Chemosphere, Vol.17, No.5, pp 943-962, 1988
Printed in Great Britain

0045-6535/88 $3.00 + .00
Pergamon Press plc

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DYNAMICS OF DIETARY BIOACCUMULATION AND FAECAL ELIMINATION OF HYDROPHOBIC ORGANIC CHEMICALS IN FISH

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ABSTRACT

A compilation of available literature data on uptake efficiencies of hydrophobic, organic chemicals from food by fish is presented. It is shown that the uptake efficiency of chemical from food (E_o) follows a relationship with the 1-octanol-water partition coefficient (K_{OW}), i.e., $1/E_o = 5.3.10^{-8}.K_{OW} + 2.3$. A model is derived for chemical uptake from food, which is shown to be consistent with the observed food-uptake data. The equations provide an explanation for the phenomenon of food chain accumulation, which is observed in natural ecosystems for several hydrophobic halogenated aromatic hydrocarbons.

INTRODUCTION

It has been suggested by several authors that uptake from food, rather than uptake directly from the water, is the major pathway by which hydrophobic organic chemicals accumulate in fish [1-5]. However there have been relatively few comparisons of the relative importance of chemical uptake from food and water, mainly because of the limited available information about chemical uptake from food. The kinetics and equilibria of chemical uptake from water have recently been described by Gobas and Mackay [6] as an extension of the work of Mackay and Hughes [7] and Gobas et al. [8]. In the present paper, an analysis is presented of the equilibria and dynamics of uptake of hydrophobic organic chemicals from food and elimination to the faeces. First, uptake efficiency data of chemicals from food are gathered from the literature and are related to the 1-octanol-water partition coefficient. Then, a model is derived for chemical uptake in fish from food, which is consistent with the observed data. In deriving this "food

uptake" model for fish, we follow the modelling work by Amidon et al. [9,10], Suzuki et al. [11], and Ho et al. [12] on oral drug absorption in mammals. The equations that are presented for uptake in fish are both in fugacity and conventional form and are similar to those derived and tested by these authors. The model is shown to fit to reported experimental food uptake data, and values are obtained for the parameters that control the rate of organic chemical absorption from food in fish and chemical elimination to the faeces.

ANALYSIS OF EXPERIMENTAL FOOD UPTAKE EFFICIENCY DATA

To derive the fundamental kinetic parameters for dietary uptake of organic chemicals in fish, absorption efficiency (E_0) data were gathered from the literature, listed in Table I and plotted versus the logarithm of 1-octanol-water partition coefficient log K_{OW} in Figure 1. The studies selected were those in which fish were exposed only to contaminated food for a relatively long period of time with a constant feeding rate. In addition, only data for single compounds were considered. The tabulated data are believed to include most of the published absorption efficiencies for halogenated hydrocarbons.

Athough there is a considerable spread in the data, Figure 1 suggests that, for chemicals with a log K_{OW} up to approximately 7, the uptake efficiency from food is constant. For chemicals with a log K_{OW} exceeding 7, the uptake efficiency from food falls with increasing K_{OW}. The following empirical

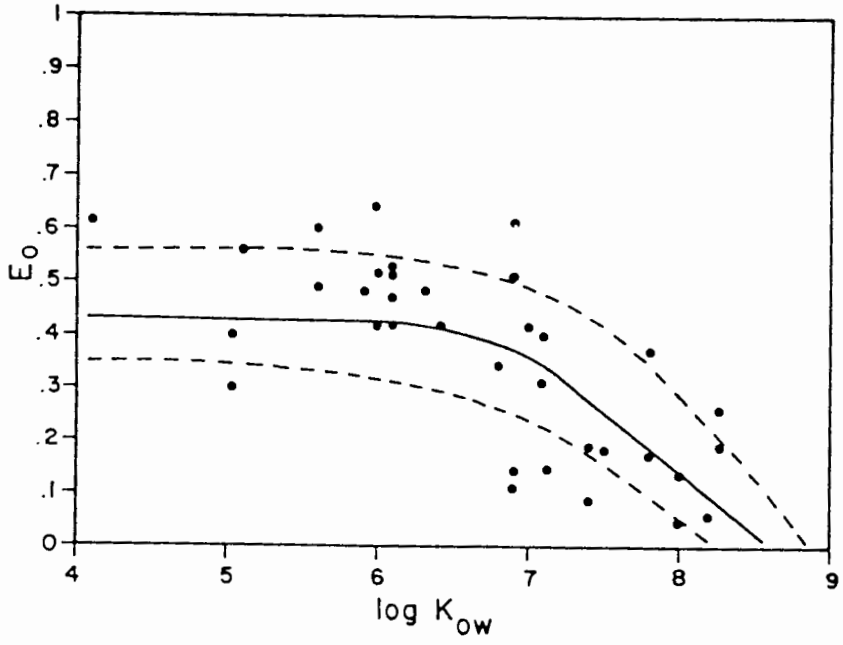

Figure 1. Observed absorption efficiencies (E_0) of hydrophobic organic chemicals in fish as a function of the 1-octanol-water partition coefficient (log K_{OW}).

Table I : Compila
absorption efficienci
selected hydrophobic

COMPOU
pentachlorobenzene
2,2',5,5' tetrachlorob
2,2',3,3',5,5' hexach
2,2',4,4',5,5' hexach
2,2',3,3',4,4',5,5' oc
decachlorobiphenyl
pentachlorobenzene
2,2',5,5' tetrachlorol
2,2',4,4',5,5' hexach
2,2',3,3',4,4',5,5' oc
decachlorobiphenyl
2,5 dichlorobipheny
2,2',5 trichlorobiphe
2,4,5 trichlorobiphe
2,2',5,5' tetrachloro
2,3,4,5 tetrachlorob
3,3',4,4' tetrachlorc
2,3,4,5 tetrabromob
2,2',4,5 te romo
2,4,5 trib iphe
mirex
4,4' DDT
trichlorobenzene
2,3,7,8 tetra-CDD
1,2,3,7 tetra-CDD
1,3,6,8 tetra-CDD
1,2,3,4,7 penta-CD
1,2,3,4,7,8 hexa-C
1,2,3,4,6,7,8 hepta
octaCDD
1,2,3,7 tetra-CDD
1,2,3,4,7 penta-CI
1,2,3,4,7,8 hexa-C
1,2,3,4,6,7,8 hept
cis-chlordane
trans-chlordane

a) calculated fr
molecule. b) CD

Table I : Compilation of 1-octanol-water partition coefficients (log K_{OW}), experimentally determined absorption efficiencies from food (E_0) and correlated absorption efficiencies from food ($E_{0,corr}$) of selected hydrophobic organic chemicals.

COMPOUND	log K_{OW}	E_0	$E_{0,corr}$	FISH SPECIES
pentachlorobenzene	5.0 [18]	0.30 [19]	0.43	**GUPPY** male
2,2',5,5' tetrachlorobiphenyl	6.1 [20]	0.51 [2]	0.42	(Poecilia reticulata)
2,2',3,3',5,5' hexachlorobiphenyl	7.0 [20]	0.42 [21]	0.35	
2,2',4,4',5,5' hexachlorobiphenyl	6.9 [20]	0.51 [2]	0.37	
2,2',3,3',4,4',5,5' octachlorobiphenyl	7.1 [20]	0.31 [2]	0.34	
decachlorobiphenyl	8.3 [20]	0.19 [2]	0.08	
pentachlorobenzene	5.0 [18]	0.40 [19]	0.43	**GUPPY** female
2,2',5,5' tetrachlorobiphenyl	6.1 [20]	0.42 [2]	0.42	(Poecilia reticulata)
2,2',4,4',5,5' hexachlorobiphenyl	6.9 [20]	0.61 [2]	0.37	
2,2',3,3',4,4',5,5' octachlorobiphenyl	7.1 [20]	0.40 [2]	0.34	
decachlorobiphenyl	8.3 [20]	0.26 [2]	0.08	
2,5 dichlorobiphenyl	5.1 [20]	0.56 [17]	0.43	**GOLDFISH**
2,2',5 trichlorobiphenyl	5.6 [20]	0.49 [17]	0.43	(Carassius auratus)
2,4,5 trichlorobiphenyl	5.6 [20]	0.60 [17]	0.43	
2,2',5,5' tetrachlorobiphenyl	6.1 [20]	0.53 [17]	0.42	
2,3,4,5 tetrachlorobiphenyl	5.9 [20]	0.48 [17]	0.43	
3,3',4,4' tetrachlorobiphenyl	6.1 [20]	0.47 [22]	0.42	**SALMON**
2,3,4,5 tetrabromobiphenyl	6.3 [a]	0.48 [22]	0.41	(Salmo salar)
2,2',4,5 tetrabromobiphenyl	6.3 [a]	0.48 [22]	0.41	
2,4,5 tribromobiphenyl	6.4 [a]	0.42 [22]	0.41	
mirex	7.5 [24]	0.18 [22,23]	0.25	
4,4' DDT	6.0 [26]	0.64 [26]	0.43	**RAINBOW TROUT**
trichlorobenzene	4.1 [18]	0.61 [27]	0.43	(Salmo gairdneri)
2,3,7,8 tetra-CDD[b]	6.8 [28]	0.34 [29]	0.38	
1,2,3,7 tetra-CDD	6.9 [28]	0.14 [26]	0.37	
1,3,6,8 tetra-CDD	7.1 [28]	0.15 [26]	0.34	
1,2,3,4,7 penta-CDD	7.4 [28]	0.19 [26]	0.28	
1,2,3,4,7,8 hexa-CDD	7.8 [28]	0.37 [26]	0.18	
1,2,3,4,6,7,8 hepta-CDD	8.0 [28]	0.133 [26]	0.13	
octaCDD	8.2 [28]	0.058 [26]	0.09	
1,2,3,7 tetra-CDD	6.9 [28]	0.11 [26]	0.37	**FATHEAD MINNOW**
1,2,3,4,7 penta-CDD	7.4 [28]	0.09 [26]	0.28	(Pimephelas promelas)
1,2,3,4,7,8 hexa-CDD	7.8 [28]	0.171 [26]	0.18	
1,2,3,4,6,7,8 hepta-CDD	8.0 [28]	0.045 [26]	0.13	
cis-chlordane	6.0 [26]	0.52 [31]	0.42	**REDHORSE SUCKER**
trans-chlordane	6.0 [26]	0.42 [31]	0.42	(Moxostoma macrolepidotum)

a) calculated from fragment constants as described by Lyman [25] using the corresponding PCB as a base molecule. b) CDD is chlorodibenzo-p-dioxin.

relationship between the uptake efficiency E_0 and K_{OW} can therefore be suggested:

$$1/E_0 = A.K_{OW} + B \qquad (1)$$

where A and B are constants. To fit the constants A and B linear regression of the data in Table 1, i.e. $1/E_0$ vs. K_{OW}, is not desirable, since K_{OW} varies over several orders of magnitude and would thus weigh heavily in favor of the data points with high K_{OW}. The most appropriate regression is believed to be on a semi-logarithmic basis of $1/E_0$ versus log K_{OW}. Non-linear regression (SAS-NLIN) can then be used to fit the parameters A and B to the data in Table 1. This results in values of 5.3 (+/-1.5). 10^{-8} for A and of 2.3 (+/-0.3) for B, such that

$$1/E_0 = 5.3.10^{-8}.K_{OW} + 2.3 \qquad (2)$$

where the confidence intervals have a 95% probability. In Figure 1, the solid line represents the correlated behaviour of E_0 with respect to log K_{OW} and the broken lines indicate the asymptotic 95% confidence intervals of the proposed correlations. It should be noted that due to the relatively large number of data points of high K_{OW}, equation 2 may somewhat underestimate E_0 values of low K_{OW} chemicals.

In order to derive a theoretical basis for the observed empirical relationship, we now discuss the process of chemical absorption from food and propose a model describing the kinetics of organic chemical uptake by fish from food and elimination to the faeces, which is consistent with the observed data.

FOOD-UPTAKE MODEL DERIVATION

Figure 2 is a schematic diagram of a fish showing the various chemical transport and transformation processes. The aim of our modelling work is to describe each of these processes with physically and physiologically realistic expressions containing a minimum number of adjustable parameters. Values for these parameters are then obtained by fitting the model to experimental data. This study focusses on chemical uptake from food and elimination by egestion in the faeces. However, to fully appreciate the implications of the "food-uptake" model, it is useful to discuss first a comprehensive bioaccumulation model combining all transfer and transformation processes depicted in Figure 2. The more complex mathematical expressions for chemical uptake from food are then derived and incorporated in the comprehensive model.

I. A Comprehensive Bioaccumulation Model

The expression describing simultaneous exchange of chemical between fish and water, and fish and food, and metabolic transformation, as depicted in Figure 2, can be expressed as

$$dC_F/dt = k_1.C_W - k_2.C_F + k_A.C_A - k_E.C_F - k_R.C_F \qquad (3)$$

where C is concentration (mol/m^3), t is time (h), and the subscripts W refer to water, A to food, E to faeces, and F to the whole fish. A fish is defined as the whole organism excluding the gill compartment and the gastro-intestinal (GI) tract. k_1, k_2, k_A and k_E are respectively the rate constants (h^{-1}) of chemical uptake from the water, elimination to the water, uptake from food, and elimination by egestion in the faeces, respectively, and k_R is the rate constant (h^{-1}) for metabolic transformation of the chemical in the fish.

Following the fugacity approach, as described by Gobas and Mackay [6] and Mackay and Paterson [13], equation 3 can also be written as

$$V_F.Z_F.df_F/dt = D_F.(f_W - f_F) + D_A.f_A - D_E.f_F - D_R.f_F \qquad (4)$$

where V is volume (m^3), Z is the chemical's fugacity capacity (mol/m^3.Pa) in a phase, and f is the chemical's fugacity (Pa). D_F is the overall transport parameter (mol/Pa.h) for chemical transfer between water and fish across the gills. D_A is the transport parameter for chemical uptake from food into the fish across the gastro-intestinal (GI)-tract. The transport parameter D_E (mol/Pa.h) describes chemical

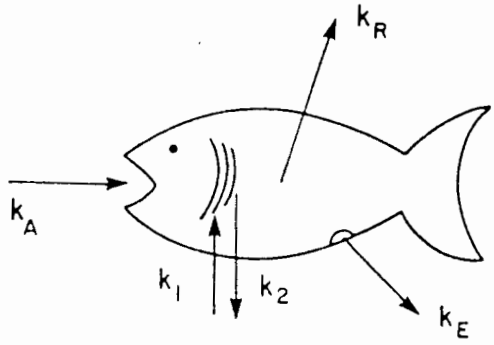

Figure 2. Schematic diagram of chemical uptake in fish from water (k_1) and food (k_A) and depuration by elimination to the water (k_2), elimination in the faeces (k_E), and metabolic transformation (k_R).

elimination in the faeces. D_R (mol/Pa.h) is the transformation parameter for metabolic transformation of chemical in the fish. The transport parameters D_F, D_A, and D_E include all transport processes involved in solute transfer between the water, food, and faeces, respectively, and the solute's final storage site in the fish.

Integration of equation 3 with a constant C_W and C_A, an initial C_F of zero and assuming a constant fish volume with time gives

$$C_F = \{C_W.[k_1/(k_2+k_E+k_R)] + C_A.[k_A/(k_2+k_E+k_R)]\}.\{1-\exp -(k_2+k_E+k_R).t\} \quad (5)$$

Since C_F is f_F/Z_F, C_W is f_W/Z_W and C_A is f_A/Z_A, it can be shown that equation 5 is equivalent to the integrated form of equation 4 with a constant f_A and f_W and an initial f_F of zero, i.e.,

$$f_F = \{f_W.[D_F/(D_F + D_E + D_R)] + f_A.[D_A/(D_F + D_E + D_R)]\}.\{1 -\exp[-(D_F + D_E + D_R).t/(V_F.Z_F)]\} \quad (6)$$

where

$$k_1 = D_F/V_F.Z_W \quad (7)$$
$$k_2 = D_F/V_F.Z_F \quad (8)$$
$$k_A = D_A/V_F.Z_A \quad (9)$$
$$k_E = D_E/V_F.Z_F \quad (10)$$
$$k_R = D_R/V_F.Z_F \quad (11)$$

Equations 5 and 6 show that at infinite exposure time a fish-water bioaccumulation factor, K_B can be defined for fish simultaneously exposed to contaminated water and food as

$$K_B = C_F/C_W = (Z_F/Z_W).\{[D_F/(D_F+D_E+D_R)] + [(f_A/f_W).(D_A/(D_F+D_E+D_R)]\} \quad (12)$$

or

$$K_B = C_F/C_W = \{k_1/(k_2 + k_E + k_R)\} + (C_A/C_W).\{k_A/(k_2 + k_E + k_R)\} \quad (13)$$

It also follows from equations 5 and 6 that in food uptake experiments, when fish are exposed to

contaminated food but
which is sometimes refer

$K_M = C_F/C_A = (Z_F/Z_A$

The bioconcentration
infinite exposure time f

$K_C = C_F/C_W = Z_F/Z_V$

Equations 12 to 15
quantities, i.e., Z_F,
but also by the re
with the faeces,
transformation occu
is small co d to
In order to make
and the rate at
controlling the exch

II. Chemical Upta

As illustrated in
chemical transpor
Chemical transfer

$V_F.Z_F.df_F/dt = D$

where D_G is t
storage site in
as being passiv
to the GI-tract
reverse flux r

contaminated food but uncontaminated water, the ratio of fish to food concentrations, i.e., C_F/C_A or K_M, which is sometimes referred to as a biomagnification factor [14], can be expressed as

$$K_M = C_F/C_A = (Z_F/Z_A).\{D_A/(D_F + D_E + D_R)\} = k_A/(k_2 + k_E + k_R) \quad (14)$$

The bioconcentration factor, K_C, which is defined as the ratio of fish and water concentrations at infinite exposure time for fish exposed to contaminated water only (i.e., $C_A = f_A = 0$), is

$$K_C = C_F/C_W = Z_F/Z_W.\{D_F/(D_F + D_E + D_R)\} \quad (15)$$

Equations 12 to 15 demonstrate that K_B, K_M, and K_C are not solely determined by the thermodynamic quantities, i.e., Z_F, Z_W and Z_A, which reflect the affinities of the chemical for the fish, water, and food but also by the relative rates of chemical uptake from water and food, release to the water, egestion with the faeces, and metabolic transformation. Equation 13 shows that even when no metabolic transformation occurs ($D_R = 0$), the bioconcentration factor only reflects fish-water partitioning when D_E is small compared to D_F.

In order to make reliable predictions about the bioaccumulation potential of hydrophobic chemicals in fish and the rate at which bioaccumulation is achieved in fish requires knowledge about the processes controlling the exchange of solute between fish, water, food, and faeces.

II. Chemical Uptake from Food

As illustrated in Figure 3, chemical uptake in fish from food can be viewed as the combined result of chemical transport through the GI-tract and the transfer of chemical between the GI-tract and the fish. Chemical transfer between the GI-tract and the fish can be described by

$$V_F.Z_F.df_F/dt = D_G.(f_G - f_F) \quad (16)$$

where D_G is the transport parameter for chemical transfer between the GI-tract and the chemical's final storage site in the fish and f_G is the chemical's fugacity in the GI-tract. We view this transfer process as being passive with a flux $D_G.f_G$ from the GI-tract to the fish and a reverse flux $D_G.f_F$ from the fish to the GI-tract. This implies that the fish can eliminate chemicals by eating uncontaminated food. This reverse flux may also include a contribution from bile excretion. Bile excretion may be expected to

enhance chemical elimination into the faeces, thus causing the transport parameter D for fish-to-GI-tract transfer to exceed the transport parameter for GI-tract-to-fish transfer. However, for the present purpose we will assume that one transport parameter i.e. D_G describes chemical exchange between the fish and the GI-tract.

As has been discussed by Amidon et al. [9,10], chemical uptake from the GI-tract can often be satisfactorily described when the gut is treated as a well mixed reactor. The concentration or fugacity (f_G) in the GI-tract then serves to promote passive diffusion across the GI-tract to the blood and organs of the fish. The same fugacity applies to the egested faeces. A steady state mass balance on the GI-tract, including food intake and excretion, results in

$$D_G.(f_G - f_F) = D_I.f_A - D_O.f_G \qquad (17a)$$

It thus follows that the GI-tract adopts a fugacity f_G of

$$f_G = (D_I.f_A + D_G.f_F)/(D_G + D_O) \qquad (17b)$$

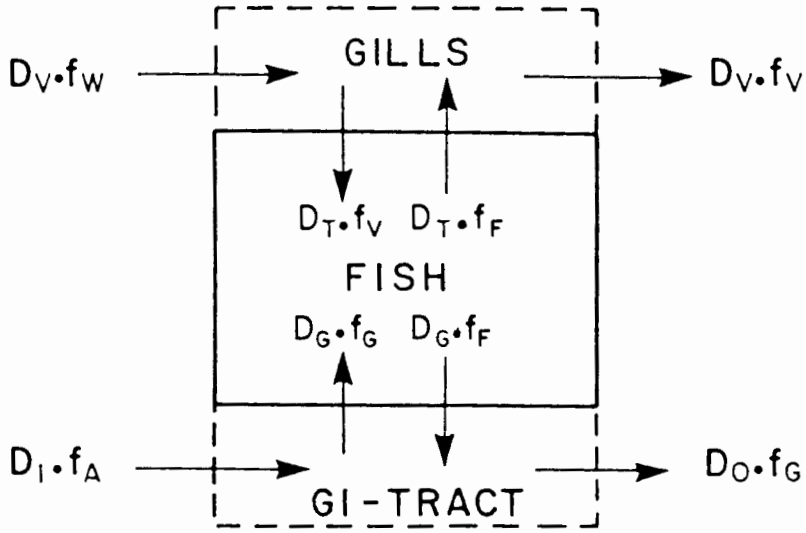

Figure 3. Schematic diagram of the chemical fluxes in and between the gill compartment, GI-tract, and the fish.

where $D_I.f_A$ is the flux with which chemical enters the GI-tract as a result of food consumption and $D_O.f_G$ is the flux with which chemical leaves the GI-tract as a result of faecal egestion. D_I is the transport parameter for chemical transport into the GI-tract and is the product of the feeding rate G_I (m^3/h) and the chemical's fugacity capacity in the food, Z_A, i.e., $G_I.Z_A$ such that $D_I.f_A$ equals $G_I.C_A$. The transport parameter for chemical transport out of the GI-tract, D_O is $G_O.Z_G$, where G_O is the faecal egestion rate (m^3/h), such that $D_O.f_G$ equals $G_O.C_G$. Substitution of equation 17b in equation 16 leads to

$$V_F.Z_F.df_F/dt = \{D_I.D_G/(D_O + D_G)\}.f_A - \{D_O.D_G/(D_O + D_G)\}.f_F \quad (18)$$

From equations 3, 4, and 18, it follows that the rate constants, k_A and k_E, are related to the transport parameters as

$$k_A = D_A/(V_F.Z_A) = \{D_I.D_G/(D_O + D_G)\}/(V_F.Z_A) \quad (19)$$

$$k_E = D_E/(V_F.Z_F) = \{D_O.D_G/(D_O + D_G)\}/(V_F.Z_F) \quad (20)$$

The absorption efficiency E is the ratio of the flux of chemical from the GI-tract into the fish, i.e., $D_G.(f_G - f_F)$, to the flux of chemical into the GI-tract, i.e., $D_I.f_A$ such that

$$E = D_G.(f_G - f_F)/D_I.f_A \quad (21)$$

Substitution of equation 17b into equation 21 shows that at the beginning of the exposure period, when no chemical is present in the fish and f_F is zero, the initial uptake efficiency, E_0, is maximal, i.e.,

$$E_0 = D_G/(D_O + D_G) \quad (22)$$

Alternatively, the absorption efficiency E can be defined in terms of the ratio of the flux out of the GI-tract ($D_O.f_G$ or $G_O.C_G$) and into the GI-tract ($D_I.f_A$ or $G_I.C_A$) as

$$E = 1 - (D_O.f_G/D_I.f_A) = 1 - (G_O.C_G/G_I.C_A) \quad (23)$$

which is equivalent to equation 21.

To convert from D-values to kinetic rate constants it may be necessary to estimate Z_F and Z_A and also Z_G, probably using the lipid or organic carbon content of the fish, food, and the faeces. Z_F, Z_A, and Z_G can then be equated to respectively, $L_F.Z_L$, $L_A.Z_L$, and $L_G.Z_L$ or $L_F.Z_O$, $L_A.Z_O$, and $L_G.Z_O$ (if Z_L = Z_O) where L_F, L_A, and L_G are the volume fractions of fish, food, and faeces with an affinity for the chemical equal to that of 1-octanol and Z_O is the chemical's fugacity capacity in 1-octanol.

At this point, it is useful to review the significance and relationships between the various D values and how these values control the absorption and excretion processes. Figure 4 shows the various chemical fluxes.

The input of chemical associated with food is $D_I.f_A$. This mixes with the contents of the GI-tract and adopts a fugacity f_G. There are two removal processes from the GI-tract, i.e., absorption and egestion, characterized by D_G and D_O, respectively. The fraction of chemical absorbed is $D_I.f_A.D_G/(D_G + D_O)$ and that egested is $D_I.f_A.D_O/(D_G + D_O)$, which total $D_I.f_A$. Chemical also enters the GI-tract by diffusion from the fish at a rate $D_G.f_F$. This flux splits into $D_G.f_F.D_G/(D_G + D_O)$, which is reabsorbed, and $D_G.f_F.D_O/(D_G + D_O)$, which is eliminated by egestion. The total flux of chemical absorbed by the fish from food ingestion and reabsorption is therefore

$$D_G.f_G = (D_G.f_F + D_I.f_A).D_G/(D_O + D_G) \qquad (24)$$

and the total flux of chemical eliminated by the fish in the GI-tract is

$$D_G.f_F = (D_G.f_F + D_O.f_F).D_G/(D_O + D_G) \qquad (25)$$

The net flux into the fish is $\{(D_G.f_G)-(D_G.f_F)\}$ or $\{(D_I.f_A)-(D_O.f_F)\}.D_G/(D_O+D_G)$, which is equation 18, or $\{(D_A.f_A)-(D_E.f_F)\}$, which are the corresponding terms in equation 4. D_A and D_E thus represent the combined result of chemical flow in the GI-tract and chemical diffusion across the GI-wall.

A similar process occurs in the gills where the gill ventilation rate is D_V, i.e., the product of the volumetric gill flow, G_V (m^3/h) and the chemical's fugacity capacity in water, Z_W. The rate of absorption is characterized by the transport parameter D_T. The gill water adopts a fugacity f_V, which can be deduced from a steady state mass balance similar to equations 17a and 17b namely

Figure 4. I
tract, and th

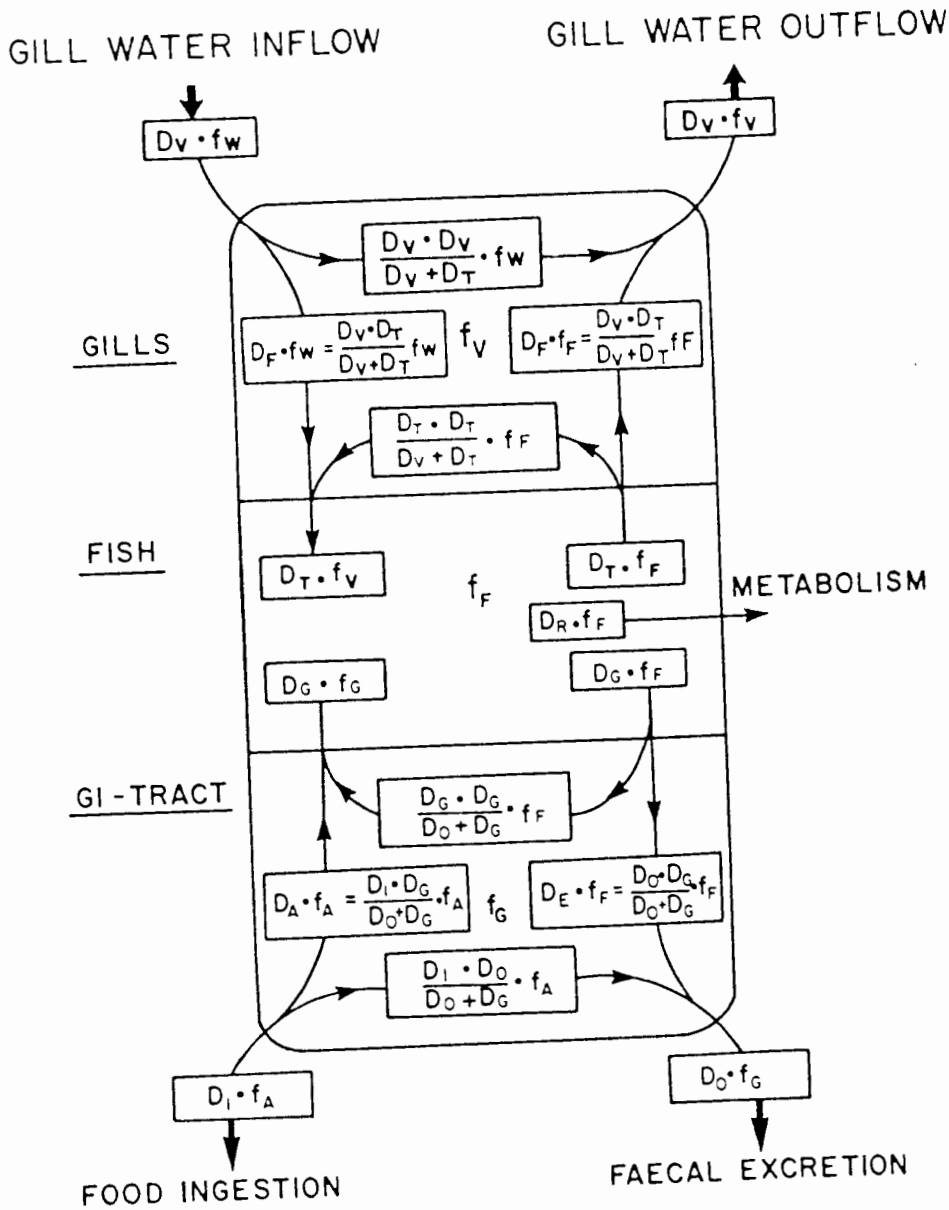

Figure 4. Detailed schematic diagram of the chemical fluxes in and between the gill compartment, the GI-tract, and the fish.

$$D_T.(f_V - f_F) = D_V.f_W - D_V.f_V \quad (26a)$$

or

$$f_V = (D_V.f_W + D_T.f_F)/(D_V + D_T) \quad (26b)$$

Figure 4 further illustrates that part of the chemical inflow $D_V.f_W$ is absorbed, whereas the other part is "by passed" in the gills and not absorbed. It follows that D_F is $D_V.D_T/(D_V + D_T)$. The significant difference between the absorption via the gills and from the GI-tract is that, whereas in the gills the inflow and outflow of chemical are characterized by a common D_V, in the GI-tract the inflow and outflow have different D values, D_I and D_O as a result of food mass loss and composition change.

Transfer across the GI-tract

To gain insight into the factors controlling D_G we can follow the approach originally suggested by Flynn and Yalkowsky [15] and applied by several authors [6,7,8,16] of describing solute transfer between the GI-tract and the solute's storage sites in the fish as a process in which the solute passes through a series of resistances in aqueous and lipid phases. Therefore, all D values applying to solute transport between the fish and the GI-tract in aqueous phases of the fish are grouped together in one term, D_W. Similarly solute transport in the lipid phases of the fish is expressed by a transport parameter, D_L. Each D term can be viewed as a product of a transport parameter, Q, with units of m^3/h, which combines all diffusion transfer terms, or flow rates (m^3/h) applicable to solute transfer in that phase and the fugacity capacity Z, i.e., $D_W = Q_W.Z_W$ and $D_L = Q_L.Z_L$. The transport parameters D_W and D_L can also be viewed as the conductivities of the water and lipid phase for chemical transport. The reciprocals $1/D_W$ and $1/D_L$ are the resistances of the water and lipid phase to chemical transport. Assuming that water and lipid transport processes apply in series and that transport resistances across lipid-water interfaces are negligible, the net transport of solute between the fish and the GI-tract can be expressed in terms of D_W and D_L as

$$1/D_G = 1/D_W + 1/D_L = 1/Q_W.Z_W + 1/Q_L.Z_L \quad (27)$$

The transport parameters Q_W and Q_L in equation 24 for food uptake are specific to transfer of chemical across the GI-tract. They are not equal to the water and lipid phase transport parameters for fish-water exchange through the gills.

Substituting equatio
19, 20, and 22, it fol

$1/k_A = (V_F/G_I).\{(G$
$1/k_E = (V_F.L_F/G_O$
$1/E_0 = (G_O.L_G/Q_V$

From equations 28
as

$k_A = E_0.G_I./V_F$

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Substituting equation 24 for D_G, $G_I.L_A.Z_O$ for D_I, $G_O.L_G.Z_O$ for D_O, and K_{OW} for Z_O/Z_W in equations 19, 20, and 22, it follows that

$$1/k_A = (V_F/G_I).\{(G_O.L_G/Q_W).K_{OW} + (G_O.L_G/Q_L) + 1\} \quad (28)$$

$$1/k_E = (V_F.L_F/G_O.L_G).\{(G_O.L_G/Q_W).K_{OW} + (G_O.L_G/Q_L) + 1\} \quad (29)$$

$$1/E_0 = (G_O.L_G/Q_W).K_{OW} + G_O.L_G/Q_L + 1 \quad (30)$$

From equations 28 and 30, it follows that k_A and E_0 are related, as proposed by Bruggeman et al. [17], as

$$k_A = E_0.G_I./V_F \quad (31)$$

The reciprocal of k_A, i.e., $1/k_A$, can be viewed as the time needed to transport chemical from the food into the fish or as the total resistance for chemical transfer from the food into the fish. Likewise, $1/k_E$ is the time required to eliminate chemical from the fish into the faeces or the total resistance for chemical elimination to the faeces. The ratios $(V_F/G_I).(G_O.L_G/Q_W).K_{OW}$ and $(V_F/G_I).(G_O.L_G/Q_L)$ can be viewed as the solute's relative transport times in the water and lipid phases of the fish, respectively, or as the relative resistances that the solute encounters in the water and lipid phases of the fish on its route from the food phase in the GI-tract to the final storage site in the body lipid of the fish. When the solute's K_{OW} increases, and aqueous solubility thus decreases, the water phase of the fish can accomodate only a lower concentration of solute molecules. As a result, the time required to transport a certain amount of solute with this lower concentration increases. The resistance of the fish's water phase toward mass transfer thus increases, whereas it remains approximately constant in the lipid phase. For high K_{OW} chemicals, this implies that the uptake rate from food and elimination rate to the faeces and thus k_A, E_0 and k_E decrease with increasing K_{OW}. For low K_{OW} chemicals, uptake from food and elimination by excretion to the faeces is predominantly controlled by transport in lipid phases, and k_A, E_0, and k_E are, therefore, expected to be approximately constant with respect to K_{OW}. Comparing equation 1 and 2 with equation 30, it can be concluded that the empirical constants A and B in equations 1 and 2 have a physical significance, i.e.,

$$A = G_O.L_G/Q_W = 5.3\ (+/-\ 1.5).10^{-8} \quad (32) \quad \text{and} \quad B = (G_O.L_G/Q_L) + 1 = 2.3\ (+/-\ 0.3) \quad (33)$$

The empirical equation 2 therefore has a theoretical basis. By experimental measurement of E_0 for a series of chemicals with varying K_{OW} under controlled conditions, i.e., a constant feeding rate and no uptake of chemical from the water, it is thus possible to determine the fundamental kinetic parameters Q_W and Q_L. Knowledge of these parameters is invaluable for a reliable estimation of organic chemical bioaccumulation from contaminated food.

TRANSPORT PARAMETER

The transport parameters Q_W and Q_L for chemical uptake from food were determined for a 0.10 g male guppy (Poecilia reticulata) as follows: G_O was experimentally determined to be 0.74(+/-0.04) mg faeces (dry weight).day^{-1} by collecting faeces over a 14 day period from 20 fish with an average weight of 0.1 g, which were fed dry fish food (Tetramin) at a constant daily feeding rate of 2.0 (+/- 0.1) mg dry fish food per fish. G_O was thus 37% of G_I. Since dry fish food increased in weight by 4.6 fold when added to the water and administered to the fish, G_I and G_O corresponded to respectively 9.2 mg wet fish food per day or approximately 9.2 µL/d and 3.4 mg wet fish food per day or 3.4 µL/d. Assuming that L_A, L_G,

Table II : Fish wet weight or volume (V_F), lipid content (L_F), reported feeding rate (g) and the volumetric feeding rate (G_I) and calculated water- and lipid phase transport parameters for gastro-intestinal absorption (resp. Q_W and Q_L) of hydrophobic organic chemicals in various fish species.

FISH SPECIES	V_F (g)	L_F	g (g/g/d)	G_I[a] (µL/d)	Q_W[b] (L/d)	Q_L[c] (µL/d)
Guppy male [2]	0.1	0.022	0.02	9.2	1.4	0.058
Guppy female [2]	0.35	0.039	0.02	32	9.1	0.36
Goldfish [17]	4.5	0.033	0.01	210	48	2.0
Salmon [22]	3.4	0.046	0.039	610	198	8.0
Rainbow trout [26]	0.75	0.085	0.015	52	31	1.3
Fathead minnow [26]	1.0	0.036	0.015	69	18	0.71

a) G_I was calculated as the product of the reported feeding rate g, the fish weight V_F and the conversion factor from dry to wet food i.e 4.6.
b) Q_W was calculated as the product of L_G (i.e. L_F) and G_O (i.e., 37% of G_I) divided by 5.3 . 10^{-8} (i.e., $L_G.G_O/Q_W$).
c) Q_L was calculated as the product of L_G (i.e. L_F) and G_O (i.e., 37% of G_I) divided by 1.3 (i.e., $L_G.G_O/Q_L$).

and L_F are approximately similar and equal to 0.022 (Table II), approximate values for Q_W of 1.4 L/d and for Q_L of $0.058 \cdot 10^{-6}$ L/d were calculated.

Following the same approach for the fish species in Table I and thus assuming a faecal egestion rate (G_O) that is approximately one-third of the reported feeding rate (G_I) and feeding rates expressed on a wet food weight basis which are 4.6 fold that of the reported dry food weight basis, approximate values for Q_W and Q_L were estimated for each fish species and listed in Table II.

DISCUSSION

Although Figure 1 demonstrates a considerable spread in the data, it is believed that, to a first approximation, the proposed model gives a satisfactory correlation of the available data and describes the kinetics of chemical uptake from food adequately, using soundly based physiological concepts. Although the values of Q_W, Q_L, and G_O determined here may contain a relatively large error, they give an indication of the relative rate of uptake of organic chemicals from dietary exposure. More, and more accurate, data are needed to test the validity of the presented approach more rigorously. Three causes for the large spread in the data can be suggested:

(i) Mechanisms for chemical transport across the gastro-intestinal wall may be different for each type of chemical species or are poorly described with the presently used parameters. However, from the present literature and this analysis, there are no indications that different transport mechanisms exist for the closely related chemicals in this study or that other structural parameters have to be used to describe transport. Only for the penta- to octachlorodibenzo-p-dioxin, which have minimal internal cross sections (MICS) exceeding 0.95 nm, has it been suggested that membrane permeation is blocked [31]. However, the absorption efficiency data for chlorodibenzo-p-dioxins with MICSs larger than 0.95 nm seem to fit the suggested model, which is based on diffusive transport through aqueous and lipid layers only. The low absorption efficiencies of these dioxins [26], as well as their decrease with increasing chlorine content may thus be explained by their extremely slow transport through aqueous phases in the fish due to their low aqueous solubilities.

(ii) The ratios $G_O \cdot L_G/Q_W$ and $G_O \cdot L_G/Q_L$ may differ considerably between the various fish species, such that a comprehensive analysis of all absorption efficiency data is not justified. Since the fish species in this analysis were fed similar diets at approximately the same feeding rate, it seems unlikely that $L_G \cdot G_O/Q_W$ and $L_G \cdot G_O/Q_L$ vary considerably between the various fish species.

(iii) Finally, experimental error and variations in methodology may contribute to the considerable spread

in the absorption efficiencies. Experimental error may be the result of (1) the presence of non-absorbed test chemical in the GI-tract during extraction and analysis of fish resulting in overestimation of the actual fish concentrations and absorption efficiencies, (2) variations in fish weight (e.g. growth) and lipid content during the often long-lasting experiments [2], (3) variations in the length of the feeding period between the different studies, which have been suggested to affect the determination of the absorption efficiency [21,32], and (4) metabolic transformation in the fish.

Procedures for food uptake experiments which control the above mentioned parameters may, therefore, result in more accurate and reproducible data which can then be more meaningfully compared with data from other studies.

One particular aspect of the food-uptake model deserves special attention since it possibly explains the phenomenon of biomagnification and food-chain accumulation observed for high K_{OW} chlorinated hydrocarbons in the field [3,5,33]. As a result of digestion and absorption of food by the organism, the volume or volumetric flow rate of food continuously decreases while food is being transported through the GI-tract. This results in a faecal excretion rate G_O which is lower than the organism's food consumption rate, G_I. For example, for the guppy, the G_I/G_O ratio is approximately 3. This process causes the chemical's fugacity and concentration in the GI-contents (i.e., f_G or C_G) to increase, resulting in a fugacity in the GI-tract which exceeds the chemical's fugacity in the food (i.e., f_A). A further increase in the chemical's fugacity in the GI-tract may occur as a result of digestion of the ingested food in the GI-tract (e.g. hydrolysis of lipids), which may lower the affinity of the GI-contents for the chemical and thus reduce the chemical's fugacity capacity Z_G in the GI-tract. When the chemical's fugacities in food and fish are equal (i.e., fish and food are in chemical equilibrium), the chemical fugacity in the GI-tract will tend to exceed the fugacity in the food such that f_G/f_A equals D_I/D_O or $G_I.Z_A/G_O.Z_G$ (equation 17a), resulting in a net flux of chemical from the GI-tract into the fish. If the rate of chemical elimination to the water is small, and especially when smaller than the chemical elimination rate to the faeces ($D_W < D_E$), and, in addition, metabolic transformation is insignificant ($D_R < D_E$), the chemical's fugacity in the fish will tend to approach the fugacity in the GI-tract such that f_F/f_A equals D_I/D_O or $G_I.Z_A/G_O.Z_G$. Halogenated hydrocarbons with a high K_{OW} values (e.g. larger than 10^6) are an example of a class of chemicals which are extremely slowly metabolized and eliminated by fish. When a fish is exposed to food and water contaminated with this type of chemical and chemical fugacities in water and food are equal ($f_A = f_W$), which seems to be a reasonable assumption for fish feeding on organisms of the lower trophic levels in the environment, the chemical fugacity in the fish will tend to exceed the

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BCF (K_C) and the fis
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chemical's fugacity in the water (i.e., $f_F/f_W > 1$). As a result, the chemical's BAF (K_B) will exceed the BCF (K_C) and the fish-water partition coefficient, Z_F/Z_W, which is usually predicted from the chemical's K_{OW} as $L_F.K_{OW}$. The extent to which K_B exceeds K_C or f_F/f_W over 1 depends on the relative values of D_A and D_E or G_I and G_O and the lipid content of the food. Bioaccumulation factors of high K_{OW} chemicals in Lake Ontario fish have indeed been shown to exceed fish-water partition coefficients [5] and calculated fugacities of these chemicals in fish to be higher than fugacities in the water [3]. As demonstrated by Connolly and Pedersen [3] and Clark et al. [33], this increase in fugacity may take place at every trophic level of the food-chain, where one organism feeds on another organism of a "lower" trophic level and may thus be viewed as the driving force of what is generally referred to as food chain accumulation [14].

ACKNOWLEGEMENT

The authors gratefully acknowledge the financial support of Natural Sience & Engineering Research Council of Canada, the Ontario Ministry of Environment and the Wildlife Toxicology Fund.

LIST OF NOMENCLATURE AND ABBREVIATIONS

C_A chemical concentration in the food (mol/m^3)

C_F chemical concentration in the whole fish (mol/m^3)

C_G chemical concentration in the GI-tract

C_W chemical concentration in the water (mol/m^3)

D_A transport parameter for chemical uptake from food in the fish (mol/Pa.h)

D_E transport parameter for chemical elimination in the faeces (mol/Pa.h)

D_F transport parameter for chemical exchange between the water and the fish (mol/Pa.h)

D_G transport parameter for chemical transfer between the GI-tract and the chemical's final storage site in the fish (mol/m^3.Pa)

D_I transport parameter for food ingestion (mol/Pa.h)

D_L transport parameter in the lipid phases of the fish for chemical exchange between the GI-tract and the final storage site in the fish (mol/Pa.h)

D_O transport parameter for faecal egestion (mol/Pa.h)

D_R transformation parameter for metabolic transformation of the chemical in the fish (mol/Pa.h)

D_T transport parameter for chemical exchange between the gill compartment and the fish (mol/Pa.h)

D_V transport parameter for gill ventilation (mol/Pa.h)

E absorption efficiency of chemical from food

E_O initial absorption efficiency of chemical from food

f_A fugacity of the chemical in the food (Pa)

f_F fugacity of the chemical in the fish (Pa)

f_G fugacity of the chemical in the GI-tract (Pa)

f_V fugacity of the chemical in the gill compartment (Pa)

f_W fugacity of the chemical in the water (Pa)

G_I feeding rate in m^3 food per hour (m^3/h)

G_O faecal excretion rate in m^3 faeces per hour (m^3/h)

G_V volumetric gill ventilation rate in m^3 water per hour (m^3/h)

GI gastro-intestinal tract

k_A rate constant for chemical uptake from food (in h^{-1} or d^{-1})

k_E rate constant for chemical elimination by egestion in the faeces (in h^{-1} or d^{-1})

k_R rate constant for metabolic transformation in the fish (in h^{-1} or d^{-1})

k_1 rate constant for chemical uptake from the water (in h^{-1} or d^{-1})

k_2 rate constant for chemical elimination to the water (in h^{-1} or d^{-1})

K_B bioaccumulation factor in fish (exposure from water and food)

K_C bioaccumulation factor in fish (exposure from water only)

K_M biomagnification factor (exposure from food only)

K_{OW} 1-octanol-water partition coefficient

L_A organic fraction of the food in grams of organic matter per gram of food

L_F organic fraction of the fish in grams of organic matter per gram of fish

L_G organic fraction of the gastro-intestinal content in grams organic matter per gram of GI content

MICS Minimal Internal Cross Section (nm)

Q_W transport parameter in the water phases of the fish for chemical exchange between the GI-tract and the final storage site in the fish (m^3/h)

Q_L transport parameter in the lipid phases of the fish for chemical exchange between the GI-tract and the final storage site in the fish (m^3/h)

t time (h)

V_F volume of the whole fish (m^3)

Z_A the chemical's fugacity capacity of the food (mol/m^3.Pa)

Z_F the chemical's fugac

Z_L the chemical's fugac

Z_O the chemical's fugac

Z_W the chemical's fuga

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Z_F the chemical's fugacity capacity of the fish (mol/m^3.Pa)

Z_L the chemical's fugacity capacity in the lipids of the fish (mol/m^3.Pa)

Z_O the chemical's fugacity capacity in 1-octanol (mol/m^3.Pa)

Z_W the chemical's fugacity capacity of the water (mol/m^3.Pa)

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GI content

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(Received in Germany 2 November 1987; accepted 8 March 1988)