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6 ASSESSING BIOACCUMULATION FACTORS OF PERSISTENT ORGANIC POLLUTANTS IN AQUATIC FOOD-CHAINS

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6.1 INTRODUCTION

As part of the Toxic Substances Management Policy (TSMP) under the revised, but not yet promulgated, Canadian Environmental Protection Act in Canada, the Waste Minimization Prioritization process of the USEPA and the Long-Range Transboundary Air Pollution (LRTAP) Protocol on Persistent Organic Pollutants (POPs) of the United Nations Environment Program, large numbers of chemical substances (*e.g.* approximately 22,500 chemicals used or imported in Canada that are currently on Canada's Domestic Substances List) are to be evaluated for their potential impact on the environment. This evaluation process involves the assessment of the toxicity, bioaccumulation and persistence of the chemical and a comparison of the assessed values to a set of standard criteria. The bioaccumulation criteria identified in the TSMP state that if the Bioconcentration Factor (BCF) or Bioaccumulation Factor (BAF) exceeds 5,000 or the logarithm of the octanol-water partition coefficient (log K_{ow}) of the chemical substance exceeds 5, the bioaccumulation criterion is exceeded. If the criteria for bioaccumulation, inherent toxicity and persistence are all exceeded, man-made chemical substances are being further evaluated in a screening level risk assessment with the purpose to consider the chemical substance for virtual elimination.

Because of the large number and great variety of chemical substances that are to be evaluated and the potential implications of the outcome of the evaluation process for industry, human and ecological health and regulators, it is important to develop sound methodologies for evaluating chemical substances for their bioaccumulation potential. This chapter summarizes and evaluates the ability of various methods to assess the bioaccumulation potential of persistent organic pollutants. The definitions

and mechanism of the bioconcentration, bioaccumulation and octanol-water partitioning of POPs are briefly reviewed. Secondly, empirical, semi-empirical and theoretical methods for the assessment of bioaccumulation properties are reviewed. Finally, the application of these methods for estimating BCFs and BAFs is evaluated and the uncertainties, merits and limitations of each method are discussed.

6.2 DEFINING BIOACCUMULATION

Since various quantities are being used to express the degree to which a chemical substance accumulates in organisms, it is useful to review their definitions. It should be recognized that there is some inconsistency in the use of these definitions in the literature. However, there is a general convergence to the use of the following definitions:

6.2.1 OCTANOL-WATER PARTITION COEFFICIENT

This is the ratio of the chemical concentrations in octanol (C_o) and in water (C_w) in an octanol-water system that has reached a chemical equilibrium:

$K_{ow} = C_o/C_w$ (equation 1)

Since octanol is a good surrogate phase for lipids in biological organisms, the octanol-water partition coefficient represents how a chemical would thermodynamically distribute between the lipids of biological organisms and water. It represents the lipophilicity and the hydrophobicity of the chemical substance. It is usually referred to as K_{ow} or P, or in its 10-based logarithmic form log K_{ow} or log P, and it is unitless.

6.2.2 BIOCONCENTRATION

Bioconcentration is a process where the chemical concentration in an aquatic organism achieves a level that exceeds that in the water as a result of exposure of the organism to a chemical concentration in the water via the respiratory surface (*e.g.* gills and/or skin).

Bioconcentration is the result of a balance between the rate of chemical uptake from the water via the respiratory surface of the organism (*e.g.* gills and skin) and the loss or elimination of chemical from the organism. Elimination of the chemical occurs predominantly via the respiratory surface (*e.g.* gills in fish), fecal egestion and metabolic transformation. However, chemical elimination can also occur through other mechanisms such as egg deposition in oviparous organisms or sperm production. Growth of the organism tends to lower or "dilute" the internal concentration in the organism. It can be viewed as a route of chemical elimination, although there is no net loss of chemical mass from the organism. It is important to

stress that growth dilution takes place at the same time as chemical uptake. Therefore as organisms grow and age, concentrations often increase because the rate of chemical uptake in the organism exceeds the rate of chemical elimination and growth dilution.

Bioconcentration typically refers to a condition, usually achieved under laboratory conditions where a chemical is absorbed by an organism from the water via the respiratory surface (*e.g.* gills) and/or the skin (*i.e.* there is no chemical uptake through food ingestion). Bioconcentration occurs if the concentration of a chemical substance in an aquatic organism achieves a level that exceeds that in the water. The extent of bioconcentration of a chemical substance is usually expressed in the form of a bioconcentration factor (BCF) which is the ratio of the chemical concentration in the organism (C_B) and the water (C_W):

$$BCF = C_B/C_W \quad \text{(equation 2)}$$

Because chemical sorption to particulate and dissolved organic matter in the water column may substantially reduce the fraction of the chemical in the water that can actually be absorbed by aquatic organisms, the BCF is more appropriately expressed in terms of the freely dissolved chemical concentration (C_{WD}):

$$BCF = C_B/C_{WD} \quad \text{(equation 3)}$$

The merit of defining the BCF in terms of the freely dissolved chemical concentration is that it is independent of the concentrations of particulate and dissolved organic matter in the water phase, which may vary from test to test, and hence more universal in its applicability. However, measurements of the freely dissolved chemical concentration in the water are difficult and while several methods have been applied, there are no generally recognized or standardized techniques available to measure freely dissolved concentrations. The chemical concentration in the organism (C_B) is usually expressed in units of gram of the chemical per kg of the organism and the BCF has units of L/kg. The weight of the organism can be expressed on a wet weight (WW), a dry weight (DW) or a lipid weight (LW) basis. Most commonly, the weight of the organism is expressed on a wet weight basis. However, when concentration measurements are made in specific tissues of the organism (rather than the whole organism), it is preferable to report the concentration on a lipid weight basis as organs and tissues can vary substantially in their lipid content. The lipid content is an important factor controlling not only the extent of chemical bioaccumulation of organic substances within an organism but also between organisms. Under conditions where lipid levels show relatively little variation over time, the extent of bioconcentration tends to be proportional to the lipid content of the organism (*e.g.* Geyer 1984, Gobas and Mackay 1987), resulting in higher BCF in organisms of higher lipid content. If lipid levels vary rapidly relative to the exchange of chemical between the organism and the water, there is a tendency for lipid based concentrations to increase with decreasing lipid content and

to decrease with increasing lipid content. The main purpose of expressing the BCF on a lipid weight basis, is to make it independent of the lipid content of the organism.

6.2.3 BIOMAGNIFICATION

Biomagnification is the process where the chemical concentration in an organism achieves a level that exceeds that in the organism's diet due to dietary absorption. The extent of chemical biomagnification in an organism is best determined under laboratory conditions where organisms are administered diets containing a certain concentration of the chemical substance while there is no chemical uptake through other routes of exposure (*e.g.* uptake from water in fish). Biomagnification can also be determined under field conditions based on chemical concentrations in the organism and its diet. Biomagnification factors derived under controlled laboratory conditions which exclude uptake through routes other than the diet, are different from those determined under field conditions because field based biomagnification factors are the results of chemical uptake through all routes of chemical uptake rather than dietary absorption alone.

The extent of chemical biomagnification is usually expressed in the form of a biomagnification factor (BMF) which is the ratio of the chemical concentration in the organism and the concentration in the organism's diet:

$$BMF = C_B/C_D \quad \text{(equation 4)}$$

The chemical concentration in the organism (C_B) and the diet of the organism (C_D) are usually expressed in units of respectively gram of the chemical per kg of the organism and gram of chemical per kg of food.

6.2.4 BIOACCUMULATION

Bioaccumulation is the process where the chemical concentration in an aquatic organism achieves a level that exceeds that in the water as a result of chemical uptake through all routes of chemical exposure (*e.g.* dietary absorption, transport across the respiratory surface, dermal absorption, inhalation). Bioaccumulation takes place under field conditions. It is a combination of chemical bioconcentration and biomagnification.

The extent of chemical bioaccumulation is usually expressed in the form of a bioaccumulation factor (BAF) which is the ratio of the chemical concentrations in the organism (C_B) and the water (C_W):

$$BAF = C_B/C_W \quad \text{(equation 5)}$$

Because chemical sorption to particulate and dissolved organic matter in the water column may substantially reduce the fraction of the chemical in the water that can

actually be absorbed by aquatic organisms (see discussion on bioavailability – section 6.2.7), the BAF can also be expressed in terms of the freely dissolved chemical concentration (C_{WD}):

$BAF = C_B/C_{WD}$ (equation 6)

The merit of defining the BAF in terms of the freely dissolved chemical concentration is that it is independent of the concentrations of particulate and dissolved organic matter in the water phase and hence more universal in its applicability from site to site. The chemical concentration in the organisms is usually expressed in units of gram of the chemical per kg of the organism. The weight of the organism can be expressed on a wet weight (WW), a dry weight (DW) or a lipid weight (LW) basis. Most commonly, the weight of the organism is expressed on a wet weight basis and the units of the BAF are L/kg. However, when concentration measurements are made in specific tissues of the organism (rather than the whole organism), it is preferable to report the concentration on a lipid weight basis as organs and tissues can vary substantially in their lipid content.

6.2.5 FOOD-CHAIN BIOACCUMULATION

Food-chain bioaccumulation is the process where chemical concentrations in organisms increase with each step in the food-chain resulting in contaminant concentrations in the predators that are greater than those in the prey. Because concentrations of many hydrophobic organic chemicals in organisms increase with increasing lipid content of the organism, the occurrence of food-chain bioaccumulation is best detected by comparing chemical concentrations in predators and prey on a lipid weight basis. If lipid based concentrations in organisms increase with increasing trophic level, there is evidence of food-chain bioaccumulation.

6.2.6 FOOD-CHAIN MULTIPLIER

The food-chain multiplier (FM) is a factor that is applied to the bioconcentration factors to account for chemical biomagnification in the food-web. It is used by the USEPA to derive bioaccumulation factors of very hydrophobic organic chemicals in higher trophic level organisms:

BAF = FM x BCF (equation 7)

6.2.7 BIOAVAILABILITY

Definitions of chemical bioavailability vary widely among environmental chemists, pharmacologists, physiologists and ecologists. In this chapter, bioavailability of a

chemical substance in particular environmental media such as water, sediment and the organism's food is defined as the fraction of the chemical in the medium that is in a form, shape or condition which can be absorbed by the organism. Bioavailability is usually expressed as fraction or a percentage and is specific to the medium in which the substance resides and the route of exposure.

6.3 METHODS FOR ASSESSING THE BCF AND THE BAF

There are three methodologies that can be used to assess the bioaccumulation behaviour of chemical substances in aquatic organisms. They include empirical methods, the application of semi-empirical relationships and theoretical models.

6.3.1 EMPIRICAL METHODS

The empirical methods that are available to assess the bioaccumulation behaviour of persistent organic pollutants include measurements of the BAF in the field and the BCF in laboratory based bioconcentration tests. Field based observations of the bioaccumulation factor typically involves the measurement of the chemical's concentration in the organism or in a particular tissue of the organism (C_B) and in the water (C_W) resulting in a BAF, which is C_B/C_W. These field derived BAFs are often the most preferred method for the assessment of a chemical's bioaccumulation behaviour because they provide the most direct evidence of the occurrence of bioaccumulation. One of the biggest difficulties associated with the determination of a BAF under field conditions involves the accurate measurement of the water concentration. Typically, water concentrations are low under field conditions and close to the analytical detection limit. This means that water concentration often cannot be measured as in many cases the actual concentration is below the detection limit. If the water concentrations are below the detection limit, it is useful to express the bioaccumulation factor relative to the concentration of the chemical in the sediment (C_S), in the form of a Biota-Sediment-Accumulation Factor (BSAF), *i.e.* C_B/C_S. However, the BSAF is typically many of orders of magnitude smaller than the BAF and therefore no substitute for a BAF. A second problem associated with the derivation of field derived BAFs concerns the difficulty associated with the measurement of the freely dissolved chemical concentration in the water. For chemicals with a log K_{ow} less than 5, measurements of the freely dissolved chemical concentration are typically of little concern because the majority of the chemical in the water is in the freely dissolved form and the total concentration in the water therefore equals the freely dissolved concentration. However, for chemicals with greater log K_{ow}, this is no longer the case and the concentration of freely dissolved chemical in the water is only a small fraction of the total concentration in the water. The remainder of the chemical is present in a "sorbed" state and is associated with particulate or dissolved organic matter in the water phase. With increasing K_{ow}, the fraction of freely dissolved chemical in the water is expected to fall and can reach

levels that are only 1% or less. When using the total water concentration in the derivation of a BAF, the ability of the chemical to bioaccumulate can be underestimated considerably, *e.g.* a 100 fold if C_{WD} is only 1% of C_W. Although there have been attempts to develop methods for the determination of freely dissolved chemical concentration (Landrum *et al.* 1984, Yin and Hasset 1986, Sproule *et al.* 1991), most of the methods are still in an experimental stage and their measurements should be treated with caution. Variations in water concentration over time can also have an important effect on the determination of accurate water concentrations (Gobas and Zhang 1992). For example, if the concentration of a chemical substance in the water falls quickly over time (*e.g.* due to a reduction in source loading, seasonally based evaporation or algae blooms) and the chemical concentration in the organism can not respond to the lower concentration quickly enough due to its slow elimination rate, the observed BAF will overestimate the bioaccumulation behaviour of the chemical substance. Likewise, a rapid increase in water concentration can result in an apparent BAF that is lower than the actual BAF, which would have been achieved given sufficient time to reach a steady-state between water and organism. This effect is expected to be more important for chemicals with high log K_{ow} (*i.e.* greater than 5) as these chemicals often exhibit slow depuration kinetics, requiring long periods of time to achieve steady-state.

The type of organism that is collected can also affect the BAF. Organisms at higher trophic levels may contain higher concentrations than organisms at lower trophic levels due to biomagnification in organisms of lower trophic level. Differences among organisms in their ability to metabolize chemical substances, growth patterns, lipid levels, contaminant exposure histories, diet compositions and habitats all will have an effect on the BAF values that are determined under field conditions. It can therefore be concluded that while field derived BAFs probably provide some of the most direct evidence of bioaccumulation of the chemical in the aquatic environment, they are difficult to extrapolate to other organisms, locations or time periods.

Bioconcentration tests are performed under laboratory conditions and result in the measurement of a BCF, which is different from a BAF as it does not include the accumulation of chemical from the diet and any possible food-chain magnification effects. Protocols for bioconcentration tests can be found in "Standard Practice for Conducting Bioconcentration Tests with Fishes and Saltwater Bivalve Molluscs" (American Standards for Testing and Materials 1988) and the "Bioaccumulation: Flow-through Fish Test" (Organization for Economic Co-operation and Development (1996), 305E). The bioconcentration tests involve aqueous exposures of organisms to the test chemical in flow-through aquaria followed by a depuration phase, in which the organisms are moved to tanks that contain uncontaminated water. The test methods and their merits and limitations have been recently reviewed by Gobas and Morrison (1999). The main advantage of bioconcentration tests, is that they are carried out under controlled conditions and the results can be reproduced by other investigators, hence providing a method of verification that is difficult to obtain when field measurements are involved. However, measurements of the BCF suffer from some of the same experimental difficulties associated with the measurement of the freely dissolved chemical concentration as the field derived BAFs. In addition,

the tests are often carried out in a 3 to 4 week time period, which for many chemical substances is too short to reach a steady-state. Given also the lack of chemical uptake from food, the BCFs derived under laboratory conditions often underestimate the bioaccumulation potential of chemical substances considerably. This underestimation is particularly significant for chemicals with a log K_{ow} greater than 5 as these chemical tend to be associated with particulate or dissolved organic mater, exhibit slow uptake and elimination kinetics and under field conditions are largely absorbed via the diet.

6.3.2 SEMI-EMPIRICAL MODELS

One of the most popular methods to assess the bioconcentration factors of organic chemicals is the application of correlations between the bioconcentration factor and the octanol-water partition coefficient, which take the following form:

$$\log BCF = \alpha \times \log K_{ow} + \beta \quad \text{(equation 7)}$$

where α and β are constants derived through linear regression of the experimental data. These correlations have a theoretical basis in that they assume that the bioconcentration process in fish is essentially a chemical partitioning process, where the chemical exchanges between the water and the tissues of the organism (via the respiratory surface). This theory, which was first proposed by Hamelink *et al.* (1971), was later explored by Veith *et al.* (1979) and thermodynamically formulated by Mackay (1982), essentially views a fish as a droplet of lipids, represented by a surrogate solvent octanol, in equilibrium with the chemical in the water. The BCF of chemicals with a log K_{ow} greater than 1 can thus be expressed as (Gobas and Mackay, 1987) as either equations 8 or 9:

$$BCF = L_B \times K_{ow} \quad \text{(equation 8)}$$

$$\log BCF = \log L_B + \log K_{ow} \quad \text{(equation 9)}$$

Where L_B is the lipid content of the organism (kg lipid/kg organism) and K_{ow} is the octanol-water partition coefficient, which mimics the chemical's partition coefficient between the organism's lipid tissues and the water.

A large number of log BCF-log K_{ow} correlations have been reported in the literature. For example, Connell (1990) summarizes 29 of these correlations with α varying between 0.54 and 1.2 and β varying between -1.71 and 1.89. Some of the reported log BCF- log K_{ow} relationships are illustrated in Figure 1. This Figure shows the large variations between the reported correlations, which span approximately 4 orders of magnitude.

A frequently used correlation is that of Veith and Kosian (1983) for a series of simple hydrophobic organic substances in fish:

$$\log BCF = 0.79 \times \log K_{ow} - 0.4 \quad \text{(equation 10)}$$

The majority of the published correlations report linear relationships between log BCF and log K_{ow} that have a slope less than 1.0, which deviates from the theoretical model and suggests that the BCF follows a parabolic relationship with K_{ow}, *e.g.* in the case of equation 11.

$$BCF = 0.40 \times K_{ow}^{0.79} \quad \text{(equation 11)}$$

Mackay (1982) suggested that the relationships between log BCF and log K_{ow} should have a slope of 1.0 and proposed that the following equation should be used:

$$BCF = 0.048 \times K_{ow} \quad \text{(equation 12)}$$

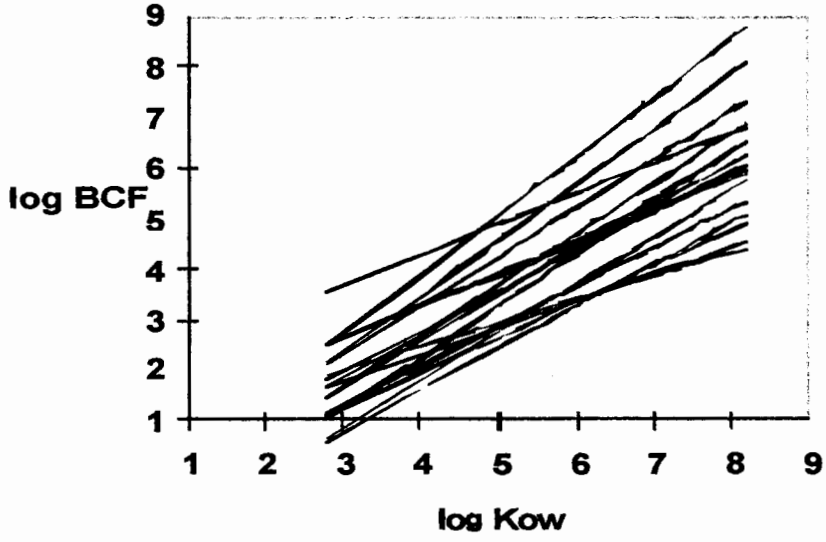


Figure 1: Some reported linear log BCF (L/kg wet weight) vs. log K_{ow} relationships for hydrophobic organic chemicals in fish.

Non-linear correlations between log BCF and log K_{ow} have also been reported. For example, Bintein *et al.* (1993) suggested a "parabolic"-type relationship, characterized by a linear relationship between log BCF and log K_{ow} for chemicals

with a log K_{ow} less than 6, an optimum log BCF for chemicals with a log K_{ow} around 6 and then a declining log BCF with increasing log K_{ow} for chemicals with a log K_{ow} greater than 6:

$$\log BCF = 0.910 \times \log K_{ow} - 1.975 \times \log(6.8 \times 10^{-7} \times \log K_{ow} + 1) - 0.786 \quad \text{(equation 13)}$$

This equation tends to represent the optimum in the log BCF- log K_{ow} relationship, which is often observed in empirical data sets. Most recently, Meylan *et al.* (1999) proposed correlations with K_{ow}, drawing from a substantial database of approximately 694 substances, that include correction factors F_i for specific classes of chemical substances:

$$\log BCF = 0.77 \times \log K_{ow} - 0.70 + \Sigma F_i \quad \text{(for log } K_{ow} \text{ between 1 and 7)} \quad \text{(equation 14)}$$

$$\log BCF = -1.37 \times \log K_{ow} + 14.4 + \Sigma F_i \quad \text{(for log } K_{ow} \text{ greater than 7)} \quad \text{(equation 15)}$$

where ΣF_i is the sum of all the correction factors.

The variation in available log BCF- log K_{ow} correlations makes it hard to select an appropriate equation for making BCF estimates. When using the log BCF- log K_{ow} correlations to assess BCFs, it is important to be aware of how the correlation was derived. One of the key issues in the relationship between the BCF and K_{ow} is that it tends to be linear but only for chemicals that are not metabolized and that have a log K_{ow} between approximately 1 and 5. The reason is that such chemicals are mainly absorbed from the water and the uptake and depuration kinetics are relatively rapid, allowing the chemical concentration in the organism to reach a steady-state with that in the water during the bioconcentration test. For chemicals with a log K_{ow} greater than approximately 5, the linear correlation between BCF and K_{ow} breaks down. For these superhydrophobic chemicals, the BCF is often much lower than expected from the chemical's octanol-water partition coefficient. The reason for this loss of linear correlation lies in a number of biological and chemical processes (*i.e.* the role of fecal egestion, growth, slow uptake and depuration kinetics) as well as experimental artifacts *i.e.* bioavailability, short exposure periods in bioconcentration tests, difficulties maintaining stable water concentrations over time) which are discussed in more detail in Gobas *et al.* (1989) and Gobas and Morrison (1999). The range of chemicals included in the correlation may therefore have a large effect on the correlation reported. In general, there is a tendency for α values to drop and for β values to increase if more higher log K_{ow} (greater than 5) chemicals are included in the correlation.

6.3.3 THEORETICAL MODELS

There are many different types of theoretical models regarding the bioconcentration

and bioaccumulation of hydrophobic organic chemicals in aquatic organisms. The models range from simple compartmental models, representing organisms or parts of organisms as a "black" box (Spacie and Hamelink 1982) to internal pharmacokinetic models describing chemical transport between various organs within the organism (*e.g.* Nichols *et al.* 1990, Law *et al.* 1991). Some of these models have recently been reviewed by Gobas and Morrison (1999). The most frequently used food-web bioaccumulation models are the models by Thomann *et al.* (1989, 1992) and Gobas (1993). Campfens and Mackay (1997) have recently developed an alternative fugacity based model. All of these models contain sub-models describing the bioaccumulation in various organisms of aquatic food-chains. The sub-models are linked to represent the transfer of the chemical substance within a food-chain or food-web from prey to predator. All of the available food-web bioaccumulation models are based on a set of mass-balance equations (one for each organism), describing the rates of chemical uptake and elimination in the organism. The mass balance equations are solved by applying a steady-state assumption, hence assuming that chemical concentrations in water, sediment and organism have achieved a steady-state. The rates of chemical uptake and elimination are assessed by different means in the models. All of these models can be parameterized to represent conditions that representative of the environment of interest. The models have all been validated for a range of organochlorines in organisms of the Lake Ontario food-chain. However, other model validation exercises have also been reported (Morrison *et al.* 1997, Gobas *et al.* (1998) and a comparison of the behaviour of some of the models has been reported in Burkhard *et al.* (1997). The models are widely used. For example, the Gobas model has been reviewed by the US-EPA (1994) and is being applied in the US-EPA's Great Lakes Water Quality Initiative (US-EPA 1995). The models are widely accessible. For example, the Gobas model is presented in a self-contained MicroSoft-Wind$_{ow}$s based program or in Excel spreadsheet and can be downloaded from http://www.rem.sfu.ca/toxicology/. The Campfens and Mackay (1997) model can be downloaded from http://www.trentu.ca/academic/aminss/envmodel/welcome.html and the Thomann model can be obtained from the author.

The strength of the models is that they represent some of the most current and in-depth insights into the bioaccumulation process. The models contain equations that can be used to assess the fraction of freely dissolved chemical in the water phase and hence derive BCFs and BAFs that are based on the freely dissolved chemical concentration in the water. They can also account for many organism and chemical specific factors, such as the lipid content of the organism, body weight, growth, feeding characteristics, and temperature, and can be used to investigate how bioaccumulation factors may vary under different environmental conditions.

6.4 EVALUATION OF METHODS FOR ASSESSING BCFs AND BAFs

Since the bioaccumulation of chemical substances is typically assessed through either semi-empirical or theoretical models, it is worthwhile to investigate to what degree these methods are able to estimate the chemical's bioaccumulation behaviour in the

environment. For that purpose, we have derived BCFs and BAFs through various log BCF-log K_{ow} correlations and through a bioaccumulation model and then compared the assessed values to the actual BAFs observed in the field. While, there are many log BCF-log K_{ow} correlations that could be used to do this, we selected the correlation reported by Veith and Kosian (1983), *i.e.* equation 10, as well as those by Mackay (1982), *i.e.* equation 12, and Bintein (1993), *i.e.* equation 13, because they are frequently used, are based on relatively large number of chemicals and represent different correlation techniques. The BCF was also assessed through equation 8, which is a theoretical log BCF-Log K_{ow} relationship following Gobas and Mackay (1987). This relationship is specific to the species of interest because it requires that the lipid content of the species is used to calculate the BCF. Model calculations of the BAFs were also conducted by using the food-chain bioaccumulation model reported in Gobas (1993). The model equations are reported in Gobas *et al.* (1993) and the spread-sheet version of the model, downloadable from http://www.rem.sfu.ca/toxicology/ was used to conduct the calculations. The model input parameters are listed in Table 1. The calculations were conducted to assess the BAFs of a set of PCBs, chlorobenzenes, DDT and its metabolites, mirex, hexachlorobutadiene, octachlorostyrene (OCS) and some others in sculpins, alewife, smelt and large salmonids (*i.e.* a combination of lake trout, rainbow trout and coho salmon) in Lake Ontario, determined by Oliver and Niimi (1988). The observed BAFs of the chemicals in these lake Ontario species were derived by dividing observed concentrations in fish by the observed total (*i.e.* freely dissolved and sorbed chemical) chemical concentration in the water reported by Oliver and Niimi (1988). Octanol-water partition coefficients were taken from Hawker and Connell (1988) for PCBs, Veith *et al.* (1979) for OCS and Mackay *et al.* (1992) for the other chemicals. Only those chemical substances for which all required data were available were included in the BAF calculations.

The extent of systematic over or underprediction of the actual BAF by the assessed BCF or BAF was characterized by the "model bias" or MB, *i.e.* respectively,

$$MB = 10^{(\Sigma^{n}_{i=1}\ \log(BAF_{obs,i}/BCF_{calc,i})/n)} \quad \text{(equation 16)}$$

$$MB = 10^{(\Sigma^{n}_{i=1}\ \log(BAF_{obs,i}/BAF_{calc,i})/n)} \quad \text{(equation 17)}$$

where $BCF_{calc,i}$ and $BAF_{calc,i}$ are the model calculated BCF and BAF and $BAF_{obs,i}$ is the observed BAF for a chemical substance i. In essence, MB is the mean of the distribution of $\log(BAF_{obs}/BAF_{calc})$ or the geometric mean of distribution of (BAF_{obs}/BAF_{calc}). If, on average, calculated and assessed BAFs are equal, then MB is 1.0 and there is no systematic over or under prediction by the bioaccumulation assessment method. If MB>1, then the observed BAFs are on average greater than the assessed BCFs or BAFs. If MB<1, then the observed BAFs are on average smaller than the calculated values. For example, a MB of 5 means that on average, the observed BAFs are 5 times greater than the assessed values; hence the method

has a tendency to underestimate the BAFs by a factor of 5. An MB of 0.2 implies that on average the observed BAFs are 5 times smaller than the assessed values.

The extent of uncertainty is expressed by the 95% confidence intervals (CI) of the distribution of $\log(BAF_{obs}/BAF_{calc})$. The CI represent the range of predicted concentrations that includes 95% of the concentration observations. Because of the log-normal distribution of (BAF_{obs}/BAF_{calc}), the 95% confidence intervals can be presented as a constant factor of the mean. For example, if $\log(BAF_{calc}/BAF_{obs})$. has a mean of 0, (*i.e.* the geometric mean of BAF_{calc}/BAF_{obs} is 1.0) and CI of 0.3 and -0.3, then the assessment method produces no systematic over - or under prediction of the observed concentrations, *i.e.* MB equals 1, and model predicted values ranging between $10^{0.3}$ (or 2) and $10^{-0.3}$ (or 0.5) times the geometric mean include 95% of the observed BAFs. The larger the CI, the greater the uncertainty of the bioaccumulation assessment methodology.

The results of the analysis are graphically illustrated in Figures 2 and 3 and in Table 2. Figure 2, which shows the relationship between the BCF and BAF, assessed through model calculations, and the BAF observed in sculpins and in Lake Ontario salmonids. The results illustrate that BCFs calculated through equation 10, tend to underestimate observed BAFs in the field, on average by a factor of 32 for sculpins and 98 for the higher trophic level salmonids (Table 2). The 95% confidence intervals are approximately an order of magnitude. The underestimation is caused in part by the role of dietary uptake that is not considered in the log BCF-log K_{ow} correlations. For this reason, BAFs in salmonids are underestimated to a much greater degree than those in sculpins. However, as Figure 3 illustrates, even chemicals with relatively low log K_{ow} (*i.e.* less than 5) and which are not expected to biomagnify in the food-chain are underestimated by equation 10 by an order of magnitude or more. The latter is likely due to experimental error in the derivation of the correlation and should be considered when applying the correlation to assess a BCF.

The extent of underestimation of the actual BAFs is less when Equation 12 is used. However, as Table 2 illustrates, the BCFs calculated are still on average underestimating the BAF by a factor of 13 to 14 for sculpins and a factor of 42 to 43 the higher trophic level salmonids. The 95% confidence intervals are approximately an order of magnitude. Compared to equation 10, the Mackay correlation does a somewhat better job estimating the BCFs of high K_{ow} chemicals due to the steeper slope of the correlation.

The non-linear equation, *i.e.* equation 13, provided estimates of the BCF that are approximately 100 to 400 fold smaller than actually observed BAFs for the same chemicals. Associated 95% CI values were also very large. The reason for the large underestimation of actual BAF values is that this correlation is most susceptible to experimental artifacts and error associated with the measurement of BCFs of high K_{ow} chemicals. This is further illustrated in Figure 3 which shows that the discrepancy between calculated BCFs and observed BAFs increases with increasing K_{ow} and can amount up to a factor of 10,000 for chemicals with a log K_{ow} of 7 to 8.

The theoretically based log BCF- log K_{ow} relationship is able to reduce the discrepancy between observed and predicted bioaccumulation factors by 3 to 8 fold

Table 1: Input parameters for the bioaccumulation model used to assess BAFs.

Parameter	Input Value(s)/Source
Chemical characteristics	
Octanol-water Partition Coefficient	Hawker and Connell (1988), Veith *et al.* (1979), Mackay *et al.* (1992)
Total water concentration	Data from Oliver and Niimi (1988)
Sediment concentration	Data from Oliver and Niimi (1988)
Environmental Properties	
Mean water temperature	8 °C (Oliver and Niimi 1988)
Organic content of water	0.00000025 kg/L
Organic carbon content of sediments	2% (Oliver and Niimi 1988)
Density of lipids	0.9 kg/L
Density of organic carbon	0.9 kg/L
Metabolic transformation rate constant	0 d^{-1}
Species characteristics	
Phytoplankton lipid content	0.5% (Oliver and Niimi 1988)
Mysids (*Mysis relicta*) lipid content	5.0% (Oliver and Niimi 1988)
Pontoporeia (*Pontoporeia affinis*) lipid content	3.0% (Oliver and Niimi 1988)
Oligochaetes (*Tubifex tubifex*) lipid content	1.0% (Oliver and Niimi 1988)
Sculpin (*Cottus cognatus*)	
Weight	5.4 g (Oliver and Niimi 1988)
Lipid content	8.0% (Oliver and Niimi 1988)
Diet	18% zooplankton, 82% *Pontoporeia* (Flint 1986)
Alewife (*Alosa pseudoharengus*)	
Weight	32 g (Oliver and Niimi 1988)
Lipid content	7.0% (Oliver and Niimi 1988)
Diet	60% zooplankton, 40% *Pontoporeia* (Flint 1986)
Smelt (*Osmerus mordax*)	
Weight	16 g (Oliver and Niimi 1988)
Lipid content	4.0 % (Oliver and Niimi 1988)
Diet	54% zooplankton, 21% *Pontoporeia*, 25% sculpins (Flint 1986)
Salmonids (*Salvelinus namaycush*, *Salmo gairdneri*, *Oncorhynchus velinus namaycush*)	
Weight	2410 g (Oliver and Niimi 1988)
Lipid content	16% (Oliver and Niimi 1988)
Diet	10% sculpin, 50% alewife, 40% smelt (Flint 1986)

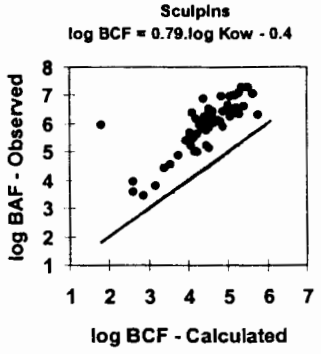
compared to the empirically based linear correlations, represented by equations 10 and 12. This simple theoretical model still underestimates BAFs in the field by 8 (for sculpins) to 13 (for salmonids) fold. One of the reasons for the improvements of this method over empirically based correlations is the ability of the method to take into account the lipid content of the organism. Typically, bioconcentration experiments are conducted with relatively small fish that tend to have lower lipid contents, while higher trophic level fish often contain higher degrees of body fat, which can lead to a greater degree of bioaccumulation. Also, this linear model is less susceptible to the duration of the bioconcentration tests by assuming that chemical equilibria between the water and the organism are achieved.

The results indicate that theoretical food-chain models, which are developed to estimate BAFs of chemicals in the field, are the best tool to assess BAFs. The model that was explored showed only a minor overestimation of the BAFs in the field for sculpins, smelt and salmonids and a small underestimation of BAFs for alewife. The main reason for the improved prediction of the BAFs is that dietary uptake, long exposure times, growth and differences in lipid content among the various organisms is taken into account. The uncertainty in the model predictions as expressed by the 95% CI ranged between a factor of 3 to 5 for the various fish species (Table 2).

Table 2: Comparison of bioconcentration and bioaccumulation factors estimated by several methods to observed bioaccumulation values for four fish species: MB represents the average extent of over- (MB<1) or underestimation (MB>1) of the actual BAF by the estimation methods; CI represents the 95% confidence interval of BAF_{obs}/BCF_{calc} or BAF_{obs}/BAF_{calc}.

	log BCF = 0.79 x log K_{OW} - 0.40 (Veith and Kosian 1983)		**BCF = 0.048 x K_{OW} (Mackay 1982)**		**log BCF = 0.910 x log K_{ow} - 1.975 x log(6.8 x 10^{-7} x log K_{ow} + 1) - 0.786 (Bintein 1993)**		**log BCF = 1.0 x log K_{OW} + log L Gobas and Mackay (1987)**		**Bioaccumulation Model Gobas (1993)**	
Species	**MB**	**CI**	**MB**	**CI**	**MB**	**CI**	**MB**	**CI**	**MB**	**CI**
Sculpins	32	11.2	13.6	14.1	114	55	8.2	14	0.78	5.5
Alewife	35	9.0	14.4	13.3	140	20	9.9	13	1.18	3.5
Smelt	34	9.3	14.3	11.9	132	29	17	12	0.83	4.4
Salmonids	98	8.7	42.7	11.6	362	32	13	12	0.74	4.2

A


Sculpins
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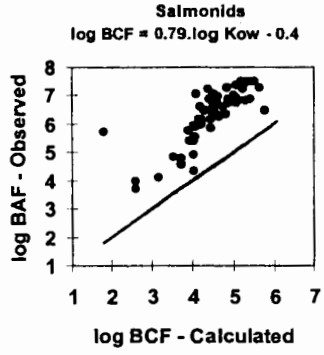
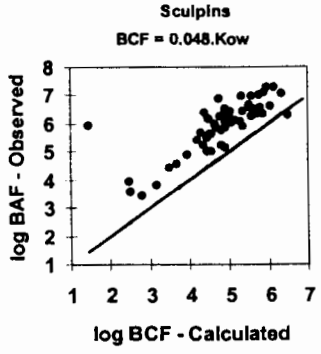
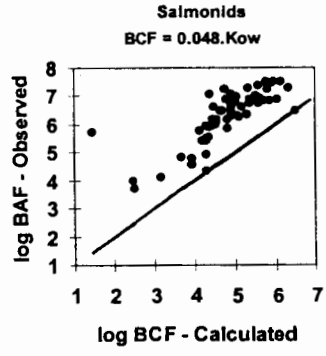
log BAF - Observed
log BCF - Calculated

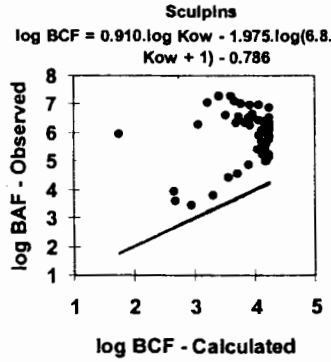

Salmonids
log BCF = 0.79.log Kow - 0.4
log BAF - Observed
log BCF - Calculated

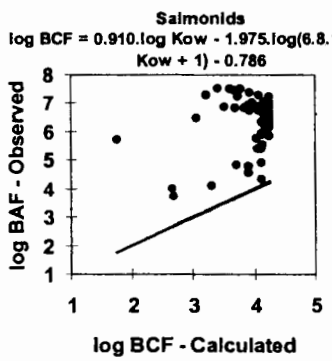
B


Sculpins
BCF = 0.048.Kow
log BAF - Observed
log BCF - Calculated

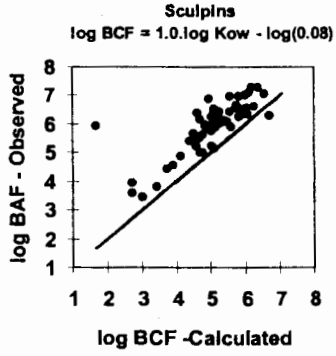

Salmonids
BCF = 0.048.Kow
log BAF - Observed
log BCF - Calculated

C


Sculpins
log BCF = 0.910.log Kow - 1.975.log(6.8.10-7.log Kow + 1) - 0.786
log BAF - Observed
log BCF - Calculated


Salmonids
log BCF = 0.910.log Kow - 1.975.log(6.8.10-7.log Kow + 1) - 0.786
log BAF - Observed
log BCF - Calculated

D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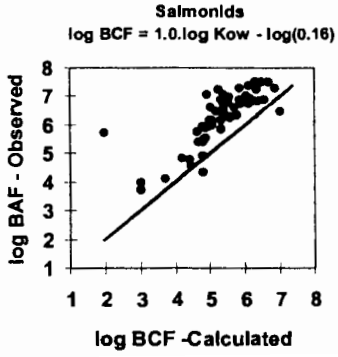
log BAF - Observed
log BCF -Calculated


Salmonids
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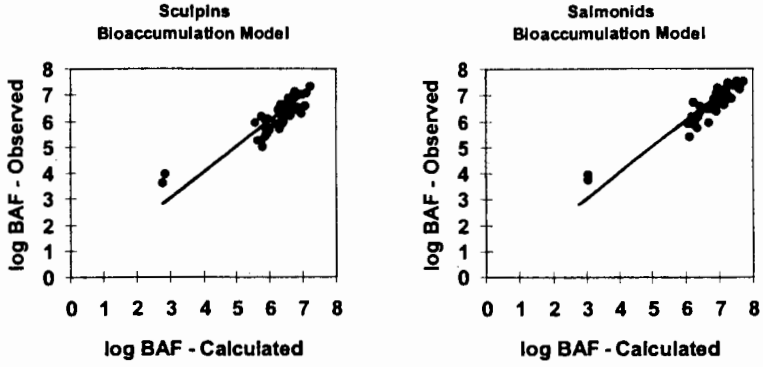
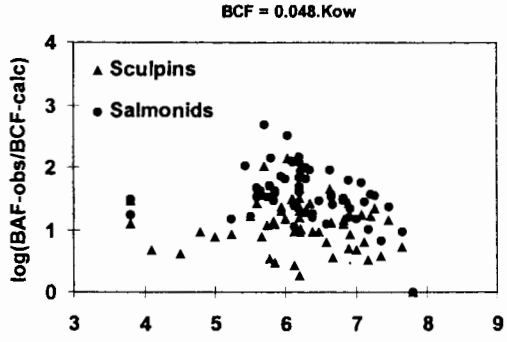
log BAF - Observed
log BCF -Calculated

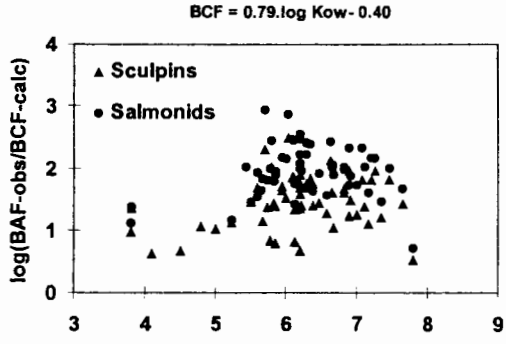


E

Figure 2: A comparison of observed BAFs with BCFs and BAF that were predicted by different log BCF-log K_{ow} correlations and theoretical models.



A



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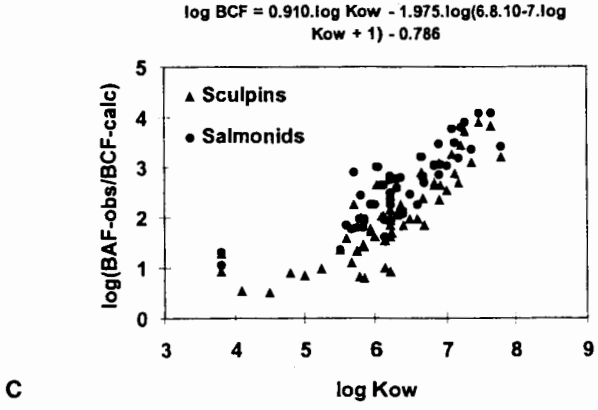

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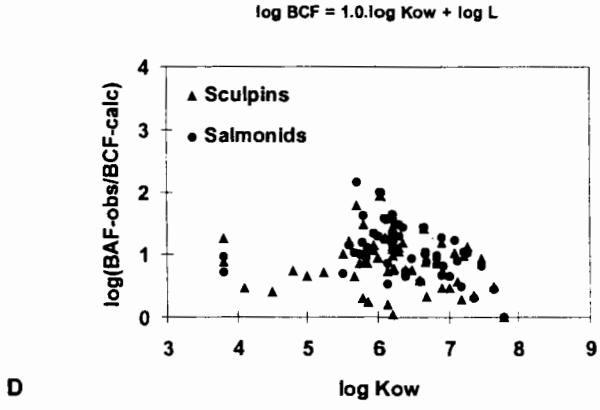

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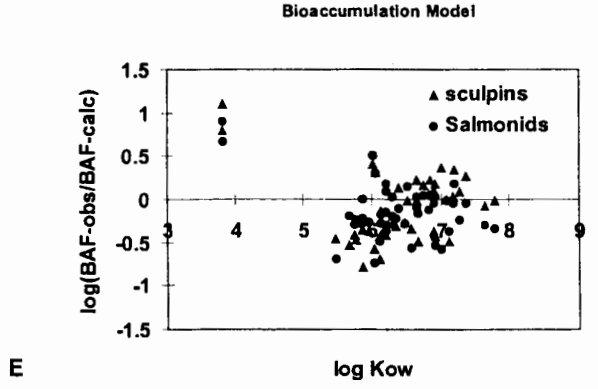

E

Figure 3: The logarithm of the ratio of the observed BAF to the calculated BCF or BAF as a function of the log K_{ow} for a series of organic chemicals The higher the ratio, the greater the overestimation.

6.5 OVERALL DISCUSSION

When evaluating chemicals on their bioaccumulation behaviour according to Canada's TSMP, Europe's UNEP or the Waste Minimization Protocol by the USEPA's Office of Solid Waste, data regarding the BCF, BAF or K_{ow} can all be used to assess whether a chemical substance meets certain bioaccumulation criteria or not. However, as explained earlier K_{ow}, BCF and BAF are very different measures of the bioaccumulation behaviour. If either of these bioaccumulation measures can be compared to a common criterion, such is the case in the TSMP and the UNEP, very different outcomes can be obtained. The data demonstrate that BAFs tend to be much greater than BCFs. This is true not only for chemicals with high log K_{ow} (*i.e.* greater than 5), which are largely absorbed via the diet (and hence expected to exhibit a BAF greater than the BCF), but also for lower K_{ow} chemicals, which are expected to be mainly absorbed from the water (and hence exhibit a BCF that should be comparable to the BAF). One of the consequences of these observations is that it is possible for the BCF of a chemical substance to be 5,000 or less while the BAF exceeds 5,000. Figure 3 illustrates that the discrepancy between BCFs derived from correlations of laboratory data and observed BAFs in the field can be considerable. Following the correlation by Bintein (1993), BAFs can be up to 10,000 times greater than BCFs for high K_{ow} chemicals. The latter illustrates the experimental difficulties obtaining reliable BCF data for very high K_{ow} chemicals in typical laboratory tests. One of the conclusions one can draw from these observations that for high K_{ow} chemicals, the BCF is an unreliable predictor of the actual bioaccumulation factor in the field and tends to underestimate the actual degree of chemical bioaccumulation in the field. If the BCF is used to assess the bioaccumulation potential of a chemical, it should be measured against a much lower criterion than the criterion (*i.e.* 5,000 in the TSMP and UNEP) for the BAF. How much lower this criterion should be depends on the quality of the bioconcentration test that was used to measure the bioconcentration potential.

The results of this analysis further illustrates the difficulties associated with the estimation of the bioaccumulation potential using semi-empirical correlations based on laboratory based bioconcentration data. The correlations that are available result in very different estimates of the BCF, which makes it difficult to determine whether a chemical substance exceeds the bioaccumulation criterion or not. Among the available BCF correlations that were investigated in this study, equation 9 results in the smallest degree of underestimation of actual BAFs in the field. The BAF models produce by far the most reliable method to assess BAFs in the field. The model produces no significant systematic over or underestimation of observed values and contains the least amount of uncertainty. The success of the models over empirical measurements can be credited to the considerable amount of knowledge of the bioaccumulation process that has been accumulated over the years and that the models attempt to express. It is recommended that this knowledge base is used in the characterization of the bioaccumulation potential of the vast number of chemicals that are in use. While it can be argued that the bioaccumulation potential of many of the chemicals that are to be evaluated may not be appropriately described by current bioaccumulation models, due to their ability to be metabolized in organisms or

dissociate or slow membrane transport, the models, in absence of reliable empirical data, are expected to provide conservative estimates of the bioaccumulation potential, which are to be preferred when attempting to "safe guard" the environment from bioaccumulative substances.

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