Development of Bioaccumulation Factors for Protection of Fish and Wildlife in the Great Lakes

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Bioaccumulation factor (BAF) development for application to the Great Lakes, and in particular for the recent Great Lakes Water Quality Initiative (GLWQI) effort of U.S. EPA and the respective Great Lakes states, illustrates the importance of the linkage between sediments and the water column and its influence on exposure of all aquatic biota. This presentation included a discussion of the development and application of bioaccumulation factors for fish, both water-based BAFs and biota-sediment accumulation factors (BSAFs), with emphasis on the role of sediments in bioaccumulation of persistent, hydrophobic non-polar organic chemicals by both benthic and pelagic organisms. Choices of bioaccumulation factors are important because they will strongly influence predictions of toxic effects in aquatic organisms, especially when chemical residue-based dose-response relationships are used.

There were two principal bioaccumulation factor expressions used by the GLWQI. The BAF_{ℓ}^{fd} is based on lipid-normalized concentration of the chemical in the organism with respect to the concentration of freely dissolved (bioavailable) chemical in the water. The BSAF is the lipid-normalized concentration in the organism with respect to organic carbon-normalized concentration in the sediments. BSAFs were used to determine BAF_{ℓ}^{fd}s for chemicals with concentrations which have not been measured in Great Lakes water but are detectable in sediments and fish. Equilibrium partitioning of persistent non-polar organic chemicals generally occurs between sediments and benthic invertebrates and a thermodynamic equilibrium or fugacity approach is useful for describing the degree of equilibrium (or disequilibrium) associated with bioaccumulation in fish. However, measured BAF_{ℓ}^{fd}s and BSAFs generally indicate a state of non-equilibrium partitioning from sediments to fish. BAF_{ℓ}^{fd}s and BSAFs may be determined and applied as steady-state relationships which incorporate degrees of disequilibrium, such as normally present between water and sediment or between fish and water due to the biomagnification phenomenon.

The bioaccumulation cube (Figure 1) is a conceptual model which includes the most important generic factors that must be considered when predicting bioaccumulation from measured or predicted concentrations of chemicals in the water and sediments of the ecosystem. The bioavailability considerations that remain, after incorporating the influence of organism lipid, organic carbon in water and sediments, and trophic level into BAF_{ℓ}^{fd}s and BSAFs to reduce uncertainty for site-specific bioavailability conditions, are shown on the z-axis. Basically, this residual bioavailability factor is the chemical distribution between water and sediment which can vary between ecosystems or vary temporally and spatially within an ecosystem. Chemical properties which influence bioaccumulation are shown on the x-axis. The octanol-water partition coefficient (K_{ow}) is the primary indicator of chemical hydrophobicity and bioaccumulation potential. A second chemical factor is metabolism by organisms in the food chain. Metabolism is strongly related to chemical structure as well as the presence or absence of specific metabolizing enzymes in different organisms in the food chain. The rates of metabolism of a bioaccumulative chemical by the different organisms in a food chain will determine the extent to which rates of elimination of the chemical will be faster than that predicted on the basis of K_{ow} in the absence of metabolism. Conceptually, the cumulative effect of metabolism in the food chain can be equated to a factor $K_{metabolism}$ which could be subtracted from K_{ow} to correct for the degree of reduced bioaccumulation associated with metabolism.

Ecosystem conditions, such as riverine/lacustrine character, temperature, and trophic condition, as illustrated on the y-axis of the bioaccumulation cube, may be an important consideration when trying to extrapolate from one ecosystem to another. The degree to which quantitative differences in bioaccumulation may be attributable to particular ecosystem conditions, apart from the influence of organic carbon which is handled as a bioavailability variable, is not well known. Bioaccumulation data of the quality needed for quantitative measurement of these relationships for different ecosystems are very limited. Finally, recognition that the food chain has to be defined when modeling bioaccumulation and biomagnification creates a fourth dimension, the trophic

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level, within the bioaccumulation cube; i.e. the bioaccumulation cube exists for each trophic level or more specific definition of food chain.

The procedures used in the GLWQI for predicting bioaccumulatation are reported in the form of a technical support document (U.S. EPA, 1995) which is available from NTIS. Although bioaccumulation factors can be specific for ecosystem conditions and for the structure of the food chain, they may be less site-specific in regard to bioavailability conditions. However, in the GLWQI, BAF_{ℓ}^{fd}s were developed based upon the concentration of freely dissolved chemical in water because this greatly reduces bioavailability conditions as a source of variability between sites. The fraction of the chemical in water which is not partitioned to particulate organic carbon and dissolved organic carbon (fraction freely dissolved) is considered to be the fraction which is bioavailable. The fraction freely dissolved (f^{fd}) chemical can be estimated as:

$$f^{fd} = \frac{1}{1 + POC \cdot K_{poc} + DOC \cdot K_{doc}} = \frac{1}{1 + POC \cdot K_{ow} + DOC \cdot K_{ow}/10} \quad (1)$$

where POC is the concentration of particulate organic carbon, DOC is the concentration of dissolved organic carbon, and K_{poc} and K_{doc} are the respective organic carbon-water partition coefficients. For the GLWQI, K_{poc} was set equal to K_{ow} for each chemical, and K_{doc}, based on Great Lakes water data, was set equal to one-tenth of K_{ow}, reflecting the lesser partitioning power of dissolved organic carbon.

The distribution of chemicals between the sediment and water column can be characterized with a sediment-water concentration quotient ($\prod_{socw}$) which is the ratio of the organic carbon-normalized concentration in surface sediments to the freely dissolved chemical concentration in water. With Lake Ontario data (Oliver and Niimi, 1988) and the POC and DOC partitioning model (equation 1), $\prod_{socw}$ can be related to the degree of chemical equilibrium or disequilibrium (Figure 2). The values of $\log \prod_{socw}$ for chemicals with varying $\log K_{ow}$ are above the line which represents a fugacity ratio of one, or $\prod_{socw}$ equal to $\log K_{ow}$. This reflects a degree of chemical disequilibrium in Lake Ontario which is probably common to most of the Great Lakes since the early 1970s. Based on linear regression, the $\prod_{socw}$ value for these data would be about 25 times K_{ow}, or about 25-fold theoretical disequilibrium between the sediment and the water column under recent conditions in Lake Ontario. A significant portion of this disequilibrium may be an ecosystem characteristic as a consequence of the difference between the fraction of organic carbon in sediments and the fraction of organic carbon associated with particulate material in the overlying water.

BAF_{ℓ}^{fd} predictions for chemicals with $\log K_{ow}$s greater than 5 are quite sensitive to variations in $\prod_{socw}$ when $\prod_{socw}/K_{ow} = 25$ (Figure 3). Using the Gobas bioaccumulation model (Gobas, 1993), Burkhard (1997) demonstrated that a 10 percent increase in the Lake Ontario $\prod_{socw}$, which is the same as increasing the sediment concentration by 10 percent while holding the water column concentration steady, results in nearly a 10 percent change in BAF_{ℓ}^{fd}s. Predictions of bioaccumulation in the form of the BAF_{ℓ}^{fd}s for organisms throughout the food chain are strongly influenced by change in the $\prod_{socw}$ value when water is at disequilibrium with surface sediments (Burkhard, 1997). In other words, BAF_{ℓ}^{fd}s for chemicals with $\log K_{ow}$s > 5 are strongly benthically linked under this condition of disequilibrium, even when the benthic food chain connection may be small. If the ratio of $\prod_{socw}$ to K_{ow} is close to one (equilibrium between the water and sediment which theoretically could occur in other locations), the sensitivity of the $\prod_{socw}$ is quite different (Figure 4). The relationship for sculpin is more sensitive, reflecting its stronger benthic connection to the sediments. The BSAF sensitivity to change in $\prod_{socw}$ is the opposite of the BAF_{ℓ}^{fd} sensitivity; i.e., when the BAF_{ℓ}^{fd} sensitivity is large, the BSAF sensitivity is small. This is not surprising since $\prod_{socw}$ equals the ratio of the BAF_{ℓ}^{fd} to the BSAF. In summary (Figure 5), the sensitivity of BAF_{ℓ}^{fd}s and BSAFs to $\prod_{socw}$ depends on the K_{ow} of the chemical, the benthic/pelagic relative contribution to the food chain, and the degree of disequilibrium between the sediment and the overlying water. The relative sensitivity of BAF_{ℓ}^{fd}s and BSAFs to $\prod_{socw}$ could be an important determinant, under particular site-specific conditions and chemical K_{ow}s, of whether a water-based or a sediment-based bioaccumulation factor should be used for prediction of bioaccumulation.

Selection of BAF_{ℓ}^{fd}s for the Great Lakes Water Quality Initiative involved a tiered approach. Preference was given to high-quality, field-measured values. Unfortunately, for many chemicals these values do not exist. Second preference was given to BAF_{ℓ}^{fd}s predicted using a BSAF methodology, which is described below. The third and fourth tier procedures involved calculation of food chain multipliers to account for biomagnification. In the third tier, the food chain multiplier is multiplied by a measured bioconcentration factor (BCF) and, in the fourth tier when BCFs are not available, the octanol-water partition coefficient is used as a surrogate for the lipid-normalized bioconcentration factor based on freely dissolved chemical in water (BCF_{ℓ}^{fd}).

The second tier method, which uses BSAFs to calculate BAF_{ℓ}^{fd}s, was derived using the following relationship between BAF_{ℓ}^{fd}, BSAF, and $\prod_{socw}$:

$$\prod_{socw} = \frac{BAF_{\ell}^{fd}}{BSAF} \quad (2)$$

For many chemicals in the Great Lakes, under present-day conditions, ratios of $\prod_{socw}$ to K_{ow} (fugacity ratios between sediment and water) are similar:

$$\frac{(\prod_{socw})_i}{(K_{ow})_i} \approx \frac{(\prod_{socw})_r}{(K_{ow})_r} \quad (3)$$

With this condition, equation 2 can be substituted into equation 3 and, following rearrangement, the resulting equation 4 can be used to calculate $(BAF_{\ell}^{fd}s)_I$ for chemicals (I) such as TCDD which cannot be routinely measured in water at this time:

$$(BAF_{\ell}^{fd})_i = \frac{(BAF_{\ell}^{fd})_r\,(BSAF)_i\,(K_{ow})_i}{(BSAF)_r\,(K_{ow})_r} \qquad (4)$$

The BSAF method uses reference chemicals (r), such as PCB congeners, for which $(BAF_{\ell}^{fd})_r$s can often be accurately measured. If a reference chemical that has the same K_{ow} as the unknown chemical is chosen, the K_{ow} ratio in the equation becomes one and the calculation is simplified further. Figure 6 illustrates BAF_{ℓ}^{fd}s calculated from Lake Ontario data with the BSAF method. The distribution of the PCB congener BAF_{ℓ}^{fd}s (circles) provides the expected increase in bioaccumulation and biomagnification with respect to magnitude of K_{ow}. In contrast, the dioxins and furans are predicted to have quite smaller bioaccumulation factors (on the basis of K_{ow}). This is primarily because of the effect of metabolism in fish which is effectively measured by the BSAFs and incorporated into the BAF_{ℓ}^{fd}s. Even though metabolism rates are slow, the increase in elimination rate of the parent chemical is significant and dramatically reduces the bioaccumulation potential with respect to PCBs with the same K_{ow}.

To evaluate the BSAF method, BAF_{ℓ}^{fd}s measured in Lake Ontario were compared to predicted BAF_{ℓ}^{fd}s calculated from Lake Ontario BSAFs (Figure 7) and were in good agreement. A further evaluation was performed by comparing BAF_{ℓ}^{fd}s calculated from BSAFs for PCBs in Lake Ontario for trout to BAF_{ℓ}^{fd}s independently calculated from BSAFs in Green Bay for brown trout (Figure 8). These values were also in agreement despite the disparate ecosystems and measurements involved.

The determination of food chain multipliers (ratio of BAF_{ℓ}^{fd} to K_{ow}) for prediction of BAF_{ℓ}^{fd}s from K_{ow}s was accomplished with a food chain model (Gobas, 1993) using Lake Ontario data and conditions. The objective was to calculate food chain multipliers for bioaccumulative organic chemicals and use them with K_{ow} to estimate BAF_{ℓ}^{fd}s. Figure 9 illustrates how the predictions with food chain multipliers compared to measured BAF_{ℓ}^{fd}s with the data reported by Oliver and Niimi (1988) for Lake Ontario. The agreement is very good, particularly for the higher K_{ow} chemicals which are not metabolized, which in this case are primarily PCBs. The food chain multipliers that were calculated using the Gobas model reflect a biomagnification potential that is a function of K_{ow} for the two top trophic levels of predator fish and forage fish. Under the conditions of the model, the zooplankton are considered to be at equilibrium with respect to the water and benthic invertebrates at equilibrium with respect to the sediment.

Bioaccumulation factors can facilitate bioaccumulation predictions in ecological risk assessments involving impacts of complex mixtures of chemicals. The joint toxicity of chemicals that share similar structure and common mode of toxic action with TCDD (2,3,7,8-tetracholorodibenzo-p-dioxin) can be predicted with an additivity model using the TCDD toxicity equivalence approach. TCDD toxicity equivalence factors (TEFs) are essentially toxicity potency estimates relative to TCDD such that a chemical with a TEF of 1 has a potency equal to that of TCDD. The toxicity equivalence concentration (TEC) is calculated as the sum of the products of the TEF times the concentration for each chemical in a mixture. Often a key question involves what media the concentrations should be based upon. TECs have been calculated based on chemical concentrations in effluents, sediments, or water. TECs based on concentrations of the chemicals in tissue are preferable because of the direct connection between concentration in the tissue and the dose-response relationship for a toxic effect. If a TEC associated with a contaminant mixture in sediments is desired, the TEC can be expressed in terms of the concentrations expected in a fish as a result of bioaccumulation (TEC_{fish}). The TEC_{fish} can be directly related to the potential for toxic effects in the fish (Cook et al., 1997a), or to wildlife or humans that eat the fish, and is calculated as the sum of products of the organic carbon-normalized concentration in sediment (C_{sac}) times the BSAF (equation 5) and the TEF for each of n chemicals. The fraction lipid (f) in the fish is included when the TEC_{fish} is calculated on the basis of whole fish, rather than lipid-normalized concentration. A TEC_{fish} can similarly be calculated for chemical concentrations in water with BAF_{ℓ}^{fd}s.

$$TEC_{fish} = \sum_{i=1}^{n} (C_{soc})_i\ (BSAF_{fish})_i\ (f_{\ell})\ (TEF_{fish})_i \qquad (5)$$

Equation 5, as adapted for lake trout eggs, was used retrospectively to determine the influence of TCDD and related chemicals on lake trout reproduction and population dynamics of lake trout in Lake Ontario since 1920 (Cook et al., 1994, 1997). Radionuclide-dated sediment sections from sediment cores were essential for construction of a historical exposure record which was then linked to effects on lake trout through the lake trout egg TCDD dose-early life stage mortality response relationship (Walker et al., 1994). The use of the lake trout egg TCDD dose-response relationship requires use of TEFs and BSAFs based on concentrations of chemicals in trout eggs to calculate TCDD toxicity equivalence concentrations which were based on lake trout eggs (TEC_{egg}s). Figure 10 summarizes the information that was generated by this analysis. The y-axis represents the chronology in years for 1 cm increments from the key reference sediment core from eastern Lake Ontario which were analyzed by high resolution gas chromatography/high resolution mass spectrometry. This core was selected to represent trends in Lake Ontario exposure conditions in this century. The toxicity equivalents of the more important congeners present in the 1 cm increments of sediment are plotted cumulatively on the x-axis such that each horizontal bar represents the TEC_{egg} predicted for lake trout on the basis of equation 5. The $BSAF_{egg}$s were adjusted to accommodate the effect of differences in $\prod_{socw}$ attributable to greater chemical loadings to the lake prior to 1970.

The relationship between predicted TEC_{egg}s and predicted degree of lake trout early life stage mortality is also indicated in Figure 10. For example, during the period from the 1940s to the 1970s, 100 percent early life stage mortality is predicted for this very sensitive fish species. The epidemiological records from Lake Ontario are consistent with this prediction, despite complications associated with the presence of non-chemical stressors such as sea lamprey predation and over-fishing during the period in which the lake trout population declined to virtual extinction by 1960. During the period of recovery of Lake Ontario after 1970, when lake trout were stocked and large populations of adult trout were restored, natural reproduction has not been achieved. However, eggs were collected from the stocked fish, fertilized, and early life stage development and survival monitored under laboratory conditions. The incidence of mortality due to blue-sac syndrome associated with TCDD was observed in the laboratory and is in good agreement with the percent mortality predicted with the TEC_{egg} model. After 1985, measured concentrations of TCDD and related chemicals in lake trout eggs were below the threshold for mortality associated with the blue-sac syndrome, and field observations of lake trout sac fry presence on spawning reefs increased with the first observations of 1- to 2- year old lake trout from natural reproduction occurring in 1994.

BAF_{ℓ}^{fd}s and BSAFs can be critical components of water and sediment criteria development. For example, to create a sediment criterion for the protection of future lake trout populations in the Great Lakes, the following factors should be considered: (1) the concentration of TCDD in the eggs that would be associated with no adverse effects to early life stages of lake trout (this includes effects at sublethal exposures that reduce survival of sac fry and alvins) and (2) the $BSAF_{egg}$s for lake trout under a $\prod_{socw}$ condition expected during the time period of interest. The concentration of TCDD in sediment that would be associated with a lack of adverse effects (sediment criterion) can be calculated from the concentration of TCDD in the egg associated with the threshold for toxic effects divided by the $BSAF_{egg}$. Similarly, a water criterion can be calculated using the BAF_{ℓ}^{fd} for TCDD.

To relate these TCDD criteria, whether they be sediment criteria or water criteria, to organisms exposed to complex mixtures of TCDD and related chemicals, differences in bioaccumulation must be considered along with the differences in toxic potency as expressed with TEFs. Bioaccumulation potentials of the different chemicals contributing to dioxin toxicity risks can be referenced to TCDD as with TEFs. In the GLWQI these were named bioaccumulation equivalency factors. The sum of TCDD toxicity equivalents is directly comparable to the water quality criterion or sediment quality criterion for TCDD under the TCDD toxicity equivalence model.

In conclusion, BAF_{ℓ}^{fd}s and BSAFs are essential for application of chemical-residue-based criteria in risk assessments and are interrelated through the sediment-water concentration quotient ($\prod_{socw}$), particularly for the more hydrophobic organic chemicals. They can incorporate elements of site-specific bioavailability. They are a specific interface between exposure assessments and effects assessments. They are a primary output in food chain bioaccumulation models used for validation of the models and comparisons to field data. Finally, measured bioaccumulation factors are effective for prediction of bioaccumulation in association with water or sediment quality criteria when used appropriately with time-averaged exposure estimates for persistent organic chemicals, especially those with a higher K_{ow}.

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Figure 1.

Framework for Predicting Bioaccumulation Factors
Applicable to Different Aquatic Ecosystems

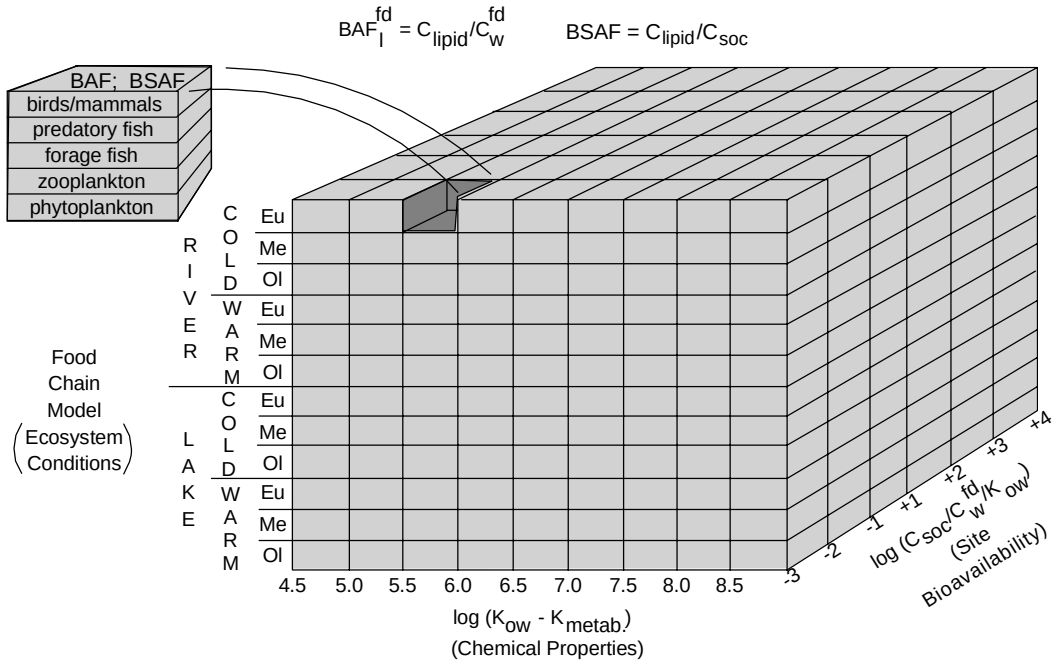


Figure 2.

Sediment-water column chemical concentration quotient
for Lake Ontario data of Oliver and Niimi (1988)

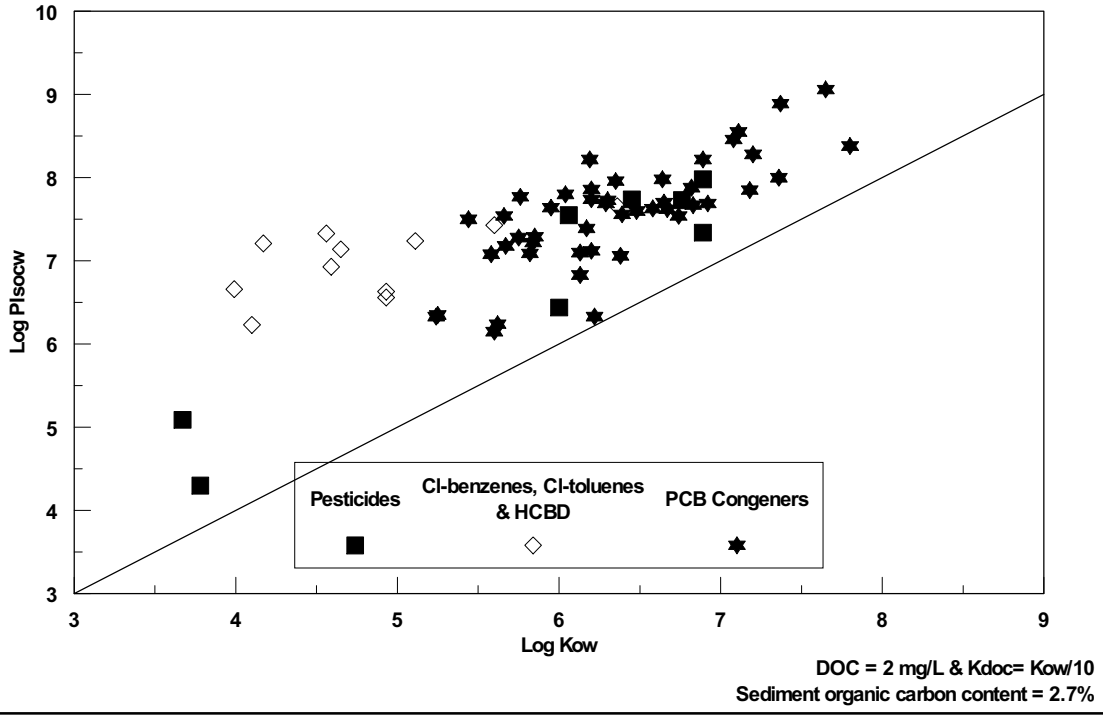


Figure 3.

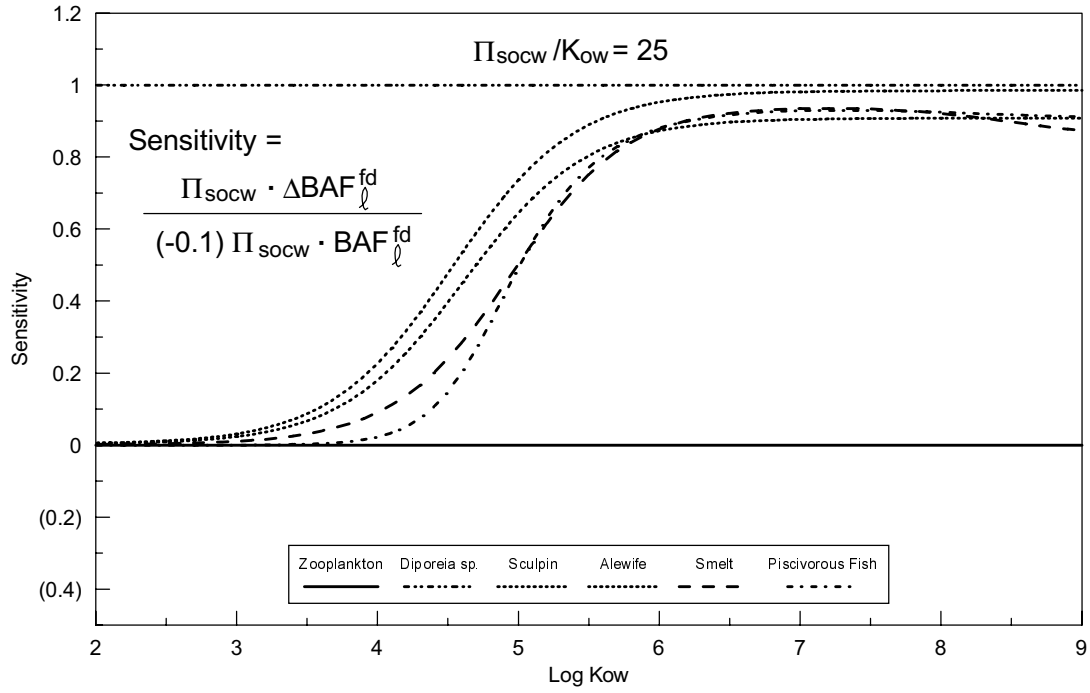


Figure 4.

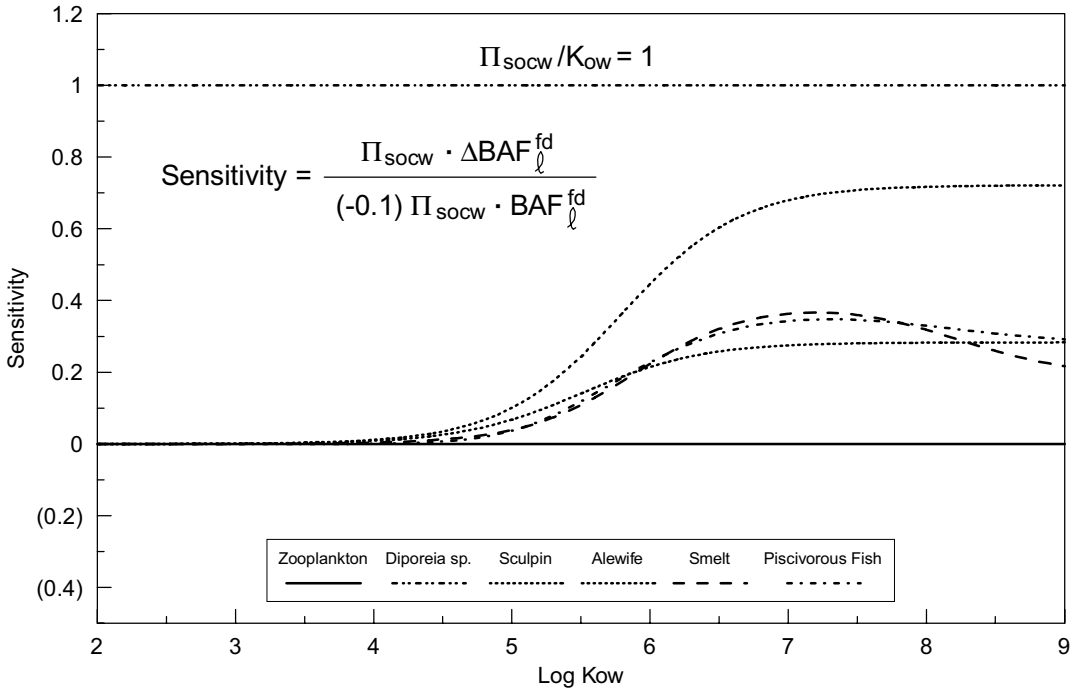
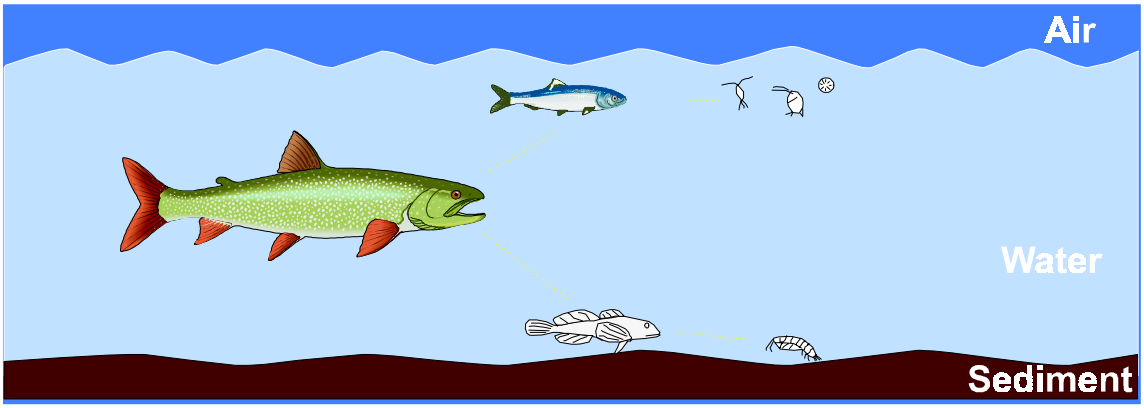


Figure 5.

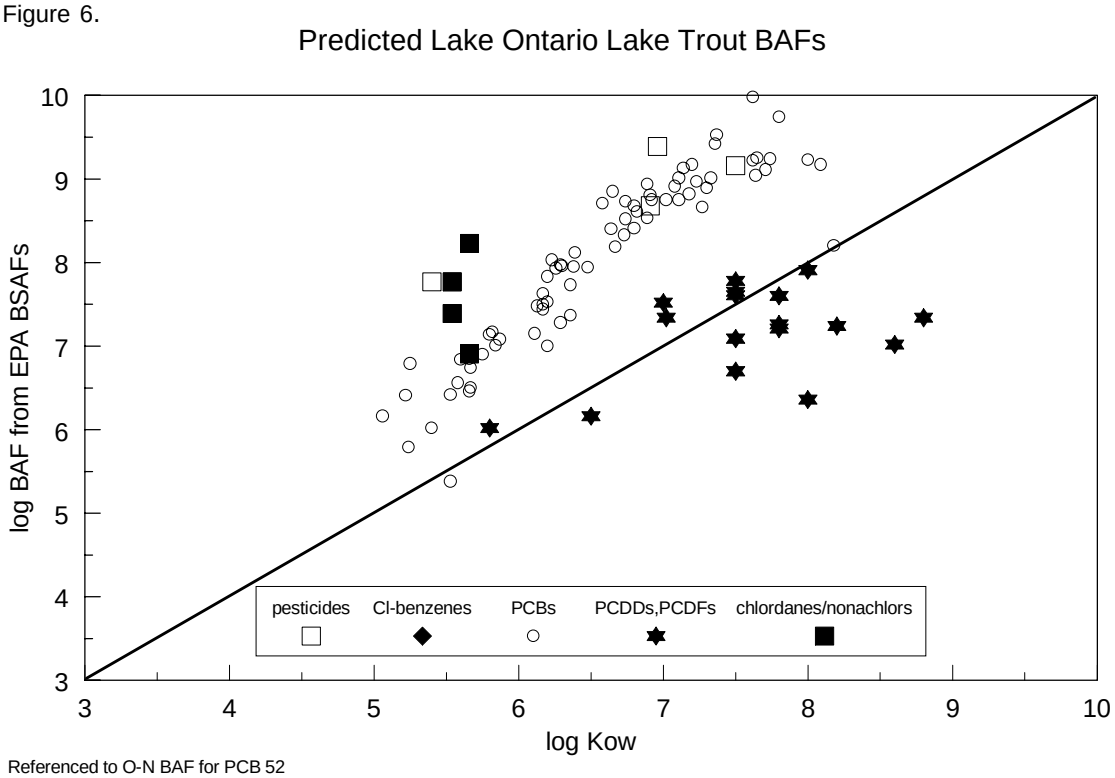


$$\Pi_{socw} = \frac{C_{soc}}{C_w^{fd}} = \frac{BAF_\ell^{fd}}{BSAF}$$

Sensitivities of BAF_ℓ^{fd}s and BSAFs to changes in Π_{socw} depend on:

1. K_{ow} of chemical
2. Benthic/pelagic contribution to food chain
3. Disequilibrium between sediment and overlying water (SOC - POC - C_w^{fd})

Figure 6.



Referenced to O-N BAF for PCB 52
Doc=2mg/L & Kdoc=Kow/10

Figure 7.

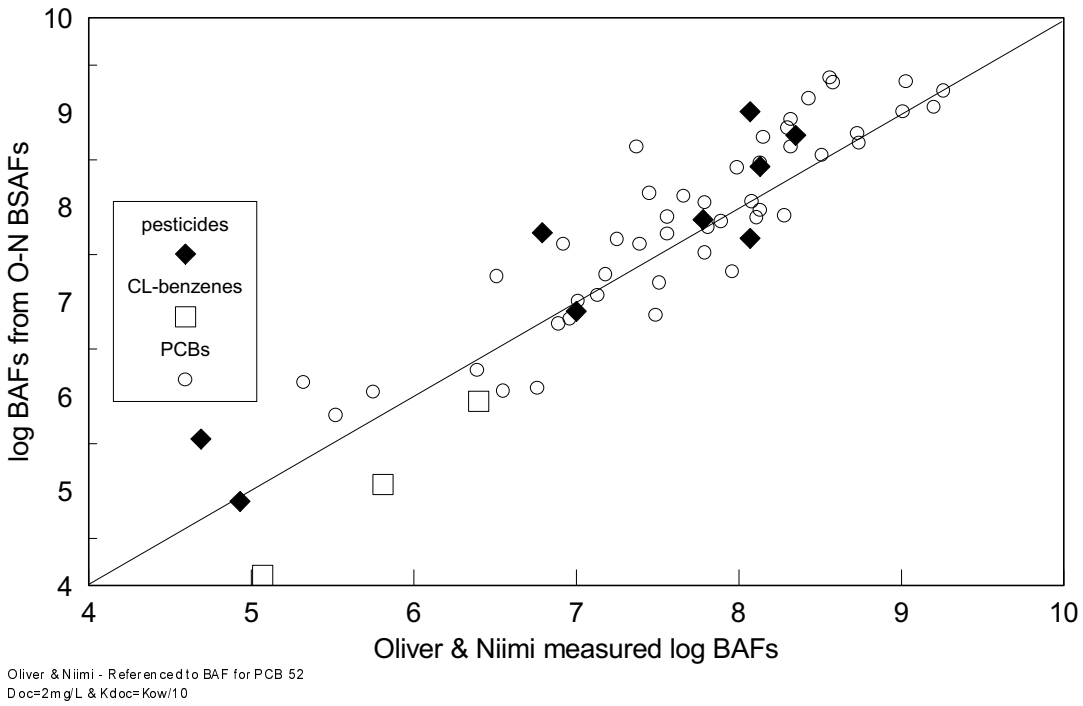


Figure 8.

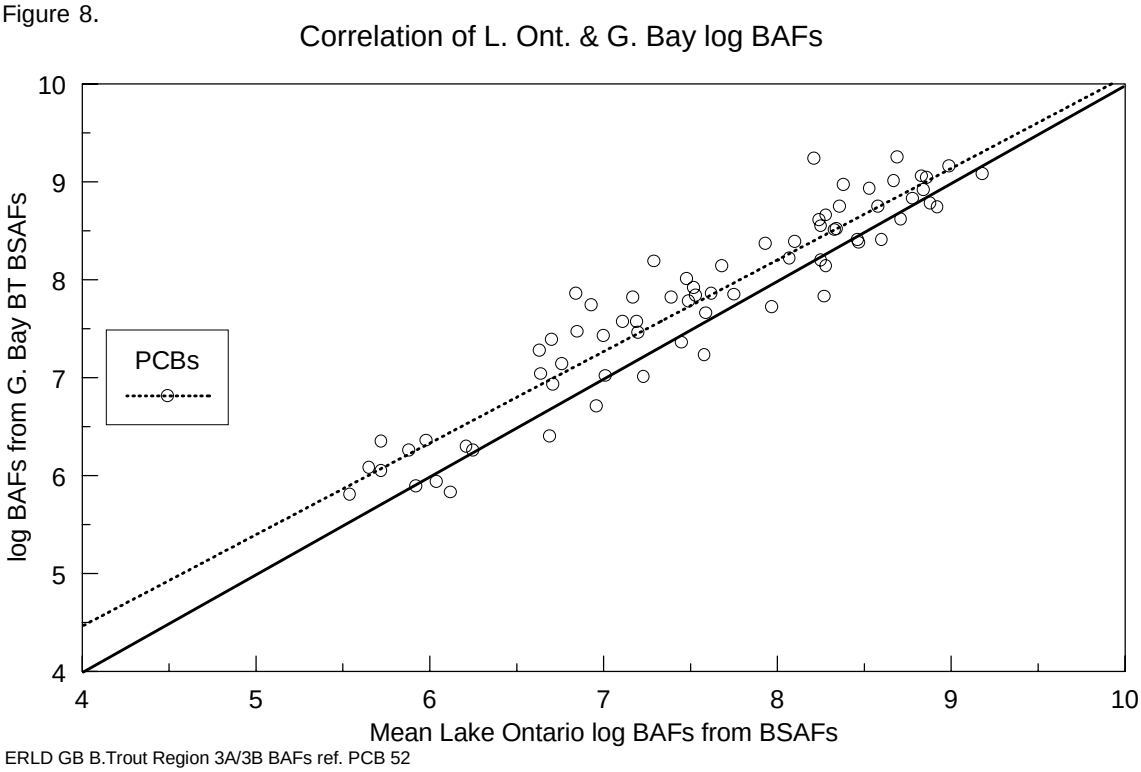


Figure 9.

Measured and Predicted BAFs for Piscivorous Fishes
Measured BAFs from Oliver and Niimi (1988)

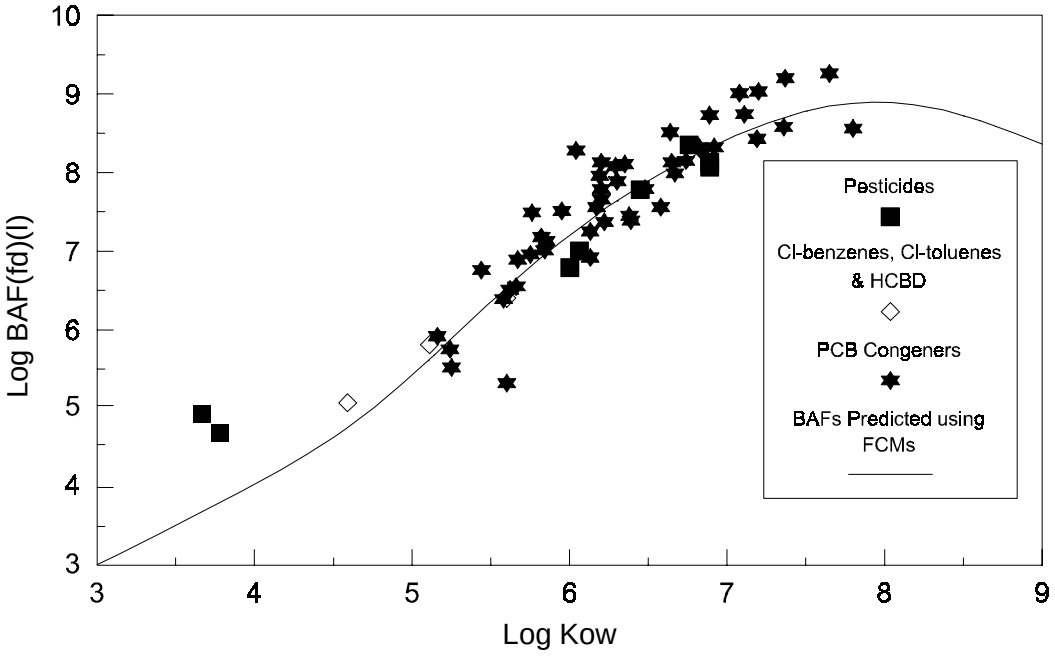
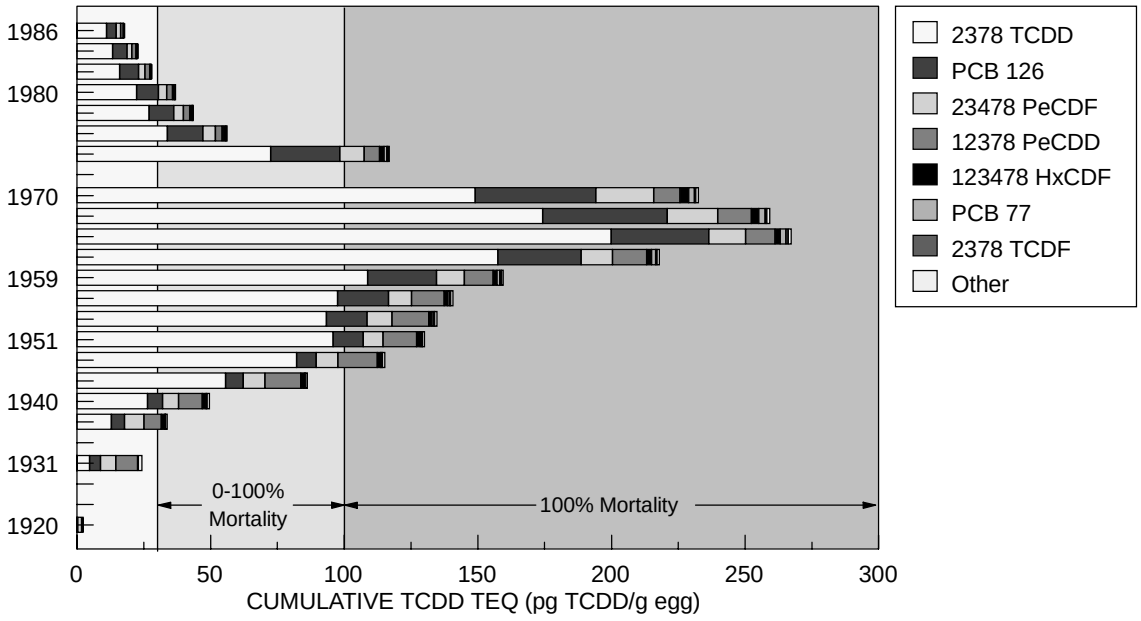


Figure 10.

Lake Ontario Lake Trout Egg RTEC Retrospective
Contribution of Individual Chemicals



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