

A Mathematical Model for Cadmium in the Stone Loach (*Noemacheilus barbatulus* L.) from the River Ecclesbourne, Derbyshire

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A mathematical model which linked metabolism of stone loach with cadmium dynamics was developed using information from laboratory experiments and field studies. Three possible sources of cadmium were distinguished: water, food, and sediment. Predicted results over 1 year were compared with field observations from three sites in Derbyshire. The model adequately predicted growth of fish for all three sites. Predicted cadmium levels in loach were in good agreement with measured levels in fish from all three sites despite the fact that concentrations of cadmium in the environment were kept constant during each simulation. The weight of fish affected the relative importance of different pathways of cadmium intake under similar conditions. Uptake from water contributed substantially to body burden even though the concentration in water was lower than that in food or in sediment. However, uptake from both food and sediment could not be ignored given the measured levels of cadmium in the field. The relative importance of uptake from the three sources also differed with site. The model showed that metabolism, affected by temperature, is important to the dynamics of cadmium in the stone loach. © 1990 Academic Press, Inc.

INTRODUCTION

The nature of the link between exposure to a contaminant in the environment and the dose received within an organism is a central problem in studies of the biological effects of pollutants in the environment: exposure determines the dose, which may then cause an effect on the organism (Doull *et al.*, 1980). There has been a long debate about the relative importance of different parts of the physical environment (e.g., food, water, sediment) as sources of persistent pollutants, such as heavy metals, for aquatic animals. Knowledge of the routes and rates of uptake of a pollutant from different sources is important for understanding and predicting effects of pollutants on wildlife.

This paper develops a mathematical model to describe results on rates of uptake and loss of cadmium from water (Douben, 1989a), food (Douben, 1989c), and sediment (Douben and Koeman, 1989) by the stone loach (*Noemacheilus barbatulus* L.). Data from laboratory experiments have been used together with field data on cadmium burden in loach from three sites in Derbyshire: River Ecclesbourne, Brailsford Brook South, and Suttonbrook (Douben, 1989b). (For a detailed description of the study sites see Douben (1989d)).

The objectives of the mathematical model have been:

- to assess the effect of body size on cadmium burden;
- to quantify the intake of cadmium from food, water, and sediment;

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- to explain the observed fluctuations in cadmium body burdens under field conditions;
- to evaluate reliability of application in other habitats.

The stone loach is a common fish in British rivers. It is a bottom-feeder (Maitland, 1965), buries itself in the mud (Hyslop, 1982), and is active during the first few hours of darkness (Welton *et al.*, 1983).

DEVELOPMENT OF THE MODEL

First Approach

The mathematical model is based on the premise that metabolism (metabolic rate) of stone loach is an important factor that affects metal burden, an approach first developed by DeFreitas and Hart (1975). Metabolism of fish (including growth) depends on body weight and on the temperature of the water, and affects rates of uptake and loss of pollutant. The model can be divided into two major parts: one part describes metabolism of the loach, the other describes the flux of cadmium between fish and its surroundings. Values of parameters and variables for the model were estimated from data for the River Ecclesbourne and validated with observations from the two other sites: the Brailsford Brook South and Suttonbrook.

Norstrom *et al.* (1976) developed a model which considered two routes of entry for mercury and PCB in yellow perch (*Perca flavescens*): food and water. A comparison between their model and that described here is made where appropriate. Their model has been used as a basis for the mathematical model described in this paper. Data for the stone loach have been used where available.

Metabolism

Two rates of metabolism can be distinguished: low routine metabolism when fish show occasionally spontaneous movements and maximum metabolism when fish are active and feeding at such quantities that growth occurs. The relationship between weight of fish and metabolic rate can be expressed as (Paloheimo and Dickie, 1966)

$$Q_{lr} = \alpha_{lr} W^y, \quad (1)$$

in which Q_{lr} is the low routine metabolism (cal day^{-1}); α_{lr} is the coefficient for low routine metabolism ($\text{cal day}^{-1} \text{ mg}^{-1}$); W is the body weight (dry weight mg); and y is the body weight exponent.

Numerous publications deal with the relationship between metabolism and size of the fish (e.g., Niimi and Beamish, 1974) or temperature (Beamish, 1974; Brett *et al.*, 1969). Data on oxygen consumption rate for the stone loach over a wide range of temperatures have been published (Douben, 1989c), and energy expenditure can be calculated by converting oxygen consumption into calories (see below). It was assumed that high activity was absent at 6°C and below, because growth of loach had ceased under those conditions (Douben, 1989b). If any growth occurs, a component for change in weight with time, dW/dt , is introduced in Eq. (1) and total metabolic rate increases. Conversely, loss of weight makes energy available thus lowering the required intake of food.

Three age groups of loach have been distinguished: fish between 0 and 1 year old (0+), between 1 and 2 years old (I+), and 2 years and older (II+) (for details see

Douben (1989b)). For each age group, a regression analysis of measured weights of fish on the time of each sampling occasion throughout 1 year was carried out and differentiation of the regression equation yielded growth rate as a function of time. Given that temperature affects growth rate and temperature of river water changed with time (Douben, 1989b), a subsequent regression analysis was carried out of growth rate on temperature, after allowing for the fact that estimates were based on growth rate over a period. The equations for growth rate on a yearly basis (dW/dt) were then for 0+ (2a), I+ (2b), and II+ fish (2c),

$$\frac{dW}{dt} = 178.3119 \quad (2a)$$

$$\frac{dW}{dt} = -194.1894 + 203.7868 * T \quad (2b)$$

$$\frac{dW}{dt} = 23.135 + 86.145 * T, \quad (2c)$$

in which T represents temperature. This approach proved to be adequate for predicting weight of loach from the River Ecclesbourne.

The model for metabolism and ration (R) is then

$$R = \frac{1}{E_f} \left[\alpha_{lr} W^\gamma + (\beta + 1) \frac{dW}{dt} \right]. \quad (3)$$

The coefficient E_f allows for food passing through the gut unassimilated and another coefficient, β , takes the energetic cost of growth into account (Norstrom *et al.*, 1976).

Uptake of Pollutant

Uptake of pollutant can occur from three sources: food, water, and sediment. The model is based on the assumption that rates of uptake from these sources are independent and that, therefore, uptake of cadmium via different pathways is additive.

Uptake of cadmium from food depends on the ingested ration (R) and the concentration of pollutant in the food (C_{pf}). However, not all of the ingested cadmium is taken up by the stone loach. Results on rates of uptake of cadmium during dietary exposure, dCd/dt , have been published (Douben, 1989c) and are implemented in Eq. (4) to estimate the efficiency of uptake of cadmium from the food (E_{pf}):

$$\frac{dCd}{dt} = E_{pf} * C_{pf} * R. \quad (4)$$

Similarly, not all of the cadmium is taken up from the water flowing over the gills. Rate of uptake of cadmium from the water is related to the concentration of cadmium in the water (C_{pw}) and the uptake of oxygen from the water. The latter is a function of the metabolic requirement which is related to the volume of water passing over the gills (V) to supply the fish with oxygen. The volume of water can be expressed as the concentration of oxygen in the water (C_{ox}) and the efficiency with which the oxygen is taken up (E_{ox}). Oxygen can be converted into calories by $Q_{ox} = 3.42 \text{ cal mg}^{-1}$ oxygen (which is equal to $3.42 \times 10^{-3} \text{ cal g}^{-1}$ oxygen) (Warren and Davis, 1967). The

coefficient for low routine metabolism is expressed as α instead of α_{lr} (for explanation see below). The model is given by

$$\frac{dCd}{dt} = \left[\frac{E_{pw} * C_{pw}}{E_{ox} * C_{ox} * Q_{ox}} \right] * \left[\alpha W^{\gamma_w} + \beta \frac{dW}{dt} \right]. \quad (5)$$

Exposure to sediment contaminated with cadmium increased cadmium levels in stone loach under laboratory conditions (Douben and Koeman, 1989). Field observations also suggested that uptake of cadmium from the sediment could occur (Douben, 1989b). Rate of uptake will depend on concentration of cadmium in the sediment (C_{ps}). For practical purposes an efficiency coefficient (E_{ps}) of less than unity would imply that not all the cadmium is taken up. It was assumed that the connection between metabolic requirements (which appears also in Eqs. (5) and (6)) and uptake of cadmium under these circumstances could be described in a way similar to that for water-borne exposure, although the pathway of uptake may be different. This does, of course, not imply uptake of oxygen from the sediment. Uptake of cadmium from sediment is then as described by

$$\frac{dCd}{dt} = \left[\frac{E_{ps} * C_{ps}}{E_{ox} * C_{ox} * Q_{ox}} \right] * \left[\alpha W^{\gamma_s} + \beta \frac{dW}{dt} \right]. \quad (6)$$

Loss of Pollutant

Loss of cadmium from loach was determined after both water-borne and dietary exposure (Douben, 1989a and 1989c). The rate constants for loss found in the laboratory during and after dietary exposure were higher than for other types of exposure. Concentrations used in food items during dietary exposure were close to levels in invertebrates (on which loach feeds) as found under field conditions (see below). Body size had no effect on the rate of loss per unit burden of cadmium, in contrast to the model used by Norstrom *et al.* (1976). Loss can be described by

$$\frac{dCd}{dt} = k * Cd \quad (7)$$

Final Model

Submodels for cadmium burden in the loach which included just one source of cadmium were used to test the working of that model and were compared with results from laboratory experiments. These submodels were then amalgamated into one major model given by

$$\begin{aligned} \frac{dCd}{dt} = & \left[\frac{E_{pf} * C_{pf}}{E_f} \right] * \left[\alpha W^{\gamma_f} + (\beta + 1) \frac{dW}{dt} \right] + \left[\frac{E_{pw} * C_{pw}}{E_{ox} * C_{ox} * Q_{ox}} \right] * \left[\alpha W^{\gamma_w} + \beta \frac{dW}{dt} \right] \\ & + \left[\frac{E_{ps} * C_{ps}}{E_{ox} * C_{ox} * Q_{ox}} \right] * \left[\alpha W^{\gamma_s} + \beta \frac{dW}{dt} \right] - k * Cd. \end{aligned} \quad (8)$$

ESTIMATION OF VARIABLES AND PARAMETERS

Metabolism

Oxygen consumption rate per day was calculated from low routine metabolism for 19 hr and maximum metabolism for 5 hr, so that α_{lr} becomes α . Stone loach were

fed different rations of *Tubifex*, from which maintenance rations were calculated (Douben, 1989c). The energetic value of the worms was taken to be 5.49 kcal g⁻¹ dry weight *Tubifex* (Warren and Davis, 1967). The ratio of the amount of energy required, from oxygen consumption rate, to the amount of energy consumed at maintenance ration is taken as the estimate for efficiency of energy uptake from the diet and yields a value of 0.70.

The value of α (in Eq. (2) α_{lr} ; for explanation see above) was estimated from the results from oxygen consumption rate at different temperatures (Douben, 1989c). The coefficient relating uptake of energy to the amount of tissue deposited β was estimated by using the results from feeding *ad libitum* (Douben, 1989c). A linear regression of growth rate on food consumption was carried out according to Eq. (9a) to obtain b and then β was estimated according to Eq. (9b) (Norstrom *et al.*, 1976),

$$\frac{dW}{dt} = a + b \cdot R \quad (9a)$$

$$b = \frac{E_f}{1 + \beta}, \quad (9b)$$

where E_f equals 0.70.

Results for exponents of body weight, y_w , y_f , and y_s (according to the route of entry: water, food, and sediment respectively), relating weight to cadmium burden, from laboratory experiments yielded values of 0.34 ± 0.08 , 0.70 ± 0.06 , and 0.88 ± 0.13 , respectively (Douben, 1989a and 1989c, Douben and Koeman, 1989). A test was carried out to use a common exponent of 0.78 (the value of intake of food).

It was assumed water was always saturated with oxygen, when oxygen concentration (mg liter⁻¹) can be described by

$$C_{ox} = 14.45 - 0.413 \cdot T + 0.00556 \cdot T^2, \quad (10)$$

in which T represents the temperature (°C) (Norstrom *et al.*, 1976).

The efficiency of oxygen uptake from the water was assumed to be 0.75 (Lloyd, 1961).

Efficiency of Cadmium Uptake

Rates of uptake of cadmium from water, food, and sediment have been published (Douben, 1989a and 1989c, and Douben and Koeman, 1989). These data should be the same as the outcome of the appropriate parts of Eq. (7), which describe uptake from these sources. Loss of weight (a negative value for dW/dt), caused by starvation during exposure to water-borne cadmium and cadmium associated with sediment particles lowered the total of the metabolic component of the respective equations. This was taken into account when the efficiencies of cadmium uptake were calculated. These efficiencies were estimated as 4.05, 6.29, and 0.05% from water, food, and sediment, respectively.

Loss of Cadmium

Loss of cadmium was higher after than during dietary exposure. Laboratory experiments indicated that the rate constant of loss (k) is dependent on temperature, and the values of 0.22 at 8°C and 9.76 at 18°C have been used (Douben, 1989c). For

TABLE 1

MINIMUM AND MAXIMUM CONCENTRATIONS OF CADMIUM IN WATER, INVERTEBRATES, AND SEDIMENT FROM THREE SITES IN DERBYSHIRE

Site	Concentration of cadmium					
	Water ($\mu\text{g liter}^{-1}$)		Invertebrates (mg kg^{-1})		Sediment (mg kg^{-1})	
	Min	Max	Min	Max	Min	Max
River Ecclesbourne	0.1	2.8	0.01	100	40	75
Brailsford Brook						
South	0.16	1.4	0.01	10	1	2
Suttonbrook	0.1	1.6	0.01	10	1	2

Note. For details of water, see Douben (1989d).

intermediate temperatures k was obtained by interpolation and below and above these k was kept constant at 0.22 and 9.76 (day^{-1}), respectively.

Concentration of Pollutant in the Environment

Water. Results from field observations on the concentration of cadmium in water (Douben, 1989d) were used to estimate maximum and minimum levels that can be expected in the River Ecclesbourne (Table 1).

Food. Samples of invertebrates were taken on four occasions (29 May, 22 June, 21 September 1987, and 18 January 1988) for metal determination. Invertebrates were sorted into taxa; samples were weighed, dried at 85°C for 3 days, and then reweighed. Also, the gut contents of some loach were analyzed to determine the taxa actually eaten. The contents found in gut of stone loach were broadly similar to the taxa found in the invertebrate samples. For all three sites the concentration of lead and cadmium varied between times of sampling and taxa (Fig. 1 and Table 2) ($P < 0.001$). Also there is probably a significant interaction between sampling time and taxa (P ranging from 0.10 to 0.05). The results (Fig. 1) suggest that the concentration of both metals is higher in samples taken later in the year.

Sediment. Sediment samples were taken over a 1-year period at the same time as fish (see Douben, 1989b). For details of sampling and chemical analysis, see Douben and Koeman (1989). Table 1 lists the results of maximum and minimum concentrations found.

Temperature

To obtain data for temperature for each day, mean values of minimum and maximum temperature for each of the sampling occasions (Douben, 1989b) were interpolated between sampling occasions.

Initial Values of the Model

Mean values of dry weight and cadmium burden measured in loach per age group in the first sample of fish, taken during the 1-year sampling program, have been used as initial values.

CONCENTRATION
RANGE (mg kg⁻¹)

CADMIUM

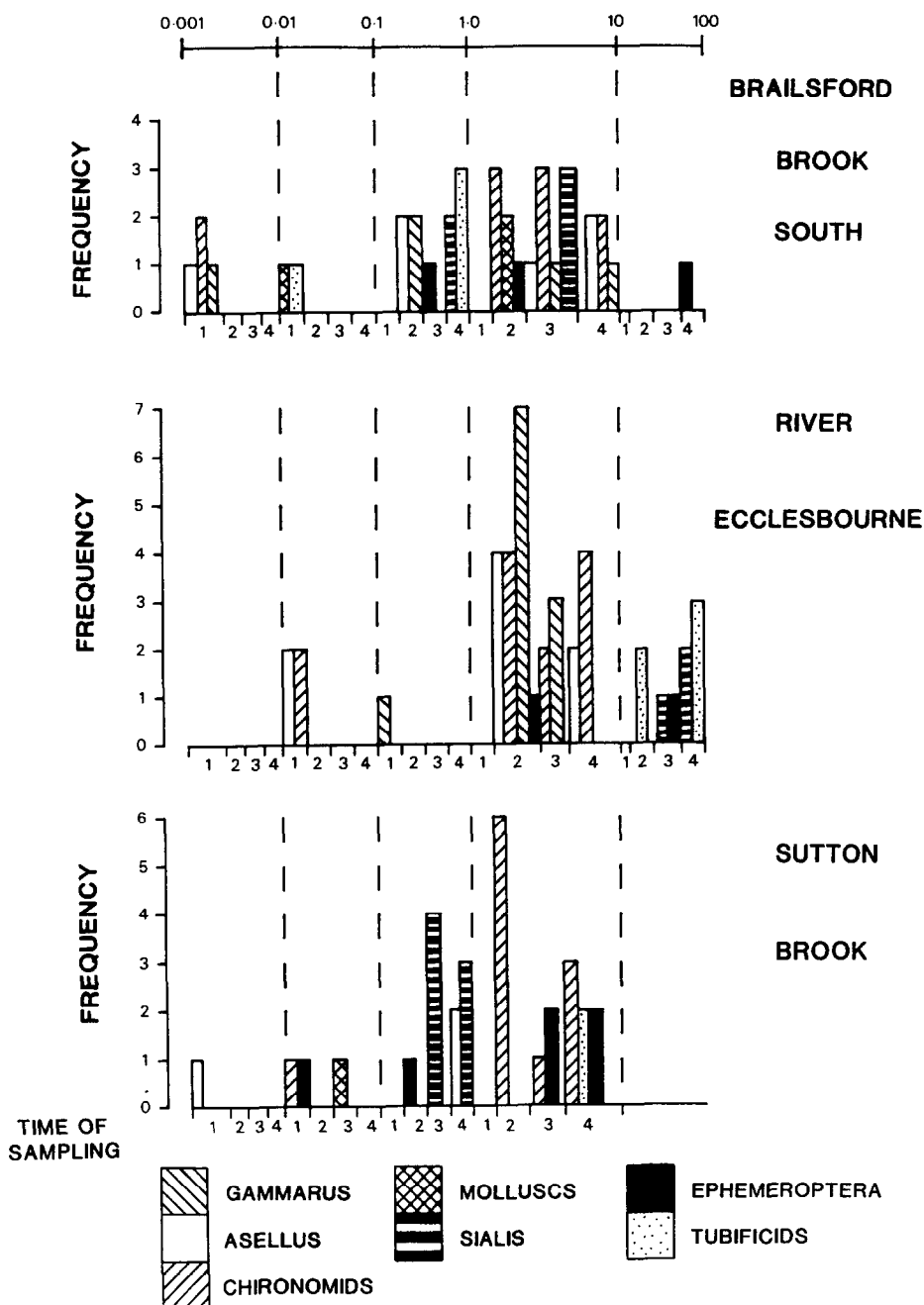


FIG. 1. Frequency distribution of concentration of cadmium in invertebrates from three sites in Derbyshire, sampled on four occasions. See text for sampling dates.

TABLE 2
DETAILS OF STONE LOACH (*Noemacheilus barbatulus* L.) AND THEIR GUT CONTENTS WITH ESTIMATED TOTAL NUMBER OF ANIMALS

Site	Fish no.	Length (mm)	Sex	Taxon										Total number
				Chironomidae	Crustacea	Erpobdellidae	Lumbriculidae	Oligochaeta	Prodiamesa	Simuliidae	Tubificidae			
R. Ecclesbourne	1	77	♂	+	—	—	—	—	—	—	+	—	>100	
	2	82	♀	+	—	—	—	—	—	—	+	—	>50	
Brailsford Brook	3	105	♀	+	+	—	+	—	+	+	+	+	>100	
	4	92	♀	—	—	—	—	—	—	—	+	—	12	
Suttonbrook	5	93	♂	+	—	—	—	+	—	—	+	—	>150	
	6	67	♂	+	—	+	—	—	—	—	+	—	>100	

TABLE 3

COMPARISON OF THE REGRESSION OF THE DIFFERENCE BETWEEN PREDICTED AND OBSERVED LOGARITHMIC DRY WEIGHT FOR STONE LOACH OF DIFFERENT AGES ON TIME OF SAMPLING: STANDARD DEVIATION ABOUT THE REGRESSION LINE (S_y), THE MEAN DIFFERENCE BETWEEN PREDICTED AND OBSERVED MEAN DRY WEIGHT (mg), AND THE CORRELATION COEFFICIENT

Age group	Standard deviation about the regression S_y	Mean difference (mg)	Correlation coefficient between predicted and observed dry weight	Number of observations
II+	0.0453	0.0268	0.833***	13
I+	0.0855	0.1679	0.916***	12
0+	0.2129	-0.4321	0.369	5

*** Significant correlation at the 0.001 probability level.

Time Constant

Metabolism was simulated on a daily basis and predicted growth rate adequately. Values of rate constants for loss of cadmium required that change of cadmium burden was calculated for each hour.

Criterion for Fit

Given that earlier work had shown that body weight was an important factor that influenced cadmium burden, comparison between observed data (Douben, 1989b) and predicted results were made for three different age groups. The differences between the logarithm of predicted and observed mean values per sample for all times were regressed on sampling time to evaluate whether the difference changed with time. The regression coefficient was not different from zero on any occasion; thus a bias in this difference with time had not occurred. The deviation of the difference about the regression line was then used as a measure for adequate fit. The mean difference indicated the overall closeness of the predicted to the observed values.

RESULTS

Prediction of Dry Weight and Effect on Cadmium Burden

Prediction of weight of I+ and II+ fish (based on Eqs. (2b) and (2c)) correlated significantly ($P < 0.001$) with the observed data (see also Table 3). Weight of 0+ fish was not adequately predicted, presumably because few field observations were available. Food accounted for more than 50% of the total intake of cadmium (Table 4). Percentage uptake from water was of similar magnitude as that from sediment for 0+ and I+ fish, but lower for II+ fish. Standard deviations of the regression of the difference between observed and predicted values were similar for I+ fish and for II+ fish but the predicted values matched those observed better for the first group of fish.

Range of Minimum and Maximum Cadmium Burden

Standard conditions refers to the values of parameters as listed in Table 5. Two levels of concentrations of cadmium in the environment (water, food, and sediment)

TABLE 4
EFFECT OF AGE OF FISH ON THE RELATIVE CONTRIBUTION OF WATER, FOOD, AND SEDIMENT TO THE INTAKE OF CADMIUM^a

Age group	Percentage intake from									Mean difference between predicted and observed mean (ng)	Number of observations
	Water			Food			Sediment				
	Min	Max	Overall	Min	Max	Overall	Min	Max	Overall		
II+	2.0	16.3	11.3	57.4	70.8	61.1	24.3	30.6	27.7	-0.5219	13
I+	0.0	35.2	21.7	53.8	71.5	58.9	10.4	29.4	19.4	-0.3079	12
0+	18.4	27.7	22.6	55.7	67.5	62.6	12.9	18.5	14.8	-0.7877	5

^a Minimum (min) and maximum (max) on 1 day and overall covering the entire simulation period, and on the regression of the difference between predicted and observed logarithmic burden of cadmium in stone loach on time of sampling, the standard deviation about the regression, and the mean difference between predicted and observed logarithmic cadmium burden. Concentrations of cadmium in water, food, and sediment were 1 $\mu\text{g liter}^{-1}$, 10 mg kg^{-1} dry weight, and 10 mg kg^{-1} dry weight, respectively.

TABLE 5
VALUES OF VARIABLES FOR STANDARD
CONDITIONS IN THE MATHEMATICAL
MODEL WHICH PREDICTS CADMIUM
BURDEN OF I+ STONE LOACH

Variable	Value
Dry weight (mg) ^a	300
Cadmium burden (ng) ^a	15
y_w	0.34
y_f	0.70
y_s	0.88
C_{pw} ($\mu\text{g liter}^{-1}$)	1.0
C_{pf} (mg kg^{-1} dry weight)	10
C_{ps} (mg kg^{-1} dry weight)	10
E_{pw}	4.05×10^{-2}
E_{pf}	6.29×10^{-2}
E_{ps}	5.211×10^{-4}
E_{ox}	0.75
Q_{ox}	3.42×10^{-3}
E_f	0.70
β	0.83

^a Initial situation for fish from the River Ecclesbourne.

have been distinguished: minimum and maximum (Table 1). Using these concentrations throughout different simulations yielded the widest range of body burden in loach that can be expected. The observed values for the three age groups fell within the respective ranges (Figs. 2A, 2B, and 2C): 8 out of 13, 11 out of 12, and 4 out of 5 sampling occasions for II+, I+, and 0+ fish, respectively. The model predicted a plateau in cadmium burden for each age group of fish during the winter, which for the maximum concentrations were higher than the observed peaks for both I+ and II+ fish. The rise in cadmium content is predicted to occur later than observed. Because I+ fish approach the maximum weight by the start of the second winter, there is hardly any difference in predicted values between I+ and II+ fish from that time onward (Figs. 2b and 2c).

Given the availability of data for I+ fish throughout the sampling period, subsequent analyses and comparisons are made for I+ fish only with standard conditions (Table 5) to obtain an overview of the effect of changes in parameters and variables on metal burden of the fish.

Effect of Change in Cadmium in Water, Food, and Sediment

All predictions of minimum intake per day of cadmium from water are zero (Table 6). This is due to the loss of weight during the winter period. The energy derived from this loss of weight is calculated to be greater than the requirements for Q_{lr} ; provisions

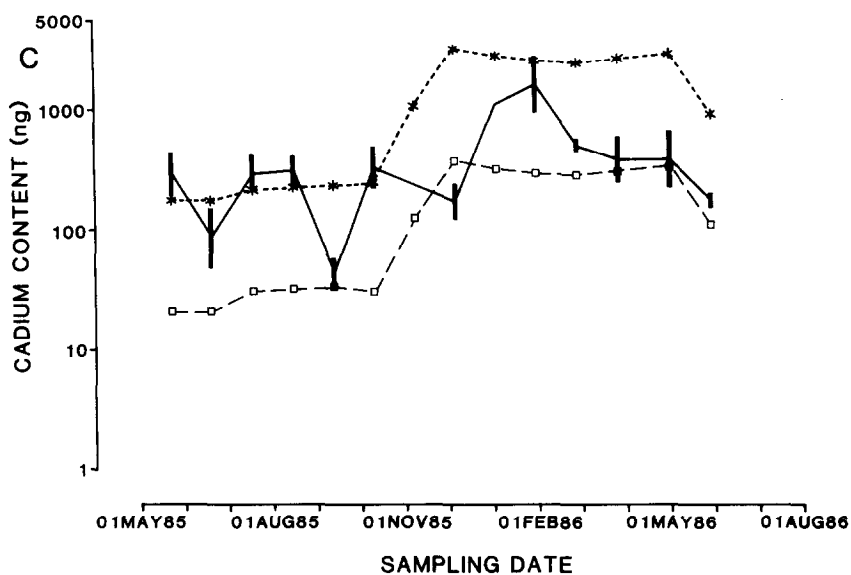
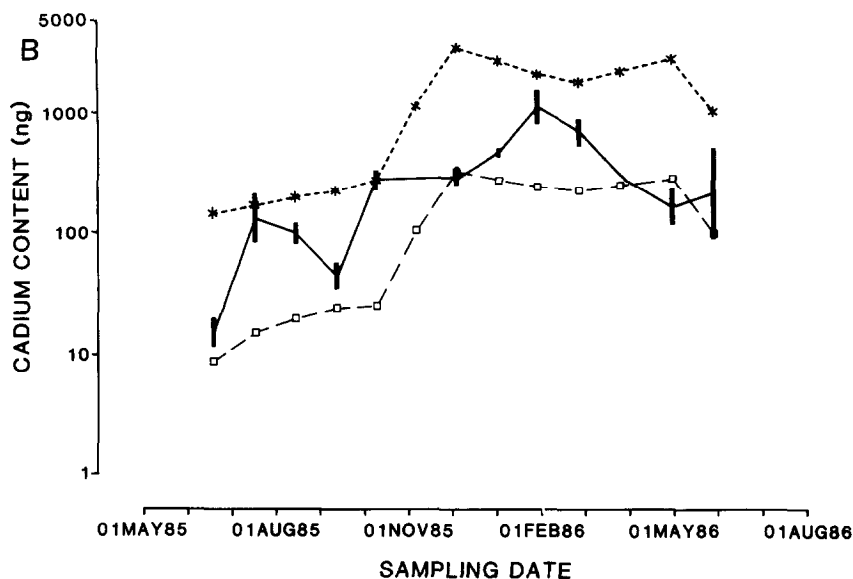
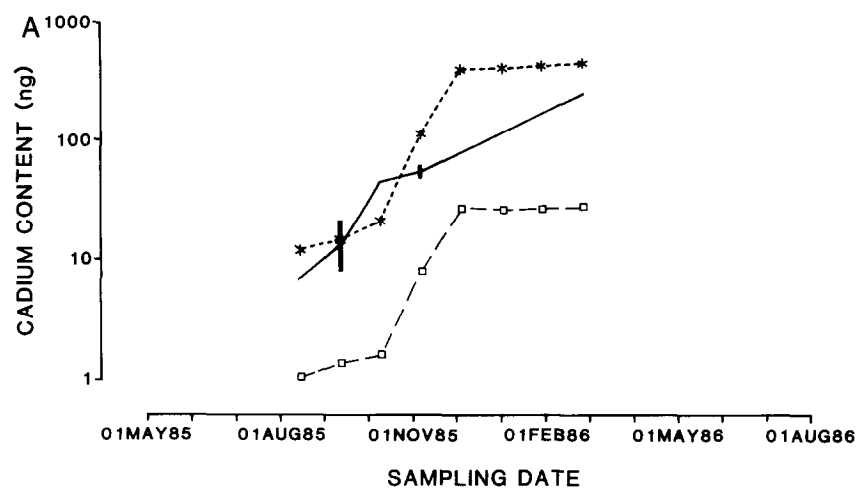


FIG. 2. Mean cadmium content (bars) with standard errors, of stone loach sampled at about 4-weekly intervals from the River Ecclesbourne, Derbyshire. Values predicted with highest (*) and with lowest (□) measured concentrations of cadmium in water, food and sediment. Three different age groups were distin-

were made that no negative intake could take place through the water, i.e., additional loss via the uptake component, which was then set to zero.

An increase in the cadmium concentration in water from 0.1 to $1.0 \mu\text{g liter}^{-1}$, with concentrations remaining constant in food and sediment, obviously increased the percentage intake of cadmium from this source while the overall percentage intake from water tends toward the higher part of the range (Table 6a). Maximum predicted intake from sediment remains unaffected but its overall contribution drops from 24.2 to 6.6%. Deviation between observed and predicted values increases.

When the concentration of cadmium in food increases from 0.01 to 1.0 mg kg^{-1} then its contribution to the total intake increases most rapidly toward the top end of the concentration range used. The increase in concentration from 10 to 100 mg kg^{-1} has considerably less effect. The deviation between the observed and predicted value drops (Table 6b).

An increase in the concentration in the sediment also reduces the difference between observed and predicted values (Table 6c). When the concentrations of cadmium in water, food, and sediment are $1.0 \mu\text{g liter}^{-1}$, 1 mg kg^{-1} , and 100 mg kg^{-1} , respectively, the least deviation for all comparisons listed in Tables 6a, 6b, and 6c is obtained and the mean of the difference is lowest: this indicates that the observed and predicted values are reasonably close.

Effect of Exponent of Body Weight

The relatively low contribution from the water component may be, at least to some extent, due to the numerically lower value of the exponent relating body weight to cadmium uptake from water. When the exponents are given the value of 0.78, the value for uptake of food, entry of cadmium through the water increases to nearly 2.5 times, the relative contribution from food drops to about 69% of its original contribution, and that from sediment drops to about 35% (Table 7). The deviation about the regression of the difference between observed and predicted values on time is reduced.

Relationship between Metabolic Rate and Cadmium Uptake from Sediment

It was assumed that the connection between metabolic rate and uptake of cadmium from sediment is similar to that for water-borne exposure. Replacing the part of metabolic rate by the equation used for dietary exposure (Eq. (3)) increases the proportions taken up from water and food at the cost of intake from sediment (Table 8). The predicted cadmium burdens do not match the observed burdens as well as the standard model does.

Effect of Rate Constant of Loss

At lower temperatures, body burden increases because rate of intake is reduced more than rate of loss. Given that cadmium burden in both I+ and II+ fish peaked in January, it seems likely that below 8°C loss is further reduced and not constant as assumed in the standard model. The same relationship between k and temperature extrapolated below 8°C with a minimum value of 0.0 results in a greater difference between the observed and predicted values (Table 9).

EFFECT OF REDUCTION OF THE VALUE FOR RATE CONSTANT OF LOSS k BELOW 8°C ON THE RELATIVE CONTRIBUTION OF WATER, FOOD, AND SEDIMENT, TO THE CADMIUM BURDEN OF THE LOACH, ON THE STANDARD DEVIATION ABOUT THE REGRESSION OF THE DIFFERENCE BETWEEN PREDICTED AND OBSERVED LOGARITHMIC CADMIUM BURDEN^a

Value of k below 8°C	Percentage intake from						Standard deviation about regression S_y	Mean difference between predicted and observed mean cadmium burden (ng)	Maximum predicted cadmium burden			
	Water			Food						Sediment		
	Min	Max	Overall	Min	Max	Overall				Min	Max	Overall
0.22	0.0	35.2	21.7	53.8	71.5	58.9	10.4	29.4	19.4	0.3911	-0.3079	425.2
Temperature dependent ^b	0.0	35.2	21.7	53.8	71.5	58.9	10.4	29.4	19.4	0.6667	0.3798	11416.1

^a Concentrations of cadmium in water, food, and sediment were $1\text{ }\mu\text{g liter}^{-1}$, 10 mg kg^{-1} dry weight, and 10 mg kg^{-1} dry weight, respectively.

^b Value of k below 8°C calculated as: $k = -7.412 + 0.945 \times \text{temperature } (^{\circ}\text{C})$ with a minimum of 0.0; see text for details.

TABLE 10

EFFECT OF CHANGE IN TEMPERATURE ON WEIGHT AND ON RELATIVE CONTRIBUTION OF CADMIUM IN WATER, FOOD, AND SEDIMENT TO THE BODY BURDEN OF LOACH, ON THE STANDARD DEVIATION ABOUT THE REGRESSION OF THE DIFFERENCE BETWEEN PREDICTED AND OBSERVED CADMIUM BURDEN ON TIME OF SAMPLING AND THE MEAN DIFFERENCE BETWEEN PREDICTED AND OBSERVED LOGARITHMIC CADMIUM BURDEN^a

Change of temperature in comparison with observed data ^b	Percentage intake from									Predicted final dry weight (mg)	Maximum predicted cadmium burden (ng)
	Water			Food			Sediment				
	Min	Max	Overall	Min	Max	Overall	Min	Max	Overall		
+2°	5.6	35.2	22.3	52.4	68.8	57.8	11.3	25.6	19.9	2153.2	464.6
+1°	2.0	35.3	22.0	53.1	70.6	58.3	10.7	27.5	19.7	1960.5	439.9
0°	0.0	35.2	21.7	53.8	71.5	58.9	10.4	29.4	19.4	1767.9	425.2
-1°	0.0	35.6	21.9	54.1	71.7	59.2	10.3	31.6	18.9	1575.3	409.9
-2°	0.0	34.0	22.3	54.3	71.8	59.4	10.3	35.5	18.3	1382.7	348.1

^a Concentrations of cadmium in water, food, and sediment were $1\text{ }\mu\text{g liter}^{-1}$, 10 mg kg^{-1} dry weight, and 10 mg kg^{-1} dry weight, respectively.

^b Observed data from the River Ecclesbourne (Douben, 1989b).

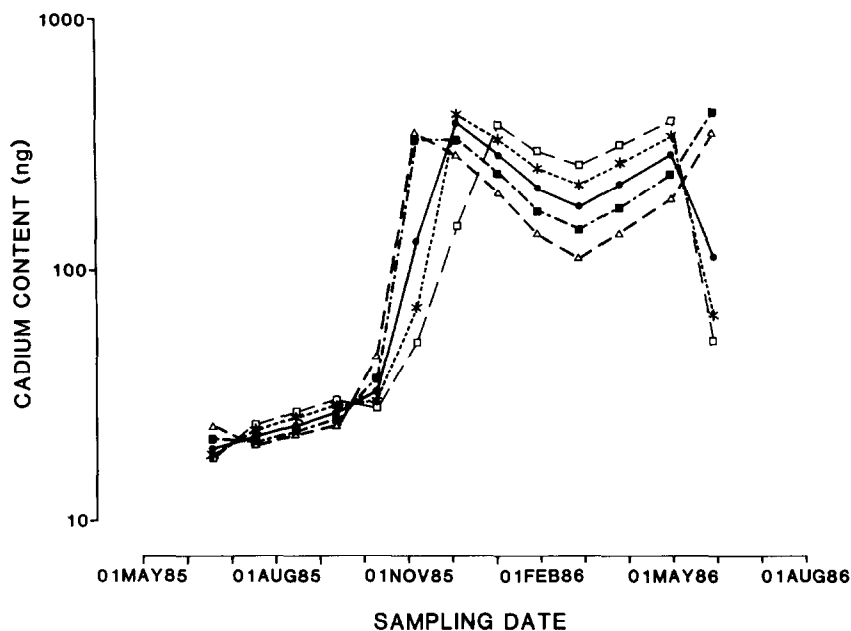


FIG. 3. Effect of change in temperature on predicted cadmium content (ng) of stone loach for standard conditions in the environment (see text for details): (●) observed set of temperatures in the River Ecclesbourne; (*) all temperatures increased by 1°C; (□) all temperatures increased by 2°C; (■) all temperatures decreased by 1°C; (▲) all temperatures decreased by 2°C.

Effect of Temperature

Hitherto temperatures used were as observed in water from the River Ecclesbourne (Douben, 1989b). Predictions were carried out with one and two degrees difference for all temperatures without adjusting for a possible change in growth rate. Entry of cadmium from water is lowest at the standard set of temperatures but the predicted minimum percentage intake from water increases with temperature (Table 10). Minimum, maximum, and overall percentage uptake from food increases with drop in temperature, while the overall relative contribution from sediment decreases with decreasing temperature.

Given that the model is based on metabolism of stone loach, it is not surprising that predicted weight of fish is higher for higher temperatures at the end of the simulation period. Also, the maximum predicted cadmium burden is increased.

There was little difference between the predicted burden of cadmium up to the middle of October for the different sets of temperatures (Fig. 3). Thereafter, the predicted increase is delayed for higher temperatures. Consequently, the maximum predicted burden is higher and occurs later. During the midwinter period there is clearly an effect of temperature on the value of the plateau: higher temperatures cause higher cadmium burden. In late spring, the cadmium load drops for temperatures at and above standard. There was little difference between these three predicted levels of cadmium at the end of the simulation period. Cadmium burden increases for temperatures below standard level at the end of the simulation period. However, given the overall tendency, it is likely that cadmium burden would drop with rise in temperature during the second summer.

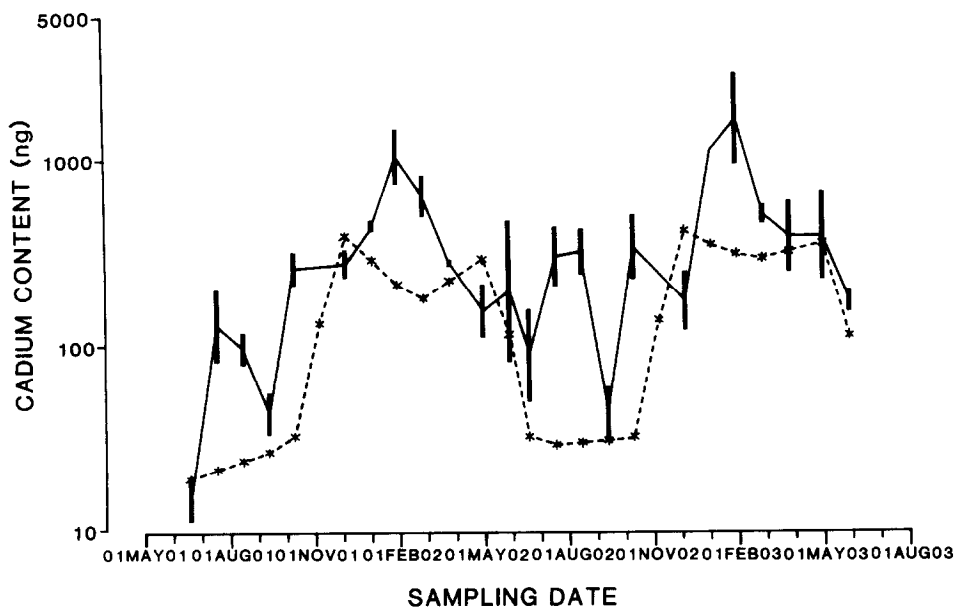


FIG. 4. Cadmium content (*) in stone loach, predicted continuously for 2 years, with concentration of cadmium in water, food, and sediment of $1.0 \mu\text{g liter}^{-1}$, 10 mg kg^{-1} dry weight, and 10 mg kg^{-1} dry weight, respectively; mean cadmium content (bars) with standard errors of loach sampled at about 4-weekly intervals from the River Ecclesbourne, Derbyshire, for I+ and II+ fish in increasing order of age. For details, see text.

Predictions from the Model

Period of simulation. Analysis of the model was performed on the results for I+ fish apart from the comparison for the effect of body weight. Assuming that environmental conditions (e.g., temperature, concentration of cadmium in water, food, and sediment) remain the same for another year, the simulation period covered 2 years continuously, using initial values of cadmium burden and dry weight for I+ fish only. Predicted results for dry weight were highly correlated ($P < 0.001$) with observed results for I+ and II+ fish caught in the River Ecclesbourne (Douben, 1989b); 89% of the variation in predicted dry weight was explained by observed values. Predicted cadmium burden follows the trend as observed (Fig. 4). The relative contributions of water, food, and sediment are, as expected, between the results obtained for I+ and II+ fish separately (compare Table 4 with Table 11).

Predictions for different sites. Maximum and minimum measured concentrations of cadmium in water, food, and sediment from Brailsford Brook South and Suttonbrook (Table 1) were used together with data for temperature at those sites (Douben, 1989b and Douben and Koeman, 1989). Only I+ fish were considered. The predicted minima were always lower than the observed cadmium burden (Figs. 5A and 5B), and, in Suttonbrook, the observed burdens were usually lower than the predicted maxima. The observed cadmium burden in fish from Brailsford Brook South was higher than the predicted burden up to September 1985, but within the range of predicted minima and maxima. Thereafter, the rise in cadmium at the end of the autumn was predicted for both sites. The drop at the end of the simulation period

TABLE 11

PREDICTED PERCENTAGE INTAKE OF CADMIUM FROM WATER, FOOD, AND SEDIMENT BY STONE LOACH DURING 2 YEARS, STARTING WITH INITIAL VALUES FOR 1-YEAR-OLD FISH AND COMPARISON OF THE REGRESSION OF THE DIFFERENCE BETWEEN PREDICTED AND OBSERVED LOGARITHMIC BURDEN OF CADMIUM, THE STANDARD DEVIATION ABOUT THE REGRESSION (S_y), THE MEAN DIFFERENCE BETWEEN PREDICTED AND OBSERVED LOGARITHMIC CADMIUM BURDEN^a

Percentage intake from									Standard deviation about regression S_y	Mean difference between predicted and observed mean cadmium burden (mg)
Water			Food			Sediment				
Min	Max	Overall	Min	Max	Overall	Min	Max	Overall		
0.0	35.2	15.5	53.8	71.5	60.1	10.4	31.7	24.4	0.4197	−0.3615

^a Concentrations of cadmium in water, food, and sediment were $1 \mu\text{g liter}^{-1}$, 10 mg kg^{-1} dry weight, and 10 mg kg^{-1} dry weight, respectively.

occurs too late in the model for Brailsford Brook South and too early for Suttonbrook (Figs. 5A and 5B).

Prediction of weight of loach with the equation for growth rate derived from observations from the River Ecclesbourne and data for temperature from the respective sites show that they are in good agreement with the observed weights (Table 12a). The standard deviation about the regression for Brailsford Brook South fish is smallest. Using the same concentrations of cadmium in water, food, and sediment ($1 \mu\text{g liter}^{-1}$, 10 mg kg^{-1} , and 1 mg kg^{-1} , respectively) for all sites, then the results show that the relative contribution of these sources are comparable both as far as the range and as far as the overall percentages are concerned (Table 12b). Predictions for Brailsford Brook South were closer to the observed data.

DISCUSSION

The approach to construct the mathematical model to predict cadmium burden in stone loach depends heavily on adequate information on both metabolism and pollutant dynamics and on the link between these two components. The predicted levels of cadmium indicated that these conditions were reasonably met: reproduction of trends follows cadmium burden of stone loach under field circumstances. Coupling of metabolism of the stone loach with pollutant dynamics helps to explain the relative importance of the different sources of cadmium.

The results of the predictions of weight of loach indicate that they are in good agreement with the observed weights in I+ fish from the three rivers, and in II+ fish from the River Ecclesbourne, while too few data are available for 0+ fish (Tables 3 and 12a).

The premise that metabolism of the loach is an important factor in explaining its metal burden seems to be justified by the similarities of predicted and observed cadmium burden. For example, the higher levels observed during the winter period were reasonably well predicted. Cadmium levels tended to be higher in bullhead (*Cottus gobio* L.) from the River Ecclesbourne in November than in those sampled in August even after allowing for differences in weight (Moriarty *et al.*, 1984). Similar observations were found in mussels (Amiard *et al.*, 1986). This phenomenon can be ex-

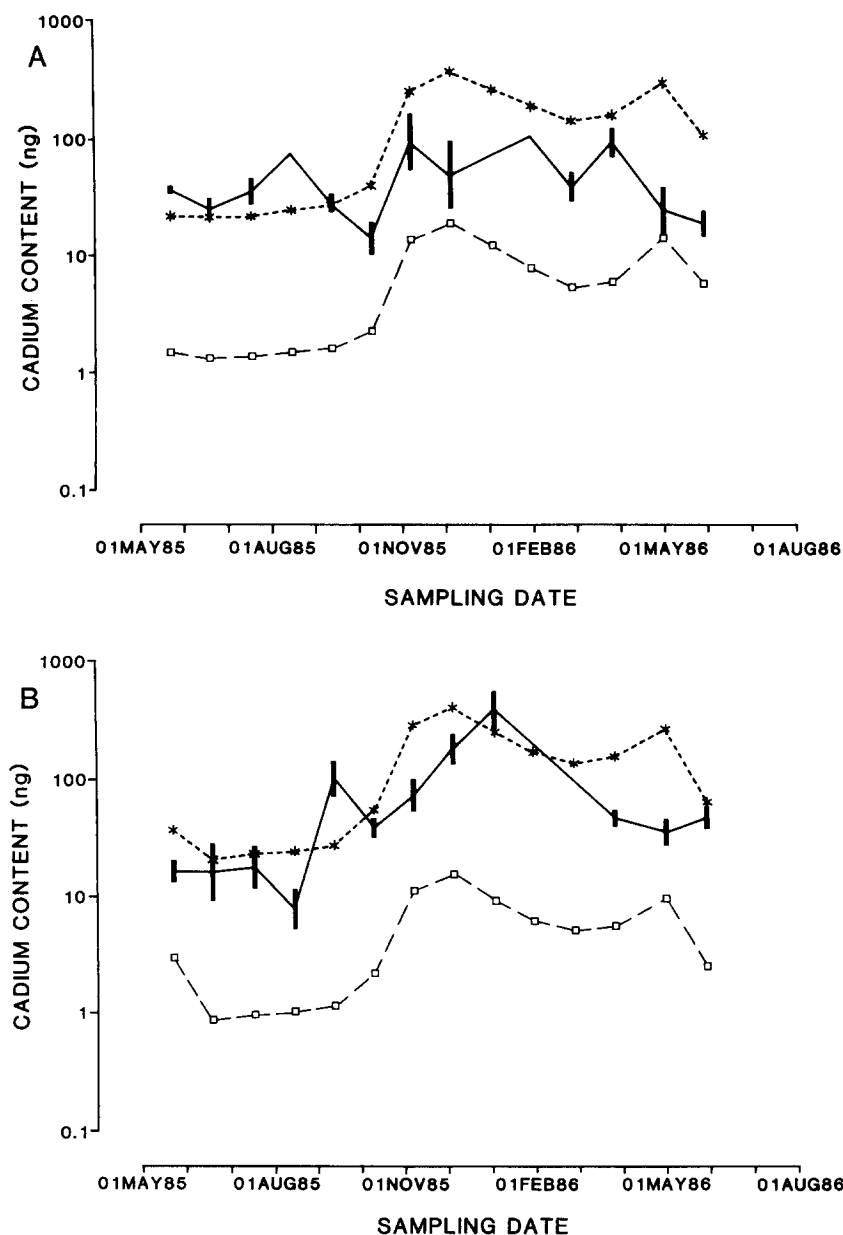


FIG. 5. Mean cadmium content (bars) with standard errors, of stone loach in the age group I+, sampled at about 4-weekly intervals from two streams in Derbyshire. Values predicted with highest (*) and with lowest (□) measured concentrations of cadmium in water, food, and sediment. (A) Brailsford Brook South and (B) Suttonbrook.

plained by the effect of temperature on rates of intake and loss: rates of intake are more affected than rates of loss. The rate constant for loss, k , was a function of temperature in this model in contrast to the model used by Norstrom *et al.* (1976), but in accordance with their suggestion. These results correspond with those found by Jimenez *et al.* (1987) for the bluegill sunfish (*Lepomis macrochirus*). Although the

TABLE 12
COMPARISON, FOR STONE LOACH IN THE AGE GROUP I+, OF THE REGRESSION OF THE DIFFERENCE BETWEEN PREDICTED
AND OBSERVED LOGARITHMIC (a) DRY WEIGHT AND (b) CADMIUM CONTENT ON TIME OF SAMPLING
FROM THREE SITES IN DERBYSHIRE (FOR DETAILS SEE DOUBEN, 1989b)^a

Site	Standard deviation about the regression S_y	Mean difference (mg)	Correlation coefficient	Number of observations							
(a) Dry weight											
River Ecclesbourne	0.0855	0.1679	0.916***	12							
Brailsford Brook South	0.0831	0.1689	0.871***	13							
Suttonbrook	0.1094	0.2639	0.864***	12							
	Percentage intake from										
	Water			Sediment							
	Min	Max	Overall	Min	Max	Overall					
(b) Cadmium content											
River Ecclesbourne	0.0	38.9	26.3	60.0	96.2	71.3	1.1	4.0	2.4	0.4003	-0.3984
Brailsford Brook South	0.0	39.3	27.0	59.7	96.2	70.9	1.0	4.0	2.1	0.2999	0.2298
Suttonbrook	0.0	38.9	27.1	60.0	96.2	70.8	1.0	4.0	2.1	0.3817	0.1739

^a Standard deviation about the regression line (S_y), the mean difference between predicted and observed mean dry weight (mg)/cadmium content (ng), the correlation coefficient between predicted and observed dry weight/cadmium content, and the relative contribution of water, food, and sediment to intake of cadmium: minimum (min) and maximum (max) per day and overall covering the entire simulation period. Concentrations of cadmium in water, food and sediment were $1 \mu\text{g liter}^{-1}$, 10 mg kg^{-1} , and 1 mg kg^{-1} dry weight, respectively.

*** Significant correlation at the 0.001 probability level.

value of k appeared to be different during and after dietary exposure (Douben, 1989c), no provision was made to allow for this phenomenon in the model because no adequate information was available for the effect of the concentration of cadmium in the environment on k .

Under field conditions, even in the unlikely event of a constant exposure, the intake of cadmium by the stone loach will be influenced by factors associated with metabolism such as change in temperature (Fig. 3). This was demonstrated by all simulations, particularly by the one run for 2 years. However, the high rate of loss of cadmium in May/June of the second year was observed later than predicted (Fig. 4). Norstrom *et al.* (1976) concluded that estimates of pollutant concentrations in the environment were most prone to errors due to inadequate definition of seasonal variation. Despite the fact that the concentration of cadmium in samples of invertebrates tended to be higher during the autumn (Fig. 1) and that the concentration of cadmium in water fluctuated due to flow rate and, perhaps, season (Douben, 1989d), predictions of cadmium in loach were in reasonable accordance with measured levels.

There are three possible routes of entry of cadmium: water, food, and sediment. Water is more important for 0+ and I+ fish than for II+ fish. Food contributes substantially to the body burden of loach in all age groups. There is still some controversy over the importance of food as a source of metal for fish (Kay, 1985; McCracken, 1987). Sediment as a source of metal is often overlooked; the results of other studies indicated that cadmium associated with sediment particles was taken up by aquatic organisms, including the stone loach (Douben and Koeman, 1989; Gillespie, 1972; Luoma, 1983), possibly through ingestion of sediment (Tessier and Campbell, 1987). The results of the predictions in this paper demonstrate that cadmium in loach originates partly from sediment; its importance increases with age (weight) of loach (Table 4). The problem of uptake from sediment particles directly or from interstitial water is outside the scope of this paper. There is increasing evidence that differences in behaviour affect routes of entry of metals in general into fish (Ney and Van Hassel, 1983).

The link between metabolism and cadmium uptake from sediment was the same as that between metabolism and uptake from water. From Eq. (5) it can be deduced that changing the link into the dietary equivalent reduces the intake of cadmium from sediment, despite the increase of the coefficient for growth rate β into $\beta + 1$, because $1/E_f$ (which is equal to $1/0.70$) is replaced by $1/(E_{ox} * C_{ox} * Q_{ox})$ ($1/0.0026 * C_{ox}$) while C_{ox} ranges from 14.45 to 8.71 mg l liter⁻¹. The results in Table 8 quantify the end result.

Comparison of the cadmium burden in loach in the age group I+ from different sites indicates that there is great similarity between the predicted cadmium burdens in loach with maximum and minimum concentration of cadmium in water, food, and sediment as far as trend is concerned as well as levels in fish from Suttonbrook and Brailsford Brook South. For the same concentrations of cadmium in the environment, the relative contribution of cadmium intake from the sediment is slightly higher for the predictions for the River Ecclesbourne in comparison with other streams due to higher temperatures during the summer which increased growth rate; predicted final weights were 1767.9, 1709.5, and 1654.2 mg dry weight for loach from the River Ecclesbourne, Brailsford Brook South, and Suttonbrook, respectively. DeFreitas *et al.* (1974) concluded that the major route of entry of methyl mercury in pike (*Esox lucius*) differed with location. Given that the concentration of cadmium in sediment is substantially higher in samples from River Ecclesbourne than in those

from Brailsford Brook South and Suttonbrook, this results in a higher percentage uptake of cadmium from the sediment. To some extent the same argument applies to food. This clearly demonstrates that conclusions about the origin of cadmium in fish depend on environmental conditions.

CONCLUSIONS

The mathematical model described in this paper couples metabolism of the stone loach with uptake and loss of cadmium in the fish. It predicts levels of cadmium in the fish with a high degree of realism. Metabolism affects cadmium burden. Cadmium is taken up from water, food, and sediment at different rates. The relative importance of these sources is affected by body size. Temperature has a major influence on the cadmium burden.

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