	8.9	ND
75-35-4	1,1-Dichloroethylene	1.73	Log Kow*FCM	2	1.8	2.1	ND	2	2.4	2.6	ND
120-82-1	1,2,4-Trichlorobenzene	4.02	Field BAFs	2,600	870	280	ND	2,800	1,500	430	ND
95-50-1	1,2-Dichlorobenzene	3.43	Log Kow*FCM	49	41	55	ND	52	71	82	ND
107-06-2	1,2-Dichloroethane	1.48	Log Kow*FCM	1.5	1.5	1.6	ND	1.6	1.8	1.9	ND
78-87-5	1,2-Dichloropropane	1.99	Log Kow*FCM	2.8	2.5	3	ND	2.9	3.5	3.9	ND
122-66-7	1,2-Diphenylhydrazine	2.94	Log Kow*FCM	17	14	18	ND	18	24	27	ND
156-60-5	1,2-Trans-Dichloroethylene	2.09	Log Kow*FCM	3	3	4	ND	3.3	4.2	4.7	ND
541-73-1	1,3-Dichlorobenzene	3.53	BCF*FCM	30	72	130	ND	31	120	190	ND
542-75-6	1,3-Dichloropropene	1.82	Log Kow*FCM	2.2	2	2.3	ND	2.3	2.7	3	ND
106-46-7	1,4-Dichlorobenzene	3.44	BCF*FCM	26	38	56	ND	28	66	84	ND
88-06-2	2,4,6-Trichlorophenol	3.69	Log Kow*FCM	88	74	98	ND	94	130	150	ND
120-83-2	2,4-Dichlorophenol	3.2	Log Kow*FCM	29	25	33	ND	31	42	48	ND
105-67-9	2,4-Dimethylphenol	2.3	Log Kow*FCM	4.6	4	5	ND	4.8	6.2	7	ND
51-28-5	2,4-Dinitrophenol	1.54	ernative BAF (BCF*F(	ND	ND	ND	3.7	ND	ND	ND	4.4
121-14-2	2,4-Dinitrotoluene	1.98	Log Kow*FCM	3	2	3	ND	2.8	3.5	3.9	ND
91-58-7	2-Chloronaphthalene	3.9	Log Kow*FCM	140	120	160	ND	150	210	240	ND
95-57-8	2-Chlorophenol	2.17	Log Kow*FCM	3.7	3.2	4	ND	3.8	4.8	5.4	ND
534-52-1	2-Methyl-4,6-Dinitrophenol	2.49	Log Kow*FCM	6.5	5.6	7.1	ND	6.8	8.9	10	ND
91-94-1	3,3'-Dichlorobenzidine	3.36	Log Kow*FCM	42	35	46	ND	44	60	69	ND
59-50-7	3-Methyl-4-Chlorophenol	3.1	Log Kow*FCM	24	20	26	ND	25	34	39	ND
50-29-3	4,4'-DDT	6.91	Field BAFs	17,000	70,000	3.9E+05	ND	35,000	240,000	1.1E+06	ND
107-02-8	Acrolein	-0.01	Log Kow*FCM	1	1	1	ND	1	1	1	ND
107-13-1	Acrylonitrile	-0.92	Log Kow*FCM	1	1	1	ND	1	1	1	ND
309-00-2	Aldrin	6.5	Log Kow*FCM	9,600	1.0E+05	2.4E+05	ND	18,000	3.1E+05	6.5E+05	ND
959-98-8	alpha-Endosulfan	3.83	Log Kow*FCM	120	100	130	ND	130	180	200	ND
71-43-2	Benzene	2.13	Log Kow*FCM	3.4	3	3.7	ND	3.6	4.5	5	ND
92-87-5	Benzidine	1.34	Log Kow*FCM	1.4	1.3	1.4	ND	1.4	1.6	1.7	ND
319-85-7	beta-BHC	3.78	Log Kow*FCM	110	91	120	ND	110	160	180	ND
33213-65-9	beta-Endosulfan	3.62	Log Kow*FCM	76	63	84	ND	80	110	130	ND
108-60-1	Bis(2-Chloro-1-Methylethyl) Eth	2.48	Log Kow*FCM	6.4	5.5	7	ND	6.7	8.8	10	ND
111-44-4	Bis(2-Chloroethyl) Ether	1.34	Log Kow*FCM	1.4	1.3	1.4	ND	1.4	1.6	1.7	ND
117-81-7	Bis(2-Ethylhexyl) Phthalate	7.5	Alternative BAF	ND	ND	ND	210	ND	ND	ND	710

Table 1. Comparison of Florida BAFs and National BAFs and Derivation Methods

CAS Number	Chemical Name	Mean Log K_{OW}	Derivation Method (for baseline BAF/BCF)	Florida BAF/BCF (L/kg-tissue)				National BAF/BCF (L/kg-tissue)			
				TL2	TL3	TL4	Alternative	TL2	TL3	TL4	Alternative
75-25-2	Bromoform	2.4	Log Kow*FCM	5.5	4.8	6	ND	5.8	7.5	8.5	ND
85-68-7	Butylbenzyl Phthalate	4.73	Alternative BAF	ND	ND	ND	11000	ND	ND	ND	19000
56-23-5	Carbon Tetrachloride	2.64	Log Kow*FCM	9	8	10	ND	9.3	12	14	ND
57-74-9	Chlordane	5.54	Log Kow*FCM	4,100	21,000	32,000	ND	5,300	44,000	60,000	ND
108-90-7	Chlorobenzene	2.84	Log Kow*FCM	13	11	15	ND	14	19	22	ND
124-48-1	Chlorodibromomethane	2.16	Log Kow*FCM	3.6	3.2	3.9	ND	3.7	4.8	5.3	ND
67-66-3	Chloroform	1.97	Log Kow*FCM	2.7	2.4	2.9	ND	2.8	3.4	3.8	ND
93-72-1	Chlorophenoxy Herbicide (2, 4, 5-TP)	3.8	Alternative BAF (BCF*FCM)	ND	ND	ND	34	ND	ND	ND	58
94-75-7	Chlorophenoxy Herbicide (2,4-D)	2.81	Alternative BAF (BCF*FCM)	ND	ND	ND	10	ND	ND	ND	13
75-27-4	Dichlorobromomethane	2.1	Log Kow*FCM	3.3	2.9	3.5	ND	3.4	4.3	4.8	ND
60-57-1	Dieldrin	6.2	Log Kow*FCM	8,200	77,000	1.7E+05	ND	14,000	210,000	4.1E+05	ND
84-66-2	Diethyl Phthalate	2.35	Alternative BAF	ND	ND	ND	580	ND	ND	ND	920
131-11-3	Dimethyl Phthalate	1.6	Alternative BAF	ND	ND	ND	2500	ND	ND	ND	4000
84-74-2	Di-n-Butyl Phthalate	4.21	Alternative BAF	ND	ND	ND	1700	ND	ND	ND	2900
1031-07-8	Endosulfan Sulfate	3.66	Log Kow*FCM	83	69	92	ND	88	120	140	ND
72-20-8	Endrin	5.47	Log Kow*FCM	3,600	17,000	25,000	ND	4,600	36,000	46,000	ND
100-41-4	Ethylbenzene	3.74	Log Kow*FCM	98	82	110	ND	100	140	160	ND
58-89-9	gamma-BHC (Lindane)	3.72	Field BAFs	1,200	1,400	1,700	ND	1,200	2,400	2,500	ND
76-44-8	Heptachlor	6.1	Log Kow*FCM	7,600	67,000	1.4E+05	ND	12,000	180,000	3.3E+05	ND
1024-57-3	Heptachlor Epoxide	5.4	Log Kow*FCM	3,200	14,000	20,000	ND	4,000	28,000	35,000	ND
87-68-3	Hexachlorobutadiene	4.78	Field BAFs	21,000	1,500	710	ND	23,000	2,800	1,100	ND
77-47-4	Hexachlorocyclopentadiene	4.52	Log Kow*FCM	570	820	850	ND	620	1500	1300	ND
67-72-1	Hexachloroethane	3.58	Field BAFs	1100	160	400	ND	1200	280	600	ND
78-59-1	Isophorone	1.67	Log Kow*FCM	1.8	1.7	1.9	ND	1.9	2.2	2.4	ND
72-43-5	Methoxychlor	4.88	Log Kow*FCM	1,200	2,600	2,800	ND	1,400	4,800	4,400	ND
74-83-9	Methyl Bromide	1.1	Log Kow*FCM	1.2	1.2	1.3	ND	1.2	1.3	1.4	ND
75-09-2	Methylene Chloride	1.3	Log Kow*FCM	1.4	1.3	1.4	ND	1.4	1.5	1.6	ND
98-95-3	Nitrobenzene	1.84	Log Kow*FCM	2.2	2	2.4	ND	2.3	2.8	3.1	ND
608-93-5	Pentachlorobenzene	5.18	Field BAFs	3,000	2,300	6,100	ND	3,500	4,500	10,000	ND
87-86-5	Pentachlorophenol	5.01	BCF*FCM	38	150	320	ND	44	290	520	ND
108-95-2	Phenol	1.46	Log Kow*FCM	1.5	1.4	1.6	ND	1.5	1.7	1.9	ND
127-18-4	Tetrachloroethylene	3.4	Log Kow*FCM	46	39	51	ND	49	66	76	ND
108-88-3	Toluene	2.72	Log Kow*FCM	10	9	11	ND	11	15	17	ND

Table 1. Comparison of Florida BAFs and National BAFs and Derivation Methods

CAS Number	Chemical Name	Mean Log K_{OW}	Derivation Method (for baseline BAF/BCF)	Florida BAF/BCF (L/kg-tissue)				National BAF/BCF (L/kg-tissue)			
				TL2	TL3	TL4	Alternative	TL2	TL3	TL4	Alternative
8001-35-2	Toxaphene	4.97	Log Kow*FCM	1,500	3,500	3,900	ND	1,700	6,600	6,300	ND
79-01-6	Trichloroethylene	2.61	Log Kow*FCM	8.3	7.1	9.1	ND	8.7	12	13	ND
75-01-4	Vinyl Chloride	1.36	Log Kow*FCM	1.4	1.3	1.5	ND	1.4	1.6	1.7	ND
83-32-9	Acenaphthene	3.98	BCF	ND	ND	ND	290	ND	ND	ND	510
120-12-7	Anthracene	4.45	BCF	ND	ND	ND	340	ND	ND	ND	610
56-55-3	Benzo (a) Anthracene	5.61	BCF	ND	ND	ND	600	ND	ND	ND	3900
50-32-8	Benzo (a) Pyrene	6.06	BCF	ND	ND	ND	600	ND	ND	ND	3900
205-99-2	Benzo (b) Fluoranthene	6.04	BCF	ND	ND	ND	600	ND	ND	ND	3900
207-08-9	Benzo (k) Fluoranthene	6.06	BCF	ND	ND	ND	600	ND	ND	ND	3900
218-01-9	Chrysene	5.16	BCF	ND	ND	ND	600	ND	ND	ND	3900
53-70-3	Dibenzo (a,h) Anthracene	6.84	BCF	ND	ND	ND	600	ND	ND	ND	3900
206-44-0	Fluoranthene	4.9	BCF	ND	ND	ND	1300	ND	ND	ND	1500
86-73-7	Fluorene	4.18	BCF	210	190	420	260	230	450	710	ND
193-39-5	Indeno (1,2,3-cd) Pyrene	6.58	BCF	ND	ND	ND	600	ND	ND	ND	3900
129-00-0	Pyrene	4.88	BCF	ND	ND	ND	370	ND	ND	ND	860
7440-41-7	Beryllium	N/A	1980 BCF	ND	ND	ND	18.9	N/A	N/A	N/A	N/A
7440-36-0	Antimony	N/A	2002 BCF	ND	ND	ND	1	N/A	N/A	N/A	N/A
57-12-5	Cyanide	0.865	2002 BCF	ND	ND	ND	1	ND	ND	ND	1
Polychlorinated Biphenyls (PCBs)		N/A	2002 BCF	ND	ND	ND	31,200	N/A	N/A	N/A	N/A
7782-49-2	Selenium	N/A	2002 BCF	ND	ND	ND	4.8	N/A	N/A	N/A	N/A

Table 2. Geometric Mean of Original and Corrected Baseline BAF Values (L/kg-lipid)

TL	Species	N	EPA Baseline (Original)	EPA Baseline (Corrected)	FL Baseline (Original)	FL Baseline (Corrected)
2	Amphipod (Pontoporeia hoyi)	1	2,470,769	**1,342,467**	2,470,769	**1,342,467**
2	Mayfly (Hexagenia limbata)	1	360,081	**195,633**	360,081	**195,633**
2	Shrimp (Mysis relicta)	1	808,223	**439,118**	808,223	**439,118**
2	Water flea (Daphnia magna)	1	294,452	**202,600**	294,452	**202,600**
2	Zebra mussel (Dreissena polymorpha)	19	2,252,602	**1,549,961**	2,252,602	**1,549,961**
2	Bluegill sunfish (Lepomis macrochirus)	4	120,798	**83,079**	11,824	**8,132**

Table 3. Geometric Mean of Original and Corrected Final BAF Values (L/kg-tissue)

TL	EPA (Final)	**EPA Final (Corrected)**	FL (Final)	**FL Final (Corrected)**
2	8,848	5,284	5,562	3,321
3	1,697	1,167	64	44
2/3	3,875	2,483	596	383

Table 4. Comparsison of Gobas Speadsheet Results and USEPA Published Values

Gobas Model Parameter	Log Kow	4	5	6	7	8	9
	Water Temperature	8° C (National Default Temperature)					
	SOWC/Kow	23					
Model Calculated Food Chain Multipliers	TL2	1	1	1	1	1	1
	TL3	1.23	3.01	9.87	13.8	9.19	1.99
	TL4	1.07	2.49	14.7	25.6	10.6	0.44
Food Chain Multipliers, EPA (2003) Table 4-6	TL2	1	1	1	1	1	1
	TL3	1.23	3	9.79	13.2	7.6	1.38
	TL4	1.07	2.51	14.9	24.3	7.23	0.21

Table 5. Sensitivity of Various Gobas Model Parameters With Respect to Calculated Food Chain Multipliers

Gobas Model Parameter	Log Kow	5							
	Water temperature	8° C (National Default Temperature)				16° C (Alternative Florida)			
	SOWC/Kow	23 (Default)	10	5	2	23 (Default)	10	5	2
Model Calculated Food Chain Multipliers	TL2	1	1	1	1	1	1	1	1
	TL3	3.01	1.86	1.42	1.15	4.08	2.34	1.66	1.26
	TL4	2.49	1.82	1.57	1.41	3.99	2.60	2.06	1.74
Gobas Model Parameter	Log Kow	6							
	Water temperature	8° C (National Default Temperature)				16° C (Alternative Florida)			
	SOWC/Kow	23 (Default)	10	5	2	23 (Default)	10	5	2
Model Calculated Food Chain Multipliers	TL2	1	1	1	1	1	1	1	1
	TL3	9.87	4.81	2.85	1.66	12.5	5.97	3.47	1.94
	TL4	14.7	7.45	4.67	3.00	22.8	11.2	6.80	4.14
Gobas Model Parameter	Log Kow	7							
	Water temperature	8° C (National Default Temperature)				16° C (Alternative Florida)			
	SOWC/Kow	23 (Default)	10	5	2	23 (Default)	10	5	2
Model Calculated Food Chain Multipliers	TL2	1	1	1	1	1	1	1	1
	TL3	13.8	6.4	3.6	1.9	16.1	7.5	4.2	2.2
	TL4	25.6	12.2	7.1	4.0	36.0	17.1	9.8	5.5

Table 6. Comparison of FCMs and BAFs Calculated With and Without Metabolism

Parameter	Trophic Level	Without Metabolism	With Metabolism
Pentachlorophenol	**log k_{ow} = 5.01**	**k_m = 1.66 day^{-1} [a]**	
FCM	**TL2**	1.0	1.0
	TL3	3.0	0.13
	TL4	2.6	0.0037
BAF/BCF	**TL2**	38	38
	TL3	150	7.4
	TL4	320	1.3
Heptachlor	**log k_{ow} = 6.10**	**k_m = 0.025 day^{-1} [b]**	
FCM	**TL2**	1.0	1.0
	TL3	11	4.1
	TL4	17	0.91
BAF/BCF	**TL2**	7600	7600
	TL3	67000	26000
	TL4	140000	7700
1,3-Dichlorobenzene	**log k_{ow} = 3.53**	**k_m = 0.578 day^{-1} [b]**	
FCM	**TL2**	1.0	1.0
	TL3	1.0	0.82
	TL4	1.0	0.22
BAF/BCF	**TL2**	30	30
	TL3	72	59
	TL4	130	29

a. Hazardous Substances Data Bank
(https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:@term+@DOCNO+894)
b. Arnot et al. (2008)

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Table 7. Lake Ontario Based Food Web Model Used to Derive National Food Chain Multipliers Adopted by FDEP

Species	Trophic Level	Lipid Content	Weight	Diet
Phytoplankton	1	0.5%	--	--
Zooplankton (mysids [*Mysis relicta*])	2	5%	100 mg	--
Benthic Invertebrates (*Diporeia*)	2	3%	12 mg	--
Sculpin (*Cottus cognatus*)	3	8%	5.4 g	18% zooplankton, 82% *Diporeia*
Alewife (*Alosa pseudoharengus*)	3	7%	32 g	60% zooplankton, 40% *Diporeia*
Smelt (*Osmerus mordax*)	3-4	4%	16 g	54% zooplankton, 21% *Diporeia* , 25% sculpin
Salmonids (*Salvelinus namaycush, Oncorhynchus mykiss, Oncorhynchus velinus namaycush*	4	11%	2,410 g	10% sculpin, 50% alewife, 40% smelt

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Table 8. Hypothetical Florida-Based Food Web Model Parameters

Species	Trophic Level	Lipid Content	Weight	Diet
Phytoplankton	1	0.5%	--	--
Zooplankton (mysids [*Mysis relicta]*)	2	5%	100 mg	--
Crayfish	2	1%	6 g	--
Panfish (sunfish)	3	3%	200 g	20% zooplankton, 80% crayfish
Largemouth bass	4	4%	2,000 g	20% crayfish, 80% panfish
Freshwater catfish	4	8%	5,000 g	20% crayfish, 80% panfish

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Table 9. Comparison of FCMs Calculated With Great Lakes and Hypothetical Florida Food Web Parameters

Gobas Model Parameter	Log Kow	4	5	6	7
	Water Temperature	16° C (Alternative Florida)			
	SOWC/Kow	5			
Great Lakes Food Web	TL2	1	1	1	1
	TL3	1.1	1.7	3.5	4.2
	TL4	1.1	2.1	6.8	9.8
Hypothetical Florida Food Web	TL2	1	1	1	1
	TL3	1.1	1.7	3.8	4.9
	TL4	1.1	1.7	5.2	7.1

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ATTACHMENT F

Review of PAH Bioaccumulation and Bioconcentration Factors used by USEPA in Derivation of 2015 Human Health Water Quality Criteria

This attachment presents annotated slides from a platform presentation on November 10, 2017 at the 37th Annual Meeting of the Society of Environmental Toxicology and Chemistry held in Orlando, Florida. The slides are the same as those presented at the conference. The text associated with each slide has been added since the platform presentation to provide context and explanation.

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REVIEW OF PAH BIOACCUMULATION AND BIOCONCENTRATION FACTORS USED BY USEPA IN DERIVATION OF 2015 HUMAN HEALTH WATER QUALITY CRITERIA

Paul Anderson, Jacqueline Iannuzzi, Michele Buonanduci

November 10, 2016

This presentation reviews the bioaccumulation/bioconcentration methodology employed by USEPA to derive the 2015 human health ambient water quality criteria (HHAWQC) and released by USEPA in January 2016. The presentation uses polynuclear aromatic hydrocarbons (PAH) as example compounds. However, many of the topics described in the presentation are applicable to other compounds for which USEPA derived HHAWQC in 2015.

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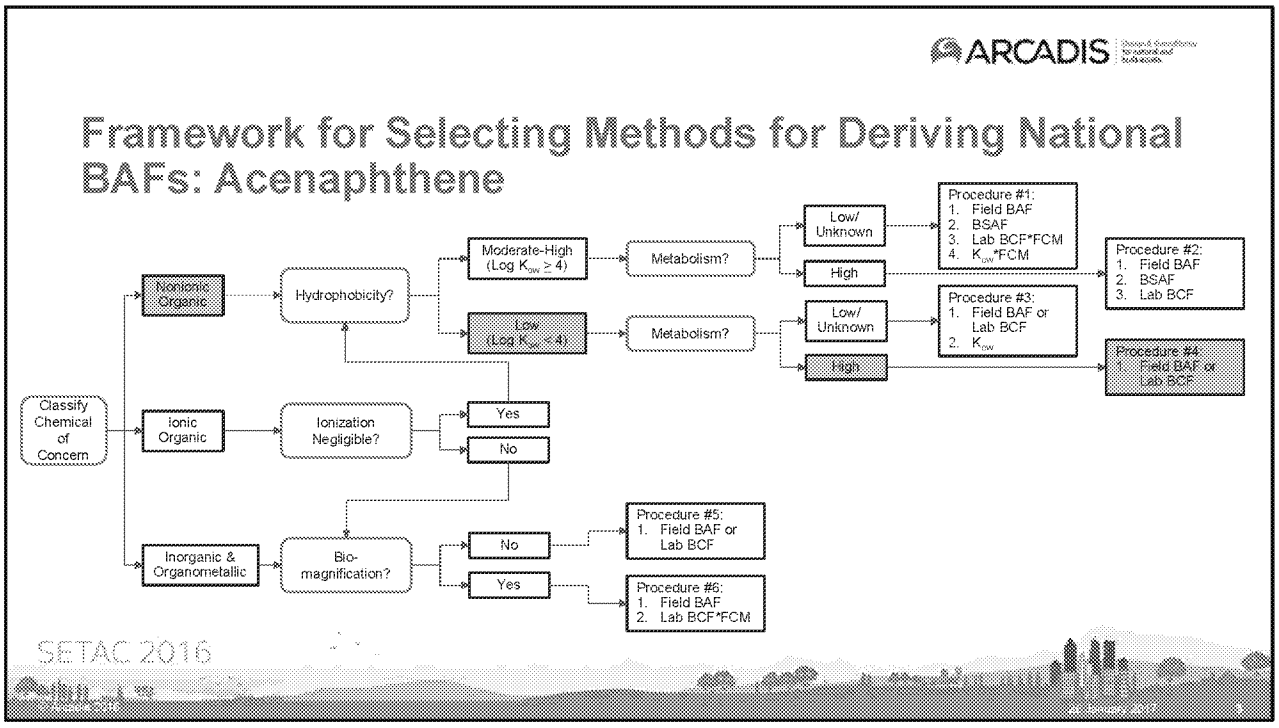
Goals Today

- Overview of process USEPA followed to develop the BAFs/BCFs used to derive the 2015 Human Health Ambient Water Quality Criteria (HHAWQC)
- Application of that process to polynuclear aromatic hydrocarbons (PAH)
- Deviations from the process
- Food chain multipliers (FCMs)
- Example of effect of other adjustments to the USEPA's default assumptions
- Comparison of BCFs/BAFs derived using alternative assumptions and effect on HHAWQC

SETAC 2016

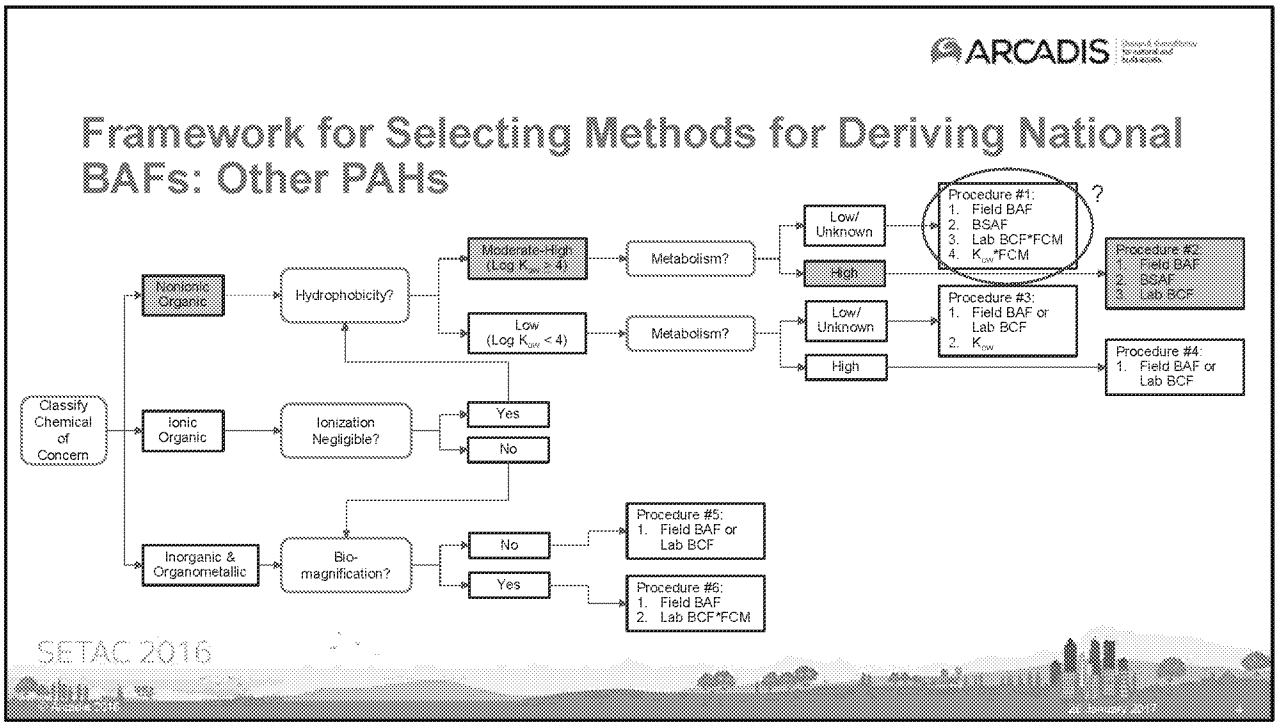
The presentation will review the overall process followed by USEPA to develop bioaccumulation factors (BAFs) and bioconcentration factors (BCFs) used to derive the 2015 HHAWQC. PAH are used as the example class of compounds to which BAF/BCF methodology was applied. The application to PAH will document ways in which USEPA deviated from the process it describes in the January 2016 methodology. The presentation also touches on the purpose, application and applicability of food chain multipliers (FCMs) to PAH. It also presents a summary of some of the other assumptions that might be appropriate to adjust before using the 2015 BAFs/BCFs when setting State-specific HHAWQC. The presentation concludes by showing how the BAFs/BCFs used by USEPA in the 2015 PAH HHAWQC can change when some of these changes are incorporated into the derivation process.



USEPA's framework for selecting a method to derive national BAFs is presented in this slide. The framework contains three decision points.

- The first is identifying whether the chemical is organic and, if it is organic, whether it is ionized in ambient surface waters.
- Second, if the compound is an organic and it is not ionized in ambient surface waters, whether the chemical has a low or moderate-high K_{ow}, where the threshold between the two categorizations of low versus moderate-high is a log K_{ow} of 4.
- Third, for non-ionized organic chemicals the degree of metabolism affects the procedure that is selected to estimate the BAF.

The boxes highlighted in green present the outcome of the above decision points for acenaphthene. USEPA classifies acenaphthene as a nonionic organic chemical with low K_{ow} and high metablolism. That results in the national BAF being based on Procedure #4, in which the national BAF is based either on a field-measured BAF or a laboratory-measured BCF. USEPA used Procedure #4 to derive the National BAF for acenaphthene.



USEPA's framework for selecting a method to derive national BAFs is presented in this slide with boxes highlighted for seven PAH for which benzo(a)pyrene is assumed to be a surrogate. USEPA classifies these seven PAH as nonionic organic chemicals with moderate-high K_{ow} and high metabolism. Based on the framework, that should result in the national BAF being based on Procedure #2, in which the national BAF is based either on a field-measured BAF, a BSAF, or a laboratory-measured BCF. However, despite the above classifications, when developing national BAFs for these seven PAH, USEPA elected to use Procedure #1 (circled in red on the slide). In that procedure, the national BAF is based either on a field-measured BAF, a BSAF, a laboratory-measured BCF multiplied by a FCM, or the K_{ow} multiplied by the FCM. USEPA does not provide an explanation for the deviation from the framework, though as described in subsequent slides, the effect on the final national BAF can be quite large.

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Food Chain Multipliers

- BCFs theoretically account for uptake from only water
- FCMs used to account for uptake from other exposure pathways (e.g. diet, sediment)
- USEPA 2016 FCMs based on modeling of Great Lakes foodweb
- Great Lakes are unique and may not be representative of many other US waters
- USEPA 2016 FCMs do not include metabolic transformation, hence why USEPA's process indicates FCMs should not be used for highly metabolized compounds

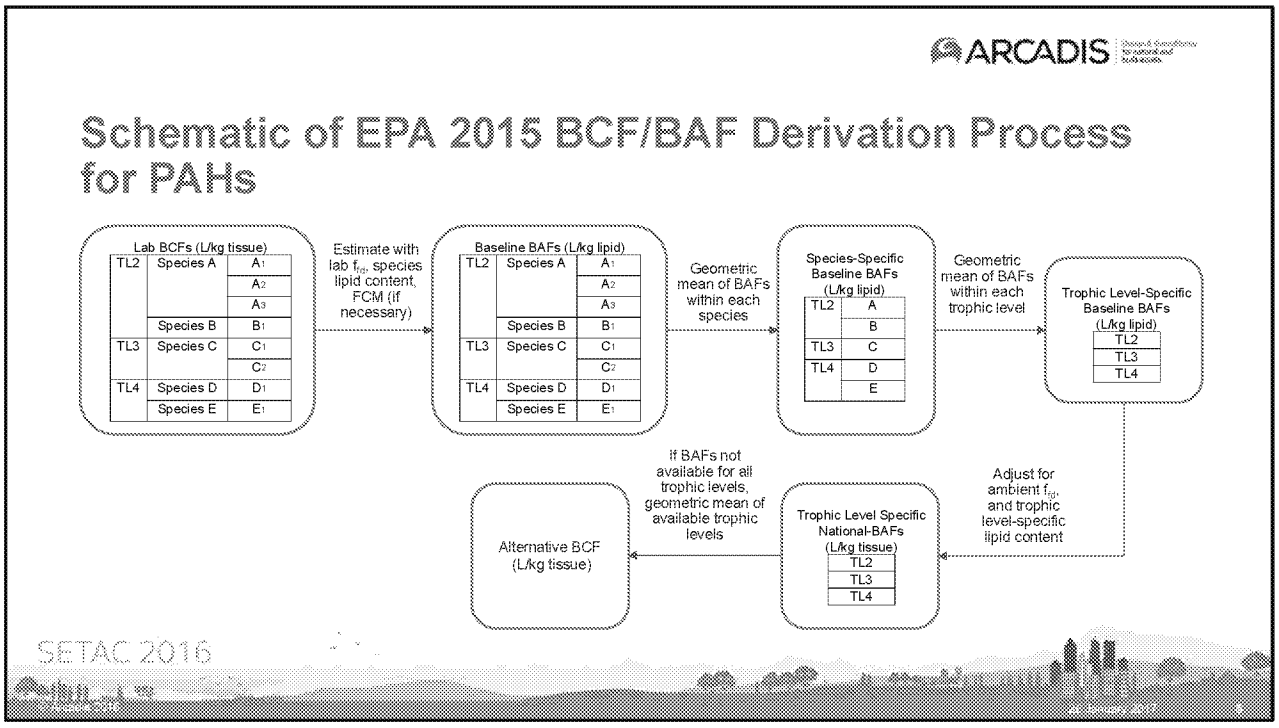
Log K_{ow}	Trophic Level 2	Trophic Level 3	Trophic Level 4	Log K_{ow}	Trophic Level 2	Trophic Level 3	Trophic Level 4	Log K_{ow}	Trophic Level 2	Trophic Level 3	Trophic Level 4
4.0	1	1.23	1.07	5.7	1	7.40	9.54	7.4	1	12.0	19.5
4.1	1	1.29	1.09	5.8	1	8.21	11.2	7.5	1	11.5	17.8
4.2	1	1.35	1.13	5.9	1	9.01	13.0	7.6	1	10.8	15.5
4.3	1	1.45	1.17	6.0	1	9.79	14.9	7.7	1	10.1	13.3
4.4	1	1.56	1.23	6.1	1	10.5	16.7	7.8	1	9.31	11.2
4.5	1	1.70	1.32	6.2	1	11.2	18.5	7.9	1	8.46	9.13
4.6	1	1.87	1.44	6.3	1	11.7	20.1	8.0	1	7.60	7.23
4.7	1	2.08	1.60	6.4	1	12.2	21.6	8.1	1	6.73	5.58
4.8	1	2.33	1.82	6.5	1	12.6	22.8	8.2	1	5.88	4.19
4.9	1	2.64	2.12	6.6	1	12.9	23.8	8.3	1	5.07	3.07
5.0	1	3.00	2.51	6.7	1	13.2	24.4	8.4	1	4.33	2.20
5.1	1	3.43	3.02	6.8	1	13.3	24.7	8.5	1	3.65	1.54
5.2	1	3.93	3.68	6.9	1	13.3	24.7	8.6	1	3.05	1.06
5.3	1	4.50	4.49	7.0	1	13.2	24.3	8.7	1	2.52	0.721
5.4	1	5.14	5.48	7.1	1	13.1	23.6	8.8	1	2.08	0.483
5.5	1	5.85	6.65	7.2	1	12.8	22.5	8.9	1	1.70	0.320
5.6	1	6.66	8.01	7.3	1	12.5	21.2	9.0	1	1.38	0.210

SETAC 2016

This slide provides some background on FCMs. The embedded table presents the FCMs used by USEPA to derive national BAFs. The concept of the FCM arose from the realization that, theoretically, BCFs only account for uptake of a chemical by aquatic biota directly from water. For many chemicals, other exposure pathways are present and can make a substantial contribution to uptake from the aquatic environment, such as diet and sediment. FCMs were developed to account for these other uptake pathways. The FCMs were based on a model of the accumulation of polychlorinated biphenyls (PCBs) in the Great Lakes food web.

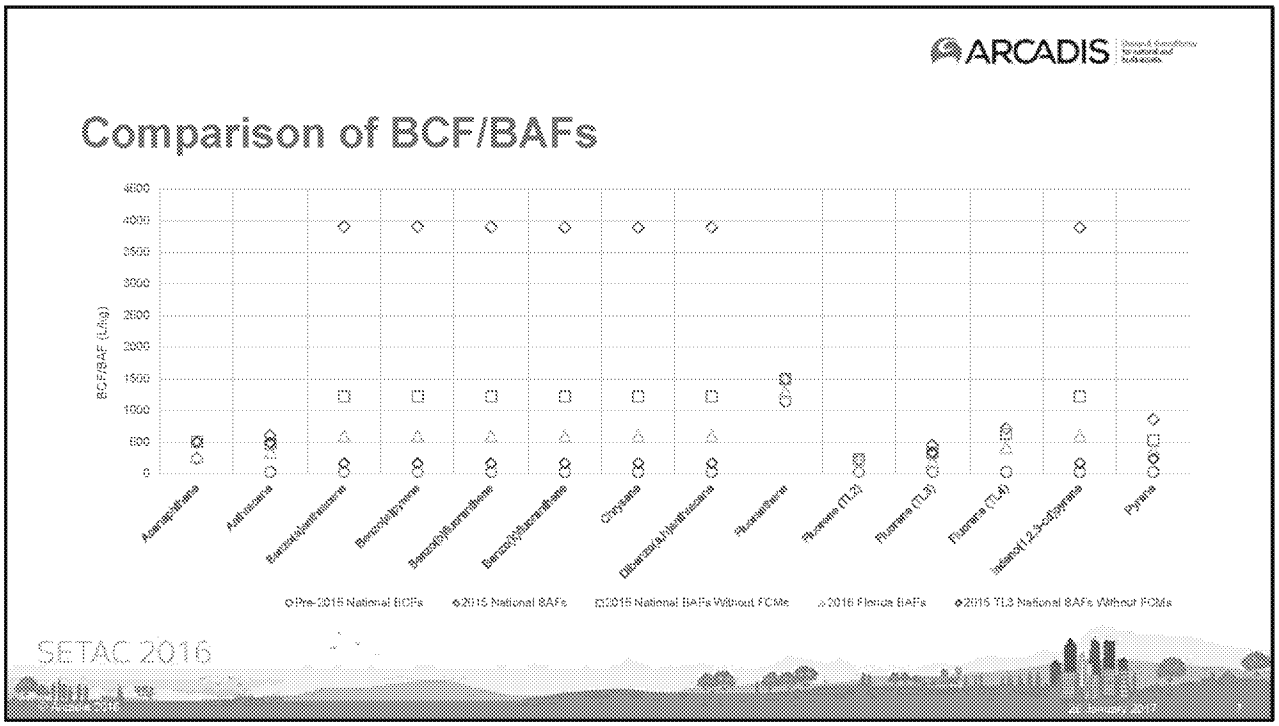
As shown in the table, FCMs are close to 1 for chemicals with a log K_{ow} of about 4 (i.e., pathways other than direct uptake from water contribute little to overall exposure meaning that total accumulation is only slightly greater than that predicted by a BCF). FCMs increase with increasing log K_{ow}, to a maximum about 13 for trophic level 3 and 25 for trophic level 4 near a log K_{ow} of 7 (i.e., pathways other than direct uptake from water contribute about 13 and 25 times more to overall exposure for these two trophic levels than just direct uptake from water). At log K_{ow}s of greater than 7, FCMs decrease with increasing log K_{ow} and approach or are less than 1 at a log K_{ow} of 9. The effect of K_{ow} on predicted FCM is why USEPA's framework contains a K_{ow}-based decision point; at log K_{ow}s of less than 4, exposure from exposure pathways other than direct uptake from water do not need to be account for.

In addition to K_{ow}, metabolism also plays a significant role in bioaccumulation of chemicals in aquatic biota. Specifically, accumulation of metabolized chemicals can be substantially lower than accumulation of non-metabolized chemicals. The model used by USEPA to develop the FCMs is based on PCBs and assumes no metabolism of PCBs. Thus, the FCMs are applicable to only compounds that have no or little metabolism and is the reason the framework includes a metabolism-based decision point. FCMs for metabolized compounds, such as PAHs, would be expected to be lower, perhaps substantially lower, than the FCMs shown in the above table.



A schematic of USEPA's application of the framework to derive national BAFs for PAHs is presented in this slide.

- The process starts with a listing of all laboratory BCFs for a specific PAH included in USEPA's database. Each measured BCF is categorized by species and trophic level.
- Each laboratory measured BCF is then converted to a Baseline BAF (expressed on a freely dissolved, 100% lipid basis). If called for by the framework, a laboratory measured BCF is multiplied by a FCM.
- For each species that has more than one Baseline BAF, the species-specific Baseline BAF is estimated by taking the geometric mean of all the Baseline BAFs measured for that species.
- For each trophic level that has more than one species-specific Baseline BAF, a Trophic Level-specific Baseline BAF is estimated by taking the geometric mean of all the species-specific BAFs measured for that trophic level.
- Trophic level-specific Baseline BAFs are converted to Trophic Level-specific National BAFs by adjusting the Baseline BAFs to account for the trophic level-specific lipid content of fish in national surface waters and fraction freely dissolved of each chemical in national surface waters. When National BAFs are available for all trophic levels, they are used to develop National HHAWQC. As discussed in subsequent slides, USEPA's framework identifies fraction freely dissolved and trophic level-specific lipid adjustments to make BAFs more water body-specific.
- If National BAFs are absent for one or more trophic levels, the geometric mean of the available Trophic Level-specific National BAFs is used to derive National HHAWQC.



This graph shown on the slide plots several different BCFs/BAFs (as described below) for 12 PAH. The value of the BCF/BAF is shown on the y-axis and the name of each PAH is shown on the x-axis. Note that fluorene is shown three times on the x-axis corresponding the availability of BAFs for all three trophic levels.

- The green circles present the BCF used to derive National HHAWQC prior to issuance of the new 2015 HHAWQC. For all PAH, these are the lowest BCF/BAFs shown on the figure. With the exception of acenaphthene and fluoranthene, the BCFs were uniform and low (30 L/kg).
- The orange diamonds present the BAF used to derive the 2015 National HHAWQC. For all PAH, these are the highest BAFs shown on the figure. For seven PAH, these are identical because the bioaccumulation of benzo(a)pyrene is used as a surrogate to represent the bioaccumulation of the other six PAH.
- The blue squares present the BAFs that would result if the FCM was not applied to the derivation of the National BAF. As described above, USEPA classifies all 12 PAH as having high metabolism. Based on the BAF framework presented in USEPA's BAF guidance (USEPA 2016) a FCM should not have been applied in the derivation of the National BAFs for PAH. The National BAF for the seven PAH represented by benzo(a)pyrene would be about three times lower than the National BAF used by USEPA in the 2015 HHAWQC, and the resulting HHAWQC would have been about three times higher. The effect of the FCM is less for the other three PAH to which it was applied (i.e., anthracene, fluorene, pyrene).
- Green diamonds present the BAF used by the Florida Department of Environmental Protection (FDEP) to derive their proposed State-specific HHAWQC. In addition to not applying a FCM when deriving BAFs for PAH, FDEP also used Florida-specific information on the lipid content of fish and dissolved and particulate organic carbon (DOC and POC) in Florida waters to derive a Florida-specific BAF from USEPA's baseline BAF for each PAH. The Florida-specific BAFs are lower for all PAH than National BAFs derived without using a FCM. The largest difference occurs for the seven PAH represented by benzo(a)pyrene. The Florida-specific BAFs are about 6.5 times lower than the National BAF used by USEPA in the 2015 HHAWQC.
- The purple diamonds represent National BAFs for the Trophic Level 3 derived without using a FCM. For most PAH, these BAFs end up being the lowest of all the BAFs based on the information used by USEPA to derive BAFs for the 2015 HHAWQC. The purpose of these BAFs is to demonstrate the effect on the

National BAF of excluding the accumulation of PAH measured for Trophic Level 2 aquatic biota which consist of invertebrates (e.g. shellfish). While consumption of invertebrates in ambient waters is likely from estuaries of coastal states, consumption of invertebrates from local freshwaters is infrequent in inland states. It turns out that because most invertebrates do not metabolize PAH, they bioaccumulate PAH at substantially higher rates than finfish. Consequently, when Trophic Level 2 BAFs (i.e., most invertebrates) are excluded from the derivation of a National BAF, the National BAF decreases substantially. A combined Trophic Level 3 and 4 National BAF is not shown on the figure because USEPA's database does not contain data on BCFs for PAH measured in Trophic Level 4 species.

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Potential Adjustments to PAH BCFs

- State-specific DOC/POC (Florida)
- State-specific lipid fraction of trophic level species (Florida)
- State-specific trophic level-specific consumption rates (e.g., freshwater invertebrates)

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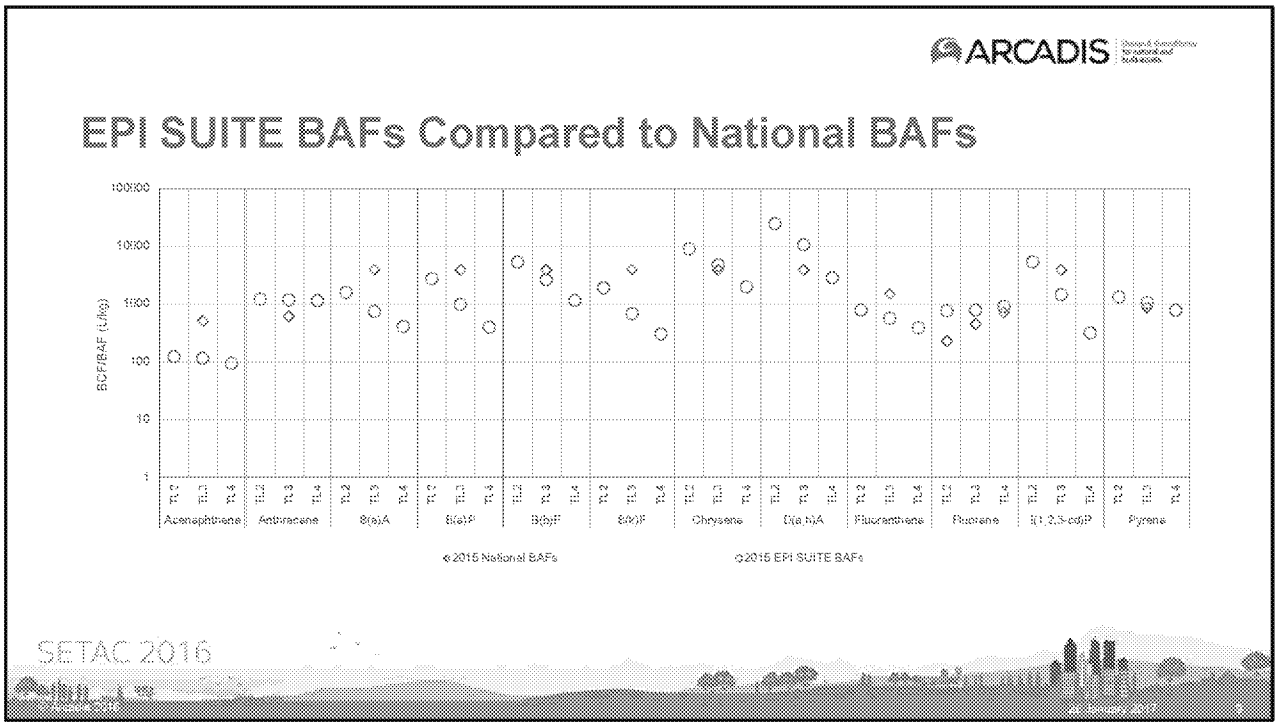
As suggested by the previous slide, several adjustments to the National BAFs could make them more applicable to a State's surface waters. The list shown on this slide is not comprehensive. It focuses on adjustments that could be made based on State-specific information.

- The concentration of DOC and POC in surface water can be used to develop a State-specific estimate of the fraction of freely dissolved chemical in surface waters. Many States are likely to have such data (see FDEP 2016). Such data can be applied to estimate a State-specific fraction freely dissolved for all organic chemicals, not just PAH.
- Some States may also have data on the lipid content of species in different trophic levels. The State-specific lipid data can be used to develop State-specific lipid fractions for each trophic level (see FDEP 2016).
- Although not a specific adjustment called out by USEPA's BAF framework, the National BAFs assume consumption of a specific amount of fish from each of three trophic levels. As noted above, trophic level 2 consists of invertebrates but consumption of aquatic invertebrates from freshwater is a relatively rare occurrence, certainly much less frequent than the consumption of shellfish such as shrimp, crabs, clams and lobster that comprise the majority of trophic level 2 species included in the National BAF trophic level 2 fish consumption rate. States should consider deriving State-specific HHAWQC based on trophic level-specific fish consumption rates that reflect the species present in and consumed from State waters.



The graph shown on the slide plots two sets of BAFs for the 12 PAH for which USEPA proposed HHAWQC in 2015. The value of the BAF is shown on the y-axis and the name of each PAH on the x-axis. The green circles present the trophic level-specific BAF derived using EpiSuite for each of the PAH. The orange diamonds present the National BAF used by USEPA to derive the 2015 HHAWQC. EpiSuite is a model used by USEPA to estimate bioaccumulation for different compounds across the three trophic levels. The EpiSuite model accounts for metabolism and some other parameters that may make it a better predictor of BAFs than the FCM model USEPA used in the framework to derive the National BAFs used to develop the 2015 HHAWQC. The EpiSuite BAFs are presented in the supporting documentation for each individual PAH.

Review of the 2015 National BAFs and the EpiSuite BAFs for PAH reveals some general trends and observations.

- For most PAH, fluorene being the exception, EpiSuite BAFs decrease with increasing trophic level. This is consistent with the expectation that PAH are metabolized and points to why FCMs, which predict increasing concentrations of PAH (and all other chemicals) with increasing trophic level, are not appropriate to use for chemicals such as PAH that are metabolized.
- For five PAH, all three trophic level-specific BAFs are lower than the 2015 National BAF. For most PAH the trophic level 3 and 4 EpiSuite BAFs are lower than the 2015 National BAF. Only fluorene has 2015 National BAFs lower than the EpiSuite BAFs for all trophic levels. The comparison suggests that the 2015 National BAFs overestimate bioaccumulation of PAH and may lead to lower HHAWQC than would be derived if USEPA's 2016 BAF methodology had been followed by USEPA when developing the 2015 HHAWQC.

Individual PAH supporting documentation:

- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Acenaphthene, 83-32-9. EPA 820-R-15-002. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0234
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Anthracene, 120-12-7. EPA 820-R-

15-008. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0236

- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Benzo(a)anthracene, 56-55-3. EPA 820-R-15-011. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0176
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Benzo(a)pyrene, 50-32-8. EPA 820-R-15-012. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0177
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Benzo(b)fluoranthene, 205-99-2. EPA 820-R-15-013. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0178
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Benzo(k)fluoranthene, 207-08-9. EPA 820-R-15-014. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0179
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Chrysene, 218-01-9. EPA 820-R-15-030. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0184
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Dibenzo(a,h)anthracene, 53-70-3. EPA 820-R-15-032. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0185
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Fluoranthene, 206-44-0. EPA 820-R-15-043. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0220
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Fluorene, 86-73-7. EPA 820-R-15-044. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0221
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Indeno(1,2,3-cd)pyrene, 193-39-5. EPA 820-R-15-053. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0187
- USEPA. 2015. Update of Human Health Ambient Water Quality Criteria: Pyrene, 129-00-0. EPA 820-R-15-062. Office of Water, Office of Science and Technology. June. https://www.regulations.gov/document?D=EPA-HQ-OW-2014-0135-0248

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Potential Adjustments to PAH BCFs (cont.)

- Applicability of Great Lakes FCMs to other waters
- Assumed fraction freely dissolved (F_{fd}) in laboratory studies
- Applicability of literature BCFs to species consumed by humans (e.g., daphnids)

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States may want to consider other adjustments to the framework and USEPA's application of the framework that do not require State-specific data but, rather, involve refinements to the data used by USEPA or the framework itself.

- As described in other attachments, the most important consideration may be the applicability of the food chain model USEPA used to derive FCMs. That model was based on PCBs in the Great Lakes. PCBs are not representative of all compounds to which FCMs may be applied and the Great Lakes are not representative of all waters of the United States.
- In the absence of data on the fraction of freely dissolved chemicals in laboratory BCF experiments, USEPA assumed the concentration of DOC and POC in test aquaria was the same as the average concentration in national ambient waters. If water in the test aquaria was filtered or treated in some way prior to use, it is possible, if not likely, that DOC and especially POC concentrations are lower than found in natural waters. If that were to be the case, then the fraction freely dissolved would be greater than USEPA estimated and the Baseline BAFs lower than USEPA reports.
- Several of the BCFs that USEPA includes in its database are measured in invertebrate species (such as daphnids) that are not consumed by humans. Before using such data, States may want to confirm BCFs reported for such species are representative BCFs in species regularly consumed by people.
- The completeness of USEPA's BCF/BAF database and the frequency at which it is updated is unclear. States may wish to review and update the data for key compounds of interest when deriving or updating State-specific HHAWQC.

Although not an adjustment used to derive National BAFs from the information presented in USEPA's database or a refinement of that process, some States may have State-specific information on bioaccumulation of chemicals in their waters. As indicated in the framework, a field BAF is the preferred measure of bioaccumulation when deriving HHAWQC. Such BAFs could be used in place of the BAFs estimated using the BAF derivation process presented in USEPA's 2016 guidance.

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Effect on HHAWQC

Compound	Pre-2015 National HHAWQC (ug/L)	2015 National HHAWQC (ug/L)		
		Using 2015 National BAFs	Using 2015 National BAFs Without FCMs	Using 2015 National TL3 BAFs Without FCMs
Acenaphthene	670	70	70	70
Anthracene	8300	300	370	360
Benzo(a)anthracene	0.0038	0.0012	0.0037	0.018
Benzo(a)pyrene	0.0038	0.00012	0.00037	0.0018
Benzo(b)fluoranthene	0.0038	0.0012	0.0037	0.018
Benzo(k)fluoranthene	0.0038	0.012	0.037	0.18
Chrysene	0.0038	0.12	0.37	1.8
Dibenzo(a,h)anthracene	0.0038	0.00012	0.00037	0.0018
Fluoranthene	130	20	20	NA
Fluorene	1100	50	60	67
Indeno(1,2,3-cd)pyrene	0.0038	0.0012	0.0037	0.018
Pyrene	830	20	30	63

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This table presents a comparison pf the pre-2015 HHAWQC to the 2015 HHAWQC for 12 PAH. The first column presents the name of each PAH included in the comparison. The second column presents the pre-2015 HHAWQC for 12 PAH. The third column presents the 2015 HHAWQC as derived by USEPA. The fourth column presents the 2015 HHAWQC without the FCM. The fifth column presents the 2015 HHAWQC without the FCM and based on only the Trophic Level 3 BAF. With the exception of benzo(k)fluoranthene and chrysene, the 2015 HHAWQC are lower than the pre-2015 HHAWQC. For about half of the PAH, the decrease is about 10-fold (or more). HHAWQC based on BAFs that do not include the FCM or that are based on only Trophic Level 3 BAFs are greater than the 2015 HHAWQC for most PAH, but are still lower than the pre-2015 HHAWQC for about seven of the 12 PAH.

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Summary

- USEPA did not follow its own guidance when deriving BAFs/alternative BCFs for PAH and the 2015 national HHAWQC
- USEPA used FCMs to adjust BCFs of 11 of 12 PAH even though guidance indicates FCMs should not be used for highly metabolized compounds
- 2015 national HHAWQC for most PAH increase when FCMs are removed from derivation – about 3.5 times higher for 7 of 12 PAH
- Other refinements also likely warranted (e.g., state-specific DOC/POC concentrations and trophic level lipid content)
- Combined, these could lead to substantially lower HHAWQC

SETAC 2016

In summary, USEPA did not follow the framework presented in its own guidance when deriving BAFs for 11 of the 12 PAH for which updated HHAWQC were recommended in 2015 because it used FCMs to adjust BCFs for those PAH even though guidance indicates FCMs should not be used for highly metabolized compounds. The 2015 national HHAWQC for most PAH increase when FCMs are removed from the HHAWQC derivation and increase by slightly more than 3-fold for the seven PAH whose bioaccumulation is represented by benzo(a)pyrene. In addition to reconsidering USEPA's application of an FCM to PAH, USEPA's framework and generally acknowledged scientific understanding of the parameters that affect bioaccumulation suggest that States should use State-specific data, if available, to develop State-specific DOC/POC concentrations and State-specific trophic level lipid contents, as well as considering the applicability to State waters and scientific basis of other aspects of USEPA's 2016 bioaccumulation methodology.

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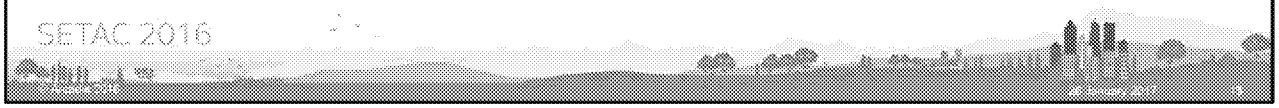
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